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INFLUENCE OF RAFTED OYSTER AQUACULTURE ON SEDIMENT PROCESSES

DRAFT

DRAFT FINAL REPORT

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PROJECT RATIONALE AND OBJECTIVES

Comparison of historical Chesapeake Bay oyster standing stocks with those existing now indicate that an important mechanism for removing phytoplankton biomass from Bay water has all but disappeared (Newell 1988; Newell et al. 1989). The Bay ecosystem appears to have changed such that a substantial portion of primary production is now dissipated by bacterial metabolism (Baird and Ulanowicz 1989), leading to increased oxygen consumption in the water column and sulfide production in sediments. These microbial processes have been chiefly responsible for increasing the intensity, duration, and spatial extent of hypoxic and anoxic conditions in mesohaline Bay waters (Tuttle et al. 1987a). A simple, benthic suspension feeding model predicts that rafted oyster population densities sufficient to reduce current phytoplankton biomass by 40% are theoretically sustainable (Gerritsen et al. 1989). All these observations lead to the hypothesis that increasing Bay oyster stocks, by rafted oyster mariculture or by augmenting oyster reef densities, could substantially improve water quality in the Chesapeake Bay and/or its tributaries and, at the same time, revitalize the declining shellfish industry in Maryland.

Field studies conducted by our laboratory in 1989 and 1990 at the St. George Oyster Company oyster mariculture facility in St. Mary's County, Maryland, demonstrated that rafted oysters can remove significant quantities of phytoplankton carbon and biochemical oxygen demand from the estuarine water column (Jonas and Tuttle 1991; Tuttle and Jonas, in preparation). The field data are consistent with the trophic consequences of increasing oyster densities predicted by a quasi-equilibrium, mass action model of the exchanges transpiring in the mid-Bay ecosystem (Ulanowicz and Tuttle, in press). Despite mounting evidence of the

efficacy of increasing oyster stocks as a useful bioremediation technique to augment the nutrient reduction strategy, it remains unclear whether increased loading of sediments with oyster feces and pseudofeces would significantly increase oxygen demand in the sediments. If so, many of the benefits gained from removing excess phytoplankton from the water column could be negated.

Based on information gained using a variety of techniques, many of which we have applied over the past eight years to examine the formation and maintenance of anoxia in the mesohaline Chesapeake Bay, we report here on the influences of oyster rafting mariculture on underlying estuarine sediments in comparison with similar, nearby sediments outside the raft area. Our goals were to establish whether oyster fecal loading substantially increases sediment oxygen deficits and to examine how this loading quantitatively and qualitatively affects key estuarine microbial sediment processes on a seasonal basis.

To attain these goals, our objectives were:

1. To compare the quantity and quality of organic carbon reaching the sediments beneath and away from rafting areas;

2. To determine integrated microbial metabolism in these sediments;

3. To compare rates of sediment sulfate reduction, the key bacterial process occurring in Chesapeake Bay sediments during the periods of rapid oyster growth; and,

4. To assess sediment oxygen demand in sediments beneath and away from rafting areas.

BACKGROUND

Ecosystem Rationale for Oyster Replenishment

Recent studies on Chesapeake Bay water quality and assessments of the current state of the mid-Bay's ecosystem (Malone et al. 1986; Tuttle et al. 1985, 1987a, 1987b; Jonas 1987; Jonas et al 1988a, 1988c; Baird and Ulanowicz 1989; Jonas and Tuttle 1990; Baird et al. 1991) all suggest that there has been a major shift in the trophic food web structure of the Bay's ecosystem. Especially during the warmer months of the year, the ecosystem now appears to be dominated by bacteria and their associated physiological processes rather than by grazer-based food webs. This trophic shift is particularly evident in the water column where increased phytoplankton production resulting from anthropogenic inputs of nitrogen and phosphorous is consumed to a major degree by free-living bacteria. In the mesohaline reaches of the Bay, for example, abundances of these microorganisms reach and remain at 10 to 20 x 10^9 cells L^{-1}. Such sustained abundances, which have been observed over several years and locations throughout the mid-Bay region (Malone et al. 1986; Tuttle et al. 1987a; Ducklow et al. 1987; Jonas and Tuttle 1990; Malone et al. 1991), are high compared to other coastal environments (Williams 1984). These elevated bacterial abundances are responsible for high rates of pelagic oxygen consumption and represent one of the primary factors driving the development and maintenance of hypoxia and anoxia commonly observed in the mainstem and subestuaries of the Bay (Tuttle et al. 1987a).

High levels of microbially labile dissolved organic carbon (DOC) fueling the production and metabolism (and thus, oxygen consumption) of the pelagic, heterotrophic bacteria derive from: 1) direct release of DOC by living phytoplankton (Malone et al. 1991); 2) indirect release of DOC through grazing and excretion by zooplankton (e.g. Caron et al.

1988; Roman et al. 1988); and 3) DOC release from decaying phytoplankton cells (Tuttle et al. 1987a; Jonas and Tuttle 1990; Bell 1990). About 11% of mainstem mid-Bay total DOC (typically 3.5 mg C L^{-1}; Malone et al. 1991) consists of highly labile organic carbon (0.38 mg C L^{-1} measured as dissolved, 5-day biochemical oxygen demand; Jonas and Tuttle 1990) which in turn is composed of such substances as carbohydrates, amino acids, and short chain organic acids (Bell et al. 1988; Jonas et al. 1988a; Bell 1990). Like bacterial abundances, rates of oxygen-consuming metabolism of this labile organic carbon are also unexpectedly high compared to other estuarine systems. In the mid-Bay mainstem, for example, dissolved monosaccharide concentrations average 1 to 2 μM (0.07 to 0.14 mg C L^{-1}), dissolved free amino acid (DFAA) concentrations approach 1 μM, and their metabolism can average 225 n mol L^{-1} h^{-1} (16.2 μg C L^{-1} h^{-1}) and 20 n mol L^{-1} h^{-1}, respectively (Bell 1990). Thus, dissolved monosaccharides, comprising up to 37% of labile DOC, represent a preferred source of carbon and energy for pelagic bacterial metabolism and production in the mid-Bay and exhibit a very rapid turnover ranging from 8.9 to 4.3 h.

Recent inter-ecosystem comparisons of the Chesapeake Bay with other coastal environments suggest that the Bay is stressed, giving rise to increased recycling of materials (i.e. fixed carbon and nutrients) via short intense loops (Baird et al. 1991). Thus, although there have been suggestions that secondary producer-based bacterial food webs may be important links to higher trophic levels in aquatic ecosystems, this phytoplankton/bacterial food web ("microbial loop") is probably unproductive in terms of transferring carbon and energy to harvestable biological resources. Factors such as increased food web length (Baird and Ulanowicz 1989) and the apparent lack of efficient bactivors (small animals which consume bacteria) seem to result in Bay planktonic food webs in which the bacteria act as an

organic carbon sink in which carbon and plant nutrients are rapidly recycled (Ducklow et al. 1986; Baird and Ulanowicz 1989; Malone and Ducklow 1990; Fig. 1). The amount of phytoplankton net production "lost" through mid-Bay water column microbial metabolism alone has been estimated at 50, 30, 28 and 25% in summer, fall, winter, and spring, respectively (Baird and Ulanowicz 1989). Indeed, the 1989 State of the Bay Report concludes: "...only a small percentage of the plant production eventually reaches the economically important finfish and shellfish levels. The task of managers is to restore the Chesapeake to a balanced ecosystem in which as much of this energy as possible is funneled into important and useful biological yields -- oysters, striped bass, and waterfowl, among others. In the Bay's current state, much of the plant production does not reach these higher levels but ends up decomposing on the Bay bottom, robbing the water of much needed oxygen."

Recent evidence indicates that increased carbon flow through microbial loop communities is occurring in Bay sediments as well as in the water column. Sulfate reduction, a process confined chiefly to sediments and catalyzed by obligately anaerobic bacteria, has increased in mid-Bay sediments since colonial times (Cooper and Brush 1991). Directly measured rates of sediment sulfate reduction (sulfide production) in the mid- and lower Bay are among the highest found in marine environments (Tuttle et al. 1987a, 1987b; Roden and Tuttle in press, in revision) and rates in the upper Bay are substantial, even at limiting sediment pore water sulfate concentrations (Roden and Tuttle in review).

Although there are probably multiple causes for this shift in trophic structure of the Chesapeake Bay ecosystem, it is likely that a key factor has been the decline in abundance of benthic suspension feeders, such as oysters and clams, and consequent reduction in cropping

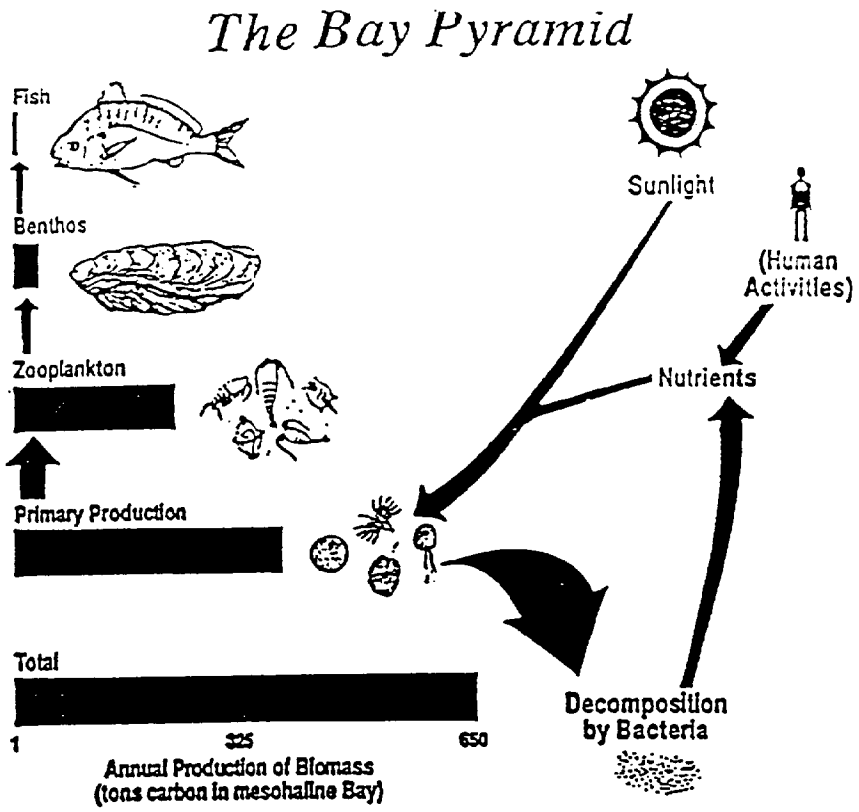

Figure 1. Current state of production (carbon flow) in the Chesapeake Bay ecosystem. Adapted from Draft 1989 State of the Bay report. (Thanks to Dr. J.A. Mihursky, CRC).

of phytoplankton. Baird and Ulanowicz (1989) noted that deposit-feeding organisms now dominate the benthic community of the Bay and that water clarity, once maintained by large populations of filter feeders, has decreased. Low dissolved oxygen concentrations, high rates of sediment deposition, overharvesting and parasitic diseases (e.g. MSX and Dermo) have all contributed to this decline of benthic suspension feeders. Newell (1988) estimates that Chesapeake Bay standing stocks of the American oyster, *Crassostrea virginica*, declined from 188 x 10^6 kg dry weight (~355 million bushels) in the late 19th century to about 1.9 x 10^6 kg dry weight (~4 million bushels) currently. Oyster landings in the 1800's amounted to about 20 million bushels annually from the northern, mesohaline portion of the Bay, whereas current harvests are of the order of 0.5 million bushels or less.

Calculations based on oyster abundances in the Bay and laboratory-determined oyster feeding rates (Newell 1988; Newell et al. 1989) suggest that oyster abundances in the late 19th century were sufficient to filter the entire volume of the Maryland portion of the Bay in three to six days. Current oyster stocks filter the same volume in about 325 days. Thus, a major biological mechanism for removing phytoplankton and organic detritus has been nearly eliminated from large areas of the Bay.

Although deposit-feeding macrobenthic invertebrates may have replaced the oyster to some extent (Baird and Ulanowicz 1989), it is possible that benthic biomass is actually reduced due to the loss of oyster feces and pseudofeces (Haven and Morales-Alamo 1986; Holland et al. 1987; Jordan 1987). Large segments of the macrobenthos may depend either on the organic materials deposited by oysters or the large surface area provided by oyster shell. In either event, inhospitable bottom water and sediment chemical conditions probably limit annual recolonization success.

It is reasonable to conclude that oysters, key filter feeders, were but are no longer a quantitatively important component of the trophic structure of the Chesapeake Bay ecosystem. Based on calculations such as those discussed above and on the current trophic state of the Bay, we (Tuttle et al. 1987b) and others (Newell 1988; Newell et al. 1989; Gerritsen et al. 1989) have proposed that replenishing oyster populations should have a major positive impact on Bay water quality as well as a revitalizing influence on the nearly extinct Chesapeake Bay shellfish industry.

Oyster Replenishment as a Bioremediation Tool

Given the likely condition that the magnitude of bacterial biomass, production, and metabolism in Chesapeake Bay is ultimately related to the amount of internal organic carbon production (autochthonous primary production) and external inputs (allochthonous carbon from terrestrial sources), it is theoretically feasible to control bacterioplankton communities by:

1. decreasing autochthonous production through nutrient reduction strategies and allochthonous carbon inputs by effective waste treatment and land management practices (bottom-up or supply side controls) and by

2. redirecting a portion of autochthonous production and allochthonous carbon through ecosystem compartments at higher trophic levels than the microbial loop (top-down or demand side control).

The first of these strategies, already implemented as the cornerstone of Bay cleanup

efforts and targeted primarily at decreasing phytoplankton biomass and production, would be expected to decrease microbial loop biomass and production as well with a concurrent decrease in oxygen consumption and improved water quality (eg. higher dissolved oxygen levels in deep waters, increased water clarity). Unfortunately, it is becoming increasingly apparent that nutrient reduction goals (40% reduction of N and P inputs) are probably not attainable, particularly in the case of N where substantial inputs as NO_x enter the Bay watershed from air pollution (see eg. Blankenship 1990, 1991). Furthermore, there is no reason to conclude *à priori* that the proportion of primary production metabolized by microbial communities would be altered, even if nutrient reduction goals were attained (i.e. even less production would be available for transfer to higher trophic levels, such that stocks of desirable species could be decreased).

The second strategy, a bioremediation procedure relying on higher trophic level consumers (oysters) whose population density could be directly managed, would permit a greater proportion of primary production to be captured by species more desirable than microorganisms. This top-down control scheme has, in fact, been proposed as a practical means to augment the nutrient reduction strategy (Gerritsen et al. 1989; Ulanowicz and Tuttle, in press).

Replenishment Strategies: Oyster Reef versus Oyster Aquaculture

Oyster standing stocks could be increased by replenishing historic oyster reefs, establishing new reefs, or by raft mariculture of oysters. Although our arguments are based on delineating those practices which will optimize water quality improvement, we are well aware of political and sociological considerations which may ultimately drive the

implementation of oyster replenishment strategies.

Gerritsen et al. (1989) used a simple, benthic suspension feeding model to predict the ability of suspension feeding bivalves to remove excess phytoplankton production from Bay waters, thereby improving water quality and decreasing oxygen deficits caused by decaying phytoplankton. Their model predicts that benthic oyster populations increased to a density sufficient to remove 40% of the phytoplankton standing crop (requiring an oyster biomass about ten-fold greater than that which existed historically in the Maryland portion of Chesapeake Bay) would be unsustainable due to problems of crowding, food limitation, and periodic hypoxic and anoxic conditions. In contrast, rafted oyster mariculture population density sufficient to meet the 40% nutrient reduction (i.e., 40% phytoplankton biomass removal) target of Maryland's Chesapeake Bay Initiatives are theoretically sustainable. It should be pointed out that this model scenario assumes the use of oyster replenishment alone to meet established water quality goals. If on the other hand oyster replenishment were used to augment nutrient reduction strategies (Ulanowicz and Tuttle, in press), oyster biomass supplementation could be reduced and oyster replenishment to the benthos would become an effective option.

There are other factors, however, which argue for oyster aquaculture. Viewed most simply, rafting of oysters within the mixed zone of the water column removes the oyster in the "Bay Pyramid" (Fig. 1) from its usual benthic position to the level between primary production and bacterial decomposition processes. In this new position, the oyster "competes" with bacterioplankton and, if successful, oysters could sequester a substantial amount of organic carbon from immediate bacterial metabolism. Redirecting the carbon flow by increasing oyster populations would be expected to reduce suspended particulate matter

(including phytoplankton, bacteria, and detritus) and oxygen demand while improving water clarity and increasing a harvestable fisheries resource. Rafted aquaculture is also likely to alleviate two major problems faced by bottom dwelling oysters. First, bottom dwelling oysters are particularly subject to deleterious influences of hydrogen sulfide arising from sulfate reduction in the sediments or from inundation by advected anoxic water. Secondly, oysters in more saline regions (e.g., the mesohaline Bay) are threatened by the parasitic disease MSX and Dermo, chronic infections often fatal to the animals before they reach market size. By suspending oysters near the surface, away from sediments, the threat of low-dissolved oxygen concentrations is greatly reduced or eliminated, and the more rapid oyster growth rates attainable in rafted aquaculture should lessen the effects of parasitic diseases.

Field and Ecosystem Modeling Validations

Although simple modeling exercises such as those discussed above suggest that increased oyster populations could improve Bay water quality and restore balance to the Bay's ecosystem, field evidence and ecosystem effects confirming the efficacy of this proposed bioremediation strategy has been lacking. During 1989 and 1990, however, our laboratory conducted at the St. George Oyster Company in St. Mary's County, MD, a small-scale demonstration study aimed at determining how rafted oyster mariculture influences phytoplankton and bacterioplankton biomass and production, water column nutrients, and organic carbon lability. Details of this work may be found elsewhere (Jonas and Tuttle 1991; Ulanowicz and Tuttle, in press) or are in preparation (Tuttle and Jonas, in prep), but several key findings are worthy of mention here. We compared parameters measured within a raft field with measurements made in adjacent, open water areas.

Over a late May - early October period, phytoplankton biomass was reduced in the raft field (60,000 oysters in a 300 m^2 area) an average of 50% (range 17% to 72%) with a concommitted reduction in primary production (average 44% reduction). Thus, suggestions that raft mariculture should decrease phytoplankton biomass but might leave primary production unaffected (Gerritsen et al. 1989) or even increased (Tenore et al. 1982) seem unfounded. Bacterioplankton abundances were reduced significantly but less dramatically (average 20%, range 10 to 40%) than phytoplankton. Bacterial production and metabolism (glucose turnover), however, were nearly identical in rafted and open water areas despite decreased abundances in the former, indicating increased cell-specific rates of both processes. This finding is consistent with observations that bacterioplankton in Bay waters respond primarily to labile DOC (Jonas and Tuttle 1990; Malone et al. 1991). Indeed, filterable (functionally dissolved) 5-day biochemical oxygen demand (BOD) was decreased an average of only 9% (range 20% decrease to 21% increase) within the oyster raft field. Total BOD, however, was reduced an average of 30% within the rafts area and particulate BOD was decreased by an average of 47% (maximum of 64%), comparable to decreases in phytoplankton biomass and production.

A quasi-equilibrium, mass action model designed to assess the influence of increasing oyster densities on the mid-Bay ecosystem (Ulanowicz and Tuttle, in press) predicts qualitatively similar changes resulting from decreasing oyster stock exploitation by 23% (oyster biomass increased by 150%). Although smaller in magnitude (the aquaculture oyster densities were much greater), the predicted changes (decreases of 11%, 6%, and 5% for phytoplankton abundance, bacterioplankton abundance, and suspended POC-attached bacterial mass, respectively) were all in the same direction as parameters measured at the aquaculture

facility. Interestingly, the ratio of phytoplankton abundance decrease:bacterioplankton abundance decrease (about 2:1) was strikingly similar to that measured in the field. Other desirable changes predicted by the model included: decreased gelatinous zooplankton (-89%); increased benthic diatoms (+29%), mesozooplankton (+5%), carnivorous fishes (+18%), filter feeding fishes (+5%); and virtually unchanged DOC (+1%). Thus, the evidence so far supports the contention that increasing oyster populations in the Bay and/or its tributaries will positively impact the Bay's ecosystem and yield improved water quality.

Potentially Negative Impacts

Despite proposed, predicted, and measured benefits of an oyster replenishment strategy, there are several possible negative impacts associated with increased oyster densities. One of these, namely increased phytoplankton production in the vicinity of the oysters, has been discounted (Jonas and Tuttle 1991; Ulanowicz and Tuttle, in press). Another, increased nutrient concentrations (particularly N) arising from oyster excretion or from increased sediment flux, has not been confirmed by our 1990 study of water quality and pelagic microbial processes at the St. George Oyster Company (Tuttle and Jonas, in prep). Indeed, levels of ammonia and nitrate + nitrite were not elevated in an oyster raft area compared to nearby open waters.

Perhaps of greatest concern is the possibility that increased oyster densities could, through increased deposition of highly labile organic material (oyster feces and pseudofeces) increase sediment microbial processes and, thereby, increase sediment oxygen demand and sediment nutrient regeneration. In one sense then, what had been a problem of excess oxygen consumption and nutrient regeneration in the water column could be relocated to the

sediments. This shift appears to occur in mariculture raft areas of Spanish rias (Tenore et al. 1982) where sediments beneath rafts exhibit higher rates of anaerobic microbial processes (e.g. sulfate reduction) than sediments in rias where aquaculture is not conducted. The Spanish ria environments, however, are not nearly so productive as the Chesapeake Bay. Interestingly, ammonia regeneration in sediments underlying rafted rias is less intense than in open rias, probably due to decreased bioturbation in the former (Tenore et al. 1982).

The potential for increased carbon loading to sediments by increased oyster densities has been pinpointed as the critical outstanding question which needs to be addressed before oyster augmentation as a water quality improvement strategy can be implemented (Gerritsen et al. 1989). The work reported here was undertaken to directly investigate this potential problem. We have hypothesized that sediments underlying rafted oysters will receive greater quantities of microbially labile organic matter than outlying sediments and that key, anaerobic processes, such as sulfate reduction, will be increased. Both aerobic decomposition of the newly deposited material and sulfide produced from sulfate reduction should increase oxygen demand beneath the rafts. Accordingly, we selected for measurement parameters to assess sediment carbon quantity (POC) and quality (PON and BOD), overall sediment microbial activity (dark assimilation of carbon dioxide), and sulfate reduction (rates and pool sizes of sulfate and sulfide).

METHODS

Study Site Description

Our proposal identified the St. George Oyster Company oyster aquaculture facility,

located along the Potomac River in St. Mary's County, MD and operated by the Stewart Petroleum Company, as our study area. We intended to examine sediments beneath "oyster bag" raft arrays set along the eastern shore of Piney Point Creek where we had conducted in 1990 a study of the influence of rafted oyster aquaculture on water quality; phytoplankton biomass and production; bacterioplankton biomass, production and metabolism; and water column carbon quality (Tuttle and Jonas, in prep). This site had the advantages that: we had already collected a substantial body of water column data to serve as a backdrop for our sediment study; the oyster raft experimental study area, consisting of adjacent rows of oyster bag rafts, bags without oysters, and surrounded by open water on all sides, remained virtually "unmanipulated" by aquaculture personnel through an agreement we had with the St. George Oyster Company; the site was within ½ hour of our laboratory in Solomons; and outside access to the site by land was controlled by Stewart Petroleum which owned the property. Unfortunately, the St. George Oyster Company was closed by Stewart Petroleum in February 1991, just before our sediment study was to begin. We are unsure of the causes which forced the closure, but continued financial losses incurred by the ambitious St. George Oyster Company undertaking and possibly infection of the aquacultured oyster stock by the disease Dermo and/or MSX (caused by the parasitic protozoans, *Perkinsus marinus* and *Haplosporidium nelsoni*, respectively) may well have been key factors.

We are indebted to our grant officer, David Bleil of the Maryland Department of Natural Resources Tidewater Administration, for identifying and arranging for our access to an alternate aquaculture site located at Pintail Point Farm (near the Wye River Institute) on Maryland's Eastern Shore. Unfortunately, this site is more than two hours from our laboratory and had lower oyster densities and smaller oysters than the Piney Point Creek site.

Perhaps more importantly, however, financial and research personnel constraints on the project inhibited us from making pelagic measurements of the sort we had done previously at the St. George facility, and it was inappropriate at such a late date for us to interfere with operations (e.g., moving oyster trays and aerating the water) critical to the success of the commercial enterprise. On the positive side, the sediments at Pintail Point Farm (Deep Cover Creek, Paynter and Burreson 1991) were softer and less shell-littered, both of which facilitated coring. Moreover, the cove environment was more protected than at Piney Point Creek, thus minimizing sediment resuspension events, and the oysters at this lower salinity site were not infected with MSX or Dermo (Paynter and Burreson 1991).

The oyster raft area of the Deep Cove Creek site is shown schematically in Fig. 2. Two oyster raft fields were located approximately 5 m from each other and 15 m out from the northerly shore. Water depth throughout the cove ranged from about 1 m (station 1) to 2 m (station 4) at mean low tide. The raft stations 2 and 3 were located in the approximate center of each of the two raft fields. Oyster culture employees set out smaller oysters in the field surrounding station 3 for initial grow up, and then moved these oysters to the raft field surrounding station 2 for further growth. The larger oysters at station 2 were transported to high salinity sites in Virginia for final grow out before they were sold commercially. This scheme is employed to take advantage of the observations that the young oysters could be grown disease-free at the low salinity site but higher growth rates could be achieved at high salinity sites, so long as the oysters were not held at the latter for time periods long enough for Dermo infection to occur (Paynter and Burreson 1991).

The oysters were rafted in mesh trays (Paynter and Burreson 1991) similar in size and design to the "bread tray" rafts used by St. George Oyster Company in 1989 (Ulanowicz and

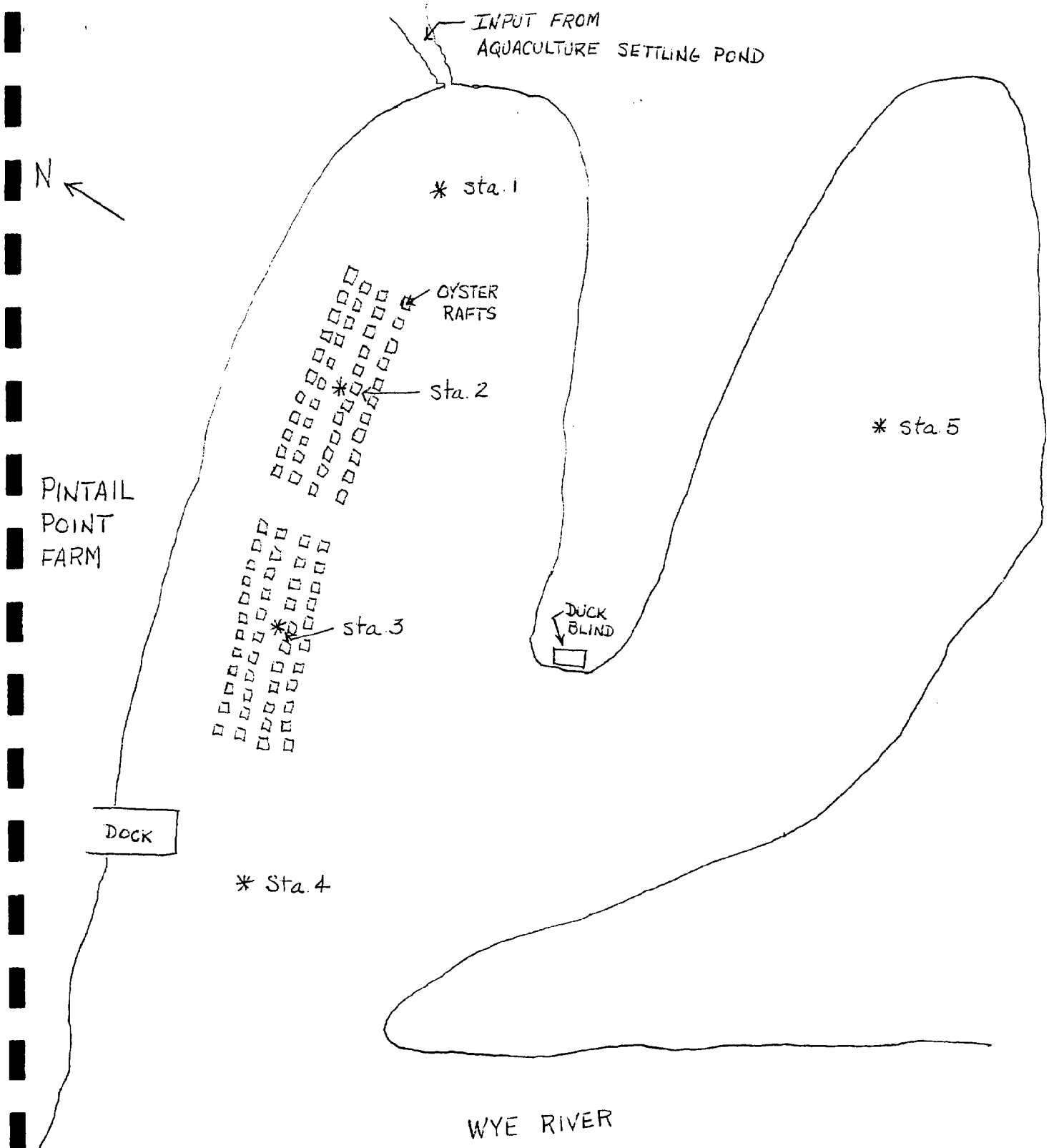

Figure 2. Schematic diagram of the Deep Cove Creek rafted oyster aquaculture site (not to scale).

Tuttle, in press). The maximum number of oysters rafted in the cove was 600,000 individuals (K. Paynter, personal communication).

Intermittent terrestrial input from an aquaculture waste pond settling at the cove's head influenced our selection of control (away from rafts) stations. Station 1 was located about 50 m down-cove from the raft field around station 2 in order to assess effects of this input. Station 4 was established about 35 m out from the cove mouth side of the raft field surrounding station 3. Thus, stations 1-4 formed a transect along the main axis of the cove which permitted us, within the bounds of original project resources, to assess oyster-related influences against the background of potential effects of non-oyster inputs. We also established a third control site (station 5) midway into a second cove whose mouth was adjacent to the mouth of the rafted cove. This cove received runoff from agricultural fields at its head and on its southern shore, but it was unaffected by aquaculture pond input and, to our knowledge, had not been used for oyster aquaculture.

Coring Device Design and Sediment Collection

In order to sample soft sediments such as those of the oyster raft fields from a small skiff, we needed to design and fabricate light, easy to use hand-held coring devices. These were constructed chiefly of light, inexpensive PVC tubing. The core barrel consisted of a 15 cm length of thin-walled, 1 in. ID PVC plumbing pipe fitted with a threaded male PVC connector. The core barrel was screwed into a 1" ID brass flapper valve with its plug removed. The flapper valve retained cores in the core barrel liner during retrieval. Core barrel liners were cut from 2.5 cm ID plexiglass stock (Read Plastics, Rockville, MD) to a length of 20-25 cm. One end was beveled to serve as a cutting edge. The core liner, which

fit easily but snugly into the core barrel, was held in place by a strip of duct tape wrapped around the bottom of the core barrel and the protruding core liner. The core handle, consisting of a thick-walled, 1" ID, 1.75 m length of PVC pipe, was connected to the top of the flapper valve by another threaded male PVC connector. The overall length of the assembled corer, about 2 m, was sufficient for most coring at the depths encountered at the site. For deeper samples, an additional 1.4 m length of pipe could be easily fitted to the handle by means of male and female connectors.

A synopsis of sampling visits is shown in Table 1. Full suites of measurements were made on June 10 (station 2 only) and on all subsequent visits (stations 1-4, occasionally 5). Cores were collected by lowering the core barrel to the sediment surface, followed by a rapid, even push of the corer into the sediment to a depth of about 15-20 cm. The cores were retrieved gently into the skiff and the bottom of the liner immediately plugged with a #5½ rubber stopper. The liner was then carefully removed from the core barrel and the top, filled to overflowing with overlying water was carefully stoppered to exclude air. Collected cores were placed upright in core racks and transported to the laboratory in coolers containing ambient temperature cove water. Eleven to 12 cores collected at each station were required for a full suite of measurements.

Hydrographic Measurements

Temperature, salinity, dissolved oxygen (DO), and Secchi disk depth were determined routinely at each station. Salinity was measured using a YSI Model 33 salinity meter, and temperature and DO with a YSI Model 57 digital dissolved oxygen meter.

Table 1 . Weather conditions and other observations made at the Pintail Point Farm oyster aquaculture facility on sediment sampling days.

DATE	WEATHER CONDITIONS	OTHER OBSERVATIONS
May 29	Fair and hot, calm.	Dissolved oxygen in rafted cove lower than in unrafted cove where the minimum % oxygen saturation (67%) was found at the head of the cove.
June 10	Fair and warm, calm.	
July 12	Fair and warm. Wind light from west (into rafted cove).	Air bubblers in operation between the two oyster raft areas (Stations 2 and 3).
Aug 1	Fair and warm. Wind light and northerly (across rafted cove).	Additional air bubblers installed along the main axis of the oyster raft areas. Bubblers in operation. "Red tide" observed at Station 4 and offshore into mouth of cove.
Sep 6	Rainy and cool. Wind gusty from the southwest. Water surface of unrafted cove most affected by wind.	Oyster rafts removed from Station 2 (largest oysters) area. Rafts still in place at Station 3. Bubblers not in operation.
Sep 27	Fair and cool. Wind moderate from north (across both coves).	Some rafts of larger oysters have been placed back at Station 2. Only a few oyster rafts at Station 3. Bubblers not in operation.
Nov 15	Fair and warm, calm.	All rafts removed from Station 2 area. Still a few rafts at Station 3. Bubblers not in operation.

Pore Water Collection

Collection of sediment pore water was required for analysis of free sulfide (HS^-), sulfate, and total inorganic carbon (TIC). Upon returning to the laboratory, three cores from each station were selected for pore water collection. Overlying water was carefully removed with a syringe from the top of the core as the core surface was gassed with O_2-free N_2. A #4 rubber stopper was inverted into the bottom of the liner and a 1.5 cm thick-walled PVC tube was applied against the stopper as a core pusher. Two cm thick segments of sediment were extruded directly into a gassed-out 50 mℓ centrifuge tube which was then tightly capped to prevent air intrusion. Two additional segments from replicate cores were removed to the tube. A total of 6 tubes were filled with sediments from each station so that profiles over a 12 cm depth at 2 cm intervals were obtained.

Capped tubes of pooled sediment were centrifuged at 3000 to 4000 rpm with an IEC swinging bucket rotor for 30 to 40 min. For pore water HS^- and sulfate analyses, the caps were removed, the pore water surface was gassed with O_2-free N_2, and 5 to 8 mL of pore water was taken up into a gassed-out syringe. The contents of the syringe were filtered through a N_2-purged, in-line filter (0.22 μm pore size membrane) into a pre-weighed scintillation vial containing 0.5 mL of 10% (w/v) zinc acetate to fix HS^- as ZnS. The vial was then weighed again so that a dilution factor to allow for the zinc acetate could be determined.

A portion of the zinc acetate-treated pore water was removed for immediate HS^- analysis or held overnight at 4°C for analysis the following day. The remainder was filtered (0.22 μm pore size membrane) to remove precipitated ZnS and the filtrate was stored at 4°C

in a plastic scintillation vial for subsequent sulfate analysis.

An additional portion of untreated pore water was removed to a small plastic vial fitted with a tight cap. The vials were stored frozen and analyzed later for TIC.

Chemical Determinations and Porosity

Pore water HS^- and total reduced sulfur (TRS) in sediments were measured according to the colorimetric method of Cline (1969). Samples analyzed for TRS consisted of appropriately diluted material from zinc acetate traps used to collect reduced sulfur from chromium distillations (see below).

Sulfate was measured with a Dionex Model 2020i ion chromatograph operated in the 30 u Siemens detector range. Ions were separated on an APS-4 column (Dionex) and eluted with filtered (0.45 μm pore size membrane) 2.8 mM $NaHCO_3$/2.25 mM Na_2CO_3. The column was regenerated with 0.025 N H_2SO_4.

Porosity of sediments is defined as the water content (by weight) of 1 g of wet (whole) sediment. Two cm thick segments were cut from fresh cores into pre-weighed aluminum pans and the wet weight determined. The segments were then dried to constant weight at 75°C.

POC and PON content of the surficial sediments (0-2 cm) was determined by elemental analysis of dried sediments, ground to a powder with a mortar and pestle. POC was also estimated from gravimetric loss from dry sediments after combustion at 450°C. TIC in pore water was estimated by acidifying samples and quantifying purged CO_2 with a carbon analyzer fitted with an infrared detector (CBL Analytical Services).

Biochemical Oxygen Demand

Five-day and 20-day biochemical oxygen demand (BOD-5 and BOD-20, respectively) estimates were made using a newly-developed procedure for sediments. A 2 cm thick surficial sediment segment was cut from a freshly collected core into a 150 mL beaker to which was added 90 mL of a nutrient-buffer solution prepared just prior to use from the two sterile stock solutions described below. Solution A had the composition: NaCl, 24 g; $MgSO_4 \cdot 7H_2O$, 7 g; KCl, 0.7 g; $MgCl_2 \cdot 6H_2O$, 5.3 g; deionized distilled water, 1 L. Solution A was sterilized by autoclaving. Solution B was composed of: K_2HPO_4, 21.75 g; KH_2PO_4, 8.5 g; $Na_2HPO_4 \cdot 7H_2O$, 33.4 g; KNO_3, 3.2 g; deionized-distilled water, 1 L. The pH was adjusted to 7.2 and the solution was filter-sterilized (0.22 μm pore size membrane). Solution A was diluted for use to the salinity of sample site surface water (usually about 8 ppt) with deionized-distilled water and solution B was added at the rate of 1 mL/L of diluted solution A to prepare the nutrient-buffer solution.

The diluted sediment was vigorously stirred and aerated for 30 min. to oxidize free sulfide which in the reduced sediments could contribute greatly to BOD. Two mL portions of well stirred sediments were transferred to each of 3-150 mL glass stoppered bottles, followed by an "inoculum" of 1 mL of surface water collected at the aquaculture site. The bottles were then filled with additional nutrient-buffer solution and DO was measured with a stirring DO probe. Two 4 mL portions of diluted sediments were filtered through pre-weighed GF/F glass fiber filters. The collected sediment was washed with two 5 mL portions of deionized water and dried to a constant weight. The dry weight data were used to normalize BOD data to unit weight of dry sediment.

BOD samples were incubated in the dark at 20°C and their DO content was measured at 5 and 20 days. Controls consisted of "inoculated" nutrient-buffer solution lacking sediments. BOD values for nutrient-buffer solution were subtracted from values for diluted sediments. Replicate cores from each station were analyzed for BOD.

Dark Assimilation of Carbon Dioxide

Dark CO_2 assimilation as a measure of integrated microbial metabolism was determined by measuring the rate of $NaH^{14}CO_3$ assimilation in duplicate intact sediment cores collected at each station and incubated at *in situ* temperature in the dark. The methods were similar to those described by Radway et al. (1987), but with some important modifications.

Overlying water was removed to a depth of 2 cm above the sediment surface. Measurements were started by injecting with a Hamilton syringe 10 μL (10 μCi) portions of $NaH^{14}CO_3$ (ICN Radiochemicals) into the sediments through silicone-sealed ports in the side of the core liner. Injections began 1 cm beneath the sediment water interface and were repeated at 2 cm intervals to a depth of 11 cm. Following incubation for 12 h (optimal incubation time was determined from time course measurements up to 24 h with station 2 sediments collected on June 10), the cores were frozen and held at -70°C until alkaline extraction of radiolabeled organic material was done.

For analysis, frozen core segments were sliced directly into tared, 125 mL wide mouth flasks which were then re-weighed to estimate sediment wet weight. Purging of thawed, acidified sediment with air to remove remaining ^{14}C-labeled inorganic carbon and boiling alkali extraction of labeled organic material was done according to Radway et al. (1987). Radioactivity of extracts was quantified using a Packard 3340 Minaxi liquid

scintillation counter (LSC) operated in the DPM mode. Water was added to 10 mL Instagel (Packard Instruments) to form a gel so that the samples did not phase during counting.

Dark CO_2 assimilation rates were calculated from turnover constants corrected for isotope discrimination (factor = 1.06). The turnover constants were also corrected for amount of radiolabel recovered when cores were frozen immediately after they had been injected (T = 0 correction). This correction factor, determined on a sediment dry weight basis, varied in magnitude with the turnover constant. For example, when extracted DPM was 0.075% of DPM injected into a segment, the T = 0 correction accounted for 65% of the turnover constant. When extracted DPM exceeded 1.2% of injected DPM, the T = 0 correction accounted for only 4.6% of the turnover constant. Turnover constants, adjusted for the T = 0 correction, were corrected for porosity (to convert to a "whole" or wet sediment basis) and multiplied by the TIC pool size of the appropriate segment. Assimilation rates used to construct core profiles have the units:

ng Carbon/g Wet Sediment x Day.

Areal rates were calculated by multiplying the per gram rate of each individual segment by wet weight of that segment and then summing the segment values to obtain an integrated value for the entire 12 cm core. These integrated values are expressed as:

mg Carbon/m^2 x Day.

Sulfate Reduction

Sediment sulfate reduction was assessed by ^{35}S- radiotracer methods (Jorgensen 1978).

Initial core preparation and injection procedures were identical to those for CO_2 assimilation measurements (see above), except that injections consisted of 10 to 15 μL portions (1.2 to 2.0 μCi) of carrier-free $Na_2{}^{35}SO_4$ (ICN Radiochemicals). Incubations were for 4 h as determined from time course incubations (0, 1, 2, 4, and 6 h) conducted with station 2 sediments collected on June 10. Sulfate reduction was stopped by injecting 200 μL of 30% (w/v) zinc acetate into the sediments through the same injection ports through which radioactivity had been added. This procedure "fixed" reduced sulfur by retarding its reoxidation. Fixed cores were immediately frozen and held at -70°C.

Total reduced ^{35}S was liberated by acidic chromium reduction (Zhabina and Volkov 1978; Fossing and Jorgensen 1989; Roden and Tuttle, in press). Cores were removed from the freezer, gently warmed so that they could be extruded from the core liner, and 2 cm thick segments cut and placed into tared 125 mL three-neck boiling flasks. The flasks were rapidly re-weighed, connected to distillation apparatus, and reduced ^{35}S was distilled into collection traps containing 100 mL of 10% (w/v) zinc acetate.

Radioactivity of $Zn^{35}S$ was quantified by LSC counting of LSC 2 mL of trap contents in 7 mL of Instagel. The TRS content of the trap material was measured as described above. Calculations made to determine sulfate reduction rates were similar to those used for the dark CO_2 assimilation measurements (see above). T = 0 corrections averaged 2.8% of sulfate reduction turnover constants. Sulfate reduction rates for core profiles have been expressed as: n mol S/g Wet Sediment x Day. Areal rates are in the units: m mol S/m^2 x Day.

RESULTS

Weather and Hydrographic Data

Weather conditions and hydrographic data collected during each of the visits to the sample sites are recorded in Table 1 and 2. All samples were collected during mid- to late-morning. Highest water temperatures, sometimes exceeding 30°C, occurred in May, although temperatures remained at 24°C or above throughout the season until late September. Salinity during the entire period ranged from about 6.8 ppt to 10.0 ppt. Surface water dissolved oxygen, when unaffected by operation of air bubblers, followed a pattern in the rafted cove of lowest DO at the head to highest values at the mouth (stations 1-4, May 29). Lowest observed DO (Table 2) occurred near the bottom of the channel of the Wye River at a depth of about 3 meters, suggesting that oxygen consuming *in situ* processes were at least as intense in the river as in the aquaculture cove area. Highest summertime DO in surface water occurred at station 4 on August 1. This coincided with the observation of an apparent "Red Tide" extending from station 4 to the mouth of the rafted cove.

Although DO values were sometimes low, <3.5 mg/ℓ, they were not biologically critical, at least during daylight hours, even without mechanical aeration. Bottom water DO tended to be lower than at the surface and this was true of both rafted and unrafted stations. When mechanical aeration commenced on July 12, bottom and surface water DO appeared to increase within the rafted cove areas relative to station 4 (Table 1). Mechanical bubbling was discontinued on or before September 6 even though oysters were still being rafted at station 3. Substantial DO sags were not noted in the period after June 10.

Secchi depths ranged from about 37 to 101 cm (Table 2). Highest Secchi depth values, indicating greatest water clarity, occurred in November likely as a result of natural seasonal variation in phytoplankton standing stocks. Usually there were no apparent significant differences in Secchi depth between rafted and unrafted areas. This suggests that oysters did

Table 2 . Hydrographic and secchi disk data collected at the Pintail Point Farm oyster aquaculture facility on days when sediments were sampled. Oysters were rafted at Stations 2 and 3. Station 6 was located in the main channel of the adjacent Wye River. ND indicates data not collected.

DATE	STATION	SURFACE TEMP deg C	BOTTOM TEMP deg C	SURFACE SALINITY ppt	BOTTOM SALINITY ppt	SURFACE DO mg/L	BOTTOM DO mg/L	SECCHI DEPTH cm
May 29	1	29.9	ND	7.0	ND	3.10	ND	>70
	2	30.1	28.9	6.9	6.9	3.51	3.42	69
	3	29.7	28.6	6.8	6.9	3.30	3.75	85
	4	30.5	28.1	6.9	7.0	6.35	5.22	68
	5	31.3	30.8	7.1	7.1	6.16	5.60	50
	6	29.6	27.3	7.1	7.5	8.44	2.89	ND
June 10	2	25.9	25.4	6.9	6.9	5.85	4.48	45
July 12	1	26.9	26.6	7.0	7.0	6.79	5.70	53
	2	27.4	27.3	7.0	7.1	6.79	5.65	52
	3	27.8	27.5	7.1	7.2	6.41	5.33	52
	4	28.2	27.5	7.1	7.1	7.49	6.13	57
Aug 1	1	26.8	26.4	8.3	8.3	5.65	4.95	53
	2	27.0	26.6	8.4	8.4	6.34	4.91	54
	3	27.1	26.8	8.8	8.8	6.35	6.09	56
	4	27.3	26.5	8.8	8.8	10.00	6.08	45
Sep 6	1	24.3	24.2	8.2	8.1	6.16	4.75	43
	2	24.9	25.0	8.2	8.2	5.91	5.61	42
	3	25.1	25.2	8.2	8.2	5.81	5.56	39
	4	25.0	25.2	8.4	8.5	6.10	5.32	47
	5	24.7	ND	8.2	ND	6.59	ND	37
Sep 27	1	20.3	20.3	7.8	7.8	5.09	5.10	55
	2	20.7	20.8	7.8	7.9	5.80	5.62	52
	3	20.5	20.6	8.0	8.0	6.07	5.85	52
	4	20.7	20.6	7.8	8.0	6.70	5.69	65
	5	20.2	ND	7.3	ND	6.43	ND	40
Nov 15	1	8.5	8.5	9.9	10.0	12.40	12.01	97
	2	8.3	8.3	9.8	9.9	13.24	13.16	98
	3	8.0	8.2	9.4	9.6	13.05	10.71	101
	4	8.9	8.3	9.3	9.5	12.27	11.80	101
	5	8.2	8.0	9.2	9.2	12.42	11.24	90

not detectably influence water clarity as determined by this relatively crude method.

Sediment Characteristics

The sediments consisted of "clayey" sand material at all stations except station 4 which was noticeably sandier. All stations, except station 4, appeared to be chemically reducing below 2 cm, as evidenced by a black appearance of the sampled cores. Surficial sediments, even in the rafted areas, often contained macrofauna, usually polychaete worms. At station 4, however, bioturbation, as indicated by worm tracks, was often apparent to a depth of at least 4 cm. Undecomposed or only partially decomposed leaves were sometimes encountered in cores taken at stations 1 through 3. These leaves were found at various depths, even as deep as 12 cm.

Porosity of the sediments exhibited a high degree of uniformity from sampling date to sampling date at individual stations (Fig. 3). Surface porosities were in the range of 0.75 to 0.80 at stations 1, 2, 3 and 5. Throughout the sediment profile, stations 1 and 2 were similar, as were stations 3 and 5. However, the profile for station 4 showed lower values than any of the others. The differences between station groups were most noticeable at the bottom of the sampled profile (10-12 cm). Mean porosity values were 0.67 to 0.68 at stations 1 and 2 (Figs. 3a and 3b), 0.60 to 0.62 at stations 3 and 5 (Figs. 3c and 3e), and 0.55 at station 4 (Fig. 3d).

Carbon: POC and PON

POC and PON, measured by elemental analysis, were analyzed only in the 0-2 cm core segments. POC decreased from station 1 to 4 (Fig. 4a). The pattern for PON was

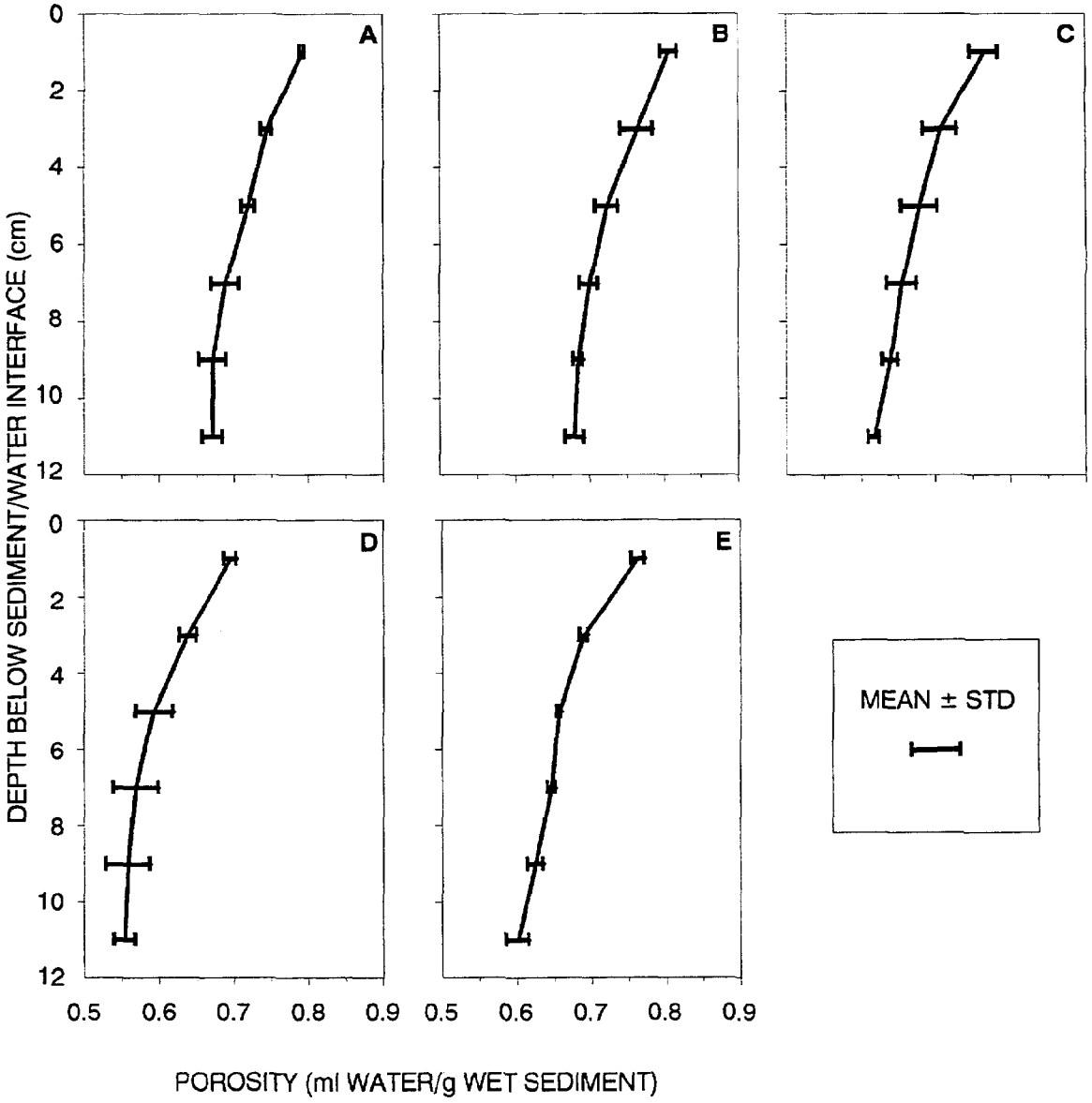

Figure 3. Porosity profiles of sediments at (A): station 1, (B): station 2, (C): station 3, (D): station 4, and (E): station 5.

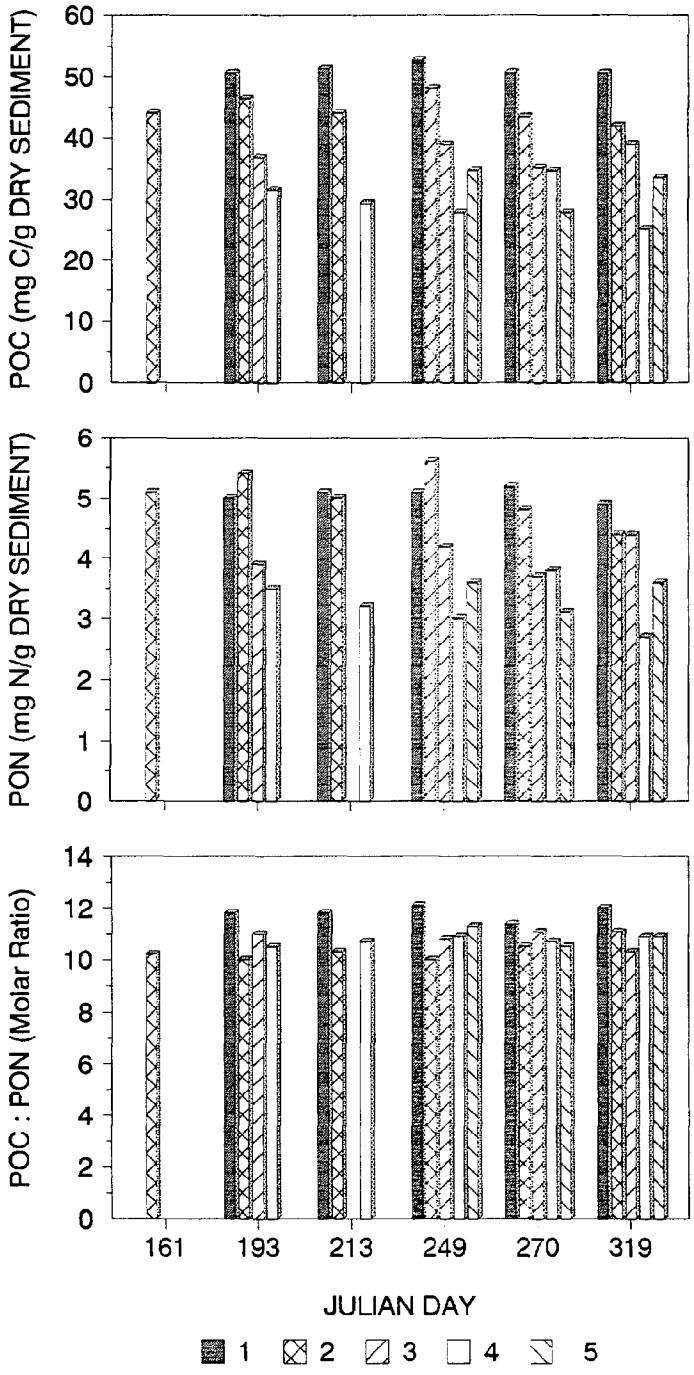

Figure 4. POC, PON, and POC:PON molar ratios in surficial (0-2 cm) sediments. Bar codes represent different stations.

similar except that PON was highest at station 2 on two occasions (Fig. 4b). It is noteworthy that station 5, having sediment characteristics most resembling station 3, consistently had both lower POC and PON values than station 3 (Figs. 4a and 4b). The consistency of this pattern suggests an oyster signal in the sediments at station 3.

The surficial sediments at all station were carbon rich compared to the Redfield Ratio, C/N = 8 (Fig. 4c), although station 1 appeared to be the most enriched (Fig. 4a, Table 3). At station 2, POC was relatively constant until removal of oyster rafts on September 6, after which POC declined slightly. PON decreased simultaneously, although the decrease in PON was slightly greater than that of POC as evidenced by an increasing POC/PON ratio (Fig. 4c). These data suggest that while oysters were present the surficial organic matter was of higher nutritional quality. Overall the POC/PON ratio at station 2 was lower than at other locations (Table 3).

POC at station 3 was variable. The relatively high values of POC and PON on November 15 might reflect deposition of primary production from a fall phytoplankton bloom. At station 4 the trends in both POC and PON were negative after July 12, except for September 27 when both were elevated. The POC/PON ratio at station 4 showed the least variability. Trends in the data from station to station (Table 3) are suggestive of two effects. Decreasing POC from station 1 to 4 implies organic inputs from upland sources such as the aquaculture sedimentation pond located in the drainage basin of the cove. Superimposed on this gradient is an oyster effect as evidenced by the lower POC/PON ratio at station 2 and higher POC and PON at station 3 than at station 5.

Table 3. Mean particulate organic carbon, particulate organic nitrogen, and molar carbon : nitrogen ratios in the surficial 2cm of sediment at stations 1 through 5.

	POC (mg C/g Dry Sed)		PON (mg N/g Dry Sed)		C:N (Molar Ratio)	
STATION	MEAN	STD	MEAN	STD	MEAN	STD
1	51.2	0.8	5.1	0.1	11.8	0.3
2	44.6	2.1	5.0	0.4	10.4	0.4
3	37.5	1.6	4.1	0.3	10.8	0.3
4	29.7	3.2	3.2	0.4	10.7	0.1
5	32.1	3.0	3.4	0.3	10.9	0.3

Carbon: Biochemical Oxygen Demand

Five-day BOD data are shown in Fig. 5a. Excluding the August 1 sampling date when values were skewed by an undetermined amount of BOD in the diluent (see Methods), BOD ranged from 0.75 to 2.75 mg C/g dry weight of sediment. Highest values were always found at station 2 except on November 15 when almost identical values were found at stations 2 and 3. Five-day BOD at stations 1 and 3 were similar except on November 15 when it was substantially higher at station 3 than at station 1. Station 4 BOD-5 was always lower than at station 1 and was usually lowest, except on August 1 where the data may be in error. On the final three sampling dates (September 6 - November 15) BOD-5 was higher at station 5 than at station 4 but they varied in the same pattern on the different dates. There was a trend of decreasing BOD-5 at each station over time (note August 1 possible error) until November 15 when it increasing at all stations. This observation supports our hypothesis of increasing rate of deposition of fresh phytoplankton derived organic carbon during this period. This effect could not be due to oysters since most had already been removed (Table 1).

The carbon in the surficial sediments at station 2 was clearly more labile than at other stations (Fig. 5a) even though POC was not the highest (Fig 4a and Table 3). This conclusion is supported by the POC/PON ratios at station 2 (Fig. 4c, Table 3). The BOD-5 data suggest the same pattern as do the POC/PON data, that of decreasing organic matter lability (nutritional quality) in the down-cove direction but with an intermediate oyster signal of increased lability.

Our goal in estimating both 5 and 20 day BOD was to develop an index of BOD lability, i.e. high BOD-5 to BOD-20 ratios would indicate increased carbon lability. On

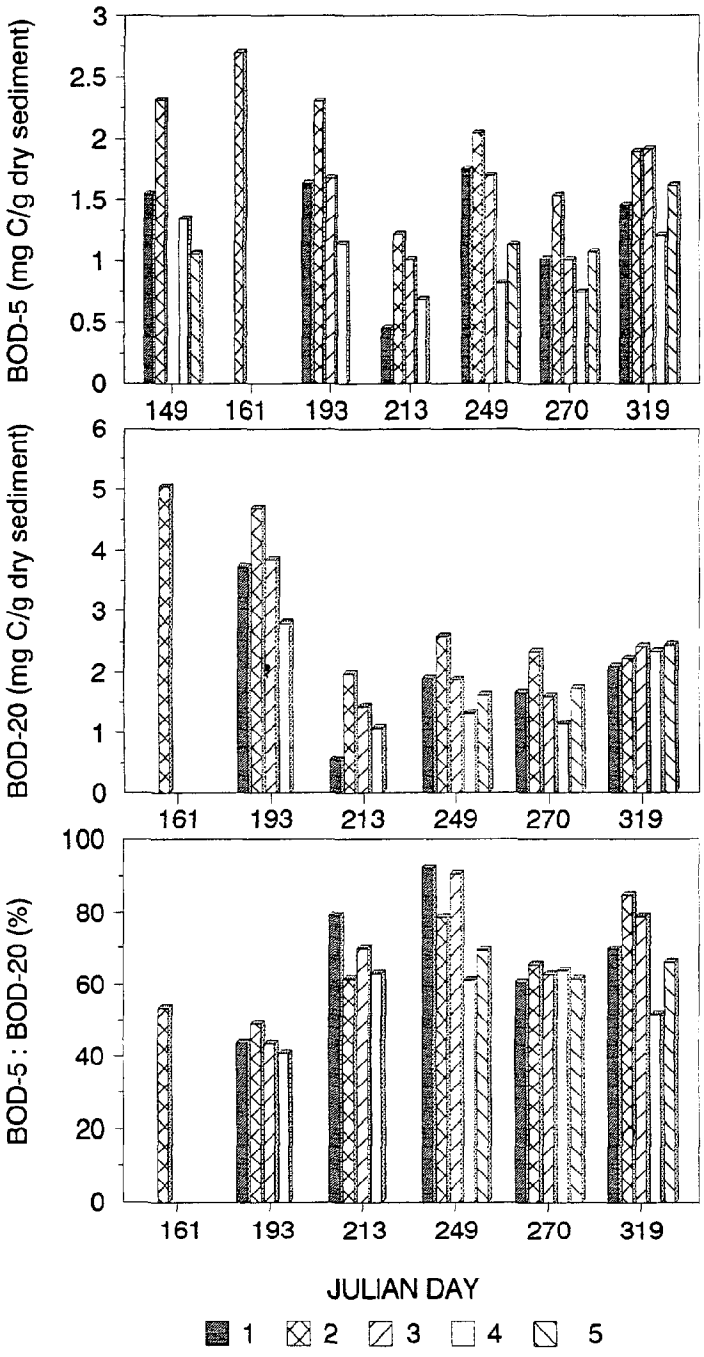

Figure 5. Five-day and twenty-day biochemical oxygen demand (BOD-5 amd BOD-20, respectively) in surficial (0-2 cm) sediments. Bar codes represent different stations.

several occasions, however, high amounts of BOD in diluent water resulted in very low or zero DO before the end of the 20-day incubation period. Obviously these 20 day values are not then useful. Reasonable data were accumulated from the July 12 (Julian Day 193) and September 27 (Julian Day 270) sampling trips. On these two dates, the trend in BOD-20 was the same as that for BOD-5 and the ratios of BOD-5/BOD-20 were not substantially different among the stations (Fig. 4c).

With the exception of one occurrence at station 3 (November 15), BOD-5 at station 2 always exceeded, by as much as 3 times, that at all other stations (Fig. 6a). This increased sediment BOD clearly indicates an organic signal in surficial sediments associated with the presence of oysters in the overlying water. Similarly, BOD-20 at station 2 also exceeded that at other locations except on November 15 (Fig. 6c). At station 3, the other oyster-raft site, BOD was greater than at station 4, the down-cove, unrafted, control site. However, station 3 BOD was variable compared to BOD at stations 1 and 5, the up-cove and out-cove control sites, respectively (Figs. 6b and 6d). On August 1 (Julian Day 213) BOD at station 3 was 2-3 times greater than at station 1, but at other times they were about the same. The oyster signal in BOD was not nearly as clear at station 3 where smaller oysters were rafted. Even where a fairly strong oyster effect was observed it appeared to be gone by November 15 in both cases. The oysters effects on labile sediment carbon seem to be local in geographic extent and of short-term duration.

From an experimental design perspective, there is a question as to the efficacy of station 1 as an up-cove control site. Terrestrial carbon inputs seemed to elevate BOD at that site compared to station 4 and 5 (Figs. 7a and 7b). There is no reason to suspect that station 5 has been influenced by oysters in the recent past. The data shown in Fig. 7c suggest no

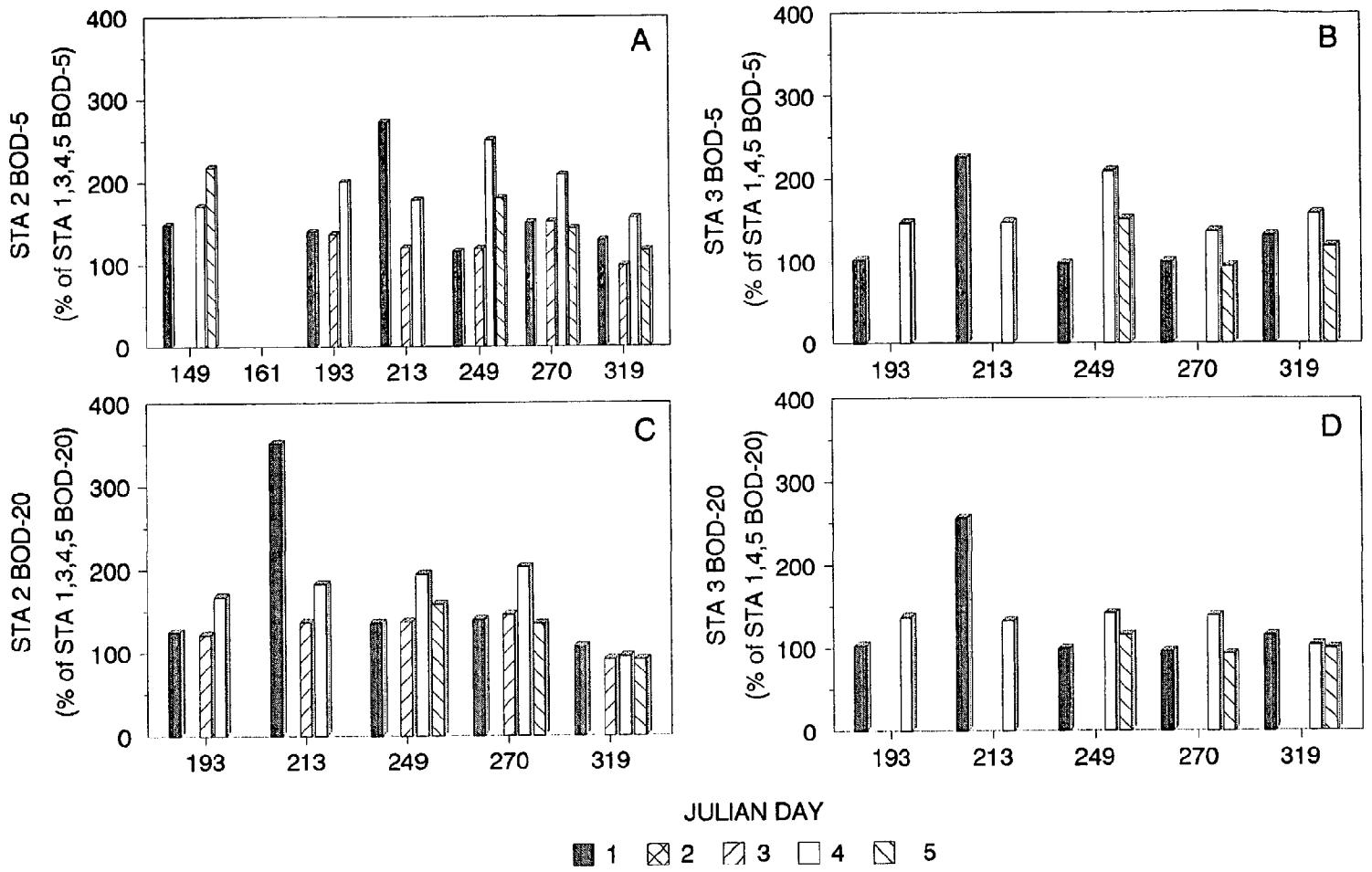

Figure 6. Comparisons of five-day and twenty-day biochemical oxygen demand values at stations 2 and 3 with values at the other stations. Panel (A): BOD-5 at station 2 compared to BOD-5 at stations 1, 3, 4, and 5; (B): BOD-5 at station 3 compared to BOD-5 at stations 1, 4, and 5; (C): BOD-20 at station 2 compared to BOD-20 at stations 1, 3, 4, and 5; and (D): BOD-20 at station 3 compared to BOD-20 at stations 1, 4, and 5. Bar codes represent different stations.

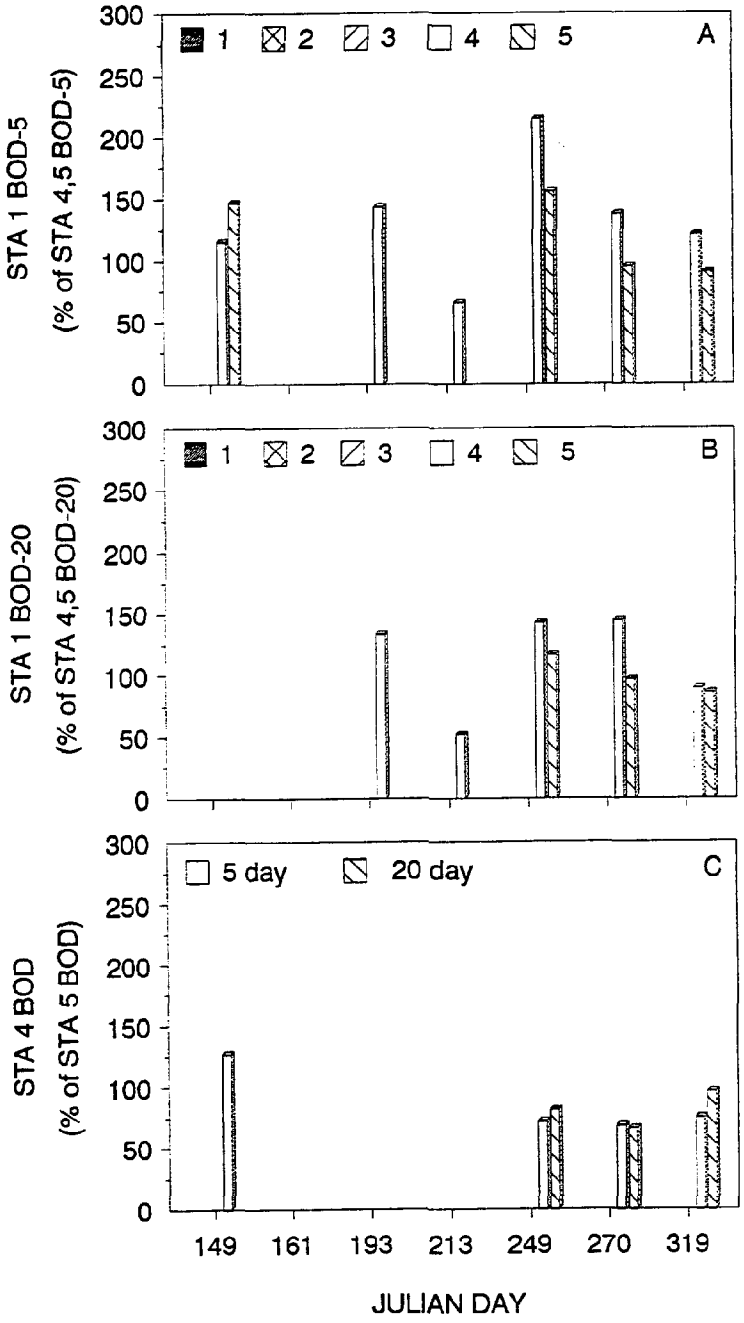

Figure 7. Intercomparison of five-day and twenty-day biochemical oxygen demand values among stations where rafts were not present. Panel (A): BOD-5 at station 1 compared to BOD-5 at stations 4 and 5; (B): BOD-20 at station 1 compared to BOD-20 at stations 4 and 5; and (C): BOD at station 4 compared to BOD at station 5. Bar codes represent different stations in panels (A) and (B) and BOD- 5 and BOD-20 in panel (C).

significant differences in BOD between stations 4 and 5.

Carbon: POC by Combustion

From a practical perspective determination of organic content of the sediments by weight loss after combustion is an inexpensive and rapid technique useful for processing multiple samples. Carbon contents of synoptic surficial sediment samples analyzed by elemental analysis and, separately, by combustion weight loss were compared (Fig. 8, Table 4). Although there is some scatter in the data, particularly at low carbon concentrations, these two estimates yielded comparable results ($r^2 = 0.83$).

In order to validate conversion of down-core combustion loss data to POC values and to characterize the oxidation state of the sediment POC, we compared mean measured POC (elemental analysis), mean POC calculated from the regression shown in Fig. 8 and POC values calculated from combustion data assuming the carbon was at the oxidation state of carbohydrate (combustion loss * 12/32). The results (Table 4) indicate that, when data from all stations were used, the three methods yielded very similar results. Therefore, it is reasonable to conclude that the POC, on average, is at or near the oxidation state of carbohydrate. POC profiles were generated using this assumption about POC oxidation state.

When we compared the stations individually, calculated POC values differed from combustion loss POC values at four of the five stations (Table 4). Stations 1 and 2 evidenced higher regression based POC values than were suggested by the carbohydrate-based calculations, whereas, these ratios of the values were lower than expected at stations 4 and 5. Similar relationships held for ratios of measured POC against combustion loss POC only at stations 1 and 5. This suggests that at station 1, and possibly station 2, POC was more

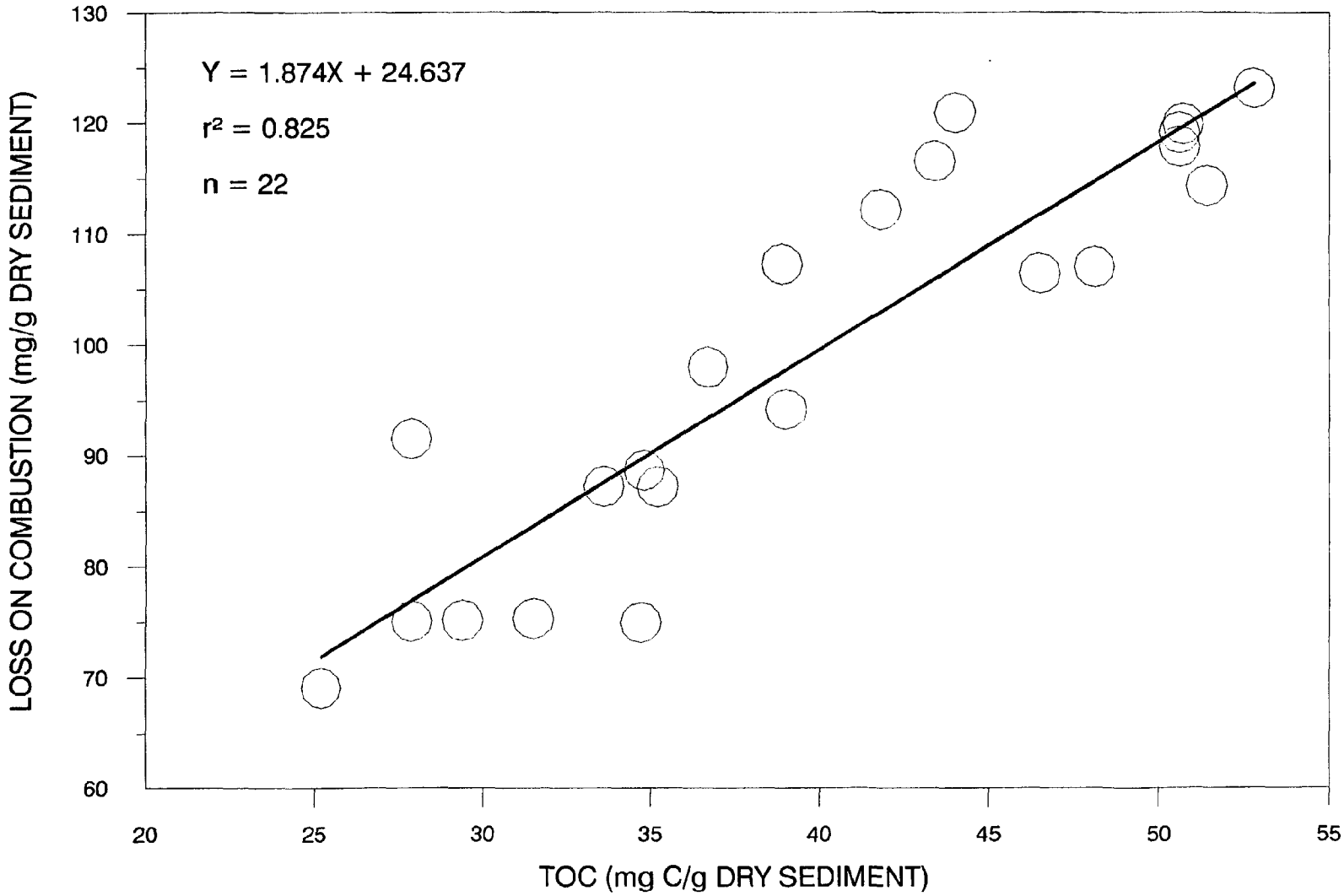

Figure 8. Regression of surficial sediment weight loss on combustion on POC determined by elemental analysis.

Table 4. Comparison of sediment POC (0-2cm depth) measured directly (by CHN analysis), calculated by regression (see Fig. 8) and estimated from loss on combustion (assuming lost material had the composition : CHOH).

STATION	n	MEAN CALCULATED POC mg C/g DRY SED	MEAN COMBUSTION LOSS POC (AS CHOH) mg C/g DRY SED	MEAN MEASURED POC mg C/g DRY SED	CALCULATED POC: COMBUSTION LOSS POC %	MEASURED POC: COMBUSTION LOSS POC %
1	5	50.30	47.57	51.22	105.7	107.7
2	5	46.96	45.06	44.76	104.2	99.3
3	4	38.42	38.66	37.45	99.4	96.9
4	5	26.30	29.57	29.74	88.9	100.6
5	3	34.41	35.66	32.10	96.5	90.0
ALL DATA	22	39.76	39.66	39.76	100.2	100.2

reduced than carbohydrate, and at station 5, and possibly station 4, it was more oxidized.

Station 1 was carbon rich throughout the sediment profile when compared to all other stations (Fig. 9a). Station 2 was enriched only at the surface, and showed the greatest decrease in carbon with depth (Fig.9b). Stations 3 and 5 had very similar profiles (Figs. 9c and 9e), while station 4 sediments had the lowest carbon content throughout the 0 - 12 cm horizon (Fig. 9d). Whereas there may be an oyster signal of increased carbon at stations 2 and 3 (note variance in 0 - 4 cm horizon at station 3), this effect appears to be small and is masked by the non-oyster related, down-cove gradient in POC.

Station 2 exhibited an unusually large decrease in carbon between the surface and the 6 cm horizon (Fig. 9b). We investigated this further by comparing decreases in POC from the surface to the 6 cm horizon on each sampling date. The largest declines were seen at station 2 and sometimes at station 3 (Table 5). This effect could be explained by carbon enrichment in the surficial sediments (i.e. deposition by oysters) or by increased microbial metabolic activity at depth. On the average, the difference at station 2 was nearly twice that at any other station.

Dark Assimilation of Carbon Dioxide

Total inorganic carbon (TIC) was measured to determine the size of the inorganic carbon pool which is necessary to convert $^{14}CO_2$ uptake rates to actual carbon assimilation values. The TIC content of sediment pore waters represents the balance between assimilatory/dissimilatory microbial processes and diffusion (abiotic transport within the sediments). Increases in TIC with depth indicate an imbalance between microbial organic carbon degradation and the sum of TIC assimilation and diffusive processes. Assimilatory

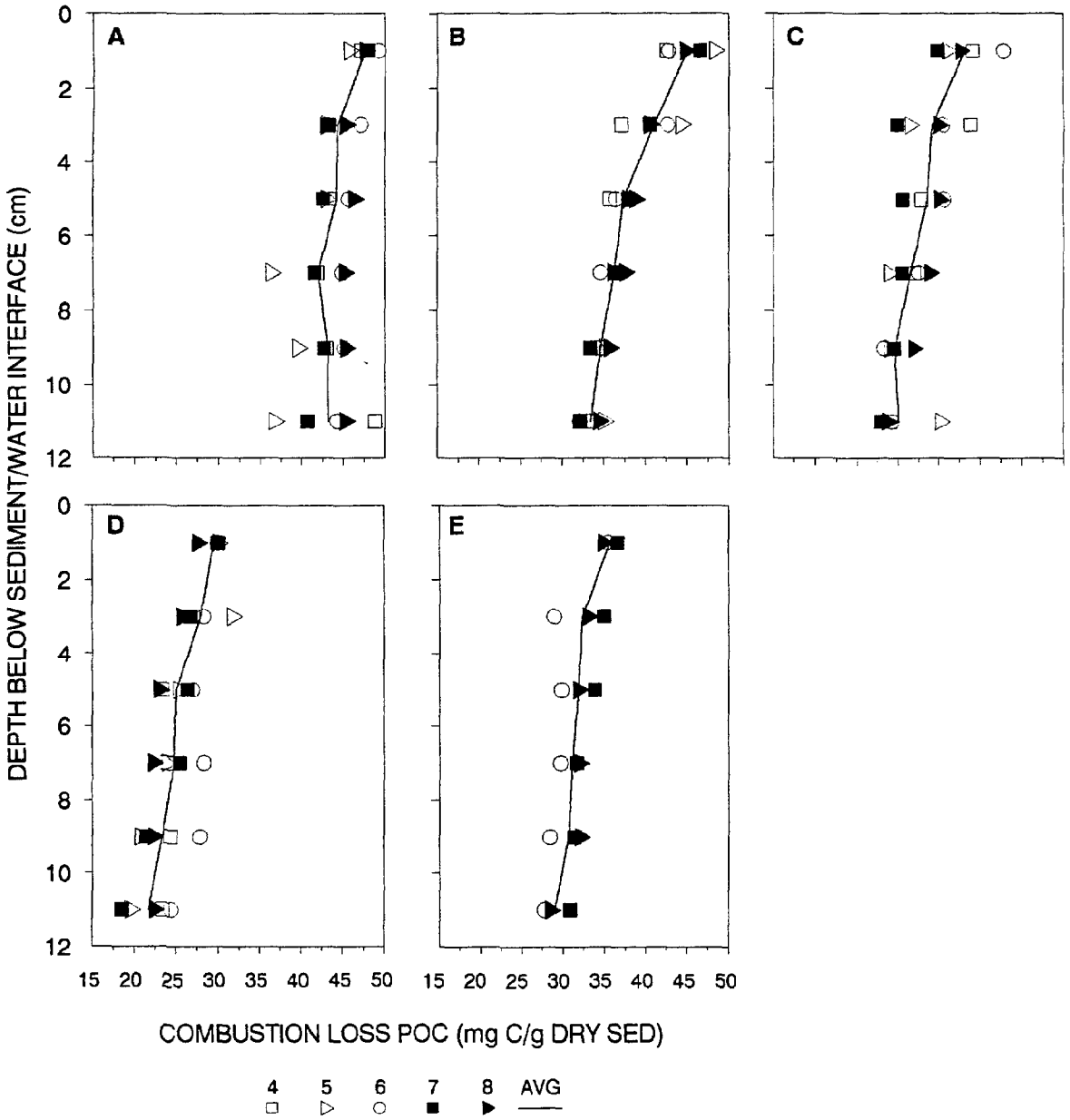

Figure 9. Distributions of POC in sediments at (A) station 1, (B) station 2, (C) station 3, (D) station 4, and (E) station 5. Different symbols represent different sampling days whose number codes are as follows: July 12 (4); August 1 (5); September 6 (6); September 27 (7); and November 15 (8).

TABLE 5. Loss of POC (determined from combustion of dry sediment) between the 0-2cm and 4-6cm segments of cores collected July 12 to September 15, 1991.

	POC LOSS (mg C/g Dry Sediment) on SAMPLE DATE :						
STATION	07-12	08-01	09-06	09-27	11-15	MEAN	STD
1	3.75	2.68	3.56	5.32	1.27	3.32	1.33
2	6.81	10.39	6.29	8.58	6.05	7.62	1.64
3	6.31	ND	7.21	4.20	2.58	4.06	2.59
4	6.75	4.69	3.02	3.58	4.59	4.53	1.28
5	ND	ND	5.59	2.76	2.98	2.27	2.10

process and diffusion out of the sediments would tend to decrease TIC whereas dissimilatory processes would increase TIC.

TIC profiles for the five stations are shown in Fig. 10. In nearly every case, TIC increased with depth. Profiles for stations 1 and 4 showed the least scatter from cruise to cruise (Fig. 10a and 10d), but TIC increased more substantially with depth at station 1. The variability in TIC among sampling dates was particularly evident at stations 2 and 3 (Fig. 10b and 10c). The profiles for station 5 were similar to stations 2 and 3 on the same sampling dates, indicating a similar balance in carbon dynamics at these three stations (Figs. 10b, 10c and 10e). The trend at station 2 was for high TIC values, particularly in surficial sediments when temperatures were high and oysters were present (samplings 3 - 5, Fig. 10b). Aeration in the water column (see Table 1) tended to depress surficial TIC. Stations 2 and 3, affected by deposition from oysters tended to have similar TIC profiles, except on July 12 (sampling 4) when the station 3 profile resembled that of station 4. Because smaller oysters were rafted at station 3, this relationship was probably due to insufficient oyster biomass to generate a detectable signal at this early date.

Dark CO_2 assimilation profiles are reported in Figures 11 - 15. Assimilation rates were generally high in the surficial sediments (100 - 300 ng C/gd) but declined rapidly with depth to less than 50 ng C/gd below the 6 cm horizon. A notable exception occurred in station 2 sediments on July 12 (Fig. 12b) where rates in the 10 - 12 cm segment of one of the replicates exceeded 1.1 μg C/gd. This was probably the result of methanogenesis (bacterial autotrophic metabolism). This explanation is supported by sulfate depletion in sediments below 9 cm on this day at station 2 (see Fig. 18b). Dark CO_2 assimilation profiles at station 4 (Fig. 14) differed from those at other stations in that maximum surficial rates (except on

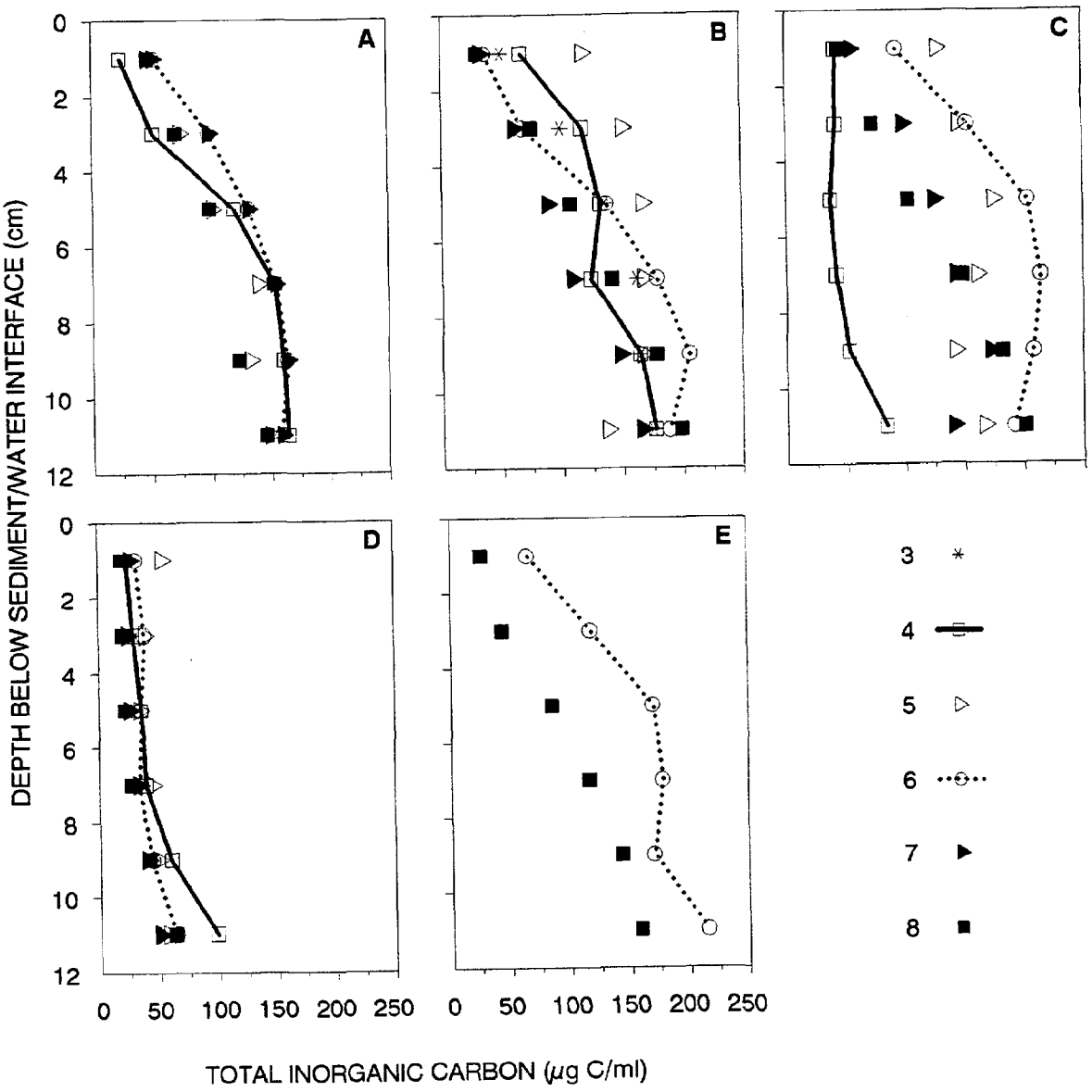

Figure 10. Distributions of total inorganic carbon (TIC) in sediments at (A) station 1, (B) station 2; (C) station 3; (D) station 4; and (E) station 5. Different symbols represent different sampling days whose number codes are as follows: June 10 (3); July 12 (4); August 1 (5); September 6 (6); September 27 (7); and November 15 (8). Lines are drawn through symbols for July 12 and September 6 to highlight the extremes at station 3.

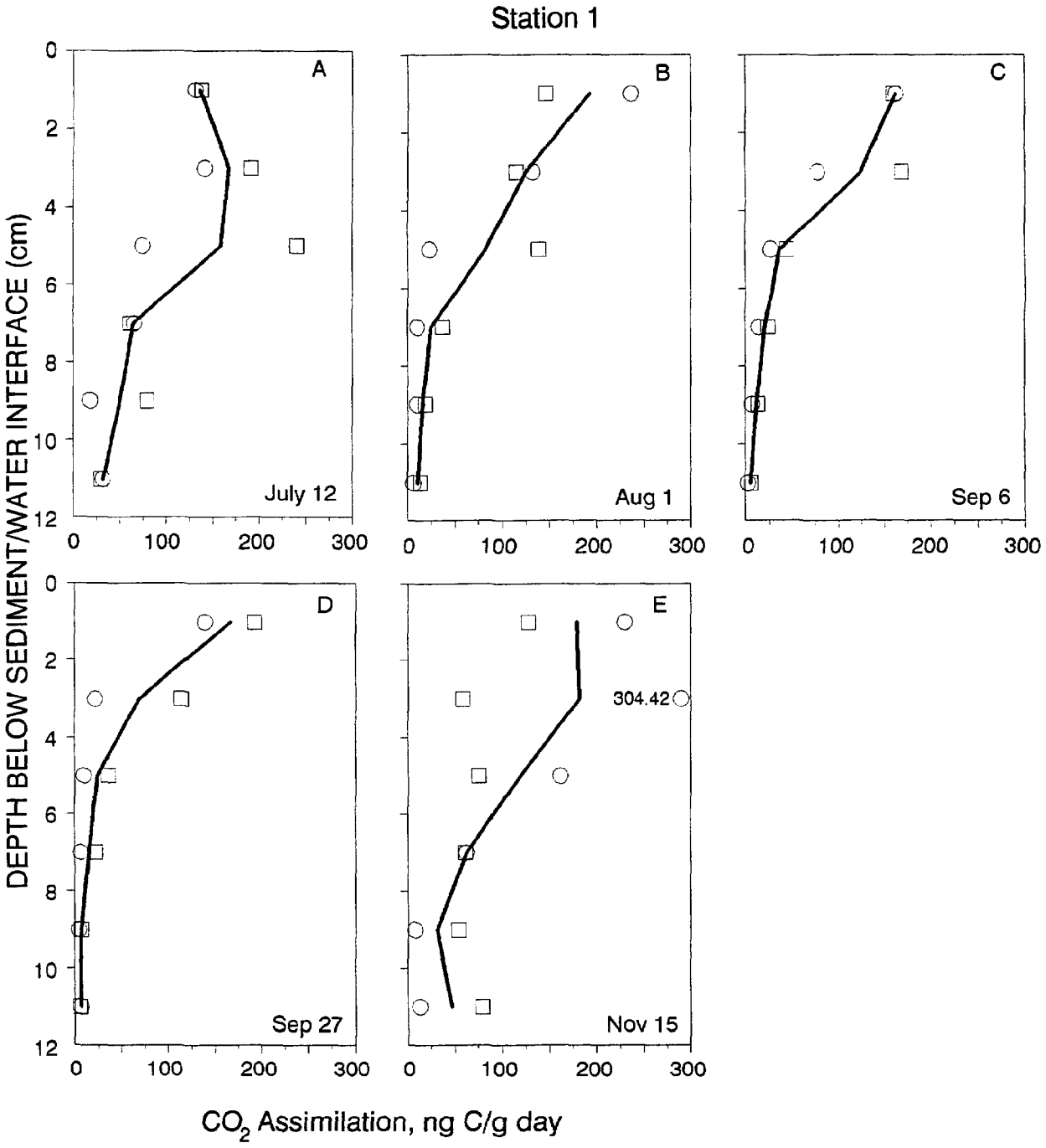

Figure 11. Rates of dark assimilation of CO_2 as a function of sediment depth at station 1. Different symbols represent values for individual cores and the line depicts the average. The number in panel (E) gives the magnitude of an offscale rate.

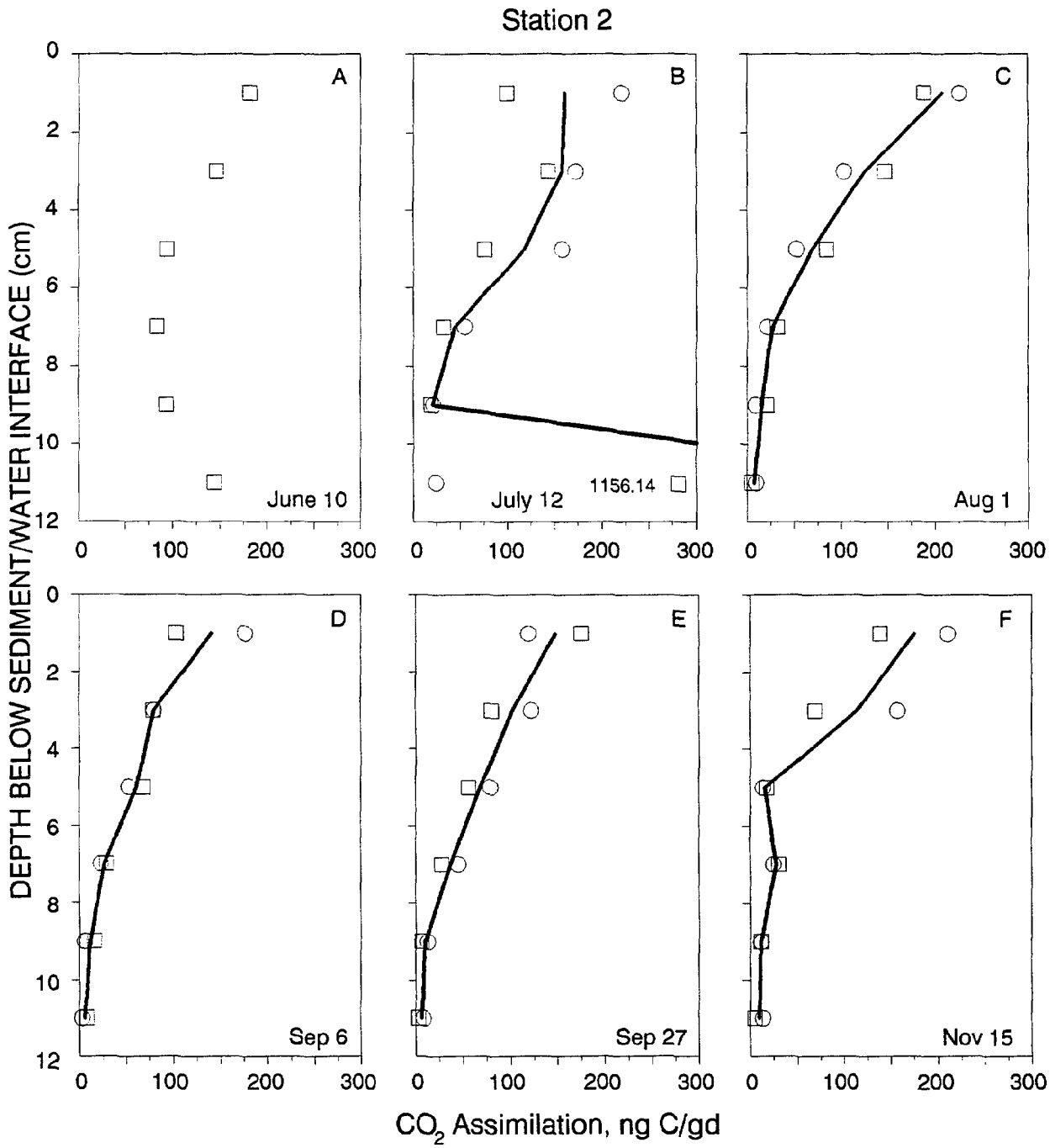

Figure 12. Rates of dark assimilation of CO_2 as a function of sediment depth at station 2. Different symbols represent values for individual cores and the line depicts the average. The number in panel (B) gives the magnitude of an offscale rate.

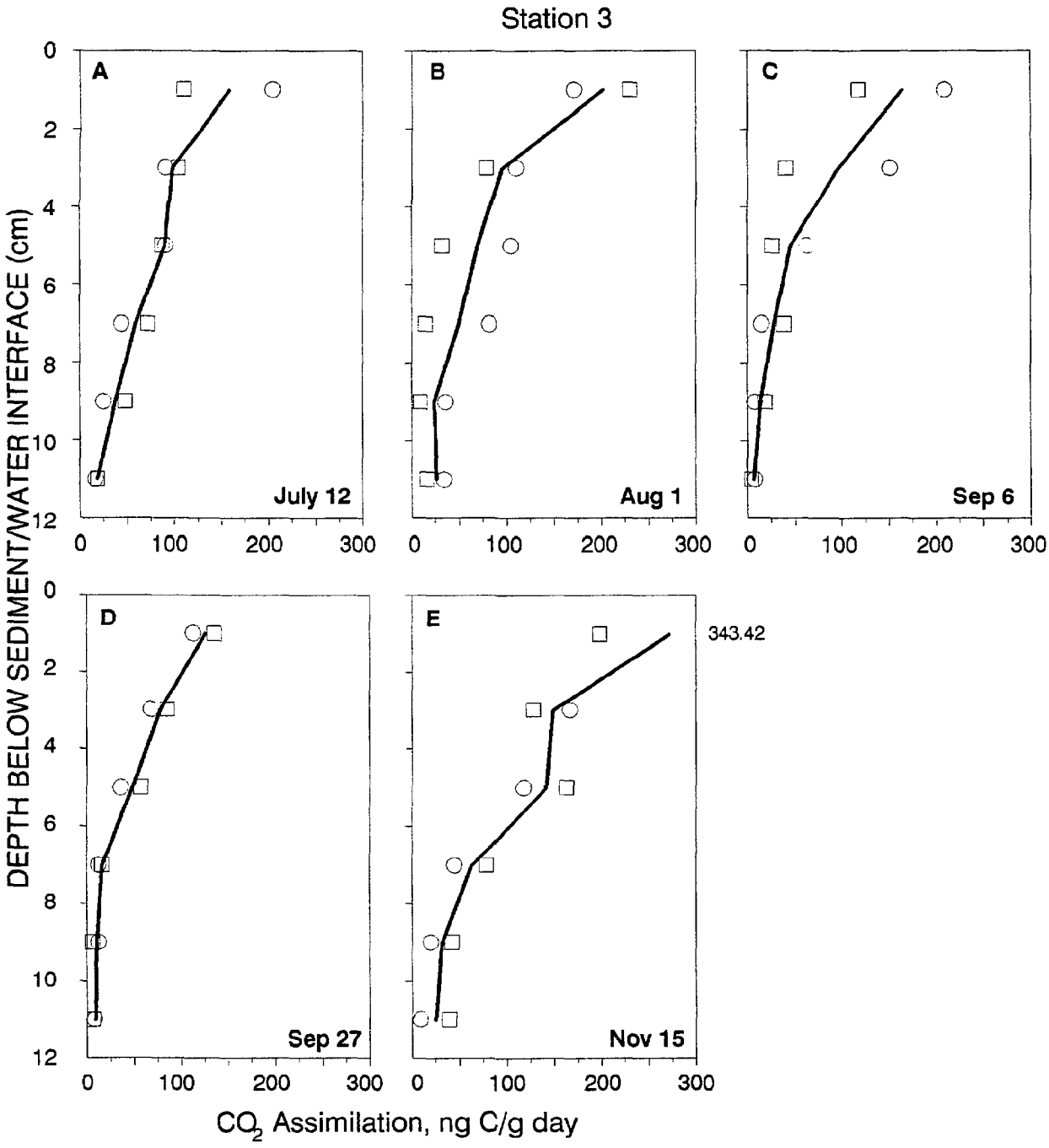

Figure 13. Rates of dark assimilation of CO_2 as a function of sediment depth at station 3. Different symbols represent values for individual cores and the line depicts the average. The number adjacent to panel (E) gives the magnitude of an offscale rate.

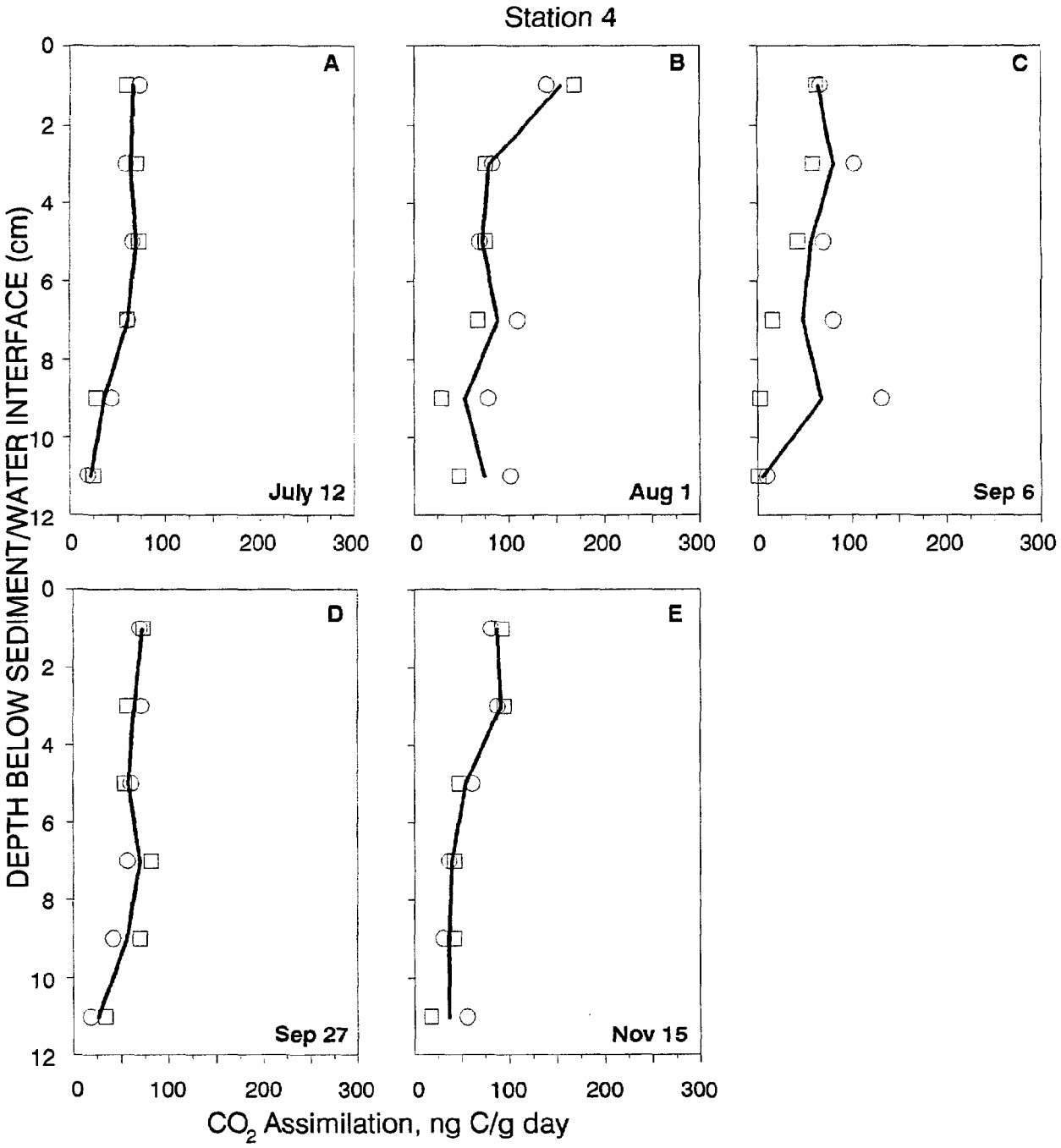

Figure 14. Rates of dark assimilation of CO_2 as a function of sediment depth at station 4. Different symbols represent values for individual cores and the line depicts the average.

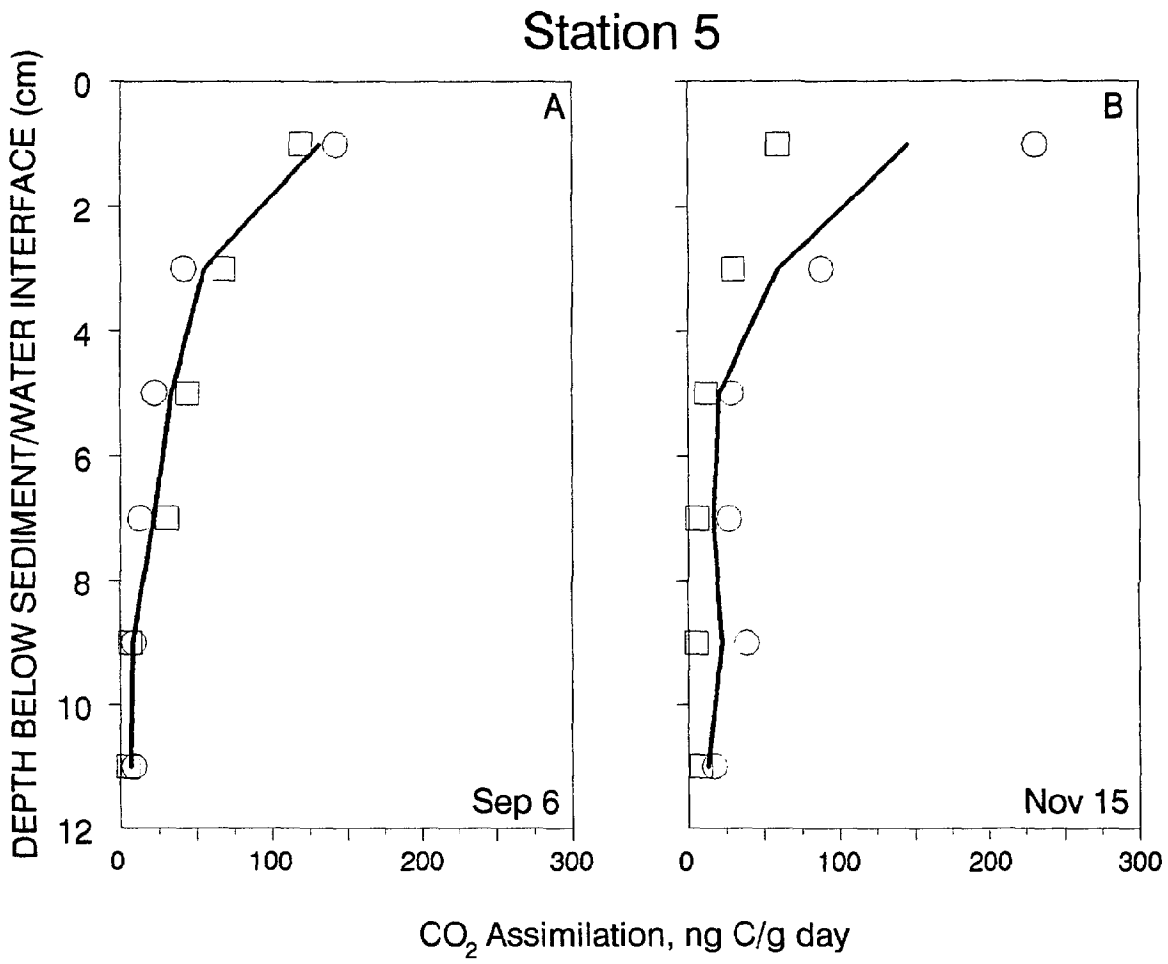

Figure 15. Rates of dark assimilation of CO_2 as a function of sediment depth at station 5. Different symbols represent values for individual cores and the line depicts the average.

August 1) never exceeded 100 ng C/gd and rates at depth were the same or higher than at other stations (note the station 2 exception, see above).

It appears that the dark CO_2 assimilation measurement, except for times when methanogenesis is occurring, estimates microbial respiratory activity which causes increasing TIC levels particularly at stations 1, 2, 3, and 5. The more uniform depth profiles at station 4 indicate reduced respiratory activity in the upper 6 cm of the sediments (compare Fig. 14 with Figs. 11 - 13 and 15). This relationship is more readily apparent when areal dark CO_2 assimilation rates are compared (Fig. 16).

There were no clear patterns among the stations in areal dark CO_2 assimilation rates integrated from 0 - 12 cm depth (Fig. 16a). In the upper 6 cm, however, the down-cove effect, decreasing rates from station 1 to station 4, could be seen from July 12 through September 27. Data for August 1 and September 27 suggest a possible oyster effect at station 2 , but this difference was probably not significant (Fig. 16b). In general, microbial respiratory activity in the top 6 cm of sediment was higher in stations 1 - 3 than at stations 4 and 5, but possible oyster effects at stations 2 and 3 were small in magnitude and/or masked by the down-cove gradient previously described. Interestingly, temperature seems not to have greatly affected dark CO_2 assimilation during sampling period.

Sulfur: Sulfate Profiles

Under anoxic conditions in marine sediments such as those studied here, sulfate reduction is the major microbial metabolic process consuming organic matter (anaerobic respiration) (Roden and Tuttle, in press). Sulfate concentrations must be known in order to calculate sulfate reduction rates from the radiotracer experiments, but they are of

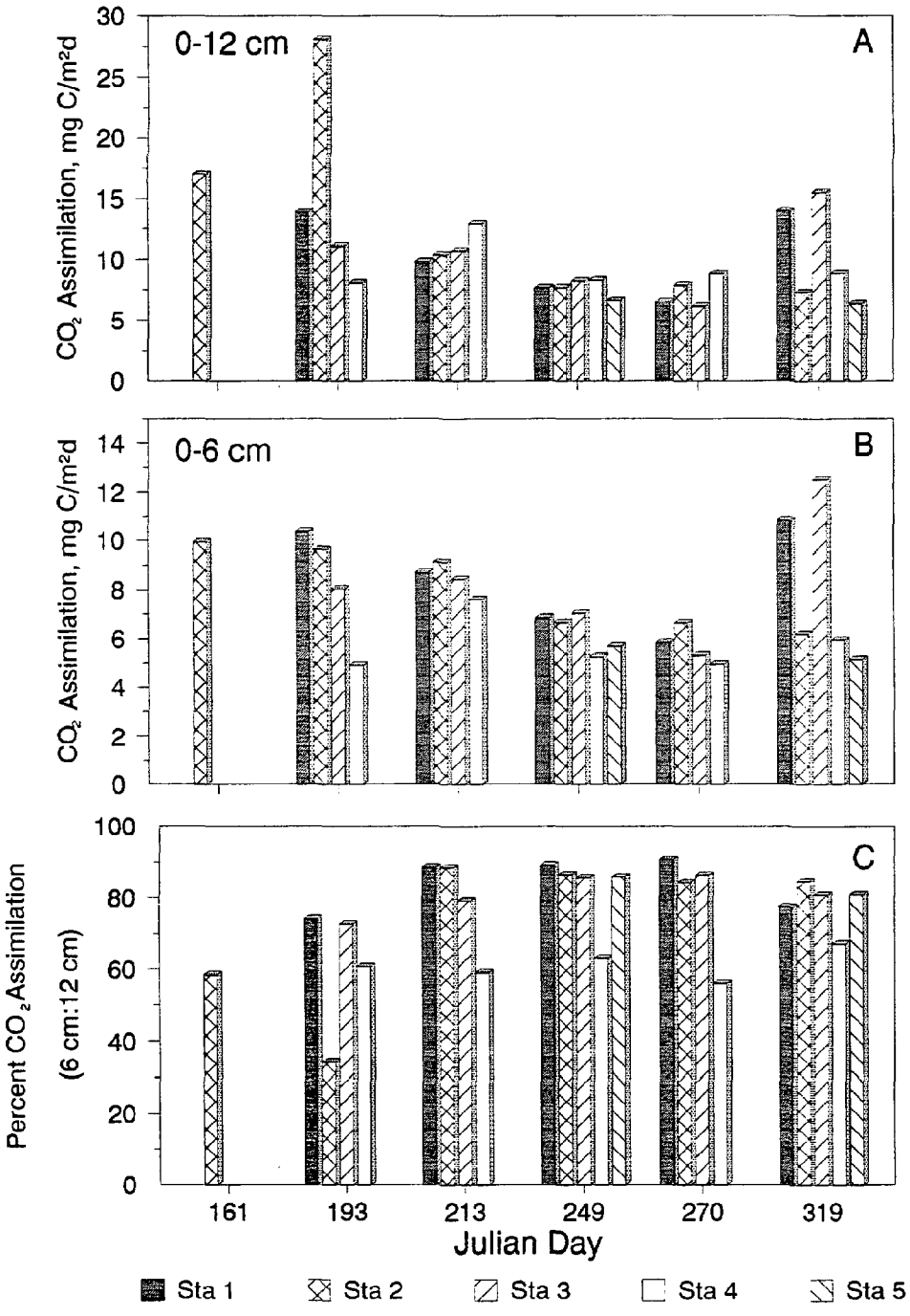

Figure 16. Depth-integrated areal rates of dark assimilation of CO_2 over the study period. Panel (A): integrated over 12 cm depth; (B): integrated over the 0-6 cm depth interval; (C): ratio of areal rate over 0-6 cm to that over 0-12 cm.

importance in their own right in that their level is indicative of the balance between sulfate supported anaerobic respiration and sulfide oxidation. In general, in sediments with active sulfate reduction, sulfate concentrations in sediment pore water are expected to be high at the surface and to decrease with depth. On the other hand, if substantial sulfate depletion is evident in pore waters of surficial sediments, sulfate reduction exceeds sulfide oxidation and/or influx of new sulfate from overlying water.

Sulfate profiles for the five stations are shown in Figures 17 - 21. The overall pattern indicates depletion of sulfate with depth except occasionally at station 4. At station 1 the profiles from July 12 to September 27 were almost identical (Fig. 17) suggesting a quasi-equilibrium between reductive and oxidative plus diffusion processes. On November 25 sulfate concentrations had increased, however, indicating that the balance shifted in favor of oxidative processes and/or diffusion. High salinity on this date (Table 2) supports increased diffusion of sulfate into sediments.

Sulfate profiles at station 2 (Fig. 18) were qualitatively similar to station 1 profiles (Fig. 17) but differed quantitatively. Specifically, throughout the profiles sulfate was more depleted than at station 1 indicating increased rates of sulfate reduction at this oyster raft site. Even in the 0 - 2 cm horizon in the presence of aeration, sulfate concentrations were substantially lower on July 12 and August 1 at station 2 (Figs. 18b and 18c) than at station 1 (Figs. 17a and 17b). In the deeper horizons on July 12 (Fig. 18b) sulfate had nearly disappeared below 7 cm and on August 1 (Fig. 18c) below 5 cm. After removal of oysters from station 2 (September 6, Table 1) sulfate concentrations in the pore waters above 6 cm depth increased dramatically (Fig. 18d) such that the concentrations were even higher than at station 1 (Fig. 17c). This strongly implicates oysters in the overlying water as a source of

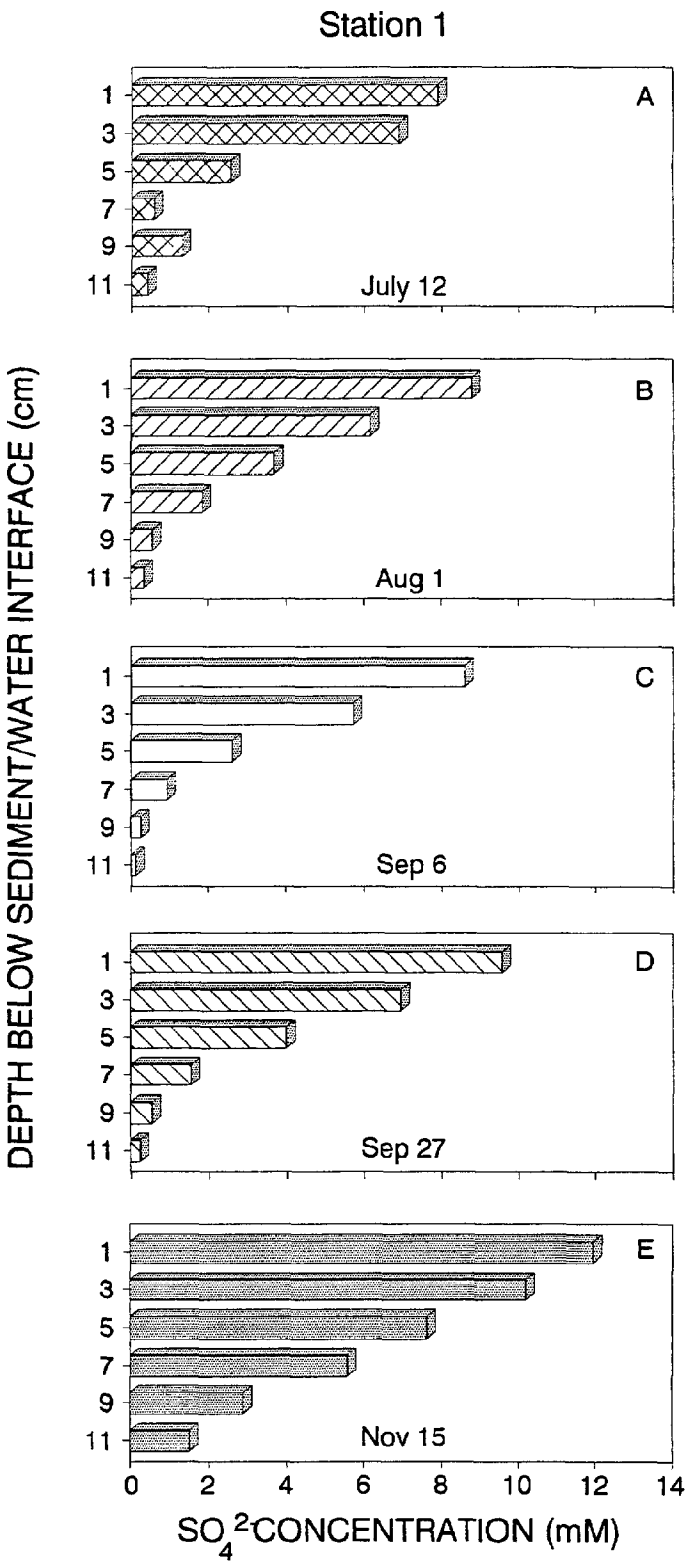

Figure 17. Depth profiles of pore water sulfate concentration at station 1.

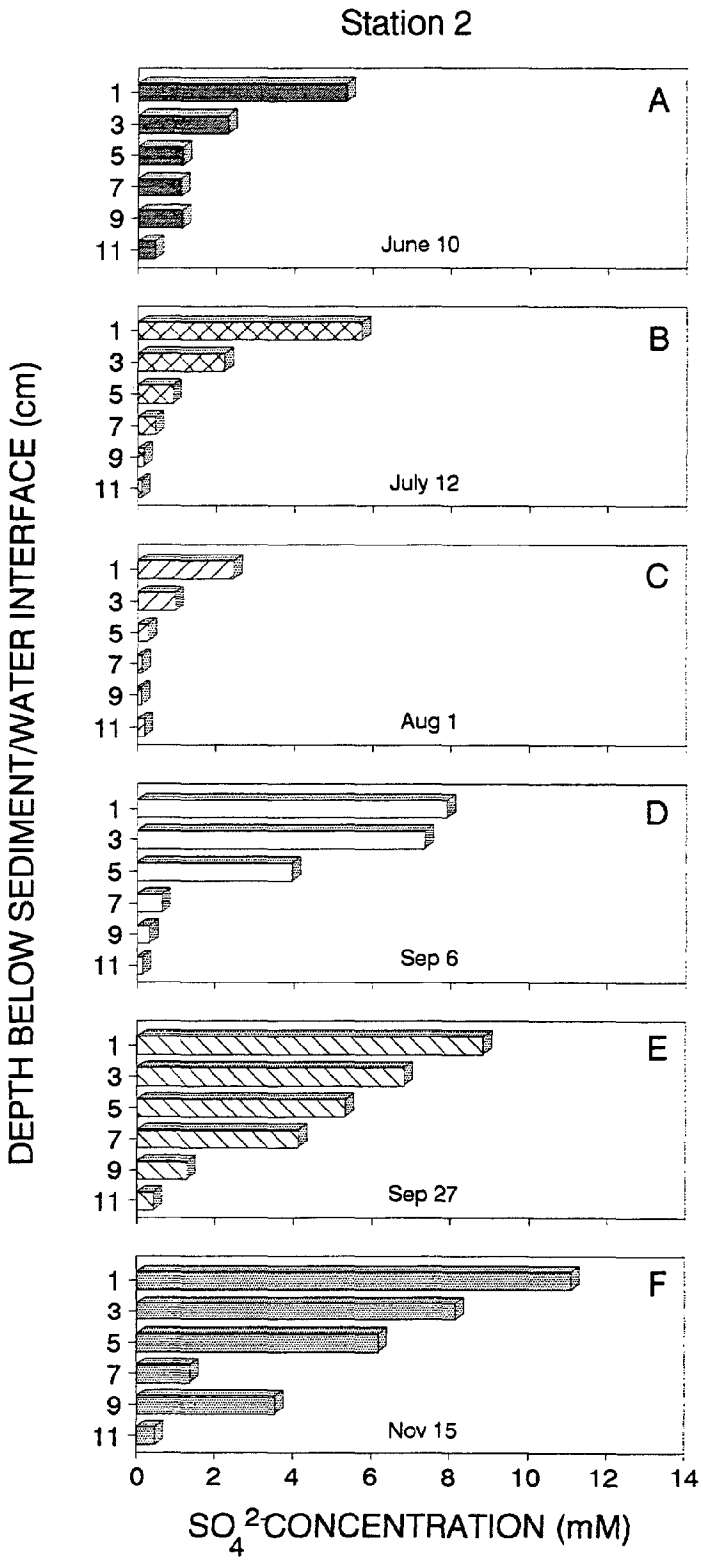

Figure 18. Depth profiles of pore water sulfate concentration at station 2.

organic matter fueling increased sulfate reduction in July and August. Sulfate continued to increase in pore waters at station 2 throughout the remainder of the study (Figs 18d - 18f). In fact, by November 15 the profiles at stations 1, 2, 3 and 5 were very similar (Figs. 17e, 18f, 19e and 21b).

At station 3, where the smaller oysters were rafted and which had less total biomass, sulfate concentrations were high relative to station 2 and were reasonably constant to a depth of 9 cm (Figs. 18b and 19a). However, by August 1 the profile at station 3 (Fig. 19b) was almost identical to that at station 2 on the same date (Fig. 18c). On September 6, when oysters were still present at station 3, sulfate concentrations were lower than at station 2, particularly in the upper 7 cm. This supports the contention that oyster deposition is responsible for increased sulfate reduction and, therefore, sulfate depletion. Oysters were kept at station 3 until almost the end of the study (Table 1). In this respect the persistent sulfate depletion in sediments at this station (Figs. 19d and 19e) compared to stations 1 (Fig. 17d and 17e) and 2 (Figs. 18e and 18f) strongly illustrate that oysters increase the rate of anaerobic sediment microbial processes.

Comparison of sulfate profiles at stations 3 and 5 on September 6 (Figs. 19c and 21a) and November 15 (Figs. 19e and 21b) indicates that, although they were qualitatively similar, sulfate was more depleted at station 3. Because these sediments were so similar in character, this depletion further supports the conclusion of an oyster effect.

Sulfate profiles at station 4 differed from those at all the other stations (Fig. 20). Apart from July 12 (Fig. 20a) there was little or no sulfate depletion throughout the entire depth profile. This is probably due to the sandy nature of these sediments, lack of oyster influences and reduced input of allochthonous organic material in this down-cove area.

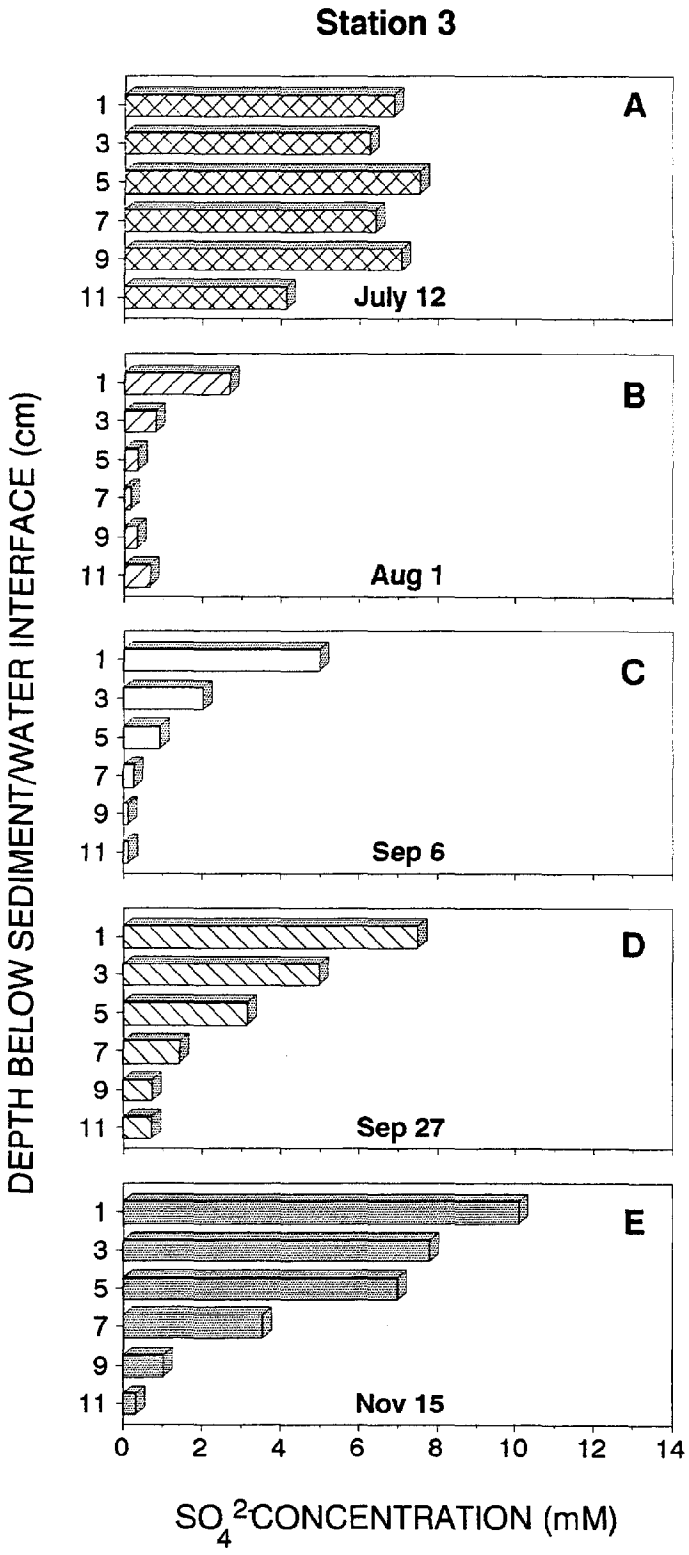

Figure 19. Depth profiles of pore water sulfate concentration at station 3.

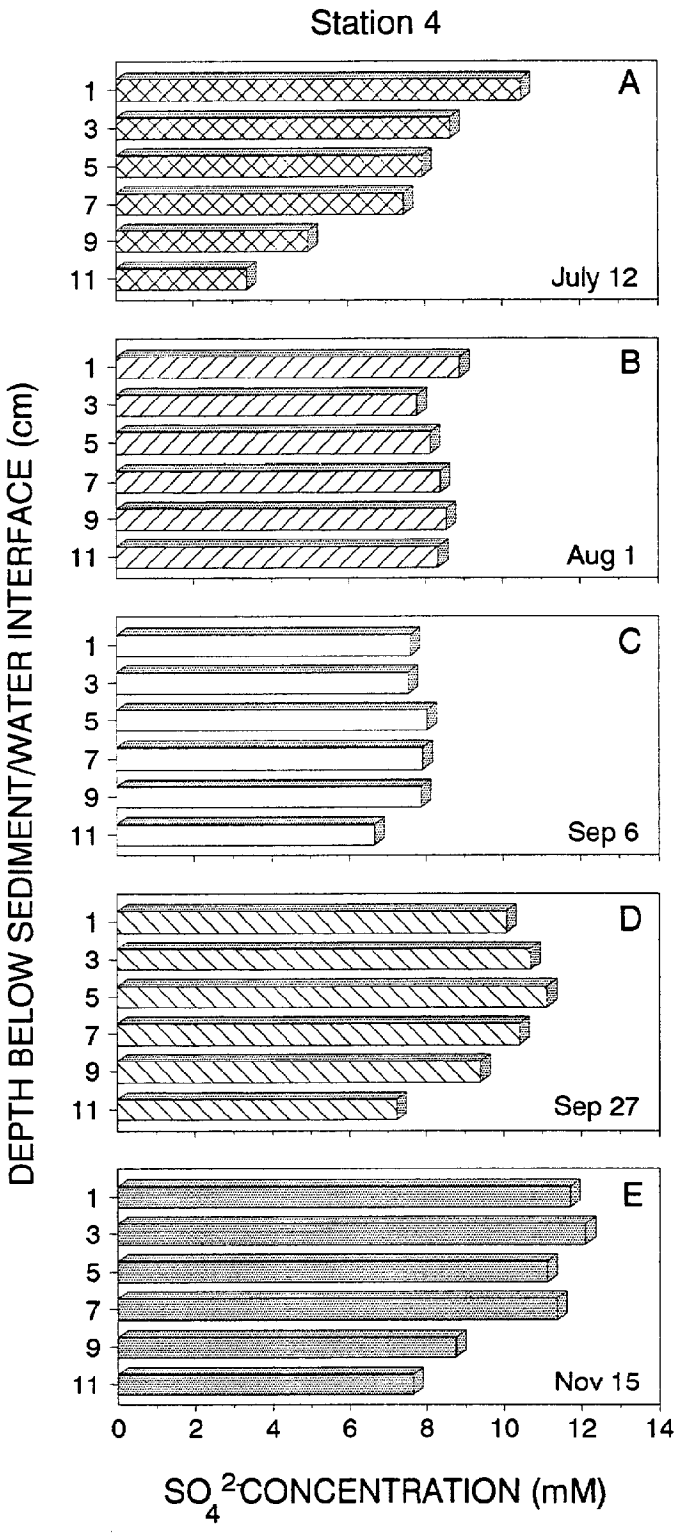

Figure 20. Depth profiles of pore water sulfate concentration at station 4.

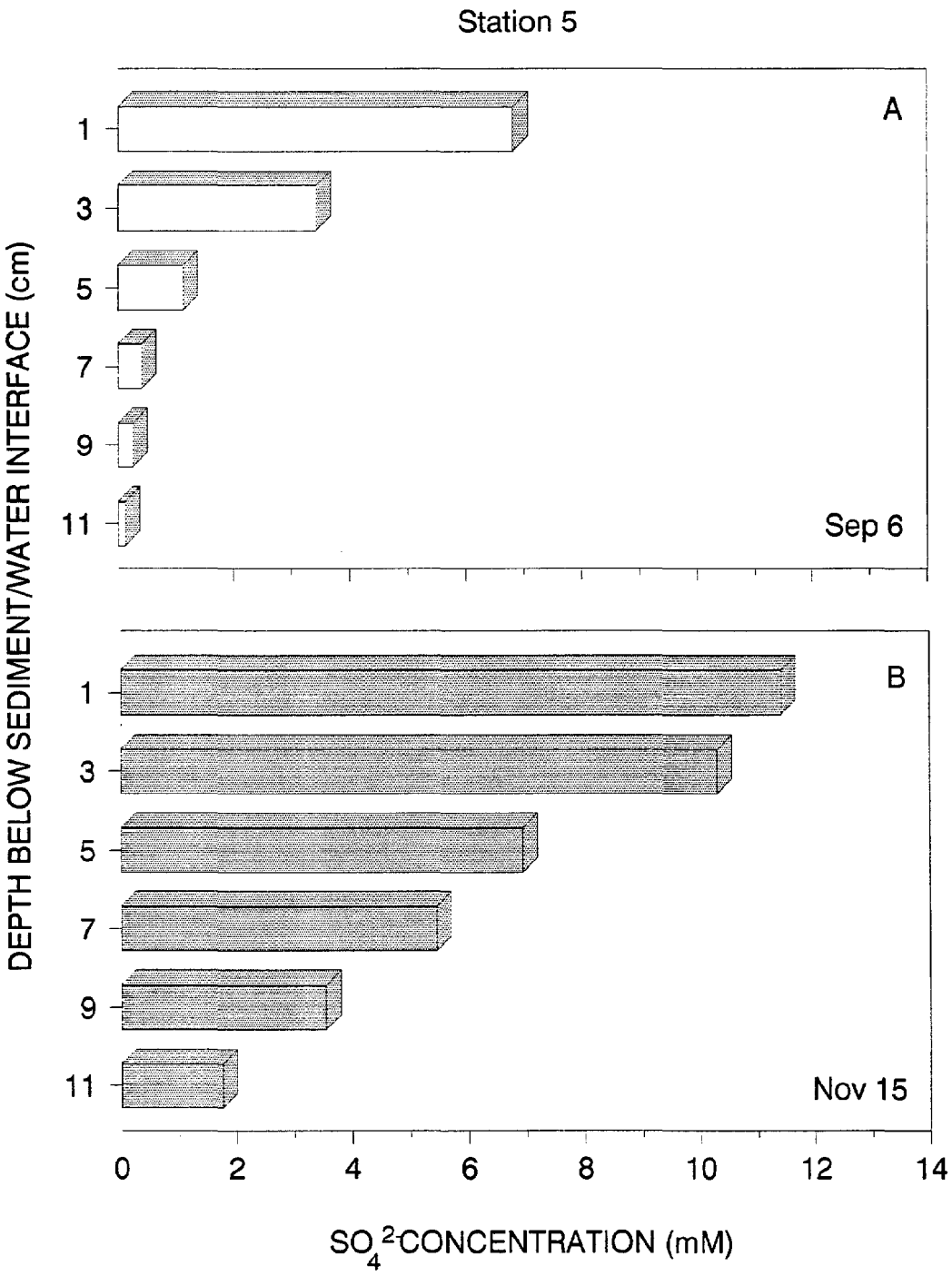

Figure 21. Depth profiles of pore water sulfate concentration at station 5.

Sulfur: Sulfate Reduction

Profiles of measured sulfate reduction rates are shown in Figs. 22 - 26. On the final two sampling dates sulfate reduction rate profiles were similar at all stations examined. Sulfate reduction rates were low, with mean values not exceeding 50 nmol S/gd throughout the sediment profiles. Maximum rates of sulfate reduction occurred during summer, warm weather conditions, probably indicating effects of temperature, redox condition and the availability of suitable substrates supporting sulfate reduction.

On June 10 the sulfate reduction profile at station 2 was bimodal, having peaks near the sediment water interface and at 8 - 10 cm (Fig 23a). On July 12 sulfate reduction was bimodal at station 1 (Fig. 22a) but at station 2 (Fig. 23b) sulfate reduction was highest near the surface and declined with depth. The replicate values were highly variable in the top 8 cm of the cores from station 2. The mean profile is probably more representative of sulfate reduction rates than is the core which yielded the lower rate estimates since sulfate at station 2 was highly depleted with depth on that date (Fig. 18b). The station 3 profile (Fig. 24a) was markedly different from stations 1 and 2. Sulfate reduction occurred mainly below 8 cm, in agreement with sulfate profiles which indicated depletion, particularly in the deeper sediments (Fig. 19a). Despite high rates of sulfate reduction at stations 1, 2 and 3, rates at station 4 on July 12 were low throughout the sediment column, never exceeding about 40 nmol S/gd (Fig. 25a).

On August 1 rates at the sediment surface at station 1 had decreased from July 12, but the minimum in the 4 - 6 cm horizon remained evident and rates below 6 cm increased (Fig. 22b). Stations 2 and 3 (Figs. 23c and 24b) exhibited very similar sulfate reduction profiles

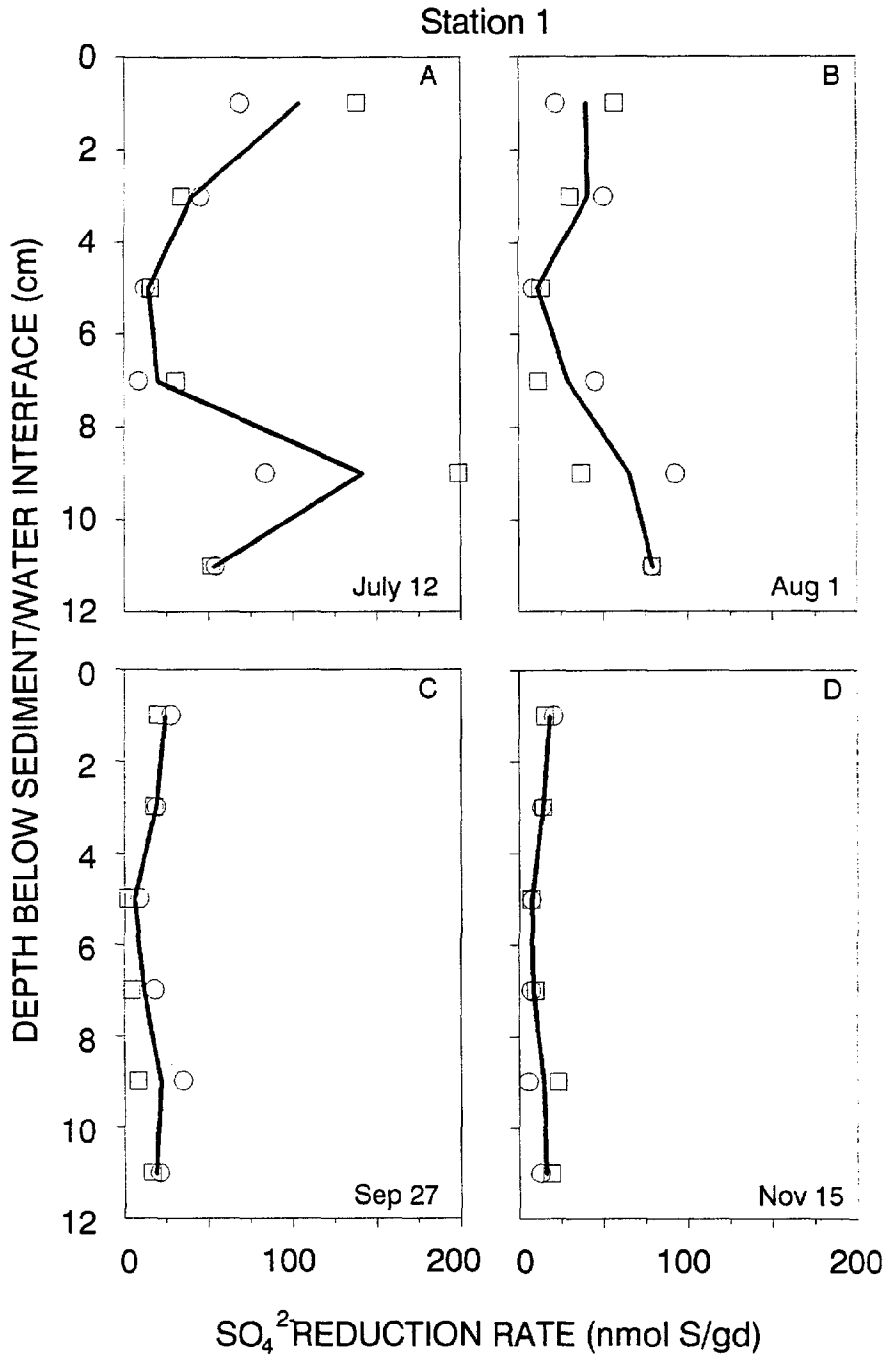

Figure 22. Sulfate reduction rate as a function of sediment depth at station 1. Different symbols represent values for individual cores and the line depicts the average.

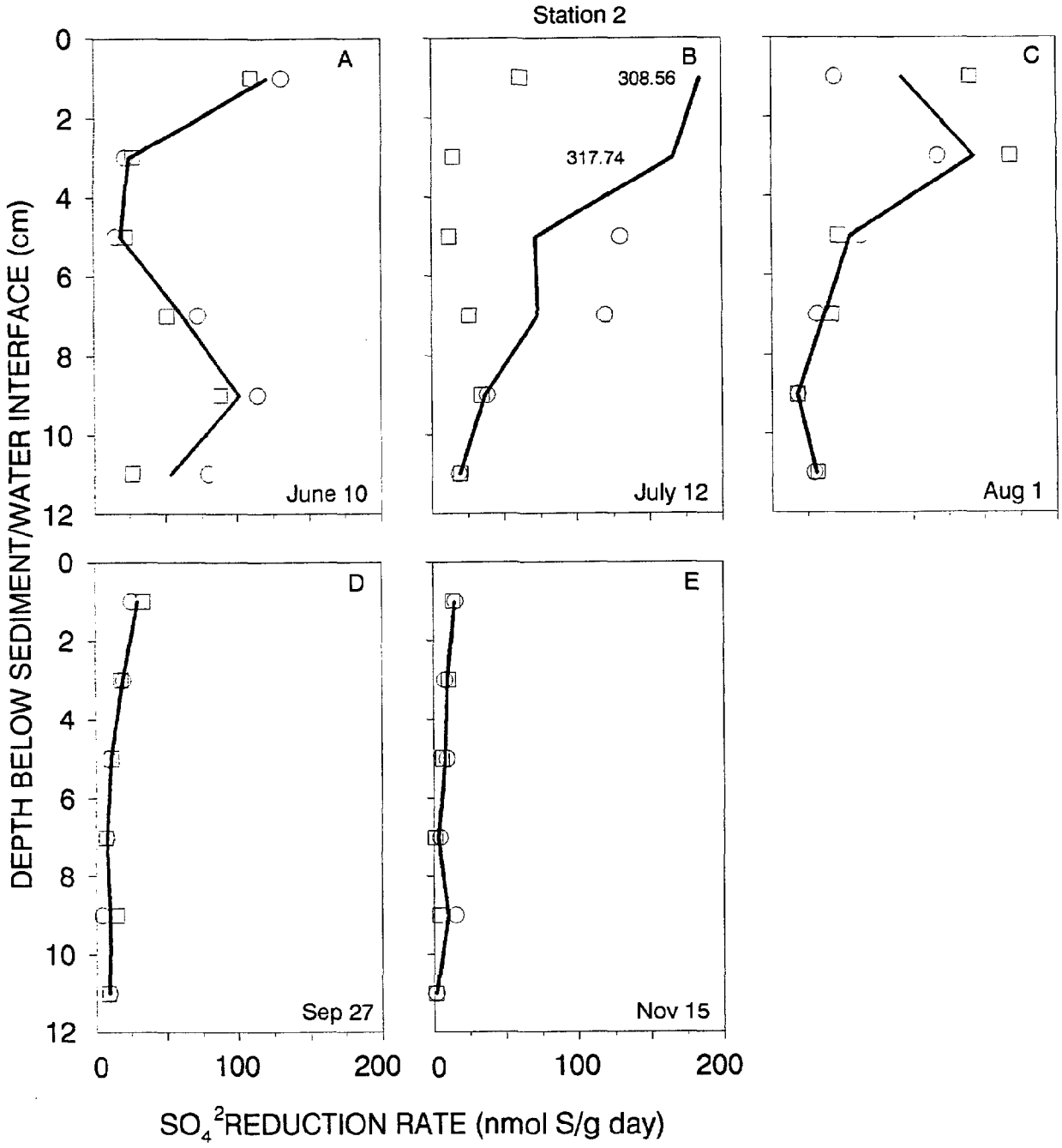

Figure 23. Sulfate reduction rate as a function of sediment depth at station 2. Different symbols represent values for individual cores and the line depicts the average. The numbers in panel (B) give values for offscale rates.

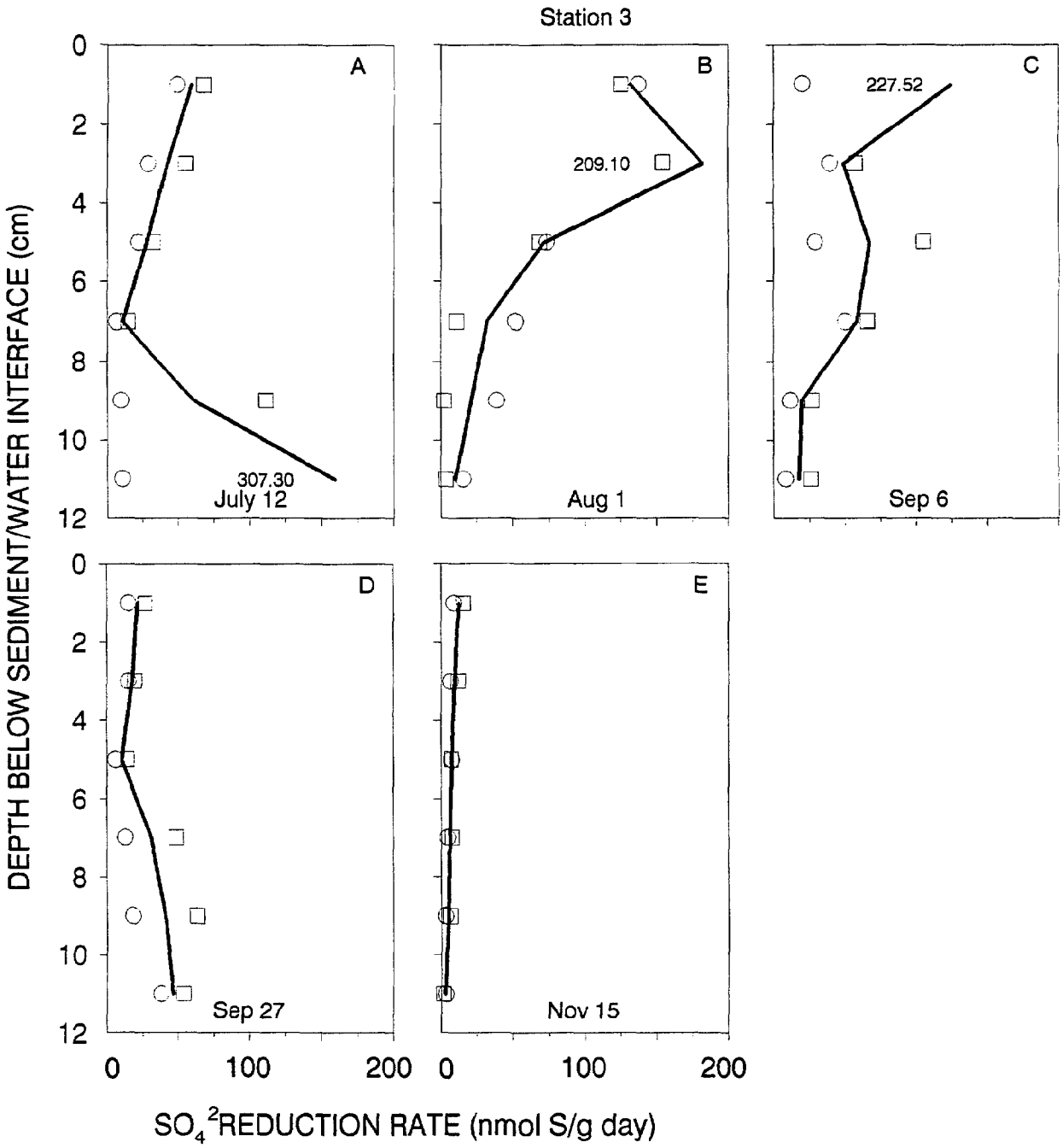

Figure 24. Sulfate reduction rate as a function of sediment depth at station 3. Different symbols represent values for individual cores and the line depicts the average. The numbers in panels (A), (B), and (C) give values for offscale rates.

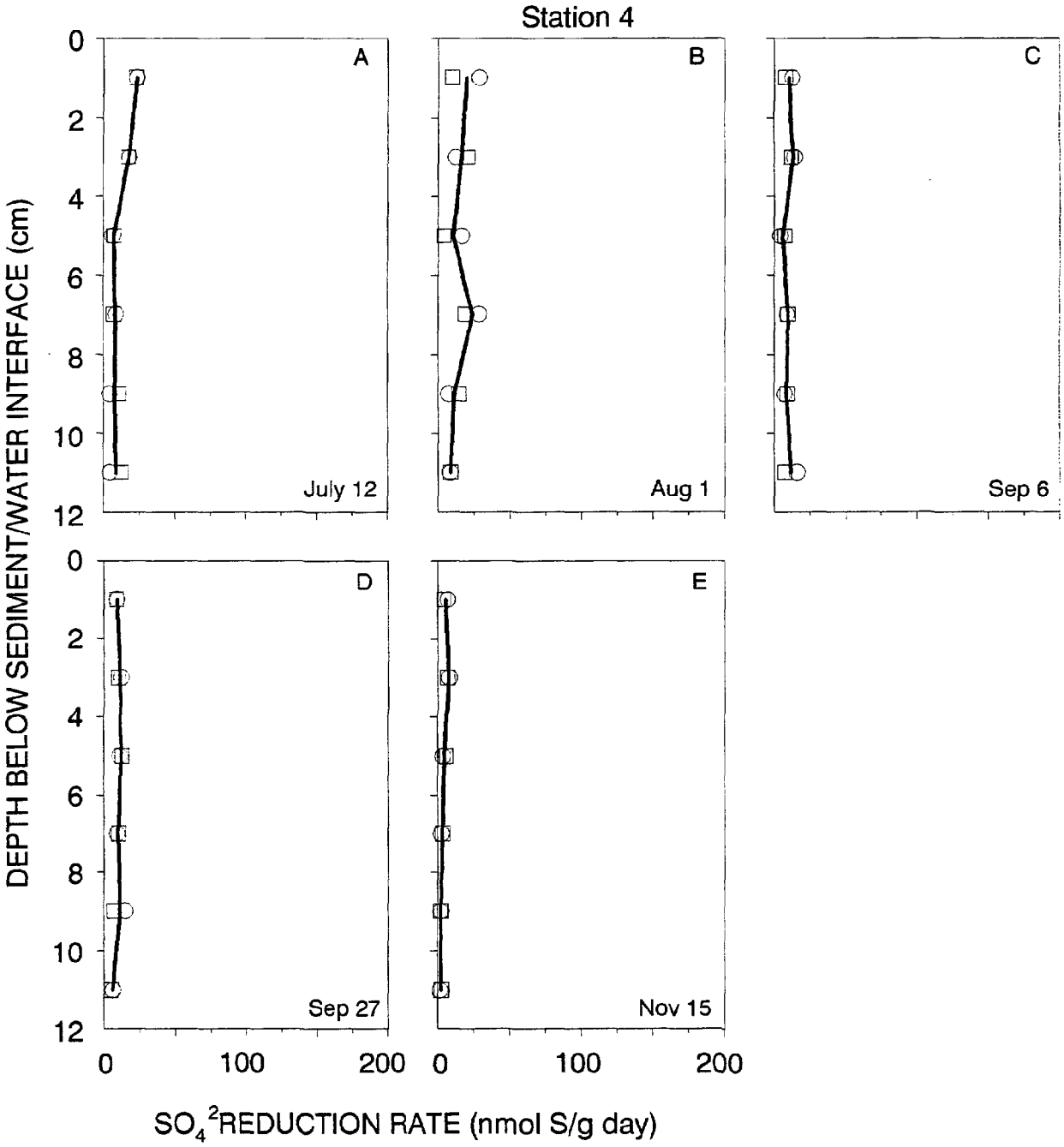

Figure 25. Sulfate reduction rate as a function of sediment depth at station 4. Different symbols represent values for individual cores and the line depicts the average.

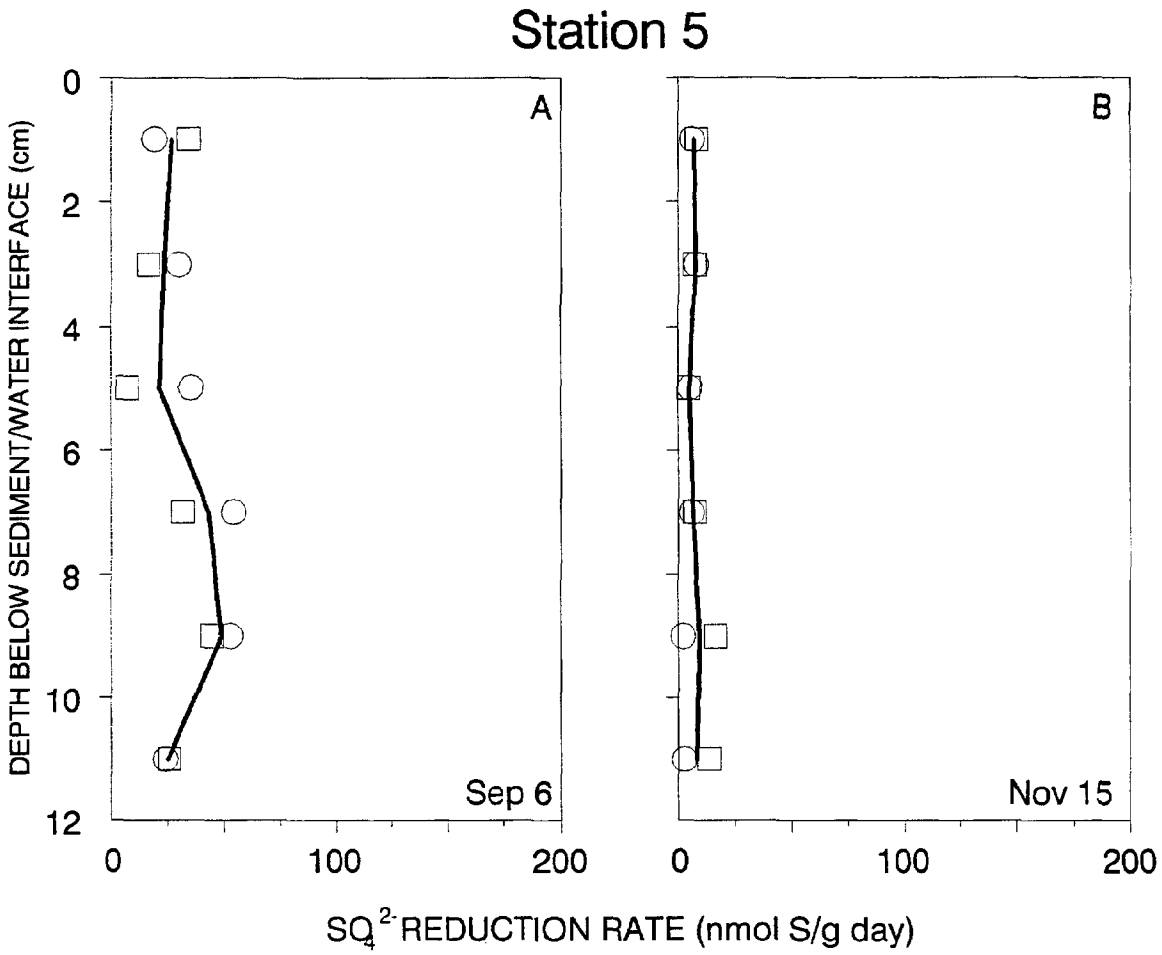

Figure 26. Sulfate reduction rate as a function of sediment depth at station 5. Different symbols represent values for individual cores and the line depicts the average.

with maxima within the 2 - 4 cm horizon. Decreased surficial rates at these two stations may have been due to oxygen input at the sediment water interface due to mechanical bubbling of the overlying water (Table 1). Despite relatively high rates at station 2 and 3 sulfate reduction at station 4 remained low (Fig. 25b).

Unfortunately, data for stations 1 and 2 on the September 6 were lost due to improper processing of cores. At station 3 (Fig. 24c), however, sulfate reduction rates remained high in contrast to the companion station 5 (Fig. 26a). Station 4 continued to evidence low sulfate reduction rates (Fig. 25c). Similarities in the magnitude and trend in the sulfate reduction rate profiles at stations 2 and 3 compared to stations 1, 4 and 5 during the summer indicate a marked oyster effect.

By September 27 sulfate reduction rate profiles at stations 1, 2 and 3 appeared to be qualitatively similar (Figs. 22c, 23d and 24d). However, mean rates in the deepest 6 cm at station 3 were noticeably higher than at the other two stations. This may represent an effect of oysters having been removed later from station 3 than from station 2 (Table 1).

Relationships among sulfate reduction rates in time and space are most easily seen by comparing depth integrated data (Fig. 27). At station 1 sulfate reduction rates decreased consistently over the period July 12 to November 15 (Julian Day 193 to 319) (Fig. 27a). Data for station 2 followed a similar pattern of change with a peak occurring on July 12. In contrast, sulfate reduction rates at station 3 peaked on August 1, whereas, integrated sulfate reduction at station 4 remained low throughout the study. Although sulfate reduction was measured at station 5 on only two occasions, the sulfate reduction rate patterns were not inconsistent with those at stations 1 and 3.

Oyster rafting had a substantial, although transient, effect on sediment sulfate

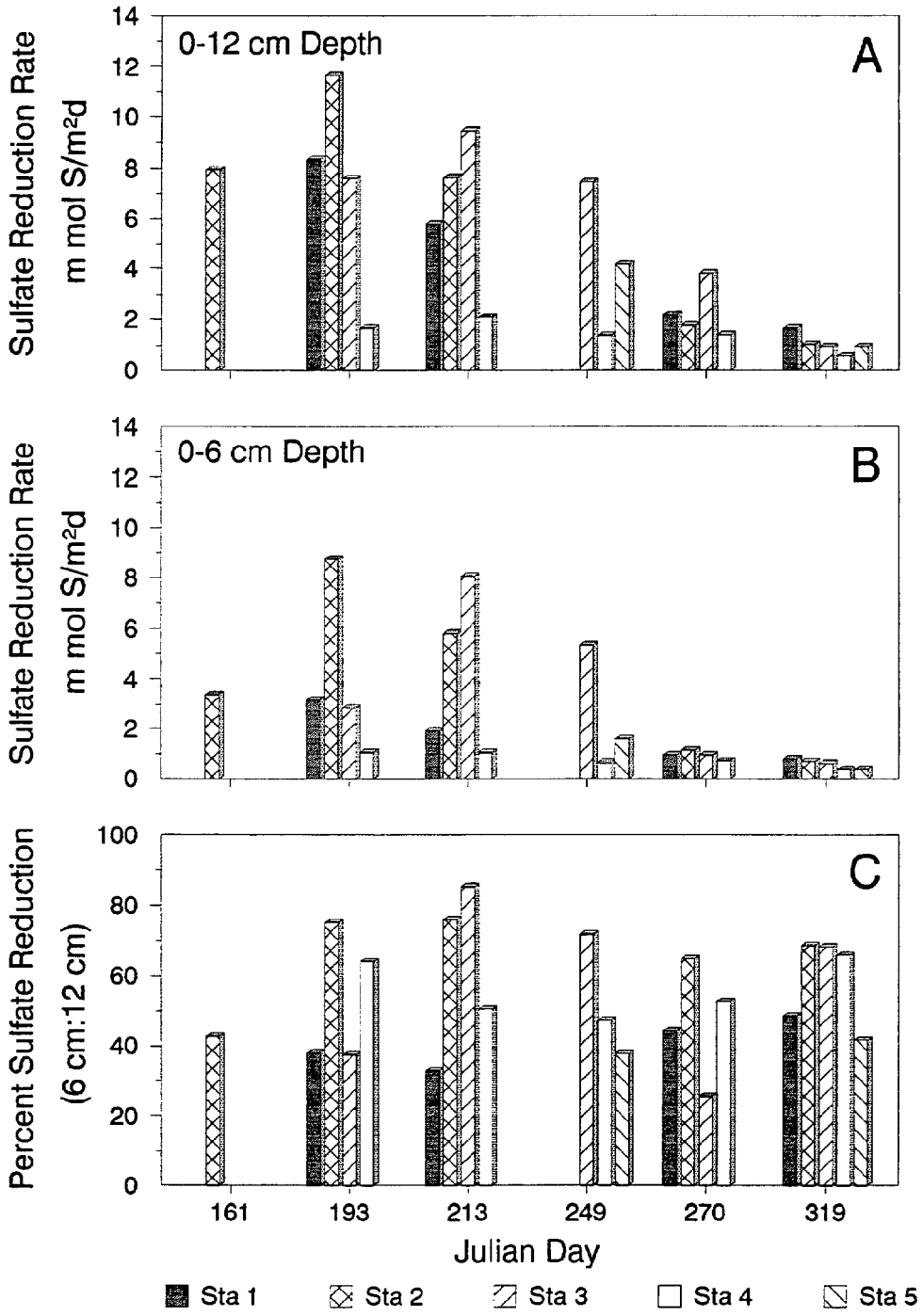

Figure 27. Depth-integrated areal sulfate reduction rates over the study period. Panel (A): integrated over 12 cm depth; (B): integrated over the 0-6 cm depth interval; (C): ratio of areal rate over 0-6 cm to that over 0-12 cm.

reduction. When oysters were present at station 2 (Table 1) sulfate reduction rates there were substantially higher than at either of the control stations 1 and 4. This effect was most noticeable in the upper 6 cm of the sediments (Fig. 27b). After oyster removal from the raft area at station 2, sulfate reduction rates in the sediments there were not significantly different from rates at any of the control stations.

Our conclusions are reinforced by comparing sulfate reduction rates at station 3 with those at stations 1, 4 and 5. Presumably the oysters at station 3 were smallest on July 12 and increased in size (biomass) as time progressed. It is interesting in this respect that the integrated rate of sulfate reduction at station 3 on July 12 was about the same as at station 1 and its distribution in the sediments was also similar to that at station 1 (Figs. 27a - 27c). Only 3 weeks later, however, the sulfate reduction rate at station 3 was substantially greater than at station 1, and this effect was most noticeable in the upper portions of the sediment. This is consistent with increased deposition of labile organic material to the sediment surface. Oysters were removed from station 3 at a date later than when they were removed from station 2. It is significant that from August 1 through September 27 sulfate reduction rates at station 3 were higher than at any of the other stations. However, by November 15 the rates were very similar across the rafted cove transect with a possible trend of decreasing sulfate reduction from the head of the cove to its mouth.

Sulfur: Sulfide Profiles

Distribution of HS^- in sediment pore water supports the sulfate reduction rate data and sulfate distribution profiles (Figs. 28 - 32). At station 1, HS^- tended to accumulate at depth rather than at the sediment surface (Fig. 28). When oysters were present at stations 2 and 3

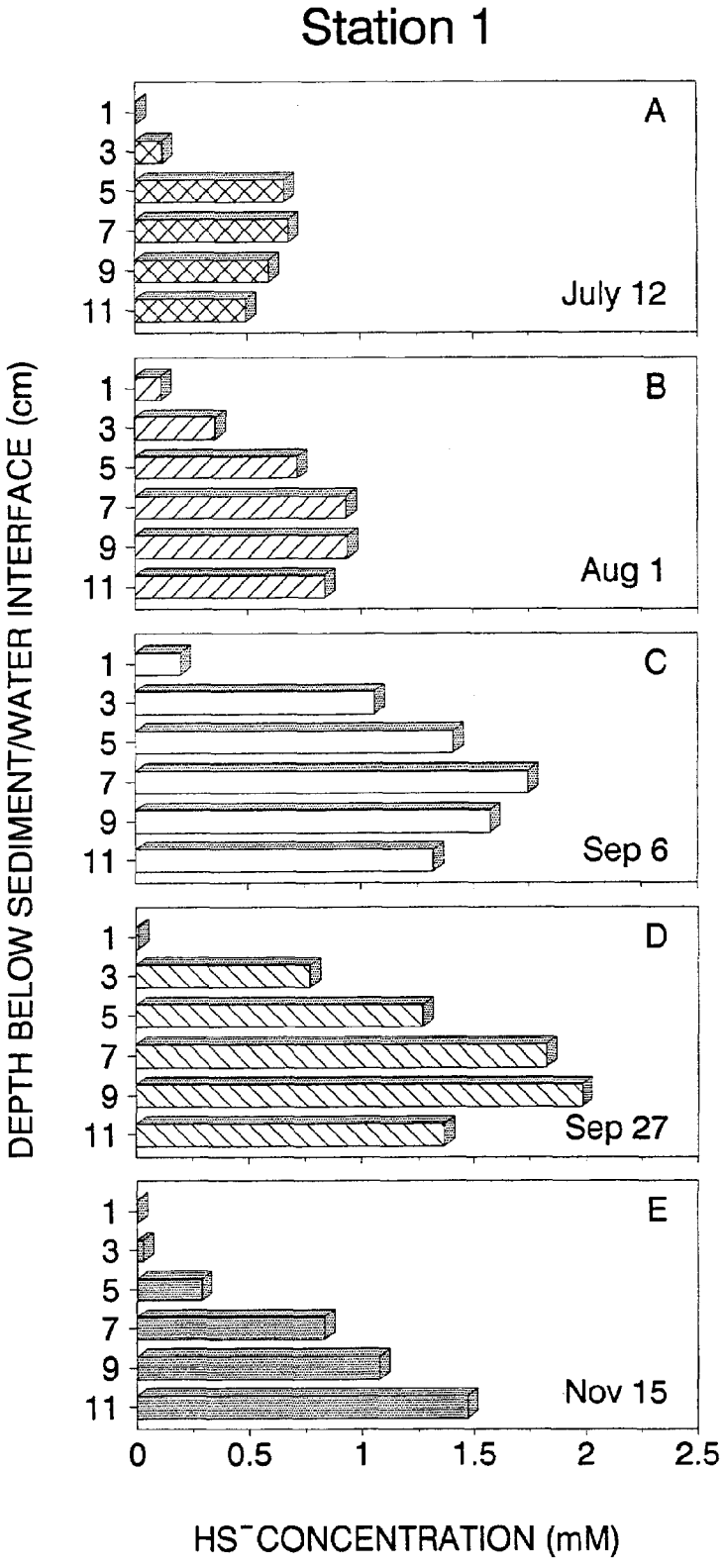

Figure 28. Depth profiles of pore water HS^- concentration at station 1.

(Figs. 29 and 30) HS^- tended to accumulate near the surficial sediments, and, were it not for mechanical aeration, it might well have contributed to anoxic conditions in the water column. Also in concert with sulfate reduction rate data, when oysters were removed from stations 2 and 3 (before September 6 and 27, respectively), HS^- rapidly disappeared from surficial sediments and the profiles had the same patterns as at station 1 (Fig. 28). In this respect, comparison of the HS^- profile on September 6 at station 3 (Fig. 30c) with station 5 (Fig. 32a) also demonstrates an effect of the oysters.

Although station 4 was only about 35 meters from the oyster rafts, HS^- concentrations were very low throughout the sediment profiles during the entire sampling period (Fig. 31). The only case in which a substantially higher than background value was detected was on July 12 in the 10 - 12 cm segment (Fig. 31a).

Sulfur: Total Reduced Sulfur

The general distribution pattern for TRS was an increase with depth in the sediment profile Figs. 33 - 37). Despite differences in sulfate reduction rates and HS^- concentrations, TRS in the sediments was reasonably similar at most of the stations (Figs. 33 - 38). A possible exception was at station 4 where TRS appeared to be lower overall (Fig. 38d). Nevertheless, there appeared to be an increase in TRS at stations 2 and 3 (Figs. 38b and 38c) at the same time that areal sulfate reduction rates peaked (Figs. 27a and 27b).

The fact that TRS levels in the sediments were relatively similar at all the stations may be related to inputs of metals which can react with sulfide, forming insoluble metal sulfides such as Fe_2S whose oxidation is very slow. Thus, at station 4 where sulfate reduction rates were low most of the sulfide produced would accumulate as metal sulfide. The failure of

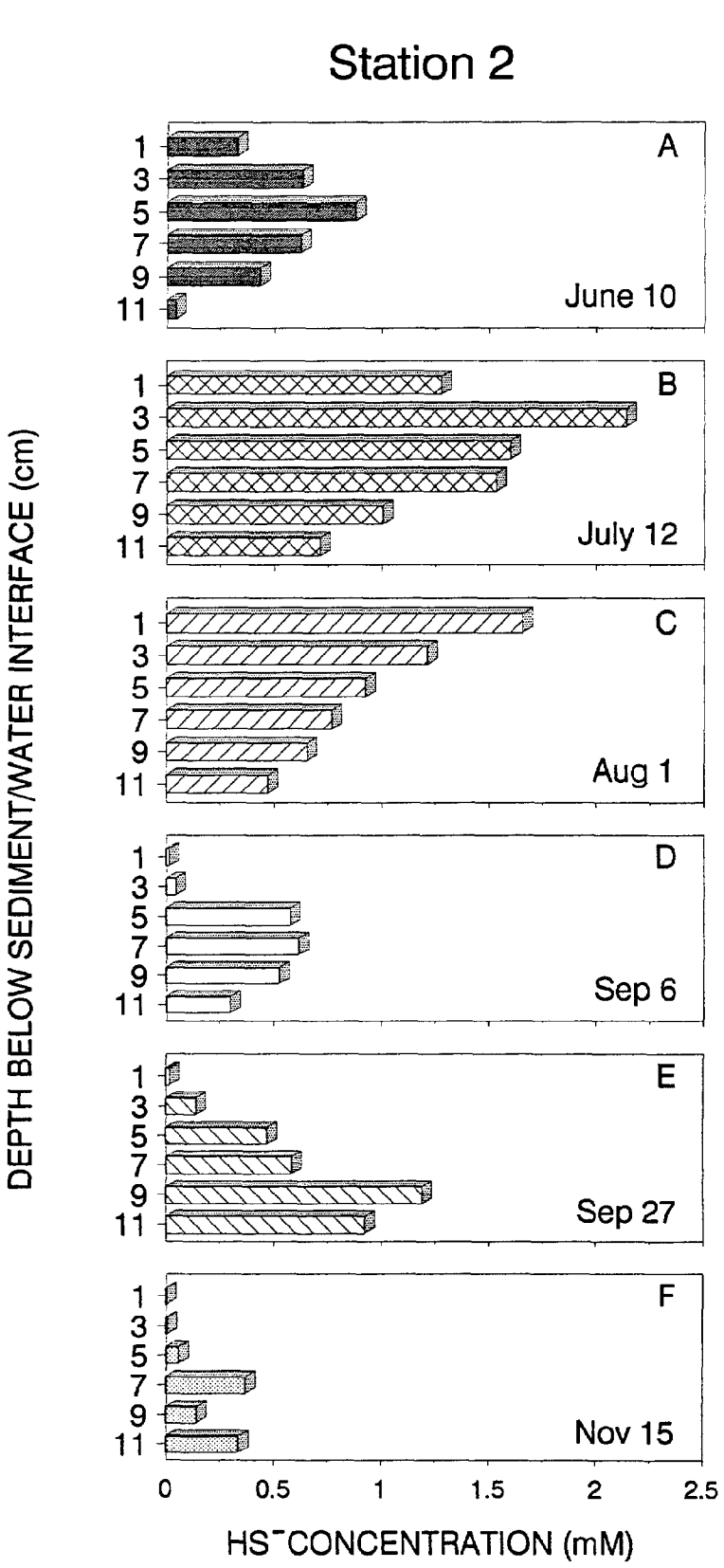

Figure 29. Depth profiles of pore water HS^- concentration at station 2.

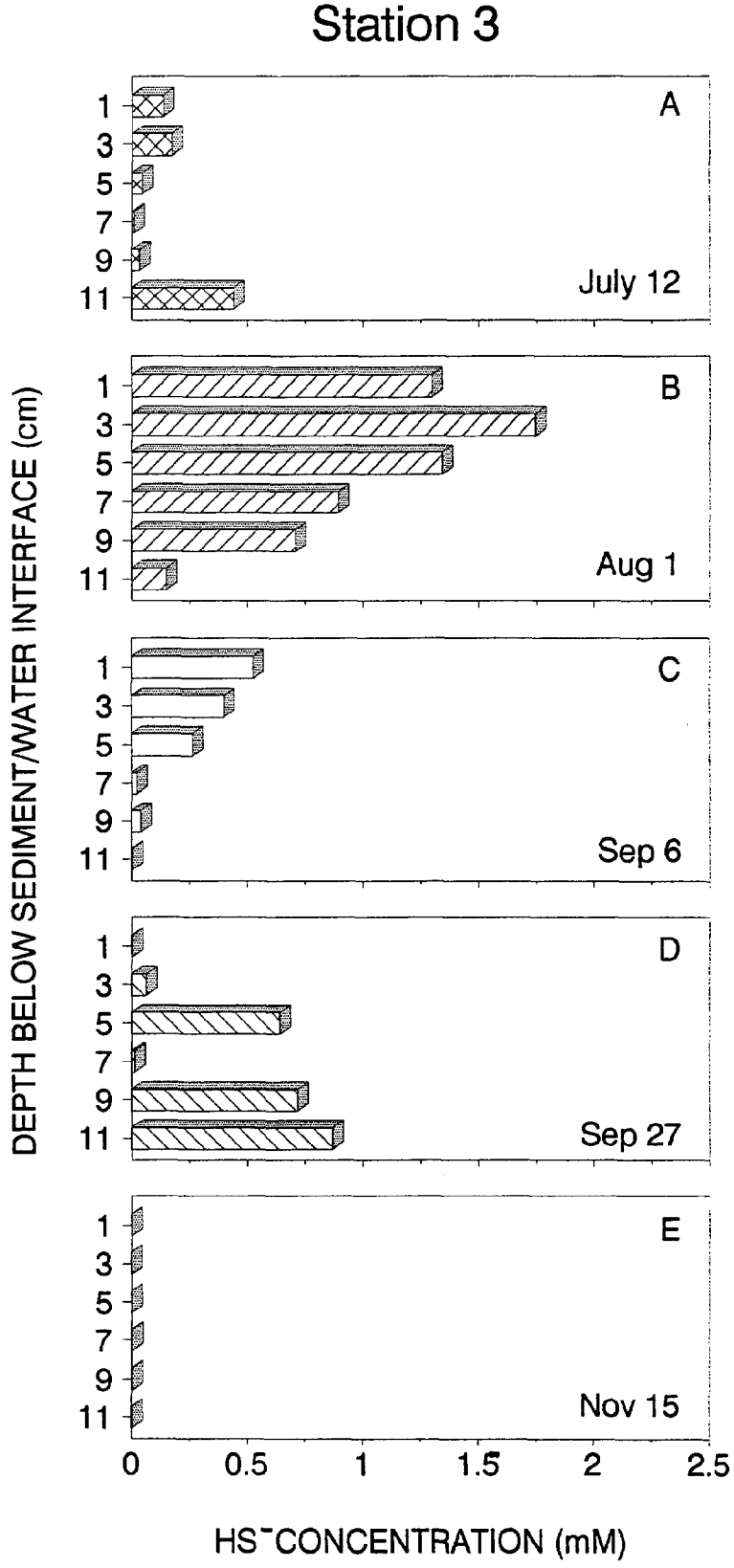

Figure 30. Depth profiles of pore water HS^- concentration at station 3.

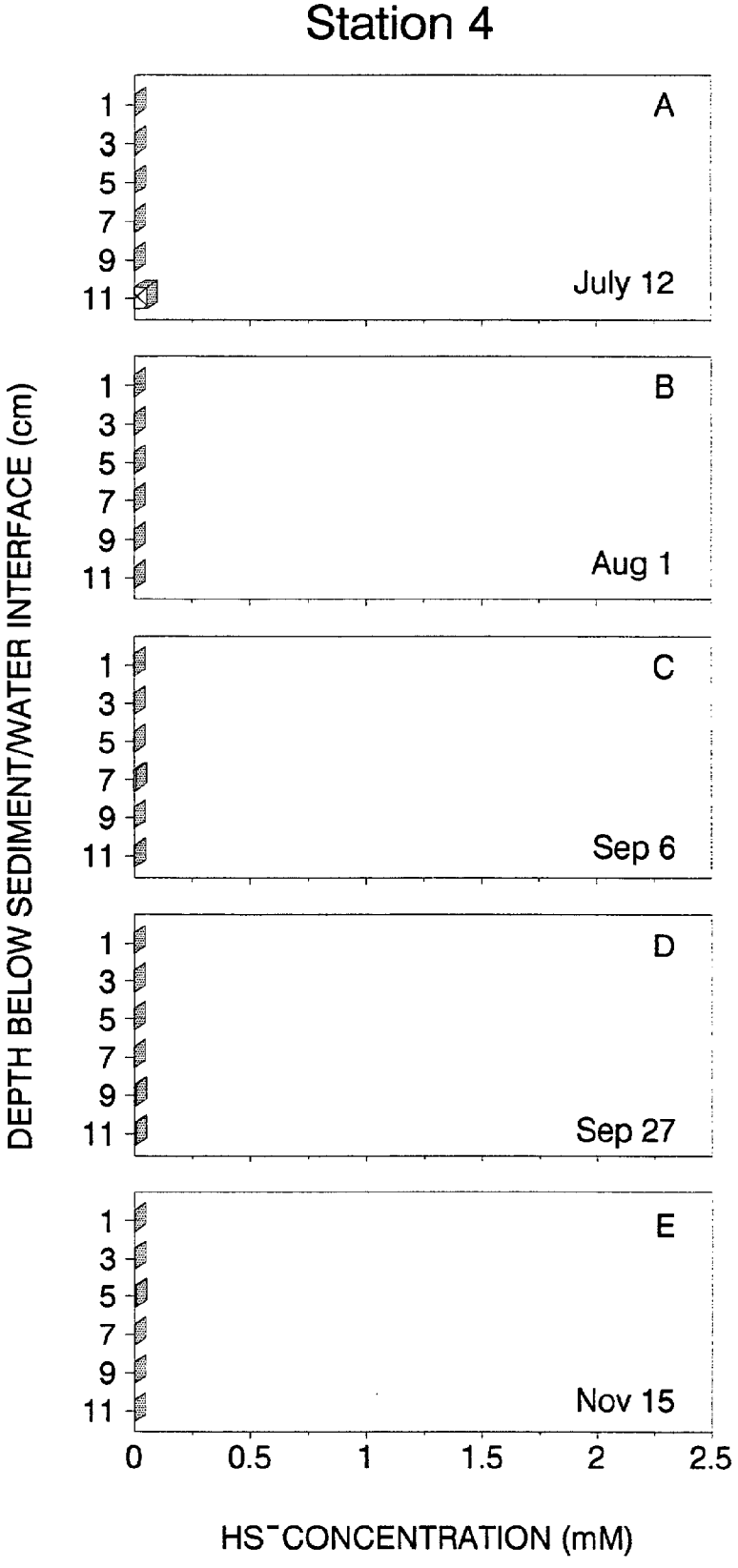

Figure 31. Depth profiles of pore water HS^- concentration at station 4.

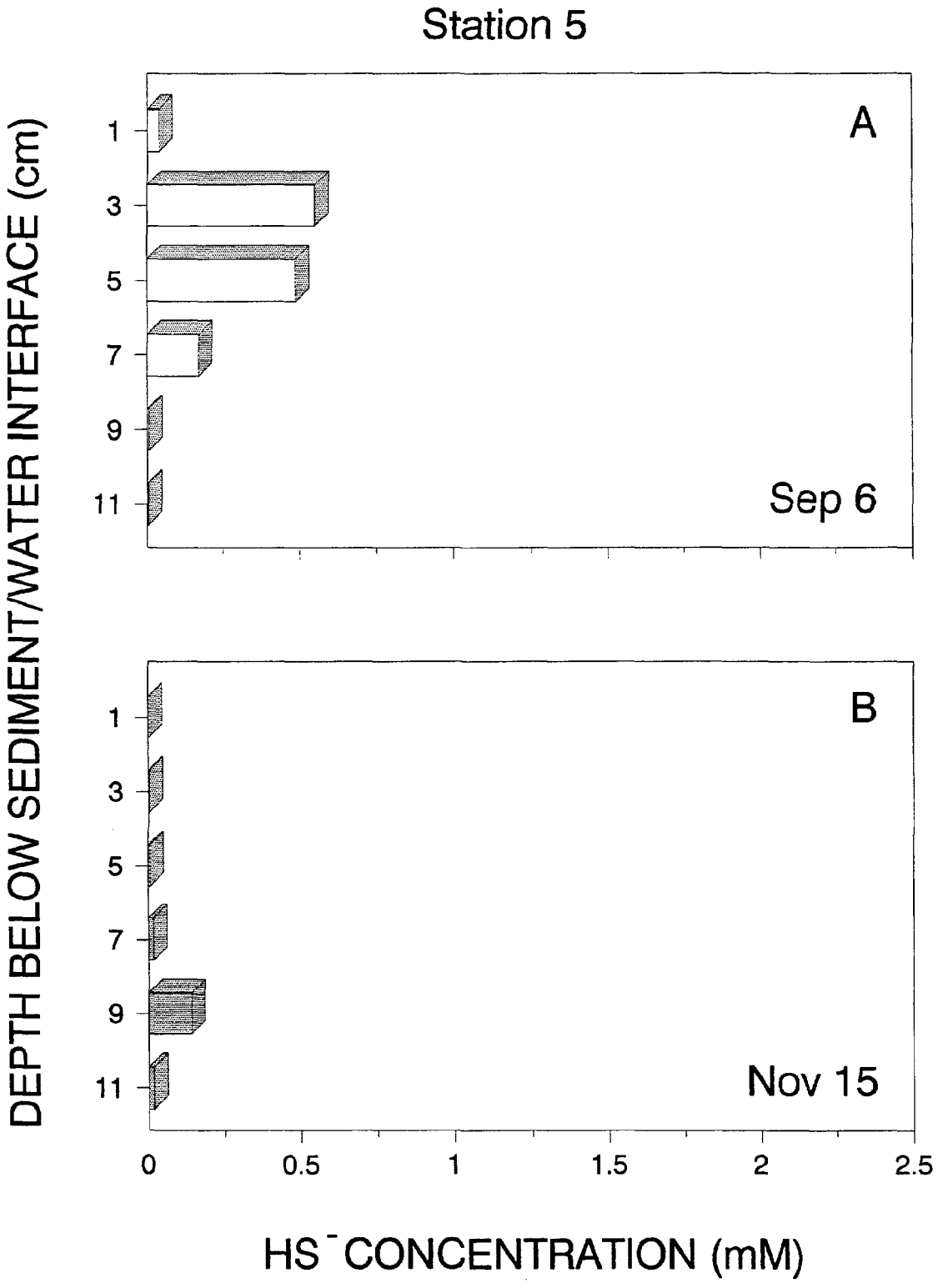

Figure 32. Depth profiles of pore water HS^- concentration at station 5.

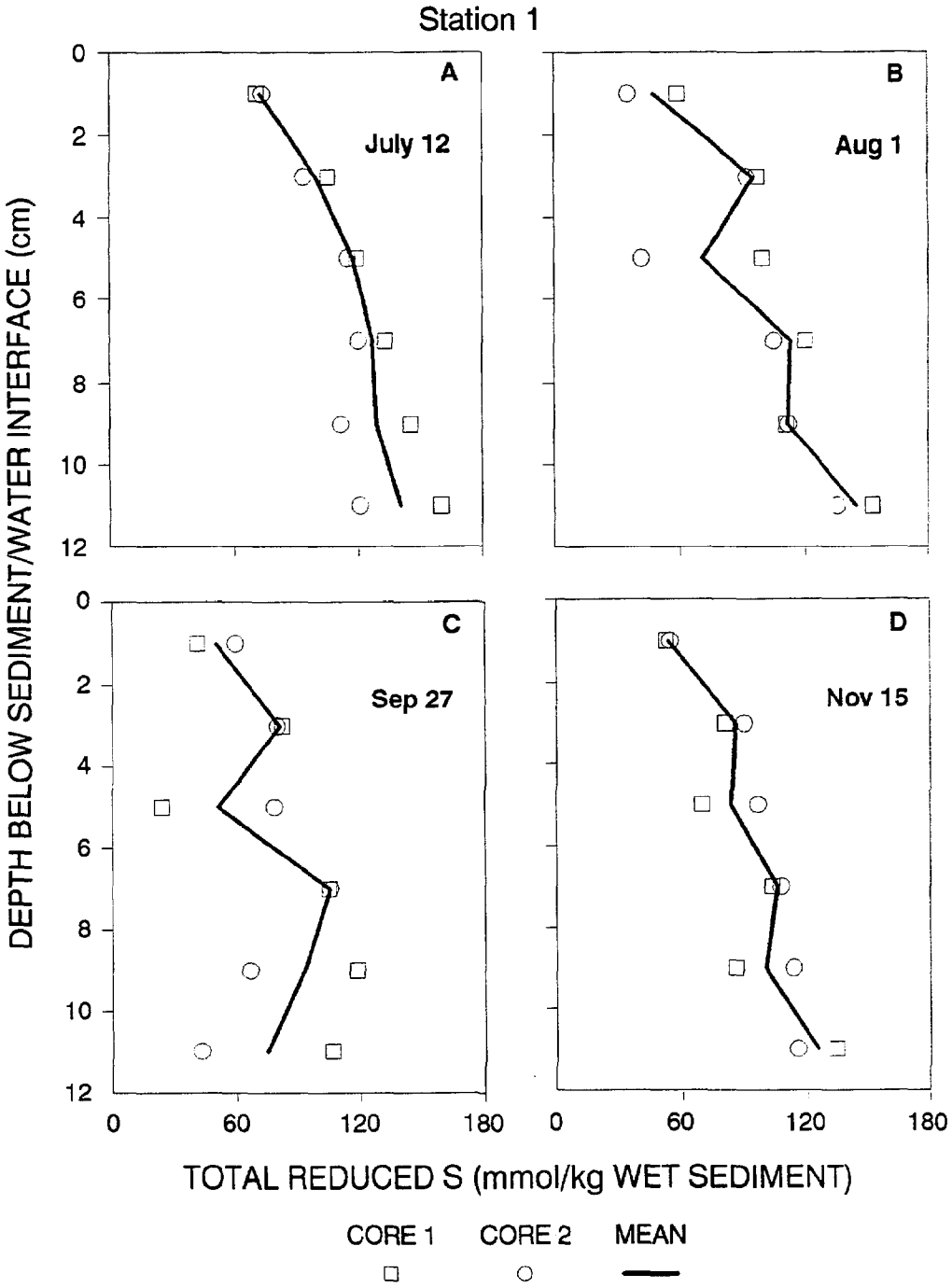

Figure 33. Distributions of total reduced sulfur (TRS) in sediments at station 1.

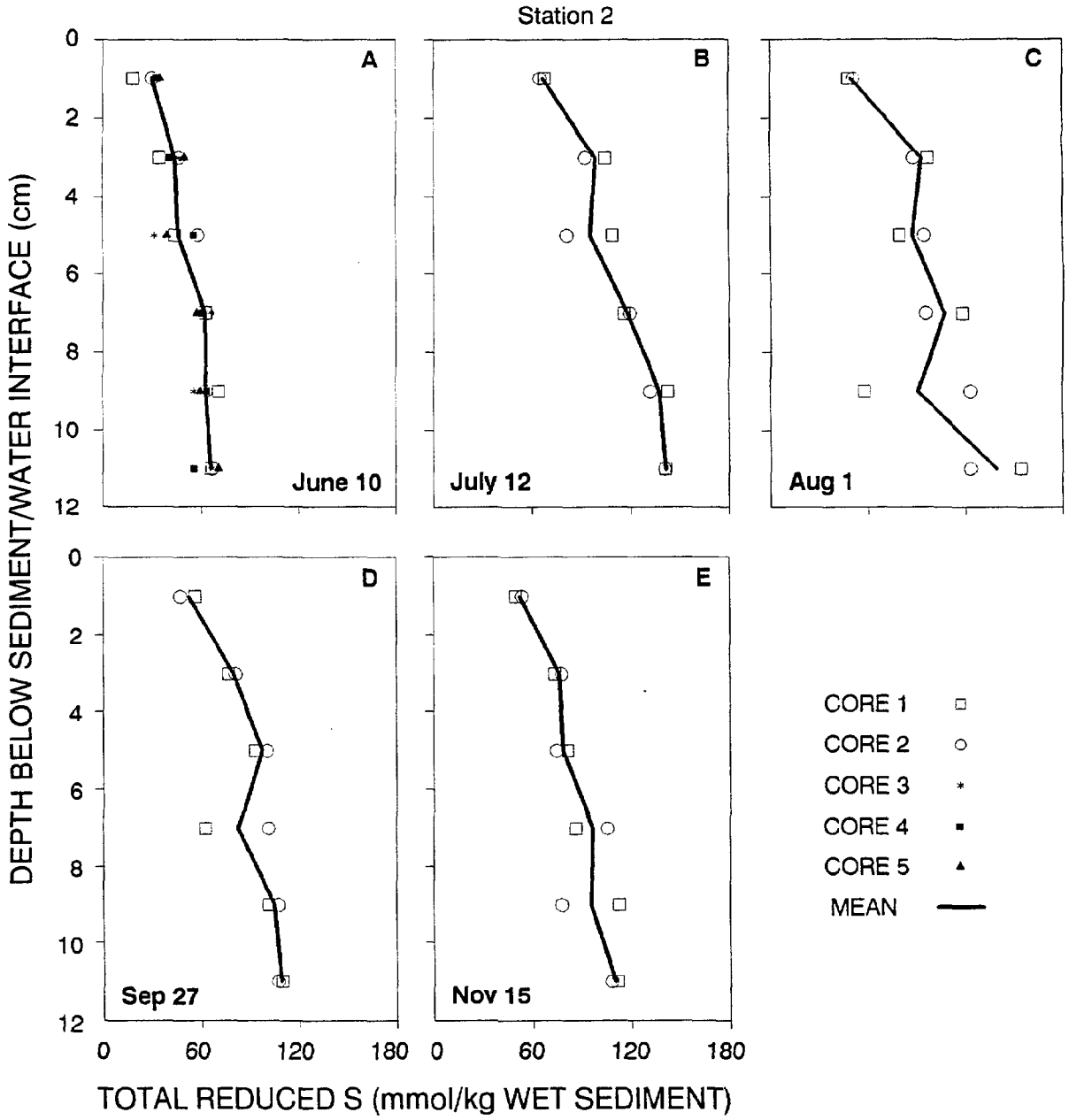

Figure 34. Distributions of total reduced sulfur (TRS) in sediments at station 2. Note in panel (A) that 5 replicate cores were examined as part of a time course sulfate reduction experiment.

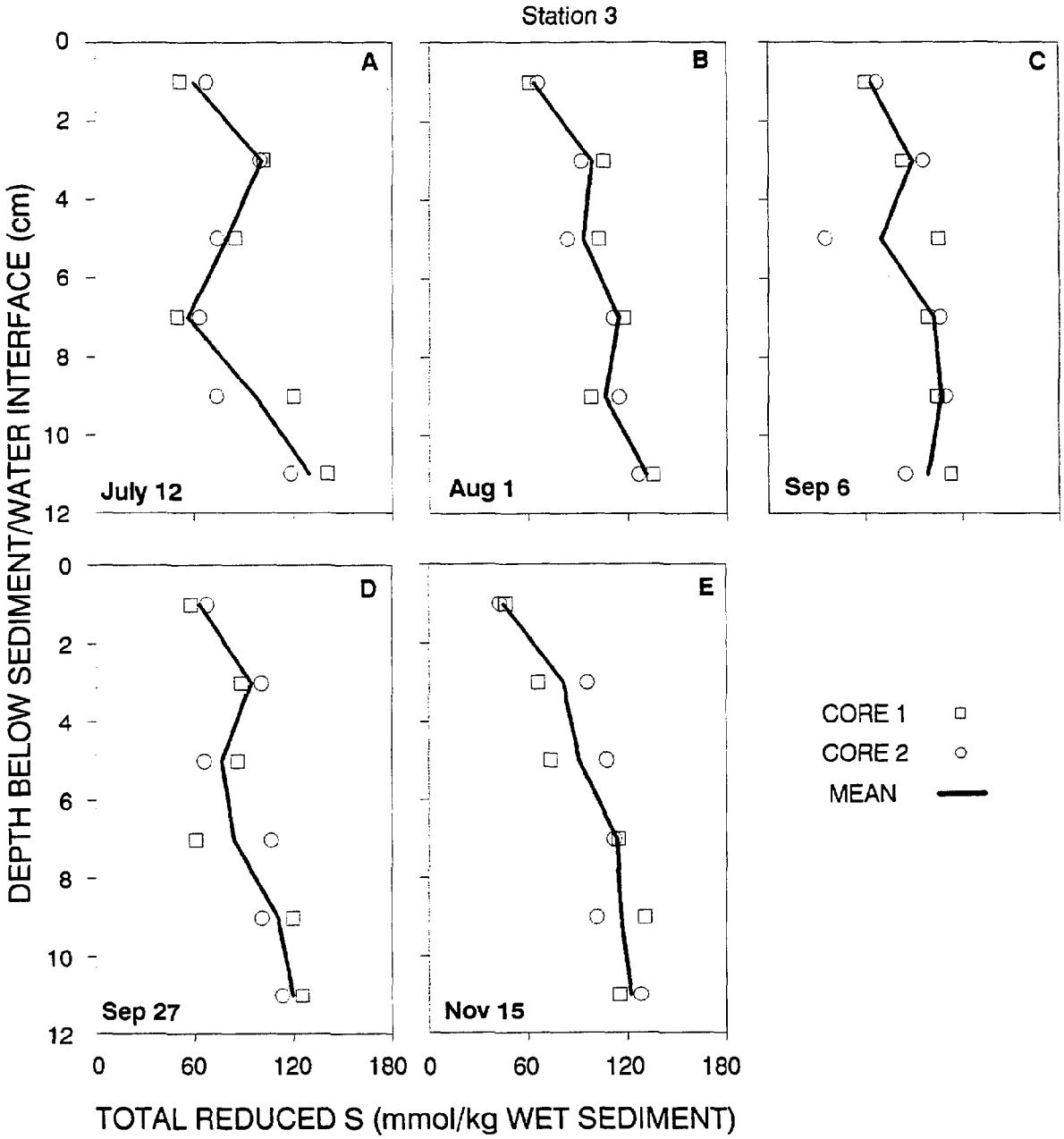

Figure 35. Distributions of total reduced sulfur (TRS) in sediments at station 3.

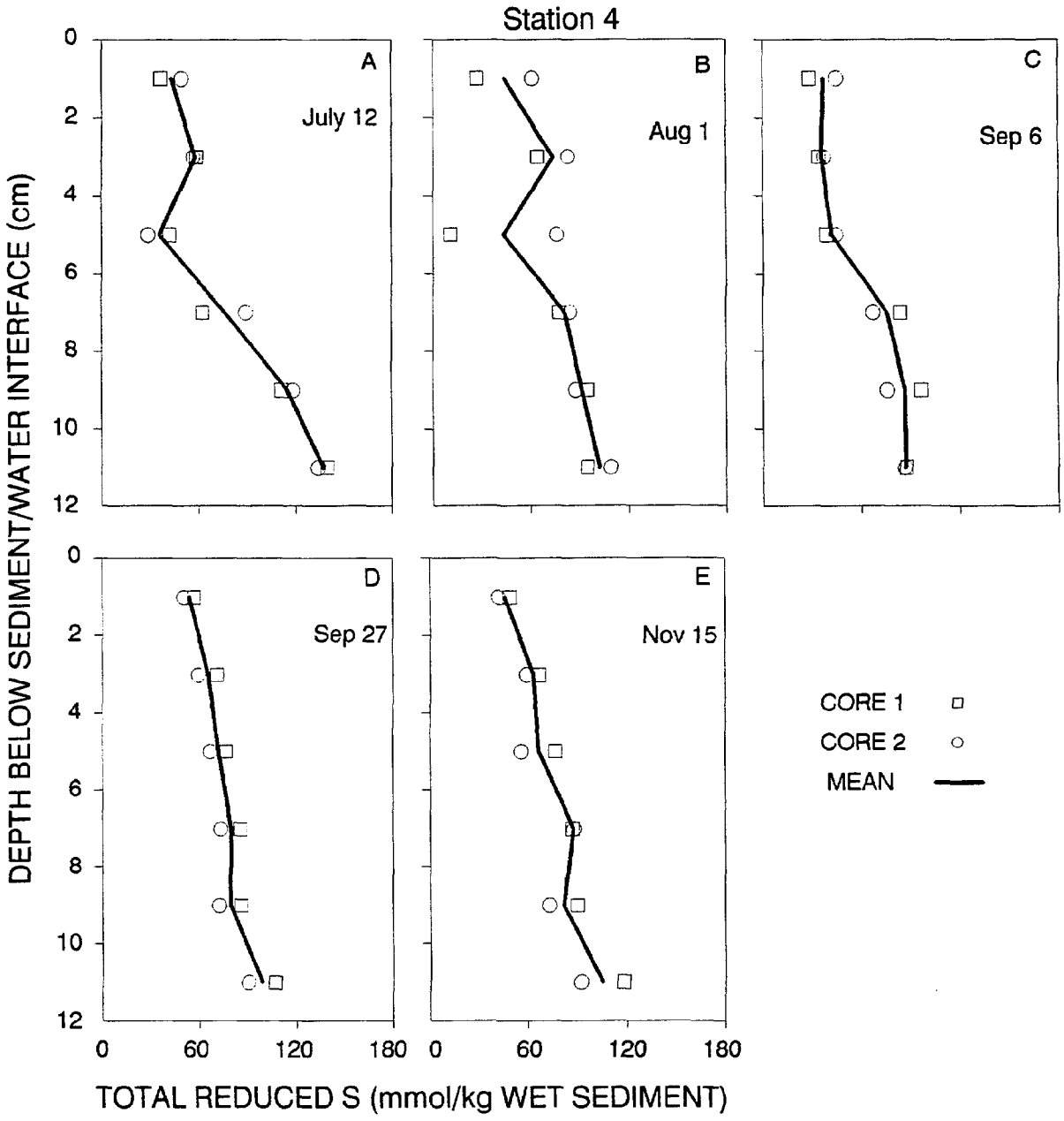

Figure 36. Distributions of total reduced sulfur (TRS) in sediments at station 4.

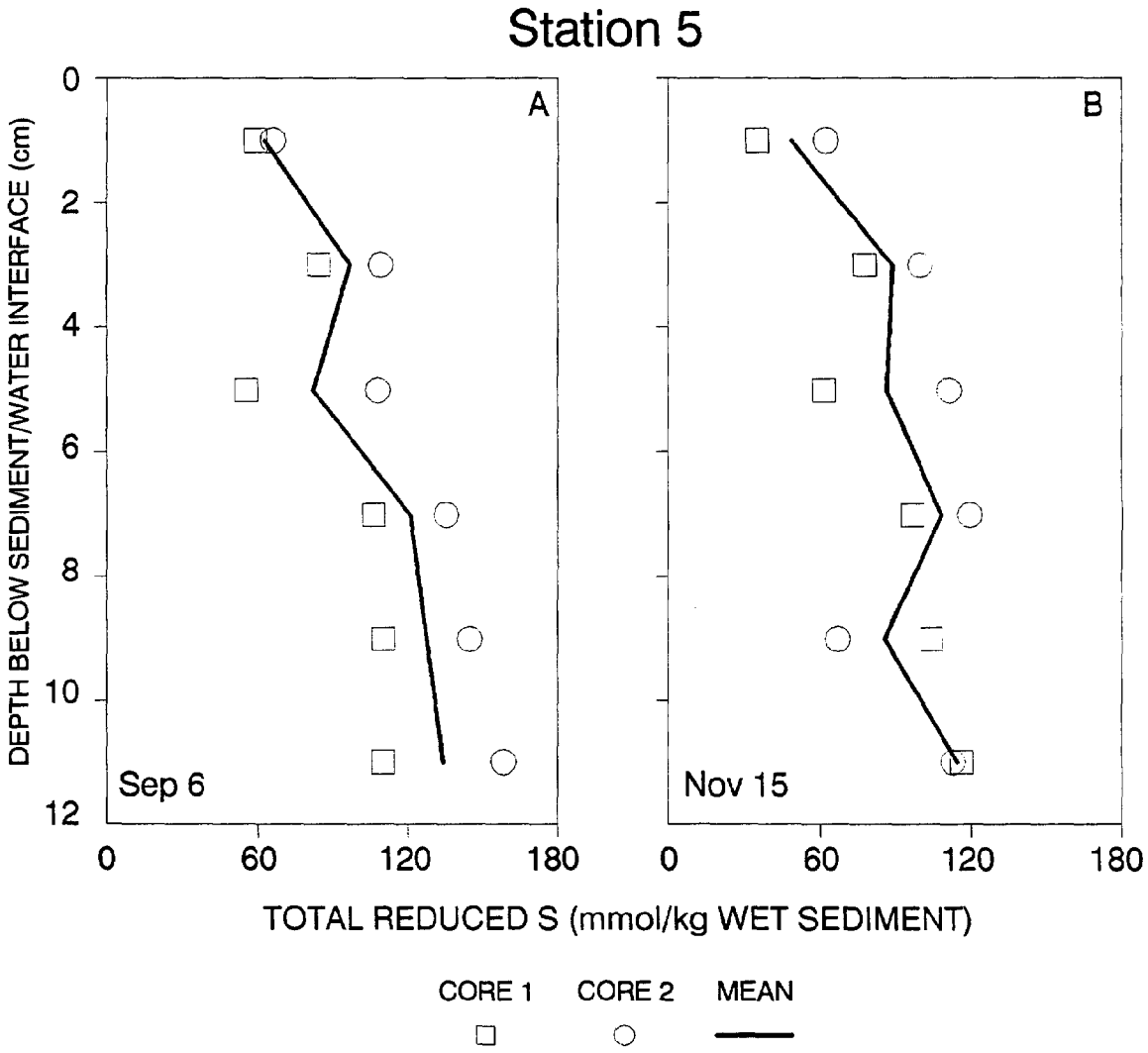

Figure 37. Distributions of total reduced sulfur (TRS) in sediments at station 5.

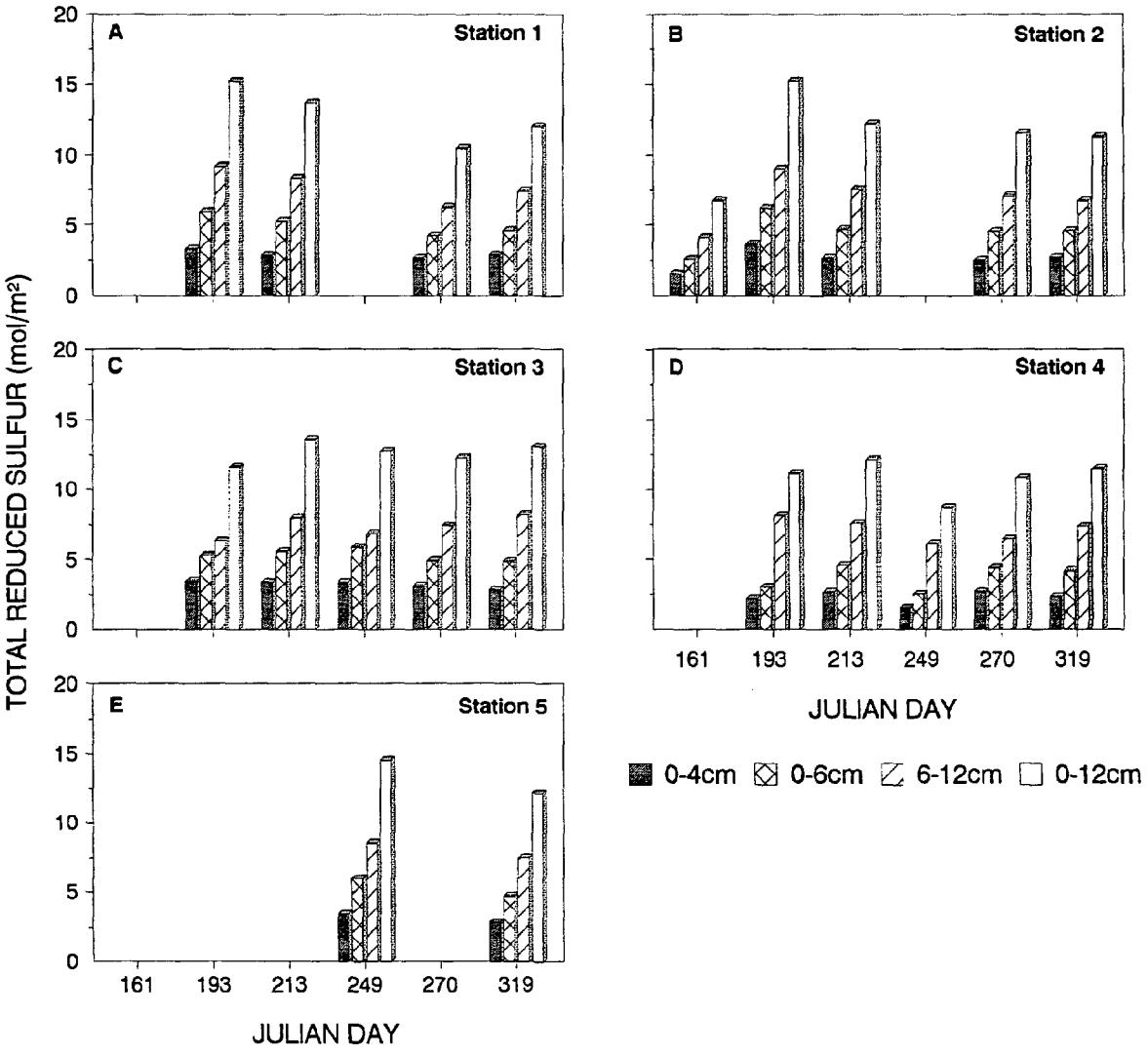

Figure 38. Depth-integrated areal total reduced sulfur (TRS) content of sediments over the study period. Bar codes indicate the depth intervals over which values for individual segments were integrated.

metal sulfides to continue accumulating at the other stations where the sulfate reduction rates were much higher probably means that the supply of metals available to react with sulfide is depleted and, thus, HS^- accumulates. This contention is supported by the data for station 2 (Figs. 34a, 34b and 38b) where TRS increased about two-fold between June 10 and July 12 and remained relatively constant thereafter.

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