

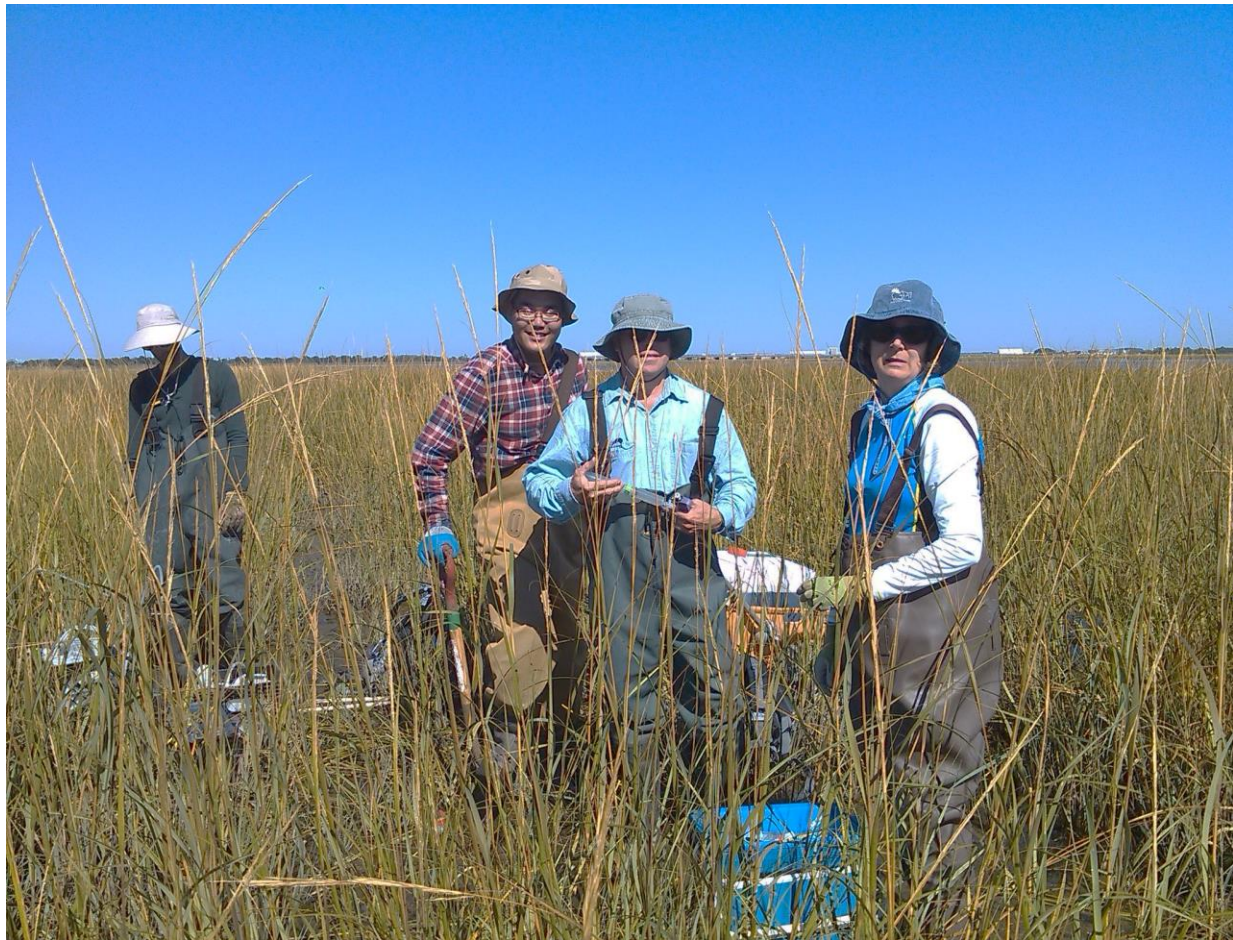


Health and Resilience of Salt Marshes in Jamaica Bay, NY

Geochemical and Dynamical Perspectives

Natural Resource Report NPS/NCBN/NRR—2018/1643





ON THIS PAGE

Elders West marsh. Late summer sampling- September 2015. Left to right: J. Tamborski, H. Yin, J. K. Cochran, C. Heilbrun
Image credit: Q. Zhu

ON THE COVER

Elders East marsh: Spring sampling- April, 2016.
Image credit: J. K. Cochran

Health and Resilience of Salt Marshes in Jamaica Bay, NY

Geochemical and Dynamical Perspectives

Natural Resource Report NPS/NCBN/NRR—2018/1643

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May 2018

U.S. Department of the Interior
National Park Service
Natural Resource Stewardship and Science
Fort Collins, Colorado

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Please cite this publication as:

Cochran, J. K., Q. Zhu, C. Heilbrun, J. Tamborski, H. Yin, P. Fitzgerald, J. Perez-Tuero, and H. Feng. 2018. Health and resilience of salt marshes in Jamaica Bay, NY: Geochemical and dynamical perspectives. Natural Resource Report NPS/NCBN/NRR—2018/1643. National Park Service, Fort Collins, Colorado.

Contents

	Page
Figures.....	vii
Tables.....	xi
Part 1: Overview and Summary of Results.....	1
Introduction and Background.....	1
Pore Water and Solid Phase Geochemistry	5
Marsh Drainage	9
Marsh Accretion Rates	10
Concluding Remarks- Are the marshes studied resilient?.....	11
References	12
Acknowledgements	13
Personnel	13
Part 2: Pore water and solid phase geochemistry of salt marshes in Jamaica Bay: Small- scale heterogeneities and seasonal variation of dissolved Fe^{2+} and H_2S	15
Introduction	15
Sample Sites and Measurements	16
Field Methods.....	16
Discrete Pore Water Sampling and Measurement.....	16
Sensor (Planar Optode) 2-Dimensional Measurements of Pore water H_2S and Fe^{2+}	25
Solid Phase Geochemistry	26
Results	33
Discussion	54
Heterogeneities of Fe^{2+} and H_2S distributions in marsh peat pore water	54
Seasonal Variation of H_2S and Fe^{2+} distributions in marsh pore water.....	56
Interaction of H_2S and Fe^{2+} distributions in marsh peat pore waters	57
Interaction of H_2S and Fe^{2+} as seen in the solid phase: Degree of Pyritization.....	57
Co-distribution of H_2S and phosphate in marsh pore water	58

Contents (continued)

	Page
Time Series of $\Sigma\text{H}_2\text{S}$ in Jamaica Bay Marshes- 2004 to 2016	59
Summary	61
Acknowledgements	63
References	63
Supplemental Information	66
Google Earth images of sampling sites (2004-2016)	66
Part 3: Accretion rates of salt marshes in Jamaica Bay, New York: JoCo and Big Egg	71
Introduction	71
Sampling and Measurements.....	71
Results	72
Discussion	83
Accretion Rates	83
Summary	89
Acknowledgements	90
References	90
Supplemental Information	91
Part 4: Investigation of pore water residence times and drainage velocities in salt marshes using short-lived radium isotopes	95
Abstract	95
Introduction	95
Methods	96
Site Description	96
Sampling & Analyses	98
Residence Time Estimates.....	99
Results	100
Geochemistry.....	100

Contents (continued)

	Page
Pore Water Velocity & Residence Time	105
Fe and H ₂ S Throughput Fluxes	108
Discussion	109
Controls on Ra Activities	109
Environmental Significance	113
Summary and Conclusions	114
Acknowledgements	115
References	115
Supplemental Information	119

Figures

	Page
Figure 1.1. Map of Jamaica Bay located within south-western Long Island, NY, showing the sampling sites mentioned in this report.....	2
Figure 1.2. Schematic diagram of a positive feedback loop (shown in red) that may contribute to marsh degradation and loss.....	3
Figure 1.3. The diagenetic cycle of sulfur in marsh peat and subtidal sediments.....	4
Figure 1.4. Tide gauge records at Sandy Hook, NJ	5
Figure 1.5. Average pore water H ₂ S concentrations in the ~5-30 cm depth zone of marshes in Jamaica Bay, as a function of sampling season	6
Figure 1.6. Example of results from in situ sensors that record the concentrations of H ₂ S (A & B) and Fe ²⁺ (C & D) in the pore water of marsh peat.....	8
Figure 1.7. ²²⁴ Ra-derived estimates of pore fluid residence time (t, in days; top) and vertical seepage velocity (v, in cm/day; bottom) at shallow (25 cm) depths in Jamaica Bay marshes, NY	9
Figure 1.8. Example of accretion chronology in JoCo marsh, Jamaica Bay, based on ²¹⁰ Pb data.....	11
Figure 2.1. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of Big Egg (BE) marsh peat in fall 2014, Jamaica Bay, NY.....	34
Figure 2.2. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of Elders East (EE) marsh peats in fall 2014, Jamaica Bay, NY.....	35
Figure 2.3. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of Elders West (EW) marsh peats in fall 2014, Jamaica Bay, NY	36
Figure 2.4. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of JoCo (JC) marsh peats in fall 2014, Jamaica Bay, NY	37
Figure 2.5. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of Big Egg (BE) marsh peats in spring 2015, Jamaica Bay, NY.....	38
Figure 2.6. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of Elders East (EE) marsh peats in spring 2015, Jamaica Bay, NY	39
Figure 2.7. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of Elders West (EW) marsh peats in spring 2015, Jamaica Bay, NY.....	40
Figure 2.8. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of JoCo (JC) marsh peats in spring 2015, Jamaica Bay, NY	41

Figures (continued)

	Page
Figure 2.9. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of Big Egg (BE) marsh peats in summer 2015, Jamaica Bay, NY	42
Figure 2.10. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of Elders East (EE) marsh peats in summer 2015, Jamaica Bay, NY	43
Figure 2.11. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of Elders West (EE) marsh peats in summer 2015, Jamaica Bay, NY	44
Figure 2.12. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of JoCo (JC) marsh peats in summer 2015, Jamaica Bay, NY	45
Figure 2.13. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of Big Egg (BE) marsh peats in spring 2016, Jamaica Bay, NY	46
Figure 2.14. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of Elders East (EE) marsh peats in spring 2016, Jamaica Bay, NY	47
Figure 2.15. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of Elders West (EW) marsh peats in spring 2016, Jamaica Bay, NY	48
Figure 2.16. H ₂ S and dissolved Fe ²⁺ distribution patterns in the pore water of JoCo (JC) marsh peats in spring 2016, Jamaica Bay, NY	49
Figure 2.17a. Total dissolved sulfide ΣH ₂ S (=H ₂ S + HS ⁻ + S ²⁻) profiles in pore water of Elders East (EE), Elders West (EW), JoCo (JC) and Big Egg (BE) in Jamaica Bay, NY, in fall 2014 and spring 2015	51
Figure 2.17b. Total dissolved sulfide ΣH ₂ S (=H ₂ S + HS ⁻ + S ²⁻) profiles in pore water of Elders East (EE), JoCo (JC) and Big Egg (BE) in Jamaica Bay, NY, in summer 2015 and spring 2016.....	52
Figure 2.18. Comparison of seasonal variations in H ₂ S, HPO ₄ and Fe average (±1 SD) concentrations in the pore water and plant root epidermis (of <i>S. alterniflora</i>) from Elders East (EE2), NY, showing an opposite variation of these elements between the pore water (top) and the root epidermis (bottom) with seasonal change	53
Figure 2.19. Temporal variation of average total dissolved inorganic sulfide (ΣH ₂ S) in pore waters of different salt marsh sites at Jamaica Bay, NY	61
Figure 2S.1. JoCo (JC) sampling sites, Jamaica Bay, NY	66
Figure 2S.2. Elders East (EE) sampling sites, Jamaica Bay, NY	67
Figure 2S.3. Elders West (EW) sampling sites, Jamaica Bay, NY	68

Figures (continued)

	Page
Figure 2S.4. Big Egg (BE) sampling sites, Jamaica Bay, NY	69
Figure 3.1. ^{210}Pb and ^{226}Ra vs depth at Big Egg 1, a restored site in Big Egg Marsh, Jamaica Bay, NY (Fig. 3S.3)	82
Figure 3.2. ^{210}Pb and ^{226}Ra vs depth at Big Egg 3, a site in Big Egg marsh, Jamaica Bay, NY	83
Figure 3.3. Ln (excess ^{210}Pb) vs. depth (for depths >15 cm) for Big Egg 1 in the restored part of the marsh, Jamaica Bay, NY	84
Figure 3.4. Ln (excess ^{210}Pb) vs. depth for Big Egg 3, from the unrestored part of the marsh, Jamaica Bay, NY	85
Figure 3.5. ^{210}Pb -based accretion chronology for JoCo 1, a marsh site in Jamaica Bay, NY	88
Figure 3.6. ^{210}Pb -based accretion chronology for JoCo 2, a marsh site in Jamaica Bay, NY. For comparison, the rate of rise of mean sea level over the period is 0.4 cm/y.	88
Figure 3.7. ^{210}Pb -based accretion chronology for JoCo 3, a marsh site in Jamaica Bay, NY. For comparison, the rate of rise of mean sea level over the period is 0.4 cm/y.	89
Figure. 3S.1. Generalized map of Jamaica Bay, New York, showing location of Big Egg and JoCo marshes that are discussed in this section of the report.	91
Figure 3S.2. JoCo marsh sampling sites, Jamaica Bay, NY.	92
Figure 3S.3. JoCo marsh sampling sites (expanded scale), Jamaica Bay, NY	92
Figure 3S.4. Big Egg marsh sampling sites, Jamaica Bay, NY.	93
Figure 3S.5. Big Egg marsh sampling sites (expanded scale), Jamaica Bay, NY.	93
Figure 4.1. Jamaica Bay, located within south-western Long Island, NY (inset, red box), with the approximate locations of the five sampled marshes.	97
Figure 4.2. Co-variation between ^{223}Ra and ^{224}Ra , arranged by marsh, for all sampling campaigns at Jamaica Bay, NY	101
Figure 4.3. Comparison of shallow (25 cm; solid) and deep (≥ 50 cm; dashed) ^{224}Ra activities for pore waters in Jamaica Bay, New York	102
Figure 4.4. Pore water ^{224}Ra vs. salinity (A), ORP (B) and pH (C), arranged by marsh in Jamaica Bay, NY, for April 2015, September 2015 and April 2016 samples	103

Figures (continued)

	Page
Figure 4.5. Mean solid-phase ^{228}Th , solid-phase (reactive) Fe and solid-phase (reactive) Mn vs. sediment grain size (10^{th} percentile), for shallow and deep sediments, arranged by marsh. Shallow (S) samples are represented by filled symbols, deep (D) samples are represented by hollow symbols.....	105
Figure 4.6. ^{224}Ra pore water profile from JoCo Marsh, New York, during November 2013, October 2014 and April 2016.....	107
Figure 4.7. Comparison of shallow (25 cm; solid) and deep (≥ 50 cm; dashed) ^{224}Ra derived estimates of vertical seepage velocity (v ; top) and residence time (τ ; bottom) of marshes in Jamaica Bay, NY	108
Figure 4.8. Shallow (25 cm) ^{224}Ra derived estimates of residence time vs. the sampling site's distance from the nearest creek bank for samples collected during April 2015, September 2015 and April 2016.	112

Tables

	Page
Table 2.1a. Marsh sampling site locations and sampling dates, Jamaica Bay, NY.	17
Table 2.1b. Elders East site pH, redox potential, and salinity data, Jamaica Bay, NY. ^A , ...	18
Table 2.1c. Elders West site pH, redox potential, and salinity data, Jamaica Bay, NY. ^A	19
Table 2.1d. Big Egg site pH, redox potential, and salinity data, Jamaica Bay, NY. ^A	20
Table 2.1e. JoCo site pH, redox potential, and salinity data, Jamaica Bay, NY. ^A	21
Table 2.2. Pore water solute data for Jamaica Bay, NY. ^A	22
Table 2.3. Solid phase geochemical data for Jamaica Bay, NY. For sampling locations and dates, see Table 2.1a. ^A	27
Table 2.4. Solid phase chromium reducible sulfide (CRS), total sulfur (Total S) and acid- leachable iron (Fe) in Jamaica Bay, NY, marsh sediments. ^A	29
Table 3.1a. Sampling locations and dates of cores for determining marsh accretion rate in Big Egg Marsh, Jamaica Bay, NY.	72
Table 3.1b. Radiometric data for Big Egg Marsh, Jamaica Bay, NY. ^A	73
Table 3.1c. Inventories of excess ²¹⁰ Pb in Big Egg Marsh cores, Jamaica Bay, NY.	76
Table 3.2a. Sampling locations and dates of cores for determining marsh accretion rates in JoCo Marsh, Jamaica Bay, NY.	77
Table 3.2b. Radiometric data and constant flux accretion rates for JoCo Marsh, Jamaica Bay, NY. ^A	77
Table 3.2c. Inventories of excess ²¹⁰ Pb in JoCo Marsh cores, Jamaica Bay, NY.	80
Table 3.3. Loss-on-ignition (organic matter content) data for Elders, Big Egg and JoCo marsh sites, Jamaica Bay, NY	81
Table 4.1. Mean ($\pm$ SD) shallow (25 cm) pore water ²²⁴ Ra activities, advective velocities and residence times for each marsh, arranged by sampling season at Jamaica Bay, NY.	101
Table 4.2. Mean ($\pm$ SD) solid-phase ²²⁸ Th and ²²⁸ Ra activities (dpm g ⁻¹) arranged by marsh, with corresponding grain size distributions (10 th and 50 th percentile) and organic content (as % loss-on-ignition)	104
Table 4.3. Steady-state Ra activities (dpm L ⁻¹) $\pm$ 1 σ counting error, taken as the highest observed pore water ²²⁴ Ra activity for each marsh site sampled in Jamaica Bay, New York.	106

Tables (continued)

	Page
Table 4.4. Mean ($\pm$ SD) pore water Fe and H ₂ S from shallow (S) and deep (D) samples, arranged by marsh in Jamaica Bay, NY	109
Table 4S.1. Marsh sampling locations, Jamaica Bay, NY.	119
Table 4S.2. ^{224,223} Ra activities and modeled advective velocities (v) and pore water residence times (τ). ^A	120

Part 1: Overview and Summary of Results

Introduction and Background

Jamaica Bay is a highly urbanized estuary (~80 km²) located between the boroughs of Queens and Brooklyn in New York City, NY (USA), with a connection to the Atlantic Ocean through Rockaway Inlet (Fig. 1.1). There are over a dozen isolated marsh islands within Jamaica Bay, some of which are natural, and many of which have been restored through engineering efforts. Four primary sewage treatment plants discharge over 300 million gallons of treated effluent into Jamaica Bay per day, which carry significant loads of dissolved nutrients and trace metals (Benotti et al., 2006).

Eutrophication in Jamaica Bay, from sewage treatment plant effluent and combined sewer overflows, is thought to be an important driver of salt marsh degradation and loss, with reduced sediment loads, dredging, boat traffic, and an increase in sea level acting as additional factors (Hartig et al., 2002).

Degradation has increased in recent years to an estimated 134 km/yr of creek and open-bay-edge marsh loss, corresponding with an increase in N loads (Hartig et al., 2002). Microbial respiration of organic matter in the water column leads to significantly low levels of dissolved oxygen, which subsequently results in coastal acidification within the bay (Wallace et al., 2014). Inputs of submarine groundwater discharge to Jamaica Bay are $(0.8 - 9.0) \times 10^9 \text{ L d}^{-1}$, estimated from a radium (Ra) isotope mass balance, with the majority of the flow composed of recirculated seawater (Beck et al., 2007). The large volumetric contribution of recirculated seawater through the coastal aquifer is a minor source of nutrients but a significant source of dissolved trace metals, with the flux of Fe, Zn, Co and Ni rivalling inputs from treated wastewater effluent (Beck et al., 2009). The high input of nutrients and metals from these various point-source and nonpoint-sources have resulted in significant environmental degradation and loss to the Jamaica Bay salt marsh ecosystem.

This report presents the results of a systematic study of salt marshes in Jamaica Bay over a two-year period from 2014 to 2016 (Fig. 1.1). The marshes studied – Big Egg, Elders Point East and West and JoCo – were selected because they spanned the range from fully restored marshes (Elders East in 2006/07, and Elders West in 2010), to partially restored (Big Egg in 2003), and to a natural marsh considered ‘healthy’ (JoCo). Three sampling sites were established in each marsh (see the Google Earth maps of sampling sites in Supplementary Information of Part 2 of this report). These sites were selected in part to complement those sampled in an earlier study (Cochran et al., 2013) and in part to coordinate with ongoing research such as accretion rates determined via Surface Elevation Tables (SETs). Pore water samples were collected at two times of the year, (spring and late summer/early fall) using “sippers” and push-point piezometers that collected water from discrete depths. These were supplemented with chemical sensors sensitive to the concentrations of H₂S and Fe²⁺ in pore water. The latter produced two-dimensional images of sulfide and iron concentrations in the upper 25 cm of the marsh peat (e.g. Fig. 1.6). Sediment cores were collected for solid phase geochemistry and for accretion rate determination (at Big Egg and JoCo) using the natural radionuclide ²¹⁰Pb. Larger volume pore water samples were analyzed for the natural radionuclide ²²⁴Ra to determine drainage rates of water through the marsh peat. Details of the sampling site locations, pore water and solid phase geochemistry, and accretion and drainage rates of the marshes studied are presented in Parts 2-4 of this report.

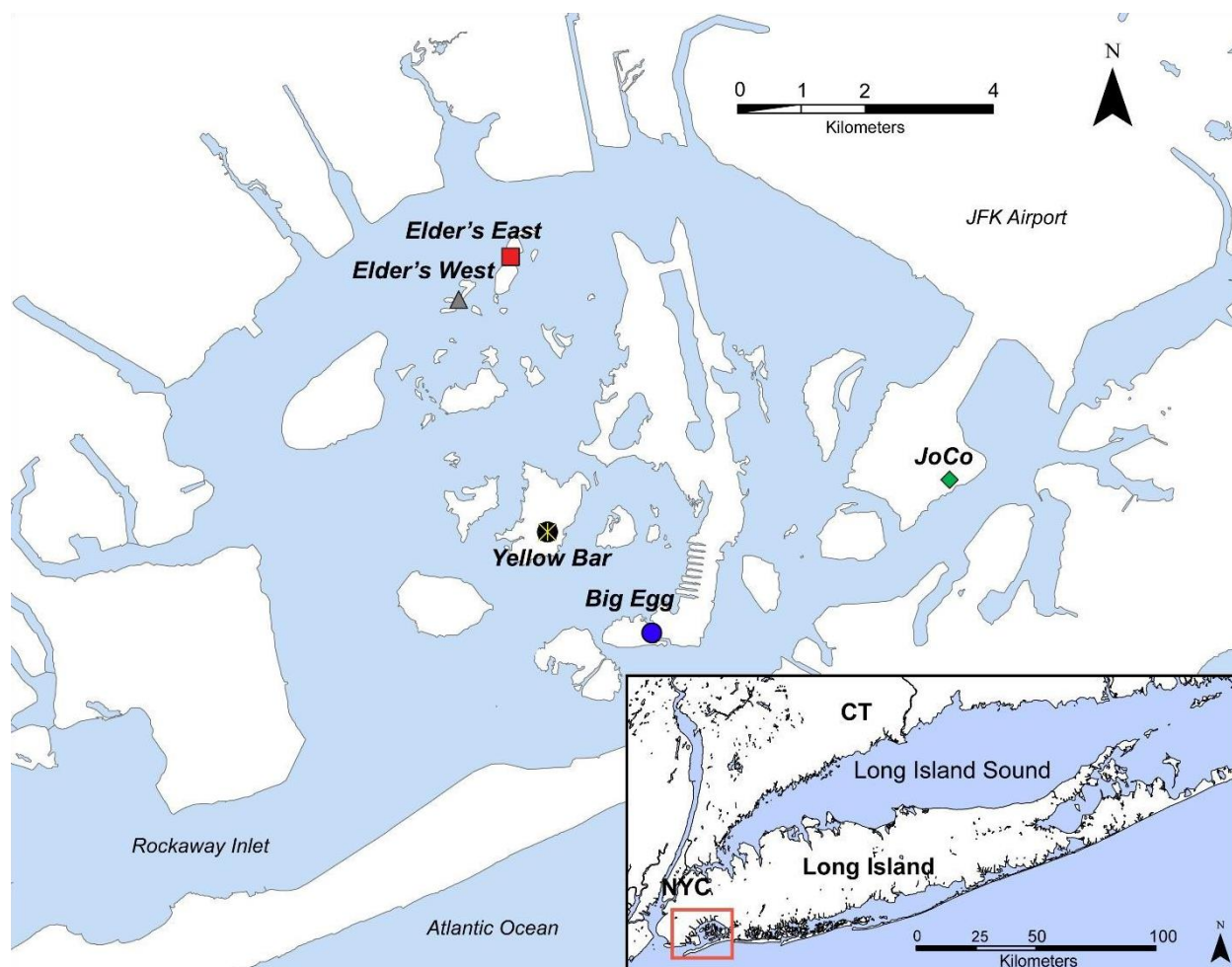


Figure 1.1. Map of Jamaica Bay located within south-western Long Island, NY, showing the sampling sites mentioned in this report.

This study has its origins in earlier work begun in 2004 to characterize salt marshes in Jamaica Bay before and after restoration (Elders East and West) and to compare them with natural marshes such as JoCo that have not suffered significant areal loss (Cochran et al., 2013). The fundamental hypothesis underlying this work was developed by Kolker (2005; Fig. 1.2) and stated that in eutrophic systems such as Jamaica Bay, enhanced organic matter production or supply can be delivered onto the marsh surface, stimulating the production of dissolved hydrogen sulfide via bacterially-mediated sulfate reduction in the pore water of the marsh peat. This process causes hydrogen sulfide (H_2S), a toxin to marsh plants, to build up to levels that are harmful to the plants (> 4 millimolar, mM), and continued exposure to elevated H_2S may contribute to marsh plant die-off and peat collapse (Fig. 1.2).

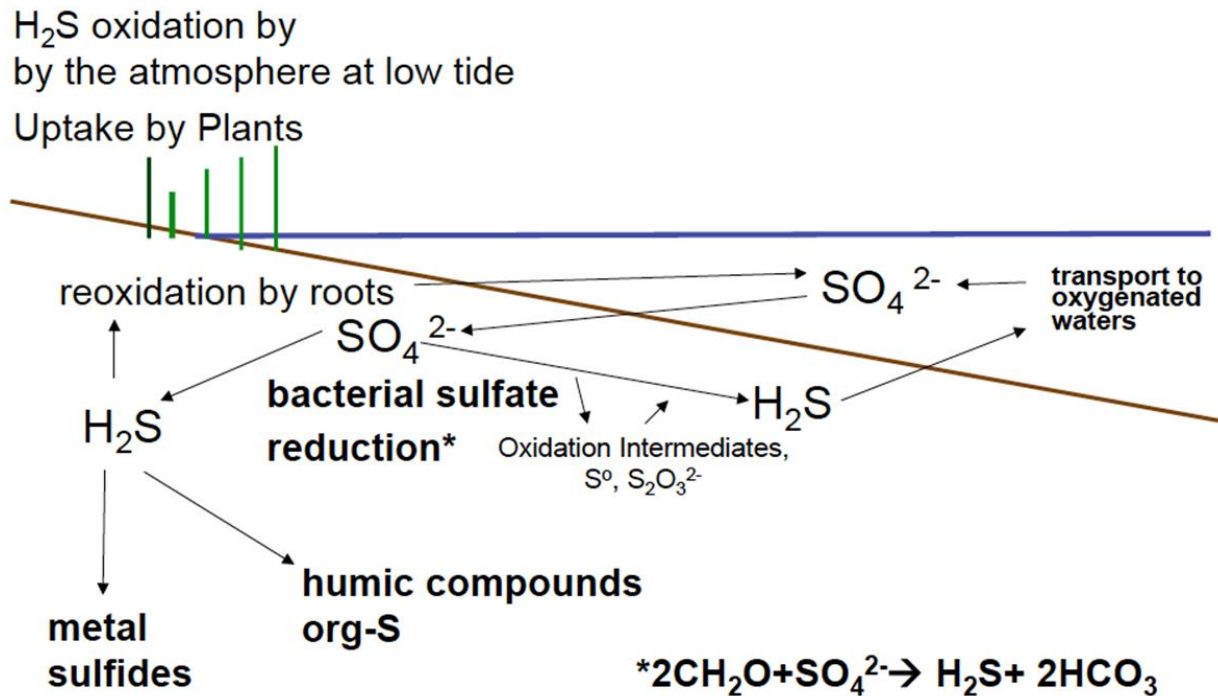


Figure 1.2. Schematic diagram of a positive feedback loop (shown in red) that may contribute to marsh degradation and loss. Enhanced nutrient inputs stimulate phytoplankton and algal blooms. This labile organic matter can be transported by tides onto the marsh surface, where it can undergo bacterial decomposition via sulfate reduction. This produces elevated concentrations of hydrogen sulfide, a phytotoxin, in the marsh peat pore water. As plants die, the peat collapses, causing lowered elevation of the marsh surface and decreased rate of accretion, facilitating further deposition of organic matter onto the marsh. Untreated sewage inputs to Jamaica Bay via Combined Sewer Overflow (CSO) events can also supply labile organic matter to the marsh surface (adapted from Kolker, 2005; Cochran et al., 2013).

The sulfur cycle in marshes can be complex and is subject to numerous feedbacks (Fig. 1.3). For example, H₂S can interact with the iron redox cycle such that Fe²⁺ in the pore water reacts with H₂S to precipitate iron monosulfide (FeS) and pyrite (FeS₂), thus removing H₂S from solution. This negative feedback helps control the concentration of H₂S in the pore water, but is dependent on the availability of reactive iron. As well, bacterial activity is dependent on temperature and is lower at colder temperatures. Thus, sulfate reduction proceeds at a slower rate in winter and spring. Impressed upon this seasonal cycle of sulfide production are the physical dynamics of the marsh system. Marshes are intertidal deposits that are flooded periodically on high tides and then drained on low. In the marsh islands of Jamaica Bay, a part of the tidal drainage is percolation of water through the marsh peat. This process also can lower H₂S concentrations or at least attenuate them by effectively flushing the marsh with low H₂S bay water. Finally, marshes must accrete or grow upward to keep pace with sea level. As sea level is rising, marshes are accreting. For Jamaica Bay, the most appropriate record of sea level rise is that available at the tide gauge at Sandy Hook, NJ (Fig. 1.4). That rate, ~0.41 cm/y, provides a long-term value to which marsh accretion may be compared.

Thus, we sought to answer three questions in this study:

- 1) What are the levels of H_2S and Fe^{2+} (and related solutes such as NH_4^+ and PO_4^{3-}) in marsh peat pore water and how do they vary with season (Part 2 of this report)?
- 2) What has been the history of marsh accretion over the past ~100 years (Part 3 of this report)?
- 3) What are the rates of flow of pore water through the marshes (Part 4 of this report)?

In the sections that follow, we briefly summarize the key results from each of the parts of this report. The reader is referred to each part for detailed discussion of that particular aspect of the study.

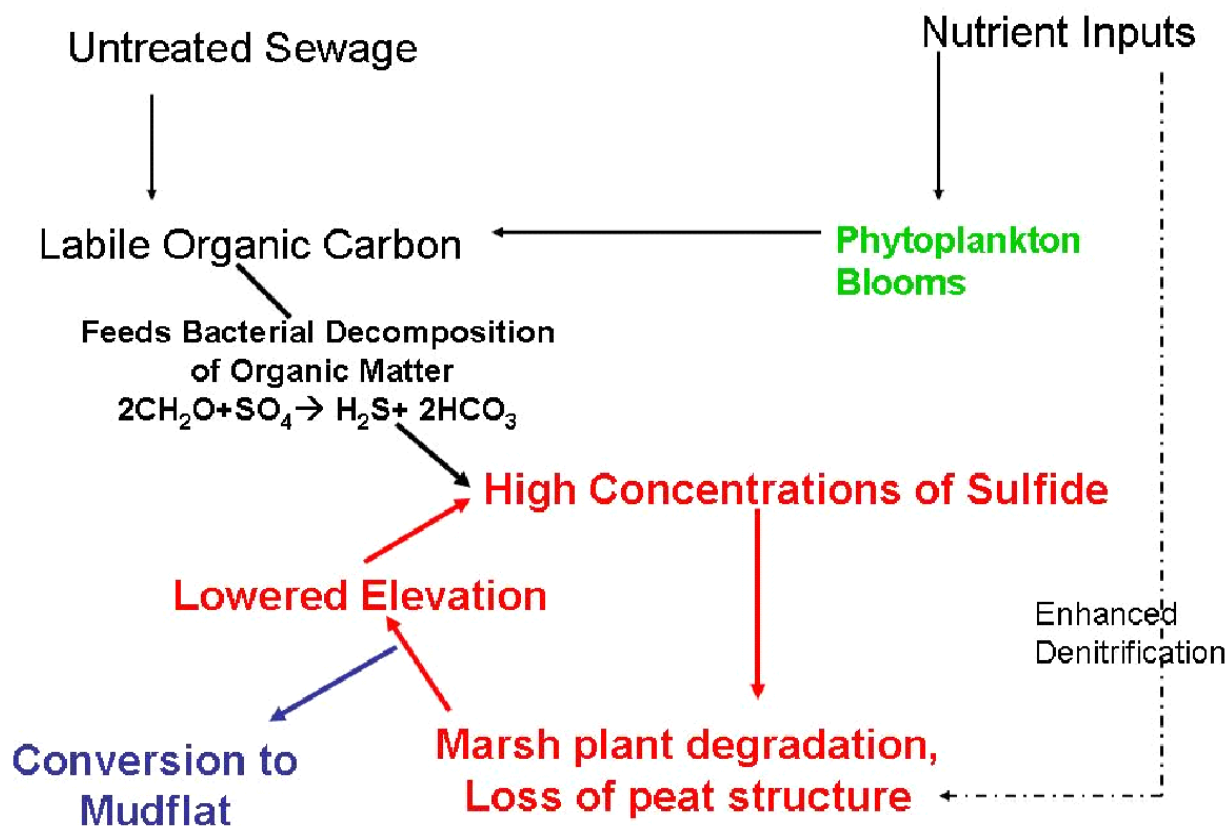


Figure 1.3. The diagenetic cycle of sulfur in marsh peat and subtidal sediments. Vertical green bars represent marsh plants. Horizontal blue bar is mean sea level. Sulfate (SO_4) supplied from seawater is used to oxidize organic matter (reaction marked with *). This produces hydrogen sulfide (H_2S) in the marsh pore water, which can be toxic to the plants but can also react with dissolved iron (as Fe^{2+}) to precipitate metal sulfides (FeS and FeS_2) (adapted from Kolker, 2005; Cochran et al., 2013).

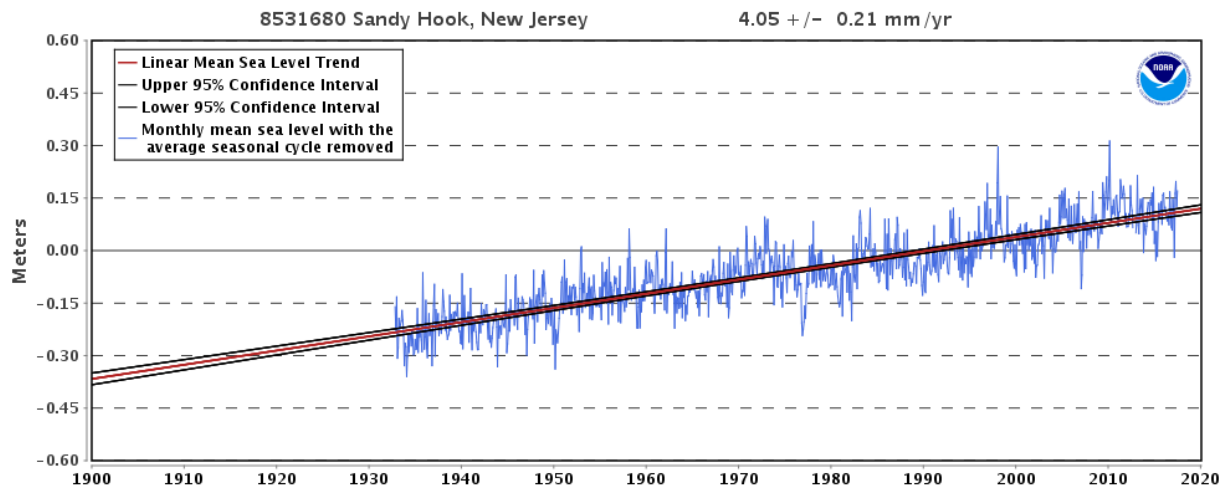


Figure 1.4. Tide gauge records at Sandy Hook, NJ. A best-fit line through the data gives a rate of sea level rise of 0.405 ± 0.021 cm/y (source: NOAA).

Pore Water and Solid Phase Geochemistry

Our goal in this phase of the study was to characterize the marsh peat pore water for key solutes that are related to organic matter cycling in the marsh, namely ammonium (NH_4^+), phosphate (PO_4^{3-}) and hydrogen sulfide (H_2S). Additionally, we measured iron because of the linkage between the reduction-oxidation (redox) cycles of sulfur and iron (Fig. 1.3). Sampling was designed to capture the geochemistry of the marshes at two critical times- following the winter cold period when the marsh plants had died back but before spring growth had advanced (designated “spring” samplings) and in late summer/early fall following the summer high temperatures, but before marsh growth died back later in the fall (designated “fall” or “summer” samplings). This sampling scheme was also designed to capture the seasonal variation in the bacterial oxidation of organic matter, a strong driver of sedimentary redox cycles and one that is especially pronounced in the sulfur and iron cycles. We collected samples of pore water at discrete depths within the root zone of the peat and, for the first time, also used in situ chemical sensors sensitive to either H_2S or Fe^{2+} . These gave us a rapid snapshot of the variation in these solutes in two dimensions. The sensor data were in broad agreement with the discrete samples analyzed in the laboratory. They showed that pore water H_2S concentrations were low at Elders East and, especially, Elders West. However, the highest values, ~ 9 mM, were observed at JoCo in the fall 2014 sampling. These levels are sufficient to cause adverse effects on marsh plants, yet JoCo is considered to have lost little area over time. Although JoCo may be at or approaching a biogeochemical “tipping point” beyond which the marsh will deteriorate further, we considered other aspects of the marsh that might moderate the effects of such elevated H_2S concentrations. One such aspect is seasonality- JoCo showed strong seasonality, with very low H_2S values in the spring samplings of 2015 and 2016. These reflect the relatively low rates of bacterial oxidation of organic matter during the cold period of the year, and thus high values of pore water sulfide at JoCo do not persist. In particular, they are low as the growing season begins in the spring.

In part, this is due to reactions such as precipitation of iron sulfides that remove sulfide from the pore water. We examined the solid phase Fe and S and found that very high fractions of the diagenetically reactive iron at JoCo and Big Egg were associated with pyrite, FeS_2 , a stable precipitate that can persist for long periods in anoxic sediments. This implies that the negative feedback associated with the linkage of the diagenetic Fe and S cycles via the formation of iron sulfide precipitates is limited at JoCo and Big Egg. In other words, there is insufficient diagenetically reactive iron to buffer the pore water hydrogen sulfide through formation of iron sulfides.

Our sampling of marshes in Jamaica Bay began in 2004 with characterization the unrestored area of Big Egg marsh, continued from 2005 to 2007 in Big Egg, JoCo and Elders, and in the same marshes from 2014 to 2016 in the present study. Sampling in Elders was designed to capture both pre- and post-restoration efforts there. We measured pore water H_2S in the upper 5-30 cm of the marsh (approximately coincident with the root zone) and the results over time are summarized in Fig. 1.5.

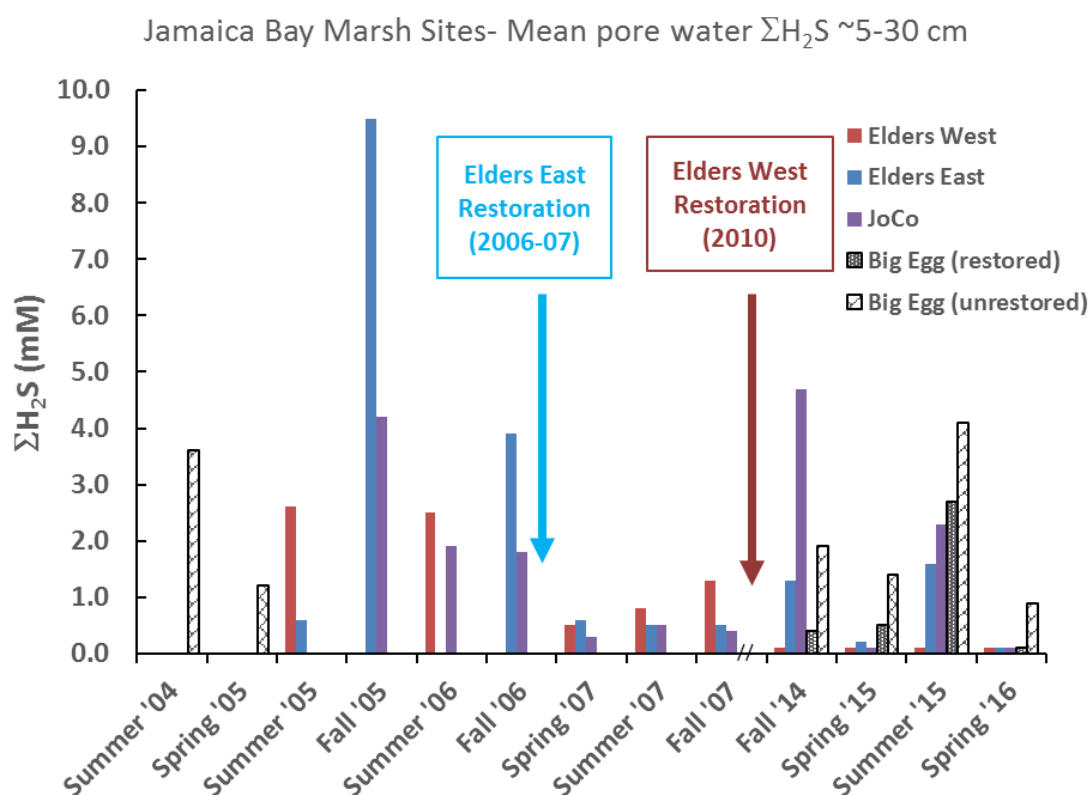


Figure 1.5. Average pore water H_2S concentrations in the ~5-30 cm depth zone of marshes in Jamaica Bay, as a function of sampling season. The method used measures several species of aqueous hydrogen sulfide, i.e., H_2S , HS^- and S^{2-} and is designated $\Sigma\text{H}_2\text{S}$. Note the break in time axis between fall, 2007 and fall, 2014. Dates of restoration for Elders East and West are indicated; Big Egg marsh was partially restored in 2003. Spring, 2007 sampling at Elders East was post-restoration. See Part 2 of this report for details.

The exceptionally high H_2S in Elders East prior to restoration, when the marsh was heavily degraded, is evident. After restoration, H_2S levels have remained low. Although H_2S at Elders West was not

that high before restoration, levels measured in the present sampling from 2014 – 2016 have indeed been low, <0.1 mM. Elders West is characterized by high concentrations of reactive iron that effectively keep the pore water H₂S low. Sites in the unrestored part of Big Egg show H₂S ranging from 1 to 4 mM, with no significant trend over time. In contrast, the restored part of Big Egg, sampled in the present study, shows lower H₂S than the unrestored part of the marsh at comparable sampling times. Finally, JoCo shows considerable variation in H₂S over time with values >4 mM in fall, 2005 and again in fall, 2014, but lower at the other sampling times, with especially low concentrations in the 2007 sampling and in spring, 2015 and 2016. The fact that we have been able to sample the same marshes repeatedly over a period of ~13 years makes it possible to put in perspective H₂S concentrations in marsh pore water as a driver of marsh loss. Thus, although even a healthy marsh such as JoCo displays H₂S concentrations in the root zone that are considered to be lethal levels in greenhouse studies, these concentrations are not maintained seasonally or from year-to-year in the same season.

Even under conditions of high sulfide, marsh plants may cope in other ways. Our use of in situ sensors revealed small-scale spatial heterogeneities in the distributions of Fe and H₂S apparently linked to the effects of the plant roots on the surrounding pore water, such that concentrations of H₂S were lowered in pore water adjacent to the roots (e.g. Fig. 1.6). Either oxidation of the H₂S to sulfate or its precipitation as an iron sulfide phase may have been involved. In the former case, the reaction results in a decrease in pH. Values of pH at JoCo marsh were among the lowest observed, generally less than 6.5 and occasionally less than 5. Motivated by this result, we collaborated with colleagues at Montclair State University and Brookhaven National Laboratory (BNL) to use the Hard X-Ray Nanoprobe at the National Synchrotron Light Source II to examine the distributions of a suite of trace elements (including Fe and S) on the scale of nanometers in the root epidermis and endodermis of *Spartina alterniflora*, collected at Elders East. The results, published in Nature Scientific Reports, showed that Fe and S co-varied, suggesting precipitation of an FeS phase or Fe-S complex (Feng et al., 2017). Additional recent work at BNL (Feng et al., 2018) showed that when pore water H₂S and Fe were high, the concentrations of these elements in the root epidermis were low (see Fig. 2.19 in Part 2 of this report).

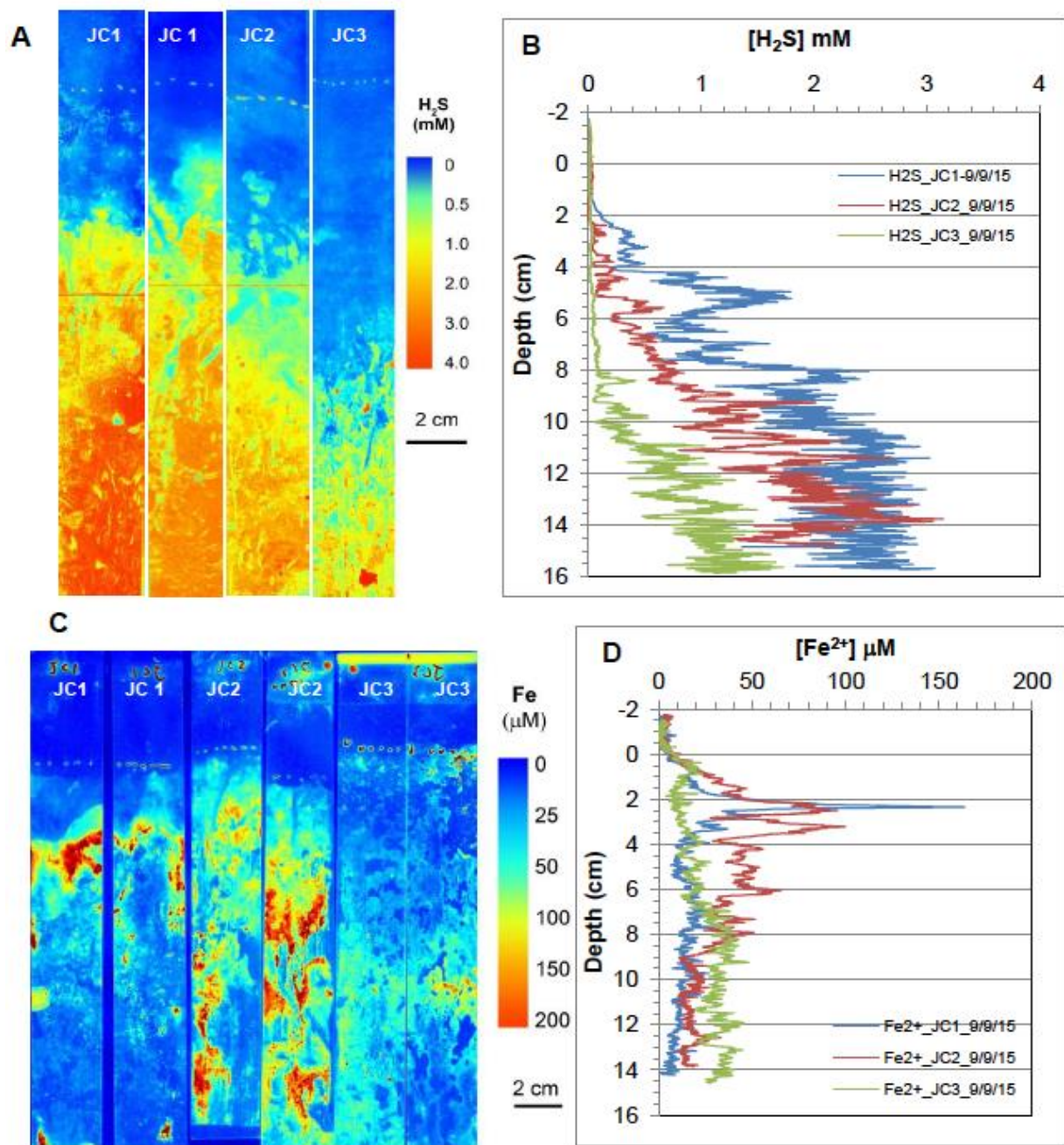


Figure 1.6. Example of results from in situ sensors that record the concentrations of H_2S (A & B) and Fe^{2+} (C & D) in the pore water of marsh peat. The sensors were emplaced in JoCo marsh in early September, 2015, representing late summer conditions. Paired sensors with the same station designation, e.g. “JC 1” are replicates from that station taken approximately 1 m apart. The horizontal dashed line on each image indicates the marsh surface and the color indicates the concentration of solute. The texture in the images is caused by the effect of plant roots on the solute concentrations. Integrating the concentrations of each solute at each depth across the respective images produces the vertical profiles of H_2S (B) and Fe^{2+} (D). In these, 0 on the vertical (depth) axis corresponds to the marsh surface, and negative values show the concentrations of H_2S and Fe^{2+} on the sensor film above the marsh surface (0 in both cases). See Part 2 of this report for details.

Marsh Drainage

An additional factor that may affect pore water hydrogen sulfide is the ability of water to percolate or drain through the marsh peat following flooding during high tides. We examined this through the use of the naturally occurring radium isotope ^{224}Ra (half-life = 3.6 days), and the methodology and results are described in full detail in Part 4 of this report. In brief, we found that the fastest drainage rates in the upper 25 cm were at the sampling sites in JoCo marsh (Fig. 1.7). Indeed, calculated vertical flow through the upper 25 cm at JoCo was ~ 25 cm/day, while it was ~ 5 cm/day at Big Egg. Thus, the residence time of water in the root zone at JoCo is of the order of 1 day. This relatively rapid flushing ensures that pore water sulfide has a short residence time, even though its rate of production via organic matter oxidation may be high. Many factors control the movement of water through marsh peat, but one factor stands out in explaining our results- the height of the marsh surface above mean sea level (MSL). Of the marshes studied, JoCo had the greatest height above MSL. We believe this is a factor in the rapid drainage observed here. This is discussed further in Part 4 of this report, which has also been published in *Marine Chemistry* (Tamborski et al., 2017).

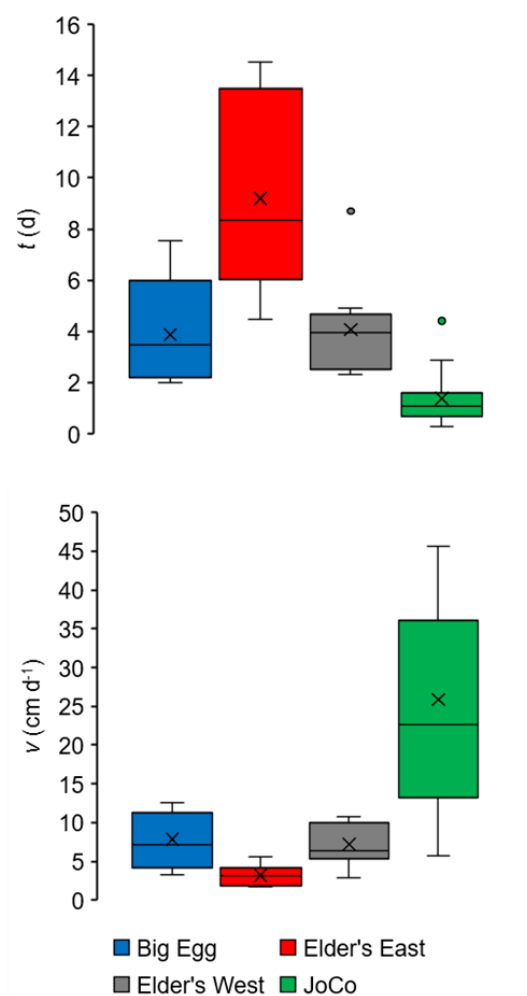


Figure 1.7. ^{224}Ra -derived estimates of pore fluid residence time (t , in days; top) and vertical seepage velocity (v , in cm/day; bottom) at shallow (25 cm) depths in Jamaica Bay marshes, NY. The mean is indicated by a solid black "X." See Part 4 of this report for details.

Marsh Accretion Rates

An additional component of marsh resiliency is the ability of a marsh to accrete to keep pace with sea level rise. Redfield (1972) proposed that salt marshes maintain an “equilibrium” with sea level and as sea level rises, the marsh accretes to keep pace. The record of sea level that is appropriate for comparison with Jamaica Bay is that of Sandy Hook, NJ (Fig. 1.4). The rate of sea level rise from that record is 0.41 cm/y. Our approach was to collect marsh cores and measure the naturally occurring radionuclide ^{210}Pb . Lead-210 is produced in the atmosphere from radioactive decay of radon-222 that emanates from rocks and soils. The ^{210}Pb atoms are quickly stripped from the atmosphere by precipitation and transported to the Earth’s surface. Thus, they are present in soils, including marsh peat, as well as in aquatic sediments. As a sediment deposit builds up, the ^{210}Pb initially at the sediment surface is buried, isolated from its source and decays with a half-life of 22.3 years. The distribution of ^{210}Pb (termed “excess” ^{210}Pb to reflect those ^{210}Pb atoms that have been delivered via the pathway described above) with depth in the deposit can be used to reconstruct the deposition rate of the deposit. In the case of salt marshes, we measure the rate at which the marsh surface grows upward or accretes.

We collected cores at each sampling site in Big Egg and JoCo marshes and analyzed them for ^{210}Pb . No cores were collected at the Elders East and West sites because the relatively recent restoration of those marshes would affect the down-core ^{210}Pb distributions and make it not possible to reconstruct accretion chronologies. Recent accretion at the Elders marshes is best determined through surface elevation tables (SETs). Because the rate of supply of ^{210}Pb to the Earth’s surface is relatively constant at a given location (although significantly variable geographically), we used a “constant flux” model to determine the rate of accretion of the marsh through time. This approach is most appropriate for the JoCo cores, and results are presented and described in detail in Part 3 of this report.

Big Egg and JoCo show radically different patterns in accretion. At Big Egg, two sites were in the unrestored part of the marsh- they showed relatively slow or no accretion. This area is extensively flooded tidally, and the effects of storms, including Hurricane Sandy, on it may be significant. In contrast, a core taken in the area of the marsh on which sediment was sprayed in 2003 showed a pattern consistent with the restoration. The ^{210}Pb profile showed accretion at about the rate of sea level rise prior to restoration. The effect of the emplacement of sprayed sediment is seen in a ~15 cm thick interval of lower excess ^{210}Pb . The upper cm or so shows higher excess ^{210}Pb , indicative of the resumption of accretion. The ^{210}Pb profiles at Big Egg are shown and discussed in Part 3 of this report.

Three cores were taken at JoCo and all permitted reconstruction of marsh accretion through the past ~100 years. Two of the cores (taken at JoCo 1 and 2; see supplementary information for site locations) show accretion at ~0.20 cm/y until around 1980, then increasing values to maxima (~0.6 – 0.8 cm/y) in 2000, well above the rate of sea level rise. Accretion then decreased progressively in both cores back to ~0.25 cm/y. (Fig. 1.8 gives an example of this pattern for JoCo 1). In part, this may be a natural process of recovering from “overshoot”, in which marsh accretion increased to values well above MSL rise, perhaps because plant growth was stimulated by increased nutrient input

to Jamaica Bay, and then was forced to go through a period of lower accretion to recover equilibrium with MSL. However, in one core (JoCo 1) the decrease in accretion continued, to ~0.15 cm/y in the most recent sample. That sample includes accretion in 2012, and any effect of Hurricane Sandy might be evident in it. The recent accretion rate obtained with ^{210}Pb can be compared with SET results. The third core from JoCo (JoCo 3) also shows accretion rate increasing to values above MSL rise and then decreasing to ~0.3 – 0.4 cm/y. The pronounced decrease seen at JoCo 1 is not apparent in that core. The accretion chronologies at JoCo are consistent with it being a “healthy” marsh, but the pronounced decrease in accretion to values less than the rate of MSL rise in at least one core may be cause for concern. It will be important to continue monitoring JoCo for hydrogen sulfide and accretion rates and to compare the ^{210}Pb accretion data with those obtained from Surface Elevation Tables (SETs).

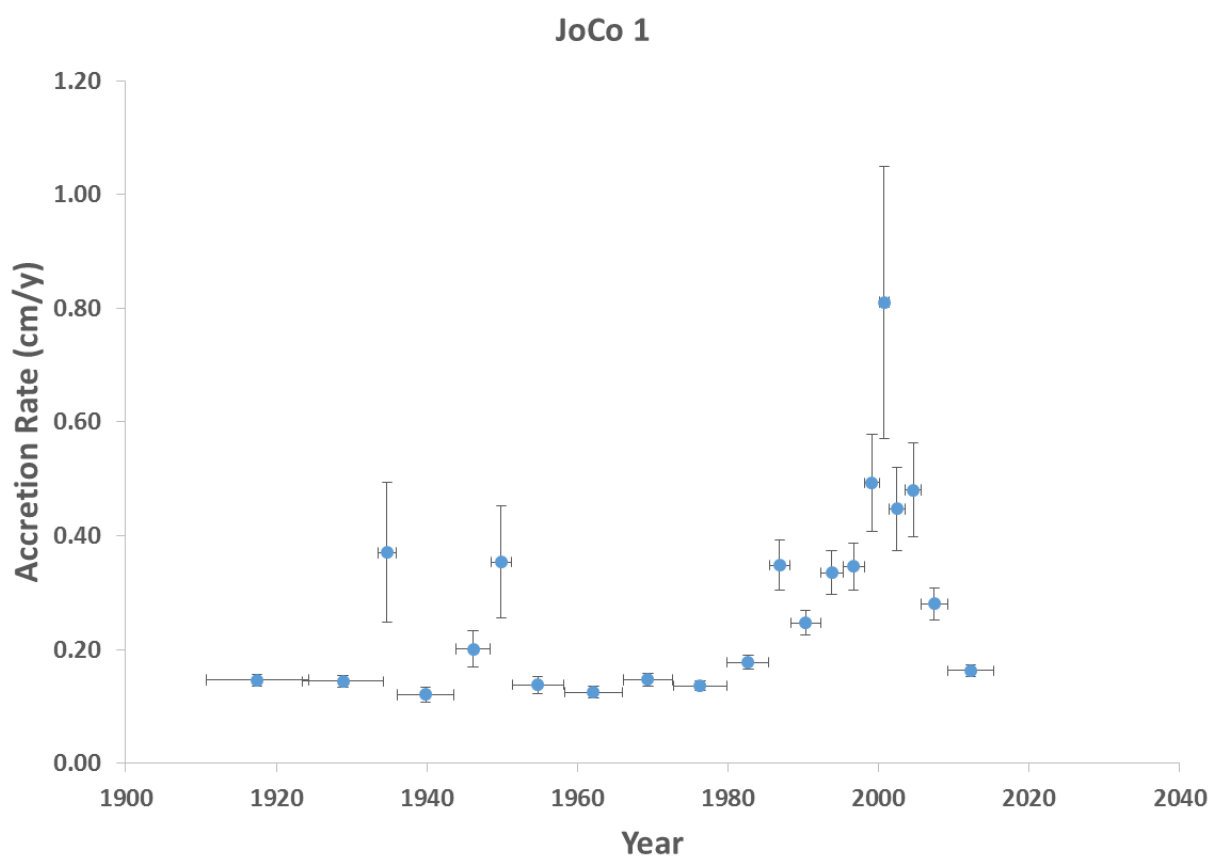


Figure 1.8. Example of accretion chronology in JoCo marsh, Jamaica Bay, based on ^{210}Pb data. The rate of sea level rise over the period covered by this record is 0.4 cm/y (see Fig. 1.4). See Part 3 of this report for details.

Concluding Remarks- Are the marshes studied resilient?

From the perspective of the effects of sediment geochemistry on marsh resilience, Elders East and West show low levels of hydrogen sulfide after restoration. The sandy sediment used to restore those marshes was ideal for “re-setting” the sulfur system to produce low pore water H_2S . The major challenge to the restored marshes seems to be physical- the possible effects of large storms such as

Sandy on the marshes while the plants continue to develop. The restored part of Big Egg marsh shows lower pore water hydrogen sulfide than the unrestored area. In contrast to the sediment used for restoration at Elders, the muddy sand sprayed onto Big Egg did not “re-set” the sulfur system there to the same extent as at Elders. The unrestored area of Big Egg is degrading. At our two sampling stations there, the marsh was either accreting very slowly (much less than sea level rise) or not at all. Degradation was visibly evident in the fragmented nature of the marsh. At JoCo, although the marsh plants were exposed to high levels of H₂S in the early fall, 2014 and late summer, 2015, that situation was not persistent. Our prior sampling at all times in 2007 showed low levels of H₂S, as was the case for the spring, 2015 and 2016 samplings. Marsh drainage rates as determined by naturally occurring radium isotopes, show the fastest drainage at JoCo, and that fact may help moderate possible effects to the plants of exposure to elevated H₂S. The ²¹⁰Pb-based accretion chronologies at JoCo show increases in accretion to values at or above the rate of sea level rise through the 1980s to 2000. However, in one core, the accretion rate decreased from the maximum in 2000 to values about half that of the rate of sea level rise in the sample representing accretion in 2012, the time of Hurricane Sandy. This may indicate that the marsh is developing problems keeping pace with sea level rise, exacerbated by the storm, although the limited spatial coverage of the cores for which accretion was measured makes it difficult to ascertain the exact cause.

Thus, the question of the resilience of JoCo in the face of future changes is difficult to answer. Our long-term data set on marsh geochemistry has been useful in assessing trends in the geochemical setting of Jamaica Bay marshes and the effects of restoration on marsh health. Continued monitoring conducted twice per year at key stations within selected marshes (e.g. JoCo and Elders) is strongly recommended.

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Acknowledgements

This work was supported by the National Park Service Task Agreement P14AC01395 to JKC and QZ and was associated with the Science and Resilience Institute of Jamaica Bay. Portions of the pore water radium study also were supported by National Park Service Award 59054 to JKC and P. Rafferty. J. Tamborski acknowledges funding by a NY Sea Grant fellowship (Project R/CMC-12). We are grateful to our colleagues H. Bokuniewicz and R. Aller (Stony Brook University) for helpful discussion, and to D. Riepe and E. Manclark (American Littoral Society) and P. Rafferty (National Park Service) for logistical support.

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Numerous people were involved in this project. A complete list is as follows:

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- Qingzhi Zhu, Co-Principal Investigator
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- Joseph Tamborski, PhD student
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- Wen Cong
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- Justin Manning

Montclair State University:

Senior Personnel-

- Huan Feng, Professor

Graduate Students-

- Yu Qian, PhD student
- Logistical and other support:
- Don Riepe, American Littoral Society
- Elizabeth Manclark, American Littoral Society
- Patricia Rafferty, National Park Service

Part 2: Pore water and solid phase geochemistry of salt marshes in Jamaica Bay: Small-scale heterogeneities and seasonal variation of dissolved Fe^{2+} and H_2S

Introduction

Iron (Fe^{2+}) and sulfur (S) are two important redox sensitive elements in marine sediment and salt marsh peat, their distribution patterns with depth in the pore water reflect multiple biogeochemical reactions and processes in deposits, for example, organic matter decomposition, sulfate reduction/sulfide oxidation, availability of reactive Fe, and accumulation rate of authigenic pyrite minerals. All these biogeochemical processes are closely coupled to the environment and ecosystem of salt marshes, including marsh peat degradation, accretion, biomass growth/decline, and species diversities. Particulate Fe is input to coastal marshes through wind-blown dust, river run-off, and tidal flooding. The oxidized Fe mineral particles can deposit directly on the marsh surface, and subsequently become involved in early diagenetic reactions in marsh peat. One important pathway for Fe in marsh is the reduction of oxidized FeOOH by organic matter to produce dissolved Fe^{2+} , which can react with sulfide, generating the authigenic minerals FeS and pyrite (FeS_2). Hydrogen sulfide in marsh pore water is generally produced from the reduction of sulfate by bacteria as organic matter is oxidized. Because of the large amount of labile organic matter in marshes (e.g. from marsh plants or combined sewer overflows), the more active electron acceptors O_2 , nitrate/nitrite, Mn-oxide and Fe-oxide are completely consumed by organic matter in a thin surficial layer of the marsh peat, resulting in an anoxic sulfidic environment in most salt marshes. Under anoxic conditions, sulfate-reducing bacteria use SO_4^{2-} as an electron acceptor for organic matter remineralization, producing H_2S as one of the reduced products. This anaerobic respiration process often dominates in organic matter-rich salt marshes, generating high concentrations of H_2S at millimolar (mM) levels. H_2S is harmful to marsh plants such as *Spartina alterniflora*, and long-term exposures to levels greater than ~ 4 mM H_2S in marsh pore water can cause plant die-off, and subsequent peat degradation and subsidence (Pezeshki et al., 1988; Koch and Mendelsohn, 1989; Koch et al., 1990; Seliskar et al., 2004). Therefore, understanding the distribution patterns and seasonal variations of dissolved Fe^{2+} and H_2S , as well as the nutrients phosphate and nitrogen, in marsh pore water is critical for the study of marsh ecosystem functions and processes.

Generally, the intense redox reactions and precipitation/dissolution reactions in the surficial marsh peat generate a sharp gradient of Fe^{2+} and H_2S in peat pore water. The H_2S concentrations can increase from 0 to several mM over depths of millimeters to centimeters, with the concentrations of Fe^{2+} changing by several hundred micromolar (μM). In addition, the growth of marsh plant roots, development of the rhizosphere network, and oxygen transport through roots create complicated and time-dependent three-dimensional distribution patterns of Fe^{2+} and H_2S in marsh peat.

In prior studies, we measured pore water solute concentrations in marsh peat using samples collected with “sippers”—short tubes that are emplaced to various depths in the peat and through which pore water is drawn into an evacuated syringe. In the present study, we have complemented this approach with chemical sensors that provide high-resolution mapping linking the structure of marsh peat with

spatial and temporal patterns of H_2S and Fe^{2+} concentrations. Using sensors made in our laboratory, our goal was to measure the 2-dimensional (2-D) distributions of Fe^{2+} and H_2S in different seasons, examine the interactions of these solutes in marsh pore water, and characterize elevated pore water levels of the phytotoxin, hydrogen sulfide (H_2S). We also sought to compare the results with those obtained through discrete sampling of pore water by conventional techniques and to examine the effects of the redox cycles of Fe and S on the solid phase reservoirs of these elements.

Sample Sites and Measurements

Field Methods

Four study sites in Jamaica Bay were chosen for this project: JoCo, Big Egg, Elders Point East and Elders point West. The marshes were selected because 1) the Elders marshes had been restored in 2006/07 (Elders East) and 2010 (Elders West), 2) Big Egg was partially restored by spraying sediment on top of a portion of the marsh, and 3) JoCo was considered a “healthy” marsh for reference. In addition, we have prior data (2004-2010) from Big Egg, Elders and JoCo marshes with which to compare the present data (Cochran et al., 2013). Three sampling sites were established in each marsh (see Table 2.1 for locations; see Fig. 1.1 for an overview map of Jamaica Bay and Figs. 2S.1-2S.4 for detailed Google Earth images of sampling sites). At each site, pore water samples were taken by “sipper” and push-point piezometer (designated “Radium Samples”) for measurements of dissolved Fe, H_2S , nutrients and ^{224}Ra . Pore water Fe^{2+} and H_2S also were measured by chemical sensors. Pore water pH and oxidation-reduction potential (ORP) were measured by electrode in the field using aliquots of the “sipper” pore water samples. Sediment cores were collected by inserting aluminum tubes (7 cm I.D.) into the peat. Samples for solid phase reactive iron, chromium reducible sulfur and total S, C and N were taken from the cores at all sites. In addition, cores were sampled for ^{210}Pb measurement at JoCo and Big Egg (see Part 3 of this report). Full details of the pore water and solid phase geochemistry are given below.

Discrete Pore Water Sampling and Measurement

Discrete pore water samples were taken using pore water “sippers” at depths of 5, 10, 15, and 25 cm in the marsh peat (Table 2.1). The sippers are hollow acrylic rods that end in a small opening. Each sipper is connected to Tygon tubing which is connected to a 50 ml plastic syringe. A valve connected to the Tygon tubing between the syringe and the sipper facilitates purging of the syringe. Pore water samples of ~50 ml are drawn into the syringe through the sipper. The samples are immediately filtered in the field through 0.45 μm filters. Aliquots for dissolved sulfide, nutrients and trace elements are collected. The sulfide aliquots are fixed in the field by adding 0.5 ml of 0.05 M $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ to each sample. The concentrations of dissolved sulfide, nutrients (NH_4^+ and HPO_4^{2-}) and dissolved Fe^{2+} in these discrete pore water samples were subsequently measured in the laboratory, and the data in Tables 2.1 – 2.2 represent measurements of single samples.

Table 2.1a. Marsh sampling site locations and sampling dates, Jamaica Bay, NY.

Site Name	Marsh Site	Location		Sampling Date			
		Latitude (°N)	Longitude (°W)	Fall 2014	Spring 2015	Summer 2015	Spring 2016
Elder East	EE1	40.63647	73.84761	10/6/14	4/16/15	9/23/15	4/18/16
	EE2	40.63715	73.84596	10/6/14	4/16/15	9/23/15	4/18/16
	EE3	40.63592	73.84628	10/6/14	4/16/15	9/23/15	4/18/16
Elder West	EW1	40.63234	73.85636	10/6/14	4/27/15	9/23/15	4/18/16
	EW2	40.63233	73.85483	10/6/14	4/27/15	9/23/15	4/18/16
	EW3	40.63192	73.85477	10/6/14	4/27/15	9/23/15	4/18/16
Big Egg	BE1	40.59604	73.82637	10/8/14	4/13/15	9/25/15	4/15/16
	BE2	40.59586	73.82814	10/8/14	4/13/15	9/25/15	4/15/16
	BE3	40.59607	73.82812	10/8/14	4/13/15	9/25/15	4/15/16
JoCo	JC1	40.61241	73.78779	10/10/14	5/1/15	9/9/15	4/22/16
	JC2	40.61212	73.78724	10/10/14	5/1/15	9/9/15	4/22/16
	JC3	40.61173	73.78591	10/10/14	5/1/15	9/9/15	4/22/16

Table 2.1b. Elders East site pH, redox potential, and salinity data, Jamaica Bay, NY. ^A

Marsh Site	Depth (cm)	pH				Redox potential (mV)				Salinity (PSU)			
		Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016
EE1	5	6.00	6.75	6.17	6.18	-190	-216	-217	-59	27	20	ND	ND
	10	6.30	6.82	6.37	6.12	-160	-222	-228	-105	27	21	ND	ND
	15	6.50	6.67	6.41	6.23	-192	-178	-254	-125	27	23	ND	ND
	25	6.95	6.68	6.72	6.9	-220	-158	-292	-146	27	23	ND	ND
EE2	5	6.64	6.14	6.04	6.00	-265	-20	-280	-142	27	27	ND	ND
	10	6.65	6.03	6.37	5.88	-249	3	-303	-127	27	20	ND	ND
	15	6.64	6.09	6.15	6.14	-248	-5	-281	-143	27	23	ND	ND
	25	6.88	6.09	6.45	6.88	-265	21	-315	-176	28	18	ND	ND
EE3	5	6.00	6.18	5.75	6.23	-265	-24	-258	-179	29	27	ND	ND
	10	6.04	6.07	6.41	5.87	-249	-105	-295	-161	29	23	ND	ND
	15	6.47	5.63	6.45	6.24	-248	-112	-286	-176	29	22	ND	ND
	25	6.62	5.82	6.71	6.38	-265	-91	-302	-177	29	24	ND	ND
EE1-25 ^B	25	ND	6.52	6.71	ND	ND	-155	-260	ND	ND	26	ND	ND
EE1-50 ^B	50	ND	6.96	7.07	ND	ND	-197	-270	ND	ND	23	ND	ND
EE2-25 ^B	25	ND	6.54	6.32	ND	ND	-136	-270	ND	ND	20	ND	ND
EE2-50 ^B	50	ND	6.68	6.50	ND	ND	-148	-270	ND	ND	22	ND	ND
EE3-25 ^B	25	ND	6.35	6.74	ND	ND	-36	-288	ND	ND	24	ND	ND
EE3-50 ^B	50	ND	6.82	7.07	ND	ND	-120	-248	ND	ND	28	ND	ND

^A Where: ND = Not determined, IV = Insufficient volume for electrode, and NS = No sample^B Radium Sample

Table 2.1c. Elders West site pH, redox potential, and salinity data, Jamaica Bay, NY. ^A

Marsh Site	Depth (cm)	pH				Redox potential (mV)				Salinity (PSU)			
		Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016
EW1	5	6.04	IV	5.94 ^C	6.17	-23	IV	-190	-36	27	30	ND	ND
	10	6.35	7.20	6.40	6.10	-44	-40	-199	-15	27	24	ND	ND
	15	3.48	7.13	6.51	6.59	-75	-40	-210	-19	27	25	ND	ND
	25	3.55	7.20	6.78	6.69	-69	-67	-207	-31	28	24	ND	ND
EW2	5	6.72	7.22	6.73	6.40	-65	-49	-97	-21	27	24	ND	ND
	10	6.72	6.97	6.53	6.45	-128	-70	-128	-24	27	23	ND	ND
	15	6.00	6.81	6.68	6.55	-50	-43	-131	-44	27	24	ND	ND
	25	6.78	6.62	6.71	6.75	-98	-50	-139	-76	27	28	ND	ND
EW3	5	6.30	7.09	6.50	6.19	-115	-90	-97	11	29	31	ND	ND
	10	6.52	7.03	6.68	6.60	-65	-55	-117	-21	29	29	ND	ND
	15	5.75	7.00	6.66	6.68	-20	-94	-124	-27	29	28	ND	ND
	25	6.39	7.10	6.34	6.83	-90	-140	-162	-39	29	29	ND	ND
EW1-25 ^B	25	ND	7.30	6.91	ND	ND	-90	-205	ND	ND	30	ND	ND
EW1-100 ^B	100	ND	7.28	6.84	ND	ND	-128	-130	ND	ND	27	ND	ND
EW2-25 ^B	25	ND	7.50	6.83	ND	ND	-120	-101	ND	ND	28	ND	ND
EW2-100 ^B	100	ND	6.90	6.60	ND	ND	-98	-106	ND	ND	29	ND	ND
EW3-25 ^B	25	ND	7.17	5.91	ND	ND	-90	-89	ND	ND	32	ND	ND
EW3-100 ^B	100	ND	6.97	6.16	ND	ND	-236	-124	ND	ND	38	ND	ND

^A Where: ND = Not determined, IV = Insufficient volume for electrode, and NS = No sample

^B Radium Sample

^C Location: 40.63234°N, 73.85577°W

Table 2.1d. Big Egg site pH, redox potential, and salinity data, Jamaica Bay, NY. ^A

Marsh Site	Depth (cm)	pH				Redox potential (mV)				Salinity (PSU)			
		Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016
BE1	5	6.12	7.01	IV	6.16	-125	-190	IV	-88	27	28	ND	ND
	10	5.74	7.09	6.79	6.02	-75	-233	-345	-129	27	27	ND	ND
	15	6.36	7.12	IV	6.13	-190	-186	IV	-58.2	27	28	ND	ND
	25	6.45	6.84	6.85	6.22	-133	-186	-367	-195	27	28	ND	ND
BE2	5	6.70	NS	7.15	ND	-27	NS	-371	ND	28	NS	ND	ND
	10	7.10	7.08	7.02	6.78	-12	-217	-374	-152	28	29	ND	ND
	15	IV	6.52	IV	6.71	IV	-230	IV	-240	30	29	ND	ND
	25	6.50	6.65	6.67	6.78	-240	-195	-383	-218	29	29	ND	ND
BE3	5	6.00	NS	NS	7.20	-130	NS	NS	-128	28	NS	NS	ND
	10	6.46	6.88	NS	6.87	-200	-250	NS	-192	28	30	NS	ND
	15	6.50	7.26	NS	6.88	-150	-187	NS	-178	29	30	NS	ND
	25	6.34	7.09	NS	6.65	-230	-186	NS	-170	29	30	NS	ND
BE1-25 ^B	25	ND	6.83	IV	ND	ND	-249	IV	ND	ND	30	ND	ND
BE1-50 ^B	50	ND	6.88	6.76	ND	ND	-247	-388	ND	ND	30	ND	ND
BE2-25 ^B	25	ND	6.65	IV	ND	ND	-195	IV	ND	ND	30	ND	ND
BE2-50 ^B	50	ND	6.70	6.56	ND	ND	-226	-376	ND	ND	31	ND	ND
BE3-25 ^B	25	ND	ND	6.9	ND	ND	ND	-331	ND	ND	ND	ND	ND
BE3-50 ^B	50	ND	ND	6.62	ND	ND	ND	-325	ND	ND	ND	ND	ND

^A Where: ND = Not determined, IV = Insufficient volume for electrode, and NS = No sample

^B Radium Sample

Table 2.1e. JoCo site pH, redox potential, and salinity data, Jamaica Bay, NY. ^A

Marsh Site	Depth (cm)	pH				Redox potential (mV)				Salinity (PSU)			
		Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016
JC1	5	6.45	4.88	6.2	5.87	-230	-41	-325	-41	28	32	ND	ND
	10	6.41	6.08	6.15	5.26	-273	-60	-325	-26	29	27	ND	ND
	15	6.50	6.04	6.35	4.79	-270	-90	-350	-18	29	28	ND	ND
	25	6.55	6.25	6.23	5.49	-290	-210	-350	-56	29	27	ND	ND
JC2	5	6.30	5.40	6.82	5.65	-185	-39	-198	-81	28	28	ND	ND
	10	6.55	5.70	6.15	5.4	-220	-113	-277	-59	28	26	ND	ND
	15	6.35	5.62	6.13	5.29	-230	-98	-307	-83	28	25	ND	ND
	25	6.60	6.30	5.77	5.79	-250	-160	-321	-90	28	24	ND	ND
JC3	5	6.13	5.87	6.64	6.06	-220	-86	-234	-69	29	35	ND	ND
	10	6.42	6.04	6.06	4.51	-270	-106	-247	-20	30	31	ND	ND
	15	6.53	6.67	6.12	4.88	-275	-128	-320	-30	32	27	ND	ND
	25	6.64	6.32	5.95	5.26	-285	-164	-235	-66	32	28	ND	ND
JC1-25 ^B	25	ND	6.35	6.17	ND	ND	-165	-292	ND	ND	30	ND	ND
JC1-50 ^B	50	ND	6.65	ND	ND	ND	-190	ND	ND	ND	27	ND	ND
JC1-100 ^B	100	ND	ND	6.64	ND	ND	ND	-320	ND	ND	ND	ND	ND
JC2-25 ^B	25	ND	6.88	6.16	ND	ND	-190	-282	ND	ND	28	ND	ND
JC2-50 ^B	50	ND	6.58	ND	ND	ND	-154	ND	ND	ND	29	ND	ND
JC2-100 ^B	100	ND	ND	IV	ND	ND	ND	IV	ND	ND	ND	ND	ND
JC3-25 ^B	25	ND	6.79	6.4	ND	ND	-184	-276	ND	ND	32	ND	ND
JC3-50 ^B	50	ND	6.57	ND	ND	ND	-209	ND	ND	ND	38	ND	ND
JC3-100 ^B	100	ND	ND	6.36	ND	ND	ND	-312	ND	ND	ND	ND	ND

^A Where: ND = Not determined, IV = Insufficient volume for electrode, and NS = No sample

^B Radium Sample

Table 2.2. Pore water solute data for Jamaica Bay, NY. ^A

Marsh Site	Depth (cm)	NH ₄ ⁺ (μM)				HPO ₄ (μM)				ΣH ₂ S (μM)				Fe (μM)			
		Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016
EE1	5	1.0	53	4.0	11	7.7	6.3	6.0	0.8	229	610	416	77	1	3	32	11
	10	0.0	32	22	4	10.8	7.9	21	2.4	261	699	1284	229	1	3	1	4
	15	2.0	58	31	16	11.3	5.7	29	8.4	114	364	2090	304	1	2	1	3
	25	61	101	45	79	29.9	5.3	25	10.7	991	224	3907	241	0.0	2	0.0	4
EE2	5	2.0	240	10	13	36.5	1.8	3.0	0.0	2028	0.0	127	38	2	24	83	61
	10	0.0	483	72	34	38.7	0.9	46	0.0	2783	63	1385	62	1	98	1	127
	15	0.0	507	16	21	39.4	1.7	14	1.3	1122	88	748	102	1	43	3	40
	25	0.0	834	56	32	38.1	5.4	45	14.3	2553	69	2387	244	2	29	10	3
EE3	5	7.0	24	0.0	12	1.3	0.0	3.0	1.7	1309	0.0	384	4	1	2	73	30
	10	0.0	164	21	17	196.3	0.0	39	25.4	256	0.0	1883	0	1	50	0.0	43
	15	0.0	121	14	39	0.4	0.0	32	20.4	2461	3	1866	283	0.0	234	1	4
	25	5.0	104	23	70	0.3	0.9	44	42.3	1865	7	2519	155	0.0	68	0.0	4
EW1	5	0.0	2.0	1.9	75	4.4	0.4	16.1	0.0	43.0	0.0	16.2	12.0	63	27	23	493
	10	10	0.0	0.0	0.7	18.0	0.0	1.3	0.0	4.0	0.0	0.0	7.0	340	66	61	33
	15	2.0	0.0	0.0	1.3	7.3	0.0	10.4	0.0	6.0	0.0	43.5	1.0	742	42	14	12
	25	1.0	0.0	0.0	2.4	0.6	0.0	25.6	0.0	12.0	0.0	0.0	2.0	254	146	53	72
EW2	5	0.0	0.6	0.0	2.8	30.2	0.0	1.1	0.0	15.0	0.0	6.5	4.0	74	24	157	136
	10	0.0	18.9	0.0	3.7	0.4	0.0	1.3	0.0	31.0	0.0	0.0	2.0	5	187	488	131
	15	0.0	9.3	3.0	2.7	0.4	0.0	1.1	0.6	27.0	0.0	1.3	0.0	66	118	410	156
	25	0.0	17.5	0.0	4.2	0.5	0.0	1.1	0.4	6.0	0.0	0.7	1.0	195	159	374	291
EW3	5	10	5.7	0.2	5.0	27.2	0.0	2.3	0.0	164.0	0.0	0.0	0.0	11	18	40	84
	10	6.9	0.0	0.0	4.3	20.3	0.0	1.3	0.0	45.0	0.0	5.3	0.0	54	30	81	166
	15	19	6.7	0.0	2.3	33.9	0.0	5.5	0.0	21.0	0.0	2.2	0.0	86	96	92	85

^A Zero (0.0) concentrations are below detection, NS = No Sample

Table 2.2 (continued). Pore water solute data for Jamaica Bay, NY. ^A

Marsh Site	Depth (cm)	NH ₄ ⁺ (μM)				HPO ₄ (μM)				ΣH ₂ S (μM)				Fe (μM)			
		Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016
EW3	25	9.0	45.0	0.0	2.4	28.8	3.1	7.5	0.0	5.0	0.0	0.0	0.0	425	366	510	88
BE1	5	14	240	111	0.5	0.1	11	90	0.00	1234	272	1200	10	5	2	11	8
	10	4.2	340	207	2.4	0.0	40	161	0.00	252	882	3015	11	5	2	5	6
	15	59	265	344	1.2	0.4	28	44	0.00	17	413	1370	9	6	4	0.0	5
	25	1.0	245	445	3.2	0.1	20	91	0.2	85	509	5381	27	6	3	1	12
BE2	5	18	882	589	101	0.2	85	115	14.2	17	2476	2962	120	2	3	0.0	5
	10	28	336	752	115	0.2	26	130	15.2	9	926	4022	184	3	3	2	6
	15	NS	160	522	186	NS	24	111	24.5	4965	2576	3178	761	4	4	5	1
	25	158	73	637	182	0.9	11	100	18.5	4436	1431	5491	3159	3	2	2	1
BE3	5	5.8	NS	582	155	0.3	NS	164	10.9	273	1846	2143	97	4	NS	3	2
	10	4.8	610	759	325	0.4	72	212	21.8	840	226	4164	361	4	1	4	1
	15	6.5	207	NS	252	2.1	13	NS	34.5	2116	368	3916	854	3	2	NS	0.0
	25	14	238	762	405	1.0	15	85	53.6	2366	NS	6722	1595	3	1	6	0.0
JC1	5	2.0	57	4.9	3.2	0.2	3.6	14	0.0	2876	4.5	2314	51	3	8	5	4
	10	23	157	41	3.0	0.2	7.9	20	1.2	6095	17	4301	22	3	3	NS	3
	15	28	193	134	4.2	0.2	8.7	20	0.0	5587	43	4658	13	7	6	NS	4
	25	77	224	96	17.7	0.3	9.2	24	1.1	6697	660	4275	160	2	7	NS	5
JC2	5	36	1.6	0.0*	2.9	0.4	0.0	4.3	0.00	846	5.4	NS	16	2	77	15	52
	10	71	2.6	0.0	3.6	0.5	0.0	1.0	0.00	1594	4.5	133	9	3	96	15	46
	15	2.6	7.3	0.0	14.0	0.3	0.0	1.1	0.00	1973	133	588	9	3	141	NS	109
	25	198	41	2.0	8.8	1.0	7.2	4.7	1.0	3487	343	1800	140	4	11	NS	8
JC3	5	10	26	31	2.1	0.2	1.1	11	0.6	3470	2.1	282	10	4	6	15	5
	10	71	181	35	2.6	0.5	4.5	11	0.0	5406	4.9	480	21	6	4	15	4

^A Zero (0.0) concentrations are below detection, NS = No Sample

Table 2.2 (continued). Pore water solute data for Jamaica Bay, NY. ^A

Marsh Site	Depth (cm)	NH ₄ ⁺ (μM)				HPO ₄ (μM)				ΣH ₂ S (μM)				Fe (μM)			
		Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016
JC3	15	102	291	11	3.2	0.1	6.4	22	0.0	9416	24	4056	64	4	3	NS	8
	25	170	248	23	8.6	0.4	7	22	1.9	8539	390	2891	195	20	6	NS	5

^A Zero (0.0) concentrations are below detection, NS = No Sample

Total dissolved sulfide (as $\Sigma\text{H}_2\text{S} = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}]$), ammonium, and phosphate were measured on the pore water samples using techniques described by Kolker (2005) and Cochran et al. (2013). Pore water sulfide was measured colorimetrically (Cline, 1969; Reese et al., 2011). Absorbances were measured at 670 nm using a spectrophotometer, and were compared with those determined for standards of different sulfide concentrations. Replicate standards, including a zero-point deionized water blank were analyzed as part of each sample run. Standard curves had a precisions of $\pm 1-5\%$.

Ammonium and phosphate were measured using a Lachat Nutrient Autoanalyzer. For each analyte a zero-point deionized water blank was run and the blank was $<10\%$ of the lowest standard for that analyte. Each sample was then blank corrected. Replicates (triplicates) were run at the beginning, middle and end of a sample run and precision was better than $\pm 5\%$. Detection limits were .001 mg N/liter for ammonium and .01 mg/liter for phosphate. Dissolved iron was measured with a modified version of the diamine method (Stookey, 1970). Replicates and blanks were analyzed within each sample run.

Pore water pH and Eh (ORP; Oxidation-Reduction Potential) were measured in the field with a YSI 1009-1 09C multi-parameter probe that measured pH on the total H^+ scale and used a Pt electrode for Eh. Salinity values were determined on selected samples in the laboratory through measurement of chloride or with a refractometer. Sampling site locations, and field data are given in Table 2.1. Pore water nutrients, $\Sigma\text{H}_2\text{S}$, and dissolved Fe^{2+} concentrations are given in Table 2.2.

Sensor (Planar Optode) 2-Dimensional Measurements of Pore water H_2S and Fe^{2+}

Dissolved Fe^{2+} in-situ measurement: 2.8×20 cm Fe^{2+} optical sensor strips (Zhu and Aller, 2012) were mounted on one side of a $5 \times 40 \times 1$ cm (width $\times$ length $\times$ thickness) polycarbonate plastic sheet with a beveled end for insertion into marsh peat. In-situ measurements were made at low tide by inserting/punching the plastic sheet with attached sensor strip vertically into the salt marsh peat and allowing it to react for 1 to 10 min, depending on the Fe^{2+} concentration in the marsh. After the reaction, the sensor film was pulled out of the marsh and rinsed with seawater. The color- changed sensing film was developed and calibrated after return to the laboratory. In-situ deployments were duplicated at each site. 2-D in-situ measurements of Fe^{2+} in pore water at each site were conducted at October 2014 (early fall), April 2015 (spring), September 2015 (late summer), and April 2016 (spring).

Dissolved H_2S in-situ measurement: 2-D H_2S distributions in Oct 2014 were measured in box cores which were collected from each site and incubated/re-equilibrated with seawater (collected from the same site) in the laboratory for 24 hours at room temperature. The 2-D H_2S distribution was imaged using a fluorescence H_2S sensor (Zhu and Aller, 2013). 2-D H_2S distributions in all other seasons, April 2015 (spring), September 2015 (late summer), and April 2016 (spring), were obtained by in-situ deployments using irreversible H_2S sensors (Yin et al., 2017). A 3.5×20 cm H_2S sensor film was mounted on one side of a $5 \times 40 \times 1$ cm (width $\times$ length $\times$ thickness) polycarbonate plastic sheet with a beveled end, and the deployment was similar to that of above Fe^{2+} sensing (Zhu and Aller, 2012), duplicate measurements were conducted at each site.

Solid Phase Geochemistry

Cores for solid phase geochemistry (chromium reducible sulfur, iron, total C, N, S) were taken by carefully inserting an aluminum tube (i.d. 7 cm) into the marsh peat. After the tube was emplaced on the marsh surface, vertical cuts were made around the perimeter to minimize compaction as the core was inserted. Immediately after return to the laboratory, the cores were frozen. They were later defrosted only enough to permit the sediment to be extruded and then were sectioned into 1-2 cm intervals. Small aliquots of sediment were removed from each section for solid phase geochemistry and the remainder was weighed, dried, weighed again to determine water content and then ground to a powder.

Solid phase reactive Fe was leached from 25-50 mg of dried, ground sediment with 1 N hydrochloric acid for 24 hours. The resulting leachate was filtered through a 0.45 μm Whatman PES filter and analyzed for Fe using the colorimetric Ferrozine reagent method (Stookey, 1970). Replicate leaches reflected the variability in the sediment samples and replicate analyses of the same leachate or standard solution gave reproducibility of $\pm 5\%$. Sulfur was measured in two pools – chromium reducible sulfides (CRS, dominantly pyrite, FeS_2) and total solid phase sulfur. Total sulfur was measured on dried, ground sediment with a CNS Analyzer and had an error of $\pm 10\%$. CRS was extracted using a passive distillation method (Kolker, 2005). The sulfide released after a 48-hour exposure of the sediment to the chromium was measured using a colorimetric method (Cline, 1969). Duplicate extractions of a sample were done as part of each sample run. Analytical replicates were within $\pm 5\%$; extraction replicates were within 10% and reflected heterogeneity of the sediment. Solid phase C, N, S and Fe are given in Table 2.3 and Fe, total S and CRS data for the summer, 2015 and spring, 2016 samplings are summarized in Table 2.4.

Table 2.3. Solid phase geochemical data for Jamaica Bay, NY. For sampling locations and dates, see Table 2.1a. ^A

Marsh Site	Depth (cm)	Nitrogen (mmol N/g)				Carbon (mmol C/g)				Sulfur (μmol S/g)				CRS* (μmol/g)				Iron (μmol Fe/g)			
		Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016
EE1	5	ND	0.005	0.011	0.69	ND	0.07	0.12	8.02	ND	10.3	17	228	ND	ND	12	4	ND	8.0	6.6	24.1
	10	ND	0.011	0.004	0.01	ND	0.14	0.04	0.17	ND	17.9	20	17	ND	ND	15	13	ND	9.2	6.2	11.3
	15	ND	0.001	0.005	<.001	ND	0.04	0.02	0.02	ND	14.0	35	18	ND	ND	35	14	ND	9.8	6.8	8.4
	25	ND	ND	0.000	<.001	ND	ND	0.99	0.01	ND	ND	16	11	ND	ND	11	9	ND	ND	9.8	9.3
EE2	5	ND	0.018	0.068	0.03	ND	0.21	1.88	0.37	ND	17.4	39	25	ND	ND	38	8	ND	7.7	11.4	7.2
	10	ND	0.004	0.004	0.00	ND	0.10	0.36	0.09	ND	9.7	11	17	ND	ND	11	11	ND	4.6	4.9	6.1
	15	ND	0.000	0.004	<.001	ND	0.01	0.23	0.02	ND	14.0	13	22	ND	ND	20	12	ND	8.6	4.5	7.9
	25	ND	ND	0.004	<.001	ND	ND	0.19	0.01	ND	ND	15	16	ND	ND	14	10	ND	ND	5.3	8.5
EE3	5	ND	0.010	0.008	1.06	ND	0.13	0.25	11.81	ND	8.7	6	283	ND	ND	7	11	ND	6.3	5.1	46.7
	10	ND	0.002	0.003	<.001	ND	0.05	0.12	0.05	ND	10.5	13	8	ND	ND	8	4	ND	6.1	6.1	5.8
	15	ND	0.001	ND	<.001	ND	0.02	ND	0.03	ND	10.1	ND	29	ND	ND	11	7	ND	7.5	ND	8.1
	25	ND	ND	ND	<.001	ND	ND	ND	0.01	ND	ND	ND	60	ND	ND	10	27	ND	ND	ND	8.7
EW1	5	ND	0.004	0.013	0.01	ND	0.04	0.12	0.07	ND	5.9	21.7	16.2	ND	ND	0	6	ND	13.0	15.1	13.6
	10	ND	0.002	0.005	0.00	ND	0.04	0.08	0.07	ND	3.5	22.0	15.3	ND	ND	22	3	ND	27.9	15.6	19.5
	15	ND	0.003	0.005	0.006	ND	0.07	0.07	0.21	ND	12.2	19.8	34.4	ND	ND	22	16	ND	17.4	17.6	28.2
	25	ND	0.004	ND	<0.001	ND	0.15	ND	0.04	ND	7.7	ND	16.6	ND	ND	ND	11	ND	24.2	ND	16.6
EW2	5	ND	0.082	0.004	0.01	ND	1.23	0.08	0.24	ND	ND	7.6	7.6	ND	ND	18	ND	ND	33.2	24.1	75.4
	10	ND	0.002	0.004	0.00	ND	0.20	0.09	0.26	ND	3.0	7.7	4.7	ND	ND	14	3	ND	28.3	18.7	43.4
	15	ND	0.003	0.020	0.00	ND	0.13	0.20	0.52	ND	0.8	22.7	1.5	ND	ND	17	5	ND	31.9	24.7	33.6
	25	ND	0.003	0.009	0.00	ND	0.15	0.24	0.16	ND	4.5	17.7	10.0	ND	ND	8	7	ND	21.2	34.3	30.1
EW3	5	ND	0.009	0.003	0.00	ND	0.91	0.05	0.08	ND	11.8	7.6	36.0	ND	ND	3	41	ND	23.4	18.0	17.7
	10	ND	0.002	0.006	<.001	ND	0.66	0.12	0.08	ND	8.6	9.3	7.9	ND	ND	4	17	ND	27.1	21.9	22.3
	15	ND	0.003	0.003	<.001	ND	0.82	0.06	0.10	ND	1.2	7.2	5.5	ND	ND	4	6	ND	20.5	25.6	26.6
	25	ND	0.002	ND	0.00	ND	0.69	ND	0.13	ND	2.1	ND	14.3	ND	ND	6	5	ND	27.8	ND	37.4
JC1	5	ND	1.03	1.37	1.61	ND	26.2	28.4	22.5	ND	432	1040	773	ND	ND	136	222	ND	13.6	12.6	8.0
	10	ND	1.09	1.18	1.52	ND	24.8	25.8	24.3	ND	354	615	907	ND	ND	121	264	ND	9.1	34.1	8.9

^A ND: Not determined, *CRS: Chromium reducible sulfur, principally pyrite (FeS₂); see text.

Table 2.3 (continued). Solid phase geochemical data for Jamaica Bay, NY. For sampling locations and dates, see Table 2.1a. ^A

Marsh Site	Depth (cm)	Nitrogen (mmol N/g)				Carbon (mmol C/g)				Sulfur (μmol S/g)				CRS* (μmol/g)				Iron (μmol Fe/g)			
		Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016	Fall 2014	Spring 2015	Summer 2015	Spring 2016
JC1	15	ND	0.94	1.00	1.65	ND	23.8	25.1	27.4	ND	344	649	829	ND	ND	84	154	ND	4.8	43.5	5.2
	25	ND	1.01	0.80	1.60	ND	24.2	20.6	24.7	ND	379	715	836	ND	ND	117	178	ND	15.6	43.6	4.4
JC2	5	0.91	0.65	0.99	1.36	0.36	15.1	23.9	18.2	514	202	660	425	ND	ND	48	86	ND	42.0	126	25.4
	10	0.83	0.59	0.94	1.20	0.51	17.4	16.0	18.7	496	266	452	694	ND	ND	127	571	ND	24.8	100	10.8
	15	0.72	0.51	0.98	0.79	0.27	13.6	16.3	11.2	5412	220	517	464	ND	ND	194	81	ND	33.7	124	44.1
	25	0.68	0.49	0.67	0.95	1.03	9.8	17.2	15.7	850	209	806	609	ND	ND	252	333	ND	39.8	163	31.9
JC3	5	1.21	0.86	1.14	1.58	0.24	24.1	23.9	22.2	749	365	724	522	ND	ND	63	20	ND	9.5	19.4	7.1
	10	1.01	0.72	1.30	1.61	0.47	25.1	22.5	26.9	602	318	647	824	ND	ND	27	179	ND	3.3	13.8	6.1
	15	1.07	0.76	1.18	1.37	0.11	20.7	25.6	21.8	668	330	530	747	ND	ND	83	179	ND	5.8	9.6	6.8
	25	0.85	0.61	ND	1.20	0.39	25.8	ND	22.2	752	377	ND	720	ND	ND	ND	109	ND	11.5	ND	8.3
BE1	5	ND	0.32	0.02	0.19	ND	7.6	0.27	2.48	ND	372	31	504	ND	ND	8	212	ND	78.9	13.5	76.7
	10	ND	ND	0.00	0.23	ND	ND	0.05	3.10	ND	ND	15	520	ND	ND	18	242	ND	121.1	5.5	73.6
	15	ND	0.26	0.16	0.55	ND	5.4	2.3	8.6	ND	584	427	711	ND	ND	166	722	ND	156.5	70.7	81.6
	25	ND	ND	0.28	0.64	ND	ND	5.1	12.1	ND	ND	1029	1970	ND	ND	418	590	ND	ND	71.7	ND
BE2	5	0.06	0.37	0.16	0.52	1.70	10.0	3.3	12.3	119	350	170	1080	ND	ND	157	343	ND	67.6	29.7	98.4
	10	0.26	0.42	0.15	0.41	5.91	15.8	3.5	8.0	402	853	264	418	ND	ND	193	160	ND	198.6	22.0	60.0
	15	0.30	0.33	0.11	0.33	7	11.0	2.3	6.8	525	668	149	791	ND	ND	82	461	ND	158.4	22.0	93.4
	25	ND	ND	0.06	0.11	ND	ND	1.1	2.7	ND	ND	100	290	ND	ND	73	85	ND	ND	19.9	30.0
BE3	5	0.40	0.32	0.43	0.45	8.25	11.0	8.4	7.7	654	436	647	819	ND	ND	355	383	ND	68.3	104	127
	10	0.28	0.21	0.40	0.41	6.30	6.0	8.4	6.9	728	256	475	894	ND	ND	244	396	ND	49.4	49.5	78.3
	15	0.27	0.21	0.26	0.35	5.95	6.1	4.4	7.0	620	150	252	831	ND	ND	192	577	ND	45.3	43.9	93.6
	25	0.28	0.15	0.17	0.35	4.67	4.0	3.2	5.6	560	69	272	693	ND	ND	150	226	ND	21.2	44.6	92.8

^A ND: Not determined, *CRS: Chromium reducible sulfur, principally pyrite (FeS₂); see text.

Table 2.4. Solid phase chromium reducible sulfide (CRS), total sulfur (Total S) and acid-leachable iron (Fe) in Jamaica Bay, NY, marsh sediments.^A

Marsh Site	Depth (cm)	Summer, 2015				Spring, 2016			
		CRS ($\mu\text{mol S/g}$)	Total S ($\mu\text{mol S/g}$)	Fe ($\mu\text{mol Fe/g}$)	DOP†	CRS ($\mu\text{mol S/g}$)	Total S ($\mu\text{mol S/g}$)	Fe ($\mu\text{mol Fe/g}$)	DOP†
BE1	5	8	31	13.5	0.23	212	504	76.7	0.58
	10	18	15	5.5	0.62	242	520	73.6	0.62
	15	166	427	70.7	0.54	722	711	81.6	0.82
	25	418	1029	–	–	590	1970	–	–
	25*	–	–	–	–	296	–	–	–
BE2	5	157	170	29.7	0.73	343	1080	98.4	0.64
	10	193	264	22.0	0.81	160	418	60.0	0.57
	15	82	149	22.0	0.65	461	791	93.4	0.71
	15*	–	–	–	–	276	–	–	–
	25	73	100	19.9	0.65	85	290	30.0	0.59
BE3	5	355	647	103.9	0.63	383	819	126.8	0.60
	10	244	475	49.5	0.71	396	894	78.3	0.72
	10*	–	–	–	–	384	895	–	–
	15	192	252	43.9	0.69	577	831	93.6	0.76
	25	150	272	44.6	0.63	226	693	92.8	0.55
BE1	38 (1:10)**	716	–	–	–	–	–	–	–
	38 (1:10)**	552	–	–	–	–	–	–	–
JC1	5	136	1040	12.6	0.84	222	773	8.0	0.93
	10	121	615	34.1	0.64	264	907	8.9	0.94
	15	84	649	43.5	0.49	154	829	5.2	0.94

^A BE = Big Egg; JC = JoCo; EW = Elders West; EE = Elders East

† DOP: degree of pyritization, where pyrite Fe (FeS_2 , Fe_{py}) = $\text{CRS}/2$ and $\text{DOP} = \text{Fe}_{\text{py}}/(\text{Fe}_{\text{py}} + \text{Fe}_{\text{leach}})$

* Duplicate analysis of select samples where indicated; “–” means no duplicate

** Replicate analyses applied to the select samples indicated, with the solution dilutions indicated; “–” means no replicate

Table 2.4 (continued). Solid phase chromium reducible sulfide (CRS), total sulfur (Total S) and acid-leachable iron (Fe) in Jamaica Bay, NY, marsh sediments.^A

Marsh Site	Depth (cm)	Summer, 2015				Spring, 2016			
		CRS (μmol S/g)	Total S (μmol S/g)	Fe (μmol Fe/g)	DOP†	CRS (μmol S/g)	Total S (μmol S/g)	Fe (μmol Fe/g)	DOP†
JC1	25	117	715	43.6	0.57	178	836	4.4	0.95
	25*	122	–	–	–	265	–	–	–
JC2	5	48	660	126.4	0.16	86	425	25.4	0.63
	10	127	452	100.0	0.39	571	694	10.8	0.96
	10*	111	453		1.00	–	–	–	–
	15	194	517	124.4	0.44	81	464	44.1	0.48
	25	252	806	163.1	0.44	333	609	31.9	0.84
	25*	–	–	–	–	257	–	–	–
JC3	5	63	724	19.4	0.62	20	522	7.1	0.59
	10	27	647	13.8	0.49	179	824	6.1	0.94
	10*	14	–	–	–	–	–	–	–
	15	83	530	9.6	0.81	179	747	6.8	0.93
	15*	23	–	–	–	–	–	–	–
	25	–	–	–	–	109	720	8.3	0.87
	25*	–	–	–	–	126	–	–	–
JC3	25 (1:05)**	–	–	–	–	291	720	8.3	0.95
	25 (1:05)**	–	–	–	–	211	720	8.3	0.93
	25 (1:05)**	–	–	–	–	363	720	8.3	0.96
	25 (1:10)**	–	–	–	–	331	720	8.3	0.95
	25 (1:10)**	–	–	–	–	226	720	8.3	0.93

^A BE = Big Egg; JC = JoCo; EW = Elders West; EE = Elders East

† DOP: degree of pyritization, where pyrite Fe (FeS_2 , Fe_{py}) = $\text{CRS}/2$ and $\text{DOP} = \text{Fe}_{\text{py}}/(\text{Fe}_{\text{py}} + \text{Fe}_{\text{leach}})$

* Duplicate analysis of select samples where indicated; “–” means no duplicate

** Replicate analyses applied to the select samples indicated, with the solution dilutions indicated; “–” means no replicate

Table 2.4 (continued). Solid phase chromium reducible sulfide (CRS), total sulfur (Total S) and acid-leachable iron (Fe) in Jamaica Bay, NY, marsh sediments.^A

Marsh Site	Depth (cm)	Summer, 2015				Spring, 2016			
		CRS ($\mu\text{mol S/g}$)	Total S ($\mu\text{mol S/g}$)	Fe ($\mu\text{mol Fe/g}$)	DOP†	CRS ($\mu\text{mol S/g}$)	Total S ($\mu\text{mol S/g}$)	Fe ($\mu\text{mol Fe/g}$)	DOP†
JC3	25 (1:10)**	–	–	–	–	359	720	8.3	0.96
EW1	5	0	22	15.1	0.00	6	16	13.6	0.18
	10	22	22	15.6	0.41	3	15	19.5	0.08
	15	22	20	17.6	0.38	16	34	28.2	0.23
	15*	22	–	–	–	13	–	–	–
	25	–	–	–	–	11	17	16.6	0.24
EW2	5	18	8	24.1	0.27	–	8	75.4	–
	5*	50	–	–	–	–	–	–	–
	10	14	8	18.7	0.27	3	5	43.4	0.03
	10*	–	–	–	–	2	–	–	–
	15	17	23	24.7	0.26	5	1	33.6	0.07
	25	8	18	34.3	0.10	7	10	30.1	0.10
EW3	5	3	8	18.0	0.08	41	36	17.7	0.54
	5*	–	–	–	–	46	–	–	–
	10	4	9	21.9	0.08	17	8	22.3	0.27
	15	4	7	25.6	0.07	6	6	26.6	0.10
	15*	6	–	–	–	–	–	–	–
	25	–	–	–	–	5	14	37.4	0.06
EW2	38 (1:05)**	–	–	–	–	13	–	–	–
	38 (1:05)**	–	–	–	–	12	–	–	–

^A BE = Big Egg; JC = JoCo; EW = Elders West; EE = Elders East

† DOP: degree of pyritization, where pyrite Fe (FeS_2 , Fe_{py}) = $\text{CRS}/2$ and $\text{DOP} = \text{Fe}_{\text{py}}/(\text{Fe}_{\text{py}} + \text{Fe}_{\text{leach}})$

* Duplicate analysis of select samples where indicated; “–” means no duplicate

** Replicate analyses applied to the select samples indicated, with the solution dilutions indicated; “–” means no replicate

Table 2.4 (continued). Solid phase chromium reducible sulfide (CRS), total sulfur (Total S) and acid-leachable iron (Fe) in Jamaica Bay, NY, marsh sediments.^A

Marsh Site	Depth (cm)	Summer, 2015				Spring, 2016			
		CRS (μmol S/g)	Total S (μmol S/g)	Fe (μmol Fe/g)	DOP†	CRS (μmol S/g)	Total S (μmol S/g)	Fe (μmol Fe/g)	DOP†
EW2	38 (1:05)**	—	—	—	—	10	—	—	—
	38 (1:10)**	—	—	—	—	12	—	—	—
	38 (1:10)**	—	—	—	—	13	—	—	—
	38 (1:10)**	—	—	—	—	10	—	—	—
EE1	5	12	17	6.6	0.48	4	228	24.1	0.08
	10	15	20	6.2	0.54	13	17	11.3	0.36
	10*	6	—	—	—	—	—	—	—
	15	35	35	6.8	0.72	14	18	8.4	0.45
	25	11	16	9.8	0.36	9	11	9.3	0.32
EE2	5	38	39	11.4	0.63	8	25	7.2	0.36
	10	11	11	4.9	0.53	11	17	6.1	0.47
	15	20	13	4.5	0.69	12	22	7.9	0.43
	25	14	15	5.3	0.57	10	16	8.5	0.37
EE3	5	7	6	5.1	0.40	11	283	46.7	0.10
	5*	8	—	6.1	0.41	4	8	—	—
	10	11	13	—	—	17	29	5.8	0.59
	10*	10	—	—	—	27	60	—	—

^A BE = Big Egg; JC = JoCo; EW = Elders West; EE = Elders East

† DOP: degree of pyritization, where pyrite Fe (FeS_2 , Fe_{py}) = $\text{CRS}/2$ and $\text{DOP} = \text{Fe}_{\text{py}}/(\text{Fe}_{\text{py}} + \text{Fe}_{\text{leach}})$

* Duplicate analysis of select samples where indicated; “—” means no duplicate

** Replicate analyses applied to the select samples indicated, with the solution dilutions indicated; “—” means no replicate

Results

The high resolution 2-D Fe^{2+} and 2-D H_2S distribution patterns revealed by optical sensors in the 12 sampling sites in JoCo (JC), Big Egg (BE), Elders Point East (EE) and Elders Point West (EW) are shown in Figs. 2.1 – 2.16. 1-D vertical profiles of H_2S and Fe^{2+} at each site were calculated by averaging the data from each horizontal pixel layer.

The results of sensor H_2S and Fe^{2+} distributions in fall 2014 are given in Fig. 2.1 - 2.4. The green panels in Figs 2.1A, 2.2A, 2.3A and 2.4A are visible images of the detected cores from Big Egg, Elders East, Elders West and JoCo, respectively. The root interweaving patterns can be clearly seen and are directly associated with the 2-D H_2S distribution patterns. The H_2S in all sites showed a gradient in the top 2 cm depth and reached maximum concentrations below 2 or at 2-4 cm. High H_2S concentrations were observed in the sequence of JC (3-6 mM) > BE3 (2 mM) > EE (~1 mM), with EW at a relatively lower level (<0.4 mM). It should be pointed out that the 2-D H_2S distributions in the fall 2014 season were measured in the laboratory using a fluorescence H_2S sensor after a 24-hour incubation of the box cores at room temperature, (see Methods, Zhu and Aller, 2013). In-situ 2-D dissolved Fe^{2+} distribution patterns showed that Fe^{2+} levels at Big Egg, Elders East and JoCo are relatively low (<40 μM) with a maximum zone at about 1-4 cm depth in fall season, but Fe^{2+} was >200 μM below 6 cm at EW associated root patterns. The iron concentrations thus vary in the sequence of EW > EE > BE > JC.

The results of in-situ 2-D H_2S and Fe^{2+} distributions in the spring samplings, 2015 and 2016, are given in Figs. 2.5 - 2.8 and 2.13 – 2.16. The levels of H_2S are generally <20 μM or even non-detectable in the top 8 cm of marsh peat and increased to <100 μM deeper in the peat. However, high levels of H_2S (1 – 3 mM) were found at the sampling sites in Big Egg 2 (BE2) in spring 2015 (Fig 2.5). Dissolved Fe^{2+} concentrations are generally lower than 40 μM at BE2, BE3, EE1-3, and JC1-3, but Fe^{2+} concentrations at Elders East and West reach higher values, 100-150 μM (EE3, spring 2016, Fig. 2.14) and 300-600 μM (EW1, 2, and 3; spring 2015, Fig. 2.7). The pore water iron concentrations vary in the sequence of EW > EE > BE > JC in spring, 2015 and 2016, comparable to the fall sampling.

The results of sensor in-situ 2-D H_2S and Fe^{2+} distributions in summer, 2015 are shown in Figs. 2.9 – 2.12. H_2S concentrations are almost non-detectable in the top 2 cm of marsh peat but increase significantly to 1-3 mM below 6 cm at the sites in Big Egg and JoCo. H_2S concentrations at sites in Elders East and at EW1 are in the range of 0.5 – 1 mM, and at sites EW2 and EW3 are <0.1 mM. Dissolved Fe^{2+} concentrations in Elders West are as high as 300-500 μM , with a maximum zone at 1-3 cm depth for EW1 and EW3. Levels of Fe^{2+} at Big Egg, Elders East and JoCo range from 50 – 200 μM , in the sequence EW > BE > EE > JC.

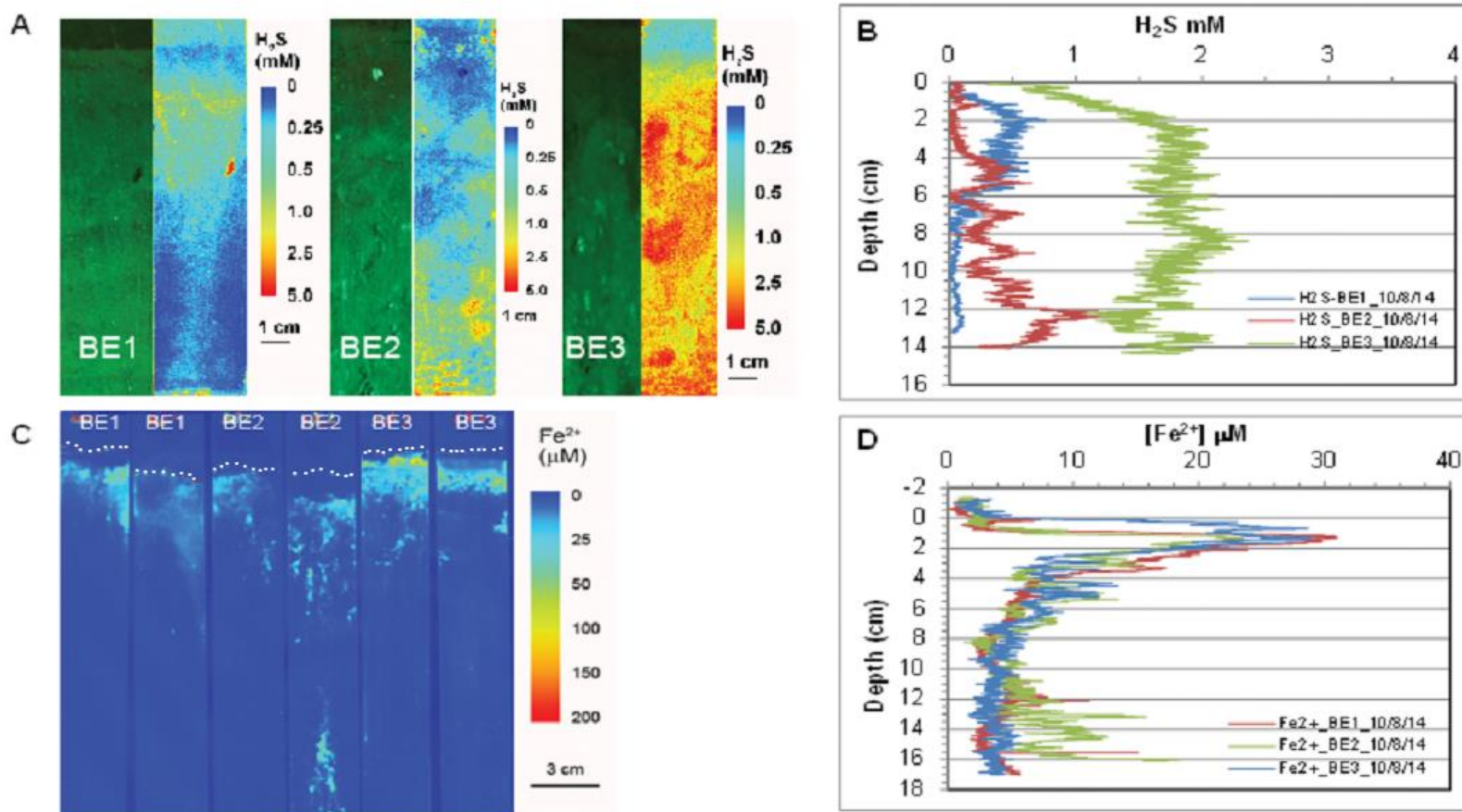


Figure 2.1. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of Big Egg (BE) marsh peat in fall 2014, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns in the sediments, which were incubated for 1 day in lab before H_2S imaging. The green panels are physical image of sediments and the color panels (pseudo-color) are the corresponding 2-D H_2S distributions. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in panel (A). (C) In-situ 2-D Fe^{2+} distribution patterns which were obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

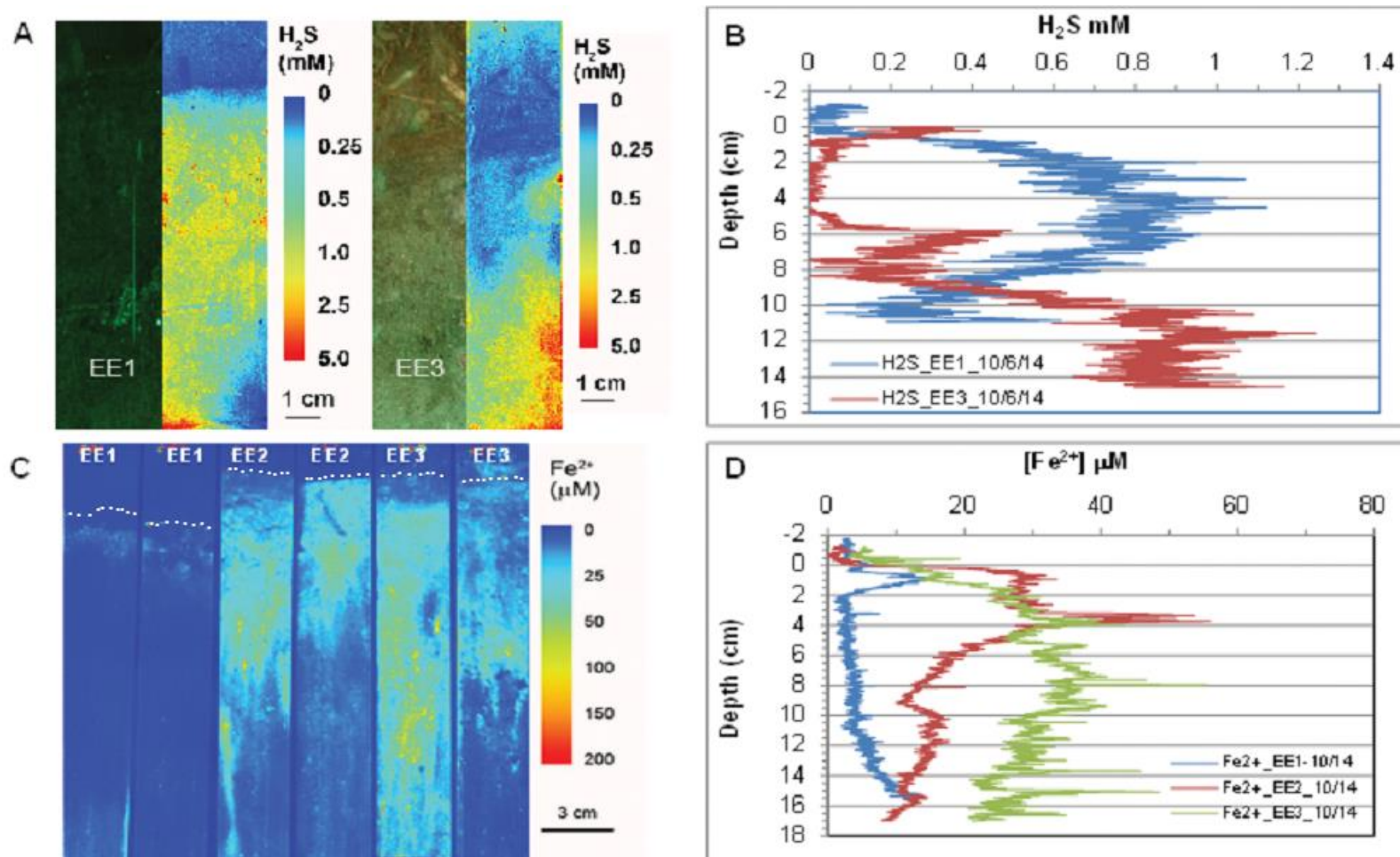


Figure 2.2. H₂S and dissolved Fe²⁺ distribution patterns in the pore water of Elders East (EE) marsh peats in fall 2014, Jamaica Bay, NY. (A) 2-D H₂S distribution patterns in the sediments, which were incubated 1 day in lab before H₂S imaging. The green panels are physical image of sediments and the color panels (pseudo color) are corresponding 2-D H₂S distributions. (B) Vertical H₂S profiles averaged from each 2-D H₂S distribution in panel (A). (C) In-situ 2-D Fe²⁺ distribution patterns which were obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe²⁺ profiles averaged from each 2-D Fe²⁺ distributions in panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

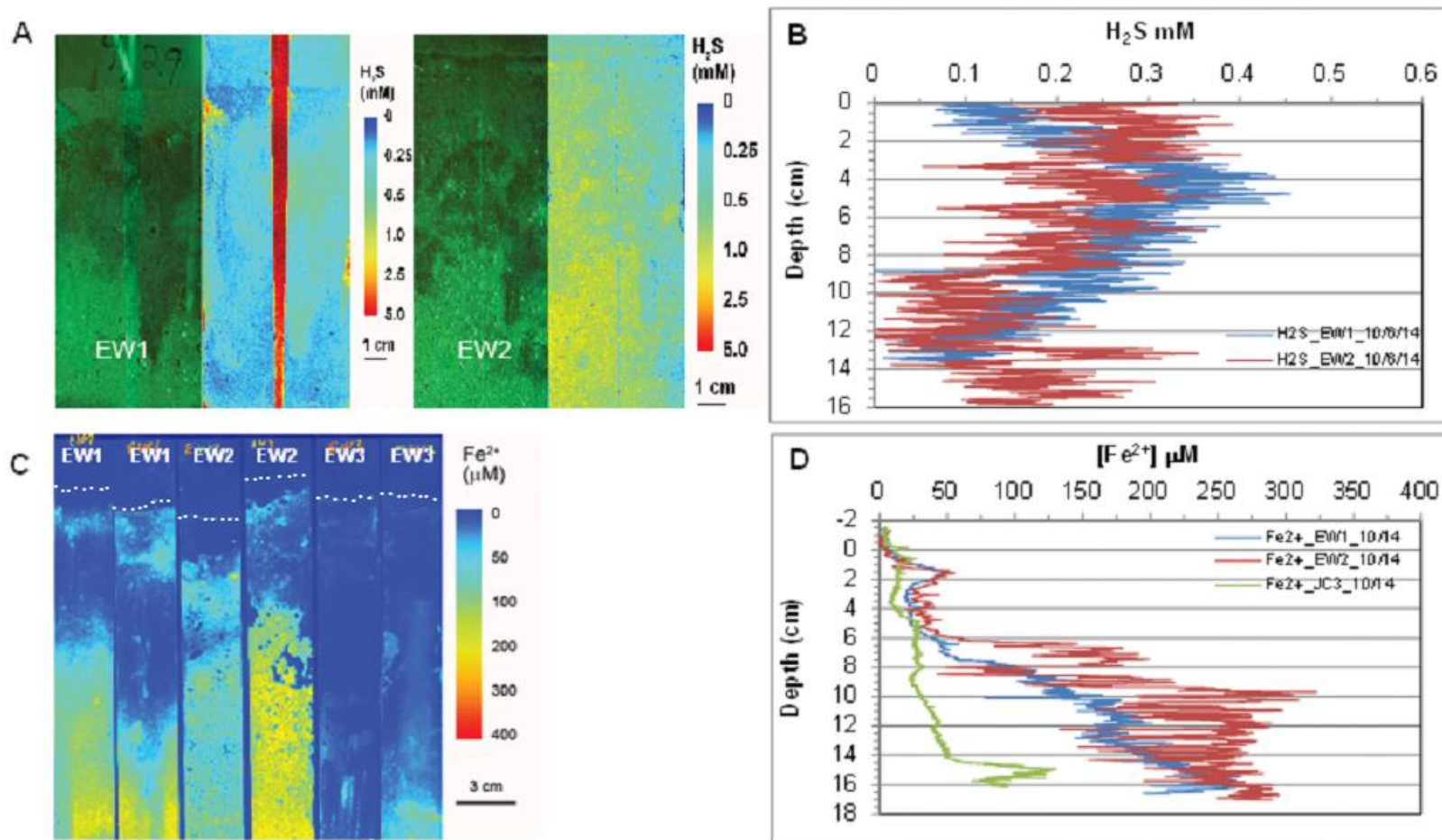


Figure 2.3. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of Elders West (EW) marsh peats in fall 2014, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns in the sediments, which were incubated for 1 day in lab before H_2S imaging. The green panels are physical image of sediments and the color panels (pseudo-color) are corresponding 2-D H_2S distributions. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in panel (A). (C) In-situ 2-D Fe^{2+} distribution patterns which were obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

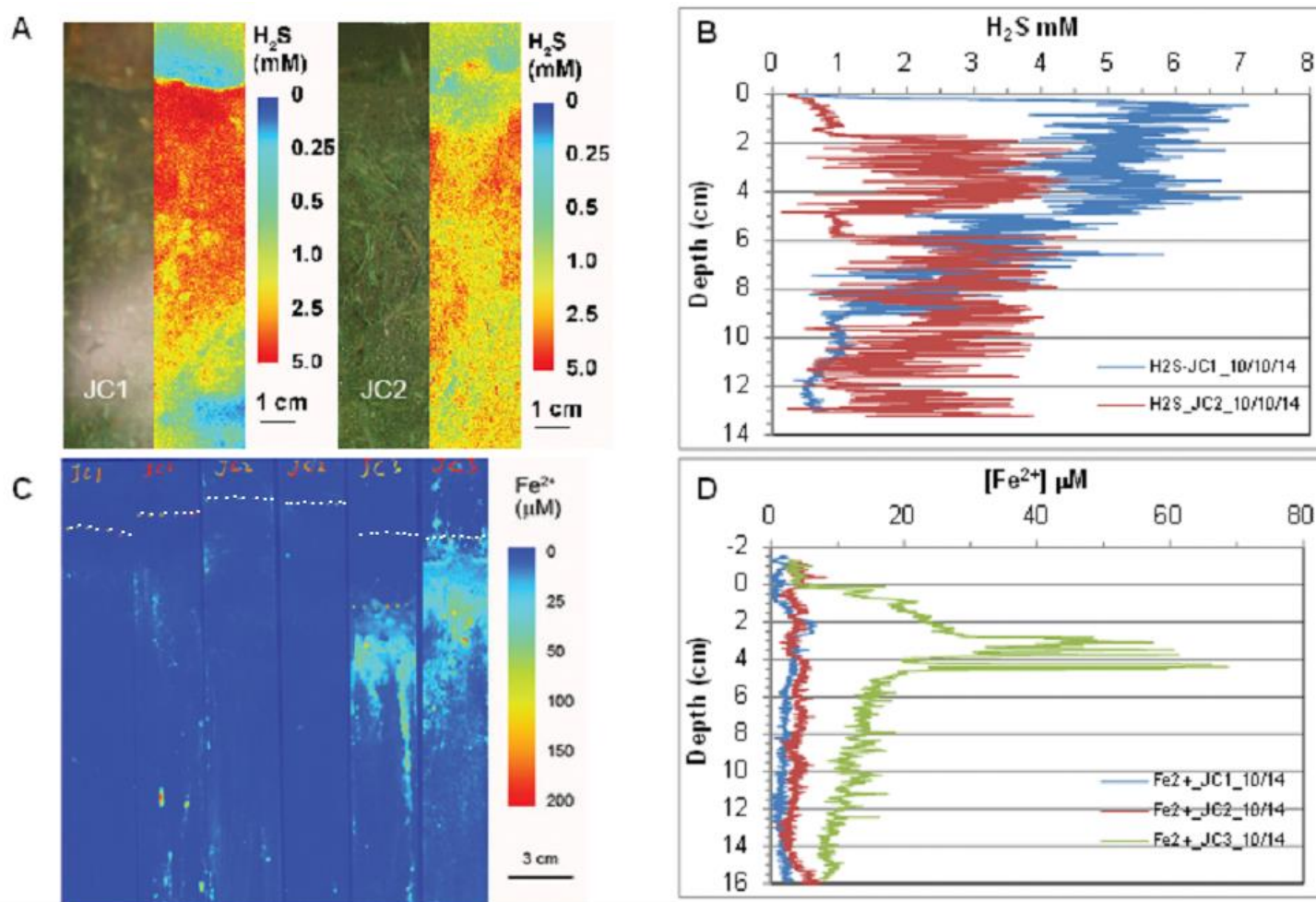


Figure 2.4. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of JoCo (JC) marsh peats in fall 2014, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns in the sediments, which were incubated for 1 day in lab before H_2S imaging. The green panels are physical image of sediments and the color panels (pseudo-color) are corresponding 2-D H_2S distributions. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in panel (A). (C) In-situ 2-D Fe^{2+} distribution patterns which were obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

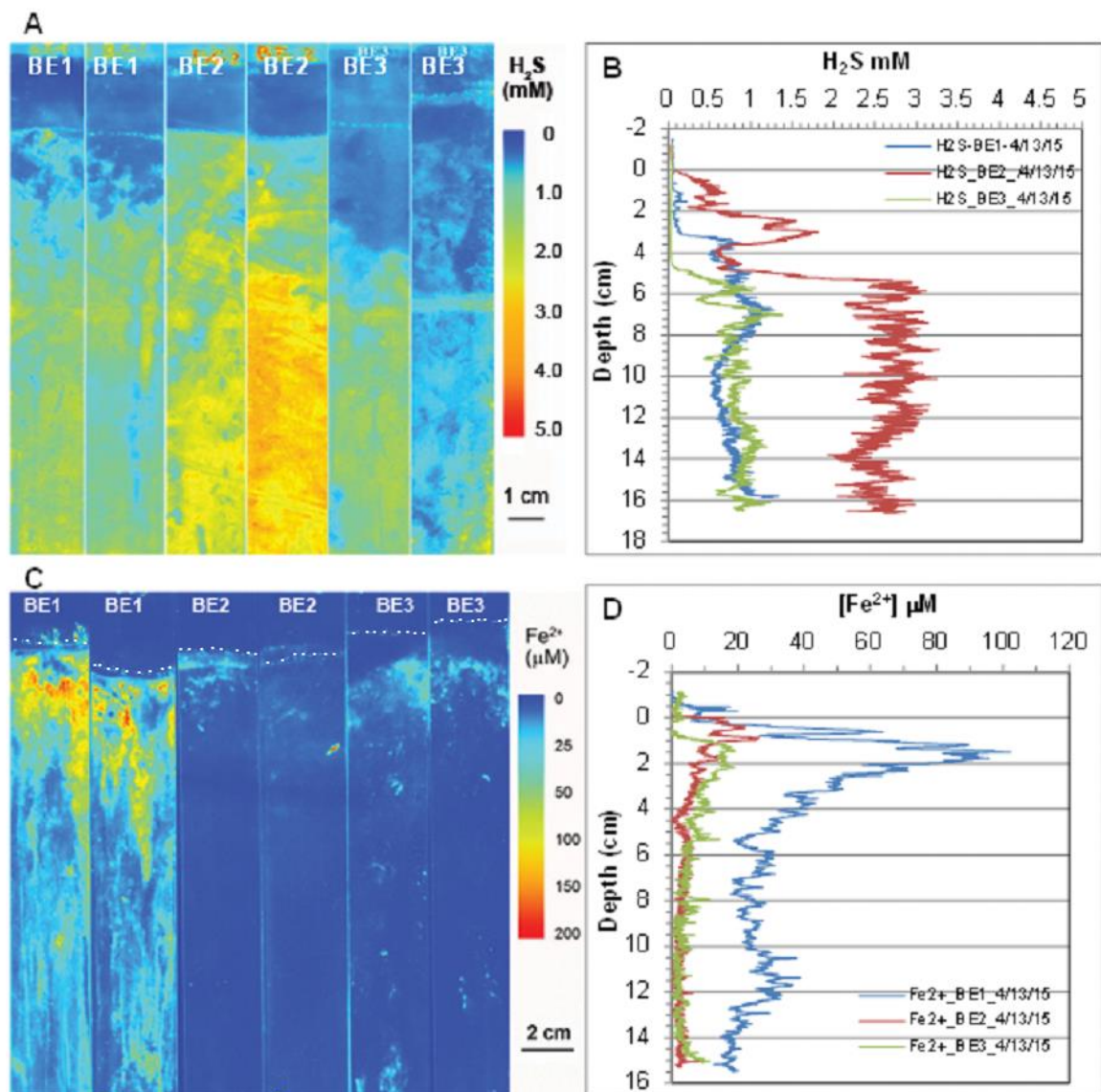


Figure 2.5. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of Big Egg (BE) marsh peats in spring 2015, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns (pseudo-color) obtained by in-situ measurements in sediments; dotted line marks the peat surface. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in the panel (A). (C) 2-D Fe^{2+} distribution patterns obtained by in-situ deployments, the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in the panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

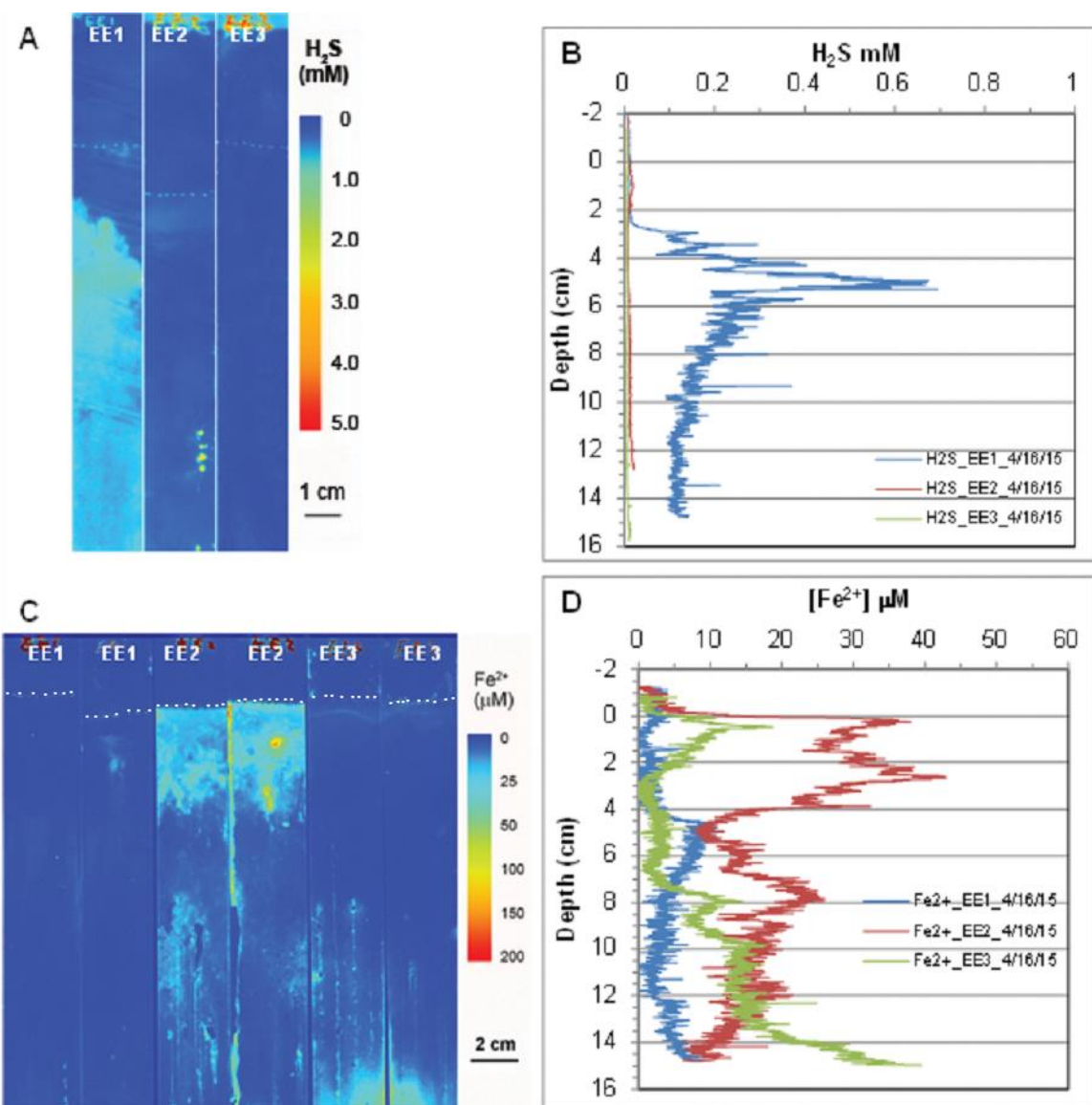


Figure 2.6. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of Elders East (EE) marsh peats in spring 2015, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns (pseudo-color) obtained by in-situ measurements in sediments; dotted line marks the peat surface. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in the panel (A). (C) 2-D Fe^{2+} distribution patterns obtained by in-situ deployments, the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in the panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

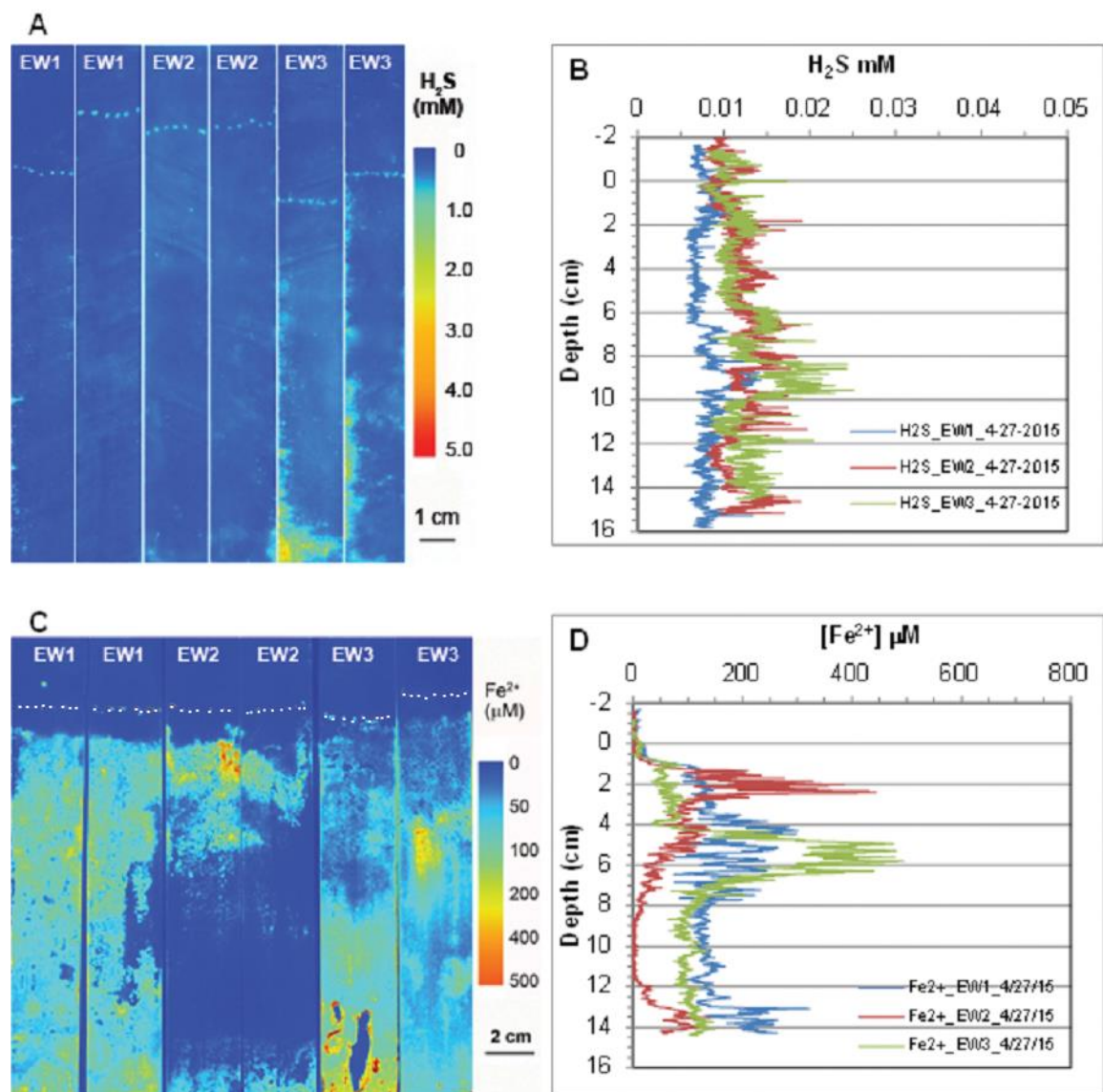


Figure 2.7. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of Elders West (EW) marsh peats in spring 2015, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns (pseudo-color) obtained by in-situ measurements in sediments; dotted line marks the peat surface. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in the panel (A). (C) 2-D Fe^{2+} distribution patterns obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in the panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

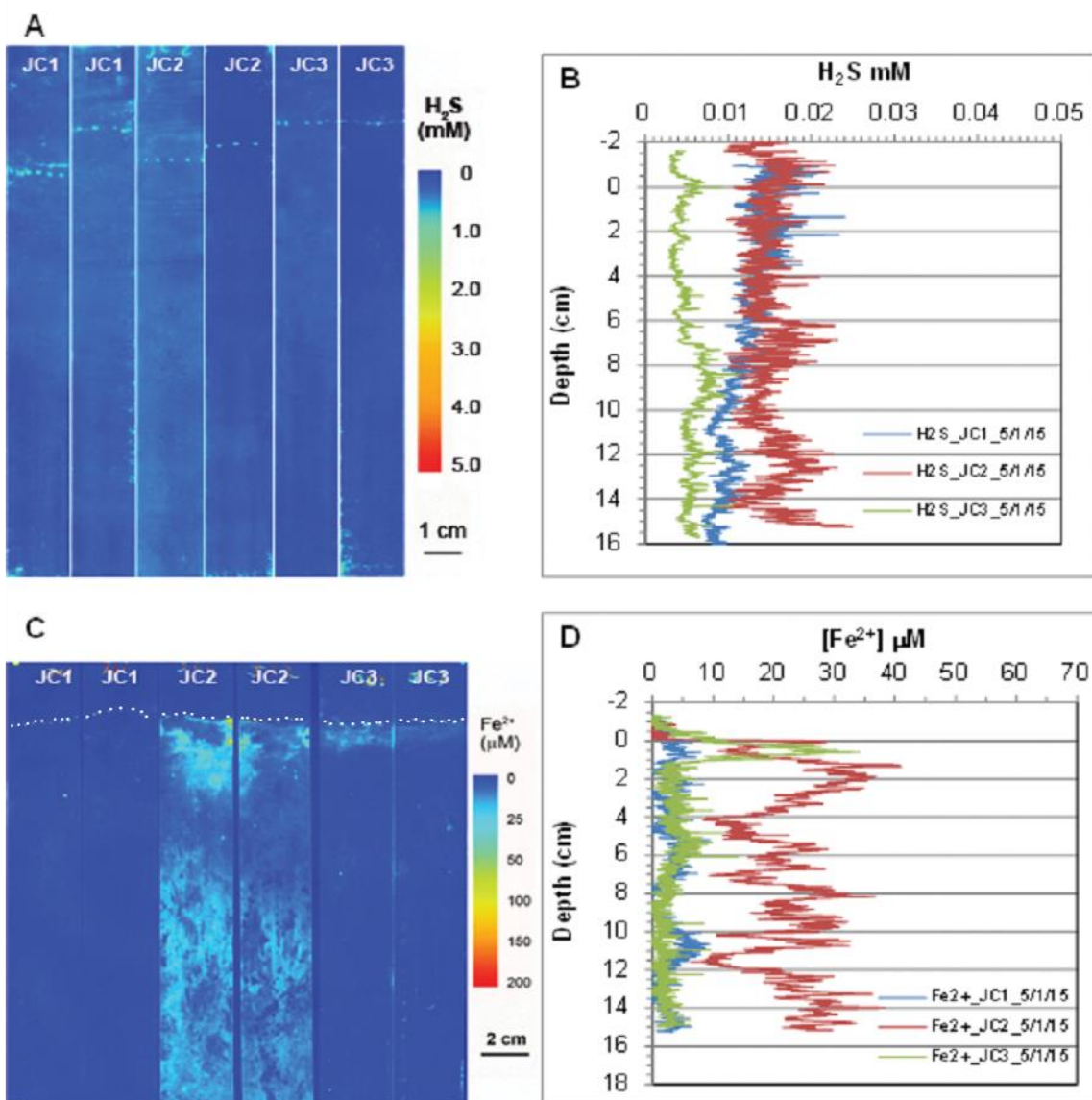


Figure 2.8. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of JoCo (JC) marsh peats in spring 2015, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns (pseudo-color) obtained by in-situ measurements in sediments; dotted line marks the peat surface. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in the panel (A). (C) 2-D Fe^{2+} distribution patterns obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in the panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

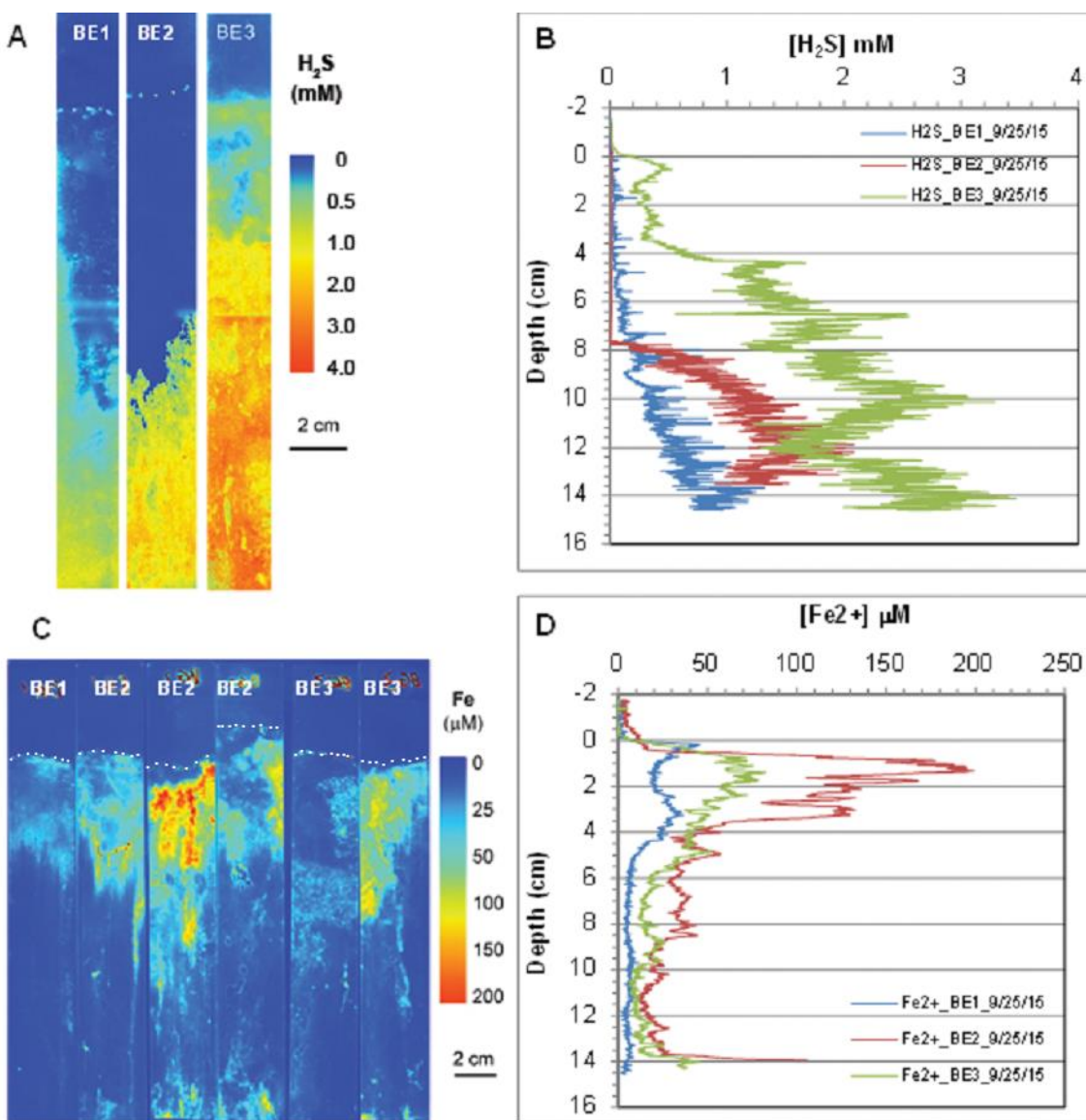


Figure 2.9. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of Big Egg (BE) marsh peats in summer 2015, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns (pseudo-color) obtained by in-situ measurements in sediments; dotted line marks the peat surface. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in the panel (A). (C) 2-D Fe^{2+} distribution patterns obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in the panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

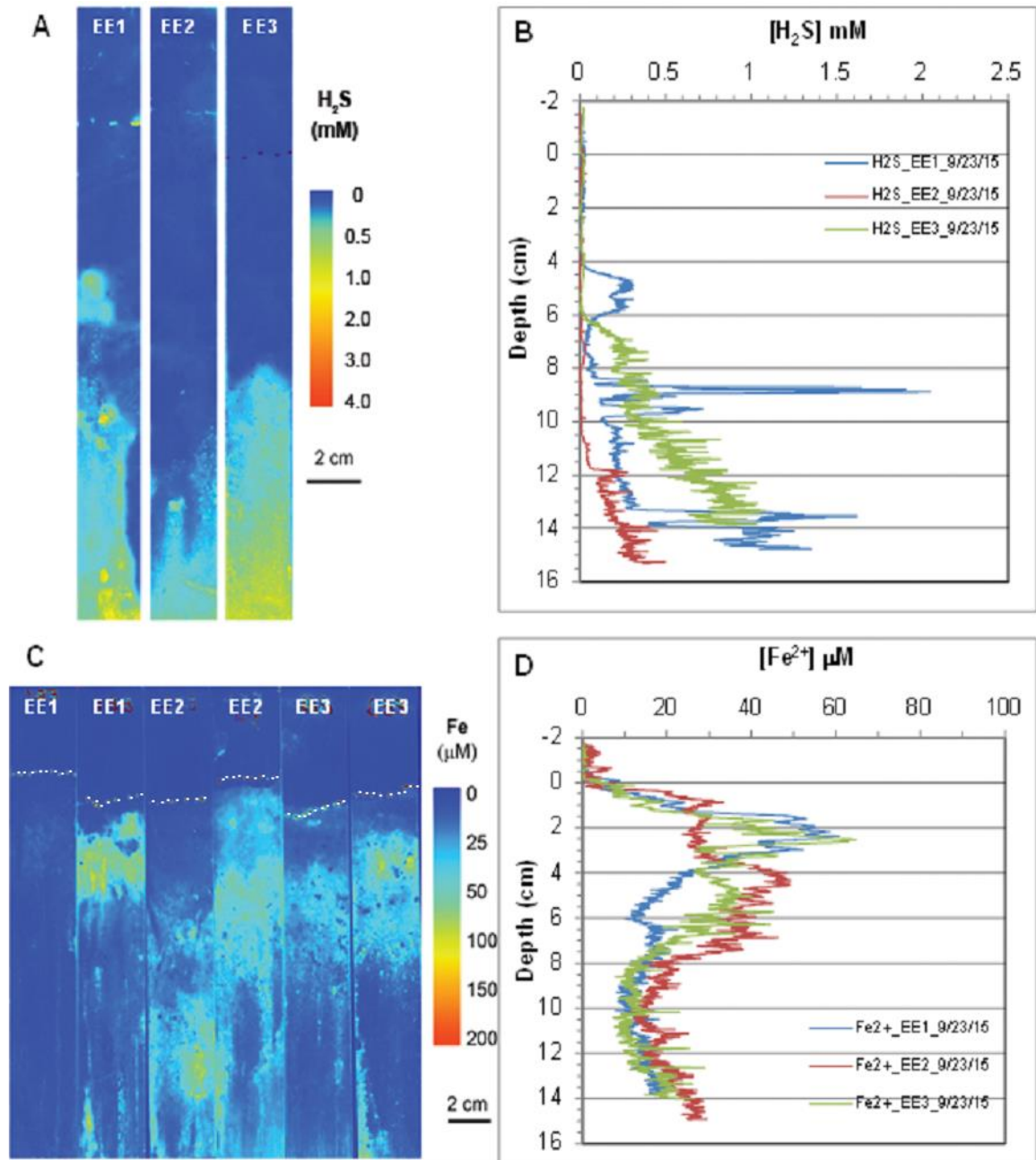


Figure 2.10. H₂S and dissolved Fe²⁺ distribution patterns in the pore water of Elders East (EE) marsh peats in summer 2015, Jamaica Bay, NY. (A) 2-D H₂S distribution patterns (pseudo-color) obtained by in-situ measurements in sediments; dotted line marks the peat surface. (B) Vertical H₂S profiles averaged from each 2-D H₂S distribution in the panel (A). (C) 2-D Fe²⁺ distribution patterns obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe²⁺ profiles averaged from each 2-D Fe²⁺ distributions in the panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

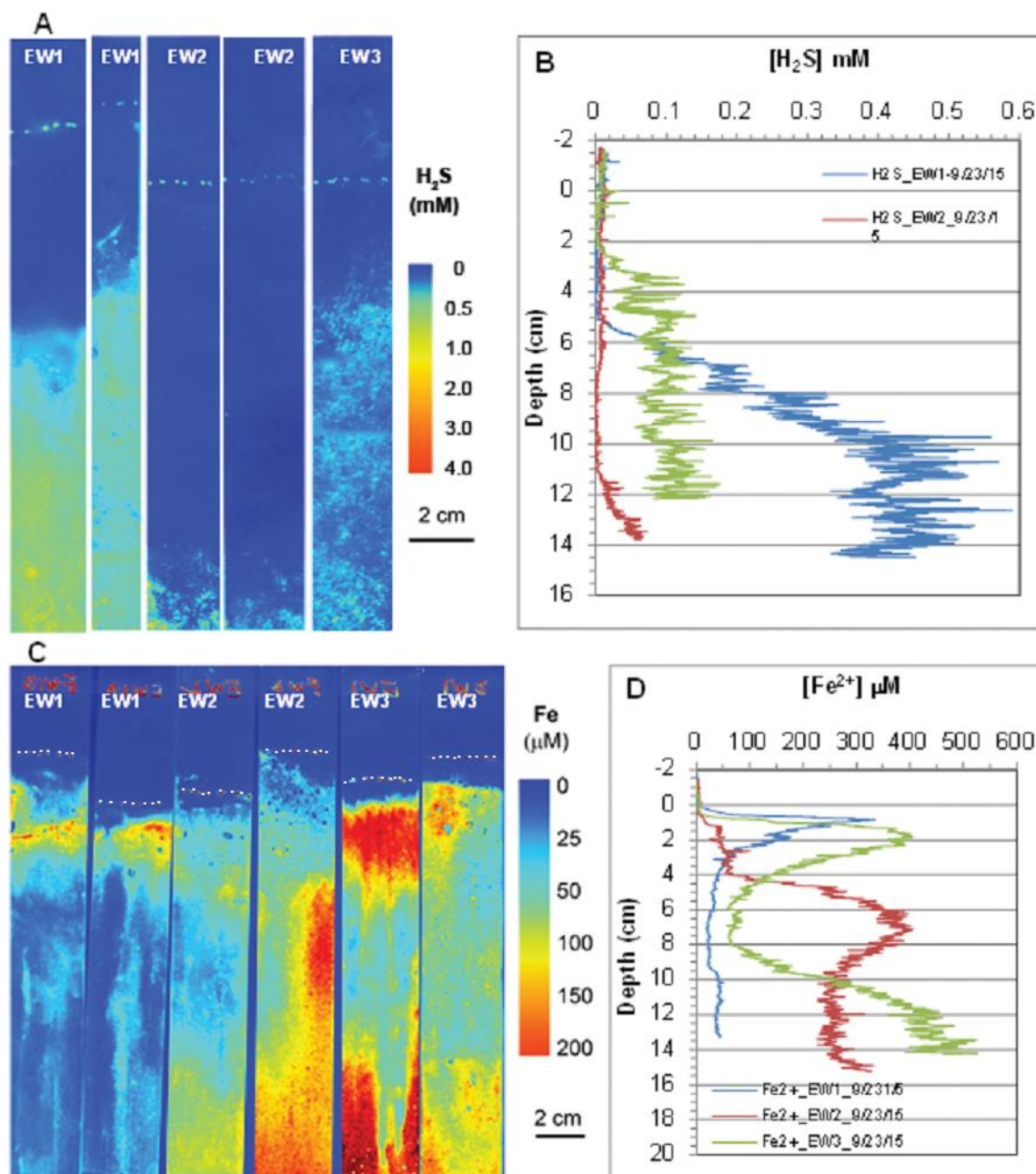


Figure 2.11. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of Elders West (EE) marsh peats in summer 2015, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns (pseudo-color) obtained by in-situ measurements in sediments; white dotted line marks the peat surface. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in the panel (A). (C) 2-D Fe^{2+} distribution patterns obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in the panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

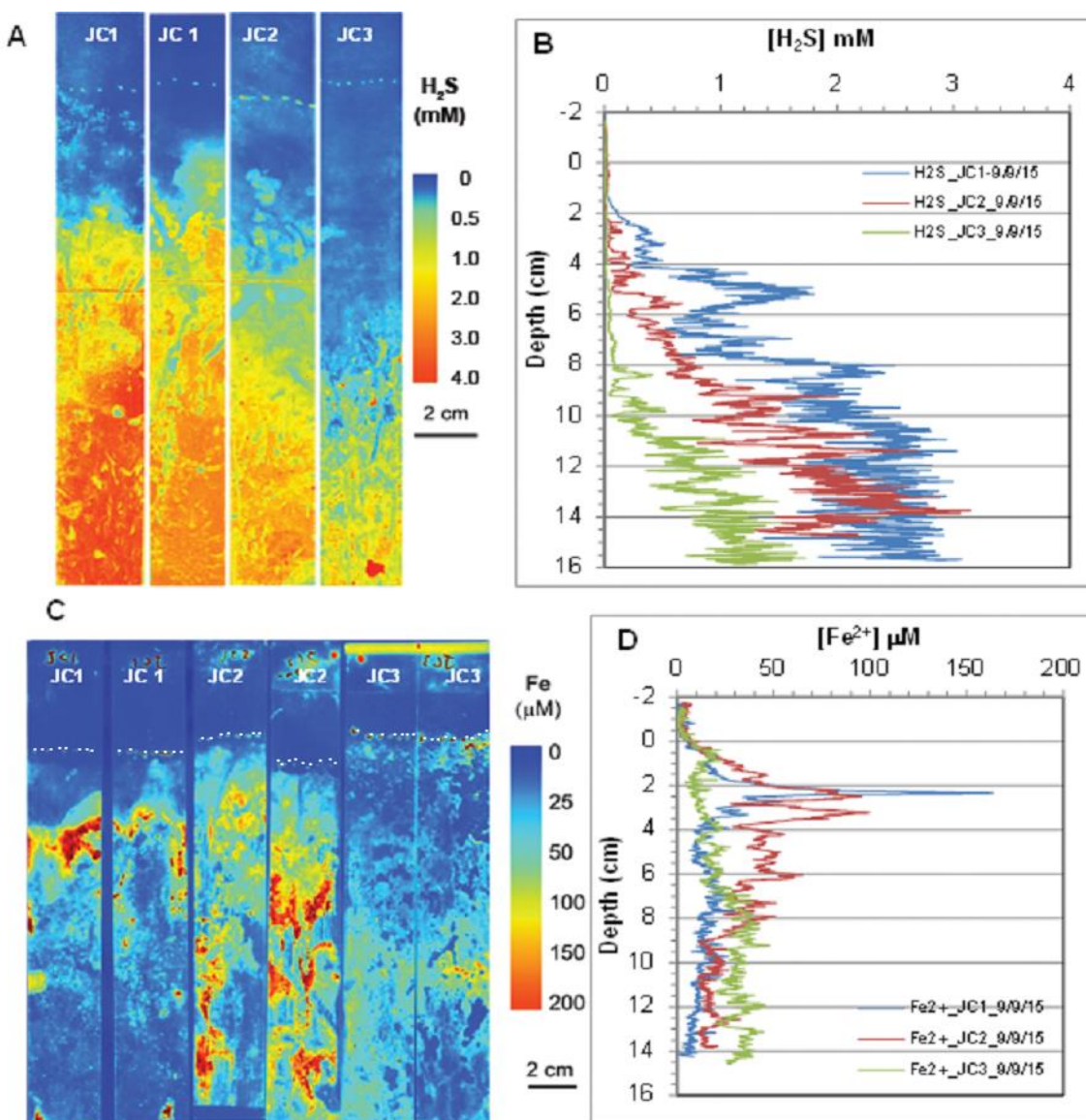


Figure 2.12. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of JoCo (JC) marsh peats in summer 2015, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns (pseudo-color) obtained by in-situ measurements in sediments; white dotted line marks the peat surface. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in the panel (A). (C) 2-D Fe^{2+} distribution patterns obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in the panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

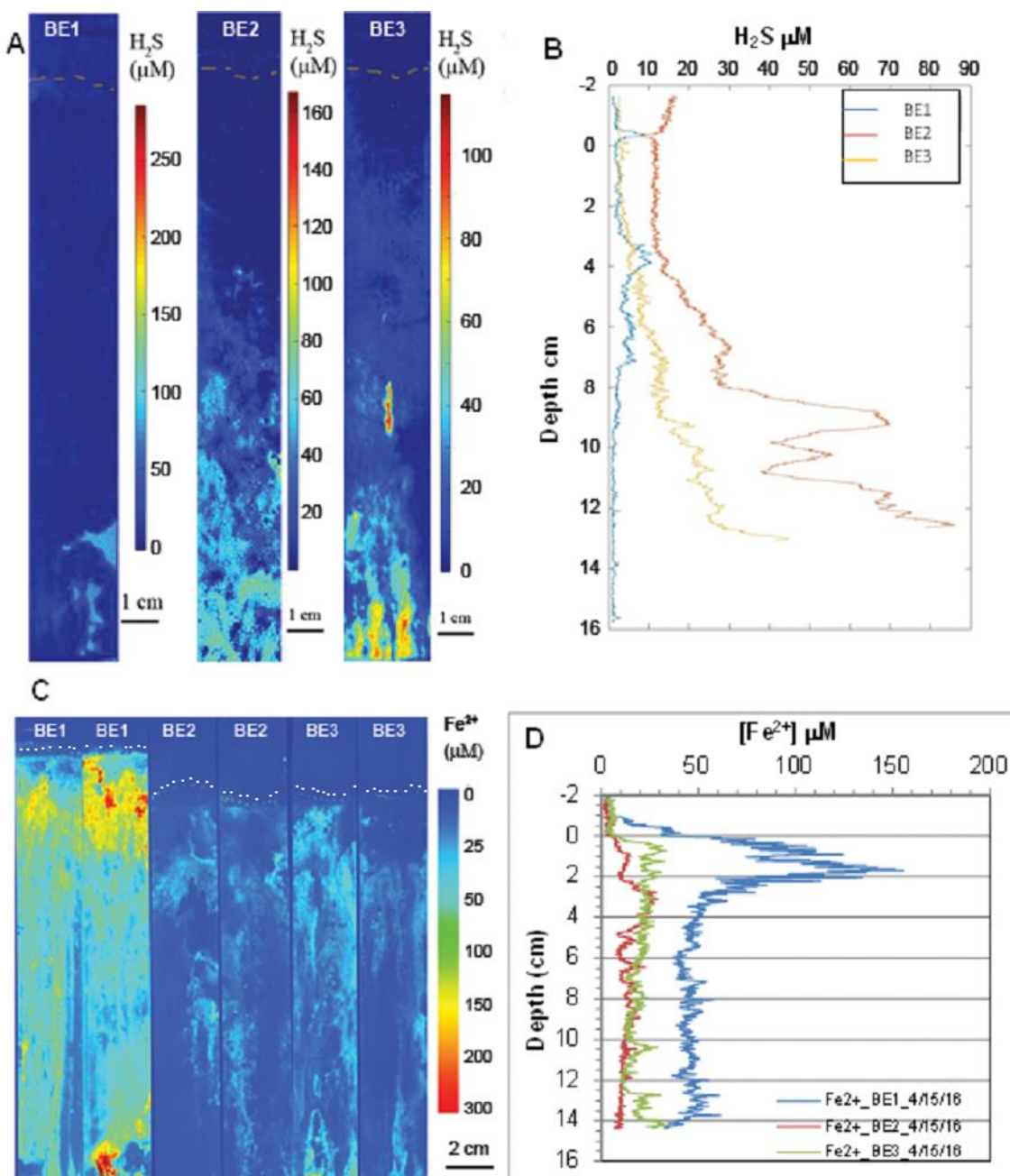


Figure 2.13. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of Big Egg (BE) marsh peats in spring 2016, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns (pseudo-color) obtained by in-situ measurements in sediments; dotted line marks the peat surface. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in the panel (A). (C) 2-D Fe^{2+} distribution patterns obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in the panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

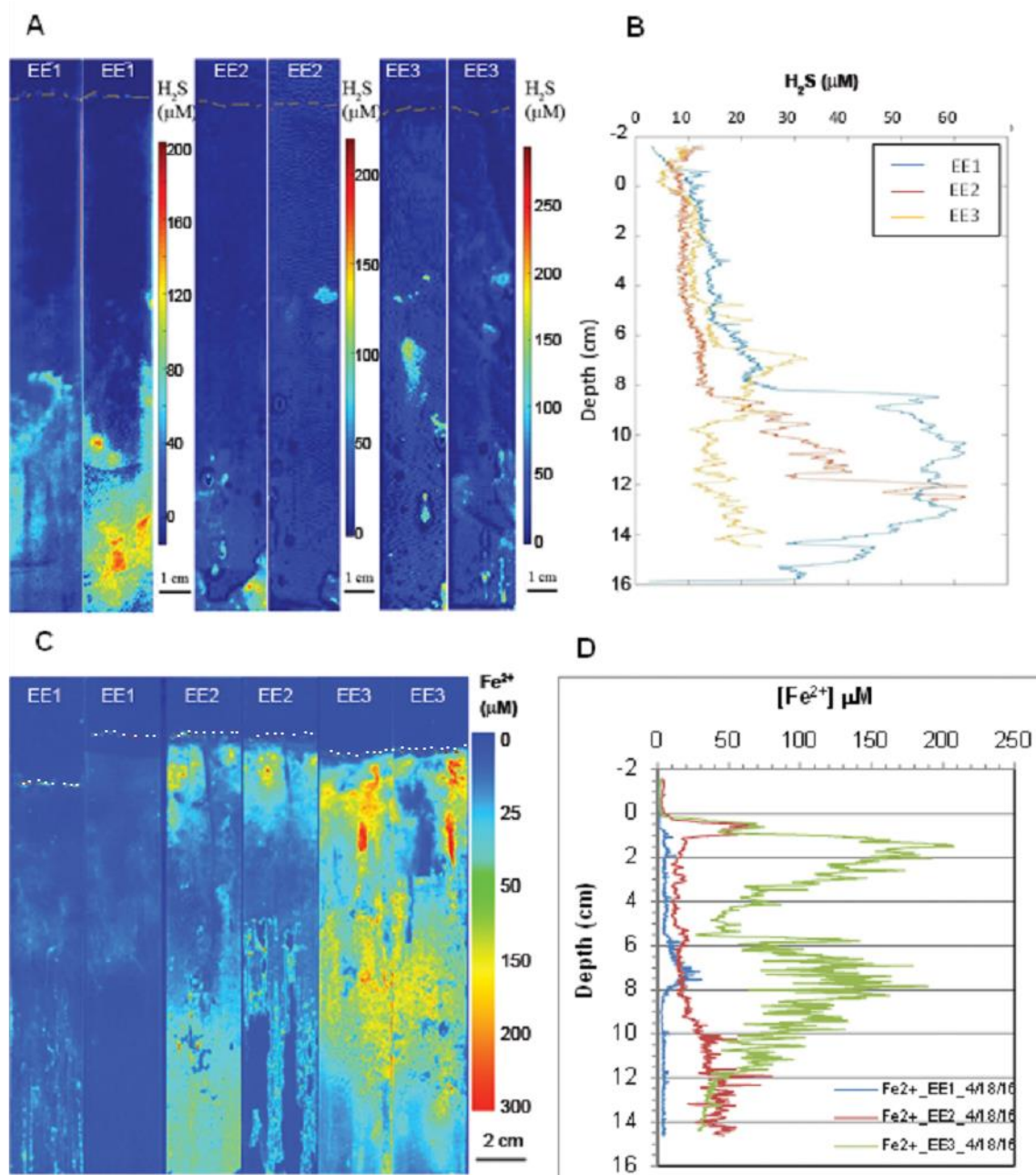


Figure 2.14. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of Elders East (EE) marsh peats in spring 2016, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns (pseudo-color) obtained by in-situ measurements in sediments; dotted line marks the peat surface. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in the panel (A). (C) 2-D Fe^{2+} distribution patterns obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in the panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

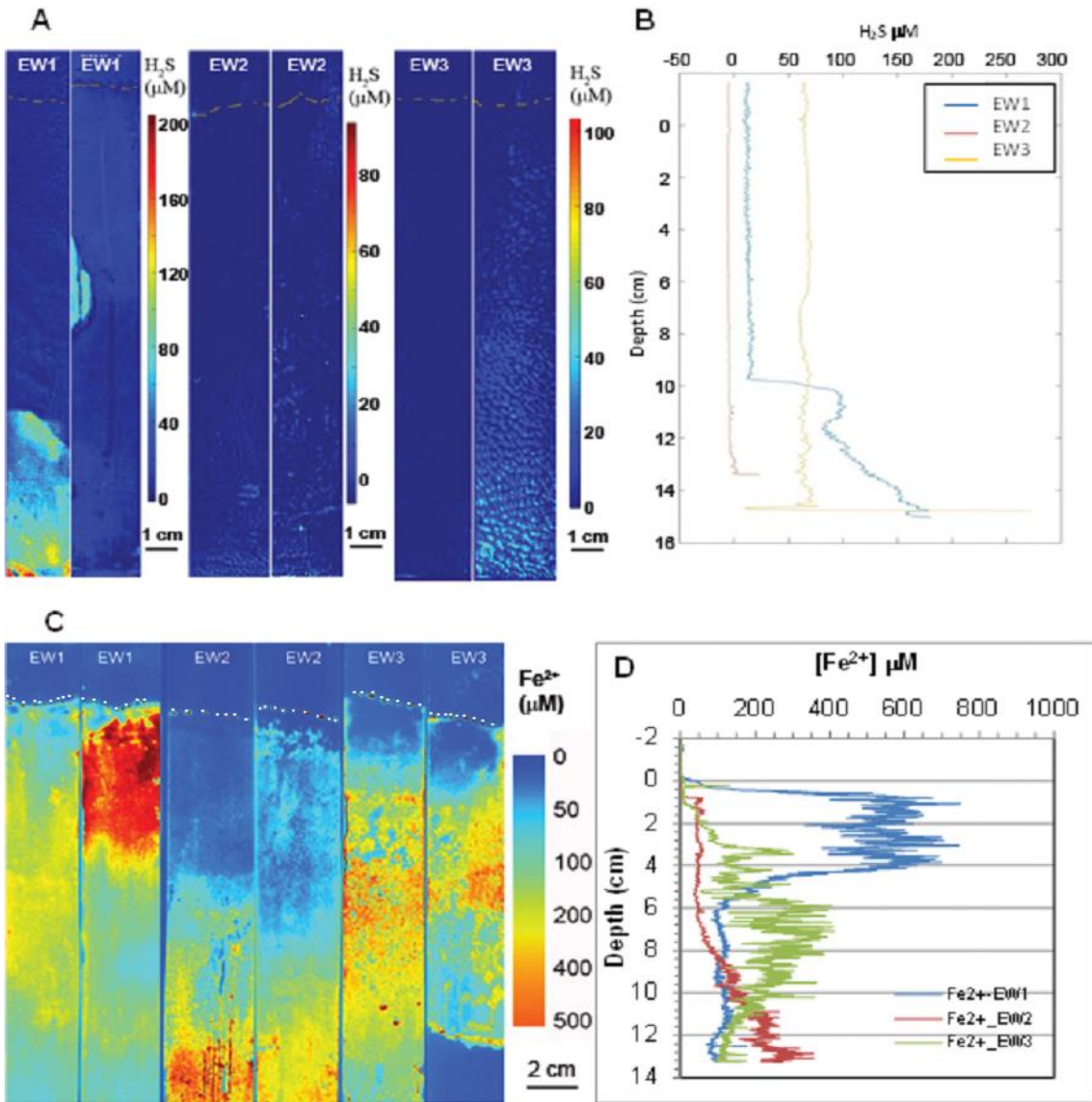


Figure 2.15. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of Elders West (EW) marsh peats in spring 2016, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns (pseudo-color) obtained by in-situ measurements in sediments; dotted line marks the peat surface. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in the panel (A). (C) 2-D Fe^{2+} distribution patterns obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in the panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

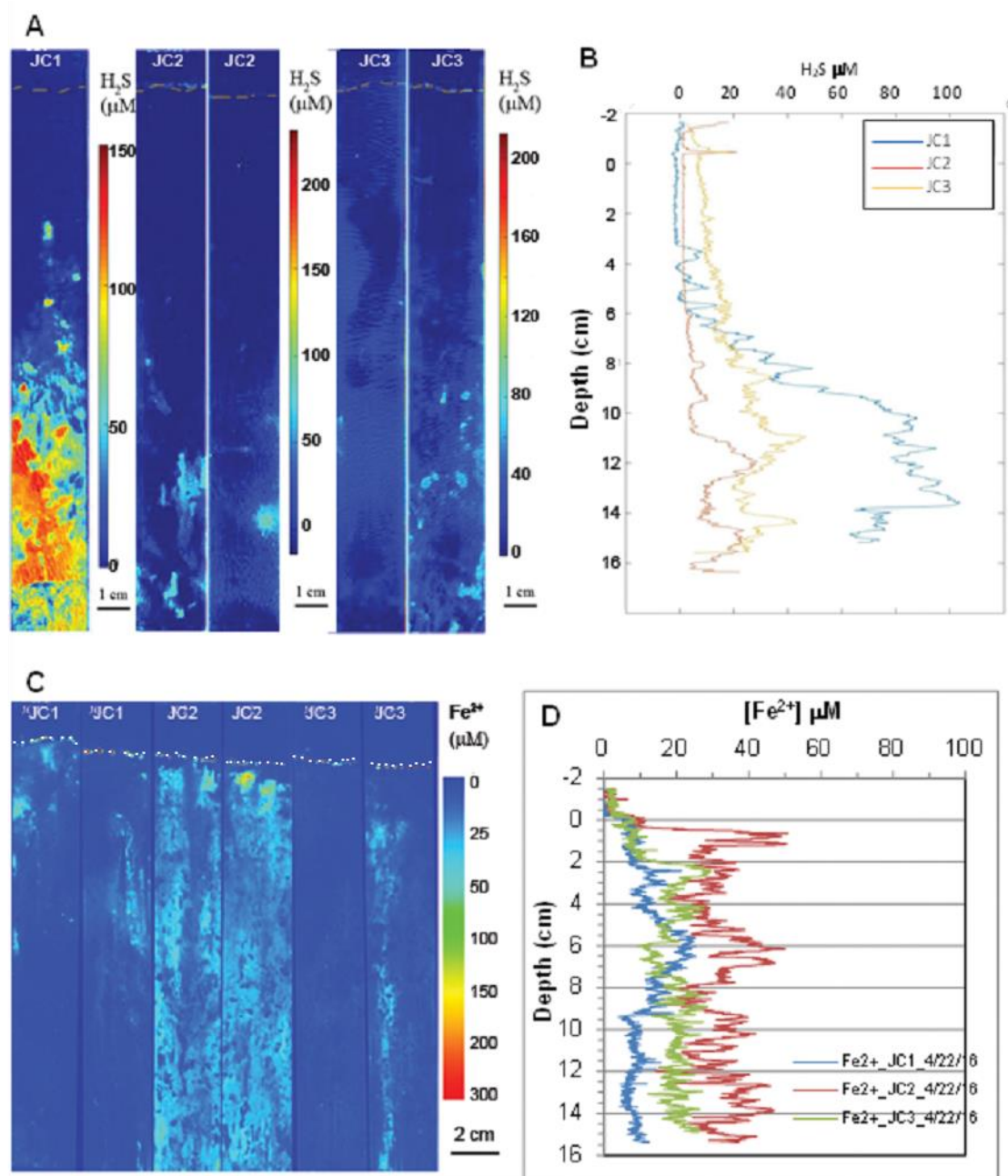


Figure 2.16. H_2S and dissolved Fe^{2+} distribution patterns in the pore water of JoCo (JC) marsh peats in spring 2016, Jamaica Bay, NY. (A) 2-D H_2S distribution patterns (pseudo-color) obtained by in-situ measurements in sediments; dotted line marks the peat surface. (B) Vertical H_2S profiles averaged from each 2-D H_2S distribution in the panel (A). (C) 2-D Fe^{2+} distribution patterns obtained by in-situ deployments; the white dotted line marks the peat surface. (D) Vertical Fe^{2+} profiles averaged from each 2-D Fe^{2+} distributions in the panel (C). “Negative” depths, where shown, represent concentrations in fluid just above the peat surface (0 on the vertical (depth) axis corresponds to the marsh surface). Paired panels (with same station designation) represent replicate sensor deployments within 1 m at a given site.

The pH, redox potentials (Eh) and salinity of the discrete pore water samples collected at 5, 10, 15 and 25 cm depth of marsh peat at various sites and seasons are summarized in Table 2.1. The pH

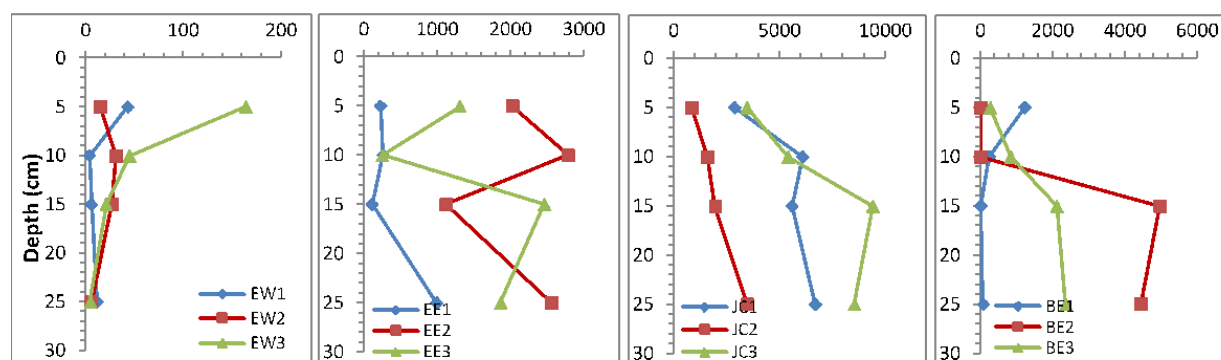
values of all sites and seasons are generally in the range of 6 - 7 at 5, 10, 15 and 25 cm depths of marsh peat, and the vertical pH data show slight increases with depth below 5 cm. No obvious seasonal variation in pH is observed, except for the spring 2015 sampling at EW, during which pH is slightly greater than 7 and thus higher than the pH values obtained in other seasons at EW. Two extremely low pH values, 3.48 and 3.55, are found in the 2014 fall sampling at 15 and 25 cm of EW1, respectively. The pH of JoCo (JC) is likely lower than pH of other sites at the same season.

Redox potential (Eh) obtained from each marsh site below 5 cm is negative. It decreases with depth in most sites and also shows a significant seasonal and spatial variation for all four marshes. At site EE, the Eh of summer and fall ranges from ~ -200 to ~ -300 mV, and it increases to $-5 \sim -170$ mV in spring. The Eh values of EW is higher than other sites, it is in the range of $-15 \sim -100$ in spring and fall, and slightly decreases to $-100 \sim -200$ mV in summer. The Eh values in BE range from -12 to about -200 mV in spring and fall, and largely decrease to about -370 mV in summer. The Eh values of JC are -18 to about -150 mV in spring, -185 to -290 mV in fall and -200 to -350 mV in summer, respectively. The salinities of all four sites don't show obvious changes either with depth or season, and range from 27 to 30.

The concentrations of dissolved Fe^{2+} , total hydrogen sulfide ($\Sigma\text{H}_2\text{S}$, $\Sigma\text{H}_2\text{S} = \text{H}_2\text{S} + \text{HS}^- + \text{S}^{2-}$), phosphate and ammonium in pore water were also determined by traditional methods via pore water “sippers” at discrete depths of 5, 10, 15 and 25 cm. The results are summarized in Table 2.2 and Fig. 2.17. Dissolved Fe^{2+} in pore water of EW is much higher than that of EE, BE and JC, and seasonal variation and vertical gradients are evident at the sampling sites in EW, EE and JC (Fig. 2-18). However, the dissolved Fe^{2+} in the pore water of BE is relative low ($< 12 \text{ } \mu\text{M}$) and shows no obvious change with depth. Total hydrogen sulfide obtained in fall and summer is much higher than in spring, and the concentrations vary in the sequence of $\text{JC} > \text{BE} > \text{EE} > \text{EW}$. Similarly, as revealed by the 2-D H_2S sensor data, the total hydrogen sulfide concentration in EW is very low or non-detectable at all depths, even in the fall or summer samplings. Ammonium concentrations also vary with season and location in Jamaica Bay. The NH_4^+ concentrations at sites in BE are as high as $100\text{-}900 \text{ } \mu\text{M}$ in spring and summer, but decrease to $< 59 \text{ } \mu\text{M}$ in fall. The NH_4^+ concentrations of EW are very low in spring, and but mostly non-detectable in fall and summer. Similar to ammonium, phosphate concentrations also show similar concentrations at the sites in JC and EW, and higher concentrations at BE and EE. Interestingly, higher phosphate is found in summer and fall at all sites.

The solid phase total sulfur (S), chromium reducible sulfur (CRS), acid-leachable Fe, solid phase C and N are summarized in Table 2.4. The degree-of-pyritization (DOP), or the extent to which the Fe in the marsh sediment is associated with FeS_2 at the different sites, is also given in Table 2.4.

$\Sigma\text{H}_2\text{S}$ Profiles in pore water (μM), Fall 2014



$\Sigma\text{H}_2\text{S}$ Profiles in pore water (μM), Spring 2015

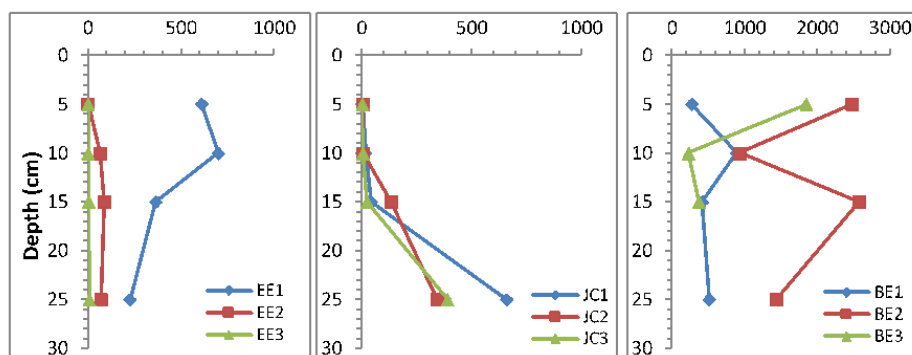
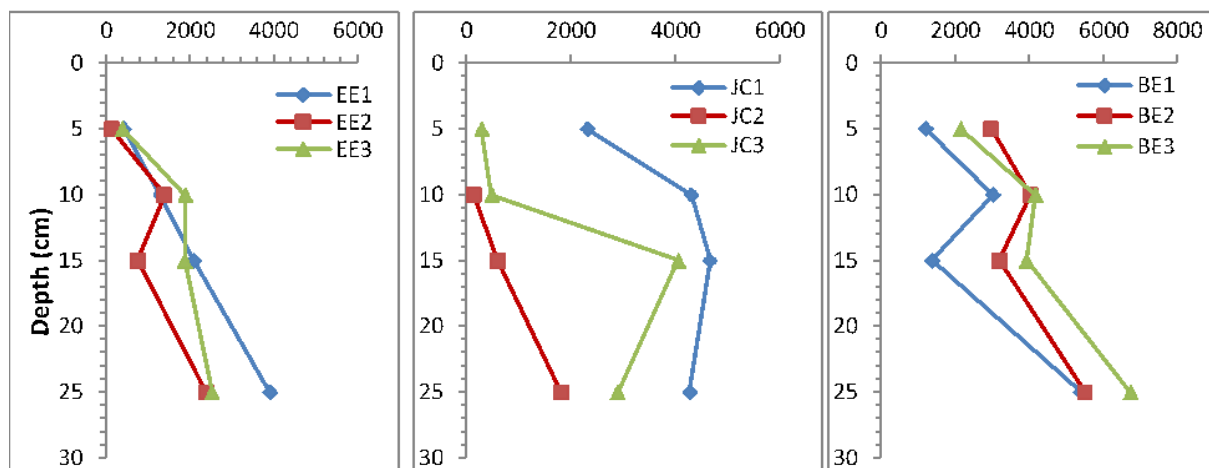


Figure 2.17a. Total dissolved sulfide $\Sigma\text{H}_2\text{S}$ ($=\text{H}_2\text{S} + \text{HS}^- + \text{S}^{2-}$) profiles in pore water of Elders East (EE), Elders West (EW), JoCo (JC) and Big Egg (BE) in Jamaica Bay, NY, in fall 2014 and spring 2015. Samples were collected using “sippers.”

$\Sigma\text{H}_2\text{S}$ profiles in pore water (μM), Summer 2015



$\Sigma\text{H}_2\text{S}$ profiles in pore water (μM), Spring 2016

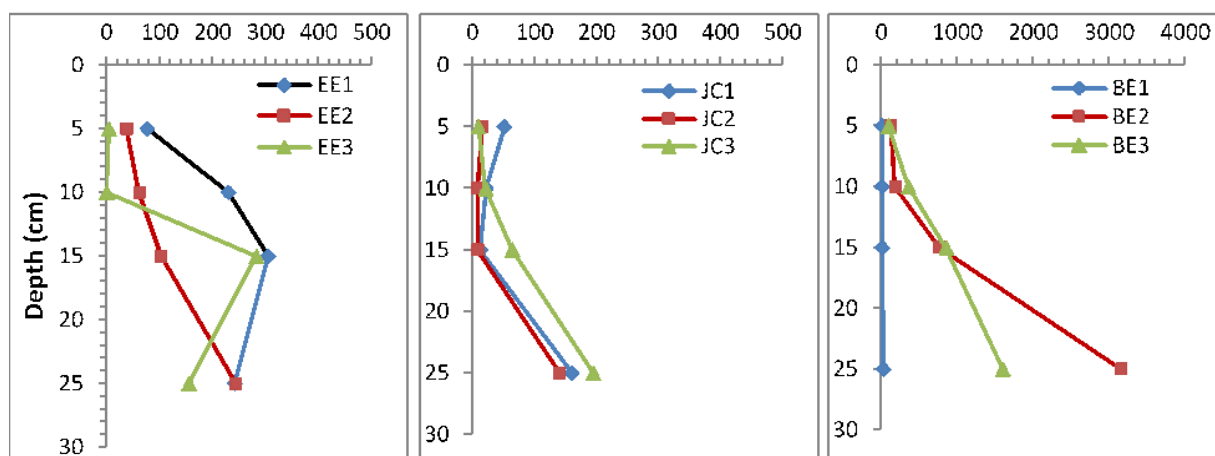


Figure 2.17b. Total dissolved sulfide $\Sigma\text{H}_2\text{S}$ ($=\text{H}_2\text{S} + \text{HS}^- + \text{S}^{2-}$) profiles in pore water of Elders East (EE), JoCo (JC) and Big Egg (BE) in Jamaica Bay, NY, in summer 2015 and spring 2016. Samples were collected using “sippers.”

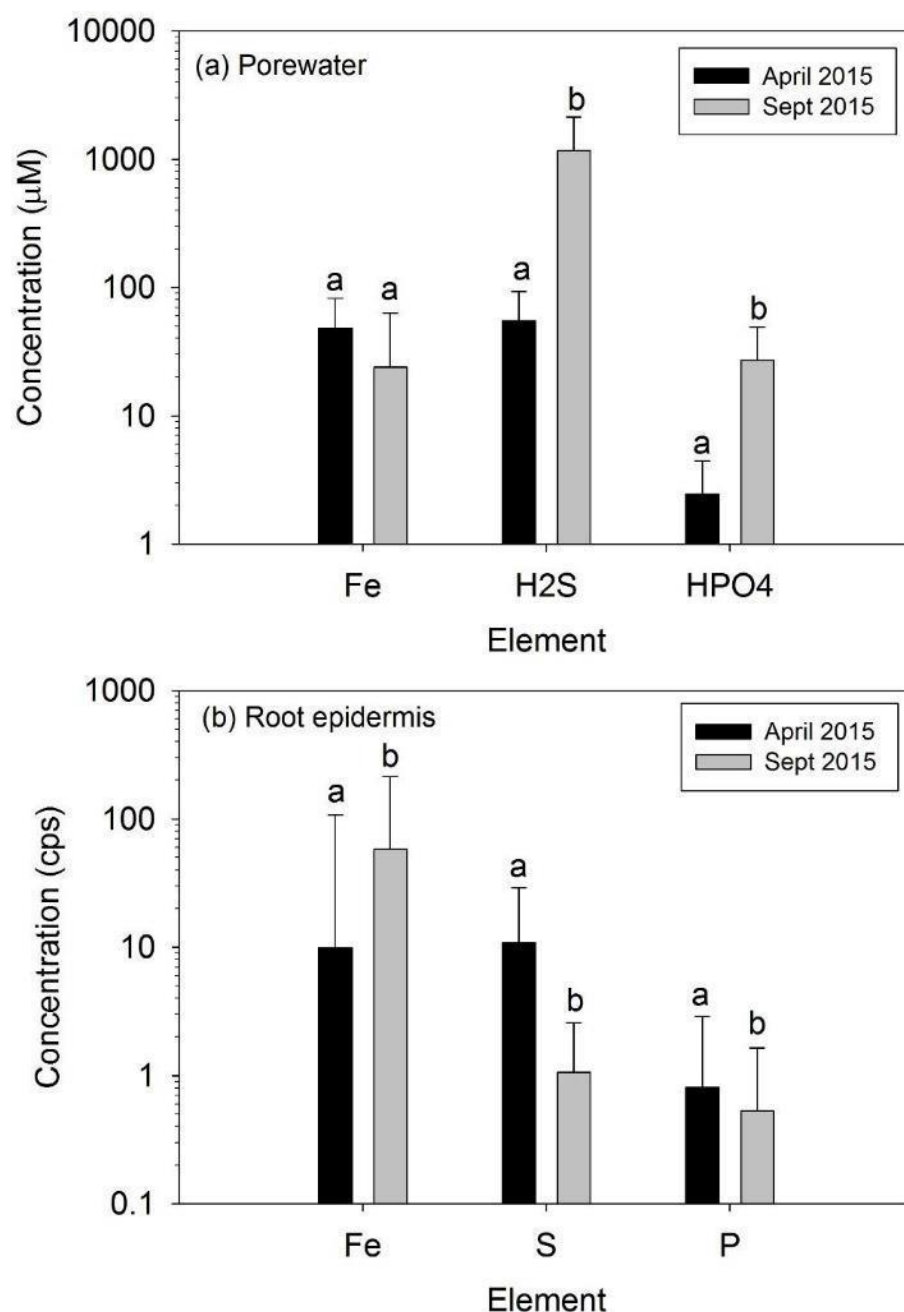


Figure 2.18. Comparison of seasonal variations in H₂S, HPO₄ and Fe average (± 1 SD) concentrations in the pore water and plant root epidermis (of *S. alterniflora*) from Elders East (EE2), NY, showing an opposite variation of these elements between the pore water (top) and the root epidermis (bottom) with seasonal change. Samples were collected in April and September 2015, respectively. Different letters on each pair of elemental concentrations indicates difference is statistically significant (t-test, $p < 0.05$; Feng et al., 2018).

Discussion

Heterogeneities of Fe²⁺ and H₂S distributions in marsh peat pore water

Salt marsh peat is the site of intense biogeochemical reactions involving anoxic organic matter remineralization, which typically result in dramatic changes in the concentration of H⁺, Fe²⁺, H₂S and other pore water species in the upper layer of marsh sediments (Bull and Taillefert, 2001; Morse et al., 1987; Canfield et al., 1992; Brendel and Luther, 1995; Zhu and Aller, 2013; Yin et al., 2017). Compositional changes of Fe²⁺ and H₂S with depth in marsh pore water are usually assumed to occur in an overall average vertical progression. Significant heterogeneity and complex three-dimensional reaction patterns over mm to cm scales can result, however, from the intense biomass growth and density (Zhu and Aller, 2013; Yin et al., 2017). The growth of plant roots and oxygen transport through the rhizosphere from plant leaves to deep marsh peat driven by plant photosynthesis create a complicated and time-dependent 3-D distribution pattern of Fe²⁺ and H₂S in marsh peat. Most of the selected study sites in Jamaica Bay are dominated by saltmarsh cordgrass *Spartina alterniflora*, in which plant roots extensively grew and were tightly linked to each other over at least the top 30 cm of the peat. Thus, it is expected that the 2-D distribution patterns of Fe²⁺ and H₂S in marsh peat are influenced by the plant root growth patterns.

In order to study Fe²⁺ and H₂S distributions and the associated biogeochemical processes in marsh peat with a high density of living plants, box cores made of clear acrylic plastic were collected from each site in October 2014. The H₂S sensor deployments were conducted in the laboratory so that the plant root features and sensor foil deployment position can be directly seen from side of the core. The 2-D H₂S distribution measured by a reversible H₂S fluorescence planar sensor was compared to the visible image of the peat core (side view). The green color of the visual images (Figs. 2.1A – 2.4A) was from the visual light source (white is not available in the image system used). The corresponding 2-D H₂S images in Figs. 2.1A – 2.4A (shown as pseudo-colors reflecting concentrations) revealed the complex concentration distribution patterns associated with the plant root structures and organic substrate distributions in marsh peat. Note that no worm burrows were found in the measurements, suggesting that bioturbation is not a factor in these sediments and therefore does not affect the accretion chronologies derived from ²¹⁰Pb distributions (see discussion of ²¹⁰Pb in Part 3 of this report). In the fall sampling, H₂S concentrations near the surface of the peat were undetectable but sharply increased below 2 cm to high H₂S levels in the fall sampling, except for the sites at JC (Fig 2.4A) and BE3 (Fig. 2.1A). The H₂S levels at sites in JoCo marsh were elevated to 4 – 6 mM just below the marsh surface, which was much higher than the threshold (2 mM) that can be harmful to *S. alterniflora* (Koch and Mendelssohn, 1989). The distribution pattern was significantly complicated by plant roots, which transport oxygen into the surrounding peat. The transport of oxygen around the roots of marsh grass in anoxic sulfidic sediment can create a thin oxic layer in which oxygen and/or nitrate (rather than sulfate) serve as the electron acceptors for organic matter remineralization, resulting in a low level of H₂S around the root. Such an interface of oxic-anoxic sediment around the roots can be seen in both visible peat images and 2-D H₂S images, indicating heterogeneous remineralization patterns. **We hypothesize that the oxic layers formed around roots help marsh plants to survive in the high levels of H₂S by blocking sulfide absorption.** It should be pointed that the 2-D H₂S distributions in the fall 2014 season (Figs 2.1A – 2.4A) were measured in the

laboratory using a fluorescence H_2S sensor after incubation of the box cores in seawater with air aeration for 24 hours at room temperature (Zhu and Aller, 2013). This was different from the in-situ H_2S measurements in other seasons with an absorption optical sensor (Yin et al., 2017). The 2-D H_2S distributions obtained by in-situ deployments (Figs. 2.5 - 2.16, panel A) showed that H_2S levels in top 4 cm were low even in the summer season, and gradually increased to higher concentrations at depth. The high H_2S concentrations just below the water-peat interface in Fig 2.1A (site BE3) and Fig 2.4A (site JC) were not found in the 2-D in-situ measurements in the field. The effect of roots on the 2-D patterns of H_2S can be seen in images with very high H_2S . This is especially evident at JoCo in the summer, a time when marsh plant growth is dense and bacterial activity is high (Fig. 2.12). In general, H_2S levels at JoCo and Big Egg were higher than at Elders East or West.

2-D Fe^{2+} distributions were measured by in-situ deployments, so visible images of the sensing marsh peat were not available for any sampling time. However, the 2-D Fe^{2+} distributions also showed the influence of roots, similar to the 2-D H_2S images, especially at the Elders sites, where pore water Fe^{2+} concentrations were high (Figs. 2.1 – 2.16, panel C). Areas of low/undetectable Fe^{2+} concentration can be clearly seen in the high Fe^{2+} zones, implying that dissolved Fe^{2+} was oxidized by oxygen in the thin oxic layers around the roots. Fe^{2+} concentrations at Big Egg, Elders East and JoCo were in the range of 10-100 μM , which is typical of coastal marsh pore water. However, Elders West had very high Fe^{2+} concentrations at all sampling times, likely due to high levels of iron in the sediment which was used to restore the Elders West marsh. High levels of Fe^{2+} may be harmful to plants because it may co-precipitate or adsorb the nutrients ammonium and phosphate in the marsh, preventing their uptake by the roots. On the other hand, the high levels of Fe^{2+} can efficiently remove sulfide in the pore water due to the formation of authigenic FeS and FeS_2 minerals, resulting in lower levels of H_2S at EW in all seasons.

We have tested the hypothesis that *S. alterniflora* can form oxic layers around roots to prevent sulfide absorption by using the National Synchrotron Light Source-II at Brookhaven National Laboratory (see Feng et al., 2018). We used the Hard X-ray Nanoprobe Beamline to obtain nanometer-scale measurements of trace elements in *S. alterniflora* root tissue. Fig. 2.18 shows the results for Fe, S and P in the root epidermis of *S. alterniflora* from Elders East (EE2) in April and September, 2015. Also shown are the corresponding average pore water Fe, $\Sigma\text{H}_2\text{S}$ and PO_4^{3-} concentrations from 5 to 25 cm. When pore water sulfide and phosphate are high, in the late summer, the root epidermis shows lower concentrations of S and P. At the same time, pore water Fe is lower than in the April sampling, but Fe in the root epidermis is high. This pattern is consistent with the roots producing an oxic microenvironment when oxygen is transported into the peat through the root, such that Fe^{2+} in the pore water is oxidized, possibly producing iron ‘plaque’ (i.e. FeOOH) on the root epidermis. This plaque prevents sulfide from entering the root tissue. Phosphate may also be excluded via adsorption onto the FeOOH or formation of an iron phosphate phase.

In addition to the vertical and horizontal heterogeneities of Fe^{2+} and H_2S distributions, there are many “hot spots” on the 2-D Fe^{2+} and H_2S images, reflecting the heterogeneous distributions of labile organic matter and the microniches of exoenzymes and microbes on sediment particles (Cao et al.,

2013). We also noted that large variation of H_2S and/or Fe^{2+} distributions may occur in same site in duplicate in-situ measurements over distances of <1 m between two deployed sensor sheets.

Typically, the high concentration of H_2S (or $\Sigma\text{H}_2\text{S}$) in anaerobic salt marshes comes from the reduction of sulfate by organic matter. Marsh peats in Jamaica Bay are periodically submerged. Oxygen in overlying water (or air) can diffuse into the surficial marsh peat or be transported into deeper sediment through roots. However, the oxygen and other electron acceptors can be quickly exhausted over spatial scales of millimeters by the decomposition of the large amount of plant biomass in the marsh peat, generating a decrease in redox potential (Eh) with depth (Hanbrick et al., 1980) and a complicated 3D pattern associated with the roots of plants. Therefore, redox potential can be used as an indicator of the degree of oxidation of marsh peat. The results summarized in Table 2.1 show that the redox potentials of all sites generally decrease from 5 to 25 cm, but exhibit a clear seasonal variation. The redox potential in the spring is higher than in summer and fall, indicating low organic matter degradation rates in spring. The data also show a clear spatial heterogeneity of the oxidation degree of different marsh sites. Redox potential of marsh peat at EW is much higher than EE, BE and JC, with sequence of $\text{EW} > \text{BE} > \text{EE} > \text{JC}$. The higher redox potential in EW is caused by the high content of FeOOH minerals (a layer of red FeOOH is visible on EW peat surface), which in turn dominate the biomass decomposition, resulting in low or undetectable H_2S in pore water (Table 2.2 and Figs. 2.3, 2.7, 2.11 and 2.15). Interestingly, the pH values of all sites and depths are in the range of 6 – 7 with vague seasonal variations, implying the intense reduction of organic matters by various electron acceptors in these sediments tend to buffer sediment pore water close to 6-7. Two extremely low pH values, < 4 , were found at depths of 15 and 25 cm of EW1 peat in fall 2014. The reason for this is not clear, although oxidation of iron sulfides can produce low pH.

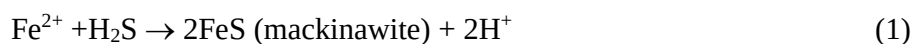
Seasonal Variation of H_2S and Fe^{2+} distributions in marsh pore water

H_2S distributions in marsh pore water in all the marshes varied seasonally, generally with higher H_2S levels in summer and fall, and lower or undetectable levels in spring (Table 2.2, Fig 2.1 – 2.17). However, H_2S in different marshes showed different concentrations in the summer and fall samplings. For example, H_2S levels at JoCo and Big Egg were as high as 2 – 6 mM, but were < 1 mM at Elders East and < 0.4 mM at Elders West, implying that the seasonal variation of H_2S was not only determined by temperature-mediated bacterial activity, but also by the availability of reactive organic substrates and reactive iron in the marsh substrate. The relatively low H_2S levels at Elders West may also be attributed to the extremely high FeOOH and Fe^{2+} concentrations in this site. A previous study showed that the exoenzymes and microbes in marine sediments have high activities in the summer and fall, but very low in winter and early spring (Cao et al., 2013). Indeed, the discrete pore water samples showed higher oxidation-reduction potential (i.e. more positive) in spring than in the summer samplings, indicating less “reducing” conditions in the peat in spring (see discussion above; Table 2.1). Thus, the seasonal dependence of H_2S distributions was a direct reflection of the change in microbial activity with temperature. The higher levels of H_2S at JoCo and Big Egg, indicate more labile organic matter was available in those two marshes. Interestingly, high H_2S distributions in the spring 2015 sampling were only found at Big Egg (Fig. 2.5A). The reason for this is not clear.

Fe²⁺ concentrations in marsh pore water also show seasonal changes (Table 2.2, Fig 2.1 – 2.17), but the seasonal changes are not very significant compared to the variations in the H₂S distributions, partially due to the low Fe²⁺ concentrations in the marsh pore water, except for EW. However, the distribution patterns of Fe²⁺ are closely associated with H₂S distribution patterns in marsh pore water, as discussed below. Generally, Fe²⁺ concentrations in pore water are relatively higher in spring than in summer and fall, due to the low H₂S concentrations in spring.

Interaction of H₂S and Fe²⁺ distributions in marsh peat pore waters

In organic-rich marsh peat, the depth of O₂ penetration is typically so shallow as to make the zones of aerobic respiration, denitrification and MnO₂ reduction very thin in the summer and fall seasons when bacterial activity is high. Thus, the organic matter decomposition processes in the upper ~30 cm are likely dominated by either iron respiration in the suboxic zone or sulfate respiration under anoxic conditions. At the depth below which Mn-oxide has been depleted, Fe-oxide reduction becomes energetically favorable as a pathway for organic matter oxidation because Fe-oxide has a higher redox potential than sulfate, resulting in increasing Fe²⁺ concentrations in pore water with depth, as shown in panel C of Figs. 2.1 – 2.16. At depths below which the reactive particulate Fe-oxide has been depleted, sulfate reduction dominates the metabolism, producing dissolved sulfide species (HS⁻, H₂S, S²⁻), and an increase in H₂S with depth in pore water below the Fe²⁺ zone (Bull and Taillefert, 2001; Jørgensen and Kasten, 2006; Johnston, 2011). The free sulfide subsequently reacts with dissolved Fe²⁺ to form the reactive solid phase FeS, resulting in a Fe²⁺ maximum above the H₂S maximum (Bull and Taillefert, 2001):



FeS is unstable and converts to the more stable form pyrite (FeS₂) by a variety of pathways (Berner, 1984; Howarth, 1979), including, for example:



The in-situ zonations of Fe²⁺ and H₂S in Figs 2.1 - 2.16 shows this sequence—maximum Fe²⁺ is generally produced at 2 – 4 cm, and the H₂S levels increase to maxima below 4 cm. The in-situ heterogeneous 2-D Fe²⁺ and H₂S distributions are useful for determining redox zonation and understanding the dominant biogeochemical processes occurring within the marsh peat.

Thus, both dissolved Fe²⁺ and H₂S can be efficiently removed by FeS₂ precipitation from pore water. When millimolar levels of H₂S occur in marsh peat pore water, the dissolved Fe²⁺ concentrations are generally < 20 μM at the same depths. On the other hand, the high pore water concentrations of Fe²⁺ at Elders West are linked to low H₂S levels in all seasons. There are some Fe²⁺ “hot spots” co-distributed with high levels of H₂S, as seen in Fig. 2.5A, C, Fig. 2.9A, C and Fig. 2.12A, C. These hot spots are likely produced in the suboxic layers around roots, caused by O₂ transport down to the deep sediment through the rhizosphere.

Interaction of H₂S and Fe²⁺ as seen in the solid phase: Degree of Pyritization

The precipitation of the solid phases FeS and FeS₂ (pyrite) as a result of elevated concentrations of H₂S and Fe²⁺ in the pore water effectively removes H₂S from solution, and is thus a geochemical

means of controlling H₂S concentrations (Berner, 1984; Howarth, 1979). The pore water data described in this section are essentially snapshots of conditions at the time of sampling. The composition of the solid phase can integrate the redox reactions occurring in the sediments over longer periods. We measured fractions of the solid phase S and Fe pools in the peat at all the sites (Table 2.3). For sulfur, the important pools include Acid Volatile Sulfide (AVS), Chromium Reducible Sulfur (CRS) and Total Sulfur. AVS is a measure of FeS-associated sulfur, CRS of the pyrite-associated sulfur and total S of the AVS, CRS and all other forms, including organosulfur compounds. For iron, we measured a fraction termed “reactive” Fe, i. e. that obtained by a 1N HCl cold leach of the dried sediment. This procedure extracts the portion of Fe that is diagenetically mobile and readily able to react with sulfide to produce the iron sulfide phases. Our prior experience in JoCo (Cochran et al., 2013) suggests that $AVS \ll CRS \leq \text{Total S}$. As noted in reactions 1 and 2, the AVS pool is quite labile and converts to pyrite, which is a longer term sink for Fe and especially S in the marsh peat. In effect, the formation of pyrite removes dissolved sulfide from the pore water and stores it, lowering the exposure of the plants to this phytotoxin. The solid phase measurements enable calculation of a parameter termed the “Degree of Pyritization” (DOP), that is, the degree to which reactive Fe in the solid phase is associated with pyrite and is thus unable to further remove dissolved sulfide from pore water. DOP is defined as:

$$DOP = Fe_{\text{pyrite}} / (Fe_{\text{pyrite}} + Fe_{\text{reactive}}) \quad (3)$$

where Fe_{pyrite} is calculated as $CRS/2$ (i.e. one mole of Fe per 2 moles of S in FeS₂), and Fe_{reactive} is the leachable Fe. Table 2.4 gives the solid phase DOP results.

Several features stand out in the data:

- The CRS-sulfur is generally less than the total sulfur at Big Egg and JoCo, but often comparable at the Elders sites. To the extent that total sulfur includes diagenetically produced organosulfur compounds and sulfur associated with the marsh plants, this difference is explainable by the higher organic content of the marsh sediments at JoCo and Big Egg. Indeed, at the Elders sites, with much lower organic content, CRS and total sulfur are comparable.
- Concentrations of pyrite are greater at JoCo and Big Egg compared with Elders. This mirrors the trend in reactive Fe, which is also greater at Big Egg and JoCo.
- There are seasonal differences in the Fe and S fractions between the summer 2015 and spring 2016 samplings. These reflect the redox cycling of the various pools of Fe and S over the year.
- The degree of pyritization among the sites varies as $JoCo > Big\ Egg > Elders\ East > Elders\ West$. Indeed, the values at JoCo can approach 1, indicating that 100% of the reactive iron is associated with pyrite. These high values suggest that any biogeochemical control of pore water H₂S via FeS₂ precipitation is close to a limit and that high H₂S but low Fe²⁺ concentrations in the pore water can be expected, as observed.

Co-distribution of H₂S and phosphate in marsh pore water

There are no 2-D phosphate data from in situ sensors available for this project, but phosphate concentrations at discrete depths of 5, 10, 15 and 25 cm in marsh peats were measured and the results

are summarized in Table 2.2 together with NH_4^+ , $\Sigma\text{H}_2\text{S}$ and Fe^{2+} . For most of the sites, the phosphate distribution patterns and concentrations in pore water showed a positive correlation with $\Sigma\text{H}_2\text{S}$ or H_2S but negative correlation with dissolved Fe^{2+} distributions. The phosphate in pore water may come from two sources. One is from the decomposition of labile organic matter, with bacteria using sulfate as electron acceptor. More elevated H_2S indicates that more inorganic phosphate was released from the organic matter, and thus elevated levels of H_2S should correlate with higher phosphate in pore water. As a result, the sulfidic zone in marsh peat would be expected to have higher pore water phosphate concentrations than suboxic zones, and this is demonstrated by the data in Table 2.2. The other phosphate source is from the reduction of particulate Fe-oxides. FeOOH particles adsorb inorganic phosphate, which can be released into pore water when the FeOOH is reduced to dissolved Fe^{2+} (Azzoni et al., 2001). However, if the content of active particulate FeOOH is high in the solid phase, phosphate can be removed from pore water by either absorbing onto iron particles or forming an $\text{Fe}_3(\text{PO}_4)_2$ precipitate in the suboxic zone. However, in the sulfidic zone, $\text{Fe}_3(\text{PO}_4)_2$ can be converted to FeS , releasing PO_4^{3-} as a result of the higher stability of FeS than $\text{Fe}_3(\text{PO}_4)_2$ (Roden and Edmonds, 1997). Thus, in late summer and early fall when the marsh peat was sulfidic and more reduced, the pore water phosphate level was high whereas in spring when the marsh was more oxidized, the iron-bound phosphate, $\text{Fe}_3(\text{PO}_4)_2$, was high due to the depleted sulfide, resulting in low levels of pore water phosphate. This pattern is evident at the Elders sites over both years of sampling and at JoCo and Big Egg in summer, 2015, compared with the two spring samplings (2015, 2016; Table 2.2). It should be pointed out that the marsh peat at Elders West was more oxidized from surface down to 25 cm deep (deeper depths were not tested) in all seasons due to the high levels of active iron oxides (which was visible as a distinct red FeOOH layer on the peat surface). Thus, the top 25 cm marsh peat at Elders West can be considered as a suboxic zone dominated by Fe diagenesis (Figs. 2.3, 2.7, 2.15, panel C), such that low pore water concentrations of PO_4^{3-} , NH_4^+ and $\Sigma\text{H}_2\text{S}$ are seen and pore water Fe is the highest of all the sites (Table 2.2). The absence of sulfate reduction (to sulfide) at Elders West also helps explain the low pyrite concentrations and degree of pyritization there (Tables 2.3 and 2.4).

Time Series of $\Sigma\text{H}_2\text{S}$ in Jamaica Bay Marshes- 2004 to 2016

Our group has studied Jamaica Bay marshes since 2004 (see Cochran et al., 2013 for data collected prior to the present study). In particular, we have pore water $\Sigma\text{H}_2\text{S}$ concentrations measured by “sipper” at the four marshes that are the subject of this report. All samples were taken in the upper 25 to 30 cm and analyzed for $\Sigma\text{H}_2\text{S}$ as described above. Analytical techniques were the same throughout and thus the values are comparable within and among the marshes. However, although sampling sites were in the same general area of each marsh, they were not identical over time. In addition, not all marsh sites were sampled in each year. The record of sampling includes: Big Egg- 2004/05, 2014-2016; Elders East and West- 2005-2007, 2014-2016; JoCo- 2005-2007, 2014-2016. These time series of samples permit us to examine changes in the average concentration of $\Sigma\text{H}_2\text{S}$ in pore water of the marsh peat in a depth zone in which root density is high and the plants can be considered susceptible to exposure to elevated levels of its phytotoxin. To do this, we calculated the average $\Sigma\text{H}_2\text{S}$ value of the pore water analyses from sippers deployed from ~5 to 30 cm. Generally, 4 to 5 sample depths were involved (e.g. 5, 10, 15, 25 cm). All sites sampled in each marsh at a given time were averaged to produce a single $\Sigma\text{H}_2\text{S}$ value, presumed to be representative of that marsh at that time. Google

Earth images of the stations sampled in each marsh are provided in the Supplemental Information section. The results are shown in Fig. 2.19. The patterns in each marsh are as follows:

Big Egg

A portion of this marsh was restored in 2003 by spraying sandy sediment from the adjacent subtidal bottom onto the marsh surface (Frame et al., 2006). The unrestored portion of the marsh was sampled in 2004/05 and again in our recent sampling (stations BE-2 and BE-3). We also sampled the restored portion of the marsh during the present study (station BE-1). The effects of the sediment spray are well documented in the ^{210}Pb profile in the core taken in this area of the marsh (see Part 3 of this report). Concentrations of $\Sigma\text{H}_2\text{S}$ in the unrestored portion of the marsh are as high as 3.5–4 mM in the summer and are quite similar between 2004/05 and 2014–16, with comparable values in comparable seasons (Fig. 2.19). Samples from the restored portion of the marsh (plotted separately in Fig. 2.19) appear to have lower $\Sigma\text{H}_2\text{S}$ in the pore water, and the offset is especially clear in the fall, 2014, and spring, 2015 and 2016 samplings.

Elders East

This marsh showed the highest concentration of $\Sigma\text{H}_2\text{S}$ seen by our group- the average value in the fall, 2005 was 9.5 mM, well above the toxic level of 4 mM. Indeed, the marsh was heavily degraded and was restored in 2006/07. Our sampling after restoration shows that levels of $\Sigma\text{H}_2\text{S}$ fell by an order of magnitude in 2007. Values remain low in the spring, 2015 and 2016 samplings, but seem to be increasing in the two warm weather samplings in fall, 2014 and summer, 2015.

Elders West

Elders West was restored in 2010. Although the pre-restoration levels of $\Sigma\text{H}_2\text{S}$ were not as high as those in Elders East, concentrations post-restoration have dropped to virtually undetectable levels in our 2014–2016 samplings (Fig. 2.19). As noted elsewhere in this report, the Elders West site appears to be dominated by Fe diagenesis. Any sulfide produced is rapidly removed as pyrite.

JoCo

JoCo presents a conundrum in that it is considered a “healthy” marsh in Jamaica Bay, yet over the period 2005 to 2016, average $\Sigma\text{H}_2\text{S}$ levels were >2 mM in summer and fall, 2006 and summer, 2015 and exceeded 4 mM in fall, 2005 and 2014. Offsetting these high concentrations is the fact that levels of $\Sigma\text{H}_2\text{S}$ were low (<0.5 mM) at other sampling times, including in the spring, summer and fall, 2007, and were exceptionally low (~0 mM) values seen in spring, 2015 and 2016. Several factors controlling $\Sigma\text{H}_2\text{S}$ are likely in play at JoCo. The large variations in $\Sigma\text{H}_2\text{S}$ from sampling to sampling may in part be due to the fact that most of the reactive iron in the JoCo peat is associated with FeS_2 and is thus not able to readily react with H_2S produced via sulfate reduction. Secondly, although temperature is a strong control on bacterial activity and hence the production of H_2S , there is no clear relationship between mean air temperature during the month or week of sampling and mean pore water $\Sigma\text{H}_2\text{S}$ (data not shown). A clue to the variation of $\Sigma\text{H}_2\text{S}$ at JoCo lies in the fact that drainage rates in JoCo are the fastest seen of the four marshes examined in this study. (See the research article by Tamborski et al. included as Part 4 of this report.) These rates may vary with time as a function of tides (neap vs. spring) and season (warm vs cold; variation in precipitation, variation in plan growth). Nevertheless, the ^{210}Pb chronologies at least at two of the sites documented in the present study

suggest that accretion in portions of the marsh may not be keeping pace with sea level rise. It is possible that at least the portion of JoCo studied is at or near a “tipping point” for degradation and we recommend continued seasonal monitoring at JoCo to document the health and resilience of this marsh.

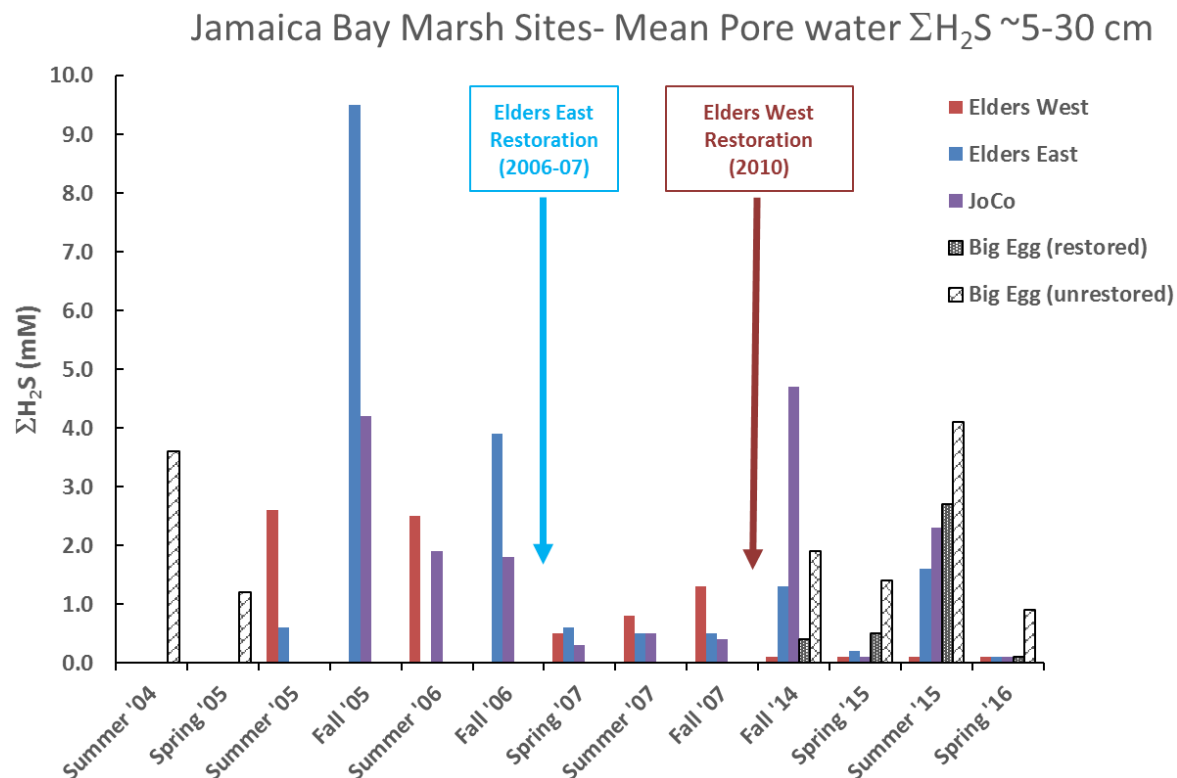


Figure 2.19. Temporal variation of average total dissolved inorganic sulfide ($\Sigma\text{H}_2\text{S}$) in pore waters of different salt marsh sites at Jamaica Bay, NY. Data were averaged from $\Sigma\text{H}_2\text{S}$ concentrations measured in samples taken at discrete depths from 5 to 30 cm. Spring, 2007 sampling in Elders East was post-restoration.

Summary

- Pore water hydrogen sulfide (H_2S) and iron (Fe^{2+}) distributions were measured at Big Egg, JoCo and Elders East and West marshes in Jamaica Bay using in-situ sensors that produced a two-dimensional (2-D) image of concentrations. Both H_2S and Fe^{2+} distributions showed significant vertical and horizontal heterogeneities, as well as seasonal variations. The complicated 2-D distribution patterns associated with the effects of roots (e.g. oxygen transport) were also revealed. The sensor measurements were generally in good agreement with those obtained from discrete pore water samples, although because the analytical procedure for the discrete samples measures all forms of dissolved sulfide (designated $\Sigma\text{H}_2\text{S}$), the latter concentrations were somewhat greater than the sensor H_2S measurements.
- Hydrogen sulfide concentrations measured by in situ sensors at JoCo and Big Egg were elevated (2-6 mM) in late summer and early fall, probably caused by loadings of labile organic matter on

the marshes in the eutrophic Bay. The elevated H₂S levels were higher than the threshold at which adverse effects on marsh plants may occur (~2 mM). On the other hand, oxic zones formed around roots may protect the plants from absorbing H₂S in an extreme sulfidic environment. Indeed, Synchrotron X-Ray imaging shows that concentrations of S and P in the epidermis of *S. alterniflora* roots at Elders East are lowest when H₂S and PO₄³⁻ pore water concentrations are high. Sensor levels of H₂S at Elders East and West were < 1 mM in summer and fall. H₂S levels in spring were < 100 μ M in all sites.

- Dissolved Fe²⁺ concentrations measured with in situ sensors at Big Egg, JoCo and Elder East were in the range of <100 to ~150 μ M, mostly < 40 μ M in all seasons. At Elders West, Fe²⁺ showed high pore water levels in all seasons, 300 – 600 μ M. Pore water Fe²⁺ measured by sensor and in discrete pore water samples were in good agreement. The 2-D Fe²⁺ distributions at Elders West suggested that a suboxic zone in the peat at that marsh could extend at least to 25 cm, resulting in low H₂S in the top 25 cm, even in summer. In addition, the high concentrations of Fe²⁺ at Elders West may be linked to low concentrations of phosphate by the formation of an Fe₃(PO₄)₂ precipitate. Elders West had the lowest pore water NH₄⁺ concentrations of all sites, possibly because NH₄⁺ also was removed by adsorption or co-precipitation with Fe phases.
- Measurement of solid phase S and Fe at Big Egg and JoCo shows that significant amounts (>50%) of diagenetically reactive Fe are associated with the phase FeS₂ (pyrite) and thus not readily able to react as pore water H₂S increases. Indeed, at JoCo, virtually all of the reactive Fe is associated with pyrite in the spring, 2016 sampling. At Big Egg and JoCo, this suggests that the negative feedback on pore water H₂S concentrations associated with the coupled Fe and S redox cycles is weak and that the ability of Fe to control pore water sulfide through pyrite formation is limited. The Elders sites are intermediate with respect to Big Egg and JoCo. Elders East also shows significant (>50%) amounts of Fe associated with pyrite, while Elders West generally has <50%.
- The present study, together with work conducted since 2004, has permitted us to document the pore water geochemistry of the Big Egg, Elders East and West, and JoCo. The greatest change is seen in the significant reduction of the phytotoxin H₂S in the pore water at Elders East and West after the respective restorations of those marshes. Sandy sediment, particularly the iron-rich material used at Elders West, is most effective at ensuring low concentrations of hydrogen sulfide. A reduction is also apparent in the restored portion of Big Egg marsh, while the unrestored portions there continue to display high pore water H₂S, especially in summer samplings. At JoCo, sampling in fall, 2005, and summer and fall, 2006 showed high (2-4 mM) average values of H₂S in the pore water. In contrast, values in spring, summer and fall, 2007 were <0.5 mM. The recent samplings in 2014-16 show strong seasonality, with high values in fall, 2014 (>4 mM) and summer, 2015, but low values (<0.2 mM) in the two spring samplings (2015, 2016). Although the marsh plants at JoCo are exposed to occasional high levels of H₂S that might be considered toxic, the marsh is relatively elevated compared with mean sea level, and drainage through the marsh peat, as traced by naturally occurring radium isotopes (see Part 4 of this report), is more rapid at JoCo than at the other marshes studied. This may help explain why JoCo

continues to be a “healthy” marsh. Relatively healthy marshes such as JoCo should especially be the subject of continued monitoring, for both geochemical and biological parameters.

Acknowledgements

We are grateful to the National Park Service and the Science and Resilience Institute at Jamaica Bay for support of this research. We thank Wen Cong and Yu Qian for assistance in the field, and Patricia Rafferty (National Park Service), Don Riepe, and Elizabeth Manclark (American Littoral Society) for logistical support.

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Supplemental Information

Google Earth images of sampling sites (2004-2016)

Images are labeled with the year(s) sampled and the station number; for example EE05/07-1 represents Elders East station sampled from 2005 to 2007.



Figure 2S.1. JoCo (JC) sampling sites, Jamaica Bay, NY. Images are labeled with the sampling year(s) and station number; for example, JC05/06-1 represents JoCo Station 1 sampled from 2005 to 2006.



Figure 2S.2. Elders East (EE) sampling sites, Jamaica Bay, NY. Images are labeled with the sampling year(s) and station number; for example, EE14/16-2 represents Elders East Station 2 sampled from 2014 to 2016.



Figure 2S.3. Elders West (EW) sampling sites, Jamaica Bay, NY. Images are labeled with the sampling year(s) and station number; for example, EW14/16-1 represents Elders West Station 1 sampled from 2014 to 2016.

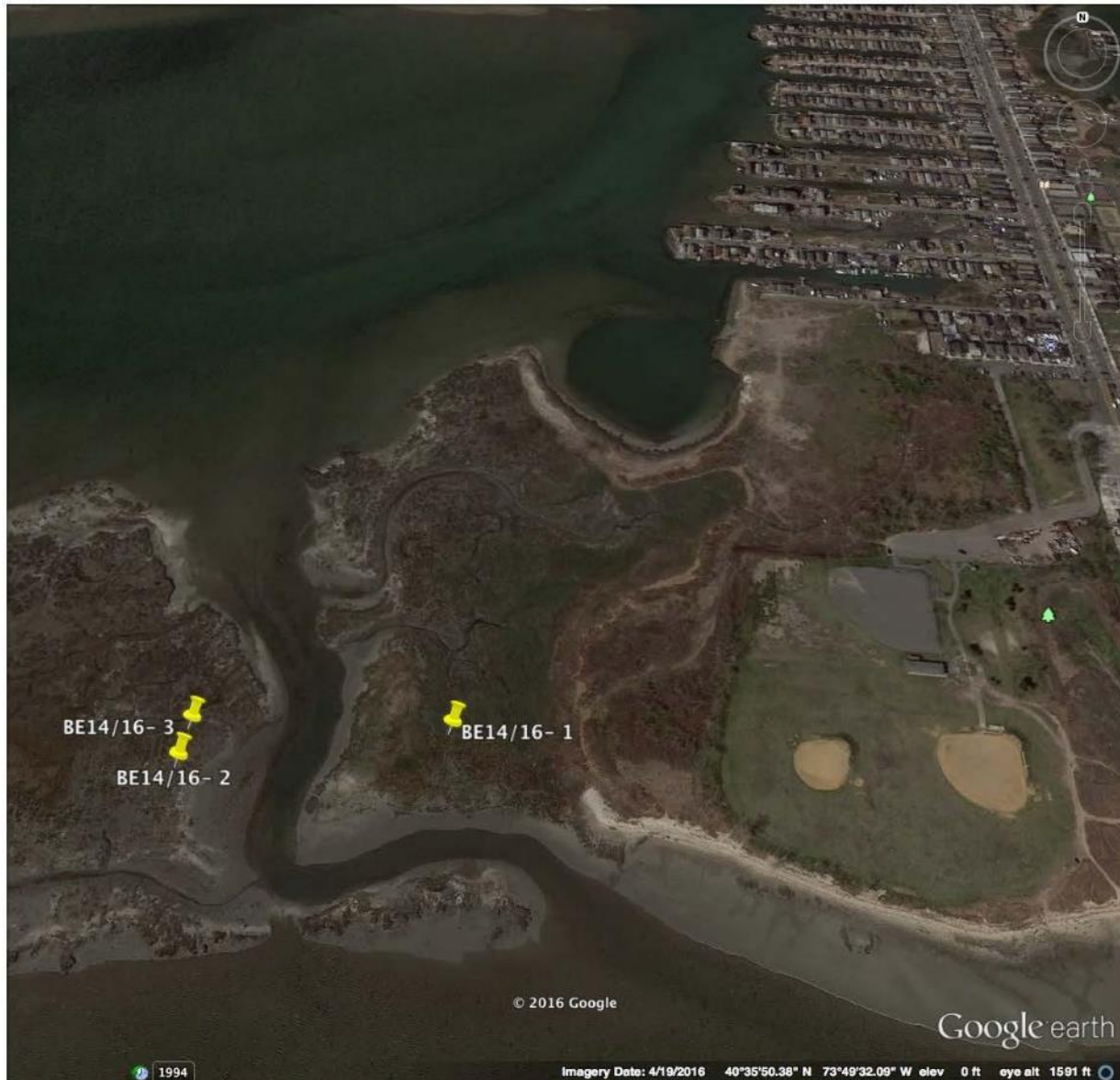


Figure 2S.4. Big Egg (BE) sampling sites, Jamaica Bay, NY. Images are labeled with the sampling year(s) and station number; for example, BE14/16-3 represents Big Egg Station 3 sampled from 2014 to 2016. Big Egg 1 is located in the restored portion of the marsh.

Part 3: Accretion rates of salt marshes in Jamaica Bay, New York: JoCo and Big Egg

Introduction

An important goal of the project is to determine whether the marshes sampled are accreting to keep pace with the rise in mean sea level (MSL; ~ 0.4 cm/y). The term ‘accretion’ in the context of salt marshes is used to represent the upward translation of the marsh surface. This process depends on both supply and accumulation of lithogenic material to the marsh, as well as the growth of marsh plants and accumulation of residual organic material in the peat. Short-term accretion rates can be determined using surface elevation tables (SETs) that also can be used to measure subsidence of a marsh, if occurring. We have evaluated long-term accretion rates of JoCo and Big Egg marshes through measurements of the naturally occurring radionuclide, ^{210}Pb (half-life = 22.3 y). ^{210}Pb is produced in the atmosphere through decay of ^{222}Rn that has emanated from continental rocks and soils. It is deposited at the marsh surface by precipitation and is supplied directly to the marsh surface in this manner, but also can be supplied in association with subtidal sediments resuspended and added tidally to the marsh. The effective time range for ^{210}Pb accretion chronologies is about 5 half-lives or 100 years.

Sampling and Measurements

Single cores were collected in 2014 and 2015 at each of the three sampling sites in JoCo and Big Egg marshes. The locations of the marshes in general are shown in Fig. 3S.1, and Google Earth images showing the core locations are presented in Figs. 3S.2 – 5. The core at Big Egg 1 was taken in the restored area, while Big Egg cores 2 and 3 were from the natural, unrestored portion of the marsh (Figs. 3S.4 and 3S.5). The three sites at JoCo were from the easternmost portion of the marsh (Figs. 3S.2 and 3S.3). These sites were chosen to be adjacent to the sites for geochemical and pore water Ra sampling (Parts 2 and 4 of this report) and to be near SET or previous well emplacements if present. Sampling locations and dates are included in Tables 3.1 and 3.2. We did not evaluate accretion at the Elders marsh sites because the extensive restoration at those marshes eliminates the natural profiles of ^{210}Pb with depth in the marsh. Accretion rates at Elders are best determined by SET emplacements. Soil augur cores were used to obtain ~ 50 cm long cores, which were transferred to aluminum tubes for transport and storage. In the laboratory, cores were frozen before eventual sampling into increments of 1 to 2 cm. The samples were weighed wet, dried and weighed again to determine water content. A limited number of the dried samples were ashed at 450°C in a muffle furnace to determine the loss on ignition, a measure of the organic content.

The samples were ground to a powder and placed in plastic containers for measurement of the gamma activities of ^{210}Pb (46 keV) and ^{226}Ra (via ^{214}Bi , 352 keV), following the method of Renfro et al. (2016). Samples were counted for 2-4 days on Canberra 3800 mm² planar Ge detectors. Self-absorption corrections for ^{210}Pb were made by counting a standard through the sample and using a previously determined calibration of ^{210}Pb counting efficiency as a function of transmission of the standard through the sample relative to counts through an empty sample container. Excess ^{210}Pb

($^{210}\text{Pb}_{\text{xs}}$) is the ^{210}Pb derived largely from the atmospheric pathway described above and was calculated as total ^{210}Pb activity – ^{226}Ra activity.

Results

The radionuclide measurements for the six sampling sites in JoCo and Big Egg are given in Tables 3.1 and 3.2, and the loss-on -ignition results are in Table 3.3. All the marsh sites in JoCo had excess ^{210}Pb distributed to ~25 cm. These lend themselves to detailed accretion chronologies (see next section). The three sites at Big Egg displayed variable excess ^{210}Pb profiles. BE-1, the restored site, showed a significant gradient in excess ^{210}Pb from 15-28 cm, low or negligible excess from 5-15 cm and significant excess in the upper 5 cm (Fig. 3.1). At the unrestored sites, in contrast, BE-2 showed negligible excess ^{210}Pb down the core (Table 3.1), while BE-3 had excess ^{210}Pb only in the upper 3-6 cm (Fig. 3.2).

Table 3.1a. Sampling locations and dates of cores for determining marsh accretion rate in Big Egg Marsh, Jamaica Bay, NY.

Site Name	Marsh Site	Sampling Date	Location	
			Latitude (°N)	Longitude (°W)
Big Egg	BE1	10/8/2014	40.59604	73.82637
	BE2	10/8/2014	40.59586	73.82814
	BE3	10/8/2014	40.59607	73.82812

Table 3.1b. Radiometric data for Big Egg Marsh, Jamaica Bay, NY. ^A

Marsh Site	Sample Depth Interval (cm)	H ₂ O content (g water/g wet sediment)	Dry Bulk Density (g/cm ³)	²¹⁰ Pb (dpm/g)	²²⁶ Ra (dpm/g)	²¹⁰ Pb _{xs} (dpm/g)	Ln(²¹⁰ Pb _{xs})
BE1	0-1	0.822	0.204	4.85 ± 0.37	1.33 ± 0.10	3.51 ± 0.39	1.26
	1-2	0.327	1.163	1.65 ± 0.13	1.13 ± 0.00	0.51 ± 0.13	-0.67
	2-3	0.346	1.106	2.06 ± 0.11	0.93 ± 0.03	1.13 ± 0.11	0.12
	3-4	0.373	1.032	2.08 ± 0.15	1.01 ± 0.04	1.07 ± 0.15	0.07
	4-5	0.256	1.384	1.63 ± 0.15	1.08 ± 0.03	0.55 ± 0.15	-0.60
	5-6	0.226	1.489	1.34 ± 0.12	1.04 ± 0.03	0.30 ± 0.12	-1.21
	6-7	0.219	1.516	1.45 ± 0.11	1.10 ± 0.03	0.35 ± 0.11	-1.05
	7-8	0.260	1.372	1.20 ± 0.13	1.11 ± 0.04	0.09 ± 0.14	-2.37
	8-9	0.217	1.524	1.18 ± 0.09	ND	ND	NC
	9-10	0.206	1.566	0.48 ± 0.08	0.78 ± 0.02	-0.30 ± 0.09	NC
	10-11	0.216	1.527	0.56 ± 0.10	0.53 ± 0.02	0.03 ± 0.10	-3.51
	11-12	0.233	1.466	0.55 ± 0.07	0.75 ± 0.02	-0.21 ± 0.08	NC
	12-13	0.349	1.100	2.28 ± 0.07	1.60 ± 0.05	0.68 ± 0.09	-0.39
	13-14	0.424	0.905	1.87 ± 0.08	1.71 ± 0.05	0.16 ± 0.10	-1.85
	14-15	0.406	0.949	2.06 ± 0.19	1.50 ± 0.05	0.56 ± 0.20	-0.59
	15-16	0.430	0.890	1.82 ± 0.07	1.57 ± 0.05	0.25 ± 0.09	-1.37
	16-17	0.690	0.389	5.04 ± 0.05	1.69 ± 0.07	3.35 ± 0.09	1.21
	17-18	0.738	0.317	4.88 ± 0.05	1.33 ± 0.06	3.55 ± 0.08	1.27
	18-19	0.772	0.270	4.37 ± 0.06	1.22 ± 0.06	3.15 ± 0.08	1.15
	19-20	0.787	0.250	3.86 ± 0.04	1.22 ± 0.05	2.64 ± 0.07	0.97
	20-22	0.796	0.238	2.16 ± 0.06	0.82 ± 0.04	1.35 ± 0.08	0.30
	22-24	0.769	0.274	2.70 ± 0.07	1.08 ± 0.06	1.62 ± 0.09	0.48
	24-26	0.731	0.328	2.07 ± 0.07	1.40 ± 0.05	0.66 ± 0.08	-0.41
	26-28	0.713	0.355	2.11 ± 0.09	1.40 ± 0.07	0.71 ± 0.11	-0.35

^A ND is not determined; NC is not calculated, “-” indicates measurement was not replicated

Table 3.1b (continued). Radiometric data for Big Egg Marsh, Jamaica Bay, NY. ^A

Marsh Site	Sample Depth Interval (cm)	H ₂ O content (g water/g wet sediment)	Dry Bulk Density (g/cm ³)	²¹⁰ Pb (dpm/g)	²²⁶ Ra (dpm/g)	²¹⁰ Pb _{xs} (dpm/g)	Ln(²¹⁰ Pb _{xs})
BE1	28-30	0.679	0.406	1.95 ± 0.09	1.58 ± 0.06	0.37 ± 0.06	NC
	30-32	0.722	0.341	1.42 ± 0.07	1.30 ± 0.04	0.12 ± 0.08	NC
	32-33	0.710	0.359	1.05 ± 0.14	1.18 ± 0.05	-0.13 ± 0.15	NC
	33-34	0.694	0.383	1.43 ± 0.07	1.51 ± 0.04	-0.08 ± 0.08	NC
	34-35	0.733	0.325	0.82 ± 0.16	1.34 ± 0.06	-0.52 ± 0.17	NC
	35-36	0.748	0.304	1.01 ± 0.13	1.23 ± 0.08	-0.23 ± 0.15	NC
BE2	0-1	0.382	1.010	0.96 ± 0.1	1.33 ± 0.04	-0.37 ± 0.10	NC
	0-1 (replicate count)	–	–	1.03 ± 0.09	1.34 ± 0.03	-0.32 ± 0.10	NC
	1-2	0.299	1.245	0.88 ± 0.09	1.27 ± 0.04	-0.39 ± 0.10	NC
	1-2 (replicate count)	–	–	1.34 ± 0.12	1.38 ± 0.04	-0.03 ± 0.12	NC
	2-3	0.393	0.981	0.76 ± 0.09	1.22 ± 0.04	-0.46 ± 0.09	NC
	3-4	0.420	0.914	0.80 ± 0.08	1.34 ± 0.04	-0.54 ± 0.09	NC
	4-5	0.462	0.815	0.87 ± 0.10	1.46 ± 0.04	-0.59 ± 0.11	NC
	5-6	0.680	0.404	0.57 ± 0.10	1.09 ± 0.04	-0.52 ± 0.10	NC
	6-7	0.619	0.506	1.06 ± 0.14	1.34 ± 0.06	-0.29 ± 0.15	NC
	7-8	0.642	0.467	1.03 ± 0.13	1.39 ± 0.05	-0.36 ± 0.14	NC
	8-9	0.676	0.411	1.10 ± 0.16	1.26 ± 0.06	-0.15 ± 0.17	NC
	8-9 (replicate count)	–	–	0.89 ± 0.07	1.50 ± 0.03	-0.61 ± 0.08	NC
	9-10	0.682	0.402	0.73 ± 0.14	1.22 ± 0.06	-0.49 ± 0.16	NC
	10-11	0.661	0.435	0.83 ± 0.10	1.37 ± 0.05	-0.55 ± 0.11	NC
	11-12	0.663	0.432	1.17 ± 0.17	1.42 ± 0.07	-0.26 ± 0.19	NC
	12-13	0.684	0.399	0.23 ± 0.01	1.23 ± 0.05	-1.00 ± 0.05	NC
	13-14	0.679	0.406	0.57 ± 0.11	1.23 ± 0.05	-0.66 ± 0.13	NC
	14-15	0.713	0.354	1.02 ± 0.11	1.39 ± 0.05	-0.37 ± 0.12	NC

^A ND is not determined; NC is not calculated, “–” indicates measurement was not replicated

Table 3.1b (continued). Radiometric data for Big Egg Marsh, Jamaica Bay, NY. ^A

Marsh Site	Sample Depth Interval (cm)	H ₂ O content (g water/g wet sediment)	Dry Bulk Density (g/cm ³)	²¹⁰ Pb (dpm/g)	²²⁶ Ra (dpm/g)	²¹⁰ Pb _{xs} (dpm/g)	Ln(²¹⁰ Pb _{xs})
BE2	15-16	0.733	0.325	1.42 ± 0.14	1.53 ± 0.06	-0.11 ± 0.15	NC
	16-17	0.746	0.307	1.03 ± 0.14	1.54 ± 0.06	-0.50 ± 0.15	NC
	17-18	0.763	0.283	1.27 ± 0.16	1.44 ± 0.06	-0.17 ± 0.17	NC
	18-19	0.749	0.302	1.71 ± 0.17	1.20 ± 0.05	0.52 ± 0.18	NC
	19-20	0.748	0.303	1.39 ± 0.16	1.32 ± 0.05	0.08 ± 0.17	NC
	20-21.5	0.718	0.348	1.90 ± 0.18	1.40 ± 0.06	0.49 ± 0.19	NC
BE3	0-1	0.708	0.362	5.01 ± 0.33	2.65 ± 0.12	2.36 ± 0.35	-0.16
	1-2	0.723	0.340	3.47 ± 0.26	1.63 ± 0.10	1.85 ± 0.28	-0.47
	2-3	0.714	0.353	2.25 ± 0.23	1.53 ± 0.09	0.72 ± 0.24	-1.36
	3-4	0.732	0.327	2.23 ± 0.16	2.21 ± 0.07	0.02 ± 0.18	-5.24
	4-5	0.743	0.311	2.57 ± 0.23	1.88 ± 0.10	0.69 ± 0.25	-1.54
	5-6	0.732	0.327	1.93 ± 0.18	1.58 ± 0.08	0.34 ± 0.20	-2.18
	6-7	0.723	0.340	2.21 ± 0.22	2.04 ± 0.09	0.17 ± 0.24	-2.85
	7-8	0.684	0.399	1.49 ± 0.10	1.84 ± 0.05	-0.35 ± 0.11	NC
	8-9	0.718	0.348	1.84 ± 0.13	1.93 ± 0.06	-0.09 ± 0.15	NC
	9-10	0.711	0.357	1.54 ± 0.14	1.64 ± 0.07	-0.10 ± 0.16	NC
	10-11	0.707	0.363	1.70 ± 0.15	1.58 ± 0.06	0.11 ± 0.16	NC
	11-12	0.696	0.381	1.15 ± 0.12	1.88 ± 0.06	-0.73 ± 0.14	NC
	12-13	–	–	1.34 ± 0.19	1.79 ± 0.08	-0.45 ± 0.20	NC
	13-14	0.705	0.367	1.16 ± 0.10	1.48 ± 0.05	-0.32 ± 0.11	NC
	14-15	0.704	0.367	1.46 ± 0.16	1.61 ± 0.05	-0.15 ± 0.17	NC
	15-16	0.731	0.328	1.36 ± 0.17	1.47 ± 0.08	-0.11 ± 0.19	NC
	16-17	0.724	0.338	1.48 ± 0.23	1.77 ± 0.07	-0.29 ± 0.24	NC
	17-18	0.707	0.364	1.87 ± 0.18	1.70 ± 0.07	0.17 ± 0.20	NC

^A ND is not determined; NC is not calculated, “-” indicates measurement was not replicated

Table 3.1b (continued). Radiometric data for Big Egg Marsh, Jamaica Bay, NY. ^A

Marsh Site	Sample Depth Interval (cm)	H ₂ O content (g water/g wet sediment)	Dry Bulk Density (g/cm ³)	²¹⁰ Pb (dpm/g)	²²⁶ Ra (dpm/g)	²¹⁰ Pb _{xs} (dpm/g)	Ln(²¹⁰ Pb _{xs})
BE3	18-19	0.707	0.363	1.22 ± 0.14	1.51 ± 0.07	-0.29 ± 0.16	NC
	19-20	0.684	0.400	0.97 ± 0.15	1.63 ± 0.06	-0.66 ± 0.16	NC
	20-22	0.684	0.398	0.98 ± 0.15	1.39 ± 0.06	-0.41 ± 0.16	NC
	22-24	0.684	0.399	1.11 ± 0.13	1.43 ± 0.06	-0.32 ± 0.15	NC
	24-26	0.689	0.391	1.22 ± 0.13	1.49 ± 0.06	-0.27 ± 0.14	NC
	26-28	0.727	0.334	0.69 ± 0.12	1.57 ± 0.05	-0.88 ± 0.13	NC
	28-30	0.732	0.327	ND	ND	ND	NC
	30-32	0.669	0.422	ND	ND	ND	NC
	32-34	0.615	0.512	0.73 ± 0.10	1.59 ± 0.06	-0.86 ± 0.12	NC
	34-36	0.627	0.491	ND	ND	ND	NC

^A ND is not determined; NC is not calculated, “-” indicates measurement was not replicated

Table 3.1c. Inventories of excess ²¹⁰Pb in Big Egg Marsh cores, Jamaica Bay, NY.

Core	ρ _{dry} (g/cm ³)*	Σ ²¹⁰ Pb _{xs} (dpm/cm ²)
BE-1	2.6	12.8 ± 0.6
BE-2	2.6	0.0
BE-3	2.6	2.1 ± 0.2

*Density of dry sediment used in inventory calculation

Table 3.2a. Sampling locations and dates of cores for determining marsh accretion rates in JoCo Marsh, Jamaica Bay, NY.

Site Name	Marsh Site	Sampling Date	Location	
			Latitude (°N)	Longitude (°W)
JoCo	JC1	5/1/2015	40.61241	73.78729
	JC2	10/10/2014	40.61212	73.78724
	JC3	10/10/2014	40.61173	73.78591

Table 3.2b. Radiometric data and constant flux accretion rates for JoCo Marsh, Jamaica Bay, NY. ^A

Marsh Site	Sample Depth Interval (cm)	H ₂ O content (g water/g wet sed)	Dry Bulk Density (g/cm ³)	²¹⁰ Pb (dpm/g)	²²⁶ Ra (dpm/g)	²¹⁰ Pb _{xs} (dpm/g)	Accretion Rate (cm/y)	Midpoint Calendar age
JC1	0-1	0.800	0.225	13.13 ± 0.26	0.88 ± 0.09	12.25 ± 0.28	0.162 ± 0.008	2012.3
	1-2	0.817	0.204	7.75 ± 0.49	1.06 ± 0.15	6.69 ± 0.51	0.282 ± 0.025	2007.4
	2-3	0.828	0.191	4.64 ± 0.43	0.82 ± 0.12	3.82 ± 0.45	0.484 ± 0.061	2004.6
	3-4	0.820	0.200	4.47 ± 0.29	0.81 ± 0.09	3.66 ± 0.30	0.451 ± 0.042	2002.5
	4-5	0.824	0.196	3.40 ± 0.44	1.45 ± 0.17	1.95 ± 0.47	0.818 ± 0.200	2000.7
	5-6	0.826	0.193	4.48 ± 0.45	1.39 ± 0.19	3.09 ± 0.49	0.497 ± 0.082	1999.1
	6-7	0.831	0.186	4.79 ± 0.43	0.56 ± 0.13	4.23 ± 0.44	0.349 ± 0.040	1996.7
	7-8	0.840	0.176	5.53 ± 0.44	1.30 ± 0.19	4.23 ± 0.48	0.339 ± 0.042	1993.8
	8-9	0.838	0.178	5.97 ± 0.45	0.89 ± 0.17	5.08 ± 0.48	0.250 ± 0.027	1990.3
	9-10	0.876	0.134	4.91 ± 0.45	0.63 ± 0.13	4.28 ± 0.47	0.353 ± 0.043	1986.9
	10-11	0.851	0.163	6.84 ± 0.41	0.76 ± 0.11	6.08 ± 0.43	0.180 ± 0.016	1982.7
	11-12	0.856	0.157	7.12 ± 0.42	0.40 ± 0.08	6.72 ± 0.43	0.139 ± 0.013	1976.3
	12-13	0.849	0.165	5.83 ± 0.47	1.07 ± 0.14	4.76 ± 0.49	0.150 ± 0.019	1969.4
	13-14	0.840	0.176	5.19 ± 0.40	1.02 ± 0.11	4.17 ± 0.42	0.128 ± 0.017	1962.1
	14-15	0.844	0.172	4.25 ± 0.38	1.19 ± 0.13	3.06 ± 0.40	0.143 ± 0.023	1954.7
	15-16	0.843	0.173	2.76 ± 0.40	1.75 ± 0.17	1.01 ± 0.44	0.368 ± 0.163	1949.9

^A NC is not calculated, “-” indicates measurement was not replicated

Table 3.2b (continued). Radiometric data and constant flux accretion rates for JoCo Marsh, Jamaica Bay, NY. ^A

Marsh Site	Sample Depth Interval (cm)	H ₂ O content (g water/g wet sed)	Dry Bulk Density (g/cm ³)	²¹⁰ Pb (dpm/g)	²²⁶ Ra (dpm/g)	²¹⁰ Pb _{xs} (dpm/g)	Accretion Rate (cm/y)	Midpoint Calendar age
JC1	16-17	0.860	0.152	2.68 ± 0.33	0.89 ± 0.12	1.79 ± 0.35	0.210 ± 0.048	1946.2
	17-18	0.865	0.147	3.20 ± 0.46	0.68 ± 0.12	2.52 ± 0.48	0.127 ± 0.029	1939.9
	18-19	0.867	0.144	1.75 ± 0.34	1.05 ± 0.11	0.70 ± 0.36	0.395 ± 0.210	1934.7
	19-20	0.863	0.149	2.51 ± 0.30	0.45 ± 0.08	1.51 ± 0.30	0.109 ± 0.024	1928.9
	20-22	0.870	0.141	1.78 ± 0.29	0.64 ± 0.10	1.15 ± 0.31	0.145 ± 0.049	1917.5
	22-24	0.856	0.158	1.32 ± 0.14	0.97 ± 0.06	0.34 ± 0.16	NC	NC
	24-26	0.827	0.191	1.42 ± 0.18	1.31 ± 0.07	0.11 ± 0.20	NC	NC
	26-28	0.854	0.159	2.07 ± 0.19	0.62 ± 0.00	1.45 ± 0.19	NC	NC
	34-36	0.842	0.174	2.14 ± 0.23	1.38 ± 0.07	0.76 ± 0.24	NC	NC
	38-40	0.844	0.171	1.01 ± 0.13	0.81 ± 0.05	0.19 ± 0.14	NC	NC
JC2	0-1	0.786	0.248	18.50 ± 0.76	1.89 ± 0.19	16.61 ± 0.78	0.334 ± 0.019	2013.3
	1-2	0.787	0.246	15.21 ± 0.57	0.91 ± 0.13	14.30 ± 0.59	0.357 ± 0.018	2010.4
	2-3	0.776	0.260	12.71 ± 0.53	1.37 ± 0.15	11.34 ± 0.55	0.392 ± 0.022	2007.7
	3-4	0.792	0.240	12.10 ± 0.67	2.60 ± 0.22	9.50 ± 0.70	0.471 ± 0.038	2005.4
	4-5	0.801	0.228	11.29 ± 0.69	1.39 ± 0.12	9.90 ± 0.70	0.445 ± 0.034	2003.2
	5-6	0.800	0.230	8.61 ± 0.53	1.04 ± 0.10	7.57 ± 0.54	0.542 ± 0.043	2001.1
	6-7	0.803	0.226	6.93 ± 0.60	1.25 ± 0.16	5.68 ± 0.62	0.700 ± 0.080	1999.5
	7-8	0.801	0.229	9.78 ± 0.54	1.01 ± 0.17	8.77 ± 0.56	0.421 ± 0.031	1997.6
	8-9	0.804	0.225	8.74 ± 0.48	1.40 ± 0.21	7.34 ± 0.53	0.478 ± 0.038	1995.4
	9-10	0.741	0.308	9.21 ± 0.51	1.21 ± 0.11	8.00 ± 0.52	0.293 ± 0.022	1992.6
	10-11	0.806	0.222	9.41 ± 0.52	1.10 ± 0.15	8.32 ± 0.54	0.355 ± 0.027	1989.5
	11-12	0.812	0.214	9.63 ± 0.53	1.41 ± 0.16	8.23 ± 0.55	0.342 ± 0.027	1986.6
	12-13	0.804	0.225	8.86 ± 0.53	2.61 ± 0.24	6.25 ± 0.56	0.393 ± 0.040	1983.9
	13-14	0.798	0.233	11.01 ± 1.05	2.63 ± 0.25	8.38 ± 1.08	0.256 ± 0.035	1980.7

^A NC is not calculated, “-“ indicates measurement was not replicated

Table 3.2b (continued). Radiometric data and constant flux accretion rates for JoCo Marsh, Jamaica Bay, NY. ^A

Marsh Site	Sample Depth Interval (cm)	H ₂ O content (g water/g wet sed)	Dry Bulk Density (g/cm ³)	²¹⁰ Pb (dpm/g)	²²⁶ Ra (dpm/g)	²¹⁰ Pb _{xs} (dpm/g)	Accretion Rate (cm/y)	Midpoint Calendar age
JC2	14-15	0.786	0.248	11.03 ± 0.86	1.88 ± 0.17	9.15 ± 0.88	0.191 ± 0.020	1976.1
	15-16	0.793	0.238	8.97 ± 0.63	1.75 ± 0.24	7.22 ± 0.67	0.216 ± 0.022	1971.2
	16-17	0.807	0.221	9.82 ± 0.70	0.77 ± 0.11	9.05 ± 0.71	0.157 ± 0.015	1965.7
	17-18	0.804	0.224	9.95 ± 0.54	2.36 ± 0.25	7.58 ± 0.59	0.151 ± 0.015	1959.2
	18-19	0.798	0.232	7.92 ± 0.63	1.65 ± 0.17	6.26 ± 0.66	0.143 ± 0.017	1952.4
	19-20	0.802	0.227	7.05 ± 0.40	1.27 ± 0.13	5.78 ± 0.42	0.125 ± 0.013	1944.9
	20-22	0.800	0.229	5.12 ± 0.39	1.70 ± 0.15	3.41 ± 0.42	0.151 ± 0.023	1934.3
	22-24	0.804	0.224	4.65 ± 0.32	1.36 ± 0.1	3.29 ± 0.34	0.095 ± 0.017	1917.4
	24-26	0.806	0.222	3.10 ± 0.34	1.20 ± 0.08	1.90 ± 0.35	NC	NC
	26-28	0.812	0.214	2.86 ± 0.34	1.03 ± 0.10	1.83 ± 0.36	NC	NC
JC3	0-1	0.836	0.183	14.4 ± 1.28	3.10 ± 0.45	11.30 ± 1.36	0.290 ± 0.040	2013.0
	0-1 (replicate count)	-	0.183	13.46 ± 2.27	1.42 ± 0.47	12.04 ± 2.32	NC	NC
	1-2	0.833	0.186	10.23 ± 0.67	2.98 ± 0.22	7.25 ± 0.71	0.403 ± 0.110	2010.1
	1-2 (replicae count)	-	0.186	8.64 ± 1.47	0.91 ± 0.26	7.73 ± 1.49	NC	NC
	2-3	0.848	0.169	8.64 ± 0.44	1.24 ± 0.12	7.40 ± 0.46	0.431 ± 0.200	2007.7
	3-4	0.634	0.460	5.64 ± 0.66	1.67 ± 0.22	3.97 ± 0.69	0.268 ± 0.080	2004.6
	4-5	0.836	0.183	8.55 ± 0.67	1.10 ± 0.21	7.45 ± 0.70	0.324 ± 0.180	2001.2
	5-6	0.837	0.181	9.13 ± 0.96	1.72 ± 0.32	7.40 ± 1.01	0.297 ± 0.110	1998.0
	6-7	0.845	0.172	5.71 ± 0.60	1.73 ± 0.20	3.97 ± 0.63	0.537 ± 0.150	1995.4
	7-8	0.849	0.167	5.11 ± 0.58	1.60 ± 0.12	3.51 ± 0.59	0.59 ± 0.170	1993.6
	8-9	0.858	0.157	6.88 ± 0.46	1.22 ± 0.14	5.66 ± 0.48	0.365 ± 0.18	1991.4
	9-10	0.856	0.159	7.48 ± 0.64	1.11 ± 0.22	6.38 ± 0.67	0.291 ± 0.110	1988.3
	10-11	0.853	0.163	7.54 ± 0.46	0.80 ± 0.17	6.74 ± 0.49	0.239 ± 0.130	1984.5
	11-12	0.699	0.363	5.65 ± 0.80	0.75 ± 0.25	4.89 ± 0.84	0.121 ± 0.100	1978.3

^A NC is not calculated, “-“ indicates measurement was not replicated

Table 3.2b (continued). Radiometric data and constant flux accretion rates for JoCo Marsh, Jamaica Bay, NY. ^A

Marsh Site	Sample Depth Interval (cm)	H ₂ O content (g water/g wet sed)	Dry Bulk Density (g/cm ³)	²¹⁰ Pb (dpm/g)	²²⁶ Ra (dpm/g)	²¹⁰ Pb _{xs} (dpm/g)	Accretion Rate (cm/y)	Midpoint Calendar age
JC3	12-13	0.844	0.173	5.93 ± 0.47	0.88 ± 0.14	5.05 ± 0.49	0.201 ± 0.190	1971.7
	13-14	0.839	0.179	5.98 ± 0.78	1.25 ± 0.25	4.74 ± 0.82	0.175 ± 0.130	1966.4
	14-15	0.845	0.172	4.34 ± 0.39	0.75 ± 0.14	3.59 ± 0.41	0.205 ± 0.200	1961.1
	15-16	0.811	0.214	3.81 ± 0.53	1.13 ± 0.16	2.67 ± 0.55	0.189 ± 0.150	1956.0
	16-17	0.858	0.156	3.32 ± 0.43	0.90 ± 0.13	2.42 ± 0.45	0.247 ± 0.230	1951.4
	17-18	0.860	0.153	2.90 ± 0.51	1.35 ± 0.17	1.55 ± 0.54	0.353 ± 0.220	1947.9
	18-19	0.858	0.156	3.06 ± 0.49	1.12 ± 0.18	1.93 ± 0.52	0.250 ± 0.370	1944.5
	19-20	0.849	0.167	3.93 ± 0.45	1.09 ± 0.13	2.84 ± 0.47	0.133 ± 0.310	1938.8
	20-22	0.859	0.155	2.58 ± 0.32	0.83 ± 0.09	1.75 ± 0.33	0.174 ± 0.250	1929.3
	22-24	0.862	0.151	2.42 ± 0.38	1.07 ± 0.12	1.35 ± 0.40	0.158 ± 0.300	1917.3

^A NC is not calculated, “-“ indicates measurement was not replicated

Table 3.2c. Inventories of excess ²¹⁰Pb in JoCo Marsh cores, Jamaica Bay, NY.

Core	ρ _{dry} (g/cm ³)*	Σ ²¹⁰ Pb _{xs} (dpm/cm ²)
JoCo-1	1.9	15.7 ± 0.1
JoCo-2	2.3	46.4 ± 0.6
JoCo-3	2.1	21.6 ± 0.6

*Density of dry sediment used in inventory calculation

Table 3.3. Loss-on-ignition (organic matter content) data for Elders, Big Egg and JoCo marsh sites, Jamaica Bay, NY. Core locations and sampling dates are given in Part 2 of this report.

Site Name	Marsh Site	Sample Season	Sample Depth (cm)	Loss-on-Ignition (%)
Elders West	EW1	Spring, 2016	25	0.39
	EW1	Spring, 2016	25 (repl) *	0.55
	EW1	Spring, 2016	26 (repl) *	0.43
	EW1	Spring, 2016	27 (repl) *	0.36
	EW1	Summer, 2015	5	0.96
	EW1	Summer, 2015	12	0.15
	EW2	Spring, 2015	23	0.26
	EW2	Summer, 2015	5	0.27
	EW3	Spring, 2015	22.5	0.25
	EW3	Summer, 2015	5	0.26
	EW3	Summer, 2015	15	0.24
Elders East	EE1	Spring, 2015	12.5	0.50
	EE1	Summer, 2015	22	0.18
	EE2	Spring, 2015	15	0.40
	EE2	Summer, 2015	5	2.40
	EE3	Spring, 2015	5	1.40
	EE3	Spring, 2015	12.5	0.30
JoCo	JC1	Spring, 2015	1.5	65.0
	JC1	Spring, 2015	1.5 (dup) *	66.0
	JC1	Spring, 2015	25	41.0
	JC1	Spring, 2015	25 (dup) *	42.0
	JC1	Spring, 2015	39	40.0
	JC1	Spring, 2015	39 (dup) *	39.0
	JC2	Fall, 2014	4.5	38.0
	JC2	Fall, 2014	4.5 (dup) *	38.0
	JC2	Fall, 2014	15.5	31.0
	JC2	Fall, 2014	15.5 (dup) *	29.0
	JC2	Fall, 2015	49	19.0
	JC3	Fall, 2014	14.5	52.0
	JC3	Fall, 2014	25	48.0
	JC3	Fall, 2014	52.5	28.0
Big Egg	BE1	Spring, 2015	15	4.5
	BE2	Fall, 2014	2.5	3.2
	BE2	Fall, 2014	2.5 (dup) *	3.2
	BE2	Spring, 2015	15	5.4
	BE3	Fall, 2014	3.5	20.0

* "repl" and "dup" refer to replicate (n = 3) or duplicate (n = 2) analyses of indicated samples

Table 3.3 (continued). Loss-on-ignition (organic matter content) data for Elders, Big Egg and JoCo marsh sites, Jamaica Bay, NY. Core locations and sampling dates are given in Part 2 of this report.

Site Name	Marsh Site	Sample Season	Sample Depth (cm)	Loss-on-Ignition (%)
Big Egg	BE3	Fall, 2014	3.5	20.0
	BE3	Fall, 2014	23	14.0
	BE3	Fall, 2014	23 (dup) *	15.0
	BE3	Fall, 2014	33	8.9
	BE3	Fall, 2014	33 (dup) *	9.3
	BE3	Spring, 2015	5	6.7
	BE3	Spring, 2015	15	6.5
	BE3	Summer, 2015	25	10.0

* "repl" and "dup" refer to replicate (n = 3) or duplicate (n = 2) analyses of indicated samples

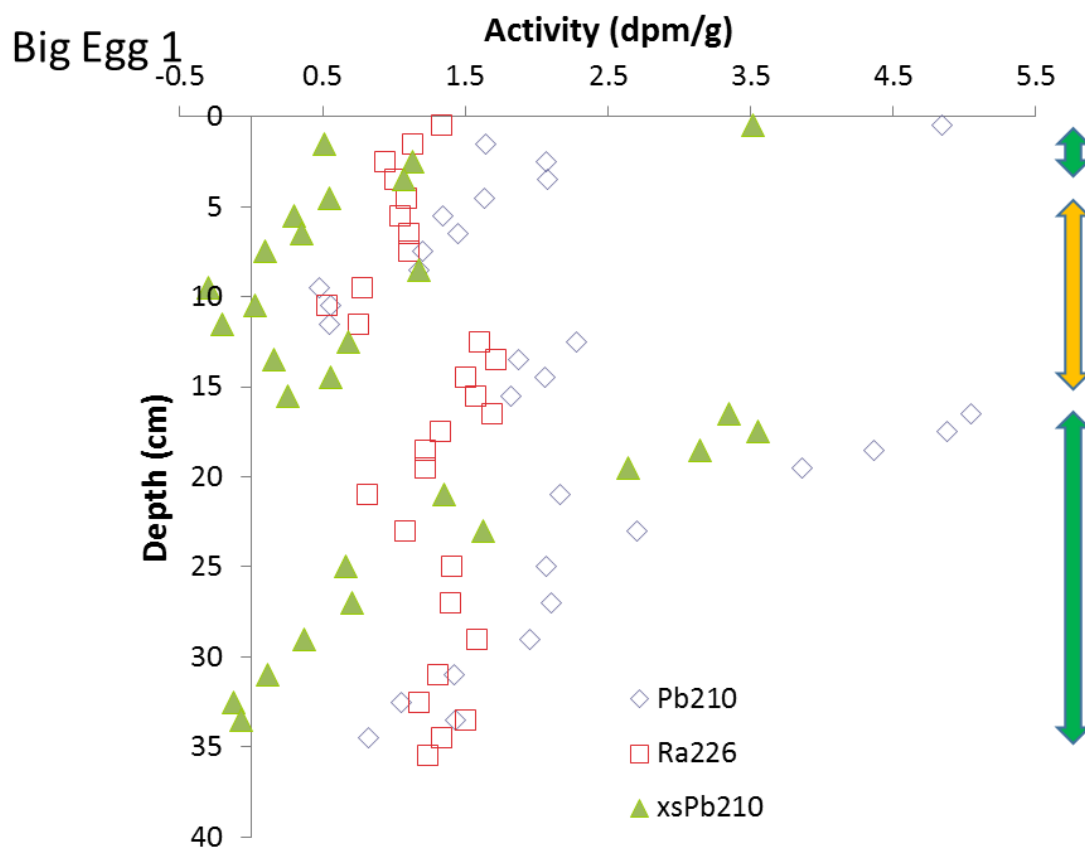


Figure 3.1. ^{210}Pb and ^{226}Ra vs depth at Big Egg 1, a restored site in Big Egg Marsh, Jamaica Bay, NY (Fig. 3S.3). Arrows indicate the interpretation of 1) accretion prior to spray restoration in 2003 (lower green arrow), 2) interpreted to be emplacement of sprayed sediment with low excess ^{210}Pb activities (middle orange arrow) and resumption of accretion (upper green arrow).

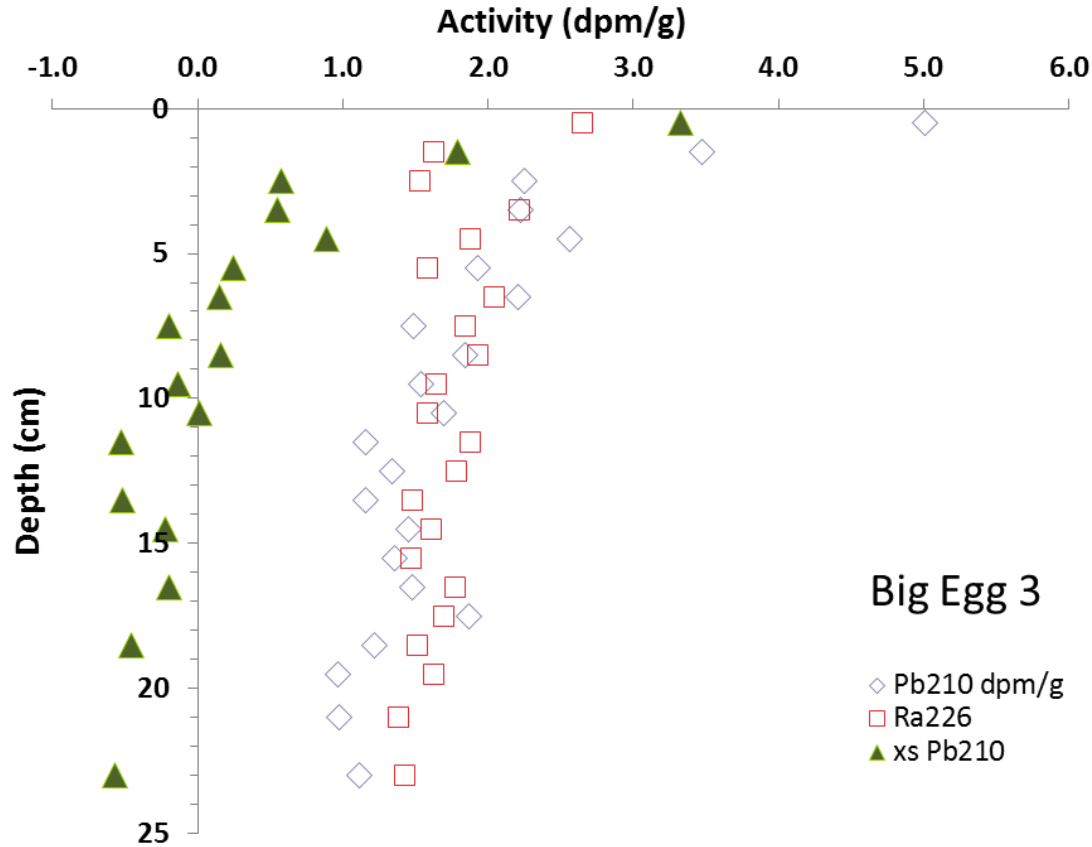


Figure 3.2. ^{210}Pb and ^{226}Ra vs depth at Big Egg 3, a site in Big Egg marsh, Jamaica Bay, NY.

Discussion

Accretion Rates

Two approaches may be used to reconstruct the depositional history of a marsh from excess ^{210}Pb data. If the specific ^{210}Pb activity (dpm/g) of freshly deposited material has remained constant with time, $^{210}\text{Pb}_{\text{xs}}$ will decrease with depth in the section according to:

$$A = A_o \exp\left(-\lambda \frac{x}{S}\right) \quad (1)$$

where $A = ^{210}\text{Pb}_{\text{xs}}$ activity at depth x , $A_o = ^{210}\text{Pb}_{\text{xs}}$ activity at the marsh surface, x = depth in marsh core, λ = decay constant of ^{210}Pb and S = accretion rate of marsh. A single value of S will result from a best-fit line through a plot of $\ln(A)$ vs x , and this approach is termed the “constant initial activity” method.

A second approach, described in more detail below, is termed the “constant flux” or constant rate-of-supply” method. This assumes that the flux of ^{210}Pb to the marsh surface has been constant with time and that the inventory of excess ^{210}Pb in the marsh core is approximated by that expected from atmosphere supply, ~18-32 dpm/cm² in Jamaica Bay marshes (Graustein and Turekian, 1996). The excess ^{210}Pb inventories in the unrestored, natural portion of Big Egg range from 0-2 dpm/cm²,

substantially less than expected from atmospheric supply (Table 3.1). In contrast, those at JoCo range from 16-46 dpm/cm² (Table 3.2).

As noted above, Big Egg 1 shows a gradient in excess ²¹⁰Pb from the bottom of the core (28 cm) to 15 cm, low and variable activities from 15 to 1 cm and then higher activities in the top-most sample (0-1 cm). Because the constant flux method is not really applicable to such profiles, we applied the constant initial activity method to the portion of the excess ²¹⁰Pb profile below 15 cm from Big Egg 1 (Fig. 3.3) and to the upper 9 cm of Big Egg 3 (Fig. 3.4). At Big Egg 1, the marsh was accumulating at a rate of ~0.36 cm/y over the 50-60 years represented by the gradient below 15 cm. This was sufficient to keep pace with sea level rise (0.41 cm/y at the Sandy Hook tide gauge; see Fig. 1.4).

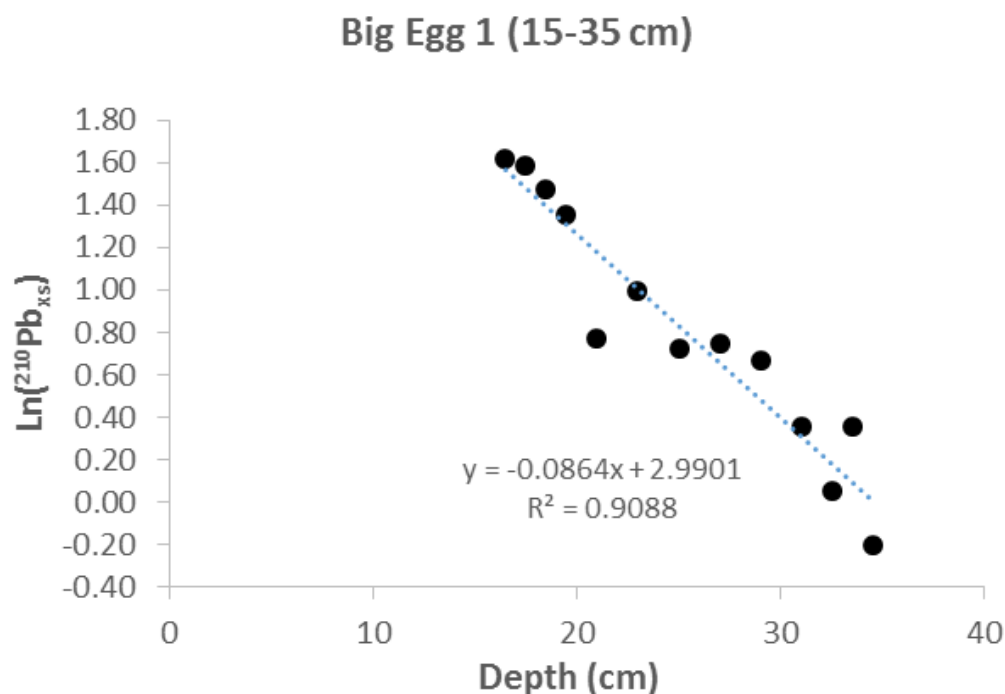


Figure 3.3. Ln (excess ²¹⁰Pb) vs. depth (for depths >15 cm) for Big Egg 1 in the restored part of the marsh, Jamaica Bay, NY. The accretion rate from the slope of the best-fit line is 0.36 cm/y.

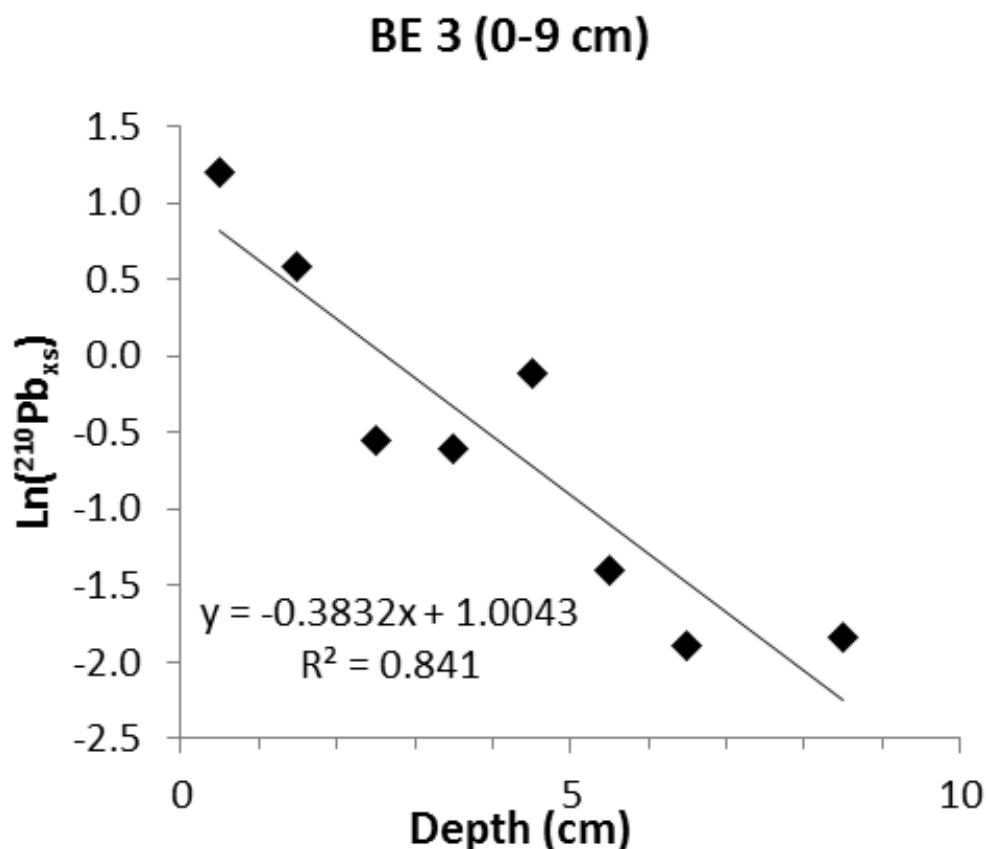


Figure 3.4. Ln (excess ²¹⁰Pb) vs. depth for Big Egg 3, from the unrestored part of the marsh, Jamaica Bay, NY. The accretion rate from the slope of the best-fit line is 0.08 cm/y.

The pattern of excess ²¹⁰Pb distribution at Big Egg 1 is consistent with the restoration history of the marsh (Frame et al., 2006). The site was restored in 2003 by spraying the marsh surface with sediment dredged from adjacent subtidal waters. Approximately 40 cm of material was emplaced by this process. Frame et al. (2006) document post-restoration losses of 20-40 cm along the NW edge of the restored area and 20 cm along the SE edge. Losses of this magnitude are consistent with the ~15 cm interval that we interpret to correspond the residual sprayed sediment, shown in Fig. 3.1 by the low excess ²¹⁰Pb activities from ~16 to 2 cm in the core (middle arrow), but it is also possible that the Big Egg 1 site received less than 40 cm of spray fill. Accretion at rates comparable to sea level rise since 2003 should have caused the marsh surface to accrete about 3-4 cm, and the higher excess ²¹⁰Pb in the upper 1 cm shows evidence of resumed accretion after restoration. In contrast, at the unrestored, natural site Big Egg 3, the marsh is currently accreting at 0.08 cm/y and is not keeping pace with mean sea level rise (Fig. 3.4). Big Egg 2 has little to no excess ²¹⁰Pb and does not appear to be accreting. In both cases, it is possible that the ²¹⁰Pb profiles show effects of Hurricane Sandy such that extensive erosion occurred in association with the storm.

A second, more powerful approach to interpreting ²¹⁰Pb data permits variations in S to be determined and is termed the “constant flux” method. This method assumes that the flux of ²¹⁰Pb to the marsh surface has remained constant with time. A₀ is permitted to vary by this method, and variations in it are related to variations in S (Appleby & Oldfield, 1978; McCaffrey & Thomson,

1980; Bricker-Urso et al., 1989; Cochran et al., 1998). The constant flux method requires calculation of the inventory of $^{210}\text{Pb}_{\text{xs}}$, Q_o (dpm/cm²), in the marsh core, determined as:

$$Q_o = \sum (A_i \rho_i x_i) \quad (2)$$

where $A_i = ^{210}\text{Pb}_{\text{xs}}$ activity of the i th depth interval, x_i = dry bulk density of the i th depth interval and x_i = thickness of the i th interval. The relationship between $^{210}\text{Pb}_{\text{xs}}$ inventory and age is expressed as:

$$Q = Q_o \exp(-\lambda t) \quad (3)$$

where Q = inventory of $^{210}\text{Pb}_{\text{xs}}$ activity below depth x , Q_o = total inventory of $^{210}\text{Pb}_{\text{xs}}$ activity in the core (eqn. 2), and t = age of horizon x (years). This method relies on the constancy of ^{210}Pb supply to the marsh. The constant flux method produces an age for the base of a given sampling interval using the $^{210}\text{Pb}_{\text{xs}}$ inventory, Q , below that depth. The error in the age is based on uncertainty in the ratio Q/Q_o (eqn. 3). Errors in Q/Q_o are determined by propagating the counting error of the ^{210}Pb measurements used to calculate Q and Q_o . Errors in t are derived from:

$$\sigma_t = \frac{\sigma_{Q/Q_o}}{\lambda(\frac{Q}{Q_o})} \quad (4)$$

Marsh accretion rates can be calculated for each depth interval in the section as:

$$S_i = \frac{x_{i+1} - x_i}{t_{i+1} - t_i} \quad (5)$$

where i = i th depth interval, x_i = depth of the top of the i th interval and t_i = age of the top of the i th interval. The uncertainty on S is largely determined by the uncertainty on t (eqn. 4).

The loss-on-ignition data indicate the organic matter content of the marsh samples and we use these data to estimate the effective dry bulk densities, assuming that organic matter has a density of 1.25 g/cm³ and the detrital lithogenic material has a density of 2.6 g/cm³. This is a factor only at JoCo because the organic content at Big Egg was relatively low (Table 3.3). The effective densities for JoCo, based on average organic contents, are given in Tables 3.1 and 3.2.

As its name implies, the “constant flux” model for determining accretion rates depends on constancy of the flux of ^{210}Pb to the marsh site. This can be tested by comparing the inventory of excess ^{210}Pb in the marsh (Q_o) with the value expected from atmospheric input. The latter ranges from 18 – 32 dpm/cm² in the northeastern USA (Graustein and Turekian, 1996; Renfro et al., 2013). The values at Big Egg range from 0 to ~13 dpm/cm² (Table 3.1c). Given the accretion dynamics at Big Egg described above, these values suggest that the marsh is not effectively retaining ^{210}Pb , especially at Big Egg 2 and 3 (Table 3.1c), and this is consistent with little or no accretion at those sites. Inventories at JoCo are ~16 dpm/cm² at JoCo 1, ~46 dpm/cm² at JoCo 2 and ~22 dpm/cm² at JoCo 3 (Table 3.2c). JoCo 1 and 3 are approximately within the range of inventories expected from atmospheric input of ^{210}Pb , while JoCo 2 is high. This suggests some redistribution of ^{210}Pb and likely the lithogenic particles with which it is associated in the marsh or the addition of subtidal

sediments (and associated ^{210}Pb) to JoCo 2. We assume that this process has been constant over time at the three JoCo sites in order to calculate the constant flux accretion chronologies for JoCo (Figs. 3.5 – 3.7).

We apply the constant flux method, rather than the constant activity method, to the JoCo cores because the former offers the ability to determine the temporal variation in JoCo over the past 100 years (Figs. 3.5 -3.7). The JoCo marsh sites show accretion at rates of 0.10 to 0.25 cm/y prior to ~1980, with rates increasing after that to values that are approximately equal to or somewhat greater than the rate of MSL rise. Both JoCo 1 and 2 show a maximum in accretion around 2000, with values decreasing toward the present. The most recent accretion rate in JoCo 1 is 0.16 cm/y, decidedly less than the rate of present sea level rise. This occurs in the interval that includes the date of Superstorm Sandy, and the impact of that storm might have reduced marsh accretion. However, the declining trend in accretion after 2000 in both cores began prior to Sandy. As well, JoCo 1 and 2 show short-term maxima in accretion: in 1935, 1950, 1987 and 2000 in JoCo 1 (Fig. 3.5) and 1934, 1984 and 2000 for JoCo 2 (Fig. 3.6). Given the temporal resolution of the sampling (~ 1 to 2 y), these maxima may mark storm events such as hurricanes or nor'easters during which flooding of the marsh sites resulted in material accumulating on the marsh surface. Small-scale spatial variations in the elevation of the marsh surface relative to sea level may cause different sites within a marsh to respond differently to the same events. Indeed, JoCo 3 does not show clear evidence of the accretion maxima that are evident in JoCo 1 and 2, nor evidence of a pronounced slowdown in accretion after 2000. As well, the accretion history of JoCo 3 is somewhat different from that of JoCo 1 and 2 (Fig. 3.7). As with JoCo 1 and 2, the accretion rate is ≤ 0.2 cm/y up to the mid-1980s, when it increases to ~ 0.6 cm/y in the mid-1990s and then decreases to values (0.29 cm/y), closer to the rate of sea-level rise, toward the core top.

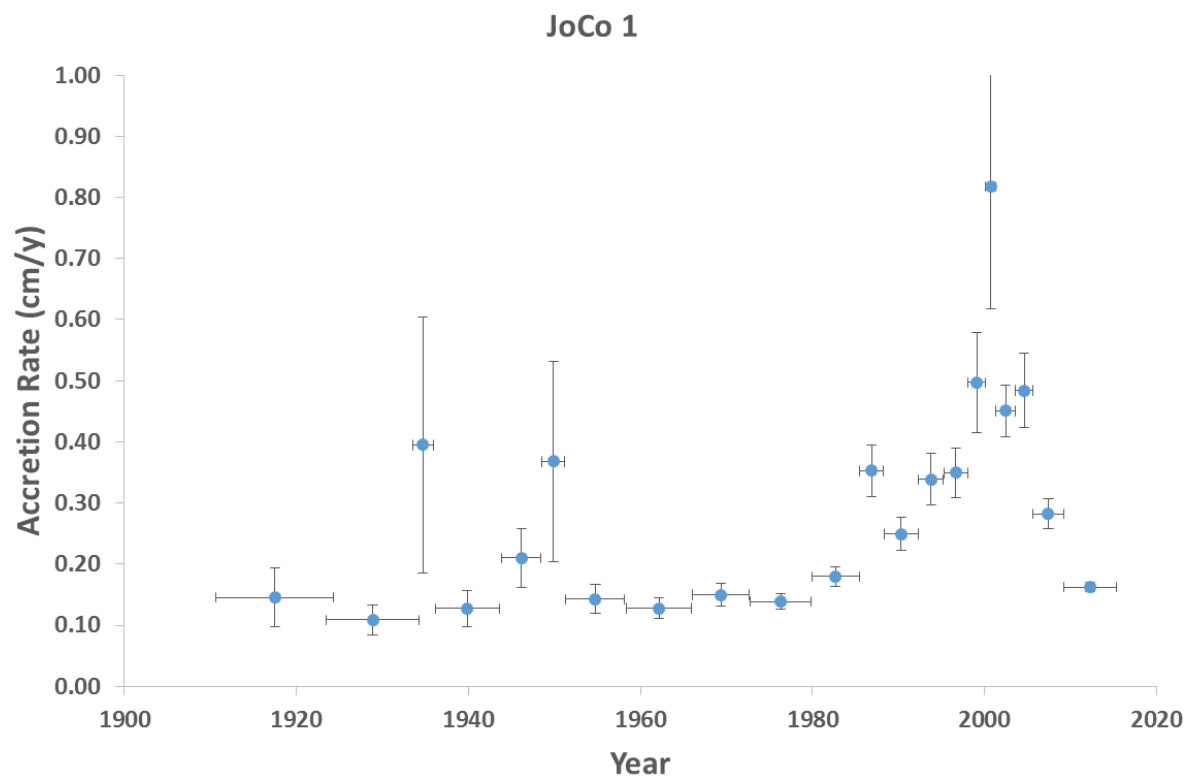


Figure 3.5. ^{210}Pb -based accretion chronology for JoCo 1, a marsh site in Jamaica Bay, NY. For comparison, the rate of rise of mean sea level over the period is 0.4 cm/y.

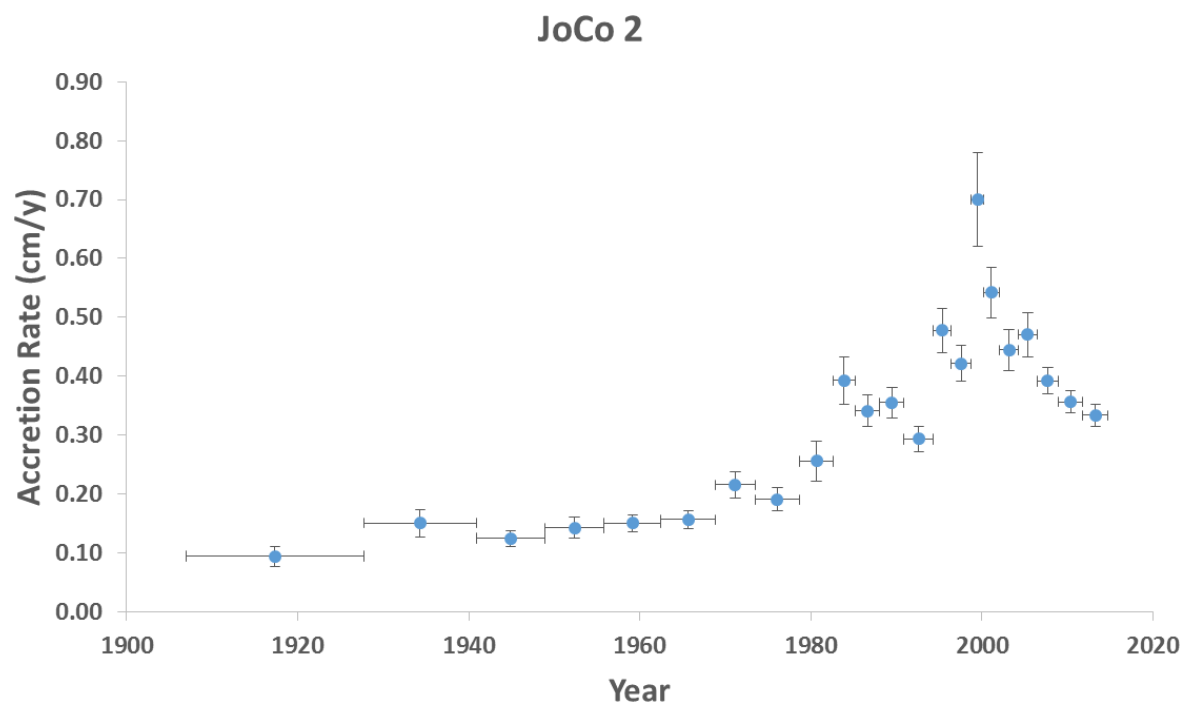


Figure 3.6. ^{210}Pb -based accretion chronology for JoCo 2, a marsh site in Jamaica Bay, NY. For comparison, the rate of rise of mean sea level over the period is 0.4 cm/y.

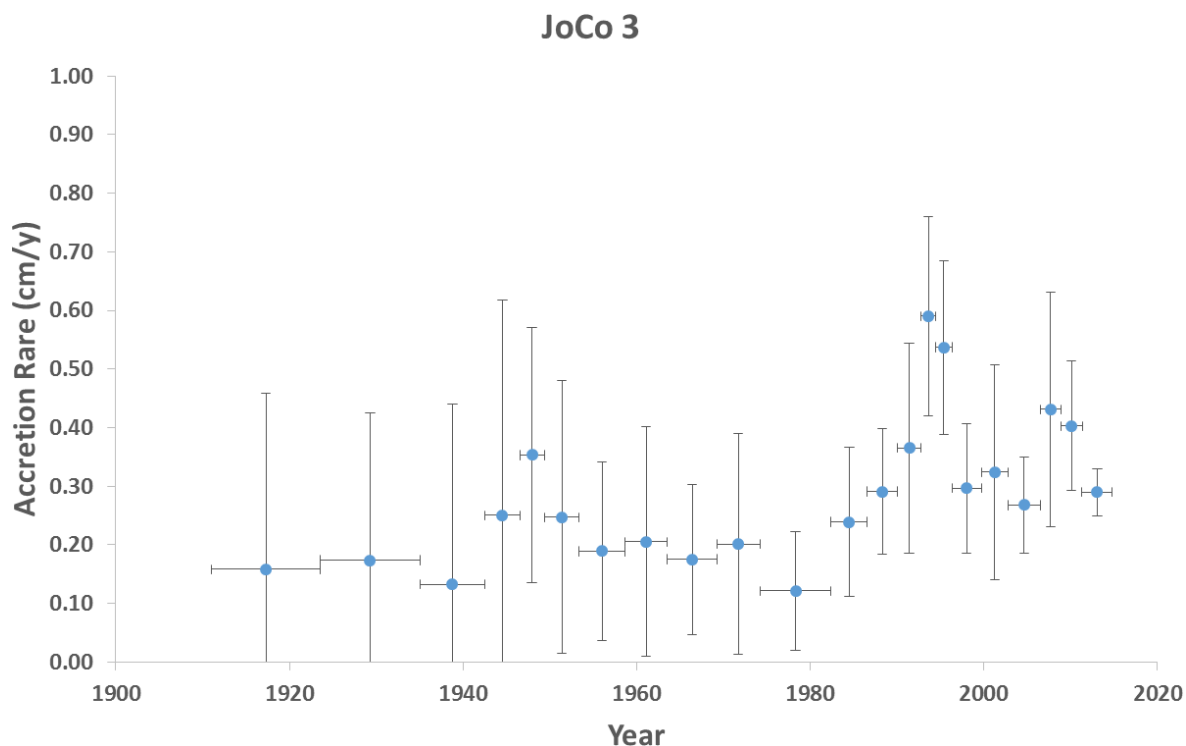


Figure 3.7. ^{210}Pb -based accretion chronology for JoCo 3, a marsh site in Jamaica Bay, NY. For comparison, the rate of rise of mean sea level over the period is 0.4 cm/y.

Summary

Big Egg and JoCo marshes show strong differences in down-core ^{210}Pb distributions and in accretion rates. Of the sites sampled at Big Egg, the two unrestored, natural sites show evidence of little accretion (Big Egg 2) or accretion at a rate insufficient to keep pace with sea level rise (Big Egg 3). The site restored by spray, Big Egg 1, shows evidence that it was accreting to keep pace with sea level in the ~50 -60 years before the spray, and that accretion has resumed after the restoration. However, the ^{210}Pb profile is just reestablishing itself after the spray and is insufficiently detailed to calculate the present rate of accretion. SET emplacements are better suited to determine recent accretion. The accretion information from the unrestored sites at Big Egg suggest that the marsh is degrading. Our own visual and qualitative observations over two years of sampling support this finding.

In contrast, ^{210}Pb profiles at the three sites sampled in JoCo marsh showed excess ^{210}Pb distributed to ~30 cm in each core and yielded detailed accretion rate chronologies over the past 100 years. All three sites show increases in accretion rate to values that exceed the rate of sea level rise by ~2- to 3-fold into the 1990s. Rates decline after that, and one site— JoCo 1— shows a progressive decline to a rate that is insufficient to keep pace with sea level rise. The other aspect of marsh dynamics that determines whether a marsh will keep pace with sea level rise is subsidence. If the marsh is subsiding, or compacting, faster than accretion, it may not be able to keep pace with sea level. SET emplacements in JoCo may help determine if subsidence is occurring there. Part 2 of this report discusses an additional stressor of JoCo marsh, namely occasional high levels of hydrogen sulfide,

but Part 4 documents the relatively rapid tidal drainage of water through the marsh that may help moderate exposure of the plants to sustained high levels of this phytotoxin (Part 4 of this report).

Acknowledgements

We are grateful to the National Park Service and the Science and Resilience Institute at Jamaica Bay for support of this research. We thank Hang Yin and Wen Cong for assistance in the field, Michael Pettito and Justin Manning for laboratory support, and Patricia Rafferty (National Park Service), Don Riepe, and Elizabeth Manclark (American Littoral Society) for logistical support.

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Supplemental Information

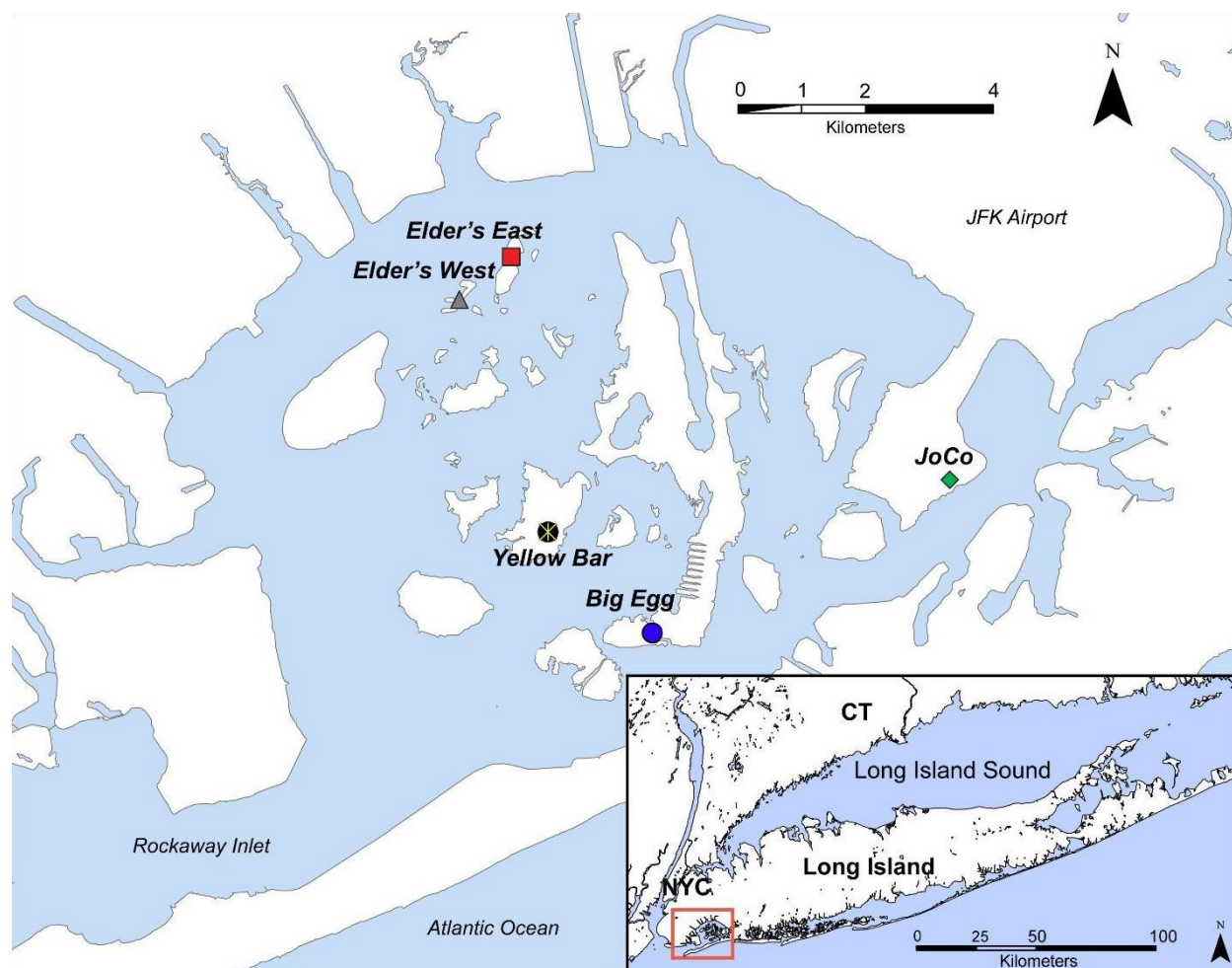


Figure. 3S.1. Generalized map of Jamaica Bay, New York, showing location of Big Egg and JoCo marshes that are discussed in this section of the report.



Figure 3S.2. JoCo marsh sampling sites, Jamaica Bay, NY.

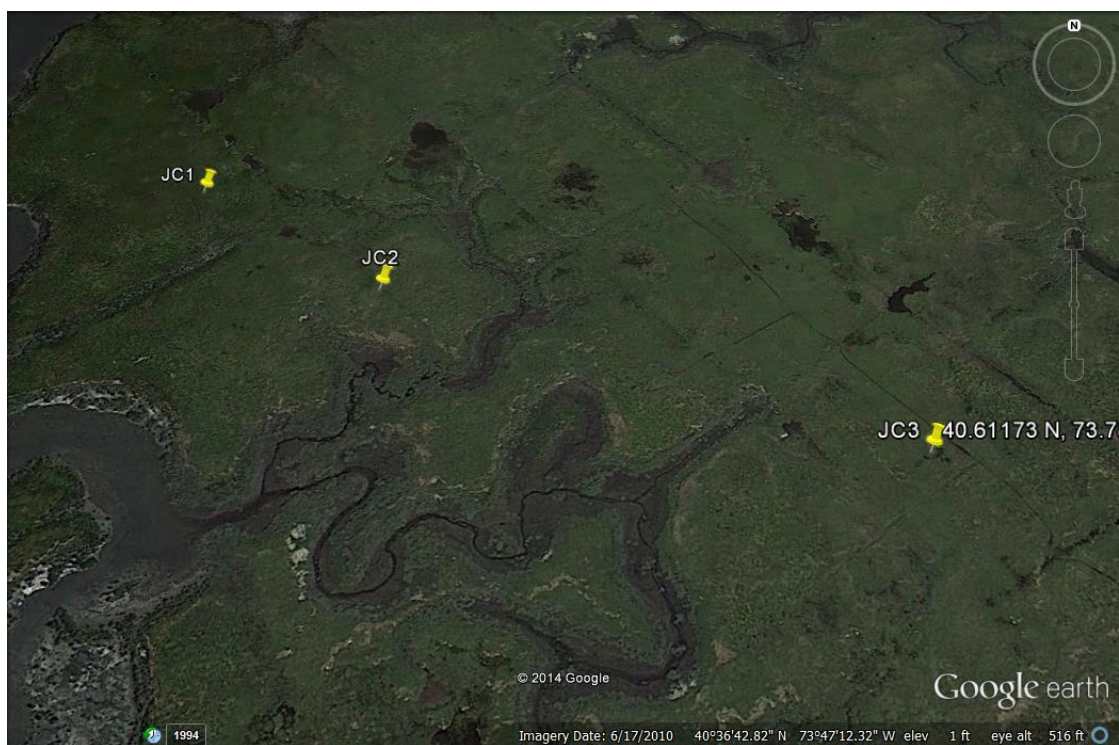


Figure 3S.3. JoCo marsh sampling sites (expanded scale), Jamaica Bay, NY.



Figure 3S.4. Big Egg marsh sampling sites, Jamaica Bay, NY.



Figure 3S.5. Big Egg marsh sampling sites (expanded scale), Jamaica Bay, NY.

Part 4: Investigation of pore water residence times and drainage velocities in salt marshes using short-lived radium isotopes

(This part of the report has been published as: Tamborski, J.T., Cochran, J.K., Heilbrun, C., Rafferty, P., Fitzgerald, P., Zhu, Q. and Salazar, C. (2017) Investigation of pore water residence times and drainage velocities in salt marshes using short-lived radium isotopes. *Marine Chemistry* 196, 107-115.)

Abstract

Pore water residence times and drainage velocities were investigated in Jamaica Bay (NY, USA), a highly urbanized estuary in New York City where salt marsh degradation and loss has accelerated in recent years. Five different marshes (natural and restored) were sampled for shallow and deep dissolved Ra isotopes over a several year period. Sediment cores and pore water were collected at each marsh site to determine solid-phase ^{228}Th , ^{228}Ra , reactive solid phase Fe and Mn, median grain size and dissolved Fe, Mn and sulfide. Taken together, these geochemical parameters were evaluated with respect to the measured pore water ^{224}Ra , in order to determine the equilibrium activity of dissolved ^{224}Ra with the marsh sediment. Pore water residence times were estimated using a one-dimensional advective transport model for ^{224}Ra , assuming that the pore water ^{224}Ra grows into the equilibrium ^{224}Ra activity, and that flow is primarily downward. Pore water ^{224}Ra and estimated residence times did not display any seasonality between the marshes. The shortest residence times were estimated for the highest elevation, fine-grained-sand marsh (0.8 – 2.6 d at 25 cm), which has the highest percent vegetation cover. We hypothesize that the faster drainage velocity of the healthy, sandy marsh, as traced by ^{224}Ra , combined with a higher mean elevation above sea-level, together limit the marsh plants exposure period to the build-up of H_2S in the pore fluid from the spring through summer. In contrast, pore water residence times were greater for marshes with a lower elevation above sea-level, where sediments were finer-grained, and fluxes of Fe and H_2S were higher throughout spring and summer seasons. This work demonstrates the utility of ^{224}Ra as a tracer of salt marsh flow dynamics, and highlights the importance of sediment heterogeneity and marsh elevation on the dynamic geochemistry of salt marshes.

Introduction

The suite of Ra isotopes ($^{223,224,226,228}\text{Ra}$) comprises effective tracers of salt marsh pore water flow dynamics (Bollinger and Moore, 1984, 1993; Charette et al., 2003; Rama and Moore, 1996). Relatively slow drainage velocities and subsequently longer pore water residence times beneath the marsh surface permit ample time for the production and recoil of short-lived Ra atoms into the surrounding pore fluid, from the alpha decay of the particle-associated parent Th isotope (Swarzenski, 2007). ^{224}Ra and ^{223}Ra have half-lives of 3.66 d and 11.4 d, respectively, making them excellent tracers of water exchange processes in coastal systems (Rodellas et al., 2017). Salt marshes are intimately connected to the ocean, and the movement of pore water from the marsh to the sea may be broadly defined as submarine groundwater discharge (Burnett et al., 2003). Pore water exchange from salt marsh drainage has been shown to be a significant source of nutrients to adjacent

coastal water bodies (Charette, 2007; Krest et al., 2000), while the degree to which pore waters exchange with the coastal ocean may be primarily dependent upon the tidal amplitude and variations in sea level (Wilson et al., 2015). In order to properly evaluate chemical fluxes from salt marshes, it is necessary to understand the time-scale in which pore water resides beneath the marsh surface.

Krest and Harvey (2003) utilized a one-dimensional advective transport model for short-lived ^{224}Ra and ^{223}Ra to quantify vertical groundwater velocities in a Florida Everglades wetland. The distribution of Ra isotopes in pore water is dependent upon fluid ionic strength (Webster et al., 1995), thus, the application of a one-dimensional advective transport model for Ra is suitable in salt marsh systems where there is little variation in pore water salinity. In a South Carolina salt marsh, shallow pore water Ra activities were greater than deeper pore waters, where there was a zone of higher permeability sands, and pore water residence times were shorter (Hughes et al., 2015). Pore water residence times were estimated to be between 1 – 26 hours within the upper 10 cm of sediment of the same marsh (Bollinger and Moore, 1993). Pore water drainage rates were determined to be influenced by subtle topographic variations in a New England salt marsh, where discharge to adjacent tidal creeks occurred between 10 and 15 m from the creek bank (Nuttle and Hemmond, 1988). However, few datasets exist in the literature to date on pore water residence times and drainage rates in salt marshes, particularly at depths greater than 25 cm.

Salt marsh degradation and loss is a global issue, fueled by eutrophication, organic loading and enhanced H_2S production, which can be harmful to marsh plant species (Bromberg Gedan et al., 2009; King et al., 1982). Vegetation zonation and root structure influence horizontally and vertically heterogeneous pore water geochemical gradients in salt marshes (Moffett and Gorelick, 2016), in addition to eco-hydrologic variables (Moffett et al., 2012). We hypothesize that the residence time of pore water within a salt marsh, and the marshes ability to drain, may vary with respect to the marsh sediment characteristics (porosity, permeability and elevation), which, taken with seasonal changes in vegetation, may influence geochemical gradients. Using ^{224}Ra , we assess the seasonality of pore water residence times within Jamaica Bay (NY, USA) marshes, with respect to differences in seasonal vegetation (spring = low biomass; summer = high biomass) and estimate throughput fluxes of dissolved Fe and H_2S .

Methods

Site Description

Jamaica Bay is a highly urbanized estuary ($\sim 80 \text{ km}^2$) located between the boroughs of Queens and Brooklyn in New York City, NY (USA), with a connection to the Atlantic Ocean through Rockaway Inlet (Fig. 4.1). There are over a dozen isolated marsh islands within Jamaica Bay, some of which are natural, and many of which are restored through engineering efforts. Four primary sewage treatment plants discharge over 300 million gallons of treated effluent into Jamaica Bay per day, which carry significant loads of dissolved nutrients and trace metals (Benotti et al., 2006). Eutrophication in Jamaica Bay, from sewage treatment plant effluent and combined sewer overflows, is thought to be an important driver of salt marsh degradation and loss, with reduced sediment loads, dredging, boat traffic, and an increase in sea level acting as additional factors (Hartig et al., 2002). Degradation has increased in recent years to an estimated 134 km/yr of creek and open-bay-edge marsh loss,

corresponding with an increase in N loads (Hartig et al., 2002). Microbial respiration of organic matter in the water column leads to significantly low levels of dissolved oxygen, which subsequently results in coastal acidification within the bay (Wallace et al., 2014). Inputs of submarine groundwater discharge to Jamaica Bay are between $(0.8 - 9.0) \times 10^9 \text{ L d}^{-1}$, estimated from a Ra isotope mass balance, with the majority of the flow composed of recirculated seawater (Beck et al., 2007). The large volumetric contribution of recirculated seawater through the coastal aquifer is a minor source of nutrients but a significant source of dissolved trace metals, with the flux of Fe, Zn, Co and Ni rivalling inputs from treated wastewater effluent (Beck et al., 2009). The high input of nutrients and metals from these various point-source and nonpoint-sources have resulted in significant environmental degradation and loss to the Jamaica Bay salt marsh ecosystem.

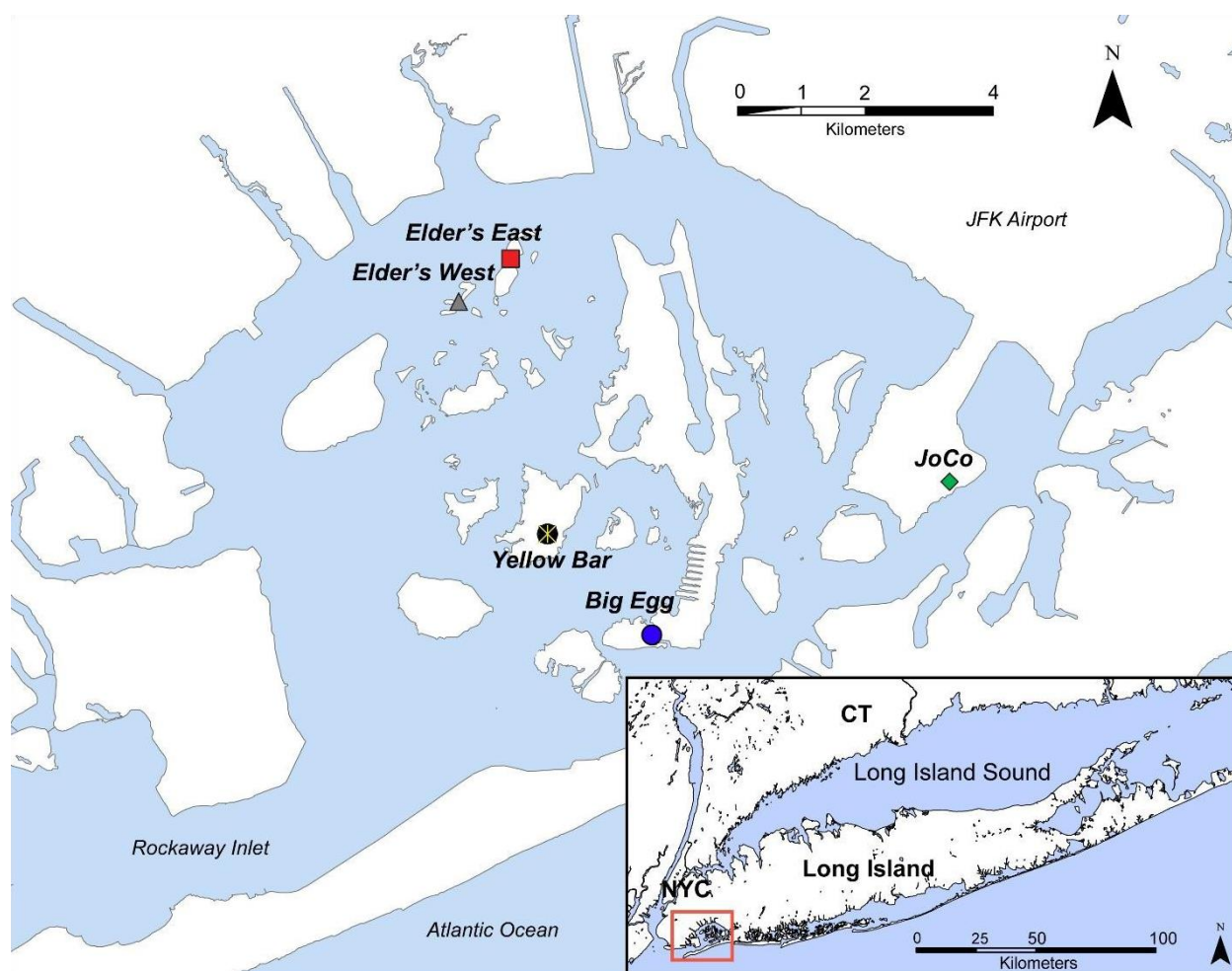


Figure 4.1. Jamaica Bay, located within south-western Long Island, NY (inset, red box), with the approximate locations of the five sampled marshes.

A total of five salt marshes were studied; sites in two natural marshes, JoCo and an unrestored portion of Big Egg, and sites in four restored marshes, Elder's East, Elder's West and Yellow Bar and a restored portion of in Big Egg (Fig. 4.1). Marsh surface elevations were measured by P. Rafferty (National Park Service) throughout 2014; JoCo had the highest mean elevation of $0.70 \pm$

0.23 m ($n = 3,120$), followed by Elder's West (0.65 ± 0.13 m, $n = 246$), Elder's East (0.54 ± 0.26 m, $n = 331$) and Big Egg (0.21 ± 0.28 m, $n = 513$). Percent total vegetation cover was estimated during this same period, using a modified Braun Blanquet method for 0.25 m^2 plots. JoCo had the lowest percentage of barren marsh surface area (5%), followed by Elder's East (25%), Big Egg (35%) and Elder's West (45%). All five marshes are dominated by *Spartina alterniflora*, while JoCo has a mixture of marsh grasses that includes *Spartina patens*, a high marsh species, indicative of JoCo's higher elevation above sea level, with respect to the other Jamaica Bay marshes. Elder's East was restored in 2006/2007, Elder's West was restored in 2010 and Yellow Bar was restored in 2012. Restoration was performed by the US Army Corps of Engineers and included demarcating the boundaries of the marshes with sand bags, dumping dredged sand from Ambrose Channel (NY/NJ) and Rockaway Inlet onto the marsh surface, and systematically planting *Spartina alterniflora* (Baron, 2016). One of the three sample sites at Big Egg (BE1) also was previously restored by spraying sandy sediment from the adjacent channel onto the marsh surface (Frame et al., 2005), but the remaining two sites sampled (BE2 and BE3) were natural. JoCo experienced a marsh loss of approximately 7% between 1974 and 1999, while losses at Big Egg were upwards of 38% (NYSDEC, 2006).

Sampling & Analyses

Sampling campaigns were carried out during June and November 2013 at Big Egg, JoCo, and Yellow Bar marshes (Fig. 4.1). During these campaigns, samples were designated as creek, mid and interior stations. Additional samples were collected at JoCo during September 2013 and October 2014. Four marshes in Jamaica Bay were sampled during April 2015, September 2015 and April 2016: Big Egg, Elder's East, Elder's West, and JoCo (Fig. 4.1), with the site locations distributed across each marsh (sites numbered 1 through 3). Additional depth horizons were sampled at JoCo during November 2013, October 2014 and April 2016. Coordinates for each marsh site are presented in Table 4S.1.

All marshes were sampled within approximately two hours of low tide, when the marsh surface was exposed. Shallow (25 cm) and deep (50 – 100 cm) pore water samples were collected at each station (areas of dense vegetation during the summer). Pore waters were sampled by inserting a steel-tip push-point piezometer (M.H.E. Products) to a specific depth below the marsh sediment, and retrieved *via* peristaltic pump at a flow rate $\leq 0.1 \text{ L min}^{-1}$. At this flow rate, with a sampling port well-screen length of 3.7 cm on the push-point piezometer, the samples would represent pore waters collected from an integrated, spherical radius of ± 4.55 cm (Beck, 2007). Pore water samples from April 2015, September 2015 and April 2016 were analyzed for temperature, pH and oxidation-reduction potential (ORP) using a laboratory calibrated YSI 1009-1 09C multi-parameter probe during sample collection; salinity was measured using a handheld refractometer. Sediment cores were collected *via* hand auger at each marsh, except for Yellow Bar.

Pore water samples (0.5 – 3 L) for Ra analysis were collected into triple-rinsed plastic containers and field filtered (10, 5 and $1 \mu\text{m}$; GWV high capacity groundwater sampling capsules). Samples were aerated, and MnO_2 impregnated acrylic fibers were added to the filtered containers to quantitatively adsorb dissolved Ra from the pore fluid onto the fiber overnight. MnO_2 fibers were rinsed with DI water, partially dried, and counted on a radium delayed coincidence counter (RaDeCC; Moore and

Arnold, 1996). ^{232}Th standards were run to determine the detector counting efficiency of the ^{220}Rn channel, while the efficiency of the ^{219}Rn channel (^{223}Ra) was determined from ^{220}Rn (Moore and Cai, 2013). Second counts were performed approximately 10 d after the first counts to measure ^{223}Ra . Third counts were run on select samples to determine the activity of ^{228}Th , in order to calculate excess ^{224}Ra .

Bulk sediment samples from discrete depths from the cores were dried, sieved to remove large root fragments, sealed, and counted on a planar Canberra Ge detector at 583 keV (^{208}Ti) and 911 keV (^{228}Ac) to determine the activity of solid-phase ^{228}Th and ^{228}Ra , respectively. NIST Material 4350B and IAEA 300 sediment were used to determine the detector counting efficiencies. Following counting, 1-3 g aliquots of sediment were taken to measure organic content by loss-on-ignition (LOI). The sediment was weighed, combusted at 450°C for 24 hours, reweighed and the mass difference was used to calculate LOI. Grain size distribution was determined for select shallow and deep sediments *via* Malvern Mastersizer 2000 laser diffractometer (Sperazza et al., 2004).

Pore water samples for trace metal analyses were collected using acid-rinsed polypropylene syringes with HEPA 0.20 μm pore space filters into 20 ml acid-rinsed bottles, and acidified with 10% HNO_3 to a pH of ~ 2 . Samples for sulfide were pipetted into 0.5 ml of 0.05M $\text{Zn}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ to fix the sulfide before analysis. Pore water samples were colorimetrically analyzed for dissolved Fe using a Ferrozine spectrophotometric reagent (Stookey, 1970), *via* polar-star plate reader, with an analytical precision of $\pm 5\%$. Dissolved Mn^{2+} (Goto et al., 1962) and H_2S (Cline, 1969) were colorimetrically analyzed, with procedures amended for the plate reader. Analytical precisions were approximately $\pm 7\%$ for Mn^{2+} and H_2S . Sediment samples were subject to a 1 N HCl cold leach (10.0 ml) for 24 hours to dissolve sediment-bound Fe and Mn-oxide coatings (Kolker, 2005; Leventhal and C., 1990; van der Zee and van Raaphorst, 2004), after which the sediment leaches were colorimetrically analyzed, as described above.

Residence Time Estimates

A simple, one-dimensional advective transport model (neglecting dispersion and molecular diffusion) for Ra (C_R) is applied to the pore water samples to calculate both residence time (τ) and advective (drainage) velocities (v ; Krest and Harvey, 2003),

$$\frac{\partial C_R}{\partial t} = -v \frac{\partial C_R}{\partial x} + \frac{P}{(1+K)} - \lambda C_R \quad (1)$$

where t is time (d), x is the sample depth (cm), P is the production rate of Ra from parent Th radionuclides in the sediment and includes recoil of the nascent Ra atoms into the pore water, K is the Ra partition coefficient, and λ is the Ra decay constant (d^{-1}). Assuming steady-state conditions, the solution to equation 1 becomes:

$$C_R = P' \lambda^{-1} + (C_R^0 - P' \lambda^{-1}) e^{-\frac{\lambda x}{v}} \quad (2)$$

where C_R^0 is the initial seawater concentration of Ra that would be supplied to the pore fluid. The production and retardation terms are simplified into one term, $P' = P/(1+K)$. P' can be determined independently for ^{224}Ra by incubating sediment in a closed system (i.e. no advective transport of pore

water) and measuring the equilibrium pore water Ra activity at steady-state (Bokuniewicz et al., 2015). The advective transport parameter v can be calculated assuming that the only source of the measured Ra ($A_R = C_R * \lambda$) is from the overlying surface waters draining vertically downward into the marsh (A_o) and *in situ* production from the sediment (P'). Alternatively, we can calculate the residence time ($\tau = x/v$) of pore fluid at a given depth beneath the marsh surface. Converting concentrations to activities, the pore water residence time may be estimated as:

$$\tau = \ln \frac{(1 - \frac{A_R}{P'})}{(1 - \frac{A_o}{P'})} * \frac{1}{-\lambda} \quad (3)$$

Here, we use an average ^{224}Ra surface water activity of 0.21 dpm L^{-1} from a previous sampling campaign in Jamaica Bay to define A_o (Beck et al., 2007). The value of P' used is taken as the highest observed ^{224}Ra pore water activity, for each respective salt marsh. Vertical advective velocities (cm d^{-1}) are evaluated with respect to each discrete pore water sampling depth ($v = x/\tau$), assuming one-dimensional, vertical flow. The assumption that flow is one-dimensional is supported by the detailed ^{224}Ra pore water profiles taken at JoCo during three separate campaigns.

Results

Geochemistry

Dissolved

Pore water ^{224}Ra and ^{223}Ra displayed a positive linear relationship between all five marshes throughout the various seasonal campaigns (Fig. 4.2). The average uncertainty of ^{224}Ra was approximately 5.0 %, while ^{223}Ra uncertainties ranged from 10 – 20 %; as a result, ^{224}Ra is the isotope of focus here. Ra activities and ancillary water parameters for all of the collected pore water samples are presented in Table S2. Ra activities varied between each marsh, with the lowest mean ($\pm$ SD) ^{224}Ra activities from the various seasonal campaigns observed at Elder's East (shallow = $3.7 \pm 0.6 \text{ dpm L}^{-1}$; deep = $3.5 \pm 0.8 \text{ dpm L}^{-1}$; Table 4.1; Fig. 4.3). From all of the sampling campaigns, the mean ($\pm$ SD) ^{224}Ra activities were greatest in the deep samples for JoCo (shallow = $4.1 \pm 2.1 \text{ dpm L}^{-1}$; deep = $8.3 \pm 4.5 \text{ dpm L}^{-1}$) and Elder's West (shallow = $6.8 \pm 1.8 \text{ dpm L}^{-1}$; deep = $7.2 \pm 2.4 \text{ dpm L}^{-1}$). Mean shallow and deep samples at Big Egg (shallow = $7.0 \pm 2.1 \text{ dpm L}^{-1}$; deep = $7.1 \pm 2.8 \text{ dpm L}^{-1}$; Table 4.1, Fig. 4.3) were approximately equal to those at Elder's West.

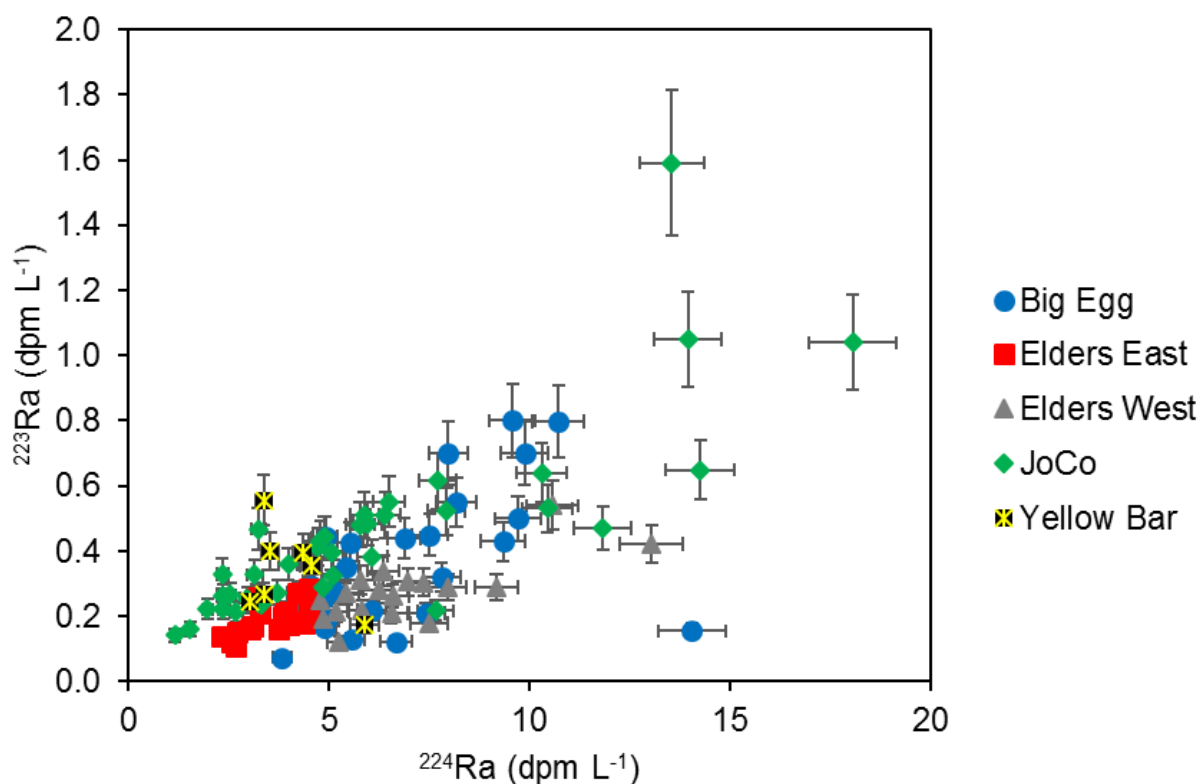


Figure 4.2. Co-variation between ^{223}Ra and ^{224}Ra , arranged by marsh, for all sampling campaigns at Jamaica Bay, NY.

Table 4.1. Mean ($\pm$ SD) shallow (25 cm) pore water ^{224}Ra activities, advective velocities and residence times for each marsh, arranged by sampling season at Jamaica Bay, NY.

Site Name	Season	^{224}Ra (dpm L $^{-1}$)	v (cm d $^{-1}$)	τ (days)
Big Egg	June 2013	5.0 ± 0.3	11.1	2.3
	November 2013	5.8 ± 0.8	9.4	2.7
	April 2015	9.3 ± 0.8	4.5	5.7
	September 2015	8.3 ± 0.9	5.5	4.7
	April 2016	6.8 ± 2.8	8.8	4.0
	Mean	7.0 ± 2.1	7.9 ± 3.2	3.9 ± 1.8
Elder's East	April 2015	3.3 ± 0.7	3.8	8.3
	September 2015	3.5 ± 0.3	3.4	7.7
	April 2016	4.2 ± 0.2	2.0	12.8
	Mean	3.7 ± 0.6	3.2 ± 1.3	9.2 ± 3.6
Elder's West	April 2015	6.6 ± 1.2	7.4	3.7
	September 2015	6.9 ± 2.6	7.6	4.6
	April 2016	6.9 ± 0.9	6.6	4.0
	Mean	6.8 ± 1.8	7.2 ± 2.5	4.1 ± 1.9

Table 4.1 (continued). Mean ($\pm$ SD) shallow (25 cm) pore water ^{224}Ra activities, advective velocities and residence times for each marsh, arranged by sampling season at Jamaica Bay, NY.

Site Name	Season	^{224}Ra (dpm L $^{-1}$)	v (cm d $^{-1}$)	τ (days)
JoCo	June 2013	3.2 ± 1.1	29.1	1.0
	September 2013	3.5 ± 1.0	26.0	1.1
	November 2013	2.7 ± 0.3	31.7	0.8
	April 2015	4.8 ± 2.3	23.3	1.7
	September 2015	6.7 ± 2.7	12.7	2.6
	April 2016	4.4 ± 1.0	15.6	1.4
	Mean	4.1 ± 2.1	25.9 ± 17.8	1.4 ± 0.9
Yellow Bar	June 2013	3.4 ± 0.1	5.7	4.4
	November 2013	4.0 ± 0.7	4.6	6.1
	Mean	3.7 ± 0.6	5.1 ± 1.3	5.2 ± 1.5

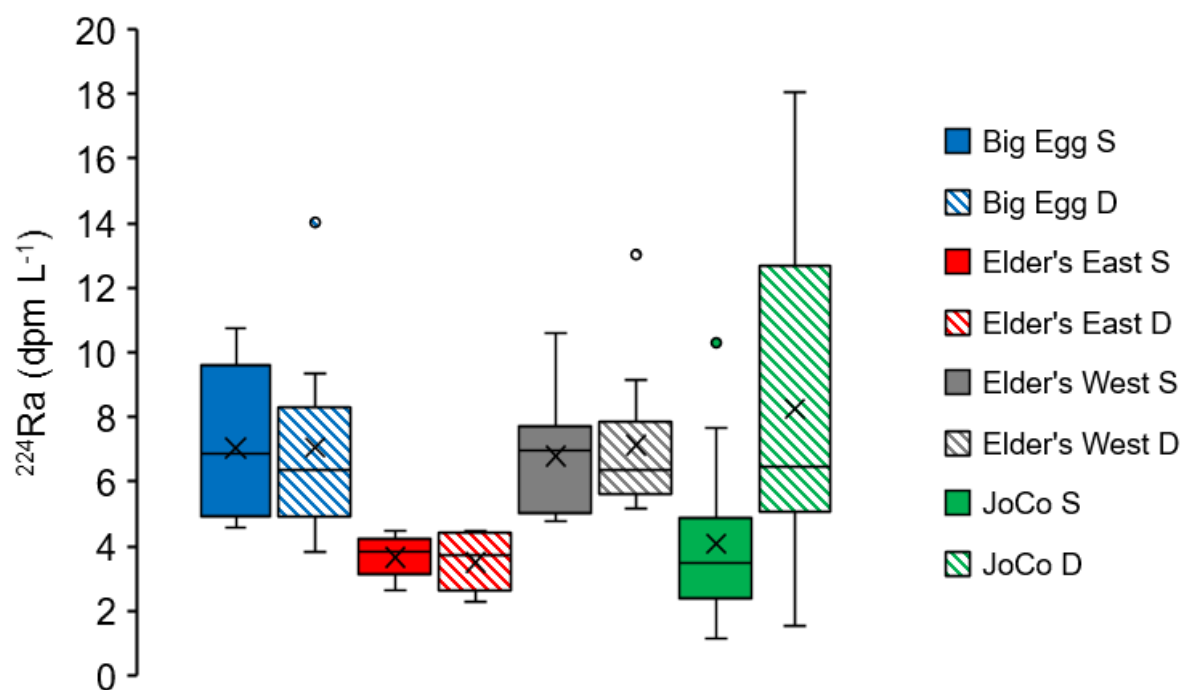


Figure 4.3. Comparison of shallow (25 cm; solid) and deep (≥ 50 cm; dashed) ^{224}Ra activities for pore waters in Jamaica Bay, New York. The mean Ra activity is indicated by a solid black "X." Small circles denote outlier values.

There were no clear seasonal differences in shallow (25 cm) pore water ^{224}Ra activities for each marsh (Table 4.1). As well, the sites at Big Egg include one site in the restored portion and two sites in the natural portion of the marsh. There were no clear differences in the shallow (25 cm) pore water ^{224}Ra activities among the Big Egg sites sampled at the same time (Table 4S.2), and they have been averaged together in Table 4.1. Mean shallow ^{224}Ra activities were highest at Big Egg during April 2015 (9.3 ± 0.8 dpm L $^{-1}$), however, ^{224}Ra activities were lower the following April (6.8 ± 2.8 dpm L $^{-1}$).

¹). Similarly, shallow ²²⁴Ra activities were highest at JoCo during September 2015 (6.7 ± 2.7 dpm L⁻¹), while activities were approximately a factor of two less during September 2013 (3.5 ± 1.0 dpm L⁻¹; Table 4.1). There was no observable relationship between pore water salinity, ORP or pH (data in Table 4S.2) with respect to the measured ²²⁴Ra pore water activities (Fig. 4.4). Results from a multiple linear regression analysis indicate that salinity, ORP and pH were not statistically significant in controlling the observed ²²⁴Ra activities at Big Egg, while ORP was statistically significant (95% CI) at Elder's East ($p = 0.045$), Elder's West ($p = 0.012$) and JoCo ($p = 0.045$).

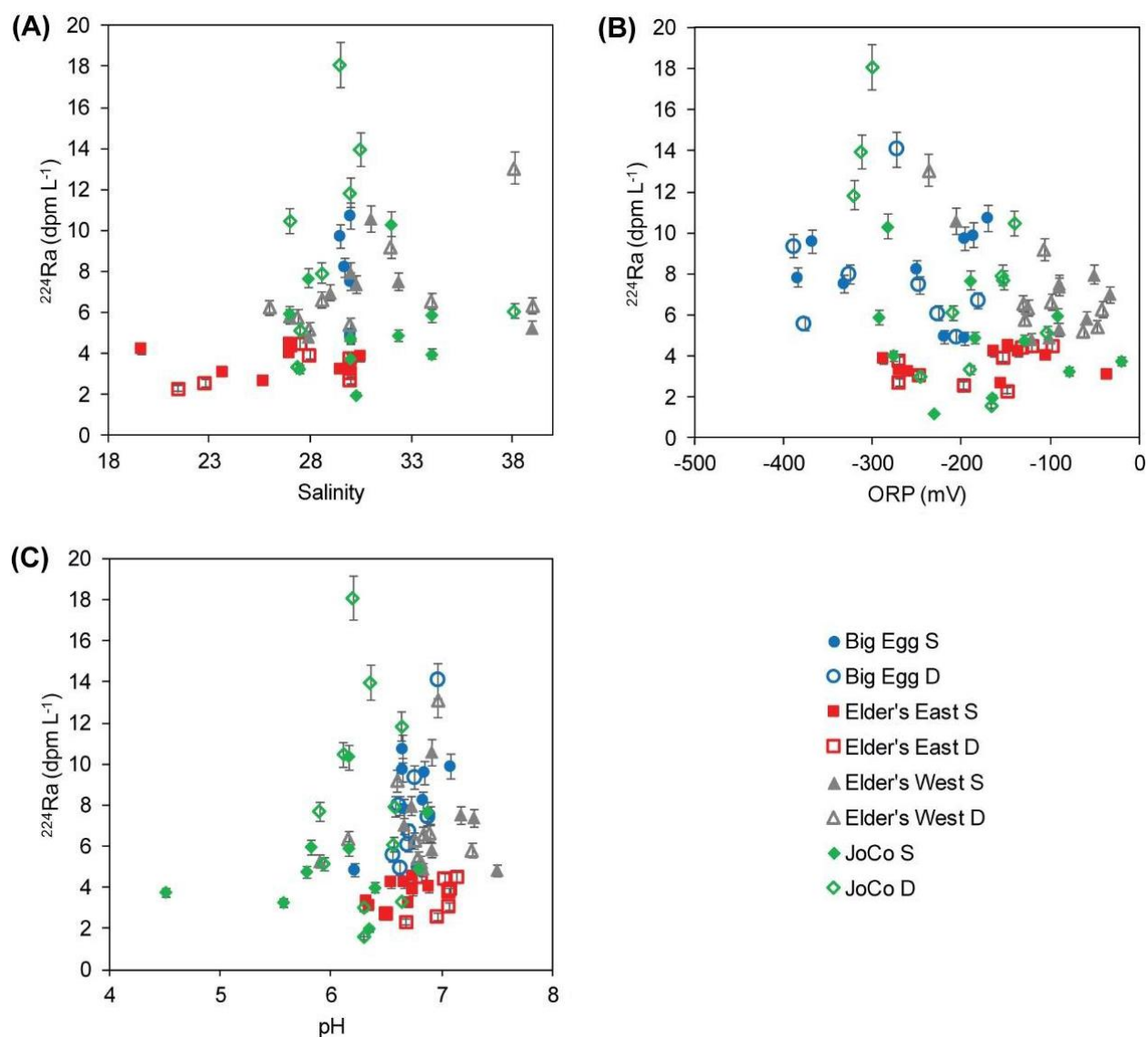


Figure 4.4. Pore water ²²⁴Ra vs. salinity (A), ORP (B) and pH (C), arranged by marsh in Jamaica Bay, NY, for April 2015, September 2015 and April 2016 samples. Shallow (S) samples are represented by filled symbols, deep (D) samples are represented by hollow symbols.

Solid-phase

Sediment samples measured for solid-phase ^{228}Th and ^{228}Ra were grouped into shallow (Big Egg and JoCo < 25 cm; Elder's East and Elder's West < 15 cm) and deep (Big Egg and JoCo 25 – 55 cm; Elder's East and Elder's West 15 – 25 cm) subsets. Cores longer than 25 cm were not recovered from Elder's East and Elder's West; no cores were recovered from Yellow Bar. Mean solid-phase activities for shallow and deep marsh sediments, along with grain size distributions and LOI, are summarized in Table 2. At Big Egg, shallow and deep sediments had a significant fraction of fine-to-coarse-silt ($D_{10} = 5 - 6 \mu\text{m}$), with an average shallow and deep ^{228}Th activity equal to 1.40 ± 0.36 and $1.74 \pm 0.25 \text{ dpm g}^{-1}$, respectively (Table 4.2). Solid-phase ^{228}Th activities were similar between Elder's East and Elder's West for both shallow and deep sediments ($0.40 - 0.52 \text{ dpm g}^{-1}$). These sediments were primarily a medium sand (D_{50}), although Elder's West had finer-grained material at depth ($D_{10} = 30 \mu\text{m}$) in comparison to Elder's East ($D_{10} = 179 \mu\text{m}$). For JoCo, the lithogenic fraction of the marsh sediments was primarily very-fine-sand ($D_{50} = 56 - 63 \mu\text{m}$), with mean solid-phase ^{228}Th activities between 1.19 and 1.13 dpm g^{-1} for shallow and deep sediments (Table 4.2).

Table 4.2. Mean ($\pm$ SD) solid-phase ^{228}Th and ^{228}Ra activities (dpm g^{-1}) arranged by marsh, with corresponding grain size distributions (10th and 50th percentile) and organic content (as % loss-on-ignition). Big Egg and JoCo shallow samples are categorized as < 25 cm depth, with deep samples between 25 and 55 cm. Elder's East and Elder's West shallow samples are categorized as < 15 cm depth, with deep samples between 15 and 25 cm.

Site Name	^{228}Th (dpm g^{-1})	^{228}Ra (dpm g^{-1})	n	d(0.1) (μm)	d(0.5) (μm)	LOI (%)
Big Egg-S	1.40 ± 0.36	1.13 ± 0.18	4	6	43	7.6
Big Egg-D	1.74 ± 0.25	1.53 ± 0.62	3	5	69	10.0
Elders East-S	0.40 ± 0.09	0.47 ± 0.10	3	19	261	0.7
Elders East-D	0.42 ± 0.05	0.48 ± 0.09	3	179	294	1.0
Elders West-S	0.52 ± 0.04	0.61 ± 0.03	5	22	223	0.5
Elders West-D	0.52 ± 0.04	0.59 ± 0.02	3	30	341	0.3
JoCo-S	1.19 ± 0.47	1.08 ± 0.48	8	12	63	37.0
JoCo-D	1.13 ± 0.27	0.75 ± 0.04	3	10	56	30.0
Yellow Bar-S	0.80	0.45	1	NM	NM	NM
Yellow Bar-D	0.96	1.28	1	NM	NM	NM

n = number of samples analyzed, S = shallow; D = deep, NM = not measured

Organic content varied among the marshes (Table 4.2). The Elder's marshes, being relatively recently restored with fine-sand, had low organic content (<1%). This reflects the fact that little time has passed since restoration for the build-up of a stable marsh peat deposit. In contrast, Big Egg and JoCo had higher average organic content between 8-10% and 30-37%, respectively.

There was a positive relationship between mean solid-phase ^{228}Th activity and solid-phase (reactive) Fe concentrations, both of which decreased with increasing sediment grain size (Fig. 4.5). Solid-phase Fe was highest in the shallow, fine-silt sediments at Big Egg ($72 \pm 52 \mu\text{mol g}^{-1}$). Solid-phase Fe concentrations were lowest at Elder's East ($7 \mu\text{mol g}^{-1}$ shallow and $8 \mu\text{mol g}^{-1}$ deep) and Elder's

West ($22 \mu\text{mol g}^{-1}$ shallow and $27 \mu\text{mol g}^{-1}$ deep). At JoCo, solid-phase Fe increased with increasing depth, with mean shallow and deep concentrations equal to $(26 \pm 33) \mu\text{mol g}^{-1}$ and $(43 \pm 40) \mu\text{mol g}^{-1}$, respectively. Solid-phase (reactive) Mn concentrations were variable among the four marshes with mean concentrations between 0.5 and $2.0 \mu\text{mol g}^{-1}$. Solid-phase Mn did not show a relationship with grain size, ^{228}Th activity or (reactive) Fe (Fig. 4.5).

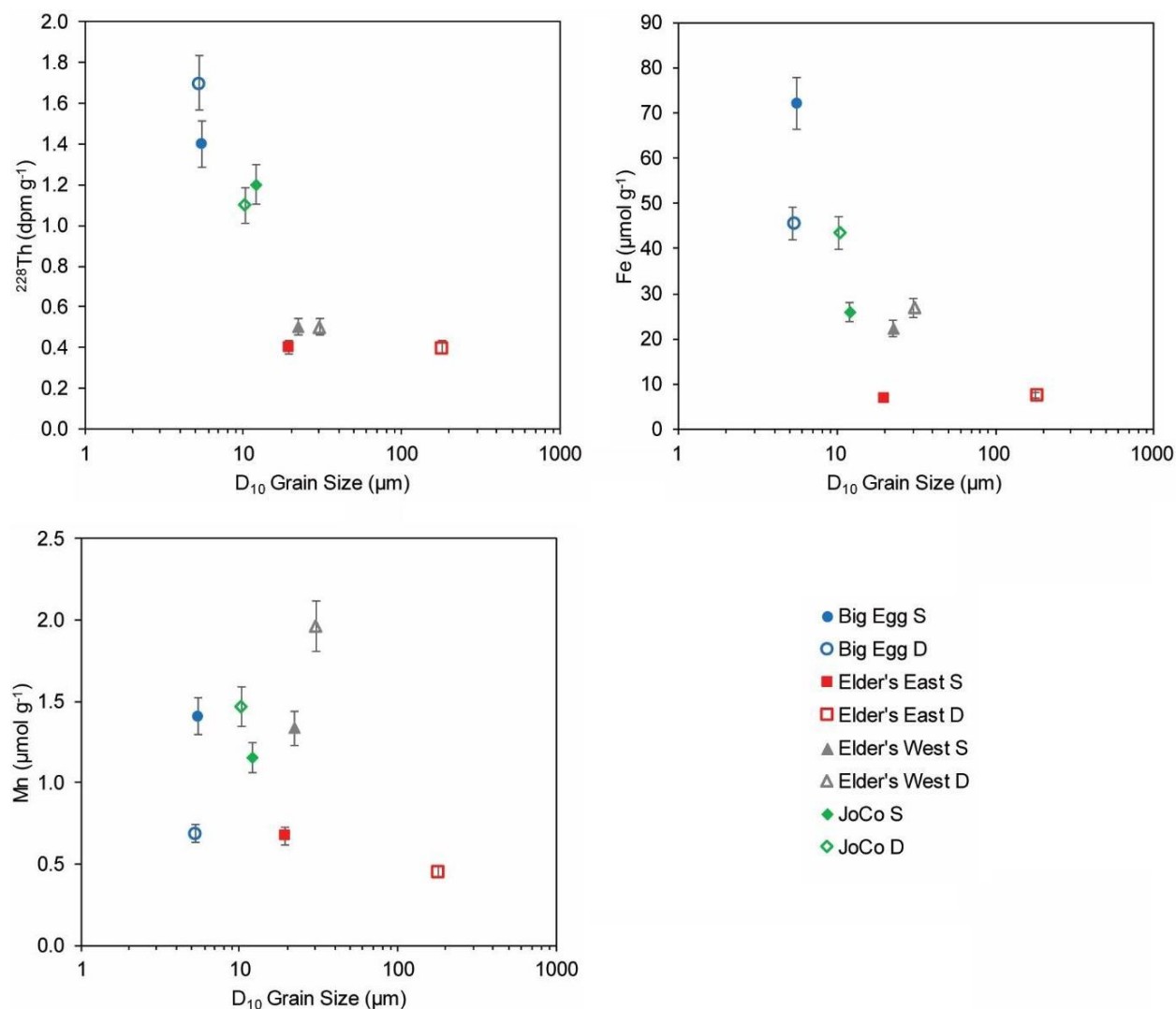


Figure 4.5. Mean solid-phase ^{228}Th , solid-phase (reactive) Fe and solid-phase (reactive) Mn vs. sediment grain size (10^{th} percentile), for shallow and deep sediments, arranged by marsh. Shallow (S) samples are represented by filled symbols, deep (D) samples are represented by hollow symbols.

Pore Water Velocity & Residence Time

Modeling pore water residence times using Ra isotopes is highly dependent upon the Ra steady-state equilibrium activity used (P' in eq. 2 & 3; Tamborski et al., 2017). Values of P' are set by the ionic strength of the pore fluid, sediment grain size, the surface-bound Th content of the sediment, and the abundance of solid-phase Fe and Mn-oxide coatings, which can adsorb Ra (Beck and Cochran,

2013). Here, we set P' as the highest observed Ra activity for each marsh, which ranged from 4.5 – 18.1 dpm L⁻¹ (Table 4.3). In comparison, experimentally determined values of ²²⁴Ra in equilibrium with coastal sediments were equal to 11.1 and 16.1 dpm L⁻¹ for a coarse-grained intertidal sand and a very-fine-grained silt taken offshore in Long Island Sound (Tamborski et al., 2017). Accordingly, these results are in relatively good agreement with the highest ²²⁴Ra values observed for Jamaica Bay. For Jamaica Bay sediment, we were unable to adequately replicate the redox conditions of the sediment in a sediment/pore water equilibration experiment, such that this method could not be used to define P' . The overarching assumption in these calculations (equations 1 – 3) is that the highest observed ²²⁴Ra activity for each marsh is representative of a steady-state system between the marsh sediment and the pore fluid, such that production is balanced by decay. Furthermore, these calculations assume that the sediments are fairly homogeneous between sites at each marsh. Finally, we assume that pore water flow is predominantly vertical and that lateral (horizontal) flow is negligible. The assumptions used in the residence time calculations, as well as other potential external controls on the pore water Ra activities, are discussed in Section 4.1. Uncertainty in the terms from equations 1 – 3 were propagated into a final residence time uncertainty, assuming a P' error of 20% (Tamborski et al., 2017), and are presented in Table 4S.2.

Table 4.3. Steady-state Ra activities (dpm L⁻¹) $\pm$ 1 σ counting error, taken as the highest observed pore water ²²⁴Ra activity for each marsh site sampled in Jamaica Bay, New York.

Site Name	²²⁴ Ra	$\pm$
Big Egg	14.1	0.7
Elder's East	4.5	0.2
Elder's West	13.1	0.5
JoCo	18.1	0.9
Yellow Bar	5.9	0.2

A composite depth profile of pore water ²²⁴Ra at JoCo, from different sampling sites and times within the marsh, is presented in Fig. 4.6. In an idealized one-dimensional system, seawater that has infiltrated into the marsh sediment will percolate vertically downward. As the pore fluid migrates downward, it will accumulate more Ra atoms *via* alpha-recoil from the ²²⁸Th present on and near the sediment grain surfaces, until production is balanced by decay at some particular depth horizon. As shown in Fig. 4.6, pore water ²²⁴Ra activities at different JoCo sites increased with depth, and fit well with modeled estimates of vertical advective velocities produced from equations 1 – 3. As a result, we assume that the Jamaica Bay marshes studied here can be simplified as one-dimensional systems, and therefore we can use our estimated residence times to simply calculate pore water advective velocities ($v = x/\tau$). It should be noted that the differences in advective velocities here may reflect heterogeneous flow between sites (Table 4S.1), rather than between seasons (Table 4.1).

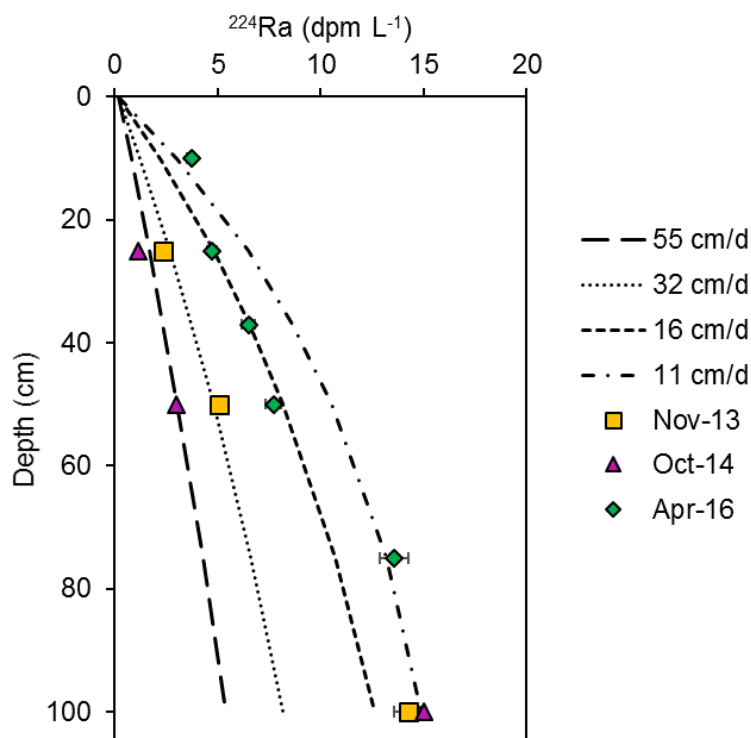


Figure 4.6. ^{224}Ra pore water profile from JoCo Marsh, New York, during November 2013, October 2014 and April 2016. The dashed lines represent a range of vertical advective velocity estimates (equations 1 – 3). November 2013 samples are from site JoCo interior, October 2014 samples are from JC1, and April 2016 samples are from JC3 (see Table S1). Plot is only of sampling dates in which ≥ 3 samples were taken at a particular site.

Pore water advective velocities and residence times, for each marsh, are presented in Fig. 4.7, with mean shallow (25 cm) sites summarized by season in Table 4.1. Elder's East and Elder's West, the two restored marshes, on average had the lowest mean ($\pm$ SD) pore water advective velocities of (3.2 ± 1.3) and (7.2 ± 2.5) cm d^{-1} at 25 cm depth, which correspond to mean residence times of (9.2 ± 3.6) and (4.1 ± 1.9) d, respectively. Advective velocities at depth (≥ 50 cm) were higher than shallow samples, with mean velocities equal to (7.5 ± 4.3) cm d^{-1} for Elder's East and (23.2 ± 6.5) cm d^{-1} for Elder's West, and residence times equal to (10.9 ± 8.7) and (3.6 ± 1.1) d, respectively (Fig. 4.7). Elder's West had significantly finer-grained sediment at depth ($D_{10} = 30 \mu\text{m}$) compared to Elder's East ($D_{10} = 179 \mu\text{m}$; Table 4.2); this difference in grain size is likely the primary driver between the large differences in the observed P' values (Table 4.3) as well as hydraulic conductivity. If residence times were estimated for Elder's East using the same P' value as Elder's West (13.1 dpm L^{-1}), then mean residence times would decrease to (1.6 ± 0.3) d for shallow pore waters and (1.5 ± 0.4) d for deep pore waters. Corresponding advective velocities would subsequently increase to (16.2 ± 3.2) and (36.0 ± 10.7) cm d^{-1} for shallow and deep pore waters, respectively. For any of the marshes studied, a minimum ^{224}Ra production rate will lead to a maximum residence time estimate. Mean velocities at Yellow Bar, the third restored marsh, were (5.1 ± 1.3) cm d^{-1} at 25 cm depth, with a mean residence time of (5.2 ± 1.5) d.

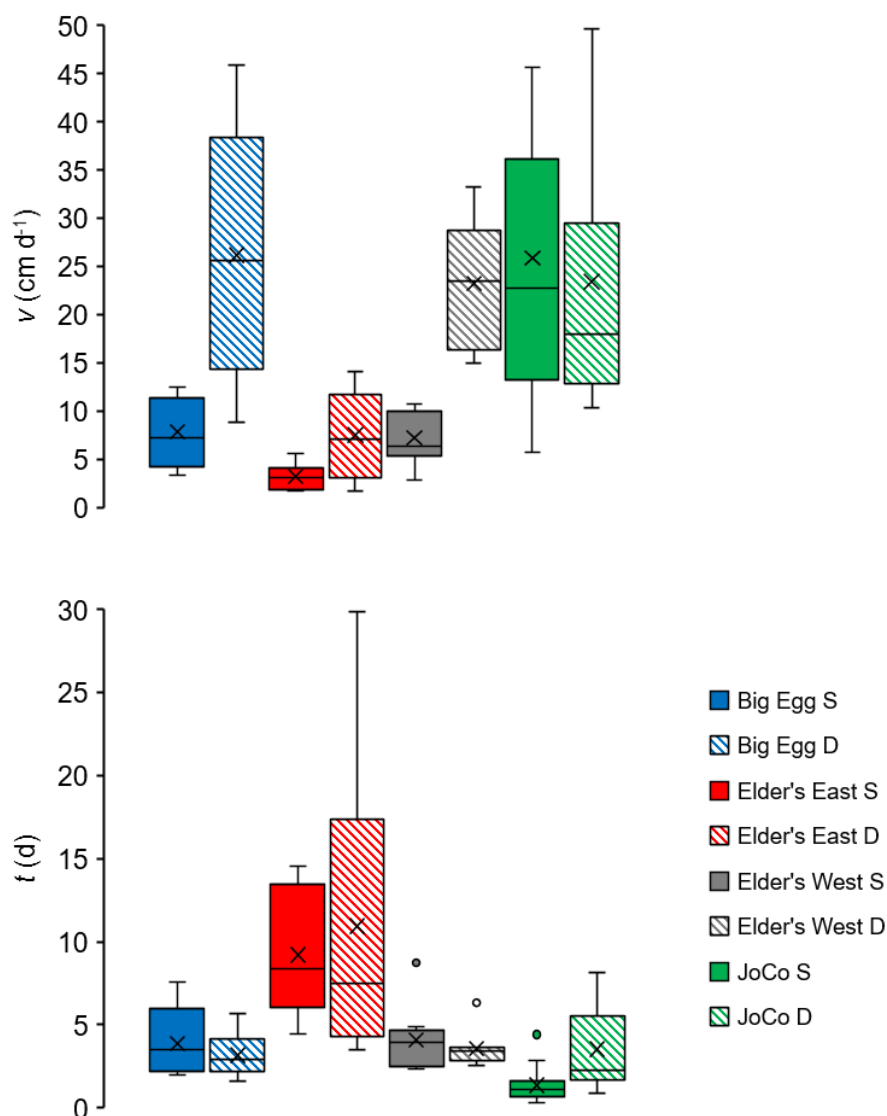


Figure 4.7. Comparison of shallow (25 cm; solid) and deep (≥ 50 cm; dashed) ^{224}Ra derived estimates of vertical seepage velocity (v ; top) and residence time (τ ; bottom) of marshes in Jamaica Bay, NY. The mean is indicated by a solid black “X.”

Mean pore water advective velocities at Big Egg were equal to (7.9 ± 3.2) cm d^{-1} at 25 cm and increased to approximately (26.2 ± 12.7) cm d^{-1} for deep samples (Fig. 4.7), where sediments were slightly coarser-grained (Table 4.2). Shallow residence times at Big Egg were equal to (3.9 ± 1.8) d and were similar at depth, equal to (3.2 ± 1.2) d. JoCo had the highest advective velocities of all the marshes. Mean advective velocities between shallow and deep samples at JoCo were similar, equal to (25.9 ± 17.8) cm d^{-1} and (23.4 ± 13.1) cm d^{-1} , respectively. Corresponding pore water residence times at 25 cm were (1.4 ± 0.9) d and increased to approximately (3.5 ± 2.4) d at depth (Fig. 4.7).

Fe and H_2S Throughput Fluxes

Fe and H_2S throughput fluxes were calculated by multiplying the measured pore water concentration at a discrete depth by the ^{224}Ra estimated vertical advective velocity at that same depth, and are

summarized by season in Table 4.4. Pore water Fe and H₂S concentrations varied considerably among the marsh sites. During the spring sampling seasons, Fe varied from 250 μ M at Elder's West to 3 μ M at JoCo, with the sites ranked as Elder's West >> Elder's East > Big Egg ~ JoCo. For H₂S, the sites varied as Big Egg > JoCo >> Elder's East ~ Elder's West, with highest concentration at Big Egg (2.7 mM) and undetectable at the Elder's sites (Table 4.4). During the summer, Fe varied from 685 μ M at Elder's West to ~0 μ M at JoCo, with the sites ranked as Elder's West >> Big Egg > Elder's East ~ JoCo. H₂S concentrations were higher in the summer compared to spring; accordingly, the sites varied as Big Egg > JoCo > Elder's East > Elder's West, with highest concentration at Big Egg (5.2 mM) and lowest concentrations at Elder's West (0.05 mM; Table 4.4). Pore water Fe and H₂S were not measured for Yellow Bar.

Table 4.4. Mean ($\pm$ SD) pore water Fe and H₂S from shallow (S) and deep (D) samples, arranged by marsh in Jamaica Bay, NY. The top table is a summary of both April sampling campaigns, the bottom table is a summary of September 2015. Fluxes are calculated using the ²²⁴Ra derived vertical advective velocities. "n" is the number of shallow (S) or deep (D) concentrations or fluxes averaged at each marsh.

Date	Marsh Site	Fe (μ mol L ⁻¹)	Fe Flux (mmol m ⁻² d ⁻¹)	H ₂ S (mmol L ⁻¹)	H ₂ S Flux (mmol m ⁻² d ⁻¹)	n
April	Big Egg-S	5.0 $\pm$ 6.7	0.5	1.8 $\pm$ 1.0	123	6
	Big Egg-D	5 $\pm$ 3	1	2.7 $\pm$ 1.1	735	5
	Elders East-S	20 $\pm$ 28	1	0.2 $\pm$ 0.1	7	6
	Elders East-D	4 $\pm$ 5	0.1	0.1 $\pm$ 0.1	11	6
	Elders West-S	194 $\pm$ 104	14	0 $\pm$ 0	0	6
	Elders West-D	250 $\pm$ 149	72	0 $\pm$ 0	0	6
	JoCo-S	7 $\pm$ 5	2	0.5 $\pm$ 0.2	83	6
	JoCo-D	3 $\pm$ 2	1	1.0 $\pm$ 0.2	217	6
September	Big Egg-S	4 $\pm$ 1	0	5.2 $\pm$ 1.1	275	3
	Big Egg-D	2 $\pm$ 1	0	4.4 $\pm$ 0.9	550	3
	Elders East-S	1 $\pm$ 1	0	2.7 $\pm$ 0.2	90	3
	Elders East-D	1 $\pm$ 1	0	1.3 $\pm$ 0.6	101	3
	Elders West-S	361 $\pm$ 306	33	0.05 $\pm$ 0.00	4	3
	Elders West-D	685 $\pm$ 350	157	0.05 $\pm$ 0.00	12	3
	JoCo-S	0 $\pm$ 0	0	2.6 $\pm$ 0.6	331	3
	JoCo-D	0 $\pm$ 0	0	3.5 $\pm$ 0.8	616	3

Discussion

Controls on Ra Activities

In a theoretical model of pore water draining vertically through marsh sediment, short-lived ²²⁴Ra activities will increase with increasing depth, until production from the sediment is balanced by decay (e.g. Fig. 4.6). The production rates used here are set by the highest observed ²²⁴Ra activity in deep pore water at each marsh (Table 4.3). Hypothetically, values of *P'* could have been higher at a

sediment depth greater than those sampled; if this were the case, then our residence times would represent maximum estimates.

The solid-phase ^{228}Th activities (Table 4.2) measure both surface-bound and structurally-bound ^{228}Th . Solid-phase $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios indicate a slight excess of ^{228}Th in marsh sediment from Big Egg and JoCo, while Elder's East and Elder's West $^{228}\text{Th}/^{228}\text{Ra}$ were approximately in equilibrium within uncertainties (Table 4.2). Excess ^{228}Th at Big Egg and JoCo provides evidence that the production of ^{224}Ra into the pore fluid was from surface-bound ^{228}Th associated with the fine-grained fraction of the marsh sediment (Fig. 4.5). The ^{228}Th parent isotope activity scales as a function of grain size such that more surface-bound ^{228}Th is linked to larger surface area (Porcelli and Swarzenski, 2003). This is further supported by the solid-phase (reactive) Fe, which is only associated with particle surfaces (based on the leaching procedures used; Fig. 4.5). Accordingly, these relationships justify our choice to use the maximum ^{224}Ra activity from each marsh as the production term in the residence time calculations. Between the five marshes, Elder's East had the lowest observed P' value (Table 4.3). While it is possible that this value is an underestimate, the coarser grain size and lower reactive Fe concentrations suggest that the sediment particles at Elder's East would have recoiled a lower percentage of ^{224}Ra atoms into the surrounding pore fluid. Furthermore, Elder's East had the lowest concentration of surface-bound (reactive) Mn between the four marshes ($\sim 0.5 \mu\text{mol g}^{-1}$; Fig. 4.5).

For several samples taken in Jamaica Bay, higher ^{224}Ra activities were observed at 25 cm compared with samples taken at ≥ 50 cm depth (Fig. 3; Table S2). This discrepancy may be caused by: (1) a difference in the sediment (porosity, permeability, grain size) and associated ^{228}Th content with depth (Hughes et al., 2015); (2) a difference in Fe and Mn-oxide coatings on sediment surfaces (Beck and Cochran, 2013; Gonnee et al., 2008); (3) bioturbation and bioirrigation (Bollinger and Moore, 1984); (4) lateral, horizontal flow (Charette, 2007) or (5) tidal influences (tidal amplitude, variations in sea level; Wilson et al., 2015).

Sediment Heterogeneity & Solid-phase Th Activity

Where sediments are coarse-grained, vertical advective velocities will be relatively fast due to a higher permeability, while sediment recoil efficiency will be lower than fine-grained sediments (Porcelli and Swarzenski, 2003). For example, shallow pore water Ra activities in a fine-grained sediment matrix were found to be greater than deeper pore waters associated with coarser-grained sediments (Hughes et al., 2015). Of the five marshes analyzed in this study, Big Egg had the finest grain size, which is reflected in the higher solid-phase ^{228}Th activities and (reactive) Fe concentrations (Table 4.2, Fig. 4.5). For Elder's East and Elder's West, mean solid-phase ^{228}Th activities were comparable between shallow and deep sediments (Table 4.2), with lower solid-phase Fe and Mn concentrations at Elder's East (Fig. 4.5). It is unlikely that the greater ^{224}Ra activities measured in the shallow pore water samples were exclusively a result of recoil efficiency from higher sediment-bound ^{228}Th , considering that solid-phase ^{228}Th activities were similar between shallow and deep sediments for all five marshes (Table 4.2).

Fe and Mn-oxides

Fe and Mn-oxide coatings on sediment surfaces can adsorb Ra from solution, while their subsequent dissolution can release Ra atoms into the surrounding pore fluid (Beck and Cochran, 2013; Gonneea et al., 2008). Surface-bound Mn-oxide concentrations were very low in the Jamaica Bay marsh sediments ($0.5 - 2.0 \mu\text{mol g}^{-1}$; Fig. 4.5), likely reflecting the oxidation of organic matter coupled to Mn-oxide reduction via microbial respiration. There was a statistically significant correlation between pore water Ra activities and ORP for Elder's East, Elder's West and JoCo. Greater reducing conditions (more negative ORP) lead to the dissolution of the Fe and Mn-oxide coatings on the marsh sediments, which could have increased pore water Ra activities independent of *in situ* production. Conversely, longer pore water residence times (higher Ra activities) permit greater opportunities for the microbial consumption of dissolved oxygen and early diagenetic redox reactions that would occur in a hypoxic or anoxic environment. The positive relationship between solid-phase ^{228}Th and solid-phase (reactive) Fe suggests that these solid-phase constituents, which control Ra activities, are together dependent on sediment grain size, while Mn was not significant (Fig. 4.5).

Bioturbation and Bioirrigation

Previously sampled subtidal sediment cores from JoCo were found to contain small bivalves, gastropods and polychaetes (Beck et al., 2007). These sediment cores were incubated for various time intervals in order to assess the diffusive flux of $^{223,224}\text{Ra}$ from the marsh sediment, as well as the input of $^{223,224}\text{Ra}$ from bioirrigation, which was determined to be significant. In the present study, our pore water sampling occurred above the subtidal zone in areas of dense vegetation, where the presence of bio-irrigating organisms was visibly less abundant in comparison to the tidal creeks. Bioirrigation in Jamaica Bay salt marshes is primarily dominated by fiddler crabs, whose burrows are visible when present, and therefore were avoided in selecting sample sites. Furthermore, our samples were collected deep enough (25 and ≥ 50 cm) to minimize the influence of bioirrigation on the sampled pore waters. The strong fit between measured ^{224}Ra and modeled ^{224}Ra activities for JoCo (Fig. 4.6) suggest that the influence of bioirrigation on the measured pore water ^{224}Ra was minimal.

Lateral Flow

Lateral, horizontal flow beneath the marsh surface may influence the measured Ra activities in a way that cannot be accounted for in the one-dimensional advective (vertical) transport model. Sampling of island marshes rather than fringing marshes (Fig. 4.1) reduces the likelihood that lateral pore water movement, or inputs from terrestrial groundwater enriched in Ra isotopes, would have contributed to the measured pore water Ra activities (Charette, 2007; Salazar, 2015). There was no apparent trend in pore water salinities to suggest that there was an external, lateral input source of Ra to the Jamaica Bay marshes (Fig. 4.4). There was approximately 0.1 cm of precipitation two days prior to sampling Elder's East during April 2015, which explains why pore water salinities were ≤ 25 , considering that pore water residence times were on the order of several days (Fig. 4.4; Table 4S.1). There was no precipitation for the remaining sampling campaigns, which is reflected in the higher pore water salinities more typical of Jamaica Bay. The agreement between the measured ^{224}Ra activities and model estimates (equations 1 – 3) at JoCo (Fig. 4.6) further support a vertical transport pathway, rather than a two-dimensional flow system.

Tidal Influence

Using a numerical model, Wilson and Gardner (2006) estimated pore water residence times between ~10 – 50 d beneath a theoretical salt marsh, where residence times increased with increasing distance from the creek bank. Additionally, pore water flow velocities were highest where the mean tide level met the creek bank, where flow predominantly occurred as groundwater discharge. At distances greater than 15 m away from the creek bank, pore water flow became primarily vertical (downward), with significantly lower advective velocities (Wilson and Gardner, 2006). For the marshes studied in Jamaica Bay, there was no observable relationship between shallow pore water advective velocity or residence time with respect to the sample site's distance from the nearest creek bank, measured using current high-resolution visible airborne imagery in Google Earth® (Fig. 4.8). The lack of any relationship between sampling distance from the creek bank and pore water velocity/residence time for Jamaica Bay may be an artifact of having too few sampling locations per marsh. Conversely, the individual sites studied here may have been adequately far from the creek banks, such that they were less affected by the tidal signal (~ 1.8 m range) propagating through the creek bank and into the center of the marsh. As a result, the observed differences in Ra activities were likely caused by differences in the downward percolation of seawater into the marsh sediment, in addition to the aforementioned processes, and not from external tidal forcing mechanisms.

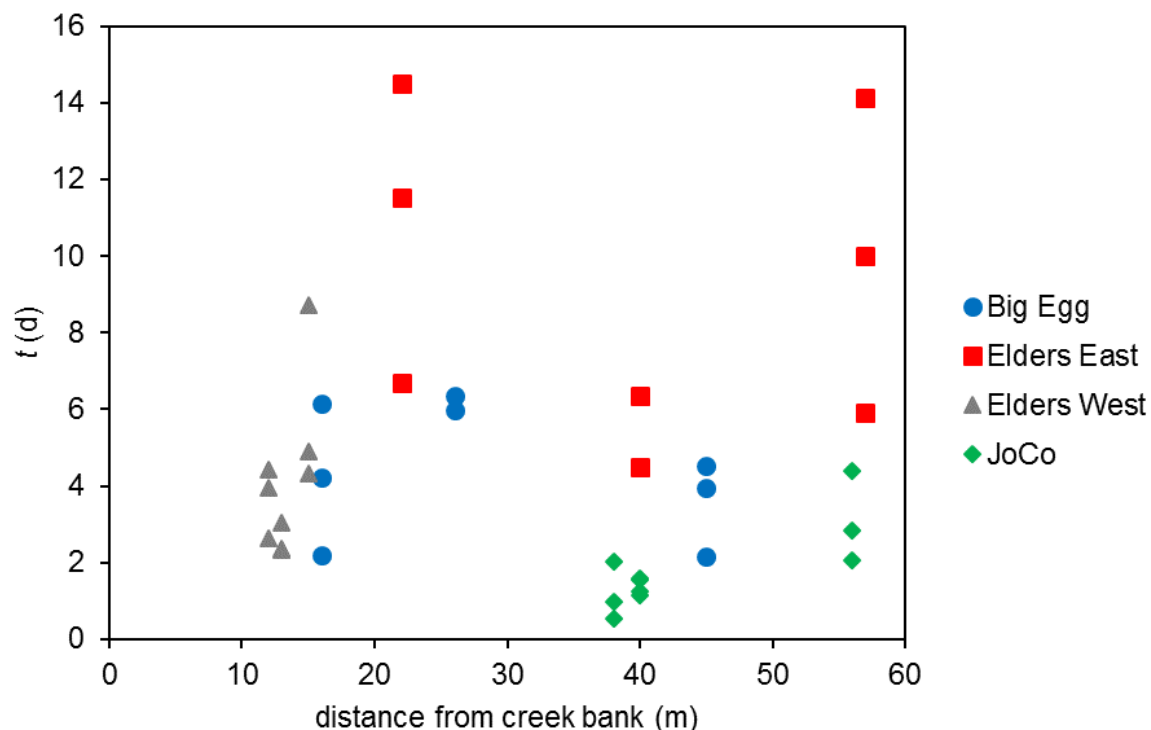


Figure 4.8. Shallow (25 cm) ^{224}Ra derived estimates of residence time vs. the sampling site's distance from the nearest creek bank for samples collected during April 2015, September 2015 and April 2016.

Environmental Significance

We did not observe any significant trends in pore water residence times between spring and summer seasons (Table 4.1). In the absence of a major storm event, the subsurface structure of the marsh (excluding biomass) remains relatively constant from year to year. As a result, it is likely that there would not be any seasonality in a marsh's capacity to drain between to 50 cm depth, assuming that the overlying sediment regime has not significantly changed and the influence of bioirrigation is minimal. Differences in seasonal pore water residence times may reflect the choice of the equilibrium ^{224}Ra activity used (Table 4.3), which could change seasonally if Fe and Mn-oxide coatings on the sediment surfaces varied seasonally. Conversely, local differences (Table 4S.1) may be attributed to site specific, small-scale heterogeneities and variable subsurface flow paths through the sediment medium, as for example, between macro-pores and matrix-pores (Harvey and Nuttle, 1995).

Conceptually, pore water advective velocities should increase with increasing grain size, reflecting an increase in hydraulic conductivity. However, shallow pore water advective velocities were lowest for Elder's East and Elder's West (Table 4.1), the two restored marshes analyzed in this study, and those with the largest median grain size (Table 4.2). Advective velocities for Big Egg were similar to the Elder's marshes (Table 4.1). The highest pore water advective velocities were calculated for JoCo, which is considered to be the most "healthy" of the five marshes studied here (based on biomass, the barren marsh surface area is $\leq 5\%$). A marsh's elevation above sea-level has a significant influence on advective pore water transport (Nuttle and Hemmond, 1988). On average, JoCo has the greatest elevation above sea-level (0.70 ± 0.23 m) with respect to the other marshes sampled during this study (Elder's West = 0.65 ± 0.13 m; Elder's East = 0.54 ± 0.26 m; Big Egg = 0.21 ± 0.28 m).

Slower advective velocities lead to longer pore water residence times beneath the marsh surface, which promotes greater build-up of pore water sulfide produced as a consequence of the microbial oxidation of organic matter by SO_4^{2-} reduction. High concentrations of H_2S may negatively affect plant height and productivity (King et al., 1982; Koch and Mendelsohn, 1989) and be implicated in marsh loss. The low H_2S concentrations at the restored Elder's marshes reflect the sandier substrate and lower concentrations of organic matter (Table 4.2), such that Elder's East and Elder's West are dominated by Fe redox conditions. Additionally, high pore water concentrations of Fe can lower pore water sulfide through the precipitation of iron sulfides. As a consequence, Elder's East and Elder's West had very low fluxes of H_2S , while Fe fluxes were highest at Elder's West (Table 4.4).

Throughput fluxes of H_2S at JoCo were much higher than at Elder's East or West and were greater during the summer compared with the spring (Table 4), reflecting the higher concentrations of H_2S in pore waters from increased microbial respiration during the summer. Sediments at Big Egg and JoCo have higher concentrations of organic matter due to a higher amount of marsh peat (Table 4.2), and therefore SO_4^{2-} reduction is an important pathway for organic matter oxidation. JoCo is considered to be the "healthiest" of the studied marshes, based on the plant density. JoCo's higher elevation above sea-level and sandy substrate (Table 4.2) together permit fast pore water advective velocities (Table 4.1, Fig. 4.7), and as a result limit the exposure of the marsh plants to H_2S building up in the pore fluid.

In contrast with JoCo, H₂S fluxes at Big Egg were comparable between spring and summer months (Table 4.4). This indicates a high exposure of the root zone to H₂S beginning in the spring as the plants begin to regenerate and continuing through the summer. Over the last several decades' marsh degradation and loss has occurred at an alarming rate at Big Egg (NYSDEC, 2006), and was clearly observable in a qualitative sense over the three-year period of this study. Big Egg 1 (BE1) was previously restored, while BE2 and BE3 remain natural. While the number of samples are limited (Table 4S.2), mean shallow pore water residence times were lower at BE1 (3.5 d) compared to BE2 (4.2 d) and BE3 (6.2 d), suggesting that the recent restoration efforts may have helped enhance marsh drainage by slightly increasing the surface elevation of the marsh at BE1. The restoration of Elder's East and Elder's West has had a positive environmental impact, in terms of vegetation density and structure, over the last several years (Elder's East = 25% barren surface-area; Elder's West = 45% barren surface area, estimated from 0.25 m² Braun Blanquet plots during 2014). The low concentration of organic matter in the marsh sediment at Elder's has resulted in low rates of SO₄²⁻ reduction and low H₂S concentrations, but the long pore water residence times (Table 4.2) may become problematic if organic matter and H₂S levels increase in the future.

The methodology outlined in this study is applicable to other salt marsh systems. Understanding pore water residence times within salt marshes will permit a better understanding of geochemical fluxes from marshes to the coastal ocean. Globally, salt marsh degradation and loss is driven by the complicating factors of eutrophication, leading to plant exposure to enhanced concentrations of phytotoxins, and the ability of marshes to accrete to keep pace with sea-level rise (Bromberg Gedan et al., 2009). The production and/or removal of phytotoxins, including H₂S, may be linked to the residence time of pore water beneath the marsh surface. The results from this study demonstrate that many interrelated factors such as porosity, permeability, sediment grain size and elevation of the marsh surface above mean sea level influence marsh drainage. This may affect the choice of sediment for marsh restoration, as well as the desired elevation gain *via* restoration efforts. For example, Big Egg 1 was restored through spraying adjacent channel sediment onto the marsh surface, while the Elder's restoration efforts involved dredged sand. As a result, the type of sediment used for future restorative marsh work, as well as the modified elevation of the marsh surface, should be carefully considered.

Summary and Conclusions

Pore waters and sediment were sampled in five distinct Jamaica Bay (NY) salt marshes over a several year period. Measurements of pore water ²²⁴Ra and solid-phase ²²⁸Th, Fe and Mn were used to assess the production of ²²⁴Ra from the marsh sediment to the surrounding pore fluids. A one-dimensional advective transport model was employed to estimate pore water residence times and vertical drainage velocities, in order to calculate throughput fluxes of Fe and H₂S. Pore water drainage velocities were highest in JoCo marsh, which had the highest elevation above mean sea-level of the marshes studied with sediments comprising very-fine-grained sand. This produces a lower exposure period to elevated concentrations of pore water H₂S, especially at the start of the spring growing season. Drainage rates and residence times varied between the marshes as a function of the marshes sediment characteristics. Residence times did not appear to be seasonal, such that variable residence times likely reflected local heterogeneities in flow. Short-lived Ra isotopes

provide a tool for assessing marsh drainage and in turn allow for improved estimates of geochemical fluxes.

Acknowledgements

This work was supported by the National Park Service Award 59054 to PR and JKC and Task Agreement P14AC01395 to JKC and QZ. The latter funding was associated with the Science and Resilience Institute of Jamaica Bay. JJT acknowledges funding by a NY Sea Grant fellowship (project R/CMC-12). We are grateful to Wen Cong and Hong Yi for field assistance and to Justin Manning for the loss-on-ignition measurements. Sampling logistics were skillfully provided by the American Littoral Society and we thank Don Riepe and Elizabeth Manclark for their help.

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Supplemental Information

Table 4S.1. Marsh sampling locations, Jamaica Bay, NY.

Site Name	Marsh Site	Latitude (°N)	Longitude (°W)
Big Egg	BE1	40.59604	73.82637
	BE2	40.59586	73.82814
	BE3	40.59607	73.82812
Elder's East	EE1	40.63647	73.84761
	EE2	40.63715	73.8460
	EE3	40.63592	73.84628
Elder's West	EW1	40.63228	73.85578
	EW2	40.63233	73.85483
	EW3	40.63192	73.85477
JoCo	JC1	40.61241	73.78729
	JC2	40.61212	73.78724
	JC3	40.61173	73.78591

Table 4S.2. ^{224,223}Ra activities and modeled advective velocities (v) and pore water residence times (τ). ^A

Site Name	Sample ID	Sample Season	Depth (cm)	²²⁴ Ra (dpm/L)	²²³ Ra (dpm/L)	Salinity	pH	ORP	v (cm/d)	τ (d)
Big Egg	BE Creek	June, 2013	25	4.6 ± 0.2	0.29 ± 0.05	NM	NM	NM	12.5	2.0 ± 0.3
	BE Mid	June, 2013	25	5.4 ± 0.3	0.35 ± 0.05	NM	NM	NM	10.0	2.5 ± 0.4
	BE Interior	June, 2013	25	5.1 ± 0.2	0.28 ± 0.04	NM	NM	NM	10.9	2.3 ± 0.3
	BE Creek	Nov, 2013	25	4.9 ± 0.2	0.19 ± 0.03	NM	NM	NM	11.3	2.2 ± 0.3
	BE Mid	Nov, 2013	25	6.9 ± 0.3	0.44 ± 0.07	NM	NM	NM	7.2	3.5 ± 0.5
	BE Interior	Nov, 2013	25	5.5 ± 0.2	0.43 ± 0.06	NM	NM	NM	9.8	2.6 ± 0.4
	BE Interior 50	Nov, 2013	50	3.8 ± 0.2	0.07 ± 0.01	NM	NM	NM	31.3	1.6 ± 0.3
	BE Interior 100	Nov, 2013	100	4.9 ± 0.2	0.17 ± 0.03	NM	NM	NM	45.9	2.2 ± 0.3
	BE1 shallow	April, 2015	25	8.2 ± 0.4	0.55 ± 0.07	29.7	6.83	-249	5.5	4.5 ± 0.7
	BE1 deep	April, 2015	100	7.4 ± 0.3	0.21 ± 0.03	29.9	6.88	-247	25.7	3.9 ± 0.6
	BE2 shallow	April, 2015	25	9.7 ± 0.5	0.50 ± 0.07	29.5	6.65	-195	4.1	6.1 ± 1.3
	BE2 deep	April, 2015	50	6.1 ± 0.3	0.22 ± 0.03	30.5	6.70	-226	17.2	2.9 ± 0.4
	BE3 shallow	April, 2015	25	9.9 ± 0.5	0.70 ± 0.11	NM	7.09	-186	3.9	6.3 ± 1.4
	BE1 shallow	Sep, 2015	25	7.5 ± 0.4	0.45 ± 0.07	30.0	6.90	-331	6.3	4.0 ± 0.6
	BE1 deep	Sep, 2015	50	8.0 ± 0.4	0.70 ± 0.09	32.5	6.62	-325	11.5	4.3 ± 0.7
	BE2 shallow	Sep, 2015	25	7.8 ± 0.4	0.32 ± 0.04	NM	6.67	-383	5.9	4.2 ± 0.7
	BE2 deep	Sep, 2015	50	5.6 ± 0.3	0.13 ± 0.02	30.0	6.56	-376	19.4	2.6 ± 0.4
	BE3 shallow	Sep, 2015	25	9.6 ± 0.6	0.80 ± 0.09	NM	6.85	-367	4.2	6.0 ± 1.2
	BE3 deep	Sep, 2015	50	9.3 ± 0.4	0.43 ± 0.06	NM	6.76	-388	8.8	5.7 ± 1.1
	BE1 shallow	April, 2016	25	4.8 ± 0.3	0.26 ± 0.03	30.0	6.22	-195	11.6	2.1 ± 0.3
	BE1 deep	April, 2016	100	6.7 ± 0.3	0.12 ± 0.03	30.0	6.71	-181	30.1	3.3 ± 0.5
	BE2 shallow	April, 2016	25	4.9 ± 0.2	0.45 ± 0.06	30.0	6.78	-218	11.4	2.2 ± 0.3
	BE2 deep	April, 2016	100	14.1 ± 0.7	0.16 ± 0.03	30.0	6.97	-272	NC	NC
	BE3 shallow	April, 2016	25	10.7 ± 0.5	0.80 ± 0.07	30.0	6.65	-170	3.3	7.5 ± 2.2
	BE3 deep	April, 2016	100	4.9 ± 0.2	0.19 ± 0.03	30.0	6.63	-205	45.5	2.2 ± 0.3
Elder's East	EE1 shallow	April, 2015	25	2.7 ± 0.1	0.11 ± 0.02	25.7	6.52	-155	5.6	4.5 ± 1.3
	EE1 deep	April, 2015	50	2.6 ± 0.1	0.12 ± 0.01	22.8	6.96	-197	11.9	4.2 ± 1.2
	EE2 shallow	April, 2015	25	4.2 ± 0.2	0.27 ± 0.03	19.7	6.54	-136	1.7	14.5 ± >14.5

^A NM means “not measured”; NC means “not calculated”

Table 4S.2 (continued). ^{224,223}Ra activities and modeled advective velocities (v) and pore water residence times (τ). ^A

Site Name	Sample ID	Sample Season	Depth (cm)	²²⁴ Ra (dpm/L)	²²³ Ra (dpm/L)	Salinity	pH	ORP	v (cm/d)	τ (d)
Elder's East	EE2 deep	April, 2015	50	2.3 ± 0.1	0.14 ± 0.01	21.5	6.68	-148	14.1	3.5 ± 1
	EE3 shallow	April, 2015	25	3.1 ± 0.1	0.17 ± 0.02	23.7	6.35	-36	4.2	5.9 ± 2.2
	EE3 deep	April, 2015	50	4.5 ± 0.1	0.22 ± 0.03	27.5	6.82	-120	NC	NC
	EE1 shallow	Sep, 2015	25	3.2 ± 0.2	0.26 ± 0.02	29.5	6.71	-260	3.9	6.4 ± 2.6
	EE1 deep	Sep, 2015	50	3.8 ± 0.2	0.16 ± 0.02	30.0	7.07	-270	5.4	9.2 ± 7.5
	EE2 shallow	Sep, 2015	25	3.3 ± 0.2	0.21 ± 0.02	30.0	6.32	-270	3.7	6.7 ± 2.9
	EE2 deep	Sep, 2015	50	2.7 ± 0.2	0.15 ± 0.01	30.0	6.50	-270	10.9	4.6 ± 1.4
	EE3 shallow	Sep, 2015	25	3.9 ± 0.2	0.20 ± 0.02	30.5	6.74	-288	2.5	10.0 ± >10.0
	EE3 deep	Sep, 2015	50	3.0 ± 0.2	0.16 ± 0.02	30.0	7.07	-248	8.8	5.7 ± 2.0
	EE1 shallow	April, 2016	25	4.5 ± 0.2	0.28 ± 0.04	27.0	6.74	-147	NC	NC
	EE1 deep	April, 2016	50	4.4 ± 0.2	0.18 ± 0.03	27.0	7.03	-132	2.6	19.6 ± >19.6
	EE2 shallow	April, 2016	25	4.0 ± 0.2	0.18 ± 0.03	27.0	6.89	-105	2.2	11.5 ± >11.5
	EE2 deep	April, 2016	50	4.5 ± 0.2	0.28 ± 0.03	27.0	7.14	-97	1.7	29.9 ± >29.9
	EE3 shallow	April, 2016	25	4.2 ± 0.2	0.18 ± 0.02	27.0	6.66	-163	1.8	14.1 ± >14.1
	EE3 deep	April, 2016	50	3.9 ± 0.2	0.21 ± 0.02	28.0	7.08	-153	4.7	10.7 ± >10.7
Elder's West	EW1 shallow	April, 2015	25	7.4 ± 0.4	0.30 ± 0.04	30.3	7.30	-90	5.8	4.3 ± 0.7
	EW1 deep	April, 2015	100	5.8 ± 0.3	0.31 ± 0.04	27.4	7.28	-128	33.3	3.0 ± 0.5
	EW2 shallow	April, 2015	25	4.8 ± 0.2	0.25 ± 0.03	27.9	7.50	-120	10.7	2.3 ± 0.4
	EW2 deep	April, 2015	100	6.6 ± 0.3	0.26 ± 0.04	28.6	6.90	-98	27.6	3.6 ± 0.6
	EW3 shallow	April, 2015	25	7.5 ± 0.3	0.18 ± 0.03	32.4	7.17	-90	5.6	4.4 ± 0.7
	EW3 deep	April, 2015	100	13.1 ± 0.5	0.42 ± 0.06	38.1	6.97	-236	NC	NC
	EW1 shallow	Sep, 2015	25	10.6 ± 0.5	0.54 ± 0.09	31.0	6.91	-205	2.9	8.7 ± 3.5
	EW1 deep	Sep, 2015	100	6.6 ± 0.3	0.21 ± 0.04	34.0	6.84	-130	27.7	3.6 ± 0.6
	EW2 shallow	Sep, 2015	25	4.8 ± 0.2	0.19 ± 0.03	30.0	6.83	-101	10.6	2.4 ± 0.4
	EW2 deep	Sep, 2015	100	9.2 ± 0.4	0.29 ± 0.05	32.0	6.60	-106	15.8	6.3 ± 1.5
	EW3 shallow	Sep, 2015	25	5.3 ± 0.3	0.12 ± 0.03	39.0	5.91	-89	9.5	2.6 ± 0.4
	EW3 deep	Sep, 2015	100	6.4 ± 0.3	0.34 ± 0.04	39.0	6.16	-124	29.1	3.4 ± 0.5
	EW1 shallow	April, 2016	25	8 ± 0.4	0.29 ± 0.04	30.0	6.73	-50	5.1	4.9 ± 0.9

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Table 4S.2 (continued). ^{224,223}Ra activities and modeled advective velocities (v) and pore water residence times (τ). ^A

Site Name	Sample ID	Sample Season	Depth (cm)	²²⁴ Ra (dpm/L)	²²³ Ra (dpm/L)	Salinity	pH	ORP	v (cm/d)	τ (d)
Elder's West	EW1 deep	April, 2016	50	5.2 ± 0.3	0.21 ± 0.03	28.0	6.81	-62	19.4	2.6 ± 0.4
	EW2 shallow	April, 2016	25	5.8 ± 0.3	0.22 ± 0.03	27.0	6.91	-59	8.2	3.0 ± 0.5
	EW2 deep	April, 2016	50	6.2 ± 0.3	0.28 ± 0.04	26.0	6.76	-41	14.9	3.4 ± 0.5
	EW3 shallow	April, 2016	25	7.0 ± 0.3	0.31 ± 0.04	29.0	6.67	-33	6.3	3.9 ± 0.6
	EW3 deep	April, 2016	50	5.4 ± 0.3	0.27 ± 0.04	30.0	6.79	-47	18.2	2.8 ± 0.4
JoCo	JoCo Creek	June, 2013	25	4.8 ± 0.2	0.43 ± 0.06	NM	NM	NM	15.9	1.6 ± 0.2
	JoCo Mid	June, 2013	25	2.3 ± 0.1	0.33 ± 0.04	NM	NM	NM	37.3	0.7 ± 0.2
	JoCo Interior	June, 2013	25	2.5 ± 0.1	0.27 ± 0.04	NM	NM	NM	34.0	0.7 ± 0.2
	JoCo Creek	Sep, 2013	25	4.9 ± 0.2	0.29 ± 0.05	NM	NM	NM	15.7	1.6 ± 0.2
	JoCo Mid	Sep, 2013	25	2.4 ± 0.1	0.22 ± 0.03	NM	NM	NM	36.8	0.7 ± 0.2
	JoCo Interior	Sep, 2013	25	3.2 ± 0.1	0.24 ± 0.04	NM	NM	NM	25.4	1.0 ± 0.2
	Joco Interior 50	Sep, 2013	50	5.8 ± 0.2	0.48 ± 0.05	NM	NM	NM	25.3	2.0 ± 0.3
	Joco Interior 50	Sep, 2013	50	6.4 ± 0.3	0.51 ± 0.07	NM	NM	NM	22.2	2.2 ± 0.3
	JoCo Creek	Nov, 2013	25	2.7 ± 0.1	0.21 ± 0.03	NM	NM	NM	31.8	0.8 ± 0.2
	JoCo Mid	Nov, 2013	25	3.1 ± 0.2	0.33 ± 0.04	NM	NM	NM	26.3	0.9 ± 0.2
	JoCo Interior	Nov, 2013	25	2.4 ± 0.1	0.26 ± 0.05	NM	NM	NM	36.8	0.7 ± 0.2
	Joco Interior 50	Nov, 2013	50	5.1 ± 0.2	0.40 ± 0.05	NM	NM	NM	29.9	1.7 ± 0.2
	JoCo Interior 100	Nov, 2013	100	14.3 ± 0.5	0.65 ± 0.09	NM	NM	NM	12.2	8.2 ± 2.4
	JC1 25	Oct, 2014	25	1.2 ± 0.1	0.14 ± 0.02	NM	6.26	-230	86.5	0.3 ± 0.2
	JC1 50	Oct, 2014	50	3.0 ± 0.1	0.26 ± 0.02	NM	6.30	-245	56.5	0.9 ± 0.2
	JC1 100	Oct, 2014	100	15 ± 1.2	0.95 ± 0.15	NM	6.30	-166	NC	NC
	JC1 shallow	April, 2015	25	2.0 ± 0.1	0.22 ± 0.03	30.3	6.35	-165	45.6	0.5 ± 0.2
	JC1 deep	April, 2015	50	3.3 ± 0.2	0.24 ± 0.03	27.4	6.65	-190	49.6	1.0 ± 0.2
	JC2 shallow	April, 2015	25	7.7 ± 0.4	0.22 ± 0.02	27.9	6.88	-190	8.8	2.9 ± 0.4
	JC2 deep	April, 2015	50	7.9 ± 0.4	0.52 ± 0.06	28.6	6.58	-154	16.7	3.0 ± 0.4
	JC3 shallow	April, 2015	25	4.9 ± 0.2	0.44 ± 0.04	32.4	6.79	-184	15.7	1.6 ± 0.2
	JC3 deep	April, 2015	50	6.1 ± 0.3	0.38 ± 0.05	38.1	6.57	-209	23.8	2.1 ± 0.3
	JC1 shallow	Sept, 2015	25	5.9 ± 0.3	0.51 ± 0.05	34.0	6.17	-292	12.4	2.0 ± 0.3

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Table 4S.2 (continued). ^{224,223}Ra activities and modeled advective velocities (v) and pore water residence times (τ). ^A

Site Name	Sample ID	Sample Season	Depth (cm)	²²⁴ Ra (dpm/L)	²²³ Ra (dpm/L)	Salinity	pH	ORP	v (cm/d)	τ (d)
JoCo	JC1 deep	Sept, 2015	100	11.8 ± 0.6	0.47 ± 0.07	30.0	6.64	-320	18.0	5.6 ± 0.9
	JC2 shallow	Sept, 2015	25	10.3 ± 0.5	0.64 ± 0.08	32.0	6.16	-282	5.7	4.4 ± 0.6
	JC2 deep	Sept, 2015	100	18.1 ± 0.9	1.04 ± 0.13	29.5	NM	NM	NC	NC
	JC3 shallow	Sept, 2015	25	4.0 ± 0.2	0.36 ± 0.05	34.0	6.40	-276	20.0	1.3 ± 0.2
	JC3 deep	Sept, 2015	100	14.0 ± 0.7	1.05 ± 0.13	30.5	6.36	-312	12.9	7.7 ± 2.1
	JC1 shallow	April, 2016	25	3.2 ± 0.2	0.47 ± 0.03	27.5	5.58	-78	25.4	1.0 ± 0.2
	JC1 deep	April, 2016	50	5.1 ± 0.3	0.33 ± 0.03	27.5	5.94	-103	29.5	1.7 ± 0.2
	JC2 shallow	April, 2016	25	6.0 ± 0.3	0.48 ± 0.05	27.0	5.82	-91	12.2	2.1 ± 0.3
	JC2 deep	April, 2016	50	10.5 ± 0.5	0.53 ± 0.06	27.0	6.12	-140	11.1	4.5 ± 0.6
	JC3	April, 2016	10	3.7 ± 0.2	0.27 ± 0.03	30.0	4.51	-20	8.7	1.2 ± 0.2
	JC3	April, 2016	25	4.7 ± 0.2	0.41 ± 0.03	30.0	5.79	-128	16.3	1.5 ± 0.2
	JC3	April, 2016	37	6.5 ± 0.3	0.55 ± 0.06	NM	NM	NM	16.2	2.3 ± 0.3
	JC3	April, 2016	50	7.7 ± 0.4	0.62 ± 0.06	NM	5.90	-152	17.4	2.9 ± 0.4
	JC3	April, 2016	75	13.6 ± 0.7	1.59 ± 0.16	NM	NM	NM	10.3	7.3 ± 1.7
Yellow Bar	YB Creek	June, 2013	25	3.5 ± 0.2	0.40 ± 0.05	NM	NM	NM	5.4	4.6 ± 1.2
	YB Mid	June, 2013	25	3.4 ± 0.2	0.56 ± 0.07	NM	NM	NM	5.8	4.3 ± 1.1
	YB Interior	June, 2013	25	3.4 ± 0.2	0.27 ± 0.04	NM	NM	NM	5.8	4.3 ± 1.1
	YB Creek	Nov, 2013	25	4.6 ± 0.2	0.36 ± 0.05	NM	NM	NM	3.3	7.6 ± 3.5
	YB Mid	Nov, 2013	25	3.0 ± 0.1	0.24 ± 0.04	NM	NM	NM	6.9	3.6 ± 0.9
	YB Interior	Nov, 2013	25	4.4 ± 0.3	0.40 ± 0.08	NM	NM	NM	3.6	6.9 ± 2.7
	YB Interior deep	Nov, 2013	50	5.9 ± 0.2	0.17 ± 0.02	NM	NM	NM	NC	NC

^A NM means “not measured”; NC means “not calculated”

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NPS 646/145098, May 2018

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