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TRACE METAL DISTRIBUTIONS IN NATURAL SALT MARSH SEDIMENTS

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TRACE METAL DISTRIBUTIONS
IN NATURAL SALT MARSH SEDIMENTS

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SUMMARY

Sediment core samples were collected from two salt marsh areas of the coast of Georgia (near Thunderbolt, Georgia and Hell Gate in Ossabaw Sound). Samples from channels were also collected from both areas. The marsh sediments show an oxidized upper zone (20-30 cm), with reduced zone below, and an increase in sulfide with depth. The clay mineral composition and the grain size of the sediment cores with depth is fairly uniform.

The distribution of trace metals in sediment cores can be explained by their post depositional mobility and diffusion in the interstitial solutions in the sediments. Elements such as Mn, Ni and Co are enriched in the upper oxidized zone. Redox reactions can account directly for the mobilization of Mn, Ni and Co. Fe and Cu do not appear to migrate significantly. This is probably due to their immobilization by sulfide in the reduced zone. Marsh sediments appear to act as a sink for Zn since it tends to diffuse downward. Hg in the sediments, possibly in a biologically active form, may be released from the sediments either due to volatilization by bacteria or uptake by plants. Marsh plants (*Spartina alterniflora*) play a major role in the uptake and removal of trace metals from the marsh sediments.

CHAPTER I

INTRODUCTION

It has been established that the Georgia estuaries and salt marshes form an effective sediment trap (Windom, *et al.*, 1971b). A reasonable estimate of the rate of accumulation of salt marsh sediments is around 1 mm/yr (Rusnak, 1967). Many studies have been made to determine the amount and composition of the material which southeastern rivers transport (Neiheisel and Weaver, 1967; Windom, *et al.*, 1971a) and their adequacy of supplying various trace metals to marine sediment. Since the southeastern estuarine sediments rather than deep sea sediment receive the bulk of this material, salt marsh sediments are of interest in terms of trace metal deposition and redistribution. Trace metal concentrations in the suspended matter found by Windom, *et al.* (1971a), in their study of three southeastern rivers, are higher than those in the salt marsh sediments. This suggests that various other processes besides sedimentation control the trace metal distribution in salt marsh sediments.

The sediment cores from the salt marsh environment show an oxidized top layer overlying reduced sediment. Chemical parameters such as Eh, pH and sulfide play a major role in controlling the trace metal distribution within sedimentary systems. Studies by Lynn and Bonatti (1965), Bezrukov (1960) and Manheim (1965) of hemipelagic sediments in various areas have shown that the oxidized zone and the interface between the oxidized and reduced zone are enriched in Mn relative to the reduced sediment below. Lynn and Bonatti (1965) calculated that ionic or molecular diffusion in the pore solution is the main mechanism by which the migration of trace metals takes place. Bonatti, et al., (1970) studied post depositional mobility, mainly by diffusion in interstitial solutions, of various trace metals in the sediments. They found that redox reactions can account directly for the mobilization of Mn, Ni, Co and Cr. Fe and Cu do not migrate significantly since they are immobilized as sulfide in the reduced zone.

The present study was designed to understand the processes that control the trace metal distribution in the salt marsh sediment system. Processes such as redox conditions, diffusion-advection, uptake by plants and sedimentation have been considered in evaluating trace metal deposition and distribution. In the present study, the distribution of Fe, Mn, Zn, Cu, Co, Ni and Hg was considered. Two salt marsh areas, Thunderbolt and Hell Gate (Fig. 1), were chosen for study. Thunderbolt (Fig. 2) is a part of the Wilmington River estuary and Hell Gate (Fig. 3) is to the immediate south of Savannah, near the Ossabaw Sound. Both of these areas are along the Intracoastal Waterways.

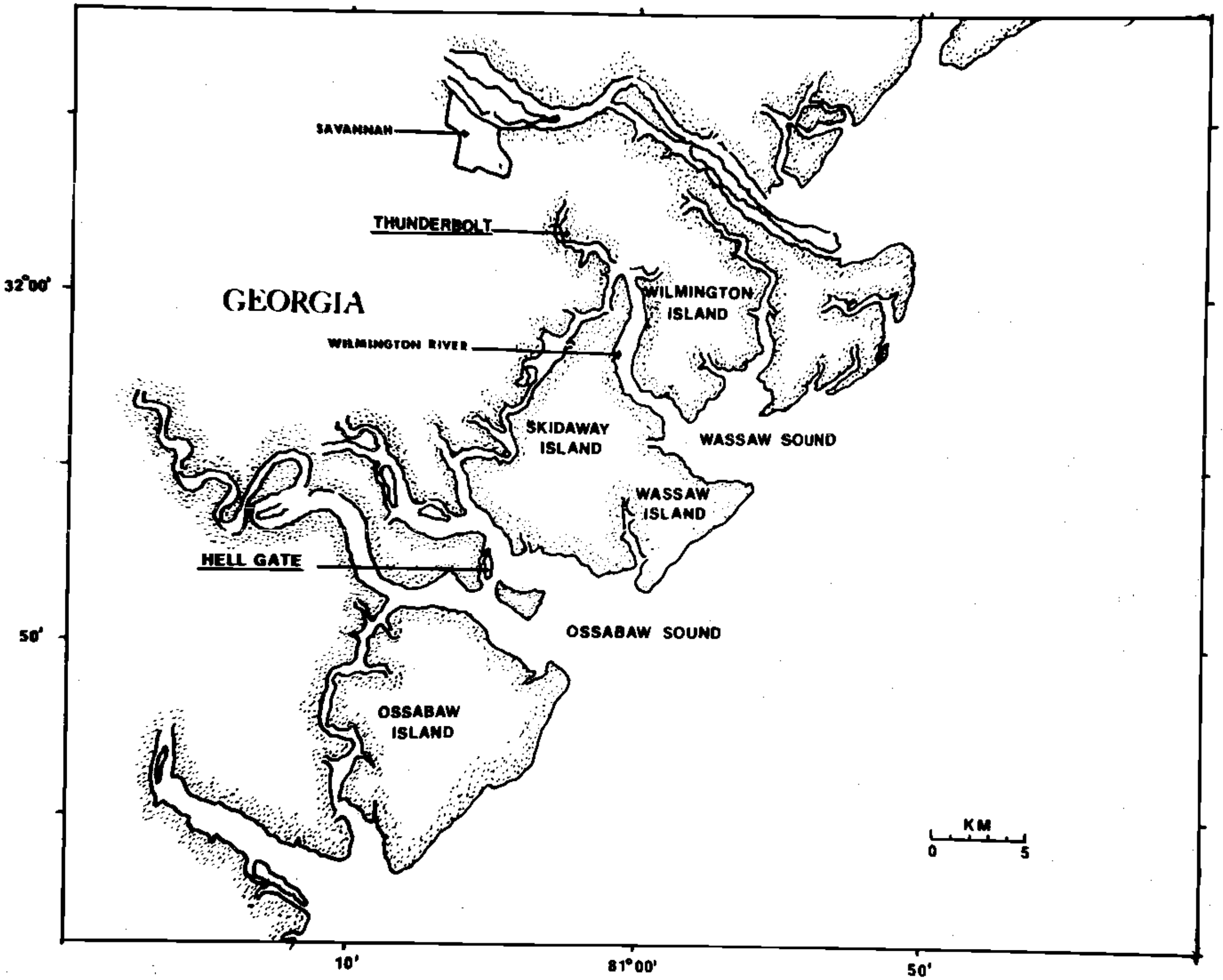


Figure 1. Index Map of the Study Area (Thunderbolt and Hell Gate)

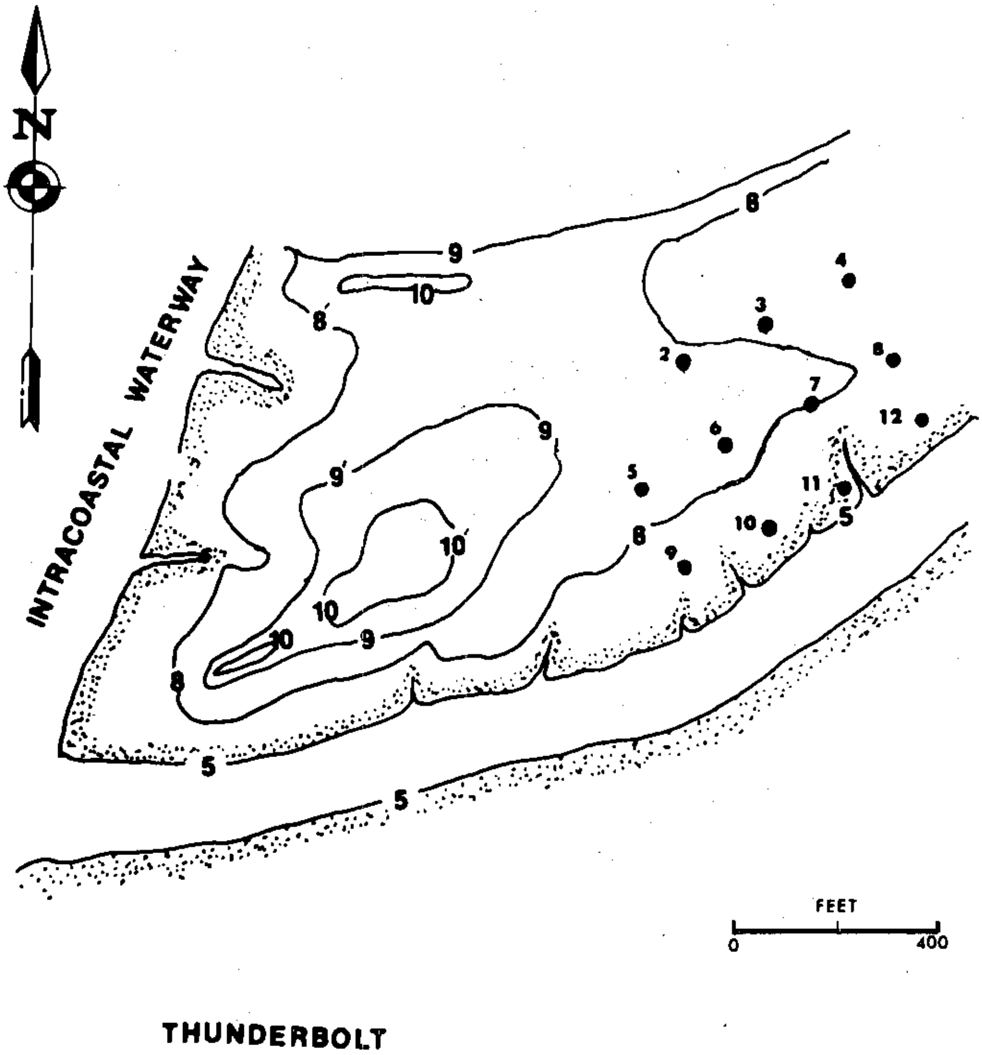


Figure 2. Thunderbolt Study Area
(Dots Indicate Locations of Coring Station.)

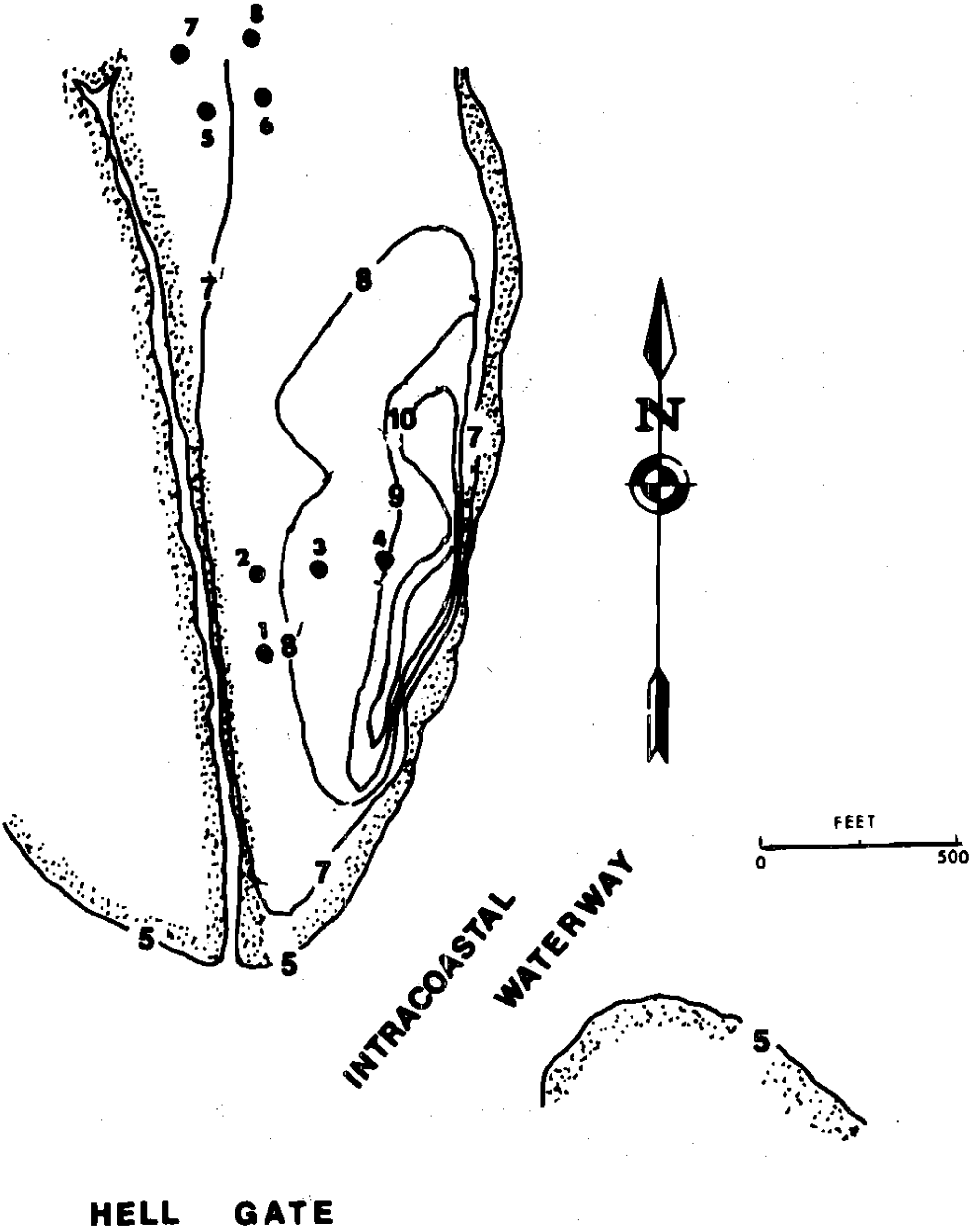


Figure 3. Hell Gate Study Area
(Dots Indicate Locations of Coring Stations.)

CHAPTER II

METHODS

Cores were collected from each study area at various stations (Figs. 2 and 3) using a piston corer mounted on tripods. Marsh grass (*Spartina alterniflora*) samples were also collected at these stations. Samples from channels adjacent to the marshes were collected using either a piston corer or a grab sampler.

Shortly after collection, the cores were extruded and analyzed at 10 cm intervals for Eh, pH and sulfide, using a platinum electrode with Zobell solution as standard for Eh, a standard combination pH electrode and a specific ion sulfide electrode with a calomel reference electrode, respectively. Samples were collected at 20 cm intervals for other analyses. The channel sediments were also analyzed for Eh, pH and sulfide and sampled similar to the marsh sediments.

Leachable and total Fe, Mn, Cu, Co, Ni and Zn were determined by the following procedure: Samples were air dried and then crushed. For the leachable fraction of the metals, approximately 100 mg of the powdered samples were treated with 10 ml solution equivalent to 1 M-hydroxylamine hydrochloride and 25 per cent (v/v) acetic acid. This treatment is used to dissolve all nondetrital (authigenic) phases and has been explained in detail by Chester and Hughes (1967). An additional portion of each of the samples amounting to approximately 100 mg was completely digested using hydrofluoric and nitric acids to allow the determination of the total metal content of the samples. The two solutions resulting from the two chemical treatments were analyzed by atomic absorption spectrophotometry using a Beckman model 495 atomic absorption system, and using as standards, solutions prepared in matrices similar to sample solutions.

To analyze the sediment for mercury, the samples were wet digested using sulphuric acid followed by reduction aeration by flameless atomic absorption. This method has been described in detail by Hatch and Ott (1968). This would represent the total mercury tied up in authigenic and organic phases.

The samples for trace metal analyses of marsh grass (Spartina alterniflora) were prepared by digesting 0.5 g of dried grass with 5.0 ml fuming nitric acid. The residue is dissolved with 1:1 HCl and brought to volume. The sample thus prepared is analyzed by atomic absorption spectrophotometry. This method has been described in detail by Middleton and Stuckey (1954).

For clay analyses the sediment sample was washed several times with deionized water using 0.6 micron candle filters to get rid of excess salts. The cleaned sediment was then dispersed in about 20 ml of deionized water. The clay fraction from the dispersed sediment was separated by centrifugation. Clay analyses were accomplished using a GE XRD-6 x-ray diffraction unit as 45 kv and 20 ma with nickel filtered Cuk_{α} radiation.

To determine clay, silt and sand fractions in the sediment, pipette analysis was used. All material coarser than 62 microns was removed from the sample by wet sieving. Material finer than 62 microns was dispersed in water and brought to 1000 ml. The clay and silt fractions were then determined by the pipette method as described by Folk (1968).

Total organic content in the samples was determined by weight loss on ignition at 600^{o} C for one hour.

CHAPTER III

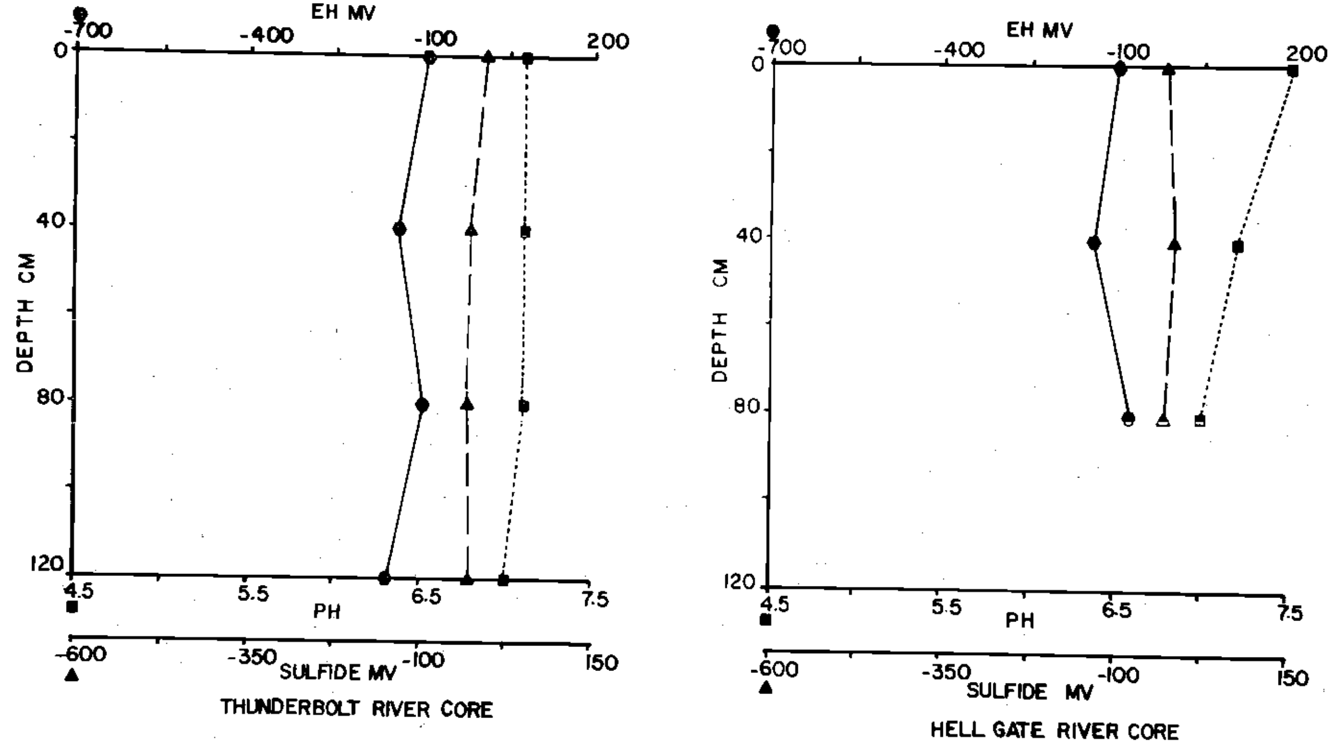
RESULTS

Eh, pH, and Sulfide

In Figure 4 the distribution of the three chemical parameters is shown for the cores in the channel sediments for the Hell Gate and Thunderbolt areas. Since calibration of the sulfide electrode for sediments is difficult, only the electrode response (in mv) is shown. These sediments are uniform in pH, Eh and sulfide ion concentration with depth. In the Thunderbolt study area (Fig. 2), all cores collected have a distribution of the three chemical parameters as shown for a few of the stations in Figure 5 and in Appendix I. Instead of uniform distribution of parameters with depth, Eh rapidly decreases, while sulfide ion rapidly increases through the oxidized layer and then maintains a uniform value at depth in the reduced sediment. This same characteristic is also observed for the Hell Gate area (Fig. 3) as can be seen from Figure 6 and Appendix I. The pH in both marsh areas shows an increasing trend with depth.

Iron

Fe is the most abundant of all the metals studied in the marsh sediments. The Thunderbolt area, in general, shows



THUNDERBOLT RIVER CORE

HELL GATE RIVER CORE

Figure 4. Eh, pH and Sulfide Variations with Depth for Channel Sediments in the Thunderbolt and Hell Gate Areas. (Increasing Negative Response of Sulfide Electrode Represents Increasing Sulfide Ion.)

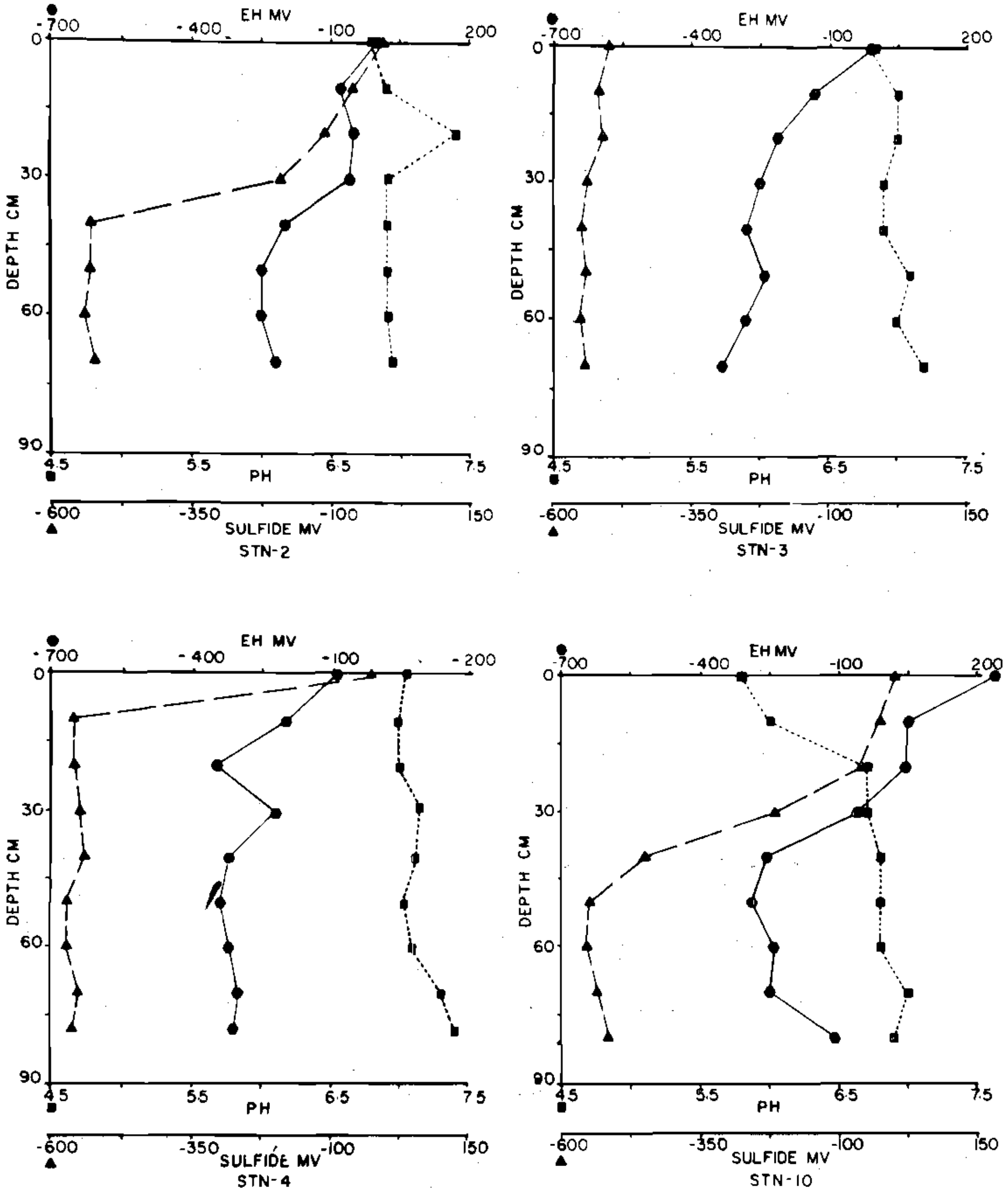


Figure 5. Eh, pH and Sulfide Variations with Depth for Representative Cores in the Thunderbolt Area

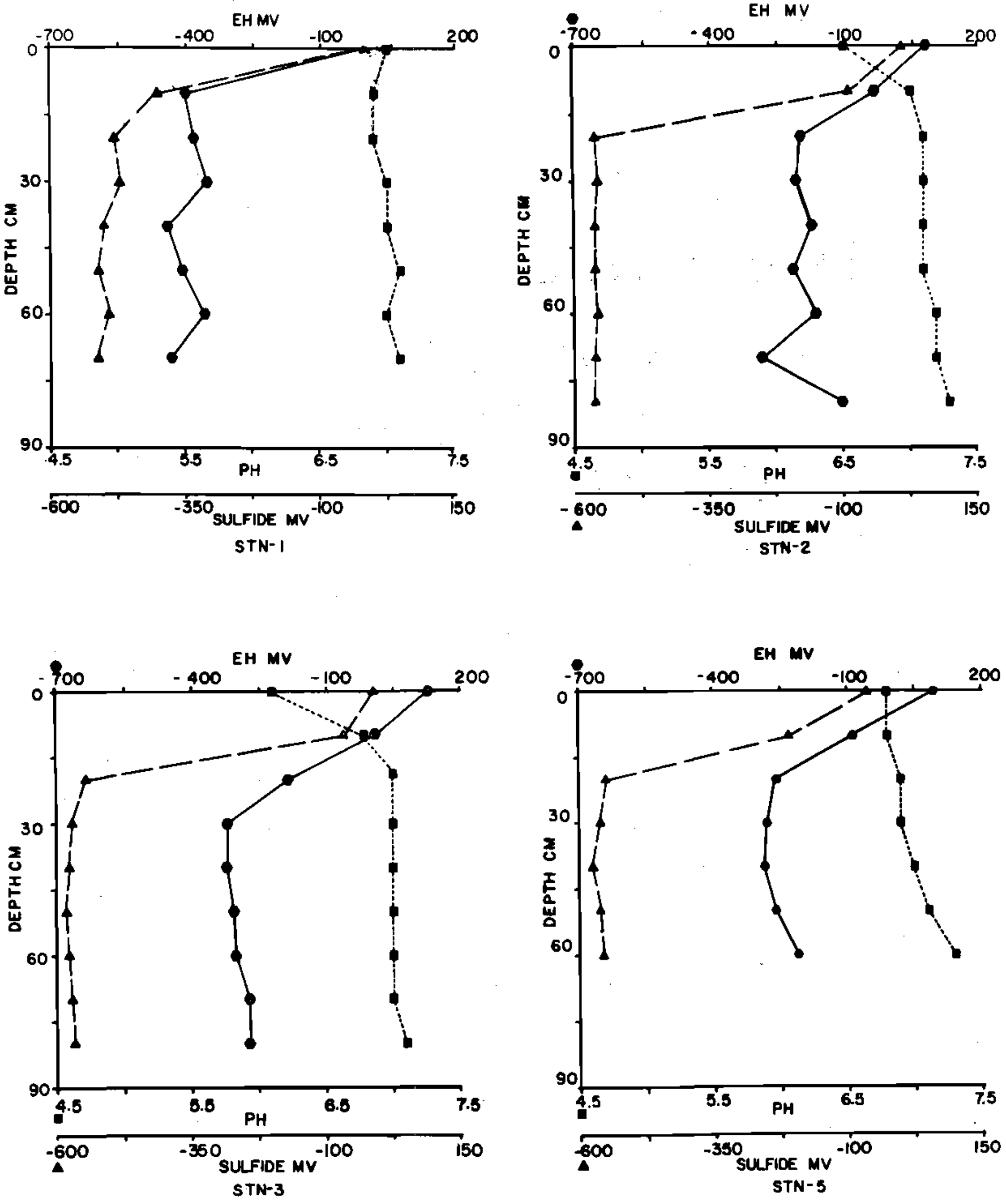


Figure 6. Eh, pH and Sulfide Variations with Depth for Representative Cores in the Hell Gate Area

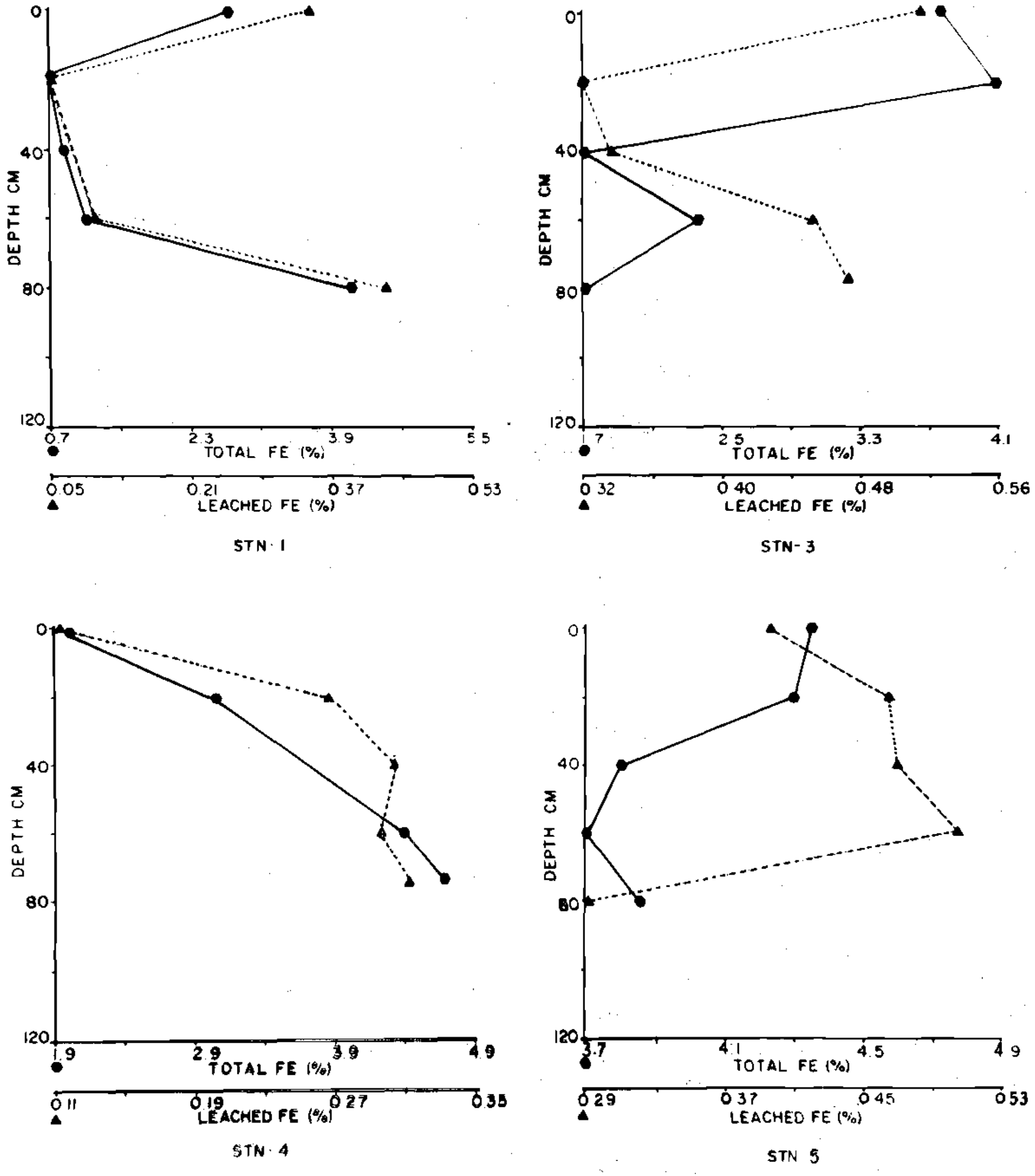
a higher Fe concentration in the total and leachable fractions than the Hell Gate area. The vertical distribution of total and leachable Fe in representative cores from both the Thunderbolt and Hell Gate areas is listed in Appendix II and illustrated in Figures 7 and 8.

The Fe concentration in the total fraction of the sediments varies between 1.3 and 7.1 per cent, with an average of 3.5 per cent in Thunderbolt and 1.3 and 4.9 per cent with an average of 3.1 per cent in the Hell Gate area. The leachable fraction in the Thunderbolt and Hell Gate areas varies between 0.14 and 1.6 per cent and 0.12 and 1.5 per cent, respectively. The average leachable Fe in Thunderbolt and Hell Gate is 0.59 per cent and 0.53 per cent, respectively. This shows that approximately 17 per cent of the total Fe in sediments in both areas is leachable.

The vertical distribution of total and leachable Fe in the Thunderbolt river core is illustrated in Figure 9. The Fe concentration with depth is uniform and is higher than the marsh sediments. The average concentration of Fe in river channel sediments is 4.3 per cent with 1.8 per cent leachable Fe, or 41 per cent of the total.

Manganese

Mn is the second most abundant metal studied in the marsh sediments. The vertical distribution of Mn in both study areas is given in Appendix II and illustrated for



STN 1

STN 3

STN 4

STN 5

Figure 7. Vertical Distribution of Total and Leachable Fe with Depth in Representative Cores from the Thunderbolt Area

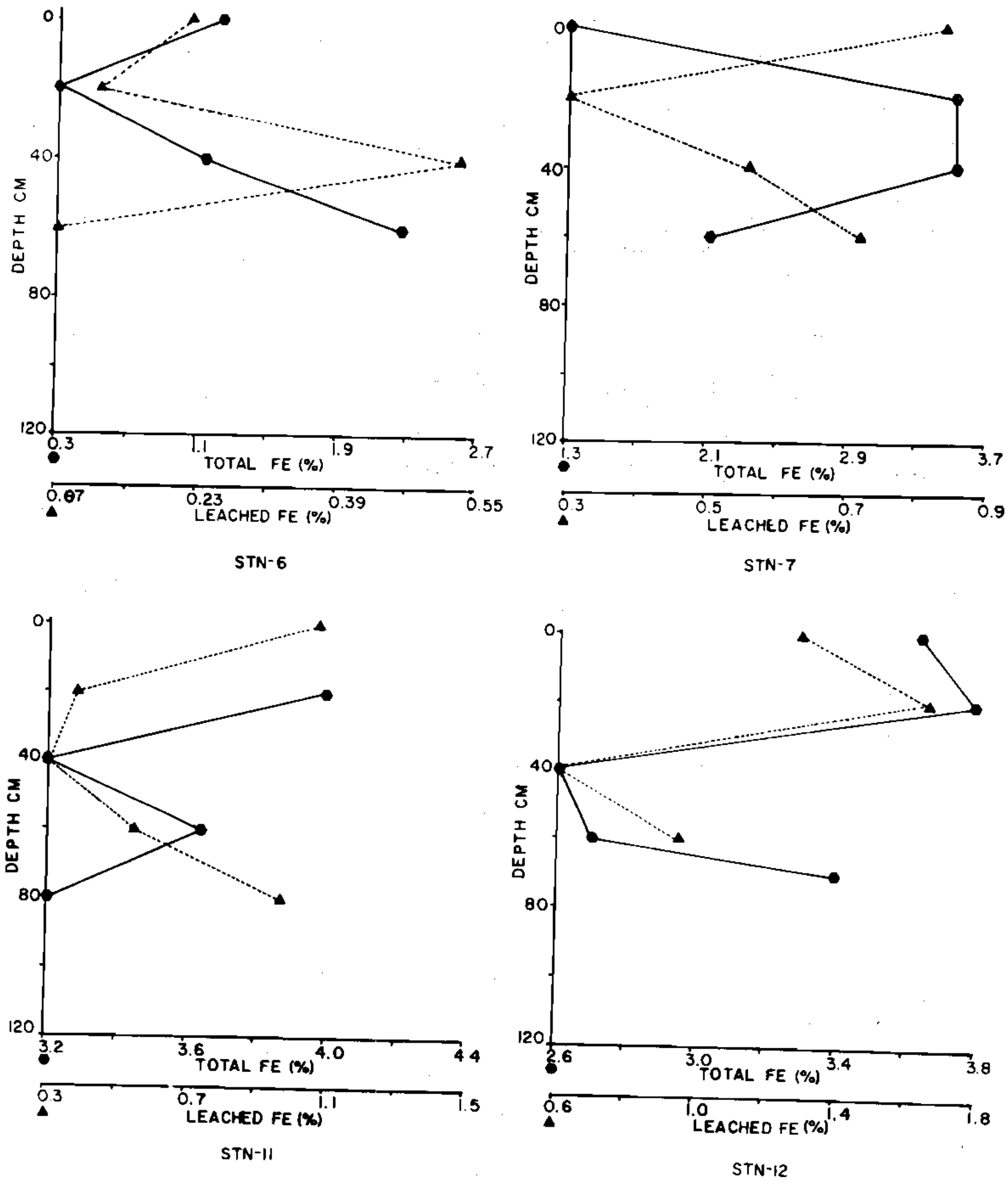


Figure 8. Vertical Distribution of Total and Leachable Fe with Depth in Representative Cores from the Hell Gate Area

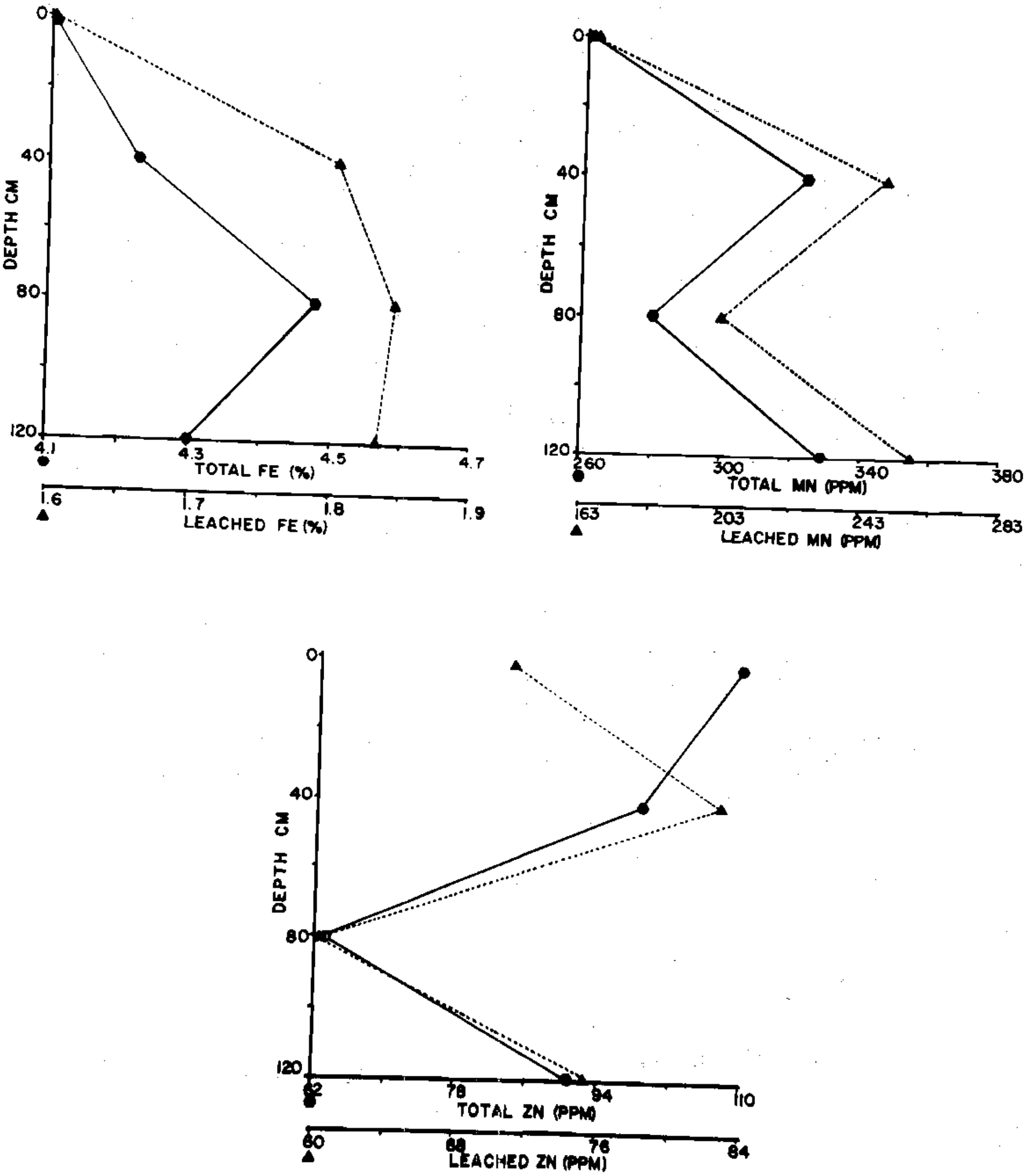


Figure 9. Vertical Distribution of Total and Leachable Fe, Mn and Zn with Depth in the Channel Sediments

representative cores in Figures 10 and 11. The Hell Gate area shows, on the average, higher concentrations of Mn than the Thunderbolt area. The total Mn in Hell Gate varies between 98 and 900 ppm, with an average 420 ppm. In Thunderbolt, Mn varies between 90 and 1280 ppm, the average being 380 ppm. The leachable Mn characteristically shows a maximum around 20-40 cm. Approximately 20-25 per cent of the total Mn is leachable.

Total and leachable Mn in the river channel sediments is uniform with depth. The vertical distribution has been listed in Appendix II and illustrated in Figure 9. The average total Mn is 300 ppm, which is lower than the marsh sediments. Approximately 60 per cent of the total Mn in channel sediments is leachable.

Zinc

Zn in the marsh sediments has a higher concentration than Cu, Co and Ni. Both areas of study show similar concentrations of Zn in the sediments. The vertical distribution of total and leachable Zn in both areas is given in Appendix II and illustrated for representative cores in Figures 12 and 13.

In the Thunderbolt area total Zn varies between 51 and 290 ppm, the average being 100 ppm. Average leachable Zn is 90 ppm. In the Hell Gate area, total Zn varies between 35 and 140 ppm with an average of 102 ppm. The average

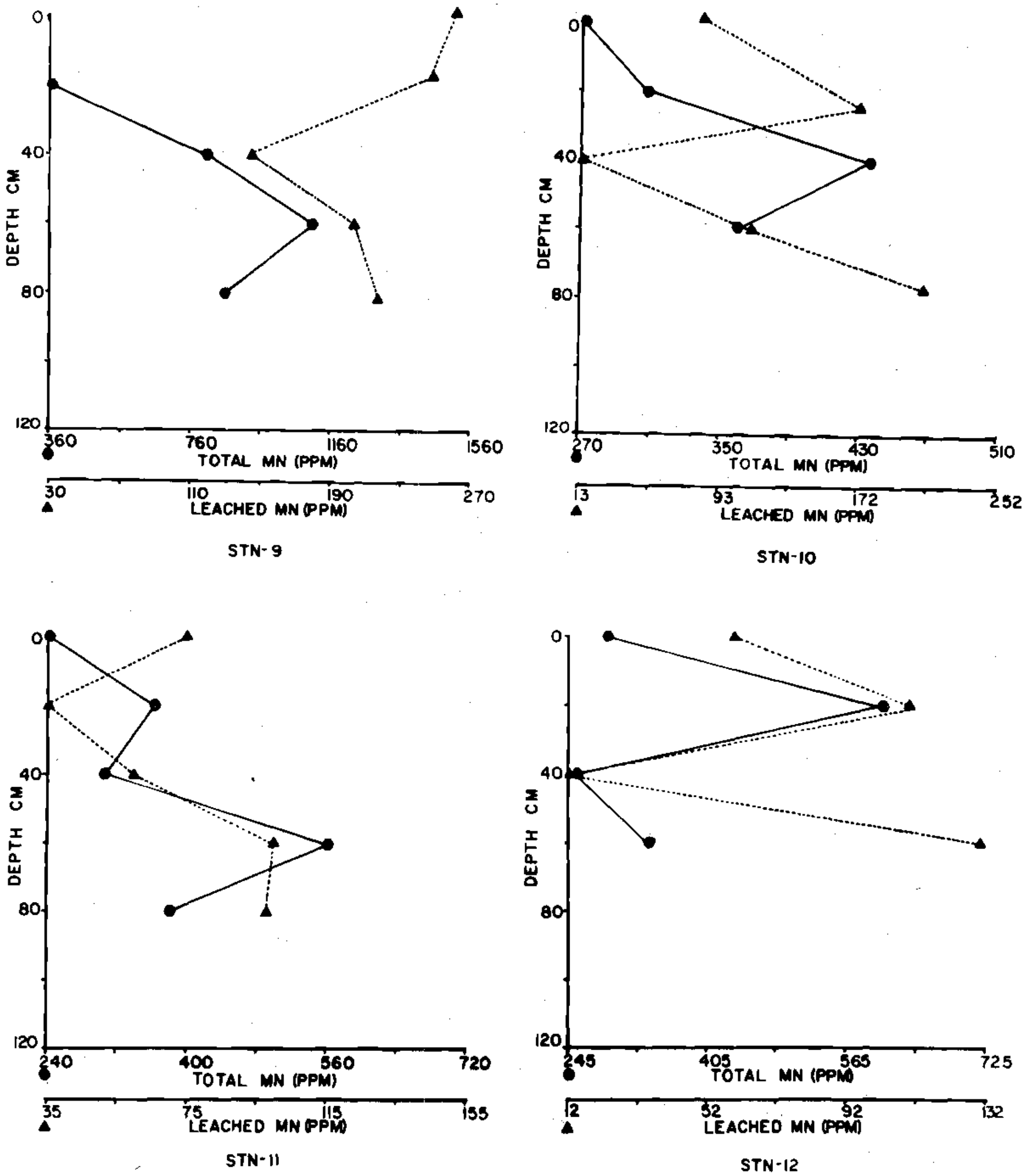


Figure 10. Vertical Distribution of Total and Leachable Mn with Depth in Representative Cores from the Thunderbolt Area

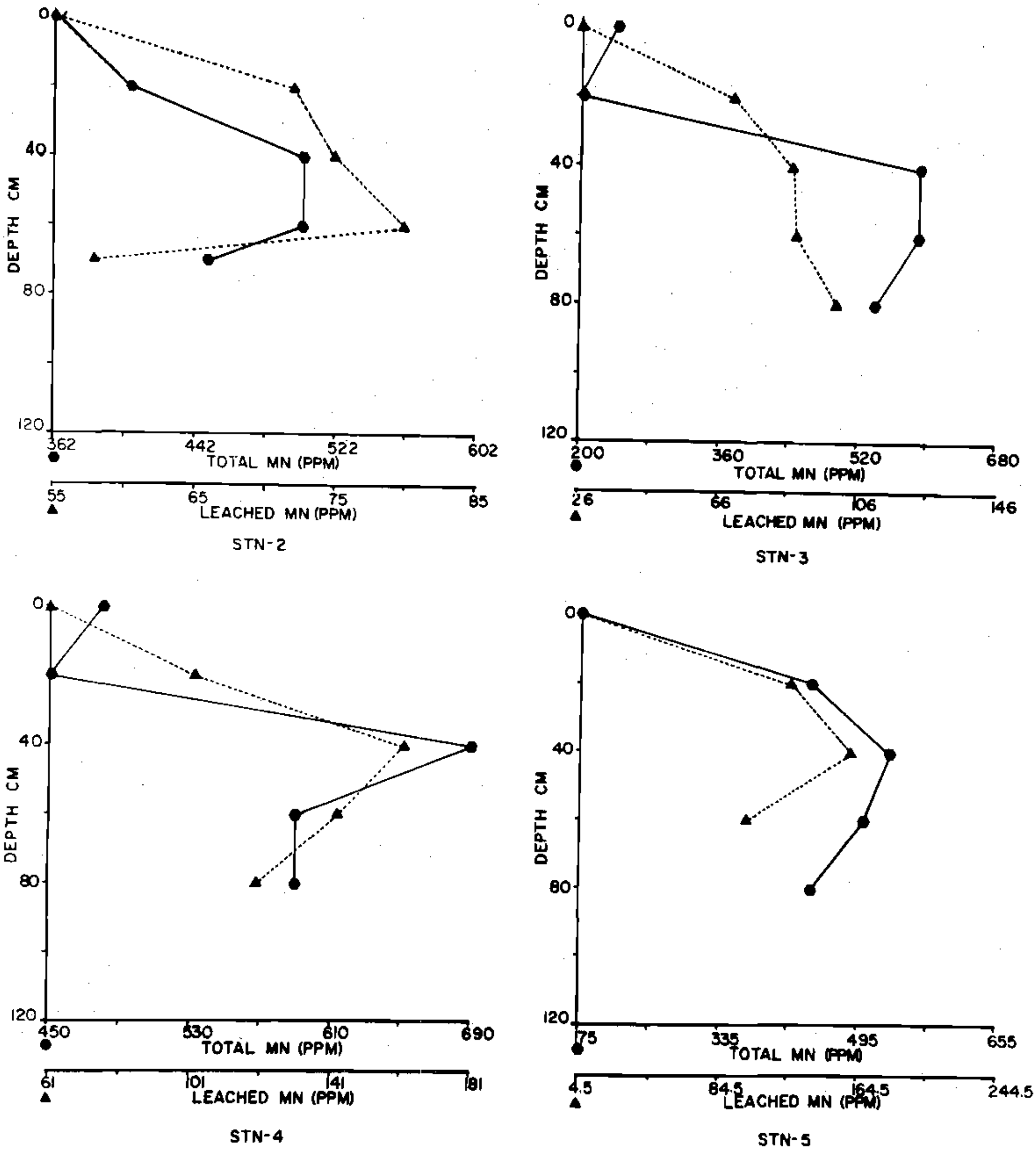


Figure 11. Vertical Distribution of Total and Leachable Mn with Depth in Representative Cores from the Hell Gate Area

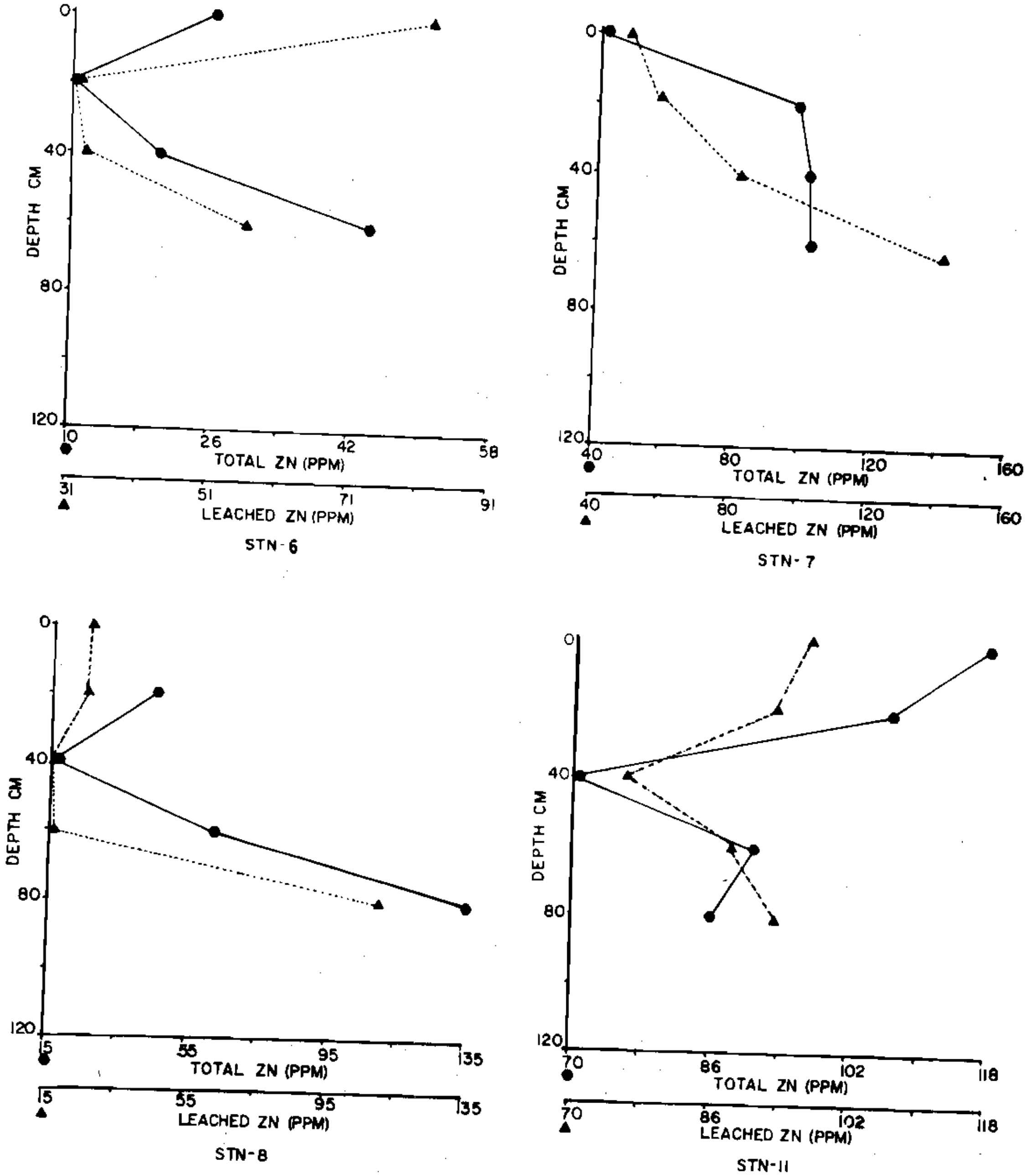


Figure 12. Vertical Distribution of Total and Leachable Zn with Depth in Representative Cores from the Thunderbolt Area

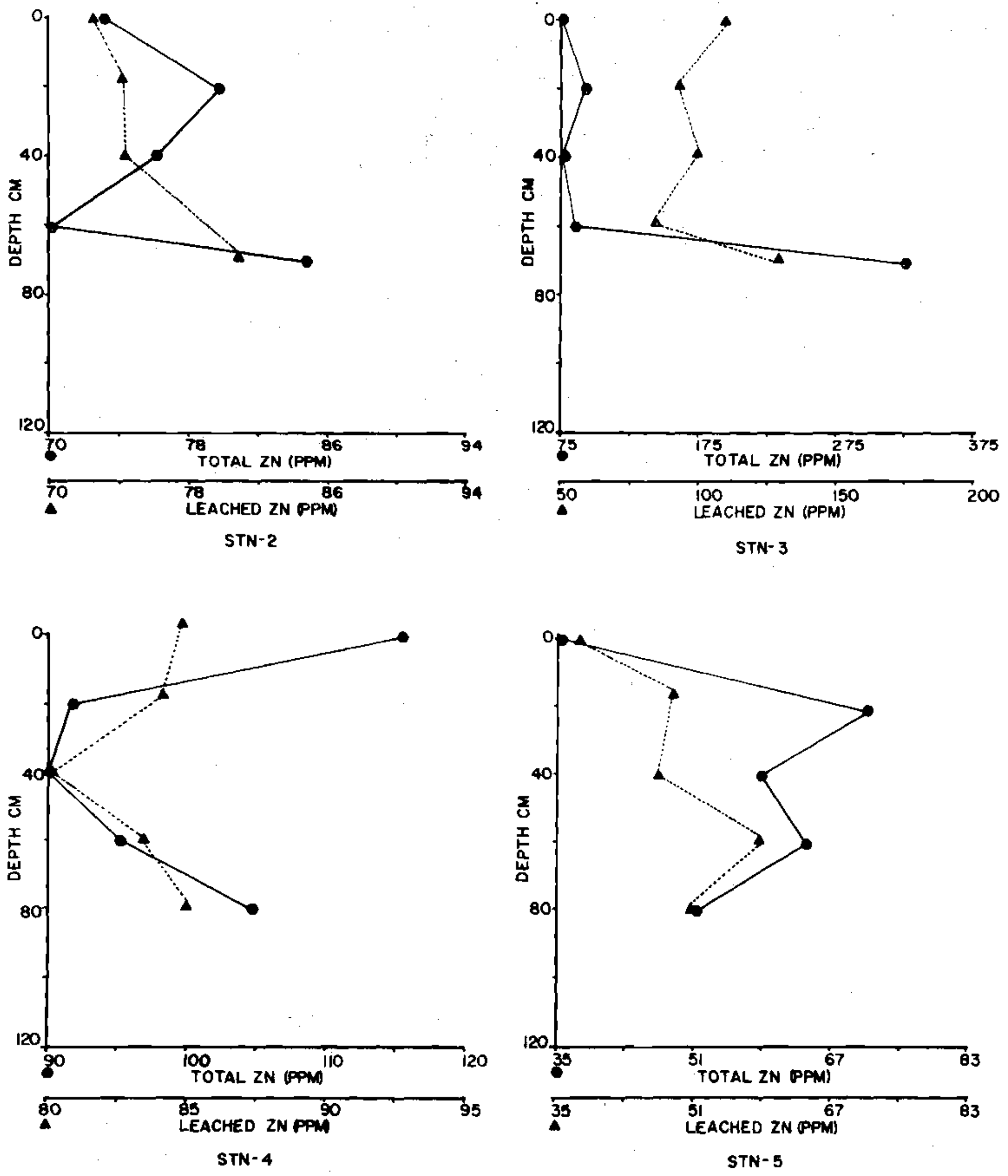


Figure 13. Vertical Distribution of Total and Leachable Zn with Depth in Representative Cores from the Hell Gate Area

leachable Zn in Hell Gate is also 90 ppm. This indicates that about 90 per cent of Zn in the marsh sediments is authigenic. The channel sediments show uniform Zn with depth (Figure 9 and Appendix II). Most of the Zn in these sediments (95 per cent) is leachable.

Copper, Cobalt and Nickel

The vertical distributions of Cu, Ni and Co with depth in representative marsh sediment cores are shown in Figures 14, 15 and 16. Cu, Co and Ni show relatively uniform distribution with depth and the average total concentration of trace metals ranges below 35 ppm. In the leached fraction, the average concentrations of Cu, Co and Ni are all below 20 ppm. The river channel sediments also show a uniform concentration of Cu, Co and Ni with depth (Figure 17).

Mercury

The concentration of Hg in the salt marsh sediments is relatively uniform (Figure 18) and low with values significantly higher occurring in adjacent channel sediments (Appendix II).

Size Analyses

The grain size analyses for the cores from both areas and the channel sediments is listed in Table 1. The Thunderbolt area sediments show a fairly uniform grain size composition with depth. Stations 1 to 4 in the Hell Gate area

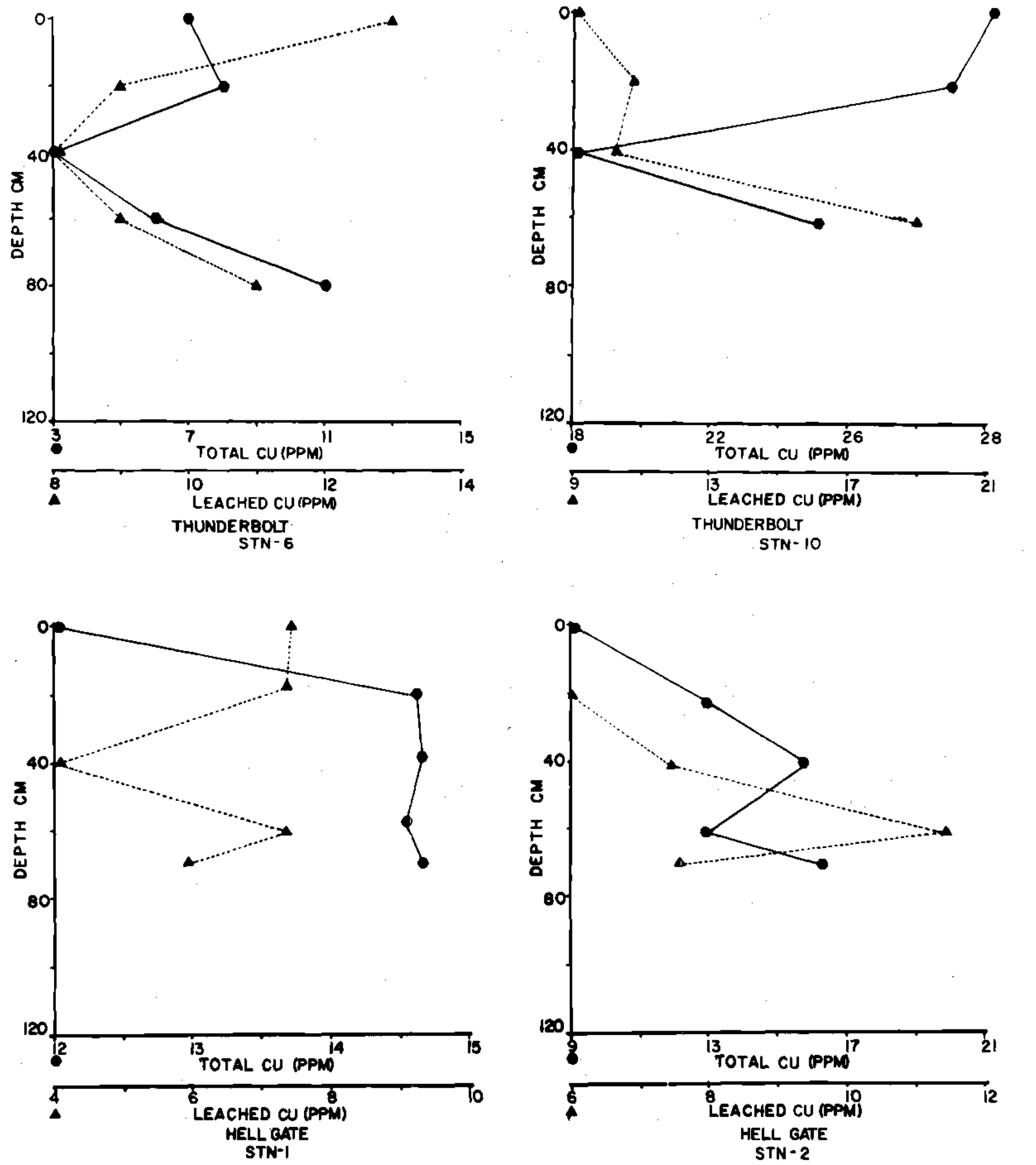


Figure 14. Vertical Distribution of Total and Leachable Cu with Depth in Representative Cores from the Thunderbolt and Hell Gate Study Areas

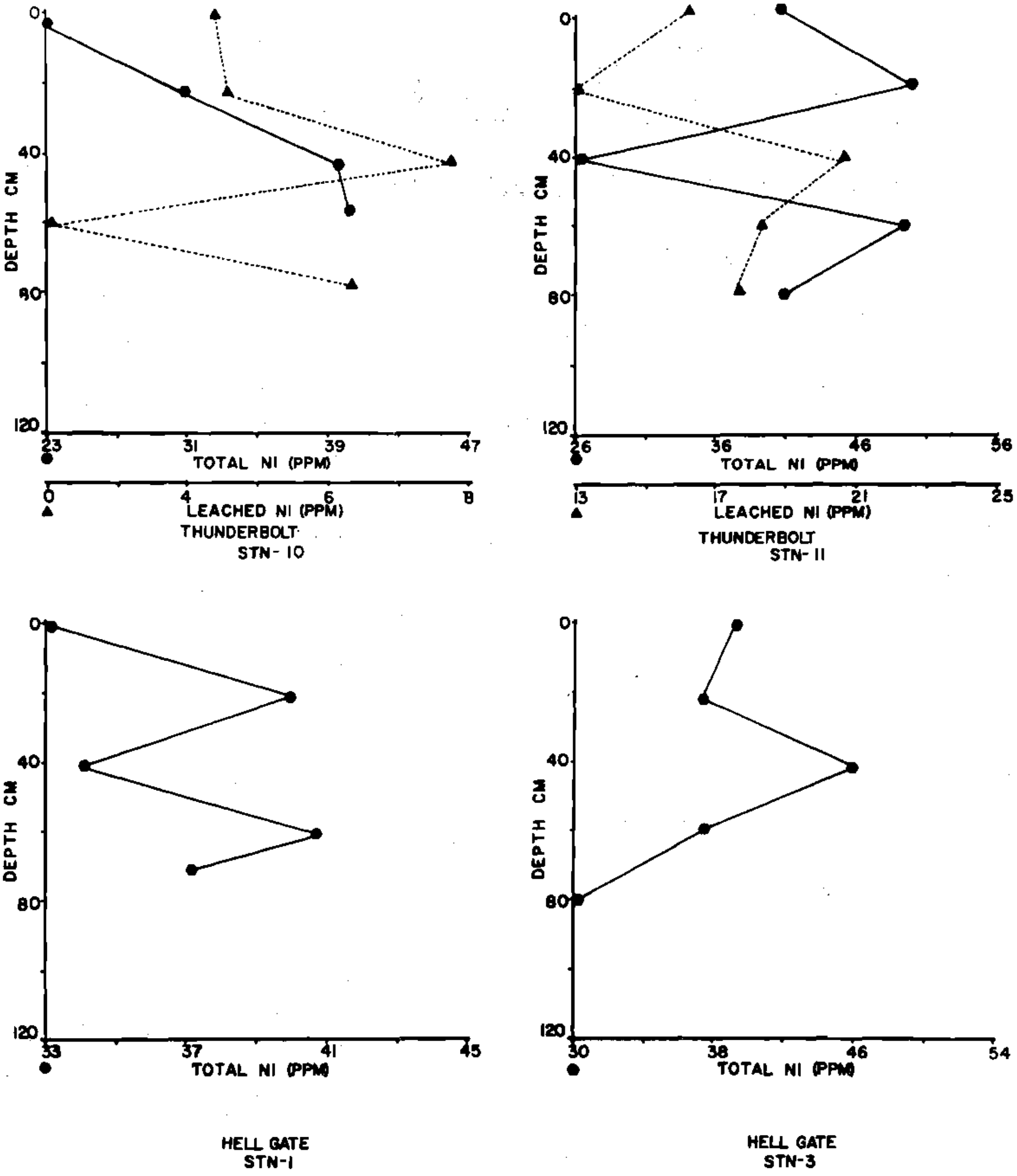
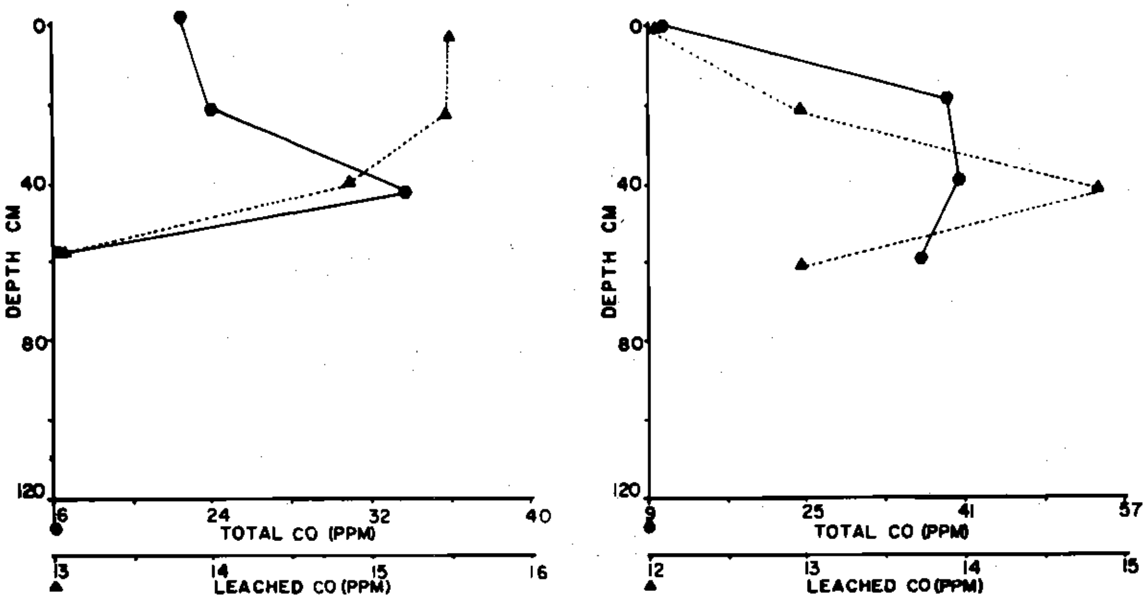
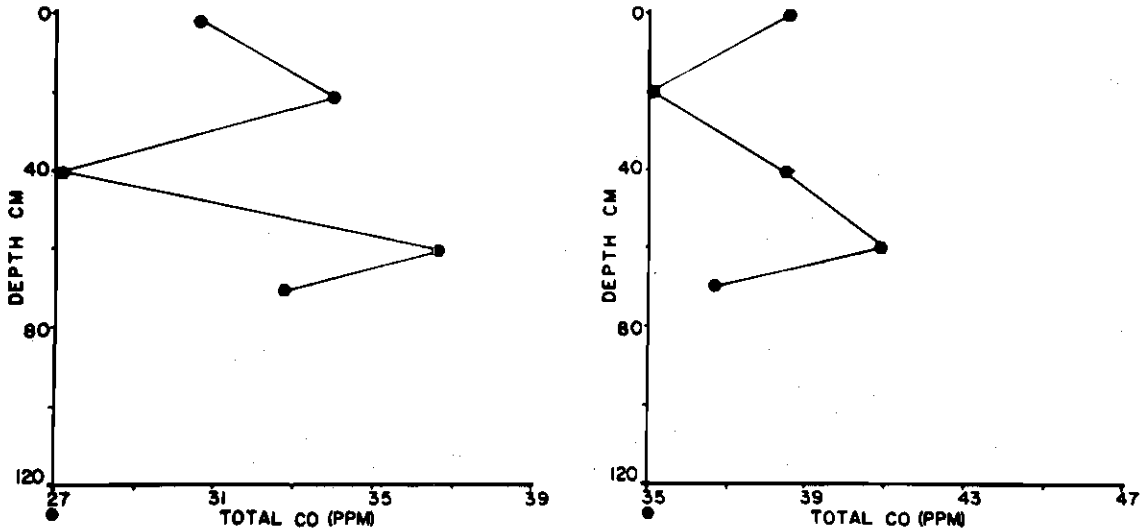


Figure 15. Vertical Distribution of Total and Leachable Ni with Depth in Representative Cores from the Thunderbolt and Hell Gate Study Areas



THUNDERBOLT
STN- 6

THUNDERBOLT
STN- 7



HELL GATE
STN-1

HELL GATE
STN-2

Figure 16. Vertical Distribution of Total and Leachable Co with Depth in Representative Cores from the Thunderbolt and Hell Gate Study Areas

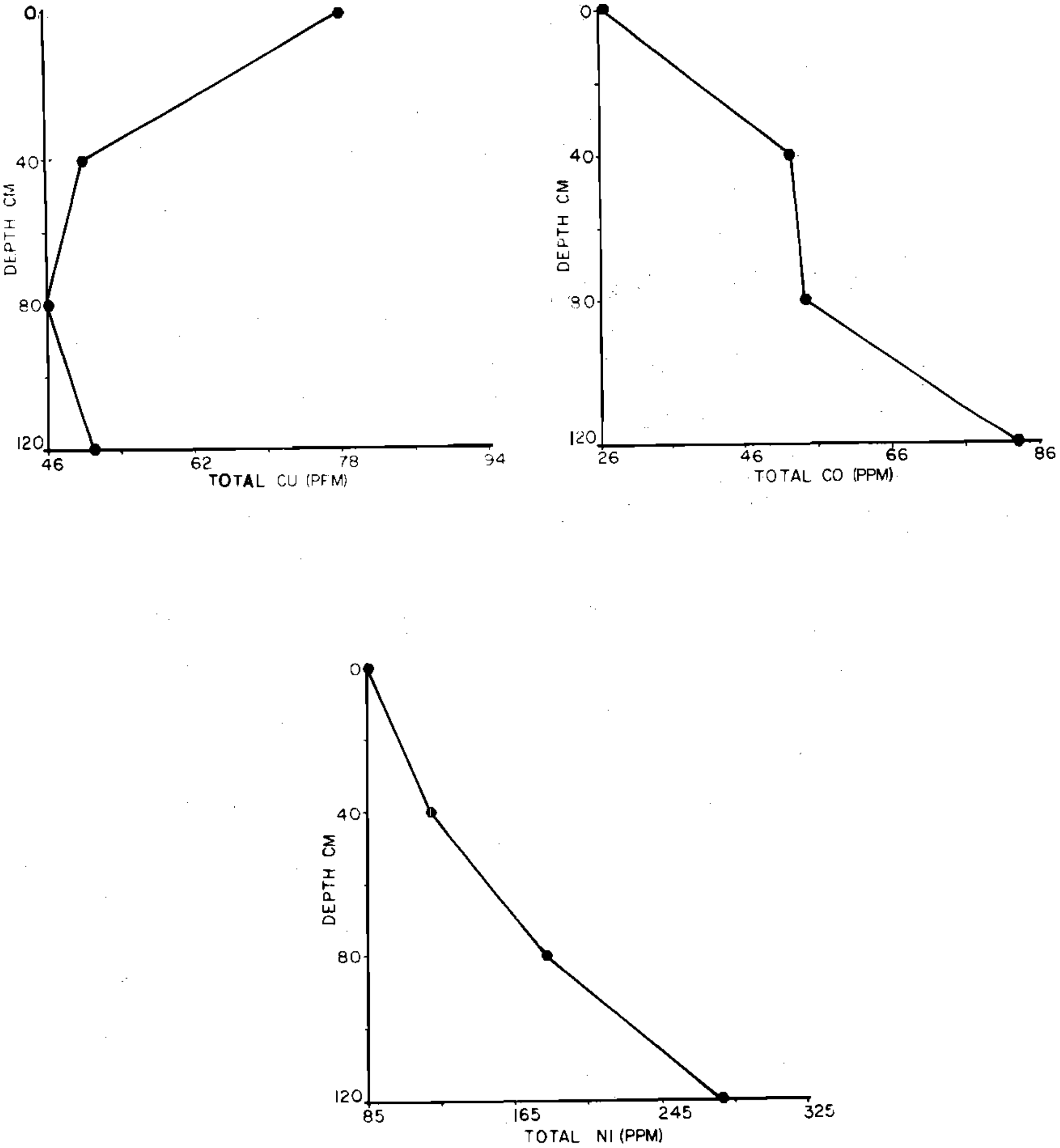


Figure 17. Vertical Distribution of Total Cu, Co and Ni with Depth in the Channel Sediments

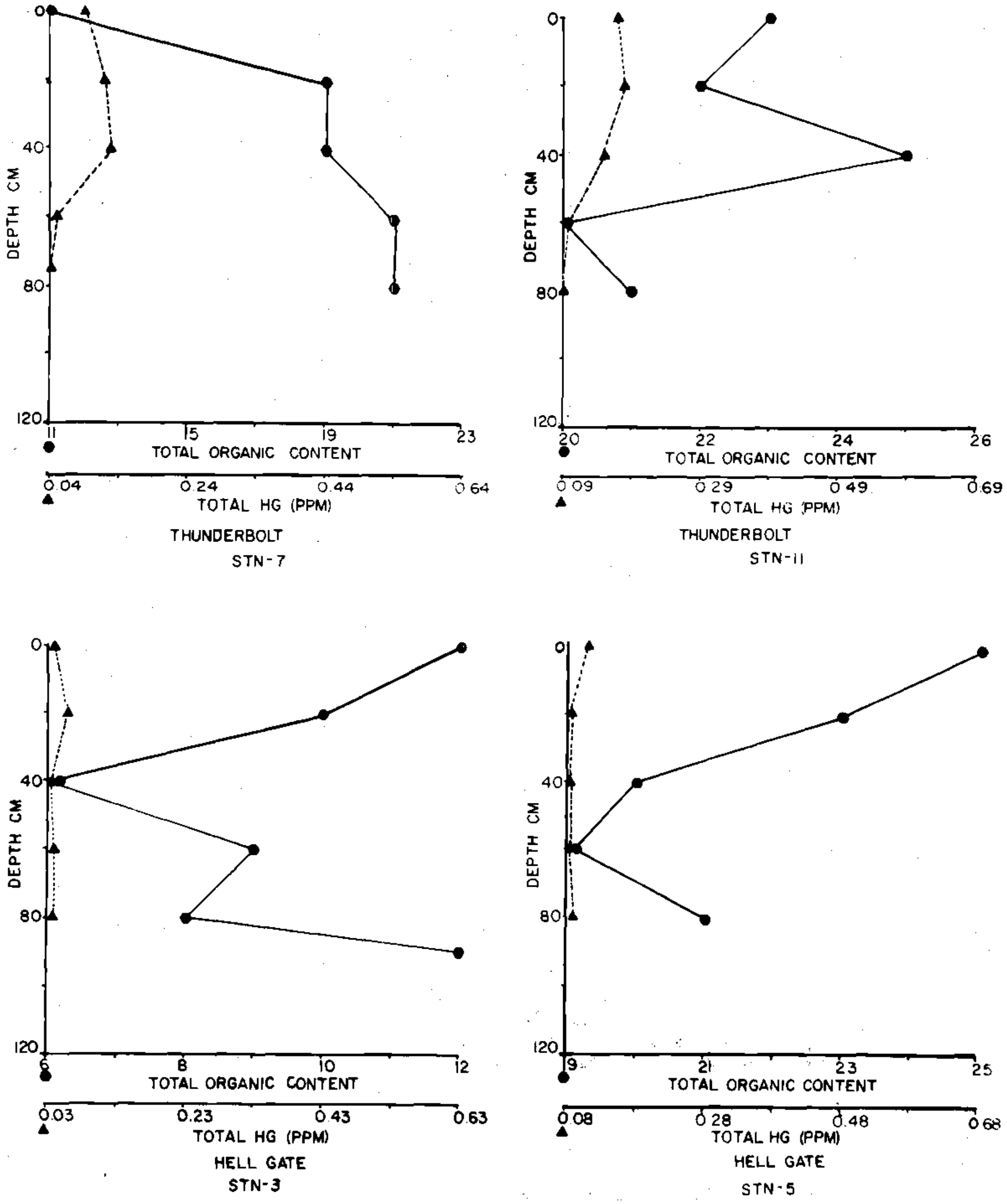


Figure 18. Vertical Distribution of Hg and Total Organic Material in Cores from the Thunderbolt and Hell Gate Study Areas

(Fig. 3) show coarser grain size with approximately 60-65 per cent of the sediment coarser than 62 microns. The channel sediments consist of approximately 80 per cent of the sediment finer than 62 microns with 54 per cent clay fraction. No significant variations in grain size with depth is found in either marsh or channel sediments.

Clay Mineralogy

The amount of clay material in sediments in both areas is also listed in Table 1. The three major clay minerals in the sediments in both areas are kaolinite (7Å), montmorillonite (14Å) and illite (10Å), with their average percentages being 35, 15 and 50 per cent, respectively. No significant variation in the clay mineral composition with depth is observed.

Organic Content

The total organic content of marsh sediments with depth in both areas is listed in Appendix II and illustrated for representative cores in Figure 18. Organic material is more closely associated with silts and clays than with sands.

Table 1. Results of Grain Size and Clay Analyses

Size Analyses

Location	Depth (cm)	Calculated Percentages		
		Clay%	Silt%	Sand%
Hell Gate				
Station 1	0	20	19	61
	20	25	17	58
	40	17	18	65
	60	25	15	60
Station 3	0	30	15	55
	20	22	15	63
	40	20	13	67
	60	20	20	60
Station 5	0	56	30	15
	20	66	26	8
	40	33	56	11
	60	53	38	9
Thunderbolt				
Station 1	0	55	37	8
	20	49	35	12
	40	53	41	9
	60	58	34	8
Station 3	0	42	48	10
	20	56	29	15
	40	48	36	16
	60	55	33	12
Station 5	0	50	35	15
	20	43	37	20
	40	56	33	11
	60	45	39	16
Thunderbolt Channel Sediment				
	0	48	42	10
	40	17	63	20
	80	40	24	36
	120	35	40	25

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CHAPTER IV

DISTRIBUTION OF METALS IN SALT MARSH SEDIMENTS

Basic Chemical Model for Salt Marsh Sediment System

The principal species of carbon and sulfur in an aerobic marine environment would be HCO_3 and $SO_4^=$ (Berner, 1970). The decrease in oxygen which makes the sediments reducing is due to oxidation of organic matter contained in the sediments and reduced metabolites of anaerobic microorganisms. Surface sediments of salt marshes are occupied by anaerobic bacteria which rapidly consume oxygen during oxidation or organic matter in this layer. The organic matter is composed mostly of the detritus of Spartina alterniflora. Due to consumption of oxygen in the surface layer, sediment beneath is dominated by anaerobic bacteria which further utilize the remaining organic matter. This results in an Eh profile in the natural marsh sediments as shown in Figures 5 and 6. These profiles are similar to those obtained by Bonatti, et al., (1970) for hemipelagic sediments which ranged from +100 Mv for the upper zone to about -400 Mv in the lower zone (∿1 m).

Sulfur is added to the sediments in two forms: organic sulfur compounds and dissolved $SO_4^=$, producing species such as H_2S, HS^- and $S^=$ depending on pH and Eh (Garrels and Christ, 1965). Evidence of this is seen from the sulfide data in the marsh sediments which show that sulfide increases as the sediments become more reducing.

The interrelation of Eh (redox potential), pH and $S^{=}$ can be demonstrated by the following oxidation-reduction reactions:

$$2\ CH_2O + SO_4^{=}\ aq \longrightarrow 2\ HCO_3^{-}\ aq + H_2S\ aq \qquad (1)$$

$$2\ CH_2O + SO_4^{=}\ aq \longrightarrow HCO_3^{-}\ aq + HS^{-}\ aq + CO_2\ aq + H_2O\ aq \qquad (2)$$

$$CH_2O + SO_4^{=} + H_2O + 4e^{-} \longrightarrow CO_2 + S^{=} + 4OH^{-} \qquad (3)$$

The reduction of $SO_4^{=}$ to $S^{=}$ (Eq 3) is an important process controlling the sulfide concentrations in the marsh sediments and its dependence on Eh and pH can be represented by the following equation:

$$Eh = Eo + \frac{0.059}{4} \log \frac{(CH_2O)\ (SO_4^{=})\ (H_2O)}{(P_{CO_2})\ (S^{=})\ (OH^{-})^4} \qquad (4)$$

Eo = +.487 volts [Calculated from the free energy values from Garrels and Christ (1965)] . For Eq (4), Eh = -.131 volts at $SO_4^{=} = 10^{-2}$ and $P_{CO_2} = 10^{-8}$. pH = 7.1.

CH_2O represents organic matter. As Eh is decreased, reduced species and OH^{-} increase as shown in Figures 5 and 6.

Model for Processes of Trace Metal Distribution in Salt Marsh Sediments

In preparing a model for salt marsh sediments, various processes controlling the distribution of trace metals must be considered. The mobilization and movement of trace metals should be controlled by the redox potential, diffusion of dissolved chemical species in interstitial waters and advection due to sedimentation and compaction. It is assumed that the movement of interstitial solutions is vertical only. Uptake of trace metals from marsh sediments brought about by plants (*Spartina alterniflora*) may be an important mechanism for removal from salt marsh sediments. Clay minerals and organic matter are natural materials that have a capacity to exchange sorbed ions with those ions in solution and may have certain effects on the trace metal distribution. The trace metals may also be tied up as their organic complexes. The present data, however, is inconclusive regarding the control of clays and organic matter on the trace metal distribution in sediments. A basic assumption in the consideration of the present model for trace metal distribution in salt marsh sediments is that the metals are supplied to the sediment surface due to sedimentation.

Oxidation-Reduction Reactions

At their reduced valence, Fe, Mn, Cu, Co and Ni are more soluble than in their oxidized states in natural systems

(Bonatti, *et al.*, 1970). As a result, a concentration gradient should be established in the pore solution across the oxidation-reduction interface of the sediments and these elements should be concentrated in pore solutions below this interface. Such a gradient should cause upward migration of trace metals by diffusion. For an oxidation reduction reaction of the type:

$$bB + cC = dD + eE + ne^-$$

the abundance of various trace metals in various redox conditions can be calculated from the equation:

$$Eh = Eo + \frac{0.059}{n} \log \frac{a_D^d a_E^e}{a_B^b a_C^c}$$

where Eh = oxidation reduction potential in volts

Eo = voltage of the reaction when all substances involved are unit activity

n = number of electrons

a = activity

Diffusion-Advection

The process regulating the distribution of dissolved chemical species in the interstitial waters is diffusion accompanied by advection. The following assumptions would have to be made to set up a model for migration of trace metals due to diffusion-advection following Anikouchine

(1967).

1) The movement of the solution is vertical only ($\frac{\partial V}{\partial X} = 0$) and a one dimensional model is possible.

2) Diffusion is through interstitial solution and the overall diffusion coefficient is proportional to porosity.

3) The sediment compacts as it is buried under thickening new layers.

4) The sediment has an impermeable base that determines the boundary conditions for the flow.

The local change in concentration is then given by:

$$\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial X^2} = \frac{V \partial C}{\partial X} \qquad (1)$$

The second order term describes Fickian diffusion with a constant coefficient of diffusivity D_s. Advection at the depth x with the fixed basement is described by the product $\frac{V \partial C}{\partial X}$, where V in the velocity of expelled interstitial water and $\frac{\partial C}{\partial X}$, the concentration gradient.

In applying equation (1) to the marsh sediment, advection can be neglected since the movement of the water towards the interface is countered by interface movement during sediment accumulation (Anikouchine, 1967). Equation (1) can therefore be simplified to:

$$\frac{\partial c}{\partial t} = D_s \frac{\partial^2 C}{\partial X2} \qquad (2)$$

From equation (2) it can be seen that the main factor controlling the movement of trace metals upwards toward the oxidizing environment can be expressed as the diffusion flux by the equation:

$$J = \Phi \, D_S \frac{\partial C}{\partial X} \qquad (3)$$

where J = diffusion flux vector in mass/area of sediment/time

C = concentration in mass per unit volume

D_S = diffusion coefficient in the sediment $\cong 10^{-5}$ cm^2/sec (Berner, 1970)

Φ = porosity = .85 (Emery, 1960)

Uptake by Plants

Williams and Murdoch (1969) have suggested the potential importance of marsh plants (*Spartina alterniflora*) in the removal of Zn, Mn and Fe from marsh sediments. The annual production of *Spartina alterniflora* is approximately 700 $g/m^2/yr$ (J. Gallager, personal communication), most of which is lost or returned to these sediments in the form of plant detritus. Trace metals are necessary for the plants to perform certain biological functions within its system. Sediments supply these trace metals to the plants. The concentration of various trace metals found in *Spartina alterniflora* from both areas have been listed in Table 2.

Supply by Sedimentation

Trace metals are added to the salt marsh by depositing

Table 2. Results of Marsh Grass (*Spartina alterniflora*) Analyses

Trace Metal Concentrations (ppm dry wt.)
in *Spartina alterniflora*
(in leaves and stalks combined)

	Fe	Mn	Zn	Cu	Co	Ni	Hg
Hell Gate Station							
1	2600	105	20	8	10	20	1.0
3	1100	50	11	5	15	25	1.0
4	1900	130	14	7	9	10	1.2
6	700	75	19	4	13	15	0.8
Thunderbolt Station							
1	1400	76	15	10	21	17	1.0
2	1600	120	17	8	8	21	1.1
5	800	55	16	4	16	11	1.0
9	1100	75	25	6	10	9	0.9

sediments. The accretion rate for various trace metals can be calculated from the trace metal concentration in the surface sediments and the sedimentation rate.

From the above considerations, a model for the supply and removal of trace metals can be set up as illustrated in Figure 19.

Iron Distribution in Salt Marsh Sediments

To obtain a more quantitative understanding of the factors controlling the distribution of Fe in the marsh sediments, information regarding the presence and abundance of species can be obtained from the Eh and pH data. Since Fe exhibits two oxidation states (Fe^{2+} and Fe^{3+}), stability of these species in solution must be a function of the redox state of the system. Goldberg (1954) has suggested that under oxidizing conditions Fe may be present as hydrated ferric oxide or hydroxide.

Many researchers (Lynn and Bonatti (1965), Jenne (1968), Chester and Hughes (1966) and Turner and Harriss (1970)) have suggested that Fe is released to interstitial fluids as ferrous iron after reduction and diffuses in response to redox potential variations. Calculations for the abundance of Fe^{2+} and Fe^{3+} can be made using Eh and pH values obtained in the natural marsh. The boundary between Fe^{2+} and Fe^{3+} stability fields can be determined by the following equations:

$$Fe^{2+}\ aq = Fe^{3+}\ aq + e$$

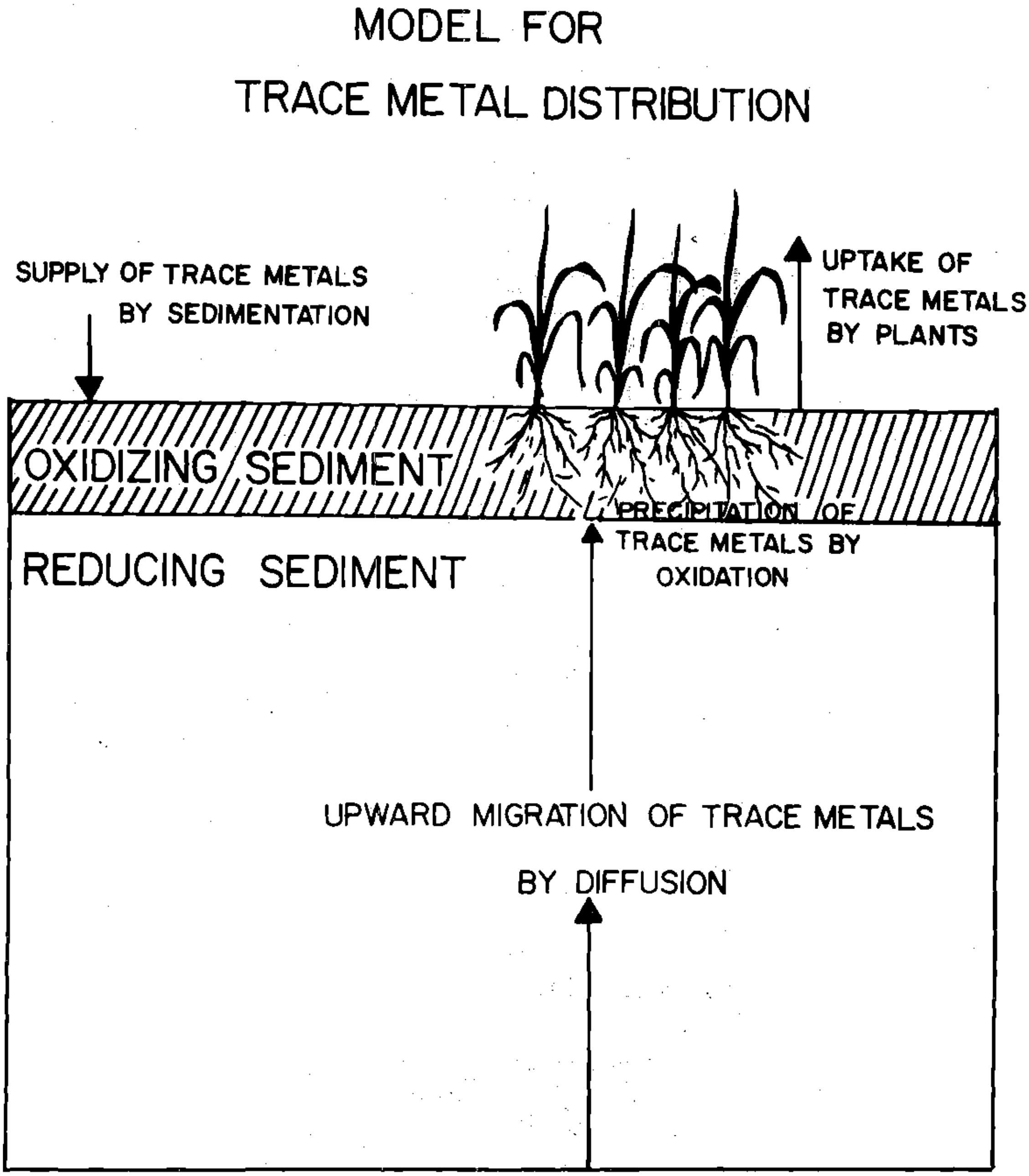

Figure 19. Model for Trace Metal Distributions in Marsh Sediments Showing Various Processes Involved in the Supply and Removal of Trace Metals from Sediments

For this reaction:

$$Eh = Eo + 0.059 \log\left[\frac{Fe^{3+}}{Fe^{2+}}\right]$$

Under the condition that Fe^{2+} aq = Fe^{3+} aq, Eh = Eo = 0.771 volts (Garrels and Christ, 1965). Hence, under the Eh, pH conditions found in natural salt marsh sediments, the major Fe species is Fe^{2+}. The abundance of Fe^{2+} would increase with a greater reducing environment. This would cause a concentration gradient in the Fe^{2+} present in the interstitial waters and the leachable fraction of the sediments, resulting in the diffusion of Fe^{2+} species upwards towards the oxidizing environment.

The iron distribution in salt marsh sediments as seen theoretically from the above discussion should show a vertical concentration gradient, if all the iron is mobile. However, due to chemical reactions within the sediment and interstitial waters, localized precipitation of Fe and other trace elements may occur. Berner (1970) has shown that in sulfate reducing sediments hydrogen sulfide formed can leach many of the non-resistant iron containing minerals to form iron monosulfide. The reaction rate of such chemical reactions, however, is extremely slow (Anikouchine, 1967). If the concentration of Fe^{2+} in the interstitial waters is only affected by diffusion and if deposition due to chemical reactions is negligible, the diffusion flux can be calculated using the following equation:

$$J = \Phi D_s \frac{\partial C}{\partial X} \qquad (3)$$

where $\frac{\partial C}{\partial X}$ is the concentration gradient with depth for Fe and can be calculated from the experimental data (Appendix II) assuming maximum mobile Fe = leachable Fe.

The calculated average flux for cores in the Thunderbolt and Hell Gate areas is listed in Table 3. The Thunderbolt area, with a higher concentration of Fe than the Hell Gate area, has a greater theoretical flux rate. It should be noted that the average calculated flux is a maximum value. From the estimations made for deposition, removal and concentration of iron in the marsh sediments (Table 3), about 2 per cent of leachable Fe supplied by sedimentation and upflux is taken up by plants.

Fe in the salt marsh can be summarized in the following way: Fe is brought to the marsh sediments in the form of particulate material. The part of Fe which is not tied up as insoluble sulfide would be mobilized by reducing conditions and would diffuse toward the surface until it is taken up by the root system of the marsh grass or concentrated in the oxidized layer. Fe may then be transported out of the marsh as plant detritus (Williams and Murdoch, 1969) or recycled within.

Table 3. Budget Calculations for Iron in Natural Salt Marsh

Marsh sedimentation rate = 1 mm/yr
or ≅ 0.50 mm/yr (dry wt)[1]

Annual production of *Spartina alterniflora*
≅ 700 $g/m^2/yr$ (dry wt)[2]

	Thunderbolt	Hell Gate
Average Maximum Fe Upflux in Reducing Sediment	127.0 $g/m^2/yr$	54.0 $g/m^2/yr$
Average Fe Accretion Rate in the Sediment	30.0 $g/m^2/yr$	20.0 $g/m^2/yr$
Leachable Fraction in Accreted Fe	5.0 $g/m^2/yr$	3.0 $g/m^2/yr$
Total Maximum Leachable Fe Available to the Plants by Upflux and Sedimentation	132.0 $g/m^2/yr$	57.0 $g/m^2/yr$
Fe Uptake by Plants	1.5 $g/m^2/yr$	0.9 $g/m^2/yr$
% Available Fe Removed by Plants	1%	2%

---

[1] Rate taken from that theoretically calculated by Rusnak (1967)

[2] Average annual production rate determined by infrared aerial photography (Gallager, 1972)

Manganese Distribution in Salt Marsh Sediments

The predominant Mn species in the reducing environment is Mn^{2+}. Dissolved Mn^{2+} is unstable in an oxidizing environment and is rapidly oxidized and precipitated as manganic oxide. The abundance of Mn^{2+} in environments of varying redox potential can be calculated from the Eh data using the following reaction:

$$Mn^{2+} + 2H_2O \longrightarrow MnO_2 + 4H^+ + 2e^-$$

For this reaction:

$$Eh = Eo + \frac{0.059}{2} \log \frac{(MnO_2)(H^+)^4}{(Mn^{++})(H_2O)^2}$$

Eo = 1.29 volts (calculated from free energy values taken from Garrels and Christ, 1965).

Solving for log Mn^{2+}:

$$\log Mn^{2+} = -\left[\frac{Eh - 1.29}{0.0295} + 4pH\right]$$

It can be seen from the above equation that under the pH conditions found in the natural salt marsh environment the log Mn^{2+} would increase as the Eh decreases (is more reducing). This would cause a concentration gradient in Mn^{2+} present in the interstitial waters and the leachable fraction of the sediments. Such a gradient between oxidizing and reducing interfaces would lead to diffusion of Mn^{2+} to the oxidizing interface where precipitation would take place. This is also seen from experimental data which shows a maximum for Mn around 20-40 cms in the marsh sediment (Figs. 10 and 11).

A flux for the upward diffusion of Mn^{2+} towards the oxidizing environment can be calculated using Eq. (3) ($J = \Phi D_s \partial C/\partial X$) assuming: $D_s = .3 \times 10^{-5}$ (Anikouchine, 1967), and maximum mobile Mn = Leachable Mn. The calculated average flux for Thunderbolt and Hell Gate areas is listed in Table 4. From the estimations made for deposition, removal and concentration of Mn in the marsh sediments (Table 4), about 6 per cent of leachable Mn supplied by sedimentation and upflux is taken up by plants.

Mn in the salt marsh can be summarized in the following way: Mn is brought in the salt marsh sediments in the form of particulate material. It is then mobilized by reducing conditions at depth and diffuses toward the surface where it concentrates and is partly taken up by the root system of the marsh grass. The manganese may be then transported out of the marsh as plant detritus (Williams and Murdoch, 1969) or recycled within.

Zinc Distribution in Salt Marsh Sediments

Most of Zn (90-95 per cent) in the marsh sediments is authigenic (leachable)(Appendix II). It has been suggested that Zn in sediments is largely associated with organic matter (Brooks, *et al.*, 1968). The present data also shows such a correlation (Fig. 20). Zn in the sediments enhibits

Table 4. Budget Calculations for Manganese in Natural Salt Marsh

Marsh sedimentation rate = 1 mm/yr
or ≅ 0.50 mm/yr (dry wt)[1]

Annaul production of *Spartina alterniflora*
≅ 700 $g/m^2/yr$ (dry wt)[2]

	Thunderbolt	Hell Gate
Average Maximum Mn Upflux in Reducing Sediment	2.00 $g/m^2/yr$	1.70 $g/m^2/yr$
Average Mn Accretion Rate in the Sediment	0.4 $g/m^2/yr$	0.3 $g/m^2/yr$
Leachable Fraction in Accreted Mn	0.08 $g/m^2/yr$	0.06 $g/m^2/yr$
Total Maximum Leachable Mn Available to the Plants by Upflux and Sedimentation	2.08 $g/m^2/yr$	1.76 $g/m^2/yr$
Mn Uptake by Plants	0.11 $g/m^2/yr$	0.13 $g/m^2/yr$
% Available Mn Removed by Plants	5%	7%

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[1] Rate taken from that theoretically calculated by Rusnak (1967)

[2] Average annual production rate determined by infrared aerial photography (Gallager, 1972)

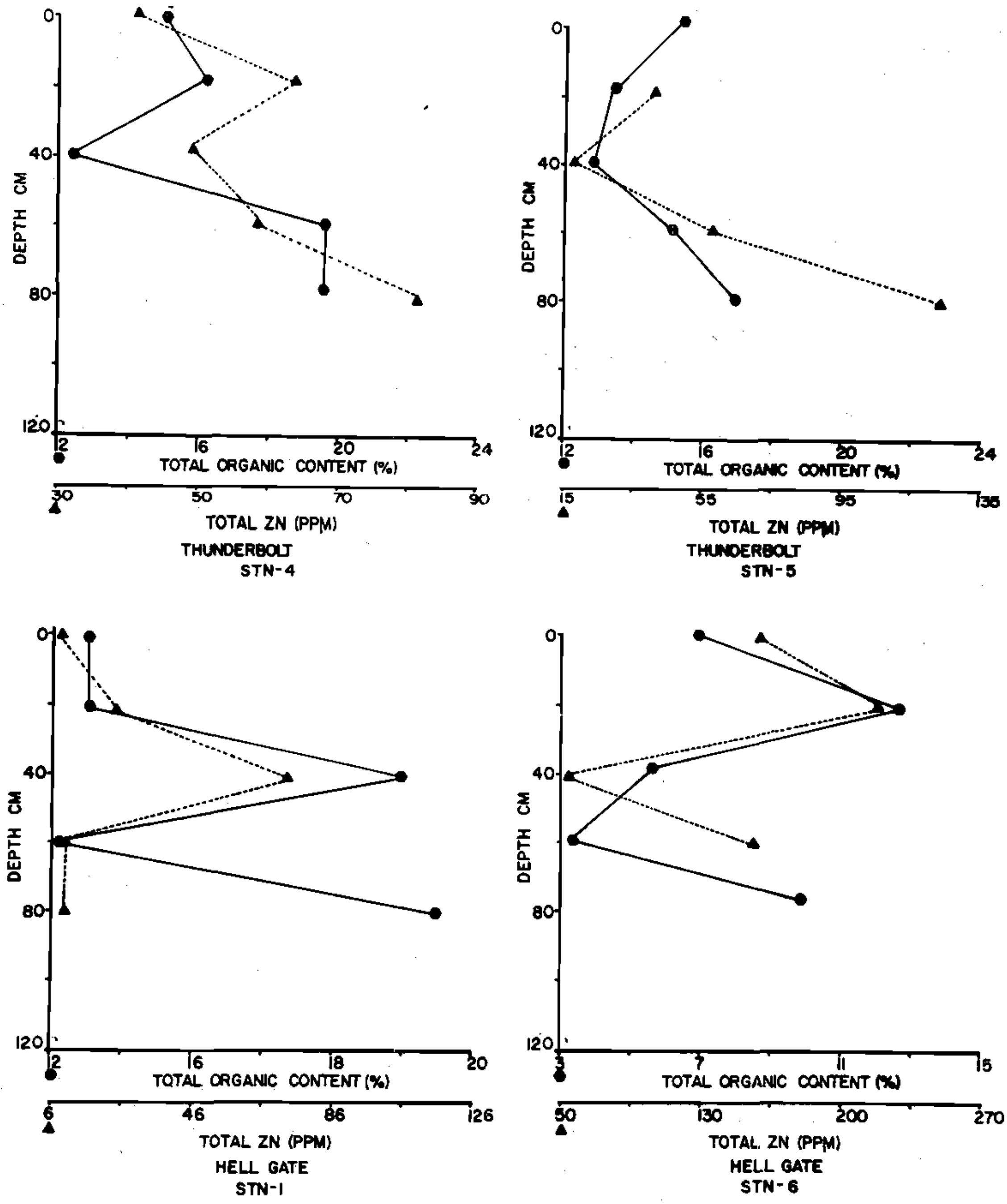

Figure 20. Correlation with Depth of Zn and Total Organic Material in the Thunderbolt and Hell Gate Study Areas

one oxidation state, Zn^{2+}. The redox potential therefore has no direct control on the distribution of Zn^{2+}. Zn distribution is mainly controlled by sulfide and oxygen concentration in the sediments which leads to its precipitation. In an oxidizing environment, Zn may be precipitated as its oxide or hydroxide. Zinc has a high affinity for sulfur. In the presence of sulfur, Zn^{2+} is very insoluble forming stable ZnS, according to the following reaction:

$$Zn^{2+} + S^{=} \longrightarrow ZnS$$

The solubility of Zn^{2+} depends upon the solubility product. Since, $K_{sp} = 1.1 \times 10^{-21}$ (Fischer, 1965)

Then

$$[Zn^{2+}] = \frac{1.1 \times 10^{-21}}{[S^{=}]}$$

From the above equation it can be seen that as $[S^{=}]$ increases more Zn^{2+} would be tied up as ZnS. Sulfide in marsh sediments increases with depth and then maintains a uniform value (Fig. 5 and 6). This would affect the abundance of Zn^{2+} present in the interstitial solution below the oxidizing interface in marsh sediments, with depth, and may cause a chemical potential gradient. Such a gradient would cause the mobile Zn^{2+} in the interstitial solutions in the marsh sediments to migrate by diffusion downward, since it would produce gradient on Zn^{2+} decreasing with depth.

The major process for the removal of Zn from the marsh sediments is uptake by plants. Since there is no upward diffusion of Zn in the marsh sediments, the principal source of supply by Zn to the surface sediments for uptake by plants would be due to sediment accretion. The estimations for the supply and uptake of Zn from the marsh sediments (Table 5) indicate that about 10-15 per cent of Zn supplied to the surface sediments by sedimentation is taken up by plants.

Zn in the marsh sediments can be summarized in the following way: Zn is brought to the salt marsh sediments mainly associated with organic matter. The salt marsh sediments appear to act as a sink for Zn since it tends to diffuse downward. The part of Zn that is taken up by the plants may be removed from the marsh as plant detritus (Williams and Murdoch, 1969) or recycled within.

Copper, Nickel and Cobalt Distribution in Salt Marsh Sediments

Cu, Ni and Co are minor metals in marsh sediments. The post depositional mobility of Cu, Ni and Co can be discussed in terms of their redox potentials.

Cu exhibits two oxidation states Cu^+ and Cu^{2+}. Calculations for the abundance of Cu^+ and Cu^{2+} can be made using the Eh and pH data obtained in the salt marsh sediments. The boundary between Cu^+ and Cu^{2+} stability fields can be determined using the following reaction:

Table 5. Budget Calculations for Zinc
in Natural Salt Marsh

Marsh sedimentation rate = 1 mm/yr
or ≅ 0.50 mm/yr (dry wt)[1]

Annual production of *Spartina alterniflora*
≅ 700 g/m^2/yr (dry wt)[2]

	Thunderbolt	Hell Gate
Average Concentration of Zn in Sediment	100 ppm	102 ppm
Average Zn Accretion Rate in the Sediment	0.1 g/m^2/yr	0.1 g/m^2/yr
Leachable Fraction in Accreted Zn	0.1 g/m^2/yr	0.1 g/m^2/yr
Total Maximum Leachable Zn Available to the Plants by Sedimentation	0.1 g/m^2/yr	0.1 g/m^2/yr
Zn Uptake by Plants	0.013 g/m^2/yr	0.015 g/m^2/yr
% Available Zn Removed by Plants	13%	15%

---

[1] Rate taken from that theoretically calculated by Rusnak (1967)

[2] Average annual production rate determined by infrared aerial photography (Gallager, 1972)

$$Cu^{+} \rightleftharpoons Cu^{2+} + e^{-}$$

For this reaction:

$$Eh = Eo + 0.059 \log \frac{[Cu^{2+}]}{[Cu^{+}]}$$

Under the condition that $Cu^{+}_{aq} = Cu^{2+}aq$, $Eh = Eo =$ $-.159$ V (calculated from the free energy values taken from Garrels and Christ, 1965). Hence, under the Eh, pH conditions found in natural salt marsh sediments, both Cu^{+} and Cu^{2+} would be present. Cu^{+} would be the predominent species when the Eh is below $-.159$ V, and would increase as the Eh decreases with depth. This would cause a concentration gradient in the reducing sediments ($<-.159$ V) causing upward migration of Cu^{+}. A similar gradient would also be established for Cu^{2+} in the sediments with Eh $>-.159$ V.

The upward migration of Cu species in the marsh sediments may, however, be controlled by their precipitation as cuprous and cupric sulfides due to their very low solubility products (Bonatti et al., 1970).

Under the oxidation reduction conditions in the natural salt marsh environment, the major species of Ni and Co would be Ni^{2+} and Co^{2+}, respectively. The redox potential in the marsh sediments would be one of the major factors controlling their abundance in the salt marsh sediment systems. Considering that these elements when in the reduced state tend to be in solution and precipitate when oxidized (Bonatti et al., 1970), it follows that as the marsh sediments become more reducing with depth, the abundance of Ni^{2+} and Co^{2+} would increase. As a result, a concentration gradient should be established in the pore solution causing upward migration of these elements. In the presence of sulfide (total sulfur species $>10^{-5}$), Ni^{2+} and Co^{2+} may be tied up as their sulfides (Garrels and Christ, 1965). NiS and CoS are relatively insoluble. It has been suggested (Goldberg, 1954) that Ni and Co do not form minerals of their own in the sediments but are contained in Mn and Fe species. Thus, a quantity of Ni and Co may be prevented from migrating in the pore solution by being captured as Fe or Mn sulfides. However, some migration of Ni and Co towards the oxidizing environment is indicated by a maximum found for Ni and Co around the oxidation-reduction interface (20-40 cms) (Figs. 15 and 16).

A flux for the upward diffusion of Cu, Ni and Co can be calculated from the present data using Eq. (3) ($J = \Phi D_s \frac{\partial C}{\partial X}$) assuming maximum mobile Cu, Ni and Co = leachable Cu, Ni and Co, respectively. From the estimations made for depositions, removal and concentration of Cu, Ni and Co (Tables 6, 7 and 8), about 27 per cent Cu, 47 per cent Ni, and 40 per cent Co in their leachable fraction, supplied by sedimentation and upflux, is taken up by plants.

Table 6. Budget Calculations for Copper in Natural Salt Marsh

Marsh sedimentation rate = 1 mm/yr
or ≅ 0.50 mm/yr (dry wt)[1]

Annual production of _Spartina alterniflora_
≅ 700 $g/m^2/yr$ (dry wt)[2]

	Thunderbolt	Hell Gate
Average Maximum Cu Upflux in Reducing Sediment	0.007 $g/m^2/yr$	0.005 $g/m^2/yr$
Average Cu Accretion Rate in the Sediment	0.021 $g/m^2/yr$	0.012 $g/m^2/yr$
Leachable Fraction in Accreted Cu	0.008 $g/m^2/yr$	0.005 $g/m^2/yr$
Total Maximum Leachable Cu Available to the Plants by Upflux and Sedimentation	0.014 $g/m^2/yr$	0.010 $g/m^2/yr$
Cu Uptake by Plants	0.004 $g/m^2/yr$	0.0025 $g/m^2/yr$
% Available Cu Removed by Plants	28%	25%

---

[1] Rate taken from that theoretically calculated by Rusnak (1967)

[2] Average annual production rate determined by infrared aerial photography (Gallager, 1972)

Table 7. Budget Calculations for Nickel in Natural Salt Marsh

Marsh sedimentation rate = 1 mm/yr
or ≅ 0.50 mm/yr (dry wt)[1]

Annual production of Spartina alterniflora
≅ 700 g/m^2/yr (dry wt)[2]

	Thunderbolt	Hell Gate
Average Maximum Ni Upflux in Reducing Sediment	0.009 g/m^2/yr	0.009 g/m^2/yr
Average Ni Accretion Rate in the Sediment	0.030 g/m^2/yr	0.040 g/m^2/yr
Leachable Fraction in Accreted Ni	0.012 g/m^2/yr	0.016 g/m^2/yr
Total Maximum Leachable Ni Available to the Plants by Upflux and Sedimentation	0.021 g/m^2/yr	0.025 g/m^2/yr
Ni Uptake by Plants	0.01 g/m^2/yr	0.014 g/m^2/yr
% Available Ni Removed by Plants	49%	45%

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[1] Rate taken from that theoretically calculated by Rusnak (1967)

[2] Average annual production rate determined by infrared aerial photography (Gallager, 1972)

Table 8. Budget Calculations for Cobalt in Natural Salt Marsh

Marsh sedimentation rate = 1 mm/yr
or ≅ 0.50 mm/yr (dry wt)[1]

Annual production of *Spartina alterniflora*
≅ 700 g/m^2/yr (dry wt)[2]

	Thunderbolt	Hell Gate
Average Maximum Co Upflux in Reducing Sediment	0.007 g/m^2/yr	0.005 g/m^2/yr
Average Co Accretion Rate in the Sediment	0.029 g/m^2/yr	0.025 g/m^2/yr
Leachable Fraction in Accreted Co	0.012 g/m^2/yr	0.010 g/m^2/yr
Total Maximum Leachable Co Available to the Plants by Upflux and Sedimentation	0.019 g/m^2/yr	0.015 g/m^2/yr
Co Uptake by Plants	0.007 g/m^2/yr	0.006 g/m^2/yr
% Available Co Removed by Plants	35%	40%

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[1] Rate taken from that theoretically calculated by Rusnak (1967)

[2] Average annual production rate determined by infrared aerial photography (Gallager, 1972)

Cu, Ni and Co in the marsh sediments can be summarized in thefollowing way: The diffusion flux of these trace metals is relatively low due to low concentrations of these trace metals in the marsh sediments in a mobile form. A major part of these trace metals which is mobilized by reducing conditions and diffuses towards the surface is taken up by the root system of the marsh grass. These trace metals may be transported out of the marsh as plant detritus or recycled within. The major source of supply of these trace metals to the surface sediment, however, would be due to sedimentation(Tables 6, 7 and 8).

Mercury Distribution in Salt Marsh Sediments

The channel sediments (Appendix II) are rather transitory and probably reflect the concentration of mercury in suspended sediment brought into the estuarine environment from continental runoff. Sediments of similar characteristics also reach the salt marsh environment as well but here they are subjected to processes which may lead to the release of mercury from the sediments either due to volatilization by bacteria or uptake by plants. The diffusion of mercury out of the sediment due to biological methylation would result in a mercury distribution following the equation (Jernelov, 1970):

$$Hg_x = Hg_o e^{-kx}$$

Where Hg_o and Hg_x are the mercury concentrations at the surface and at depth x respectively, k is the diffusion constant. The observed distribution of mercury does not follow this equation and might better fit a model where mercury is taken up by the roots of _Spartina_ _alterniflora_ in the upper layers of the sediments. Budget calculations for the supply and removal of mercury are shown in Table 9.

Mercury in the marsh sediments appears to be in a biologically active state and is lost from the sediment by its rapid uptake by plants. Mercury may then be transported out of the marsh as plant detritus, part of which may be recycled within.

Table 9. Budget Calculations for Mercury in Natural Salt Marsh

Marsh sedimentation rate = 1 mm/yr
or ≅ 0.50 mm/yr (dry wt)[1]

Annual production of *Spartina alterniflora*
≅ 700 $g/m^2/yr$ (dry wt)[2]

	Thunderbolt	Hell Gate
Average Concentration of Hg in Sediment	0.13 mg/gm	0.09 mg/gm
Average Hg Accretion Rate in the Sediment	$1.3 \times 10^{-4} gm/m^2/yr$	$.9 \times 10^{-4} gm/m^2/yr$
Hg Uptake by Plants	$7.7 \times 10^{-4} gm/m^2/yr$	$6.3 \times 10^{-4} gm/m^2/yr$
% Available Hg Removed by Plants	> 100%	> 100%

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[1] Rate taken from that theoretically calculated by Rusnak (1967)

[2] Average annual production rate determined by infrared aerial photography (Gallager, 1972)

CHAPTER V

CONCLUSIONS

1) Sediments from both salt marsh areas studied show an upper oxidizing layer (20-30 cm) with a reducing layer below, which is due to oxidation of organic matter in the sediments. The Eh rapidly decreases while sulfide ion rapidly increases through the oxidized layer and then maintains a uniform value in the reduced sediment. pH shows an increasing trend with depth.

2) Iron, manganese and zinc are the major transition metals in the salt marsh sediments. Copper, nickel, cobalt and mercury show relatively low concentrations. The post depositional redistribution of all the elements studied (except zinc and mercury) is controlled by redox reactions which cause a concentration gradient, causing upward migration of these trace metals by diffusion.

3) Approximately 2 per cent of available leachable iron in the sediments is taken up by plants. The reduced species of iron may be tied up as sulfides.

4) Manganese appears to be the most mobile of the metals in reduced zone and is precipitated at the oxidation-reduction interface. (Vertical profiles for manganese show a maximum around 20-40 cm in the leachable fraction.)

Approximately 6 per cent of available leachable manganese is taken up by plants.

5) The marsh sediments tend to act as a sink for zinc since it tends to diffuse downwards. Approximately 14 per cent of zinc supplied to the salt marsh by sedimentation is taken up by plants.

6) Copper, nickel and cobalt with low and relatively uniform concentrations with depth have low upflux. However, nickel and cobalt appear to have greater mobility than copper since they show a maximum in the leachable fraction around the oxidation reduction interface (20-40 cm). Approximately 27 per cent of the copper, 47 per cent of the nickel and 40 per cent of the cobalt, available (leachable) by sedimentation and upflux, are taken up by plants.

7) Mercury is rapidly removed from the sediments by uptake by plants.

APPENDIX I

Depth (cm)	pH Units	Eh (mv)	Sulfide (mv)
Thunderbolt Station 1			
000	6.5	130.0	60.0
010	7.0	30.0	-90.0
020	6.9	-20.0	-120.0
030	6.8	-20.0	-220.0
040	6.9	10.0	-210.0
050	6.9	-120.0	-420.0
060	6.9	-60.0	-500.0
070	7.4	-50.0	-540.0
Thunderbolt Station 2			
000	6.8	0.0	-5.0
010	6.9	-80.0	-60.0
020	7.4	-50.0	-110.0
030	6.9	-60.0	-190.0
040	6.9	-200.0	-530.0
050	6.9	-250.0	-530.0
060	6.9	-250.0	-540.0
070	6.9	-110.0	-520.0
Thunderbolt Station 3			
000	6.8	0.0	-500.0
010	7.0	-130.0	-520.0

APPENDIX I (CONTINUED)

Depth (cm)	pH Units	Eh (mv)	Sulfide (mv)
020	7.0	-210.0	-510.0
030	6.9	-250.0	-540.0
040	6.9	-280.0	-550.0
050	7.1	-240.0	-540.0
060	7.0	-280.0	-550.0
070	7.2	-330.0	-540.0
Thunderbolt Station 4			
000	7.2	-90.0	-30.0
010	6.9	-200.0	-560.0
020	6.9	-350.0	-560.0
030	7.5	-220.0	-550.0
040	7.3	-320.0	-540.0
050	7.0	-340.0	-570.0
060	6.9	-320.0	-570.0
070	7.3	-300.0	-550.0
078	7.4	-310.0	-560.0
Thunderbolt Station 5			
000	4.5	150.0	30.0
010	5.8	105.0	-15.0
020	6.5		-50.0
030	6.5	-15.0	-485.0
040	6.6	-160.0	-420.0
050	6.5	-130.0	-530.0

APPENDIX I (CONTINUED)

Depth (cm)	pH Units	Eh (mv)	Sulfide (mv)
060	6.5	-180.0	-510.0
070	6.6	-145.0	-495.0
080	6.9	-25.0	-350.0
Thunderbolt Station 6			
000	7.1	125.0	13.0
010	6.8	103.0	-24.0
020	7.0	155.0	-56.0
030	6.9	85.0	-175.0
040	6.8	-15.0	-455.0
050	6.9	30.0	-442.0
060	6.9	-215.0	-470.0
Thunderbolt Station 7			
000	6.2	30.0	-35.0
010	6.7	-255.0	-521.0
020	7.1	-105.0	-560.0
030	7.0	-200.0	-540.0
040	6.8	-140.0	-555.0
050	6.8	-135.0	-540.0
060	6.9	-275.0	-560.0
070	7.0	-85.0	-540.0
Thunderbolt Station 8			
000	5.8	153.0	-5.0

APPENDIX I (CONTINUED)

Depth (cm)	pH Units	Eh (mv)	Sulfide (mv)
010	6.6	25.0	-30.0
020	6.8	14.0	-45.0
030	6.9	-20.0	-225.0
040	6.9	-310.0	-520.0
050	7.0	-218.0	-565.0
060	7.0	-310.0	-550.0
070	7.0	-338.0	-440.0
075	7.1	-130.0	-545.0
Thunderbolt Station 9			
000	6.6	140.0	-30.0
010	7.1	100.0	-40.0
020	7.1	100.0	-40.0
030	7.1	90.0	-50.0
040	7.2	50.0	-50.0
050	7.4	70.0	-70.0
060	7.4	70.0	-90.0
070	7.4	30.0	-90.0
080	7.6	20.0	-120.0
087	7.6	60.0	-90.0
Thunderbolt Station 10			
000	5.8	240.0	4.0
010	6.0	49.0	-25.0

APPENDIX I (CONTINUED)

Depth (cm)	pH Units	Eh (mv)	Sulfide (mv)
020	6.7	44.0	-60.0
030	6.7	-60.0	-215.0
040	6.8	-257.0	-450.0
050	6.8	-290.0	-550.0
060	6.8	-240.0	-555.0
070	7.0	-250.0	-535.0
080	6.9	-105.0	-515.0
Thunderbolt Station 11			
000	5.6	115.0	13.0
010	6.7	35.0	-20.0
020	6.8	35.0	-30.0
030	6.6	05.0	-60.0
040	6.8	-45.0	-65.0
050	6.7	-95.0	-90.0
060	6.8	-30.0	-155.0
070	6.8	-40.0	-170.0
080	6.7	-80.0	-195.0
Thunderbolt Station 12			
000	5.6	70.0	-35.0
010	6.4	0.0	-95.0
020	6.6	-40.0	-115.0
030	6.3	-240.0	-425.0

APPENDIX I (CONTINUED)

Depth (cm)	pH Units	Eh (mv)	Sulfide (mv)
040	6.3	-185.0	-495.0
050	6.4	-110.0	-495.0
060	6.5	-90.0	-510.0
070	6.7	-40.0	-450.0
Thunderbolt River Core			
000	7.1	-90.0	-6.0
040	7.1	-140.0	-26.0
080	7.1	-95.0	-30.0
120	7.0	-155.0	-25.0
Hell Gate Station 1			
000	6.8	95.0	-60.0
010	6.8	-85.0	-205.0
020	6.9	-260.0	-550.0
030	6.9	-280.0	-560.0
040	7.0	-285.0	-575.0
050	7.1	-260.0	-560.0
060	7.3	-210.0	-555.0
Hell Gate Station 2			
000	6.5	83.0	10.0
010	7.0	-30.0	-90.0
020	7.1	-195.0	-560.0
030	7.1	-205.0	-555.0

APPENDIX I (CONTINUED)

Depth (cm)	pH Units	Eh (mv)	Sulfide (mv)
040	7.1	-170.0	-560.0
050	7.1	-210.0	-560.0
060	7.2	-160.0	-555.0
070	7.2	-280.0	-560.0
080	7.3	-100.0	-560.0
Hell Gate Station 3			
000	6.1	130.0	-10.0
010	6.8	10.0	-65.0
020	7.6	-185.0	-545.0
030	7.0	-320.0	-570.0
040	7.0	-320.0	-575.0
050	7.0	-305.0	-580.0
060	7.0	-300.0	-575.0
070	7.0	-270.0	-570.0
080	7.1	-270.0	-565.0
Hell Gate Station 4			
000	6.4	-30.0	-35.0
010	6.8	-10.0	-200.0
020	6.9	-90.0	-540.0
030	6.8	-305.0	-545.0
040	6.8	-240.0	-535.0
050	6.8	-130.0	-560.0

APPENDIX I (CONTINUED)

Depth (cm)	pH Units	Eh (mv)	Sulfide (mv)
060	6.8	-245.0	-550.0
070	6.9	-285.0	-555.0
080	7.3	-85.0	-495.0
Hell Gate Station 5			
000	6.6	110.0	-15.0
010	6.8	70.0	-40.0
020	6.9	-150.0	-520.0
030	7.0	-250.0	-550.0
040	7.0	-260.0	-555.0
050	6.9	-245.0	-560.0
Hell Gate Station 6			
000	6.3	75.0	-20.0
010	7.3	-15.0	-60.0
020	7.3	-250.0	-485.0
030	6.9	-320.0	-560.0
040	6.9	-300.0	-565.0
050	7.0	-225.0	-555.0
060	6.9	-285.0	-560.0
070	7.0	-180.0	-530.0
Hell Gate Station 7			
000	6.7	135.0	-40.0
010	7.0	100.0	-360.0

APPENDIX I (CONTINUED)

Depth (cm)	pH Units	Eh (mv)	Sulfide (mv)
020	6.9	-65.0	-545.0
030	6.9	-205.0	-525.0
040	6.9	-200.0	-550.0
050	7.0	-305.0	-545.0
060	6.9	-290.0	-550.0
070	7.0	-250.0	-535.0
Hell Gate Station 8			
000	5.4	130.0	-15.0
010	6.6	60.0	-50.0
020	6.9	35.0	-565.0
030	6.9	-15.0	-565.0
040	6.9	-290.0	-560.0
050	6.9	-305.0	-560.0
060	6.9	-125.0	-470.0
070	7.0	-70.0	-520.0
080	7.3	-65.0	-390.0
Hell Gate River Core			
000	7.5	-100.0	-28.0
040	7.2	-140.0	-15.0
080	7.0	-65.0	-25.0

APPENDIX II

Depth (cm)	Total Fe (%)	Total Mn (ppm)	Total Cu (ppm)	Total Co (ppm)	Total Ni (ppm)	Total Zn (ppm)
Thunderbolt Station 1						
0	5.3	510	32	35	120	245
20	5.3	720	35	35	145	145
40	3.8	410	16	13	230	110
60	4.1	370	15	27	240	94
80	3.7	670	16	25		115
Thunderbolt Station 2						
0	3.2	140	19	60	30	134
20	3.2	190	13	31	35	70
40	5.0	420	9	53	15	76
60	4.2	240	30	82	25	133
80	4.8	490	31	85	40	106
Thunderbolt Station 3						
0	3.5	130	22	49	33	104
20	2.8	330	10	31	21	62
40	5.2	680	29	86	30	130
60	4.2	550	30	56	15	80
80	3.0	600	25	50	25	110
Thunderbolt Station 4						
0	2.1	310	8	25	32	75

APPENDIX II (CONTINUED)

Depth (cm)	Total Fe (%)	Total Mn (ppm)	Total Cu (ppm)	Total Co (ppm)	Total Ni (ppm)	Total Zn (ppm)
20	5.6	490	29	55	23	112
40	2.8	240	35	87	31	134
60	3.5	300	25	80	15	80
80	4.2	400	20	78	25	110
Thunderbolt Station 5						
0	2.4	160	32	18	36	98
20	3.5	480	36	50	45	96
40	3.1	425	30	38	45	102
60	3.2	406	23	46	44	105
80	3.9	295	33	38	48	101
Thunderbolt Station 6						
0	1.3	225	5	22	21	73
20	.83	200	6	24	18	77
40	1.7	270	13	34	30	123
57	1.1	225	11	16	19	44
Thunderbolt Station 7						
0	1.3	137	30	9	13	40
20	3.5	737	29	39	42	98
40	3.5	362	18	41	43	102
60	2.1	450	25	37	43	102
Thunderbolt Station 8						
0	2.1	190	11	22	20	52

APPENDIX II (CONTINUED)

Depth (cm)	Total Fe (%)	Total Mn (ppm)	Total Cu (ppm)	Total Co (ppm)	Total Ni (ppm)	Total Zn (ppm)
20	2.9	245	8	17	18	50
40	3.7	406	32	50	50	102
60	2.5	250	32	49	64	75
Thunderbolt Station 9						
0	7.1	360	26	121	21	123
40	5.4	805	33	57	65	155
60	6.0	1110	30	110	40	130
80	5.7	860	32	78	35	130
Thunderbolt Station 10						
0	1.9	270	9	19	23	57
20	2.1	306	22	40	39	91
40	3.5	435	37	39	57	110
60	2.6	362	30	65	55	110
Thunderbolt Station 11						
0		240	29	50	42	118
20	4.0	362	35	64	50	107
40	3.2	306	11	34	25	70
60	3.7	560	24	50	50	91
80	3.2	380	17	46	41	86
Thunderbolt Station 12						
0	3.7	290	27	49	46	111
20	3.8	606	33	39	40	118

APPENDIX II (CONTINUED)

Depth (cm)	Total Fe (%)	Total Mn (ppm)	Total Cu (ppm)	Total Co (ppm)	Total Ni (ppm)	Total Zn (ppm)
40	2.6	245	26	40	50	91
60	2.7	337	23	44	45	98
70	3.4		24	50		
Thunderbolt River Core						
0	4.1	260	78	26	85	110
40	4.2	323	50	52	120	99
80	4.4	280	46	54	182	62
120	4.3	329	51	83	278	92
Hell Gate Station 1						
0	2.2	362	12	31	33	73
20	3.4	560	15	34	40	80
40	3.6	502	15	27	34	76
60	3.1	560	14	37	41	70
70	3.5	380	15	33	37	85
Hell Gate Station 2						
0	2.6	362	9	38	37	75
20	2.4	405	13	35	42	92
40	2.7	504	16	38	42	76
60	3.1	504	13	41	36	85
70	1.7	450	16	36	50	325
Hell Gate Station 3						
0	1.8	240	14	32	39	114

APPENDIX II (CONTINUED)

Depth (cm)	Total Fe (%)	Total Mn (ppm)	Total Cu (ppm)	Total Co (ppm)	Total Ni (ppm)	Total Zn (ppm)
20	1.3	200	15	36	37	66
40	1.9	590	12	34	46	74
60	1.7	590	13	36	37	83
80	2.1	540	14	34	30	86
Hell Gate Station 4						
0	1.9	480	16	37	38	113
20	2.1	450	15	32	36	90
40	1.8	690	12	28	33	88
60	1.9	590	12	35	37	93
80	2.1	590	19	41	34	103
Hell Gate Station 5						
0	1.3	175	7	30	30	35
20	3.9	440	14	27	40	71
40	3.4	530	13	29	47	58
60	2.5	500	9	29	47	64
80	3.0	440	14	35	33	51
Hell Gate Station 6						
0	3.5	230	18	10	52	71
20	3.4	310	1	33	59	50
40	3.5	480	9	18	47	67
60	2.3	435	7	18	56	55
80	2.3	415	12	18	38	54

APPENDIX II (CONTINUED)

Depth (cm)	Total Fe (%)	Total Mn (ppm)	Total Cu (ppm)	Total Co (ppm)	Total Ni (ppm)	Total Zn (ppm)
Hell Gate Station 7						
0	3.9	350	11	12	40	76
20	3.9	380	9	35	44	58
40	3.1	440	11	20	45	59
60	3.1	500	11	22	35	57
80	2.5	490	13	18	55	51
Hell Gate Station 8						
0	2.5	120	14	15	49	67
20	4.9	385	11	30	39	76
40	3.2	290	11	15	28	74
60			10	20	33	70
80	2.6	415	8	25	42	66

APPENDIX II (CONTINUED)

Leached Fe (ppm)	Leached Mn (ppm)	Leached Cu (ppm)	Leached Co (ppm)	Leached Ni (ppm)	Leached Zn (ppm)	Total Organic Content	Total Mercury (ppm)
Thunderbolt Station 1							
14650	230	11			292	22	0.12
12400	120	10			224	23	0.12
4350	24	5			109	16	0.05
1700	75	2			98	18	0.03
1300	50				68	17	0.02
Thunderbolt Station 2							
4259	10	11			132		
4231	10	12			29		
2011	19	13			47		
5393	38	13			76		
6063	65	15			27		
Thunderbolt Station 3							
6161	10	24			76		
1840	10	12			52		
6291	79	10			115		
4356	140	12			72		
5390	123	11			70		
Thunderbolt Station 4							
2174	10	19			99		
4186	33	7			57		
6809	117	10			30		

APPENDIX II (CONTINUED)

Leached Fe (ppm)	Leached Mn (ppm)	Leached Cu (ppm)	Leached Co (ppm)	Leached Ni (ppm)	Leached Zn (ppm)	Total Organic Content	Total Mercury (ppm)
7345	222	8			29		
	163	8			19		
					32		
Thunderbolt Station 5							
3100	8	7	13	10		21	0.10
5800	120	9	17	10		24	0.17
7400	110	11	19	11		19	0.09
5900	105	8	21	20		18	0.07
1900	35	8	12	17		21	0.10
Thunderbolt Station 6							
1300	0	5	15	15		3	0.20
700	28	6	15	14		7	0.25
2300	55	6	15	15		19	0.16
2100	50	6	14	13		21	0.10
Thunderbolt Station 7							
8500	35	9	12	24	26	11	0.09
3100	170	11	13	19	38	19	0.12
5700	135	10	14	12	25	19	0.13
7300	37	19	13	20	32	21	0.05
					26	21	0.04
Thunderbolt Station 8							
8800	12	7	13	16			
3700	60	8	8	15			

APPENDIX II (CONTINUED)

Leached Fe (ppm)	Leached Mn (ppm)	Leached Cu (ppm)	Leached Co (ppm)	Leached Ni (ppm)	Leached Zn (ppm)	Total Organic Content	Total Mercury (ppm)
3800	52	10	16	32			
4700	58	16	12	33			
Thunderbolt Station 9							
12197	30	10	12	18	38		
6233	245	6	12	18	48		
7235	204	10	14	18	30		
8500	200	10	15	20	35		
Thunderbolt Station 10							
4300	35	8	6	10			
6600	65	12	14	10			
3700	12	21	12	23			
2900	110	13	14				
12100	210	10	14	17			
Thunderbolt Station 11							
10600	75	8	16	16		27	0.21
3700	35	9	19	13		25	0.20
2900	60	11	14	21		21	0.11
5400	100	13	16	18		26	0.09
9600	98	11	12	18			
Thunderbolt Station 12							
12500	60	11	10	22		23	
16200	110	9	18	17		30	

APPENDIX II (CONTINUED)

Leached Fe (ppm)	Leached Mn (ppm)	Leached Cu (ppm)	Leached Co (ppm)	Leached Ni (ppm)	Leached Zn (ppm)	Total Organic Content	Total Mercury (ppm)
5600	12		9	15		21	
9100	130	14	11	17		20	
						22	
Thunderbolt River Core							
15748	163				71		0.34
17778	249				83		0.34
18200	203				60		0.38
18081	258				76		0.23
Hell Gate Station 1							
4700	189	8			65	22	
3400	175	8			26	2	
3250	136	4			30	3	
1860	120	8			39	4	
3000	80	6			46	19	
Hell Gate Station 2							
3700	55	5			73	12	
1850	72	5			76	29	
3100	75	7			76	26	
2200	80	11			81	23	
1350	58	7					

APPENDIX II (CONTINUED)

Leached Fe (ppm)	Leached Mn (ppm)	Leached Cu (ppm)	Leached Co (ppm)	Leached Ni (ppm)	Leached Zn (ppm)	Total Organic Content	Total Mercury (ppm)
Hell Gate Station 3							
2400	26	8			100		
3200	70	8			90	7	
1550	87	6			100	13	
1200	88	8			80	3	
1360	100	6			125	22	
Hell Gate Station 4							
3700	61	11			85	11	
4500	102	11			84	14	
2900	162	11			80	16	
2300	143	6			84	19	
2400	120	7			85	21	
Hell Gate Station 5							
1150	4	8			36	25	0.11
3350	125	8			50	23	0.08
2200	160	7			46	20	0.08
1550	100	7			59	21	0.09
					50	21	0.09
Hell Gate Station 6							
6600	37	3			120		
7600	80	2			38		
5800	120	3			110		

APPENDIX II (CONTINUED)

Leached Fe (ppm)	Leached Mn (ppm)	Leached Cu (ppm)	Leached Co (ppm)	Leached Ni (ppm)	Leached Zn (ppm)	Total Organic Content	Total Mercury (ppm)
6800	168	3			120		
6500	97	3					
Hell Gate Station 7							
11400	112	3				20	0.10
24200	88	6				24	0.11
6700	165	3				23	0.11
6600	172	2				22	0.15
6700	163	4				23	
Hell Gate Station 8							
4500	15	2				20	
12600	146	2				24	
7050	88	2				22	
4200	115	3				23	
14800	133	2				21	

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