

Studies on heavy metal accumulation in aquatic macrophytes from Sevan (Armenia) and Carambolim (India) lake system

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Summary

Aquatic macrophytes are unchangeable biological filters and they carry out purification of the water bodies by accumulating dissolved metals and toxins in their tissue. In view of their potential to entrap several toxic heavy metals, 45 macrophytes belonging to 8 families collected from two different physiographic locations (36 from Sevan lakes Armenia; 9 from Carambolim Lake, Goa, India) were studied for estimation of 14 heavy metals. The study was aimed at understanding the importance of these macrophytes in accumulation of toxic metals and suggesting the remedial measures, if any, for the preservation and restoration of lake ecosystem.

Inductively Coupled Plasma- Atomic Emission Spectrometric (ICP-AES) analysis of these aquatic macrophytes have shown the importance of aquatic macrophytes in accumulation of heavy metals and maintaining the clarity of water bodies beside their role in trophic systems. Accumulation of most of the heavy metals was higher in root system. The representative macrophytes from two different physiographic locations show similar trend and order in accumulating different heavy metals. Of the 14 metals investigated, 9 (Ca, Fe, Al, Cr, Cu, Ba, Ti, Co, and Pb) showed higher rate of accumulation in the root whereas 3 (Mn, Zn and Mg) showed more accumulation in stem and 1 (Ca) showed higher accumulation in the leaves. In most of the samples Cu was accumulated more in the roots ($50 \pm 47.15 \mu\text{g/g}$) and less in flower ($9.52 \pm 3.97 \mu\text{g/g}$). On an Average the occurrence of heavy metal was much higher in macrophytes of Sevan lakes than Carambolim Lake. The accumulation of 14 elements was in order of $\text{Ca} > \text{Mg} > \text{Fe} > \text{Al} > \text{Mn} > \text{Ba} > \text{Zn} > \text{Ti} > \text{Cu} > \text{Cr} > \text{Co} > \text{Ni} > \text{Pb} > \text{Cd}$.

The present study revealed that the aquatic macrophytes play a very significant role in removing the different metals from the ambient environments. They probably play a major role in reducing the effect of high concentration of heavy metals. Therefore, the macrophyte community of the Sevan lakes area needs to be protected and restored on a priority basis. Accumulation of highly toxic metals like – Cr, Cd, Pb and Ni was lower as compared to the essential metals like Ca, Fe and Mn in all the macrophytes from both the lake systems, consequently high metal concentrations observed in both the areas may not directly reflect on the pollution level.

Keywords: Aquatic macrophytes, toxic metals, accumulation, Sevan Lakes; Armenia; Carambolim Lake, Goa, India.

Introduction

Macrophytes are aquatic plants, growing in or near water that are either emergent, submerged or floating. Macrophytes are beneficial to lake because they provide food and settler for fish and aquatic invertebrates. They also produce oxygen, which helps in overall lake functioning, and provide food for some fish and other wildlife.

Macrophytes are considered as important component of the aquatic ecosystem not only as food source for aquatic invertebrates, but also act as an efficient accumulator of heavy metals (Devlin, 1967; Chung and Jeng, 1974). They are unchangeable biological filters and play an important role in the maintenance of aquatic ecosystem. Aquatic macrophytes are taxonomically closely related to terrestrial plants, but are aquatic phanerogams, which live in a completely different environment. Their characteristics to accumulate metals make them an interesting research objects for testing and modeling ecological theories on evolution and plant succession, as well as on nutrient and metal cycling (Forstner and Whittman, 1979). Therefore, it is very important to understand the functions of macrophytes in aquatic ecosystem.

Heavy metals are metals having a density of 5 g/cc, (Nies et al., 1999). These metals include elements such as copper, cadmium, lead, selenium, arsenic, mercury, chromium and etc. Some sources of heavy metals are industry, municipal wastewater, atmospheric pollution, urban runoff, river dumping, and shore erosion. Heavy metals in surface water systems can be from natural or anthropogenic sources. Currently, anthropogenic inputs of metals exceed natural inputs. High levels of Cd, Cu, Pb, Fe can act as ecological toxins in aquatic and terrestrial ecosystems (Guilizzoni, 1991; Balsberg-Påhlsson, 1989). Excess metal levels in surface water may pose a health risk to humans and to the environment.

The water, sediments and plants in wetlands receiving urban runoff contain higher levels of heavy metals than wetlands not receiving urban runoff. Large aquatic plants are known to accumulate heavy metals in their tissues. Macrophytes take up heavy metals mainly through the root, although uptake through the leaves may also be of significance. As the macrophytes die and

decay, the accumulated metals in the decaying macrophytes can increase in the concentration of heavy metals in the sediments. Aquatic plants often grow more vigorously where nutrient loading is high. They are capable of removing water-soluble substances from solution and temporarily immobilize them within the system (HO, 1988; Untawale et al., 1980).

Bioavailability and bioaccumulation of heavy metals in aquatic ecosystems is gaining tremendous significance globally. Several of the submerged, emergent and free-floating aquatic macrophytes are known to accumulate and bioconcentrate heavy metals (Bryan, 1971; Chow et al., 1976). Aquatic macrophytes take up metals from the water, producing an internal concentration several fold greater than their surroundings. Many of the aquatic macrophytes are found to be the potential scavengers of heavy metals from water and wetlands (Gulati et al., 1979). Yet research has focused mainly on the interaction between biological factors such as competition, co-existence, grazing, life cycles, adaptation, and environmental factors (salinity, depth, wave exposure) of importance for structuring brackish macrophyte and algal communities (Alloway and Davis, 1971).

Many industrial and mining processes cause heavy metal pollution, which can contaminate natural water systems and become a hazard to human health. Therefore, colonization of macrophytes on the sediments polluted with heavy metals and the role of these plants in transportation of metals in shallow coastal areas are very important. The present investigation was planned and executed considering the potentials of macrophytes as a biological filter of the aquatic environment.

Results confirm that aquatic plants can play an important role as a transportation link for metals from the sediments up into shoots. The metals are thereby made available to grazing molluscs and, thus, reintroduced into the food web via fish to birds and humans. In addition, macrophytes in shallow coastal zones function as living filters for nutrients and metals that become bound to living plant material. Additionally, vascular aquatic macrophytes are involved in the biogeochemical cycles of nutrient and non-essential elements in many aquatic ecosystems. These plants often take up elements in excess of need and can

accumulate essential as well as non-essential elements to concentration many times higher than those of the surrounding waters.

In view of the increasing aquatic pollution, the initial survey was undertaken to acquire an estimation of the range of variability in accumulation of heavy metals in the aquatic plants from the lake Sevan, Armenia and Carambolim Lake, Goa, India. The study was aimed at understanding the importance of these macrophytes in accumulation of toxic metals and suggesting the remedial measures, if any for the preservation and restoration of the lake ecosystem.

Materials and Methods

Study areas:

Lake Sevan (Armenia): ..“ A piece of blue sky fallen”, "...mountain mirror" - Lake Sevan is the second highest in the world and is situated at the altitude of 1896 meters in hollow of picturesque Geghama Mounts. Lake Sevan contains 80% of Armenian water resources and plays an important role in regulating the country's water balance. The lake has two parts – Minor Sevan and Major Sevan differentiated by age and origin.



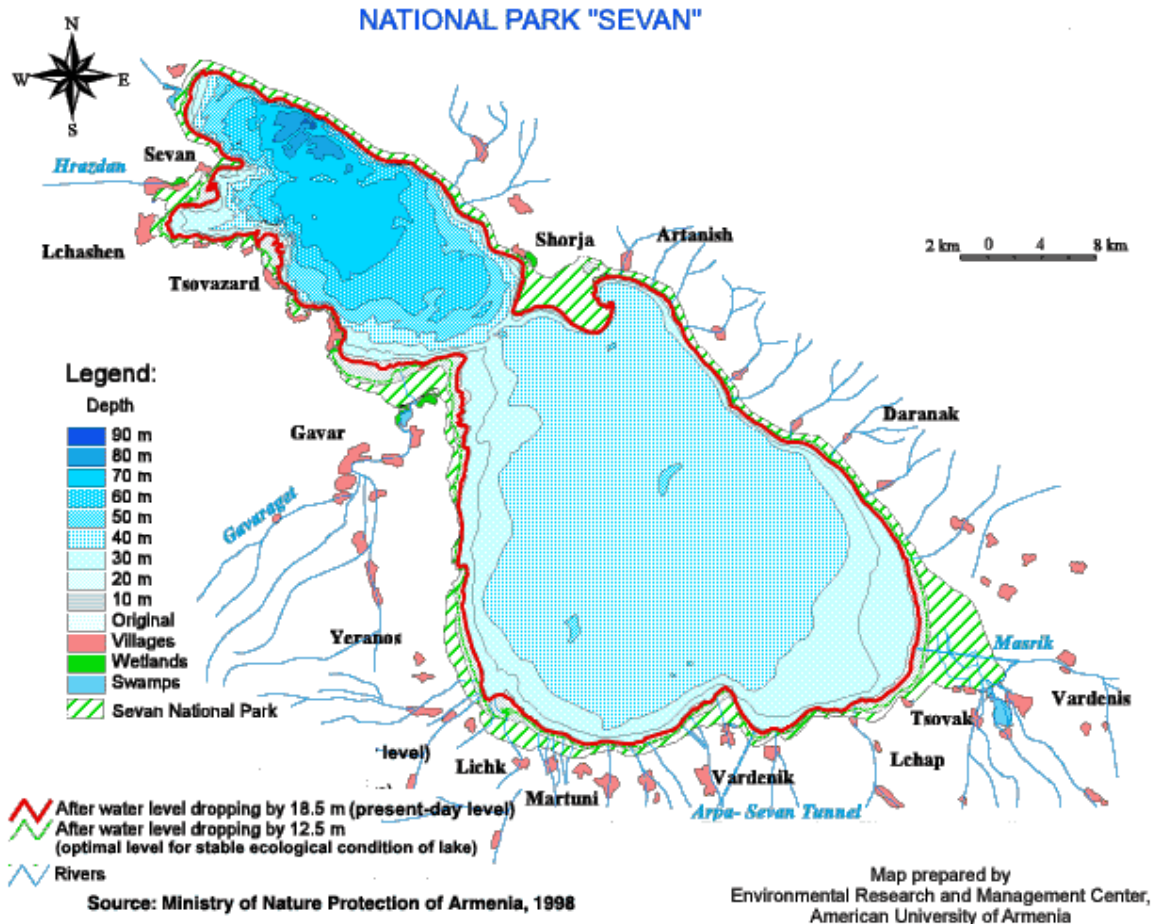


Fig. 1. Sevan Lake basin, Armenia.

Lake Sevan lies at the eastern part of Armenia between 40°9' - 40°38' N latitudes and 62°36' - 63°19' E longitudes (Fig.1). The basin of Lake Sevan (4890km²) belongs to the basin of the river Araks. Water level before the artificial fall was 1916 m height, the surface was 1416 km², and max length of 98,7km (Hovhannissyan, 1994), and now - correspondingly 1896m, 1243 km², 78,4km (Anon, 1999). The riverine part is an important freshwater feeding area for the surrounding regions. Lake Sevan belongs to the water column of those lakes, where macrophytes form the main part of the organic substance. Sevan Basin is a unique high mountain ecosystem with rich and diverse flora and fauna (Vardanian, 1998; Vardanian and Barseghian, 1999). The plant groups that grow in and around the rivers are diverse enough not only by their floristic ingredients, but by their construction as well. Aquatic macrophytes are unchangeable biological filters for the rivers that pour into the Sevan and they carry out purifying function. Sevan

basin's aquatic plants play an important role in the normal maintenance of the ecosystem of the lake, at the same time serving as a regulator of food and oxygen regimes for various animals that live in water, and the latter's in their turn, for the ichthyofauna.

However, the misuse of this resource over several decades lowered the water level by 20 meters and changed the morphometrics of the lake. As a result more than 10,000 hectares of marshes, and Gilly Lake in the south end of Lake Sevan, have been drained and lost through the lowering of Lake Sevan. Many of the former macrophytes have disappeared from the catchments that created about 60,000 tons of biomass, about 25,000-hectare sand soils, about 10,000-hectare mosses have dried. Studies on the chemical, physical and biological characteristics of water quality prove the important changes caused due to destroying bio-balance in the ecosystem. Many of the streams entering lake carry pollutants and as a result, it has become more eutrophic. All these changes collapsed the ecological balance of the Sevan Basin (Vardanian, 2000) causing desertification. Thus the Sevan Basin has become subject of investigation and concern for the whole world. The changes in the conditions within the lake have led to degradation of the whole ecosystem, and changes in various processes within the area of the lake.

Carambolim Lake, Old Goa (India): Located at $15^{\circ} 30'N$ $73^{\circ} 55'E$ along the side of the Mandovi River in central Goa, India, Carambolim Lake is a man-made wetland covering about 70 hectares catchment area (Fig.2). This is the main source of water for irrigation for the agricultural lowland in the Karmali area. The lake is situated 5-10m above mean sea level. It has a water depth of about 3-5 m during the monsoon. The wetland is flooded for about five months from October to March. The water level is raised to about 2 m by closing a sluice gate, enabling farmers to grow *Rabi crop* (dry season) rice on the low-lying land around the wetland. It reaches the maximum water depth in January. The sluice gate is normally opened in April and the water is used for irrigation.

This is a unique wetland of the region and a dreamland for birds. The birds feed on algae, grasses, insects, crustaceans, mollusks and fishes. The diverse and abundant avifauna attracts the human visitors, bird watchers and natural

lovers (Walia and Shanbhag, 1999). Periodic exposure of most of the lake bed during premonsoon and total draining of wetland at far end of summer as practiced at Carambolim appear to be a strategic management components, conducive for the sustenance of diverse and rich avifauna (Walia and Shanbhag, 1999). However, this ecologically important wetland is facing lots of problems especially due to the growing of weeds and surrounding land use pattern, which is reducing the catchments area and water depth.

Sample collection and identification: Macrophytes were hand picked from the freshwater habitat. In the laboratory, they were sorted species-wise following standard taxonomic manuals and one set was kept for preparation of herbarium and confirmation of taxonomic identification (Tables 1A and 1B).

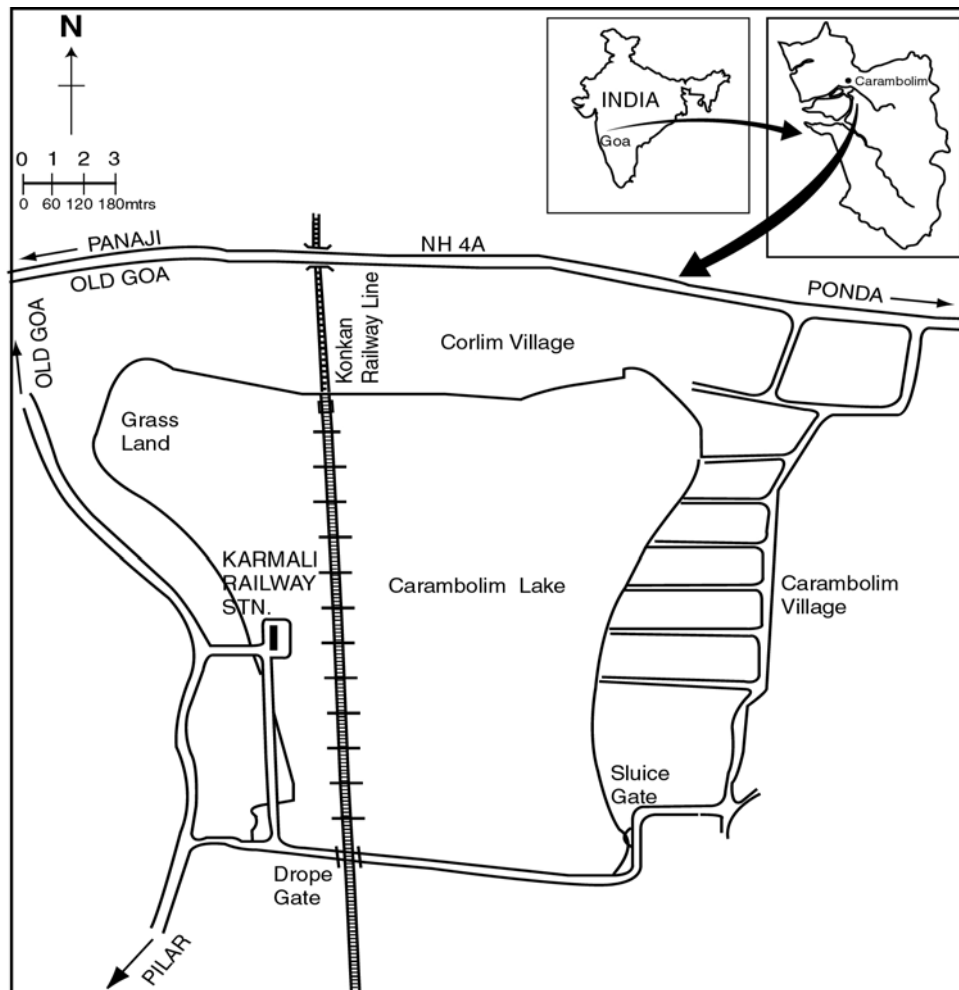


Fig. 2. SITE MAP OF CARAMBOLIM LAKE, OLD GOA.

Table 1A: Macrophyte samples from Lake Sevan (Armenia)

No.	NAME	FAMILY	LOCATION	DATE
A1	<i>Potamogeton pectinatus</i> L.	Potamogetonaceae	Argichi (Madina)	5 th Aug,2000
A2	<i>Potamogeton pussilus</i> L.	Potamogetonaceae	Argichi (Madina)	5 th Aug,2000
A3	<i>Batrachium divaricatum</i> (Schrank) Wimm.	Ranunculaceae	Makenis	5 th Aug,2000
A4	<i>Hippuris vulgaris</i> L.	Hippuridaceae	Argichi (Martuni)	5 th Aug,2000
A5	<i>Myriophyllum spicatum</i> L.	Haloragaceae	Argichi (Madina)	5 th Aug,2000
A6	<i>Lemna minor</i> L.	Lemnaceae	Argichi (Madina)	5 th Aug,2000
A7	<i>Chara vulgaris</i>	Characeae	Makenis	5 th Aug,2000
A8	<i>Potamogeton crispus</i> L.	Potamogetonaceae	Argichi (Madina)	5 th Aug,2000
A9	<i>Potamogeton pussilus</i> L.	Potamogetonaceae	Makenis	5 th Aug,2000
A10	<i>Rorippa islandica</i> (Oeder) Borb.	Brassicaceae	Makenis	5 th Aug,2000
A11	<i>Holosteum umbellatum</i> L.	Caryophyllaceae	Makenis	5 th Aug,2000
A12	<i>Lepidium latifolium</i>	Brassicaceae	Makenis	5 th Aug,2000
A13	<i>Lythrum salicaria</i> L.	Lythraceae	Makenis	5 th Aug,2000
A14	<i>Puccinellia sevangensis</i> (Grossh.)	Poaceae	Makenis	5 th Aug,2000
A15	<i>Eleocharis palustris</i> (L.) Roem. Et. Schult	Cyperaceae	Argichi (Madina)	5 th Aug,2000
A16	<i>Bolboschoenus maritimus</i> (L.) Palla	Cyperaceae	Argichi (Martuni)	5 th Aug,2000
A17	<i>Calamagrostis epigeios</i> (L.) Roth.	Poaceae	Argichi (Madina)	5 th Aug,2000
A18	<i>Equisetum rammosimum</i> Desf.	Equisetaceae	Argichi (Madina)	5 th Aug,2000
A19	<i>Mentha arvensis</i> L.	Lamiaceae (Labiatae)	Argichi (Madina)	5 th Aug,2000
A20	<i>Glyceria plicata</i> Fries	Poaceae	Argichi (Martuni)	5 th Aug,2000
A21	<i>Scirpus tabernaemontani</i> C. C. Gel.	Cyperaceae	Argichi (Martuni)	5 th Aug,2000
A22	<i>Bidens tripartite</i> L.	Asteraceae	Argichi (Madina)	5 th Aug,2000
A23	<i>Sparganium erectum</i> L.	Sparganiaceae	Makenis	5 th Aug,2000
A24	<i>Juncus articulatus</i> L.	Juncaceae	Makenis	5 th Aug,2000
A25	<i>Ranunculus sceleratus</i> L.	Ranunculaceae	Argichi (Madina)	5 th Aug,2000
A26	<i>Polygonum amphibium</i> L.	Polygonaceae	Makenis	5 th Aug,2000
A27	<i>Scrophylaria alata</i> Gilib.	Scrophulariaceae	Makenis	5 th Aug,2000
A28	<i>Myosotis caespitosa</i> L. F. Schultz.	Boraginaceae	Makenis	5 th Aug,2000
A29	<i>Alopecurus myosoroides</i> Huds.	Poaceae	Argichi (Madina)	5 th Aug,2000

A30	<i>Potentilla anserine</i> L.	Rosaceae	Argichi (Madina)	5 th Aug,2000
A31	<i>Chara vulgaris</i>	Characeae	Makenis	12 th Sept,2000
A32	<i>Fontinalis anthipiretica</i>	Fontinalaceae	Aighr lake	5 th Aug,2000
A33	<i>Fontinalis anthipiretica</i>	Fontinalaceae	Argichi (Madina)	5 th Aug,2000
A34	<i>Filago arvensis</i> L.	Asteraceae	Argichi (Martuni)	5 th Aug,2000
A35	<i>Asperula humifusa</i> (Biele) Bess	Rubiaceae	Argichi (Madina)	5 th Aug,2000
A36	<i>Potamogeton crispus</i> L.	Potamogetonaceae	Makenis	5 th Aug,2000

Table 1B: Macrophyte samples from the Carambolim Lake and surrounding areas Goa, India.

Sample No.	NAME	LOCATION	FAMILY	DATE
I1	<i>Pistia stratiotes</i> L.	Karmali	Araceae	24 th Mar,2002
I2	<i>Nelumbium speciosum</i> Willd	Karmali	Nymphaeaceae	24 th Mar,2002
I3	<i>Ludwigia perennis</i> L.	Ela Farm (Old Goa)	Onagraceae	24 th Mar,2002
I4	<i>Nymphoides Hill cristatum</i> (Roxb.) O.Kuntze	Ela Farm (Old Goa)	Menyanthaceae (nom.Alt. Gentinaceae)	24 th Mar,2002
I5	<i>Lemna trisulca</i> L.	Ela Farm (Old Goa)	Lemnaceae	24 th Mar,2002
I6	<i>Sagittaria sagittifolia</i> L.	Ela Farm (Old Goa)	Alismataceae	24 th Mar,2002
I7	<i>Sesuvium portulacastrum</i> L	Azoshim	Ficoideae	24 th Mar,2002
I8	<i>Nymphae stellata</i> Willd	Sulabatt	Nymphaeaceae	24 th Mar,2002
I9	<i>Sargassum ilicifolius</i>	Chapora	Sargassaceae	19 th Feb,2002

Sample processing: Individual species were washed carefully. Different plant parts such as root, stem, leaves and flowers (if available) were washed in distilled water and dried at 70° C in hot air oven for 48 hours. Dried samples were homogenized and ground to yield fine powder.

The sample processing and analytical procedures for ICP-AES analysis were as follows:

- ≈0,050 g of dried and powdered bulk samples were moistened with 1-2 ml of deionised water.
- 10 ml of concentrated HNO₃ was added slowly and the mixture was left for reaction overnight

- the mixture was heated on a hot plate until incipient boiling for achieving complete leaching/digestion of the tissue. The digest was allowed to cool.
- cool mixture was filtered through No 40 filter paper to remove gelatinous precipitates, if any, followed by filtering through No 42 filter paper to remove any fine crystalline residues.
- Finally, the filtrate was made to 50 ml with deionised water.

The solution, blank and calibration standard were spiked with 2 µg/ml scandium (Sc) as the internal standard. This internal standard method monitors and compensates the variation in emission signals due to varying nebulization of solutions having different viscosity.

Sample analysis by ICP-AES: Perkin-Elmer plasma-400 ICP-AES operating in sequential mode was used for all the analysis. Since every element has its own characteristic set of energy levels and thus the set of emission wavelengths makes the atomic spectrometer useful for element specific analytical techniques. The wavelengths at which the various metals were detected are as follows, Ca 317.933 nm, Mg 285.213nm, Fe 238.204, Al 396.153, Cr 267.716, Cu 327.393, Ni 231.604, Ba 233.527, Mn 257.610, Zn 206.200, Pb 220.353, Cd 228.802, Ti 334.940 and Co 228.616.

The accuracy of the analytical results was assessed by several analyses of standard reference material in duplicate over a period of time. The averages of six such analyses were used to calculate percent error in the results. Analysis of the most of the elements is accurate within 3% analytical error.

Results and Discussions

Analyses of metals accumulation in plants have practical values in outlining ore deposits of variety of metals and also in making of new discovery (Antonovics et al., 1971). The concentration of heavy metals in 36 aquatic macrophytes from Lake Sevan (Armenia) and 09 from the Carambolim Lake and surrounding areas, Old Goa, India is given in tables 2A-2M. The literature survey suggests that investigations on the heavy metals accumulation in Lake Sevan catchments basin have been carried out for the first time. The comparative study on macrophytes

and accumulation of heavy metals in different macrophytes from these two different geographical areas are also done probably for the first time. Hence, the present study has greater significance; especially as the water from both these habitat is being used for drinking (Sevan Lakes) and irrigation. Generally the accumulations of heavy metals in Lake Sevan were very high as compared to the Carambolim Lake. There has been considerable decrease in the water level of Sevan Lake in the last few decades since 1934-2000 (Hovhannissyan, 1994; (Vardanian and Barseghian, 1999) and could be the main reason for high accumulation of metals in the lake water and the catchments basin.

As shown in tables 2A-2M, distribution of different elements in the macrophytes was very unique and interesting. In general, calcium (Ca) was accumulated more in leaves than in stem. On an average 24814.94 ± 12713.68 $\mu\text{g/g}$ Ca was observed in leaves, and maximum of 40976.23 $\mu\text{g/g}$ Ca was in *Nelumbium speciosum*, collected from the Carambolim Lake, Goa. At the same time, on an average 12441.31 ± 5879.13 $\mu\text{g/g}$ Ca was accumulated in roots. The accumulation of Mg was more in stem (10124.77 ± 10602.48 $\mu\text{g/g}$) and least (5048.08 ± 2005.17 $\mu\text{g/g}$) in leaves. Maximum of 33090.44 $\mu\text{g/g}$ Mg was observed in stem of *Sesuvium portulacastrum* collected from Goa. Iron (Fe) was mostly accumulated in root and on an average of 60842.57 ± 42610.45 $\mu\text{g/g}$ Fe was found in roots. Flowers were the portion where Fe was least accumulated (4560 ± 818.98 $\mu\text{g/g}$). As shown in Table 2M, Iron concentration was maximum (111212 $\mu\text{g/g}$) in *Pistia stratiotes* collected from the Carambolim Lake.

Similar to the Fe, Aluminum (Al) was also more in roots with mean value of 28170 ± 20113.69 $\mu\text{g/g}$ and as in case of Fe, the minimum concentration (2354.82 ± 851.37 $\mu\text{g/g}$) was observed in flowers. Except in *Sesuvium portulacastrum* where maximum chromium (Cr) value of 27.44 $\mu\text{g/g}$ was in stem, the accumulated of Cr was more in roots (79.56 ± 59.34 $\mu\text{g/g}$) and the least value were observed in the flowers (6.11 ± 2.8 $\mu\text{g/g}$). *S. portulacastrum* was collected from a local freshwater pond at Azoshim near Carambolim, however the Cr concentration of 186 $\mu\text{g/g}$ was in the roots of *Ludwigia perennis* collected from an agricultural field near Old Goa. Higher accumulation of Cr in *L. perennis* could be

due to the extensive use of Cr in adjoining horticulture fields, which is the major commercial activity in the surrounding area. In most of the plants, copper (Cu) was found more in the roots ($50 \pm 47.15\mu\text{g/g}$) and less ($9.52 \pm 3.97\mu\text{g/g}$) accumulation was in flowers. Nickel (Ni) was not detected in stem and flowers but was recorded in roots ($9.81 \pm 16.67\mu\text{g/g}$). Barium (Ba) was accumulated more in roots ($80.9 \pm 58.22 \mu\text{g/g}$), whereas flowers showed low value of Ba ($10.55 \pm 6.87\mu\text{g/g}$).

Manganese (Mn) was accumulated more in stem ($708.19 \pm 428.31\mu\text{g/g}$) followed by leaves. Zinc (Zn) was found more in stem (on an average of $115.75 \pm 55.95\mu\text{g/g}$). The accumulation of Lead (Pb) was high in roots (on an average of $29.22 \pm 27.95\mu\text{g/g}$) and in most of the macrophytes it was higher by a factor of 2 in roots as compared to stem and leaves.

Ti was accumulated more in root ($303.42 \pm 125.63\mu\text{g/g}$) and the lowest accumulation of Ti was observed in flower ($51.43 \pm 36.62\mu\text{g/g}$). Cobalt (Co) was also observed in the samples but in very little quantity. The highest accumulation of Co was in the roots ($6.17 \pm 5.35 \mu\text{g/g}$). Cadmium (Cd) was observed only in *Sargassum* sp. ($10.23\mu\text{g/g}$), which was collected from the marine intertidal area (Chapora coast, Goa, India).

Of the 14 metals investigated, 09 (Ca, Fe, Al, Cr, Cu, Ba, Ti, Co, and Pb) showed higher rate of accumulation in the root whereas 03 (Mn, Zn and Mg) showed more accumulation in stem and 1 (Ca) showed higher accumulation in the leaves (Table 2). A plant with numerous thin roots would accumulate more metals than one with few thick roots. Factors such as light intensity, oxygen tension and temperature are known to affect the uptake of minerals (Devlin, 1967). Moreover, the energy derived from photosynthesis and the oxygen released can improve conditions for the active absorption of elements. However, interactions between metals are often complex, and they are dependent on the metal concentration and pH of the growth medium (Balsberg-Påhlsson, 1989).

Goa is well known for mining activities and major contribution to the economy is from the export of over 10 million tonnes per year of iron and manganese ore (Parulekar et al., 1986). The availability of iron and manganese in the surrounding environment and their accumulation in aquatic organisms like

macrophytes were therefore obvious and can be correlated with the mineral deposits in the adjacent areas (Ramadhas et al., 1974). The present investigation, therefore, provides important information on the leaching of metals from the mining field and its subsequent accumulation in aquatic organisms. Hence, studies on the accumulation of heavy metals in aquatic plants can be used effectively to assess the health of the environment.

In case of the Sevan Basin River, large variations were observed in concentrations of all metals in aquatic plants (Table, 2A-H; Fig.3-8). Of the 36 macrophytes *Chara vulgaris* shows the greatest ability to accumulate Ca up to 414300µg/g; Table, 2D). *Lytrum salicaria* showed the better ability to accumulate Zn (3981µg/g; Table, 2D) and *Potamogeton pectinatus* shows the highest concentration of Mn (39,890 µg/g; Table, 2A). The role of these three metals in respiration as activators of enzymes involved in glycolysis and Krebs' cycle has been documented. Cadmium (Cd) was not observed in freshwater macrophytes collected from both study areas. However, 10.23 µg/g Cd was recorded in one of the marine macrophyte, *Sargassam ilicifolius*, collected from intertidal rocky area at Chapora, Goa. Further, Cd has also been recorded in a mangrove clam *Polymesoda erosa* (Ingole pre. obs.) collected from Chapora mangrove area. Presence of Cd in both the marine organisms (i.e seaweed *S. ilicifolius* sp and clam *Polymesoda erosa*) suggests the possible accumulation of cadmium in marine environment along the west Goa coast. While, monitoring the heavy metals (Pb, Hg, Cd) in aquatic plants (algae, mosses, macrophytes) and sediment Zakova and Kockova (1998) reported the high accumulation of Pb and Cd in the macrophytes of Dyje/Thaya River basin in Czech Republic. According to Untawale et al (1980), although there was a marked seasonality in heavy metal concentrations in mangrove foliage copper, Nickel and cobalt showed uniform pattern of concentration during different season. It emphasize that Cd in macrophytes of Sevan and Carambolim Lake was perhaps below the detection level. When arranged according to their accumulation, the following order was observed for the 14 elements - Ca> Mg> Fe> Al> Mn> Ba> Zn> Ti> Cu> Cr> Co> Ni> Pb> Cd.

It is well documented that aquatic plants due to photosynthetic activity change the oxygen regime of the rivers, which in turn has great importance for the growth and multiplication of the hydrobionts (Butterworth et al., 1972; Bowen, 1977). These macrophytes offers good condition for sediment, which in turn plays a very important role in propogation of benthic community (Allan et al., 1975). However, the positive role of aquatic macrophytes may become reverse in case of their massive growth.

The effects of trace elements in an aquatic ecosystem can be assessed by changes in the community structure, physiological activity and ultrastructural components of macrophytes (Chester and Stoner, 1974; Bohn, 1975; Pulich et al., 1976; Bradford, 1976). However, comparison of metal content in macrophytes is often difficult because of differences in sampling time (ageing of plants) and presence of pollution sources. Moreover, the metal data cannot be extrapolated from one species to another or even within the same species, largely due to different accumulation rates. Nevertheless, copper (Cu) is known to reduce photosynthesis rates and respiration of aquatic moss, *Fontinalis antipyretica* (Vazquez et al., 2000). In eutrophic lakes such as Sevan Lake, very high local concentrations of metals often occur as a result of the strong reducing environment coupled with industrial and municipal discharges (Vardanyan, unpublished data). The low availability of heavy metals in the Sevan Basin Rivers as compared to Carambolim Lake, Goa seemed to be the precipitation of heavy metals as sulphides. Further, as compared to the Carambolim Lake the Sevan Basin Rivers has higher in-and out flow of freshwater that may reduce the rate of metal accumulation in aquatic macrophytes. Nonetheless, as suggested by Corcoran and Alexander (1964) and Bryan (1976) plants frequently accumulated large amounts of metals. As the concentration of highly toxic metals like – Cr, Cd, Pb and Ni was lower compared to the essential metals like Ca, Fe and Mn, therefore, high metal concentrations in aquatic macrophytes observed in both the study area may not directly reflect on the pollution level of these areas.

Driel and Groot (1974) and Bower et al (1978) have studied the metal uptake, translocation and effects in plants growing on naturally polluted and unpolluted sediments. Their results suggest that aquatic plants may facilitate the

transportation of metals from sediments up into shoots. The metals are thereby made available to grazing molluscs and, thus, reintroduced into the food web via fish to birds and humans (Brown and Chow, 1977). In addition, macrophytes in shallow coastal zones function as living filters for nutrients and metals that become bound to living plant material and remain in the inner archipelago areas (Sawidis et al., 1995).

Conclusion

From the present observations, it is concluded that there is a uniform pattern of heavy metal variation in the macrophytes of Carambolim Lake and surrounding area. In general, values of some metals like iron, calcium and copper are higher in almost all the specimens. Similar trend of heavy metal accumulation in the Armenian samples shows the universal importance of these macrophytes in cleaning up of the aquatic environment. Since the investigations on the heavy metals accumulation in macrophytes of Lake Sevan were carried out for the first time, hence the results presented here could be very useful for environmental monitoring and checking the health of the water body. The data presented here is indispensable information for comparison for studies of related nature. The aquatic macrophytes were found to be the potential source for accumulation of heavy metals from water and wetlands. Therefore, such studies should become an integral part of the sustainable development of the ecosystems and pollution assessment program.

Average level of all heavy metal accumulation in most of the macrophytes from Sevan Lake was much higher than macrophytes from Carambolim Lake. This indicates that occurrence of heavy metal is far more in the Sevan Lake than that of Carambolim Lake. This emphasizes that the macrophyte of both these lake system needs protection.

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Table 2A. Heavy metal concentrations in Potamogetonaceae

Heavy metal ($\mu\text{g/g}$ dry wt.)	Potamogetonaceae*				
	A1 ^a (0.0501)	A2 (1.1001) ^b	A8 (0.0503)	A9 (0.0503)	A36 (0.0504)
Ca	119800	31110	37450	268800	24830
Mg	29360	10620	20410	7804	5819
Fe	19930	17950	25180	30680	111600
Al	11640	19320	29250	2441	4599
Cr	26.14	3380	38.73	8.01	24.02
Cu	139.4	3695	24.21	4.31	38.11
Ni	17.89	2033	26.71	1.77	0.83
Ba	1765	386.5	394.6	390.5	276.1
Mn	39890	4361	9556	7535	3889
Zn	586.3	133.7	288.8	84.66	186.2
Pb	60.38	10.89	4.19	4.43	6.93
Cd	2.03	0.39	0.71	1.55	5.58
Ti	523.6	536.8	697.3	94.05	217.8
Co	55.0	14.4	13.9	1.88	49.6

Table: 2B Heavy metal concentrations in Poaceae and Lemnaceae

Heavy metal ($\mu\text{g/g}$ dry wt.)	Poaceae				Lemnaceae
	A14 (0.0502)	A17 (0.0504)	A20 (0.05)	A29 (0.0501)	A6 (0.0505)
Ca	33420	45210	21240	18430	127700
Mg	6142	15110	8320	10580	23630
Fe	1147	1495	3888	790.1	14320
Al	1262	1240	4021	440.7	4560
Cr	3.68	6.89	8.70	4.82	13.48
Cu	15.86	17.99	30.20	61.12	23.56
Ni	0.31	0.72	0.31	1.30	0.58
Ba	76.89	109.1	117.1	328.0	226.1
Mn	183.8	190.1	1432	1686	3000
Zn	98.25	169.1	147.1	330.2	212.5
Pb	7.85	0.25	3.38	3.68	7.17
Cd	0.08	0.17	0.21	0.24	0.79
Ti	36.56	56.82	134.4	21.07	152.3
Co	6.47	14.2	11.5	13.8	16.0

Table: 2C: Heavy metal concentrations in Lemnaceae, Hippuridaceae and Haloragaceae

Heavy metal ($\mu\text{g/g}$ dry wt.)	Cyperaceae			Hippuridaceae	Haloragaceae
	A15 (0.0503)	A16 (0.0503)	A21 (0.0504)	A4 (0.0505)	A5 (0.0506)
Ca	36200	42390	16120	133900	104200
Mg	12630	17970	11390	41180	29990
Fe	1284	1874	1241	2651	18600
Al	383.1	6877	4310	2871	17870
Cr	2.21	7.20	4.93	6.47	3123
Cu	12.71	33.98	5.00	18.12	4654
Ni	0.08	0.08	0.15	1.48	1409
Ba	222.4	381.5	94.90	144.9	1896
Mn	1791	1855	235.2	2478	27040
Zn	108.3	136.9	146.5	210.6	156.0
Pb	3.29	2.16	1.31	4.18	7.21
Cd	0.04	0.28	0.05	0.19	1.39
Ti	16.97	76.51	46.39	138.8	524.6
Co	10.2	6.97	16.1	7.60	44.4

Table: 2D: Heavy metal concentrations in Ranunculaceae, Characeae and Lythraceae

Heavy metal ($\mu\text{g/g}$ dry wt.)	Ranunculaceae		Characeae		Lythraceae
	A3 (0.0501)	A25 (0.05)	A7 (0.1002)	A31 (0.0505)	A13 (0.05)
Ca	118200	37420	414300	216100	156400
Mg	38140	12990	5725	15100	46620
Fe	8706	1091	15150	8299	3010
Al	8480	1023	929.5	4211	2992
Cr	31.43	5.49	3.95	10.93	9.65
Cu	250.5	18.68	17.49	15.04	52.83
Ni	28.45	2.44	0.64	9.01	1.71
Ba	104.0	71.16	503.8	351.9	77.93
Mn	5454	209.9	6749	1542	454.6
Zn	1266	107.1	28.84	42.86	3981
Pb	24.77	0.82	5.24	4.36	10.39
Cd	0.83	0.37	1.44	0.45	0.21
Ti	278.9	69.68	27.58	205.2	168.0
Co	21.2	21.9	0.093	11.7	11.4

Table: 2E: Heavy metal concentrations in Brassicaceae, Asteraceae and Equisetaceae

Heavy metal ($\mu\text{g/g}$ dry wt.)	Brassicaceae		Asteraceae		Equisetaceae
	A10 (0.0504)	A12 (0.0502)	A22 (0.05)	A34 (0.0505)	A18 (0.0501)
Ca	169300	241200	29470	106300	43050
Mg	24160	12110	13150	33170	12100
Fe	1461	722.5	1432	7570	458.9
Al	1277	3408	1271	8205	282.8
Cr	8.34	4.08	5.59	20.51	4.32
Cu	29.03	13.06	11.78	54.09	6.82
Ni	1.52	1.85	2.28	0.62	0.84
Ba	43.15	36.30	20.07	198.8	118.3
Mn	350.2	118.1	537.0	475.0	71.26
Zn	290.3	196.8	161.4	104.4	79.79
Pb	6.10	2.77	0.88	6.33	1.31
Cd	0.33	0.24	0.02	0.00	0.23
Ti	63.22	16.25	92.03	386.5	17.15
Co	0.046	11.9	5.32	6.30	1.18

Table: 2F: Heavy metal concentrations in Fontinalaceae, Lamiaceae, Sparganiaceae and Juncaceae

Heavy metal ($\mu\text{g/g}$ dry wt.)	Fontinalaceae		Lamiaceae	Sparganiaceae	Juncaceae
	A32 (0.0503)	A33 (0.0501)	A19 (0.05)	A23 (0.0503)	A24 (0.025)
Ca	207500	136400	132000	84710	40340
Mg	5282	9873	28570	26700	21160
Fe	495.8	2011	4258	1128	1936
Al	363.9	1337	3805	613.9	1332
Cr	61.56	44.98	12.37	5.39	10.38
Cu	54.26	35.75	65.28	37.79	50.06
Ni	10.25	45.15	0.68	1.16	1.18
Ba	33.01	52.40	895.6	258.3	485.4
Mn	81.470	302.4	392.5	5844	6524
Zn	82.46	91.19	308.7	261.6	458.1
Pb	1.42	1.78	6.71	2.52	2.73
Cd	0.34	0.23	0.17	0.30	0.30
Ti	14.74	47.25	184.5	35.08	65.68
Co	0.098	3.26	12.9	21.1	2.74

Table: 2G: Heavy metal concentrations in Polygonaceae, Scrophulariaceae and Boraginaceae.

Heavy metal ($\mu\text{g/g}$ dry wt.)	Polygonaceae	Scrophulariaceae	Boraginaceae
	A26 (0.0505)	A27 (0.0501)	A28 (0.0503)
Ca	102100	84910	45560
Mg	43050	31340	8499
Fe	1780	2438	4174
Al	1557	1632	4202
Cr	7.15	7.87	12.81
Cu	39.42	88.13	58.56
Ni	0.61	0.85	0.34
Ba	195.95	96.55	395.5
Mn	630.2	345.5	446.9
Zn	262.5	463.2	185.0
Pb	4.27	4.46	8.84
Cd	0.16	0.05	0.00
Ti	94.89	94.40	227.4
Co	17.0	18.9	6.44

Table: 2H: Heavy metal concentrations in Rosaceae, Rubiaceae and Caryophyllaceae

Heavy metal ($\mu\text{g/g}$ dry wt.)	Rosaceae	Rubiaceae	Caryophyllaceae
	A30 (0.0503)	A35 (0.05)	A11 (0.0505)
Ca	114200	90100	41320
Mg	27830	12930	30160
Fe	3967	19390	1305
Al	3517	22070	1397
Cr	11.00	41.14	4.97
Cu	51.92	48.88	14.34
Ni	0.12	32.99	2.00
Ba	693.5	586.3	88.69
Mn	352.7	692.0	355.9
Zn	358.4	193.6	261.2
Pb	6.12	7.10	6.46
Cd	0.31	0.90	0.42
Ti	263.2	1084	98.85
Co	16.7	20.6	12.8

Table: 2I: Heavy metal concentrations in *Nelymbium speciosum*

Heavy metal (µg/g dry wt.)	<i>Nelymbium speciosum</i>			
	Root (0.0505)	Stem (0.0504)	Leaf (0.0503)	Flower (0.0503)
Ca	13688.69	24728.66	40976.23	10612.88
Mg	2322.96	7163.61	6023.53	7711.45
Fe	49207.41	25654.51	18235.80	3981.16
Al	29642.62	3076.29	3238.56	1752.81
Cr	51.93	6.29	4.39	4.13
Cu	28.36	9.34	5.00	12.32
Ni	0.15	0.00	0.00	0.00
Ba	82.63	20.04	55.44	15.41
Mn	158.45	1090.03	1749.00	269.03
Zn	131.19	166.31	105.95	148.51
Pb	22.48	2.16	2.27	4.04
Cd	0.00	0.00	0.00	0.00
Ti	351.52	70.04	49.35	25.54
Co	7.16	2.99	3.33	0.25

Table: 2J: Heavy metal concentrations in *Ludwigia perennis* and *Nymphoides Hill cristatum*

Heavy metal (µg/g dry wt.)	<i>Ludwigia perennis L.</i>			<i>Nymphoides Hill cristatum</i>		
	Root (0.0501)	Stem (0.05)	Leaf (0.05)	Root (0.0505)	Stem (0.0503)	Leaf (0.0505)
Ca	15590.72	52554.76	32641.14	4401.18	8139.24	10527.48
Mg	3413.80	11614.41	5493.66	1050.04	1745.57	3276.95
Fe	101706.33	19054.75	16770.12	27570.90	10355.92	13740.33
Al	65422.71	15717.83	16526.46	16838.79	16452.20	18952.98
Cr	185.95	41.66	44.37	50.92	40.08	47.65
Cu	146.76	47.74	26.09	16.49	11.03	17.86
Ni	45.27	0.00	0.00	0.00	0.00	0.00
Ba	169.59	95.00	45.01	57.52	64.09	80.01
Mn	234.45	613.29	407.28	248.84	514.22	830.97
Zn	164.70	203.24	129.87	76.47	87.02	113.26
Pb	82.66	11.35	9.58	8.57	4.24	8.70
Cd	0.00	0.00	0.00	0.00	0.00	0.00
Ti	348.63	235.77	217.55	210.95	356.15	383.57
Co	15.67	2.66	1.29	1.97	1.34	7.78

Table: 2K: Heavy metal concentrations in *Sagittaria sagittifolia* and *Sesuvium portulacastrum*.

Heavy metal ($\mu\text{g/g}$ dry wt.)	<i>Sagittaria sagittifolia</i> L.			<i>Sesuvium portulacastrum</i> L.		
	Root (0.0503)	Stem (0.0505)	Leaf (0.0504)	Root (0.0504)	Stem (0.0502)	Leaf (0.05)
Ca	18975.12	32893.26	32912.91	7854.46	11165.30	6803.29
Mg	2336.74	5117.81	5012.74	20782.34	33090.44	8046.24
Fe	97358.79	2719.82	24069.30	986.10	10922.22	503.21
Al	37488.94	2829.78	23042.97	938.61	11630.05	432.44
Cr	106.29	6.82	62.98	2.05	27.44	0.48
Cu	74.05	14.05	61.45	41.56	37.74	52.32
Ni	14.92	0.00	1.29	0.00	0.00	0.00
Ba	98.35	29.26	58.23	3.54	29.65	0.06
Mn	180.24	244.53	524.93	274.79	1363.18	53.97
Zn	100.11	98.43	108.11	22.67	76.31	29.80
Pb	48.61	5.04	19.51	3.01	3.76	3.43
Cd	0.00	0.00	0.00	0.00	0.00	0.00
Ti	414.09	102.85	407.88	58.70	669.38	21.02
Co	6.59	0.00	2.34	0.00	4.50	0.00

Table: 2L: Heavy metal concentrations in

Heavy metal ($\mu\text{g/g}$ dry wt.)	<i>Nymphae stellata willd</i>			
	Root (0.0505)	Stem (0.0503)	Leaf (0.0505)	Flower (0.0505)
Ca	7540.65	9684.13	30081.15	14153.39
Mg	2873.39	8060.19	2435.35	4661.58
Fe	37856.41	7783.69	17209.05	5139.37
Al	19204.66	2209.09	5556.23	2956.83
Cr	52.44	5.72	20.42	8.09
Cu	14.39	3.39	4.25	6.71
Ni	0.00	0.00	0.00	0.00
Ba	24.40	5.28	18.44	5.70
Mn	86.18	423.90	897.53	215.82
Zn	55.22	63.21	38.11	54.69
Pb	12.12	2.75	6.05	5.02
Cd	0.00	0.00	0.00	0.00
Ti	389.84	129.67	141.82	77.33
Co	2.39	0.23	1.37	0.00

Table: 2M: Heavy metal concentrations in

Heavy metal (µg/g dry wt.)	<i>Pistia stratiotes L.</i>		<i>Lemna trisulca L.</i>	<i>Sargassum ilicifolius</i>
	Root (0.0503)	Leaf (0.0505)	Whole sample (0.0502)	Whole sample (0.0502)
Ca	19038.32	19762.37	23041.22	121982.15
Mg	5626.16	4081.34	3749.32	64924.52
Fe	111212.02	8339.26	70476.83	5591.53
Al	27653.89	2966.80	19238.09	4175.34
Cr	107.32	11.15	55.30	13.43
Cu	28.41	7.53	217.06	142.05
Ni	8.34	0.00	0.00	0.00
Ba	130.27	42.09	107.69	173.18
Mn	1168.34	100.03	472.16	432.59
Zn	110.16	91.56	1308.56	219.67
Pb	27.07	1.76	233.38	3.00
Cd	0.00	0.00	0.00	10.23
Ti	350.22	84.84	314.53	176.88
Co	9.43	0.16	2.94	14.54

*(Please see table 1A and AB for further details on sampling location and species).

Legends to figure:

Figure 3-8: (6 graphs) shows concentration of various metals in different parts of the macrophytes collected from Goa, India (11-*Pistia stratiotes L.*; 12-*Nelymbium speciosum willd.*; 13-*Ludwigia perennis L.*; 14-*Nymphoides Hill cristatum.*; 15-*Lemna trisulca L.*; 16-*Sagittaria sagittiflia L.*; 17-*Sesuvium portulacastrum L.*; 18-*Nymphae stellata willd.*; 19-*Sargassum ilicifolius.*

