

THE CHEMISTRY OF
SUSPENDED PARTICULATE MATTER:
FIRTH OF FORTH

by

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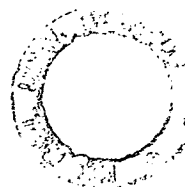
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1978



Declaration

This thesis has been composed by me,
and except where specified in the text,
all the work presented here is my own.

ABSTRACT

The Firth of Forth is a wide, shallow, marine-dominated coastal embayment on the east coast of Scotland. The concentration of suspended particulate matter ranges from $<1 \text{ mg l}^{-1}$ at the seaward end to $>30 \text{ mg l}^{-1}$ in the west, with intermediate values along the south shore and in bottom waters.

Studies of the major-element chemistry (Al, Si, Ca, Fe, Ti, K, Mg, P and S) of local suspended matter are reported. An attempt is made to account for the observed areal, vertical and temporal changes in the chemistry of this material in terms of its concentration, gross composition, mineralogy, particle size characteristics and the partitioning of major elements among terrigenous, biogenic and organic components. The extent to which these factors are influenced by hydrodynamic processes and resuspension of bottom sediments is examined.

Suspended matter in the Forth is dominated by terrigenous debris, particularly to the west. Locally, variations in inter-element ratios of this material as a function of water depth indicate increasing particle size and loading of terrigenous matter in bottom waters. Particulate Al resides almost exclusively in detrital aluminosilicates. All the elements examined are present to some degree in the terrigenous fraction, their abundance relative to Al being a function of particle size-specific mineralogy. Biogenic associations of Si, Ca (skeletal debris) and P (organics) are quantified. Pollutant phases of particulate P and Fe occur in direct association (organics and possibly ferriphosphates) and in independent forms (sewage organics and ferruginous waste).

Seaward and northward flux of particulate matter occurs in surface waters, ensuring some dispersal of pollutant material and mixing with terrigenous debris. As this settles, however, it is subject to net landward transport in the bottom waters along with material winnowed from local sediments. Some degree of hydrodynamic sorting of particles is expressed in their chemistry. Relative to the amount of material in suspension, only negligible escape of particulate matter from the Forth appears to occur.

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CHAPTER 1

INTRODUCTION

The purpose of this thesis is to observe and account for variations in the major element chemistry of suspended particulate matter ($> 0.4 \mu\text{m}$) in a shallow coastal estuary (the Firth of Forth).

The distribution of suspended particulate matter in estuaries has been examined previously in terms of loading, sediment transport, and to a lesser degree, particle size characteristics and mineralogy. Gravimetric loading, however, has formed the basis of most studies (e.g. Postma, 1967 ; Schubel, 1968, 1971a; Meade, 1972; Buller, 1975; d'Angejan and Ingram, 1976). Such studies, even if they include particle size analyses, provide insufficient information as to the nature of the suspended material, since equivalent loadings do not guarantee equivalent composition in different samples. The term 'suspended sediment' is a misnomer for estuarine particulate matter, which consists of terrigenous debris of widely varying particle size and mineralogy, biogenic constituents (both skeletal and soft parts) and pollutants from municipal and industrial effluents. Very few studies of the chemistry of suspended particulate matter have been reported, despite the fact that chemical analyses in conjunction with loading studies would provide the best definition of the nature of the suspended matter.

Further, the role of particulate matter in the estuary extends beyond that of passively transported material. Aggregation, disaggregation and solution processes may play a major role in determining the fate of this material. Products of non-conservative mixing of river and marine waters may involve spontaneous precipitation of unsupported material, usually in association with organic complexes (Aston and Chester, 1973; Boyle et al, 1974; Sholkovitz, 1976). Many

processes of such removal, however, are dependent upon or enhanced by the presence of suspended particulate matter. This material acts as a catalyst through its function as nuclei for flocculation and aggregation phenomena, and provides microsubstrates for major and trace-element sorption-desorption reactions, cation exchange, microbiological activity and precipitation of metallic oxides and/or phosphates (Burton and Liss, 1976; Turekian, 1977). Although such studies are beyond the scope of this thesis, future recognition of these authigenic associations in particulate matter depends upon a full appreciation of the extent to which the observed changes in particulate chemistry reflect physical sorting and particle size variations within the existing background of suspended material.

In this thesis, suspended particulate matter collected from the Firth of Forth will be examined with respect to its concentration, grain size distribution characteristics, gross composition, mineralogy and major element chemistry. The data will then be applied to account for the distribution of this material as observed in the estuary, and to determine the extent to which the chemical characteristics of this material reflect its source, particle size, major element partitioning and/or hydrodynamic processes. The Firth of Forth provides a useful template for other such studies as it typifies the shallow, tidally-dominated coastal plain estuaries which host many of the world's large population centres. Although river flow is minimal, sufficient distinct sources of particulate components exist to permit definition of the major constituents of the suspended load.

Most previous studies of particulate chemistry have been restricted to oceanic and shelf waters (Joyner, 1964; Atkinson and Stefannson,

1969; Spencer and Sachs, 1970; Baker, 1976; Feely, 1975, 1976; Bishop et al, 1977). These are far outnumbered by gravimetric or light-scattering studies of total load. Recently, attention has been directed towards the chemistry of coastal particulates from large estuaries (d'Anglejan and Smith, 1973), sea lochs (Price and Calvert, 1973) and fjords (Skei et al, 1973; Taylor, 1974; Price and Skei, 1975; Skei, 1975). Within these areas, the loadings of suspended particulate matter and the terrigenous component in particular are very small compared to those observed in nearshore environments. Only Sholkovitz's (1978) study of particulate chemistry in the Tay estuary can be closely compared to the present study. Nevertheless, it is within these nearshore waters that the character and fate of particulate matter is of greatest importance, particularly when it involves the discharge of pollutant material. This thesis, therefore, represents an early attempt to investigate the factors which dictate coastal particulate chemistry.

The chemical analyses in this programme were determined by means of 'thin-film' X-ray fluorescence (XRF) spectroscopy of filtered particulate samples. Although this analytical procedure has been applied before, it is based on certain assumptions which have not been challenged fully by previous workers. As a result of the nature of chemical data obtained by XRF analyses of size-variant samples (Chapter 6), potentially significant flaws became evident in these assumptions. A detailed theoretical study was undertaken to ensure that the analytical trends as indicated in this thesis reflect real chemical variations. This work is the only such study which is directly applicable to the analysis of natural coastal particulate matter, and its implications for future studies by this method must be

considered. The theoretical derivation and its significance are discussed in Appendix A. This work has been set apart because it is tangential to the main study, but it constitutes an integral part of this thesis.

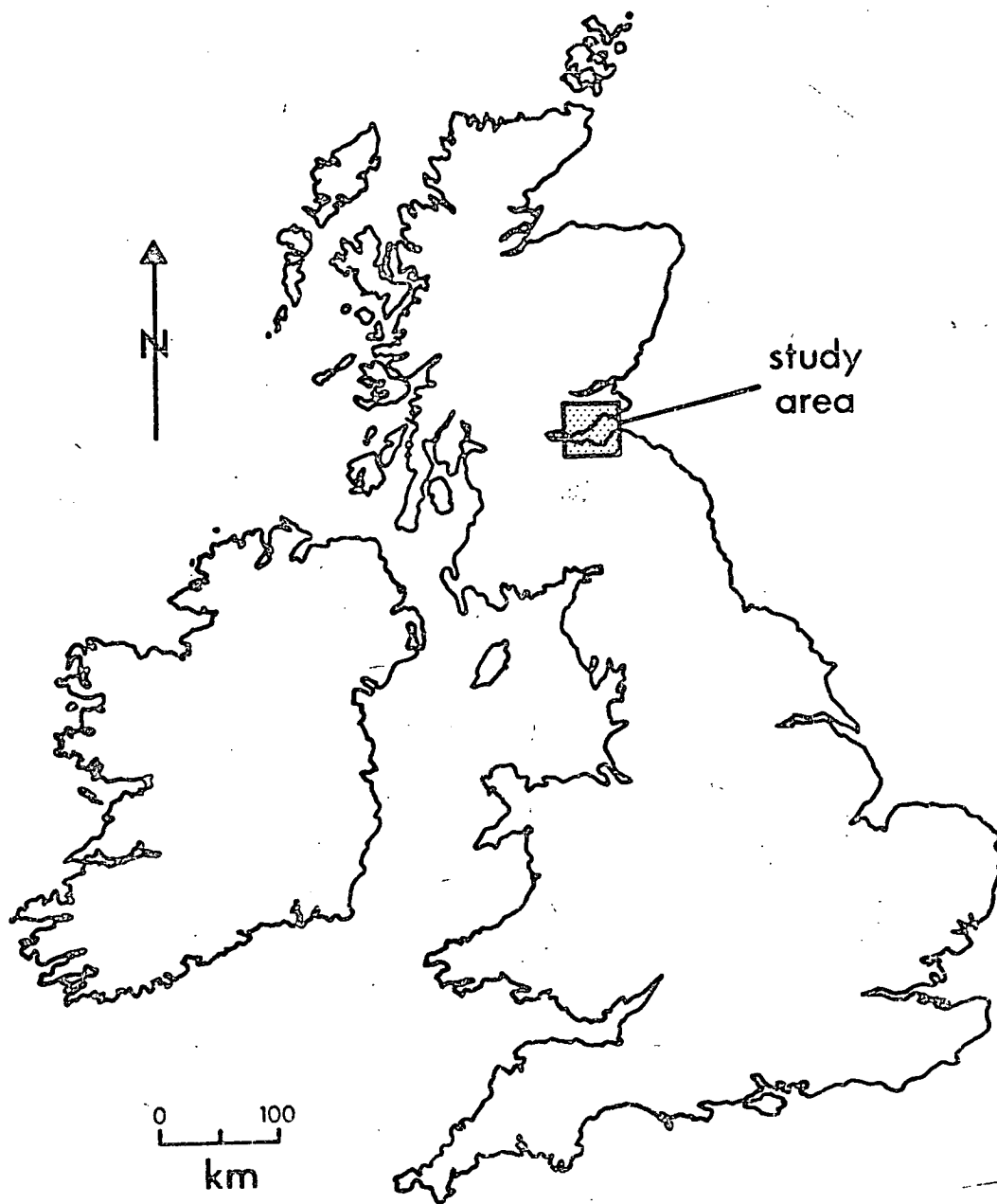
CHAPTER 2

THE PHYSICAL SETTING OF THE STUDY AREA

The Firth of Forth is a large, dominantly river- and glacially-defined shallow coastal embayment on the east coast of Scotland at the eastern extremity of the Midland Valley (Figure 2.1). It is geographically subdivided into two main portions. A narrow, shallow inner estuary extends from Stirling to the Forth bridges, and the wide, semi-enclosed embayment of the Firth of Forth itself extends eastward to the North Sea as shown in Figure 2.2. This latter zone, subsequently referred to as the Forth, constitutes the study area of this thesis. Its seaward limit is defined arbitrarily here by a line extending southwards from Anstruther to North Berwick, as shown in Figure 2.2.

The geology in the immediate vicinity of the study area (Figure 2.3) is dominated by calcareous sandstones, limestones and coal-bearing strata of Carboniferous age. West of Stirling, Silurian shales, Devonian sandstones and Dalradian mica schists are prominent. The study area contains many volcanic necks and lavas from Devonian and Carboniferous igneous activity, and is well faulted. Broad synclines to the east and west of Edinburgh contain coal-bearing strata of economic importance.

The bathymetry of the Firth of Forth is illustrated in Figure 2.4. The Forth is characterized by shallow waters, which exceed 40 m only in narrow channels and in the seaward end of the main basin. Detailed calculations of the area and volume were conducted, as reported in Appendix D. This study indicates a surface area of 670 km^2 , a total water volume of 13 km^3 and an average depth of 20 m within the study area. The Forth is essentially funnel-shaped. Despite the varying width of the estuary, the cross-sectional area along the five transects shown in Figure 2.4 increase progressively seaward, as shown in



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Fig. 2.1 Map of the British Isles, showing the location of the Firth of Forth.

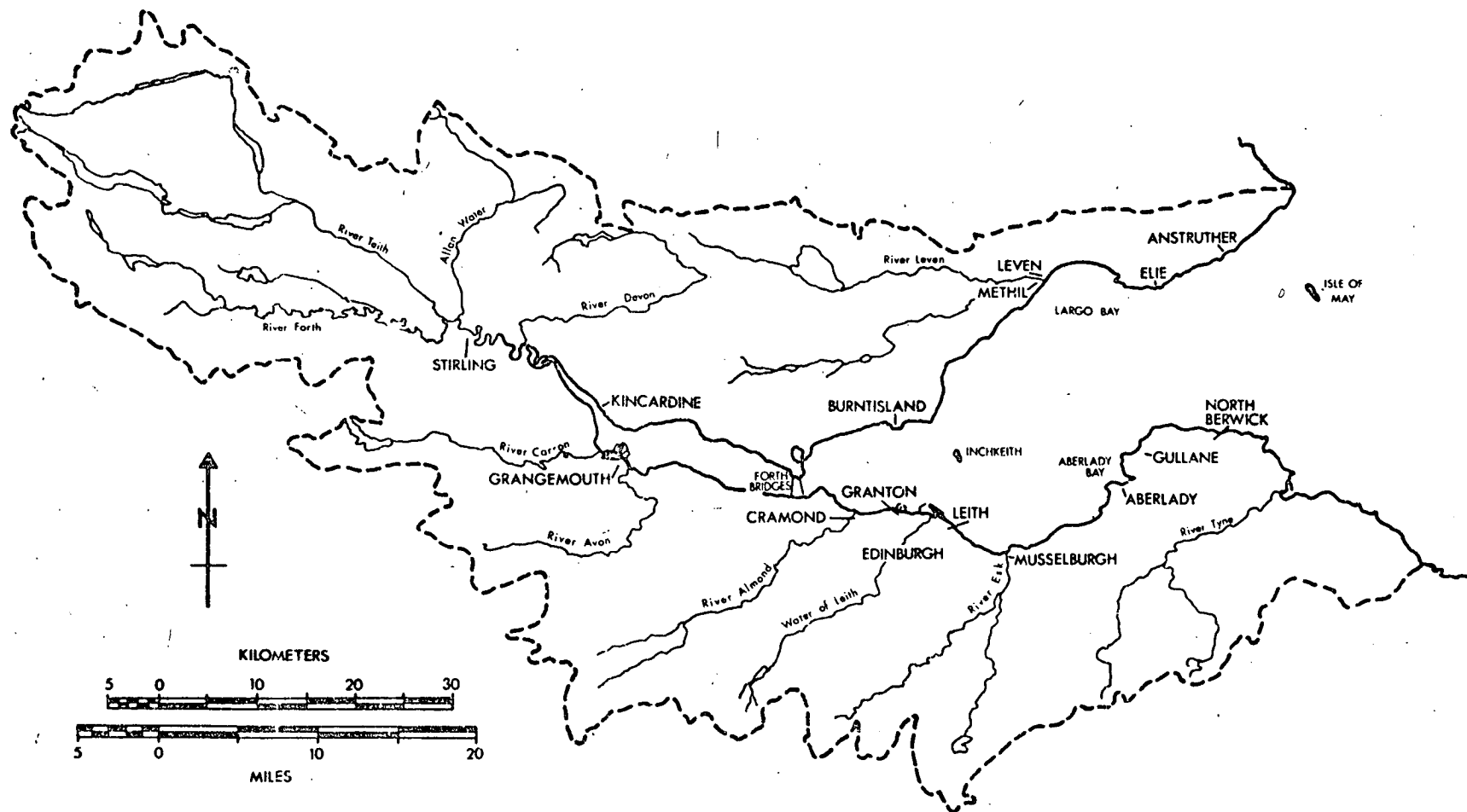


Fig. 2.2 Geography of the catchment area of the Firth of Forth.

FIRTH OF FORTH CATCHMENT AREA GEOLOGICAL MAP

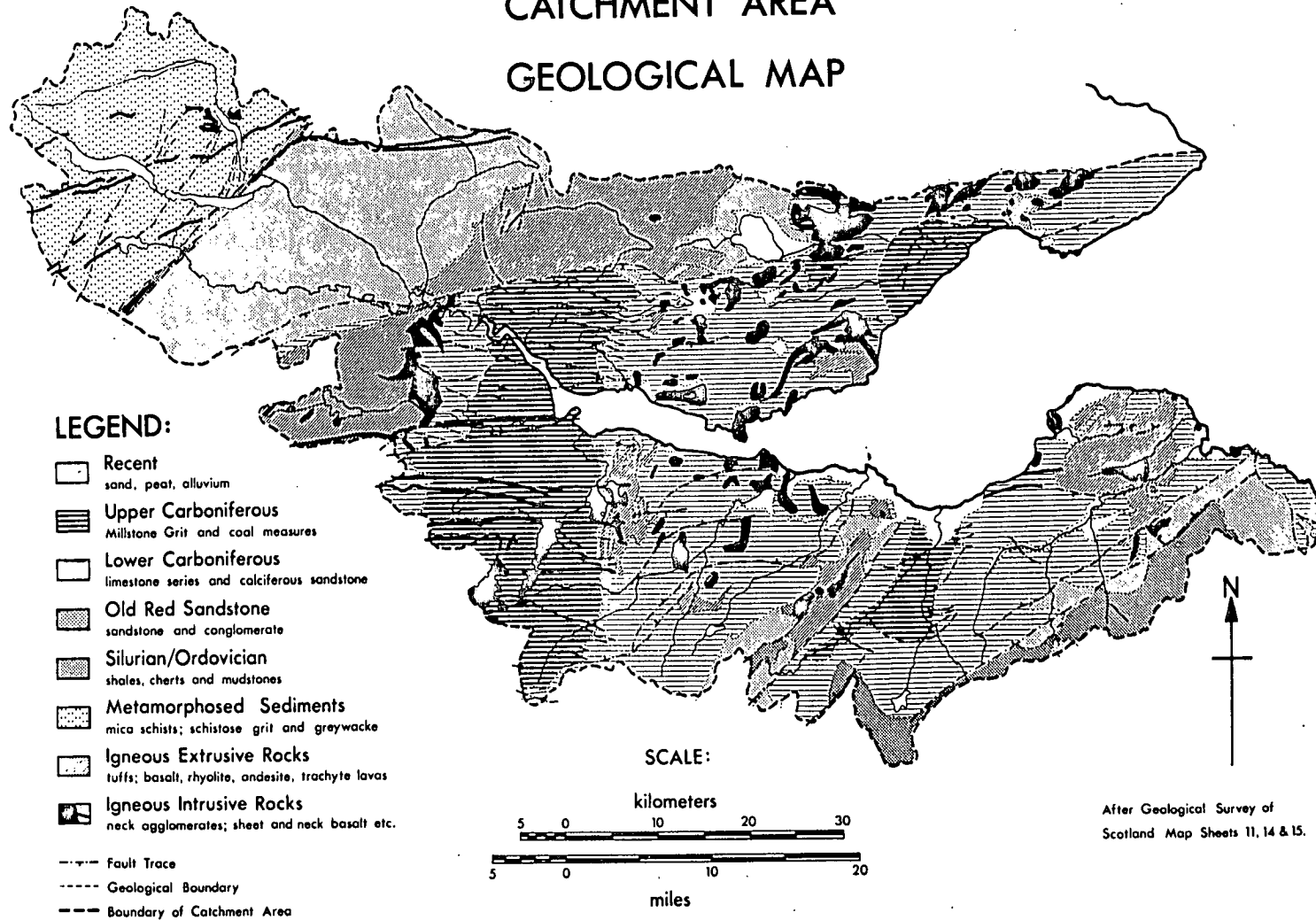


Fig. 2.3 Local Geology.

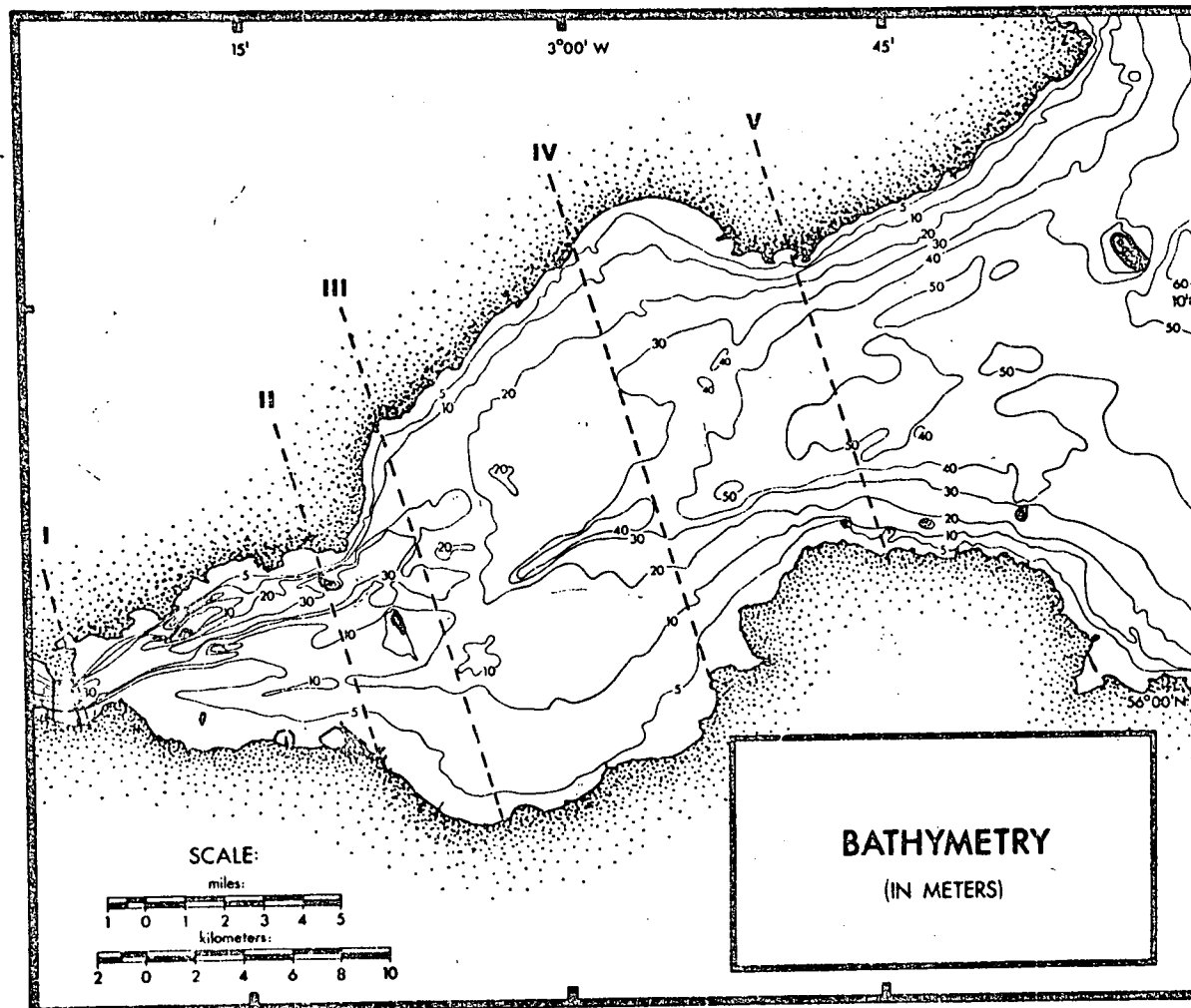


Fig. 2.4 Bathymetry of the Firth of Forth.
See text for discussion of sections I-V.

Table 2.1.

TABLE 2.1

Cross-sectional areas (perpendicular to the axis of the main channel) along the transects shown in Figure 2.4.

<u>Transect</u>	<u>Area (km²)</u>
I	0.027
II	0.090
III	0.202
IV	0.374
V	0.416

Two channels are seen to the west. Both the main channel to the north and the 'Narrow Deep' between Inch Keith and Leith reach depths in excess of 30 m. Thomson (1978) points out that these are merely surface expressions of much deeper channels cut into the bedrock. The present gross channel configurations were established by late pre-glacial times (McManus, 1972). Incised river erosion during periods of lower sea level and further erosion of the existing channels by subglacial meltwater and/or ice scour resulted in the present configuration of overdeepened channels infilled by post-glacial sedimentation.

Glacial and postglacial deposition of gravels, sands, silts and clays contribute to the local sediment overburden, which is thickest (~60 m) in the aforementioned channels and in Largo Bay. Elsewhere, this material varies in thickness, averaging <20 m, but is completely absent in some areas. The surficial sediments of the study area are shown in Figure 2.5 to be dominated by muds and sandy muds. Sands are concentrated near the shore in Largo Bay and near Aberlady, while exposed bedrock outcrops along each shore to the east of the study area.

The geographic area shown in these figures supports a population of approximately 700,000 people. Local industries include coal mining, power generation, chemical and petrochemical industries, paper manufacturing, brewing and distilling and heavy construction. Direct discharge of municipal and industrial effluents into the study area average $4 \text{ m}^3 \text{ s}^{-1}$. Colliery waste and dredging spoil are also introduced locally. Covill (1972) summarized these inputs as follows:

Crude Sewage and Industrial Effluent Discharge:

City of Edinburgh	$241 \times 10^3 \text{ m}^3$ per day
Midlothian (Esk Valley)	$68 \times 10^3 \text{ m}^3$ per day
Remaining south shore	$15 \times 10^3 \text{ m}^3$ per day

Pit, mine and washery waters (National Coal Board)

Four collieries	$15 \times 10^3 \text{ m}^3$ per day
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The character and significance of specific outfalls and physical characteristics of the Forth will be discussed further as they affect the data in this thesis.

CHAPTER 3

HYDROGRAPHIC SETTING

3.1 Introduction.

Before the character of the suspended particulate matter in the Firth of Forth may be examined in detail, the hydrographic environment of this material must be determined. There is an unfortunate lack of published material on circulation and mixing in the Forth. A brief appraisal of existing results will be supplemented by the data collected in conjunction with the sampling of suspended particulate matter in this study.

Salinity levels in the Forth were first reported by Murray (1816), with later elaboration and monitoring by Mill (1884a, 1884b). These studies indicated that the estuary is marine-dominated, its northern half being characterised by relatively high salinities ($\sim 34.5\%$), with slightly lower values near the south shore ($\sim 32 - 34\%$). Craig (1972) estimated a 5% dilution of seawater by land drainage. The mean river flow is approximately $65 \text{ m}^3 \text{ s}^{-1}$, with the majority of this flow ($\sim 50 \text{ m}^3 \text{ s}^{-1}$) being discharged into the inner estuary, mainly via the rivers Forth, Teith and Allan (Figure 2.2) (Forth River Purification Board Annual Report, 1975). Municipal and industrial effluent discharge to the outer estuary itself averages $4 \text{ m}^3 \text{ s}^{-1}$, much of this being associated with sewage discharge along the south shore. A flushing time of 8 months for the study area has been suggested by Craig (1972), while Bowden (1963) (reported in Corlett, 1972) estimates a 'mixing half life' of 41.5 days, compared to 2.4 days for the inner estuary.

Mass westward flow on the flood tide and eastward flow during ebb tide characterise the gross water movement in the study area, and tidal currents are most rapid in the constricted portion of the

channel west of Edinburgh (Watson and Watson, 1971; Watts, 1975, 1977).

3.2 Sampling procedures.

The major field sampling programme for this study consisted of one areal survey and three fixed-position tidal station monitoring programmes. The D.A.F.S. research vessel Mara was used in March 1975 for a one-week multidisciplinary research survey. The areal sampling grid consisted of 29 sampling stations as shown in Figure 3.1, on which all sampling locations referred to in this thesis are based. The samples studied here were collected over a two-day period as shown in Appendix B. Hydrographic parameters were determined by the D.A.F.S. marine laboratory, and were kindly made available for this study; the author is solely responsible for their mode of presentation and interpretation here.

Fixed-position monitoring through a 12-hour semidiurnal tidal cycle was conducted at each of three stations selected to represent the western end of the study area (Station 26, January 20, 1977), the central Forth (Station 15, February 8, 1977) and the Edinburgh area (Station 7, April 19, 1977) (see Figure 3.1).

Water samples were collected at four or five depths hourly throughout the tidal cycle, using two-litre N.I.O. bottles. Temperature, salinity and total suspended load determinations were made on aliquots of these samples. Salinities were determined on board using a Plessey 6230N salinometer for the tidal sampling at station 26, and in the laboratory after field sampling for stations 15 and 7. Temperature determinations were made using a simple thermometer immediately after sample retrieval, and are unlikely to be accurate. At all tidal stations, measurements of the speed and direction of tidal currents were made at several depths on a half-hourly basis by personnel of

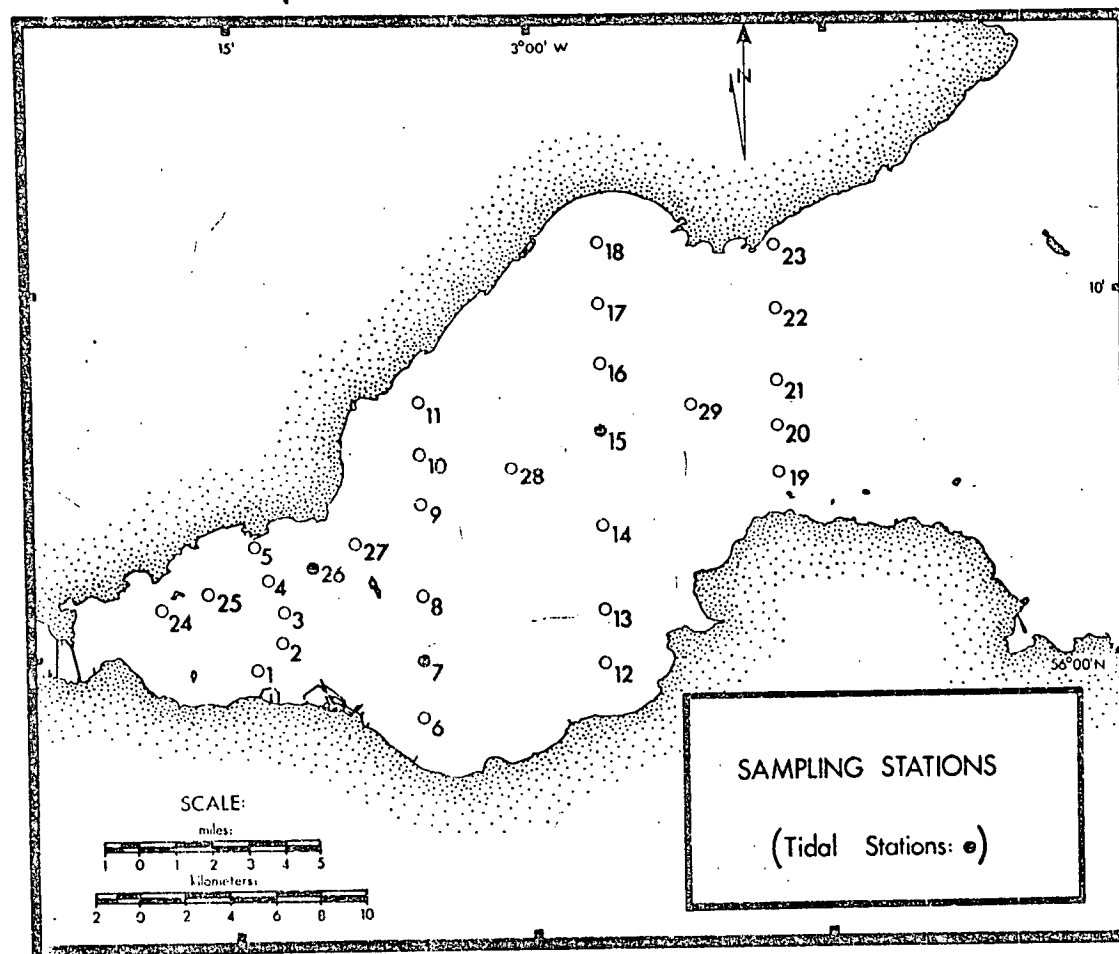


Fig. 3.1 Location of sampling stations.

the Forth River Purification Board. These raw data have been freely made available for inclusion in this thesis, their presentation and interpretation being the responsibility of the author.

For all sampling programmes, subsamples of the hydrographic casts were vacuum filtered through pre-weighed $0.4\ \mu\text{m}$ pore-sized 37 mm diameter Nuclepore[®] membrane filters to obtain samples of suspended particulate matter. These samples were immediately washed with filtered distilled water to remove sea salts. In all cases, the samples were filtered within 24 hours of sampling. During the tidal station programmes, all samples were filtered on board except for the last two hourly collections, which were filtered on the following day.

The filters were stored in acid-washed plastic containers, and after being returned to the laboratory, were dessicated and reweighed on a Mettler H2OT 5-place balance (areal sampling) or a Perkin Elmer AD2-autobalance (tidal stations) to determine the gravimetric loading. The filters were then retained for later chemical analysis (Chapters 6, 7 and 8).

3.3 Results.

Areal patterns of hydrography.

The major hydrographic trends observed during the March 1975 sampling period are consistent with the areal trends reported in the literature. Salinities range from $<33\%$ in the west to $>34\%$ in the northeastern end of the study area as shown in Figure 3.2. The five sections presented in this and subsequent figures show (from top to bottom) the four north-south transects indicated in Figure 3.1 (north to the left), and a longitudinal profile from the bridges to the east end of the study area. Station numbers are indicated above each

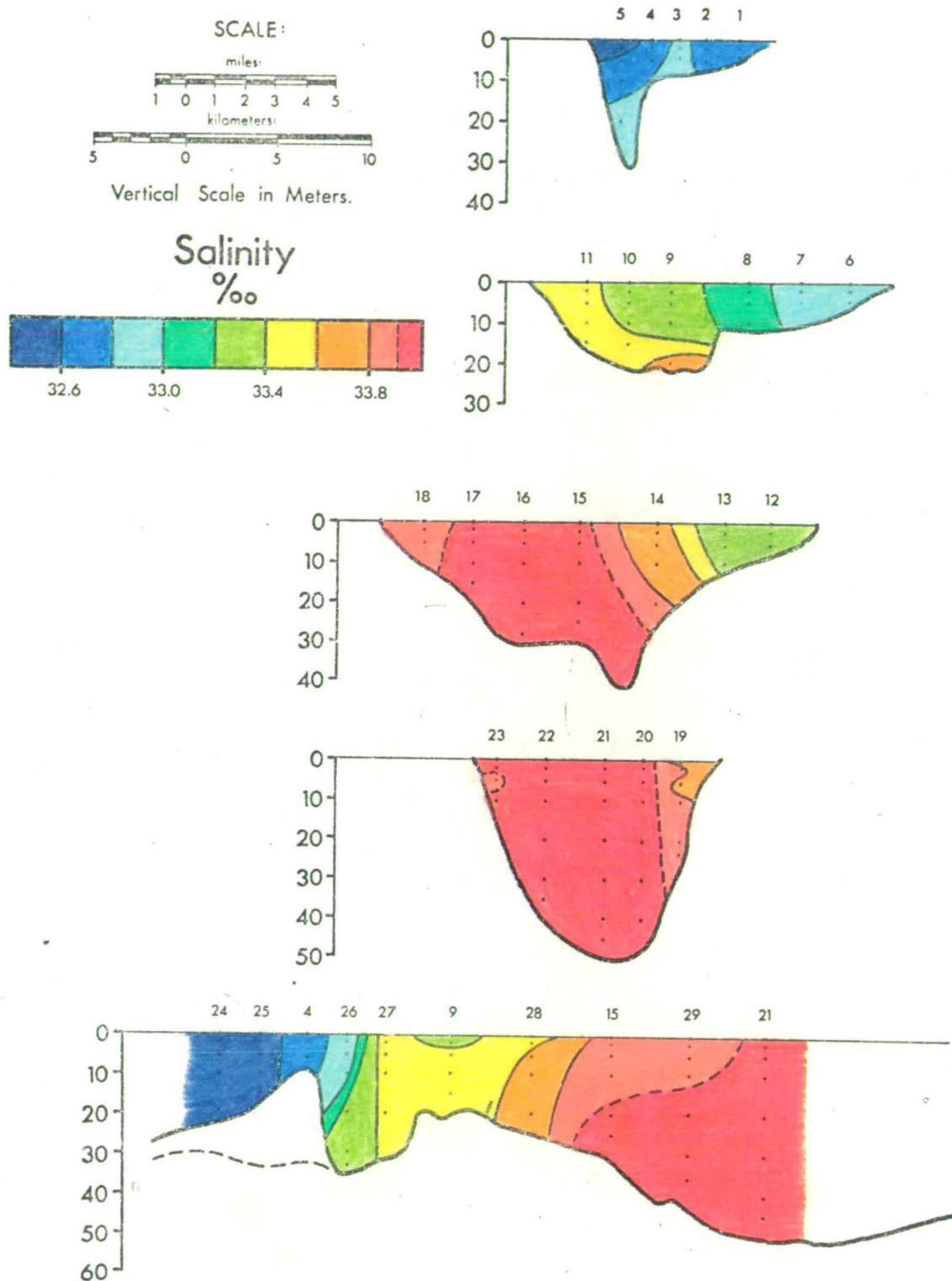


Fig. 3.2 Salinity distributions, March 17-18, 1975. See text for explanation of the format of this and similar figures.

section. The apparent sill at station 4 in the bottom section is an artefact of the sampling location, as this station was located on the southern flank of the channel.

Despite the narrow range of salinities, a distinctly estuarine pattern is indicated, with the lowest salinities to the west and along the south shore. The most abrupt salinity gradient occurs at the point of restriction of the basin (near stations 26 and 27). Values increase seaward, to the north, and with depth. The saline bottom waters in the central basin may have an impounding effect on the waters of lower salinity above the wide sediment flanks along the south shore.

Water temperatures vary with salinity (Appendix D), ranging from 5.2°C in the west to 5.7°C in the bottom waters of the central Forth.

The D.A.F.S. nutrient analyses (Appendix D) indicate a correlation between high silicate levels and the waters of low salinity. Silicate concentrations range from 4.5 to $16.2\ \mu\text{g-at l}^{-1}$. Dilution alone cannot account for all the variation in dissolved silicate levels. It is likely that biological utilization contributes to the observed seaward decrease in concentration. Dissolved phosphate is also higher in waters of low salinity, but the highest concentrations occur near Edinburgh rather than in the less saline waters to the west (Figure 3.3), suggesting that local sewage effluent constitute the primary source. The concentrations in this area ($> 4\ \mu\text{g-at l}^{-1}$) represent pollution as defined by Yentch (in Ketchum, 1969). Phosphate concentrations here compared to the rest of the study area suggest that the extent of this pollution is very limited; dilution, biological utilization and/or scavenging of dissolved phosphate by particulate matter may account for its rapid depletion.

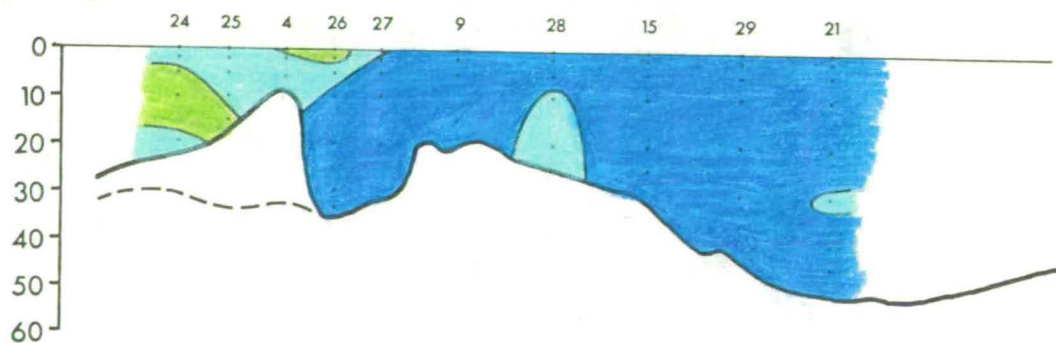
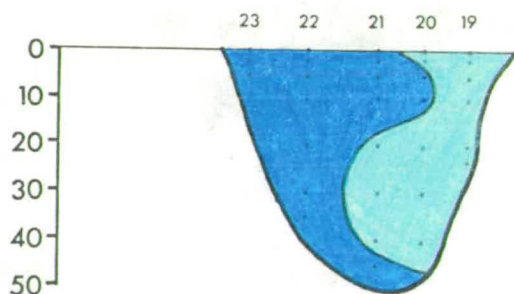
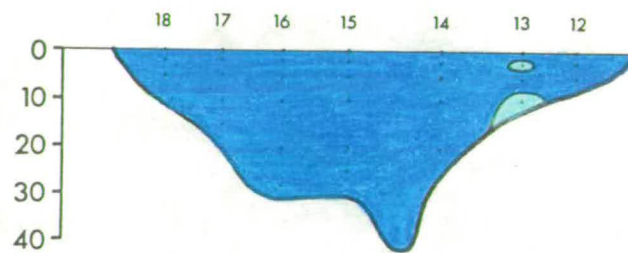
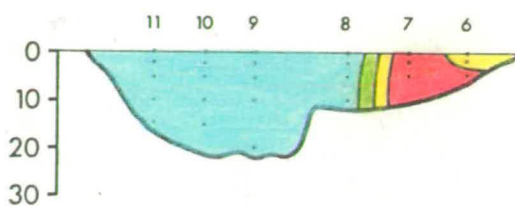
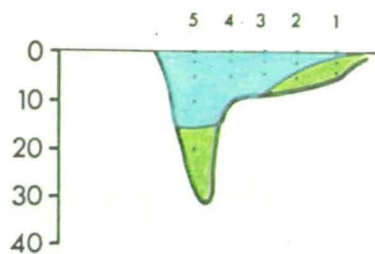
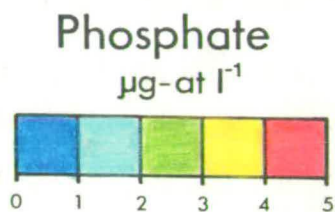
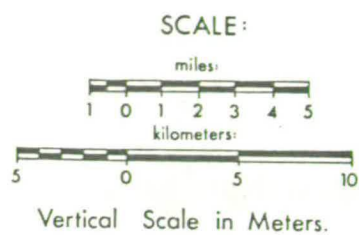


Fig. 3.3 Distribution of dissolved phosphate, March 17-18, 1975.

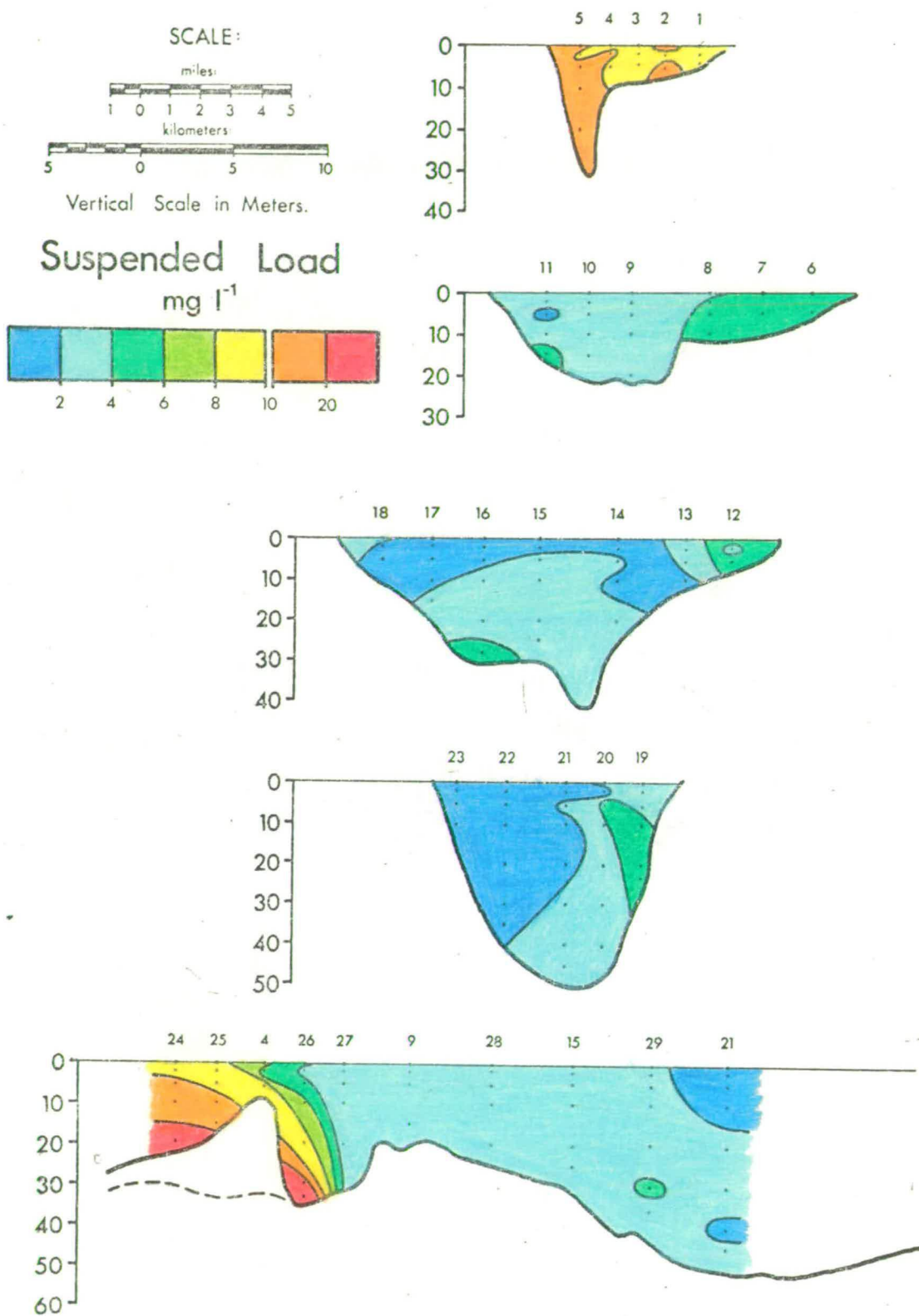


Fig. 3.4 Concentration of suspended particulate matter, March 17-18, 1975.

The areal distribution of suspended particulate matter is shown in Figure 3.4 as total suspended load in mg l^{-1} . Loadings ranged from $< 2 \text{ mg l}^{-1}$ to $> 30 \text{ mg l}^{-1}$ at the time of sampling. The highest loads were found in bottom waters to the west, with the most pronounced vertical gradient occurring at the point of channel constriction (Station 26). To the east, loads range from $> 4 \text{ mg l}^{-1}$ near the south shore to $< 4 \text{ mg l}^{-1}$ throughout most of the central basin. The lowest loads ($< 2 \text{ mg l}^{-1}$) are found in surface waters in the central Forth and to greater depths in the north-eastern extremity of the study area.

Hydrography of tidal stations.

Salinity, temperature, suspended load and current data collected during tidal cycle monitoring at stations 26, 15 and 7 may be used to determine the nature of local tidal circulation patterns and the relationship between local short-term hydrodynamic events and the suspended load. In the following figures, these parameters are shown graphically with water depth indicated on the vertical axis (with the surface water as a datum), and time through the tidal cycle is indicated horizontally. Contours are not intended to represent the movement of water masses; they simply enclose sampling points with similar data.

Waters at station 26 in the west end of the study area are typified by low salinities (consistent with the areal survey) as shown in Figure 3.5a. These range from $< 32.6\%$ in surface waters two hours after low tide to $> 33.6\%$ in bottom waters at high tide. Salinity increases with depth at all times, with the most pronounced vertical gradient occurring at the onset of flood tide. Current speeds here range from 2 to 77 cm s^{-1} (Figure 3.5b). Flood tide currents exceed 50 cm s^{-1} throughout the water column during flood tide, while stronger

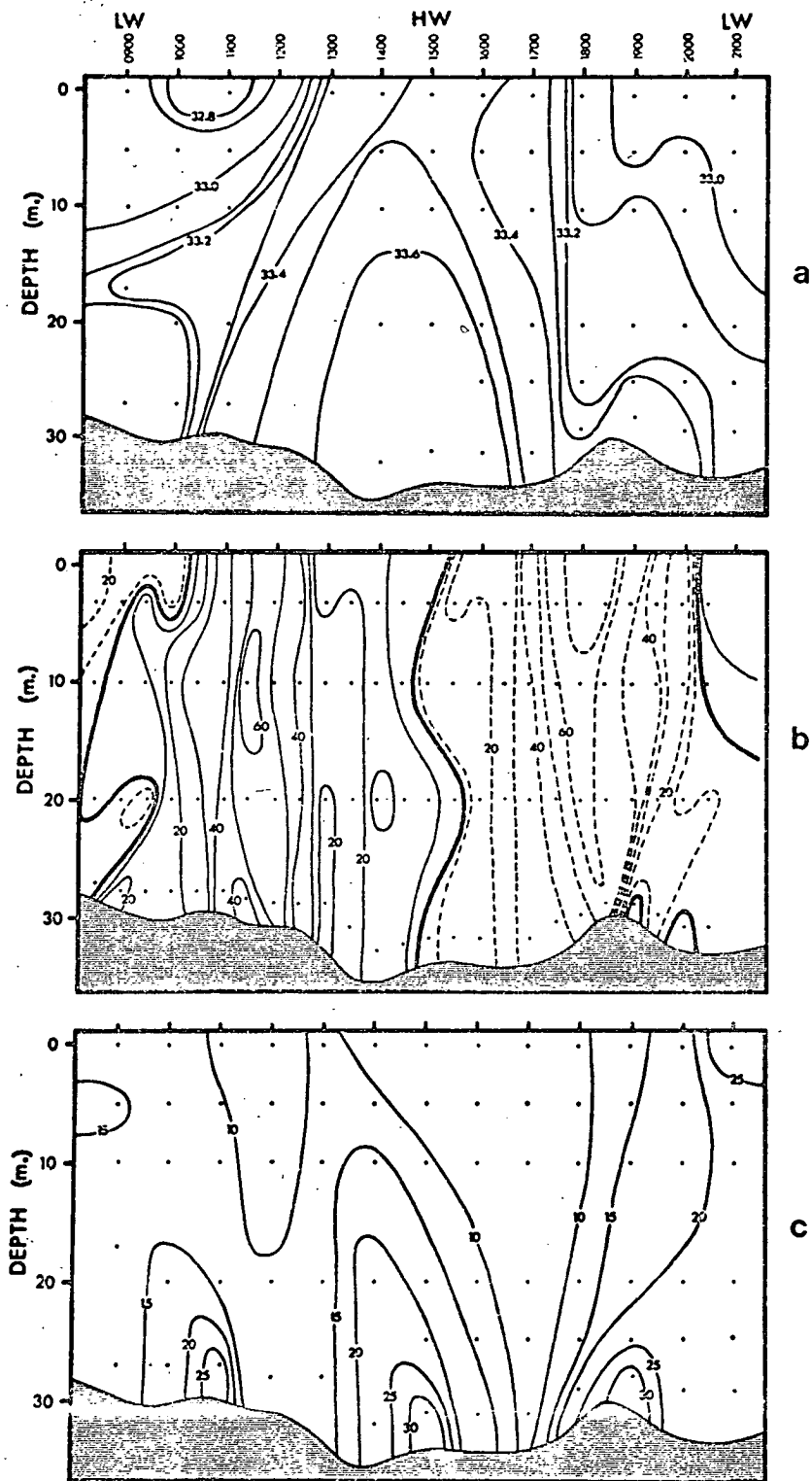


Fig. 3.5 Tidal cycle sampling at station 26, January, 20, 1977.
 a) Salinity (‰)
 b) Current speed (cm s⁻¹) (Flood tide —; Ebb tide - - -)
 c) Concentration of suspended matter (mg l⁻¹).

currents ($>60 \text{ cm s}^{-1}$) are found in the upper half of the water column during ebb flow. This pattern of accentuated ebb flow is consistent with ebb tide flow in most estuaries (Schubel, 1971b; Dyer, 1973).

Loadings of suspended particulate matter range from 6 to 31 mg l^{-1} . Three significant zones, with loads greater than 15 mg l^{-1} occur in the bottom waters after the onset of flood tide and near high water, and throughout the water column toward the end of ebb tide (Figure 3.5c). Local resuspension may account for the increased concentrations of suspended matter in the bottom waters during the onset of flood tide (1000 - 1100 hrs) and during peak ebb flow (1800 - 1900 hrs). The high concentrations in the upper water column at low water (2000 - 2100 hrs) likely result from cross-channel transport of material resuspended from the southern flank of the channel by wind-induced turbulence. The cause of the increased loadings in the bottom waters near high tide (1400 - 1500 hrs) is unclear. These occur during a period of southward flow in the bottom waters and may represent a resuspension of sediments from the side of the channel.

The tidal pattern observed at station 15 in the central basin exhibits higher overall salinities but lower energy conditions and lower loadings of suspended particulate matter than those noted at station 26. The most important hydrographic feature at this station is the abrupt vertical salinity gradient which is maintained throughout the tidal cycle (see Figure 3.6a). Salinities are consistently lower than 33.6‰ in surface waters, and exceed 34.2‰ at depths $>20 \text{ m}$. Maximum tidal flow appears to occur from 10 - 20 m depth, and is distributed symmetrically about slack water (Figure 3.6b), indicating a standing wave pattern (Dyer, 1973). The marked increase in the depth of the more saline deep waters during flood tide does not indicate

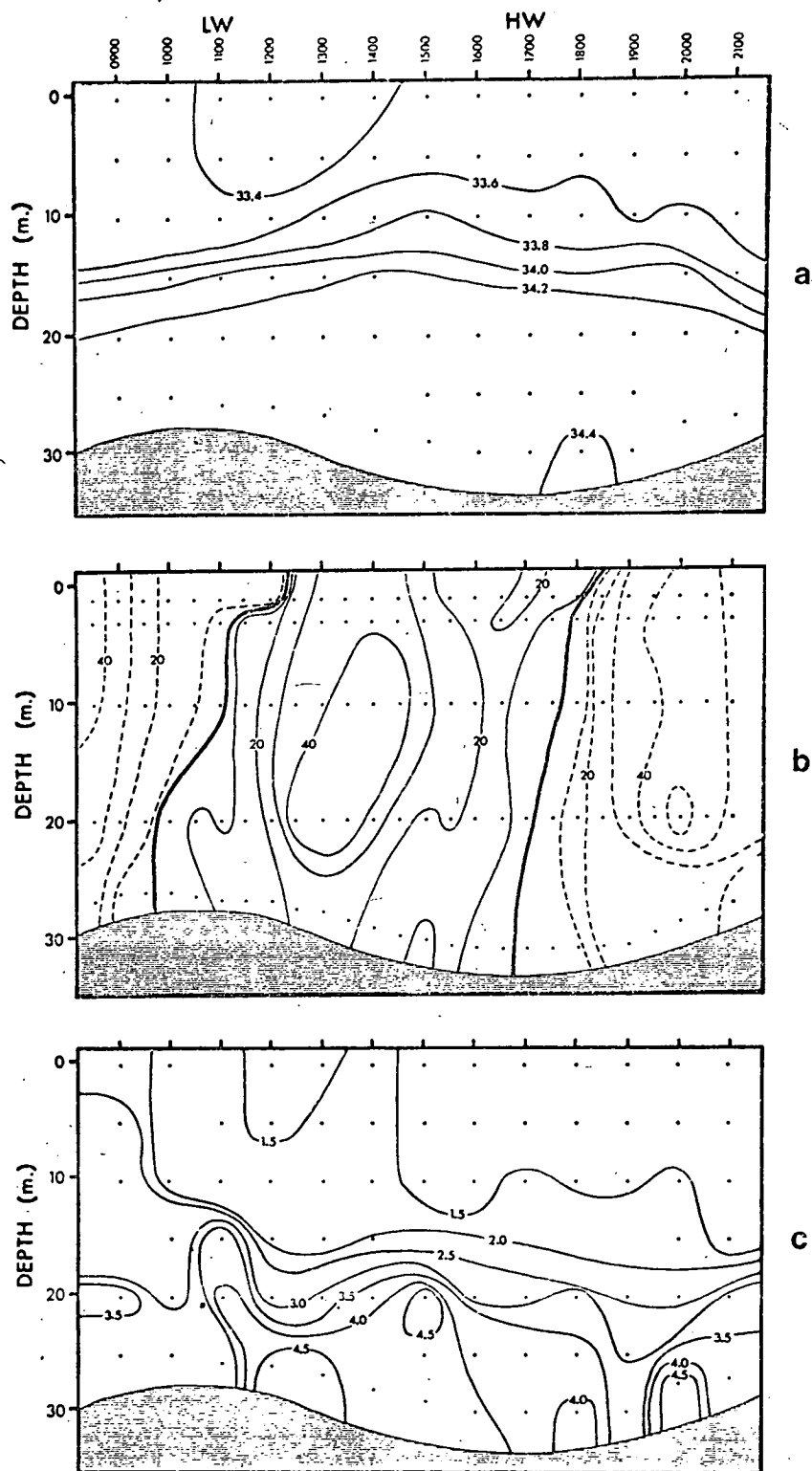


Fig. 3.6 Tidal cycle sampling at station 15, February 8, 1977.
a) Salinity ($^{\circ}/_{\infty}$)
b) Current speed (cm s^{-1}) (Flood tide —; Ebb tide - - -)
c) Concentration of suspended matter (mg l^{-1}).

the incursion of a tidal wedge, since maximum flow appears to occur in the central basin. Bottom waters consistently flow more slowly than those at ~ 20 m depth, and thus must indicate bottom drag effects by the sediment substrate. Both flood and ebb tidal movement appear to be initiated in the bottom waters.

The loadings of suspended particulate matter show little gross variation, and are far less than those seen at station 26. However, a consistent difference in suspended load concentrations is evident between surface and bottom waters at station 15 (see Figure 3.6c). Concentrations of 2.0 mg l^{-1} typify the upper half of the water column (< 15 m), while loads in excess of 3.0 mg l^{-1} are common at depths > 20 m. Slightly higher loads ($> 4 \text{ mg l}^{-1}$) are found in bottom waters during flood tide, and may reflect resuspension of local sediments at this time.

The south side of the estuary, as represented by tidal cycle sampling at station 7 (Figure 3.1) on April 4, 1977, is typified by a shallow (~ 12 m), relatively homogenous water column with the lowest energy conditions of the three stations studied. Salinities here range from 33.7 to 33.9‰ (Figure 3.7a), with only a slight indication of higher values in the bottom waters. These values are intermediate between those noted at stations 26 and 15.

Maximum tidal current speeds occur in the surface waters at station 7 (< 5 m) during ebb tide. The flow here is asymmetrical about slack water. The highest flood tide currents occur 4 to 5 hours after low water, while seaward movement is initiated soon after high tide and is characterised by stronger and more prolonged flow. Unfortunately, strong southwest winds which reinforced the surface currents late in the sampling programme took the boat almost 2 km off

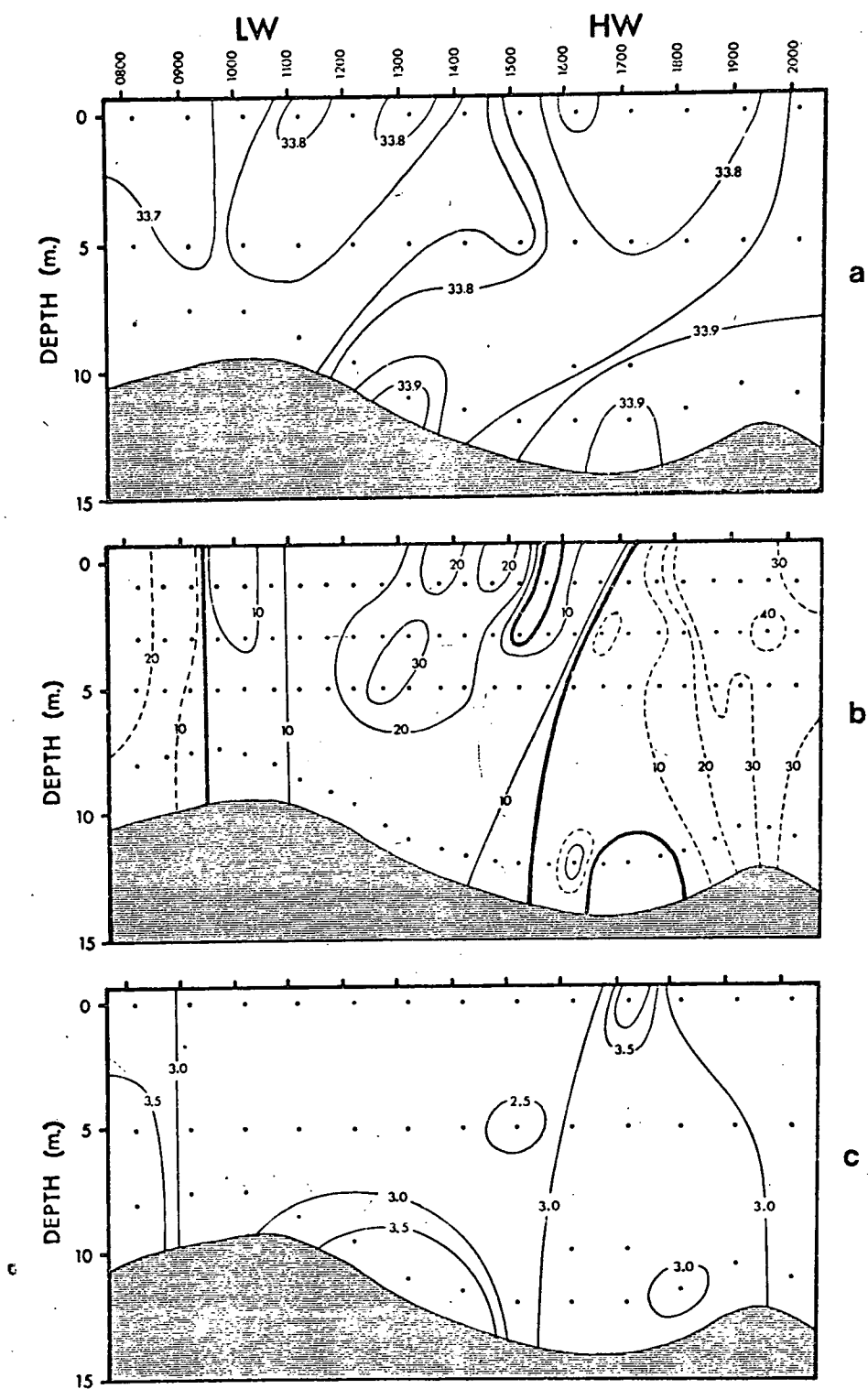


Fig. 3.7 Tidal cycle sampling at station 7, April 19, 1977.
 a) Salinity (‰)
 b) Current speed (cm s^{-1}) (Flood tide —; Ebb tide - - -).
 c) Concentration of suspended matter (mg l^{-1}).

the original station in the last three hours of sampling, so data toward the end of the day are somewhat tenuous.

Loadings of suspended particulate matter vary between 2.4 and 4.1 mg l^{-1} (see Figure 3.7c). Little vertical gradation is apparent, and the essentially homogeneous nature of the particulate loading at any one time is an important characteristic of this area, reflecting effective mixing of the shallow water column. The highest concentrations of suspended particulate matter occur in the early stages of ebb tide, and in the near-bottom samples during peak flood tide flow.

3.4 The hydrodynamic environment of particulate matter.

The areal salinity distributions observed during the March 1975 sampling programme (Figure 3.2) are consistent with the gross pattern of a partially mixed estuary as defined by Pritchard and Carter (1971). The narrow range of salinities noted at that time and during tidal station monitoring indicate a marine-dominated environment with little dilution of North Sea waters (salinity 34.5‰ (Corlett, 1972)) by freshwater flow.

Average salinities were determined on the basis of the volumetric study described in Appendix C, using the salinity data from the areal sampling programme. Dilution of seawater by river flow was found to range from ~5‰ in the west to ~1.4‰ in the east. With a volume of $1.3 \times 10^{10} \text{ m}^3$ (Chapter 2) and an average freshwater discharge of $\sim 65 \text{ m}^3 \text{ s}^{-1}$, this indicates an approximate flushing time of 54 days, according to the freshwater dilution method of Dyer (1973).

Two important aspects of the loading of suspended particulate matter in the Forth have been demonstrated here for the first time. The first is the areal distribution of this material. The markedly high concentrations in the west may indicate local sources and

possibly entrapment of suspended matter in this area. Along the south shore, concentrations are higher than in the main basin of the Forth. It is unclear from gravimetric analyses alone whether this indicates dilution and transport of suspended matter or partial impoundment of locally derived and reworked material.

The second major point shown in the preceding figures is the marked difference in the patterns of suspended matter concentrations at the three tidal stations. In the west (Station 26), high loads ($>10 \text{ mg l}^{-1}$) persist through most of the tidal cycle, while pronounced short-term increases occur in the bottom water at three times: early in flood tide, at high water, and during peak ebb flow. During late ebb tide, high concentrations throughout the water column likely reflect the effect of wind-induced turbulence and transport. The combined effects of high energy conditions and the restrictions imposed by a narrow channel are reflected in the complex patterns of loading. By contrast, the data from Station 15 indicate a two-phase system, with slightly higher concentrations in the bottom half of the water column. This demarcation between top and bottom waters is stable throughout the tidal cycle, but some further enhancement of bottom water loads is evident during flood tide. In the shallow waters to the south (Station 7), an essentially homogeneous suspension persists throughout the tidal cycle.

Because the distribution of suspended particulate matter appears to be controlled by physical processes, more detailed assessment of water movement is necessary. The tidal current data were resolved into longitudinal (upstream/downstream) and cross-channel vectors to permit better distinction of the flow characteristics (see Appendices C and D). The axis of the main channel was taken to be 070° .

The derived vector components are shown in Appendix D.

This study showed that the major upstream and downstream tidal current vectors are essentially consistent with the current speeds shown in Figures 3.6b, 3.8b and 3.9d, and dominate cross-channel flow except at slack water. Basin configuration, therefore, largely dictates tidal flow.

At station 26, cross-channel flow varies considerably, indicating a mild 'sloshing' effect in the narrow channel. Pronounced northward flow during ebb tide is indicated in the surface waters, however, and may account for the introduction of much of the particulate material at the end of the sampling period. At station 15, cross-channel flow is minimal compared to the upstream/downstream movement, but a fairly consistent southward movement toward the end of flood tide is indicated in the surface waters, while northward flow occurs at depths > 20 m throughout much of the tidal cycle.

Cross-channel effects are most pronounced at station 7, where this component constitutes over 30% of the net flow. Westward flow during flood tide is accompanied by a southward cross-channel flow, particularly in the bottom waters. Near slack water, and consistently throughout ebb tide, surface waters here flow seaward and pronouncedly northward, toward the central basin of the estuary.

On the basis of areal salinity distributions, Craig (1972) hypothesised an outflow of less saline water along the south shore of the Forth as a result of Coriolis deflection of ebb tide currents. The present study, however, suggests that tidal movement is dictated by basin configuration and the sheer volume of the tidal incursion. Mass upstream movement during flood tide, particularly in the deep waters of the central basin, appears to force the ambient water upstream and inshore, shouldering the local waters landward above the

shallow southern flanks of the Forth. Release of this impounded waterhead results in an eastward and northward spilling due to gravitational flow. The reduced salinities along the south shore probably reflect local freshwater input rather than classical estuarine flow.

Estimates of the average flow and the flux of suspended particulate matter were derived using the longitudinal and cross-channel current vectors and suspended loads from each tidal station for the first 12 hours of monitoring. The suspended sediment flux at a point in time is the product of the suspended load and the measured current velocity, yielding a flux in $\text{g m}^{-2} \text{s}^{-1}$ (cf. Buller (1975) and d'Anglejan and Ingram (1976)). Rather than integrating these values to depth at each sampling time as was done by Buller (1975), the author elected to derive a value for average current velocity and suspended sediment flux at each sampling depth through the tidal cycle by vector analysis. This procedure is outlined in Appendix C.

The net flow at station 26 is seaward at depths < 20 m, and upstream in deeper waters (see Figure 3.8a). A similar pattern is indicated in Figure 3.8b for the net flux of suspended particulate matter, except that the upstream movement in the bottom waters is accentuated. Smith and Parsons (1965) noted a net westward transport of silt in the northern channel near by means of radioactive tracers. Smith et al (1965) showed net seaward movement in the south channel (in Craig, 1972). Average cross-channel flow varies from northward ($\sim 6 \text{ cm s}^{-1}$) in surface and bottom waters to southward at depths of 10 - 20 m, but net sediment flux is northward at all depths, notably in the surface waters, indicating that much of the material in suspension is derived from the south.

In the central estuary, net seaward flow occurs only in the

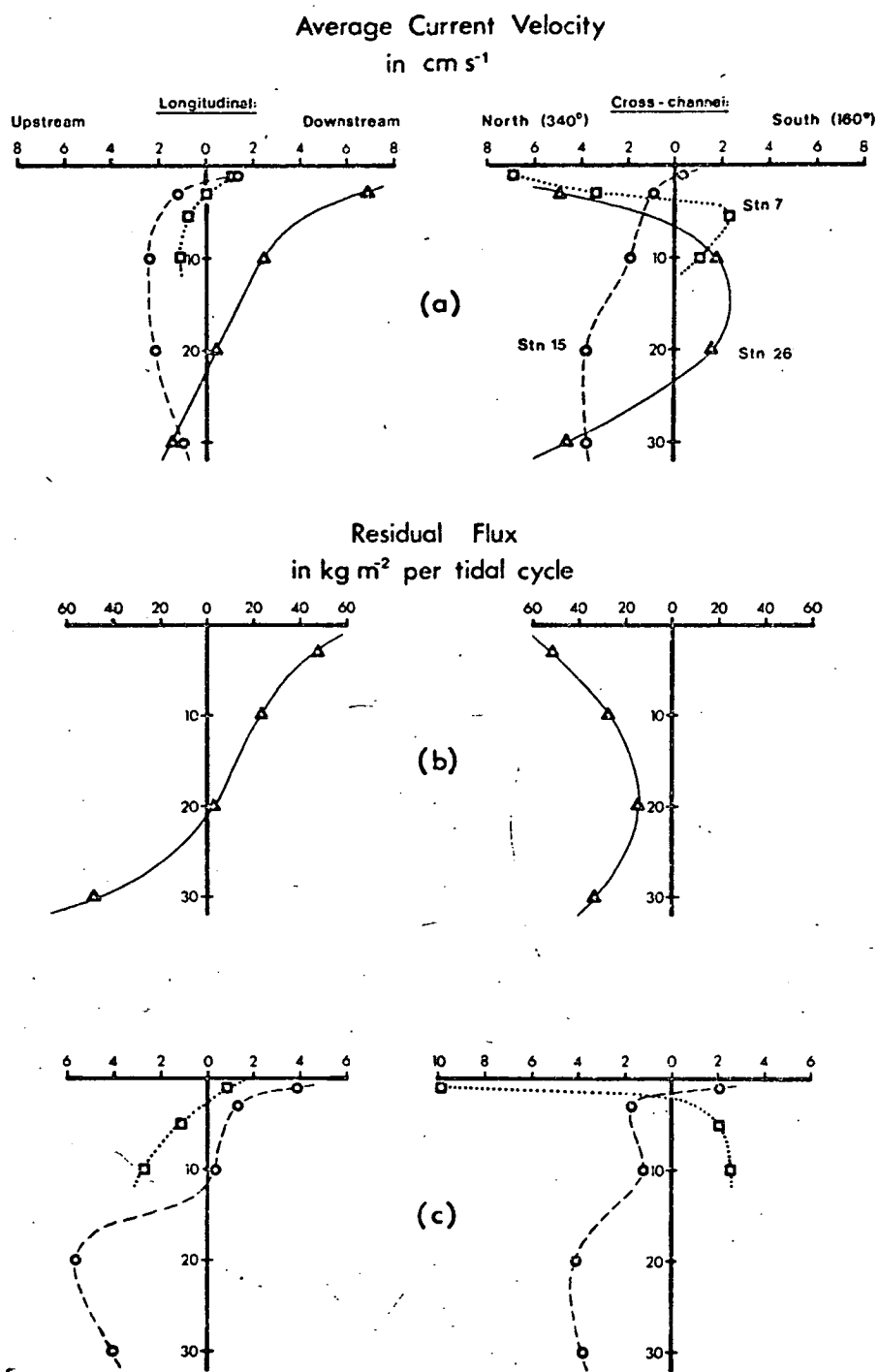


Fig. 3.8 Mean water movement and net flux of suspended matter during tidal station monitoring

- a) Average current velocity in longitudinal and cross-channel components
- b) Residual flux of suspended matter, station 26
- c) Residual flux of suspended matter, stations 15 and 7.

surface waters (~ 1 m), with upstream movement in deeper waters, mainly at 10 - 20 m depth. Cross-channel flow is progressively more northward with depth. Here, a net seaward flux of suspended matter is indicated at depths < 10 m, but more pronounced upstream and northward transport occurs with increasing depth.

At station 7, the residual cross-channel flow and sediment flux exceed the magnitude of the longitudinal components. Pronounced northward flow and sediment transport are indicated in surface waters, with net movement in the opposite direction at depths > 5 m. Residual seaward movement appears to occur only in the surface waters (< 3 m).

These findings provide some evaluation of the environment and transport of the suspended particulate matter in the Forth at the time of sampling. Before further interpretation is possible, much more detailed investigations into the composition and particle size characteristics of the suspended matter as functions of location, water depth and energy conditions are necessary. Gravimetric loading data alone are insufficient indicators of the fate of specific particulate components.

CHAPTER 4

LOADING AND PARTICLE SIZE

4.1 Introduction.

The purpose of this chapter is to determine the size distribution characteristics of suspended particulate matter samples collected from the Firth of Forth in conjunction with tidal station monitoring. Modified pipette analyses were performed at half-phi intervals on 16 particulate and 6 sediment samples. Of prime interest are the basic size distribution characteristics, the relationship between loading and particle size, and the degree of similarity between particulate matter and the underlying sediments. Further, samples from different areas of the Forth and from the inner estuary may be compared to determine the extent to which the loading of suspended particulate matter may be indicative of variations in character.

Several previous estuarine studies have involved size analyses of particulate matter, usually by visual means (Bond and Meade, 1966; d'Anglejan and Smith, 1973) or by automatic counting methods (Schubel, 1968). Volume-weighted calculations have been applied by Schubel (1971a) to provide better approximation of particle mass. In the present study, the physical separation of successive size fractions by pipette analysis permits a more direct evaluation of weight distribution with size and also provides samples of varying maximum size for later chemical determinations.

Previous studies have shown that nearly all estuarine particulates are smaller than 100 μm , with the majority being much finer-grained (Meade, 1972). Material of size less than 1 μm constitutes a significant proportion, while the abundance of very coarse particles often varies with the speed of tidal currents (Schubel, 1971; Nicholls, 1972). Differences in size distribution characteristics between samples may

indicate different sources (Bond and Meade, 1966). In the present study, such hypotheses will be examined in the light of later mineralogical (Chapter 5) and chemical (Chapter 6) studies.

4.2 Methods.

Field procedures were similar at all stations. The most detailed sampling in conjunction with tidal flow took place at station 26. Here, eight five-litre water samples were collected for pipette analysis, representing top and bottom waters at various stages of the tidal cycle. Further, a shallow gravity core with a relatively undisturbed sediment-water interface was retrieved, and samples of particulate matter from immediately above the core top (10 cm) and from the surface of the sediment itself were retrieved using narrow plastic tubing attached to a 50 ml syringe. In addition, ambient water was discharged rapidly from the syringe from a height of ~20 cm above the core top, and a sample of artificially resuspended sediment was extracted.

All storage containers had been pre-washed, soaked for 24 hours in 10% hydrochloric acid and rinsed several times with filtered distilled water. Particulate samples were stored in five-litre polythene bottles; sediment and resuspended sediment samples were stored in 75 ml glass vials. All pipette analyses were initiated within 48 hours of sampling.

In the central estuary (station 15) only one particulate sample was collected from the bottom water, because little accuracy of pipette data was anticipated with samples of such low load. Here a sample of the bottom sediment (core top) was obtained by the method described earlier.

Six five-litre water samples were collected from top and bottom waters at station 7 during three stages of the tidal cycle during a sampling programme in August 1976. Inclement weather forced the

abandonment of this sampling programme, and these samples do not correlate directly with the tidal station sampling at this station as presented in the previous chapter. A bottom sediment sample was retrieved for analysis.

Two additional samples were obtained from the inner estuary at a sampling location near Grangemouth for comparative purposes. One five-litre sample representing suspended particulate matter was collected, and one sample of the material at the sediment-water interface was retrieved as described earlier.

On return to the laboratory, all pipette analyses were initiated within 48 hours of field sampling. Suspended particulate samples were agitated and pipetted directly from the five-litre storage containers. Sediment and resuspended sediment samples were dispersed in 1 litre of filtered distilled water and sampled from a graduated cylinder.

Aliquots of these suspensions were withdrawn by pipette at times and depths consistent with standard half-phi pipette sampling procedures (Müller, 1967; Royse, 1970) as indicated in Appendix C, and were vacuum-filtered through preweighed 0.4 μm pore-size, 37 mm diameter Nuclepore[®] membrane filters. The volume of each aliquot was selected to ensure that the filtered particulate sample was within weight limits which would permit later X-ray fluorescence analysis (0.1 - 2 mg). Each sample was rinsed with filtered distilled water immediately after filtering to remove sea salts.

The data of particulate loadings as presented here and in Appendix E refer to the weight of material in the pipette sample containing particles of size less than or equal to the stated diameter. Phi-units have been used to indicate particle size ($\phi = -\log_2$).

(particle size in mm)) (see Table 4.I). These designate hydraulically equivalent settling rates, and do not necessarily indicate a measured diameter. The accuracy of these size estimates will be examined further in the next chapter.

TABLE 4.I

Metric equivalents (in μm) of phi size (ϕ) intervals.			
PHI	μm	PHI	μm
3.0	125	6.5	11.0
3.5	88.4	7.0	7.8
4.0	62.5	7.5	5.5
4.5	44.2	8.0	3.9
5.0	31.2	8.5	2.8
5.5	22.1	9.0	2.0
6.0	15.6	10.0	1.0

4.3 Results.

The weights of suspended particulate matter and sediment samples from Station 26 in the western end of the Forth are shown for successive pipette subsamples in Figure 3.1. Total loads range from $<10 \text{ mg l}^{-1}$ in surface waters to $>20 \text{ mg l}^{-1}$ in bottom waters. The weights shown are fairly accurate, but due to problems of humidity in the weighing room, the lighter sample loads in particular may reflect some moisture content.

All bottom water loads exceed those of their respective surface waters, except at low water at the end of the sampling period. At this time, the flow direction in the surface waters is opposite to that at depth. The higher loadings of coarse-grained material here probably reflect lateral transport, possibly of resuspended sediment from the southern flank of the channel. It is important to note that differences in loading are primarily expressed in material of size

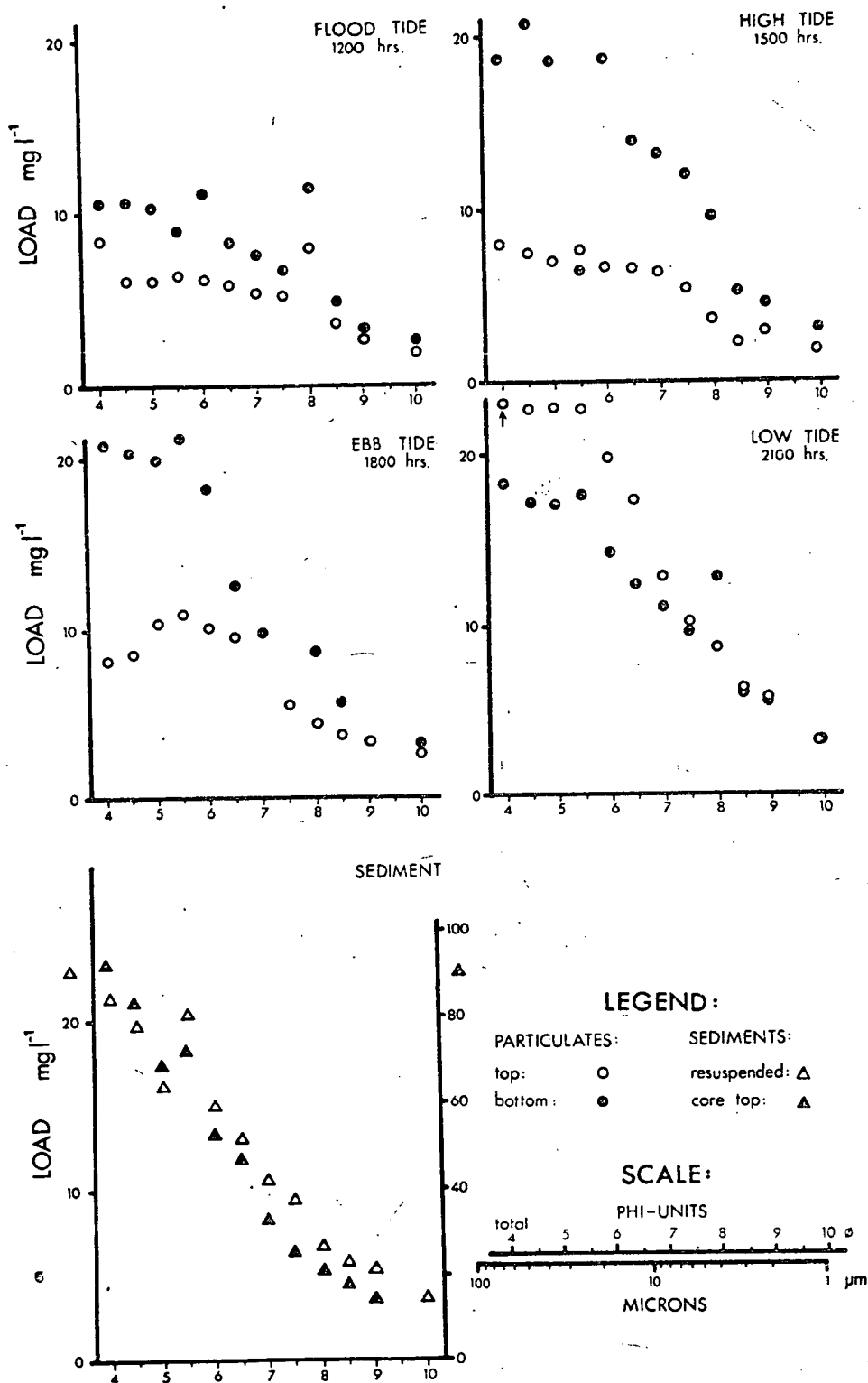


Fig. 4.1 Concentration of suspended matter and sediments (mg l^{-1}) versus maximum particle size in pipette samples from station 26.

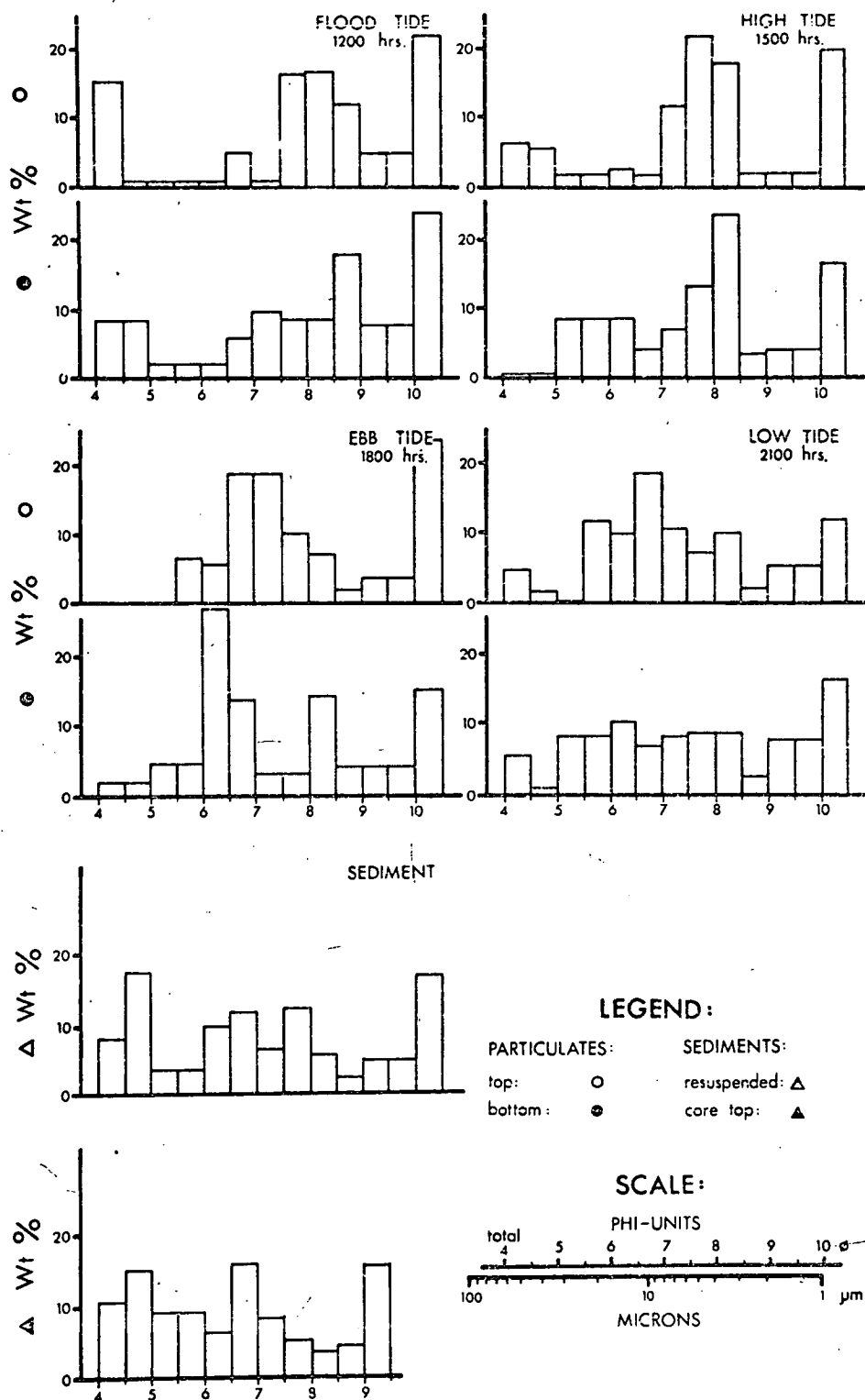


Fig. 4.2 Histograms of particle size distribution by weight for samples from station 26.

NOTE: Due to low pipette sample weights, these and subsequent histograms are subject to minor interpretive error.

greater than 8ϕ . Despite the differences in the original concentration ($8-24 \text{ mg l}^{-1}$), the finest fractions (10ϕ) of all particulate samples are present in roughly equal concentrations ($1.5 - 3.0 \text{ mg l}^{-1}$) in top and bottom waters. This indicates that a relatively uniform fine-grained suspension occurs, while more coarse-grained matter is intermittently introduced and lost.

From these data, histograms of the frequency distribution were prepared as shown in Figure 4.2. These indicate a multimodal size distribution. Clay-sized particles (10ϕ) account for 10-20% of the total sample weight. A second size mode varies from 6ϕ to 8ϕ , and can be identified in most samples. The relative amount of this material appears to be greater in bottom water samples. The prominence of the coarsest mode (coarse silt) varies, but is most notable in the sediment samples.

At station 15, only one suspended particulate matter sample was pipetted, due to anticipated problems of accuracy with the low concentrations of material. This was collected from the bottom waters at 1400 hours. Only this sample and the bottom sediment sample are shown in Figure 4.3, since the weights of the resuspended sediment pipette suite were too inconsistent to permit gravimetric interpretation.

The most significant feature of both the particulate and sediment samples at station 15 is the abundance of coarse-grained material. Over 60% by weight of both samples consists of material of size greater than 6ϕ , compared to $\sim 20\%$ for similar size modes at station 26. Loadings of the suspended particulate sample range from 8.6 mg l^{-1} in total to 1.33 mg l^{-1} in the finest fraction. The first value is anomalously high relative to the loadings noted in the previous chapter

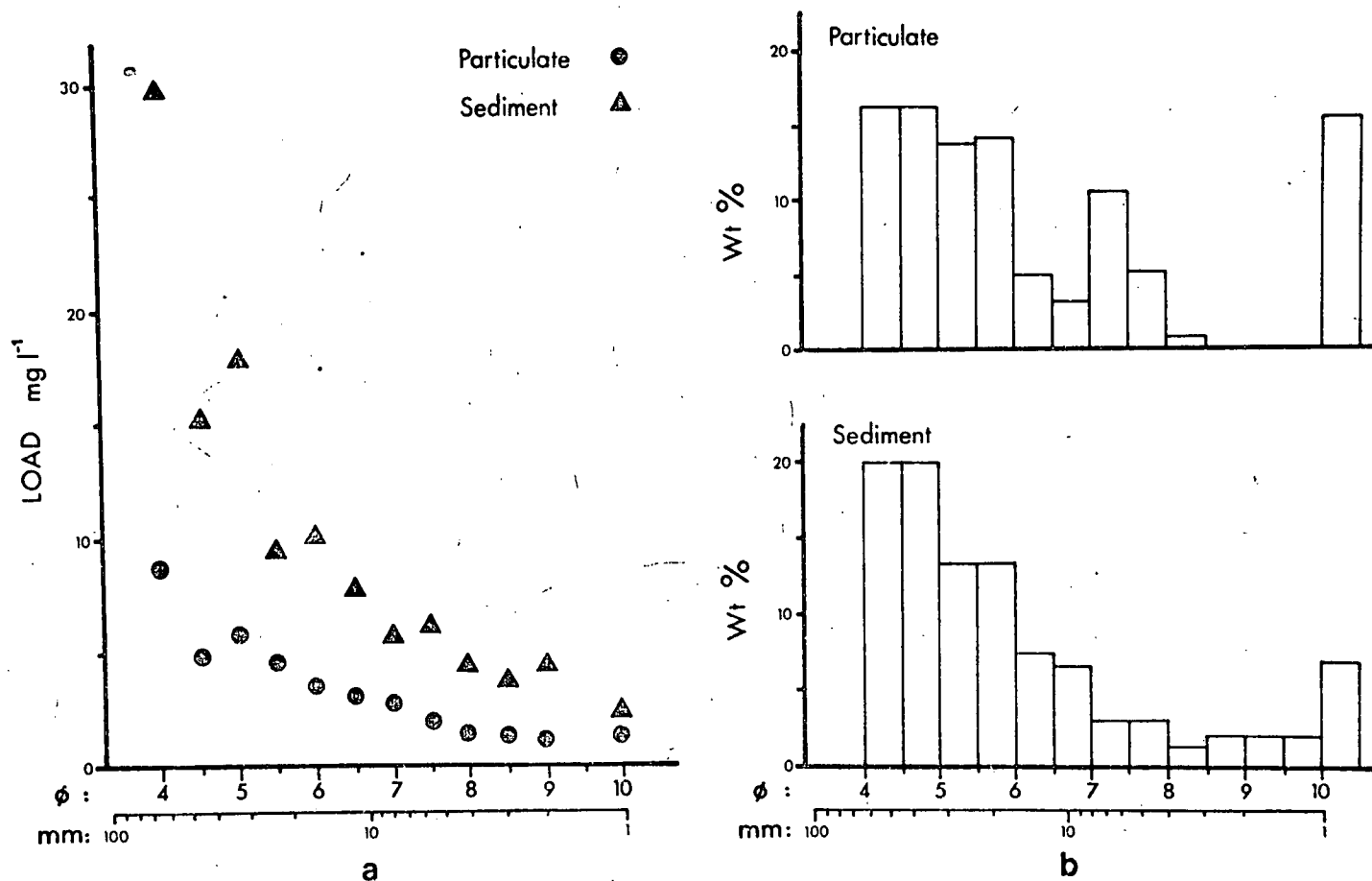


Fig. 4.3 Particle size characteristics of pipette samples from station 15
 a) Concentration versus maximum particle size
 b) Histograms of size distribution.

(Figure 3.6c), and may reflect random capture of large particles; at sizes less than 4.5ϕ , however, the concentration of suspended material is more consistent with the values reported earlier. The similarity between the particle size distribution characteristics of the suspended matter and the bottom sediments here indicates the likelihood of some relationship between them. However, energy conditions here are far lower than those noted at station 26; both this fact and the low total suspended loads in this area argue against a solely mineralogenic character of the coarse-grained material. It is more likely to be biogenic in origin, but this will be examined further in subsequent chapters.

The samples from station 7 (Figures 4.4 and 4.5) are anomalous in that they show pronounced coarse-grained modes in the particulate matter. The concentrations of suspended matter here range from 10 to 36 mg l^{-1} . These far exceed the loadings noted during tidal station monitoring (Chapter 3), and probably reflect the storm conditions experienced at the time of collection (August 26, 1976). Loadings of the clay-sized fraction (10ϕ) are similar in all samples, ranging from 0.9 to 1.4 mg l^{-1} . Most samples show similar loadings for all the material of size less than 4.5ϕ of $\sim 7 \text{ mg l}^{-1}$. The prominence of coarse-grained constituents in the suspended samples in conjunction with the lack of such material in the underlying sediment suggests that this fraction is introduced from other sources, possibly as biogenic material or waste from nearby effluent sites. The abundance of this material masks small-scale size modes in Figure 4.5, but some indication of the three basic size fractions described earlier is apparent.

The loading and size distribution characteristics of one particulate

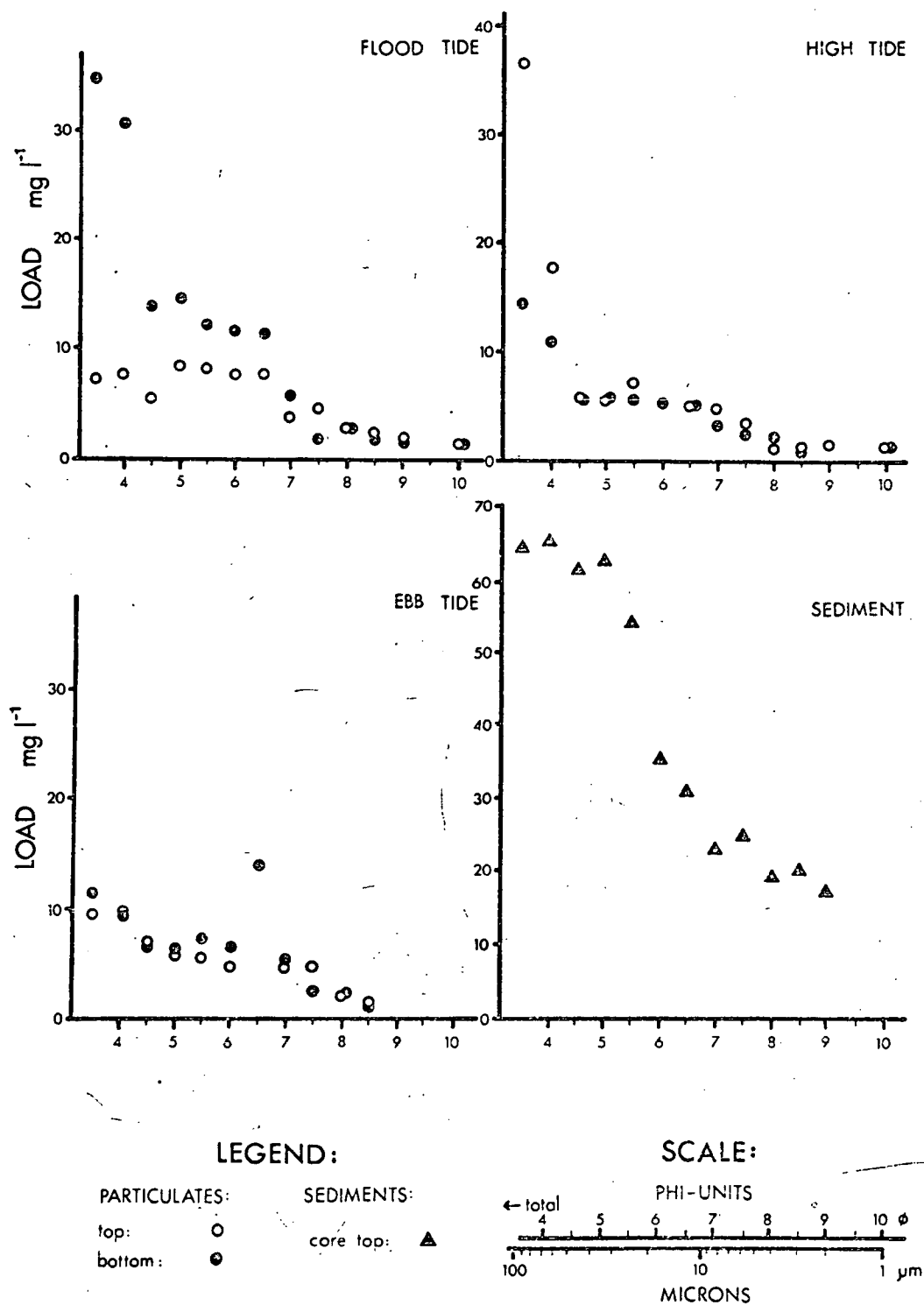


Fig. 4.4 Concentration of suspended matter versus maximum particle size in pipette samples from station 7.

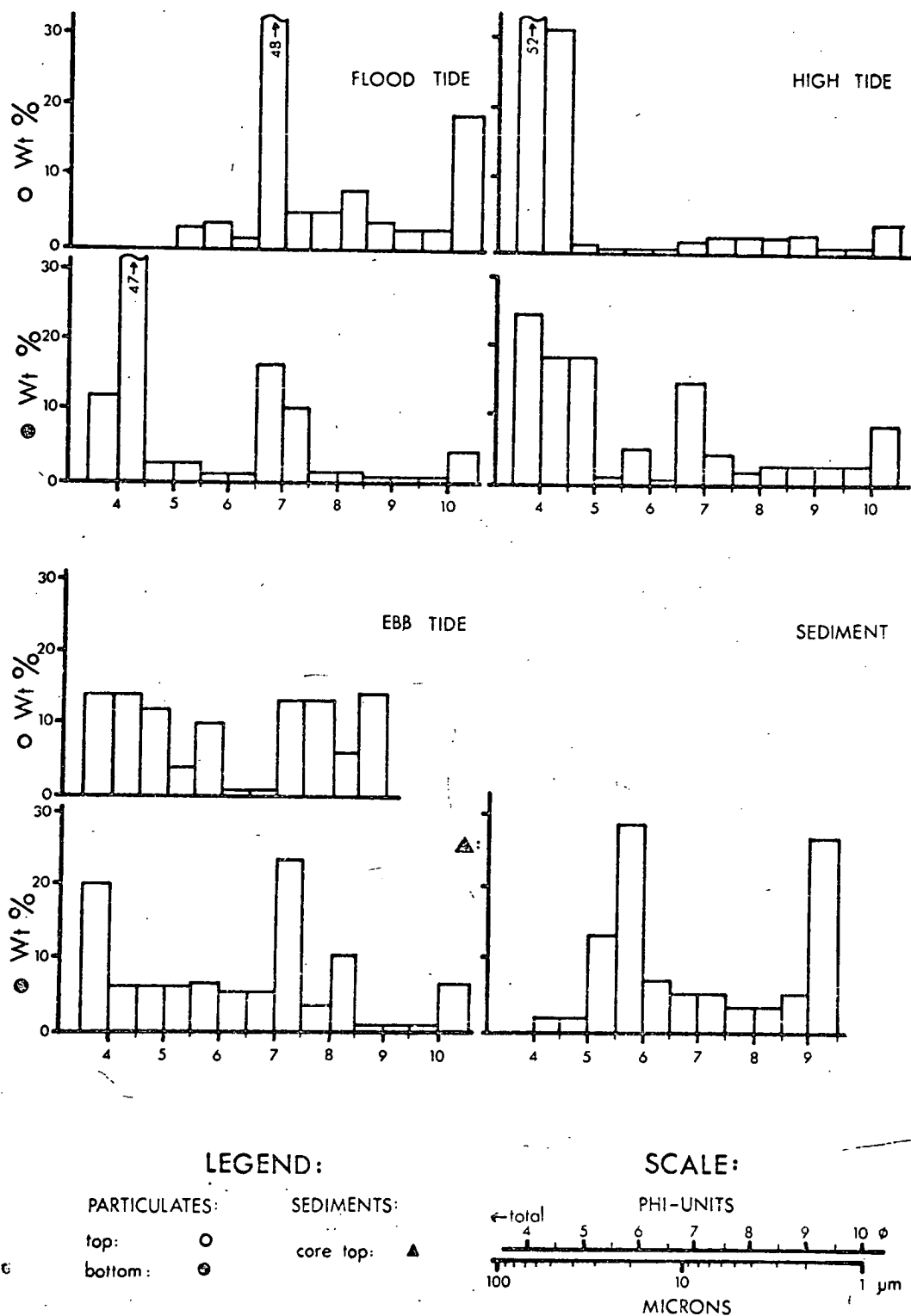


Fig. 4.5 Particle size distribution, station 7.

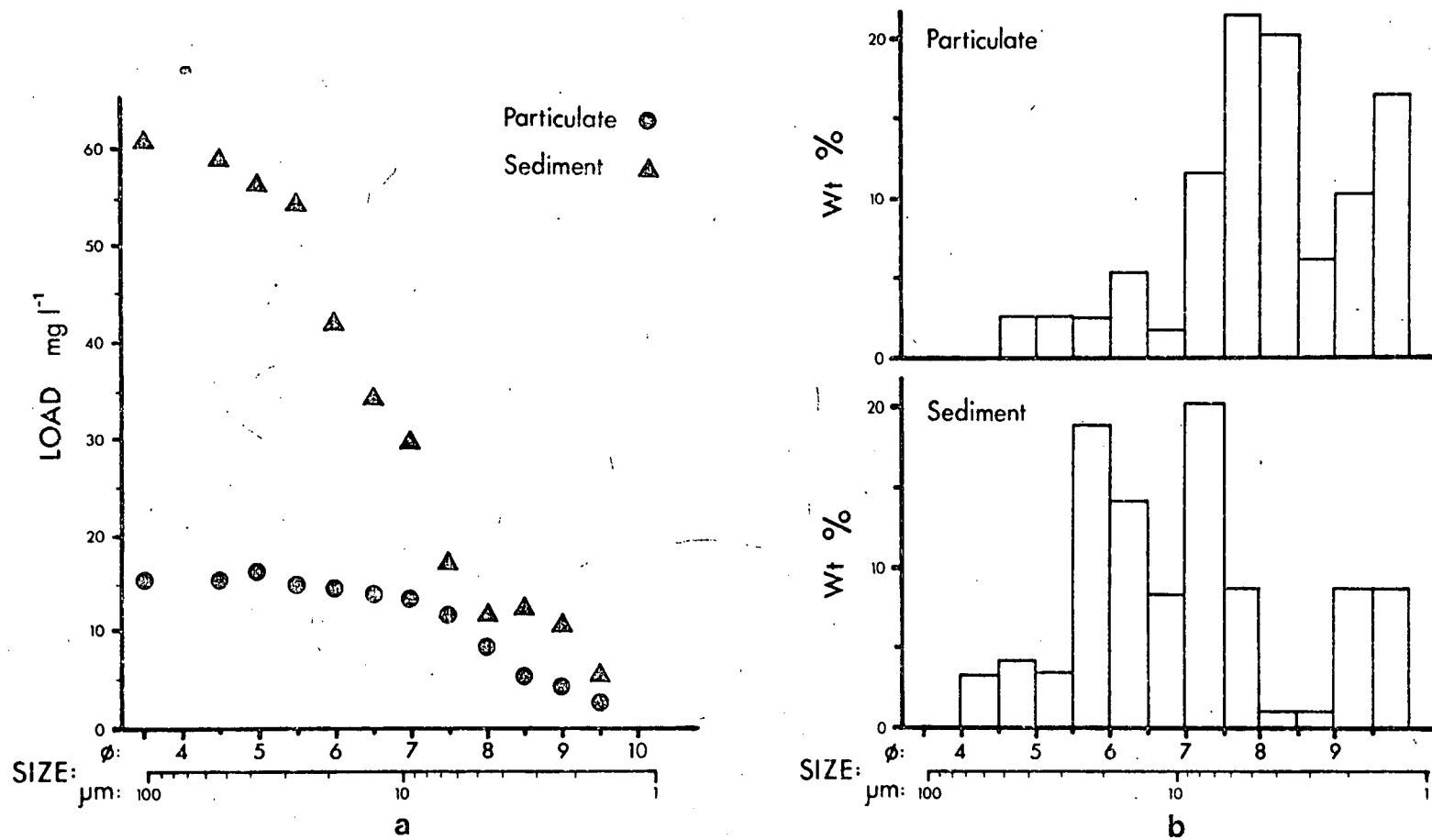


Fig. 4.6 Particle size characteristics of samples from the inner estuary (near Grangemouth)

a) Concentration versus maximum particle size

b) Histograms of size distribution.

sample and one sediment sample from the inner estuary near Grangemouth are shown in Figure 4.6. The suspended particulate sample shows a total loading of 15.6 mg l^{-1} , which is consistent with the range noted at station 26, but it consists of much finer-grained material than was noted at any of the other stations. Both this and the sediment sample show significant percentages of fine-grained material and a second mode of fine silt-sized particles of size $\sim 7 - 8\phi$. Only the underlying sediment contains significant amounts of coarser material.

4.4 The gravimetric character of suspended particulates.

From the presentation of these results, it appears that a multimodal size distribution characterises the suspended particulate matter and sediments in the Firth of Forth. Variations in the character of the samples from different areas and depths reflect different local energy conditions, differential settling rates and/or different sources of at least some of the material. Clay-sized material ($10\phi, \leq 1 \mu\text{m}$) is present in significant amounts in all samples. A second size mode from $6 - 8.5\phi$ ($15 - 4 \mu\text{m}$) represents fine silt-sized particles, while the abundance of coarser material ($\phi < 6$) varies considerably in the samples. Locally, the abundance of this last mode appears to dictate the overall differences in suspended loads between samples.

A summary of the loading and partitioning of material among these size modes is shown in Table 4.II. The multimodal character of the samples and the limited accuracy of size distribution calculations preclude detailed statistical evaluation, but the mean particle size has been calculated from cumulative frequency distribution curves by the formula:

$$M\phi = \frac{\phi_{84} - \phi_{16}}{2}$$

TABLE 4.I

Summary of the loading and size distribution characteristics of pipetted samples.

STATION	TIDE	DEPTH	LOADING (mg l^{-1})		WEIGHT DISTRIBUTION (%)			MEAN SIZE ϕ
			4 ϕ	10 ϕ	c.silt	f.silt	clay	
26	flood	surface	8.32	1.85	17.3	60.5	22.2	7.62
	flood	bottom	10.58	2.50	19.9	56.5	23.6	7.67
	slack hw.	surface	7.86	1.60	16.0	63.6	20.4	7.82
	slack hw.	bottom	18.70	3.08	17.0	66.5	16.5	7.53
	ebb	surface	7.97	2.54	6.5	69.8	23.7	7.97
	ebb	bottom	20.62	3.12	12.1	72.8	15.1	7.35
	slack lw.	surface	24.45	3.00	18.7	69.0	12.3	7.30
	slack lw.	bottom	18.27	3.03	22.5	60.9	16.6	7.47
	-	resp. sed	21.32*	3.48*	30.2	53.5	16.3	6.95
15	flood	sediment	93.18*	14.52*	43.1	41.3	15.6	6.43
		bottom	8.60	1.33	60.2	24.3	15.5	5.78
		sediment	29.92*	2.10*	66.6	26.4	7.0	5.83
7	flood	surface	8.24	1.55	6.3	74.9	18.8	7.65
	flood	bottom	34.60	1.38	66.2	29.8	4.0	4.92
	slack hw.	surface	36.10	1.29	85.8	10.6	3.6	3.70
	slack hw.	bottom	14.20	1.10	64.8	27.5	7.7	5.18
	ebb	surface	9.60	1.36	53.3	32.7**	14.0**	5.88
	ebb	bottom	11.40	0.88	44.9	46.7**	8.6**	5.88
	-	sediment	64.30*	17.44*	44.7	28.4**	26.9**	7.02
Inner Estuary	slack hw.	bottom	15.62	2.56	7.4	76.2	16.4	7.97
		sediment	60.84*	5.24*	29.5	61.9	8.6	6.97

* - The weights of these samples are artefacts of the procedure.

** - The percentages of fine silt and clay-sized modes have been approximated by extending the cumulative weight percent curves due to loss of the 10 ϕ samples.

(Folk and Ward, 1957; Royse, 1970) to provide a gross evaluation of the average particle size of the samples.

In previous studies, the covariance between total suspended load, depth in the water column, current speed and particle size has been interpreted as indicating the resuspension of local sediments (Schubel, 1971a; Nicholls, 1972; Meade, 1972; Sholkovitz, 1978). In the Forth, however, the most significant coarse-grained components are found in the central and southern portions of the main estuary, where energy conditions and total loads are below those to the west. Bond and Meade (1966) observed a similar seaward increase in the relative abundance of coarse-grained material in Chesapeake Bay suspended particulate matter, and attributed this to local resuspension of the more coarse-grained sediments.

The relative abundance of clay- and fine silt-sized fractions appears to be independent of loading or of the abundance of coarse-grained material in all suspended particulate and sediment samples from the Forth as shown in Figure 4.7. The ratio by weight of fine silt to clay averages 3.5. Although resuspension may account for local variations in particle size distribution, variations in the nature of the suspended material as functions of source and lateral transport are more likely responsible for this pattern for the coarse fraction at least, although finer material ($< 15 \mu\text{m}$, 6ϕ) may be uniformly derived from a single source.

Despite the range of total suspended load observed in these samples, a relatively uniform loading of $1 - 3 \text{ mg l}^{-1}$ of the finest fraction (10ϕ) is evident in all areas. A similar pattern was noted in the turbidity maximum described by Schubel (1971a) in a restricted channel in Chesapeake Bay. He described two populations of suspended

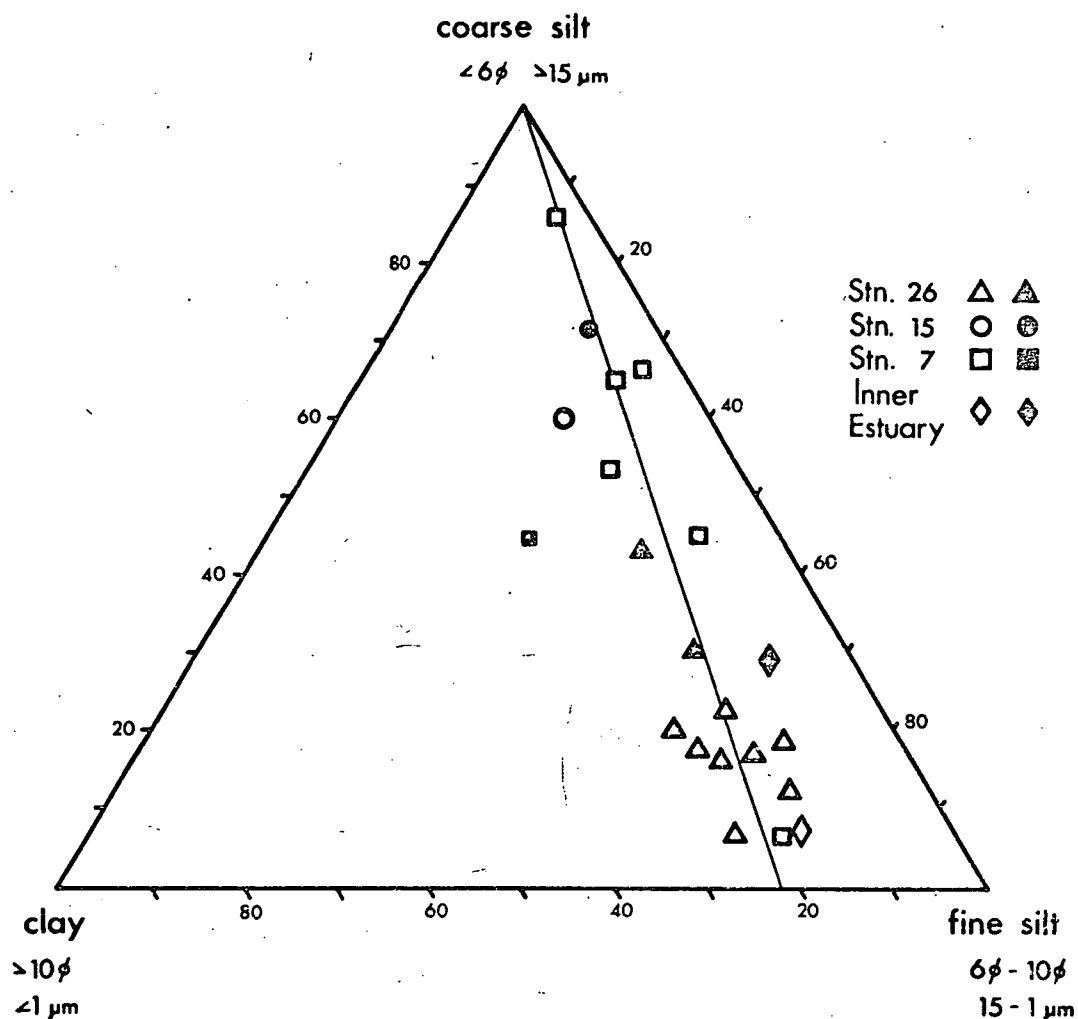


Fig. 4.7 Ternary plot diagram of the weight distribution among the three size ranges discussed in the text. Open symbols represent suspended particulate matter samples. Solid symbols represent sediment samples.

particulate matter in this area - a fine-grained fraction which is maintained in suspension, and a coarse-grained component which is intermittently introduced into the water column by resuspension of local sediments due to tidal flow, then lost the sediments due to the higher settling rate of this material. Resuspension and rapid settling of coarse-grained material should be accompanied by resuspension and progressively slower settling of medium and fine-grained fractions.

At station 26 and upriver (and for most sediment samples) the loading of the finest pipette fraction varies with the total suspended load as shown in Figure 4.8a. This pattern is consistent with the local sediments' being a likely source material. No such association is apparent in samples from station 7, however. Further, Figure 4.8b, which illustrates the relationship between loading and mean particle size, suggests little relationship between the size-specific gravimetric character of particulate samples from different areas of the Forth. Samples from station 26 conform to the trend indicated for most sediment samples, as does the material from the inner estuary. Samples from the other areas, however, are distinctly anomalous, although each group shows a covariance between mean particle size and loading.

The relationships between particle size characteristics and loading of suspended particulate samples indicate that the coarse-grained fraction, at least, in the different areas of the Forth may reflect differences in the character and source of the suspended matter. Although better consistency in the relative abundance and loading of the fine silt and clay-sized modes may indicate their primary association with terrigenous material derived from local sediments or maintained in suspension during transport within the Forth, this cannot

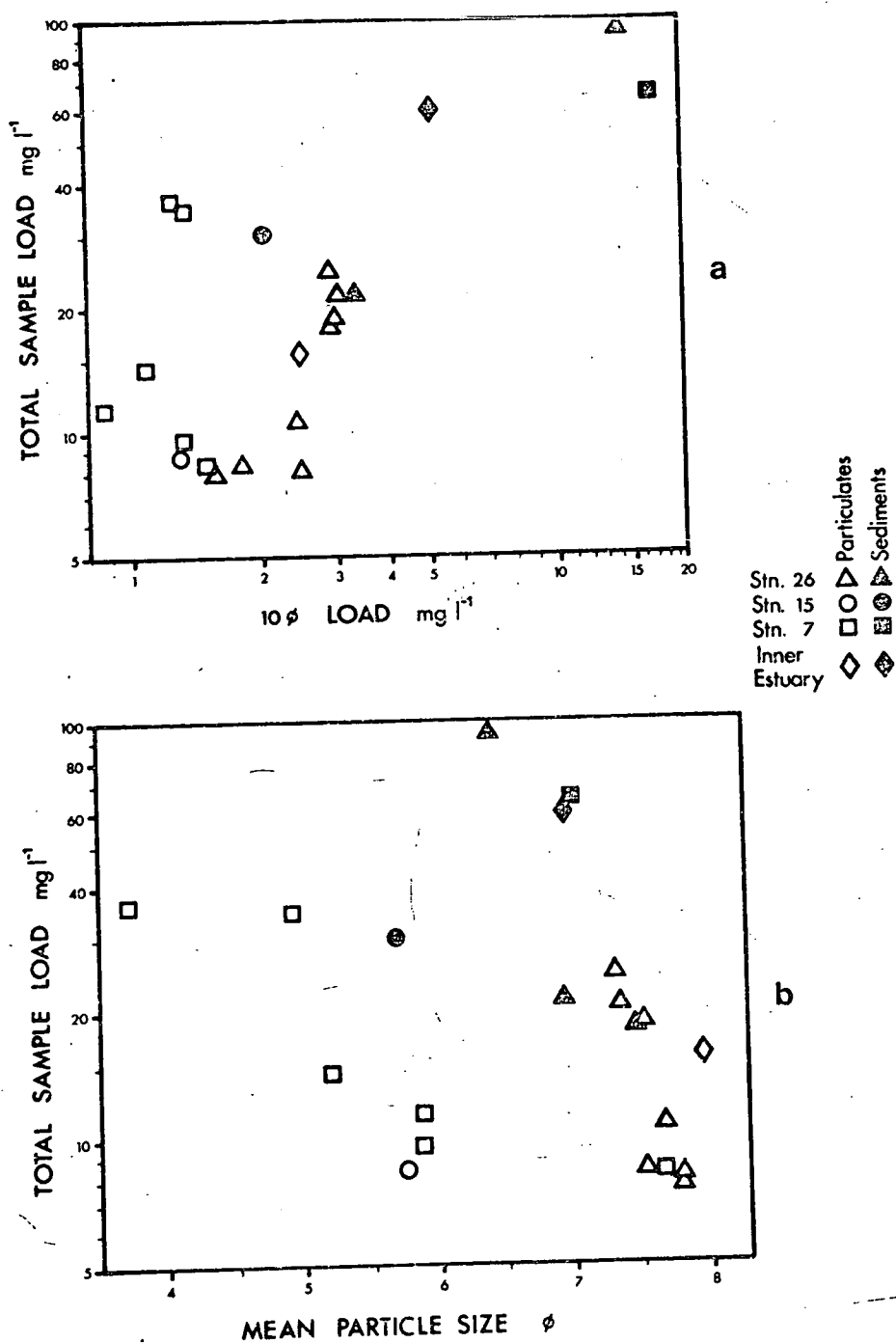


Fig. 4.8 Loading and particle size characteristics of pipetted samples

a) Concentration of total sample versus concentration of finest fraction

b) Concentration of total sample versus estimated mean particle size.

be proven by gravimetric analysis alone. The loading of suspended particulate matter in coastal waters provides insufficient information on its own for detailed consideration of its source and distribution characteristics.

CHAPTER 5

VISUAL AND MINERALOGICAL CHARACTER OF PARTICULATE MATTER

5.1 Introduction.

The anomalous loading characteristics of suspended particulate matter samples from the study area suggest pronounced variations in the nature of this material as a function of particle size, geographical location and depth in the water column. These are likely to be reflected in subsequent chemical analyses. In order that these, in turn, may be interpreted realistically, qualitative visual examination of the suspended matter and bottom sediment samples was conducted to identify their major components and to estimate the degree of similarity between samples. Further, the suggestion that terrigenous material from bottom sediments may constitute a significant proportion of the suspended matter necessitates examination of gross mineralogical trends.

5.2 Visual examination.

Reflected light microscopic examination revealed that the amount of terrigenous material in the samples varies considerably in different areas. Those from the west end of the study area, with loads consistently $>10 \text{ mg l}^{-1}$, contain coarse-grained coal fragments, quartz and minor amounts of other minerals in addition to abundant quantities of fine-grained terrigenous debris. Only a few biogenic skeletal fragments (diatoms and foraminifera) are evident.

Biogenic debris dominates the samples to the east. Few coarse-grained minerals are present here, except in some bottom water samples, but aggregates of finer particles occur. Near the municipal effluent sites, diatom frustules, other biogenic debris and abundant quantities of organic detritus (attributed to sewage effluent) characterise the particulate samples. Although significant amounts of terrigenous

debris occur here, few coarse-grained minerals are present.

Because of the poor resolution of reflected light microscopy with such fine-grained particles, a scanning electron microscope (SEM) was used to provide more detailed visual information on the composition of the particulate samples. Eighteen samples from areal, tidal station and pipette sample suites were examined. Representative SEM micrographs are presented in Plates 5-I and 5-II.

At low magnification (Plate 5-I), the areal trends described above are substantiated. Top and bottom water particulate samples in the western end of the study area (Plates 5-I a and b) consist mainly of mineralogenic debris, and indicate greater loading, particle size and angularity of mineral fragments in the bottom waters. Particles of size $\geq 15 \mu\text{m}$, many with monoclinic cleavage, are common to top and bottom water samples. Cleavage and fracture characteristics of coarse-grained particulates (e.g. quartz, feldspar etc.), allow general identification, while coal fragments are made obvious by their cellular imprints, angularity and/or conchoidal fracture.

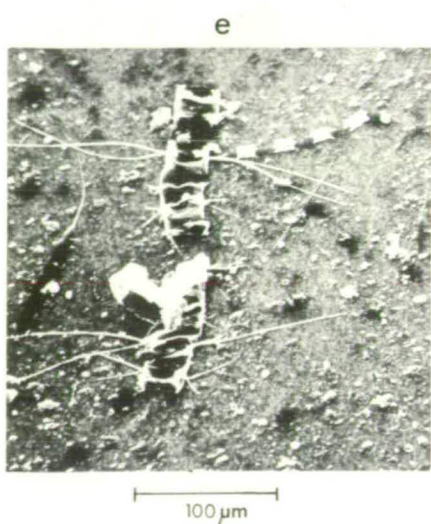
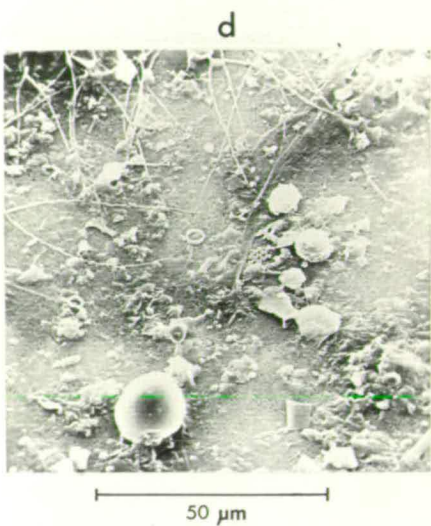
Biogenic debris in the east end of the study area (Plate 5-I c and d) consist primarily of Skeletonema sp., with subordinate silicoflagellate, dinoflagellate and crustacean fragments. Fine fibrous material observed in a sample at station 21 (Figure 3.1) was identified as artificial fibre due to its lack of any apparent biological features. Terrigenous debris here consists of fine-grained micaceous and clay material. Few mineral grains exceed $10 \mu\text{m}$ in size, and most appear to be associated with aggregates of organic debris.

Samples from the south shore (Plate 5-I e) contain skeletal debris, mostly diatoms of a variety of species, and include Skeletonema sp., Bidulaphia sp. and some crustacean fragments. Amorphous organic debris

PLATE 5.I

Selected scanning electron micrographs of suspended particulate matter from the Firth of Forth (see text for discussion)

- a) Station 26, surface water particulate sample. Concentration 5.2 mg l^{-1} . March 17, 1975.
- b) Station 26, bottom water particulates showing angular mineral grains, large ($>30 \mu\text{m}$) fragments of minerals with monoclinic cleavage and coal fragment with organic (floral) imprint. Concentration $\sim 34 \text{ mg l}^{-1}$. March 17, 1975.
- c) Station 21, surface water particulates consisting of biogenic debris, aggregated (?) fine-grained minerals and occasional discrete mineral fragments. Concentration $\sim 5 \text{ mg l}^{-1}$. March 17, 1975.
- d) Station 21, 40 m depth, March 17, 1975. Concentration $\sim 3 \text{ mg l}^{-1}$.
- e) Station 7. Surface water particulate sample showing biogenic and organic debris and accessory mineralogenic material. April 19, 1977.
- f) Particulate sample from the inner estuary (near Grangemouth), showing the dominance of terrigenous material. February 14, 1977.



introduced by local sewage discharge occurs in aggregates which also contain significant amounts of terrigenous material. Few coarse-grained minerals are apparent.

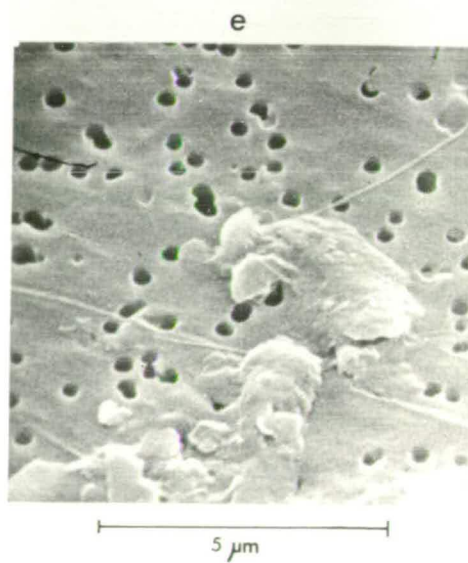
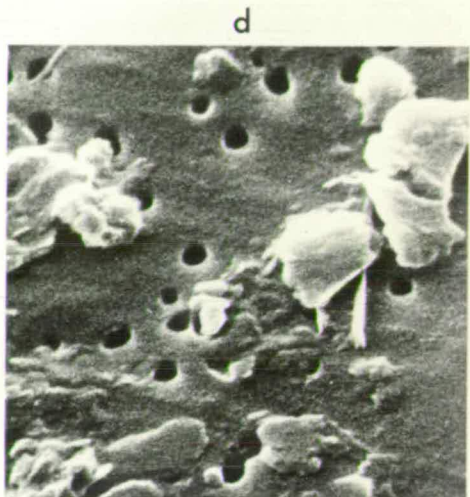
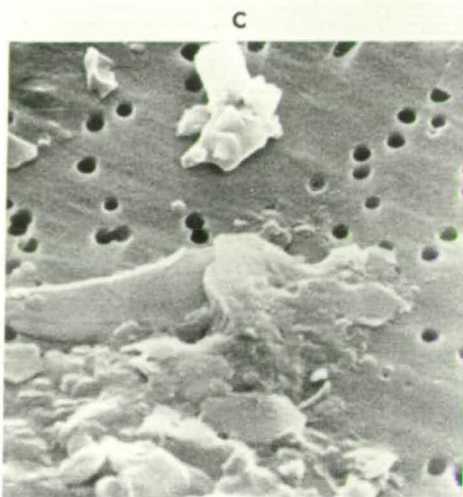
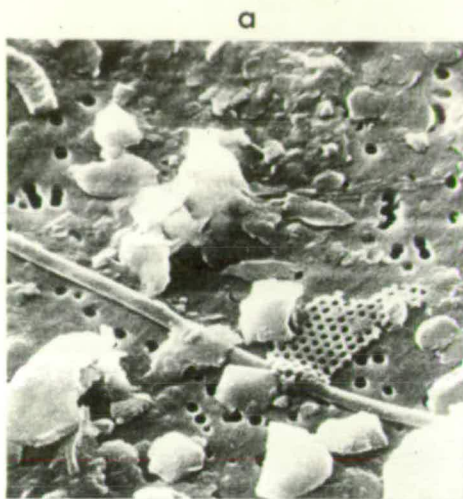
Suspended particulate matter from the inner estuary near Grangemouth is dominated by fine-grained minerals as shown in Plate 5-I f. Compared to samples from the west end of the study area (station 26), this sample shows relatively greater amounts of biogenic debris but fewer coarse-grained mineral fragments.

High magnification photomicrographs of fine-grained components (Plate 5-II) show that their appearance is similar in both sediments and suspended particulate samples. These consist primarily of fine-grained phyllosilicates and occasional skeletal fragments.

An attempt was made to determine the accuracy of the maximum particle size as indicated by the phi (ϕ) scale in pipette experiments (Chapters 4 and 6). Detailed examination of selected subsamples revealed that only biogenic debris and coal fragments exceed the maximum particle size indicated. For angular mineral fragments of size $\sim 15\mu\text{m}$, the maximum dimension of the grains is approximately indicated by phi measure. Finer-grained minerals of angular character ($\sim 10\mu\text{m}$) show their minimum dimension (perpendicular to the filter) to be roughly equivalent to the maximum particle size indicated. The lateral dimensions of flat-lying, micas and clays exceed their theoretical particle dimensions, but their thickness perpendicular to the membrane is considerably less.

5.3 Mineralogy.

The presence of significant amounts of terrigenous debris in these samples necessitates some examination of the mineralogy of this material. Qualitative identification of the major mineralogenic



constituents of suspended particulate matter have been reported in earlier studies (d'Anglejan and Smith, 1973; Baker, 1976; Price and Calvert, 1973; Feely, 1975; Skei, 1975; Sholkovitz, 1978a). Because of the small amounts of material available for analysis, little detailed information is available. Studies of clay mineralogy are particularly tenuous in such samples, but more detailed studies of their size relationships have been conducted in sediments (e.g. Grim, 1968; Archer, 1969).

Methods.

Both suspended particulate matter and sediments were collected for X-ray diffraction (XRD) studies on Whatman glass-fibre filters (GFF) and on Nuclepore[®] membrane filters during the tidal station sampling periods. Selected samples from the areal sampling program were also examined. The Nuclepore[®]-filtered samples are those referred to in other chapters, and thus provide a direct link between gravimetric, visual, mineralogical and chemical observations. The glass-fibre-filtered samples contain more material and may provide better definition of mineral reflections, but the flat surface of the Nuclepore[®] filters (Plate 5-II) tend to orient the fine-grained phyllosilicates, thus providing better clay-mineral response. Pipette subsamples were also examined to investigate mineralogical changes with particle size.

The mineralogy of the samples was determined using a Philips PW-1010 X-ray diffractometer, equipped with an AMR 3-202 X-ray focussing graphite monochromator which reduces background scatter. The X-ray source was Cu $K\alpha_1$ radiation ($\lambda = 1.54\text{\AA}$). The untreated samples were scanned at $\frac{1}{4}^\circ$ 2 θ per minute. Background effects were determined by scanning blank filters, and are discussed at greater

length in Appendix C.

The major minerals identified in the XRD scans were quartz, chlorite, illite (clay mica) and feldspar. The criteria on which these and accessory mineral identifications were made are summarized in Table 5-I (Chao, 1970; Müller, 1967; Doff, 1969; Carroll, 1970; Millot, 1970).

TABLE 5-I

Diagnostic 2θ reflection angles and respective d-spacings are shown for minerals identified in particulate and sediment samples in the Firth of Forth.

Mineral	2θ	$\text{\AA}$
quartz	26.66	3.34
quartz	20.85	4.26
feldspar	27.8	3.19
feldspar	27.5	3.24
chlorite	25.5	3.5
chlorite	12.4	7
chlorite	6.3	14
illite	8.5 - 9.5	10
calcite	29.4	3.03
amphibole (hbld)	10.5	8.5
pyrite	35.0	2.71
halite	31.7	2.82
gypsum	11.6	7.6

The quartz $3.34\text{\AA}$ peak was detectable in all the samples. The $4.26\text{\AA}$ reflection, however, was observed only on scans of glass-fibre filtered samples and in some heavily-loaded Nuclepore[®] samples. The $3.19\text{\AA}$ feldspar reflection may be attributed to plagioclase with possible interference from orthoclase, while the $3.24\text{\AA}$ reflection represents alkali feldspars and possibly includes microcline (Jørgensen, 1965).

The $7\text{\AA}$ and $3.5\text{\AA}$ chlorite peaks ($[002]$ and $[003]$) may also indicate kaolinite ($[001]$ and $[002]$). However, as weathering at 56° north latitude is unlikely to produce kaolinite in significant quantities (Turekian, 1968), it is assumed that these reflections

primarily indicate chlorite. D'Anglejan and Smith (1973) noted average chlorite/kaolinite abundance ratios of over 3.5, with higher values (>23) in the upper reaches of the St. Lawrence estuary.

Figure 5.1 illustrates a series of representative XRD traces obtained from a suite of pipette samples of suspended particulate matter from station 26. The decreasing peak intensities reflect the lesser amounts of material on successive samples, as will be discussed later.

The low $14\text{\AA}/7\text{\AA}$ peak area ratios of the assumed chlorite reflections shown in Figure 5.1 typify 'soil chlorites' as noted in the sediments of Oslofjord by Doff (1969). He assumed that besides the possibility of certain septochlorites being present, this trend could represent iron-rich chlorite. The very diffuse $14\text{\AA}$ reflection does suggest some soil chlorite in the samples, although its proportion to the total chlorite is unknown.

Illite, defined here as material having a $\sim 10\text{\AA}$ reflection, was identified in all samples. The sharpness of the illite peak in some samples indicates the relative amounts of well-crystallized mica (muscovite, biotite) versus poorly-crystallized hydrated micas (Weaver, 1961).

Halite ($2.8\text{\AA}$) and gypsum ($7.6\text{\AA}$) reflections were evident only in glass-fibre filtered samples. Because these were not rinsed with filtered distilled water after filtration, the presence and apparent covariance of halite and gypsum probably indicate the formation of salts from the evaporated residual sea water.

The results of specific XRD analyses will be considered firstly with respect to particle size, then on an areal basis.

Particle size and mineralogy.

Pipette-separated samples of suspended particulate matter and underlying sediments at one- or two-phi intervals were examined on Nuclepore[®] filters for their changes in mineralogy. Unfortunately, progressively finer-grained pipette samples contained less material, and exhibited reduced mineral reflections as shown in Figure 5.1. This effect was minimised somewhat by increasing the volume of the pipette aliquots of the finer-grained samples. The loadings on the filters are listed in Figure 5.1. Due to the low sensitivity at these sample weights and the variable loadings, true comparisons of mineral abundances are difficult, and quantitative calculations based on peak areas (cf. Biscaye, 1965) are highly unlikely to be accurate. Even so, gross trends in mineralogy with changing particle size may be illustrated by direct examination of the traces and by changes in the ratios of specific peak areas.

Quartz and feldspar peaks are most prominent in samples containing very coarse-grained material. With decreasing size, the illite peaks appear to decrease in sharpness and to degrade from a single peak to multiple reflections. This trend is consistent even in samples of roughly equivalent loading, and probably reflects the preferential settling of coarse-grained, well crystalline micas (seen in SEM micrographs) versus the finer-grained, more hydrated varieties and mixed layer clays. The chlorite 7Å reflections also exhibit decreasing sharpness, but remain single peaks, possibly indicating the loss of detrital chlorites from a suspension dominated by poorly crystalline soil chlorites of small size.

An attempt was made to determine the relative changes in mineralogy by comparing specific peak area ratios. These are summarized

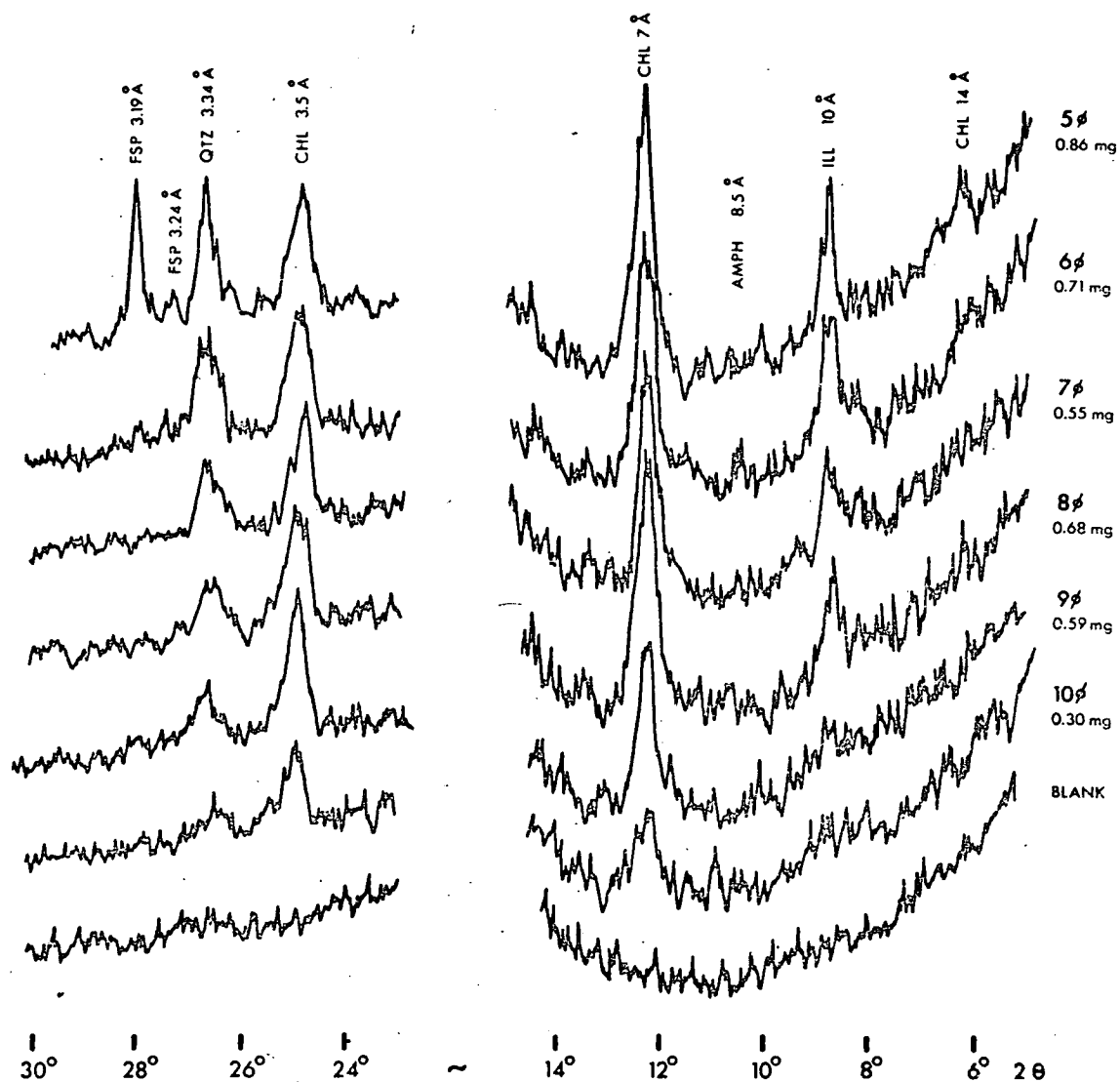


Fig. 5.1 Representative X-ray diffractograms from a pipette suite of suspended particulate matter (station 26, 30 m, 2100 hours). The gaps between 14-24° 2θ omits a wide background peak from the Nuclepore filter.

in Table 5-II. Measurements were made with a Haff-813 planimeter, and are subject to error due to the poor reproducibility of the XRD traces, primarily caused by a 'noisy' background and poor peak definition.

The only consistent relationship apparent in these measurements is the decreasing quartz ($3.34\text{\AA}$)/chlorite ($3.5\text{\AA}$) peak area ratios with decreasing particle size. This suggests that quartz is more associated with coarse-grained material ($>15\text{ }\mu\text{m}$), while chlorite may exist in all samples, although it is likely to vary with composition and origin. A similar size relationship is indicated for feldspar, which is detectable only in the coarse-grained samples, but poor peak definition precludes detailed evaluation.

TABLE 5-II

X-ray diffraction peak area ratios for selected pipette suites.

Sample	Filter	Phi	1	2	3	4
Station 26 particulate 2100 hours 30 m depth	Nucl.	Tot.	0.43	1.00	0.15	0.78
		5 ϕ	0.75	1.00	0.16	1.20
		6 ϕ	0.35	0.74	0.19	1.26
		7 ϕ	n.m.	0.59	0.11	1.18
		8 ϕ	n.m.	0.50	0.13	1.15
		9 ϕ	n.m.	0.52	n.m.	0.52
		10 ϕ	n.m.	0.58	n.m.	0.67
Station 26 bottom sediment	Nucl.	Tot.	0.28	1.7	0.08	0.63
		6 ϕ	0.16	0.84	0.11	0.40
		8 ϕ	0.40	0.65	0.15	0.95
		10 ϕ	0.26	0.63	n.m.	0.47
Inner estuary (sediment)	GFF	Tot.	0.32	1.7	1.20	0.15
		9 ϕ	n.m.	1.3	0.20	0.91

1 - Feldspar (total)/Chlorite ($3.5\text{\AA}$)

2 - Quartz ($3.34\text{\AA}$)/Chlorite ($3.5\text{\AA}$)

3 - Chlorite ($14\text{\AA}$)/Chlorite ($7\text{\AA}$)

n.m. - not measured (peak too small for accurate measurement)

The chlorite $14\text{\AA}/7\text{\AA}$ peak area ratios do not vary markedly, but they do indicate relatively less $14\text{\AA}$ chlorite in the fine-grained fractions. To some degree, this may reflect poor peak definition, but this trend and the low overall $14\text{\AA}/7\text{\AA}$ ratios suggest the existence of both fine-grained soil chlorites and coarser detrital fragments. This trend is also illustrated in the glass-fibre filtered sediment samples. The illite $10\text{\AA}/\text{chlorite } 3.5\text{\AA}$ peak area ratios of the suspended particulate matter samples show a maximum in the 5 ϕ - 8 ϕ samples. The reason for this is unclear, but this trend appears to be independent of loading effects. These samples show the sharpest illite peaks, and may contain significant amounts of micaceous material relative to chlorites. However, the sediment pipette samples do not substantiate this relationship. Qualitative examination of the illite peak character as discussed earlier provides a more dependable evaluation of the distinction between detrital micas and finer-grained clays.

Areal trends in mineralogy.

Eight surface water suspended particulate samples from the March 1975 sampling programme were analysed by XRD techniques. Five of these (from stations 24, 26, 9, 15 and 21 as shown in Figure 3.1) represent a seaward trend. The XRD traces of these are shown in Figure 5.2.

Peak area ratios for the areal samples proved of little use, due to the differences in loading and changes in the character of individual peaks. Decreasing quartz ($3.34\text{\AA}$)/chlorite ($3.5\text{\AA}$) ratios were noted from stations 24 - 9, but these increased again seaward. This principally reflects the disproportionate collapse of the chlorite $3.5\text{\AA}$ peak at station 15 as shown in Figure 5.2. This seaward loss

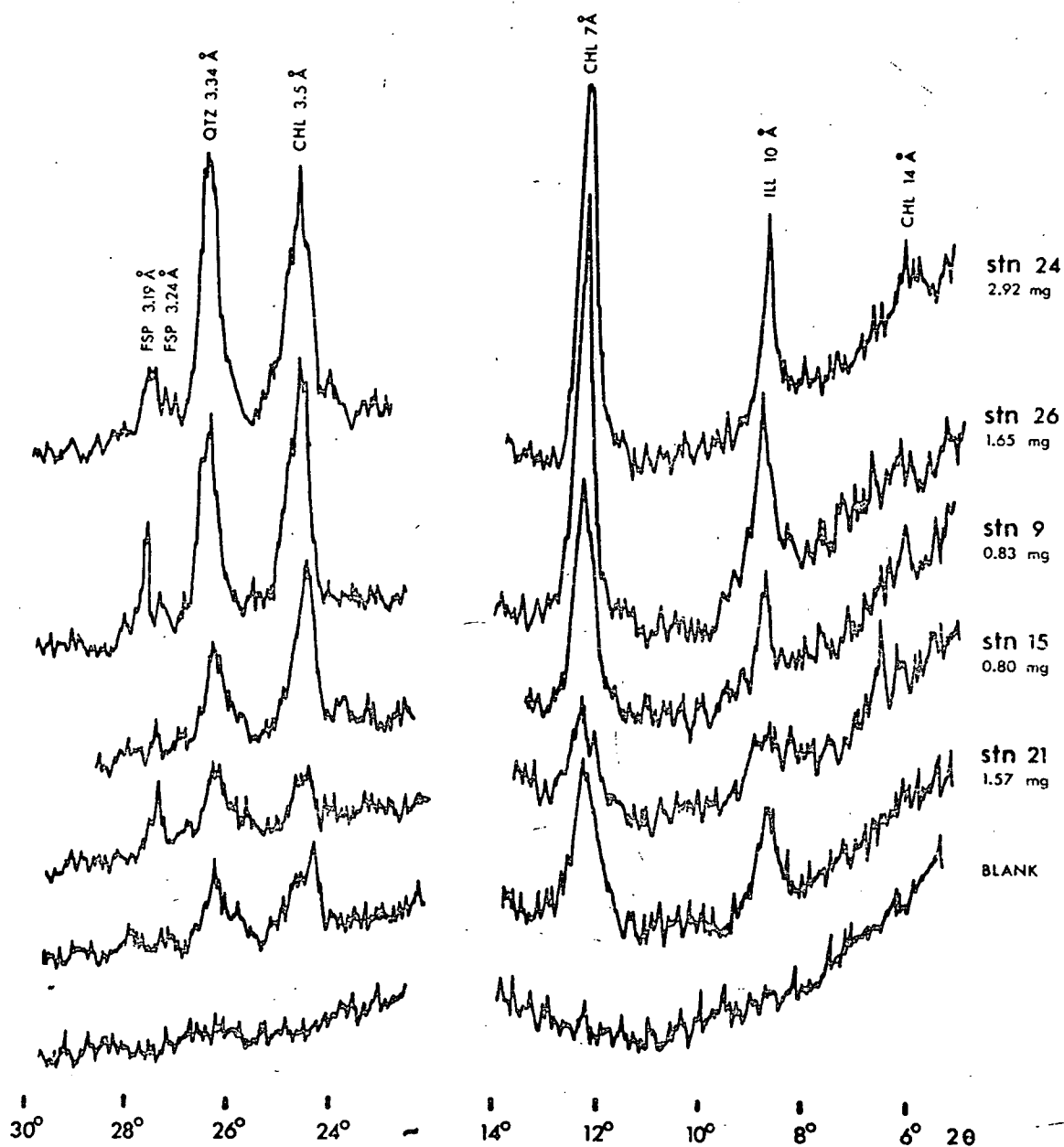


Fig. 5.2 Representative X-ray diffractograms of surface water particulate samples from successively seaward stations.

in peak sharpness is not entirely due to loading effects, and may reflect a lack of coarse-grained, well-crystallized detrital chlorites in the central Forth. Here, the illite peaks are also less sharp than those noted in pipette samples from the west (Figure 5.1) of equivalent loading.

Surface and bottom water samples were collected at stations 26 and 15 during tidal station monitoring. At station 15, the bottom water sample showed pronouncedly higher quartz ($3.34\text{\AA}$)/chlorite ($3.5\text{\AA}$) peak area ratios than seen in the top water sample scan (1.9 versus 0.6). Feldspar peaks were noted only in the bottom water samples. Less marked but similar trends were noted at station 26, with quartz/chlorite ratios of 1.2 in the surface water and 1.9 in bottom water particulates. These values are consistent with an increasing particle size landward and with depth in the Forth.

5.4 The gross composition of suspended matter.

Mineralogical studies principally have served to identify the major constituents of the terrigenous fraction of the local particulate matter. Quartz and to some degree feldspar exist primarily in the coarse-grained fraction. Some indication of a size distinction between detrital, well-crystallized chlorites and micas and finer-grained soil-chlorites, poorly crystalline hydrated micas and mixed-layer clays has been suggested, but quantitative evaluation of such trends is severely limited due to the poor peak definition and the uncertainty of loading effects.

Visual examination reveals that the terrigenous component of this material, though abundant in all samples, is progressively finer-grained towards the east, so the hypothesised correlation between the character of chlorite and illite peaks in the central Forth and

those of fine-grained samples of pipette suites from the west may be substantiable. The lack of very distinct mineralogical trends likely indicates that similar terrigenous constituents occur in all samples, particularly in the fine silt and clay-sized modes. Little obvious mineralogical variation, therefore, might be expected, except during periods of pronounced resuspension. Quantitative definition of size-specific mineralogy in the fine-grained material is beyond the sensitivity of the XRD procedure.

The visual and mineralogical studies indicate that distinction between terrigenous, biogenic and organic constituents of suspended particulate matter in the Forth is probably more important than mineralogical variations alone.

CHAPTER 6

THE CHEMICAL SIGNIFICANCE OF PARTICLE SIZE VARIATIONS

6.1 Introduction.

X-ray diffraction studies of suspended particulate matter have revealed some mineralogical variation with changing particle size, but the analytical procedure is slow, and suffers from limited sensitivity, accuracy and precision, particularly for small samples. "Thin-film" X-ray fluorescence (XRF) techniques have been adapted to provide chemical analyses of natural particulate samples (Price and Angell, 1968; Price and Calvert, 1973; Taylor, 1974; Skei, 1975; Price and Skei, 1975; Baker and Piper, 1976). This procedure is fast and non-destructive, and due to the high sensitivity of the instruments, only very small amounts of sample are required.

Suspended particulate matter and sediment samples from the Firth of Forth were analysed for a suite of major elements by XRF "thin-film" techniques as a means of determining the partition of these elements in estuarine particulate matter. Very few previous studies have considered the chemical characteristics of particulate matter, while those which have done so have depended almost entirely upon analyses of "bulk" samples (those which contain the full range of particle sizes present in the natural suspension). Before such analyses are considered in bulk samples from the Firth of Forth, their chemical composition as a function of particle size will be examined in detail.

Because of the wide range of loadings of these pipette samples (Chapter 4), direct examination of the abundances of each element in the samples is of little practical use. Inaccuracies in weighing preclude direct comparison between sample weights and the chemical determinations, so inter-element ratios will be employed to illustrate

varying size-specific chemical associations. Of the three major constituents of suspended particulate matter described earlier, the terrigenous fraction is dominated by the elements Si, Al, Fe, K, Ti, Mg and to some degree, Ca, in association with various minerals. Biogenic skeletal debris consists primarily of Si and Ca, while P and S probably reside mainly in organic constituents (Spencer and Sachs, 1970; D'Anglejan and Smith, 1973; Price and Calvert, 1973; Broecker, 1974; Price and Skei, 1975; Skei, 1975; Sholkovitz, 1978).

Aluminium may be used as an indicator of detrital aluminosilicate mineral abundances since it resides mainly in the lattices of phyllosilicates (clays, micas) and in lesser amounts in tectosilicates (e.g. feldspars and plagioclase) and other detrital forms. The ratios of specific elements to Al, therefore, may be used to examine size-specific chemical trends within the terrigenous fraction. Once these have been defined, the relationship between suspended particulate and bottom sediment samples will permit definition of the chemical attributes of true resuspended sediments than would gravimetric data alone.

6.2 Methods.

Samples were collected and filtered according to the techniques detailed in Chapters 3 and 4. Subsamples of suspended particulate matter and sediments from pipette studies (Chapter 4) were analysed by XRF techniques on Nuclepore[®] membrane filters. Quantitative determinations were made for Al, Si, Ca, Fe, Ti, K, Mg, P and S, using a series of prepared standards and secondary standards to calibrate the signal response from each element. The calibration curves used are consistent with those from other studies in this department (Price, Doff, pers. comm.). The pipette methods are discussed in Appendix C.

Details of the analytical procedure are presented in Appendix C,

and a re-evaluation of its limitations appears in Appendix A. A total of 261 samples from the 22 pipette suites presented in Chapter 4 were analysed. Semi-quantitative analyses of chlorine were conducted to verify effective rinsing of sea salts from the samples. Thus, K, Mg and Ca as determined in the samples may be presumed to represent these elements in direct association with particulate matter.

6.3 Results.

The results of these studies will be presented in two stages. Firstly, data from the eight pipette suites at station 26 will be examined to determine size-specific chemical variations at a single location. Secondly, these will be compared to chemical data from other areas on a particle-size basis.

The Si/Al ratios of material from station 26 fall from ~ 1.80 - 1.95 in bulk particulate samples (4ϕ) to ~ 1.56 in the fine-grained components. Pronounced variation of this ratio with changing particle size is shown at about 6ϕ ($15\ \mu\text{m}$) in those particulate samples with significant coarse-grained constituents (see Figure 4.2). This is consistent with the prominence of quartz in the coarse-grained terrigenous fraction as suggested by XRD studies. Sediments and resuspended sediments show slightly higher Si/Al ratios than the overlying particulates, indicating more abundant coarse-grained minerals which are not subject to prolonged suspension.

Ratios of K to Al (Figure 6.2) show similar trends, and are consistent with the pronounced abundance of feldspars in the coarser fraction as suggested in Chapter 5. As with Si/Al, K/Al ratios are highest in the coarse-grained sediments, but all particulate samples show values similar to those of the sediments at particle sizes less than $15\ \mu\text{m}$.

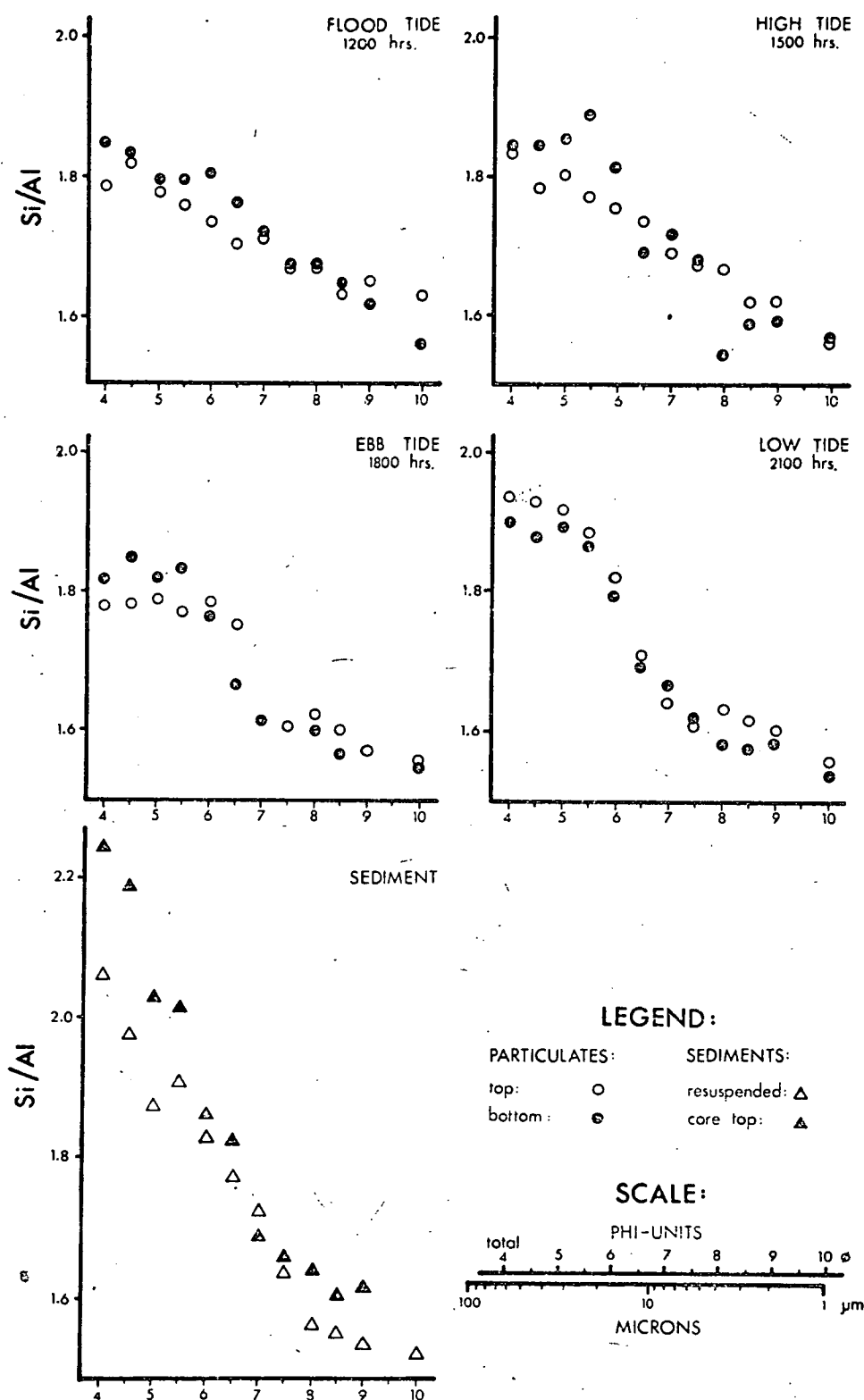


Fig. 6.1 Si/Al ratios versus maximum particle size in pipette samples from station 26.

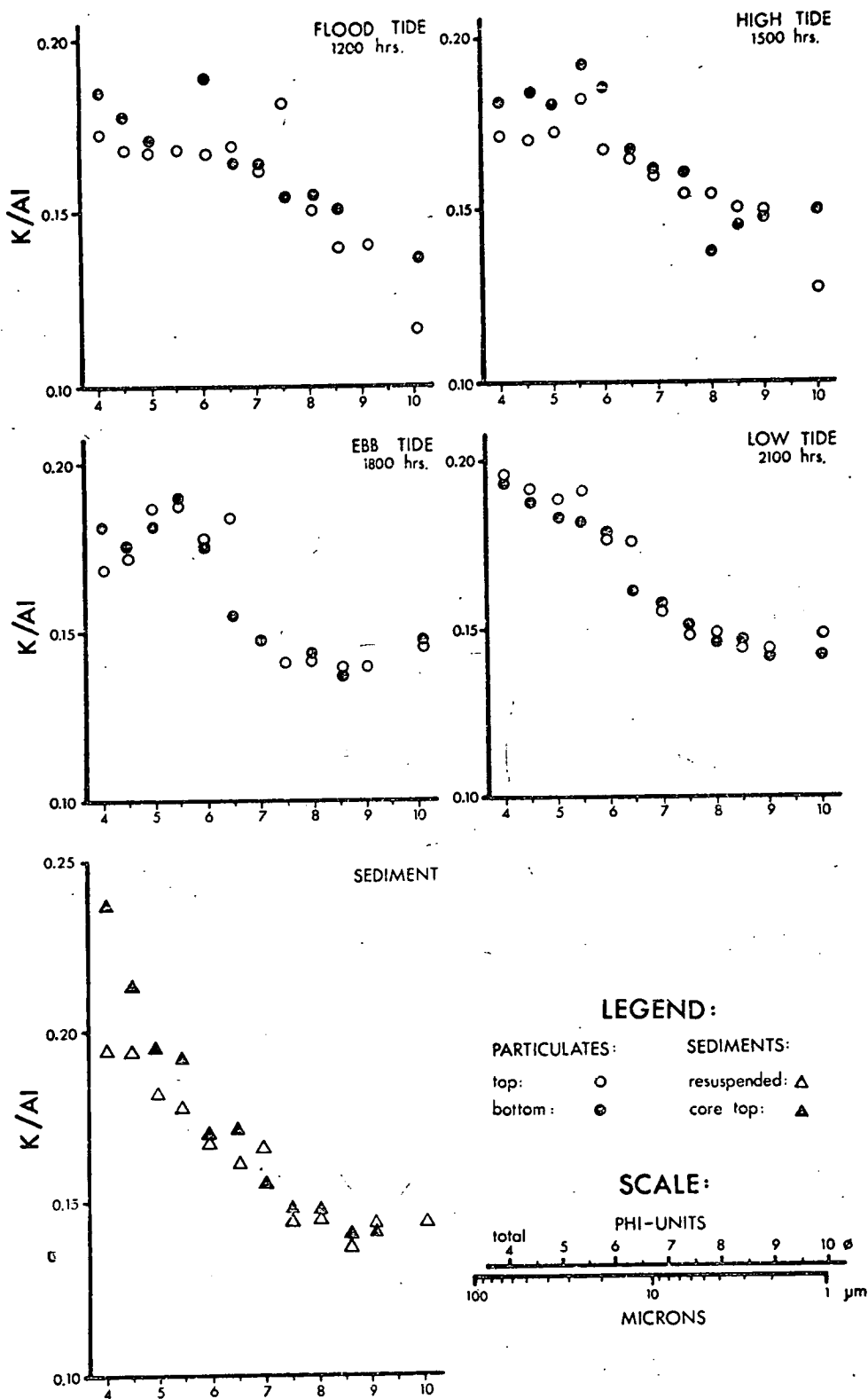


Fig. 6.2 K/AI ratios versus maximum particle size, station 26.

In contrast, Mg/Al ratios in these samples are virtually constant with changing particle size, averaging about 0.15 in all pipette suites. This suggests close association of Mg and Al within the predominantly fine-grained detrital aluminosilicates, with no significant coarse-grained Mg-rich phase.

The ratios of Fe and Ti to Al decrease markedly with decreasing particle size. Further, the greatest changes in these occur at sizes which represent distinct size modes as shown in Figure 4.2, suggesting strongly size-specific chemical variation. The Fe/Al ratios range from 0.48 in total particulates to over 0.55 in the sediment samples, while the fine-grained components of all samples are roughly similar, ranging from 0.40 in the 6 ϕ aliquot to 0.35 in the finest fraction. This may indicate partitioning of Fe between fine-grained detrital aluminosilicates (chlorite, illite), in detrital micas and chlorites, and in coarse-grained minerals such as ilmenite, magnetite or amphiboles. Similar trends of Ti/Al ratios may indicate that in addition to its association with clay minerals ($\text{Ti/Al} \sim 0.04$), Ti may also be found in coarse-grained material such as ilmenite or minor amounts of sphene, rutile or anatase. The increasing ferruginous and titaniferous nature of many sediments with increasing grain size has been shown in comparisons between different studies (e.g. Goldschmidt, 1954; Hirst, 1962; see Table H.2).

The close comparison between these inter-element ratios in both suspended particulate and sediment samples suggest a dominantly mineralogenic association of Si, K, Fe and Ti in the suspended material at station 26.

The Ca/Al ratios of suspended particulate samples (Figure 6.5) vary directly with particle size, ranging from ~ 0.25 in the total

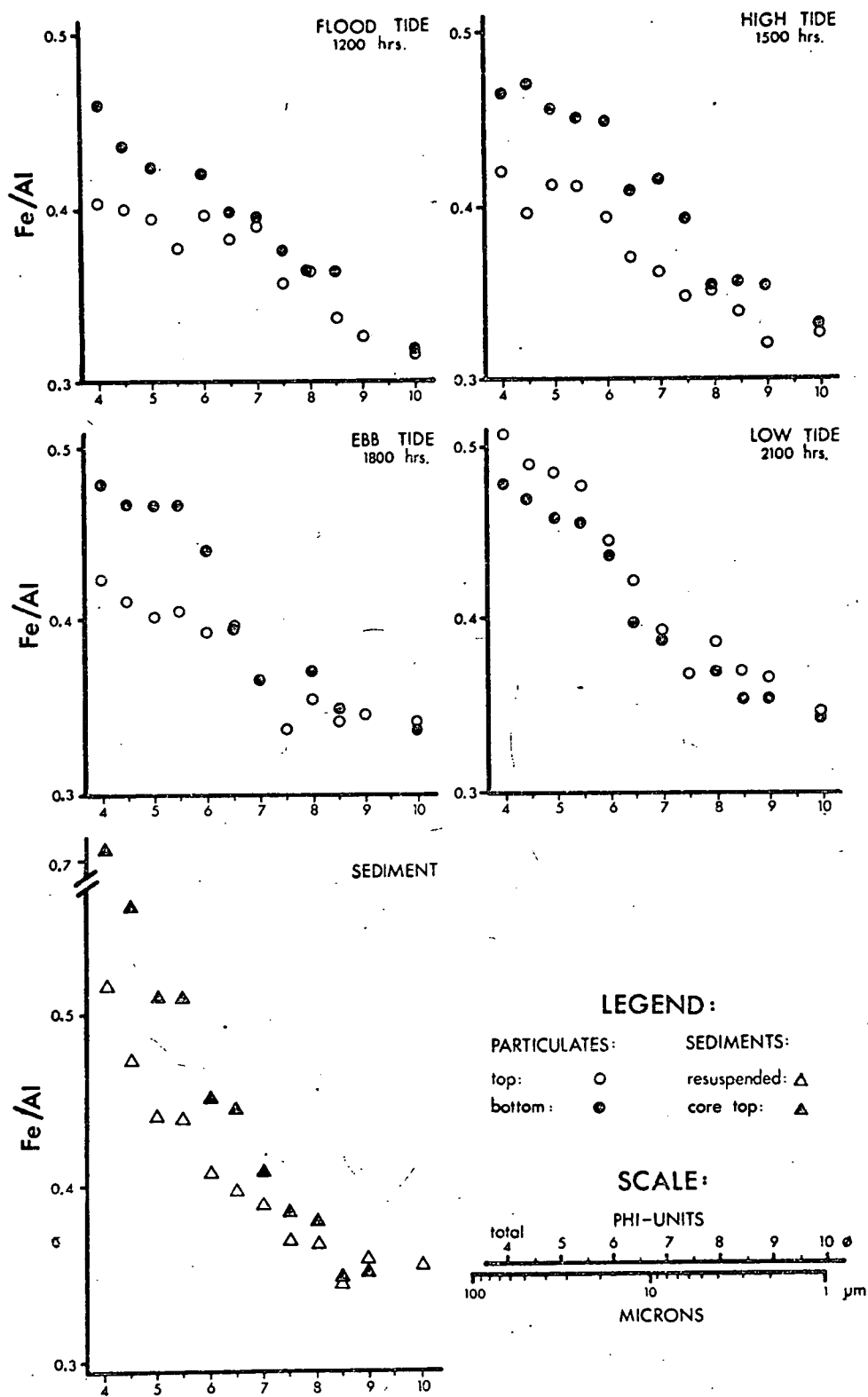


Fig. 6.3 Fe/Al ratios versus maximum particle size, station 26.

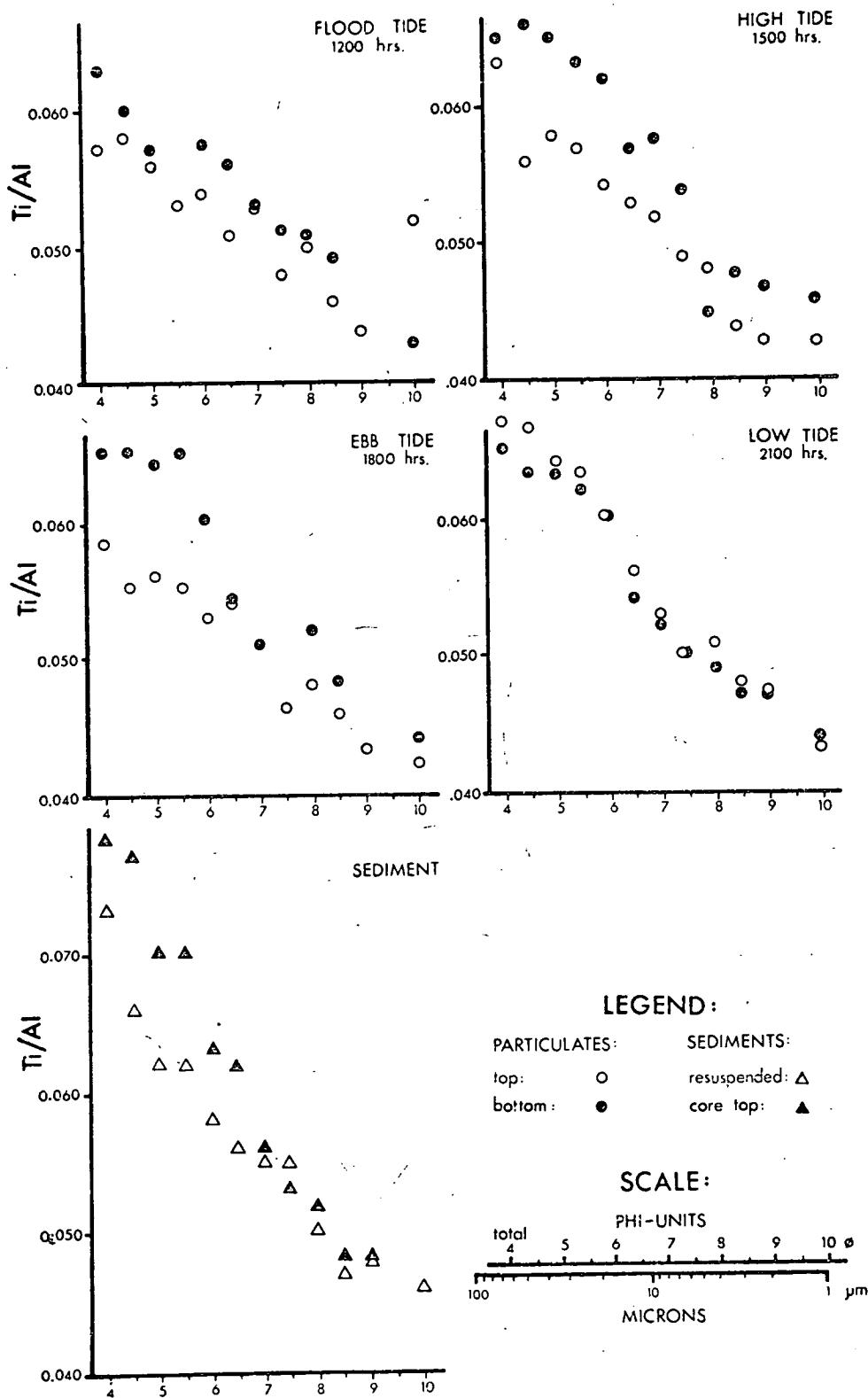


Fig. 6.4 Ti/Al ratios versus maximum particle size, station 26.

sample to ~ 0.15 in the fine-grained component. This variation is essentially linear in these plots (notably at low and high tide) compared to the sinusoidal curves shown by Fe/Al and Ti/Al ratios. This suggests that the association of Ca to mineralogenic phases is less exclusive than that noted for the other elements studied thus far. The most significant feature of the Ca/Al ratios shown in Figure 6.5, however, is the marked difference between sediment and particulate samples, particularly in fine-grained samples. These ratios are roughly equivalent in the total samples (the sediment is slightly lower, i.e. 0.20 versus 0.25), but with decreasing size, the Ca/Al ratios of the sediments fall to 0.03 (10%) compared with values of 0.16 in equivalent particulate samples. This low value is consistent with that reported by Goldberg (1954) for glacial clays (0.033). The reason for this difference between suspended and deposited material is unclear.

Because the sediment samples were pipetted from filtered distilled water rather than the ambient seawater used for particulate samples, this trend might reflect solution due to the lower pH of this water (~ 5.5). However, suspended particulate matter samples which were resuspended into filtered distilled water during subsidiary experiments showed no reduction whatsoever in their Ca/Al ratios after remaining in this medium for periods equivalent to the duration of the pipette experiments. Consequently, much of this apparent loss of Ca relative to Al must be considered a natural process in the sediments, representing either solution of the fine-grained Ca at the sediment-water interface or "swamping" of this material by fine-grained, Al bearing terrigenous matter, so reducing the Ca/Al ratios. Particulate Ca resides primarily in calcareous skeletal fragments of varying

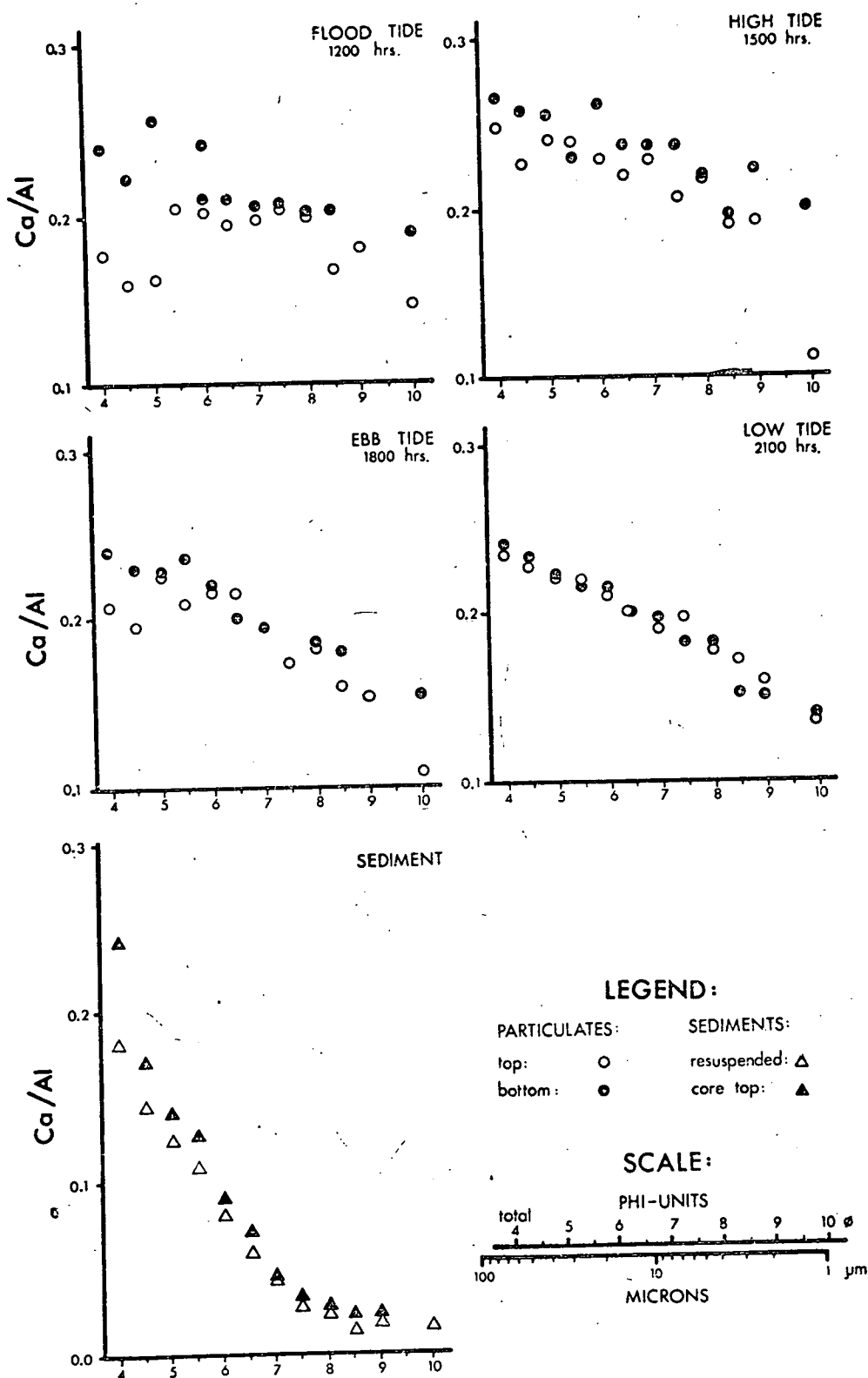


Fig. 6.5 Ca/Al ratios versus maximum particle size, station 26.

particle size due to physical degradation in the high energy conditions at station 26.

Ratios of P to Al at station 26 are low, averaging ~ 0.013 in most samples, with some increase (> 0.015) in the finest fraction of some lightly-loaded particulates (Figure 6.6). The sediment samples have lower P/Al ratios which fall with decreasing particle size from ~ 0.010 to 0.006 . The general range of P/Al ratios for all samples at this station are consistent with those reported for fine-grained sediments by previous workers (Garrels and MacKenzie, 1972; Hirst, 1962; Wright, 1972) as well as for some coastal particulates (Sholkovitz, 1978). Decreased fine-grained P relative to Al in the sediments may indicate decomposition of organic matter at the sediment-water interface as suggested by Berner (1974), or may, as with Ca, represent a masking effect of large amounts of terrigenous debris.

The S/Al ratios shown in Figure 6.7 exhibit much more scatter than those of P/Al, but a direct relationship between particle size and the S/Al ratio is apparent in all samples, ranging from 0.020 in the total sample to ~ 0.005 in the finest fraction. Ratios of S to P exceed unity in the coarse-grained samples and fall below 1.0 in finer material. In the sediment samples, higher S/Al ratios are associated with the bottom sediment than with the artificially resuspended sample, and may indicate the presence of sulphide minerals.

The results presented thus far have illustrated variations in size-specific chemical/mineralogical trends within the terrigenous component of the suspended matter at station 26, and have shown differences between some elemental associations (notably Ca and P) in specific size ranges of particulates and underlying sediments. Although areal trends in particulate chemistry will be examined in detail in later chapters,

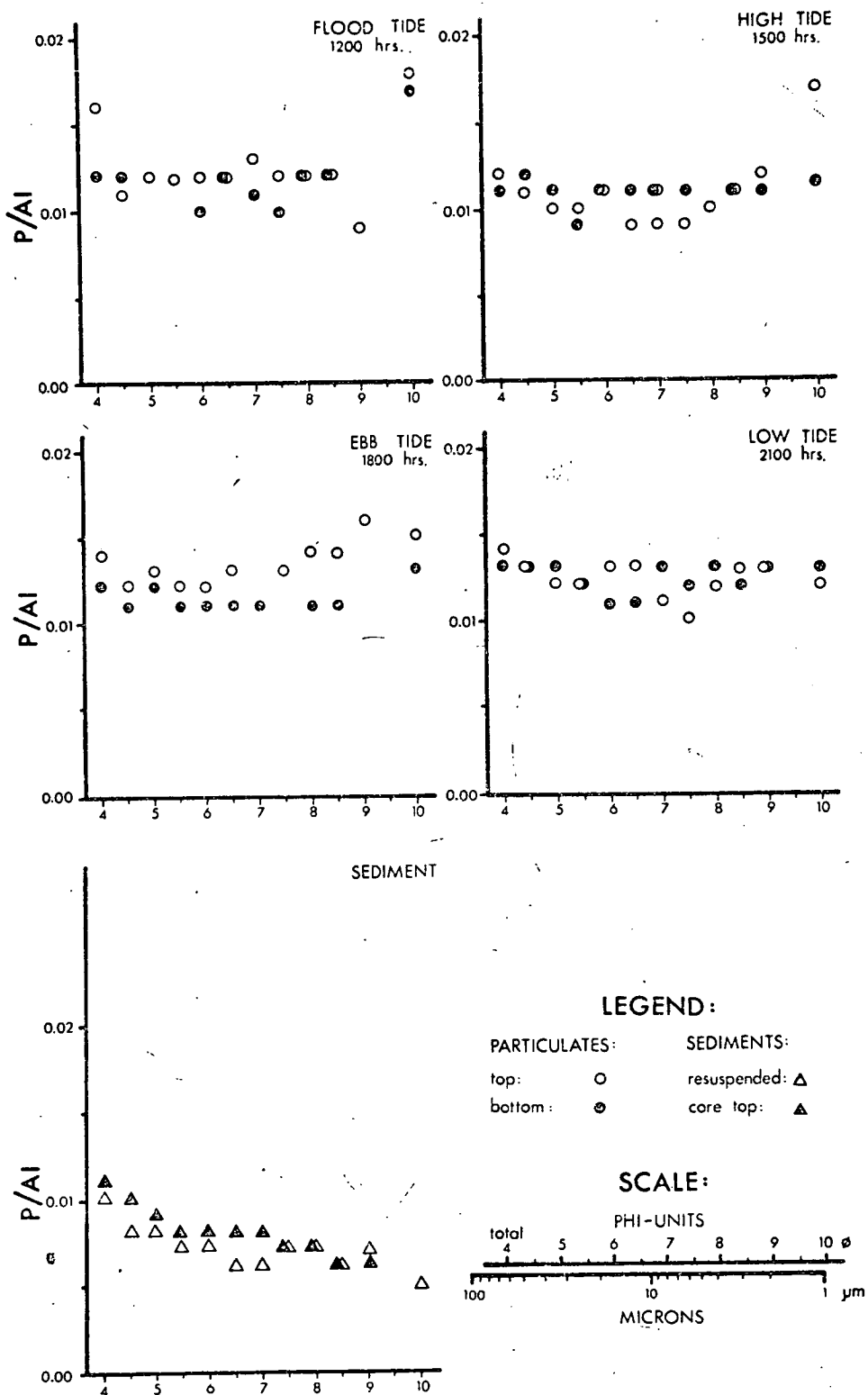


Fig. 6.6 P/AI ratios versus maximum particle size, station 26.

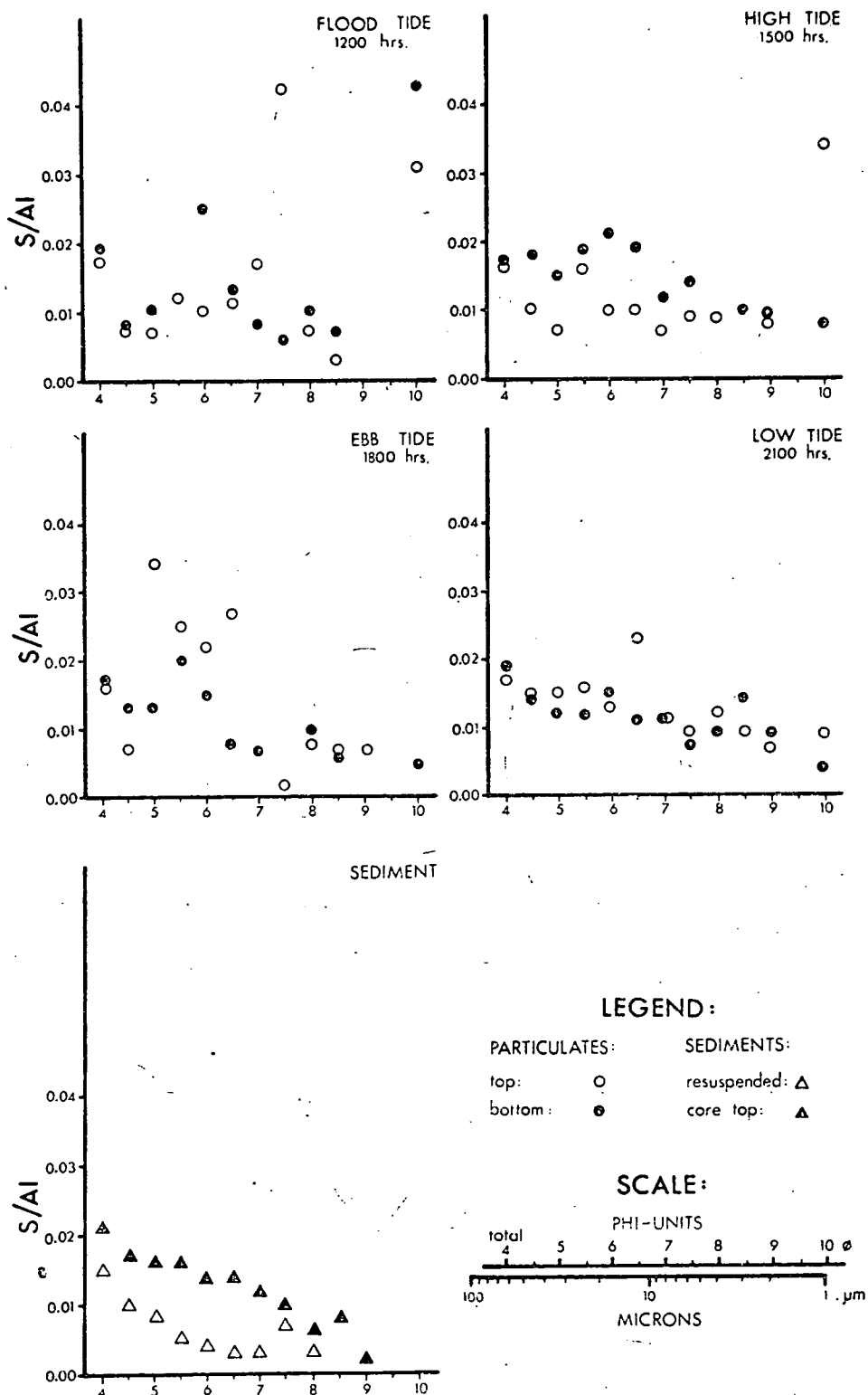


Fig. 6.7 S/Al ratios versus maximum particle size, station 26.

direct comparison between particulates at station 26 and those from other areas (stations 15 and 7) will help to clarify and elaborate on the relative importance of specific elemental associations.

Figure 6.8a summarizes the percentages of Al found in particulate and sediment samples from stations 26, 15 and 7. Aluminium comprises $\sim 10\%$ by weight of the total sediments, but with decreasing particle size, this rises to a maximum of $\sim 20\%$ in all fractions finer than 8ϕ ($< 4 \mu\text{m}$). Dilution of aluminosilicate minerals by quartz and coal fragments (Chapter 5) could account for the lower percentages of Al in the bulk sediment samples. Particulate samples from station 26 differ slightly from the sediments in that Al reaches a maximum of $\sim 20\%$ at $4 \mu\text{m}$, with lower percentages in both the coarse ($\sim 15\%$) and the fine-grained ($\sim 16\%$) samples. Here, clay-sized aluminosilicates in suspension may be accompanied by small but significant amounts of organic matter which could account for this reduction.

The weight percentages of aluminosilicates (denoted from Al concentrations) are much reduced at station 15 (central estuary), and especially at station 7 (near Edinburgh). This can be attributed to a dilution of the reduced terrigenous loads by biogenic skeletal debris at station 15, and by skeletal and particularly organic matter at station 7. These trends are substantiated by SEM examinations as shown in Chapter 5, and the chemical trends described below.

Figure 6.8b shows that the Ti/Al ratios of particulate samples are similar to or less than those of sediment samples of equivalent size. Values range from 0.07 in sediment samples and particulates with abundant coarse-grained components to ~ 0.04 in fine-grained fractions.

In contrast, while the K/Al ratios of western particulate samples

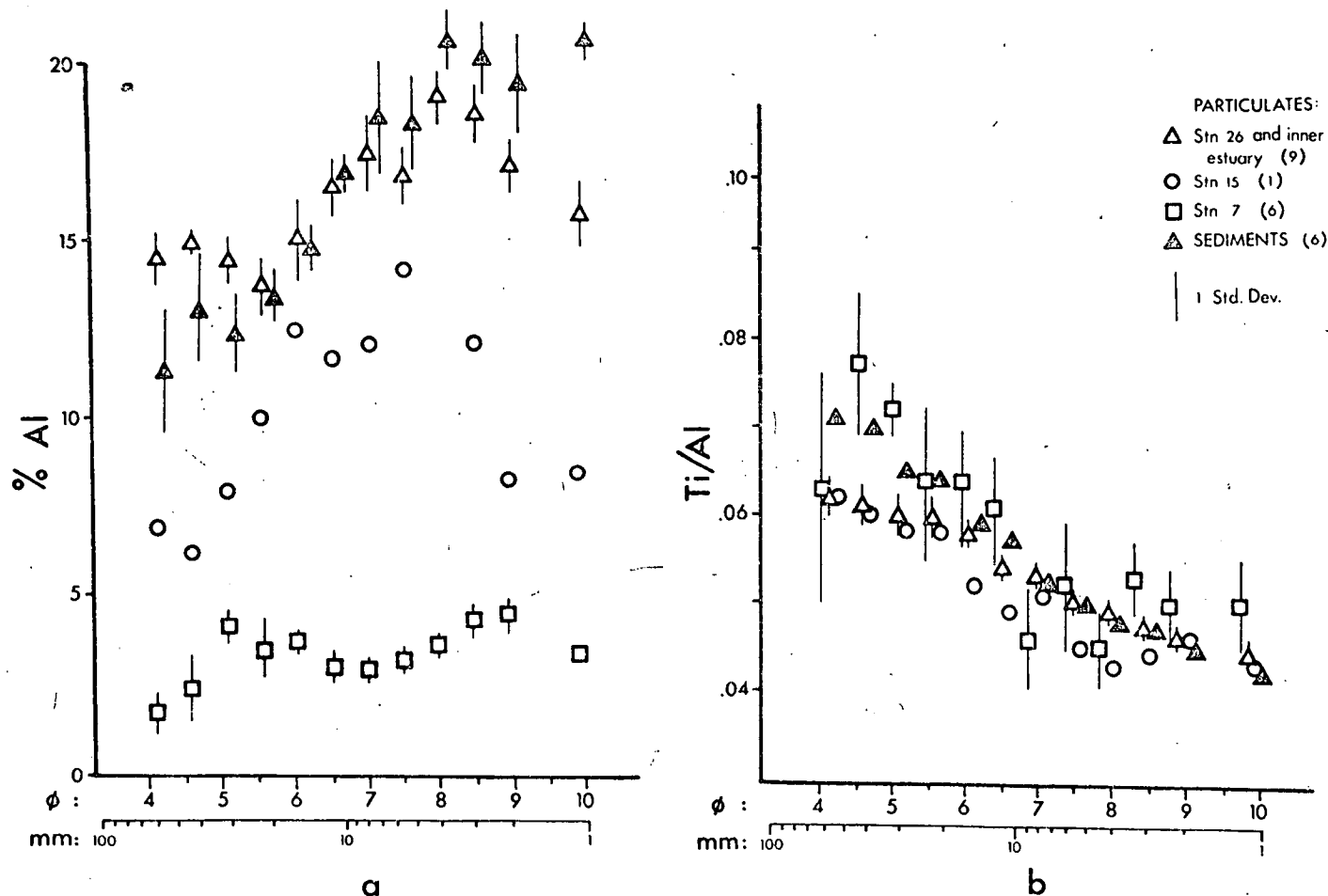


Fig. 6.8 Comparison of pipette data

a) Percentage of Al versus maximum particle size

b) Ti/Al ratios versus maximum particle size.

'Error' bars are equal to 1 standard deviation (1σ) of the analyses of different samples at each location. They do not represent analytical precision.

are similar to those of the sediments throughout the size range studied (Figure 6.9a), particulate matter from stations 15 and 7 show consistently higher K/Al ratios. Similar trends are noted in the particulate Mg/Al ratios. These samples show very prominent coarse-silt modes (Chapter 4). However, the lack of very high Ti/Al and Fe/Al ratios, and the persistence of slightly higher K/Al ratios at all sizes argue against a mineralogenic role for this excess K. It is likely associated with biogenic material. Although these vary little with particle size, they average 0.15 in particulates from station 26 and the inner estuary, and are only slightly higher than those noted in sediment samples. However, particulate Mg/Al ratios at other stations are distinctly higher, roughly 0.26 at station 15 and 0.43 at station 7. Very high Mg/Al and K/Al ratios have been reported in samples containing much biogenic debris (Price and Calvert, 1973; Skei, 1975) and this may indicate substantial amounts of marine organic matter at these stations relative to the terrigenous loads. Further, high Mg/Al and K/Al ratios have been noted in filtered samples of sewage particulates from the Edinburgh area (Table 6.I), so some of the increase in these ratios, particularly at station 7, may reflect an addition pollutant influence.

TABLE 6.I

Approximate inter-element ratios determined from particulate sewage collected from various municipal plants prior to discharge.

Station	Si/Al	Ca/Al	Fe/Al	Ti/Al	K/Al	Mg/Al	P/Al
Leith	0.31	2.4	3.4	0.013	0.43	0.05	3.2
Musselburgh	1.8	2.6	50	0.046	0.70	0.54	4.2
Wallyford	0.87	11.5	3.7	0.038	1.5	1.3	5.6

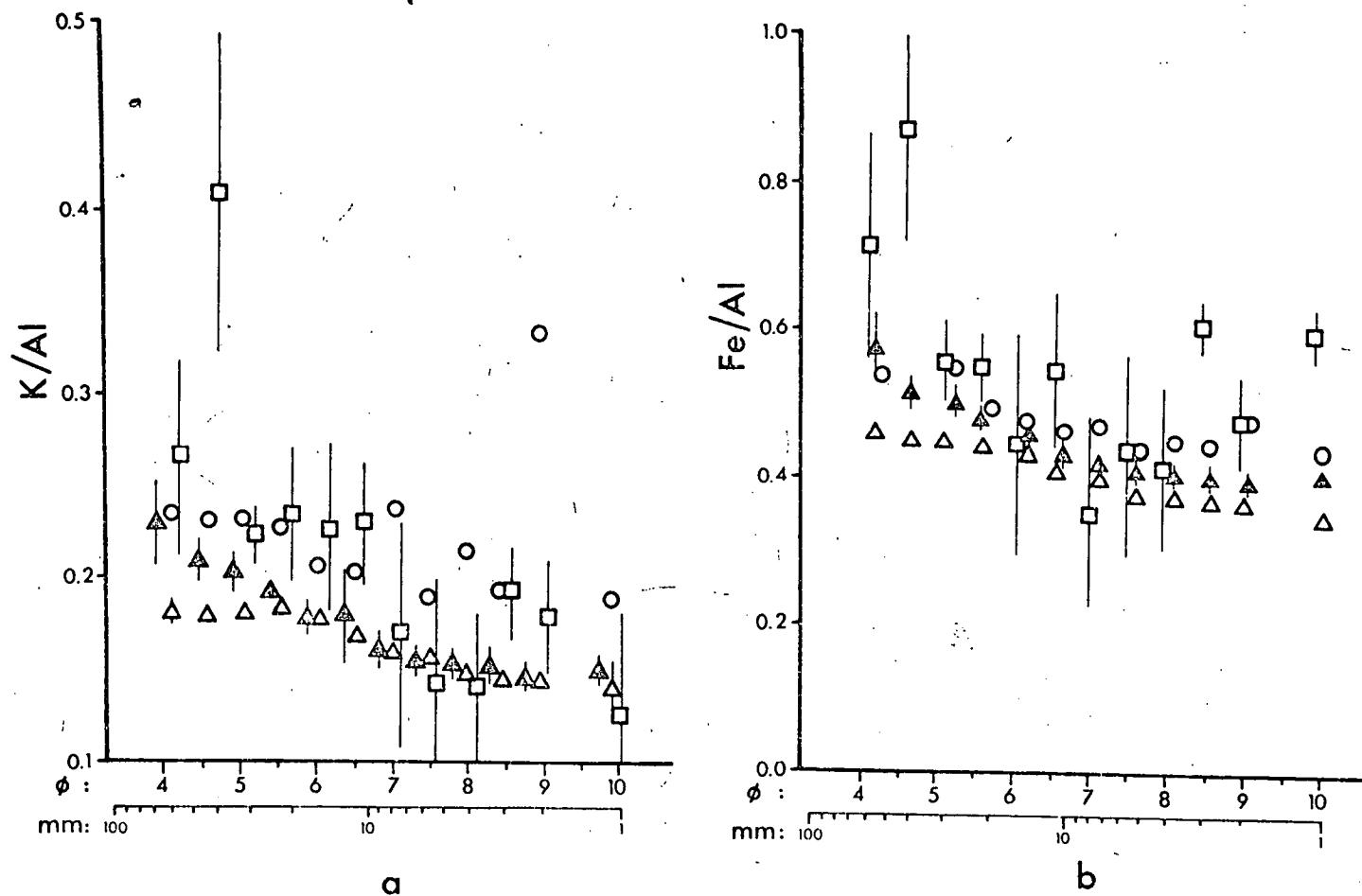


Fig. 6.9 Comparison of (a) K/Al and (b) Fe/Al ratios in different pipette suites versus maximum particle size. See Fig. 6.8 for legend.

The close association between the Fe/Al ratios of the particulate samples and the underlying sediments is shown in Figure 6.9b, with values ranging from ~ 0.6 in the total samples to ≥ 0.4 in the fine-grained material. Only at station 7 are there significantly higher values (> 0.6) in the finest particulates. As high Fe/Al ratios are also seen in sewage samples (Table 6.I), these may again represent the presence of organically associated Fe from municipal effluents.

Much greater variations in Si/Al ratios occur between particulate samples from different areas shown in Figure 6.10a. Si/Al ratios of particulates from station 26 vary with particle size and closely approximate those seen in the sediments here and at other stations. Such ratios range from ~ 2 in the total samples to ~ 1.6 in the finest fraction. At station 15, very high Si/Al ratios of 5.4 are seen in the particulate matter coarser than 5ϕ ($30 \mu\text{m}$). Finer-grained material at this station shows only a moderate increase in values over those of the sediments. The large diatom fragments shown in Plate 5-I undoubtedly account for the anomalously high Si/Al ratios here. The local sediments showed slightly elevated Si/Al ratios compared to those at other stations (Appendix E), and may indicate some local sedimentation of skeletal debris. A high biological productivity at station 7 at the time of sampling (August, 1976) may also account for the apparently non-terrigenous associations of Si as evidenced by Si/Al ratios of > 3.0 . Here, however, even the finest particulate material shows Si/Al ratios significantly in excess of those in the sediments. This might be interpreted as indicating some scavenging of dissolved Si onto existing fine-grained particulates as suggested by Bien et al (1958), and Liss and Spencer (1970), but a much more likely explanation

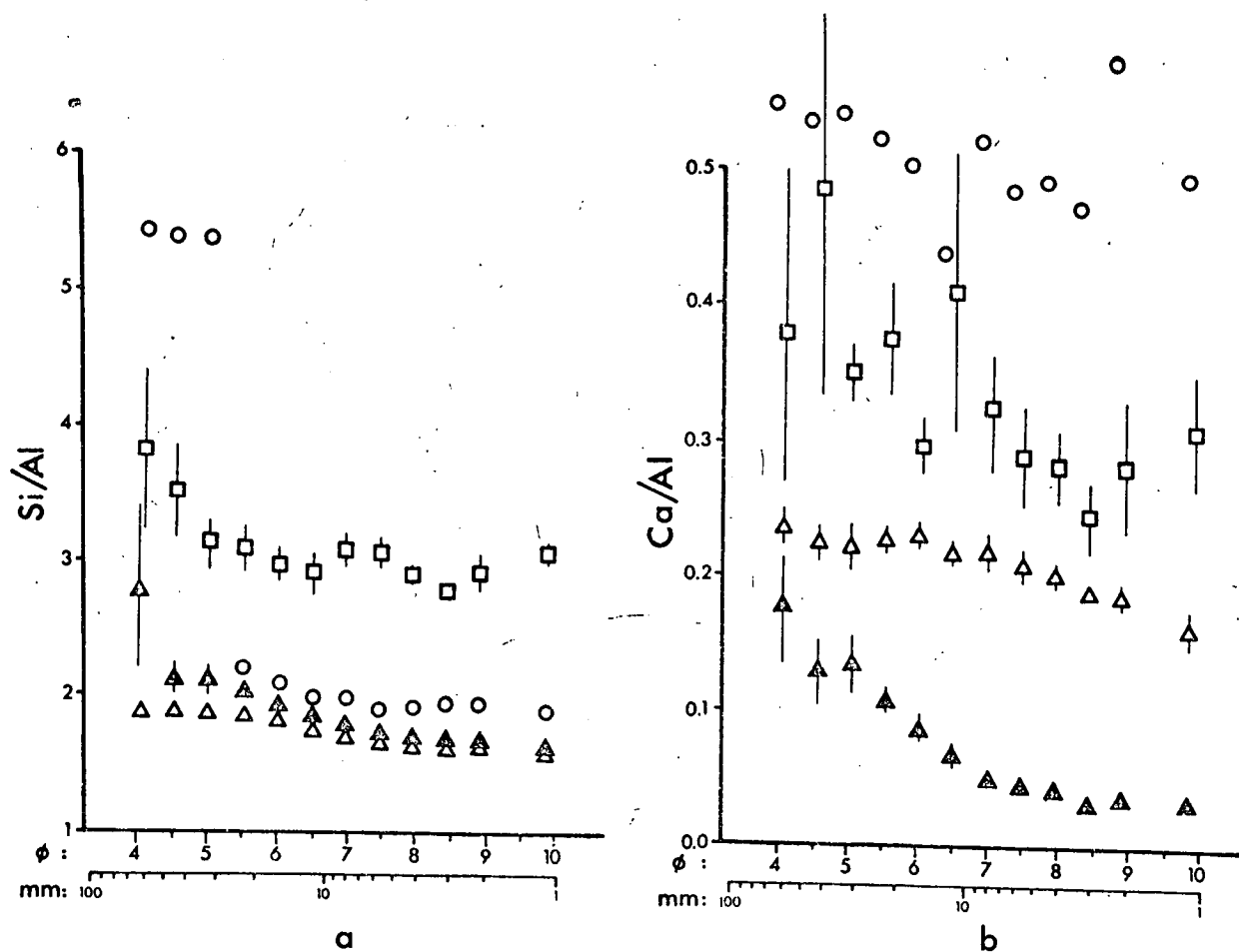


Fig. 6.10 Comparison of (a) Si/Al and (b) Ca/Al ratios in different pipette suites versus maximum particle size. See Fig. 6.8 for legend.

is that the high Si/Al ratios in this fraction reflect the buoying of siliceous skeletal debris through its incorporation into organic aggregates of low density. Further, significant amounts of fine-grained biogenic fragments were seen in SEM photographs to account for these anomalous inter-element ratios.

The Ca/Al ratios of different samples (Figure 6.10b) show the greatest range of values of the parameters studied. The lowest values consistently occur in fine-grained sediments. All particulate samples show Ca/Al ratios which decrease linearly with decreasing particle size, probably indicating a continuum of sizes of biogenic debris which is masked to varying degrees by detrital aluminosilicates. High Ca/Al ratios typify sewage particulates (Table 6.I), so to some degree its effect may account for the high values noted at station 7. Before such assertions are accepted, however, some estimate as to the effect of masking of this material by the terrigenous fraction must be gained.

Ratios of P and S to Al as a function of particle size are shown in Figure 6.11a and b. Both elements show pronounced enrichment relative to Al in particulate samples from station 7, suggesting that their primary non-terrigenous associations are with organic (sewage) detritus, while a further association with marine organic matter may be indicated by the high levels of these ratios in particulate samples from station 15. These, although much lower than those at station 7, are consistently higher than those noted in western areas or in sediment samples. P/Al ratios vary inversely with particle size in all samples except the bottom sediments at station 26. S/Al ratios show similar trends in some samples, but as they vary directly with particle size in the particulate samples from station 26 and in the underlying sediments here, it is possible that the mineralogy as well as the

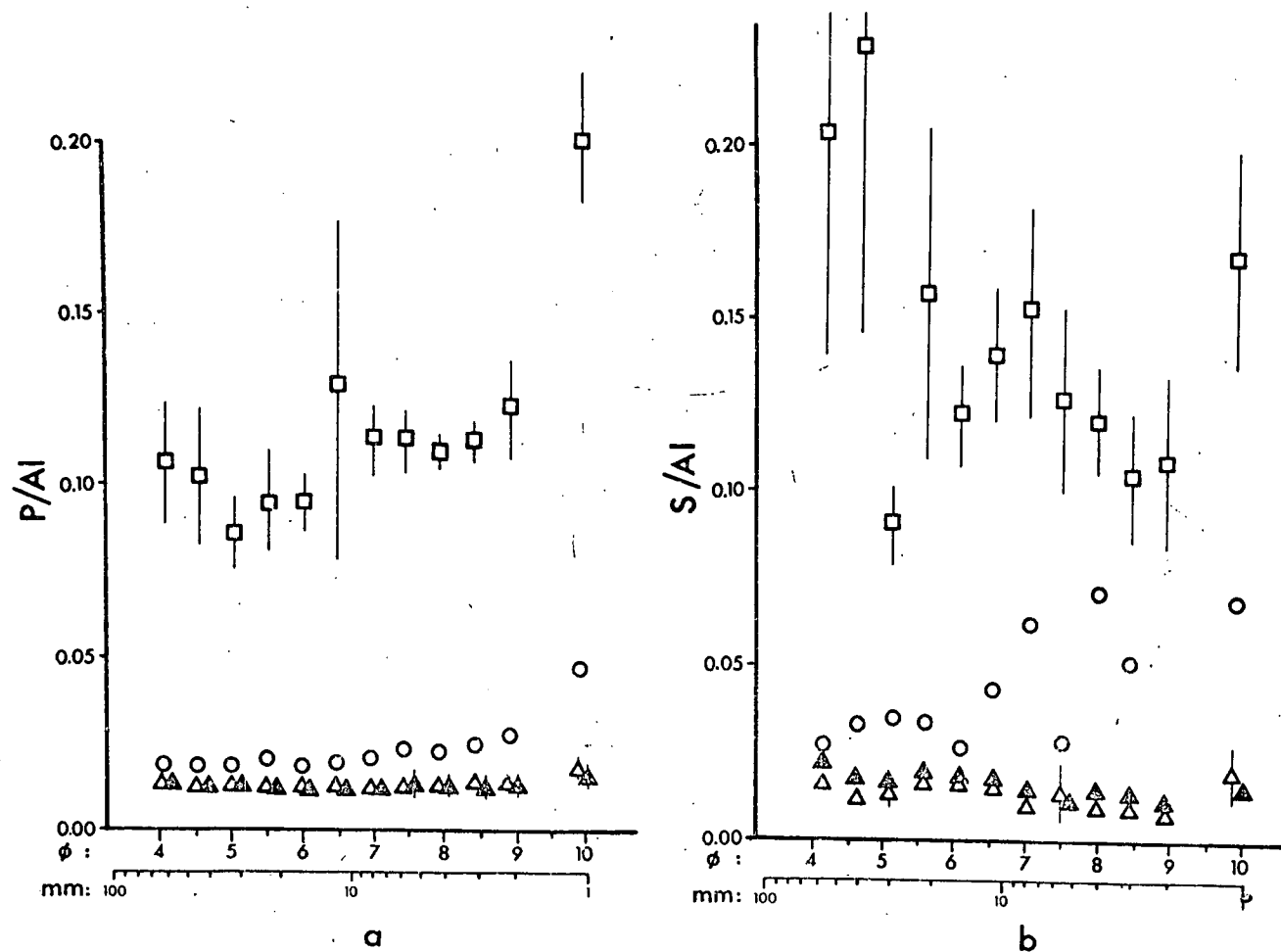


Fig. 6.11 Comparison of (a) P/AI and (b) S/AI ratios in different pipette suites versus maximum particle size. See Fig. 6.8 for legend.

organic matter is influencing these ratios.

6.4 The application of particle-size studies.

Good correlation between the size-specific Ti/Al ratios of sediments and particulate samples was noted in these samples, regardless of the fluctuations in other elemental ratios in samples from different areas. Progressively poorer correlation suggests a decreasing degree of exclusive association with the terrigenous fraction for Fe, K, Si, Mg, Ca, S and P. Speculations as to mineralogical associations may be tenable for Ti, Fe, K and Si within particulate samples shown to be consistent with underlying sediments with respect to these elements. Decreasing element-to-aluminium ratios of these may be interpreted as indicating some preferentially coarse-grained minerals such as quartz and feldspars (as shown in XRD studies), and possibly pyrite (FeS_2), iron oxides such as magnetite (Fe_3O_4) and ilmenite (FeTiO_3) and possibly some rutile, sphene and garnet.

Decreasing Si/Al and Fe/Al ratios in the pipette samples of size progressively less than $15\ \mu\text{m}$ (6ϕ) are consistent with a decreasing mean particle size (and physical separation) of biotite, chlorite and illite (Mudroch *et al.*, 1976). The K/Al ratios substantiate this trend for biotite, illite and muscovite¹. This may be a tenuous extrapolation of the data, but it is a far more dependable speculation than estimating clay mineralogy by comparison of the inter-element ratios of different bulk samples (cf. Baker, 1976). Further, these trends are best expressed in samples unlikely to contain coarser material artificially maintained in suspension by organic aggregates.

1. Both the conclusions of the theoretical study in Appendix A and the results of subsequent comparisons between XRF and wet chemical analyses (Doff, *pers. comm.*) indicate that these chemical trends are real, and must therefore represent mineralogical variations as opposed to matrix absorption effects.

It is unclear whether the anomalously low Ca/Al and P/Al ratios of fine-grained sediments reflect real chemical variation. This pattern is consistent with slow digestion of fine-grained Ca-rich dust in an environment of reduced pH (Krauskopf, 1967). Such conditions could result from the decomposition of organic material at the sediment-water interface (Berner, 1974). It is equally likely, however, that these trends reflect varying 'mixes' of biogenic Ca and clay-sized aluminosilicates due to the more rapid accumulation of the latter in the sediments.

In samples from different areas, however, speculations as the actual abundance of biogenic skeletal matter (Si and Ca) or organic detritus (P and S) become very tenuous on the basis of inter-element ratios alone. Although these have proved valuable in speculating size-specific trends and qualitative estimates of major-element partitioning, they reflect both variations in chemical association and the mixture of terrigenous and non-terrigenous components. Some method of determining the abundance of non-terrigenous components must be used before bulk samples may be examined in detail.

In previous studies of the chemistry of suspended particulate chemistry, such methods have been proposed. Spencer and Sachs (1970) suggested that direct multiplication of the particulate Al abundance might provide a useful estimate of the loading of detrital aluminosilicates, from which the amounts of other elements in excess of this material could be calculated. Price and Calvert (1973) used inter-element ratios (to Al) which were taken to be representative of local inorganic detritus (for Si/Al) or sedimentary material from the literature (Ca/Al and Fe/Al), and used these in conjunction with loadings of particulate Al to estimate the amounts of specific elements in

excess of the levels attributable to such association. Skei (1975) selected specific inter-element ratios of river-borne detritus entering Sorfjorden as being representative of the terrigenous end-member, and performed similar calculations.

Although these techniques may be useful in areas with low suspended loads and fairly uniform sizes of terrigenous constituents, they are inapplicable to the study of nearshore particulate matter samples because of their demonstrable variations in particle sizes (Chapter 4), and the degree to which inter-element ratios may vary as a function of this factor. A more detailed method is required in estuarine work, and the pipette studies presented here suggest a useful possibility.

As mentioned earlier, the Ti/Al ratios of these samples show the best correlation between suspended particulate matter and sediment samples. The latter usually show higher Ti/Al ratios in the total sample by virtue of their greater abundance of coarse-grained minerals. These ratios in particulate samples are not affected by partitioning of the other major elements between the terrigenous fraction and other components. Therefore, it would appear that the Ti/Al ratios of samples from the Forth at least, may be used to approximate the maximum size of the terrigenous fraction of a given particulate sample. Once this is done, the abundance of this material may be derived from the absolute loading of particulate Al, and the abundances of non-terrigenous elements in the sample may be approximated using the equation:

$$X_{\text{excess}} = X_{\text{total}} - (Al_{\text{total}} * X/Al_i) \quad \text{Eq. 6.1}$$

where X_{excess} is the abundance of element X attributed to non-terrigenous associations,

X_{total} is the abundance of element X as analysed,

Al_{total} is the abundance of particulate Al as analysed, and

X/Al_i is the inter-element ratio which characterizes the terrigenous source material of maximum size 'i', as determined by the Ti/Al ratio of the sample.

Although subject to some unavoidable errors in data manipulation, this method constitutes an improvement on existing techniques, as it accounts for variations in loading and particle size, both of which may vary considerably in coastal waters. It is best suited to determination of excess levels of those elements which occur mainly in non-terrigenous forms (e.g. P), but may be used to indicate gross variations in other elements as well.

The size-specific criteria on which these calculations are based in later chapters of this thesis are shown in Table 6.II. These were derived from the sediment sample at station 26, as this sample appeared on close examination of the chemical trends (Appendix E) and SEM studies to be least affected by non-terrigenous material.

This method may be applied in other study areas as well, but the size-specific criteria on which it is based must be established locally. Applied to samples from the Forth, it will provide a locally-calibrated means of accounting for observed variations in particulate chemistry.

Table 6.1

SUMMARY OF THE SIZE-SPECIFIC INTER-ELEMENT RATIOS DETERMINED
BY PIPETTE ANALYSES TO BE REPRESENTATIVE OF TERRIGENOUS MATERIAL (SEE TEXT).

MAX SIZE		INTER-ELEMENT RATIO OF TERRIGENOUS FRACTION							
PHI	μM	SI/AL	CA/AL	FE/AL	TI/AL	K/AL	MG/AL	P/AL	S/AL
4.0	62.5	2.250	0.240	0.630	0.082	0.235	0.145	0.011	0.021
4.5	44.2	2.230	0.198	0.564	0.077	0.220	0.145	0.011	0.020
5.0	31.2	2.130	0.160	0.520	0.073	0.205	0.145	0.010	0.018
5.5	22.1	2.020	0.128	0.488	0.068	0.192	0.145	0.010	0.017
6.0	15.6	1.875	0.096	0.450	0.065	0.180	0.145	0.009	0.015
6.5	11.0	1.770	0.072	0.435	0.061	0.170	0.145	0.009	0.014
7.0	7.8	1.710	0.054	0.415	0.058	0.162	0.145	0.008	0.012
7.5	5.5	1.675	0.040	0.398	0.055	0.155	0.145	0.008	0.011
8.0	3.9	1.645	0.030	0.384	0.053	0.150	0.145	0.007	0.010
8.5	2.8	1.625	0.028	0.372	0.051	0.147	0.145	0.007	0.008
9.0	2.0	1.610	0.024	0.366	0.049	0.144	0.145	0.006	0.007
9.5	1.4	1.595	0.024	0.358	0.048	0.142	0.145	0.006	0.005
10.0	1.0	1.570	0.023	0.354	0.046	0.140	0.180	0.005	0.004

CHAPTER 7

TIDAL INFLUENCES ON PARTICULATE CHEMISTRY

7.1 Introduction.

In the preceding chapters, variations in the chemistry of suspended particulate matter of specific mineralogy, source and particle size have been examined, and some appreciation of the degree to which bulk (total sample) analyses represent these trends has been gained. These findings may now be applied to the interpretation of the character of samples in situ. Firstly, chemical determinations of particulate samples collected in conjunction with tidal cycle monitoring will be examined to augment the purely gravimetric loadings discussed in Chapter 3. The purpose of this examination is to determine whether significant differences in particulate chemistry are indicated at different states of the tide, and to provide a first evaluation of the extent to which hydrodynamic processes affect the chemistry of this material.

7.2 Methods.

Samples of suspended particulate matter were collected at several depths at hourly intervals during full semi-diurnal tidal cycles at Stations 26, 15 and 7 according to field techniques described in Chapter 3. The volumes of water filtered were ~66 ml at station 26, ~200 ml at station 15 and ~130 ml at station 7. The samples were analysed on Nuclepore® 0.45 μm membrane filters for Al, Si, Ca, Fe, Ti, K, Mg, P and S by techniques detailed in Appendix C. Gravimetric and hydrographic data from these stations are shown in Chapter 3.

7.3 Results.

The abundance of particulate Al is shown for the three tidal station sampling periods in Figure 7.1. In each case, the abundance of aluminosilicates, as indicated by Al, appears to vary with total

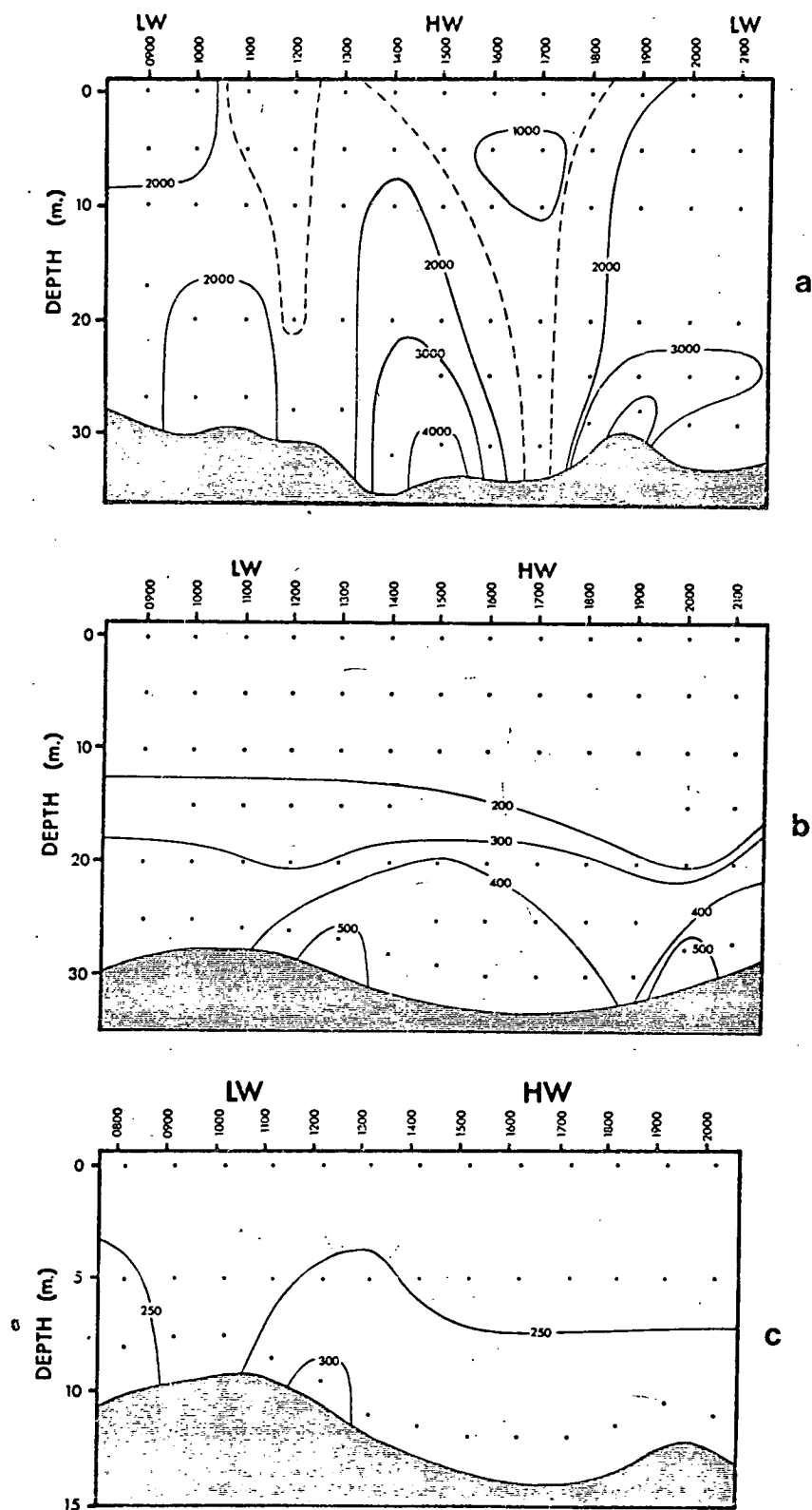


Fig. 7.1 Concentration of particulate Al (in $\mu\text{g l}^{-1}$) during tidal station monitoring - a) station 26; b) station 15; c) station 7.

load (Chapter 3), indicating the importance of fine-grained terrigenous debris in these samples.

At station 26, the zones of the highest Si/Al ratios correlate with those of high total suspended load, ranging from >1.9 in bottom waters near high tide and in highly loaded samples at the end of the sampling period to <1.8 through the water column just after high water when total loadings are reduced (see Figure 7.2a). These values are consistent with the range noted in pipette studies, and indicate the preferential settling of coarse-grained minerals in response to hydrodynamic influences. The distribution of Ca/Al ratios over the tidal cycle (Figure 7.2b) are more independent of the loading of aluminosilicates. These exceed 0.23 in the bottom waters symmetrically about high water, but are lower in the surface waters and toward low tide. The Ca/Al ratios of these samples appear to correlate better with salinity (Figure 3.5a) than with suspended load, and may indicate the presence of significant amounts of biogenic Ca in suspension, derived from the east.

A subtle relationship between Fe/Al ratios and suspended load concentrations is apparent in Figure 7.3a. These range from <0.45 in surface waters and at times of low ($<10 \text{ mg l}^{-1}$) loading to >0.45 in bottom waters and at low tide. These values are consistent with those noted in the total pipette samples from this area, and as for Si/Al ratios, argue towards a dominant particle-size influence.

The patterns of P/Al ratios at station 26 contrast to those of Si/Al and Fe/Al as shown in Figure 7.3b. P/Al ratios are low, and range only from 0.010 to 0.014. These are consistent with the values noted in pipette studies, but show no marked variation through the tidal cycle as a function of loading.

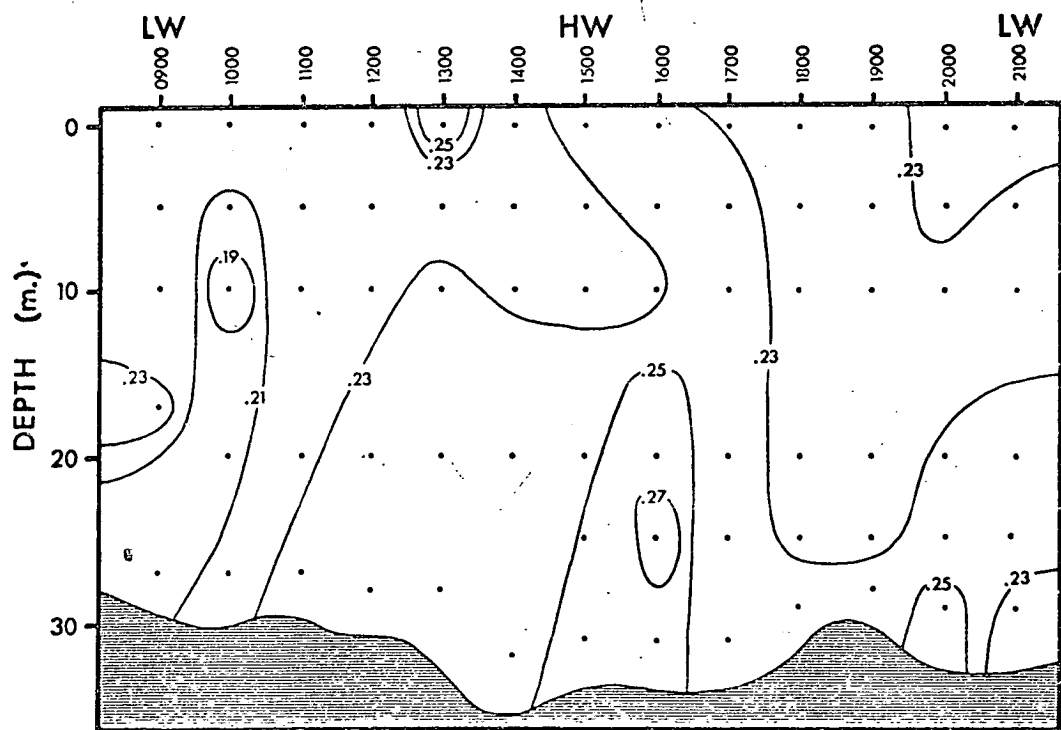
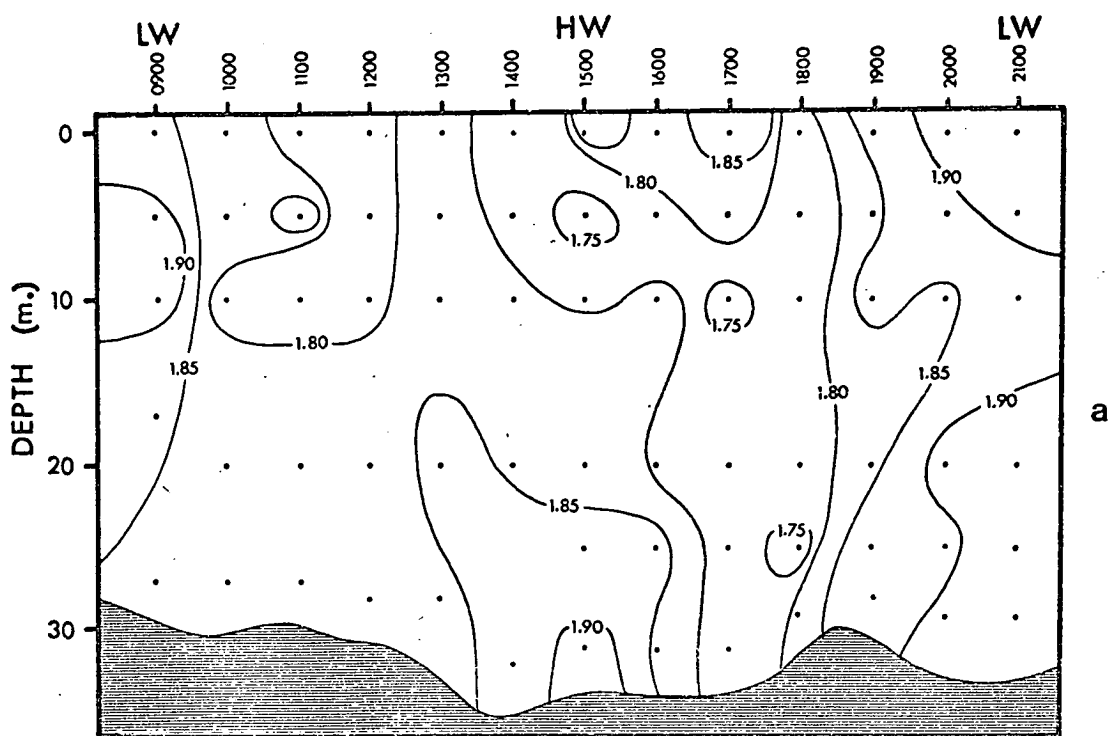


Fig. 7.2 Inter-element ratios of suspended matter during tidal cycle monitoring, station 26.
a) Si/Al b) Ca/Al.

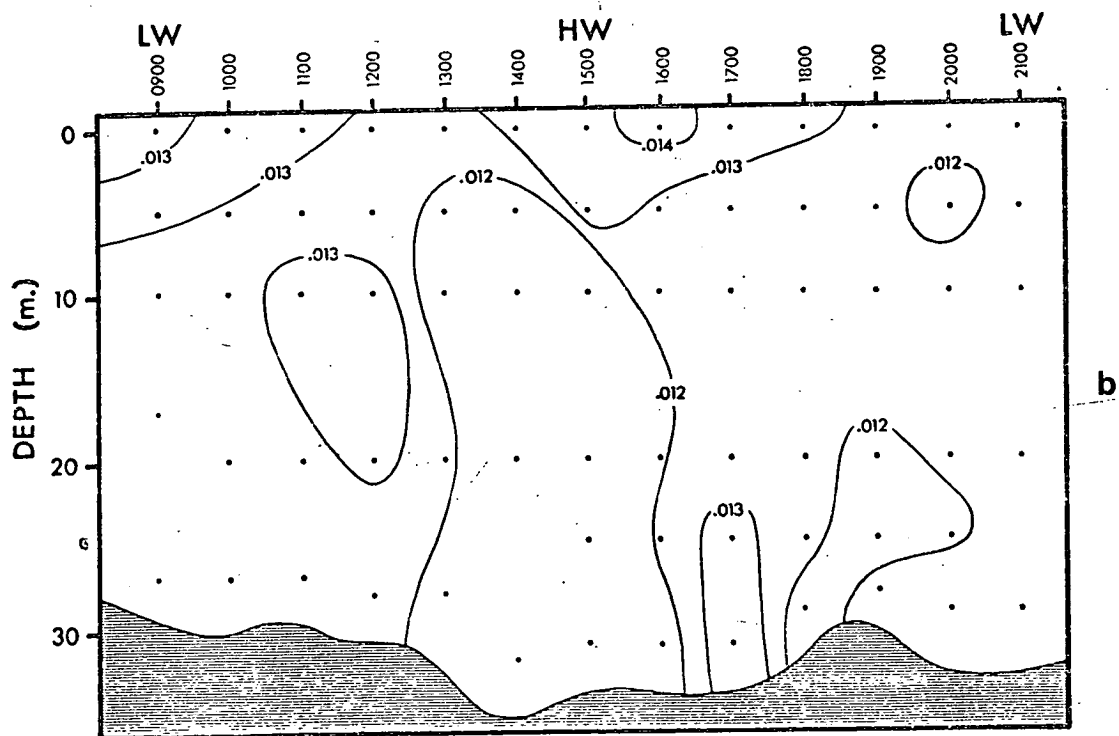
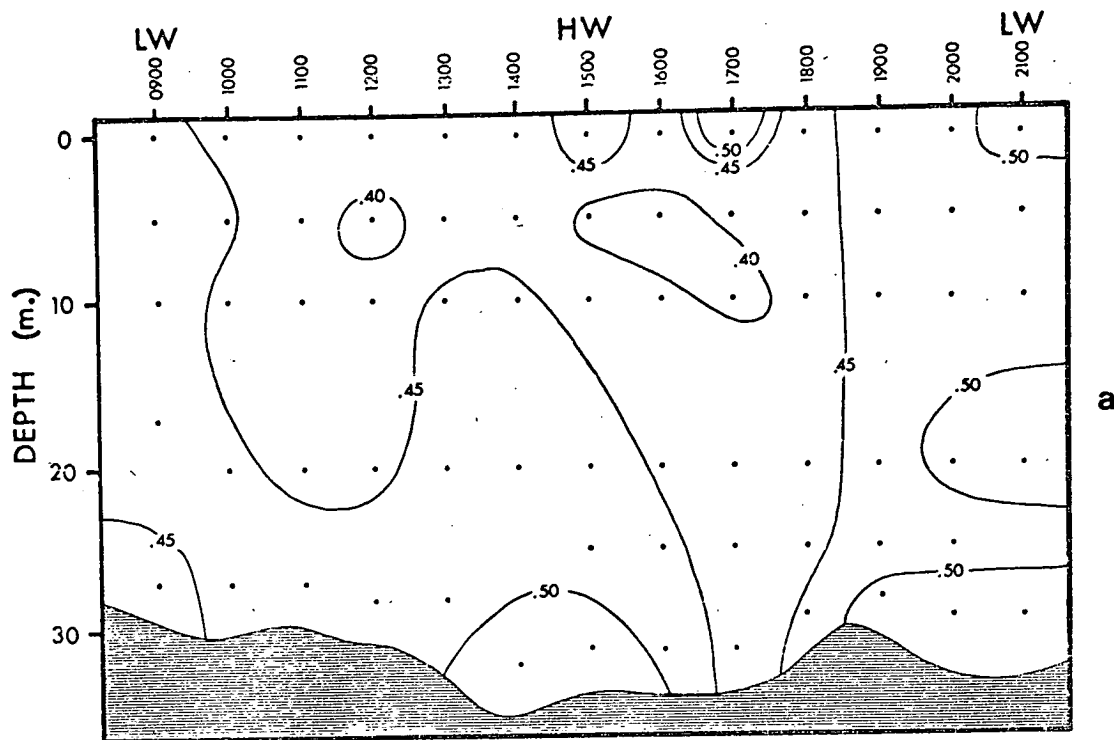


Fig. 7.3 Inter-element ratios of suspended matter during tidal cycle monitoring, station 26.
a) Fe/Al b) P/Al.

The pronounced distinction between top and bottom waters at station 15, as discussed for salinity and suspended matter concentrations (Chapter 3) is also expressed in the chemical characteristics of the suspended material. In contrast to station 26, Si/Al ratios (Figure 7.4a) are higher here ($\sim 1.7 - 3$). Samples from depths >15 m consistently show Si/Al ratios in excess of 2.0, while still higher values (>2.2) typify the bottom water samples during times of peak flow. These ratios are in excess of those noted in sediment samples in Chapter 6, and indicate the presence of significant amounts of coarse-grained biogenic Si in the samples. The lowest Si/Al ratios (<1.8) are found in surface samples (<10 m). These compare to the ratios noted for total samples at station 26, but their occurrence in this area of low energy and suspended load concentrations argues against only a mineralogical association for Si.

Similar vertical gradients were noted for particulate Ca/Al ratios. These also exceed the ratios noted at station 26, ranging from 0.1 to 0.7, with most falling between 0.3 and 0.6. Deeper water particulate samples (>15 m) have Ca/Al ratios consistently greater than 0.4, while the highest values (>0.5) are associated with the bottom waters, particularly after low tide.

Particulate samples at depths >15 m have Fe/Al ratios in excess of 0.45 throughout the tidal cycle at this station. Lower values are found in surface water samples regardless of the state of the tide, while in deeper waters (>20 m), the highest Fe/Al ratios are apparent during flood and ebb flow. Ratios of K and Ti to Al show similar trends, suggesting that particle size and settling effects dictate the particulate chemistry of these elements.

The most significant chemical trends noted at station 15 are

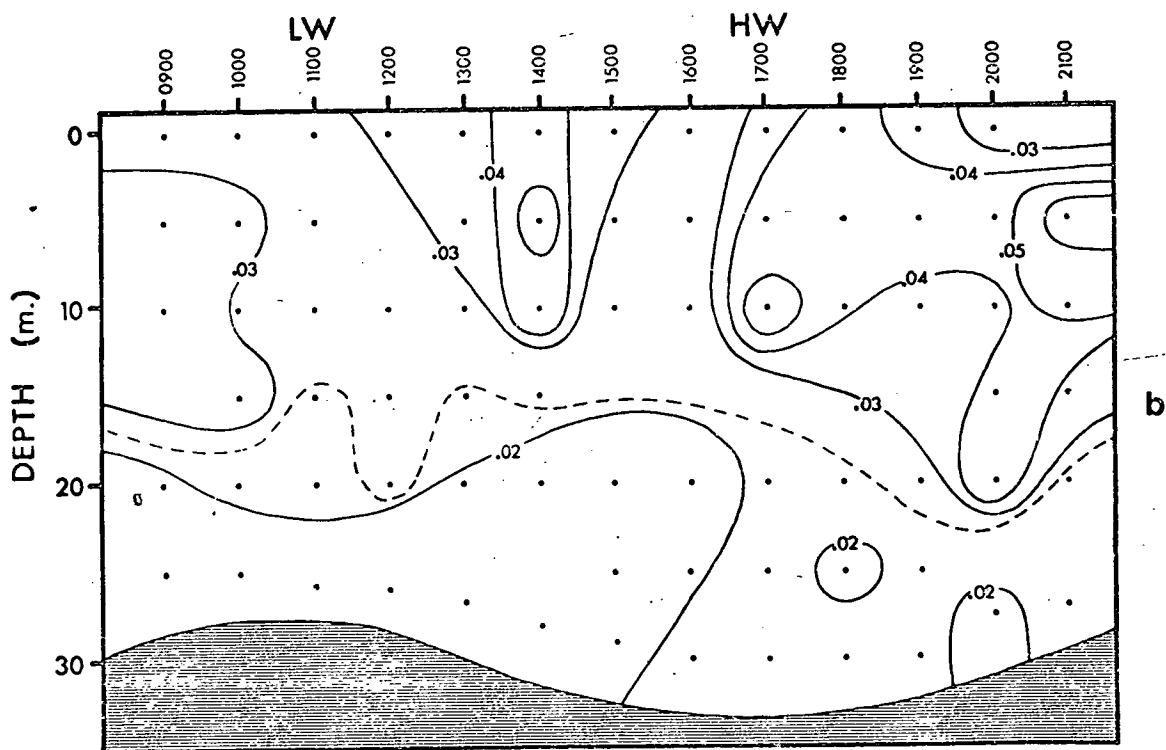
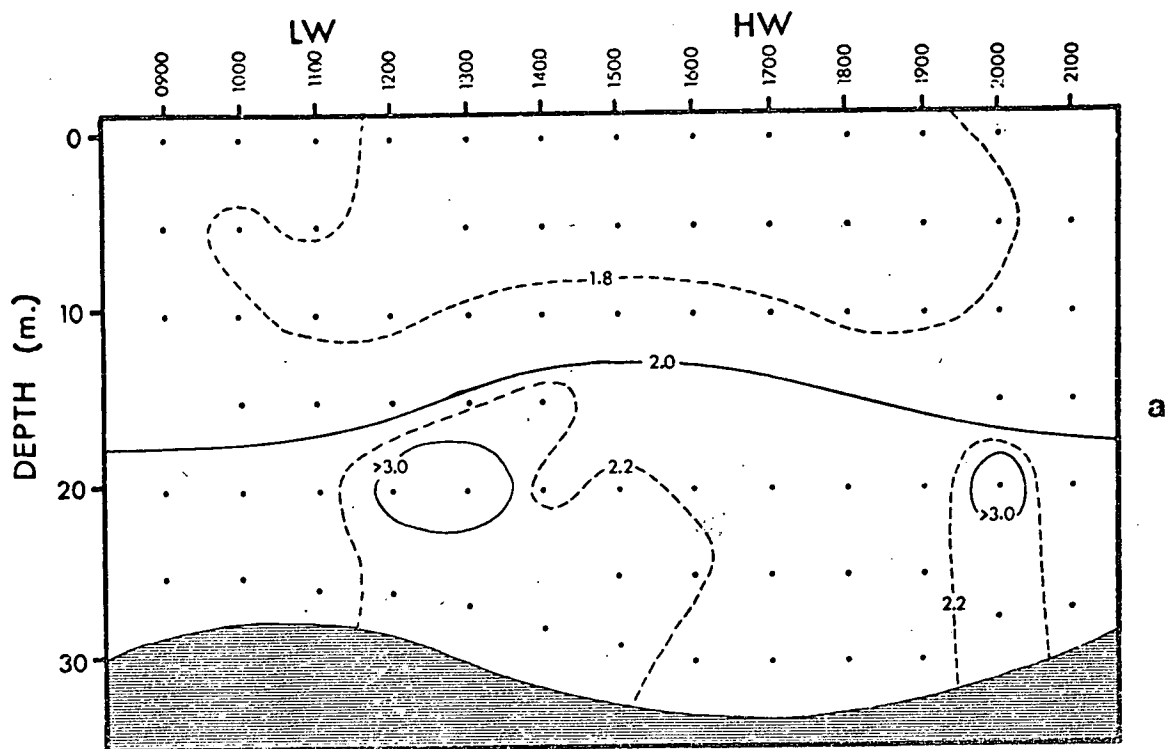


Fig. 7.4 Inter-element ratios of suspended matter, station 15.
a) Si/Al b) P/Al.

those of the P/Al ratios of particulate samples which show patterns opposite to those of Si/Al, Ca/Al and Fe/Al throughout the tidal cycle (Figure 7.4b). Values range from 0.018 to >0.060 , far exceeding the range noted for other ratios, and are also much higher than the P/Al ratios seen at station 26, indicating the importance of organic material relative to terrigenous debris. P/Al ratios <0.025 typify bottom waters (>20 m), while values >0.030 are found only in surface waters, particularly during ebb tide.

Compared with the data from the two previous stations, little significant vertical or tidal variations in particulate inter-element ratios are apparent at station 7 (Figure 7.6), particularly with respect to Si/Al, Ca/Al and Fe/Al. The gravimetric and hydrodynamic studies as described in Chapter 3 indicate a fairly homogeneous water mass and particulate suspension, a factor which appears to be reflected in most elemental ratios. For instance, Si/Al ratios range only from 2.4 to 2.8, while Ca/Al values vary between the narrow limits of 0.22-0.32, and Fe/Al ratios range only from 0.45 to 0.53. It is significant, however, that the Si/Al ratios (and to some degree Ca/Al) are higher than those seen at station 26, reflecting the importance of biogenic material here relative to low concentrations of aluminosilicates. Little variation with the state of the tide is apparent for those elements predominantly associated with terrigenous and biogenic constituents.

The most significant chemical trends at station 7 are those shown by the P/Al ratios (Figure 7.5b). At all times, these are very high, and range from 0.04 to 0.12, with most falling between 0.04 and 0.08. These exceed even those ratios shown in the surface waters at station 15, where loadings of particulate Al are equivalent. The highest values

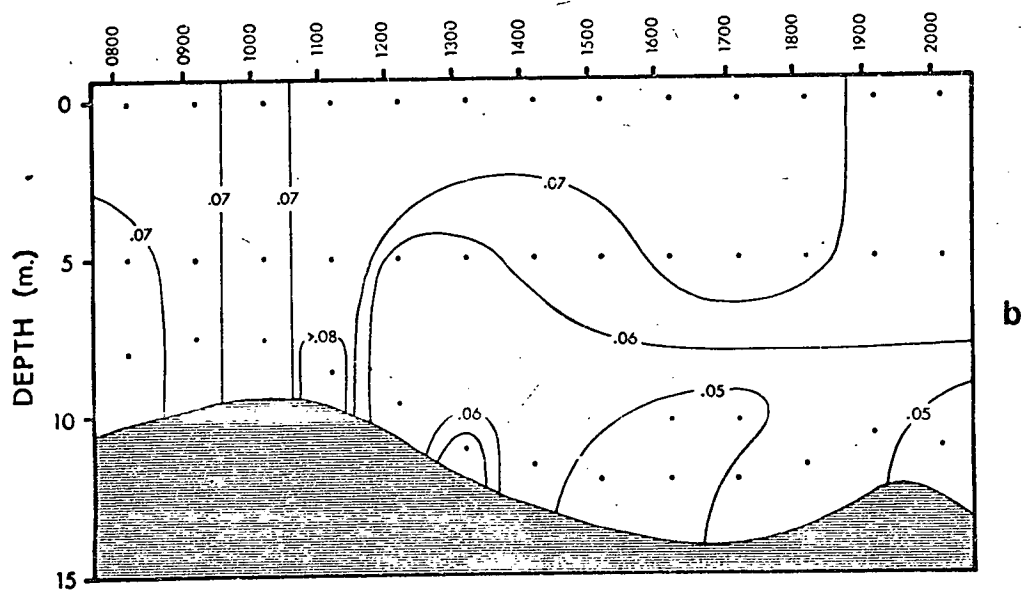
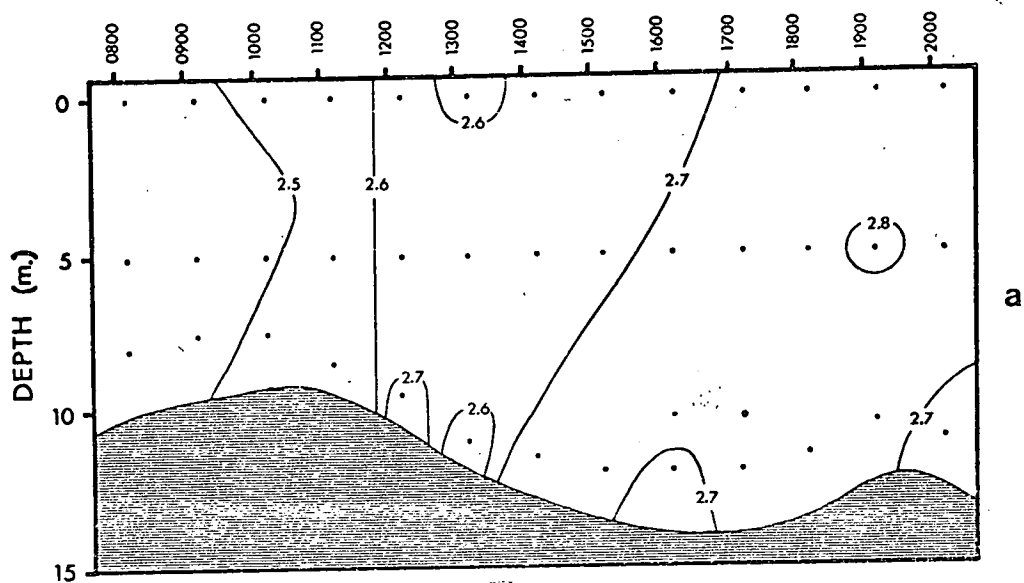


Fig. 7.5 Inter-element ratios of suspended matter, station 7.
a) Si/Al b) P/Al.

(>0.06) are consistently found in the surface waters (<5 m) throughout the tidal cycle, and through the entire water column at low tide. These undoubtedly reflect the influence of organic detritus as seen in Plate 5.I.

7.4 Particulate chemistry and the tidal phase.

In the western and central areas of the Firth of Forth, the loadings of particulate Al and the Si/Al and Fe/Al ratios of the particulate samples appear to vary locally with the concentration of suspended matter. Similar trends are shown for K and Ti. Although poorer correlation is evident for Ca/Al ratios, these broadly show similar characteristics. The relatively homogeneous suspensions at station 7 are typified by minimal variations in these ratios. These trends indicate that hydrodynamic processes and chemical changes as a function of particle size play a major role in dictating the vertical and temporal characteristics of particulate chemistry. To some degree, the inverse relationships between P/Al ratios and loading also conform to this pattern.

Although inter-element ratios are of some value in defining chemical variation, they are affected by both real chemical changes and varying relative loads of different components. The method developed in the previous chapter for determining the abundance of major elements in non-terrigenous form was applied to these samples in order to distinguish real chemical trends from mixing effects. These data (see Appendix H) show considerable scatter, but the general trends may be described briefly. These have been summarized in Table 7.I, which lists the mean concentrations of non-terrigenous Si, Ca, Fe and P in the upper and lower half of the water column at each station as a function of the state of the tide.

TABLE 7-I

Average abundance (in $\mu\text{g l}^{-1}$) of non-terrigenous elements in suspension during tidal station monitoring.

Station	Tide	Depth	Excess Si	Excess Ca	Excess Fe	Excess P
26	flood	surface	26	204	3	5.0
		bottom ¹	4	276	8	4.1
	ebb	surface	24	239	29	5.4
		bottom ¹	9	291	23	4.7
15	flood	surface	30	54	7	3.8
		bottom ¹	211	165	25	4.0
	ebb	surface	26	54	7	5.2
		bottom ¹	148	162	28	4.9
7	flood	surface	183	42	10	13.5
		bottom ²	201	50	6	11.8
	ebb	surface	136	32	3	14.2
		bottom ²	187	44	6	11.8

¹Depth 15 m

²Depth 5 m.

The most significant aspects of these data are the different concentrations of non-terrigenous elements at the three stations, particularly for P. Despite the difference in P/Al ratios at stations 26 and 15, it appears that the abundance of particulate organic P is roughly similar, being only slightly higher in the west. Very high levels of organic P ($9-16 \mu\text{g l}^{-1}$) are indicated at station 7, however, undoubtedly reflecting the presence of sewage waste. Here, the levels of organic P are highest at low tide and in the surface waters during flood tide (see Figure 7.6a). This pattern conforms to that indicated by the P/Al ratios (Figure 7.5b). By contrast, the levels of particulate organic P at the other stations show little vertical variation, despite the differences in loading. This is particularly significant at station 15 where the distinction between top and bottom waters is expressed in all other chemical parameters. In this sense, the organic P appears to be relatively independent of the total load, and is not subject to short-term settling effects. This suggests its occurrence either as small particles, or more likely as organic aggregates of low density. As such, this material may be subject to transport in a manner which is independent of terrigenous material, resulting in selective chemical sorting of particulate matter by physical means.

At station 15, the pronouncedly higher concentrations of (presumably) biogenic Si and Ca in the bottom waters may indicate a net accumulation of skeletal debris which accumulates at, and is resuspended from, the local sediments (see Figure 7.6b). The reason for the apparent increase in non-terrigenous Fe in these waters (Figure 7.6c) is unclear as yet, but the pronounced vertical gradients again argue towards the importance of resuspension of this material in some form. The sediment sample by which these excess elements were defined

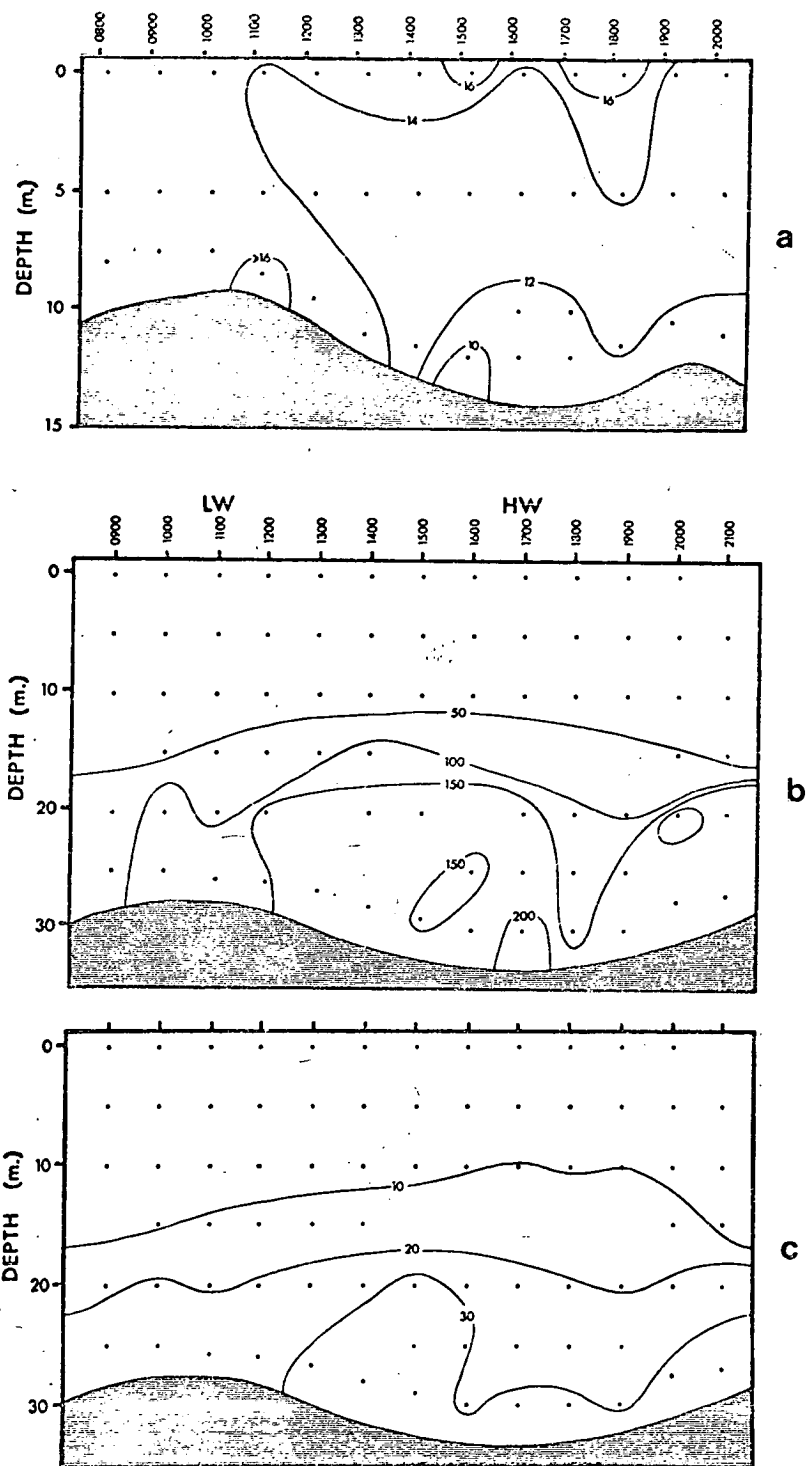


Fig. 7.6 Estimated concentrations of representative 'excess' (non-terrigenous) elements in particulate matter during tidal cycle monitoring.

a) excess P, station 7; b) excess Si, station 15;
c) excess Fe, station 15.

was that at station 26 (Chapter 6), which had lower Si/Al and Ca/Al ratios than the sediment at station 15. As such, some of the excess Si and Ca may reflect mineralogenic variation in addition to biogenic material. Nevertheless, the Fe/Al ratios of these sediments were equivalent, so the levels of excess Fe here must reflect a non mineralogenic influence.

The highest concentrations of biogenic Si occur at station 7. This may result from local biological production in the early spring (April) compared to the mid-winter sampling times at the other stations. These levels are roughly comparable to those of the bottom waters at station 15. At both stations, very slightly higher concentrations of excess Si are indicated during the flood tide. Some preferred landward transport of siliceous skeletal material may be indicated. By contrast, excess Ca concentrations at station 7 are low, and compare to those in the surface waters at station 15. The reason for this is unclear. The high levels of excess Ca indicated at station 26 are to some degree a function of the high overall loadings here and the marked dichotomy between the Ca/Al ratios of particulate material and the underlying sediment. The dominant mineralogenic association of Si and Fe renders the distinction of low levels of these excess elements at station 26 very tenuous because of the vast quantities of terrigenous material. The marked increase in the abundance of excess Fe during ebb flow may, however, indicate the seaward movement of terrigenous waste.

Perhaps the most important point in the data is the illustration that differences in particulate chemistry as a function of location appear to exceed those attributed to local influences. On the whole, little pronounced change in the loading of specific non-terrigenous

constituents occurs due to tidal effects. Areal trends, however, are difficult to assess from these data due to the different sampling times and the distances between stations. Before further interpretation of the transport of particulate matter is considered further, therefore, a more detailed study of the distribution and chemical characteristics of this material in the study area as a whole will be necessary for two reasons. Firstly, this will permit some determination of the net transport resulting from the cumulative effects of many tidal cycles (as indicated by particulate chemistry). Further, these major variations may be used to better define the modes of chemical associations in the samples.

CHAPTER 8

AREAL VARIATIONS IN PARTICULATE CHEMISTRY

8.1 Introduction.

The character of suspended particulate matter in the Firth of Forth has been discussed with respect to loading, particle size distribution, mineralogy, hydrodynamic influences and the relationship between these parameters and the chemistry of the material. In the course of these investigations, data from selected stations in the estuary have been compared to aid the interpretation of gravimetric and chemical studies. The gross areal trends noted in this manner are as follows:

Gravimetric analyses (Chapter 3) indicate that suspended loads at the time of areal sampling ranged from 0.7 to 34 mg l^{-1} . The lightest loadings are associated with surface waters in the central and eastern portions of the study area, the heaviest loadings being found in bottom waters to the west, the intermediate loads ($\sim 6 \text{ mg l}^{-1}$) along the south shore. Particle size analysis indicated a multimodal size distribution in the samples, with modes representing fine silt ($< 6\phi$) and clay-sized fractions (10ϕ) covarying in relative abundance (Figure 3.7). This material is intermittently augmented by coarser ($> 6\phi$) material in response to tidal flow and cross-channel transport. On a gravimetric basis, at least two distinct populations were tentatively identified (Figure 3.8). Within each, maximum particle size varies with load, but samples from the west end of the study area are dominated by high loads of terrigenous components while eastern samples have coarse-grained material which is dominantly biogenic in origin. All samples, however, contain significant mineralogenic assemblages.

A complicated relationship between particle size and the type of constituent particles (terrigenous, biogenic, organic) is reflected in

the chemistry of the particulate samples. Coarse and fine-grained terrigenous components (characterised by associations of Al, Mg, Ti, Fe, K and Si) constitute a variable background to which may be added coarse-grained siliceous skeletal fragments, calcareous debris of widely varying particle size, and organic matter (reflected in P and S abundances) in both soft parts of marine organisms and municipal effluents.

Because of the wide range of loadings observed to date and the apparent seaward fining of at least the terrigenous fraction (indicated by SEM studies in Chapter 5), it has been difficult to quantify the abundance of non-terrigenous components or to hypothesise their mode of occurrence using data from only a few widely-separated stations. In this chapter, a 'point-in-time' areal sampling survey will be examined, and the findings of the previous chapters will be applied in an attempt to interpret the significance of observed chemical trends.

8.2 Methods.

A suite of 160 suspended particulate samples were collected over a two day period (March 17 and 18, 1975) according to the field techniques detailed in Chapter 3.

Major element determinations were performed on a Philips PW-1210 X-ray fluorescence spectrometer for Al, Si, Ca, Fe, Ti, K, Mg, P and S, using the same set of particulate standards which were applied to samples from pipette and tidal station sample suites. Semi-quantitative analyses of Cl were performed to verify the effective removal of sea salts by the earlier rinsing. No salt corrections, therefore, have been applied to the data.

8.3 Results.

The results of gravimetric and chemical analyses are tabulated in Appendix G. Due to the wide range of loadings noted during this sampling period and the association to some degree of all the major elements with the terrigenous component of the samples, direct examination of relative elemental abundances provides little information on the small-scale lateral and vertical changes in elemental associations. Figure 8.1 illustrates the relationships between particulate Al and both Si and P. Each plot demonstrates a gross similarity in elemental ratios, reflecting the dominance of terrigenous detritus in determining particulate chemistry. Some variations in these associations are apparent, but they cannot be related to geographical location or water depth using this mode of data presentation. In order to provide optimum definition of both areal and vertical trends in chemical associations, the following figures will be presented by means of cross-channel and longitudinal profiles (as in Figures 3.2 - 3.4) showing ratios of the major elements to aluminium.

Figure 8.2 shows the loading of particulate aluminium during this sampling period. Loads range from $<200 \mu\text{g l}^{-1}$ to $>1200 \mu\text{g l}^{-1}$, the highest values being found in bottom waters in the west. This pattern is consistent with the distribution of total particulate loads (Figure 3.4), indicating a close association between the abundance of detrital aluminosilicates and total suspended load. The differences in the range of these parameters reflects the importance of coarse-grained minerals and other material, particularly to the west (see page 48). These loadings fall within the range noted by Sholkovitz (1978) in the Tay estuary, but are much higher than those reported in deeper coastal waters such as fjords ($<50 \mu\text{g l}^{-1}$)

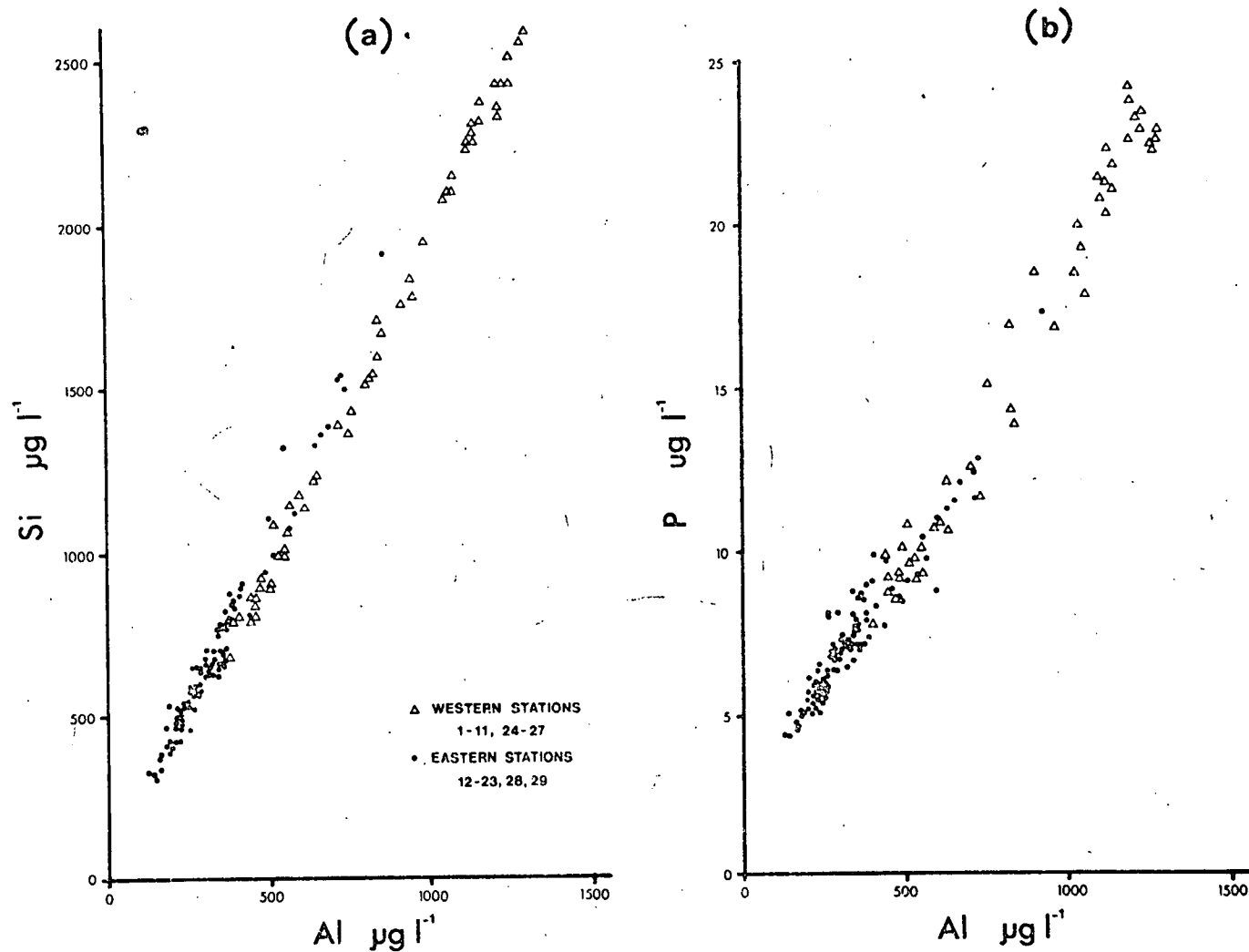


Fig. 8.1 Representative inter-element plots of particulate chemical data from areal sampling.
a) Si versus Al b) P versus Al.

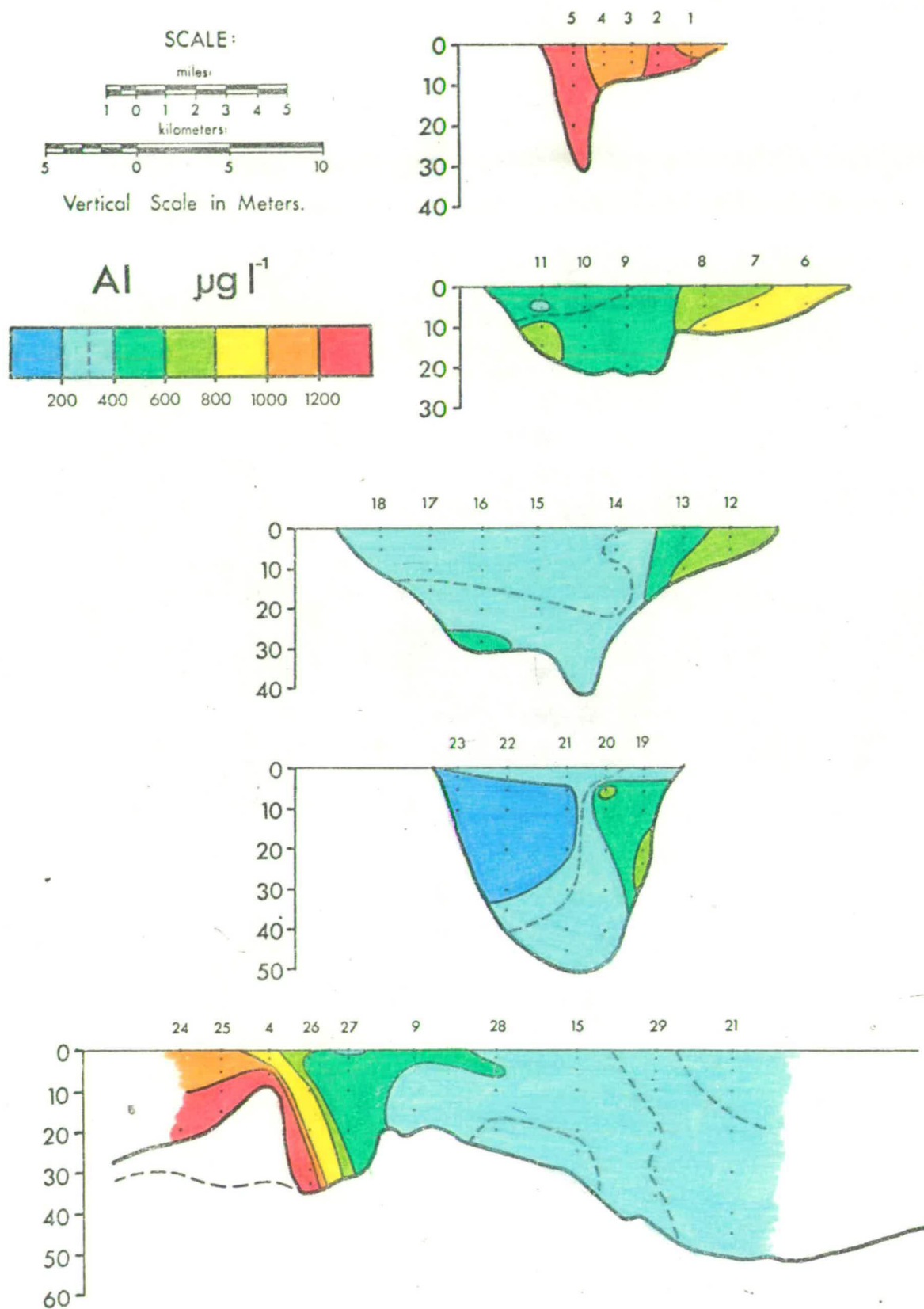


Fig. 8.2 Concentration of particulate Al in the Firth of Forth.
(The station numbers shown refer to Fig. 3.1).

(Taylor, 1974; Skei, 1975; Price and Skei, 1975), sea lochs ($< 75 \mu\text{g l}^{-1}$) (Price and Calvert, 1973) or offshore and oceanic waters ($< 2 \mu\text{g l}^{-1}$) (Spencer and Sachs, 1970; Baker, 1973; Feely et al, 1971; Feely, 1975; and others).

A close covariance between Al loadings and Ti/Al ratios is indicated by Figure 8.3. These values range from < 0.060 in surface waters of the central and eastern estuary to > 0.070 in bottom waters in the west. High Ti/Al ratios in the bottom waters of the central study area and along the south shore, particularly on the ebb tide (Station 19) attest to local resuspension effects and seaward transport of terrigenous components. Pipette studies (Chapter 6) indicated exclusive association of Ti with the terrigenous fraction of these samples, with covariance between the increasing particle size and the Ti/Al ratio. The range and distribution of Ti/Al ratios in Figure 8.3 are consistent with the suggestion of a progressive seaward fining of the terrigenous material.

Similar associations between Fe/Al ratios and suspended load are indicated in Figure 8.4. Here, however, accentuated ratios in the seaward samples are not directly correlative with particle size as indicated by Ti/Al ratios, suggesting the existence of non-terrigenous Fe in these samples. Potassium shows very similar trends, with values ranging from 0.18 in surface waters to 0.22 in bottom waters at both the western and eastern extremities of the study area. The former is accompanied by high Ti/Al ratios, and may be attributed to resuspension of coarse feldspars, but in the east, the higher K/Al ratios must be considered anomalous. No consistent areal or vertical trends are apparent in the Mg/Al ratios (Appendix G), which average from 0.18 to 0.20.

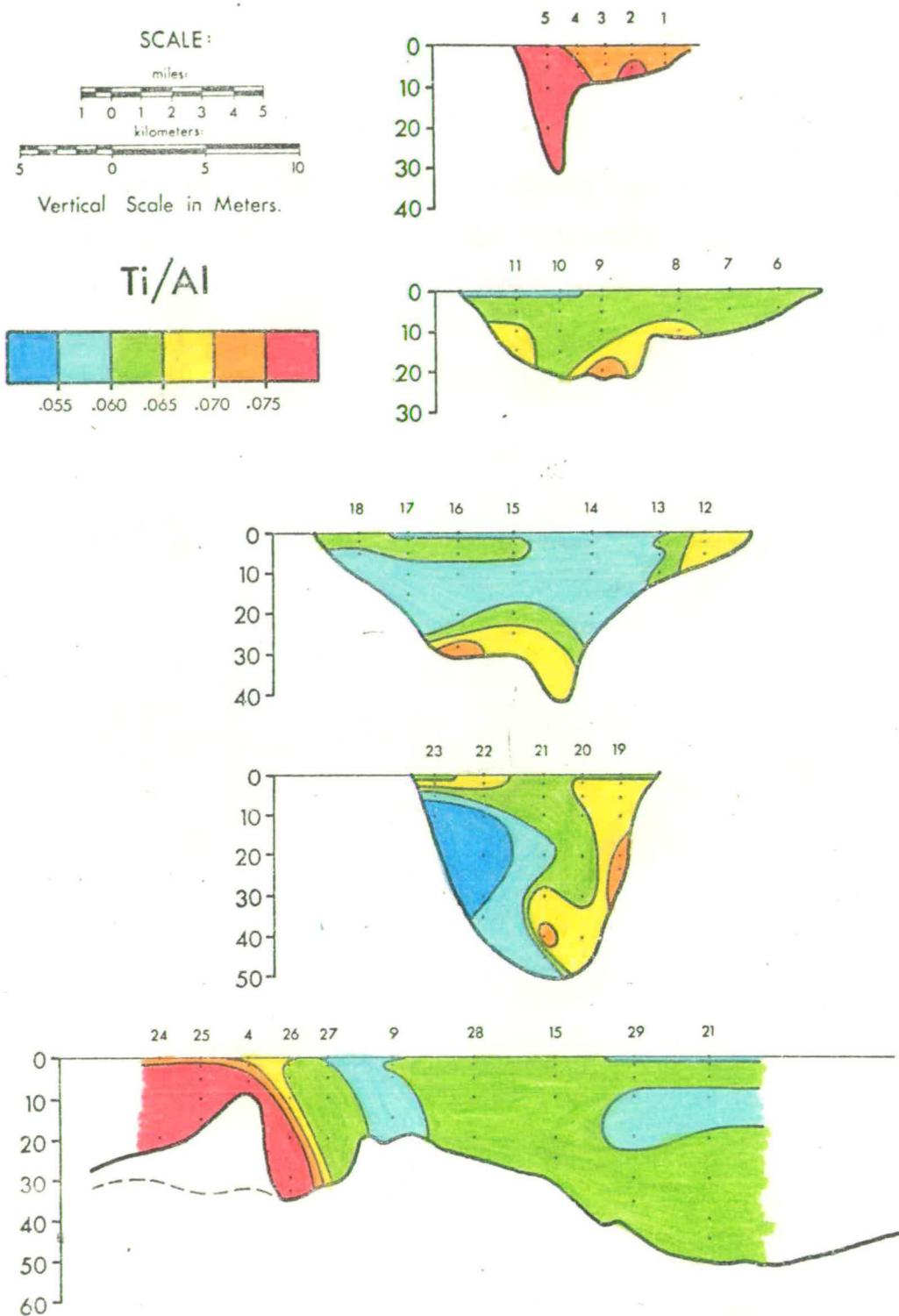


Fig. 8.3 Areal variation of the Ti/Al ratio of suspended particulate matter.

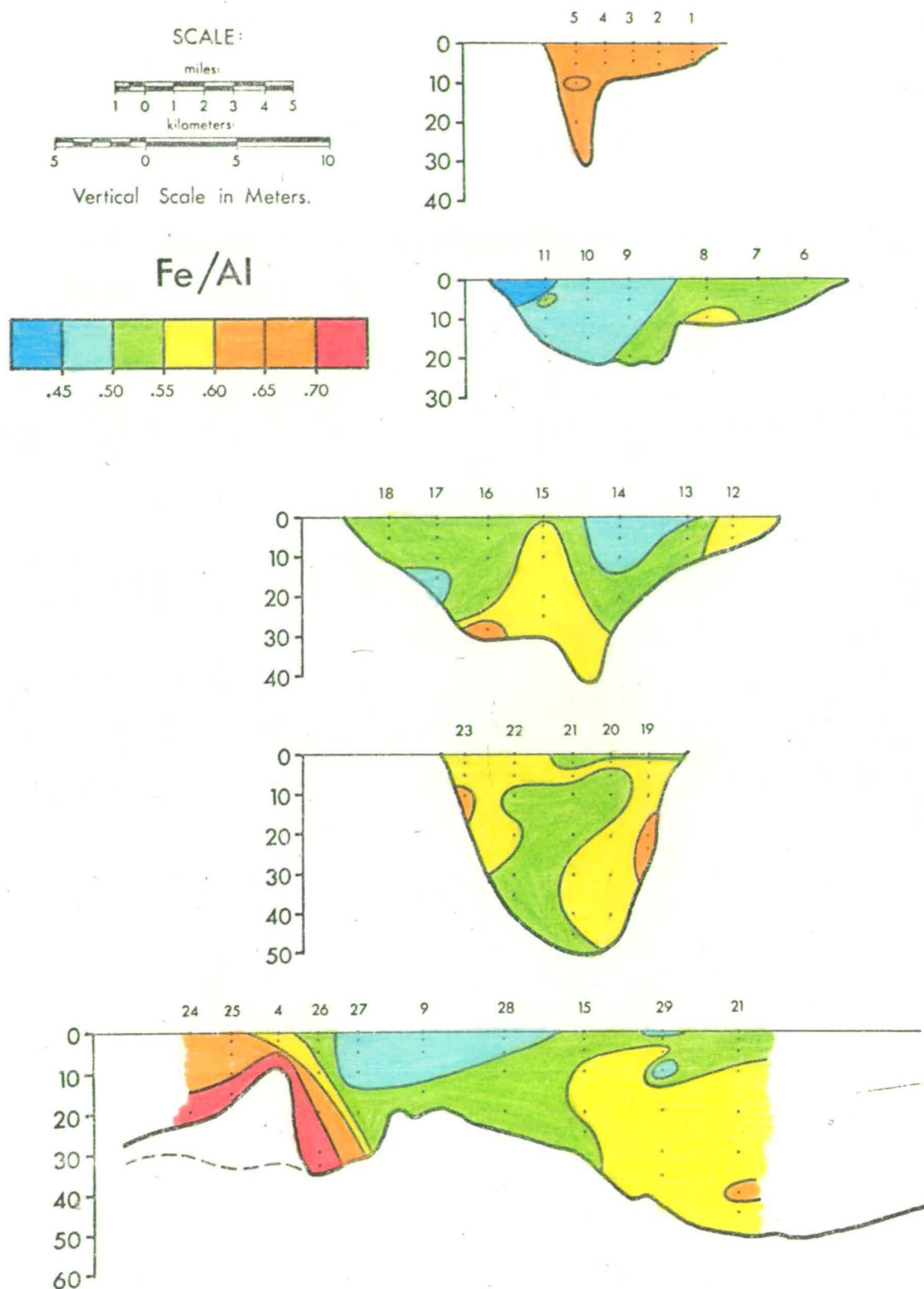


Fig. 8.4 Areal variation of the Fe/Al ratio of suspended particulate matter.

The variation in Si/Al ratios is shown in Figure 8.5. These range from 1.8 to 2.3. In the west, Si/Al ratios vary with depth and with sample loading, in keeping with the varying abundance of coarse-grained quartz and feldspars derived from local sediments and lateral transport (Chapters 6 and 7), but the highest values (>2.2) are found in samples from the bottom waters at the eastern extremity of the study area, particularly along the north shore. This inverse correlation between loading and element-to-aluminium ratios is even more pronounced for the Ca/Al and P/Al ratios shown in Figures 8.6 and 8.7 respectively. The Ca/Al ratios range from 0.25 to 0.55, a range which is consistent with that noted in pipette samples (Chapter 6), but the range of P/Al ratios (<0.020 to >0.030) is far below that noted in either pipette or tidal station sampling, and may reflect dilution of the minor levels of particulate P by varying amounts of detrital aluminosilicates.

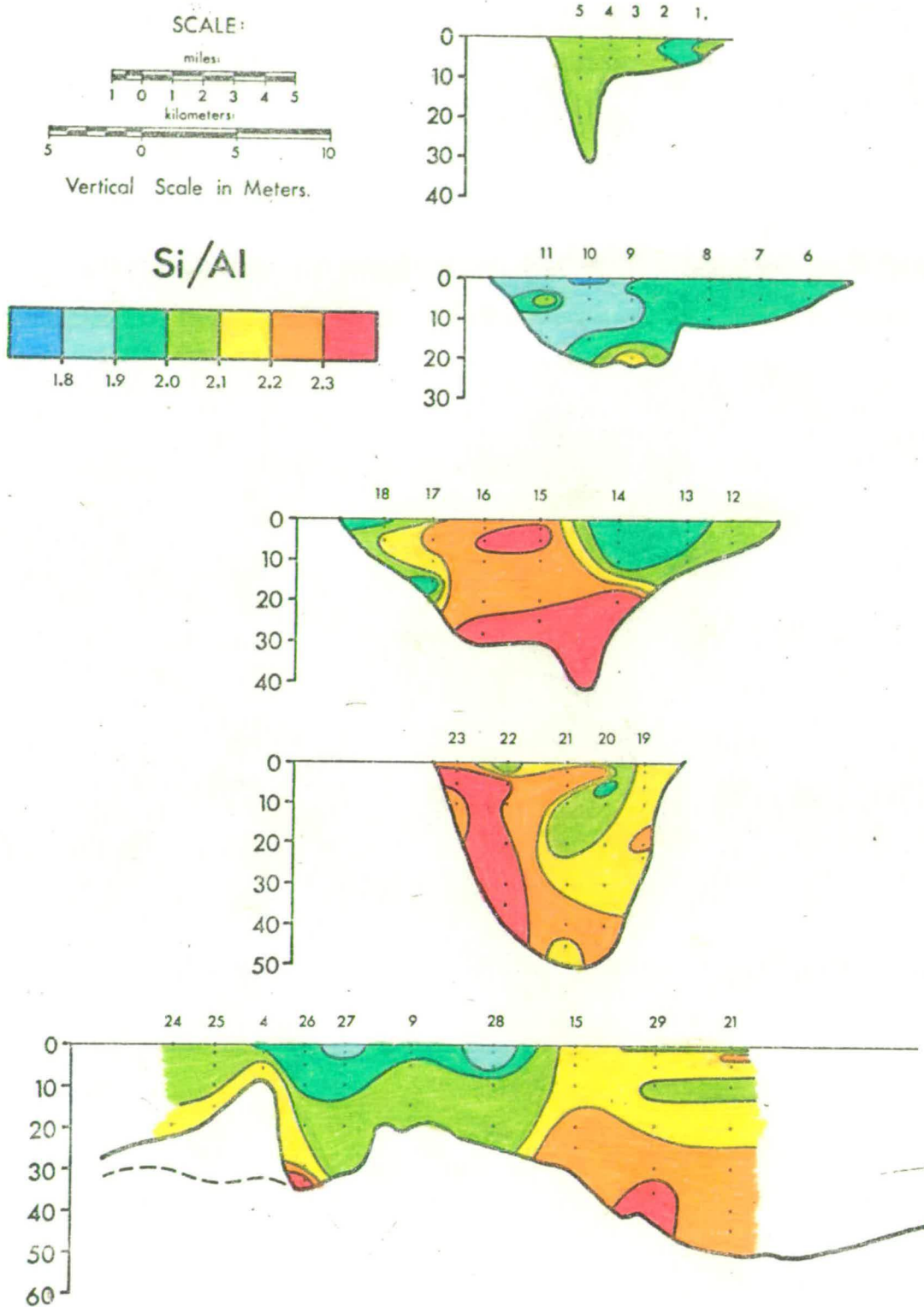


Fig. 8.5 Areal variation of the Si/Al ratio of suspended particulate matter.

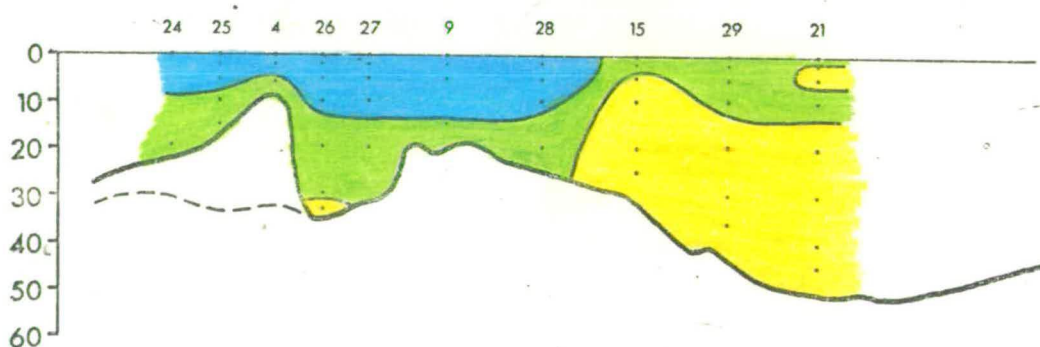
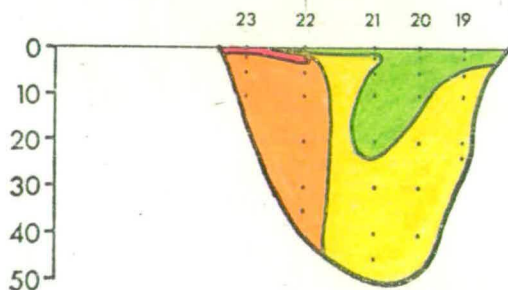
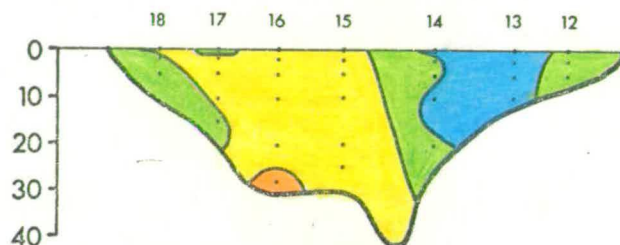
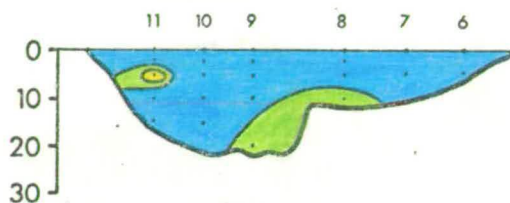
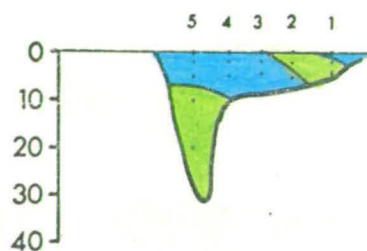
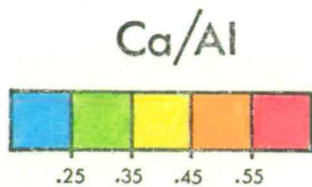
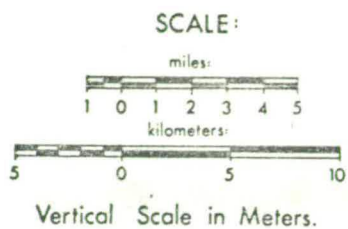


Fig. 8.6 Areal variation of the Ca/Al ratio of suspended particulate matter.

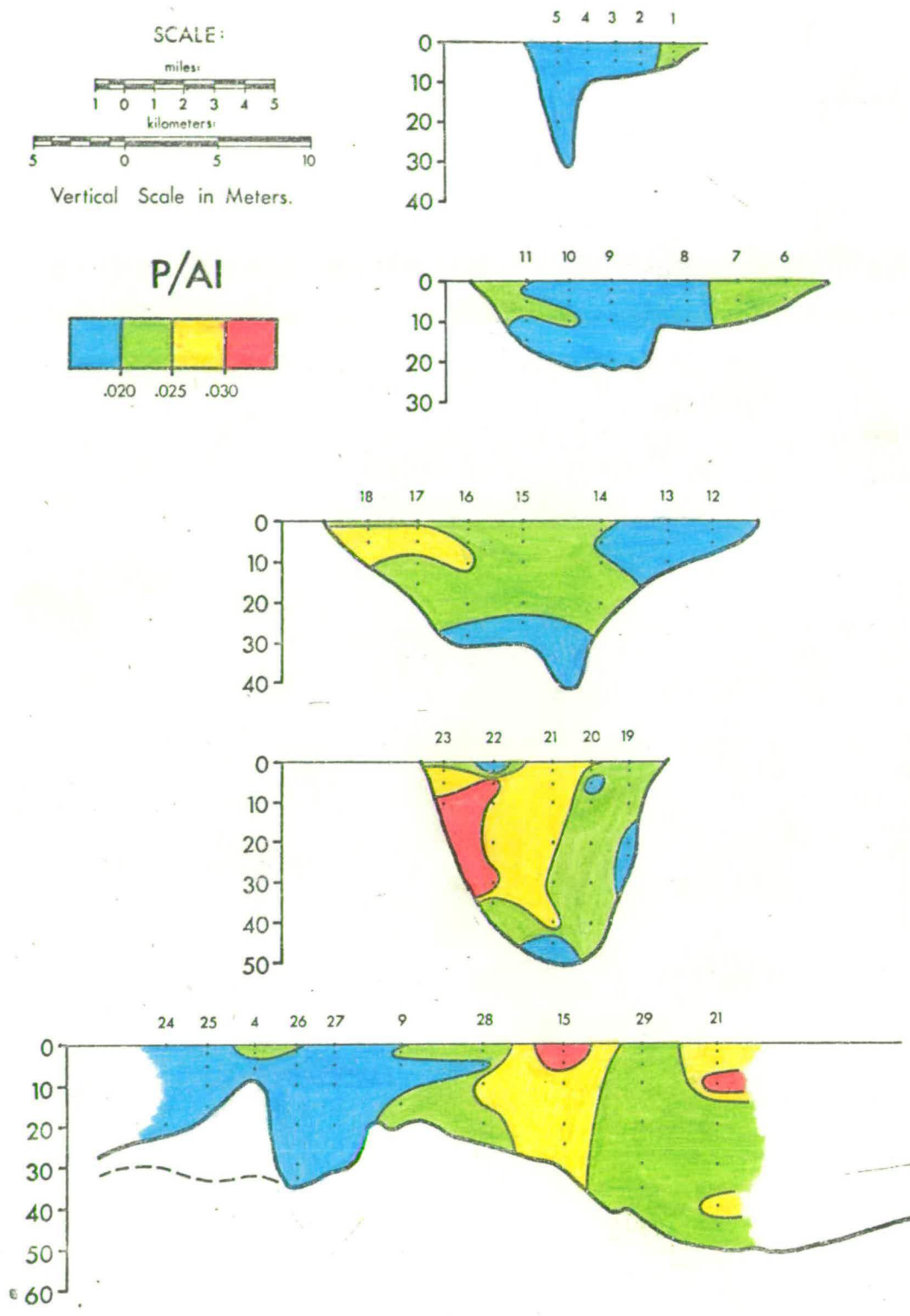


Fig. 8.7 Areal variation of the P/AI ratio of suspended particulate matter.

8.4 Discussion.

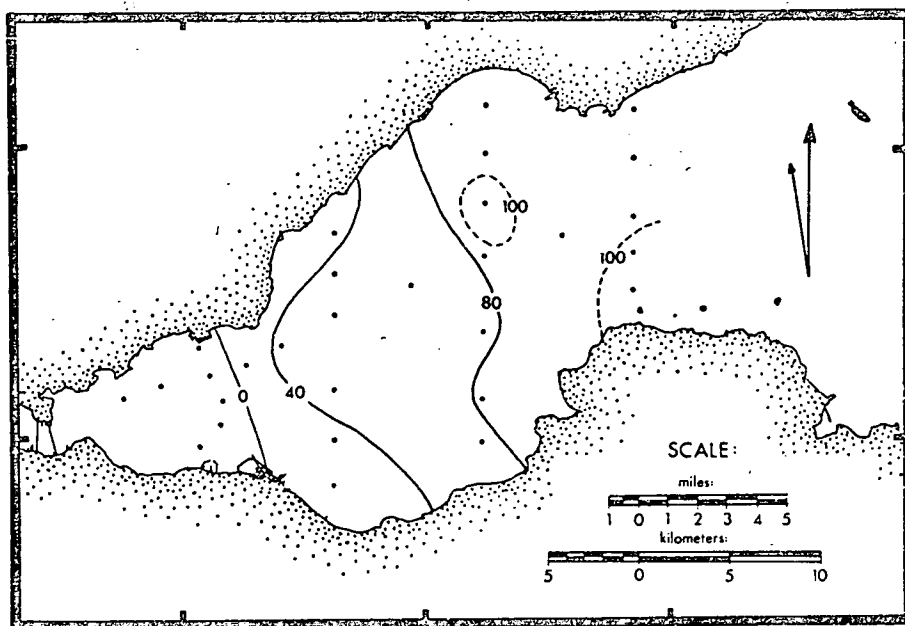
The application of inter-element ratios to the interpretation of major element associations in particulates is valuable in that it permits gross comparison between these and underlying sediment samples, and between given 'bulk' samples and selected pipette fractions. Those elements principally indicative of varying grain size within the terrigenous fraction (Ti and less so, Fe) show ratios to Al which are broadly consistent with the model of a seaward decrease in the size and loading of the terrigenous fraction. Progressively less exclusive association with this material is indicated for Fe, K, Si, Ca and P, but due to their partition between terrigenous, biogenic, organic and possibly authigenic phases coupled with a widely varying background of size and loading of detrital minerals, the degree to which these variations indicate real chemical trends is suspect. Extrapolations which are substantiable in studies of oceanic particulates cannot be applied to estuarine and nearshore waters, since loading effects may influence the apparent chemical associations.

The inter-element ratios at station 26 in this study are consistent with those noted in previous chapters; loadings of particulate Al at this station were equivalent (subject to tidal fluctuations) at all sampling times. At station 7, however, although the Ti/Al ratios are consistent in different studies (indicating roughly similar particle size relationships) loadings of particulate Al averaged $\sim 800 \mu\text{g l}^{-1}$ during areal sampling, compared to $\sim 200 \mu\text{g l}^{-1}$ during tidal station monitoring (April, 1977) and $\sim 150 \mu\text{g l}^{-1}$ in the total pipette samples (August, 1976). Ratios to Al of Si, Ca and particularly P are reduced in these samples with high Al loads, and are presumed to reflect masking of biogenic and organic phases by detrital

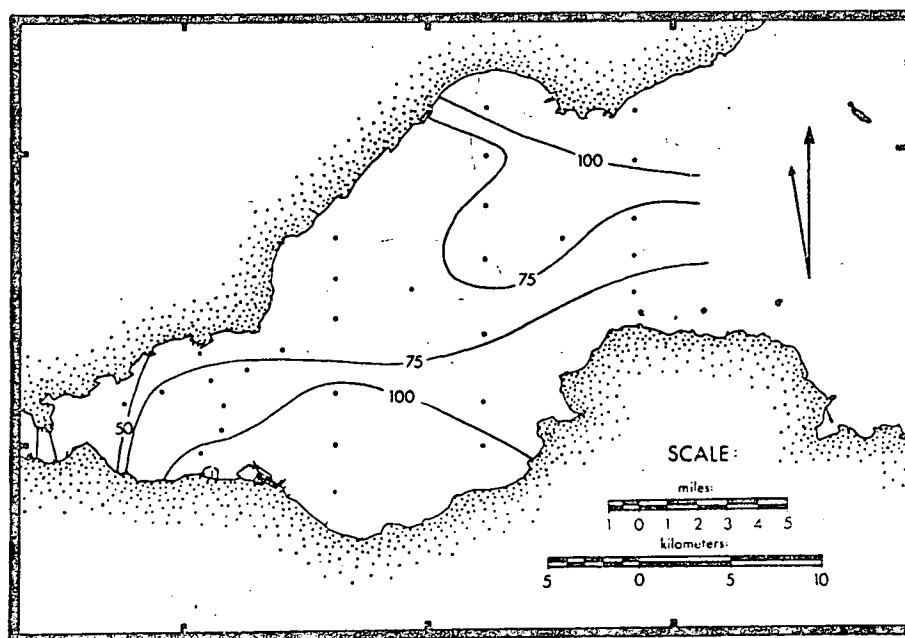
aluminosilicates. This effect was also noted (but was less severe) at station 15. The high winds during the areal sampling programme undoubtedly account for this effect, and have been mentioned previously as having profound effects on water movement in the Forth (Craig, 1972; Watson and Watson, 1971). This influence appears to be restricted to the south shore with its wide sediment banks, but it may provide significant amounts of terrigenous debris from cross-channel transport as observed in the latter stages of the tidal station sampling at station 26. Here, however, the good correlation between particulate chemistry at different sampling times suggests that tidal currents dominate wind effects in determining the character of particulates. This appears to be true in the deeper waters of station 15, but the opposite condition appears to apply to the Edinburgh area.

An attempt has been made to quantify the abundance of 'excess' (non-terrigenous) Si, Ca, Fe and P by means of the technique developed in Chapter 6, based on estimating the maximum size of the terrigenous fraction.

The estimated abundances of non-terrigenous Si and Ca in surface waters are shown in Figure 8.8. Excess Si was found to vary in abundance from virtually zero in the western areas to $\sim 100 \mu\text{g l}^{-1}$ to the east. Here, the excess Si concentrations vary with depth, indicating a subsurface maximum of biogenic activity, a net settling of tests, or resuspension of siliceous debris from the bottom sediments. No indication of high biogenic Si in the vicinity of the sewage outfalls is evident. This may reflect the limitations of this method due to the prominence of Si in the terrigenous fraction, but the areal trends indicated in pipette studies are substantiated, and suggest a real



(a)



(b)

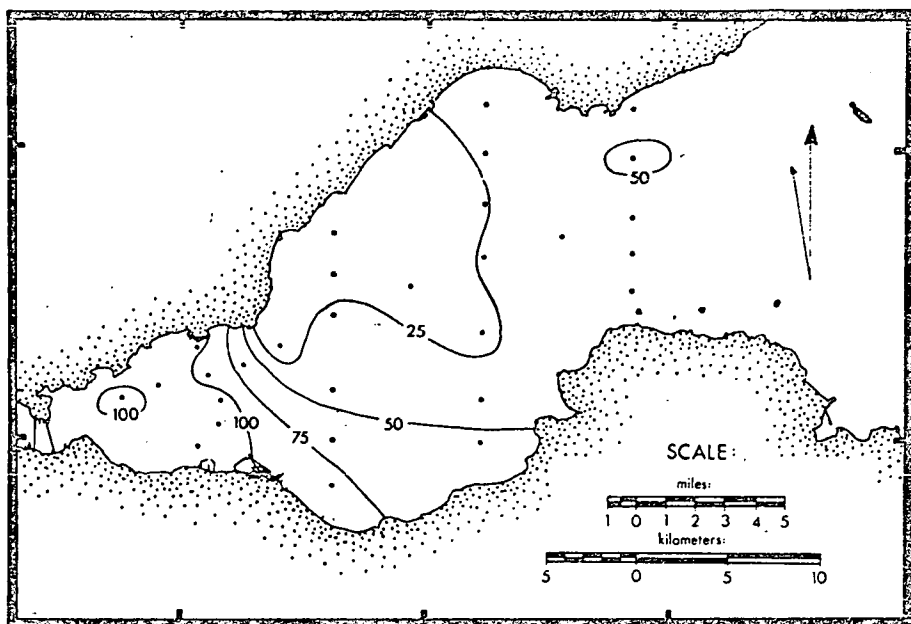
Fig. 8.8 Estimated areal distribution of 'excess' (non-terrigenous)
a) Si and b) Ca in $\mu\text{g l}^{-1}$.

trend toward higher biological activity progressively eastward in the estuary.

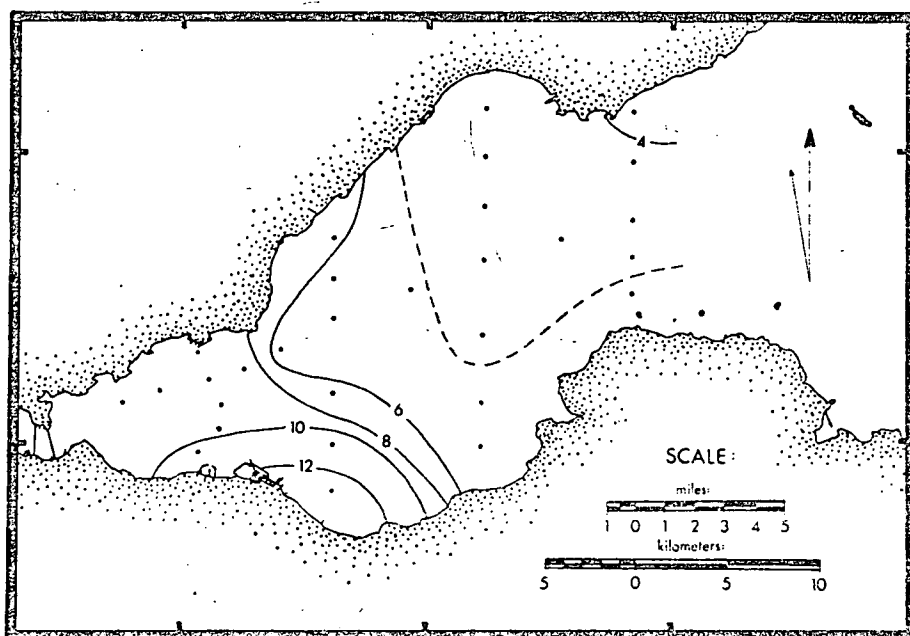
Excess Ca was found to range from $\sim 50 \text{ ug l}^{-1}$ to $>100 \text{ ug l}^{-1}$. The highest levels (Figure 8.8b) are found along the south shore of the estuary and in the north-east. The latter maximum undoubtedly reflects biological activity. In the Edinburgh area, however, high levels of non-terrigenous Ca correlate with neither tidal studies nor pipette analyses. The most likely explanation is that shell fragments (gastropod and pelecypod as well as microfauna) have been resuspended from nearby shell banks by the wind-induced turbulence.

'Excess' Ca in samples from eastern stations constitutes 80% of the total particulate Ca in the samples. This value agrees with that determined in preliminary studies when a sample from station 22 was leached with HCl fumes, rinsed with filtered distilled water, and re-analysed. This indicates a high proportion of CaCO_3 in this sample, and lends some credence to the method used here to determine excess amounts. Excess Ca averages only 20-50% of the total Ca in western samples, possibly reflecting the presence of particulate Ca in plagioclase and/or amphiboles as determined by XRD. Further, the sediment pipette suite on which this procedure is based may contain significant amounts of coarse shell debris, rendering it similar to the highly-loaded resuspended samples to the west, and hindering accurate assessment of the chemical associations.

The abundance of non-terrigenous particulate Fe ranges from $<25 \text{ ug l}^{-1}$ to $>100 \text{ ug l}^{-1}$ (Figure 8.9 a). The highest levels are consistently found in the western extremity of the Forth, and may indicate the outflow of pollutant Fe in various forms. The levels reported here are consistent with those observed during tidal station monitoring.



(a)



(b)

Fig. 8.9 Estimated areal distribution of 'excess' (non-terrigenous)
a) Fe and b) P (in $\mu\text{g l}^{-1}$).

These indicate seaward transport of this excess Fe from the inner estuary and offshore dispersal from the south shore in the Edinburgh area.

The almost exclusive non-terrigenous associations of P render it most suitable for determination of excess levels by the method developed in this study. In Figure 8.9b, the abundance of excess P is shown to range from $>12 \text{ ug l}^{-1}$ near Edinburgh to $\sim 4 \text{ ug l}^{-1}$ at the seaward end of the estuary. A similar trend was indicated in particulate carbon levels (Davies, pers. comm.) measured by the D.A.F.S. laboratory, and in carbon/nitrogen ratios, which ranged from >12 in the west (>15 at station 7) to <8 in the samples from the eastern stations. The high levels of particulate P are attributed to sewage waste.

Particulate P levels are approximately 6% of those noted for particulate C in the Edinburgh area, compared to 3% eastward. This may indicate scavenging of dissolved phosphate by organic material, and/or flocculation of organic material from municipal effluents as removal mechanisms in addition to biological utilization and dilution processes as suggested earlier.

At the eastern stations, the levels of non-terrigenous Si, Ca and P are attributed to the hard and soft parts of marine organisms. Biogenic Si abundances in this area correlate well with those reported by Price and Calvert (1973) in Loch Etive, but exceed those of Skei (1975) in Sorfjord. Both those studies based estimates of biogenic Si on a fixed Si/Al ratio, and may not be as dependable as the present method. The covariance of excess Si and Ca is apparent only in the samples from the east end of the estuary (with low loadings of detrital aluminosilicates) (Figure 8.10b). In these samples, biogenic Si levels

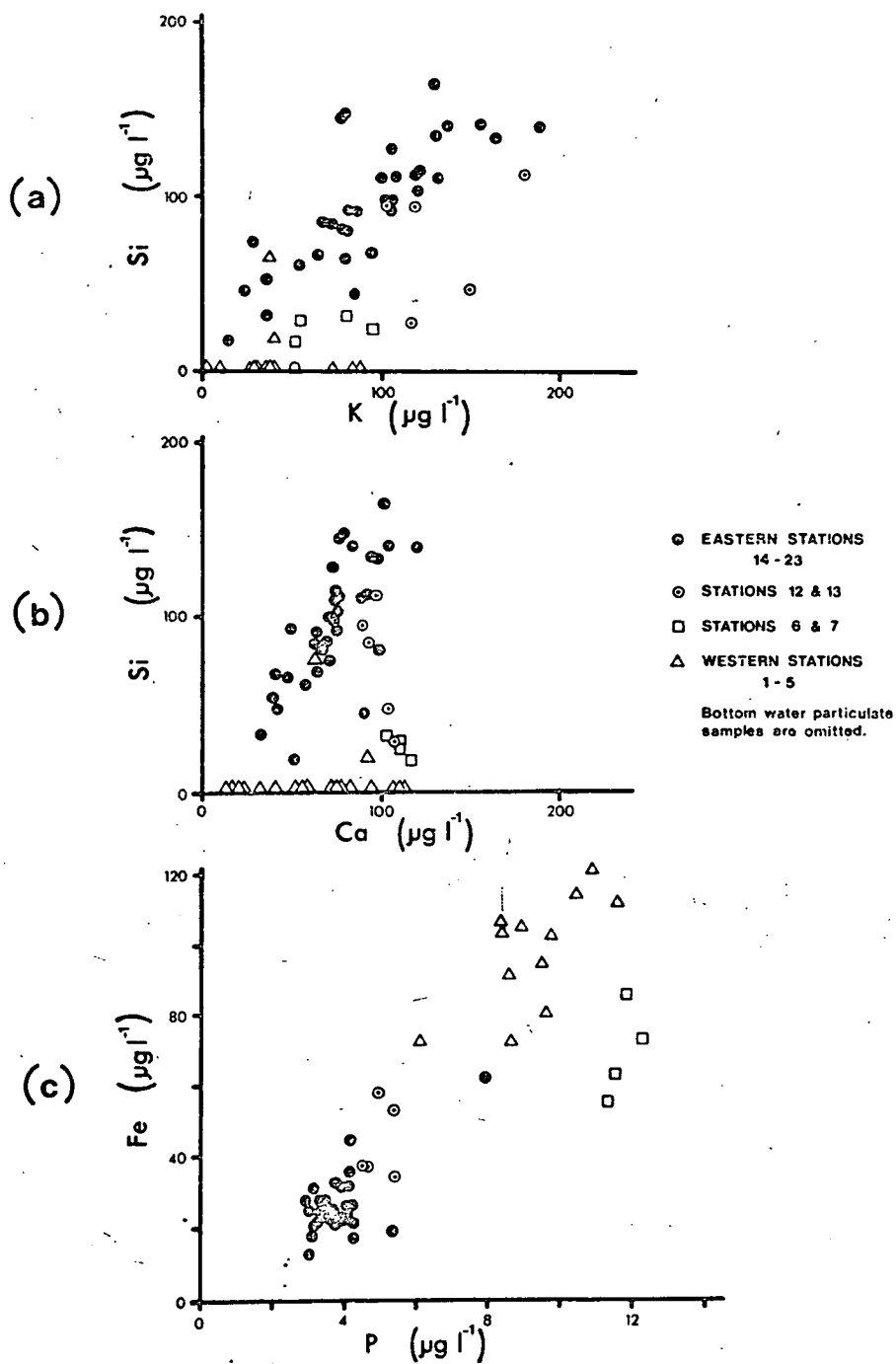


Fig. 8.10 Relationships between elements in non-terrigenous particulate form
 a) Si versus K; b) Si versus Ca; c) Fe versus P.

exceed those of biogenic Ca. The positive Ca intercept of the eastern samples may reflect a uniform suspension of fine-grained Ca as indicated in pipette studies, while high levels of biogenic Ca in western areas are attributed to resuspended shell debris.

Covariance between excess Si and K is indicated in the eastern samples (Figure 8.10a), and may indicate the uptake of K by marine plankton (Fujita, 1971; Skei, 1975; Bishop *et al.*, 1977). No such association is apparent for Mg and Si or Mg and Ca due to the low levels of sensitivity in analysis and the poorly defined size-specific trends of Mg in terrigenous matter (Chapter 6). High levels of excess Mg in the western samples are thought to represent only an artefact of the difficulty in defining non-terrigenous Mg.

A positive correlation between excess Fe and P is indicated in Figure 8.10c. Since particulate P correlates with particulate carbon (D.A.F.S. data) and varies in abundance and chemical trends with organic carbon (from Sholkovitz, 1978a), this may indicate the association of Fe and organic flocs as products of non-conservative estuarine mixing, scavenging of these elements by pollutant organic particulates, and/or more probably a direct association of Fe with the original municipal organic waste. Boyle *et al.* (1974) and others (Aston and Chester, 1973; Sholkovitz, 1976, 1978 ; Boyle *et al.*, 1977) have demonstrated effective removal of dissolved Fe as a result of flocculation processes. Such products, and direct complexes of Fe and P (Burton, 1976) would be unstable at the sediment-water interface (Berner, 1974). The low levels of P in fine-grained sediments (relative to detrital aluminosilicates) compared to overlying particulates (Chapter 6) may indicate the decomposition of these complexes. No equivalent loss was noted in the Fe/Al ratios of the same samples,

but this may simply reflect the dominant association of Fe with fine-grained clays.

In the Firth of Forth, high levels of pollutant discharge and low river flow complicate the determination of chemical associations of Fe and P. The close geographical proximity of the suggested sources of Fe and P could conceivably result in their similar distribution due to hydrodynamic influences without definite interaction. In earlier preliminary studies four particulate samples representing the eastern and western ends of the study area were subjected to mild leaching (30 seconds in hot 0.1N NaOH as per Jackson, 1958) and re-analysed. This treatment had virtually no effect on any of the other major elements (apart from a very slight increase attributed to particulate matter in the leaching agent), but it did result in significant removal of Fe and P as shown in Table 8.I.

TABLE 8.I

Results of leaching experiments on particulate samples.

SAMPLE	P				Fe				leachable
	1	2	3	4	1	2	3	4	Fe/P
Stn 23 (2 m)	8.36	5.29	3.07	37%	140	131	9	6.4%	2.93
Stn 22 (5 m)	6.96	3.41	3.28	47%	94	86	8	8.9%	2.56
Stn 4 (2 m)	29.0	13.3	15.8	54%	583	555	28	4.8%	1.77
Stn 25 (2 m)	37.4	16.4	21.0	56%	894	852	42	4.7%	2.00

- (1 - Weight before leaching (in μg);
 2 - Final weight (μg);
 3 - Weight loss (μg);
 4 - Percentage loss.)

This loss indicates that at least some of the excess P and Fe may occur in unstable ferriphosphates in particulate form. In the

two seaward samples in Table 8.I, which contain little or no raw sewage, the ratios of leachable Fe to P average 2.75, which is almost exactly that of vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) as speculated in samples from Loch Etive by Price and Calvert (1973). No such assertion is possible here, however, since this treatment is likely to affect humic acids and their associated Fe. The abundance of pollutant Fe and P from municipal and industrial effluents and the high levels of organic matter suggest a more likely association between Fe and organic flocs. Both excess Fe and P were found to be primarily associated with material of size $>10 \mu\text{m}$. As such, they are susceptible to settling along with much of the terrigenous material in the western end of the estuary. High levels of trace metals are also associated with the sewage waste (Craig, 1972; Covill, 1972; F.R.P.B., pers. comm.) and may be expected to be associated with this material as well, resulting in their accumulation in local sediments (Morel et al, 1975).

Calculated ratios of excess Fe to P in the areal survey exceed those indicated by the leaching studies, and range from 3 to 6 in most samples, with ratios >10 to the west. In all areas, the abundance of non-terrigenous Fe increases with depth, and enhanced excess Fe/P ratios typify bottom water samples. Other forms of non-terrigenous Fe are likely to be present besides those mentioned previously. Ferruginous waste from industrial effluents and mine waters is intermittently discharged into the Forth, mainly into the inner estuary, but also at Musselburgh, and notably via the River Leven (F.R.P.B., pers. comm.). High levels of dissolved or colloidal Fe in these low pH waters might be expected to precipitate as unsupported ("free") Fe or onto the surface of existing particles. Aston and Chester (1973)

suggested that the abundance of suspended matter is of greater importance in determining Fe removal than are changes in salinity. Higher levels of excess Fe in bottom waters of the central estuary may reflect settling of pollutant particulate Fe or the maintenance of 'nepheloid' suspensions of free Fe-oxides in the turbulent bottom waters along with resuspension of low-P surface sediments.

Sholkovitz (1978) reported that due to the high levels of major elements within the terrigenous fraction of estuarine particulate matter, it is difficult to detect the products of estuarine mixing or to account for variations in non-terrigenous components beyond particle-size linked chemical trends in the detrital fraction. This factor is also evident in samples from the Firth of Forth, but the procedure of determining non-terrigenous abundances as developed in this thesis has proved effective in defining at least major biogenic and pollutant chemical associations.

CHAPTER 9

THE CHARACTER OF COASTAL PARTICULATES.

The determination of major element abundances in suspended particulate matter has provided a far better evaluation of the nature of this material than does simple gravimetric analysis. Both inter-element ratios and calculations of the abundance of specific non-terrigenous components aid in clarifying mineralogical variation within the terrigenous component, and major-element partitioning among terrigenous, biogenic and organic constituents.

In the sediment samples from the Firth of Forth, ratios between elements which are principally associated with the terrigenous fraction (Al, Ti, Fe, K, Mg) show good agreement with values for average shale (Turekian and Wedepohl, 1961; Krauskopf, 1967), and in some respects with other coastal sediments and glacial clays (Taylor, 1974; Skei, 1975). With decreasing particle size, the Forth samples show inter-element ratios more consistent with finer-grained recent sediments (Grim and Johns, 1954; Hirst, 1962) (see Table H.2). These similarities are not necessarily consistent for all elements; the differences principally attest to changes in mineralogy in samples where the non-terrigenous fraction is quantitatively unimportant.

The close correlation between the size-specific chemistry of major elements in suspended particulate matter from the west end of the Firth of Forth and that of the underlying sediments reflects the dominance of terrigenous debris in these samples. The ranges of inter-element ratios of suspended particulate matter throughout the Forth conform favourably to those reported by Sholkovitz (1978) in the Tay estuary. He attributed most of the observed changes in ratios to particle size factors within a dominantly terrigenous loading. In the Forth, however, studies of the underlying sediment have indicated

that although the western particulates are completely dominated by this material, those from other areas have anomalously high Ca/Al, P/Al and S/Al ratios, and little correlation between these samples and the sediment, particularly in the fine-grained components, is indicated.

Locally in the study area, variations in inter-element ratios with depth are consistent with an increase in particle size in the bottom water particulates, indicating that physical settling characteristics, subject to hydrodynamic influences, dictate the vertical variations in particulate chemistry. The size-specific trends of Ti/Al ratios were determined to be consistent in particulate and sediment samples, and provide the best indication of size variations in the terrigenous fraction. Progressively poorer correlation with particle size in the areal sampling (Chapter 8) was indicated for Fe, K, Si, Ca and P. To some extent, this indicates progressively less exclusive association with the terrigenous fraction, but it also reflects various degrees of mixing between terrigenous and non-terrigenous constituents. This fact illustrated that the use of inter-element ratios alone is of limited value in identifying chemical relationships in estuarine particulates. The range of P/Al ratios observed in the vicinity of station 7 at different sampling times and the varying Ca/Al ratios in the finest pipette samples illustrate the extent to which dilution of a relatively constant suspension of organic particulates or fine-grained Ca-rich material by varying amounts of aluminosilicates can affect inter-element ratios without indicating gross differences in chemical associations.

This problem is particularly acute in nearshore waters. Farther offshore, the relatively uniform and very small abundances of detrital

minerals in suspension permit fairly direct evaluation of chemical variation by inter-element ratios alone, except perhaps in outflowing surface waters (Price and Skei, 1975) or bottom nepheloid layers (Baker, 1976; Feely, 1975). Here, some difficulty may be experienced in applying more than qualitative estimates of major element partitioning, but in estuaries, even these may be precluded by highly variable loadings of different constituents.

Using the same method described in Chapter 3 for determining net flux of suspended particulate matter, the abundances of specific constituents (particulate Al, non-terrigenous Si, Ca, Fe and P) as calculated during tidal station sampling periods were applied to the determination of net longitudinal and cross-channel flux at each sampling depth as illustrated for station 26 in Figure 9.1, and detailed in Table 9.1.

At each station, in the frame of reference for which opposite directions of net flux are indicated with depth (cross-channel at station 7, upstream/downstream at stations 26 and 15), the relative magnitude of the flux in either direction varies for the different elements. In all cases, the landward flux of particulate P in the bottom waters constitutes a smaller percentage of the surface water counterdirectional transport than is shown by the other elements, regardless of the direction of net flux.

Other chemically specific anomalies are indicated, particularly for Fe at station 26 and for biogenic Si and Ca at station 15. The flux for non-terrigenous (pollutant) Fe at station 26 appears to be seaward at all depths. At station 15, the relative landward flux of biogenic Si and Ca, in bottom waters is disproportionate to that of total load, relative to the eastward surface flux. The great

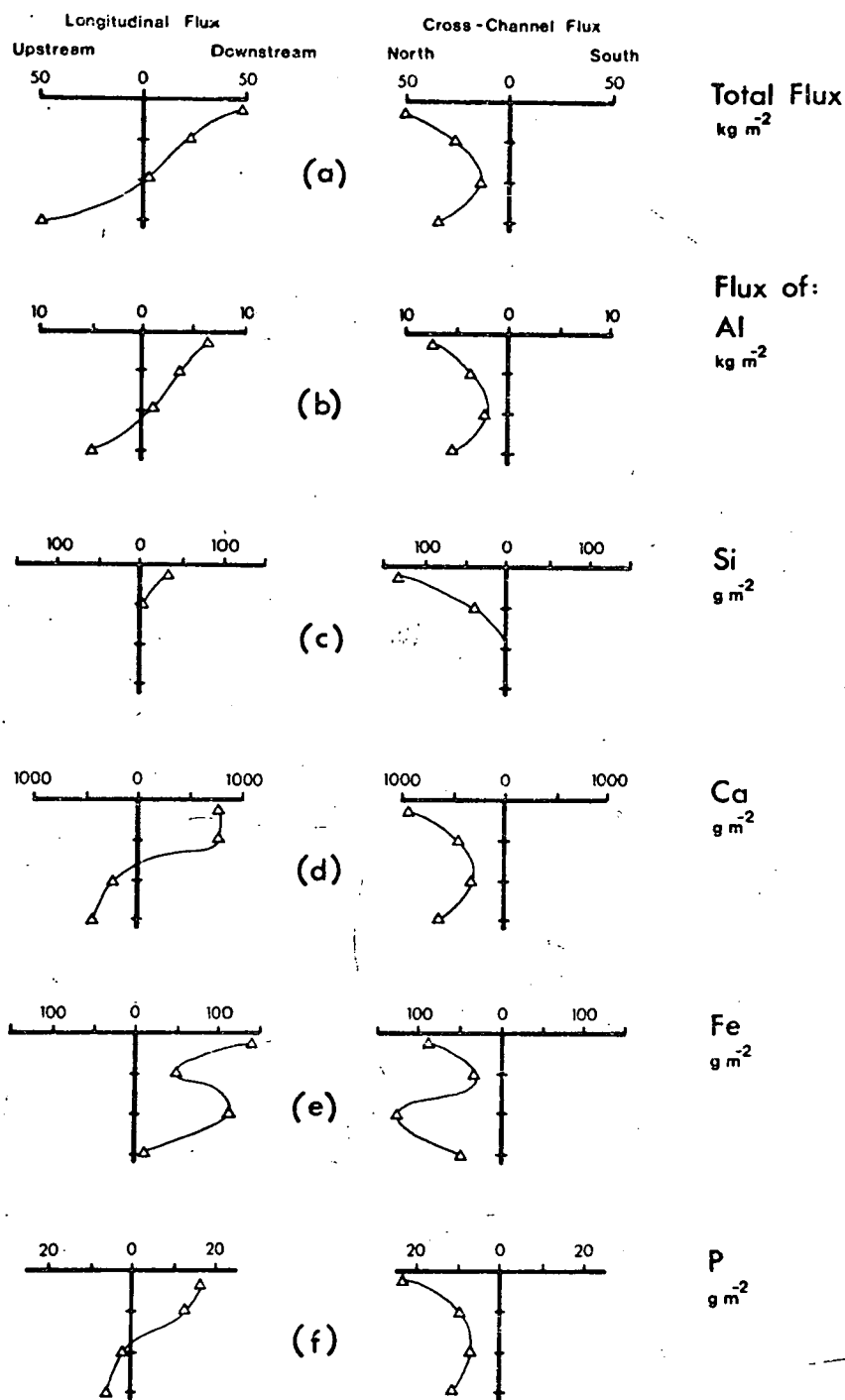


Fig. 9.1 Estimated flux of suspended matter and of specific chemical constituents. The values stated for Si, Ca, Fe and P refer to non-terrigenous associations.

discrepancies between the magnitude of total suspended load flux and those of the 'excess' elements attest to the dominance of terrigenous detritus in the suspended material. A preferential landward transport of coarser material in the bottom waters likely occurs within the terrigenous fraction. However, the differences in the relative magnitude of flux of specific parameters with depth (e.g. Si, Ca and P versus Al at station 15) argue towards a sorting of the components of the suspended matter by physical processes which are ultimately expressed in the chemical characteristics of the material.

In order to account for the net flux at a given point, these data were simplified for each station by integrating these curves to depth. The resultant net flux at each station for these constituents is summarized in Table 9.2. Net seaward transport of all constituents is indicated at station 26, with a net upstream flux of much smaller magnitude at the other two stations. A net northward cross-channel flux is indicated in all areas. This is particularly prominent at station 26, less so at station 15, while near Edinburgh (station 7), the onshore (southward) flux in bottom waters essentially counteracts the opposing net transport in the surface waters.

At station 26, all components of the suspended particulate matter show a pronounced northward flux with varying seaward components. The magnitude of seaward versus cross-channel flow is greater for P and particularly Fe than for the other parameters. At both stations 15 and 7, the net flux is landward, but relative to the longitudinal flux, the northward cross-channel component is more pronounced for P than for the other non-terrigenous components. This indicates some degree of preferential dispersal (probably in surface waters) of organic P due to its occurrence in flocs and organic aggregates of low density

TABLE 9.1

NET FLUX PER TIDAL CYCLE AT SPECIFIC DEPTHS

Stn.	Depth (m)	Load (kg m^{-2})		Al (kg m^{-2})		Si* (g m^{-2})		Ca* (g m^{-2})		Fe* (g m^{-2})		P* (g m^{-2})	
		Long.	XChan.	Long.	XChan.	Long.	XChan.	Long.	XChan.	Long.	XChan.	Long.	XChan.
26	3	-47.3	51.9	-6.2	7.3	-29	135	-779	970	-138	90	-15.8	23.3
	10	-22.9	27.9	-3.5	3.7	-4	41	-775	433	-47	32	-12.2	9.8
	20	-2.4	14.8	-0.9	2.2	-	-	249	325	-114	125	1.0	7.1
	bottom	48.8	33.4	5.1	5.3	-	-	438	618	-9	47	5.7	11.7
15	1	-3.9	-2.1	-0.32	-0.22	-77	-16	-103	-33	-17	45	-3.3	-6.5
	3	-1.3	1.7	0.04	0.19	-6	33	56	65	-4	10	2.7	7.6
	10	-0.3	1.2	0.11	0.12	81	10	62	45	10	-1	5.7	3.0
	20	5.7	4.1	0.63	0.50	232	149	219	215	26	26	-3.9	2.3
	bottom	4.1	3.8	0.40	0.40	118	126	139	162	14	24	1.5	3.5
7	1	-0.8	9.9	0.00	0.74	97	484	33	104	1.7	1.0	1.4	48.0
	5	1.2	-2.0	0.21	-0.13	384	-183	54	-8	2.4	-0.1	10.7	-7.3
	bottom	2.7	-2.6	0.21	-0.21	150	-180	39	-50	-0.2	-1.0	16.1	-11.3

* - Non-terrigenous associations.

(The line of the main channel was taken to be 070° . Longitudinal flux is shown as positive for upstream movement (250°) and negative for downstream flux (070°). Cross-channel transport is shown as positive for net northward (340°) transport, and negative for the opposite movement (160°).)

TABLE 9.2

Summary of net flux of suspended load and specific constituents.

Stn.	Parameter	Net flux per tidal cycle (Kg m ⁻¹)	
		Long.	X Channel
26	Load	-200	960
	P-Al	-47	140
	excess Si	-0.25*	1.2*
	excess Ca	-5.9	18
	excess Fe	-2.7	2.6
	excess P	-0.17	0.37
15	Load	64	76
	P-Al	8.6	8.9
	excess Si	3.5	3.1
	excess Ca	3.5	3.7
	excess Fe	0.37	0.55
	excess P	0.025	0.082
7	Load	16	10.5
	P-Al	2.2	0.6
	excess Si	2.6	-0.13
	excess Ca	0.51	0.055
	excess Fe	0.014	-0.002
	excess P	0.13	0.060

(The line of the main channel was taken to be 070°. Longitudinal flux is shown as positive for upstream movement (250°) and negative for downstream flux (070°). Cross-channel transport is shown as positive for net northward (340°) transport, and negative for the opposite movement (160°).)

*The values for excess (non-terrigenous) Si at station 26 are particularly subject to interpretive error.

(see Chapters 6 and 7).

Impoundment of particulates in the Forth and reworking of local sediments apparently contribute to the bulk of the total suspended load. This would indicate that this material is subject to local sedimentation as well. To some degree, this may be substantiated by data from sediment samples. Material from municipal effluents in the Edinburgh area contains high levels of trace elements, notably Cu, Pb and Zn (Covill, 1972; Forth River Purification Board, pers. comm.). Covill (1972) and Nicholson and Moore (1970) showed that concentrations of these heavy metals were highest in the sediments to the west, and in the immediate vicinity of Edinburgh. Shallow cores collected during the March 1975 sampling period by the author, and analysed in peripheral studies showed that these high levels occurred in the upper 20 - 25 cm of the sediments (Figure 9.2), but further studies by the Forth River Purification Board have indicated that the depth of such 'enrichment' is variable, and may average greater depths in the local sediments (Stock, pers. comm.). The core from station 2 (near Granton) in Figure 9.2 was analysed by the author for major elements, and it was determined that the surface enrichment was not due to lithologic variations. The enriched core top was also characterised by higher water and carbon contents than the lower sediments.

These trace metal levels are higher than those reported in most other British estuaries (Table 9.IV), but are restricted to the southern and western extremities of the Forth. The levels of Zn do not exceed those attributable to natural processes of surface enrichment as noted in Loch Etive by Malcolm (pers. comm.), and may reflect progressive early diagenetic release of this element from the sediments and/or particulate matter. However, high levels of Cu and Pb at least,

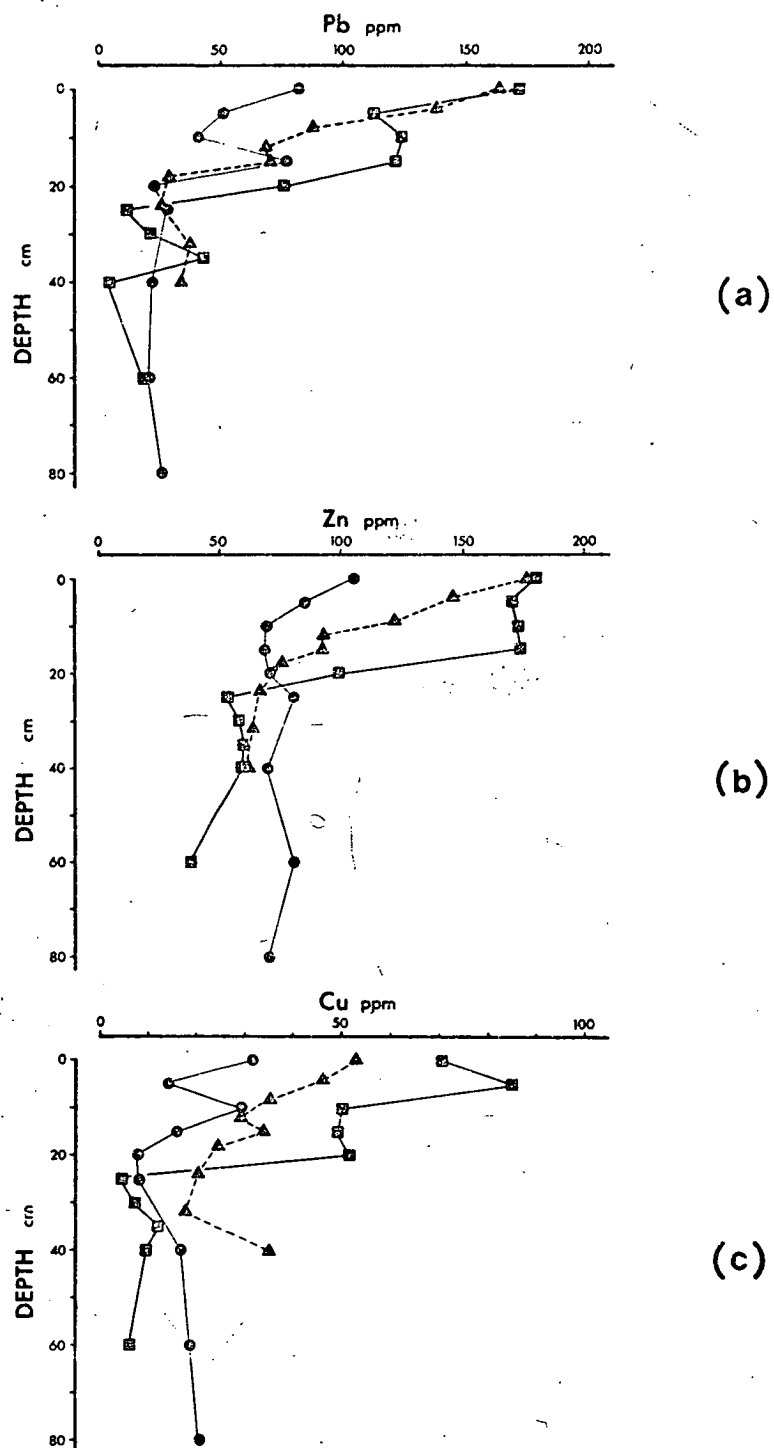


Fig. 9.2 Trace element concentrations (ppm) versus depth in core samples from stations 1 (▲), 7 (■) and 13 (●).
a) Pb; b) Zn; c) Cu.

undoubtedly reflect pollutant input (Bruland et al, 1973).

TABLE 9.4

Levels of trace metals in selected recent surface sediments.

	1	2	3	4	5	6	7	8
Cu (ppm)	48	10	37	225	35	15-20	30-35	70
Pb (ppm)	20	37	86	528	158	100	60	171
Zn (ppm)	95	63	165	1680	265	270	260	180

1 - Average nearshore sediment (Wedepohl, 1960); 2 - Solway Firth (Perkins et al, 1973); 3 - Firth of Clyde (Mackay et al, 1972); 4 - Clyde estuary (Perkins et al, 1973); 5 - Oslo-fjord (Price, 1967); 6 - Loch Etive, outer basin (Malcolm, pers. comm.); 7 - Loch Etive, inner basin (ibid); 8 - this study, core 7 (Figure 9.2).

Rough estimates of the present average rate of discharge of suspended solids from rivers and municipal effluents in the whole Forth estuary/Firth were found to account for only a small percentage of the dry weight of sediment present in a uniform layer of 20 cm depth in the southern and western portions of the Forth. It is likely that coastal erosion during storm action, reworking of local sediments, higher river discharge during peak flow and the addition of material derived from land fill and dredging spoil contribute significantly to the local sediments in sporadic episodes, while net onshore migration of winnowed sediments from the east may contribute significant amounts of material. Similar calculations of the rate of discharge of heavy metals from the Edinburgh area suggest that only a small proportion of this material is fixed in the sediment. Dilution of pollutant metals by natural terrigenous material (Müller and Förstner, 1975) cannot

account for the local discrepancy. It is likely that most of the trace metals associated with sewage waste are solubilized on discharge into marine waters (Morel et al, 1975). Further considerations of the trace metal associations are beyond the scope of this thesis, but have been examined in more detail by deGroot et al (1971), Duinker et al (1974), Murray and Meinke (1974), Troup and Bricker (1975), Carpenter et al (1975), Windom (1975), de Groot et al (1976), and many others.

The physical characteristics and major element chemistry of particulate samples in the Firth of Forth have indicated potential flaws in previous assumptions of local sediment transport based on salinity distributions (Craig, 1972; Corlett, 1972). Mass upstream and downstream tidal flow of the entire water column result in a dynamic physical environment for local suspended material, but little is likely to escape unless the flow of the surface waters is profoundly affected by the dominant south-westerly winds. Tidal flow alone, in conjunction with the settling characteristics of the suspended matter, appears to result in a net accumulation of sediments in the estuary as a mixture of material from sources to the west, south and east. Net northward flux assures some degree of dispersal of pollutant particulate material and dilution by the terrigenous load. Zones of high bacterial populations and depletion of dissolved oxygen are very restricted geographically to the Edinburgh area (Covill, 1972), indicating that local biological utilization of sewage waste occurs as well as physical dilution and sedimentation processes.

At stations 15 and 7, residual longitudinal flux is sufficiently small that minor variations in tidal patterns due to wind effects and small scale aberrations in tidal flow or phase (spring/neap) may significantly alter the magnitude and direction of the flux in surface

waters. Landward flux is likely to occur at depth due to tidal influences, resulting in a net influx of marine biogenic material and terrigenous and pollutant phases winnowed from the sediments in the main basin. The anomalous hydrographic and chemical characteristics noted along the south shore appear to be more indicative of the effects of local input and resuspension than of pronounced seaward transport along the south shore due to Coriolis deflection of ebb tide currents. Impoundment of this water by bathymetric constraints on tidal flow patterns and the complex directions of tidal flow result in a fairly static local particulate load.

The distribution of particulates in the areal sampling period argues towards some degree of seaward transport, at least in surface waters, but the net balance of particulates in the Forth cannot be calculated with the data available at present. The wide spacing of the tidal stations and the different sampling times preclude calculations of total flux of suspended matter in the Forth.

This study represents an early attempt to determine and interpret the chemistry of nearshore particulates. The importance of hydrodynamic influences and the particle size distribution characteristics of the samples have been demonstrated, and must be considered in future work. To a great degree, these parameters influence the chemical character of particulate samples. From detailed considerations of the extent to which physical factors are reflected in particulate chemistry, the partitioning of major elements and the character and abundance of the major constituents of coastal suspended particulate matter may be determined.

CHAPTER 10

SUMMARY AND CONCLUSIONS

A detailed study of the suspended particulate matter in a shallow coastal embayment (the Firth of Forth) was conducted to determine the partition of major elements within this material, to define the source and character of the major components, and to examine the extent to which the abundance, physical character and chemical composition of estuarine particulates may be influenced by physical processes.

Marine waters dominate the estuary. Salinities range from 32.5‰ to 34.5‰. The lowest salinities are found in the western extremity of the Forth, with slightly higher salinities along the south shore and in surface waters north of Edinburgh. Highest values are found in the central estuary and toward the eastern end. Dilution of North Sea water ($\sim 34.5\%$) by land-derived drainage ranges from $\sim 5\%$ to the west to $\sim 1.5\%$ to the east. Freshwater discharge is low, totalling $\sim 65 \text{ m}^3 \text{ sec}^{-1}$, indicating a freshwater flushing time of ~ 54 days.

Flow regimes in the Forth are complex, with pronounced cross-channel flow due to basin configuration, tidal gyres and wind effects. The gross pattern is essentially riverine, with mass movement upstream during flood tide and gravitational release of impounded waters during ebb flow. No distinct water masses were identified. High levels of dissolved phosphate ($> 4 \text{ } \mu\text{g-at l}^{-1}$) and silicate ($> 16 \text{ } \mu\text{g-at l}^{-1}$) in the less saline waters fall to normal marine levels within geographically small areas. High SiO_4^{4-} levels are principally associated with waters to the west, while the high PO_4^{3-} levels result from the input of municipal sewage in the Edinburgh area. Dilution and biological utilization combine to limit the areas affected by these inputs.

Tidal currents, largely controlled by bathymetric configuration, dominate the local circulation patterns. The basin of the Forth is

essentially funnel-shaped, with cross-sectional areas decreasing by over 90% from the seaward end to the bridges. Pronounced restriction of the channel west of Edinburgh results in enhanced current velocities in this area. Here, tidal currents reach a maximum of 0.7 m sec^{-1} in surface waters ($< 20 \text{ m}$) during ebb tide, when flow patterns are essentially riverine. Peak flood and ebb flow occur symmetrically about slack water. A weak vertical salinity gradient is apparent, and is most pronounced during peak flood tide. A residual flow toward the main channel from the south shore is indicated in surface waters. This is attributed to wind effects and a spilling of tidally-impounded water from the southern flank of the estuary.

Near Edinburgh, the shallow (12 m) water column is essentially homogeneous ($\sim 33.8\%$ salinity). Tidal flow here is asymmetrical about slack water. Maximum flood current speeds average 0.2 m sec^{-1} , and occur 4 to 5 hours after low water. Ebb flow is concentrated in the surface waters, and has a pronounced northward component. A shouldering of water onto the wide southern flanks of the estuary by flood waters in the main channel is indicated, with a corresponding gravitational release of the impounded waters at ebb tide.

In the central estuary, a marked salinity gradient from $\sim 33.5\%$ in surface waters to $\sim 34.3\%$ at depths $> 20 \text{ m}$ is maintained throughout the tidal cycle. Maximum flow ($> 0.4 \text{ m sec}^{-1}$) occurs from 10 - 20 m depth. The salinity gradient, therefore, represents only slight density stratification and does not indicate independently moving water masses. Ebb flow exceeds flood tide movement in both velocity and duration. The average flow is seaward at all depths, ranging from $> 4 \text{ cm sec}^{-1}$ in surface waters to $\sim 2 \text{ cm sec}^{-1}$ at depths $> 5 \text{ m}$.

Loadings of suspended particulate matter range from $< 1 \text{ mg l}^{-1}$

in the north-eastern extremity of the Forth to $>30 \text{ mg l}^{-1}$ in bottom waters to the west. High loads ($>15 \text{ mg l}^{-1}$) typify all waters in the latter area; this pattern is consistent with a landward increase in suspended load in most estuaries (Dyer, 1973). Intermediate loadings ($\sim 6 \text{ mg l}^{-1}$) are found along the south shore.

Locally, loading of particulate matter varies with depth, and is subject to the influence of tidal currents (resuspension) and lateral transport.

The suspended matter exhibits a multimodal size distribution. Clay-sized particles (10ϕ) comprise 5 - 30% of the material. Fine silt-sized particles (6ϕ - 8ϕ) comprise the bulk of the samples (~ 20 - 70% by weight). These two modes covary in abundance in all samples. In the west, they are intermittently augmented by mineralogenic particles of size greater than 6ϕ ($15 \mu\text{m}$). Despite the range of loadings noted in the estuary, a fairly uniform suspension of the clay-sized fraction was observed in all areas, ranging from $\sim 2.5 \text{ mg l}^{-1}$ in the west to $<1.5 \text{ mg l}^{-1}$ in the central estuary. A coarse-silt mode ($>15 \mu\text{m}$) is extremely prominent in particulate samples from the central and southern Forth, where it consists of biogenic skeletal debris. Coarse-grained mineralogenic constituents are never as important, and occur only in the bottom waters to the west under high energy conditions.

Net suspended sediment flux is upstream in the bottom waters at the three tidal monitoring stations studied. Surface waters show a net seaward flux, while in the Edinburgh area, the main residual transport is northward toward the centre of the estuary.

The major minerals present in suspension and in bottom sediments are quartz, feldspar, chlorite and illite. Quartz and feldspar are more associated with the coarse-grained material ($>15 \mu\text{m}$).

Fine-grained chlorite, illite and poorly crystallized, mixed-layer clays dominate the terrigenous fraction, but coarser well-crystallized mica and detrital chlorite occur where higher energy conditions exist. Progressively seaward samples show mineral characteristics roughly analogous to those of decreasing particle size. X-ray diffraction analyses are of limited use for determining relationships within the clay fraction of lightly-loaded samples, but size-specific chemical analyses are consistent with a decreasing particle size in the order biotite > chlorite > illite.

Chemical determinations of 9 major elements (Al, Si, Ca, Fe, Ti, K, Mg, P and S) were conducted on both 'bulk' (total sample) and size-separated pipette samples of suspended particulate matter and sediments. All elements are present to some extent within the terrigenous fraction. Loadings of particulate Al ranged from $200 \mu\text{g l}^{-1}$ to $1200 \mu\text{g l}^{-1}$, and varied closely with total suspended load. This element was assumed to reside principally in the residual structure of detrital aluminosilicates. The percentage of particulate Al varies inversely with the maximum particle size, reaching a maximum percentage in all sediment material of size $>8\phi$ ($<4 \mu\text{m}$). Dilution of detrital aluminosilicate minerals by coarse-grained minerals and coal fragments accounts for this pattern. In particulate samples, a maximum percentage of Al is also evident in the 8ϕ pipette samples, but a subsequent fall in the finer fraction attests to the presence of fine-grained organics or flocs.

In the central estuary, the percentage of Al is lower than in sediment samples at all particle sizes, in the absence of coarse-grained minerals. Scanning electron microscopy revealed that the coarse fraction of these samples is dominated by biogenic debris. To the west, a closer association between particulates and the underlying sediments

is indicated both by the similar percentages of Al and by similar inter-element ratios.

The ratios of Ti, Fe, K and Si to Al covary closely with the maximum size of the samples, indicating the presence of coarse-grained minerals which are intermittently introduced into suspension, and are subject to removal due to their differential settling rates. Virtually constant Mg/Al ratios are attributed to the primary association of Mg with residual clay lattices. The P/Al ratios vary inversely with particle size. Throughout the study area, Ca/Al ratios vary with particle size in a manner which is independent of the small-scale size distribution characteristics of the samples, indicating a continuum of particle sizes attributed to fragmented biogenic debris.

Pipetted samples of bottom sediments show that Ti/Al, Fe/Al, Si/Al and K/Al ratios vary with particle size in a manner which is consistent with that observed in the overlying particulate samples. In the coarse-grained sediments, these ratios exceed those of suspended matter, but at sizes $< 15 \mu\text{m}$ more consistent values occur between samples. Sediment samples are characterized by anomalously low Ca/Al and P/Al ratios in the fine-grained fractions compared to the overlying suspended matter. This may indicate decomposition of organic matter and solution of fine-grained calcareous 'dust' at the sediment-water interface, or simply dilution of these phases by aluminosilicates due to differential accumulation rates.

Locally, variations in the inter-element ratios of suspended particulate matter with depth in the water column indicate increasing particle sizes and loading of terrigenous matter in the bottom waters. Hydrodynamic influences and differential settling rates dictate the composition of particulate matter to a great degree. On an areal basis,

seaward fining of the terrigenous fraction is indicated by the decreasing Ti/Al ratios of particulate samples. Progressively poorer correlations with these areal patterns are apparent for ratios to Al of Fe, K, Si, Ca, Mg, S and P. These relationships are indicative of the degree to which these elements are exclusively associated with the terrigenous fraction. Inter-element ratios alone, however, are insufficient for the determination of chemical partitioning in estuarine particulates, since they reflect both real chemical variations and the mixture of terrigenous and non-terrigenous components.

The Ti/Al ratios of bulk particulate samples may be used to determine the 'effective' maximum particle size of the terrigenous component. In conjunction with the loading of particulate Al and size-specific ratios of other elements (determined from pipette analyses of material known to be dominated by terrigenous debris), the abundance of other elements in non-terrigenous particulates can be calculated by the equation:

$$X_{\text{non-terr}} = X_{\text{tot}} - (Al_{\text{tot}} \cdot X/Al_i)$$

where X/Al_i is the ratio of element X to Al in terrigenous samples of maximum particle size i. This procedure is more applicable to the varying particulate load concentrations and particle size characteristics of coastal particulates than in the use of a single diagnostic inter-element ratio. The size-specific chemical characteristics of likely source materials must be determined locally before this method is applied.

The abundance of non-terrigenous Si in the Forth ranges from virtually zero in the west end of the estuary to $>100 \text{ ug l}^{-1}$ in the east. This occurs principally as coarse-grained ($>30 \text{ }\mu\text{m}$) biogenic

debris in the central estuary and near the sewage outfalls. Excess Si in the finest pipette fractions occurs as fine skeletal fragments and larger particles whose settling rate is retarded by their incorporation into organically-bound aggregates. The abundance of excess Ca ranges from $<75 \mu\text{g l}^{-1}$ to $>100 \mu\text{g l}^{-1}$. Of this, $\sim 50 \mu\text{g l}^{-1}$ occurs as fine-grained ($\leq 1 \mu\text{m}$) Ca of uncertain origin in uniform suspension throughout the Forth. The remainder reflects biological productivity in the seaward end of the estuary and resuspended shell debris along the south shore in periods of high wind action. In the former area, excess K correlates with biogenic Si and Ca, and is thought to indicate uptake of K by marine organisms.

Pollutant Fe and P account for most of the non-terrigenous fraction of these elements. The abundance of excess P ranges from $>12 \mu\text{g l}^{-1}$ near the Edinburgh sewage outfalls to $<4 \mu\text{g l}^{-1}$ in seaward samples. Of this, $\sim 2 \mu\text{g l}^{-1}$ is attributed to the soft parts of marine organisms. The levels of pollutant Fe range from $>100 \mu\text{g l}^{-1}$ in the west to $<50 \mu\text{g l}^{-1}$ eastward. Discharge of ferruginous waste from the inner estuary could constitute the major source of this material. The abundance of non-terrigenous Fe and P appear to covary and probably exist as organic aggregates and to some degree as ferriphosphates. Increased Fe/P ratios in bottom waters indicate the possible existence of unsupported oxides of Fe, either from mine wastewaters or as Fe liberated by the decomposition of organic associations at the sediment-water interface.

The suspended particulate matter of the Firth of Forth is sufficiently dominated by terrigenous debris to effectively mask any authigenic chemical associations. Biogenic, pollutant and organic components, however, may be identified. Preferential seaward flow of

fine-grained components and pollutant organic material in surface waters assures some dispersal of these and mixing with terrigenous debris. As they settle, however, they are subject to landward transport in the bottom waters (along with coarse-grained terrigenous material) and possible incorporation into the local sediments. This pattern is substantiated by studies of heavy metal contents in selected core samples.

Minor degrees of sorting are indicated in the chemistry of suspended particulate matter due to hydrodynamic effects. Organic P in particular is subject to more seaward and northward net flux than are terrigenous components, probably due to its low density in aggregated form, resulting in longer residence times in the surface waters with more pronounced net seaward movement.

The systematic consideration of loading, particle size-distribution, gross composition, mineralogy and detailed chemical studies of coastal suspended particulate matter is unique to this study. Further, the hydrographic studies during tidal station monitoring have provided new information on the hydrodynamic environment of the Forth, and the local flux of suspended material. This work has also stimulated a fresh consideration of the XRF 'thin-film' analytical technique (Appendix A), the implications of which must be considered in future studies.

APPENDIX A

Mass absorption effects in "thin-film" X-ray
fluorescence analysis of particulate matter.

i) INTRODUCTION.

Thin-film X-ray fluorescence (XRF) analytical techniques are being employed in steadily increasing numbers of chemical studies of natural and pollutant particulate matter because they require only small amounts of sample and provide a fast, non-destructive method of analysis. Usually, fine-grained samples are mounted onto membrane filters and the chemical composition is determined by normal XRF analysis, using artificially prepared standards of known composition for calibration. The term "thin-film" implies that as a result of minimal particle size, virtually none of the primary (tube X-rays) or secondary (elemental signal) radiation is absorbed by the sample, and that the signal received by the detector is proportional to the amount of a given element in the sample.

Baines (1966) suggested that closely-grouped particles would absorb part of the secondary signal from surrounding grains by shielding them from the detector, and argued against the use of the procedure. However, experimental studies have shown that signal response is proportional to sample load for lightly loaded material (less than approximately 0.3 mg cm^{-2}), while excessive loading results in reduced signal per unit weight (Price and Angell, 1968; Cann and Winter, 1971; Baker and Piper, 1976; Meier and Unger, 1976; Spatz and Lieser, 1976a, 1976b).

Absorption effects within a given particle will vary in magnitude as a function of the wavelength of the signal and the size, composition and density of the sample matrix (Leibhafsky et al, 1960; Jenkins and deVries, 1967, 1970; Adler, 1968; Jenkins, 1968, 1970a, 1970b).

Although particle size effects have been considered in the preparation of pressed disc powder samples, few attempts have been made to quantify

these effects for filtered samples. Baker and Piper (1976) reported linearity of signal response with increasing rock powder sample weights, but they noted that analysis of two suites of chemically identical rock powders with different size characteristics resulted in two distinct calibration lines of different slope. Absorption due to particle size was suggested, and the authors warned that nearshore particulate matter (as opposed to oceanic samples) may be subject to absorption effects.

Criss (1976) presented a model based on computer studies to predict absorption effects on primary (tube) X-rays in different chemical matrices. This model, however, suffers from lack of experimental evidence and oversimplification, particularly with respect to the size distribution characteristics of samples, and is inapplicable to natural particulate analysis.

Few studies of absorption effects for the range of sizes and chemical compositions found in natural particulate matter have been conducted. Experimental evidence for the existing studies is lacking or inconclusive. The assumption of true thin film response, based on simple loading experiments (Baker and Piper, 1976; Meier and Unger, 1976; and others) may be untenable since the loss of signal noted with excessive sample weights may reflect particle shielding rather than size effects. Finally, no satisfactory formulae have been derived for the application of size/absorption models to samples with complex size distribution characteristics.

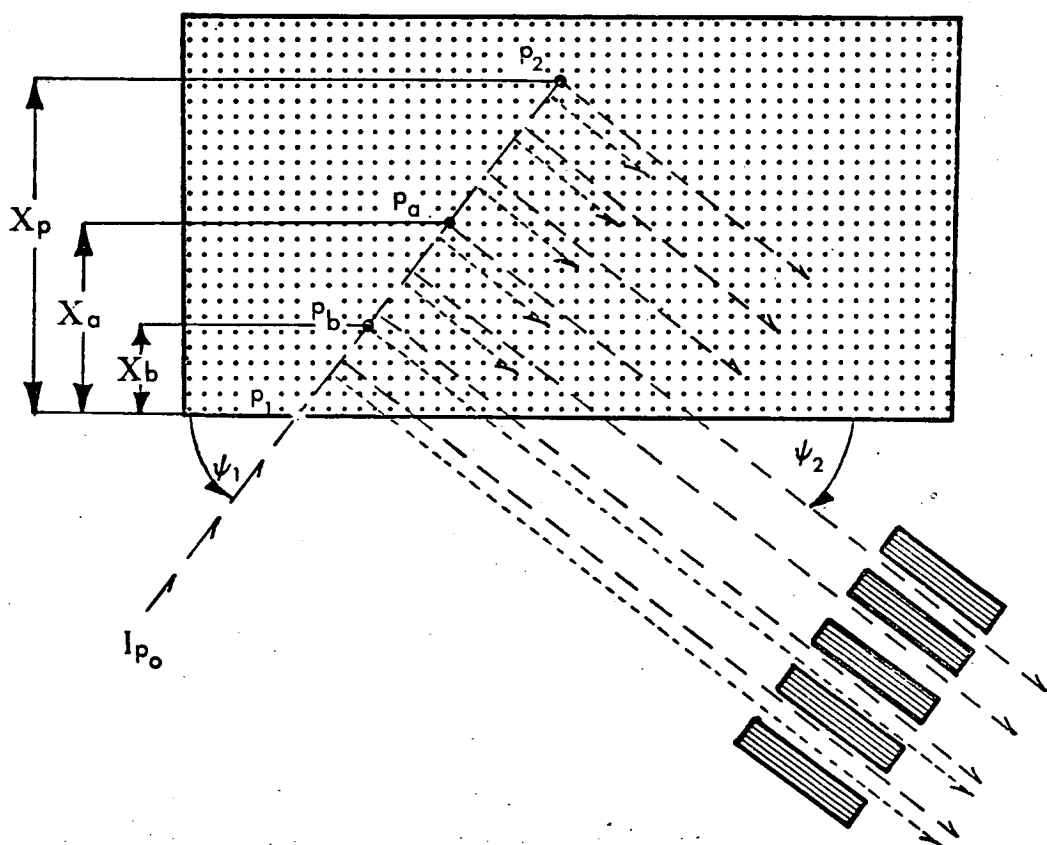
The purposes of this study are to develop a theoretical model which is applicable to the study of absorption effects in particulate samples, to test this model experimentally and to use these results to re-evaluate the limitations of XRF thin-film techniques in the study of natural and pollutant particulate matter as presented in this thesis and elsewhere.

ii) MATRIX ABSORPTION THEORY.

Matrix effects which may produce analytical inaccuracy fall into two classifications: elemental interactions (primary and secondary absorption and signal enhancement) and physical effects (particle size and effects due to chemical state)(Jenkins and deVries, 1967). Matrix absorption theory will be discussed here.

An expression of the matrix absorption effect for primary X-rays is given by Jenkins and deVries (1967) with respect to the following situation:

Figure A.1



The absorption of the incident radiation of intensity I_{p_0} may be calculated at a point p_2 by determining the final intensity I_{p_2} at depth X_{p_2} in the matrix by the following equation:

$$I_{p_2} = I_{p_0} \cdot e^{-\mu(\lambda)\rho \cdot \frac{X_{p_2}}{\sin \psi_1}} \quad \text{Eq. A.1}$$

$$I_{p_2} = I_{p_0} \cdot e$$

where λ is the wavelength of the radiation,

$\mu(\lambda)$ is the absorption coefficient of the specific matrix with respect to radiation of wavelength λ ,

ρ is the density of the matrix,

X_{p_2} is the depth in the sample at which the X-ray intensity is being determined, and

ψ_1 is the angle of incidence of the X-rays with the surface of the film.

The coefficient of absorption for a matrix of known composition is given by:

$$\text{matrix } \mu(\lambda) = \sum (C_A \cdot \mu_A(\lambda)) \quad \text{Eq. A.2}$$

where C_A is the concentration of a specific element in the matrix (expressed as a decimal percent), and

$\mu_A(\lambda)$ is the absorption coefficient of the element A with respect to the signal of wavelength λ , as determined from tables in Jenkins and deVries (1967).

Equation A.1 may be modified to illustrate a similar absorption effect on the secondary signal from a specific fluorescing element. In Figure A.1, the depth X_B represents the maximum depth from which secondary signal from element B may be expected to escape from the matrix and reach the detector. The relationship between the original signal intensity I_{XB} and that of the escaping signal I may be expressed as follows:

$$I = I_{XB} \cdot e^{-\mu(\lambda)\rho \cdot \frac{X_B}{\sin \psi_2}} \quad \text{Eq. A.3}$$

where ψ_2 is the angle between the edge of the sample and the path to the detector.

In this situation, the 'escape pathlength' of element A is greater than that of element B; therefore, if the depth of the sample should exceed X_B , an increase in signal ratio between elements A and B will result. Although signal from element B from shallower depths in the sample will still be received, beyond the critical depth X_B , no further increase in total signal with film thickness will occur.

For theoretical considerations, a simplified model may be used wherein the detector and beam angles are taken to be 90° and it is assumed that 1° (tube) X-rays are not absorbed by the sample matrix. If the elemental signal intensity at any point in the matrix is now designated as I_0 (intensity of secondary signal from a given element of wavelength λ), the intensity of that signal as it reaches the detector may be expressed as:

$$I = I_0 \cdot e^{-\mu(\lambda)\rho X} \quad \text{Eq. A.4}$$

Even when the signal intensity I from depth X is zero, the detector receives secondary signal from that element from depths less than X at an intensity indicated by the integral of equation A.4.

This integral may be determined as follows:

$$\int_0^x I dx = I_0 \int_0^x e^{-\mu(\lambda)\rho X} dx \quad \text{Eq. A.5}$$

Let

$$\vartheta = -\mu(\lambda)\rho X$$

Therefore,

$$\frac{d\vartheta}{dx} = -\mu(\lambda)\rho$$

Substituting in equation A.5,

$$\begin{aligned} \int_0^x I dx &= -I_0 \int_0^x \frac{1}{\mu(\lambda)\rho} e^{\vartheta} d\vartheta \\ &= -\frac{I_0}{\mu(\lambda)\rho} \int_0^x e^{\vartheta} d\vartheta \\ &= -\frac{I_0}{\mu(\lambda)\rho} (e^{-\mu(\lambda)\rho X} - 1) \end{aligned}$$

Therefore,

$$\int_0^x I dx = \frac{I_0 \cdot (1 - e^{-\mu(\lambda)\rho X})}{\mu(\lambda)\rho} \quad \text{Eq. A.6}$$

This equation may be used to determine the total signal received from a particular element in a given matrix or film of thickness X in the simplified model described earlier.

If there is no significant absorption of the primary (tube) X-rays, the intensity of the secondary signal from any given element will be uniform throughout the homogeneous sample. If, in addition, there is no absorption by the matrix of these secondary X-rays as they pass toward the detector, the received signal will be proportional to the mass of

the sample, or in the case of the uniform film model, to the thickness of the film (signal received $\propto X$). Or,

$$\int_0^x I dx_{\text{thin-film}} = kX \quad \text{Eq. A.7}$$

where k is a proportionality constant representing primary X-ray intensity, tube excitation efficiency and other analytical factors.

When the above expression is satisfied, true thin-film conditions apply, and XRF analysis provides an accurate indication of composition.

Similarly, the general expression for the signal received at the detector is

$$\int_0^x I dx_{\text{received}} = \frac{k \cdot I_0 \cdot (1 - e^{-\mu(\lambda)\rho x})}{\mu(\lambda)\rho} \quad \text{Eq. A.8}$$

An expression which indicates the degree to which observed or theoretically received signal approximates thin-film response has been assigned the symbol Γ , where

$$\Gamma = \frac{\text{signal received}}{\text{thin-film response}}$$

Therefore,

$$\Gamma = \frac{\left(\frac{k \cdot I_0 \cdot (1 - e^{-\mu(\lambda)\rho x})}{\mu(\lambda)\rho} \right)}{kX}$$

or,

$$\Gamma = \frac{\int_0^x I dx}{X} \quad \text{Eq. A.9}$$

The value of Γ may be considered to represent the decimal percentage to which the received signal approximates thin-film conditions.

If true-film response for a sample were 1000 counts per μm sample thickness but at $4\mu\text{m}$ thickness absorption effects were such that only 3000 counts were received as opposed to the 4000 expected, the value

of Γ for this thickness of this sample would be 0.750.

The values of Γ for signals with varying matrix absorption coefficients ($\mu(\lambda)\rho$) as calculated using the simplified model developed thus far are shown in Figure A.2; Table A.I lists the matrix absorption coefficients which correspond to selected major element secondary signal wavelengths in a variety of natural matrices. If one were planning to analyse for Fe in a matrix of composition and density equivalent to that of obsidian, the associated matrix absorption coefficient could be found from Table A.I to be 183, while reference to Figure A.2 would show that for this model, if the sample were a film of thickness $10\ \mu\text{m}$, the signal received from Fe would be predicted to be 0.91 times that of true thin-film response.

iii) A MORE REALISTIC MODEL

The theoretical study to this point has been developed on the basis of a very simplified model with no absorption of primary X-rays and orientation of the primary beam and the path to the detector of $\psi_1 = \psi_2 = 90^\circ$. In order that these formulae may be applied to real particulate analyses, assumptions made to this point must be eliminated. Two of these refer to the machine settings (beam and detector angles and tube effects), while the remainder refer to the physical characteristics of the sample itself (particle shape and size distribution). Even with some of these parameters corrected, the more realistic model will lack full detail; since beyond a given point, the theory must be demonstrated experimentally.

Detector Angle.

In actual analytical conditions, the beam and detector angles (ψ_1 and ψ_2) are approximately 45° . When analysing a thin film, this

TABLE A.I

Matrix absorption coefficients ($\mu(\lambda)\rho$)
of selected elements in natural matrices.

(* = primary $K\alpha$ X-rays.)

¹Krauskopf (1967); ²Broecker (1974); ³Stach et al (1976)(averaged bituminous and anthracite values); ⁴Millot (1970); ⁵ibid; ⁶equal proportions magnetite and hematite;

⁷based on XRF analysis of fraction $\leq 1 \mu\text{m}$, Chapter 6.

ELEMENT BEING ANALYSED:

MATRIX COMPOSITION:	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr*	Fe	Mo*	W*
Crustal average ¹	4874	3527	2938	3973	2792	1955	1045	784	558	343	211	17	1
Obsidian (this study)	4907	3130	2452	2966	2795	1953	1043	815	509	301	183	11	1
Granite (UGSG-G2)	4885	3161	2682	4055	3266	2010	1074	847	557	331	204	13	1
Av. Oceanic Particulates ²	3306	2059	1311	1647	1143	802	425	294	347	209	129	7	1
Av. Oceanic Organics ²	1219	747	467	316	206	146	73	56	30	17	11	1	0
Coal ³	1523	931	583	394	257	194	97	66	29	23	14	1	0
Orthoclase	4399	2752	2513	3721	2625	1838	982	1035	651	388	239	13	1
Quartz	4358	2738	1751	4296	3044	2128	1140	794	496	290	144	10	1
Montmorillonite ⁴	3807	2496	2444	3504	2468	1725	921	640	399	232	141	8	1
Av. Mica ⁵	6838	4813	3656	3609	2522	1764	1044	728	453	266	162	24	1
Hornblende	7589	5398	5034	4582	3201	2244	1197	839	674	506	318	33	1
Sphene	8103	5195	3349	3631	2497	1753	945	650	909	976	629	37	1
Pyrite	13064	8893	6146	4418	3157	6903	3709	2624	1706	993	628	114	4
Iron Oxides ⁶	18851	13065	9010	6462	4620	3268	1763	1267	717	481	295	145	5
Firth of Forth Pipette ⁷													
Samples, Average Composition of 10 ϕ samples ($\leq 1\mu\text{m}$).	4030	2806	2982	3632	2569	1811	967	729	502	328	203	16	1

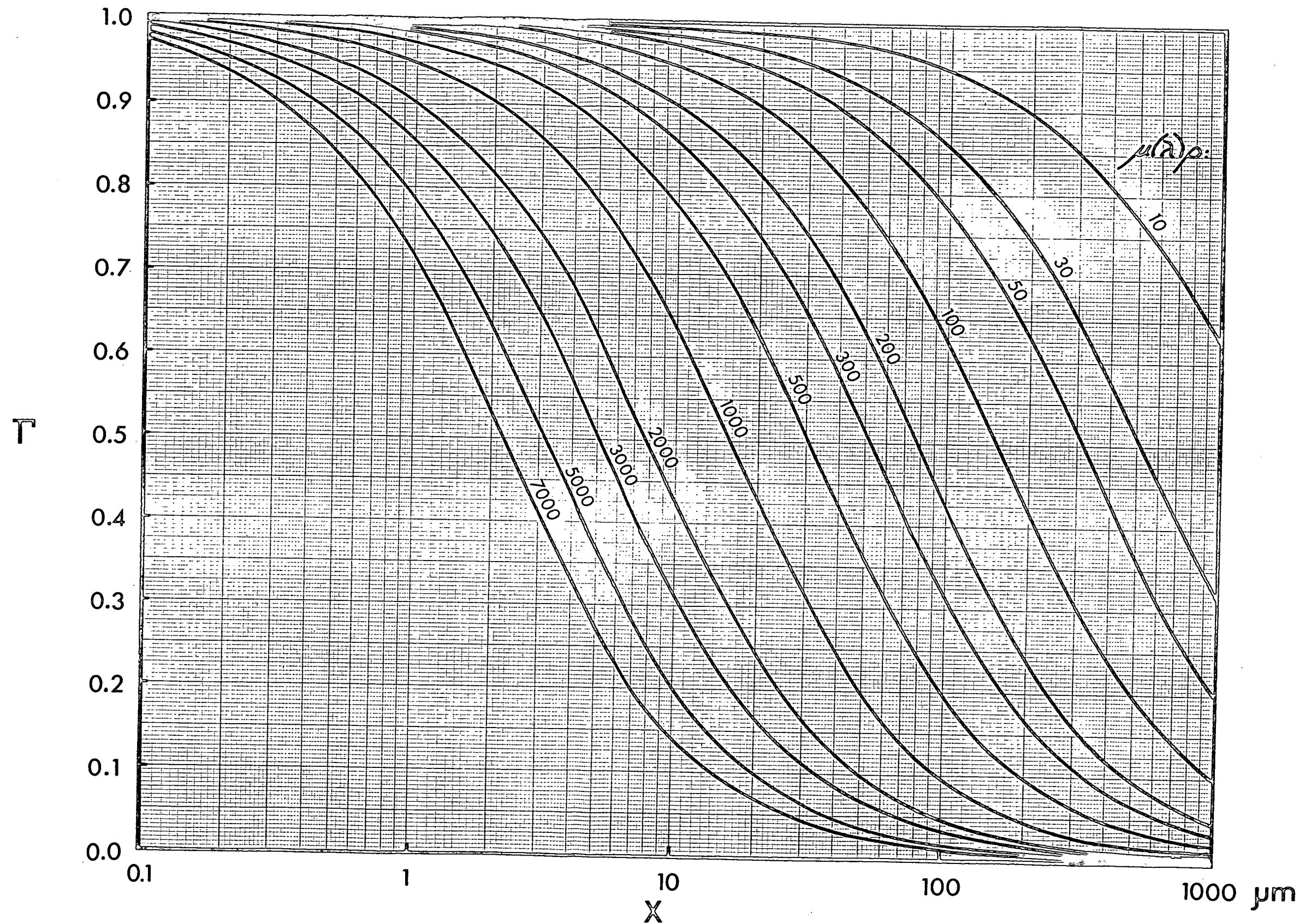


FIGURE A.2

Theoretical curves of Γ - values are shown as a function of X (X = film thickness when $\psi_1 = \psi_2 = 90^\circ$, or X = minimum dimension of a particle of 'average' shape when $\psi_1 = \psi_2 = 45^\circ$). The matrix is obsidian as examined in this chapter. These curves are based on the assumption that no absorption of primary X-rays occurs.

means that the pathlength of the primary or secondary signal within the matrix of the film is increased over that of the simplified model by a factor of $\sin^{-1} 45^\circ$. This results in a displacement to the left of all the curves shown in Figure A.2 by a factor of $0.41 \cdot X$.

Instead of the Γ of Fe in crustal rocks at $X = 10 \mu\text{m}$ being 0.91 as shown previously, it would become ~ 0.85 , since the real pathlength of the secondary signal in a matrix $10 \mu\text{m}$ thick would be $14.1 \mu\text{m}$ ($10 \mu\text{m} \cdot \sin 45^\circ$). The effect of this correction to the simplified model, then, is a simple geometric adjustment of the theoretical curves.

Particle Shape.

The model thus far applies to films only, i.e. those samples for which the thickness normal to the membrane is a small fraction of the lateral dimensions of the sample. This is particularly applicable in the analysis of sheet silicates. Natural particulates, however, consist of large numbers of discrete particles with variable size and shape. A film and a sphere may be considered the extremes of regular particle shape as regards the amount of matrix within a given percentage of the film thickness/spherical diameter X . (Rods are roughly spherical in section, and with the effect of the spinner during analysis, particles of varying shape will provide a response somewhere between these two extremes.) This argument is based on the assumption that the minimum particle dimension is common to both shapes.

A detailed study was conducted into the geometry of spheres to determine the distribution of their mass with depth into the matrix of the sphere in the direction of the detector. This work is not presented here because of space limitations, but the basic conclusions are these: signal response from spheres (diameter = X) is better than that from films (thickness = X) except when X is far less than the critical

depth at which significant signal loss occurs. In a sphere whose diameter is roughly 0.8 to 1.5 times that of the critical depth, signal response will exceed that of a film of equivalent thickness by roughly 30%. When X significantly exceeds the critical depth (and the detector angle is 45°), signal response from the sphere may exceed that of the film by a factor of 2. The progression in shape from films to spheres to angular semibladed particles is associated with an increase in light element to heavy element signal ratio. The theoretical curves as shown in Figure A.2 represent the average response over the range of expected particle shapes. With a detector angle of 45° , response from films will be represented by a leftward shift of the curves by a factor of $X \cdot \sin^{-1} 45^\circ$ while response from spheres may be represented by a right-displacement of the curves from 0 to $0.3x$. Given the variety of particle shapes observed in natural particulate samples, the values of X stated in Figure A.2 may be considered to be roughly representative of the thickness of sample particles normal to the membrane, regardless of their shape.

Visual examinations revealed that the maximum dimension for particles usually does not represent the matrix thickness at an angle of the detector. Many particles were found to be bladed in shape to some degree, and the thickness of the particle normal to the membrane was a small fraction of the maximum dimensions. In these particles, signal response falls somewhere between those of the film and the sphere. Care must be taken to ensure that the stated value of X is measured perpendicular to the membrane surface. Rather than working through problems of hydraulic equivalence and particle shape solutions for settling rates, the accuracy of size-separation techniques should be verified visually (preferably by SEM) before the curves in Figure A.2 are used.

Tube Effects.

In the simplified model, the assumption has been made throughout that no significant absorption of primary X-rays takes place. Reference to Table A.1 shows that primary radiation from the Cr tube is subject to absorption phenomena to a greater degree than is the secondary signal from Fe. The relative efficiencies of different excitation sources and the wavelength of the exciting beam have not been considered in detail. For the Cr tube, the continuum, in addition to the K α peak, contributes significantly toward excitation of the sample (Adler, 1968). The matrix absorption coefficients of the X-ray sources in Table A.I, therefore, must be considered very approximate, since they are based on the K α wavelength.

Secondary signal at its point of origin is proportional to the primary X-ray intensity at that point in the sample matrix. Since the model assumed that there was no absorption of primary X-rays, this initial intensity was uniform throughout the depth of the sample. When primary X-rays are absorbed, the secondary signal intensity becomes less with increasing matrix depth, subject to the same integration mentioned earlier. Since the matrix absorption coefficient for Cr in crustal rocks is considerably less than that of most of the other major elements, little overall effect is noted; however, Ti and Fe and other elements with mass absorption coefficients in the same order of magnitude are affected somewhat as shown in Figure A.3. This set of curves represents the Γ values calculated for secondary signal received from a matrix of composition and density equivalent to that of average crustal rocks with a Cr tube as the excitation source. Particle shape affects displacement of these curves by the same factors mentioned previously.

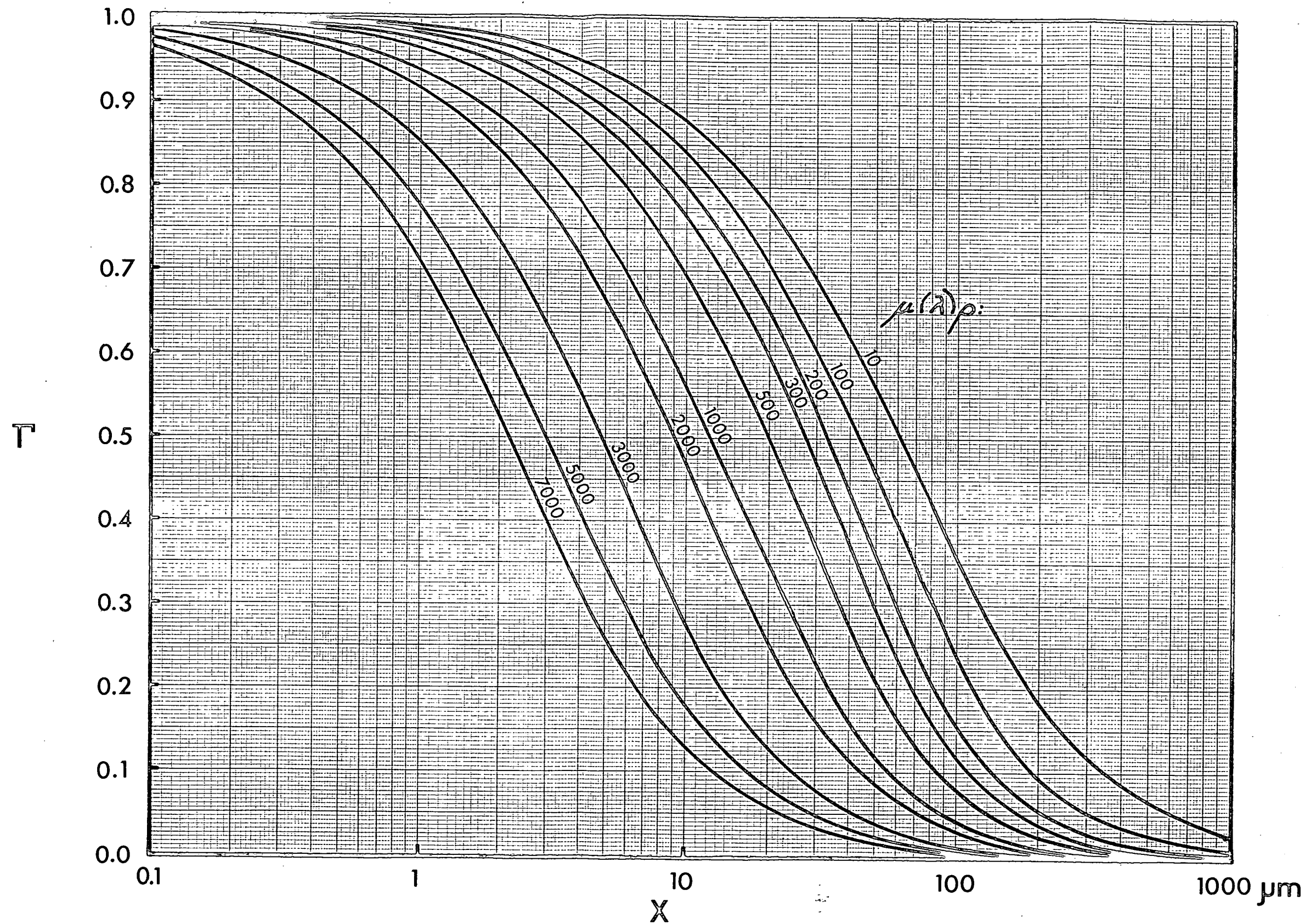


FIGURE A.3

Theoretical curves of T - values as a function of X are shown for analytical conditions where absorption of primary X-rays occurs. The value of X is as detailed in Figure A.3. The theoretical matrix is obsidian, and Cr K α radiation ($\lambda = 2.29\text{\AA}$) is used as the source of primary X-rays.

Particle Size Distribution.

The theory developed thus far is essential in determining the anticipated signal loss from a given particle, but is of little use in establishing estimated signal loss through the sample as a whole. Natural particulate samples tend to be multimodal with a significant percentage of very fine particles and secondary modes of more coarse material (see Chapter 4).

Baker and Piper (1976) correctly assumed that particle size effects may be significant in XRF analysis of coastal particulates. They prepared two sets of chemically identical standards, one from the original U.S.G.S. rock standard powder (AGV-1), the other a specially re-ground subsample of the same powder; the authors claimed linear increase of signal from each sample with increasing weight, but different slopes were apparent, attributed to some function of mean particle size and Z (atomic number). These results are to be expected in the light of the preceeding discussion; the key to this problem is the definition of the size at which significant absorption begins to affect the analyses of real samples.

The relationship between the signal received from element X (σ_x) in the particulate sample and the theoretical signal which would be directly proportional to the amount of that element present based on true thin-film response (σ_{x_r}) would be:

$$\sigma_{x_r} = \sum_{i=1}^n \left(\frac{\sigma_{x_i} \omega_i}{\Gamma_{x_i}} \right) \quad \text{Eq. A.10}$$

where i represents an individual size interval in the sample (defined by pipette or other size determination),

- n is the number of such sample intervals,
 ω_i is the decimal weight percent of the subsample
 within the size interval i ,
 σ_{x_i} is the signal from element X in particles within
 the size interval i , and
 Γ_{x_i} is the Γ factor for element X at the intermediate
 particle diameter within the size interval i .

The estimated degree of signal loss for element X through the sample as a whole may be determined by a direct comparison between the estimated true thin-film signal as above and the signal actually received, as shown in equation A.9, where Γ_{x_τ} is the Γ factor for element X in the total sample.

$$\Gamma_{x_\tau} = \sum_{i=1}^n (\omega_i \Gamma_{x_i}) = \frac{\sigma_x}{\sigma_{x_\tau}} \quad \text{Eq. A.11}$$

It may be demonstrated that these equations account for theoretical changes in signal response in multimodal samples which show vastly different signal response despite equal sample weight and mean particle size. The magnitude of such signal loss through the range of particle size observed in natural particulates must be determined before any researcher can say that, for instance, oceanic samples are free from absorption effects because of their size, let alone coastal particulates or aerosol particulate matter. Only through size-variant studies may an order of magnitude be assigned to these phenomena. Because this is the first study of this subject from this frame of reference, the efficacy of these formulae in predicting experimental results must be demonstrated before going further.

- n is the number of such sample intervals,
 ω_i is the decimal weight percent of the subsample
 within the size interval i ,
 σ_{x_i} is the signal from element X in particles within
 the size interval i , and
 Γ_{x_i} is the Γ factor for element X at the intermediate
 particle diameter within the size interval i .

The estimated degree of signal loss for element X through the sample as a whole may be determined by a direct comparison between the estimated true thin-film signal as above and the signal actually received, as shown in equation A.9, where Γ_{x_T} is the Γ factor for element X in the total sample.

$$\Gamma_{x_T} = \sum_{i=1}^n (\omega_i \Gamma_{x_i}) = \frac{\sigma_x}{\sigma_{x_T}} \quad \text{Eq. A.11}$$

It may be demonstrated that these equations account for theoretical changes in signal response in multimodal samples which show vastly different signal response despite equal sample weight and mean particle size. The magnitude of such signal loss through the range of particle size observed in natural particulates must be determined before any researcher can say that, for instance, oceanic samples are free from absorption effects because of their size, let alone coastal particulates or aerosol particulate matter. Only through size-variant studies may an order of magnitude be assigned to these phenomena. Because this is the first study of this subject from this frame of reference, the efficacy of these formulae in predicting experimental results must be demonstrated before going further.

iv) EXPERIMENTAL STUDIES.

A sample of obsidian glass was powdered to yield a particulate sample of uniform chemistry throughout and with a chemical composition approximately that of average crustal rocks. Size separation was performed by a standard pipette analysis adjusted so as to yield less than 0.3 mg cm^{-2} of material on the most heavily loaded sample. Each of the pipette aliquots was filtered through preweighed $0.40 \mu\text{m}$ pore size 37 mm diameter Nuclepore[®] membrane filters. These samples were dried and analysed by XRF techniques for Al, Si, Ti and Fe. No standards were used, since prepared standards are subject to the same error as particulate samples. A fused disc sample of the powder was prepared and analysed separately to establish the composition of the samples by a method not subject to the effects being considered here.

Data from this experiment are shown in Table 4.II. Table 4.IIa shows the counts for each sample (which consists of a known maximum particle size and a representative sample of all finer material) in the pipette experiment. Table 4.IIb shows the half-phi interval data derived from this, wherein the weight percentages of each size interval have been determined by subtraction as in standard pipette analyses; in this case, the same subtraction has been applied to the counts as well, to produce an estimate of the counts which are attributable to material within each size fraction.

These counts were correlated for intercept and blank values. In addition, their original trends in changing count rate with maximum size have been smoothed by weight-linked proportioning in half-phi steps between the fixed coarse and fine-grained end members.

The obsidian "particulate" sample had a size distribution pattern as shown in Figure A.4.

TABLE A.II

Corrected counts for obsidian experiment

(a)

Summary of adjusted cumulative counts.

Max ϕ	Max Size (μm)	Wt (μg)	Counts			
			Al	Si	Ti	Fe
4.0	62.5	1090	24907	143898	8850	15303
5.0	31.2	1090	24907	143898	8850	15303
5.5	22.1	970	24337	143451	8329	14688
6.0	15.6	760	22381	131175	7059	12544
6.5	11.0	580	19225	111302	5706	10198
7.0	7.8	500	17094	103868	5153	8507
7.5	5.5	460	16040	95719	4765	7862
8.0	3.9	340	12893	72158	3630	5945
8.5	2.8	330	12461	70637	3489	5795
9.0	2.0	320	11992	67298	3299	5535
9.5	1.4	260	9804	55063	2718	4432
10.0	1.0	190	7251	40790	2041	3145

(b)

Summary of calculated ϕ -interval data

ϕ -Int	Wt (μg)	Wt%	Cum Wt%	Counts			
				Al	Si	Ti	Fe
5	0	.000	.000	0	0	0	0
5 - 5 $\frac{1}{2}$	120	.110	.110	570	447	521	615
5 $\frac{1}{2}$ - 6	210	.193	.303	1956	12276	1270	2144
6 - 6 $\frac{1}{2}$	180	.165	.468	3156	19873	1353	2346
6 $\frac{1}{2}$ - 7	80	.073	.541	2131	7434	553	1691
7 - 7 $\frac{1}{2}$	40	.037	.578	1054	8149	388	645
7 $\frac{1}{2}$ - 8	120	.110	.688	3147	23561	1135	1917
8 - 8 $\frac{1}{2}$	10	.009	.697	432	1521	141	150
8 $\frac{1}{2}$ - 9	10	.009	.706	469	3339	190	260
9 - 9 $\frac{1}{2}$	60	.055	.761	2188	12235	581	1103
9 $\frac{1}{2}$ - 10	70	.064	.826	2553	14273	677	1287
10	190	.174	1.000	7251	40790	2041	3145

FIGURE A.4

Particle size frequency distribution (by weight)
of obsidian sample.

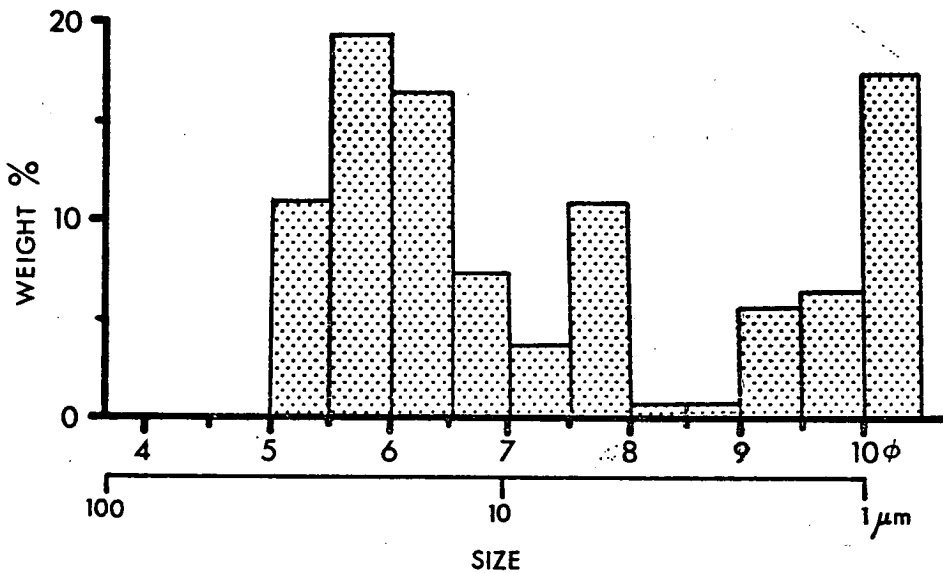


Figure A.5 (a-d) shows the count rates (counts/weight) of the original samples versus maximum particle size. These curves refer to the samples for which the maximum particle size present is shown on the abscissa (the sample contains this and all finer material) and the count rate is shown on the ordinate axis.

The signal drop with increasing particle size illustrates that size-related absorption phenomena affected the signal to a great degree. Constant signal response would be indicated by a horizontal trend. The net fall in signal response (roughly 40% for Al, 38% for Si, 22% for Ti and 17% for Fe) is in keeping with the theory. The fact that these curves seem to level off below 8φ (3.9 μm) does not necessarily indicate that thin-film conditions have been satisfied; this simply reflects that of the material smaller than 4 μm, over half is less than 1 μm (10φ) and over threequarters is less than 1.4 μm. This very fine-grained material provides a 'buffering' effect against apparent signal loss from the few particles in the size range of less than 8φ.

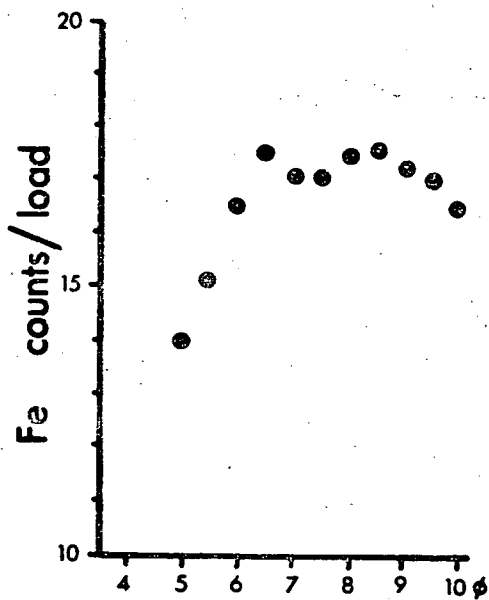
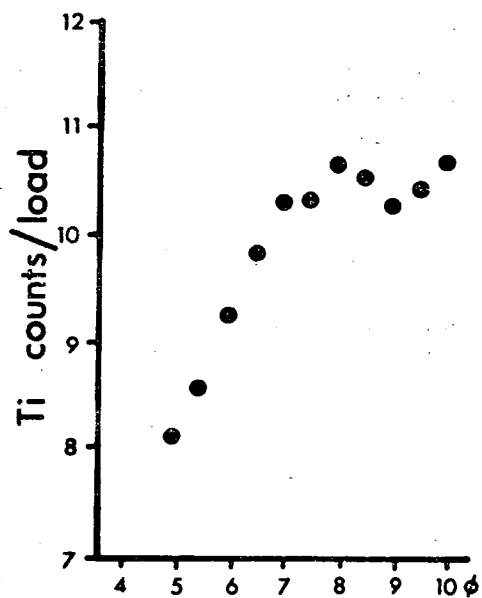
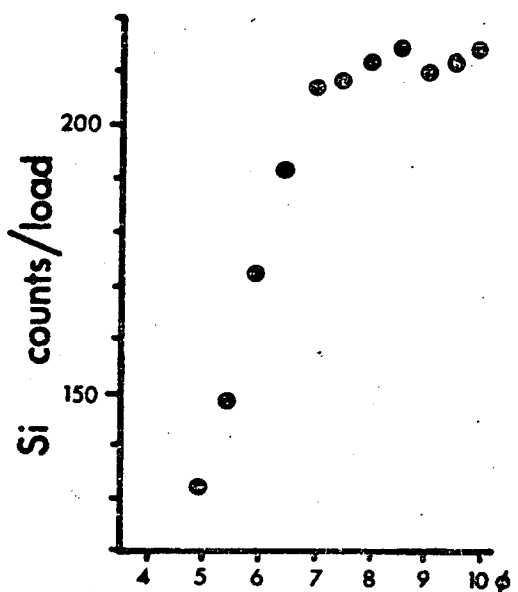
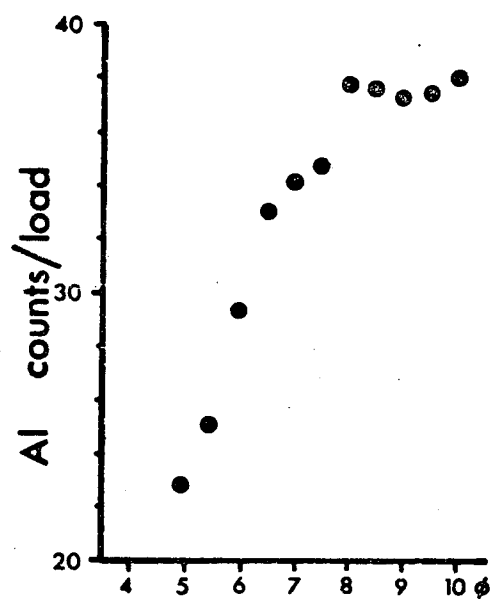


Fig. A.5 Ratios of counts received to load of obsidian powder in successive pipette samples.

Each of the elements in Figure A.5 is subject to the effects of size distribution. The best independent evaluation of signal return from individual particle sizes is provided by studying the response from each size interval. The data for such calculations are illustrated in Figure A.6 (a-d). The points shown in parentheses are those size fractions with calculated weights less than $10\ \mu\text{g}$. Such calculations are of limited accuracy, but these figures are presented to illustrate the first signal return versus size plot that is independent of the parameters which have hindered accurate evaluation of this phenomenon in other studies.

In Figure A.6, nowhere in the size range studied does the Al signal show a linear relationship with weight. The other elements appear to be fairly constant at size less than 8ϕ .

Testing the model.

The real proof of the model must depend on its comparison with the experimental data. Working strictly from Table A.I and Figure A.3 (Cr tube was used), and based on the weight distribution data, the Γ_{x_r} of the obsidian sample as a whole was determined for Al, Si, Ti and Fe. This calculation represents the theoretical degree to which received signal approximates thin-film response. The same calculation was performed for the 10ϕ sample (where 100% of this sample is less than $1\ \mu\text{m}$, with an assumed average diameter of $0.5\ \mu\text{m}$). The predicted ratio of these count rates (whole sample over material less than $1\ \mu\text{m}$) were then calculated. These were then compared with the observed countrates from experimental data.

The theoretical efficiency of signal return from the total sample (Γ_{x_r}) and the finest fraction of the obsidian pipette suite were determined using Equation A.9, the gravimetric data (Table A.IIb) and

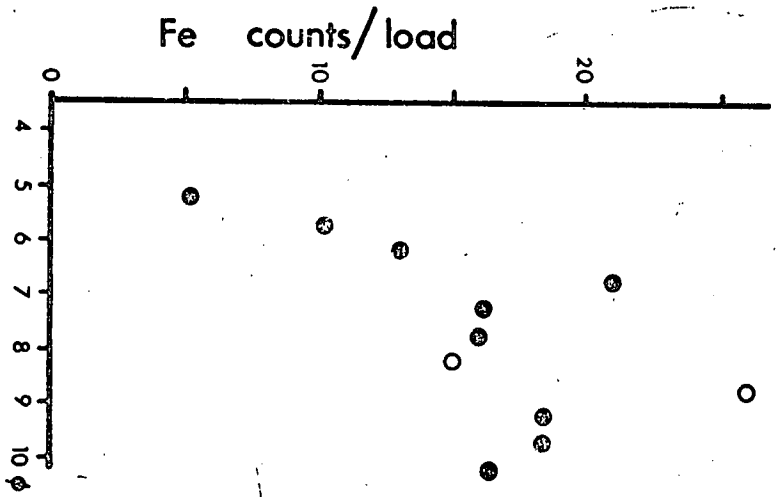
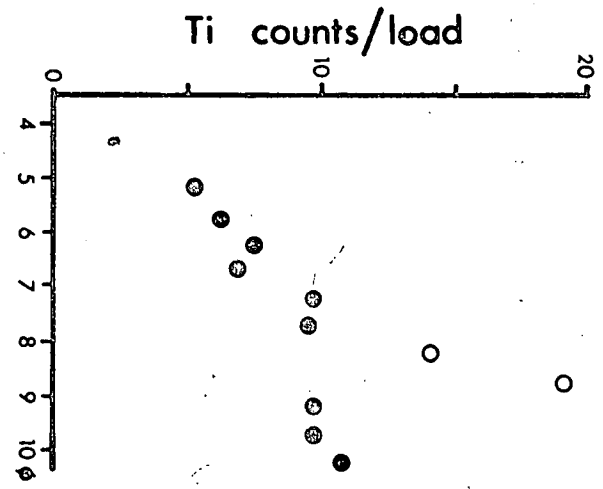
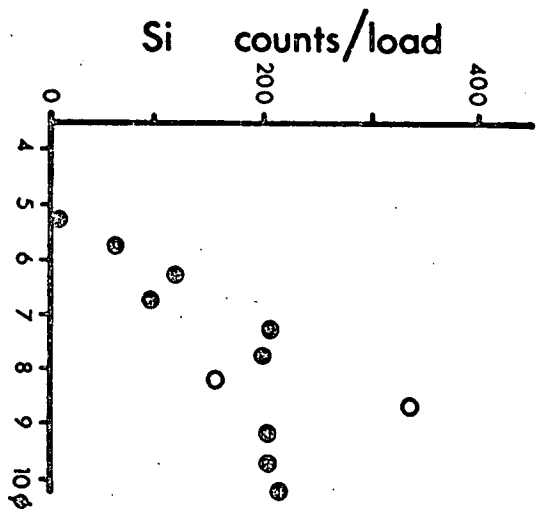
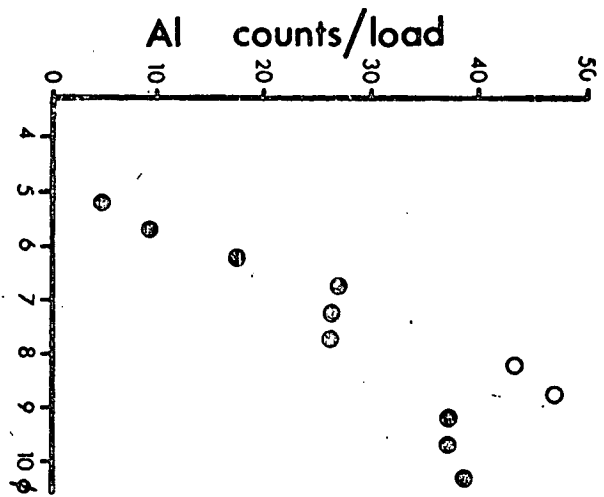


Fig. A.6 Ratios of estimated signal return (counts/load) from material within each size interval for the obsidian sample.

the known chemical composition of the sample. The values of $\Gamma_x^{10\phi}$, A and $\Gamma_x^{10\phi}$, B in Table A.III represent calculations for a fine fraction with an average particle size (by weight) of 0.5 and 1.0 μm respectively. Scanning electron microscopy studies indicate that the latter is a better approximation of the real situation.

The ratios of these Γ_x factors for each element represent the predicted change in signal response between the two pipette subsamples, and may be compared directly to the ratios of equivalent countrates as determined experimentally (Table A.III).

TABLE A.III

		ELEMENT			
		Al	Si	Ti	Fe
THEORY	Γ_{x_T}	0.40	0.50	0.72	0.81
	$\Gamma_{x10\phi}$ A	0.92	0.94	0.98	0.99
	$\Gamma_{x10\phi}$ B	0.79	0.86	0.95	0.97
	$\Gamma_{x_T} / \Gamma_{x10\phi}$ A	0.44	0.53	0.73	0.82
	$\Gamma_{x_T} / \Gamma_{x10\phi}$ B	0.51	0.58	0.76	0.84
DATA	Countrate (tot)	22.85	132.0	8.12	14.04
	Countrate (10 ϕ)	39.58	214.7	10.74	16.55
	CR (tot)/CR (10 ϕ)	0.58	0.62	0.76	0.84

The experimental evidence agrees very well with the theoretical predictions. Slightly enhanced light-element signal probably reflects the angularity of the particles as discussed earlier.

v) DISCUSSION.

The theoretical study presented here successfully accounted for the experimental evidence of matrix absorption due to particle size effects. If the curves shown in Figures A.2 and A.3 are indeed accurate, then absorption effects must be pronounced in XRF analysis of natural particulate matter. Credible analyses have been obtained by many authors, however, and have been offered as proof of efficient signal return. Enough information is at hand now to re-evaluate the significance of previous procedural studies.

The effective signal return has been shown to vary as a function of the specific element being analysed, the excitation efficiency of the X-ray source, the wavelength and intensity of the primary X-ray beam, the chemical composition and density of the sample matrix and the particle shape and size distribution characteristics of the sample. Reference to Table A.I and Figure A.2 or A.3 will permit determination of the magnitude of absorption effects for a specific matrix of given particle size, while application of equation A.10 or A.11 permit a similar calculation for a whole sample of known particle size distribution characteristics.

Oceanic particulates have been assumed to have sufficiently fine-grained to guarantee near-true thin-film response (Baker and Piper, 1976). Carder, Beardsley and Pak (1971) reported size distribution characteristics of particulates in the eastern equatorial Pacific in terms of the number of particles of size greater than a specific series of "threshold" values. These data were used to determine numbers of particles within each size interval for representative top water and 1000 meter samples (Stn. YPT-34). A rough estimate of particulate volume was made by assuming sphericity (original data were based on

Coulter Counter analysis) and Equation A.9 was applied to the resultant volume ratios, based on approximate compositions of crustal rocks for those particles less than $10\text{ }\mu\text{m}$ and of organics and biogenic skeletal debris for larger material. The resultant estimated signal accuracy (Γ_{x_r}) was calculated and found to be as follows: for the top water sample, Γ_{x_r} was determined to be 0.51 for Al and 0.92 for Fe; the equivalent values for the 1000 m sample were 0.56 and 0.91. This suggests a potential absorption problem with Al at least, even in fine-grained oceanic particulate samples.

Carder et al (1971) did not report particle counts for grains less than $2\text{ }\mu\text{m}$. A sample was postulated wherein the reported data represented only half the sample, with another half represented by a fine-grained mode ($<1\text{ }\mu\text{m}$). Assuming an average particle size within this mode of $0.5\text{ }\mu\text{m}$ (based on weight distribution) this theoretical sample was examined using Equation A.11. The resultant Γ_x values were found to be 0.72 and 0.92 for Al and Fe in the surface sample and 0.74 and 0.95 for the respective elements in the 1000 m sample. The Fe signal response may be within acceptable limits, but the signal received from Al is inaccurate by a factor of over 25%. The similar ratios between Γ_{Al} and Γ_{Fe} suggest that changes in observed inter-element ratios from top to bottom waters may reflect true chemical variation, but the Al signal in particular may be subject to absorption.

Estuarine particulates are even more subject to absorption effects due to their composition and size distribution (Chapters 4 and 5).

A linear relationship between sample load and signal return in prepared standards has been cited as proof of the accuracy of signal return (Meier and Unger, 1976). Many applications of XRF particulate analysis have been based on similar assumptions. Such sample suites

are invariably prepared such that all standard samples have the same composition and size distribution characteristics. Under these conditions, the signal received must vary directly with the weight of the sample (as long as no shielding takes place) regardless of the magnitude of absorption effects. Linear calibration curves do not, therefore, indicate the lack of significant absorption effects as claimed in previous studies. They may still be used for accurate chemical determinations, however, subject to conditions which will be explored later.

The constancy of inter-element ratios within sets of standards has also been claimed as being indicative of accuracy. Since signal response from each element must show linear response with sample weight, it follows that inter-element ratios must remain constant as well, regardless of the accuracy of each (until loading becomes excessive and particle shielding begins to result in preferential loss of light element signal).

A problem arose in the course of this study when two sets of standards prepared from different materials showed good agreement for count rates on all elements except Si, for which two distinct but independently linear calibration curves were obtained. One of these suites was found to contain many relatively large ($>10\ \mu\text{m}$) quartz grains while the other lacked such material. Loss of Si signal from the material within these grains is the likeliest reason for the lower Si response from this sample. The remaining elements, being associated with finer-grained material common to each set of standards, provided equivalent count rates.

This pattern is much simpler than that described by Baker and Piper (1976) for two sets of chemically identical rock powder samples

with different particle size characteristics due to grinding. Their study showed a progressively greater loss of signal in the coarse sample for those elements with high matrix absorption coefficients, indicating that large particles in the unground samples were of more complicated mineralogy than simple quartz. If the coarsest particulate matter in a suite of actual samples is of simple or predictable mineralogy, the matrix absorption problem may be simplified considerably.

A similarity in particle size distribution characteristics between particulate standards and samples is crucial if XRF analyses are to be accurate. When a set of particulate standards is first calibrated, a count rate for each element is assigned on the basis of total standard weight and known composition.

Methods of preparation of standards are sufficiently similar (Price and Calvert, 1973; Taylor, 1974; Skei, 1975; Baker and Piper, 1976; Sholkovitz and Price, pers. comm.) to result in samples of roughly equivalent size distribution and composition in most cases. Baker and Piper (1976) showed colinearity of standards prepared from different rock powders. Differences in absorption effects between such suites due to minor variations in coarse-grained constituents and mineralogy were probably masked (if present) by the signal received from the more prominent fine-grained constituents common to all samples.

Despite the magnitude of absorption effects indicated by Figures A.2 and A.3, artificially prepared suites of particulate standards may be used to determine the chemical composition of natural particulate matter as long as the size distribution of the samples is similar to that of the standards. Chemical determinations in this thesis were originally based on rock powder standards which, due to the character of ground powders (Jenkins and deVries, 1967; Baker and Piper, 1976),

probably bore a very close resemblance to the particle size distributions described for natural samples in Chapter 3.

Analysis of bulk particulate samples is rendered more accurate by the stabilizing influence of the signal from the fine-grained component common to both standards and samples. Only size-variant data may be used to evaluate the extent of matrix absorption effects, and these have not been applied to theoretical studies in the past.

Analyses of selected pipette samples of suspended particulate matter and sediments from station 26 in the Firth of Forth (Chapters 4, 5 and 6) were examined to determine the extent to which particle size effects could account for the changes in inter-element ratios with increasing particle size as shown for particulate samples of constant chemical composition in the experiment with obsidian powder as discussed previously. The assumption was made that chemical composition was constant throughout the sample, regardless of particle size.

The changes in signal response of all elements measured exceeded those predicted by the theoretical model by the percentages indicated in Table A.IV. The order of elements showing increased independence from theoretical constrictions is entirely independent of that indicated by their matrix absorption coefficients (Table A.I), suggesting that real chemical variation with particle size accounts for much of the inter-element variation shown in Chapter 5. Sulfur and calcium were found to be most independent of particle size effects, followed by silicon, titanium, aluminium, potassium and iron. The existence of matrix absorption effects due to particle shielding is best shown in the one sample with a load of 0.68 mg cm^{-2} (shielded sediment).

Several particulate samples were prepared into fused disc form (Doff, Price, pers. comm.) for major element analysis by XRF techniques

TABLE A.IV

The percentage by which observed changes in signal response exceed those predicted by absorption theory alone, based on the assumption of constant composition.

Sample	S	Ca	Si	Ti	Al	K	Fe
Surface Part.	217	167	108	84	81	69	56
Bottom Partic.	393	80	91	65	60	53	44
Sediment	950	555	90	39	37	51	22
Shielded sed.	950	630	58	29	11	33	-17

independent of the effects discussed previously. Due to the minimal sample weights (< 2 mg), accuracy of the analyses was questionable. Nevertheless, in bulk samples (not size-separated) better agreement between methods was observed for ratios of elements to Al than for absolute abundances.

The "thin-film" data (presented as absolute and/or inter-element ratios) increased as an inverse function of the matrix absorption coefficient of the element being analysed (Table A.1) in bulk samples (those containing all particle sizes). This indicates that mass absorption effects probably do occur during this film analysis of these natural particulate samples. These trends become poorly defined to indistinguishable with decreasing size in pipette samples.

Despite the inaccuracies indicated by the fusion study, the use of standards with size distribution and composition similar to those of the samples being analysed may still result in accurate analyses as shown by the intercalibration of different rock powder standards prepared by the same grinding techniques (Baker and Piper, 1976).

vi) SUMMARY AND SIGNIFICANCE TO THIS THESIS.

Matrix absorption effects have been shown to affect signal return during XRF "thin-film" analysis of natural particulate matter. A theoretical model has been derived which accounts for this signal loss, and experimental corroboration has been presented. Even very fine grained material may absorb a significant percentage of the signal. Reference to Table A.1 and Figures A.2 or A.3 will permit determination of the absorption effects to be anticipated in a given matrix.

In natural particulate matter, these effects are minimized by several factors, including chemical inhomogeneity as a function of particle size, the dominance of fine-grained material (less susceptible to absorption) by weight, the more simple mineralogy of coarse-grained material, the orientation of grains on the membrane (short axis perpendicular to the filter) and the enhanced light-element signal return from very angular particles.

When the particle size and composition of the samples analysed are similar to those of the standards used for preparing calibration curves, quite accurate analyses may be derived, but absolute accuracy cannot be claimed until further corroborative analytical studies (fusion disc, atomic absorption) have been completed.

In the present thesis, the size distribution of the standards and samples were quite similar, but many particulate samples contained more coarse-grained material. Most of this, however, occurred as X-ray transparent material (organic debris and coal fragments), porous biogenic skeletal debris (of simple chemistry and minimal shielding capability), or size-specific minerals which were chemically distinct from the fine-grained constituents. In addition, visual and mineralogical studies (Chapter 5) substantiated the chemical data trends, and inter-element

ratios were consistent with analyses by other techniques.

Due to the similarity of the matrix absorption coefficients of some elements (e.g. Si and Al, Table A.1), changes in their inter-element ratios due to particle size effects alone are minimal. The pronounced variations in Si/Al ratios in Chapters 6, 7 and 8, therefore, must be considered real. Trends of elemental abundance (as a percentage of total suspended load or ratioed to other elements) which are contrary to those predicted theoretically must be considered representative of true chemical variation. Gross differences in the analyses of Ca, S and P in samples with equivalent size characteristics, loads and other chemical associations (Chapter 6) must reflect real chemical variation. Signal return from other elements exceeds the limits predicted by the model with varying particle size.

Exhaustive examination of the chemical data in this thesis has indicated that inter-element ratios as shown represent real chemical trends, and that the values stated are approximately accurate.

This theoretical study has resulted in a continuing re-examination of the XRF "thin-film" technique as it is applied to the study of natural particulate matter. Whether or not the accuracy of the procedure is established, sufficient evidence has been presented here to prove that the term "thin-film" is inapplicable and should be discarded. "XRF particulate analysis" is suggested as an alternative.

APPENDIX B

Locations and times of sample collection.

TABLE B.I

The locations of the sampling stations referred to in this thesis are shown in the order of their sampling during the March 1975 survey.

The areal sampling took place just after spring tide (March 14, 1975). The tidal station sampling at stations 26 (January 20, 1977), 15 (February 8, 1977) and 7 (April 4, 1977) was conducted at or very near to spring tide.

The states of the tide as shown in the table are based on high water times of 0453 and 1710 hours on March 17, and 0530 and 1749 hours on March 18, 1975. The tidal amplitude was 5.0 m (Watts, 1975).

TABLE B.I

Stn	Latitude			Longitude			Date	Time (GMT)	Tide
18	56	11	33	02	56	50	17/3/75	0705	Ebb
17	56	09	67	02	56	50	"	0730	Ebb
16	56	08	00	02	56	50	"	0745	Ebb
15	56	06	17	02	56	50	"	0811	Ebb
14	56	03	58	02	56	50	"	0840	Ebb
13	56	01	33	02	56	50	"	0911	Ebb
12	55	59	50	02	56	50	"	0937	Ebb
1	55	59	92	03	14	00	17/3/75	1053	Flood
2	56	00	58	03	13	33	"	1106	Flood
3	56	01	17	03	12	67	"	1123	Flood
4	56	01	67	03	12	67	"	1137	Flood
5	56	02	50	03	14	00	"	1154	Flood
24	56	01	17	03	18	67	17/3/75	1225	Flood
25	56	01	58	03	16	33	"	1249	Flood
4	56	01	67	03	12	67	"	1321	Flood
26	56	02	25	03	11	53	"	1345	Flood
27	56	03	00	03	09	00	"	1434	Flood
9	56	04	17	03	05	50	"	1458	Flood
28	56	05	17	03	00	67	"	1538	Flood
15	56	06	17	02	56	50	"	1607	Flood
29	56	06	92	02	51	50	"	1640	Flood
21	56	07	58	02	47	00	"	1720	Ebb
23	56	11	25	02	47	00	18/3/75	0735	Ebb
22	56	09	58	02	47	00	"	0755	Ebb
21	56	07	58	02	47	00	"	0828	Ebb
20	56	06	33	02	47	00	"	0903	Ebb
19	56	05	08	02	47	00	"	0932	Ebb
6	56	58	58	03	05	50	18/3/75	1125	Ebb
7	55	59	92	03	05	50	"	1146	Flood
8	56	01	67	03	05	50	"	1250	Flood
9	56	04	17	03	05	50	"	1315	Flood
10	56	05	67	03	05	50	"	1340	Flood
11	56	07	00	03	05	50	"	1412	Flood
15	56	06	17	02	56	50	18/3/75	1441	Flood

APPENDIX C

Methods.

METHODS

The field sampling techniques employed in this thesis have been summarized in the main text and will not be repeated here. Certain aspects of the laboratory procedures and specific methods of data manipulation, however, require further explanation and will be considered in their order of appearance in the thesis.

Physical characteristics of the Firth of Forth.

Calculations of the volume of the study area were derived from a large scale bathymetric chart, with the mean water depth contoured in meters (derived from DECCA Navigational chart LD3 114a). The study area was divided into 10 sectors as shown in Figure C.1, on the basis of the March 1975 sampling grid. Within each sector, the map area between successive bathymetric contours was determined using a Haff-813 planimeter. Scale factors were applied to yield actual areas in m^2 . Water volumes were calculated by determining the volume present between successive depth intervals by the equation:

$$V_{x(n-D \ n)} = \frac{(A_n - A_{n-D})D}{2} \quad \text{Eq. C.1}$$

where n is the lower depth limit of the interval,
 D is the thickness of the depth interval,
 A_n is the area of the sector with depth $< n$ meters,
 A_{n-D} is the area of the sector of depth less than the next more shallow contour, and
 $V_{x(n-D \ n)}$ is the volume of water in the sector between the depths n and $n-D$.

The volumes thus determined were summed to yield a total volume for each sector and for the entire study area. The areas of selected

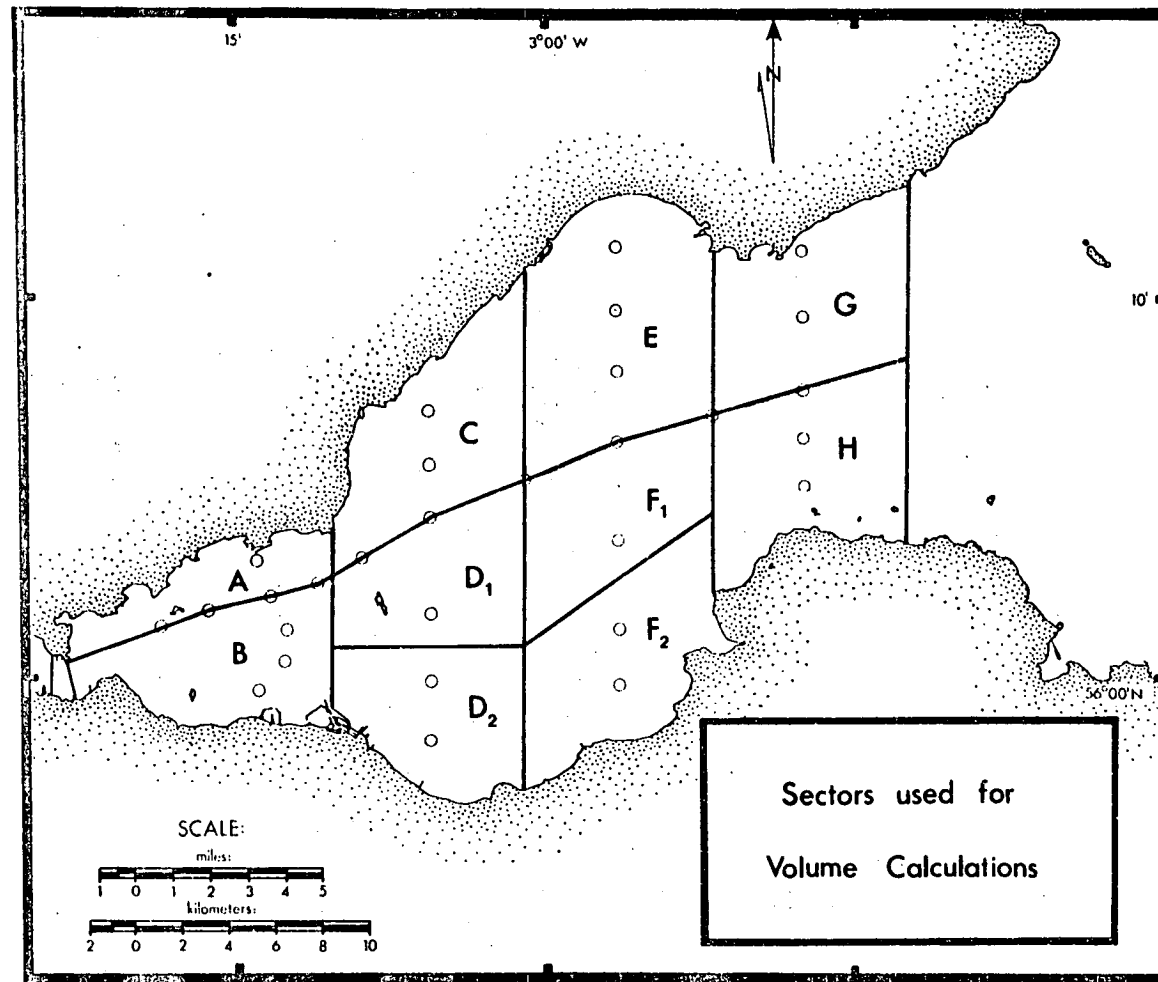


Fig. C.1

cross-channel transects (Chapter 2) were also calculated by means of planimetry and scale factoring.

The total volume of the Forth as calculated by this method ($\sim 13 \text{ km}^3$) is less than half that quoted by Craig (1972) of 30 km^3 . Craig's figure implies an average water depth of over 40 m, and appears unfeasible even if the study area is extended considerably seaward.

Estimates of the 'average' salinity and concentration of suspended particulate matter were determined by planimetry of these parameters as plotted in Figures 3.2 and 3.4. These were averaged within each 10 m depth interval of each sector (Figure C.1), and were extrapolated to the volume of water within that depth interval. In this manner, a more detailed evaluation of the average salinity and loading of particulate matter was possible here than in previous studies, although this is still based only on a point-in-time survey. Table C.1 summarizes the calculations of area, volume and average salinity and load for the sectors shown in Figure C.1.

TABLE C.1

Gross physical characteristics of the Firth of Forth.

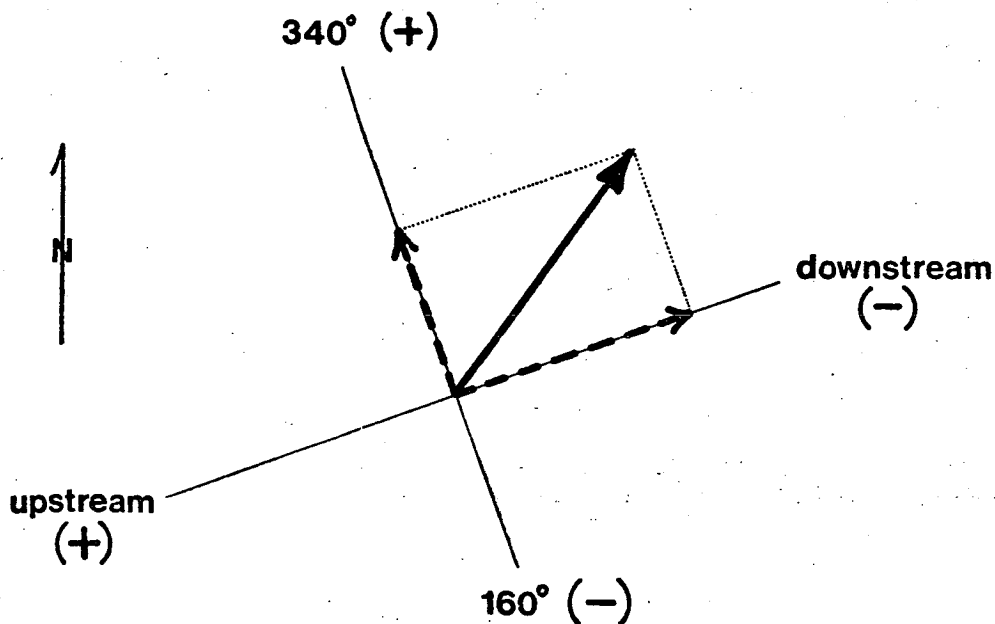
Sector	Area (km^2)	Volume (km^3)	Average Depth (m)	Suspended Load Conc. (mg l^{-1})	Total $\times 10^6 \text{ kg}$	Salinity Av %	% fresh water dilution
A	32.4	0.46	14.0	10.4	4.8	32.69	5.25
B	60.1	0.53	8.8	9.2	4.9	32.77	5.01
C	72.8	1.22	16.8	3.0	3.7	33.43	3.10
D ₁	53.3	0.96	18.0	4.1	3.9	33.25	3.62
D ₂	62.4	0.48	7.7	4.8	2.3	32.95	4.49
E	105	2.14	20.4	2.6	5.6	33.98	1.51
F ₁	58.1	1.75	30.1	2.5	4.4	33.88	1.80
F ₂	76.8	0.70	9.1	3.6	2.5	33.33	3.39
G	74.7	2.50	33.5	1.6	4.0	34.00	1.45
H	74.3	2.43	32.7	2.9	7.0	33.99	1.48
Total/ Average	670	13.17	19.6	3.4	45	33.71	2.29

Water movement and flux calculations.

For the tidal station monitoring data, each measurement of the speed and direction of currents was resolved into a longitudinal (upstream/downstream) and a cross-channel vector as shown in Figure C.2, assuming a main channel orientation of 070° . Upstream movement and northward cross-channel flow were arbitrarily defined as positive. The original data and the derived vectors are listed in Appendix D.

Figure C.2

Resolution of vector components.



The average current speed at a given depth was determined by averaging the half-hourly data from the first 12 hours of each tidal station. The flux of suspended material (in $\text{kg m}^{-2} \text{s}^{-1}$) was determined by multiplying the concentration of the particulate matter (in kg m^{-3}) by the current velocity (in m s^{-1}) in each frame of reference (Buller, 1975; d'Anglejan and Ingram, 1976). This calculation was performed for each of the first 12 hourly sampling times at each station. At station 26, the loadings of the 1 m and 5 m particulate samples were

averaged and multiplied by the current velocity at 3 m depth. At station 15, the 3 m depth current vectors were combined with the 5 m loading data. Elsewhere, the depths of current measurements and loading were taken to be equivalent.

The net flux for a tidal cycle was determined by assuming each flux calculation to be representative of a one-hour period ($1 \text{ g m}^{-2} \text{ s}^{-1} \times 3600 \text{ s} = 3.6 \text{ kg m}^{-2} \text{ hr}^{-1}$) and summing these vectors in each frame of reference.

This method permits integration to depth (yielding a net flux through the sampling point in kg m^{-1} (cf. Buller, 1975)), and it is advantageous in that it permits definition of varying directions of flux as a function of depth.

Pipette analyses.

The theory of pipette analysis, based on Stokes' (1851) equations of particle settling velocities is detailed at length elsewhere (Krumbein & Pettijohn, 1938; Müller, 1967; Royse, 1970).

In the present study, five-litre water samples were collected for particle-size analyses of suspended particulate matter. Aliquots from bottom sediments were retrieved for later dispersal in one litre of filtered distilled water for pipette analysis. The procedure is that described by Royse (1970), with a few modifications. Because of the light suspensions encountered, large-volume samples were used, and the volumes of individual aliquots were chosen to provide sufficient material for chemical analysis. The volumes of the pipette samples are listed in Appendix E. These are usually 50 ml for particulate samples of size greater than 8ϕ and 100 ml for finer samples. The pipette suites from station 7 (performed first) were based on smaller water volumes, which may contribute to the irregularities of gravimetric

and chemical data curves for these samples.

The times and depths of the pipette sampling are shown in Table C.2.

TABLE C.2

Sampling conditions for pipette analysis.

Size ϕ	Time			Depth cm.
	hr.	min.	sec.	
4.0		1	30	20
4.5		1	30	10
5.0		2	59	10
5.5		6	00	10
6.0		11	59	10
6.5		23	53	10
7.0		48	02	10
7.5	1	36		10
8.0	3	12		10
8.5	6	25		10
9.0	8	58		7
9.5	12	45		5
10.0	25	23		5

In Appendix E, the first sample of each pipette suite (designated as 3 ϕ for station 7 and 4 ϕ for all other samples) in fact represents the total sample. This was extracted by agitating the container and pouring the sample into a container of known volume. The suspension was then re-agitated and the standard pipette analysis was begun. All samples were immediately vacuum-filtered through pre-weighed 0.4 μ m pore-size 37 mm diameter Nuclepore[®] membrane filters, and were washed with a volume of filtered distilled water equivalent to that of the sample. The filters were dessicated, transferred to the weighing room and allowed to equilibrate with the ambient humidity conditions before weighing on a Perkin-Elmer AD-2 autobalance. Repetitive weighings of selected filters were performed throughout this period to ensure consistency. The precision of weighing was estimated at $\pm 5 \mu$ g.

Scanning electron microscopy.

Nuclepore[®]-filtered samples were examined by reflected light microscopy to determine their gross characteristics and to select representative subsamples for SEM examination. Sections were cut from the filters and mounted on aluminium stubs using double-sided Sellotape[®]. The samples were carbon-coated and examined on an S4 Stereoscan scanning electron microscope at the Bush Agricultural Research Station, Terrestrial Sciences Unit.

X-ray diffraction.

Untreated suspended particulate matter and sediment samples were examined by X-ray diffraction on both Nuclepore[®] and glass-fibre filters, using a Philips PW-1010 X-ray diffractometer fitted with an AMR 3-202 X-ray focussing monochromator. The machine settings are listed in Table C.3.

TABLE C.3

Machine setting for X-ray diffraction studies.

kV	36
mA	20
Scale factor	1
Divergence slit	1°
Receiving slit	0.1°
Time constant	8 seconds
Scan rate	$\frac{1}{4}$ ° per minute
X-ray source	Ni-filtered Cu K α radiation ($\lambda = 1.54 \overset{0}{\text{\AA}}$)

Each filter was cut in half and mounted on an aluminium plate by means of silicon grease. Although this procedure was useful for glass-

fibre filtered samples, severe background effects were encountered with Nuclepore[®] filters, particularly from 10-14° and 16-20° 2θ.

The second of these is a background peak from the filter itself, but the 10-14° 2θ peak was determined to be due to the silicon grease.

This was eliminated by 'tacking' the filters to the aluminium plate by peripheral dabs of grease which were not irradiated, and by holding the straight edge of the half-filter flush with the plate by means of the spring-clip in the sample chamber.

Due to the smooth surface of the Nuclepore[®] filters, these samples should be considered as oriented mounts. The sensitivity of the XRD analyses suffered as a result of the small amounts of sample available.

Major elements in particulate samples.

The major elements studied (Si, Ca, Fe, Ti, K, Mg, P and S) were determined by X-ray fluorescence spectrometry according to 'thin-film' techniques as detailed by Taylor (1974) and discussed at greater length in Appendix A.

A Philips PW1212 multi-channel XRF spectrometer was used to analyse samples from the areal sampling programme, the pipette samples from station 7, and all particulate and sediment samples from station 26 and the inner estuary. The remaining samples were analysed on a PW1450 XRF spectrometer.

All analyses were based on the same set of standards, which were run with each suite of samples. These standards consisted of natural particulate matter (N. B. Price, pers. comm.) which were originally calibrated from rock powder standards of known composition. Subsequent wet chemical analyses (D. Doff, pers. comm.) have shown that the analyses of the Forth particulate sample analyses are consistent with those of other studies in this department. The calibration curves

were plotted by hand to verify their linearity. Count manipulations were then performed by means of computer programmes based on least squares linear regression analysis. Several blank filters from each factory order were rinsed with filtered distilled water in the filtration unit in the course of preparing actual samples, and were analysed to determine background levels. These were small for all elements, but were subtracted from the original analyses.

The samples were analysed in groups of three, according to the machine settings listed in Table C.4. A monitor was left in the machine at all times to permit corrections for machine drift. Semi-quantitative analyses of Cl were performed which verified total removal of sea salts. No salt corrections, therefore, have been applied to the analyses of Ca, K, Mg or S.

Three cycles of analyses were conducted on all samples analysed on the PW1212 machine. Due to the higher sensitivity and greater stability of the PW1450 spectrometer, however, only two cycles were run on that instrument. The estimated precision is summarised in Table C.5.

TABLE C.4

Machine settings for XRF analyses.

Element	Line	Tube	kV	mA	Crystal	Peak	Background	Counter	Time (s)	Coll.	Vacuum
Al	K α	Cr	60	24	PET	144.95	-	F	20	C	yes
Si	K α	Cr	60	24	PET	109.12	-	F	20	C	yes
Ca	K α	Cr	40	24	PET	45.19	-	F	20	F	yes
Fe	K α	Cr	60	24	LiF(200)	57.60	-	S	20	F	yes
Ti	K α	Cr	60	24	LiF(200)	86.26	-	F	20	F	yes
K	K α	Cr	60	24	PET	50.68	-	F	20	C	yes
Mg	K α	Cr	40	32	ADP	136.85	133.85	F	40	C	yes
P	K α	Cr	60	24	PET	89.47	87.47	F	40	F	yes
S	K α	Cr	60	24	PET	75.62	-	F	20	F	yes
*Cu	K α	W	80	24	LiF(200)	45.00	45.60	S	40	F	no
*Pb	L β	W	80	24	LiF(200)	28.25	27.85	S	40	F	no
*Zn	K α	W	80	24	LiF(200)	41.76	40.80	S	40	F	no

* = Accessory analyses of sediments (Chapter 9).

TABLE C.5

Estimated precision of XRF major-element analyses of
suspended particulate matter samples
(based on 6 repetitive analyses).

Element	Precision	
	Skei (1975)	This Study
Al	2%	1%
Si	5%	1%
Ca	2%	1%
Fe	1%	1%
Ti	5%	1%
K	2%	1%
Mg	3%	1%
P	4%	1%
S	2%	2%

The discrepancies in precision between this study and that of Skei to some degree reflect the fact that more material was available for analysis in Forth samples. However, the precision calculations for this study were based on six repeated analyses performed over a short period of time (~ 12 hours), and are somewhat enhanced as a result.

Trace elements in sediments.

The concentrations of Cu, Pb and Zn as quoted in Chapter 9 and Appendix H are derived from subsidiary studies of core samples conducted in 1975 by the author. The sediment was retrieved using a stainless steel gravity corer with unsupported polycarbonate core barrels. On return to the laboratory, the cores were frozen, split and stripped

of the possibly contaminated outer layer. Subsamples were taken over 5 cm intervals. These were oven-dried, then crushed for 1 minute in a Tema tungsten carbide mill. The powdered samples were prepared as pressed discs for XRF analysis according to techniques detailed by Taylor (1974). Calibration curves were derived from USGS rock powder standards, based on the values reported by Flanagan (1973). Matrix absorption effects were corrected following the methods of Reynolds (1963). The machine settings used are shown in Table C.4.

APPENDIX D

Hydrographic Data.

- i) Hydrographic data - March 1975
 - areal (grid) sampling (Table D.1)
- ii) Salinity, temperature, total suspended load
 - (concentration) - tidal station 26 (Table D.2)
- iii) Current data - tidal station 26 (Table D.3)
- iv) Current vector components - tidal station 26 (Table D.4)
- v) Salinity, temperature, total suspended load
 - (concentration) - tidal station 15 (Table D.5)
- vi) Current data - tidal station 15 (Table D.6)
- vii) Current vector components - tidal station 15 (Table D.7)
- viii) Salinity, temperature, total suspended load
 - (concentration) - tidal station 7 (Table D.8)
- ix) Current data - tidal station 7 (Table D.9)
- x) Current vector components - tidal station 7 (Table D.10)

TABLE D.1

Hydrographic data - March 1975
areal (grid) sampling.

SUMMARY OF HYDROGRAPHIC DATA FROM MARCH 1975 GRID SAMPLING.
DATA PROVIDED BY THE DEPARTMENT OF AGRICULTURE AND FISHERIES
FOR SCOTLAND (DRS. JOHNSTON AND DAVIES).

TEMPERATURE IN DEGREES CENTIGRADE, SALINITY IN PARTS PER THOUSAND.
PO4, NO3 AND SIO4 IN UG-AT/L.

N.A. = NOT ANALYSED (DATA NOT AVAILABLE)

TEMP	SAL	PO4	NO3	SIO4	NAME
5.49	33.82	0.21	10.80	11.40	15-18-0
5.49	33.81	0.21	2.60	10.80	15-18-02
5.51	33.83	0.19	8.10	10.80	15-18-05
5.50	33.92	0.14	9.90	N.A.	16-17-0
5.50	33.93	0.21	10.10	9.10	16-17-02
5.51	33.93	0.19	9.80	N.A.	16-17-05
5.51	33.93	0.19	9.80	9.90	16-17-10
5.49	33.92	0.13	N.A.	9.90	16-17-15
5.53	33.94	0.18	6.40	9.50	17-16-0
5.53	33.95	0.18	9.80	9.80	17-16-02
5.56	33.95	0.77	8.80	9.50	17-16-05
5.56	33.95	0.77	9.40	8.70	17-16-10
5.57	33.94	0.19	8.10	9.90	17-16-20
5.58	33.96	0.79	9.60	9.90	17-16-28
5.57	33.97	0.79	4.50	10.70	18-15-0
5.60	33.97	0.87	9.20	9.00	18-15-02
5.61	34.00	0.29	10.10	9.80	18-15-05
5.61	33.98	0.29	6.80	9.50	18-15-10
5.62	33.99	0.26	9.60	9.20	18-15-20
5.62	33.98	0.27	9.60	9.50	18-15-25
5.48	33.73	0.31	11.00	11.20	19-14-0
5.48	33.71	0.27	10.60	10.70	19-14-02
5.49	33.70	0.24	11.10	10.50	19-14-05
5.51	33.72	0.26	10.50	10.50	19-14-10
5.49	33.82	0.26	8.60	N.A.	19-14-20
5.36	33.27	0.32	3.30	11.90	20-13-0
5.36	33.25	1.05	N.A.	11.70	20-13-02
5.36	33.26	0.34	N.A.	11.30	20-13-05
5.36	33.27	1.43	7.90	12.50	20-13-10
5.26	33.34	0.29	6.70	13.00	21-12-0
5.27	33.33	0.21	13.30	11.40	21-12-02
5.27	33.33	0.19	11.40	11.30	21-12-05
5.32	32.74	1.87	12.30	12.90	22-1-0
5.26	32.74	2.21	12.80	14.10	22-1-02
5.24	32.76	2.32	9.80	14.20	22-1-04
5.27	32.72	1.58	9.10	13.10	23-2-0
5.28	32.70	1.50	11.10	14.70	23-2-02
5.27	32.71	2.62	12.30	13.80	23-2-05
5.31	32.86	1.13	14.00	13.50	24-3-0
5.33	32.87	1.21	6.00	12.90	24-3-02
5.31	32.86	1.21	11.80	15.40	24-3-04
5.37	32.73	1.42	13.20	14.20	25-4-0
5.36	32.74	1.13	N.A.	13.60	25-4-02
5.37	32.76	1.14	13.90	13.60	25-4-05
5.45	32.55	1.37	13.20	14.50	26-5-0
5.45	32.55	1.67	N.A.	13.40	26-5-02
5.41	32.61	1.16	9.90	15.10	26-5-05
5.37	32.72	1.50	11.10	13.80	26-5-10
5.45	32.97	2.13	3.70	13.00	26-5-20

TABLE D.1

(continued)

TEMPERATURE IN DEGREES CENTIGRADE, SALINITY IN PARTS PER THOUSAND.
PO4, NO3, SIO4 AND NH3 IN UG-AT/L.

N.A. = NOT ANALYSED (DATA NOT AVAILABLE)

TEMP	SAL	PO4	NO3	SIO4	NAME
5.47	32.28	1.66	12.70	14.40	27-24-0
5.47	32.27	1.66	N.A.	14.80	27-24-02
5.37	32.40	2.00	8.60	15.00	27-24-05
5.37	32.47	2.08	7.70	14.50	27-24-10
5.40	32.58	1.69	9.60	14.40	27-24-20
5.46	32.26	1.63	12.00	14.80	28-25-0
5.45	32.26	1.55	N.A.	14.90	28-25-02
5.37	32.59	1.35	8.70	15.40	28-25-05
5.39	32.43	1.55	8.70	16.20	28-25-10
5.39	32.50	2.69	8.20	15.00	28-25-15
5.46	32.70	2.35	11.60	15.00	29-4-0
5.46	32.70	0.93	N.A.	14.30	29-4-02
5.43	32.77	1.35	8.50	14.00	29-4-05
5.44	32.83	2.19	12.40	14.10	30-26-0
5.45	32.83	2.03	9.20	14.50	30-26-02
5.43	32.86	1.18	5.20	13.70	30-26-05
5.36	32.87	0.97	9.30	14.40	30-26-10
5.50	33.29	0.40	9.80	13.00	30-26-20
5.52	33.37	0.61	N.A.	11.40	30-26-30
5.52	33.36	1.17	8.60	12.70	30-26-33
5.50	33.44	1.03	7.60	11.40	31-27-0
5.51	33.44	0.29	8.80	11.10	31-27-02
5.47	33.46	0.29	8.20	10.80	31-27-05
5.47	33.55	0.97	8.50	8.96	31-27-10
5.48	33.59	0.19	5.70	9.62	31-27-20
5.49	33.35	0.31	6.90	10.16	32-9-0
5.50	33.30	0.21	9.40	68.96	32-9-02
5.46	33.45	0.19	8.00	9.73	32-9-05
5.50	33.57	0.21	5.70	9.62	32-9-10
5.48	33.59	0.16	N.A.	9.62	32-9-15
5.58	33.59	0.23	7.40	9.62	33-28-0
5.59	33.59	0.97	N.A.	9.84	33-28-02
5.59	33.60	0.97	11.70	9.40	33-28-05
5.55	33.62	1.08	11.10	9.15	33-28-10
5.53	33.68	1.03	N.A.	9.51	33-28-20
5.57	33.80	0.26	2.20	8.31	34-15-0
5.57	33.81	0.23	10.20	8.85	34-15-02
5.57	33.81	0.23	6.60	8.42	34-15-05
5.57	33.87	0.95	6.70	9.18	34-15-10
5.58	33.92	0.23	8.40	7.54	34-15-20
5.59	33.93	0.23	7.00	7.65	34-15-25
5.52	33.83	0.23	11.70	8.42	35-29-0
5.53	33.83	1.00	9.30	8.31	35-29-02
5.52	33.82	0.97	10.10	8.52	35-29-05
5.52	33.83	0.24	6.30	8.31	35-29-10
5.62	33.92	0.31	N.A.	8.09	35-29-20
5.62	33.98	0.24	7.80	6.88	35-29-30
5.62	34.01	0.19	9.90	7.76	35-29-35
5.55	33.91	0.56	7.60	7.98	36-21-0
5.58	33.91	0.18	10.70	8.20	36-21-02
5.58	33.90	0.87	9.90	8.20	36-21-05
5.57	33.90	0.89	9.30	8.63	36-21-10
5.62	33.95	0.95	9.70	7.98	36-21-20
5.64	33.99	1.00	8.60	8.31	36-21-30
5.67	33.99	0.90	9.60	8.20	36-21-40
5.68	33.99	0.87	N.A.	8.31	36-21-45

TABLE D.1

(continued)

TEMPERATURE IN DEGREES CENTIGRADE, SALINITY IN PARTS PER THOUSAND,
PO4, NO3, SiO4 AND NH3 IN UG-AT/L.

N.A. = NOT ANALYSED (DATA NOT AVAILABLE)

TEMP	SAL	PO4	NO3	SiO4	NAME
5.47	33.90	0.23	11.30	7.32	37-23-0
5.45	33.92	0.21	N.A.	7.45	37-23-02
5.49	33.88	0.21	8.30	7.54	37-23-05
5.48	33.90	0.39	9.70	7.65	37-23-10
5.49	33.92	0.71	9.70	7.65	38-22-0
5.50	33.92	0.82	9.10	7.54	38-22-02
5.50	33.91	0.82	8.90	7.76	38-22-05
5.51	33.96	0.81	7.70	7.76	38-22-10
5.51	33.95	0.77	9.30	7.54	38-22-20
5.51	33.94	0.79	9.50	7.54	38-22-30
5.51	33.96	0.79	9.30	7.21	38-22-35
5.51	33.92	0.45	N.A.	8.31	39-21-0
5.51	33.91	0.93	6.50	8.63	39-21-02
5.52	33.91	0.87	7.90	8.20	39-21-05
5.52	33.92	0.98	N.A.	8.20	39-21-10
5.62	33.91	1.05	7.00	8.20	39-21-20
5.61	33.98	1.00	9.90	9.20	39-21-30
5.64	33.99	1.00	9.90	9.30	39-21-40
5.65	33.99	0.87	9.90	9.10	39-21-45
5.47	33.91	1.03	10.70	9.20	40-20-0
5.50	33.91	1.03	10.60	9.30	40-20-02
5.50	33.92	0.95	10.30	9.70	40-20-05
5.50	33.93	0.98	10.10	9.30	40-20-10
5.49	33.90	1.00	10.70	9.50	40-20-20
5.51	33.93	1.00	N.A.	9.20	40-20-30
5.51	33.94	1.05	10.30	9.30	40-20-40
5.51	33.94	0.87	8.80	9.20	40-20-45
5.41	33.79	1.00	10.50	9.70	41-19-0
5.41	33.82	1.00	10.50	9.70	41-19-02
5.42	33.79	1.00	10.40	9.70	41-19-05
5.47	33.85	1.00	10.80	9.40	41-19-10
5.50	33.89	0.93	10.50	9.30	41-19-20
5.50	33.89	1.08	10.50	9.10	41-19-25
5.24	33.88	3.83	14.00	14.00	42-6-0
5.23	33.85	3.78	14.00	14.00	42-6-02
5.22	32.84	4.11	16.10	12.60	42-6-05
5.29	32.97	4.11	13.80	12.30	43-7-0
5.28	32.96	4.56	13.50	12.30	43-7-02
5.28	32.96	4.83	13.30	12.40	43-7-05
5.46	33.13	1.85	12.50	11.90	44-8-0
5.44	33.14	1.93	12.60	11.90	44-8-02
5.40	33.18	1.72	13.50	11.26	44-8-05
5.42	33.19	1.79	14.00	11.26	44-8-10
5.56	33.24	1.67	13.50	10.60	45-9-0
5.57	33.23	1.38	13.60	11.15	45-9-02
5.47	33.23	1.35	13.90	11.26	45-9-05
5.49	33.39	1.29	13.50	10.60	45-9-10
5.48	33.65	1.29	12.70	10.40	45-9-20
5.52	33.31	1.32	13.70	10.71	46-10-0
5.51	33.30	1.50	13.60	10.71	46-10-02
5.49	33.33	1.50	13.20	10.71	46-10-05
5.55	33.36	1.35	12.20	10.71	46-10-10
5.52	33.57	1.08	N.A.	10.16	46-10-15
5.55	33.51	1.21	12.19	10.05	47-11-0
5.53	33.51	0.24	12.30	9.94	47-11-02
5.49	33.55	1.13	12.40	10.05	47-11-05
5.51	33.56	1.05	12.30	9.40	47-11-10
5.51	33.56	1.14	12.40	10.05	47-11-15
5.51	33.50	1.19	12.20	9.73	48-28-0
5.48	33.49	1.21	12.40	9.94	48-28-02
5.46	33.55	1.16	12.80	10.71	48-28-05
5.53	33.67	1.09	12.00	12.68	48-28-10
5.53	33.67	1.09	12.00	12.68	48-28-20
5.61	33.40	1.30	12.60	10.49	49-15-0
5.61	33.60	1.09	12.30	10.27	49-15-02
5.57	33.63	1.11	11.90	9.51	49-15-05
5.52	33.63	1.00	10.10	9.40	49-15-10
5.53	33.67	1.08	4.20	9.73	49-15-20
5.52	33.66	1.14	9.90	9.94	49-15-25

TABLE D.2

Salinity, Temperature, Total Suspended Load
- Tidal Station 26

TIME	DEPTH (m)	SALINITY (ppt)	TEMPERATURE (°C)	T.S.L. (mg/l)
0855	0	32.939	-	14.3
	5	32.961	-	15.2
	10	32.989	-	13.5
	17	33.209	-	14.6
	27	33.092	-	11.9
0955	0	-	-	13.8
	5	32.999	-	13.8
	10	33.003	-	13.4
	20	33.030	-	15.2
	27	33.028	-	15.1
1055	0	32.688	-	7.8
	5	32.968	-	11.4
	10	33.068	-	12.0
	20	33.279	-	13.7
	27	33.461	-	25.5
1155	0	-	5.6	8.2
	5	-	5.8	7.5
	10	-	5.5	7.0
	20	-	5.4	10.3
	28	-	5.3	14.2
1301	0	33.389	5.5	11.1
	5	-	5.6	11.1
	10	-	5.4	13.1
	20	-	5.2	12.4
	28	-	5.0	12.7
1400	0	33.395	6.2	7.3
	5	33.503	5.8	10.6
	10	33.555	5.7	18.3
	20	33.631	5.7	20.8
	30	33.651	6.0	24.0
1500	0	33.414	5.7	8.9
	5	33.421	5.6	8.0
	10	33.535	6.3	11.0
	20	33.632	5.6	18.6
	33	33.663	5.6	31.6
1600	0	33.412	5.6	7.2
	5	33.348	5.6	5.8
	10	33.431	5.4	7.3
	20	33.594	5.2	10.5
	25	33.616	5.3	12.4
	30	33.615	5.1	18.8

TABLE D.2

(continued)

TIME	DEPTH (m)	SALINITY (ppt)	TEMPERATURE (°C)	T.S.L. (mg/l)
1700	0	33.351	5.4	9.2
	5	33.359	5.0	6.7
	10	33.377	4.9	6.3
	20	33.415	5.0	7.1
	25	33.426	4.8	8.0
	30	33.435	4.7	7.7
1800	0	33.039	5.3	9.5
	5	33.043	4.7	9.2
	10	33.069	4.6	9.4
	20	33.155	4.6	11.9
	25	33.164	4.5	10.5
	29	33.278	4.6	25.0
1900	0	32.938	4.8	14.5
	5	32.981	5.0	14.8
	10	33.137	5.0	18.9
	20	33.151	-	16.2
	25	33.386	4.7	24.7
	29	33.367	-	31.5
2000	0	32.967	5.0	19.8
	5	33.002	5.0	17.1
	10	33.028	5.0	16.8
	20	33.132	5.0	22.4
	25	33.214	4.9	22.8
	29	33.362	5.0	22.3
2100	0	32.966	5.1	30.0
	5	32.974	-	22.6
	10	32.966	-	21.0
	20	33.093	-	23.2
	25	33.127	4.9	23.2
	29	33.163	5.0	22.3

TABLE D.3
Current Data (in cm/sec)

Tidal Station 26

TIME	DEPTH (m)	3 m		10 m		20 m		Bot.	
		Azimuth	Speed	Azimuth	Speed	Azimuth	Speed	Azimuth	Speed
0830	28.5	105	024	075	006	215	009	190	002
1910	29.7	025	015	345	008	080	008	305	026
0934	30.3	310	017	265	009	125	012	310	016
1004	30.3	055	010	295	028	290	010	310	018
1033	29.5	205	019	250	034	255	028	295	025
1100	29.6	250	038	230	037	250	040	250	044
1134	30.5	250	049	235	061	230	052	250	036
1205	30.9	265	057	275	042	270	050	280	057
1230	30.9	245	044	250	039	260	041	285	034
1307	33.0	270	017	235	022	245	017	230	016
1333	35.2	240	020	240	024	255	021	215	023
1409	35.5	170	010	265	015	250	007	200	014
1437	34.4	235	009	210	008	250	011	220	010
1504	33.7	265	007	140	012	210	014	020	004
1534	33.6	105	024	145	012	200	007	045	010
1605	33.9	090	015	050	017	105	016	045	015
1633	34.2	050	027	085	028	095	028	050	024
1703	33.7	040	048	065	035	080	034	070	032
1734	33.0	035	062	085	053	090	047	035	036
1807	31.2	040	077	080	064	085	061	060	043
1836	28.4	065	071	085	050	060	053	085	059
1856	28.4	050	053	040	048	015	054	350	007
1933	32.1	100	037	100	046	100	028	085	011
2005	32.9	020	023	045	022	095	004	205	010
2033	33.0	275	017	320	009	170	010	110	007

TABLE D.4

Current Vector Components (see Appendix C) Tidal Station 26								
Time	Longitudinal Flow (cm s^{-1})				Cross-channel Flow (cm s^{-1})			
	(Upstream (250°) = +ve)				(North (340°) = +ve)			
	3 m	10m	20m	Bot	3 m	10m	20m	Bot
0830	-20	-6	7	1	-14	-1	-5	-2
0910	-11	-1	-8	15	11	8	-1	21
0934	9	9	-7	8	15	2	-10	14
1004	-10	20	8	9	3	20	6	16
1033	13	34	28	18	-13	-0	2	18
1100	38	35	40	44	-0	-13	-0	-0
1134	49	59	49	36	-0	-16	-18	-0
1205	55	38	47	49	15	18	17	29
1230	44	39	40	25	-4	-0	7	18
1307	16	21	17	15	6	-6	-1	-5
1333	20	24	21	19	-3	-4	2	-13
1409	2	14	7	9	-10	4	-0	-11
1437	9	6	11	9	-2	-5	-0	-5
1504	7	-4	11	-3	2	-11	-9	3
1534	-20	-3	4	-9	-14	-12	-5	4
1605	-14	-16	-13	-14	-5	6	-9	6
1633	-25	-27	-25	-23	9	-7	-12	8
1703	-42	-35	-33	-32	24	3	-6	-0
1734	-51	-51	-44	-29	36	-14	-16	21
1807	-67	-63	-59	-42	39	-11	-16	7
1836	-71	-48	-52	-57	6	-13	9	-15
1856	-50	-42	-31	-1	18	24	44	7
1933	-32	-40	-24	-11	-19	-23	-14	-3
2005	-15	-20	-4	7	18	9	-2	-7
2033*	15	3	2	-5	7	8	-10	-4
Average	-6.9	-2.4	-0.4	1.5	4.9	-1.8	-1.5	4.6

*Not included in 12-hour cycle.

TABLE D.5

Salinity, Temperature, Total Suspended Load
- Tidal Station 15

TIME	DEPTH (m)	SALINITY (ppt)	TEMPERATURE (°C)	T.S.L. (mg/l)
0902	0	33.412	5.0	2.45
	5	33.423	5.0	2.53
	10	33.460	5.0	2.56
	20	34.225	6.5	3.74
	25	34.274	6.3	3.27
1006	0	33.404	5.0	1.98
	5	33.400	4.9	6.68
	10	33.398	5.2	1.67
	15	33.848	5.5	2.58
	20	34.205	5.5	2.91
	25	34.240	5.6	3.21
1104	0	33.372	4.9	3.38
	5	33.383	5.0	1.93
	10	33.415	4.9	1.67
	15	34.151	5.5	3.72
	20	34.238	5.5	4.23
	26	34.279	5.6	3.03
1205	0	33.377	4.9	1.43
	5	33.386	5.0	1.43
	10	33.407	5.5	1.80
	15	34.167	5.5	1.85
	20	34.303	5.6	2.80
	26	34.337	5.5	4.51
1304	0	33.401	5.0	1.40
	5	33.437	5.0	1.75
	10	33.645	5.1	1.58
	15	34.193	5.5	1.79
	20	34.314	5.6	3.12
	26	34.418	5.5	4.54
1410	0	33.438	5.0	1.77
	5	33.444	5.2	1.70
	10	33.628	5.5	1.58
	15	34.176	5.6	2.00
	20	34.354	5.7	3.56
	28	34.373	5.7	4.27
1500	0	33.467	5.4	1.49
	5	33.491	5.5	1.43
	10	33.940	5.7	1.40
	20	34.37	6.0	4.78
	25	34.392	6.0	4.46
	29	34.390	5.9	3.60

TABLE D.5

(continued)

TIME	DEPTH (m)	SALINITY (ppt)	TEMPERATURE (°C)	T.S.L. (mg/l)
1600	0	33.488	5.2	1.50
	5	33.580	5.7	1.44
	10	-	5.5	1.29
	20	34.372	6.0	2.99
	25	34.386	5.9	3.76
	30	34.390	5.9	3.60
1700	0	33.491	5.1	1.39
	5	33.547	5.1	1.40
	10	33.617	5.2	1.56
	20	34.377	6.0	2.97
	25	34.395	6.0	3.87
	30	34.387	5.9	3.89
1800	0	33.462	5.0	1.40
	5	33.574	5.1	1.17
	10	33.761	5.1	1.35
	20	34.381	5.7	3.01
	25	34.393	5.8	3.88
	30	34.419	5.7	4.03
1900	0	33.484	4.9	1.36
	5	33.511	5.0	1.35
	10	33.563	5.0	1.44
	20	34.369	5.6	2.21
	25	34.376	5.7	2.72
	30	34.375	5.7	3.18
2000	0	33.456	5.0	-
	5	33.464	5.0	1.43
	10	33.647	5.0	1.54
	15	34.041	5.3	1.66
	20	34.297	5.5	2.11
	27+	34.336	5.6	4.91
2100	0	33.431	4.9	1.29
	5	33.435	4.8	1.45
	10	33.446	4.8	1.34
	15	33.846	5.1	1.48
	20	34.302	5.5	3.10
	27	34.286	5.5	3.73

TABLE D.6

Current Data (in cm/sec)

Tidal Station 15

TIME	DEPTH (m)	1 m		3 m		10 m		20 m		Bot.	
		Azimuth	Speed	Azimuth	Speed	Azimuth	Speed	Azimuth	Speed	Azimuth	Speed
0833	29.0	075	041	065	043	060	048	080	036	075	028
0900	28.5	075	035	075	033	055	039	085	029	030	006
0933	28.0	040	023	045	026	045	025	050	011	065	006
1007	27.8	040	018	070	013	080	013	185	003	285	006
1035	27.8	045	011	040	016	040	010	185	013	260	009
1102	27.8	085	011	055	007	090	005	260	009	290	017
1131	28.0	000	013	265	011	260	013	270	017	320	019
1203	28.4	070	017	250	019	265	021	240	028	290	019
1230	29.0	270	020	240	027	280	032	255	043	285	028
1302	30.0	240	031	260	035	235	038	275	048	260	025
1337	30.9	235	037	255	035	245	044	270	045	275	029
1407	31.5	240	031	250	039	215	041	270	030	235	017
1435	32.0	260	032	255	030	240	041	285	026	270	013
1501	32.4	245	022	255	028	260	036	285	017	290	008
1530	32.8	210	018	215	024	250	024	295	020	295	011
1602	33.0	205	015	235	019	260	021	265	016	285	009
1632	33.2	210	016	205	020	240	018	285	011	315	007
1704	33.3	200	024	235	012	260	009	255	004	085	002
1729	33.2	250	014	215	009	270	009	040	006	050	005
1802	33.0	180	010	070	009	065	009	070	014	070	008
1833	32.6	030	011	055	027	065	020	075	025	070	023
1900	32.1	065	031	070	033	070	035	050	036	085	020
1932	31.5	040	036	085	041	075	037	050	045	080	027
1958	30.9	060	043	015	040	035	045	085	050	080	026
2029	30.4	060	044	065	043	055	043	050	048	095	022
2058	29.7	045	036	065	036	070	038	090	038	045	016

TABLE D.7

Current vector components (See Appendix C), tidal station 15.

Time	Longitudinal Flow (cm s^{-1})					Cross-channel Flow (cm s^{-1})				
	(Upstream (250°) = +ve)					(North (340°) = +ve)				
	1 m	3 m	10m	20m	Bot	1 m	3 m	10m	20m	Bot
0833	-41	-43	-47	-35	-28	-4	4	8	-6	-2
0900	-35	-33	-38	-28	-5	-3	-3	10	-8	4
0933	-20	-24	-23	-10	-6	12	11	11	4	1
1007	-16	-13	-13	1	5	9	-0	-2	-3	3
1035	-10	-14	-9	5	9	5	8	5	-12	2
1102	-11	-7	-5	9	13	-3	2	-2	2	11
1131	-4	11	13	16	6	12	3	2	6	18
1203	-17	19	20	28	15	-0	-0	5	-5	12
1230	19	27	28	43	23	7	-5	16	4	16
1302	31	34	37	44	25	-5	6	-10	20	4
1337	36	35	44	42	26	-10	3	-4	15	12
1407	31	39	34	28	16	-5	-0	-24	10	-4
1435	32	30	40	21	12	6	3	-7	15	4
1501	22	28	35	14	6	-2	2	6	10	5
1530	14	20	24	14	8	-12	-14	-0	14	8
1602	11	18	21	15	7	-11	-5	4	4	5
1632	12	14	18	9	3	-10	-14	-3	6	6
1704	15	12	9	4	-2	-18	-3	2	0	-1
1729	14	7	8	-5	-5	-0	-5	3	3	2
1802	3	-9	-9	-14	-8	-9	-0	1	-0	-0
1833	-8	-26	-20	-25	-23	7	7	2	-2	-0
1900	-31	-33	-35	-34	-19	3	-0	-0	12	-5
1932	-31	-40	-37	-42	-27	18	-11	-3	15	-5
1958	-42	-23	-37	-48	-26	7	33	26	13	-5
2029*	-43	-43	-42	-45	-20	8	4	11	16	-9
2058*	-33	-36	-38	-36	-15	15	3	0	-13	7
Average	-1.2	1.2	2.4	2.2	1.0	-0.3	0.9	1.9	3.8	3.8

*Not included in 12-hour cycle.

TABLE D.8

Salinity, Temperature, Total Suspended Load
- Station 7

TIME	DEPTH (m)	SALINITY (ppt)	TEMPERATURE (°C)	T.S.L. (mg/l)
0815	0	33.698	5.8	3.21
	5	33.722	5.8	3.72
	8	33.725	5.9	3.70
0915	0	33.699	5.9	2.50
	5	33.699	6.0	2.55
	7.5	33.739	6.0	2.73
1015	0	33.716	6.0	2.79
	5	33.750	6.0	2.94
	7.5	33.747	6.0	2.73
1115	0	33.801	6.2	2.65
	5	33.730	6.1	2.63
	8.5	33.707	6.2	3.38
1215	0	33.756	6.2	2.57
	5	33.734	6.0	2.94
	9.5	33.826	6.0	3.65
1315	0	33.820	6.8	2.98
	5	33.742	6.5	2.82
	11	33.907	6.5	3.58
1415	0	33.743	6.9	2.76
	5	33.754	6.4	2.86
	11.5	33.903	6.0	3.72
1515	0	33.820	6.8	2.57
	5	33.747	6.5	2.41
	12	33.881	6.1	2.80
1615	0	33.745	6.5	2.76
	5	33.813	6.2	3.12
	10	33.866	6.0	3.16
1715	0	33.764	6.4	4.04
	5	33.778	6.2	3.17
	10	33.908	6.0	3.26
1815	0	33.786	6.2	2.94
	5	33.810	5.0	3.18
	11.5	33.900	5.9	2.93
1915	0	33.777	6.3	2.78
	5	33.826	6.2	2.68
	10.5	33.915	6.0	3.45
2015	0	33.861	6.4	2.66
	5	33.888	6.2	2.89
	11	33.939	6.0	2.84

TABLE D.9

Current Data

Station 7

TIME	DEPTH (m)	1 m		3 m		5+ m		Bot.	
		Azimuth	Speed	Azimuth	Speed	Azimuth	Speed	Azimuth	Speed
0815	10.2	040	023	025	026	045	023	075	013
0845	9.9	030	017	030	019	055	017	045	011
0915	9.6	080	012	065	016	050	010	050	007
0945	9.5	325	012	235	004	295	002	315	002
1015	9.4	325	014	340	021	330	015	270	005
1045	9.4	250	008	240	005	240	007	195	004
1115	9.6	260	017	230	014	240	013	220	012
1145	10.0	270	013	230	015	215	016	250	015
1215	10.6	265	018	230	026	220	020	240	018
1245	11.2	240	016	240	025	235	030	245	019
1315	12.0	280	021	230	031	235	025	250	019
1345	12.4	270	017	260	021	225	028	215	011
1415	12.9	245	028	240	029	220	026	215	011
1445	13.2	270	011	205	013	245	013	215	006
1515	13.5	305	023	075	013	235	011	320	009
1545	13.7	035	006	235	007	195	013	145	009
1615	14.0	315	011	255	016	180	018	170	021
1645	14.0	345	011	090	016	020	003	240	007
1715	14.0	050	008	020	006	145	009	305	002
1745	13.8	060	014	040	008	060	015	220	004
1815	13.4	050	031	035	017	065	019	020	008
1845	13.0	055	031	015	033	090	032	015	019
1915	12.3	050	034	050	036	050	029	075	024
1945	12.2	045	030	040	048	050	033	075	033
2015	12.8	045	026	030	038	050	032	075	021

TABLE D.10

Current vector components (see Appendix C), tidal station 7.

Time	Longitudinal Flow (cm s^{-1})				Cross-channel Flow (cm s^{-1})			
	(Upstream (250°) = +ve)				(North (340°) = +ve)			
	1 m	3 m	5+m	Bot	1 m	3 m	5+m	Bot
0815	-20	-18	-21	-13	12	18	10	-1
0845	-13	-15	-16	-10	11	12	4	5
0915	-12	-16	-9	-7	-2	1	3	2
0945	3	4	1	1	12	-1	1	2
1015	4	0	3	5	14	21	15	2
1045	8	5	7	2	-0	-1	-1	-3
1115	17	13	13	10	3	-5	-2	-6
1145	12	13	14	15	4	-5	-9	-0
1215	17	24	17	18	5	-9	-10	-3
1245	16	25	29	19	-3	-4	-8	-2
1315	18	29	24	19	11	-11	-6	-0
1345	16	21	25	9	6	4	-12	-6
1415	28	29	23	9	-2	-5	-13	-6
1445	10	9	13	5	4	-9	-1	-3
1515	13	-13	11	3	19	-1	-3	8
1545	-5	7	7	-2	3	-2	-11	-9
1615	5	16	6	4	10	1	-17	-21
1645	-1	-15	-2	7	11	-5	2	-1
1715	-8	-4	-2	1	3	5	-9	2
1745	-14	-7	-15	3	2	4	3	-2
1815	-29	-14	-19	-5	11	10	2	6
1845	-30	-19	-30	-11	8	27	-11	16
1915	-32	-34	-27	-24	12	12	10	-2
1945	-27	-42	-31	-33	13	24	11	-3
2015*	-24	-29	-30	-21	11	24	11	-2
Average	-1.0	0.0	0.8	1.0	7.0	3.4	-2.2	-1.0

*Not included in 12-hour cycle.

APPENDIX E

Gravimetric and chemical data for pipette studies of suspended particulate matter and sediment samples.

The sample names for pipette suites at stations 26 and 7 refer to the state of the tide (see Appendix D), the depth (TOP/BOT) and the maximum particle size (ϕ) of the samples. For station 15 and the inner estuary, PCT indicates a bottom water suspended particulate matter sample. In all tables, RSP-SED indicates an artificially resuspended sediment, and BOT-SED refers to a core top sample (see Chapter 4). BDL (below detection limit) indicates that the XRF counts received were exceeded by those of the blank filter.

- i) Original analyses (less blank values) - pipette samples,
station 26 (Table E.1)
- ii) Concentration of particulate elements - pipette samples,
station 26 (Table E.2)
- iii) Ratios to Al - pipette samples, station 26 (Table E.3)
- iv) Original analyses (less blank values) - pipette samples,
station 15 (Table E.4)
- v) Concentration of particulate elements - pipette samples,
station 15 (Table E.5)
- vi) Ratios to Al - pipette samples, station 15 (Table E.6)
- vii) Original analyses (less blank values) - pipette samples,
station 7 (Table E.7)
- viii) Concentration of particulate elements - pipette samples,
station 7 (Table E.8)
- ix) Ratios to Al - pipette samples, station 7 (Table E.9)
- x) Original analyses (less blank values) - pipette samples,
inner estuary (Table E.10)
- xi) Concentration of particulate elements - pipette samples,
inner estuary (Table E.11)
- xii) Ratios to Al - pipette samples, inner estuary (Table E.12)

TABLE E.1

Original analyses (less blank values) -
pipette samples, station 26.

ORIGINAL DATA (SAMPLE SUITE: STN26PPT)
VOLUME IN L. TSL IN MG. ELEMENTAL ABUNDANCES IN MICROGRAMS

VOL	TSL	AL	SI	CA	FE	TI	K	MG	P	S	NAME
0.066	0.549	73.0	130.3	12.98	29.51	4.19	12.63	11.14	1.15	1.22	FLO-TOP-04.0
0.050	0.353	55.8	101.6	8.83	22.23	3.21	9.45	BDL	0.64	0.40	FLO-TOP-04.5
0.050	0.362	56.8	100.9	9.25	22.37	3.19	9.57	6.70	0.68	0.42	FLO-TOP-05.0
0.050	0.370	53.0	93.0	10.93	19.97	2.82	8.94	7.91	0.63	0.64	FLO-TOP-05.5
0.050	0.363	54.7	94.7	10.96	21.71	2.97	9.18	6.85	0.68	0.53	FLO-TOP-06.0
0.050	0.341	49.2	83.7	9.56	18.84	2.51	8.35	6.79	0.59	0.54	FLO-TOP-06.5
0.050	0.321	54.3	93.3	10.70	21.20	2.86	8.79	6.64	0.70	0.91	FLO-TOP-07.0
0.050	0.317	40.8	68.0	8.96	14.52	1.95	7.43	7.75	0.48	1.82	FLO-TOP-07.5
0.050	0.406	84.1	140.2	16.80	30.67	4.19	12.69	11.94	0.97	0.58	FLO-TOP-08.0
0.100	0.361	64.1	104.2	10.76	21.53	2.95	8.98	9.49	0.75	0.22	FLO-TOP-08.5
0.100	0.260	44.6	73.5	8.09	14.50	1.95	6.31	5.66	0.42	BDL	FLO-TOP-09.0
0.100	0.185	26.0	42.3	3.86	8.25	1.36	3.03	3.88	0.46	0.84	FLO-TOP-10.0
0.066	0.698	98.9	182.3	23.75	45.43	6.19	18.27	13.68	1.19	1.84	FLO-BOT-04.0
0.050	0.534	81.5	149.1	18.11	35.55	4.90	14.50	11.59	0.95	1.07	FLO-BOT-04.5
0.050	0.445	77.6	139.1	12.03	32.89	4.39	13.30	BDL	BDL	0.81	FLO-BOT-05.0
0.050	0.564	74.9	135.0	18.08	31.42	4.46	14.26	13.39	0.77	1.90	FLO-BOT-06.0
0.050	0.413	69.9	123.3	14.71	27.84	3.89	11.53	9.49	0.85	0.90	FLO-BOT-06.5
0.050	0.383	71.7	123.1	15.72	28.29	3.81	11.77	10.69	0.77	0.58	FLO-BOT-07.0
0.050	0.333	66.0	110.4	13.54	24.82	3.39	10.22	8.67	0.66	0.37	FLO-BOT-07.5
0.050	0.576	95.5	159.1	20.27	34.74	4.85	14.81	16.47	1.10	0.98	FLO-BOT-08.0
0.100	0.491	86.4	142.0	17.36	31.43	4.24	13.01	12.13	1.06	0.60	FLO-BOT-08.5
0.100	0.250	35.3	54.9	6.65	11.22	1.53	4.85	4.23	0.59	1.53	FLO-BOT-10.0
0.066	0.519	82.4	151.0	20.26	34.75	5.23	14.18	12.54	1.02	1.29	HW-TOP-04.0
0.050	0.369	56.2	100.1	12.61	22.32	3.13	9.58	13.47	0.60	0.55	HW-TOP-04.5
0.050	0.346	55.5	100.0	13.33	23.00	3.20	9.54	6.97	0.56	0.40	HW-TOP-05.0
0.050	0.382	54.6	96.8	13.00	22.58	3.12	9.92	9.55	0.54	0.87	HW-TOP-05.5
0.050	0.330	54.7	96.0	12.46	21.55	2.96	9.14	7.55	0.58	0.53	HW-TOP-06.0
0.050	0.319	52.3	90.9	11.40	19.32	2.77	8.56	7.18	0.47	0.50	HW-TOP-06.5
0.050	0.312	45.5	78.9	10.47	16.87	2.36	7.34	BDL	0.39	0.32	HW-TOP-07.0
0.050	0.265	42.5	71.0	8.72	14.78	2.09	6.52	6.07	0.38	0.12	HW-TOP-07.5
0.100	0.355	61.1	101.9	13.17	21.45	2.91	9.39	9.96	0.64	0.55	HW-TOP-08.0
0.100	0.212	37.8	61.3	7.04	12.95	1.67	5.62	4.34	0.40	BDL	HW-TOP-08.5
0.100	0.275	40.5	65.8	7.71	13.00	1.76	6.03	6.75	0.49	0.34	HW-TOP-09.0
0.100	0.160	25.9	40.3	2.83	8.45	1.11	3.25	2.49	0.43	0.27	HW-TOP-10.0
0.066	1.234	166.9	308.1	44.60	77.58	10.77	30.16	25.88	1.89	2.86	HW-BOT-04.0
0.050	1.037	141.2	260.6	36.44	66.50	9.33	25.87	20.42	1.73	2.58	HW-BOT-04.5
0.050	0.931	137.9	256.4	35.35	62.86	9.01	24.76	22.46	1.50	2.05	HW-BOT-05.0
0.050	0.323	39.9	75.4	9.23	17.98	2.52	7.66	6.49	0.37	0.75	HW-BOT-05.5
0.050	0.949	131.6	238.3	34.36	59.18	8.21	24.34	BDL	1.50	2.72	HW-BOT-06.0
0.050	0.699	123.3	208.3	29.10	50.29	7.03	20.65	21.30	1.34	2.30	HW-BOT-06.5
0.050	0.663	122.5	209.9	29.16	51.04	7.06	19.79	19.74	1.29	1.41	HW-BOT-07.0
0.050	0.599	109.1	183.5	25.87	42.91	5.89	17.48	BDL	1.24	1.49	HW-BOT-07.5
0.100	0.952	54.0	83.3	1.23	18.96	2.43	7.39	7.66	0.27	0.02	HW-BOT-08.0
0.100	0.515	109.0	174.0	21.80	39.13	5.28	15.82	17.75	1.10	1.04	HW-BOT-08.5
0.100	0.453	85.0	135.7	18.01	30.20	4.03	12.62	14.66	0.96	0.77	HW-BOT-09.0
0.100	0.308	52.7	82.6	11.56	17.52	2.41	7.80	8.48	0.62	0.43	HW-BOT-10.0
0.066	0.526	91.5	162.8	18.91	38.72	5.28	15.48	BDL	1.30	1.44	EBB-TOP-04.0
0.050	0.416	64.6	115.2	12.63	26.64	3.58	11.10	8.27	0.76	0.48	EBB-TOP-04.5
0.050	0.509	68.5	122.4	15.50	27.48	3.83	12.83	12.36	0.88	2.30	EBB-TOP-05.0
0.050	0.535	65.6	116.0	13.65	26.64	3.62	12.29	11.46	0.81	1.62	EBB-TOP-05.5
0.050	0.500	65.1	115.7	14.23	25.52	3.47	11.56	10.59	0.80	1.44	EBB-TOP-06.0
0.050	0.470	65.1	115.4	14.29	26.26	3.59	12.17	12.26	0.83	1.77	EBB-TOP-06.5
0.050	0.269	49.6	79.4	8.66	16.59	2.28	7.00	BDL	0.63	0.09	EBB-TOP-07.5
0.100	0.430	88.8	144.1	16.04	31.33	4.24	12.62	BDL	1.26	0.67	EBB-TOP-08.0
0.100	0.356	70.7	112.5	11.16	24.07	3.25	9.90	10.65	1.00	0.47	EBB-TOP-08.5
0.100	0.333	57.9	90.8	8.79	20.06	2.50	8.09	12.15	0.91	0.43	EBB-TOP-09.0
0.100	0.254	39.1	60.6	4.21	13.34	1.63	5.70	5.32	0.59	BDL	EBB-TOP-10.0
0.066	1.361	195.3	354.3	46.73	93.60	12.75	35.61	24.12	2.43	3.33	EBB-BOT-04.0
0.050	1.016	151.9	280.4	34.75	70.75	9.88	26.80	20.86	1.73	2.05	EBB-BOT-04.5
0.050	0.999	146.3	266.0	33.48	68.44	9.41	26.63	20.67	1.70	1.90	EBB-BOT-05.0
0.050	1.062	144.6	264.9	34.15	67.38	9.35	27.12	20.57	1.61	2.91	EBB-BOT-05.5
0.050	0.906	144.4	253.8	32.08	63.53	8.69	25.24	20.38	1.62	2.16	EBB-BOT-06.0
0.050	0.627	127.6	212.3	25.48	50.44	6.94	19.83	17.97	1.46	1.07	EBB-BOT-06.5
0.050	0.488	91.4	147.2	17.60	33.25	4.65	13.62	13.76	1.01	0.64	EBB-BOT-07.0
0.100	0.854	171.5	273.7	31.12	63.65	8.94	24.64	24.10	1.84	1.65	EBB-BOT-08.0
0.100	0.561	113.6	177.4	20.37	39.53	5.48	15.70	15.56	1.30	0.64	EBB-BOT-08.5
0.100	0.312	52.4	80.8	8.06	17.62	2.29	7.71	8.45	0.69	0.27	EBB-BOT-10.0

TABLE E.1

(continued)

ORIGINAL DATA (SAMPLE SUITE: STN26PPT)
VOLUME IN L. TSL IN MG. ELEMENTAL ABUNDANCES IN MICROGRAMS

VOL	TSL	AL	SI	CA	FE	TI	K	MG	P	S	NAME
0.066	1.614	208.7	403.9	48.54	105.92	14.03	40.60	32.08	2.96	3.47	LV-TOP-04.0
0.050	1.134	168.5	324.1	38.03	82.35	11.07	32.22	24.52	2.18	2.48	LV-TOP-04.5
0.050	1.143	158.7	304.0	34.90	76.85	10.22	29.80	21.93	1.97	2.36	LV-TOP-05.0
0.050	1.141	158.6	299.3	34.72	75.44	9.99	30.11	23.24	1.89	2.51	LV-TOP-05.5
0.050	0.994	156.7	285.0	32.89	69.64	9.35	27.67	25.17	1.99	2.02	LV-TOP-06.0
0.050	0.870	136.6	233.2	27.21	57.70	7.70	24.05	22.56	1.79	3.21	LV-TOP-06.5
0.050	0.643	126.1	206.5	23.99	49.82	6.64	19.74	20.30	1.44	1.43	LV-TOP-07.0
0.050	0.513	81.6	130.8	16.20	29.92	4.11	12.10	10.06	0.85	0.73	LV-TOP-07.5
0.100	0.856	166.1	270.2	29.21	64.05	8.43	24.53	23.48	2.01	1.95	LV-TOP-08.0
0.100	0.612	120.2	194.4	20.52	44.50	5.82	17.31	17.48	1.53	1.13	LV-TOP-08.5
0.100	0.562	106.4	169.9	16.99	39.12	4.99	15.26	17.34	1.41	0.79	LV-TOP-09.0
0.100	0.300	53.9	83.8	7.28	18.58	2.30	8.00	7.40	0.67	0.51	LV-TOP-10.0
0.066	1.206	153.6	292.1	37.08	73.47	9.99	29.58	22.83	2.05	2.99	LV-BOT-04.0
0.050	0.863	129.4	242.9	30.13	60.82	8.17	24.22	19.51	1.67	1.85	LV-BOT-04.5
0.050	0.856	120.0	227.3	26.51	54.87	7.57	22.01	17.43	1.52	1.45	LV-BOT-05.0
0.050	0.884	118.7	221.1	25.41	52.87	7.39	21.46	17.84	1.48	1.44	LV-BOT-05.5
0.050	0.708	112.6	201.6	24.19	49.08	6.76	19.88	16.83	1.26	1.69	LV-BOT-06.0
0.050	0.615	116.9	196.9	23.26	46.57	6.34	18.81	14.84	1.34	1.30	LV-BOT-06.5
0.050	0.552	93.5	155.8	18.25	36.23	4.82	14.69	16.55	1.19	1.01	LV-BOT-07.0
0.050	0.476	83.0	134.4	15.14	30.53	4.15	12.57	21.64	1.01	0.56	LV-BOT-07.5
0.050	0.681	136.2	214.9	24.97	50.06	6.67	19.89	19.49	1.82	1.21	LV-BOT-08.0
0.100	0.635	101.3	159.0	17.21	35.76	4.75	14.94	17.09	1.25	1.45	LV-BOT-08.5
0.100	0.593	94.8	149.6	16.17	33.47	4.42	13.45	13.94	1.22	0.84	LV-BOT-09.0
0.100	0.303	55.0	84.3	7.73	18.81	2.40	7.81	7.42	0.70	0.20	LV-BOT-10.0
0.066	1.407	176.9	363.9	31.98	90.93	12.91	34.35	23.04	1.78	2.64	RSP-SED-04.0
0.025	0.493	66.8	131.9	9.64	31.49	4.39	12.97	12.34	0.54	0.67	RSP-SED-04.5
0.025	0.401	58.7	110.0	7.35	25.84	3.64	10.67	6.87	0.45	0.46	RSP-SED-05.0
0.025	0.509	59.6	113.9	6.58	26.21	3.68	10.62	BDL	0.44	0.28	RSP-SED-05.5
0.025	0.372	56.2	102.8	4.82	23.67	3.26	9.43	7.05	0.42	0.20	RSP-SED-06.0
0.025	0.322	50.7	89.9	3.00	19.51	2.86	8.15	6.53	0.29	0.14	RSP-SED-06.5
0.025	0.263	46.1	79.4	2.08	18.34	2.53	7.60	6.70	0.27	0.15	RSP-SED-07.0
0.050	0.464	79.8	130.6	2.09	29.29	4.35	11.49	11.41	0.58	0.59	RSP-SED-07.5
0.050	0.336	67.5	105.3	1.55	24.88	3.35	9.79	8.66	0.46	0.22	RSP-SED-08.0
0.050	0.280	54.4	84.2	0.71	18.66	2.57	7.42	6.98	0.31	BDL	RSP-SED-08.5
0.050	0.261	51.3	78.8	0.97	18.37	2.49	7.31	8.66	0.35	BDL	RSP-SED-09.0
0.050	0.174	34.7	52.8	0.62	12.28	1.59	4.96	7.66	0.19	BDL	RSP-SED-10.0
0.066	6.150	504.9	1134.7	121.18	354.94	46.13	118.95	71.36	5.54	10.57	BOT-SED-04.0
0.025	2.084	245.5	537.3	41.72	137.61	18.86	52.25	33.58	2.34	4.15	BOT-SED-04.5
0.025	1.735	216.3	438.9	30.56	110.13	15.16	42.17	34.88	1.87	3.41	BOT-SED-05.0
0.025	1.817	230.5	464.0	29.43	116.99	16.17	44.32	36.89	1.93	3.72	BOT-SED-05.5
0.025	1.326	216.1	401.7	19.94	97.20	13.56	36.72	28.19	1.72	3.36	BOT-SED-06.0
0.025	1.187	201.4	367.5	14.42	89.47	12.53	34.36	28.08	1.59	2.84	BOT-SED-06.5
0.025	0.821	168.4	284.3	7.51	62.49	9.37	26.05	22.72	1.27	1.99	BOT-SED-07.0
0.025	0.638	138.1	229.0	4.58	53.17	7.32	20.44	17.52	1.02	1.38	BOT-SED-07.5
0.025	0.526	108.0	177.1	3.08	41.03	5.60	15.88	17.57	0.77	0.63	BOT-SED-08.0
0.025	0.453	87.1	139.6	2.12	30.42	4.17	12.20	11.50	0.54	0.69	BOT-SED-08.5
0.025	0.363	72.8	118.0	1.73	25.56	3.51	10.23	10.26	0.44	0.15	BOT-SED-09.0

(BDL = BELOW DETECTION LIMIT; N.A. = NOT ANALYSED)

TABLE E.2

Concentration of particulate elements -
pipette samples, station 26.

RATIOS TO VOLUME (SAMPLE SUITE: STN26PPT)
TSL IN MG/L, ELEMENTS IN MICROGRAMS/L

TSL/VOL	AL/VOL	SI/VOL	CA/VOL	FE/VOL	TI/VOL	K/VOL	MG/VOL	P/VOL	S/VOL	NAME
8.32	1107.	1973.	196.7	447.1	63.5	191.4	168.8	17.4	18.5	FLO-TOP-04.0
7.06	1116.	2032.	176.6	444.6	64.2	189.0	BDL	12.8	8.0	FLO-TOP-04.5
7.24	1137.	2017.	185.0	447.4	63.8	191.4	134.0	13.6	8.4	FLO-TOP-05.0
7.40	1061.	1859.	218.6	399.4	56.4	178.8	154.2	12.6	12.8	FLO-TOP-05.5
7.26	1094.	1894.	219.2	434.2	59.4	183.6	137.0	13.6	10.6	FLO-TOP-06.0
6.82	985.	1674.	191.2	376.8	50.2	167.0	135.8	11.8	10.8	FLO-TOP-06.5
6.42	1086.	1867.	214.0	424.0	57.2	175.8	132.8	14.0	18.2	FLO-TOP-07.0
6.34	816.	1360.	179.2	290.4	39.0	148.6	155.0	9.6	36.4	FLO-TOP-07.5
8.12	1681.	2803.	336.0	613.4	83.8	253.8	238.8	19.4	11.6	FLO-TOP-08.0
3.61	641.	1042.	107.6	215.3	29.5	89.8	94.9	7.5	2.2	FLO-TOP-08.5
2.60	446.	735.	80.9	145.0	19.5	63.1	56.6	4.2	BDL	FLO-TOP-09.0
1.85	260.	424.	38.6	82.5	13.6	30.3	38.8	4.6	8.4	FLO-TOP-10.0
10.58	1499.	2763.	359.8	688.3	93.8	276.8	207.3	18.0	27.9	FLO-BOT-04.0
10.68	1631.	2982.	362.2	711.0	98.0	290.0	231.8	19.0	21.4	FLO-BOT-04.5
8.90	1552.	2783.	240.6	657.8	87.8	266.0	BDL	BDL	16.2	FLO-BOT-05.0
11.28	1499.	2700.	361.6	629.6	89.2	285.2	267.8	15.4	38.0	FLO-BOT-06.0
8.26	1399.	2465.	294.2	556.8	77.8	230.6	189.4	17.0	18.0	FLO-BOT-06.5
7.66	1434.	2461.	314.4	565.8	76.2	235.4	213.8	15.4	11.6	FLO-BOT-07.0
6.66	1320.	2208.	270.8	496.4	67.8	204.4	173.4	13.2	7.4	FLO-BOT-07.5
11.52	1910.	3182.	465.4	694.8	97.0	296.2	329.4	22.0	19.6	FLO-BOT-08.0
4.91	864.	1420.	173.6	314.3	42.4	130.1	121.3	10.6	6.0	FLO-BOT-08.5
2.50	353.	550.	66.5	112.2	15.3	48.5	42.3	5.9	15.3	FLO-BOT-10.0
7.86	1249.	2287.	307.0	526.5	79.2	214.8	190.0	15.5	19.5	HW-TOP-04.0
7.38	1124.	2002.	252.2	446.4	62.6	191.6	269.4	12.0	11.0	HW-TOP-04.5
6.92	1111.	1999.	266.6	460.0	64.0	190.8	139.4	11.2	8.0	HW-TOP-05.0
7.64	1092.	1936.	260.0	451.6	62.4	198.4	191.0	10.8	17.4	HW-TOP-05.5
6.60	1095.	1919.	249.2	431.0	59.2	182.8	151.0	11.6	10.6	HW-TOP-06.0
6.38	1046.	1817.	228.0	386.4	55.4	171.2	143.6	9.4	10.0	HW-TOP-06.5
6.24	911.	1578.	209.4	337.4	47.2	146.8	BDL	7.8	6.4	HW-TOP-07.0
5.30	849.	1420.	174.4	295.6	41.8	130.4	121.4	7.6	2.4	HW-TOP-07.5
3.55	612.	1019.	131.7	214.5	29.1	93.9	99.6	6.4	5.5	HW-TOP-08.0
2.12	378.	613.	70.4	129.5	16.7	56.2	43.4	4.0	BDL	HW-TOP-08.5
2.75	405.	658.	77.1	130.0	17.6	60.3	67.5	4.9	3.4	HW-TOP-09.0
1.60	259.	403.	28.3	84.5	11.1	32.5	24.9	4.3	8.7	HW-TOP-10.0
18.70	2529.	4669.	675.8	1175.5	163.2	457.0	392.1	28.6	43.3	HW-BOT-04.0
20.74	2823.	5213.	728.8	1330.0	186.6	517.4	408.4	34.6	51.6	HW-BOT-04.5
18.62	2758.	5127.	707.0	1257.2	180.2	495.2	449.2	30.0	41.0	HW-BOT-05.0
6.46	798.	1509.	184.6	359.6	50.4	153.2	129.8	7.4	15.0	HW-BOT-05.5
18.98	2632.	4766.	687.2	1183.6	164.2	486.8	BDL	30.0	54.4	HW-BOT-06.0
13.98	2466.	4166.	582.0	1005.8	140.6	413.0	426.0	26.8	46.0	HW-BOT-06.5
13.26	2450.	4198.	583.2	1020.8	141.2	395.8	394.8	25.8	28.2	HW-BOT-07.0
11.98	2182.	3670.	517.4	858.2	117.8	349.6	BDL	24.8	29.8	HW-BOT-07.5
9.52	540.	833.	12.3	189.6	24.3	73.9	76.6	2.7	0.2	HW-BOT-08.0
9.15	1090.	1740.	218.0	391.3	52.8	158.2	177.5	11.0	10.4	HW-BOT-08.5
4.53	850.	1357.	180.1	302.0	40.3	126.2	146.5	9.6	7.7	HW-BOT-09.0
3.08	527.	826.	105.6	175.2	24.1	78.0	84.8	6.2	4.3	HW-BOT-10.0
7.97	1387.	2466.	286.5	586.7	80.0	234.5	BDL	19.7	21.8	EBB-TOP-04.0
8.32	1292.	2303.	252.6	532.8	71.6	222.0	165.4	15.2	9.6	EBB-TOP-04.5
10.18	1369.	2448.	310.0	549.6	76.6	256.6	247.2	17.6	46.0	EBB-TOP-05.0
10.70	1312.	2320.	273.0	532.8	72.4	245.8	229.2	16.2	32.4	EBB-TOP-05.5
10.00	1302.	2314.	284.5	510.4	69.4	231.2	211.8	16.0	28.8	EBB-TOP-06.0
9.40	1321.	2308.	285.8	525.2	71.8	243.4	245.2	16.6	35.4	EBB-TOP-06.5
5.38	993.	1587.	173.2	331.8	45.6	140.0	BDL	12.6	1.8	EBB-TOP-07.5
4.30	888.	1441.	160.4	313.3	42.4	126.2	BDL	12.6	6.7	EBB-TOP-08.0
3.56	707.	1125.	111.6	240.7	32.5	99.0	106.5	10.0	4.7	EBB-TOP-08.5
3.33	579.	908.	87.9	200.0	25.0	80.9	121.5	9.1	4.3	EBB-TOP-09.0
2.54	391.	606.	42.1	133.4	16.3	57.0	53.2	5.9	BDL	EBB-TOP-10.0
20.62	2959.	5368.	708.0	1418.2	193.2	539.5	365.5	36.8	50.5	EBB-BOT-04.0
20.32	3039.	5608.	695.0	1415.0	197.6	536.0	417.2	34.6	41.0	EBB-BOT-04.5
19.98	2926.	5319.	669.6	1368.8	188.2	532.6	413.4	34.0	38.0	EBB-BOT-05.0
21.24	2891.	5298.	683.0	1347.6	187.0	542.4	411.4	32.2	58.2	EBB-BOT-05.5
18.12	2887.	5077.	641.6	1270.6	173.8	504.8	407.6	32.4	43.2	EBB-BOT-06.0
12.54	2553.	4247.	509.6	1008.8	138.8	396.6	359.4	29.2	21.4	EBB-BOT-06.5
9.76	1828.	2944.	352.0	665.0	93.0	272.4	275.2	20.2	12.8	EBB-BOT-07.0
8.54	1715.	2737.	311.2	636.5	89.4	246.4	241.0	18.4	16.5	EBB-BOT-08.0
5.61	1136.	1774.	203.7	395.3	54.8	157.0	155.6	13.0	6.4	EBB-BOT-08.5
3.12	524.	809.	80.6	176.2	22.9	77.1	84.5	6.9	2.7	EBB-BOT-10.0

TABLE E.2
(continued)

RATIOS TO VOLUME (SAMPLE SUITE: STN26PPT)
TSL IN MG/L, ELEMENTS IN MICROGRAMS/L

TSL/VOL	AL/VOL	SI/VOL	CA/VOL	FE/VOL	TI/VOL	K/VOL	MG/VOL	P/VOL	S/VOL	NAME
24.45	3162.	6120.	735.5	1604.8	212.6	615.2	486.1	44.8	52.6	LW-TOP-04.0
22.68	3369.	6481.	760.6	1647.0	221.4	644.4	490.4	43.6	49.6	LW-TOP-04.5
22.86	3174.	6080.	698.0	1537.6	204.4	596.0	438.6	39.4	47.2	LW-TOP-05.0
22.82	3173.	5985.	694.4	1508.8	199.8	602.2	464.8	37.8	50.2	LW-TOP-05.5
19.88	3135.	5701.	657.8	1392.8	187.0	553.4	503.4	39.8	40.4	LW-TOP-06.0
17.40	2732.	4665.	544.2	1154.0	154.0	481.0	451.6	35.8	64.2	LW-TOP-06.5
12.86	2523.	4130.	479.8	996.4	132.8	394.8	406.0	28.8	28.6	LW-TOP-07.0
10.26	1632.	2615.	324.0	598.4	82.2	242.0	201.2	17.0	14.6	LW-TOP-07.5
8.56	1661.	2702.	292.1	640.5	84.3	245.3	234.8	20.1	19.5	LW-TOP-08.0
6.12	1202.	1944.	205.2	445.0	58.2	173.1	174.8	15.3	11.3	LW-TOP-08.5
5.62	1065.	1699.	169.9	391.2	49.9	152.6	173.4	14.1	7.9	LW-TOP-09.0
3.00	539.	838.	72.8	185.8	23.0	80.0	74.0	6.7	5.1	LW-TOP-10.0
18.27	2328.	4426.	561.8	1113.2	151.4	448.2	345.9	31.1	45.3	LW-BOT-04.0
17.26	2588.	4857.	602.6	1216.4	163.4	484.4	390.2	33.4	37.0	LW-BOT-04.5
17.12	2401.	4547.	530.2	1097.4	151.4	440.2	348.6	30.4	29.0	LW-BOT-05.0
17.68	2374.	4423.	508.2	1057.4	147.8	429.2	356.8	29.6	28.8	LW-BOT-05.5
14.16	2251.	4032.	483.8	981.6	135.2	397.6	336.6	25.2	33.8	LW-BOT-06.0
12.30	2337.	3938.	465.2	931.4	126.8	376.2	296.8	26.8	26.0	LW-BOT-06.5
11.04	1869.	3116.	365.0	724.6	96.4	293.8	331.0	23.8	20.2	LW-BOT-07.0
9.52	1661.	2688.	303.6	610.6	83.0	251.4	232.8	20.2	11.2	LW-BOT-07.5
13.62	2724.	4299.	499.4	1001.2	133.4	397.8	389.8	36.4	24.2	LW-BOT-08.0
6.35	1013.	1590.	172.1	357.6	47.5	149.4	170.9	12.5	14.5	LW-BOT-08.5
5.93	948.	1496.	161.7	334.7	44.2	134.5	139.4	12.2	8.4	LW-BOT-09.0
3.03	550.	843.	77.3	188.1	24.0	78.1	74.2	7.0	2.0	LW-BOT-10.0
21.32	2680.	5514.	484.5	1377.7	195.6	520.5	349.1	27.0	40.0	RSP-SED-04.0
19.72	2673.	5275.	385.6	1259.6	175.6	518.8	493.6	21.6	26.8	RSP-SED-04.5
16.04	2348.	4400.	294.0	1033.6	145.6	426.8	274.8	18.0	18.4	RSP-SED-05.0
20.36	2386.	4557.	263.2	1048.4	147.2	424.8	RDL	17.6	11.2	RSP-SED-05.5
14.88	2247.	4112.	192.8	946.8	130.4	377.2	283.6	16.8	8.0	RSP-SED-06.0
12.88	2028.	3595.	120.0	780.4	114.4	326.0	261.2	11.6	5.6	RSP-SED-06.5
10.52	1844.	3175.	83.2	733.6	101.2	304.0	268.0	10.8	6.0	RSP-SED-07.0
9.28	1596.	2611.	41.8	585.6	87.0	229.8	228.2	11.6	11.8	RSP-SED-07.5
6.72	1349.	2105.	31.0	497.6	67.0	195.8	173.2	9.2	4.4	RSP-SED-08.0
5.60	1088.	1685.	14.2	373.2	51.4	148.4	139.6	6.2	RDL	RSP-SED-08.5
5.22	1026.	1576.	19.4	367.4	49.8	146.2	173.6	7.0	RDL	RSP-SED-09.0
3.48	694.	1056.	12.4	245.6	31.8	99.2	153.2	3.8	RDL	RSP-SED-10.0
93.18	7650.	17193.	1836.1	5377.9	698.9	1802.3	1081.2	83.9	160.2	BOT-SED-04.0
83.36	9819.	21491.	1668.8	5504.4	754.4	2090.0	1343.2	93.6	166.0	BOT-SED-04.5
69.40	8652.	17556.	1222.4	4405.2	606.4	1686.8	1395.2	74.8	136.4	BOT-SED-05.0
72.68	9221.	18562.	1177.2	4679.6	646.8	1772.8	1235.6	77.2	148.8	BOT-SED-05.5
53.04	8644.	16067.	797.6	3888.0	542.4	1468.8	1127.6	66.8	122.4	BOT-SED-06.0
47.48	8055.	14700.	576.8	3578.8	501.2	1374.4	1123.2	63.6	113.6	BOT-SED-06.5
32.84	6734.	11371.	300.4	2739.6	374.8	1042.0	908.8	50.8	79.6	BOT-SED-07.0
25.52	5526.	9160.	183.2	2126.8	292.8	817.6	700.8	40.8	55.2	BOT-SED-07.5
21.04	4320.	7086.	123.2	1641.2	224.0	635.2	702.8	30.8	25.2	BOT-SED-08.0
18.12	3485.	5584.	84.8	1216.8	166.8	488.0	460.0	21.6	27.6	BOT-SED-08.5
14.52	2912.	4719.	69.2	1022.4	140.4	409.2	410.4	17.6	6.0	BOT-SED-09.0

(RDL = BELOW DETECTION LIMIT; N.A. = NOT ANALYSED)

TABLE E.3

Ratios to Al -

pipette samples, station 26.

RATIOS TO AL (SAMPLE SUITE: STN26PPT)

SI/AL	CA/AL	FE/AL	TI/AL	K/AL	MG/AL	P/AL	S/AL	NAME
1.78	0.178	0.404	0.057	0.173	0.153	0.016	0.017	FLD-TOP-04.0
1.82	0.158	0.398	0.058	0.169		0.011	0.007	FLD-TOP-04.5
1.77	0.163	0.394	0.056	0.168	0.118	0.012	0.007	FLD-TOP-05.0
1.75	0.206	0.377	0.053	0.169	0.149	0.012	0.012	FLD-TOP-05.5
1.73	0.200	0.397	0.054	0.168	0.125	0.012	0.010	FLD-TOP-06.0
1.70	0.194	0.383	0.051	0.170	0.138	0.012	0.011	FLD-TOP-06.5
1.72	0.197	0.390	0.053	0.162	0.122	0.013	0.017	FLD-TOP-07.0
1.67	0.220	0.356	0.048	0.182	0.190	0.012	0.045	FLD-TOP-07.5
1.67	0.200	0.365	0.050	0.151	0.142	0.012	0.007	FLD-TOP-08.0
1.63	0.168	0.336	0.046	0.140	0.146	0.012	0.003	FLD-TOP-08.5
1.65	0.181	0.325	0.044	0.141	0.127	0.009		FLD-TOP-09.0
1.63	0.148	0.317	0.052	0.116	0.149	0.018	0.032	FLD-TOP-10.0
1.84	0.240	0.459	0.063	0.185	0.138	0.012	0.019	FLD-BOT-04.0
1.83	0.222	0.436	0.060	0.178	0.142	0.012	0.013	FLD-BOT-04.5
1.79	0.155	0.424	0.057	0.171			0.010	FLD-BOT-05.0
1.80	0.241	0.420	0.060	0.190	0.179	0.010	0.025	FLD-BOT-06.0
1.76	0.210	0.398	0.056	0.165	0.136	0.012	0.013	FLD-BOT-06.5
1.72	0.219	0.395	0.053	0.164	0.149	0.011	0.008	FLD-BOT-07.0
1.67	0.205	0.376	0.051	0.155	0.131	0.010	0.006	FLD-BOT-07.5
1.67	0.212	0.364	0.051	0.155	0.172	0.012	0.010	FLD-BOT-08.0
1.64	0.201	0.364	0.049	0.151	0.140	0.012	0.007	FLD-BOT-08.5
1.56	0.188	0.318	0.043	0.137	0.120	0.017	0.043	FLD-BOT-10.0
1.83	0.246	0.421	0.063	0.172	0.152	0.012	0.016	HW-TOP-04.0
1.78	0.224	0.397	0.056	0.170	0.240	0.011	0.010	HW-TOP-04.5
1.80	0.240	0.414	0.058	0.172	0.125	0.010	0.007	HW-TOP-05.0
1.77	0.238	0.413	0.057	0.182	0.175	0.010	0.016	HW-TOP-05.5
1.75	0.228	0.394	0.054	0.167	0.138	0.011	0.010	HW-TOP-06.0
1.74	0.218	0.370	0.053	0.164	0.137	0.009	0.010	HW-TOP-06.5
1.73	0.230	0.370	0.052	0.161		0.009	0.007	HW-TOP-07.0
1.67	0.205	0.348	0.049	0.154	0.143	0.009	0.003	HW-TOP-07.5
1.67	0.215	0.351	0.048	0.154	0.163	0.010	0.009	HW-TOP-08.0
1.62	0.186	0.342	0.044	0.149	0.115	0.011		HW-TOP-08.5
1.62	0.190	0.321	0.043	0.149	0.167	0.012	0.008	HW-TOP-09.0
1.56	0.109	0.327	0.043	0.126	0.096	0.017	0.034	HW-TOP-10.0
1.85	0.267	0.465	0.065	0.181	0.155	0.011	0.017	HW-BOT-04.0
1.85	0.258	0.471	0.066	0.183	0.145	0.012	0.018	HW-BOT-04.5
1.86	0.256	0.456	0.065	0.180	0.163	0.011	0.015	HW-BOT-05.0
1.89	0.231	0.451	0.063	0.192	0.163	0.009	0.019	HW-BOT-05.5
1.81	0.261	0.450	0.062	0.185		0.011	0.021	HW-BOT-06.0
1.69	0.236	0.408	0.057	0.167	0.173	0.011	0.019	HW-BOT-06.5
1.71	0.238	0.417	0.058	0.162	0.161	0.011	0.012	HW-BOT-07.0
1.68	0.237	0.393	0.054	0.160		0.011	0.014	HW-BOT-07.5
1.54	0.023	0.351	0.045	0.137	0.142	0.005	0.000	HW-BOT-08.0
1.60	0.200	0.359	0.048	0.145	0.163	0.010	0.010	HW-BOT-08.5
1.60	0.212	0.355	0.047	0.148	0.172	0.011	0.009	HW-BOT-09.0
1.57	0.200	0.332	0.046	0.148	0.161	0.012	0.008	HW-BOT-10.0
1.78	0.207	0.423	0.056	0.169		0.014	0.016	EBB-TOP-04.0
1.78	0.195	0.412	0.055	0.172	0.128	0.012	0.007	EBB-TOP-04.5
1.79	0.226	0.401	0.056	0.187	0.181	0.013	0.034	EBB-TOP-05.0
1.77	0.208	0.406	0.055	0.187	0.175	0.012	0.025	EBB-TOP-05.5
1.78	0.219	0.392	0.053	0.178	0.163	0.012	0.022	EBB-TOP-06.0
1.75	0.216	0.397	0.054	0.184	0.186	0.013	0.027	EBB-TOP-06.5
1.60	0.174	0.334	0.046	0.141		0.013	0.002	EBB-TOP-07.5
1.62	0.181	0.353	0.048	0.142		0.014	0.008	EBB-TOP-08.0
1.59	0.158	0.341	0.046	0.140	0.151	0.014	0.007	EBB-TOP-08.5
1.57	0.152	0.346	0.043	0.140	0.210	0.016	0.007	EBB-TOP-09.0
1.55	0.108	0.341	0.042	0.146	0.136	0.015		EBB-TOP-10.0
1.81	0.239	0.479	0.065	0.182	0.124	0.012	0.017	EBB-BOT-04.0
1.85	0.229	0.466	0.065	0.176	0.137	0.011	0.013	EBB-BOT-04.5
1.82	0.229	0.468	0.064	0.182	0.141	0.012	0.013	EBB-BOT-05.0
1.83	0.236	0.466	0.065	0.188	0.142	0.011	0.020	EBB-BOT-05.5
1.76	0.222	0.440	0.060	0.175	0.141	0.011	0.015	EBB-BOT-06.0
1.66	0.200	0.395	0.054	0.155	0.141	0.011	0.008	EBB-BOT-06.5
1.61	0.193	0.364	0.051	0.149	0.151	0.011	0.007	EBB-BOT-07.0
1.60	0.182	0.371	0.052	0.144	0.141	0.011	0.010	EBB-BOT-08.0
1.56	0.179	0.348	0.048	0.138	0.137	0.011	0.006	EBB-BOT-08.5
1.54	0.154	0.336	0.044	0.147	0.161	0.013	0.005	EBB-BOT-10.0

TABLE E.3

(continued)

RATIOS TO AL (SAMPLE SUITE: STN26PPT)

SI/AL	CA/AL	FE/AL	TI/AL	K/AL	MG/AL	P/AL	S/AL	NAME
1.94	0.233	0.508	0.067	0.195	0.154	0.014	0.017	LW-TOP-04.0
1.92	0.226	0.489	0.066	0.191	0.146	0.013	0.015	LW-TOP-04.5
1.92	0.220	0.484	0.064	0.188	0.138	0.012	0.015	LW-TOP-05.0
1.89	0.219	0.476	0.063	0.190	0.146	0.012	0.016	LW-TOP-05.5
1.82	0.210	0.444	0.060	0.177	0.161	0.013	0.013	LW-TOP-06.0
1.71	0.199	0.422	0.056	0.176	0.165	0.013	0.023	LW-TOP-06.5
1.64	0.190	0.395	0.053	0.156	0.161	0.011	0.011	LW-TOP-07.0
1.60	0.198	0.367	0.050	0.148	0.123	0.010	0.009	LW-TOP-07.5
1.63	0.176	0.386	0.051	0.148	0.141	0.012	0.012	LW-TOP-08.0
1.62	0.171	0.370	0.048	0.144	0.145	0.013	0.009	LW-TOP-08.5
1.60	0.160	0.367	0.047	0.143	0.163	0.013	0.007	LW-TOP-09.0
1.56	0.135	0.345	0.043	0.148	0.137	0.012	0.009	LW-TOP-10.0
1.90	0.241	0.478	0.065	0.193	0.149	0.013	0.019	LW-BOT-04.0
1.88	0.233	0.470	0.063	0.187	0.151	0.013	0.014	LW-BOT-04.5
1.89	0.221	0.457	0.063	0.183	0.145	0.013	0.012	LW-BOT-05.0
1.86	0.214	0.445	0.062	0.181	0.150	0.012	0.012	LW-BOT-05.5
1.79	0.215	0.436	0.060	0.177	0.150	0.011	0.015	LW-BOT-06.0
1.68	0.199	0.398	0.054	0.161	0.127	0.011	0.011	LW-BOT-06.5
1.67	0.195	0.388	0.052	0.157	0.177	0.013	0.011	LW-BOT-07.0
1.62	0.183	0.368	0.050	0.151	0.140	0.012	0.007	LW-BOT-07.5
1.58	0.183	0.368	0.049	0.146	0.143	0.013	0.009	LW-BOT-08.0
1.57	0.170	0.353	0.047	0.147	0.165	0.012	0.014	LW-BOT-08.5
1.58	0.170	0.353	0.047	0.142	0.147	0.013	0.009	LW-BOT-09.0
1.53	0.140	0.342	0.044	0.142	0.135	0.013	0.004	LW-BOT-10.0
2.06	0.181	0.514	0.073	0.194	0.130	0.010	0.015	RSP-SED-04.0
1.97	0.144	0.471	0.066	0.194	0.185	0.008	0.010	RSP-SED-04.5
1.87	0.125	0.440	0.062	0.182	0.117	0.008	0.008	RSP-SED-05.0
1.91	0.110	0.439	0.062	0.178		0.007	0.005	RSP-SED-05.5
1.83	0.086	0.421	0.058	0.168	0.126	0.007	0.004	RSP-SED-06.0
1.77	0.059	0.385	0.056	0.161	0.129	0.006	0.003	RSP-SED-06.5
1.72	0.045	0.398	0.055	0.165	0.145	0.006	0.003	RSP-SED-07.0
1.64	0.026	0.367	0.055	0.144	0.143	0.007	0.007	RSP-SED-07.5
1.56	0.023	0.369	0.050	0.145	0.126	0.007	0.003	RSP-SED-08.0
1.55	0.013	0.343	0.047	0.136	0.128	0.006		RSP-SED-08.5
1.54	0.019	0.358	0.049	0.143	0.159	0.007		RSP-SED-09.0
1.52	0.018	0.354	0.045	0.143	0.221	0.005		RSP-SED-10.0
2.25	0.240	0.703	0.091	0.236	0.141	0.011	0.021	BOT-SED-04.0
2.19	0.170	0.561	0.077	0.213	0.137	0.010	0.017	BOT-SED-04.5
2.03	0.141	0.509	0.070	0.195	0.161	0.009	0.016	BOT-SED-05.0
2.01	0.128	0.507	0.070	0.192	0.134	0.008	0.016	BOT-SED-05.5
1.86	0.092	0.450	0.063	0.170	0.130	0.008	0.014	BOT-SED-06.0
1.82	0.072	0.444	0.062	0.171	0.139	0.008	0.014	BOT-SED-06.5
1.69	0.045	0.407	0.056	0.155	0.135	0.008	0.012	BOT-SED-07.0
1.66	0.033	0.385	0.053	0.148	0.127	0.007	0.010	BOT-SED-07.5
1.64	0.029	0.380	0.052	0.147	0.163	0.007	0.006	BOT-SED-08.0
1.60	0.024	0.349	0.048	0.140	0.132	0.006	0.008	BOT-SED-08.5
1.62	0.024	0.351	0.048	0.141	0.141	0.006	0.002	BOT-SED-09.0

TABLE E.4

Original analyses (less blank values) -
pipette samples, station 15.

ORIGINAL DATA (SAMPLE SUITE: GHISPPY)

VOLUME IN L. TSL IN MG. ELEMENTAL ABUNDANCES IN MICROGRAMS

VOL	TSL	AL	SI	CA	FE	TI	K	MG	P	S	NAME
0.100	0.860	59.5	320.8	32.21	31.70	3.68	13.88	13.07	1.06	1.58	PCT-04.0
0.100	0.484	44.5	236.4	23.58	13.40	2.65	10.23	10.52	0.80	1.46	PCT-04.5
0.100	0.581	45.9	244.1	24.52	25.02	2.68	10.57	10.68	0.82	1.57	PCT-05.0
0.100	0.463	46.3	101.1	23.95	22.66	2.69	10.44	11.03	0.93	1.56	PCT-05.5
0.100	0.342	42.8	88.0	21.40	19.82	2.23	8.77	9.65	0.76	1.13	PCT-06.0
0.100	0.301	35.3	68.5	15.24	15.92	1.72	7.12	8.90	0.66	1.51	PCT-06.5
0.100	0.274	33.0	64.2	17.11	15.23	1.67	7.84	8.01	0.65	2.06	PCT-07.0
0.100	0.188	26.7	49.9	12.75	11.39	1.19	4.99	6.65	0.62	0.74	PCT-07.5
0.100	0.139	19.1	35.9	9.29	8.42	0.79	4.07	5.92	0.42	1.35	PCT-08.0
0.100	0.133	16.1	30.8	7.52	7.06	0.67	3.10	4.22	0.39	0.82	PCT-08.5
0.100	0.113	9.2	17.6	5.27	4.35	0.42	3.07	3.30	0.25	1.26	PCT-09.0
0.100	0.133	11.2	20.8	5.48	4.78	0.46	2.33	3.48	0.51	0.77	PCT-10.0
0.102	0.678	101.6	515.8	13.15	48.72	6.00	21.12	20.81	1.39	1.98	RSP-SED-04.0
0.050	0.096	4.9	14.0	1.00	7.49	0.86	2.83	0.49	0.16	0.23	RSP-SED-04.5
0.050	0.381	54.8	117.6	7.52	25.93	3.20	11.42	11.06	0.79	1.09	RSP-SED-05.0
0.050	0.319	49.5	101.7	5.74	22.72	2.84	9.92	8.89	0.66	1.14	RSP-SED-05.5
0.050	0.286	46.4	89.7	3.96	20.56	2.42	8.74	9.64	0.66	1.17	RSP-SED-06.0
0.050	0.056	9.6	17.2	0.41	3.64	0.42	1.66	2.02	0.15	0.00	RSP-SED-06.5
0.050	0.111	30.7	54.8	1.44	12.63	1.42	5.36	6.68	0.48	0.65	RSP-SED-07.0
0.050	0.174	33.3	59.6	1.77	14.18	1.58	5.69	7.40	0.49	0.65	RSP-SED-07.5
0.050	0.136	24.7	43.5	1.16	10.41	1.16	4.26	5.64	0.40	0.65	RSP-SED-08.0
0.050	0.062	11.7	19.9	0.40	4.67	0.45	1.81	2.60	0.22	0.20	RSP-SED-08.5
0.050	0.128	24.7	43.0	1.08	10.06	1.11	4.26	5.38	0.44	0.51	RSP-SED-09.0
0.100	0.185	38.3	161.3	1.48	15.63	1.65	6.45	8.31	0.71	0.92	RSP-SED-10.0
0.038	1.137	72.7	214.5	21.53	48.84	5.58	21.08	13.85	1.00	0.00	BOT-SED-04.0
0.025	0.377	39.9	96.2	7.44	21.68	2.73	9.41	7.99	0.54	0.65	BOT-SED-04.5
0.025	0.449	39.2	96.0	7.98	21.81	2.67	9.25	7.87	0.50	0.64	BOT-SED-05.0
0.025	0.233	33.3	68.8	3.40	15.55	1.91	6.72	6.77	0.46	0.71	BOT-SED-05.5
0.025	0.250	34.9	70.9	3.74	16.46	2.00	6.95	6.95	0.42	0.72	BOT-SED-06.0
0.025	0.195	31.2	62.7	3.02	14.66	1.82	6.99	6.65	0.43	0.93	BOT-SED-06.5
0.025	0.145	24.7	45.8	1.33	10.54	1.21	4.47	5.23	0.36	0.47	BOT-SED-07.0
0.025	0.155	27.8	50.9	1.48	11.89	1.35	4.84	5.81	0.36	0.31	BOT-SED-07.5
0.025	0.101	21.0	37.8	1.50	8.99	0.99	3.68	4.43	0.26	0.55	BOT-SED-08.0
0.025	0.093	17.9	32.3	0.67	7.74	0.82	3.12	3.78	0.22	0.37	BOT-SED-08.5
0.025	0.110	15.6	27.4	0.66	6.57	0.68	2.57	3.45	0.23	0.23	BOT-SED-09.0
0.050	0.105	20.5	34.9	0.67	8.22	0.83	3.29	4.70	0.31	0.33	BOT-SED-10.0

(BDL = BELOW DETECTION LIMIT; N.A. = NOT ANALYSED)

TABLE E.5

Concentration of particulate elements -
pipette samples, station 15.

RATIOS TO VOLUME (SAMPLE SUITE: GH15PPT)
TSL IN MG/L, ELEMENTS IN MICROGRAMS/L

TSL/VOL	AL/VOL	SI/VOL	CA/VOL	FE/VOL	TI/VOL	K/VOL	MG/VOL	P/VOL	S/VOL	NAME
8.60	595.	3208.	322.1	317.0	36.8	138.6	130.7	10.6	15.8	PCT-04.0
4.84	445.	2364.	235.8	134.0	26.5	102.3	105.2	8.0	14.6	PCT-04.5
5.81	459.	2441.	245.2	250.2	26.8	105.7	106.8	8.2	15.7	PCT-05.0
4.63	463.	1011.	239.5	226.6	26.9	104.4	110.3	9.3	15.6	PCT-05.5
3.42	428.	880.	214.0	198.2	22.3	87.7	96.5	7.6	11.3	PCT-06.0
3.01	353.	685.	152.4	159.2	17.2	71.2	89.0	6.6	15.1	PCT-06.5
2.74	330.	642.	171.1	152.3	16.7	78.4	80L	6.5	20.6	PCT-07.0
1.88	267.	499.	127.5	113.9	11.9	49.9	66.5	6.2	7.4	PCT-07.5
1.39	191.	360.	92.9	84.2	7.9	40.7	59.2	4.2	13.5	PCT-08.0
1.33	161.	308.	75.2	70.6	6.7	31.0	42.2	3.9	8.2	PCT-08.5
1.13	92.	176.	52.7	43.5	4.2	30.7	33.0	2.5	12.6	PCT-09.0
1.33	112.	208.	54.8	47.8	4.6	23.3	34.8	5.1	7.7	PCT-10.0
6.65	996.	5056.	128.9	477.6	58.8	207.1	204.0	13.6	19.4	RSP-SED-04.0
1.92	98.	280.	20.0	149.8	17.2	56.6	9.8	3.2	4.6	RSP-SED-04.5
7.62	1095.	2352.	150.4	518.6	64.0	228.4	221.2	15.8	21.8	RSP-SED-05.0
6.38	990.	2033.	114.8	454.4	56.8	198.4	177.8	13.2	22.8	RSP-SED-05.5
5.72	928.	1794.	79.2	411.2	48.4	174.8	192.8	13.2	23.4	RSP-SED-06.0
1.12	192.	344.	8.2	72.8	8.4	33.2	40.4	3.0	0.0	RSP-SED-06.5
2.22	614.	1095.	28.8	252.6	28.4	107.2	133.6	9.6	13.0	RSP-SED-07.0
3.48	665.	1193.	35.4	283.6	31.6	113.8	148.0	9.8	13.0	RSP-SED-07.5
2.72	494.	870.	23.2	208.2	23.2	85.2	112.8	8.0	13.0	RSP-SED-08.0
1.24	234.	398.	8.0	93.4	9.0	36.2	52.0	4.4	4.0	RSP-SED-08.5
2.56	495.	860.	21.6	201.2	22.2	85.2	107.6	8.8	10.2	RSP-SED-09.0
1.85	383.	1613.	14.8	156.3	16.5	64.5	83.1	7.1	9.2	RSP-SED-10.0
29.92	1914.	5644.	566.6	1285.3	146.8	554.7	364.5	26.3	0.0	BOT-SED-04.0
15.08	1597.	3848.	297.6	867.2	109.2	376.4	319.6	21.6	26.0	BOT-SED-04.5
17.96	1567.	3840.	319.2	872.4	106.8	370.0	314.8	20.0	25.6	BOT-SED-05.0
9.32	1330.	2751.	136.0	622.0	76.4	268.8	270.8	18.4	28.4	BOT-SED-05.5
10.00	1378.	2838.	149.6	658.4	80.0	278.0	278.0	16.8	28.8	BOT-SED-06.0
7.80	1249.	2508.	120.8	586.4	72.8	279.6	266.0	17.2	37.2	BOT-SED-06.5
5.80	990.	1834.	53.2	421.6	48.4	178.8	209.2	14.4	18.8	BOT-SED-07.0
6.20	1112.	2038.	59.2	475.6	54.0	193.6	232.4	14.4	12.4	BOT-SED-07.5
4.04	842.	1513.	60.0	359.6	39.6	147.2	177.2	10.4	22.0	BOT-SED-08.0
3.72	716.	1292.	26.8	309.6	32.8	124.8	151.2	8.8	14.8	BOT-SED-08.5
4.40	626.	1095.	26.4	262.8	27.2	102.8	138.0	9.2	9.2	BOT-SED-09.0
2.10	411.	699.	13.4	164.4	16.6	65.8	94.0	6.2	6.6	BOT-SED-10.0

(80L = BELOW DETECTION LIMIT; N.A. = NOT ANALYSED)

TABLE E.6

Ratios to Al -

pipette samples, station 15

RATIOS TO AL (SAMPLE SUITE: GH15PPT)

SI/AL	CA/AL	FE/AL	TI/AL	K/AL	MG/AL	P/AL	S/AL	NAME
5.39	0.542	0.533	0.062	0.233	0.220	0.018	0.027	PCT-04.0
5.32	0.530	0.301	0.060	0.230	0.237	0.018	0.033	PCT-04.5
5.32	0.534	0.545	0.058	0.230	0.233	0.018	0.034	PCT-05.0
2.18	0.518	0.490	0.058	0.226	0.238	0.020	0.034	PCT-05.5
2.06	0.500	0.463	0.052	0.205	0.226	0.018	0.026	PCT-06.0
1.94	0.432	0.452	0.049	0.202	0.252	0.019	0.043	PCT-06.5
1.94	0.518	0.461	0.051	0.237		0.020	0.062	PCT-07.0
1.87	0.478	0.427	0.045	0.187	0.249	0.023	0.028	PCT-07.5
1.88	0.486	0.441	0.041	0.213	0.310	0.022	0.071	PCT-08.0
1.91	0.466	0.437	0.042	0.192	0.261	0.024	0.051	PCT-08.5
1.91	0.572	0.472	0.046	0.333	0.358	0.027	0.137	PCT-09.0
1.86	0.489	0.427	0.041	0.208	0.311	0.046	0.069	PCT-10.0
5.08	0.129	0.480	0.059	0.208	0.205	0.014	0.019	RSP-SED-04.0
2.85	0.204	1.525	0.175	0.576	0.100	0.033	0.047	RSP-SED-04.5
2.15	0.137	0.474	0.058	0.209	0.202	0.014	0.020	RSP-SED-05.0
2.05	0.116	0.459	0.057	0.200	0.180	0.013	0.023	RSP-SED-05.5
1.93	0.085	0.443	0.052	0.188	0.208	0.014	0.025	RSP-SED-06.0
1.79	0.043	0.379	0.044	0.173	0.210	0.016	0.000	RSP-SED-06.5
1.78	0.047	0.411	0.046	0.175	0.218	0.016	0.021	RSP-SED-07.0
1.79	0.053	0.426	0.048	0.171	0.222	0.015	0.020	RSP-SED-07.5
1.76	0.047	0.421	0.047	0.172	0.228	0.016	0.026	RSP-SED-08.0
1.70	0.034	0.398	0.038	0.154	0.222	0.019	0.017	RSP-SED-08.5
1.74	0.044	0.407	0.045	0.172	0.217	0.018	0.021	RSP-SED-09.0
4.21	0.039	0.408	0.043	0.168	0.217	0.019	0.024	RSP-SED-10.0
2.95	0.296	0.671	0.077	0.290	0.190	0.014	0.000	BOT-SED-04.0
2.41	0.186	0.543	0.068	0.236	0.200	0.014	0.016	BOT-SED-04.5
2.45	0.204	0.557	0.068	0.236	0.201	0.013	0.016	BOT-SED-05.0
2.07	0.102	0.468	0.057	0.202	0.204	0.014	0.021	BOT-SED-05.5
2.06	0.109	0.478	0.058	0.202	0.202	0.012	0.021	BOT-SED-06.0
2.01	0.097	0.470	0.058	0.224	0.213	0.014	0.030	BOT-SED-06.5
1.85	0.054	0.426	0.049	0.181	0.211	0.015	0.019	BOT-SED-07.0
1.83	0.053	0.428	0.049	0.174	0.209	0.013	0.011	BOT-SED-07.5
1.80	0.071	0.427	0.047	0.175	0.210	0.012	0.026	BOT-SED-08.0
1.80	0.037	0.432	0.046	0.174	0.211	0.012	0.021	BOT-SED-08.5
1.75	0.042	0.420	0.043	0.164	0.221	0.015	0.015	BOT-SED-09.0
1.70	0.033	0.400	0.040	0.160	0.229	0.015	0.016	BOT-SED-10.0

TABLE E.7

Original analyses (less blank values) -
 pipette samples, station 7.

ORIGINAL DATA (SAMPLE SUITE: STN7-PP)
 VOLUME IN L, TSL IN MG, ELEMENTAL ABUNDANCES IN MICROGRAMS

VOL	TSL	AL	SI	CA	FE	TI	K	MG	P	S	NAME
0.025	0.175	2.5	12.0	2.19	5.20	0.57	1.74	0.93	0.54	0.50	FLD-TOP-03.0
0.025	0.186	7.1	22.0	2.04	5.35	0.64	1.82	2.22	0.61	0.55	FLD-TOP-04.0
0.025	0.131	1.0	4.6	0.95	1.39	0.24	0.71	0.35	0.15	0.51	FLD-TOP-04.5
0.025	0.206	9.0	26.5	3.30	4.22	0.61	1.97	3.18	0.76	0.74	FLD-TOP-05.0
0.025	0.200	3.0	10.3	1.01	BDL	0.10	0.47	2.33	0.41	0.84	FLD-TOP-05.5
0.025	0.193	7.3	21.1	2.16	4.92	0.54	2.24	2.82	0.66	0.91	FLD-TOP-06.0
0.025	0.191	6.9	20.3	2.75	4.63	0.48	1.84	3.67	0.49	0.74	FLD-TOP-06.5
0.025	0.093	3.0	10.3	0.60	0.32	0.14	0.19	0.39	0.30	0.12	FLD-TOP-07.0
0.025	0.115	3.2	10.3	1.28	2.20	0.25	1.01	1.82	0.37	0.43	FLD-TOP-07.5
0.050	0.145	5.6	16.5	1.32	1.68	0.25	0.56	2.78	0.58	0.54	FLD-TOP-08.0
0.050	0.113	3.8	10.6	1.20	2.49	0.19	0.80	1.63	0.48	0.60	FLD-TOP-08.5
0.100	0.196	6.6	21.0	2.49	3.85	0.39	1.29	2.66	1.04	1.07	FLD-TOP-09.0
0.100	0.155	4.2	13.6	1.62	2.95	0.26	1.47	2.56	0.97	1.04	FLD-TOP-10.0
0.010	0.346	5.5	15.6	0.45	4.32	0.41	1.15	1.76	0.34	0.50	FLD-BOT-03.0
0.010	0.303	5.3	13.4	1.04	2.26	0.35	0.69	1.54	0.23	0.44	FLD-BOT-04.0
0.025	0.348	18.8	48.8	5.22	13.33	1.50	4.96	5.11	0.85	1.21	FLD-BOT-04.5
0.025	0.364	20.8	53.4	7.13	14.09	1.70	5.56	4.57	1.07	1.16	FLD-BOT-05.0
0.025	0.301	19.2	50.2	5.46	12.83	1.53	4.77	4.45	0.89	0.85	FLD-BOT-05.5
0.025	0.292	13.6	35.1	4.07	8.84	0.98	3.38	3.16	0.93	1.16	FLD-BOT-06.0
0.025	0.285	10.5	27.2	3.03	4.90	0.69	2.01	4.97	0.77	1.09	FLD-BOT-06.5
0.025	0.143	4.7	12.5	1.35	0.73	0.21	0.52	1.98	0.50	0.63	FLD-BOT-07.0
0.050	0.112	4.4	11.5	0.92	0.47	0.18	0.31	0.66	0.50	0.32	FLD-BOT-07.5
0.050	0.143	6.6	18.0	1.89	3.35	0.38	1.26	2.21	0.72	0.86	FLD-BOT-08.0
0.100	0.170	9.4	24.2	2.19	5.01	0.46	1.53	2.27	1.01	0.82	FLD-BOT-08.5
0.100	0.172	9.2	24.1	1.74	3.17	0.42	1.00	1.94	1.02	0.58	FLD-BOT-09.0
0.100	0.138	4.8	14.2	1.17	2.62	0.23	0.82	1.75	1.15	0.73	FLD-BOT-10.0
0.010	0.361	3.7	12.8	1.00	0.47	0.20	0.61	0.82	0.31	0.68	HW-TOP-03.0
0.010	0.171	1.1	6.4	0.65	1.20	0.09	0.42	0.13	0.15	0.46	HW-TOP-04.0
0.025	0.144	1.3	4.6	0.54	1.25	0.11	0.40	1.11	0.17	0.35	HW-TOP-04.5
0.025	0.136	4.3	14.7	1.37	2.18	0.31	0.97	1.09	0.44	0.44	HW-TOP-05.0
0.025	0.175	4.1	13.2	1.93	2.52	0.29	1.23	2.67	0.37	1.06	HW-TOP-05.5
0.025	0.124	3.4	11.2	1.03	2.31	0.22	0.82	1.62	0.31	0.54	HW-TOP-06.5
0.025	0.112	2.3	7.2	0.75	BDL	0.07	0.21	1.90	0.25	0.58	HW-TOP-07.0
0.025	0.090	1.8	5.9	0.45	BDL	0.08	0.02	1.10	0.17	0.38	HW-TOP-07.5
0.100	0.102	3.4	9.6	0.94	BDL	0.14	0.21	1.86	0.33	0.38	HW-TOP-08.0
0.100	0.118	6.1	16.6	1.27	3.49	0.33	0.89	1.53	0.60	0.37	HW-TOP-08.5
0.100	0.136	5.8	16.9	1.53	2.89	0.26	1.34	1.87	0.59	0.60	HW-TOP-09.0
0.100	0.129	4.4	13.9	1.31	2.52	0.26	0.65	1.53	0.76	0.44	HW-TOP-10.0
0.010	0.142	1.5	4.1	0.28	BDL	0.08	BDL	1.17	0.16	0.33	HW-BOT-03.0
0.010	0.108	1.3	5.4	0.17	BDL	0.03	BDL	0.98	0.17	0.23	HW-BOT-04.0
0.025	0.136	2.1	7.1	1.62	1.44	0.13	0.78	3.38	0.26	0.64	HW-BOT-04.5
0.025	0.145	4.8	16.5	1.84	2.99	0.33	1.04	1.18	0.44	0.50	HW-BOT-05.0
0.025	0.142	4.3	13.6	1.85	2.31	0.26	1.12	2.48	0.45	0.69	HW-BOT-05.5
0.025	0.125	3.5	11.0	1.01	0.21	0.16	0.38	3.45	0.40	0.51	HW-BOT-06.0
0.025	0.125	4.3	11.4	1.26	0.86	0.18	0.62	2.34	0.46	0.57	HW-BOT-06.5
0.050	0.151	5.1	15.7	2.14	2.46	0.28	1.25	2.92	0.75	1.12	HW-BOT-07.0
0.050	0.123	4.1	12.5	1.19	2.64	0.21	0.71	1.82	0.56	0.52	HW-BOT-07.5
0.050	0.113	3.4	10.3	0.67	0.22	0.12	0.16	1.79	0.41	0.31	HW-BOT-08.0
0.100	0.099	4.0	10.7	1.14	2.35	0.17	0.72	1.41	0.51	0.50	HW-BOT-08.5
0.100	0.110	3.9	11.6	0.80	0.29	0.14	0.19	1.87	0.59	0.48	HW-BOT-10.0

TABLE E.7
(continued)

ORIGINAL DATA (SAMPLE SUITE: STA7-PP)
VOLUME IN L. TSL IN %G. ELEMENTAL ABUNDANCES IN MICROGRAMS

VOL	TSL	AL	SI	CA	FE	TI	K	MG	P	S	NAME
0.010	0.095	1.3	4.6	BDL	BDL	0.09	BDL	0.53	0.11	0.19	EBB-TOP-03.0
0.010	0.097	1.2	4.2	0.87	BDL	0.05	BDL	1.43	0.14	0.29	EBB-TOP-04.0
0.010	0.069	1.3	4.6	0.27	0.94	0.11	0.63	0.12	0.11	0.19	EBB-TOP-04.5
0.025	0.144	4.8	15.1	1.78	3.00	0.32	1.13	1.59	0.52	0.54	EBB-TOP-05.0
0.025	0.135	4.5	13.0	1.25	1.04	0.24	0.60	1.56	0.39	0.47	EBB-TOP-05.5
0.025	0.112	4.6	14.8	1.58	2.82	0.34	1.43	1.86	0.48	0.72	EBB-TOP-06.0
0.025	0.111	3.3	10.1	1.26	2.12	0.20	1.23	1.75	0.42	0.55	EBB-TOP-07.0
0.025	0.119	3.9	12.0	1.35	2.16	0.21	0.85	0.90	0.50	0.59	EBB-TOP-07.5
0.050	0.096	3.2	9.0	1.09	1.94	0.17	0.71	1.47	0.36	0.55	EBB-TOP-08.0
0.100	0.136	6.3	17.2	1.49	3.44	0.33	1.09	1.45	0.67	0.76	EBB-TOP-08.5
0.010	0.114	2.5	6.9	0.71	2.02	0.18	0.72	2.74	0.14	0.35	EBB-BOT-03.0
0.010	0.091	1.5	5.4	0.49	0.81	0.11	0.42	0.26	0.19	0.34	EBB-BOT-04.0
0.025	0.165	6.6	20.4	1.84	4.72	0.49	1.95	1.90	0.50	0.56	EBB-BOT-04.5
0.025	0.152	7.0	20.5	2.01	2.80	0.54	1.21	1.79	0.51	0.62	EBB-BOT-05.0
0.025	0.175	7.4	21.7	3.07	4.93	0.56	2.22	1.85	0.65	0.71	EBB-BOT-05.5
0.025	0.157	5.0	14.5	1.20	1.09	0.26	0.78	2.09	0.46	0.52	EBB-BOT-06.0
0.025	0.348	4.3	12.8	3.25	2.97	0.28	1.32	2.27	1.32	0.85	EBB-BOT-06.5
0.025	0.128	3.2	9.2	0.85	0.80	0.12	0.40	1.64	0.29	0.56	EBB-BOT-07.0
0.050	0.121	4.9	14.5	1.07	0.79	0.20	0.36	1.90	0.43	0.34	EBB-BOT-07.5
0.050	0.103	3.6	10.2	1.18	2.00	0.18	0.80	1.59	0.42	0.45	EBB-BOT-08.0
0.100	0.088	2.7	7.8	0.44	1.92	0.18	0.75	0.60	0.30	0.21	EBB-BOT-08.5
0.100	0.107	3.3	9.5	1.33	1.81	0.16	0.61	1.73	0.69	0.73	EBB-BOT-10.0
0.010	0.644	58.6	115.5	3.49	26.94	3.66	10.23	10.19	0.62	0.99	BOT-SED-03.0
0.010	0.652	66.3	139.7	5.67	35.01	4.44	13.00	11.93	0.74	1.49	BOT-SED-04.0
0.025	10.547	178.9	382.9	15.04	90.28	11.69	34.60	26.21	1.55	3.39	BOT-SED-04.5
0.010	0.627	77.1	160.8	5.52	38.31	5.05	14.53	12.61	0.87	1.27	BOT-SED-05.0
0.010	0.543	71.4	143.4	4.62	33.29	4.37	13.29	11.75	0.60	1.43	BOT-SED-05.5
0.025	0.896	162.4	301.8	7.76	68.63	9.03	26.57	26.92	1.37	2.57	BOT-SED-06.0
0.025	0.788	160.8	276.4	7.04	66.51	8.21	24.55	24.32	1.48	2.29	BOT-SED-06.5
0.025	0.581	81.1	136.0	2.84	32.79	3.92	11.92	12.08	0.82	1.03	BOT-SED-07.0
0.025	0.625	143.0	234.0	5.63	55.50	6.81	20.56	23.28	1.28	1.88	BOT-SED-07.5
0.025	0.497	119.7	186.9	4.10	45.19	5.14	16.49	21.06	1.21	1.57	BOT-SED-08.0
0.025	0.524	113.5	184.1	3.80	45.13	5.19	15.96	18.33	1.13	1.32	BOT-SED-08.5
0.025	0.436	97.1	155.0	3.07	35.33	4.21	13.05	17.11	0.90	1.06	BOT-SED-09.0

(BDL = BELOW DETECTION LIMIT; N.A. = NOT ANALYSED)

TABLE E.8

Concentration of particulate elements -
 pipette samples, station 7.

RATIOS TO VOLUME (SAMPLE SUITE: STN7-PP)
 TSL IN MG/L, ELEMENTS IN MICROGRAMS/L

TSL/VOL	AL/VOL	SI/VOL	CA/VOL	FE/VOL	TI/VOL	K/VOL	MG/VOL	P/VOL	S/VOL	NAME
7.00	102.	479.	87.6	208.0	22.8	69.6	37.2	21.6	20.0	FLD-TOP-03.0
7.44	284.	878.	81.6	214.0	25.6	72.8	88.8	24.4	22.0	FLD-TOP-04.0
5.24	40.	184.	38.0	55.6	9.6	28.4	14.0	6.0	20.4	FLD-TOP-04.5
8.24	360.	1060.	132.0	168.8	24.4	78.8	127.2	30.4	29.6	FLD-TOP-05.0
8.00	118.	413.	40.4	80L	4.0	18.8	93.2	16.4	33.6	FLD-TOP-05.5
7.72	292.	844.	86.4	196.8	21.6	89.6	112.8	26.4	36.4	FLD-TOP-06.0
7.64	277.	812.	110.0	185.2	19.2	73.6	146.8	19.6	29.6	FLD-TOP-06.5
3.72	121.	413.	24.0	12.8	5.6	7.6	15.6	12.0	4.8	FLD-TOP-07.0
4.60	129.	412.	51.2	88.0	10.0	40.4	72.8	14.8	17.2	FLD-TOP-07.5
2.90	112.	330.	26.4	33.6	5.0	11.2	55.6	11.6	10.8	FLD-TOP-08.0
2.26	76.	213.	24.0	49.8	3.8	16.0	32.6	9.6	12.0	FLD-TOP-08.5
1.96	66.	210.	24.9	38.5	3.9	12.9	26.6	10.4	10.7	FLD-TOP-09.0
1.55	42.	136.	16.2	29.5	2.6	14.7	25.6	9.7	10.4	FLD-TOP-10.0
34.60	548.	1557.	45.0	432.0	41.0	115.0	176.0	34.0	50.0	FLD-BOT-03.0
30.30	526.	1344.	104.0	226.0	35.0	69.0	154.0	23.0	44.0	FLD-BOT-04.0
13.92	750.	1953.	208.8	533.2	60.0	198.4	204.4	34.0	48.4	FLD-BOT-04.5
14.56	830.	2136.	285.2	563.6	68.0	222.4	182.8	42.8	46.4	FLD-BOT-05.0
12.04	767.	2009.	218.4	513.2	61.2	190.8	178.0	35.6	34.0	FLD-BOT-05.5
11.68	542.	1405.	162.8	353.6	39.2	135.2	126.4	37.2	46.4	FLD-BOT-06.0
11.40	422.	1088.	121.2	196.0	27.6	80.4	198.8	30.8	43.6	FLD-BOT-06.5
5.72	188.	501.	54.0	29.2	8.4	20.8	79.2	20.0	25.2	FLD-BOT-07.0
2.24	87.	230.	18.4	9.4	3.6	6.2	13.2	10.0	6.4	FLD-BOT-07.5
2.86	131.	360.	37.8	67.0	7.6	25.2	44.2	14.4	17.2	FLD-BOT-08.0
1.70	94.	242.	21.9	50.1	4.6	15.3	22.7	10.1	8.2	FLD-BOT-08.5
1.72	92.	241.	17.4	31.7	4.2	10.0	19.4	10.2	5.8	FLD-BOT-09.0
1.38	48.	142.	11.7	26.2	2.3	8.2	17.5	11.5	7.3	FLD-BOT-10.0
36.10	371.	1282.	100.0	47.0	20.0	61.0	82.0	31.0	68.0	HW-TOP-03.0
17.10	108.	639.	65.0	120.0	9.0	42.0	13.0	15.0	46.0	HW-TOP-04.0
5.76	52.	186.	21.6	50.0	4.4	16.0	44.4	6.8	14.0	HW-TOP-04.5
5.44	174.	588.	54.8	87.2	12.4	38.8	43.6	17.6	17.6	HW-TOP-05.0
7.00	163.	528.	77.2	100.8	11.6	49.2	106.8	14.8	42.4	HW-TOP-05.5
4.96	134.	448.	41.2	92.4	8.8	32.8	64.8	12.4	21.6	HW-TOP-06.5
4.48	91.	286.	30.0	80L	2.8	8.4	76.0	10.0	23.2	HW-TOP-07.0
3.60	73.	236.	18.0	80L	3.2	0.8	44.0	6.8	15.2	HW-TOP-07.5
1.02	34.	96.	9.4	80L	1.4	2.1	18.6	3.3	3.8	HW-TOP-08.0
1.18	61.	166.	12.7	34.9	3.3	8.9	15.3	6.0	3.7	HW-TOP-08.5
1.36	59.	169.	15.3	28.9	2.6	13.4	18.7	5.9	6.0	HW-TOP-09.0
1.29	44.	139.	13.1	25.2	2.6	6.5	15.3	7.6	4.4	HW-TOP-10.0
14.20	150.	410.	28.0	80L	8.0	80L	117.0	16.0	33.0	HW-BOT-03.0
10.80	133.	542.	17.0	80L	3.0	80L	98.0	17.0	23.0	HW-BOT-04.0
5.44	86.	286.	64.8	57.6	5.2	31.2	135.2	10.4	25.6	HW-BOT-04.5
5.80	192.	659.	73.6	119.6	13.2	41.6	47.2	17.6	20.0	HW-BOT-05.0
5.68	171.	542.	74.0	92.4	11.2	44.8	99.2	18.0	27.6	HW-BOT-05.5
5.00	140.	439.	40.4	8.4	6.4	15.2	138.0	16.0	20.4	HW-BOT-06.0
5.00	173.	455.	50.4	34.4	7.2	24.8	93.6	18.4	22.8	HW-BOT-06.5
3.02	102.	314.	42.8	49.2	5.6	25.0	58.4	15.0	22.4	HW-BOT-07.0
2.46	82.	250.	23.8	52.8	4.2	14.2	36.4	11.2	10.4	HW-BOT-07.5
2.26	67.	207.	13.4	4.4	2.4	3.2	35.8	8.2	6.2	HW-BOT-08.0
0.99	40.	107.	11.4	23.5	1.7	7.2	14.1	5.1	5.0	HW-BOT-08.5
1.10	39.	116.	8.0	2.9	1.4	1.9	18.7	5.9	4.8	HW-BOT-10.0

TABLE E.8
(continued)

RATIOS TO VOLUME (SAMPLE SUITE: STN7-PP)
TSL IN MG/L. ELEMENTS IN MICROGRAMS/L

TSL/VOL	AL/VOL	SI/VOL	CA/VOL	FE/VOL	TI/VOL	K/VOL	MG/VOL	P/VOL	S/VOL	NAME
9.50	131.	461.	BDL	BDL	9.0	BDL	53.0	11.0	19.0	EBB-TOP-03.0
9.70	124.	419.	87.0	BDL	5.0	BDL	143.0	14.0	29.0	EBB-TOP-04.0
6.90	126.	459.	27.0	94.0	11.0	63.0	12.0	11.0	19.0	EBB-TOP-04.5
5.76	190.	605.	71.2	120.0	12.8	45.2	63.6	20.8	21.6	EBB-TOP-05.0
5.40	182.	521.	50.0	41.6	9.6	24.0	62.4	15.6	18.8	EBB-TOP-05.5
4.48	186.	590.	63.2	112.8	13.6	57.2	74.4	19.2	28.8	EBB-TOP-06.0
4.44	132.	404.	50.4	84.8	8.0	49.2	70.0	16.8	22.0	EBB-TOP-07.0
4.76	156.	478.	54.0	86.4	8.4	34.0	36.0	20.0	23.6	EBB-TOP-07.5
1.92	64.	181.	21.8	38.8	3.4	14.2	29.4	7.2	11.0	EBB-TOP-08.0
1.36	63.	172.	14.9	34.4	3.3	10.9	14.5	6.7	7.6	EBB-TOP-08.5
11.40	252.	692.	71.0	202.0	18.0	72.0	274.0	14.0	35.0	EBB-BOT-03.0
9.10	149.	545.	49.0	81.0	11.0	42.0	26.0	19.0	34.0	EBB-BOT-04.0
6.60	265.	815.	73.6	188.8	19.6	78.0	76.0	20.0	22.4	EBB-BOT-04.5
6.08	280.	820.	80.4	112.0	21.6	48.4	71.6	20.4	24.8	EBB-BOT-05.0
7.00	295.	868.	122.8	197.2	22.4	88.8	74.0	26.0	28.4	EBB-BOT-05.5
6.28	199.	581.	48.0	43.6	10.4	31.2	83.6	18.4	20.8	EBB-BOT-06.0
13.92	174.	513.	130.0	118.8	11.2	52.8	90.8	52.8	34.0	EBB-BOT-06.5
5.12	129.	370.	34.0	32.0	4.8	16.0	65.6	11.6	22.4	EBB-BOT-07.0
2.42	97.	289.	21.4	15.8	4.0	7.2	38.0	8.6	6.8	EBB-BOT-07.5
2.06	72.	204.	23.6	40.0	3.6	16.0	31.8	8.4	9.0	EBB-BOT-08.0
0.88	27.	78.	4.4	19.2	1.8	7.5	6.0	3.0	2.1	EBB-BOT-08.5
1.07	33.	95.	13.3	18.1	1.6	6.1	17.3	6.9	7.3	EBB-BOT-10.0
64.40	5865.	11552.	349.0	2694.0	366.0	1023.0	1019.0	62.0	99.0	BOT-SED-03.0
65.20	6627.	13972.	567.0	3501.0	444.0	1300.0	1193.0	74.0	149.0	BOT-SED-04.0
421.88	7155.	15318.	601.6	3611.2	467.6	1384.0	1048.4	62.0	135.6	BOT-SED-04.5
62.70	7711.	16078.	552.0	3831.0	505.0	1453.0	1261.0	87.0	127.0	BOT-SED-05.0
54.30	7139.	14337.	462.0	3329.0	437.0	1329.0	1175.0	60.0	143.0	BOT-SED-05.5
35.84	6498.	12071.	310.4	2745.2	361.2	1062.8	1076.8	54.8	102.8	BOT-SED-06.0
31.52	6431.	11057.	281.6	2660.4	328.4	982.0	972.8	59.2	91.6	BOT-SED-06.5
23.24	3245.	5440.	113.6	1311.6	156.8	476.8	483.2	32.8	41.2	BOT-SED-07.0
25.00	5720.	9358.	225.2	2220.0	272.4	822.4	931.2	51.2	75.2	BOT-SED-07.5
19.88	4789.	7474.	164.0	1807.6	205.6	659.6	842.4	48.4	62.8	BOT-SED-08.0
20.96	4540.	7364.	152.0	1805.2	207.6	638.4	733.2	45.2	52.8	BOT-SED-08.5
17.44	3885.	6202.	122.8	1413.2	168.4	522.0	684.4	36.0	42.4	BOT-SED-09.0

(BDL = BELOW DETECTION LIMIT; N.A. = NOT ANALYSED)

TABLE E.9

Ratios to Al -

pipette samples, station 7

RATIOS TO AL (SAMPLE SUITE: STN7-PP)

SI/AL	CA/AL	FE/AL	TI/AL	K/AL	MG/AL	P/AL	S/AL	NAME
4.72	0.862	2.047	0.224	0.685	0.366	0.213	0.197	FLD-TOP-03.0
3.10	0.288	0.755	0.090	0.257	0.313	0.086	0.078	FLD-TOP-04.0
4.60	0.950	1.390	0.240	0.710	0.350	0.150	0.510	FLD-TOP-04.5
2.95	0.367	0.469	0.068	0.219	0.354	0.085	0.082	FLD-TOP-05.0
3.49	0.341		0.034	0.159	0.787	0.139	0.284	FLD-TOP-05.5
2.89	0.296	0.674	0.074	0.307	0.386	0.090	0.125	FLD-TOP-06.0
2.93	0.397	0.668	0.069	0.266	0.530	0.071	0.107	FLD-TOP-06.5
3.42	0.199	0.106	0.046	0.063	0.129	0.099	0.040	FLD-TOP-07.0
3.20	0.398	0.683	0.078	0.314	0.565	0.115	0.134	FLD-TOP-07.5
2.94	0.235	0.299	0.045	0.100	0.496	0.103	0.096	FLD-TOP-08.0
2.81	0.317	0.657	0.050	0.211	0.430	0.127	0.158	FLD-TOP-08.5
3.17	0.376	0.582	0.059	0.195	0.402	0.157	0.162	FLD-TOP-09.0
3.20	0.382	0.696	0.061	0.347	0.604	0.229	0.245	FLD-TOP-10.0
2.84	0.082	0.788	0.075	0.210	0.321	0.062	0.091	FLD-BOT-03.0
2.56	0.198	0.430	0.067	0.131	0.293	0.044	0.084	FLD-BOT-04.0
2.60	0.278	0.711	0.080	0.264	0.272	0.045	0.064	FLD-BOT-04.5
2.57	0.343	0.679	0.082	0.268	0.220	0.052	0.056	FLD-BOT-05.0
2.62	0.285	0.669	0.080	0.249	0.232	0.046	0.044	FLD-BOT-05.5
2.59	0.300	0.652	0.072	0.249	0.233	0.069	0.086	FLD-BOT-06.0
2.58	0.287	0.464	0.065	0.191	0.471	0.073	0.103	FLD-BOT-06.5
2.67	0.288	0.156	0.045	0.111	0.422	0.107	0.134	FLD-BOT-07.0
2.64	0.211	0.108	0.041	0.071	0.151	0.115	0.073	FLD-BOT-07.5
2.74	0.288	0.510	0.058	0.192	0.336	0.110	0.131	FLD-BOT-08.0
2.56	0.232	0.531	0.049	0.162	0.241	0.107	0.087	FLD-BOT-08.5
2.61	0.189	0.344	0.046	0.109	0.211	0.111	0.063	FLD-BOT-09.0
2.99	0.246	0.552	0.048	0.173	0.368	0.242	0.154	FLD-BOT-10.0
3.46	0.270	0.127	0.054	0.164	0.221	0.084	0.183	HW-TOP-03.0
5.92	0.602	1.111	0.083	0.389	0.120	0.139	0.426	HW-TOP-04.0
3.58	0.415	0.962	0.085	0.308	0.854	0.131	0.269	HW-TOP-04.5
3.39	0.316	0.502	0.071	0.224	0.251	0.101	0.101	HW-TOP-05.0
3.23	0.473	0.618	0.071	0.301	0.654	0.091	0.260	HW-TOP-05.5
3.33	0.307	0.687	0.065	0.244	0.482	0.092	0.161	HW-TOP-06.5
3.15	0.330		0.031	0.093	0.837	0.110	0.256	HW-TOP-07.0
3.24	0.247		0.044	0.011	0.604	0.093	0.209	HW-TOP-07.5
2.84	0.277		0.041	0.062	0.549	0.097	0.112	HW-TOP-08.0
2.73	0.209	0.575	0.054	0.147	0.252	0.099	0.061	HW-TOP-08.5
2.90	0.262	0.494	0.044	0.229	0.320	0.101	0.103	HW-TOP-09.0
3.12	0.295	0.568	0.059	0.146	0.345	0.171	0.099	HW-TOP-10.0
2.73	0.187		0.053		0.780	0.107	0.220	HW-BOT-03.0
4.08	0.128		0.023		0.737	0.128	0.173	HW-BOT-04.0
3.34	0.757	0.673	0.061	0.364	1.579	0.121	0.299	HW-BOT-04.5
3.44	0.384	0.624	0.069	0.217	0.246	0.092	0.104	HW-BOT-05.0
3.18	0.433	0.541	0.066	0.262	0.581	0.105	0.162	HW-BOT-05.5
3.14	0.289	0.050	0.045	0.109	0.989	0.115	0.146	HW-BOT-06.0
2.63	0.291	0.199	0.042	0.143	0.540	0.106	0.132	HW-BOT-06.5
3.07	0.419	0.481	0.055	0.245	0.571	0.147	0.219	HW-BOT-07.0
3.05	0.290	0.644	0.051	0.173	0.444	0.137	0.127	HW-BOT-07.5
3.07	0.199	0.065	0.036	0.048	0.533	0.122	0.092	HW-BOT-08.0
2.70	0.286	0.590	0.043	0.181	0.354	0.128	0.126	HW-BOT-08.5
2.97	0.205	0.074	0.036	0.049	0.478	0.151	0.123	HW-BOT-10.0

TABLE E.9
(continued)

RATIOS TO AL (SAMPLE SUITE: STN7-PP)

SI/AL	CA/AL	FE/AL	TI/AL	K/AL	MG/AL	P/AL	S/AL	NAME
3.52			0.069		0.405	0.084	0.145	EBB-TOP-03.0
3.38	0.702		0.040		1.153	0.113	0.234	EBB-TOP-04.0
3.64	0.214	0.746	0.087	0.500	0.095	0.087	0.151	EBB-TOP-04.5
3.18	0.375	0.632	0.067	0.238	0.335	0.109	0.114	EBB-TOP-05.0
2.87	0.275	0.229	0.053	0.132	0.344	0.086	0.104	EBB-TOP-05.5
3.18	0.341	0.608	0.073	0.368	0.401	0.103	0.155	EBB-TOP-06.0
3.06	0.382	0.642	0.061	0.373	0.530	0.127	0.167	EBB-TOP-07.0
3.06	0.345	0.552	0.054	0.217	0.230	0.128	0.151	EBB-TOP-07.5
2.80	0.339	0.602	0.053	0.220	0.457	0.112	0.171	EBB-TOP-08.0
2.74	0.237	0.548	0.053	0.174	0.231	0.107	0.121	EBB-TOP-08.5
2.75	0.282	0.802	0.071	0.286	1.087	0.056	0.139	EBB-BOT-03.0
3.66	0.329	0.544	0.074	0.282	0.174	0.128	0.228	EBB-BOT-04.0
3.07	0.276	0.712	0.074	0.294	0.287	0.075	0.084	EBB-BOT-04.5
2.93	0.268	0.401	0.077	0.173	0.256	0.073	0.089	EBB-BOT-05.0
2.95	0.417	0.669	0.076	0.301	0.251	0.088	0.096	EBB-BOT-05.5
2.92	0.241	0.219	0.052	0.157	0.420	0.092	0.104	EBB-BOT-06.0
2.95	0.747	0.683	0.064	0.303	0.522	0.303	0.195	EBB-BOT-06.5
2.87	0.264	0.248	0.037	0.124	0.509	0.090	0.174	EBB-BOT-07.0
2.97	0.220	0.162	0.041	0.074	0.390	0.088	0.070	EBB-BOT-07.5
2.84	0.329	0.557	0.050	0.223	0.443	0.117	0.125	EBB-BOT-08.0
2.89	0.162	0.708	0.066	0.277	0.221	0.111	0.077	EBB-BOT-08.5
2.85	0.398	0.542	0.048	0.183	0.518	0.207	0.219	EBB-BOT-10.0
1.97	0.060	0.459	0.062	0.174	0.174	0.011	0.017	BOT-SED-03.0
2.11	0.086	0.528	0.067	0.196	0.180	0.011	0.022	BOT-SED-04.0
2.14	0.084	0.505	0.065	0.193	0.147	0.009	0.019	BOT-SED-04.5
2.09	0.072	0.497	0.065	0.188	0.164	0.011	0.016	BOT-SED-05.0
2.01	0.065	0.466	0.061	0.186	0.165	0.008	0.020	BOT-SED-05.5
1.86	0.048	0.422	0.056	0.164	0.166	0.008	0.016	BOT-SED-06.0
1.72	0.044	0.414	0.051	0.153	0.151	0.009	0.014	BOT-SED-06.5
1.68	0.035	0.404	0.048	0.147	0.149	0.010	0.013	BOT-SED-07.0
1.64	0.039	0.388	0.048	0.144	0.163	0.009	0.013	BOT-SED-07.5
1.56	0.034	0.377	0.043	0.138	0.176	0.010	0.013	BOT-SED-08.0
1.62	0.033	0.398	0.046	0.141	0.161	0.010	0.012	BOT-SED-08.5
1.60	0.032	0.364	0.043	0.134	0.176	0.009	0.011	BOT-SED-09.0

TABLE E.10

Original analyses (less blank values) -
pipette samples, inner estuary.

ORIGINAL DATA (SAMPLE SUITE: GHFRSPPT)
VOLUME IN L. TSL IN MG. ELEMENTAL ABUNDANCES IN MICROGRAMS

VOL	TSL	AL	SI	CA	FE	TI	K	MG	P	S	NAME
0.050	0.753	114.7	208.0	29.75	52.25	6.72	19.62	19.25	1.99	2.32	PCT-04.0
0.050	0.781	115.6	210.2	29.58	52.80	6.80	20.49	20.33	2.01	2.79	PCT-04.5
0.050	0.806	93.8	179.1	25.92	44.48	5.75	17.68	18.36	1.74	3.27	PCT-05.0
0.050	0.742	116.5	208.6	30.20	52.14	6.72	20.02	19.96	1.86	2.55	PCT-05.5
0.050	0.723	115.9	207.0	30.42	52.22	6.66	19.89	19.94	1.99	2.80	PCT-06.0
0.050	0.682	94.1	168.2	23.82	41.33	5.30	15.64	15.48	1.59	1.93	PCT-06.5
0.050	0.669	109.3	191.4	27.71	47.26	6.03	17.76	18.64	1.88	2.12	PCT-07.0
0.050	0.579	93.5	159.3	22.97	38.93	4.86	14.72	16.52	1.64	2.09	PCT-07.5
0.050	0.412	74.0	122.4	17.00	29.43	3.62	10.87	13.43	1.37	1.45	PCT-08.0
0.050	0.254	46.4	74.7	9.71	17.79	2.16	6.59	8.37	0.91	1.09	PCT-08.5
0.050	0.208	36.9	60.2	7.65	13.94	1.67	5.41	6.94	0.79	1.25	PCT-09.0
0.050	0.128	16.2	25.8	3.16	5.86	0.66	2.53	3.96	0.52	1.02	PCT-09.5
0.025	1.521	207.4	403.9	23.80	113.25	14.10	39.72	34.34	3.63	4.30	BOT-SED-04.0
0.025	1.473	203.5	397.2	25.13	111.41	13.83	38.95	34.61	3.65	4.11	BOT-SED-04.5
0.025	1.410	174.0	333.8	20.40	92.74	11.52	32.58	29.30	3.04	3.54	BOT-SED-05.0
0.025	1.360	198.5	380.2	23.02	106.05	13.16	37.24	33.98	3.51	4.01	BOT-SED-05.5
0.025	1.072	152.7	275.2	14.59	75.57	9.19	26.51	26.30	2.71	3.00	BOT-SED-06.0
0.025	0.858	153.3	265.6	12.09	72.87	8.77	25.31	26.23	2.69	2.92	BOT-SED-06.5
0.025	0.734	131.8	221.9	8.34	59.84	7.13	20.63	22.83	2.25	2.00	BOT-SED-07.0
0.025	0.424	86.0	140.4	4.25	37.42	4.27	12.74	15.42	2.33	1.31	BOT-SED-07.5
0.025	0.293	64.7	102.7	2.68	27.03	3.08	9.29	11.61	1.20	0.92	BOT-SED-08.0
0.025	0.307	63.7	102.2	2.61	26.91	3.08	9.39	11.52	1.21	0.90	BOT-SED-08.5
0.025	0.262	58.2	92.9	2.40	24.24	2.72	8.31	10.73	1.09	0.86	BOT-SED-09.0
0.025	0.131	27.7	43.2	1.05	11.14	1.16	3.86	5.47	0.59	0.51	BOT-SED-09.5

(BDL = BELOW DETECTION LIMIT; N.A. = NOT ANALYSED)

TABLE E.11

Concentration of particulate elements -
pipette samples, inner estuary.

RATIOS TO VOLUME (SAMPLE SUITE: GHFRBPPT)
TSL IN MG/L. ELEMENTS IN MICROGRAMS/L

TSL/VOL	AL/VOL	SI/VOL	CA/VOL	FE/VOL	TI/VOL	K/VOL	MG/VOL	P/VOL	S/VOL	NAME
15.06	2293.	4160.	595.0	1045.0	134.4	392.4	385.0	39.8	46.4	PCT-04.0
15.62	2313.	4204.	591.6	1046.0	136.0	409.8	406.6	40.2	55.8	PCT-04.5
16.12	1876.	3582.	518.4	889.6	115.0	353.6	367.2	34.8	65.4	PCT-05.0
14.84	2330.	4173.	604.0	1042.8	134.4	400.4	399.2	37.2	51.0	PCT-05.5
14.46	2318.	4140.	598.4	1044.4	133.2	397.8	398.8	39.8	56.0	PCT-06.0
13.64	1883.	3364.	476.4	826.6	106.0	312.8	309.6	31.8	38.6	PCT-06.5
13.38	2185.	3828.	554.2	945.2	120.6	355.2	372.8	37.6	42.4	PCT-07.0
11.58	1871.	3187.	459.4	778.6	97.2	294.4	330.4	32.8	41.8	PCT-07.5
8.24	1481.	2449.	340.0	588.6	72.4	217.4	268.6	27.4	29.0	PCT-08.0
9.08	929.	1494.	194.2	355.8	43.2	131.4	167.4	18.2	21.8	PCT-08.5
4.16	739.	1204.	153.0	278.8	33.4	108.2	138.8	15.8	25.0	PCT-09.0
2.56	324.	515.	63.2	117.2	13.2	50.6	79.2	10.4	20.4	PCT-09.5
60.84	8296.	16158.	952.0	4530.0	564.0	1588.8	1373.6	145.2	172.0	BOT-SED-04.0
58.92	8140.	15889.	1005.2	4456.4	553.2	1558.0	1384.4	146.0	164.4	BOT-SED-04.5
56.40	6961.	13352.	816.0	3709.6	460.8	1303.2	1172.0	121.6	141.6	BOT-SED-05.0
54.40	7941.	15209.	920.8	4242.0	526.4	1489.6	1359.2	140.4	160.4	BOT-SED-05.5
42.88	6108.	11006.	583.6	3022.8	367.6	1060.4	1052.0	108.4	120.0	BOT-SED-06.0
34.32	6134.	10622.	483.6	2914.8	350.8	1012.4	1049.2	107.6	116.8	BOT-SED-06.5
29.36	5273.	8878.	333.6	2393.6	285.2	825.2	913.2	90.0	80.0	BOT-SED-07.0
16.96	3442.	5617.	170.0	1496.8	170.8	509.6	616.8	93.2	52.4	BOT-SED-07.5
11.72	2590.	4109.	107.2	1081.2	123.2	371.6	464.4	48.0	36.8	BOT-SED-08.0
12.28	2548.	4089.	104.4	1076.4	123.2	375.6	460.8	48.4	36.0	BOT-SED-08.5
10.48	2329.	3716.	96.0	969.6	108.8	332.4	429.2	43.6	34.4	BOT-SED-09.0
5.24	1108.	1727.	42.0	445.6	46.4	154.4	218.8	23.6	20.4	BOT-SED-09.5

(BDL = BELOW DETECTION LIMIT; N.A. = NOT ANALYSED)

TABLE E.12

Ratios to Al -
 pipette samples, inner estuary.

RATIOS TO AL (SAMPLE SUITE: GHFRBPPT)

SI/AL	CA/AL	FE/AL	TI/AL	K/AL	MG/AL	P/AL	S/AL	NAME
1.81	0.259	0.456	0.059	0.171	0.168	0.017	0.020	PCT-04.0
1.82	0.256	0.457	0.059	0.177	0.176	0.017	0.024	PCT-04.5
1.91	0.276	0.474	0.061	0.188	0.196	0.019	0.035	PCT-05.0
1.79	0.259	0.448	0.058	0.172	0.171	0.016	0.022	PCT-05.5
1.79	0.262	0.451	0.057	0.172	0.172	0.017	0.024	PCT-06.0
1.79	0.253	0.439	0.056	0.166	0.164	0.017	0.020	PCT-06.5
1.75	0.254	0.433	0.055	0.163	0.171	0.017	0.019	PCT-07.0
1.70	0.246	0.416	0.052	0.157	0.177	0.018	0.022	PCT-07.5
1.65	0.230	0.397	0.049	0.147	0.181	0.019	0.020	PCT-08.0
1.61	0.209	0.383	0.047	0.142	0.180	0.020	0.023	PCT-08.5
1.63	0.207	0.377	0.045	0.146	0.188	0.021	0.034	PCT-09.0
1.59	0.195	0.362	0.041	0.156	0.244	0.032	0.063	PCT-09.5
1.95	0.115	0.546	0.068	0.192	0.166	0.018	0.021	ROT-SED-04.0
1.95	0.123	0.547	0.068	0.191	0.170	0.018	0.020	ROT-SED-04.5
1.92	0.117	0.533	0.066	0.187	0.168	0.017	0.020	ROT-SED-05.0
1.92	0.116	0.534	0.066	0.188	0.171	0.018	0.020	ROT-SED-05.5
1.80	0.096	0.495	0.060	0.174	0.172	0.018	0.020	ROT-SED-06.0
1.73	0.079	0.475	0.057	0.165	0.171	0.018	0.019	ROT-SED-06.5
1.68	0.063	0.454	0.054	0.156	0.173	0.017	0.015	ROT-SED-07.0
1.63	0.049	0.435	0.050	0.148	0.179	0.027	0.015	ROT-SED-07.5
1.59	0.041	0.418	0.048	0.143	0.179	0.019	0.014	ROT-SED-08.0
1.60	0.041	0.422	0.048	0.147	0.181	0.019	0.014	ROT-SED-08.5
1.60	0.041	0.416	0.047	0.143	0.184	0.019	0.015	ROT-SED-09.0
1.56	0.038	0.402	0.042	0.139	0.197	0.021	0.018	ROT-SED-09.5

APPENDIX F

Gravimetric and chemical data for suspended particulate matter samples collected during tidal station monitoring.

The sample names shown (e.g. 26-0855-00) refer to the station location, the time of sampling (GMT) and the sampling depth in meters. BDL indicates that the XRF counts received were exceeded by those of the blank filter.

- i) Concentration of particulate elements - tidal station 26
(Table F.1)
- ii) Ratios to Al - tidal station 26 (Table F.2)
- iii) Concentration of particulate elements - tidal station 15
(Table F.3)
- iv) Ratios to Al - tidal station 15 (Table F.4)
- v) Concentration of particulate elements - tidal station 7
(Table F.5)
- vi) Ratios to Al - tidal station 7 (Table F.6)

TABLE F.1

Concentration of particulate elements -
tidal station 26.RATIOS TO VOLUME (SAMPLE SUITE: GP26TYD)
TSL IN MG/L, ELEMENTS IN MICROGRAMS/L

TSL/VOL	AL/VOL	SI/VOL	CA/VOL	FE/VOL	TI/VOL	K/VOL	MG/VOL	P/VOL	S/VOL	NAME
14.20	2028.	3822.	435.3	955.2	127.1	365.0	305.5	25.3	56.7	26-0855-00
15.09	2158.	4122.	475.8	1009.1	136.2	395.0	334.1	27.3	57.7	26-0855-05
13.38	1940.	3596.	421.8	908.5	120.0	351.1	80L	23.2	62.0	26-0855-10
14.55	1953.	3653.	459.5	921.8	127.0	354.2	317.4	23.5	66.8	26-0855-17
11.85	1771.	3222.	352.9	777.0	106.8	302.3	151.5	18.6	43.8	26-0855-27
13.74	2145.	3897.	461.8	962.7	131.2	372.0	200.0	27.9	59.5	26-0955-00
13.64	2070.	3786.	427.6	933.5	123.6	366.5	203.0	24.5	57.1	26-0955-05
13.29	1804.	3225.	325.3	763.8	105.3	308.9	170.3	20.8	47.3	26-0955-10
15.09	2282.	4129.	467.4	1071.8	141.8	407.3	220.8	26.7	66.4	26-0955-20
15.06	2179.	4003.	477.4	996.1	135.5	387.6	210.3	26.8	66.4	26-0955-27
7.76	1297.	2260.	275.0	520.8	71.5	210.0	160.5	16.7	43.6	26-1055-00
11.30	1672.	3159.	359.8	748.9	103.6	289.7	258.8	20.6	50.8	26-1055-05
11.91	1825.	3276.	401.2	786.8	111.8	302.1	80L	22.9	48.0	26-1055-10
13.61	2090.	3777.	471.7	930.6	131.1	358.2	188.6	24.7	56.4	26-1055-20
25.39	3653.	203.	852.9	1760.6	242.6	8.3	365.3	42.3	85.5	26-1055-27
8.20	1252.	2241.	275.3	508.0	70.6	201.4	120.6	15.6	36.7	26-1155-00
7.55	1112.	1937.	173.5	436.8	63.8	167.1	94.7	13.8	41.2	26-1155-05
7.02	1072.	1849.	224.1	432.1	61.2	164.2	122.1	13.9	45.8	26-1155-10
10.26	1335.	2411.	332.3	584.4	80.9	238.8	133.9	17.9	59.4	26-1155-20
14.17	1959.	3623.	468.6	953.6	128.6	357.9	196.4	22.9	62.1	26-1155-28
11.00	1544.	2866.	398.5	687.3	98.5	267.0	238.5	19.1	52.9	26-1301-00
11.09	1661.	3044.	373.3	739.5	105.2	285.0	214.5	18.9	46.7	26-1301-05
13.08	1891.	3476.	466.2	862.6	115.9	337.4	184.8	21.5	60.0	26-1301-10
12.44	1780.	3338.	438.8	826.8	115.3	314.1	322.3	21.2	51.1	26-1301-20
12.62	1874.	3424.	457.0	809.5	114.4	322.4	168.0	21.1	52.1	26-1301-28
7.26	1159.	2076.	262.3	492.6	68.8	188.6	209.7	15.0	37.1	26-1400-00
10.58	1616.	2867.	360.5	677.9	96.1	265.2	147.4	18.5	42.6	26-1400-05
18.29	2778.	4947.	577.1	1288.9	181.5	476.1	257.4	29.2	72.4	26-1400-10
20.74	2977.	5477.	719.7	1419.2	198.0	533.8	277.6	32.4	68.2	26-1400-20
24.05	3292.	6175.	779.1	1690.8	237.4	614.1	490.6	33.9	81.4	26-1400-30
8.89	1148.	2171.	317.4	518.0	72.9	204.2	184.5	14.8	44.1	26-1500-00
7.98	1161.	2000.	245.6	452.1	65.0	178.3	114.4	13.0	34.7	26-1500-05
11.79	1707.	3065.	385.6	727.4	104.7	280.2	138.3	19.4	40.6	26-1500-10
18.64	2662.	4834.	663.9	1267.6	177.7	473.5	238.3	28.2	56.4	26-1500-20
31.64	4075.	7767.	1032.0	2210.2	297.6	798.2	616.7	43.2	92.6	26-1500-33
7.18	1052.	1907.	262.6	463.9	62.0	174.5	165.2	14.7	35.5	26-1600-00
5.76	918.	1615.	212.1	336.1	49.7	137.7	80L	11.2	24.4	26-1600-05
7.26	1187.	2160.	263.6	515.0	74.7	200.5	181.5	13.8	39.4	26-1600-10
10.39	1580.	2835.	405.0	691.8	93.8	273.2	155.3	17.6	41.7	26-1600-20
12.41	1697.	3158.	465.9	794.8	107.9	319.5	351.1	20.6	41.5	26-1600-25
18.67	2676.	4892.	711.4	1298.2	175.9	485.3	257.6	30.8	59.2	26-1600-30
9.15	1293.	2405.	273.3	647.4	78.9	223.3	134.7	16.7	34.5	26-1700-00
6.74	917.	1660.	225.5	373.6	53.3	154.5	152.7	11.2	37.4	26-1700-05
6.24	922.	1602.	213.0	354.1	50.9	140.5	80L	11.1	23.6	26-1700-10
7.11	1046.	1861.	248.3	423.2	62.3	162.3	181.1	13.0	23.0	26-1700-20
7.98	1190.	2068.	244.1	477.6	69.7	185.2	133.5	15.3	29.2	26-1700-25
7.65	1181.	2113.	275.0	480.9	71.4	190.0	167.9	15.9	26.1	26-1700-30
9.41	1450.	2572.	324.8	612.9	84.2	238.9	157.9	19.4	37.1	26-1800-00
9.14	1400.	2477.	307.9	577.7	83.0	227.4	127.6	17.3	29.7	26-1800-05
9.39	1597.	2810.	342.9	667.0	92.7	263.0	129.1	19.2	33.9	26-1800-10
11.88	1862.	3301.	415.0	833.3	113.2	315.3	165.0	21.7	41.2	26-1800-20
10.44	1677.	2929.	363.6	730.5	101.4	280.3	162.3	20.6	39.4	26-1800-25
24.85	3523.	6442.	856.7	1720.9	235.2	628.0	80L	40.2	63.8	26-1800-30
14.45	1448.	2726.	315.5	658.6	90.3	260.3	228.8	17.0	33.3	26-1900-00
14.73	2276.	4192.	501.2	1025.6	137.3	395.0	222.6	27.1	45.9	26-1900-05
18.85	2627.	4950.	594.1	1280.8	172.6	477.4	288.8	31.8	57.1	26-1900-10
16.14	2439.	4476.	548.0	1180.6	156.2	436.5	232.0	27.0	45.2	26-1900-20
24.58	3448.	6360.	790.9	1687.9	224.0	631.5	307.9	39.4	70.2	26-1900-25
31.32	4147.	7765.	1018.9	2146.2	281.5	814.2	392.6	49.2	100.5	26-1900-30
19.74	2585.	4995.	607.1	1283.3	171.8	485.0	212.7	29.8	50.3	26-2000-00
16.97	2512.	4746.	577.4	1201.8	161.4	466.1	225.0	28.6	49.1	26-2000-05
16.70	2364.	4377.	538.9	1141.5	151.8	427.9	214.1	28.3	47.0	26-2000-10
22.24	2844.	5517.	669.1	1428.2	192.7	543.6	280.9	32.9	60.5	26-2000-20
22.67	3110.	5860.	734.7	1546.4	204.0	576.7	274.4	33.3	56.8	26-2000-25
22.15	2803.	5516.	705.0	1416.5	194.8	539.2	402.4	32.4	56.7	26-2000-30
29.83	3856.	7536.	910.2	2037.4	264.1	765.6	395.2	45.5	62.4	26-2100-00
22.48	3123.	5890.	700.8	1540.0	203.2	550.9	304.5	35.9	60.0	26-2100-05
20.49	2914.	5477.	645.9	1445.3	187.1	537.1	238.3	33.6	55.2	26-2100-10
23.11	2990.	5817.	714.8	1575.9	208.2	586.3	292.4	37.7	74.7	26-2100-20
23.08	3034.	5888.	766.5	1502.4	198.8	583.8	272.1	36.4	65.9	26-2100-25
22.14	2634.	5100.	583.5	1347.4	176.8	499.5	80L	29.1	51.2	26-2100-30

(80L = BELOW DETECTION LIMIT; N.A. = NOT ANALYSED)

TABLE F.2

Ratios to Al -
tidal station 26.

RATIOS TO AL (SAMPLE SUITE: GH26TYD)

SI/AL	CA/AL	FE/AL	TI/AL	K/AL	MG/AL	P/AL	S/AL	NAME
1.88	0.215	0.471	0.063	0.180	0.151	0.012	0.028	26-0855-00
1.91	0.220	0.468	0.063	0.183	0.155	0.013	0.027	26-0855-05
1.85	0.217	0.468	0.062	0.181		0.012	0.032	26-0855-10
1.87	0.235	0.472	0.065	0.181	0.163	0.012	0.034	26-0855-17
1.82	0.199	0.439	0.060	0.171	0.086	0.011	0.025	26-0855-27
1.82	0.215	0.449	0.061	0.173	0.093	0.013	0.028	26-0955-00
1.83	0.207	0.451	0.060	0.177	0.098	0.012	0.028	26-0955-05
1.79	0.180	0.423	0.058	0.171	0.094	0.012	0.026	26-0955-10
1.81	0.205	0.470	0.062	0.178	0.097	0.012	0.029	26-0955-20
1.84	0.219	0.457	0.062	0.178	0.097	0.012	0.030	26-0955-27
1.74	0.212	0.402	0.055	0.162	0.124	0.013	0.034	26-1055-00
1.89	0.215	0.448	0.062	0.173	0.155	0.012	0.030	26-1055-05
1.79	0.220	0.431	0.061	0.166		0.013	0.026	26-1055-10
1.81	0.226	0.445	0.063	0.171	0.090	0.012	0.027	26-1055-20
0.06	0.233	0.482	0.066	0.002	0.100	0.012	0.023	26-1055-27
1.79	0.220	0.406	0.056	0.161	0.096	0.012	0.029	26-1155-00
1.74	0.156	0.393	0.057	0.150	0.085	0.012	0.037	26-1155-05
1.73	0.209	0.403	0.057	0.153	0.114	0.013	0.043	26-1155-10
1.81	0.249	0.438	0.061	0.179	0.100	0.013	0.044	26-1155-20
1.85	0.239	0.487	0.066	0.183	0.100	0.012	0.032	26-1155-28
1.86	0.258	0.445	0.064	0.173	0.154	0.012	0.034	26-1301-00
1.83	0.225	0.445	0.063	0.172	0.129	0.011	0.028	26-1301-05
1.84	0.247	0.456	0.061	0.178	0.098	0.011	0.032	26-1301-10
1.88	0.246	0.464	0.065	0.176	0.181	0.012	0.029	26-1301-20
1.83	0.244	0.432	0.061	0.172	0.090	0.011	0.028	26-1301-28
1.79	0.226	0.425	0.059	0.163	0.181	0.013	0.032	26-1400-00
1.77	0.223	0.420	0.059	0.164	0.091	0.011	0.026	26-1400-05
1.78	0.208	0.464	0.065	0.171	0.093	0.011	0.026	26-1400-10
1.84	0.242	0.477	0.067	0.179	0.093	0.011	0.023	26-1400-20
1.88	0.237	0.514	0.072	0.187	0.149	0.010	0.025	26-1400-30
1.89	0.276	0.451	0.063	0.178	0.161	0.013	0.038	26-1500-00
1.72	0.212	0.390	0.056	0.154	0.099	0.011	0.030	26-1500-05
1.80	0.226	0.426	0.061	0.164	0.081	0.011	0.024	26-1500-10
1.82	0.249	0.476	0.067	0.178	0.090	0.011	0.021	26-1500-20
1.91	0.253	0.542	0.073	0.196	0.151	0.011	0.023	26-1500-33
1.81	0.250	0.441	0.059	0.166	0.157	0.014	0.034	26-1600-00
1.76	0.231	0.366	0.054	0.150		0.012	0.027	26-1600-05
1.82	0.222	0.434	0.063	0.169	0.153	0.012	0.033	26-1600-10
1.79	0.256	0.438	0.059	0.173	0.098	0.011	0.026	26-1600-20
1.86	0.275	0.469	0.064	0.188	0.207	0.012	0.024	26-1600-25
1.83	0.266	0.485	0.066	0.181	0.096	0.011	0.022	26-1600-30
1.86	0.211	0.501	0.061	0.173	0.104	0.013	0.027	26-1700-00
1.81	0.246	0.408	0.058	0.169	0.167	0.012	0.041	26-1700-05
1.74	0.231	0.384	0.055	0.152		0.012	0.026	26-1700-10
1.78	0.237	0.405	0.060	0.155	0.173	0.012	0.022	26-1700-20
1.75	0.241	0.405	0.059	0.157	0.113	0.013	0.025	26-1700-25
1.79	0.233	0.407	0.060	0.161	0.142	0.013	0.022	26-1700-30
1.77	0.224	0.423	0.058	0.165	0.109	0.013	0.026	26-1800-00
1.77	0.220	0.413	0.059	0.162	0.091	0.012	0.021	26-1800-05
1.76	0.215	0.418	0.058	0.165	0.087	0.012	0.021	26-1800-10
1.77	0.223	0.444	0.061	0.169	0.089	0.012	0.022	26-1800-20
1.75	0.217	0.436	0.060	0.167	0.097	0.012	0.023	26-1800-25
1.83	0.243	0.488	0.067	0.178		0.011	0.018	26-1800-30
1.88	0.218	0.435	0.062	0.180	0.158	0.012	0.023	26-1900-00
1.84	0.220	0.451	0.060	0.174	0.098	0.012	0.020	26-1900-05
1.88	0.226	0.488	0.066	0.182	0.110	0.012	0.022	26-1900-10
1.83	0.225	0.484	0.064	0.179	0.095	0.011	0.019	26-1900-20
1.85	0.229	0.490	0.066	0.183	0.089	0.011	0.020	26-1900-25
1.87	0.246	0.518	0.068	0.196	0.095	0.012	0.024	26-1900-30
1.93	0.235	0.496	0.066	0.188	0.082	0.012	0.019	26-2000-00
1.89	0.230	0.478	0.064	0.186	0.090	0.011	0.020	26-2000-05
1.85	0.228	0.482	0.064	0.181	0.090	0.012	0.020	26-2000-10
1.94	0.235	0.502	0.068	0.191	0.099	0.012	0.021	26-2000-20
1.88	0.236	0.497	0.067	0.185	0.088	0.011	0.018	26-2000-25
1.97	0.252	0.505	0.070	0.192	0.144	0.012	0.020	26-2000-30
1.95	0.236	0.528	0.068	0.199	0.102	0.012	0.021	26-2100-00
1.90	0.226	0.497	0.066	0.187	0.099	0.012	0.019	26-2100-05
1.88	0.222	0.496	0.064	0.184	0.082	0.012	0.019	26-2100-10
1.94	0.240	0.526	0.070	0.197	0.098	0.013	0.025	26-2100-20
1.94	0.233	0.495	0.065	0.192	0.090	0.012	0.022	26-2100-25
1.94	0.221	0.511	0.067	0.190		0.011	0.019	26-2100-30

TABLE F.3

Concentration of particulate elements -
tidal station 15.

RATIOS TO VOLUME (SAMPLE SUITE: 015127)
TSL IN MG/L, ELEMENTS IN MICROGRAMS/L

TSL/VOL	AL/VOL	SI/VOL	CA/VOL	FE/VOL	VI/VOL	K/VOL	MG/VOL	P/VOL	S/VOL	NAME
2.44	195.	365.	26.2	81.8	10.9	30.2	30.4	4.8	4.1	15-0902-00
2.52	180.	337.	58.3	80.6	10.0	28.8	36.4	5.5	5.8	15-0902-05
2.55	182.	337.	66.7	73.3	10.5	35.3	48.3	5.6	12.9	15-0902-10
3.75	560.	762.	167.3	180.8	22.0	73.8	78.2	6.9	10.6	15-0902-20
3.28	555.	751.	175.6	181.5	21.8	75.8	76.3	6.2	12.1	15-0902-25
1.96	186.	344.	67.6	82.7	10.5	32.7	58.0	5.0	8.9	15-1006-00
6.68	182.	321.	57.0	78.1	9.9	26.6	31.6	5.8	3.5	15-1006-05
1.66	165.	303.	61.1	78.8	9.2	31.8	32.6	4.8	7.1	15-1006-10
2.58	213.	399.	78.2	98.3	12.0	36.4	42.2	7.1	6.2	15-1006-15
2.92	319.	661.	152.7	157.0	18.4	66.0	68.1	6.5	9.1	15-1006-20
3.21	361.	761.	173.7	176.7	20.9	76.8	76.2	7.0	7.4	15-1006-25
3.39	171.	311.	58.9	76.2	8.8	27.6	34.0	4.7	5.6	15-1104-00
1.94	163.	294.	55.9	75.4	9.0	26.8	31.8	4.5	2.9	15-1104-05
1.67	134.	236.	43.0	57.3	6.6	20.8	24.7	3.7	3.4	15-1104-10
3.73	218.	427.	98.2	99.9	12.3	41.6	44.4	5.3	5.0	15-1104-15
4.24	355.	739.	171.1	178.6	21.8	80.7	83.0	7.1	12.0	15-1104-20
3.04	334.	701.	156.5	163.9	19.0	69.2	65.2	6.3	6.6	15-1104-26
1.43	169.	301.	56.9	69.8	8.6	26.9	32.1	6.1	4.5	15-1205-00
1.61	172.	309.	61.5	73.5	8.9	30.6	41.1	4.9	8.8	15-1205-10
1.41	247.	492.	117.2	107.8	13.4	49.7	58.3	6.1	7.7	15-1205-15
2.81	209.	663.	155.9	151.8	17.7	65.3	80.1	7.4	6.9	15-1205-20
4.52	422.	920.	215.4	214.5	26.3	99.1	99.1	7.4	15.0	15-1205-26
1.41	137.	247.	47.7	57.1	7.1	22.0	27.1	4.2	4.7	15-1304-00
1.76	179.	310.	58.0	70.4	8.9	31.5	32.8	6.9	5.2	15-1304-05
1.58	195.	362.	65.8	82.1	9.9	32.7	37.7	4.9	4.7	15-1304-10
1.79	230.	465.	107.6	102.9	12.2	44.9	47.7	5.0	4.5	15-1304-15
3.13	369.	1898.	182.6	177.1	21.1	78.2	78.7	6.5	6.7	15-1304-20
4.50	508.	1128.	259.9	264.8	32.1	115.5	107.9	9.0	9.2	15-1304-26
1.77	145.	248.	46.0	57.6	95.1	21.9	26.3	5.8	1.3	15-1410-00
1.70	152.	281.	50.3	63.1	7.6	22.7	27.0	8.1	3.5	15-1410-05
1.59	152.	282.	57.8	67.4	7.9	26.1	31.5	6.6	4.3	15-1410-10
2.01	202.	451.	97.3	86.1	10.2	38.1	43.1	5.0	4.7	15-1410-15
3.56	358.	764.	186.4	175.2	20.7	76.6	73.9	6.1	6.1	15-1410-20
4.28	426.	929.	219.6	219.2	25.5	94.8	90.4	6.8	9.5	15-1410-28
1.50	147.	262.	51.3	62.1	7.3	24.0	30.8	4.4	6.0	15-1500-00
1.44	162.	290.	55.1	69.1	8.1	26.1	31.3	4.0	4.3	15-1500-05
1.41	162.	305.	71.2	67.1	6.8	28.3	32.8	4.6	3.6	15-1500-10
4.79	457.	1029.	251.3	243.7	28.4	105.5	97.5	8.1	9.0	15-1500-20
4.47	474.	1066.	256.0	246.6	32.3	108.2	102.0	8.3	9.1	15-1500-25
3.57	477.	1068.	256.4	246.8	30.3	108.1	102.2	6.5	9.5	15-1500-29
1.50	174.	298.	48.7	216.2	102.8	26.0	29.9	4.3	4.0	15-1600-00
1.43	159.	276.	53.9	63.0	8.5	25.5	31.9	4.3	3.6	15-1600-05
1.29	165.	298.	58.6	66.9	8.1	25.8	30.9	4.3	2.5	15-1600-10
3.00	346.	729.	185.2	165.7	211.4	73.1	73.3	5.9	5.2	15-1600-20
3.77	432.	962.	237.4	220.3	26.2	97.2	90.6	8.0	7.4	15-1600-25
4.08	433.	954.	235.2	220.3	27.4	103.1	92.0	10.3	10.6	15-1600-28
1.39	177.	306.	55.4	78.7	9.0	27.6	35.1	6.4	5.0	15-1700-00
1.40	169.	301.	59.4	73.4	9.2	27.6	34.8	7.3	6.4	15-1700-05
1.56	170.	339.	75.4	73.8	8.6	29.1	36.1	9.8	6.5	15-1700-10
2.96	352.	766.	192.1	169.8	19.4	77.6	77.0	8.4	7.7	15-1700-20
3.88	450.	991.	254.0	230.5	27.5	105.3	97.2	11.5	10.1	15-1700-25
3.90	449.	978.	234.4	227.7	26.5	100.4	96.1	9.3	8.9	15-1700-30
1.41	174.	284.	50.3	75.4	8.5	24.0	30.4	7.1	4.7	15-1800-00
1.17	159.	278.	48.4	66.5	8.0	24.1	29.1	5.8	4.0	15-1800-05
1.35	167.	275.	53.5	65.2	7.7	23.6	28.9	7.0	2.1	15-1800-10
3.62	315.	660.	172.8	153.7	17.9	71.2	67.6	7.3	7.5	15-1800-20
3.89	372.	805.	199.1	182.0	21.2	81.6	80.2	6.8	7.0	15-1800-25
4.04	432.	931.	224.9	219.5	21.2	95.4	91.0	8.7	8.0	15-1800-29
1.37	156.	279.	57.1	66.4	8.0	26.5	32.4	5.4	7.2	15-1900-00
1.35	174.	307.	59.8	72.5	8.5	28.8	34.0	9.4	3.4	15-1900-05
1.45	167.	298.	57.3	73.9	8.7	26.9	31.5	6.0	4.3	15-1900-10
2.21	264.	548.	147.6	124.0	14.5	56.9	62.5	7.0	6.9	15-1900-20
2.73	319.	689.	170.3	153.3	17.9	68.8	69.9	6.6	7.9	15-1900-25
3.18	393.	842.	213.0	192.4	23.4	87.3	88.7	9.4	10.2	15-1900-30
16.79	158.	286.	56.6	68.3	8.0	27.3	31.4	3.4	5.5	15-2000-00
1.44	147.	248.	40.9	69.6	8.4	28.8	30.1	7.6	6.1	15-2000-05
1.54	177.	327.	71.0	76.4	9.2	31.6	37.3	6.8	6.5	15-2000-10
1.66	189.	364.	89.6	81.4	9.4	36.0	42.7	7.6	6.5	15-2000-15
2.12	161.	307.	138.6	124.9	14.8	56.5	58.4	7.3	5.2	15-2000-20
4.92	523.	1167.	279.0	281.7	32.4	122.5	111.7	10.1	10.3	15-2000-30
1.45	158.	287.	58.0	68.5	8.2	26.9	35.4	5.5	5.7	15-2100-05
1.35	157.	282.	58.5	66.5	8.2	26.5	34.8	8.3	6.3	15-2100-10
1.49	174.	337.	70.7	78.0	10.0	31.8	38.3	5.8	5.7	15-2100-15
3.11	308.	785.	184.9	180.5	21.3	78.9	79.7	8.5	8.2	15-2100-20
3.74	436.	929.	220.4	220.4	24.5	96.0	96.2	6.7	9.9	15-2100-28

(BOL = BELOW DETECTION LIMIT; N.A. = NOT ANALYSED)

TABLE F.4

Ratios to Al - tidal station 15.

RATIOS TO AL (SAMPLE SUITE: GH15TYD)

SI/AL	CA/AL	FE/AL	TI/AL	K/AL	MG/AL	P/AL	S/AL	NAME
1.87	0.103	0.420	0.056	0.155	0.158	0.025	0.021	15-0902-00
1.87	0.324	0.448	0.056	0.160	0.202	0.030	0.032	15-0902-05
1.85	0.366	0.402	0.060	0.194	0.265	0.032	0.071	15-0902-10
2.12	0.464	0.502	0.061	0.205	0.217	0.019	0.029	15-0902-20
2.12	0.496	0.512	0.062	0.214	0.215	0.017	0.034	15-0902-25
1.91	0.364	0.445	0.056	0.176	0.205	0.027	0.048	15-1006-00
1.76	0.312	0.428	0.054	0.146	0.173	0.032	0.019	15-1006-05
1.84	0.370	0.454	0.056	0.193	0.198	0.029	0.043	15-1006-10
1.87	0.366	0.451	0.056	0.171	0.198	0.033	0.029	15-1006-15
2.07	0.480	0.493	0.058	0.267	0.214	0.021	0.029	15-1006-20
2.11	0.481	0.489	0.059	0.213	0.211	0.019	0.020	15-1006-25
1.82	0.344	0.446	0.051	0.162	0.199	0.027	0.033	15-1104-00
1.84	0.344	0.464	0.055	0.160	0.195	0.028	0.018	15-1104-05
1.78	0.322	0.429	0.050	0.156	0.185	0.027	0.025	15-1104-10
1.96	0.451	0.459	0.056	0.191	0.204	0.024	0.023	15-1104-15
2.09	0.483	0.504	0.061	0.228	0.234	0.020	0.034	15-1104-20
2.10	0.469	0.491	0.057	0.207	0.195	0.019	0.020	15-1104-26
1.78	0.336	0.412	0.051	0.159	0.190	0.036	0.026	15-1205-00
1.80	0.358	0.427	0.052	0.178	0.239	0.028	0.051	15-1205-10
1.99	0.475	0.437	0.054	0.201	0.236	0.025	0.031	15-1205-15
3.17	0.746	0.727	0.085	0.313		0.035	0.033	15-1205-20
2.18	0.510	0.508	0.062	0.235	0.235	0.017	0.036	15-1205-26
1.80	0.348	0.416	0.051	0.161	0.198	0.031	0.034	15-1304-00
1.74	0.325	0.394	0.050	0.177	0.184	0.039	0.029	15-1304-05
1.86	0.358	0.420	0.051	0.167	0.193	0.025	0.024	15-1304-10
2.02	0.467	0.447	0.053	0.195	0.207	0.022	0.019	15-1304-15
5.14	0.495	0.479	0.057	0.212	0.213	0.018	0.018	15-1304-20
2.22	0.511	0.521	0.063	0.227	0.212	0.018	0.018	15-1304-26
1.71	0.317	0.396	0.055	0.151	0.181	0.040	0.009	15-1410-00
1.71	0.328	0.415	0.050	0.149	0.178	0.053	0.023	15-1410-05
1.86	0.380	0.444	0.052	0.172	0.207	0.044	0.028	15-1410-10
2.23	0.481	0.426	0.051	0.189	0.213	0.025	0.023	15-1410-15
2.13	0.521	0.489	0.058	0.214	0.206	0.017	0.017	15-1410-20
2.18	0.516	0.515	0.061	0.223	0.212	0.021	0.022	15-1410-28
1.78	0.348	0.421	0.049	0.162	0.209	0.030	0.041	15-1500-00
1.79	0.339	0.425	0.050	0.161	0.193	0.025	0.027	15-1500-05
1.89	0.440	0.415	0.054	0.175	0.203	0.029	0.022	15-1500-10
2.25	0.550	0.534	0.062	0.231	0.214	0.018	0.020	15-1500-20
2.25	0.540	0.520	0.068	0.228	0.215	0.018	0.019	15-1500-25
2.24	0.542	0.518	0.063	0.227	0.214	0.018	0.020	15-1500-29
1.71	0.280	0.444	0.0591	0.150	0.172	0.025	0.023	15-1600-00
1.74	0.339	0.396	0.054	0.161	0.201	0.027	0.022	15-1600-05
1.81	0.356	0.404	0.049	0.156	0.187	0.026	0.015	15-1600-10
2.11	0.535	0.479	0.061	0.211	0.212	0.017	0.015	15-1600-20
2.23	0.550	0.510	0.061	0.225	0.210	0.019	0.017	15-1600-25
2.20	0.543	0.509	0.063	0.238	0.213	0.024	0.025	15-1600-28
1.73	0.312	0.444	0.051	0.155	0.198	0.036	0.028	15-1700-00
1.78	0.352	0.415	0.055	0.163	0.200	0.043	0.038	15-1700-05
1.82	0.444	0.434	0.051	0.171	0.224	0.058	0.038	15-1700-10
2.18	0.546	0.483	0.057	0.221	0.219	0.024	0.022	15-1700-20
2.20	0.564	0.512	0.061	0.234	0.216	0.026	0.022	15-1700-25
2.18	0.522	0.507	0.059	0.224	0.214	0.021	0.020	15-1700-30
1.66	0.289	0.433	0.049	0.138	0.175	0.041	0.027	15-1800-00
1.75	0.304	0.418	0.050	0.151	0.183	0.036	0.025	15-1800-05
1.65	0.321	0.391	0.047	0.142	0.174	0.042	0.012	15-1800-10
2.10	0.549	0.488	0.057	0.226	0.215	0.023	0.024	15-1800-20
2.16	0.535	0.489	0.057	0.219	0.216	0.018	0.019	15-1800-25
2.16	0.521	0.509	0.049	0.221	0.211	0.020	0.018	15-1800-29
1.79	0.366	0.426	0.051	0.170	0.208	0.035	0.046	15-1900-00
1.76	0.344	0.417	0.049	0.165	0.195	0.054	0.020	15-1900-05
1.79	0.343	0.443	0.052	0.161	0.189	0.036	0.026	15-1900-10
2.08	0.559	0.470	0.055	0.216	0.237	0.027	0.026	15-1900-20
2.10	0.533	0.480	0.056	0.215	0.219	0.021	0.025	15-1900-25
2.14	0.542	0.490	0.060	0.222	0.226	0.024	0.025	15-1900-30
1.82	0.358	0.431	0.051	0.172	0.198	0.021	0.035	15-2000-00
1.79	0.365	0.419	0.050	0.173		0.045	0.037	15-2000-05
1.84	0.401	0.431	0.052	0.178	0.210	0.038	0.037	15-2000-10
1.92	0.475	0.431	0.050	0.191	0.226	0.040	0.034	15-2000-15
3.51	0.859	0.774	0.092	0.350	0.362	0.045	0.032	15-2000-20
2.23	0.534	0.539	0.062	0.234	0.214	0.019	0.020	15-2000-30
1.82	0.368	0.435	0.052	0.170	0.225	0.060	0.036	15-2100-05
1.80	0.374	0.424	0.052	0.182	0.222	0.053	0.040	15-2100-10
1.89	0.442	0.438	0.056	0.179	0.215	0.033	0.032	15-2100-15
2.13	0.502	0.490	0.058	0.214	0.216	0.023	0.022	15-2100-20
2.14	0.507	0.507	0.061	0.221	0.221	0.020	0.023	15-2100-28

TABLE F.5

Concentration of particulate elements -
tidal station 7.

RATIOS TO VOLUME (SAMPLE SUITE: GH77TYD)
TSL IN MG/L, ELEMENTS IN MICROGRAMS/L

TSL/VOL	AL/VOL	SI/VOL	CA/VOL	FE/VOL	TI/VOL	K/VOL	MG/VOL	P/VOL	S/VOL	NAME
4.86	228.	564.	69.2	106.8	14.5	39.8	39.1	16.1	7.7	77-0815-00
5.64	260.	633.	92.6	136.1	18.0	44.7	46.7	17.7	18.3	77-0815-05
5.61	268.	660.	79.8	143.2	21.8	46.2	52.1	17.9	12.3	77-0815-08
1.91	226.	559.	57.6	106.0	12.1	39.3	40.2	15.9	9.2	77-0915-03
1.95	232.	567.	72.4	111.3	21.6	39.2	41.3	17.3	9.0	77-0915-05
2.08	232.	576.	62.7	109.2	14.8	40.8	44.5	16.3	8.4	77-0915-08
2.13	234.	595.	67.1	114.7	14.8	39.7	43.8	16.0	9.2	77-1015-06
2.24	249.	619.	64.0	120.3	13.2	43.0	46.1	16.0	12.9	77-1015-05
2.08	241.	620.	67.3	117.6	15.0	42.3	43.8	15.0	8.9	77-1015-08
2.02	218.	552.	60.0	103.4	12.9	38.6	40.7	15.4	7.9	77-1115-00
2.01	236.	604.	63.4	109.9	14.8	42.0	42.9	16.9	2.5	77-1115-05
2.58	276.	701.	106.6	129.5	17.0	48.9	54.3	32.1	12.7	77-1115-09
1.96	218.	577.	58.9	102.6	12.0	39.2	40.8	15.4	8.9	77-1215-00
2.24	262.	680.	66.9	130.5	16.6	47.6	44.1	15.0	9.2	77-1215-05
2.79	306.	847.	90.8	155.6	20.6	59.2	55.5	17.3	13.4	77-1215-10
2.27	221.	570.	51.8	99.7	12.6	37.6	37.6	16.0	6.2	77-1315-00
2.15	303.	820.	78.5	141.5	18.2	56.2	52.5	14.9	11.1	77-1315-05
2.73	217.	560.	61.5	107.0	13.4	38.1	41.4	16.2	8.9	77-1315-12
2.11	206.	545.	62.7	96.8	10.9	36.4	41.7	17.3	13.2	77-1415-00
2.18	203.	556.	50.8	98.9	12.4	35.1	34.6	14.0	6.2	77-1415-05
2.84	278.	761.	61.8	129.7	17.1	52.7	52.5	14.7	14.0	77-1415-12
1.96	200.	533.	51.7	95.4	17.9	35.8	37.3	15.1	5.9	77-1515-00
1.84	205.	549.	52.3	98.9	13.3	35.3	35.6	13.8	6.5	77-1515-05
2.14	269.	735.	70.9	125.2	16.8	47.9	44.3	11.6	4.7	77-1515-12
2.11	200.	534.	60.8	92.0	13.1	36.6	37.6	16.9	9.8	77-1615-00
2.38	189.	524.	36.0	84.6	11.9	32.7	34.2	14.1	11.0	77-1615-05
2.41	259.	705.	77.3	125.2	18.2	51.7	45.3	12.1	10.3	77-1615-10
2.57	292.	777.	81.9	141.8	17.5	54.4	49.1	12.7	9.1	77-1615-13
3.08	200.	554.	51.9	96.7	12.7	37.4	38.2	18.2	8.9	77-1715-00
2.42	192.	521.	53.0	89.4	13.1	34.9	38.9	15.7	6.0	77-1715-05
2.49	285.	776.	84.2	139.6	18.6	54.3	51.8	13.9	7.4	77-1715-10
2.48	260.	706.	74.7	123.8	18.4	50.5	50.5	13.7	8.3	77-1715-13
2.24	201.	559.	58.9	93.8	12.9	38.7	40.5	17.9	7.6	77-1815-00
2.43	211.	597.	60.9	103.1	14.4	36.9	38.2	15.5	5.2	77-1815-05
2.24	272.	738.	72.6	129.8	16.3	53.0	50.4	15.1	5.3	77-1815-12
2.12	217.	602.	63.9	104.6	19.8	38.9	37.3	14.6	4.5	77-1915-00
2.35	217.	600.	60.0	106.7	14.8	39.3	38.9	14.7	6.6	77-1915-05
2.63	258.	715.	81.8	123.8	14.7	48.0	47.2	13.1	7.9	77-1915-11

(BOL = BELOW DETECTION LIMITS; N.A. = NOT ANALYSED)

TABLE F.6

Ratios to Al - tidal station 7.

RATIOS TO AL (SAMPLE SUITE: GH77TYD)

SI/AL	CA/AL	FE/AL	TI/AL	K/AL	MG/AL	P/AL	S/AL	NAME
2.47	0.303	0.468	0.064	0.174	0.171	0.070	0.034	77-0815-00
2.43	0.356	0.523	0.069	0.172	0.179	0.068	0.070	77-0815-05
2.46	0.298	0.534	0.081	0.172	0.194	0.067	0.046	77-0815-08
2.47	0.255	0.469	0.053	0.174	0.178	0.070	0.041	77-0915-00
2.44	0.311	0.479	0.093	0.169	0.178	0.075	0.039	77-0915-05
2.49	0.271	0.471	0.064	0.176	0.192	0.070	0.036	77-0915-08
2.54	0.287	0.490	0.063	0.169	0.187	0.068	0.039	77-1015-00
2.49	0.258	0.484	0.053	0.173	0.186	0.064	0.052	77-1015-05
2.57	0.279	0.488	0.062	0.175	0.182	0.062	0.037	77-1015-08
2.53	0.275	0.475	0.059	0.177	0.187	0.071	0.036	77-1115-00
2.56	0.269	0.465	0.063	0.178	0.182	0.071	0.036	77-1115-05
2.54	0.387	0.470	0.062	0.177	0.197	0.116	0.046	77-1115-09
2.65	0.270	0.471	0.055	0.180	0.188	0.071	0.041	77-1215-00
2.60	0.256	0.499	0.063	0.182	0.169	0.058	0.035	77-1215-05
2.76	0.296	0.508	0.067	0.193	0.181	0.056	0.044	77-1215-10
2.58	0.235	0.452	0.057	0.171	0.170	0.073	0.028	77-1315-00
2.71	0.259	0.468	0.060	0.186	0.174	0.049	0.037	77-1315-05
2.58	0.283	0.492	0.061	0.175	0.190	0.074	0.041	77-1315-12
2.64	0.304	0.469	0.053	0.177	0.202	0.084	0.064	77-1415-00
2.67	0.244	0.475	0.059	0.169	0.166	0.067	0.030	77-1415-05
2.74	0.222	0.467	0.062	0.190	0.189	0.053	0.050	77-1415-12
2.66	0.258	0.477	0.089	0.179	0.187	0.076	0.029	77-1515-00
2.68	0.255	0.483	0.065	0.172	0.174	0.067	0.032	77-1515-05
2.74	0.264	0.466	0.062	0.178	0.165	0.043	0.017	77-1515-12
2.67	0.305	0.461	0.065	0.184	0.189	0.085	0.049	77-1615-00
2.78	0.191	0.448	0.063	0.173	0.181	0.075	0.058	77-1615-05
2.72	0.298	0.482	0.070	0.199	0.174	0.047	0.040	77-1615-10
2.66	0.280	0.485	0.060	0.186	0.168	0.043	0.031	77-1615-13
2.77	0.260	0.484	0.063	0.187	0.191	0.091	0.045	77-1715-00
2.72	0.276	0.466	0.068	0.182	0.203	0.082	0.031	77-1715-05
2.72	0.295	0.490	0.066	0.190	0.182	0.049	0.026	77-1715-10
2.71	0.287	0.476	0.071	0.194	0.194	0.053	0.032	77-1715-13
2.79	0.294	0.468	0.064	0.193	0.202	0.089	0.038	77-1815-00
2.82	0.288	0.488	0.068	0.175	0.181	0.073	0.025	77-1815-05
2.71	0.267	0.477	0.060	0.195	0.185	0.056	0.020	77-1815-12
2.77	0.294	0.481	0.091	0.179	0.172	0.067	0.021	77-1915-00
2.77	0.277	0.492	0.068	0.181	0.179	0.068	0.031	77-1915-05
2.77	0.317	0.480	0.057	0.186	0.183	0.051	0.031	77-1915-11

APPENDIX G

Gravimetric and chemical data for suspended particulate matter - areal sampling programme.

The sample names shown (e.g. 15-18-0) refer to a D.A.F.S. hydrographic code (15), the station number as shown in Figure 3.1 (18) and the sampling depth in meters.

- i) Concentration of particulate elements (Table G.1)
- ii) Ratios to Al (Table G.2)

TABLE G.1

Concentration of particulate elements.

 RATIOS TO VOLUME (SAMPLE SUITE: GRID-PCT)
 TSL IN MG/L, ELEMENTS IN MICROGRAMS/L

TSL/VOL	AL/VOL	SI/VOL	CA/VOL	FF/VOL	TI/VOL	K/VOL	MG/VOL	P/VOL	S/VOL	NAME
2.38	277.	656.	121.2	152.5	16.7	60.1	66.5	6.7	15.6	15-16-0
1.97	270.	524.	78.1	143.0	17.1	50.0	46.4	6.8	N.A.	15-18-02
1.90	274.	583.	80.4	138.8	15.2	51.6	44.4	6.9	15.4	15-18-05
1.48	225.	465.	77.9	120.2	12.4	44.7	35.3	6.0	15.2	16-17-0
1.52	228.	519.	96.4	125.1	14.5	49.8	47.5	5.8	N.A.	16-17-02
1.62	225.	509.	91.6	122.9	14.5	47.3	40.8	5.8	N.A.	16-17-05
1.93	279.	590.	108.9	141.9	15.8	57.0	46.2	6.4	15.6	16-17-10
2.45	347.	652.	92.1	163.2	18.6	61.2	62.3	7.7	17.8	16-17-15
1.00	247.	534.	89.5	125.0	13.8	51.0	36.8	6.0	15.1	17-16-0
1.24	261.	597.	113.9	140.3	15.8	57.6	53.3	5.9	N.A.	17-16-02
1.66	258.	594.	114.0	138.0	15.9	56.5	52.4	6.2	N.A.	17-16-05
1.97	219.	503.	85.0	113.8	12.1	46.1	38.7	5.5	14.3	17-16-10
2.66	300.	672.	125.9	164.2	17.8	66.7	61.2	6.9	15.8	17-16-20
5.76	539.	1324.	258.8	342.9	39.6	141.2	108.4	9.3	19.8	17-16-28
2.45	254.	576.	97.9	137.3	14.2	55.0	44.2	6.0	15.4	18-15-0
1.38	220.	528.	94.7	129.9	14.3	51.8	46.0	5.2	N.A.	18-15-02
3.21	234.	543.	98.5	133.4	14.6	54.3	47.6	5.1	N.A.	18-15-05
2.14	288.	643.	118.4	157.6	16.7	65.4	48.4	6.4	15.8	18-15-10
3.03	339.	774.	152.0	197.1	20.9	79.9	74.6	7.2	16.6	18-15-20
3.21	374.	880.	164.2	216.9	24.3	90.4	64.4	7.2	16.8	18-15-25
1.31	252.	461.	49.9	111.3	13.1	40.1	35.2	5.6	14.3	19-14-0
1.76	322.	631.	81.2	148.5	19.1	50.3	54.7	6.5	N.A.	19-14-02
3.31	363.	717.	97.0	171.1	21.4	64.6	60.5	7.0	N.A.	19-14-05
1.34	224.	429.	49.2	107.1	12.2	38.3	29.8	5.4	14.0	19-14-10
2.03	283.	654.	85.3	142.4	15.7	53.4	51.0	6.9	15.1	19-14-20
3.48	558.	1082.	130.3	277.2	32.4	105.2	89.5	10.4	19.6	20-13-0
4.17	570.	1123.	137.1	285.5	34.2	115.0	107.5	9.8	N.A.	20-13-02
3.45	508.	994.	119.2	257.9	30.1	98.3	83.8	9.1	18.5	20-13-05
1.76	634.	1322.	142.7	325.2	38.5	123.6	102.2	11.3	19.8	20-13-10
5.07	655.	1370.	188.3	377.5	42.8	140.8	124.7	11.6	21.9	21-12-0
6.93	674.	1390.	193.8	382.1	44.0	141.2	120.3	12.1	N.A.	21-12-02
5.69	729.	1504.	219.2	423.2	47.5	156.3	135.1	12.8	22.6	21-12-05
9.17	1199.	2335.	298.6	735.4	84.3	253.1	203.1	23.7	34.7	22-1-0
8.55	1133.	2280.	295.4	711.5	81.7	241.0	199.3	22.2	N.A.	22-1-02
9.00	1201.	2370.	306.0	734.9	84.4	251.0	196.3	24.1	34.1	22-1-04
10.21	1272.	2572.	329.4	822.0	93.9	276.4	238.5	22.4	34.3	23-2-0
8.86	1228.	2446.	307.9	754.7	86.2	255.8	211.8	22.8	N.A.	23-2-02
10.59	1201.	2443.	280.7	793.8	92.9	266.0	213.1	22.5	33.7	23-2-05
8.91	1126.	2260.	276.5	692.0	81.9	239.3	208.9	20.2	31.1	24-3-0
8.75	1067.	2158.	245.2	674.2	79.2	228.2	183.0	17.8	N.A.	24-3-02
8.81	1033.	2084.	237.2	632.5	75.3	217.6	187.6	18.5	29.8	24-3-04
7.81	1054.	2105.	228.5	640.8	74.5	219.1	186.5	19.2	30.9	25-4-0
8.12	1044.	2106.	240.2	638.6	75.7	216.8	183.1	19.9	N.A.	25-4-02
8.75	1107.	2238.	273.1	691.4	82.7	238.5	203.6	21.3	31.3	25-4-05
10.31	1283.	2600.	307.4	831.1	96.1	280.6	225.8	22.5	35.4	26-5-0
9.81	1224.	2442.	260.5	771.3	91.4	259.5	200.5	23.1	N.A.	26-5-02
10.09	1235.	2528.	286.3	799.4	94.5	272.7	203.2	23.3	N.A.	26-5-05
11.19	1290.	2645.	333.9	845.8	102.4	295.7	234.0	22.8	37.2	26-5-10
10.62	1272.	2552.	324.1	814.8	98.3	276.5	230.3	22.1	34.6	26-5-20

TABLE G.1
(continued)

RATIOS TO VOLUME (SAMPLE SUITE: GRID-ECT)
TSL IN MG/L, ELEMENTS IN MICROGRAMS/L

TSL/VOL	AL/VOL	SI/VOL	CA/VOL	FE/VOL	TI/VOL	K/VOL	MG/VOL	P/VOL	S/VOL	NAME
9.12	1124.	2318.	243.6	723.0	82.6	246.7	194.7	21.2	35.3	27-24-0
24.09	1944.	4263.	607.3	1813.3	198.3	545.0	321.8	36.0	56.8	27-24-20
9.16	1143.	2322.	267.3	716.6	83.0	247.8	216.0	21.0	33.1	28-25-0
3.47	1149.	2385.	285.7	739.7	85.8	255.2	200.8	21.7	N.A.	28-25-02
9.16	1108.	2259.	241.4	723.2	84.7	243.4	200.0	20.7	N.A.	28-25-05
14.00	1378.	2861.	345.0	949.7	107.2	311.3	229.8	26.0	37.6	28-25-10
14.81	1469.	3122.	376.9	1143.1	128.8	359.5	274.1	26.2	44.3	28-25-15
7.78	906.	1768.	193.6	529.6	61.0	176.7	160.0	18.5	27.1	29-4-0
5.00	828.	1713.	197.3	481.5	57.9	173.3	143.0	16.9	N.A.	29-4-02
18.06	1757.	3702.	507.7	1420.4	159.7	443.1	306.9	29.4	49.1	29-4-05
5.16	755.	1434.	165.0	389.7	48.9	139.9	132.7	15.1	23.6	30-26-0
6.69	593.	1178.	120.1	315.2	37.4	110.5	93.9	10.7	N.A.	30-26-02
6.75	830.	1605.	190.6	458.7	55.4	163.1	173.6	14.3	25.0	30-26-10
8.62	972.	1956.	244.1	632.2	78.3	209.1	159.2	16.8	29.0	30-26-20
20.37	1863.	3952.	561.7	1570.1	186.5	476.7	286.2	25.6	48.6	30-26-30
34.56	2251.	5032.	808.1	2427.4	271.7	667.1	352.4	30.7	61.5	30-26-33
2.07	373.	684.	80.2	165.3	20.1	63.4	61.2	7.0	15.6	31-27-0
2.55	404.	804.	100.8	205.7	24.2	75.0	67.5	7.8	N.A.	31-27-05
3.34	472.	923.	86.5	230.5	28.4	87.6	75.9	8.5	17.9	31-27-10
3.66	567.	1141.	148.8	293.8	35.8	109.8	77.4	9.3	18.9	31-27-20
2.86	468.	892.	101.3	222.8	25.8	82.5	59.3	9.0	17.4	32-9-0
3.06	442.	868.	101.0	220.7	27.6	81.7	78.7	9.7	N.A.	32-9-02
2.52	389.	790.	87.8	190.0	23.0	71.0	64.1	7.4	N.A.	32-9-05
1.94	257.	518.	67.5	128.4	15.2	49.8	39.7	5.7	13.7	32-9-15
2.25	341.	626.	73.9	149.4	20.3	54.5	49.4	8.1	15.7	33-28-0
2.53	353.	669.	81.6	169.2	22.8	57.2	57.6	8.6	N.A.	33-28-02
2.62	436.	814.	100.1	188.8	27.7	69.7	67.1	7.8	N.A.	33-28-05
2.25	284.	585.	64.4	152.5	19.3	54.5	42.2	7.1	16.0	33-28-10
2.50	350.	706.	99.7	184.4	21.9	69.1	60.6	7.9	16.2	33-28-20
2.50	276.	597.	90.4	146.2	17.7	57.9	54.4	8.5	15.6	34-15-0
2.41	269.	591.	76.0	147.7	17.4	54.9	54.6	8.0	N.A.	34-15-02
1.44	267.	585.	97.7	145.1	17.7	57.8	50.6	8.1	N.A.	34-15-05
2.91	295.	630.	105.2	162.8	18.8	61.2	54.8	6.1	15.1	34-15-10
2.19	238.	536.	98.9	136.5	14.5	56.1	44.5	6.6	14.8	34-15-20
2.56	304.	666.	112.8	164.7	19.0	65.8	57.7	7.5	15.3	34-15-25
2.56	316.	633.	93.7	156.0	18.2	61.7	60.3	7.2	16.6	35-29-0
2.03	307.	657.	105.7	155.4	19.1	62.4	63.0	7.4	N.A.	35-29-02
3.24	382.	857.	132.9	211.3	25.9	82.3	72.5	8.1	N.A.	35-29-05
2.22	333.	679.	108.9	162.4	19.4	65.2	65.8	7.2	15.8	35-29-10
2.25	292.	641.	118.4	155.3	17.1	64.6	47.4	7.1	15.2	35-29-20
4.12	343.	781.	142.6	197.1	21.6	79.6	69.0	7.6	16.2	35-29-30
2.56	298.	704.	118.7	177.2	19.5	72.2	58.4	6.7	15.0	35-29-35
4.91	201.	417.	64.1	108.7	11.3	43.5	40.1	5.5	16.2	36-21-0
1.62	216.	478.	77.7	114.8	13.4	45.1	43.5	5.5	N.A.	36-21-02
4.62	219.	478.	79.6	118.1	13.7	45.7	46.2	5.8	N.A.	36-21-05
1.44	205.	426.	70.6	117.2	12.2	41.4	36.2	6.2	15.4	36-21-10
2.62	326.	709.	130.1	182.2	20.2	71.6	60.8	7.3	16.2	36-21-20
1.84	338.	747.	133.6	192.6	21.6	76.2	62.0	7.4	16.0	36-21-30
2.97	220.	500.	93.7	138.1	14.4	53.4	41.8	5.5	15.0	36-21-40
1.56	364.	626.	157.6	210.1	23.3	85.9	77.7	7.8	18.2	36-21-45

TABLE G.1

(continued)

 RATIOS TO VOLUME (SAMPLE SUITES GP17-PCT)
 TSL IN MG/L, ELEMENTS IN MICROGRAMS/L

TSL/VOL	AL/VOL	SI/VOL	CA/VOL	FE/VOL	TI/VOL	N/VOL	MS/VOL	P/VOL	S/VOL	NAME
1.59	216.	486.	119.4	122.4	13.6	46.9	41.0	5.1	14.5	37-23-0
0.72	192.	532.	100.4	114.2	13.0	44.6	35.9	5.2	N.A.	37-23-02
1.31	181.	468.	92.2	102.3	10.7	38.7	26.7	5.2	13.8	37-23-05
0.72	143.	327.	74.2	86.3	8.1	32.1	23.7	5.1	14.2	37-23-10
5.17	930.	1847.	219.8	516.3	62.5	183.6	157.5	17.3	N.A.	38-22-02
1.69	129.	332.	76.0	75.8	8.0	33.8	32.1	4.4	N.A.	38-22-05
1.24	166.	378.	79.9	89.7	8.8	36.1	27.6	4.8	14.1	38-22-10
1.17	168.	392.	81.1	94.8	9.0	39.3	31.2	4.7	15.6	38-22-20
1.52	142.	330.	75.0	76.8	7.1	31.6	24.0	4.4	13.6	38-22-30
1.52	266.	654.	138.1	144.8	15.5	59.8	53.4	6.4	15.1	38-22-35
1.56	199.	433.	60.4	106.8	11.3	40.4	36.1	5.7	14.0	39-21-0
1.44	234.	524.	85.8	122.5	15.1	49.5	47.6	6.4	N.A.	39-21-02
2.16	186.	416.	58.7	105.5	11.7	40.1	37.5	5.0	N.A.	39-21-05
1.34	167.	345.	50.2	87.4	10.6	33.6	26.5	4.6	13.1	39-21-10
1.59	190.	391.	57.9	104.2	10.9	38.8	34.3	5.2	13.4	39-21-20
2.19	245.	527.	87.8	137.2	15.9	53.5	39.7	5.7	16.2	39-21-30
3.09	342.	771.	145.7	196.8	23.8	76.6	73.4	6.8	16.9	39-21-40
3.06	366.	793.	143.1	197.7	21.8	80.7	74.7	7.1	16.9	39-21-45
2.34	280.	580.	100.2	145.8	15.8	57.4	53.6	7.2	14.8	40-20-0
1.66	250.	557.	85.6	139.5	16.4	53.8	49.9	6.1	N.A.	40-20-02
4.00	600.	1132.	137.7	282.2	41.2	101.4	91.0	8.8	N.A.	40-20-05
2.09	310.	641.	107.0	160.3	18.1	63.7	52.0	7.2	15.8	40-20-10
2.25	313.	664.	117.6	179.3	20.0	68.8	58.6	7.1	15.7	40-20-30
2.78	386.	833.	153.3	218.3	24.3	85.9	78.3	7.9	17.6	40-20-40
3.56	385.	856.	154.8	227.6	26.1	87.8	74.4	9.0	N.A.	40-20-45
2.91	365.	777.	125.1	199.2	22.2	75.7	72.1	8.7	16.6	41-19-0
3.25	402.	873.	138.0	223.4	26.6	86.4	78.0	9.1	N.A.	41-19-02
3.75	406.	892.	157.9	239.2	27.2	90.0	79.4	9.9	N.A.	41-19-05
4.12	412.	906.	156.8	241.7	27.5	97.2	80.2	6.3	17.7	41-19-10
5.22	491.	1107.	211.2	334.1	36.5	118.9	98.4	9.5	21.4	41-19-20
6.00	709.	1535.	274.6	451.8	50.4	164.3	137.6	12.5	22.7	41-19-23
5.21	803.	1536.	179.5	435.7	49.1	152.5	146.1	15.6	27.4	42-6-0
5.21	944.	1792.	200.7	512.2	55.0	179.3	159.8	20.3	26.9	42-6-05
4.97	796.	1522.	188.8	414.4	48.9	148.8	145.9	18.5	24.3	43-7-0
3.59	815.	1544.	195.3	430.9	50.3	151.8	147.7	18.9	25.2	43-7-05
3.79	633.	1223.	153.4	320.8	38.5	119.8	109.7	12.1	20.6	44-8-0
4.07	641.	1237.	146.2	322.2	39.3	121.2	112.6	10.6	N.A.	44-8-02
5.07	707.	1392.	163.2	378.9	45.4	138.3	131.4	12.4	22.7	44-8-05
5.10	841.	1679.	214.4	462.6	56.8	169.4	165.3	13.9	24.6	44-8-10
2.97	487.	897.	97.0	243.0	29.3	82.0	74.9	9.3	18.4	45-9-0
3.09	521.	995.	108.7	246.0	32.3	88.9	82.4	9.7	N.A.	45-9-02
2.66	536.	994.	114.8	241.3	32.4	88.9	83.9	9.8	N.A.	45-9-05
3.75	543.	1010.	122.3	255.3	33.1	96.7	92.4	9.2	19.4	45-9-10
1.41	514.	1089.	129.2	271.3	38.0	99.3	91.0	10.8	19.5	45-9-20
2.93	451.	808.	87.7	205.6	26.0	75.6	65.6	9.2	18.3	46-10-0
2.24	457.	861.	91.4	207.2	28.1	76.3	72.9	8.8	N.A.	46-10-02
2.28	489.	896.	101.7	226.8	29.7	80.6	76.8	9.2	N.A.	46-10-05
3.03	499.	905.	105.5	222.4	30.2	84.2	76.4	10.1	19.7	46-10-10
1.83	555.	1064.	138.0	266.9	33.3	103.6	100.4	10.1	19.5	46-10-15
2.72	441.	795.	89.0	190.1	26.2	70.3	59.9	9.9	18.9	47-11-0
2.90	454.	840.	101.7	202.2	28.6	75.4	70.7	8.8	N.A.	47-11-02
2.10	281.	599.	98.4	151.4	17.1	56.6	56.9	6.8	N.A.	47-11-05
4.00	604.	1135.	121.2	291.6	41.2	104.7	92.4	11.0	20.4	47-11-10
5.07	738.	1372.	178.3	352.6	50.0	129.8	134.8	11.7	22.1	47-11-15
1.79	355.	665.	66.0	156.8	18.4	60.4	54.8	7.6	16.9	49-15-0
2.19	360.	691.	69.2	167.2	21.7	64.7	58.8	7.2	N.A.	49-15-02
2.00	345.	655.	84.7	157.2	20.5	59.2	56.3	6.7	N.A.	49-15-05
1.55	365.	796.	86.0	161.0	20.4	63.5	51.7	7.2	18.1	49-15-10
3.69	483.	938.	132.6	241.3	29.6	88.9	83.4	8.6	27.7	49-15-20
5.31	718.	1550.	241.9	403.6	50.7	156.7	135.3	11.6	24.4	49-15-25

(BDL = BELOW DETECTION LIMIT; N.A. = NOT ANALYSED)

TABLE G.2

Ratios to Al

RATIOS TO AL (SAMPLE SUITE: GRID-PCT)

SI/AL	CA/AL	FE/AL	TI/AL	K/AL	MG/AL	P/AL	S/AL	NAME
2.37	0.437	0.550	0.060	0.217	0.240	0.024	0.056	15-18-0
1.94	0.290	0.530	0.064	0.185	0.172	0.025		15-18-02
2.13	0.293	0.506	0.056	0.186	0.162	0.025	0.056	15-18-05
2.07	0.346	0.535	0.055	0.199	0.157	0.027	0.068	16-17-0
2.28	0.423	0.549	0.064	0.216	0.206	0.025		16-17-02
2.26	0.406	0.545	0.064	0.210	0.181	0.026		16-17-05
2.12	0.390	0.509	0.057	0.205	0.166	0.023	0.056	16-17-10
1.88	0.265	0.470	0.054	0.176	0.179	0.022	0.051	16-17-15
2.16	0.362	0.506	0.056	0.206	0.149	0.024	0.061	17-16-0
2.28	0.436	0.537	0.061	0.220	0.204	0.023		17-16-02
2.30	0.442	0.536	0.062	0.219	0.203	0.024		17-16-05
2.29	0.388	0.519	0.055	0.210	0.176	0.025	0.065	17-16-10
2.24	0.419	0.547	0.059	0.222	0.204	0.023	0.052	17-16-20
2.46	0.480	0.636	0.073	0.262	0.201	0.017	0.037	17-16-28
2.27	0.385	0.540	0.056	0.216	0.174	0.024	0.060	18-15-0
2.40	0.430	0.591	0.065	0.235	0.209	0.024		18-15-02
2.32	0.420	0.569	0.062	0.232	0.203	0.022		18-15-05
2.24	0.412	0.548	0.058	0.227	0.168	0.022	0.055	18-15-10
2.29	0.449	0.582	0.062	0.236	0.220	0.021	0.049	18-15-20
2.35	0.438	0.579	0.065	0.241	0.172	0.019	0.045	18-15-25
1.83	0.198	0.442	0.052	0.159	0.140	0.022	0.057	19-14-0
1.96	0.252	0.461	0.059	0.187	0.170	0.020		19-14-02
1.98	0.267	0.471	0.059	0.178	0.167	0.019		19-14-05
1.91	0.220	0.478	0.055	0.171	0.133	0.024	0.062	19-14-10
2.31	0.302	0.504	0.056	0.189	0.180	0.024	0.054	19-14-20
1.94	0.234	0.497	0.058	0.189	0.160	0.019	0.035	20-13-0
1.97	0.240	0.501	0.060	0.202	0.189	0.017		20-13-02
1.96	0.235	0.508	0.059	0.194	0.165	0.018	0.036	20-13-05
2.08	0.225	0.513	0.061	0.195	0.161	0.018	0.031	20-13-10
2.09	0.287	0.576	0.065	0.215	0.190	0.018	0.033	21-12-0
2.06	0.287	0.567	0.065	0.209	0.178	0.018		21-12-02
2.06	0.301	0.580	0.065	0.214	0.185	0.017	0.031	21-12-05
1.95	0.249	0.613	0.070	0.211	0.169	0.020	0.029	22-1-0
2.01	0.261	0.628	0.072	0.213	0.176	0.020		22-1-02
1.97	0.255	0.612	0.070	0.209	0.163	0.020	0.028	22-1-04
2.02	0.259	0.646	0.074	0.217	0.186	0.016	0.027	23-2-0
1.99	0.251	0.614	0.070	0.206	0.172	0.019		23-2-02
2.03	0.234	0.661	0.077	0.222	0.177	0.019	0.028	23-2-05
2.01	0.246	0.615	0.073	0.212	0.185	0.018	0.028	24-3-0
2.02	0.230	0.632	0.074	0.214	0.171	0.017		24-3-02
2.02	0.229	0.612	0.073	0.211	0.182	0.018	0.029	24-3-04
2.00	0.217	0.608	0.071	0.208	0.177	0.018	0.029	25-4-0
2.02	0.230	0.611	0.072	0.208	0.175	0.019		25-4-02
2.02	0.247	0.624	0.075	0.215	0.184	0.019	0.028	25-4-05
2.03	0.240	0.648	0.075	0.219	0.176	0.018	0.028	26-5-0
2.00	0.213	0.630	0.075	0.212	0.164	0.019		26-5-02
2.05	0.232	0.647	0.077	0.221	0.165	0.018		26-5-05
2.08	0.259	0.687	0.079	0.229	0.181	0.018	0.029	26-5-10
2.01	0.255	0.641	0.077	0.217	0.181	0.017	0.027	26-5-20

TABLE G.2
(continued)

RATIOS TO AL (SAMPLE SUITE: GRID-PCT)

SI/AL	CA/AL	FE/AL	TI/AL	M/AL	MG/AL	P/AL	S/AL	NAME
2.06	0.217	0.643	0.073	0.220	0.173	0.019	0.031	27-24-0
2.19	0.312	0.933	0.102	0.280	0.166	0.020	0.029	27-24-20
2.03	0.234	0.627	0.073	0.217	0.189	0.018	0.029	28-25-0
2.08	0.249	0.644	0.075	0.222	0.175	0.019		28-25-02
2.04	0.218	0.652	0.076	0.220	0.180	0.019		28-25-05
2.08	0.250	0.689	0.078	0.226	0.167	0.019	0.027	28-25-10
2.13	0.258	0.778	0.088	0.245	0.187	0.018	0.030	28-25-15
1.95	0.214	0.584	0.067	0.195	0.176	0.020	0.030	29-4-0
2.07	0.238	0.582	0.070	0.209	0.173	0.020		29-4-02
2.11	0.289	0.808	0.091	0.252	0.175	0.017	0.028	29-4-05
1.90	0.219	0.516	0.065	0.185	0.176	0.020	0.031	30-26-0
1.99	0.203	0.532	0.063	0.186	0.158	0.018		30-26-02
1.93	0.230	0.553	0.067	0.196	0.209	0.017	0.030	30-26-10
2.01	0.251	0.650	0.081	0.215	0.164	0.017	0.030	30-26-20
2.12	0.302	0.843	0.100	0.256	0.154	0.014	0.026	30-26-30
2.24	0.359	1.078	0.121	0.296	0.157	0.014	0.027	30-26-33
1.83	0.215	0.443	0.054	0.170	0.164	0.019	0.042	31-27-0
1.99	0.250	0.509	0.060	0.186	0.167	0.019		31-27-05
1.96	0.183	0.488	0.060	0.186	0.161	0.018	0.038	31-27-10
2.01	0.263	0.518	0.063	0.194	0.137	0.016	0.033	31-27-20
1.91	0.217	0.476	0.055	0.176	0.127	0.019	0.037	32-9-0
1.96	0.228	0.499	0.062	0.185	0.178	0.022		32-9-02
2.03	0.226	0.488	0.059	0.183	0.165	0.019		32-9-05
2.02	0.263	0.500	0.059	0.194	0.155	0.022	0.054	32-9-15
1.84	0.217	0.438	0.060	0.160	0.145	0.024	0.046	33-28-0
1.89	0.231	0.479	0.065	0.162	0.163	0.024		33-28-02
1.87	0.229	0.433	0.063	0.160	0.154	0.018		33-28-05
2.06	0.227	0.537	0.068	0.192	0.149	0.025	0.056	33-28-10
2.02	0.285	0.527	0.063	0.197	0.173	0.023	0.046	33-28-20
2.16	0.328	0.530	0.064	0.210	0.197	0.031	0.057	34-15-0
2.19	0.282	0.548	0.065	0.204	0.203	0.030		34-15-02
2.19	0.366	0.544	0.066	0.217	0.190	0.030		34-15-05
2.13	0.356	0.551	0.064	0.207	0.186	0.027	0.051	34-15-10
2.25	0.415	0.573	0.061	0.236	0.187	0.028	0.062	34-15-20
2.20	0.372	0.543	0.062	0.217	0.190	0.025	0.050	34-15-25
2.01	0.297	0.494	0.058	0.195	0.191	0.023	0.052	35-29-0
2.14	0.345	0.507	0.062	0.203	0.205	0.024		35-29-02
2.24	0.348	0.554	0.068	0.216	0.190	0.021		35-29-05
2.04	0.327	0.487	0.058	0.196	0.197	0.022	0.047	35-29-10
2.19	0.405	0.532	0.059	0.221	0.162	0.024	0.052	35-29-20
2.28	0.416	0.575	0.063	0.232	0.201	0.022	0.047	35-29-30
2.36	0.398	0.595	0.066	0.242	0.196	0.022	0.050	35-29-35
2.08	0.319	0.541	0.056	0.217	0.200	0.028	0.081	36-21-0
2.21	0.359	0.531	0.062	0.209	0.201	0.025		36-21-02
2.18	0.363	0.538	0.063	0.208	0.211	0.027		36-21-05
2.07	0.344	0.570	0.059	0.201	0.176	0.030	0.075	36-21-10
2.18	0.399	0.560	0.062	0.220	0.187	0.022	0.050	36-21-20
2.21	0.395	0.570	0.064	0.225	0.184	0.022	0.047	36-21-30
2.27	0.426	0.628	0.065	0.243	0.190	0.025	0.068	36-21-40
2.27	0.432	0.576	0.064	0.236	0.213	0.022	0.050	36-21-45

TABLE G.2

(continued)

RATIOS TO AL (SAMPLE SUITE: GRID-PCT)

SI/AL	CA/AL	FE/AL	TI/AL	K/AL	MG/AL	P/AL	S/AL	NAME
2.25	0.553	0.566	0.063	0.217	0.190	0.023	0.067	37-23-0
2.78	0.524	0.596	0.068	0.233	0.187	0.027		37-23-02
2.59	0.510	0.566	0.059	0.214	0.148	0.029	0.076	37-23-05
2.29	0.519	0.604	0.056	0.224	0.165	0.035	0.100	37-23-10
1.99	0.236	0.555	0.067	0.198	0.169	0.019		38-22-02
2.58	0.590	0.588	0.062	0.263	0.249	0.034		38-22-05
2.27	0.481	0.539	0.053	0.217	0.166	0.029	0.085	38-22-10
2.33	0.482	0.563	0.054	0.233	0.185	0.028	0.093	38-22-20
2.32	0.528	0.540	0.050	0.222	0.169	0.031	0.096	38-22-30
2.46	0.518	0.543	0.058	0.225	0.200	0.024	0.057	38-22-35
2.18	0.304	0.537	0.057	0.203	0.181	0.029	0.070	39-21-0
2.24	0.366	0.523	0.064	0.211	0.203	0.027		39-21-02
2.23	0.315	0.566	0.063	0.215	0.201	0.027		39-21-05
2.07	0.301	0.524	0.064	0.202	0.159	0.028	0.079	39-21-10
2.05	0.305	0.548	0.057	0.204	0.180	0.028	0.070	39-21-20
2.15	0.359	0.561	0.065	0.219	0.162	0.023	0.066	39-21-30
2.26	0.427	0.576	0.070	0.230	0.215	0.026	0.050	39-21-40
2.16	0.391	0.539	0.059	0.220	0.204	0.019	0.046	39-21-45
2.08	0.358	0.521	0.056	0.205	0.192	0.026	0.053	40-20-0
2.23	0.342	0.557	0.066	0.215	0.199	0.024		40-20-02
1.89	0.229	0.470	0.069	0.169	0.152	0.015		40-20-05
2.07	0.346	0.518	0.058	0.206	0.168	0.023	0.051	40-20-10
2.12	0.375	0.572	0.064	0.220	0.187	0.023	0.050	40-20-30
2.16	0.397	0.566	0.063	0.223	0.203	0.021	0.046	40-20-40
2.22	0.402	0.591	0.066	0.228	0.193	0.023		40-20-45
2.13	0.343	0.546	0.061	0.207	0.198	0.024	0.045	41-19-0
2.17	0.343	0.555	0.066	0.215	0.194	0.023		41-19-02
2.20	0.389	0.589	0.067	0.222	0.195	0.024		41-19-05
2.20	0.380	0.587	0.067	0.236	0.195	0.020	0.043	41-19-10
2.25	0.430	0.680	0.074	0.242	0.200	0.019	0.044	41-19-20
2.17	0.387	0.637	0.071	0.232	0.194	0.018	0.032	41-19-23
1.91	0.224	0.543	0.061	0.190	0.182	0.024	0.034	42-6-0
1.90	0.213	0.543	0.062	0.190	0.169	0.022	0.028	42-6-05
1.91	0.237	0.521	0.061	0.187	0.183	0.023	0.030	43-7-0
1.90	0.240	0.529	0.062	0.186	0.181	0.023	0.031	43-7-05
1.93	0.242	0.507	0.061	0.189	0.173	0.019	0.033	44-8-0
1.93	0.228	0.502	0.061	0.189	0.176	0.016		44-8-02
1.97	0.231	0.536	0.064	0.196	0.186	0.018	0.032	44-8-05
2.00	0.255	0.550	0.068	0.202	0.197	0.016	0.029	44-8-10
1.84	0.199	0.499	0.060	0.168	0.154	0.019	0.038	45-9-0
1.91	0.209	0.472	0.062	0.171	0.158	0.019		45-9-02
1.85	0.214	0.450	0.060	0.166	0.156	0.018		45-9-05
1.86	0.225	0.470	0.061	0.178	0.170	0.017	0.036	45-9-10
2.12	0.251	0.528	0.074	0.193	0.177	0.021	0.038	45-9-20
1.79	0.195	0.456	0.058	0.168	0.146	0.021	0.041	46-10-0
1.88	0.200	0.453	0.061	0.171	0.159	0.019		46-10-02
1.83	0.208	0.464	0.061	0.165	0.157	0.019		46-10-05
1.81	0.211	0.446	0.060	0.169	0.157	0.020	0.040	46-10-10
1.92	0.249	0.481	0.060	0.187	0.181	0.018	0.035	46-10-15
1.80	0.202	0.431	0.059	0.159	0.136	0.023	0.043	47-11-0
1.85	0.224	0.446	0.063	0.166	0.156	0.019		47-11-02
2.13	0.350	0.538	0.061	0.208	0.202	0.024		47-11-05
1.88	0.200	0.483	0.068	0.173	0.153	0.018	0.034	47-11-10
1.86	0.242	0.478	0.068	0.176	0.183	0.016	0.030	47-11-15
1.87	0.186	0.442	0.052	0.170	0.154	0.021	0.047	49-15-0
1.92	0.248	0.465	0.060	0.180	0.163	0.020		49-15-02
1.90	0.245	0.456	0.059	0.172	0.163	0.019		49-15-03
2.18	0.235	0.441	0.056	0.174	0.142	0.020	0.050	49-15-10
1.94	0.275	0.500	0.061	0.184	0.173	0.018	0.057	49-15-20
2.16	0.337	0.562	0.071	0.218	0.166	0.016	0.034	49-15-25

APPENDIX H

Summary tables and accessory data

- i) Summary of major element ratios for particulate samples
(and comparison with the literature) (Table H.1)
- ii) Summary of major element ratios for sediment samples
(and comparison with the literature) (Table H.2)
- iii) Non-terrigenous element abundance, tidal station 26
(Table H.3)
- iv) Non-terrigenous element abundance, tidal station 15
(Table H.4)
- v) Non-terrigenous element abundance, tidal station 7
(Table H.5)
- vi) Non-terrigenous element abundance, areal sampling
(Table H.6)
- vii) Trace element analyses of sediment samples (Table H.7)

TABLE H.1

Summary of major element ratios for particulate samples
(and comparison with the literature).

REFERENCE	LOCATION	LOAD mg/l	P/Al $\mu\text{g/l}$	Si/Al	Ca/Al	Fe/Al	Ti/Al	K/Al	Mg/Al	P/Al	S/Al
This study, Stn 26 (Av. 8 pipette suites) (20/1/77)	Total sample (46)	14.6	2028	1.84	0.23	0.46	0.062	0.18	0.15	0.013	0.017
	66 ($\leq 15 \mu\text{m}$)	13.3	1987	1.78	0.23	0.43	0.058	0.18	0.15	0.012	0.016
	106 ($\leq 1 \mu\text{m}$)	2.6	425	1.56	0.16	0.34	0.044	0.14	0.15	0.017	0.019
This study, Stn 15 (1 pipette suite) (8/2/77)	Total sample (46)	8.6	595	5.39	0.54	0.53	0.062	0.23	0.22	0.018	0.027
	66 ($\leq 15 \mu\text{m}$)	3.4	428	2.06	0.50	0.46	0.052	0.21	0.23	0.018	0.026
	106 ($\leq 1 \mu\text{m}$)	1.3	112	1.86	0.49	0.43	0.041	0.21	0.31	0.016	0.069
This study, Stn 7 (Av. 6 pipette suites) (29/7/76)	Total sample (46)	18.8	259	3.78	0.38	0.71	0.063	0.27	0.47	0.11	0.20
	66 ($\leq 15 \mu\text{m}$)	6.7	249	2.94	0.29	0.44	0.063	0.23	0.49	0.09	0.12
	106 ($\leq 1 \mu\text{m}$)	1.3	45	3.03	0.31	0.59	0.050	0.18	0.46	0.20	0.17
This study, Inner Estuary (1 pipette suite) (14/2/77)	Total sample (46)	15.1	2293	1.81	0.26	0.46	0.059	0.17	0.17	0.017	0.020
	66 ($\leq 15 \mu\text{m}$)	14.5	2318	1.79	0.26	0.45	0.057	0.17	0.17	0.017	0.024
	9.56 ($\leq 1.4 \mu\text{m}$)	2.6	324	1.59	0.20	0.36	0.041	0.16	0.24	0.032	0.063
This study, tidal station monitoring, Station 26 (20/1/77)	Minimum:	7.2	918	1.73	0.16	0.37	0.055	0.15	0.39	0.011	0.018
	Maximum:	31.3	4147	1.95	0.27	0.54	0.073	0.20	0.21	0.014	0.041
This study, tidal station monitoring, Station 15 (8/2/77)	Minimum:	1.4	137	1.65	0.28	0.42	0.049	0.14	0.16	0.017	0.017
	Maximum:	4.9	523	5.14	0.54	0.54	0.068	0.23	0.27	0.060	0.051
This study, tidal station monitoring, Station 7 (19/4/77)	Minimum:	1.9	192	2.43	0.19	0.45	0.053	0.17	0.17	0.043	0.020
	Maximum:	5.6	306	2.82	0.38	0.53	0.093	0.20	0.20	0.116	0.061
This study, areal sampling programme (17-18/3/75)	Minimum:	0.7	181	1.80	0.18	0.43	0.052	0.16	0.14	0.014	0.03
	Maximum:	34.5	2251*	2.78	0.59	>0.70*	>0.080*	0.29	0.25	0.034	0.10
d'Anglejan and Smith (1973)	Av. 23 samples, St. Lawrence Estuary	1-30	-	3.26	0.29	0.62	0.100	0.33	0.31	-	-
Feely (1975)	Gulf of Mexico: Normal particulates	0.02	0.51	3.62	1.46	0.87	-	-	0.49	-	2.1
	Nepheloid layer	0.05	1.52	3.7	0.9	0.7	-	-	0.2	-	2.8
Price and Calvert (1973)	Loch Etive: Minimum:	-	7.6	2.34	-	0.47	0.033	0.21	0.19	-	-
	Maximum:	-	74	9.54	-	1.56	0.072	0.42	0.41	-	-
Price and Skei (1975)	Hardangerfjord: Minimum:	-	0.9	1.47	-	0.72	0.020	0.21	0.24	-	-
	Maximum:	-	36.5	33.3	-	2.33	0.113	0.81	1.50	-	-
	Av. River samples	-	-	2.25	-	1.10	0.072	0.38	0.30	-	-
Sholkovits (1978)	Tay estuary: Minimum:	(3.7)	-	3.5	0.05	0.62	0.070	0.24	0.19	0.012	-
	Maximum:	-	-	4.5	0.23	0.85	0.085	0.29	0.22	0.015	-
	River Tay: Minimum:	-	-	3	0.15	0.9	0.04	0.20	0.18	0.02	-
	Maximum:	(145)	-	8	0.55	1.8	0.12	0.30	0.4	0.2	-
Taylor (1974)	West Norwegian fjord Maximum:	0.19	0.5	1.14	0.04	-	0.020	0.12	0.08	-	-
	Minimum:	1.93	24.5	10.8	8.27	-	0.102	2.20	1.65	-	-
	Av. 4 river samples	-	-	2.12	0.13	-	0.040	0.24	0.12	-	-

* Samples significantly above these values are thought to reflect artefact problems due to overloading.

TABLE H.2

Summary of major element ratios for sediment samples
(and comparison with the literature)

REFERENCE	LOCATION	Si/Al	Ca/Al	Fe/Al	Ti/Al	K/Al	Mg/Al	P/Al	S/Al
This study, mean of 6 sediment pipette suites	Total sample (44)	2.73	0.18	0.57	0.071	0.23	0.18	0.013	0.022
	66 samples ($\leq 15 \mu\text{m}$)	1.89	0.09	0.46	0.059	0.18	0.17	0.011	0.018
	106 samples ($\leq 1 \mu\text{m}$)	1.59	0.03	0.39	0.042	0.14	0.21	0.015	0.015
Chester (1965) (in Taylor, 1974)	Average argillaceous pelagic sediment	2.7	0.07	0.61	0.053	0.29	0.22	0.006	-
Clark (1924) (in Taylor, 1974)	Average sandstone	14.5	1.56	0.39	0.060	0.43	0.28	0.014	0.012
Doff (1969)	Average of 13 Oslofjord Sediments	3.2	0.36	0.79	0.056	0.38	0.20	0.021	0.145
Grim & Johns (1954) (in Peely, 1975)	1 μm fraction, 2 sediment samples, the Gulf of Mexico	2.24	0.09	0.49	0.03	0.19	0.19	-	-
Hougen et al (1925) + Goldschmidt (1954) (in Doff, 1969)	Average of 78 Norwegian Glacial clays	3.3	0.26	0.62	0.057	0.39	0.24	0.011	0.012
Hirst (1962)	Gulf of Paria: 12 Platform sands	11.3	1.48	1.01	0.083	0.29	0.17	0.015	-
	6 Basin clays	2.9	0.13	0.58	0.049	0.22	0.15	0.009	-
Krauskopf (1967)	Av. world shale	3.0	0.31	0.59	0.056	0.29	0.17	0.010	0.003
Moore (1963) (in Calvert, 1976)	Average of 125 sands and muddy sands, Buzzard's Bay, Mass.	-	0.23	0.40	0.081	0.39	0.10	-	-
Pettijohn (1957)	Average greywacke	3.9	0.28	0.52	0.038	0.20	0.17	0.011	0.05
Skel (1975)	15 'anomalous' surface sediments	3.4	2.0	5.3	0.075	0.36	0.24	0.050	-
	13 'normal' surface sediments (Sorfjorden)	3.8	0.3	0.77	0.076	0.38	0.23	0.009	-
Taylor (1974)	Av. sediment, 2 west Norwegian fjords	3.5	0.44	0.62	0.064	0.34	0.18	0.019	0.20
Turekian and Wedepohl (1961)	Average Shale	3.4*	0.28	0.59	0.058	0.33	0.19	0.009	0.03
	Average sandstone	14.7	1.56	0.39	0.060	0.42	0.28	0.007	0.01
	Av. Deep sea clay	3.0	0.34	0.77	0.055	0.30	0.25	0.018	0.015
Wedepohl (1968)	Average greywacke	4.3	0.25	0.54	0.053	0.23	0.18	0.009	0.017
	Average shale	3.1	0.18	0.53	0.052	0.34	0.18	0.008	0.027
White (1970)	Sands and silts, Oregon-Washington continental shelf	4.4	0.34	0.44	0.078	0.23	0.26	-	-
Wright (1972)	Barents Sea: Sands	9.69	0.15	0.28	0.025	0.41	0.08	0.008	-
	Silts	5.89	0.22	0.30	0.073	0.32	0.14	0.009	-
	Clays	2.25	0.06	0.66	0.058	0.29	0.19	0.016	-
	Total sediment	4.9	0.15	0.52	0.057	0.34	0.17	0.009	-
Price and Skel (1975)	Average sediment, Hardangervjord	2.25	-	1.10	0.072	0.38	0.30	-	-

* Turekian and Wedepohl (1961) - The stated 7.5% Si is assumed to be a misprint for 27.5%

TABLE H.3

Non-terrigenous element abundance, tidal station 26.

NON-TERRIGENOUS ELEMENT ABUNDANCE (UG/L):						
SI	CA	FE	K	MG	P	SAMPLE NAME
19.2	240.6	42.4	0.0	11.3	7.0	26-0855-00
75.3	268.5	37.9	6.5	21.1	7.8	26-0855-05
0.0	235.5	35.2	1.7	0.0	5.7	26-0855-10
0.0	209.5	0.0	0.0	34.1	3.9	26-0855-17
88.3	225.4	6.7	1.2	0.0	2.7	26-0855-27
0.0	255.9	0.0	0.0	0.0	8.5	26-0955-00
120.9	278.5	32.8	14.5	0.0	5.9	26-0955-05
32.3	195.4	0.0	2.2	0.0	4.5	26-0955-10
0.0	244.3	44.9	0.0	0.0	6.1	26-0955-20
0.0	268.2	15.5	0.0	0.0	7.2	26-0955-27
42.8	204.9	0.0	0.0	0.0	6.2	26-1055-00
24.4	199.3	0.0	0.0	16.4	5.5	26-1055-05
0.0	226.0	0.0	0.0	0.0	6.4	26-1055-10
0.0	271.0	0.0	0.0	0.0	5.8	26-1055-20
0.0	385.2	0.0	0.0	0.0	5.7	26-1055-27
101.1	207.7	0.0	0.0	0.0	5.5	26-1155-00
35.7	113.4	0.0	0.0	0.0	4.8	26-1155-05
16.1	166.2	0.0	0.0	0.0	5.3	26-1155-10
47.1	236.1	3.5	11.7	0.0	5.8	26-1155-20
0.0	217.8	0.0	0.0	0.0	3.2	26-1155-28
0.0	250.2	0.0	0.0	14.5	5.1	26-1301-00
0.0	213.9	0.0	0.0	0.0	3.9	26-1301-05
0.0	284.6	11.6	0.0	0.0	4.5	26-1301-10
0.4	267.8	25.7	0.0	64.1	5.1	26-1301-20
0.0	277.0	0.0	0.0	0.0	4.1	26-1301-28
23.9	178.8	0.0	0.0	41.5	4.5	26-1400-00
7.3	244.1	0.0	0.0	0.0	3.9	26-1400-05
0.0	221.5	0.0	0.0	0.0	1.4	26-1400-10
0.0	338.7	0.0	0.0	0.0	2.6	26-1400-20
0.0	252.3	0.0	0.0	13.2	1.0	26-1400-30
17.6	207.1	1.2	0.0	18.0	4.5	26-1500-00
15.5	182.9	0.0	0.0	0.0	3.7	26-1500-05
0.0	221.6	0.0	0.0	0.0	4.0	26-1500-10
0.0	323.2	0.0	0.0	0.0	1.5	26-1500-20
0.0	225.1	0.0	0.0	25.7	0.0	26-1500-33
44.9	186.8	6.2	0.0	12.5	5.2	26-1600-00
76.8	175.3	0.0	0.0	0.0	3.8	26-1600-05
0.0	149.6	0.0	0.0	9.3	3.1	26-1600-10
38.5	291.2	4.5	4.5	0.0	3.3	26-1600-20
0.0	303.0	31.4	14.1	105.0	5.3	26-1600-25
0.0	366.8	0.0	0.0	0.0	4.0	26-1600-30
0.0	149.1	65.4	0.0	0.0	5.0	26-1700-00
37.7	159.4	0.0	0.0	19.0	2.9	26-1700-05
24.9	163.2	0.0	0.0	0.0	3.6	26-1700-10
9.5	173.0	0.0	0.0	29.3	3.6	26-1700-20
0.0	199.1	0.0	0.0	0.0	4.6	26-1700-25
22.5	189.9	0.0	0.0	0.0	5.2	26-1700-30
5.3	220.4	0.0	0.0	0.0	6.3	26-1800-00
0.0	207.0	0.0	0.0	0.0	4.6	26-1800-05
0.0	227.9	0.0	0.0	0.0	4.8	26-1800-10
5.8	260.9	23.4	0.0	0.0	4.9	26-1800-20
0.0	242.9	1.0	0.0	0.0	5.5	26-1800-25
0.0	405.7	1.7	0.0	0.0	4.9	26-1800-30
9.7	176.4	6.8	0.0	18.7	3.9	26-1900-00
163.5	337.3	35.6	8.1	0.0	6.6	26-1900-05
0.0	257.9	0.0	0.0	0.0	5.5	26-1900-10
0.0	313.8	82.8	0.0	0.0	5.0	26-1900-20
0.0	349.5	5.2	0.0	0.0	4.9	26-1900-25
0.0	488.1	122.7	18.1	0.0	7.7	26-1900-30
0.0	276.2	21.7	0.0	0.0	4.0	26-2000-00
36.8	336.3	71.5	13.9	0.0	6.0	26-2000-05
0.0	311.5	75.5	1.5	0.0	7.0	26-2000-10
0.0	305.0	40.1	0.0	0.0	4.4	26-2000-20
0.0	336.6	28.9	0.0	0.0	3.2	26-2000-25
0.0	256.5	0.0	0.0	0.0	4.4	26-2000-30
0.0	293.2	32.5	0.0	0.0	4.9	26-2100-00
0.0	353.9	26.9	0.0	0.0	4.9	26-2100-05
23.2	366.1	133.9	12.5	0.0	7.4	26-2100-10
0.0	239.8	19.2	0.0	0.0	7.7	26-2100-20
0.0	317.6	19.7	0.4	0.0	5.9	26-2100-25
0.0	246.2	61.8	0.0	0.0	2.7	26-2100-30

TABLE H.4

Non-terrigenous element abundance, tidal station 15.

NON-TERRIGENOUS ELEMENT ABUNDANCE (UG/L):						
SI	CA	FE	K	PG	P	SAMPLE NAME
31.6	9.6	0.9	0.0	2.3	3.2	15-0902-00
29.4	48.6	5.9	0.0	10.2	4.0	15-0902-05
14.8	51.5	0.0	4.3	21.9	4.1	15-0902-10
86.6	132.7	16.7	8.9	26.0	3.7	15-0902-20
88.0	141.7	21.9	11.9	24.8	2.9	15-0902-25
36.2	57.5	5.6	2.5	11.0	3.4	15-1006-00
15.6	49.6	5.5	0.0	5.1	4.3	15-1006-05
20.8	52.1	5.3	5.0	8.6	3.5	15-1006-10
34.3	66.7	7.7	1.8	11.2	5.3	15-1006-15
116.0	135.5	24.8	14.4	21.8	4.0	15-1006-20
143.8	154.1	26.8	18.3	23.9	4.0	15-1006-25
29.7	53.7	10.5	2.0	9.2	3.4	15-1104-00
20.3	47.0	7.9	0.0	8.1	3.2	15-1104-05
20.6	39.2	7.6	1.1	5.3	2.7	15-1104-10
54.4	86.4	9.5	6.3	12.7	3.5	15-1104-15
74.4	137.1	19.1	16.8	31.5	3.9	15-1104-20
130.8	158.4	25.4	15.1	16.8	3.6	15-1104-26
25.5	52.1	6.8	1.9	7.5	4.9	15-1205-00
26.1	56.3	7.4	4.7	16.1	3.6	15-1205-10
78.4	107.2	9.6	11.4	22.5	4.1	15-1205-15
193.0	105.7	20.2	16.2	0.0	5.1	15-1205-20
128.6	174.8	24.5	23.1	37.8	3.5	15-1205-26
20.9	43.5	4.4	1.4	7.2	3.2	15-1304-00
19.9	52.9	3.9	5.2	6.9	5.6	15-1304-05
45.0	64.3	9.4	3.9	9.4	3.5	15-1304-10
85.6	100.7	14.4	10.3	14.3	3.4	15-1304-15
1265.6	162.8	23.7	18.3	24.1	3.5	15-1304-20
174.6	211.0	36.0	24.0	34.2	4.4	15-1304-26
0.0	11.1	0.0	0.0	5.2	4.2	15-1410-00
13.5	45.7	6.5	0.3	4.9	7.0	15-1410-05
32.5	53.2	9.0	3.3	9.4	5.5	15-1410-10
122.3	91.6	10.9	8.4	13.7	3.5	15-1410-15
151.6	167.0	26.6	18.6	21.9	3.2	15-1410-20
174.8	188.9	33.9	22.4	28.6	4.9	15-1410-26
22.7	47.1	7.2	2.2	9.4	3.3	15-1500-00
26.3	50.5	8.6	2.2	7.7	2.8	15-1500-05
34.2	64.7	2.7	3.2	9.3	3.3	15-1500-10
172.5	207.4	38.2	23.3	31.3	4.0	15-1500-20
56.2	180.1	0.1	11.0	33.2	3.5	15-1500-25
174.5	212.6	32.2	22.3	35.1	4.1	15-1500-29
0.0	7.0	106.6	0.0	4.7	2.3	15-1600-00
9.9	47.5	0.0	0.8	8.8	3.0	15-1600-05
32.3	54.8	6.3	2.0	6.9	3.2	15-1600-10
0.0	107.1	0.0	0.0	23.1	2.1	15-1600-20
197.9	206.3	32.5	23.8	28.0	4.1	15-1600-25
162.3	193.6	25.4	25.2	29.2	6.3	15-1600-28
17.9	50.4	12.7	1.4	9.3	5.1	15-1700-00
17.9	52.6	6.2	1.3	9.2	5.9	15-1700-05
33.1	70.6	10.5	4.1	13.4	4.6	15-1700-10
164.7	173.1	23.8	20.6	25.9	5.5	15-1700-20
146.6	210.7	27.8	24.2	31.8	7.4	15-1700-25
183.7	202.0	32.3	24.0	31.0	5.2	15-1700-30
8.0	46.0	11.6	0.0	5.1	6.0	15-1800-00
19.3	43.9	7.2	0.6	5.9	4.6	15-1800-05
13.9	49.6	6.2	0.2	0.0	6.1	15-1800-10
121.4	135.8	23.0	20.2	21.9	4.7	15-1800-20
168.8	179.3	27.6	21.3	26.2	3.7	15-1800-25
229.6	212.7	58.9	31.9	28.4	5.7	15-1800-29
22.9	52.4	6.5	3.1	9.8	4.2	15-1900-00
24.0	54.9	7.8	3.2	8.7	8.2	15-1900-05
23.9	57.2	9.8	1.8	7.2	4.8	15-1900-10
97.2	133.3	14.5	14.1	24.2	4.8	15-1900-20
123.0	153.0	20.8	17.0	23.6	4.1	15-1900-25
146.5	184.7	21.4	20.4	31.7	5.9	15-1900-30
30.5	52.3	9.4	4.0	8.4	2.2	15-2000-00
27.4	56.2	7.8	4.2	0.0	6.4	15-2000-05
35.1	65.7	4.3	5.0	11.5	3.5	15-2000-10
56.6	84.3	11.1	8.2	15.3	6.2	15-2000-15
203.5	99.8	23.2	18.5	34.9	5.4	15-2000-20
186.7	228.6	46.5	28.4	35.9	5.4	15-2000-30
28.1	53.2	8.0	3.2	12.5	8.3	15-2100-05
24.1	53.8	6.3	5.0	12.1	7.1	15-2100-10
32.8	69.0	4.1	2.9	12.4	4.4	15-2100-15
155.4	165.9	27.5	19.2	26.2	6.8	15-2100-20
160.1	149.0	31.3	22.1	33.2	4.7	15-2100-26

TABLE H.5

Non-terrigenous element abundance, tidal station 7.

NON-TERRIGENOUS ELEMENT ABUNDANCE (UG/L):						SAMPLE NAME
SI	CA	FE	K	MG	P	
135.5	47.3	4.0	0.0	5.9	14.0	77-0815-00
79.2	50.9	0.7	0.0	8.9	15.1	77-0815-05
56.9	15.5	0.0	0.0	13.2	14.9	77-0815-08
180.2	49.5	15.9	4.2	7.4	14.0	77-0915-00
44.4	16.6	0.0	0.0	7.6	14.7	77-0915-05
141.8	40.5	4.9	0.0	10.9	14.1	77-0915-08
156.0	44.6	9.3	0.0	9.8	13.9	77-1015-00
202.6	54.1	21.3	4.4	10.0	13.9	77-1015-05
168.6	44.1	9.1	0.0	8.2	12.8	77-1015-08
166.1	44.3	8.7	1.6	9.1	13.4	77-1115-00
161.2	40.7	3.6	0.0	8.6	14.7	77-1115-05
184.6	80.1	5.4	0.0	14.3	29.5	77-1115-09
204.6	47.0	12.2	3.8	9.2	13.6	77-1215-00
189.5	41.7	12.7	0.5	6.2	12.6	77-1215-05
228.0	51.5	6.0	0.4	11.0	14.1	77-1215-10
192.4	39.8	8.1	1.8	5.5	14.2	77-1315-00
284.4	56.6	9.9	4.7	8.6	12.1	77-1315-05
152.5	40.5	9.1	0.0	9.8	14.2	77-1315-12
205.8	56.4	17.4	5.4	11.7	15.8	77-1415-00
188.0	35.8	8.3	0.0	4.4	12.1	77-1415-05
239.6	35.0	4.5	2.7	12.2	12.1	77-1415-12
82.6	3.6	0.0	0.0	8.3	12.9	77-1515-00
164.9	32.6	6.7	0.0	5.9	11.9	77-1515-05
231.4	45.1	4.2	0.0	5.3	9.1	77-1515-12
130.6	35.2	6.0	0.0	8.7	14.9	77-1615-00
169.9	17.9	0.0	0.0	6.8	12.4	77-1615-05
152.8	35.7	0.0	0.0	7.6	9.5	77-1615-10
259.5	60.8	14.6	4.6	6.7	10.0	77-1615-13
179.1	32.7	6.7	1.4	9.2	16.4	77-1715-00
112.7	22.3	0.0	0.0	11.1	13.8	77-1715-05
200.6	47.7	0.0	0.0	10.4	11.0	77-1715-10
152.0	33.1	0.0	0.0	12.7	11.1	77-1715-13
182.8	39.6	3.5	2.6	11.3	16.0	77-1815-00
169.7	33.8	0.0	0.0	7.5	13.3	77-1815-05
255.7	53.0	11.4	6.7	10.9	12.6	77-1815-12
112.3	11.7	0.0	0.0	5.8	12.1	77-1915-00
137.8	25.2	0.0	0.0	7.4	12.4	77-1915-05
274.3	67.8	16.8	6.2	9.8	10.9	77-1915-11

TABLE H.6

Non-terrigenous element abundance, areal sampling

NON-TERRIGENOUS ELEMENT ABUNDANCE (UG/L):						
SI	CA	FE	K	MG	P	SAMPLE NAME
165.2	101.2	31.9	13.0	26.2	4.2	15-18-0
17.8	52.2	21.5	1.4	7.3	4.3	15-18-02
114.2	65.6	24.9	7.1	4.6	4.7	15-18-05
80.4	65.7	26.9	8.2	3.7	4.1	16-17-0
91.8	74.5	22.5	8.7	14.4	3.7	16-17-02
86.3	69.9	21.5	6.7	8.0	3.7	16-17-05
112.9	93.8	26.2	11.8	5.7	4.2	16-17-10
70.7	78.2	25.0	7.5	11.9	4.8	16-17-15
111.5	76.1	22.4	10.9	1.0	4.0	17-16-0
134.6	95.1	26.6	13.1	15.4	3.5	17-16-02
110.7	89.2	22.0	10.0	15.0	3.8	17-16-05
128.0	73.2	22.8	10.6	6.8	3.7	17-16-10
140.8	104.2	33.5	15.6	17.6	4.1	17-16-20
121.7	152.0	38.8	22.5	30.2	3.4	17-16-28
141.1	84.1	31.7	13.8	7.3	3.9	18-15-0
115.4	73.5	30.9	12.1	14.1	3.2	18-15-02
103.4	75.9	27.9	12.1	13.6	2.9	18-15-05
133.8	97.7	32.4	16.5	6.7	3.8	18-15-10
139.5	119.5	44.7	18.9	25.5	4.1	18-15-20
177.5	128.2	48.3	23.0	10.1	3.8	18-15-25
47.1	42.3	14.6	2.3	0.0	3.8	19-14-0
60.9	58.0	8.4	5.5	8.0	3.6	19-14-02
74.7	70.8	13.2	2.9	7.9	3.7	19-14-05
53.4	40.2	17.9	3.6	0.0	3.5	19-14-10
170.7	70.0	25.0	7.6	10.0	4.6	19-14-20
94.7	90.1	34.5	10.4	4.6	5.4	20-13-0
113.4	96.0	37.4	18.0	24.8	4.7	20-13-02
95.1	82.6	37.0	11.9	10.2	4.5	20-13-05
199.3	97.0	49.3	15.8	10.2	5.6	20-13-10
46.6	104.4	57.8	15.0	29.7	5.0	21-12-0
27.6	107.4	53.0	11.7	22.5	5.3	21-12-02
31.2	125.8	67.4	16.2	29.3	5.4	21-12-05
0.0	106.7	112.0	7.3	29.3	11.6	22-1-0
0.0	114.2	122.5	8.8	35.1	10.9	22-1-02
0.0	113.7	110.1	4.7	22.1	12.0	22-1-04
0.0	77.5	104.5	0.0	54.0	8.4	23-2-0
0.0	111.3	115.9	3.9	33.7	10.5	23-2-02
0.0	0.0	37.4	0.0	38.9	9.3	23-2-05
0.0	96.3	106.4	8.4	45.6	8.9	24-3-0
0.0	33.8	72.3	0.0	26.2	6.0	24-3-02
0.0	71.8	95.1	5.7	37.7	8.2	24-3-04
0.0	59.9	92.9	3.1	33.7	8.6	25-4-0
0.0	73.0	95.5	2.7	31.6	9.4	25-4-02
0.0	53.8	66.7	0.0	42.9	9.1	25-4-05
0.0	53.4	107.6	0.0	39.8	8.4	26-5-0
0.0	18.1	80.9	0.0	23.0	9.6	26-5-02
0.0	41.7	102.7	0.9	24.1	9.7	26-5-05
0.0	24.4	73.3	0.0	47.0	8.6	26-5-10
0.0	18.8	13.4	0.0	45.8	8.0	26-5-20

TABLE H.6

(continued.)

NON-TERRESTRIAL ELEMENT ABUNDANCE (UG/L):

SI	CA	FE	N	MG	P	SAMPLE NAME
0.0	21.0	89.1	0.0	31.7	8.8	27-24-0
0.0	140.7	588.5	88.1	39.8	16.6	27-24-20
0.0	84.3	122.0	13.3	50.2	9.6	28-25-0
0.0	58.2	91.8	2.5	34.2	9.1	28-25-02
0.0	21.9	98.0	0.0	39.2	8.4	28-25-05
0.0	14.2	81.4	0.0	29.9	10.8	28-25-10
0.0	26.3	217.5	14.3	61.1	10.0	28-25-15
0.0	77.6	87.2	2.6	28.5	9.4	29-4-0
0.0	64.8	50.9	3.6	22.9	8.6	29-4-02
0.0	86.0	313.4	30.1	52.0	10.1	29-4-05
19.2	92.5	50.1	4.0	23.2	8.3	30-26-0
66.3	63.2	48.4	3.7	7.9	5.4	30-26-02
0.0	84.4	53.7	3.7	53.2	5.9	30-26-10
0.0	10.8	19.9	0.0	18.2	6.0	30-26-20
0.0	114.5	396.3	38.9	16.1	5.0	30-26-30
0.0	267.8	1009.1	138.0	26.0	5.8	30-26-33
59.4	65.2	16.9	5.6	7.1	4.0	31-27-0
88.5	71.7	29.8	6.3	8.9	4.1	31-27-05
87.5	52.5	25.2	7.4	7.4	4.2	31-27-10
77.7	94.4	38.7	7.8	0.0	4.2	31-27-20
92.2	76.0	28.7	6.7	0.0	5.2	32-9-0
38.7	58.5	21.7	2.1	14.6	5.7	32-9-02
101.2	59.7	20.7	4.8	7.7	3.9	32-9-05
64.2	48.9	16.7	6.1	2.5	3.3	32-9-15
23.0	49.3	1.1	0.0	0.0	5.0	33-28-0
6.4	47.6	10.2	0.0	6.4	5.3	33-28-02
0.0	58.2	0.0	0.0	3.8	3.8	33-28-05
11.7	28.0	14.0	0.0	1.0	4.2	33-28-10
50.0	66.1	26.8	6.0	9.8	4.7	33-28-20
79.4	63.9	21.9	8.2	14.4	6.0	34-15-0
85.8	50.1	26.5	6.4	15.5	5.6	34-15-02
46.1	63.5	14.8	6.6	11.8	5.4	34-15-05
76.3	76.8	29.8	8.0	11.9	5.4	34-15-10
114.8	81.7	32.9	15.6	10.0	4.4	34-15-20
98.7	83.7	28.1	11.2	13.6	4.8	34-15-25
93.5	76.6	25.0	10.5	14.5	4.7	35-29-0
81.8	76.2	17.4	7.1	18.5	4.6	35-29-02
85.5	84.0	25.0	9.0	17.1	4.2	35-29-05
88.9	84.9	17.3	8.5	17.4	4.2	35-29-10
123.7	97.4	28.2	14.9	5.0	4.4	35-29-20
138.3	109.7	42.8	17.8	19.3	4.4	35-29-30
101.8	80.5	31.7	15.0	15.1	3.7	35-29-35
73.4	53.2	25.3	10.9	11.0	3.9	36-21-0
72.5	56.9	17.5	6.1	12.1	3.5	36-21-02
67.0	58.5	19.3	6.2	14.4	3.8	36-21-05
62.2	55.8	27.8	6.4	6.3	4.3	36-21-10
98.5	98.8	35.6	12.9	13.5	4.3	36-21-20
113.8	101.1	40.6	15.3	13.0	4.4	36-21-30
56.0	65.5	50.7	11.2	9.8	3.3	36-21-40
142.5	122.5	48.1	20.3	24.8	4.5	36-21-45

TABLE H.6

(continued)

NON-TERRIGENOUS ELEMENT ABUNDANCE (UG/L):						
SI	CA	FE	K	MG	P	SAMPLE NAME
80.9	98.7	25.1	7.9	9.6	3.1	37-23-C
144.7	75.8	20.6	7.8	8.0	3.2	37-23-02
147.7	79.1	23.6	7.9	0.5	3.5	37-23-05
82.9	66.5	27.0	8.9	2.9	3.9	37-23-10
0.0	100.7	62.7	5.1	22.7	8.0	38-22-02
90.6	63.6	17.8	10.6	13.4	3.2	38-22-05
99.1	73.2	23.5	13.3	3.4	3.5	38-22-10
109.6	74.3	27.7	13.1	6.8	3.3	38-22-20
98.6	71.0	23.9	10.6	3.4	3.4	38-22-30
182.5	118.9	28.8	14.5	14.7	4.0	38-22-35
93.3	49.6	24.2	8.2	7.2	4.1	39-21-0
84.6	63.3	17.1	7.3	13.6	4.3	39-21-02
66.8	40.8	21.6	6.5	10.4	3.3	39-21-05
32.1	34.2	12.3	3.6	2.2	3.1	39-21-10
65.2	47.6	25.2	7.9	6.7	3.7	39-21-20
67.7	54.3	27.3	9.4	4.2	3.4	39-21-30
44.0	91.0	19.2	8.6	23.8	5.4	39-21-40
144.7	116.7	38.2	18.3	21.6	3.7	39-21-45
102.2	85.1	29.7	12.1	13.0	4.9	40-20-0
51.5	53.5	17.3	5.7	13.5	3.6	40-20-02
0.0	41.6	0.0	0.0	4.0	2.8	40-20-05
92.9	94.6	25.6	11.1	7.1	4.4	40-20-10
76.8	87.5	38.3	12.3	13.1	4.3	40-20-30
109.8	116.2	44.7	16.5	22.4	4.4	40-20-40
78.2	105.5	39.6	13.9	18.5	5.1	40-20-45
131.2	98.8	40.4	13.6	19.1	5.4	41-19-0
59.5	86.4	26.9	9.1	19.6	5.0	41-19-02
71.0	105.9	41.0	12.0	20.5	5.8	41-19-05
73.8	104.0	40.6	18.1	20.5	4.1	41-19-10
11.2	113.9	56.9	10.7	27.1	4.1	41-19-20
25.4	161.1	83.2	19.0	34.8	5.4	41-19-23
30.7	102.4	74.3	7.9	29.6	12.3	42-6-0
22.8	110.1	87.5	9.4	23.0	11.8	42-6-05
29.0	112.3	56.1	5.4	30.4	11.3	43-7-0
16.8	117.0	64.3	5.2	29.5	11.6	43-7-05
102.0	107.8	45.2	12.1	17.8	6.3	44-6-0
34.7	84.6	33.5	5.7	19.5	4.7	44-6-02
66.3	95.3	60.8	11.0	28.8	6.0	44-6-05
0.0	106.7	52.3	8.0	43.4	5.4	44-6-10
34.9	61.9	31.0	0.0	4.3	4.9	45-9-0
18.8	58.7	11.6	0.0	6.8	5.0	45-9-02
44.0	76.1	7.9	0.0	6.1	4.9	45-9-05
98.3	83.1	18.9	4.3	13.5	4.2	45-9-10
0.0	27.4	0.0	0.0	16.5	5.1	45-9-20
37.2	63.3	18.5	2.5	0.4	5.6	46-10-0
3.2	47.5	1.3	0.0	6.5	4.6	46-10-02
30.1	66.4	14.0	3.3	5.8	4.8	46-10-05
21.6	69.5	5.2	0.0	5.9	5.5	46-10-10
81.6	98.0	25.4	9.1	19.9	5.1	46-10-15
13.9	57.2	0.0	0.0	0.0	5.9	47-11-0
0.0	58.0	0.0	0.0	4.8	4.6	47-11-02
100.7	78.2	29.1	10.7	16.1	4.2	47-11-05
0.0	24.4	0.0	0.0	4.7	4.9	47-11-10
0.0	83.8	0.0	0.0	27.7	4.3	47-11-15
81.3	55.3	20.4	7.1	3.2	5.1	49-15-0
54.0	63.2	10.7	3.5	6.6	3.9	49-15-02
44.9	59.8	7.2	0.5	6.3	3.5	49-15-05
171.4	66.2	9.5	4.3	6.0	4.2	49-15-10
32.4	86.2	24.0	2.0	11.4	4.2	49-15-20
20.8	127.0	30.2	9.5	31.2	4.4	49-15-25

TABLE H.7

Trace element analyses of sediment samples.

Core	Depth (cm.)	Pb (ppm.)	Zn (ppm.)	Cu (ppm.)
1	0-4	163.7	176.5	53.3
	4-8	137.6	146.4	46.4
	8-12	87.8	122.4	35.5
	12-15	69.0	93.4	29.0
	15-18	70.5	92.7	34.3
	18-21	29.9	76.0	24.9
	24-28	25.9	66.8	20.6
	32-36	38.0	64.1	17.8
	40-44	34.2	61.3	35.1
7	0-5	171.3	180.2	70.4
	5-10	112.0	169.8	85.4
	10-15	124.1	173.2	50.3
	15-20	121.9	173.7	49.4
	20-25	75.6	99.0	21.7
	25-30	11.1	53.0	4.7
	30-35	20.8	57.8	7.5
	35-40	42.9	60.0	12.2
	40-50	3.9	60.8	9.6
	60-70	9.4	38.5	6.3
13	0-5	81.6	105.9	31.6
	5-10	50.5	84.3	14.3
	10-15	40.7	69.4	29.6
	15-20	66.7	69.0	16.0
	20-25	23.3	71.3	7.8
	25-30	28.4	81.9	8.3
	40-50	22.1	70.0	17.0
	60-70	20.3	81.3	19.9
	80-90	25.8	70.7	21.6

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