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UNITED STATES
NAVAL POSTGRADUATE SCHOOL



THESIS

EDB STAGE SURFACE CIRCULATION IN AN
ESTUARY BY CALCIUM ELECTRODE MEASUREMENT

by

David B. Gibson

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OCT 13 1967

June 1967

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EBB STAGE SURFACE CIRCULATION
IN AN ESTUARY BY
CALCIUM ELECTRODE MEASUREMENT

by

David Bruce Gibson
Lieutenant, United States Navy

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN OCEANOGRAPHY

from the

NAVAL POSTGRADUATE SCHOOL
June 1967

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ABSTRACT

The Calcium Activity Electrode was used to study the ebb stage circulation in a coastal plain estuary. Moss Landing estuary receives a large amount of calcium waste from the manufacture of magnesia brick at the Kaiser Refractory plant located adjacent to one of the tributaries of the estuary. One hundred and eighty-nine water samples were collected and analysed to provide calcium distribution data at the confluence of three tributaries in the estuary. A continuity model is described that determines the surface layer circulation pattern in the confluence area using the calcium data. The circulation pattern determined by electrode is in good agreement with supporting information provided by current and dye studies in the confluence area.

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1. INTRODUCTION

Chemical analysis has previously been used to trace ocean water masses; for example, by tracing phosphate rich water (Sverdrup, 1942). However, while chemical techniques have been suitable for the large scale sluggish movements, they have been too laborious and insensitive to apply to the study of detail circulation. The prolonged laboratory techniques of most chemical analyses make the analysis of a significant number of samples prohibitive. Modern electrode techniques offer a rapid and sensitive measurement of many elements, and therefore have potential application in chemical tracer studies.

The purpose of this paper is to present an evaluation of the Calcium Activity Electrode as an effective instrument in studying a detailed circulation.

The specific problem selected for study, with the aid of electrode analysis, was a description of the ebb tide surface circulation pattern at the confluence of several tributaries in the Moss Landing estuary, Moss Landing, California. The electrode was to aid in determining this circulation pattern by tracing a calcium pollutant being discharged into one of the three tributaries. Figure 1 is an aerial photograph of Moss Landing showing the geographical relationship between the pollutant source, tributaries, mixing zone and estuary outlet. Figure 2 is an enlarged aerial photograph showing bounds of the mixing zone, which is the turning basin for the small boat harbor. Tributaries labeled A, B and C are also shown.

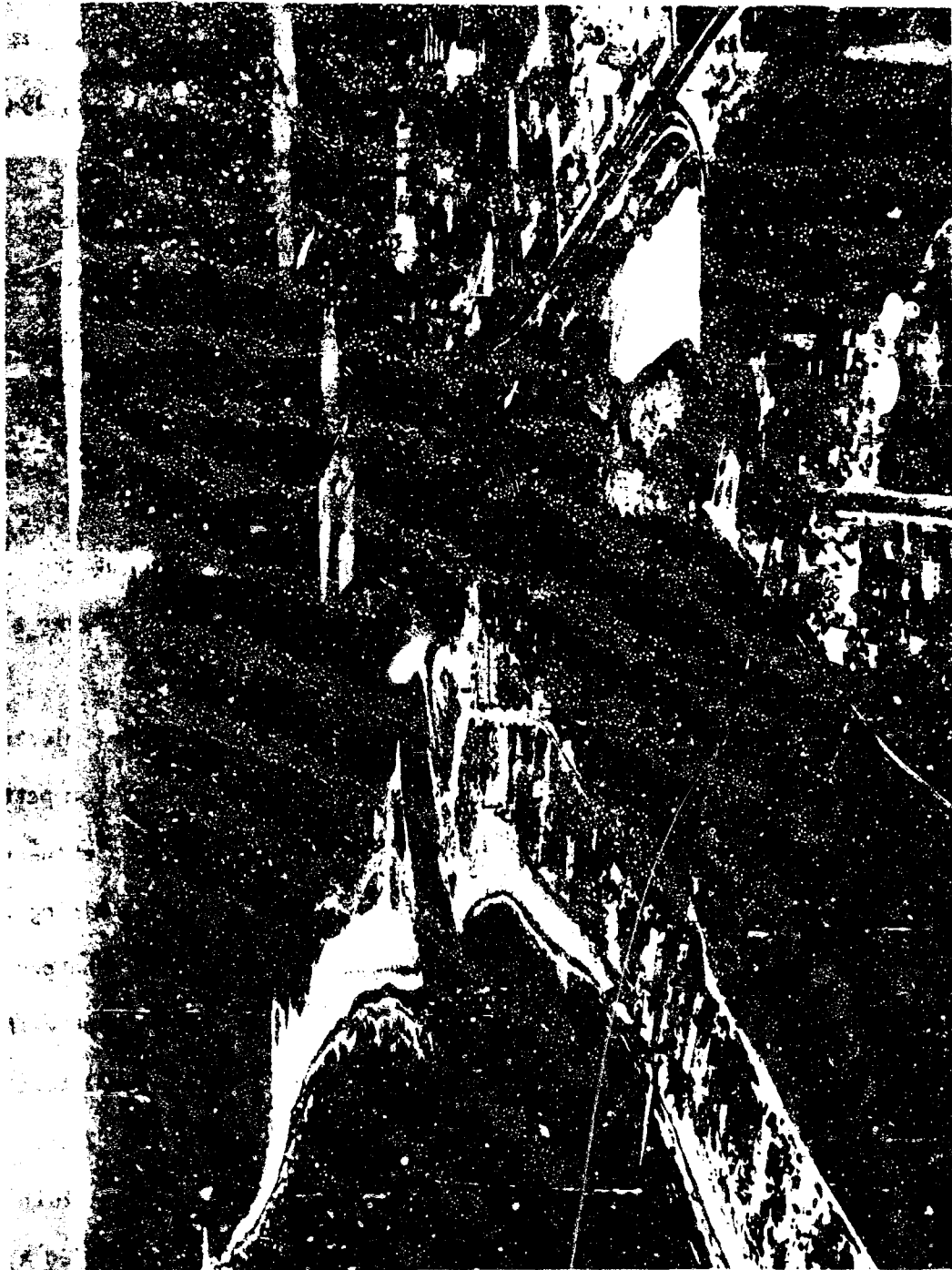


FIGURE 1

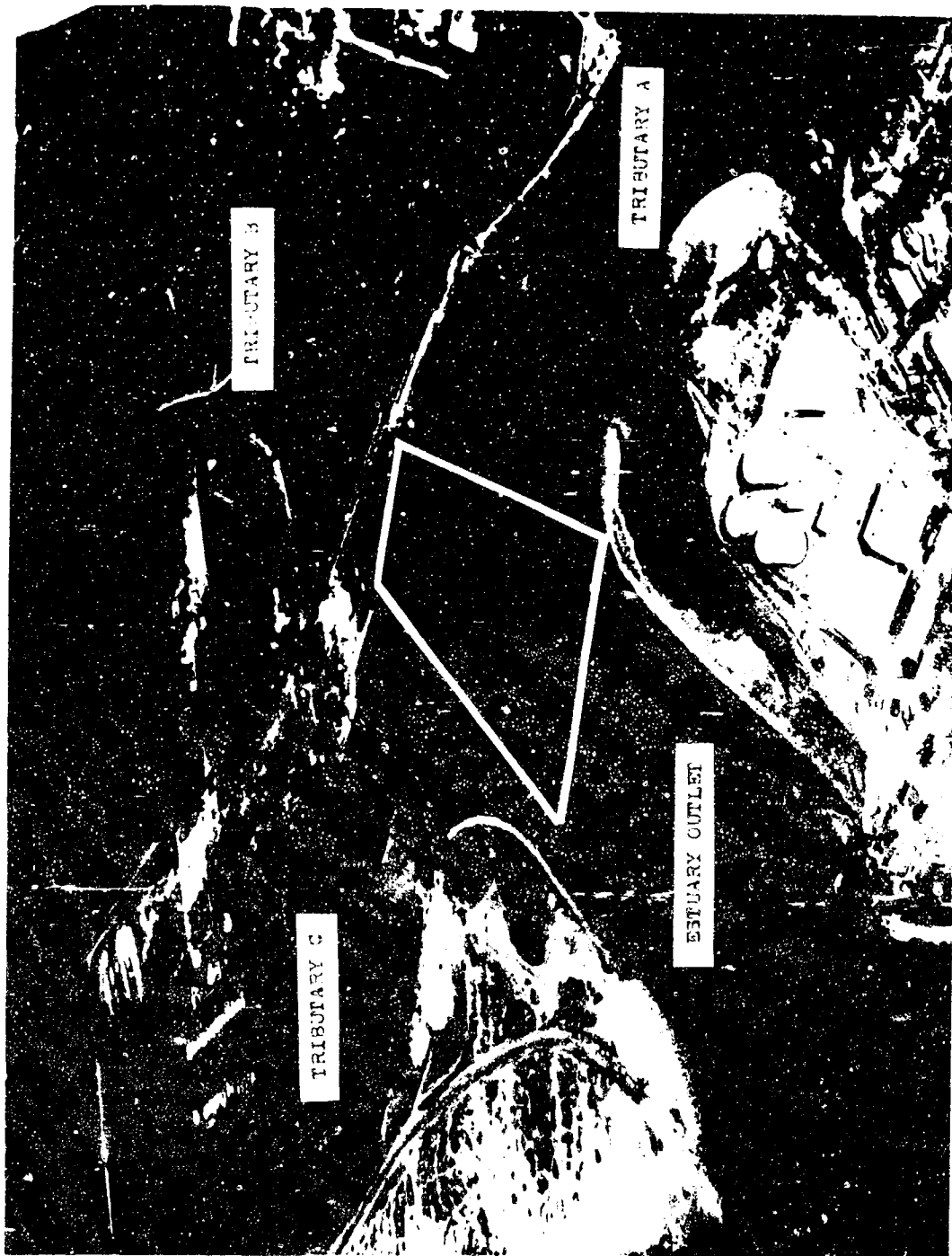


FIGURE 2

One hundred and eighty nine water samples, and supporting physical oceanographic data were collected on four field trips. Formulating a continuity model within the turning basin, we used the calcium distribution to determine the circulation. The resulting circulation pattern was supported by dye studies taken on a subsequent field trip.

Vertical thermal profiles and a water budget study were conducted for the purposes of strengthening the postulates of the continuity model and for providing further evidence in support of the circulation shown by the chemical analysis.

II. BACKGROUND

The Moss Landing estuary was selected for this study for the following reasons:

1. Close proximity to Monterey and research facilities;
2. The estuary receives an industrial waste product high in calcium concentration;
3. The bottom topography and configuration of the estuary are known in sufficient detail;
4. No previous definitive studies have been conducted in the estuary.

Area Description. The Moss Landing estuary, Elkhorn Slough, was created in 1947 by the Army Corps of Engineers, by cutting a channel through the sand dunes which separated Monterey Bay from a body of fresh water covering about the same surface area as the waters of the estuary today.

The characteristics of coastal plain estuaries have been described by Williams (1962). Moss Landing estuary appeared to be two layered during this study. In this type of estuary, the salt wedge intrusion moves into the estuary on the flood tide adjacent to the bottom with fresher water being found nearer the surface. The estuary was previously shown to be two layered from the results of surface to bottom salinity measurements conducted over a two month period by the Kaiser Refractory plant located at Moss Landing. The analyses were conducted prior to Kaiser's construction of a sea water intake within the estuary.

The estuary is composed of three tributaries meeting in a confluence area referred to in this paper as a turning basin (Figure 2).

Tributary A, the turning basin and the estuary outlet are periodically dredged by the Army Corps of Engineers in order to maintain the navigational channel at an approximate depth of eighteen feet at mean lower low water. Once a year the Army Corps of Engineers sounds the dredged areas of the estuary and reports the results in a published sounding survey for Moss Landing Harbor. Tributary C is dredged as often as necessary by Elkhorn Yacht Club to an approximate depth of ten feet at mean lower low water, and recent soundings are available for this tributary.

Only a few isolated soundings have been taken in tributary B by the Pacific Gas and Electric Company in the area of their cooling water discharge line. These soundings are considered to be of little value since they were obtained over ten years ago.

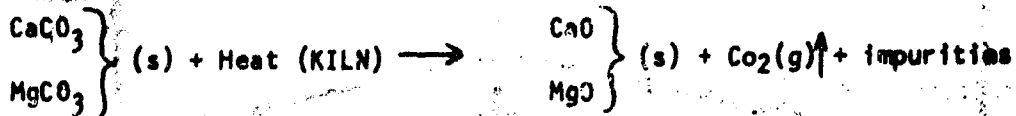
The Moss Landing estuary is a small estuary. Not considering the surrounding land which it drains, its surface area is less than one square mile.

Calcium Pollutant. Calcium pollutant is discharged into tributary A by the Kaiser Refractory plant at Moss Landing as a waste product in the manufacture of magnesia brick. This pollutant has been discharged by Kaiser at a steady rate and on a continuous basis for over a fifteen year period. Calcium pollutant is discharged into the estuary in aqueous solution containing a calcium concentration 3.9 times that of water analysed from the adjacent water of Monterey Bay.

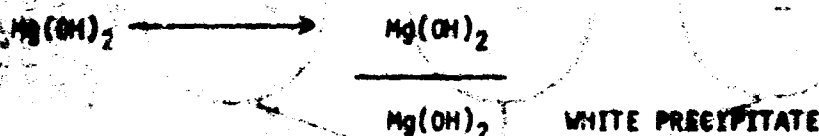
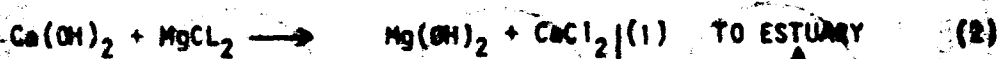
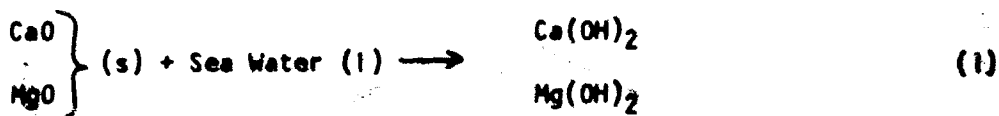
Kaiser manufactures magnesium oxide brick using dolomite from Natividad, California. Dolomite ($MgCa(CO_3)_2$) is first crushed and heated in a kiln at Natividad. This process yields a granulated solid composed of calcium oxide (CaO) and magnesium oxide (MgO) as described by the following equation:

DOLOMITE

COMPOUND



The CaO/MgO mixture is then transported to the Kaiser plant at Moss Landing where it is placed into one of two reaction tanks containing filtered sea water (Plate 1). The process extracts 90% of the magnesium contained in the sea water as a white precipitate of magnesium hydroxide [Mg(OH)₂]. The slurry is pumped from the reaction tanks and equally divided into three settling tanks. In these tanks the products are separated by gravity. The concentrated calcium chloride solution is drawn off into a discharge line leading back to the estuary. The magnesium hydroxide precipitate is pumped into two washing tanks. The magnesium hydroxide is allowed to settle through fresh water in these washing tanks purging any calcium chloride carried along with the precipitate. The fresh water from these tanks containing dilute calcium chloride is spilled into the pollutant discharge line where it dilutes the waste from the settling tanks by a factor of 25%. The chemical reaction equations describing these processes are:



The calcium pollutant having a concentration of $2.2 \times 10^{-2} M$ is discharged into the estuary at a rate of 20,000 gpm for a total discharge of 125 pounds of calcium per minute.

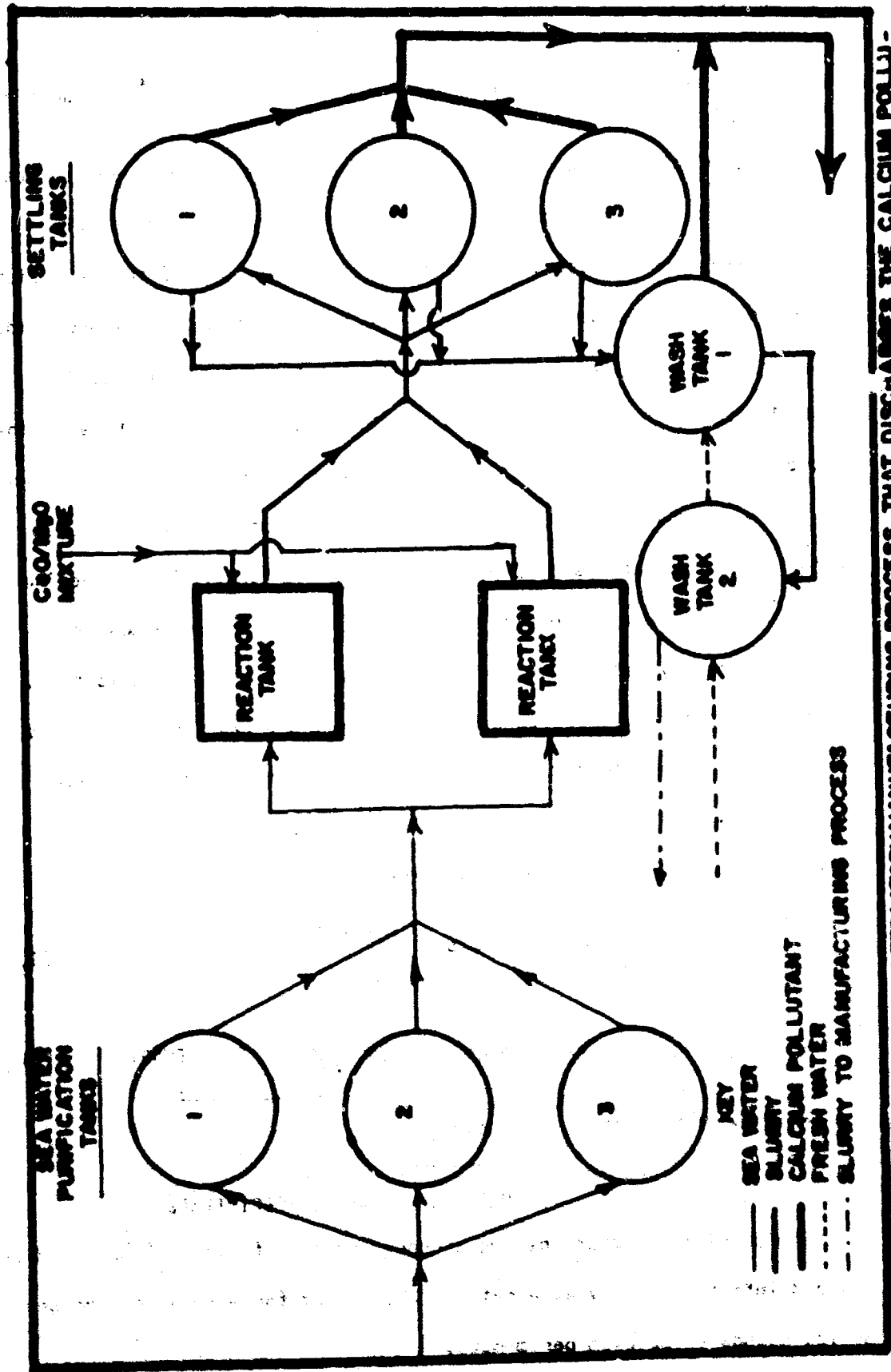


PLATE I. A SECTION OF KAISER REFRACTORY MANUFACTURING PROCESS THAT DISCHARGES THE CALCIUM POLLU-

Previous Electrode Studies. Thompson (1966) compared the electrode analysis of Copenhagen Water ($Cl = 19.37\%$) to results reported by Garrels and Thompson (1962) using the classical technique. The results agreed within 3% of the measured value. Experimental error in the electrode measurement is $\pm 2\%$ and that of Garrels and Thompson was approximately $\pm 2\%$. The precision of the electrode measurement is therefore comparable with the measurements by classical means (Thompson, 1966). Thompson's results show that values measured by the electrode are as good or better than values obtained by the classical method.

The calcium electrode reduces the laboratory analysis time from at best hours for the classical technique to approximately fifteen seconds per sample. The classical technique includes two precipitations, two filtrations and a titration with permanganate. The analysis is time consuming due to slow crystallizations of the precipitates obtained. Filtration of these precipitates is also difficult to perform without loss of calcium. Extreme care must be maintained throughout the analysis in order to obtain accuracy comparable to the electrode capability.

III. EXPERIMENTAL PROCEDURES

Field Trips. Data was collected on four field trips: October 15, 1966; November 27, 1966; January 8, 1967; February 8, 1967. These dates are in the fall-winter season of this area and were selected using the following criteria;

1. Daylight sampling hours.
2. The same tide range (within ± 1.5 feet) during each field trip and for the preceding two days.
3. Similar weather conditions prior to and during each field trip. Specifically, winds were to be less than five knots during a field trip, and no rain for at least four days preceding data collection.

Each field trip was designed to provide specific information. Field Trip I showed the traceability of the pollutant using the electrode to determine its distribution. A more detailed identification of the pollutant movement within its source tributary was the objective of Field Trip II. The purpose of Field Trip III was to study the circulation within the turning basin by using the calcium distribution within the estuary. In addition, current measurements and tide staff readings were obtained and used as supporting data. Dye studies were conducted on Field Trip IV as an independent method of studying the circulation in the turning basin and to estimate the rate of vertical diffusion in the turning basin.

General Data Collection. Field data was collected from thirteen foot rowboats powered by five horsepower outboard motors. Predetermined sampling stations were marked at the beginning of each field trip using

moored plastic floats. Stations were reliably located because navigation in the estuary can be accurately done due to the nearness of numerous prominent landmarks. The estimated positioning error is ± 10 feet.

Sampling stations were easily occupied and maintained during sampling. The mooring method used is shown diagrammatically in Plate 2.

Sampling Equipment. Water samples of 250 ml were collected at the surface and at depth. Frautchy and Van Dorn sampling bottles were used to collect sub surface samples, while surface samples were hand drawn.

A ten foot tide staff marked at three inch intervals was secured to the forward range light in the turning basin on Field Trip III. At least two visual tide staff readings were taken each hour during the ebb tidal stage.

Current velocities were measured near the boundary between each tributary and the turning basin, and half way down the estuary outlet using a Hydro Products current speed and direction sensors, model numbers 460 and 465-A respectively. The operational precision claimed by the manufacturer for the current speed sensor is $\pm 3\%$ when used in a position not exceeding five degrees from the vertical for speeds of from 0.1 to 5 knots. The current direction sensor is precise to within ± 5 degrees when used in a position not exceeding twenty degrees from the vertical.

A Hydro Products thermistor was used to obtain vertical temperature profiles at selected positions in the estuary. The precision of the thermistor is $\pm .5^\circ\text{C}$.

Calcium Analysing Equipment. The principle tool in this study is the Calcium Activity Electrode, model 92-90 manufactured by Orion Research Incorporated of Cambridge, Massachusetts. The electrode is shown in cross section in Plate 3.

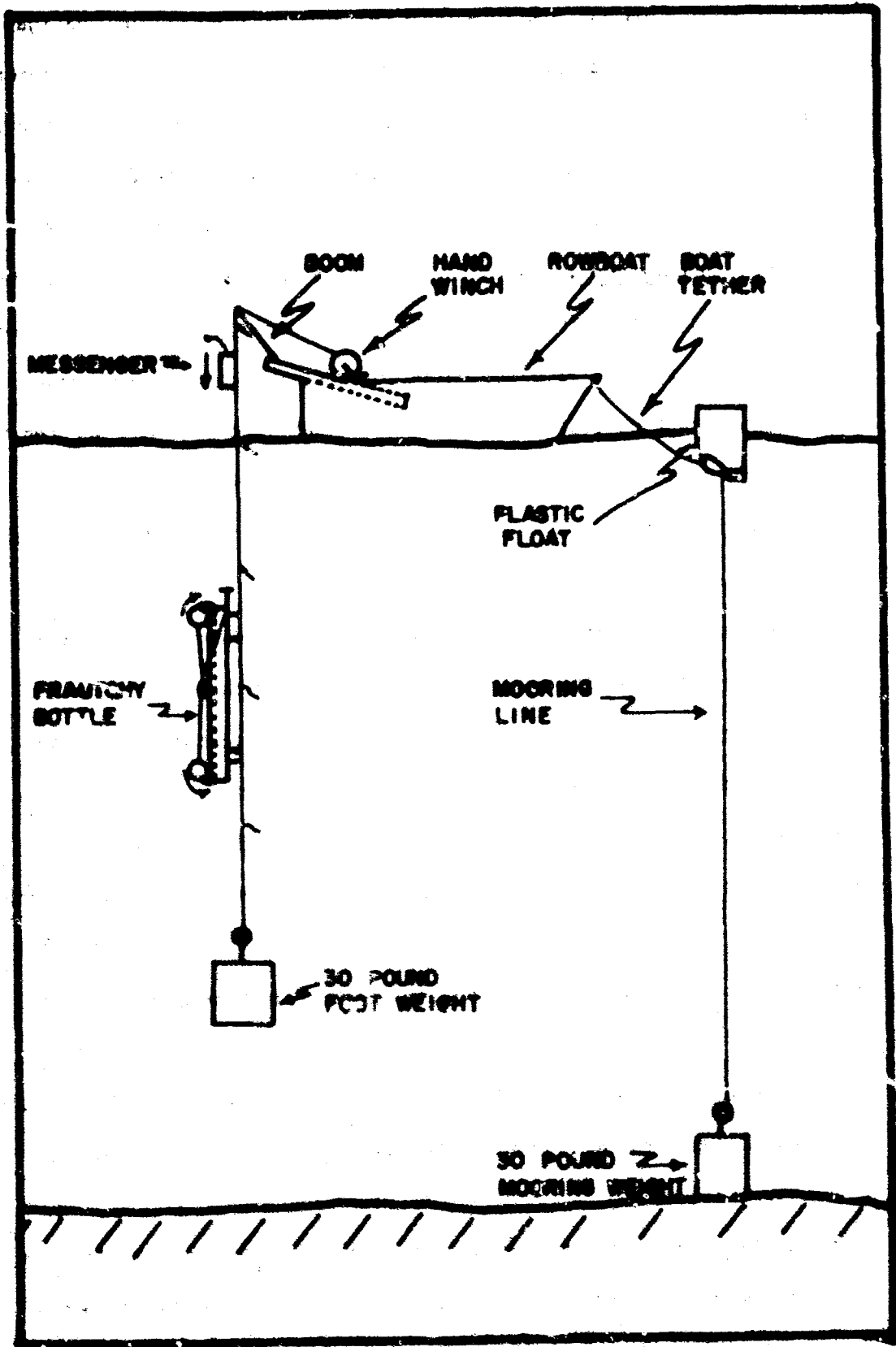


PLATE 2. SAMPLING SYSTEM.

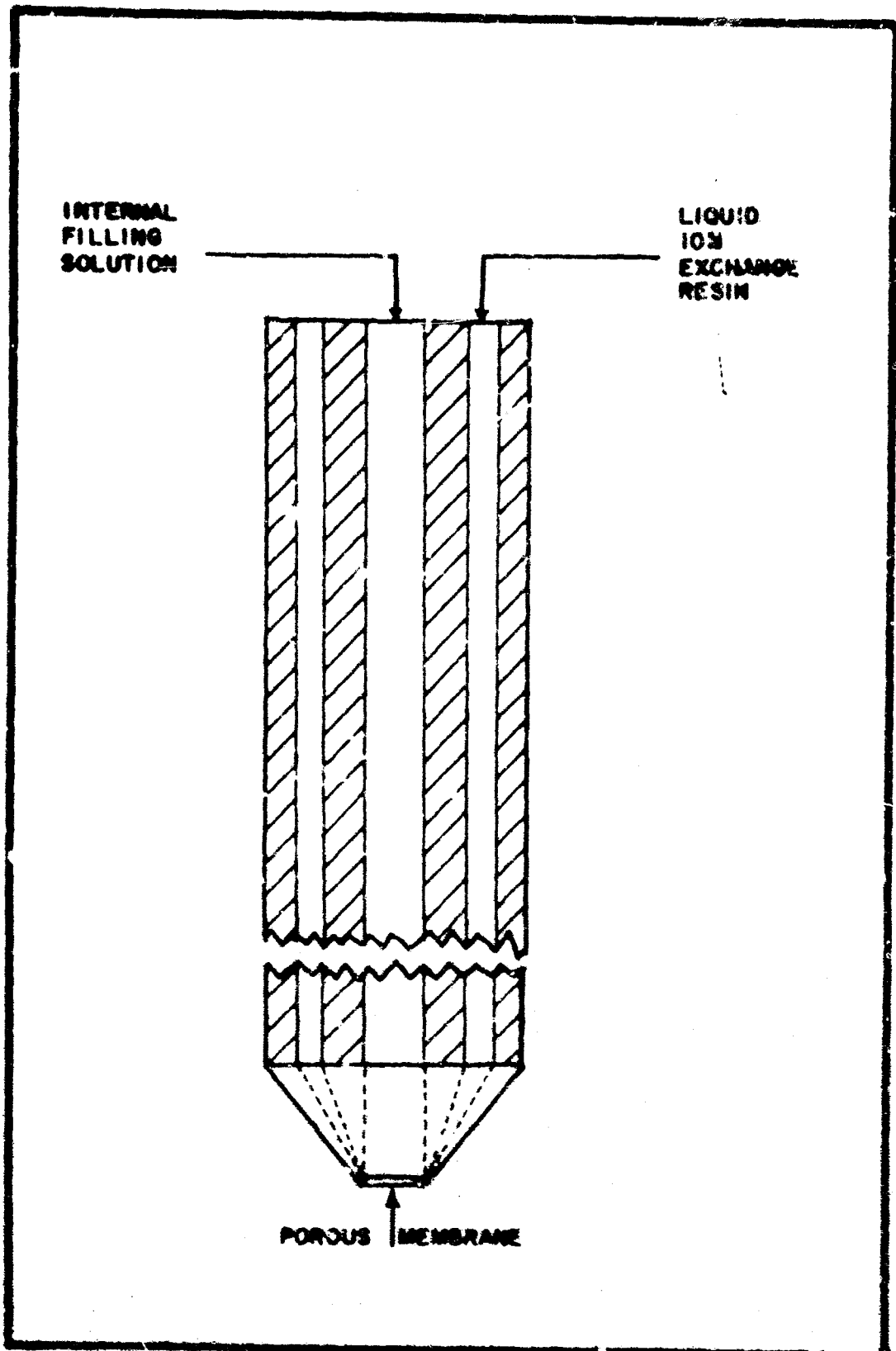


PLATE 3. CROSS SECTION OF CALCIUM ELECTRODE.

The calcium electrode was developed in 1965. The calcium electrode detects ionized or unbound calcium in aqueous solution as a pH electrode detects hydrogen ion. The pH electrode develops a potential across a fritted glass membrane, whereas the calcium electrode develops the potential across a thin layer of water-immiscible liquid ion exchange resin. The potential developed between the electrode and a calcium sample is described by means of the Nernst Equation (Patterson, 1967):

$$E = E_0 - \frac{0.059}{N} \log Q \quad (3)$$

E = Resultant EMF

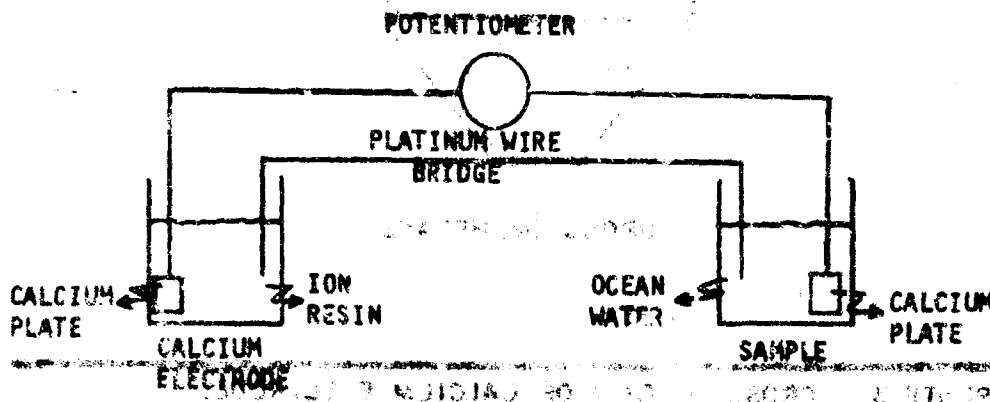
E_0 = Standard EMF

N = Number of electrons transferred

Q = Analogous to an equilibrium constant which in this case is the ratio of the calcium activity of the sample over the activity of the ion exchange resin.

This equation is fundamental in describing the potentials of any concentration gradient.

The principle of operation in making a calcium determination with the electrode can best be explained by a simple beaker model. In the schematic diagram below the beaker on the right represents the sample to be measured, and the one on the left a calcium electrode.



The equilibrium equation describing this model takes the following form because the potentiometer imposes an equal and opposite EMF:



The standard EMF, E_0 , is zero because the EMF of each of the half-cell reactions in the model is equal in magnitude but opposite in sign. Standard half-cell potentials are based on one molar solutions.

If the calcium values are not equal then an EMF can be measured. The second term on the right hand side of the Nernst Equation takes into account the unequal calcium concentration between sample and electrode. The Nernst Equation is thus reduced to the following form:

$$E = \frac{-0.059}{N} \log Q \quad (5)$$

The remaining unknowns (N and Q) are determined from the equilibrium equation. The number of electrons transferred is two, hence $N = 2$. The expression Q is equal to the ratio of the calcium activity of the sample over the calcium activity of the electrode. This expression in the equation can be written in this form because the activity of a pure solid phase is always unity. Therefore, the Nernst Equation can be written:

$$E = \frac{-0.059}{N} \log A_{\text{Ca}^{++}(\text{SAMPLE})} + \frac{0.059}{2} A_{\text{Ca}^{++}(\text{ELECTRODE})} \quad (6)$$

This equation contains one unknown if the activity of the calcium ion in the electrode is maintained at a fixed value.

The specific ion electrode takes advantage of the characteristic concentration stability of ion exchange resins to provide this constant activity.

The potential measured by the calcium electrode is a direct measure of calcium activity. This potential represents an effective calcium concentration less than the actual unbound calcium in the sample.

Conversion of this potential to the corresponding calcium concentration is obtained by dividing the activity by an appropriate activity coefficient.

By plotting a calibration curve using the potentials of ten standard calcium chloride solutions, diluted by a one molar NaCl solution to maintain a nearly constant activity coefficient, the potential readings can be directly interpreted in terms of relative calcium concentrations. This plot yields a near straight line when constructed on semi-logarithmic paper because the ionic strength of the standardizing solutions was constant (Appendix II). Once the calibration curve is drawn, the concentration of any sample within the range of the standard calcium chloride solutions can be determined to a precision of 1.0% over the range used.

The calcium electrode can satisfactorily measure calcium activity in solutions ranging down to 5.0×10^{-6} m/l. Below this range the natural diffusion from the ion exchange resin becomes significant. The values measured in our study ranged from 10^{-3} m/l to 10^{-2} m/l.

The electrode potential measurements were read on a Beckman Expanded Scale pH meter. Electrode measurements on samples were repeated several times and the reproducibility was found to be ± 0.05 millivolts which represents a range in calcium concentration of approximately 1.0% of the observed value.

IV. ESTUARY CIRCULATION MODEL

The relatively large amount of calcium discharged into the estuary provides a means to trace the movement of water by identifying the calcium distribution within the estuary. Since the electrode shows a sensitivity of 1% over the range used, it can be utilized to describe the turning basin circulation.

Water volume conservation in the turning basin can be expressed in the following form:

$$\gamma_A + \gamma_B + \gamma_C = \gamma_T \quad (7)$$

$\gamma_A, \gamma_B, \gamma_C$ = Fractional volume of water emptying into the turning basin from each tributary.

γ_T = Total volume of water being transported through the turning basin during the ebb tidal stage which in the above equation is equal to unity. This volume is also the flow out to sea.

Considering the calcium concentration to be conservative its continuity is expressed in the following form:

$$\gamma_A C_A + \gamma_B C_B + \gamma_C C_C = C_{TB}$$

C_A, C_B, C_C = The calcium concentration from each tributary expressed in moles/liter.

C_{TB} = Calcium concentration in the turning basin expressed in moles/liter.

If the calcium distribution in each tributary is known, then the calcium concentration at any point in the turning basin can be determined by a weighted average of these distributions. The undiluted

volume of water from each tributary at any point in the turning basin, when multiplied by its concentration, provides the contribution from that tributary to the total concentration. The sum of these terms is the value measured in the mixing zone.

In this study two tributaries, B and C, were found to be constant and equal in calcium concentration. This result simplifies the calcium conservation equation to the following form:

$$Y_A C_A + (Y_B + Y_C)C_{BC} = C_{TB} \quad (9)$$

$$Y_A C_A + (1 - Y_A)C_{BC} = C_{TB} \quad (10)$$

The above equation can be solved for Y_A at any point in the turning basin if C_A , C_{BC} and C_{TB} are known. The distribution of Y_A values reveals the circulation pattern when an isopleth field is contoured connecting equal Y_A values.

V. DATA ANALYSIS

Field Trip I. The purpose of Field Trip I was to investigate the distribution of calcium concentration in Moss Landing estuary. Sampling station locations are shown in Plate 4. Water samples were collected at each station at depths of four and ten feet over a six hour period of the ebb stage. The calcium concentration of each sample was determined in the laboratory by using the calcium electrode. Laboratory data for all field trips is shown in Appendix I. Additional samples collected about one mile west of the estuary outlet, in Monterey Bay, were found to have a near constant calcium concentration of 5.10×10^{-3} m/l.

The time variation of calcium at stations I, II and III is shown in Plates 5 and 6 at the four and ten foot levels respectively. Station I, due to its close proximity to the pollutant source, definitely shows the effects of the calcium discharge at the four foot level. The concentration at this location increases markedly throughout the ebb stage. Similar trends of calcium concentration exist at station II and III, located in the center of the turning basin and in the estuary outlet respectively, except the concentrations are lower. However, all stations have a significantly higher calcium concentration than the adjacent water of Monterey Bay. On the other hand the concentrations at ten feet are low in relation to those at four feet. The concentrations at this depth increase only slightly with time into the ebb stage.

The significantly higher calcium concentration at the four foot depth supports the earlier conclusion that the estuary is two layered at least with respect to calcium. Attenuation of the calcium concentration at stations II and III is most likely due to horizontal mixing

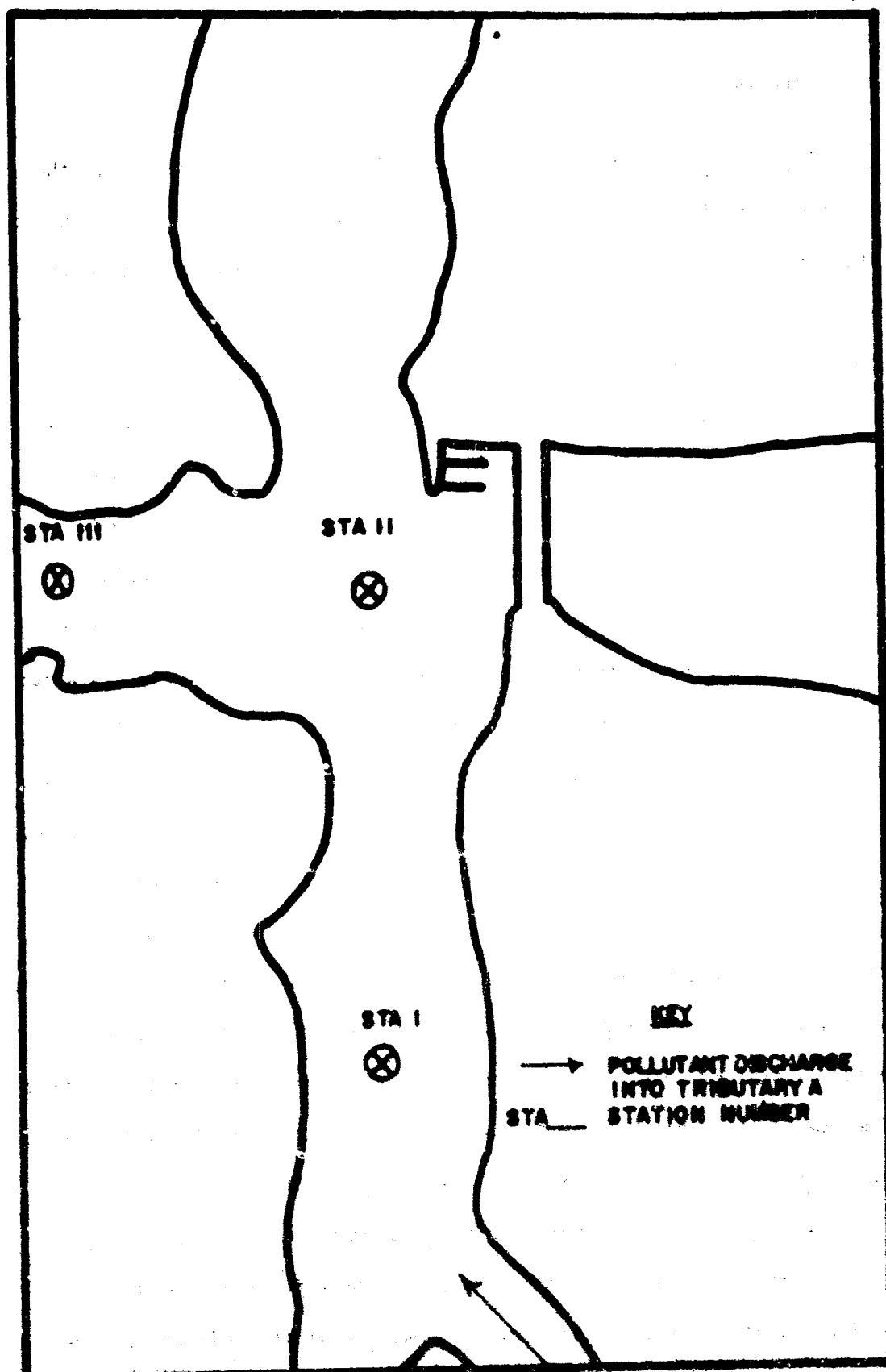
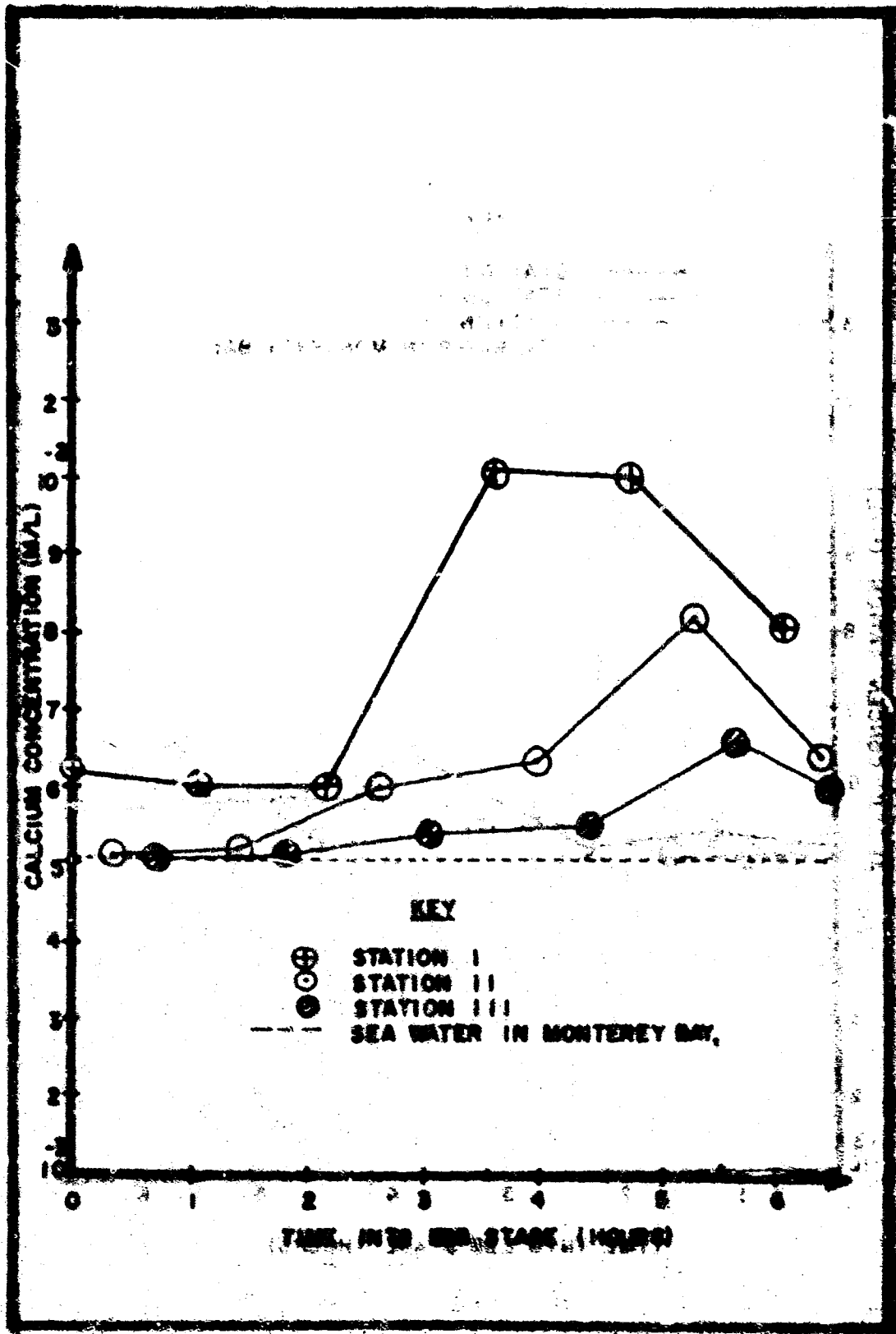
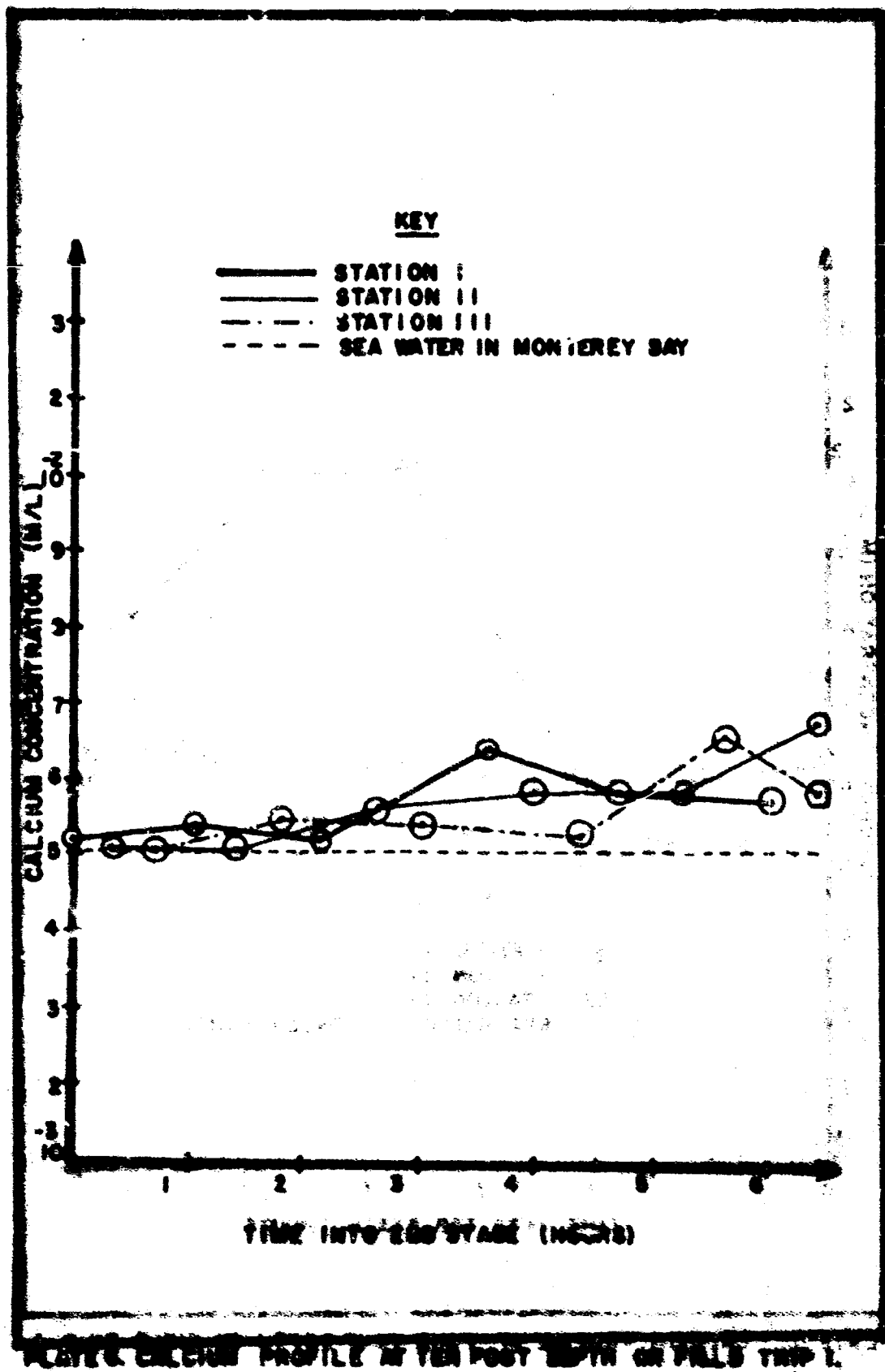


PLATE 4. STATION LOCATIONS FIELD TRIP 1.





with water from tributary B as the increase in concentration at depth is not significant.

Data from this field trip indicated the existence of a calcium maximum which moves down tributary A, through the turning basin and out to the ocean on the ebb stage. On the flood stage, this calcium maximum is probably located opposite the pollutant source. Pollutant movement analogous to this was described by Pritchard (1960). However, a more detailed understanding of the calcium distribution in each tributary over the ebb stage was required prior to attempting to describe the circulation in the turning basin. The determination of these distributions formed the basis of Field Trip II.

Field Trip II. The calcium distribution of the surface and at four feet along the length of tributaries A, B and C was investigated. Calcium samples were collected in tributaries B and C only at the commencement of the ebb stage, while more detailed sampling was conducted in tributary A over the duration of the ebb stage.

Two stations separated by 1000 feet were occupied in each of the tributaries, B and C, as shown in Plate 7. The calcium concentration of all samples collected in tributary B and C were equal within the precision of the analytical technique at 6.80×10^{-3} m/l. Since both tributary B and C are shallow and narrow and receive no calcium directly, mixing should assure uniformity in concentration over the ebb stage.

More detailed sampling was undertaken in tributary A, at one hour intervals, over the ebb stage. Five stations were established in tributary A as shown in Plate 7. These stations extended from a position directly opposite the location of the pollutant discharge to a point on the boundary of the turning basin.

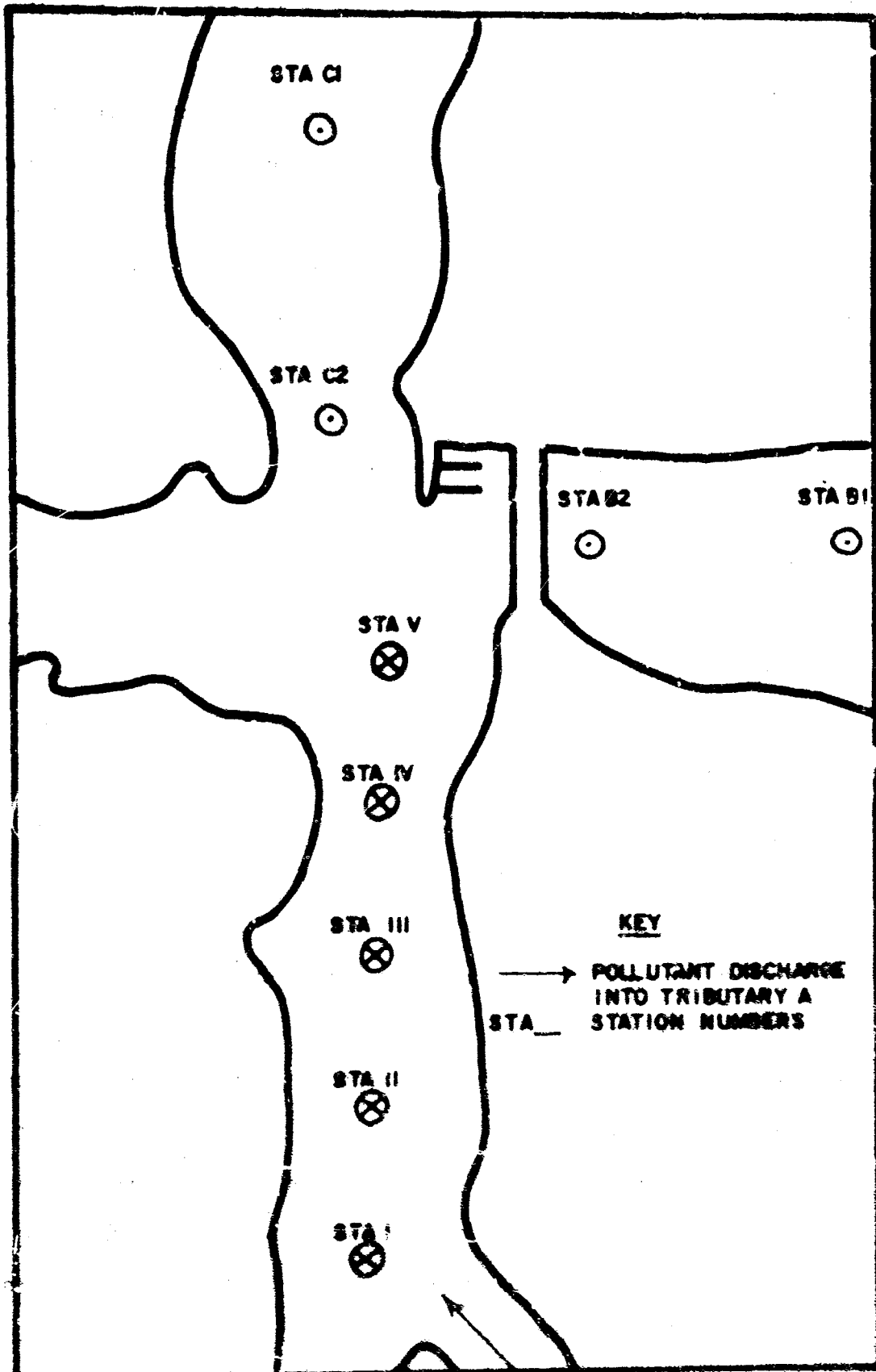


PLATE 7. STATION LOCATIONS FIELD TRIP II.

The distribution of calcium at the surface and at the four foot depth in tributary A at successive times into the ebb stage is shown in Plates 8 to 11. Plate 8 shows the calcium distribution at the beginning of the ebb stage. The concentration decreases from the source to the turning basin at the surface and four foot level. Plates 9 to 11 show that in the upper portion of tributary A the surface concentration drops soon after the commencement of the ebb stage and continues to drop throughout the remainder of the stage. At the same time the concentration at the four foot depth shows only a relatively small change over the ebb until a sharp increase is noted toward the end of the stage in the upper portion of tributary A. At the midpoint of tributary A the surface concentration decreases throughout the ebb stage to the extent of falling below the concentration at the four foot depth. At station V, closest to the turning basin, the concentration remains relatively uniform. The reason for the decreases noted in total calcium concentration at the surface in tributary A is due to the intrusion of additional water. This additional water is undoubtedly fresh water run-off from the surrounding land behind the pollutant source. This explanation is based on the 2.53 inches of rain recorded in Monterey for the week of November 18 just prior to Field Trip II. This was an abnormally large amount of precipitation for this period.

Plates 12 to 16 show the time variation of calcium concentration at each station in tributary A. These plates show that the surface and four foot concentrations become equal at successively later times into the ebb stage proceeding from a point opposite the pollutant source toward the turning basin. This is probably due to the movement of the fresh water intrusion into the tributary. The rate of movement of this fresh water intrusion down tributary A is similar to the rate of the

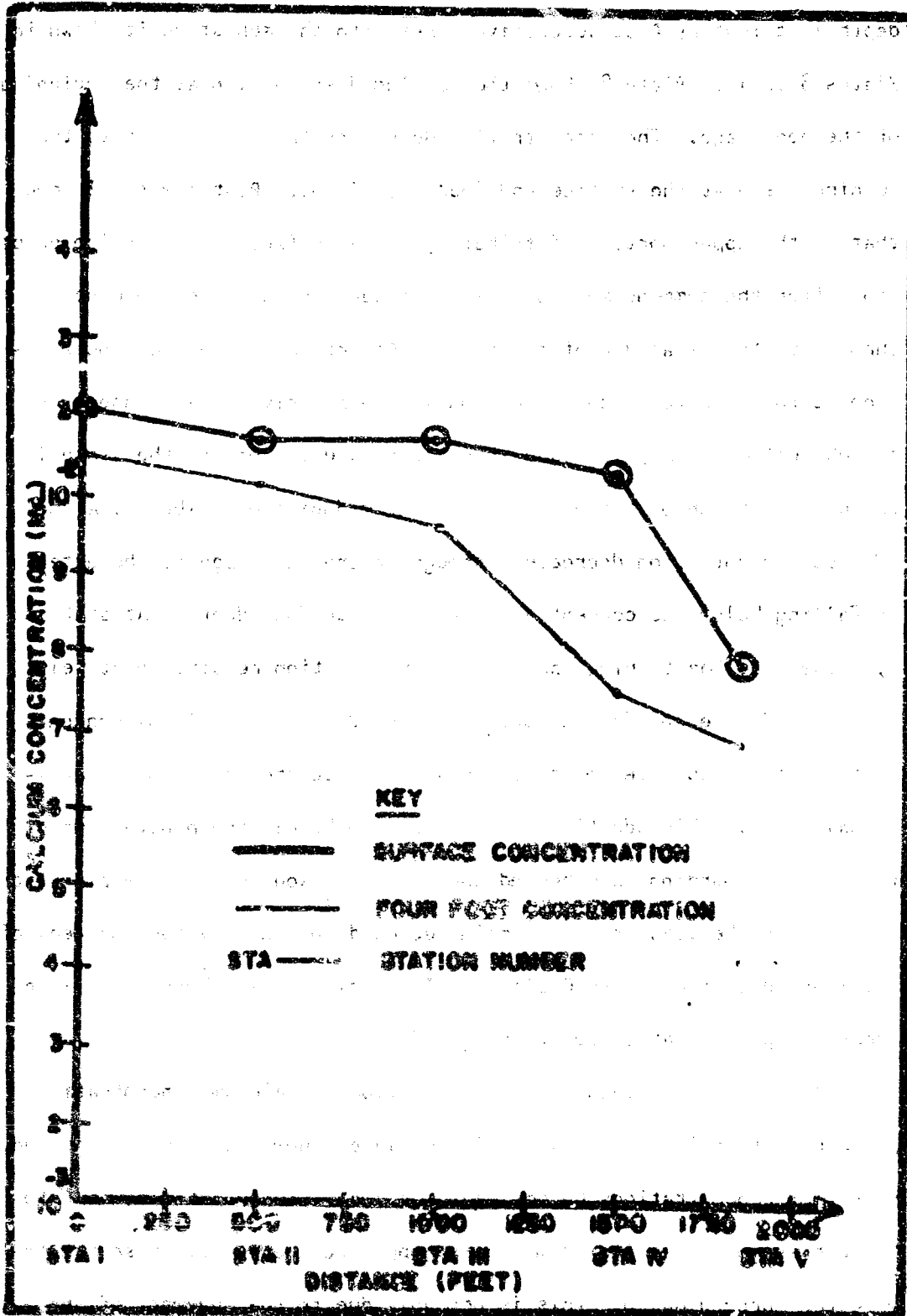


PLATE B. CALCIUM DISTRIBUTION IN TRIBUTARY A, FIELD TRIP N, AT COMMENCEMENT OF EGG STAGE.

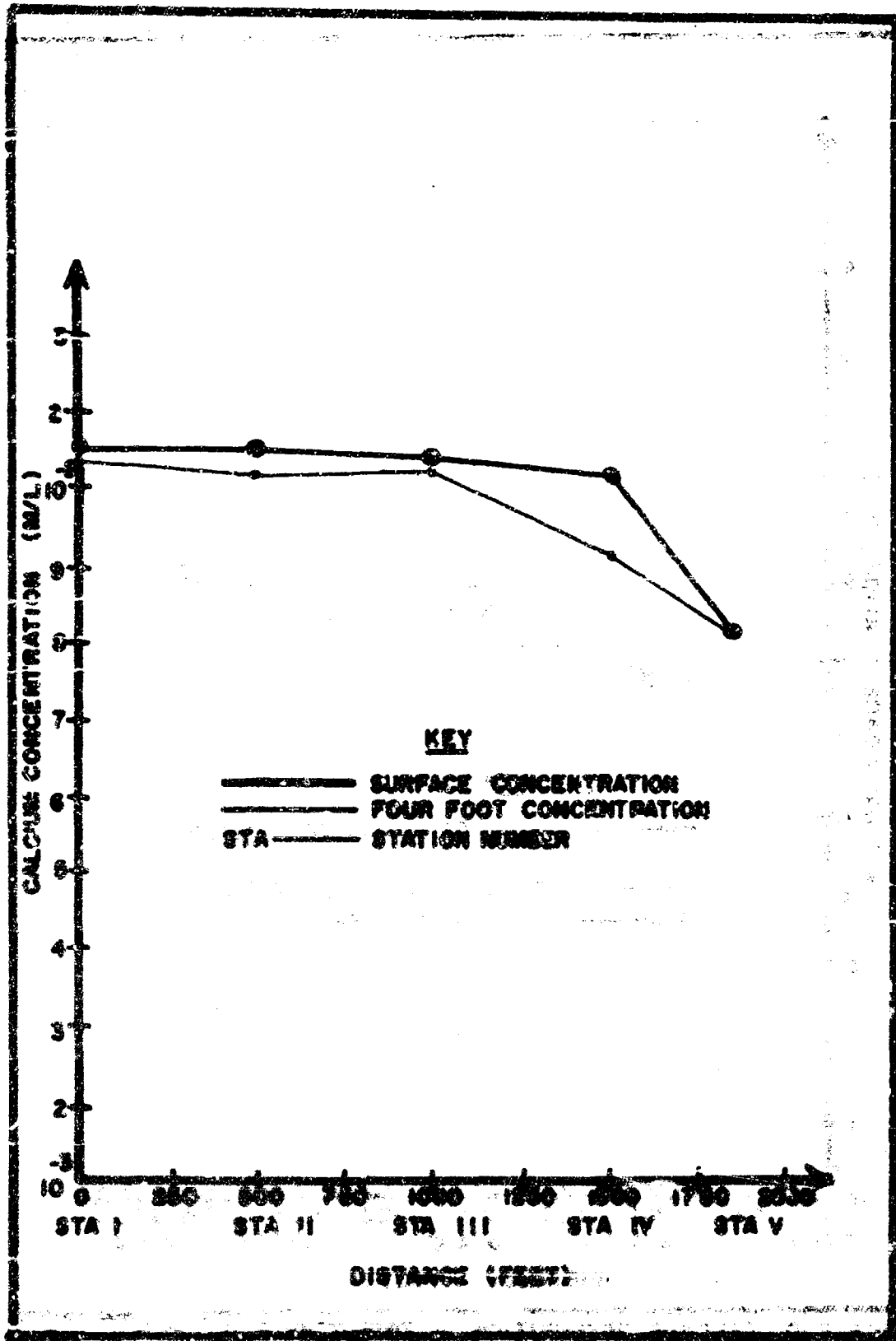


PLATE 9. CALCIUM DISTRIBUTION IN TRIBUTARY A AT 2.5 HOURS INTO THE ESB STAGE, FIELD TRIP II.

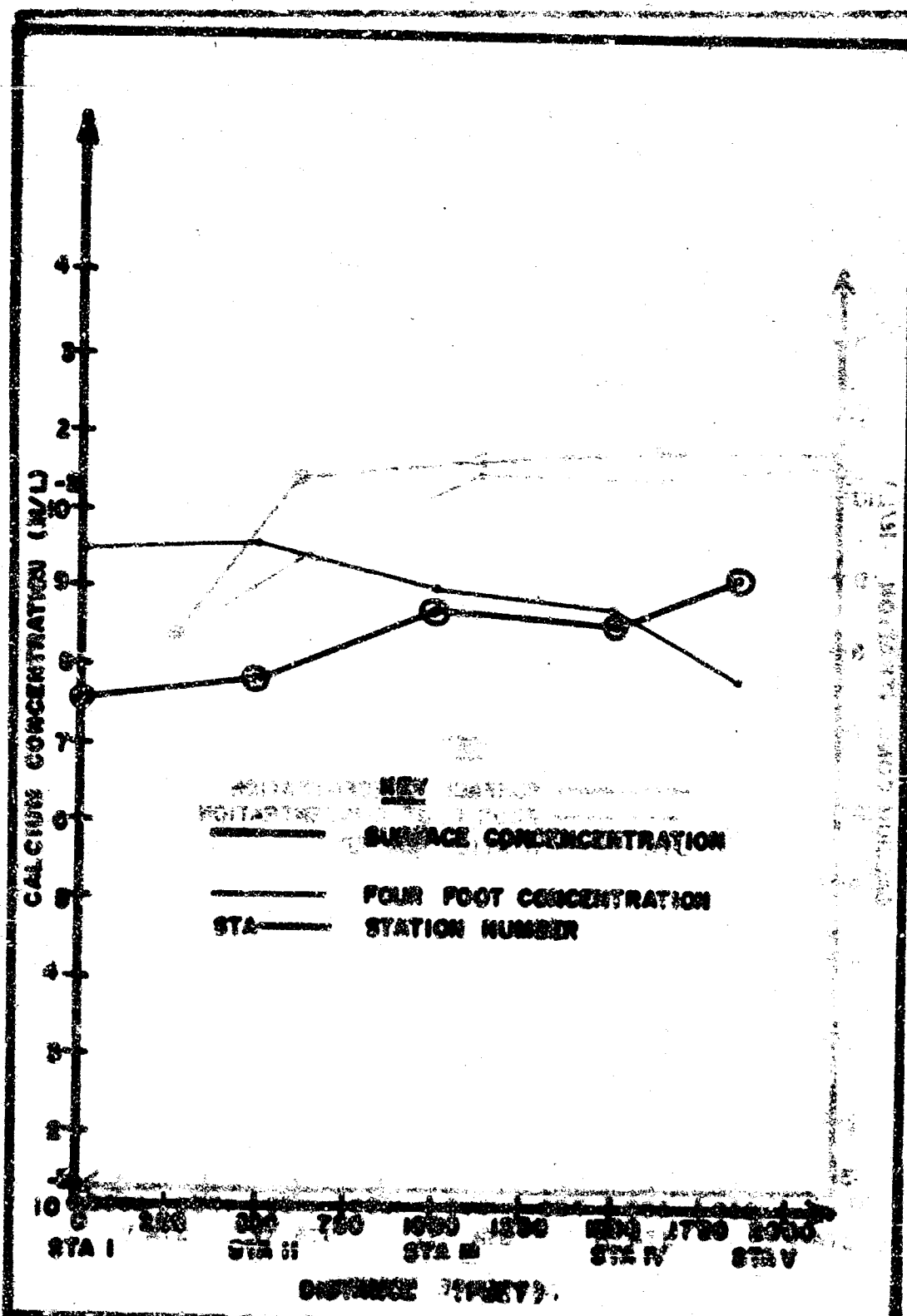


PLATE 10. CALCIUM DISTRIBUTION IN TERRACE A, FIELD TRIP 2, AT FIVE POINTS INTO THE RED STRATA

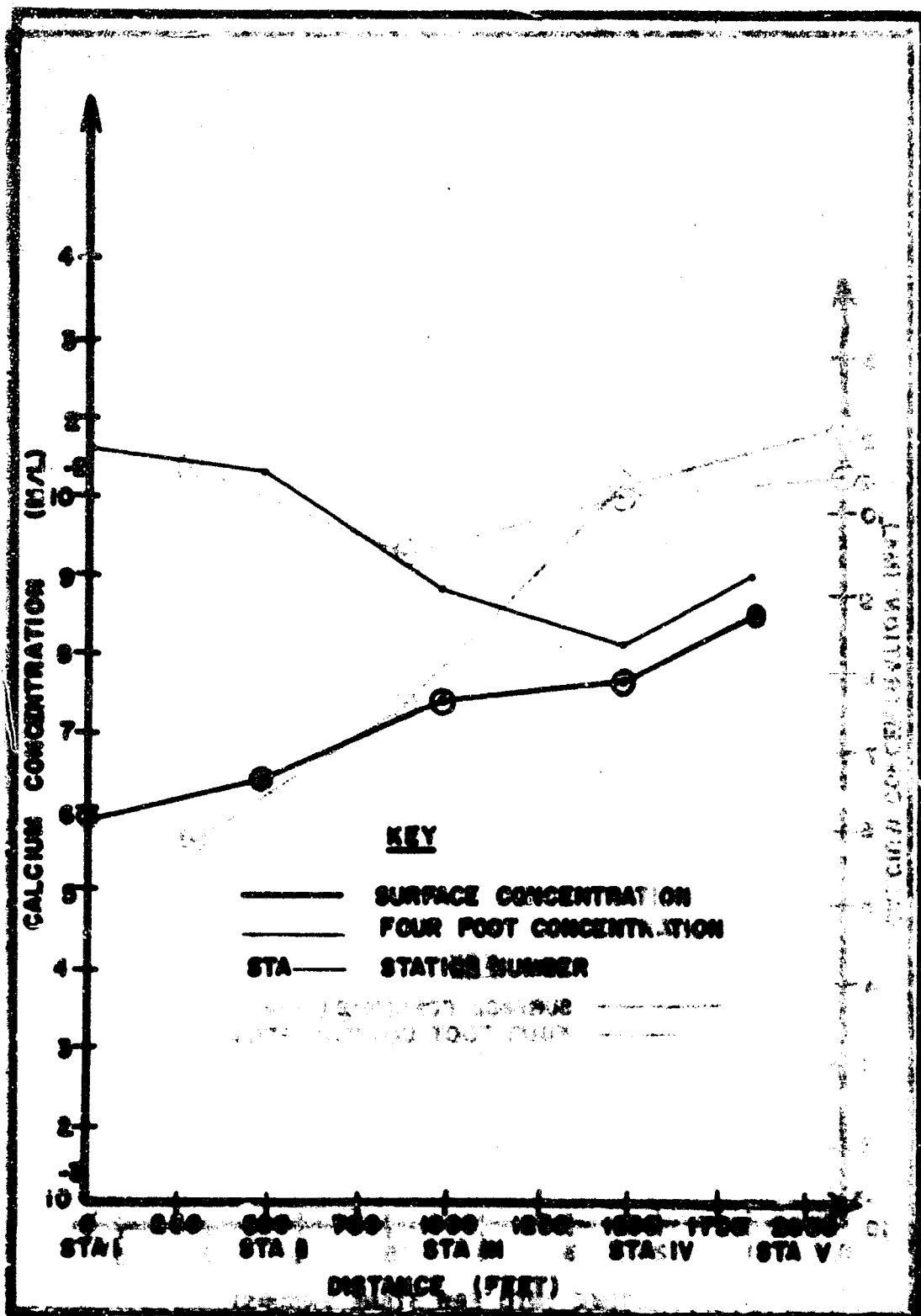


PLATE II. CALCIUM DISTRIBUTION IN TRIBUTARY A, FIELD TRIP II, AT SEVEN HOURS INTO THE EGG STAGE.

U.S. GEOLOGICAL SURVEY, WATER RESOURCES DIVISION, WASHINGTON, D.C.

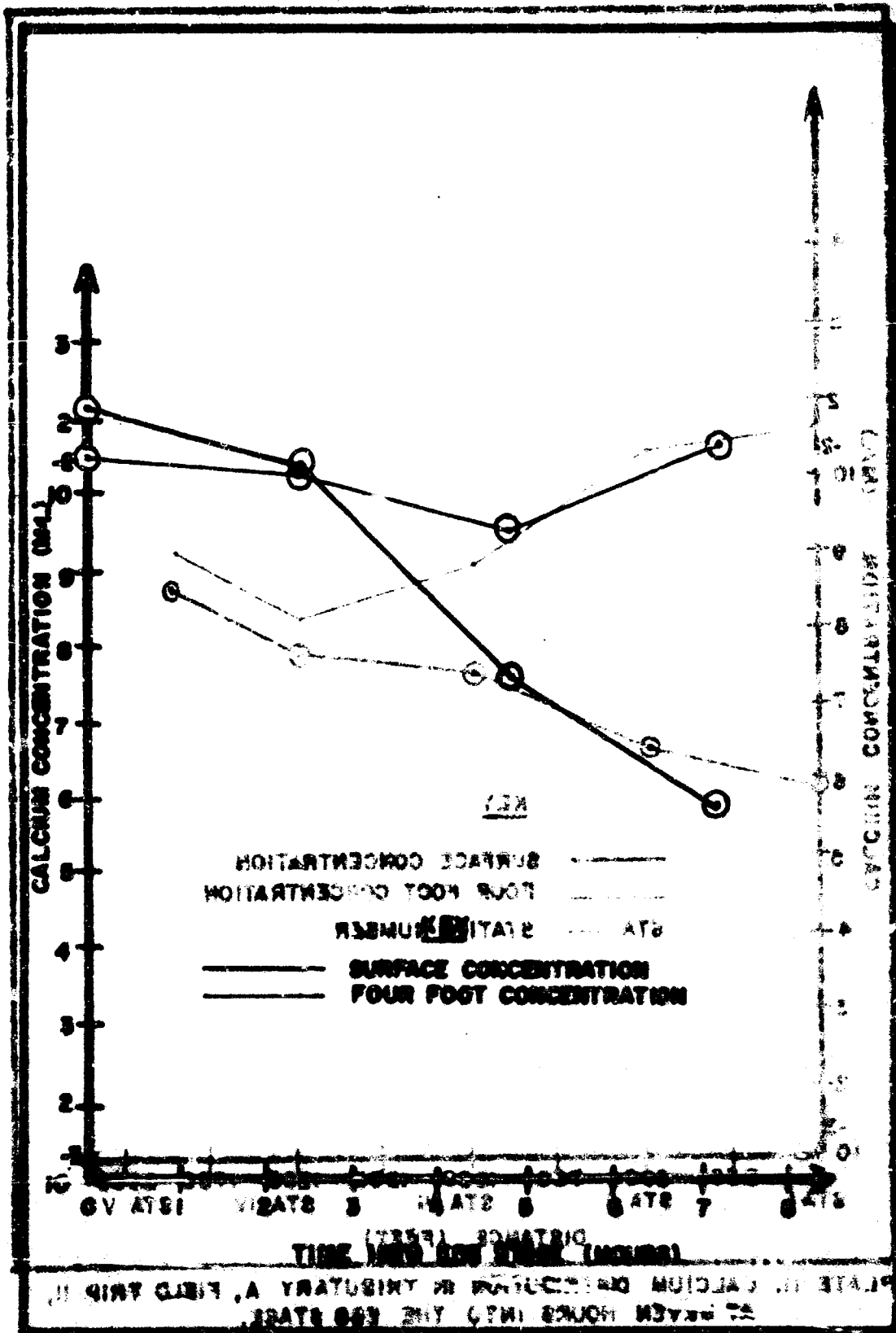


PLATE 12. CALCIUM VARIATION, STATION 1, FIELD TRIP II

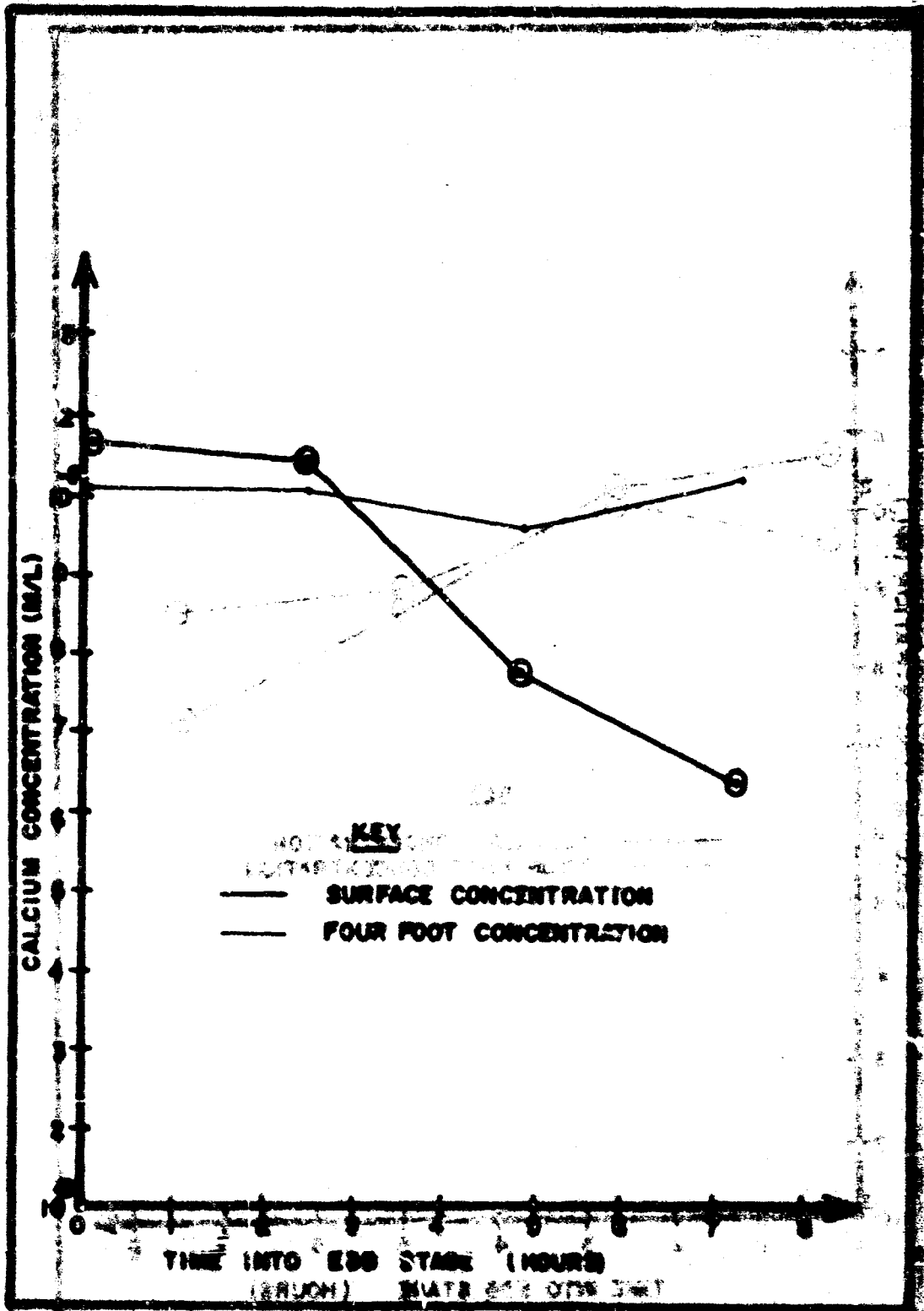


PLATE 13. CONCENTRATION VARIATION, STATION H, FIELD TRIP 11.

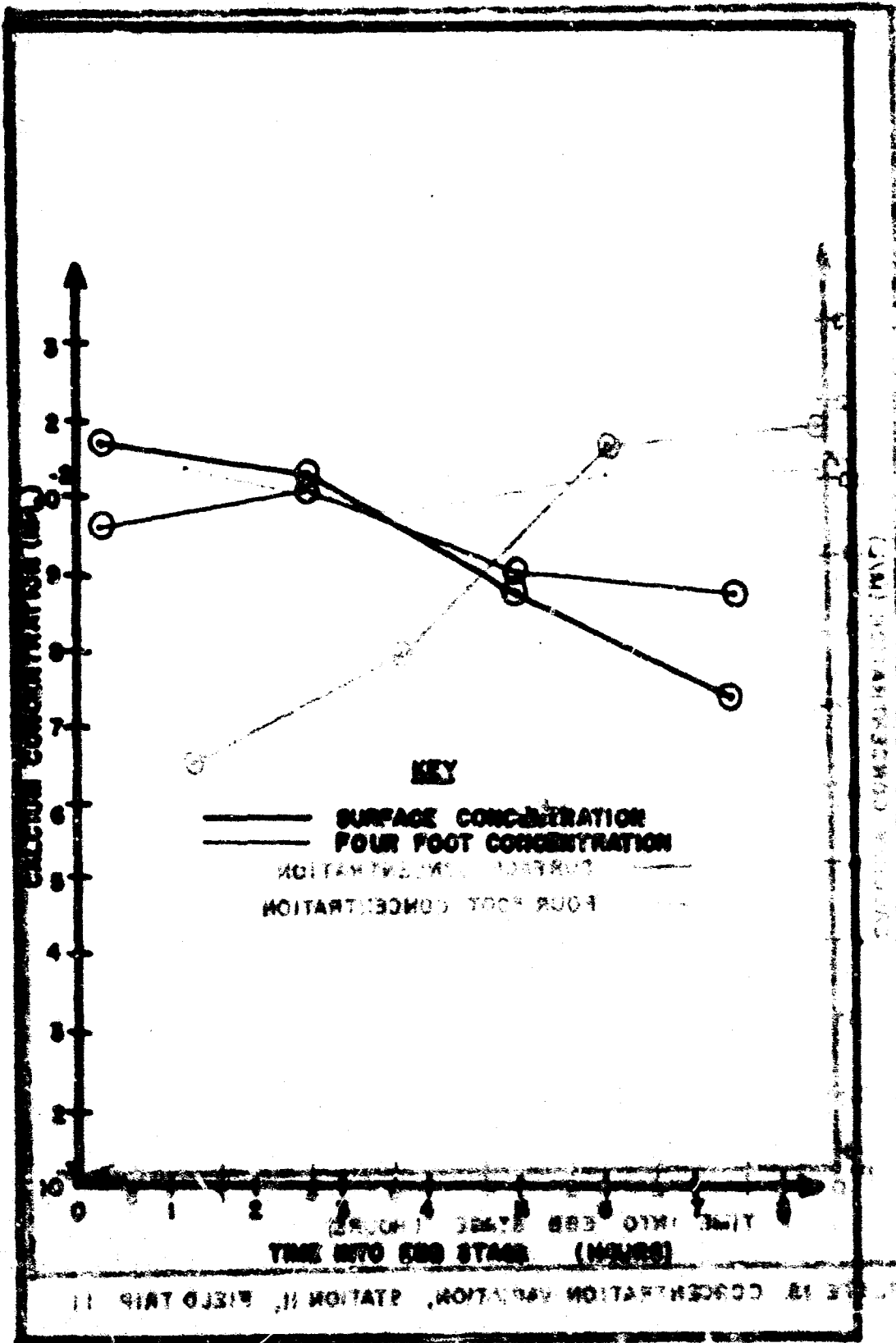


PLATE 14. CALCIUM VARIATION, STATION 14, FIELD TRIP.

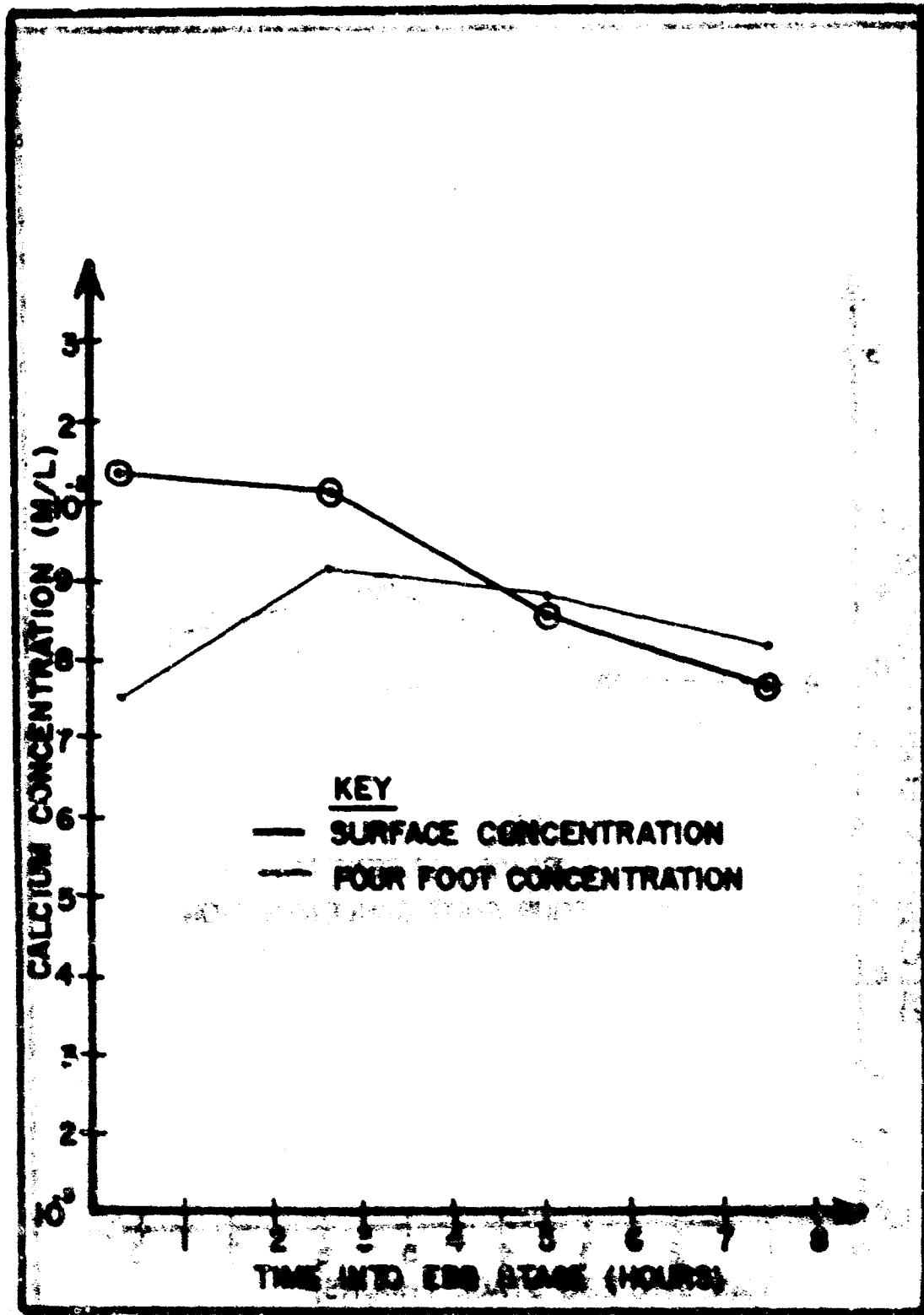


PLATE 15. CONCENTRATION VARIATION STATION IV, FIELD TRIP N.

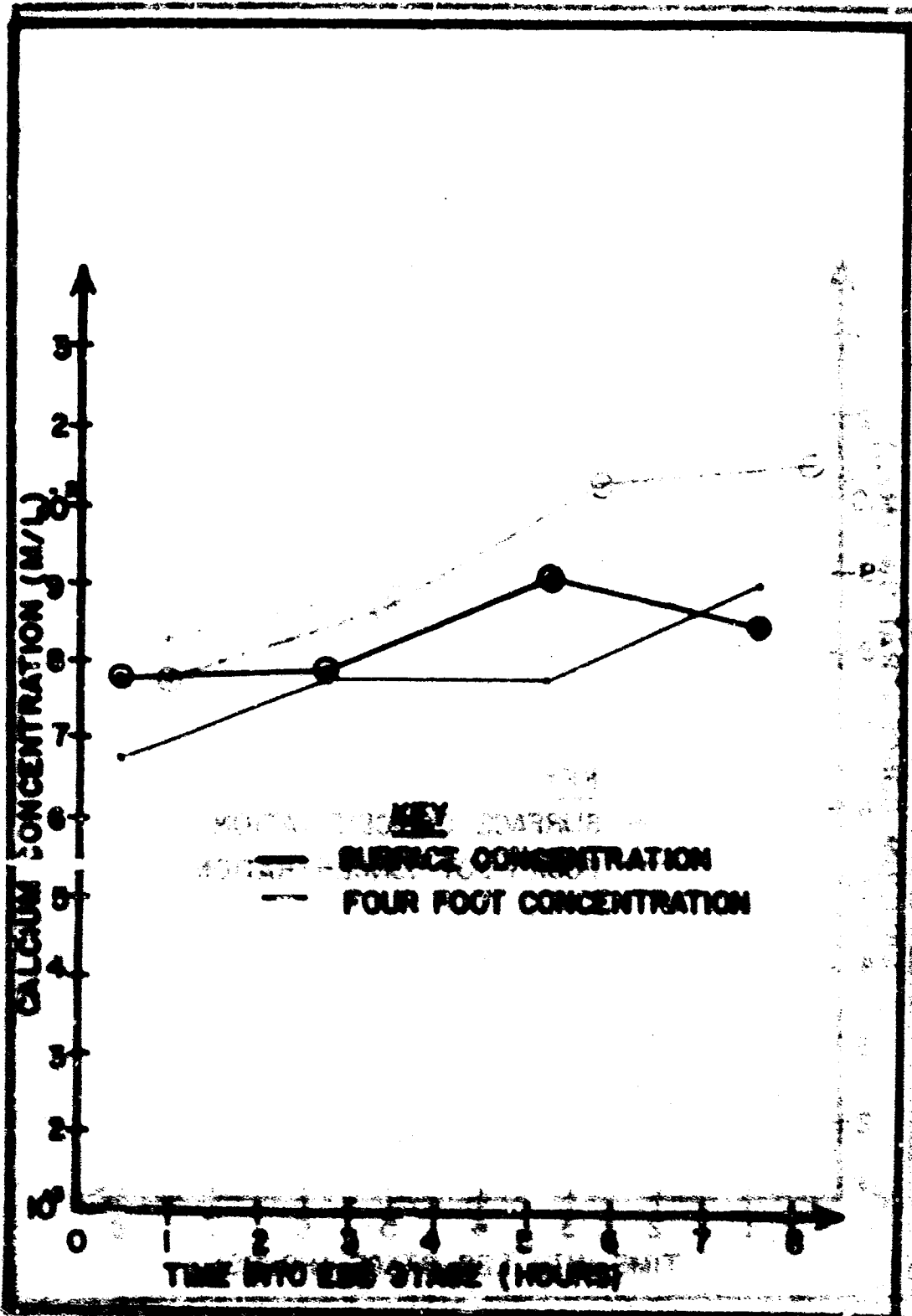


PLATE 8. CONCENTRATION VARIATION, STATION V, FIELD TRIP II.

calcium maximum movement seen in this tributary on Field Trip I.

Since we had obtained sufficient field experience and understanding of the processes in tributary A, a final experiment was designed to determine the circulation in the turning basin by use of the calcium distributions within the estuary.

Field Trip III. Two and one half hours into the ebb stage was selected as the time to apply the continuity equations to the turning basin in order to obtain an explicit result for the surface circulation pattern.

A grid of stations was established to provide good area coverage of the confluence area as shown in Plate 17. These stations were established in such a way as to facilitate the determination of the calcium distribution in tributaries A, B and C as well as the estuary outlet. Samples were collected directly into sample jars at the surface and at a depth of two feet. The Arabic numbered stations were used to determine the calcium distribution in the turning basin. Those stations with Roman numeral or alphabetical designations were used to determine the calcium distribution in the tributaries at the sampling times. Stations marked X_n were sampled at $2\frac{1}{2}$ and $3\frac{1}{2}$ hours into the ebb stage while those marked (N) were sampled at 2 and 3 hours into the ebb. At the crosshatched circles (⊗) water samples and current measurements were obtained over $5\frac{1}{2}$ hours of the ebb stage. The calcium concentrations of the collected water samples were normalized to $2\frac{1}{2}$ hours into the ebb by linear approximations.

The calcium concentration values determined for $2\frac{1}{2}$ hours into the ebb stage for the turning basin, tributary A, B and C are shown in Plates 18, 19, and 20 respectively. The calcium concentrations within the turning basin show a decreasing trend in values proceeding across

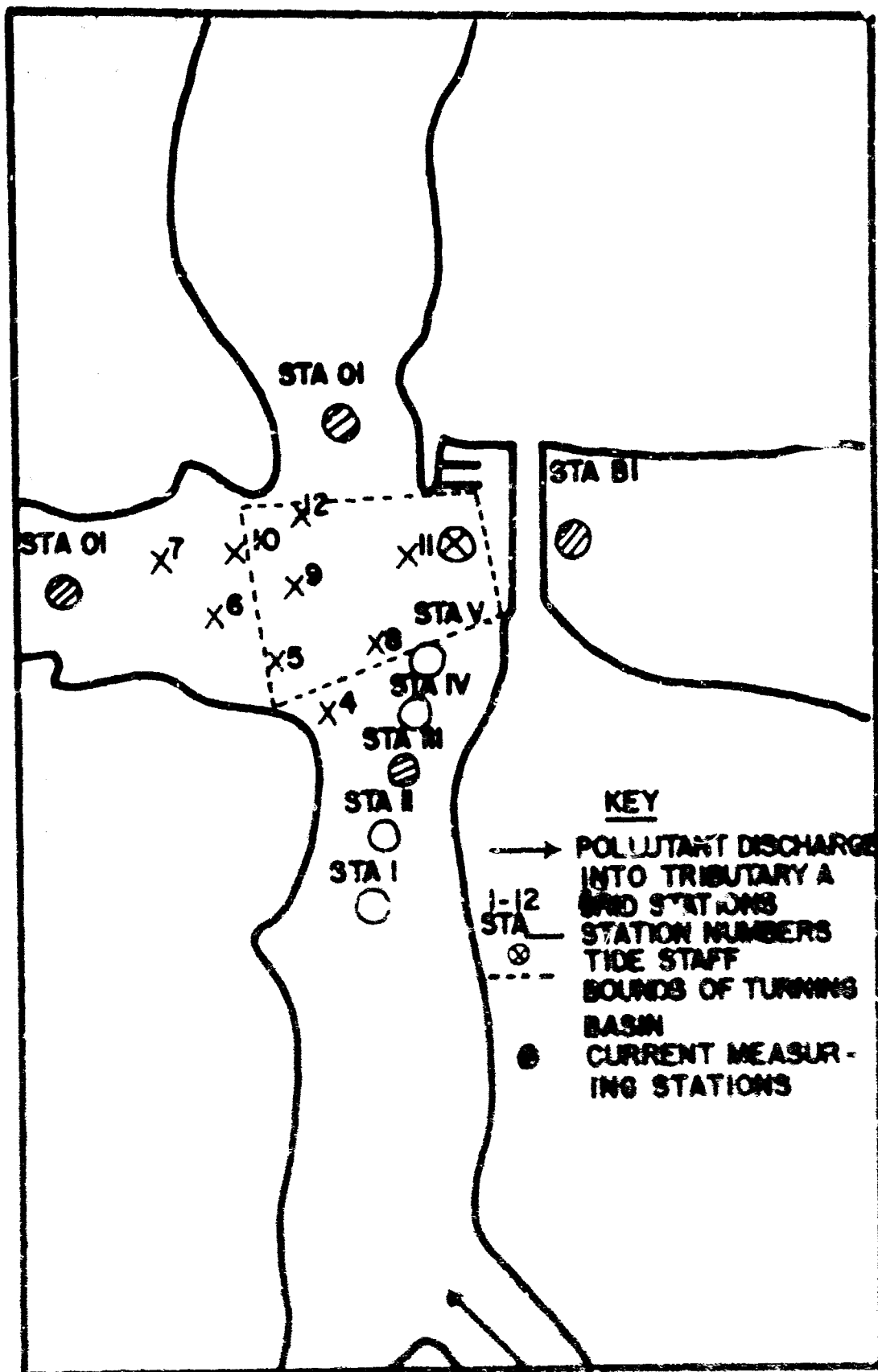
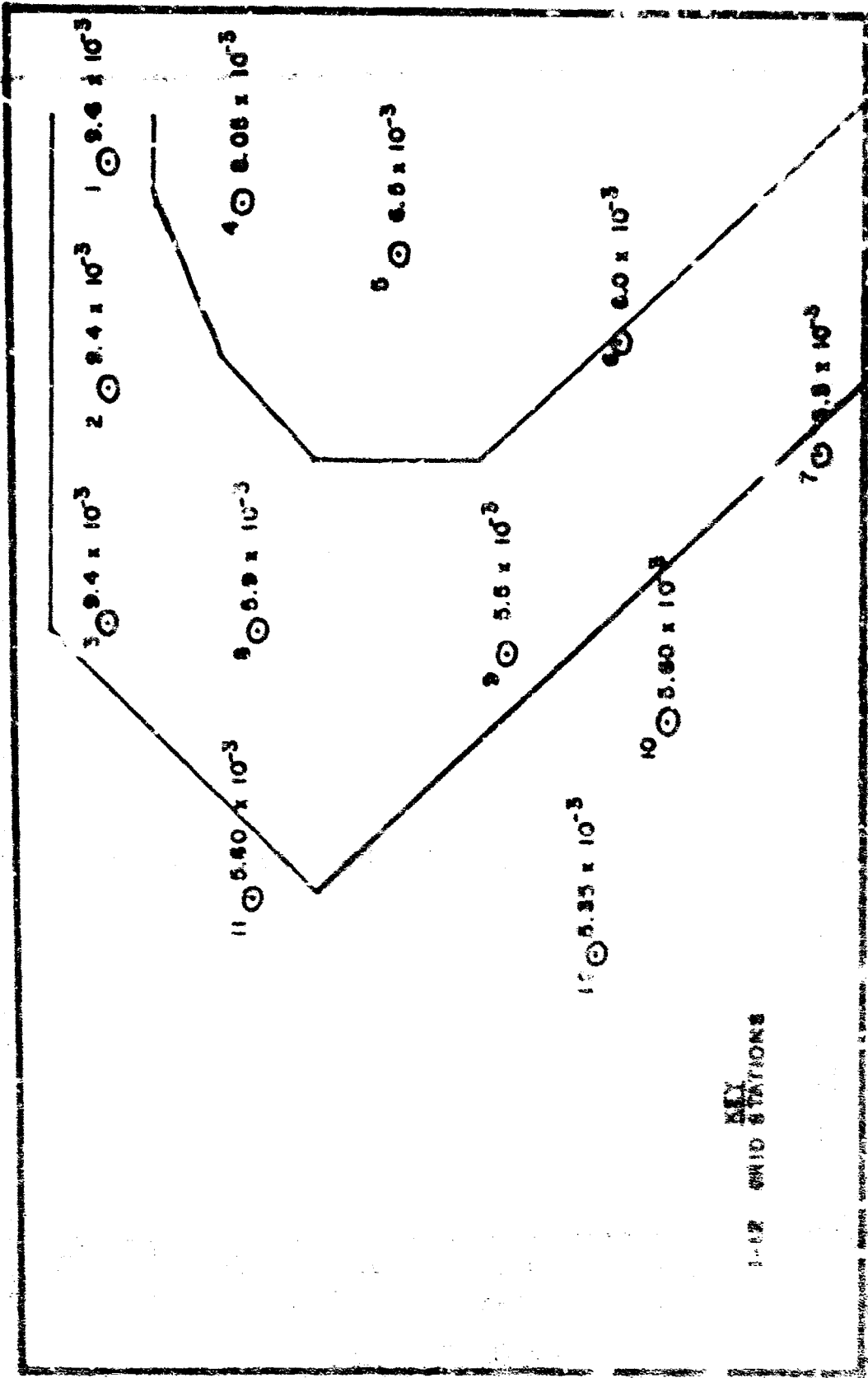


PLATE 17. STATION LOCATIONS FIELD TRIP 51



KEY
GRID STATIONS

CALCIUM CONCENTRATION AT EACH GRID STATION 2.3 HOURS INTO THE EBB TIDE.

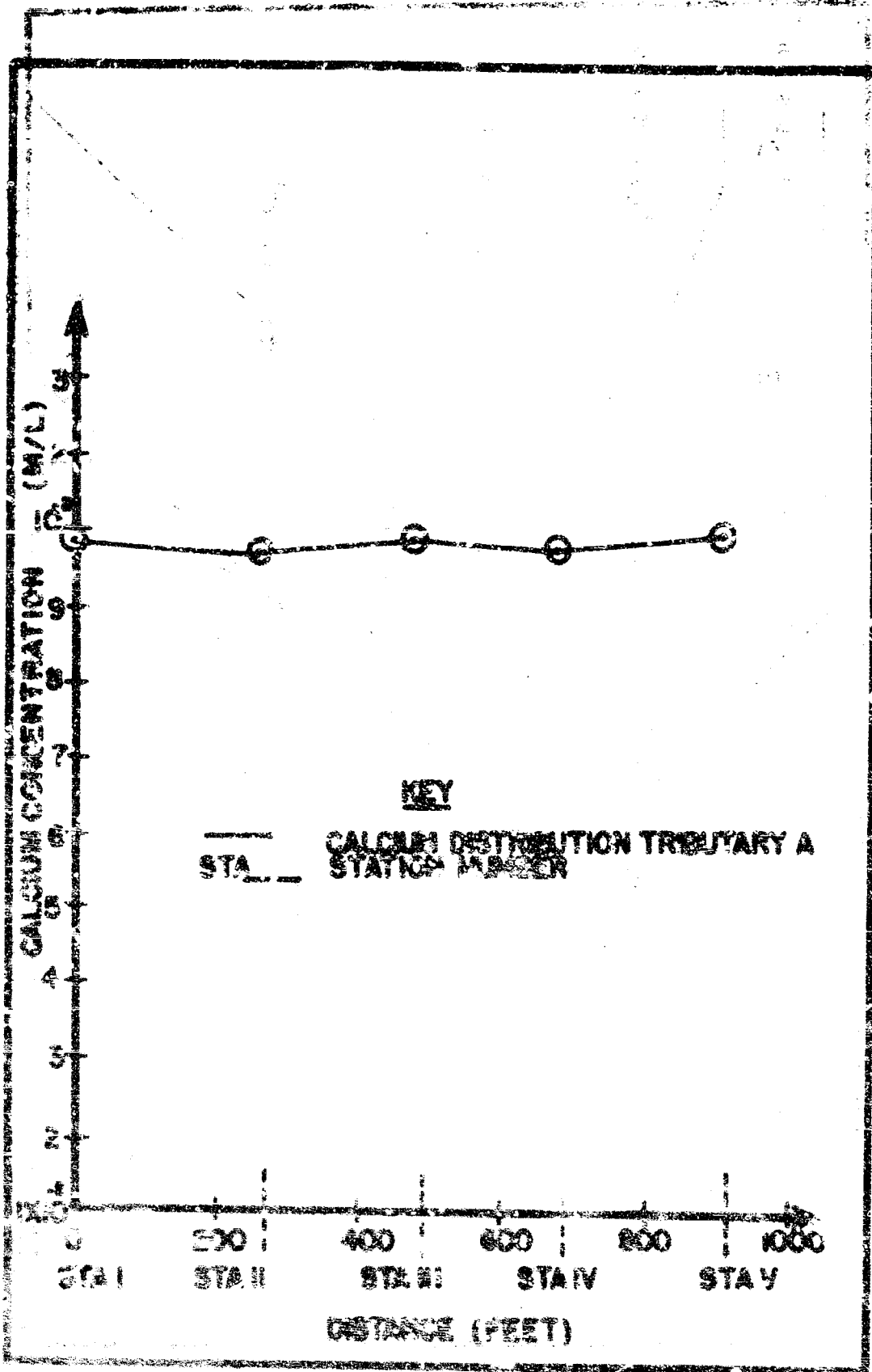


PLATE 12. CALCIUM DISTRIBUTION IN TRIBUTARY A AT 2.5 HOURS INTO THE END STAGE, FIELD TRIP III.

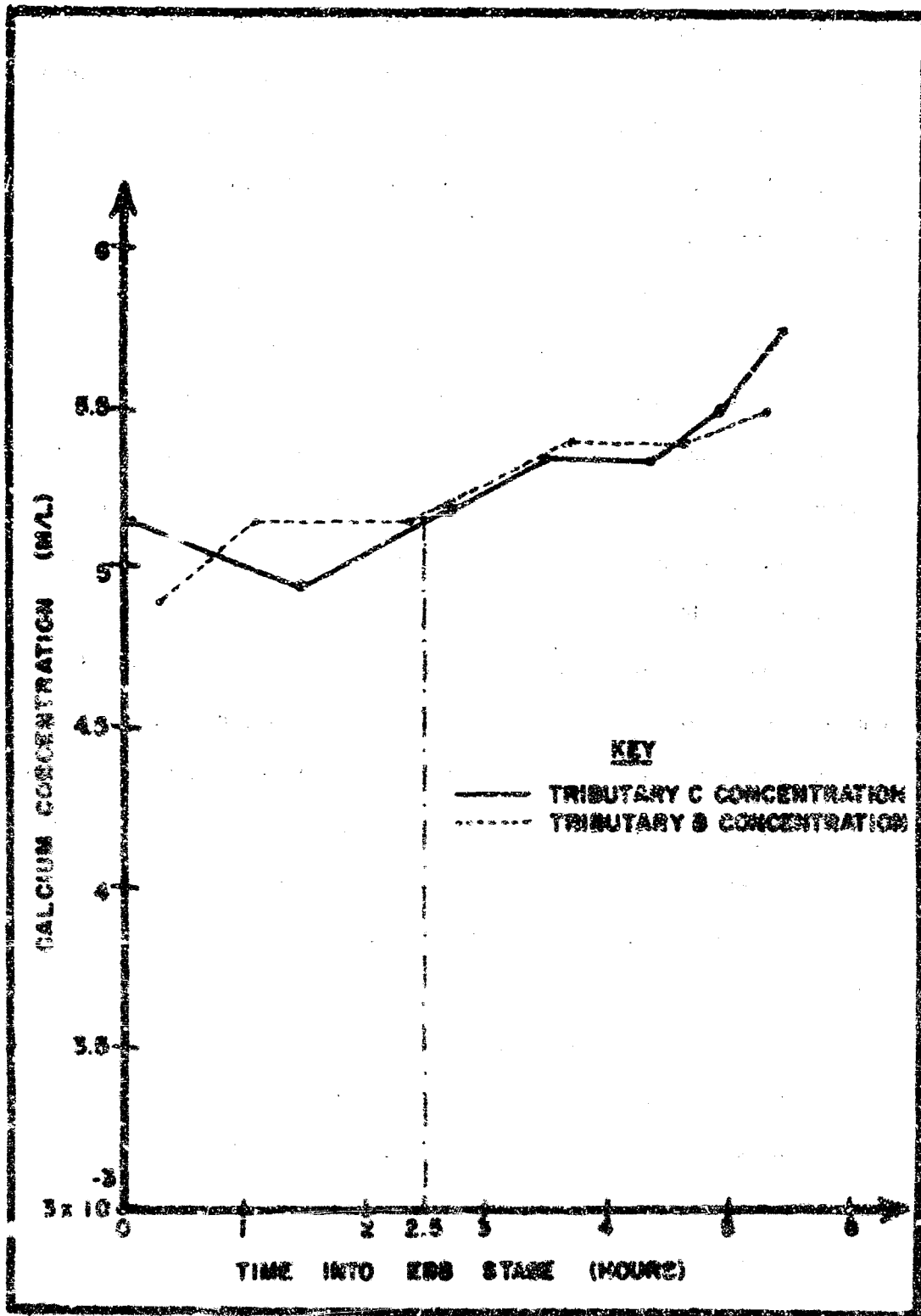


PLATE 20. CALCIUM VARIATIONS FROM TRIBUTARIES B AND C.

the turning basin and seaward down the estuary outlet from the discharge boundary of tributary A. The calcium values in tributary A revealed that the calcium distribution in this tributary can be considered a flat field at least to 1000 feet into the tributary. Tributaries B and C show equal concentration values at 2½ hours, with only a slight overall rise over the entire ebb stage.

In order to obtain a better understanding of the movement of the calcium maximum in tributary A, surface samples were collected at a line of stations along the center line of the tributary at about five hours into the ebb stage. The location of each station and the resulting calcium distribution is shown in Plate 21. This plate clearly shows that the calcium maximum has just reached the turning basin boundary at this time into the ebb.

In addition to the collection of water samples for analysis, current measurements were taken in each tributary and in the estuary outlet over a five hour period commencing at the beginning of the ebb stage. Current measuring locations are shown in Plate 17. Current speeds at each station were plotted against time into the ebb stage and are shown in Plate 22. The current speed at each station is seen to increase to a maximum value approximately four hours into the ebb stage. Current speeds in tributary B and the estuary outlet are approximately equal throughout the ebb stage, but are about six times the magnitude of current speeds measured in tributaries A and C at their respective maximum values.

Tide staff readings were taken over a five hour period commencing at the beginning of the ebb stage at the location shown in Plate 17. These readings were plotted and compared against readings of the standard tide gauge at Monterey and are shown in Plate 23. The error in

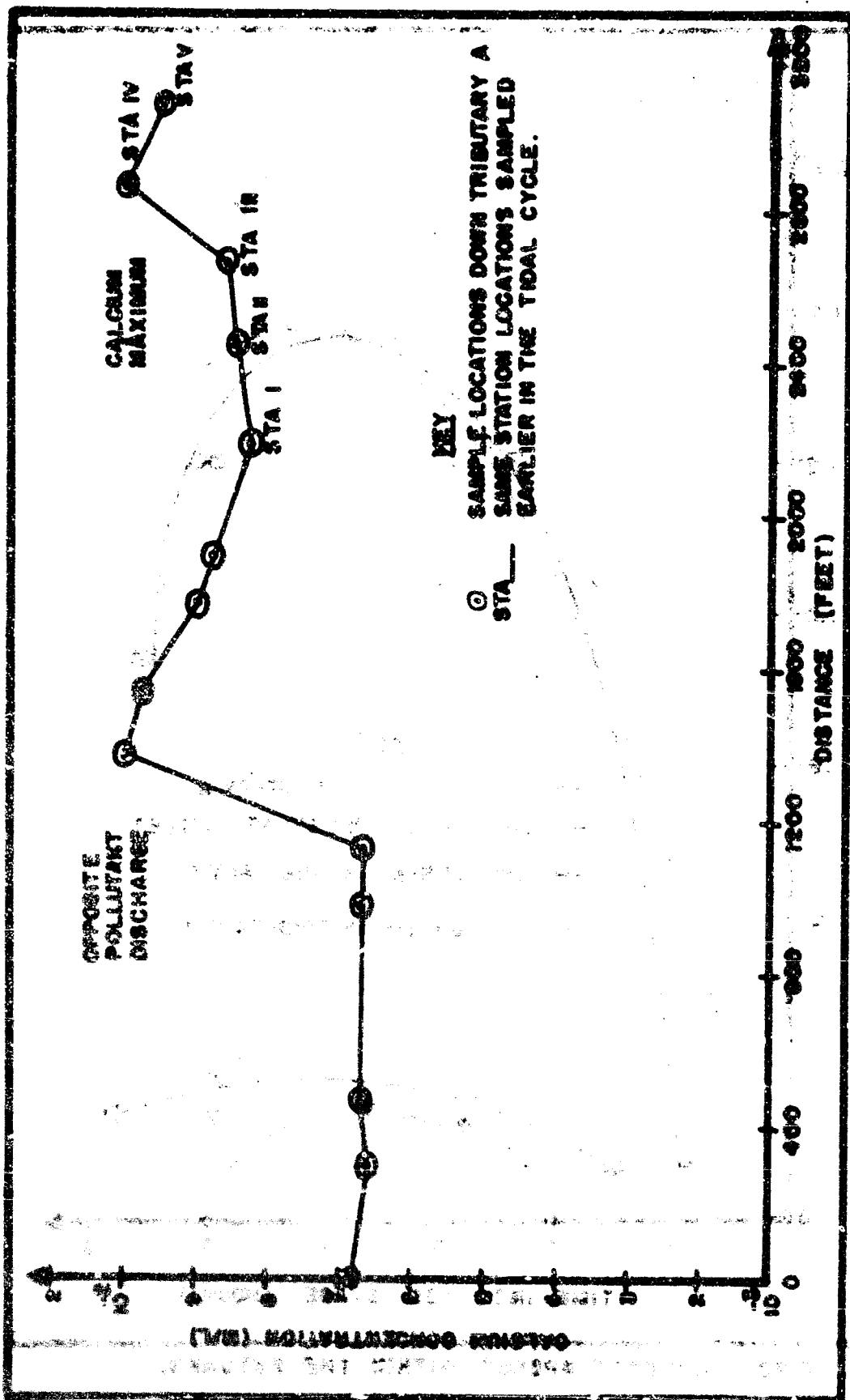


PLATE 21. CALCIUM DISTRIBUTION IN TRIBUTARY A AT 3:00 P.M. INTO THE EBB STAGE, FIELD TRIP III.

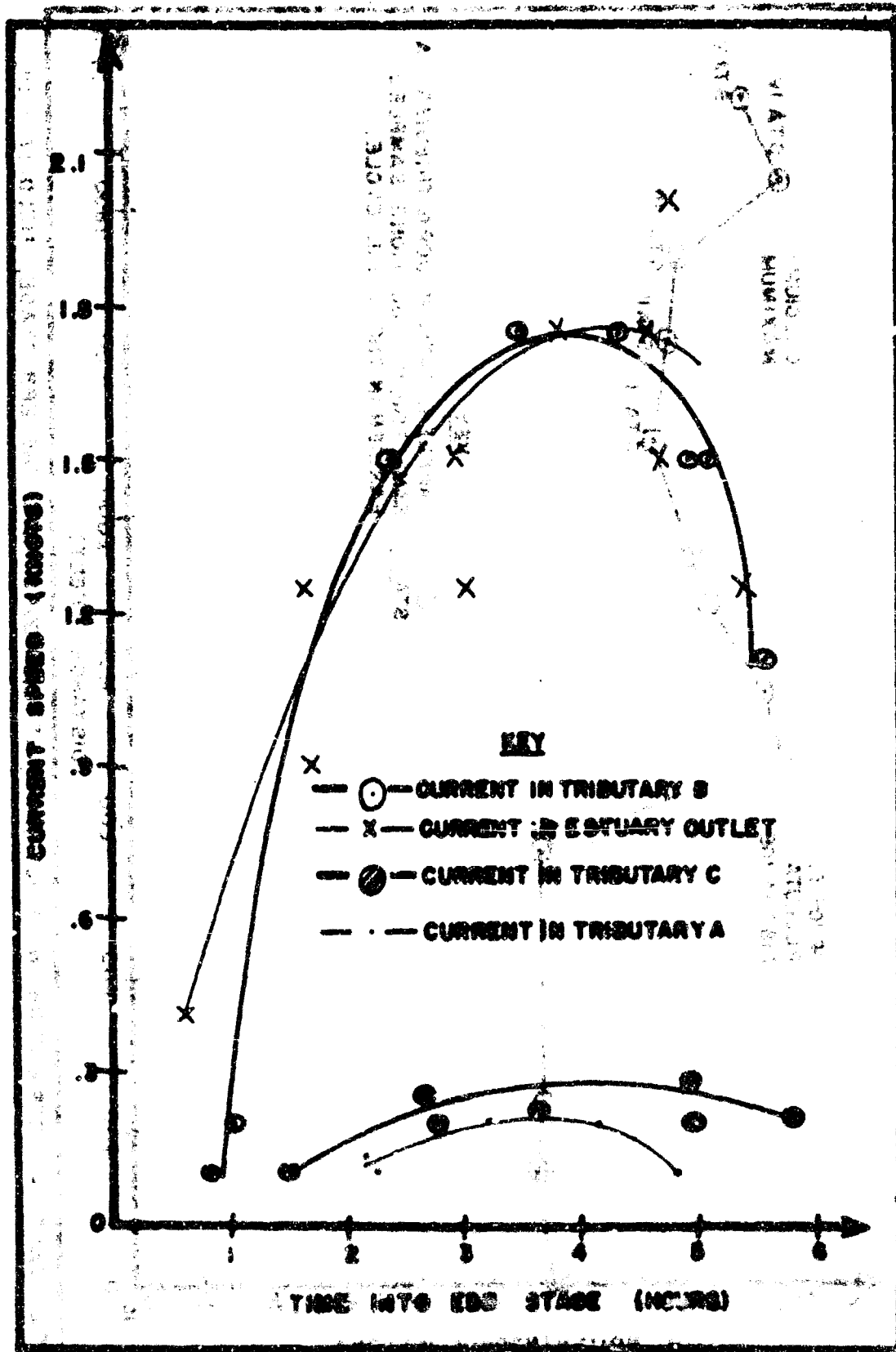


PLATE 22. CURRENT SPEEDS WITHIN THE ESTUARY.

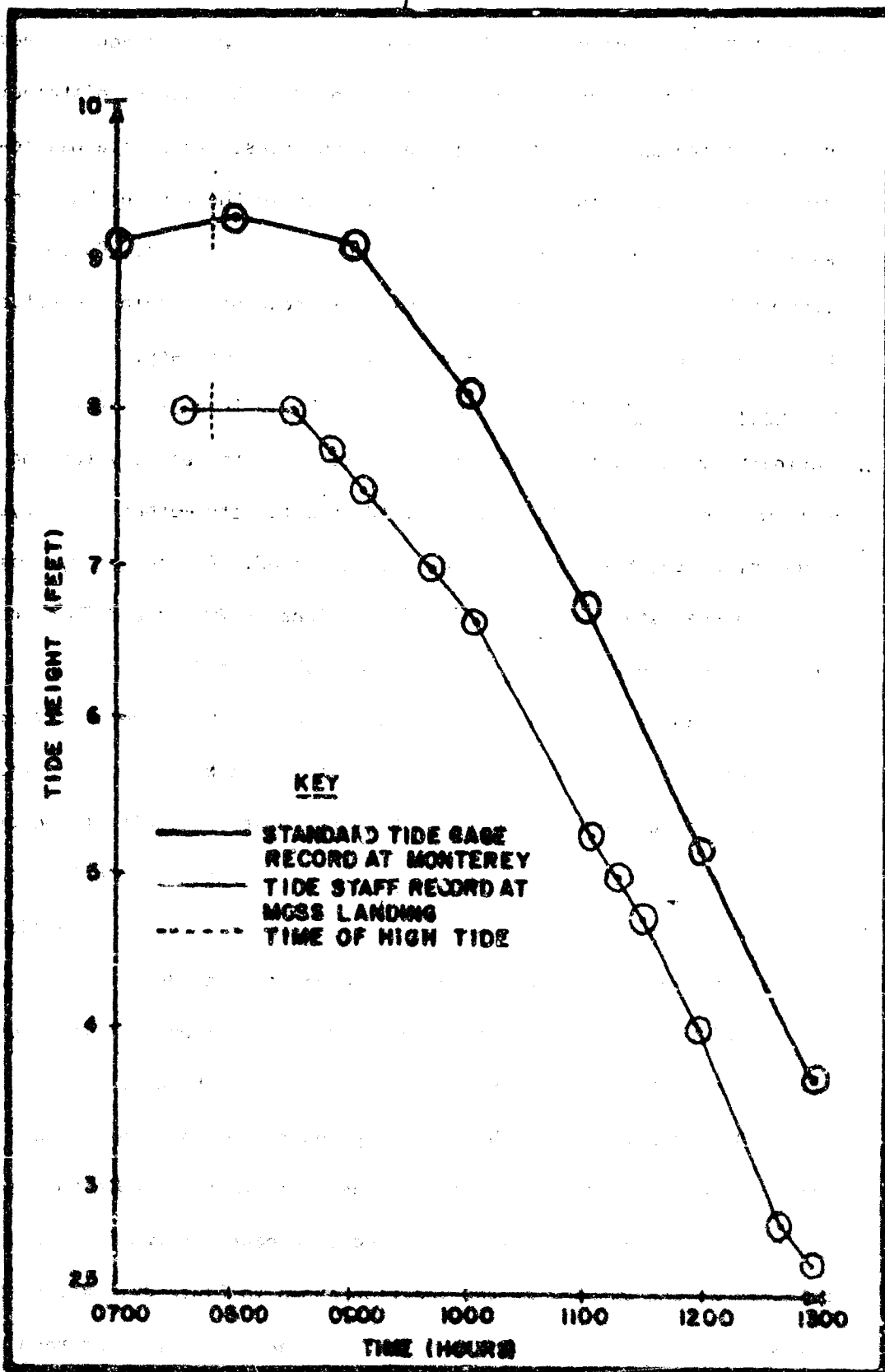


PLATE 2A. COMPARISON OF EBB TIDAL STAGE MOVEMENT RATES BETWEEN MONTEREY AND MOSS LANDING.

reading the tide staff is less than ± 3 inches. The plotted ebb tidal stage of Monterey Harbor and Moss Landing estuary were in good agreement.

Data collected on this field trip provided the calcium distribution in the turning basin and the adjacent tributaries. This data was required for the description of the circulation in the turning basin by application of the continuity equations described earlier. Furthermore, determination of current speeds at various locations within the estuary permitted an evaluation of a water budget for the estuary.

Field Trip IV. The data collected on Field Trip III satisfied the continuity model, and the circulation pattern in the estuary turning basin was determined. On Field Trip IV an alternate method using dye to determine the basin circulation was attempted. Fluorocene dye was placed in the estuary at three fixed locations at $2\frac{1}{2}$, $4\frac{1}{2}$ and $5\frac{1}{2}$ hours into the ebb stage. Station locations are shown in Plate 24.

Color photographs using a Pacemaker Speed Graphic camera (127 mm lens) were taken at predetermined intervals from a Navy C-45 airplane at an altitude of about 1000 feet. A representative result of the circulation pattern revealed is shown in Figure 3. The dye entering the turning basin from the two stations in tributary B revealed a meander-like pattern in the center of the turning basin. The dye stain placed near the discharge of tributary A remained concentrated near its source diffusing slightly toward the center line of the tributary.

At $3\frac{1}{2}$ hours into the ebb stage a dye packet was attached to a thirty pound weighted nylon line at a position two feet above the weight. This dye packet was then quickly lowered to a depth of two feet above the floor of the estuary at the location shown in Plate 24. After approximately two minutes when the initial surface dye stain had been carried out of the basin by the current, no evidence of dye returning

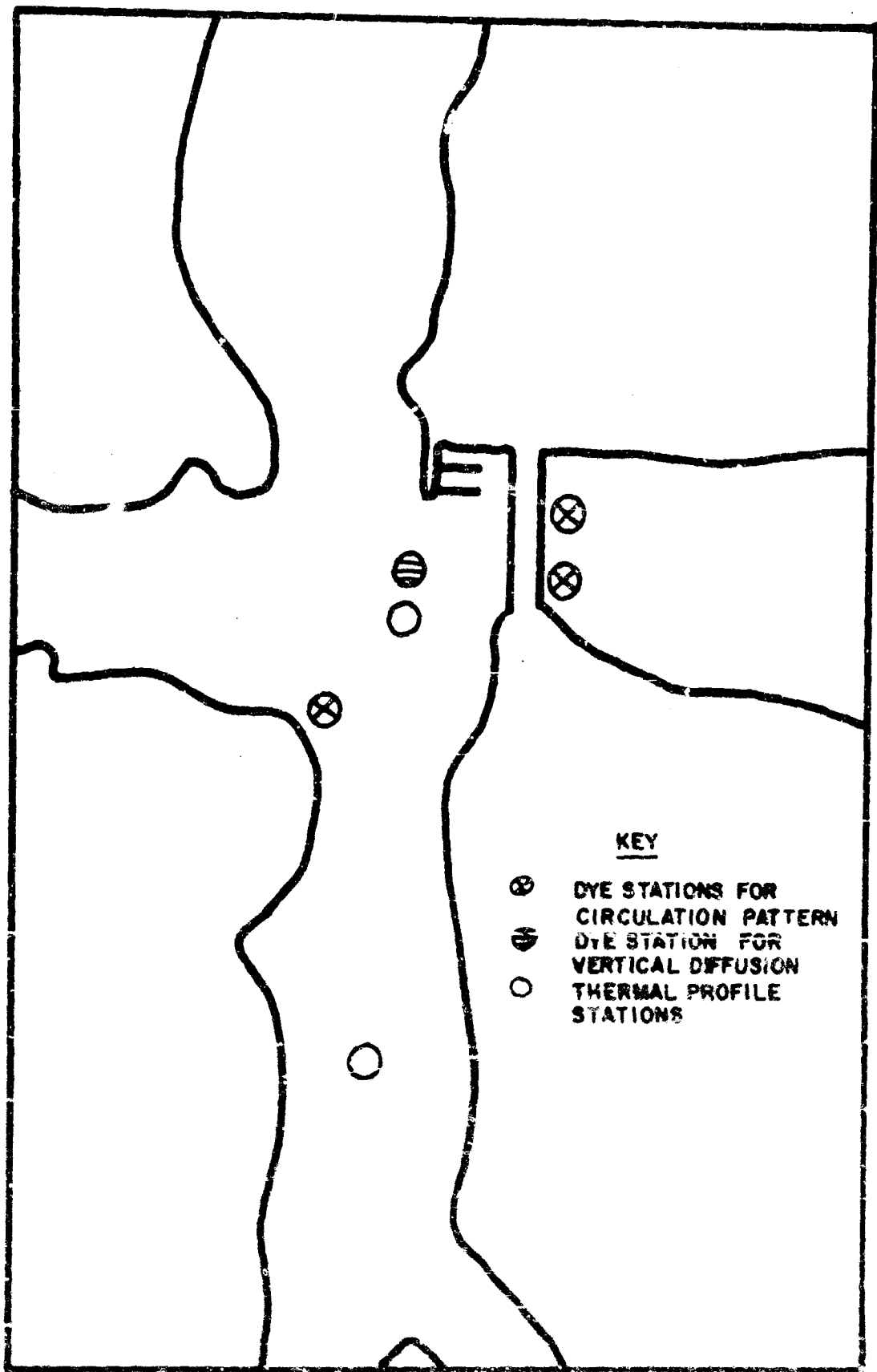


PLATE 24. STATION LOCATIONS FIELD TRIP M.

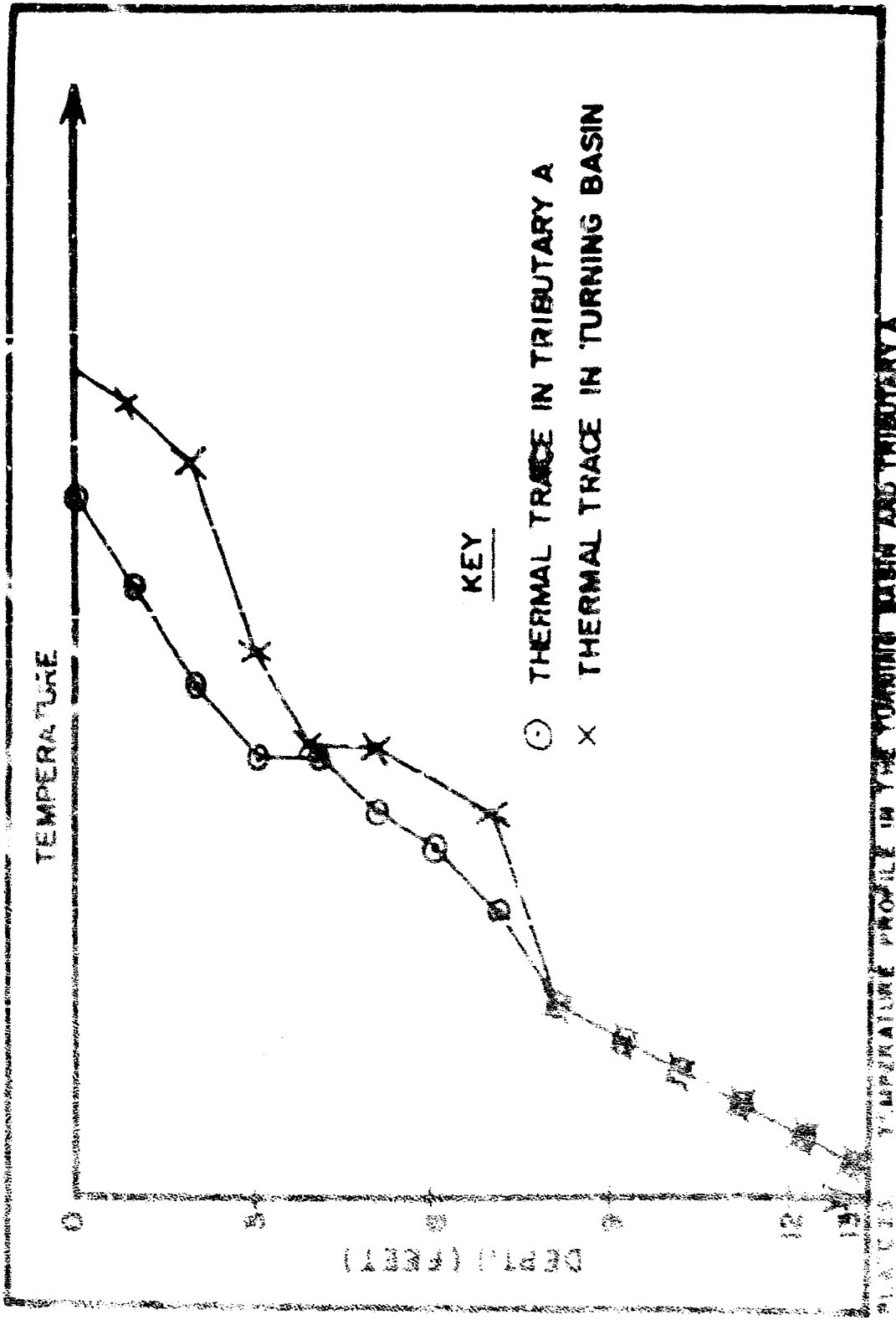


to the surface was observed from the airplane or by ground observers using field glasses. Upon retrieving the dye packet at the end of fifteen minutes it was observed that only 10% of the dye remained unexpanded. Thus, vertical diffusion must be of minor significance in the turning basin.

Upon completion of the dye studies two vertical thermal profiles were measured, one in tributary A and the other in the turning basin at the stations shown in Plate 24. Unfortunately, the temperature calibration of the probe was faulty and quantitative values are not available. However, the qualitative results shown in Plate 25 indicate that there is a stable stratification at a depth of eight feet throughout tributary A and the turning basin.

Dye study results; thermal profiles, known fresh water dilution of the calcium pollutant and the large difference in calcium concentration between the four and ten foot depths lead us to believe that the continuity equations are satisfied in the upper layer of the turning basin.

On the basis of these results vertical diffusion, if present, can be neglected.



TEMPERATURE PROFILE IN THE TURNING BASIN AND TRIBUTARY A

VI. DATA DISCUSSION

Having obtained an understanding of the calcium movement and distribution within the estuary on Field Trips I and II, we applied the calcium distribution data from Field Trip III to the continuity equations. Since it was our purpose to use the calcium distribution to study the circulation pattern in the turning basin, the continuity model described in section IV was applied to the data using the following equations:

$$Y_A + Y_B + Y_C = Y_T \quad (7)$$

$$Y_A C_A + Y_B C_B + Y_C C_C = C_{TB} \quad (8)$$

Recall that equation (7) represents continuity of volume with Y_{A-C} representing fractional volumes from each tributary. The right hand term Y_T is equal to unity and represents the total volume passing through the estuary outlet. Equation (8) describes the conservation of calcium resulting if equation (7) is satisfied.

Field data from Field Trip III showed the concentration in tributary B and C to be equal at 2½ hours into the ebb stage. Under these conditions equation (8) reduces to the following form:

$$Y_A C_A + (1 - Y_A) C_{BC} = C_{TB} \quad (9)$$

Field Trip III data also provided the value of C_A , C_{BC} and C_{TB} . Therefore, the fractional volume Y_A was determined at each station in the turning basin. Isoleths connecting points of equal Y_A were contoured revealing the circulation pattern shown in Plate 26. Plate 26 shows a

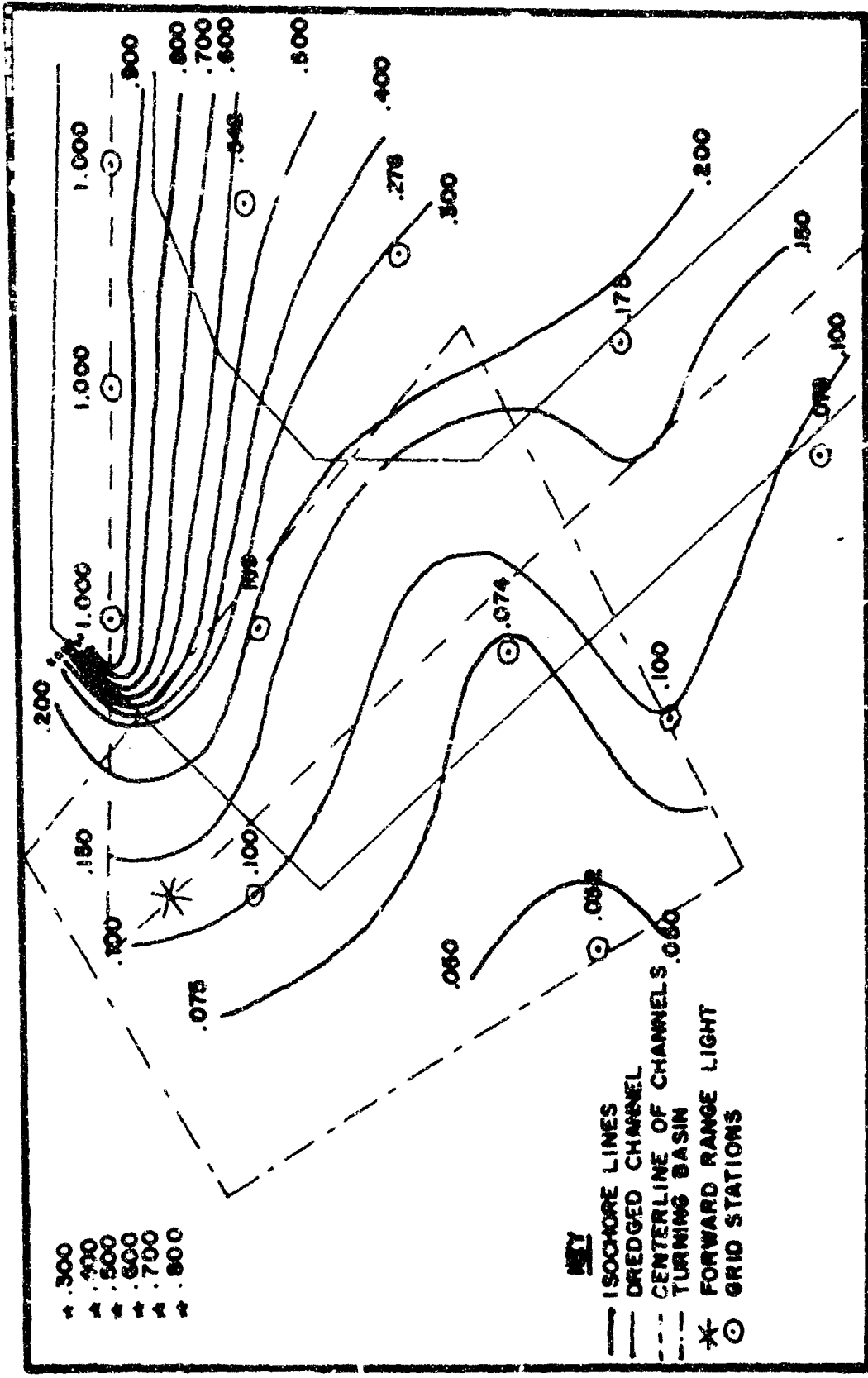
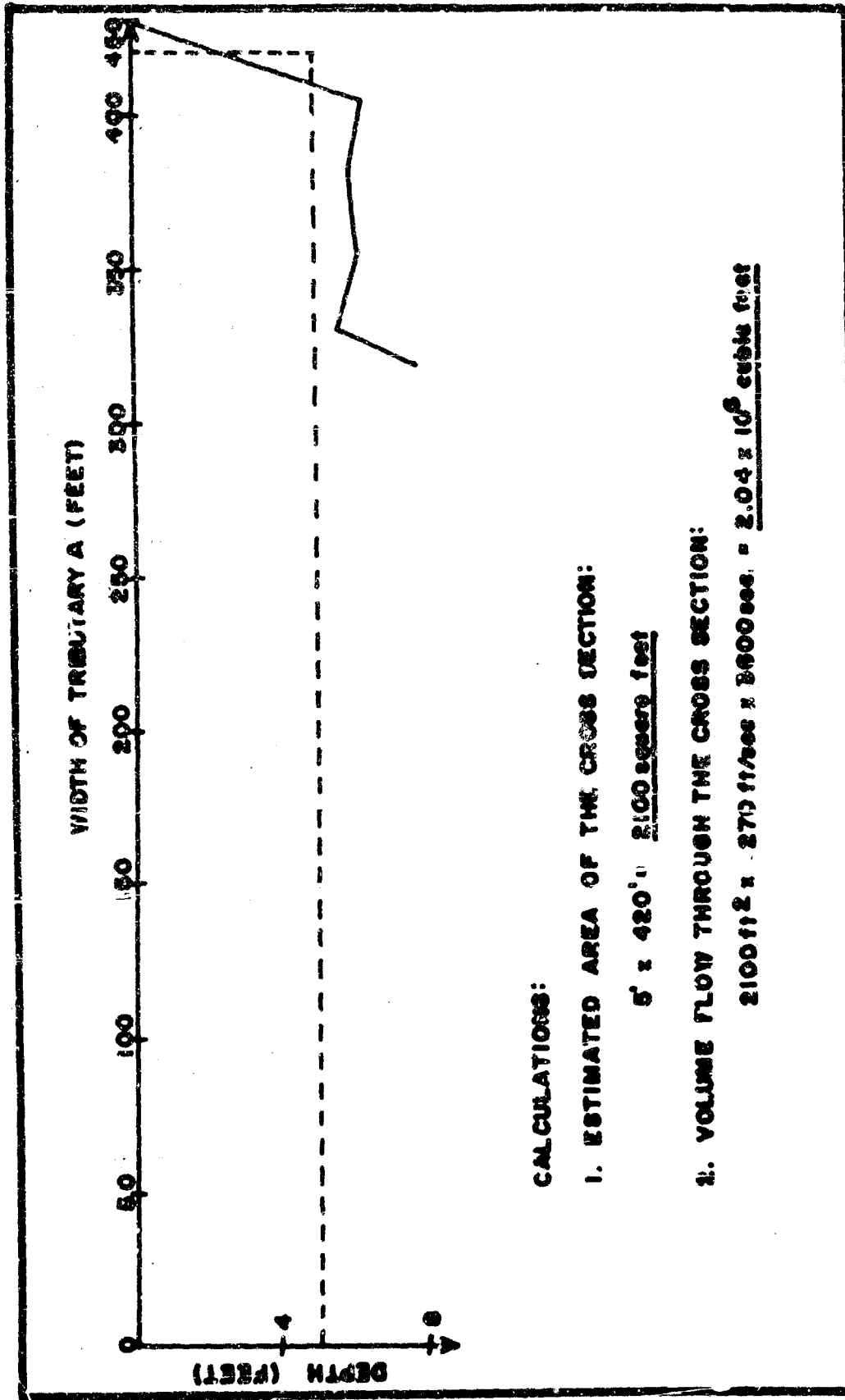


PLATE 26. CIRCULATION IN TURNING BASIN BY ELECTRODE MEASUREMENT.

meander-like pattern through the center of the turning basin.

Evidence supporting the correctness of this circulation pattern is the agreement between the value of γ_A contributed to the turning basin as determined by electrode and independently by a water budget study. Through the use of the water budget γ_A was computed for a six minute interval centered around $2\frac{1}{2}$ hours into the ebb stage. This fractional volume was determined by calculating the volume of water transported through a cross section in tributary A, C and the estuary outlet for the six minute period by multiplying the time interval (six minutes) times the product of the current speed and the cross sectional area at each current measuring station. These calculations are shown in Plates 27 to 29. The volume transported through tributary B cannot be directly determined in the same manner due to the lack of soundings in the tributary. However, since the volume transported through tributary A, C and the estuary outlet is known, the volume transported through tributary B can be determined. γ_A was determined to be approximately 9.6% using the method summarized in Table I. The determination of γ_A by electrode analysis was calculated by numerically integrating over the areas between isopleths of γ_A in the turning basin. These calculations are shown in Plate 30 which show a value of approximately 10.2% which is in good agreement with 9.6%. This agreement between γ_A values supports the circulation pattern determined by the calcium electrode.

Further corroborative evidence substantiating the correctness of the circulation pattern revealed by the electrode comes from the dye studies of Field Trip IV. There is close similarity between the two patterns as shown in Plate 31.



CALCULATIONS:

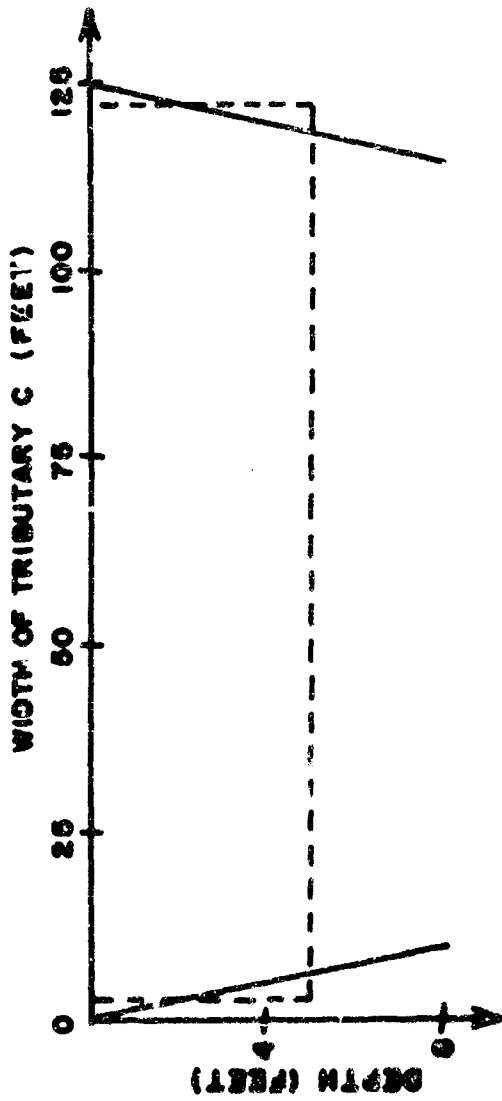
1. ESTIMATED AREA OF THE CROSS SECTION:

$5' \times 420' = \underline{2100 \text{ square feet}}$

2. VOLUME FLOW THROUGH THE CROSS SECTION:

$2100 \text{ ft}^2 \times 270 \text{ ft/sec} \times 3600 \text{ sec.} = \underline{2.04 \times 10^8 \text{ cubic feet}}$

PLATE 17. CROSS SECTIONAL AREA OF SURFACE LAYER AT CURRENT MEASURING STATION IN TRIBUTARY A.



CALCULATIONS:

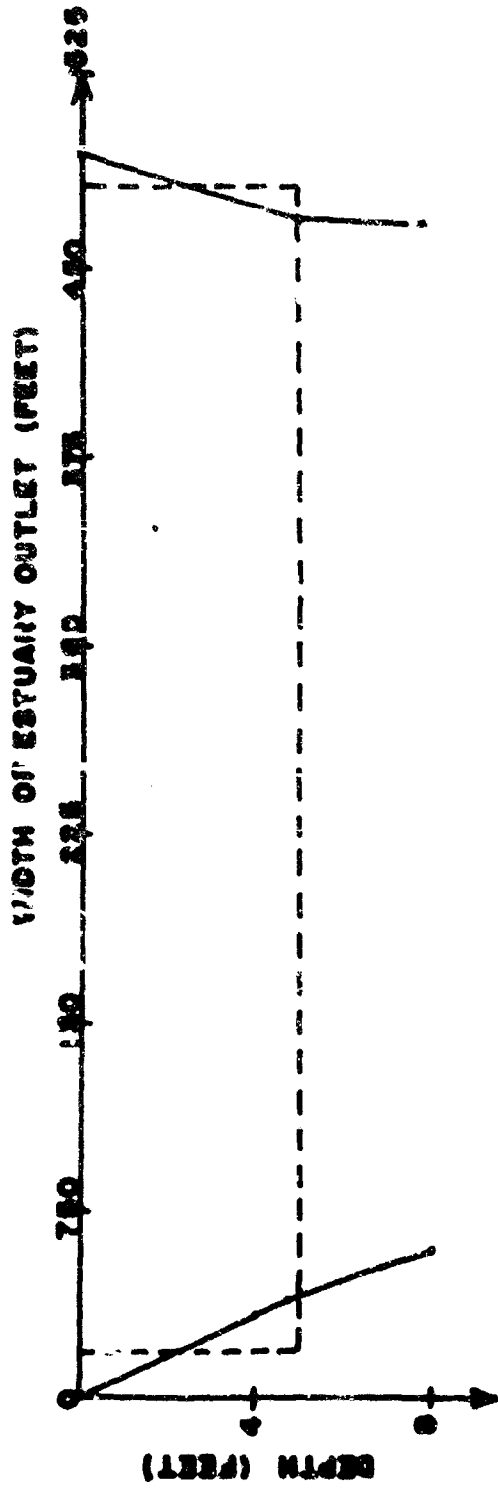
1. ESTIMATED AREA OF THE CROSS SECTION:

$6' \times 116' = 690 \text{ SQUARE FEET}$

2. VOLUME FLOW THROUGH THE CROSS SECTION:

$690 \text{ FT}^2 \times .379 \text{ FT}^3/\text{SEC} \times 3600 \text{ SEC.} = 906 \times 10^6 \text{ CUBIC FEET}$

PLATE 20. CROSS SECTIONAL AREA OF SURFACE LAYER AT CURRENT MEASURING STATION IN TRIBUTARY C.



CALCULATIONS:

1. ESTIMATED AREA OF THE CROSS SECTION:

$$5' \times 466' = \underline{2320 \text{ SQUARE FEET}}$$

2. VOLUME FLOW THROUGH THE CROSS SECTION:

$$2320 \text{ FT}^2 \times 2.56 \text{ FT/SEC} \times 3600 \text{ SEC.} = 21.35 \times 10^6 \text{ CUBIC FEET}$$

PLATE 29. CROSS SECTIONAL AREA OF SURFACE LAYER AT CURRENT MEASURING STATION IN ESTUARY OUTLET.

TABLE I

WATER BUDGET DETERMINATION OF TRIBUTARY A
 PERCENTAGE VOLUME CONTRIBUTION TO THE
 TURNING BASIN 2.5 HOURS INTO THE EBB STAGE

I. BASIC EQUATION USED: $Y_A + Y_B + Y_C = Y_T$

Y_{A-C} = FRACTION OF TOTAL VOLUME FLOW OUT OF EACH TRIBUTARY

Y_T = TOTAL VOLUME OUT OF THE ESTUARY OUTLET IN A SIX
 MINUTE PERIOD. DROP OF TIDE NEGLECTED DUE TO SMALL
 DROP IN RELATION TO THE DEPTH OF THE SURFACE LAYER.

II. DATA FROM PLATES 27 TO 29.

$Y_A = 2.04 \times 10^6$ CUBIC FEET IN A SIX MINUTE PERIOD

$Y_C = .805 \times 10^6$ CUBIC FEET IN A SIX MINUTE PERIOD

$Y_T = 21.35 \times 10^6$ CUBIC FEET IN A SIX MINUTE PERIOD

NOTE: SIX MINUTE PERIOD CENTERED AROUND 2.5 HOURS INTO THE
 EBB STAGE.

III. CALCULATIONS:

1. Y_B DETERMINED FROM THE BASIC EQUATION IN PARAGRAPH I.
 DIVIDE THROUGH THE BASIC EQUATION BY A FACTOR OF 10^6 .

$2.04 + Y_B + .805 = 21.35$

$Y_B + 2.85 = 21.35$

$Y_B = \underline{18.50 \times 10^6 \text{ CUBIC FEET}}$

2. DETERMINATION OF THE PERCENTAGE OF Y_A WITH RESPECT TO THE
 TOTAL WATER VOLUME IN THE TURNING BASIN:

a. $Y_T = 21.35 \times 10^6$ CUBIC FEET

b. $\frac{Y_A}{Y_A + Y_B + Y_C} = \frac{2.04 \times 10^6 \text{ CUBIC FEET}}{21.35 \times 10^6 \text{ CUBIC FEET}} = .0955 = 9.55\%$

TABLE I. WATER BUDGET CALCULATIONS

CALCULATIONS

1. AREA OF THE TURNING BASIN: 290,000 FT²
2. AREA OF ZONE I-IX IN TURNING BASIN MULTIPLIED BY PERCENTAGE OF TRIBUTARY WATER IN ZONE

ZONE	AREA (FT ²)	X % WATER	AREA (FT ²)
I	22,000	.026	563
II	91,000	.0625	5680
III	67,000	.0625	4160
IV	66,000	.125	8250
V	34,000	.175	5950
VI	7,500	.250	1875
VII	2,700	.350	945
VIII	600	.450	270
IX	200	.550	110
			<u>28,643</u>

3. PERCENTAGE TRIBUTARY WATER IN TURN-

$$\text{ING BASIN: } \frac{28,643}{290,000} = 10.22\% \approx .01\%$$

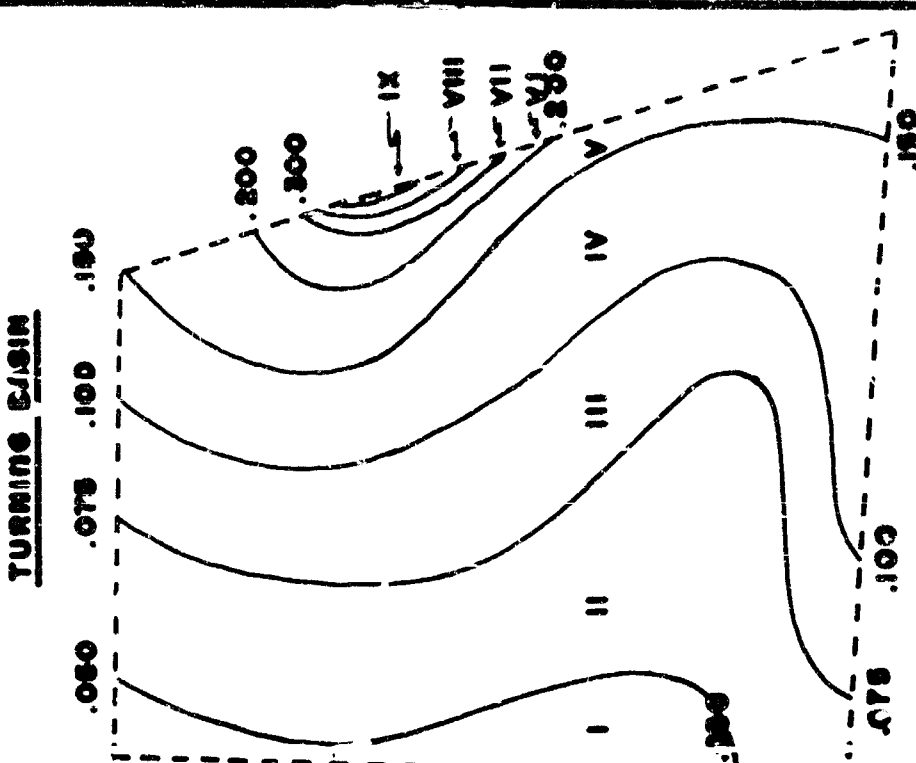
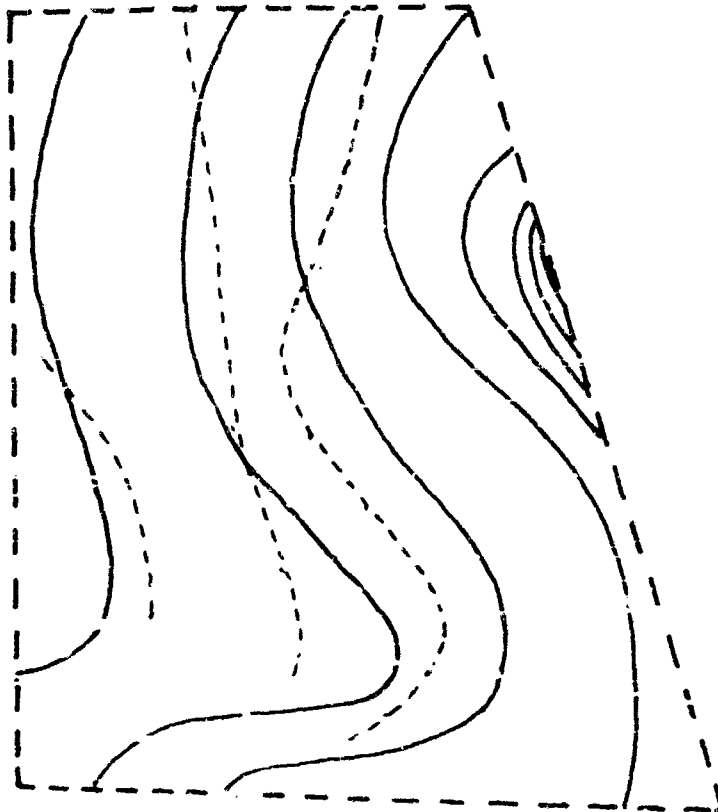


PLATE 34 AVERAGE PERCENTAGE OF TRIBUTARY WATER IN THE TURNING BASIN.



KEY

- CIRCULATION PATTERN ELECTRODE
- CIRCULATION PATTERN BY DYE STUDIES

PLATE N. CIRCULATION PATTERN BY ELECTRODE AND DYE STUDY.

VII. SUMMARY AND RECOMMENDATIONS

Summary. The applicability of the Calcium Activity Electrode to describe water circulations was evaluated in the Moss Landing estuary. This was accomplished by determining the circulation pattern in the turning basin of the estuary which contains a high concentration of calcium with respect to its adjacent oceanic environment. Excellent agreement was obtained between the upper layer circulation pattern revealed by use of the electrode, current and dye studies.

This study shows the Calcium Activity Electrode to be a quick and sensitive analytical instrument to describe water movements in this environment.

Recommendations. Subsequent investigations involving the use of the Calcium Activity Electrode can be improved by the development of an in situ electrode model. Its development appears feasible and would allow a quicker and more detailed evaluation of circulation patterns. Future studies using an in situ model would be more detailed by allowing an increase in the quantity of data obtained per unit surface area. This increase would be possible through a reduction in the handling of presently required sampling equipment.

The application of other specific ion electrodes such as the perchlorate (ClO_4^-) electrode should be evaluated. Since perchlorate does not exist naturally in the marine environment, the addition of perchlorate into small water bodies such as rivers, lakes and small estuaries would allow study of their circulations in a manner similar to that described in this thesis.

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APPENDIX I

FIELD TRIP DATA

FIELD TRIP I.

A. Tide Data Height of high tide 6.4 feet at 1138.

Height of low tide -0.7 feet at 1822.

B. Sample Data from each Station (Plate 4):

<u>Station No. I</u>				
<u>Run No.</u>	<u>Consecutive Sample No.</u>	<u>Time Into Ebb Stage (min.)</u>	<u>Depth of Sample (ft.)</u>	<u>Calcium Concentration (m/l)</u>
1	1	Ø	4	6.20×10^{-3}
1	2	Ø	10	5.20×10^{-3}
2	7	65	4	6.00×10^{-3}
2	8	65	10	5.40×10^{-3}
3	13	134	4	6.00×10^{-3}
3	14	134	10	5.20×10^{-3}
4	19	214	4	1.12×10^{-2}
4	20	214	10	6.40×10^{-3}
5	25	289	4	1.08×10^{-2}
5	26	289	10	5.85×10^{-3}
6	31	365	4	8.10×10^{-3}
6	32	365	10	5.80×10^{-3}

<u>Station No. II</u>				
1	3	20	4	5.10×10^{-3}
1	4	20	10	5.10×10^{-3}
2	9	85	4	5.20×10^{-3}
2	10	85	10	5.10×10^{-3}
3	15	157	4	6.00×10^{-3}

3	16	157	10	5.60×10^{-3}
4	21	239	4	6.30×10^{-3}
4	22	239	10	5.80×10^{-3}
5	27	316	4	8.40×10^{-3}
5	28	316	10	5.85×10^{-3}
6	33	378	4	6.40×10^{-3}
6	34	378	10	6.80×10^{-3}

Section No. III

1	5	39	4	5.10×10^{-3}
1	5	39	10	5.10×10^{-3}
2	11	109	4	5.15×10^{-3}
2	12	109	10	5.50×10^{-3}
3	17	182	4	5.40×10^{-3}
3	18	182	10	5.40×10^{-3}
4	23	266	4	5.50×10^{-3}
4	24	266	10	5.30×10^{-3}
5	29	336	4	6.60×10^{-3}
5	30	336	10	6.20×10^{-3}
6	35	390	4	5.90×10^{-3}
6	36	390	10	5.85×10^{-3}

FIELD TRIP II.

A. Tide Data: Height of high tide 5.9 feet at 0856.
 Height of low tide -0.6 feet at 1614.

B. Sample Data from each Station (Plate 7):

<u>Station No. C₁</u>				
<u>Run No.</u>	<u>Consecutive Sample No.</u>	<u>Time Into Ebb Stage (min.)</u>	<u>Depth of Sample (ft.)</u>	<u>Calcium Concentration (m/l)</u>
1	1	-42	0	6.8×10^{-3}
1	2	-42	4	6.8×10^{-3}
<u>Station No. C₂</u>				
1	3	-29	0	6.8×10^{-3}
1	4	-29	4	6.8×10^{-3}
<u>Station No. B₁</u>				
1	5	-18	0	6.8×10^{-3}
1	6	-18	4	6.8×10^{-3}
<u>Station No. B₂</u>				
1	7	-13	0	6.8×10^{-3}
1	8	-13	4	6.8×10^{-3}
<u>Station No. I</u>				
1	9	01	0	2.10×10^{-2}
1	10	01	4	1.46×10^{-2}
2	19	146	0	1.42×10^{-2}
2	20	146	4	1.28×10^{-2}
3	29	289	0	7.60×10^{-3}
3	30	289	4	9.50×10^{-3}
4	39	430	0	5.90×10^{-3}
4	40	430	4	1.60×10^{-2}

Station No. II

1	11	08	0	1.67×10^{-2}
1	12	08	4	1.12×10^{-2}
2	21	151	0	1.45×10^{-2}
2	22	151	4	1.12×10^{-2}
3	31	296	0	7.80×10^{-3}
3	32	296	4	9.60×10^{-3}
4	41	440	0	6.40×10^{-3}
4	42	440	4	1.23×10^{-2}

Station No. III

1	13	14	0	1.70×10^{-2}
1	14	14	4	9.60×10^{-3}
2	23	157	0	1.35×10^{-2}
2	24	157	4	1.17×10^{-2}
3	33	302	0	8.70×10^{-3}
3	34	302	4	9.00×10^{-3}
4	43	446	0	7.40×10^{-3}
4	44	446	4	8.80×10^{-3}

Station No. IV

1	15	20	0	1.27×10^{-2}
1	16	20	4	7.45×10^{-3}
2	25	162	0	1.14×10^{-2}
2	26	162	4	9.10×10^{-3}
3	35	307	0	8.50×10^{-3}
3	36	307	4	8.70×10^{-3}
4	45	451	0	7.60×10^{-3}
4	46	451	4	8.10×10^{-3}

Station No. V

1	17	27	0	7.80×10^{-3}
1	18	27	4	6.80×10^{-3}
2	27	166	0	7.90×10^{-3}
2	28	166	4	7.80×10^{-3}
3	37	313	0	9.10×10^{-3}
3	38	313	4	7.80×10^{-3}
4	47	455	0	8.50×10^{-3}
4	48	455	4	9.00×10^{-3}

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FIELD TRIP III.

A. Tide Data: Height of high tide 6.5 feet at 0744.

Height of low tide -1.3 feet at 1526.

B. Sample data from each Station (Plate 17):

Station No. C₁

<u>Run No.</u>	<u>Consecutive Sample No.</u>	<u>Time Into Ebb Stage (min.)</u>	<u>Depth of Sample (ft.)</u>	<u>Calcium Concentration (m/l)</u>
1	1	01	0	5.15×10^{-3}
2	4	91	0	4.95×10^{-3}
3	32	164	0	5.20×10^{-3}
4	54	224	0	5.40×10^{-3}
5	66	271	0	5.40×10^{-3}
6	68	316	0	5.50×10^{-3}

Station No. B₁

1	2	16	0	4.90×10^{-3}
2	3	66	0	5.15×10^{-3}
3	19	144	0	5.15×10^{-3}
4	45	209	0	5.35×10^{-3}
5	65	261	0	5.35×10^{-3}
6	67	296	0	5.50×10^{-3}
7	83	336	0	5.75×10^{-3}

Station No. I

1	5	119	0	1.10×10^{-2}
1	6	119	2	1.15×10^{-2}
2	35	180	0	9.2×10^{-3}
2	36	180	2	1.0×10^{-2}

Station No. II

1	7	121	0	1.09×10^{-2}
1	8	121	2	1.09×10^{-2}
2	37	182	0	9.0×10^{-3}
2	38	182	2	9.6×10^{-3}

Station No. III

1	9	124	0	1.10×10^{-2}
1	10	124	2	1.10×10^{-2}
2	39	185	0	9.6×10^{-3}
2	40	185	2	9.6×10^{-3}

Station No. IV

1	11	129	0	1.23×10^{-2}
1	12	129	2	9.6×10^{-3}
2	41	189	0	9.6×10^{-3}
2	42	189	2	9.2×10^{-3}

Station No. V

1	13	132	0	1.23×10^{-2}
1	14	132	2	1.23×10^{-2}
2	43	192	0	9.20×10^{-3}
2	44	192	2	9.60×10^{-3}

Station No. 1

2	15	140	0	8.30×10^{-3}
2	16	140	2	7.80×10^{-3}
3	46	210	0	5.77×10^{-3}
3	47	210	2	5.77×10^{-3}

Station No. 2

2	17	143	0	6.60×10^{-3}
2	18	143	2	6.40×10^{-3}

3	48	212	0	5.80×10^{-3}
3	49	212	2	5.80×10^{-3}

Station No. 3

2	20	146	0	6.10×10^{-3}
2	21	146	2	5.90×10^{-3}
3	50	214	0	5.75×10^{-3}
3	51	214	2	5.75×10^{-3}

Station No. 4

2	22	152	0	5.50×10^{-3}
2	23	152	2	5.50×10^{-3}
3	52	224	0	5.40×10^{-3}
3	53	224	2	5.35×10^{-3}

Station No. 5

2	24	155	0	6.00×10^{-3}
2	25	155	2	5.80×10^{-3}
3	55	228	0	6.50×10^{-3}
3	56	228	2	6.50×10^{-3}

Station No. 6

2	26	158	0	5.50×10^{-3}
2	27	153	2	5.50×10^{-3}
3	57	232	0	5.50×10^{-3}
3	58	232	2	5.60×10^{-3}

Station No. 7

2	28	160	0	5.60×10^{-3}
2	29	160	2	5.65×10^{-3}
3	59	234	0	5.60×10^{-3}
3	60	234	2	5.75×10^{-3}

		<u>Station No. 8</u>		
2	30	163	0	5.5×10^{-3}
2	31	163	2	5.75×10^{-3}
3	61	237	0	5.50×10^{-3}
3	62	237	2	5.40×10^{-3}

		<u>Station No. 9</u>		
2	33	167	0	5.35×10^{-3}
2	34	167	2	5.35×10^{-3}
3	63	239	0	5.75×10^{-3}
3	64	239	2	5.60×10^{-3}

		<u>Stations Mrs A₁ - A₁₄ *</u>			<u>No.</u>
1	69	317	0	5.8×10^{-3}	A ₁
1	70	318	0	6.6×10^{-3}	A ₂
1	71	320	0	6.7×10^{-3}	A ₃
1	72	322	0	6.7×10^{-3}	A ₄
1	73	323	0	6.7×10^{-3}	A ₅
1	74	324	0	1.02×10^{-2}	A ₆
1	75	325	0	9.8×10^{-3}	A ₇
1	76	327	0	9.0×10^{-3}	A ₈
1	77	328	0	8.8×10^{-3}	A ₉
1	78	330	0	8.3×10^{-3}	A ₁₀
1	79	332	0	8.5×10^{-3}	A ₁₁
1	80	333	0	8.60×10^{-3}	A ₁₂
1	81	334	0	1.01×10^{-2}	A ₁₃
1	82	335	0	9.5×10^{-3}	A ₁₄

* Station locations shown on page 21.

C. Miscellaneous Sample Data (Plate 17):

<u>Station No.</u>	<u>Consecutive Run No.</u>	<u>Sample No.</u>	<u>Time into Ebb Stage (min.)</u>	<u>Depth of Sample (ft.)</u>	<u>Calcium Concentration (m/l)</u>
4	1	B	89	0	1.08×10^{-3}
	1	C	89	4	9.40×10^{-3}
5	1	D	94	0	6.50×10^{-3}
6	1	E	97	0	6.20×10^{-3}
7	1	F	100	0	5.80×10^{-3}
	1	G	100	2	5.40×10^{-3}
8	1	I	104	0	7.20×10^{-3}
	1	J	104	2	6.10×10^{-3}
9	1	K	107	0	5.60×10^{-3}
	1	L	107	2	5.20×10^{-3}
10	1	M	109	0	5.40×10^{-3}
	1	N	109	2	5.40×10^{-3}
11	1	O	112	0	5.20×10^{-3}
	1	P	112	2	5.15×10^{-3}
12	1	Q	115	0	5.10×10^{-3}
	1	R	115	2	5.10×10^{-3}
01	1	A	11	0	5.20×10^{-3}
	2	H	101	0	5.15×10^{-3}
	3	S	176	0	5.40×10^{-3}
	4	T	234	0	5.60×10^{-3}
	5	U	276	0	5.60×10^{-3}
	6	V	326	0	6.00×10^{-3}

D. Current Data shown in Plate 22.

E. Tide Staff Data shown in Plate 23.

FIELD TRIP IV.

- A. Tide Data: Height of high tide 6.1 feet at 0914.
Height of low tide -0.8 feet at 1632.
- B. Results of Dye Study for Circulation In Turning Basin shown in Figure 3.
- C. Data from Thermal Profiles in Plate 25.

APPENDIX II
ELECTRODE CALIBRATION CURVE

