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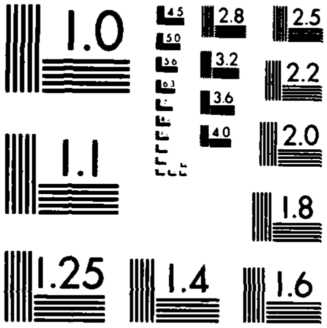

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October 1985

SURVEY OF COPPER IN KINGS BAY AND CUMBERLAND SOUND

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The work described herein was performed by the Marine Environment Branch, Code 522, Naval Ocean Systems Center (NAVOCEANSYSCEN), for the Chief of Naval Operations, Naval Facilities Engineering Command, and Officer in Charge of Construction, Trident.

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A multiparameter survey consisting of physical, chemical, and biological measurements was performed to map the copper distribution in Kings Bay and Cumberland Sound, Georgia. The results of this study suggest (1) Kings Bay was probably not a source of elevated copper levels during the study interval, (2) dewatering of the dredge spoil containment area does not appear to be a source of copper pollution, and (3) concentrations in the Lower Turning Basin of Kings Bay were slightly higher than levels in the Upper Basin or in Cumberland Sound, suggesting possible input from copper antifouling coatings.

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SUMMARY

OBJECTIVE

A multiparameter survey consisting of physical, chemical, and biological measurements was performed to map the copper distribution in Kings Bay and Cumberland Sound, Georgia.

METHOD

Continuous real-time measurements were made on board the survey craft for temperature, salinity, oxygen, pH, chlorophyll *a* fluorescence, light transmission, cupric ion electrode response, and bottom depth. Discrete samples were collected for copper analysis by anodic stripping voltammetry (ASV) and atomic absorption (AA) spectrophotometry. Data are presented from underway mapping surveys of Kings Bay and Cumberland Sound during ebb and flood tidal conditions, tidal studies at a fixed location in Kings Bay, and an effluent monitoring station in an area receiving effluent from a dredge spoil containment area undergoing dewatering.

RESULTS

Results ranged from 1.2 to 5.8 µg/L for discrete AA samples, 0.3 to 2.2 µg/L for discrete ASV samples, and -200 to -40 mV for cupric ion electrode response. A two-way nested analysis of variance (ANOVA) showed no significant difference ($P>0.05$) for ASV samples and a highly significant difference ($P<0.0001$) for AA samples with respect to sample location. The results of this study suggest that (1) Kings Bay was probably not a source of elevated copper levels during the study interval, (2) dewatering of the dredge spoil containment area does not appear to be a source of copper pollution, and (3) concentrations in the Lower Turning Basin of Kings Bay were slightly higher than levels in the Upper Basin or in Cumberland Sound, suggesting possible input from copper antifouling coatings.

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INTRODUCTION

Recent analyses of water in Kings Bay and Cumberland Sound show elevated and increasing levels of copper. Values of total copper as high as 38 µg/L have been reported (Naval Facilities Engineering Command (NAVFACENGCOM), 1984). Monitoring during 1982-1983 frequently showed values in excess of the suggested Environmental Protection Agency (EPA) criterion of 23 µg/L for marine waters (EPA, 1980). These values contrast with concentrations of approximately 2 µg/L measured in comparable estuarine systems in Georgia (Windom et al., 1983). Although results to date are based on a limited number of discrete samples, there is concern about the apparent trend towards higher concentrations. The question arises whether Navy activity, including dredging operations in Kings Bay, may be responsible for these elevated copper levels.

In response to this concern, a comprehensive environmental study of copper in Kings Bay and Cumberland Sound was conducted in January 1985. Detailed measurements of copper and supporting physical, chemical, and biological parameters were made to evaluate the distribution of copper in Kings Bay and vicinity. The field measurement program was conducted using the Naval Ocean System Center's (NOSC) Marine Environmental Survey Craft (MESC), which uses a system of in situ and flowthrough monitoring devices (Zirino & Hightower, 1984). Measurements are made from a towed conductivity-temperature-depth (CTD) "fish" or on a flowing stream of seawater provided by a pumped seawater system. Instrumentation aboard the MESC permits continuous measurement of uncomplexed copper (i.e., ionic Cu^{2+}) on the pumped seawater stream and near-real-time analysis of total dissolvable copper by automated anodic stripping voltammetry (AASV). A data acquisition system records and displays information from all continuous sensors (temperature, salinity, oxygen, pH, chlorophyll, light transmission, Cu^{2+}, and bottom depth) at rates up to 30 samples a minute. This provides the capability for tracking plumes and/or locating point sources while the craft is underway or measuring variability as a function of time when the craft is moored at a fixed location. The chemical and physical data are combined with navigational data to generate underway maps of the environmental parameters of interest. In addition, real-time display of copper data and supporting environmental data provide a mechanism for selecting sample sites for collection of discrete samples for copper analysis by traditional laboratory procedures.

This report presents the results of measurements made from 15 to 23 January 1985 Data are presented from underway mapping surveys of Kings Bay and Cumberland Sound during ebb and flood tidal conditions, tidal studies at a fixed location in the vicinity of the Navy facilities in Kings Bay, and a monitoring station in which the survey platform was moored in an area receiving effluent from a dredge spoil containment area that was undergoing dewatering. Results from discrete samples collected for copper analyses by traditional laboratory procedures are also reported.

Measurements made during this study are used to address several specific questions: (1) Is there any evidence of a point source of copper that might be contributing to the apparent elevation of copper levels in Kings Bay or Cumberland Sound? (2) Are levels of copper significantly higher in Kings Bay than in Cumberland Sound? (i.e., Is the Navy responsible for the elevated copper levels?) and (3) What effect does the dewatering of dredge spoils have on the level of copper in this estuarine system?

METHODS

Field Measurement Program. Underway mapping, tidal monitoring, and effluent monitoring were conducted from the NOSC MESC. The MESC is a self-contained, self-propelled, 38-foot shallow-draft survey platform that houses a suite of on-board physical, chemical, and biological sensors and a data acquistion and processing system. Speed of the craft during underway mapping was approximately 2 knots. Position of the craft during mapping events was determined using dead-reckoning techniques with reference to fixed navigational markers and landmarks. The dead-reckoning method gives an estimated position resolution of ±20 meters. Position of discrete samples collected during underway mapping surveys was determined by interpolation between navigational fixes bracketing the time the sample was collected (Johnston, 1983). During tidal monitoring, the craft was secured to the medium auxiliary repair drydock (ARDM) pier. During effluent monitoring, the craft was anchored approximately 10 meters from the mouth of the channel carrying effluent from the Mainside Disposal Area into Kings Bay at a location approximately 150 meters southeast of the USS SIMON LAKE (AS 33).

Instrumentation. Two types of copper measurements were made on board the craft during the field study. Ionic or "free" copper was monitored continuously using a copper ion-selected electrode (Cu-ISE) (Zirino & Seligman, 1981). Total "dissolvable" copper was measured by AASV on discrete samples acidified to pH 2 with 50-percent Ultrex HNO_3 (J.T. Baker Chemical Co.) (Zirino & Lieberman, 1975). Seawater for both measurements was pumped on board the survey craft through approximately 5 meters of noncontaminating polyethylene hose using a Jabsco Model 18630-0003 sealless magnetic drive pump. The pump, which does not have any metal parts that contact the sample, was used to pull seawater from an intake attached to a CTD fish towed off the starboard side of the survey craft. The fish was maintained at a depth of approximately 1 meter below the surface of the water. Flow rate of the pumping system was approximately 40 gal/min.

In addition to the copper measurements, supporting environmental data were measured using in situ sensors on the towed CTD system and sensors that made measurements on a pumped seawater stream on board the craft. A list of parameters measured and the instrumentation used is given in Table 1. Figure 1 is a schematic of the on-board manifold system.

Signals from the various sensors were sampled and recorded using a data acquisition and processing system based on a dual processor microcomputer. Analog signals from the CTD system, copper and pH electrodes, fluorometers, etc., were subjected to an integrating analog to digital (A-D) conversion and sampled in conjunction with the digital signal from the fathometer using an Analog Devices μMac 5000 measurement and control subsystem. The data were telemetered to an IBM-compatible personal computer (PC) and recorded on floppy disks. The PC was also used to perform real-time calibration and hard-copy graphics display. Two-second sampling rates were used during underway mapping periods. For a nominal craft speed of 2 knots, this corresponds

Table 1. Parameters measured and instrumentation.

Sensor Type	Parameter	Instrumentation
In Situ	Temperature Conductivity Dissolved Oxygen Light Transmission	Interoceans 513D CTD
	Bottom Depth	Fathometer with Thru-Hull Transducer
Pumped	Realitive Cu^{2+}	Ag/AgCl ISE
	"Dissolvable" Cu	Automated Anodic Stripping Voltammetry (Zirino & Lieberman, 1975)
	pH	Glass Electrode
	Nephelometry	Turner Designs with Flow Attachment
	Chlorophyll a	Turner Designs with Flow Attachment
Discrete	Total Cu	Graphite Furnace AA

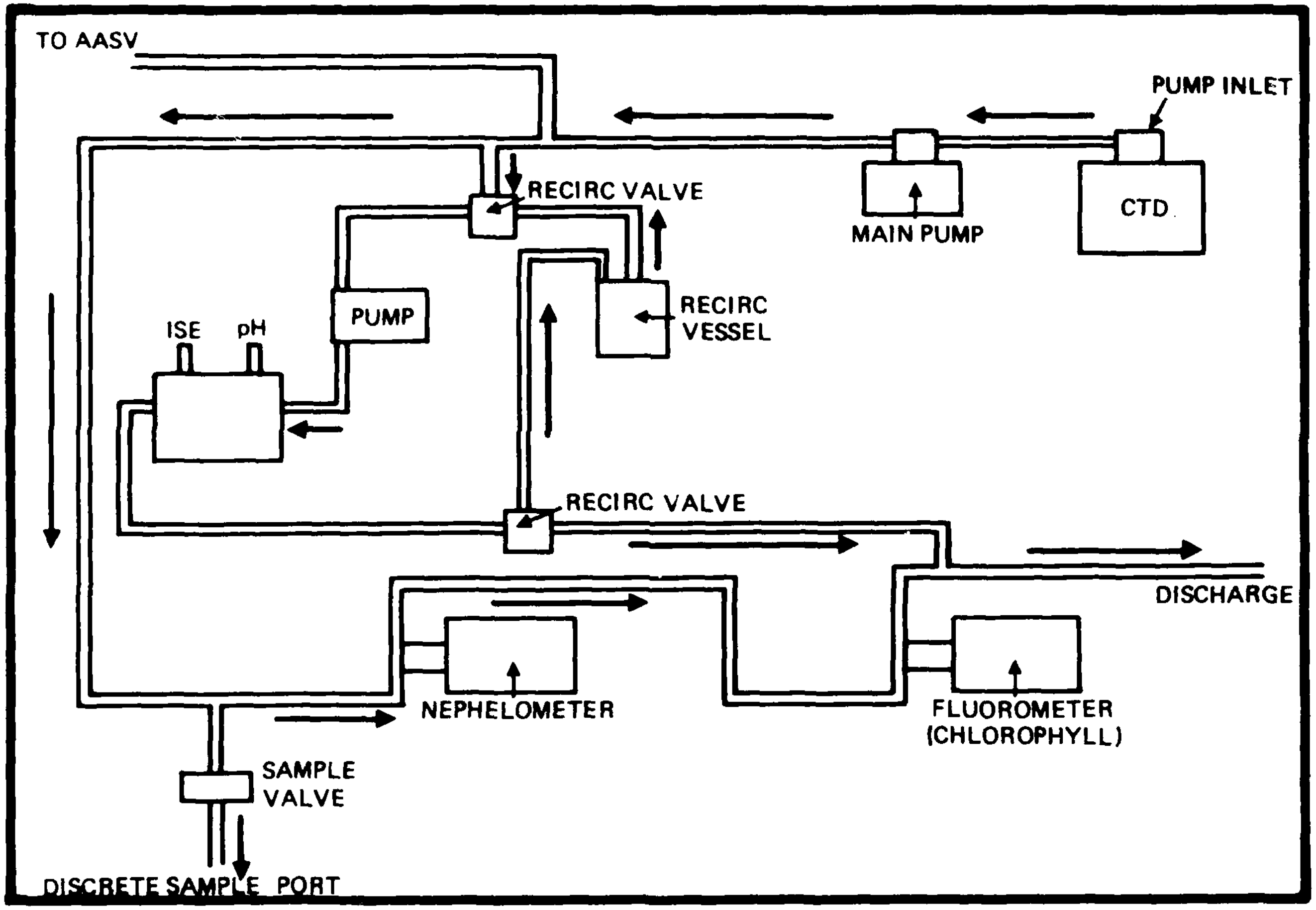


Figure 1. Schematic of the MESC measurement/instrumentation system.

to a spatial resolution of 2 meters. Five- to thirty-second sampling intervals were used for tidal stations.

Calibration Procedures. The CTD system (temperature, conductivity, percent transmittance, dissolved oxygen, and probe depth) was calibrated by the manufacturer (Interocean Systems, San Diego) prior to the field operation. The pH electrode was calibrated against standard buffer solutions periodically during the operation. Nephelometer measurements were calibrated against a standard curve generated by adding formazine standard to 0.45 μ-filtered seawater (American Public Health Association, 1980).

Cu-ISE mV response was recorded directly. No attempt was made to calibrate the ISE in terms of Cu^{2+} because measured potentials in seawater do not represent equilibrium potentials in the thermodynamic sense (Zirino & Seligman, 1981). In spite of the non-Nerstian behavior of the electrode, measurements in seawater (Williams & Baldwin, 1976; Zirino et al. 1980) have shown increasingly positive potentials correlate with higher copper concentrations as measured by other analytical techniques. In addition, Sunda and Guillard (1976) have presented convincing evidence showing it is the Cu^{2+} activity (a quantity closely related to the copper measured by the ISE) and not the total copper concentration that determines the toxicity to planktonic organisms. With the above qualifications in mind, the Cu-ISE potential should be viewed as an indicator of Cu^{2+} in seawater and not as a measure of the total copper. Even though the Cu-ISE measurements are not directly comparable with other copper measurements, the electrode provides useful information because it is the only method that provides a continuous signal. Furthermore, the potential measured by the electrode appears to have important significance with respect to the fraction of copper that is toxic to organisms.

ASV measurements are also sensitive to the form or speciation of copper in seawater. Under acid conditions, ASV measures that fraction of the total copper in the free or ionic state and all complexes that can be reduced at the electrode. Metal strongly bound to dissolved complexes or associated with the particulate material may not be measured by this technique. ASV measurements are useful because they provide a near-real-time means of field analysis not possible with traditional laboratory procedures.

Cu-ISE and ASV measurements both provide a framework for selecting sampling sites and interpreting results for discrete measurements of copper by atomic absorption (AA) spectrophotometry. This provides a unique capability for tracking plumes and locating point sources.

Discrete Sampling Procedures. All samples collected for discrete copper analyses were collected in 250-mL polyethylene bottles soaked in a nonionic detergent for several hours, rinsed with deionized water several times, soaked in 8 N HNO_3 for at least 48 hours, and then rinsed at least three times with ultrahigh purity (Milli-Q) deionized water (Millipore Corp.). In the field, each sample bottle was rinsed with three aliquots of the sample before the final sample was collected. Several workers have shown that rigorous cleaning of sample containers and careful sample handling procedures are required to avoid sample contamination (e.g., Bruland et al., 1979). After collection, samples were acidified to pH 2 with Ultrex nitric acid.

Samples for ASV analyses were either collected automatically by the ASV instrument, which was connected to the pumped seawater system, or collected from the sampling port on the manifold in precleaned sample bottles. ASV samples collected online were acidified and analyzed immediately. Samples collected in bottles were acidified to pH 2 and analyzed within 24 hours.

Copper samples analyzed by graphite furnace AA spectrophotometry were collected from the sample port on the pumping system. Samples were stored in precleaned polyethylene bottles, acidified to pH 2 immediately after collection, and returned to the laboratory for analysis.

Laboratory Copper Analyses. Copper was determined using the atomic absorption-furnace technique (Method 220.2, EPA 1983). Measurements were made on a Perkin-Elmer 5000 spectrophotometer equipped with an HGA-2000 graphite furnace. For all analyses, 75-µL injections of a 1:4 dilution of the acid-digested sample were used. The detection limit of the method for these conditions is approximately 1 µg/L.

Experimental Plan. To determine whether there was a significant difference in the concentrations of copper in specific regions within Kings Bay and Cumberland Sound, the study area was divided into three regions: UPPER - the Upper Turning Basin of Kings Bay, LOWER - the Lower Turning Basin of Kings Bay, and SOUND - the Cumberland Sound area (see Figure 2). Horizontal mapping and discrete copper samples were taken in each region during flood and ebb tide. Six copper ASV samples and six copper AA samples were taken in each region during both tidal states. An analysis of variance (ANOVA) was performed on the data to determine whether significant differences exist between tidal state, location, and the interaction between tidal state and location. The effect of tidal variability was observed by collecting continuous data while the craft was moored to the ARDM pier. The effect of dewatering the dredge spoil containment area was observed by anchoring the survey platform in an area receiving the effluent and collecting continuous data during the dewatering operation.

RESULTS

Table 2 lists the date, time, and type of measurement conducted during the study. The complete suite of data from the three measurement series (i.e., underway mapping survey, tidal monitoring stations, and effluent monitoring station) is presented in Appendices A, B, and C, respectively. Locations of the outfall station, tidal monitoring station, and underway mapping areas are shown in Figure 2. So data can be referenced to tidal state, Figure 3 shows times and heights of high and low waters calculated for the period of 15 to 24 January at the Crooked River entrance station.

Underway Mapping Surveys. For each underway mapping survey (Appendix A), a time-series plot showing Cu-ISE response, chlorophyll fluorescence, pH, percent relative light transmission, dissolved oxygen, salinity, temperature, and bottom depth is presented. This is followed by a map (or maps) showing the corresponding cruise track of the survey craft. Times corresponding to turning points and/or navigational fixes are

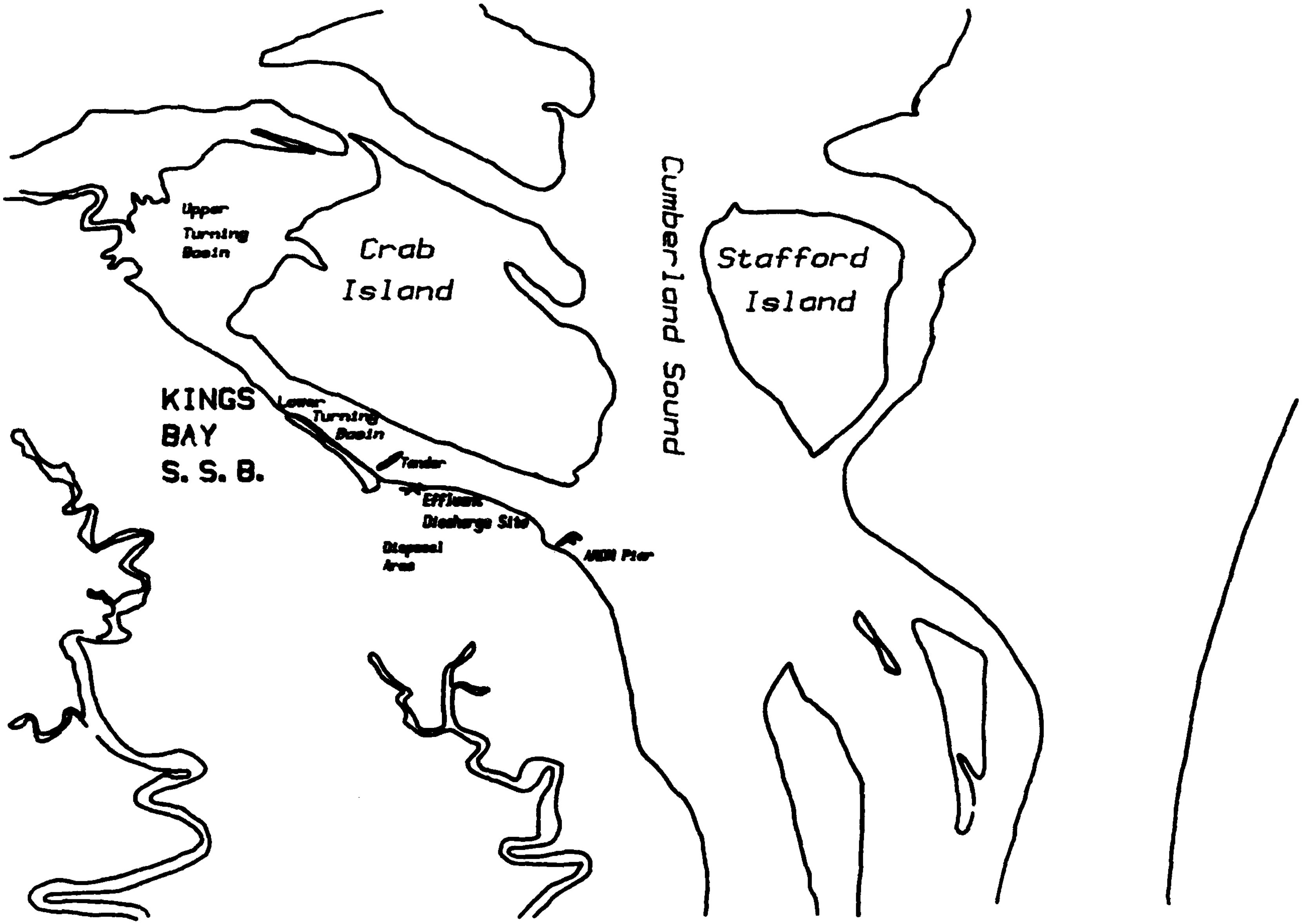


Figure 2. Location of sampling areas in the Kings Bay-Cumberland Sound region.

Table 2. Date, time, type of measurement, and location

Date	Time	Type of Measurement	Location
15-16 Jan	1918-0700	Tidal Monitoring	ARDM Pier
16 Jan	1640-1806	Underway Mapping	CS
16-17 Jan	1840-1010	Tidal Monitoring	ARDM Pier
17 Jan	1105-1155	Effluent Monitoring	Outfall
17 Jan	1336-1656	Effluent Monitoring	Outfall
17 Jan	1735-1750	Effluent Monitoring	Outfall
17-18 Jan	1818-0130	Effluent Monitoring	Outfall
19 Jan	1048-1215	Underway Mapping	LB,UB
19 Jan	1229-1345	Underway Mapping	UB,LB
19 Jan	1346-1524	Underway Mapping	LB,CS
19 Jan	1524-1654	Underway Mapping	CS,LB,UB
19 Jan	1655-1819	Underway Mapping	UB,LB,CS
19-20 Jan	1953-0611	Tidal Monitoring	ARDM Pier
20-21 Jan	1615-1206	Tidal Monitoring	ARDM Pier
21 Jan	1524-1650	Underway Mapping	LB
22 Jan	1537-1922	Tidal Monitoring	ARDM Pier
22-23 Jan	2057-1154	Tidal Monitoring	ARDM Pier

Key: CS=Cumberland Sound
LB=Lower Turning Basin-Kings Bay
UB=Upper Turning Basin-Kings Bay

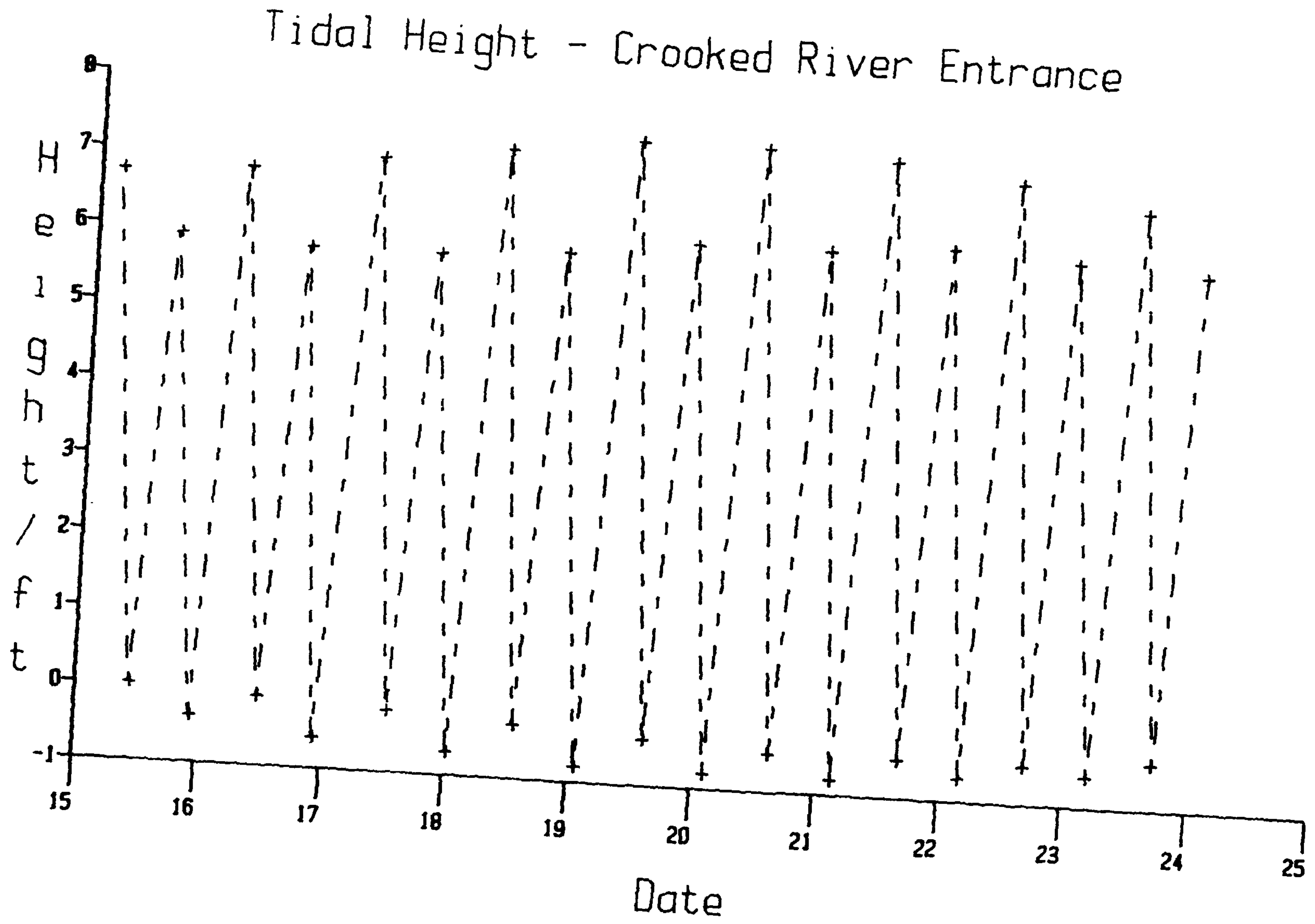


Figure 3. Tidal height versus time for 15 to 24 January 1985 at the Crooked River entrance.

provided along the cruise track to relate the time-series data to geographic location. Finally, a map (or maps) shows the location, as determined by interpolation from the time of collection and bracketing navigational fixes, of each discrete copper sample collected during that set of time-series measurements. The discrete sample chart facilitates comparison of discrete copper measurements with ancillary underway data.

Measurements (Figure A-1) conducted 16 January along a cruise track (Figure A-2) proceeding from ARDM pier into Cumberland Sound to the north end of Stafford Island and back along approximately the same cruise track show only minor changes. Because nearly the same track was followed on the northern transect as on the return transect to the south, there is an obvious symmetry to the data. The most significant feature is a small temperature-salinity front (temperature gradient less than 0.5°C-salinity gradient less than 0.5°/oo) located approximately midway along the axis of Stafford Island. Although dissolved oxygen and light transmission showed higher values in this colder, less saline water, chlorophyll fluorescence and Cu-ISE response remained nearly constant.

The most intensive mapping of the Kings Bay-Cumberland Sound area was conducted on 19 January. Figures 4a and 4b show a composite cruise track of the coverage obtained. Because of the overlap in coverage resulting from repeated transects through the area, the data are divided into separate segments. Separate track charts are given in Appendix A for each segment of the time-series data.

The comprehensive mapping program conducted on January 19 is the result of the experimental sampling plan designed to test for differences in copper concentrations between the Upper Basin, Lower Basin, and Cumberland Sound during ebb and flood tides. In addition to continuous underway mapping with the Cu-ISE, at least six samples for ASV and laboratory AA analysis were collected in each of the three areas during each tidal stage. Figures 5a and 5b show the location of the discrete samples collected. Charts showing the time each copper sample was measured or collected and the corresponding value from each of the three methods (Cu-ISE, ASV, and AA) are given in Appendix D.

Sampling to determine differences in copper concentrations within the study area was conducted during one tidal cycle to minimize variability from other sources. For example, if measurements are made on different days, an event such as a storm could produce changes in fresh water input, physical mixing, sediment load, etc. These processes introduce a source of temporal variability that is difficult to resolve from the spatial variability of interest in this study.

Data from underway measurements on January 19 (Figures A-4, A-9, A-12, A-17, and A-22) show that waters in Kings Bay and Cumberland Sound are, in general, quite well mixed. Relatively small changes in water quality parameters were observed over the survey area. Nominal ranges in values were as follows: temperature - 11.0 to 11.5°C, salinity - 30.5 to 31.5°/oo; dissolved oxygen - 8.0 to 8.5 mg L^{-1}; percent light transmission - 65 to 85 percent; and pH - 7.9 to 8.2. The Cu-ISE electrode response showed the greatest range in values, varying between -40 and -200 mV.

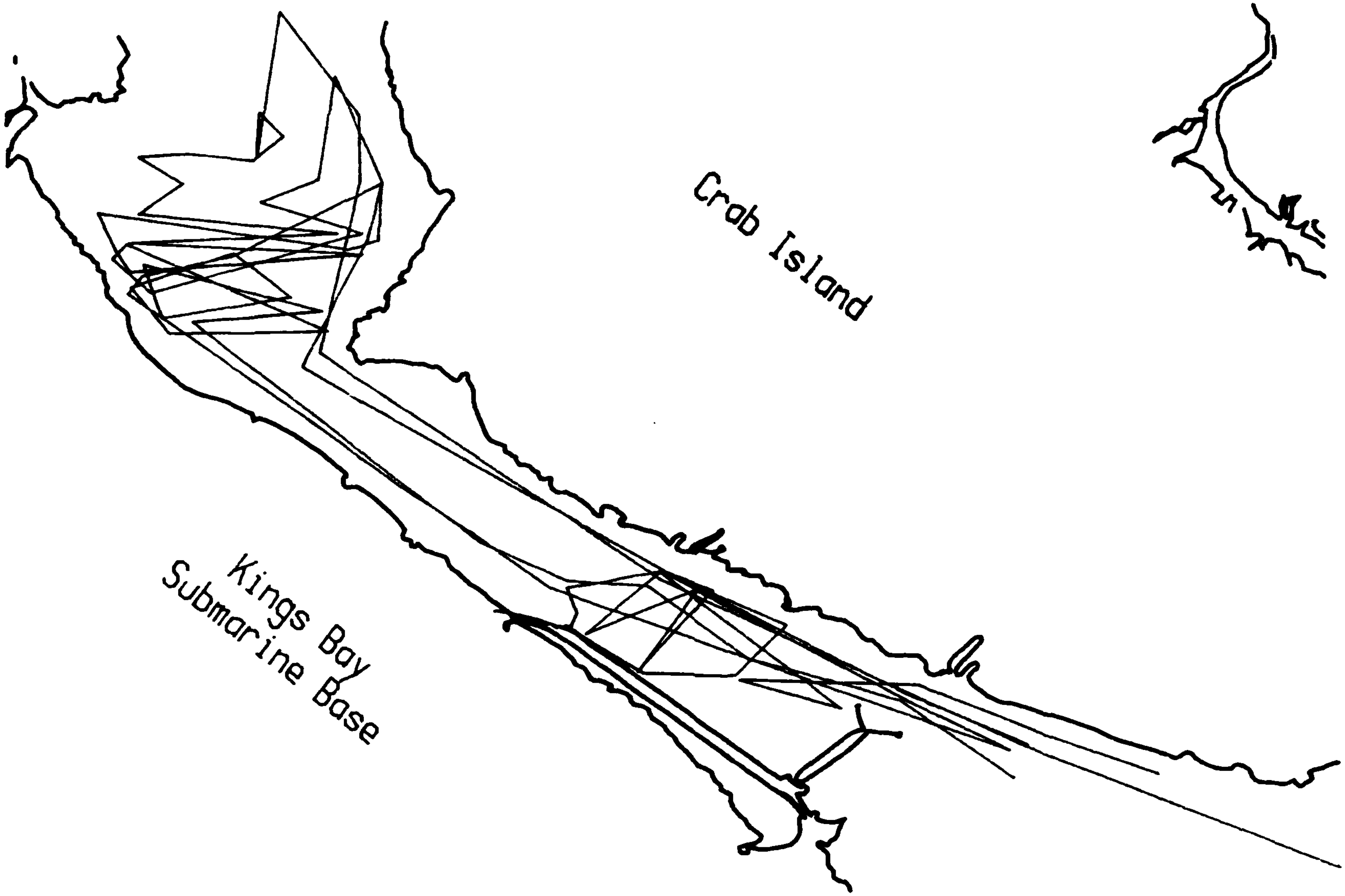


Figure 4a. Composite cruise track showing area coverage obtained during underway mapping conducted 19 January 1985: Upper Turning Basin and Lower Turning Basin. Time-series data from underway measurements are divided into separate segments, each with a corresponding track chart, in Appendix A.

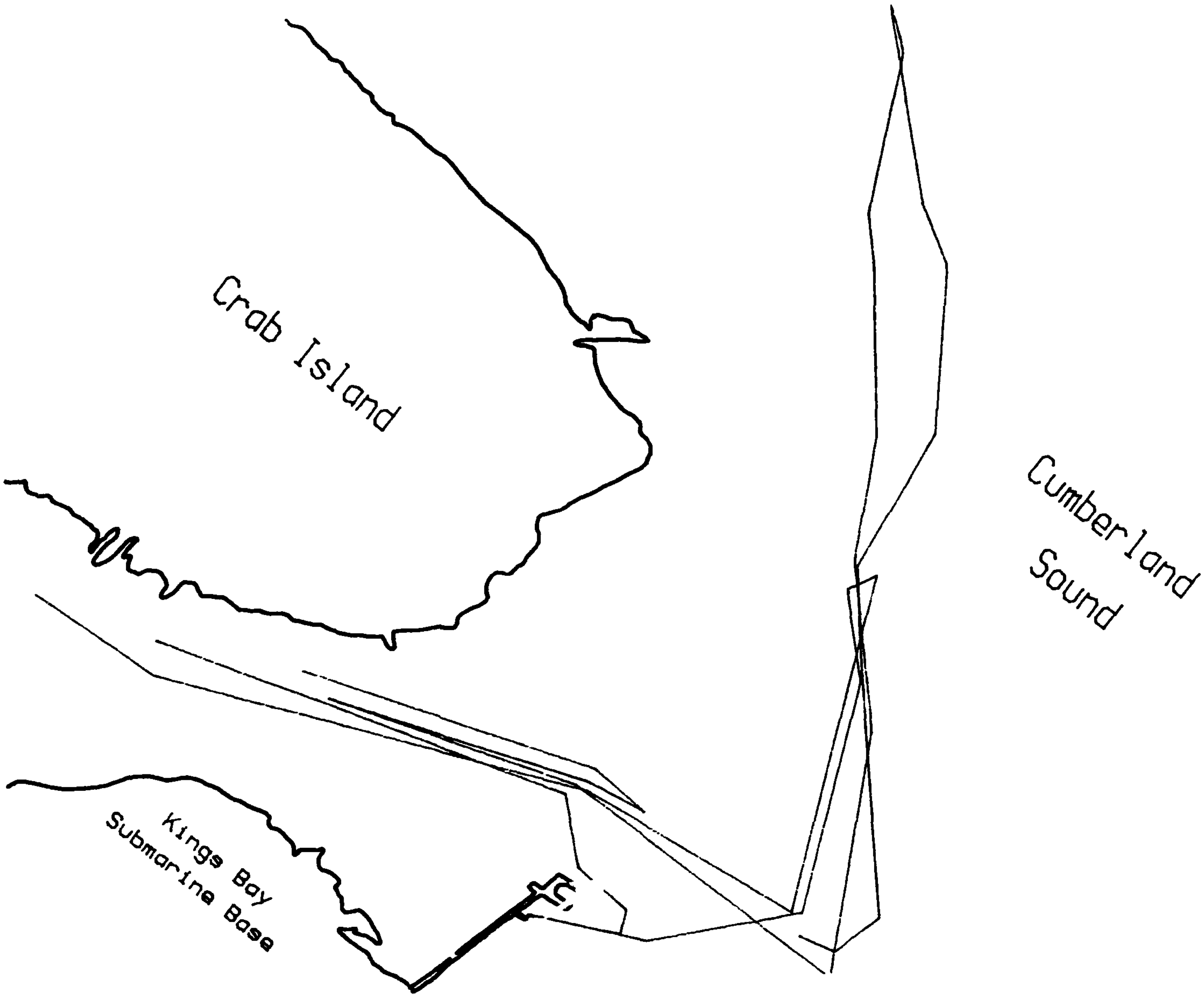


Figure 4b. Composite cruise track showing area coverage obtained during underway mapping conducted 19 January 1985: Cumberland Sound. Time-series data from underway measurements are divided into separate segments, each with a corresponding track chart, in Appendix A.

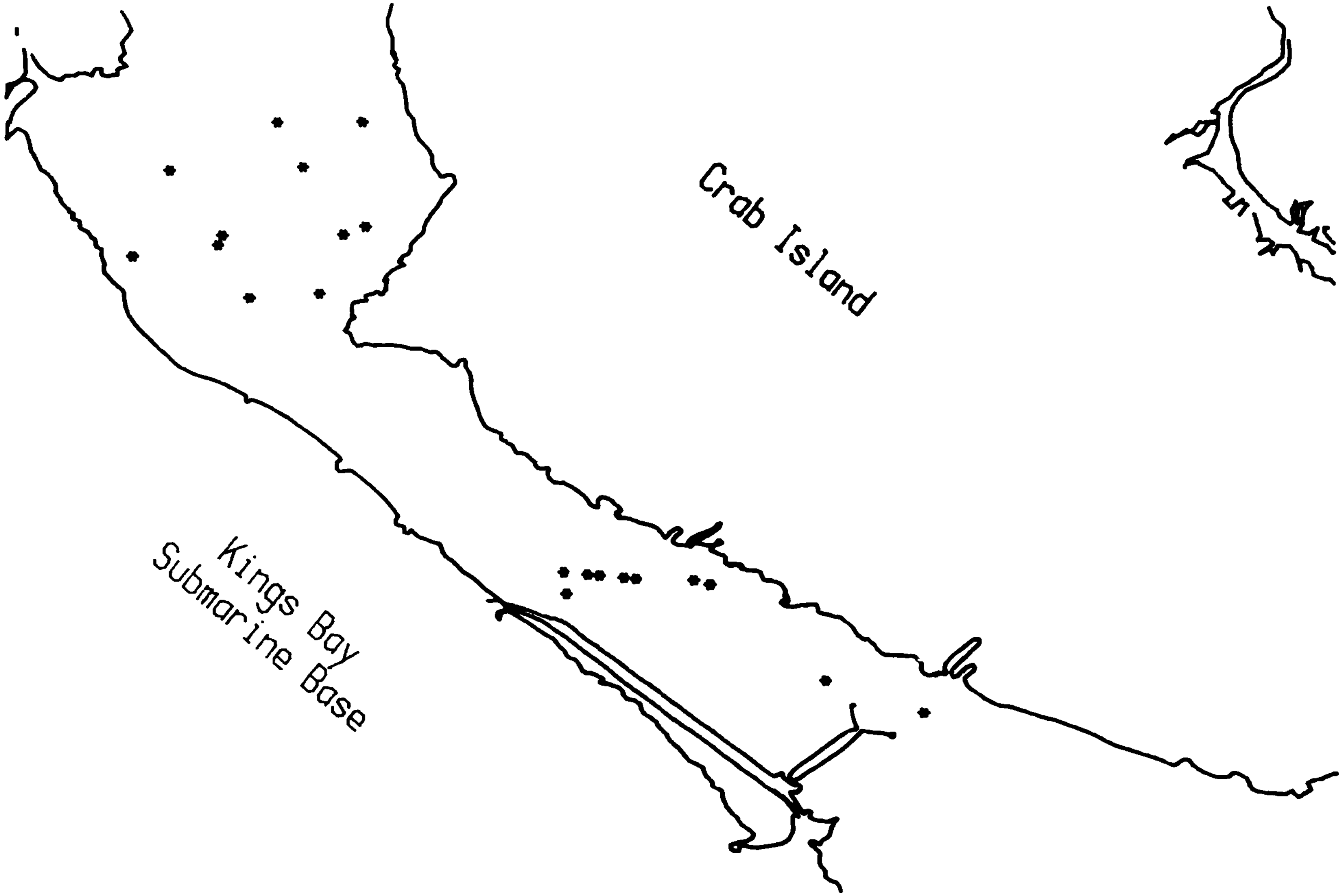


Figure 5a. Locations of discrete samples collected during sampling on 19 January 1985: Upper Turning Basin and Lower Turning Basin. Charts showing copper values determined by graphite furnace AA, automated ASV, and Cu-ISE as a function of location and tidal stage are presented in Appendix D.

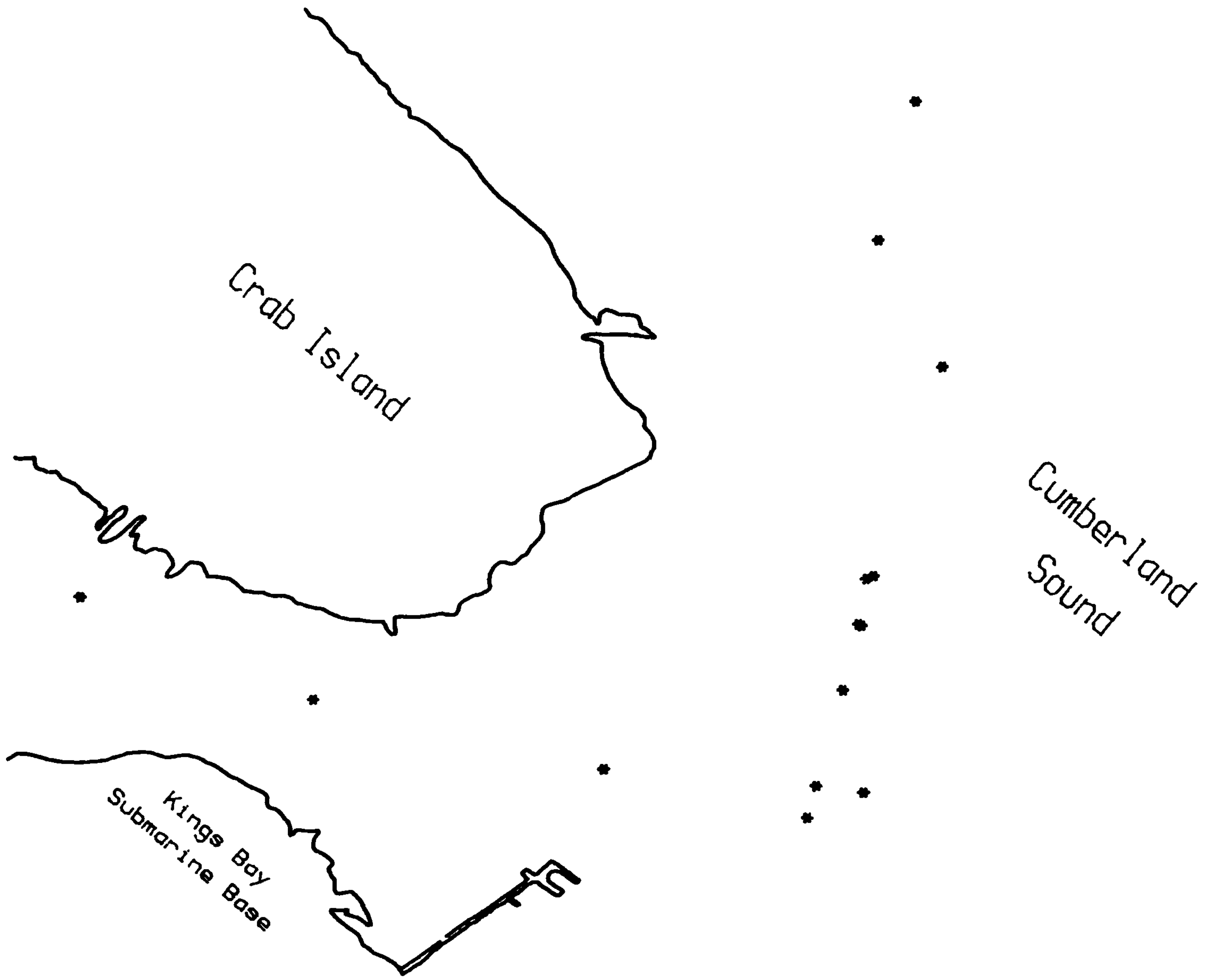


Figure 5b. Locations of discrete samples collected during sampling on 19 January 1985: Cumberland Sound. Charts showing copper values determined by graphite furnace AA, automated ASV, and Cu-ISE as a function of location and tidal stage are presented in Appendix D.

The greatest change in copper electrode response was observed in the Lower Basin in the shallow waters (shoal waters) along the coast of Crab Island. Figure A-12 shows that when the survey craft approached the shore of Crab Island, as indicated by decreasing bottom depth, decreases were observed in light transmission and Cu^{2+} activity measured with the Cu-ISE. Details of these events are more easily seen in Figures 6 and 7, which show two segments of the time-series data replotted using expanded scales. The data show decreases in Cu^{2-} activity (more negative potential) associated with decreases in bottom depth and light transmission and increases in temperature every time the survey craft approached the shore of Crab Island. The effect of temperature on the Cu-ISE in natural seawater has been determined to be -1.5 mV/°C (Rice & Jasinski, 1976). During mapping intervals, observed temperature changes were less than 1°C and observed changes in Cu-ISE were frequently greater than 100 mV. Therefore, temperature effects on the Cu-ISE were negligible. Note that decreases in Cu^{2+} activity were not observed in shallow waters in Cumberland Sound (e.g., Figure A-12, 1454 to 1524) or in shallow waters in the Upper Basin (e.g., Figure A-9, 1228 to 1300).

Results of copper measurements for the Upper Basin, Lower Basin, and Sound under ebb and flood tidal conditions are presented in Table 3. Discrete samples for shipboard ASV analysis and laboratory graphite furnace-AA analysis were collected from the pumped seawater system using procedures described in the methods section. Sampling was coordinated to provide complementary samples for both methods. Cu^{2-} activity measured using the Cu-ISE was obtained by extracting values from the continuous record that correspond to the times discrete samples were collected for ASV and AA analysis. AA values ranged from 1.2 to 5.8 µg/L and ASV values ranged from 0.3 to 2.2 µg/L. These values are much lower than those recently reported for Kings Bay and Cumberland Sound (NAVFACENGCOM, 1984). Cu^{2-} electrode response ranged from a low of -120 mV to a high of -40 mV.

Mean values measured by AA, ASV, and the Cu-ISE are compared as a function of location (area) and tidal state using bar graphs in Figures 8a, 8b, and 8c. Compared to the Upper Basin and the Sound, AA values indicate higher copper concentrations in the Lower Basin of Kings Bay under both ebb and flood tides. Both ASV and Cu^{2+} electrode measurements suggest slightly higher values in all areas during the flood tidal stage.

A two-way nested ANOVA was performed to determine whether a significant difference exists in the mean copper concentration between/within different locations and tidal stages. The sample groupings compared by the model are listed in Table 4. The three locations are as defined earlier in Figure 2 (Upper Turning Basin, Lower Turning Basin, and Cumberland Sound). The ANOVA results are shown in Tables 5a and 5b. Separate analyses were run on ASV and AA measurements. No significant differences were found between any groupings for ASV-determined concentrations ($p>0.05$). However, for the AA-analyzed samples, a highly significant difference was found for sample location ($p<0.0001$). The major source of variability was attributed to sample location. Levels measured in the Lower Turning Basin were higher than those determined in the Upper Turning Basin or Cumberland Sound.

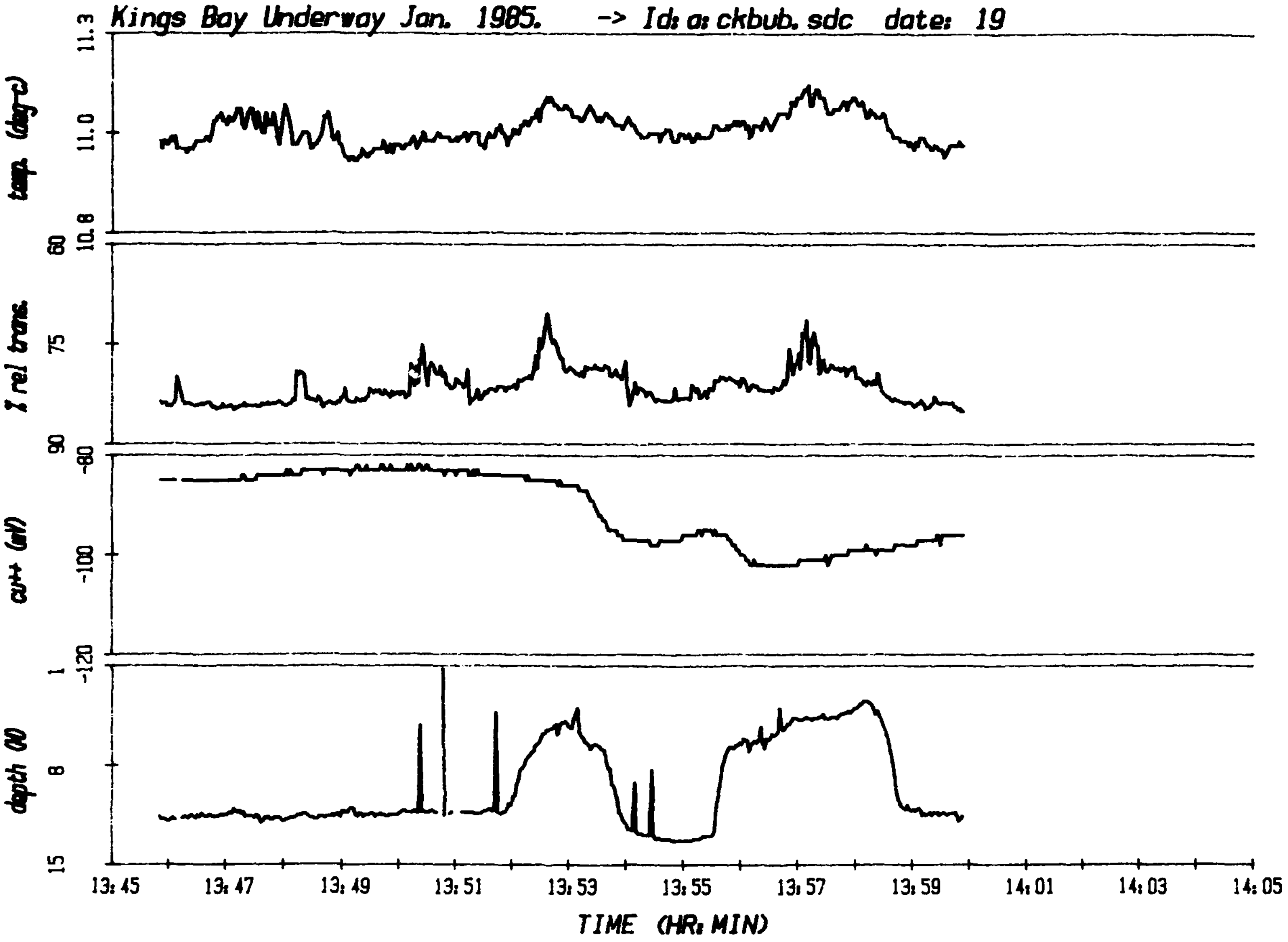


Figure 6. Expanded plot of time-series data from underway mapping conducted on 19 January 1985 in the Lower Turning Basin, Kings Bay. Note, more negative Cu-ISE potentials correlate with decreased bottom depth, higher water temperature, and lower light transmission.

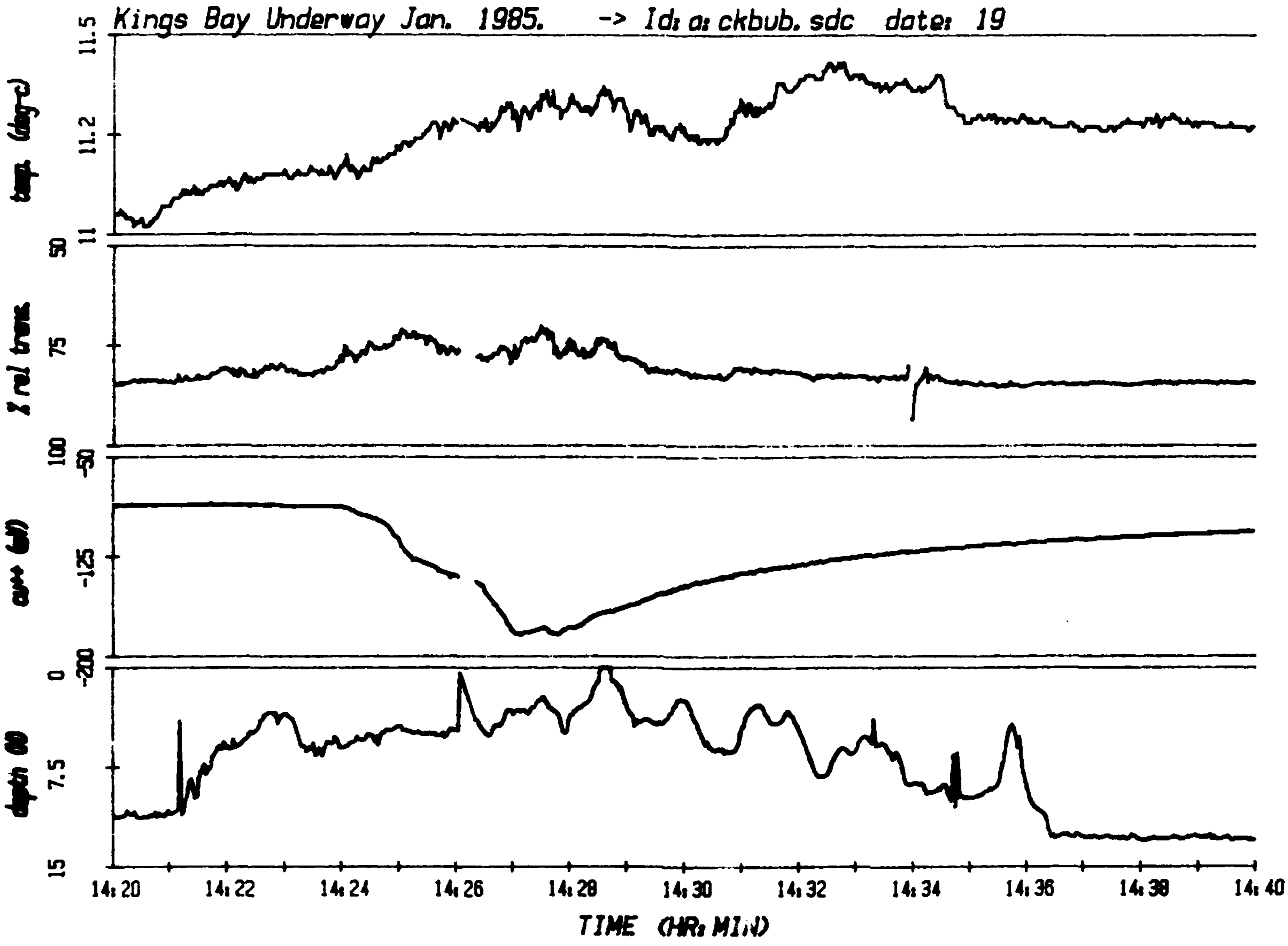


Figure 7. Expanded plot of time-series data from underway mapping conducted 19 January 1985 in the Lower Turning Basin, Kings Bay.

Table 3. Discrete copper ASV, AA values, and Cu electrode responses for Kings Bay and Cumberland Sound (19 January 1985).

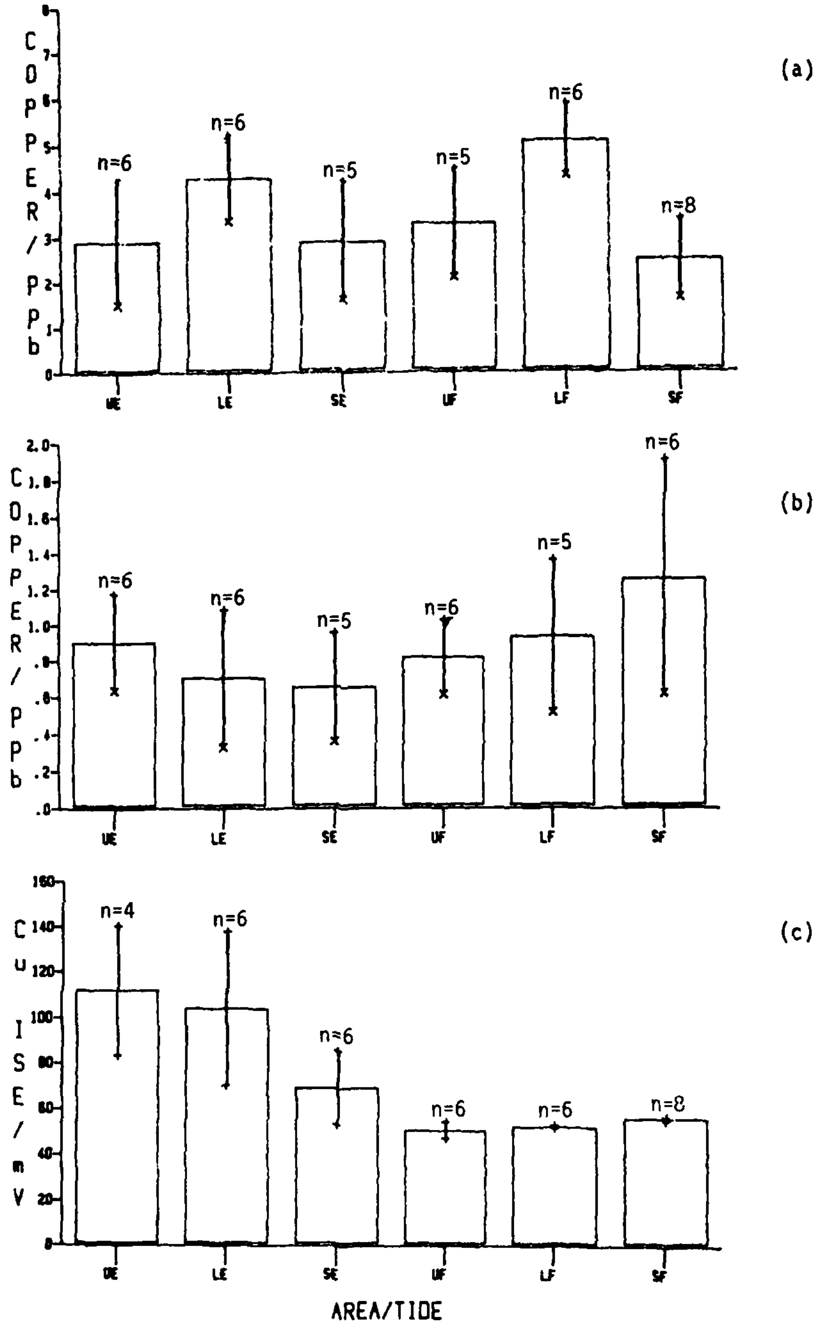
Area/Tide	Time		Cu^{2+} (mV)	ASV (μg/L)	AA (μg/L)
Upper/Ebb	1183		-56	1.26	3.2
"	1150		-60.5	0.81	3.5
"	1204		-229*	0.76	5.2
"	1218		nd	0.51	1.8
"	1231		-113	1.15	1.8
"	1244		-102	0.92	1.8
		Mean =	-89.9	0.90	2.9
		*SD =	-28.5	0.27	1.4
Lower/Ebb	1330		-83	0.58	4.0
"	1350		-83	0.65	5.4
"	1355		-96	0.97	5.3
"	1407		-86	0.39	2.9
"	1421		-86	1.33	4.5
"	1434		-121	0.31	3.9
		Mean =	-104	0.71	4.3
		*SD =	-33.9	0.38	0.94
Sound/Ebb	1504		-85	0.45	3.5
"	1515		-80	0.48	3.7
"	1528		-70	1.16	4.1
"	1540		-70	0.72	1.9
"	1554		-43	0.46	1.2
		Mean =	-69.6	0.65	2.9
		*SD =	-16.2	0.30	1.3

* Contamination suspected; value not included in statistics.

Table 3. Discrete copper ASV, AA values, and Cu electrode responses for Kings Bay and Cumberland Sound (19 January 1985). (continued)

Area/Tide	Time	Cu^{2+} (mV)	ASV (μg/L)	AA (μg/L)
Upper/Flood	1631	-53	0.57	3.3
"	1644	-44	1.11	3.6
"	1657	-51	0.69	5.2
"	1711	-51	1.05	1.9
"	1720	-53	0.75	2.6
"	1724	-54	0.75	
	Mean =	-51.0	0.82	3.3
	±SD =	-3.6	0.21	1.2
Lower/Flood	1731	-52	12.3	3.7
"	1733	-53	1.3	5.3
"	1734	-52	0.77	5.2
"	1736	-53	0.32	5.1
"	1737	-53	1.37	5.8
"	1740	-53	0.93	5.8
	Mean =	-53	0.94	5.1
	±SD =	-0.5	0.43	0.77
Sound/Flood	1750	-56	0.60	3.9
"	1751	-56	0.62	3.2
"	1752	-56		3.1
"	1753	-56		1.8
"	1754	-56	1.86	2.4
"	1756	-57	1.09	1.6
"	1757	-57	2.19	2.4
"	1759	-58	1.23	1.6
	Mean =	-56.5	1.27	2.5
	±SD =	-0.8	0.65	0.88

* Contamination suspected; value not included in statistics.



UE = Upper Turning Basin/ebb tide
UF = Upper Turning Basin/flood tide
LE = Lower Turning Basin/ebb tide
LF = Lower Turning Basin/flood tide
SE = Cumberland Sound/ebb tide
SF = Cumberland Sound/flood tide

Standard deviations about each mean are indicated on the figure.

Figure 8. Bar graphs showing mean copper concentrations measured by (a) Graphite Furnace AA, (b) Automated ASV, and (c) CU-ISE as a function of location (area) and tidal stage.

Table 4. Sample categories used in the ANOVA.

Category	Description
Tidal State	Comparison of pooled samples taken at ebb versus flood tide.
Location	Comparison of pooled ebb and flood tide measurements in the three areas.
Tidal State X Location Interaction	Comparison of mean concentrations at three locations of ebb versus flood tide measurements.

Table 5a: ANOVA table for ASV data.

Source of Variation	df	SS	MS	F	P
Tidal State	1	0.51297	0.51297	3.34519	NS .10 > P > .05
Location	2	0.182437	0.091219	0.56373	NS P > .10
Tide X Location Interaction	2	0.64492	0.32246	1.99278	NS P > .10
Error	28	4.53078	0.16184		

Critical $F_{[.05]:1,28} = 4.2$ $F_{[.10]:1,28} = 2.89$

$F_{[.05]:2,28} = 3.34$ $F_{[.10]:2,28} = 2.50$

Table 5b. ANOVA table for AA data.

Source of Variation	df	SS	MS	F	P
Tidal State	1	0.253195	0.253195	0.21973	NS P > .10
Location	2	29.221566	14.61078	12.6795	** P < .0001
Tide X Location Interaction	2	2.583314	1.296155	1.12092	NS P > .10
Error	30	34.569448	1.152315		

Critical $F_{[.05]:1,30} = 4.17$ $F_{[.10]:1,30} = 2.88$

$F_{[.05]:2,30} = 3.32$ $F_{[.10]:2,30} = 2.49$

Tidal Monitoring Stations. Tidal monitoring stations were established to evaluate variability in copper and other data as a function of time. The ARDM pier location was selected because of its relative proximity to Cumberland Sound and the ease of sample collection. We reasoned that if there were any significant differences between the waters of Kings Bay and Cumberland Sound, this location would provide an opportunity to document these differences as a function of tidal state. Time-series data are presented in Appendix B. The parameters are the same as those in the underway measurements. Because position is fixed, bottom depth can be used as a measure of the tidal state.

Continuous tidal monitoring data (Figures B-1 to B-10) show the variability observed at a fixed location in a dynamic estuarine environment. For example, Figure B-6 shows that for a tidal range of approximately 2 meters, temperature ranged approximately 2°C, percent of light transmission varied by 40 percent, and Cu-ISE response varied by more than 100 mV. A common feature observed in all the tidal station data was a decrease in Cu-ISE electrode response (more negative potentials), a decrease in light transmission, and a decrease in temperature that usually occurred just after low tide. Because the sensors were fixed to the survey craft, which moved up and down with the tide, we could not be sure whether the observed changes were a function of the distance the sensors were off the bottom or were due to resuspension of bottom sediments by tidal currents.

Effluent Monitoring. During the study period, dewatering of the Mainside Disposal Area was conducted. Effluent from the dewatering operation flowed through a channel and entered Lower Kings Bay at a point southeast of SIMON LAKE (Figure 2). This provided an opportunity to attempt to locate and characterize the effluent from the dredge spoils containment area at its point of entry into Kings Bay. Continuous data were (Figure C-1) collected as the survey craft moved from its ARDM pier berth to a location where the effluent was draining into Kings Bay, and data were collected while the craft was anchored at the mouth of the drainage channel through a tidal cycle (Figures C-2, C-3, and C-4) show the effluent could easily be distinguished from ambient Kings Bay water by major differences in its properties. Figures C-1, C-2, and C-4 show that the effluent water was warmer, more saline, showed lower relative light transmission, higher pH, higher fluorescence, and a dramatically more negative Cu-ISE response. We believe the sharp gradients observed in the continuous data were due to the effluent plume drifting in and out of the vicinity of the CTD and hose intake.

Mean values for discrete ASV and AA samples (Table 6) collected during the effluent monitoring were similar to mean values determined for the Lower Basin during the mapping survey. When time-series data were used to separate the discrete samples on the basis of whether the craft was sampling the effluent plume or the ambient water (Table 5), a standard t-test showed there was no significant difference between the means of ASV ($p>0.25$) and AA values ($0.25>p>0.10$) for the two waters.

DISCUSSION

A significant result from this study was that copper concentrations were lower than the 10 to 38 μg/L levels measured during the 1982-83 period (NAVFACENGCOM, 1984). During this survey, concentrations determined by graphite furnace AA did not exceed

Table 6. Discrete copper ASV and AA values in the area of the effluent outfall.

Time	ASV (µg/L)	AA (µg/L)
1250	0.80	2.6
1322	0.2	2.6
1400	0.74	1.9
1438	0.50	2.6@
1508	0.43	3.3
1604	0.71	3.3
1643	0.57	4.0
1719	1.0	3.3
1734	0.50	1.2
1758	0.65	2.6
1931	1.5	3.3
2012	0.58	5.8
2048	1.0	5.1@
2139	0.53	5.1@
2205	0.97	5.8@
2245	0.24	6.6@
2324	0.52	2.4@
0003	1.0	2.4@
0041	0.41	2.4@

		ASV	AA
All Data -	Mean =	0.73	3.7
	*SD =	0.32	1.6
In Plume	Mean =	0.64	4.1
	*SD =	0.30	1.8
Out of Plume	Mean =	0.72	3.3
	*SD =	0.36	1.5

@ In Effluent Plume

6 μg/L. Mean AA values for the Upper and Lower Turning Basins in Kings Bay ranged from 2.5 to 5.1 μg/L. There are several possible explanations for the lower values observed in this study.

Major construction dredging activity concurrent with the 1982-83 sampling period may have produced short-term increases in copper levels in Kings Bay and Cumberland Sound. Construction dredging could lead to higher concentrations of copper in the water column through resuspension and/or oxidation with subsequent solubilization of insoluble copper complexes from the bottom sediments. Release of copper from bottom sediments and resuspension of bottom sediments have been proposed (Windom et al., 1983) to explain dissolved copper concentrations measured at salinities between 30 and 36°/oo in other estuarine waters in Georgia.

Another possible source of copper is dissolution of carbonaceous material blasted during construction dredging. Chemical analyses of carbonate sediment slurry mixtures showed higher concentrations of dissolved copper than did slurries of clays and silts (Alvarez, Lehman & Associates, Inc., 1984).

In contrast to the 1982-83 period, no dredging activity had taken place for 1 to 2 months prior to the sampling effort reported here. The lower copper values measured in this study suggest that whatever the mechanism responsible for increased copper levels in the water column (resuspension of bottom sediments, release from carbonaceous sediments, etc.), the effect is probably only short term.

Values of copper measured in Kings Bay and Cumberland Sound during this study approach concentrations determined in other estuarine systems along the southeast coast of the US. Windom et al. (1983) measured total copper concentrations (dissolved + particulate) in waters with salinities greater than 25°/oo of about 1.3 and 1.0 μg/L-1 for the Savannah and Ogeechee estuaries, respectively. The ranges of copper concentrations documented for water samples from Kings Bay are reported in NAVFACENGCOM (1984). The ranges reported were 2 to 18 μg/L for the 1976-77 Environmental Impact Statement (EIS), <10 to 20 μg/L for 1980-81 environmental monitoring, 38 to 55 μg/L for 1981-82 environmental monitoring, and 10 to 38 μg/L for 1982-83 environmental monitoring. These values suggest increases in copper associated with increased dredging occurring from 1978 to 1983.

Great care must be taken when comparing concentrations measured by different analytical techniques. Various methods for measuring copper measure different fractions of the total copper present in the seawater sample. Total copper is often divided into a dissolved and a particulate fraction defined by filtration of the sample through a 0.45 μm filter. The dissolved fraction can be further divided into three classes: (1) the ionic and labile forms, (2) inorganic complexes and colloids and weak organic complexes, and (3) strongly bound organic complexes and colloids (Zirino, 1981). The Cu-ISE measures only the ionic fraction. Analysis by ASV at pH 2 measures the ionic and labile as well as some of the copper associated with weakly bound complexes and colloids. Analysis by AA spectroscopy following acid digestion measures the copper associated with classes 1,

2. and 3 as well as copper leached from the particulate component during acid digestion. Copper measured after acid digestion of the sample is designated as the "total soluble" fraction because this procedure transcends the fractionation produced by filtering. The important point is there is no single correct procedure for measuring copper or any other trace metal. Different methods measured different fractions of the total. These different fractions may have special significance depending on the chemical, biological, or geological process of concern.

Collection of noncontaminated copper samples is a nontrival exercise and could be one possible reason why the 1982-83 copper values were higher. Only recently have copper measurements in the marine environment produced results that give distributions consistent with controlling physical, chemical, and biological processes (Boyle & Edmond, 1977). These results were obtained only after instituting special procedures, including rigorous cleaning of sample containers and extremely careful sampling and analytical techniques. Procedures described for collecting samples for the 1982-83 samples do not mention how sample containers were cleaned (NAVFACENGCOM, 1984). In addition, the report stated that water samples were introduced directly into bottles containing required amounts of acid. This obviously precluded rinsing of the sample container with the sample.

A second important observation is the results of this survey do not support the existence of a point source of copper in Kings Bay. In fact, Cu-ISE measurements showed increasingly negative potentials (indicating lower Cu^{2+} activities) in the effluent stream entering Kings Bay from the Mainside Disposal Area and in the shallow waters along the shore of Crab Island. We believe that higher concentrations of dissolved organics may be responsible for the more negative Cu-ISE potentials in these waters. This hypothesis is supported by the correlation of higher levels of chlorophyll fluorescence and lower light transmission with more negative Cu-ISE potentials in the effluent waters. Lower light transmission and more negative ISE potentials were also observed in the shoal waters off Crab Island. The implication is that organic compounds complex dissolved copper, which lowers the Cu^{2+} activity. Compared to ambient waters in Kings Bay, measurements have shown that the effluent from the Mainside Disposal Area has significantly higher concentrations of total organic carbon, ammonia, and nitrogen (Alvarez, Lehman & Associates, Inc., 1985). In the shoal waters off Crab Island, negative Cu-ISE potentials may reflect the influence of organic ligands associated with the resuspension of bottom sediments in the shallow water column. Increasingly, negative Cu-ISE values associated with decreasing light transmission were also observed following low tide at tidal monitoring stations. Resuspension of organic rich bottom sediments may be responsible for these observations as well.

Another possible explanation is the numerous streamlets that drain the marsh on Crab Island may contain relatively high concentrations of dissolved organics from the marsh itself or, possibly, organics that have percolated through the dike of the Crab Island dredge spoils containment area. Some indirect evidence in support of the latter mechanism is the observation that orange bands (presumbably iron oxide) have been observed on the outside of containment area dikes (Personal communication from Peter W. Havens, ecologist, OICC Trident, Kings Bay, January 1985). This suggests there is some transport of dissolved constituents through the dikes surrounding the containment areas.

Note that differences observed in Cu-ISE response between ambient waters and effluent waters and between the Lower Basin and offshore Crab Island were not reflected in ASV and AA values. This suggests that Cu^{2-} activity may vary significantly due to complexation by organics, but levels of total Cu appear to be nearly the same in the different waters.

Based on analyses of samples collected during dewatering of the Mainside Disposal Area, we do not believe that the effluent represents a source of Cu to the Kings Bay and Cumberland Sound region. ASV and AA values are indistinguishable from ambient values. Cu-ISE potentials actually suggest that effluent waters show lower levels of the toxic Cu^{2+} ion.

A nonpoint source of Cu is suggested by the observation that AA Cu values were significantly higher in the Lower Turning Basin than in the Upper Turning Basin or Cumberland Sound during both ebb and flood tidal stages. Although values are still quite low (the highest value measured was 5.8 μg/L), compared to the suggested EPA criterion of 23 μg/L, the situation should probably be monitored closely as Navy activity increases at Kings Bay Submarine Base to determine whether this is a persistent feature. Elevated copper levels have been observed in several other bays and harbors where there are a large number of boats painted with copper antifoulant coatings (Young et al., 1979; Zirino et al., 1978).

The variability observed during tidal monitoring (see Figures B-1 to B-10) illustrates the dynamic nature inherent in the estuarine environment of Kings Bay. The data show fluctuations occurring over the tidal cycle that could influence the comparability of samples collected at different phases of the tide. Couple this tidally induced variability with seasonal changes and short-term weather events, and one begins to understand the difficulty and complexity involved in comparing and interpreting monitoring data. To distinguish between natural variability and the impact of man, knowledge must first be obtained to assess the natural variability and thereby identify the "background noise" of the system being studied (Buffington & Little, 1980).

The effect of natural variability on the comparability of data acquired during a long-term monitoring effort cannot be totally eliminated. However, the magnitude of the variability can be reduced by establishing a controlled sampling regimen. The following guidelines should be used to minimize the natural variability factor.

1. Annual and seasonal sampling should be conducted during restricted periodic windows. For example, sample as close as possible to the third week in March each year.

2. Sampling should be conducted during periods of representative weather conditions within the seasonal interval. Collection during periods of extreme weather tend to inject a large variability component.

3. Sampling should not be conducted during periods of extreme tidal flux.

4. Sample collection should be performed during comparable tidal states from sample interval to sample interval.

5. Sample locations should be known and repeatable. In a small estuary, such as Kings Bay, a small difference in sample location can cause a large variability component. Generally, sampling within a 10-meter radius may be desirable.

6. *Establish sampling stations in well mixed, homogeneous areas.* Shoals and sites of fresh water influx, such as creeks and drainage ditches, are highly variable areas. It may be best to establish midchannel stations.

7. The number of stations, areas, and samples per area or station should be predetermined and not varied from year to year or sampling interval. Statistical comparisons require adequate sample populations to derive valid conclusions. The statistical test to be used and the sites to be sampled should be established prior to field operations.

SUMMARY AND CONCLUSIONS

Results from this study show that copper concentrations in Kings Bay and Cumberland Sound are considerably lower than values reported during the 1982-83 period. Because earlier measurements were made during periods of active dredging, this suggests (assuming previous measurements were based on noncontaminated samples) that increases in Cu concentrations due to dredging activity are probably only short term.

Several important questions posed at the beginning of this study can now be answered.

1. No evidence was found to support the existence of a point source of Cu in Kings Bay or Cumberland Sound. Obviously, the importance of this question was diminished to a large extent by the finding that copper levels are within the range of values measured from 1976 to 1977 (NAVFACENGCOM, 1984), before dredging activity was initiated.

2. Dewatering of dredge spoil containment areas does not appear to be a source of copper. Levels of copper measured by ASV and AA were not significantly different from values measured in ambient waters. Cu-ISE measurements suggest less available free (ionic) Cu^{2+} in effluent water than in ambient water.

3. Concentrations of copper measured in the Lower Turning Basin of Kings Bay were slightly higher than levels in the Upper Basin or in Cumberland Sound, suggesting possible input from copper antifouling coatings.

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APPENDIX A

UNDERWAY MAPPING DATA

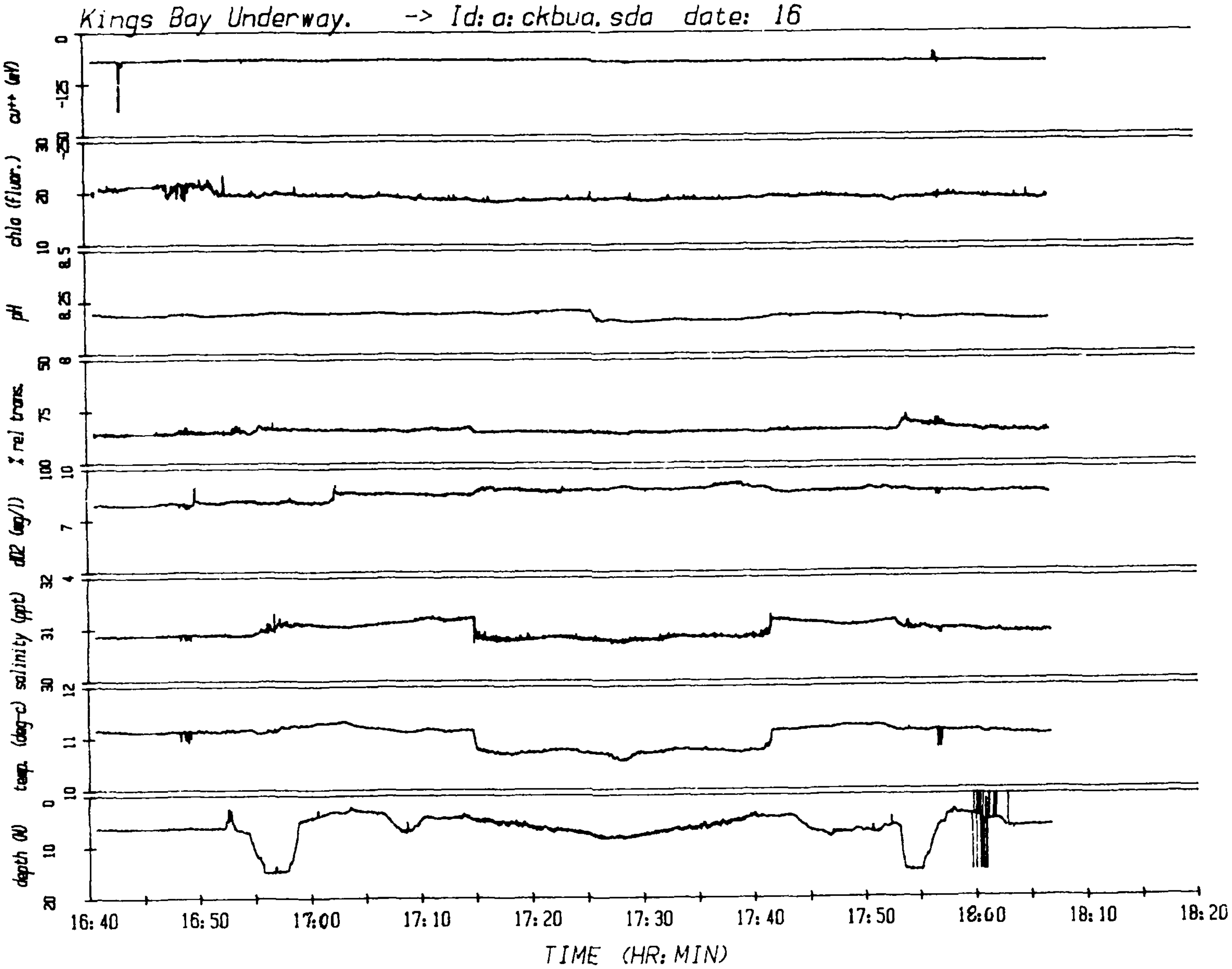

Figure A-1. Time-series data: 1640-1806, 16 January 1985.

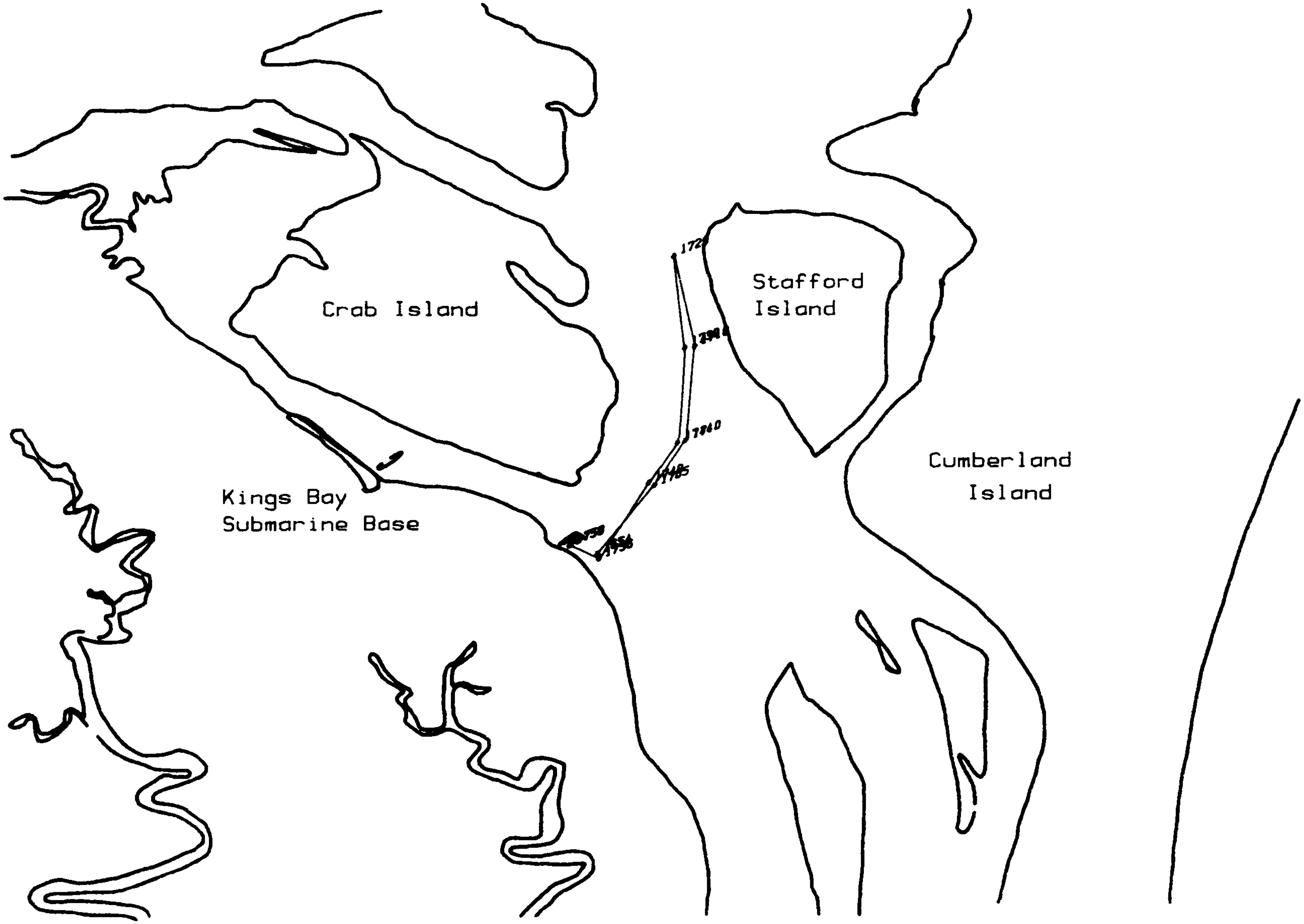

Figure A-2. Cruise track: 1640-1806, 16 January 1985.

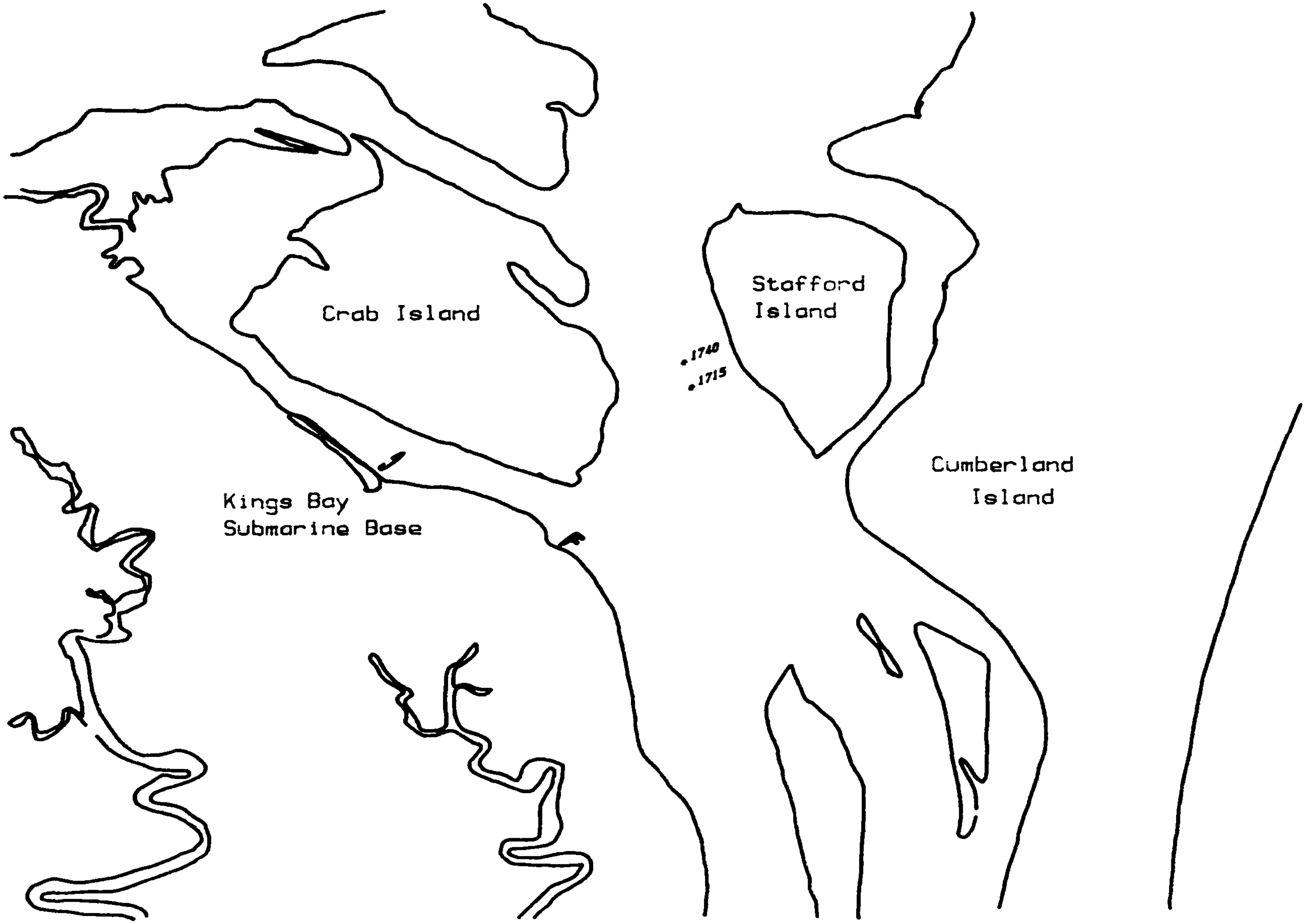

Figure A-3. Discrete samples collection sites: 1640-1806, 16 January 1985.

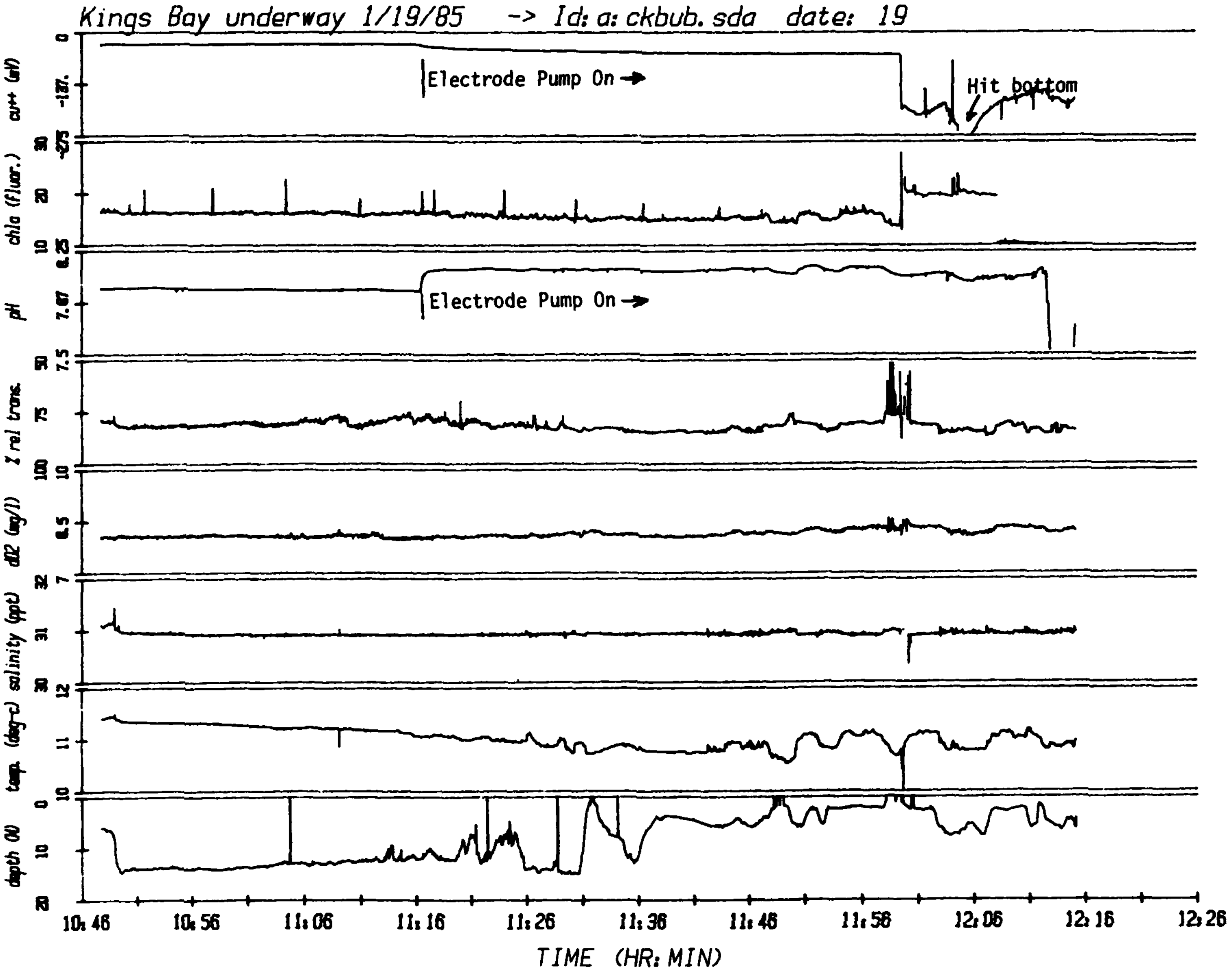

Figure A-4. Time-series data: 1048-1215, 19 January 1985.

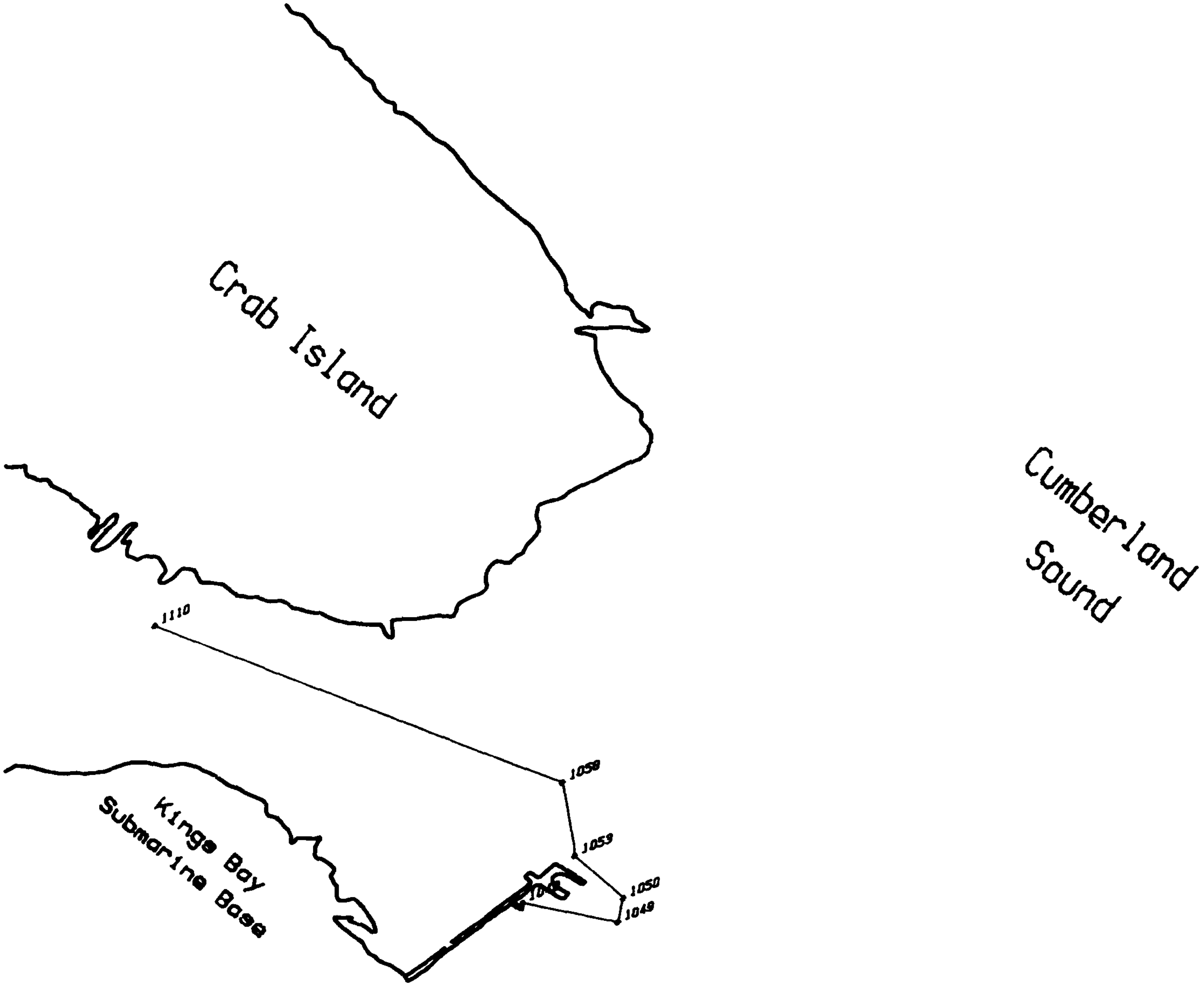

Figure A-5. Cruise track: 1048-1215, 19 January 1985.

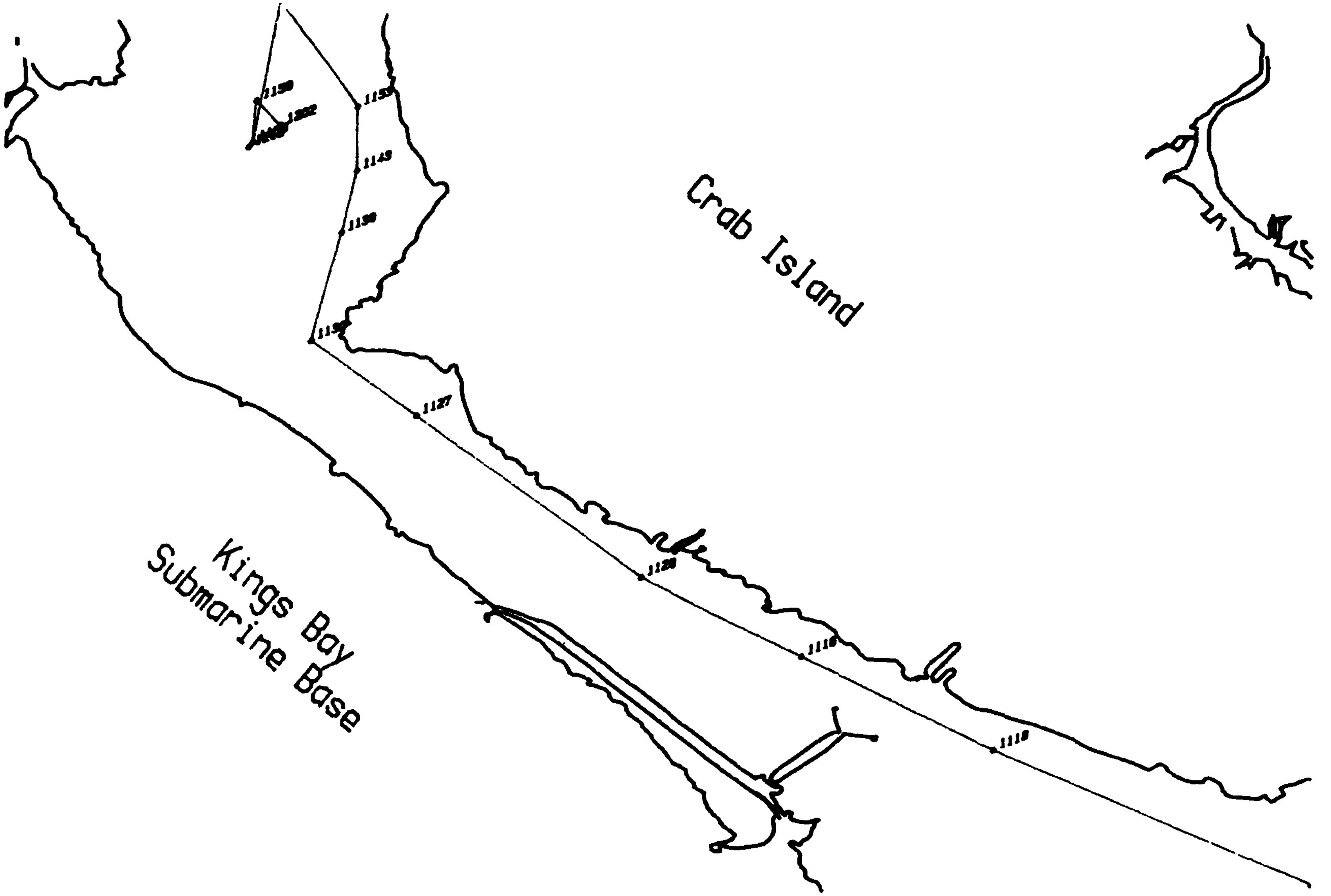

Figure A-6. Cruise track sites: 1048-1215, 19 January 1985.

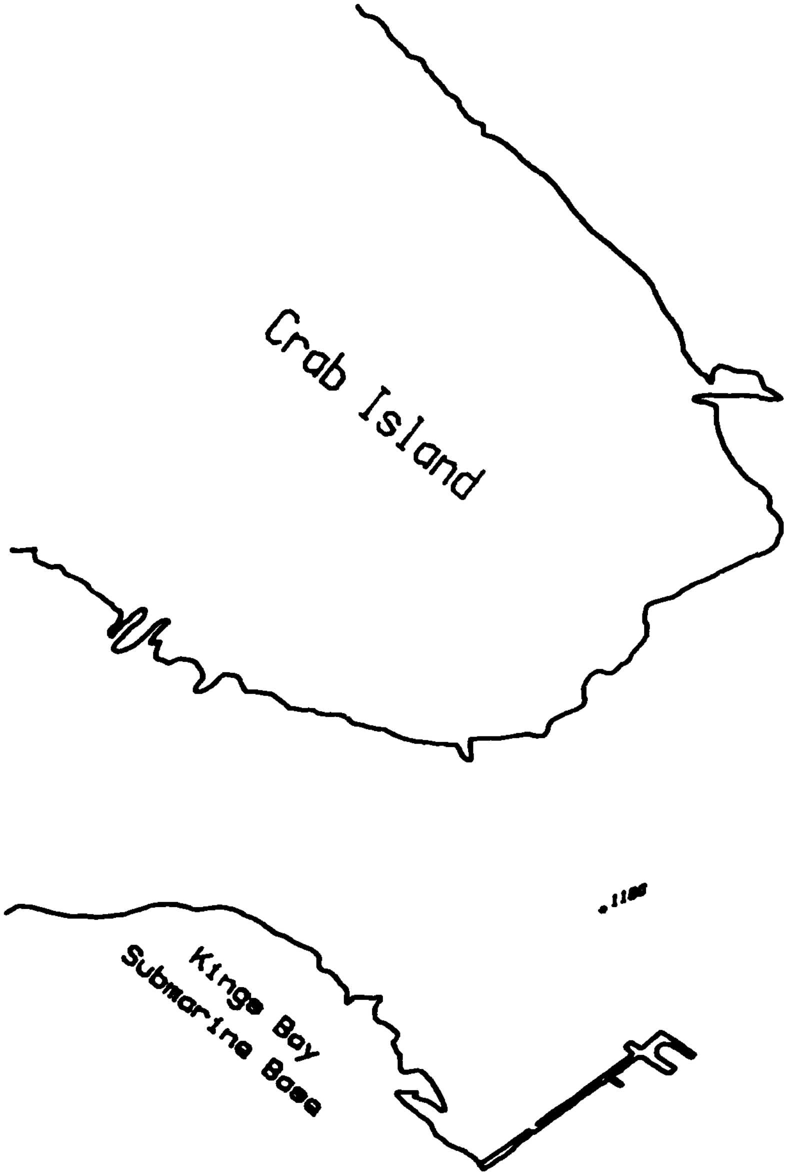

Figure A-7. Discrete sample collection sites: 1048-1215, 19 January 1985.

Figure A-8. Discrete sample collection sites: 1048-1215, 19 January 1985.

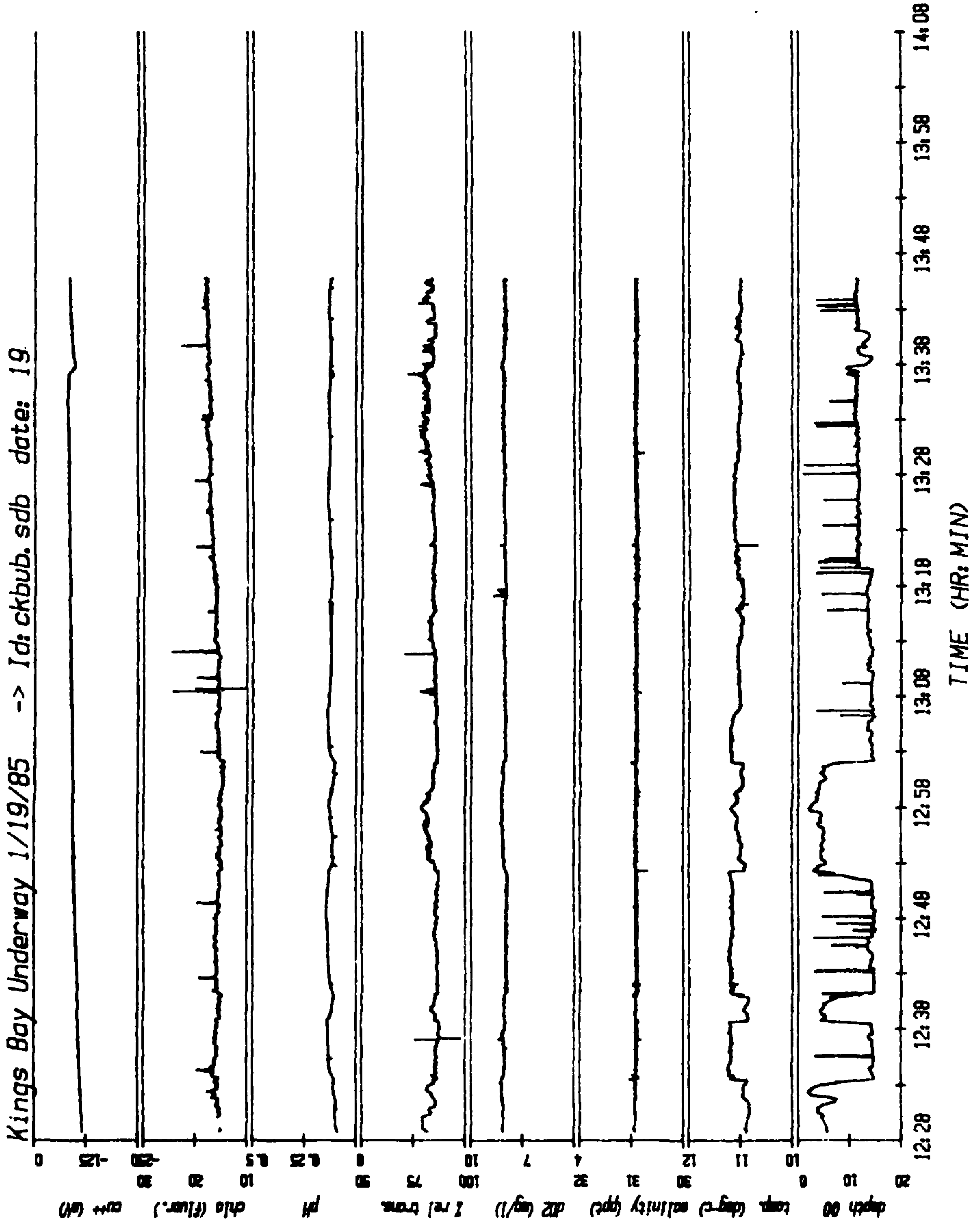

Figure A-9. Time-series data: 1229-1345, 19 January 1985.

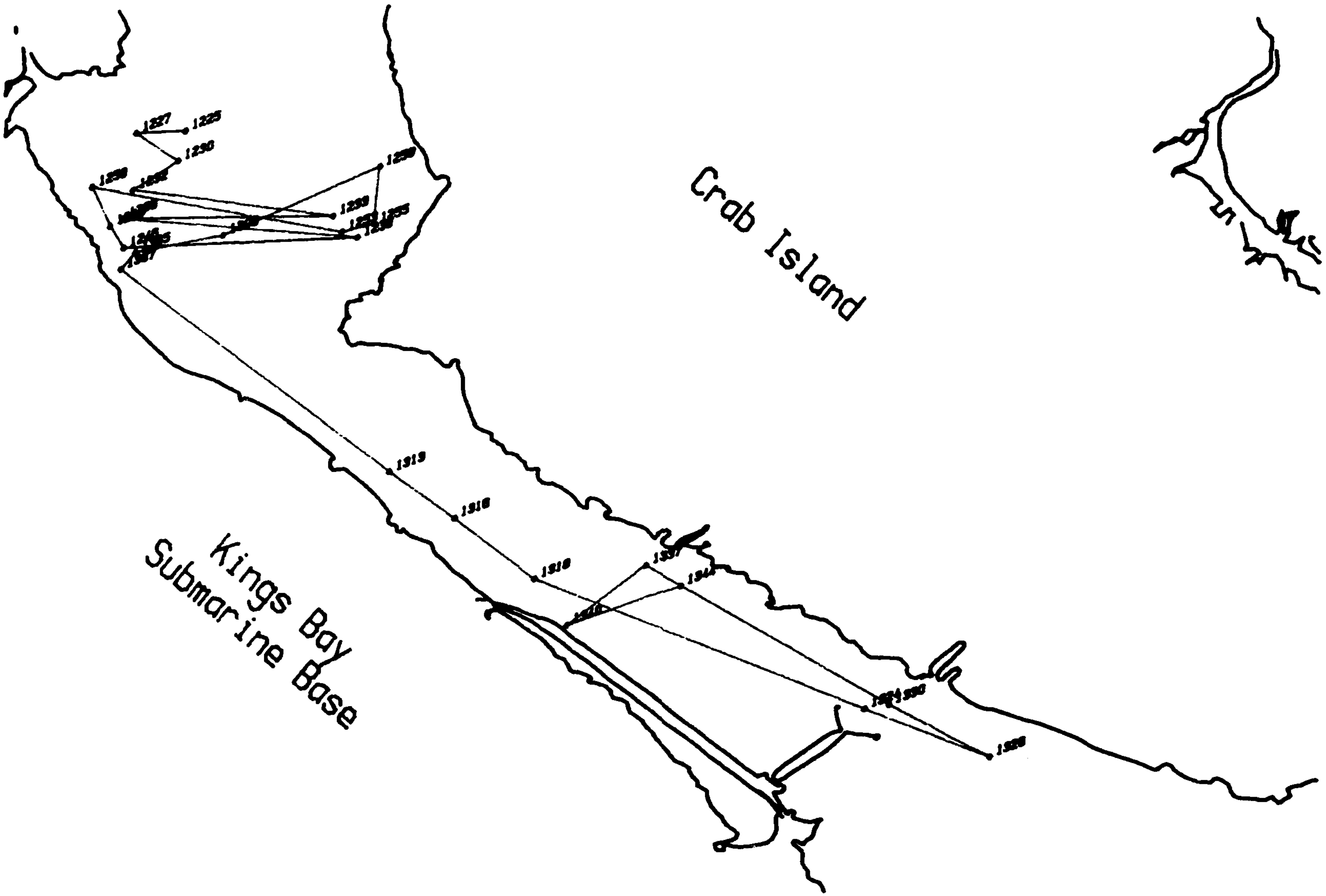

Figure A-10. Cruise track: 1229-1345, 19 January 1985.

Figure A-11. Discrete sample collection sites: 1229-1345, 19 January 1985.

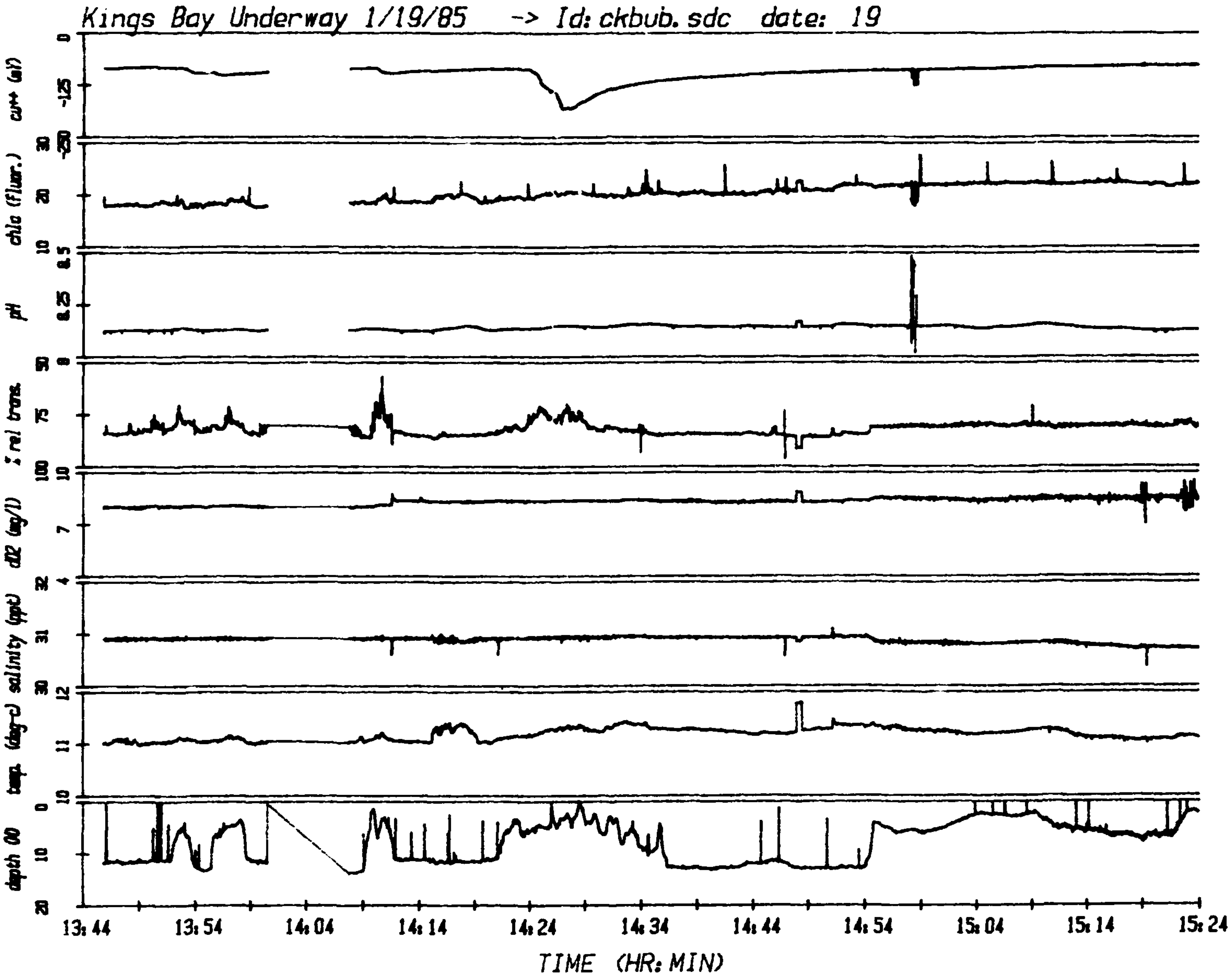

Figure A-12. Time-series data: 1346-1524, 19 January 1985.

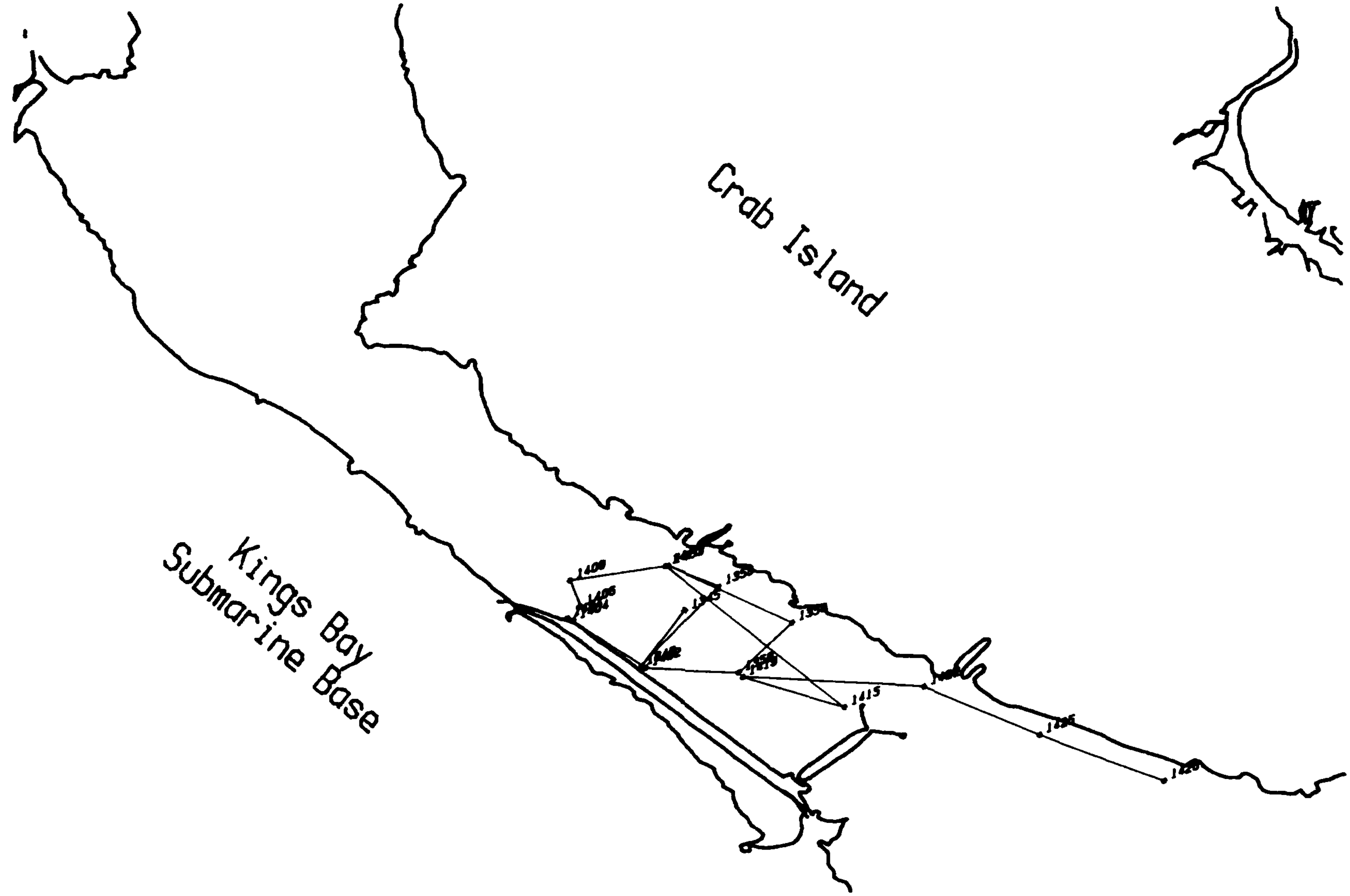

Figure A-13. Cruise track: 1346-1524, 19 January 1985.

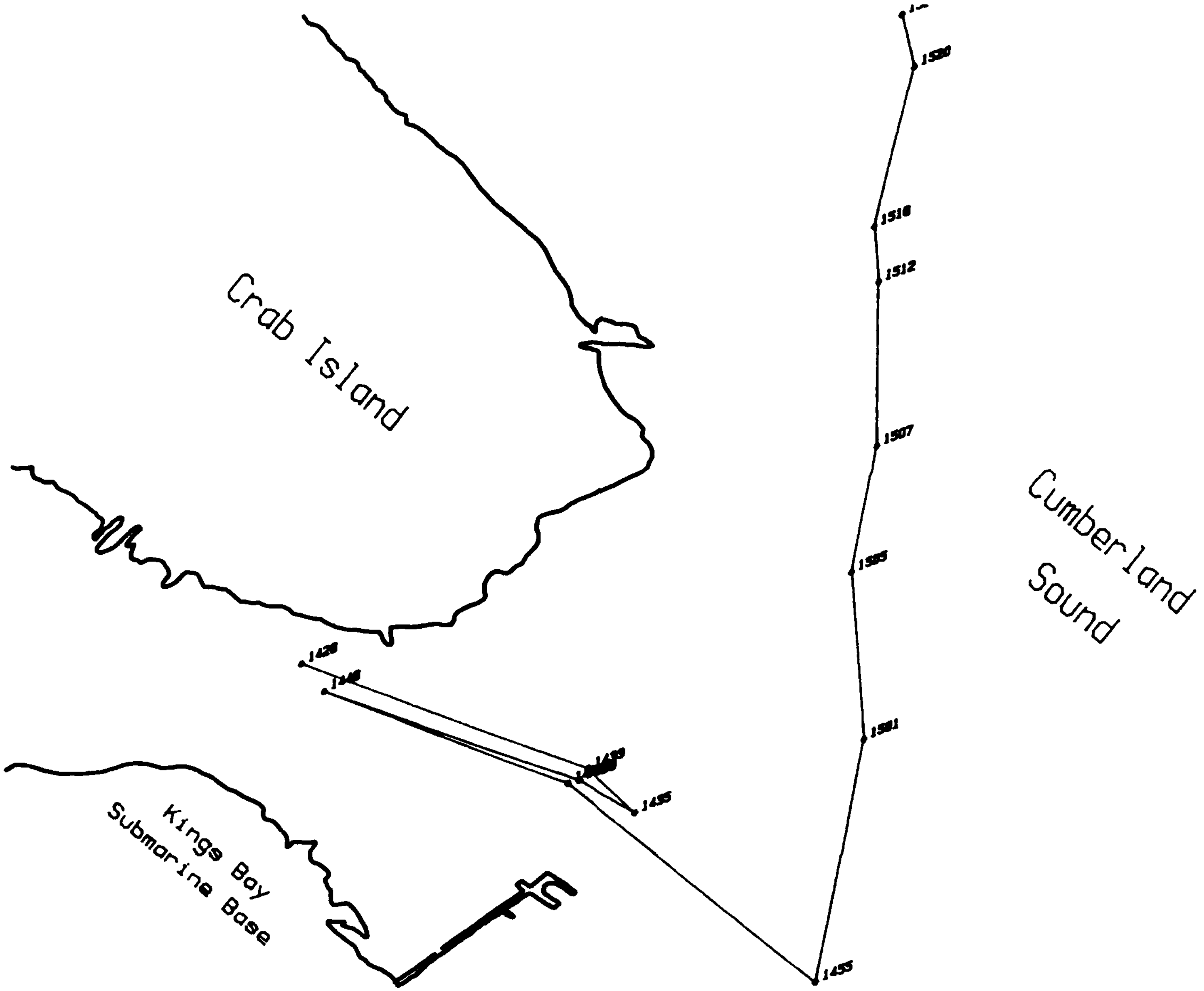

Figure A-14. Cruise track: 1346-1524, 19 January 1985.

Figure A-15. Discrete sample collection sites: 1346-1524, 19 January 1985.

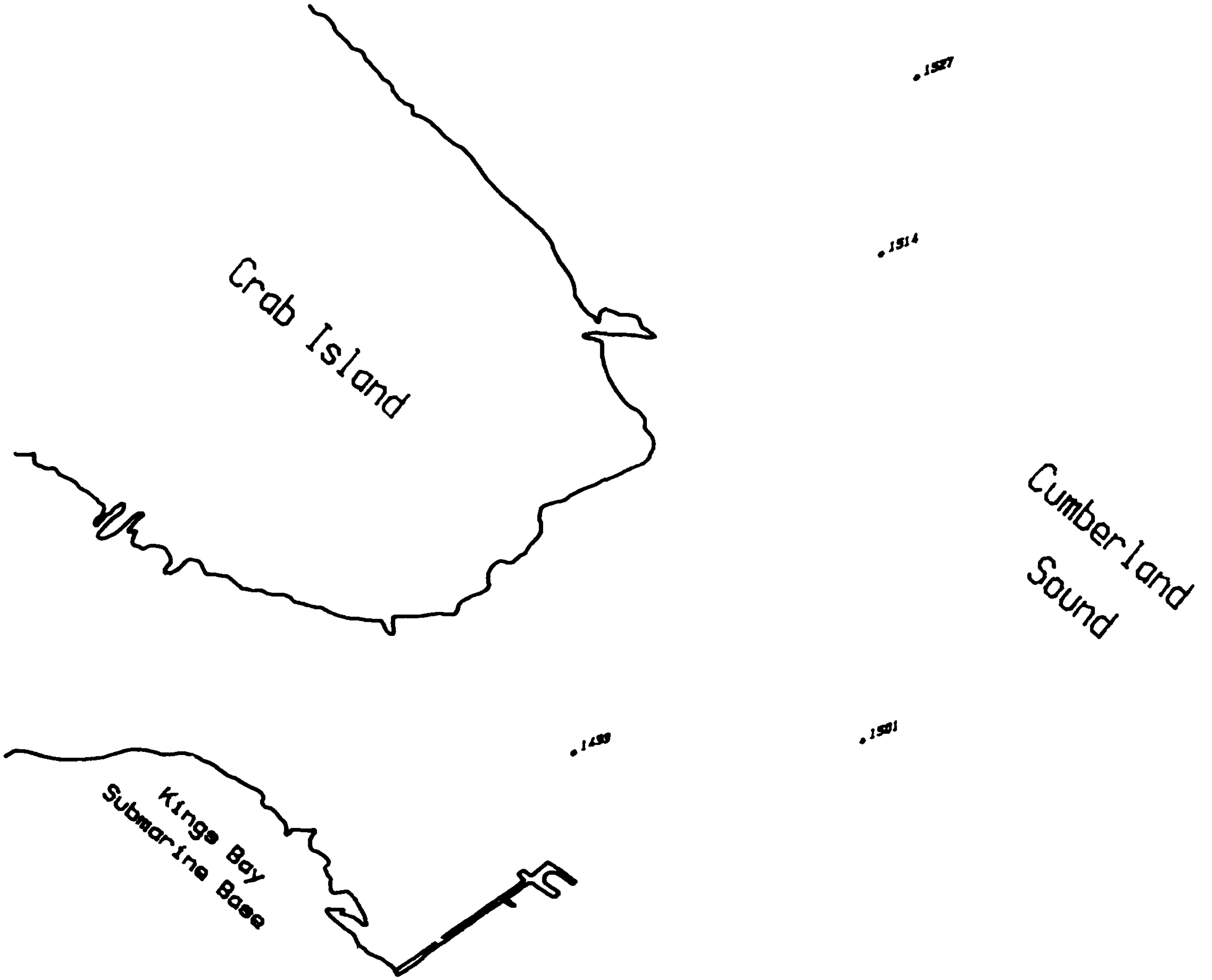

Figure A-16. Discrete sample collection sites: 1346-1524, 19 January 1985.

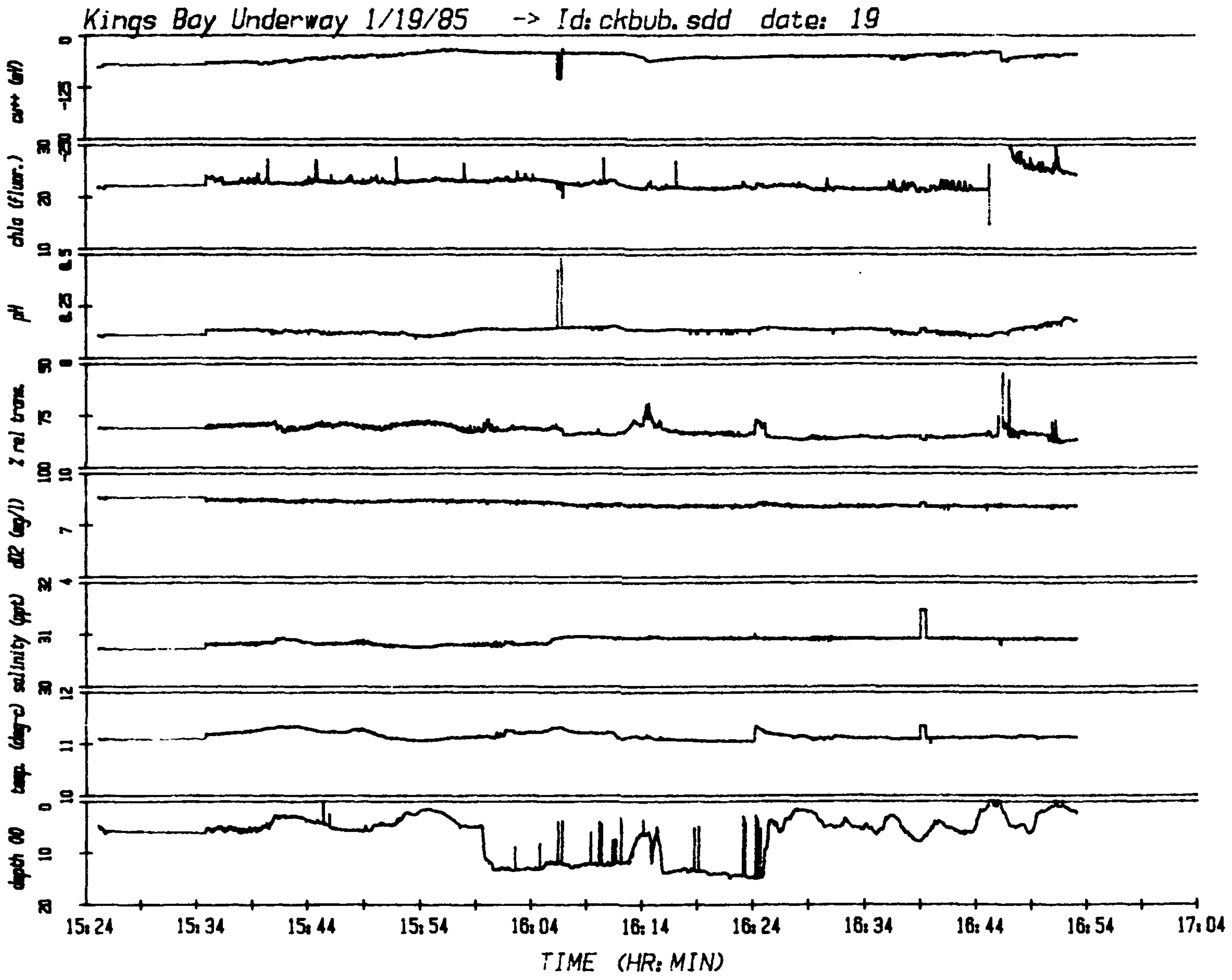

Figure A-17. Time-series data: 1524-1654, 19 January 1985.

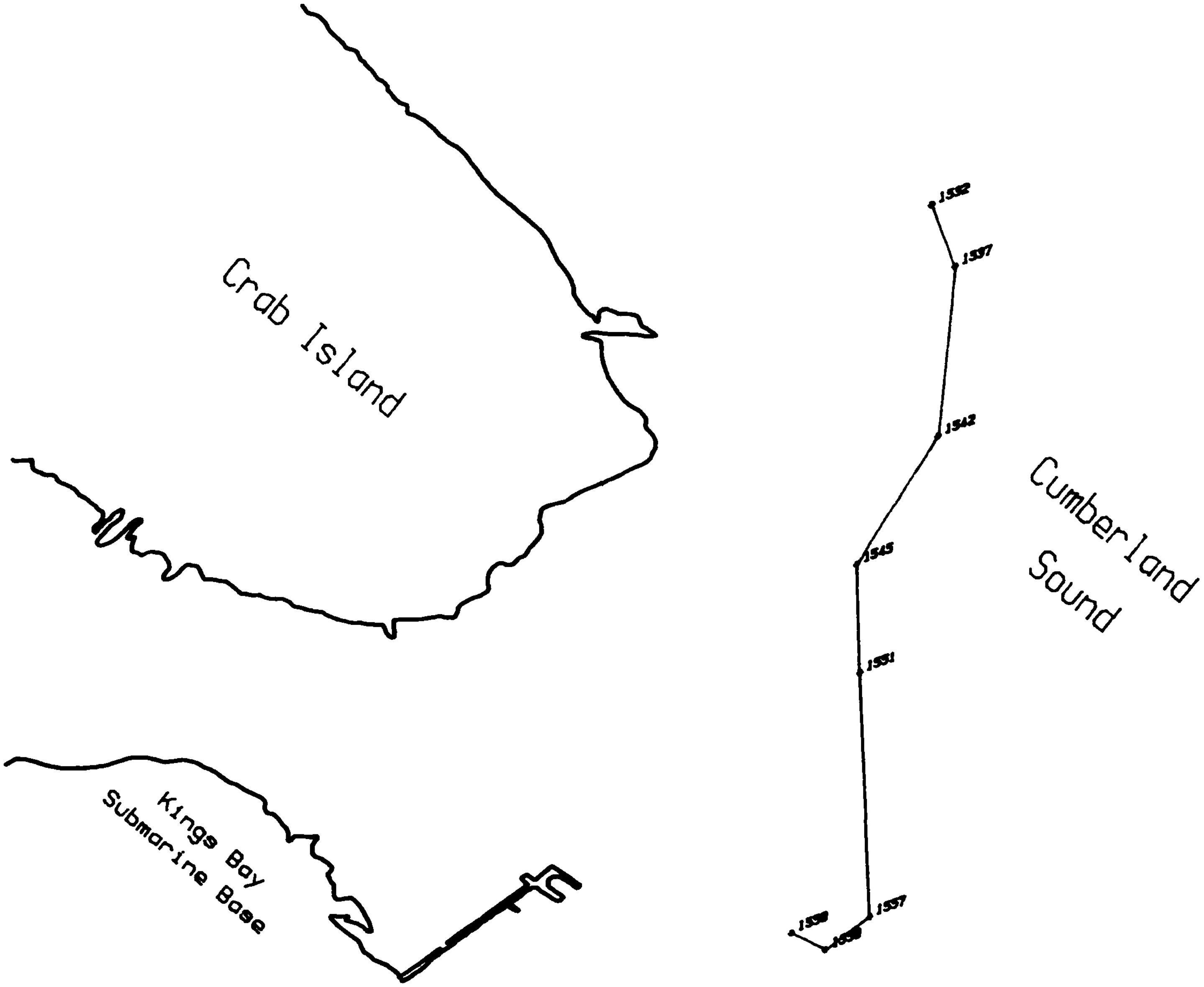

Figure A-18. Cruise track: 1524-1654, 19 January 1985.

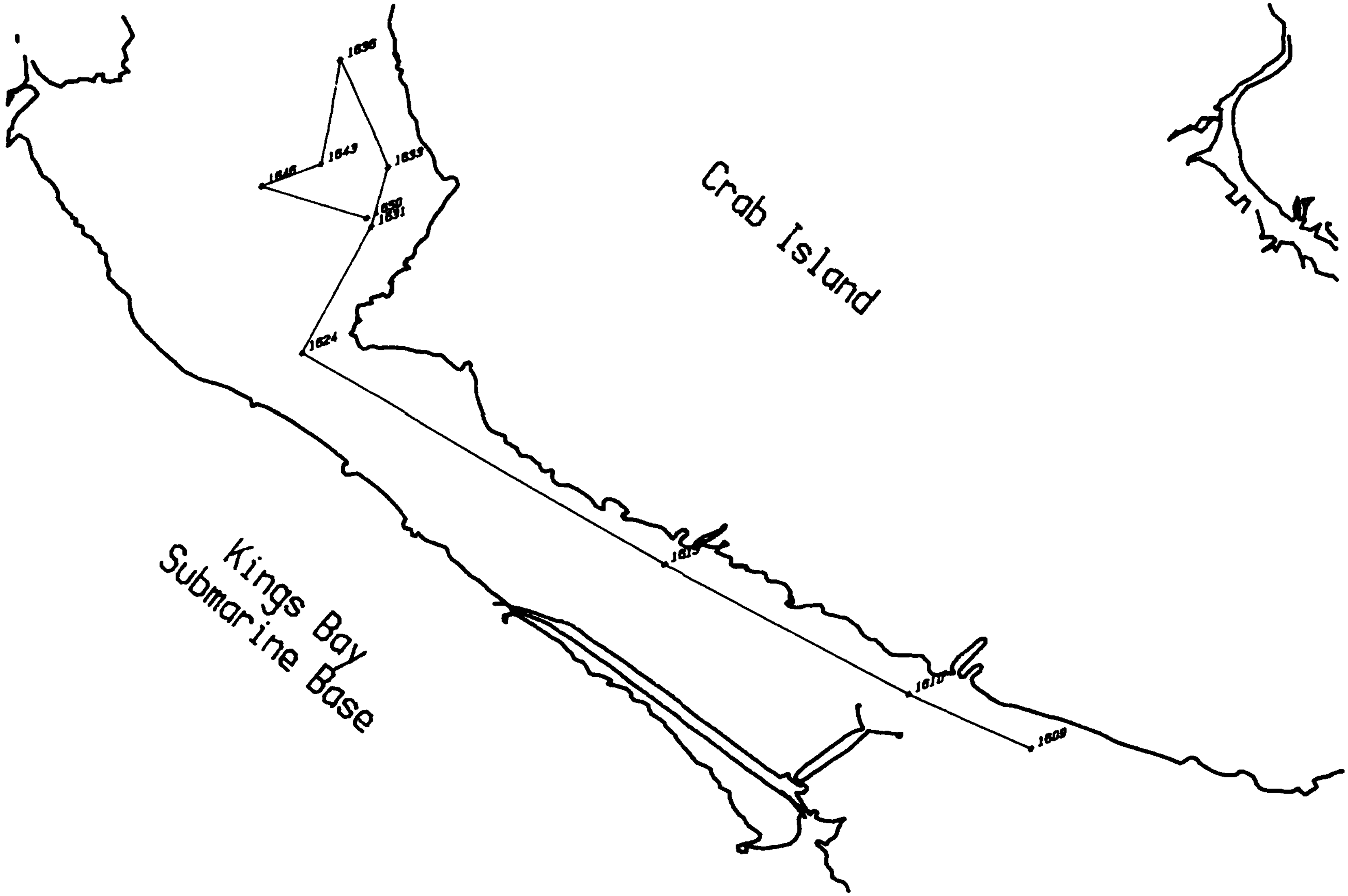

Figure A-19. Cruise track: 1524-1654, 19 January 1985.

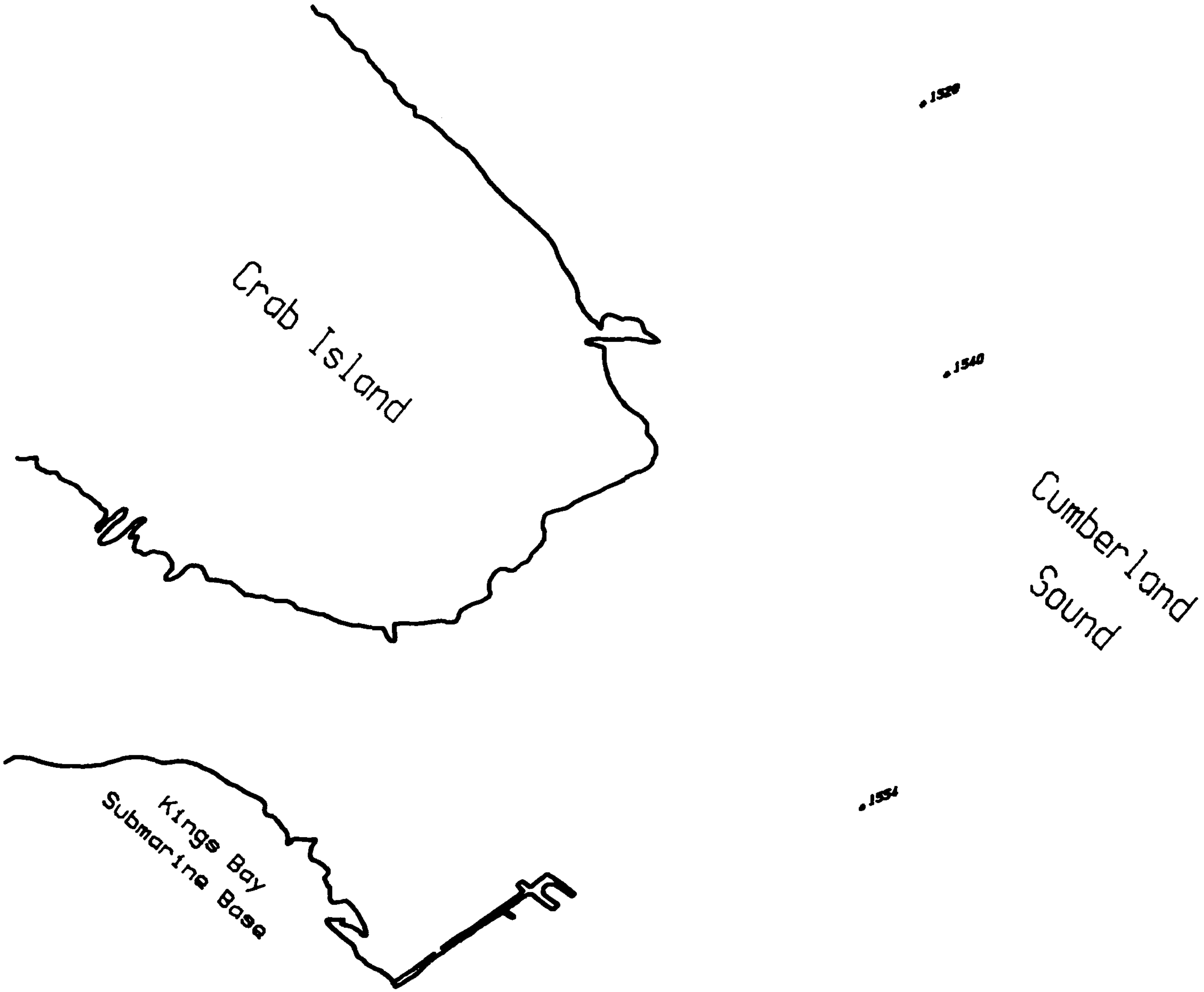

Figure A-20. Discrete sample collection sites: 1524-1654, 19 January 1985.

Figure A-21. Discrete sample collection sites: 1524-1654, 19 January 1985.

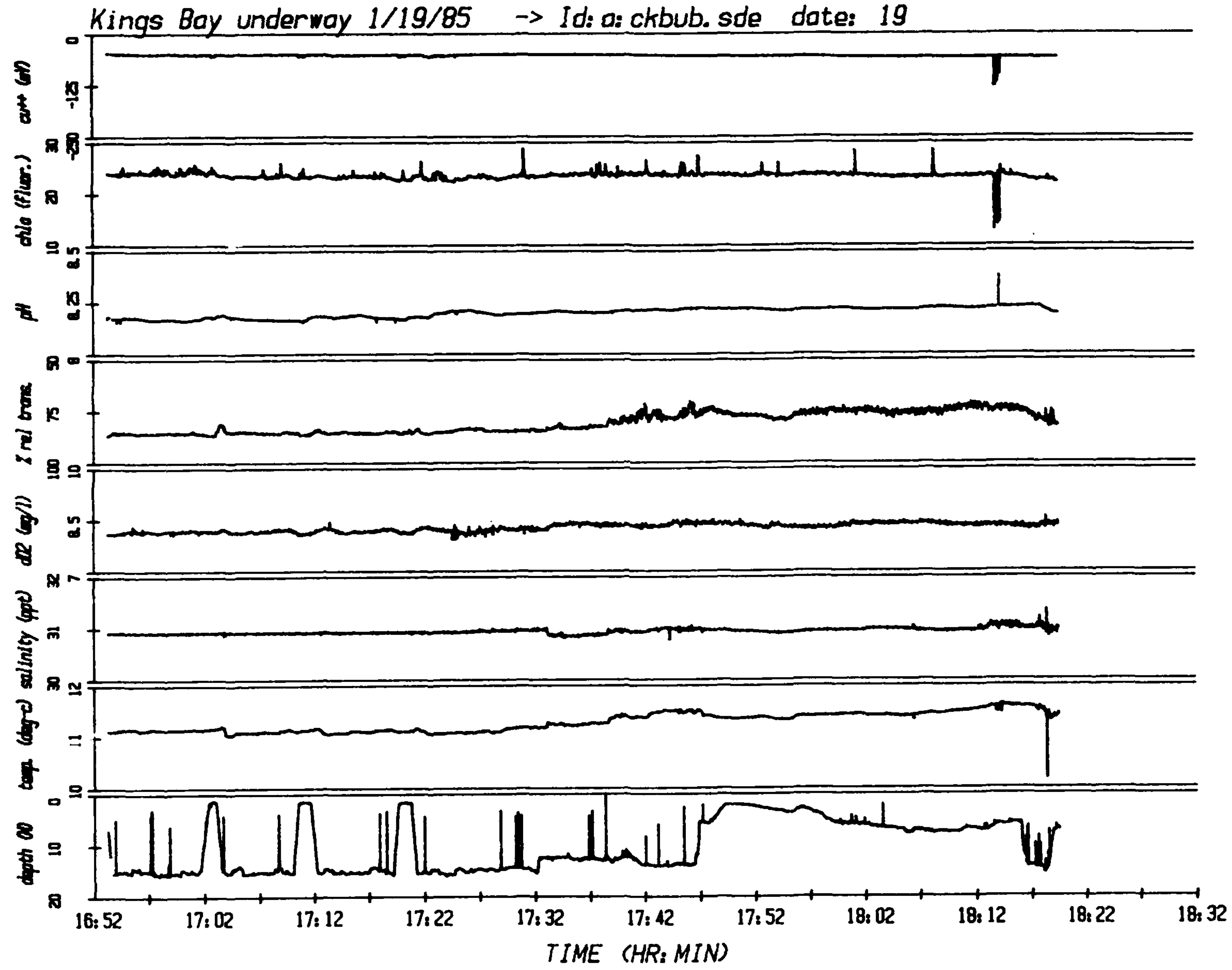

Figure A-22. Time-series data: 1655-1819, 19 January 1985.

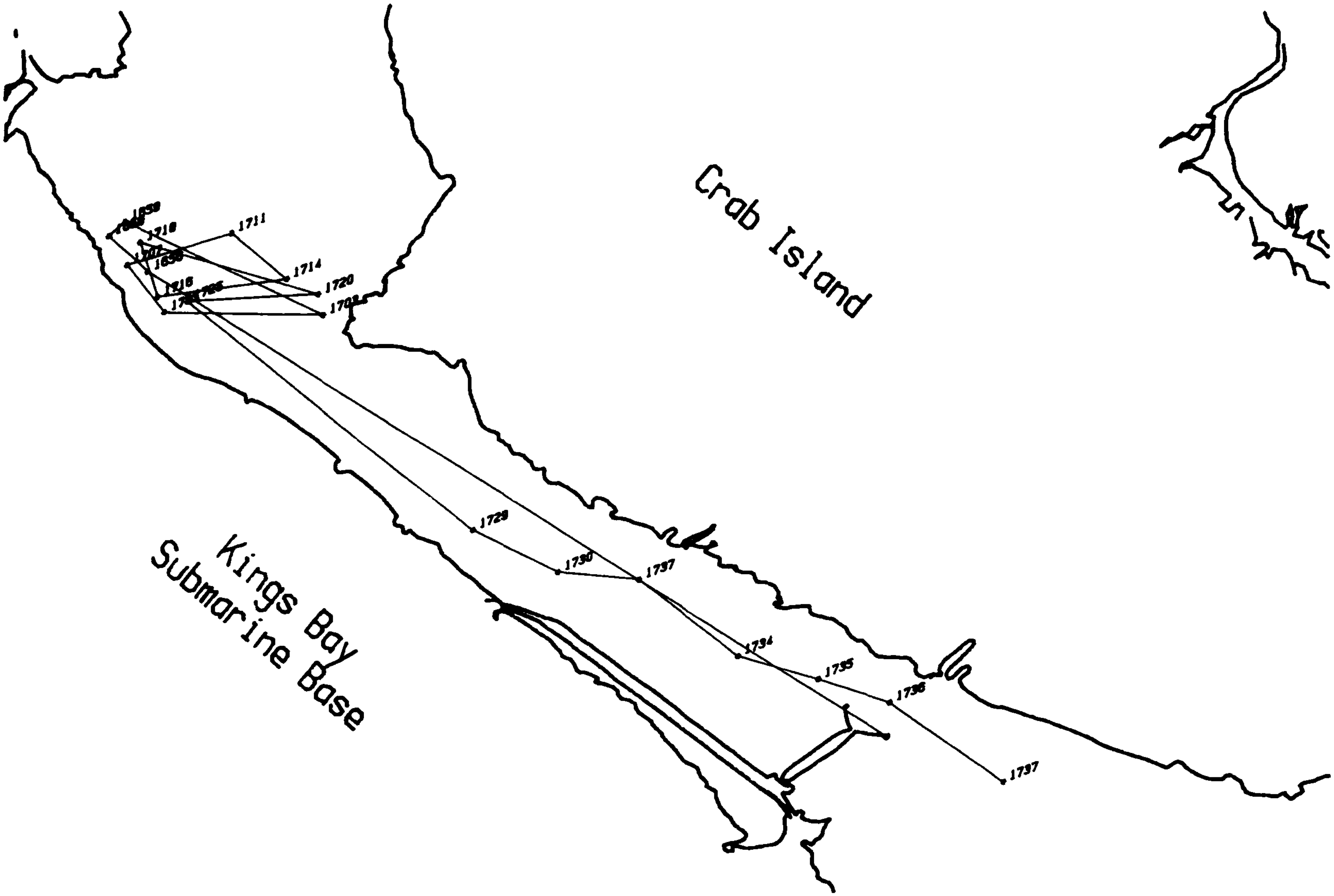

Figure A-23. Cruise track: 1655-1819, 19 January 1985.

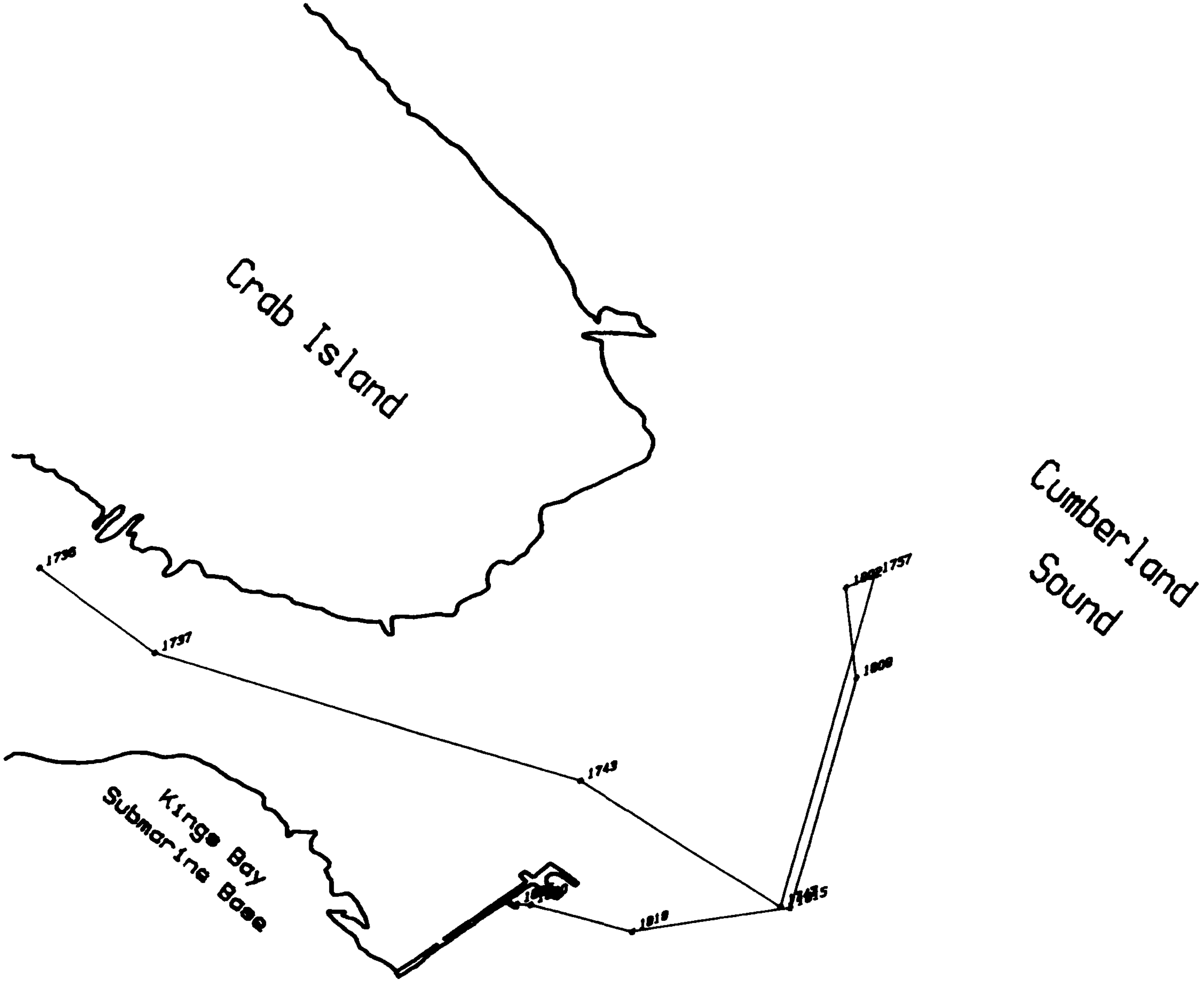

Figure A-24. Cruise track: 1655-1819, 19 January 1985.

Figure A-25. Discrete sample collection sites: 1655-1819, 19 January 1985.

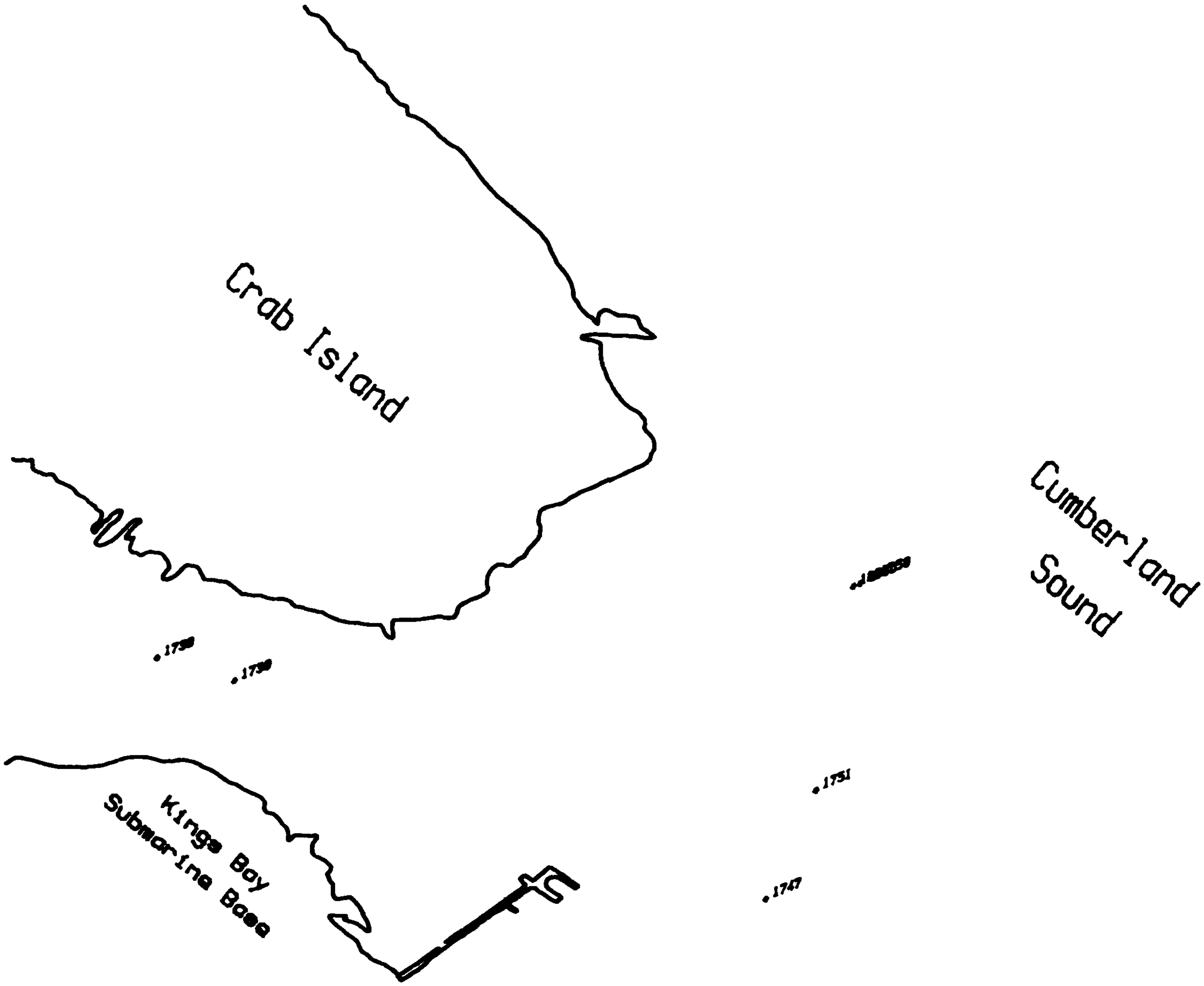

Figure A-26. Discrete sample collection sites: 1655-1819, 19 January 1985.

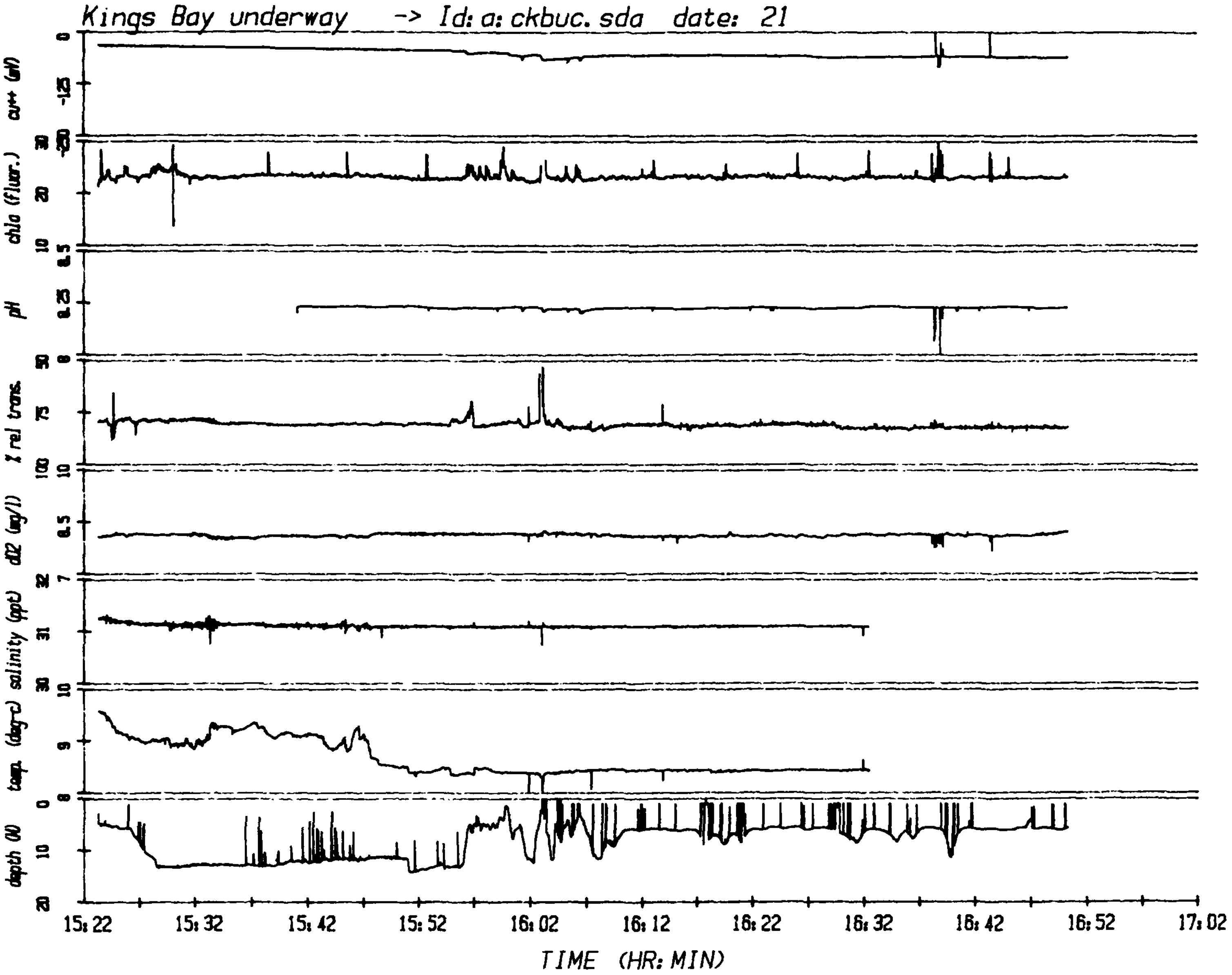

Figure A-27. Time-series data: 1524-1650, 21 January 1985.

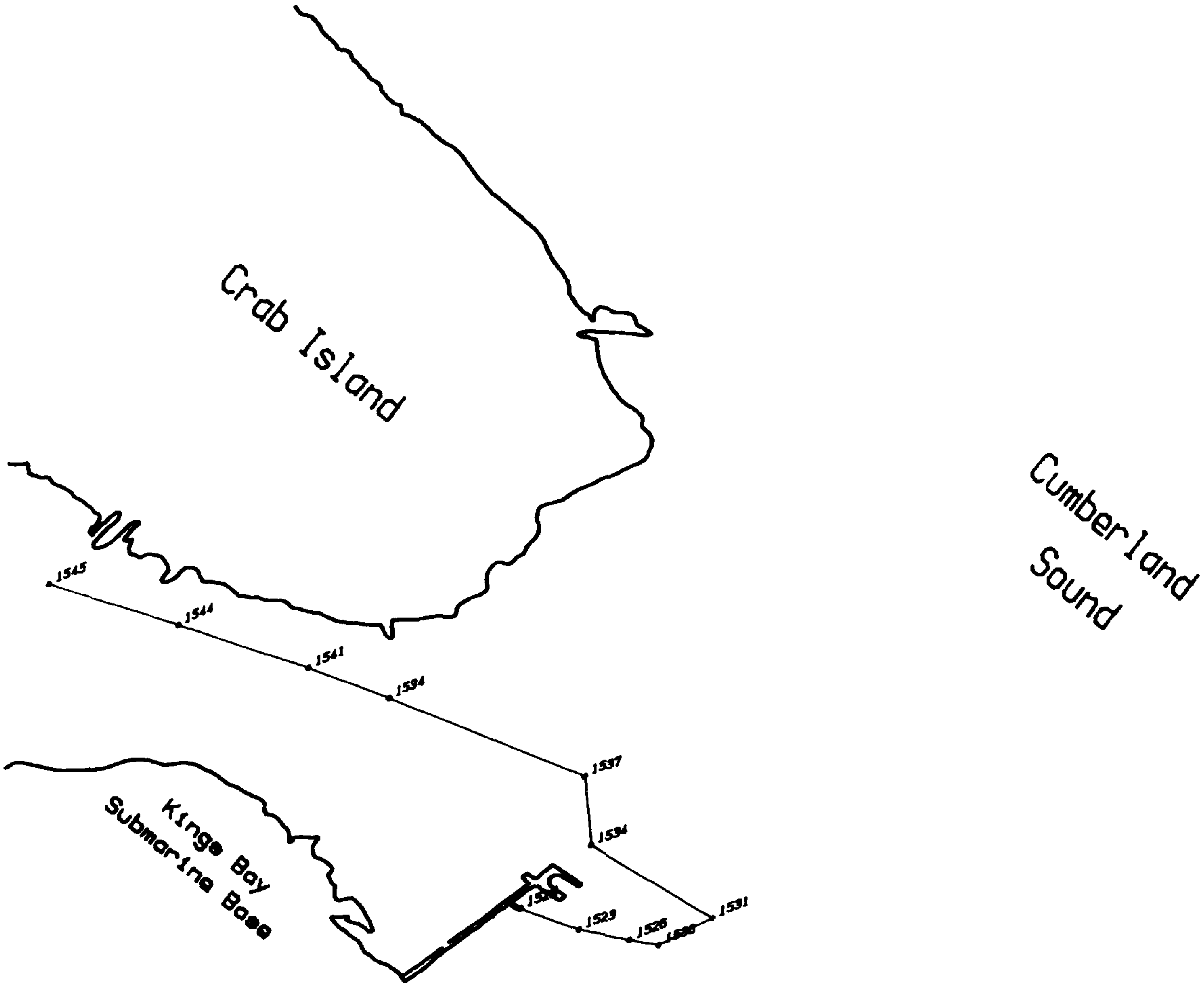

Figure A-28. Cruise track: 1524-1650, 21 January 1985.

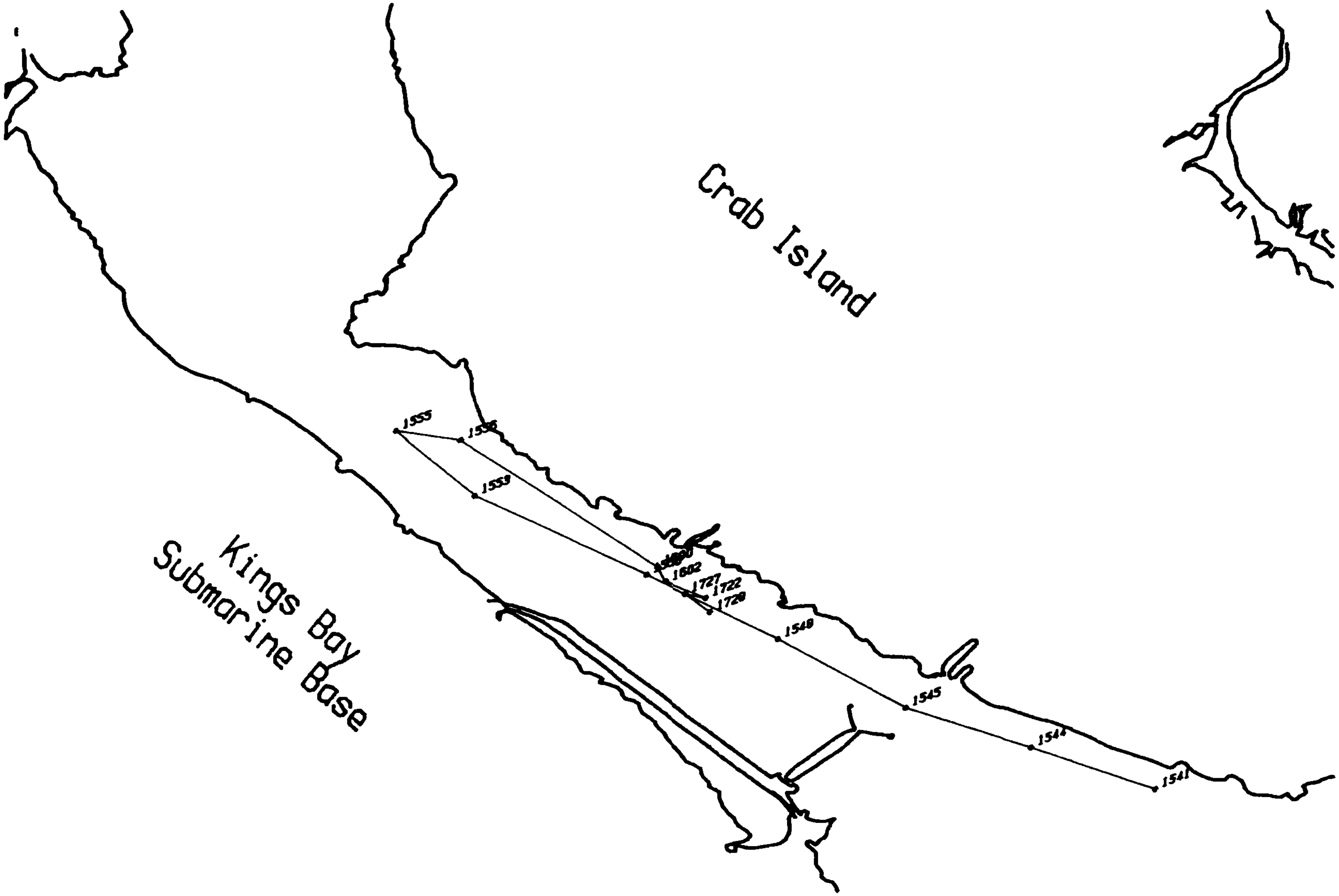

Figure A-29. Cruise track: 1524-1650, 21 January 1985.

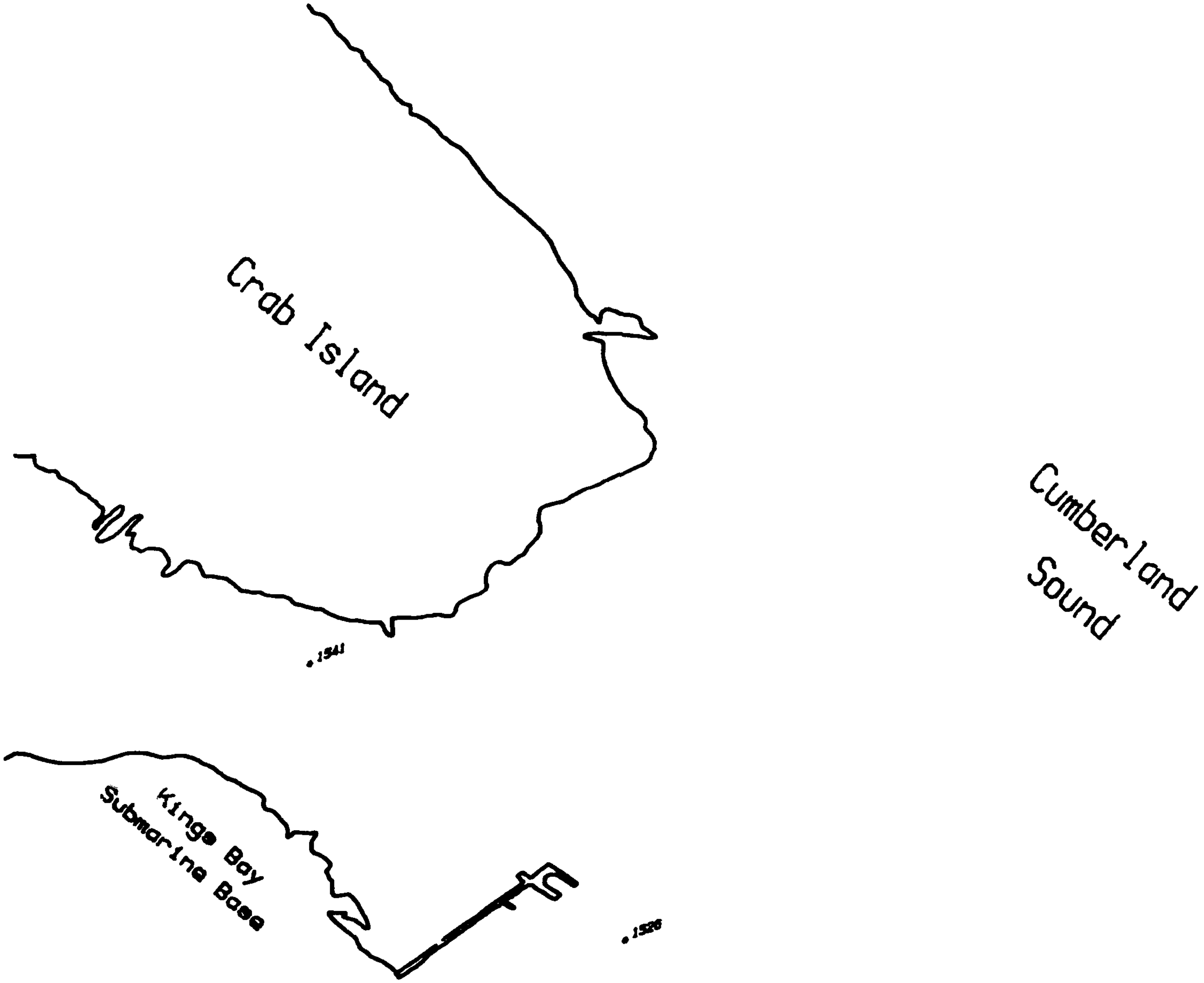

Figure A-30. Discrete sample collection sites: 1524-1650, 21 January 1985.

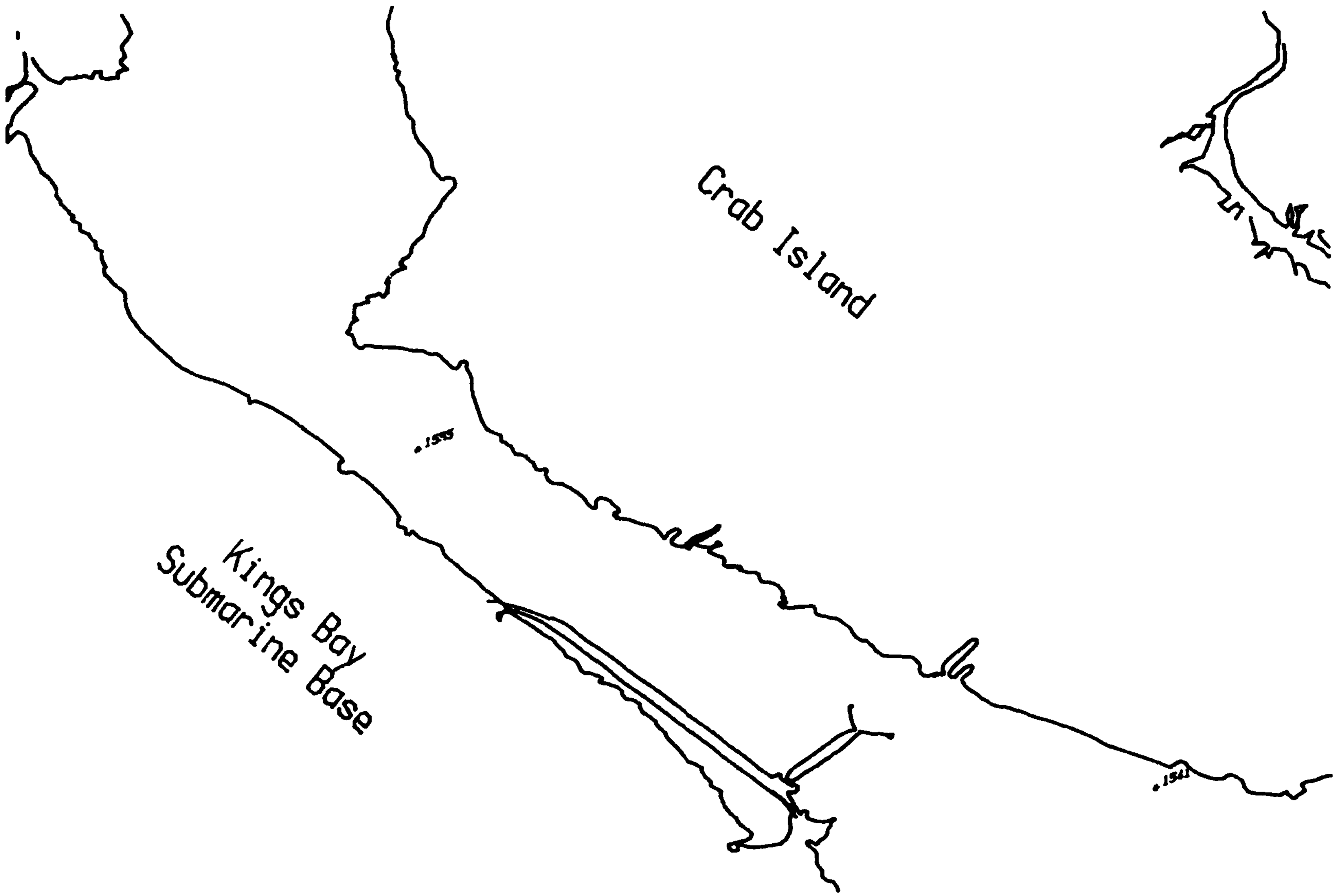

Figure A-31. Discrete sample collection sites: 1524-1650, 21 January 1985.

APPENDIX B

TIDAL MONITORING DATA

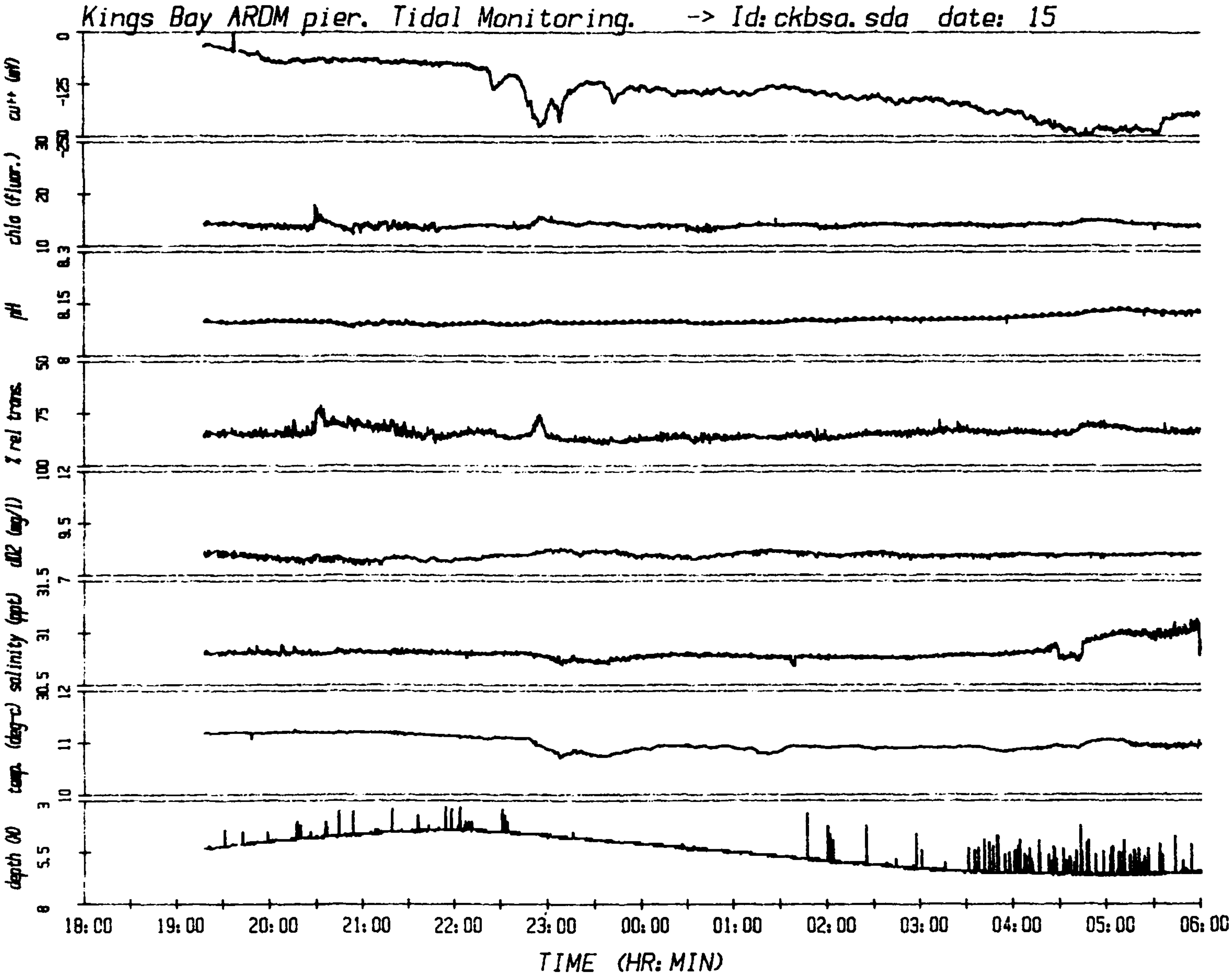

Figure B-1. ARDM pier tidal monitoring: 1918-0600, 15-16 January 1985.

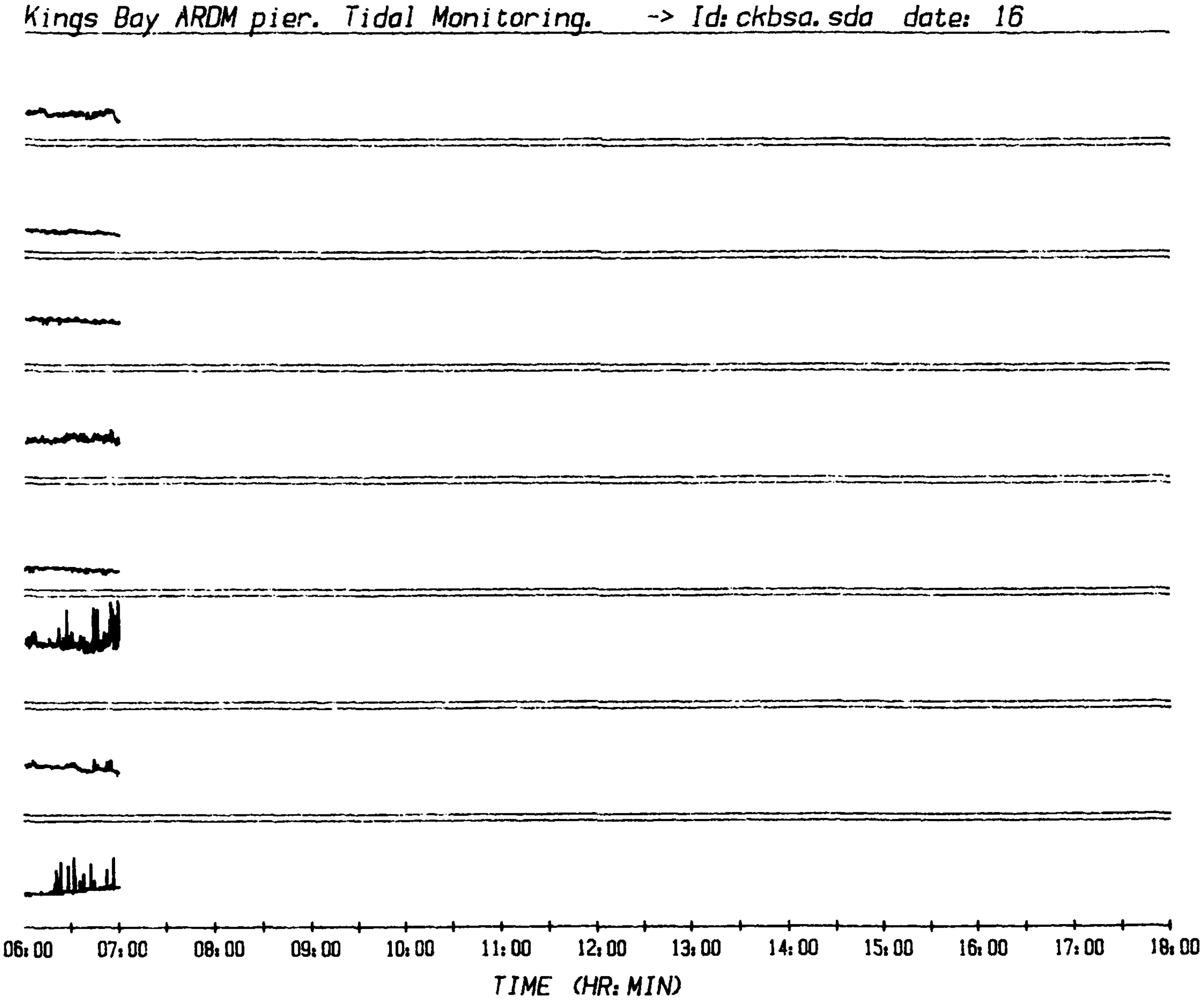

Figure B-2. ARDM pier tidal monitoring: 0600-0700, 16 January 1985.

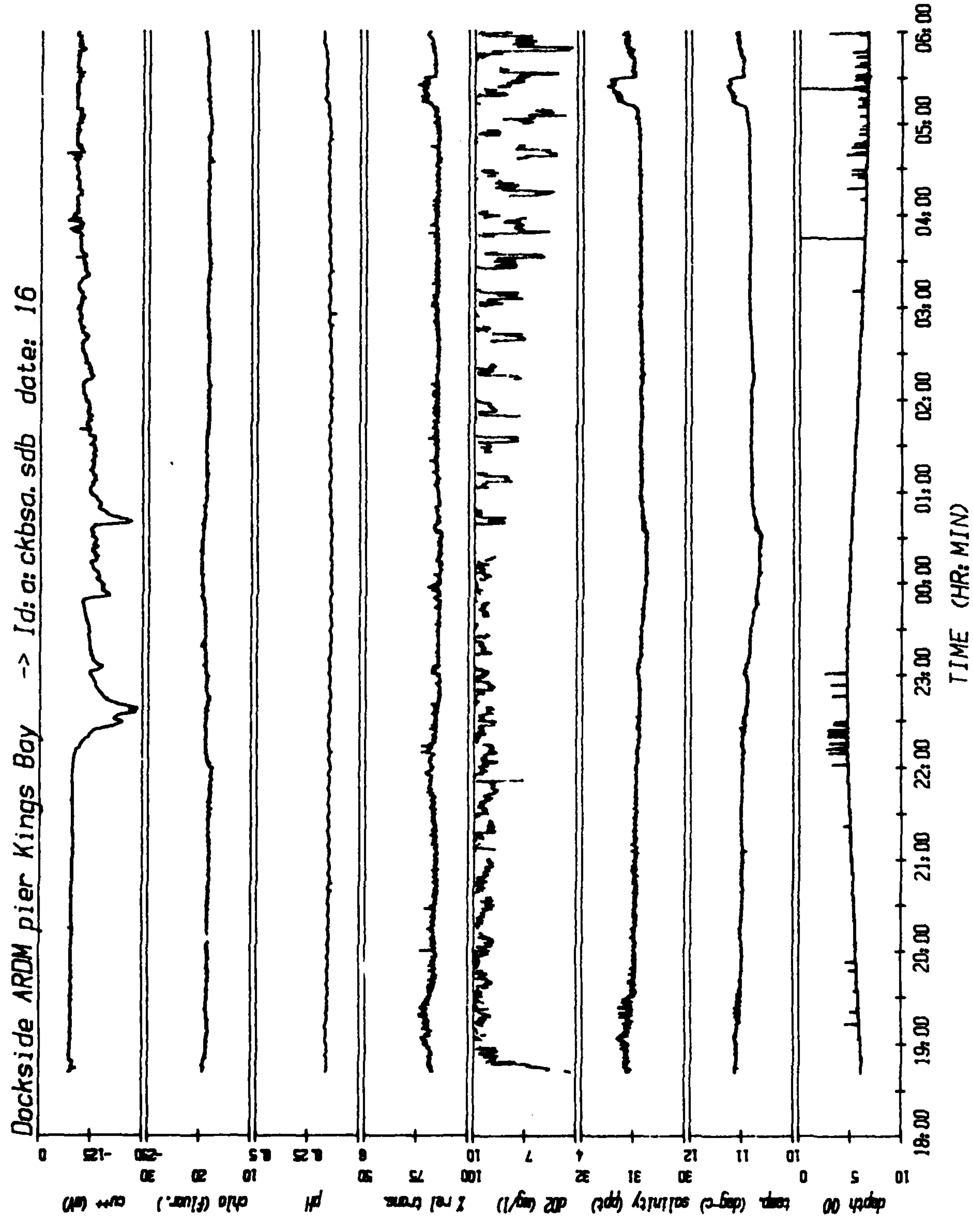

Figure B-3. ARDM pier tidal monitoring: 1840-0800, 16-17 January 1985.

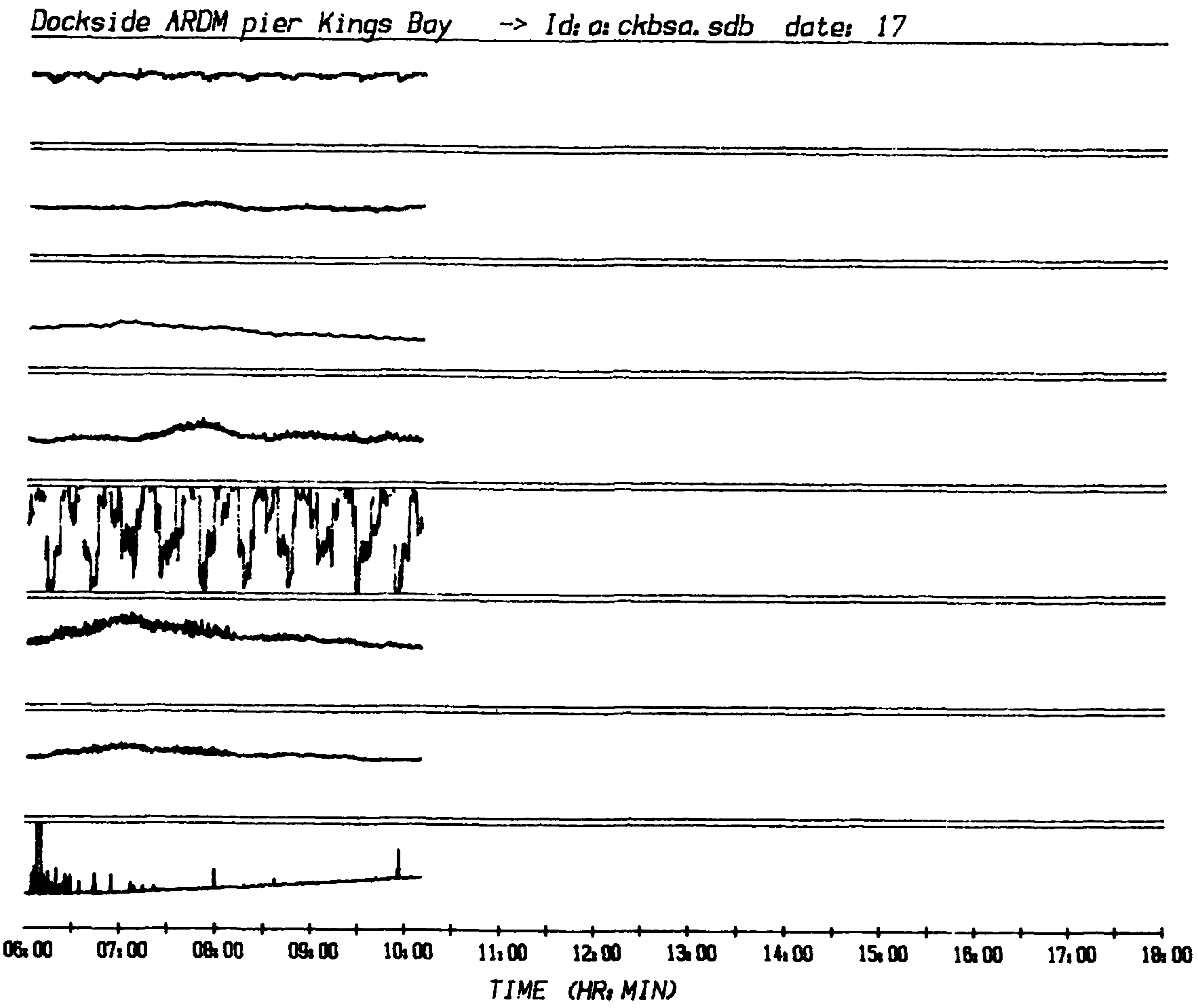

Figure B-4. ARDM pier tidal monitoring: 0800-1010, 17 January 1985.

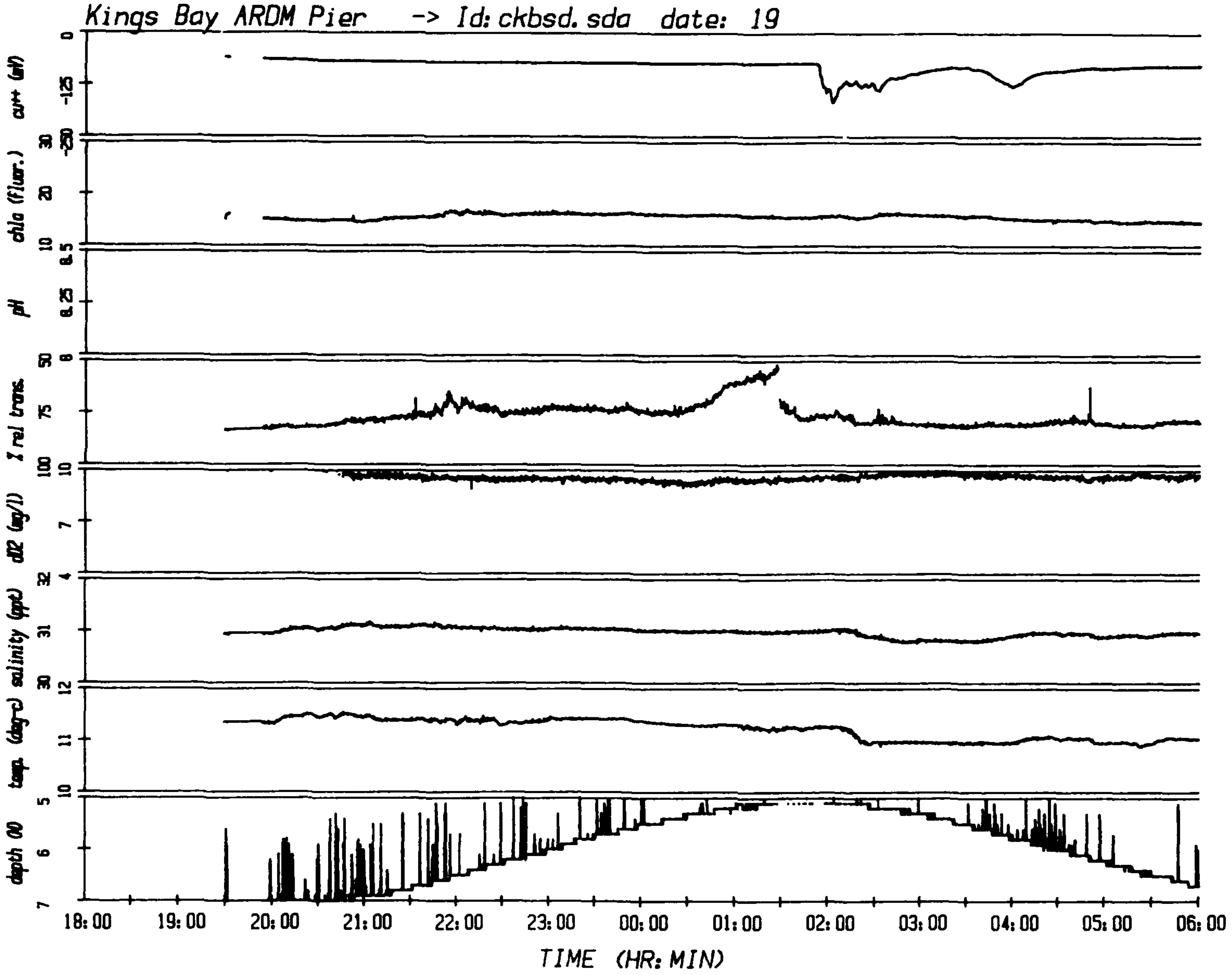

Figure B-5. ARDM pier tidal monitoring: 1953-0600, 19-20 January 1985.

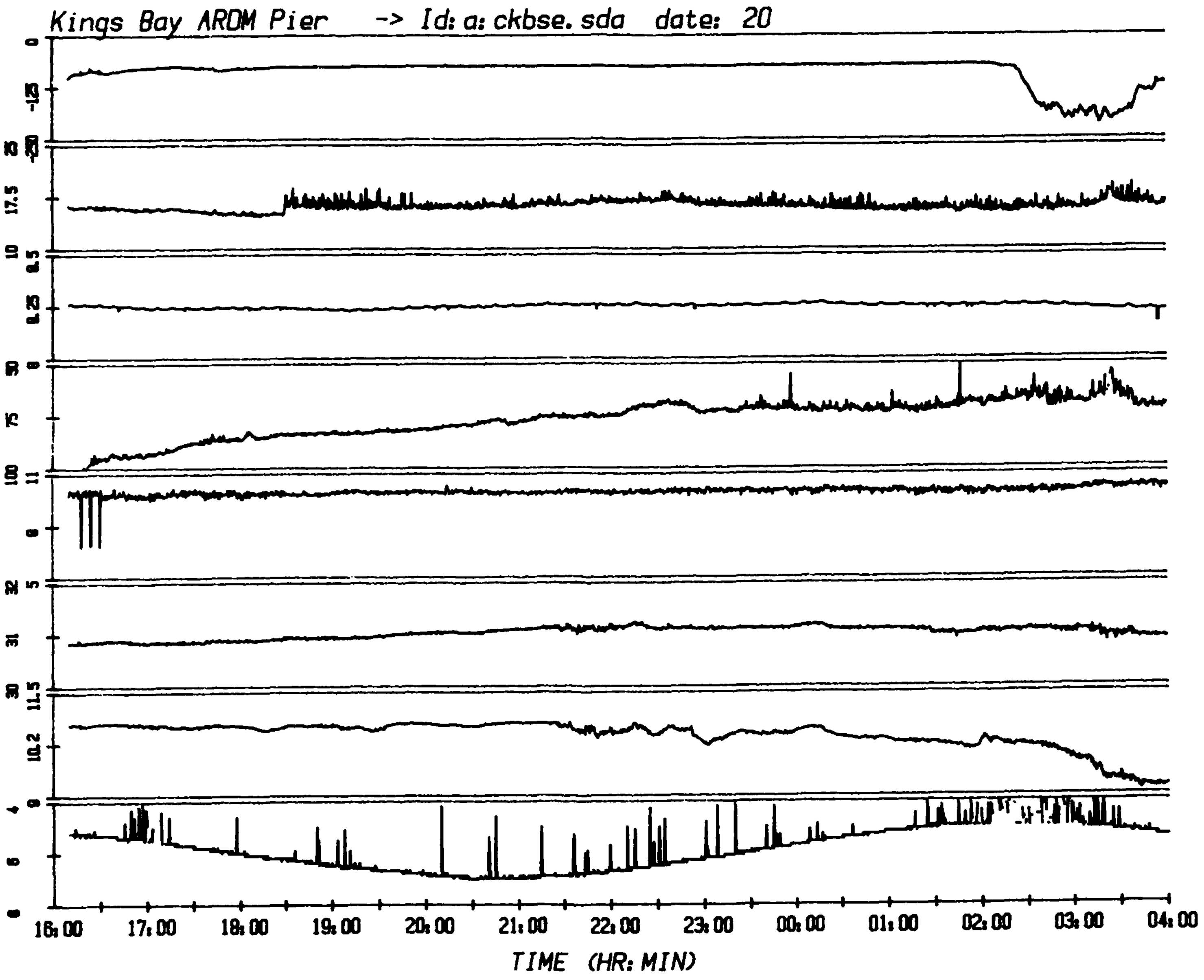

Figure B-6. ARDM pier tidal monitoring: 1615-0400, 20-21 January 1985.

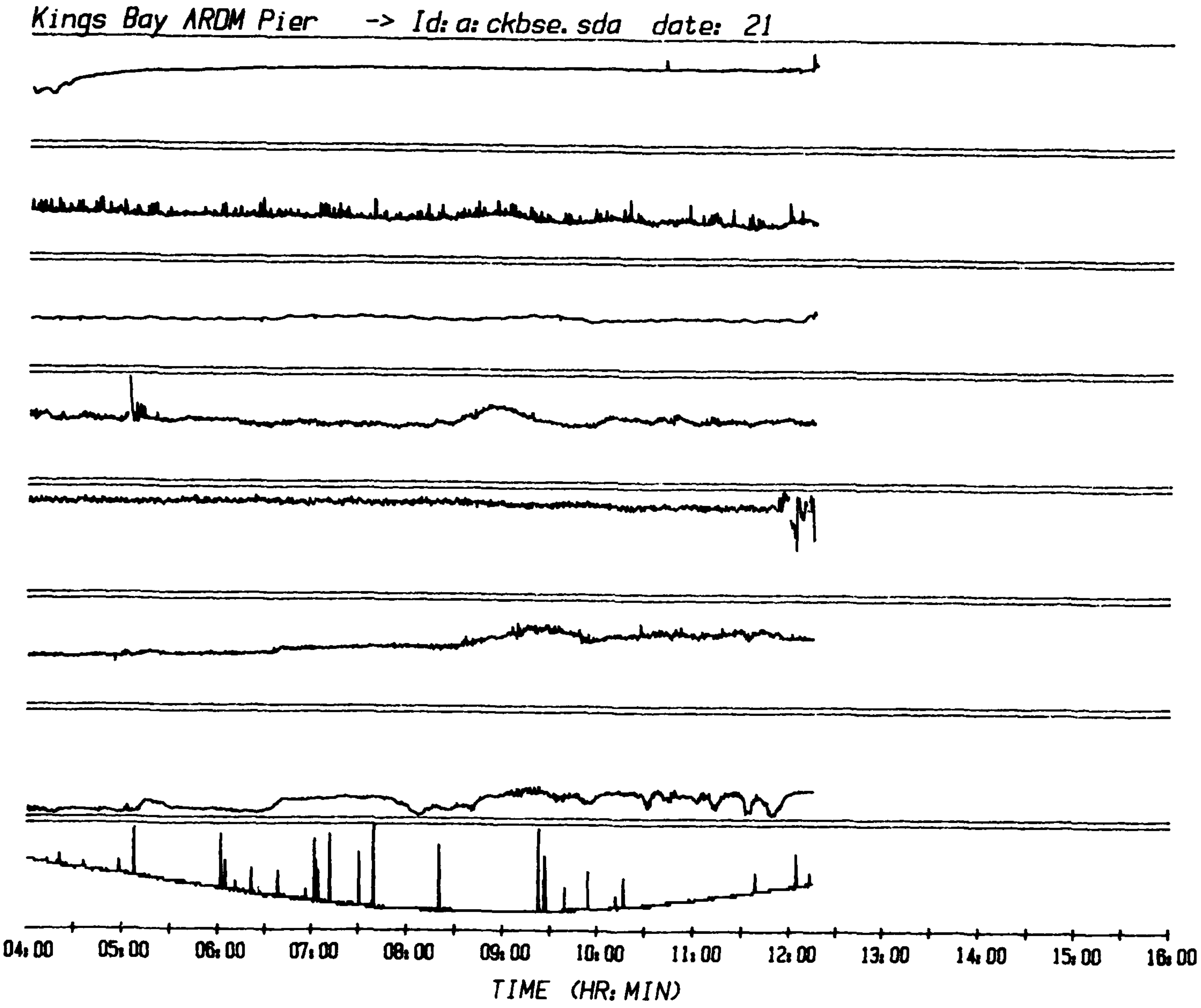

Figure B-7. ARDM pier tidal monitoring: 0400-1206, 21 January 1985.

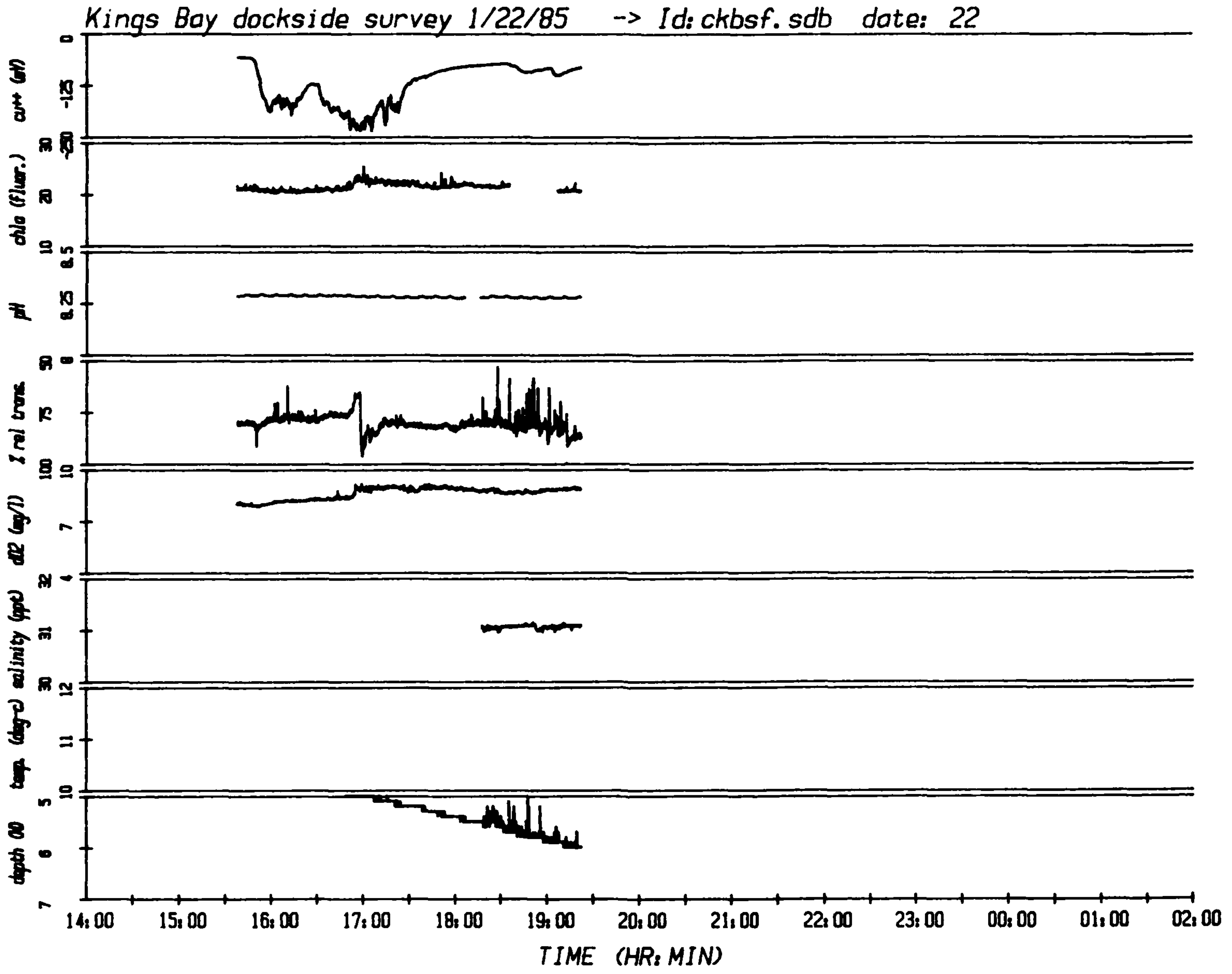

Figure B-8. ARDM pier tidal monitoring: 1537-1922, 22 January 1985.

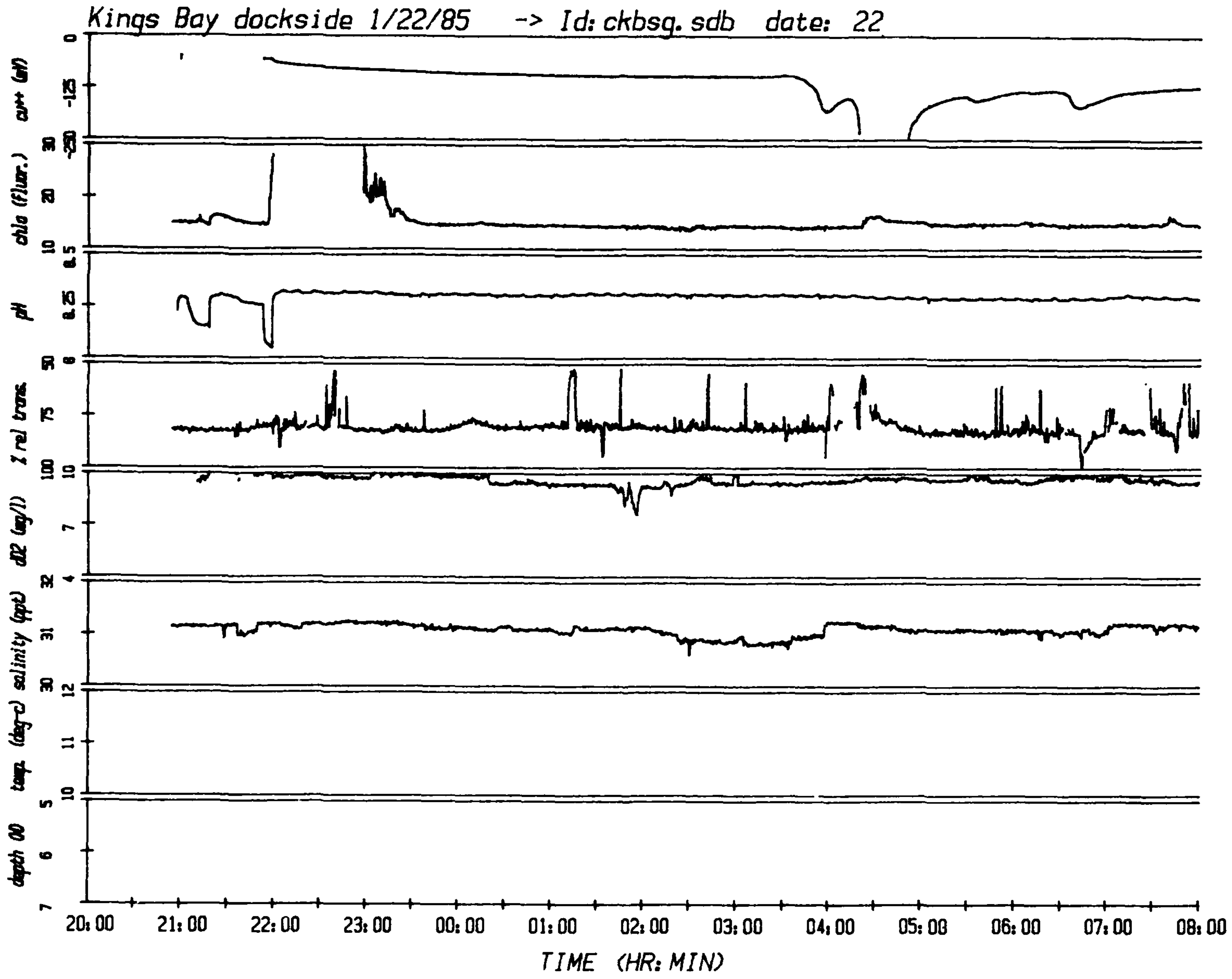

Figure B-9. ARDM pier tidal monitoring: 2057-0800, 22-23 January 1985.

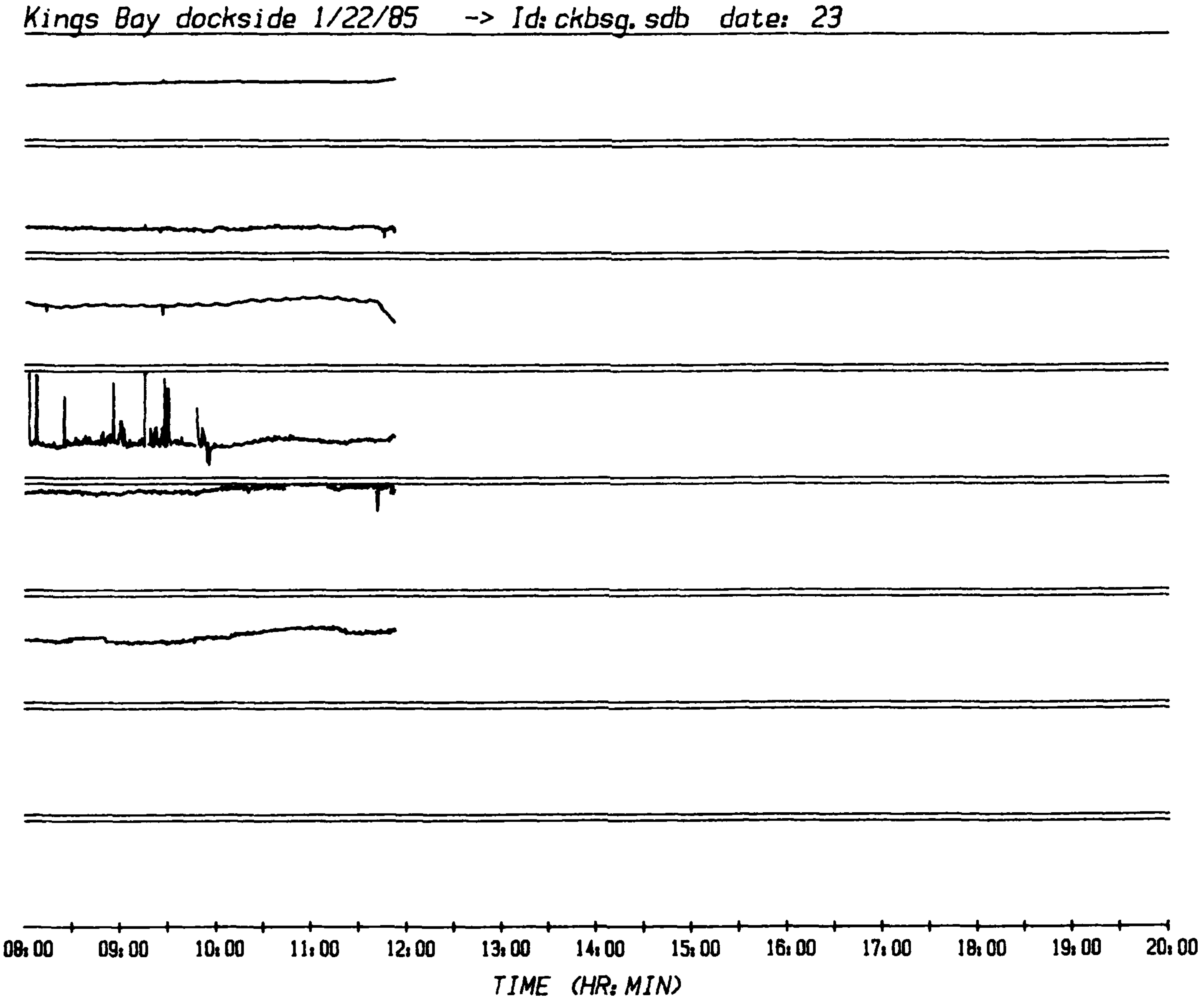

Figure B-10. ARDM pier tidal monitoring: 0800-1154, 23 January 1985.

APPENDIX C

EFFLUENT MONITORING DATA

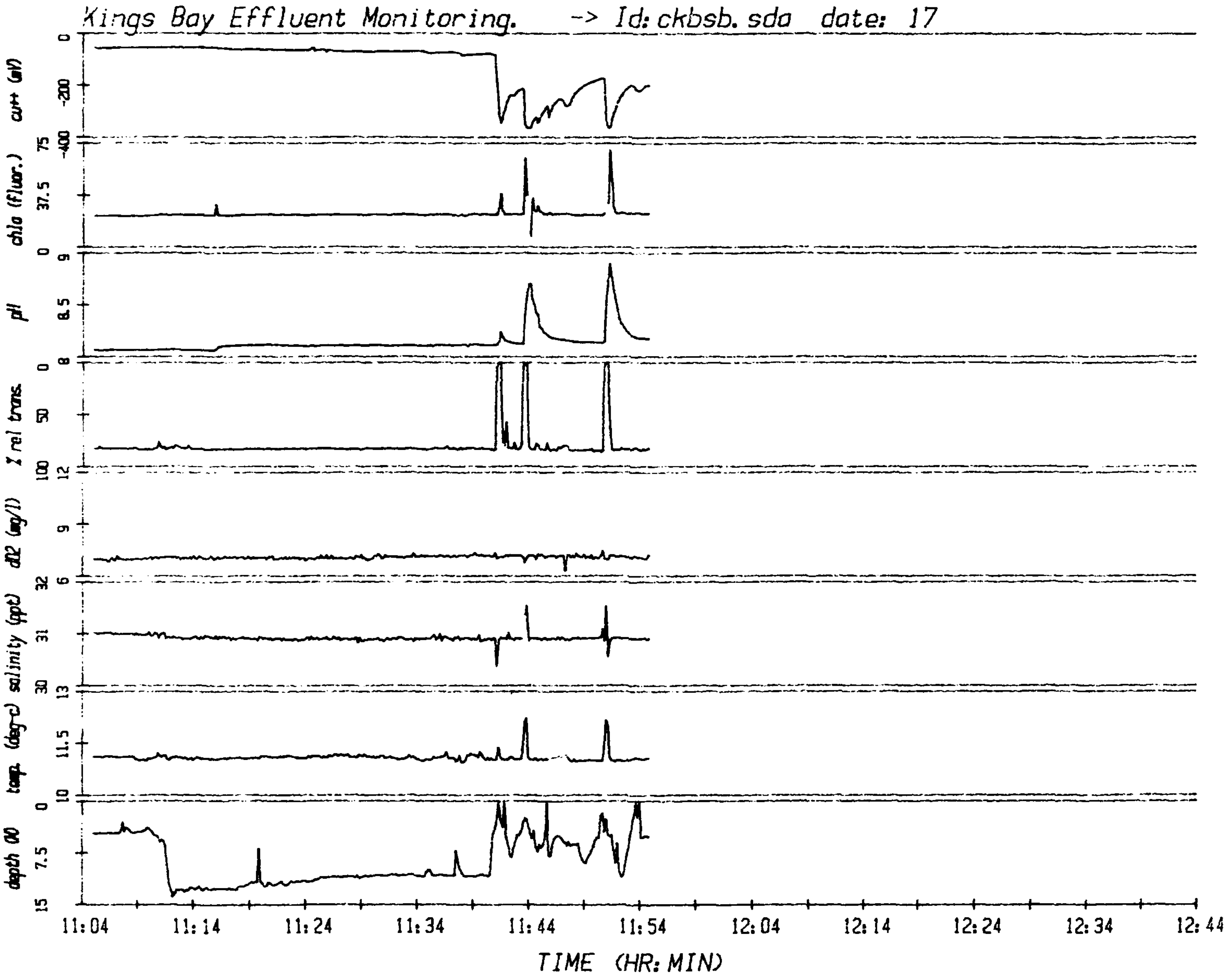

Figure C-1. Effluent monitoring: 1105-1155, 17 January 1985.

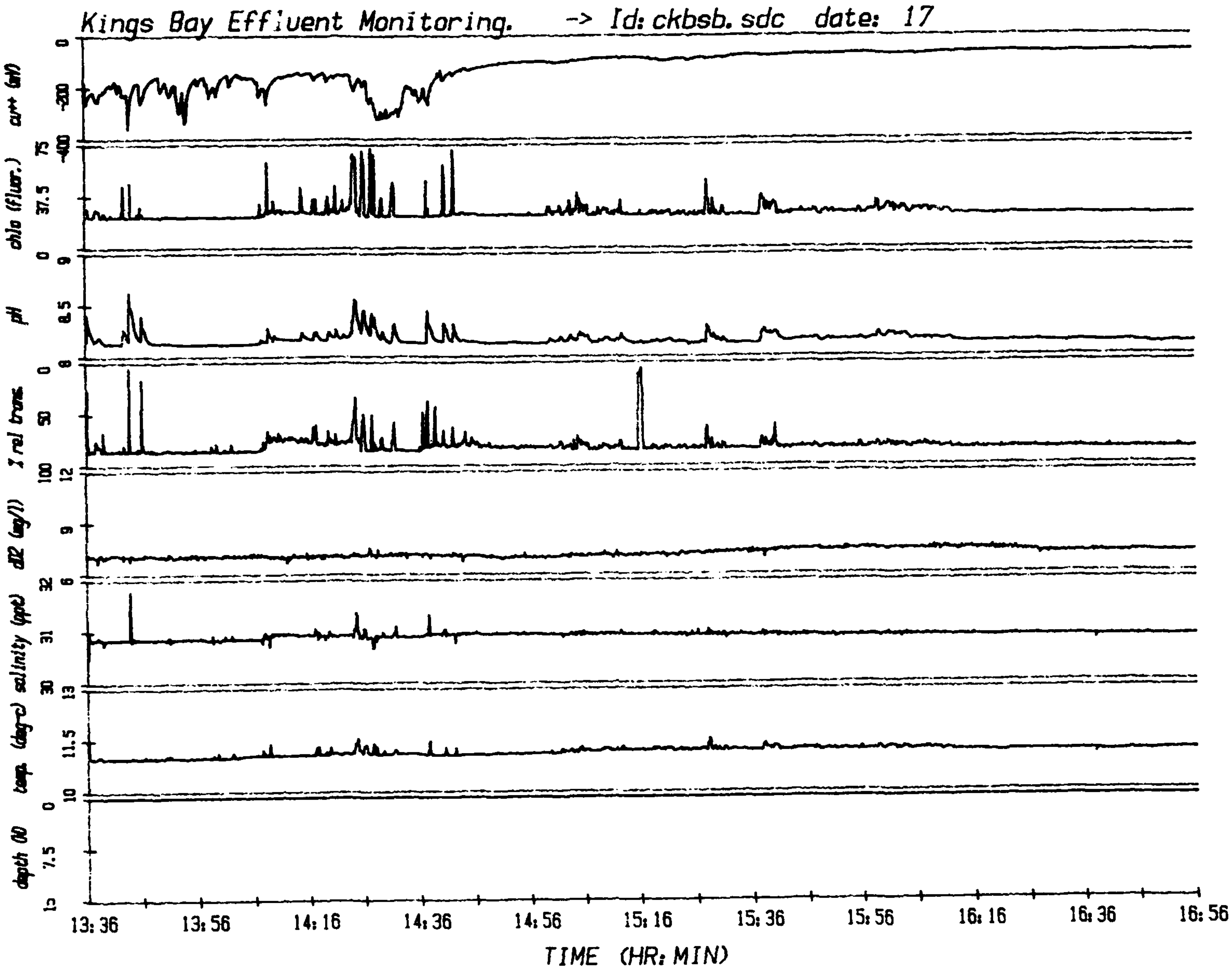

Figure C-2. Effluent monitoring: 1336-1656, 17 January 1985.

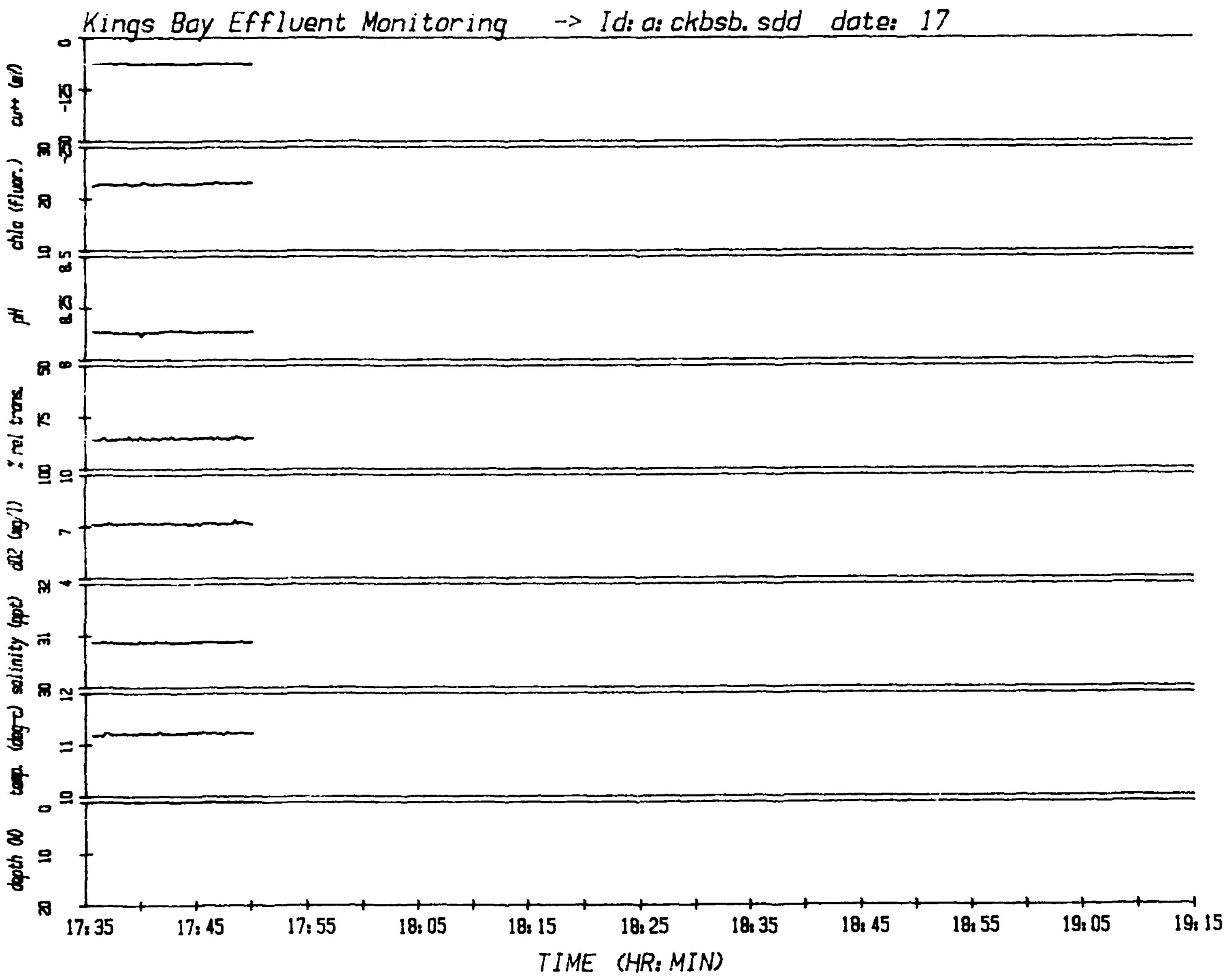

Figure C-3. Effluent monitoring: 1735-1750, 17 January 1985.

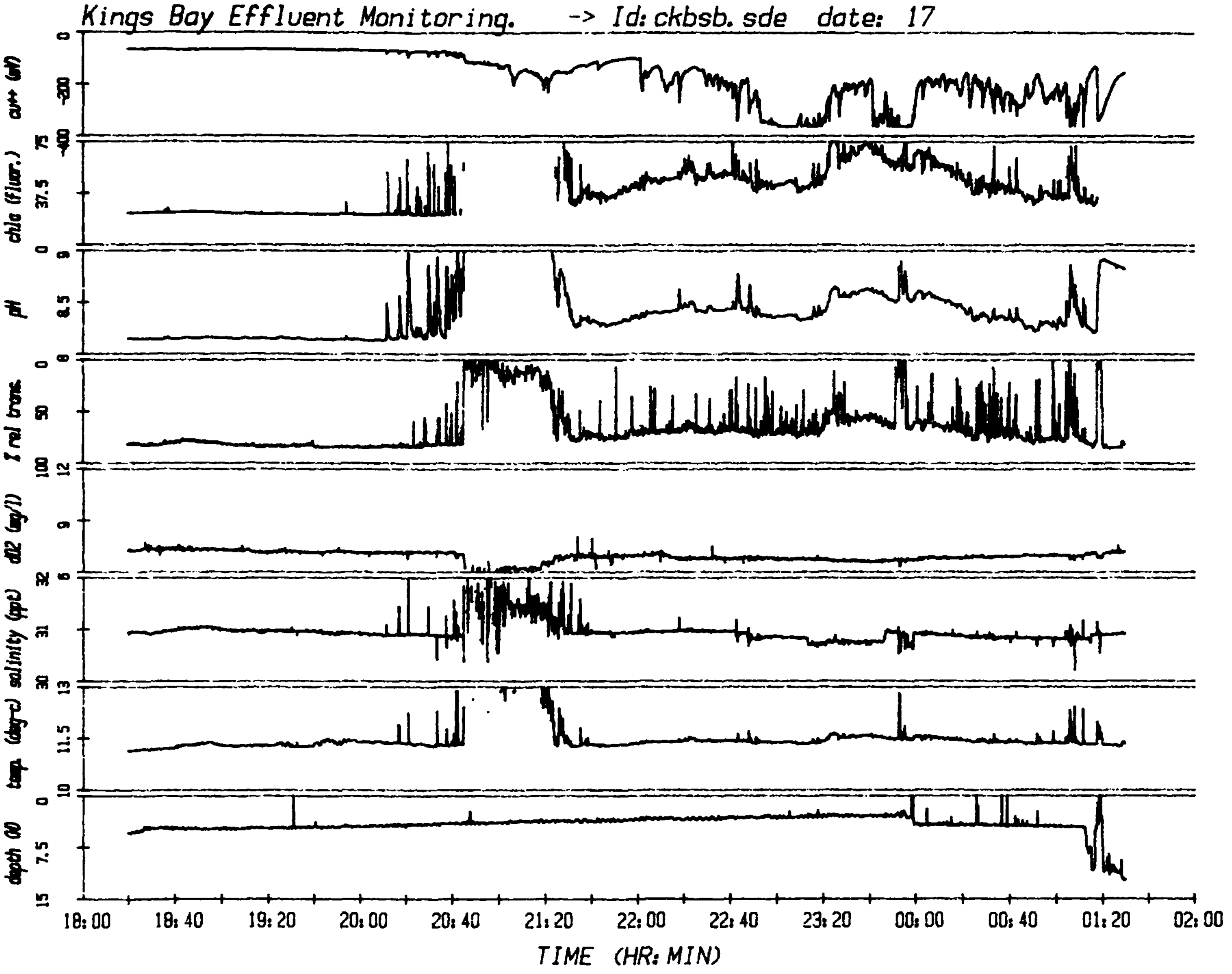

Figure C-4. Effluent monitoring: 1818-0130, 17-18 January 1985.

APPENDIX D

COPPER DATA: CHARTS SHOWING SAMPLE LOCATIONS AND VALUES FOR SAMPLES COLLECTED/MEASURED 19 JANUARY 1985.

AA and ASV values are in mV; Cu-ISE values are in relative mV.

Figure D-1. Copper AA data: Upper turning basin-ebb tide.

Figure D-2. Copper ASV data: Upper turning basin-ebb tide.

Figure D-3. Copper-ISE data: Upper turning basin-ebb tide.

Figure D-4. Copper AA data: Lower turning basin-ebb tide.

Figure D-5. Copper AA data: Lower turning basin-ebb tide.

Figure D-6. Copper ASV data: Lower turning basin-ebb tide.

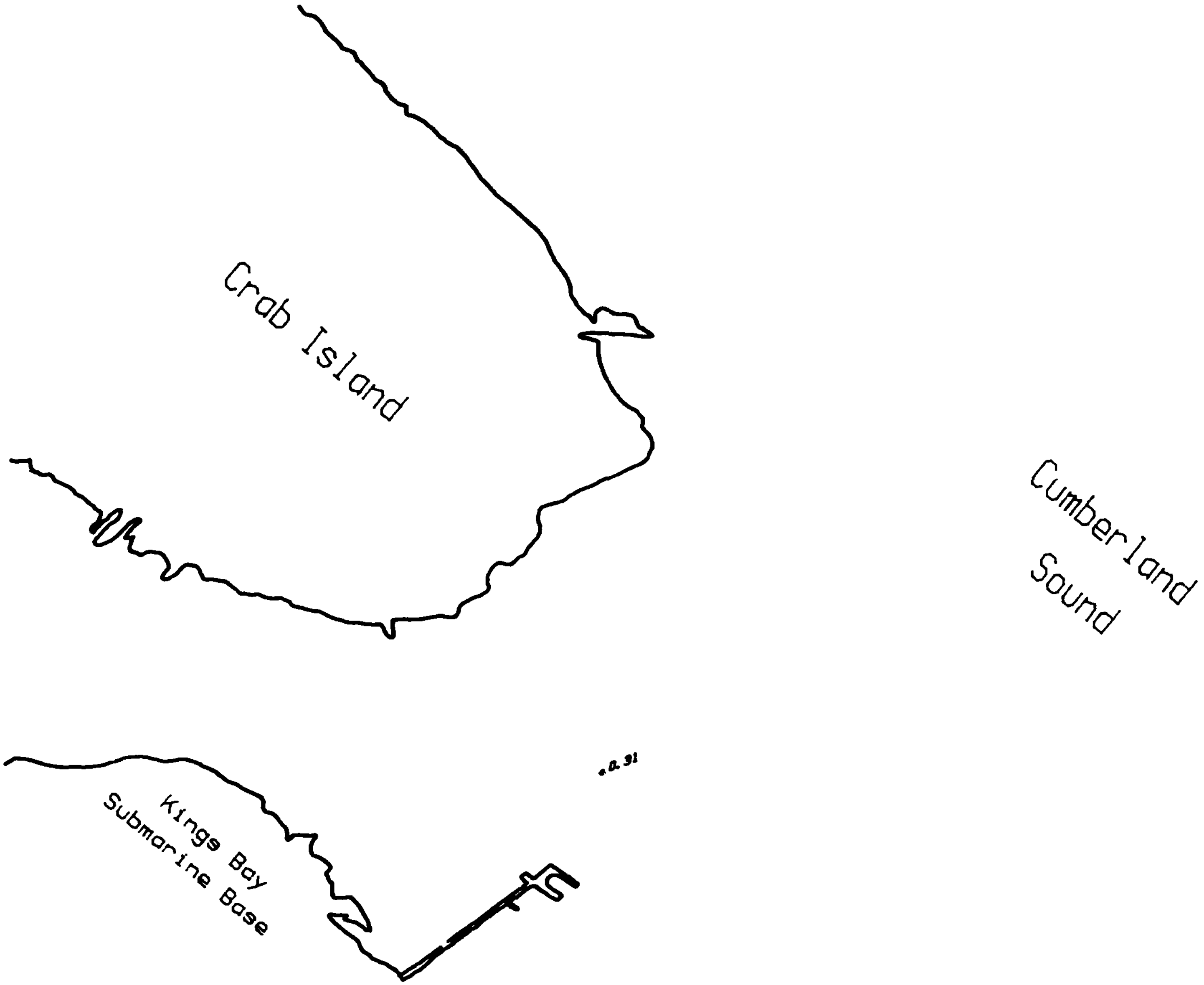

Figure D-7. Copper ASV data: Lower turning basin-ebb tide.

Figure D-8. Copper-ISE data: Lower turning basin-ebb tide.

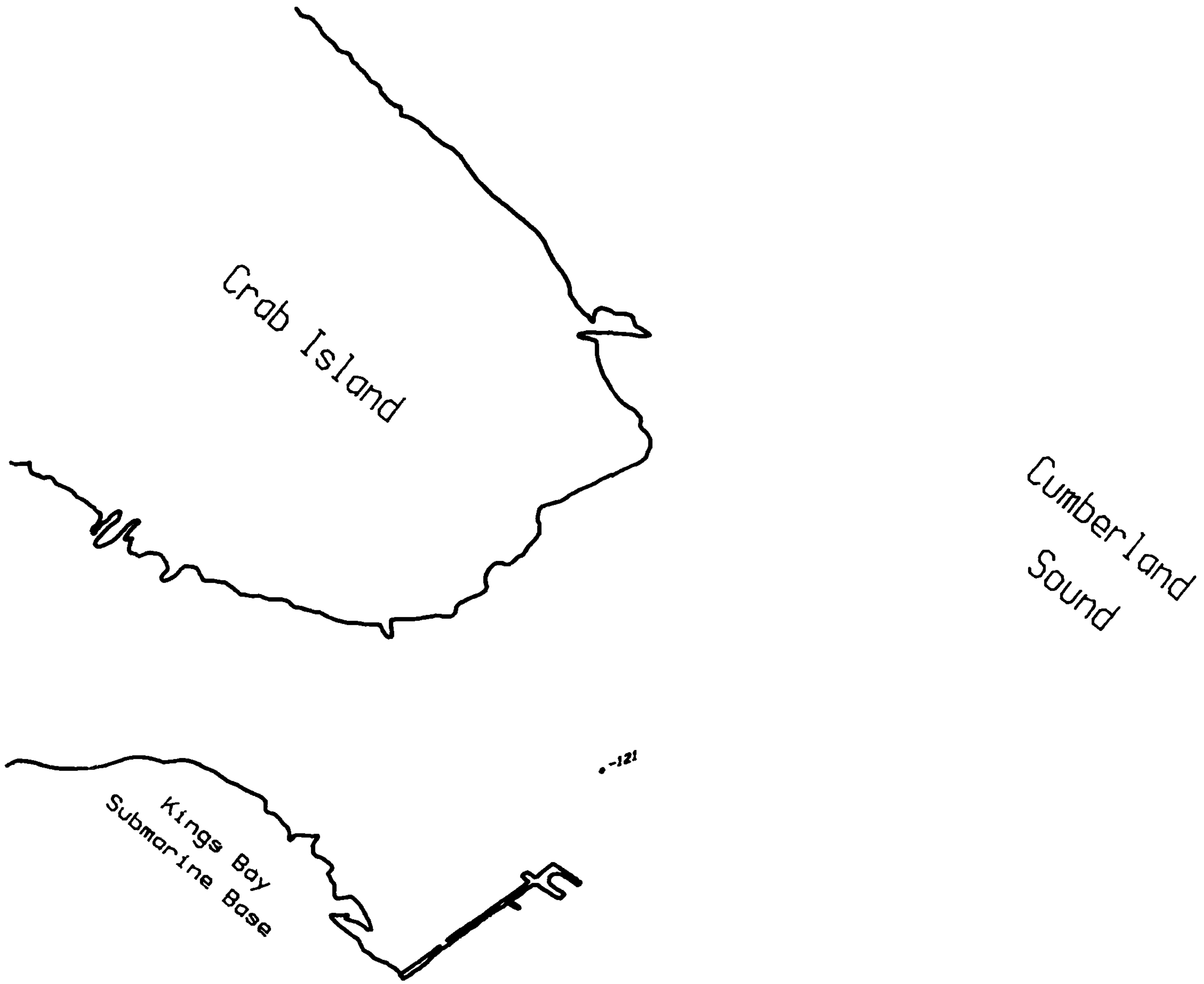

Figure D-9. Copper-ISE data: Lower turning basin-ebb tide.

Figure D-10. Copper AA data: Sound-ebb tide.

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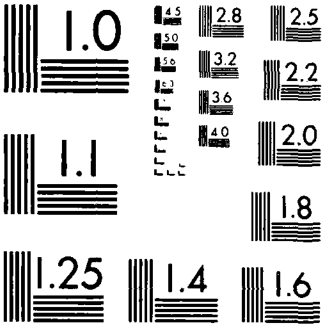
NAVAL OCEAN SYSTEMS CENTER SAN DIEGO CA
S H LIEBERMAN ET AL OCT 85 NOSC/TR-1062
UNCLASSIFIED F/G 13/2 NL



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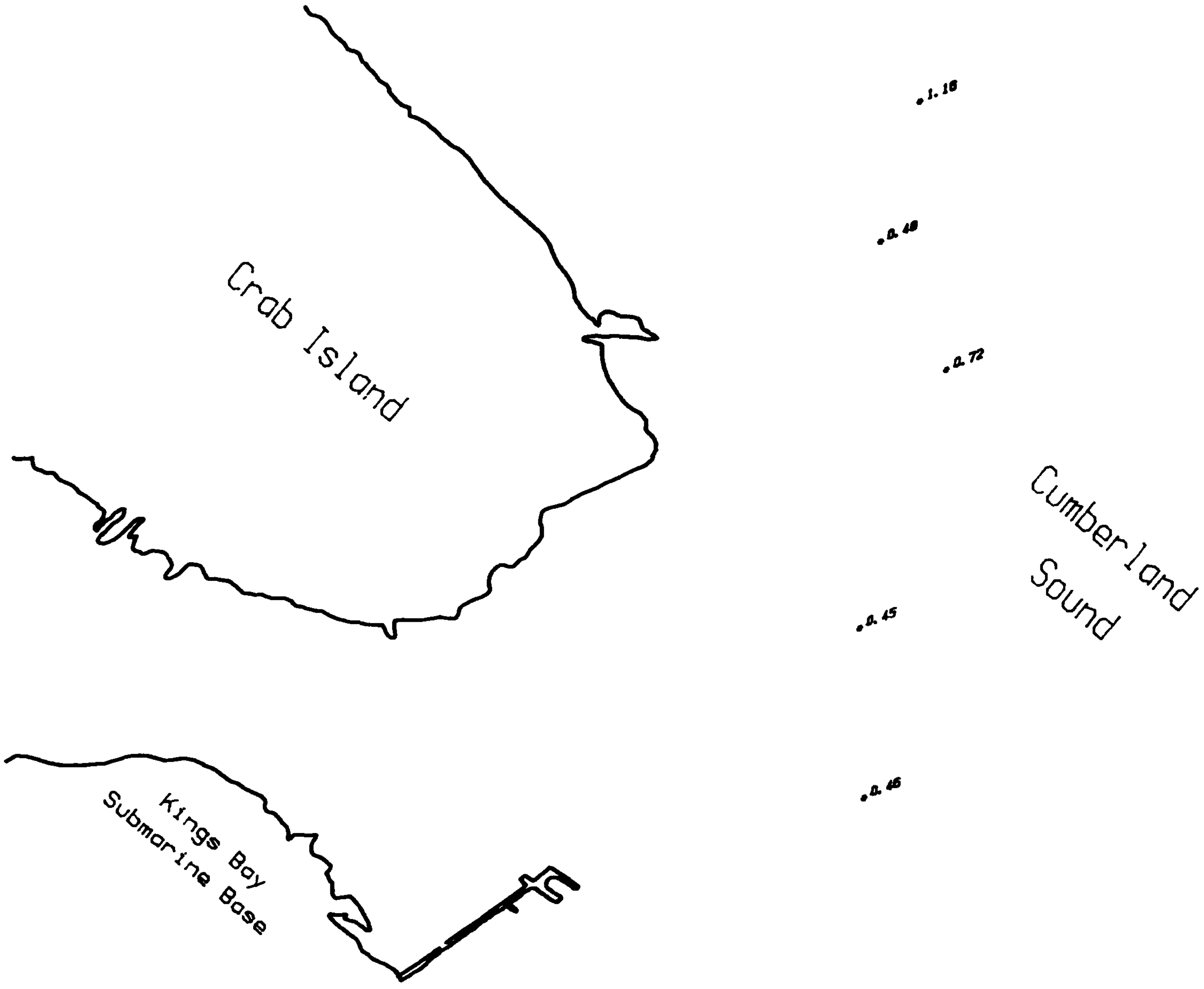

Figure D-11. Copper ASV data: Sound-ebb tide.

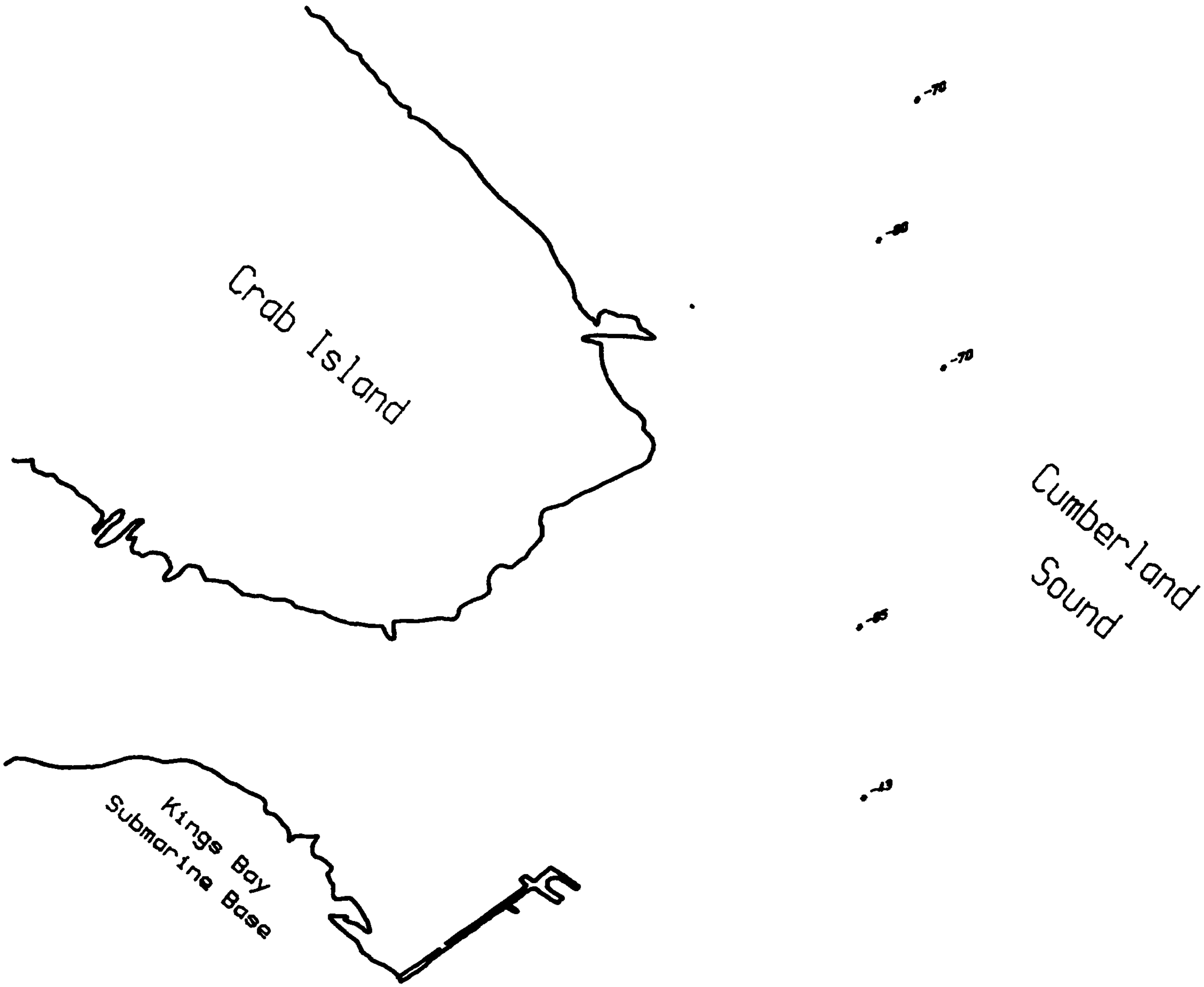

Figure D-12. Copper-ISE data: Sound-ebb tide.

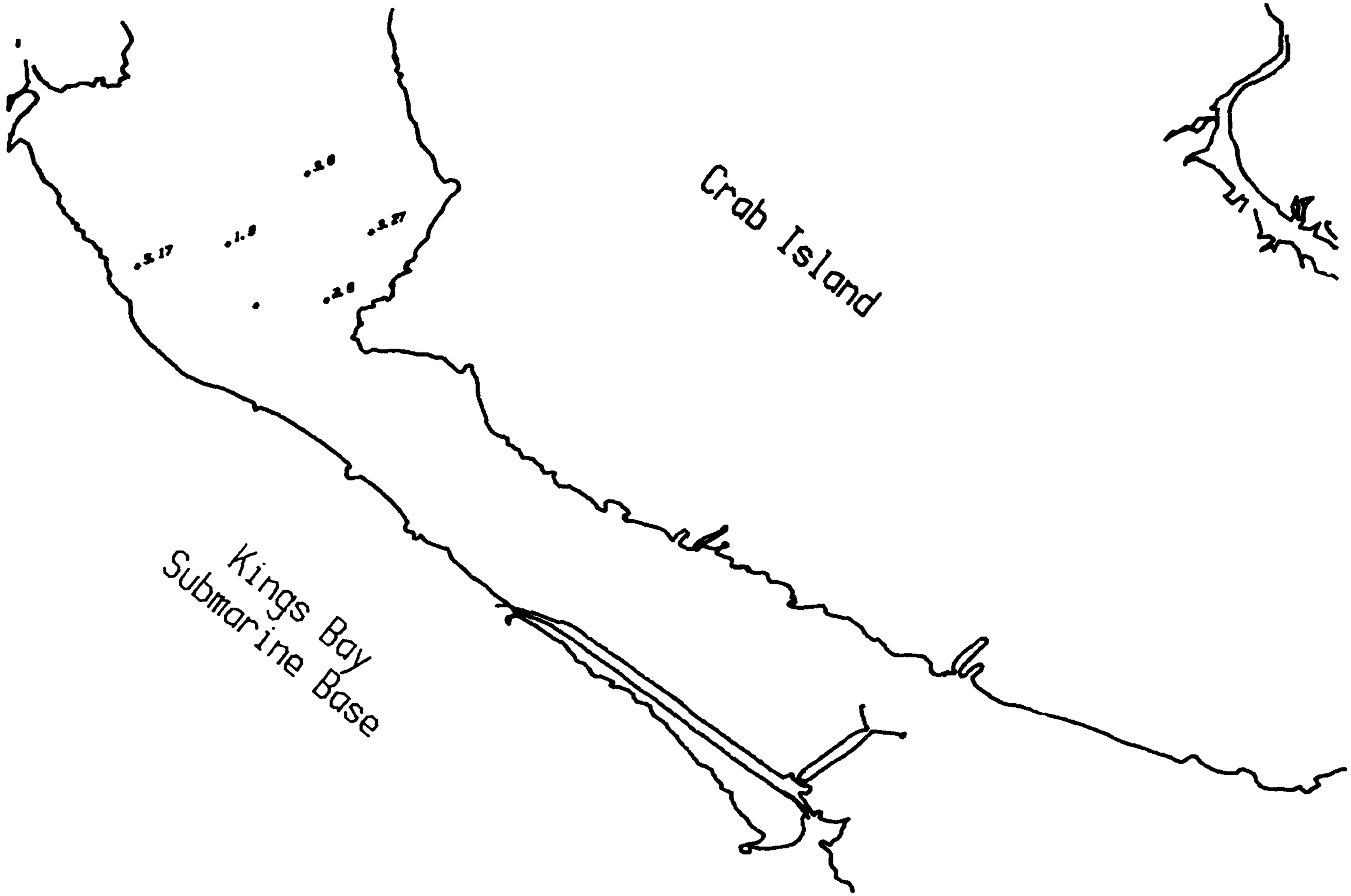

Figure D-13. Copper AA data: Upper turning basin-flood tide.

Figure D-14. Copper ASV data: Upper turning basin-flood tide.

Figure D-15. Copper-ISE data: Upper turning basin-flood tide.

Figure D-16. Copper AA data: Lower turning basin-flood tide.

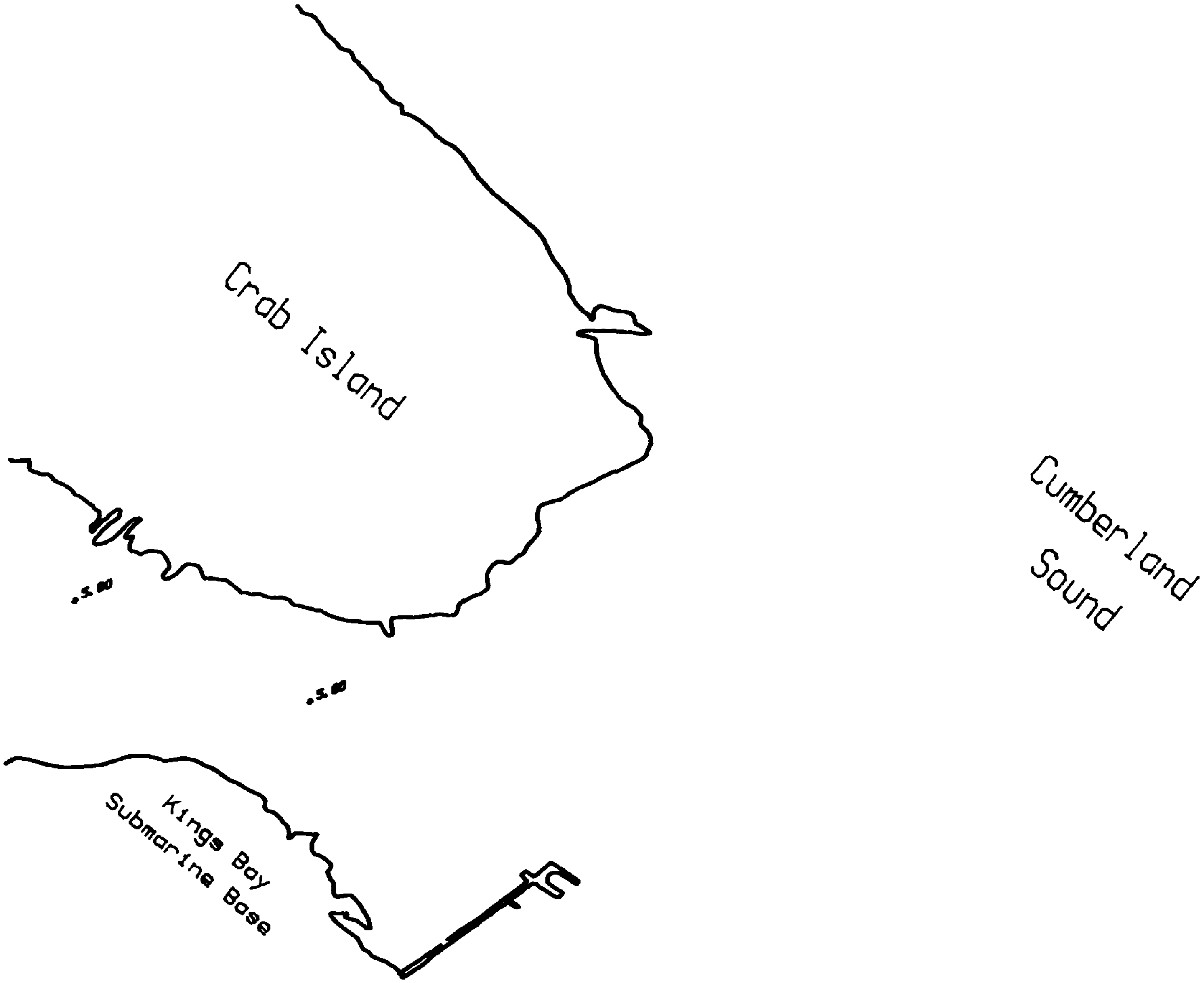

Figure D-17. Copper AA data: Lower turning basin-flood tide.

Figure D-18. Copper ASV data: Lower turning basin-flood tide.

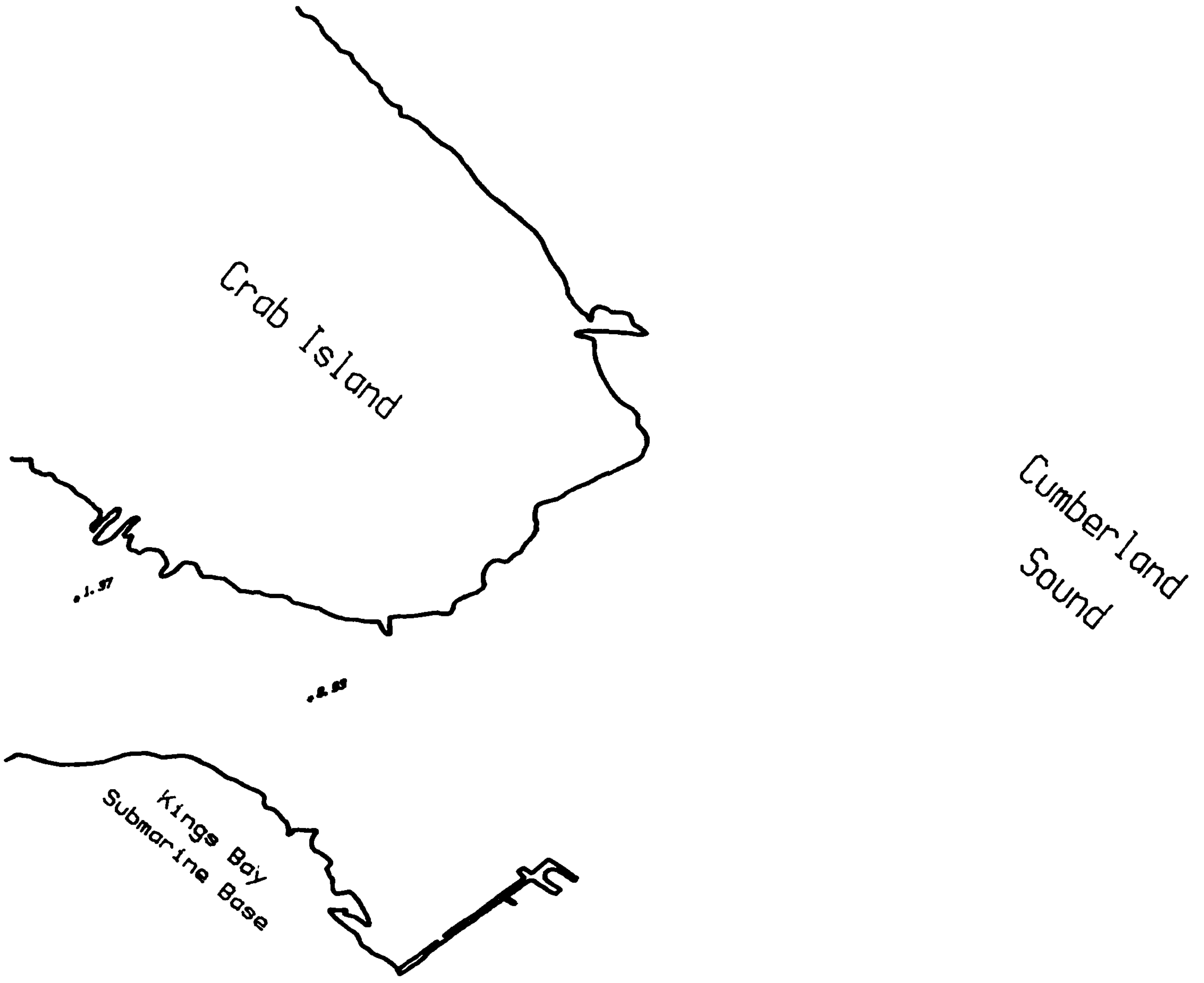

Figure D-19. Copper ASV data: Lower turning basin-flood tide.

Figure D-20. Copper-ISE data: Lower turning basin-flood tide.

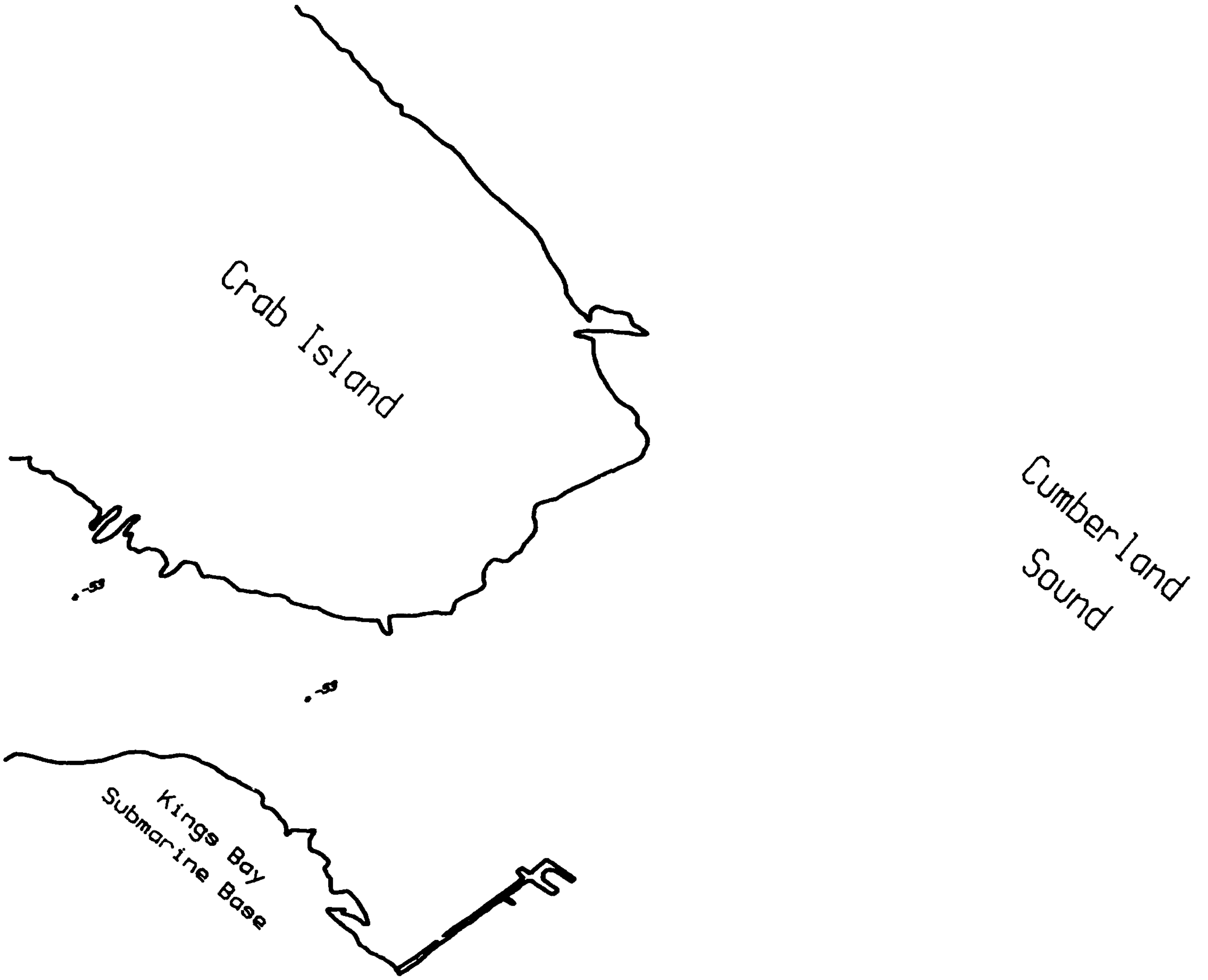

Figure D-21. Copper-ISE data: Lower turning basin-flood tide.

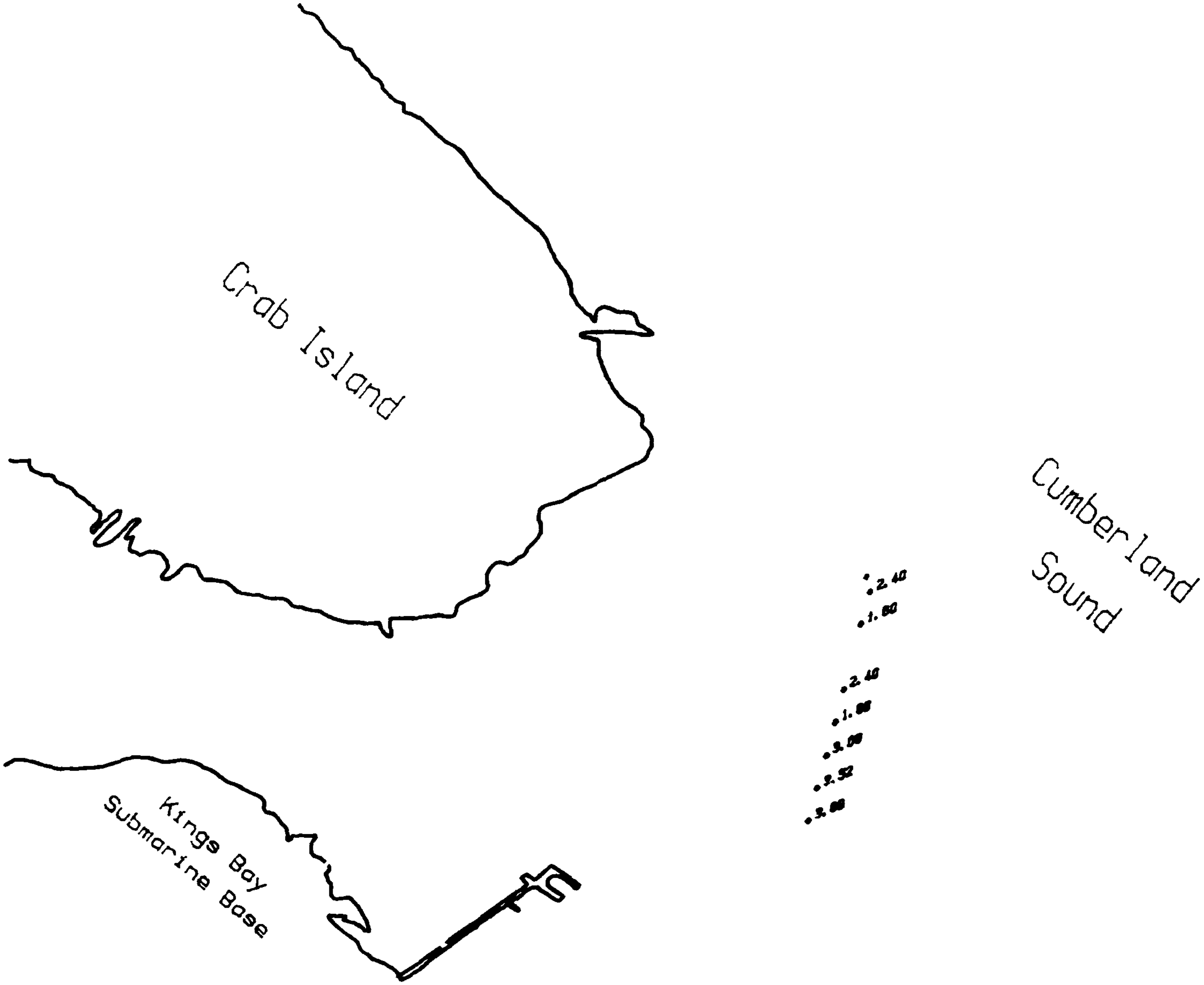

Figure D-22. Copper AA data: Sound-flood tide.

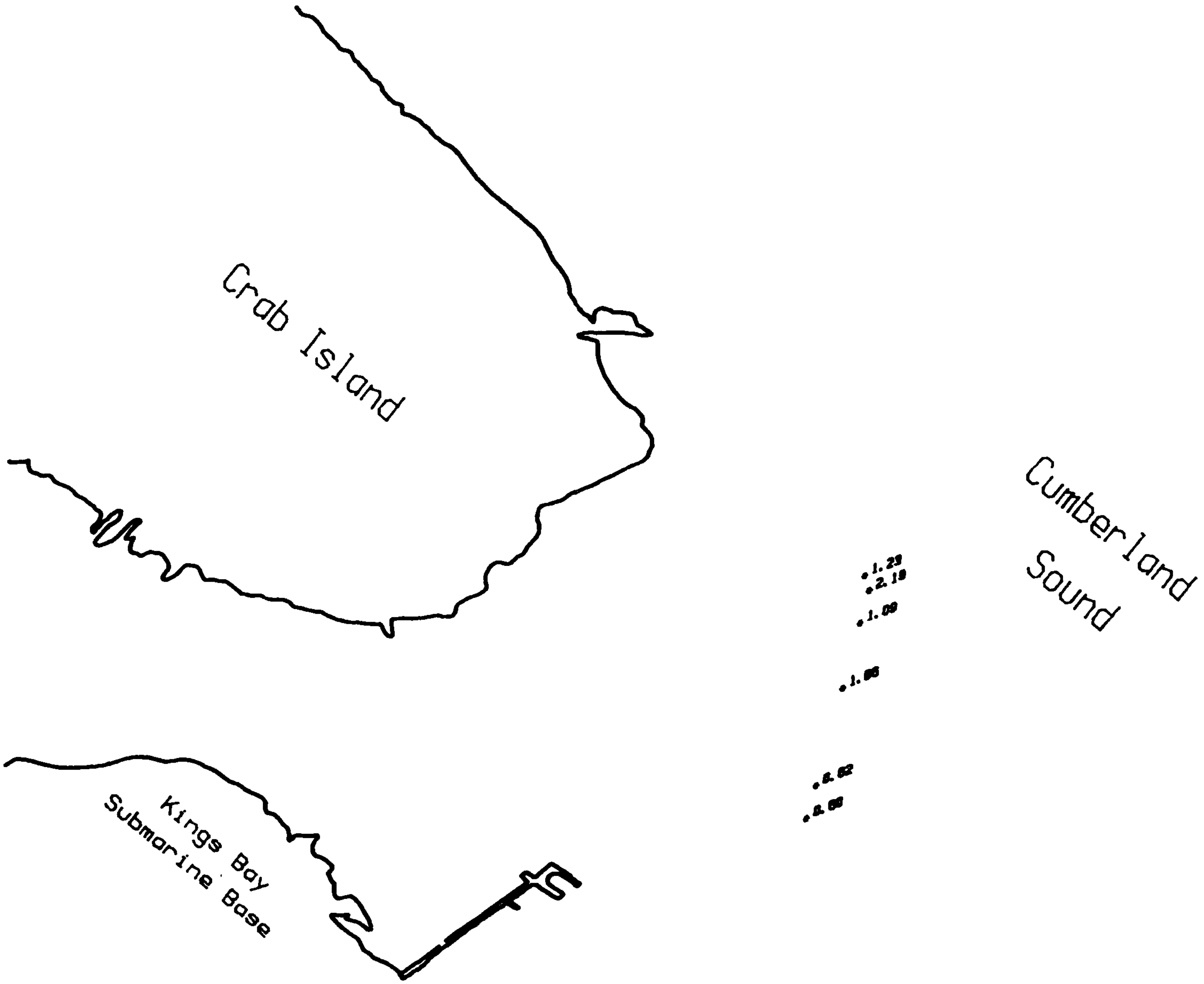

Figure D-23. Copper ASV data: Sound-flood tide.

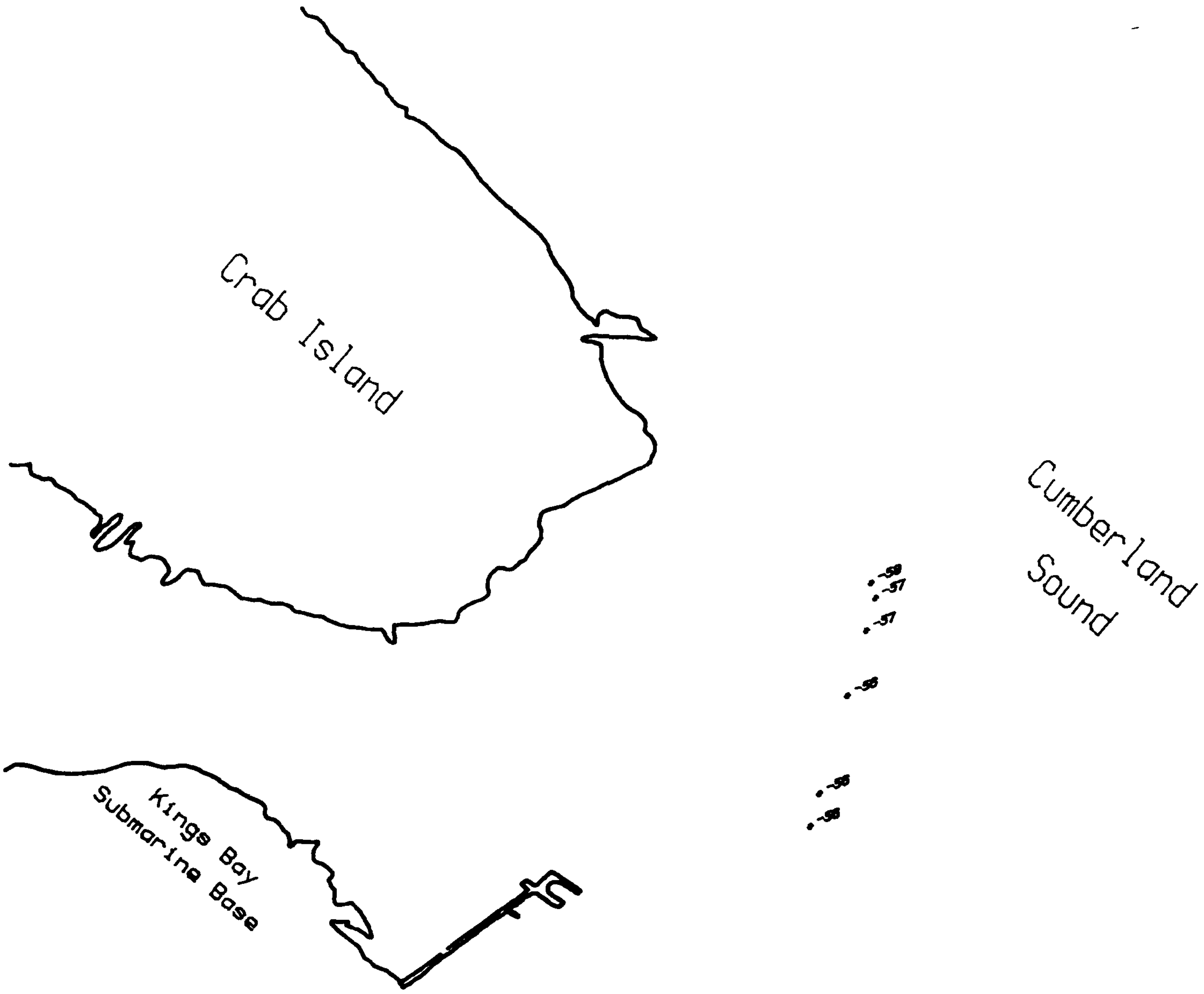

Figure D-24. Copper-ISE data: Sound-flood tide.

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