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Contaminant Migration Via Sediment Porewater Through A Sub-aqueous Cap Over Hamilton Harbour Sediments

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CONTAMINANT MIGRATION VIA SEDIMENT POREWATER THROUGH A SUB-AQUEOUS CAP OVER HAMILTON HARBOUR SEDIMENTS

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Abstract

Sub-aqueous capping is one method that has been employed to isolate contaminated sediment from overlying water and biota. In this report, we present data from a demonstration *in situ* capping site (100 m x 100 m) in Hamilton Harbour, Lake Ontario, Canada. The objectives of this study were to assess the long-term mobility of different pore water elements through the cap material and to measure the quality and quantity of harbour sediments accumulating on the cap surface. Results show variable concentration gradients of major ions, nutrients and major elements, within the sand cap. Concentration profiles for silica and chloride are similar to those in the original sediments due to downward diffusion of chloride from the overlying water and high silica content in the sand material. Concentrations of Fe and NH_3-N are higher than expected and are due to the sand Fe content and de-nitrification processes producing NH_3-N. The concentration profiles for Mn and SRP show that the sand cap is restricting diffusion to the top and bottom 10 cm of the approximately, 35 cm cap, with minimum concentrations being found in the middle of the cap. Concentrations have been decreasing over time and seem to have achieved a steady state in the year 2000 for Mn and 2003 for SRP. The results demonstrate that the sand cap is effective in reducing diffusional fluxes of some contaminants. The mean sedimentation rate of particulate matter at bottom minus 2 m is 6.2 g/m2/day, which is equivalent to a sediment accumulation rate of 6.5 cm over the eight-year study period. All major and trace elements in the bottom sediment cores, show decreasing depth concentrations, with the exception of calcium and magnesium. The major and trace element concentrations in the surficial sediments of the three cores are 25 to 50% lower than the mean concentrations in the trapped material. Also these surficial sediment concentrations for Fe are 50 to 70% lower than those reported by other investigators for sediments sampled in 1996. Over the study period the mean accumulation rate is ~0.5 to 0.6 cm/yr. These results compare extremely well with ^{210}Pb rates of 0.599 cm/yr, calculated by other investigators as the mean sedimentation rate for Hamilton Harbour.

Migration dans l'eau interstitielle des sédiments de contaminants à travers une couche de recouvrement sous-marine mise en place au-dessus des sédiments de fond dans le port de Hamilton

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Résumé

La mise en place d'une couche de recouvrement sous-marine est une méthode d'atténuation qui a déjà été utilisée pour isoler des sédiments contaminés de l'environnement aquatique sus-jacent et des organismes qui y vivent. Dans ce rapport, nous présentons les résultats obtenus dans un site de démonstration de recouvrement *in situ* (100 m x 100 m), dans le port de Hamilton, lac Ontario, Canada. Cette étude visait à évaluer la mobilité à long terme des divers éléments de l'eau interstitielle à travers la couche de recouvrement et à mesurer la qualité et la quantité de sédiments du port s'accumulant sur la surface de la couche de recouvrement. L'étude a mis en évidence la présence de gradients de concentration variables d'ions majeurs, d'éléments nutritifs et d'éléments majeurs à l'intérieur de la couche de recouvrement de sable. Les profils de concentration de la silice et des chlorures sont semblables à ceux observés dans les sédiments originaux à cause de la diffusion vers le bas des chlorures à partir de l'eau sus-jacente et de la forte teneur en silice de la couche de recouvrement de sable. Les concentrations de Fe et de NH_3-N sont plus élevées que prévu à cause de la teneur en Fe du sable et des processus de dénitrification produisant le NH_3-N. Les profils des concentrations de Mn et de PRS montrent que la couche de recouvrement de sable d'environ 35 cm d'épaisseur limite la diffusion des contaminants vers les 10 premiers centimètres du haut et du bas de la couche, les concentrations étant minimales au centre de la couverture. Les concentrations ont progressivement diminué avec le temps et semblent s'être stabilisées en 2000 dans le cas du Mn et en 2003 dans celui du PRS. Les résultats montrent que la couche de recouvrement de sable réduit les flux diffusionnels de certains contaminants. Le taux de sédimentation moyen à 2 m du fond, évalué à 6,2 g/m^2/jour, est équivalent au taux d'accumulation des sédiments de 6,5 cm observé au cours de la période de huit ans couverte par l'étude. Les concentrations de tous les éléments majeurs et éléments traces dans les carottes de sédiments de fond diminuent en fonction de la profondeur, à l'exception du calcium et du magnésium. Les concentrations d'éléments majeurs et éléments traces dans les sédiments de surface des trois carottes sont 25 à 50 % plus faibles que les concentrations moyennes dans le matériel piégé. Les concentrations de Fe dans ces échantillons de sédiments de surface sont 50 à 70 % plus faibles que les concentrations observées par d'autres chercheurs dans des échantillons de sédiments prélevés en 1996. Au cours de la période couverte par l'étude, le taux d'accumulation moyen s'élève à environ 0,5 à 0,6 cm/an. Ces résultats sont très similaires aux taux de sédimentation moyen de 0,599 cm/an établis d'après le profil du 210Pb pour le port de Hamilton par d'autres chercheurs.

Introduction

Hamilton Harbour is a 2,150 hectare embayment (Fig. 1) draining a 49,400 hectare watershed and is connected to Lake Ontario by the Burlington ship canal. Hamilton and Burlington are the two largest communities in the watershed. Both cities obtain drinking water from Lake Ontario and discharge treated sewage to the harbour. Two large steel producers, known at the time of the study as Stelco and Dofasco, occupy about 30% of the harbour waterfront shoreline.

Harbour sediments are highly contaminated with heavy metals and other inorganic and organic contaminants as a result of historical discharges from industry, sewage treatment plants, and urban storm water runoff. The harbour sediments exceed the Ontario Ministry of Environmental and Energy (OMEE) sediment quality guidelines at the severe effect level for many inorganic and organic contaminants (HHRAP 1992). The harbour has been identified as one of the Great Lakes Areas of Concern (IJC 1985).

In the summer of 1995 Environment Canada carried out a pilot-scale sediment capping project in Hamilton Harbour. Clean sand (medium to coarse grain size) was placed over an area of bottom sediment, approximately 100 m by 100 m, to an average thickness of 35 cm. The average water depth of the capped area is 15 m and the maximum slope of the site is about 1.9°. Several factors, such as bottom currents, ship traffic and wave induced shear stress were considered in the selection of the site (Zeman 1994). Results of the pre-capping geotechnical and sedimentological testing were discussed by Zeman *et al* (1995).

The first capping projects were carried out in the United States (Bokuniewicz *et al* 1978) and thereafter in other countries, such as Japan (Kikegawa 1983), Norway (Skei 1992; Instanes 1994), and Canada. Presently, capping is considered as one of several possible sediment remediation measures.

The objectives of this study were to assess the long-term mobility of different pore water elements through the cap material and to measure the quality and quantity of harbour sediments resettling on the cap surface. Suspended sediment and sediment porewater are the mediums for migration of different elements in the water column and within the sediment respectively and play important roles linking bottom sediment with overlying lake water.

Materials and Methods

Dialysis samplers or "peepers" (Hesslein 1976) were used *in situ* to collect sediment porewater at 1 cm depth intervals at the cap site and in the original sediment adjacent to the capped area. Each peeper contained either 60 or 100 compartments (CELLS) which were filled with oxygen-free de-ionized, double distilled water. The open side was covered with a 0.45 micron, pore size, cellulose membrane (Gelman Scientific Inc.). The peepers were assembled following standard procedures recommended by Rosa and Azcue (1993) and kept in oxygen free double distilled water until they were vertically deployed by divers through the sand cap. A permanent mooring (railway wheel), with a subsurface buoy, was deployed at a depth of 13.0 m in the north west corner of the cap site, after cap placement had been completed. The peepers were always inserted in undisturbed substrate on the circumference of a three-metre circle around the mooring. Upon retrieval the peepers were quickly rinsed with lake water to dislodge adhering sediment particles. The porewater from each compartment was immediately removed using disposable syringes. The samples were stored in polystyrene vials and acidified with ultra pure concentrated acids to pH<2, according to Rosa and Azcue (1993) and stored at 4°C prior to analysis. Samples used for nutrient analyses were stored in vials containing 10 µL of 7% H_2SO_4; the samples used for metal analyses were preserved with 50 µL of ultra pure Seastar concentrated HNO_3. All yearly pore water samples for Fe and Mn were analyzed by ICP/AES, and the occasional extra peeper was used for a trace element scan, using ICP/MS. If data are not reported for a specific year, they were not measured. The porewater samples were analyzed for a wide range of parameters by the National Laboratory for Environmental Testing (NLET) in Burlington using Environment Canada Protocol (1979).

A resuspension sediment sampler (RSS), with triplicate cylindrical traps at three depths (0.2, .05 and 2.0 m) above the sediment water interface, was used to collect sedimenting particulate matter (Rosa *et al* 1991). The sampler was deployed from April to November and refurbished on a monthly basis. In the fall, of each year, the sampler was deployed and left until the following spring, to collect sedimenting particulate matter over the winter months. The trapped matter from the three traps at each level was combined, and freeze dried. The material collected was oven dried at 60° C, and the sedimentation rate of total trapped matter (TTM) was calculated. In the spring of 2003 six replicate short cores were hand taken by divers, using core liners 6 cm in diameter and 15 cm long. These cores were sectioned at half centimetre intervals, until a layer of pure sand was reached, freeze dried and oven dried at 60° C before analysis. Chemical analyses for organic and inorganic constituents were done by the National Laboratory for Environmental Testing (NLET) in Burlington using Environment Canada Protocol (1979).

Results and Discussion

Temporal and spatial variations in the concentrations of dissolved oxygen are common in Hamilton Harbour. The concentration of dissolved oxygen rapidly decreases from

saturation in early spring to approximately 0.2 mg/1 (anoxia) in the hypolimnion during late summer (Fig. 2). Knowledge of the oxygen regimes is essential as diffusional fluxes are dependent on oxygen levels (redox conditions) when the concentration approaches zero. Phosphorus and iron fluxes can be 10 to 15 times greater under reduced conditions (Penn *et al* 2000). This would alter the pore water profile especially at the sediment-water interface and the first few centimetres of the overlying lake water. For this reason all the peepers were retrieved in the spring (early June) or fall (late October) when oxygen concentrations are high, (Fig. 2).

From the fall of 1995 to the spring of 2003, dialysis chambers (peepers) (Fig. 3) were deployed on the cap site to monitor pore water movement from the contaminated sediment through the sand cap to the overlying water. This was accomplished by measuring yearly, either in the spring or fall, sediment pore water profiles for nutrients and trace elements, over a period of eight years. Changes in the concentration of selected elements within the sand cap over time will determine if upward diffusion of contaminants is occurring.

The thickness of the sand cap, based on twenty one cores taken over the whole area, varies from 24 to 48 cm; but, based on three cores taken near the peeper mooring (Zeman and Patterson 2000), the cap thickness there was 32, 34 and 37 cm. A thickness of 34cm will be assumed for the purpose of pore water data interpretation.

A. Pore water profiles

Chemical exchange between sediment pore water and the overlying water is an important pathway for transport of nutrients and other contaminants. Whether sediments act as nutrient source or sink depends on sediment composition and limnological conditions. The exchange across sediment-water interface is regulated by precipitation/dissolution, mineral equilibria, redox conditions, sorption/desorption processes and microbial activity in sediments (Penn *et al* 2000). The pore water profiles of nutrients, PO_4-P (SRP) and NH_3-N (NH_3); major ions, SO_4 and Cl; major elements, Fe, Si (SiO_2) and Mn, are the principal elements measured on a yearly bases; although on occasion, multiple peepers were deployed to measure other trace elements.

The pore water concentration profiles of the measured elements in the original sediments prior to capping are shown in Figure 4. All the profiles show a continuous increase below the sediment water interface, except for Cl, and the elements remained in solution at high concentrations in the deeper sections of the sediment. The concentrations of Fe, Si and Mn in pore water at 30 cm sediment depth were 80, 40, and 50 times higher, respectively, than in the overlying lake water. The Fe and NH_3 concentration profiles in the original sediment pore water from the capped area showed strong similarities (R^2=0.77); and even stronger similarities (R^2=0.84) are shown by Mn and SRP (Fig. 4). The diagenetic accumulation of Mn and SRP in the oxic layer (0 to 3 cm) of the sediment is evident in Figure 5. This may be due to the fact that under oxygenated conditions Mn will persist in solution longer than Fe (Förstner and Wittmann 1981). The concentration profile of Fe, Mn, SRP, and SIO_2 in the pore water indicated remobilization of these

elements in the anoxic sediments and precipitation in the oxic interface especially for Mn and SRP. The shape of all the pore water profile is typical of contaminated fresh water systems.

When the cap is placed over the existing sediment, the original sediment water interface will become the sediment-sand interface, and a new sediment-water interface will be established. This new interface will change in character as freshly deposited sediment accumulates on the sand cap over time. The amount of sediment accumulation will depend on the net sedimentation rate.

Now we have two different interfaces where exchange processes will occur and they are dependent on different physico-chemical factors. Since the sand cap is a relatively clean medium (Zeman and Patterson 2000), some upward diffusion of contaminants at the sediment-sand interface; and downward diffusion at the sediment-water interface will occur. Unidirectional ion migration (diffusion) always occurs in a solution/substrate that exhibits a concentration gradient, until homogeneity is achieved. Similarly in sediment pore water ion exchange is always occurring and is controlled not only by concentration gradients, but other physico-chemical factors such as organic content, redox conditions, adsorption/desorption processes, etc. The amount of diffusion that occurs in the sand cap, will determine its efficacy to deter contaminant migration from the contaminated sediments to the overlying lake water.

Yearly pore water concentration profiles of major ions, nutrients and major elements are shown in Figures 6 to 13, for the capped sediments. The major ions (Fig. 6, 7) show typical profiles. The SO_4 concentrations are highest in the overlying water, decreasing to a minimum at approximately 3 to 5 cm below the sediment-water interface (Fig. 6). The elevated concentration levels below that depth could be due to oxidation (oxygen exposure) during sample processing. It would be expected that concentrations below this depth would be close to zero because of reduced conditions. The Cl concentration profiles are fairly constant with depth (Fig. 7). The concentration differences in the overlying water are due to seasonal changes. The highest concentrations (85-100 mg/l) correspond to late spring sampling and are due to road salt input during spring freshet. At this time the sand cap is acting as a sink. The lower concentrations (~60 mg/l) in the overlying water correspond to the fall sampling periods when Cl depletion has occurred and the sand cap is acting as a source. These results confirm that the sand cap is not acting as a deterrent to major ion movement. It appears that Cl concentrations at the top of the sand cap are mainly controlled by ambient lake water concentrations and those below 10 cm are fairly constant.

The annual nutrient pore water concentration profiles in the capped sediments are shown in Figures 8 and 9. The 1995 and 1996 profiles show quite distinct differences than those in the other years. Near maximum concentration seems to be occurring in the sand cap, 10 to 30 cm below the sand-water interface, especially for NH_3-N, (Fig. 8) although SRP shows concentration minimum at 13 cm below the sand water interface (Fig. 9). Higher concentrations in the lower section of the sand cap could be due to sand cap placement, which shifted the redox potential in the original sediments and in the sand cap toward reducing conditions. This encourages NH_3-N production by de-nitrification and

anaerobic decomposition of organic substances present in the oxic layer (0-3 cm) of the original sediments. This results in an increase of pore water species within the sediments in the short term. Since contaminant diffusion is proportional to concentration gradients, upward diffusion at the sediment sand interface will increase pore water concentrations within the sand cap. These concentration maxima seem to have dissipated by the spring of 1997 and were not repeated. The NH_3-N profiles (Fig. 8) seem to show a quasi-linear concentration change, from a minimum at the sediment-water interface to a maximum between 30 and 40 cm depth, with no obvious time trend. The diagenetic accumulation of SRP in the oxic layer (0 to 3 cm) of the sand cap is quite evident (Fig. 9). The SRP profiles show a significant time trend of decreasing concentrations with time and the lowest concentration appearing near the mid-section of the sand cap (Fig.9a). The highest concentrations are below the 60 cm depth, which is well within the original contaminated sediments.

The concentration profiles of the major elements are shown in Figures 10-12. All three elements show higher concentrations for 1995 and 1996, within the sand cap. Higher nutrient concentrations can be attributed to sediment compaction. The SIO_2 profiles (Fig. 10) don't show a time trend and are very similar to the original sediments (Fig.4). This is due to the fact that, both the original sediments and the sand cap have SIO_2 concentrations greater than 40% (Azcue et al 1998) and thus high concentrations within the sand cap are expected. The Fe concentrations (Fig. 11) are lowest at the top 20 cm of the sand cap and increase to a maximum at the bottom (10 to 15 cm) of the cap and, into the original sediments. The higher concentrations within the cap can be due to reasonably high concentration of Fe (1.5%) in the sand material according to Azcue *et al* (1998). The Mn profiles (Fig. 12) show decreasing concentrations with time. The lowest concentrations appear towards the middle section (~22 cm depth) of the cap (Fig. 13). The highest concentrations are below the 50 cm depth, which are the original sediments.

Based on these results, all of the pore water elements seem to show elevated concentrations especially at the lower section of the sand cap. Cap placement caused considerable sediment compaction of the original sediment -- approximately 14 cm in the top one metre of the sediments. This compaction resulted in a substantial reduction in the porosity, thus forcing the ambient pore water in a lateral and upward direction, into the sand cap. Although this is temporary, it did increase the pore water contaminant concentration in the lower part of the cap. This influx of contaminants is in addition to the influx due to molecular diffusion. There is substantial contamination in the original sediment pore water, according to these findings, and gradually these contaminants will diffuse in the bottom section of the sand cap. The amount of entrainment into the middle and upper section of the cap is dependant mainly on the physico-chemical (adsorption/desorption, etc.) characteristics of the sand cap, and can only be determined by continuous measurements over time. Most trace metals tend to be enriched in the modern organic sediments relative to inorganic sediments, a factor which is most probably due to the nature of the metal-organic binding strength and perhaps increased ion-exchange capacity of organic sediments over inorganic types. As a result, the highest and most uniform concentrations of trace metals generally occur in the modern-organic sediment found in the deep central areas of most lakes (Coker *et al* 1979). Because of the

low ion-exchange capacity of inorganic sediments, such as sand, the entrainment by molecular diffusion into the sand cap will probably be minimized due to the low organic carbon content of the sand material, relative to the original sediments, 0.1% and 3%, respectively, according to Zeman and Patterson (2000).

B. Sand cap sediment accumulation

Sedimentation of suspended particulate matter (SPM) is a fundamental processes of aquatic ecosystems and important in the transport of pollutants (Allan 1986), as well as the input of particulate organic carbon to the benthic food chain (Smetacek 1984). Sediment transport, deposition and resuspension are processes mainly driven by meteorological forces and currents (Hilton and Allen 1986). Particles are transformed by physical, chemical, and biological processes such as decomposition, mineralization, adsorption, and bacterial degradation (Wassmann 1990). The residence time of particles in the water column is of crucial importance in transformation processes and is usually limited by the downward flux and water depth rather than loss through outflow. The determination of contaminant flux is an important step in evaluating remediation priorities and assessing progress in solving water quality problems. Sediment trap measurements yield valuable information about total mass flux, composition of particulate matter, and changes of particle composition with depth.

Resuspension, at the sediment water interface, distributes particles back into the water column, which will again settle to the bottom. This continuing process of colliding particles forms flocs of variable size and results in a dynamic equilibrium between aggregation and disaggregation (Lick and Lick 1988). During this process there is also an associated change in surface area of the particles, which affects metal sorption/desorption equilibrium. Calvo *et al* (1991) showed in calibrated experiments that the particulate metal concentration is greater in the suspension than the original sediments. Hamilton Harbour is a closed embayment at the western end of Lake Ontario (Fig. 1), with an area of 2150 ha and, mean and maximum depths of 13 and26 m respectively. Hamilton Harbour receives municipal, industrial and CSO discharges and the only outlet is via the ship canal to Lake Ontario. The ratio of the harbour surface area to the cap is approximately 2000:1; therefore, the likelihood of contaminated sediment resettling over the sand cap, are very high.

The sedimentation rates of total trapped matter (TTM) from November 1995 to June 2004, at the cap site, are shown in Figure 14. *In situ* experiments with replicate traps, either positioned in parallel moorings (in open waters) or fixed at the same site, result in coefficients of variation <15%, including the errors of sub-sampling and chemical analyses (Rosa *et al* 1991). The mean sedimentation rate for the three trap depths over the study period is 8.67 g/m^2/day (Table 1A), with minimum and maximum rates of 0.2 and 32.5 g/m^2/day, respectively. The highest TTM sedimentation rates always occur in the spring and fall of each year and the lowest rates occur in the summer (Fig. 14). These higher rates are due to the resuspension of bottom sediments during isothermal periods. The mean summer rates are 55% lower for TTM and the mean organic carbon content and % loss on ignition (LOI) are 14 and 30% higher, respectively (Table 1B, 1C). The higher organic content is due to abundant production of phytoplankton in

the photic zone during the summer (Charlton and Le Sage, 1996), which settles through the water column to the bottom sediments. The % LOI for the study period is shown in Figure 15, which clearly shows that the trapped material has a much higher organic content over the summer periods. Also, in the summer, the harbour is thermally stratified. Thus, resuspension of reduced sediment (low organic content, due to decomposition of organic matter) is much less than the spring and fall periods. The mean LOI at the mid-harbour station (19%) is slightly higher than the LOI at the cap site (17%). The mid-harbour station is about 8m deeper and is not as prone to resuspension of less organic sediments as is the shallower near-shore cap site.

There is no significant difference in the mean concentrations of major and trace elements in the trapped material between the summer and the rest of the year (Table 1); although, plots of individual data (Fig. 16) seem to show inverse relationships, which are not statistically significant (R^2 <0.1). The individual data plots for four elements; iron, lead, chromium and titanium, seem to indicate that metal concentration in the trapped matter during the summer (low sedimentation and high organic content) could be higher than the rest of the year. This is most probably due to the nature of the metal-organic binding strength in the presence of dissolved oxygen; however, under reducing conditions in the bottom sediments, they are solubilised and may result in decreasing concentrations in the particulate fraction.

This implies that suspended material in the water column has higher metal concentrations than the bottom sediments. Plots of element concentrations in TTM over time (from 1995 to 2003) show no change for Fe (not plotted) and Cr and, also show a somewhat decreasing concentration trend for Pb and Ti (Fig. 17), which is not statistically significant ($R^2 < 0.07$).

C. Sand cap core samples

Hand coring, by divers, is probably one of the best methods to retrieve an intact core with minimum sediment disturbance and sediment compaction, at least in natural sediments consisting of soft muds. In natural, soft sediments, core liners can be easily inserted with minimum pressure. This was not the case obtaining cores on the sand cap. Divers had to apply considerable pressure to insert the core liner once it reached the sand substrate. As a result, some cores were taken on a slight angle and the surface sediments were disturbed. Visual inspection revealed some sediment smearing along the inside walls of the core liner next to the sand substrate had occurred. Some difficulty was also encountered during extrusion (core slicing).

The main problem was the loss of surficial sediment dripping down along the sides, between the core liner and the sand substrate; a condition that could not be overcome. This will certainly result in an under-estimate of the sediment thickness and bias the sand substrate towards a higher organic content. After all the cores were extruded, only four were deemed usable for organic content and three of these were sent for major and trace element analysis. The sand substrate for most cores was reached at a depth of 4 to 5 cm. This depth may be an under-estimate, since surficial sediments were lost during core sectioning. The concentration of major and trace elements in the three cores is shown in Table 2. All the elements show a concentration decrease with depth, with the exception of calcium and magnesium, which actually show an increasing trend. The major and trace element concentrations of the surficial

sediments in the three cores (Table 2) are 25 to 50% lower than the mean concentrations in the trapped material (Table 1A). These results agree with the findings of Calvo et al (1991). Also, these concentrations are 50 to 70% lower than those reported by Azcue *et al* (1998).

The depth profile for % LOI, organic carbon (OC) and density are shown in Figure 18. All three parameters seem to show a quasi-linear depth trend with decreasing organic content and increasing density. Based on the mean of four cores, the best fit linear trend line has a very high correlation coefficient (R^2) of 0.88, 0.99 and 0.99 for LOI, OC and density, respectively. A one cm slice of sand from core # 5, at a depth of 10 cm, was analysed for organic content and density. The results showed that sand contains 2.1% LOI, a 0.16% organic carbon and a density of 2.72 g/cc. Using the equations from Figure 18, and substituting the above values for "y", we can calculate the depth where pure sand occurs by extrapolation. The calculated depths for the three parameters are: 5.6, 4.8 and 5.4 cm for LOI, OC and density, respectively, with a mean depth of 5.3 cm. The mean sedimentation rate of TTM for the study period, from the three trap levels, is 8.67 g/m2/day (Table 1A). Thus, from October 1995 to June 2004, 27167 g/m2 of sediment settled on top of the sand cap. Assuming water content of 80% and a bulk density of the newly deposited sediments of 1.5 g/cc, the volume of accumulated sediment per metre square would be 90544 cc. This corresponds to a sediment accumulation of 9.05cm (after dividing by 10,000 cm^2). Since sediment traps measure gross rates, which includes resuspension, this value is overestimated. Assuming that the sedimentation rate at two metres above the sediment is equal to the net rate (although, this can still be slight overestimate) and using the mean sedimentation rate for this depth of 6.2 g/m^2/day for the study period, the sediment accumulation would be 6.5 cm. This estimated value is 30% less than the previous estimate, and the difference is resuspension of bottom sediments below this trap depth. This sediment accumulation estimate is higher than the measured accumulation value from coring (~4 cm) and the calculated accumulation by extrapolation (5.3 cm, or 0.624 cm/yr). These values compare extremely well with ^{210}Pb rates of 0.599cm/yr, calculated by Rukavina and Versteeg (1996), as the mean rate for Hamilton Harbour.

Summary and Conclusions

The results of a nine-year study at the Hamilton Harbour *in situ* sand capping site have been reported. Results of monitoring the migration of major ions, nutrients and major elements, within the sand cap, show variable concentration gradients. Concentration profiles for silica and chloride are similar to those in the original sediments due to downward diffusion of chloride from the overlying water and high silica content in the sand material. The amount of pore water Fe within the sand cap is due to the higher concentration of Fe (1.5%) present in the sand material. Ammonia concentration profiles within the cap are similar to those for Fe, and both show a quasi-linear concentration from a minimum at the sediment water interface to a maximum between 30 and 40 cm depth. These concentrations, which are higher than expected are due to the sand Fe content and de-nitrification processes producing NH_3-N. The concentration profiles for Mn and SRP confirm that diffusion is restricted to the top and bottom 10 cm of the cap. These concentrations have been decreasing over time and seem to have

achieved a steady state in the year 2000 for Mn and 2003 for SRP. The sand cap is effective in reducing diffusional fluxes of some contaminants, likely due to its low organic content. Inorganic sediments, such as sand, have low ion-exchange capacity; therefore, entrainment by molecular diffusion into the sand cap is probably minimal relative to the original sediments.

The average sedimentation rate for the study period, for all trap levels, is 8.67 g/m2/day. The mean rate at bottom-2 m is 6.2 g/m2/day and the lower rate is attributed to lower sediment resuspension at this level. All major and trace elements show a concentration decrease with depth, with the exception of calcium and magnesium, which actually show an increasing trend. Major and trace element concentrations in the surficial sediments of the three cores are 25 to 50% lower than the mean concentrations in the trapped material. Also, the surficial sediment concentrations for Fe are 50 to 70% lower than those reported by other investigators for sediment sampled in 1996. This is a substantial difference is attributed to decreasing harbour concentrations from 1996 to 2003. Coring results show that there is 4 to 5 cm of newly deposited sediment over the sand cap. Also, the sediment thickness was calculated by extrapolation of sediment core chemistry relationships at 5.3 cm. By using the downward flux of particulates measured over the study period the sediment accumulation was estimated to be 6.5 cm. Coring results underestimate sediment thickness and downward flux calculation overestimates it; thus, the sediment thickness calculated by extrapolation (5.3 cm) seems the most correct. Over the study period the mean accumulation rate is ~0.5 to 0.6 cm/yr. These results compare extremely well with ^{210}Pb rates of 0.599 cm/yr, calculated by other investigators as the mean rate for Hamilton Harbour.

Molecular diffusion and resuspension are natural processes; therefore, contaminated sediments will always be a source of pollutants to the water column. If external loadings are eliminated, then sedimentation of freshly produced material will act as a natural cap. Sand capping appears to be very effective in eliminating the resuspension of contaminated sediments but it is not as effective in eliminating molecular diffusion of contaminants. However, due to its inorganic composition, it does substantially decrease diffusion processes. An impermeable barrier would be the ideal choice and probably could be created as a thin layer within the sand cap.

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Table 1 Whole Year and Temporal Mean Sed. Rates and Concentrations at the Cap Site

1A Mean from 1995 to 2003 (All Data)

	Org. C. as % of Total	%LOI	TTM g/m2/day	Cu µg/g	Fe Pct	Cr µg/g	Pb µg/g	Ti µg/g	Li µg/g	Ni µg/g	Sn µg/g
	Det.Limit 1	1	0.5	1	0.01	1	1	1	1	1	2
MEAN	68.4	17.5	8.67	118	4.97	92	186	224	23	43	66

1B Mean from 1995 to 2003 (Mid August to Mid May)

	Org. C. as % of Total	%LOI	TTM g/m2/day	Cu µg/g	Fe Pct	Cr µg/g	Pb µg/g	Ti µg/g	Li µg/g	Ni µg/g	Sn µg/g
	Det.Limit 1	1	0.5	1	0.01	1	1	1	1	1	2
MEAN	65.0	15.8	10.3	117	5.03	94	186	226	23	43	70

Element Sedimentation Rate from Mid August to Mid May

Cu	0.44	g/m2/yr
Pb	0.70	g/m2/yr
Ni	0.16	g/m2/yr
Fe	189	g/m2/yr

1C Mean from 1995 to 2003 (Mid May to Mid August)

	Org. C. as % of Total	%LOI	TTM g/m2/day	Cu µg/g	Fe Pct	Cr µg/g	Pb µg/g	Ti µg/g	Li µg/g	Ni µg/g	Sn µg/g
	Det.Limit 1	1	0.5	1	0.01	1	1	1	1	1	2
MEAN	74.1	20.5	4.74	118	4.85	86	185	218	24	45	58

Element Sedimentation Rate from Mid May to Mid August

Cu	0.2	g/m2/yr
Pb	0.32	g/m2/yr
Ni	0.08	g/m2/yr
Fe	83.9	g/m2/yr

Table 2 Element Concentrations in Three Sandcap Cores Sampled in The Spring of 2003 (ug/g)

Core # 2																							
Depth	CD	CO	GA	LA	LI	NI	PB	RB	TL	U	AL	BA	CR	CU	FE	MN	P	SR	V	ZN	CA	MG	K
0.5	1.9	8.7	6.93	15.4	20.8	25.8	102	41.7	0.561	0.73	23800	135	82	58	37200	1630	1750	144	54	761	90900	19800	6920
1	1.5	7.3	5.44	14.1	17.4	21.3	79.2	31.5	0.418	0.65	16400	88	52	46	25900	1150	1310	132	37	534	96900	19100	5860
1.5	1.7	8.4	6.43	15.9	20.1	24.5	92.8	38.1	0.472	0.73	20600	112	69	53	30800	1320	1460	132	46	640	90000	18800	7100
2	1.6	7.8	6.04	14.1	18.9	23	83.9	35	0.42	0.68	18300	99	59	49	27700	1190	1270	131	42	563	95400	19500	6590
2.5	1.4	7	5.45	12.8	17.6	21.2	74.2	31.9	0.36	0.61	16900	91	55	43	25100	1090	1150	134	39	517	99100	19800	5990
3	1.1	6.2	4.72	12.6	15.5	18.3	61.1	27.1	0.287	0.59	14800	79	46	37	21800	954	1030	135	34	428	100000	21100	5330
3.5	0.7	4.7	3.73	11.1	12.6	14.1	41.0	20.8	0.193	0.55	11500	61	34	27	16400	733	747	140	27	297	113000	21200	3920
4	0.3	3.2	2.61	11.3	9.4	9	21	13	0.16	0.43	7940	39	21	16	10900	506	438	120	19	153	127000	20000	2520
Core # 3																							
0.5	2	8.8	6.88	15.2	19.9	25.2	103	42.2	0.538	0.71	22800	129	72	58	34900	1630	1610	133	52	713	85400	18400	7850
1	1.6	7.6	6	16.1	17.7	22.1	82.8	35.1	0.456	0.66	19300	105	60	50	29100	1230	1460	139	44	588	95600	18000	6690
1.5	1.4	7.2	5.85	15	17.1	21	76.5	34.5	0.422	0.69	18300	100	54	45	26800	1150	1270	133	41	527	95300	18500	6370
2	1.1	6.1	4.97	13.1	14.7	17.8	62.2	28.2	0.331	0.63	15900	86	46	38	23700	990	1090	141	38	442	104000	18700	5660
2.5	1.1	6	4.91	12.4	15	17.9	60.4	28.1	0.305	0.57	15400	83	46	36	22500	986	1040	137	35	424	103000	18900	5370
3	0.8	5.1	4.21	12.8	12.8	14.7	46	22.8	0.245	0.56	12400	66	38	28	19100	853	875	138	32	320	111000	20500	4190
3.5	0.6	4.3	3.43	11.8	11.7	12.5	35.1	18.3	0.178	0.51	10100	53	26	23	14900	703	715	161	25	241	125000	19900	3520
4	0.6	4.1	3.37	10	11.2	11.9	34.2	18.3	0.175	0.51	10500	55	31	22	14800	693	665	141	25	250	113000	20700	3670
4.5	0.6	4	2.8	10.3	10.8	11.8	34	14.4	0.167	0.45	8170	43	26	22	13000	604	590	142	21	231	116000	20600	2500
Core # 5																							
0.5	2.7	12.5	9.51	18.7	30.5	36.4	148	58.4	0.798	0.91	30600	171	99	86	46200	1890	2100	120	65	1000	65800	18100	10900
1	2.3	10.1	8.12	17.4	23.6	30.4	124	49.9	0.671	0.83	27000	151	84	69	40000	1660	1830	130	58	865	79900	18600	9890
1.5	1.7	7.9	6.19	14.4	18.9	23.6	89.6	36.4	0.46	0.69	20100	109	68	52	31600	1350	1600	130	46	647	93800	19600	7060
2	1.5	7.4	5.6	14.1	18.3	22	80.3	33	0.402	0.63	18000	98	58	46	28400	1240	1390	135	42	576	97900	19200	6200
2.5	1.5	7.1	5.32	13.6	17.7	21.2	75.6	30.4	0.361	0.63	16900	90	53	44	27100	1170	1270	135	39	542	101000	19000	5810
3	1.4	7.4	5.71	13.4	18.4	22.1	75.7	32.5	0.348	0.67	17200	91	53	44	26100	1090	1140	131	40	505	100000	19500	5870
3.5	1	6.1	4.51	14.4	15.7	18.4	58.7	24.2	0.269	0.59	13100	70	44	36	22100	917	1040	134	33	395	105000	20000	4350
4	0.7	4.8	3.81	11.1	12.4	14	41	19.6	0.184	0.54	11400	59	36	26	17800	772	789	138	29	289	113000	20700	3770

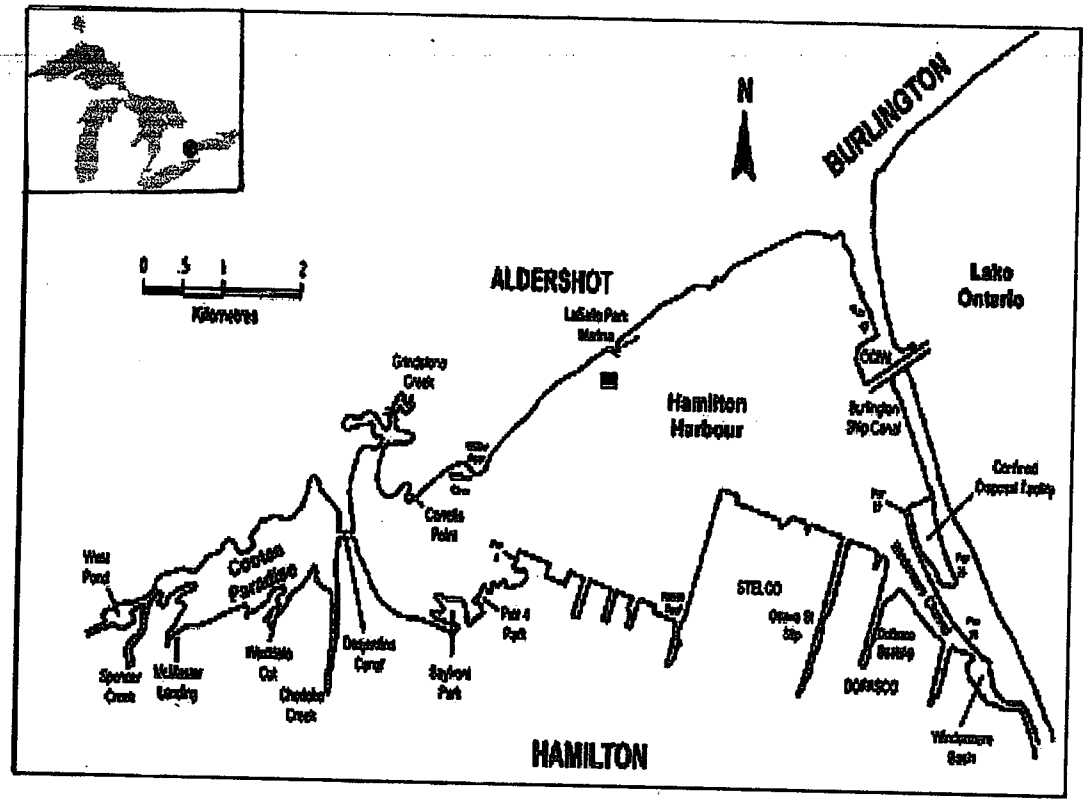


Figure 1. Hamilton Harbour Area , showing The Cap Site (■), and The Harbour Relative to Lake Ontario and Cootes Paradise

Figure 2 Seasonal Dissolved Oxygen Concentrations (mg/l) at 30cm Above The Sandcap

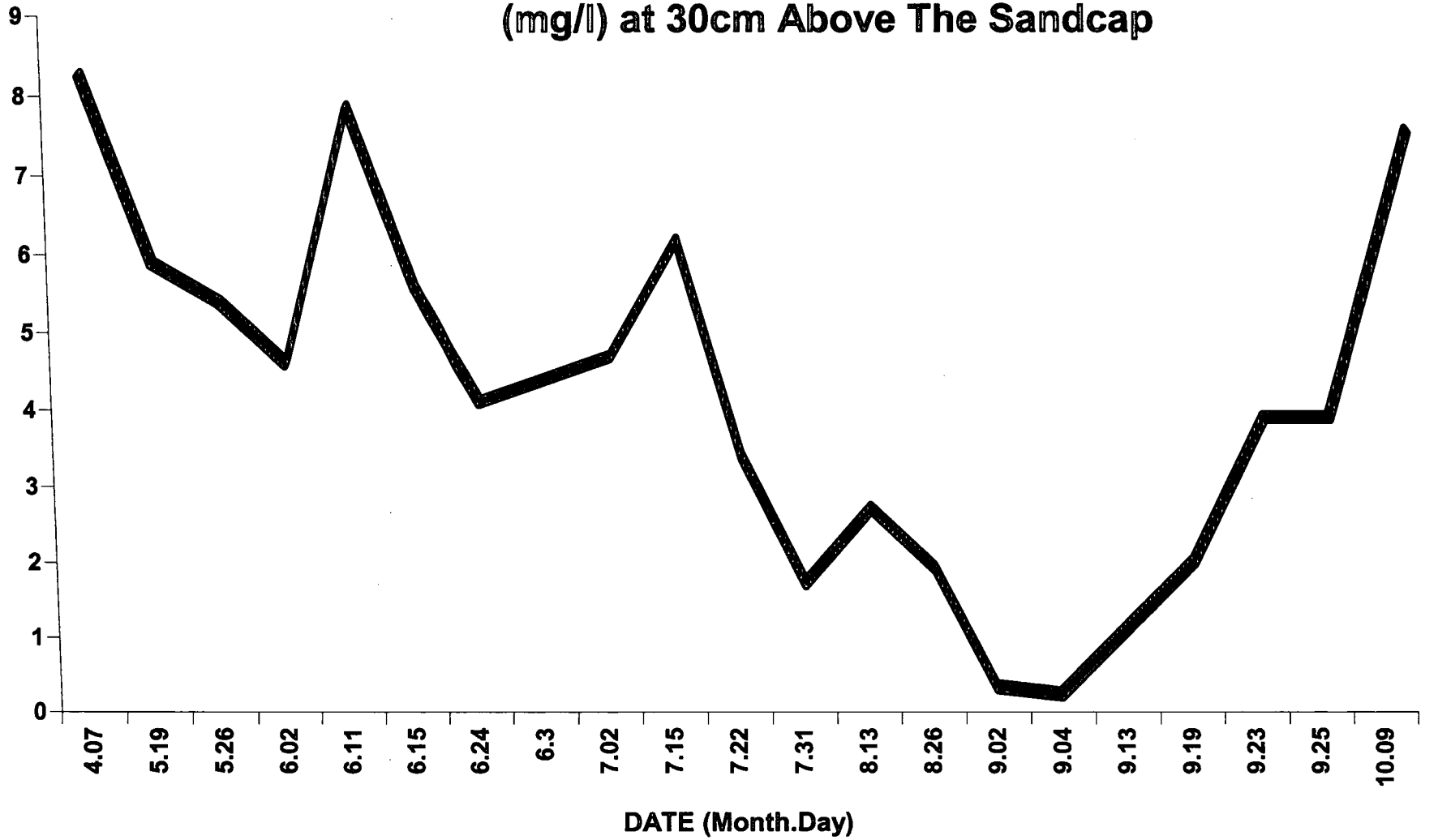


Fig. 3 Dialysis Sampler

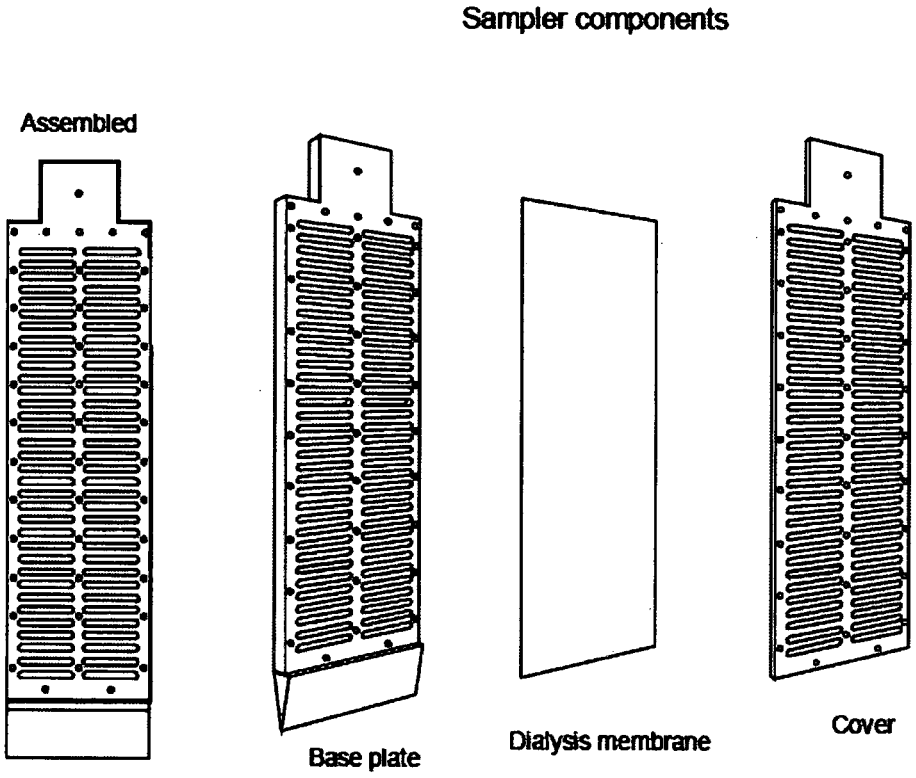


Fig. 4 Pore Water Profiles Taken in 1995 Prior to Cap Placement (mg/l)

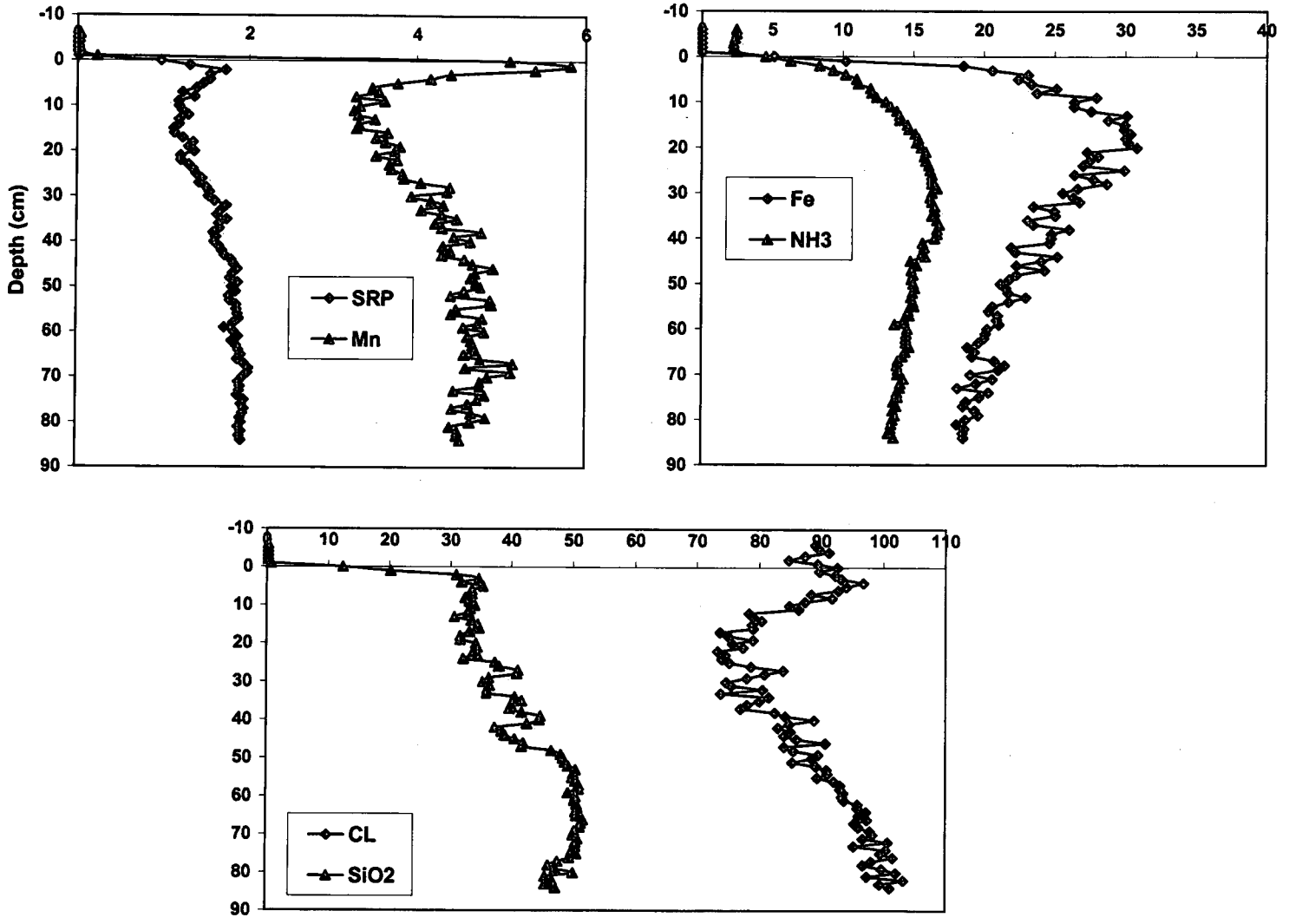
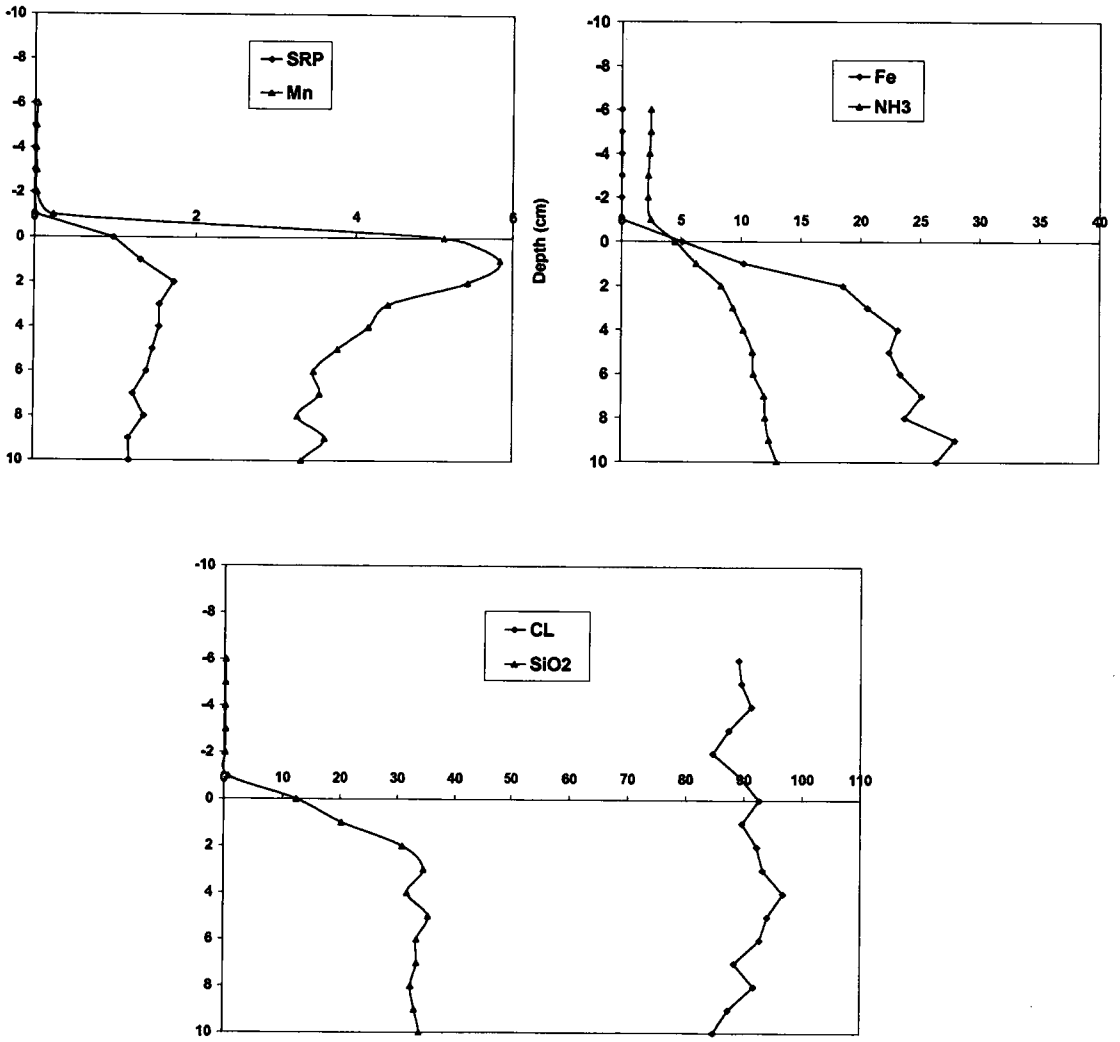


Fig. 5 Pore Water Profiles at the Sediment Water Interface Prior to Capping (mg/l)



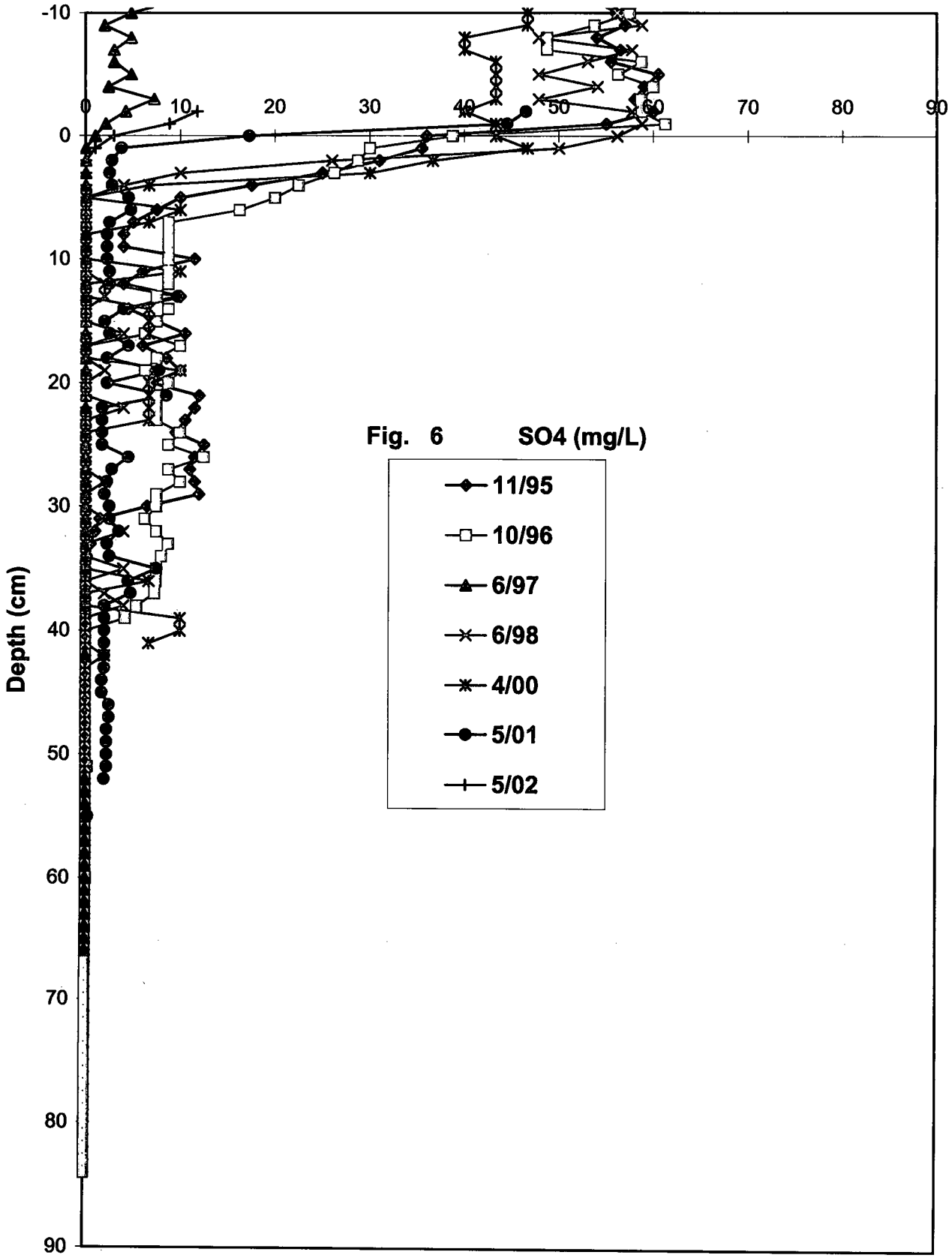
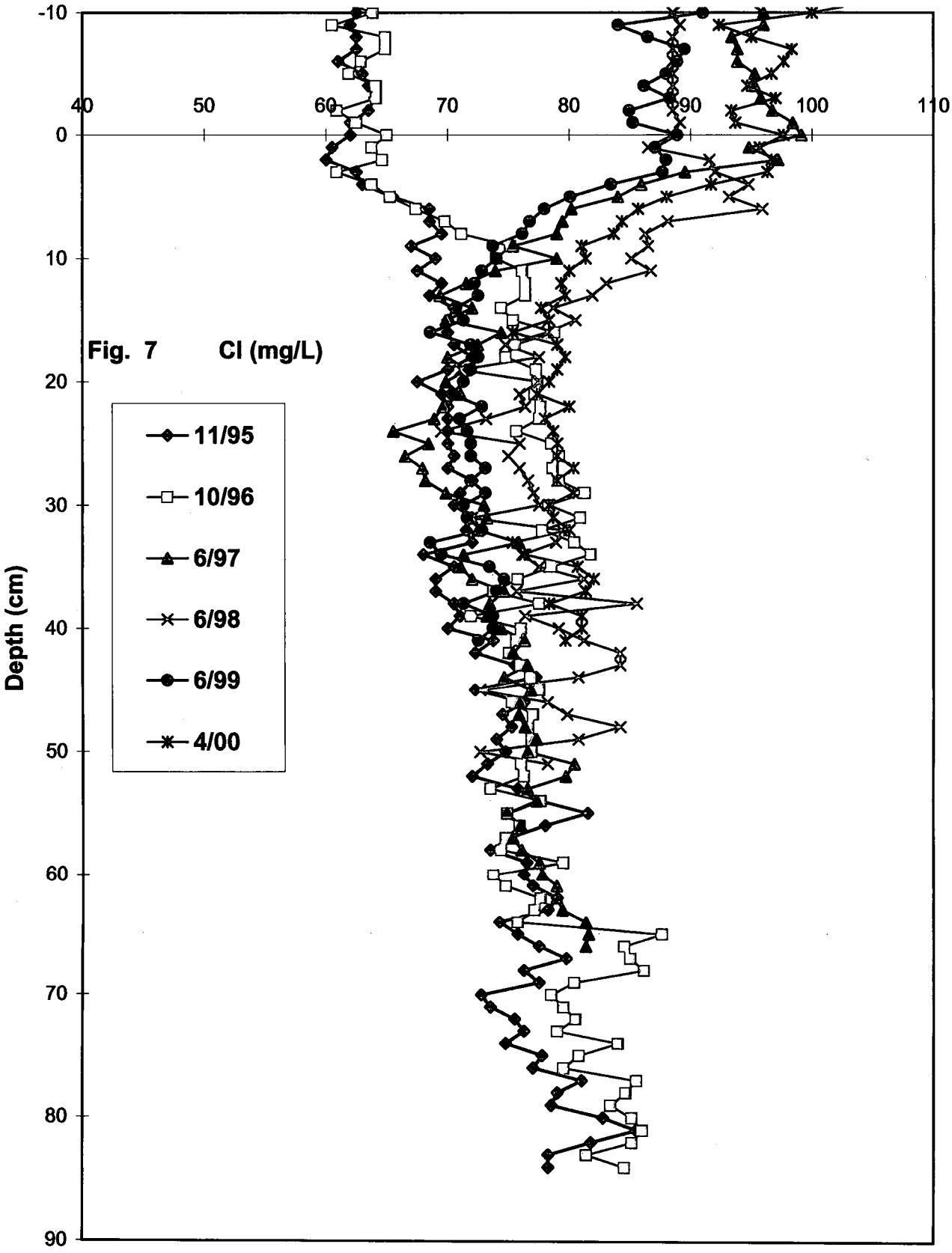

-10
0
10
20
30
40
50
60
70
80
90
Depth (cm)
0
10
20
30
40
50
60
70
80
90
11/95
10/96
6/97
6/98
4/00
5/01
5/02

Fig. 6 SO4 (mg/L)


-10
0
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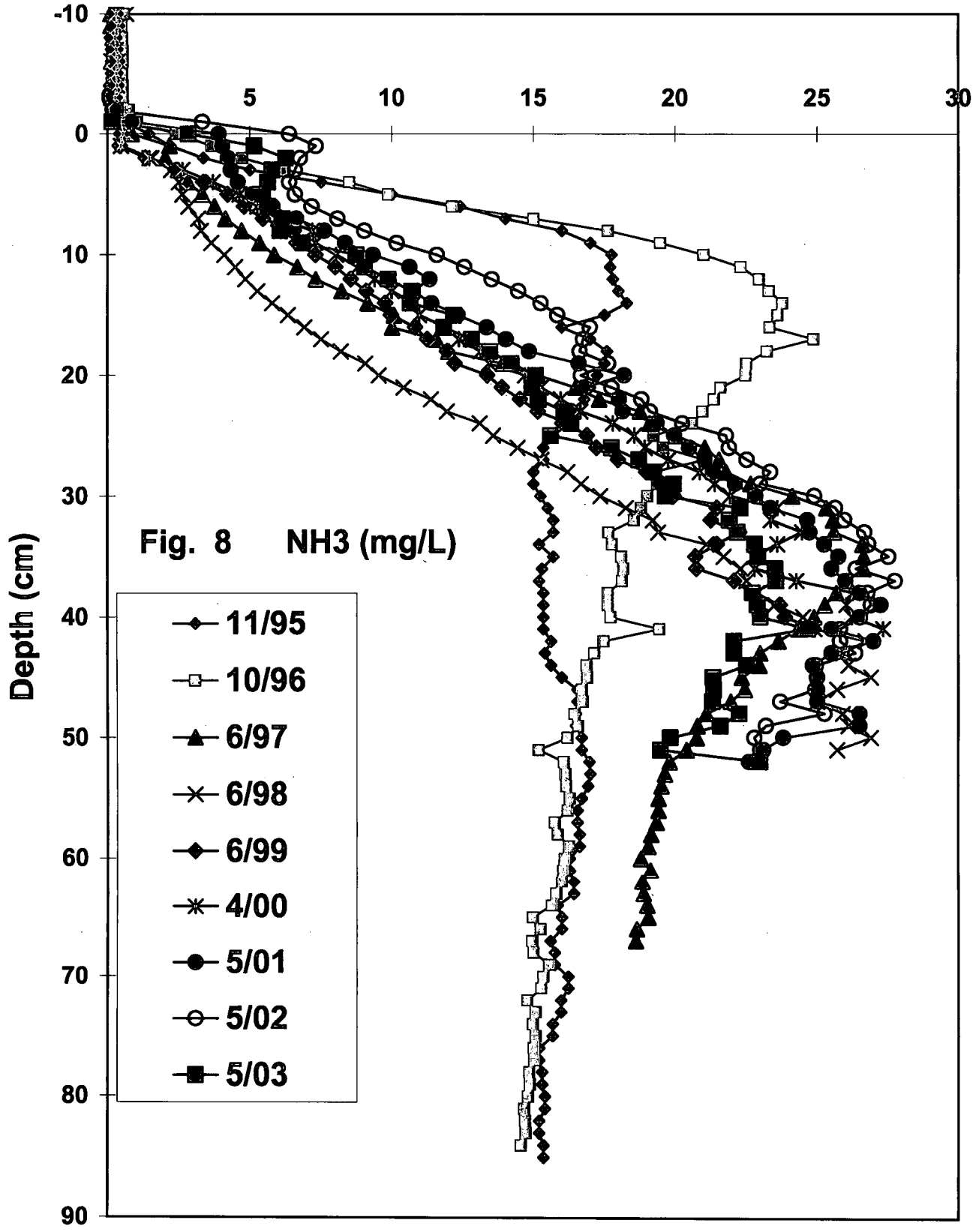
30
40
50
60
70
80
90
40
50
60
70
80
90
100
110
Depth (cm)
11/95
10/96
6/97
6/98
6/99
4/00

Fig. 7 Cl (mg/L)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70
80
90
5
10
15
20
25
30
Depth (cm)
Fig. 8 NH3 (mg/L)
11/95
10/96
6/97
6/98
6/99
4/00
5/01
5/02
5/03

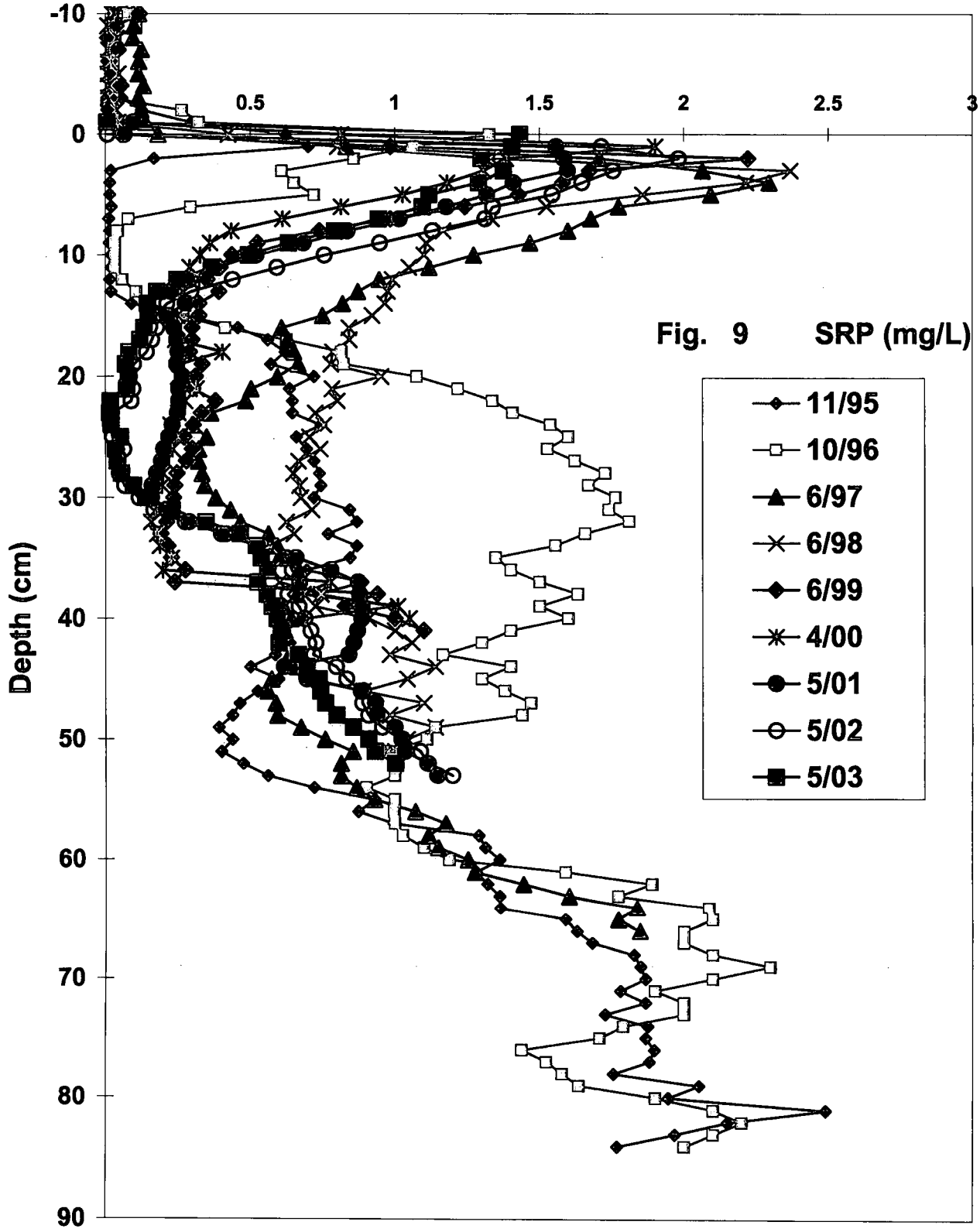
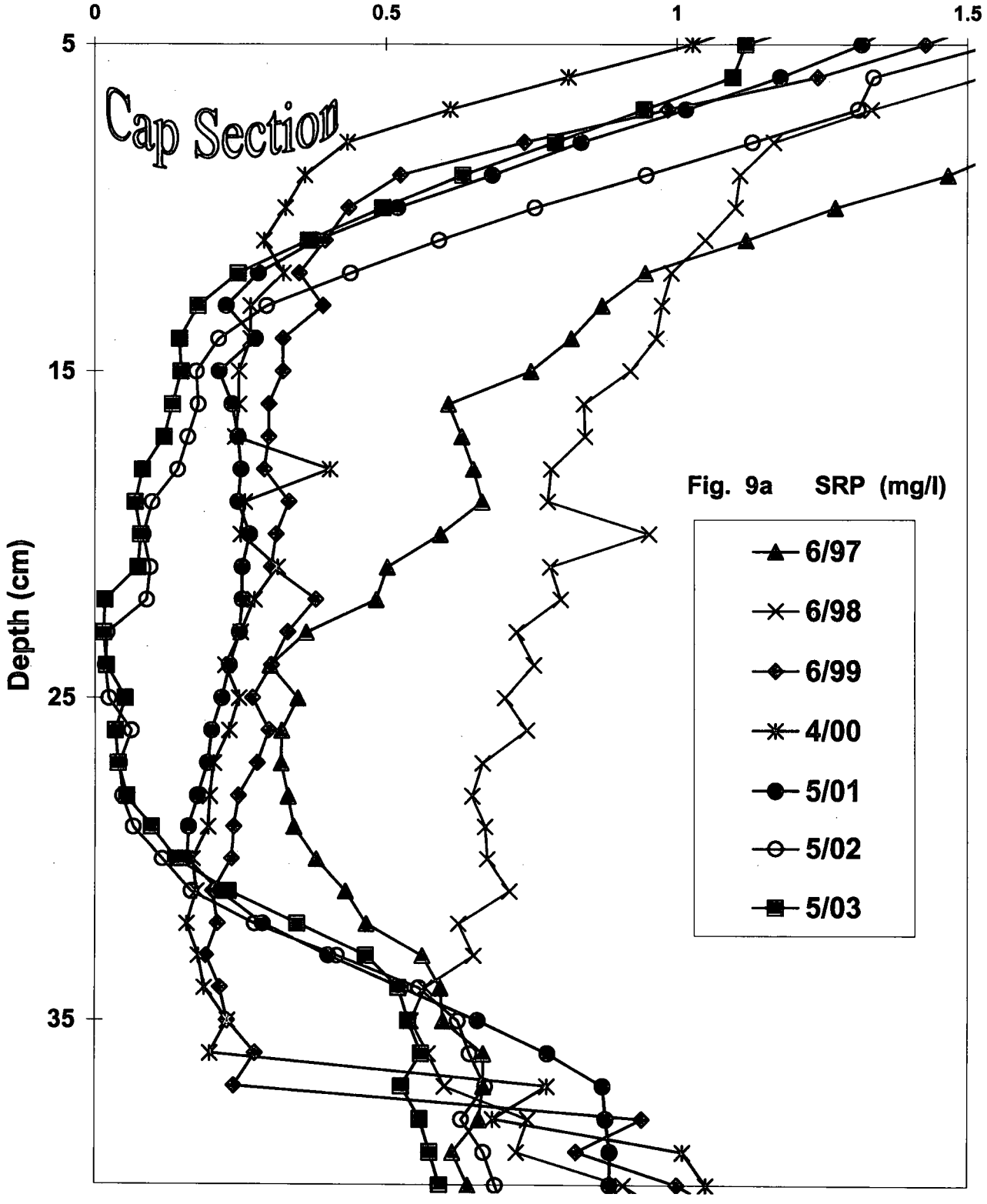
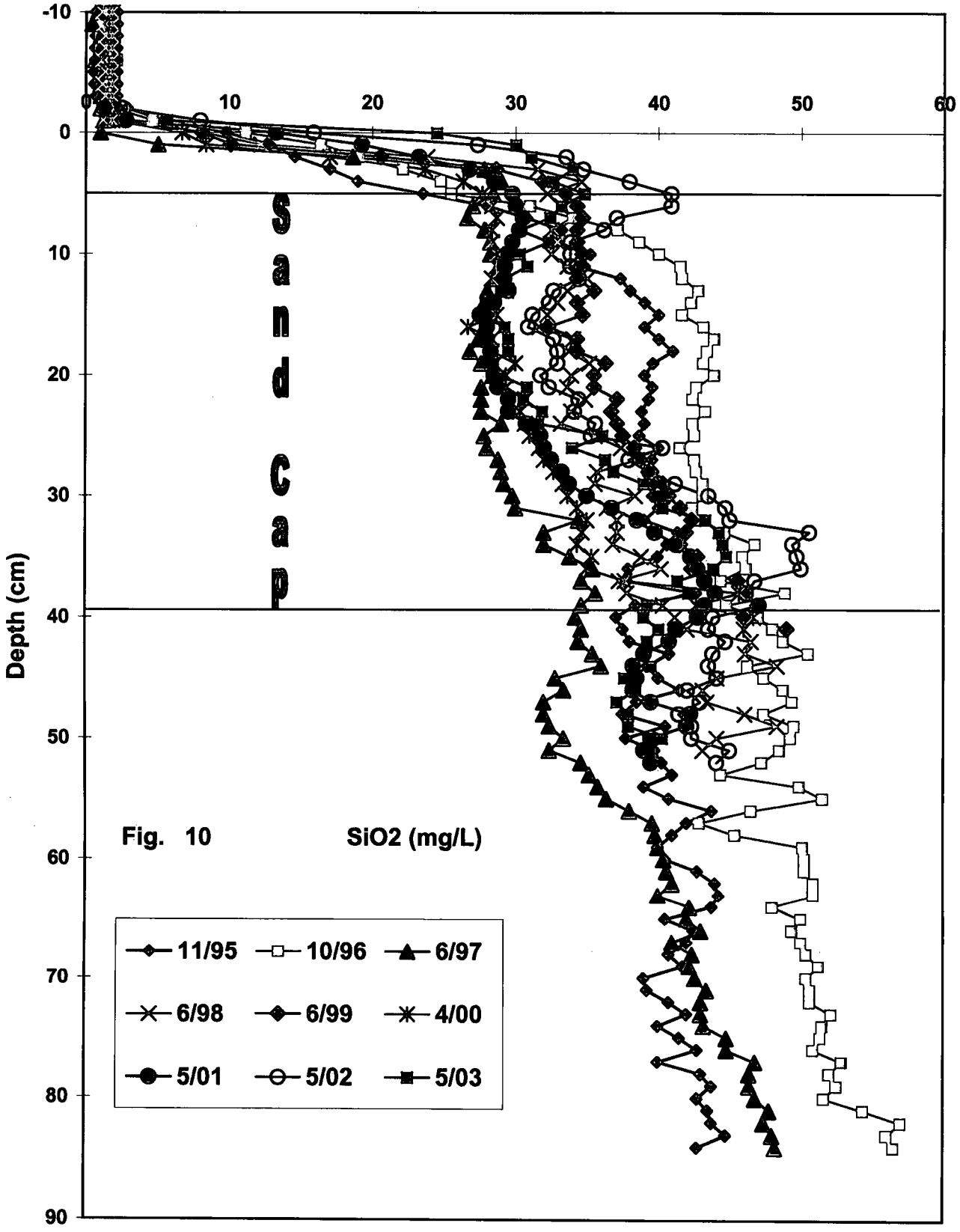

-10
0
10
20
30
40
50
60
70
80
90
0.5
1
1.5
2
2.5
3
Depth (cm)
11/95
10/96
6/97
6/98
6/99
4/00
5/01
5/02
5/03

Fig. 9 SRP (mg/L)


0
0.5
1
1.5
5
15
25
35
Depth (cm)
Cap Section
Fig. 9a SRP (mg/l)
6/97
6/98
6/99
4/00
5/01
5/02
5/03


-10
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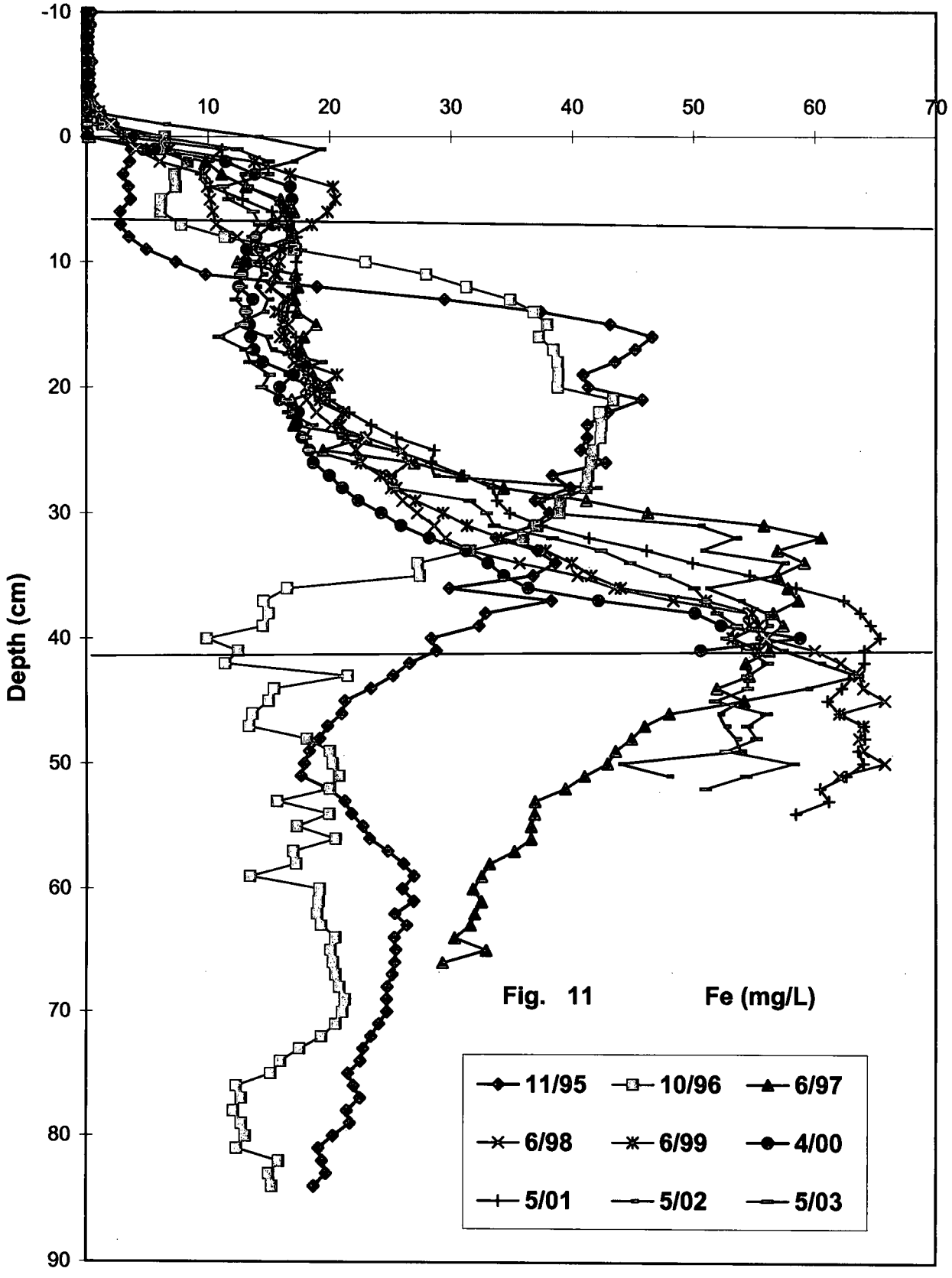
10
20
30
40
50
60
0
10
20
30
40
50
60
70
80
90
Depth (cm)
Sand Cap
SiO2 (mg/L)
11/95
10/96
6/97
6/98
6/99
4/00
5/01
5/02
5/03

Fig. 10


-10
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70
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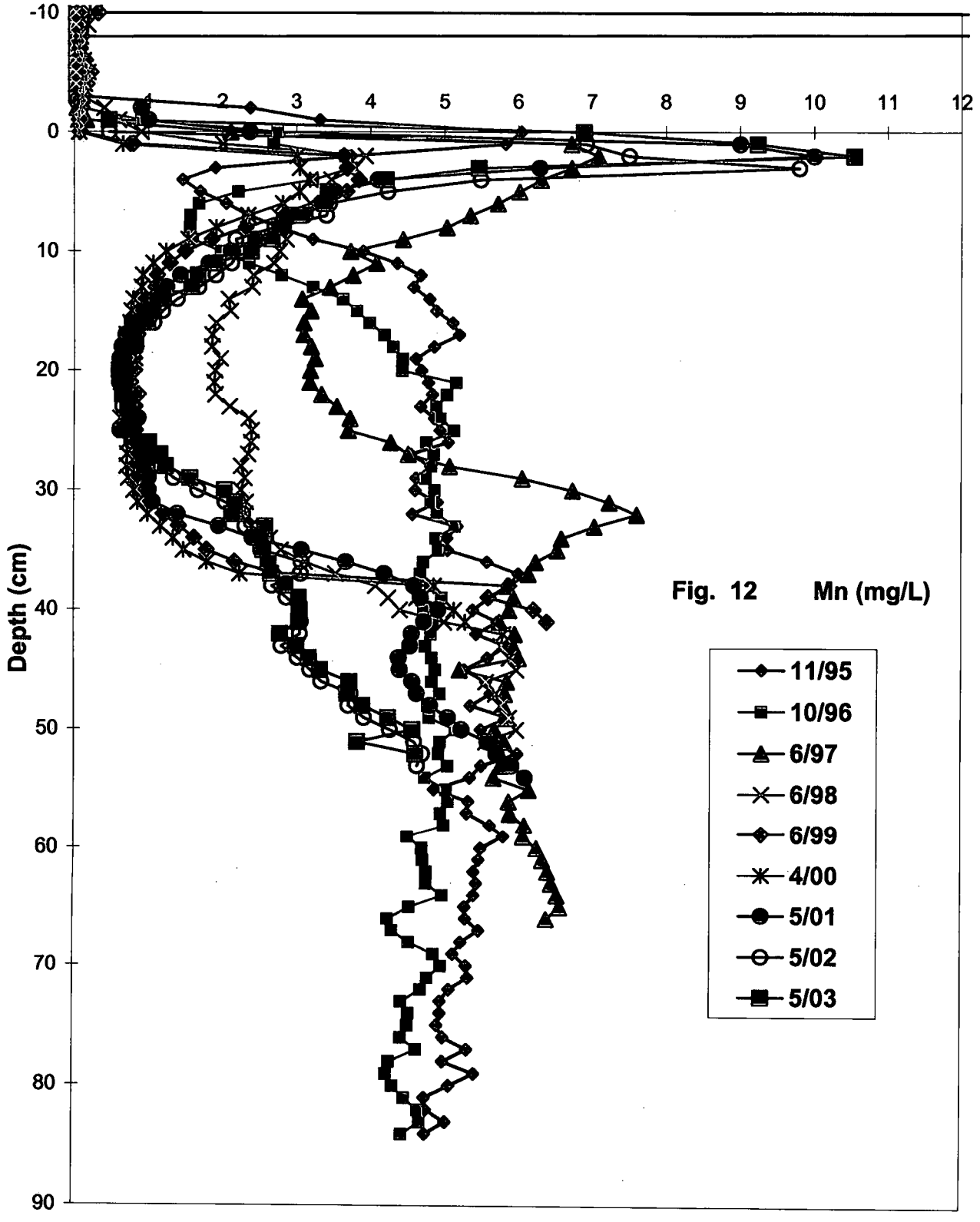
60
70
80
90
Depth (cm)
11/95
10/96
6/97
6/98
6/99
4/00
5/01
5/02
5/03

Fig. 11 Fe (mg/L)


-10
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20
30
40
50
60
70
80
90
Depth (cm)
2
3
4
5
6
7
8
9
10
11
12
Mn (mg/L)
11/95
10/96
6/97
6/98
6/99
4/00
5/01
5/02
5/03

Fig. 12

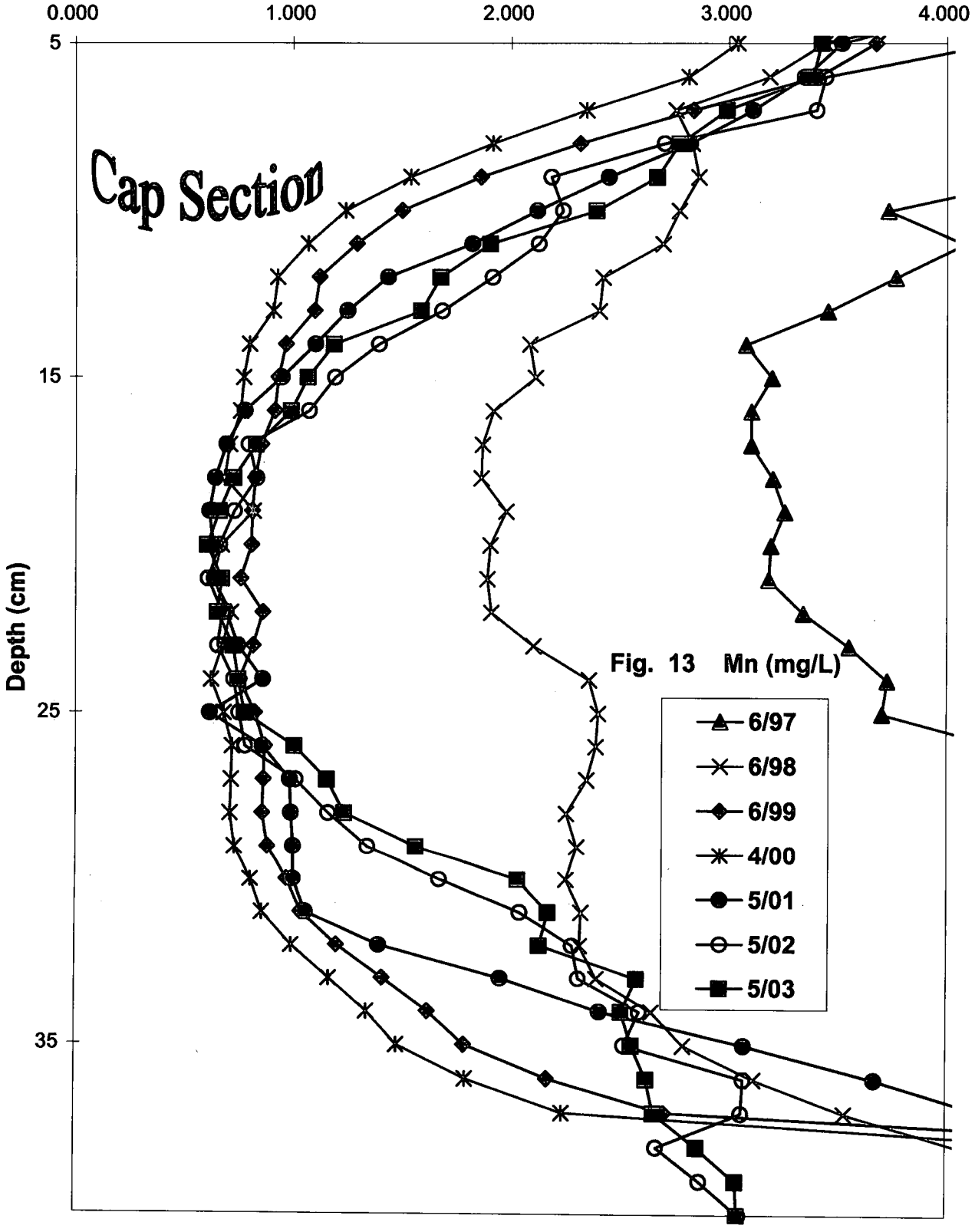

0.000
1.000
2.000
3.000
4.000
5
15
25
35
Depth (cm)
Cap Section
6/97
6/98
6/99
4/00
5/01
5/02
5/03

Fig. 13 Mn (mg/L)

Fig. 14 Sedimentation Rates of Total Trapped Matter (TTM) At The Sand Cap Site

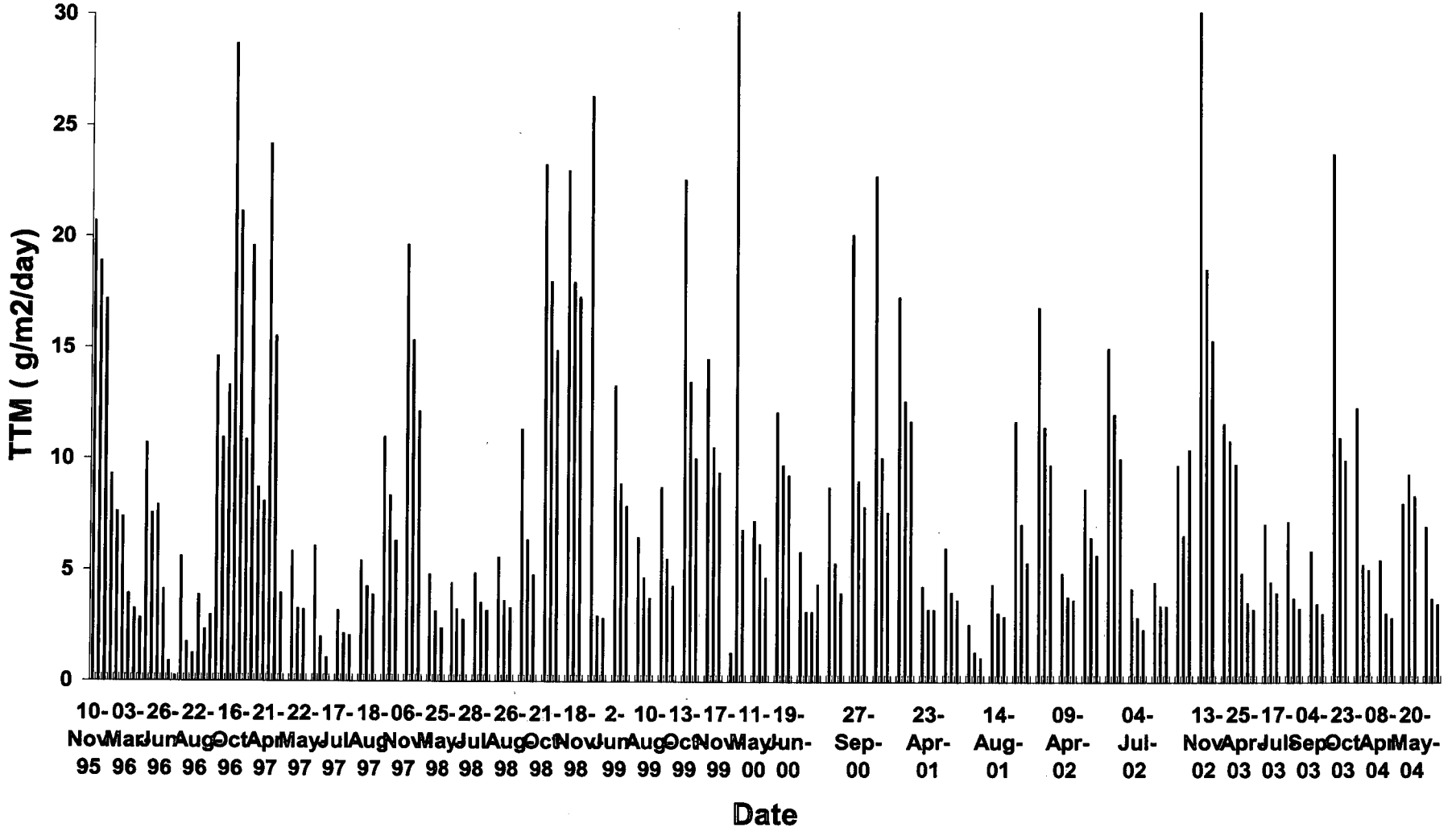


Fig. 15 % LOI in the Total Trapped Matter (TTM)
At The Sand Cap Site

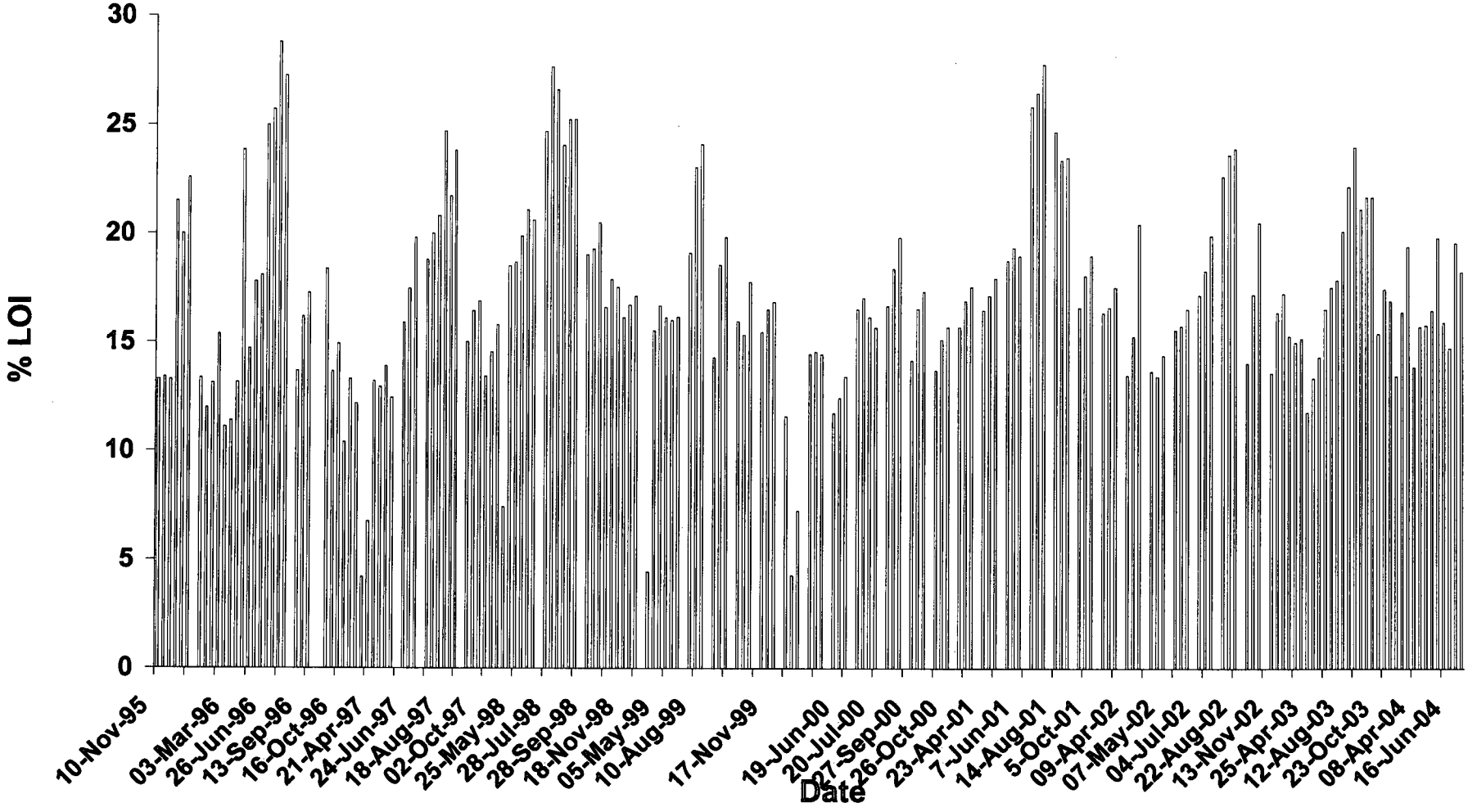
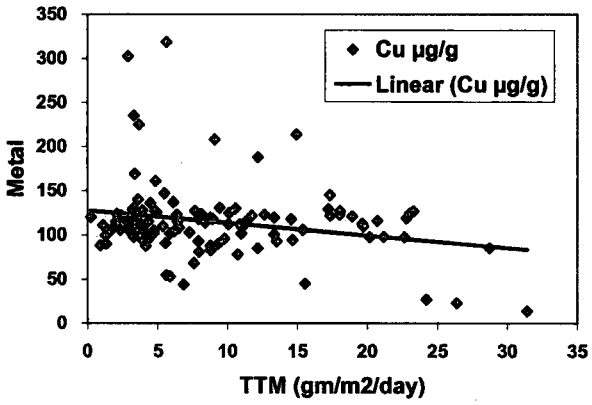
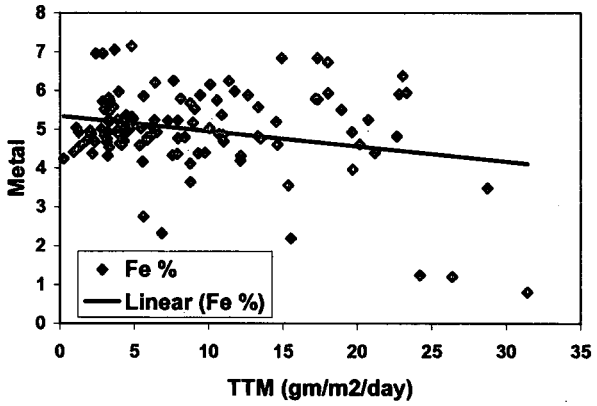
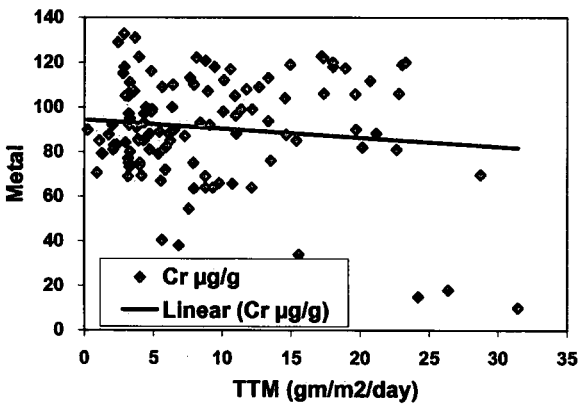
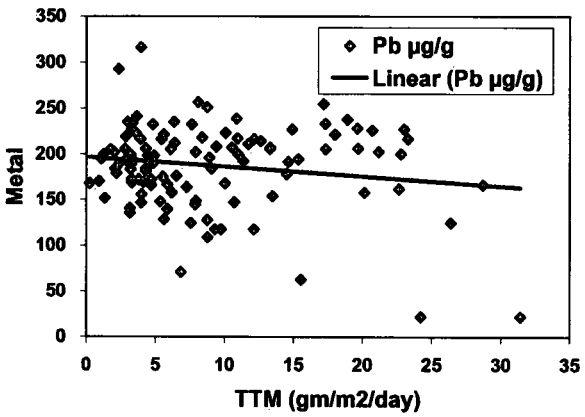


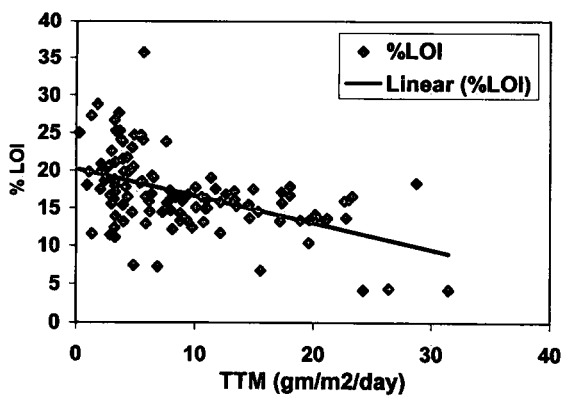
Fig. 16 Concentration of Metals and % LOI in the Total Trapped Matter at the Cap Site











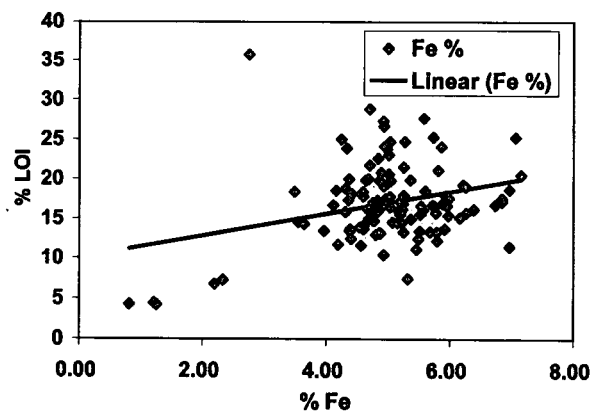


Fig. 17 Element Concentrations in TTM During the Study Period at the Sand cap Site

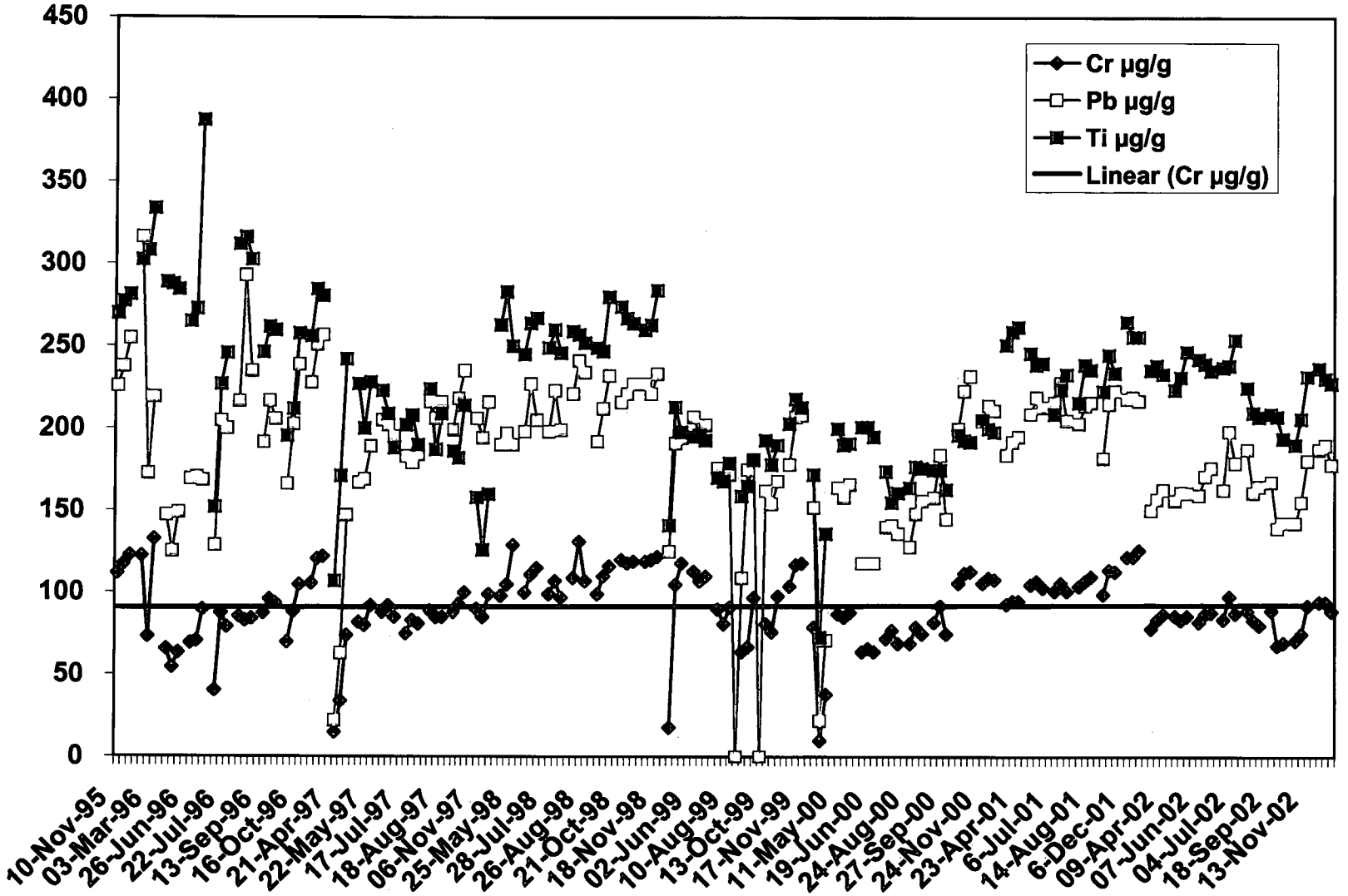
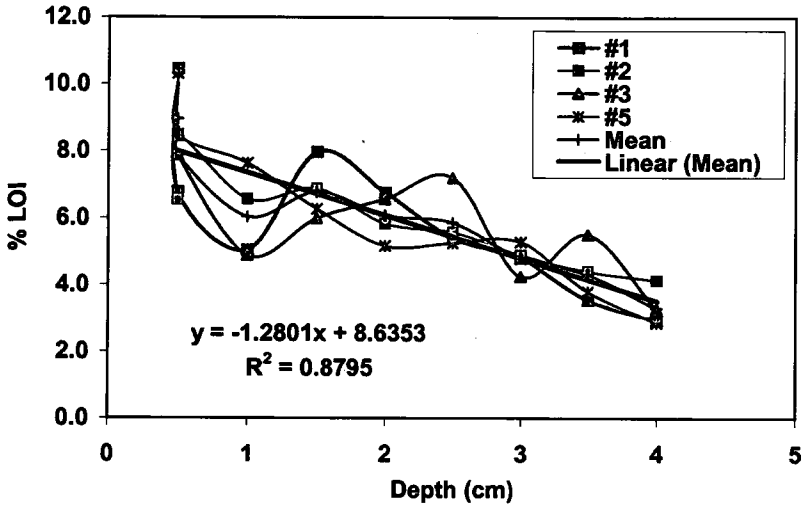
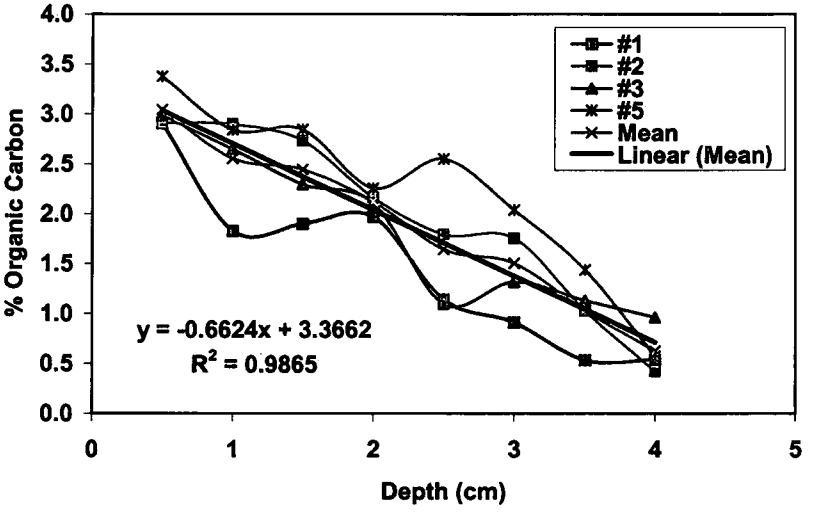
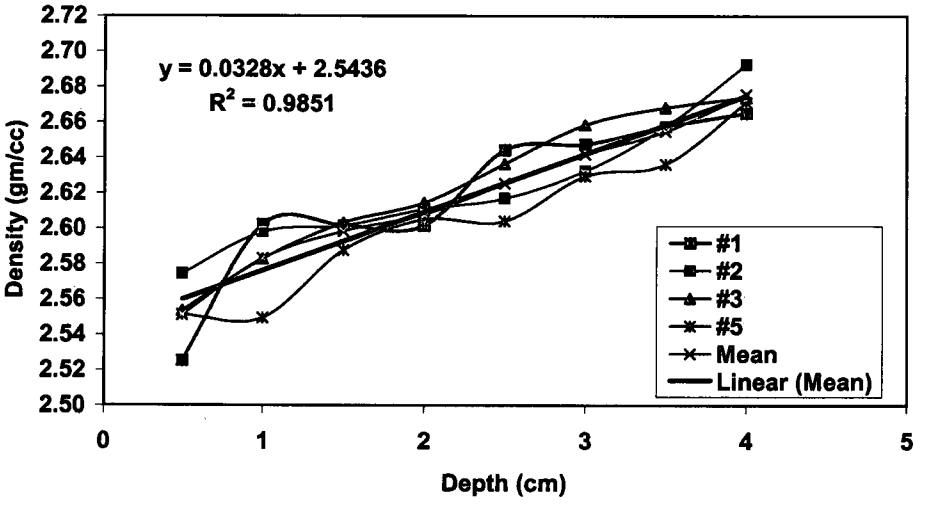


Fig. 18 Organic Content and Density Profiles in Sediment Cores at the Sandcap Site







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