THE CYCLING OF MERCURY IN *SPARTINA* MARSHES AND ITS AVAILABILITY TO SELECTED BIOTA

by

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ABSTRACT

A procedure is described for the accurate determination of mercury in fibrous marsh peat. Two dosages of a mercury-containing sewage sludge were added bimonthly for 4 and 7 years, respectively, to duplicate experimental salt marsh plots; and spacial patterns of mercury concentrations, soil organic matter contents, and specific densities were determined. Mercury was retained in the soil of the upper intertidal zone; but was lost (half-life 4 years) from marsh soils adjacent to tidal creeks due to export and dilution processes, rather than chemical or biological transformations. Marsh plants and organisms did not respond to mercury enrichments of the soil, but tissue concentrations increased with decreasing soil organic contents. Natural mercury was very firmly bound by humic compounds, while added mercury remained associated with the sludge. During the decay of Spartina alterniflora, mercury and other trace metal concentrations increased to manyfold those of live plants. These enrichments were controlled by adsorption-desorption processes of mercury complexes adhered loosely to the litter.

RÉSUMÉ

On décrit un procédé pour la détermination précise du mercure dans la tourbe fibreuse de marais. Deux doses de boue d'égout contenant du mercure ont été ajoutées deux fois par mois pendant 4 et 7 ans, respectivement, dans plusieurs zones expérimentalles de marais salins. On decrit les distributions spatialles de concentration en mercure, du contenu organique du sol, et des densités spécifiques. La mercure était retenu dans la tourbe dans la zone des marées hautes; mais était perdu (demi-vie 4 ans) des sédiments des zones inférieures du marais à cause des processus de dilutions et d'entraînement direct, plutôt que par des transformations chimiques ou biologiques. Les plantes et organismes du marais ne réagissaient pas aux enrichissement en mercure du sol, mais les concentrations des tissus augmentaient quand le contenu organique du sol décroîssait. Le mercure naturel était lié très fermement par les composés de terre végétale, tandis que le mercure ajouté restait associé à la boue d'égout. Pendant la décomposition de Spartina alterniflora, les concentrations en mercure et en d'autres traces de metal augmentaient jusqu'à plusieurs fois celles des plantes vivantes. Ces enrichissements étaient contrôlés par des processus d'adsorption-désorption des composés organo-metalliques adhérant lâchement aux plantes mortes.

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PREFACE

This dissertation consists of three papers which have been presented as individual chapters, and which deal with different aspects of mercury cycling in a salt marsh environment. The thesis format conforms to the requirements set out by the Faculty of Graduate Studies and Research in a document titled "Guidelines Concerning Thesis Preparation", which reads as follows:

> MANUSCRIPT AND AUTHORSHIP
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> The candidate has the option, subject to the approval of the Department, of including as part of the thesis the text of an original paper, or papers, suitable for submission to learned journals for publication. In this case the thesis must still conform to all other requirements explained in this document, and additional material (e.g. experimental data, details of equipment and experimental design) may need to be provided. In any case abstract, full introduction and conclusions must be included, and where more than one manuscript appears, connecting texts and common abstract, introduction, and conclusions are required. A mere collection of manuscripts is not acceptable; nor can reprints of published papers be accepted.
>
> While the inclusion of manuscripts co-authored by the Candidate and others is not prohibited for a test period, the Candidate is warned to make an explicit

statement on who contributed to such work and to what extent, and Supervisors and others will have to bear witness to the accuracy of such claims before the Oral Commitee. It should also be noted that the task of the External Examiner is much more difficult in such cases.

Chapter 1 of this dissertation describes the procedure developed for the determination of total mercury in various marsh samples. This chapter further documents the fate of mercury in sludge-treated soils, based on mass balance calculations. Chapter 2 examines the availability of sedimentary mercury to marsh grasses, mussels, and fiddler crabs. This chapter further evaluates some of the mechanisms which control the bioavailability of mercury in a salt marsh system. Chapter 3 deals with the decompositional changes in the concentrations of mercury and five other heavy metals in S. alterniflora, and further elucidates the mechanisms underlying this phenomenon.

The research towards this dissertation was carried out during three years of residence as a guest student at the Woods Hole Oceanographic Insitution in Woods Hole, Massachusetts, under the supervision of Dr. John M. Teal. I made use of existing experimental salt marsh plots laid out in Great Sippewissett Marsh, twelve kilometers north of Woods Hole, which have been treated since 1970 with a mercury and other heavy metals containing fertilizer made from sewage sludge (see Methods in Chapters 1-3).

Measurements of Eh and determinations of heavy metals,

excepting mercury, were performed by students from the Boston University Marine Program at Woods Hole, who carried out these analyses routinely as part of their doctoral thesis research.

Originality

This dissertation is the first study of biogeochemical behavior of mercury in the peaty coastal marshes of the northeastern part of North America. It has considered both the fate of anthropogenic mercury and its availability to plants and animals in the salt marsh. It has further evaluated the natural background concentrations of this element in organisms in relation to environmental parameters.

A unique opportunity for this study existed in Great Sippewissett Marsh in which experimental plots surrounding single drainage creeks had been fertilized with a mercury-containing sludge. The soil enrichments of mercury resulting from these treatments remained unaltered at high marsh elevations, but mercury dissipated from the vegetated low marsh habitats following first-order kinetics with a half-life of about four years. This field observation of mercury dissipation provides a basis for assessing the residence time of this element in sludge-treated wetlands, and is likely to be applicable to other forms of added mercury as well.

This dissertation further discussed the bioavailability of mercury in salt marsh ecosystems under both natural and mercury-contaminated (fertilized) conditions. The contention is made that mercury levels of plants and animals may not

necessarily be related to the total mercury content of the sediments. A careful consideration of the interrelations between mercury speciation, its contents in sediments and biota, and relevant environmental variables may therefore be essential in monitoring and baseline studies. This study demonstrated a further need for such considerations by showing that natural processes are involved in the trace-metal enrichments of plant materials during decay. This phenomenon results in a detritus which has a mercury content higher than that found in live grasses.

Besides providing new knowledge of the behavior of mercury in the salt marshes of the northwest Atlantic coast, the findings have an immediate importance for regulatory agencies in handling problems of mercury contamination of salt marshes, and in implementing decisions concerning the disposal of municipal sewage wastes.

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to Drs. John Teal and Ivan Valiela for the many ways in which they have contributed to this work. They provided me with the opportunity to become part of the "Salt Marsh Project", and it has been a privilege to work with them. As a courtesy to their interest, helpful comments and financial assistance, I have included John and Ivan as junior authors in the three papers of which this dissertation consists. I further gratefully acknowledge Professor Gilles LaRoche, my thesis advisor, for his continuous interest in the research progress and in other matters.

I have benefited from discussions with many students and staff members of the Woods Hole Oceanographic Institution and other laboratories in Woods Hole and elsewhere. The assistance and encouragements of Dr. M.H. Bothner were of great value. Several students, particularly Anne Giblin and Brian Howes, often lent a patient ear and shared aspects of their own work with me. Dr. D.C. Mortimer provided critical insights during a daylong visit at this laboratory, while discussions with Drs. H.L. Windom and W.F. Fitzgerald helped me along the way. The cheerful assistance of Cynthia Wigley, who helped me with field work during the summer of 1978, was much appreciated.

The Woods Hole Oceanographic Institution provided office and laboratory space as well as many other facilities. I thank Dorothea and the late Arnold B. Gifford for allowing me to use

their salt marsh property, and members of the Hackensack Meadowlands Development Commission for their assistance in sampling the Hackensack marshes.

I received financial support from many sources. A cultural scholarship from the Canada Council made it possible to pursue a doctoral degree at McGill University. Furthermore, I received graduate fellowships from the Agricultural University of Wageningen, the Netherlands, the Faculty of Graduate Studies and Research of McGill University, and the ICES/Mercury Foundation of Duke University. Funding for research as well as personal support came from grants from the Victoria Foundation and the Pew Memorial Trust Foundation.

Finally, I would like to acknowledge my mother and two brothers in Holland for their interest and support; and, last but not least, my wife Wendy Nelson for being such a good friend throughout these past four years. Without her my acclimatization to life in the United States would have taken much longer, and the past years would have been less pleasant than they have been.

INTRODUCTION

Sewage contamination is a widespread problem in many coastal areas of North America (Officer & Ryther, 1977). Municipal sewage wastes often contain significant amounts of heavy metals, such as mercury (Klein & Goldberg, 1970; Van Loon, 1971). It is important to be able to assess the fate and effect of anthropogenic mercury inputs in coastal wetlands, as waters adjoining vegetated salt marshes are rich feeding and nursery grounds for large populations of commercially important fish and shellfish.

The retention and dissolution of sediment-bound mercury in the estuarine environment may be controlled by geochemical and microbiological processes. In addition, mercury may dissipate from marsh soils by biophysical and mechanical means, such as surface run off and erosion, bioturbation, biodeposition, and dilution of metal-enriched sediments with uncontaminated materials. Following the discovery that various mercury compounds may be converted into the harmful methylated form (Wood et al., 1968; Jensen & Jernelöv, 1969), biogeochemical processes of this element have been investigated extensively (De Groot et al., 1971; Bothner & Carpenter, 1973; Lindberg et al., 1975; Windom, 1975). To a large extent these studies have focussed on subtidal river and estuarine sediments, and little attention has thus far been given to the intertidal salt marsh system.

Natural background and anthropogenic mercury have been studied in coastal marshes along the southeastern United States by workers from the University of Georgia (Windom ,1973 & 1975; Windom et al., 1976; and Gardner et al., 1978). These marshes are characterized by fine and compact sediments containing relatively large amounts of silt and clay (Duff & Teal, 1965; Windom, personal communication), and pH values as high as 10 (Pomeroy, 1959). In contrast, salt marshes along the northeastern coastline largely consist of fibrous peat, are a rich source of humic compounds and generally have pH values between 5-6.5 (Howarth, 1979). Consequently, a detailed knowledge of the biogeochemical behavior of mercury in these high organic marshes is imparative.

This dissertation had the following objectives: 1) The assessment of the fate and retention of mercury associated with sewage wastes in the vegetated habitats of the marsh environment; 2) The study of the response of marsh grasses and animals to mercury enrichments of the sediments; 3) The elucidation of the environmental variables which control the bioavailability of mercury in the marsh system; 4) The understanding of processes involved in the trace-metal enrichments during the decay of marsh grasses.

The determination of total mercury is currently most widely performed by the flameless atomic absorption spectrophotometric method originally introduced by Hatch and Ott (1968)

and since then modified by several workers. Recent review articles by Reimers et al. (1973) and Ure (1975) critically discussed several of these procedures. Due to the heterogeneous nature of the marsh peat, special attention needs to be given to ensure the representativity of small (< 0.5 gm) samples. The successful breakdown of organo-mercury complexes present in the soil matrix into ionic forms is complicated by the high stability of the mercury-organic matter associations and the volatility of several forms of this element. An additional objective of this study therefore was the development of a reliable procedure for the determination of total mercury, applicable to salt marsh soils, grasses and animals.

The availability of mercury to marsh biota depends on such variables as pH, Eh, temperature, and the mercury binding capacity of the soil. The interrelationships between these closely related variables and their effects on the bioavailability of mercury are still poorly understood. For example, Burton and Leatherland (1971) reported mercury concentrations in shellfish collected from a non-polluted estuary in excess of those commonly found in uncontaminated coastal areas. In the study presented here mercury contents of marsh biota appeared to fluctuate between different marshes independent of their soil mercury concentrations. These findings emphasize the need for clarification not only of natural background concentrations of mercury but also for their relation to critical environmental variables.

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CHAPTER 1

RETENTION AND FATE OF EXPERIMENTALLY ADDED MERCURY IN A MASSACHUSETTS SALT MARSH TREATED WITH SEWAGE SLUDGE

ABSTRACT

A simple, rapid, precise and reproducible procedure is described for sample preparation, extraction and measurement of total mercury in peaty sediments, plants and animal tissues. Various amounts of a heavy metal containing dried sewage sludge were applied to experimental plots in a New England salt marsh. This treatment resulted in elevation of mercury levels in the surface 5 cm of the soil. Discrepancies in the bulk density of marsh sediments corresponded with interparticle spaces and detritus/mineral ratios in the peat matrix. Mass balance calculations showed that wetlands covered with tall Spartina alterniflora lost mercury considerably faster than higher marsh locations which retained virtually all mercury added. The shortest half-life of mercury calculated was four years. Grain size analysis of peat and sewage sludge suggested that mercury in the higher intertidal range remained associated with sludge components. Biochemical and physical processes affecting the dissipation of mercury from creekside sediments are discussed.

INTRODUCTION

Municipal sewage may contain considerable amounts of mercury (van Loon, 1974; de Haan, 1977). Experimental plots in Great Sippewissett Marsh have received dosages of a commercial fertilizer that contains sewage sludge since 1970. This furnishes an opportunity to study the behavior and effects of mercury in the sludge on the sediments and organisms of a salt marsh. In this paper we report on the fate of mercury in these marsh sediments. A subsequent study will deal with the availability of this element to salt marsh biota (Breteler et al., in preparation).

A major problem is the adequate and routine analysis of mercury in sediments of heterogeneous nature. We present here an adaptation and development of methods for the determination of total mercury in environmental samples. The technique presented is accurate, reproducible and applicable for peaty sediments, plants and animal tissues.

METHODS

Characterization of Study Area

Samples were collected during 1977 and 1978 from Great Sippewissett Marsh (Cape Cod, Massachusetts). Circular plots of 10 m radius, drained by a single creek, have been treated with a commercial fertilizer containing sewage sludge from a secondary treatment plant (Kerr McGee Chemical Corporation, Chicago). Two replicate plots received high dosages of this

sludge (HF, 50.4 g/m^2/2 weeks) since 1970, while two additional plots, added in 1974, received extra large dosages (XF, 151.2 g/m^2/2 weeks). In addition, duplicate, untreated plots with similar layout were used as controls. The sludge contained 0.94 $\pm$ 0.05 mg Hg/kg (standard error) and was spread manually during low tides at intervals of two weeks from April to early November. Details of the sludge composition and treatment effects have been presented elsewhere (Valiela et al., 1973, 1974, 1975, 1976; Banus et al., 1974, 1975; Krebs et al., 1974). Levels of mercury in the sludge fertilizer applied after 1976 were less than 3% of the initial mercury concentration. This curtailment of added mercury allowed us to study its rate of release from the marsh surface under natural conditions.

The experimental plots each contained three habitats, characterized by dominant vegetation types. Tall low marsh extended a few meters on each side of the tidal creeks, was flooded twice daily and was covered with a tall form of Spartina alterniflora. Short low marsh contained predominantly a dwarf growth form of Spartina alterniflora and was considered a transitional zone to high marsh, which was covered by tidal water only during spring tides, and dominated by Spartina patens and Distichlis spicata.

Field Sampling and Preparation

Marsh samples were taken from all habitats inside, 0-10 m outside, and away from experimental plots. Plexiglas corers were used to obtain 20 cm cores (6.7 cm diameter) and 5 cm cores (4.75 cm diameter). All 20 cm core samples were kept frozen inside the corer (-20°C) until analysis, extruded after slight

thawing and divided into sections of 0-2, 2-5, 5-10, 10-15 and 15-20 cm. All 5 cm cores were extruded immediately into whirl-pak bags and frozen upon returning to the laboratory until analysis. Sediments were oven-dried (50°C, overnight), pulverized with a glass mortar and pestle, and sieved through a 1 mm mesh sieve. The coarser fraction was ground in a Wiley mill and mixed with the finer fraction, unless tha sample contained coarse inorganic materials which were not adequately ground by the mill. In this case heavier particles were separated by placing the sample in a 600 ml glass beaker held inside a 1 l beaker. The larger beaker was closed off with a plastic lid equipped with a movable pipe through which a stream of air was directed at the sample. The air pressure was adjusted to blow lighter particles from the heavier fraction. Coarse, inorganic sediments containing mostly mercury-free minerals were weighed and discarded.

Soil Analyses

Organic matter was measured by combustion of oven-dried (110°C) samples at 500°C for 4 hours. Freeze-dried peat samples were seived over a set of five screens (USA Standard Sieve Series), stacked and shaken overnight on a gyratory shaker to obtain particle size fractions of 0-0.063, 0.063-0.125, 0.125-0.25, 0.25-0.5, 0.5-1.0 and > 1.0 mm.

Analysis of Total Mercury

Glassware used for the digestion of samples was washed and brushed clean with Alconox detergent, soaked in a saturated

$K_2Cr_2O_7$ in 8N HNO_3 solution, and rinsed with concentrated HNO_3 and several rinses with deionized water (18 megaohms/cm resistivity).

The procedure used for the digestion and measurement of mercury was based upon modifications of methods described by Agemian & Chau (1976), Iskandar et al. (1972), and Ure & Shand (1974). All reagents used were certified grade, used without further purification. A sample between 0.1 and 0.5 g, depending upon the expected mercury concentration, was weighed into a 125 ml ground-glass stoppered Erlenmeyer flask, and 5 ml deionized water and 0.03 ml anti-foaming agent (tributylphosphate) were added. Next, a mixture of 20 ml concentrated H_2SO_4/HNO_3 (2:1) was slowly added, the flask was stoppered, placed in a gyratory water-bath shaker and gently rotated for 2 hours at 70°C. The sample was cooled, diluted with 30 ml deionized water, cooled again and oxidized overnight with 20 ml 6% $KMnO_4$. Next, 30 ml deionized water, and 5 ml 10% $NH_2OH.HCL$ were added. Precipitated MnO_2 was dissolved by gentle manual swirling of the flask and leaving it unstoppered for several hours.

An aliquot of 25 ml was pipetted into a 250 ml round-bottom ground-glass flask, to which an egg-shaped Teflon-covered stirring bar had been added. Next, 5 ml 20% $SnCl_2$ dissolved in 6N HCl was added and the flask quickly closed with an impinger stopper fitted with a four-way valve. The contents of the flask were stirred at maximum speed and splashing for 2 min to allow complete partitioning of reduced mercury between liquid and

air phase (Ure & Shand, 1974). The four-way valve was turned to allow the nitrogen flow (0.7 l/min) to sweep the mercury vapor through the drying cell (anhydrous $Mg(ClO_4)_2$) into an atomic absorption spectrophotometer (mercuryMonitor, Model 1235, Laboratory Data Control). The resulting response was recorded on a strip chart recorder at 10 mV (chart speed 3cm/min). The reduction flask and pipet were rinsed with deionized water prior to the next measurement to prevent cross contamination. Ten samples could be processed in one hour.

Calibration

A matrix effect was observed in the blank solutions containing all chemicals. Peak absorption of these blanks spiked with mercury were consistently lower than similar spikes in deionized water. Standards were therefore obtained from blanks spiked with aliquots from a freshly prepared 1 ppm Hg solution. No difference was noted between blanks spiked prior to the digestion phase or just before measurement. A linear regression of the standard curve ($r > 0.999$) was used to calculate mercury in samples.

The precision and accuracy of the method was checked by analyzing a reference material (NBS No. 1571) in ten consecutive runs. The mean value 153 $\pm$ 19 ng Hg/g compared well with the certified value (155 $\pm$ 15 ng Hg/g; 2 S.D.). Recovery of 200 ng Hg spikes from $HgCl_2$ and HgS to this material was 99% and 86% respectively. The lower detection limit, calculated as 2 S.D.

above the mean blank value, was 10 ng Hg/dry sediment.

RESULTS

Sediment Characterizations

Vegetated creekbank sediments (0-5 cm) in Great Sippewissett Marsh had significantly lower amounts of organic matter than sediments found in the higher intertidal zones (Table 1). The percentage organic matter and specific densities (g/cm^3) of surface sediments were not significantly elevated in any of the habitats (Students t-test, $p > 0.1$), and we therefore did not distinguish between control, HF, and XF treated sediments with respect to these variables. The specific gravity of salt marsh sediments, reflecting the lower weight of organic matter relative to the mineral fraction, was significantly lower in short low and high marsh than in tall low marsh habitats. Variations of this kind are commonly found in salt marsh sediments (Cotnoir, 1974).

In 20 cm cores the surface 0-2 cm showed a statistically significant higher organic matter content compared to the deeper layers. Bulk densities decreased with increasing depths (Table 2). To better understand this trend, replicate samples of freeze-dried, sieved (1mm mesh) peat obtained from various depths in the surface 20 cm were compressed inside a glass syringe to a total volume of 5 cm^3, weighed and analysed for ash-free organic matter content. Uniform compression of this spongy material was attained by maximizing the manual pressure

TABLE 1

PERCENT ORGANIC MATTER (MEAN ± STD. ERROR) AND SPECIFIC DENSITY (MEAN ± STD. ERROR, G/CM^3) IN SURFACE (0-5) SEDIMENTS OF DIFFERENT SALT MARSH HABITATS. VERTICAL LINES JOINING THE MEANS INDICATE NO SIGNIFICANT DIFFERENCE AMONG THOSE MEANS (STUDENT-NEWMAN-KEULS TEST) AT THE 0.05 LEVEL.

	N	*Organic matter (%)*	*Specific density (g/cm^3)*
Tall low marsh	52	41.1 ± 1.45	0.244 ± 0.009
Short low marsh	44	50.5 ± 1.54	0.212 ± 0.008
High marsh	36	54.6 ± 1.42	0.207 ± 0.008

TABLE 2

PERCENT ORGANIC MATTER (MEAN ± STD. ERROR N=4) AND SPECIFIC DENSITY (MEAN ± STD. ERROR, G/CM^3) AT INTERVALS OF DEPTH IN SURFACE (0-20 CM) SALT MARSH SEDIMENTS. VERTICAL LINES JOINING THE MEANS INDICATE NO SIGNIFICANT DIFFERENCE AMONG THOSE MEANS (STUDENT-NEWMAN-KEULS TEST) AT THE 0.05 LEVEL.

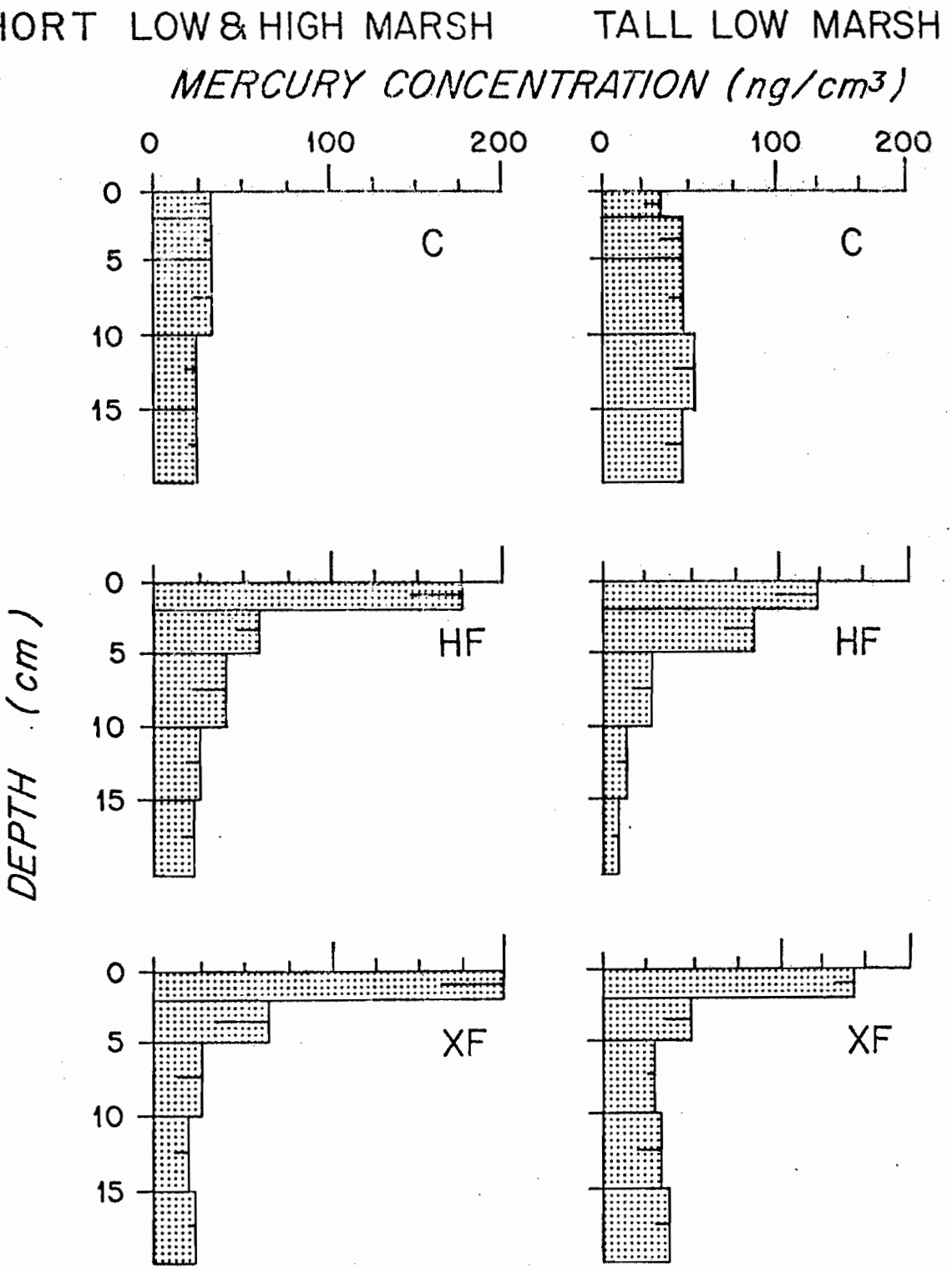
Depth (cm)	*Organic matter (%)*	*Specific density (g/cm^3)*
0-2	44.8 ± 2.9	0.266 ± 0.023
2-5	50.4 ± 2.3	0.223 ± 0.064
5-10	52.9 ± 3.1	0.185 ± 0.053
10-15	53.1 ± 3.2	0.175 ± 0.051
15-20	56.1 ± 2.4	0.145 ± 0.042

applied to the plunger (coefficient of variation 1%). This experiment showed that the specific density of these sediments at any depth was determined primarily by differences in the interstitial volumes and to a lesser extent by the relative amounts of organic matter and minerals. The heterogeneous nature of marsh peat makes comparisons of trace constituents between marshes difficult. In this study we chose to convert mercury concentrations to g Hg/cm^3 and g Hg/m^2 units.

Possible differences in the added amounts of applied fertilizer were examined by comparing the weight percentages of acid-soluble (0.5 N HCl) sludge constituents in the sediments of different marsh habitats. Since approximately equal amounts of these components were recovered throughout the treated marsh plots, discrepancies in residual Hg contents of various habitats were attributed to factors other than discrepancies in the fertilization treatments.

Vertical Profile of Mercury

The sewage sludge additions increased the concentration of mercury in the 0-5 cm layer of the marsh soil (Figure 1). No significant differences (one-way analysis of variance, $p \geq 0.25$) were found in the mercury contents of subsurface (5-20 cm) control, HF, or XF treated sediments. Discontinuities in the mercury concentration profiles occasionally found at various depths could be attributed to anomalous detritus/sand ratios. Increased concentrations in the surface sediments of fertilizer-treated plots were more pronounced in higher intertidal habitats than


SHORT LOW & HIGH MARSH
TALL LOW MARSH
MERCURY CONCENTRATION (ng/cm³)
0
100
200
0
5
10
15
C
HF
XF
DEPTH (cm)

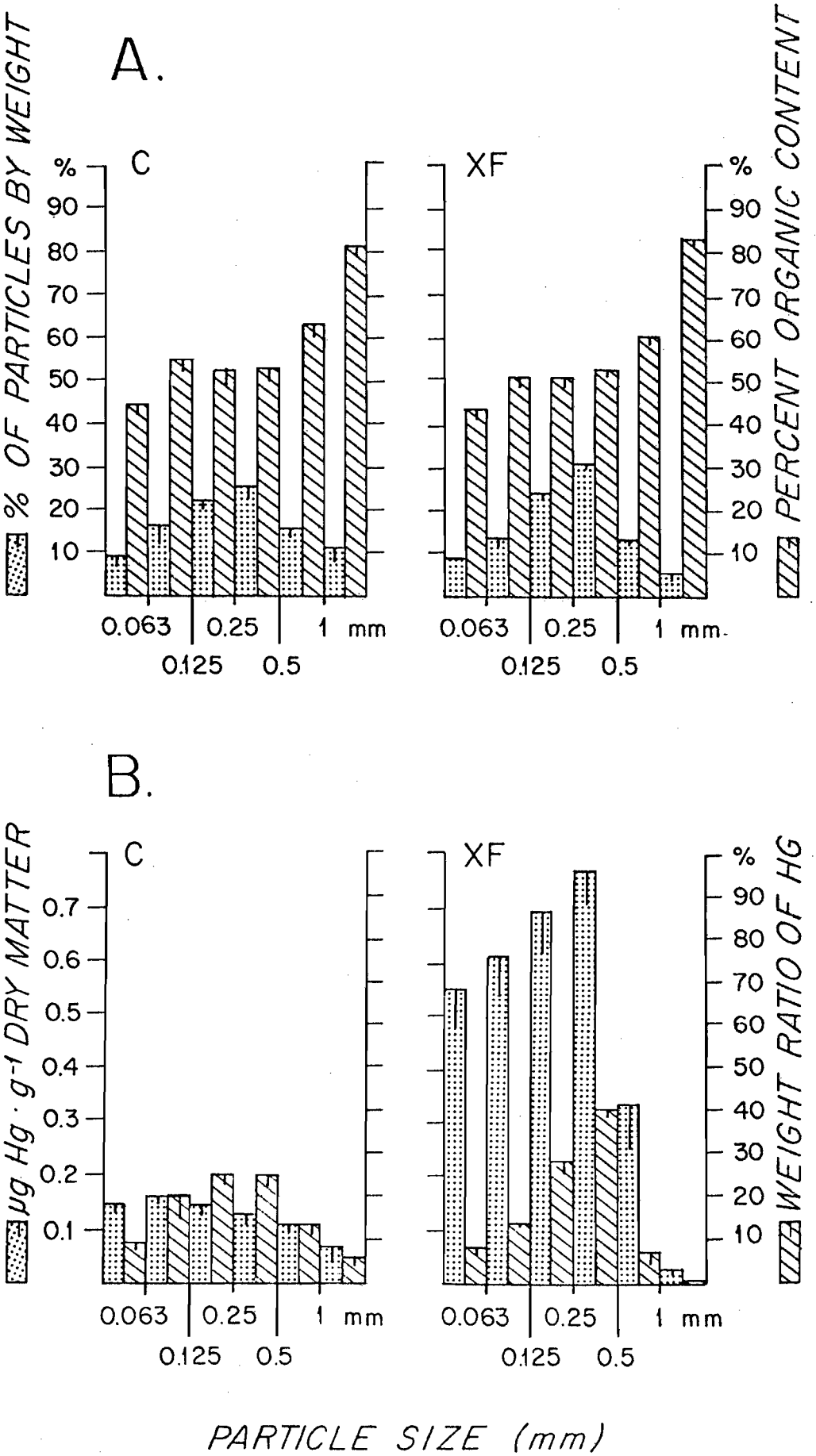
in low marsh zones. Further quantification of this observation, discussed below, indicated that a loss of mercury had taken place from this latter marsh region.

Particle Size Fractionations

Peat from Great Sippewissett Marsh consisted primarily of decaying Spartina grass. The weight % abundance of particle size fractions in these sediments peaked between 0.25-0.5 mm (Figure 2^a). The fraction > 1mm contained translucent live as well as dead roots and rhizomes. This larger material was mainly organic and contained the least amount of mercury (Figure 2^b). Smaller particles consisted mostly of plant detritus with a minor component of algal and animal detritus and occasionally mixed with minerals. The increase in mercury in sludge-treated sediments was limited to particles smaller than 1 mm and was maximal in the 0.25-0.5 mm fraction, which contained 41% of the total sedimentary mercury (Figure 2^b).

Particles of decreasing size contained significantly less organic matter ($r^2 = 0.77$; $p < 0.002$). Since the state of decomposition of detritus is directly proportional to particle size (Fenchel, 1970), this relationship suggested that mercury was progressively concentrated during the breakdown of Spartina grass. This finding agreed with results obtained for above-ground tissues of these plants (Breteler et al., in preparation).

In Figure 3 the weight percentages and mercury concentrations of particle size fractions have been plotted against

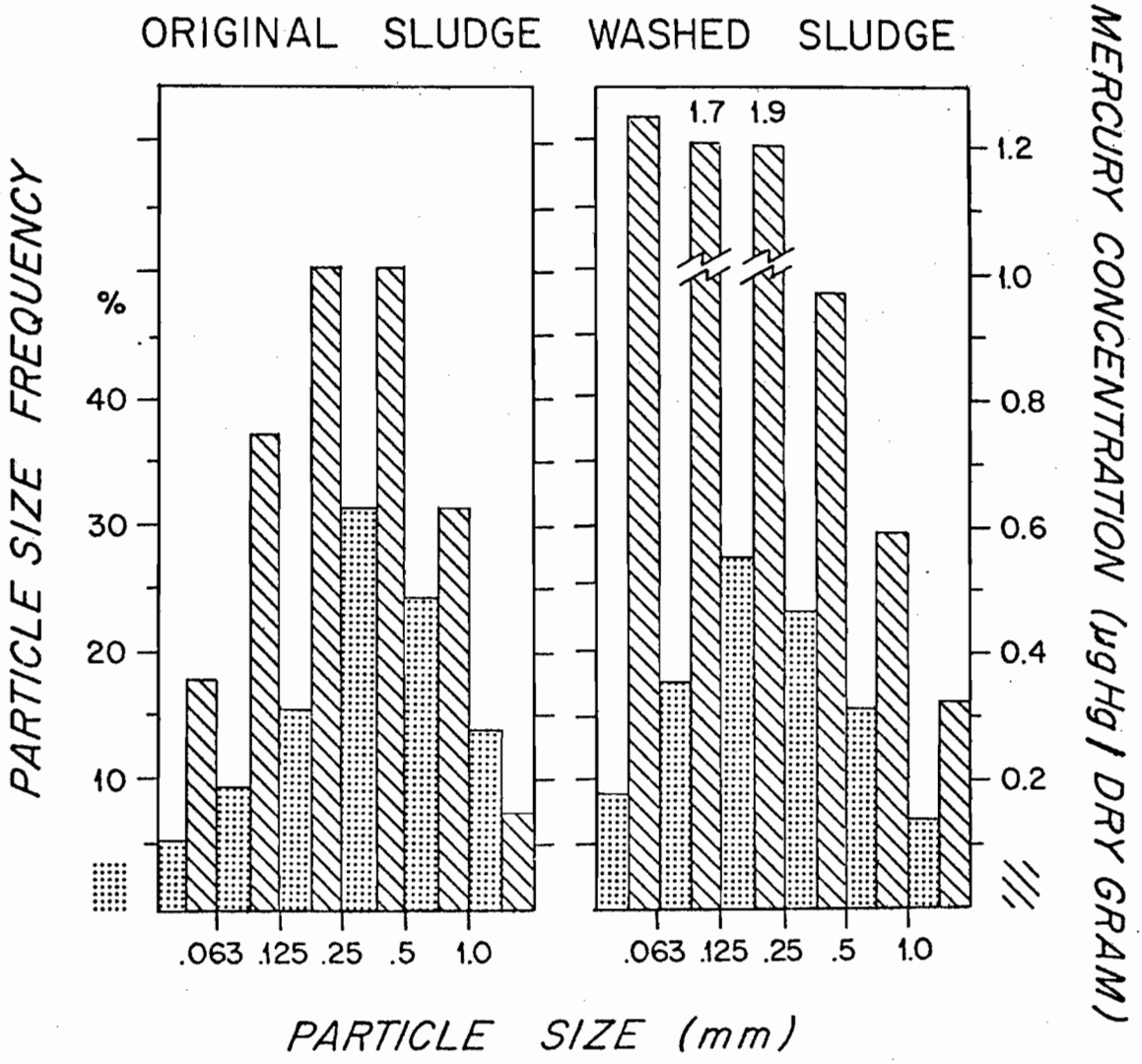

A.
C
XF
% OF PARTICLES BY WEIGHT
PERCENT ORGANIC CONTENT
%
90
80
70
60
50
40
30
20
10
0.063
0.125
0.25
0.5
1 mm
B.
µg Hg · g⁻¹ DRY MATTER
WEIGHT RATIO OF HG
0.7
0.6
0.5
0.4
0.3
0.2
0.1
PARTICLE SIZE (mm)

particle sizes for representative samples of original, i.e. untreated sludge fertilizer. A portion of this fertilizer was also washed with deionized water to simulate natural weathering of this material on the marsh surface. The degradation of organic agglomerates and dissolution of water-soluble fertilizer components resulted in a sharp increase in the mercury concentration of smaller size particles (Figure 3).

From the data presented in Figures 2 and 3 we computed the mercury concentrations of particle size fractions in extra high fertilized, 0-5 cm marsh sediments. We used realistic weight portions of fertilizer and sediments and compensated for the degradation of the sludge by taking 7 parts original and 3 parts washed fertilizer. Using this ratio a very close resemblance of calculated mercury concentrations and measured values resulted in all size ranges below 1 mm. From this we concluded that the transfer of mercury from the sludge to marsh sediments had been negligible, inferring that desorption-adsorption processes are unlikely to play an important role in the deminution of mercury in sludge-treated salt marsh sediments.

Mercury Budget in Experimental Plots

Mercury concentrations in high fertilized (HF) and extra-high fertilized (XF) marsh sediments were significantly higher


ORIGINAL SLUDGE
WASHED SLUDGE
PARTICLE SIZE FREQUENCY
%
40
30
20
10
1.7
1.9
1.2
1.0
0.8
0.6
0.4
0.2
.063
.125
.25
.5
1.0
PARTICLE SIZE (mm)
MERCURY CONCENTRATION (µg Hg / DRY GRAM)

than values found outside these experimental plots (Table 3). The concentrations inside XF plots exceeded those of HF plots in all marsh habitats, while the mercury content of tall low marsh was considerably less elevated than that of sediments higher in the intertidal range. Analysis of variance of the mean mercury concentrations of sediments outside the XF-treated plots as well as the control plots in the three marsh habitats showed that a significant increase in mercury had taken place in the tall low marsh region exclusively (Student-Newman-Keuls test for 6 means, $p<0.05$). This result suggested a lateral loss of mercury from creekside sediments consistent with the considerable dissipation of mercury from sludge-treated tall low marsh sediments.

Table 4 presents the complete balance sheet for mercury in HF and XF plots. Mercury concentrations inside these plots were based upon measurements two years after the original sludge fertilizer had been replaced by a material containing only 0.03 mg Hg/kg dry fertilizer. The mean sludge Hg concentration presented in Table 4 for HF plots was based on the average concentration of this sludge after 1979, although sludge used in earlier years had been obtained from the same source. The residual mercury in HF and XF plots (Table 4) were computed from data from Table 3. The amount of mercury remaining in the 0-5 cm sediments over a period of two years following curtailment of this element, was highest in the higher intertidal ranges of the treated plots

TABLE 3

MERCURY CONCENTRATION (MEAN ± STD. ERROR, MG Hg/ M^2) IN 0-5 CM SEDIMENTS OF SALT MARSH HABITATS IN EXPERIMENTAL PLOTS RECEIVING EXTRA HIGH (XF) AND HIGH (HF) DOSAGES OF DRIED SEWAGE SLUDGE, AS WELL AS IN SEDIMENTS LESS THAN 10M OUTSIDE XF PLOTS, AND IN CONTROL PLOTS. MEAN VALUES ARE BASED ON 7-20 SAMPLES.

	Mercury concentration (mg Hg/ m^2)		
	Tall low marsh	*Short low marsh*	*High marsh*
Inside XF plots	4.05 ± 0.42	6.96 ± 0.74	6.41 ± 0.45
Inside HF plots	3.79 ± 0.55	6.12 ± 0.46	6.04 ± 0.50
Outside XF plots	1.73 ± 0.15	1.11 ± 0.09	1.29 ± 0.09
Control plots	1.21 ± 0.11	0.99 ± 0.06	1.09 ± 0.09

TABLE 4

MASS BALANCE OF MERCURY IN A SALT MARSH CONTAINING DUPLICATE EXPERIMENTAL PLOTS (10 M RADIUS), TREATED BI-WEEKLY (APRIL-NOVEMBER) WITH VARYING AMOUNTS OF A DRIED SEWAGE SLUDGE.

	XF Treatment	*HF Treatment*
Years of treatment	1974 - 1976	1970 - 1976
Total sludge input	6.19 kg/m^2	4.82 kg/m^2
Concentration of Hg in sludge ($\pm$ 2 SE)	0.94 $\pm$ 0.09 mg Hg/kg	0.94 mg Hg/kg
Hg input during each application	0.142 mg Hg/m^2/ 2wks.	0.047 mg Hg/m^2/ 2wks.
Mean annual Hg input	1.94 mg Hg/m^2	0.65 mg Hg/m^2
Total Hg input	5.82 mg Hg/m^2	4.53 mg Hg/m^2
Residual Hg in:		
Tall low marsh	2.84 mg Hg/m^2	2.58 mg Hg/m^2
Short low marsh	5.97 mg Hg/m^2	5.13 mg Hg/m^2
High marsh	5.32 mg Hg/m^2	4.95 mg Hg/m^2

which retained virtually all Hg added. In contrast, only 50% of residual mercury was left in the tall Spartina zone.

Clearance Rate of Mercury from Contaminated Marsh Sediments

Assuming that the mercury loss from the enriched marsh surface was proportional to the residual mercury concentration (Bothner et al., in press) we calculated the mercury concentration in sediments in 1976 by adding the annual input I and subtracting a fraction r of the total residual mercury at the end of each experimental year. For example, the residual mercury concentration (RC) at the end of the first year of treatment (RC_{1970} in HF plots; RC_{1974} in XF plots) was I - rI, that of the following year: (I - rI) + I - r(2I - rI), etc. Carrying out this task and collecting terms, neglecting power values larger than three, a polynomial function of the form

$$RC_{1976}, XF = 3I - 6rI + 4r^2I - r^3I \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

resulted for XF plots. For HF plots, started in 1970, the function obtained the form

$$RC_{1976}, HF = 7I - 28rI + 56\ r^2I - 70\ r^3I \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Similarly, but taking the added mercury after 1976 as zero, the polynomials for 1978 took the form

$$RC_{1978}, XF = 3I - 12rI + 19r^2I - 15\ r^3I \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and

$$RC_{1978}, HF = 7I - 42rI + 119r^2I - 210r^3I \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Inserting I and RC_{1978} values from Table 4, the annual

clearance rates (r) were computed for tall low marsh habitats (r_{XF} = 0.166 ± 0.030; r_{HF} = 0.089 ± 0.033). Because a negative r-value is nonsensical, clearance rates were taken as zero for all other marsh habitats, inferring that export of mercury from higher intertidal zones had been negligible.

The general differential equation for first-order reactions

$$C_t = C_o \cdot e^{-rt} \quad \text{.....(5)}$$

with C_t = background mercury concentration

C_o = total sedimentary mercury in 1976

r = clearance rate

t = clearance time (in years)

was used to describe the mercury loss from the lowest Spartina region. The estimated time required for the dissipation of all added mercury was thus 9-14 years, and the half-life of mercury ($C_t = \frac{1}{2}C_o$) 4 ± 1 and 8 ± 3 years for XF and HF plots respectively. These values, obtained from replicate plots receiving varying amounts of mercury during 4 respectively 7 years agreed within precision. An additional check for the validity of the above calculations was provided by the mean mercury concentration of 8 tall low marsh cores obtained in 1977 from XF plots (4.7 ± 0.5 mg Hg/m^2). This value agreed favorably with the calculated concentration of 4.5 mg Hg/m^2 for that year, obtained from equation 5 for t=1.

DISCUSSION

The release rate of mercury from salt marsh sediments depends on the geochemical properties of the forms in which this element is present. Experimental results showed that mercury had not dissociated from the sludge, and that this element was present in the marsh mainly in highly stable organo-metallic complexes (Breteler et al., in preparation), although the presence of mercuric sulfide was not excluded. Unfortunately, no reports of studies dealing specifically with the rate of mercury loss from marsh sediments were found in the literature. However, several references are available for coastal and marine sediments. For example, Bothner et al. (in press) calculated a half-life of 1.3 years in the mercury-enriched estuarine sediments of Bellingham Bay (Washington). Comparison with the half-life reported by us of 4 years, which was the most reliable estimate, is not very realistic because of the large differences in the natural chelating capacity of the estuarine and marsh environments. Nevertheless, mercury is eliminated from tall low marsh at almost the same rate as from estuarine sediments. In contrast, mercury is completely retained by the marsh at higher intertidal elevations.

These differences may be explained by one or more of the mechanisms by which mercury may be lost from sediments. These include: (1) adsorption-desorption processes; (2) biological transformation processes; (3) bioaccumulation, followed by

migration of organisms or export of dead grasses; and (4) physical removal processes.

Aspects of chemical desorption processes leading to the mobilization and transfer of mercury from the sediments have been discussed by many workers. Mercury mobilization as an organo-metallic complex has been proposed as an effective mechanism of solubilization of sediment-bound mercury in river systems (de Groot et al., 1971; Cline et al., 1973). However, mercury present in the river sediment-water interphase may be of a more readily exchangable form, or may be associated largely with humic and fulvic acids. In contrast, mercury in the marsh is firmly bound by humic compounds insoluble in acid and base solution (Breteler et al., in preparation). Khalid et al. (1977) studied the release of mercury from Mississippi River sediments under controlled pH and redox conditions and concluded that these parameters greatly influence the rate of exchange of mercury between sediments and water. These results were in accordance with the findings of Kudo et al. (1975) and Bothner et al. (in press), who noted a more rapid release from reducing sediments than from oxidizing sediments. By contrast, mercury was almost entirely retained at higher marsh elevations which were considerably more reduced than the low intertidal sediments (Howes et al., in preparation). Differences in the retention of mercury between low and high intertidal sediments are therefore not well explained by geochemical processes.

The biological formation of methylmercury from various forms of mercury in aquatic sediments has been widely recognized

as a means of mercury loss from contaminated sediments, both in aquatic systems (Ramamoorthy et al., 1977; Colwell et al., 1976; Bisogni et al., 1975; Olson & Cooper, 1974; Jacobs & Keeney, 1974; and Langley, 1973), and in terrestrial soils (Landa, 1978; Rogers, 1976; and Beckert et al., 1974). Of interest in this respect is the finding that the volatile loss of mercury is greatly enhanced when sediments are alternatively exposed to air and water (Fagerstrom & Jernelov, 1972). These results suggest a high potential loss of mercury from the periodically flooded marsh sediments. Moreover, Olson & Cooper (1976) found reducing conditions to be more favorable for the production of methylmercury than oxidizing conditions. Yet, the reducing higher marsh sediments did not release measurable amounts of mercury over a seven year period. One possible explanation is that the abundance of organic matter in the marsh reduces the availability of mercury for methylation (Hamdy et al. 1977). Although concentrations of methylmercury are extremely low in salt marsh sediments (Andren & Harriss, 1973; and Windom et al., 1976), and in situ production has not been reported in the literature, its presence in certain marsh organisms has been attributed to its formation in the sediments (Gardner et al. 1978). Overall, microbial transformations of mercury into water soluble or volatile forms can not adequately explain the loss of mercury from the low intertidal marsh. Neither does the uptake of mercury by marsh grasses and animals explain these losses, since the measured concentrations in biota were too low

to account for the diminution of mercury (Breteler et al., in preparation).

Erosional loss of creekside sediments is an infrequently occurring phenomenon, occasionally observed during severe winters due to ice rafting. Of more general importance however, is the loosening of marsh sediments by the stirring activities of mussels and fiddler crabs inhabiting these habitats. Thus, enriched sediments can be exported with the tides. In addition, gradual dilution of the sediments with new materials takes place during the accretion of the marsh. Richard (1978) measured an accretion rate of 2-4 mm/year in tall S. alterniflora habitats. Although the marsh build-up may be less rapid in Great Sippewissett Marsh, the dilution of the sludge waste components with uncontaminated materials could nonetheless constitute an important mechanism by which mercury concentrations drop in tall low marsh sediments. The high bioturbation activity in this habitat may further contribute to this process. Reimers & Krenkel (1974) and Bothner (1973) proposed that mercury transport in river and estuarine systems takes place largely by physical transport of inorganic and organic constituents enriched in mercury. This same mechanism, coupled with the dilution process, may be of equal importance to the dissipation of sediment mercury in the salt marsh system.

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CHAPTER 2

THE AVAILABILITY OF MERCURY TO SALT MARSH ORGANISMS

ABSTRACT

mercury concentrations were measured in sediments, marsh grasses, mussels, and fiddler crabs in salt marsh plots treated with a mercury-containing commercial sludge fertilizer and in clean and industrially contaminated marshes. Mercury accumulated in the roots of the marsh grass Spartina alterniflora, rather than in rhizomes or above-ground tissues. Mercury concentrations did not increase in marsh organisms within the plots treated with sewage sludge. Highest concentrations of mercury were found in animals living in the least organic marsh sediments. Mercury was closely associated with small (<0.5 mm) detrital particles. Only between 10 and 30% of the total soil mercury was complexed by the humic and fulvic acid fraction of the marsh soil.

INTRODUCTION

In recent years the discharge of mercury compounds to the coastal environment has led to an increase in concentrations of mercury in sediments in a number of salt marshes along the east coast of the United States.

The release of mercury from these sediments depends on a wide range of biological and chemical factors, including its chemical form (Hogg et al., 1978a), the presence of organic soil colloids (Cline et al., 1973; Alberts et al., 1974; Miller et al., 1975), physical turbidity processes (Bothner et al., in press), reduction-oxidation potentials (Kudo et al., 1975; Khalid et al., 1977) and chlorinity (Reimers and Krenkel, 1974). This sedimentary mercury may become available for uptake by coastal organisms, resulting in elevated levels of this element in body tissues (Klein & Goldberg, 1970; Burton & Leatherland, 1971; Jones et al., 1972; Fujiki, 1973; Windom et al., 1976; and Gardner et al., 1978).

The mercury concentration of organisms is not necessarily related to the total soil mercury concentration but rather to the form of this metal in the sediments. The role of the biological formation of methylmercury in the transfer of this element from sediments to biota has been widely recognized (see e.g. Bisogni & Lawrence, 1975). Additional factors, such as the species-specific regulatory mechanisms (Bryan, 1976), age and body weight (Cross et al., 1973) have been discussed. To date, little attention has been given to the effect of the sediment itself on the availability of

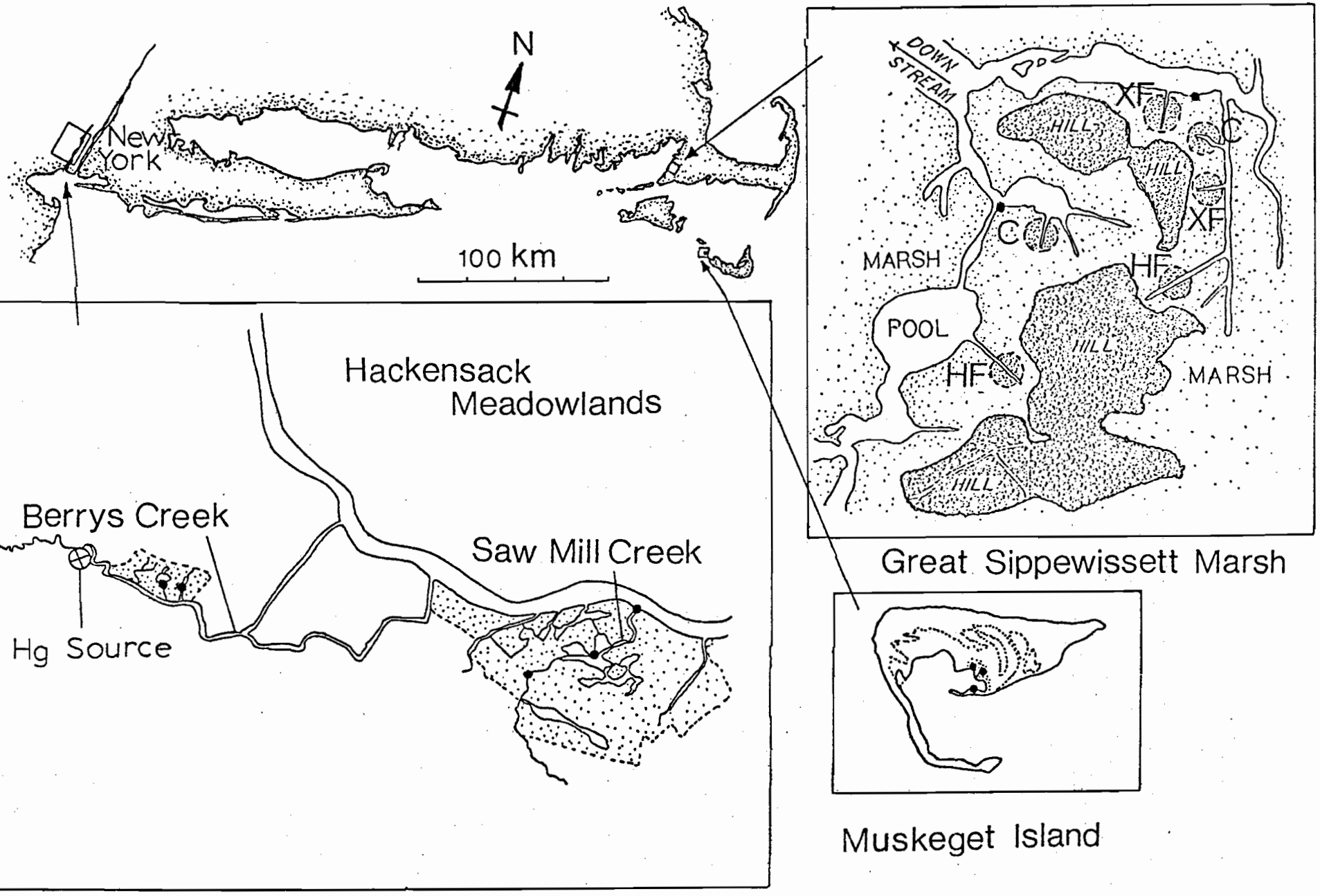
soil-bound mercury to biota.

In this report we present data of mercury concentrations in plants and organisms from salt marsh plots experimentally treated with mercury and from marshes where heavy industrial pollution provided mercury for long periods. In addition, we assess the effects of the organic content, soil texture, pH, and reduction-oxidation potential (Eh) of the sediment on the availability of mercury to marsh organisms and plants. The long-term fate of mercury in a salt marsh environment as well as the retention capacity of marsh soils for this element are discussed elsewhere (Breteler et al., in preparation).

EXPERIMENTAL

Duplicate experimental plots with a radius of 10 m were laid out in Great Sippewissett Marsh (Figure 1). These plots were treated throughout the growing season (April-November) with a fertilizer made from a metal-containing sewage sludge with an approximate mercury content of 1 ppm. This material was spread by hand twice monthly during low tide at two levels: 50.4 g/m^2 (HF plots) and 151.2 g/m^2 (XF plots). Two additional untreated plots were maintained as controls (C). Further details of the procedures used and the treatment effects are given in Valiela & Teal (1974), Valiela et al. (1973, 1974, 1975, 1976, 1978), Banus et al. (1974, 1975), Giblin et al. (in press), and Breteler et al. (in preparation).

Figure 1. Study areas in Great Sippewissett Marsh (C = control marsh; HF = high fertilized marsh plots; XF = extra high fertilized marsh plots), Muskeget Island Marsh, and the Saw Mill Creek and Berrys Creek Marshes in the Hackensack Meadowlands.Solid circles indicate sampling stations.


N
New York
100 km
Hackensack
Meadowlands
Berrys Creek
Saw Mill Creek
Hg Source
DOWN STREAM
XF
HILL
C
MARSH
HF
POOL
Great Sippewissett Marsh
Muskeget Island

Samples for this study were taken during 1977 and 1978 from Great Sippewissett Marsh (Cape Cod, Massachusetts)(Figure 1). Both marshes were dominated by the marsh cord grass Spartina alterniflora Loisel., but differed in makeup of the sediments. The sediments of Muskeget marshes were light textured, contained a large component of coarse sand, and were oxidized. Surface sediments from Great Sippewissett Marsh were finer grained and highly organic, contained only a minor component of sand or silt, and were oxidized along the creeksides but reduced at higher intertidal elevations. Samples were also obtained from two marshes in the Hackensack Meadowlands (New Yersey), which have for many years received discharges of mostly elemental mercury from industrial sources. Berrys Creek Marsh (3-9‰ salinity) and Saw Mill Creek Marsh (9-15‰ salinity) were situated 2 and 10 km downstream of the principal source of mercury respectively (Figure 1). While both marshes were dominated by Phragmites communis, all samples for this study were collected from patchy stands of tall S. alterniflora.

Fiddler crabs (Uca pugnax and U. minax) from all marshes, and mussels (Modiolus demissus), collected from the Massachusetts marshes, were rinsed with tap water on return to the laboratory. Mussels were shucked immediately, and 3-5 crabs and mussels were pooled, frozen, freeze-dried, and ground with glass mortar and pestle. Whole plants of S. alterniflora were cut from isolated stands bordering on or in tidal creeks from the Hackensack and Great Sippewissett marshes, rinsed with tap water, and divided into roots, rhizomes, culms, leaves, and flowers. Ten plants were used for each sample. They were oven-

dried (50°C, overnight) and ground in a Wiley mill. Sediments were collected from the same sites as the grasses and invertebrates. They were stored frozen, freeze-dried, and subsamples were used for the determination of organic matter by weight loss on ignition (4 h at 500°C) and total mercury.

Details of the analytical procedure used for mercury determinations are described elsewhere (Breteler *et al.*, in preparation). The analytical uncertainty (2 SD) was less than 10% of mean peat values and 5% for biological samples. To evaluate the loss of mercury due to pretreatment procedures we analyzed replicate subsamples before any pretreatment (wet), after freeze-drying, oven-drying, and after freeze-drying and grinding. These three ways of handling samples did not result in significant differences in mercury contents. Redox potentials were measured *in situ* during low tide, using a bare platinum electrode and an $Ag/AgCl_2$ reference after equilibration for 15 min. pH was measured in core samples with a glass electrode and separate reference.

Marsh sediments were extracted with 0.5 N NaOH, 0.5 N HCl, and 6 N HCl, respectively. Approximately 5 g of a sieved (0.5 mm mesh), washed and freeze-dried soil sample, obtained by pooling three 0-5 cm surface cores, was mixed with 100 ml of the extractant in 150 ml Corex glass centrifuge tubes, shaken overnight, centrifuged (15,000 × g for 1 h), and the supernatant decanted. Solids were washed with deionized water, freeze-dried and weighed. The treated sediments were analyzed for total mercury content. Subsamples of the extracted material were used for the determination of wet/dry ratios and organic

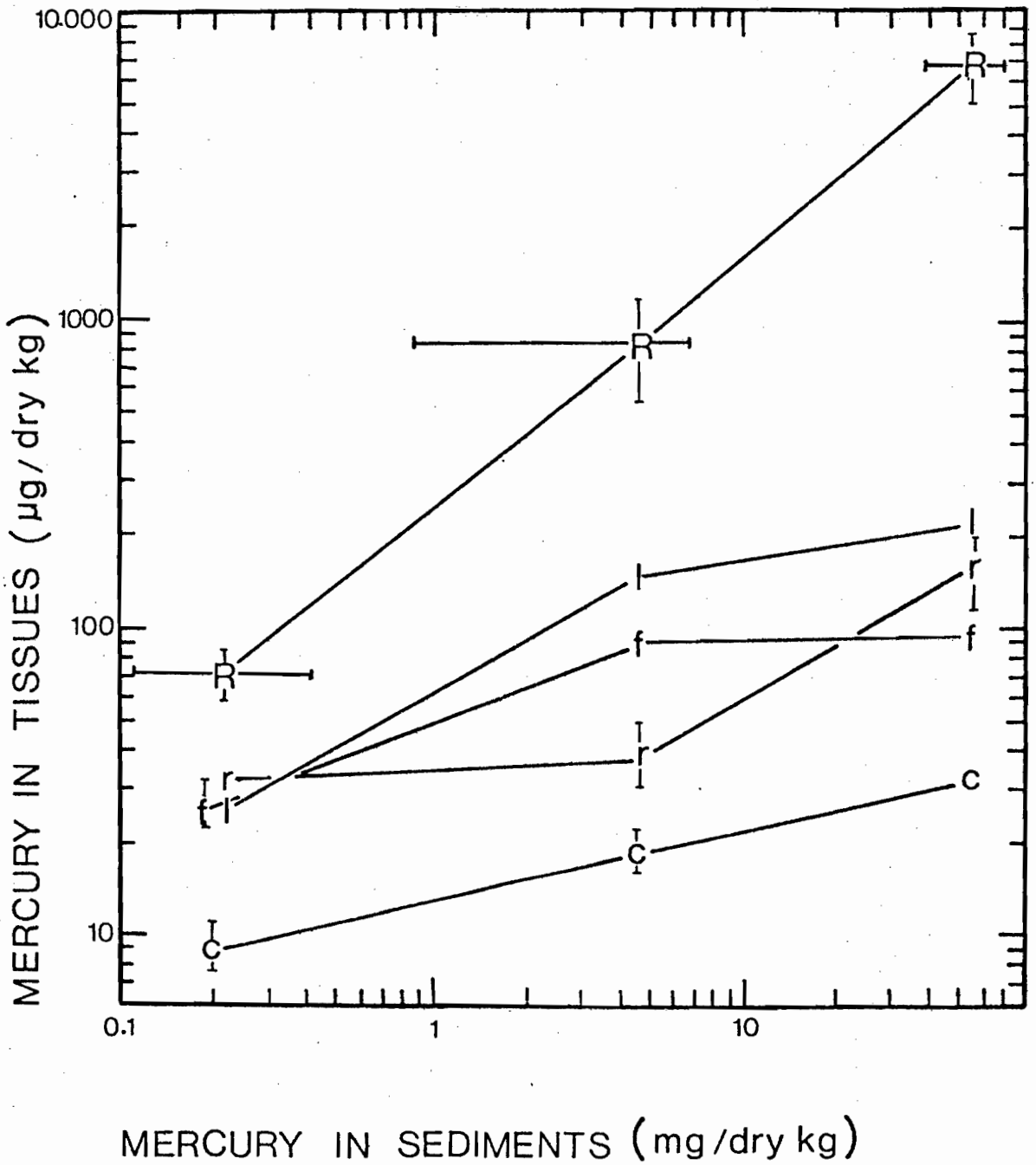
matter content.

RESULTS AND DISCUSSION

Mercury in Spartina alterniflora

All plant parts of S. alterniflora showed a certain amount of increase in mercury contents as levels of this element increased in sediments (Figure 2). Roots had the highest concentrations and also showed the steepest increase relative to increases in sediment mercury. Thus, while root concentrations were only slightly higher than those of other plant parts under natural conditions, up to two orders of magnitude differences were observed in grasses from mercury contaminated areas. If mercury had been adsorbed on the epidermal cells of below-ground parts of S. alterniflora, rhizomes and the part of the stem growing below-ground would have elevated levels of mercury similar to those of the roots. Figure 2 shows that this is not the case, and mercury therefore evidently penetrated epidermal cells and subsequently associated with cell metabolites. Assimilation of mercury by plants may not be limited to ionic forms alone, but may include organo-mercury complexes (Tiffin, 1977). The large difference between the mercury concentrations in roots and other parts of S. alterniflora indicates that transfer of this element is limited, suggesting the presence of a blocking mechanisms (Beauford et al., 1977; Wallace & Romney, 1977; and Hogg et al., 1978b). Even when the marsh cord grass was grown hydroponically in the presence of $HgCl_2$

Figure 2. Mean mercury concentrations (ng Hg/g dry weight) ± S.E. in roots (R), rhizomes (r), culms (c), leaves (l) and flower structures (f) of tall morphology *Spartina alterniflora*. Horizontal bars, depicted only around (R) symbols, give the range of soil mercury contents (mg Hg/kg dry weight) of ambient sediments. Vertical error bars are presented when larger than the symbol used.


10,000
1000
100
10
0.1
1
10
MERCURY IN TISSUES (µg/dry kg)
MERCURY IN SEDIMENTS (mg/dry kg)
R
r
f
c

(Rahn, 1973), only 1% of the total amount of mercury assimilated by the roots was transferred to the leaves, and 3% to the culms. Under field conditions Windom (1973) and Gardner et al. (1978) also found a considerably higher accumulation of mercury by roots of S. alterniflora than by its rhizomes.

Mean mercury concentrations in leaf tissues of grasses from the Hackensack Meadowlands attained values 4-fold of those of the culms. These differences were found in the whole range of sediment mercury concentrations observed (Figure 2). By contrast, Gardner et al. (1978) reported mercury levels of culms and grass blades to be of approximately the same value. We expect that at least part of the mercury in the leaves is taken up directly from the water column, although the possibility that mercury is retained by storage tissues of the foliage may not be excluded. In the first place, grasses collected from the upper limit of the intertidal range contained significantly less mercury than those from the lower intertidal zone (83 vs. 121 ppb Hg; paired t-test, $p<0.01$). Moreover, the mercury concentration of the below-ground part of the grass stems (125 ppb Hg) was intermediate between the lower above-ground part (0-10 cm; 273 ppb Hg) and the higher culm to which the blades were attached (33 ppb Hg). This is consistent with the theory that the section of the grass most frequently contacted by the river water adsorbed the highest amount of mercury from the water column. The soluble mercury content (passing a 0.45 µm Millipore filter) in the waters adjoining the creek sides averages 100 ng Hg/ℓ (P. Galluzzi, pers. comm.).

Under experimental conditions, Rahn (1973) also found that mercury could be adsorbed from the water phase by leaves of S. alterniflora, while Erikson & Mortimer (1975) and Mortimer & Kudo (1975) reported a similar mechanism for submerged plants.

In Great Sippewissett Marsh the total annual above-ground production of S. alterniflora amounted to less than 2 kg/m^2 in fertilized, and about 0.5 kg/m^2 in untreated marsh (Valiela et al., 1976). An amount of organic particles equivalent to 40% of above-ground production is lost by tidal export (Valiela et al., 1978). If 0.025 mg Hg/kg S. alterniflora were taken up from the sediments alone, then the total annual loss of this element from the marsh surface would amount to less than 1% of the soil mercury concentration. In contaminated marshes this percentage would be even lower, because a rise in the sediment mercury concentration caused a much less steep increase in the above-ground S. alterniflora tissues (Figure 2). Export of this grass from the marsh system to adjoining waters therefore does not seem to substantially deplete mercury from the soil of northeastern salt marshes. This finding is in contrast with reports for southern marshes (Windom, 1973 & 1975; Dunstan & Windom, 1975). In the latter study, however, mercury concentrations of S. alterniflora, probably whole plants, exceeded those of the sediments by 4-fold, both on a dry weight basis; and mercury therefore appears to have been better available for uptake than was the case in our study.

Mercury in Mussels and Fiddler Crabs

Mercury concentrations did not increase in the fiddler

crabs U. pugnax, mussels, and marsh grasses from the experimentally fertilized plots, in spite of the 3-6 fold increase in sediment mercury (Table 1). Perhaps fiddler crabs and mussels obtained at least part of the detrital food from the uncontaminated marsh adjacent to the treated plots. However, these animals did accumulate considerable amounts of copper and cadmium from the metal-enriched plots (Giblin et al., in press). It therefore seems likely that the mercury, which we added in association with the sewage sludge, was unavailable for uptake by invertebrates and grasses alike. Since it is difficult to extract mercury from the enriched sediments (Table 3, discussed below), the organomercury complexes apparently were too stable to be assimilated by the organisms after ingestion.

In the Hackensack Meadowlands, U. pugnax and U. pugilator were found abundantly in marshes where mercury levels reached 5 ± 0.4 mg Hg/dry kg sediment. In contrast, no fiddler crabs lived in salt marshes closer to the former source of mercury discharge (> 50 ppm Hg). Fiddler crabs apparently tolerated moderately contaminated conditions but were unable to withstand high levels of sediment mercury.

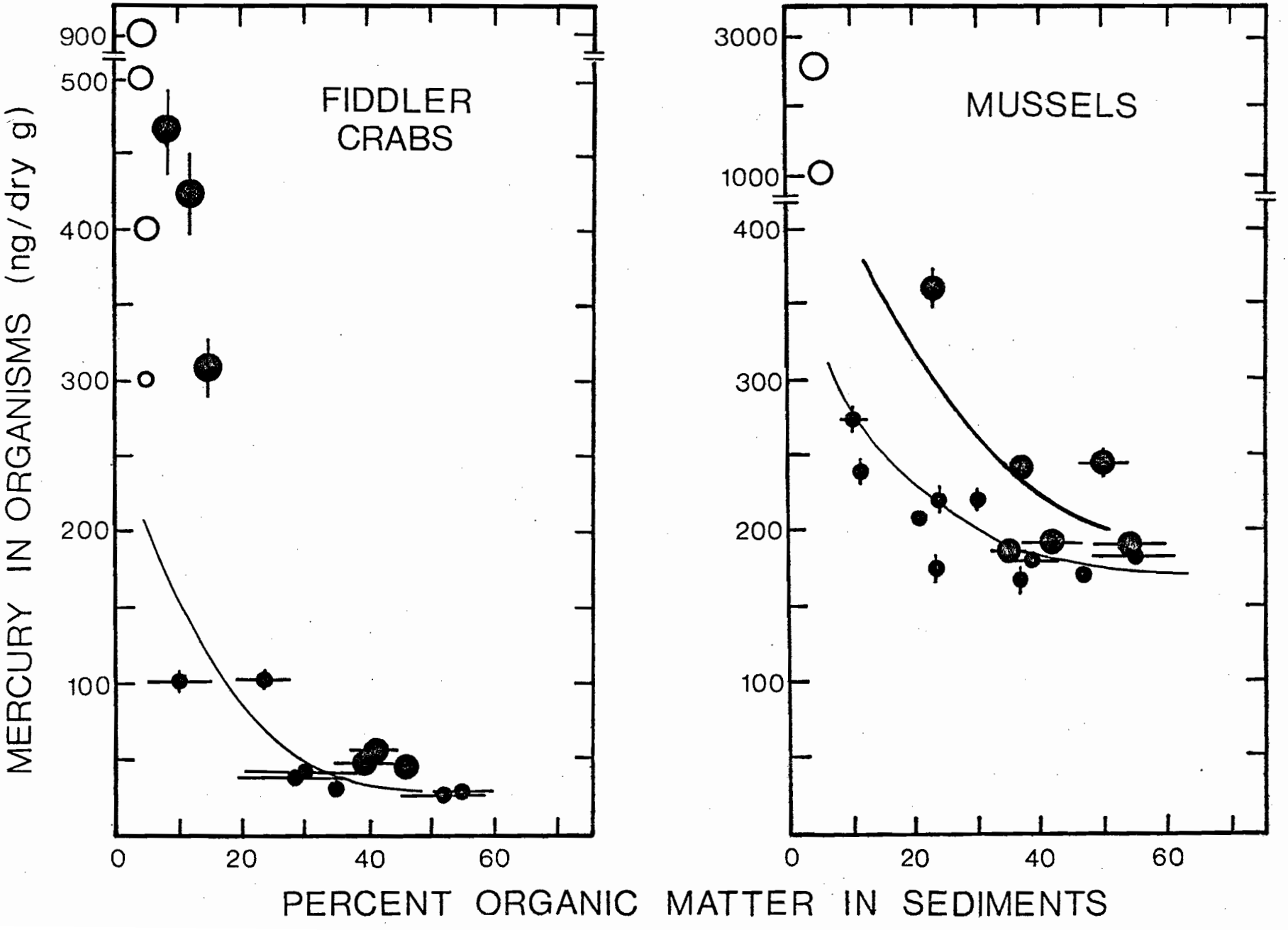
Effects of Sediment Organic Matter on the Bioavailability of Mercury

Mercury concentrations of mussels and fiddler crabs increased rapidly with decreasing organic matter content of the soil (Figure 3). This inverse relation was particularly evident when organisms were grouped according to the mercury

TABLE 1. Mercury concentrations (ng Hg/g dry weight) ± S.E. of marsh soils and common grass and animal species. Samples are from experimental plots in Great Sippewissett Marsh. C=untreated marsh; HF and XF stand for high and extra high dosages of a mercury-containing fertilizer.

	Mercury concentration (ng Hg/g dry weight)		
	C	HF	XF
Sediments covered with:			
Tall *S. alterniflora* (creek sides)	100± 9	308±44	330±34
Short *S. alterniflora* (low marsh)	100± 6	506±38	575±61
S. patens (high marsh)	112±10	539±45	572±40
Marsh grasses			
S. alterniflora (tall form)	19±1.9	-	21±1.5
S. alterniflora (short form)	22±3.2	-	21±1.5
S. patens	25±1.8	-	22±1.8
Marsh animals:			
Uca pugnax (fiddler crabs)	57±16	31± 3	48± 3
Modiolus demissus (ribbed mussels)	178± 8	190± 5	218±12
Crassostrea virginica (oysters)	568±47	516±15	-
Mercenaria mercenaria (soft clams)	305±45	266±13	-

Figure 3. Mean mercury concentrations (ng Hg/g dry weight) ± S.E. of fiddler crabs and mussels, plotted against the sediment organic matter content (range given). n = 3-5. Increasing sizes of the symbols indicate increases in the mercury contents of the ambient sediments: (●) 0.05 - 0.29 mg Hg/dry kg; (●) 0.3 - 0.6 mg Hg/kg; (●) 1.5 - 6 mg Hg/kg. Open circles present data from Gardner *et al.* (1978). Curves are drawn by eye.


MERCURY IN ORGANISMS (ng/dry g)
900
500
400
300
200
100
FIDDLER CRABS
3000
1000
400
300
200
100
MUSSELS
0
20
40
60
0
20
40
60
PERCENT ORGANIC MATTER IN SEDIMENTS

contents of the ambient sediments. The relationship appeared to take the form of first-order reactions with a steep drop in mercury accumulation initially, followed by a gradual leveling in predominantly organic marshes. Thus, while the tissue mercury contents of these animals clearly depend on those of the ambient sediments under mostly sandy conditions, elevated levels of sediment mercury were unavailable for bioaccumulation in peaty marshes. For comparison, we included data from silty southeastern salt marshes which contain only 4 ± 2% organic matter (Windom, 1975).

At any level of soil organic content, more mercury was accumulated by mussels than by fiddler crabs, even if differences in the ash-free organic contents of mussels (89%) and fiddler crabs (55%) were taken into consideration. Since both groups of organisms feed on detritus with similar mercury contents, the tissue concentration of mercury reflects their ability to regulate mercury uptake.

While mercury concentrations of estuarine sediments generally correlate well with the organic matter content (Lindberg & Harriss, 1974; Windom, 1975; and Bothner et al., in press), such relationship was less evident in the peaty New England marshes. This was largely due to the presence of coarse fibrous plant remains which had comparatively low mercury contents (Breteler et al., in preparation). However, since such materials were largely absent in the Hackensack Meadowlands, mercury levels in these latter marshes closely followed the organic matter content of the sediments. This relation could be clearly demonstrated in the surface layer

of sediment cores (Figure 4), but was less evident when mercury concentrations approached background levels. The large fluctuations in mercury contents at various depths indicate that dilution processes, resulting from variations in the deposition of minerals, may distort evidence of past anthropogenic mercury discharges. The correlation between mercury and organic matter in the sediments would suggest that marsh soils with low organic matter contents contain relatively little mercury. Conversely, organisms living under those conditions appear to attain higher levels of this element.

Table 2 shows the concentrations of mercury in live roots of S. alterniflora and of ambient sediments. The results show that mean mercury concentrations of S. alterniflora roots from the predominantly sandy marsh soil attained levels up to 40-fold of those from the peaty marshes. This finding is consistent with the observation that mercury is better available to animals when the marsh soil contains little organic matter.

Although a single explanation for this phenomenon can not be presented at this time, the results suggest that certain conditions existing in low organic marsh soils favor the physico-chemical and perhaps biological transformation of mercury into forms more readily available for uptake by biota. Alternatively, these conditions may retard the formation of stable organo-mercurials from naturally introduced mercury of aquatic and atmospheric origin. Table 3 shows sediment characteristics of the marsh soils, including pH, Eh, and the

Figure 4. Percent organic matter (○) and mercury concentrations (▲) in mg Hg/kg dry sediment at various depths in vegetated marsh soils along Saw Mill Creek and Berrys Creek (Hackensack Meadowlands).

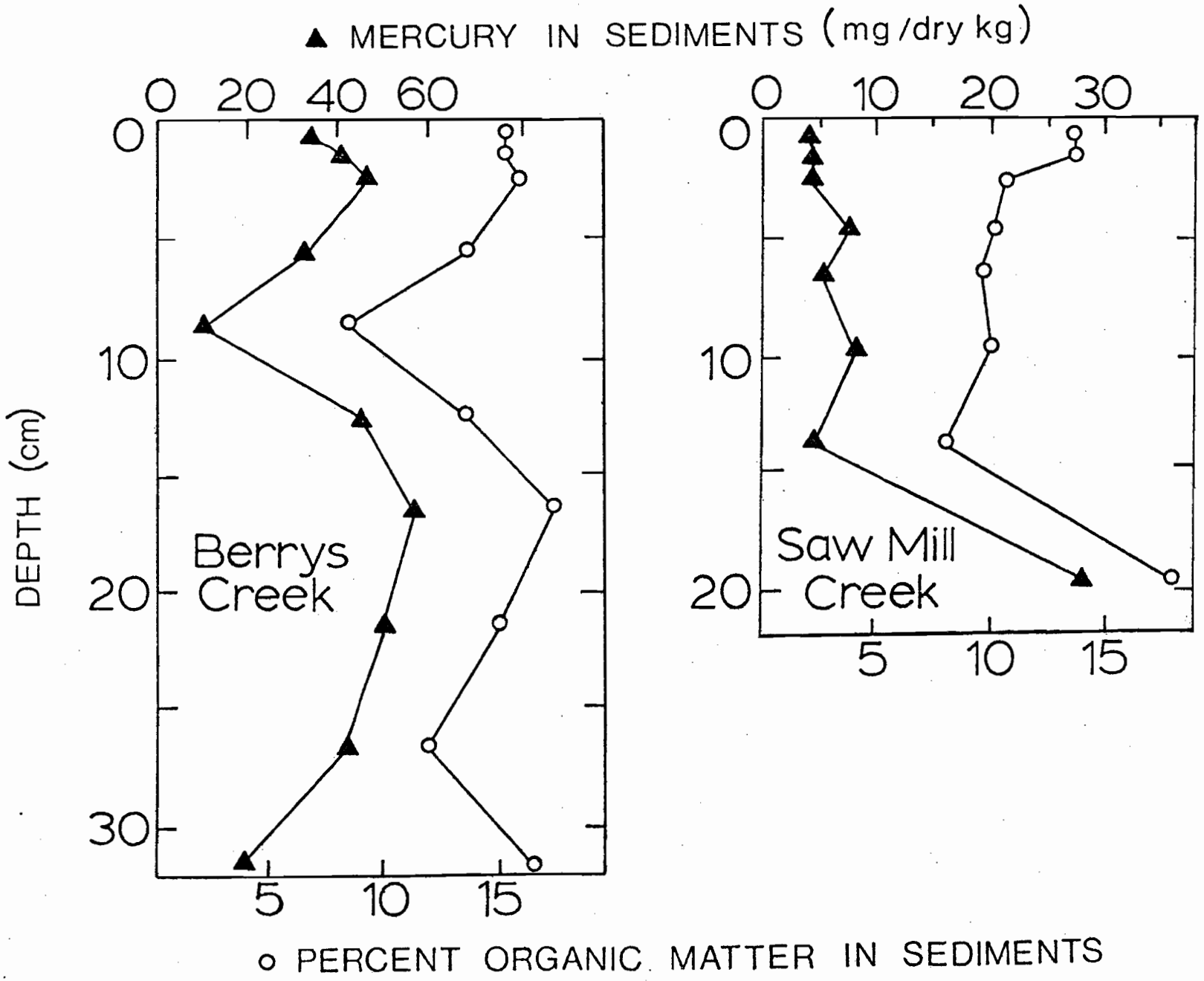

▲ MERCURY IN SEDIMENTS (mg/dry kg)
0 20 40 60
0 10 20 30
DEPTH (cm)
0
10
20
30
Berrys Creek
Saw Mill Creek
5 10 15
5 10 15
o PERCENT ORGANIC MATTER IN SEDIMENTS

TABLE 2. Mercury concentrations (mean ± S.E.) in mg/kg dry weight in live roots of *S. alterniflora* and in ambient sediment of salt marshes in New England and the Hackensack Meadowlands.

Marsh sites	Number of stations	Mercury concentrations (mg/kg	
		Live roots	Sediments
Massachusetts marshes			
Great Sippewissett	2	0.04±0.01	0.18±0.05
Muskeget	3	1.4 ±0.09	0.05±0
Hackensack Meadowlands			
Berrys Creek	3	6.8 ±1.7	55.7 ±7.5
Saw Mill Creek #1	4	0.42±0.06	4.9 ±0.7
Saw Mill Creek #2	2	2.0 ±0.5	2.3 ±1.5

percentage organic matter content. Eh values were determined under carefully standardized conditions and provide a measure of the relative oxidation state of the soil. It is interesting to speculate concerning the role of the soil texture on the availability of mercury. Due to the large quantity of coarse minerals in Muskeget Island marshes, its soil was considerably more open than that of Great Sippewissett Marsh. Hogg et al. (1978b) showed that under experimental conditions roots of bromegrass attained the highest levels of mercury when growing on the lightest textured Hg-treated soils with the lowest organic content. A similar relation appeared to exist for tall morphology S. alterniflora in the New England marshes. We are not certain about the role of Eh concerning the latter relationship. No differences were found between the oxidation states of the rhizosphere of Muskeget and Great Sippewissett Marsh. Both marshes were largely oxidized, although reducing conditions were occasionally observed in the latter marsh at depths of 15 cm (Table 3). Nonetheless, with the majority of the root productivety taking place in the surface 5 cm (Valiela et al., 1976), Eh did not seem to play an important role in the uptake of mercury by the grasses.

In Great Sippewissett Marsh pH values fluctuate between 5 and 6 in the subsurface (2-30 cm) soil. Values are higher in the surface zone, reaching up to 8. Due to the sandy nature of the Muskeget Marsh soil, acidic conditions were generally found only below the rhizosphere. We are unsure about the significance of these differences with respect to mercury mobilization, but do not see how pH could account for the

TABLE 3. Sediment parameters of salt marsh sediments in New England and in the Hackensack Meadowlands. Eh (mV) and pH are means ± S.E. (n=4-8).

Marsh sites	Organic matter content (%)	Eh (mV)			pH		
		Depth in sediments			Depth in sediments		
		1 cm	5 cm	15 cm	0 cm	5 cm	15 cm
New England marshes							
Great Sippewissett	34±11	350±75	275±75	60±100	6.0±0.5	5.5±0.5	5.5±0.5
Muskeget	7±1	437±10	251±60	182±113	7.0±1.0	6.5±0.5	6.0±0.5
Hackensack Meadowlands							
Berrys Creek	16±1	284±38	64±14	189± 48	6.2±0.1	6.0±0.1	5.8±0.1
Saw Mill Creek #1	14±1	21±33	-16±17	-66± 23	5.7±0.1	5.6±0.1	5.8±0.1
Saw Mill Creek #2	9±1	-56±20	0±50	-144± 16	5.6±0.1	5.2±0.5	3.6±1.0

high mercury levels of the roots of the latter marsh in the ranges observed.

Sediment characteristics in Berrys Creek Marsh were generally uniform between stations, and no relation of the nature discussed above could therefore be discerned. In contrast, distinct differences in pH and, to a lesser extent, Eh were found between the mid-creek stations (station #1) and the mouth of Saw Mill Creek (station #2)(Table 3). Station #2 was somewhat less oxidized than station #1, and significantly more acidic. Concurringly, sediment mercury levels were lower in the latter station, while those of the roots were high (Table 2). Moreover, we measured a reduction in the mean grass length of 23% compared to grasses from station #1. Since the pH optimum for the synthesis of methylmercury is 4.5 (Wood, 1974), conditions at station #2 would appear ideal for the formation of this harmful and mobile form of mercury. The acidity of the latter marsh site therefore may partially explain the lower mercury content of the sediments and relatively high levels of the plant-root system. Worth noting in connection with this is the finding by Khalid et al. (1977) who concluded that redox potential and pH regulate the chemical form as well as the bioavailability of mercury in riverbed sediments depending on the amount of mercury present. Our results suggest that under moderately contaminated conditions mercury becomes better available for bioaccumulation under more acidic conditions.

Altogether, mercury concentrations in plants and animals in marshes are controlled by multiple environmental factors including organic content, pH, and redox potential of the soil.

When these factors favor the mobilization of sediment-bound mercury into available forms, an increase in the concentrations of mercury in biota inhabiting this intertidal system may occur.

Chemical Extractions of Mercury from Marsh Soils

Twelve percent of the mercury added to the marsh as a result of the sludge treatments and 30% of naturally present mercury was extracted after treatment of surface sediments from Great Sippewissett Marsh with 0.5 N NaOH (Table 4). These percentages presumably indicate the mercury fraction bound by humic and fulvic acids (Holtzclaw et al., 1978). We found a similar portion of mercury to be associated with soil organic acids in the contaminated sediments of the Hackensack Meadowlands. Between 30 and 50% of the total ash-free organic matter of the marsh soils was comprised of humic and fulvic acids. Since mercury concentrations and organic contents of the marsh soils correlated well (Figure 4), and coarse (> 1.0 mm) plant remains contained only minor amounts of mercury (Breteler et al., in preparation), the results of Table 4 suggest that this element was predominantly associated with small detritus particles. Treatment of marsh soils with dilute and concentrated HCl progressively hydrolyzes organic matter and dissolves inorganic colloids. The results show that the bonding of mercury with the soil colloids was very firm, especially in the uncontaminated marsh soils. Thirty percent of this element was released from the peat after treatment with 6 N HCl. In contrast, Hogg et al. (1978a) found up to 90% release of mercury from loamy sand and from loam soils using similar

TABLE 4. Mercury and organic matter losses (in % of original contents) ± S.E. after extraction with 0.5 N NaOH, 0.5 N HCl, and 6 N HCl. Samples consist of 5 cm surface cores from untreated (C) and from extra high fertilized (XF) plots within Great Sippewissett Marsh (GS) and from Saw Mill Creek (SM) and Berrys Creek (BC) in the Hackensack Meadowlands (HM). ppm = mg/kg dry weight. OM = organic matter.

		Mercury loss (%)				Organic matter loss (%)		
	Intact soil	NaOH	HCl		Intact soil	NaOH	HCl	
Marsh	ppm Hg	0.5 N	0.5 N	6 N	%OM	0.5 N	0.5 N	6 N
GS								
C	0.20±0.03	29.5±3.0	-7.9±9.0	30.7±15.6	42.0±10.1	47.6±3.7	8.8±5.8	31.2±2.2
XF	0.65±0.07	12.0±2.0	-4.8±3.0	71.8± 3.7	45.2± 1.8	39.5±1.6	13.7±2.4	29.3±2.4
HM								
SM	12.4±2.9	25.7±4.6	25.0±6.4	78.3±3.7	10.3±2.9	31.6±6.8	0.5±0.5	15.7±2.0
BC	80.0±10.0	10.0±1.5	7.7±2.3	83.3±4.3	14.3±0.6	32.9±2.5	1.1±0.6	16.4±0.2

extraction conditions. This result indicates that mercury was bound tightly by the detrital soil particles. The stability of the mercury-organic matter associations in the soil colloids of coastal wetlands may, at least in part, explain the poor availability of this element to marsh biota.

CONCLUSIONS

The data presented here indicate that the application of a sludge fertilizer containing mercury to salt marshes covered with S. alterniflora does not result in an increase of the mercury content of shellfish, fiddler crabs, and marsh vegetation types. However, when salt marshes are subject to very high anthropogenic mercury inputs, a considerable accumulation of this metal results in the S. alterniflora root system; but translocation of mercury to above-ground tissues is very limited.

The availability of mercury to plants and marsh invertebrates appears to increase exponentially with decreasing amounts of organic matter. Therefore, even small increases of sediment mercury may seriously affect the biota in marshes with light-textured soils of low organic matter content, resulting in the possible contamination of species of importance to man. This study further demonstrates the need for a careful evaluation of the interrelations between mercury speciation, its contents in sediments and biota, and relevant environmental variables, especially with respect to monitoring and baseline studies.

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CHAPTER 3

TRACE ELEMENT ENRICHMENTS DURING THE DECOMPOSITION OF *SPARTINA ALTERNIFLORA*

ABSTRACT

Concentrations of mercury, copper, zinc, chromium, iron, and manganese were measured at intervals of 5, 10, and 24 weeks in decaying Spartina alterniflora. Litter samples were obtained from: 1) low marsh habitats, flooded a major portion of each tidal cycle, 2) high marsh habitats, flooded for shorter periods during most high tides. The study included experimental marsh plots, treated with a metal-containing sewage sludge, and untreated marsh. Overall, highly significant increases were found in the concentrations of Hg, Cu, Fe, and Zn. Significant increases were further observed in Cr and Mn in tall form, untreated litter. The metal concentration increases were related to the strength with which metals were bound by the decaying plant material. Metal concentrations of decomposed plants were therefore higher in short S. alterniflora than in the more frequently inundated tall form. Decay weight losses may partially account for the metal enrichments, depending on the bonding strength and location of the elements. Differences in the nitrogen content of certain litter types could not explain the magnitude of the metal increases observed. In general, no metals were adsorbed from the sludge-treated marsh soil.

INTRODUCTION

Spartina alterniflora Loisel, the smooth marsh cord grass, is commonly found along the east coast of the United States of America, and may be found growing from a tall form (1-3 m in height) to a dwarf form (10-40 cm in height). The dominant habitats, morphological differences, as well as some of the factors controlling the growth forms of this grass have been described earlier (Squiers and Good, 1974; Valiela et al., 1978).

Concentrations of several trace metals in litter of *S. alterniflora* were found to be higher than those of the living grasses (Williams and Murdoch, 1969; Pellenbarg, 1978; Giblin et al., in press). Lindberg and Harriss (1974) reported a substantial increase in mercury in dead leaves of red mangroves relative to live foliage, and hypothesized that this was due to an active sorption of the metal by the microfauna growing on the decomposing litter. Alternatively, the mercury increase could have been caused by the strong association between the element and those components of the plants most resistent to degradation. Pellenbarg (1978) reported increases in Cu, Zn, and Fe in litter of *S. alterniflora* higher than explained by the loss of weight through decay. These processes are of interest, since it is well established that detritus from *S. alterniflora* forms a major link between primary and secondary productivity in coastal salt marshes (Odum and de la Cruz, 1967; Teal, 1962).

Three concurring and interacting processes are involved in metal concentration changes of dead plants during decomposition. These processes are: (1) relative metal increases due to decay losses of plant components with below average metal content, (2) absolute concentration increases caused by an adsorption of metal-enriched components by the plant material; and (3) loss of trace metals by desorption processes, or by decay losses of metal-enriched plant parts. This study deals with the relative changes in the concentrations of Hg, Cu, Fe, Zn, Cr, and Mn during the decomposition of litter of short and tall S. alterniflora.

We tested the hypotheses that metals supplied to the marsh sediment were important in determining the metal contents of the dead plants, and that these concentrations were further influenced by the location of the litter in the intertidal range. To ascertain if metal concentrations were related to the chemical composition of the grasses, we monitored the contents of carbon, nitrogen, and sulfur in the litter during the decay.

METHODS

Litter was collected from Great Sippewissett Marsh, Cape Cod, Massachusetts. In this marsh experimental plots have been treated since 1974 with a metal-containing fertilizer based on sewage sludge. This material was spread over the marsh surface during the low tide, twice every month, in

dosages of 151.2 g/m^2. The metal additions took place throughout the growing seasons (April-October) of 1974-1976. Further details of experimental procedures and treatment effects on S. alterniflora are presented elsewhere (Valiela et al., 1974, 1975, 1976).

Senescing S. alterniflora, collected in October 1977 from control as well as from fertilized marsh, were divided into equal portions of approximately 400 grams (wet weight), and put inside duplicate, nylon bags (mesh opening 8 mm). These bags were attached to the location where the grasses were growing with aluminum pins. Thus the taller grasses were placed lower in the intertidal range than the short grasses. Grasses were collected at the start of the experiment and after 32, 70, and 168 days of litter exposure, respectively. Each time samples were collected from the litter bags, we also took duplicate samples of 10 standing dead plants from each site.

Litter was carefully rinsed with deionized water, freeze-dried, ground in a Virtis stainless steel micro-homogenizer and analyzed for Hg, Cu, Fe, Zn, Cr, and Mn. From each duplicate set of samples we analyzed one sample for C, N and S contents. Details of the analytical procedure for the determination of mercury have been described elsewhere (Breteler et al., in preparation). Other heavy metals were analyzed by atomic absorption spectrometry (Perkin Elmer 403) after hot ($60^{o}C$) digestion of the homogenized sample in nitric acid and oxidation with hydrogen peroxide. C, N, and S were measured using a Perkin Elmer 240 elemental analyzer.

RESULTS AND DISCUSSION

No significant differences in metal contents were found between litter collected from litter bags and as standing dead (two-way analysis of variance; $p < 0.05$). To obtain more precise estimates of the mean metal concentrations, we pooled the data obtained from samples collected by the two different procedures so that four metal concentration values were available for each experimental condition and sampling time.

Changes in the metal concentrations during the decay of short and tall S. alterniflora are shown in Figure 1 for litter from both control and fertilized marsh. We tested the overall significance of the metal concentration increases with time, i.e., independent of growth forms or fertilization vs. control treatments of the litter (three-factor factorial analyses of variance). We found highly significant increases in the concentrations of Hg, Cu, Fe, ($p < 0.001$) and Zn ($p < 0.01$). There were no significant statistical interactions ($p < 0.05$) among decomposition times, growth forms of S. alterniflora, and fertilized vs. control grasses for any of the metals. We further tested whether differences among the metal concentrations of the litter under various experimental conditions were significant (Figure 1; one-way analysis of variance).

While concentrations of Cr in the fertilized litter appeared to rise during the first 7 weeks of litter decay, levels had dropped markedly towards the end of the experimental

FIGURE 1A (Chapter 3)

Relative concentrations of mercury (Hg), copper (Cu) and iron (Fe) in aging litter of short and tall S. alterniflora from control and sludge-treated marsh plots in Great Sippewissett Marsh. Concentrations are in mg metal/ kg litter (dry weight) ± S.E. Asterisks indicate the level of significance of differences between mean concentrations within each curve (one-way analyses of variance). * = 95%; ** = 99%; *** = 99.9%. D=dwarf S. alterniflora, T= tall S. alterniflora.

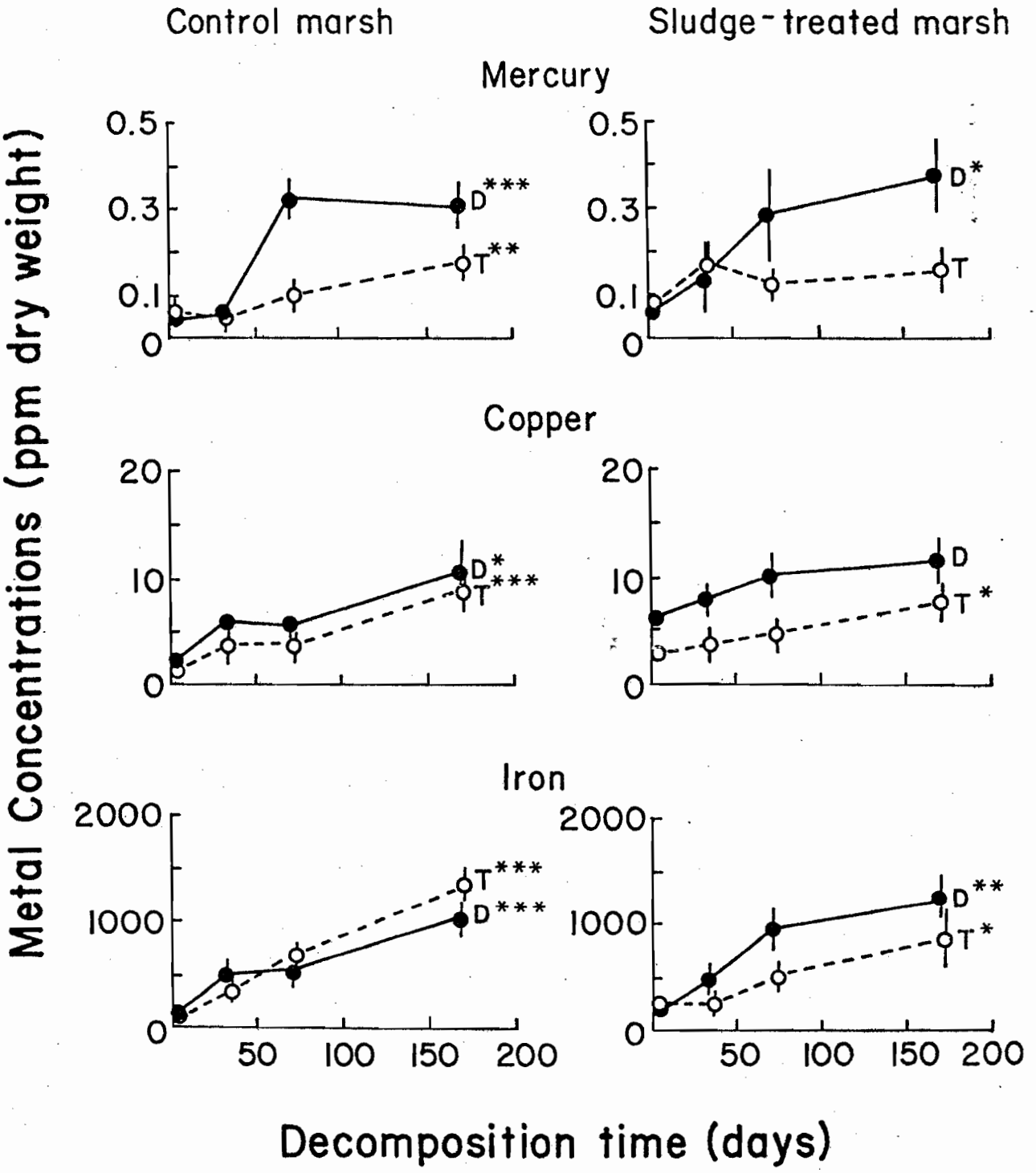
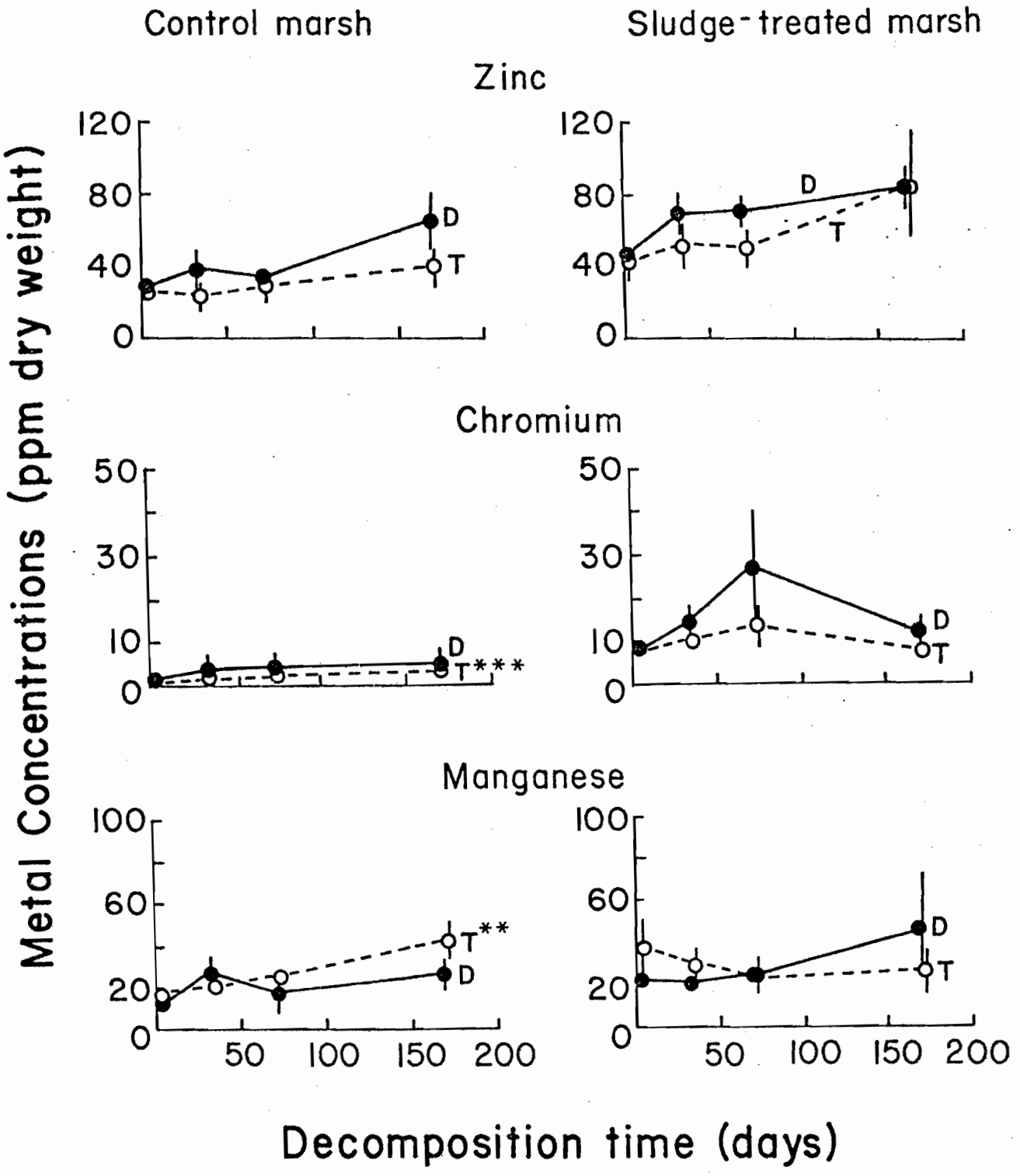

Control marsh
Sludge-treated marsh
Mercury
Copper
Iron
Metal Concentrations (ppm dry weight)
Decomposition time (days)
0.5
0.3
0.1
0
20
10
2000
1000
50
100
150
200
D***
T**
D*
T
D*
T***
D
T*
T***
D***
D**
T*

FIGURE 1B (Chapter 3)

Relative concentrations of zinc (Zn), chromium (Cr) and manganese (Mn) in aging litter of short and tall S. alterniflora from control and sludge-treated marsh plots in Great Sippewissett Marsh. Concentrations are in mg metal/kg litter (dry weight) ± S.E. Asterisks indicate the level of significance of differences between mean concentrations within each curve (one-way analyses of variance) * = 95%; ** = 99%; *** = 99.9%. D = dwarf S. alterniflora; T = tall S. alterniflora.


Control marsh
Sludge-treated marsh
Zinc
Chromium
Manganese
Metal Concentrations (ppm dry weight)
Decomposition time (days)
120
80
40
0
50
30
10
100
60
20
50
100
150
200
D
T
T***
T**

period. We are uncertain whether this trend was real; but we believe it may be, since it was observed in six out of eight cases. The gradual concentration increases of zinc were not steep enough to be significant at the 95% confidence level. However, the pattern of concentration increases was consistent under all experimental conditions and significant when the data were treated simultaneously. Mercury enrichments were considerably more pronounced in the short form than in tall litter. No differences in the mercury contents were found between control and fertilized plants, in agreement with earlier findings that this element was unavailable for uptake and accumulation under the tested conditions (Breteler et al., in preparation). Although copper was accumulated by the live grasses, and concentrations of fertilized plants were higher than those of control plants during senescence, no differences in copper contents were found at the end of the experimental period. Manganese exhibited the least consistent pattern of change during the litter decay; although the mean values of Mn were higher after six months of liter exposure than at the end of the growing season.

To ascertain whether the observed metal increases could be explained by the decay loss of plant matter, we calculated the maximum metal increase possible through this mechanism (Table 1). We obtained decay weight losses of the grasses from a decomposition study carried out parallel with and at the location of the experiment described in this report (Valiela et al., unpublished data). We concluded that adsorption took

TABLE 1

Heavy metal concentrations (mean ±3.182 SE) in short and tall *S. alterniflora* during decomposition. Litter kept on untreated and sludge-fertilized marsh plots. In parentheses are calculated concentrations assuming no loss of metal during plant decay.

S. alterniflora litter	Sampling date	% Decay wt.loss	Metal concentrations in *S. alterniflora* (mg M.kg litter dw^{-1}) Mercury	Copper	Iron
CONTROL MARSH					
Short form	Oct 11	0	0.047±0.015 (0.047)	1.60±2.23 (1.60)	126± 32 (126)
	Nov 12	22	0.052±0.033 (0.060)	5.84±0.37 (2.05)*	497±266 (162)*
	Dec 20	26	0.326±0.125 (0.064)*	5.47±2.98 (2.16)*	573±490 (170)
	Mar 28	36	0.304±0.170 (0.073)*	10.7 ±9.27 (2.50)	1143±461 (197)*
Tall form	Oct 11	0	0.058±0.053 (0.058)	1.51±0.72 (1.51)	112± 71 (112)
	Nov 12	36	0.048±0.070 (0.091)	3.73±3.27 (2.36)	354±117 (177)*
	Dec 20	40	0.098±0.061 (0.097)	3.96±3.20 (2.52)	701±197 (188)*
	Mar 28	54	0.174±0.087 (0.126)	9.25±3.32 (3.28)*	1357±432 (246)*
FERTILIZED MARSH					
Short form	Oct 11	0	0.057±0.014 (0.057)	6.10±1.41 (6.10)	195± 68 (195)
	Nov 12	27	0.135±0.253 (0.078)	8.02±3.35 (8.36)	484±326 (267)
	Dec 20	36	0.286±0.348 (0.089)	10.3 ±5.40 (9.52)	953±648 (304)*
	Mar 28	50	0.378±0.266 (0.114)*	11.8 ±6.15 (12.2)	1240±734 (390)*
Tall form	Oct 11	0	0.079±0.041 (0.079)	2.85±1.47 (2.85)	248±182 (248)
	Nov 12	42	0.172±0.156 (0.136)	3.70±1.93 (4.91)	272±219 (428)
	Dec 20	48	0.125±0.061 (0.152)	4.78±2.20 (5.48)	529±312 (477)
	Mar 28	59	0.157±0.154 (0.193)	8.21±4.84 (6.95)	870±861 (605)

*Hypothetical value outside 95% confidence limits

TABLE 1 (CONTINUED)

S. alterniflora litter	Sampling date	% Decay wt.loss	Metal concentrations in *S. alterniflora* (mg M.kg litter dw^{-1}) Zinc	Chromium	Manganese
CONTROL MARSH					
Short form	Oct 11	0	23.9± 1.6 (23.9)	1.50± 1.31 (1.50)	10.5± 7.7 (10.5)
	Nov 12	22	37.9± 32.6 (30.6)	3.11± 2.49 (1.92)	26.7±12.4 (13.5)*
	Dec 20	26	31.9± 4.2 (32.3)	3.79± 2.33 (2.03)	18.3±22.8 (14.2)
	Mar 28	36	64.8± 52.0 (37.3)	4.25± 2.32 (2.34)	26.6±17.4 (16.4)
Tall form	Oct 11	0	25.0± 9.0 (25.0)	0.76± 0.28 (0.76)	16.6± 4.6 (16.6)
	Nov 12	36	23.4± 13.8 (39.1)	1.37± 0.89 (1.19)	21.3± 7.3 (25.9)
	Dec 20	40	28.8± 9.1 (41.7)	2.45± 0.54 (1.27)*	25.7± 5.2 (27.7)
	Mar 28	54	39.8± 23.1 (54.4)	3.62± 1.01 (1.65)*	44.8±23.1 (36.1)
FERTILIZED MARSH					
Short form	Oct 11	0	45.4± 11.0 (45.4)	6.93± 3.81 (6.93)	22.3± 6.4 (22.3)
	Nov 12	27	69.4± 37.7 (62.2)	14.3 ±12.4 (9.49)	20.4± 6.0 (30.0)
	Dec 20	36	71.7± 19.9 (70.9)	34.9 ±50.0 (10.8)	25.4±24.5 (34.8)
	Mar 28	50	84.3± 45.2 (90.8)	12.6 ± 9.73 (13.9)	48.4±75.7 (44.6)
Tall form	Oct 11	0	42.6± 28.5 (42.6)	8.10± 2.96 (8.10)	38.3±43.6 (38.3)
	Nov 12	42	52.3± 33.7 (73.5)	10.9 ± 4.83 (14.0)	30.5±24.3 (66.0)
	Dec 20	48	51.2± 26.0 (81.9)	13.6 ±13.1 (15.6)	24.2±10.2 (73.6)
	Mar 28	59	86.5± 95.5 (103.9)	8.00± 5.75 (19.8)	20.6±21.8 (93.4)

*Hypothetical value outside 95% confidence limits

place when the calculated metal increase was less than the lower 95% confidence limit of the measured values. It is important to keep in mind that the calculated concentrations presume no loss of the metal during the plant decay, so that the relative importance of the metal sorption process is likely to be underestimated by these calculations. This may be especially true in cases when the natural variability of metal concentrations of the litter resulted in large confidence intervals. Therefore, we have no certainty that metal sorption had not taken place in those cases that the calculated concentrations fell within the confidence range of the actual metal values. Conversely, we may be reasonably certain that metal sorption was important when the measured means were significantly higher than the theoretical concentration increases. The results of Table 1 indicate that Cu, Fe, Hg, Cr, and perhaps Mn were adsorbed by the litter under certain conditions, most frequently in litter from unfertilized plots.

Metal concentration increases in the litter may be related to the strength with which the metals are bound within the sediment. Metals which are strongly bound to insoluble soil colloids are not available for uptake by the live grasses or by the decomposing litter. Some metals may be available for uptake, but are also leached easily from the grasses. We have observed this phenomenon for Cr, Zn and Cd (Giblin et al., in press). With the exception of Cr, no evidence was available that metals were sorbed from the metal-enriched fertilized

TABLE 2

Rate and magnitude of trace metal enrichment in litter of *Spartina alterniflora*. f_e stands for enrichment factor.

Metal	Litter type	Marsh treatment	Regression slope (SE)	r^2= Correlation coefficient	f_e= $[M]_{t=168}/[M]_{t=0}$
Hg	Short	Control	1.65 (0.92)	0.62	6.5
		Fertilized	0.76 (0.14)	0.94	6.6
	Tall	Control	1.89 (0.44)	0.90	3.0
		Fertilized	- *	0.27	2.0
Cu	Short	Control	0.049 (0.011)	0.90	6.7
		Fertilized	0.032 (0.008)	0.88	1.9
	Tall	Control	0.044 (0.006)	0.97	6.1
		Fertilized	0.032 (0.001)	1.0	2.9
Fe	Short	Control	5.7 (0.78)	0.96	9.1
		Fertilized	7.4 (0.33)	1.0	6.4
	Tall	Control	6.1 (1.47)	0.89	12.1
		Fertilized	3.9 (0.48)	0.97	3.5
Zn	Short	Control	0.23 (0.060)	0.88	2.7
		Fertilized	0.20 (0.075)	0.77	1.9
	Tall	Control	0.10 (0.020)	0.93	1.6
		Fertilized	0.23 (0.050)	0.78	2.0
Cr	Short	Control	0.014 (0.006)	0.73	2.8
		Fertilized	0.017 (0.002)	0.96	1.8
	Tall	Control	-	0.02	4.8
		Fertilized	-	0.03	1.0
Mn	Short	Control	-	0.39	2.5
		Fertilized	0.17 (0.012)	0.99	2.2
	Tall	Control	0.17 (0.040)	0.90	2.7
		Fertilized	-0.10 (0.032)	0.82	0.5

*Value not given because of poor correlation.

marsh. The source of the metals causing the enrichment by sorption therefore may be the aqueous surface film, as proposed by Pellenbarg (1978), rather than the sediment. To test this hypothesis, we compared the magnitude of metal increases in control and fertilized plots (Table 2). If metals were being made available by the marsh surface, we would expect metal concentrations to increase more rapidly in the sludge treated plots. To measure the total metal increase during the experimental period we used two parameters: (1) the regression slope of the linear regression equations describing the relationship between the metal content of the litter and the decomposition time. The use of this parameter was restricted to those instances that a high correlation coefficient was found, (2) the enrichment factor, computed as the ratio between the final and initial metal concentration. This parameter was less useful for metals which had been enriched during the life of the plants. We furthermore assumed that the same enrichment mechanism accounted for the metal increases of corresponding litter types. Evaluation of the result of Table 2 shows that metals were generally not taken up preferentially from the fertilized marsh. However, zinc uptake in tall S. alterniflora litter appeared to be higher in the fertilized marsh, although the total increase of zinc may be accounted for by weight loss of plant material during decay (Table 1). Evaluation of the results of Table 2 further indicated that the Cr and Cu concentrations of control plants increased parallel with those of the fertilized plant.

This was noteworthy, since the initial concentrations of these metals were enriched by four-fold in the sludge-treated marsh plots. This trend therefore typifies a metal sorption mechanism from aquatic sources, adding similar amounts of the metals to the litter, irrespective of the initial concentrations.

Comparison of the enrichment factors and regression slopes of the metal increases between litter employed at high marsh sites (short form) and lowest in the intertidal range (tall form) made it possible to evaluate combined effects of tidal flooding, reduction-oxidation potentials, temperature, and other factors related to the marsh sites on the metal increases. Tall form grasses decompose more rapidly than the short form (Table 1). These grasses are also more often in contact with the aqueous surface film, which is enriched in a number of heavy metals (Pellenbarg and Church, 1979). We therefore might expect a steeper rise in the metal concentrations of the tall form grasses. The results of Table 2, however, show the inverse trend; and differences in rate and magnitude of the metal enrichments between the growth forms therefore seem to be related to some other factor.

Table 3 presents the chemical component analyses of the dead grasses from all treatment combinations. The results show that the percentages of C, H and S in the decaying grasses fluctuated with time. The nitrogen contents of the fertilized grasses dropped considerably during the first weeks of plant decay and remained unchanged thereafter. No single

TABLE 3

Decompositional changes in C, N, and S in tall and short *Spartina alterniflora* from untreated and from fertilized marsh plots. Mean percentages (n=2) ± S.E.

Element	Marsh treatment	Growth form	Decomposition time 0 Days	32 Days	70 Days	168 Days
Carbon (%)	Control	Short	43.1±0.7	40.8±0.9	42.0±0.0	41.8±1.7
		Tall	41.9±0.05	40.1±1.3	41.4±0.2	42.4±1.1
	Fertilized	Short	41.9±0.8	37.7±1.6	39.7±1.5	40.6±1.0
		Tall	41.7±0.4	38.7±0.1	39.9±0.1	42.1±1.0
Nitrogen (%)	Control	Short	0.77±0.10	1.00±0.10	0.73±0.09	0.90±0.11
		Tall	0.53±0.09	0.54±0.03	0.48±0.06	0.72±0.04
	Fertilized	Short	2.54±0.01	1.48±0.0	1.60±0.56	1.63±0.38
		Tall	1.20±0.17	0.82±0.05	0.92±0.06	0.83±0.18
Sulfur (%)	Control	Short	1.22±0.07	1.16±0.02	1.60±0.48	1.25±0.12
		Tall	1.10±0.07	1.11±0.03	1.21±0.08	1.08±0.02
	Fertilized	Short	1.29±0.06	1.33±0.17	1.71±0.60	1.24±0.25
		Tall	1.23±0,15	1.10±0.04	1.17±0.13	1.30±0.01

pattern could be discerned for the sulfur content as a function of the decomposition time. Significantly higher contents of sulfur ($p < 0.05$) and nitrogen ($p < 0.001$) were found in the short form S. alterniflora in comparison with the tall form. This trend was of interest because sulfhydryl and amino groups are known to be active in the binding of heavy metals. Nitrogen contents were also significantly higher in the fertilized grasses ($p < 0.001$) due to increased uptake of nitrogen from the sludge-treated marsh (Valiela et al., 1978). However, heavy metal increases of the litter did not appear to be enhanced due to the fertilization of the marsh. The results therefore do not support the hypothesis that quantitative differences in nitrogenous compounds affect the heavy metal uptake of dead S. alterniflora. Since we could not make a similar comparison for sulfur, we are uncertain about the role of this element in the metal enrichment process.

Squiers and Good (1974) measured a larger crude fiber (cellulose and hemicellulose) content in the tall form litter. These structural carbohydrates, low in nitrogenous compounds, form an effective sorbent for organo-metallic complexes (Pellenbarg, 1978). Thus, dead tall S. alterniflora may potentially be a better sorbent for surfactant, metal-rich compounds than the short form. Since metal concentrations were generally lower in the tall form grasses, we hypothesize that a more intensive desorption takes place in these grasses. The immediate explanation for this process is the physical removal of metal-enriched materials, adhered loosely to the

litter. Such a desorption process may, perhaps, result from the more prolonged tidal submergence of plants found lower in the intertidal range. Thus the net accumulation of heavy metals during the detritus formation of S. alterniflora may be controlled by a balance between adsorption and desorption mechanisms. A relative enrichment by selective weight loss of the grasses during decay may further add to these processes, depending both on the nature of the metal and the rate of decomposition of the plants.

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SUMMARY AND CONCLUSIONS

(1) Application of a mercury containing sewage sludge to experimental salt marsh plots resulted in a three to six-fold enrichment of the surface soil (0-5 cm) of vegetated marsh habitats, with the majority retained in the top 2 cm.

(2) Mercury losses in low intertidal marsh regions followed first order kinetics with a half-life of about 4 years. Mass balance calculations showed that mercury was quantitatively retained by the soil at higher marsh elevations.

(3) Physical and mechanical processes, such as sediment transport, erosion and dilution of enriched sediments with uncontaminated materials accounted for the diminution of low-intertidal sediment mercury concentrations, rather than biological methylation or geochemical dissolution processes.

(4) The bulk density (specific gravity) of the marsh soil was primarily related to the degree of compactness of the peat. Waterlogged soils expanded and decreased the dry weight volume weight values, while the presence of minerals markedly increased the bulk density. A detailed knowledge of the specific density is therefore needed when establishing mass balances and distribution profiles for trace metals in peaty soils.

(5) Background concentrations of mercury in marsh soils are largely dependent on their mineral content, and vary considerably from one marsh system to another. In the low mineral, high organic Sippewissett Marsh a fairly uniform distribution was found in the surface 20 cm, with mercury

levels ranging between 100 and 200 ng Hg/dry gram.

(6) Soil-bound mercury is associated with the detritus particles smaller than 1 mm in diameter. The complexation of mercury with these constituents is very stable: No dissociation took place when the marsh soil was treated with either 0.5 N NaOH or 0.5 N HCl, and only 30% was dissolved in concentrated HCl.

(7) In sludge-treated soils mercury remained bound by the sludge constituents, probably in the form of organo-mercury complexes and as mercuric sulphide. At higher marsh elevations the soil mercury content compared well with the weighted sum of the natural mercury concentrations of the marsh sediment and that of the sewage sludge.

(8) Anthropogenic mercury in the marshes of the Hackensack Meadowlands was closely related to the soil organic matter content in the surface 25 cm of the vegetated marsh. It appears that dilution processes during events of high mineral deposition resulted in distortion of the historic mercury discharge records.

(9) Marsh grasses and organisms inside experimental plots did not concentrate mercury from the enriched sediments. At very high sediment mercury levels a considerable accumulation was found in the roots of S. alterniflora, but an apparent blocking mechanism prevented transfer to above-ground tissues. Export of dead marsh grasses therefore appears to be unimportant in the mass balance of anthropogenic mercury in the estuarine environment.

(10) The bioavailability of mercury in the salt marsh system was found to be inversely related to the organic matter content of the soil. This relationship was observed for mussels, fiddler crabs and S. alterniflora roots. Tissue concentrations of mercury in organisms reflect predominant sediment conditions, and therefore may vary largely between different uncontaminated marshes. Sediment variables such as pH, redox potential and metal chelating capacity are involved in the transfer of soil mercury to biota.

(11) Concentrations of mercury, copper, zinc and iron increased in S. alterniflora when these grasses started senescence, and continued throughout the detritus formation. Levels of chromium and manganese only increased in the tall form. Metals generally increased more steeply in the short growth form. This phenomenon could not be explained by differences in the chemical composition of the grasses.

(12) Generally, no uptake of trace metals was found from the metal-enriched experimental plots. Metal enrichments resulted from litter contact with the organo-metallic complexes accumulated in the surface film of adjoining marsh waters, and to a lesser degree from decay weight losses of relatively low metal containing plant parts. The ultimate enrichment in trace metals during the aging process of S. alterniflora is related to the extent that the sorbed metal complexes are held by the exposed litter.

APPENDIX 1-A

List of chemicals used, manufacturer, and label identified mercury content, if available.

Chemical	Catalog Number	Manufacturer	Mercury content
H_2SO_4	5-9685	Baker Scientific Co.	0.0003 ppm
HNO_3	3-9603	Baker Scientific CO.	0.0003 ppm
HCl	3-9535	Baker Scientific Co.	n.a.*
$KMnO_4$	1-3227	Baker Scientific Co.	0.02 ppm
$SnCl_2$	11-3980	Baker Scientific Co.	0.03 ppm
	T-142	Fisher Scientific Co.	n.a.
$NH_2OH.HCl$	1-2196	Baker Scientific Co.	0.05 ppm
$Mg(ClO_4)_2$	0828	Baker Scientific Co.	n.a.
NaOH	S-318	Fisher Scientific Co.	0.1 ppm
$HgCl_2$	M-156	Fisher Scientific Co.	n.a.
HgS, powder	M-195	Fisher Scientific Co.	n.a.
TBP**	8-W432	Baker Scientific Co.	n.a.

*not available

** $(CH_3CH_2CH_2CH_2O)_3PO$

APPENDIX 1-B

Preparation of chemical solutions

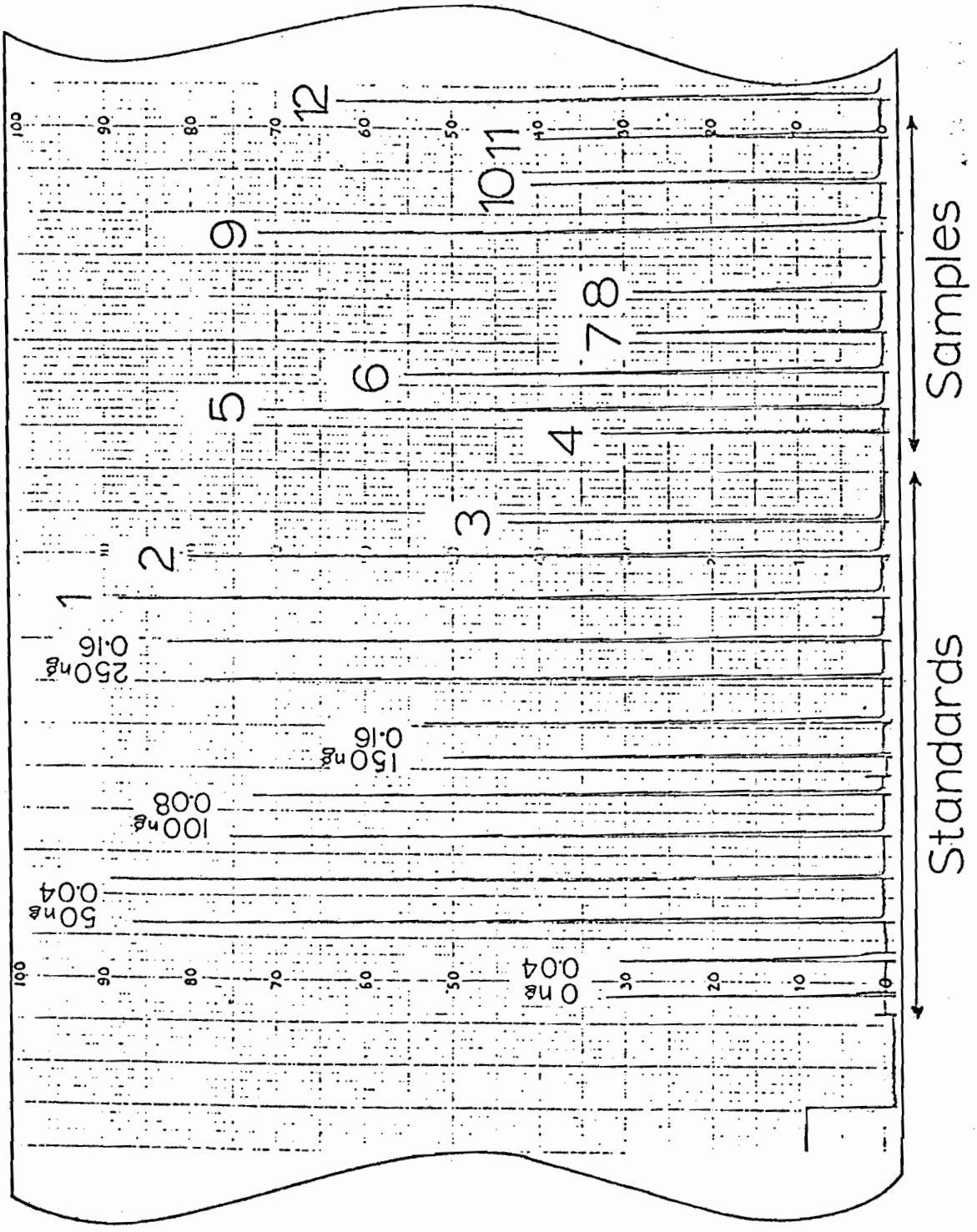
Acid mixture	1 volume conc HNO_3* and 2 volumes conc H_2SO_4. Stir, cool, keep inside dark container.
6% $KMnO_4$	60 g $KMnO_4$ and 1 L water**. Heat, stir, keep inside dark container for one month maximum.
10% $NH_2OH.HCl$	100 g $NH_2OH.HCl$ and 1 L water.
20% $SnCl_2$	300 g $SnCl_2$ and 1500 mL 60% HCl (v/v). Mercury-free air was bubbled through the solution to rid it of mercury contamination. Air was led through drying tube filled with silver-coated glass beads.
1000 ppm Hg solution	1.3535 g $HgCl_2$ and 1 L 5% nitric acid (v/v). Heat, shake. Good for several months.
1 ppm Hg solution	0.1 mL 1000 ppm Hg solution and 100 mL 5% nitric acid (volumetric flask). Accurate micropipet was used. Prepare fresh each day.

* Reagent-grade chemicals were used. (See appendix 1-A).

** Deionized water was used. (Ultra Pure Water Systems; Hydro Service & Supplies, Inc.; Specific resistance in excess of 18 megohms/cm).

FIGURE 1 (Appendix). Typical recorder output of a sample run with standards (in duplicate) obtained by the method of standard addition. Mercury spikes to the blank solution included, in this case, 0, 50, 100, 150, and 250 ng Hg. The attenuation setting of the "mercuryMonitor" is shown by the lower number given for each standard peak. At mercury spikes < 300 ng Hg a very linear response typically results. The peakheights of the standards in the example presented in Figure 1 has been plotted against the added quantity of mercury in Figure 2.

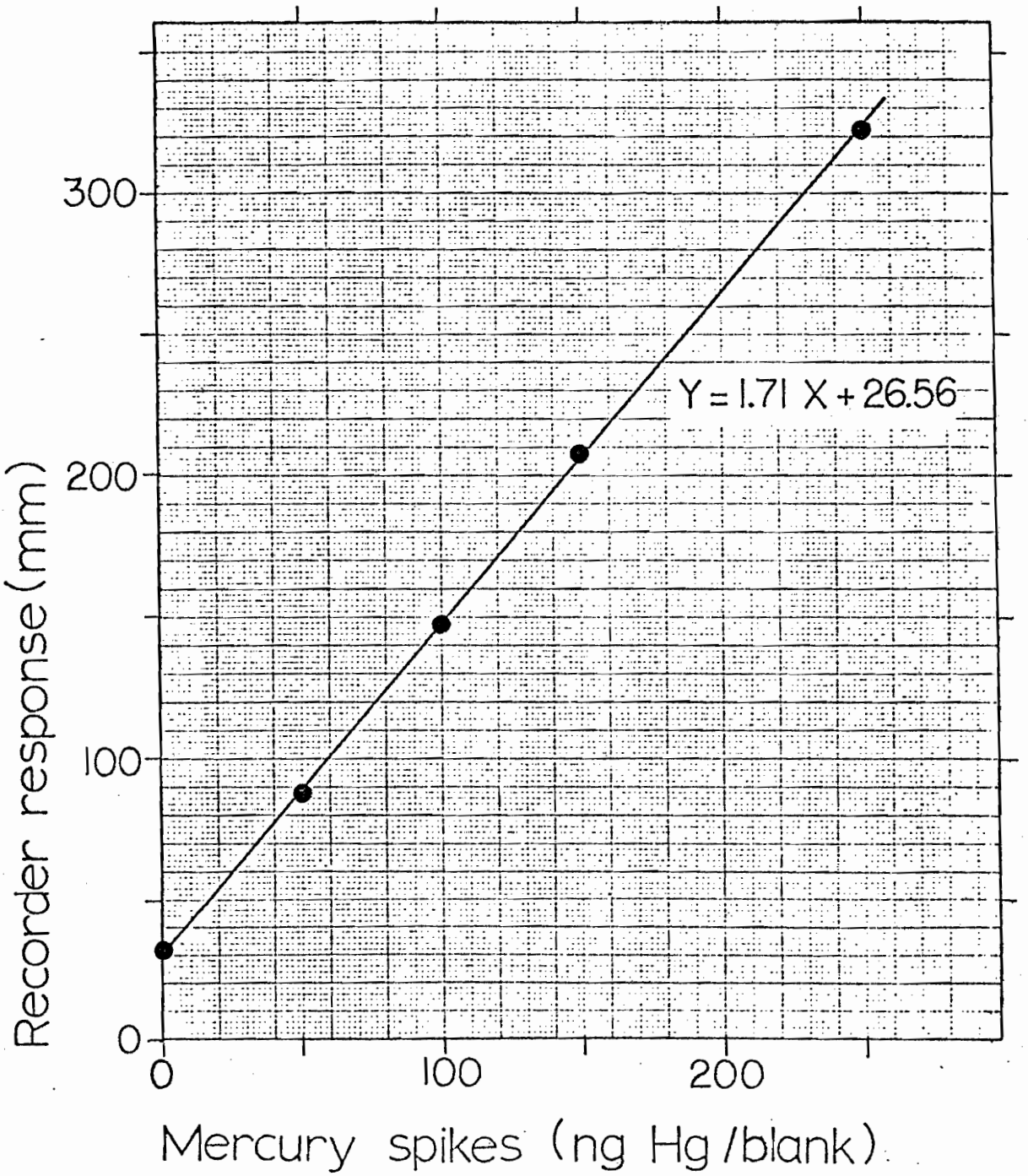
The density of the mercury vapor carried into the measuring cell of the flameless atomic absorption unit is measured at a wavelength of 253.7 nm, and is corrected for background absorption by measuring the absorption of the carrier gas in the second cell of the dual cell absorption chamber. The optical system uses a source of uv radiation, located at the optical axis of the cells. This essentially monochromatic light is passed through two cells (7.5 cm in diameter and 30 cm long) and falls on a dual solid state transducer which has been sensitized to convert 253.7 nm radiation falling upon it to an electric signal. These signals are fed into a Wheatstone bridge circuit, and the bridge voltage thus has an output proportional to the concentration of mercury in the carrier gas (nitrogen) flow.


Standards
Samples
0 ng
0.04
50 ng
0.04
100 ng
0.08
150 ng
0.16
250 ng
0.16
1
2
3
4
5
6
7
8
9
10
11
12

APPENDIX 2-B

FIGURE 2 (Appendix)

Linear relationship between the mercury content of the standard solution and the recorder response. The responses, registered on the recorder, are taken from the example presented in Figure 1 of this appendix. The mercury content of the sample is read directly from the regression equation, after correction for sample weight.


Y = 1.71 X + 26.56
Recorder response (mm)
0
100
200
300
0
100
200
Mercury spikes (ng Hg /blank)

APPENDIX 3

Mercury analyses of NBS Standard Reference Material No. 1571 (orchard leaves). Values were obtained during ten consecutive sample runs. The certified value of dried total material is 155 ng Hg/g (2 standard deviations 15 ng/g)

Date of analysis	Mercury concentration (ng Hg/g dry weight)* Replicate 1	Replicate 2	Mean
Oct. 28, 1977	158	154	156
Nov. 4	150	147	149
Nov. 18	154	133	144
Dec. 2	172	161	166
Dec. 9	156	149	153
Jan. 13, 1978	166	142	154
Jan. 27	159	160	160
Feb. 10	149	n.d.**	149
Feb. 17	133	133	133
Mar. 2	160	n.d.	160
Mean $\pm$ 2 stand. dev.	156 $\pm$ 21	147 $\pm$ 22	152 $\pm$ 19
Coëff. variation	6.8%	7.4%	6.1%

*Dry weight determined after drying subsamples overnight at 110°C

** n.d. means not determined

APPENDIX 4

Study of possible losses of mercury due to sample pretreatment procedures in S. alterniflora (marsh cord grass), M. demissus (ribbed mussel), and tidal creek muds. Means ± S.E. and individual measurements are presented in ng Hg/dry gram.

Sample pretreatments	Mercury (ng Hg/dry g)	
	Replicates	Means±S.E.
S. alterniflora		
Wet analyzed	72, 80, 61	71 ± 6
Oven-dried (105°C)	73, 119, 72	88 ± 16
Freeze-dried, closed vacuum gauge	84, 135, 90	103 ± 16
M. demissus		
Wet analyzed	225, 247	236 ± 11
Wet analyzed, homogenized*, frozen thawed inside digestion flask	226, 234	230 ± 4
Same, but thawed and exposed to air for several days	256, 274	265 ± 9
Same, but freeze-dried, open vacuum gauge	311, 315	313 ± 2
Same, but freeze-dried, closed vacuum gauge	261, 287	274 ± 13
Same, but oven-dried at 50°C	259, 264	259 ± 5
Mud		
Wet analyzed	225, 120, 141, 186	168 ± 23
Oven-dried at 50°C	153, 172, 155, 131	153 ± 8

* Polytron ultrasonic homogenizer

APPENDIX 5

Possible sources of error in the determination of total mercury. The level of relative importance, or the degree with which these errors may affect the accuracy, reproducibility or reliability of the determination have been indicated by + signs (+ least important; +++ most important), based on the experience of the author.

SAMPLE PRETREATMENT	
Incomplete homogeneity of samples	+++
Samples contain various amounts of moisture	++
Hg is lost during freeze-drying, oven-drying, or air-drying	+
Hg is lost during storage, freezing and thawing, or homogenizing	+
Samples with low mercury content are contaminated	+
MERCURY EXTRACTION (DIGESTION AND OXIDATION)	
Incomplete digestion due to lack of sample agitation	+++
Inadequate amount of oxidant (highly organic sample)	+++
Sample size too large, causing incomplete mercury extraction	+++
Temperature too low during digestion	++
Temperature too high, causing loss of volatile mercury	++
Hg losses after dilution of extract and dissolution of MnO_2	+
REDUCTION AND MEASUREMENT	
Insufficient stirring time	+++
Nitrogen flow outside the limits of 0.7 ± 0.3 liter/minute	+
Hg absorbed by wet magnesium perchlorate	++
Hg lost after addition of reductant and before closing of flask	++
Hg lost due to adsorption onto incompletely dissolved MnO_2	+
Hg lost during period less than 24 hours after dilution of extract	+

APPENDIX 6

Mercury concentration (ng Hg/g dry weight) of Modiolus demissus with shell lengths less than 6 mm and greater than 6 mm ($\bar{X}$ ± S.E. as well as the range are presented). Samples consist of 3-9 individuals ($\bar{N}$ = 5). Concentrations of mercury represent single measurements. Analytical uncertainty is less than 5%. Stations represent small (< 2 m^2) areas inside or outside experimental plots in Great Sippewissett Marsh.

Station	Mercury concentration (ng Hg/g)	Shell length $\bar{X}$ ± S.E. (range) (mm)
1	243	5.5 ± 0.2 (4.9-5.8)
	223	6.5 ± 0.3 (6.1-7.2)
2	173	5.3 ± 0.3 (4.6-6.0)
	187	7.1 ± 0.3 (6.3-8.0)
3	282	4.5 ± 0.3 (3.2-5.8)
	201	7.3 ± 0.2 (6.6-7.8)
4	269	5.1 ± 0.3 (4.1-5.8)
	298	7.7 ± 0.5 (6.5-9.7)
5	141	5.6 ± 0.2 (5.2-6.0)
	110	6.6 ± 0.2 (6.1-6.9)
6	133	5.9 ± 0.1 (5.6-6.0)
	194	6.3 ± 0.2 (6.1-6.4)
7	172	4.9 ± 0.3 (4.3-5.2)
	112	6.9 ± 0.1 (6.8-7.1)

APPENDIX 7-A

Mean mercury concentrations in ng Hg/g dry matter ± S.E. in live Spartina alterniflora, S. patens, and Distichlis spicata from Great Sippewissett Marsh. The grasses were obtained from untreated marsh plots and from experimental plots treated with extra-high (XF) dosages of a mercury-containing dried sewage sludge. All dates refer to 1978.

	Mercury concentrations (ng Hg/g)				
	6/20	7/20	8/21	9/28	10/23
Control plots					
Tall *S. alterniflora*	22±1	13±0	26±3	18±1	16±3
Dwarf *S. alterniflora*	21±6	14±0	37±9	20±1	18±1
*S. patens & D. spicata**	20±5	21±2	32±6	27±1	25±3
XF-fertilized plots					
Tall *S. alterniflora*	18±2	16±1	23±4	22±2	23±1
Dwarf *S. alterniflora*	24±1	15±4	23±1	20±1	19±3
*S. patens & D. spicata**	19±1	16±0	29±3	23±1	21±2

*S. patens and D. spicata grasses were pooled, since these plants usually are found growing together in densely vegetated high marsh locations and could not be differentiated easily.

APPENDIX 7-B

Mercury distribution in above-ground part of S. alterniflora. Various plant parts include the base stalk (0-5 cm part of the culm above-ground), the stalk (part of culm remaining after leaves and flower structure has been removed), the blades (including the base part surrounding the culm), and the flower structure (which includes the top part of the stem to which the seeds are attached). ppm = ng Hg/g dry weight.

Plant part	Weight Distribution	Mercury distribution in Spartina alterniflora					
		Berrys Creek marsh		Saw Mill Creek marsh		Great Sippewissett marsh	
	%	ppm	%	ppm	%	ppm	%
Base stalk	5.8	273	10.6	13	0.8	11	3.2
Stalk	27.8	33	6.2	19	5.6	10	14.7
Blades	54.5	208	75.9	143	82.3	23	65.0
Flower structure	11.9	93	7.4	90	11.3	27	17.0
Total	100	150	100.1	95	100	19	99.9

APPENDIX 8

Specific gravity of marsh peat (oven-dried at 110 °C, overnight) before and after compression (See Chapter 1: Results; Sediment characteristics). Also presented is the percentage organic matter content of the soil samples. Values are means ± S.E.

Number of samples (N)	Specific density before compression (g/cm^3)	Specific density after compression (g/cm^3)	Organic matter content (%)
6	0.11 ± 0.01	0.52 ± 0.02	60.1 ± 2.0
6	0.15 ± 0.0	0.49 ± 0.02	64.4 ± 2.6
4	0.19 ± 0.01	0.55 ± 0.02	56.0 ± 3.1
4	0.26 ± 0.02	0.59 ± 0.02	54.0 ± 3.6

APPENDIX 9

Appendix 9 shows that the mercury concentration of each particle size range of the sludge-treated marsh soil (0-5 cm) can be computed by summing the mercury contents of the original, unfertilized peat and the added sludge component (see Chapter 1, Results).

The surface layer of the XF-treated marsh soils contains 61% peat and 39% sludge by weight, calculated from the total amount of sludge added from 1974-1976. The effect of sludge desintegration due to weathering on the distribution of mercury with particle size was determined experimentally (Figure 4, Chapter 1). The calculated mercury concentrations of particle size ranges approximated the measured values. The calculation presented in appendix 9 was based on 7 parts original sludge and 3 parts desintegrated sludge. This ratio provided the closest approximation of calculated values and measured concentrations (least sum-of-squares method).

The results show that mercury added to the vegetated marsh surface as waste component of municipal sewage remains associated with the sludge component even after this material has decomposed and desintegrated. The tight bonding of this element with sewage sludge has important consequences for its bioavailability in the salt marsh system.

	Particle size fractions (mm)					
	0–0.63	0.067–0.125	0.025–0.25	0.25–0.5	0.5–1.0	1.0
Mercury distribution						
0.61 g peat	8.02	16.01	19.82	20.22	10.96	4.74
0.273 g original sludge	6.50	23.47	53.45	114.17	52.10	6.84
0.117 g degraded sludge	15.33	44.63	75.14	32.91	13.34	3.35
A. Total mercury content of each particle size (ng)	29.85	84.11	148.41	167.30	76.40	14.93
Weight distribution						
0.61 g peat	0.055	0.100	0.135	0.156	0.097	0.068
0.273 g original sludge	0.015	0.026	0.093	0.085	0.067	0.038
0.117 g degraded sludge	0.010	0.021	0.032	0.027	0.018	0.008
B. Total weight of each particle size range (g)	0.080	0.147	0.210	0.268	0.182	0.114
A/B. Calculated mercury concentration (ng/g)	373	572	707	624	420	121
Measured mercury concentration (ng/g)	550	613	695	770	334	29
3.182 standard error	322	341	290	272	354	48

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