

**INORGANIC CONTAMINANTS IN SUSPENDED SOLIDS  
FROM HAMILTON HARBOUR**

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## MANAGEMENT PERSPECTIVE

Hamilton Harbour is one of the most polluted bodies of water in North America and was identified by the International Joint Commission (IJC) as one of the 17 Areas of Concern in Ontario. This report presents results of 1986 study on suspended solids in Hamilton Harbour. The data presented here indicate that the highest concentrations of contaminants (phosphorus and heavy metals) are found in areas adjacent to the sources. Anthropogenic forms of iron wustite and hematite showed to be good tracers of the industrial input. The contaminants tend to be confined close to the surface of the water column. The results of the study have important implications because they suggest that only about 33% of contaminated solids are deposited within the Harbour while remaininig 67% of solids may be exported into Lake Ontario via Burlington Ship Canal.

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ABSTRACT

Concentrations of heavy metals and phosphorus were measured in suspended solids collected from Hamilton Harbour in the spring and late summer of 1986. Forms of iron were determined using Mossbauer spectroscopy and related to the concentrations of heavy metals and phosphorus. The highest metal concentrations are found in deep water and in areas adjacent to outfalls. Wustite and hematite, originating from anthropogenic activities, are good tracers of the industrial input, and their concentrations are consistent with the concentrations of heavy metals, particularly Zn and Pb. Heavy metals in suspended solids exceed guidelines for open water disposal of dredged sediments. Annual loadings of heavy metals to the sediments, calculated from the heavy metal concentrations in suspended solids are  $\sim 477 \times 10^3$  kg Fe,  $16 \times 10^3$  kg Zn,  $3 \times 10^3$  kg Pb, 958 kg Cu, 469 kg Ni and 56 kg Cd. Phosphorus concentrations in suspended solids are high and range between  $3100 \text{ mg kg}^{-1}$  and

7300 mg kg<sup>-1</sup>. Higher than average non-apatite inorganic P (NAI-P) concentrations in solids are observed in samples taken from the vicinity of municipal discharges. Manganese and iron were released from bottom sediments during summer anoxia in the hypolimnion of the deep water; however no phosphorus release was observed.

ADDITIONAL INDEX WORDS: Phosphorus, iron, heavy metals, sediments, Mossbauer spectroscopy, hematite, wustite.

Running title: Contaminants in Hamilton Harbour

PERSPECTIVE-GESTION

Le port de Hamilton est l'un des plans d'eau les plus pollués d'Amérique du Nord et a été, à ce titre, identifié par la Commission mixte internationale (CMI) comme étant l'un des 17 secteurs de préoccupation en Ontario. Le présent rapport donne les résultats d'une étude réalisée en 1986 sur les matières solides en suspension dans le port de Hamilton. Les données présentées ici indiquent que les concentrations les plus élevées de contaminants (phosphore et métaux lourds) se retrouvent dans les zones voisines des sources. Des formes anthropiques d'hématite et de wüstite de fer se sont révélées être de bons traceurs des polluants industriels. Les contaminants ont tendance à être confinés près de la surface dans la colonne d'eau. Les résultats de l'étude sont intéressants parce qu'ils indiquent que seulement 33 % environ des matières solides contaminées sont déposées dans le port de Hamilton, alors que les 67 % qui restent pourraient bien être transportés par le canal de Burlington et se déposer dans le lac Ontario.

## RÉSUMÉ

Les concentrations de métaux lourds et de phosphore ont été mesurées dans des matières solides en suspension prélevées dans le port de Hamilton au printemps et à la fin de l'été de 1986. La présence de certaines formes de fer a été déterminée à l'aide de la spectroscopie de Mossbauer et liée aux concentrations de métaux lourds et de phosphore. Les teneurs en métaux les plus élevées ont été mesurées en eau profonde et dans les zones voisines des exutoires. La wüstite et l'hématite, provenant d'activités anthropiques, représentent de bons traceurs des polluants industriels; leur concentration est conforme aux concentrations de métaux lourds, notamment le Zn et le Pb. La teneur en métaux lourds dans les matières solides en suspension était supérieure aux directives pour l'élimination de sédiments de dragage au milieu d'un plan d'eau. Les charges annuelles de métaux lourds ou sédiments, calculées à partir des teneurs en métaux lourds dans les matières solides en suspension sont d'environ  $477 \times 10^3$  kg Fe,  $16 \times 10^3$  kg Zn,  $3 \times 10^3$  kg Pb, 958 kg Cu, 469 kg Ni et 56 kg Cd. Les teneurs en phosphore dans les matières solides en suspension sont élevées et varient de 3 100 mg kg<sup>-1</sup> à 7 300 mg kg<sup>-1</sup>. Des concentrations de phosphore inorganique autre que l'apatite, supérieures à la moyenne, ont été observées dans des échantillons

de matières solides prélevés au voisinage des effluents municipaux. Les sédiments de fonds ont libéré du manganèse et du fer au cours de l'anoxie d'été dans l'hypolimnion en eau profonde; aucun phosphore n'a semblé être libéré.

## INTRODUCTION

Hamilton Harbour is a natural embayment at the western end of Lake Ontario with a surface area of  $2.2 \times 10^7 \text{ m}^2$  and mean depth 13 m (MOE 1974). The lake and the Harbour are separated by a sandbar and linked together by the Burlington Ship Canal, through which considerable water exchange takes place. The Harbour, which is connected at its western end with the shallow turbid waters of Cootes Paradise also receives water from several streams. The general limnology of the Harbour was described in detail by Harris et al. (1980).

Hamilton Harbour is one of the most polluted bodies of water in North America and was identified in 1985 by the International Joint Commission as an Area of Concern. The Harbour receives treated sanitary sewage and storm water runoff from the surrounding cities of Hamilton and Burlington and is also the source and the recipient of cooling water for the steel industry located on the south shore. High concentrations of metals and organic contaminants, eutrophication and oxygen depletion in the summer severely impair water quality.

Although numerous studies have been conducted on Hamilton Harbour (Harris et al. 1980; Haffner et al. 1982; Nriagu et al. 1983; MOE 1981; MOE 1985; Poulton 1987), little information is available on the speciation of particulate iron (Manning et al. 1980) and phosphorus in suspended solids and sediments and their relation to heavy metals. Thus, in 1986 a study on Hamilton Harbour was initiated, focussing on suspended solids, firstly



because they represent the major net loadings from the two steel companies Stelco and Dofasco, secondly because they play an important role in removing/or remobilizing contaminants to/from the water column. The main aim of the study is to determine the forms and concentrations of iron, phosphorus, and heavy metals in suspended solids in order to (a) assess the relative importance of municipal and industrial point sources and (b) evaluate the fate of anthropogenic material within the Harbour.

#### MATERIALS AND METHODS

To evaluate the partitioning of contaminants between the solid and aqueous phases, water samples and suspended solids were collected at six stations in Hamilton Harbour (Fig.1) on two occasions (April and September 1986). The stations were chosen to reflect distinct zones (MOE 1985), influenced by water exchange with Lake Ontario, deep-water deposition and the near-by discharges. At each station, a temperature profile and an oxygen profile were obtained, using the EBT and oxygen profiler (Ford and Charlton 1984). Temperature profiles showed that the water column in April was well mixed, whereas in September the water column was strongly stratified and anoxic conditions persisted in deeper water, in the middle of the Harbour (Fig. 2).

On both occasions, water samples and suspended solids were taken from 1 m below the surface and 1 m above the sediment-water interface. The suspended solids were collected using a continuous-flow Westphalia separator. The collected solids were

frozen immediately and freeze-dried later in the laboratory. The water samples were used to determine the concentrations of suspended solids, phosphorus and heavy metals in water. The concentrations of suspended solids in water were determined after filtration of 500 mL of water through prewashed and preweighed 47-mm glass fiber filters, which were later dried and reweighed. Water samples for total P, total filterable P and total metals were preserved and analyzed as described in "Analytical Methods Manual" (Environment Canada 1979).

Concentrations of total P, non-apatite inorganic P (NAI-P), and apatite-P in suspended solids were measured according to Williams et al. (1976a) and Mayer and Williams (1981). Inorganic and organic carbon were determined with a Leco induction furnace, organic carbon being measured after removal of carbonate carbon with sulfurous acid (Kemp 1971). Total concentrations of metals in suspended solids were determined by acid dissolution and subsequent atomic absorption spectrometry (Desjardins 1978). To complement the information, bottom sediments (0-1 cm) taken by Benthos corer from all six locations were analyzed for the same parameters as the suspended solids.

The principal iron compounds were determined by Mossbauer spectroscopy. Mossbauer spectra were recorded at room temperature using a  $\text{Co}^{57}/\text{Fe}^{57}$  source. The spectra of all samples were recorded at low velocities with an electromechanical transducer. Some spectra were recorded also at higher velocities to confirm the concentrations of magnetically-ordered

Fe species seen only weakly at the lower velocities. Spectra were computed using the programs of Stone (1967). The peak half-width and the peak-areas within a quadrupole doublet were assumed to be equal. Chi-square values and visual examination were used for goodness of fit. The isomer shifts are reported relative to Fe-metal foil, which was used for the calibration of the spectrometer.

## RESULTS AND DISCUSSION

### Particulate and Dissolved Phosphorus

The areal distribution of phosphorus in water shows considerable variation (Fig. 3). Total P concentrations in water exceeded the provincial guidelines (0.02 mg/L) at all stations and on both sampling occasions. The total P concentrations were highest at the mouth of the Windermere Basin (station #4), which receives effluent from the Hamilton sewage treatment plant (STP), and at station #6, which is close to the discharge from the Burlington sewage treatment plant.

The high P concentrations in the Harbour result from high P loadings (520 kg/day) (RAP 1988), mainly from point sources (municipal STPs, storm water runoff) and to a much lesser extent from non-point (diffuse) sources (RAP 1988). Although the P concentrations in the effluents of the Hamilton and Burlington STPs are in compliance with the provincial guidelines (1mg/L), the residence time of water (90-140 days) (MOE 1985) is

sufficient to allow effective utilization of P by biota (Haffner et al. 1982). Due to these factors, the Harbour waters are hypereutrophic with large phytoplankton standing crops (Haffner et al. 1982; MOE 1985). The response of the biological community is however mediated by the influx of oligotrophic to mesotrophic lake water, light limitation by suspended matter (Harris 1976; Harris and Piccinin 1980) and frequent perturbation of the Harbour thermal structure caused by harmonic oscillations of Lake Ontario (Barica 1988; Sephton and Harris 1984). Blue green algae are noticeably absent (Harris and Piccinin 1980; Murphy 1987), due to high N:P ratios, which favour green algal species (Schindler 1977; Barica et al. 1980).

Total P concentrations in suspended solids averaged ~5900 mg/kg with higher P concentrations in April than in September (Fig. 3). The seasonal differences are small and the average total P concentration of benthic sediments (3935 mg/kg) suggests that the differences are not due to resuspension of benthic sediments. The concentrations of Al (Table 4) in suspended solids favour this conclusion. Generally, total P concentrations were higher in the surface solids than in the solids from just above the sediment-water interface (Fig. 3). Similar trends were observed for organic P, which accounted for more than half of the total particulate P (~63% in April and ~55% in September) and NAI-P (Table 1). The most likely explanation for this is that the surface solids, containing particles of biogenic origin (from algal tissue and organic debris) enriched in organic P, are quite buoyant and, due to their low settling velocities, tend to be

confined to the surface. Apatite P (Table 1) comprised only a minor fraction of the total P (~2.5% in April and 5.6% in September).

In April, concentrations of the NAI-P at stations adjacent to the municipal point sources (stn. #4 and #6) were higher than those of the remaining Harbour stations, although the concentration of NAI-P in surface solids at station #5 (Table 1) was also high. As seen in Fig. 1, this station is located at the entrance of the Windermere Canal in 20 m of water. Water enriched with nutrients from Hamilton STP effluent, discharged into Windermere Basin, moves via this area towards the Burlington Canal, rather than dispersing through the entire area of the Harbour. This phenomenon known as "short circuiting" has been proposed by several investigators (MOE 1986; Barica 1988; Charlton, pers. comm.). Such water movement, confined to the surface would result in the transport of particles, enriched in P in the same direction.

In September during stratification, no P release from sediments (Fig. 3) was observed, despite the low oxygen conditions at station #2, located in the deepest part of the central basin. The oxygen concentration at this station dropped to 0 mg/L while concentrations of ~5 mg/L of oxygen were measured in the bottom waters of the other stations. The September concentrations of Fe and Mn in near-bottom solids, which will be discussed later, indicate regeneration of Mn and Fe from benthic sediments at this time of the year. High concentration of Fe<sup>3+</sup> in

benthic sediment at stn. #2, resulting in a high molar  $\text{Fe}^{3+}/\text{NAI-P}$  ratio (7.3) (Table 2), is probably responsible for the absence of observed P release. Mole ratios of ~3 have been reported for benthic sediments (Shiller et al. 1985).

The high total particulate P concentration of bottom solids from station #3 in September is probably due to the collapsed algal population sinking to the bottom. Organic carbon values (Table 1) support this conclusion.

As in April, the NAI-P concentrations in September were higher in solids from the stations close to municipal discharges (stns. #4 and #6). The results suggest that the influence of the point sources on the particulate P is most pronounced in the NAI-P fraction. This fraction would include the phosphates precipitated and discharged by the STPs as well as phosphates precipitated authigenically within the water column. Several investigators (Williams et al. 1980; DePinto et al. 1981; Young et al. 1985) suggested that the NAI-P category includes a fraction of particulate P which would be most readily available for biological utilization upon depletion of dissolved P.

In September, the particulate organic P from near-bottom solids at station #4 accounted for much less of  $P_T$  (~17% of  $P_T$ ) than in all other solids collected at that time of year (Org. P ~56% of  $P_T$ ). It is believed that the input of abiotic components, most likely from resuspension of benthic sediment is responsible for low organic P in the solids. The resuspension is also evident

from the high concentration (11.8 mg/L) of suspended solids in water (Table 3) collected from station #4 at 1 m above the bottom. Consistent with this are the apatite-P and Al concentrations of near-bottom solids at this station (Table 1 and 4), which are similar to those found in benthic sediments (Table 2). While on average the apatite-P in suspended solids accounted only for ~5.6% of  $P_T$  in September, this form of P constituted ~16% of  $P_T$  in bottom solids collected at this station. Apatite-P and Al concentrations in suspended solids showed a close correlation (Mayer and Manning, 1989) reflecting resuspension of benthic sediments.

Although the total P concentrations in Harbour benthic sediments are considerably higher than those of the Great Lakes sediments (Williams and Mayer 1972; Williams et al. 1976 a, b; Kemp et al. 1978), they are 1.5 times lower than the total P concentrations of the settling material. The differences are due mainly to lower organic P content of benthic sediments. The particulate organic P, originating presumably mainly from algae and other plankters is mineralized during settling through the water column and at the sediment-water interface. The suspended solids and sediment organic P data show that as much as 77% of organic P is mineralized. Mineralization of organic matter results in consumption of oxygen from the water column. The Redfield equation (Redfield et al., 1963) indicates that as much as 3.5 mg/L oxygen is required to mineralize 1 mg of organic carbon. The organic carbon content of material collected just above the sediment was between 83 mg/g-196 mg/g, thus at least

290 mg of oxygen is needed to mineralize the organic material from suspended solids. Such consumption of oxygen, in addition to nitrification, leads to anoxic conditions in the bottom waters of the Harbour in the summer.

### Mossbauer Spectral Interpretations

Mossbauer or nuclear  $\gamma$ -ray spectroscopy is particularly useful in determining the major forms of iron in sediments and suspended solids. A representative Mossbauer spectrum of suspended solids from the Harbour is shown in Fig. 4. All spectra are qualitatively similar. Four doublets, corresponding to four Fe-compounds can be readily identified in the somewhat complicated spectra. In addition to two naturally occurring Fe-forms ( $\text{Fe}^{2+}$  from chlorite and clays and  $\text{Fe}^{3+}$  from amorphous iron oxides) two more Fe forms can be identified, namely ferric ions in crystalline hematite ( $\text{Fe}_2\text{O}_3$ ) and ferrous ions in wustite ( $\text{Fe}_{1-x}\text{O}$ ). The hematite doublets are well defined at the energies -1.77 and 0.84 mm/s and they match those of  $\text{Fe}_2\text{O}_3$  (Ruskov and Tomov 1975; Manning et al. 1980). The source of the latter two forms of Fe is the steel industry, although minute amounts of hematite are derived from the red soils in the Harbour watershed. Wustite, the lowest oxide of iron that contains less Fe than corresponds to the stoichiometric composition of  $\text{FeO}$  (Bodsworth 1963), forms as a scale when hot iron or steel contacts air (Manning et al. 1980). The most abundant Fe form in Hamilton Harbour suspended solids is  $\text{Fe}^{3+}$  (Table 4). The average computed values of isomer shift, quadrupole splitting and line width of



all identified Fe forms are listed in Table 5. Wustite and hematite half-width were constrained in most computations using values derived from computations of spectra of samples which had the highest concentrations of these two compounds. The values of isomer shift, quadrupole splitting and half-width (Table 5) are in good agreement with those of Manning et al. (1980) and are good to  $\pm 0.1$  mm/s.

X-ray diffraction methods have confirmed the presence of wustite, hematite and chlorite. High velocity spectra show the presence of the outer spectral peaks which in addition to hematite may include some (~10%) magnetite. The X-ray diffraction however, showed no evidence of a ferric compound other than hematite, hence most of the  $\text{Fe}^{3+}$  is present in amorphous ferric oxides and hematite. The proportions of four identified forms of Fe were obtained from the ratios of areas beneath the respective doublets, taking into account the areas of remaining two outer doublets corresponding to hematite. The four forms of iron account for > 95% of the total Fe. Concentrations of each iron species were then calculated using the ratios of respective iron species and total Fe concentrations.

#### Distribution of Particulate Iron

Loadings of iron to Hamilton Harbour far exceed those of the other heavy metals (MOE 1985). Although, generally not toxic, at very high concentrations (1500 ug/L) iron, precipitated as hydroxide in fine floc can kill fish and fish eggs by smothering

(Harlow and Hodson 1988). Acute and chronic toxicity was apparently observed at total iron concentrations higher than 1000 ug/L and was shown to be closely related to concentrations of dissolved ionic ferrous (II) iron species (Harlow and Hodson 1988). At no time did we measure such high iron concentrations in Harbour water, although the total Fe concentrations at several stations exceeded the provincial guidelines (0.3 mg/L) on both sampling occasions. Iron was largely present (~104%) in the particulate form (Tables 6 and 7).

Considerable spatial and temporal differences were found in concentrations of iron in suspended solids and consequently in iron concentrations in water. In April, elevated concentrations of Fe were observed in surface solids from stations close to industrial outfalls (stns. #3, #5). While the average Fe concentration in solids in April was 46.0 mg/g, values as high as 100.5 and 87.5 mg/g were measured at stations #3 and #5, respectively. The trend was similar in September, with the concentrations of Fe in solids close to industrial outfalls higher than the overall Harbour average (59.7 mg/kg) for that time of year. In September, however, the concentration of Fe at stn #5 was higher in bottom suspended solids than that of the surface solids.

Consistent with the total Fe concentration in solids is the distribution of Fe compounds in particles, which differs considerably, depending on the sampling location. Figs. 5a and 5b show, that the proportion of iron compounds from anthropogenic activities, wustite and hematite, is also higher in solids

collected at locations close to industrial sites. The main input of iron is most likely from the steel mill effluent.

The natural distribution of iron forms is highly distorted by the industrial inputs. Whereas, the ratios of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in suspended solids and benthic sediments in Great Lakes are ~1 (Manning et al. 1984; Mayer and Manning 1989) ratios as high as 27 were found in solids from the Harbour (Table 4). Solids collected from stations close to the steel companies have the highest ratios. Generally, the ratios were higher for the surface solids than for bottom solids. The distorted ratios can be attributed to a greater proportion of Fe from wustite and hematite on the account of terrigenous  $\text{Fe}^{2+}$  from chlorite.

The effect of particulate Fe from wustite and hematite on aquatic organisms has not been reported, since these Fe compounds are not commonly found at high concentrations in natural environments. However, it is not expected that at concentrations found in the Harbour, these compounds would pose any obvious environmental problem (Manning et al. 1980). The two Fe compounds, wustite and hematite however, prove to be good and readily measurable tracers of industrial input.

As suspended solids, benthic sediments also show increased proportion of wustite and hematite at locations adjacent to industrial sites and in the middle of depositional basin (Table 8). Deposition of anthropogenic particles is however evident in all areas of the Harbour. The relative contribution of naturally occurring  $\text{Fe}^{2+}$  from chlorite and clays to total Fe is higher in benthic sediments than in suspended solids, as reflected in lower

$Fe^{3+}/Fe^{2+}$  ratios (1.2 average value for the top 1 cm layer of sediment from all 6 locations).

The degree of Fe enrichment in suspended solids can be calculated by comparing Al and Fe ratios of Harbour material with that of the background material. If the input of Fe to the Harbour solids is from natural sources (uncontaminated benthic sediments, soils from surrounding watershed, etc.) only and if Al, bound mainly in clay minerals, is regarded as a conservative element (Kemp and Thomas 1976; Kemp et al. 1976; Manning and Jones 1982), the following expression can be written:

$$\frac{Al_{seds.}}{Al_{susp.s.}} = \frac{Fe_{seds.}}{Fe_{susp.s.}} \quad (1)$$

where  $Al_{seds.}$  and  $Al_{susp.s.}$  represent concentrations of aluminum in benthic sediments and suspended solids, respectively and  $Fe_{seds.}$  and  $Fe_{susp.s.}$  represent concentrations of iron in benthic sediments and suspended solids, respectively.

The concentrations of Al in sediments from terrigenous sources are ~4.5% (Kemp et al. 1976; Thomas et al. 1972) and concentrations of  $Fe_T$  ~4% (Mudroch and Capobianco 1979; Kemp et al. 1976; Thomas et al. 1972). Fe concentration in suspended solids greater than 4% would lower the  $Fe_{seds.}/Fe_{susp.s.}$  ratio (Table 9) and suggest additional input of Fe either from anthropogenic sources or from internal loadings from sediments by precipitation of previously released dissolved Fe.

Equation (1) after rearrangement yields:

$$\frac{Al_{seds.}}{Al_{susp.s.}} \times \frac{Fe_{susp.s.}}{Fe_{seds.}} = 1 \quad (2)$$

Equation (2) shows that the product of two fractions will be close to 1, if input from anthropogenic contamination and/or anoxic Fe regeneration from benthic sediments is absent. The values obtained from equation (2), therefore can be considered enrichment factors (E.F.).

Our data (Table 9) reveal that the values are close to 1 in most samples. The exceptions are solids collected from locations close to industrial sites (stn #3, #5) and samples collected close to STPs. The enrichment factor of surface suspended solids at stations #3 and #5 was 13.2 and 4.8 in April, and 8.8 and 3.1 in September, respectively. In April the enrichment factors of suspended solids from the vicinity of Burlington STP were 3.1 and 2.7, whereas the value of 2 was calculated for a sample from the vicinity of the mouth of Windermere basin. Furthermore, in September, enrichment factor values of about 2.5 were calculated for samples from stn. #2, suggesting additional Fe input, probably from the precipitation of iron previously released from the anoxic bottom sediments.

Using the enrichment factor, the total Fe concentrations in uncontaminated suspended solids can be calculated. These values should then be in reasonable agreement with the sum of  $Fe^{2+} + Fe^{3+}$ . Comparison of data indeed confirms the agreement of the two sets of values in most cases. Discrepancies, however, appear in the particulate solids from locations affected by industrial input

and those affected by reprecipitation of previously released  $\text{Fe}^{3+}$ .

Knowing the total concentration of Fe in suspended solids and sedimentation rates, Fe loadings to the sediments can be calculated. Recent sedimentation rates in Harbour, determined by the Pb-210 dating method, are about  $410 \text{ g m}^{-2} \text{ y}^{-1}$  (Nriagu et al. 1983). Using this value and an average Fe concentration in suspended solids of  $52.85 \text{ mg/g}$ , an annual loading of  $\sim 477 \times 10^3 \text{ kg}$  Fe to sediments is obtained. This value may slightly overestimate the loadings since sediments are deposited in only about 90% of the Harbour area (Nriagu et al. 1983) and some Fe, measured in suspended solids is regenerated from benthic sediments. The loadings calculated here are however, lower by a factor of nearly 2 when compared to  $880 \times 10^3 \text{ kg}$ , calculated from sediment metal concentrations by Nriagu et al. (1983). Our results are also lower than the  $760 \times 10^3 \text{ kg}$  annual loadings to the Harbour sediments calculated by MOE (1985). The discrepancies may be due to decreased loadings to the Harbour from industrial sources and STPs in recent years. The loadings calculated by Nriagu et al. (1983) and MOE (1985) are based on data from earlier studies. Over the last 15 years, an 80% reduction in iron loadings was achieved by improvements in the effluent treatment facilities of steel mills and STPs (RAP 1988). In 1987, iron loadings to the Harbour from industrial and municipal sources were  $\sim 4000 \text{ kg/day}$  or  $1460 \times 10^3 \text{ kg y}^{-1}$  (RAP 1988). From a comparison of this value with Fe loadings to the sediments, calculated above, we suggest that  $\sim 33\%$  of Fe is retained by sediments within the Harbour.

## Iron-Phosphorus Interaction

Of the iron compounds present in suspended solids and sediments, x-ray amorphous ferric oxide has the greatest potential for interaction with phosphorus (NAI-P) and heavy metal ions. The surfaces of hydrated ferric oxides are the principal binding sites for NAI-P in Great Lakes sediments (Manning et al. 1984; Williams et al. 1976a). Freshly-precipitated ferric hydroxide can bind as much as ~ 10% of its weight of NAI-P (Manning et al. 1984). Concentrations of ferric iron and of NAI-P are highly elevated in Harbour suspended solids and benthic sediments (relative to Lake Erie and Lake Ontario sediments) (Manning et al. 1984). The concentration ratio  $Fe^{3+}/NAI-P$  in Harbour suspended solids is in the range 6-30, with most values being ~10. Hence, there is sufficient ferric iron available to bind the high inputs of P, thus reducing its bioavailability.

Concentrations of  $Fe^{3+}$  and NAI-P are well correlated in April ( $r=0.74$ ,  $p>0.01$ ) for  $N=12$ , but are poorly correlated in the September ( $r=-0.16$ ) for  $N=12$ . Statistical correlations in a body of water such as Hamilton Harbour are fraught with difficulties because of the point source nature of the inputs, which leads to "non-equilibrium conditions" at source stations. As already mentioned, the main sources of the NAI-P are the STPs, which are situated close to stations #4 and #6, whereas the main sources of iron are the industrial outfalls which are located close to stations #3 and #5. The amorphous ferric oxide, originating from the steel industry should have adsorption sites available for

binding phosphate ion. The ferric iron compounds are therefore beneficial in reducing the effects of high nutrient levels.

Although the regeneration of Fe and Mn during summer anoxia was observed at station #2 (Table 6), no release of P from benthic sediments was observed. Anoxic release of Fe is frequently accompanied by P-release (Mortimer 1941; Burns and Ross 1972). Phosphorus retention may be explained by the short duration of anoxia at this location. Summer anoxia is occasionally interrupted by influx of oxygenated bottom lake water (MOE 1985). Alternatively, ferric iron reduction in the enriched Harbour sediments may lead to the formation of an insoluble  $\text{Fe}^{2+}$ -other metal-P phase, as Filipek and Owen (1981) suggested for marine sediments.

No vivianite peaks were detected in the Mossbauer spectra of benthic sediments, despite the high Fe and P concentrations and anoxia conditions in the summer. If all the NAI-P in the bottom sediments of stations 3, 4, 5 and 6 (0.26 to 0.45 wt.% P, Table 2) is in vivianite, the required  $\text{Fe}^{2+}$  content is ~0.9 wt.%, i.e. >10% of total Fe. The high energy vivianite peak (at ~3.02 mm/s) is well separated from the  $\text{Fe}^{2+}$  clay/chlorite peak (energy ~2.44 mm/s) and would be readily distinguished.

#### Heavy Metals in Water and in Suspended Solids

The toxicity of heavy metals to aquatic organisms has been well documented (Wong et al. 1978; Hodson et al. 1979; Hodson 1986). Although some metals (Cu and Zn) are micronutrients for most organisms, at higher concentrations most of the heavy metals



have adverse effects on the mortality rates, growth and reproduction of organisms (Harlow and Hodson 1988).

In Hamilton Harbour, concentrations of heavy metals in water (dissolved and particulate) are above the background levels reported for waters of Lake Ontario (Poulton 1987). Furthermore, the concentrations of heavy metals in water exceed the provincial guidelines (MOE 1985) at several stations (Table 7). Generally, the elevated concentrations of the heavy metals in water are consistent with the concentrations of the suspended solids in the water.

Since the geochemistry of iron is dealt with separately in the previous chapter, we will discuss here the distribution of Mn, Zn, Pb, Cu, Ni and Cd. As for Fe, all Mn (100%) was present in the particulate form, whereas the remaining metals were largely present in dissolved form.

Distinct zones of heavy metals enrichment occur in the Harbour. The zones of enriched suspended solids are located close to industrial outfalls and STPs. Close correlations between Fe and Pb ( $r=0.82$   $p>0.001$ ) for  $N=24$ , and Fe and Zn ( $r=0.84$   $p>0.001$ ) for  $N=24$  were observed in suspended solids collected on both sampling occasions suggesting common or adjacent source of both metals. Pb is not an important contaminant from the steel industry but is derived mainly from automobile emissions. Pb enters the Harbour via storm water run-off, which passes through the STPs, however under overflow conditions Pb enters the Harbour via storm sewers, one of which is adjacent to the main Stelco

discharge. The eastern end of the Harbour can be considered a mixing zone in which Pb and other heavy metal ions adsorb onto iron oxides. Zinc is derived mainly from the recycling of galvanized iron at the steel plant. Close to industrial sources (e.g. stations 3 and 5) Fe, Zn and Pb are present at higher concentrations in the near-surface solids than in the near-bottom solids (Fig. 6), suggesting a surface plume from these areas. The surface plume is probably due to warm water in the effluent. The particles enriched in these metals are transported rapidly within the Harbour and some eventually into the Lake Ontario prior to their deposition. The presence of such a plume is important because of its proximity to the Burlington Canal and because of the potential for export of contaminants to Lake Ontario.

The concentrations of Zn in suspended solids (Table. 6) and benthic sediments (Table 10) greatly exceed the MOE guidelines of open water disposal for dredged sediment at all stations. Similarly, Pb exceeded the MOE guidelines for open water disposal at all stations. According to Chapman (1986), Pb levels greater than 50 ug/g have adverse effects on the biota. The levels of Pb in suspended solids (307 ug/g, average) and sediments (281 ug/g, average) exceed this value and together with high levels of PCBs and PAHs, may be responsible for the low diversity of benthos (Harlow and Hodson 1988).

The remaining heavy metals in suspended solids, Cu, Ni, and Cd (Table 6), exceed the guidelines at several stations. Higher than average concentration of these metals (Fig. 7) are observed

in solids collected from stations #4, #5 which are close to the Windermere Basin, the receiving water body of the Hamilton STP.

A seasonal trend is observed in the concentration of manganese in suspended solids. In September, when low oxygen conditions occurred, the concentration of Mn sharply increased to nearly 3% and 6% (Fig. 6) in near-bottom solids at station #1 and #2, respectively. The average concentration of Mn at that time of the year was 1.21%, with the surface solids averaging only ~0.6%. The Mn concentration of solids in April averaged only at 0.7%. The most probable explanation for such high particulate Mn concentration is the oxidation and precipitation of dissolved Mn during the sample collection and centrifugation process. The high concentration of dissolved Mn in the water is obviously a result of anoxic release of this element from the sediments at this time of year.

Using the average suspended solids metal concentrations and a sedimentation rate of  $410 \text{ g m}^{-2} \text{ y}^{-1}$ , annual loadings of metals to sediments have been calculated. The loadings are  $16 \times 10^3 \text{ kg y}^{-1}$  Zn,  $3 \times 10^3 \text{ kg y}^{-1}$  Pb,  $958 \text{ kg y}^{-1}$  Cu,  $469 \text{ kg y}^{-1}$  Ni and  $56 \text{ kg y}^{-1}$  Cd.

Although the loadings of most nutrients and contaminants to the Harbour are steadily decreasing and the water quality has been improving, further reduction in P loadings is required to reduce algal production, caused by high P concentrations in water. Total P concentrations in water, similarly as the NAI-P concentrations in solids were highest in the vicinity of

municipal point sources. During the summer, when low oxygen conditions occurred, no significant release of P from the sediments was observed, although Mn and Fe release occurred in the deep area of the Harbour. Consequently, algal production is driven mainly by STP-phosphorus. Our results indicate that wustite and hematite are good tracers of industrial input and correlate well with Zn and Pb in the suspended solids. The highest concentrations of the  $Fe^{3+}$ , wustite and hematite are in suspended solids from areas adjacent to the industrial park. Similarly, the concentrations of the heavy metals are highest in areas close to industrial and municipal sources and in deep water. The particles originating from industrial sources are more abundant in the near-surface solids than those in the near-bottom.

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TABLE 1  
FORMS AND CONCENTRATIONS OF CARBON AND PHOSPHORUS  
IN SUSPENDED SOLIDS

STATION	SAMPLING DEPTH m	NAI-P mg/kg	APATITE-P mg/kg	ORGANIC P mg/kg	TOTAL P mg/kg	TOTAL C %	ORGANIC C %
APRIL 1986							
HH-1	1	1792	110	3903	5805	23.4	22.1
	12	1857	153	3470	5480	15.4	14.0
HH-2	1	1628	65	5440	7133	28.2	25.9
	21	1644	127	4087	5858	15.9	14.8
HH-3	1	1904	72	4881	6857	26.8	25.0
	14	1957	127	4067	6151	17.3	15.9
HH-4	1	3789	405	2990	7184	13.7	11.8
	4	3587	465	3184	7236	13.2	11.2
HH-5	1	2609	190	4506	7305	20.5	18.7
	20	1762	175	4025	5962	16.3	14.7
HH-6	1	2259	67	4617	6943	24.1	21.8
	5	2187	85	4619	6891	22.2	19.6
SEPTEMBER 1986							
HH-1	1	1390	230	3636	5256	20.0	16.3
	12	1419	342	1704	3465	11.8	9.6
HH-2	1	1667	110	4322	6099	24.7	22.4
	21	1865	240	2720	4825	14.6	12.7
HH-3	1	2010	162	3669	5841	22.5	20.7
	14	1737	205	3727	5669	20.6	17.6
HH-4	1	2785	315	3068	6168	16.6	14.2
	4	2095	487	521	3103	11.7	8.3
HH-5	1	1772	120	4431	6323	24.4	21.0
	20	1567	360	1521	3448	12.6	10.5
HH-6	1	2900	162	3933	6995	22.9	16.7
	5	2270	247	3152	5669	17.6	12.9

TABLE 2

PHOSPHORUS AND CARBON CONCENTRATIONS AND  $\text{Fe}^{3+}$ /NAI-P RATIOS  
IN HAMILTON HARBOUR SEDIMENTS

STATION	TOTAL C %	ORGANIC C %	NAI-P mg/g	APATITE-P mg/g	ORGANIC P mg/g	TOTAL P mg/kg	$\text{Fe}^{3+}$ /NAIP
1 HH 0-1	6.60	3.92	1035	446	1209	2690	13.1
2 HH 0-1	7.07	4.65	1969	497	947	3413	7.3
3 HH 0-1	7.21	4.86	2585	497	245	3327	6.7
4 HH 0-1	8.43	6.53	3140	583	482	4205	3.4
5 HH 0-1	8.47	6.31	3097	428	336	3861	6.0
6 HH 0-1	6.78	3.70	4458	604	1055	6117	2.1

TABLE 3

TOTAL SUSPENDED SOLIDS  
HAMILTON HARBOUR 1986

STATION	SAMPLING DEPTH (m)	APRIL TSS mg/L	SEPTEMBER TSS mg/L
HH-1	1	4.5	4.4
	12	3.9	5.6
HH-2	1	4.9	3.8
	21	3.0	2.8
HH-3	1	5.5	3.8
	14	2.9	2.6
HH-4	1	5.6	4.8
	4	5.8	11.8
HH-5	1	3.2	4.4
	20	3.3	7.0
HH-6	1	3.6	6.2
	5	3.3	4.4

TABLE 4  
 CONCENTRATIONS OF ALUMINUM AND DIFFERENT FORMS OF IRON  
 IN SUSPENDED SOLIDS

STATION	SAMPLING DEPTH m	Al mg/g	Fe <sup>2+</sup> mg/g	Fe <sup>3+</sup> mg/g	wustite hematite		Fe <sup>3+</sup> /Fe <sup>2+</sup>
					mg/g	mg/g	
APRIL 1986							
HH-1	1	19.9	4.1	11.8	1.1	2.7	2.9
	12	31.0	5.3	12.9	1.5	5.3	2.4
HH-2	1	13.5	2.4	9.0	1.5	5.2	3.8
	21	25.6	4.7	15.9	3.6	10.0	3.4
HH-3	1	8.8	0.8	22.3	29.4	52.5	27.0
	14	23.5	4.0	20.7	5.0	11.8	5.2
HH-4	1	41.6	15.6	26.6	5.5	7.3	1.7
	4	44.0	16.0	26.2	4.3	7.5	1.6
HH-5	1	19.7	3.2	21.9	9.5	52.9	6.8
	20	21.2	4.9	19.7	6.0	13.2	4.1
HH-6	1	12.1	2.3	14.0	5.8	11.6	6.2
	5	14.0	2.7	14.2	5.3	12.5	5.3
SEPTEMBER 1986							
HH-1	1	30.4	8.5	18.6	1.9	5.6	2.2
	12	44.7	13.5	34.8	5.4	10.0	2.6
HH-2	1	14.8	3.4	17.9	3.8	8.9	5.3
	21	34.2	9.0	60.2	6.7	4.2	6.7
HH-3	1	15.6	3.3	30.2	26.0	60.9	9.3
	14	26.8	8.4	26.7	8.4	17.0	3.2
HH-4	1	35.9	11.1	29.1	6.4	20.3	2.6
	4	45.0	20.9	20.1	3.1	2.1	1.0
HH-5	1	13.9	3.9	18.5	5.0	11.4	4.8
	20	42.7	14.0	33.3	17.7	32.6	2.4
HH-6	1	25.8	5.1	17.7	1.8	5.1	3.4
	5	36.3	8.6	20.2	3.2	8.6	2.3

TABLE 5  
MOSSBAUER PARAMETERS

Fe compound	IS (mm/s)	QS (mm/s)	HW (mm/s)
Fe <sup>2+</sup> , chlorite	1.13	2.56	0.44
Fe <sup>3+</sup> , amorphous	0.37	0.70	0.53
wustite, Fe <sub>1-x</sub> O	0.97	0.73	0.48
hematite, Fe <sub>2</sub> O <sub>3</sub>	0.43	2.57	0.39

TABLE 6

CONCENTRATIONS OF Fe, Mn, Zn, Pb, Cu, Ni AND Cd IN SUSPENDED SOLIDS

STATION	SAMPLING DEPTH m	Fe mg/g	Mn mg/g	Zn ug/g	Pb ug/g	Cu ug/g	Ni ug/g	Cd ug/g
APRIL 1986								
HH-1	1	19.7	4.4	1350	183	100	22	3.1
	12	25.0	5.9	1700	206	50	42	2.6
HH-2	1	18.0	4.8	1500	112	31	12	3.5
	21	34.2	12.0	2400	194	92	62	4.9
HH-3	1	105.0	5.5	2650	454	69	32	6.7
	14	41.5	9.7	2325	242	77	72	5.4
HH-4	1	55.0	2.8	1700	301	199	52	7.6
	4	54.0	2.2	1600	407	207	72	8.5
HH-5	1	87.5	10.6	2900	443	123	47	7.6
	20	43.7	10.9	2300	313	77	47	5.8
HH-6	1	33.6	7.4	1875	230	47	22	6.3
	5	34.7	7.6	1925	230	54	42	5.4
SEPTEMBER 1986								
HH-1	1	34.5	4.9	1075	206	77	47	4.4
	12	63.7	29.2	1500	253	112	47	6.7
HH-2	1	34.0	7.7	1037	230	62	42	2.6
	21	80.0	59.4	1725	301	154	62	4.9
HH-3	1	123.7	5.9	3212	655	112	62	7.6
	14	60.6	8.4	1800	324	115	102	9.9
HH-4	1	66.9	7.2	2262	443	161	87	8.5
	4	46.2	1.3	950	206	131	47	5.4
HH-5	1	38.7	5.7	1150	513	73	72	4.9
	20	97.5	8.0	2612	431	157	62	10.8
HH-6	1	29.7	3.5	675	183	115	32	8.5
	5	40.7	4.5	900	313	127	47	9.0

TABLE 7  
CONCENTRATIONS OF Fe, Mn, Zn, Cu IN WATER

STATION	SAMPLING DEPTH m	Fe ug/L	Mn ug/L	Zn ug/L	Cu ug/L
APRIL 1986					
HH-1	1	73	22	13	4
	12	153	25	28	7
HH-2	1	82	22	36	3
	21	81	36	30	5
HH-3	1	367	38	31	5
	14	167	38	30	4
HH-4	1	417	111	36	8
	4	591	95	41	8
HH-5	1	265	54	29	5
	20	136	34	22	5
HH-6	1	126	31	20	2
	5	168	28	20	3
SEPTEMBER 1986					
HH-1	1	174	22	11	9
	12	177	25	17	10
HH-2	1	168	25	9	6
	21	123	54	8	11
HH-3	1	100	22	7	8
	14	100	22	6	10
HH-4	1	279	44	26	10
	4	687	86	48	10
HH-5	1	138	18	11	12
	20	595	66	25	12
HH-6	1	263	28	7	6
	5	165	25	9	4

TABLE 8

RELATIVE CONTRIBUTION OF DIFFERENT Fe FORMS AND  $\text{Fe}^{3+}/\text{Fe}^{2+}$  RATIOS  
IN HAMILTON HARBOUR SEDIMENTS

STATION	$\text{Fe}^{2+}$ %	$\text{Fe}^{3+}$ %	wustite %	hematite %	$\text{Fe}^{3+}/\text{Fe}^{2+}$
1 HH 0-1	31.5	38.0	8.1	22.4	1.2
2 HH 0-1	23.3	29.9	12.6	34.3	1.3
3 HH 0-1	21.7	29.7	17.5	31.1	1.4
4 HH 0-1	44.5	42.5	6.3	6.8	1.0
5 HH 0-1	25.2	38.3	9.5	27.0	1.5
6 HH 0-1	43.6	32.2	7.6	16.6	0.7



TABLE 9

## RATIOS OF AL AND FE IN SUSPENDED SOLIDS AND SEDIMENTS AND ENRICHMENT FACTORS CALCULATED FOR SUSPENDED SOLIDS

STATION	SAMPLING DEPTH m	APRIL		SEPTEMBER		APRIL	SEPTEMBER
		Al <sub>r</sub> *	Fe <sub>r</sub> **	Al <sub>r</sub> *	Fe <sub>r</sub> **	E. F.	
HH-1	1	2.20	2.00	1.45	1.15	1.10	1.26
	12	1.41	1.60	0.98	0.62	0.88	1.58
HH-2	1	3.25	2.20	2.90	1.18	1.48	2.46
	21	1.72	1.90	1.29	0.50	0.90	2.58
HH-3	1	5.00	0.38	2.82	0.32	13.16	8.81
	14	1.87	0.96	1.64	0.66	1.95	2.48
HH-4	1	1.06	0.73	1.22	0.60	1.45	2.03
	4	1.00	0.74	0.98	0.86	1.35	1.14
HH-5	1	2.20	0.46	3.16	1.03	4.78	3.07
	20	2.07	0.92	1.03	0.41	2.25	2.51
HH-6	1	3.64	1.19	1.70	1.35	3.06	1.26
	5	3.14	1.15	1.21	0.98	2.73	1.23

\* Al<sub>r</sub> are Al<sub>sed.s.</sub>/Al<sub>susp.s.</sub> ratios, where Al<sub>sed.s.</sub> is the average Al concentration in sediments (4.5%) and Al<sub>susp.s.</sub> is Al concentration in suspended solids, as measured

\*\* Fe<sub>r</sub> are Fe<sub>sed.s.</sub>/Fe<sub>susp.s.</sub> ratios, where Fe<sub>sed.s.</sub> is average background Fe concentration in sediments (4%) and Fe<sub>susp.s.</sub> is Fe concentration in suspended solids, as measured

E.F. is the enrichment factor, calculated from the equation (2)

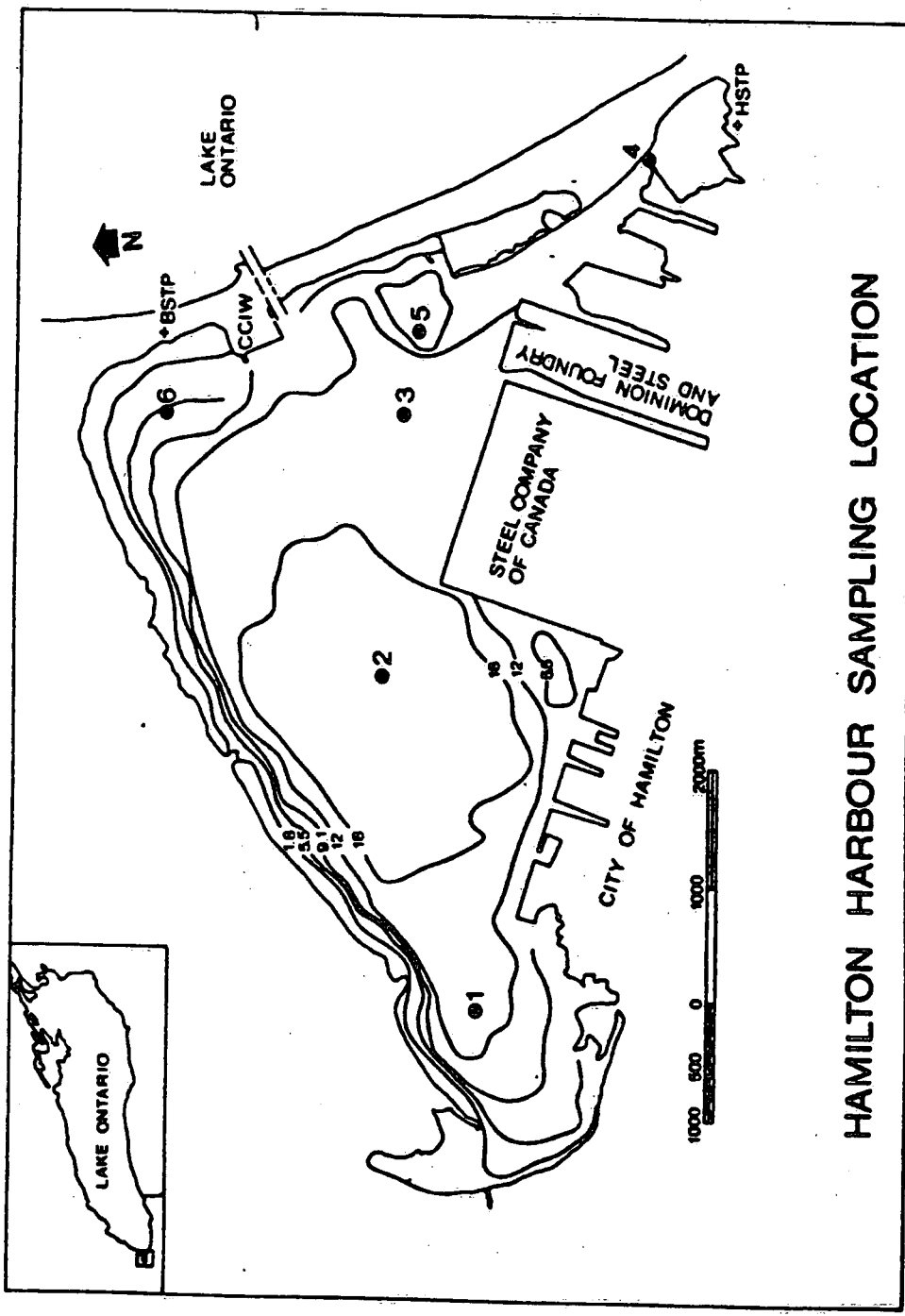
TABLE 10

CONCENTRATIONS OF Fe, Mn, Zn, Pb, Cu, Ni AND Cd  
IN HAMILTON HARBOUR SEDIMENTS

STATION	Fe mg/g	Mn mg/g	Zn ug/g	Pb ug/g	Cu ug/g	Ni ug/g	Cd ug/g
1 HH 0-1	64.4	2.3	2200	301	119	47	6.7
2 HH 0-1	87.0	2.3	2900	405	156	63	14.4
3 HH 0-1	104.8	2.6	2725	355	150	59	13.8
4 HH 0-1	46.0	1.1	1050	154	161	59	12.4
5 HH 0-1	87.5	3.0	2850	280	138	71	17.1
6 HH 0-1	52.6	1.3	1350	192	222	31	20.5

## LIST OF FIGURES

1. Location of the sampling sites
2. Oxygen and temperature profiles of water column in September
3. Total P, NAI-P concentrations in suspended solids and total P, and total filterable P (TFP) in water a) April 1986, b) September 1986
4. Room temperature Mossbauer adsorption spectrum of suspended solids from station HH-3
5. Distribution of iron forms in suspended solids a) April 1986, b) September 1986
6. Concentrations of Fe, Mn, Zn and Pb in suspended solids a) April 1986 b) September 1986
7. Concentrations of Cu, Ni and Cd in suspended solids a) April 1986 b) in September 1986



HAMILTON HARBOUR SAMPLING LOCATION

Fig 1

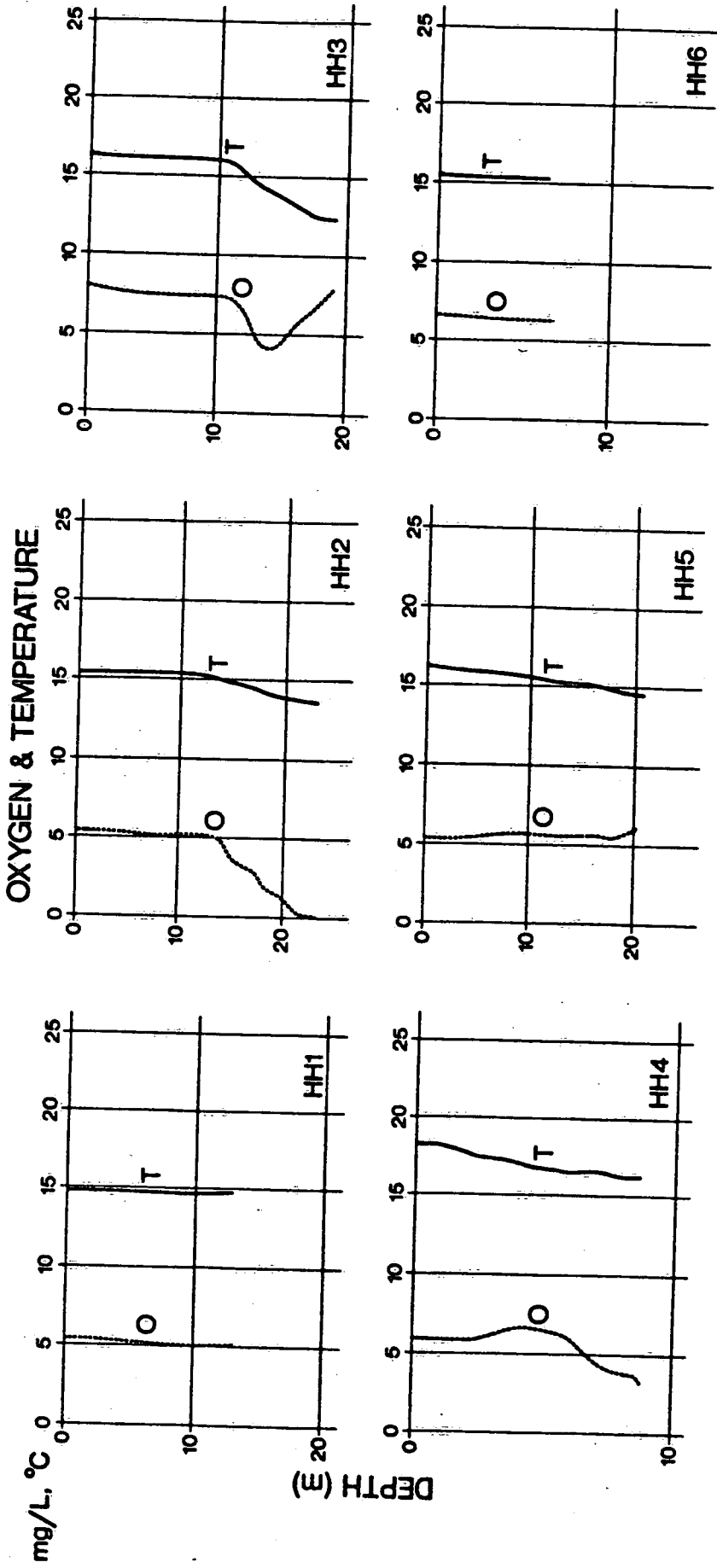
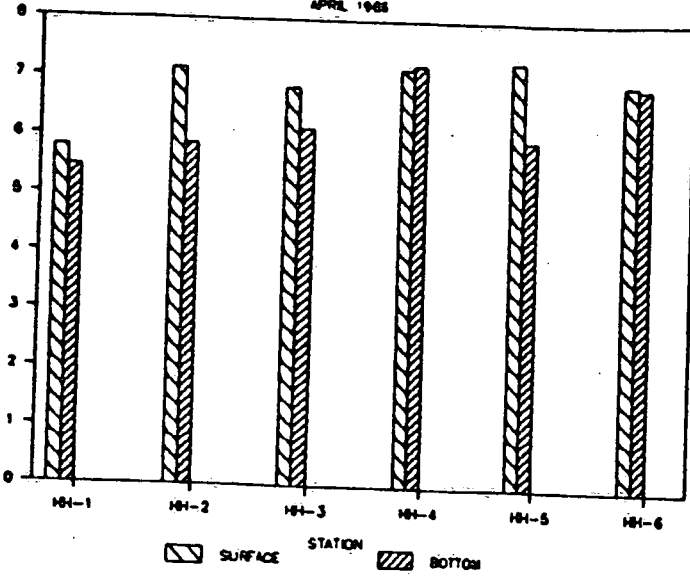


Fig 2

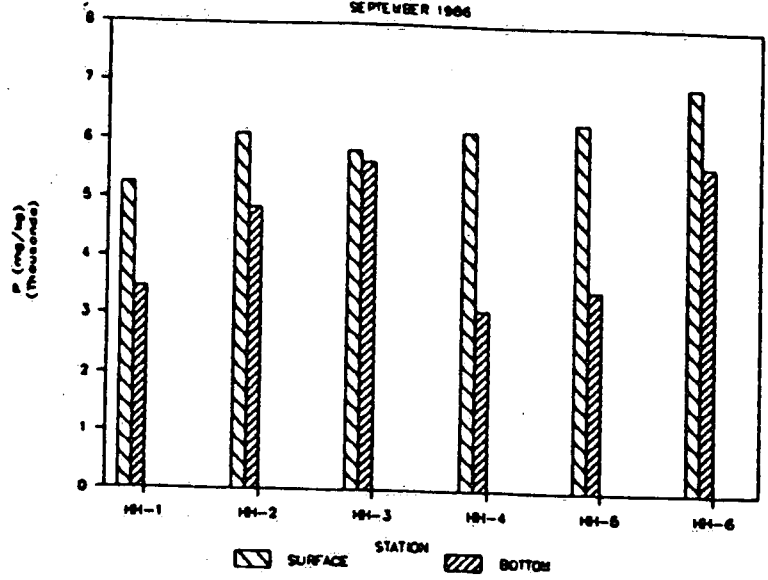
TOTAL P IN SUSPENDED SOLIDS

APRIL 1988



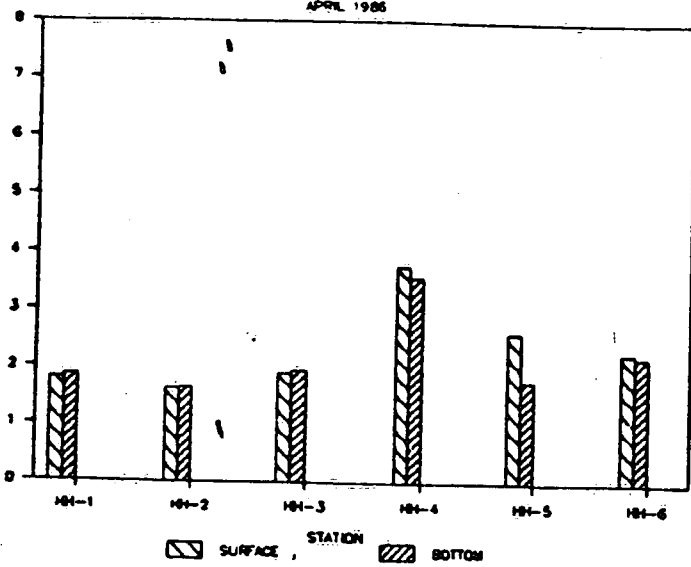
TOTAL P IN SUSPENDED SOLIDS

SEPTEMBER 1988



NAI-P IN SUSPENDED SOLIDS

APRIL 1988



NAI-P IN SUSPENDED SOLIDS

SEPTEMBER 1988

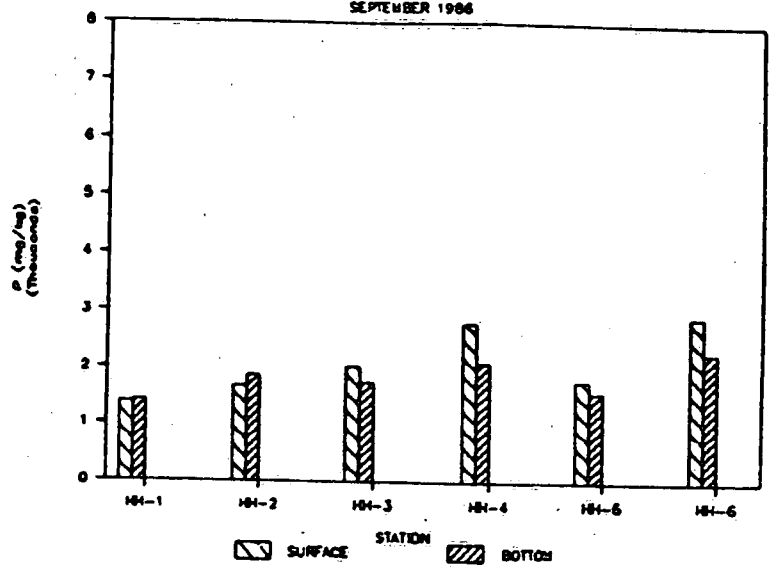
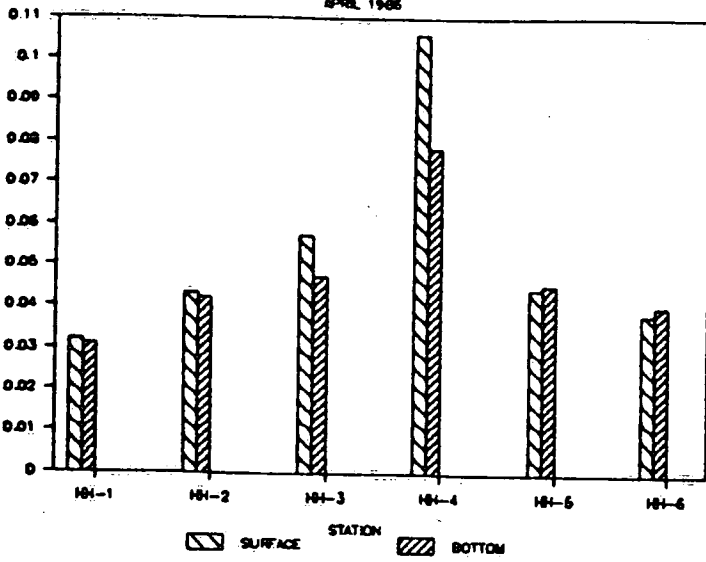
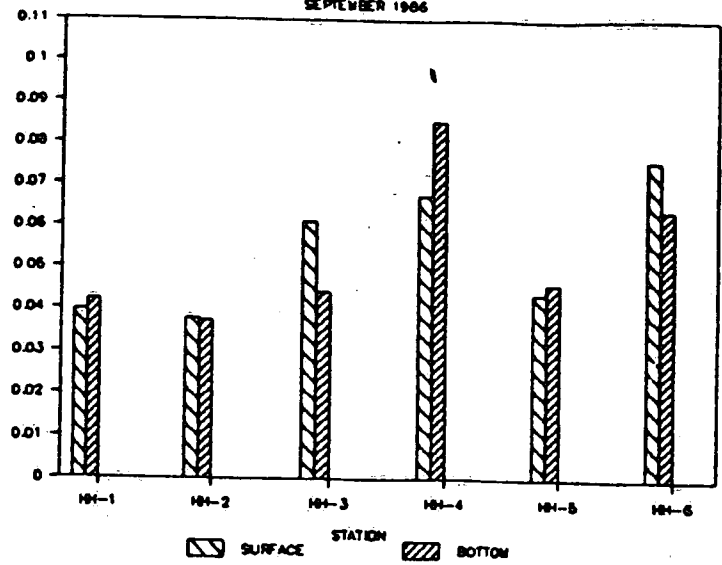


Fig. 3

TP IN WATER  
APRIL 1966



TP IN WATER  
SEPTEMBER 1966



TFP IN WATER  
SEPTEMBER 1966

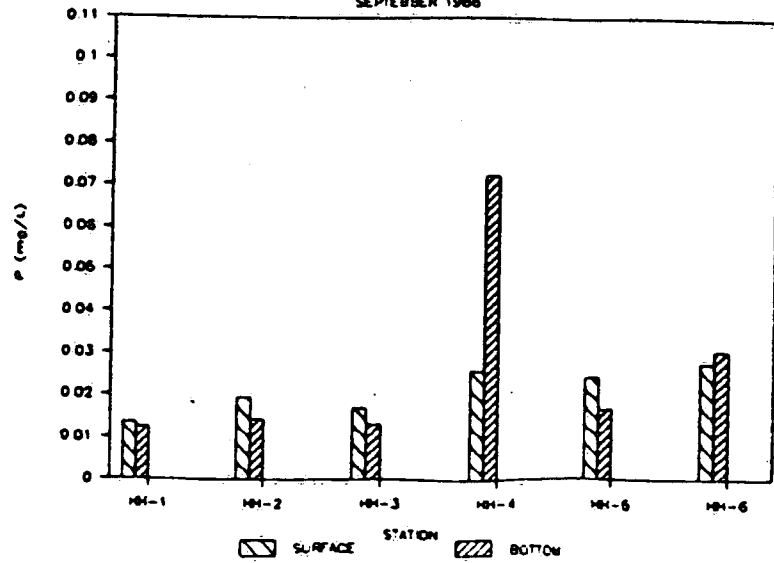


Fig 3

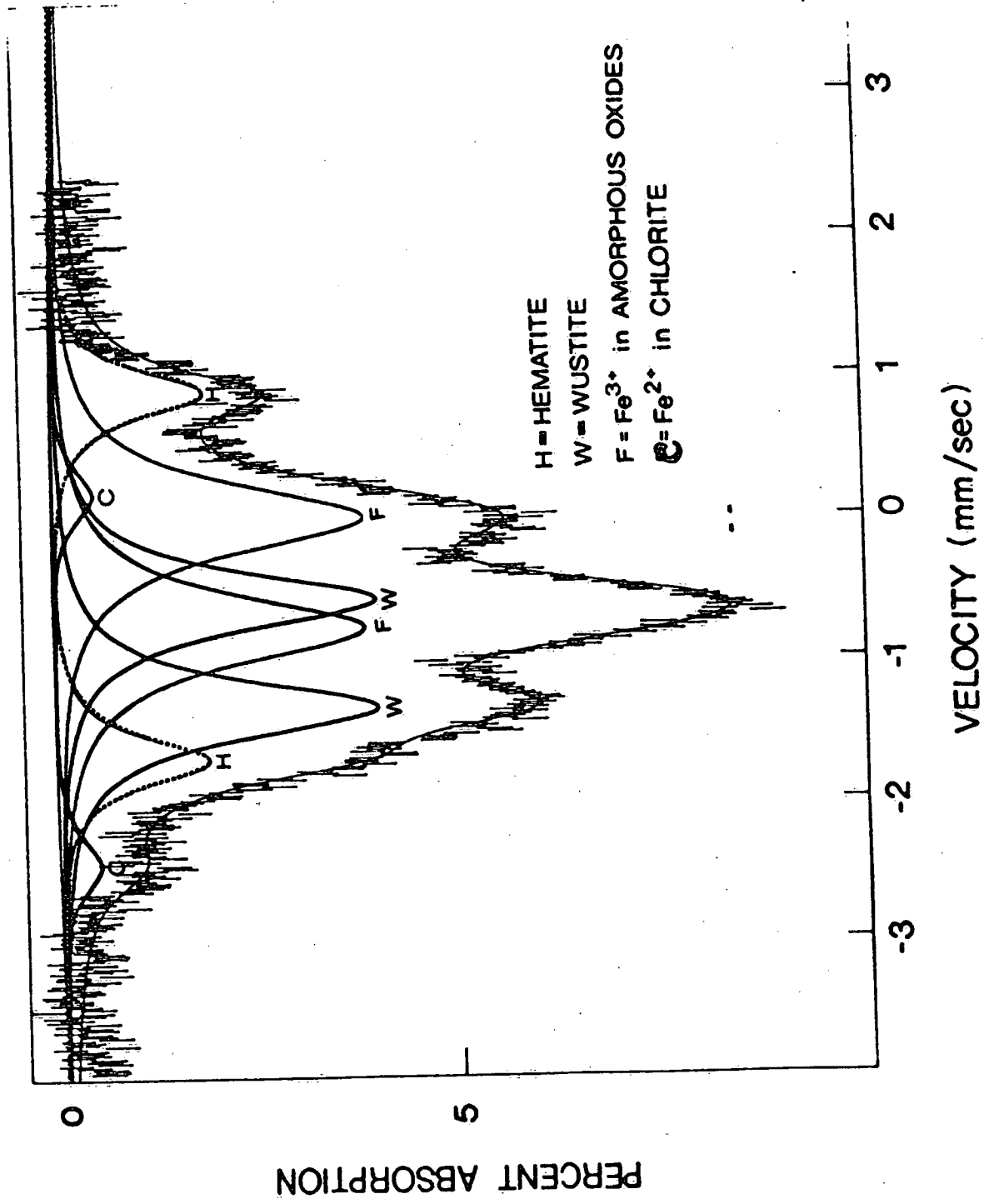
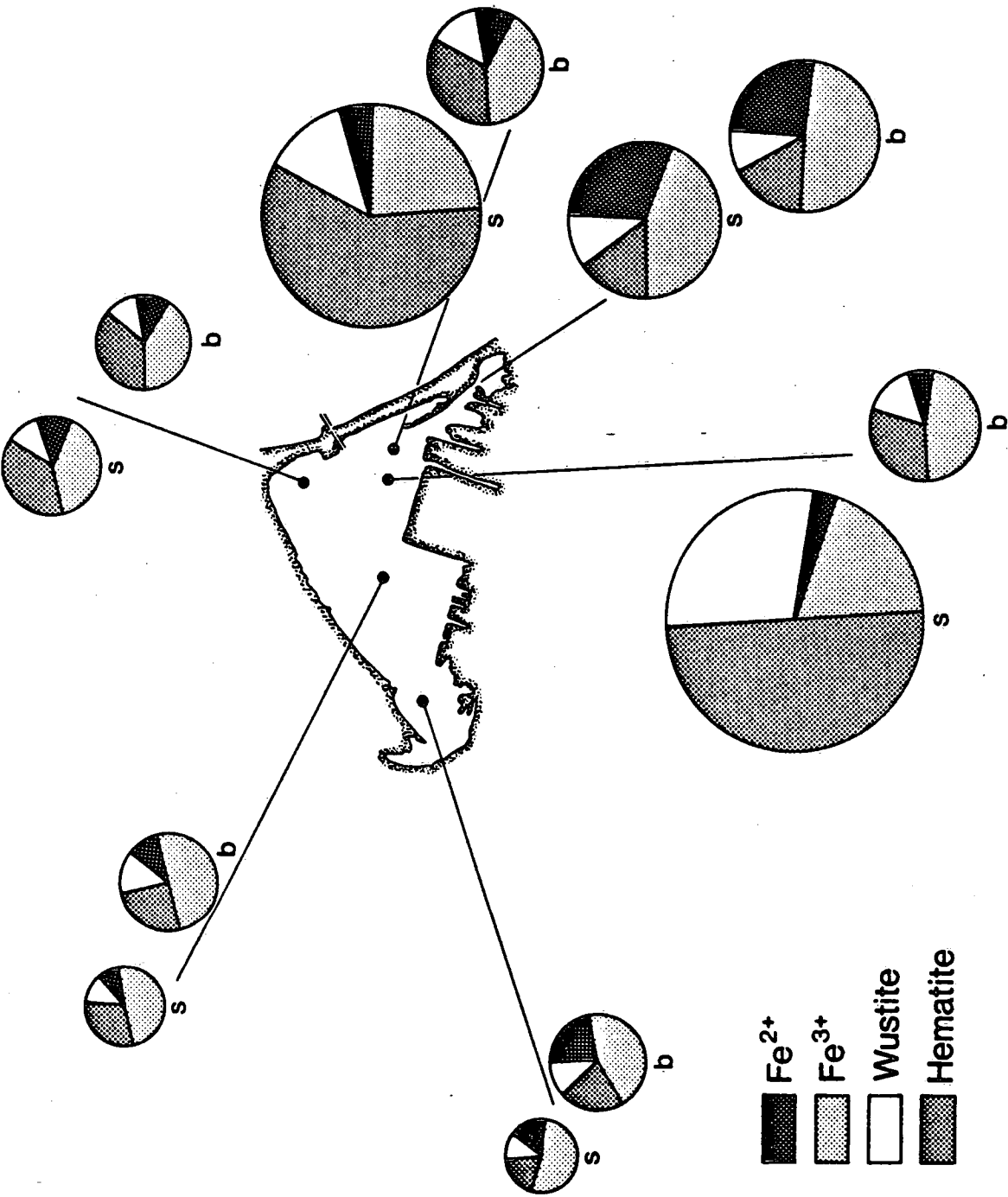


Fig. 4

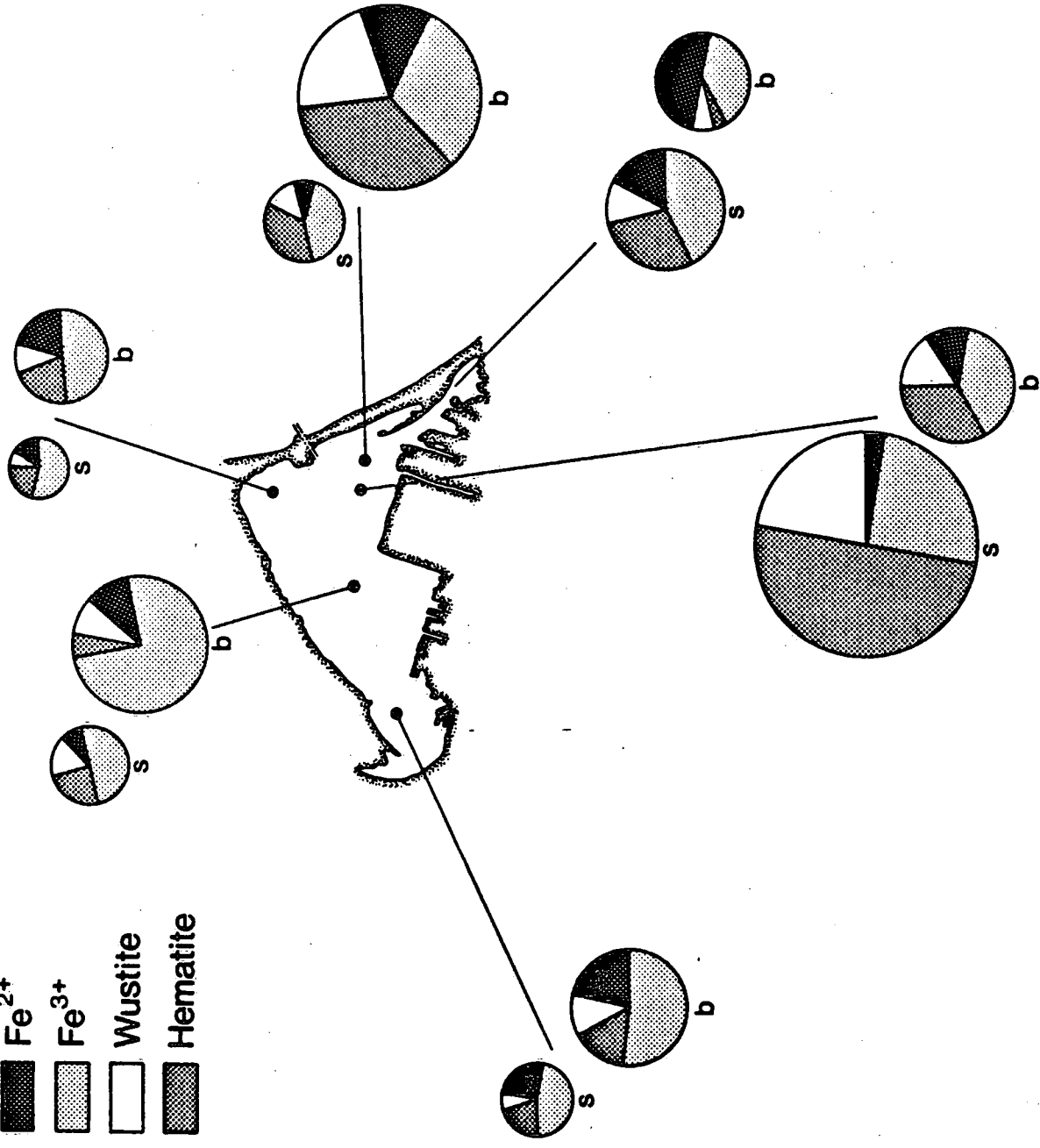




DISTRIBUTION OF IRON FORMS IN SUSPENDED SOLIDS (APRIL, 1986)

779

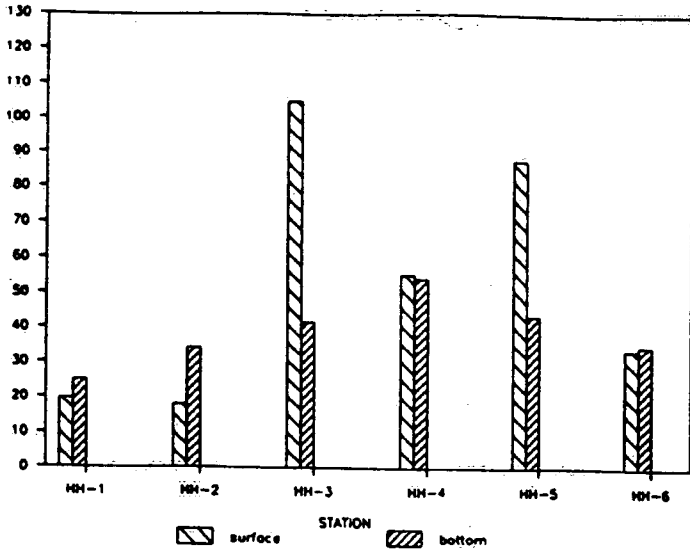
$Fe^{2+}$   
  $Fe^{3+}$   
 Wustite  
 Hematite



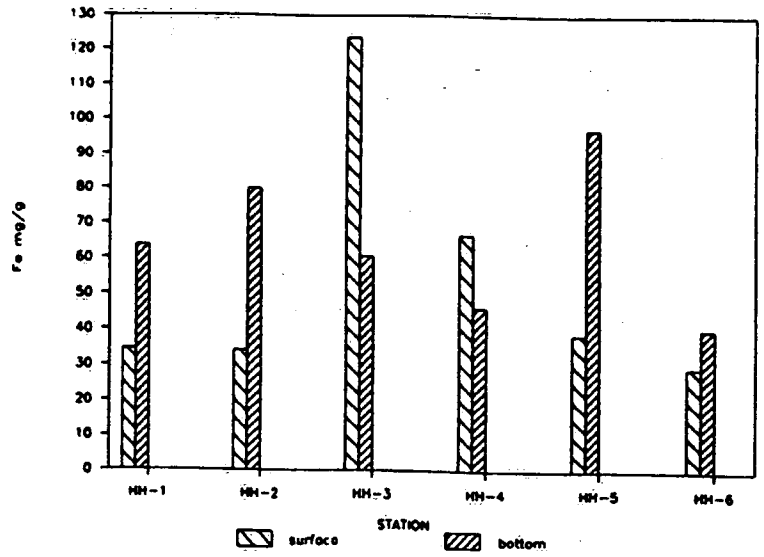
DISTRIBUTION OF IRON FORMS IN SUSPENDED SOLIDS (SEPT. 1986)

Fig 5.2

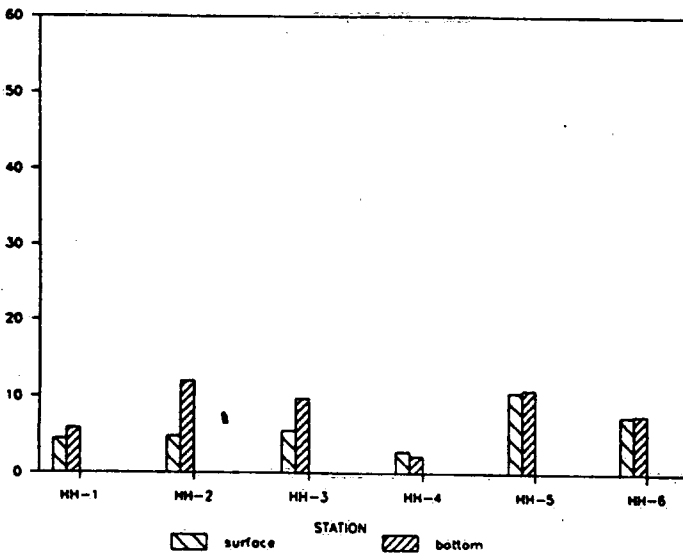
FE IN SUSPENDED SOLIDS, APRIL



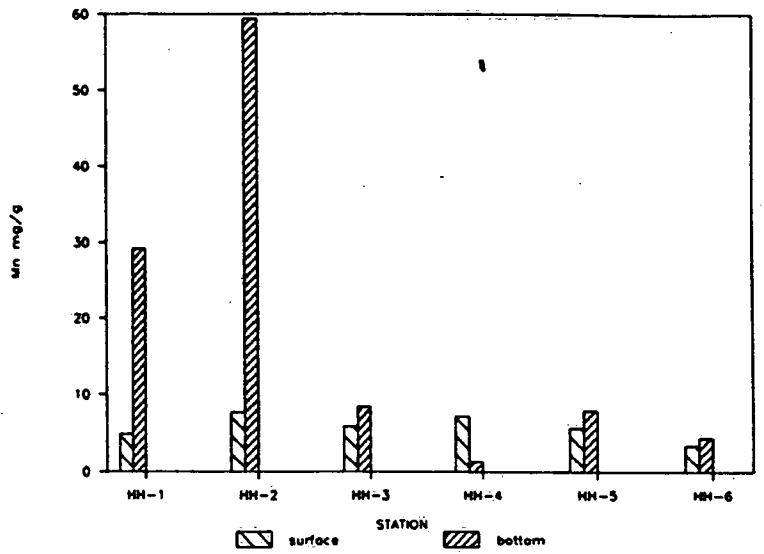
FE IN SUSPENDED SOLIDS, SEPTEMBER



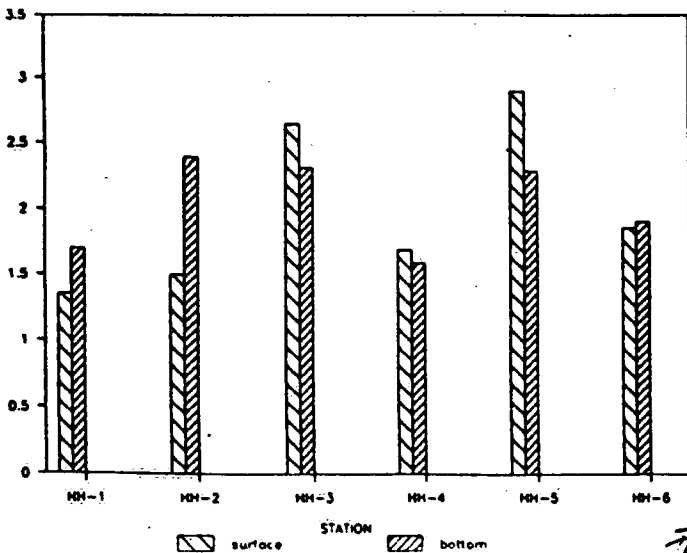
MN IN SUSPENDED SOLIDS, APRIL



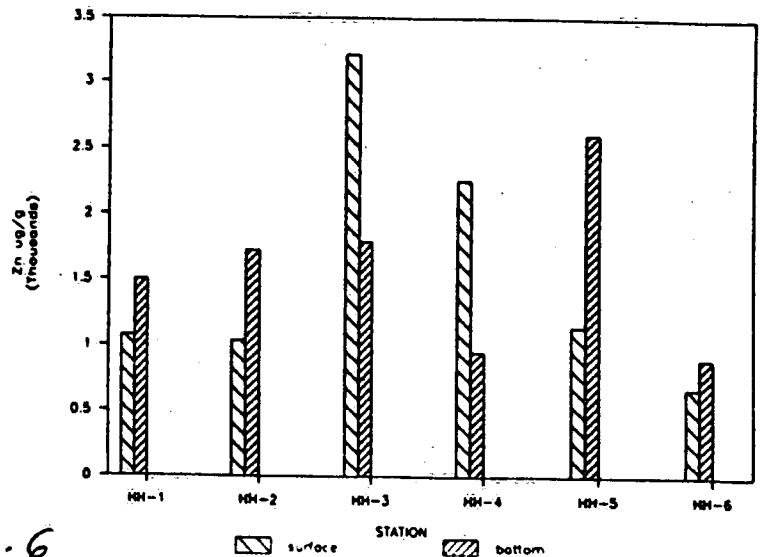
MN IN SUSPENDED SOLIDS, SEPTEMBER



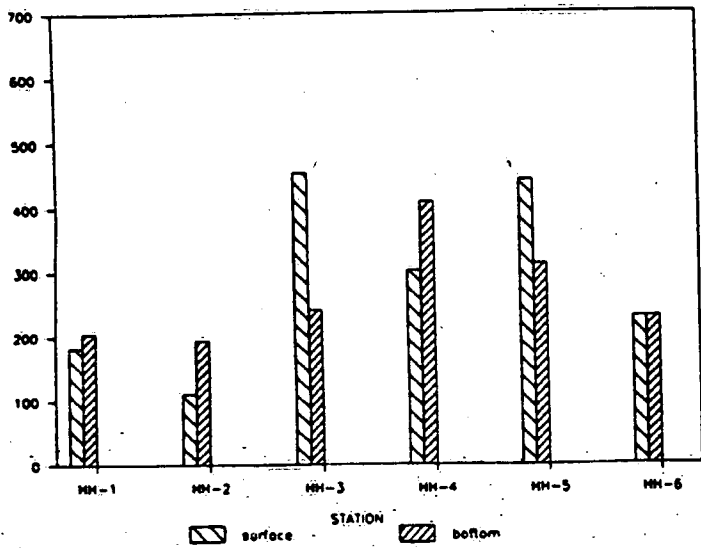
ZN IN SUSPENDED SOLIDS, APRIL



ZN IN SUSPENDED SOLIDS, SEPTEMBER



PB IN SUSPENDED SOLIDS, APRIL



PB IN SUSPENDED SOLIDS, SEPTEMBER

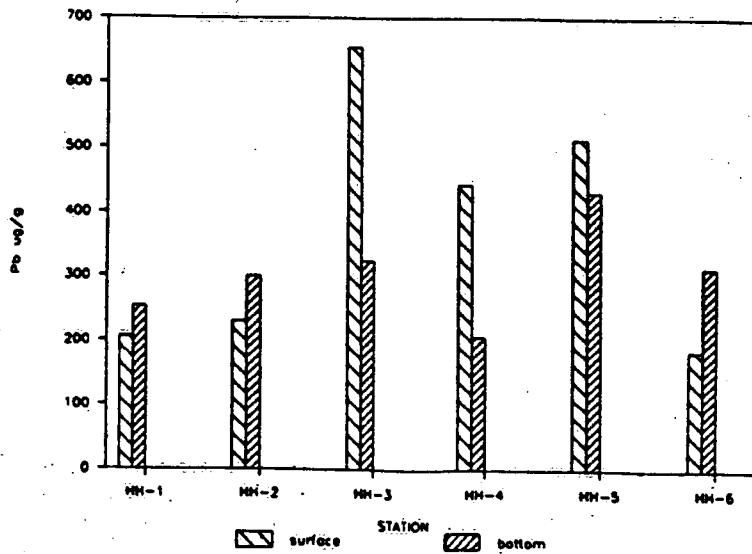
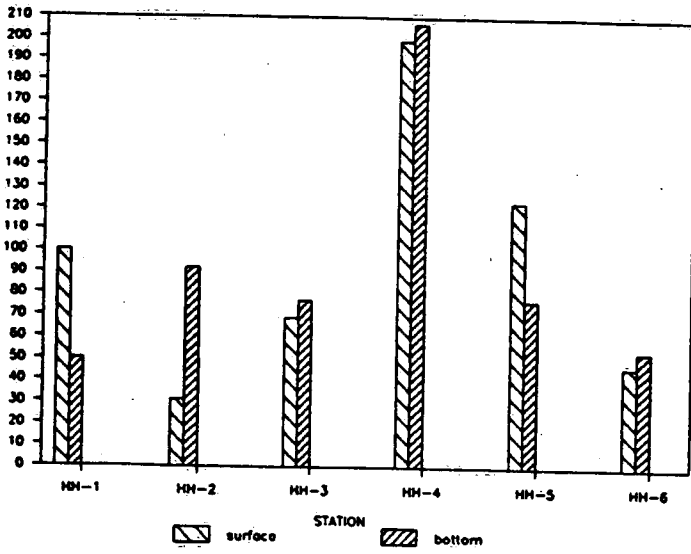
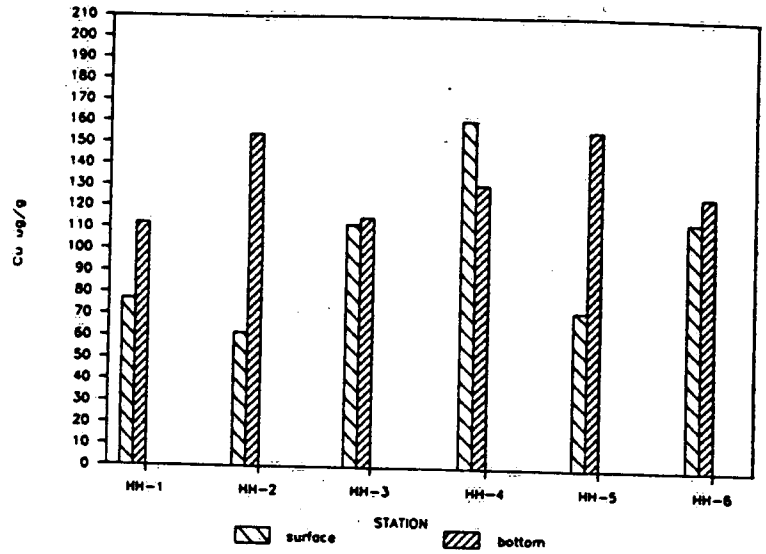


Fig. 6

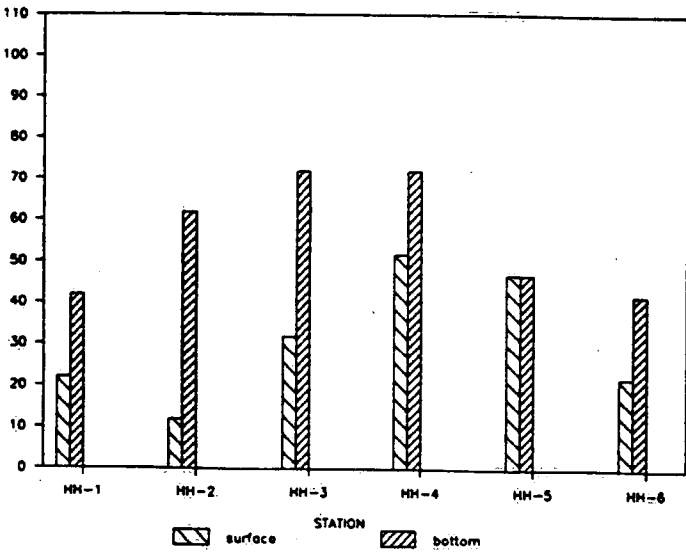
CU IN SUSPENDED SOLIDS, APRIL



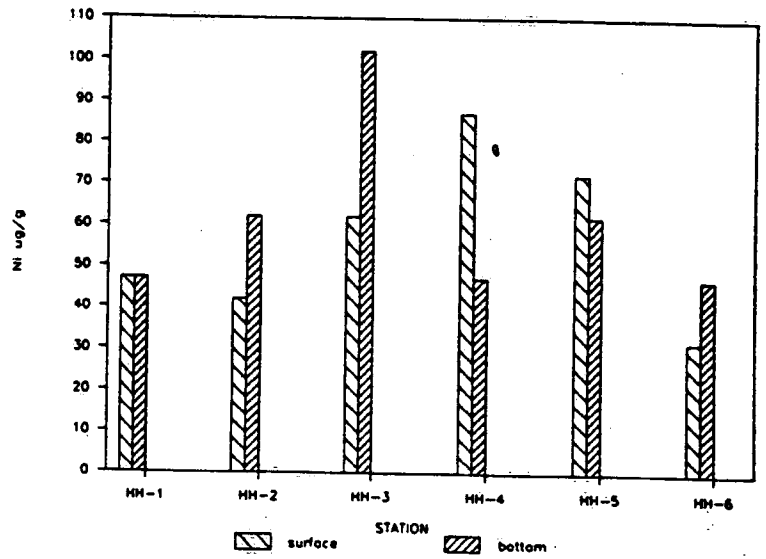
CU IN SUSPENDED SOLIDS, SEPTEMBER



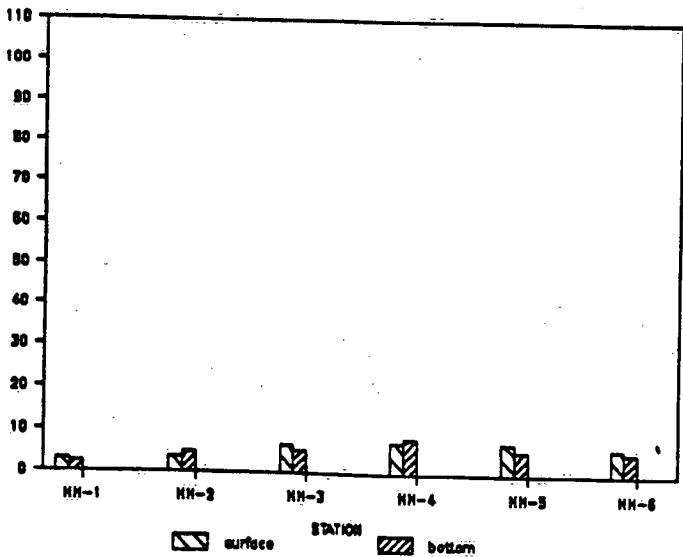
NI IN SUSPENDED SOLIDS, APRIL



NI IN SUSPENDED SOLIDS, SEPTEMBER



CD IN SUSPENDED SOLIDS, APRIL



CD IN SUSPENDED SOLIDS, SEPTEMBER

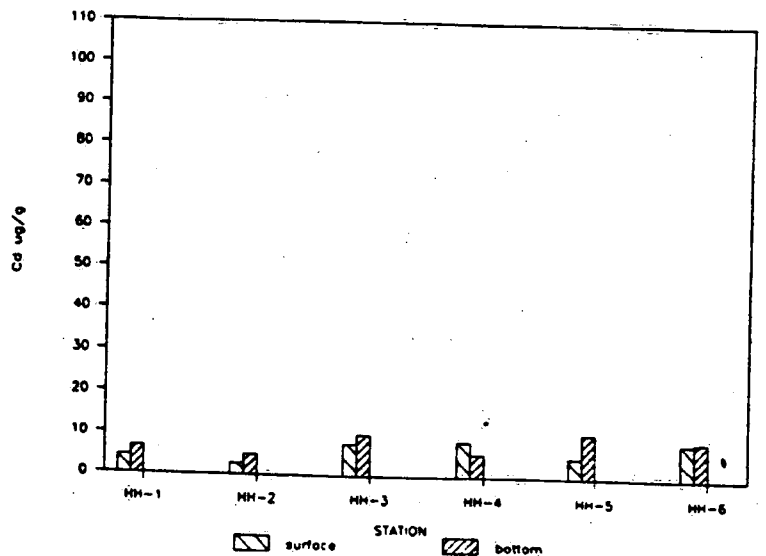


Fig 7