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Alkalinity and pH in the southern Chesapeake Bay and the James River estuary¹

Abstract—The ranges of alkalinity and pH in the southern Chesapeake Bay and the James River estuary were $2.25 \text{ meq} \cdot \text{liter}^{-1}$ at 32‰ to <0.85 at salinities below 6‰ and 7.5–8.3 during the sampling period. Alkalinity is linearly related to salinity in southern Chesapeake Bay. In the James River estuary, the relationship is more complicated as a result of the mixing of various sources of water or the removal of alkalinity. pH values increase with salinity. The variations in pH may be caused by the salinity-dependence of the apparent dissociation constants of carbonic acid.

Alkalinity and pH play a central role in determining the environmental setting and the geochemistry of estuaries and oceans (Mackenzie and Garrels 1966; Garrels and Mackenzie 1967; Sillén 1967; Stumm and Morgan 1970). Mook and Koene (1975) have proposed a theoretical model for predicting the pH distribution in an estuary as a result of changes in the apparent dissociation constants of carbonic acid with salinity. I here present detailed alkalinity and pH distributions in the southern Chesapeake Bay and the James River estuary and use the data to test the model of Mook and Koene (1975) and to evaluate the potential of alkalinity as a mixing indicator in a complex estuarine system.

R. Johnson supervised the collection of

the samples of surface waters during cruises A, B, and C. T. Aardrup, B. Hester, and the crew of RV *Linwood Holton* assisted me during cruises. R. Peace made some of the salinity determinations.

The Chesapeake Bay is one of the largest estuaries in North America, with a drainage basin of $166,200 \text{ km}^2$ (Pelczar 1972). In the northern Chesapeake Bay, the Susquehanna and Potomac Rivers are by far the most important sources of freshwater, contributing 49 and 18% of the total inflow; in the southern Chesapeake Bay, the James River is the only major river, contributing 16% of the annual freshwater inflow to the bay (Pritchard 1952). Thus, the southern Chesapeake Bay may be considered as a mixture of Susquehanna and Potomac River water mixing with seawater and James River water.

The James River is a coastal plain river (Pritchard 1952). It is about 640 km long and has a drainage area $>26,000 \text{ km}^2$. The mean freshwater discharge is about $200 \text{ m}^3 \cdot \text{s}^{-1}$; extremes of 9–9,200 $\text{m}^3 \cdot \text{s}^{-1}$ have been recorded. Tidal influence may extend 150 km upstream (Brehmer and Haltiwanger 1966). The James River has many tributaries; the Pagan River, the Warwick, and the Chickahominy River are some of the major ones within the study area.

Samples at various depths at a number

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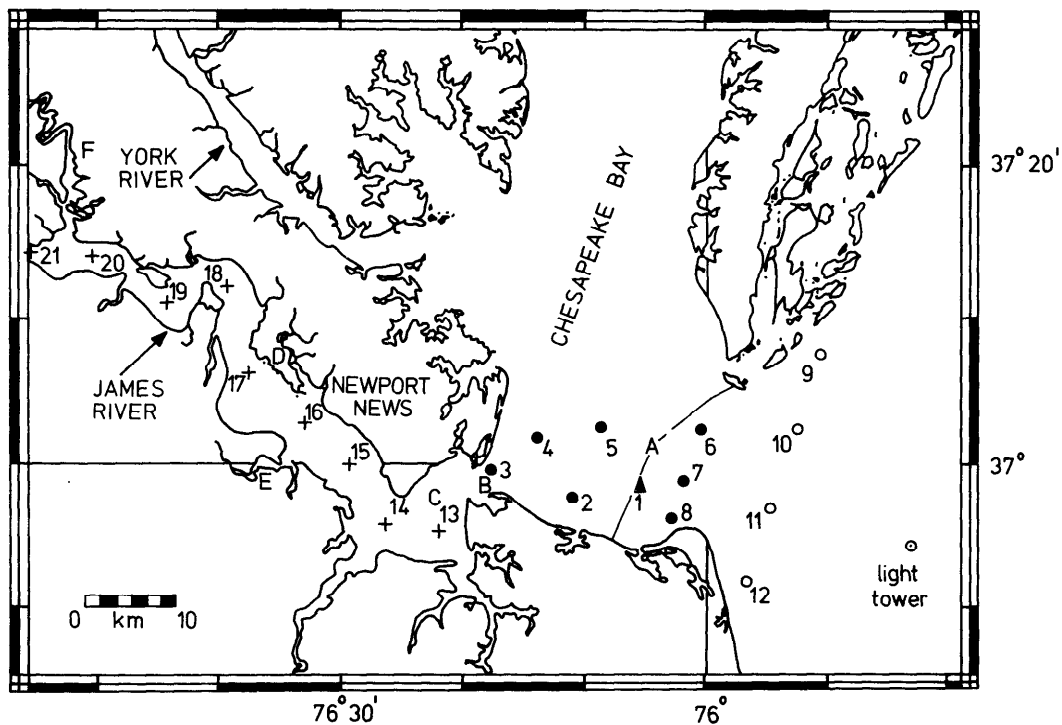


Fig. 1. Station locations during Cruise Carbonate, July–August 1977. \blacktriangle —Leg 1, 12 July; \bullet —leg 2, 19 July; \circ —leg 3, 2 August; $+$ —leg 4, 13 August. A—Chesapeake Bay Bridge; B—Hampton Roads Tunnel; C—Hampton Roads; D—Warwick River; E—Pagan River; F—Chickahominy River.

of stations in the southern Chesapeake Bay and James River estuary were collected during four legs of Cruise Carbonate between 12 July and 13 August 1977 (Fig. 1). Polypropylene (Natl. Inst. Oceanogr., U.K.) sampling bottles were used, as metal samplers are not satisfactory (Park 1968). Samples for pH measurements were drawn into iodine flasks by the procedure for oxygen samples (Strickland and Parsons 1972) and the flasks tightly and carefully stoppered to avoid trapping air bubbles. The samples were stored in a cooler filled with ice, returned to the laboratory on the same day, and stored refrigerated until analysis. Samples for alkalinity measurements were stored in similar fashion in 1-liter polyethylene bottles. Salinity samples were stored at room temperature in polyethylene bottles. Alkalinity and pH were determined as soon as practical at the lab.

Additional samples of surface waters were taken with a polyethylene bucket on three other cruises with stations stretching from the Chesapeake light tower to offshore of Newport News (Fig. 2). Each position was occupied twice at slack before floodtide and slack before ebftide. These samples were analyzed for alkalinity and salinity only.

Salinity was determined from conductivity measurements with a salinometer (Guildline Instr.). The precision is $\pm 0.01\%$. For pH measurements, the electrode was standardized at pH 4 and 7 at 25°C with buffers prepared according to the recommended procedure of NBS (Durst 1975). Each sample in the iodine flask was first equilibrated at 25°C in a constant temperature water bath ($\pm 0.1^{\circ}\text{C}$). The precision is about ± 0.05 pH unit. Alkalinity was determined by the method of Edmond (1970) as modified by Gieskes

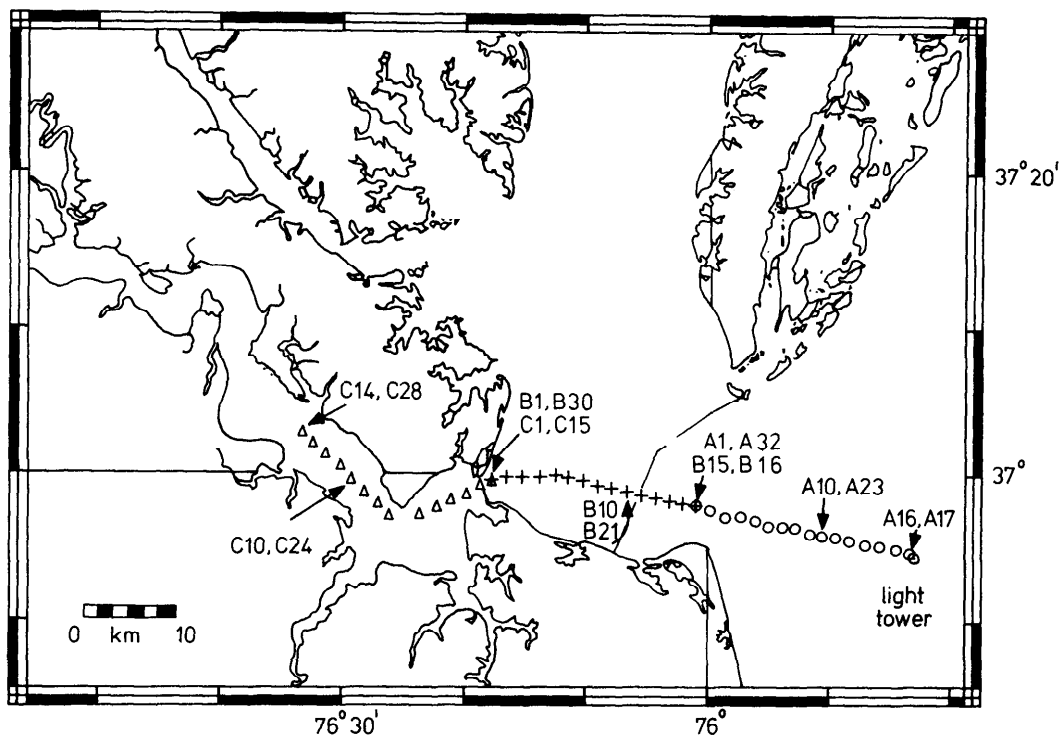


Fig. 2. Station locations for sampling surface waters, July 1977. ○—Cruise A, stations A1 to A32, 9 July; +—Cruise B, stations B1 to B30, 16 July; △—Cruise C, stations C1 to C28, 23 July.

and Rogers (1973). Fifty milliliters of water was titrated with a 0.1 N hydrochloric acid solution in an open beaker immersed in a constant temperature water bath at 25°C. The hydrochloric acid was prepared from Baker DILUT-IT solution without further purification or standardization. The bicarbonate end point of the titration was determined by the Gran method. The precision of the alkalinity measurements is about $\pm 1\%$.

Figure 3 shows that pH increases with salinity from about 7.6 at 3‰ salinity to 8.15 at 32‰. The increase in pH is primarily below a salinity of 15‰; beyond this, the average pH value is relatively constant, although with considerable scatter within the range of 20–26‰. At any single salinity, the bottom samples have systematically lower pH. Within each station, there is also a slight decrease in pH with depth. The distribution of pH in samples from the surface

waters and middepths seems to follow one trend while that in the bottom samples follows an approximately parallel line with an offset of about 0.2 pH units. This may be caused by the summer conditions in the estuary. An abundance of organic matter supplied to the bottom water or surface sediments where oxidation could take place would release carbon dioxide and reduce pH, while the thermal gradient and low river flow would tend to stratify the estuary and impede vertical mixing.

The solid line in Fig. 3 gives the predicted distribution of pH in the surface and middepth waters for the estuary from mixing oceanic water (salinity 32.094‰, pH 8.119, and alkalinity 2.246 meq·liter⁻¹ at station 9) with riverine water (salinity 3.367‰, pH 7.603, and alkalinity 0.842 meq·liter⁻¹ at station 21). The model used is similar to the one proposed by Mook and Koene (1975). As a first ap-

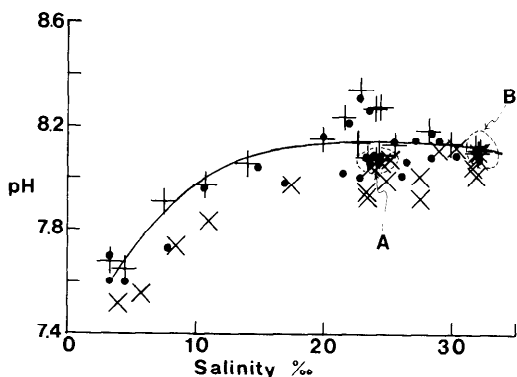


Fig. 3. Relationship between pH and salinity in southern Chesapeake Bay and James River Estuary. +—Samples from surface waters; x—bottommost sample at each station (usually within 2–3 m of bottom); ●—samples at intermediate depths. Solid line represents theoretically predicted relationship between pH and salinity in samples of surface waters and waters of intermediate depths. Enclosures A and B each contain six ●, three +, and three x.

Table 1. Notation for model calculation.

a_H	activity of hydrogen ions, defined by $\text{pH} = -\log a_H$
Cl	chlorinity of water in ‰
S	salinity of water in ‰ and $S = 1.80655 Cl$ (Cox et al. 1967)
K'_1	first apparent dissociation constant of carbonic acid and $\text{p}K'_1 = -\log K'_1$
K'_2	second apparent dissociation constant of carbonic acid and $\text{p}K'_2 = -\log K'_2$
K'_B	first apparent dissociation constant of boric acid and $\text{p}K'_B = -\log K'_B$
$T(\text{CO}_2)$	total dissolved inorganic carbon
TA	titration alkalinity
CA	carbonate alkalinity
$T(B)$	Total dissolved boron concentration
Q	$T(\text{CO}_2)/CA$
X	$(CA)_r/(CA)_o$
Subscript r	riverine end member
Subscript o	oceanic end member
b	degree of brackishness

Table 2. Calculation of pH in an estuary by considering pH, TA, and Cl of riverine and oceanic end members.

$$\frac{T(\text{CO}_2)}{CA} = \frac{a_H^2 + a_H K'_1 + K'_1 K'_2}{a_H K'_1 + 2K'_1 K'_2} = Q \quad (1)$$

Q_o and Q_r can be determined from measured pH of oceanic and riverine end members and apparent dissociation constants estimated with equations of Edmond and Gieskes (1970) and Mook and Koene (1975) for various chlorinity regimes.

If estuary (first approximation) is conservative with respect to total inorganic carbon and carbonate alkalinity, then, at any point in it

$$T(\text{CO}_2) = (1 - b)T(\text{CO}_2)_r + bT(\text{CO}_2)_o \quad (2)$$

$$CA = (1 - b)CA_r + bCA_o \quad (3)$$

By rearranging Eq. 2 and 3,

$$Q = \frac{T(\text{CO}_2)}{CA} = \frac{(1 - b)Q_r X + bQ_o}{(1 - b)X + b} \quad (4)$$

$$\text{where } b = \frac{Cl - Cl_r}{Cl_o - Cl_r} \quad (5)$$

$(CA)_r$ and $(CA)_o$ can be estimated from

$$TA = CA + \frac{K'_B \cdot T(B)}{K'_B + a_H} \quad (6)$$

where $T(B) = 2.2 \times 10^{-2} \cdot Cl \text{ mmol} \cdot \text{kg}^{-1}$ (Culkin 1965) (7)

and K'_B can be estimated from equation of Edmond and Gieskes (1970). Thus, Q can be determined for any given chlorinity. By rearranging Eq. 1,

$$a_H^2 + a_H K'_1(1 - Q) + K'_1 K'_2(1 - 2Q) = 0 \quad (8)$$

$\therefore a_H$ and, thus, pH can be calculated at any given chlorinity by solving Eq. 8.

proximation, total inorganic carbon and carbonate alkalinity are considered conservative. Then, the distribution of pH in the estuary can be predicted if the properties of the oceanic end member and the riverine end member are known and the variations of the apparent dissociation constants of carbonic acid with salinity can be determined. The terminology used in the model calculation and a summary of the model are given in Tables 1 and 2. The agreement between the model-generated and the observed distribution of pH in the estuary is reasonably good.

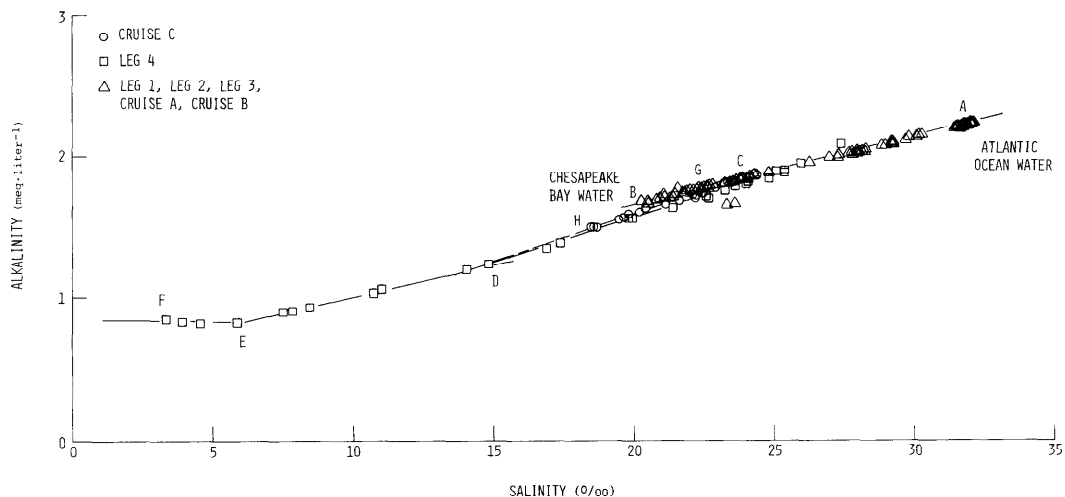


Fig. 4 Relationship between alkalinity and salinity in southern Chesapeake Bay and James River estuary. There are 105 open triangles on line ACGB.

The relationship between alkalinity and salinity is shown in Fig. 4. The data points seem to form linear segments. All the data from southern Chesapeake Bay between the James River Bridge and the Chesapeake light tower (stations 1 to 12, A1 to A32, and B1 to B30) fall on line AB; this line may represent mixing between inflowing Atlantic Ocean water (point A) and water from northern Chesapeake Bay (point B). An extension of this line will give an alkalinity of about $2.39 \text{ meq} \cdot \text{liter}^{-1}$ at 35‰ —a value similar to those reported for North Atlantic surface waters (Edmond 1974). The intercept of this line at zero salinity yields a residual alkalinity of about $0.7 \text{ meq} \cdot \text{liter}^{-1}$. Carpenter et al. (1975) reported residual alkalinity values of $0.4\text{--}0.5 \text{ meq} \cdot \text{liter}^{-1}$ at zero salinity in northern Chesapeake Bay in July and August 1959 and 1960. The agreement between these values seems good in view of the possible inherent temporal variations and the different analytical methods used.

The data from stations 13 to 21, within the James River estuary, show a distinctly different relationship with salinity (line CDEF in Fig. 4; Fig. 5). Point C lies within line AB; thus, line CDEF may represent the mixing of James River

water with Chesapeake Bay water. D and E show samples from stations 17 and 20 and form inflexion points, so that line CDEF may be described either as a combination of three linear lines (CD, DE, and EF) or as a concave curve. With the former interpretation, alkalinity is considered a conservative tracer and waters with different alkalinity to salinity ratios are assumed to be entering the James River at these inflexion points. A number of tributaries flow into the James River: the Warwick River and the Pagan River flow into it near station 17, the Chickahominy River near station 20 (Fig. 1). If line CDEF is considered a curve, then removal of alkalinity within the estuary is implied. My data cannot unequivocally rule out either possibility.

Samples of surface waters from the James River estuary from another cruise (stations C1 to C30) also yield a linear relationship between alkalinity and salinity (line GH in Figs. 4 and 5). However, this line does not coincide with line CD although the samples came from the same area (Fig. 2). The Chesapeake Bay water end member at point G is different from that at point C, although both fall on line AB. Since the samples were taken on different dates and at different tidal

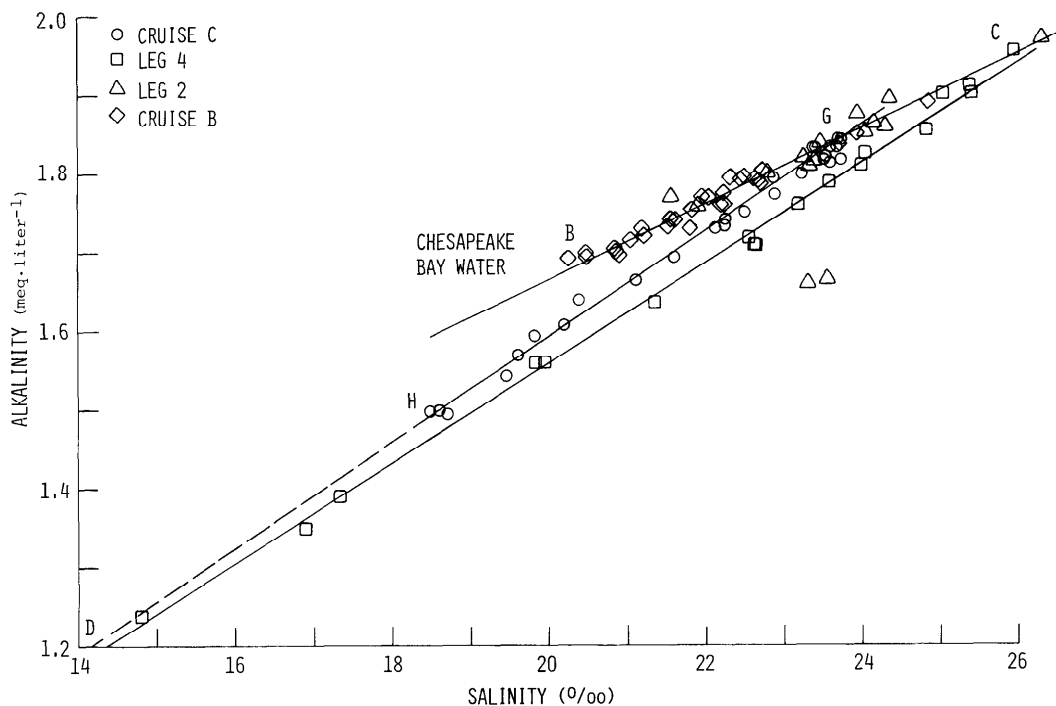


Fig. 5. An expanded section of Fig. 4 showing mixing of James River water and Chesapeake Bay water.

stages, the data suggest that the composition of the Chesapeake Bay water flowing into the James River may shift with time along the mixing line AB between upper Chesapeake Bay water and Atlantic Ocean water.

There is no evidence suggesting mixing of three end members (that is, Chesapeake Bay water, James River water, and Atlantic Ocean water) in Chesapeake Bay. The linearity of line AB is not noticeably affected at points C and G, which presumably represent outflow of the James River; this implies that during the sampling period, mixing in the bay was caused primarily by freshwater flowing south from northern Chesapeake Bay and the northward seawater intrusion. The amount of James River water that had entered Chesapeake Bay proper was relatively small. In the cruises up the James River, the relationship between alkalinity and salinity did not deviate from line AB until station 14 in leg 4 (Fig. 1) and about station C20 in Cruise C (Fig.

2). Both stations were well within Hampton Roads. This shows that the Chesapeake Bay-Atlantic Ocean water mixture had intruded into Hampton Roads and the mixing between this mixture and James River water did not occur in Chesapeake Bay proper at all. These observations probably reflect the fact that sampling took place in a season of low flow; furthermore, summer 1977 was extraordinarily dry.

Figure 6 shows the distribution of salinity and specific alkalinity (that is, the titration alkalinity to salinity ratio) in the surface waters in southern Chesapeake Bay and the James River estuary from legs 1 through 4 of Cruise Carbonate. The salinity contours clearly show that the fresh Chesapeake Bay water hugs the western side of the bay and flows into the Atlantic Ocean through the southern side of its mouth while saline Atlantic Ocean water enters the bay through the northern side of the mouth. This circulation pattern has been described in detail by

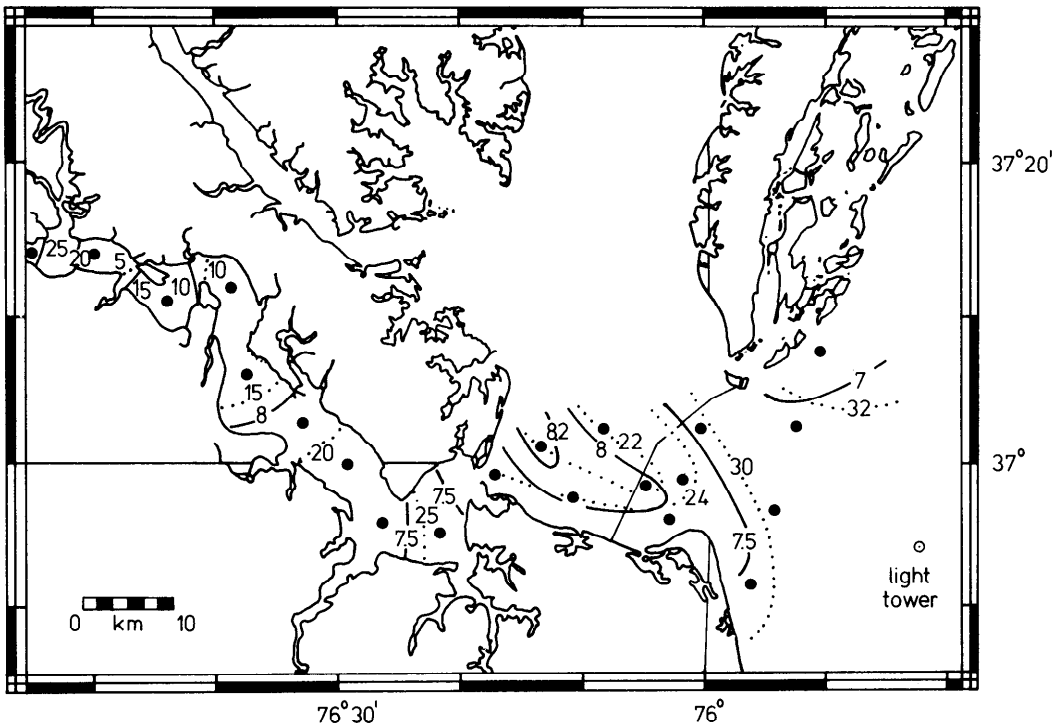


Fig. 6. Distribution of salinity and specific alkalinity in southern Chesapeake Bay and the James River estuary. Solid curves—specific alkalinity (unit of contours: 10^{-2} meq·liter $^{-1}$ ·‰ $^{-1}$). Dotted curves—salinity (unit of contours: ‰).

Pritchard (1952). The contours of specific alkalinity seem to run parallel to the salinity contours. The bay water is characterized by high specific alkalinity $>8 \times 10^{-2}$ meq·liter $^{-1}$ ·‰ $^{-1}$, whereas the Atlantic Ocean water has specific alkalinity of $<7 \times 10^{-2}$ meq·liter $^{-1}$ ·‰ $^{-1}$. In the James River, the specific alkalinity increases to 25×10^{-2} meq·liter $^{-1}$ ·‰ $^{-1}$ at station 21. In neither salinity nor specific alkalinity is there evidence suggesting a plume of James River water in the Chesapeake Bay. James River water and Chesapeake Bay water seem to mix in Hampton Roads, as suggested earlier.

The present data can provide only a crude description of the circulation. A more refined picture may be obtained if more data points become available and if the tidal effects can be evaluated. In a complex estuary, such as the Chesapeake Bay, where waters from a number of rivers mix with seawater, the influence of

each individual river on the composition of the water in the estuary is difficult to assess. My data suggest that alkalinity may be a property unique to each river and might be used as an indicator for studying mixing processes in such a complex situation.

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Modifications to the Mackereth corer

Abstract—The 6-m Mackereth corer has proved excellent for many aspects of Quaternary research, particularly in the growing field of paleomagnetic work on lake sediments. A 12-m version of the corer is described together with a magnetic orientation system.

Mackereth (1958) presented an elegant and efficient solution to the problem of obtaining long (6 m) continuous cores of soft sediment in water depths up to 100 m using lightweight equipment. Mackereth (1969) described a 1-m version of the long corer for recovering undisturbed samples of the water-sediment surface and upper sediments, which are generally disturbed or missing from 6-m cores.

An attractive feature of Mackereth corers is that the core tubes (and barrel) can

be made of PVC water pipes, which are cheap, can serve as permanent core retainers, and are easily sliced open. This makes the cores particularly suitable for paleomagnetic work on lake sediments. There is an obvious need for some means of orientating cores for such work.

The ease and reliability with which the Mackereth corer recovers 6-m cores of soft sediment indicates the feasibility of a longer version. Mackereth (1958) had suggested a practical limit of 9 m. In addition to the engineering difficulties of making longer corers, there is the problem of exceeding the mechanical strength of the sediment, when the core tube can advance without collecting any new material.

In selecting a design for a Mackereth