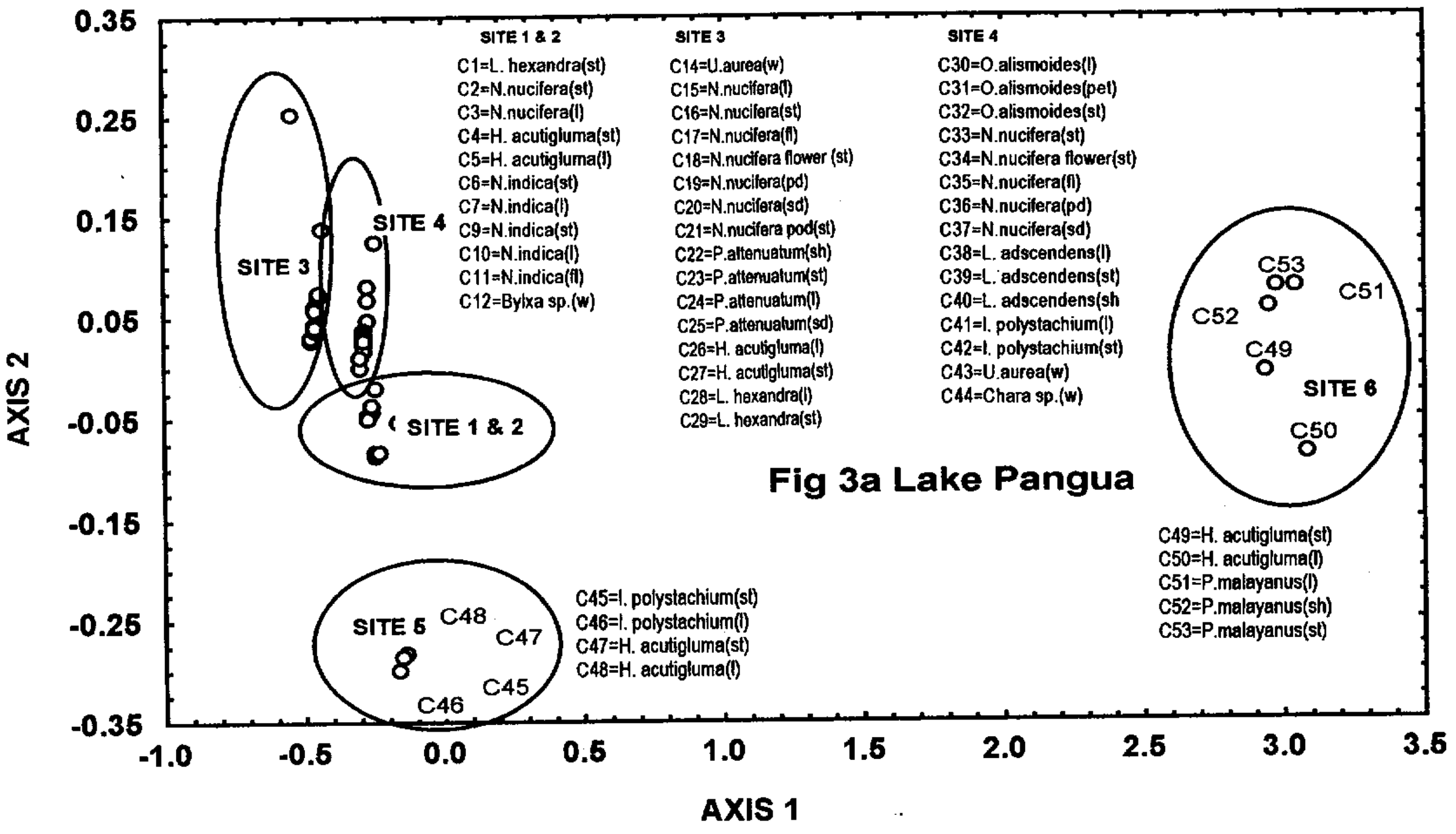
Figure 3a Multidimensional ordination using metal concentrations (Al, Cd, Fe, Mn, Mo, Pb, and Zn) in plants and sediment, redox potential (Eh), pH, sulphur and sediment organic matter from Lake Pangua.



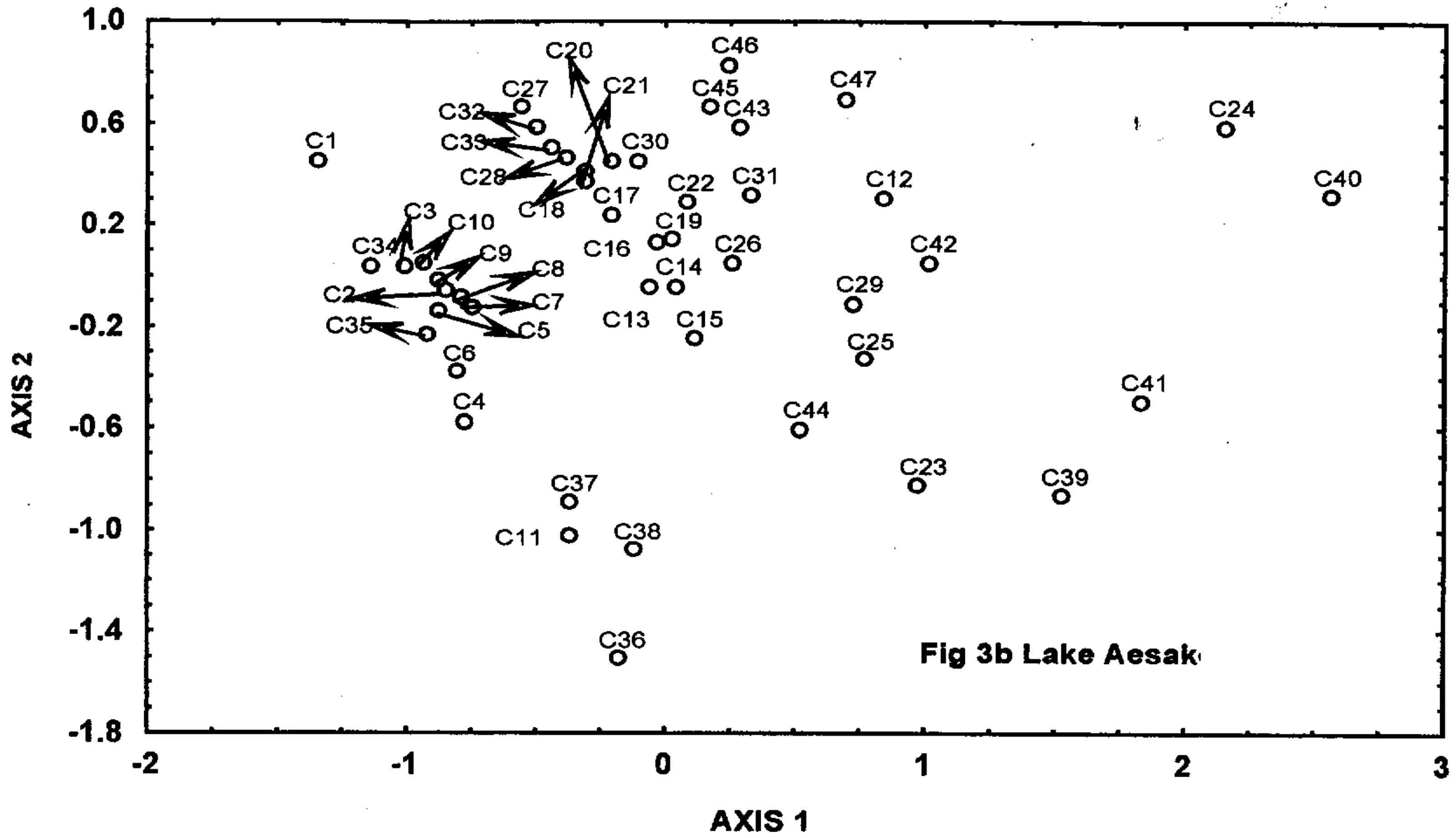


Figure 3b  Multidimensional ordination using metal concentrations (Al, Cd, Fe, Mn, Mo, Pb, and Zn) in plants and sediment, redox potential (Eh), pH, sulphur and sediment organic matter from Lake Aesake (control site). (C1 *Coix gigantica* leaves C2 *C.gigantica* stems C3 *Ischaemum polystachium* leaves C4 *I. polystachium* stems C5 *Leguminoceae trifoliate* shoots C6 *L. trifoliate* stems C7 *L. trifoliate* leaves C8 *Ipomea* sp. Leaves C9 *Ipomea* sp. Shoots C10 *Ipomea* sp. Stems C11 *Ludwigia hyssopifolia* leaves C12 *L. hyssopifolia* stems C13 *L. hyssopifolia* shoots C14 *L. hyssopifolia* seeds C15 Site 2 *Polygonum attenuatum* leaves C16 *P. attenuatum* stems C17 *P. attenuatum* shoots C18 *I. polystachium* leaves C19 *I. polystachium* stems C20 *L. trifoliate* leaves C21 *L. trifoliate* stems C22 *L. trifoliate* shoots C23 *L. hyssopifolia* leaves *C24 L. hyssopifolia* stems C25 *L. hyssopifolia* shoots C26 *L. hyssopifolia* seeds C27 *Echinocloa praestans* leaves C28 *E. praestans* stems C29 *E. praestans* Sample C30 Site 2 *Ludwigia adscendens* leaves C31 *L. adscendens* stems C32 *L. adscendens* shoots C33 *Hymenachne acutigluma* leaves C34 *H. acutigluma* stems C35 Site 3 *I. polystachium* leaves C36 *I. polystachium* stems C37 *L. hyssopifolia* leaves C38 *L. hyssopifolia* shoots C39 *L. hyssopifolia* stems C40 Site 4 *L. hyssopifolia* leaves *C41 L. hyssopifolia* stems C42 *L. hyssopifolia* shoots C43 *L. hyssopifolia* seeds C44 *L. trifoliate* leaves C45 *L. trifoliate* stems C46 *L. trifoliate* shoots C47 *I. polystachium* leaves C48 *I. polystachium* stems).

Table 5 Comparing the metal concentration in aquatic plant species common at the various categories of contamination. All concentrations are expressed at mg/kg. Refer to Table SSS (page GG) for a abbreviated physiognomy of each plant.

| Plant species at | p Cu | p Cd | p Fe | p Mn | p Pb | p Zn | p Al | p Mo |
|---|---|---|---|---|---|---|---|---|
| 0-70mg/kg Cu control (unaffected) sites. | | | | | | | | |
| *Utricularia aurea*(n=2) | 32.3±9.8 | 0.21±0.03 | 30673±13247 | 1937±431 | 3.97±1.7 | 70±20 | 1283±516 | 7.5±0.8 |
| *Nelumbo nucifera*(n=17) | 16.1±9.3 | 0.08±0.09 | 336±229 | 605±553 | 1.13±3.3 | 57±30 | 42±72 | 10.5±37 |
| *Ludwigia hyssopifolia*(n=16) | 14.8±11.7 | 0.04±0.04 | 772±1081 | 858±420 | 1.01±1.5 | 125±26 | 93±335 | 4.2±7.7 |
| *Leersia hexandra*(n=6) | 6.3±4.5 | 0.04±0.02 | 127±43 | 181±125 | 0.23±0.15 | 89±72 | 14±11 | 3.9±2.8 |
| *Hymenachne acutigluma*(n=4) | 2.4±0.7 | 0.02±0.02 | 89±26 | 146±54 | 0.13±0.04 | 33±12 | 11±9 | 1.5±1.6 |
| *Leguminoceae trifoliate*(n=9) | 6.9±2.7 | 0.01±0.01 | 192±68 | 185±108 | 0.39±0.21 | 69±24 | 14±9 | 1.4±1.8 |
| *Ischaemum polystachium*(n=8) | 12.6±16.9 | 0.01±0.01 | 95±36 | 174±46 | 0.20±0.19 | 79±57 | 7±4 | 1.1±0.4 |
| *Polygonum attenuatum*(n=9) | 6.2±1.3 | 0.03±0.01 | 233±118 | 462±302 | 0.17±0.13 | 75±25 | 10±15 | 2.6±1.5 |
| *Echinocloa praestans*(n=6) | 8.2±5.4 | 0.02±0.01 | 95±30 | 184±179 | 0.41±0.23 | 61±38 | 12±8 | 4.5±3.8 |
| 70-500mg/kg Cu moderately contaminated sediment. | | | | | | | | |
| *Utricularia aurea*(n=6) | 242.0±322 | 0.77±1.09 | 16605±15696 | 4100±5285 | 17.78±31.49 | 77±46 | 2622±3910 | 8.6±7 |
| *Chara* sp.(n=2) | 54.5±54 | 0.14±0.10 | 16625±22997 | 1346± | 2.18±3.0 | 75±40 | 592±824 | 4.1±2 |
| *Nelumbo nucifera*(n=19) | 19.9±11 | 0.16±0.13 | 235±253 | 299±390 | 1.02±3.4 | 50±24 | 17±26 | 15.4±35 |
| *Cyperaceae* sp.(n=4) | 4.4±1.7 | 0.01±0.00 | 68±27 | 75±56 | 0.09±0.06 | 23±8 | 2±2 | 2.9±2.2 |
| *L adscendence*(n=6) | 37.2±14 | 0.07±0.04 | 755±475 | 597±372 | 0.83±0.91 | 103±24 | 135±139 | 3.2±1.9 |
| *L hyssopifolia*(n=11) | 61.0±96 | 0.16±0.31 | 514±392 | 759±673 | 1.88±5.6 | 179±128 | 182±561 | 20.2±29 |
| *L hexandra*(n=16) | 18.9±44.6 | 0.10±0.19 | 297±395 | 266±174 | 0.75±1.2 | 101±75 | 41±52 | 7.2±5.4 |
| *H acutigluma*(n=14) | 6.8±4.2 | 0.04±0.03 | 129±130 | 149±105 | 0.44±1.0 | 44±24 | 25±38 | 18.7±39 |
| *I polystachium*(n=6) | 10.4±3.0 | 0.04±0.02 | 104±70 | 212±117 | 0.11±0.06 | 58±27 | 15±10 | 3.4±1.5 |
| *P karkar*(n=4) | 8.6±4.8 | 0.01±0.01 | 60±39 | 67±57 | 0.14±0.05 | 31±15 | 10±6 | 2.9±2.6 |
| 500->1000 mg/kg Cu, severely contaminated sediment. | | | | | | | | |
| *U aurea*(n=4) | 404±365 | 0.57±0.31 | 43706±14558 | 5093±1730 | 38.00±35 | 123±63 | 6181±4016 | 11.5±4.8 |
| *N nucifera*(n=14) | 26.4±14.1 | 0.43±0.37 | 404±440 | 786±1006 | 2.49±4.4 | 55±21 | 60±121 | 202.7±211 |
| *L hexandra*(n=4) | 12.7±4.0 | 0.09±0.07 | 180±106 | 420±281 | 0.42±0.34 | 107±149 | 63±72 | 15.6±23 |
| *H acutigluma*(n=10) | 9.3±2.9 | 0.35±0.87 | 119±66 | 222±113 | 0.37±0.49 | 74±42 | 11±6 | 237.1±618 |
| *I polystachium*(n=16) | 23.1±9.5 | 0.06±0.05 | 174±110 | 222±126 | 0.77±1.0 | 98±95 | 64±82 | 19.3±29 |
| *E praestans*(n=12) | 16.4±8.8 | 0.18±0.18 | 177±111 | 215±87 | 0.46±0.28 | 52±30 | 87±82 | 117.6±142 |
| *S robustum*(n=6) | 12.5±4.2 | 0.10±0.06 | 83±34 | 245±66 | 0.11±0.08 | 61±36 | 10±4 | 53.8±53 |

Generally, the results presented in Table 4 show that cadmium and lead concentrations are low, although increases in both these metals are evident. The apparent increases mentioned for these two elements are not significant ($p>0.05$) due to the high variability in the results. The concentration for Fe, Mn and Al were consistent throughout all plants at all sites. The signals from mine-derived sediments for these three elements were swamped by background signals, including a high variability within and amongst the various plants species. Molybdenum appeared to be the only element following the same trend as copper, and showed significant ($p<0.01$) increases due to the presence of mine-derived sediment.

The general observations above are confirmed when individual metal concentration in plants common to affected and unaffected sites is compared (Table 5). The increase in concentration of elements in aquatic plants as a result of the presence of mine-derived sediments was found to be significant (ANOVA $p<0.05$) for *U. aurea*, *L. hexandra* and *I. polystachium*, while *N. nucifera* and *H. acutigluma* were not significant. *Utricularia aurea* is the only submerged plant species that was present at all three sediment categories. This plant has very fine stem and branches that were observed to trap fine sediment material. The elevated concentrations of Cu, Fe and Mn were consistent with the concentration of these metals in sediment. The increase in concentration for *L. hyssopifolia* was also significant (ANOVA $p<0.05$) when data from affected and moderately affected sites were tested.

Plant-Sediment-Water Metal Interactions

Dissolved metals generally did not correlate well with plant metals, except for molybdenum. The pH of sediment appears to be significant in the correlation of Mo with the same in plants. Significant interrelations between dissolved Cu, Al and Mo with other metals in plants (Table 6). In addition, significant ($p\leq0.05$) correlations were observed between dissolved and sediment metals. Molybdenum and lead in sediment correlated with the same element in plants. Meanwhile, all metals except Cd and Al in sediments appear to determine other metal concentration in plants. For instance, the relationship between plant Cu, Cd and Mo is significant in the presence of all metals analysed in the sediment. In addition, plant Al and Pb are also affected by all sediment metals except Fe, Al and Cd.

The sediment pH, Eh and organic matter content were found to correlate with some plant metals, for example $r=-0.18$ (Cd vs SOM, $p<0.05$, $n=253$), $r=0.24$ (Cd vs pH, $p<0.05$, $n=253$) and $r=0.16$ (Pb vs Eh, $p<0.05$, $n=253$). In particular sediment organic matter was found to correlate negatively for all plant metals. However, this relationship was only significant for Cd, Fe, Al and Mo. Both Eh and pH correlation was positive, but only significant for a selection (see Table 6). The relationship between SOM and plant metals show that increases in plant metals are possible when SOM concentration decreases. This is especially true when sediment redox becomes more oxidising, a condition whereby more organic matter degradation occurs and the pH changes from a mildly acidic condition to higher pH.

The increase factor of each element for these plants relative to background concentrations were calculated by dividing the average concentration in selected plants from contaminated sites with the average for each species from uncontaminated sites (Table 7). Copper concentrations in these plants are also included for comparison. The increase factors show that increases in metal concentration in the selected plants is evident. It is also evident from the data

Table 6 Correlation data for plant metal content against dissolved metals, sediment metals, sediment sulphur, sediment organic matter, redox (Eh) and pH. Significant correlation ($p \leq 0.05$) are highlighted bold-italics.

| | pCu | pCd | pFe | pMn | pPb | pZn | pAl | pMo |
|---|---|---|---|---|---|---|---|---|
| dCu | 0.09 | ***0.26*** | 0.01 | 0.06 | 0.07 | ***0.13*** | 0.09 | ***0.32*** |
| dCd | 0.01 | 0.03 | 0.00 | -0.02 | 0.03 | 0.10 | 0.03 | 0.06 |
| dFe | -0.04 | 0.01 | 0.11 | 0.06 | -0.01 | -0.01 | -0.02 | 0.01 |
| dMn | -0.02 | -0.05 | 0.02 | 0.11 | -0.04 | 0.06 | -0.04 | -0.05 |
| dPb | -0.03 | -0.02 | -0.05 | -0.07 | -0.04 | 0.05 | -0.03 | 0.04 |
| dZn | -0.07 | -0.09 | -0.12 | -0.09 | -0.09 | 0.00 | -0.10 | -0.07 |
| dAl | 0.01 | ***0.21*** | 0.01 | 0.02 | 0.02 | ***0.14*** | 0.04 | ***0.32*** |
| dMo | ***0.17*** | ***0.33*** | 0.03 | 0.10 | ***0.13*** | 0.11 | ***0.13*** | ***0.35*** |
| sAl | 0.04 | 0.05 | -0.03 | 0.03 | 0.01 | -0.03 | -0.01 | -0.01 |
| sCd | -0.01 | 0.04 | -0.06 | -0.05 | -0.02 | 0.04 | -0.01 | 0.11 |
| sCu | ***0.16*** | ***0.31*** | 0.08 | 0.05 | ***0.15*** | 0.06 | ***0.17*** | ***0.31*** |
| sFe | ***0.15*** | ***0.24*** | 0.11 | 0.12 | 0.10 | 0.09 | 0.11 | ***0.23*** |
| sMn | ***0.14*** | ***0.26*** | 0.07 | 0.08 | ***0.13*** | 0.08 | ***0.14*** | ***0.29*** |
| sMo | ***0.19*** | ***0.31*** | 0.10 | 0.07 | ***0.18*** | 0.02 | ***0.18*** | ***0.29*** |
| sPb | ***0.20*** | ***0.27*** | 0.07 | 0.03 | ***0.19*** | 0.03 | ***0.19*** | ***0.20*** |
| sZn | ***0.19*** | ***0.29*** | 0.07 | 0.08 | ***0.16*** | 0.10 | ***0.18*** | ***0.25*** |
| sS | -0.01 | 0.03 | -0.07 | -0.03 | -0.03 | -0.07 | -0.03 | 0.09 |
| SOM | ***-0.13*** | ***-0.18*** | ***-0.13*** | -0.11 | -0.11 | -0.04 | ***-0.12*** | ***-0.13*** |
| Eh | ***0.13*** | 0.01 | ***0.16*** | 0.01 | ***0.16*** | 0.12 | ***0.17*** | -0.06 |
| pH | ***0.13*** | ***0.24*** | 0.04 | 0.09 | 0.08 | -0.06 | 0.11 | ***0.18*** |

Table 7 The increase factors for all metals relative to background concentrations of the same species from control sites.

| 70-500 mg/kg Cu | Cu | Cd | Fe | Mn | Pb | Zn | Al | Mo |
|---|---|---|---|---|---|---|---|---|
| *Utricularia aurea* | 7 | 4 | 1 | 2 | 4 | 1 | 2 | 1 |
| *Nelumbo nucifera* | 1 | 2 | 1 | 0 | 1 | 1 | 0 | 1 |
| *L hyssopifolia* | 4 | 4 | 1 | 1 | 2 | 1 | 2 | 5 |
| *L hexandra* | 3 | 2 | 2 | 1 | 3 | 1 | 3 | 2 |
| *H. acutigluma* | 1 | 1 | 1 | 0 | 3 | 1 | 2 | 7 |
| *I. polystachium* | 1 | 3 | 1 | 1 | 1 | 1 | 2 | 3 |
| 500->1000 mg/kg Cu | | | | | | | | |
| *U aurea* | 13 | 3 | 1 | 3 | 10 | 2 | 5 | 2 |
| *N nucifera* | 2 | 6 | 1 | 1 | 2 | 1 | 1 | 19 |
| *L hexandra* | 2 | 2 | 1 | 2 | 2 | 1 | 5 | 4 |
| *H. acutigluma* | 4 | 5 | 1 | 1 | 2 | 2 | 1 | 29 |
| *I. polystachium* | 13 | 0 | 95 | 174 | 0 | 79 | 7 | 1 |
| *E. praestans* | 2 | 9 | 2 | 1 | 1 | 1 | 7 | 26 |

that plants growing in the severely contaminated sites have higher metal concentration. In addition, the increase factors for particular metals appear for individual species appear to be less significant. For example, Fe, Mn and Zn do not appear to increase in the other species except for *Ischaemum polystachium*. The increases for *U. aurea* is obvious, considering their interaction with colloidal particles as mentioned previously.

## Discussion

The concentrations of dissolved metals revealed that elevated concentrations observed were associated with the presence of Fly River water. This observation also confirms the movement of Fly River water to sites further away from the main Fly River channel and the subsequent deposition of mine-derived sediments. The presence of elevated concentrations of dissolved metals investigated were also observed to be a direct result of the presence of sediments contaminated by mining residue (Yaru and Buckney, 2000). While metals in the dissolved phase may be taken up by aquatic plants, the observed increase in dissolved metals at these sites did not correlate with an increase in plant metal concentration. Molybdenum was the only element with a direct relationship between its plant concentration and both the sediment and water Mo content. The lack of correlation between plant and dissolved metals confirm previous observation by (Jackson 1992, Jackson et al 1991) that metals and nutrients are predominantly sediment derived. However, this is only true for the plants that have roots in the sediment, while floating plants take up nutrients from the water column. Dissolved copper and aluminum had some positive effect on plant-Cd, Zn and Mo, whilst dissolved molybdenum had the same effect on plant-Cu, Cd, Pb and Al. Dissolved Mo was positively correlated with plant-Mo, suggesting that plant Mo was derived from the water column.

These result confirm that the higher the sediment concentration the higher the plant metal concentration. This is consistent with observed patterns reported for copper (Yaru et al., 1999). In fact, it is distinctly illustrated by the clustering of data during multidimensional ordination, corresponding to higher metal concentrations associated with the mine-derived sediments (Yaru et al., 1999). There is evidence in the literature showing that metals in plants are primarily derived from the sediment (Dietz, 1973; Bole and Allen, 1978; Kovacs, 1978; Welsh and Denny, 1979; Barko et al., 1991; Jackson, 1992; Jackson et al., 1991). Jackson (1992) and Jackson et al. (1991) have observed positive correlation between plant-metal composition and sediment metals.

Other sediment variables such as redox, pH, sediment organic matter correlate positively or negatively to the plant metal concentrations. Jackson et al (1992) showed that redox and pH were important in the cycling of metals from sediment and therefore affects uptake by aquatic plants. It is certainly an important proposition, since the availability of copper and other heavy metals associated with the mine-derived sediment will depend on these sediment physico-chemical parameters. In fact, the results from this study show that plant metal concentrations are highly dependent on the Eh, pH and organic matter. The significant negative relationship between SOM and plant metals (with Cd, Fe, Al and Mo) reveal that these metals are bound up as organic matter complex. However, these can then become available as the organic matter complexes breakdown during oxidation. Similarly, under reduced conditions most metals are bound up as metal sulphides, however, changes in the redox status of the sediment from reducing to oxidising also renders these metals available for uptake. The positive correlation between plant metals (Cd and Mo) and pH is attributed to the uptake of these two metals from a high-pH, oxidised environment, compared metals originating from a highly mobile low-pH environment.

Correlation data for plant-metal content against dissolved and sediment metals, and various sediment characteristics reveal that metals are sediment derived (Table 6). Increase factors ranging between 2-13 for Cu, 2-9 for Cd, 2-95 for Fe, 2-174 for Mn, 2-10 for Pb, 2-79 for Zn, 2-7 for Al and 2-29 for Mo were observed for plants growing at contaminated sites. The results (Table 7) show that these factors increase with the degree of impact. *Utricularia aurea* and *Ischaemum polystachium* appear to show any potential for their use as biomonitors. Species that are fully submerged, such as *U. aurea*, have a tendency to trap fine particles. High concentrations of metals are transported in suspension in fine/colloidal particles. Consequently, *U. aurea* must be disregarded as a potential biomonitor because of difficulties in cleaning during sample preparation. Meanwhile, other plant species also show potential for their selection as biomonitors, however the increase factors do not appear to be significant.

Whilst it appears reasonable that most of these plants can be used as bio-monitors, based on the analysis of the data presented in this study, the monocots *L. hexandra, H. acutigluma* and *I. polystachium* could be targeted for further study. Only *I. polystachium* appear to be the best choice for monitoring of the impact of mine-derived sediment on aquatic plants species in the Fly River. Metal concentrations in individual organs for plants in Table 5 were plotted (Figure 4) to determine if trends were evident for each species. The individual plots show that leaves generally have higher metal concentration than stems in the monocots. Of the two dicots which were compared, *L. hyssopifolia* displayed a trend common at all sites, where metal concentrations decrease in the following pattern seeds<stems<shoots<leaves. The following general trend was observed for *N. nucifera* leaves<stems<flowers<pods<seeds for all elements except aluminum and manganese. The opposite was observed for Fe and Pb in *N. nucifera* at the control site. Meanwhile, variations in some plant species observed for sites with similar sediment metal concentrations may be related to a range of factors such as grouping different aged leaves and shoots for analysis, stress due to diseases, shading and competition (Pip, 1990). However, the trend observed was similar for all species for all sites, A single factor ANOVA (Statsoft, 1997) performed for this variation was significant ($p<0.05$). In the absence of any data relating to plant available metals, it is difficult to ascertain what fraction of the sediment-metal is available when there is evidence of a general increase in plant metals. Determining accumulation factors using dissolved metals concentrations may result in error due to the presence of various metal complexes. A small percentage of the dissolved concentration may exist in a form readily available for uptake by aquatic plants from the water column. Yaru and Buckney (2000) confirm that copper exists in the form of colloids with aluminum and iron, and as Cu-organic matter complex.

In conclusion, concentrations of metals in plants at contaminated sites were elevated, compared to those observed for plants growing at non-contaminated or pristine sites. When compared to control sites within each raunwara, a significant increase in metal loading was observed for plants growing in areas receiving mine derived sediment. A general increase in metal concentrations in observed for dicots compared to monocots, however, the high variability of the data necessitates further investigations for accumulation and the use of dicots as biomonitors. The increase

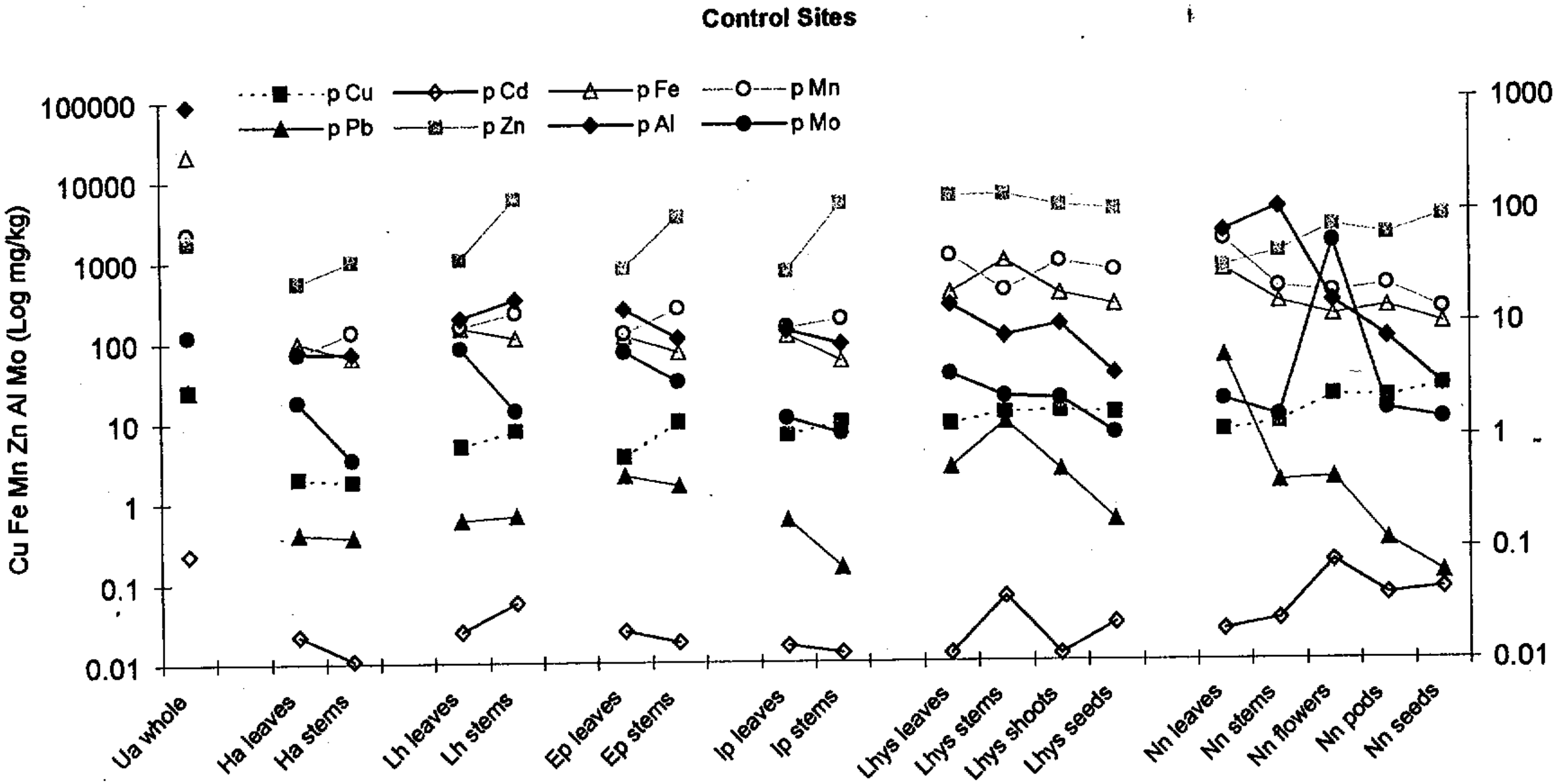


Figure 4 Plot of metal concentrations for species common to control, moderately and severely contaminated sites. Copper results are included in the plots for comparative purposes, however, Cu results are reported in Yaru et al (1999).

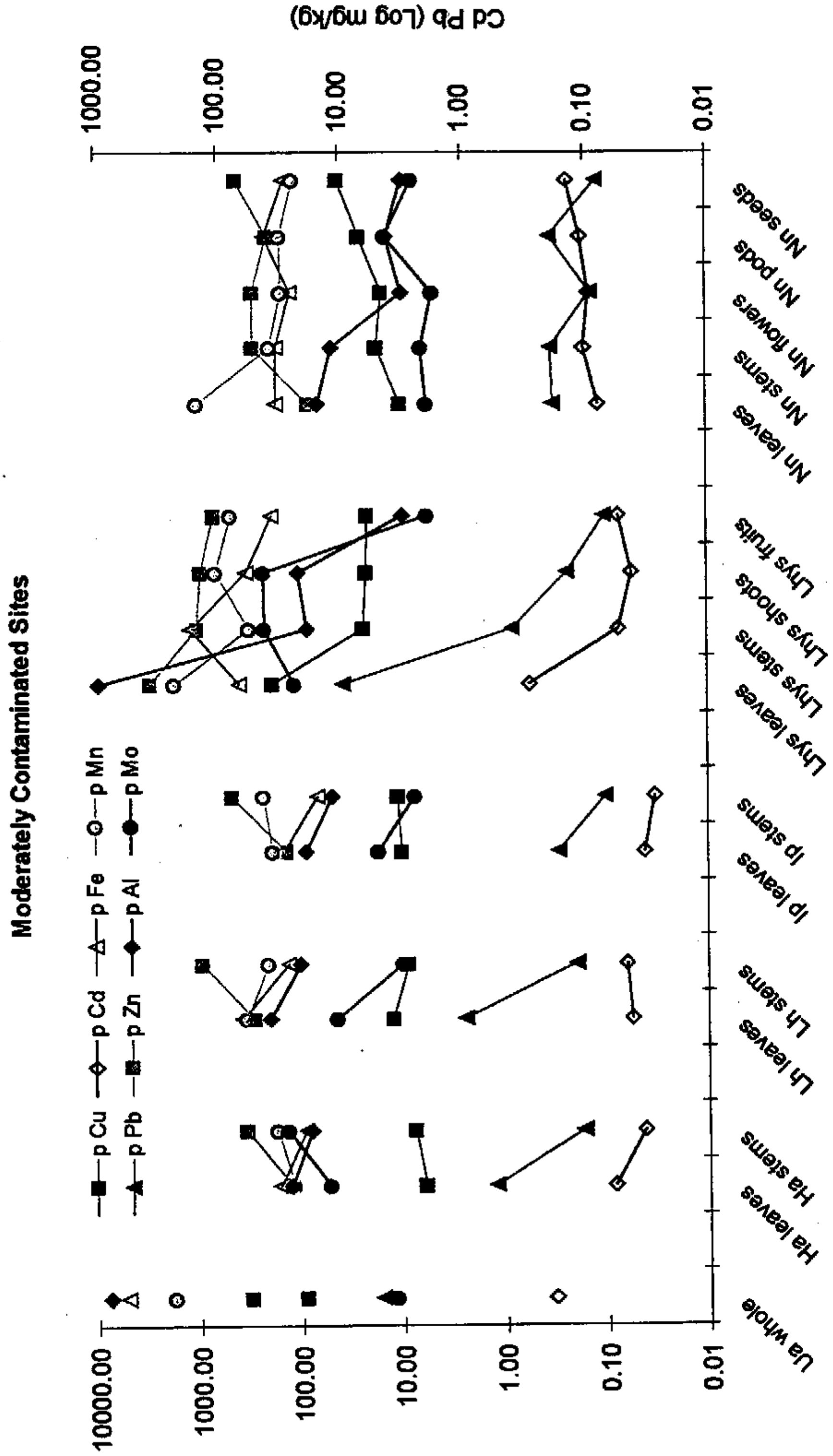


Figure 4 cont.

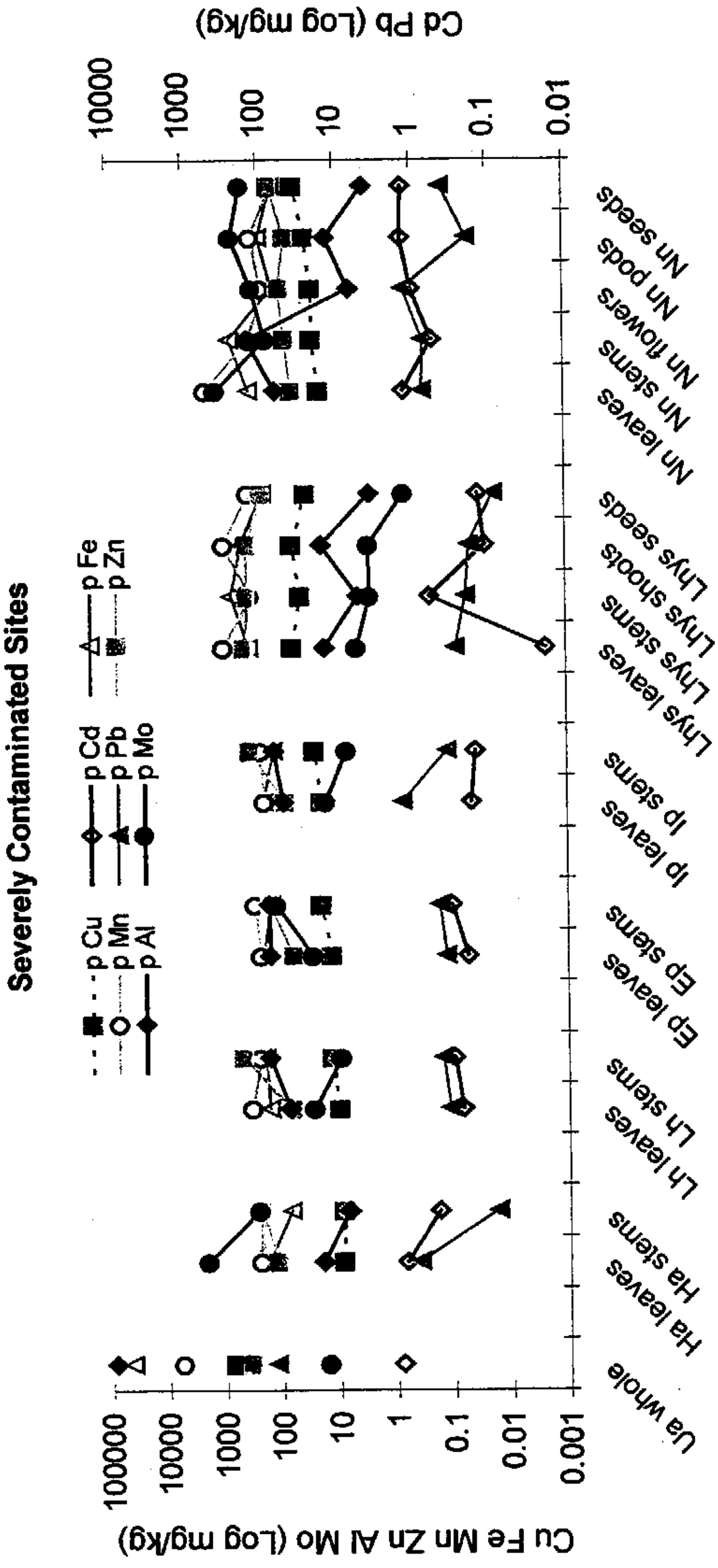


Figure 4 cont.

similar, however, *I. polystachium* appear to show accumulation. In fact, there was 13 times more copper in *I. polystachium* at sites with >500mg/kg Cu in sediment compared to the same species from control sites. In addition, the results presented reveal the potential for other monocot species such as *Hymenachne acutigluma* and *Leersia hexandra*. Data from a previous study (OTML, 1998) agree that *Hymenachne acutigluma* and *Leersia hexandra* may qualify as metal accumulators. The reported general trend was that, mature and younger shoots had more metals than stems and older leaves (in that order).

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