

Metal accumulation and its spatio-temporal variation in Negombo and Rekawa lagoons of Sri Lanka

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Abstract

Metal (Cr, Mn, Tl, Ni, Cu, Zn, As, Pb, U, Cd, Ba, Sr) concentrations in water, sediments and aquatic plants in two coastal lagoons of Sri Lanka were determined by Inductively Coupled Plasma Spectroscopy (ICP-MS). The main sources of heavy metals were observed as industrial effluents and agricultural runoff respectively for Negombo and Rekawa lagoons. There are 86 industries including metal use industries such as leather tanning, metal plating, manufacturing of metal etc. in the Katunayake Export Processing Zone and treated, partially treated or untreated effluents are released to the Negombo lagoon. Concentrations of most metal ions in water, sediments and aquatic plants were relatively higher in Negombo lagoon compared to Rekawa lagoon. The concentration ranges of Cu, As, U, Cd and Sr in water of Negombo lagoon were 0.37-1.89, 0.03-2.16, 0.03-0.29, 0.01-0.12 and 4.24-481 µg/l respectively and varied significantly ($P < 0.05$) with the sampling occasions. It would be related to the seasonal variations of rainfall and discharges of effluents to the lagoon. Only the concentrations of U, Ba and Sr in sediments (3-22, 16.5-257, 17-101 µg/l respectively) and Zn and U (21-152, 0.7-12 µg/l respectively) in aquatic plants of Negombo lagoon varied significantly with the sampling occasions ($P < 0.05$). The concentrations of Mn, Zn and Ba (193-1510, 31-88, 20-46 µg/l respectively) in sediments of Rekawa lagoon varied significantly with the sampling occasions ($P < 0.05$).

Principal component analysis (PCA) was used to study distribution and accumulation of metals in water, sediment and in algae. PCA shows that Cr, Tl, Pb and As accumulate more in sediments than in aquatic plants. Meanwhile Mn, Cd, Ba and Sr would concentrate more in aquatic plants than in sediments. Likewise metal accumulation in sediments and in algae depends on metal binding properties of sediments and algae. However, concentrations of metal ions in water were low and therefore their distribution was not shown on the selected axes of PCA.

Introduction

Metal concentrations in water and sediments of different aquatic ecosystems were studied by different authors. Estuarine and marine sediments are a sinking ground for various metals transported from the land by natural and anthropogenic activities (Liaghati *et al.*, 2003). Heavy metals like Cu, Zn and Mn are essential for metabolism of organisms while some others such as Hg, Cd and Pb have no known role in biological systems (Canli and Atli 2003). Once in water, metals may remain in solution as free ions or as soluble complexes of organic and inorganic anions. Insoluble complexes with organic particulate or inorganic anions, such as carbonates, precipitate to the sediments. Aquatic sediments can act as both a sink and a source for contaminants, whereby long-term input of contaminants can lead to sediment concentrations that can exceed water concentrations (Burger *et al.*, 2002). Therefore, exposure of aquatic biota is most often via direct uptake of free ions from water or directly across cell membranes of biota. To understand bioconcentration of metal in aquatic ecosystems, it is essential to examine several metals in a range of biotic and abiotic components.

This study was carried out to evaluate the spatio-temporal variations of metal concentrations in water, sediments and aquatic plants and to study the distribution and inter-intra group correlations of metal concentrations in the above three environmental components. It was hypothesised that habitat characteristics would be presented by metal concentrations in water, sediments and aquatic plants.

Materials and methods

Site description

Negombo and Rekawa lagoons (Fig. 1) were selected for water, sediment and aquatic plant sampling. Negombo lagoon was selected because it is located in an industrialized area whilst Rekawa lagoon is located in an agricultural area. Negombo lagoon (35.02 km²) is a semi-enclosed water body, open to the sea at its northern part. It receives fresh water through Dandugam Oya and Ja-Ela at its Southern tip. The central sewage treatment plant of the Katunayaka Export Processing Zone (KEPZ, 1.90 km²) treats the effluents of 86 industries such as tanneries, several textile-processing units, chemical processing, battery manufacturing, distilleries and fiber mills. Various types of small scale industries including boat manufacturing and painting, garages etc. are located in the vicinity of Negombo lagoon. These industries release treated, untreated or partially treated effluents to the fresh water flow of the lagoon directly or indirectly. Rekawa lagoon (2.5 km²) is bounded on the seaward side by a long sandy beach, almost 10 km in length. Therefore, the lagoon mouth is closed during most periods of the year. The lagoon has fresh water input from several small sources, although these have been reduced to some extent because of the demands of rice paddy irrigation.

Six sampling locations were selected in the Negombo lagoon (Fig. 2). Three of them were located at the Southern part of the lagoon and the other three were located at the Western part of the lagoon to represent fresh water inflow and sea water inflow to the lagoon respectively. Four locations were selected in the Rekawa lagoon (Fig. 3) to represent the whole lagoon area.

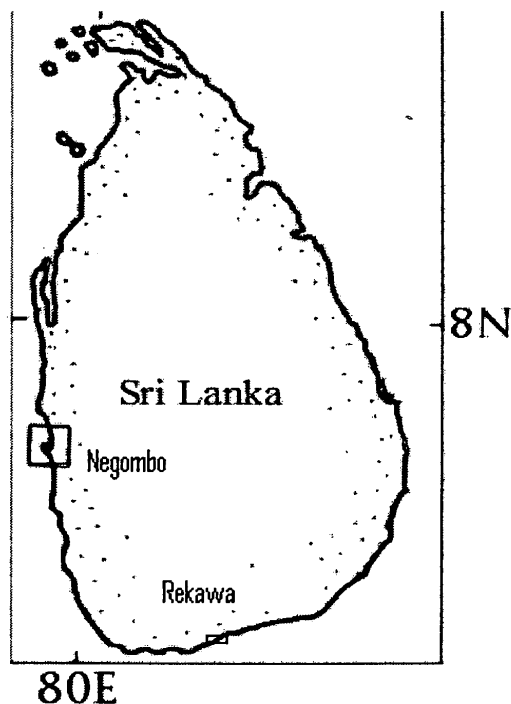


Fig 1. Locations of two lagoons in Sri Lanka

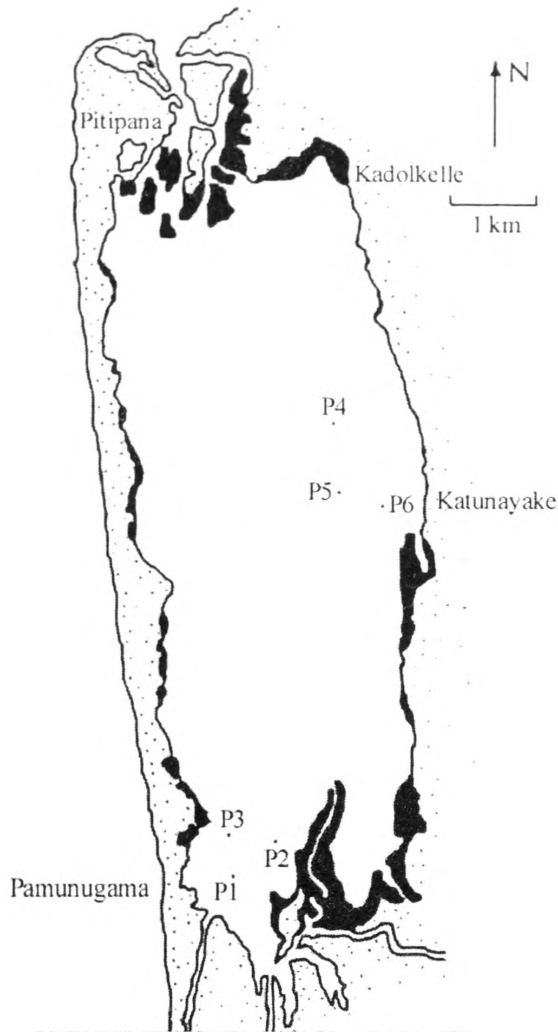


Fig 2. Sampling sites in Negombo lagoon (modified after Amarasinghe *et al.*, 2002)
P1-P6: Sampling locations

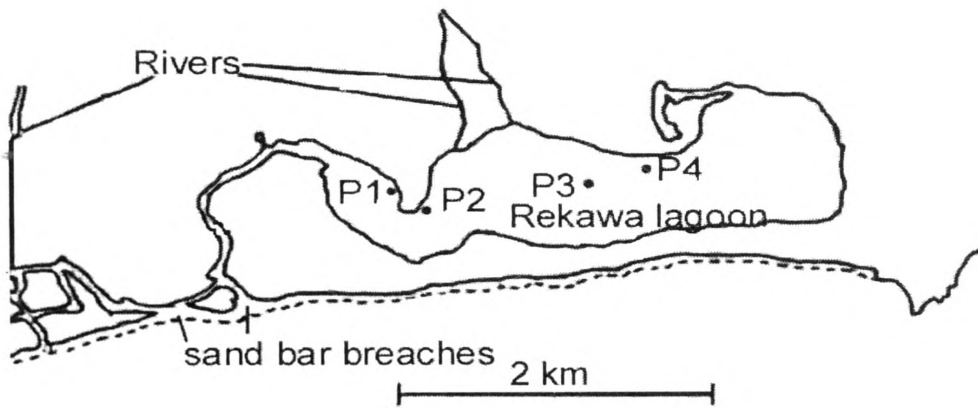


Fig 3. Sampling locations in Rekawa lagoon. P1-P4: sampling locations

Sampling and analytical methods

Water samples were taken from the surface layer of each sampling location using clean plastic bottles. Sediment samples were taken by a core sampler at each location. Aquatic plants or algae were collected using a scoop net at each location. Sampling was conducted at each location during three periods, (during three seasons), one sample from each location in each season. These three seasons were the dry season (from January to March 2004), the wet season (from May to July 2004) and the intermonsoon season (from October to December 2004). Extra sampling was carried out after the tsunami only from Rekawa lagoon which was partially damaged by the disaster.

Water samples were filtered and the pH adjusted at 2 using concentrated HNO₃. Sediment samples were oven dried at 100°C until of a constant weight. The dried samples were milled and sieved through a 200 µm mesh. About 100 mg of dried sediment were digested with 5 ml HNO₃ and 2 ml H₂O₂ under the pressure 10 bar, 600 W and 200°C in a microwave oven (3000 Anton Paar) for 30 minutes. About 50 mg of dried aquatic plant samples were digested in the microwave oven following the same procedure that was used for sediments. Each digested sample was diluted upto 50 ml using milli-Q water. Twelve metals (Cr, Mn, Tl, Ni, Cu, Zn, As, Pb, U, Cd, Ba, Sr) were analysed by ICP-MS (VG Plasma Quad PQ2 Turbo Plus). The instrument was calibrated using two standard solutions containing all the metals considered at 5 and 10 µg/l. An internal standard solution containing Bi 209 and In 115 was added to each sample at 10 µg/l. Limit detection (LOD) and limit of quantification (LOQ) were calculated using the following formulas.

$$\text{LOD} = [(b_{LI} \times f.d) + \Sigma b_l] / f.d \quad b_{LI}: \text{blank for the instrument} \quad b_l: \text{blank used}$$

$$\text{LOQ} = \text{LD} \times 5 \quad f.d: \text{dilution factor}$$

Certified reference materials were not used for these analytical methods.

Statistical analysis

One way ANOVA was used separately for the two lagoons to analyse seasonal effects on metal concentrations in water, sediments and aquatic plants. Principal component analysis (PCA) was used to simplify the data set and transform the data on the selected axes (www.statsoft.com). These axes were taken according to the clouds of data point and the tests were used to determine the distribution of metal concentrations in the three components (water, sediments and algae) on the selected axes and to demonstrate homogeneity or heterogeneity of metal concentrations in the three components. The distribution of each metal on the selected axes was represented by absolute contribution (AC) and relative contribution (RC) as percentages. Further, correlation between metal concentrations was shown by finding the Eigen vectors and Eigen values of the covariance matrix.

Between group and within group PCA were used to analyse metal concentrations in the three components (water, sediment and algae). The between group analysis was used to focus on the difference between groups (water, sediments and algae); it seeks four axes that will discriminate the center of gravity of each group (Blanc *et al.*, 2001).

Results

Metal concentrations in water

Mean metal concentrations in water of the two lagoons during each sampling occasion are given in Table 1. Significant effects of sampling seasons were observed for certain metals (Cu, As, U, Cd and Sr) and the significant levels are included in the same table.

Table 1. Mean metal concentrations in water of the two lagoons during the sampling occasions (Mean ± SD), Values in a row for each metal with no symbols are not significantly different during the sampling seasons *: P<0.05 *: P<0.001**

Metal (µg/l)	Negombo lagoon			Rekawa lagoon			
	Dry (n=6)	Wet (n=6)	Intermons (n=6)	Dry (n=4)	Wet (n=4)	Intermonsoon (n=4)	After tsunami (n=4)
Cr	0.40± 0.1	0.05± 0.0	0.18± 0.1	0.22± 0.1	0.35± 0.2	0.35 ± 0.1	0.23 ± 0.2
Mn	0.45± 0.1	0.6 ± 0.3	0.5 ± 0.3	0.33 ± 0.1	0.3 ± 0.1	0.4 ± 0.2	0.22 ± 0.1
Ni	0.27± 0.1	0.1 ± 0.1	0.3 ± 0.3	0.1 ± 0.1	0.1 ± 0	0.03 ± 0.02	0 ± 0
Cu	1.11± 0.4 *	0.7 ± 0.3 *	0.7± 0.2 *	0.5 ± 0.1	0.6 ± 0.1	0.5 ± 0.1	0.3 ± 0.2
Zn	3.6 ± 1	3.5 ± 2.5	5.6 ± 2	2.2 ± 1.1	2.4 ± 1.4	1.9 ± 0.5	12 ± 7
As	1.76± 0.3 ***	0.1 ± 0.1 ***	0.32 ± 0.2 ***	0.2 ± 0 *	0.17± 0.1 *	0.16 ± 0.0 *	0.7 ± 0.5 *
Pb	0.06± 0.0	0.03± 0.01	0.04 ± 0.0	0.03 ± 0.01	0.04 ± 0.03	0.04 ± 0.01	0.02 ± 0
U	0.24 ± 0.0 ***	0.005± 0.0 ***	0.03 ± 0.0 ***	0.02 ± 0.0 *	0.02± 0.0 *	0.02 ± 0.0 *	0.06 ± 0.02 *
Cd	0.06± 0.0 ***	0.01± 0.0 ***	0.06 ± 0.0 ***	0.05 ± 0.0	0.03 ± 0.01	0.04 ± 0.02	0.04 ± 0.0
Ba	8 ± 1.5	9 ± 3	8 ± 4	6 ± 3	8 ± 3	7 ± 1	10 ± 4
Sr	381± 77 ***	28 ± 25 ***	65 ± 41 ***	49± 22 *	46 ± 25 *	41± 20 *	111 ± 38 *

Metal concentrations in sediments

Mean metal concentrations in sediments of the two lagoons during each sampling occasion are given in Table 2, including effects of sampling seasons. Significant seasonal effects were observed for metals such as U, Ba and Sr in Negombo lagoon. Meanwhile, metals like Mn, Zn and Ba in Rekawa lagoon showed significant occasional variation. Relatively higher metal concentrations were found in Negombo lagoon than in Rekawa lagoon. However, content of certain metals in sediments of Rekawa lagoon increased after the tsunami.

Table 2. Mean metal concentrations in sediments of the two lagoons during the sampling occasions (Mean ± SD), Values in a row for each metal with no symbols are not significantly different. *: P<0.05 **: P<0.01

Metal (µg/gdw)	Negombo lagoon			Rekawa lagoon		
	Dry (n=6)	Wet (n=6)	Intermonsoon (n=6)	Wet (n=4)	Intermonsoon (n=4)	After tsunami (n=4)
Cr	153 ± 77	84 ± 48	85± 29	34 ± 2	47 ± 20	65 ± 14
Mn	576 ± 157	466 ± 137	493±124	313 ± 104 **	636 ± 285 **	969 ± 338 **
Ni	59 ± 46	20 ± 6	30 ± 12	0 ± 0	12 ± 0.9	14 ± 11
Cu	53 ± 33	16 ± 6	26 ± 16	19 ± 4	25 ± 2	33 ± 10
Zn	205 ± 106	148 ± 131	118 ± 53	31± 1 **	53 ± 7 **	60 ± 14 **
As	22 ± 9	23 ± 19	18 ± 8	3.4 ± 2.2	4 ± 0.3	8 ± 5
Pb	52 ± 28	25 ± 13	26± 10	5 ± 0.2	6.8 ± 2.3	9 ± 2
U	11± 5 *	7 ± 2 *	6 ± 2 *	1.5 ± 0.2	1.1 ± 0.2	2 ± 1
Cd	0.44±0.27	0.4 ± 0.4	0.24 ± 0.1	0.23 ± 0.05	0.26 ± 0.06	0.2 ± 0.1
Ba	121 ± 79 *	50± 36 *	56 ± 34 *	22 ± 2.6 *	35 ± 5 *	31 ± 5 *
Sr	69 ± 25 *	50 ± 24 *	38 ± 18 *	23 ± 3	36 ± 28	77 ± 27

Metals in aquatic plants

Mean metal concentrations in aquatic plants of the two lagoons during each sampling occasion are given in Table 3, including the effects of sampling seasons. Metal concentrations in aquatic plants were also relatively higher in Negombo lagoon than in Rekawa lagoon. However, aquatic plants were not identified upto species level and the occasionally available varieties were taken for metal analysis. Mn is the most available metal in both sediments and in aquatic plants in the lagoons.

Table 3: Mean metal concentrations in aquatic plants of the two lagoons during the sampling occasions (Mean \pm SD), Values with no symbols are not significantly different *: P < 0.05 ND: Not Detected

Metal ($\mu\text{g/gdw}$)	Negombo lagoon			Rekawa lagoon	
	Dry (n=6)	Wet (n=3)	Intermonsoon (n=6)	Wet (n=2)	Intermonsoon (n=3)
Cr	56 \pm 33	58 \pm 40	33 \pm 16	73 \pm 39	13 \pm 4
Mn	4066 \pm 1130	1993 \pm 726	1314 \pm 750	1809 \pm 784	763 \pm 158
Ni	34 \pm 14	39 \pm 6	22 \pm 8	9 \pm 4	0 \pm 0 (ND)
Cu	25 \pm 9	28 \pm 13	19 \pm 8	33 \pm 4	35 \pm 2
Zn	91 \pm 47 *	119 \pm 28 *	36 \pm 13 *	72 \pm 25	50 \pm 29
As	13 \pm 8	9 \pm 3	7 \pm 5	0 \pm 0 (ND)	0 \pm 0 (ND)
Pb	21 \pm 9	22 \pm 12	6.6 \pm 3	9 \pm 2	3.65 \pm 0.5
U	7 \pm 5 *	6 \pm 4 *	2.8 \pm 2 *	3 \pm 2	3.7 \pm 0.7
Cd	0.7 \pm 0.6	0.4 \pm 0.2	0.3 \pm 0.1	0.5 \pm 0.05	1.13 \pm 0.6
Ba	47 \pm 25	70 \pm 10	34 \pm 12	119 \pm 81	31 \pm 3
Sr	106 \pm 28	165 \pm 24	194 \pm 81	162 \pm 107	143 \pm 54

Distribution of metal concentrations

Principal component analysis (PCA) gives distribution of metal concentrations in water, sediments and algae in the two lagoons. All of the analysed metals were considered in this PCA because no certified materials were used to take an idea about accuracy of the analytical method.

PCA 1 (Fig. 4) describes the distribution of 12 metals (as variables) and 81 concentration values (observations). The raw data were normalized by mean values to take into account small values in water and large values in sediments and algae. Four principal axes represented 69.5% of the total initial variance (37.1%, 14.4%, 9.9%, and 7.9% respectively on the four axes). The contribution percentage of initial variance on axis 3 and axis 4 is very low (<20%). Based on PCA 1, metal accumulation is different to each other within the three environmental components (water, sediments and algae) and the variance on the two axes is displayed in Fig 4.

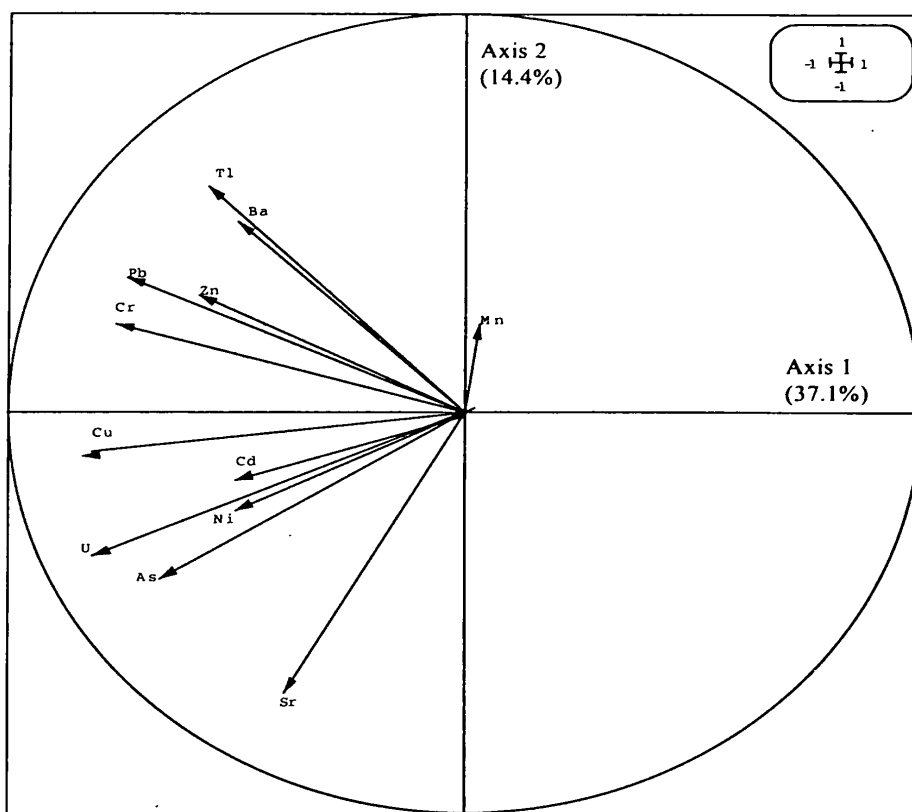


Fig 4. PCA 1 for distribution of twelve metals (in water, sediments and algae) on the two axes

PCA 2 (Fig 5) describes inter and intra group correlation for water, sediments and algae by considering intra and inter group variances between each group. The differences between lagoons, locations, seasons and metal effects were considered within the three components. Most metals contributed negatively to the axis 1 and a few metals (Mn, Cd) contributed negatively to axis 2. Axis 1 contributed 85.3% of the initial variance and axis 2 contributed 14.7% of the initial variance. Certain metals such as, Cr, Tl, Cu, Cd, and Mn are more highly correlated than the other metals (Fig 5).

PCA 2 describes the metal concentrations in sediments, which were higher in Negombo lagoon than in Rekawa lagoon such as, Cu, Cr, Tl, U, Zn, Pb and As (Fig 6). This was already observed in Negombo lagoon when considering mean metal concentrations. Also, Cr, Tl, Pb and As were higher in sediments than in algae. Metal concentrations in water were not well represented on the PCA. Therefore, most of the values were concentrated within a short distance. Water in Negombo lagoon particularly during the dry season can be separated from others. When considering mean values, higher concentrations were observed during the dry season in Negombo lagoon. Higher concentrations of Mn, Cd, Ba and Sr were found in algae than in sediment. Also, higher concentrations of most metals were observed in Negombo lagoon. However, concentrations of Sr and Cd in algae were higher in Rekawa lagoon. Seasonal variations of metal concentrations between lagoons are represented on the PCA and they are dependent on the metal and the components. For example, the highest concentration of Cr and As in sediments was observed in Negombo lagoon during the dry season (N2D and N1D around 3 in Fig 6); the highest concentrations of Cr, As and Mn in algae were found in Negombo lagoon during the dry season (N2D, N1D and N4D around 1 in Fig 6).

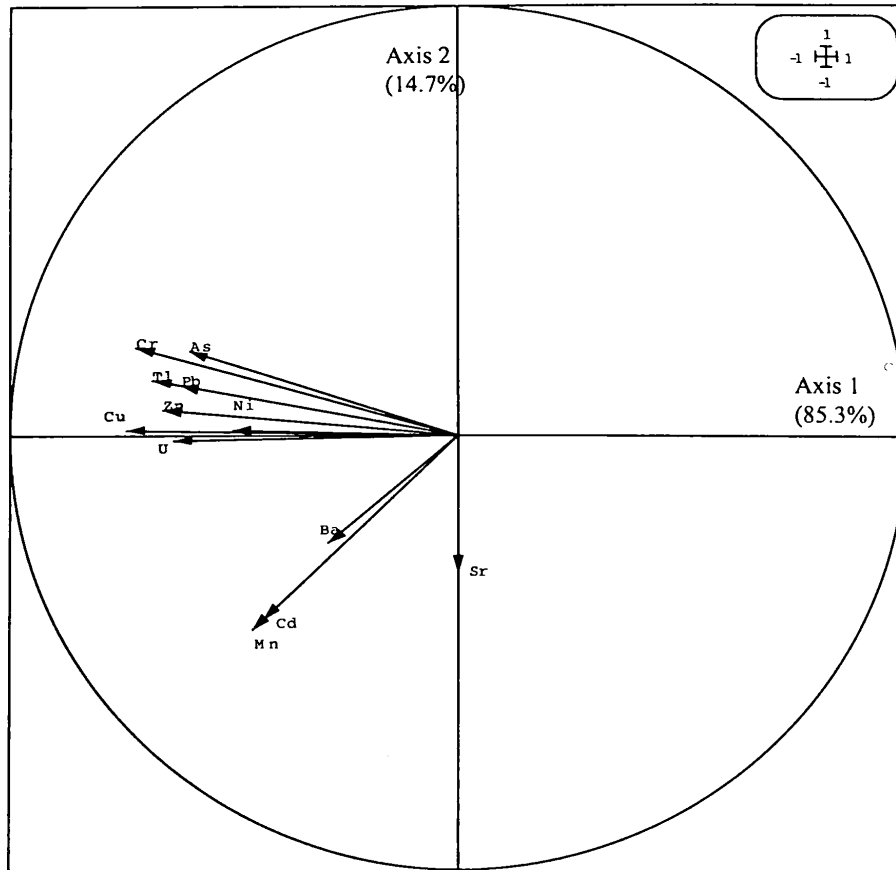


Fig 5. PCA 2 - Correlation of metal concentrations between groups (lagoons, locations, seasons)

Discussion

Concentrations of Mn, Cu, Zn and Pb in water of the studied two lagoons are within or lower than the reported range (19-34, 10-60, 116-100 and 0.5-2 µg/l respectively) in Lunawa lagoon, Sri Lanka (Mubarak, 2000). The Lunawa lagoon is one of the most polluted water bodies in Sri Lanka. Bhuvendralingam and Azmy (1995) have reported concentrations of Cu, Zn and Pb (12, 160, 12 -123 µg/g dw respectively) in sediments from the extreme northern part of Negombo lagoon. The observed concentrations of the same metals in both lagoons are within the above reported range. Since industrial effluents are more effective metal sources, higher metal concentrations in the environmental components were observed in Negombo lagoon than in Rekawa lagoon. However, certain metals such as Cu, Zn and Cd were higher in the samples taken after the tsunami than during other periods.

Certain metal concentrations (Cr, Ni, Cu, As and Zn) in sediments of Negombo lagoon exceeded the low effect range (81, 20.9, 34, 5 and 150 µg/g dw respectively) for metals in sediments published by the Australian National Oceanic Administrative Agency NOAA (1999). Metal concentrations in sediments can exceed water concentrations by 3 to 5 orders of magnitude (Burger *et al.*, 2002). Therefore, determination of metal concentrations in sediments is also important.

Metal concentrations in aquatic plant and algae have also been studied by different authors. However, most of the research was done on marine algae. Concentrations of certain metals such as Cu, Zn, Cd and Pb in *Ulva fasciata* from the Syrian coast has been reported by Al_Masri *et al.* (2003). Concentrations of these metals in aquatic plants from

both Negombo and Rekawa lagoons exceeded the reported range by Al_Masri *et al.* (2003) for *Ulva fasciata*. However, in the present study, aquatic plants were not identified up to species level.

The lowest metal concentrations were observed in water than in algae except for Sr in Negombo lagoon. Certain metals (Mn, Sr, Cd, Ba) were higher in algae compared to sediments and some metals showed the reverse tendency according to PCA. Metal concentrations in sediment were more important than in algae in Negombo lagoon. Mean concentrations of Cd were higher in algae than in sediment and other metals were higher in sediment of Negombo lagoon. Metal concentration in algae is more important than in sediment of Rekawa lagoon. Mean concentrations of most metals were higher in algae except for Cr, As, Pb and Tl. Concentrations of certain metals in sediments were higher after the tsunami and that may be a reason for increasing the metal concentrations in sediment more than in algae of Rekawa lagoon. According to the observations, aquatic plants and algae density in brush parks of Negombo lagoon were higher than in brush parks of Rekawa lagoon. This may also be a reason why metal concentration in algae was more important in Rekawa lagoon than in Negombo lagoon. However, less number of algae samples were analysed from Rekawa lagoon and those were not sufficient for any statistical analysis.

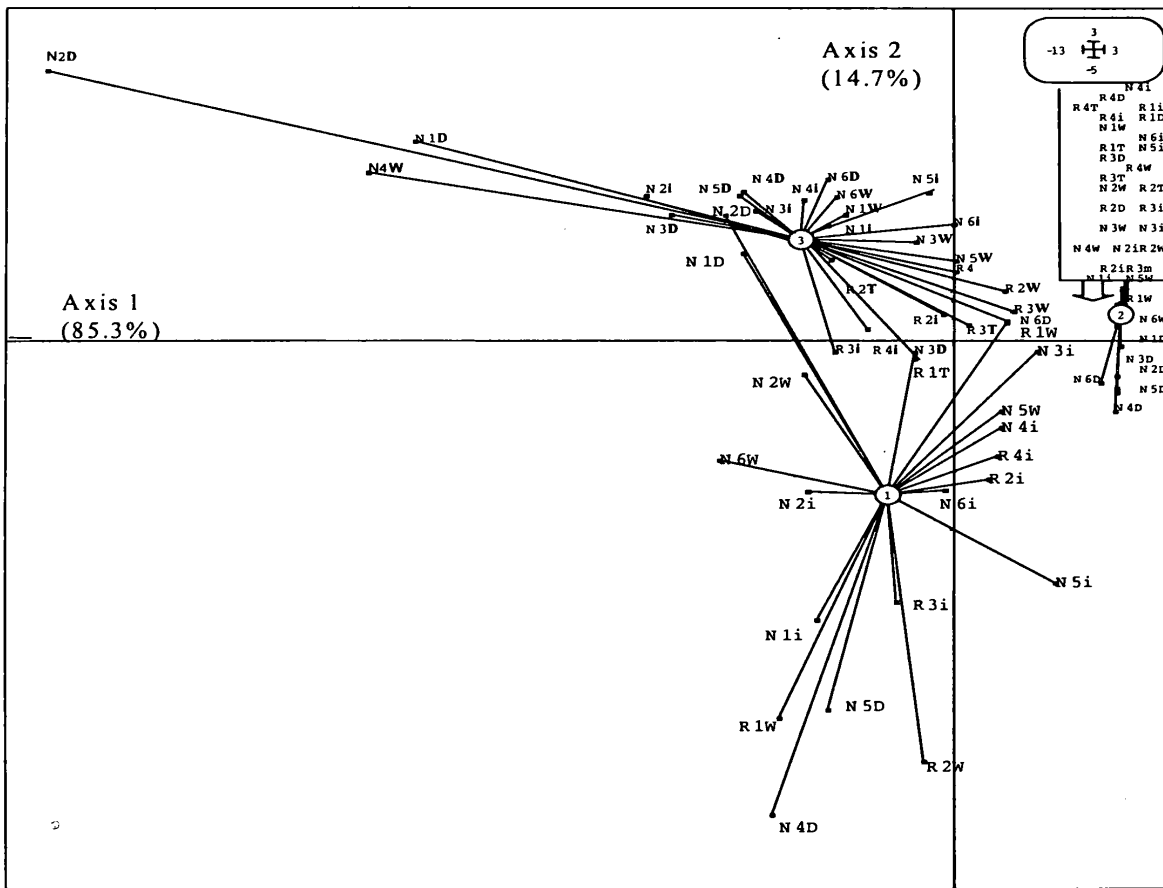


Fig 6. Distribution of individual metal concentrations between groups (lagoons, locations, seasons)

- | | | |
|--------------|------------------------|---|
| 1: Algae | D: Dry season | N: Negombo |
| 2: Water | W: Wet season | R: Rekawa |
| 3: Sediments | i: Intermonsoon season | N1 to N6: Sampling locations in Negombo |
| | T: After tsunami | R1 to R4: Sampling locations in Rekawa |

Conclusions

Significant seasonal variations for certain metals were found in the two lagoons but it depended on the type of metal and the lagoon. Also, metal concentrations are different to each other in water, sediments and algae. However, according to PCA, higher concentrations for certain metals were observed in Negombo lagoon. Sources of metals in the two lagoons should be considered for further studies in evaluation of metal concentrations in different environmental components.

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