THE APPLICATION OF LASER-RAMAN LIGHT SCATTERING TO THE DETERMINATION OF SULFATE IN SEA AND ESTUARINE WATERS

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ABSTRACT

It has been shown that laser-Raman light scattering is a fast and reliable technique for determining sulfate concentrations in sea and estuarine waters with apparently none of the interferences inherent in the gravimetric and titrametric methods. The Raman measurement involved the ratioing of the peak heights of an unknown sulfate concentration and a nitrate internal standard. This ratio was used to calculate the unknown sulfate concentration from a standard curve. The standard curve was derived from the Raman data on prepared nitrate-sulfate solutions. At the 99.7% confidence level, the accuracy of the Raman technique was 7 to 8.6 percent over the concentration range of the standard curve.

The sulfate analyses of water samples collected at the mouth of the James River, Hampton, Virginia, demonstrated that in most cases sulfate had a constant concentration relative to salinity in this area. However, abnormally low sulfate concentrations were found in deep water near the bottom. These low values were attributed to the persistance of thermoclines and haloclines for a sufficient length of time so that anaerobes in the sediments could remove measureable amounts of sulfate from the bottom water.

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CHAPTER I

INTRODUCTION

Sulfate in sea water is usually determined gravimetrically by precipitation as barium sulfate. This method, used almost exclusively since 1819, has many interferences, the most serious being cation and anion coprecipitation. Due to the low solubility of barium sulfate, errors caused by coprecipitation cannot be eliminated by repeated precipitations.

In sea water, the coprecipitation of calcium, as calcium sulfate, is the most serious problem. Carrying out the analysis in hydrochloric acid can reduce the presence of calcium, but it also increases the solubility of barium sulfate. The alkali metals also interfere by coprecipitating with barium sulfate. Bather and Riley (1954) investigated the problem of calcium and alkali metal coprecipitation and developed a method that gave quantitative recovery of barium sulfate with negligible amounts of calcium and the alkali metals. Their technique, however, is long, tedious, and difficult, which makes routine sulfate analyses prohibitively time consuming.

Various titrametric methods of sulfate analyses (Page and Spurlock, 1965; Fritz and Schenk, 1969) have been developed which are fast and easy. These methods, however, are of lower precision than that of Bather and Riley (op. cit.)

primarily because of the interferences described above.

The objective of this research was to demonstrate that Raman light scattering is a fast and reliable technique for sulfate analysis. Raman light scattering is a molecular phenomenon that produces an energy difference between the light that is incident upon, and the light that is scattered by, a molecule or molecular ion. This scattered light involves the polarization of the species by the electric field of the light. This electric field induces an oscillating dipole moment in the molecule which emits radiation with a frequency shifted from the incident light frequency by an amount equal to the frequency of the molecule vibration.

Using conservation of energy, Raman light scattering can be described by the following expression:

$$h\nu + E = h\nu' + E'$$

Here $h\nu$ and $h\nu'$ are the energy of the incident and scattered light respectively, and E and E' are the molecular energy before and after interaction respectively. Rearranging, one obtains

$$E' - E = h(\nu - \nu'),$$

which shows explicitly that the change in frequency of the light is a measure of the change in molecular energy. The change in energy is the result of transitions between the vibrational-rotational energy levels of the particle. Because the transitions are unique for each scattering species, the change in light frequency can be used for the identification of these species.

At room temperature, most molecules and ions are in the ground vibrational state and therefore, must gain energy to undergo energy level transitions. The resulting scattered light has a longer wavelength than the incident light (Stokes Raman scattering). When the incident light interacts with a particle in an excited state, the particle can undergo a transition to a lower energy level. This interaction results in the scattered light having a shorter wavelength than the incident light (anti-Stokes Raman scattering). In vibrational Raman spectroscopy, the Stokes lines are generally studied because they are more intense than the anti-Stokes lines. The greater intensity of the Stokes lines is due to the high population of the ground state relative to that of the excited levels.

A list of the major ions found in sea water is given in Table 1 together with the vibrational Raman frequencies of the polyatomic ions.* Inspection of Table 1 reveals that the Raman bands of the major polyatomic ions do not interfere in the analysis of sulfate by Raman scattering because they are displaced from the sulfate band. Other naturally occurring polyatomic ions such as nitrate and phosphate are usually in such low concentrations in sea and estuarine waters (less than 0.001 gm/1) that normally they are not detectable with Raman scattering.

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* Monoatomic ions are not Raman active and therefore, cannot interfere in the analysis of sulfate by Raman scattering.

Table 1. Concentrations and Raman vibrational frequencies of the major ionic constituents of sea water

Ion	Concentration (gm/kg) in sea water of 35 ppt*	Vibrational frequency (cm^{-1})[a]
Cl^{-1}	19.353	
Na^{+1}	10.760	
SO_4^{-2}	2.712	981**
Mg^{+2}	1.294	
Ca^{+2}	0.413	
K^{+1}	0.387	
HCO_3^{-1}	0.142	1069***
Br^{-1}	0.067	
Sr^{+2}	0.008	
B	0.004	
F^{-1}	0.001	

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*Riley and Skirrow, 1965, parts per thousand (ppt)
**Szymanski, 1967
***Nakamota, 1970

[a] Monoatomic ions are not Raman active.

A secondary objective of this research was to measure the sulfate concentrations of water samples collected at the mouth of the James River, Hampton Roads, Virginia, between Old Point Comfort and Willoughby Spit. This area was ideal for study because the location was near the laboratory and a small boat was adequate for sampling. Also, the area was suitable for determining if sulfate remains constant relative to salinity in the James River Estuary.

CHAPTER II

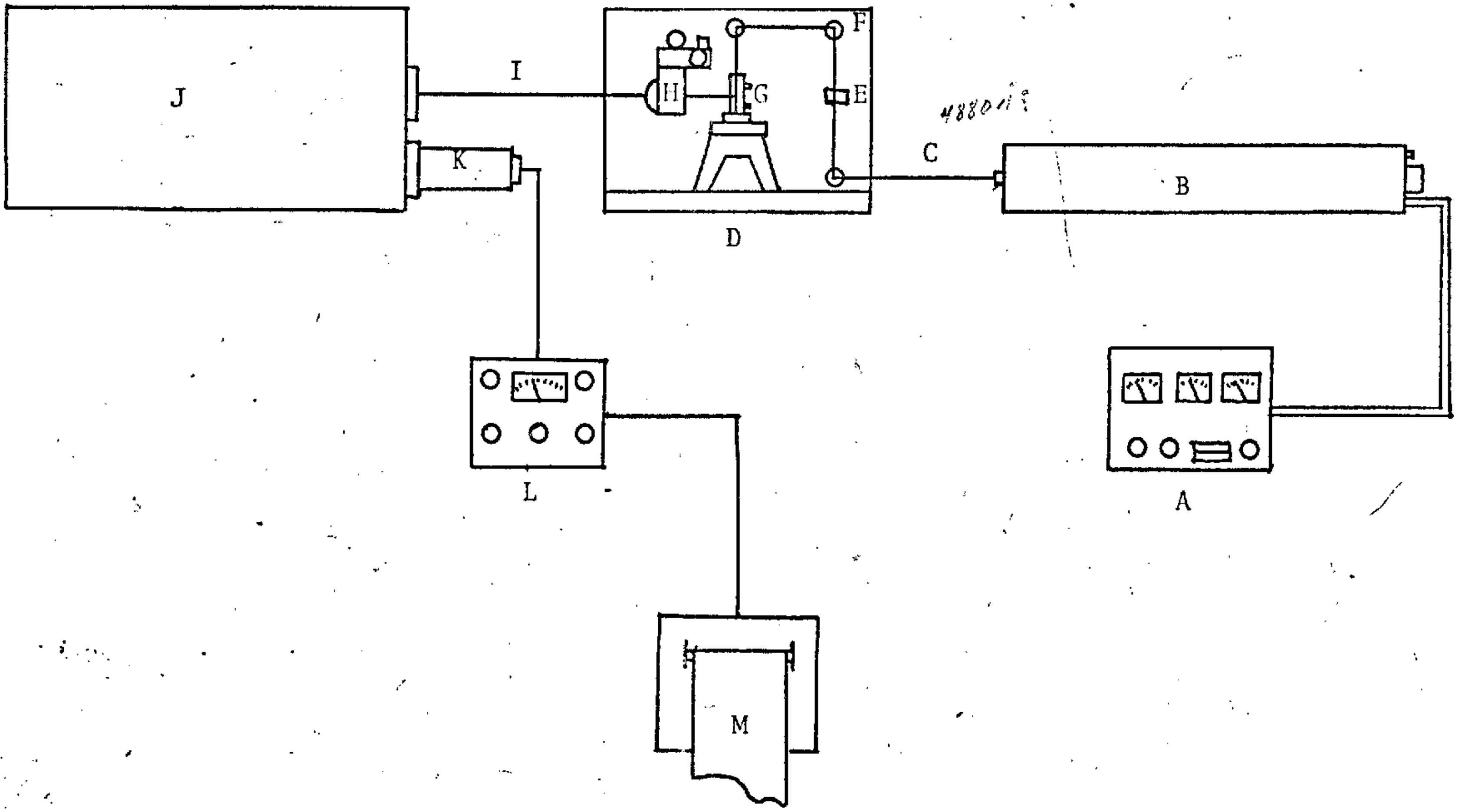
EXPERIMENTAL PROCEDURE

The Laser Raman instrument used in this research (Fig. 1) utilized the 4880 Å line of a Coherent Radiation (Palo Alto, California) Model 52 G argon ion laser for Raman excitation. The mirrors, sample holder, focusing and collection lenses were mounted on a Model 25-410 Jarrell-Ash (Waltham, Massachusetts) Raman Sample Chamber. Once aligned, each component could be removed and kinematically remounted with ease, since alignment was retained.

A Jarrell-Ash Model 25-538 double pass sample cell was used for sulfate analysis. This cell had a silvered mirrored bottom that reflected the laser light back through the sample, which effectively doubled the Raman scattering of the sample. A Spex Industries (Metuchen, New Jersey) Model 1400 double monochromator, with gratings blazed at 7000 Å, was employed for dispersion of Raman spectra in second order. The detection system was a Centronic Model 4249 BA (Bailey Instruments, Saddle Brook, New Jersey) photomultiplier in a Products for Research (Danvers, Massachusetts) Model 51772Q4249RF housing. The photomultiplier was coupled to either an SSR Instruments Company (Santa Monica, California) Model 1105 photon counting system or a Keithley Instruments (Cleveland, Ohio) Model 417 picoammeter. The spectra were displayed on an Esterline-Angus (Indianapolis,

Fig. 1. Laser-Raman instrument. The instrument assembled for this research consisted of the following:

A. laser power supply.
B. laser
C. laser light
D. Raman sample chamber.
E. focusing lens
F. mirror
G. sample cell
H. collection lens
I. scattered light
J. monochromator
K. photomultiplier and housing
L. detection device
M. recorder


J
I
H
G
F
E
D
4880115
C
B
K
L
A
M

Indiana) Model E1101E strip chart recorder.

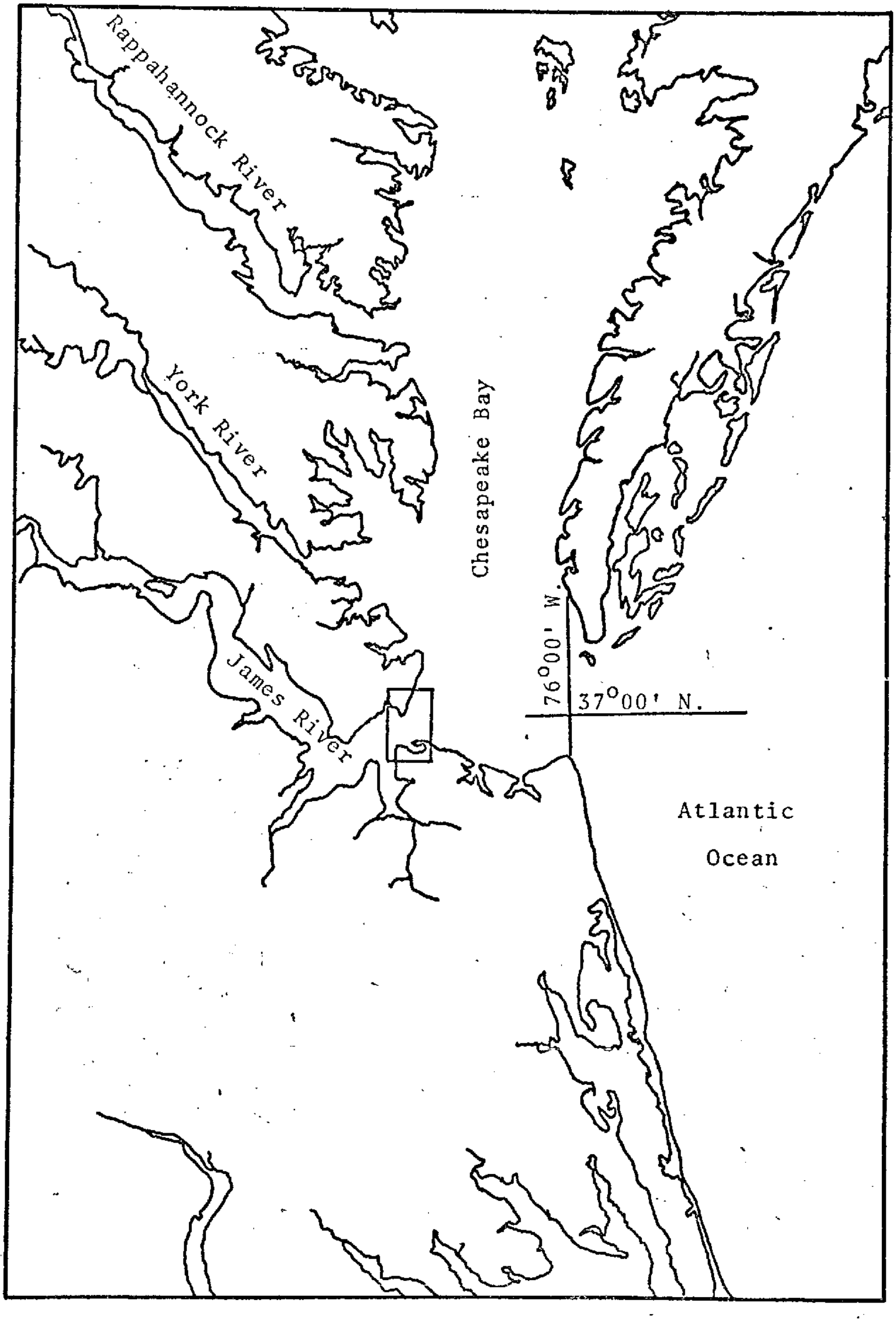
Water Sample Collection

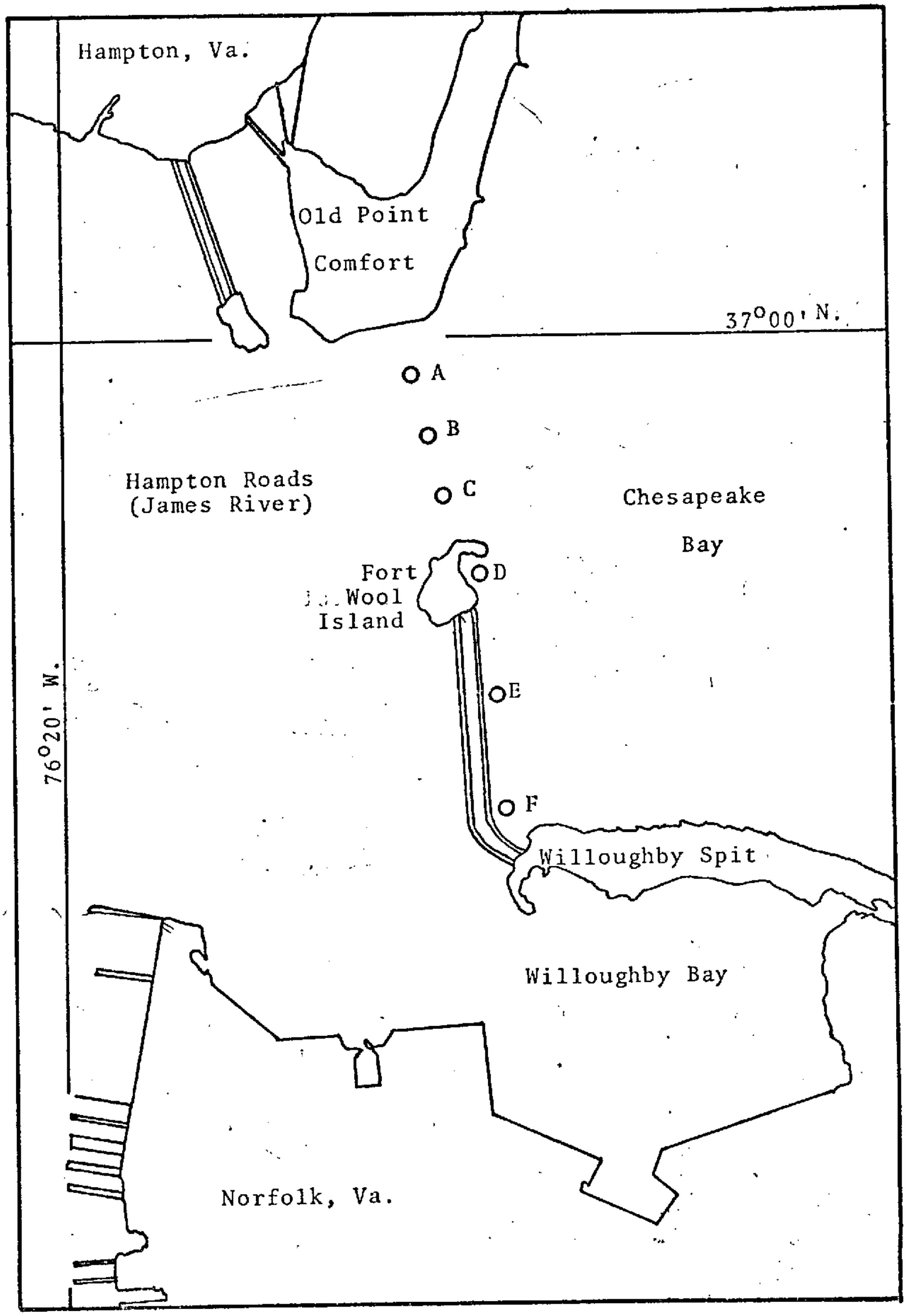
Water samples were collected between Old Point Comfort, Hampton, Virginia, and Willoughby Spit, Norfolk, Virginia, at the mouth of the James River. Six stations were chosen between these two points at approximately equal distance from each (see Figs. 2a and 2b). Three stations were located across the ship channel between Fort Wool and Old Point Comfort, (lettered A to C). The average depth was 45-50 feet at these stations and samples were taken near the bottom, at middle depth, and at the surface.

The last three stations were located on the east side of the Hampton Roads Bridge and Fort Wool Island (lettered D to F). Only surface samples were collected because at these stations the water was shallow (average of six feet). Samples were taken twice on each sampling day, once at maximum high water and once at minimum low water. A total of 24 water samples were collected each day.

Stations were occupied with a 17-foot boat, and water samples were collected using a home-made winch and nylon line for raising and lowering a N.I.O. (National Institute of Oceanography, Wormley, Godalming, Surrey, England) water sampling bottle. Once collected, the samples were stored in salinity bottles to prevent evaporation. The depth of sampling was determined by counting colored marks every three feet on the nylon line. To compensate for

Fig. 2a. The east coast of Virginia and southern portion of the Chesapeake Bay. The sampling area (insert, Fig. 2b) was located at the mouth of the James River.


Rappahannock River
York River
James River
Chesapeake Bay
76°00' W.
37°00' N.
Atlantic Ocean


Hampton, Va.
Old Point
Comfort
37°00' N.
76°20' W.
A
B
C
D
E
F
Hampton Roads
(James River)
Chesapeake
Bay
Fort
Wool
Island
Willoughby Spit
Willoughby Bay
Norfolk, Va.

bottle drift due to currents, the boat was moved to keep the hydrographic line vertical. Station location was accomplished by visual sightings of landmarks and navigation buoys.

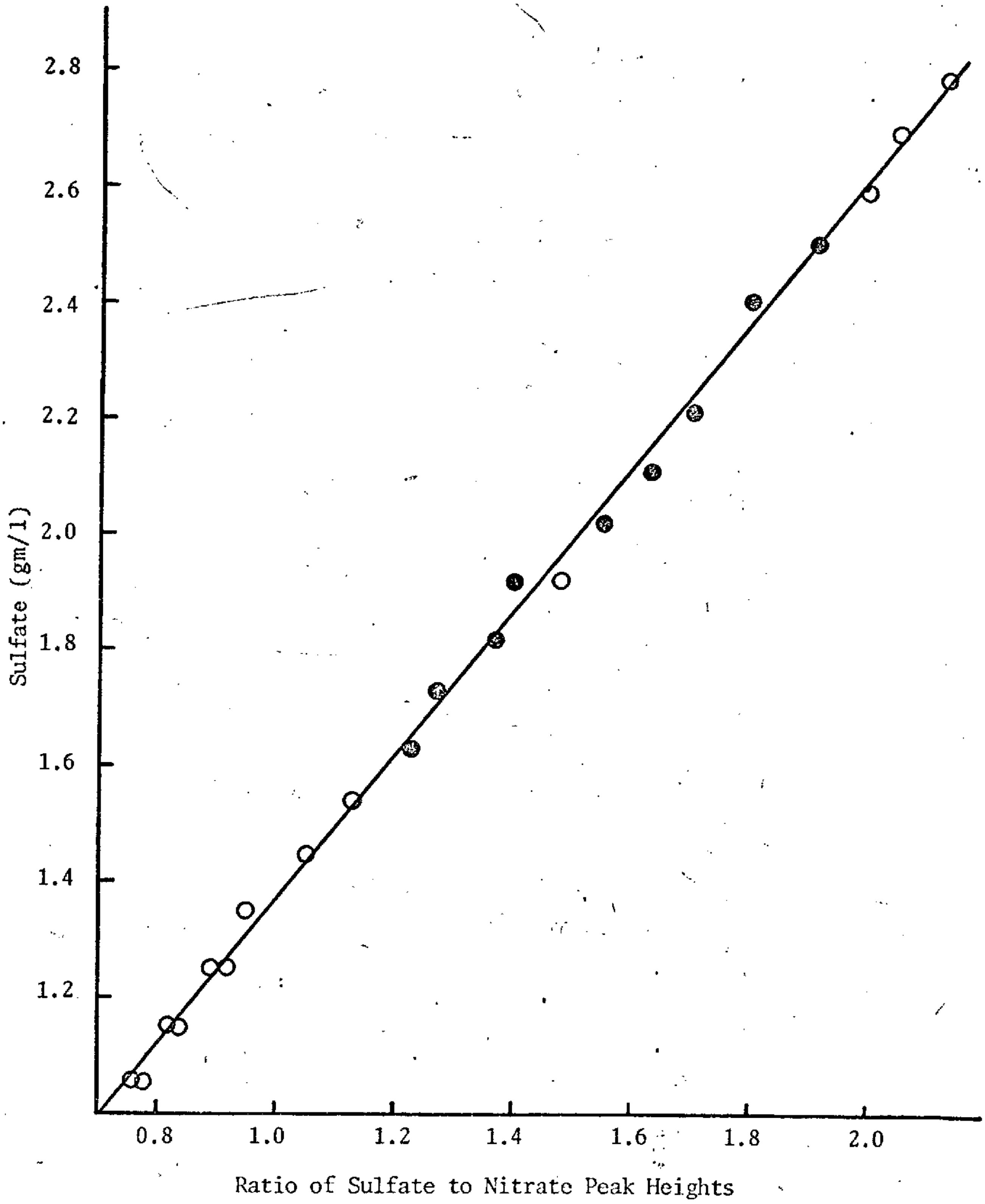
Samples were collected on August 3, August 17, September 15, and October 2, 1972. Within several days after collection, the sample salinities were determined on a Bisset Berman Corporation (San Diego, California) Model 6220 salinometer.

Preparation of Standard Curve

The molar concentration of polyatomic ions or molecules are proportional to the integrated intensities of their vibrational Raman transitions (Szymanski, 1967). The intensities of these vibrational Raman transitions are, however, dependent upon many other experimental variables such as laser power, optics alignment, optics efficiency and sample cell alignment. A convenient way of minimizing the effects of many of these variables was to measure the Raman intensities of the species of unknown concentration relative to an internal standard. Nitrate was the internal standard for sulfate determinations in this study because its Raman band was near that of sulfate. Peak heights were used as a measure of Raman intensity for sulfate and nitrate.

A standard curve (Fig. 3) obtained from Raman data on prepared nitrate-sulfate solutions, was employed to determine unknown sea water sulfate concentrations. These solutions were prepared by adding 1 ml of acidified 1.5 M

Fig. 3. The relationship between sulfate to nitrate peak height ratios and sulfate concentrations. The circles represent the sulfate concentrations of prepared nitrate-sulfate solutions as a function of the average sulfate to nitrate peak height ratios. Nine of the prepared solutions had been treated with powdered activated charcoal (dark circles). The least squares line drawn through the circles was used to calculate the unknown sulfate concentrations of the natural water samples.


Sulfate (gm/1)
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Ratio of Sulfate to Nitrate Peak Heights

reagent grade potassium nitrate to known amounts of 0.4 M reagent grade potassium sulfate and then diluted to the mark (100 ml) with deionized water. The sulfate concentrations of the prepared samples covered the sulfate range one would expect to find in sea and estuarine waters between the salinities of 13 and 35 parts per thousand (ppt).

For each prepared solution, a minimum of four scans were taken to determine the average sulfate to nitrate peak height ratio. Therefore, errors in the peak height ratio, caused primarily by laser power drift, were averaged. To eliminate the necessity of knowing the exact concentration of nitrate internal standard, the standard nitrate solution was also used in spiking the natural water samples. The accuracy of the standard curve depended only on the accuracies of the standard sulfate concentrations and the average peak height ratios.

Nine of the points on the standard curve (see Fig. 3, solid circles) came from solutions that were treated with powdered activated charcoal (Darco® G-60*, Fisher Scientific Co., Fair Lawn, New Jersey). These points did not affect the slope or the intercept of the least squares line found from the remaining 13 points determined from untreated samples. Therefore, the treatment of samples with activated carbon did not affect sulfate concentrations or the nitrate internal

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* Trademark of Atlas Chemical Industries, Inc., Fairfax, Wilmington, Delaware.

standard concentrations within the sensitivity of the technique.

Sample Preparation

In the preparation of sea water for sulfate analysis by Raman scattering, 1.0 ml of 1.5 M reagent grade potassium nitrate was added to a 100 ml volumetric flask and then filled to the mark with sea water. The nitrate solution had been acidified (pH ∿ 1), to prevent algal and bacterial growth. After dilution by sea water, the nitrate concentration was in the same range as the sulfate concentration. Several grams of powdered activated charcoal (Darco G-60 activated carbon, Fisher Scientific Co., Fair Lawn, New Jersey) were added to the sea water-nitrate solution and then shaken vigorously to remove organics that interfere by giving a broad fluorescent background. After allowing the charcoal to settle out for a few minutes, a portion of the solution was filtered using a syringe equipped with a 45 μm Millipore filter. The sample was then introduced into the sample cell. Sample preparation required approximately ten minutes and could be done while the previous sample was analyzed.

CHAPTER III

EXPERIMENTAL RESULTS

A statistical analysis was performed on the data obtained from the prepared nitrate-sulfate solutions. The results of this analysis were used to determine the sulfate concentrations of the natural water samples and to evaluate the accuracy of the Raman scattering technique for sea water sulfate analysis.

Statistical Analysis of Data Obtained from the Prepared Solutions

The slope and intercept of the least squares line through the calibration points (Fig. 3) was used to calculate sample sulfate concentrations. The linear regression equations (Youden, 1951) for the points on Fig. 3 gave a slope of 1.2440gm$SO_4^=$/1 and an intercept of 0.1217gm$SO_4^=$/1. The standard deviations of the slope and intercept (Youden, op. cit.) were 0.0145gm$SO_4^=$/1 and 0.0205gm$SO_4^=$/1 respectively. The non-zero intercept and its large standard deviation were partially attributed to the use of a straight line regression for calculating the intercept of a function which is in general non-linear. However, the linear correlation coefficient (Miller and Freund, 1965) of 0.9986 which was calculated from the calibration data, and the small standard deviation of the slope obtained from peak heights, suggested that a straight line regression was valid for calculating sulfate concentrations, if the concentrations were within the range of the standard curve.

A propagation of errors technique was used to determine the standard deviation of an unknown sulfate concentration calculated from the standard curve. Assuming that the unknown sulfate concentration, y, slope, b, intercept, a, and peak height ratio, x, in the line equation

$$y = bx + a \tag{1}$$

had standard deviations that were governed by a gaussion distribution (i.e., negative and positive values for each were equally possible), then the variance in the unknown sulfate concentration, $\sigma_y{}^2$, is given by

$$\sigma_y{}^2 = \left(\frac{\partial y}{\partial a}\right)^2 \sigma_a{}^2 + \left(\frac{\partial y}{\partial b}\right)^2 \sigma_b{}^2 + \left(\frac{\partial y}{\partial x}\right)^2 \sigma_x{}^2 \tag{2}$$

where $\sigma_a{}^2$, $\sigma_b{}^2$ and $\sigma_x{}^2$were the variances of a, b and x respectively. The partial derivatives in eq. 2 can be obtained by differentiating eq. 1:

$$\left(\frac{\partial y}{\partial a}\right)^2 = 1 \tag{3}$$

$$\left(\frac{\partial y}{\partial b}\right)^2 = x^2 \tag{4}$$

$$\left(\frac{\partial y}{\partial x}\right)^2 = b^2 \tag{5}$$

Substitution of eqs. 3, 4, and 5 into eq. 2 yields

$$\sigma_y{}^2 = \sigma_a{}^2 + x^2\sigma_b{}^2 + b^2\sigma_x{}^2 \tag{6}$$

Substituting the standard deviations of a, b and x (estimated to be two percent of x), and the appropriate values for b and x into eq. 6 gave a σ_y of .0284gm$SO_4^=$/1, for y = 1.00gm$SO_4^=$/1, and a σ_y of .0581gm$SO_4^=$/1 for y = 2.500 gm$SO_4^=$/1. At three standard deviations (the 99.7 percent confidence level) the estimated error in y was 8.6 percent at y = 1.00gm$SO_4^=$/1 and 6.8 percent at y = 2.50gm$SO_4^=$/1 (see Fig. 4 for the estimate of the error as a function of sulfate concentration). The experimental error in y decreased as y increased because the errors associated with the intercept became less significant as the sulfate concentration increased. An error in the sulfate concentration of 6.8 percent to 8.6 percent at the 99.7 percent confidence level was small when one considered the number of factors contributing to that error.

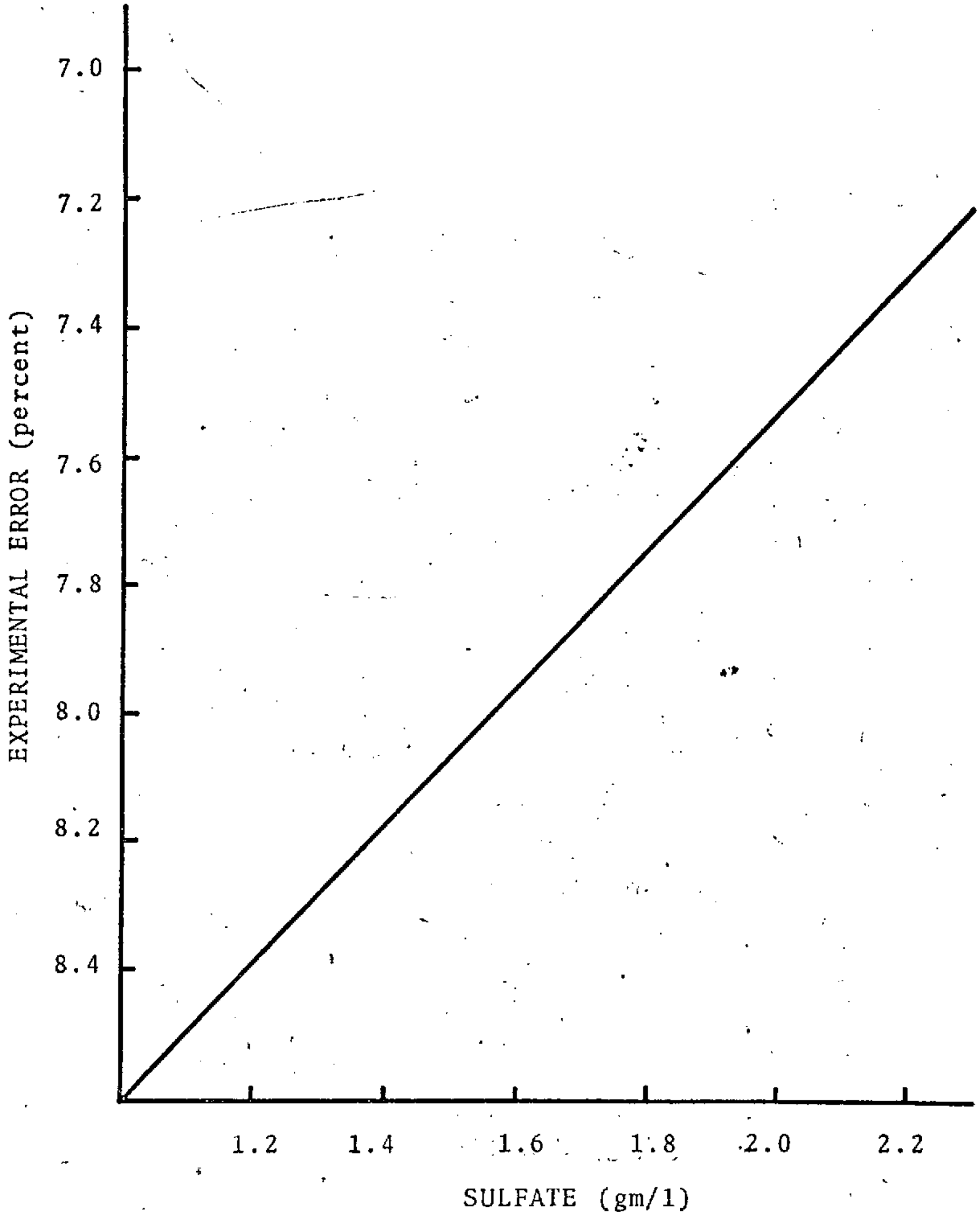
Results from Natural Water Samples

The experimentally determined sulfate concentrations and the concentrations predicted from the salinities are listed in Tables AI-1, AI-2, AI-3, and AI-4 for the samples collected on August 3, August 17, September 15, and October 2, 1972. Also listed are the salinities of the samples, the weather and tidal conditions during sample collection, the station and depth from which each sample was obtained and the percent differences between the experimentally determined and the predicted sulfate concentrations.

The depth of the bottom and middle samples varied because of the uneven bottom topography in the area and the difficulty in determining the exact station locations. Large

Fig. 2b. Sampling area. Six stations were located between Old Point Comfort, Hampton, Virginia and Willoughby Spit, Norfolk, Virginia. Three of these stations were perpendicular to the ship channel (A, B, and C) and three were near the Hampton Roads Bridge (D, E, and F).

Fig. 4. Accepted experimental error as a function of sulfate concentration. The percent error represented the uncertainty in the experimentally found sulfate concentration at the 99.7 percent confidence level. If the percent difference between the sulfate value predicted from salinity and the sulfate value found experimentally was larger than the accepted error, the two values were considered different.


EXPERIMENTAL ERROR (percent)
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
1.2
1.4
1.6
1.8
2.0
2.2
SULFATE (gm/1)

salinity gradients existed on August 3, August 17, and September 15, 1972, and the salinity distribution (Tables AI-1, AI-2, and AI-3) suggested that haloclines occurred at approximately 30 feet. Salinities at the bottom and middle depth on these days were higher at minimum low water than at maximum high water. This result is reportedly not unusual for the James River (Pritchard, 1952), and may be associated with early flooding at the bottom of the channel.

Sea surface conditions were calm on August 3 and August 17, but September 15 was choppy and October 2 was rough with approximately six to eight foot swells in the sampling area. Winds were gentle with a 7 mph average over one week before sampling on August 3. For two days before sampling on August 17, wind speeds average 13.75 mph. Winds averaged 12 mph for three days before September 15, and the highest average for one day was 13.4 mph. The rough conditions encountered on October 2 were due to a 16.2 mph average wind speed for two days before sampling. Total rainfall was less than one inch for a week before each sampling day (see Local Climatological Data, 1972, for source of wind speeds and rainfall discussed above.)

If a sea water sample were diluted with distilled water there would be a linear relationship between sulfate concentration and salinity (i.e., sulfate would be a function of salinity, and the linear correlation between the two would unity). The distribution of sulfate, as a function of salinity, for each day during the sampling period is illustrated by the points in Figs. 5, 6, 7, and 8. The points in each figure had linear correlation coefficients (Table 2) greater than 0.95, which demonstrated the close linear relationship that esixted between sulfate and salinity. Only one data group, which was from the samples taken on October 2, had a correlation coefficient less than 0.98. This result was probably due to the narrow range for the salinity and sulfate data for this group which was caused by wind and wave induced mixing of the water column (see Table AI-4).

The slope and intercept of sea water dilution curve would be 0.078gm/l and zero gm/l respectively, assuming that the salt content of sea water can be represented by the artificial sea water formula of Lyman and Fleming (1940). The slopes and intercepts for the samples gathered on August 17 and October 2 were within two standard deviations of the slope and intercept of the sea water dilution curve (Table 2). This result implies that the linear least squares regressions, for these two sample groups, were not different from a sea water dilution curve, therefore, the sulfate concentrations of these samples represented sulfate values one would predict using salinity and the concept of constant composition (Riley and Skirrow, 1965). However, a perfect correlation of unity, was not found between sulfate and salinity for these two groups. This result was attributed to the experimental error in determining sulfate. For the samples collected on August 3 and September 15, the slopes and one of the intercepts were not within three standard deviations

Fig. 5. Sulfate concentration as a function of salinity, August 3, 1972. Note that sulfate and salinity appear to have a linear relationship.

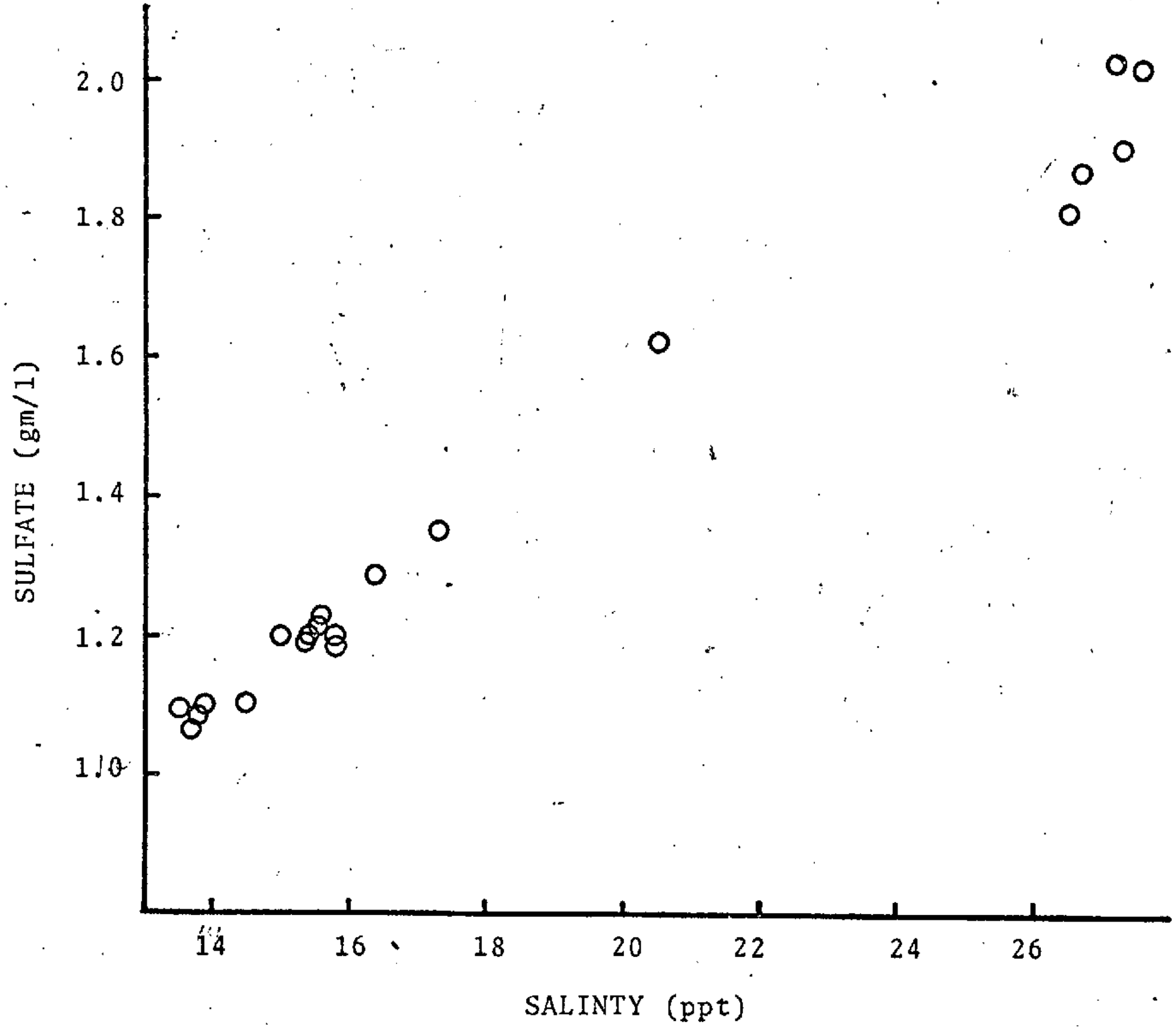

SULFATE (gm/l)
2.0
1.8
1.6
1.4
1.2
1.0
14
16
18
20
22
24
26
SALINTY (ppt)

Fig. 6. Sulfate concentration as a function of salinity, August 17, 1972. Salinity and sulfate appear to have a linear relationship.

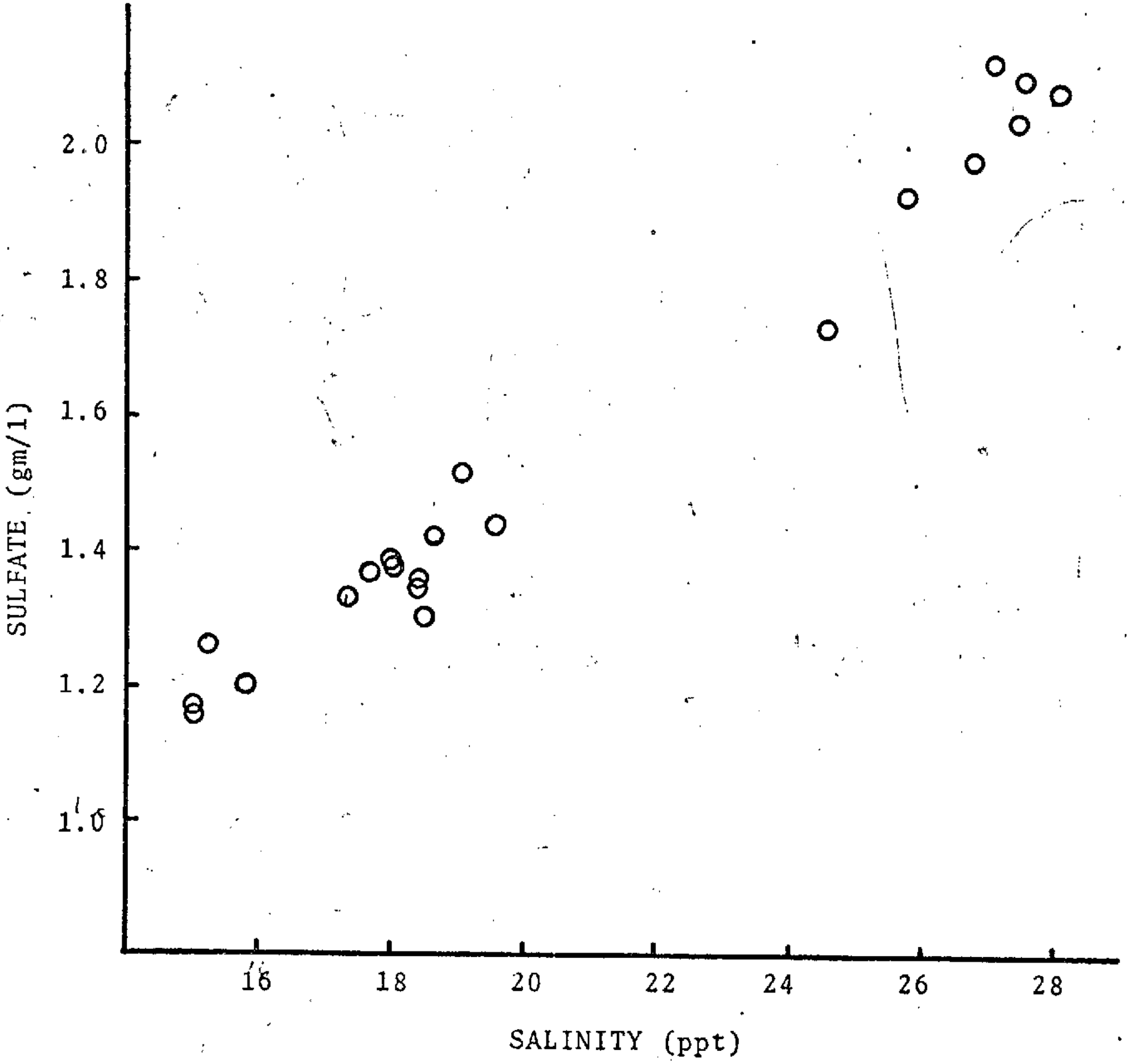

SULFATE (gm/1)
2.0
1.8
1.6
1.4
1.2
1.0
16
18
20
22
24
26
28
SALINITY (ppt)

Fig. 7. Sulfate concentration as a function of salinity, September 15, 1972. Sulfate and salinity appear to have a linear relationship.

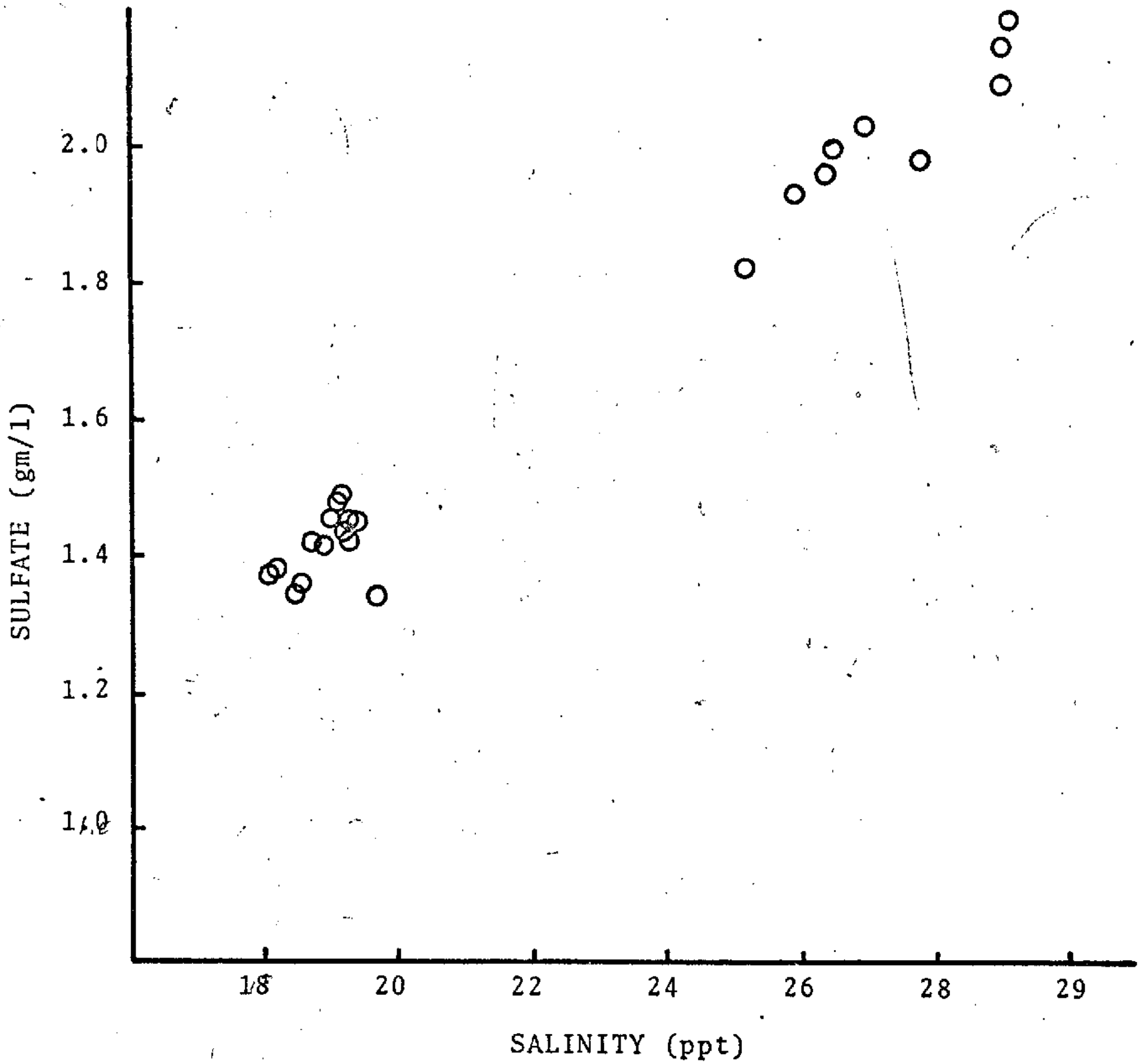

SULFATE (gm/l)
2.0
1.8
1.6
1.4
1.2
1.0
18
20
22
24
26
28
29
SALINITY (ppt)

Fig. 8. Sulfate concentration as a function of salinity, October 2, 1972. Note the narrow range of salinities in this sample group and that a linear relationship appears to exist between sulfate and salinity.

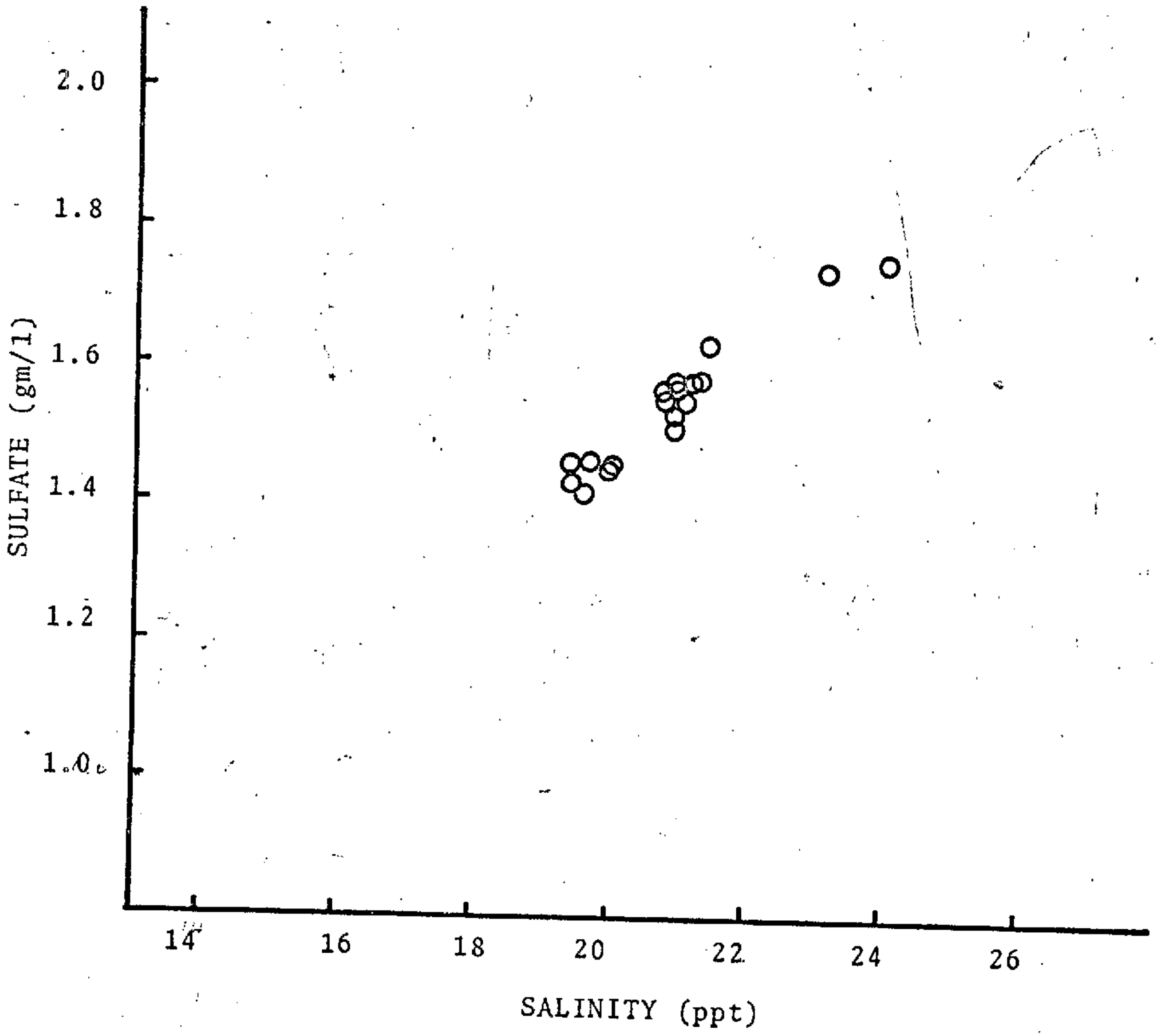
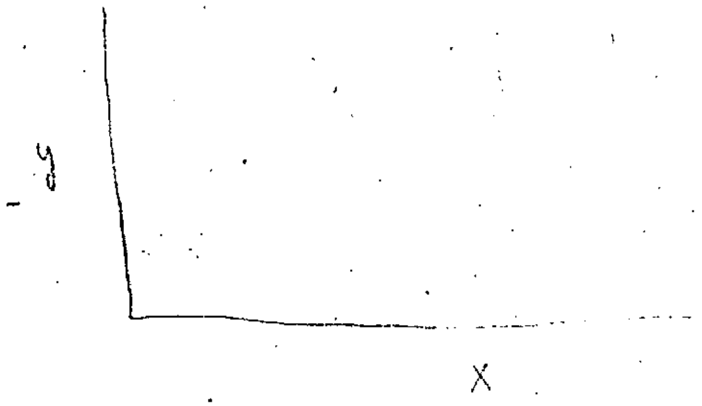

2.0
1.8
1.6
1.4
1.2
1.0
SULFATE (gm/1)
14
16
18
20
22
24
26
SALINITY (ppt)

TABLE 2. Statistical data for sulfate-salinity relationship

Date Samples Collected	Slope (gm$SO_4^{=}$/1)	Intercept (gm$SO_4^{=}$/1)	S.D. of Slope* (gm$SO_4^{=}$/1)	S.D. of Intercept* (gm$SO_4^{=}$/1)	Linear Correlation Coefficient
August 3, 1972	0.06345	0.22044	0.00191	0.03576	0.9911
August 17, 1972	0.07383	0.06607	0.00248	0.05154	0.9880
September 15, 1972	0.07017	0.08537	0.00213	0.04821	0.9904
October 2, 1972	0.07737	-0.07231	0.00517	0.10803	0.9542

Windy

well mixed



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* One standard deviation (S.D.).

of the slope and intercept of the dilution curve. This result implied that a portion of the samples in these two groups did not have sulfate concentrations that would be expected if sea water were diluted according to the concept of constant composition. Some factor other than dilution by low sulfate fresh water may have affected sulfate concentrations.

Horizontal and vertical sulfate distribution plots (see Figs. 9-20) were examined to determine which samples had sulfate concentrations not predicted by the artificial sea water dilution curve. Triangles were used to represent the sulfate concentrations one would expect if artificial sea water were diluted to the salinity of the sample and circles were used to represent the experimentally determined sulfate concentrations.

The surface distribution of sulfate (Figs. 9 and 10), with respect to station position, illustrated that all of the predicted sulfate concentrations were within the error of the experimentally determined sulfate concentrations (the curve in Fig. 4 was used to determine the error in the experimentally found sulfate concentrations). For these 44 samples, with salinities between 12ppt and 20ppt, the concept of constancy of composition was valid. The points in Figs. 11 and 12 were used to illustrate the middle depth sulfate concentrations for stations A, B, and C with respect to station position. Most of these points did not differ from the predicted values. However, one sample collected on August 3 and one collected on September 15 had markedly low

Fig. 9. Surface sulfate distribution, August 3 and August 17, 1972. The letters (A, B, C, D, E and F) were used to identify the station location (see Fig. 2b). All of the sulfate concentrations predicted from sample salinities (triangles) were within the uncertainty of the experimentally determined sulfate concentrations (circles).

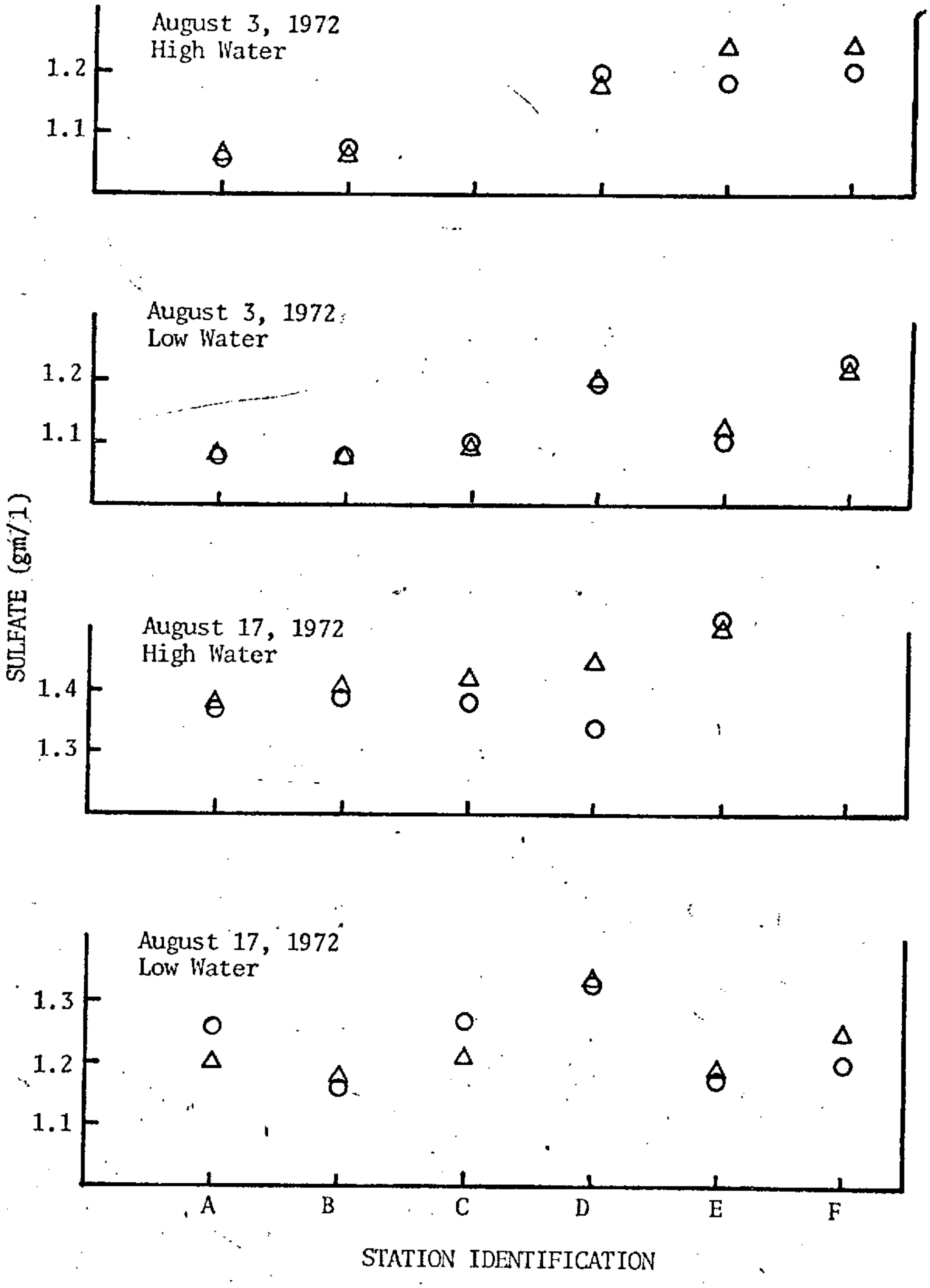

August 3, 1972
High Water
1.2
1.1
August 3, 1972
Low Water
1.2
1.1
SULFATE (gm/1)
August 17, 1972
High Water
1.4
1.3
August 17, 1972
Low Water
1.3
1.2
1.1
A
B
C
D
E
F
STATION IDENTIFICATION

Fig. 10. Surface sulfate distribution, September 15 and October 2, 1972. The letters (A,B,C,D,E and F) were used to identify the station location (see Fig. 2b). All of the surface concentrations predicted from sample salinities (triangles) were within the uncertainty of the experimentally determined sulfate concentrations (circles).

FIGURE 10

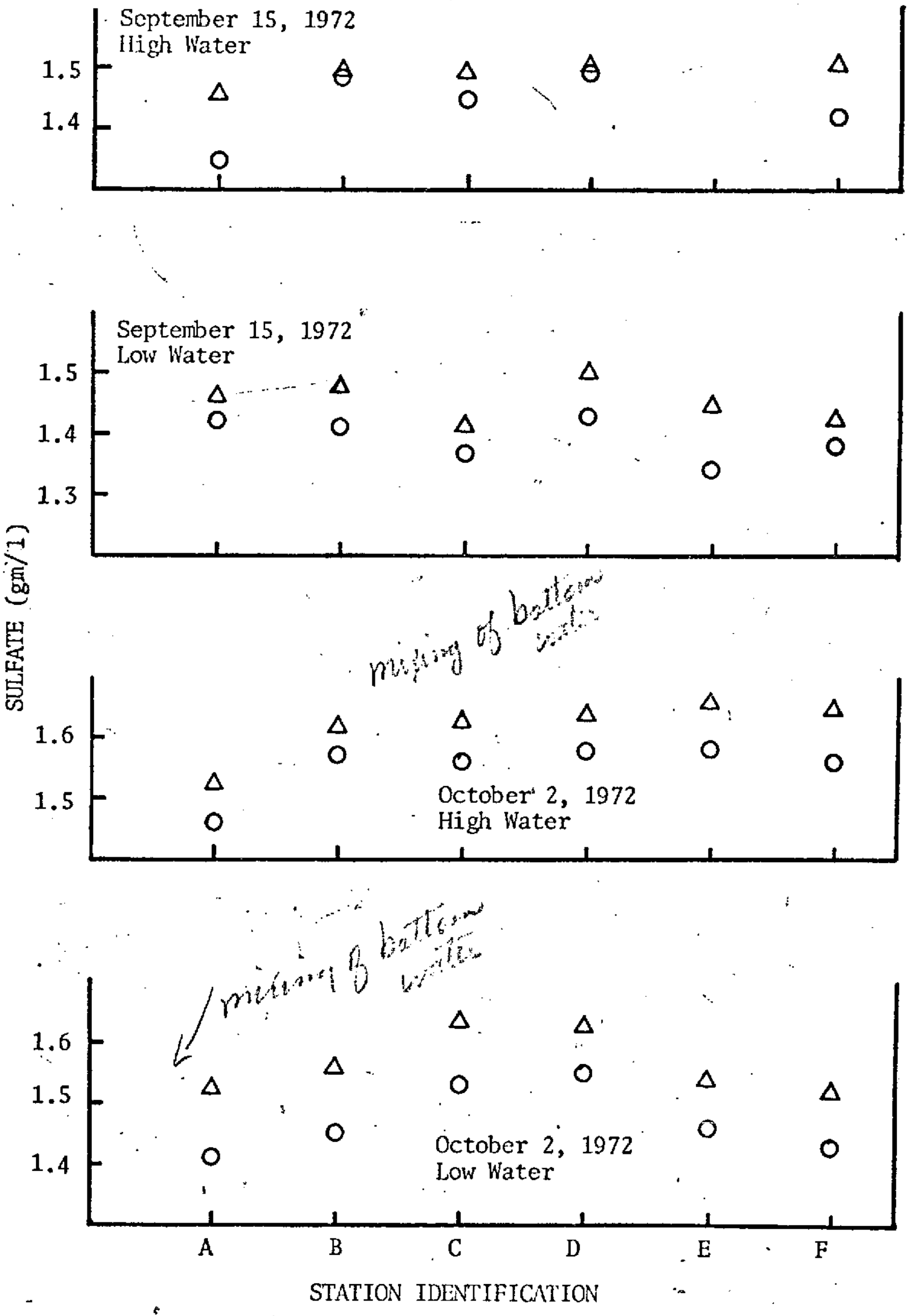

September 15, 1972
High Water
1.5
1.4
September 15, 1972
Low Water
1.5
1.4
1.3
SULFATE (gm/1)
mixing of bottom water
1.6
1.5
October 2, 1972
High Water
mixing of bottom water
1.6
1.5
1.4
October 2, 1972
Low Water
A
B
C
D
E
F
STATION IDENTIFICATION

Fig. 11. Middle depth sulfate distribution, August 3 and August 17, 1972. The letters (A, B and C) were used to identify the station location (see Fig. 2b). Note that the experimentally found sulfate concentration (circle) of the sample collected at station A at low water on August 3 was markedly lower than the sulfate concentration predicted from the sample salinity (triangle).

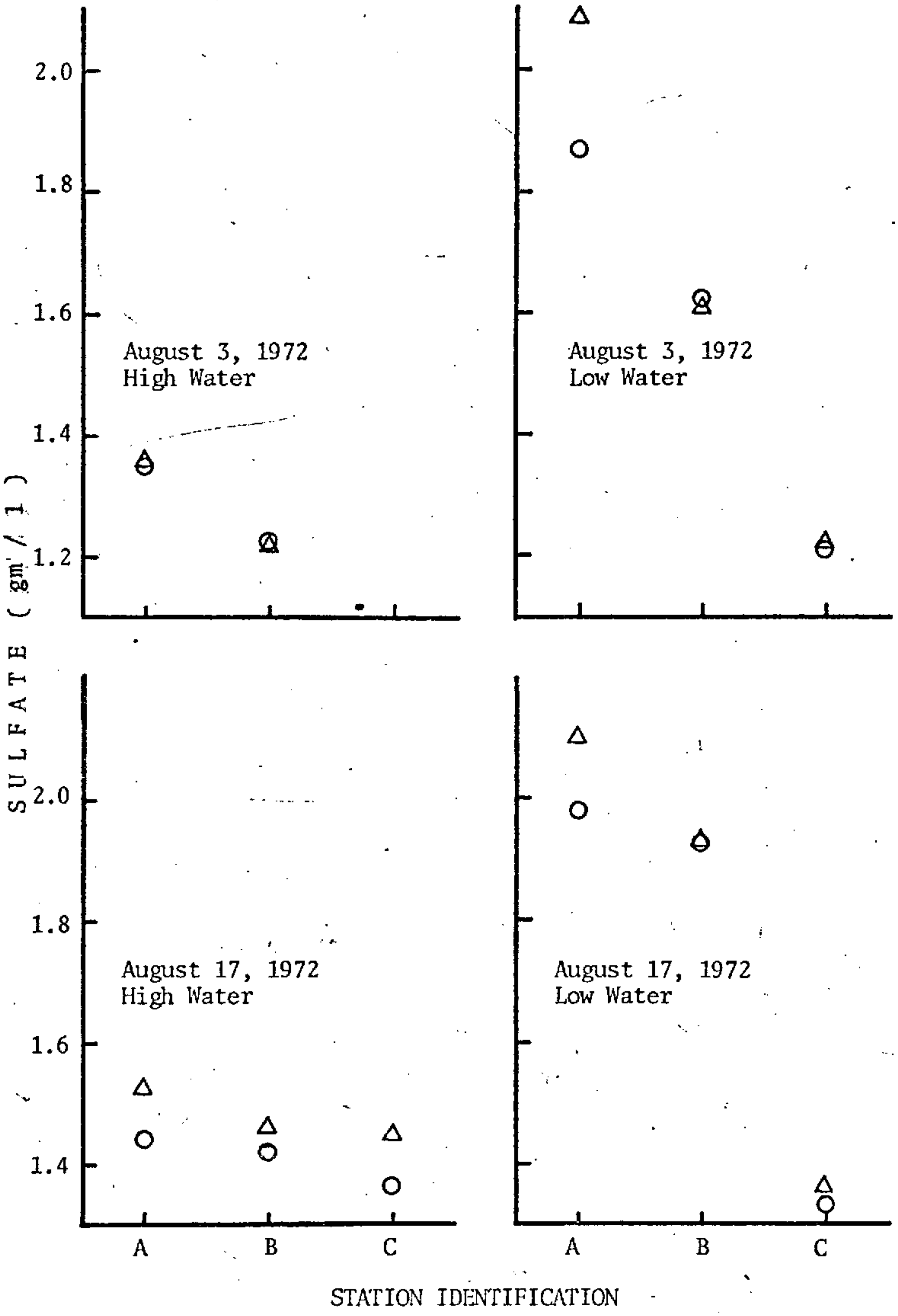
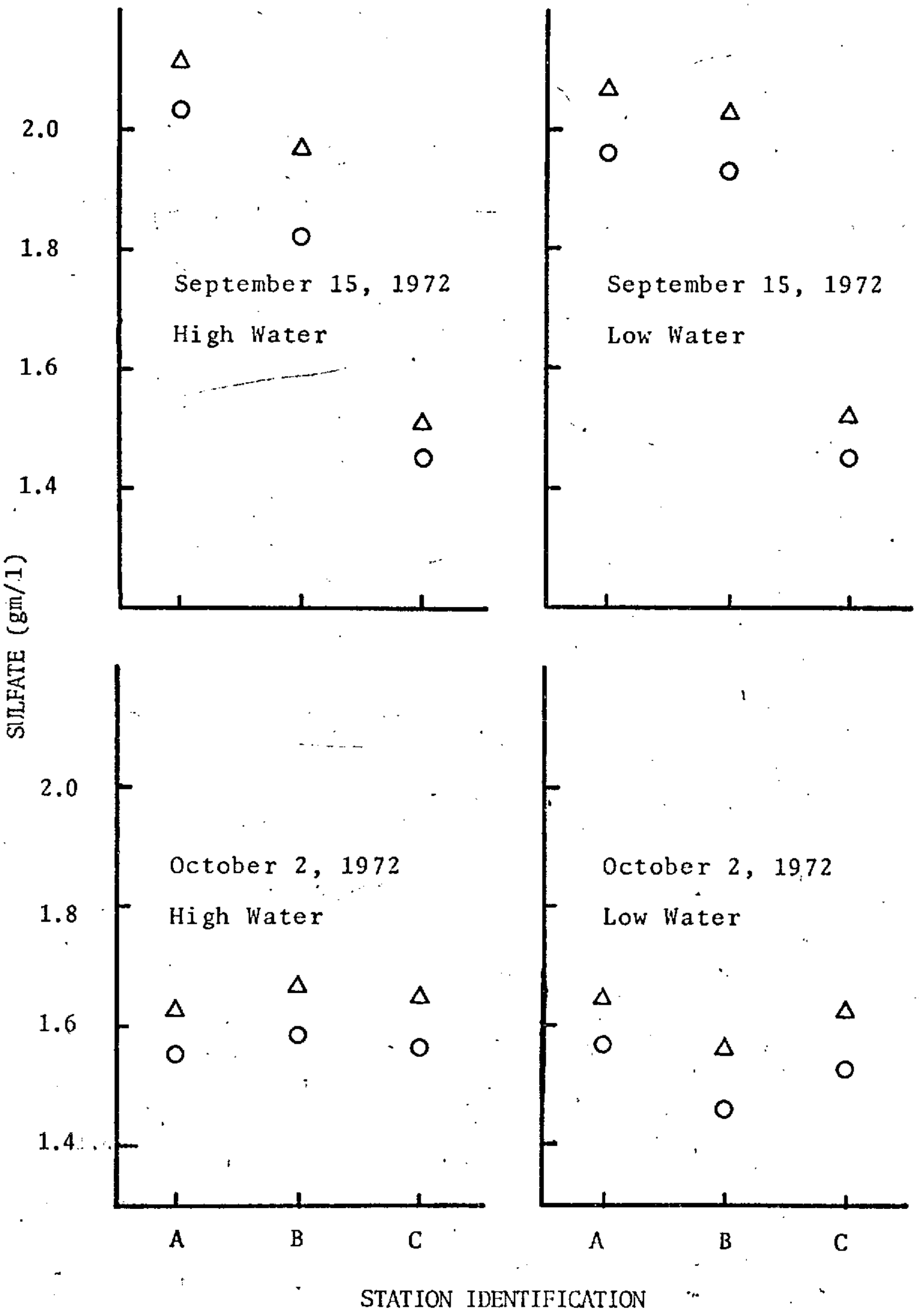

2.0
1.8
1.6
1.4
1.2
August 3, 1972
High Water
August 3, 1972
Low Water
SULFATE (gm / 1)
2.0
1.8
1.6
1.4
August 17, 1972
High Water
August 17, 1972
Low Water
A
B
C
A
B
C
STATION IDENTIFICATION

Fig. 12. Middle depth sulfate distribution, September 15 and October 2, 1972. The letters (A, B and C) were used to identify the station location (see Fig. 2b). One sample collected on September 15 at station B at high water had an experimentally found sulfate concentration (circle) lower than the predicted value (triangle), and the difference between these two values was larger than the experimental uncertainty.


2.0
1.8
1.6
1.4
September 15, 1972
High Water
September 15, 1972
Low Water
SULFATE (gm/l)
2.0
1.8
1.6
1.4
October 2, 1972
High Water
October 2, 1972
Low Water
A
B
C
A
B
C
STATION IDENTIFICATION

experimentally determined sulfate concentrations. Also, note that the least squares regressions for sulfate as a function of salinity for the groups collected on August 3 and September 15 were different from the sea water dilution curve (see Table 2).

Bottom distribution plots of sulfate concentrations were made for stations A, B, and C with respect to station position (Figs. 13 and 14). The samples gathered on October 2 agreed with values expected for diluted sea water, however, one sample collected on August 17 had a low sulfate concentration. The sulfate data for samples collected on August 3 and September 15 clearly demonstrated that several samples had sulfate concentrations lower than predicted by the dilution of sea water. These deviations appeared to be larger for samples collected at maximum high water than at minimum low water, and in fact, were so much greater than the experimental error that they must be considered real deviations. The sulfate concentrations of the bottom samples collected on August 3 and September 15, and the low sulfate concentrations at middle depth found on the same days, were far enough below normal to effect the slopes and intercepts for their sample groups.

Vertical sulfate profiles were constructed for station A for the four data groups (Figs. 15 and 16). The profiles for August 17 and October 2 indicated normal sulfate concentrations from the surface to bottom. No unexpected sulfate concentrations occurred at the surface on August 3

Fig. 13. Bottom depth sulfate distribution, August 3 and August 17, 1972. The letters (A, B and C) were used to identify the station location (see Fig. 2b). Three samples gathered on August 3 had experimental sulfate concentrations (circles) much lower than the concentrations predicted from the salinities of the samples (triangles). Note that the largest deviation was at high water.

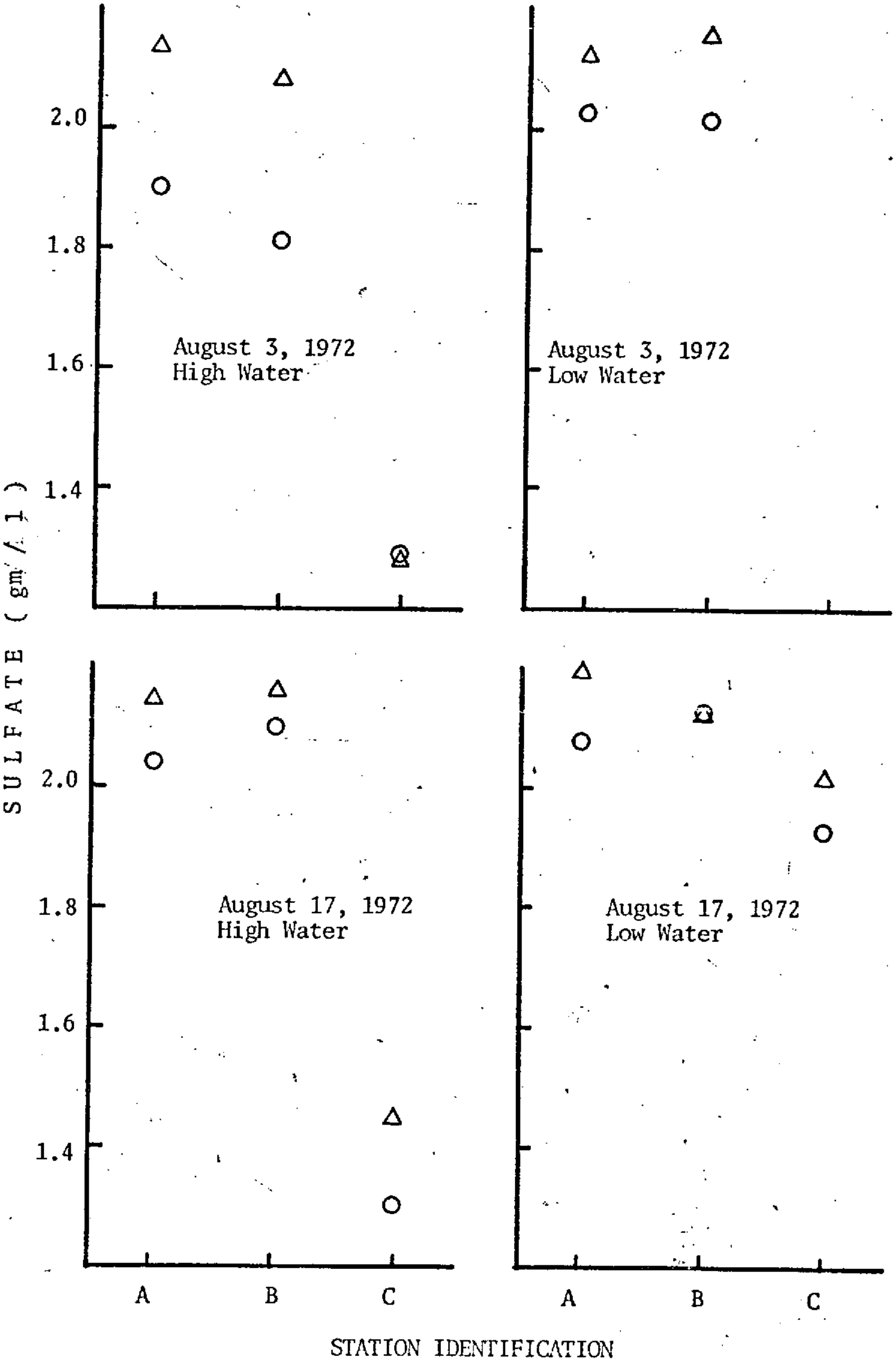

2.0
1.8
1.6
1.4
August 3, 1972
High Water
August 3, 1972
Low Water
August 17, 1972
High Water
August 17, 1972
Low Water
SULFATE (gm / l)
A
B
C
A
B
C
STATION IDENTIFICATION

Fig. 14. Bottom depth sulfate distribution, September 15 and October 2, 1972. The letters (A, B and C) were used to identify the station location (see Fig. 2b). Clearly four samples collected on September 15 had experimental sulfate concentrations (circles) much lower than the predicted values (triangles). Note that the largest deviations were found at high water.

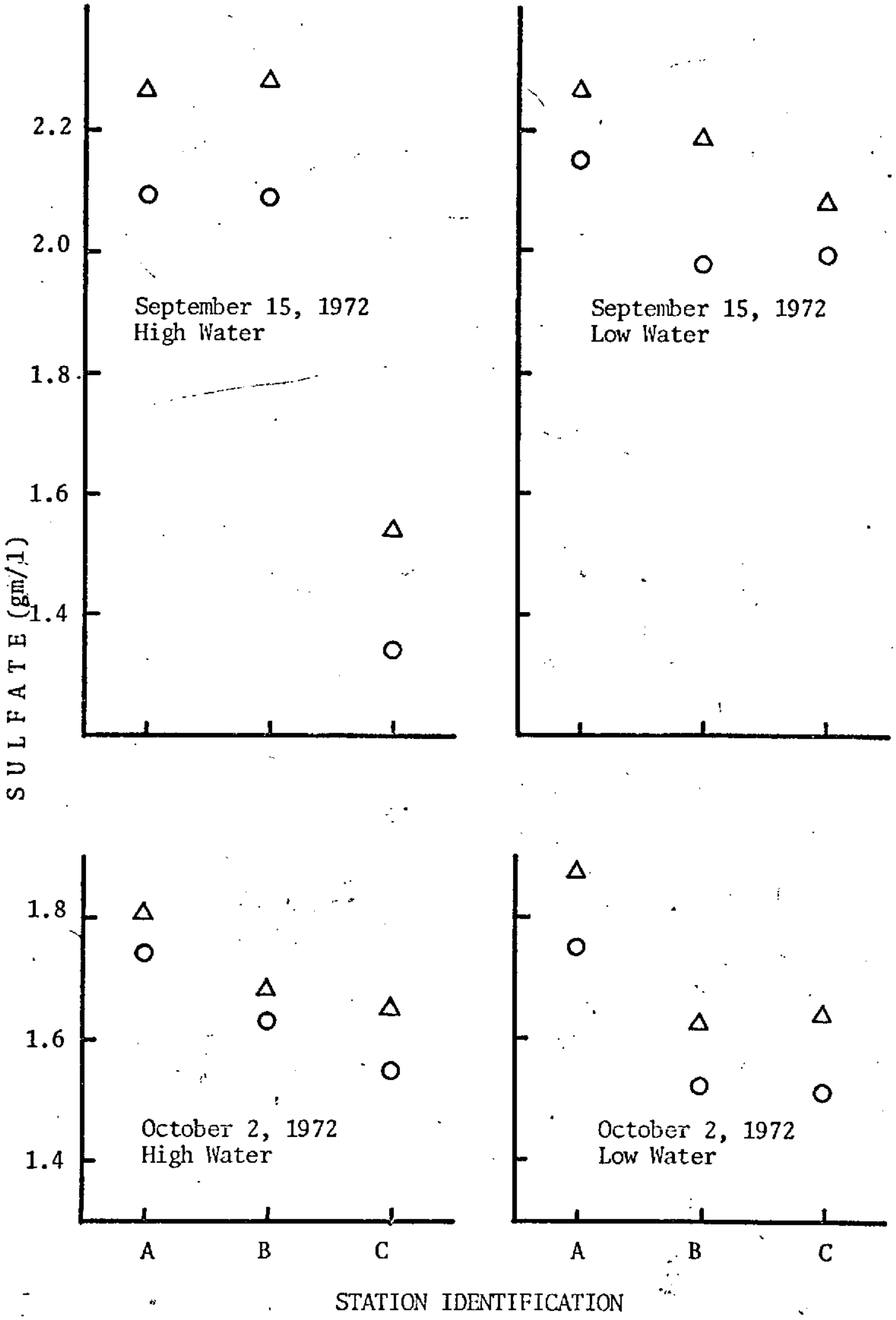
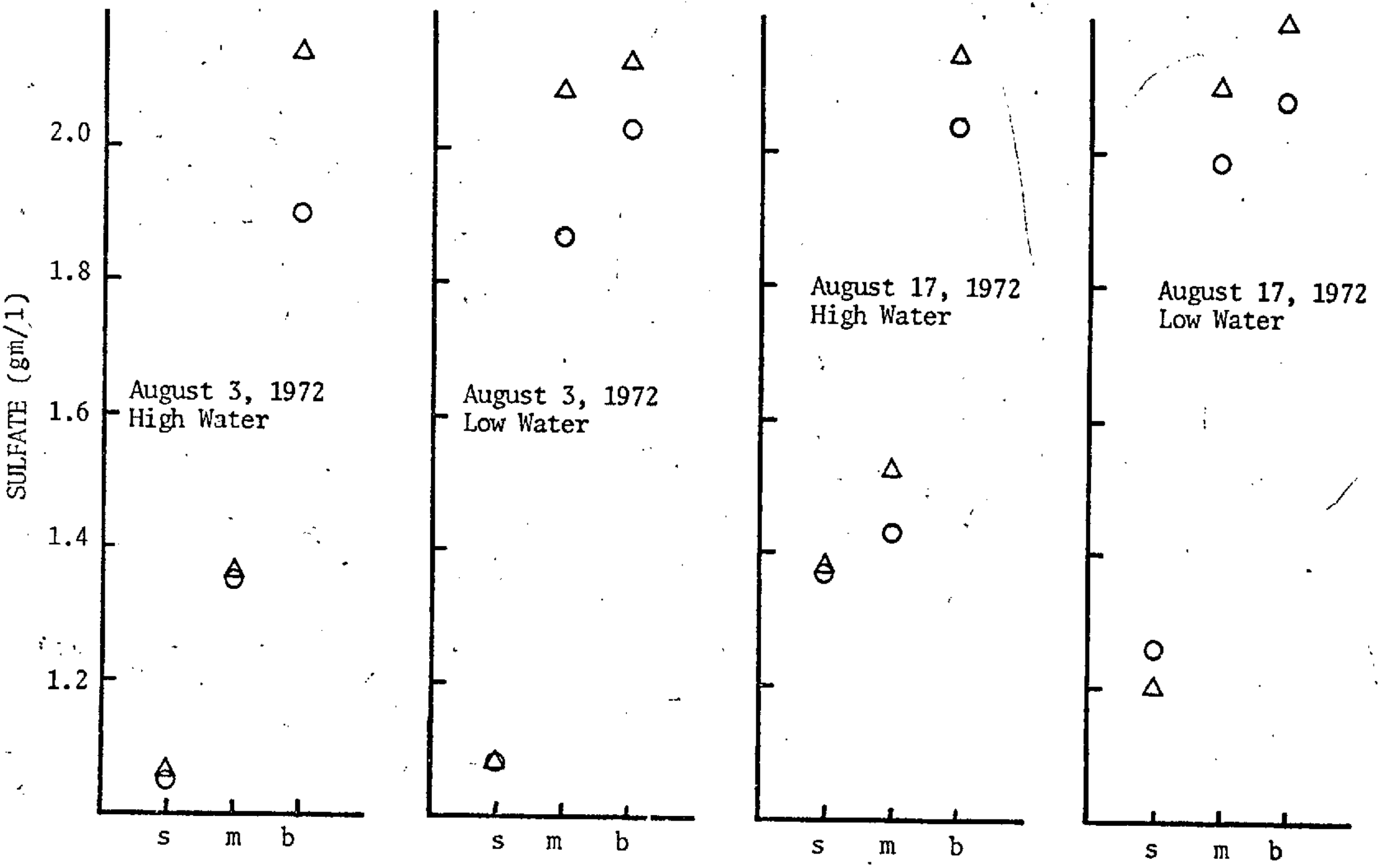

SULFATE (gm/l)
2.2
2.0
1.8
1.6
1.4
September 15, 1972
High Water
September 15, 1972
Low Water
1.8
1.6
1.4
October 2, 1972
High Water
October 2, 1972
Low Water
A
B
C
A
B
C
STATION IDENTIFICATION

Fig. 15. Vertical sulfate distribution at station A, August 3 and August 17, 1972. Two samples collected on August 3 had experimental sulfate concentrations (circles) much lower than the predicted values (triangles).

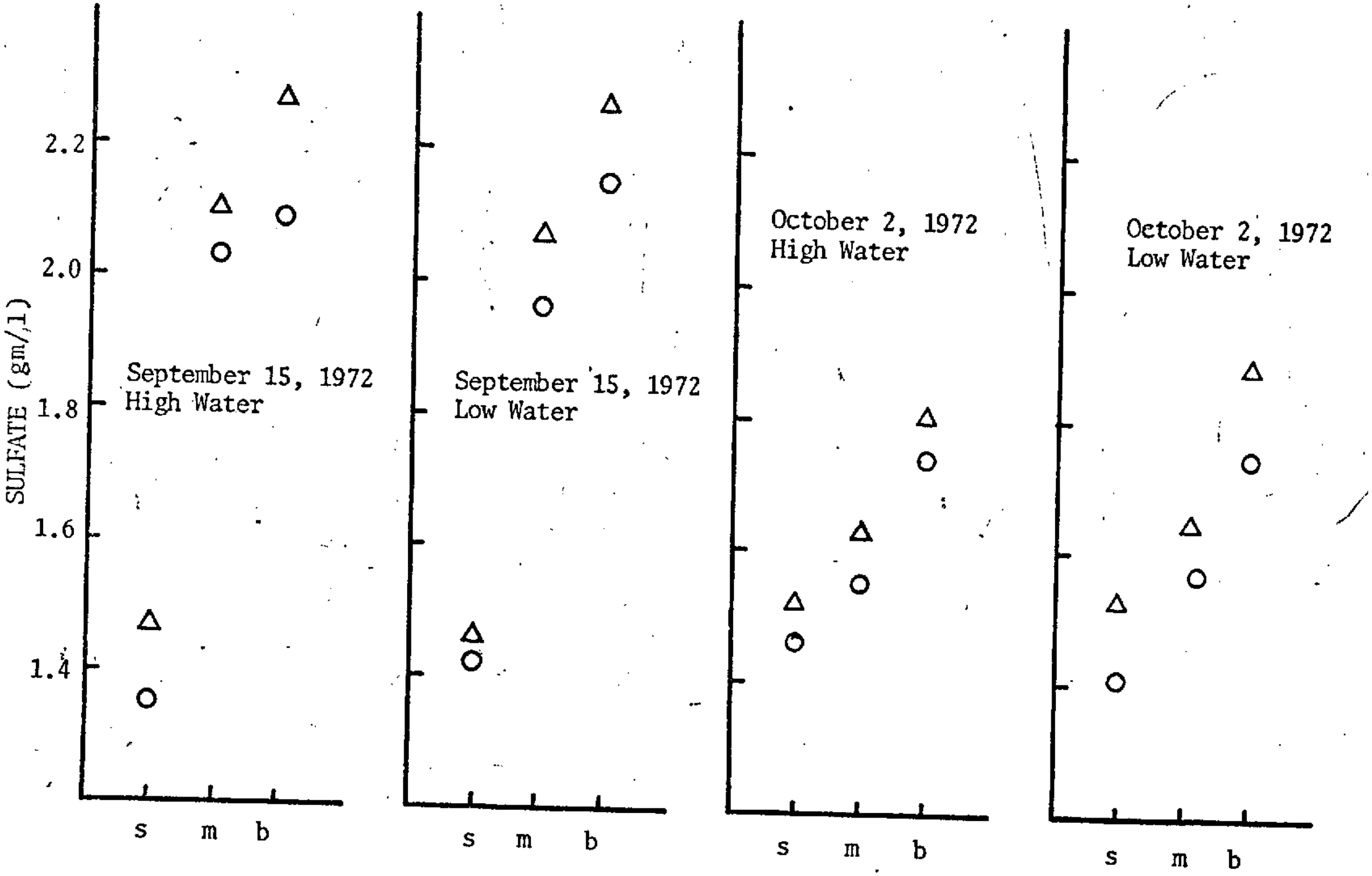
FIGURE 13



s = Surface Depth, m = Middle Depth, b = Bottom Depth

Fig. 16. Vertical sulfate distribution at station A, September 15 and October 2, 1972. One sample collected on September 15 at the bottom at high water had an experimental sulfate concentration (circle) significantly lower than the value predicted from the salinity (triangle).

FIGURE 16



s = Surface Depth, m = Middle Depth, b = Bottom Depth

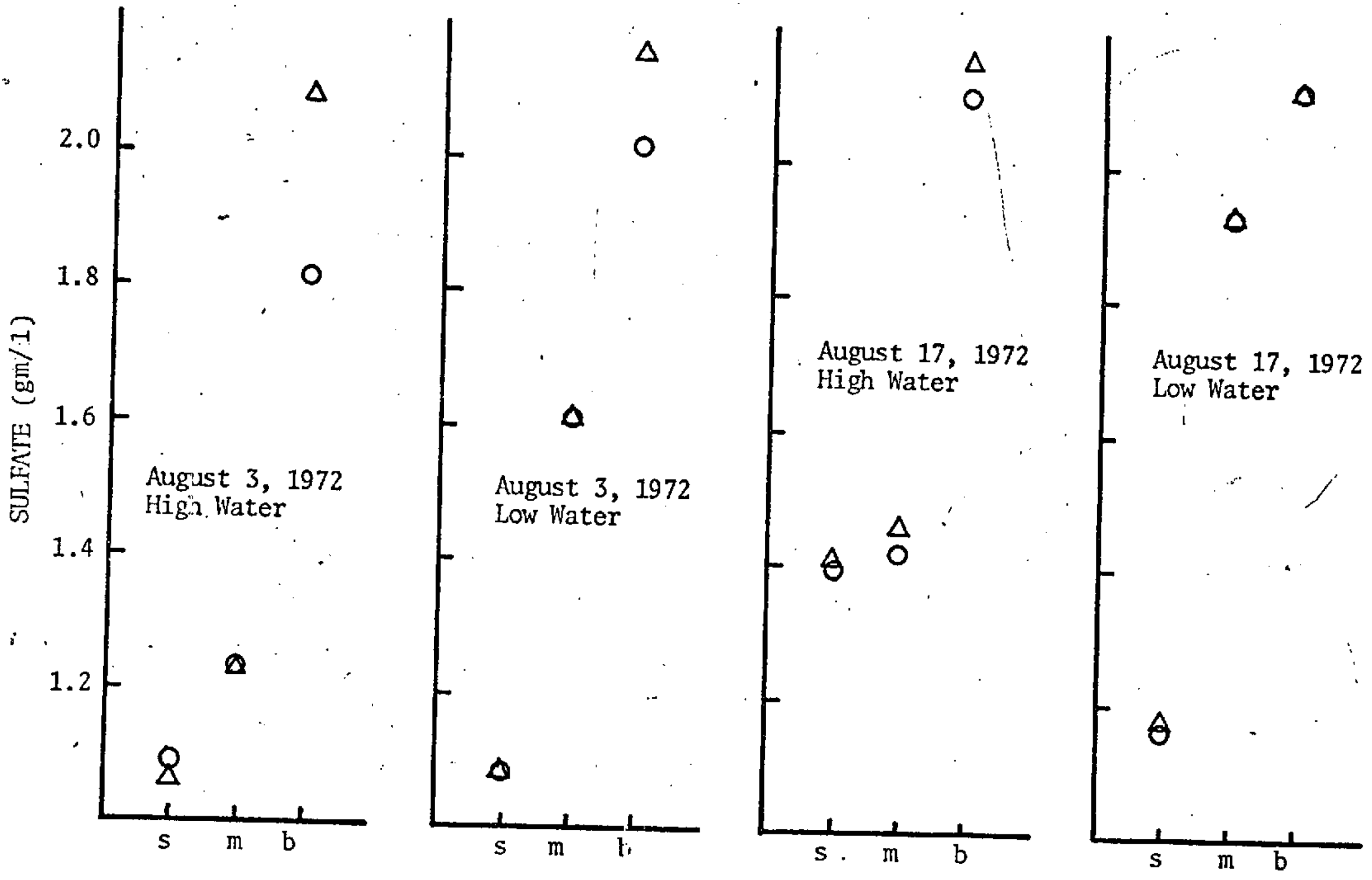
and September 15; however, one low sulfate concentration at middle depth and two low sulfate concentrations at bottom depth were detected.

The vertical sulfate distribution for station B for the four data groups are illustrated in Figs. 17 and 18. Again, no abnormal sulfate value was evident for August 17 and October 2. There were no sulfate deviations at the surface on August 3 and September 15, but there was one low sulfate concentration at middle depth and four low sulfate concentrations at bottom depth.

The points in Figs. 19 and 20 were used to represent the vertical sulfate distribution of three sample groups at station C. Station C was a shallow water station where two low sulfate values occurred. The low concentration found on September 15 was from a low salinity sample which suggested that the abnormally low sulfate concentrations found at stations A and B were not related to salinity. The low value found on August 17, the only low concentration found on that day, appeared to be insignificant when the trend in the rest of the sulfate data collected on August 17 was considered.

Fig. 17. Vertical sulfate distribution at station B, August 3 and August 17, 1972. Two experimental sulfate values (circles) were much lower than the predicted values (triangles) on August 3. Both of these low values were from bottom depth samples.

FIGURE 17



s = Surface Depth, m = Middle Depth, b = Bottom Depth

Fig. 18. Vertical sulfate distribution at station B, September 15 and October 2, 1972. On September 15 one middle depth and two bottom depth samples had experimental sulfate concentrations (circles) significantly lower than the concentrations predicted from salinities (triangles).

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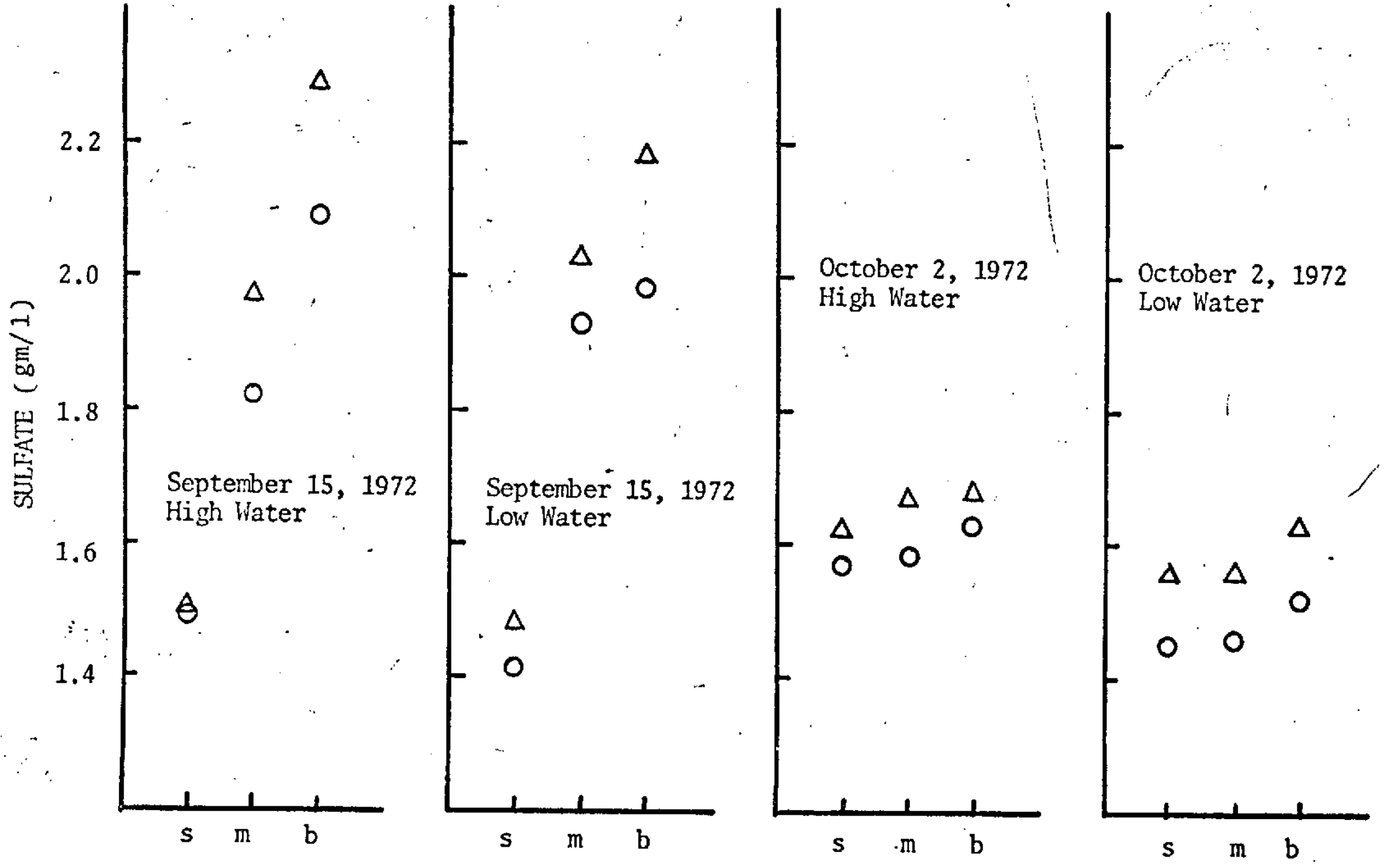
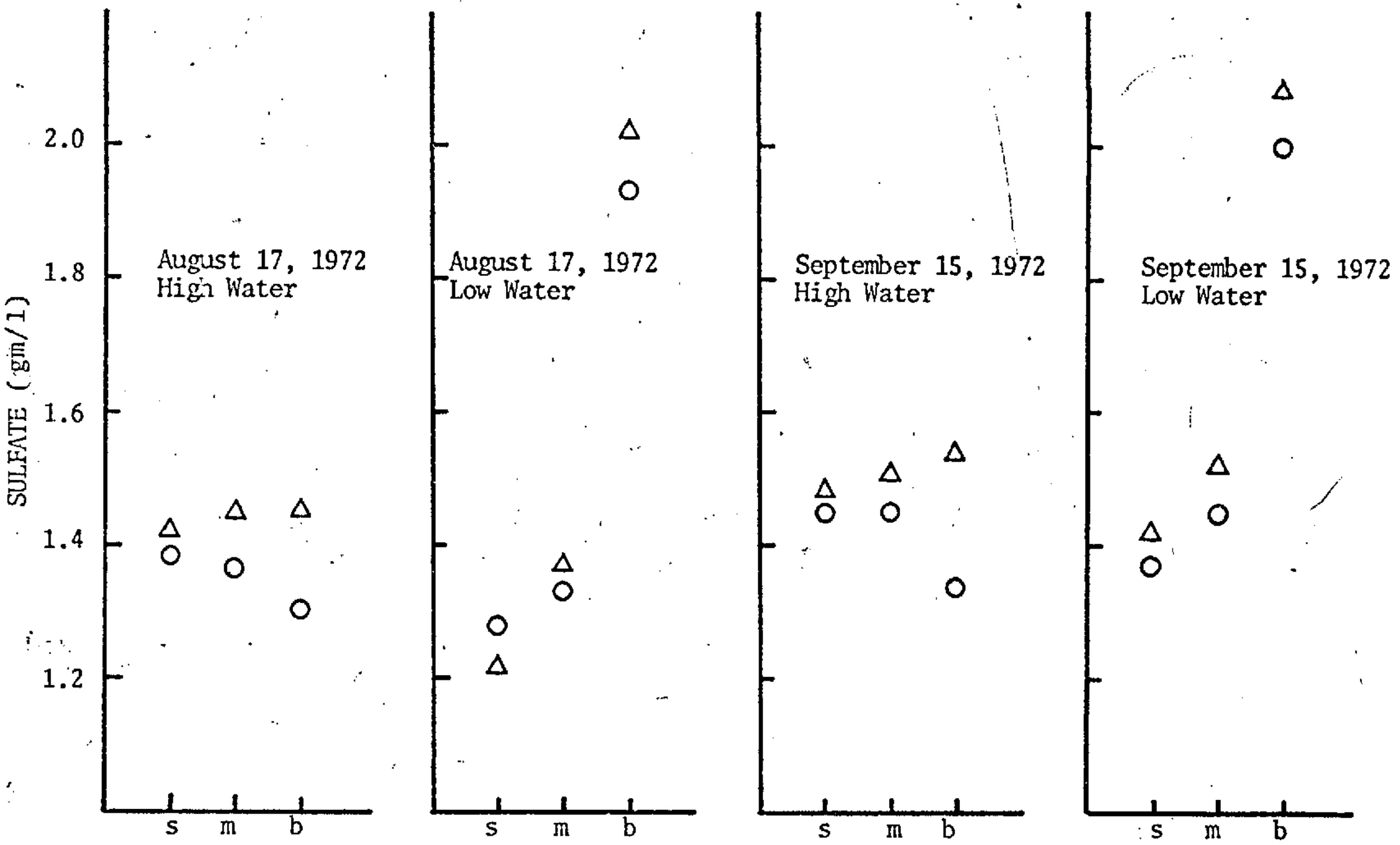


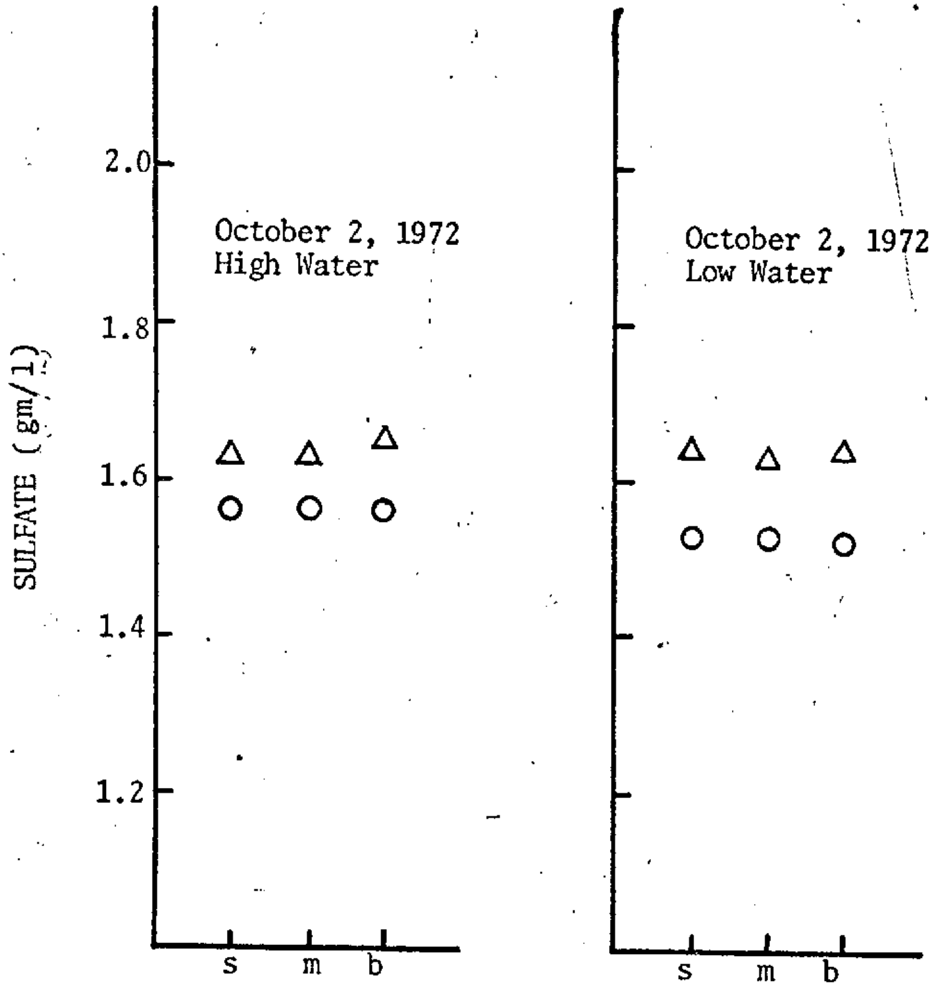
s = Surface Depth, m = Middle Depth, b = Bottom Depth

Fig. 19. Vertical sulfate distribution at station C, August 17 and September 15, 1972. Only one sample, collected on September 15, appeared to have an experimental sulfate value (circle) far below the predicted value (triangle).



s = Surface Depth, m = Middle Depth, b = Bottom Depth

Fig. 20. Vertical sulfate distribution at station C, October 2, 1972. No experimental sulfate values (circles) were significantly lower than the values predicted from salinities (triangles).



s = Surface Depth, m = Middle Depth, b = Bottom Depth

CHAPTER IV

DISCUSSION

The majority of samples analyzed had sulfate concentrations predicted by the concept of constant composition. However, low sulfate values were found below 30 feet and nine out of the eleven low values were found near the bottom (Tables AI-1, AI-2, and AI-3). This result suggested that either sulfate was removed from the water column by sediments below 30 feet, or that the other major ions increased relative to sulfate. Sulfate is a major constituent of sea water (Riley and Skirrow, 1965) and appears not to deviate from its constant composition to any significant extent in open ocean water, with the exception of the Baltic Sea (Bather and Riley, 1954; Kwiencinski, 1965; Morris and Riley, 1966; Thompson, Johnson, and Wirth, 1931; and Richards, 1965). Therefore, variations in the sulfate concentration in relationship to that of salinity were not expected to be caused by changes in the salt content of ocean water entering the Chesapeake Bay and Hampton Roads.

Factors, found to affect the sulfate to salinity relationship in coastal, estuarine, or partially landlocked marine environments, were river run off, industrial sulfate pollution (H_2SO_4), and bacterial sulfate reduction. Rivers usually produced low sulfate concentrations near their source, however, this depended upon the types of rocks which were weathered in the water shed area (Kwiencinski, 1965). In most cases, sulfate rather than chloride, is the dominant ion in river water (Riley and Skirrow, 1965), but the concentration of sulfate in river water is usually not great enough to affect the sulfate concentration in most estuaries in free exchange with the open ocean (Kimata, et al., 1958). Therefore, James River water was not expected to be the cause of the below normal sulfate concentrations found near the bottom.

Industrial pollution could increase sulfate concentrations relative to salinity in fresh river water (Bather and Riley, 1954; Kimata, et al., 1958). The effect of industrial sulfate pollution on this type of environment usually disappeared as mixing with ocean water became more significant near the river mouth (Bather and Riley, 1954; Kimata, et al., 1958). Therefore, industrial pollution was not expected to have any effect on the sulfate concentrations in the sampling area.

Sulfate reduction by bacteria was found to be responsible for the decrease in sulfate with depth in the Black Sea (Richards, 1965). Sulfate reducing bacteria could tolerate wide ranges in salinity, redox potential, acidity, temperature and oxygen, although sulfate reduction was negligible in water where the dissolved oxygen content was greater 0.1 l/ml (Riley and Skirrow, 1965; Kimata et al., 1958; and Zobell and Rittenberg, 1948). This wide range of tolerance exhibited by these anaerobes illustrated that they could exist in many different types of sediments and under a variety of conditions. The amount of organic carbon available to the bacteria in anoxic sediments was usually the limiting factor for sulfate reduction in high salinity environments (Kimata, et al., 1955, 1958). The concentration of oxidizable organic carbon was also correlated to the number of anaerobes present and to the extent of hydrogen sulfide production (Kimata, et al., 1955). In fresh water or in low salinity environments, sulfate concentration, rather than organic carbon, limited the production of hydrogen sulfide (Kimata, et al., 1958).

Studies of sulfate reduction and sulfate concentrations in estuarine systems were done by Kimata, et al., (1958, 1955) and Biggs (1967). Bay and river water and sediments which received organic pollution from industries were studies in Japan by Kimata and his co-workers (op.cit.). Although Kimata et al., (op.cit.) found low sulfate concentrations when these were compared to salinity, in some of his water samples, the cause was not attributed to sulfate depletion of the water column by reducing bacteria in the sediments. Biggs (op.cit.) focused his study on an area in the middle Chesapeake Bay, Maryland, where low dissolved oxygen concentrations in the water below 30 feet were known to exist during the summer (Hires, Stroup, and Seitz, 1963) and were responsible for crab kills (Carpenter and Cargo, 1952). Oxygen replenishment of the bottom water in this area was inhibited during the summer months because of the strong temperature and salinity stratification. Indications of sulfate reduction (Biggs, 1967) were ferrolite and pyrite in the sediments and low sulfate concentrations in the interstial water of the sediments (sulfide, produced by sulfate reducing bacteria, reacts with iron to form ferrolite and pyrite; see Berner, 1970). Several variations in sulfate concentrations relative to the salinity of the water column were reported by Biggs (op. cit.) for the sampling area.

The areas studied by these investigators had three environmental conditions in common that appeared to be necessary for the occurrence of sulfate reduction. These conditions, which were also found in the waters of Hampton Roads, were low oxygen concentrations in the water and sediments, sufficient concentrations of oxidizable organic carbon, and a plentiful supply of dissolved sulfate. Low dissolved oxygen concentrations in the water near the bottom were found in the Hampton Roads and in the Elizabeth River in September and October of 1972.* These oxygen values (as low as 0.1 ppm) were probably caused by the oxidation of organic matter and the presence of temperature and salinity gradients that inhibited the replenishment of oxygen to the bottom water. The presence of thermoclines and haloclines are not unusual in the James River (Pritchard, 1952)). Sufficient organic material, which would provide an oxidizable substrate for sulfate reduction, was indicated by the data for sedimentary

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* Personal communication of unpublished data from William A. Miloski, 2074 Cunningham Drive, Hampton, Virginia 23366.

chemical oxygen demand in the James River (U. S. Army Corps of Engineers, 1971). Tidal inflow from the Chesapeake Bay and the Atlantic Ocean would provide sufficient dissolved sulfate for bacterial reduction of sulfate in the waters or sediments of Hampton Roads.

Indications that active sulfate reduction had occurred in the Hampton Roads were the negative redox potentials* (Moncure and Maynard, 1968) and the high concentrations of trace metals in the James River sediments (U. S. Army Corps of Engineers, 1971). Active sulfide production was correlated to a negative redox potential in marine sediments (Berner, 1963), and trace metals such as lead, mercury, and zinc probably accumulated in the sediments as insoluble sulfides formed from the reaction of the metal ions with sulfide, (Riley and Skirrow, 1965).

The low sulfate concentrations found below 30 feet on August 3 and September 15 also were the result of active sulfate reduction. It is probable that bottom water became trapped by the formation of persistant pycnoclines and that this water remained in the Hampton Roads area for a sufficient length of time so that sulfate-reducing bacteria in the sediments could remove measurable amounts of sulfate from the water column. Wind induced mixing of the water column before sampling on August 15 and October 2 (Table 3)

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* Personal communication of unpublished data from William A. Miloski, 2074 Cu ingham Drive, Hampton, Virginia, 23366.

probably caused replenishment of sulfate to the bottom water and therefore, the small sulfate variations found on these sampling days.

The chemical oxygen demand of the James River sediments, which were collected from the Hampton Roads were found to be greater than similar chemical tests of sediments collected at the mouth (U. S. Army Corps of Engineers, 1971). This finding indicated that sulfate reduction was probably more prevalent inside the Hampton Roads than in the Chesapeake Bay. Therefore, more sulfate was expected to be removed from water that had remained in the James River Basin for a tidal cycle than from water that had remained in the Chesapeake Bay. The trend in the sulfate data for August 3 and September 15 illustrated that the larger sulfate variations did occur in water that had remained in the Hampton Roads for a tidal cycle (see Figs. 13 and 14). The larger sulfate variations occurred at maximum high water and at the time of sampling during high water, water below 30 feet was flowing out of the James River.

Low sulfate concentrations relative to salinity at or near the surface were neither expected nor found because of the constant replenishment of oxygen in the surface waters. This would supply enough oxygen for the oxidation of organic matter in the surface waters, and thus the waters would not be suitable for sulfate reduction. If sulfate reduction did occur near the surface, river water, which usually contains more sulfate than chloride (Riley and Skirrow, 1965), probably would tend to replenish these waters with sulfate. Thus, a combination of oxygen replenishment and river run off probably kept the sulfate concentrations in surface waters within the normal range which was found during the study.

CHAPTER V

CONCLUSION

This study has shown that laser-Raman scattering was a reliable laboratory technique for determining sulfate concentrations in natural water samples. The accuracy of the technique, which depended upon a standard curve and nitrate-internal standards was 7 to 8.6 percent over the concentration range of the standard curve.

From the sulfate analysis of water samples collected at the mouth of the James River, Virginia during August, September, and October of 1972, sulfate was found to have a constant concentration relative to salinity in most cases. Low values in sulfate concentration relative to salinity were found below 30 feet in the study area. These variations probably occur only in late summer and early fall, when weather conditions produce a stratified water column and trap the bottom water long enough so that sulfate is removed from the water. This depletion of sulfate was attributed to bacterial sulfate reduction in the organic-rich sediments within the study area.

APPENDIX I

Data obtained from natural water samples

TABLE AI-1. Data obtained from samples collected on August 3, 1972.

Weather Conditions, August 3, 1973: Average temperature, 81°F.; Precipitation, too little to measure; Average wind speed, 6.8 mph; Wind direction, West. (Local Climatological Data, 1972).

Sea Conditons: No chop, one foot swells, (observed).

Samples Collected at Minimum Low Water (0800-0900 E.S.T.)

Station (see Fig. 2b)	Depth (feet)	Salinity (ppt)	$SO_4^=$ (gm/l) Found	$SO_4^=$ (gm/l) Predicted	% Difference between Found and Predicted*
A	93	27.189	2.03	2.13	4.9
A	46	26.674	1.87	2.09	11.8
A	3	13.849	1.08	1.09	0.9
B	54	27.571	2.02	2.16	6.9
B	27	20.543	1.62	1.61	0.6
B	3	13.798	1.08	1.08	0.0
C	12	15.583	1.21	1.22	0.8
C	5	13.856	1.10	1.09	0.9
D	7	15.410	1.19	1.21	1.7
D	3	15.417	1.20	1.21	0.8
E	6	14.460	1.10	1.13	2.7
F	3	15.612	1.23	1.22	0.8

TABLE AI-1. continued...

Station (see Fig. 2b)	Depth (feet)	Salinity (ppt)	$SO_4^{=}$ (gm/l) Found	$SO_4^{=}$ (gm/l) Predicted	% Difference between Found and Predicted*
Samples Collected at Maximum High Water (1505-1605 E.S.T.)					
A	72	27.321	1.90	2.14	12.6
A	36	17.310	1.35	1.36	0.7
A	3	13.661	1.06	1.07	0.9
B	48	26.527	1.81	2.08	14.9
B	24	15.581	1.23	1.22	0.8
B	3	13.496	1.09	1.06	2.7
C	24	16.362	1.29	1.28	0.8
C	4	15.222			
D	6	15.026	1.20	1.18	1.7
E	3	15.813	1.18	1.24	5.1
F	3	15.836	1.20	1.24	3.3

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* The percentage difference accepted as experimental error for the different experimentally found sulfate concentrations can be determined from the curve on Fig. 4.

TABLE AI-2. Data obtained from water samples collected on August 17, 1972.

Weather Conditions, August 17, 1972: Average temperature, 68°F. (lowest daily average for the month); Precipitation, 0.06 in.; Average wind speed, 7.8 mph; Wind direction, South. (Local Climatological Data, 1972).

Sea Conditions: One to two foot chop with two to three foot swells (observed).

Station (see Fig. 2b)	Depth (feet)	Salinity (ppt)	$SO_4^=$(gm/l) Found	$SO_4^=$(gm/l) Predicted	% Difference between Found and Predicted
Samples Collected at Minimum Low Water (0700-0800 E.S.T.).					
A	78	28.086	2.08	2.20	5.8
A	39	26.767	1.98	2.10	6.1
A	0	15.306	1.26	1.20	4.8
B	54	27.113	2.13	2.12	0.5
B	27	24.605	1.93	1.93	0.0
B	0	15.089	1.16	1.18	1.7
C	36	25.840	1.93	2.02	4.7
C	18	17.425	1.33	1.37	3.0
C	0	15.457	1.27	1.21	4.7
D	4	17.110	1.33	1.34	0.8
E	3	15.141	1.17	1.19	1.7
F	3	15.941	1.20	1.25	4.2

TABLE AI-2. continued...

Station (see Fig. 2b)	Depth (feet)	Salinity (ppt)	$SO_4^=$ (gm/l) Found	$SO_4^=$ (gm/l) Predicted	% Difference between Found and Predicted*
Samples Collected at Maximum High Water (1350-1550 E.S.T.).					
A	78	27.488	2.04	2.15	5.4
A	39	19.568	1.44	1.53	6.2
A	0	17.658	1.37	1.38	0.7
B	51	27.563	2.10	2.16	2.9
B	25	18.669	1.42	1.46	2.8
B	0	18.031	1.39	1.41	1.4
C	27	18.560	1.30	1.45	11.5
C	14	18.491	1.36	1.45	6.6
C	0	18.105	1.38	1.42	2.9
D	3	18.486	1.34	1.45	8.2
E	3	19.136	1.52	1.50	1.3
F	3	17.017			

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*The percentage difference accepted as experimental error for the different experimentally found sulfate concentrations can be determined from the curve on Fig. 4.

TABLE AI-3. Data obtained from water samples collected on September 15, 1972.

Weather Conditions, September 15, 1972: Average temperature, 71°F.; Precipitation, too little to measure; Average wind speed, 10.9 mph; Wind direction, North. (Local Climatological Data, 1972).

Sea Conditions: One to two foot chop with one to two foot swells (observed).

Station (see Fig. 2b)	Depth (feet)	Salinity (ppt)	$SO_4^=$(gm/l) Found	$SO_4^=$(gm/l) Predicted	% Difference between Found and Predicted*
Samples Collected at Minimum Low Water (0700-0800 E.S.T.).					
A	66	28.961	2.15	2.27	5.6
A	33	26.376	1.96	2.07	5.6
A	0	18.655	1.42	1.46	2.8
B	60	27.773	1.98	2.18	10.1
B	30	25.943	1.93	2.03	5.2
B	0	18.901	1.41	1.48	5.0
C	39	26.524	1.99	2.08	4.5
C	19	19.398	1.45	1.52	4.8
C	0	18.084	1.37	1.42	3.6
D	6	19.180	1.43	1.50	4.9
E	3	18.471	1.34	1.45	8.2
F	3	18.246	1.38	1.43	3.6

TABLE AI-3. continued...

Samples Collected at Maximum High Water (1445-1545 E.S.T.).

Station (see Fig. 2b)	Depth (feet)	Salinity (ppt)	$SO_4^=$(gm/l) Found	$SO_4^=$(gm/l) Predicted	% Difference between Found and Predicted*
A	81	28.991	2.09	2.27	8.6
A	40	26.922	2.03	2.11	3.9
A	0	18.603	1.35	1.46	8.1
B	78	29.134	2.09	2.28	9.1
B	39	25.165	1.82	1.97	8.2
B	0	19.124	1.48	1.50	1.4
C	33	19.679	1.34	1.54	14.9
C	16	19.254	1.45	1.51	4.1
C	0	19.026	1.45	1.49	2.7
D	6	19.156	1.49	1.50	0.7
E	3	19.115			
F	3	19.260	1.42	1.51	6.3

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* The percentage difference accepted as experimental error for the different experimentally found sulfate concentrations can be determined from the curve on Fig. 4

TABLE AI-4. Data obtained from water samples collected on October 2, 1972.

Weather Conditions, October 2, 1972: Average temperature, 62°F.; Precipitation, none; Average wind speed, 14.1 mph; Wind direction, North. (Local Climatological Data, 1972).

Sea Conditions: Heavy chop and six to seven foot swells (observed).

Station (see Fig. 2b)	Depth (feet)	Salinity (ppt)	$SO_4^=$ (gm/l) Found	$SO_4^=$ (gm/l) Predicted	% Difference between Found and Predicted*
Samples Collected at Minimum Low Water (1045-1245 E.S.T.).					
A	75	23.959	1.75	1.88	7.4
A	37	21.043	1.57	1.65	5.1
A	0	19.585	1.41	1.53	8.5
B	54	20.781	1.52	1.63	7.2
B	27	19.950	1.46	1.56	6.8
B	0	19.955	1.45	1.56	7.6
C	42	20.938	1.51	1.64	8.6
C	21	20.779	1.53	1.63	6.5
C	0	20.925	1.53	1.64	7.2
D	6	20.783	1.55	1.63	5.2
E	0	19.679	1.46	1.52	4.1
F	0	19.411	1.43	1.52	6.3

TABLE AI-4. continued...

Samples collected at Maximum High Water (1720-1920 E.S.T.).

Station (see Fig. 2b)	Depth (feet)	Salinity (ppt)	$SO_4^=$ (gm/l) Found	$SO_4^=$ (gm/l) Predicted	% Difference between Found and Predicted*
A	66	23.135	1.74	1.81	4.0
A	33	20.831	1.55	1.63	5.2
A	0	19.422	1.46	1.52	4.1
B	60	21.419	1.63	1.68	3.1
B	30	21.289	1.58	1.67	5.7
B	0	20.743	1.57	1.63	3.8
C	15	21.117	1.55	1.65	6.4
C	7	20.845	1.56	1.63	4.5
C	0	20.783	1.56	1.63	4.5
D	0	20.912	1.58	1.64	3.8
E	0	21.170	1.58	1.66	5.1
F	0	21.029	1.56	1.65	5.7

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* The percentage difference accepted as experimental error for the different experimentally found sulfate concentrations can be determined from the curve on Fig. 4.

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