

**ASSESSMENT OF ORGANIC & HEAVY METAL POLLUTION IN MANGROVE AREAS OF KRISHNA RIVER BASIN, ANDHRA PRADESH****CH.S.R.G.KALYANI**

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**ABSTRACT**

Overlying water, sediment and mangrove seedlings in the Krishna river basin mangrove forest were analyzed for heavy metals and organic pollution. Polluted marine waters, surface waters joining the marine waters will be identified that leave the contamination into the ground water, sediment, aquatic biota will be identified. A radial distance of 0.5 to 1 km from the focused polluted surface water point in different directions covering the geographical area will be identified. The results showed that mangrove plant acidified sediment and increased organic matter contents. These findings provide actual heavy metal accumulations in sediment-plant ecosystems in mangrove forest, being important in designing the long-term management and conservation policies for managers of mangrove forest. Water and soil samples were taken from these mangroves in duplicates and analyzed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Heavy metal levels in the mangroves were then obtained. Within the seven location in the study area especially reserve forest mangroves studied, levels of heavy metals in water samples were similar, as there are no clear trends of any mangroves having elevated levels of an element and being more contaminated. Levels of heavy metals were not found to be consistently high. According to our results for the sediment sample analysis, Lankivanidibba sample has the highest level of Cu, Pb, Fe and Cr levels. In general, the whole Lankivanidibba mangrove has a higher level of Cu, Pb, Fe and Cr compared to the Kottapalem, RF, Molagunta RF, Adavuladivi RF mangroves and Yelichetladibba RF. However, Sorlagondi Reserve Forest (RF), has a higher level of Zn compared to the Nachugunta RF mangrove has the lowest level of all the heavy metals tested.

©KY Publications**Introduction**

A mangrove is a forest consisting of various species of mangrove trees growing with their bases submerged in water, at the interface between land and sea. Mangrove environments are influenced by a complex interaction of biotic and abiotic factors, which control the metallic and non-metallic nutrients available to plants species. Their soil receives and retains metals coming from different sources such as freshwater, saltwater, as well as water runoff due to natural processes, or anthropogenic activities. In terms of ecosystem, metals can be classified either as nutrients or, depending on their density, trace ($d < 1 \text{ g kg}^{-1}$), or heavy metals ($d > 5 \text{ g cm}^3$). When they act as micronutrients, heavy metals supply plants metabolic



necessities and their lack may impair the whole enzymatic system. Nonetheless, since their excess can alter cell membrane permeability, they can inhibit enzyme activity and interfere with photosynthesis. Therefore, plants usually react differently in terms of use, storage and tolerance of metals in their different parts [1-5] .

The analysis of metals concentration in different organs of mangrove plants has proved to be a more accurate instrument than mere soil analysis. The analytical procedures do not consistently reveal the complexity of bioavailability, distribution, and assimilation processes of the elements affecting the plants. Despite this limitation, altogether, these procedures suggest that mangroves act as an efficient biogeochemical barrier to metal transport [6]. The dual role of Cu, Fe, Mn, and Zn, which can be either nutrients, or toxic elements in mangrove ecosystems, has been addressed by several studies. They also have been investigated for their physiological functions together with the mechanisms that control their absorption or exclusion in the plants that grow in this ecosystem [7]. Scientific reviews elucidated the fate and effects of trace metals (22 metals) released from anthropogenic sources in the mangrove ecosystem. The metal concentrations in mangrove sediment, along with their bioavailability and bioaccumulation in tissues were studied by several workers[3]. Different species have shown different degree of metal accumulation potential [4].

Estimates of the area of India's mangrove wetlands range from 5,00,000 ha. to 6, 81,000 ha. Mangrove wetlands of India can be classified into a) tide-dominated (Sunderbans and Mahanadi mangroves), b) river dominated (Godavari, Krishna, Muthupet, Pichavaram mangroves) and c) drowned river valley (Gujarat mangroves). Andhra Pradesh has a geographical area of 2,76,000 sq.km, of which 63,770 sq.km. or 23% is under forests. Mangrove forests account for only 582 sq.km, representing only about 0.9% of the State's total forest area.

The sediments in such areas have a large capacity to retain heavy metals from tidal waters, fresh water rivers and storm water runoff and they often act as sinks for heavy metals. The cycling of organic matter through litter production, decomposition and tidal transport may eventually export a fraction of the accumulated heavy metals and, therefore, convey it to detritus food chains in adjacent coastal waters. Despite their potential exposure to metal contaminated sediments, mangroves appear to be highly tolerant to heavy metals. Mangrove sediments are anaerobic and reduced, as well as being rich in sulphides and organic matter. They therefore favour the retention of water-borne heavy metals. Hence, the present study gives comparative account of accumulation of the heavy metals concentration in water, sediment and mangroves (leaves and root) was carried out [7].

The aim of this study was three fold: 1) to provide a preliminary study to determine current levels of eight commonly polluting metals: manganese (Mn), copper (Cu), zinc (Zn), nickel (Ni), lead (Pb), iron (Fe), chromium (Cr) and cadmium (Cd) distribution of these heavy metals in overlying water, sediments, and mangrove seedlings; (2) evaluate heavy metal contamination degrees and potential ecological risk in sediment; (3) investigate the speciation of heavy metals in sediment and Mangroves.

Study Area

The mangroves of Krishna Basin in Andhra Pradesh are located in the coastal plains of Krishna delta. According to the Forest Department, the total area under mangroves is 5,000 ha. The Krishna mangroves lie between 15°2' N and 15° 55' N in latitude and 80° 42' - 81° 01' E [Figure 1]. in longitude spread across Krishna and Guntur districts. The Krishna wildlife sanctuary has been established in a part of the mangrove wetland - the total area of this sanctuary is 19,481 ha (194.81) sq.km.; it includes **Sorlagondi Reserve Forest (RF), Nachugunta RF, Yelichetladibba RF, Kottapalem, RF, Molagunta RF, Adavuladivi RF and Lankivanidibba RF**. They occupy the islands of the delta and the adjacent mainlands of both districts. A part of the mangroves is located far from the main mangrove area; it's near Machilipatnam on its eastern side and Nakshatranagar on



its western side. Fishermen in surrounding areas use the mangrove resources for fishing, house construction and firewood and to obtain fencing material for their houses. A devastating cyclone that hit the Machilipatnam coast during 1977 led to large areas of the forest getting degraded. The important soil types found in the basin are black soils, red soils, laterite and lateritic soils, alluvium, mixed soils, red and black soils and saline and alkaline soils.

Need for the Present Investigation

Aquatic ecosystems have long been used as a medium for transportation and disposing human, agriculture and industrial waste, discharged directly and indirectly into the water course. Pollutants including microbes nutrients, heavy metals, organic chemicals, oil and sediments, heat which rises the temperature of the receiving water are typically the cause of major water quality degradation around the world. Major nutrient sources to ecosystems include agriculture runoffs, domestic sewage, industrial effluents and atmospheric inputs.

Another interesting source of Pollution of waters near these Mangrove areas in KG Basin region is also possible due to Oil spill and is the release of a liquid Petroleum Hydrocarbon into the environment especially in Marine areas due to human activity. Oil spills at sea are generally much more than damaging than those on land, since they can spread for hundreds of nautical miles in a thin oil slick which can cover because with a thin coating of oil. This can kill sea birds, mammals, shellfish and other organisms in coats. Ship breaking activities is a threat to both the terrestrial and marine environment as well as to public health.

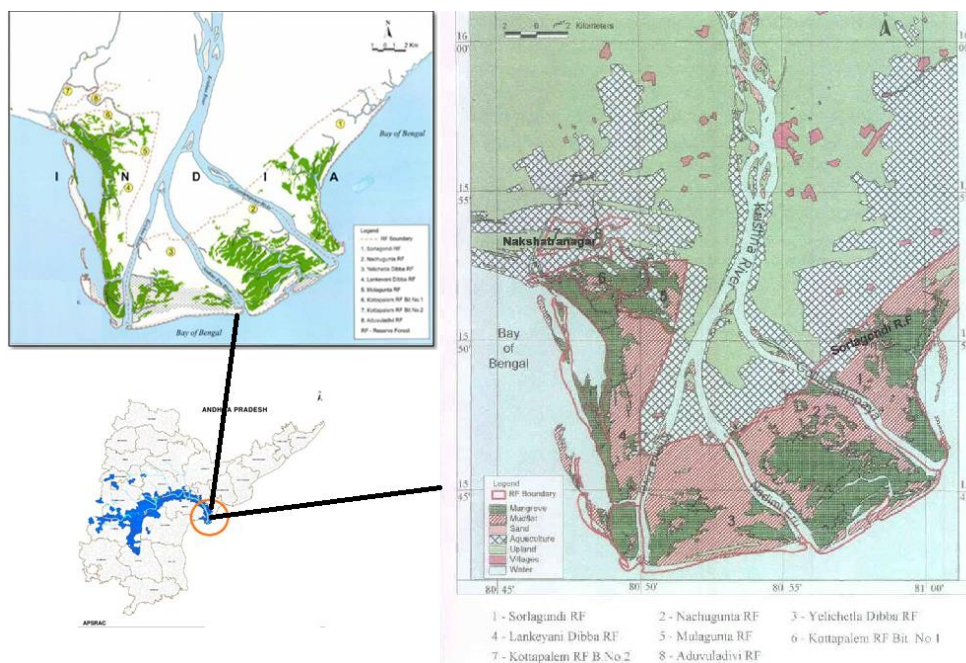


Figure-1: Mangrove forest area in Krishna River A.P., India

Sampling

For each sampling point, one subsurface liquid sample (depth about 5 to 10cm, 150ml) was collected by immersing a pre-cleaned polyethylene bottle at arm's length from the water's edge. One millilitre of 10% nitric acid was added to each liquid sample within 5 days. This was done to adhere to accepted protocols for the preservation of trace elements in water samples by lowering sample pH to two pH units and below. (U.S.



Environmental Protection Agency, 1979). This provided the benefits of minimizing precipitation of heavy metal cations and adsorption of trace elements onto the container wall of the samples. A flaw with this procedure is that the added acid may solubilise certain elements found in the container, as it has been for glass ampoules. Liquid samples were filtered with a 0.45 micron syringe filter to remove suspended particulate, with 10 to 15 of the filtrate collected in centrifuge tubes.

At each sampling point, two sediment samples, 30 cm and 4 m from the water's edge, were collected using a pre-cleaned hand auger. Sediments were taken from a soil depth of 30 cm, as the inability to perform detailed soil analysis and the lack of a standard protocol led us to choose the depth where roots of mangrove trees and many essential bacteria were situated. Extracted sediment was mixed in a bucket, ignoring sediment characteristic. For each bucket of mixed sediment, 3 hand-scoops of the sediment were stored in clean zip lock bags, compressed to limit the gaseous exchange of samples. Sediment samples were air-dried, aggregates and lumps were broken up and samples were sieved to obtain true soil component. 10 to 15 ml of each remaining sample was collected in centrifuge tubes. Soil samples were treated with hot-plate digestion, before both soil and liquid samples were analysed with ICP-MS.

Mangrove samples: matured Leaves of *Jatropha glandulifera*, *Crotalaria verrucosa*, *Acacia nilotica*, *Pithecellobium dulce*, *Azadirachta indica*, *Ficus religiosa* and *Ficus bengalensis* plants were collected in the October 2013 and washed thoroughly, shade-dried and powdered. Samples were digested for heavy metal analysis with a 90°C mixture of concentrated nitric acid and hydrogen peroxide, after the method by MacFarlane et al. (2003)[8], and made to 25 ml volume. Digested samples were stored in labelled, acid-washed glass vials. Metal analysis was carried out immediately on ICP-MS with standard procedure.



Figure 2: Sample collection by the researcher

Table1: GPS coordinates of Samples locations (Longitudes and Latitudes)

Station No	Station	GPS Coordinates (Long/Lati)	
1.	Sorlagondi RF	15° 51' 50.3604" N	80° 58' 1.4700" E
2.	Nachugunta RF,	15° 47' 16.8324" N	80° 53' 17.8008" E
3.	Yelichetladibba RF,	15° 46' 14.3245" N	80° 57' 16.2654" E



4.	Kottapalem RF,	15° 46' 37.3008" N	80° 51' 40.2588" E
5.	Molagunta RF	15° 53' 14.0712" N	80° 50' 14.7588" E
6.	Adavuladivi RF	15° 54' 55.2384" N	80° 46' 19.2504" E
7.	Lankivanidibba RF	15° 53' 14.3245" N	80° 49' 40.2588" E

Persistent Organic Pollutants (POP's)

Persistent organic pollutants (POPs) are substances that even at low concentrations may cause hazard to human health as well as to the environment. Some examples of POPs are the polycyclic aromatic hydrocarbons (PAHs) and the organochlorine compounds (OCs). In aquatic environments, both PAHs and OCs, due to their physical and chemical characteristics, tend to be retained in bottom sediments. Therefore, sediments may be used as indicators of environmental contamination. The study of sediment cores has shown to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments.

Sampling for POP's analysis

The seven sediment samples were collected in 2014 using a PVC tube, with 10 cm of diameter. The samples taken from the river junctions had 50-100cm of depth. The sample cores were sectioned in 3 cm thick discs. Each layer was dried at room temperature (27 °C) and stored in acetone rinsed glass jars until analysis.

POP extraction

We chose a POP extraction methodology that was simple, easy, and didn't use many glass materials. This method required only one Erlenmeyer flask and one shaker, items that are commonly found in laboratories. On the other hand, it used large amounts of reagents, compared to other extraction methodologies, such as soxhlet, microwave and/or sonication. All used flasks were pre-cleaned with acetone and heated to 300 °C during 24 h. All solvents used were HPLC grade. The POP mixtures and the individual standard components were acquired from Merck & Loba co PVT Ltd. The POPs were extracted using 10 g of sediment and a 100 mL acetone in an Erlenmeyer flask. After that, 50 mL of petroleum ether was added, and shaken continuously for 30 min. The suspension was filtered, the acetone was removed with water, and the excess water was removed with Na₂SO₄. The organic solution was submitted to a cleanup process, which used Al₂O₃ and Na₂SO₃ in a chromatographic column eluted with hexane in order to remove humic material and elemental sulfur. The same procedure adopted from ElciaMargareth Souza Brito et al (2005). The solution was divided in two fractions, one for PAHs and the other for OCs analysis.

The PAH concentrations were analyzed after an injection of 20 µL of the concentrated samples on the HPLC with UV-VIS Detector (Shimadzu LC10-AS pump, ODS-II reverse-phase column – 250 X 4,0 mm, Shimadzu SPD-10A UV-Vis detector). An isocratic mixture of acetonitrile/water (80:20) as the mobile phase was used.

The OC analysis was performed by gas chromatography coupled to an electron capture detector (ECD-GC) (Shimadzu GC-14B with autosampler AOC-17) with capillary columns (Shimadzu CBP1 and CBP5). The carrier gas was hydrogen. The injector and detector temperatures were 300 and 310 °C, respectively. The oven temperature program starts at 110 (for 1 min), rising to 170 (at 20 °C per min) and subsequently to 290 °C (at 7.5 °C per min), where it remained for 12 min.

Sampling analysis

In this study, the selected metals (manganese (Mn), copper (Cu), zinc (Zn), nickel (Ni), lead (Pb), iron (Fe), chromium (Cr) and cadmium (Cd) were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, ELAN DRC-e, Perkin Elmer). The accuracy of the ICP-MS performance for water analysis was assessed



by external standards, which were prepared by diluting the ICP Multi-Element Mixed Standard III (Perkin Elmer) into series of concentrations with the same acid mixture used for sample dissolution. Meanwhile, for sediment analysis, it was assessed by analyzing the standard reference material NIST, SRM 1646a (estuarine sediment). The descriptive statistic was performed to calculate maximum, minimum, mean, standard deviation (SD), and coefficient of variance (CV).

Assessment of sediment contamination and Geoaccumulation index

In this study, Two different indices were used to assess the degree of heavy metal contamination in the surface sediments of the Krishna River basin mangrove areas. For the comparison purpose, the average upper continental crust (UCC) values [11] were chosen as the reference background values in all of the following related indices (Table 3).

Enrichment factor (EF).

Contamination Factor (CF).

The degree to which sediment is contaminated is often express as Contamination Factor (CF)

$$CF = \frac{C_{metal}}{C_{background\ value}}$$

Where C_{metal} is the total metal concentration and $C_{background}$ represent the average background value of the element in sediment. The geochemical background values in shale of the metals under investigation (earlier reported by [12] were used as background values. The CF value could fall into either of the levels of contamination. Where $CF < 1$ refers to low contamination; $1 \leq CF < 3$ indicates moderate contamination; $3 \leq CF \leq 6$ means considerable (high) contamination and $CF > 6$ refers to very high contamination [13].

Geoaccumulation index (Igeo).

Igeo is also a contamination index which is defined by the following equation:

$$I - geo = \log 2(C_n / 1.5 B_n)$$

Where C_n is the measured concentration of metal n; B_n is the geochemical background concentration of metal n. Correction index 1.5 is usually used to characterize the sedimentary and geological characteristics of rocks and other effects. The geoaccumulation index consists of seven classes: $I_{geo} \leq 0$ (Class 0, practically uncontaminated); $0 < I_{geo} \leq 1$ (Class 1, uncontaminated to moderately contaminated); $1 < I_{geo} \leq 2$ (Class 2, moderately contaminated); $2 < I_{geo} \leq 3$ (Class 3, moderately to heavily contaminated); $3 < I_{geo} \leq 4$ (Class 4, heavily contaminated); $4 < I_{geo} \leq 5$ (Class 5, heavily to extremely contaminated); $5 < I_{geo}$ (Class 6, extremely contaminated) [14].

Results and Discussions

Sediments act as an ultimate sink for POPs brought into the aquatic environment from direct discharges, surface run-off and atmospheric fall out. Results are presented in Table 1. These studies showed that few organochlorine compounds were observed in the Krishna Reservoir sediment samples (Kottapalem RF, Lankivanidibba RF, Nachugunta RF). 24% of the OC's found in the Krishna Reservoir were PCBs, 09% DDT, 08% Drins (aldrin, dieldrin and endrin) and 5% other pesticides (HCB, Heptachlor, Heptachlorepoxide, and a-Endosulfan). We suppose that the introduction of chemically persistent organochlorine pesticides depends mainly on the intensity and the kind of agricultural activities. Small amounts of PCBs were found (Table 1), from < DL to 17.5 ng/g at 82 cm of depth. It was concluded that substances such as PCBs DDTs and PAHs in the Krishna River Delta sediments were the results of trace discharges in stormwaters, sewage, industrial waste, agricultural runoff, atmosphere deposition and were of long term significance to



the quality of waters in this area. These studies commented that DDT is officially banned for agricultural use in India, but it maybe illegally used in trace amounts recently for some agricultural practices. Furthermore, with recent liberalization of the agrochemicals market, there has been a tendency towards the application of cheaper pesticides and there are concerns that some banned OCPs, including DDT, maybe available to farmers and result in widespread environmental contamination

Table 2 : POP concentrations (ng/g) of sediment samples from Krishna River basin , Mean (Min-Max)

S.No	Station	PAH's	PCBs	DDT	Drins
1.	Sorlagondi RF	12.4-21.25	3.24-3.98	1.2-3.1	2-2.21
2.	Nachugunta RF,	24.14-25	3.95-3.99	2.14-2.33	3-3.54
3.	Yelichetladibba RF,	27.24-30.24	3-84-4.20	2.44-3.02	2.1-2.8
4.	Kottapalem RF,	24.68-28.95	2.35-3.95	2.68-2.99	2.4-2.9
5.	Molagunta RF	14.58-28.36	2.14-5.21	1.02-2.44	1.5-2.5
6.	Adavuladivi RF	11.25-18.34	2-44-2.99	1.44-2.09	1.2-2.6
7.	Lankivanidibba RF	13.62-27.25	1.94-2.08	1.07-2.07	1.1-2.8

Table 3: Comparison of water, sediment and leaf metal levels (ppm dry wt)

S.No	Station	Sample	Ni	Fe	Cr	Cd	Cu	Mn	Zn	Pb
1	Sorlagondi RF	Sediment	3.09	4.63	1.26	1.82	2.61	3.81	2.59	2.73
		water	2.69	3.69	1.27	1.37	3.96	2.97	1.78	1.88
		Leaf	1.34	2.06	1.14	0.37	1.67	0.72	0.19	0.58
2	Nachugunta RF,	Sediment	3.91	4.64	1.59	2.3	2.98	4.07	2.77	2.74
		water	2.28	3.68	1.07	1.16	2.93	2.96	1.77	1.88
		Leaf	1.34	2.17	1.15	0.37	1.82	0.76	0.21	0.61
3	Yelichetladibba RF	Sediment	3.04	4.31	1.24	1.8	2.52	3.75	2.55	2.54
		water	2.08	3.66	0.98	1.06	2.09	3.05	1.83	1.87
		Leaf	1.08	2.1	0.93	0.3	2.59	0.7	0.19	0.59
4	Kottapalem RF	Sediment	1.92	4.22	0.78	1.13	1.26	3.58	2.43	2.49
		water	2.55	3.72	1.2	1.3	2.8	2.88	1.73	1.9
		Leaf	1.05	2.05	0.9	0.29	2.57	0.69	0.19	0.57
5	Molagunta RF	Sediment	2.8	4.41	1.14	1.65	2.96	4.05	2.76	2.6
		water	1.97	3.88	0.93	1.01	2.61	3.37	2.02	1.98
		Leaf	0.92	2.05	0.78	0.26	1.64	0.71	0.19	0.57
6	Adavuladivi RF	Sediment	1.92	4.22	1.26	1.13	2.26	3.58	2.43	2.49
		water	2.55	3.72	1.27	1.3	2.8	2.88	1.73	1.9
		Leaf	1.05	2.05	1.14	0.29	1.57	0.69	0.19	0.57
7	Lankivanidibba RF	Water	2.8	4.41	1.59	1.65	1.96	4.05	2.76	2.6
		Sediment	1.97	3.88	1.07	1.01	1.61	3.37	2.02	1.98
		Leaf	0.92	2.05	1.15	0.26	1.64	0.71	0.19	0.57



Table 3a: Statistical Comparison of water, sediment and leaf metal levels (ppm dry wt)

Samples		Ni	Fe	Cr	Cd	Cu	Mn	Zn	Pb
water	Minimum	1.97	3.66	0.93	1.01	2.80	2.88	1.73	1.87
	Maximum	2.69	3.88	1.27	1.37	261	3.37	2.02	1.98
	Mean	2.30	3.75	1.11	1.17	1.11	3.07	1.84	1.91
	SD	0.30	0.09	0.14	0.15	0.35	0.21	0.13	0.05
Sediment	Minimum	1.92	4.22	0.78	1.13	2.26	3.58	2.43	2.49
	Maximum	3.91	4.64	1.59	2.30	2.98	4.07	2.77	2.74
	Mean	2.78	4.41	1.27	1.64	1.65	3.84	2.61	2.60
	SD	0.70	0.17	0.28	0.41	0.32	0.22	0.15	0.10
Leaf extracts	Minimum	0.92	2.05	0.78	0.26	2.57	0.69	0.19	0.57
	Maximum	1.34	2.17	1.15	0.37	2.82	0.76	0.21	0.61
	Mean	2.51	4.35	1.33	1.48	2.73	3.89	2.65	2.56
	SD	0.51	0.11	0.23	0.30	0.40	0.27	0.19	0.06

Table 4: Levels of pH measured in Water, Sediment and Plant samples

Station no.	Water	Sediment	Leaf
1	7.02	6.20	6.23
2	7.10	5.90	6.32
3	7.20	6.10	6.41
4	6.81	6.50	6.06
5	6.90	7.10	6.14
6	7.06	6.30	6.28
7	6.99	6.10	6.22

The pH range of 6.81 – 7.2 was determined in the water and 5.9 – 7.1 in the sediment and 6.06 to 6.41 in the leaf samples. The lower limit of the pH in water was determined at station 4 and the upper limit at station 3. The lower limit of the pH in the sediment was determined at station 2 and the upper limit at station 5, whereas the lower limit of the pH in the leaf sample was determined at station 4 and the upper limit at station 3. The pH of the water was higher in the water than in the sediment and leaf (Table 4).

Table 5. Contamination Factor (CF) values for heavy metal concentrations in sediment

Station	Cr	Mn	Ni	Cd	Cu	Fe	Zn	Pb
Sorlagondi RF	1.65	1.56	0.02	0.03	1.40	1.18	1.35	2.06
Nachugunta RF,	1.88	1.79	0.02	0.03	1.60	1.35	1.55	2.36
Yelichetladibba RF	1.62	1.54	0.02	0.03	1.38	1.16	1.33	2.03
Kottapalem RF	1.12	1.06	0.01	0.02	0.95	0.80	0.92	1.40
Molagunta RF	1.81	1.72	0.41	0.03	1.54	1.29	1.49	2.26
Adavuladivi RF	2.07	1.96	0.28	0.04	1.76	1.48	1.70	2.59
Lankivanidibba RF	1.78	1.69	0.45	0.03	1.52	1.27	1.46	2.23



Table 6. Geoaccumulation Index (I-geo) values for heavy metal concentrations in sediment

Station	Cr	Mn	Ni	Cd	Cu	Fe	Zn	Pb
Sorlagondi RF	1.33	0.02	0.02	0.03	1.26	1.20	1.82	1.30
Nachugunta RF,	1.52	0.02	0.02	0.03	1.44	1.37	2.09	1.49
Yelichetladibba RF	1.31	0.01	0.02	0.02	1.24	1.18	1.80	1.28
Kottapalem RF	0.90	0.01	0.01	0.02	0.86	0.81	1.23	0.88
Molagunta RF	1.46	0.14	0.33	0.01	0.36	0.35	0.53	1.43
Adavuladivi RF	1.67	0.16	0.23	0.01	0.31	0.30	0.45	1.63
Lankivanidibba RF	1.44	0.14	0.36	0.00	0.22	0.21	0.31	1.41

The highest CF in all the sampling stations were recorded for Fe with the CF values of 1.04-2.26 respectively for all stations. The least values were however recorded for Ni and Cd with CF values of 0.02 to 0.3 each at stations; 0.00 (Below detectable limit) to 0.3 at all stations. I-geo index values of the metals under investigation are presented in Table 6. Similar to CF, I-geo values are found

The present study was concentrated on river junctions where the river is combined with Bay of Bengal only. In the graphical representation of heavy metal concentration in mangrove sediments/Water/Leaf extract samples, the vertical scale showing concentration of element in ppm and the horizontal scale represent the sites of location as shown in Figs. 3-8. Analysis of variance was performed on all data and the completely Randomized Block Design (CRBD) was used to compare the means. Completely randomized block design was adopted to allow for the comparison of heavy metal concentration in sediment and water, as well as the difference in the level of the heavy metals in the polluted and non-polluted rivers.

Heavy metals are found in many parts of ships such as in paints, coatings, anodes and electrical equipment. These are taken apart with no protective measures in place and reused. Exposure can result in lung cancer, cancer of the skin, intestine, kidney, liver or bladder. It can also cause damage to blood vessels. In addition to this the sources for heavy metals are sewages, Agricultural and Irrigation run offs containing Pesticide residues.

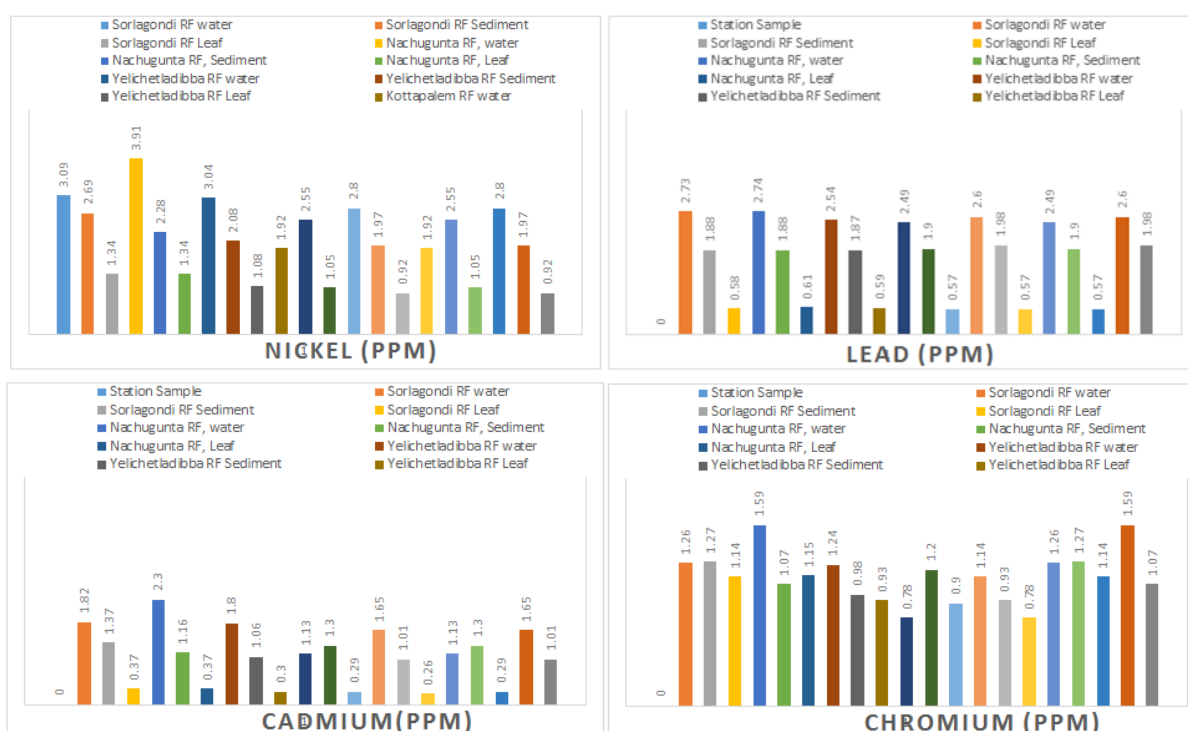
A number of elements are normally present in relatively low concentrations, usually less than a few ppm, in conventional irrigation waters and are called trace elements. Heavy metals are a special group of trace elements which have been shown to create definite health hazards when taken up by plants. Under this group are included, Cr, Cd, Ni, Zn, Cu, Pb and Fe. These are called heavy metals because in their metallic form, their densities are greater than 4 g/cc.

The heavy metals were detected in the water sample at varying concentrations in all seven stations. Table 2 shows the mean concentrations of the trace metals in the water sample. From Figure (s) 3, the mean trace metal concentrations depicted a varying trend from the different stations in Reserve forest. However, one thing has been observed that the concentrations were well above the standard level. The highest levels were recorded in that are located upstream of the river in Nachugunta RF. The presence of some trace metals as seen could be due largely to background levels in the water as a result of the use of fertilizers and also carried by wind from elsewhere. The experimental data on concentration (ppm) of toxic heavy metals like Pb, Cu and Mn in the water samples collected along sampling stations Nachugunta RF, Kottapalem RF is presented in Table 2. The trend in average concentration of these metals at different sampling stations graphically represented in Figure 3, generally, suspended sediment adsorbed pollutants from flowing water in rivers and deposits onto the bed. The accumulation of pollutants in the river bed sediment however, can affect the bio-community through food chain for a long period of time. As a result, assessment of the river sediments



through weak digestion for all the sediment samples were conducted to have an idea on the labile fraction of metal contaminants available in river sediments that could easily be released into the aquatic environment. The results are presented in Table 2. The high level of metal concentration in the river sediment relative to levels in the water as dissolved and suspended is expected since sediments have been described as a sink or reservoir for pollutants in water [10]. Again, for the sediment samples, Cu and Pb recorded highest metal concentrations at all sampled points, and Mn Ni also in higher levels. Which reaffirm the hypothesis that the river is heavily polluted in Pb and Cu. Moreover, the metal concentration levels for the other heavy metals (Pb, Zn, Ni, Fe, and Cr) for almost all sites in the reserve forest were relatively high. Interestingly, Cr was found in the sediment samples very lower values. This may be as a result of the digestion method used and/or the absence of precipitates or complexes of Cr in the sediments of the river. These results suggest that consumption of the polluted water by animals or human beings could be hazardous to their health. Larger sediment sinks to the bottom but later re-enters the aquatic system when floodplain materials are reworked by erosion [11].

The metal concentration level of heavy metals in plant leaf samples is shown in Table 2. The highest concentration of copper was recorded in Yelichentla dibba RF with the least in Kottapalem RF. Zinc concentration level in plant samples range from 2.77 to 0.17 ppm, whereas Lead also in higher values from 4.64 to 2.05. Highly toxic concentrations of manganese in soils (2.59ppm) can cause swelling of cell walls, withering of leaves and brown spots on leaves. In the present investigation it was observed that Mn concentration was found to be 2.59, 2.39 and 2.45 in Soil, sediment and plant samples at different sampling stations [12]. The levels of heavy metals, namely Fe, Zn, chromium, copper, iron, nickel and lead analyzed in the study areas were generally, above W.H.O. standards recommended for surface waters. This is an indication of pollution.



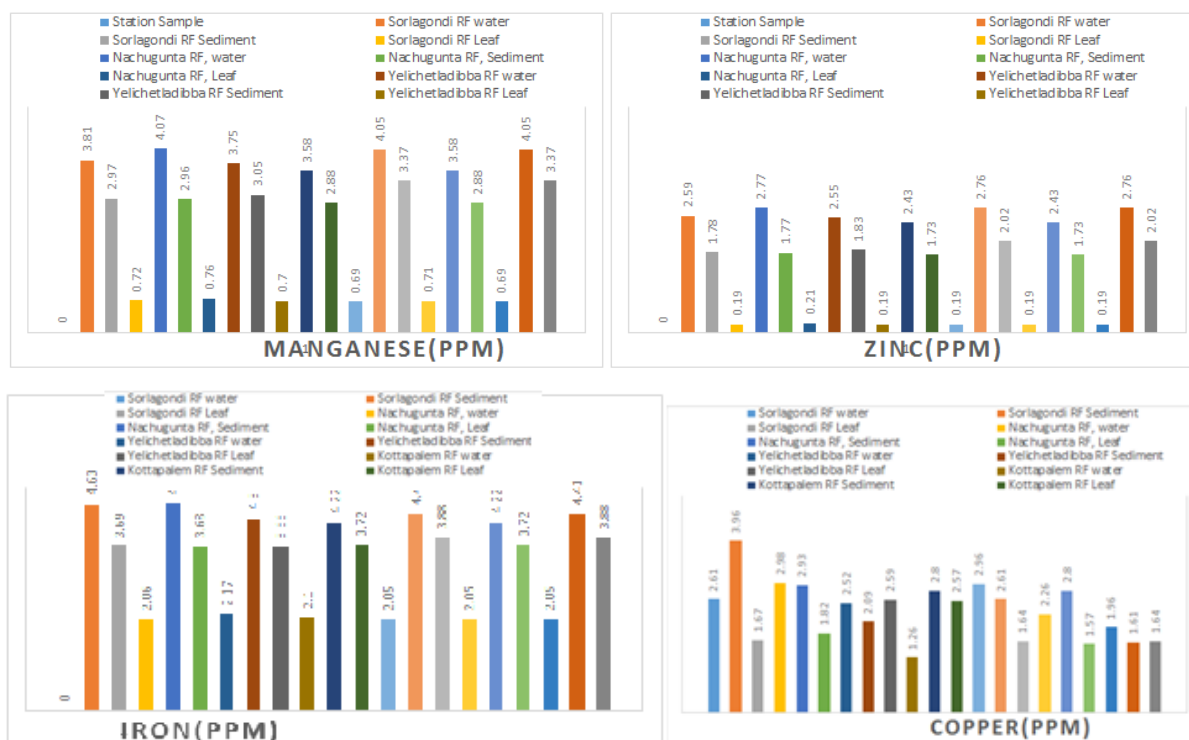


Figure 3: Concentration of selected heavy metals (ppm) in water, Leaf extracts and sediments from Krishna river basin mangrove reserve forest during the period of 2013-14

Conclusions

Based on the above-mentioned points, it is clear that the water and sediments of the Krishna River mangrove forests were contaminated by heavy metals and, therefore, using this water for recreational purposes, washing, and fishing is detrimental to human health and the environment. It is, thus, necessary to take serious and essential measures to control the entry of the sewage, treat it before entering the river, manage the quality of water and the sediments of the river, and utilize water for various purposes. This is the first study to reveal heavy metals in sediment-mangrove plant system in mangrove forest, in seven reserve forests located in Krishna reserve basin. In the present study, mangrove modified the physicochemical properties of sediments by acidifying soils and increasing organic matter contents. Heavy metals like lead, cadmium, chromium and zinc are highly toxic pollutants which could be significantly associated with bioaccumulation within a myriad of ecological systems because they cannot be biologically degraded and instead get concentrated within sediments. To summarize, indicator species are important because they can be utilized to reflect the level of pollutants including heavy metals within biological systems. Interestingly, the bio-concentration of various metals in this plant differs according to the type of tissue. For instance mangrove leaves tend to accumulate lower levels of metals as compared with mangrove roots and sediments. Mangroves and their sediments have an important ecological value because they can act as natural sinks for heavy metals owing to the high capacity of this organism to sequester such metals from tidal waters and rivers and other sources. Ambitious urban structure framework plans within mangrove habitat biotas should always consider the establishment of a comprehensive environmental risk assessment and mitigation plan due to the highly likely chances of pollution caused by anthropogenic chemicals.



Studies on POPs in environment of the Krishna River Delta demonstrate that the levels of DDTs and PAHs in various environmental media are of great concern. The PCBs is also concerned in sediments of some areas of the river basin. There is evidence from the distribution profiles of DDT and its degradation products that inputs of fresh DDT still continues in some regions of the Krishna River Delta. In the future study on POPs in this region, investigation should be enhanced on fully characterizing and remedying the POPs data gap first, their occurrence in marine and terrestrial living organisms, their transfer from food web to human, and subsequently their air–land/air–sea exchange, their land–sea interaction and cycling between Krishna River Delta and Bay of Bengal, and finally, the contributions of POPs from this sub-tropical region to the pollution of global environment.

Although in India the Central Pollution Control Board (CPCB) is responsible for restoration and maintaining the wholesomeness of aquatic resources under Water Prevention and Control of Pollution Act 1974 passed by Indian Parliament, it is expected that to maintained or restored the water quality at desired level it is important to have monitoring on regular basis. Also to address water quality related environmental problems, it is must to have accurate information and to know precisely what the problem is, where it is occurring, how serious it is, and what is causing it. Such information is necessary for determining cost effective and lasting solutions to water related problems. Hence it is expected that the regular water quality monitoring study as performed in the present investigation will help in understanding the water quality trends over a period of time and prioritising pollution control efforts. The present study will also be useful to assess assimilative capacity of a water body thereby reducing cost on pollution control; to assess the fitness of water for different uses.

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References

- [1]. Na GS, Fang XD, Cai YQ, Ge LK, Zong HM, Yuan XT, et al. (2013) Occurrence, distribution, and bioaccumulation of antibiotics in coastal environment of Dalian, China. *Mar Pollut Bull* 69: 233–237. doi: 10.1016/j.marpolbul.2012.12.028. PMID:23465572
- [2]. Li R, Chai M, Qiu GY (2016) Distribution, Fraction, and Ecological Assessment of Heavy Metals in Sediment-Plant System in Mangrove Forest, South China Sea. *PLoS ONE* 11(1): e0147308. doi:10.1371/journal.pone.0147308
- [3]. M. Lewis, R. Pryor and L. Wilking, "Fate and Effects of Anthropogenic Chemicals in Mangrove Ecosystems: A Review," *Environmental Pollution*, Vol. 159, No. 10, 2011, pp. 2328-2346. <http://dx.doi.org/10.1016/j.envpol.2011.04.027>
- [4]. S. Maiti and A. Chowdhury, "Effects of Anthropogenic Pollution on Mangrove Biodiversity: A Review," *Journal of Environmental Protection*, Vol. 4 No. 12, 2013, pp. 1428-1434.
- [5]. Madi, Ana Paula Lang Martins, Boeger, Maria Regina Torres, &Reissmann, Carlos Bruno. (2015). Distribution of Cu, Fe, Mn, and Zn in Two Mangroves of Southern Brazil. *Brazilian Archives of Biology and Technology*, 58(6), 970-976.
- [6]. Cuzzuol GRF, Rocha AC. Interação do regime hídrico com as relaçõesnutricionaisemecosistemamanguezal. *Acta Bot Bras.* 2012; 26:11-19
- [7]. Kannappan T, Shanmugavelu M, Karthikeyan MM. Concentration on heavy metals in sediments and mangroves from Manakudy Estuary (South West Coast of India). *Eur J Biol Sci.* 2012; 4:109-113.



- [8]. MacFarlane, G.R., 2002. Leaf biochemical parameters in *Avicennia marina* (Forsk.) Vierh as potential biomarkers of heavy metal stress in estuarine ecosystems. *Marine Pollution Bulletin* 44, 244–256.
- [9]. Brito, ElciaMargareth Souza, Vieira, Elisa Diniz Reis, Torres, João Paulo Machado, &Malm, Olaf. (2005). Persistent organic pollutants in two reservoirs along the Paraíba do Sul-Guandu River system, Rio de Janeiro, Brazil. *Química Nova*, 28(6), 941-946.
- [10]. do, M. et al., 2011. Water quality and level of some heavy metals in- water and sediments of Kpeshie Lagoon, La-Accra, Ghana.
- [11]. Miller, J. and Lechler, P., 2003. Importance of temporal and spatial scale in the analysis of mercury transport and fate: an example from the Carson River system, Nevada. *Environmental Geology*, 43(3): 315-325.
- [12]. Rodricks, J. V., 1992. *Calculated Risks: Understanding the toxicity and human health risks of chemicals in our environment*. Cambridge University Press.
- [13]. Gao XL, Chen CTA (2012) Heavy metal pollution status in surface sediments of the coastal Bohai Bay. *Water Res* 46: 1901–1911. doi: 10.1016/j.watres.2012.01.007
- [14]. Taylor SR, McLennan SM (1995) The geochemical evolution of the continental crust. *Rev Geophys* 33: 241–265. doi: 10.1029/95rg00262
- [15]. Martin, J. M. and Meybeck, M. Elemental mass balance of materials carried by major world rivers, *Mar Chem*, 7: 173-206, 1979.
- [16]. Nasr, S.M., Okbah, M. A. and S.M. Kasem. Environmental assessment of heavy metal pollution in bottom sediment of Aden port, Yemen. *Int. J. Ocean oceanography*, 1(1): 99-109. 2006
- [17]. Müller G (1969) Index of geoaccumulation in sediments of the Rhine River. *Geojournal* 2: 108–118.