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Selective scavenging of copper, zinc, and arsenic by iron and manganese oxyhydroxide coatings on plankton in lakes polluted with mine and smelter wastes: Results of energy dispersive x-ray micro-analysis

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SELECTIVE SCAVENGING OF COPPER, ZINC, AND ARSENIC BY IRON AND MANGANESE OXYHYDROXIDE COATINGS ON PLANKTON IN LAKES POLLUTED WITH MINE AND SMELTER WASTES: RESULTS OF ENERGY DISPERSIVE X-RAY MICRO-ANALYSIS

Togwell A. Jackson and Thomas Bistricki[1]

Lakes Research Branch, National Water Research Institute, Canada Centre for Inland Waters, P.O. Box 5050, Burlington, Ontario L7R 4A6, Canada

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[1] Present address: 2704 - 555 Sherbourne St., Toronto, Ontario M4X 1W6, Canada.

MANAGEMENT PERSPECTIVE

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The powerful technique of energy dispersive X-ray micro-analysis, which permits elemental analysis of microscopic objects such as algal cells individually, was used in conjunction with more conventional analytical methods to investigate the accumulation of potentially toxic heavy metals and metalloids by different kinds of planktonic organisms. Micro-analyses were performed on plankton samples from several lakes polluted with smelter fallout and (in one case) tailings pond effluent. Sediment samples from the same lakes were analysed in detail for a wide range of constituents and physicochemical characteristics using various other methods. The source of pollution was a base metal mining and smelting complex at Flin Flon, Manitoba. Possible practical applications of the research results to problems of pollution prevention and abatement were examined and discussed.

The paper demonstrates that iron and manganese oxide coatings on hard parts of various planktonic organisms readily scavenged heavy elements such as copper, zinc, lead, and arsenic from the surrounding water. Adsorption of the trace elements was a selective process, as iron and manganese oxides differed from one another in their affinities for particular elements. Thus, iron oxide preferentially bound copper and arsenic, whereas manganese oxide preferentially accumulated zinc; consequently, variations in iron/manganese ratios in the surface coatings gave rise to variations in trace element ratios, and the concentrations of trace elements depended on the concentrations of oxide surface deposits. The sedimentary environment - in particular, oxidation-reduction conditions and sulfide concentrations - controlled the bio-accumulation of heavy metals by determining (1) the solubility and availability of the metals in the sediments and (2) the absolute and relative abundances of iron and manganese oxide coatings deposited on plankton surfaces. The lake that is contaminated with tailings pond effluent also receives municipal sewage effluent, which engenders dense algal blooms; the remains of dead algae together with sulfate from the tailings create highly reducing, sulfide-rich bottom conditions. The result of this combination of circumstances is that the metals in the bottom sediments, though much more abundant than in the other lakes, were found to be much less bio-available; accordingly, the plankton of this lake was anomalously poor in oxide deposits and heavy metals.

The results of the study suggest that iron and manganese oxide coatings on armoured surfaces of plankton play an important role in the biogeochemical cycling of heavy metals. They efficiently remove the metals from water and convey them to the bottom as the carrier particles settle out. This process may render the metals less toxic to plankton but could also promote the uptake of metals by animals which feed on plankton. In any event, the observed phenomena could conceivably be applied to problems of pollution control - for instance, in the design of settling ponds for efficient removal of metals from industrial effluents. Thus, a pond that is fertilised with sewage effluent (a cheap, widely available, and limitless source of nutrients) together with sulfate, has dense plankton blooms (including species such as euglenophytes which, as observed in this study, characteristically possess abundant oxide coatings), is deep enough to undergo thermal stratification, has anoxic bottom water, and has highly anoxic, sulfide-rich sediments should be particularly efficient in trapping and retaining heavy metals. Finally, the study demonstrated the advantages of energy dispersive X-ray micro-analysis and the importance of integrating micro-analytical data with a wide spectrum of relevant information on the ecosystem and conditions and processes that control the biogeochemical pathways of metals.

ABSTRACT

The technique of energy dispersive X-ray micro-analysis was used along with more conventional methods to investigate the accumulation of heavy metals and other elements by various planktonic organisms in three Canadian Shield lakes polluted with Cu, Zn, and SO_4^{2-} and smaller amounts of Cd, Pb, and As from a base metal mine and smelter. The results showed that appreciable quantities of Cu and Zn were bound to exoskeletons of crustaceans, loricae of the rotifer *Keratella*, and loricae of the euglenophytes *Trachelomonas* and *Strombomonas*; euglenophyte loricae also contained As and Pb. The trace elements were associated with Fe and Mn, implying that Fe and Mn oxyhydroxides deposited on the organisms' armour had scavenged them from the water. Moreover, the inferred FeOOH and MnOOH phases discriminated between different elements, Zn being selectively bound by MnOOH whereas Cu and As were bound by FeOOH. The adsorbed Cu and Zn were associated with S to a significant degree only in the lake whose sediments had the lowest sulfide content, suggesting that the metals were complexed by thiol compounds secreted by organisms as a defense against metal toxicity wherever environmental sulfide levels were too low to provide protection. The Fe, Mn, Zn, and Cu concentrations and Mn/Fe and Zn/Cu ratios of plankton hard parts decreased with the Eh of the bottom sediments irrespective of total metal concentrations in the sediments. Fe and Mn released into solution from anaerobic but sulfide-poor sediments presumably precipitated as FeOOH and MnOOH on surfaces of planktonic organisms wherever the water was sufficiently aerated, the MnOOH/FeOOH ratio - and hence the Zn/Cu ratio - increasing with ambient O_2; but strongly reducing conditions and H_2S production in sediments interfered with the formation of both FeOOH and MnOOH, Fe precipitating as FeS in the sediments whilst Mn remained in solution. Sulfides inhibited bio-accumulation of Cu and Zn, both by hindering the formation of FeOOH and MnOOH coatings and by suppressing the release of dissolved Cu and Zn from the sediments. The Cu, Zn, Fe, and Mn concentrations and Zn/Cu and Mn/Fe ratios of plankton hard parts *and* the concentrations of *bio-available* (DTPA-extractable) Cu and Zn in the sediments were lowest in a lake whose sediments had aberrantly low Eh and high sulfide levels because of (a)

algal blooms produced by sewage effluent and (b) an ample supply of SO_4^{2-}, even though the sediments of this lake had the highest *total* Cu and Zn content. In brief, our data support the following general conclusions: (1) FeOOH and MnOOH are deposited on exposed surfaces of a wide range of plankton hard parts in different freshwater environments; (2) the FeOOH and MnOOH coatings are important scavengers of trace elements and provide the principal means whereby plankton hard parts accumulate these elements; (3) FeOOH and MnOOH have different trace element affinities, thus affecting the proportions as well as the quantities of the elements bound to the plankton; (4) the accumulation of trace elements by plankton is controlled by environmental factors such as Eh, sulfides, and O_2, because they determine the abundance and proportions of the FeOOH and MnOOH deposits and affect the solubility and bio-availability of sediment-bound trace elements; (5) rates of heavy metal uptake by plankton depend on metal speciation, which varies with environmental factors, and may be independent of total metal abundance in the sediments; and (6) heavy metal bio-availability and toxicity are limited primarily by sulfides produced in sediments, or, if these are lacking, by special thiol compounds produced by the plankton itself. These conclusions have significant implications for the cycling and ecological effects of toxic and nutritional trace elements and for the monitoring, abatement, and prevention of water pollution due to mining, smelting, and other industrial activities.

INTRODUCTION

The scavenging of heavy metals by plankton and its nonliving products (such as loricae, moulted exoskeletons, and faecal pellets) in lakes and oceans is probably of considerable biogeochemical and ecological importance, and it has implications for the monitoring and control of pollution (Fowler, 1977; Jackson, 1978, 1988, 1991; Subramian, 1978; Bistricki and Munawar, 1982; Lindahl *et al.*, 1983; Suder and Wightman, 1983; Showell and Gaskin, 1992). However, the phenomenon is only superficially understood, as it is extremely complex and poses serious technical difficulties for those who would investigate it in depth. Plankton consists of many different kinds of organisms which may differ widely in their tendency to accumulate, exclude, or excrete particular metals, and its taxonomic makeup varies greatly through time and space in response to variations in environmental conditions; mechanisms of metal bio-accumulation vary, ranging from passive adsorption to active uptake and assimilation (from food as well as water); and factors such as nutrient levels, temperature, and light intensity, by controlling the organisms' growth, reproduction, metabolic rates, and biomass, influence the uptake and excretion rates of metals and the concentrations of metals in the plankton. The uptake and retention of a metal by an organism are also regulated by other phenomena, notably metal speciation, which varies with environmental factors; the binding of the metal by nonliving particles and complexing agents such as humic matter and biogenic chelators, which may impede or promote bio-accumulation of the metal; and synergistic and antagonistic interactions with other metals.

There is indirect evidence that the ability of plankton to bind heavy metals depends largely on the species composition of the plankton (Briand *et al.*, 1978; Jackson, 1978), but proof of such specificity appears to be lacking. The purpose of the present study was to seek direct evidence for preferential accumulation of particular heavy metals by specific members of natural plankton communities in metal-polluted lakes. As chemical analysis of bulk plankton samples by conventional methods is incapable of determining the composition of individual components of the plankton, the technique of energy dispersive X-ray microanalysis was employed. Though subject to limitations, difficulties, and uncertainties of its own, this powerful, refined method offers the salient advantage of allowing different identifiable components of heterogeneous mixtures of microscopic organisms and particles to be analysed *individually* for a wide range of elements (Bistricki and Munawar, 1982; Lindahl *et al.*, 1983). Information on environmental conditions and processes, contaminant levels, and metal speciation in the lakes was acquired by ordinary methods of analysis. A brief account of our findings has been published elsewhere (Jackson and Bistricki, 1993); here the results of our research are discussed more fully.

FIELD SITES, MATERIALS, AND METHODS

The samples were collected from Hamell Lake (HL), West Nesootao Lake (WNL), and the Northwest Arm of Schist Lake (NWSL), which are located in the Boreal forest zone of the Canadian Shield near a base metal mine and smelter at Flin Flon, Manitoba (Canada). (For a map of the field area, see Fig. 14.1 of Jackson (1984)). On a molar basis, the principal pollutants from the mining and smelting complex are Zn, Cu, and SO_4^{2-} with smaller quantities of Cd, Pb, and As (Franzin, 1984). The lakes have been polluted with smelter fallout, and NWSL also receives tailings pond effluent and municipal sewage effluent, which gives rise to dense algal blooms. Unlike the other lakes, NWSL has sulfide-rich sediments owing to ample supplies of decomposing organic matter and SO_4^{2-} (Jackson, 1978, 1984).

The field work was done during 24-25 July, 1979. Plankton was sampled by collecting epilimnion water from offshore sites and pouring it through a 10 μm net; HL and NWSL water was collected by lowering a flexible plastic tube to depths of 4 and 5 m respectively, but at the WNL site, where the water was only 1.5 m deep, a van Dorn bottle was used. The depth, pH, and conductivity of the water, and water temperatures at different depths, were recorded for each sampling site, and the surficial bottom sediments, which were very fine-grained, were sampled with an Ekman dredge. Some characteristics of the water and sediments are summarised in Table 1; also see Jackson (1984).

The laboratory work was started immediately after sample collection. The plankton samples were frozen in 99% ethanol at -40°C, freeze-dried, and kept at room temperature, and the sediments were stored at 4°C. Replicate samples of sediment and pore water were analysed for a wide range of properties using methods described elsewhere (Jackson, 1984). Energy dispersive X-ray microanalyses were done during the period 1980-1982. Freeze-dried plankton specimens were dispersed in water, collected on Nuclepore filters of various pore sizes down to 0.45 μm, air-dried at room temperature, coated with C in a vacuum evaporator, and examined and analysed using an AMR-1000 scanning electron microscope equipped with a Tracor-Northern TN-11 analytical system (Bistricki and Munawar, 1982). The electron beam was focused on a selected spot on the surface of each specimen, the resulting X-ray spectrum was printed as a series of peaks on chart paper, and element abundances were estimated by measurement of peak heights with respect to the baseline, the values being expressed as counts/sec normalised to a 240 sec lifetime. A few analyses were also performed with a Philips-505 scanning electron microscope and EDAX 9100/60 X-ray micro-analysis system, which estimated elemental composition automatically. A 20 kV electron beam was used in all analyses. The plankton specimens analysed comprised (1) chitinous exoskeletons of crustaceans and particles identified with a greater or lesser degree of confidence as fragments thereof (Fig. 1, A-E); (2) chitinous loricae of the rotifer *Keratella* (Fig. 2A), which were found only in NWSL and WNL; (3) Mn- and Fe-impregnated "pectic" or "mucilaginous" loricae of the euglenophyte genera *Trachelomonas* and *Strombomonas* (Bold and Wynne, 1985; Dunlap and Walne, 1985) (Fig. 2, B & C), which were found only in HL; and (4) a siliceous chrysophyte cyst (statospore) from HL (Fig. 2D). Five to seven crustacean remains and two to four *Keratella* loricae were analysed per lake, but only single analyses are available for the other specimens. Two *Strombomonas* specimens from HL were analysed, but the two sets of data are not comparable because they were generated by different instruments. Typical examples of sample and background spectra are shown in Fig. 3.

RESULTS AND DISCUSSION

All plankton samples contained measurable quantities of Cu and Zn, but few had detectable As or Pb, and none had detectable Cd. Micro-analysis of remains of crustacean exoskeletons revealed a significant positive correlation between Cu and Fe in each lake (Table 2), and the data for all three lakes conform to a single highly significant regression line (Fig. 4A); suspended algal cells and mineral grains in the Wabigoon River, Ontario showed a similar relationship (Jackson and Bistricki, unpublished data). In contrast, Zn increased with increasing Fe only up to a critical Fe concentration, then dropped abruptly almost to the detection limit and leveled off (Fig. 4B). Cu had a much weaker affinity for Mn than for Fe (Table 2, Fig. 4C; compare Fig. 4A), but Zn showed a strong positive correlation with Mn (Table 2; Fig. 4D; compare Fig. 4B). The Zn/Cu ratio varied in essentially the same way as Zn concentration with respect to the Mn and Fe concentrations (Fig. 5A, 5B). The close association of Zn with Mn suggests that the complex relationship between Zn and Fe was a secondary manifestation reflecting variation of Mn as a function of Fe (Fig. 6; compare Fig. 4B). In brief, the data demonstrate a specific affinity between Cu and Fe and between Zn and Mn, and this applies to all three lakes, both individually and collectively. Cu and Zn in *Keratella* loricae gave similar patterns of variaton with respect to Fe and Mn, making allowances for the fact that their Fe content fell within the range of concentrations in which Zn and Fe were positively correlated (Fig. 7, 8). The observed relationships are not limited to chitinous material, as the data for a *Strombomonas* lorica conformed to the same trends as data for crustacean remains (Fig. 9). Note, however, that the *Strombomonas* lorica was richer in Fe and Mn, and therefore richer in Cu and Zn, than the crustacean remains; for that reason, presumably, it was the only specimen in which Pb was detected (not shown). Another point of interest is that HL, whose sediments were poorest in free, or volatile, sulfide (H_2S), was the only lake in which the Zn bound to crustacean exoskeletons was associated to a significant degree with S (Table 2; Fig. 10). Among the crustacean specimens from the three lakes as a whole, the correlation coefficients representing the affinity of Cu and Zn for S increase progressively as the free sulfide content of the sediment decreases (Fig. 11). The percentages of the total sedimentary Cu and Zn that were extractable with the chelating agent DTPA also increase with decreasing free sulfide concentration (Fig. 12), demonstrating that sulfides depress the bioavailability of the metals. (Note: The plots in Fig. 12 include data for Phantom Lake, which is situated near the other three lakes (Jackson, 1984)). These observations suggest that much of the Cu and Zn bound to hard parts of plankton is in the form of complexes of thiol compounds such as metallothioneins and phytochelatins (Gekeler *et al.*, 1988; Robinson, 1989) released into the water by aquatic organisms as a defense against metal toxicity wherever environmental sulfide levels are too low to provide adequate protection by immobilising the metals in the bottom sediments.

Analysis of plankton hard parts yielded only scant information about As, but the available data indicate a strong affinity between As and Fe (Fig. 13). Detectable As occurred in the Fe-rich *Trachelomonas* and *Strombomonas* loricae in HL plankton but not in the associated Fe-poor chrysophyte cyst (Fig. 13).

The accumulation of Cu, Zn, Pb, and As by hard parts of plankton can be attributed to adsorption by, and coprecipitation with, Fe and Mn oxyhydroxide coatings precipitated on the armoured surfaces of the organisms as spatially separated phases. Oxyhydroxide deposits are known to occur on loricae of *Trachelomonas* (Dunlap and Walne, 1985; Dunlap *et al.*, 1983) and exoskeletons of aquatic insects (Cain *et al.*, 1992; Hare, 1992); the ability of oxyhydroxides to adsorb trace elements is well established (Jenne, 1968; Lee, 1975); and there is evidence that oxyhydroxide coatings on aquatic insects scavenge trace elements from water (Cain *et al.*, 1992; Hare, 1992). Our data suggest, moreover, that the adsorbed Cu and Zn species include thiol complexes as well as inorganic ions. A particularly interesting result of our research is the evidence that the FeOOH and MnOOH phases discriminate between different trace elements, FeOOH accumulating Cu and As in preference to Zn whereas MnOOH preferentially binds Zn. Selective adsorption of elements has also been observed in Fe- and Mn-enriched phases of Mn nodules (Burns and Fuerstenau, 1966; Calvert and Price, 1970 and 1977), and there is indirect evidence that FeOOH and MnOOH discriminate between different Hg species (Jackson, 1988), suggesting that such effects are common in aquatic environments, although more information is required to explain them. It also remains to be determined whether the precipitation of oxyhydroxides on plankton is a specific epitaxial phenomenon - that is, whether the molecular structure of the biopolymer on which the FeOOH and MnOOH coatings are deposited determines which polymorphs of the minerals are formed. In any case, the data shown in Fig. 9 and 13, though preliminary, suggest that the mucilagenous, or pectic, matrices of euglenophyte loricae provide more favourable surface environments for the precipitation of FeOOH and MnOOH than do the chitinous products of zooplankton and the siliceous cysts of chrysophytes. Accordingly, euglenophyte loricae appear to be particularly effective scavengers of Cu, Zn, As, and Pb.

Relationships between the composition of the plankton specimens and physicochemical properties of the associated bottom sediments and pore water indicate that the Mn, Fe, Zn, and Cu concentrations and Mn/Fe and Zn/Cu ratios of plankton hard parts depend on the oxidation-reduction conditions and abundance of sulfides in the environment. Thus, the Mn/Fe ratios of crustacean exoskeletons increase with the Eh of the sediment (Table 3; Fig. 14), reflecting the fact that Mn is more soluble than Fe under O_2-deficient or reducing conditions. Similarly, Eh correlates positively with the Mn/Fe ratio of the $NH_2OH \cdot HCl$-extractable ("amorphous oxyhydroxide") fraction of the sediment but inversely with the Mn/Fe ratio of the DTPA-extractable ("bio-available") fraction of the sediment and the Mn content of the pore water (Table 3), indicating that Mn is relatively soluble at low Eh whereas Fe remains immobilised as FeOOH or is precipitated as FeS. Consequently, exposure of zooplankton to different oxidation-reduction conditions along a vertical gradient in the water column because of its diurnal migrations or transport by water movements, or as a result of sinking, probably explains the complex relationship between Mn and Fe (Fig. 6), and hence between Zn and Fe (Fig. 4B), in crustacean exoskeletons. The variation in Mn content with increasing Fe is interpreted as follows (going from left to right in Fig. 6): (1) The low levels of both Mn and Fe in most NWSL specimens reflect the extremely reducing conditions and abundant H_2S in the sediments combined with thermal stratification of the water (Table 1) and presumed lack of dissolved O_2 in the hypolimnion; dissolved Mn diffusing into the hypolimnion from the sediments remained in solution, whilst Fe was immobilised as FeS in the sediments. (2) Specimens showing an increase in Mn with increasing Fe had been exposed to anaerobic but H_2S-poor sediments overlain by O_2-rich water; both Fe and Mn were released from the sediment and then precipitated as oxyhydroxides on plankton surfaces in the water. (3) The abrupt drop in Mn content with further increase in Fe demonstrates the combined effect of anaerobic but H_2S-poor sediments and O_2-deficient water; both Fe and Mn were released from the sediment, whereupon most of the Fe precipitated as FeOOH on plankton surfaces, whereas most of the Mn remained in solution.

The effects of sedimentary environment on the accumulation of FeOOH and MnOOH deposits and adsorbed Cu and Zn on surfaces of chitinous plankton hard parts are illustrated in a series of bar diagrams comparing characteristics of samples from the three field sites (Fig. 15-19). NWSL sediment is sharply distinguished from WNL and HL sediments by its anomalously high concentrations of free and bound (volatile and nonvolatile) sulfide and organic matter and its low Eh (Fig. 15). Accordingly, NWSL sediments were deficient in $NH_2OH{\cdot}HCl$-extractable Mn, though rich in $NH_2OH{\cdot}HCl$-extractable Fe, and their $NH_2OH{\cdot}HCl$ extracts had low Mn/Fe ratios (Fig. 16); in contrast, the NWSL sediments were rich in DTPA-extractable Mn and interstitial dissolved or dispersed Mn but had a low DTPA-extractable Fe content (Fig. 16). These results demonstrate weak bonding, preferential solubilisation, and high bio-availability of Mn accompanied by immobilisation of Fe in an unavailable form (probably FeS). The NWSL sediments had the highest total Cu and Zn levels owing to continual loading of Cu and Zn by tailings pond effluent and atmospheric fallout followed by entrapment of the metals in the sediments owing to the combined effects of accumulation by algal blooms, precipitation due to alkaline conditions created by photosynthesis and SO_4^{2-} reduction, and, above all, precipitation of CuS and ZnS by H_2S and coprecipitation with FeS (Fig. 17) (Jackson, 1978). However, the concentrations of DTPA-extractable Cu and Zn were lowest in NWSL (Fig. 17) owing to immobilisation of the metals by sulfides. The NWSL sediment had the lowest Zn/Cu ratio (based on total Zn and Cu content), but its DTPA extracts had the highest Zn/Cu ratios (Fig. 17), showing that Zn was more readily solubilised than Cu. Preferential solubilisation of Zn may may have been due to the dearth of MnOOH in the sediments (Fig. 16) but may also reflect differential partitioning of Cu and Zn between sulfide and organic matter: In NWSL, Cu has a greater affinity for sulfide than Zn does because the standard entropy of CuS exceeds that of ZnS, whereas Zn has a greater affinity for organic matter (Jackson, 1978, 1979). In brief, NWSL sediments, because of their highly reducing, sulfide-rich environment, are distinguished by high Mn solubility, low

Fe solubility, and an "oxyhydroxide" fraction with a low Mn/Fe ratio, as well as low bio-availability of both Cu and Zn, and a high proportion of Zn to Cu in their bio-available metal pool. The situation in the sediments and hypolimnion is reflected in the composition of NWSL crustacean exoskeletons and *Keratella* loricae, which are poor in Fe, Mn, Zn, and Cu and have low Mn/Fe and Zn/Cu ratios (Fig. 18, 19). From inspection, it is obvious that the median Mn, Fe, Zn, and Cu concentration and Mn/Fe and Zn/Cu ratios of the plankton specimens from the three lakes (Fig. 18, 19) decrease progressively with sediment Eh (Fig. 15). We conclude that the reducing conditions and abundance of sulfides in the sediments of NWSL (together with O_2 deficiency in the hypolimnion) interfered with the accumulation of Cu and Zn by the plankton and lowered its Zn/Cu ratio, both by preventing release of dissolved Mn and Fe from the sediments and subsequent reprecipitation as MnOOH and FeOOH on plankton surfaces *and* by depressing the solubility and bio-availability of sediment-bound Cu and Zn. Biodilution of Cu and Zn by the algal blooms of NWSL may also help to explain the low levels of these metals in NWSL plankton specimens. Regarding the bio-availability of sedimentary Cu and Zn as affected by partitioning between sulfides and organic binding agents, note that sulfides appear to be more effective than organic matter in depressing the availability of Cu to crustacean exoskeletons, but with Zn the reverse is true (Table 4). In view of the relationships shown in Fig. 4-9 and the fact that the Zn/Cu ratios of NWSL plankton are low (Fig. 19) despite the high Zn/Cu ratio of the DTPA-extractable fraction of NWSL sediment (Fig. 17), it would seem that the accumulation of Zn and Cu by MnOOH and FeOOH coatings on plankton is mainly controlled by the amounts of MnOOH and FeOOH precipitated on the plankton, although effects of sulfides, organic matter, and other metal-binding agents on Cu and Zn availability undoubtedly play a role as well. The quantities of MnOOH and FeOOH deposited, and the MnOOH/FeOOH ratio of the deposit, depend, in turn, on the Eh and sulfide content of the sediments and, presumably, on the dissolved O_2 and sulfide content of the overlying water; and the Mn/Fe ratio of the oxyhydroxide deposit on the plankton largely determines the Zn/Cu ratio of the plankton.

In conclusion, the scavenging of toxic and nutrient heavy metals and metalloids by oxyhydroxide coatings on planktonic organisms may have an important bearing on the cycling and biological effects of these elements - for instance, by removing the elements from solution and hastening their transfer to the sediments through the settling out of biogenic carrier particles, or accelerating their uptake by animals that feed on plankton; by rendering them less available for bio-accumulation and toxic or beneficial biochemical effects; and by altering the proportions of bio-available elements in natural waters and aquatic food chains. Furthermore, the process could conceivably be applied to problems of pollution control, as in the design of settling ponds for more efficient removal of metals from industrial effluents (see Jackson, 1978); for instance, a pond that is fertilised with sewage effluent and SO_4^{2-}, has dense plankton blooms which include numerous euglenophytes, is deep enough to be stratified, has anoxic bottom water, and has highly reducing sediments rich in free sulfide should be particularly efficient in trapping and retaining heavy metals. Finally, our findings show that utilisation of plankton for pollution monitoring may not be appropriate, as it could give misleading results. Metal concentrations in plankton depend on environmental conditions that control metal speciation and bio-availability and the formation of MnOOH and FeOOH coatings on the organisms, and may vary with the taxonomic composition and biomass of the plankton community. The results of plankton analysis may be unrelated to the total abundance of pollutants in the ecosystem, as in NWSL, where Cu and Zn levels in plankton were lowest owing to depressed bio-availability of these metals and unfavourable conditions for the formation of metal-scavenging FeOOH and MnOOH coatings (and possibly biodilution of metals by plankton blooms), even though the total Cu and Zn concentrations in the sediments were highest in that lake.

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Table 1. Some characteristics of the water and sediments at the sampling sites. Abbreviations: Cond. = conductivity. The pH and conductivity values are medians of three replicate measurements.

Lake	Depth of water (m)	Surface water		Water temp. (°C)		Water stratified (+) or unstratified (−)	H_2S odour present (+) or absent (−)	Comments
		pH	Cond. (μS/cm)	surface	bottom			
Hamell	7	7.05	68	20.2	19.9	−	−	Brown bottom mud.
West Nesootao	1.5	7.20	40	19.7	19.5	−	−	Brown bottom mud with plant fragments. Abundant aquatic vascular plants.
Schist (N.W. Arm)	15	7.20	580	20.3	11.5	+	+	Black, foul-smelling bottom mud.

Table 2. Relationships between Cu, Zn, Fe, Mn, and S in crustacean exoskeleton remains. Explanation of symbols: r = correlation coefficient; P = significance probability.

Lake		Correlation matrix					
		Cu		Zn		S	
		r	P	r	P	r	P
Hamell	Fe	0.893	>0.02, <0.05	0.651	>>0.1	0.721	>0.1
	Mn	0.568	>>0.1	0.897	>0.02, <0.05	0.913	>0.02, <0.05
	S	0.884	>0.02, <0.05	0.989	>0.001, <0.01	-	-
West Nesootao	Fe	0.913	>0.02, <0.05	0.969	>0.001, <0.01	0.868	>0.05, <0.1
	Mn	0.905	>0.02, <0.05	0.980	>0.001, <0.01	0.562	>>0.1
	S	0.861	>0.05, <0.1	0.846	>0.05, <0.1	-	-
Schist (N.W. Arm)	Fe	0.998	<0.001	0.811	>0.02, <0.05	0.282	>>0.1
	Mn	0.641	>0.1	0.989	<0.001	0.399	>>0.1
	S	0.399	>>0.1	0.443	>>0.1	-	-

Table 3. Correlation matrix showing variation of the Mn and Fe content and Mn/Fe ratios of crustacean exoskeletons and various extractable fractions of the sediments as functions of the Eh of the bottom sediments. The regression analyses were performed on median values of data for Hamell Lake, West Nesootao Lake, and Schist Lake (N.W. Arm). Explanation of symbols: r = correlation coefficient; P = significance probability.

		Eh of sediment	
		r	P
Crustacean exoskeletons	Mn/Fe	0.99998	>0.001, <0.01
	Mn	0.966	>0.1
	Fe	0.966	>0.1
$NH_2OH{\cdot}HCl$ extract of sediment	Mn/Fe	0.919	<0.001
	Mn	0.847	<0.001
	Fe	-0.524	>0.05, <0.1
DTPA extract of sediment	Mn/Fe	-0.953	<0.001
	Mn	-0.938	<0.001
	Fe	0.957	<0.001
Mn in pore water of sediment	Mn	-0.862	<0.001

Table 4. Correlation matrix showing variation of the Cu and Zn content of crustacean exoskeletons with respect to the concentrations of bound sulfide and organic matter (estimated as % loss of weight on digestion with H_2O_2) in the bottom sediments. The regression analyses were performed on median values of data for Hamell Lake, West Nesootao Lake, and Schist Lake (N.W. Arm). Explanation of symbols: r = correlation coefficient; P = significance probability.

	Crustacean exoskeletons			
	Cu		Zn	
	r	P	r	P
Bound sulfide in sediment	-1.000	<0.001	-0.898	>0.1
Organic matter in sediment	-0.978	>0.1	-0.998	>0.02, <0.05

FIGURE CAPTIONS

Fig. 1. Electron micrographs of the remains of crustacean exoskeletons from Schist Lake (A, C, D), Hamell Lake (B), and West Nesootao Lake (E). Arrows indicate spots where energy dispersive X-ray micro-analyses were done. The microscopy was performed with an AMR-1000 scanning electron microscope.

Fig. 2. Electron micrographs of a *Keratella* lorica from Schist Lake (A) and a *Trachelomonas* lorica (B), *Strombomonas* lorica (C), and chrysophyte cyst (D) from Hamell Lake. The microscopy was performed with a Philips-505 scanning electron microscope.

Fig. 3. Energy dispersive X-ray micro-analysis spectrum of a *Strombomonas* lorica from Hamell Lake (A) and associated background spectrum (B) (generated by AMR-1000 scanning electron microscope interfaced with Tracor Northern TN-11 analytical system).

Fig. 4. Relationships between Cu and Fe (A), Zn and Fe (B), Cu and Mn (C), and Zn and Mn (D) in remains of crustacean exoskeletons from Schist Lake, Hamell Lake, and West Nesootao Lake. Analyses were done with AMR-1000/TN-11 system.

Fig. 5. Variation of Zn/Cu ratio with respect to Mn (A) and Fe (B) in crustacean exoskeletons in Schist Lake, Hamell Lake, and West Nesootao Lake. Analyses were done with AMR-1000/TN-11 system.

Fig. 6. Relationship between Mn and Fe in crustacean exoskeletons from Schist Lake, Hamell Lake, and West Nesootao Lake. Analyses were done with AMR-1000/TN-11 system.

Fig. 7. Relationships between Cu and Fe (A), Zn and Fe (B), Cu and Mn (C), and Zn and Mn (D) in *Keratella* loricae from Schist Lake and West Nesootao Lake.

Analyses were done with AMR-1000/TN-11 system.

Fig. 8. Variation of Zn/Cu ratio with respect to Mn in *Keratella* loricae from Schist Lake and West Nesootao Lake. Analyses were done with AMR-1000/TN-11 system.

Fig. 9. Relationships between Cu and Fe (A) and Zn and Mn (B) in crustacean exoskeletons and a *Strombomonas* lorica from Hamell Lake. Analyses were done with AMR-1000/TN-11 system.

Fig. 10. Relationship between Zn and S in crustacean exoskeletons from Hamell Lake. Analyses were done with AMR-1000/TN-11 system.

Fig. 11. Correlation coefficients relating Cu to S (A) and Zn to S (B) in crustacean exoskeletons plotted against the free sulfide content of the bottom sediments. The data represent Schist Lake, West Nesootao Lake, and Hamell Lake. Analyses of exoskeletons were done with AMR-1000/TN-11 system.

Fig. 12. Relationships between the percentages of sediment-bound Cu (A) and Zn (B) extracted with DTPA and the free sulfide content of the sediments. The data represent Schist Lake, Phantom Lake, West Nesootao Lake, and Hamell Lake.

Fig. 13. Relationship between As and Fe in euglenophyte loricae and a chrysophyte cyst from Hamell Lake. The analyses were done with the Philips-505/EDAX 9100/60 system.

Fig. 14. Relationship between median Mn/Fe ratios of crustacean exoskeletons and Eh values of sediments in Schist Lake, Hamell Lake, and West Nesootao Lake. Analyses of exoskeletons were done with AMR-1000/TN-11 system.

Fig. 15. The free sulfide (A), bound sulfide (B), and organic content (C) and

Eh values (D) of sediments from Schist Lake, West Nesootao Lake, and Hamell Lake (medians and ranges).

Fig. 16. Mn and Fe data for sediments from Schist Lake, West Nesootao Lake, and Hamell Lake (medians and ranges): $NH_2OH{\cdot}HCl$-extractable Mn and Fe content (A), Mn/Fe ratios of $NH_2OH{\cdot}HCl$ extracts (B), DTPA-extractable Mn and Fe content (C), and Mn concentrations in interstitial water (D).

Fig. 17. Zn and Cu data for sediments from Schist Lake, West Nesootao Lake, and Hamell Lake (medians and ranges): total Zn and Cu content (A), Zn/Cu ratios (B), DTPA-extractable Zn and Cu content (C), and Zn/Cu ratios of DTPA extracts (D).

Fig. 18. Mn and Fe content of crustacean exoskeletons (A) and *Keratella* loricae (B), and Mn/Fe ratios of crustacean exoskeletons (C) and *Keratella* loricae (D), from Schist Lake, West Nesootao Lake, and Hamell Lake (medians and ranges). Analyses were done with AMR-1000/TN-11 system.

Fig. 19. Zn and Cu content of crustacean exoskeletons (A) and *Keratella* loricae (B), and Zn/Cu ratios of crustacean exoskeletons (C) and *Keratella* loricae (D), from Schist Lake, West Nesootao Lake, and Hamell Lake (medians and ranges). Analyses were done with AMR-1000/TN-11 system.

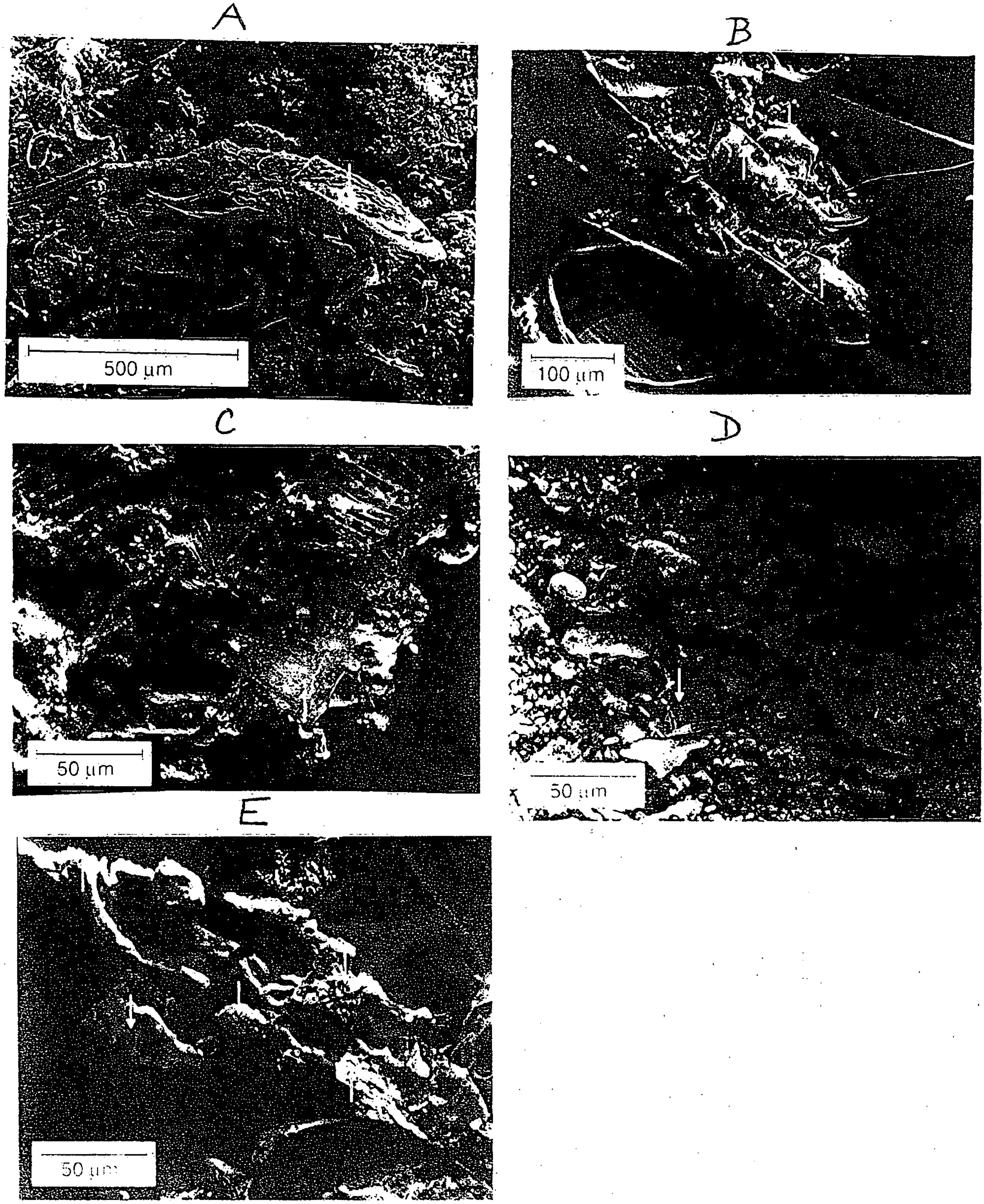


Fig. 1

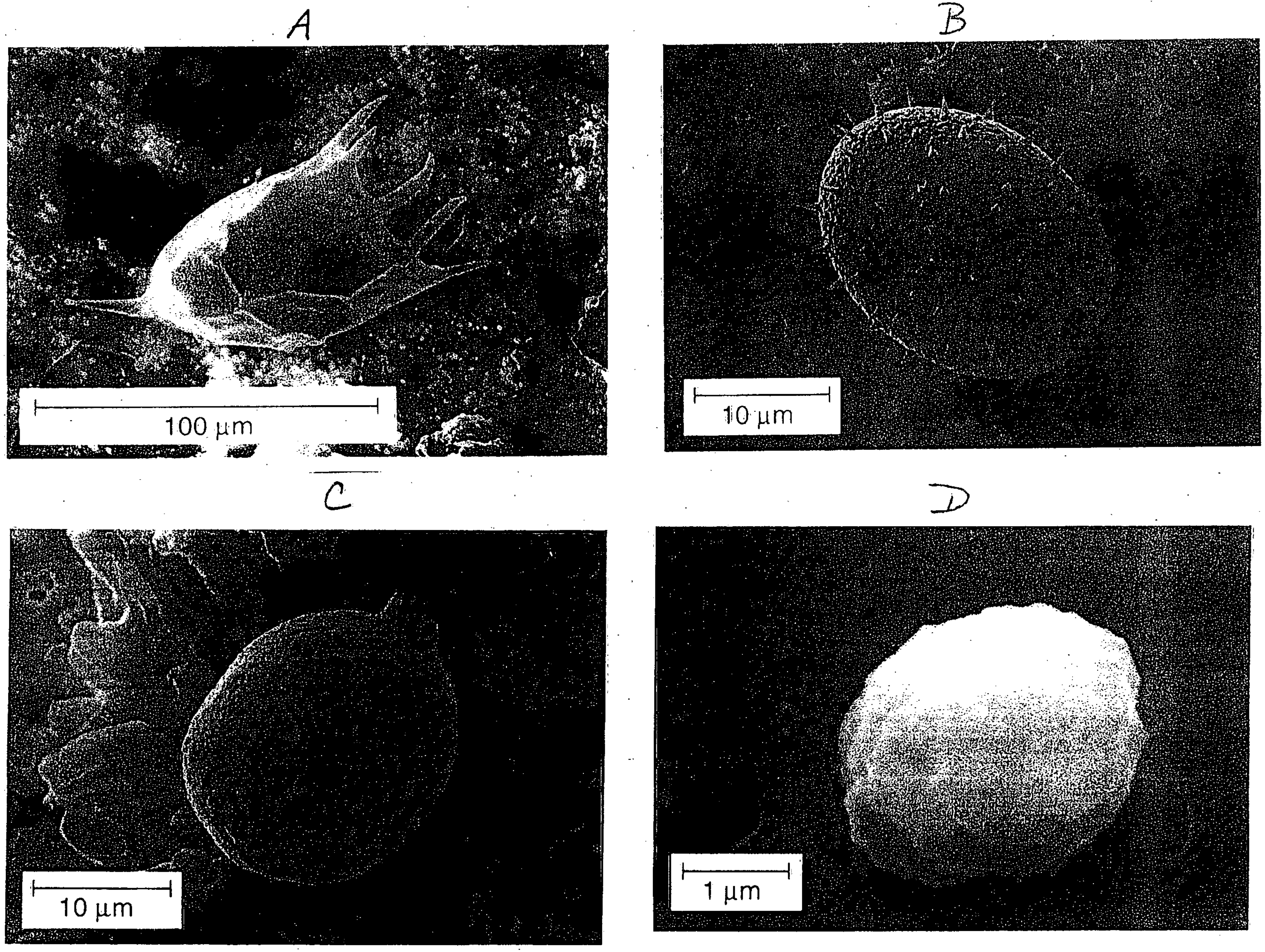


Fig. 2

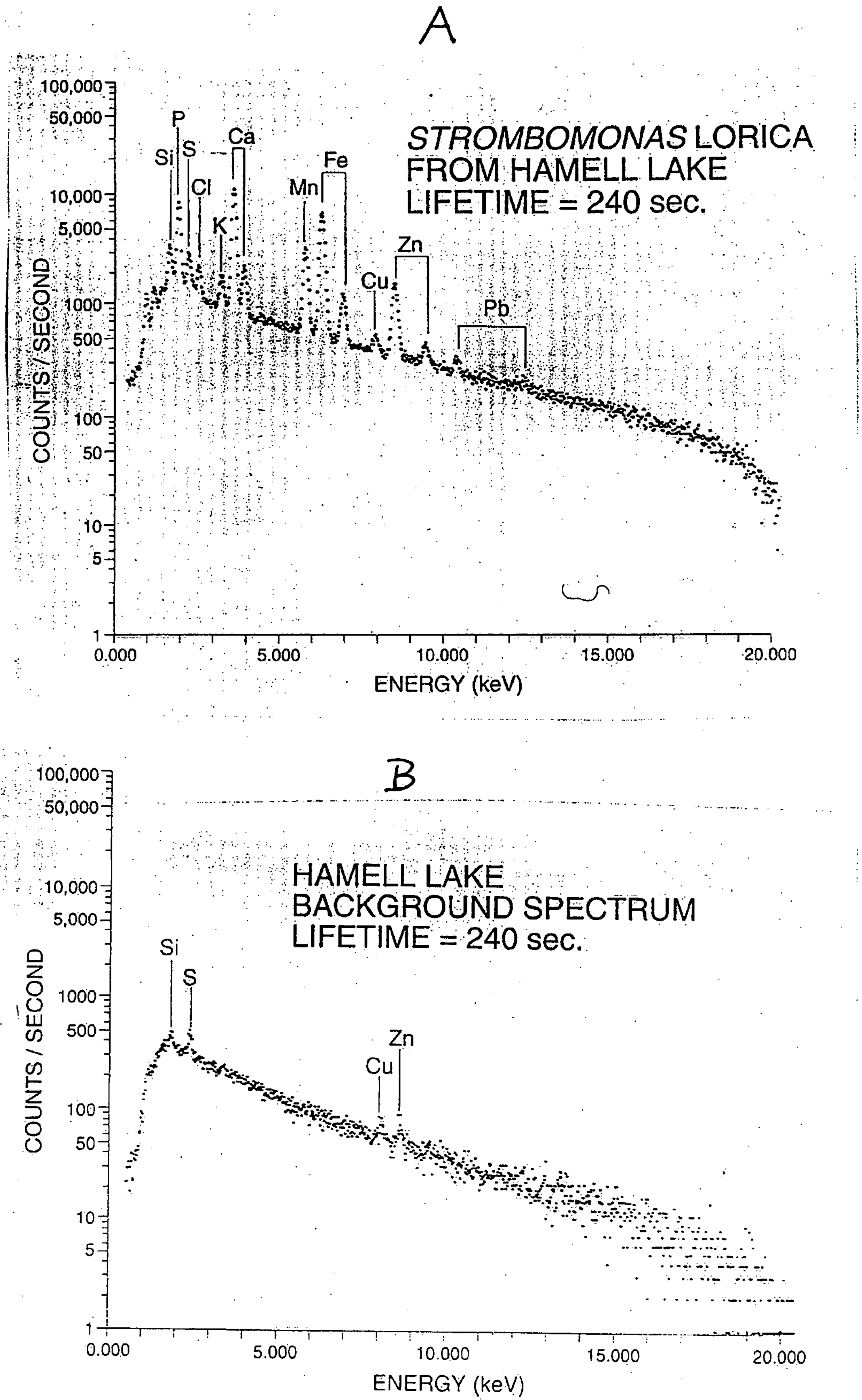

A
STROMBOMONAS LORICA
FROM HAMELL LAKE
LIFETIME = 240 sec.
Si
P
S
Cl
K
Ca
Mn
Fe
Cu
Zn
Pb
COUNTS / SECOND
100,000
50,000
10,000
5,000
1000
500
100
50
10
5
1
0.000
5.000
10.000
15.000
20.000
ENERGY (keV)
B
HAMELL LAKE
BACKGROUND SPECTRUM
LIFETIME = 240 sec.
Si
S
Cu
Zn
COUNTS / SECOND
100,000
50,000
10,000
5,000
1000
500
100
50
10
5
1
0.000
5.000
10.000
15.000
20.000
ENERGY (keV)

Fig. 3

CRUSTACEAN EXOSKELETONS IN SCHIST L. (●), HAMELL L. (■), AND W. NESOOTAO L. (▲)

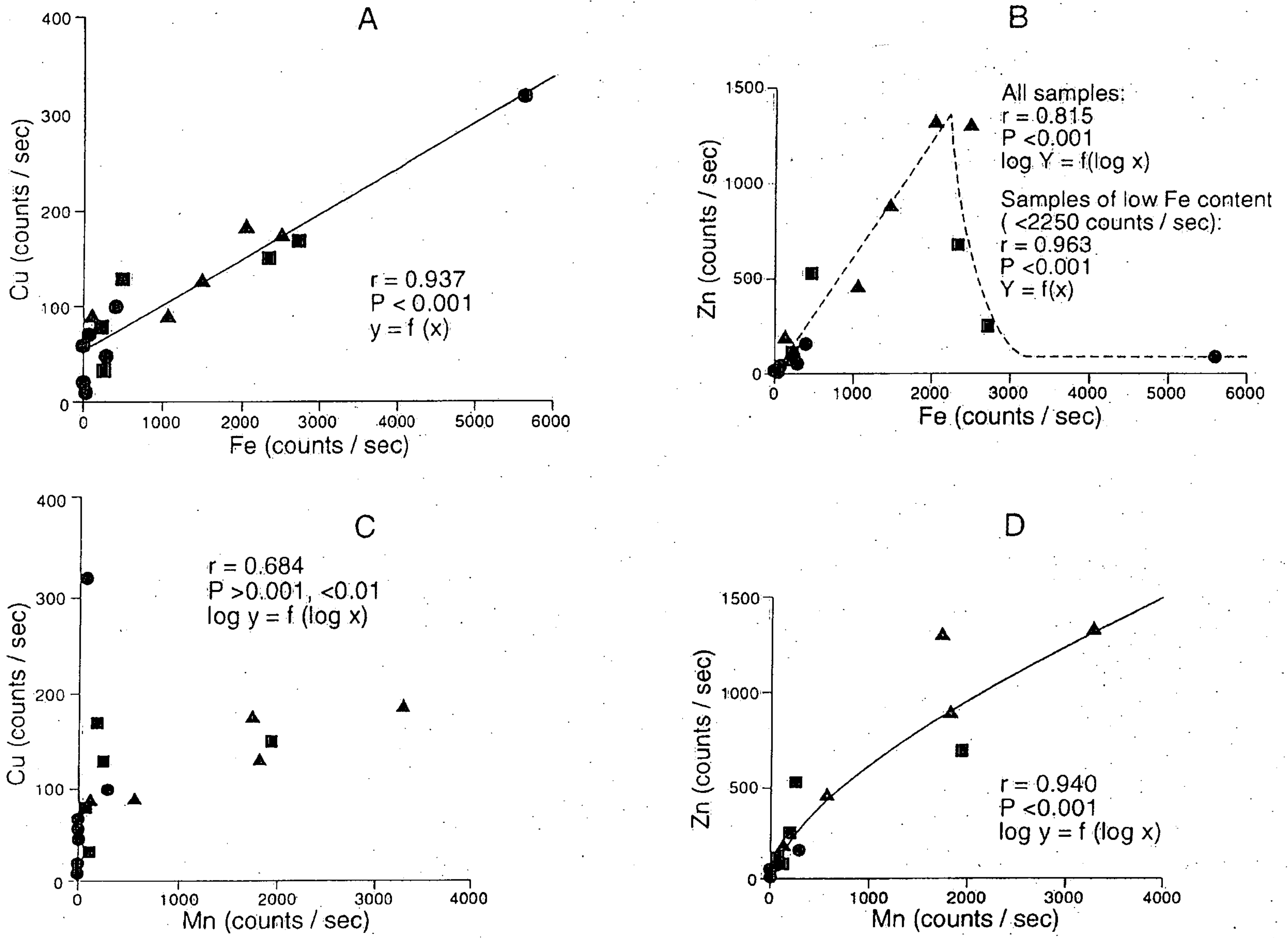


Fig. 4

CRUSTACEAN EXOSKELETONS IN SCHIST L. (●), HAMELL L. (■), AND W. NESOOTAO L. (▲)

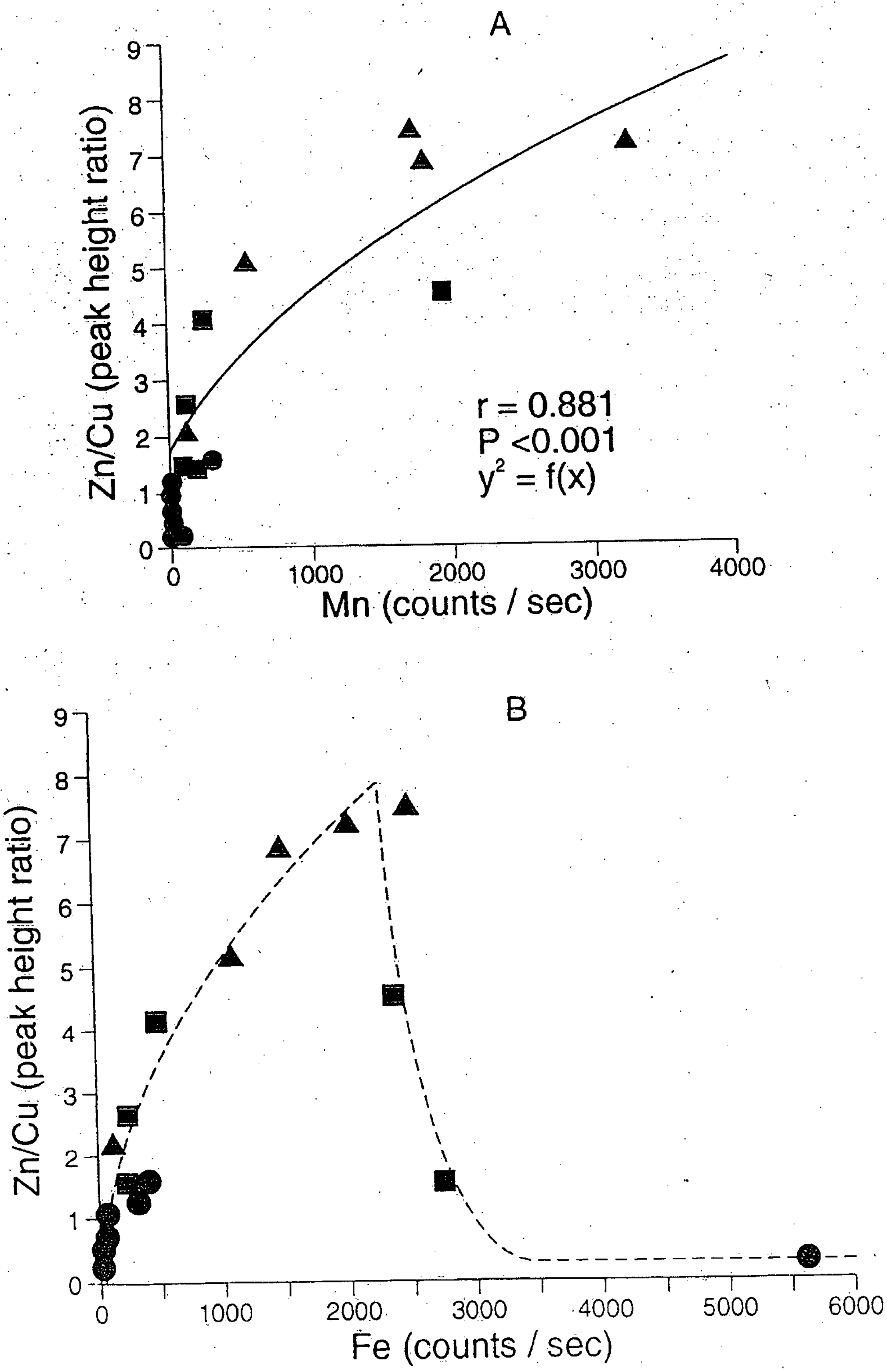


Fig. 5

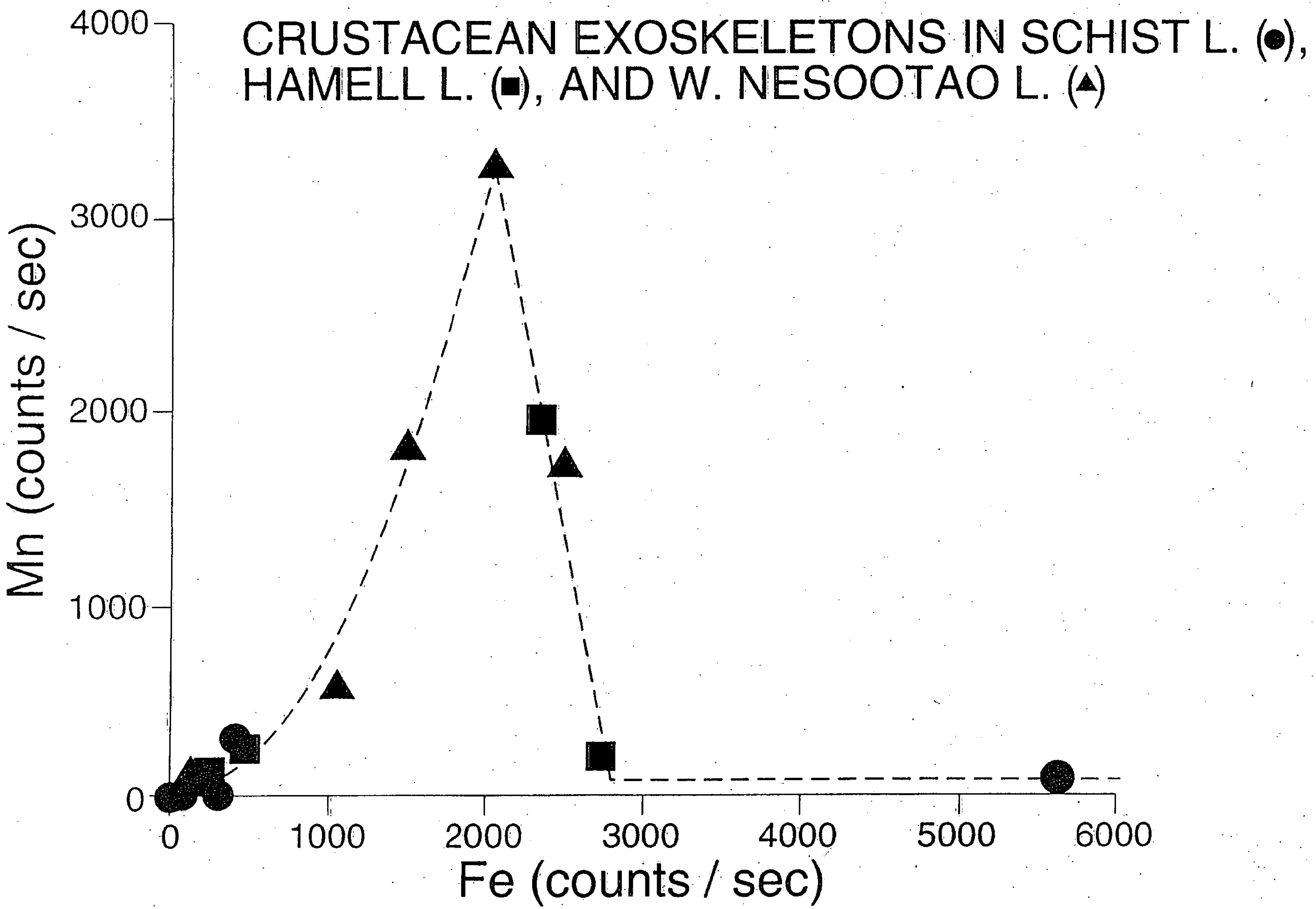
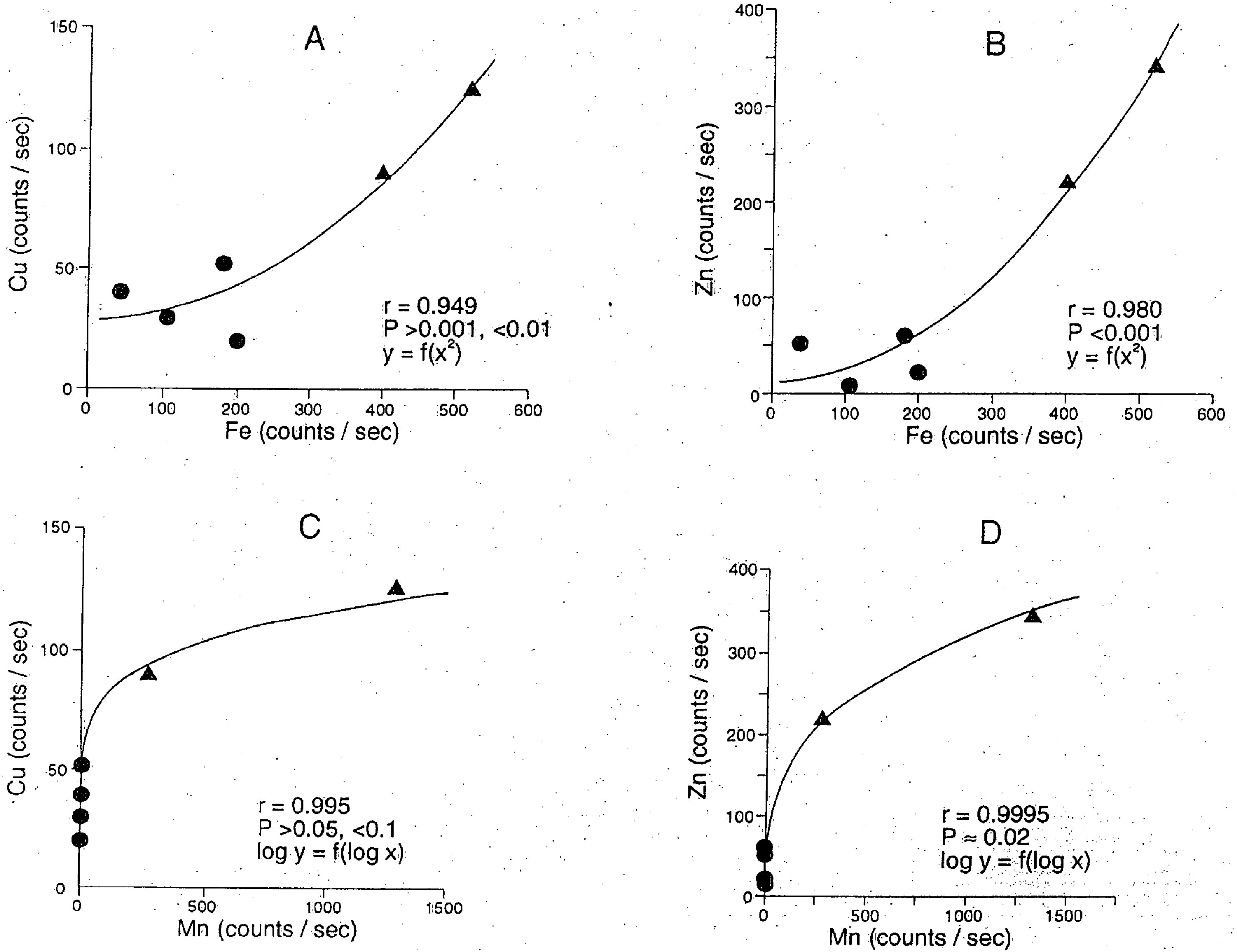

CRUSTACEAN EXOSKELETONS IN SCHIST L. (●),
HAMELL L. (■), AND W. NESOOTAO L. (▲)
Mn (counts / sec)
4000
3000
2000
1000
0
Fe (counts / sec)
0
1000
2000
3000
4000
5000
6000

Fig. 6



KERATELLA IN SCHIST L. (●) AND W. NESOOTAO L. (▲)

Fig. 7

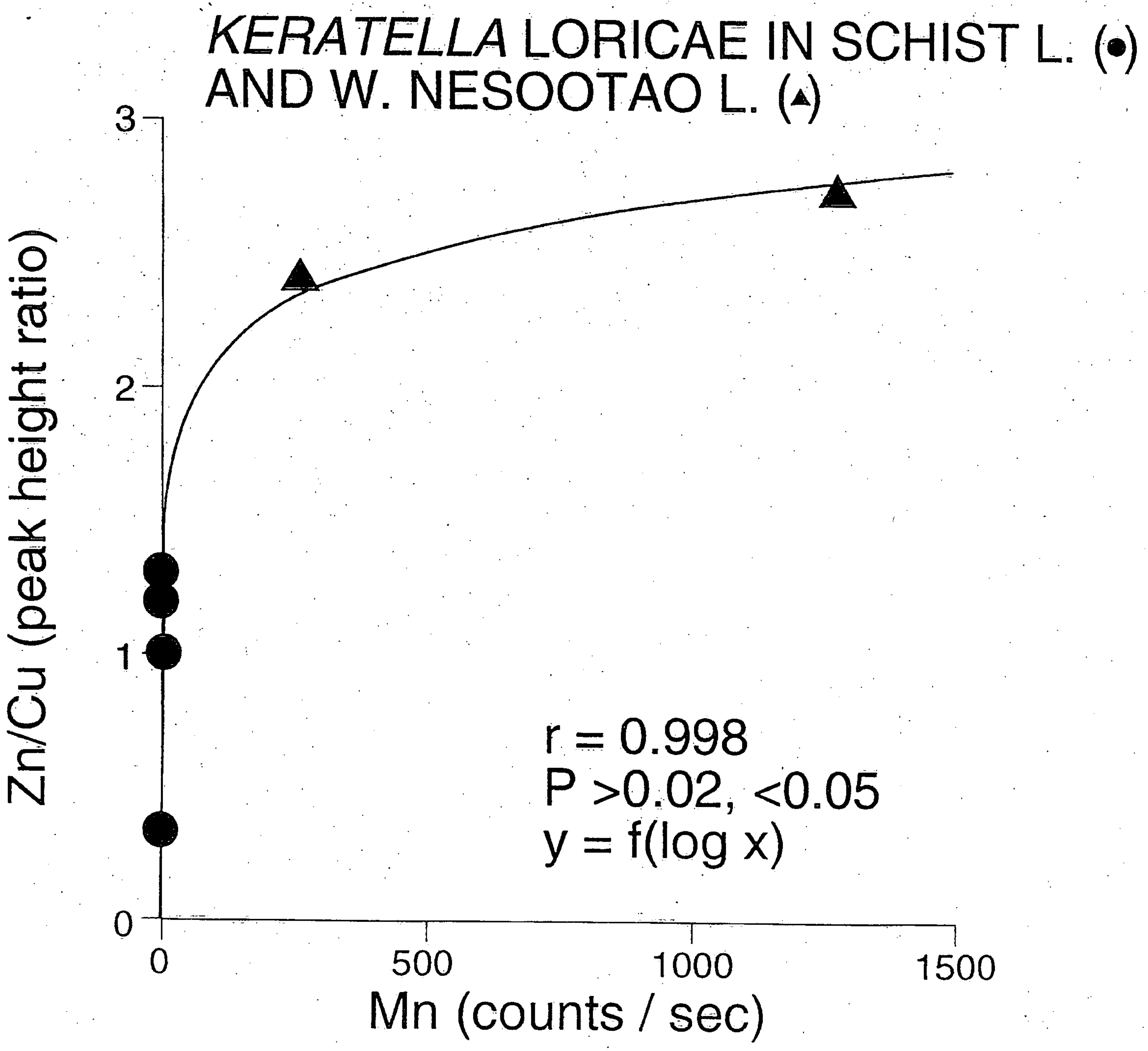

KERATELLA LORICAE IN SCHIST L. (●)
AND W. NESOOTAO L. (▲)
Zn/Cu (peak height ratio)
3
2
1
0
0
500
1000
1500
Mn (counts / sec)
r = 0.998
P >0.02, <0.05
y = f(log x)

Fig. 8

CRUSTACEAN EXOSKELETONS (●) AND *STROMBOMONAS* LORICA (▲) IN HAMELL LAKE

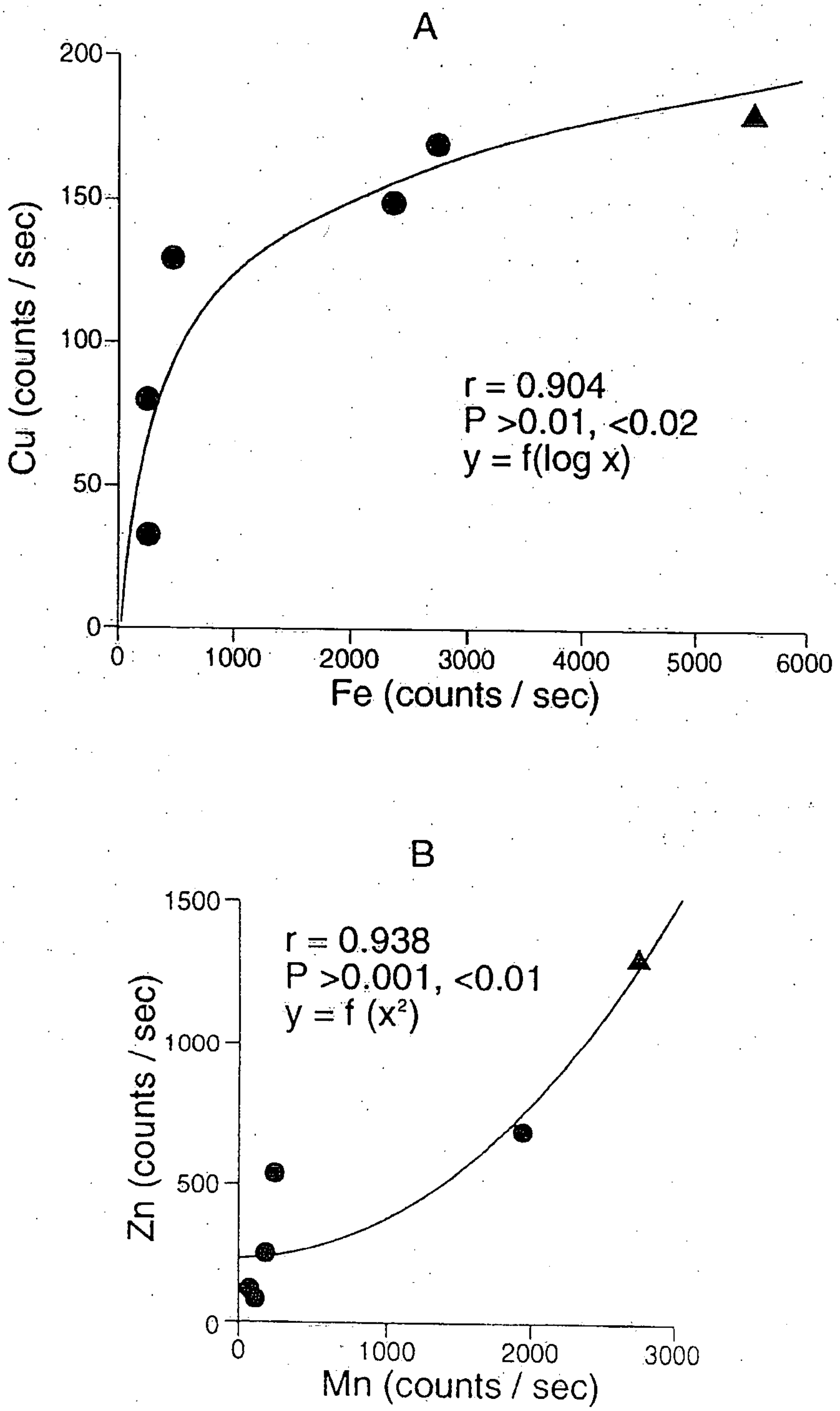


Fig. 9

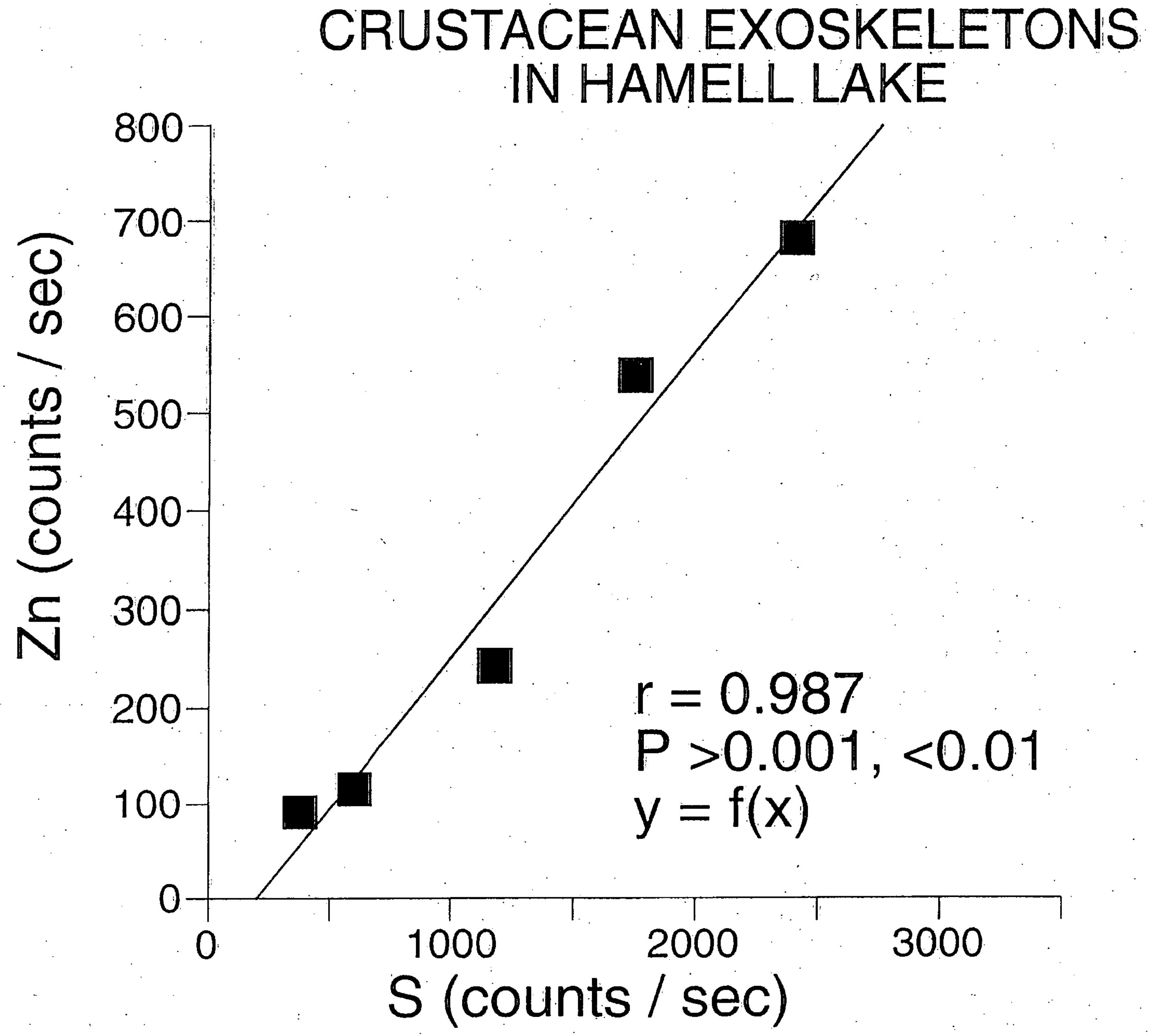

CRUSTACEAN EXOSKELETONS
IN HAMELL LAKE
Zn (counts / sec)
800
700
600
500
400
300
200
100
0
0
1000
2000
3000
S (counts / sec)
r = 0.987
P >0.001, <0.01
y = f(x)

Fig. 10

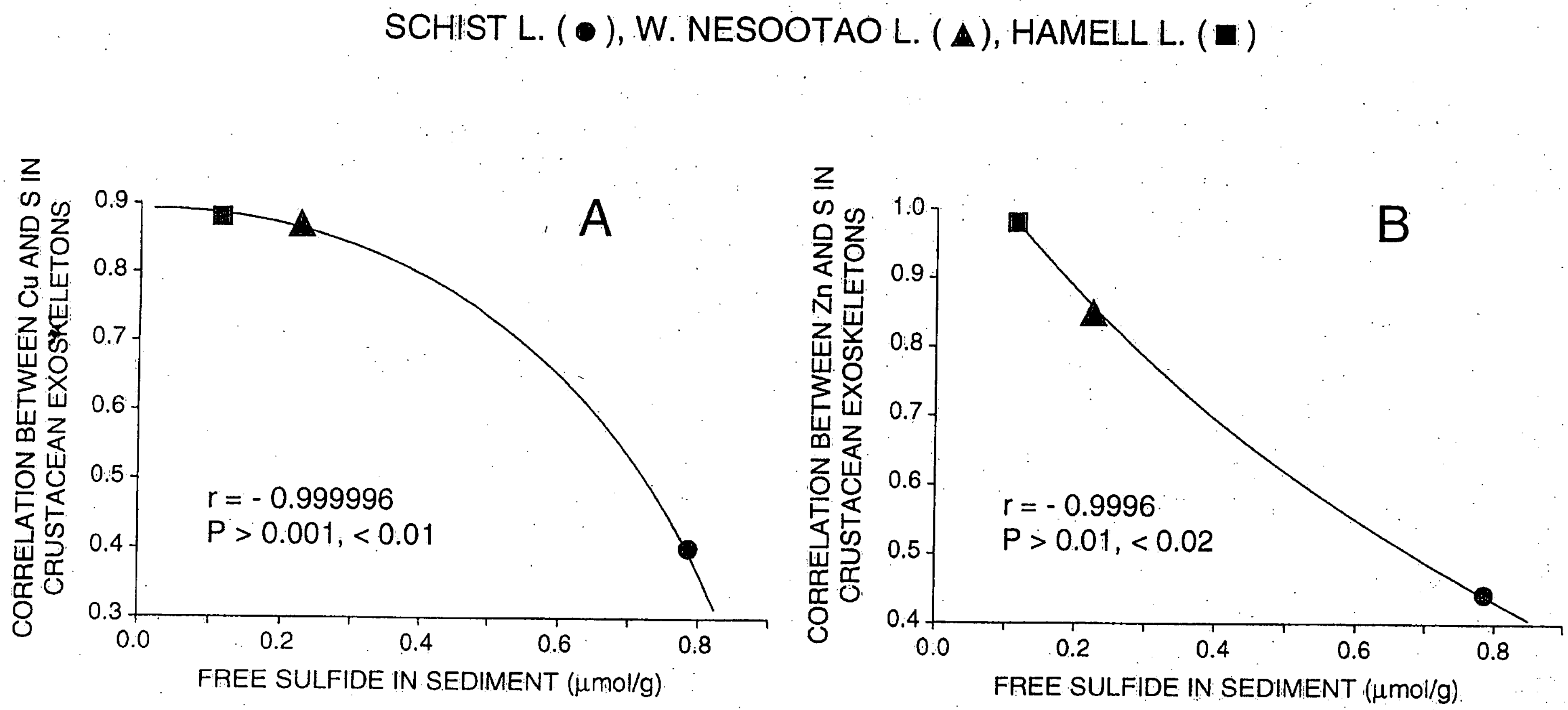

SCHIST L. (●), W. NESOOTAO L. (▲), HAMELL L. (■)
A
CORRELATION BETWEEN Cu AND S IN CRUSTACEAN EXOSKELETONS
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.0
0.2
0.4
0.6
0.8
r = - 0.999996
P > 0.001, < 0.01
FREE SULFIDE IN SEDIMENT (µmol/g)
B
CORRELATION BETWEEN Zn AND S IN CRUSTACEAN EXOSKELETONS
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.0
0.2
0.4
0.6
0.8
r = - 0.9996
P > 0.01, < 0.02
FREE SULFIDE IN SEDIMENT (µmol/g)

Fig. 11

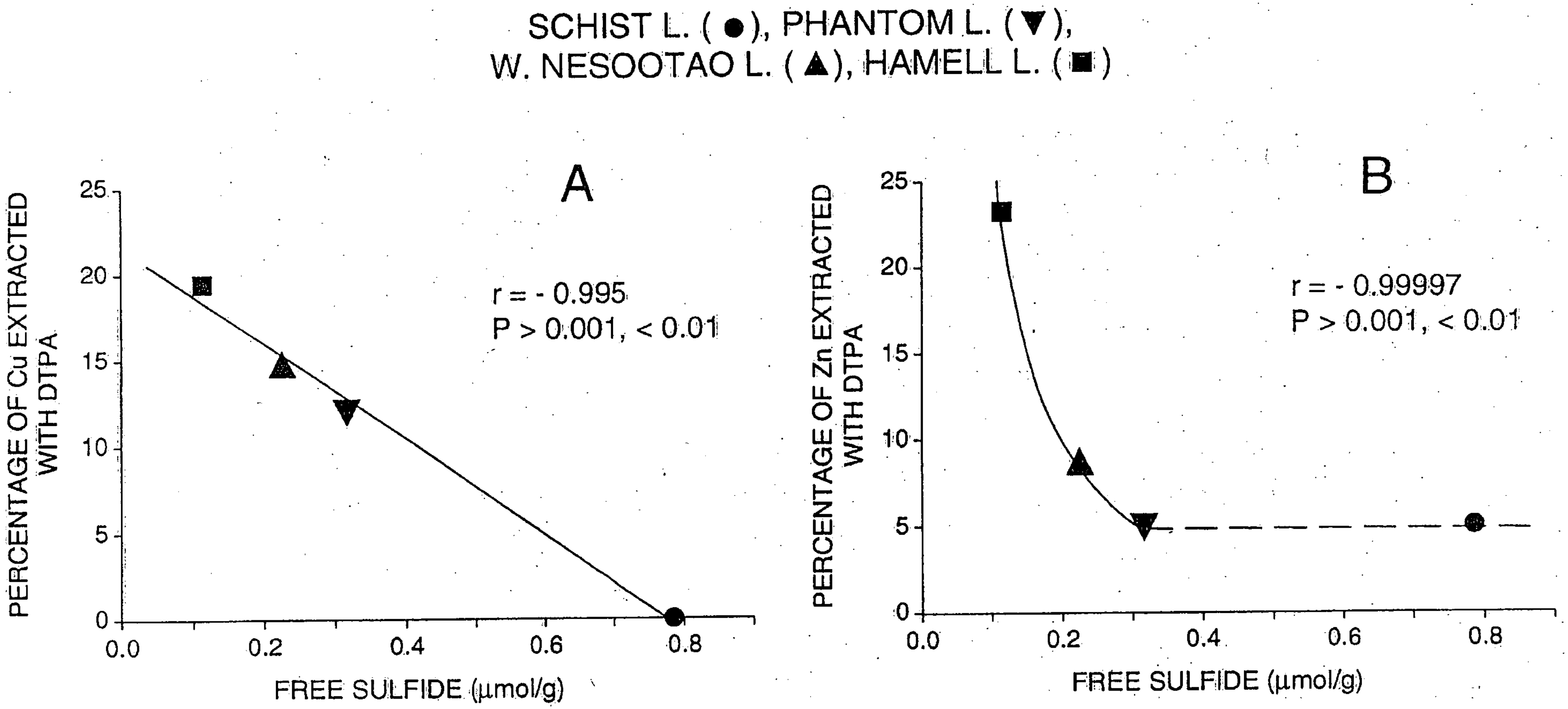

SCHIST L. (●), PHANTOM L. (▼),
W. NESOOTAO L. (▲), HAMELL L. (■)
A
PERCENTAGE OF Cu EXTRACTED WITH DTPA
25
20
15
10
5
0
0.0
0.2
0.4
0.6
0.8
FREE SULFIDE (µmol/g)
r = - 0.995
P > 0.001, < 0.01
B
PERCENTAGE OF Zn EXTRACTED WITH DTPA
25
20
15
10
5
0
0.0
0.2
0.4
0.6
0.8
FREE SULFIDE (µmol/g)
r = - 0.99997
P > 0.001, < 0.01

Fig. 12.

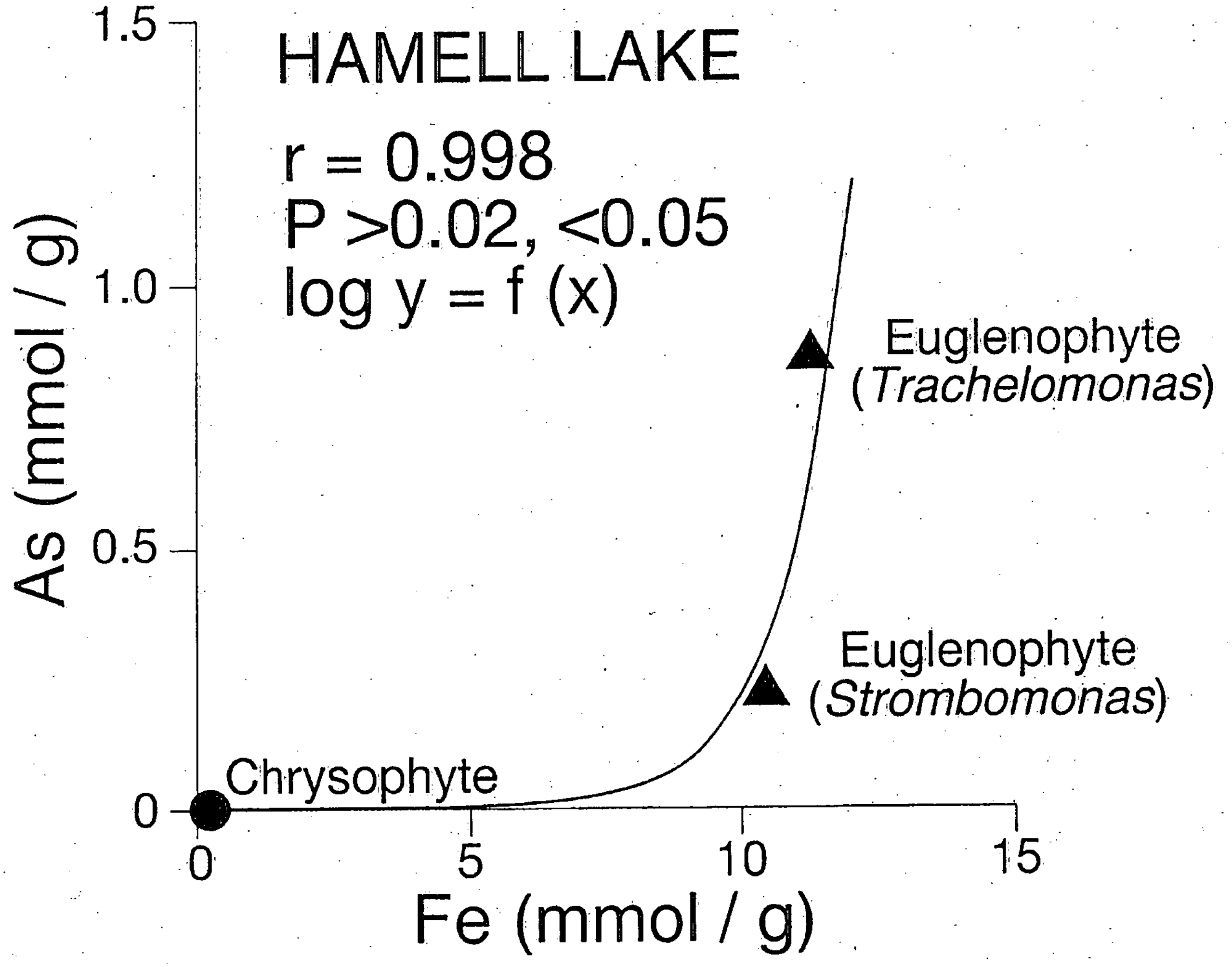

HAMELL LAKE
r = 0.998
P >0.02, <0.05
log y = f (x)
As (mmol / g)
1.5
1.0
0.5
0
Fe (mmol / g)
0
5
10
15
Chrysophyte
Euglenophyte
(*Trachelomonas*)
Euglenophyte
(*Strombomonas*)

Fig. 13

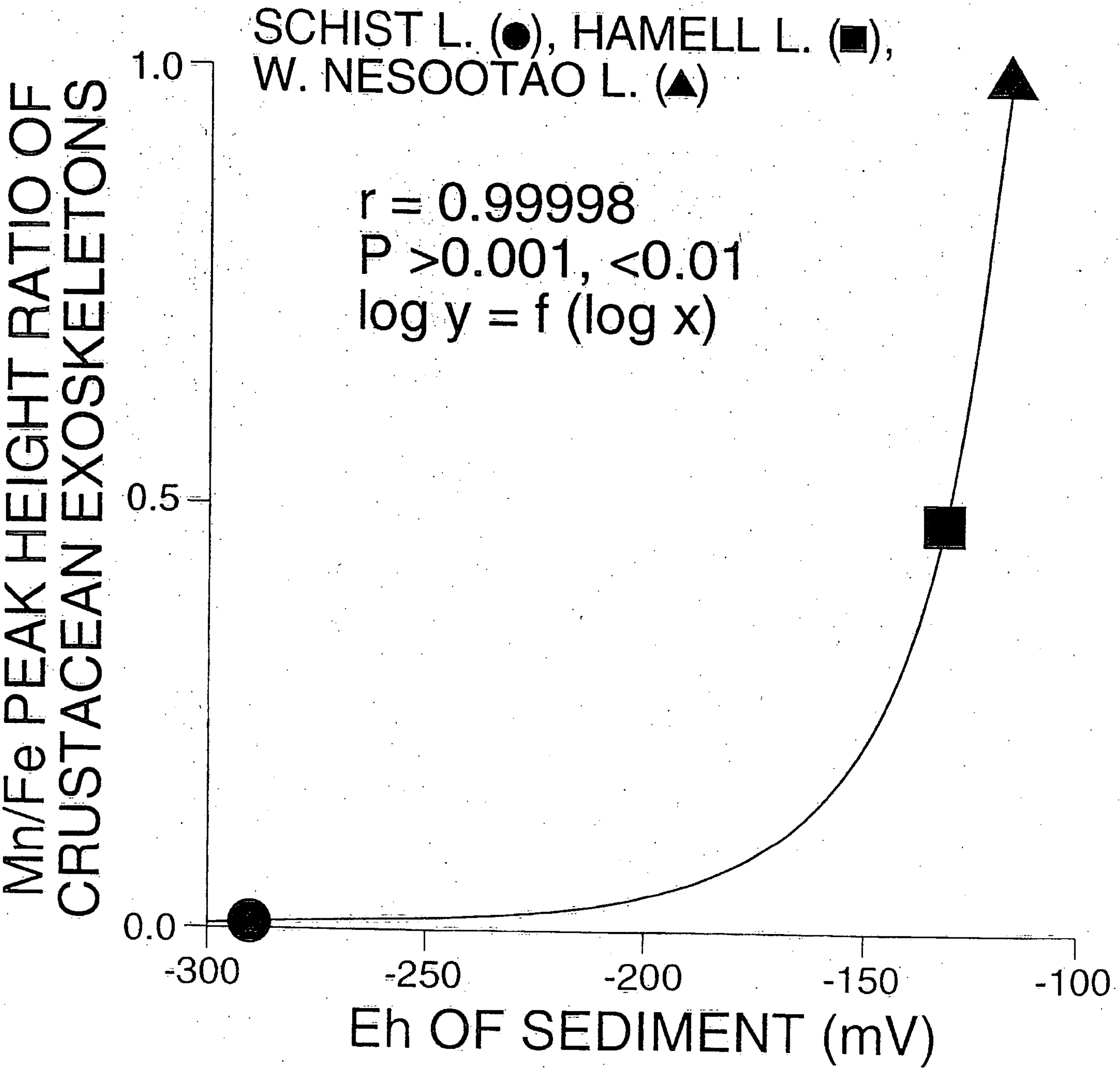

SCHIST L. (●), HAMELL L. (■),
W. NESOOTAO L. (▲)
r = 0.99998
P >0.001, <0.01
log y = f (log x)
1.0
0.5
0.0
-300
-250
-200
-150
-100
Mn/Fe PEAK HEIGHT RATIO OF CRUSTACEAN EXOSKELETONS
Eh OF SEDIMENT (mV)

Fig. 14

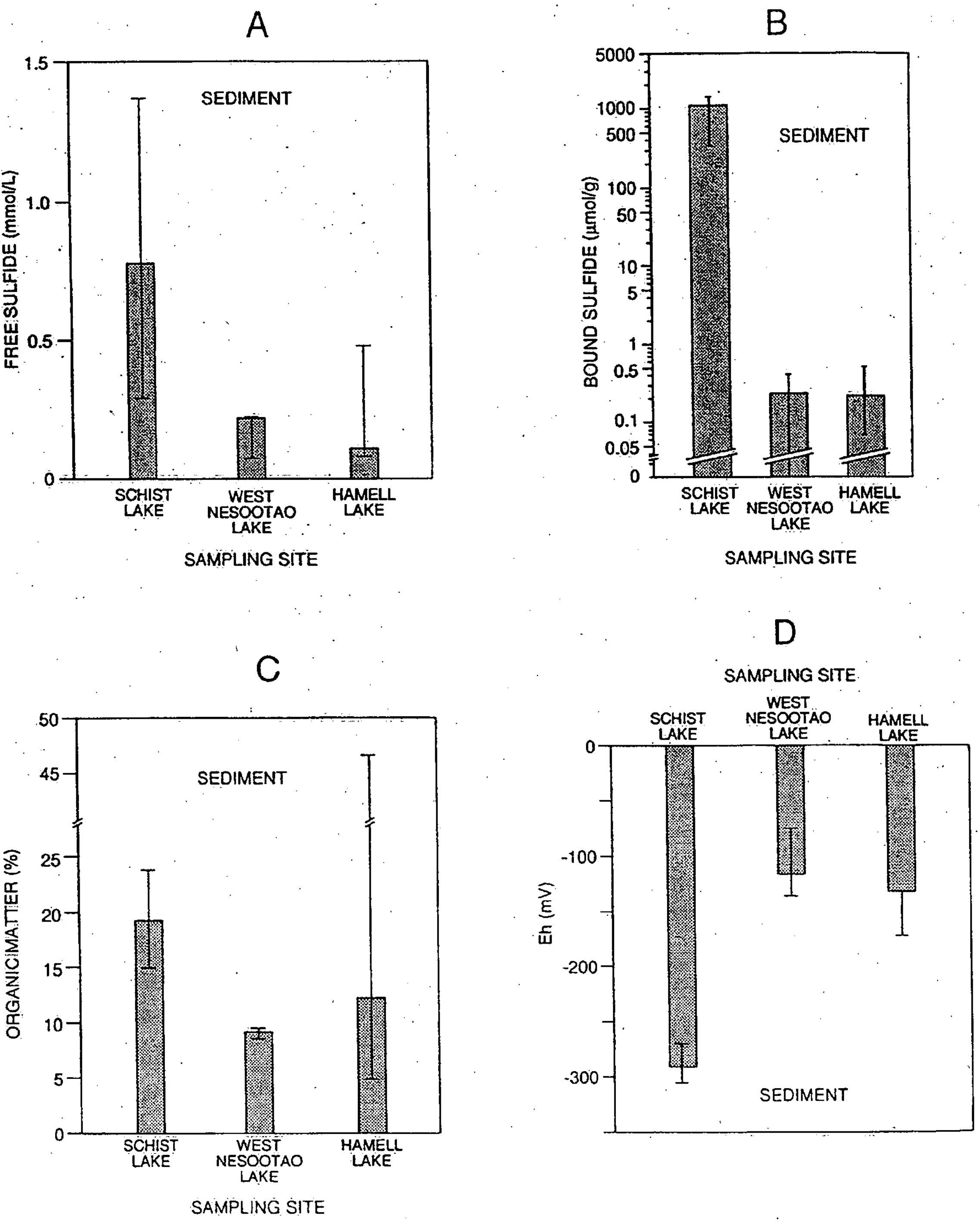

A
1.5
1.0
0.5
0
FREE SULFIDE (mmol/L)
SEDIMENT
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
B
5000
1000
500
100
50
10
5
1
0.5
0.1
0.05
0
BOUND SULFIDE (µmol/g)
SEDIMENT
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
C
50
45
25
20
15
10
5
0
ORGANIC MATTER (%)
SEDIMENT
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
D
SAMPLING SITE
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
0
-100
-200
-300
Eh (mV)
SEDIMENT

Fig. 15

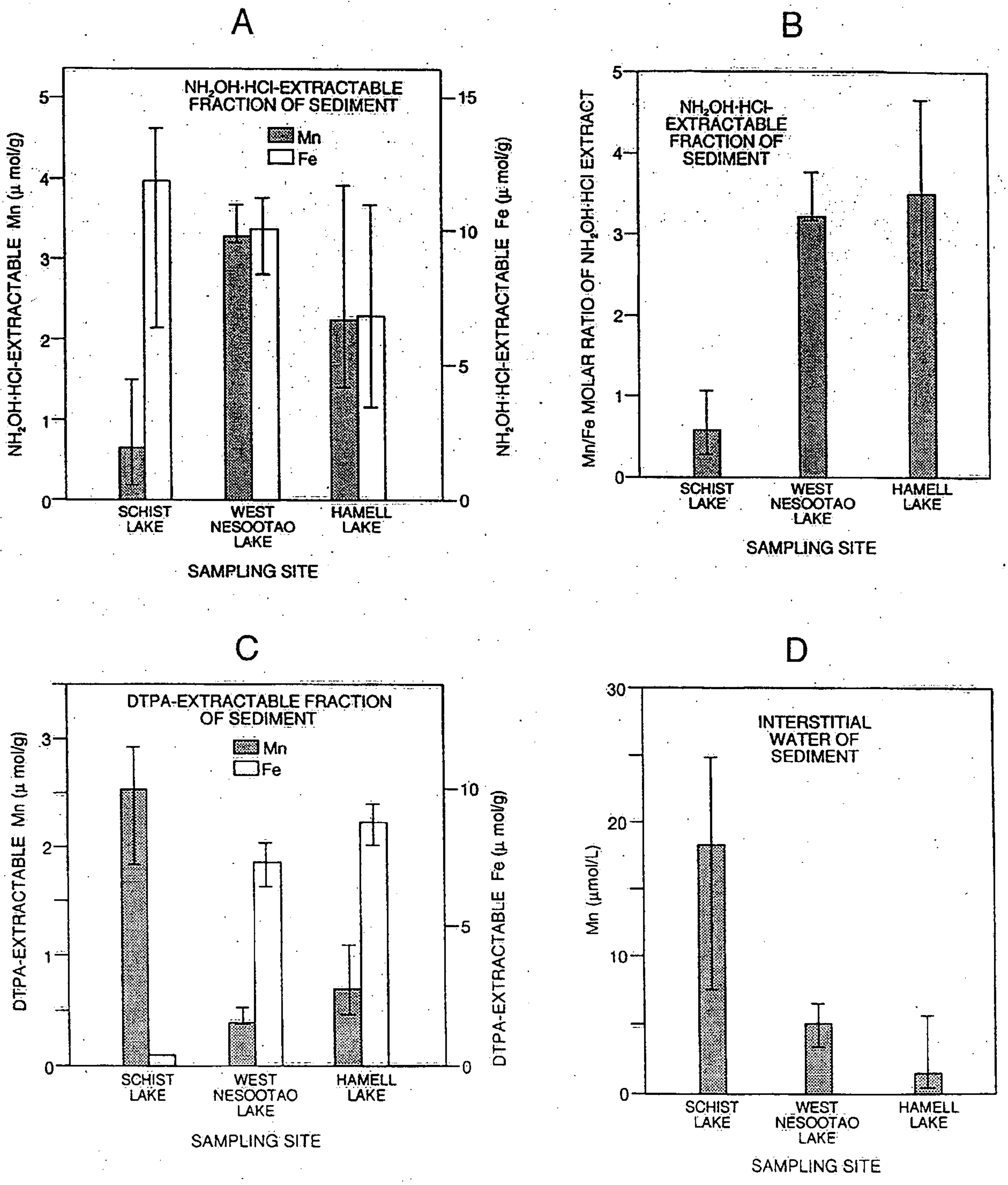

A
NH2OH·HCl-EXTRACTABLE FRACTION OF SEDIMENT
Mn
Fe
NH2OH·HCl-EXTRACTABLE Mn (µ mol/g)
NH2OH·HCl-EXTRACTABLE Fe (µ mol/g)
0
1
2
3
4
5
0
5
10
15
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
B
NH2OH·HCl-EXTRACTABLE FRACTION OF SEDIMENT
Mn/Fe MOLAR RATIO OF NH2OH·HCl EXTRACT
0
1
2
3
4
5
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
C
DTPA-EXTRACTABLE FRACTION OF SEDIMENT
Mn
Fe
DTPA-EXTRACTABLE Mn (µ mol/g)
DTPA-EXTRACTABLE Fe (µ mol/g)
0
1
2
3
0
5
10
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
D
INTERSTITIAL WATER OF SEDIMENT
Mn (µmol/L)
0
10
20
30
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE

Fig. 16

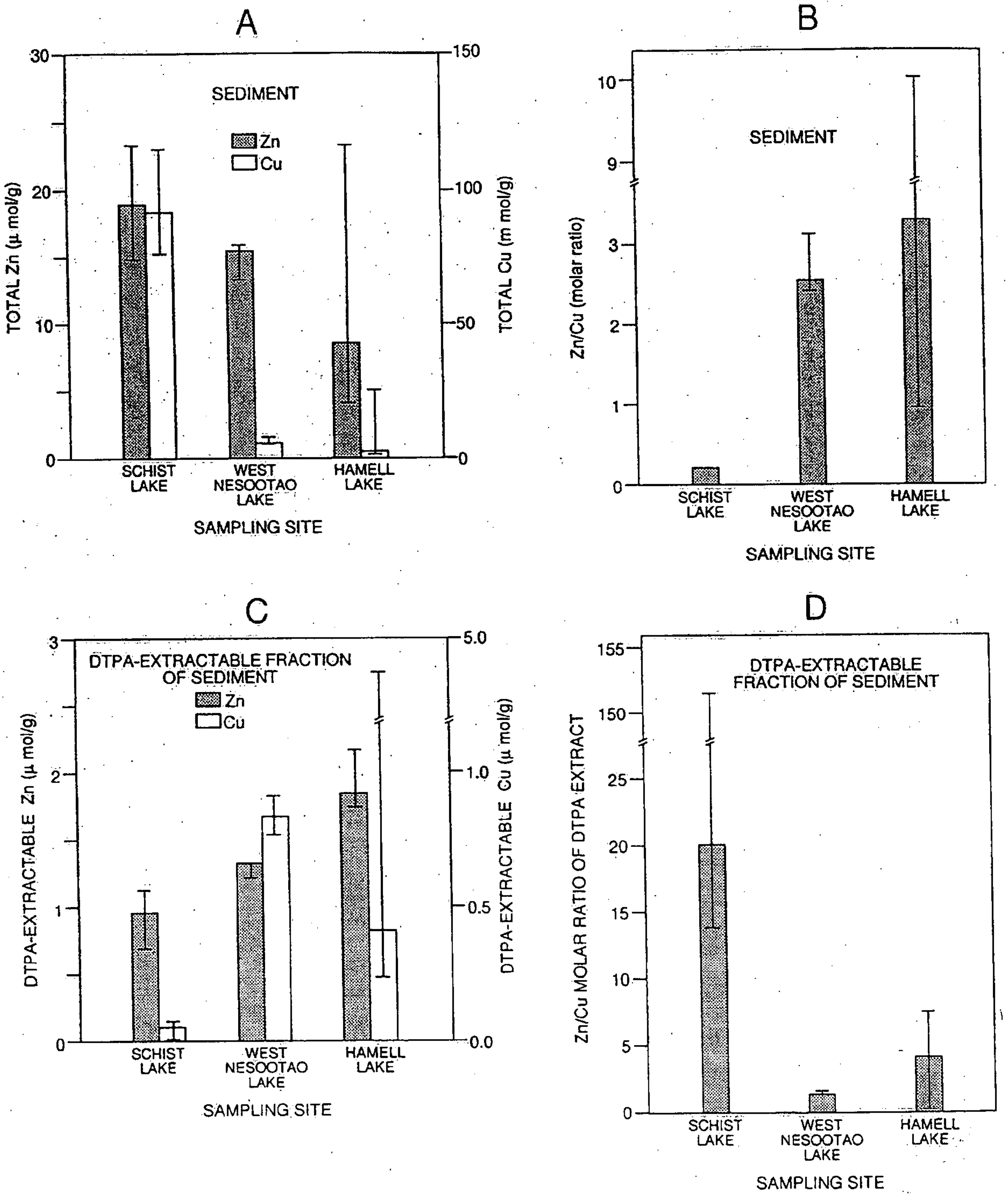

A
SEDIMENT
▨ Zn
☐ Cu
TOTAL Zn (μ mol/g)
TOTAL Cu (m mol/g)
0
10
20
30
0
50
100
150
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
B
SEDIMENT
Zn/Cu (molar ratio)
0
1
2
3
9
10
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
C
DTPA-EXTRACTABLE FRACTION OF SEDIMENT
▨ Zn
☐ Cu
DTPA-EXTRACTABLE Zn (μ mol/g)
DTPA-EXTRACTABLE Cu (μ mol/g)
0
1
2
3
0.0
0.5
1.0
5.0
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
D
DTPA-EXTRACTABLE FRACTION OF SEDIMENT
Zn/Cu MOLAR RATIO OF DTPA EXTRACT
0
5
10
15
20
25
150
155
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE

Fig. 17

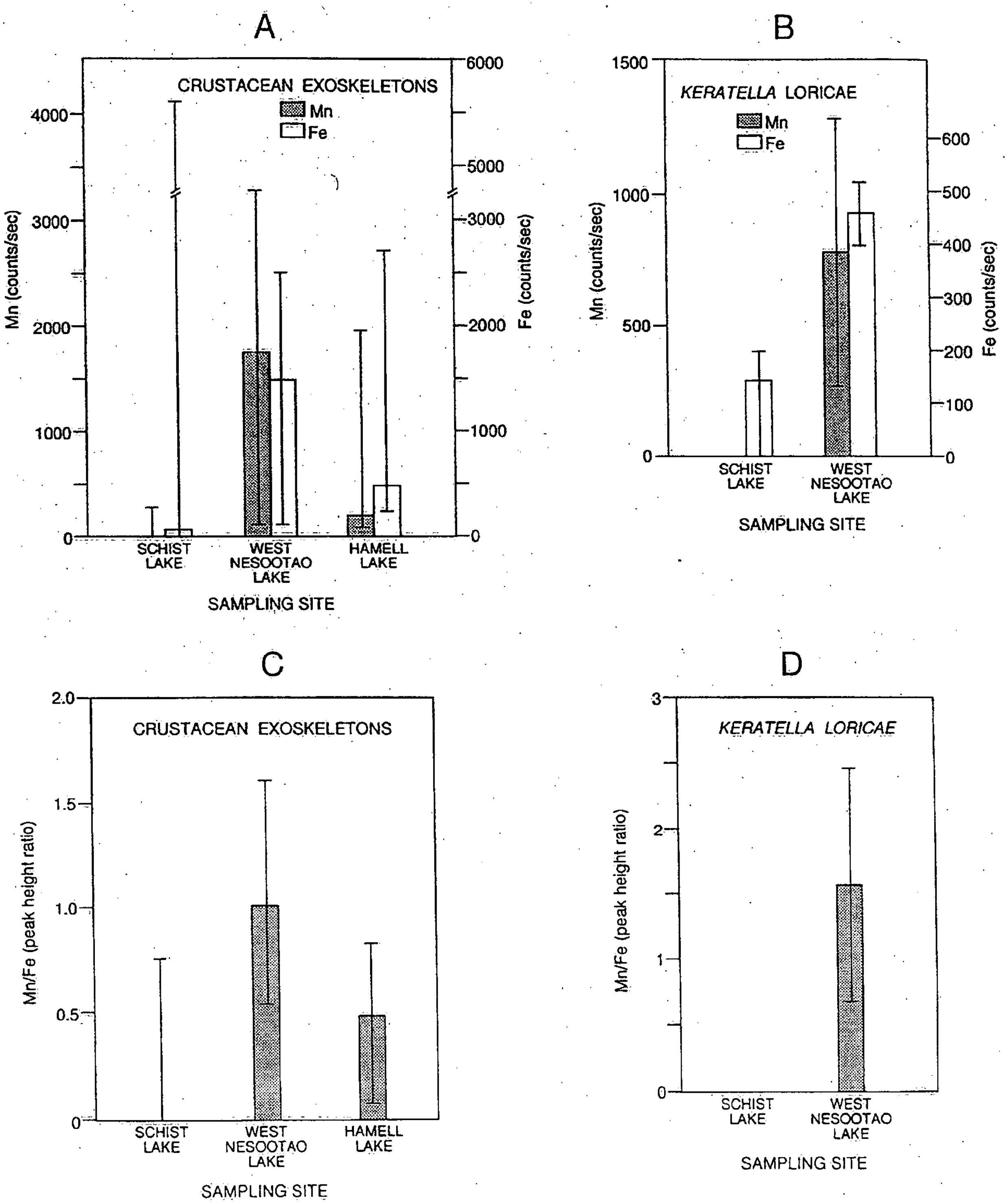

A
CRUSTACEAN EXOSKELETONS
Mn
Fe
Mn (counts/sec)
Fe (counts/sec)
0
1000
2000
3000
4000
0
1000
2000
3000
5000
6000
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
B
KERATELLA LORICAE
Mn
Fe
Mn (counts/sec)
Fe (counts/sec)
0
500
1000
1500
0
100
200
300
400
500
600
SCHIST LAKE
WEST NESOOTAO LAKE
SAMPLING SITE
C
CRUSTACEAN EXOSKELETONS
Mn/Fe (peak height ratio)
0
0.5
1.0
1.5
2.0
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
D
KERATELLA LORICAE
Mn/Fe (peak height ratio)
0
1
2
3
SCHIST LAKE
WEST NESOOTAO LAKE
SAMPLING SITE

Fig. 18

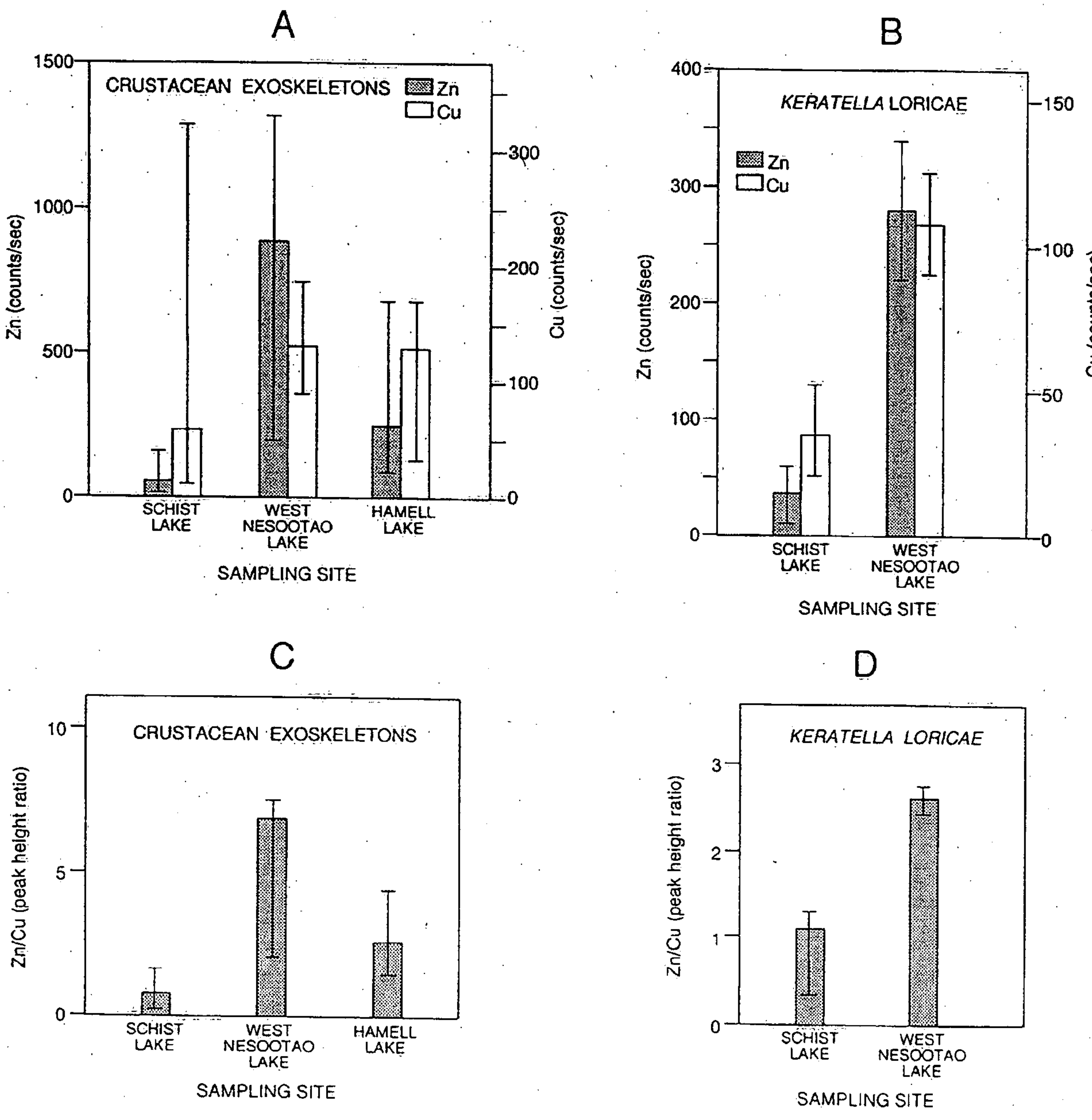

A
CRUSTACEAN EXOSKELETONS
Zn
Cu
Zn (counts/sec)
Cu (counts/sec)
1500
1000
500
0
300
200
100
0
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
B
KERATELLA LORICAE
Zn
Cu
Zn (counts/sec)
Cu (counts/sec)
400
300
200
100
0
150
100
50
0
SCHIST LAKE
WEST NESOOTAO LAKE
SAMPLING SITE
C
CRUSTACEAN EXOSKELETONS
Zn/Cu (peak height ratio)
10
5
0
SCHIST LAKE
WEST NESOOTAO LAKE
HAMELL LAKE
SAMPLING SITE
D
KERATELLA LORICAE
Zn/Cu (peak height ratio)
3
2
1
0
SCHIST LAKE
WEST NESOOTAO LAKE
SAMPLING SITE

Fig. 19

Environment Canada Environnement Canada

Canada

Canada Centre for Inland Waters
P.O. Box 5050
867 Lakeshore Road
Burlington, Ontario
L7R 4A6 Canada

National Hydrology Research Centre
11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

St. Lawrence Centre
105 McGill Street
Montreal, Quebec
H2Y 2E7 Canada

Place Vincent Massey
351 St. Joseph Boulevard
Gatineau, Quebec
K1A 0H3 Canada

Centre canadien des eaux intérieures
Case postale 5050
867, chemin Lakeshore
Burlington (Ontario)
L7R 4A6 Canada

Centre national de recherche en hydrologie
11, boul. Innovation
Saskatoon (Saskatchewan)
S7N 3H5 Canada

Centre Saint-Laurent
105, rue McGill
Montréal (Québec)
H2Y 2E7 Canada

Place Vincent-Massey
351 boul. St-Joseph
Gatineau (Québec)
K1A 0H3 Canada