

This manuscript has been submitted to  
J. Great Lakes Research  
and the contents are subject to change.  
This copy is to provide information  
prior to publication.

**TRACE METALS AND BENTHIC INVERTEBRATES  
IN SEDIMENTS OF NEARSHORE LAKE ONTARIO  
AT HAMILTON HARBOUR**

D.J. Poulton<sup>1</sup>, K.J. Simpson<sup>1</sup>, D.R. Barton<sup>2</sup>  
and K.R. Lum<sup>3</sup>

NWRI Contribution No. 86-196

<sup>1</sup>Water Resources Branch  
Ontario Ministry of the Environment  
135 St. Clair Avenue West  
Toronto, Ontario M4Év 1P5

<sup>2</sup>Barton Biological Consulting  
68 William Street West  
Waterloo, Ontario N1L 1J7

<sup>3</sup>Environmental Contaminants Division  
National Water Research Institute  
Canada Centre for Inland Waters  
Burlington, Ontario, Canada L7R 4A6

• Environment Canada

## MANAGEMENT PERSPECTIVE

This article is the result of work done in collaboration with Water Resources Branch, OME, on samples collected by NWRI in 1983. The objective was to assess the impact of discharges of metallic contaminants and PAH's from Hamilton Harbour on nearshore sediments and the benthic invertebrate community as a component of concurrent work by OME for their report on "Technical Summary and Management Options for Hamilton Harbour".

The results show that operationally-defined geochemical phases are important in determining the distributions of metals and benthic macroinvertebrates in the study area. The distribution diagrams show that portions of the metals exported from the Harbour via the Ship Canal are deposited in the nearshore zone in plumes which are oriented either directly offshore from the Canal, or more or less parallel to shore in either direction.

The benthic invertebrate distributions were mainly influenced by depth. However, within the appropriate depth ranges, most taxa showed consistently positive or negative correlations with concentrations of most metals. The strongest correlations were found most frequently with metals bound to organic matter.

## PERSPECTIVE DE GESTION

Le présent article est le fruit de travaux effectués en collaboration avec la Direction des ressources en eau du MEO sur des échantillons prélevés par l'INRE en 1983. L'objectif était d'évaluer les répercussions des émissions de contaminants métalliques et des PAH du port d'Hamilton sur les sédiments précôtiers et la communauté d'invertébrés benthiques, dans le cadre d'un travail concomitant du MEO pour son rapport "Technical Summary and Management Options for Hamilton Harbour".

Les résultats indiquent que les phases géochimiques définies pour ce travail sont importantes pour connaître la répartition des métaux et des macro-invertébrés dans la région à l'étude. Les diagrammes de répartition indiquent qu'un certain pourcentage des métaux exportés de la région du port par le canal de navigation sont déposés dans la zone précôtière sous forme de panaches qui sont orientés soit directement vers le large par rapport au canal, soit plus ou moins parallèlement au rivage dans les deux directions.

La répartition des invertébrés benthiques était principalement influencée par la profondeur. Cependant, dans les gammes de profondeurs appropriées, la plupart des taxons dénotaient des corrélations constamment positives ou négatives avec les concentrations de la plupart des métaux. Les corrélations les plus fortes se trouvaient le plus souvent avec des métaux liés à la matière organique.

## ABSTRACT

The impact of metallic contaminants from Hamilton Harbour has been studied on the sediments in the nearshore zone (up to 30 m depth) in western Lake Ontario. These metals are exported from Hamilton Harbour through the Burlington Ship Canal mainly in association with fine-grained particles. Although the total concentrations of most metals are 3 to 20 times lower than at an offshore location (100 m depth), the application of a grain-size correction to the raw data indicates the existence of plumes which are oriented either directly offshore from the canal or relatively parallel to shore in either direction. Sequential chemical extraction indicates that while most of the metals are present as lattice-bound forms, smaller amounts of bioavailable organically-bound metals are also found. The benthic invertebrate community is similar in composition to that observed in other Great Lakes nearshore areas impacted by metal and organic pollution. Although depth appeared to have the strongest influence on the distribution of most common taxa, consistent positive or negative correlations were found with most metals (particularly the organic fraction). Whether this indicates a response to metal toxicity or organic enrichment is not presently known.

Additional key words: contaminants, biota, bioavailability, geochemistry, extractions, particle sizes.

## RÉSUMÉ

Les répercussions des contaminants métalliques provenant du port d'Hamilton sur les sédiments de la zone précôtière (jusqu'à 30 m de profondeur) dans la partie occidentale du lac Ontario ont été étudiées. Ces métaux sont exportés du port d'Hamilton par le canal de navigation de Burlington, principalement en association avec des particules finement granulées. Bien que les concentrations totales de la plupart des métaux soient 3 à 20 fois moindres qu'au large (100 m de profondeur), la pondération des données brutes en fonction de la granulométrie indique l'existence de panaches orientés soit directement vers le large par rapport au canal, soit relativement parallèlement au rivage dans les deux directions. L'extraction chimique séquentielle indique que de petites quantités de métaux biodisponibles organiquement liés s'y trouvent également, bien que la plupart des métaux soient présents sous forme complexée. La composition de la communauté des invertébrés benthiques est semblable à celle observée dans les autres zones précôtières des Grands Lacs polluées par les métaux et les matières organiques. On a trouvé des corrélations constamment positives ou négatives pour la plupart des métaux (particulièrement pour la fraction organique), bien que la profondeur semble avoir la plus forte influence sur la répartition de la plupart des taxons. On ne sait pas encore si cela indique une réaction à la toxicité métallique ou à l'enrichissement organique.

Autres mots clés : contaminants, biote, biodisponibilité, géochimie, extractions, granulométrie des particules.

## INTRODUCTION

The impact of toxic substances on the environment is increasingly being recognized as one of the most important issues related to ecosystem management. Eventual control of toxic contaminants such as heavy metals depends upon understanding the mechanisms of contaminant transport within the environment and the resultant impacts upon the biota. As a step towards a complete description of these processes, we need a thorough knowledge of the chemical forms in which toxic metals exist in deposited sediments and their respective interaction with the benthic macroinvertebrate community.

Industries in Hamilton Harbour at the western end of Lake Ontario (Figure 1) discharge a variety of materials in their wastewaters, including heavy metals such as zinc, cadmium, mercury, copper and lead. Consequently, both suspended and deposited sediments in the bay have high metal contents in the form of adsorbates to clay minerals, co-precipitates with secondary iron-manganese oxides, diagenetic sulphides and carbonates, and metal-organic complexes. Heavy metals in the harbor water, and their loadings to Lake Ontario have recently been discussed (Poulton 1987). Mass exchange of water through the Burlington Ship Canal is important in diluting the pollutants within the harbor and in discharging them into the western end of Lake Ontario (Palmer and Poulton 1976; Kohli 1978, 1979, 1984; Klapwijk and

Snodgrass 1985; MOE 1985). During summer stratification, warm harbor epilimnetic waters generally flow to the lake over colder incoming lake water, although the reverse (lake water overlying harbor water) can occasionally occur. Alternating unidirectional flow of lake and harbor water is the normal flow regime under unstratified conditions.

Johnson and Matheson (1968) found that benthic macroinvertebrate communities at the extreme western end of Lake Ontario were strongly influenced by pollutants discharged through the Burlington Ship Canal. Pollution-tolerant organisms such as Limnodrilus hoffmeisteri, Tubifex tubifex and Chironomus attenuatus organisms were dominant off the mouth of the ship canal in the area of sediment enriched with iron and organic matter.

This paper describes the results of a study undertaken in August 1983, to describe the forms and distributions of selected heavy metals and benthic invertebrates in the nearshore zone of western Lake Ontario adjacent to Hamilton Harbor. The emphasis has been placed on those forms of metals most likely to be available to the biota.

## MATERIALS AND METHODS

Sediment samples were collected on August 22, 1983 from the C.S.S. Limnos using a Shipek grab sampler, at 24 stations (#360 to 383) located in the western end of Lake Ontario adjacent to Hamilton Harbour (Figure 1).

Particle size distribution in one sample from each station was determined on a Microtrac particle-size analyzer (Cooper et al. 1984). This instrument partitions sediment particles into 25 size ranges between 0.2 and 1000  $\mu\text{m}$ . For an overview of the distribution of grain sizes in the study area, these ranges were combined into 6 categories representing coarse and fine portions of each of sand, silt and clay.

Sediment samples were homogenized and a subsample was dried at 105°C to determine moisture content. Duplicate subsamples (equivalent to 2 g dry weight) of wet sediment were then analyzed for cadmium, chromium, copper, iron, manganese, nickel, lead and zinc. Sequential chemical extractions were performed to partition trace metals into five fractions likely to be affected by various environmental conditions: exchangeable, bound to carbonates, bound to iron-manganese oxides, bound to organic matter and residual metals. The procedure was similar to that used by Tessier (1979) and Tessier et. al., (1980).



### Fraction 1 - Exchangeable Metal Ions

This is a measure of those trace metals which are released most readily into the environment. Sediment samples were agitated at room temperature continuously for 1 hour with 0.75 M LiCl + 0.25 M CsCl in 60% v/v methanol at pH 7 (Lum and Edgar 1983). After centrifuging (4,000 rpm, 1 hr.) and decanting, the sample was rinsed with distilled water and re-centrifuged. This washing solution was then combined with the original extract and diluted to 20 mL.

Concentrations of heavy metals were determined by atomic absorption spectrophotometer (A.A.S.) using a Varian Model AA-475 calibrated with standards made up in the same matrix.

### Fraction 2 - Bound to Carbonates

Significant trace metal concentrations are associated with sediment carbonates (Tessier et. al., 1979), which in turn makes this fraction susceptible to changes in pH. The residue from Fraction 1 was agitated for 1 hour with 10 mL of dilute HCl (pH 3) at room temperature. After centrifuging, washing and re-centrifuging with distilled water, the extract was analyzed for heavy metal content by A.A.S.

### Fraction 3 - Bound to Iron-Manganese Oxides

Iron and manganese oxides may occur as nodules, concretions or simply as a coating on particles. These oxides are good adsorbents for trace metals and are thermodynamically unstable under anoxic conditions.

This step in the analysis involved the agitation of the residue from Fraction 2 with 10 mL of 0.1 M hydroxylamine hydrochloride (pH 2.5, HCl) for 6 hours at 96°C. The sample was then centrifuged, washed, re-centrifuged and analyzed by A.A.S.

### Fraction 4 - Bound to Organic Matter

Trace metals can be bound or complexed with naturally occurring organic matter, including humic and fulvic acids, living organisms, detritus and coatings on mineral particles. Such metals may be released into solution under oxidizing conditions (Tessier *et. al.*, 1980). The residue from Fraction 3 was digested with 3 mL of 0.02 M HNO<sub>3</sub> and 5 mL of 30% H<sub>2</sub>O<sub>2</sub> (pH 2.0 with HNO<sub>3</sub>) for 2 hours at 85°C with occasional agitation. An additional 3 mL of 30% H<sub>2</sub>O<sub>2</sub> (pH 2, HNO<sub>3</sub>) was then added, and the extraction continued for 3 hours at 85°C with occasional agitation. After cooling, 5 mL of 3.2 M ammonium acetate in 20% (v/v) HNO<sub>3</sub> was added, the solution was diluted to 20 mL and agitated continuously for 30 minutes. After centrifuging, washing and re-centrifuging, the extract was analyzed by A.A.S.

### Fraction 5 - Residual Metals

This final procedure extracted trace metals mainly held within the crystalline structure of primary and secondary minerals. These are the most tightly bound elements and are very rarely released under normal circumstances. The residue from Fraction 4 was digested with a mixture of HF, HClO<sub>4</sub>, and HNO<sub>3</sub> until near dryness. The digestion was repeated once if the residue showed any persistent color. An additional 1 mL of HClO<sub>4</sub> was added and the solution evaporated until the appearance of white fumes. Finally, the residue was re-dissolved in HCl, and diluted to 20 mL for trace metals analysis by A.A.S.

As a check on the results of the sequential extractions, duplicate raw sediment samples were analyzed for total heavy metal content using only the procedure outlined for Fraction 5. No discrepancies were found when these values were compared with the combined results of Fractions 1-5.

Analysis of duplicate samples allowed the calculation of the analytical precision over a relatively large range of element concentrations.

Since trace element data are typically log-normally distributed, all data were log transformed prior to statistical analyses. Analysis of variance (ANOVA) was used to examine differences of element concentrations between duplicate samples and among sampling stations.

Variations between duplicate determinations were not significant

( $p > 0.05$ ) for any metal. The precision of replicate measurements of total concentration of most metals were  $>90\%$  (averaged across the study area); because of lower average concentrations, the average precision was about 60-80% for Cd and Ni. In most cases the precision of results of Fractions 4 (organic) and 5 (residual) were similar or only slightly poorer. Precision could not be estimated for Fractions 1-3 since many values were near detection limits.

Duplicate Shipek samples of benthic invertebrates were obtained from 19 stations; single samples were obtained from stations 369, 373, 378, and 381 (Figure 1). Samples were preserved in 10% formalin solution and returned to the laboratory where they were washed through a 210  $\mu\text{m}$  sieve and organisms were sorted from the residue. Samples containing very large numbers of animals were subsampled. All organisms removed from the samples were identified to the lowest practical taxonomic level. Immature Tubificidae were assigned to species according to the proportional abundance of mature individuals in each sample. All counts were log transformed prior to statistical analyses.

## RESULTS AND DISCUSSION

Sand was the predominant type of sediment at nearshore stations at depths <10m, and silt became more important offshore (Table 1). Depth and mean particle size were strongly correlated ( $r = -0.800$ ). The percentage of clay also increased with depth; station 361 was exceptional in having more than 10% clay at a depth of 10 m.

The spatial distributions of the various metals generally reflected the sorting of fine-grained material toward the deeper parts of the study area (Figure 2). Concentrations of all metals increased with depth and the higher values were generally found at stations where the mean sediment particle size was less than about 50  $\mu\text{m}$ . The only exceptions were Fe and Mn which were found at moderately high concentrations inshore in the southern part of the study area. Comparison of the average concentrations of metals at nearshore stations 360-383 with those measured in the uppermost 1 cm of cores from a depth of 100 m in the Niagara Basin (K.Lum, unpublished data) shows that amounts are 3-20x greater in the active depositional zone (Table 3). These distributions appear to suggest that metallic discharges from Hamilton Harbor do not have a significant impact on sediment quality in the area immediately adjacent to the Burlington Ship Canal. This is consistent with studies which indicate that most trace metals are exported from the harbor in association with fine particles (eg. McIsaac et al. 1982, Nriagu et al. 1983) which would have a short residence time in the nearshore zone.

Although chemical extraction procedures suffer from a lack of phase specificity, they are nonetheless regarded as providing a valuable operational separation of metal forms with varying (increasing) strength of binding to the sediment substrate (Fraser and Lum 1983). The sequence of extraction can be viewed as an inverse scale of metal ion availability - the so-called extrinsic factors regulating bioavailability to organisms. The organically bound fraction (4) probably has a biological impact more significant than suggested by the strength of the chemical binding, since organic detritus is an important food for many benthic invertebrates. The residual fraction (5) is unlikely to have biological importance, nor does it reflect anthropogenic inputs other than alterations in erosion patterns.

Table 2 lists the average percentage contributions of the 5 phases to the total amounts of the various metals. The sum of exchangeable (Fraction 1), carbonate- (Fraction 2) and Fe/Mn oxide (Fraction 3) bound forms was less than 5% of the total amounts of all metals except Mn. Indeed, at most stations, analytically significant amounts of fractions 1, 2 and 3 were obtained only for Fe, Mn and Zn. Mn<sup>2+</sup> was significant at only a few offshore locations. Significant amounts of Mn as exchangeable forms has been reported by several others (eg. Tessier et al. 1980, McIsaac et al. 1982), so our results are in agreement with the generally observed lability of Mn in aquatic systems. The organically-bound phase was an important part of the

total amounts of Cd, Cu, Mn, Pb and Zn. Large amounts of organically bound Cu appear to be common due to the high stability constants of organic-Cu complexes (Stumm and Morgan 1970). The abundance of Cd in the organic phase is unusual; Tessier et al. (1980) and Lum and Edgar (1983) found large amounts of Cd in the exchangeable and carbonate phases, but only negligible quantities in the organic fraction.

The proportion of all metals in the residual fraction is much greater in the lake sediments sampled in this study, and the first 3 fractions are far less important than in suspended material inside Hamilton Harbour (McIsaac et al. 1982). This is most likely attributable to the adsorption of more available metal forms on the surfaces of small particles which would make up the bulk of suspended material. In coarser lake sediments the residual fraction incorporated within the crystalline structure of mineral particles could be expected to be more significant, especially in a high energy environment where disturbance by waves limits the incorporation of fine particles into the surface sediments in shallow water.

As with total metals, the spatial distributions of relatively available metals (sum of Fractions 1-4) for the most part reflected the sorting of fine-grained materials towards the deeper areas (Figure 3).

However, Fe and Mn showed anomalous distributions, with general northwest to southeast increases in concentration. These increases are attributable to higher values of Fe<sub>4</sub>, Mn<sub>3</sub> and Mn<sub>4</sub> in the southeastern part of the study area and mask the fact that the highest Fe<sub>1</sub>, Fe<sub>2</sub> and Mn<sub>1</sub> values are found at most stations in the far northern part of the area. The latter include most of the stations exhibiting >1% of fine clay particles (<1.0 μm; Table 1) and indicate the importance of size fractionation in determining the areas of dominance of these operationally-defined geochemical phases.

A linkage between sediment grain-size and concentration of at least some metals has been demonstrated in numerous studies cited by Forstner and Wittmann (1983), who suggested that application of a grain-size correction can greatly clarify patterns of contaminant enrichment. Mudroch and Duncan (1986) found that most metals of anthropogenic origin in the sediments of the Niagara River were associated with particles <13 μm in diameter. When we correlated metal concentrations in our samples with sediment fractions below various size ranges, highly significant (p<0.001) relationships were found for total and Fraction 4 concentrations of Cd, Cr, Cu, Ni, Pb and Zn and the proportion of sediment <21 μm in diameter. Among the more labile fractions, Fe<sub>2</sub>, Mn<sub>1</sub>, Mn<sub>2</sub> and Zn<sub>2</sub> were very strongly correlated with the percentage of particles <5.3 μm in diameter. Station averages for



these parameters were corrected for grain-size as described in Forstner and Wittmann (1983). Since no grain-size relationships were found with Fe<sub>1</sub>, Fe<sub>3</sub>, Mn<sub>3</sub>, Zn<sub>1</sub> or Zn<sub>3</sub>, no correction was applied to those data.

Figures 4 and 5 show the grain-size corrected metal concentrations within the study area. In most cases, the highest concentrations were found at Stations 369 and 373, at depths of 5 m on either side of the Burlington Ship Canal, but the distributions further away varied somewhat among elements and geochemical fractions. Although the total metal concentrations were very low at stations 369 and 373, both had very sandy sediment, with very few fine particles (Table 1).

Exchangeable (Fraction 1) iron, manganese and zinc formed more or less distinct plumes extending eastward from the Burlington Ship Canal with the highest concentrations offshore. The extended region of intermediate levels of iron to the northeast suggests an additional source of contaminants near station 360.

Concentrations of carbonate-bound (Fraction 2) metals were highest immediately adjacent to the Burlington Ship Canal, with intermediate levels along the shore in both directions. The distributional patterns

of metals extracted in Fraction 3 also indicated enrichment along the shore, but with an area of high concentration in deeper water opposite the mouth of the ship canal. The large amounts of iron found at stations 360 and 361 again suggest another source of input in addition to Hamilton Harbour.

Stations 369 and 373 had the highest concentrations of all organically bound (Fraction 4) metals in the study area. Sediments in deeper water directly off the Ship Canal appeared to be enriched with Pb, Cd, Cr and Cu. Intermediate levels of Fe and Mn were found along the shore in both directions from the canal, and offshore to the east. High concentrations of Fe, Cr, Cu and Ni at station 379 may represent another local input. The zone of slightly elevated concentrations of certain metals (eg. Cr, Cu, Ni, Zn) directly offshore from the Burlington Ship Canal is consistent with input from Hamilton Harbour, but comparison of the distribution of iron (Figures 4 and 5) with data from Johnson and Matheson (1968) suggests a reduction in the magnitude of the inputs.

### Benthos

The largest numbers and greatest variety of benthic invertebrates occurred in samples from stations adjacent to the Burlington Ship Canal, and to the northeast at depths of 10-20 m. Neither total

abundance nor number of taxa varied in any systematic way with depth, type of substratum or concentration of any metals. Benthic communities were similar to those described from the same area by Nalepa and Thomas (1976) and Barton (1986), with Limnodrilus hoffmeisteri, Tubifex tubifex, Stylodrilus heringianus or Pontoporeia hoyi dominant at most stations. Differences in sampling techniques preclude direct quantitative comparisons, but the common taxa and their distributions were virtually identical to those reported by Johnson and Matheson (1968).

Of the 43 taxa recognized during this study, 15 occurred at 6 or more stations and the distributions of these were examined in detail (Figures 6 and 7). Only 3 taxa (Potamothenis moldaviensis, L. hoffmeisteri and Pisidium casertanum) were distributed independently of depth and, hence, sediment particle size. Shallow water invertebrates included Pagastia, Chironomus (both generally found only at depths <12 m), Heterotrissocladius and Pisidium henslowanum (both restricted to depths <16 m). Five taxa were found mainly at intermediate depths (9-20 m): Potamothenis vejdoskyi, Spirosperma ferox, Asellus racovitzai, Procladius and Micropsectra. The remaining species, I. tubifex, S. heringianus and P. hoyi, were not found, or were distinctly less abundant, at the shallowest stations.

Pearson correlation coefficients ( $r$ ) were calculated between the concentrations of metals (with or without the particle size correction, as described above) and the abundances of these taxa at stations within the depth zones listed above (Table 4). Heterotrissocladus, Procladius, Asellus and S. ferox were not considered due to inadequate numbers of occurrences or lack of variation among counts. The variables were plotted graphically for all correlations which appeared to be meaningful (i.e.  $>0.5$ ) in order to detect spurious relationships. The abundance of each taxon within each depth zone was examined with respect to mean particle size, but no significant relationships were found.

Most correlations between individual taxa and metals were weak, only 28 of 198 exceeded 0.5, of which half were rejected after inspection of the plotted variables. The 14 that remained are about the number that might be expected by chance in such a large matrix, but most of the apparently significant relationships were confined to only certain taxa or metals, especially the organically bound fractions. The abundance of Chironomus at depths of  $<12\text{m}$  was positively related to the concentrations of Fe<sub>4</sub>, Mn<sub>4</sub>, Zn<sub>4</sub>, Ni<sub>4</sub> and Pb<sub>4</sub>. At depths  $>9\text{ m}$ , the number of Tubifex tended to increase with increasing concentrations of Fe<sub>1</sub>, Mn<sub>1</sub>, Cd<sub>4</sub> and Cr<sub>4</sub>, and decrease relative to Mn<sub>3</sub>. Three taxa (Pagastia, P. hoyi, P. casertanum) exhibited strongly negative relationships to Fe<sub>3</sub>. Only 3 other metal fractions showed clear relationships with as many as 2 taxa: Mn<sub>4</sub> and Zn<sub>4</sub>, positive with Pagastia and Chironomus; and Fe<sub>4</sub>, positive with Chironomus, negative

with P. henslowanum. It is more significant that values of  $r$  for a given taxon tended to have the same sign (positive or negative) with all metals. Thus Pagastia, Chironomus and Tubificidae all tended to be more abundant in sediments with high metal content, while the opposite applied to Micropsectra, S. heringianus, P. hoyi and Sphaeriidae.

The apparent responses of these two groupings of animals to different levels of metals are much the same as would be expected relative to organic enrichment (e.g. Cook and Johnson 1974, Lauritsen et al. 1985). This is not unusual in field situations. For example, the areas of Port Hope Harbour which were most heavily contaminated with a variety of heavy metals supported benthic communities dominated by L. hoffmeisteri, T. tubifex, Quistadrilus multisetosus and Chironomus (Hart et al. 1986). Concentrations of Fe, Mn, Zn and Cu in the inner harbor at Port Hope were similar to those at stations 369 and 373 near the Burlington Ship Canal. Chironomus was the most abundant benthic invertebrate in parts of the Keweenaw Waterway where the average concentration of Cu in sediments was 589  $\mu\text{g/g}$  (Kraft and Sypniewski 1981).

In contrast, Chapman et al. (1982a, b) found that S. heringianus was more tolerant of Cd under a variety of experimental conditions than were several tubificids (including T. tubifex and L. hoffmeisteri), and

cautioned against assigning organisms the same 'indicator' status with respect to both organic and inorganic contaminants. These apparent incongruities may represent different threshold responses. In an area of nearshore Lake Superior polluted by copper tailings, there was no clear relationship between numbers of P. hoyi and amounts of sediment copper except that amphipods were found only where concentrations were <395 µg/g Cu (Kraft 1979). Both L. hoffmeisteri and T. tubifex can occur in very large numbers in metal-enriched sediments (eg. Brinkhurst 1970), but actively avoid sediments with 500 µg/g Cu and 1000 µg/g Zn under laboratory conditions (McMurtry 1984). Each of these 'threshold' concentrations is higher than was observed in western Lake Ontario.

Johnson and Matheson (1968) concluded that the distribution of benthic macroinvertebrates in extreme western Lake Ontario reflected the influence of pollution from Hamilton Harbour but did not attempt to distinguish between the effects of organic and metallic contaminants. Barton (1986) found that the composition of benthic invertebrate communities throughout the Ontario nearshore of Lake Ontario was strongly influenced by organic enrichment. We have no data on the organic content of sediments in our study area, so we cannot rule out this factor as a determinant of community structure. Clearly, the distributions of individual taxa were influenced by depth, sediment

texture and, at least in a general way, metal concentrations. It is likely that both metals and organic matter are distributed away from the Ship Canal by similar mechanisms so that the correlations among metal concentrations and abundances of animals merely reflect the biologically more significant distribution of organic pollution. An alternative hypothesis is that sublethal amounts of metals act as a general stress on benthic communities and lead to structural changes similar to those observed in response to excessive nutrient enrichment.

## CONCLUSIONS

This study showed that operationally-defined geochemical phases of heavy metals are important in determining the distributions of heavy metals and benthic macroinvertebrates in Western Lake Ontario sediments. Portions of the metals exported from Hamilton Harbor via the Burlington Ship Canal are deposited in the nearshore zone of western Lake Ontario in plumes which are oriented either directly offshore from the canal, or more or less parallel to shore in either direction. In most cases this was only discernible after applying a grain-size correction to the raw data, but the similar patterns observed for those metals which did not require correction strongly suggests that the areas of apparent metal enrichment are not artifacts of the analysis. Metal - particle size correlations and variations in the shapes of the plumes among the sequentially extracted fractions suggest that different fractions are associated with particles of different sizes. Coarser particles tend to be deposited alongshore, finer ones directly offshore.

The effect of metal enrichment on the distribution of benthic invertebrates was less clear, at least in part because of the small number of Shipek samples available for analyses. Among the commonly and abundantly occurring taxa, depth appeared to have the strongest influence on distributions. Within the appropriate depth ranges,



however, most taxa exhibited consistently positive or negative correlations with concentrations of most metals. The strongest, and most likely significant, correlations were found most frequently with metals bound to organic matter. The apparent responses to metal contamination among the taxa examined were generally similar to those usually associated with organic enrichment. Whether this represents some general response to stress from sublethal amounts of metals, or simply that metals are deposited in the same areas as is organic matter from domestic sewage, is a problem for future research.

## ACKNOWLEDGEMENTS

Chemical extractions and identification and enumeration of benthic invertebrates were performed by Barringer-Magenta Ltd., 304 Carlingview Drive, Rexdale, Ontario, under contract to the Ontario Ministry of the Environment.

## REFERENCES

- Barton, D.R. 1986. Nearshore benthic invertebrates of the Ontario waters of Lake Ontario. *J. Great Lakes Res.* 12: 270-280.
- Brinkhurst, R.O. 1970. Distribution and abundance of tubificid (*Oligochaeta*) species in Toronto Harbour, Lake Ontario. *J. Fish Res. Bd. Canada* 27: 1961-1969.
- Chapman, P.M., M.A. Farrell and R.O. Brinkhurst. 1982a. Relative tolerances of selected aquatic oligochaetes to individual pollutants and environmental factors. *Aquatic Toxicol.* 2: 47-67.
- \_\_\_\_\_, \_\_\_\_\_ and \_\_\_\_\_ 1982b. Relative tolerances of selected aquatic oligochaetes to combinations of pollutants and environmental factors. *Aquatic Toxicol.* 2: 69-78.
- Cook, D.G., and M.G. Johnson. 1974. Benthic macroinvertebrates of the St. Lawrence Great Lakes. *J. Fish. Res. Bd. Canada* 31: 763-782.
- Cooper, L.R., R.L. Haverland, D.M. Hendriks and W.G. Knisel. 1984. Microtrac particle-size analyzer: an alternative particle-size determination method for sediment and soils. *Soil Sci.* 138: 138-146.
- Forstner, U., and G.T.W. Wittmann. 1983. Metal pollution in the aquatic environment. Springer-Verlag, New York.

Fraser, J.L. and K.R. Lum. 1982. Availability of elements of environmental importance in incinerated sludge ash. *Env. Sci. Tech.* 17: 52-54.

Hart, D.R., P.M. McKee, A.J. Burt and M.J. Goffin. 1986. Benthic community and sediment quality assessment of Port Hope Harbour, Lake Ontario. *J. Great Lakes Res.* 12: 206-220.

Johnson, M.G., and D.H. Matheson. 1968. Macrobenthic communities of sediments of Hamilton Bay and adjacent Lake Ontario. *Limnol. Oceanogr.* 13: 99-111.

Klapwijk, A., and W.J. Snodgrass. 1985. Model for lake-bay exchange flow. *J. Great Lakes Res.* 11: 43-52.

Kohli, B. 1978. Hamilton Harbor physical processes. Ontario Ministry of the Environment (MOE), Water Resources Branch. 53 pp.

\_\_\_\_\_ 1979. Mass exchange between Hamilton Harbour and Lake Ontario. *J. Great Lakes Res.* 5: 36-44.

\_\_\_\_\_ 1984. Hamilton Harbor: physical characteristics. Ontario Ministry of the Environment (MOE), Water Resources Branch. 22 pp.

Kraft, K.J. 1979. Pontoporeia distribution along the Keweenaw shore of Lake Superior affected by copper tailings. *J. Great Lakes Res.* 5: 28-35.

\_\_\_\_\_ and R.H. Sypniewski. 1981. Effect of sediment copper on the distribution of benthic macroinvertebrates in the Keweenaw Waterway. J. Great Lakes Res. 7:258-263.

Lauritsen, D.D., S.C. Mozley and D.C. White. 1985. Distribution of oligochaetes in Lake Michigan and comments on their use as indices of pollution. J. Great Lakes Res. 11: 67-76.

Lum, K.R., and D.G. Edgar. 1983. Determination of the chemical forms of cadmium and silver in sediments by Zeeman effect flame atomic-absorption spectrometry. Analyst 108: 918-924.

McIsaac, G., R. Karim, J.S. Betteridge, R.R. MacDonald and K.R. Lum. 1982. The chemical form and potential availability of trace metals in the southeastern part of Hamilton Harbor. National Water Research Institute. 29 pp.

McMurtry, M.J. 1984. Avoidance of sublethal doses of copper and zinc by tubificid oligochaetes. J. Great Lakes Res. 10: 267-272.

Mudroch, A., and G.A. Duncan. 1986. Distribution of metals in different size fractions of sediment from the Niagara River. J. Great Lakes Res. 12: 117-126.

Nalepa, T.F., and N.A. Thomas. 1976. Distribution of macrobenthic species in Lake Ontario in relation to sources of pollution and sediment parameters. J. Great Lakes Res. 2: 150-163.

Nriagu, J.O., H.K.T. Wong and W.J. Snodgrass. 1983. Historical records of metal pollution in sediments of Toronto and Hamilton Harbours. J. Great Lakes Res. 9: 365-373.

Ontario Ministry of the Environment. 1974. Hamilton Harbour study. Water Resources Branch.

\_\_\_\_\_ 1985. Hamilton Harbour technical summary and general management options. Water Resources Branch.

Palmer, M.D. and D.J. Poulton. 1976. Hamilton Harbour: periodicities of the physiochemical process. Limnol. Oceanogr. 21: 118-127.

Poulton, D.J. 1987. The trace contaminant status of Hamilton Harbour. J. Great Lakes Res. 13: 000-000.

Stumm, W., and J.J. Morgan. 1979. Aquatic chemistry. John Wiley & Sons, New York. 583 pp.

Tessier, A. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51: 844-851.

\_\_\_\_\_ P.G.C. Campbell and M. Bisson. 1980. Trace metal speciation in the Yamaska and St. Francois Rivers (Quebec). Can. J. Earth Sci. 17: 90-105.

**TABLE 1**

**Percentages of Sediments in Various Particle-size Categories in Western Lake Ontario.**

Station	Sand		Silt		Clay	
	>250 µm	62- 250 µm	15- 62 µm	3.7- 15 µm	1.0- 3.7 µm	<1.0 µm
360	25.19	59.92	5.42	6.71	1.84	0.92
361	0.00	0.00	43.58	42.77	10.01	3.64
363	0.00	14.16	43.28	32.68	7.60	2.28
364	0.72	1.84	34.08	48.00	10.56	4.80
365	0.00	85.46	5.71	6.53	1.66	0.64
366	0.00	72.27	10.72	13.50	2.43	1.08
367	0.00	40.85	29.75	23.10	4.72	1.58
368	0.00	22.00	38.22	31.98	6.24	1.56
369	0.00	97.40	1.14	1.23	0.18	0.05
370	0.00	80.50	7.41	9.94	1.56	0.59
371	0.00	54.56	27.96	14.06	2.66	0.76
372	0.00	37.00	47.88	13.23	1.26	0.63
373	1.94	94.91	1.07	1.67	0.32	0.09
374	4.20	70.56	14.36	8.00	2.24	0.64
375	0.00	66.36	23.56	8.16	1.44	0.48
376	0.00	58.00	28.62	10.21	2.26	0.91
377	0.00	45.76	39.99	11.40	1.99	0.86
378	0.00	7.54	55.92	29.58	6.09	0.87
379	0.00	81.94	12.06	4.30	1.16	0.54
380	0.00	9.90	68.26	17.94	3.90	0.00
381	0.00	27.90	53.95	14.30	3.30	0.55
382	0.90	5.30	64.10	24.30	5.40	0.00
383	1.28	1.60	51.04	36.48	7.68	1.92

**TABLE 2**

**Percentages of Total Heavy Metal Concentrations  
in Sequential Extracts 1-5**

Metal	EXTRACT #									
	1		2		3		4		5	
	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
Cd	0.3	1.3	0	0	0	0	67	32	32	33
Cr	0	0	0	0	1.1	3.5	11	7	88	8
Cu	0	0	0.1	0.3	0.2	0.3	40	11	60	8
Fe	0.1	0	0.1	0	0.1	0	1.3	0.7	98.5	0.6
Mn	1.8	3.1	0.02	0.06	8.8	3.9	27	8	62	12
Ni	0.7	1.4	0	0	0	0	7.4	4.1	91.9	45
Pb	0	0	0	0	0	0	24	5	76	5
Zn	0.7	0.3	0.11	0.07	0.6	0.4	20	6	78	6



**TABLE 3**

**Comparison of Trace Metal Concentration ( $\mu\text{g/g}$ ) in  
Sediments from nearshore and offshore  
Western Lake Ontario.**

Metal	Nearshore (this study)		Offshore (K.Lum, unpublished)
	Mean	s.d.	
Cd	0.68	0.50	6.0
Cr	30	19	98
Cu	28	18	104
Mn	616	307	13400
Ni	16	10	110
Pb	29	26	182
Zn	102	59	490

TABLE 4

Coefficients of correlation between common invertebrate taxa and concentrations of various metal fractions.

Indicates significant correlations ( $p \leq 0.05$ )

Station	TAXON										
	S. heringianus	P. moldaviensis	P. vej dovskiy	L. hoffmeisteri	T. tubifex	Pagastia	Chironomus	Microspectra	P. hoyi	P. casertanum	P. henslowenium
1	.377	-.123	.221	.466	.718*	.091	-.038	.300	-.112	.084	.374
2	.283	.337	.306	.423	.231	.360	.325	.249	-.176	.045	-.244
3	-.412	.150	.272	-.188	.049	-.680*	-.243	-.271	-.637*	-.680*	-.456
4	-.154	.410	-.400	-.114	-.462	.477	.686*	-.407	-.226	-.171	-.547*
1	.131	.090	.379	.634	.614*	.449	.381	.589	.207	.155	.245
3	-.498	.269	-.273	-.451	-.686*	.206	.333	-.558*	-.089	-.055	-.252
4	-.294	.450	-.416	-.082	-.469	.519*	.734*	-.506	-.266	-.248	-.505
1	-.345	-.091	-.106	-.152	-.012	.293	.265	-.019	-.027	-.352	-.144
2	.300	.479	.354	.438	.402	.472	.473	.086	-.186	-.228	-.344
3	-.411	.315	.296	.157	.048	-.318	-.193	-.389	-.405	.060	.139
4	-.170	.581	.141	.407	.449	.626*	.627*	-.404	-.206	-.324	-.156
4	.008	.451	.419	.413	.572*	.425	.471	.051	.055	-.344	-.196
4	.113	.345	.659	.370	.591*	.108	.119	.175	-.123	-.387	-.259
4	.196	.461	.381	.268	.551	.217	.447	-.299	-.253	-.456	-.472
4	-.507	.409	.047	.040	-.140	.346	.553*	-.397	-.313	-.461	-.534
4	.242	.403	.089	.437	.511	.520	.539*	-.142	-.222	-.347	-.192



LAKE  
ONTARIO

BURLINGTON

HAMILTON HARBOUR

STELCO

DOFASCO

HAMILTON

QEW

QEW

403

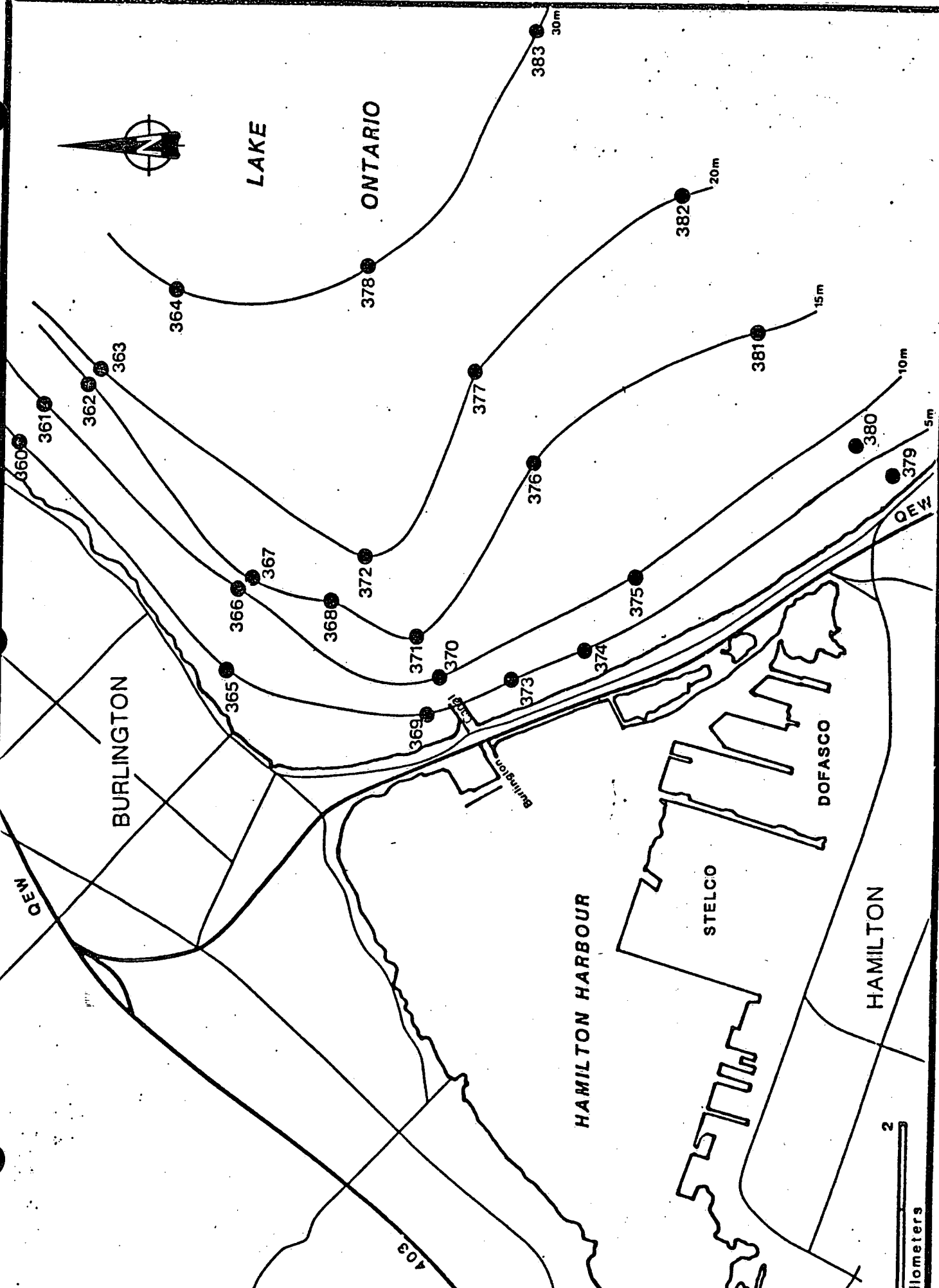
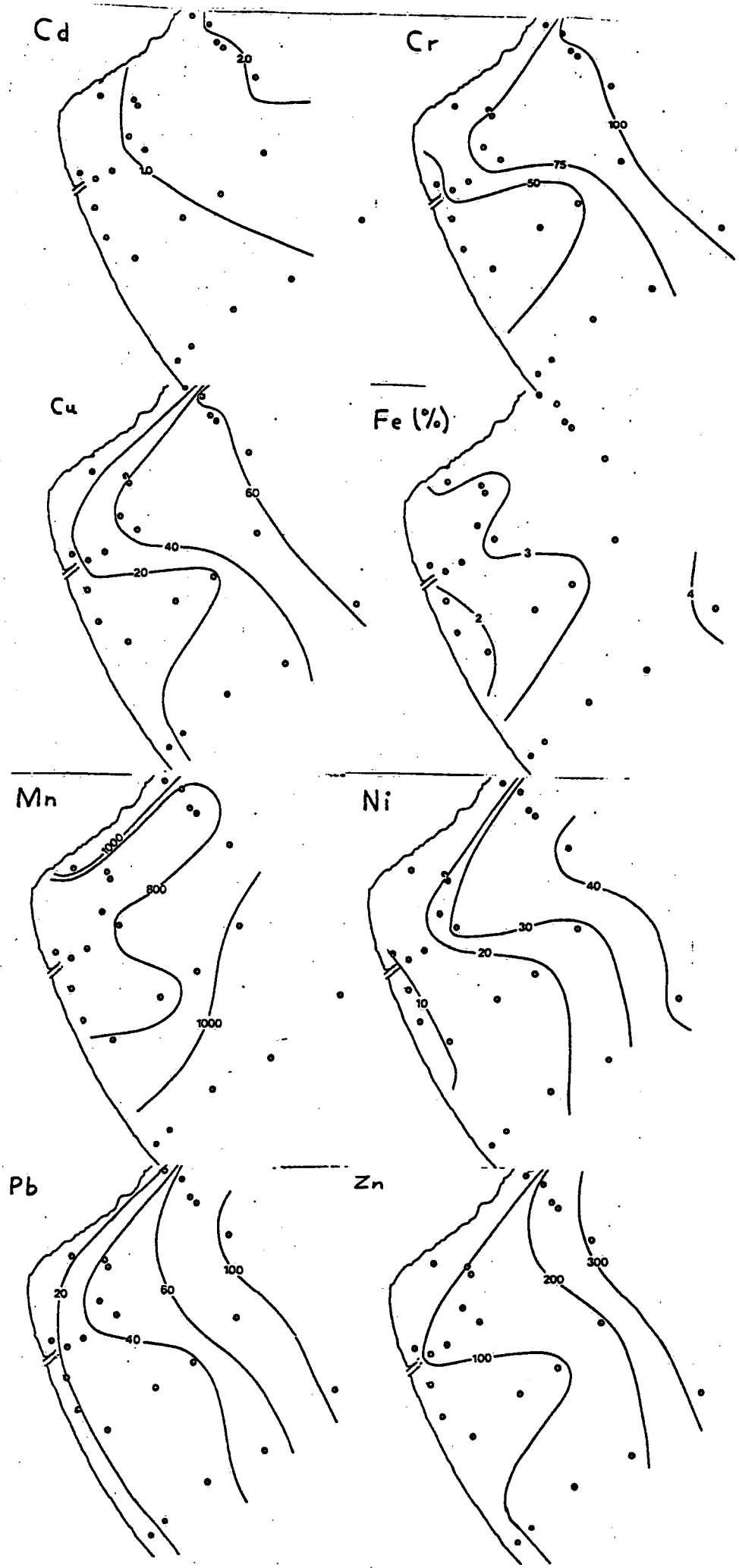
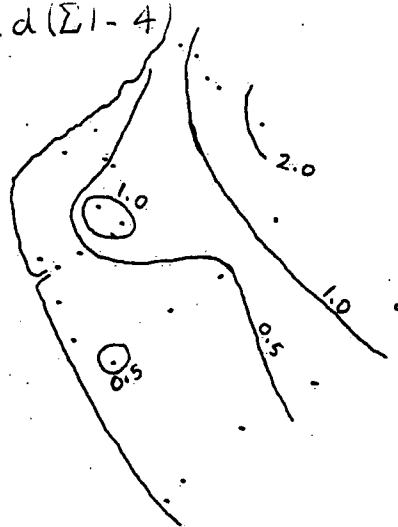


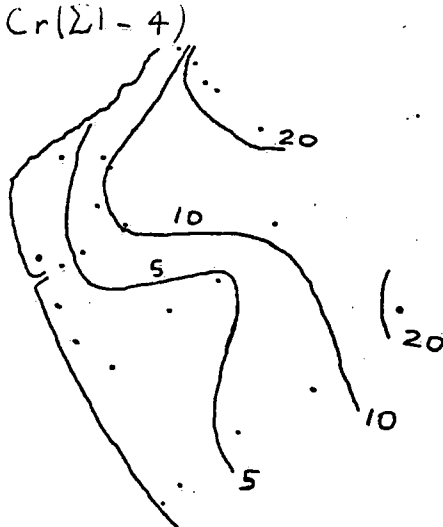
Fig. 2



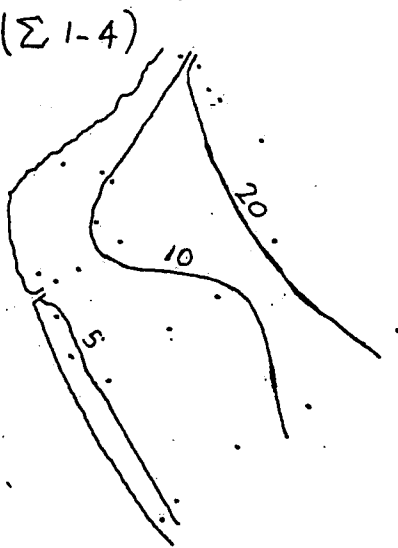
Cd ( $\Sigma 1-4$ )



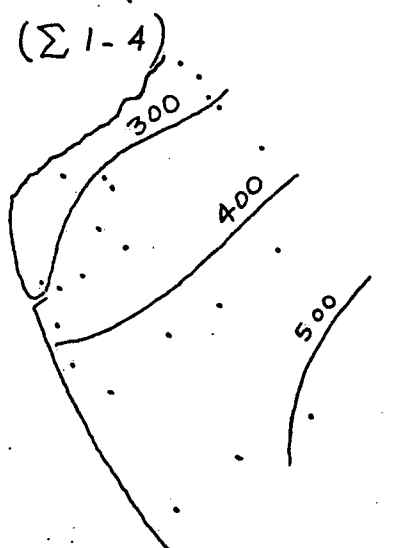
Cr ( $\Sigma 1-4$ )



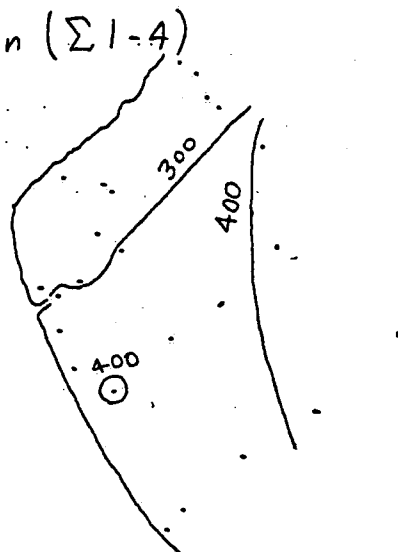
Cu ( $\Sigma 1-4$ )



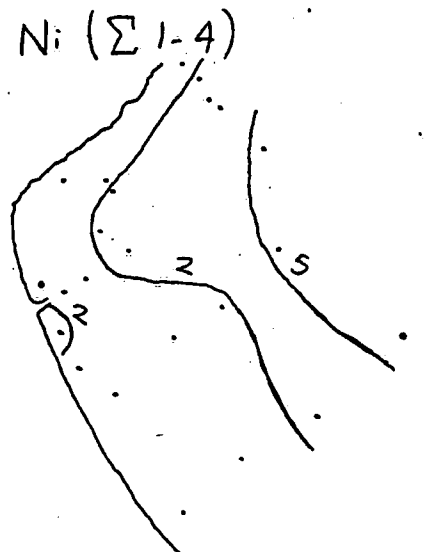
Fe ( $\Sigma 1-4$ )



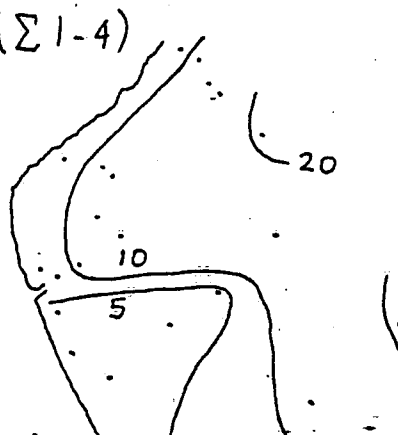
Mn ( $\Sigma 1-4$ )



Ni ( $\Sigma 1-4$ )



Pb ( $\Sigma 1-4$ )



Zn ( $\Sigma 1-4$ )

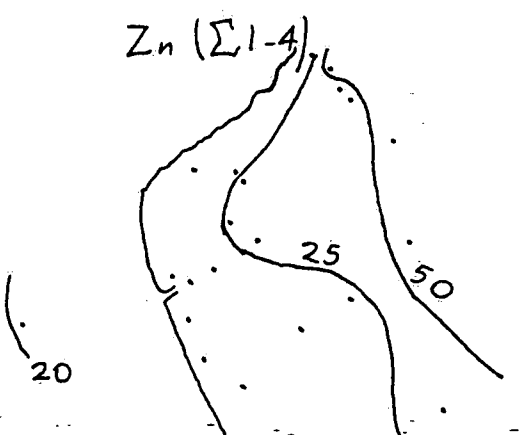


Fig. 4

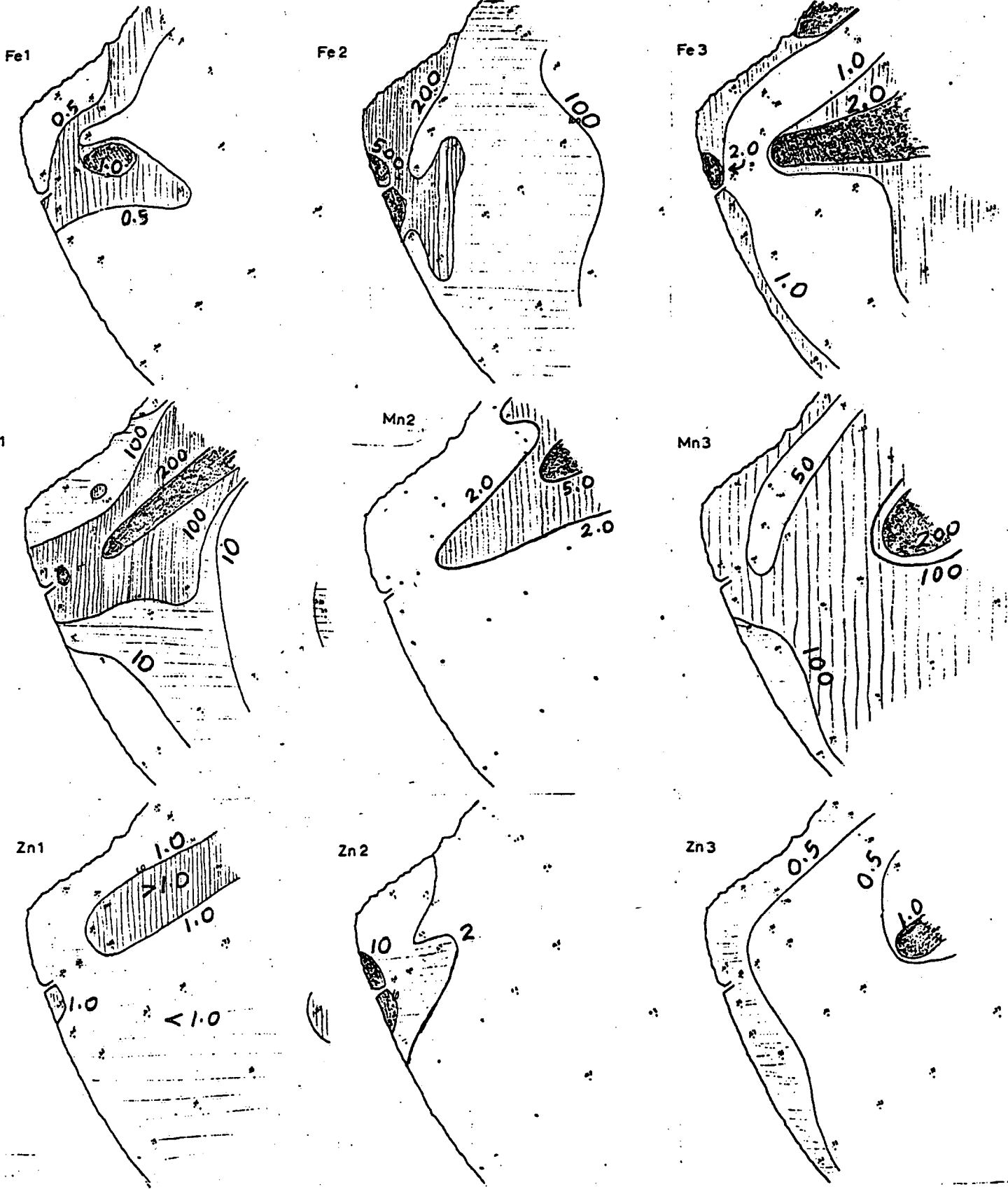
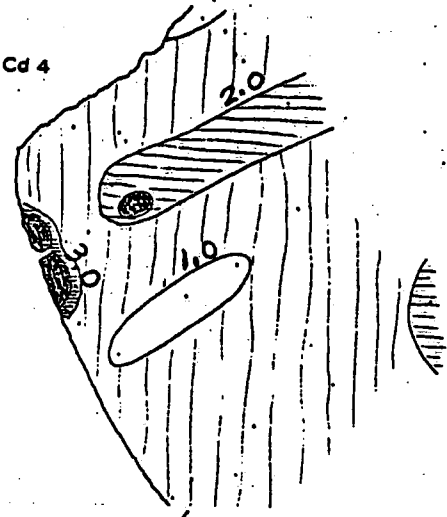
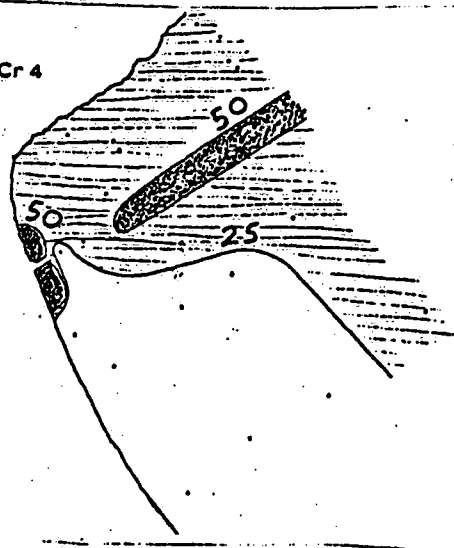


Fig-5

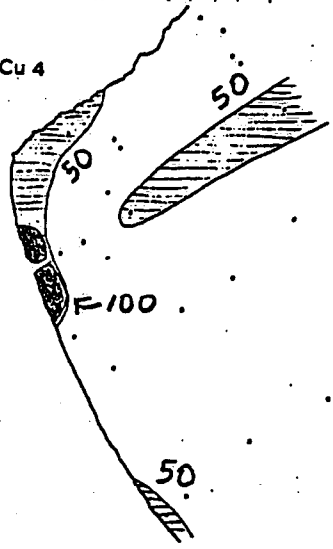
Cd 4



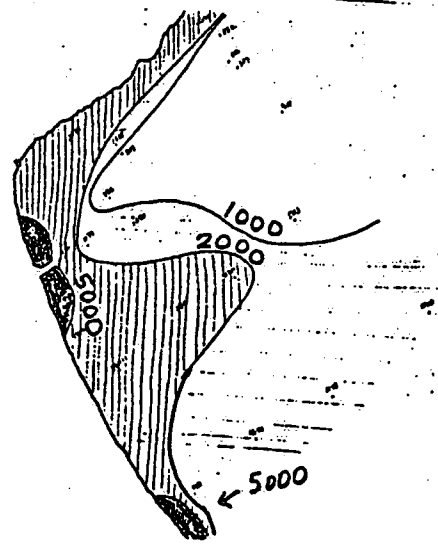
Cr 4



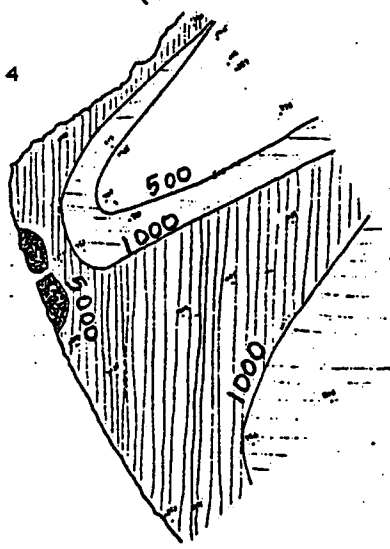
Cu 4



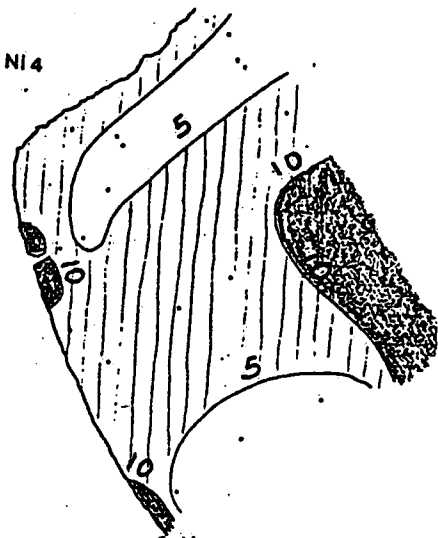
Fe 4



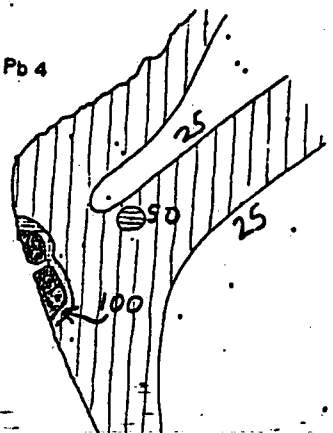
Mn 4



Ni 4



Pb 4



Zn 4

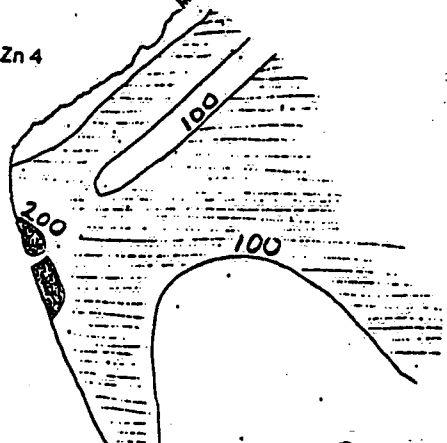
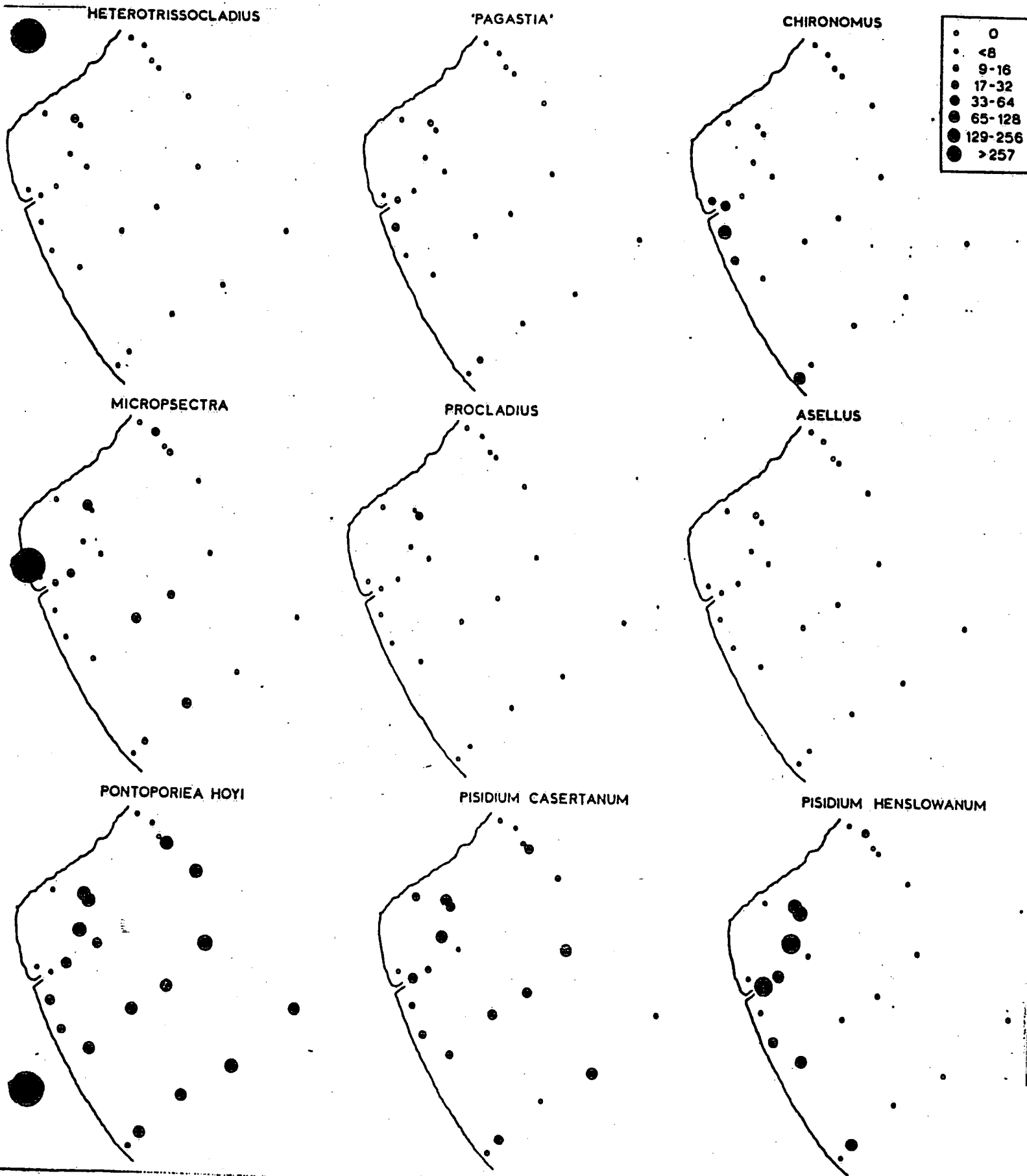


Fig. 6

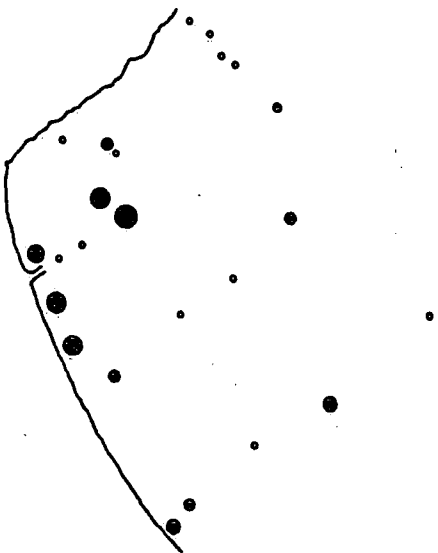




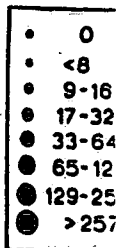
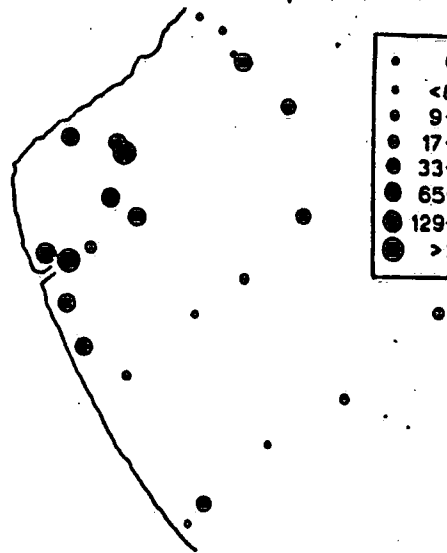
TUBIFEX TUBIFEX



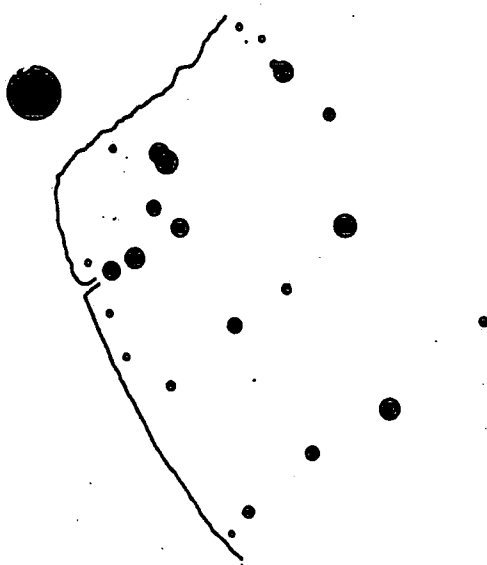
POTAMOTHRIX MOLDAVIENSIS



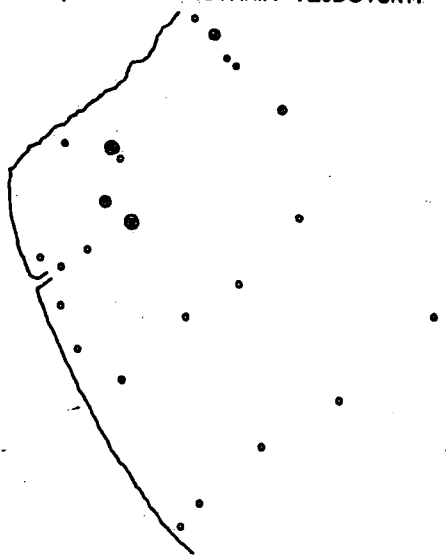
LIMNODRILUS HOFFMEISTERI



STYLODRILUS HERINGIANUS



POTAMOTHRIX VEJDOVSKYI



SPIROSPERMA FEROX

