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MANAGEMENT PERSPECTIVE

In 1985 International Join Commission (IJC) identified Hamilton Harbour as one of the 17 Areas of Concern in Ontario. Quantifying the contaminant export into Lake Ontario from the harbour has been important for closing the mass balance for heavy metals in the harbour and in assessing its relative impact on Lake Ontario.

By tracking industrially-derived particulate iron compounds (hematite and, in particular, wustite) the extent of the plume of contaminated Harbour water entering Lake Ontario was estabilished. The quantification of metal contaminants loadings from Hamilton Harbour to Lake Ontario, presented in this report, contributes significantly to the few and somewhat inconsistent loading estimates, obtained mainly by mass balance between loadings to the Harbour and fluxes to the sediments. The results of this study suggest that only a small portion of metals entering the Harbour is exported into Lake Ontario, most of the metal loading accumulates in the sediments of the harbour. The data presented in this report also suggest that metal loadings from the Harbour to Lake Ontario are low when compared to loadings from the Niagara River.

PERSPECTIVES DE LA DIRECTION

En 1985, La Commission internationale mixte (CIM) a évalué le port de Hamilton comme l'une des 17 zones problèmes en Ontario. L'analyse quantitative des exportations de contaminants à partir de ce port vers le lac Ontario s'est révélée très importante pour la détermination du bilan massique pour les métaux lourds dans le port et pour l'évaluation de leurs effets relatifs sur le lac Ontario.

En retraçant les composés particulaires d'origine industrielle à base de fer (hématite et, surtout, wüstite), on a pu évaluer l'étendue du panache d'eau contaminée pénétrant dans le lac Ontario depuis le port. L'analyse quantitative des charges de contaminants métalliques dans le lac Ontario en provenance du port de Hamilton, présentée dans ce rapport, complète utilement les rares estimations quelque peu incohérentes, obtenues principalement par évaluation du bilan massique entre les charges introduites dans le port et le flux vers les sédiments. Les résultats de cette étude laissent supposer que seule une faible fraction des métaux déversés dans le port rejoindra le lac Ontario, la majeure partie de la charge métallique s'accumulant dans les sédiments du port. Les données présentées dans ce rapport laissent également supposer que les charges métalliques présentes dans le lac Ontario et provenant du port de Hamilton sont faibles, comparativement aux charges originaires de la rivière Niagara.

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Abstract

The presence and the extent of the plume of Hamilton Harbour water extending into Lake Ontario was determined in order to assess the importance of metal contaminant transport from the Hamilton Harbour into Lake Ontario. Industrially derived iron compounds, wustite and hematite, were used as plume tracking parameters. Wustite, particularly, proved to be a good tracer of the plume.

Annual loadings of particulate heavy metals to Lake Ontario were calculated using the concentrations of heavy metals in suspended solids from the connecting Burlington Canal, Hamilton Harbour and western Lake Ontario. Annual loadings of heavy metals to Lake Ontario are ~266×10^3 kg Fe, 9.33×10^3 kg Zn, 1356 kg Pb, 273 kg Cu, and 8.7 kg Cd. The relative contribution of the total metal load from Hamilton Harbour to Lake Ontario is negligible when compared to the load from the Niagara River. Lake-harbour water exchange and the high Fe concentrations in benthic sediments of Hamilton Harbour increase phosphorus retention in the harbour sediments, thus are beneficial to water quality in Hamilton Harbour.

RÉSUMÉ

On a évalué l'étendue du panache d'eau contaminée s'étirant du port de Hamilton jusque dans le lac Ontario afin de déterminer l'importance du transport de contaminants métalliques dans le lac Ontario à partir du port de Hamilton. Des composés du fer d'origine industrielle, soit la wüstite et l'hématite, ont servi comme paramètres pour localiser le panache.

Les charges annuelles de métaux lourds particulaires gagnant le lac Ontario ont été calculées en utilisant les concentrations de métaux lourds dans les matières solides en suspension provenant du canal Burlington, du port de Hamilton et de la partie occidentale du lac Ontario. Ces charges annuelles se répartissent comme suit : 266 x 10^3 de Fe, 9,33 x 10^3 de Zn, 1 356 kg de Pb, 273 kg de Cu et 8,7 kg de Cd. La contribution relative de la charge métallique totale du port de Hamilton provenant du lac Ontario est négligeable, comparativement à la charge issue de la rivière Niagara. L'échange d'eau lac-port et les fortes concentrations de fer des sédiments benthiques du port de Hamilton entraînent une augmentation de la rétention de phosphore dans les sédiments du port, ce qui se révèle bénéfique pour la qualité de l'eau du port de Hamilton.

1. Introduction

Hamilton Harbour is one of the most heavily polluted bodies of water in North America. The harbour is situated at the western end of Lake Ontario (Figure 1). 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 receives effluent from the sewage treatment plants (STPs) of the surrounding cities of Hamilton and Burlington. Furthermore, the harbour is the source of and the recipient of cooling water from the steel industry, located on the south shore. High concentrations of organic and inorganic contaminants, eutrophication and oxygen depletion in the summer severely impair water quality in the harbour.

The exchange of water between the harbour and Lake Ontario is responsible for loadings of nutrients and contaminants to the lake. For most of the year, the exchange of water takes place via unidirectional (plug) flow to and from the lake (MOE, 1986). In summer, during stratified conditions, warmer harbour water frequently flows into the lake above a counterflow of cooler lake water (Matheson, 1963; Dick and Marsalek, 1973; Palmer and Poulton, 1976; Klapwijk and Snodgrass, 1985; MOE, 1986; Barica et al., 1988). The flow of harbour water results in a plume which may extend far into the lake. Plume tracking studies, based on the measurements of chloride, chlorophyll, conductivity and suspended solids concentrations (MOE, 1986; Barica, 1988) were carried out in order to delineate the extent of the plume. However, chlorophyll was found to be an unreliable tracer, as its levels may increase due to the photosynthesis in lake water during daylight (MOE, 1986). Similarly, suspended solids were found to be poor tracers of the plume, as their concentrations are effected by nearshore processes such as shoreline erosion, rain-induced runoff and resuspension of sediments (MOE, 1986).

Suspended solids play an important role in the transport of nutrients and contaminants in aquatic ecosystems and as such they contribute significantly to total nutrient and contaminant loads to the lake. An earlier study (Mayer and Manning, 1990a) indicated that forms of particulate iron, notably hematite and wustite, originating from the iron and steel industry, are good tracers of the anthropogenic input to Hamilton Harbour. Here, we describe the use of wustite in tracking the plume of harbour water in the nearshore area of western Lake Ontario.

Published data on metal loadings from Hamilton Harbour to Lake Ontario are scarce and inconsistent. Hence, an attempt is made in this study to quantify these loadings.

The objectives of this study are: (1) to determine the presence and the extent of the plume of harbour water in Lake Ontario; (2) to evaluate the loadings of particulate heavy metals from Hamilton Harbour to Lake Ontario; and (3) to report on the beneficial effect of lake-harbour water exchange on the Fe-P cycle in the harbour.

2. Materials and Methods

Water samples and suspended sediments were collected at several stations in Hamilton Harbour and in Western Lake Ontario (Figure 1) at approximately one month intervals between April and November of 1987. Not all stations were sampled at all times. The sampling locations on each sampling trip were selected to reflect limnological conditions (seasonal mixing, summer stratification) in the harbour and in the lake, water exchange between the harbour and the lake and the presence of a plume in the lake. At each station, a temperature profile and a conductivity measurement were taken, using the EBT and a conductivity meter. The conductivity was corrected to 25^{o}C. Oxygen concentrations measured in the bottom water at deep stations in the harbour during summer stratification indicated that hypolimnetic anoxia developed during the latter part of June.

Water samples and suspended solids were taken from 1 m below the water surface and 1 m above the sediment-water interface at harbour stations. At the lake stations, the 1 m depth only was sampled, when the presence of a plume was observed. The suspended solids were collected using a continuous-flow Westfalia separator. The collected solids were frozen immediately and subsequently freeze-dried in the laboratory. Concentrations of total suspended solids (TSS), total P (TP) and total filterable phosphorus (TFP) and total metals in water were determined according to the protocol of Environment Canada (1979). During the hypolimnion anoxia, concentrations of filterable metals in harbour water from deep stations were also measured.

Concentrations of total P in suspended solids were determined by ignition of samples at 550^{o}C and subsequent 16-hour 1N HCl extraction. The coefficient of variation determined from triplicate analyses was 1.1%. Biologically available P (BAP) in suspended solids was estimated using the procedure of Williams et al. (1980), employing a 0.1N NaOH/1.0N NaCl solution as extractant.

Concentrations of 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). The coefficient of variation of carbon analyses was $\pm$10%. Total concentrations of metals in suspended solids were determined by acid dissolution and subsequent atomic absorption spectrometry (Desjardins, 1978). The coefficients of variation for metal analyses ranged between 0.62% (for Cu) and 11.07% (for Pb). Metal analyses revealed that four of the suspended sediment samples were contaminated with stainless steel from the centrifuge, a consequence of excessive movement of the boat during centrifugation. To our knowledge, no source of stainless steel exists anywhere near the harbour. Mössbauer analyses confirmed the presence of the stainless steel.

The principal iron compounds were determined by Mossbauer spectroscopy, using an $^{57}Co/^{57}Fe$ source. The spectra of all samples were recorded at room temperatures on a 512-channel microprocessor-based spectrometer calibrated against Fe-metal foil. Spectra were recorded at low Doppler velocities (-4 to +4 mm s^{-1}), and some spectra were recorded at high velocities in order to confirm the presence and abundance of magnetically ordered species, such as hematite; the stronger outermost peaks of hematite can be detected only at high velocities. Commercially obtained hematite was used to confirm the hematite peaks, and the stainless steel plate was used to confirm the peak attributed to stainless steel. The spectra were computed using the programs of Stone (1967). Areas and half-widths within a quadrupole doublet were constrained to be equal. Chi squared values were used to assess the goodness of fit.

3. Results and Discussion

3.1. PHOSPHORUS IN WATER AND IN SUSPENDED SOLIDS

Phosphorus concentrations in the water show considerable seasonal and spatial variation. The mean total P (TP) concentration in water from Hamiton Harbour averaged at 0.072 mg/L (Table I), while the average total filterable P (TFP) concentration of the harbour water was 0.034 mg/L. These concentrations are significantly higher ($p<0.001$, $t=6.21$; $t=5.50$, respectively) than corresponding P concentrations in the lake water (Table I).

The differences between the P concentrations in the lake and harbour water (Mayer and Manning, 1990b) are less pronounced during the summer months, probably a result of increased primary productivity in the nearshore area of Lake Ontario. Similarly, the concentrations of bioavailable P (BAP) and total P (TP) in suspended solids from Hamilton Harbour are significantly higher ($p<0.001$, $t=4.85$, $t=5.62$, respectively) than corresponding particulate P concentrations from the lake (Table I). The average P concentrations in water and in suspended solids from Burlington Canal fall, as expected, between the harbour and the lake values (Table I).

Although hypolimnion anoxia persists in the harbour during the summer, no P release from sediments was observed at any station in 1986 (Mayer and Manning, 1990a). The absence of observed P release is, at least partially, a result of high Fe^{3+}/NAI-P ratios in benthic sediments. The molar Fe^{3+}/NAI-P ratio (7.3) of benthic sediments (Mayer and Manning, 1990a) at the deepest location of Hamilton Harbour is more than double that of other benthic sediments (Shiller et al., 1985).

More frequent sampling in 1987, however, revealed the influx of oxygenated bottom lake water on some occasions, even to the deep station in the middle of the harbour (station HH 2). In August, when the harbour was strongly stratified, only a slight increase in the concentration of the TFP in hypolimnetic water was observed, despite large increases in TP and BAP concentrations in solids at station HH 2 (Figure 2). Conductivity and oxygen concentrations measurements indicate the influx of oxygenated hypolimnetic lake water, resulting in large difference between the conductivities of surface and bottom waters (367 umhos/cm versus 240 umhos/cm). Such infusion of an O_2- rich lens of lake water results in dilution of suspended solids concentration (9.8 mg/L at the surface versus 3.2 mg/L at the bottom) and precipitation of the phosphorus released previously from benthic sediments into the overlying water.

In September, however, the temperature, conductivity and oxygen data indicate uninterrupted anoxic conditions at this station, resulting in high concentrations of TP and dissolved P (TFP) in hypolimnetic water (Figure 2). The total P concentration in water in September reached a value of ~0.165 mg/L, with TFP (~0.060 mg/L) accounting for about 36% of the total P (Figure 2). This TFP value is probably underestimated, since some of the TFP may have precipitated during sample collection and processing. The Fe concentrations in water and solids changed concomitantly with the P concentrations, confirming the association of the two elements. As P concentrations in hypolimnetic water increased due to anoxic release from sediments (in September), the Fe concentration in water at the same location reached a value of 1.65 mg/L (Figure 2), of which approximately 30% of total Fe was in the dissolved form.

With the exeption of hypolimnetic P-release at station HH 2 in September, the pool of dissolved P decreased in the summer in harbour water (Mayer and Manning, 1990b) as a result of biological utilisation. In July and August similar concentrations of dissolved P were measured in harbour (0.0214 mg/L, average) and in lake water (0.0175, average).

Although phosphorus concentrations in water and in suspended solids of Hamilton Harbour are high, their use in tracking the plume is limited by the variability in P concentrations in the nearshore zone of Lake Ontario, resulting from temporal changes in biological productivity and physical processes .

3.2. MÖSSBAUER SPECTRAL INTERPRETATION

Mössbauer spectral methods are highly suitable for the speciation of particulate iron. In particular, the identification and quantification of industrially derived Fe compounds in Hamilton Harbour solids showed promise in tracking the plume of harbour water containing effluent from the steel industry (Mayer and Manning, 1990a). A representative Mössbauer spectrum of suspended solids from the harbour is shown in Figure 3. Four doublets, corresponding to four Fe compounds, can be resolved in the majority of spectra of harbour samples and in spectra of some lake samples. Of these four compounds, Fe^{2+} from chlorite and clay is naturally occurring, whereas Fe^{3+} in hydrated iron oxides, is derived from both natural and industrial sources. In addition to these compounds, two more Fe forms can be identified, namely ferric ions in crystalline hematite (α-Fe_2O_3) and ferrous ions in wustite ($Fe_{1-x}O$). The source of the latter two forms is the steel industry, although small amounts of hematite are derived from the surrounding watershed. Hematite, being a heavy mineral, is likely associated with rapidly settling particles and its transport from the nearshore area toward the middle of the basin is, therefore, limited. Thus, suspended solids from the nearshore zone will contain a small quantity of hematite of natural origin. Wustite, which forms as a scale when hot iron or steel contacts air, is metastable in the aquatic environment (Bodsworth, 1963) and eventually oxidizes to higher oxides of Fe. The proportion of wustite in most of the solids in the lake is very small and therefore the error associated with its estimation is relatively large.

The most abundant form of Fe in suspended solids is Fe^{3+} in hydrated oxides (Table IV). At concentrations of wustite >5% of total Fe, the presence of wustite is indicated by a significant shoulder at ~1.3 mm s^{-1}. The average computed values of isomer shift, quadrupole splitting and the line width of all identified Fe forms are listed in Table II. In most computations, the half-widths of wustite and hematite were constrained using the values estimated from computations of spectra of samples with the highest concentrations of these two compounds. The values of the Mössbauer parameters are in good agreement with those of Manning et al. (1980) and Mayer and Manning (1990a) and are good to better than ± 0.1 mm s^{-1}. The proportions of the four identified forms of Fe were obtained from ratios of areas beneath the respective doublets, taking into account the areas of the four outer hematite peaks, not seen in the low velocity spectra.

3.3. DISTRIBUTION OF PARTICULATE IRON AND ITS IMPLICATION IN PLUME TRACKING

The average Fe concentrations were calculated for the whole data set and separately for each zone of studied area (Table I). The iron concentrations of four samples contaminated by stainless steel were corrected for the contamination. In one sample only, that for station 372 (November), was stainless steel a major contaminant, in this case amounting to 61.1% of total Fe. In the August samples, stainless steel contamination amounted to 6.7 and 24.2% of total Fe in surface and bottom solids from the canal station,respectively, and 8.1% in surface solids from station 370.

The Fe concentrations of solids collected from the harbour are significantly higher ($p<0.001$, $t= 6.091$) than of those collected from the lake (Table I), a result of loadings from point sources and to a lesser degree iron regeneration from anoxic benthic sediments. Elevated concentrations of Fe (Mayer and Manning, 1990b) in suspended solids from the nearshore area of the lake are a result of resuspension induced by seasonal mixing or rough weather conditions.

In the harbour, the partitioning of Fe between the solid and aqueous phase may be described by a distribution coefficient, K_D, which is indicative of the affinity of metal for particulate matter in aquatic systems (Balistrieri and Murray, 1986). The distribution coefficient, K_D, can be expressed as:

$$K_D = \frac{(Fe_p)}{(Fe_d)} \times \frac{1}{c_p} \qquad (1)$$

where (Fe_p) and (Fe_d) represent concentrations of particulate and dissolved Fe in water, respectively, and c_p is the suspended solids concentration in water. As seen from equation (1), K_D is directly proportional to the concentration of particulate metal and indirectly proportional to concentrations of dissolved metal and particulate matter. The values of K_D depend on, e.g., the pH and the redox potential in water column. Of these, redox potential reflecting the redox conditions govern largely the distribution of Fe between particulate and aqueous phase in Hamilton Harbour. The K_D values (Table III) estimated here are similar in magnitude to those of Balistrieri and Murray (1986) and Moran and Moore (1989), obtained from adsorption studies. A sharp decrease in K_D is apparent as the concentration of dissolved Fe increases in the hypolimnion: the ~24-fold decrease in the value of K_D from August to September is far greater than the ~6.3-fold decrease in K_D between July and August at station

HH 2 (Table III). The trend in the K_D values is consistent with changes in TFP and particulate TP and BAP concentrations, and confirms the association of P and Fe-oxides.

Consistent with total Fe concentrations in solids is the distribution of Fe compounds in particulates, which differs considerably, depending on the sampling location. The contribution of industrially derived wustite in solids decreases from the harbour towards the lake. Wustite forms a significantly greater ($p<0.001$, Table IV) fraction of total iron in solids collected from the harbour than those from the lake. The Fe^{3+} and hematite fractions of total Fe are similar in harbour and in lake suspended solids. On average, wustite and hematite account for about 10.6 and 20.6%, respectively, of total Fe in suspended solids collected from the harbour (Table IV). In August, however, when hypolimnetic precipitation of dissolved Fe occurred as a result of influx of oxygenated lake water, wustite and hematite accounted only for ~1.8 and 0% of total iron (152 mg/g) in bottom solids from station HH 2. The low contributions of industrially derived Fe-compounds at this time, provides further evidence of the influx of oxygenated lake water, responsible for a temporary interuption of the hypolimnetic anoxia at the harbour station HH 2.

Generally, the surface solids are enriched in wustite and to lesser degree in hematite (Mayer and Manning, 1990b), suggesting the presence of a surface plume emanating from industrial areas. This observation is in agreement with our earlier findigs (Mayer and Manning, 1990a).

Our sampling in July and August revealed a visible, sharply-defined surface plume of turbid Harbour water entering Lake Ontario via Burlington Canal. This visual observation was confirmed by higher than background conductivity readings within the area of the plume.

In July, a plume of a semicircle of radius ~500 m from the mouth of the harbour, extending ~3/4 km further in the north-northeasterly direction, was observed. Although on most occasions the proportion of wustite in lake solids was barely measurable (0 to 4%), between 6.0 and 7.0% of total Fe was present as wustite in lake solids in July (Figure 4a). In August, the plume followed the shore 3/4 km southward and a shorter distance northward (Figure 4b). The proportion of total Fe in wustite form at this time was between 6.8 and 7.8%. Although no visible plume was observed in November, the presence of wustite and high turbidity of water at ~500 m directly from the mouth of the harbour (station 370) confirms the presence of harbour water, probably a result of two days of south-westerly winds which forced the flow of harbour water to the lake. In November, wustite accounted for about 14 and 5% of the total Fe concentrations in surface and bottom suspended solids collected from station 370, respectively. This is comparable to the proportion of wustite measured in suspended solids from sites adjacent to the industrial areas in the harbour (Mayer and Manning 1990b). The relative proportions of anthropogenic Fe compounds in suspended solids within the plume are not significantly different from those of the canal (Figure 4a, 4b).

The following calculation permits the quantifying of trends in a plume tracking parameter, wustite:

$$\Delta W = \frac{(W - W_b)}{(W_{HH} - W_b)} \qquad (2)$$

where ΔW=elevation above the background, W=wustite proportion of the total Fe in solids from any location, W_b=background wustite proportion of Fe in natural uncontaminated suspended solids and W_{HH}=average wustite proportion of total Fe in harbour suspended solids. Since W_b=0, the equation (2) assumes the form:

$$\Delta W = \frac{W}{W_{HH}} \qquad (3)$$

The results of this calculation (Table V) show that relative elevation (100 x ΔW) of plume tracking parameter, wustite, can be at the time of the plume in the lake as much as 73% of harbour wustite proportion. Canal values (Table V) suggest that a significant proportion of industrially derived wustite makes it to the canal and is eventually exported into the lake.

Overall, the Mössbauer data (Mayer and Manning, 1990b) show decreasing concentrations of wustite and hematite in solids with the increasing distance from the mouth of the harbour, suggesting a good dilution. The dissipation of the turbulent energy of the Burlington Canal discharge is probably responsible for the effective dilution observed in the nearshore area of western Lake Ontario (Barica et al., 1988; Barica, 1989; MOE, 1986).

The loadings (L) of particulate iron from the harbour to the lake via the Burlington Canal may be calculated according to following expression:

$$L = A \times v \times c \qquad (4)$$

where c is the product of the concentrations of suspended solids and iron in corresponding layer of the canal, A is the cross-sectional area of the layer determined as the product of the layer width and layer depth ($A = w \times d$), and v is the velocity of the flow. Since no significant differences were found between the midcanal currents and those within 2 m of the wall (Barica et al., 1988), the whole canal width (89.3 m) is used as the width of the layer. Current velocities measured by Barica and Vieira (1988) and Technical Operations (unpublished data) were used to calculate the velocities of the flow. The flow of water out to the lake is assigned a positive sign, while flow of lake water into the harbour is assigned a negative sign. The net load is estimated as a sum of the layer loads (MOE, 1986) taking signs into consideration. A positive value of net loading indicates export of harbour material into Lake Ontario. Stratified flow in and out of the harbour was used in calculations for the stratified period of the year (June to September). Loadings during the remaining part of the year were calculated assuming unidirectional (plug) flow in and out of the harbour, using MOE (1986) estimates of flows during that period of the year. Average values of TSS and Fe concentrations in harbour and lake solids, respectively, were used in conjunction with flow values for calculations of loads by the plug flow. Using these calculations, the estimated net load of particulate Fe from harbour to the lake is 266×10^3 kg/yr. This value is higher than the Fe loads of 74×10^3 and 194×10^3 kg/yr, estimated by MOE in 1982 and 1979, respectively. The load calculated here is, however, about 3.7 times lower than that estimated in our earlier study (978×10^3 kg/yr, Mayer and Manning, 1990a), using the available sedimentation rates (410 g m^{-2} yr^{-1}, Nriagu et al., 1983) and loadings of Fe to the Harbour from industrial and municipal sources (RAP, 1988). The difference is probably due to uncertainties in the geochronology of Hamilton Harbour sediments, reflecting frequent perturbation of natural sedimentation processes by dredging and spoils disposal (Nriagu et al.,1983; M. Johnson, private commun.). In 1987, estimated (RAP, 1988) iron loadings to the Harbour from industrial and municipal sources were ~1460×10^3 kg/yr. Comparison of this value with the above calculated loads of Fe to the lake shows that ~18% of the total Fe load from the point sources is exported to the lake, the remainder (~82%) being retained in Harbour sediments. The beneficial effects of high Fe concentrations in the sediments are clear from phosphorus and heavy metal geochemistry. The load of Fe to Lake Ontario from Hamilton Harbour is, however, low when compared to the load of 79.4×10^6 kg/yr carried by the Niagara River (Kuntz, 1984).

3.4. IRON-PHOSPHORUS INTERACTION

The close relation between iron and phosphorus in benthic sediments has been well documented. In particular, x-ray amorphous ferric oxide has the greatest potential for interaction with phosphorus. Data from our earlier study on Hamilton Harbour (Mayer and Manning, 1990a) showed a good correlation ($r=0.74$, $n=12$) between Fe^{3+} and non-apatite inorganic P (NAI-P) concentrations for samples collected in April 1986, whereas a poor correlation ($r=0.16$, $n=12$) was observed for data from September 1986. The 1986 data set contained only the harbour Fe^{3+} and NAI-P concentrations. Assuming that the NAI-P concentration is dependent on the total Fe concentration and that P is associated mainly with Fe^{3+} and Fe^{2+} rather than with industrially derived forms of Fe (wustite and hematite) which crystalized in the absence of phosphate, the following equation can be written (after Manning 1989):

$$(\text{NAI-P}) = k_1(Fe^{3+}) + k_2(Fe^{2+}) \tag{5}$$

or

$$\frac{(\text{NAI-P})}{(Fe^{2+})} = k_1 \frac{(Fe^{3+})}{(Fe^{2+})} + k_2 \tag{6}$$

where (Fe^{3+}), (Fe^{2+}) and (NAI-P) represent the concentrations of ferric and ferrous iron and non-apatite inorganic P, respectively and k_1 and k_2 are constants. The plot of NAI-P/Fe^{2+} against Fe^{3+}/Fe^{2+} (Figure 5a) reveals a highly significant ($p<0.001$) correlation with $r=0.915$ ($n=24$). The outlier point corresponds to hypolimnetic reprecipitation of dissolved Fe, originating from the anoxic release from benthic sediments. The equation (6) provides a better fit for all the data from the harbour than just the simple NAI-P and Fe^{3+} relation. The calculated values of k_1

and k_2 are 0.0807 and 0.0919, respectively.

The 1987 data set contains data on the bioavailable P (BAP) and Fe^{3+} from the harbour, canal and from the western part of Lake Ontario. Bioavailable P, estimated by the NaOH/NaCl extraction, is the most readily available form of P (DePinto et al., 1981; Young et al., 1985) and accounts for ~70% of the NAI-P (Williams et al., 1980; Mayer, 1984). If the 1987 data set is examined, a similar linear relation is found between BAP/Fe^{2+} and Fe^{3+}/Fe^{2+} (Figure 5b) with a statistically significant ($p<0.001$) correlation coefficient, $r=0.653$ ($n=67$). The slope of the line k_1 (0.0711) is similar to that for NAI-P/Fe^{2+} against Fe^{3+}/Fe^{2+} (0.0807 and 0.0711, respectively), confirming similar association of BAP and NAI-P with Fe^{3+}, independent of the sampling time.

3.5. HEAVY METALS IN WATER AND IN SUSPENDED SOLIDS

In the past, loadings of heavy metals to Hamilton Harbour from point sources were high. Reductions in loadings of copper, iron, zinc, chromium, cadmium, and lead since 1977 (RAP, 1988) have resulted in a decline in metal concentrations in harbour water. Excluding Mn and Fe, highly significant differences ($p<0.001$) were found only between concentrations of Zn in harbour and in lake water (Table VI). The other mean metal concentrations were similar for both harbour and lake water. The concentrations of heavy metals, other than Fe, in harbour water (Mayer and Manning, 1990) meet the Provincial Water Quality Objectives on most occasions. On a few occasions, only, did Cu and Cd (Mayer and Manning, 1990b) exceed the Objectives. The frequency of exceedences of Fe concentrations in water was higher due to loadings from point sources and anoxic sediment regeneration. Concentrations of metals in harbour suspended solids were, however, significantly higher (Cu, Cd $p<0.05$ and Pb, Zn $p<0.001$) than those from the lake (Table VII). This is probably due to differences in origin and consequent differences in physico-chemical characteristics of harbour and lake particles. Most of the metals have a high affinity for particulate matter and concentrate on the surfaces of the particles.

In water, highly significant correlations ($p<0.001$) were observed only between Fe and Mn, Pb, Zn and between Zn and Pb (Table VIII). In suspended solids, however, strong intercorrelations were observed between the majority of the metals (Table IX). Heavy metals such as Cd, Pb and Zn are known to adsorb strongly onto iron oxides (Jenne, 1968; 1977; Tessier et al., 1980; Lion et al., 1982), hence the high correlation coefficients. Adsorption of the heavy metals onto Fe-oxides reduces the soluble metals concentrations in water, and hence reduces their bioavailability. Thus, the high Fe concentrations in the suspended solids, are beneficial in scavenging of the heavy metals from the harbour water column.

Although sufficient information is available on metal contaminant loadings to the harbour, the information on the export of metal contaminants from harbour to the lake is scarce. The loadings of metals from the harbour to the lake were calculated using the equation (4). Calculations were carried out similarly as for Fe loads, using the stratified flow in and out of the harbour for the stratified period of the year (June to

September) and unidirectional flow for remaining part of the year. Suspended solids and respective metal concentrations in corresponding layers of the canal were used for load calculations during the stratified conditions. For the remainder of the year, average values of harbour and lake suspended solids and metal concentrations were used in conjunction with the flow data (Barica et al., 1988).

The calculated loadings to the lake are 9.33×10^3 kg/yr Zn, 1356 kg/yr Pb, 273 kg/yr Cu and 8.7 kg/yr Cd. The calculated Zn loadings to the lake compare favourably with the 9.0×10^3 kg/yr, estimated by MOE (1986). A discrepancy appears in Cu loadings; the MOE (1986) data indicate net loadings of Cu from the lake to the harbour. A comparison of the above calculated metal export to the lake with metal loadings to the harbour (RAP, 1989) suggest that most of the metals are retained in Hamilton Harbour sediments. The metal loadings from the harbour to the lake, obtained in this study, are low when compared to loadings from Niagara River (Kuntz, 1984).

In summary, it can be stated that industrially derived Fe compounds, particularly wustite, are reliable tracers of the plume of harbour water in Lake Ontario. On two occasions, our sampling revealed a surface plume of harbour water, extending ~3/4 km from the mouth of the harbour into the lake. The excursions of harbour water into the lake are responsible for export of particle associated metals from the harbour. Even though the concentrations of some metals in harbour suspended solids are high, the relative contribution of Hamilton Harbour to the total metal load to Lake Ontario is low, when compared to loads from the Niagara River. Lake-harbour water exchange introduces oxygen-rich water to much of the deep areas of the harbour, breaking up, temporarily, hypolimnetic anoxia, thus hinderimg the P regeneration from benthic sediments. These infusions of lake water along with high Fe concentrations in benthic sediments of the harbour are, therefore, beneficial to phosphorus cycling in Hamilton Harbour.

Acknowledgment

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LIST OF FIGURES

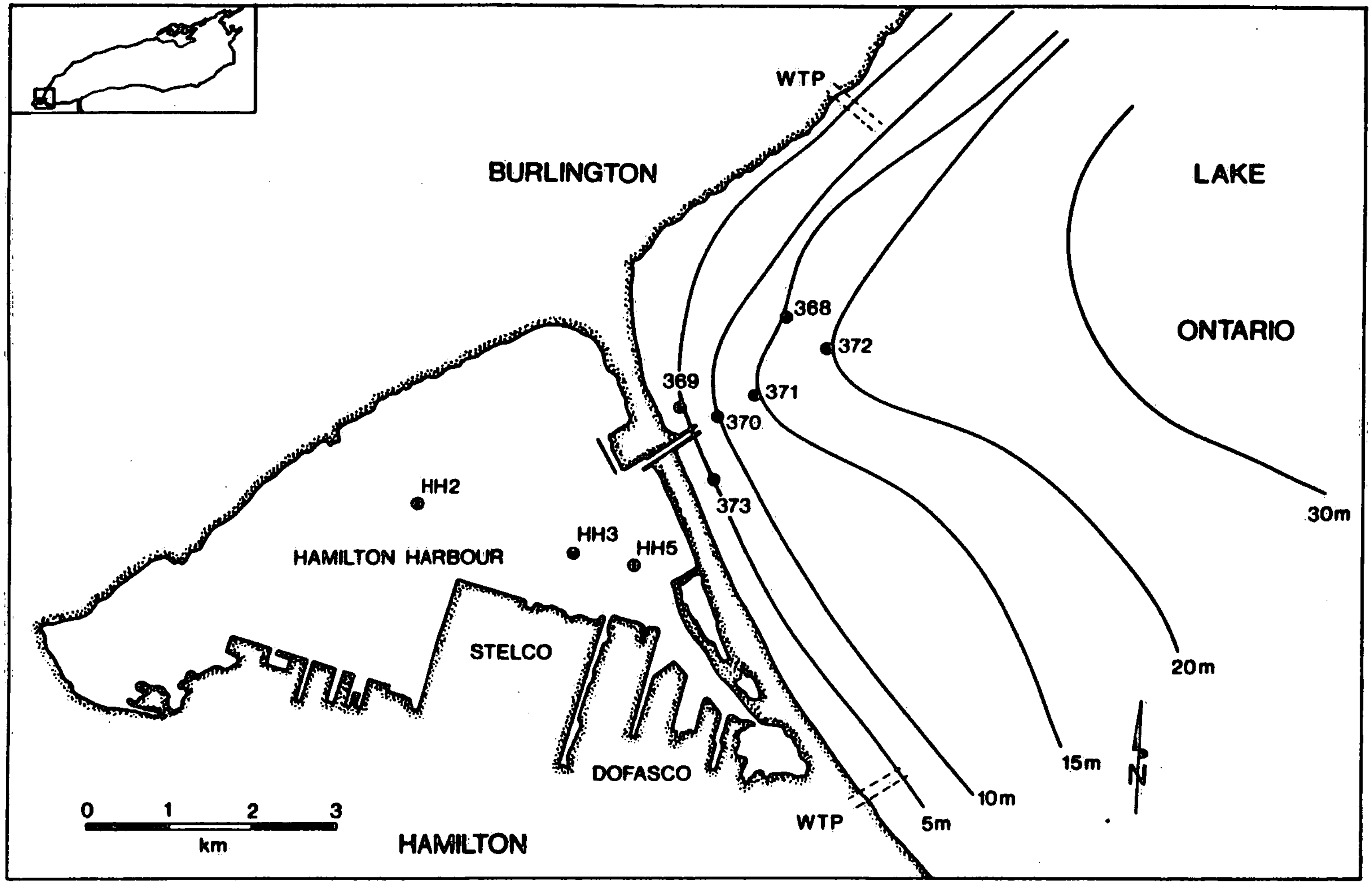
BURLINGTON
LAKE
ONTARIO
WTP
368
372
369
371
370
373
HH2
HH3
HH5
HAMILTON HARBOUR
STELCO
DOFASCO
30m
20m
15m
10m
5m
WTP
N
0
1
2
3
km
HAMILTON

Fig. 1.

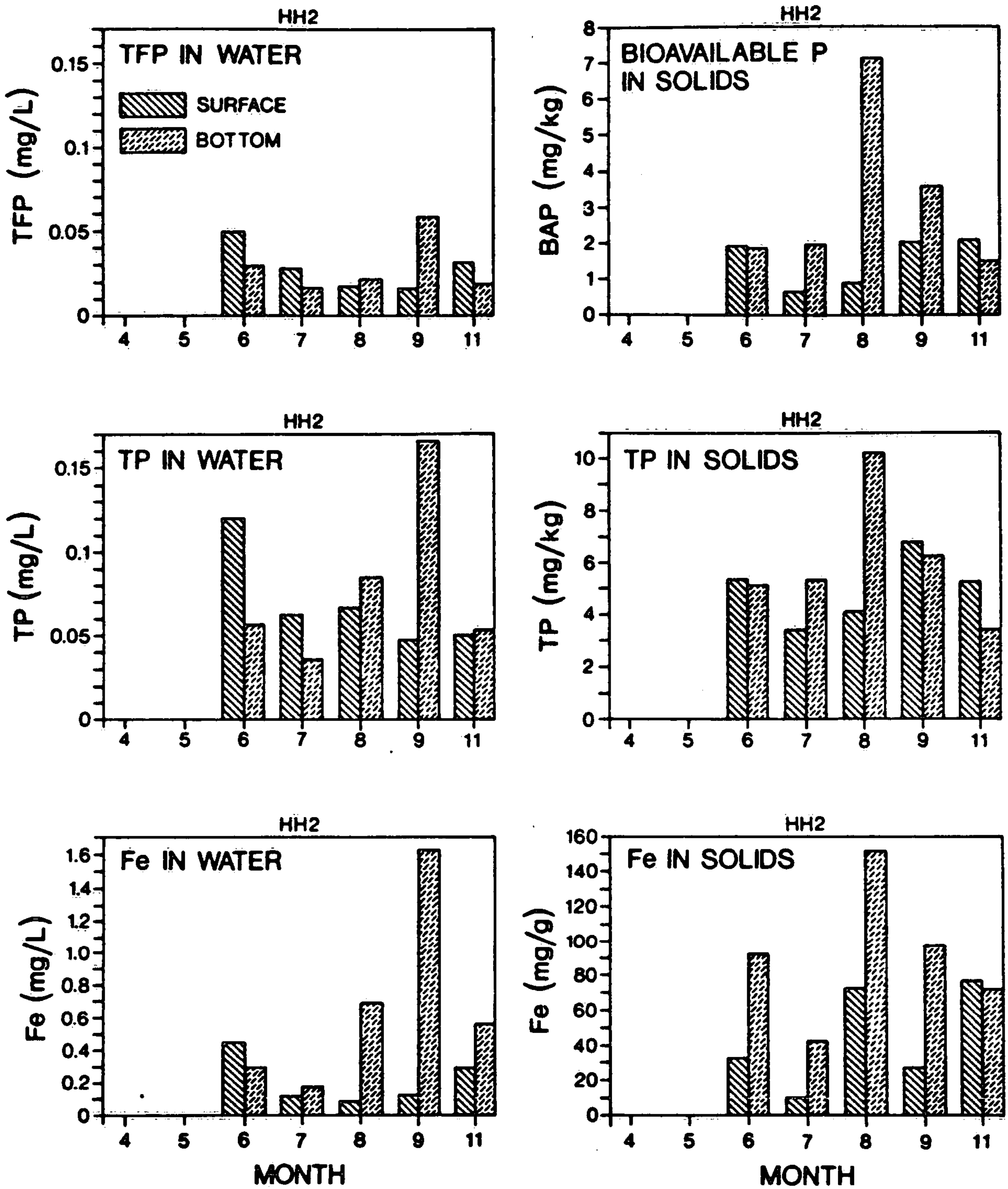
HH2
TFP IN WATER
SURFACE
BOTTOM
TFP (mg/L)
0.15
0.1
0.05
0
4
5
6
7
8
9
11
HH2
BIOAVAILABLE P
IN SOLIDS
BAP (mg/kg)
HH2
TP IN WATER
TP (mg/L)
HH2
TP IN SOLIDS
TP (mg/kg)
HH2
Fe IN WATER
Fe (mg/L)
MONTH
HH2
Fe IN SOLIDS
Fe (mg/g)
MONTH

Fig. 2.

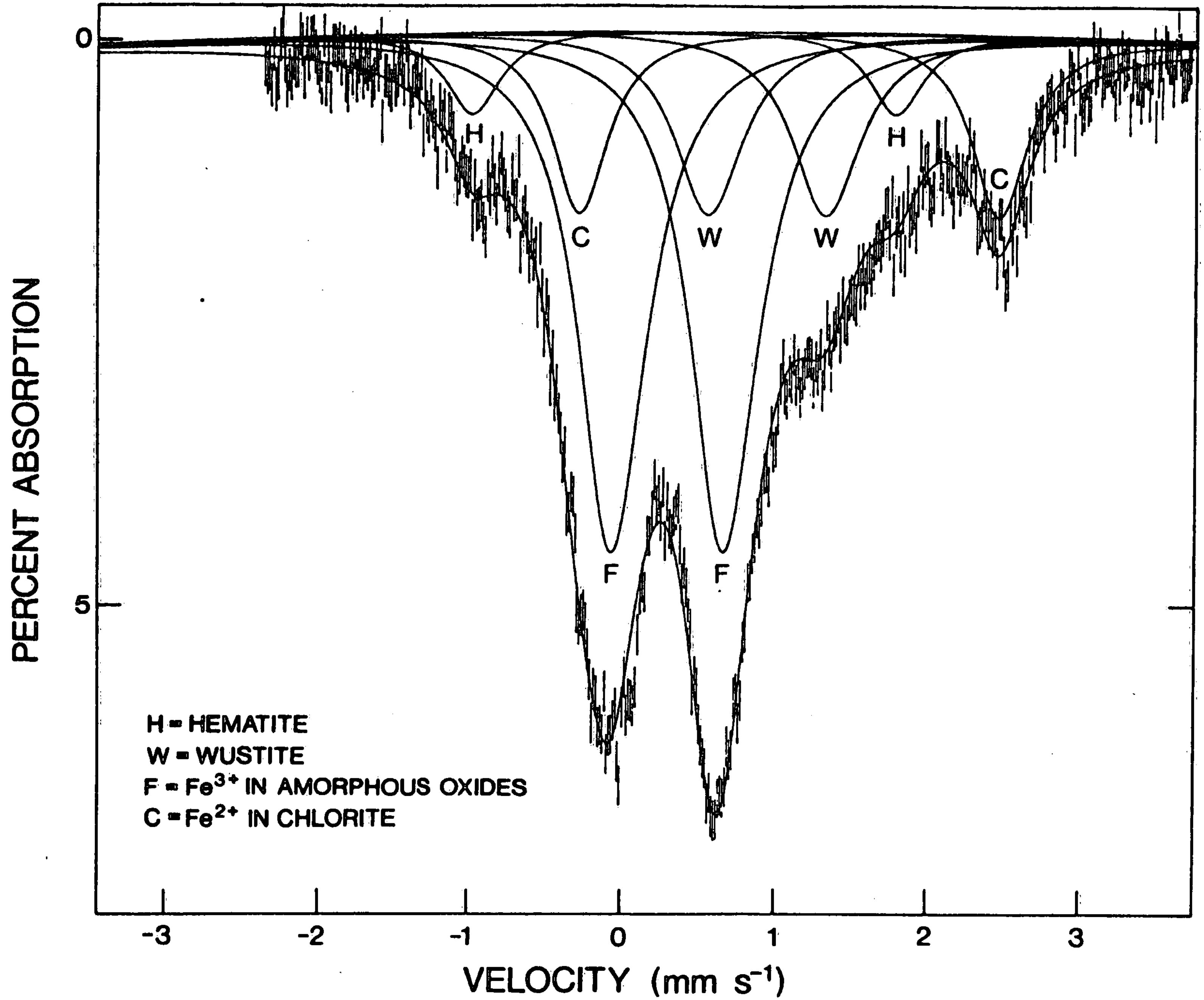
PERCENT ABSORPTION
0
5
H
C
W
W
H
C
F
F
H = HEMATITE
W = WUSTITE
F = Fe3+ IN AMORPHOUS OXIDES
C = Fe2+ IN CHLORITE
-3
-2
-1
0
1
2
3
VELOCITY (mm s-1)

Fig. 3.

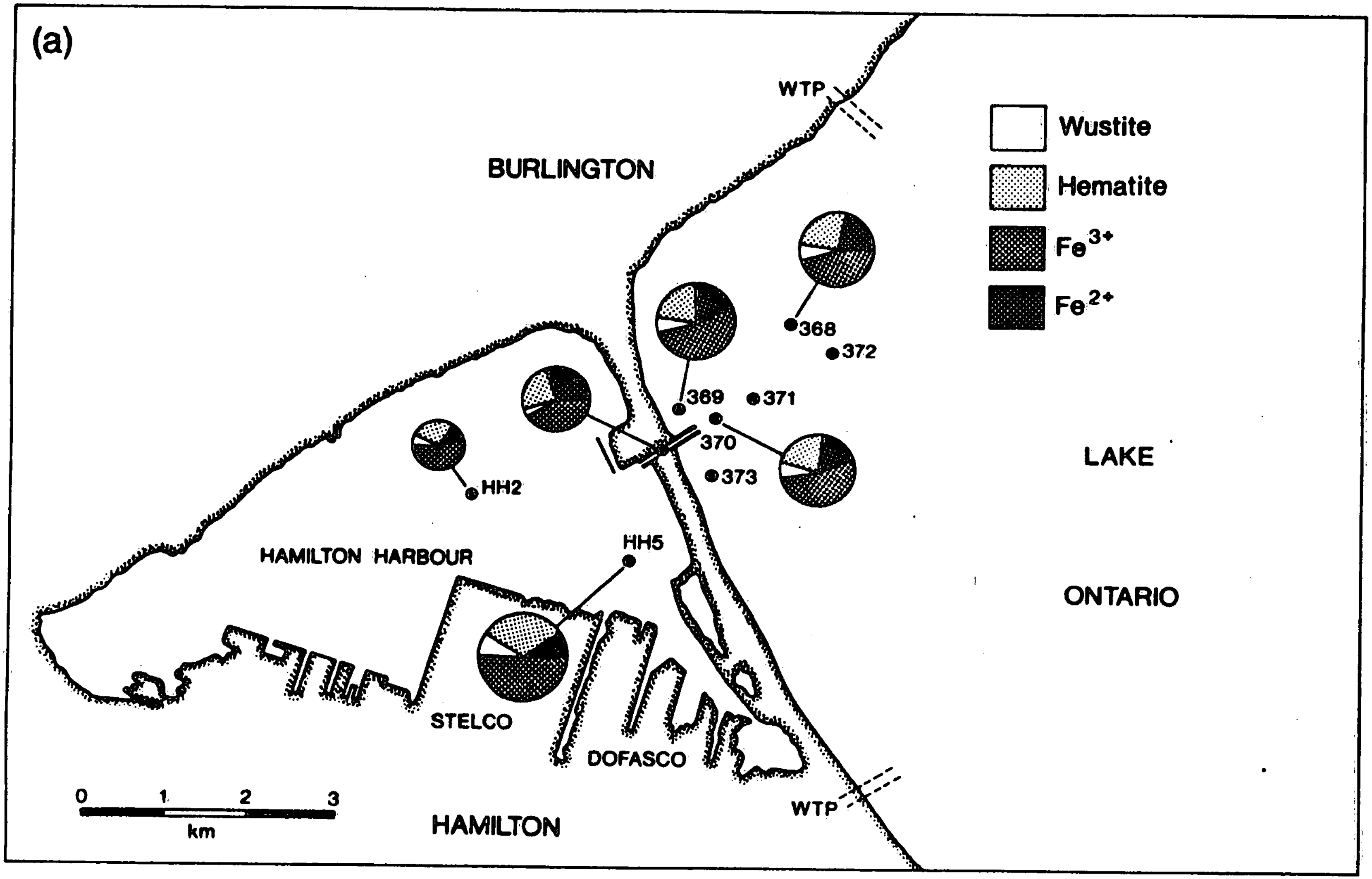
(a)
WTP
BURLINGTON
Wustite
Hematite
Fe3+
Fe2+
368
372
369
371
370
373
HH2
LAKE
HAMILTON HARBOUR
HH5
ONTARIO
STELCO
DOFASCO
0
1
2
3
km
WTP
HAMILTON

Fig. 4a

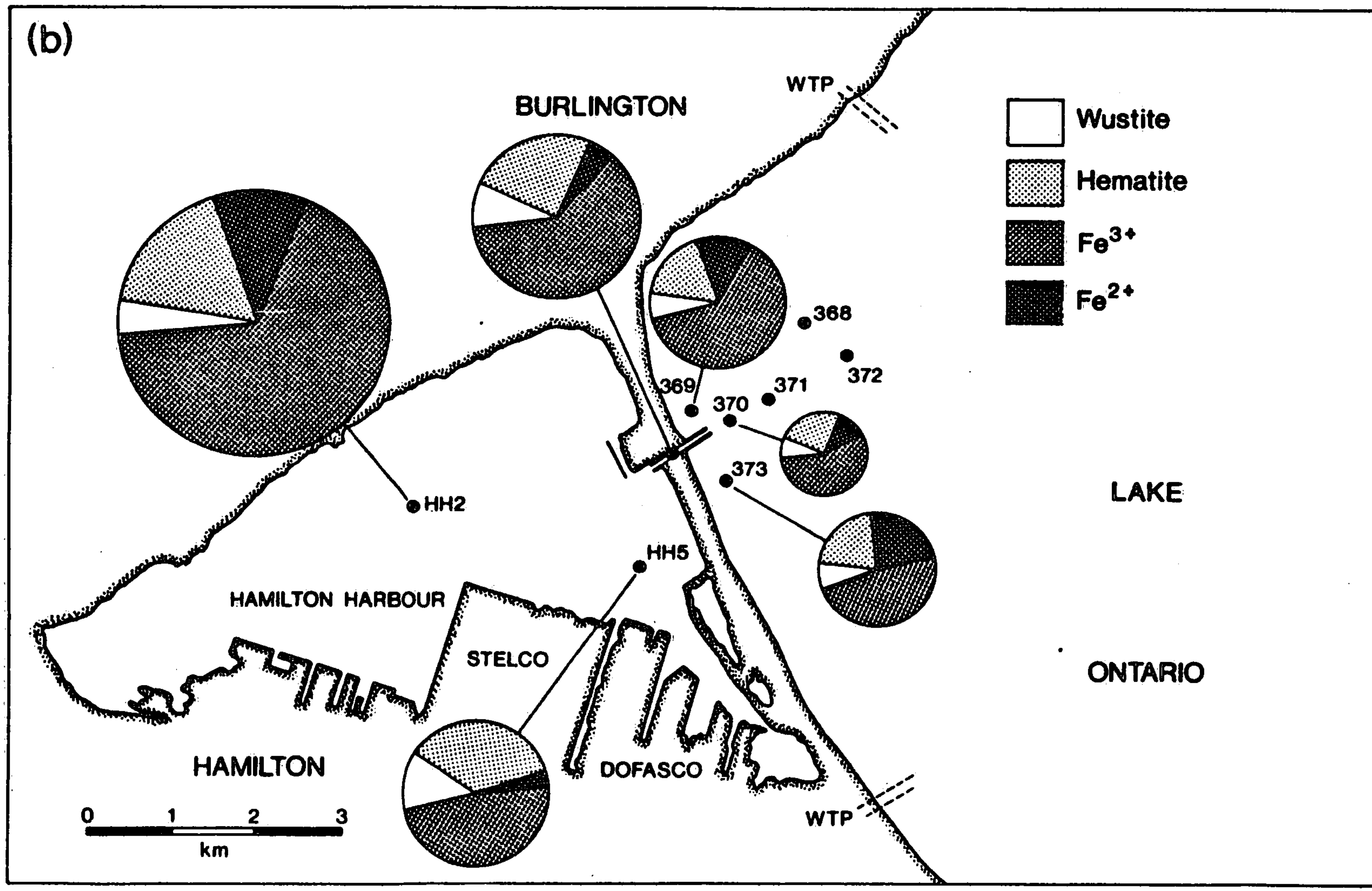
(b)
BURLINGTON
WTP
Wustite
Hematite
Fe3+
Fe2+
368
369
370
371
372
373
HH2
HH5
LAKE
ONTARIO
HAMILTON HARBOUR
STELCO
DOFASCO
HAMILTON
WTP
0
1
2
3
km

Fig 4

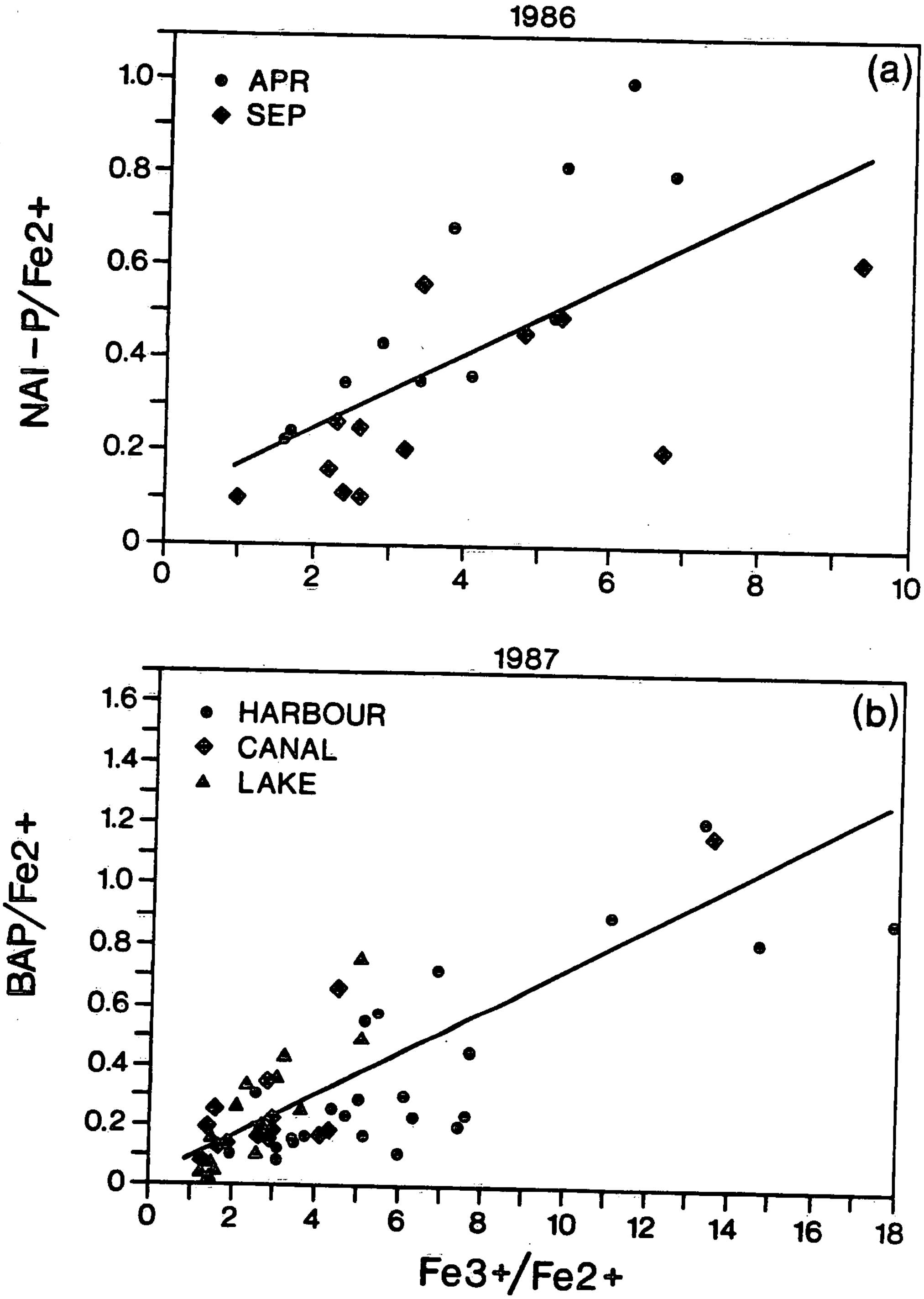
1986
(a)
APR
SEP
NAI-P/Fe2+
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
1987
(b)
HARBOUR
CANAL
LAKE
BAP/Fe2+
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
16
18
Fe3+/Fe2+

Fig. 5.

TABLE I

Mean concentrations of phosphorus and iron in water and in suspended solids. Numbers in parentheses are standard errors of means and n is number of cases.

	solids			water		
	BAP mg/kg	TP mg/kg	Fe mg/g	TP mg/L	TFP mg/L	Fe mg/L
LAKE n=23	871 (384)	3294 (1278)	25.0 (8.0)	0.029 (0.015)	0.012 (0.006)	0.124 (0.097)
HARBOUR n=30	2053 (1116)	5303 (1299)	73.6 (37.5)	0.072 (0.030)	0.034 (0.018)	0.432 (0.336)
CANAL n=14	1356 (441)	4424 (1082)	37.7 (18.2)	0.056 (0.025)	0.028 (0.016)	0.228 (0.105)
CANAL (1m) n=7	1414 (503)	4775 (1220)	40.2 (23.3)	0.068 (0.026)	0.034 (0.017)	0.265 (0.112)
CANAL (8m) n=7	1297 (360)	4073 (780)	35.2 (10.4)	0.043 (0.016)	0.023 (0.012)	0.191 (0.082)

TABLE II

Average values of Mossbauer parameters. Numbers in parentheses are standard errors of means and n is number of cases.

Fe compound	IS (mm/s)	QS (mm/s)	HW (mm/s)
Fe^{2+}, chlorite n=65	1.11 (0.02)	2.63 (0.04)	0.38 (0.03)
Fe^{3+}, amorphous n=65	0.36 (0.01)	0.69 (0.05)	0.51 (0.04)
wustite, $Fe_{1-x}O$ n=64	0.95 (0.05)	0.74 (0.05)	0.46 (0.05)
hematite, Fe_2O_3 n=64	0.45 (0.02)	2.61 (0.09)	0.36 (0.02)

TABLE III

Values of iron distribution coefficient, K_D calculated from dissolved and particulate Fe concentrations in Hamilton Harbour.

station depth	month	K_D(Fe) $\times 10^6$ mL/g
HH2 (1m)	6	4.02
HH2 (1m)	7	1.82
HH2 (1m)	8	1.40
HH2 (1m)	9	13.07
HH2 (21m)	6	2.86
HH2 (21m)	7	32.25
HH2 (21m)	8	5.12
HH2 (21m)	9	0.21
HH5 (1m)	6	10.63
HH5 (1m)	7	2.90
HH5 (1m)	8	7.09
HH5 (1m)	9	9.97
HH5 (20m)	6	8.83
HH5 (20m)	7	7.36
HH5 (20m)	8	10.76
HH5 (20m)	9	19.90

TABLE IV

Relative contributions of iron species to total Fe in suspended solids. Numbers in parentheses are standard errors of means and n is number of cases.

	Fe2+ %	Fe3+ %	wustite %	hematite %
LAKE n=23	27.5 (9.3)	51.0 (4.0)	4.0 (3.5)	17.5 (7.5)
HARBOUR n=30	12.2 (5.0)	56.6 (12.1)	10.6 (5.1)	20.6 (9.8)
CANAL n=14	18.1 (7.8)	47.3 (5.4)	9.7 (4.3)	24.6 (2.6)
CANAL (1m) n=7	17.5 (9.9)	47.4 (6.5)	10.2 (4.8)	24.5 (3.2)
CANAL (8m) n=7	18.8 (4.8)	47.2 (4.0)	9.2 (3.6)	24.8 (1.9)

TABLE V

Elevation in wustite fraction of the total Fe in suspended solids from Hamilton Harbour and western Lake Ontario. (N/A=not applicable)

station	plume	ΔW	100ΔW %
CANAL (average)	N/A	0.91	91
CANAL (1m, average)	N/A	0.96	96
CANAL (8m, average)	N/A	0.86	86
LAKE (average)	N/A	0.38	38
369 (1m, April)	no	0.06	6
368 (1m, July)	yes	0.66	66
369 (1m, July)	yes	0.57	57
370 (1m, July)	yes	0.61	61
369 (1m, August)	yes	0.64	64
370 (1m, August)	yes	0.73	73
373 (1m, August)	yes	0.70	70

TABLE VI

Mean concentrations of total heavy metals in water. Numbers in parentheses are standard errors of means and n is number of cases.

	Mn mg/L	Cd mg/L	Cu mg/L	Pb mg/L	Zn mg/L
LAKE n=23	0.009 (0.007)	0.0001 (0.000)	0.0069 (0.008)	0.001 (0.000)	0.0026 (0.002)
HARBOUR n=30	0.177 (0.280)	0.0002 (0.000)	0.0047 (0.006)	0.002 (0.001)	0.0138 (0.005)
CANAL n=14	0.031 (0.017)	0.0002 (0.000)	0.004 (0.003)	0.0016 (0.001)	0.0088 (0.004)
CANAL (1m) n=7	0.036 (0.016)	0.0002 (0.000)	0.0035 (0.002)	0.0018 (0.001)	0.0103 (0.004)
CANAL (8m) n=7	0.026 (0.015)	0.0001 (0.000)	0.0045 (0.004)	0.0013 (0.001)	0.0072 (0.004)

TABLE VII

Mean concentration of heavy metals in suspended solids. Numbers in parentheses are standard errors of means and n is number of cases.

	Mn mg/g	Cd mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg
LAKE n=21	1.4 (0.8)	1.79 (2.16)	79 (57)	238 (61)	464 (256)
HARBOUR n=30	7.1 (8.1)	3.90 (3.31)	138 (78)	404 (109)	1979 (737)
CANAL n=12	4.5 (3.1)	2.35 (2.35)	88 (47)	284 (77)	1045 (688)
CANAL (1m) n=6	4.6 (3.2)	2.07 (2.53)	66 (37)	297 (94)	1158 (770)
CANAL (8m) n=6	4.4 (3.0)	2.63 (2.12)	110 (45)	271 (53)	931 (574)

TABLE VIII

Correlation coefficient matrix for heavy metals in water.

	Fe	Mn	Cd	Cu	Pb	Zn
Fe						
Mn	0.796					
Cd	0.071	0.002				
Cu	0.044	0.135	0.286			
Pb	0.635	0.287	0.113	0.022		
Zn	0.713	0.362	0.170	0.136	0.731	

n=67, f=65

TABLE IX

Correlation coefficient matrix for heavy metals in solids.

	Fe	Mn	Cd	Cu	Pb	Zn
Fe						
Mn	0.190					
Cd	0.520	0.387				
Cu	0.445	0.277	0.678			
Pb	0.718	0.592	0.746	0.628		
Zn	0.824	0.441	0.678	0.543	0.882	

n=62, f=60

APPENDIX

CONCENTRATIONS OF TOTAL SUSPENDED SOLIDS (TSS), PHOSPHORUS AND IRON IN WATER

station	month	TSS mg/L	TP mg/L	TFP mg/L	Fe mg/L
HH 2 (1m)	6	7.4	0.1202	0.0502	0.458
HH 2 (1m)	7	7.6	0.0626	0.0280	0.120
HH 2 (1m)	8	9.8	0.0668	0.0171	0.090
HH 2 (1m)	9	2.2	0.0473	0.0157	0.125
HH 2 (1m)	11	2.4	0.0500	0.0313	0.297
HH 2 (21m)	6	2.0	0.0568	0.0298	0.304
HH 2 (21m)	7	1.4	0.0366	0.0168	0.180
HH 2 (21m)	8	3.2	0.0852	0.0218	0.693
HH 2 (21m)	9	11.2	0.1664	0.0584	1.630
HH 2 (21m)	11	8.8	0.0528	0.0193	0.567
HH 3 (1m)	4	7.0	0.0818	0.0413	0.792
HH 3 (1m)	6	5.8	0.0926	0.0480	0.350
HH 3 (1m)	9	3.6	0.0703	0.0218	0.336
HH 3 (1m)	11	3.0	0.0555	0.0357	0.235
HH 3 (14m)	4	4.8	0.0654	0.0381	0.209
HH 3 (14m)	6	3.4	0.0537	0.0287	0.309
HH 3 (14m)	9	1.8	0.0564	0.0338	0.202
HH 3 (14m)	11	2.6	0.0498	0.0297	0.313
HH 5 (1m)	4	5.6	0.1397	0.0966	0.357
HH 5 (1m)	6	6.0	0.1117	0.0656	0.583
HH 5 (1m)	7	7.0	0.0589	0.0194	0.160
HH 5 (1m)	8	5.6	0.0861	0.0256	0.358
HH 5 (1m)	9	4.0	0.1042	0.0646	0.654
HH 5 (1m)	11	2.4	0.0610	0.0412	0.319
HH 5 (20m)	4	5.0	0.0724	0.0402	0.238
HH 5 (20m)	6	7.4	0.0546	0.0246	0.597
HH 5 (20m)	7	2.0	0.0277	0.0158	0.220
HH 5 (20m)	8	2.4	0.0525	0.0162	0.585
HH 5 (20m)	9	7.6	0.0866	0.0134	1.340
HH 5 (20m)	11	4.0	0.0459	0.0270	0.336
CANAL (1m)	4	4.4	0.0683	0.0360	0.266
CANAL (1m)	5	4.8	0.0769	0.0241	0.285
CANAL (1m)	6	6.0	0.1090	0.0694	0.342
CANAL (1m)	7	7.0	0.0536	0.0219	0.130
CANAL (1m)	8	5.2	0.0904	0.0323	0.359
CANAL (1m)	9	1.8	0.0187	0.0142	0.074
CANAL (1m)	11	3.6	0.0627	0.0400	0.398
CANAL (8m)	4	2.4	0.0715	0.0386	0.285
CANAL (8m)	5	2.4	0.0307	0.0092	0.166
CANAL (8m)	6	5.0	0.0597	0.0389	0.232
CANAL (8m)	7	3.0	0.0230	0.0090	0.091
CANAL (8m)	8	0.8	0.0292	0.0144	0.059
CANAL (8m)	9	2.0	0.0499	0.0325	0.237
CANAL (8m)	11	2.4	0.0366	0.0193	0.271
368 (1m)	7	3.8	0.0426	0.0186	0.089
369 (1m)	4	4.4	0.0267	0.0070	0.282
369 (1m)	6	5.0	0.0259	0.0091	0.292
369 (1m)	7	3.0	0.0447	0.0136	0.065
369 (1m)	8	1.8	0.0524	0.0192	0.144
370 (1m)	4	6.6	0.0241	0.0079	0.234
370 (1m)	6	3.2	0.0627	0.0222	0.109
370 (1m)	7	4.8	0.0374	0.0165	0.085
370 (1m)	8	1.8	0.0402	0.0168	0.054
370 (1m)	11	1.4	0.0240	0.0108	0.117
370 (9m)	4	9.0	0.0327	0.0094	0.404
370 (9m)	6	1.6	0.0186	0.0208	0.088
370 (9m)	11	1.2	0.0127	0.0056	0.029
371 (1m)	4	4.8	0.0211	0.0065	0.181
371 (1m)	6	0.8	0.0258	0.0116	0.037
371 (14m)	4	4.4	0.0255	0.0096	0.177
372 (1m)	4	3.2	0.0176	0.0087	0.089
372 (1m)	9	1.8	0.0192	0.0089	0.050
372 (1m)	11	0.8	0.0117	0.0051	0.017
372 (22m)	4	2.0	0.0159	0.0076	0.085
372 (22m)	9	1.2	0.0186	0.0071	0.048
372 (22m)	11	0.4	0.0106	0.0056	0.024
373 (1m)	8	3.0	0.0655	0.0259	0.143

CONCENTRATIONS OF HEAVY METALS IN WATER

station	month	Mn mg/L	Cd mg/L	Cu mg/L	Pb mg/L	Zn mg/L	Cr mg/L
HH 2 (1m)	6	0.050	<0.0001	0.0029	0.0025	0.0149	0.0015
HH 2 (1m)	7	0.015	<0.0001	0.0055	0.0011	0.0100	0.0012
HH 2 (1m)	8	0.014	<0.0001	0.0020	0.0009	0.0042	<.0003
HH 2 (1m)	9	0.018	0.0002	0.0016	0.0007	0.0079	0.0007
HH 2 (1m)	11	0.042	0.0003	0.0018	0.0008	0.0124	0.0015
HH 2 (21m)	6	0.142	0.0001	0.0013	0.0022	0.0096	0.0012
HH 2 (21m)	7	0.514	<0.0001	0.0050	0.0009	0.0083	0.0008
HH 2 (21m)	8	0.786	<0.0001	0.0012	0.0009	0.0091	0.0006
HH 2 (21m)	9	1.120	0.0003	0.0017	0.0029	0.0198	0.0024
HH 2 (21m)	11	0.124	0.0003	0.0021	0.0026	0.0192	0.0021
HH 3 (1m)	4	0.083	0.0002	0.0170	0.0035	0.0257	0.0034
HH 3 (1m)	6	0.050	0.0001	0.0029	0.0026	0.0133	0.0015
HH 3 (1m)	9	0.031	<0.0001	0.0018	0.0016	0.0168	0.0015
HH 3 (1m)	11	0.042	0.0004	0.0023	0.0011	0.0134	0.0013
HH 3 (14m)	4	0.052	<0.0001	0.0215	0.0015	0.0119	0.0016
HH 3 (14m)	6	0.156	0.0001	0.0023	0.0013	0.0090	0.0012
HH 3 (14m)	9	0.034	0.0001	0.0015	0.0019	0.0104	0.0012
HH 3 (14m)	11	0.059	0.0003	0.0030	0.0020	0.0145	0.0018
HH 5 (1m)	4	0.067	0.0001	0.0107	0.0022	0.0158	0.0011
HH 5 (1m)	6	0.059	0.0002	0.0027	0.0041	0.0223	0.0023
HH 5 (1m)	7	0.016	<0.0001	0.0046	0.0008	0.0095	0.0014
HH 5 (1m)	8	0.027	<0.0001	0.0049	0.0031	0.0133	0.0043
HH 5 (1m)	9	0.043	0.0002	0.0027	0.0030	0.0272	0.0028
HH 5 (1m)	11	0.045	0.0003	0.0021	0.0010	0.0135	0.0015
HH 5 (20m)	4	0.105	<0.0001	0.0239	0.0015	0.0121	0.0016
HH 5 (20m)	6	0.095	0.0001	0.0031	0.0038	0.0166	0.0021
HH 5 (20m)	7	0.151	<0.0001	0.0048	0.0013	0.0081	0.0014
HH 5 (20m)	8	0.375	0.0001	0.0018	0.0034	0.0119	0.0011
HH 5 (20m)	9	0.939	<0.0001	0.0019	0.0031	0.0213	0.0024
HH 5 (20m)	11	0.067	0.0003	0.0017	0.0009	0.0132	0.0018
CANAL (1m)	4	0.056	<0.0001	0.0059	0.0009	0.0103	0.0015
CANAL (1m)	5	0.047	<0.0001	0.0033	0.0035	0.0118	0.0019
CANAL (1m)	6	0.050	0.0001	0.0052	0.0028	0.0151	0.0020
CANAL (1m)	7	0.019	0.0004	0.0046	0.0019	0.0096	0.0007
CANAL (1m)	8	0.030	0.0001	0.0023	0.0016	0.0096	0.0010
CANAL (1m)	9	0.009	0.0003	0.0014	<0.0007	0.0014	0.0006
CANAL (1m)	11	0.043	0.0003	0.0020	0.0013	0.0146	0.0017
CANAL (8m)	4	0.060	<0.0001	0.0054	0.0030	0.0124	0.0017
CANAL (8m)	5	0.014	<0.0001	0.0129	0.0011	0.0045	0.0014
CANAL (8m)	6	0.019	0.0001	0.0018	0.0013	0.0080	0.0014
CANAL (8m)	7	0.011	<0.0001	0.0048	0.0013	0.0042	0.0008
CANAL (8m)	8	0.023	0.0001	0.0030	0.0007	0.0015	0.0003
CANAL (8m)	9	0.030	0.0001	0.0017	0.0009	0.0111	0.0014
CANAL (8m)	11	0.023	0.0003	0.0018	0.0007	0.0084	0.0015
368 (1m)	7	0.015	0.0001	0.0016	0.0008	0.0056	0.0008
369 (1m)	4	0.009	<0.0001	0.0035	0.0014	0.0014	0.0010
369 (1m)	6	0.016	0.0001	0.0027	0.0011	0.0023	0.0013
369 (1m)	7	0.009	0.0002	0.0032	0.0014	0.0067	0.0006
369 (1m)	8	0.023	<0.0001	0.0052	0.0016	0.0055	0.0007
370 (1m)	4	0.006	<0.0001	0.0224	0.0012	0.0014	0.0007
370 (1m)	6	0.011	<0.0001	0.0037	0.0016	0.0044	0.0015
370 (1m)	7	0.013	<0.0001	0.0027	0.0010	0.0049	0.0008
370 (1m)	8	0.020	<0.0001	0.0017	<0.0007	0.0024	0.0007
370 (1m)	11	0.009	0.0003	0.0019	<0.0007	0.0058	0.0012
370 (9m)	4	0.014	<0.0001	0.0268	0.0012	0.0018	0.0011
370 (9m)	6	0.010	<0.0001	0.0019	0.0015	0.0020	0.0012
370 (9m)	11	<0.002	0.0003	0.0014	<0.0007	0.0019	0.0007
371 (1m)	4	0.005	<0.0001	0.0086	0.0009	0.0003	0.0007
371 (1m)	6	0.003	<0.0001	0.0034	0.0012	0.0006	0.0007
371 (14m)	4	0.003	<0.0001	0.0253	0.0011	0.0013	0.0010
372 (1m)	4	0.002	<0.0001	0.0177	0.0010	0.0006	0.0008
372 (1m)	9	<0.002	0.0002	0.0014	<0.0007	0.0014	0.0006
372 (1m)	11	<0.002	0.0003	0.0013	<0.0007	0.0009	0.0006
372 (22m)	4	0.004	0.0001	0.0177	0.0008	0.0003	0.0006
372 (22m)	9	0.003	0.0002	0.0014	<0.0007	0.0012	0.0006
372 (22m)	11	<0.002	0.0003	0.0012	<0.0007	0.0009	0.0007
373 (1m)	8	0.026	0.0001	0.0027	0.0007	0.0057	0.0014

CONCENTRATIONS OF TOTAL AND ORGANIC C, BAP AND TOTAL P IN SUSPENDED SOLIDS

STATION DEPTH	MONTH	Ctotal %	Corg %	BAP mg/kg	TP mg/kg
HH 2 (1m)	6	21.2	21.2	1940	5368
HH 2 (1m)	7	33.4	20.7	648	3480
HH 2 (1m)	8	26.5	22.6	914	4114
HH 2 (1m)	9	31.4	31.8	1995	6790
HH 2 (1m)	11	18.5	17.3	2107	5267
HH 2 (21m)	6	11.2	9.6	1866	5129
HH 2 (21m)	7	15.7	13.9	1952	5360
HH 2 (21m)	8	12.5	8.8	7139	10235
HH 2 (21m)	9	14.2	13.5	3571	6269
HH 2 (21m)	11	13.4	11.5	1512	3458
HH 3 (1m)	4	15.4	13.9	1379	4402
HH 3 (1m)	6	17.8	15.1	1468	4845
HH 3 (1m)	9	29.2	30.3	2493	6671
HH 3 (1m)	11	18.5	17.1	1940	5034
HH 3 (14m)	4	13.5	11.3	1429	4766
HH 3 (14m)	6	12.1	10.9	2426	6868
HH 3 (14m)	9	20.4	19.8	2363	6061
HH 3 (14m)	11	15.4	13.0	1862	4381
HH 5 (1m)	4	14.1	12.4	1912	5232
HH 5 (1m)	6	17.2	16.1	1884	5220
HH 5 (1m)	7	21.3	12.5	1023	4901
HH 5 (1m)	8	26.7	21.2	1272	4956
HH 5 (1m)	9	30.9	29.5	1770	5804
HH 5 (1m)	11	16.8	15.6	1957	4957
HH 5 (20m)	4	14.3	12.0	1428	4845
HH 5 (20m)	6	11.0	8.1	1677	3857
HH 5 (20m)	7	6.7	11.6	2140	4147
HH 5 (20m)	8	12.0	8.6	3027	6093
HH 5 (20m)	9	13.3	12.8	2766	6497
HH 5 (20m)	11	14.4	12.6	1732	4081
CANAL (1m)	4	14.2	12.5	1204	4255
CANAL (1m)	5	18.9	19.5	2044	6379
CANAL (1m)	6	18.8	14.6	1567	4823
CANAL (1m)	7	20.4	22.1	794	4092
CANAL (1m)	8	27.6	17.1	1827	6585
CANAL (1m)	9	18.1		647	2847
CANAL (1m)	11	16.8	14.5	1817	4445
CANAL (8m)	4	13.5	19.1	1265	4561
CANAL (8m)	5	20.2	15.6	1718	4311
CANAL (8m)	6	8.8	13.2	1337	4152
CANAL (8m)	7	16.9	11.3	514	2311
CANAL (8m)	8	18.1	10.4	1258	4246
CANAL (8m)	9	20.8	19.1	1630	4976
CANAL (8m)	11	18.2		1359	3957
368 (1m)	7	21.1	13.3	1012	4042
369 (1m)	4	14.0	11.0	375	1686
369 (1m)	6	10.1	7.3	504	1972
369 (1m)	7	21.4	14.0	1003	3765
369 (1m)	8	23.4	14.2	1685	5907
370 (1m)	4	22.4	9.9	393	1891
370 (1m)	6	16.1	17.1	1328	5131
370 (1m)	7	25.5	15.6	1144	4639
370 (1m)	8	24.5	13.7	1462	5907
370 (1m)	11	19.8	18.0	1503	4396
370 (9m)	4	9.3	7.6	391	1800
370 (9m)	6	13.8	6.4	815	3207
370 (9m)	11	19.3	17.2	662	2897
371 (1m)	4	10.9	9.2	469	2062
371 (1m)	6	18.4	14.5	827	3251
371 (14m)	4	10.4	9.8	466	2119
372 (1m)	4	13.5	11.1	609	2505
372 (1m)	9	16.1	12.9	674	2902
372 (1m)	11	18.3	16.4	691	2254
372 (22m)	4	13.2	9.4	1017	2675
372 (22m)	9	15.8	12.2	707	2830
372 (22m)	11	18.2	16.3	919	3012
373 (1m)	8	19.9	11.2	1375	4912

RELATIVE CONCENTRATION OF DIFFERENT Fe FORMS IN SUSPENDED SOLIDS

Station Depth	Month	Fe^{2+} %	Fe^{3+} %	Wustite %	Hematite %
HH 2 (1m)	6	19.0	49.2	7.4	24.4
HH 2 (1m)	7	10.7	55.3	5.6	28.4
HH 2 (1m)	8	11.2	67.6	4.2	17.0
HH 2 (1m)	9	9.8	67.2	7.8	15.2
HH 2 (1m)	11	8.9	54.8	7.6	28.7
HH 2 (21m)	6	12.0	62.1	7.6	18.3
HH 2 (21m)	7	10.0	77.2	4.5	8.4
HH 2 (21m)	8	5.2	93.0	1.8	0.0
HH 2 (21m)	9	12.6	63.7	7.6	16.1
HH 2 (21m)	11	16.4	50.7	9.3	23.6
HH 3 (1m)	4	4.3	27.4	21.5	46.8
HH 3 (1m)	6	22.0	64.4	8.8	4.8
HH 3 (1m)	9	4.5	49.8	17.9	27.7
HH 3 (1m)	11	12.5	55.3	10.1	22.0
HH 3 (14m)	4	19.1	53.3	9.2	18.3
HH 3 (14m)	6	9.8	74.7	4.8	10.7
HH 3 (14m)	9	15.2	55.6	11.8	17.4
HH 3 (14m)	11	13.4	50.7	11.8	24.0
HH 5 (1m)	4	17.5	45.8	13.4	23.2
HH 5 (1m)	6	16.2	56.8	20.0	6.9
HH 5 (1m)	7	9.4	51.4	8.3	30.8
HH 5 (1m)	8	3.6	47.9	13.0	35.5
HH 5 (1m)	9	3.6	52.9	14.4	29.1
HH 5 (1m)	11	10.1	48.3	14.9	26.6
HH 5 (20m)	4	18.2	50.5	8.1	23.2
HH 5 (20m)	6	17.4	53.7	23.2	5.6
HH 5 (20m)	7	19.7	39.1	12.8	28.4
HH 5 (20m)	8	9.5	63.8	7.9	18.7
HH 5 (20m)	9	9.1	68.0	7.2	15.6
HH 5 (20m)	11	14.0	48.3	14.1	23.6
CANAL (1m)	4	17.8	47.0	8.2	24.0
CANAL (1m)	5	9.8	43.9	18.2	28.0
CANAL (1m)	6	16.3	49.2	10.5	24.0
CANAL (1m)	7	29.5	42.3	3.4	24.8
CANAL (1m)	8	4.6	62.2	8.9	24.2
CANAL (1m)	9	33.8	41.9	6.5	17.9
CANAL (1m)	11	10.4	45.3	15.8	28.4
CANAL (8m)	4	18.8	50.1	7.0	24.0
CANAL (8m)	5	14.8	42.4	15.4	27.3
CANAL (8m)	6	24.3	45.9	8.1	21.6
CANAL (8m)	7	13.1	54.5	7.2	25.2
CANAL (8m)	8	26.9	43.0	4.2	25.8
CANAL (8m)	9	18.5	49.4	9.2	22.8
CANAL (8m)	11	15.1	44.9	13.4	26.6
368 (1m)	7	19.9	46.9	7.0	26.2
369 (1m)	4	31.3	48.9	0.6	19.2
369 (1m)	6	38.3	48.5	1.3	11.9
369 (1m)	7	17.6	54.3	6.0	22.1
369 (1m)	8	12.4	63.3	6.8	17.4
370 (1m)	4	31.8	49.9	1.5	16.8
370 (1m)	6	23.2	49.2	6.3	21.2
370 (1m)	7	16.7	54.0	6.5	22.7
370 (1m)	8	11.3	56.9	7.8	23.9
370 (1m)	11	12.3	45.4	14.3	28.0
370 (9m)	4	34.7	49.0	1.1	15.2
370 (9m)	6	33.6	50.4	4.1	11.9
370 (9m)	11	27.9	48.3	5.0	18.7
371 (1m)	4	34.2	55.7	0.7	9.4
371 (1m)	6	32.4	50.2	0.0	17.4
371 (14m)	4	34.3	53.1	0.7	11.9
372 (1m)	4	35.5	53.3	0.8	10.4
372 (1m)	9	37.9	51.4	2.1	8.4
372 (1m)	11	17.2	45.0	0.0	37.8
372 (22m)	4	40.3	52.7	1.3	5.7
372 (22m)	9	39.2	51.2	3.6	6.0
372 (22m)	11	27.2	47.1	6.1	19.6
373 (1m)	8	22.4	48.6	7.4	21.6

CONCENTRATIONS OF HEAVY METALS IN SUSPENDED SOLIDS

station	month	Fe mg/g	Mn mg/g	Cd mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg
HH 2 (1m)	6	33.6	2.0	0.00	46	337	1008
HH 2 (1m)	7	10.9	1.1	0.90	21	195	671
HH 2 (1m)	8	73.8	1.0	0.00	99	156	320
HH 2 (1m)	9	28.1	3.2	0.62	60	260	987
HH 2 (1m)	11	77.9	11.6	7.15	134	500	2336
HH 2 (21m)	6	93.1	2.4	2.56	159	440	2090
HH 2 (21m)	7	43.3	37.5	4.49	157	594	1373
HH 2 (21m)	8	152.0	1.6	2.00	107	391	1609
HH 2 (21m)	9	98.4	1.1	4.08	137	423	2383
HH 2 (21m)	11	72.6	6.5	8.06	160	409	2253
HH 3 (1m)	4	139.0	0.7	1.52	100	453	2965
HH 3 (1m)	6	42.7	4.8	0.00	118	344	1227
HH 3 (1m)	9	61.0	3.9	0.97	50	309	2024
HH 3 (1m)	11	60.9	11.8	7.47	150	444	2200
HH 3 (14m)	4	39.0	12.4	0.10	54	288	1625
HH 3 (14m)	6	104.0	1.8	7.12	249	438	1974
HH 3 (14m)	9	61.9	10.8	3.50	125	395	2254
HH 3 (14m)	11	83.0	15.0	11.60	234	540	2640
HH 5 (1m)	4	54.8	1.1	2.57	90	468	2208
HH 5 (1m)	6	75.4	3.1	2.60	63	365	2320
HH 5 (1m)	7	18.9	0.9	0.00	21	215	836
HH 5 (1m)	8	28.9	1.1	4.74	347	369	1422
HH 5 (1m)	9	59.4	3.1	3.96	251	386	2122
HH 5 (1m)	11	82.0	11.7	7.55	214	509	2578
HH 5 (20m)	4	37.4	16.3	0.00	68	320	1480
HH 5 (20m)	6	111.0	7.0	3.78	153	490	2913
HH 5 (20m)	7	102.0	22.9	6.23	266	564	3221
HH 5 (20m)	8	133.0	1.3	9.75	195	525	2829
HH 5 (20m)	9	151.0	2.2	4.22	176	504	2921
HH 5 (20m)	11	78.8	14.2	9.50	150	496	2576
CANAL (1m)	4	42.2	9.4	2.07	75	366	1443
CANAL (1m)	5	31.4	3.7	0.43	58	251	898
CANAL (1m)	6	44.5	6.2	1.08	76	376	1374
CANAL (1m)	7	13.8	1.5	0.00	13	217	621
CANAL (1m)	8	33.7	1.6	0.98	39	235	853
CANAL (1m)	9	23.6	1.1	1.87	57	177	156
CANAL (1m)	11	92.0	8.6	8.03	143	454	2761
CANAL (8m)	4	37.9	11.0	0.60	57	318	1371
CANAL (8m)	5	33.4	1.9	1.42	146	288	804
CANAL (8m)	6	39.5	4.5	2.05	49	245	946
CANAL (8m)	7	23.1	1.1	0.00	71	175	163
CANAL (8m)	8	18.4	3.3	3.11	162	229	102
CANAL (8m)	9	44.7	5.5	5.05	137	335	1642
CANAL (8m)	11	49.5	3.6	6.18	151	306	1492
368 (1m)	7	15.2	1.3	1.01	33	227	456
369 (1m)	4	29.5	0.9	0.00	30	204	320
369 (1m)	6	30.3	1.1	1.08	55	178	382
369 (1m)	7	15.6	1.4	0.00	268	221	436
369 (1m)	8	27.2	2.2	2.85	980	318	562
370 (1m)	4	28.0	0.9	0.00	32	207	354
370 (1m)	6	21.1	1.7	0.92	56	217	457
370 (1m)	7	15.7	1.6	0.00	19	252	601
370 (1m)	8	16.9	2.8	2.99	55	222	448
370 (1m)	11	47.8	3.7	6.15	134	378	1511
370 (9m)	4	36.2	1.0	0.00	36	173	328
370 (9m)	6	31.2	1.8	0.00	41	156	450
370 (9m)	11	17.1	0.1	5.31	166	316	414
371 (1m)	4	28.0	0.8	0.00	56	186	282
371 (1m)	6	15.4	0.6	0.57	113	239	367
371 (14m)	4	29.5	0.8	0.00	45	153	298
372 (1m)	4	22.1	0.6	0.00	79	235	328
372 (1m)	9	19.3	1.0	0.97	82	201	319
372 (1m)	11	37.3	1.2	6.12	1816	750	1317
372 (22m)	4	23.4	0.7	1.09	64	361	331
372 (22m)	9	22.1	1.3	2.90	78	269	427
372 (22m)	11	23.6	1.5	5.97	144	292	732
373 (1m)	8	23.0	2.4	3.22	86	306	503

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