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Publication Date

2011-10-04

Geochemistry of Sedimentary Pore Fluids in Venice Lagoon
Results of the SIOSED Program from 2005-2007
A Background Report

by

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This report presents information on the pore water geochemistry of sediments in Venice Lagoon, obtained through the sponsorship of the SIOSED (Scripps Institution of Oceanography SEDiment research) program. Sediments were cored in a variety of environments as well as on artificial sediment banks constructed in the Lagoon.

The material will serve as a background for several papers to be written for publication in the reviewed literature.

Introduction

As part of the SIOSED (Scripps Institution of Oceanography SEDiment research group; Deheyn and Shaffer, 2007) we have made an investigation of the geochemistry of interstitial waters of sediments recovered in this program. SIOSED studies were carried out from March 2005 to November 2007 at various times of the year. Our studies of interstitial waters were initiated in May 2005 and carried out through February 2007. At first we studied interstitial waters recovered from piston cores of variable lengths (1.1 m to 1.5 m), but later we emphasized also the studies of 20 - 25 cm long tube cores, especially in areas where new sediment banks were constructed from materials of a dredged canal (Deheyn and Shaffer, 2007). In this report we present the data obtained under the auspices of program, intended as a back ground for already published information (Han et al., 2007, 2008, 2010a,b, 2011) as well as for future papers on the geochemistry of Venice Lagoon sediments obtained under SIOSED.

Previous work on the pore fluids of Venice Lagoon sediments has emphasized work on near surface sediments, with particular reference to the measurement of nutrients and their potential fluxes in the upper 10 – 20 cm of the sediment column (e.g., Scholten et al., 2000; MAV-CVN, 2003). Additional attention has been given to distributions and potential fluxes of trace metals in near surface sediments emphasizing those of dissolved manganese, iron, copper, and zinc (MAV-CVN, 2003; 2004). Available data for the year 2001 suggest interstitial water dissolved copper concentration levels in the vicinity of Porto Marghera (Station 9B of MAV-CVN, 2003) generally below 150 nM, and concentrations of zinc below 300 nM (c.f., Figure 3.6-7 of MAV-CVN, 2003). On the other hand, data of Turetta et al. (2005) suggest copper concentrations of < 30 nM and zinc concentrations of generally < 450 nM in short cores off the islands of Campallo and Trezze in the vicinity of Venice. Variability was quite large, but the concentrations are high compared with recent data in other coastal and estuarine sediments (c.f. Table 3 of Rivera-Duarte and Flegal, 1997). Overlying waters ranged in concentration for Cu of $\sim 61 \text{ nM} \pm 11$ in the central north and central parts of the Venice lagoon, and for Zn $\sim 80 \text{ nM} \pm 15$ in the same areas. Turetta et al. (2005) report overlying water Cu of < 50 nM and Zn up to 450 nM, with much higher concentrations at the sediment water interface in the Porto Marghera area.

In the present study we did not measure trace metal concentrations. However, extensive data on the bio-geochemistry of mercury, including the pore water chemistry, are discussed elsewhere in this report.

The locations of the SIOSED coring sites are presented in Figure 1. Sites C, SO-2, and S1 are located in areas of potentially greater contamination (near shore, off the industrial zones), whereas most of the other sites are located in the south central basin of the lagoon or close to the entrances to the Adriatic sea. Note that Site SO-2 is located in a dredge channel and that nearby Site S1 is located in normal lagoon sediments.

Of principal interest are the early diagenetic processes involving the bacterial decomposition of organic matter in the sediments of Venice Lagoon. Figure 2 presents the general reduction sequence of compounds utilized by the bacteria in the oxidation of organic carbon (Sholkovitz, 1973; Froelich et al., 1979; Shaw et al., 1990; Luther et al., 2007). In the lagoonal sediments, dissolved oxygen is often rapidly utilized in the upper 2 cm or considerably less, as has been established by *in situ* micro-electrode measurements (A. Barbanti, unpublished data – Venice Lagoon). This is also demonstrated from data on dissolved manganese and iron in cores from Venice Lagoon (Figure 3; Station 2B - Palude Della Rose - is in the northern Lagoon; Station 9B – Fusina - is in the Industrial zone). Dissolved Mn^{2+} is essentially generated in the upper 0.5 cm. Generation of nitrate will occur above the depth of the Mn^{2+} maximum, and this component will subsequently be reduced rapidly (MAV-CVN, 2003). Similar results were obtained in shallow cores near Trezza and Campalto, located between Venice and Porto Marghera (Turetta et al., 2005). Thus, oxygen depletion, nitrate generation, and subsequent de-nitrification, as well as reduction of manganese oxides and dissolved manganese production are generally restricted to the upper part of the sediments. These observations imply that important bacterially induced processes are very active in the upper few cm of the sediments. Subsequent iron oxide reduction occurs at somewhat greater depths, with cores in the Porto Marghera sites having a very shallow maximum (see section below). In more remote sites a much broader maximum in dissolved Fe^{2+} characterizes the upper 10 cm or deeper. Below the depth in which iron oxide reduction is dominant, the sulfate reduction process becomes the major contributor to organic matter oxidation, often mirrored in the appearance of dissolved sulfide (HS^-). With the continued reduction of iron oxides, however, removal of sulfide typically leads to the formation of iron sulfides, e.g., FeS and FeS_2 (c.f., Bertolin et al., 1995; Bertolin et al., 1997). When all sulfate has been utilized, the reduction of carbon dioxide as well as the fermentation of organic matter typically lead to the formation of methane in the sediments. All these oxidation/reduction processes involving buried organic matter are accompanied by the production of both ammonium and dissolved phosphate, as is evident from

previous work in the Venice Lagoon (Scholten et al., 2000; MAV-CVN, 2003).

Methodology

Interstitial waters were extracted from the sediments by means of centrifugation at about 5,000 RPM speed under nitrogen atmosphere to prevent oxidation of potential sulfide. This allows collection of enough pore fluids towards the analysis of both nutrients and related components (alkalinity, ammonium, phosphate) and of major constituents (calcium, magnesium, sulfate, sulfide, chloride). The methodology has been described in detail in Gieskes et al. (1991).

Sulfide was determined as soon as possible using a modification of the method originally published by Strickland and Parsons (1978), or the sulfide was preserved as zinc sulfide through precipitation of sulfide by addition of zinc acetate on 3-5 cm³ sub-samples, with subsequent analysis in the home (SIO) laboratory.

Alkalinities were determined by means of a potentiometric titration (Gieskes et al., 1991). Dissolved iron, ammonium, phosphate were determined on the preserved alkalinity samples in the home laboratory, and sulfate was determined on non-acidified samples.

Results and Discussion

In this report first the observations on long cores (100 – 120 cm) obtained during the initial survey of the program will be presented. This allows establishment of the sedimentary conditions in many parts of the Venice Lagoon.

Part one – Pore Fluid Chemistry of the Long Cores

Results on the Venice long cores (0 - < 150 cm) include chloride, alkalinity, dissolved iron, sulfate, sulfide, ammonium, phosphate, calcium, and magnesium. The first two cores S0-2 and S1 may have “over-cored” a little thus leading to a potential loss of the surface sediment. All other cores were taken with enough overlying water to assure a good chance of success with the recovery of the actual surface of the sediment. Thus, in S0-2 and perhaps in S1 some sediment may have been lost, probably no more than ~ 10 cm. This means that the significance of the results on the long cores remains the fact that it allows a look deeper into the system than short coring of the upper 20-25 cm allows.

Chloride

Chloride concentrations (actually assuming constant Br of ~ 0.86 mM) indicate that in many of the cores (Figure 4), with the possible exception of long Core S2 and long Core SSO, there occurs a gradual downward trend in the chloride profiles. Linear regressions through many of the profiles often fit the data. This indicates, of course, that the profiles appear diffusive in nature and that lower chloride fluids must occur deeper in the sediments, possibly related to fresh water inputs at greater depths. Literature data on the Venice Lagoon indicate lower salinities towards the landward end of the lagoon, although variations do occur (Sfriso *et al.*, 2000; MAV-CVN, 2004; Solidoro *et al.*, 2004a,b; Umgieser *et al.*, 2004). Toward the seaward end of the lagoon usually higher salinities occur, as a result of exchange with the Adriatic Sea. Although annual and seasonal changes in the salinities of the lagoon are quite normal, the chloride depth profiles do not appear to show this measurably in the long core concentration profiles (except, perhaps, in core SO-2), suggesting that diffusive exchange with deeper lower salinity waters is dominant in determining the nature of the gradients, leaving linear profiles. This seems even true for site C, where fairly large seasonal changes in chlorinity have been reported (Sfriso *et al.*, 2000). In the second part of this communication, while emphasizing Sites SS1 and S2 in the Venice Lagoon, as well as artificial sediment banks at these locations, shallow cores of ~ 20 cm length are shown to have variable chloride concentrations in the upper 10 - 20 cm of the sediments.

Our data for the drill Hole SM-3 in the vicinity of Porto Marghera (Figure 4) also show that the underlying sediments of pre-lagoonal nature (deeper than 11 meters) are characterized by rapidly decreasing chloride concentrations. A gradient into the lagoonal section of the sediments suggests slow diffusion of chloride into the deeper sediments. Chloride concentrations in the upper 5 meters of SM3 are similar to those of Site C.

Of interest with regards the observed decreases in chloride concentrations with depth are the studies of the hydrology of the lagoon (Rapaglia, 2005; Rapaglia *et al.*, 2010a; 2010b; Garcia-Solsona *et al.*, 2008). In the area of the Porto Marghera (Fusina) and also in the direct vicinity of Isola la Cura (Northern part of the Lagoon), the introduction of waters from deeper aquifers through the sediments has been demonstrated, opening the possibility that the input of waters from aquifers may balance the water budget of the Lagoon and the waters carried to the Lagoon through river contributors (Rapaglia, 2005). In later studies by Rapaglia and coworkers indicated that much of this water component could be recycled seawater, or, perhaps, a mixture of fresh water and seawater, especially based on the study

of Radium isotope geochemistry. In addition fresh water wells have been demonstrated along the landward periphery of the lagoon (Garcia-Solsona et al., 2008). We postulate, therefore, that the decreases in chloride may be related to diffusive and, perhaps, in some cases advective exchange from underlying shallow fresh water aquifers in pre-lagoonal sediments. The submarine ground water discharge (GDW) has been estimated to be important in the Venice Lagoon.

Alkalinity

Increases in alkalinity (mostly HCO_3^- and, if present, HS^-) are observed in all cores, but especially in Cores SO- 2 and C (Figure 5). All processes of organic matter oxidation lead to increases in the total carbon dioxide and ammonium content of the interstitial waters, usually in the form of bi-carbonate ion and NH_4^+ in the pH range of 7.5 – 8.5, i.e., as measured in the pore fluids.

Especially in the levels below 50 cm substantial increases in alkalinity are evident, indicating that in the entire lagoon processes of organic matter decay play an important role in the sediments.

Dissolved Iron

Dissolved iron is observed in many of the cores (S1, S2, B, top of C, SS1, and SSO) as shown in Figure 6. This indicates that immediately below the sediment-water interface, certainly below 1-3 cm, the primary process involving the diagenesis of organic matter is iron oxide reduction (with perhaps manganese oxide reduction taking place in the same zone, or slightly above it (*cf* Figure 3)). Iron is often rapidly removed through the formation of iron sulfides, as is shown in Figure 6. Of interest are the data in Core SO-2, showing elevated iron concentrations below the sulfate reduction zone, i.e., in the methane formation zone. Perhaps the presence of Yellow Substance (“Gelbstoff”; yellowish colored humic substance rich samples) can explain the presence of this dissolved iron as a result of complexation processes. Though a yellow color also characterized the deeper samples from Core SSO, iron concentrations are not as high as in Core SO-2. The same is true for Site C.

Dissolved sulfate

Immediately below the zone of iron reduction sulfate reduction becomes the major process of organic matter oxidation (Figure 7). In Cores SO-2 and C sulfate is depleted within the upper 30 cm or less, and this rapid loss is reflected not only in high alkalinities, but also in high sulfides

especially noticeable in Core S0-2 (Figure 8). In the latter core (Andrea Barbanti, personal communication) rapidly accumulated organic rich material has been deposited upon already quite reducing sediments. Hence, the high sulfide concentrations close to the sediment water interface are not unexpected. Of course, in none of the cores there is absolute certainty that the top of the core was obtained. On the other hand, Core C shows great similarities to Core SO-2. Core SSO also shows a complete removal of sulfate below a depth of about 70 cm, accompanied by a sulfide zone between ~ 50 and ~ 100 cm depth. Core SO-2 was obtained in a dredge channel, as was Core SSO. It appears that in these sediments deeper sediment occurs at relatively shallow depth as a result of the dredging process.

The very high alkalinities in cores S0-2 and C suggest that below the sulfate reduction zone, further organic matter diagenesis leads to CO₂ reduction and methanogenesis. Typically no sulfide is present below the sulfate reduction zone. High alkalinities have also been observed in the organic matter rich sediments in various other settings, e.g., in Saanich Inlet in British Columbia (Murray et al., 1978; Mahn and Gieskes, 2001) as well as in Po Delta sediments (Barbanti et al, 1992, 1995).

Dissolved Ammonium

The profiles of ammonium (Figure 9) show again that this component is associated with the organic matter oxidation processes, but especially in Cores S0-2 and C, very high concentrations occur (note that in the figure NH₄ concentrations for SO-2, C, and SSO are in mM rather than μM). Again this has analogies with the Saanich Inlet and Po delta sediments. The sharp increases in NH₄ occur only below a depth of ~ 100 cm, i.e., below the zone of sulfide presence. It appears that below 100 cm the presence of methane characterizes core SSO, which is the case at much shallower depths in cores C and SO-2. Unfortunately no measurements have been made of dissolved methane, but the formation of methane would be in accord with high alkalinities and ammonium concentrations.

The correlation between alkalinity and ammonium is presented in Figure 10. From the sulfate and ammonium concentrations (Figures 7 and 9) it is evident that ammonium concentrations (above 7-9 mM) keep on increasing in the zone below the sulfate reduction zone.

Dissolved phosphate

Data for dissolved phosphate are presented in Figure 11. It is clear that similar to the case of ammonium, dissolved phosphate is generated

during the process of organic carbon oxidation. This generation is especially evident in the sulfate reduction zone and the deeper sediments.

Calcium and Magnesium

The data on calcium and magnesium reveal two major effects (Figure 12). First the surface concentrations of these components show the differences in salinity (reflected in the chloride concentrations; Figure 4), with cores C and SO-2 showing much lower calcium and magnesium concentrations. The second effect is caused by calcium (magnesium) carbonate formation in the high alkalinity environments of these cores, leading to lower calcium concentrations in cores C and SO-2. Core S2 also shows these lower concentrations in the lower part of the core, i.e., in the high alkalinity zone. The amount of carbonate precipitation will be difficult to discern in these high carbonate sediments.

30 m Drill Hole SM-3

Data on alkalinity, sulfate, ammonium, phosphate, and iron for the drill hole SM-3 are presented in Figure 13. The upper ~ 11m are part of the sediments that formed after the formation of Venice Lagoon. Below this depth low chlorides define a zone of pre-lagoonal sediments. In the upper part of the drill hole very high alkalinities reflect the part of the sediment column that has formed in very recent times, as is also evident from the increased concentrations of copper and zinc (Gieskes et al. – in preparation). The data for the various pore water components reflect those of Sites SO-2 and C (c.f., Figure 14). Below the depth zone between 4-5 m the pore fluids show much lower concentrations to a depth below 10 m.

Discussion of long core interstitial water chemistry

Interstitial water analyses of “long cores” of up to 1.5 meter length have revealed some interesting features with regard the depth distributions of several relevant constituents. Whereas cores C, SO-2, and SSO indicate processes of sulfate reduction that lead to the complete removal of sulfate from the pore fluids, the other cores do show much less sulfate removal, probably as a result of slower accumulation of the sediments and also because of lesser organic carbon contents. Composite concentration depth profiles of sulfate, sulfide, ammonium, and chloride are presented in Figure 14.

As mentioned before, sulfate, sulfide, and ammonium are representative of major diagenetic processes affecting the organic carbon in

Venice Lagoon sediments. Whereas cores in the vicinity of Porto Marghera and the industrial zone (cores C, SO-2) typically lose sulfate at very shallow depths, core SSO (the source of the materials used for the construction of experimental banks near sites SS1 and S2 – see part two) is also characterized by the complete loss of sulfate below ~ 70 cm depth, associated with large increases in ammonium below 100 cm. Core SSO originates from a channel that is regularly dredged, thus consisting of sediments that are not usually found in the vicinity of core SSO, e.g., Core SS1. This observation is probably applicable to many locations in the lagoon, especially in the areas of the industrial zones as well as in dredged canals, where the upper sections of the sediments are removed on regular time scales. In other areas of the lagoon this situation will be much reduced in nature, as is evident from Cores A, B, S1, S2, and SS1. Nonetheless, at greater depths sulfate reduction processes can become of greater importance. As noted before, Core S1 is in the vicinity of Core SO-2, situated in a dredged canal, but Core S1 was located slightly offset from a canal.

The chloride concentrations are representative of the changes in chloride in response to the salinity variations in the overlying waters, ranging from $S \sim 30$ at Station C (Porto Marghera), $S \sim 32$ (Fusina), to $S \sim 35.5$ at Station SS1 (near the Malamoco inlet). Similar gradients in salinity are implied in the data previously reported in Venice Lagoon (MAV-CVN, 2003; 2004). The data imply that, notwithstanding potential variations over short time periods, the overall distribution of salinity has remained very similar over a relatively long period of time. Downward concentration gradients of chloride in many of the cores, are most likely due to potential sinks for chloride in underlying aquifers.

Part two - Short and Long Cores in Sediment Banks

Between October 25, 2005 and November 6, 2005 sediment banks were constructed at Sites SS1 (V1) and S2 (V2) in Venice Lagoon (Figure 1B; Deheyn and Shaffer, 2007). In both cases material dredged from a canal at Site SSO was used. The operation of the bank building is demonstrated in Figure 15. Sediments of Site SSO were obtained from a previously dredged channel near the Malamocco Inlet of Venice Lagoon. The bank sediments constitute a layer of 50 - 70 cm thickness on top of the existing sediments of Sites SS1 and S2. On average the sediments of Cores V1 and V2 are, therefore, characterized by the presence of low sulfate concentrations as well as high alkalinities and high ammonium concentrations, with even very low concentrations at the sediment-water interface shortly after construction.

The upper sediments at Sites SS1 and S2 are much less reducing in nature, with only relatively minor changes in the above constituents (c.f., Part One). As a result the nature of the sediment chemistry in the upper ~ 50 - 70 cm of the sites V1 and V2 is very different from the underlying sediments of SS1 and S2. The implication of this bank construction process, therefore, is the creation of potential transitional concentration depth distributions of the various dissolved constituents of the pore waters. Shortly after the completion of both V1 and V2, the sediments were sampled for the first time on November 15, 2005 for the study of pore fluids of long cores (up to 140 cm in length). As a result of the construction process of the banks, one would not necessarily expect the sediments in the banks to be homogeneous, but certain comparisons can be made. Here we present results on several constituents that indicate the effects of this sediment transfer on the interstitial water chemistry. Towards this end the distributions of chloride, dissolved iron, sulfate, sulfide, ammonium, and phosphate are used. Comparisons are made with the data obtained in the pre-bank sites SS1 and S2 (June 2005), which served as the sites for the construction of the banks, thus providing a comparison for the pore fluids of bank sites V1 and V2. The results of the program on the distribution of mercury, both in pore fluids and solid phases in association with background data on pore fluids compositions have already been published (Han et al., 2007; 2008; 2010a,b; 2011).

Dissolved Chloride

Dissolved chloride is an important component to study in these sediments. Because in the overlying waters salinities are not constant, being influenced by rain input, evaporation, as well as considerable exchange with the Adriatic Sea through the three major inlets of Venice Lagoon, the chloride concentrations in the pore fluids should reflect the chlorides in the overlying waters. Because chloride is a non-reactive element, the distribution of this component will help to evaluate the physical processes affecting the pore fluids in the Venice Lagoon sediments, in particular on the banks (Sites V1 and V2) and the reference sites (Sites SS1 and S2). The concentration depth distributions of chloride (Cl) in Sites SS1 and S2 are presented in Figure 16A. It is evident that in the upper ~ 20 - 25 cm of the sediments of SS1 and S2, chlorides are variable, but all trend to similar values below this depth ($\sim 540 \text{ mM} \pm 2 \%$), representing an average chloride in the deeper sections. We interpret these distributions in terms of exchange of Cl between the overlying waters and the sediments. In some cases the exchange leads to linear profiles, but sometimes the profiles are non-linear. We interpret these distributions in terms of enhanced diffusive/advective

exchange through disturbance of the sediments as a result of bio-turbation and/or tidal mixing processes. The overlying waters are at times less saline or more saline. On the assumption that the near surface concentrations of Cl are representative of those of the overlying waters we demonstrate in Figure 16B the variability in the chloride concentrations in the lagoon bottom waters at sites SS1 and S2. A more detailed paper on this subject is in preparation. Clearly there is considerable variability in Cl (and salinities) at the sediment sites under consideration, with usually the more inward Site S2 being somewhat less saline. Similar variation in chlorides of the overlying waters has been reported in the vicinity of the sites of interest in this study (Sfriso et al., 2000; MAV-CVN, 2004).

Site S2 is also of interest because of the variability in Cl in the deeper parts of the sediments, with gradients in the fluids indicating diffusive exchange between the sediment and deeper sources, mostly with underlying aquifers. This is common in many of the cores taken in the Venice Lagoon as part of SIOSED (see Part one of this communication).

Data from the original long core SSO (August, 2005) are presented in Figures 4 and 17. Unfortunately only acidified samples were available for the original long core work (Figure 4), thus rendering the data less accurate than desirable. It is evident, however, that below ~ 20 cm the data show similar trends in this core. A comparison of surface sediment data for SSO and S2 (obtained from separate short cores), using both titrated samples and calculations from sulfate data, indicates that there is reasonable agreement between the various data sets. All other chloride data have been obtained using non-acidified pore waters.

On average the banks were built with materials from the upper 50 – 70 cm of Site SSO, with an average of Cl ~ 540 mM. We submit that the chloride concentrations in both V1 and V2 were $530 \text{ mM} \pm 5$ ($\sim 1\%$) during their construction, possibly implying some admixture of overlying lagoonal waters during the period of bank construction (Figure 15). Pore water chloride concentrations in the Banks V1 and V2 are given in Figure 17. Typically in most of the cores the profiles in the upper ~ 20 cm indicate variability in the chloride concentrations in response to chloride concentration changes in the overlying waters (see above discussion of Sites SS1 and S2). At greater depths chloride concentrations show a slight downward slope. A notable exception is the Cl profile of V2 in November 2006. This profile suggests a diffusive profile all the way to the surface. We submit that in this case the core was obtained at the edge of the sediment bank, and that chloride gradients to some extent are similar to those in Site S2 (Figure 4), with the upper part of Site S2 missing (50-60 cm). This may

be due to the close vicinity of this core to the sediment bank V2.

Alkalinity

Increases in alkalinity (mostly bi-carbonate and bi-sulfide) are principally due to processes of oxidation of organic matter during sulfate reduction and, when sulfate is completely depleted, as a result of methanogenesis. These processes also lead to the formation of ammonium and dissolved phosphate, as will be discussed below.

Alkalinity data were obtained at a lesser frequency than most other data, but data are available for most long cores at Sites V1, V2, and SSO, as well as for some short cores. The data are presented in Figure 18.

Both in May 2006 and November 2006 the alkalinity profiles of Site SSO indicate rapid increases in alkalinity below a depth of 10-15 cm in the long cores. Considering that between 50 to 70 cm of the sediments of SSO were used for the construction of the Banks V1 and V2, a maximum in alkalinity is expected in the upper ~ 50 cm of the banks. Below ~ 50 cm the alkalinities return to values expected from the upper parts of Sites SS1 and S2. In Site V2 in November 2006 lesser increases in alkalinity in the long core are in agreement with the observations on chloride concentrations. As pointed out before, presumably this core was taken at or near the edge of the bank.

The short cores taken at Sites V1 and V2 confirm the steep increases of alkalinities in both banks. Small discrepancies may be to the possibility of more compaction in the long cores compared with the short cores.

Dissolved Iron

Data for dissolved iron are presented in Figure 19. The original long core (see also Figure 6) show that in the long cores SS1 and S2 dissolved iron is enriched in the upper 20 to 30 cm of the sediments. In addition the iron concentrations in cores S-SS1 and S-S2 (short cores) suggest that dissolved iron is enriched in a variable manner in the upper 10 to 20 cm of these sediments. On the other hand, dissolved iron distributions in the short cores S-V1 and S-V2 are usually enriched only in the upper 5 cm of the cores, with a possible anomaly in December 2005 in Core S-V2.

The iron distributions in V1 and V2, therefore, are mostly restricted to the upper ~ 3-5 cm of the sediments, i.e., in the zone of enhanced mixing. Below we demonstrate that sulfide concentrations in many of our cores in V1 and V2 increase in the upper 5 cm also, thus causing the diminishing values of dissolved iron in the upper 3 – 5 cm through iron sulfide precipitation.

Dissolved Sulfate

Sulfate concentrations in the sediments of Site SSO (Figure 20) diminish rapidly below 15 cm, to reach zero concentrations below 50 to 70 cm. It is difficult to determine the exact nature of the sulfate profiles, with variability to be expected because these sediments stem from a dredged channel, which is probably not uniform with regards the pore water compositions. Thus, again, the sulfate profiles of Sites V1 and V2 should reflect this, i.e., minima should occur in the upper portion of V1 and V2. This is confirmed by the observations at both banks. Of course, again, the sulfate data for the November 2006 V2 profile are different from the trends in the V1 and V2 cores. The minima are located at depths of about 30 – 40 cm, except for the cores obtained in November 2005.

Note the very low sulfate concentrations at the surface in November 2005, the long cores having been taken shortly after the construction of the banks. The sulfate concentrations in the surface layer of the both V1 and V2 were well below the overlying water values in November 2005 in the surface sediments. These sulfate concentrations are expected, mostly because of the recent processes of deposition of SSO derived sediments. Diffusive sulfate exchange processes both above and below the minimum concentration levels have subsequently smoothed the gradients, but there is little doubt about the return to original Site SS1 and S2 concentrations below about 70 cm depth in V1 and V2.

Dissolved Sulfide

Data for dissolved sulfide are presented in Figure 21. Of special interest are the original long core results for Site SS1, SSO, and S2 (Figure 8). Sulfide concentrations in SS1 are relatively low, increasing below ~ 50 cm; in S2 sulfide concentrations are significant below depths of ~ 50 cm, reaching concentrations of ~ 7 mM at depths of 120 to 130 cm. On the contrary, in Site SSO a broad maximum in sulfide characterizes the sediments between 30 and 110 cm. If indeed the banks at V1 and V2 were constructed with SSO materials from depths of the upper 50 – 70 cm, the low concentrations of sulfate and the elevated concentrations of sulfide can be explained for the upper parts of the banks V1 and V2 (Figures 20 and 21). The non-homogenous nature of the concentration depth distributions in both components in the upper 50 – 70 cm of the banks, especially in November 2006, can be understood in terms of the somewhat random processes involved in the bank construction.

The short core data of V1 and V2 show sulfide maxima in the upper

10 – 20 cm.

Of importance is to consider the correlation between the dissolved iron and dissolved sulfide concentrations. The data of Figures 22A and 22B indicate a generally tight relationship, suggesting that the precipitation of iron sulfide (FeS) plays an important role in maintaining low iron concentrations in the sulfide zone. A few exceptions are noticeable in Figure 22A, presumably due to some erroneous data in iron and/or sulfide. With a measurement limit between 3 – 5 μM in dissolved iron, we submit that the zone of dissolved iron occurs mostly above the zone of sulfide presence in the bank sediments (see also Han et al., 2007).

Dissolved Ammonium

The distribution of ammonium (Figure 23) indicates an advanced signal of diagenesis of organic matter, resulting from sulfate reduction processes in Site SSO. The original (September 2005) SSO ammonium profile was quite different from those of the later SSO profiles. However, as Site SSO is in a dredged channel, spatial heterogeneity at this site is to be expected. In any case, Sites V1 and V2 should reflect the imposition of SSO derived sediments on sediments of Sites SS1 and S2, thus having relatively high ammonium contents. Again distributions of dissolved ammonium in November 2005, shortly after completion of the banks, show high concentrations at the surface, which diminish with time as a result of diffusive exchange with the overlying waters. This is especially evident from the distributions of ammonium in V1 and V2. Maxima in ammonium occur both in V1 and V2 at about 20 – 30 cm depth, except for long core V2 of November 2006. The variability of the slopes in the upper part of the sediments of V1 and V2 is mostly due to variability of these sediments (probably constructed in a non-homogenous manner (c.f., Fig. 15). It is evident that ammonium gradients in all short cores are very steep, implying important exchange of this component with the overlying waters.

Dissolved Phosphate

Though samples for phosphate were examined at a lesser frequency, the data presented in Figure 24 clearly indicate distributions similar to those of sulfate and ammonium in Sites SSO, V1, and V2. Maxima of $\sim 180 - 190 \mu\text{M}$ occur in both V1 and V2 at depth levels between 20 – 30 cm. These extrema can again be traced back to the high values in the sediments of Site SSO.

Mercury in Pore Fluids

Bloom et al. (2004) report dissolved Hg concentrations constrained to the range of approximately 3–15 pM. Monomethyl mercury ranged from about 0.1–2 pM in unfiltered samples and 0.03–1 pM in the dissolved phase. On the other hand total Hg concentrations were often higher, especially in the vicinity of the industrial zones. Bloom et al. (2004) argue that this is likely due to suspended matter in the water column.

The mean mercury mean concentrations in the top 20 cm of the sediments and the pore fluids are reported in Table 1 of Han et al. (2011), see also Han et al. (2007; 2008; 2010a; 2010b). The solids data are compatible with the data of Bloom et al. (2004). In addition data on the depth distribution of the solid Hg concentrations are presented in Figure 25. Most of the concentrations in the sediments of SS1 and S2 are below 500 ng/g, i.e., characteristic of Class A sediments. On the other hand V1 and V2 indicate concentrations above this threshold, which reflects the higher concentrations of the source sediments of Site SSO. Pore fluid Hg concentrations are quite variable (Figure 26), but there do not appear significant differences between concentrations in the reference sediments (SS1 and S2) from the bank sediments (V1 and V2), with the possible exception of data obtained in December 2005. We speculate that solid FeS present in these sediments, particularly in those of V1 and V2, which can lead to removal of Hg into the sulfide phase.

Discussion of V1 and V2 pore fluid results

The pore water chemistry of the banks V1 and V2 is radically different from that of the reference sites SS1 and S2, mostly because the building of the banks involved the use of sediments from Site SSO dredged from an existing canal and thus potentially constituting deeper sediments, characterized by higher alkalinities, ammonium, and sulfide concentrations, as well as lower sulfate concentrations. This yielded the opportunity to study pore fluid compositions in a presumed state of transition, mainly involving diffusive exchange with lower sediments and with the overlying waters.

The concentration depth profiles in both Sites SS1 and S2 clearly show a large variability in chloride profiles in the upper 20-25 cm of both sites (Figure 16). This variability is, albeit to a somewhat lesser extent, reflected in the profiles of Sites V1 and V2 with a limit of < 15 cm (Figure 17).

Because of the variability in the near surface profiles as a result of exchange processes with the overlying lagoon waters, it is worthwhile to consider the problem of simple molecular diffusion of chloride ions in a

porous medium. Assuming a diffusion coefficient of $D = 2 \times 10^{-5} \text{ cm}^2/\text{sec}$ (Li and Gregory, 1974) one can calculate a diffusive path-length of

$$Z = (2Dt)^{1/2}$$

Over a period of $t = 1$ month this path-length will be ~ 10.2 cm. If $D = 10^{-5} \text{ cm}^2/\text{sec}$ this path-length is ~ 7.2 cm and with $D = 7.5 \times 10^{-6} \text{ cm}^2/\text{sec}$ the path-length would be ~ 6.3 cm. At a porosity of $\phi = \sim 0.85$, we estimate that at about 25°C the diffusion coefficient would be $\phi^2 \times 2 \times 10^{-5} = 1.4 \times 10^{-5} \text{ cm}^2/\text{sec}$, thus suggesting a path-length of roughly 8 cm. If, therefore, molecular diffusion would be the only process affecting chloride ions, then over one month of time a signal of changes in overlying water conditions would penetrate less than 10 cm. However, typically many of the pore water chloride profiles penetrate much deeper in a relatively short time, sometimes with almost constancy, i.e., not commonly expected from diffusive exchange only (see profiles of chloride in SS1 of Figure 16A). We postulate that both bioturbation and tidally enhanced “diffusion” processes are the cause of the deeper penetration of the variable chloride signals. With a depth of penetration of the chloride signal of about 15 cm in V1 and V2, we would calculate an “effective” diffusion coefficient (including the additional perturbation effects – tidal effects, bioturbation) of $5 \times 10^{-5} \text{ cm}^2/\text{sec}$.

The above discussion is of importance when considering the concentration depth profiles of sulfate and ammonium (Figures 20 and 23). Whereas shortly after the construction of the banks pore waters at the surface of Sites V1 and V2 showed large anomalies, the profiles showed a diffusive nature by about 15 February 2006, not long after December 15, 2005. Thus the near surface sulfate and ammonium anomalies do not persist for much more than a few months after the construction of the banks. After that the diffusive exchange process has been well established, implying a slow exchange of sulfate and ammonium (as well as other constituents, e.g., alkalinity ($\sim \text{HCO}_3^-$), phosphate) between the sediments and the overlying waters. On the other hand the continued existence of the concentration maxima in ammonium at about 30 – 40 cm, implies that diffusive exchange with the overlying waters and the underlying sediments is very slow even if no continued consumption of sulfate and production of ammonium were to occur in these sediments.

As shown above, with a penetration depth of the chloride signal in one month of about 15 cm, we estimate the “effective” diffusion coefficient of NH_4^+ to be roughly $5 \times 10^{-5} \text{ cm}^2/\text{sec}$. If the gradient of ammonium concentrations is roughly 4 mM/10 cm or 0.4 mM/cm (see Figure 22 D&E),

one calculates a flux out of the sediments by means of the formula:

$$J = - DdC/dz$$

This yields a flux of ~ 16.5 mmoles/m²-day. Considering the near surface profiles of Figure 23, this flux can be 16.5 ± 10.0 mmoles/m²-day. This flux is a similar magnitude as reported by Scholten et al. (2000) and in document MAV-CVN (2003), in the vicinity of the Site C in the Venice Lagoon. On the contrary, Scholten et al. (2000) report very minor fluxes in the area of Site SS1.

With a standing stock of roughly 1, 500 mmoles/m² in the upper 50 cm of the pore water column this flux would diminish the pore fluids in about 3 months time. Clearly this is not the case and we submit that substantial production of ammonium resulting from sulfate reduction processes must continue in the upper 50 – 70 cm of both Sites V1 and V2. Thus, with an almost steady state of ammonium concentrations in V1 and V2, the diffusive out-flux of ammonium appears to be reasonably well balanced by the *in situ* production of ammonium. In other words, the banks will retain their special pore water signatures for a considerable period of time. We have also discussed this process elsewhere (Han et al., 2011).

Conclusions of Artificial Banks Studies

Detailed studies of the pore water chemistry in sediment banks constructed for intensive biological and chemical studies under the auspices of Magistrato alle Acque di Venezia, have revealed that potentially non steady state conditions have been established in the upper 70-80 cm of the sediment column. Typically the dredging of sediments of Site SSO and subsequent building of banks V1 and V2 using this material (Figure 15) has caused the situation in which sediments with enhanced contents of ammonium, alkalinity, and sulfide, as well as lower contents of sulfate, are superimposed on sediments normally present in the areas of Sites SS1 and S2. This established typical maxima or minima in the distribution of pore water components of potential interest to the biology of these sediments. Compared with available information on concentration depth distributions of pore water components in Venice Lagoon (see, e.g., Scholten et al., 2000 and MAV-CVN, 2003), almost all pore water components of the banks have near surface concentration gradients of a much steeper nature than in most other locations in Venice Lagoon, with the exception the sediments in the vicinity of the industrial zone of Venice Lagoon.

Typically concentration gradients in sulfide and ammonium are steeper in Sites V1 and V2 when compared with any other sites in Venice Lagoon. Thus exchange fluxes of ammonium and other components with the overlying waters of the lagoon will be among the highest measured in the lagoon. An estimate for the potential flux of ammonium into the lagoonal waters is ~ 17 mmol/m²-day⁻¹, compared to ~ 5 mmol/m²-day⁻¹ (Scholten et al., 2000) and $\sim 2-5$ mmol/m²-day⁻¹ (MAV-CVN, 2003). Estimates of this flux, combined with the nearly steady state of the concentration depth profiles of ammonium in the banks, suggest that there is still considerable organic matter diagenesis taking place in the SSO derived section (upper ~ 70 cm) of Sites V1 and V2. This process would also support the nature of the sulfate, ammonium, alkalinity, and phosphate profiles.

We conclude that the dredging of Venice Lagoon canals associated with the deposition of the dredged materials in the lagoon to form subtidal banks can lead to enhanced exchange of nutrients with the overlying lagoon waters. These enhanced fluxes of ammonium and phosphate can to some extent be beneficial to the water column biological productivity of the Venice Lagoon. As relatively small areas of the lagoon would be involved the overall impact, however, will be relatively small.

Most of the observed depletions in sulfate and increases in the ammonium, phosphate in the pore fluids indicate that bacterial degradation of buried organic matter of essentially marine origin is responsible for these observed changes.

Disclaimer

The material of this report has been produced in the framework of SIOSED Project, supported by Magistrato alle Acque di Venezia, Italy (Venice Water Authority) throughout Consorzio Venezia Nuova and Thetis S.p.A. Any opinions, findings, and conclusions or recommendations expressed in this report are those of the authors and do not necessarily reflect the views of the Magistrato alle Acque di Venezia (Venice Water Authority), Consorzio Venezia Nuova or Thetis S.p.AA.

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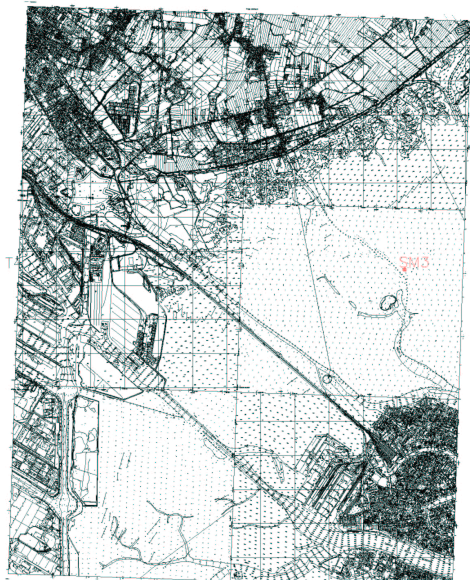
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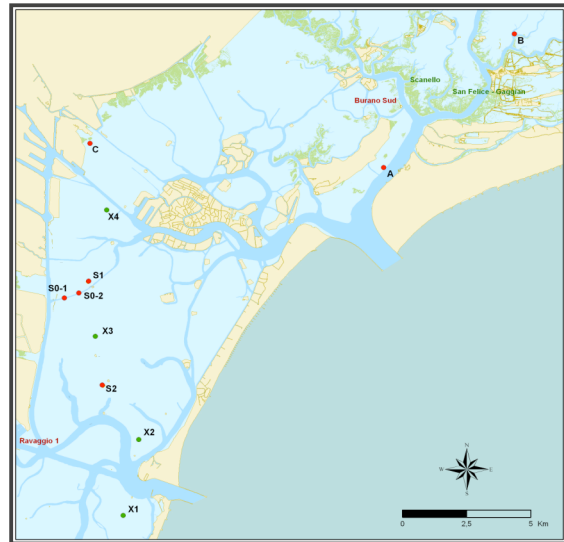
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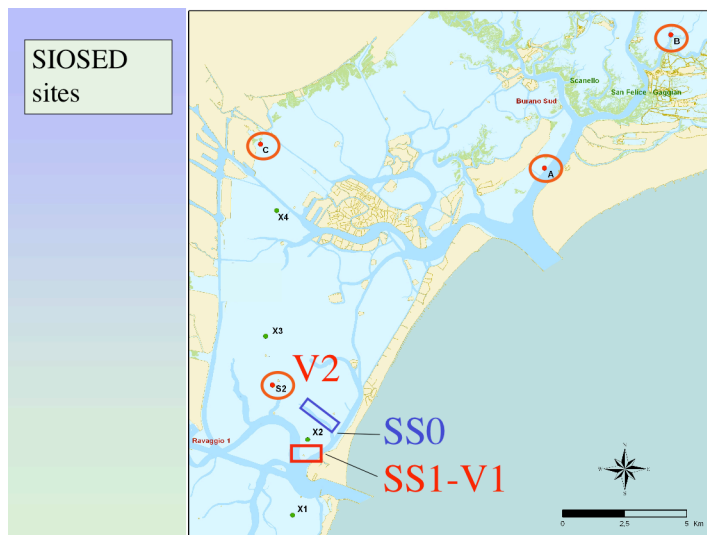
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Drill Hole SM3

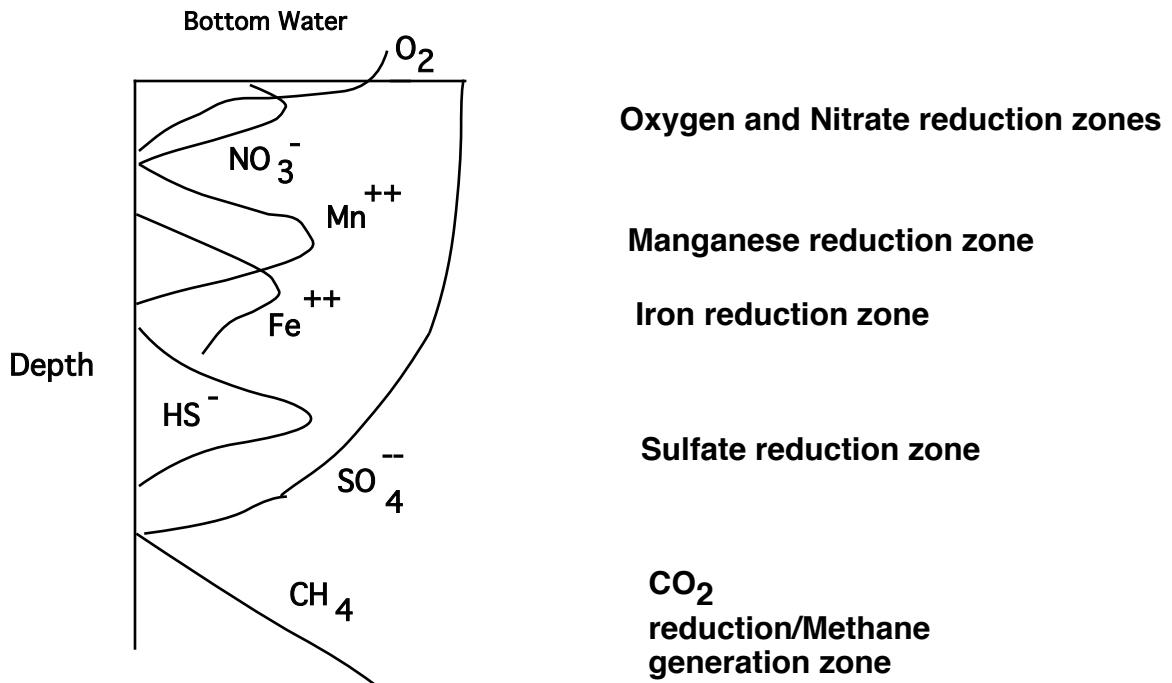


Long Core Stations (red)



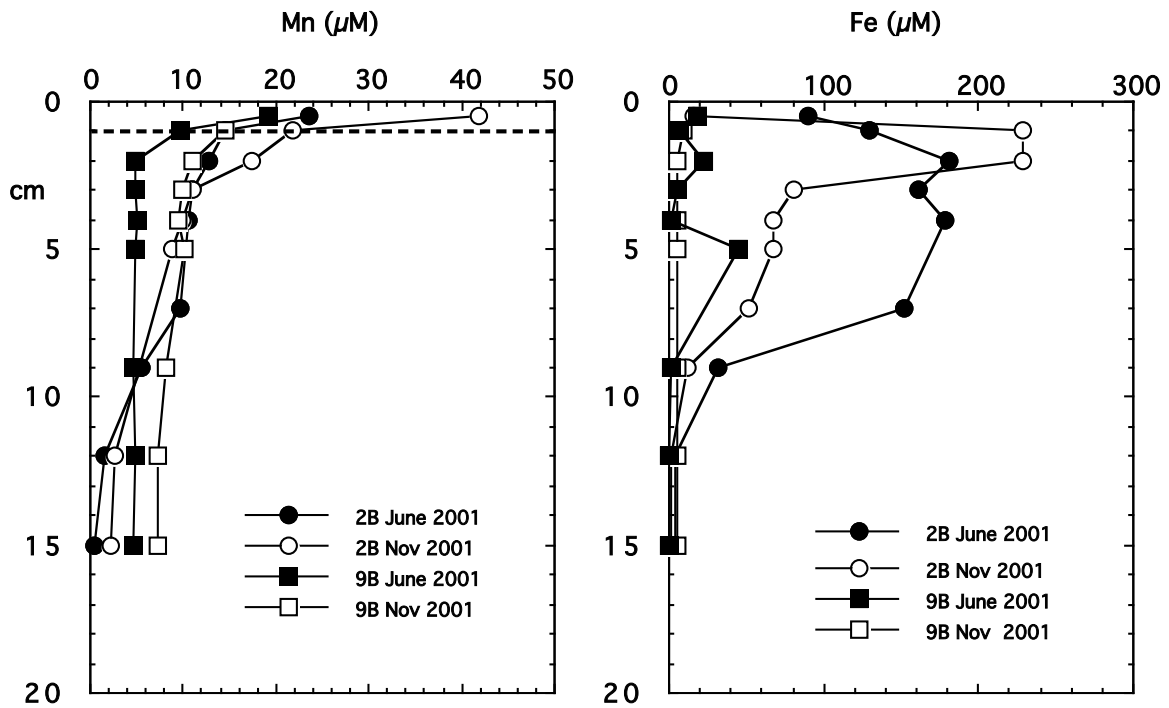
**Stations of Banks V1 (SS1) and V2 (S2)
SS0 source of banks**

Figure 1



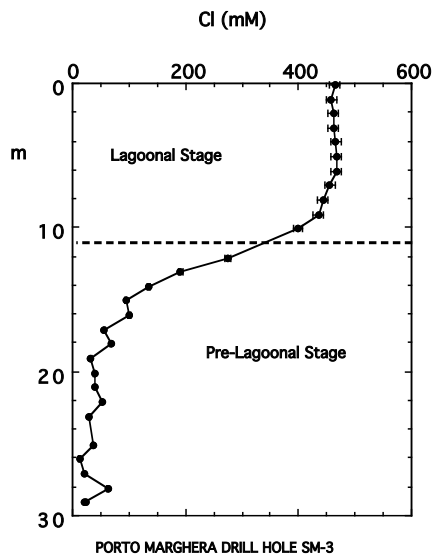
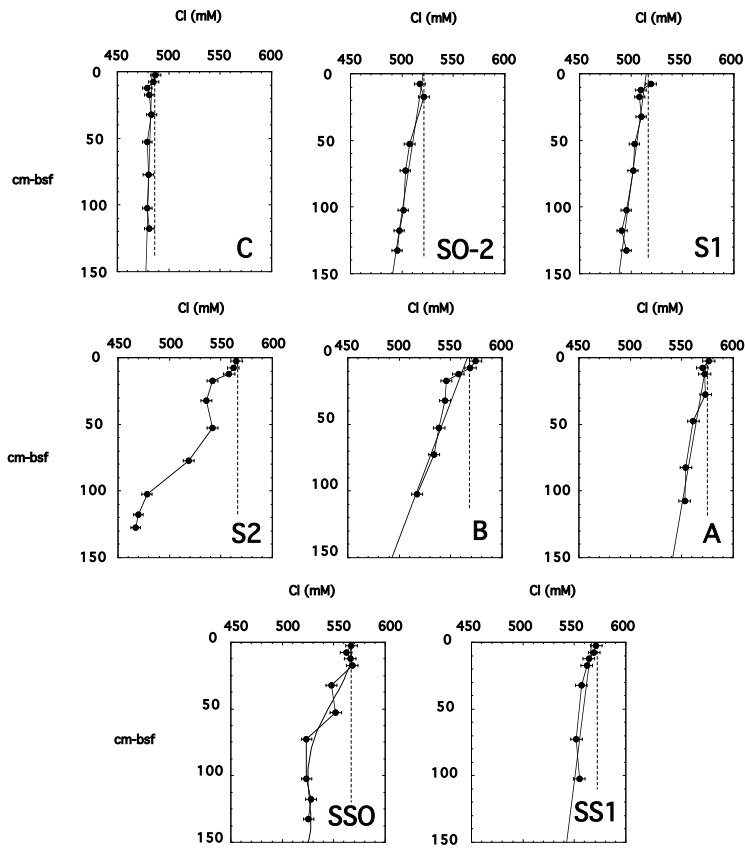
Redox sequence in Marine Sediments

Figure 2



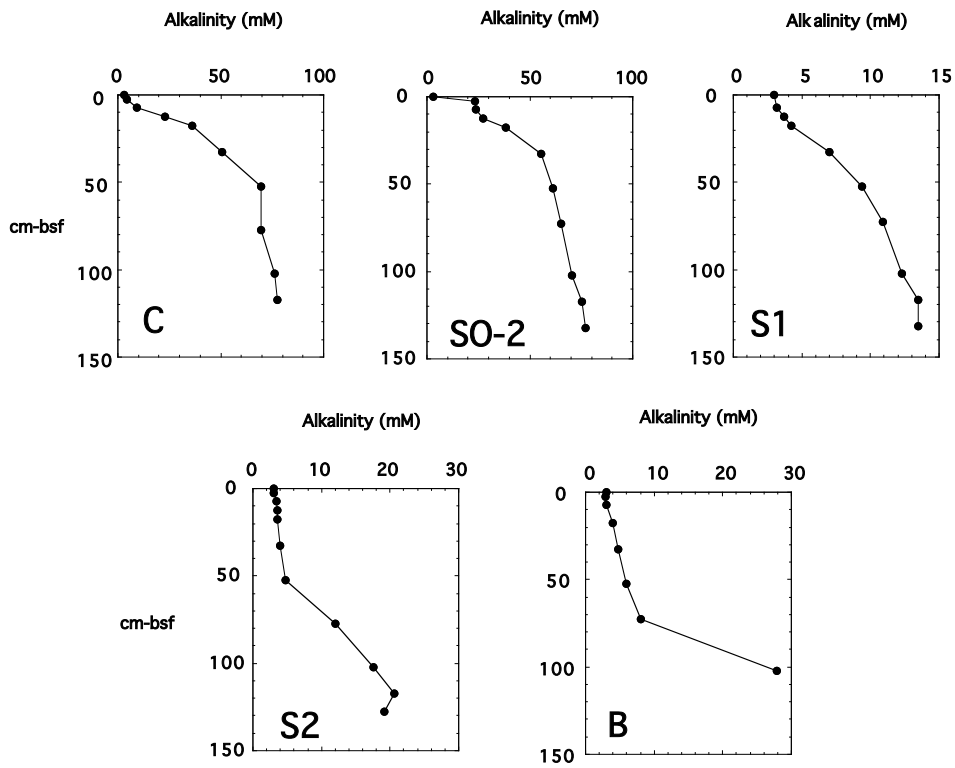
**Dissolved Manganese and Iron in Venice Lagoon pore fluids
(MAVCVN, 2003)**

Figure 3



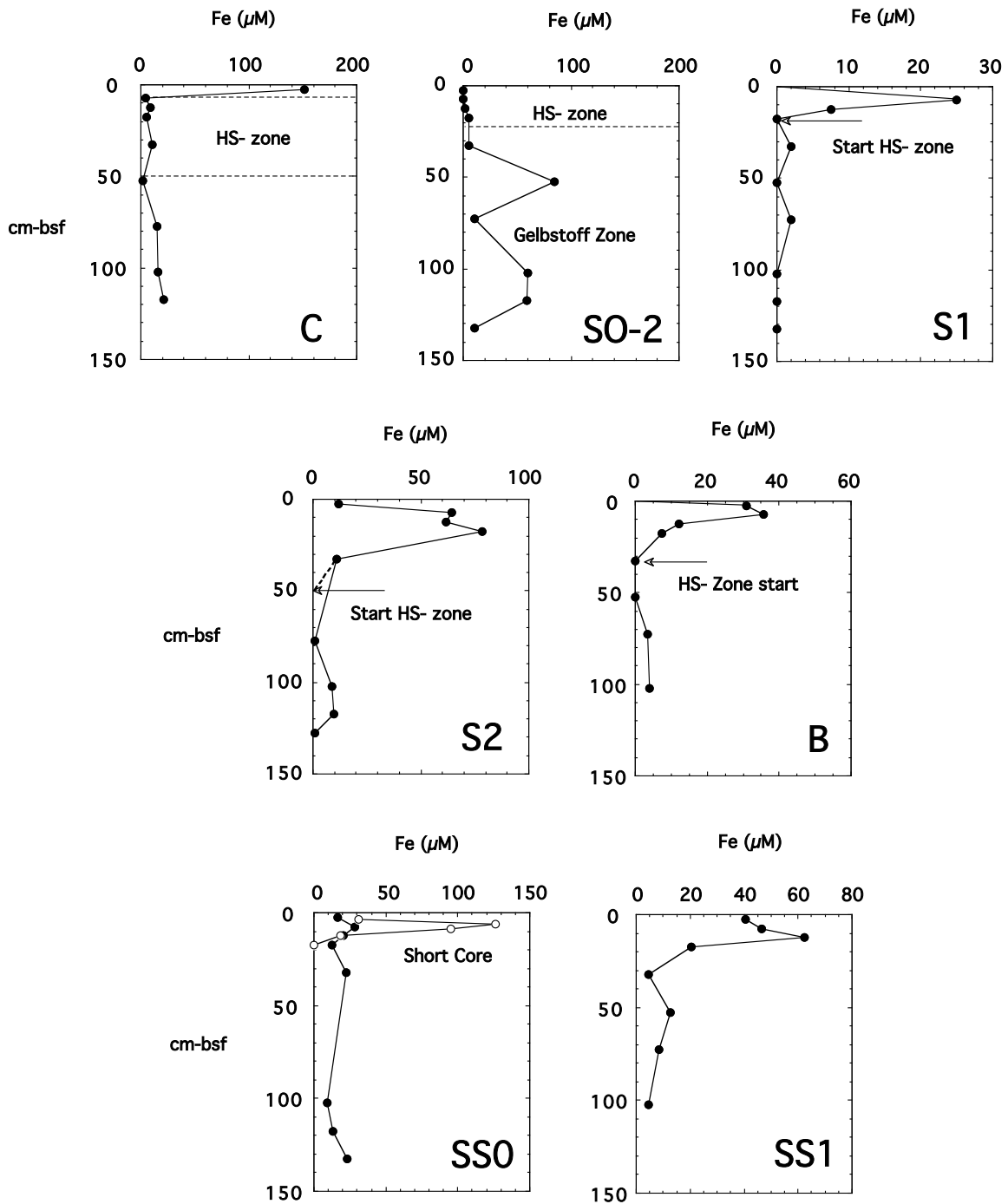
Dissolved Chloride in Pore fluids of Long Cores and Drill Hole SM3 Venice Lagoon

Figure 4



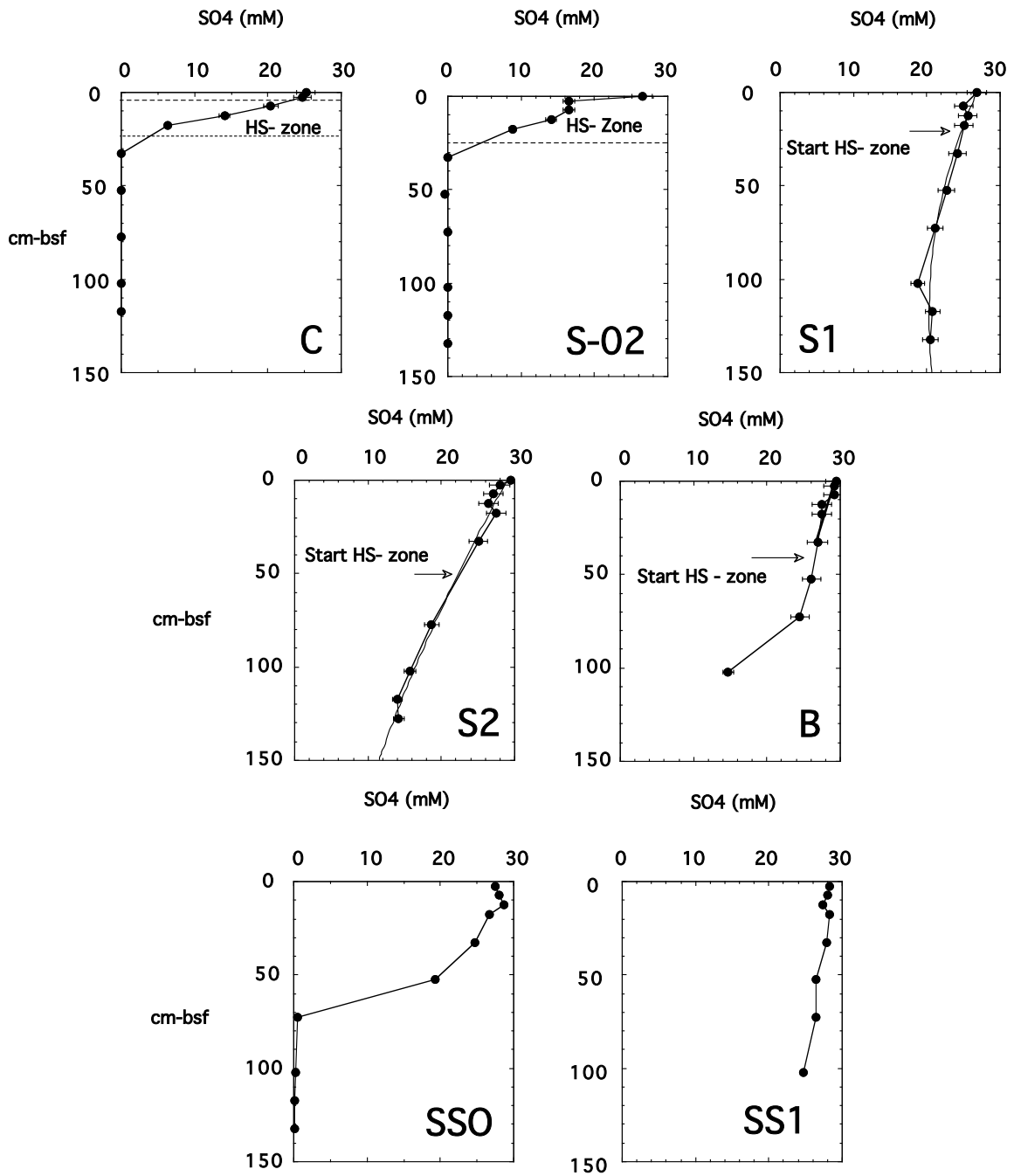
Alkalinity of Pore Fluids of Long Cores Venice Lagoon

Figure 5



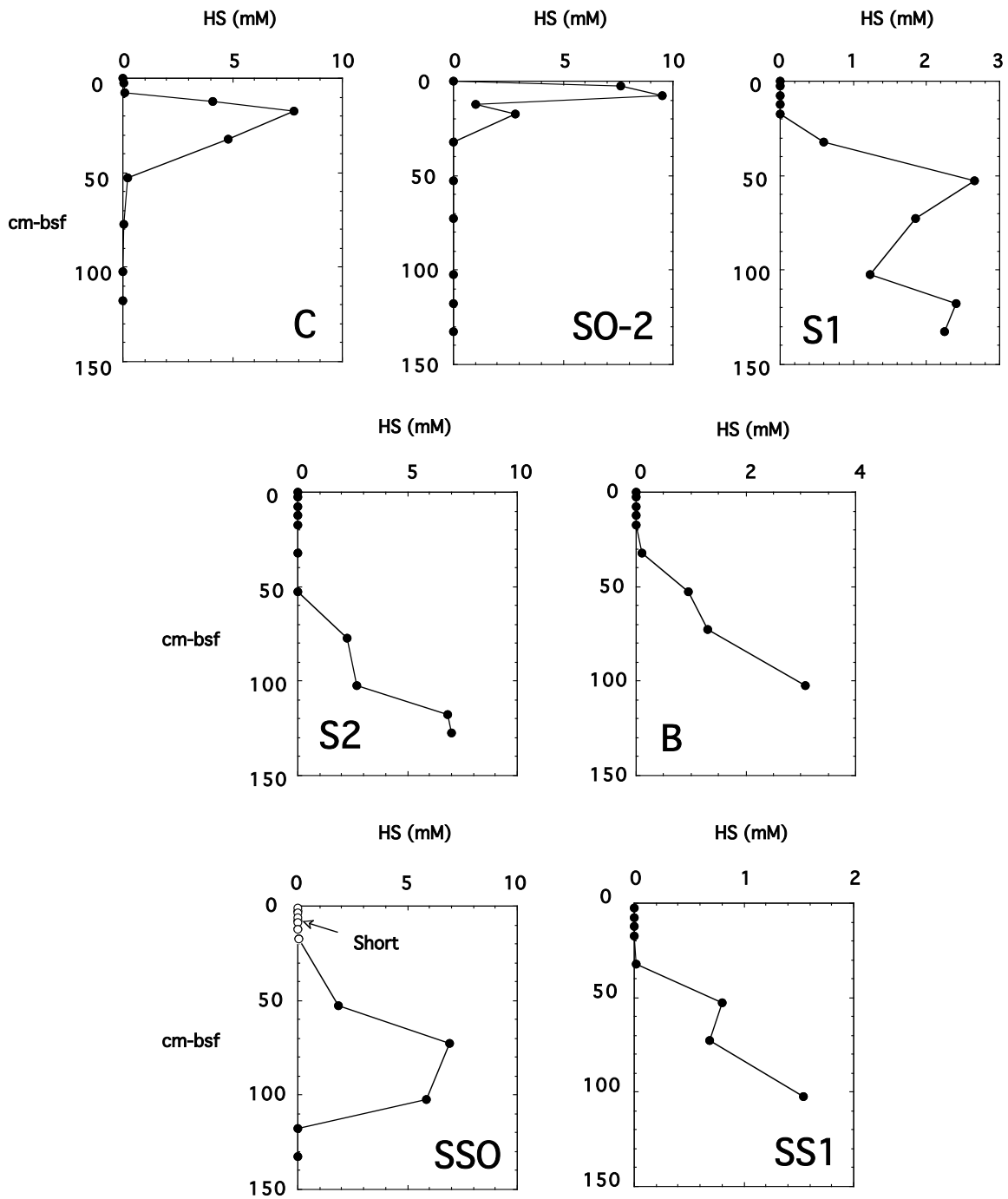
Dissolved Iron in Pore Fluids of Long Cores Venice Lagoon

Figure 6



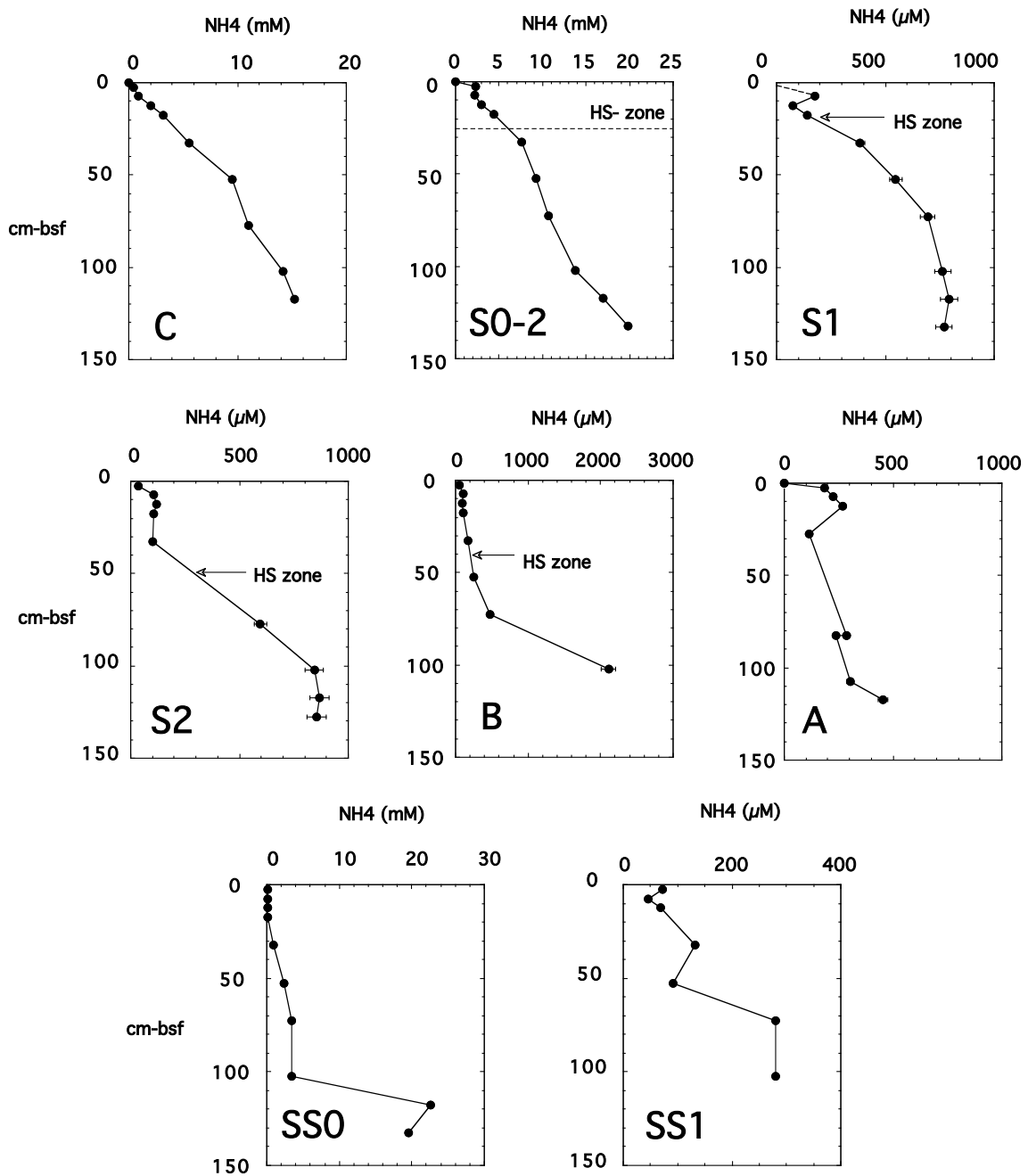
Dissolved Sulfate in Pore Fluids of Long Cores Venice Lagoon

Figure 7



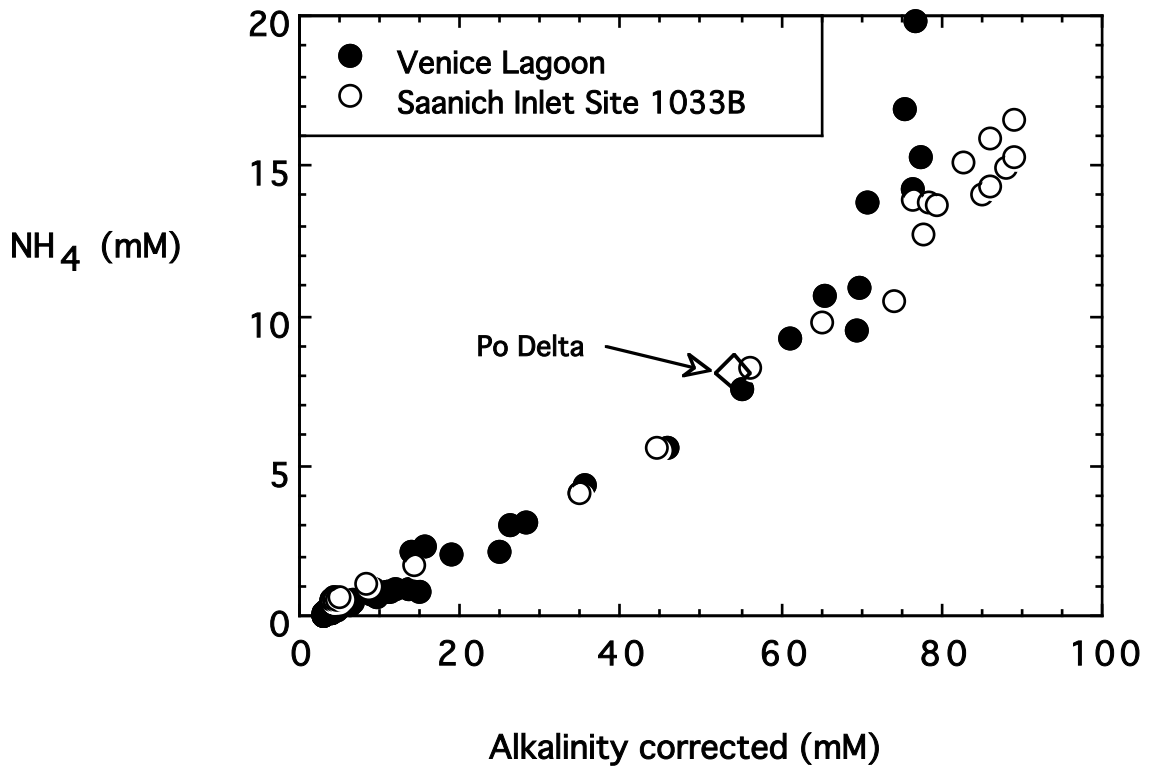
Dissolved Sulfides in Pore Fluids of Long Cores Venice Lagoon

Figure 8



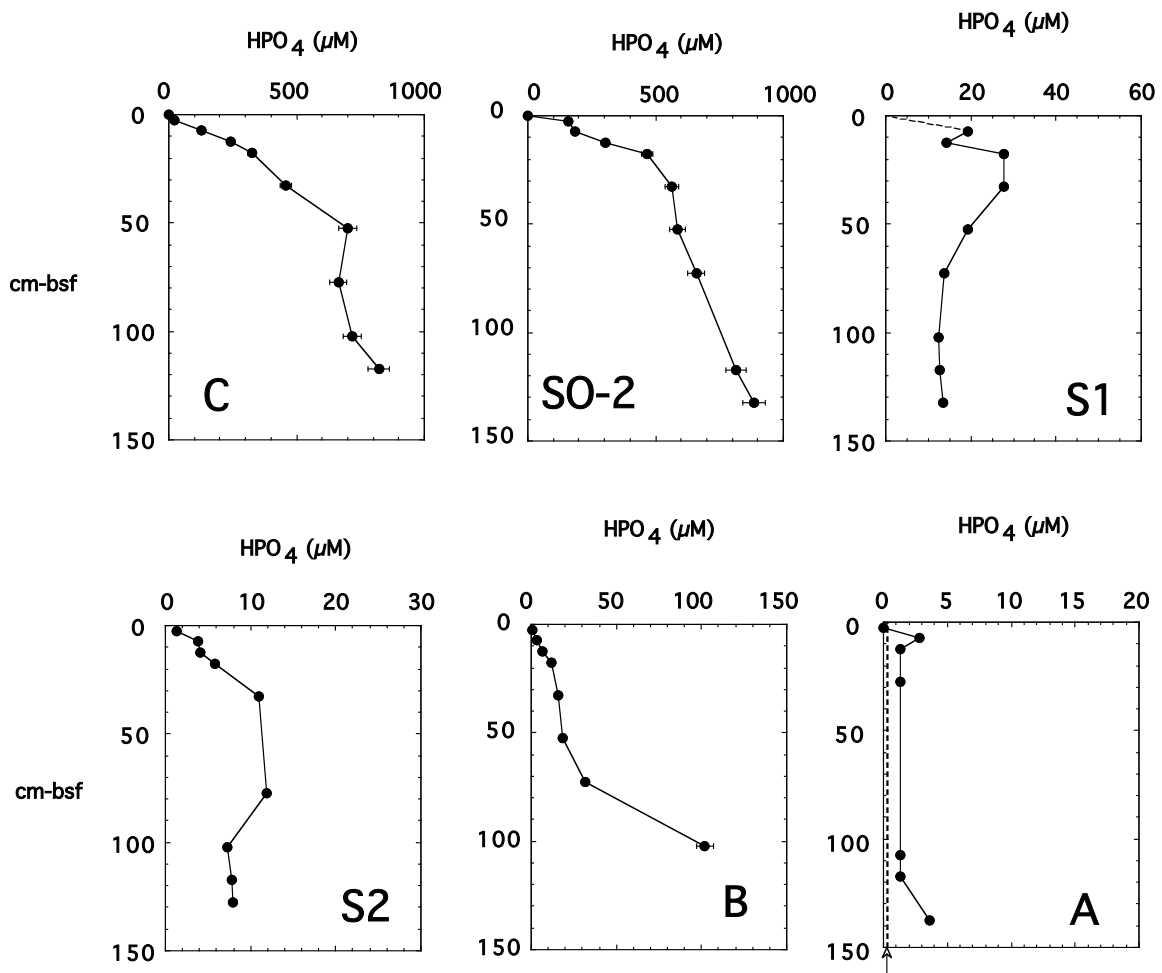
Dissolved Ammonium in Pore Fluids of Long Cores Venice Lagoon

Figure 9



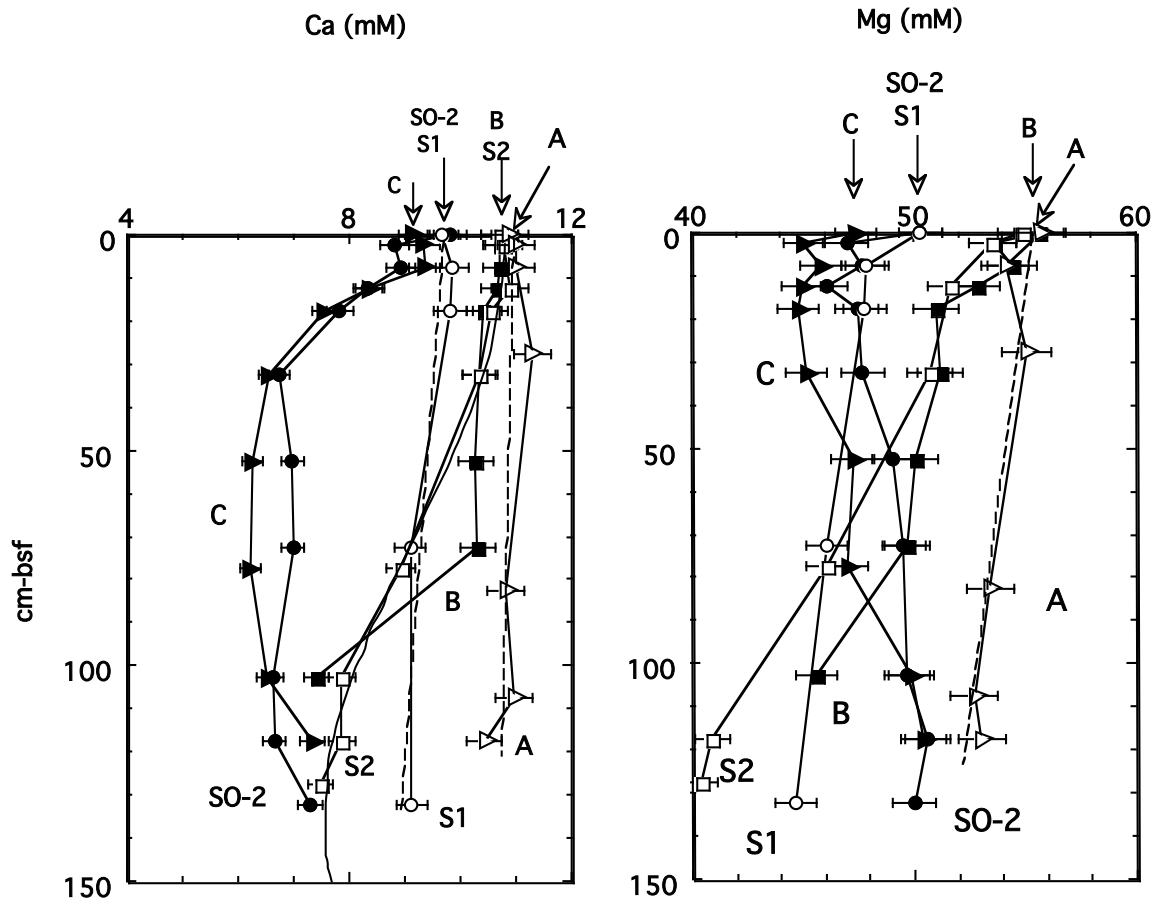
Correlation between corrected alkalinity (Alkalinity – HS⁻) and ammonium. Zero sulfate concentrations occur at ~7 - 8 mM in cores C and SO-2. Further production of ammonium in the methane zone.

Figure 10



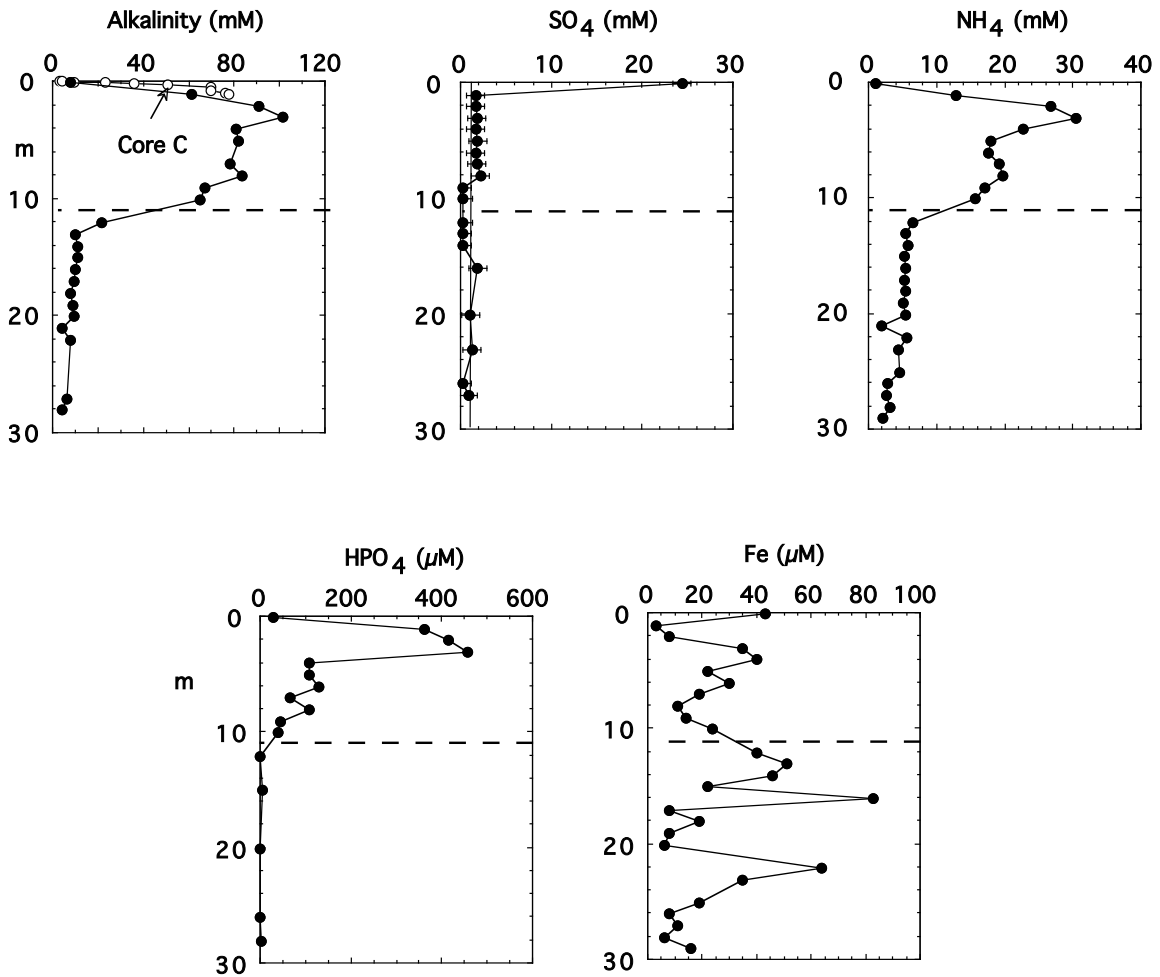
**Dissolved Phosphate in Pore Fluids of Long Cores
Venice Lagoon**

Figure 11



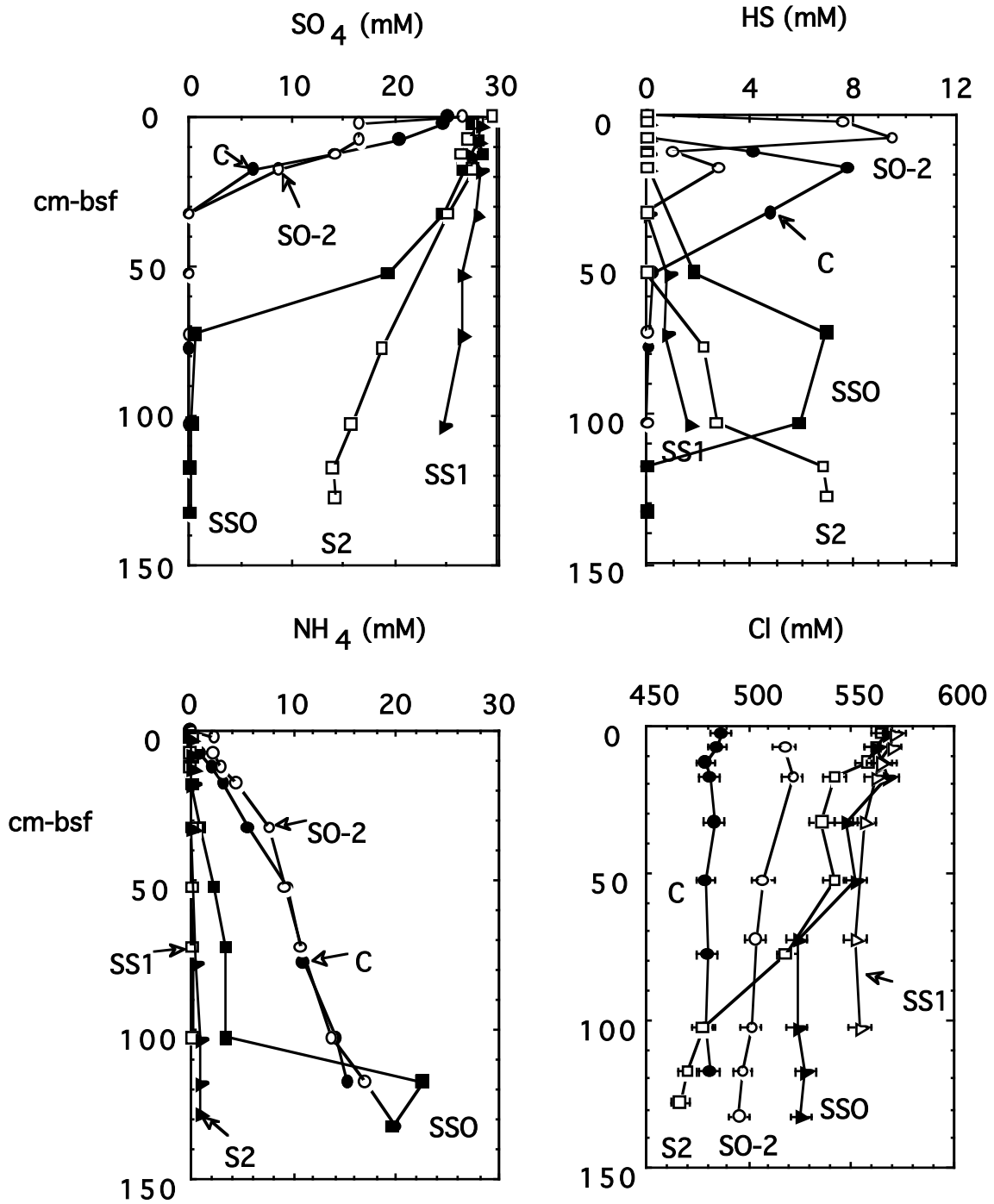
Composite Pore Fluid Profiles in Long Cores of Calcium and Magnesium Venice Lagoon

Figure 12



**Pore Fluid Profiles of Drill Hole SM3
Venice Lagoon**

Figure 13



**Composite profiles in Pore Fluids of Long Cores
Venice Lagoon
Sulfate, Sulfide, Ammonium, and Chloride**

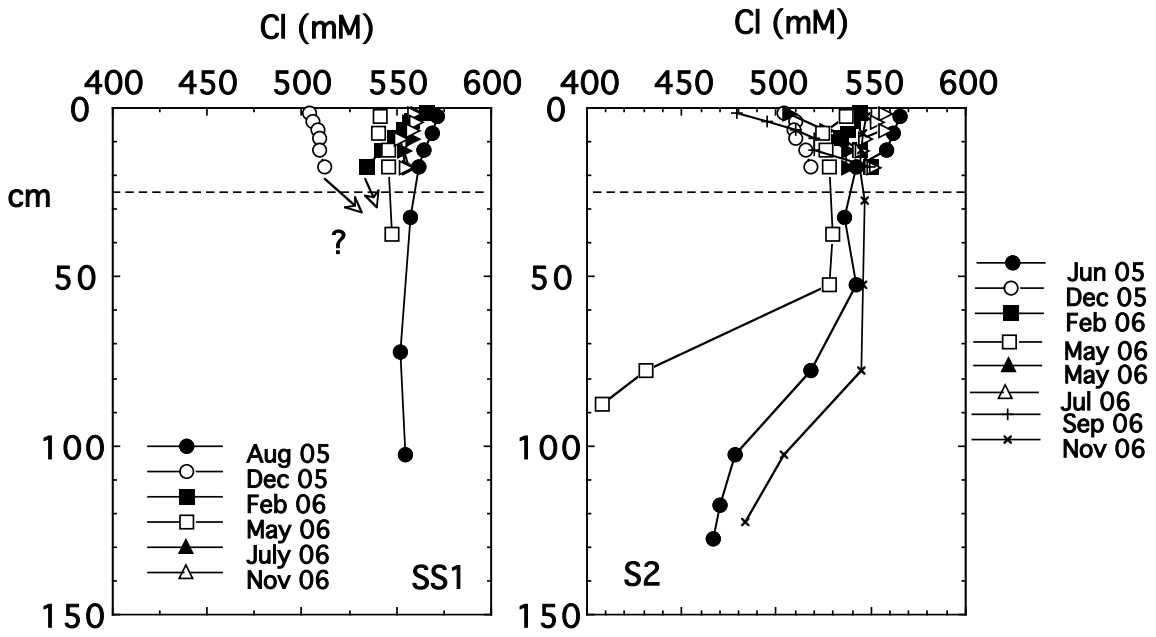
Figure 14



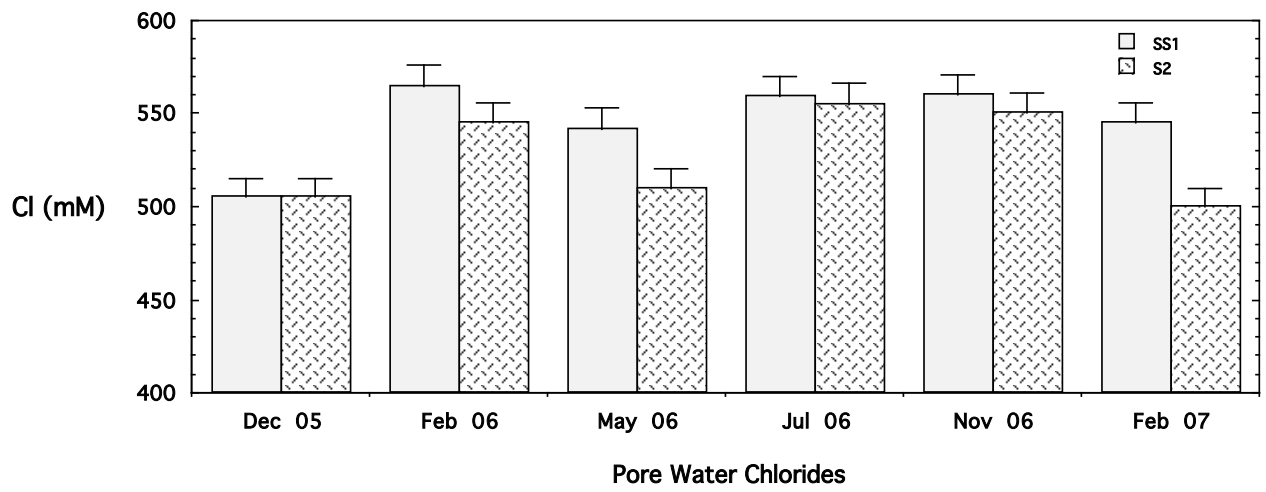
Photo credit D.D. Deheyne

Construction of Banks V1 and V2 using Sediments of Site SSO

Figure 15



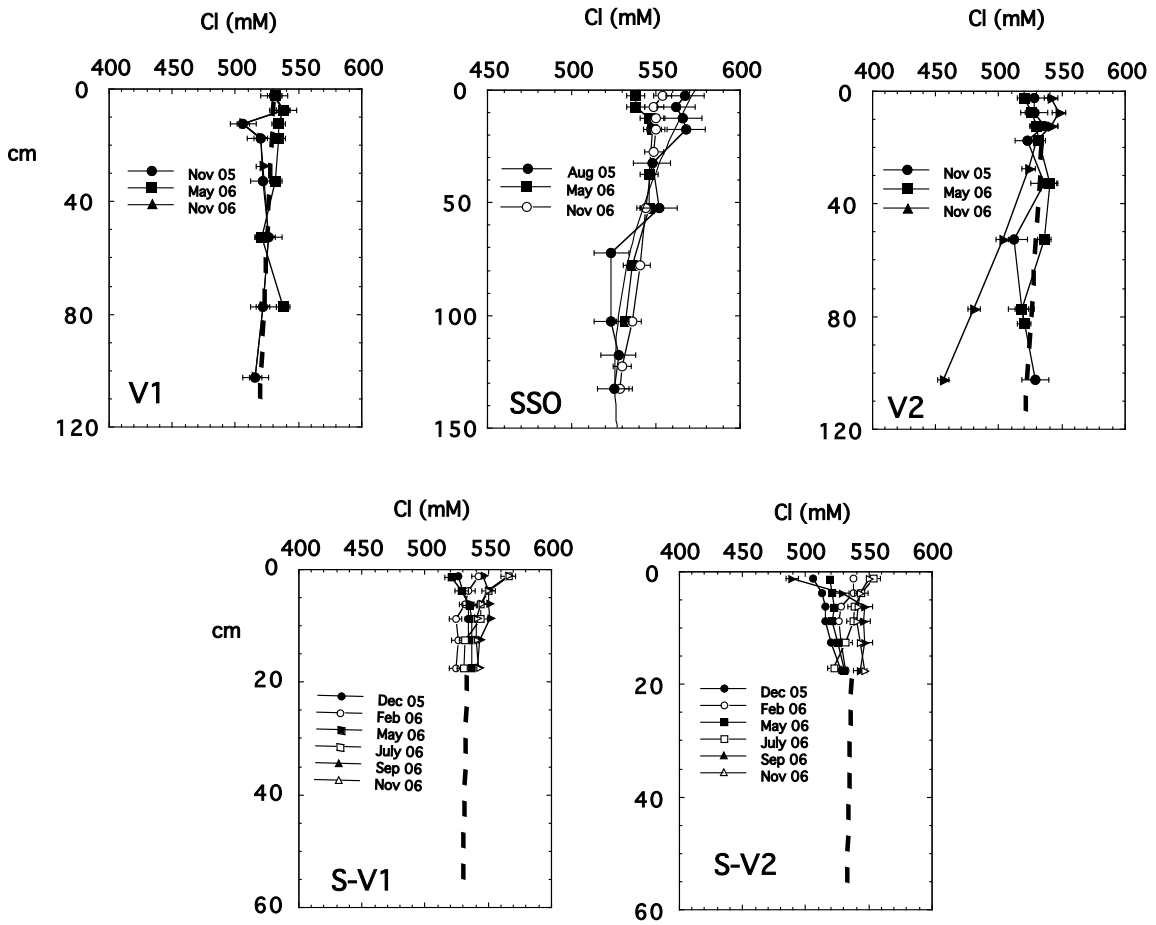
A



B

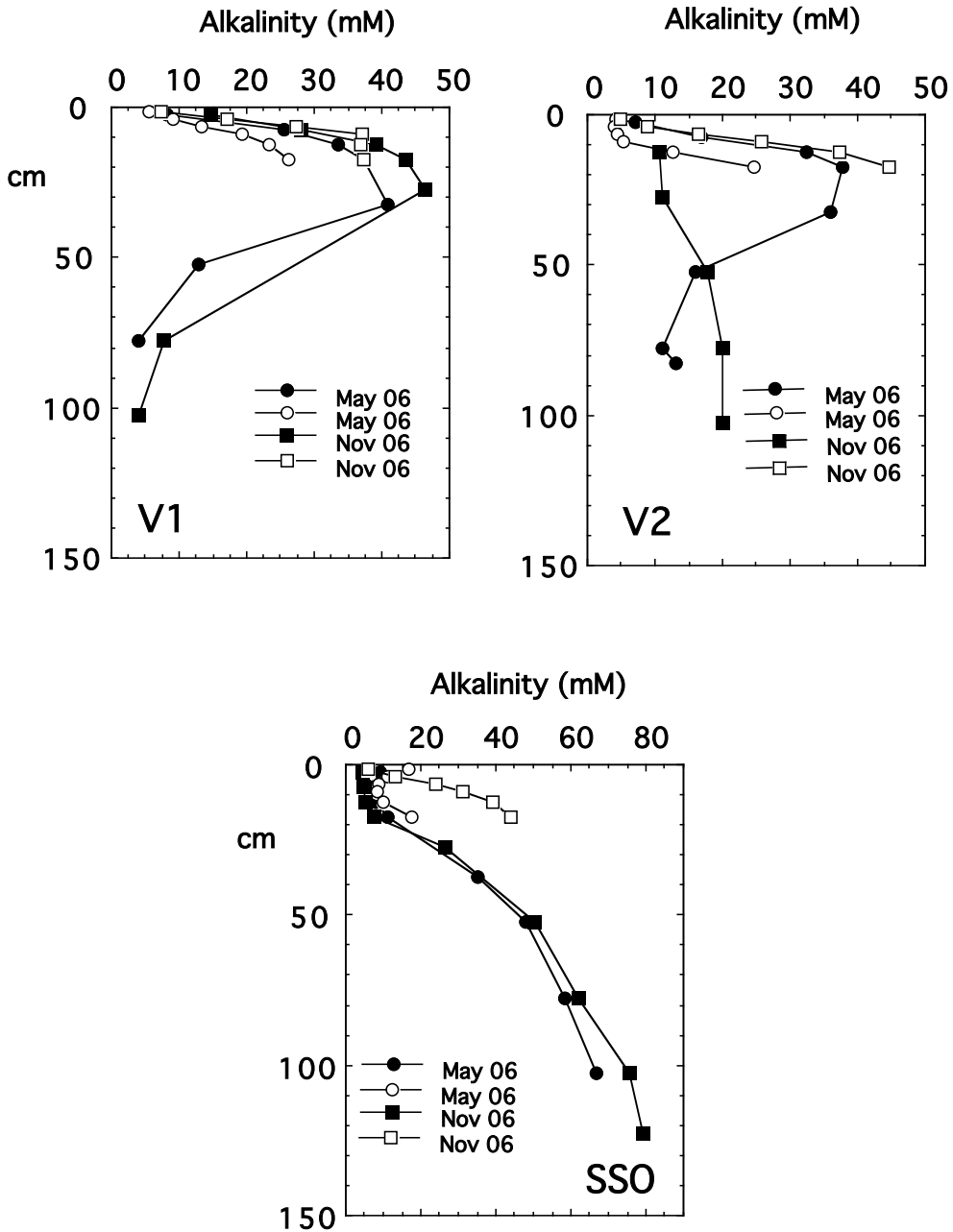
Chlorides in Reference Sites SS1 and S2

Figure 16



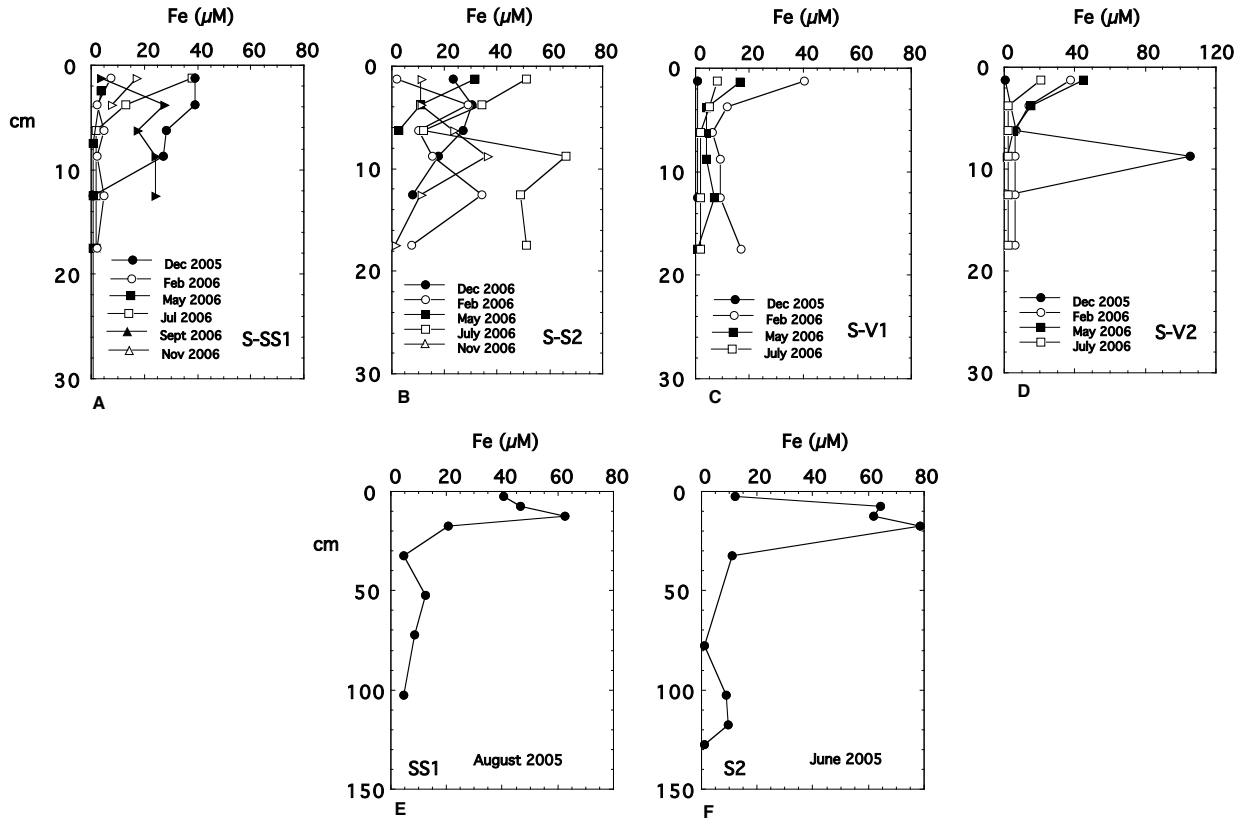
**Chlorides in Sites Long Cores V1, SSO, and V2,
and short Cores S-V1 and SV-2**

Figure 17



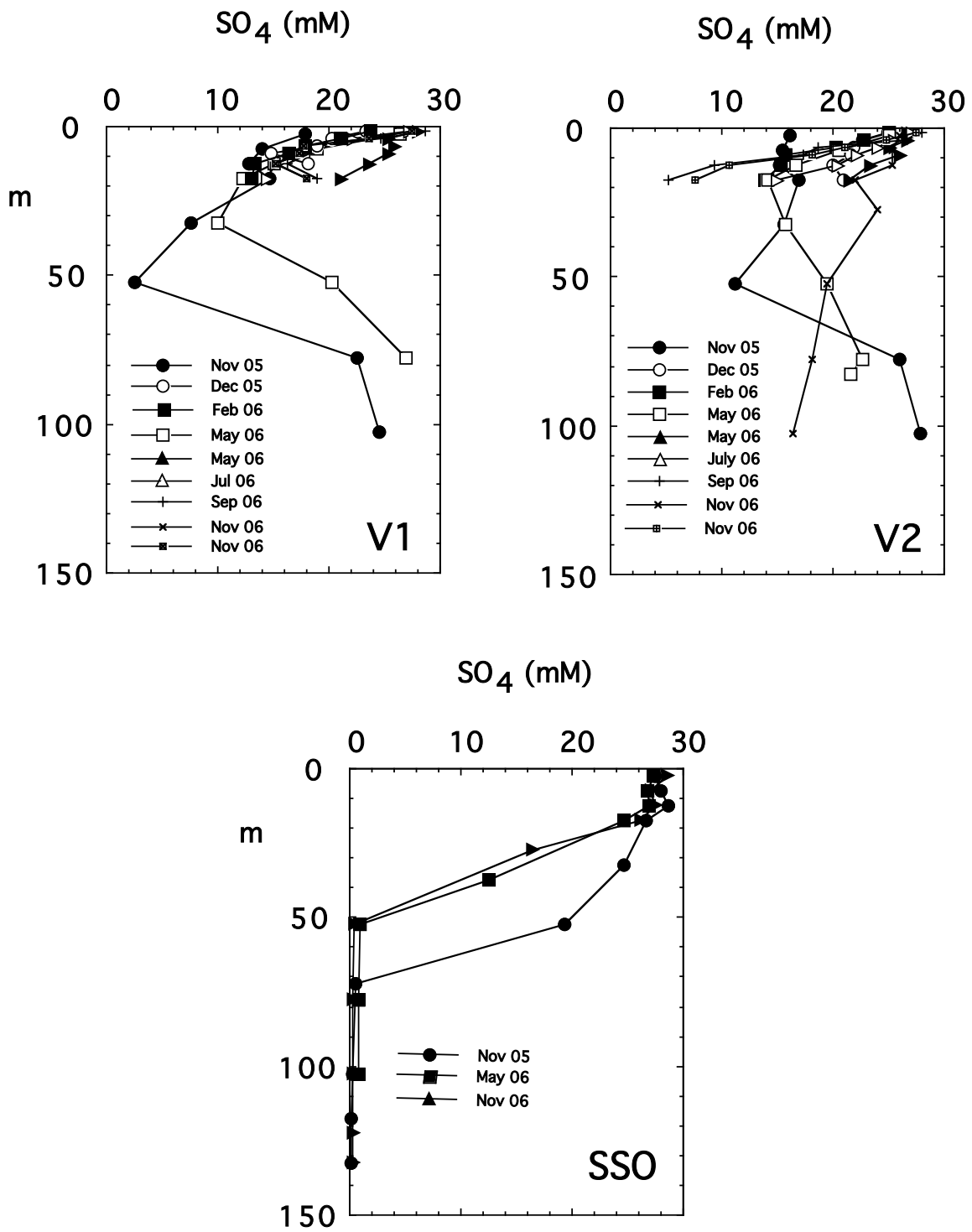
Alkalinity in V1, V2, and SSO Cores
Closed symbols: long cores; open symbols: short cores

Figure 18



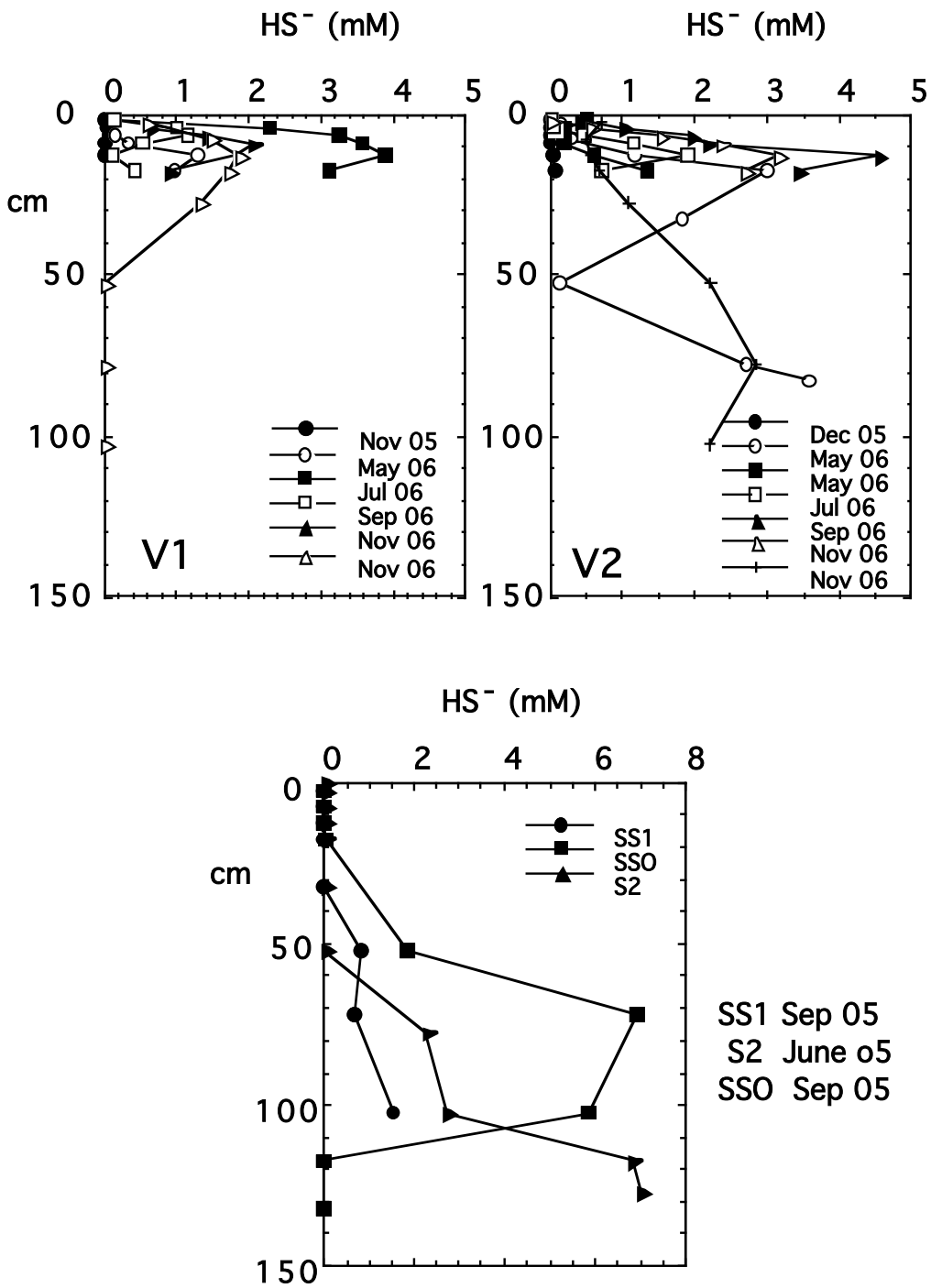
Dissolved Iron in Short Cores and Long Reference Cores

Figure 19



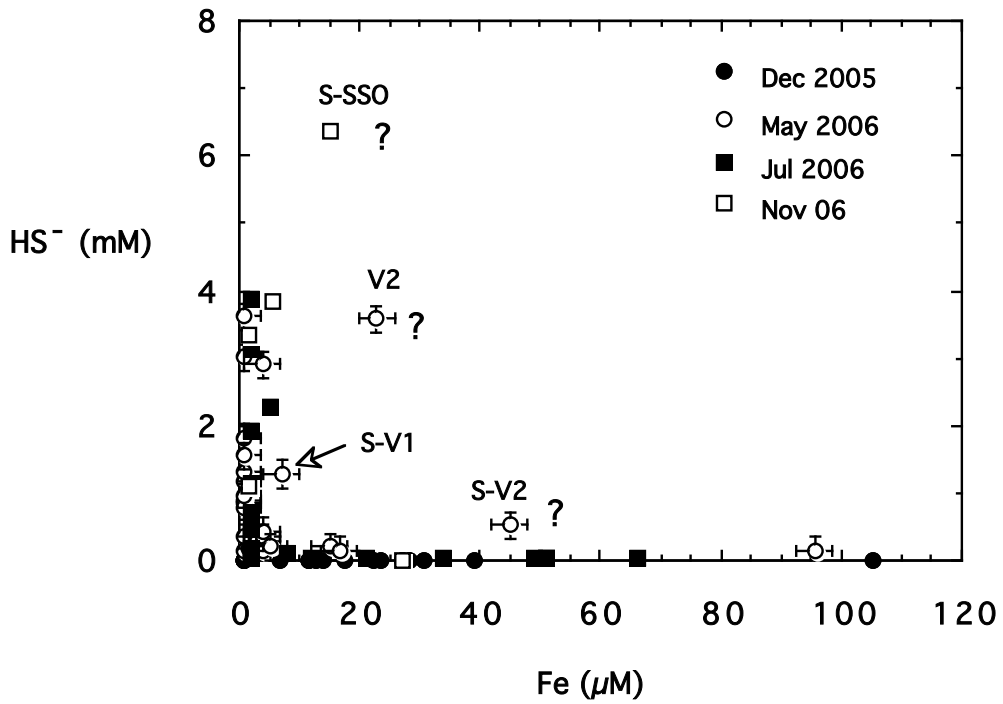
Sulfate in Long Cores V1, V2, and SSO

Figure 20

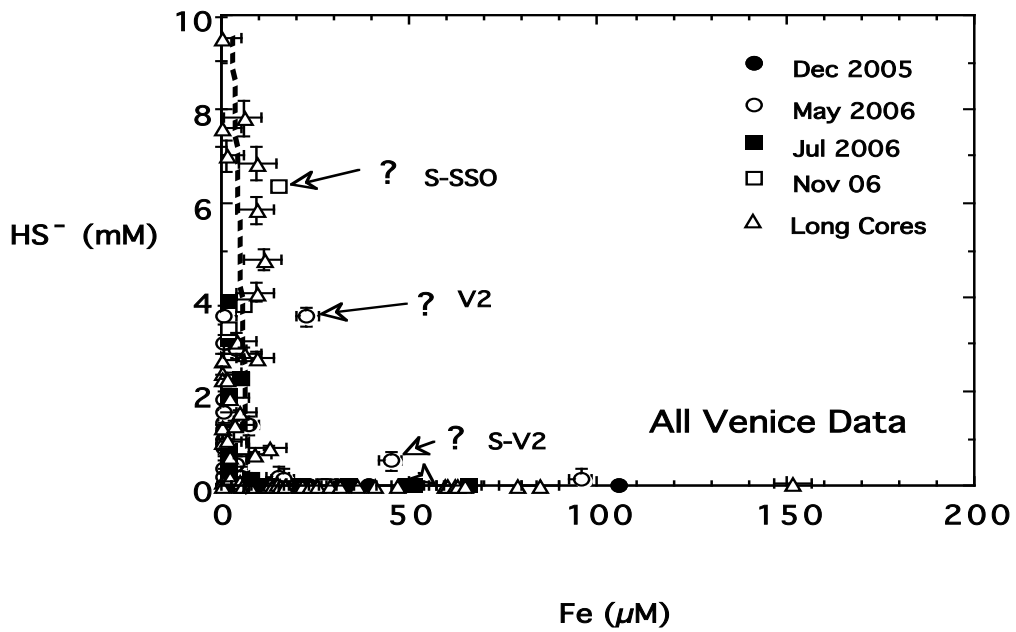


Sulfides in Long Cores from V1, V2, and SSO

Figure 21



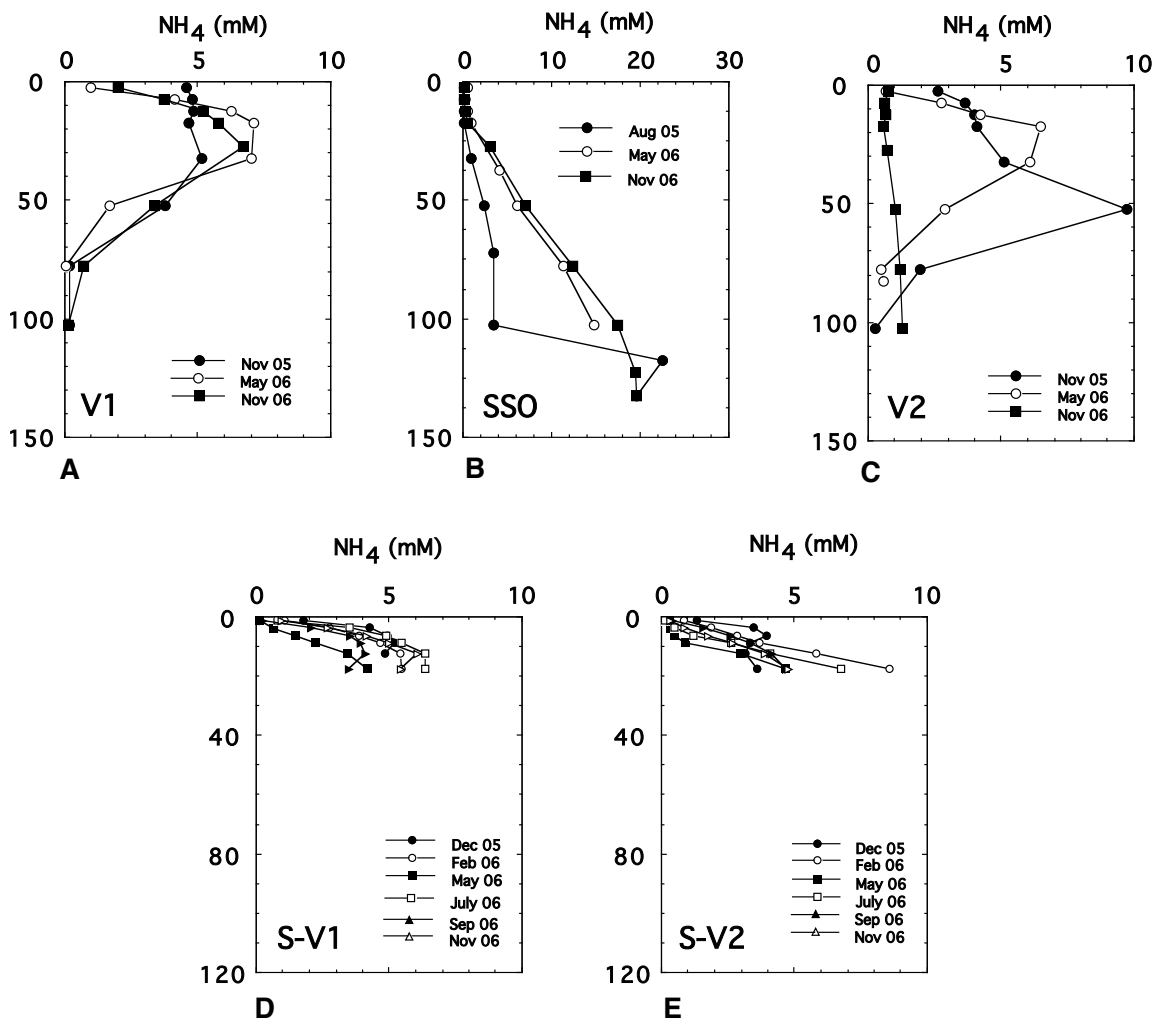
A



B

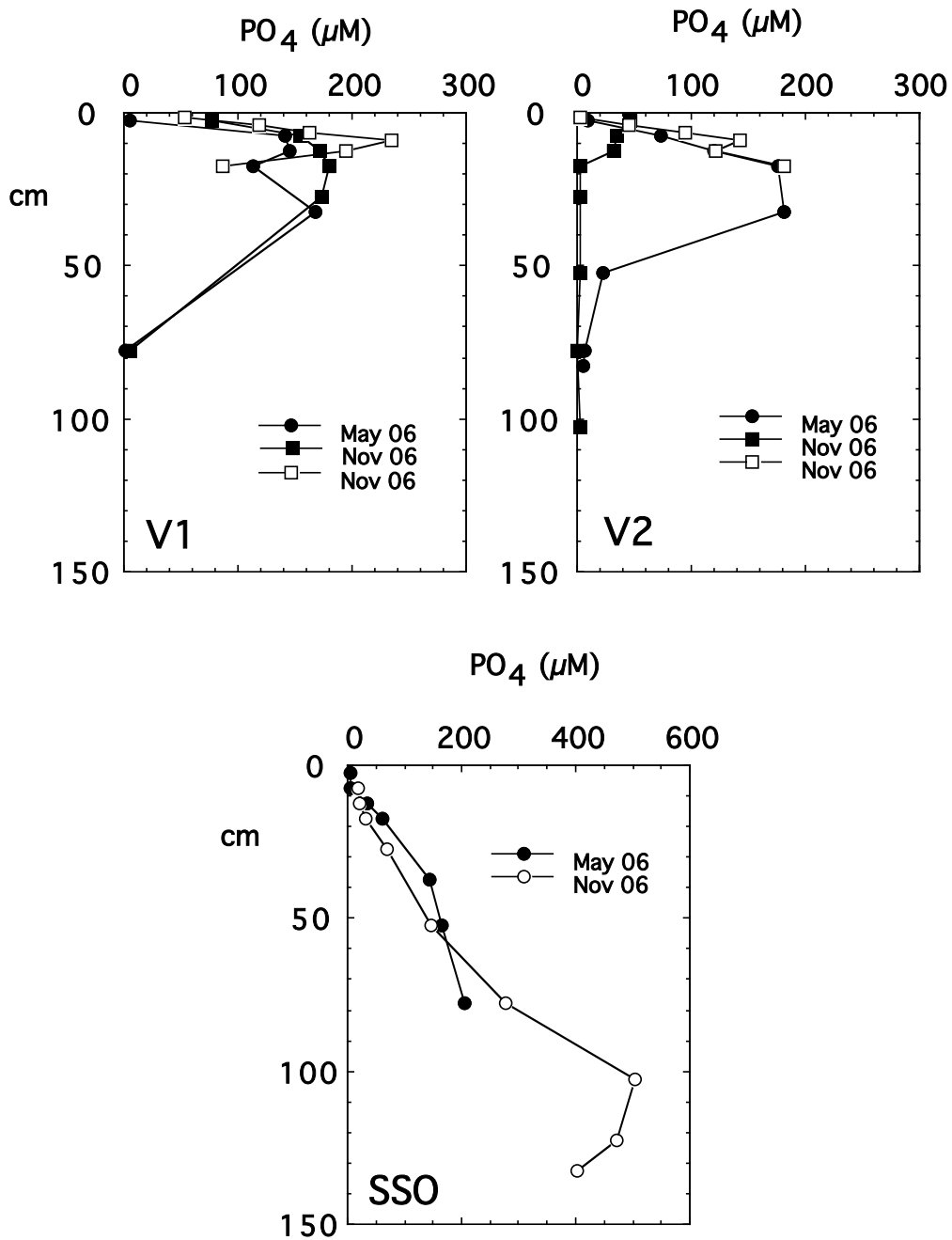
Fe²⁺ vs. HS⁻ A: Banks; B: All Venice data

Figure 22



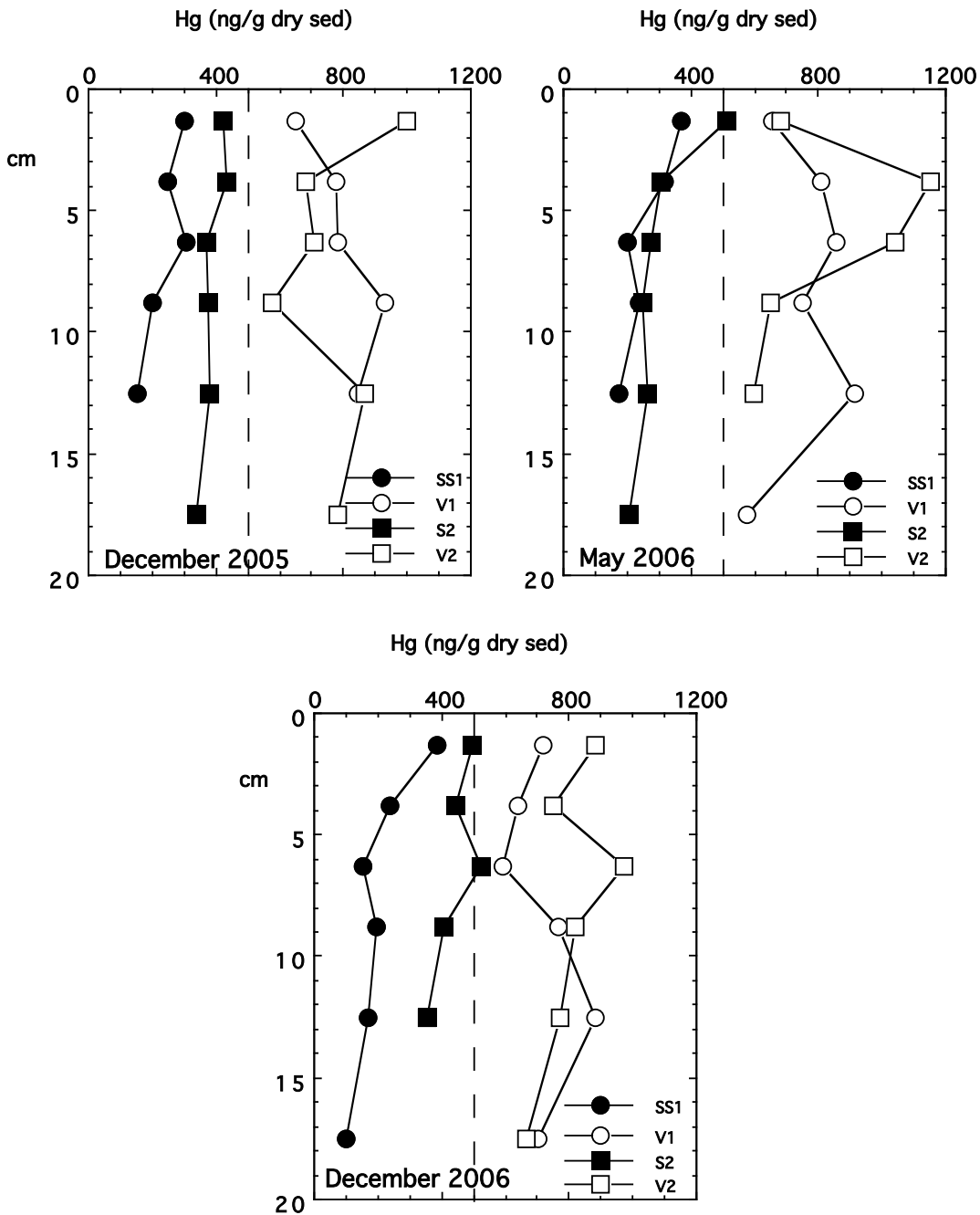
Ammonium in Long Cores V1, SSO, and V2 and Short Cores S-V1 and S-V2

Figure 23



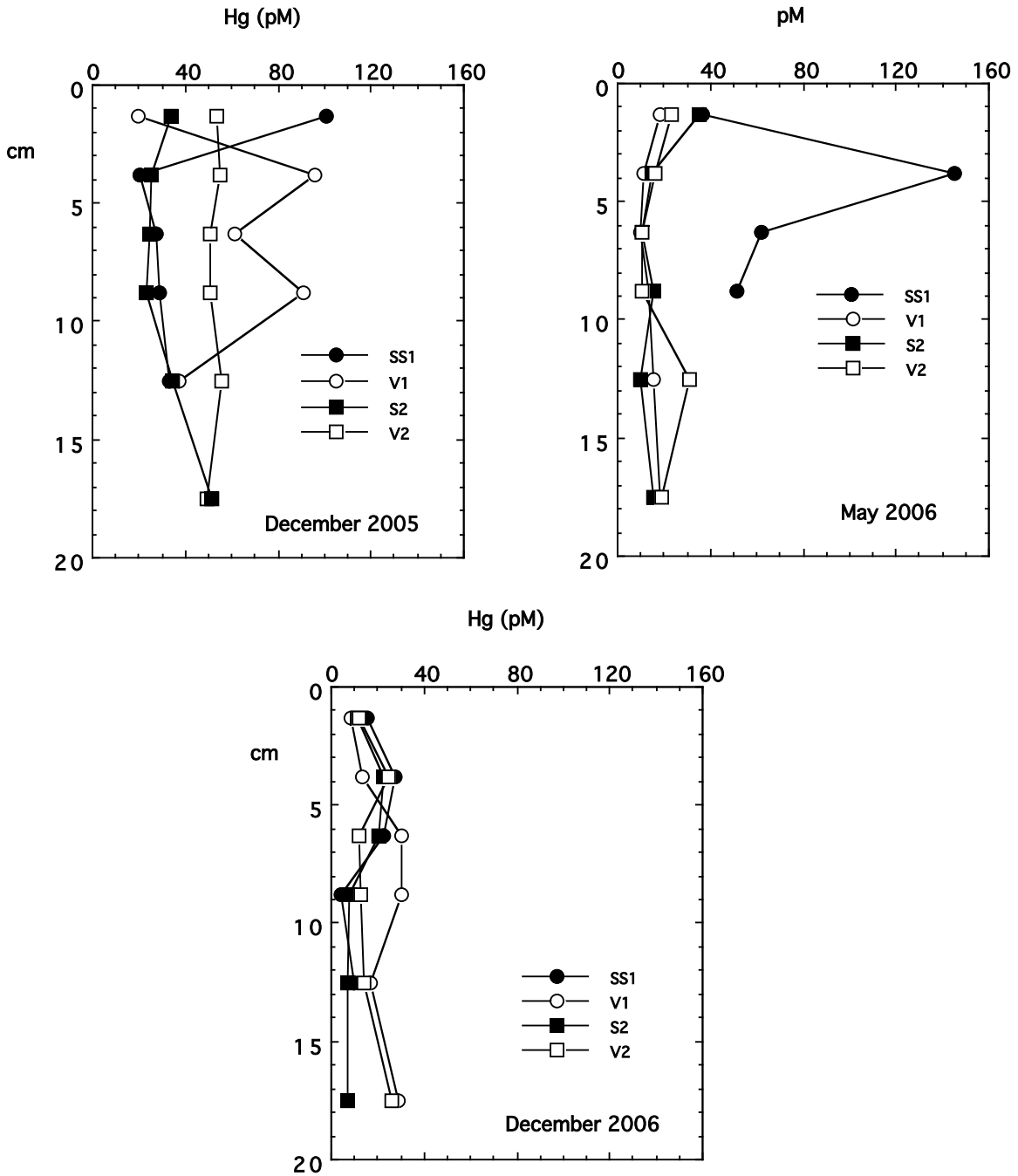
Phosphate in Long Cores V1, V2, and SSO

Figure 24



Solid phase concentrations of total mercury in upper sediments of banks V1 and V2 and reference sites SS1 and S2. Note much higher concentrations in banks reflecting source sediments of Sites SSO

Figure 25



Pore water dissolved mercury concentrations in sediments of reference sites SS1 and S2, and in bank sites V1 and V2. Overlying waters 3-15 pM (Bloom et al., 2004).

Figure 26