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## A RECORD OF THE ACCUMULATION OF SEDIMENT AND TRACE METALS IN A CONNECTICUT SALT MARSH

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### 1. INTRODUCTION

Salt marshes occur over a wide latitudinal range from above the Arctic circle to the tropics (Chapman, 1960). Some occur inland in association with brackish waters, but most are intertidal grasslands found along sea-coasts in relatively protected areas. This work concerns a salt marsh on the Connecticut coast, formed since the last glaciation, during a prolonged period of sea-level rise relative to land.

Salt marshes are conveniently classified into zones of so-called high marsh and low marsh. As a first approximation, high marsh may be described as a grass-covered horizontal platform near the mean-high-water level. The characteristic, benchlike nature of the high marsh and its associated, distinctive set of salt-tolerant plant species distinguish this zone from low marsh. High marsh in the study area is covered with dense stands of grasses, typically dominated by *Spartina patens* (Ait.) Muhl (salt hay). The tall grass, *Spartina alterniflora* Loisel (salt thatch), almost

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exclusively occupies the low areas fringing the high marsh, however, a short form of this species may be found at some higher elevations (Miller and Egler, 1950).

The elevational distribution of these and other species is generally considered to reflect tolerance to immersion in saline water (Johnson and York, 1915). Adams (1963), working along coastal North Carolina, found that a given species tends to occupy a limited elevational range above mean sea level for a given tidal regime. Stalter and Batson (1969) showed that survival of high-marsh grass, notably *S. patens*, was unlikely after transplanting to a lower tidal position. Other environmental factors, such as nutrient availability (Adams, 1963; Valiela and Teal, 1974) and competition for space (Blum, 1968; Niering and Warren, 1974) may also affect distribution.

As grasslands, salt marshes are one of the productive facets of the near-shore environment. A portion of the net production appears as thick stands of characteristic vegetation, the remainder as subsurface roots and rhizomes. Silt and clay-sized deposits from outside sources also accumulate within the interstices of the organic matrix. Data from Connecticut salt marshes indicate that peat accumulations of about 1 m are common (Hill and Shearin, 1970), although depths of several meters have been noted elsewhere in southern New England (Johnson, 1967) and more than 3 m in at least one site at nearby Clinton, Connecticut (Bloom and Ellis, 1965).

Extensive, qualitative evidence of relative vertical motion of land and sea in this area has now been developed. This evidence includes relicts of former uplands beneath the salt marshes of New England, such as soil profiles, *in situ* tree stumps, and freshwater peat now overlain by considerable thicknesses of salt-marsh deposits (Cook, 1857; Dawson, 1855; Bloom, 1961). Archeological evidence, numerous anecdotal references to datable historical artifacts, and other evidence supports arguments that relative submergence has been a widespread and generally continuing phenomenon in this area (Davis, 1910, 1913; Johnson, 1967; Knight, 1934; Chapman, 1974).

The advent of <sup>14</sup>C-dating technique provided an opportunity to more closely describe the rise in relative sea level since the last worldwide glaciation. Application of the technique to salt-marsh samples yielded quantitative evidence for the continuity and vertical extent of sea-level rise both worldwide (Shepard, 1963; Scholl and Stuiver, 1967; Milliman and Emory, 1968) and in southern New England (Barghoorn, 1953; Fairbridge, 1961; Redfield, 1967). Radiocarbon dating of salt marshes revealed that the vertical development of the deposits has evidently kept pace with

relative sea-level rise over the last few thousand years (Redfield and Rubin, 1962; Bloom and Stuiver, 1963). In nearby Clinton, Connecticut about 3 m of salt-marsh deposit has accumulated during the last 3500 years (Bloom, 1967). Dated samples are spaced hundreds to thousands of years apart, however, and the most recent sample is more than 900 years old; so possible variations within the intervals and in historical time cannot be resolved. Accumulation during the colonial and industrial eras is very poorly defined, but the marker bed experiments begun in 1962 by Bloom (1967) and recently updated and extended (Harrison and Bloom, 1974; Harrison, 1975) show that increasing thicknesses of peat are generally found above the marker layers in subsequent years, evidently due to new peat formation. Measurements at monthly intervals in Flax Pond salt marsh on the south shore of Long Island Sound show that accretion in an established *S. alterniflora* area is practically monotonic and in reasonably good agreement with long-term average peat-accumulation rate (Amantano and Woodwell, 1975; Flessa *et al.*, 1977; Richard, 1978).

The manner of accretion, chemical properties, and the considerable physical protection afforded by the peat framework suggest that these deposits may contain useful depositional records.

Coastal wetlands are generally considered to be sinks for waterborne particulate matter (Meade, 1972). Sediment storage areas such as mudflats and channels, however, often fail to show stratification, perhaps because these deposits tend to be uniformly fine-grained and/or intensely bioturbated (Ellis, 1962; Rhoads, 1967). In addition, their susceptibility to cycles of erosion and deposition severely limits their scope as historical repositories. Sediment incorporated within the peat matrix, however, is relatively well protected from physical disturbance and, therefore, its depth distribution may reflect historical sediment-generating processes in the environment.

The mass of sediment incorporated into the peat is supplied from offshore and in riverine runoff. Ellis (1962) found that the proximate source of sediment input to the Great Marsh, a coastal marsh near Norwalk, Connecticut, was suspended material carried shoreward by tidal currents. Circulation studies of Long Island Sound show that bottom water flows westward into the Sound, then veers northward toward the coast in shoal water (Gordon and Pilbeam, 1975). Thus, sediment entering north-shore coastal salt marshes would tend to originate in the east. The proportioning between offshore and riverine sources, however, will strongly depend on local circumstances, e.g., proximity to the coast and intensity of stratification of adjacent waters. Salt marshes alongside well-stratified rivers some distance from the coast, as is the study marsh, may be expected to receive a much larger share directly from land sources. The present

work will give evidence of salt-marsh deposition dominated by riverine runoff.

Knowledge of the chemical properties of salt-marsh deposits, notably their organic-matter rich, reducing, sulfidic nature, suggests that certain substances may be fixed in place by natural processes, thus possibly forming a record of chemical deposition.  $H_2S$  is generated in these kinds of deposits, on occasion evidently to excess, by bacterial sulfate reduction (Galliher, 1933). Chemical principles predict that any available metal whose sulfide salt is sufficiently insoluble will spontaneously precipitate as metal sulfide. Berner (1970) has shown in laboratory experiments that iron minerals will react with  $H_2S$  to rapidly form monosulfides and, ultimately, pyrite ( $FeS_2$ ), a process believed to be ubiquitous in anaerobic marine sediments containing metabolizable organic matter. Formation of metal sulfides besides iron has not yet been demonstrated in salt marshes, but there is good reason to suppose that certain trace-metal sulfides do form in these deposits. For example, Cu, Zn, and Pb sulfides are known to form in the laboratory when sulfide produced by bacterial sulfate reduction reacts with trace metals added in the form of soluble salts (Baas Becking and Moore, 1961; Bubela and McDonald, 1969). Furthermore, the addition of sulfide or precursor sulfate is found to effectively control heavy-metal toxicity in anaerobic digesters by precipitation of the metals as their sulfides (Lawrence and McCarty, 1965). Locally, Siccama and Porter (1972) showed that the Pb content was higher in the surface layer of the Farm River marsh than at depth and that the surface concentration decreased in salt marshes further east (away from New Haven), a phenomenon they felt to be due mainly to automotive Pb brought to the marsh surface in freshwater runoff and then chemically fixed.

Vertical profiles, by themselves, are generally insufficient to identify sources or to rule out postdepositional rearrangement. Simple deposition, for example, cannot be credibly distinguished from deposition modified by mixing or remobilization.

The present work investigates the possibility that a useful, historical record of deposition might be found in the salt marsh. After selecting a site thought to optimize chances of finding a physically intact record (see site selection criteria, Section 2.1), a series of investigations of the vertical distribution of indicator materials in both solid and pore-water phases was begun. The three trace metals, Cu, Zn, and Pb, were selected, *a priori*, as likely to be chemically immobilized through formation of their insoluble sulfides.

Fe and Mn were also included in the study because of their reputed involvement in the conservation of trace elements (Jenne, 1968) and because of their sensitivity to redox conditions. Authigenic iron sulfide

( $FeS_2$ ) is of special interest because it is *de facto* evidence of the operation of the sulfate reduction process and the persistence of reducing conditions. It is conceivable that processes resulting in pyrite formation, in addition to exemplifying the sulfide-precipitation process, may actually include other trace metals in a chemical sense. A study of the vertical distribution of  $^{210}Pb$  was undertaken because of its utility as a tracer and as a potential means to establish a sediment chronology. This natural radionuclide is produced in the atmosphere by decay of gaseous  $^{222}Rn$ , is rapidly attached to the atmospheric aerosol, and is deposited on all exposed surfaces. After deposition, its chemical behavior is believed to mimic elements with similar chemical properties. Unlike stable elements, however,  $^{210}Pb$  decays with a 22-yr half-life (Hohndorf, 1969) and, under suitable conditions, its vertical distribution within the deposit may be used to define a chronology.

## 2. EXPERIMENTAL METHODS AND RESULTS

### 2.1. Site Selection

Choice of site for detailed study was based on the following criteria: (1) the surface and subsurface vegetation should be typical high-marsh species, e.g., *S. patens*; (2) the surface relief should be minimal; (3) the core should penetrate into peat formed before human influence became significant; and (4) the probability of physical disturbance in the past should be low.

Salt hay has been cut on many Connecticut salt marshes in historical times for fodder and mulch, and drainage ditches were dug through almost all of them in the early 20th century to control mosquito breeding (Connecticut Agric. Exp. Stn. Rep., 1912). Many ditches are still maintained, so their location is usually obvious and easy to avoid. Relict ditches and areas previously hayed—implying disturbance by men or animals—are harder to avoid. It is possible, however, to minimize the probability of such disturbance by selecting areas that are difficult to approach due to the impediment of the natural drainage pattern. Aerial photographs (Connecticut Department of Environmental Protection, 1971 series, 1 in = 200 ft especially No. 30-1-4) proved valuable for this purpose, and also for identifying relict ditches or other anomalous features, and for finding areas of desirable high-marsh vegetation.

Once promising areas within the Farm River marsh were selected, they were examined in the field. Several trial cores were raised using a tool designed for this task (McCaffrey, 1977) and local residents were inter-

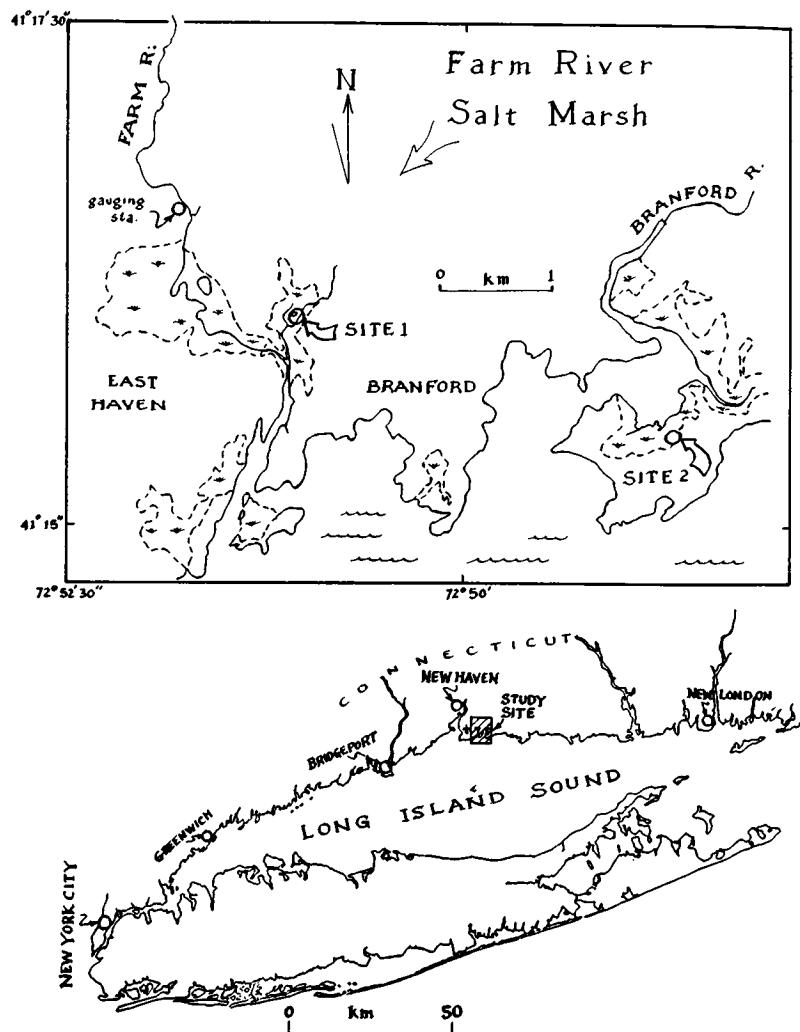


FIG. 1. Map of the study area.

viewed about the candidate sites. A part-time farmer (Stanley Kaczynski, b. 1915, personal communication), who had personally cut hay on the accessible parts of the salt marsh before 1935 and still lives within view of it, did not recollect anyone cutting hay or otherwise physically disturbing the area eventually chosen for intensive study.

The chosen area (Fig. 1) is located in the eastern lobe of the Farm River salt marsh ( $41^{\circ}16'00''N$ ,  $72^{\circ}51'06''W$ ), 7.9 km southwest of the center of

the city of New Haven. This marsh fills its valley to a remarkably uniform level and straddles tidal channels carrying freshwater runoff from a 66-km<sup>2</sup> watershed (Thomas, 1972). The site selected for detailed analysis is located near the center of a rectangular area bounded on two sides by parallel drainage ditches and on the other sides by a natural channel and a small upland "island." The deep stratigraphy (Fig. 2) was determined with a Davis peat sampler. All sampling was done at this site, except for a few cores taken from a similar salt marsh about 3 km to the east, on the north side of Indian Neck peninsula.

Human influence on the watershed was very likely negligible prior to the arrival of European colonists in the 17th century. Since then, the naturally forested watershed has been subjected to extensive clearing and cultivation, and the area is now a rapidly developing suburb of the nearby urban and industrial center of New Haven.

Man's impact on the watershed can be inferred from demographic and land-use trends for this general area. According to Hicock (1970), about 95% of the land was forested before colonization. Reduction of forested areas began after imposition of a colonial economy based on subsistence agriculture. By 1800 about a third of Connecticut's forests had been cleared to replace nutrient-impoverished farmland or for fuel or timber. The percentage of forested land passed through a minimum around the end of the Civil War (1865) (MacDonald, 1968; Harper, 1918). After this war the rate of farm abandonment exceeded the rate of establishment. This initiated an era of net decline in the area devoted to agriculture and permitted spontaneous reforestation to begin. As farming declined as an occupation, industrialization intensified and urban centers developed.

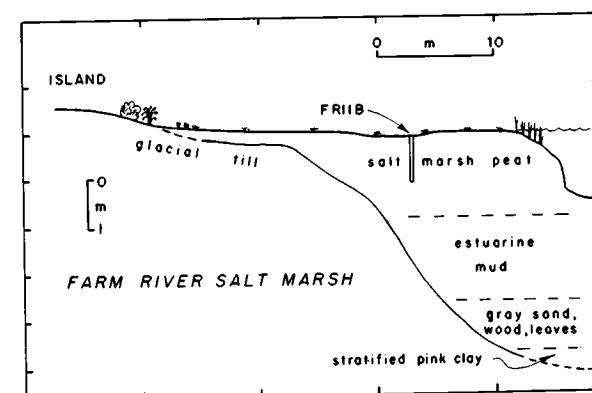


FIG. 2. Vertical section of the Farm River salt marsh, showing position of the dated core and general stratigraphy.

Census data for New England (cited by Harper, 1918) revealed that the percentage of the population employed in agriculture diminished from 62% in 1840 to 10% in 1910, while industrial employment increased from 28% to over 49%. Demographic trends during this time, shown in Fig. 3, portray the early rapid development of urban centers such as New Haven and the subsequent spillover onto outlying second-growth farmland, typified by the study area in East Haven.

## 2.2. Peat Properties

Cores were obtained at low tide by first excavating a vertical access hole with a post-hole digger, then cutting one or more meter-length cores of about 9 cm × 24 cm cross section from the exposed sides, using the special coring tool.

It is a common experience among those who stand in place on the high marsh that the surface slowly depresses and forms a water-filled pool around one's feet. Based on this observation and the generally water-saturated condition of the peat, we anticipated that water would soon fill

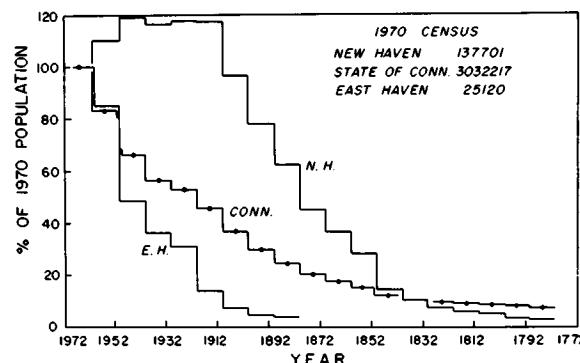


FIG. 3. The population of New Haven burgeoned shortly before the Civil War, in part due to the general movement from rural areas to manufacturing centers, and in part (about a third) due to a surge in immigration (Gilbert and Olmstead, 1910). This rapid increase was sustained until World War I, when census records for the city show an abrupt flattening. This behavior appears to be an artifact produced by growth across fixed political boundaries; suburbs such as East Haven tended to accumulate the spillover. More than 85% of the population of East Haven was added since 1920, especially since World War II. The pace of change on the watershed has continued to accelerate to the present: by 1970 over 7400 housing units and more than 140 km of roads had been constructed (East Haven, 1970). Despite the population boom, there is still no known discharge from industry into the Farm River, and at least 75% of the domestic sewage is carried out of the watershed through the municipal sewage system.

the cavity by seepage, but this proved minimal. The few liters of water that accumulated in the hole during the approximately 15-min coring operation appeared to enter near the top of the hole, rather than by subsurface flow.

Vertical zonation, in the form of diffuse colored bands, is apparent in fresh cores, especially within the upper 50 cm. The same general features of the zonation were found to extend laterally over most of the high marsh, except near the creek banks. FR11B, the core examined in greatest detail, featured: (1) *S. patens* growing at the top of the core, with apparently live roots and rhizomes extending to about 10–12 cm depth; (2) a thin ( $\lesssim$  1-cm), pink-colored layer of sediment present at the surface, presumably a result of oxidation; (3) a generally brown-colored peat beneath the surface oxidized layer, but visibly blackened at a depth of roughly 5–10 cm; and (4) a zone of gray-colored fine sediment, conspicuous in the peat between 26 and 42 cm depth, hereafter called the "clay band."

The meter-length core was cut parallel with the marsh surface at 2-cm depth intervals, then the peripheral 1–2 cm was trimmed, leaving a neat, firm, rectangular prism of peat. The prisms were placed in thin-wall plastic bags and the length of each of the 12 edges measured. Peat of this type held its shape well if handled carefully, allowing accurate measurements to be made. The peat samples were weighed in Petri dishes while fresh, after drying to constant weight at about 100°C, and again after ashing at  $500 \pm 25^\circ\text{C}$ .

The organic matter of the salt marsh is photosynthesized by grasses growing at the surface. The net primary productivity is apportioned between the conspicuous above-ground growth and the inconspicuous, but appreciable, below-ground growth. The internal structure of the peat is conveniently studied by x radiography. X radiographs of FR11A, a core raised from the same hole as FR11B, are presented as Fig. 4. Another x radiograph, Fig. 5, was made of a very large *S. patens* tussock from nearby marsh. These x-ray images provide valuable evidence of growth processes and are helpful for identifying zones of apparently homogeneous peat within the cores.

A key to the identification of the various grass species forming the peat has been developed by Niering *et al.* (1977), based mainly on their distinctive rhizome cross sections. Using an x radiograph as a map, subsamples representing the homogeneous zones may be selected for species identification. In this way it is possible to estimate the proportions of species present, and to assign a peat type based on dominance in each zone. Whether or not a significant preservational bias exists is yet to be demonstrated, so inference of the *original* species composition from old peat remains uncertain.

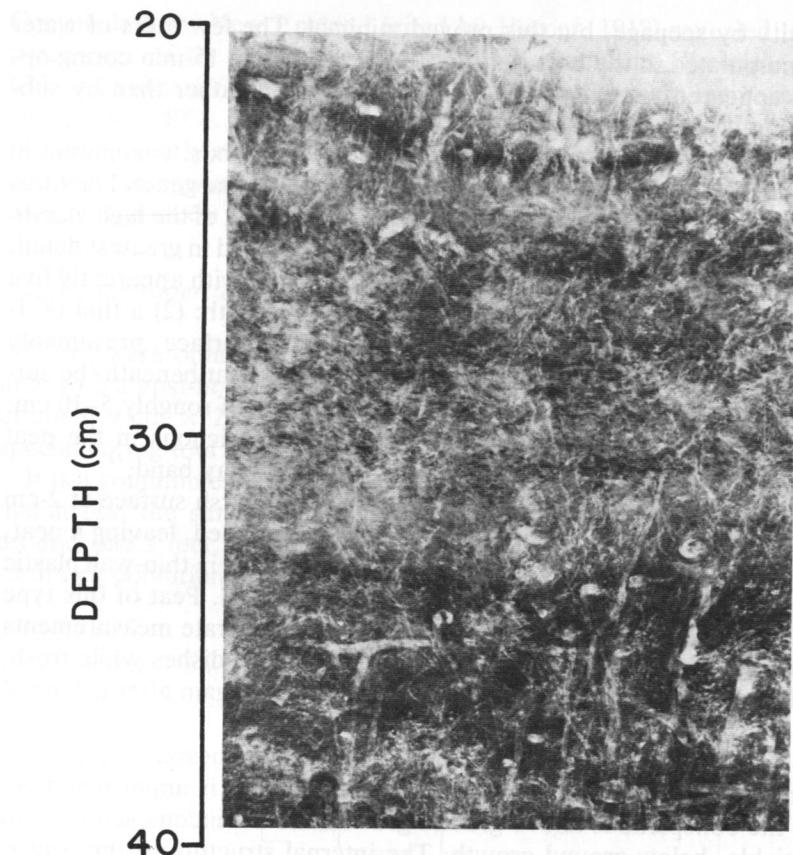


FIG. 4. X radiographs of 1-cm-thick vertical slices of core FR11A show details of the structure of high-marsh peat. As the percentage of space at any given position occupied by organic matter increases, the penetrability to x rays and consequent lightness of the photographic print also increases. The plant parts visible in the print, mainly consisting of roots and rhizomes of <0.1–1-cm diam., occupy much of the available space and form an intricate, interwoven organic matrix. The light-shaded subround objects appearing throughout most of the core are plant parts viewed in cross section or, in a few cases, holes.

The interstices of the plant matter contain inorganic sediment and are generally saturated with saline water. The mass content of a given volume of material may be conveniently described in terms of bulk densities of its component phases. Mean-bulk densities for a core may be calculated from the weight and volume data averaged over all slices.

Examination of the bulk density data for the entire core in Table I reveals that water constitutes over four-fifths of its mass, whereas dry

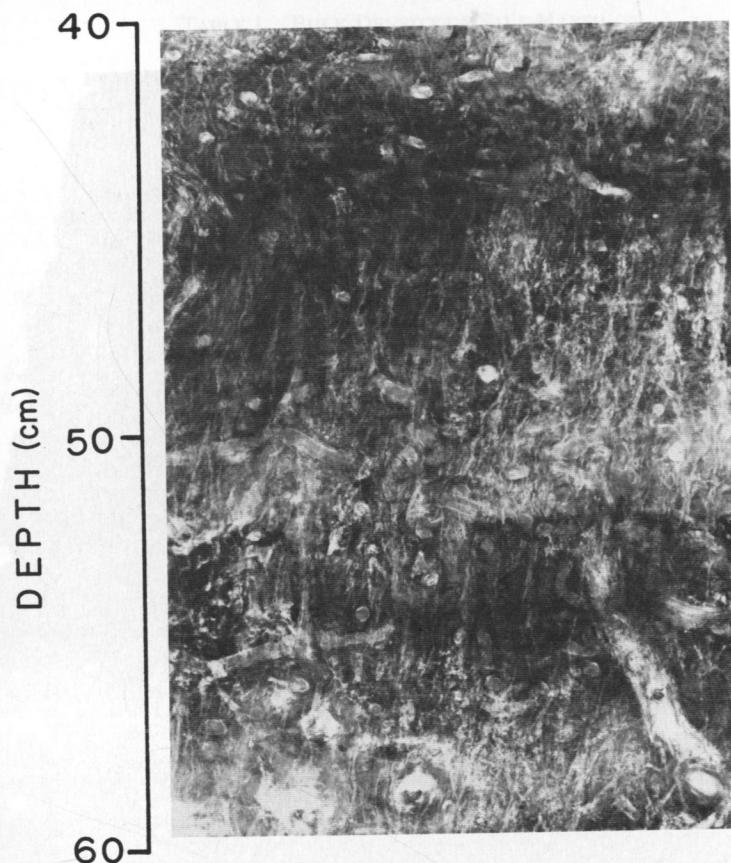


FIG. 4. (Continued.)

matter accounts for less than one-fifth. Of the dry-matter fraction, about 70% is inorganic and the remaining 30% is organic. Water dominates the mass, to the extent that the mean-bulk density of a fresh core is a mere  $1.011 \text{ gm/cm}^3$ , which demonstrates that this material is essentially neutrally buoyant in water of the estuary. Conversely, the overall mean-bulk density of dry matter is only  $0.2 \text{ gm/cm}^3$ , compared to about  $0.65 \text{ gm/cm}^3$  for Long Island Sound sediment (Thomson *et al.*, 1975) and about  $1.9 \text{ gm/cm}^3$  for sandy upland soil. The surface of the salt marsh is not supported on a column of particles. Also note that the organic fraction mean-bulk density ( $0.056 \text{ gm/cm}^3$ ) is not much greater than Sound sediment ( $0.04 \text{ gm/cm}^3$ ). The reputation of the salt-marsh peat as an organic-rich material is hardly justifiable on a mass basis. The impressions of observers are

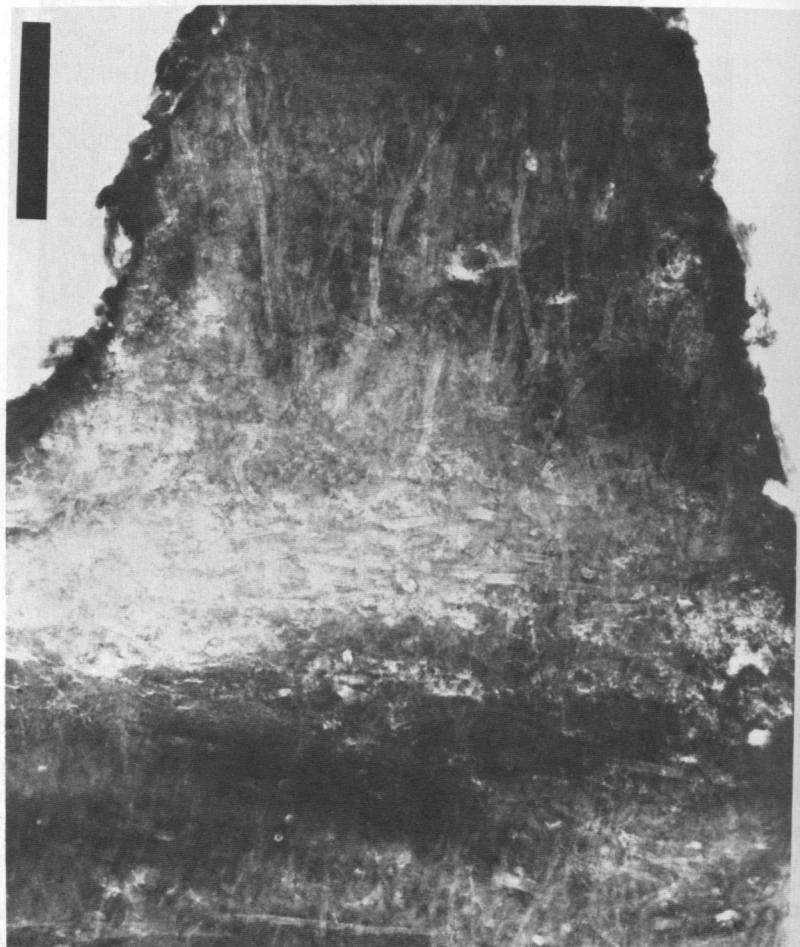


FIG. 5. X radiograph of an *S. patens* tussock. This x radiograph shows details of the internal structure of a relatively large tussock. The darker portions on the periphery and lower central part of the x radiograph are relatively rich in silt. The light-shaded region traversing the base of the tussock is composed of a mass of intertwined, 2-3-mm diam., rhizomes of, presumably, *S. patens*. A number of similar plant parts are oriented vertically within the tussock, and very fine rootlets are evidently well dispersed throughout its entire volume, which extends some 10-12 cm above the adjacent surface of the marsh. Bar is 5 cm long.

TABLE I. BULK DENSITY OF SALT-MARSH SEDIMENTS<sup>a</sup>

| Condition | Fraction  | Depth interval (cm) | Mean bulk density (gm cm <sup>-3</sup> ) |
|-----------|-----------|---------------------|------------------------------------------|
| Wet       | Total     | 0-100               | 1.011                                    |
| Dry       | Total     | 0-100               | 0.194                                    |
| Dry       | Total     | 26-42               | 0.265                                    |
| Dry       | Organic   | 0-100               | 0.058                                    |
| Dry       | Inorganic | 0-100               | 0.135                                    |
| Dry       | Inorganic | 0-5                 | 0.200                                    |
| Dry       | Inorganic | 10-25               | 0.142                                    |
| Dry       | Inorganic | 26-42               | 0.201                                    |
| Dry       | Inorganic | 42-50               | 0.137                                    |

<sup>a</sup> Mean bulk-density values are based on the measured weights and dimensions of all 50 slices of core FR11B, corrected for saw kerf. Values for the various subsections were estimated graphically using an expanded version of Fig. 6 and are considered accurate to within  $\pm 0.003$  ( $1\sigma$ ).

evidently biased by the fact that the salt-marsh organic matter is voluminous and still largely intact, whereas in bottom sediment it is comminute and diffuse. Even though the mass of organic matter is in fact small, the x radiographs show that the *volume* occupied or enclosed by roots and rhizomes is extensive.

The bulk density of dry matter present in individual slices varies over the length of the core. When the accumulated mass per unit area is plotted against depth, the curves (Fig. 6) show that dry-matter accumulation has varied in a complex way during the period of accretion. Further insight into the nature of this variation is gained by separating the dry matter into its inorganic and organic phases, also shown in the Fig. 6. It is immediately obvious that essentially all of the variation in dry-matter accumulation is due to a varying inorganic-matter contribution; the organic material, in striking contrast, accumulates in a highly linear manner over depth. This suggests that inorganic and organic matter accumulate independently. Furthermore, the uniformity of the organic-accumulation process suggests that this process is controlled in some manner.

The inorganic-matter bulk density is greater in the upper half of the core, reaching highest concentrations within the 0-5 cm and 26-42 cm depth intervals, where it averages  $0.2 \text{ gm/cm}^3$ , or 50% above the mean for the whole core. The mean-bulk density over limited depths was estimated from the slope of the line through the appropriate segment of the

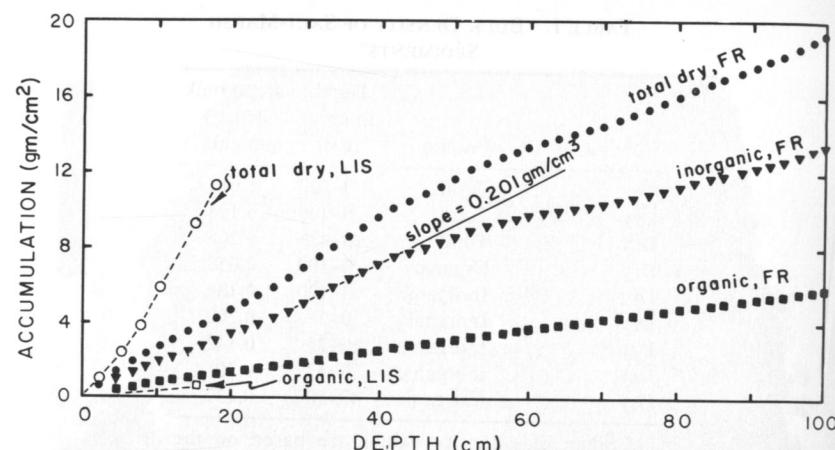


FIG. 6. Accumulation of high-marsh peat. The variation in accumulated total dry-matter content ( $\text{gm cm}^{-2}$ ) of Farm River salt-marsh core FR11B and Long Island Sound bottom-sediment core LIS 72-6 are plotted over each increment of depth. Total dry matter is broken down into inorganic (500°C residue) and organic (weight loss on ignition) fractions for the salt-marsh core. The line corresponding to the organic fraction is very nearly straight over the entire core, except for a region of changing slope within the upper 10 cm or so; whereas the inorganic-matter accumulation varies in a complex manner. The curve representing the accumulated total dry weight of sediment in Long Island Sound is shown for comparison. It exhibits the upward concavity expected for deposits where porosity decreases with depth. In contrast, there is no clear evidence of compaction in the salt marsh, even below the relatively dense layer at 26–42 cm, and the water content remains about 80% throughout.

accumulation curve, as shown in Fig. 6 for the 26–42 cm interval, and summarized in Table I. It is clear that the gray clay band noticed in the fresh core does indeed correspond to a zone of relatively high inorganic-matter content at 26–42 cm. The presence of the 0–5 cm zone of relatively high inorganic-matter content was not apparent in fresh cores, but is also indicated by its bulk density.

Direct evidence for the formation of authigenic metal sulfide comes from x-ray microprobe and light-microscope examination of the salt-marsh sediments. In the presence of sulfur, iron monosulfides react to form pyrite,  $\text{FeS}_2$ , which is known to occur as distinctive, characteristic aggregates of octahedral microcrystals of  $\text{FeS}_2$  (framboids; Berner, 1970; Sweeney and Kaplan, 1973). In the Farm River samples, frambooidal  $\text{FeS}_2$  was found to be common within at least the upper 14 cm of core examined, either as discrete framboids of  $\sim 10\text{-}\mu\text{m}$  diam. (Fig. 7) or as ordered clusters of framboids. Inspection of polished thin sections reveals a frequent association with the organic matrix, which appears to act as a template for their formation (see Fig. 8).

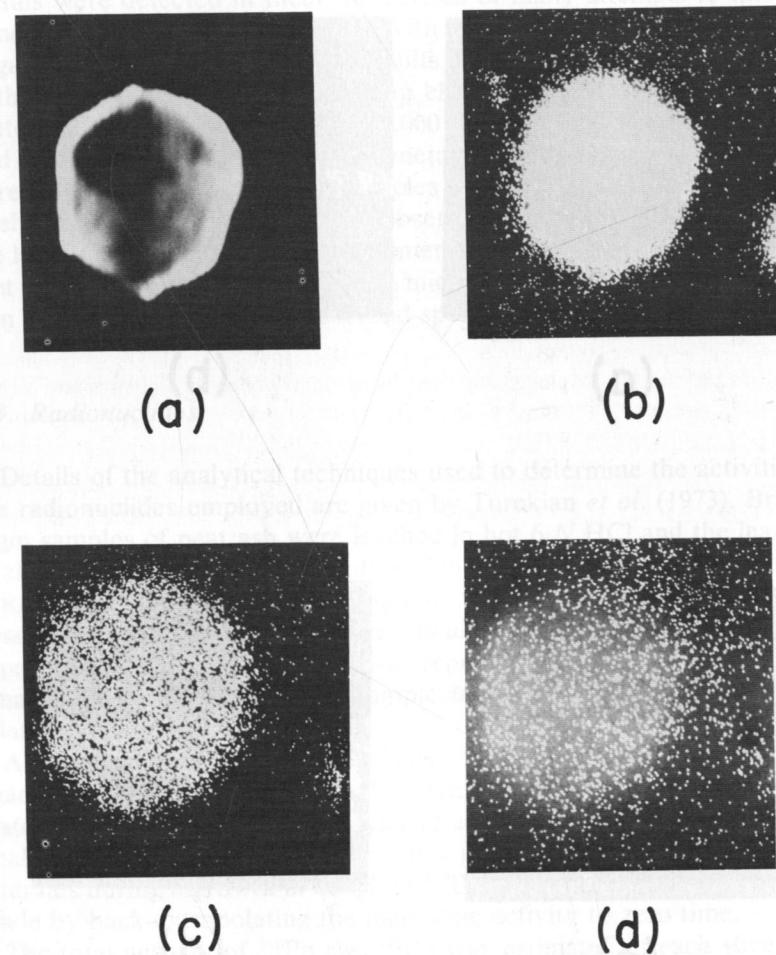


FIG. 7. A single pyrite framboid about 20- $\mu\text{m}$  diam. Specimen current image (a) shows the subround cross section of the framboid. X-Ray images of sulfur (b) and iron (c) are shown for the same specimen. The scan for copper (d), initiated before the phosphor completely faded (faint grey background), failed to detect a significant concentration within the framboid.

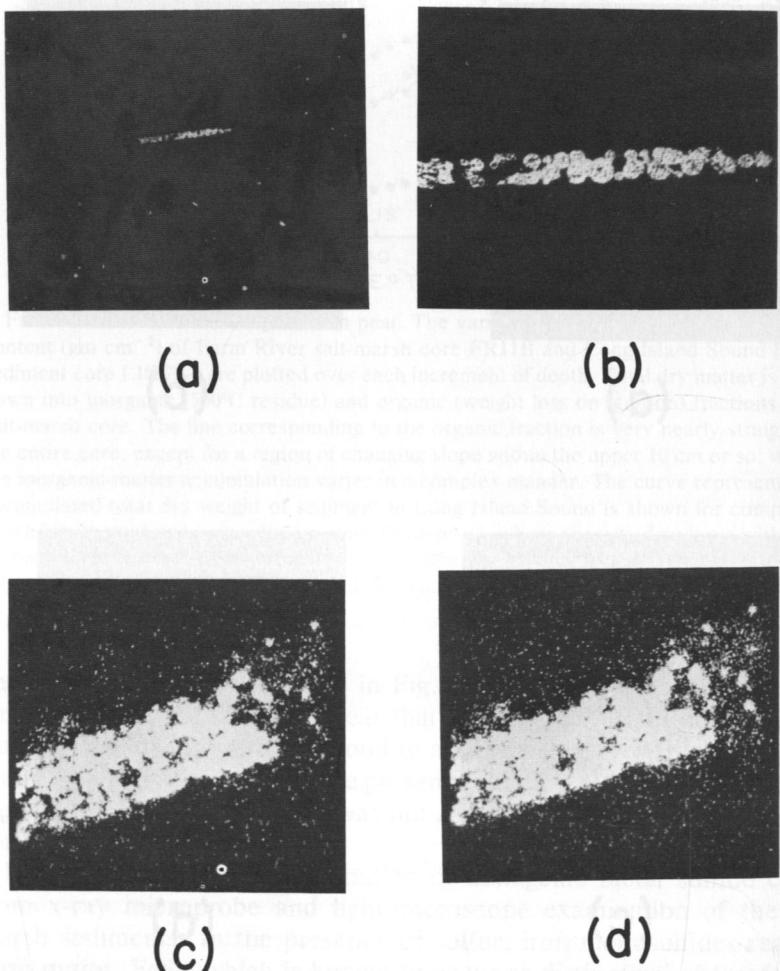


FIG. 8. Ordered distribution of iron sulfide. The photomicrograph (a) shows individual pyrite grains dispersed throughout the matrix and clustered inside an organic (?) envelope, 70 $\times$ . The graininess typical of pyrite framboids is evident at 320 $\times$  (b). X-Ray images of sulfur (c) and iron (d) portray the tendency of pyrite to conform to organic templates.

These pyrite framboids, considered possible sites for incorporation of other metals, were scanned under the microprobe for iron, sulfur, and trace elements, including Mn, Cu, Zn, and Pb. Iron and sulfur were identified as major components of the framboids, as expected, but no trace metals were detected in them. In fact, all of many attempts to find evidence of trace metals in association with mineral or organic phases proved negative, in agreement with the results of Sweeney and Kaplan (1973). Although the detection limits during element scans were probably not better than 100 or perhaps even 10,000 ppm, depending on the element and instrument conditions, if trace metals had been present in relatively pure phases in pyrite or other particles over a few microns in size, it is likely that they would have been observed. Since these trace elements are known to be present in bulk sediment, failure to detect them suggests that they are dispersed, perhaps as micron or submicron-size particles, thin surface coatings, or as absorbed species.

### 2.3. Radionuclides

Details of the analytical techniques used to determine the activities of the radionuclides employed are given by Turekian *et al.* (1973). Briefly, 5 gm samples of peat ash were leached in hot 6 N HCl and the leachate analyzed for  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$ . Radium-226 was determined by recovery of  $^{222}\text{Rn}$  gas produced by decay of parent  $^{226}\text{Ra}$  in solution within a closed vessel for at least ten days, followed by alpha scintillation counting of the separated radon. The procedure was repeated at least twice. Blanks, estimated by extraction without sample in the recycle loop, were small relative to sample activity.

After completing the  $^{226}\text{Ra}$  analysis,  $^{210}\text{Pb}$  was separated by ion exchange in the presence of stable Pb carrier, then precipitated as the chromate, mounted, covered with Mylar to absorb  $^{210}\text{Po}$  alpha particles, and finally determined by beta-counting in a proportional gas-flow counter at intervals during ingrowth of daughter  $^{210}\text{Bi}$ . Background corrections were made by back-extrapolating the ingrowing activity to zero time.

The total activity of  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  was estimated in each slice from core FR11B.  $^{210}\text{Pb}$  analyses were performed on contiguous, nominally 2-cm-thick slices from the upper two-thirds of the 1-m-long core.  $^{226}\text{Ra}$  was determined at discontinuous intervals throughout the upper half.

The total  $^{210}\text{Pb}$  activity comes from two sources:  $^{210}\text{Pb}$  in equilibrium with parent nuclides naturally present in sediment ("supported"), and  $^{210}\text{Pb}$  continually produced in the atmosphere from  $^{222}\text{Rn}$  and deposited on all exposed surfaces ("unsupported" or "excess"). Once isolated from

the atmosphere, the excess activity decays with its characteristic 22-yr half-life, which makes it possible to determine the age of a given layer of sediment. Excess activity is estimated by subtracting the supported activity from the total. The level of supported activity may be estimated from the activity of the parent nuclide if it is in secular equilibrium with its daughter, or it may be allowed to define itself by measuring the activity in sufficiently old sediment of similar composition.

The latter course was followed in this work since the  $^{210}\text{Pb}$  activity deep in the core reaches a level that is higher than  $^{226}\text{Ra}$ —its long-lived precursor nuclide. The empirical, or self-defined, supported  $^{210}\text{Pb}$  activity of 0.83 dpm/gm ash, used to calculate excess  $^{210}\text{Pb}$  higher in the core, was taken as the mean activity over the 34–40-cm level. Below 50 cm the peat was distinctly different in appearance, and the  $^{210}\text{Pb}$  values probably represent a different depositional regime.

The estimated excess activity  $A$  and associated uncertainty  $\sigma_A$  for each slice of core are listed in Table II. The error, associated with each count is estimated using the propagation-of-errors method (Bevington, 1969). Counting statistics account for most of the imprecision, although uncertainties associated with counter background and efficiency also contribute.

Measurements of the integrated standing crop of excess  $^{210}\text{Pb}$  were made on core FR11B and on a nearby upland-soil core. The upland core was taken from the center of a small (60-m diam.) "island" of till in the middle of the salt marsh. The integrated, standing crop in the upland-soil core was taken as the sum of excess  $^{210}\text{Pb}$  in each of three subsamples of soil plus the root activity in the surface horizon. The results are itemized in Table IV. All of the excess  $^{210}\text{Pb}$  present was in the upper 10 cm of soil, about equally divided between the 0–5-cm and the 5–10-cm layers. Over the interval 10–40 cm there was no measurable excess. Although the root fraction contained the greatest specific activity (dpm/gm) of  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$ , it contributed a relatively small fraction (13%) of the standing crop of excess  $^{210}\text{Pb}$  within that layer. The integrated standing crop in core FR11B was calculated from  $^{210}\text{Pb}$  activity in contiguous 2-cm-thick slices:

$$(2.1) \quad Q_i = \sum_{i+1}^n \rho_{i+1}(A_{i+1} - 0.83)(z_{i+1} - z_i) = 34.5 \text{ dpm/cm}^2$$

where  $i$  increments from 0;  $n$  is 16, the number of slices containing excess activity;  $\rho$  is the density (gm ash/cm<sup>3</sup>);  $A$  is the total  $^{210}\text{Pb}$  activity (dpm/gm ash);  $z$  is the depth (cm); and 0.83 dpm/gm ash is the supported  $^{210}\text{Pb}$  activity assumed throughout the core.

#### 2.4. Trace-Metals Analysis

Results of trace-metal analyses of cores FR11B and FR5A are presented as Tables II and III, respectively. Samples of ash material (500°C) were treated by exhaustive leach in hot 6 N HCl, with the weight of ash taken for analysis ranging from 1 to 0.1 gm, depending on the anticipated abundance of the elements. Typically, the sample was leached with 50–100 ml of hot, partially refluxing acid in a covered Pyrex beaker, for at least 12 hr, until the residue was bleached to a light color. Afterward, the slurry was evaporated to near dryness and the soluble material was taken up in 0.1 N HCl and passed through filters pre-washed in HCl. The filtrate was added directly to a volumetric flask and diluted with repeated washings of the insoluble residue with 0.1 N HCl. Solutions were analyzed by standard methods (Perkin-Elmer, 1964, 1968) using a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer equipped with a strip-chart recorder.

Filters containing insoluble residue were transferred to Teflon beakers and totally dissolved by treatment with concentrated HNO<sub>3</sub>, HF, and HClO<sub>4</sub> in the proportion 15:10:2. The mixture was refluxed for at least 24 hr, then allowed to evaporate until dense white fumes evolved. The nearly dry material was finally taken up in hot 6 N HCl, filtered, and diluted to the mark.

The small amount of residue sometimes found despite this treatment consisted of two components: a light-colored crystalline material, identified by x-ray techniques as K<sub>2</sub>NaAlF<sub>6</sub>, and a dark-colored, graphitic material. Neither residue was processed further.

To detect systematic error in the peat analyses, vegetation and rock reference samples of known composition were analyzed (McCaffrey, 1977). National Bureau of Standards Standard Reference Material 1971 (orchard leaves) was dried at 85°C, then wet ashed using HNO<sub>3</sub>–HClO<sub>4</sub> and also dry ashed at 500°C. Both the orchard leaves and the United States Geological Survey (USGS) silicate standards G-2 and BCR-1 were also treated by the usual 6 N HCl leach, as well as by total dissolution. The results of these analyses show that both wet- and dry-ashing techniques yielded accurate, reproducible results for organic matter; thus metals associated with the organic portion of the peat are probably quantitatively leached by the procedures employed. The results for the standard silicates, if these materials are assumed to represent the inorganic matter deposited in the marsh, indicate that not all of the trace metals are efficiently leached by present methods. Acid leach of granitic silicate (G-2) was accurate for Fe, Mn, Cu, and Zn, but underestimated Pb by about 50%. Total dissolution results were satisfactory for all metals except Pb,

TABLE II. TRACE-METAL, RADIOCHEMICAL, AND BULK-DENSITY DATA FOR FARM RIVER SALT-MARSH CORER  
FRIIB (41°16'00"N; 72°51'06"W)<sup>a</sup>

| Slice | Sample depth<br>(cm) | Density                  |                          | <sup>210</sup> Pb<br>(dpm/gm) | <sup>226</sup> Ra<br>(dpm/gm) | Fe<br>(mg/gm) | Mn<br>( $\mu\text{g/gm}$ ) | Cu<br>( $\mu\text{g/gm}$ ) | Zn<br>( $\mu\text{g/gm}$ ) | Pb<br>( $\mu\text{g/gm}$ ) |
|-------|----------------------|--------------------------|--------------------------|-------------------------------|-------------------------------|---------------|----------------------------|----------------------------|----------------------------|----------------------------|
|       |                      | (gm/cm <sup>3</sup> dry) | (gm/cm <sup>3</sup> ash) |                               |                               |               |                            |                            |                            |                            |
| 1     | 0-2.3                | 0.299                    | 0.217                    | 14.38 ± 0.10                  | 1.0                           | 45.4          | 896                        | 124                        | 213                        | 79                         |
| 2     | 2.3-4.7              | 0.300                    | 0.219                    | 13.88 ± 0.11                  | —                             | 42.1          | 453                        | 130                        | 222                        | 148                        |
| 3     | 4.7-6.8              | 0.249                    | 0.166                    | 12.40 ± 0.11                  | 0.23                          | 43.3          | 374                        | 126                        | 226                        | 101                        |
| 4     | 6.8-8.6              | 0.243                    | 0.160                    | 9.16 ± 0.07                   | 0.27                          | 44.4          | 345                        | 147                        | 192                        | 66                         |
| 5     | 8.6-10.5             | 0.218                    | 0.150                    | 10.58 ± 0.06                  | —                             | 40.9          | 337                        | 137                        | 233                        | 132                        |
| 6     | 10.5-12.3            | 0.183                    | 0.118                    | 8.85 ± 0.07                   | —                             | 44.0          | 345                        | 149                        | 234                        | 146                        |
| 7     | 12.3-14.3            | 0.186                    | 0.135                    | 9.24 ± 0.06                   | 0.27                          | 39.1          | 323                        | 128                        | 195                        | 217                        |
| 8     | 14.3-16.2            | 0.211                    | 0.161                    | 7.01 ± 0.05                   | —                             | 36.6          | 301                        | 96                         | 193                        | 50                         |
| 9     | 16.2-18.1            | 0.194                    | 0.150                    | 5.00 ± 0.06                   | 0.20                          | 34.6          | 303                        | 102                        | 191                        | 189                        |
| 10    | 18.1-20.0            | 0.226                    | 0.181                    | 2.78 ± 0.05                   | —                             | 35.7          | 310                        | 73                         | 130                        | 67                         |
| 11    | 20.0-21.9            | 0.191                    | 0.137                    | 4.89 ± 0.06                   | —                             | 39.4          | 300                        | 56                         | 165                        | 81                         |
| 12    | 21.9-23.8            | 0.203                    | 0.146                    | 4.04 ± 0.09                   | 0.29                          | 41.2          | 315                        | 44                         | 162                        | 62                         |
| 13    | 23.8-25.9            | 0.224                    | 0.171                    | 3.01 ± 0.07                   | —                             | 38.1          | 322                        | 33                         | 99                         | 50                         |
| 14    | 25.9-27.9            | 0.239                    | 0.184                    | 2.25 ± 0.07                   | 0.22                          | 36.4          | 349                        | 20                         | 68                         | 33                         |
| 15    | 27.9-29.9            | 0.282                    | 0.225                    | 1.79 ± 0.10                   | —                             | 33.8          | 324                        | 15                         | 71                         | 28                         |
| 16    | 29.9-32.0            | 0.277                    | 0.208                    | 1.31 ± 0.08                   | —                             | 32.7          | 329                        | 15                         | 55                         | 12                         |
| 17    | 32.0-33.9            | 0.269                    | 0.208                    | 0.99 ± 0.08                   | —                             | —             | 322                        | 13                         | 52                         | 22                         |
| 18    | 33.9-36.0            | 0.263                    | 0.203                    | 0.82 ± 0.08                   | 0.11                          | —             | 312                        | 11                         | 63                         | 18                         |
| 19    | 36.0-37.9            | 0.261                    | 0.195                    | 0.75 ± 0.07                   | —                             | —             | 268                        | 9                          | 54                         | 17                         |
| 20    | 37.9-39.9            | 0.267                    | 0.205                    | 0.67 ± 0.06                   | 0.19                          | —             | 246                        | 12                         | 46                         | 17                         |
| 21    | 39.9-41.9            | 0.238                    | 0.177                    | 0.79 ± 0.07                   | —                             | —             | 237                        | 13                         | 49                         | 20                         |
| 22    | 41.9-44.1            | 0.177                    | 0.107                    | 0.99 ± 0.08                   | —                             | —             | 229                        | 15                         | 41                         | 22                         |
| 23    | 44.1-46.4            | 0.175                    | 0.136                    | 0.71 ± 0.07                   | —                             | —             | 185                        | 13                         | 33                         | 17                         |
| 24    | 46.4-48.4            | 0.185                    | 0.127                    | 0.85 ± 0.06                   | 0.24                          | —             | 261                        | 13                         | 50                         | 17                         |
| 25    | 48.4-50.3            | 0.216                    | 0.153                    | 1.07 ± 0.06                   | —                             | —             | 245                        | 10                         | 58                         | 14                         |
| 26    | 50.3-52.4            | 0.232                    | 0.161                    | 0.59 ± 0.05                   | —                             | —             | 274                        | 12                         | 53                         | —                          |

|    |            |       |       |             |   |   |     |    |    |    |
|----|------------|-------|-------|-------------|---|---|-----|----|----|----|
| 27 | 52.4-54.4  | 0.156 | 0.119 | 0.62 ± 0.07 | — | — | 245 | 11 | 47 | 17 |
| 28 | 54.4-56.6  | 0.155 | 0.095 | 0.38 ± 0.05 | — | — | 200 | 10 | 36 | 8  |
| 29 | 56.6-58.4  | 0.141 | 0.085 | 0.75 ± 0.07 | — | — | 187 | 6  | 38 | 11 |
| 30 | 58.4-60.2  | 0.167 | 0.104 | 0.48 ± 0.08 | — | — | 182 | 10 | 33 | 26 |
| 31 | 60.2-62.2  | 0.126 | 0.072 | 0.16 ± 0.06 | — | — | 158 | 9  | 29 | 13 |
| 32 | 62.2-64.2  | 0.101 | 0.052 | 0.28 ± 0.09 | — | — | 120 | 10 | 19 | 8  |
| 33 | 64.2-66.3  | 0.110 | 0.062 | 0.47 ± 0.07 | — | — | 119 | 8  | 20 | 23 |
| 34 | 66.3-68.3  | 0.114 | 0.063 | —           | — | — | 139 | 13 | 42 | 18 |
| 35 | 68.3-70.2  | 0.107 | 0.061 | —           | — | — | 130 | 9  | 31 | 9  |
| 36 | 70.2-72.3  | 0.138 | 0.080 | —           | — | — | 169 | 12 | 36 | 17 |
| 37 | 72.3-74.3  | 0.157 | 0.099 | —           | — | — | 204 | 12 | 37 | 16 |
| 38 | 74.3-76.4  | 0.155 | 0.095 | —           | — | — | 209 | 15 | 42 | 28 |
| 39 | 76.4-78.3  | 0.164 | 0.102 | —           | — | — | 211 | 7  | 47 | 5  |
| 40 | 78.3-80.4  | 0.154 | 0.095 | —           | — | — | 260 | 16 | 51 | 14 |
| 41 | 80.4-82.5  | 0.184 | 0.126 | —           | — | — | 274 | 17 | 61 | 23 |
| 42 | 82.5-84.6  | 0.159 | 0.105 | —           | — | — | 290 | 17 | 60 | 23 |
| 43 | 84.6-86.4  | 0.137 | 0.082 | —           | — | — | 224 | 16 | 54 | —  |
| 44 | 86.4-88.7  | 0.146 | 0.089 | —           | — | — | 206 | 17 | 48 | 12 |
| 45 | 88.7-90.7  | 0.148 | 0.098 | —           | — | — | 147 | 15 | 40 | 15 |
| 46 | 90.7-92.5  | 0.168 | 0.116 | —           | — | — | 224 | 14 | 49 | 10 |
| 47 | 92.5-94.3  | 0.165 | 0.112 | —           | — | — | 253 | 18 | 55 | —  |
| 48 | 94.3-96.4  | 0.183 | 0.129 | —           | — | — | 303 | 23 | 55 | 27 |
| 49 | 96.4-98.3  | 0.200 | 0.138 | —           | — | — | 274 | 13 | 55 | 5  |
| 50 | 98.3-100.0 | 0.227 | 0.167 | —           | — | — | 257 | 13 | 55 | 5  |

<sup>a</sup> Depths are corrected for saw kerf. Densities refer to bulk or whole sediment. Concentrations and activities are based on a hot 6 N HCl leach of ash material. All weights refer to 500°C ash material except for dry density (third column), which refers to 110°C dry material. The wet:dry:ash weight ratios for the 100-cm length of core are 7.49:1.44:1, respectively. Precision ( $\sigma$ ) of sample activity, based on repeated counts during ingrowth, is derived from a propagation of errors analysis as discussed in the text.

TABLE III. LEACHABLE METAL CONCENTRATIONS, CORE FR5A<sup>a</sup>

| Slice | Sample depth<br>(cm) | Fe<br>(mg gm <sup>-1</sup> ) | Mn<br>( $\mu\text{g gm}^{-1}$ ) | Cu<br>( $\mu\text{g gm}^{-1}$ ) | Zn<br>( $\mu\text{g gm}^{-1}$ ) | Pb<br>( $\mu\text{g gm}^{-1}$ ) |
|-------|----------------------|------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 1     | 0-2.0                | 52.9                         | 1200                            | 114                             | 168                             | 152                             |
| 2     | 2.0-4.0              | 44.9                         | 497                             | 125                             | 188                             | 156                             |
| 3     | 4.0-6.1              | 45.1                         | 394                             | 135                             | 153                             | 143                             |
| 4     | 6.1-8.1              | 40.4                         | 340                             | 144                             | 154                             | 142                             |
| 5     | 8.1-10.2             | 51.0                         | 341                             | 230                             | 166                             | 170                             |
| 6     | 10.2-12.2            | 72.1                         | 378                             | 192                             | 395                             | 249                             |
| 7     | 12.2-14.3            | 63.9                         | 355                             | 150                             | 186                             | 145                             |
| 8     | 14.3-16.2            | 38.6                         | 322                             | 126                             | 144                             | 91                              |
| 9     | 16.2-18.3            | 41.3                         | 331                             | 118                             | 182                             | 114                             |
| 10    | 18.3-20.2            | 39.6                         | 330                             | 78                              | 165                             | 81                              |
| 11    | 20.2-22.2            | 54.2                         | 329                             | 84                              | 163                             | 84                              |
| 12    | 22.2-24.3            | 49.2                         | 329                             | 32                              | 153                             | 69                              |
| 13    | 24.3-26.2            | —                            | —                               | 39                              | 136                             | 133                             |
| 14    | 26.2-28.3            | —                            | —                               | —                               | 83                              | —                               |
| 15    | 28.3-30.4            | —                            | —                               | 13                              | 83                              | 59                              |
| 16    | 30.4-32.1            | 34.5                         | 338                             | 10                              | 66                              | 40                              |
| 17    | 32.1-34.1            | 35.1                         | 355                             | 6                               | 59                              | 29                              |
| 18    | 34.1-36.1            | 28.7                         | 285                             | 7                               | 54                              | 26                              |
| 19    | 36.1-38.0            | 29.9                         | 222                             | 6                               | 58                              | 24                              |
| 21    | 40.0-41.9            | 29.1                         | 232                             | 8                               | 48                              | 19                              |
| 22    | 41.9-43.9            | 12.9                         | 180                             | 8                               | 44                              | 19                              |
| 23    | 43.9-46.0            | —                            | —                               | 6                               | 29                              | 14                              |
| 24    | 46.0-48.0            | 16.8                         | 256                             | 6                               | 46                              | 14                              |
| 30    | 58.1-60.3            | 11.6                         | 168                             | 9                               | 60                              | 19                              |
| 35    | 67.9-69.8            | 17.2                         | 143                             | 8                               | 29                              | 16                              |
| 40    | 77.8-79.7            | 34.5                         | 272                             | 7                               | 61                              | 12                              |
| 45    | 87.7-89.9            | 37.6                         | 193                             | —                               | —                               | —                               |

<sup>a</sup> Approximately 2-gm samples of 500°C ash were leached for 6 hours in hot 6*N* HCl with occasional stirring and allowed to evaporate to near dryness before taking up in 0.1 *N* HCl. Concentrations are reported on an ash-weight basis. Sample depths were corrected for saw kerf.

which was overestimated by about 37%. The basalt standard (BCR-1) was generally less efficiently leached. Total dissolution gave more accurate results, but tended toward overestimation of trace metals, again, especially Pb. Leaching and total dissolution experiments carried out on ash samples from the upper (metal-rich) and lower (presumably preindustrial) sections of core FR11B show that all metals in the upper portion (except Mn) are efficiently leached ( $\geq 87\%$ ), but at depth the leaching of Zn, Pb, and perhaps Cu appears to be only 70-80% efficient.

To estimate the excess concentration  $C_{xs}$  of Cu, Zn, and Pb in the metal-rich upper third of the core, relative to the estimated background values

at depth, the average metal concentration  $C_b$  between 30 and 50 cm was subtracted from the total concentration  $C$  at any depth in the core;

$$(2.2) \quad C_{xs} = C - C_b$$

Excess metal concentrations calculated in this way are presented in Table V.

With the exception of FR5A, cores destined for pore water analysis were squeezed at room temperature with a minimum of delay (normally within 24 hours) and minimum exposure to the atmosphere. Since core tops are normally exposed to the atmosphere, only subsurface peat is likely to be sensitive to oxidation. To minimize this possibility, a core of larger cross section than necessary was transported in a plastic bag to the laboratory for slicing and squeezing. Just before squeezing, an outer rind of a few centimeters was trimmed away, and each slice was placed in a sealed plastic bag and excess air was expelled. Pore water was obtained by squeezing in a press (Manheim, 1966) while still confined in the plastic bag. Initial effluent was used to flush the apparatus; later portions were collected in a plastic syringe, filtered (Millipore HA 0.45  $\mu\text{m}$ ) directly into a plastic vial, then analyzed immediately or acidified and stored cold. Aliquots of the filtered pore water were taken for analysis of pH, chloride, and sulfate. Chloride was determined by titration with  $\text{AgNO}_3$  to a  $\text{K}_2\text{CrO}_4$  end point; sulfate was determined gravimetrically by precipitation with  $\text{BaCl}_2$  (Kolthoff and Sandell, 1956). Trace metals were determined by flame atomic absorption spectrophotometry.

TABLE IV. STANDING CROP OF EXCESS  $^{210}\text{Pb}$  IN FARM RIVER UPLAND SOIL<sup>a</sup>

| Depth<br>(cm) | Soil fraction               | $^{210}\text{Pb}$<br>(dpm/gm ash) | $^{226}\text{Ra}$<br>(dpm/gm ash) | Sample weight<br>(gm dry) | Organic matter<br>(% dry wt.) | Standing crop excess<br>$^{210}\text{Pb}$<br>(dpm/cm <sup>2</sup> ) |
|---------------|-----------------------------|-----------------------------------|-----------------------------------|---------------------------|-------------------------------|---------------------------------------------------------------------|
| 0-5           | Roots,<br>Sieved (<1<br>mm) | 53.4 $\pm$ 0.3                    | 2.13 $\pm$ 0.09                   | 36                        | 82.6                          | 1.5                                                                 |
|               |                             | 7.9 $\pm$ 0.1                     | 0.81 $\pm$ 0.02                   | 611                       | 14.5                          | 17.0                                                                |
|               |                             |                                   |                                   |                           | Subtotal:                     | 18.5                                                                |
| 5-10          |                             | 2.2 $\pm$ 0.1                     | 0.81 $\pm$ 0.04                   | 1345                      | 4.0                           | 7.7                                                                 |
| 10-40         |                             | 0.8 $\pm$ 0.1                     | 1.02 $\pm$ 0.02                   | 8240                      | 2.0                           | 0                                                                   |
|               |                             |                                   |                                   |                           | Total                         | 26.2                                                                |

<sup>a</sup> Soil and root samples were combusted at 475°C then leached in hot 6*N* HCl.  $^{226}\text{Ra}$  activity is obtained by measurement of the activity of daughter  $^{222}\text{Rn}$ , which is assumed to be in secular equilibrium.  $^{210}\text{Pb}$  flux = Total standing crop/Mean life = 0.82 dpm  $\text{cm}^{-2}$   $\text{yr}^{-1}$ .

TABLE V. HISTORICAL INCREASE IN THE FLUX OF TRACE METALS TO A CONNECTICUT SALT MARSH

| Slice | Depth $z$<br>(cm) | Excess conc. $C_{xs}$<br>( $\mu\text{g gm}^{-1}$ ash) |     |     | Excess flux $M \pm \sigma$<br>( $\mu\text{g cm}^{-2} \text{yr}^{-1}$ ) |                |             |
|-------|-------------------|-------------------------------------------------------|-----|-----|------------------------------------------------------------------------|----------------|-------------|
|       |                   | Cu                                                    | Zn  | Pb  | Cu                                                                     | Zn             | Pb          |
| 1     | 0-2.3             | 112                                                   | 163 | 61  | $8.0 \pm 2.0$                                                          | $11.7 \pm 2.7$ | $4 \pm 1$   |
| 2     | 2.3-4.7           | 118                                                   | 172 | 130 | $6.9 \pm 1.5$                                                          | $10.0 \pm 2.1$ | $8 \pm 2$   |
| 3     | 4.7-6.8           | 114                                                   | 176 | 83  | $5.6 \pm 1.7$                                                          | $8.6 \pm 2.5$  | $4 \pm 1$   |
| 4     | 6.8-8.8           | 135                                                   | 142 | 48  | $7.9 \pm 3.2$                                                          | $8.3 \pm 3.1$  | $3 \pm 1$   |
| 5     | 8.8-10.5          | 125                                                   | 183 | 114 | $5.2 \pm 1.6$                                                          | $7.7 \pm 2.3$  | $5 \pm 1$   |
| 6     | 10.5-12.3         | 137                                                   | 184 | 128 | $5.7 \pm 2.4$                                                          | $7.7 \pm 3.0$  | $5 \pm 2$   |
| 7     | 12.3-16.2         | 116                                                   | 145 | 199 | $3.8 \pm 1.0$                                                          | $4.7 \pm 1.2$  | $6 \pm 2$   |
| 8     | 16.2-18.1         | 84                                                    | 143 | 32  | $2.8 \pm 0.8$                                                          | $4.8 \pm 1.3$  | $1 \pm 0$   |
| 9     | 18.1-20.0         | 90                                                    | 141 | 171 | $3.5 \pm 1.3$                                                          | $5.5 \pm 1.9$  | $7 \pm 3$   |
| 10    | 20.0-21.9         | 61                                                    | 80  | 49  | $4.0 \pm 0.8$                                                          | $5.3 \pm 1.8$  | $3 \pm 1$   |
| 11    | 21.9-23.9         | 44                                                    | 115 | 63  | $1.1 \pm 0.3$                                                          | $3.0 \pm 1.0$  | $2 \pm 1$   |
| 12    | 23.9-25.9         | 32                                                    | 112 | 44  | $0.5 \pm 0.2$                                                          | $1.7 \pm 0.7$  | $1 \pm 0.3$ |
| 13    | 25.9-27.9         | 21                                                    | 49  | 32  | $0.8 \pm 0.1$                                                          | $1.9 \pm 0.3$  | $1 \pm 0.2$ |
| 14    | 27.9-29.9         | 8                                                     | 18  | 15  | $0.2 \pm 0.0$                                                          | $0.4 \pm 0.0$  | $0 \pm 0.0$ |
| 15    | 29.9-32.0         | 3                                                     | 21  | 10  | $0.0 \pm 0.0$                                                          | $0.3 \pm 0.0$  | $0 \pm 0.0$ |
| 16    | 32.0-33.9         | 3                                                     | 5   | —   | $0.0 \pm 0.0$                                                          | $0.0 \pm 0.0$  | $0 \pm 0.0$ |

<sup>a</sup> Excess stable metal concentrations are total concentrations less natural background, which is taken as the mean concentration ( $\pm 1\sigma$ ) within the 30-50-cm-depth interval and is  $12 \pm 2$ ,  $50 \pm 9$ , and  $18 \pm 3 \mu\text{g gm}^{-1}$  ash for Cu, Zn, and Pb, respectively. Precision of the excess concentrations is taken to be  $\pm 10\%$ .

Analyses of trace metal and sulfate in pore water provide evidence of diagenetic change in salt-marsh sediment. Rapidly processed cores from the Indian Neck and Farm River sites showed normalized  $\text{SO}_4/\text{Cl}$  ratios of greater than 1 at certain depths (Table VI). The cores also contained measurable concentrations of dissolved Mn and, at the Farm River site, Fe. The high Mn concentrations seen in Figs. 9 and 10 coincide with the maximum  $\text{SO}_4/\text{Cl}$  ratio. Other metals were not detected, with the possible exception of trace amounts of Zn in one Indian Neck core.

Very high sulfate concentrations and low pH values spontaneously developed in cores stored in air for several weeks (Table VII). Sulfate concentration more than double that of seawater and pH values below 3 were measured at certain depths. Trace metals were also found at very high concentrations at the same depths, but only in cores exposed to the atmosphere (Table VIII). This result appears to be analogous to the phenomenon of acid-mine drainage, where acidic, sulfate-rich waters develop in response to oxidation of pyrite (Stumm and Morgan, 1970). The si-

multaneous appearance of high-metal and high-sulfate concentrations when these reduced sediments are exposed to oxygen is most simply explained as oxidation of metals present in the sediment in the form of sulfides.

### 3. DISCUSSION

#### 3.1. $^{210}\text{Pb}$ Dating of the Deposit and Evaluation

The flux of  $^{210}\text{Pb}$  from the atmosphere to the surface and its subsequent decay during burial can, under suitable conditions, be used to establish an age-depth relationship in sediments.  $^{210}\text{Pb}$  has been used to determine accumulation rates of snowfields (Goldberg, 1963; Crozaz *et al.*, 1964), glaciers (Windom, 1969), lake sediments (Krishnaswami *et al.*, 1971; Bru-

TABLE VI. RATIO  $(\text{SO}_4/\text{Cl})_{\text{pore water}} / (\text{SO}_4/\text{Cl})_{\text{seawater}}$  VERSUS DEPTH<sup>a</sup>

| Depth<br>(cm) | FR5A <sup>b</sup> | FR13  | IN5  | IN6  | FR14C | FR14D |
|---------------|-------------------|-------|------|------|-------|-------|
| 0-2           | —                 | 0.795 | 1.48 | 2.43 | —     | 0.87  |
| 2-4           | —                 | 0.772 | 1.22 | 2.16 | —     | 0.69  |
| 4-6           | 4.14              | 0.734 | 0.96 | 1.41 | 0.90  | —     |
| 6-8           | 4.02              | 0.728 | 0.85 | 1.01 | 0.78  | 1.11  |
| 8-10          | 4.84              | 0.782 | 0.81 | 0.89 | 0.76  | 1.34  |
| 10-12         | 4.70              | 0.767 | 0.80 | 0.84 | 0.72  | 1.22  |
| 12-14         | 4.29              | 0.752 | 0.74 | 0.89 | 0.68  | 0.80  |
| 14-16         | 3.12              | 0.757 | 0.70 | 0.86 | 0.56  | 0.71  |
| 16-18         | 2.75              | 0.749 | 0.67 | 0.82 | 0.70  | 0.76  |
| 18-20         | 2.56              | —     | —    | —    | 0.66  | 0.77  |
| 20-22         | 2.54              | 0.668 | —    | —    | 0.68  | 0.77  |
| 22-24         | —                 | 0.701 | —    | —    | 0.67  | 0.69  |
| 24-26         | 2.37              | 0.688 | —    | —    | —     | 0.74  |
| 26-28         | 1.99              | 0.681 | —    | —    | —     | —     |
| 28-30         | —                 | 0.609 | —    | —    | —     | 0.67  |
| 32-34         | —                 | —     | —    | —    | —     | —     |
| 34-36         | 1.52              | —     | —    | —    | —     | —     |
| 46-48         | 1.09              | —     | —    | —    | —     | —     |
| 66-68         | 0.96              | —     | —    | —    | —     | —     |
| 84-86         | 1.20              | —     | —    | —    | —     | —     |
| 88-90         | 1.21              | —     | —    | —    | —     | —     |

<sup>a</sup>  $(\text{SO}_4/\text{Cl})$  designates the molal concentration ratio of sulfate to chloride. In seawater this ratio is 0.0516.

<sup>b</sup> Core FR5A stored several weeks in air, all others processed rapidly.

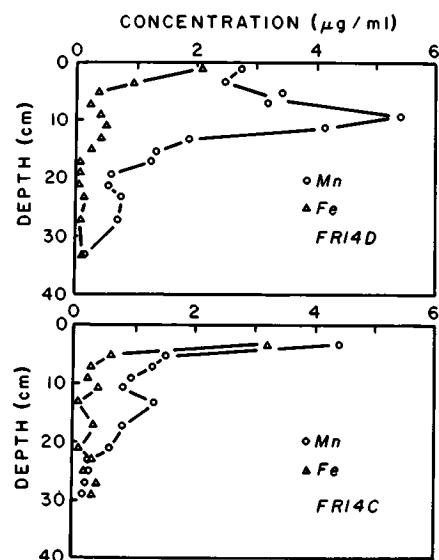


FIG. 9. Variation in dissolved manganese and iron with depth in cores FR14C and FR14D. Core FR14D was taken from a *S. patens* tussock and core FR14C was taken from an adjacent mud surface some 10-cm lower in elevation.

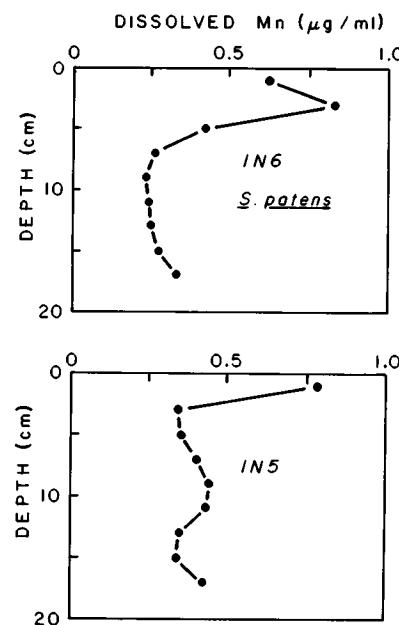


FIG. 10. Variation in dissolved manganese with depth in cores IN5 and IN6. Core IN6 was taken from a *S. patens* plateau and IN5 from the lower adjacent surface.

TABLE VII. PORE WATER ANALYSIS OF STORED-CORE FR5A

| Depth<br>(cm) | $\text{SO}_4^{2-}$<br>(mM) | $\text{Cl}^-$<br>(M) | pH   | Trace metals ( $\mu\text{g}/\text{ml}$ ) |     |      |      |    |
|---------------|----------------------------|----------------------|------|------------------------------------------|-----|------|------|----|
|               |                            |                      |      | Fe                                       | Mn  | Cu   | Zn   | Pb |
| 0-2           | —                          | 0.345                | 6.67 | 1                                        | 1.8 | 0.4  | 2.1  | —  |
| 2-4           | —                          | 0.272                | 3.98 | 5                                        | 2.6 | 0.5  | 1.4  | <1 |
| 4-6           | 54.0                       | 0.253                | 3.24 | 9                                        | 4.4 | 1.4  | 8.2  | 2  |
| 6-8           | 53.5                       | 0.258                | 3.00 | 23                                       | 7.7 | 3.1  | 16.8 | 3  |
| 8-10          | 66.0                       | 0.264                | 2.90 | 47                                       | 6.0 | 6.5  | 22.1 | 5  |
| 10-12         | 64.7                       | 0.267                | 2.85 | 112                                      | 7.1 | 6.9  | 62.6 | 10 |
| 12-14         | 60.4                       | 0.273                | 2.92 | 97                                       | 6.5 | 4.0  | 30.1 | 4  |
| 14-16         | 47.0                       | 0.292                | 3.55 | 6                                        | 5.5 | 0.9  | 16.3 | 1  |
| 16-18         | 42.2                       | 0.297                | —    | 1                                        | 4.7 | 0.2  | 17.3 | <1 |
| 18-20         | 38.9                       | 0.294                | 4.00 | 1                                        | 3.7 | <0.1 | 7.4  | <1 |
| 20-22         | 40.0                       | 0.305                | 3.71 | —                                        | 3.5 | <0.1 | 2.7  | <1 |
| 22-24         | 40.2                       | —                    | 3.83 | 2                                        | 4.0 | <0.1 | 6.4  | <1 |
| 24-26         | 38.6                       | 0.315                | 4.01 | <1                                       | 4.2 | <0.1 | 3.1  | <1 |
| 26-28         | 32.8                       | 0.319                | 4.40 | <1                                       | 1.9 | —    | 0.6  | —  |
| 28-30         | 29.2                       | —                    | —    | <1                                       | 0.5 | —    | 0.2  | —  |
| 30-32         | —                          | —                    | 4.75 | —                                        | 0.5 | —    | <0.1 | —  |
| 32-34         | —                          | —                    | —    | —                                        | 0.4 | —    | 1.0  | —  |
| 34-36         | 26.6                       | 0.340                | 5.80 | —                                        | 0.3 | —    | <0.1 | <1 |
| 36-38         | —                          | —                    | 6.53 | <1                                       | 0.2 | <0.1 | <0.1 | <1 |
| 38-40         | —                          | —                    | 6.61 | —                                        | 0.2 | —    | —    | —  |
| 40-42         | —                          | —                    | 6.90 | —                                        | 0.2 | —    | —    | —  |
| 42-44         | —                          | —                    | —    | —                                        | 0.3 | —    | <0.1 | <1 |
| 44-46         | —                          | —                    | —    | —                                        | 0.2 | —    | —    | —  |
| 46-48         | 20.2                       | 0.359                | —    | —                                        | 0.1 | <0.1 | —    | —  |
| 48-50         | —                          | —                    | 6.93 | —                                        | 0.2 | —    | —    | —  |
| 50-52         | —                          | —                    | —    | —                                        | 0.2 | —    | —    | —  |
| 52-54         | —                          | —                    | 6.80 | <1                                       | 0.2 | —    | —    | <1 |
| 54-56         | —                          | —                    | —    | —                                        | 0.3 | —    | <0.1 | <1 |
| 56-58         | —                          | —                    | —    | —                                        | 0.4 | —    | —    | —  |
| 58-60         | 19.4                       | —                    | 7.19 | —                                        | 0.3 | —    | —    | —  |
| 60-62         | —                          | —                    | —    | —                                        | 0.4 | —    | —    | —  |
| 62-64         | —                          | —                    | —    | —                                        | 0.7 | <0.1 | <0.1 | —  |
| 64-66         | —                          | —                    | 6.90 | <1                                       | 0.8 | —    | —    | —  |
| 66-68         | 19.3                       | 0.386                | 7.17 | —                                        | 0.3 | —    | —    | —  |
| 68-70         | —                          | —                    | 6.80 | —                                        | 0.3 | —    | —    | —  |
| 70-72         | —                          | —                    | 7.10 | —                                        | 0.3 | <0.1 | —    | —  |
| 72-74         | 20.9                       | —                    | 7.06 | —                                        | 0.3 | —    | —    | —  |
| 74-76         | —                          | —                    | 6.63 | <1                                       | 0.5 | —    | —    | <1 |
| 76-78         | —                          | —                    | 6.08 | —                                        | 1.0 | —    | —    | <1 |
| 78-80         | —                          | —                    | 5.59 | —                                        | 1.5 | —    | <0.1 | —  |
| 80-82         | —                          | —                    | 5.77 | —                                        | 1.4 | —    | —    | —  |
| 82-84         | —                          | 0.407                | 6.00 | —                                        | 1.4 | —    | —    | —  |
| 84-86         | 25.2                       | —                    | —    | —                                        | 1.4 | —    | —    | —  |
| 86-88         | —                          | —                    | 5.19 | <1                                       | 0.8 | <0.1 | <0.1 | —  |
| 88-90         | 25.4                       | 0.408                | —    | —                                        | 0.7 | —    | —    | <1 |
| 90-91.5       | —                          | 0.441                | 5.98 | —                                        | 1.3 | —    | —    | —  |

TABLE VIII. CHANGES IN CONCENTRATION OF TRACE METALS AND pH IN PORE WATER OF CORES STORED IN AIR VERSUS THOSE PROCESSED RAPIDLY WITHOUT STORAGE

| Core | Treatment           | Trace metals ( $\mu\text{g}/\text{ml}$ ) |                      |                 |                 |                    |
|------|---------------------|------------------------------------------|----------------------|-----------------|-----------------|--------------------|
|      |                     | Fe                                       | Mn                   | Cu              | Zn              | Pb                 |
| IN4  | Stored <sup>a</sup> | 200                                      | 8.9                  | 14.9            | 66              | 6                  |
|      | Not stored          | —                                        | 0.3                  | nd <sup>c</sup> | tr <sup>d</sup> | nd                 |
| IN5  | Not stored          | —                                        | 0.3–0.8 <sup>b</sup> | nd              | nd              | 6.5–5 <sup>b</sup> |
| IN6  | Not stored          | —                                        | 0.2–0.6 <sup>b</sup> | nd              | nd              | 6.5–5 <sup>b</sup> |

<sup>a</sup> Stored at ca. 20°C for 7 weeks after squeezing.

<sup>b</sup> Range among subsamples.

<sup>c</sup> None detected.

<sup>d</sup> Trace.

land *et al.*, 1975; Robbins and Edginton, 1975; Brugam, 1976), and coastal marine sediments (Koide *et al.*, 1972, 1973; Krishnaswami *et al.*, 1973; Bruland *et al.*, 1974; Thomson *et al.*, 1975; Amentano and Woodwell, 1975; Goldberg *et al.*, 1977).

In many of these deposits, bioturbation, physical disruption, or compaction may occur. Autocompaction of certain deep-peat deposits has been reported (Kaye and Barghoorn, 1964). Bioturbation of sedimentary deposits, due to the activities of living animals or plants, can be a source of disturbance in either upland (Lutz, 1940; Lyford, 1963) or marine (Rhoads, 1967) environments, and appropriate care must be taken in interpreting results.

If the rate of accumulation of sediment and excess  $^{210}\text{Pb}$  have both been constant, as is often assumed, and the deposit is undisturbed, then the accumulation rate  $S$  can be estimated from the best-fit straight-line equation describing radioactive decay:

$$(3.1) \quad \ln A_z = \ln A_0 - (\lambda/S)z$$

where  $A_0$  and  $A_z$  are activities of excess  $^{210}\text{Pb}$  at depths 0 and  $z$ , respectively,  $\lambda$  is the decay constant, and  $S$  is the rate of accumulation of sediment ( $\text{cm}/\text{yr}$ ). The age  $t$  or time elapsed since a given horizon  $z$  occupied the surface is then simply  $z/S$ . By inspection of Fig. 11 it is evident that the data for the salt marsh do not exhibit such a linear decrease with depth. On the other hand, if the vertical growth of the salt marsh is indeed keeping pace with a long-term, varying rate of sea-level rise, then a simple linear decrease is not expected, rather, the age-depth relationship implicit in the observed distribution of excess  $^{210}\text{Pb}$  should agree with independent historical records of sea-level rise.

To test whether or not the salt marsh has accreted at a rate comparable

to the rate of rise of relative sea level requires a different approach, one that does not demand accretion rate to have been constant. The observed, complex distribution of excess  $^{210}\text{Pb}$  activity may be used to develop a chronology in a manner similar to that used by Sackett (1965) for dating ocean sediments. Although this method allows the accretion rate to vary, it does assume that the flux of excess  $^{210}\text{Pb}$  to the surface has been constant and that there has been no significant redistribution after deposition. In an accumulating deposit, the rate of storage of excess activity beneath a unit surface area,  $dQ/dt$ , is equal to the rate of deposition on the surface minus loss due to decay:

$$(3.2) \quad dQ/dt = F - \lambda Q$$

where  $Q$  is the standing crop ( $\text{dpm cm}^{-2}$ ),  $F$  is the flux to the surface ( $\text{dpm cm}^{-1} \text{yr}^{-1}$ ),  $\lambda$  is the decay constant ( $\text{yr}^{-1}$ ), and  $t$  is time ( $\text{yr}$ ). If  $F$  is constant and the core contains the entire standing crop of excess activity, then a steady state exists, i.e.,  $dQ/dt = 0$ , and the flux to the

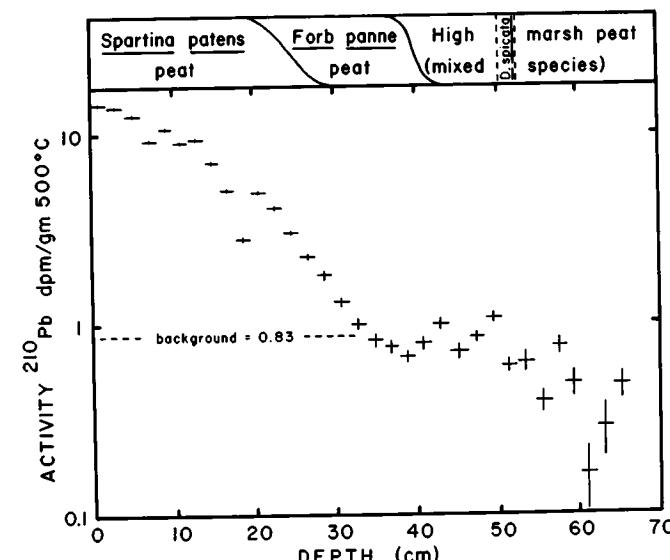


FIG. 11. The depth distribution of total activity of  $^{210}\text{Pb}$  in contiguous slices of peat from the Farm River salt marsh shows that the semilog plot is convex in the region about 34 cm. Below 34 cm to the top of the distinct *D. spicata* rhizome layer at 50 cm, the activity is low and approximately constant, averaging 0.83  $\text{dpm gm}^{-2}$ , which is taken as supported background. Below this layer, the supported  $^{210}\text{Pb}$  activity is irregularly lower. The dominant species of vegetation varies with depth as indicated, but all species found are characteristic of high marsh.

surface may be readily calculated from the equation

$$(3.3) \quad F = \lambda Q$$

As long as the steady state persists, the total standing crop beneath the surface at any time is the constant  $Q_0$ . Continued accumulation will bury the surface to some depth  $z$  in time  $t$ . If  $^{210}\text{Pb}$  is conserved except for decay, then the steady-state standing crop of excess activity  $Q_0$  will have decayed at a rate governed by the familiar decay law:

$$(3.4) \quad Q_i = Q_0 \exp(-\lambda t_i)$$

where  $Q_i$  is the standing crop remaining below depth  $z_i$ , the bottom of the  $i^{\text{th}}$  slice. When data is available in small depth increments, the following

TABLE IX.  $^{210}\text{Pb}$  CHRONOLOGY OF THE FARM RIVER SALT MARSH<sup>a</sup>

| Slice   | Depth $z$<br>(cm) | Standing crop of<br>excess $^{210}\text{Pb}$<br>$Q \pm \sigma$ (dpm/<br>cm $^2$ ) | Age<br>$t \pm \sigma$ (yr) |
|---------|-------------------|-----------------------------------------------------------------------------------|----------------------------|
| Surface | 0                 | 34.5 ± 1.0                                                                        | 0 (1972)                   |
| 1       | 2.3               | 27.7 ± 0.9                                                                        | 7.0 ± 1.4                  |
| 2       | 4.7               | 21.0 ± 0.8                                                                        | 16.0 ± 1.5                 |
| 3       | 6.8               | 16.8 ± 0.6                                                                        | 23.1 ± 1.6                 |
| 4       | 8.8               | 14.4 ± 0.6                                                                        | 28.0 ± 1.6                 |
| 5       | 10.5              | 11.7 ± 0.5                                                                        | 34.8 ± 1.6                 |
| 6       | 12.3              | 10.0 ± 0.4                                                                        | 39.9 ± 1.6                 |
| 7       | 14.3              | 7.7 ± 0.3                                                                         | 48.2 ± 1.6                 |
| 8       | 16.2              | 5.8 ± 0.3                                                                         | 57.3 ± 1.8                 |
| 9       | 18.1              | 4.6 ± 0.2                                                                         | 64.6 ± 2.0                 |
| 10      | 20.0              | 3.9 ± 0.2                                                                         | 69.8 ± 1.9                 |
| 11      | 21.9              | 2.9 ± 0.2                                                                         | 79.8 ± 2.2                 |
| 12      | 23.9              | 2.0 ± 0.1                                                                         | 97.7 ± 2.5                 |
| 13      | 25.9              | 1.2 ± 0.1                                                                         | 107 ± 3                    |
| 14      | 27.9              | 0.7 ± 0.1                                                                         | 125 ± 4                    |
| 15      | 29.9              | 0.3 ± 0.1                                                                         | 155 ± 7                    |
| 16      | 32.0              | 0.1 ± 0.0                                                                         | 203 ± 16                   |

<sup>a</sup> Depth is corrected for saw kerf and has a 1σ precision of ±0.05 cm. Total standing crop  $Q_0$  of excess  $^{210}\text{Pb}$  is the activity accumulated beneath the surface, corrected for self-defined background activity of 0.83 dpm gm $^{-3}$ . The flux of  $^{210}\text{Pb}$  to the surface ( $=\lambda Q_0$ ) is calculated to be  $1.07 \pm 0.03$  dpm cm $^{-2}$  yr $^{-1}$ .

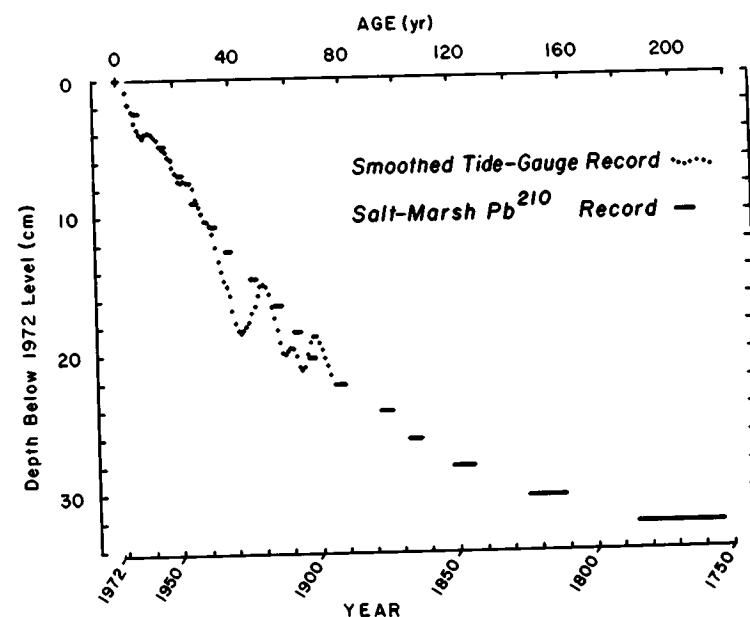


FIG. 12. Comparison of salt-marsh and tide-gauge records. The ages of salt-marsh peat calculated from the distribution of excess  $^{210}\text{Pb}$  are plotted as horizontal bars of length  $2\sigma$  centered at depth increments corresponding to the bottom of each slice. The record of annual mean sea level, based on the New York City tide gauge, was smoothed to remove most fluctuations having a period of about 5 yr or less (Hicks, 1973) and is shown as a dotted line. Smoothing caused truncation of the first 3 and last 3 yr of records, so the latest datum (1969) is indefinitely located relative to 1972 elevation. For the purpose of comparison, the curve has been located so that extrapolation from the 1969 datum along a line with the same slope as the relatively linear sea-level rise since 1940 (0.31 cm/yr, Hicks and Crosby, 1974) intersects the surface at the end of 1972. In actuality, the surface of the salt marsh is elevated about 1 m above mean sea level.

approximation may be used:

$$(3.5) \quad Q_i = \sum_{i+1}^n \rho_{i+1} A_{i+1} (z_{i+1} - z_i)$$

where  $n$  is the number of increments containing excess activity,  $\rho$  is the bulk density of sediment (gm cm $^{-3}$ ), and  $A$  is the specific activity of excess  $^{210}\text{Pb}$  (dpm gm $^{-1}$ ).

Solving the decay equation explicitly for  $t_i$  yields

$$(3.6) \quad t_i = \ln(Q_0/Q_i)/\lambda$$

Since a new value of  $Q_i$  is available at the bottom of each slice, an age

may be calculated at each depth interval. The standing crop below each slice and the resulting chronology for core FR11B are presented in Table IX and compared to the tide-gauge record in Fig. 12.

Strict adherence to the assumption of constant  $^{210}\text{Pb}$  flux is somewhat relaxed in practice, depending on the time scale of interest. Because  $^{210}\text{Pb}$  deposition in precipitation is a stochastic process, the actual flux will vary widely over short periods. These fluctuations are effectively integrated, however, by taking samples representing the accumulation of several years. No long-term measurements of atmospheric  $^{210}\text{Pb}$  are available, but the lack of a significant secular trend in annual precipitation recorded in New Haven over the last century or so (Kirk, 1939; U.S. Dept. of Commerce, 1972), and the lack of demonstrable fission-produced  $^{210}\text{Pb}$  (Beasley, 1969; Feeley and Seitz, 1970), make the assumption of a constant  $^{210}\text{Pb}$  flux seem reasonable.

Benninger's (1976) measurements of monthly total  $^{210}\text{Pb}$  deposition in New Haven further indicate that the long-term average flux is rapidly approached. Although monthly deposition varied by a factor of 4 without obvious seasonality, after only 1 yr the integrated annual average deposition rate was found to be indistinguishable from long-term averages based on standing crops of soils (Table X).

The responses of a salt marsh and tide gauge to changes in sea level must be presumed to differ. A tide gauge responds reversibly with a time constant measured in minutes. Although the salt marsh appears to keep pace with sea level over the years, the fact that it is regularly flooded by tides demonstrates its relative sluggishness. In addition, accretion of the salt marsh is generally irreversible—erosion, when it does occur, is usually confined to the seaward perimeter of exposed coastal marshes (Bloom, 1967). Slow, irreversible accretion appears to be a normal result of peat formation in New England-type salt marshes.

The nature of the response of the salt marsh suggests that the annual sea-level data should be further smoothed to make the comparison. This

TABLE X. INTEGRATED FLUX OF EXCESS  $^{210}\text{Pb}$

| Site                                    | Flux<br>(dpm $\text{cm}^{-2}$ yr $^{-1}$ ) | Method                     | Ref.            |
|-----------------------------------------|--------------------------------------------|----------------------------|-----------------|
| Branford, Connecticut                   | 1.07                                       | Standing crop, salt marsh  | This work       |
|                                         | 0.82                                       | Standing crop, forest soil | This work       |
| New Haven, Connecticut                  | 1.0                                        | Total precipitation        | Benninger, 1976 |
| Cook Forest State Park,<br>Pennsylvania | 1.0                                        | Standing crop              | Lewis, 1976     |
| Maryland                                | 1.2                                        | Standing crop, soil        | Fisenne, 1968   |

has been done using the method of Hicks (1972), which reportedly attenuates oscillations of  $\leq 5\frac{1}{2}$  yr by at least 90%, but allows long-period oscillations, which account for most of the variance in tide-gauge records (Walcott, 1975), to survive. The mean sea-level data, smoothing program, and results are given in McCaffrey (1977). It should be noted that the degree of smoothing is arbitrary and does influence the comparison. If annual or shorter period average values had been used, the increased scatter would envelop the salt-marsh curve, whereas greater smoothing would, of course, further dampen the oscillations.

Using the smoothed sea-level curve, as plotted in Fig. 12, the agreement between the rate of salt-marsh accretion and tide-gauge record is reasonably good, except in that part of the record where temporary reversals in the sea-level curve appear.

If the intermediate degree of smoothing used is accepted, then the discrepancies between the curves may provide insight into the accretion process. Note that the temporary fluctuations in the New York City tide gauge are not explained by changes in Hudson River discharge (U.S.G.S., 1960) and the 1920–1930 hiatus, at least, is also apparent in other East Coast gauges, thus they appear to be real sea-level changes of some years in duration.

There are several ways the salt marsh could conceivably have responded to sea-level reversals of this type. Direct tracking through relative minima by removal of accumulated peat can be discounted with confidence on the basis of observation: General loss of up to 10 cm of surface material, even if somehow possible, could hardly have gone unnoticed, yet no such loss has been reported. An independent line of evidence against loss of peat, discussed in a later section, is that there is no deficiency in the expected standing crop of excess  $^{210}\text{Pb}$ . Other conceivable responses, such as dewatering and compression, or simply temporary cessation of organic growth are, perhaps, somewhat more probable. However, two lines of argument indicate that these responses are also unlikely. First, the magnitude of the reversal, 4 or 5 cm, will decrease the fraction of the time the marsh is flooded by only a few percent, according to Fig. 13. This level of change is probably insignificant, given that the "noise level" of the yearly record is of the same order of magnitude. The second, more powerful argument is that  $^{210}\text{Pb}$  deposition will continue, independent of accretion. If so, cessation of surface accretion will result in accumulation of  $^{210}\text{Pb}$  and produce a zone of relatively high activity.

The ratio of the amount of activity that would have accumulated ( $Q'$ ) compared to that actually found ( $Q$ ) can be calculated. If deposition of  $^{210}\text{Pb}$  continued unchanged during a 13-yr pause in surface accretion, as

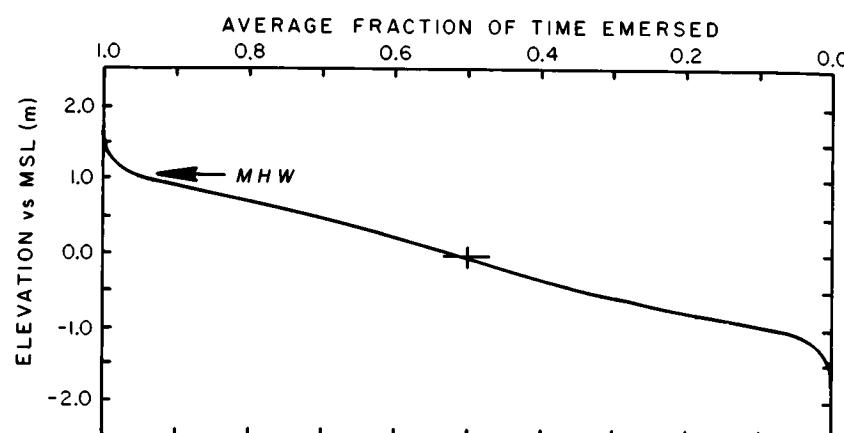


FIG. 13. The portion of the time a given intertidal position is exposed to the atmosphere depends mainly upon elevation and local tidal regime. This relationship has been determined for Bridgeport, Connecticut, where emersion for an elevation at MHW is well over 0.9.

the material in slice No. 8 accumulated, then the present ratio, under the condition that the actual interval of  $^{210}\text{Pb}$  accumulation  $t$  (= 9.1 yr) had been extended by an additional  $t'$  (= 13 yr) years, would be

$$(3.7) \quad Q'/Q = [1 + (t'/t)] \exp [-(\lambda t')] \approx 3$$

This would have been readily apparent in the 1972 data, but no such feature is found in Fig. 11, thus it is likely that accretion continued at some finite rate during this interval.

In summary, the change in relative sea level measured independently by the New York City tide gauge generally overlies the record of salt-marsh accretion derived from  $^{210}\text{Pb}$ . This agreement is considered the best evidence that the assumptions made in calculating the  $^{210}\text{Pb}$  ages are valid; in particular, that  $^{210}\text{Pb}$  has not been grossly redistributed since burial. This implies that elements with chemical properties similar to Pb, such as Cu and Zn, primarily reflect depositional rather than diagenetic processes.

### 3.2. Physical and Chemical Evidence on Lack of Disturbance and Chemical Immobility

In addition to the evidence based on  $^{210}\text{Pb}$ , other physical and chemical evidence exist by which to assess the possible importance of compaction, mixing, and chemical diagenesis at the coring site.

If substantial compaction occurred during burial, and loss of organic matter is negligible, then an upward-opening concavity would be expected in the plot of organic-matter accumulation, Fig. 6. In fact, the curve is highly linear, which demonstrates that bulk density of organic matter is practically uniform over the depth of the core, and indicates that no substantial compaction has occurred. Beneath the core, compaction is judged to be even less likely, because no compacted organic layer was present and muddy estuarine deposits occur within the next meter. The lack of measurable compaction is perhaps understandable, given that (1) fresh peat is neutrally buoyant in seawater, (2) salt-marsh peat is an extensive, intricately interwoven, space-filling, resilient, spongelike organic material, and (3) the general tendency of the high marsh to remain saturated with water throughout the tidal cycle, except for a few centimeters at the surface. This buoyant-peat model is consistent with the observations of Harrison (1975), who measured the variation in elevation of the marsh surface, relative to a bedrock outcrop, during the flood half-cycle of the tide. She detected an increase in elevation of several millimeters as the tide rose, which is the response expected for a buoyant material. The limited range of the buoyant response is thought to be due to the facts that (1) the water table is perched near the surface of the marsh, (2) changes in the free-water level in the peat are restricted by the finite permeability of this material, and (3) most of the floodwater reaches the interior surface of the high marsh by overland flow rather than by flow through the porous medium: Holes fill from above, not below.

Another feature of salt-marsh peat restricting its buoyant response is the interconnectedness of the bulk material: Peat near the surface is not isolated, but is enmeshed by its roots into a semiinfinite layer of peat some tens of centimeters thick. The buoyant-peat model predicts that if periodic recharge of this perched-water table was prevented, then substantial de-watering and compression would occur. As it turns out, this experiment has already taken place: Diking of salt marshes was one of the means used in the past to reclaim them for agricultural purposes, and following that treatment the marshes were reported to have shrunk considerably, in some cases as much as 3 feet (Smith, 1907).

The study site was selected on the basis of its a priori low probability of disturbance, but the effects of biological mixing need be neither obvious nor trivial. Physical disturbance could occur as a byproduct of the macrofauna or macroflora. For example, W. A. Niering (Connecticut College, personal communication) suspects that cropping of salt-marsh vegetation by rodents may be significant adjacent to upland refuges, but Nixon and Oviatt (1973) felt that the impact of mammals was slight. Marsh snails (*Melampus bidentatus*) and the ribbed mussel (*Modiolus demissus*)

either do not dig burrows, or inhabit the perimeter of the marsh, away from the core site.

The burrowing crab, *Uca pugnax*, is evidently present in considerable numbers on the marsh and probably represents the single greatest threat to the sedimentary record. This crab reportedly occurs in mean densities of 205/m<sup>2</sup> in the *S. alterniflora* marshes of Georgia, but in Rhode Island only 2.7 ± 3.8/m<sup>2</sup> were counted in early fall (Teal, 1962; Nixon and Oviatt, 1973). In this study area their burrows were obvious under the relatively open stands of *S. alterniflora*, but the dense stands of *S. patens* grass often prevented observation of the high-marsh surface.

To assess the significance of their burrowing activity under the *S. patens* covering the sample site, a study of the distribution of crab burrows in three zones along a transect crossing the sample site was undertaken in midsummer, when crabs were present in relative abundance. The results of this census, presented in Table XI, show that the number density of burrows along the *S. alterniflora* margin of the channel is high, approximately equal to densities reported for the Georgia *S. alterniflora* marsh. In a *S. patens* zone 2-m away, the densities dropped to ~¼ of the *S. alterniflora* value. Near the sample site, 15 m inland, one burrow was found in one 0.25-m<sup>2</sup> plot and none in the other. Evidently, crab-burrowing activity is highly skewed toward the channel margins and is uncommon at the sample site.

The substrate under each type of grass differs markedly and may explain this result. Along the perimeter of the marsh where *S. alterniflora* thrives, the surface between the emergent shoots is soft mud. In contrast, under *S. patens* there is a dense, tangled root mat, as seen in the x radiograph (Fig. 4), and it seems likely that this substrate inhibits burrowing by the fiddler crab. Whatever reason for this site preference, it appears that bioturbation by burrowing crabs is practically negligible at the interior sample site. The relative freedom from bioturbation enjoyed by the high marsh distinguishes this location from other aerobic marine sediments where mixing may be intense (Aller, 1977).

Perhaps the best available evidence to evaluate the impact of displacement of solids by plant growth comes from the experiments of Bloom (1967). In order to establish the rate of accretion of the salt marsh, he spread colored-aluminum flakes over small areas of the surface at repeated intervals over a period of years. These marker horizons were later recovered by taking small cores through the overgrown peat and measuring their depth. The fact that recovery was feasible during at least the next decade and that in almost all cases the original sequence had been preserved during growth of several centimeters of new peat is good evidence of the lack of massive physical disturbance of such layers within the critical upper levels of peat.

TABLE XI. DENSITY OF *Uca pugnax* BURROWS ON THE SURFACE OF THE FARM RIVER SALT MARSH

| Zone                                       | Burrow count <sup>a</sup><br>$N \pm \sigma$<br>(m <sup>-2</sup> ) |
|--------------------------------------------|-------------------------------------------------------------------|
| <i>S. alterniflora</i> (bordering channel) | 254 ± 40                                                          |
| <i>S. patens</i> (2-m inland of site 1)    | 64 ± 20                                                           |
| <i>S. patens</i> (midmarsh sample area)    | 2 ± 3                                                             |

<sup>a</sup> Data represent the total number of open (not necessarily occupied) burrows present on 7 August 1973 on two ¼-m<sup>2</sup> plots within each zone.

Additional evidence for or against diagenesis may be found in depth profiles of the stable elements and other chemical species of interest. The source strengths of the stable elements, unlike <sup>210</sup>Pb, cannot be hindcast with confidence, even though it is generally conceded that emission and deposition rates for many of them have increased over the last century. Although a quantitative, historical-deposition model is unavailable, we can examine the existing data for internal evidence of diagenesis.

All stable metals in both cores FR11B (Table II) and FR5A (Table III) show increased concentrations toward the surface. The magnitude and pattern of the increase varies among metals, but three types may be distinguished. Cu, Zn, and Pb are all relatively low and uniform in concentration below 30 cm. At about 30 cm, the concentrations of each of these metals simultaneously increases to a high plateau around 10 cm. The magnitude of the increases in concentration, comparing the upper third of the cores to the lower two-thirds, ranges from roughly 5 times for Zn and Pb to 9 times or more for Cu. The profiles of Fe and Mn are distinct from the trace metals and from each other. Mn exhibits no sustained trends until the surface is approached, where its concentration abruptly increases, almost tripling in core FR5A. Unlike Mn, Fe shows no abrupt surface maximum, although its concentration does increase irregularly by a factor of roughly 2 times over the upper third of the core.

Not all of the elements selected for study are expected to behave in the same way, based on general chemical properties, when buried in a reducing, sulfide-rich, marine environment. As a first approximation, the expected concentrations of dissolved metals can be estimated from published solubility-product constants, by assuming a free-sulfide concentration and neglecting complex formation, as has been done in Table XII. The calculated equilibrium concentrations are extremely low, except for Mn and possibly Fe, which suggests that Cu, Zn, and Pb should be fixed as their insoluble sulfides, whereas Mn might be chemically mobile.

TABLE XII. EXPECTED EQUILIBRIUM CONCENTRATIONS OF SELECTED METALS IN SALT-MARSH PORE WATERS, ASSUMING A TOTAL SULFIDE CONCENTRATION OF  $10^{-3}$  m<sup>a</sup>

| Element | Solubility product <sup>b</sup><br>log $K_{sp}$<br>(25°C) | Expected conc. <sup>c</sup><br>log [M <sup>2+</sup> ] <sub>e</sub> |
|---------|-----------------------------------------------------------|--------------------------------------------------------------------|
| Mn      | -12.6                                                     | -2.6                                                               |
| Fe      | -17.2                                                     | -7.2                                                               |
| Cu      | -35.2                                                     | -25.2                                                              |
| Zn      | -24.1                                                     | -14.1                                                              |
| Pb      | -26.6                                                     | -16.6                                                              |

<sup>a</sup> Total sulfide concentration  $\Sigma H_2S$  ( $= [H_2S] + [HS^-]$ ) of about 1 mM has been measured in a Louisiana salt marsh by Brannon (1973), a value not unusual for reducing marine sediments. Total dissolved sulfide-ion concentration  $[S^{2-}]$ , may then be calculated for pH (7.5) typical of the salt marsh, using the apparent dissociation constant of hydrogen sulfide ( $\log K'_1 = -6.9$ ,  $\log K'_2 = -13.6$ ) measured by Goldhaber and Kaplan (1975):

$$[S^{2-}]_e = \frac{K'_2 \Sigma H_2S}{(H^+) \{1 + [(H^+)/K'_1] + [K'_2/(H^+)]\}}$$

$$= 2.5 \times 10^{-9} \text{ m}$$

<sup>b</sup> Solubility product constants were selected from Bjerrum *et al.* (1958) compilation.

<sup>c</sup> Expected metal-ion concentrations were calculated from the expression:

$$K^{sp} = \gamma_{M^{2+}} [M^{2+}]_e \gamma_{S^{2-}} [S^{2-}]_e$$

where the activity coefficients for divalent ions are assumed equal to 0.2 and the effects of complexing ignored.

There is no guarantee that equilibrium conditions prevail, of course, especially within the biologically active surface zone of marine sediments (Presley *et al.*, 1972), and a number of complicating factors could act to support trace-metal concentrations at levels above or below those expected on the basis of simple solubility considerations, such as the tendency to absorb on peat (Fraser, 1961a,b; Bertine, 1972) or to form soluble complexes. However, there is reason to expect that immobilization via sulfide formation occurs rapidly. Goldhaber and Kaplan (1975) showed that free sulfide exists mostly as  $HS^-$ , the chemical form that Pohl (1975) demonstrated to be active in precipitation of at least Fe, Zn, and Cd

sulfides. Lawrence and McCarty (1965) found that in anaerobic digesters, where conditions are similar to those in the salt marsh, addition of sulfate to the reducing system rapidly eliminated heavy-metal toxicity, presumably by precipitating dissolved metals as their sulfides.

That sulfide is in fact produced in the salt marsh and reacts to form metal sulfides comes from several lines of evidence. The well-defined color change—pink over black—found at  $\leq 1$  cm under live *S. patens* is generally a good indication that iron hydroxyoxides are being converted to iron mono- and disulfides (Galliher, 1933; Berner, 1970). The fact that the normalized  $SO_4/Cl$  ratio under field conditions is usually less than unity (Table VI) strongly suggests that sulfate-reducing bacteria are active. Direct evidence of formation of authigenic metal sulfide comes from x-ray-microprobe and light-microscope examination of this section of the sediment, where pyrite (Fig. 7) is common within the sediment, often in close association with organic fibers (Fig. 8).

Although Fe was the only metal identified in the pyrite grains, there is indirect evidence that trace metals exist in the sediment as sulfides. One piece of evidence comes from the results of oxidation of salt-marsh sediment during prolonged storage in air. During this experiment, high-sulfate concentrations developed in the upper part of core FR5A, which coincided with the appearance of high Fe and trace-metal concentrations in the pore water. The concentrations are far greater than concentrations found in rapidly processed cores (Table VIII). Because the  $SO_4/Cl$  ratio exceeds unity, the appearance of  $SO_4^{2-}$  must be due to oxidation of a reduced form of sulfur. Thus it is likely that iron sulfide(s) and trace metals present as dispersed sulfides are oxidized during exposure to the atmosphere, yielding soluble trace metals and sulfate.

We can evaluate the observed distribution of Cu, as an example of an element tending to form highly insoluble sulfide, and Mn, which is often mobilized in reducing sediments. The depth profiles of Cu and Mn are plotted in Figs. 14 and 15, respectively. Two facts are outstanding:

(1) There is excellent agreement between the concentration ( $\mu\text{g/gm ash}$ ) profiles of the two cores, with the exception of two Cu points near 10 cm. In the case of Mn, the two profiles are practically congruent. Within a given core the Mn concentrations vary over a factor of about 2, but the detailed agreement between the two cores indicates the variation is real and laterally extensive on a scale of at least meters.

(2) The depth profiles of Cu and Mn are distinctly different: Mn concentration exhibits no sustained increase until just beneath the surface, whereas the increases in Cu concentration begins at about 30-cm depth. The Cu concentration appears to reach a maximum around 10 cm, then declines somewhat toward the surface.

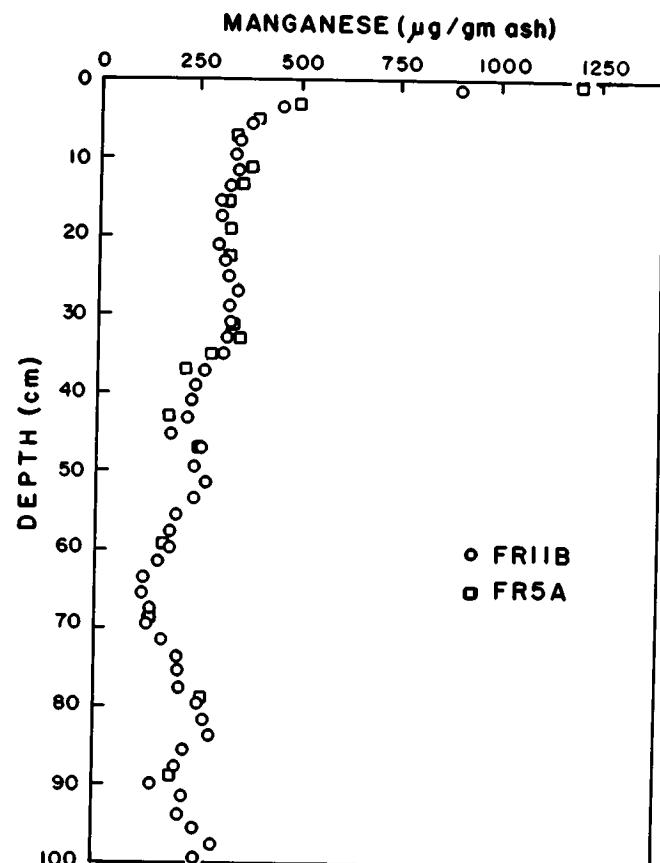


FIG. 14. Variation in the concentration of leachable Mn with depth in cores FR11B and FR5A.

The decline in specific concentration of Cu toward the surface may indicate that a complex explanation is necessary, such as a recent relative decline in Cu-deposition rate or relative increase in clay deposition. Because the inorganic-matter bulk density does vary appreciably (Fig. 17), dilution by clay merits further examination. If the relationship between copper content and ash content in core FR11B (Fig. 16) is examined, however, we find that (1) a proportionality (12- $\mu\text{g}$  Cu/gm ash) exists in the "deep peat," which is within the range expected for soils, and (2) higher in the core, above the lower clay band, copper content becomes independent of ash content. This suggests, first, that a new Cu source is contributing and, second, that the trend in concentration might be better expressed on a bulk-density basis ( $\mu\text{g}/\text{cm}^3$ ), rather than as specific gravity

( $\mu\text{g}/\text{gm}$ ). It is important to note here that if the inorganic matter in the upper part of the core still has the same concentration as it does in the deep peat, then only about 10% of the total Cu is attributable to this source, and dilution by clay cannot account for the decline in the specific concentration of Cu toward the surface in Fig. 15. Indeed, when the Cu data are replotted on a bulk-density basis, as in Fig. 18, the subsurface maximum is eliminated, at least for the dated core. Concentrations expressed in this way increase monotonically toward the surface, within the precision of the measurements. The evidence indicates that there is a new source of Cu, contributing to the salt-marsh sediment, and this source appears to be increasing in strength relative to soil-derived Cu.

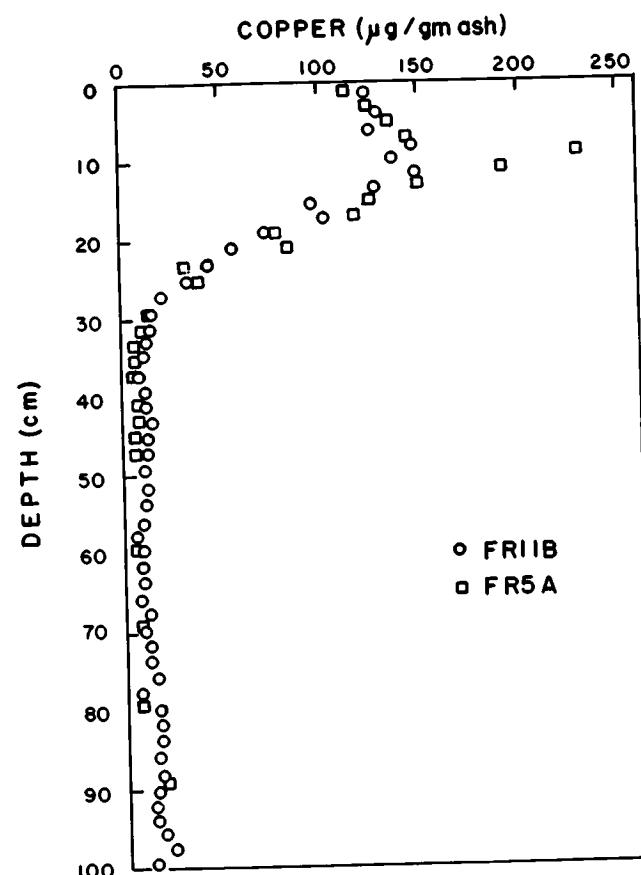


FIG. 15. Variation in the concentration of leachable Cu with depth in cores FR11B and FR5A.

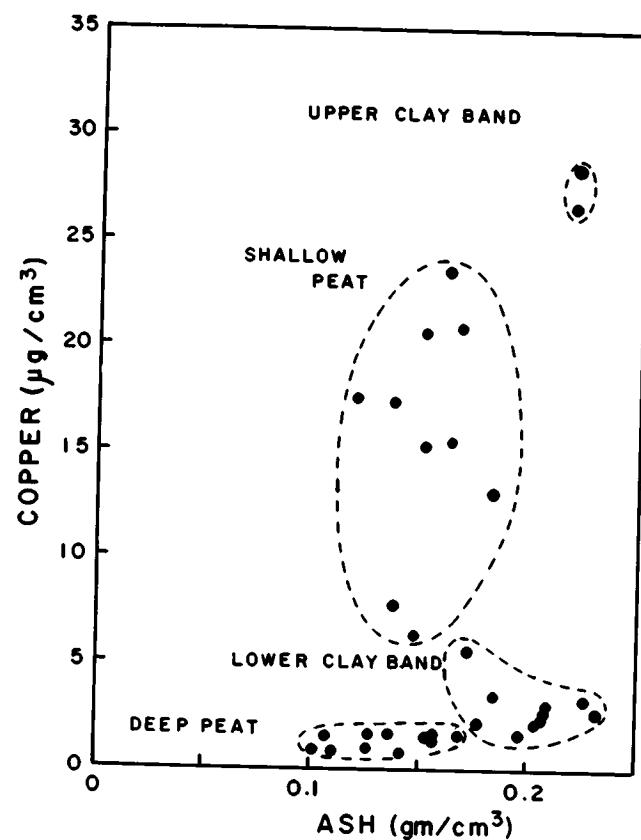


FIG. 16. Scatter diagram showing the relationship of Cu bulk density to inorganic-matter bulk density in various levels of core FR11B.

In contrast to that of Cu, the Mn profile can be adequately explained only by diagenetic remobilization. If eroded-upland soil (typically containing about 800- $\mu\text{g}$  Mn/gm ash) is the major source of Mn deposited on the salt-marsh surface, and the Mn profile is a steady-state feature, then it is clear that partial remobilization indeed must occur as the surface layer is buried. Profiles of dissolved Mn are shown in Figs. 9 and 10. In all cases Mn concentration in the pore water is highest in the uppermost sample or reaches a maximum at shallow depth. The samples exhibiting a shallow maximum were those taken from beneath grassy tussocks; the samples having a surface maximum were taken from adjacent areas of relatively low elevation. The evidence for remobilization of Mn beneath the surface of the salt marsh is qualitatively in accord with reports of

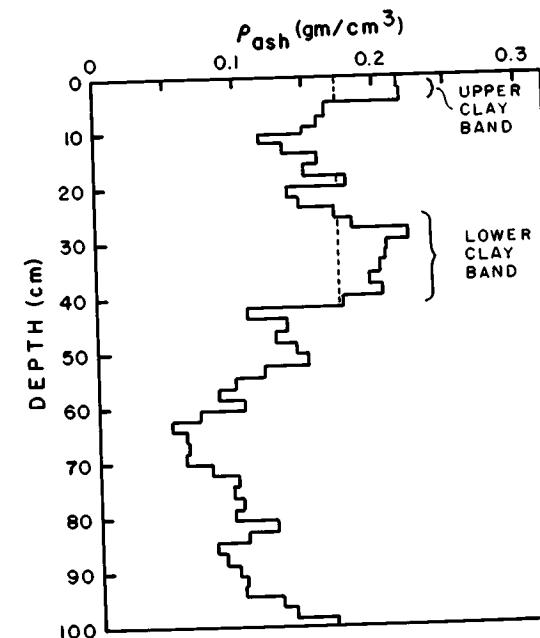


FIG. 17. Vertical distribution of inorganic matter in core FR11B. Samples with a density greater than 0.175 (dotted lines) appear as gray-colored "clay bands" due to their relatively high silt-clay content.

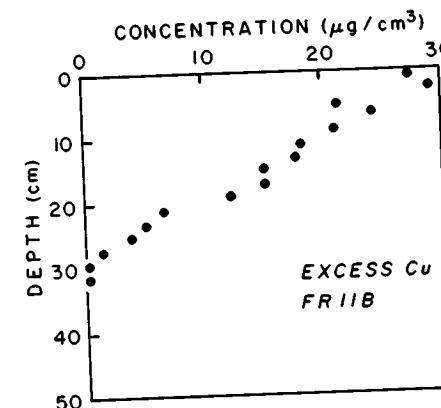


FIG. 18. Depth distribution of excess Cu in core FR11B, where Cu concentration ( $\mu\text{g cm}^{-3}$ ) =  $\text{Cu}(\mu\text{g gm}^{-1}) \times \rho (\text{gm cm}^{-3})$  for each slice of the core.

postdepositional migration of Mn in coastal marine sediments (Thomson *et al.*, 1975; Graham *et al.*, 1976), lake sediments (Robbins and Callender, 1975), and saturated soils (Ponnamperuma, 1972). A subsurface maximum in pore water concentration has also been reported beneath the land-water interface of Chesapeake Bay (Holdren *et al.*, 1975; Sanders, 1978) and Long Island Sound (Aller, 1977). In an accumulating body of reducing sediment, the occurrence of a maximum in dissolved Mn beneath a surface layer that contains very high Mn concentrations in the solid phase strongly suggests a diagenetic model involving reductive dissolution of Mn. Furthermore, the fact that the dissolved Mn concentration diminishes strongly below the maximum indicates that a removal process, as yet unidentified, is active in the deeper peat.

The relatively low leachable Mn concentrations at depth (Fig. 14) are much lower than expected for soils (Wright *et al.*, 1955), which indicates that some of the Mn escapes the sediment and reenters the estuary. Since Mn is fixed below the zone of dissolution, then both the fraction of the deposited Mn that escapes and the rate of escape may be estimated. If the Mn concentration associated with incoming soil particles is taken to be within the range reported for similar gray-brown podzolic soils ( $800 \pm 200 \mu\text{g/gm}$ ), then the concentration below 30 cm in Fig. 14 may be used to estimate the fraction lost:

$$\begin{aligned}
 \text{fraction lost} &= 1 - \text{fraction retained} \\
 &= 1 - \frac{\text{conc. at } 30 \text{ cm/leach. eff.}}{\text{incoming soil conc.}} \\
 &= 1 - \frac{(330/0.76) \pm 10\% \mu\text{g/gm}}{800 \pm 200 \mu\text{g/gm}} \\
 &= 0.46 \pm 0.14 \text{ or about half}
 \end{aligned} \tag{3.8}$$

The average rate of loss may be calculated from the average deposition rate times the fraction lost, where average deposition rate is estimated from soil concentration and total mass of inorganic matter accumulated within the length of  $^{210}\text{Pb}$ -dated core. Figure 6 shows that  $5.5 \text{ gm cm}^{-2}$  of inorganic matter, estimated to contain  $800 \pm 200 \mu\text{g Mn/gm}$  accumulated in about  $203 \pm 16 \text{ yr}$ , so the input is

$$\frac{5.5 \text{ gm cm}^{-2} \times 800 \pm 200 \mu\text{g/gm}}{200 \pm 16 \text{ yr}} \quad \text{or} \quad 22 \pm 6 \mu\text{g cm}^{-2} \text{ yr}^{-1} \tag{3.9}$$

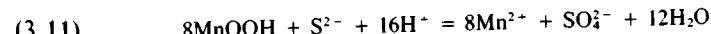
and the loss rate is

$$22 \pm 6 \times 0.46 \pm 0.14 \quad \text{or} \quad 10 \pm 4 \mu\text{g cm}^{-2} \text{ yr}^{-1} \tag{3.10}$$

Not all of the soluble Mn escapes, however. A portion evidently precipitates, presumably as insoluble oxyhydroxides, as dissolved Mn diffuses to the surface, resulting in transient storage of Mn and high total concentrations in the surface layer.

The rate of loss of Mn from the salt marsh is lower by 1–2 orders of magnitude than measured fluxes from the offshore marine sediments of nearby Long Island Sound (Aller, 1977) and Narragansett Bay, Rhode Island (McCaffrey *et al.*, 1980). If the Branford salt marsh, one of the New England types, is generally representative of other marshes in this area, then their contribution of Mn to the estuary-at-large is probably negligible compared to subtidal sediments. This result is more a consequence of the paucity of inorganic-matter deposition rather than the efficiency of remobilization.

Some notion of the actual remobilization process may be obtained by comparing the dissolved Mn concentration profile to the  $\text{SO}_4/\text{Cl}$  ratios in Table VI. The  $\text{SO}_4/\text{Cl}$  ratio in core FR13 is everywhere less than unity. The nature of the profile indicates that sulfate reduction is very active near the surface, but that sulfate reduction deeper in the core is less intense. In the other cores (FR14C and D, IN5 and 6) sulfate reduction ultimately proceeds to roughly the same degree; however, the fact that the  $\text{SO}_4/\text{Cl}$  ratio is greater than unity at certain depths indicates that oxidation processes are also active. It is possible that transport of molecular  $\text{O}_2$  via uninterrupted gas spaces in *S. alterniflora* might act as an oxygen source in its root zone (Teal and Kanwisher, 1966). However, this has not been shown to be true for *S. patens*, and the coincident appearance of  $\text{SO}_4^{2-}$  and dissolved Mn (normally rapidly removed from oxygenated waters) is difficult to reconcile with simple oxidation with molecular oxygen, at least as an equilibrium condition. Morgan (1967) has pointed out a possible alternative, spontaneous oxidation process, namely the reduction of the higher oxides of Mn in the presence of dissolved sulfide yielding dissolved Mn and sulfate:



Some form of manganese oxide is available near the sediment surface and, as it is buried, it is exposed to an environment where bacterial-sulfate reduction is generally active. If manganese oxides do act as oxidants for sulfide, then it is possible to explain, at least qualitatively, the simultaneous appearance of dissolved Mn and  $\text{SO}_4^{2-}$  in the pore water. There is sufficient solid Mn present to produce the amount of dissolved Mn found, but this reaction alone cannot begin to account for the amount of  $\text{SO}_4^{2-}$  generated. Also, the fact that the normalized  $\text{SO}_4/\text{Cl}$  exceeds unity means that some form of previously accumulated sulfide is oxidized. No trace

metals other than Mn and Fe were detected in these samples, but the stored-core experiment does show that under sufficiently extreme oxidizing conditions, trace metals can be mobilized. No single, spontaneous oxidation process seems adequate to explain the observations. It is conceivable that the observations refer to transient conditions in the salt marsh rather than equilibrium conditions, and further study is needed to understand them.

### 3.3. Atmospheric Fluxes Recorded in the Salt Marsh

The special circumstances of  $^{210}\text{Pb}$  deposition allow the hypothesis of quantitative retention of  $^{210}\text{Pb}$  to be tested. This may be done by comparing  $^{210}\text{Pb}$  deposition in the salt marsh to independent estimates of local deposition.

Although there is continual deposition of  $^{210}\text{Pb}$  to the salt-marsh surface, the quantity of excess  $^{210}\text{Pb}$  that accumulates beneath a unit surface area (the standing crop) is finite due to radioactive decay. As  $^{210}\text{Pb}$  deposition proceeds, the standing crop in a closed system will increase only until its decay rate equals the depositional flux of  $^{210}\text{Pb}$ ; thereafter a steady state exists. At steady-state, the  $^{210}\text{Pb}$  flux  $F$  may be calculated from the standing crop  $Q$  and the mean life  $\tau$  of  $^{210}\text{Pb}$ :

$$(3.12) \quad F = Q/\tau = \lambda Q$$

if the flux of  $^{210}\text{Pb}$  from the atmosphere is quantitatively retained by the salt marsh, then the flux calculated in this way should agree with independent estimates of the atmospheric  $^{210}\text{Pb}$  flux.

Such independent estimates are available from direct measurements of  $^{210}\text{Pb}$  in total precipitation and from the standing crops present in undisturbed soils. Previous measurements of the atmospheric flux have been made in New Haven by Benninger (1976) using open-bucket collectors sampled at monthly intervals. Soil-standing crops have been measured at various sites in the eastern U.S., including a forested upland site within the Farm River salt marsh, and are compared in Table X. It is evident that the  $^{210}\text{Pb}$  flux derived from salt-marsh core FR11B is indistinguishable from the current rate of deposition of  $^{210}\text{Pb}$  from the atmosphere in nearby New Haven.

The salt-marsh flux is also in substantial agreement with estimates from soil-standing crops, but may be greater than the flux estimated from the Branford forested-soil sample by about 20%. Circumstances suggest that the standing crop measured in nearby soil may tend to underestimate the atmospheric  $^{210}\text{Pb}$  flux. The site is on a small island covered with deciduous forest surrounded by an extensive area of salt marsh and, therefore,

must be presumed to act as a net source of organic matter to its surroundings. Since vegetation intercepts  $^{210}\text{Pb}$  deposited by rainfall (Hill, 1960; Francis *et al.*, 1968), leaves and other tree surfaces will contain excess  $^{210}\text{Pb}$ . Net loss of such material from the island would depress the residual standing crop below that expected on a unit-area basis. Second, the ages of the largest trees in the canopy, based on counts of annual rings, are not more than 60 years (McCaffrey, 1977), suggesting that the forest cover may have been removed within the past century by man or natural causes. An additional loss mechanism may be drainage of soil leachate containing excess  $^{210}\text{Pb}$  from the upper part of the profile into the groundwater. Overall, the exchange processes between the island and its environment all seem directed toward net loss of  $^{210}\text{Pb}$ , so a systematic deficit in the island standing crop is to be expected relative to semiinfinite forest sites or the salt marsh.

It is important to understand the relationship between intertidal position and atmospheric exposure. Due to the periodic nature of the tidal cycle, a given elevation within the tidal range may be frequently submerged by tides, but the average fraction of the time a given position is emersed depends strongly upon its elevation relative to mean-sea level. In nearby Guilford, Connecticut, where tide-gauge data are available, the surface of the high marsh was found to lie between mean-high water (MHW) and MHW neaps (R. Gordon, Yale University, personal communication), and the Farm River high marsh is believed to be similarly elevated. The relationship between elevation and exposure has been worked out for Bridgeport, Connecticut (P. Marshall, Yale University, personal communication) and is reproduced as Fig. 13. This curve may be used to estimate the average exposure time for other stations experiencing the semidiurnal tide characteristic of Long Island Sound. It is evident that exposure to direct atmospheric input increases rapidly from slightly more than half-time for a surface positioned at mean-sea level to more than 0.9 of the time for surfaces located at MHW. If this tidal regime is applied to the Farm River salt marsh, then it is clear that the high marsh is exposed to direct atmospheric input most of the time.

In summary, deposition from the atmosphere almost always impinges directly upon the high-marsh surface. Moreover, the standing crop of excess  $^{210}\text{Pb}$  now found beneath the salt-marsh surface or nearby soil is in essential agreement with that expected from measured atmospheric fluxes. Therefore, the salt-marsh standing crop of excess  $^{210}\text{Pb}$  seems best explained as quantitative retention of atmospheric deposition.

If an atmospheric source of  $^{210}\text{Pb}$  accounts within experimental error for the salt-marsh deposition, then the  $^{210}\text{Pb}$  contribution from all other sources must be small to nonexistent. If we take the simple difference in

the fluxes calculated for the salt marsh and New Haven sites,  $0.07 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ , as a probable upper limit for inorganic-matter sources, this severely constrains them. Since the present rate of accumulation of inorganic matter, judged from the mass found in the surface slice of known age, is

$$(3.13) \quad 0.217 \text{ gm/cm}^3 \times 2.32 \text{ cm}/7.07 \text{ yr} = 0.071 \text{ gm cm}^{-2} \text{ yr}^{-1}$$

then the probable maximum specific activity of inorganic material transported to the marsh via the water column is:  $0.07 \text{ dpm cm}^{-2} \text{ yr}^{-1}$  or  $\gtrsim 1 \text{ dpm } ^{210}\text{Pb}_{\text{xs}}/\text{gm ash}$ .

This estimate is compared to the specific activity of likely sources (upland and marine) in Table XIII. It appears that neither material scoured from the mud-water interface of Long Island Sound nor material eroded from the upland surface is an allowable source, since only material from beneath these surfaces is of sufficiently low activity. It is relatively difficult to effect deep (18–20 cm) erosion of submarine sediment in Long Island Sound, but common for upland soil to erode deeply, especially when land is disturbed by agriculture or construction. This indicates that the source of low-specific-activity inorganic matter is the eroding subsurface material of the watershed.

An upland-soil source is also consistent with the metal concentrations found at lower levels in the salt-marsh cores. The iron content is generally proportional to the mass of inorganic sediment and is found in concentrations (almost 4%) considered reasonable for soil (Bowen, 1966). In an analogous plot for Cu, Fig. 16, the concentrations in deep peat and many of the lower clay-band samples are also typical of soil.

This explanation cannot account for the increasingly high trace-metal concentrations found nearer the surface. Above 30 cm, the concentrations of Cu and other trace metals simultaneously begin a sustained increase

TABLE XIII. EXCESS  $^{210}\text{Pb}$  ACTIVITY IN POTENTIAL DETRITAL SOURCE MATERIAL

| Source                                    | Excess $^{210}\text{Pb}$<br>(dpm/gm ash) | Reference                    |
|-------------------------------------------|------------------------------------------|------------------------------|
| <b>Long Island Sound Sediment</b>         |                                          |                              |
| Surface                                   | 4.6                                      | Thomson <i>et al.</i> , 1975 |
| 18–20 cm                                  | 1.1                                      | Thomson <i>et al.</i> , 1975 |
| <b>Upland soil, Branford, Connecticut</b> |                                          |                              |
| 0–5 cm                                    | 5.4                                      | This work                    |
| 5–10 cm                                   | 1.5                                      | This work                    |
| 10–40 cm                                  | 0.0                                      | This work                    |

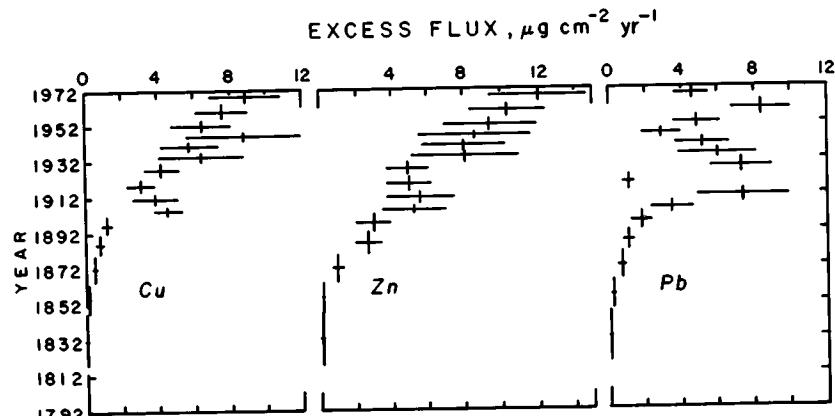


FIG. 19. Increased rate of deposition of trace metals from the atmosphere as recorded in a Connecticut salt marsh.

(Fig. 15) and become independent of inorganic matter in peat above the lower clay band (Fig. 16).

It is possible to calculate the trace-metal flux to the salt-marsh surface using the sediment chronology based on  $^{210}\text{Pb}$ , the excess concentrations of metals within each slice  $C_{\text{xs}}$  ( $\mu\text{gm/gm ash}$ ), and the bulk density  $\rho$  ( $\text{gm ash/cm}^3$ ), from the equation

$$(3.14) \quad M = \rho C_{\text{xs}} z / t$$

where  $z$  is the slice thickness (cm),  $t$  is the age (yr), and  $M$  is the metal flux ( $\mu\text{gm cm}^{-2} \text{ yr}^{-1}$ ), averaged over each slice. The flux of trace metals over the historical period are listed in Table V.

The first indication of an increase in the flux of each of the trace metals begins simultaneously in Fig. 19. This corresponds to the final stage of deposition of the lower clay band, at about the time of the U.S. Civil War (1860–1865), when industrialization in this area greatly intensified. The rate of increase since then has been generally sustained to the present. The increase is nearly linear in the case of Cu and Zn, but deviates considerably from a smooth rise in the case of Pb, and there is no obvious acceleration due to the introduction of leaded gasoline in the 1920s.

The trace-metal flux at the time the core was raised (1972) may be calculated by extrapolating the excess flux versus time curves to zero depth. This is a short, linear extrapolation in the case of Cu and Zn and may be carried out with confidence. Because of the large changes in flux with time for Pb, however, the extrapolation is less precise.

Deposition from the atmosphere and water column both contribute to

the total flux of material accumulating at the surface of the salt marsh. Their relative contributions will depend strongly on the material in question. The atmospheric contribution of inorganic mass is likely to be small relative to deposition from the water column. The total inorganic-matter flux, calculated from the known bulk density, age, and depth of the surface sample, is about  $0.07 \text{ gm cm}^{-2} \text{ yr}^{-1}$ , whereas annual dust fall measured near the sample site at Tweed-New Haven Airport (DeLouise, 1968) was found to be about  $0.004 \text{ gm cm}^{-2} \text{ yr}^{-1}$ . Dust fall at an airport is likely to be an overestimate of actual values in the relatively dust-free salt marsh, so at least 94% of the inorganic mass is deposited from the water column.

Since the mass of inorganic matter deposited from the atmosphere can account for only a small fraction of the total inorganic-matter accumulation rate, and surface Long Island Sound sediments are excluded on the basis of their high- $^{210}\text{Pb}$  specific activity, then the principal source is almost certainly the eroding soil of the watershed, carried to the surface of the salt marsh while suspended in runoff. If this is true, then the flux of trace metals associated with the soil may be estimated from the rate of accumulation of inorganic matter and its trace-metal concentration. Although data for soils of the Farm River watershed are not available, the trace-metal content for typical brown-podzolic forest soils may be used as an approximation. Data used in the model calculations are listed in Table XIV. Multiplying the mass flux by the soil concentrations yields the estimated trace-metal fluxes from the water column (Table XV).

The results of the model calculations show that the atmospheric contribution to the Fe and Mn flux is negligible compared to deposition from the water column. This is in accord with the estimated atmospheric deposition of Fe to the area of the New York Bight of about  $37 \mu\text{gm cm}^{-2} \text{ yr}^{-1}$  (Duce *et al.*, 1976). In the case of the trace elements Cu, Zn, and Pb, contribution from the water column is generally small relative to the atmosphere.

The atmospheric contribution to the salt marsh may be estimated in two ways: (1) by attempting to place the study site appropriately within the broad picture of available deposition data at various other sites; and (2) by making model calculations using local atmospheric data and, lacking local information, deposition-rate parameters determined elsewhere.

Using the first approach, the trace-metal fluxes calculated for the salt marsh are compared to measured deposition rates for other sites in Table XVI. These sites were selected to represent circumstances that would be expected to yield fluxes of comparable magnitude, as well as establish reasonable limits to be expected. The station on Hawaii receives deposition from air masses that have presumably been scavenged over the ocean of most of their pollution burden, whereas the large fluxes measured

TABLE XIV. SOIL CONCENTRATION C, DRY-DEPOSITION VELOCITIES  $V_g$ , WASHOUT RATIOS W, AND AEROSOL CONCENTRATIONS X USED IN MODEL CALCULATIONS

| Data                                    | Fe     | Mn    | Cu               | Zn   | Pb  |
|-----------------------------------------|--------|-------|------------------|------|-----|
| C ( $\mu\text{g/gm ash}$ ) <sup>a</sup> | 38,000 | 666   | 14               | 66   | 19  |
| $V_g$ (cm/sec) <sup>b</sup>             | 1.1    | 0.5   | 0.7 <sup>c</sup> | 0.6  | 0.3 |
| W <sup>d</sup>                          | 250    | 370   | 140              | 180  | 76  |
| X ( $\mu\text{g/m}^3$ ) <sup>e</sup>    | 0.54   | 0.011 | 0.16             | 0.33 | 1.0 |

<sup>a</sup> Soil data from Wright *et al.* (1955), except for Fe (Bowen, 1966).

<sup>b</sup> Cawse (1974), except where noted otherwise. The deposition velocities used above are somewhat lower than values measured within New York City (Kneip and Eisenbud, 1974) by factors of 2–4, but may be a better approximation to the regional values expected at the study site, where the largest particles have already been partially removed from the aerosol.

<sup>c</sup> Estimated from an average MMD (mass median diameter) for Cu of  $1.35 \mu\text{m}$ , based on the work of Lee *et al.* (1968) and read from the curve of  $V_g$  versus MMD of Cawse (1974).

<sup>d</sup> Dimensionless ratio, ( $\mu\text{g/kg rain}$ )/( $\mu\text{g/kg air}$ ), from Gatz (1975). Probably reliable within a factor of 2.

<sup>e</sup> Mean values for Tweed-New Haven Airport (1969–1973; Connecticut DEP 1975). Uncertainty is estimated to be  $\pm 50\%$ .

in New York City and Philadelphia represent deposition in major urban-industrial centers on the East Coast. The total fluxes at Wraymires, U.K., a site about 18 km from significant industrial sources, may be representative of semirural deposition in temperate regions. Measurements at Nantucket and Woods Hole, Massachusetts, and the New York Bight, all nonindustrialized East-Coast sites, may indicate depositional fluxes to be expected for the eastern seaboard, away from intense sources. Although the reliability of these estimates varies and is difficult to assess, it is probably not better than  $\pm 50\%$  and could easily vary by factors of 2 or 3 or more, depending upon experimental technique, length of the observation period, and other factors. Taken as a whole, however, the various

TABLE XV. RESULTS OF MODEL CALCULATIONS OF THE CONTRIBUTION OF TRACE METALS FROM THE WATER COLUMN AND ATMOSPHERE TO THE SAMPLE SITE COMPARED TO TOTAL FLUXES TO THE SALT MARSH<sup>a</sup>

| Proximate source                 | Fe   | Mn  | Cu | Zn | Pb |
|----------------------------------|------|-----|----|----|----|
| Atmosphere                       |      |     |    |    |    |
| Dry deposition                   | 20   | 0.2 | 3  | 7  | 10 |
| Wet deposition                   | 10   | 0.4 | 2  | 6  | 7  |
| Atmospheric subtotal:            | 30   | 0.6 | 5  | 13 | 17 |
| Water column, suspended sediment | 2700 | 47  | 1  | 5  | 1  |
| Model, total                     | 2730 | 48  | 6  | 18 | 18 |
| Salt marsh, total                | 3600 | <78 | 10 | 17 | ~9 |

<sup>a</sup>  $\mu\text{g cm}^{-2} \text{ yr}^{-1}$ .

TABLE XVI. CALCULATED EXCESS METAL FLUX TO THE SURFACE OF THE FARM RIVER SALT MARSH COMPARED TO MEASURED ATMOSPHERIC DEPOSITION RATES AT SELECTED SITES<sup>a</sup>

| Site                                    |           | Year               | Collection data | Cu     | Zn    | Pb                            | Ref. |
|-----------------------------------------|-----------|--------------------|-----------------|--------|-------|-------------------------------|------|
| Branford, Connecticut                   | 1972      | Dry                | 8 ± 2           | 12 ± 3 | 7 ± 4 | This work                     |      |
| Wraymires, U.K.                         | 1970-1972 | Total              | 0.07            | 0.61   | <0.6  | Peterson <i>et al.</i> , 1973 |      |
| New York Bight                          | May 1972  | Total              | 3.2             | 12     | 5.5   | Peterson <i>et al.</i> , 1973 |      |
| New York City <sup>b</sup>              | 1970      | Wet                | 5.3             | 8.1    | 6.0   | Duce <i>et al.</i> , 1976     |      |
|                                         | 1972-73   | Dry                | 26              | 21     | 12    | Volchok and Bogen, 1971       |      |
|                                         | 1969-1970 | Total              | 9.8             | 36     | 23    | Kneip and Eisenbud, 1974      |      |
|                                         | 1977-1979 | Wet                | -               | 32     | 35    | Volchok and Bogen, 1971       |      |
|                                         |           | Dry                | -               | 4      | 7     | Feeley and Larsen, 1979       |      |
|                                         |           | Total <sup>f</sup> | -               | 5      | 0.5   | Feeley and Larsen, 1979       |      |
| Philadelphia, Pennsylvania <sup>c</sup> | 1966-1967 | Wet                | 4.9             | 23     | 8     | Feeley and Larsen, 1979       |      |
| Nantucket, Massachusetts <sup>d</sup>   | 1966-1967 | Wet                | 5.6             | 7.6    | 13    | Lazrus <i>et al.</i> , 1970   |      |
| Woods Hole, Massachusetts <sup>e</sup>  | 1977-1979 | Wet                | -               | 4      | 8.5   | Lazrus <i>et al.</i> , 1970   |      |
|                                         |           | Dry                | -               | 4      | 2     | Feeley and Larsen, 1979       |      |
|                                         |           | Total <sup>f</sup> | -               | 6      | 3     | Feeley and Larsen, 1979       |      |
| Hawaii <sup>f</sup>                     | 1966-1967 | Wet                | 1.1             | 0.6    | 0.4   | Lazrus <i>et al.</i> , 1970   |      |

<sup>a</sup>  $\mu\text{g cm}^{-2} \text{yr}^{-1}$ .

<sup>b</sup> Environmental Measurements Laboratory, U.S. Department of Energy.

<sup>c</sup> Weather Bureau Airport Station. Filtered rainwater.

<sup>d</sup> Redfield Laboratory.

<sup>e</sup> Weather Bureau Research Station, Mauna Loa Observatory, Hawaii. Filtered rainwater.

<sup>f</sup> Independent measurement by open bucket.

estimates are generally self-consistent and probably are the best means available to assess the deposition expected at the study site.

It is evident from Table XVI that the rates of deposition at the study site generally fall within the range of atmospheric deposition rates represented on the high side by New York and Philadelphia, and on the low side by Hawaii. In fact, the Branford results are in good agreement with intermediate sites taken to represent total deposition along the northeastern U.S. coast. This widespread consistency suggests that the salt marsh is collecting deposition more or less representative of the region, rather than some local source. The good agreement with Wraymires, U.K., presumably reflects the similar composition and behavior of regional aerosols originating in other temperate, industrialized areas.

In the second approach, the trace-metal flux from the atmosphere may be divided into two components: wet and dry deposition. The sum of these two components of the atmospheric flux will be calculated, using local atmospheric concentration and precipitation data, estimates of dry deposition velocity as defined by Chamberlain (1960) and reported by Cawse (1974), and washout ratios from Gatz (1975), all listed in Table XV.

The concentrations  $\chi$  of the trace metals were measured quarterly in the ambient air over Connecticut at as many as 50 stations during 1969-1973 by personnel of the Department of Environmental Protection (DEP) and the Department of Health (Connecticut DEP., 1975). The values used in the present calculation are arithmetic means of measurements made on samples taken on the roof of the Tweed-New Haven Airport terminal building, which are not significantly different from New Haven (6 stations) or the state as a whole.

The wet-deposition contribution, due to the combined effects of rainout and washout, was calculated as  $W\chi h/\rho$ , where  $W$  is the washout ratio, i.e., the concentration in rain/concentration in air;  $\rho$  is the density of air ( $1200 \text{ gm/m}^3$ ); and  $h$  is the precipitation rate (mean 1965-1972 =  $112 \text{ cm}^3 \text{ cm}^{-2} \text{ yr}^{-1}$ ; Bridgeport, 1972). The flux of trace metals associated with dry deposition is taken as  $V_d \chi$ , where  $V_d$  is the dry deposition velocity. The results of the model calculations of dry and wet deposition to the total atmospheric flux is shown in Table XV.

The results clearly show that the atmospheric contribution to the Fe and Mn flux is negligible compared to deposition from the water column. For the trace elements, however, atmospheric deposition dominates. The sum of wet and dry atmospheric deposition expected for Cu, Zn, and Pb falls within a factor of 2 of the surface fluxes found in the salt marsh. The relative contribution of wet and dry deposition is in accord with the measurements of Volchok and Bogen (1971) for New York City, but disagrees

with the Wraymire, U.K., data (Peirson *et al.*, 1973), where dry deposition accounted for a relatively small fraction of the total.

The generally good agreement may be fortuitous, and the local application of  $V_g$  and  $W$  values determined elsewhere is questionable. The lack of consistent results for the same elements at different stations (Peirson *et al.*, 1973; Kneip and Eisenbud, 1974) may be due to the differences in collection techniques as well as in the aerosols. Therefore, the agreement (within a factor of 2) between the model predictions and the calculations based on the salt-marsh results should be considered provisional for the trace metals Cu, Zn, and Pb.

Although the atmosphere behaves as a local source of Cu, Zn, and Pb, it is undoubtedly carrying material from more remote sites. In general, evidence that trace metals in polluted air are being transported considerable distances comes from the decline in concentrations away from source areas, their accumulation in remote sediments, and from mass-balance calculations. Industrialized urban atmospheres generally contain higher concentrations of many trace metals than suburban areas (Lee *et al.*, 1968; Stern *et al.*, 1973), and lowest concentrations are characteristic of remote land (Rahn, 1971; Zoller *et al.*, 1974; Struempler, 1975) and ocean sites (Hoffman *et al.*, 1972; Duce *et al.*, 1975). Fuel combustion, incineration, various industrial processes, and automobiles have been identified as major contributors to the pollution burden (Winchester and Nifong, 1971; Lee and von Lehmden, 1973; Kneip and Eisenbud, 1974). Such sources have been implicated as major contributors via the atmosphere to Lake Michigan (Winchester and Nifong, 1971; Edgington and Robbins, 1976). In the Los Angeles Basin about a third of the lead emitted by automobiles is carried at least 150-km downwind before being deposited (Huntzicker *et al.*, 1975). Various sedimentary deposits, such as coastal southern California (Bruland *et al.*, 1974), the Baltic Sea (Erlenkeuser *et al.*, 1974), Long Island Sound (Thomson *et al.*, 1975), and Narragansett Bay (Goldberg *et al.*, 1977) also show increased concentrations in recent deposits.

Local atmospheric data may be examined for clues to the relative importance of remote and local sources. The long-term average atmospheric concentrations of Cu, Zn, and Pb at certain stations along the north shore of Long Island Sound (Fig. 20) show no apparent trend along the W-E transect from New York City (Morrow and Brief, 1971; Kneip and Eisenbud, 1974) along the shore to eastern Connecticut (Connecticut DEP., 1975). Measured concentrations in the New York Bight area, however, under conditions where aerosols are being mixed and advected out across the Atlantic, show a general decline away from the coast (Duce *et al.*, 1976). Model calculations indicated that roughly 6% of the Pb and 24%

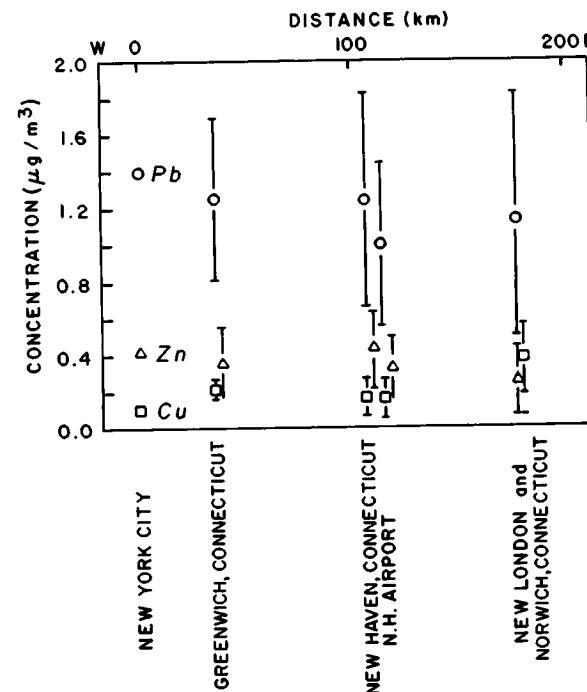


FIG. 20. Atmospheric concentrations of Cu, Zn, and Pb along the Connecticut coast.

of the Zn will be deposited within 100 km of the coast, even if there is no rain.

It may also be significant that the Nantucket station of Lazarus *et al.* (1970) was not measurably less polluted than stations in the northeastern U.S. Taken at face value, this suggests either that the sample sites are immersed in a regional atmosphere of generally similar trace-metal concentration, or that each station resides within an "island" of pollution of comparable concentration.

It would be interesting to compare the historical record of atmospheric quality found in the salt marsh to independent records of atmospheric burdens of trace metals, but such information is not available. It is possible, however, to use metal-production figures as a crude index of atmospheric emission. As an example, the historical increase in the primary production of Cu in the U.S. as a whole is compared to the increase in Cu deposition recorded in the Farm River salt marsh in Fig. 21. It is evident that the increase in Cu flux recorded in the salt marsh is in general agreement with the production trend over the period of record.

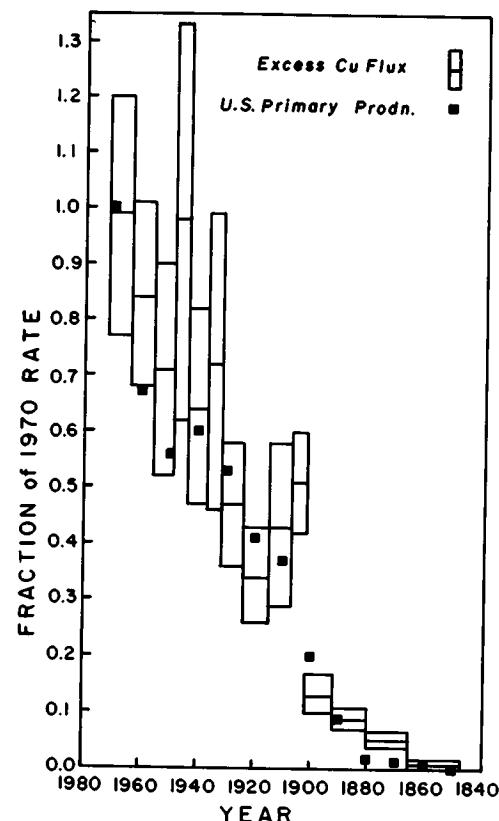


FIG. 21. Historical increase in the flux of excess Cu to the salt marsh compared to the trend in U.S. primary copper production over the same interval. Both trends are normalized by dividing the rate at any time by the 1970 rate. In the case of the salt marsh, the flux is averaged over several years accumulation, while the primary-production figures represent the rate for a single year, arbitrarily taken at the beginning of every decade from 1850–1970 (U.S. Dept. Interior, 1973).

Contributions from local sources are presumably important, but aerosol residence-time considerations and the general flow of air masses across the continent suggest that there is a very extensive areal contribution to the atmospheric burden of trace metals at the study site. Mean-residence time in the atmosphere depends on particle size and climatic regime. Esmen and Corn (1971) found that the mean-residence time of submicron-size particles in urban air in the absence of wet precipitation was roughly  $10^2$ – $10^3$  hr and decreased to 10–100 hr for 1–10  $\mu\text{m}$  particles. Moore *et al.* (1973) recently reevaluated the mean-residence time of the tropospheric aerosol and concluded that 4–6 days is the most probable value.

Turekian *et al.* (1977), using a different worldwide model, arrived at the same value for reasonable mean-transit times of global zonal winds. Rodhe and Grandell (1972) estimated the expected life of aerosol particles in the lower troposphere subjected to precipitation scavenging and found residence times on the order of 100–300 hr in summer and 35–80 hr in winter (Stockholm rainy season). Even when the effects of wet deposition are included, a mean-residence time on the order of days is still likely.

Based on a mean-residence time of days, the general eastward sweep of air across the continent (Van Cleef, 1908) and analyses of back trajectories of air masses (Cogbill and Likens, 1974) indicate that virtually any source east of the Mississippi or in southern Canada must be considered a possible contributor to the record of trace metals uncovered in the Farm River salt marsh.

### 3.4. Salt-Marsh Accretion

There is little direct evidence of the actual mechanism(s) of salt-marsh accretion, but the two processes generally offered in explanation are silt deposition and organic productivity. Silt deposition (more generally, particle deposition from the water column) has received emphasis in the past, depending on the observer and his area of study. Ganong (1903), who observed the marshes along the Bay of Fundy, felt that vegetative growth was not involved in accretion, but that salt marshes were "built up in a subsiding basin out of organic red mud brought in from the sea by the rush of the tides. . . ." His viewpoint represents one extreme, observers elsewhere came to recognize the importance of organic-matter production (i.e., peat formation) in salt-marsh accretion.

One of the earliest and most succinct statements of the peat-formation hypothesis of salt-marsh accretion was made by Mudge (1862), after he examined a section of the Romney Marsh, near Lynn, Massachusetts. He said:

The surface of the marsh is nearly a dead level, about one foot above ordinary high water mark and only overflowed by the higher Spring tides. The appearance of the marsh soil indicates a gradual formation from the grasses, aided by the fine, rich sediment which the high tides occasionally deposit. The saline grasses grow only above ordinary high water mark, and as the roots in the lowest part of the soil, even eight or more feet below the surface, are in their natural position, showing no distortion, we must conclude that their *situs* was above the high water line, and that subsidence has been so gradual that the growth of the plants has never been interrupted.

Mudge's concept of salt-marsh accretion clearly incorporates the notion that the grasses of the high marsh maintain their position during a gradual change in relative sea level, by upward growth. However, the special

mechanism he invoked as a driving force (undercutting of the peat by "a current of water in the diluvium under the clay") curtailed general application of his ideas. When Mudge made his report, glacial theory had not yet been fully accepted (Flint, 1971), and it was not until somewhat later that the real driving force was recognized to be the general rise in sea level in postglacial time (Davis, 1910). The description enunciated by Mudge contains the tracking hypothesis in embryonic form, but other than mentioning growth of grass, he is vague about the mechanism(s) involved.

Shaler's (1885) conception of salt-marsh accretion, in contrast to Mudge's, was primarily derived from his observations of the seaward perimeter of salt marshes; he hypothesized that formation of peat occurred during advance of salt-tolerant grass over silted-up mud flats. According to Shaler's theory, *S. alterniflora* is sufficiently tolerant to thrive at such a low intertidal level, and since other species cannot withstand such prolonged immersion in marine waters, it is the colonizing grass of aggrading mud flats. As *S. alterniflora* colonizes a mud flat, suspended sediment is more efficiently trapped and, once deposited, it is protected from erosion. Colonization thus promotes relatively rapid peat formation, to a level commensurate with local tidal range. The overall phenomenon, Shaler believed, was one aspect of the slow redistribution of sediment on a "steadfast" coast, long after the changes in sea level associated with deglaciation had ended. Accumulations of sediment built up in this way should show a thin surface layer of high-marsh peat overlying muddy *S. alterniflora* peat, itself overlying mud flat deposits.

These two hypotheses of salt-marsh formation were later reconciled by Johnson (1967, originally published in 1925). He recognized that each was based on observations of related but different aspects of salt-marsh formation—and were not necessarily conflicting. Stratigraphic evidence linking the two models has since been discovered in Granite Bay, Branford, Connecticut, where almost a meter of *S. patens* peat was found overlying *S. alterniflora*, itself overlying estuarine mud (Knight, 1934). Redfield (1972) has convincingly documented the overall process at Barnstable, Massachusetts: After *S. alterniflora* colonizes the mud flats, these stands of grass promote sediment accumulation and rapidly build to a level where high-marsh grasses can become established. Continued rise in relative sea level promotes development of a thick section of high-marsh peat. Eventually, the expanding, thickening wedge of high-marsh peat overrides the upland. As a result, sections through the landward edge reveal a stratigraphy consistent with the Mudge–Davis model, whereas sections through the seaward edge are consistent with the Shaler model.

The tracking hypothesis (Redfield and Rubin, 1962; Bloom and Stuiver,

1963), that the vertical growth of the high marsh is keeping pace with the rise in relative sea level, implies that (1) salt-marsh grasses are able to track the long-term change in relative mean sea level, even in the presence of relatively high-amplitude, short-period tidal fluctuations, and (2) that there is some factor related to sea level that is controlling marsh accretion in such a fashion that, ideally, it maintains but does not exceed a given elevational offset.

The idea that salt-marsh accretion is a function of the supply of silt is probably correct for Fundy-type salt marshes and during the Shaler stage of the development of the New England type, but this idea seems inadequate to account for accretion in the Mudge–Davis zone of peat formation. The historical emphasis on silt supply is perhaps an outgrowth of the crucial role of sand or silt in early marsh buildup (Shaler, 1885; Ganong, 1903; Chapman, 1960) and of the high inorganic-matter content of many marshes found along the shores of the North Atlantic and coastal plains states (Johnson, 1967). Many deposits referred to as salt marshes do, in fact, consist largely of inorganic-particulate detritus, with only incidental plant remains (Dawson, 1855; Bouma, 1963, 1969; Redfield, 1972). The botanical studies of Richards (1934) and the x radiographs of Bouma (1963) show that inorganic-particle deposition can indeed lead vertical development where supplies are adequate.

On the other hand, salt marshes are found in areas lacking an abundant silt supply. Johnson (1967) recognized that the New England-type salt marsh contained a relative lack of inorganic matter and relative excess of organic remains compared to the Fundy type, and used this property as a basis of classification. New England-type salt marshes occur from the mid-Maine coast to northern New Jersey.

This work deals with the high-marsh zone of one of the New England-type salt marshes and confirms the relative paucity of inorganic matter. Viewed at low tide, the high marsh stands exposed as an elevated volume of apparently firm, but actually highly unconsolidated material, containing over 80% of water by weight and only  $0.2 \text{ gm cm}^{-3}$  of inorganic matter. Such a low bulk density means that individual grains of inorganic matter are well-dispersed and by themselves are clearly inadequate to support an accreting high marsh. Another mechanism is needed to explain it, presumably related to high-marsh peat formation and the bulk properties of the deposit.

The salt marsh is composed largely of plant remains and more or less silt and clay-sized inorganic matter. The detailed structure of the subsurface organic matter is aptly described by Davis (1910) as:

... an extensive system of slender, tough, underground stems, from which arise

long, fibrous, branching roots; together, these form a turf-like structure, that is a mass of intermingled fine fibers, usually whitish or grayish, from intermingled silt . . . it differs from the turf formed by sedges in the persistence with which the underground stems retain their form and individuality, instead of collapsing and flattening . . . (and) in the presence of white or light-colored finely branching roots, which penetrate the mass in every direction and make up the great bulk of the material.

It is important to recognize that the material forming the peat is not the emergent portion of the grasses, rather, it is the organic matter grown in place at or just below the surface. Traditional studies of salt-marsh-grass productivity have focused on only the accessible above-ground shoots (Keefe, 1972), but there is reason to believe below-ground productivity is substantial (Valiela and Teal, 1974), perhaps equaling or exceeding above-ground productivity. For example, Broome *et al.* (1972) showed that more of the net growth of *S. alterniflora* seedlings is stored below-ground than above. Similarly, Amentano and Woodwell (1975) report that 20–40% of the total net production may be stored below ground each year in an established Long Island salt marsh. The plant parts formed below ground, in contrast to aerial parts, are well preserved in the resulting saline peat (Barghoorn, 1949). Even in 4000–5000-yr-old peat, epidermal root structures remained largely intact even though central-core tissues were often degraded.

The bulk properties of the high-marsh peat seem to be largely a consequence of this organic growth. The x radiographs (Figs. 4 and 5) reveal that a major portion of the subsurface space is occupied by or enclosed within the plant structures. This may account for the apparent low permeability of this material, as manifest in the failure of core holes to fill with water from below, despite the generally water-saturated condition of the deposit. Even at low tide the relatively low permeability of the peat in concert with tidal flooding is apparently sufficient to maintain the water-saturated condition within a few centimeters of the high-marsh surface. The uniform distribution of organic matter seen in Fig. 6 indicates that compaction is negligible and that vertical growth is somehow controlled, as if either an upper limit or some sufficient condition had been attained. This combination of circumstances seems to suggest that the primary mechanism of accretion is the formation of neutrally buoyant peat within a perched body of water.

If true, this model would account for a number of observations: lack of autocompaction, small, reversible increases in elevation of the surface during tidal flooding, and long-term tracking of the rise in relative sea level. One can speculate on how tracking might be accomplished: Normal changes in relative sea level (at tidal frequency) serve to establish the quasi-steady-state exposure at about the mean high-water level for these

moderately salt-tolerant plants. A long-term upward trend in relative sea level, as is occurring in this area, would increasingly stress the plants by increasing immersion; thus new growth would have obvious survival value. Direct evidence of the conditions causing the stress and the growth response of the plants has yet to be developed. The need to respond to a long-term trend in the midst of tidal fluctuations suggests that a highly damped signal, such as the mean height of the perched watertable, might be involved. Whatever the detailed mechanism, the response of the plants appears to be new growth both below and above ground. A rather extreme example of this is shown in the x radiograph of a large tussock in Fig. 5. The result is to move upward along the emersion curve (Fig. 13) and decrease stress. It also may be more than coincidence that the surface elevation of the high marsh is closely located at that singular point in the emersion curve where further increases in elevation have a rapidly diminishing effect on emersion time, but any lesser elevation would rapidly increase emersion. The overall effect of this growth would be to maintain the plant species within their tolerance limits and to track the rise in relative sea level.

If the inorganic matter is incorporated into the peat in proportion to its availability in suspension, then the salt marsh should be a recorder of sediment-generating processes in its vicinity.

The inorganic matter occupying the interstices of the peat originates either directly from the land or from offshore sites. Meade (1972) argues that very little of the sediment load of rivers actually escapes to the deep-ocean basin, but that most of the sediment is temporarily deposited offshore then returned, via landward bottom drift associated with estuarine circulation, to accumulate in estuaries and coastal marshlands. Evidence that offshore marine sediments are supplying silt and clay to certain coastal marshes along the Connecticut shore has been presented (Ellis, 1962; Hill and Sherin, 1970). However, as the standing crop of excess  $^{210}\text{Pb}$  in the Farm River marsh is almost entirely accounted for by atmospheric deposition, the source of silt and clay now depositing on this salt marsh seems not to be the relatively high specific-activity material present at either the marine or upland surface, but a low-specific-activity material, probably from the subsurface of the watershed.

The general features of the distribution of clay with depth are shown in Fig. 17. Moving from the oldest peat toward the present, we see that the earliest clay accumulation is beyond the reach of reliable  $^{210}\text{Pb}$  dating, but if accumulation is reasonably assumed to have averaged 0.1–0.2 cm  $\text{yr}^{-1}$ , then accelerated deposition must have begun during the 18th century. After a long period of increase, clay content remained high for roughly a century, until the time of the U.S. Civil War. Thereafter, clay

content decreased and remained low until after WWII, when renewed high concentrations began and continued at least to the time of sampling in 1972. These general features of the inorganic-matter distribution are in qualitative agreement with the temporal pattern of sediment-generating processes described by Wolman (1967) and appear to be a record of the variation in erosion taking place on a watershed in response to changing land-use activities. Two-thirds of the naturally forested land of Connecticut was cleared for agriculture between the time of settlement in the 17th century and the Civil War (MacDonald, 1968). This generally corresponds to the interval of high-inorganic-matter content forming the lower clay band at 26–42 cm. The subsequent decrease in inorganic-matter content is probably a result of extensive abandonment of farms following the Civil War.

The change in the percentage of land area devoted to farming in New Haven County is shown in Table XVII. Farm acreage decreased from a high of 87% at the time of the Civil War, to 21% by 1950, and presumably further decreased in subsequent years. In New England, farmland spontaneously reverts to forest (Lutz, 1928), thus reestablishing cover and diminishing erosion.

The increasing inorganic-matter content within the upper few centimeters of peat corresponds to a period of rapidly rising population and urbanization of the watershed. Land-development activities associated with urbanization promote erosion by increasing the rainfall/runoff ratio (Lull and Reinhart, 1972) and by increasing stream velocity in channels adapted to lesser flows (Hewlett and Nutter, 1969). Erosion of soil from the watershed and its transport to the salt marsh was directly observed in the field.

Indeed, salt marshes like the Farm River marsh, which lie adjacent to well-stratified tidal rivers, seem biased to receive soil from upland

TABLE XVII. PERCENTAGE OF NEW HAVEN COUNTY LAND AREA IN FARMS<sup>a</sup>

| Year | Area (%) | Year | Area (%) |
|------|----------|------|----------|
| 1850 | 73.0     | 1910 | 64.3     |
| 1860 | 87.3     | 1920 | 48.8     |
| 1870 | 72.9     | 1925 | 50.6     |
| 1880 | 71.8     | 1930 | 38.9     |
| 1890 | 63.7     | 1950 | 31.2     |
| 1900 | 67.5     |      |          |

<sup>a</sup> Census of Agriculture (1933); U.S. Census (1950).

sources rather than marine sources. This occurs because the runoff flood stage of the Farm River characteristically lasts a matter of days after any substantial rainfall, but the tidal period is only 12 hours, thus the entering salt wedge will repeatedly displace the overlying relatively fresh water above the banks of the tidal channel. As this water and its suspended load overspread the marsh, velocity slackens and suspended matter, strongly biased toward upland sources, is deposited on the surface.

#### 4. SUMMARY AND CONCLUSIONS

Peat from the Farm River salt marsh, an estuarine marsh on the submerging coast of Connecticut near New Haven, was sampled by raising essentially undisturbed, meter-long cores, and was found to record trace-metal deposition from the atmosphere and sediment erosion from the land during the past century.

The activity of  $^{210}\text{Pb}$  and concentrations of Fe, Mn, Cu, Zn, and Pb were measured in contiguous, 2-cm-thick slices of peat. The distribution of excess  $^{210}\text{Pb}$  with depth in the salt marsh, by assuming a constant flux to the surface, is used to estimate the age of sediment at the bottom of each slice. The resulting age-depth relationship was compared to the independent measure of sea-level rise recorded by the New York City tide gauge and was found to be in good general agreement.

The standing crop of excess  $^{210}\text{Pb}$  activity beneath the salt marsh is equivalent to a constant deposition rate of  $1.07 \pm 0.03 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ . This long-term average flux is the same as the total atmospheric deposition of excess  $^{210}\text{Pb}$  measured recently in nearby New Haven and is within 20% of the standing crop of excess  $^{210}\text{Pb}$  found in local upland soil.

These results are considered the best evidence that  $^{210}\text{Pb}$  is quantitatively retained within the salt marsh and is not significantly redistributed after deposition. They also support the idea that stable elements with analogous chemical properties also represent a depositional record.

Fixation of metals as their insoluble sulfides is clearly evident for Fe and is considered the likely method for fixing the other trace metals, except for Mn. The blackened sediment beneath the thin-surface-oxidized layer, the lower  $\text{SO}_4/\text{Cl}$  ratio than that of marine water, and the presence of pyrite frambooids ( $\text{FeS}_2$ ) show that sulfate is actively reduced to sulfide in the salt marsh. No discrete metal sulfides, besides pyrite frambooids, were detected by microprobe examination; however, the simultaneous appearance of  $\text{SO}_4^{2-}$  and trace metals in the interstitial water of cores stored in air suggests that other trace metals may be present as finely dispersed insoluble sulfides.

If Cu, Zn, and Pb are fixed after deposition, then the historical flux of trace metals to the surface may be calculated from the  $^{210}\text{Pb}$  chronology and sediment chemical composition. The flux of excess metals calculated in this way increased from about the time of the Civil War to the present high values. The fluxes observed at the study site fall within the range expected, based on reported measurements of deposition at selected sites, and also agree generally with model calculations based on concentrations reported for the local aerosol. The atmosphere is thus the principal source of  $^{210}\text{Pb}$  and trace metals now being deposited in the salt marsh, and this repository appears to contain a useful record of atmospheric quality over the past century or so. The trace metals in the atmospheric aerosol are no doubt partly of local origin, however, their likely residence time of a few days and the sweep of air masses across the continent requires practically any source in the eastern half of the U.S. to be regarded as a probable contributor.

In the case of Fe and Mn, the atmospheric supply is practically negligible, so terrestrial and/or marine sources must account for most of the Fe and Mn content. On the other hand, the standing crop of excess  $^{210}\text{Pb}$  in the salt marsh is almost entirely accounted for by atmospheric deposition, so the material arriving via the water column apparently contains little or no additional excess activity. Because the excess activity at the surface of both Long Island Sound sediment and the upland soil is relatively high, only material found at much deeper levels (1–2 decimeters) is sufficiently low in activity to act as source of inorganic matter. It is obvious that disturbed soils on the watershed are eroding and that the particulate matter suspended in runoff is deposited on the surface of the marsh during flood tides; indeed, the well-stratified estuary favors terrestrial over marine sources. For these reasons, the origin of the inorganic matter is considered to be upland soil.

The temporal pattern of land use on the Farm River watershed provides a qualitative explanation for the distribution of inorganic matter in the peat. A decline in forest cover due to clearing for agriculture proceeded until about 1865, the end of the U.S. Civil War. This was followed by a period of farm abandonment and intensifying industrial development in neighboring New Haven. Aggravated erosion during the conversion to agriculture was followed by gradual amelioration of erosion during spontaneous reforestation of abandoned farmland. This cycle is believed to have produced the feature recognized as the lower clay band. The recent upper clay band appears to be a consequence of intensive construction activities attendant to development of the watershed as a suburb of New Haven.

The vertical development of the high-marsh surface is governed by vegetative growth, not particle deposition. The extensive, interwoven,

space-filling, resilient roots and rhizomes of the high-marsh grasses deter burrowing by macrofauna and act as a matrix for retention of available, particulate-inorganic matter. The resultant peat has a varying inorganic-matter concentration, but is sufficiently impermeable so that the free-water table of the interior high marsh is usually found only a few centimeters beneath the surface.

A rise in relative sea level will tend to force an offset increase in the mean height of the interstitial water table, which is perched near mean high water. Peat beneath the water table in neutrally buoyant and not measurably compressed. Salt-tolerant grasses in the active-growing zone near the surface are forced by this relative rise in water level to occupy new space, by forming tussocks. The overall result is to track the rise in relative sea level by peat formation.

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## DIAGENETIC PROCESSES NEAR THE SEDIMENT-WATER INTERFACE OF LONG ISLAND SOUND. I. Decomposition and Nutrient Element Geochemistry (S, N, P)

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