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If Mapping Contaminated Sediment in Hamilton Harbour, Ontario

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Article abstract

Hamilton Harbour lies at the western end of Lake Ontario, and has a long history of industrial activity and urban development. Elevated levels of metals and organic compounds in bottom sediments led the International Joint Commission to designate Hamilton Harbour as an Area of Concern. Development of a remediation strategy requires definition of the distribution of the contaminants. Direct measurement of contamination by chemical analysis is prohibitively expensive. Previous studies on subsampled cores have shown that magnetic susceptibility closely tracks contaminant levels. This paper show show non-destructive measurements of magnetic susceptibility (ê) on unopened cores can be used to map the distribution of post-industrial contaminated sediments and determine areas of recent sediment disturbance.

Series

Mapping Contaminated Sediment in Hamilton Harbour, Ontario

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SUMMARY

Hamilton Harbour lies at the western end of Lake Ontario, and has a long history of industrial activity and urban development. Elevated levels of metals and organic compounds in bottom sediments led the International Joint Commission to designate Hamilton Harbour as an Area of Concern. Development of a remediation strategy requires definition of the distribution of the contaminants. Direct measurement of contamination by chemical analysis is prohibitively expensive. Previous studies on subsampled cores have shown that magnetic susceptibility closely tracks contaminant levels. This paper shows how non-destructive measurements of magnetic susceptibility (κ) on unopened cores can be used to map the distribution of post-industrial contaminated sediments and determine areas of recent sediment disturbance.

RÉSUMÉ

Le Port de Hamilton que est situé à l'extrémité ouest du lac Ontario, a connu une longue suite d'activités industrielles et de développements urbains. L'existence de niveaux élevés de métaux et de composés organiques dans les sédiments du fond du lac a amené la Comission conjointe internationale à accorder le statut de Secteur préoccupant au Port de Hamilton. L'élaboration d'une stratégie de restauration exige d'abord que l'on connaisse la distribution des polluants. L'évaluation de degré de contamination par des analyses chimiques sur échantillons s'avère beaucoup trop dispendieuse. Des études effectuées sur des sous-échantillons ont montré que les mesures de la susceptibilité magnétique suivent de près les niveaux de contamination. Le présent article montre comment une méthode de mesure de la susceptibilité magnétique (κ) sur des carottes d'échantillonnage vierges peut être utilisée pour cartographier la distribution des sédiments contaminés post-industriels, permettant ainsi de localiser les endroits de remaniement récents.

INTRODUCTION

Hamilton Harbour is a triangular-shaped embayment located at the western end of Lake Ontario (Fig. 1). During the past century, extensive urbanization and industrialization have resulted in the direct discharges of untreated sewage and industrial effluent into the harbour. Current daily discharge of water into the harbour is $2.6\text{-}3.8\times10^6$ m^3, of which 2-19% is runoff, 7-16% is from sewage treatment plants (STPs), and 72-87% is exchange with Lake Ontario. Two major iron and steel industries (Stelco and Dofasco) withdraw and return 2×106 m$^3\cdot$d^{-1} which is used for contact cooling (Remedial Action Plan, 1989). The presence of heavy metals, toxic organics in fish, contaminated sediments, eutrophication and poor aesthetics led the International Joint Commission (IJC) to designate Hamilton Harbour an Area of Concern (International Joint Commission, 1985). Presently, a plan is being developed to study and restore the ecosystem of the harbour (Remedial Action Plan, 1989, 1991). Central to the development of this plan is an understanding of the distribution and volume of contaminated sediments.

The main limitation of previous attempts to estimate the extent of the contaminated sediment is that they are based on only a few cores. When one compares estimates of the thickness of contaminated sediments from isolated cores, it rapidly becomes apparent that there are large variations in thickness throughout the harbour and that the variation is dependent upon the sample location. While in theory, the solution would be to analyze more cores, in practice, this is often not feasible due to manpower requirements and consequent economic restraints. What is needed is a rapid, cost-efficient method that can identify the boundary between contaminated and non-contaminated sediments and be used to map the three-dimensional distribution of contaminated sediments.

Magnetic susceptibility is a measure of the ease of magnetization of a sample, and is related to the amount, size and composition of the magnetic minerals it contains (Thompson and Oldfield, 1986). A direct linkage between magnetic susceptibility and contamination in Hamilton Harbour sediments has been demonstrated in studies by Morris *et al.* (1994) and Versteeg *et al.* (1995). An order of magnitude increase in magnetic susceptibility in the upper 30-70 cm is related to a rise in magnetic mineral content and an increase in magnetic mineral grain size typical of industrial and urban sources. Confirmation that this magnetic mineral boundary represents the base of the post-industrial sediment is provided by concomitant increases in both polycyclic aromatic hydrocarbons (PAH) (Morris *et al.*, 1994) and metal content (Versteeg *et al.*, 1995). A detailed discussion of the geochemistry of contaminants found in Hamilton Harbour is given by Coakley and Mudroch, in press and Bolton and Evans, in press.

In this paper, magnetic susceptibility was measured rapidly and non-destructively on 40 whole, unopened cores that were collected on a 500-m grid. The thickness of contaminated sediment was determined from these profiles, and contoured to produce a map of the distribution of contaminated sediments. Additional maps were produced by contouring magnetic susceptibility values averaged over 10-cm-thick sections, to map the distribution of contaminated sediments at various sediment depths.

Background

European settlement of the harbour region began in 1786 (Campbell, 1966), and has had a dramatic impact on the harbour ecosystem. In 1823, the Burlington Ship Canal between Lake Ontario and Hamilton Harbour was constructed, allowing the exchange of large volumes of water between the two waterbodies (Fig. 1). A similar canal, the Desjardins Canal, was constructed to join Cootes Paradise to the harbour in 1853, and the old fluvial channel filled in to make way for railroad construction. Since 1926, 25% of the open-water area in the harbour has been lost, as the marshes along the south shore were filled in to reclaim land for industrial use. Steel production began in Hamilton around the turn of the century, and the south shore of the harbour is home to two large steel-manufacturing facilities, Stelco and Dofasco. Historically, these industries discharged untreated process effluent containing contaminants such as metals, aromatic hydrocarbons, and cyanide. In recent years, pollution control equipment, which greatly reduces or eliminates these contaminant loadings, has been installed, but a historical legacy of contaminated sediments remains.

Contaminated sediments have been investigated in Hamilton Harbour in two ways. The first involves assessing surficial sediments over a broad area to establish the distribution of contamination (Poulton, 1987; Poulton *et al.*, 1988; Remedial Action Plan, 1989; Murphy *et al.*, 1990); the second involves studying the historical record of pollution by analyzing sediment cores (Nriagu *et al.*, 1983; Mayer and Johnson, 1993; Yang *et al.*, 1993).

Studies that focus on the distribution of contaminants in surficial sediments point to enhanced levels of PAHs, PCBs and heavy metals in areas such as the sewage treatment outfalls and the steel mill outfalls (Remedial Action Plan,

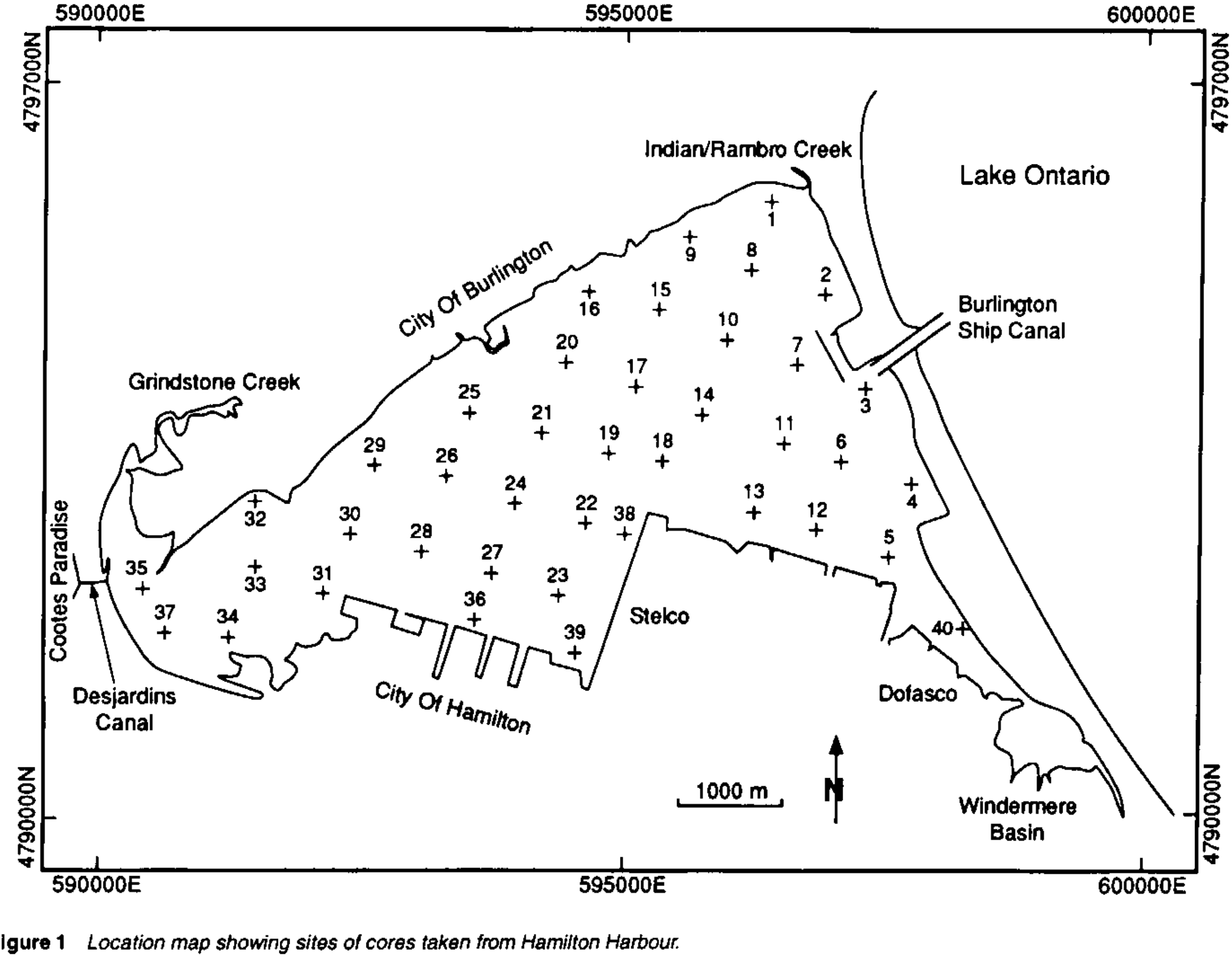

Figure 1 *Location map showing sites of cores taken from Hamilton Harbour.*

1989). The main limitation of these studies is that they do not assess the depth of contamination and, therefore, have no way of computing volumes of contaminated material that may require remediation.

Studies of the depth variations of physical and chemical properties such as organic matter, bulk density, heavy metal and phosphorus concentration in cores (Mayer and Johnson, 1993) demonstrate the impact of settlement and industrialization on the sediment deposited in the harbour. Zinc, lead and cadmium concentrations in surficial sediments are 160, 28 and 19 times, respectively, those in the pre-colonial sediments (approximately 50 cm depth; Nriagu *et al.*, 1983). PAH concentrations, associated with high-temperature combustion of fossil fuels, also have higher concentrations in the upper 70 cm relative to the deeper sediments (Morris *et al.*, 1994). Yang *et al.* (1993) have reported microfossil changes which they interpret as being indicative of the eutrophication and pollution that accompanied the deforestation and settlement of the harbour's drainage basin. These methods, all of which show contamination of the upper sediments, require extensive sample preparation in order to acquire data. An additional limitation of existing studies is that they are often based on cores which are too short to penetrate the anthropogenic horizon.

A possible alternative approach to contaminated sediment mapping is through the use of magnetic properties, especially magnetic susceptibility. There is a demonstrated relationship between increased magnetic susceptibility in sediments and contamination *via* industrial processes and urbanization. Coal fly ash, a by-product of the combustion of coal, contains spherules of magnetite (Locke and Bertine, 1986; Dekkers and Pietersen, 1992) which can be transported atmospherically. The enhanced susceptibility in the upper layers of cores from peat bogs has been related to increased atmospheric loading of magnetic particles related to increased coal burning associated with the Industrial Revolution (Thompson and Oldfield, 1986). Automobiles and urban construction materials can also lead to the formation of magnetic minerals (Beckwith *et al.*, 1984). While these iron-rich magnetic materials are not toxic themselves, they are often associated, either directly or indirectly, with true contaminants (*i.e.*, PAHs and heavy metals). Indirectly, contaminants that are produced by the same processes as the magnetic materials will follow the same pathways to sedimentation. Contaminants may adsorb onto the iron-rich particles (Stumm and Morgan, 1981).

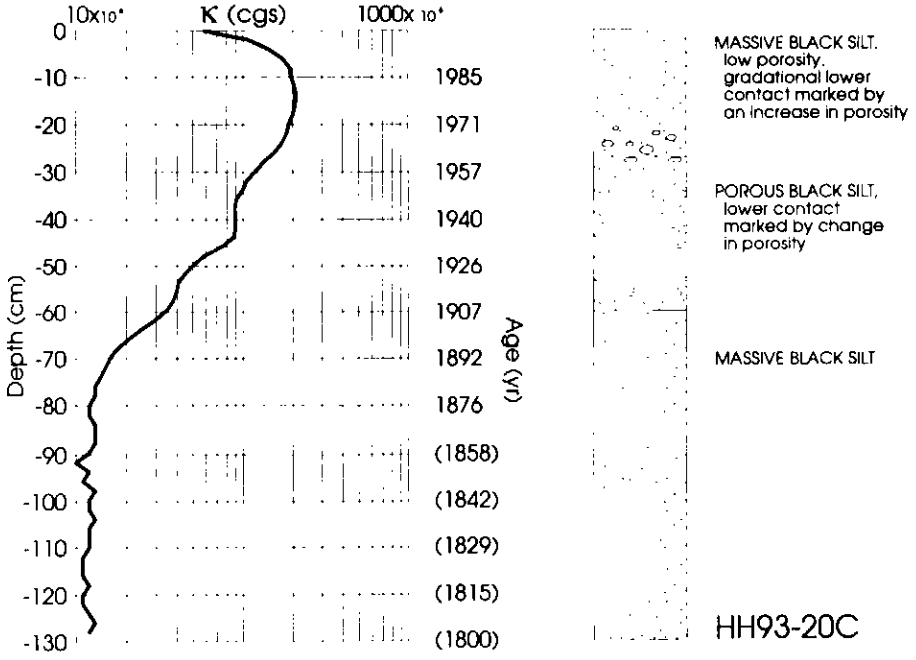

Figure 2 *Typical profile of magnetic susceptibility for Hamilton Harbour core taken at site 20 (Fig. 1). Measurement techniques are described in the text. Ages are ^{210}Pb ages. Ages in parentheses are extrapolated using calculated sedimentation rates.*

In Hamilton Harbour, there are several possible sources that could result in elevated magnetic mineral production levels. The relative impact of each individual source may have changed with progressive urbanization, industrialization and environmental monitoring of the watershed. Original settlement of the area was first accomplished by burning much of the native forest (Weaver, 1982). This would certainly have been marked by an enhancement of fine-grained magnetite in the soils, and subsequently the sediments, as demonstrated in other areas (Bloemendal *et al.*, 1979; Rummery *et al.*, 1979; Bloemendal, 1982; Rummery, 1983). As the local population grew, sewage and runoff were discharged directly into the harbour. This effluent contained magnetic Fe-oxides from construction materials, coal fly-ash, and eventually automobiles. Since the turn of the century, the production of steel in Hamilton has released large quantities of Fe into the harbour, through the atmospheric release of coal fly-ash and by direct discharge of process effluent high in Fe into the harbour. These combined sources have produced a rise in the content of highly magnetic particles in recent sediments.

Measurements of magnetic susceptibility have several advantages over direct measures of contamination: they are rapid (10-15 seconds per measurement, *i.e.*, 10 minutes to analyze a 1-m long core, with measurements every 2 cm); they are non-destructive (measurements can be taken on unopened cores through plastic core tubes); and they are economical (a susceptibility meter is inexpensive).

METHODS

In July 1993, sediment cores were collected at 40 sites in Hamilton Harbour (Fig. 1), with a standard Benthos Corer, with 40 kg of weights and a 2-m, 7.5-cm ID plastic core, tube. The corer was lowered to within 2 m from the bottom, and then allowed to free-fall into the sediment. Recovery varied from 60 cm up to 140 cm long. Immediately upon collection, the cores were examined through the liner for colour and structural variations. The cores were then sealed and stored upright in their tubes, at 4°C.

Volume-specific magnetic susceptibility (κ) was measured on the whole core by passing it through a 100-mm ID coil attachment for a Bartington MS2 susceptibility meter. Measurements were made every 2 cm, from the sediment-water interface down. The instrument resolution is 1×10^{-6} cgs emu, (or 4 $\text{Pi}\times10^{-6}$ SI). Three repeat measurements made on one core (HH93-20a) show that the real precision is approximately ± 5% of the instrument reading, although this is as great as ±20% for values less than 5×10^{-6} cgs. These errors are small in comparison to the variability of the data, which ranges over an order in magnitude.

RESULTS

Profiles

For each core, the profile of magnetic susceptibility was plotted *versus* depth (using a log-normal plot). Figure 2 shows a typical κ profile, along with lithologic descriptions. Many features of the κ profile are common to most cores. In general, low ($<2\times10^{-6}$ cgs) background values are followed by an order of magnitude rise in susceptibility at sediment depths ranging from 20-70 cm. Above the initial rise in κ, there is a plateau (45-35 cm in Fig. 2), followed by a second rise which peaks just below the surface, and then falls slightly. ^{210}Pb data (Turner, 1994) indicates that the date of the initial rise in κ at 70 cm is 1892, and that the second rise at 35 cm corresponds to a ^{210}Pb date of 1945.

Variations in the κ profiles can be used to identify correlatable horizons. Each horizon is characterized by a local peak or trough in the κ profile. As seen in Figure 3, features between adjacent cores define several magneto-stratigraphic units with a resolution of 6 cm (*i.e.*, 3 κ data points), which represent a combination of changes in magnetic mineral content and grain size. There is a reasonable correlation between these magneto-stratigraphic units and lithological units.

There are a number of cores from the south shore (*i.e.*, Fig 3B, cores 38 and 39) for which it is not possible to identify any obvious correlatable horizons. Lack of correlation indicates that these sediments have been disturbed. The distribution of these disturbed sediments, in a zone that includes the south-central and southeastern areas of the harbour, suggests that the disturbance may be related to shipping and dredging activity which is prominent in this area (Holmes and Whillans, 1984; Holmes, 1986). Other factors include the dumping of coarse-grained, highly magnetic sediment during land reclamation (Ozanian, 1957) and the proximity to a source of highly magnetic material, *i.e.*, an industrial discharge or spills from iron ore ships.

Spatial Variations

For each core, the measured κ values were averaged for each successive 10 cm of sediment, *i.e.*, 0-10 cm, 10-20 cm, etc. A colour contour map of the magnetic susceptibility distribution across Hamilton Harbour was created for each slice between successive 10 cm isobaths below the sediment-water interface. The averaged κ values were gridded by the Geosoft RANGRID random-gridding algorithm, using a 250-m grid cell size with a 750-m blanking distance. The maps produced by this procedure provide a broad estimate of observed distributions within the harbour. Caution must be exercised in the interpretation of features along the shoreline, as the gridding process does not incorporate the boundary conditions necessarily imposed by the shoreline.

To emphasize the relationship between κ distribution and the shape of the depositional basin, the colour contour maps were draped over a three-dimensional projection of the bathymetry of the harbour, using the NETVIEW package by Geosoft. The bathymetry grid was interpolated from water depths measured at each station during core collection, and gridded using the same procedure as described above.

The depth-slices provide a picture of the variations in the distribution of κ at various sediment depths. Four of these are presented in Figure 4 representing a gradation from deep to surficial sediments. The deepest section (80-90 cm, Fig. 4A) shows a zone of high κ which is restricted to the south shore. At this sediment depth, the remainder of the harbour has low (*i.e.*, background) κ values and shows no other regional features. Moving up through the sedimentary column, this zone of high κ sediment appears to migrate northward (60-70 cm, Fig. 4B). A sharp boundary

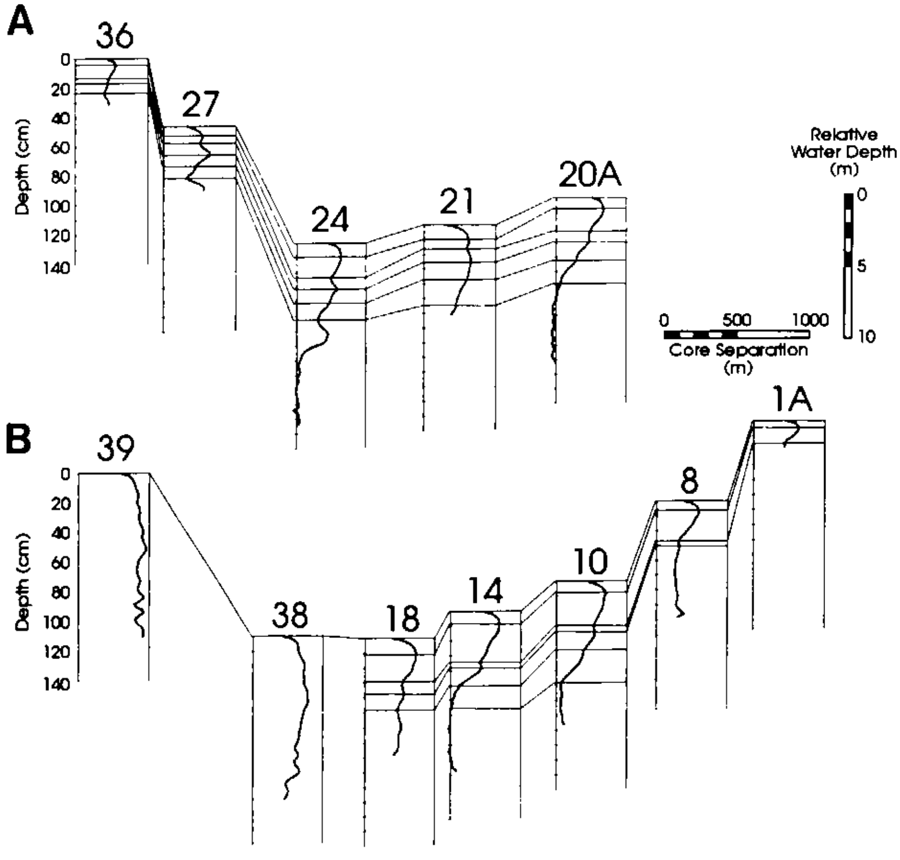

Figure 3 *Correlated cross-sections in Hamilton Harbour.* (**A**) *section next to Randle Reef, showing non-disturbed zone.* (**B**) *section through Randle Reef showing disturbed sediments along south shore at sites 38 and 39 (Fig. 1). For susceptibility scale, see Figure 2.*

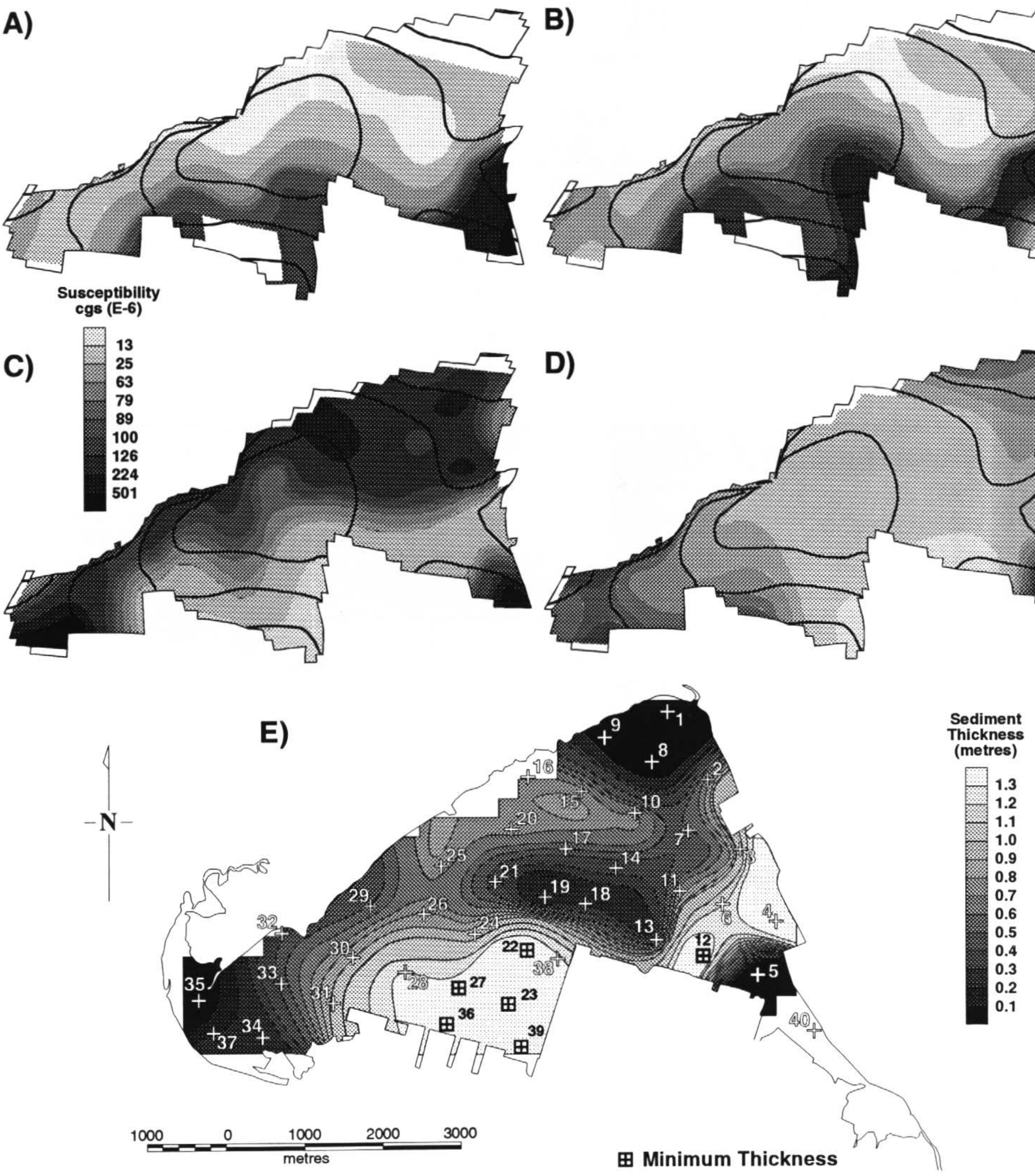

Figure 4 *Contour map of average susceptibility for 10-cm depth slices, draped onto the bathymetry of the harbour.* (**A**) *80-90 cm,* (**B**) *60-70 cm,* (**C**) *40-50 cm,* (**D**) *10-20 cm, bathymetry shown by red lines, depths in metres. Note northward expansion of comtamination in successively shallower depth slices.* (**E**) *isopach map showing thickness of contaminated sediment in Hamilton Harbour. Thickness and horizontal scale in metres.*

separating high and low κ is maintained until the 40-50 cm section (Fig. 4C). At this point, the values of κ begin to rise above background in the sediment over the remainder of the northern part of the harbour. With decreasing depth, the zonation of the harbour becomes gradually less distinct. In the near-surface sediments (10-20 cm, Fig. 4D), the previously distinct south shore zone is all but non-existent, having been succeeded by relatively uniform, high κ sediment covering most of the harbour.

There is a clear relationship between the shape of the boundary separating high and low κ, and the bathymetry of the harbour. As the boundary advances from south to north, it first progresses into deeper parts of the basin (Fig. 4B, 60-70 cm; Fig. 4C, 40-50 cm). The presence of a plume of high κ sediments into the deep basin is consistent with κ values being associated with the finest grain size fraction, which would be subject to depositional focussing into the deeper waters of the central basin.

A prominent feature brought out in Figure 4 is the effect on the distribution of κ of the influx of extraneous sediment introduced by tributaries into the harbour. The mouth of the Desjardins Canal, at the western end of the harbour, is marked by a persistent low κ value which is likely a result of the influx of fine-grained, silicate-rich sediments from Cootes Paradise, a wetland marsh drained by the canal. These sediments would be relatively non-magnetic, since the highly magnetic sediments are generally related to industrial sources, and Cootes Paradise drains a predominantly agricultural watershed. Another low κ zone in the southeastern harbour, at the mouth of Windermere Basin, in Figures 4B, C and D, is interpreted as being the result of dredging.

One must be careful in the interpretation of depositional pictures presented by these depth-slice images. It is tempting to treat them as being directly equivalent to time slices. Such a model would require uniform sedimentation rates at all points in the harbour, but currently available ^{210}Pb ages are inconclusive.

Contaminated Sediment Thickness

Previous chemical analyses have shown that there is a direct relationship between highly magnetic sediments and contaminants (Morris *et al.*, 1994; Versteeg *et al.*, 1995). It is possible to operationally define contaminated sediment as sediment having κ values above background. Since the rise of κ is so dramatic in most cores, there is little difficulty in picking the depth of this transition. Ambiguity does arise, however, when κ does not fall to a background value. Where this occurs (cores 12, 22, 23, 27, 36 and 39), we have assumed a minimum thickness of contaminated sediment, based on the profiles of adjacent cores. An isopach map of contaminated sediment thickness was derived using a gridding procedure similar to that used for the depth slices. In general, contaminant thickness appears to decrease with increasing water depth. The region of thinnest contaminated sediment corresponds to the deepest part of the harbour (Fig. 4E), which is in contrast to what is expected if the fine-grained contaminated sediments are being focussed in the central basin. It is possible that focussing is occuring, but sediment accumulation is miminized because of the small grain sizes (due to more efficient packing). Superimposed on this regional pattern are a number of localized features. The zone along the south shore, west of Stelco Pier, has the thickest zone of contaminated sediment, over 1.4 m. This zone includes Randle Reef, an area well known for high levels of contamination (Murphy *et al.*, 1990). Another thick zone of contaminated sediment occurs at the mouth of Windermere Basin.

The total volume of contaminated sediment, as estimated by this κ procedure, is over 12×10^6 m^3. Some caution should be applied in the use of this estimate of contaminated sediment thickness and volume. First of all, the thickness of contaminated sediment has been interpolated between cores which were spaced 500 m apart, and could, therefore, have missed localized variations. Greater confidence in the distribution could be obtained by analyzing more cores, with a finer sampling resolution. Second, it is possible that part of the inferred contamination could be related to colonial settlement activities (*i.e.*, forest clearance), and not solely to industrial operations. We propose that the κ maps be used as a reconnaissance tool, to identify the potentially contaminated zones, which can be verified through additional chemical analysis. This would significantly reduce the number of samples for chemical analysis, and since the κ analysis is non-destructive, the same samples can be used, eliminating the need to collect more cores.

DISCUSSION

By exploiting a previously demonstrated relationship between magnetic susceptibility and contaminants, the distribution of potentially contaminated sediment in Hamilton Harbour has been mapped. In comparison to conventional methods of contaminant detection, magnetic susceptibility measurements have the advantage of being completely non-destructive, rapid and inexpensive. Although susceptibility does not directly determine the presence of contamination, it is a rapid, inexpensive non-destructive tool which could identify potentially contaminated sediments. Such knowledge can substantially reduce the number of chemical analyses required to map the distribution of contaminated sediments in urban harbours.

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