Assessment of Heavy Metals Contamination Level in Estuarine Sea Sediment from Kollidam, India

K. Shameem Rani

Department of Zoology, M.S.S.Wakf Board College, Madurai-625 020, India

Abstract: ***A study was conducted during January to December of 2010.The accumulation of some heavy metals such as Pb, Cd, Cu Fe and Cr was determined in sediment collected from kollidam,Tamil nadu. The results showed that these metals are found widespread throughout the study area, but metal concentrations in the water samples are below the detection limits (BDL). Pb, Cd, Cu and Cr contamination were determined in sediments. The lower and higher ranges of Pb values observed for the sediment samples of both Kollidam estuaries are many times lower than NOAA recommended ER (46.7mg/kg dry weight) and ERM (218mg/kg dry weight) values and PDEP recommended TEL (30.2mg/kg) and PEL (112mg/kg) values. The lower and higher ranges of chromium observed from Kollidam estuary are significantly higher. Moreover, the above mentioned lower and higher ranges of these chromium concentrations in Kollidam estuary are significantly lower than the ER value 81mg/kg and ERM value 370mg/kg,these ranges are many times lower than the NOAA recommended ER and ERM values.***

Keywords: Kollidam, heavy metals, sediments

1. Introduction

Many of the sediments in our rivers, lakes, and oceans have been contaminated by pollutants mainly heavy metals. Some of these pollutants are straight discharged by industrial plants and municipal sewage treatment plants others come from polluted runoff in urban and agricultural areas. These Contaminated sediments can warn creatures in the benthic environment, exposing worms, crustaceans and insects to hazardous concentrations of toxic chemicals. Some kinds of toxic sediments kill benthic organisms, reducing the food available to larger animals such as fish. The cycling of heavy metals, because of their toxicity, bio-accumulation capacity and persistence, is a serious problem recently addressed by many studies on mangrove environments (Harbison, 1986; Lacerda et al., 1988; Mackey and Hodgkinson, 1995).

The use of Organo chlorine insecticides and heavy metals in industry has lead to widespread environmental contamination. Some of these compounds are the object of study on account of their toxicity and ubiquity and moreover, they are known to remain stable in the aquatic environment such as water, sediment and fishes (Fernandez et al., 1992; Ayas and Kolankaya, 1996; Heiny and Tate, 1997; Samanta et al., 2005; Singh and Singh, 2006). The domestic and industrial effluents from the settlements located along the upstream of the reservoir, as well as irrigation and surface runoff. Therefore, there has been continuous flow of pollutants into the river and the reservoir, and pollution in these water systems became significant during the last two decades.

In contrast with organic pollutants, heavy metals cannot be biologically or chemically degraded, and thus may either accumulate locally or be transported over long distances. In natural environments, the associations of metals and their distributions depend on various parameters including redox conditions (Guo et al., 1997) and organic contents (Nissenbaum and Swaine, 1976; Mounier et al., 2001). These parameters may influence the toxicity of metals through processes like mercury methylation (Mason et al., 1994), and by controlling their availability for living organisms. In addition, metals can be adsorbed onto the surface of minerals, like clay minerals, Fe or Mn oxihydroxides (Dong et al., 2000) the high concentrations of heavy metals can accumulate in sediments, and especially in fine-grained oozes, which present high mineral specific surfaces. Mangrove ecosystems, developing in the intertidal zone of most tropical and subtropical regions, are characterized by major contrasts in redox conditions and high rates of organic carbon accumulations (Huc, 1980). Harbison, 1986 reported the heavy metals may act as a sink or a source of heavy metals in coastal environments because of their variable physical and chemical properties.

The aim of the present study is to determine the concentrations of Cd (Cadmium), Cr (Chromium), Cu (Copper), Fe (Iron) and Pb (Lead) in sediment from different location of Kollidam estuary. It is expected that the results of this research will assist in acquiring information about the level of toxic metals in this region.

2. Materials and methods

2.1 Study Sites

All sample sites in Kollidam estuary are selected only in an edge of the estuary with alternative position on two sides of the ridge. In kollidam estuary, all 15 sediment sample sites were denoted as KS-1, KS-2, KS-3, KS-4, KS-5, KS-6, KS-7, KS-8, KS-9, KS-10, KS-11, KS-12, KS-13, KS-14 and KS-15. The sediment sample collection site was fixed at the beginning of each segment. So totally 15 locations were fixed throughout the estuary and they were denoted as S- I (Site-I), S- II, S-III, S- IV, S-V, S-VI, S-VII, S-VIII, S-IX, S-X, S-XI, S-XII, S-XIII, S-XIV and S-XV for our convenience. All fifteen sample sites are located on the earth at 11º22'42.75''N 79º 45'46.08''E, 11º23'08.09''N 79º 45'51.96''E, 11º23'09.66''N 79º 46'19.71''E, 11º22'57.77''N 79º 46'44.09''E, 11º22'38.13''N 79º

47’03.08’’E, 11º22’20.13’’N 79º 47’24.81’’E, 11º22’08.25’’N 79º 47’50.52’’E, 11º21’57.43’’N 79º 48’16.00’’E, 11º21’48.49’’N 79º 48’42.83’’E, 11º21’42.17’’N 79º 49’11.50’’E, 11º21’31.90’’N 79º 49’39.26’’E, 11º21’21.44’’N 79º 50’04.51’’E, 11º21’45.53’’N 79º49’47.85’’E, 11º22’12.45’’N 79º49’38.47’’E, and 11º22’39.66’’N 79º49’47.48’’E respectively.

2.2 Processing of Sediment Samples for Heavy Metals Analysis

The sediments taken out from the ice chest was dried, ground and homogenized. They were then sieved through a 2 mm stainless steel mesh. 0.5g of the resulting homogenous sample was weighed placed into a 120 ml of acid cleaned Teflon microwave vessel. After adding 5ml of ultrapure nitric acid and 2ml ultrapure hydrofluoric acid, they were digested for 30min at 200°C. After allowing at least 2 hours for cooling, the vessels were opened and 0.8g boric acid was added to dissolve the fluoride precipitates. The final volume was made-up to 50 ml by deionized water and then taken to detect the heavy metals by Atomic Absorption Spectrometer.

3. Results and Discussion

The cadmium concentrations in all fifteen sediment samples sites of Kollidam estuary from January to December are reported in Table 1. However, the cadmium concentration in all fifteen sediment sampling points from January to December of 2010-2011 ranged from 0.19±0.02 mg/g to 2.08±0.53mg/g. The lowest range was observed at KS-VIII and highest range was recorded at KS-XV. The distance between the minimum and maximum ranges were too long, therefore, the percentage of maximum range over minimum range was calculated as 994.74 % and the fluctuation peak is highly varied within the sample sites. For the sample site KS-II, the minimum range 0.38±0.03 was observed in June and the maximum 0.81±0.18 in August. The Amazon discharge partly migrates northwestward in the form of mud waves moving towards the Orinoco River, following the direction of both the current of the Guianas (Allison et al., 2000) and the coastal dynamic influences. The components of mangrove deposits can be stabilized for a few decades, like sand grains in a major dune, until they are reset in suspension when erosion reaches their settling place. Many studies, regarding heavy-metal pollution, have been done to the south of the Amazon River (Silva et al., 1998; Lacerda et al., 1999).

The mean concentrations of chromium in sediment samples of the Kollidam estuary were measured and reported in Table 2. According to the table value, mean levels of chromium in sediment samples obtained from all fifteen sample sites of Kollidam estuary system ranged from 10.76±0.9mg/kg to 94.07±04. The highest level 94.07±10.4mg/kg was obtained at KS-VIII in the month of February and the lowest 11.3±0.98mg/kg at sampling point KS-I in the same month. The mean heavy metal concentrations were (μmol g-1): Fe (789.29) > Mn (9.82) > Zn (2.51)> Cr (1.15) > Ni (0.54) > Co (0.32) > Cu (0.28) > Pb (0.13) > Hg (0.41 nmol g-1)(Marchand et al 2006). Hong Kong mangroves, receiving industrial, livestock and domestic sewage were considered as seriously contaminated by Tam and Wong (2000), reporting higher concentrations in Pb and Cu but similar concentrations in Zn and lower concentrations in Cr.

The concentrations of copper for sediments of all samples sites of Kollidam estuary are reported in Table 3. According to the table value, the mean copper concentration in all sediment samples of Kollidam estuary was within the range of 7.76±0.09mg/kg to 53±3.12mg/kg. The minimum concentration was observed at the site KS-XV in the month of February and at the site KS-VII in the month of November. he industrial Brisbane estuary (Australia), mangroves were considered as moderately polluted with similar concentrations of Ni, Cu, Pb and lower concentrations in Cr and Zn (Mackey and Hodgkinson, 1995).The concentrations of Iron for the sediments of all samples sites of Kollidam estuary are reported in Table 4. However, the Iron concentration in sediments for all the fifteen sampling points for all months ranged from 21.42±2.48 mg/g at sampling point KS- XV (in March) to 2825±175.35 mg/g at sampling point KS-VII (in October). The distance between the minimum and maximum ranges were too long and therefore, the percentage of maximum range over minimum range was calculated as 13088.61% and the fluctuation peak is highly varied within the sample sites.

In this study, the seasonal fluctuation of lead concentration during the year 2011-2012 for ten selected sampling sites of Kollidam estuary were tabulated in Table 5. According to the table report, the maximum level of lead for all sampling sites such as KS-I, KS-II, KS-III, KS-IV, KS-V, KS-VI, KS-VII, KS-VIII, KS-IX, KS-X were recorded as 25.37±3.61mg/kg, 35.2±2.88mg/kg, 49.7±4.87mg/kg, 69.17±4.11mg/kg, 76.97±4.74mg/kg, 91.27±5.44mg/kg, 97±8.45mg/kg, 91.77±10.95mg/kg at September 86.33±10.02mg/kg, 73.2±8.26mg/kg at August, 66.59±7.42mg/kg, 46.75±5.24mg/kg at September, 33.15±2.60mg/kg at August 34.39±2.75mg/kg at September and 23.83±3.40mg/kg at July respectively. Worldwide, various levels of cadmium concentration have been reported to be present in the sediments of estuary ecosystem 0.4-10 during 2001 (Riba *et al.*, 2005), 0.059-0.223mg/kg 0.059-0.223 mg/kg in mangrove sediments (Rathees Kumar, 2010), 0.4-1.6 in Ennore estuary and 0.3-0.9 in Adayar estuary (Joseph and Srivastava, 1993), 0.04±0.03 μg g-1 in Proxin river estuary (Elisangela de adrade passos *et al.*, 2010), 1.7-6.3 μg/ g-1in Tagus estuary (Susana France *et al.*, 2005) and 14.94 mg kg-1in Cochin estuary (Balachandran *et al.*, 2005). Similarly, both the Kollidam and Vellar estuaries also have been contaminated with the heavy metal cadmium. Moreover, the maximum and the minimum mean levels of Cd in the sediment samples obtained in the Kollidam estuaries ranged from 0.19±0.02 mg/kg to 2.08±0.53mg/kg. The lowest and highest ranges of cadmium observed in all fifteen sediment sampling points of Kollidam estuary were six to eight folds lower than the ranges observed in the thirteen sample sites of Vellar estuary. The above mentioned cadmium level in the sediments of Kollidam estuaries are slightly lower than the RRL and ERM ranges 1.2 to 9.6 mg/kg recommended by NOAA (Long and Morgan, 1990) but, the lower ranges observed in sediments of Vellar estuaries is one fold lower and one fold higher than the NOAA. The overall lower and higher ranges of cadmium in the surface water of Kollidam and Vellar estuaries were 0.55±0.09µg/l and 2.97±0.28 µg/l and the other values that fall in between these two ranges are reported in Table 10.3 and depicted in 11.2. The previous researches done worldwide to find out the cadmium level in various estuaries - l0.003-0.09 µ/L in San Francisco estuary, 0.17 µg/L^{-1} in Cochin Arabian sea along the Southeast Coast of India (Robin *et al.*, 2012), 0.12 µg/L^{-1} in Alleppy Arabian sea along the Southeast Coast of India (Robin *et al.*, 2012), 0.4 in µg/L^{-1} in Kayamkulam Arabian sea along the Southeast Coast of India (Robin *et al.*, 2012), 0.16 µg/L^{-1} in Neendakara Arabian sea along the Southeast Coast of India (Robin *et al.*, 2012), 0.14 µg/L^{-1} in Paravur Arabian sea along the Southeast Coast of India (Robin *et al.*, 2012), 0.14 µg/L^{-1} in Veli Arabian sea along the Southeast Coast of India (Robin *et al.*, 2012), 0.001-0.010 mg/L in Likas estuary.

4. Conclusion

The Kollidam estuary located very near to Sirkali also opens into the Bay of Bengal. The section of the estuary investigated was the lowermost 6 km, which is straight, about 300 m wide, and averages about 1.5 m deep. Just inside the mouth, lagoons exist on either side behind a wide sandy beach, the breakpoint bar forming the essential feature of a typical bar-built estuary. The estuary is characterized by salinity gradients. Based on these salinity gradients, the entire estuary is demarcated into four zones. The diurnal cycle in the estuary brings some hydrological and biological changes. Variations in salinity gradients also exist from surface to bottom over the tidal cycle. The water current speed in the estuary is almost 0.5 m/set associated with a normal tide range of 70 cm. This estuary is highly polluted with anthropogenic activities due to river bed human settlement and industrial constructions. Hence in the present investigation, the sediment was collected from estuaries to analyze the level of heavy metal load in the estuaries and their impact on estuary inhabiting biota. An estuary is a coastal area where freshwater from rivers and streams mixes with salt water from the ocean. Estuaries are important places for rich plant growth because of high level nutrients. Estuaries are often called nurseries of the ocean. Many fish species lay their eggs in estuaries. The abundant plant life in estuaries provides a safe place for young fishes to live. Birds are also abundant in estuaries as food is available in plenty in the form of marine fishes. Therefore protecting the estuaries from pollution is essential to save the teeming life in it.

Table 1: Mean concentrations of Cadmium (mg/kg) in the sediment samples of 15 sites of Kollidam estuary

Site/ Month	January	March	May	July	September	November
KS-I	0.28±0.03	0.31±0.03	0.27±0.01	0.20±0.01	0.49±0.02	0.39±0.013
KS-II	0.57±0.05	0.49±0.08	0.45±0.04	0.39±0.04	0.72±0.09	0.62±0.06
KS-III	0.60±0.04	0.51±0.03	0.47±0.02	0.39±0.01	0.74±0.05	0.65±0.04
KS-IV	0.8±0.07	0.71±0.04	0.61±0.03	0.45±0.03	1.03±0.27	0.91±0.05
KS-V	0.99±0.15	0.92±0.04	0.76±0.03	0.67±0.50	1.29±0.07	1±0.34
KS-VI	1.31±0.05	1.22±0.07	1.12±0.06	0.81±0.04	1.42±0.08	1.327±0.06
KS-VII	1.65±0.08	1.54±0.08	1.44±0.13	1.12±0.25	1.76±0.17	1.71±0.07
KS-VIII	1.83±0.10	1.82±0.09	1.73±0.09	1.12±0.08	1.90±0.15	1.87±0.11
KS-IX	1.81±0.12	1.64±0.38	1.60±0.30	1.55±0.22	1.88±0.21	1.84±0.21
KS-X	1.47±0.16	1.34±0.14	1.23±0.41	0.97±0.11	1.76±0.20	1.62±0.17
KS-XI	1.26±0.09	1.00±0.200	0.87±0.13	0.82±0.07	1.37±0.10	1.34±0.12
KS-XII	1.24±0.15	1.1±0.11	1.03±0.20	0.77±0.08	1.43±0.24	1.36±0.15
KS-XIII	0.90±0.11	0.89±0.09	0.77±0.08	0.58±0.06	1.11±0.12	0.98±0.10
KS-XIV	0.73±0.06	0.67±0.08	0.45±0.35	0.41±0.04	0.88±0.10	0.80±0.03
KS-XV	0.32±0.03	0.29±0.03	0.24±0.02	0.19±0.02	0.47±0.04	0.43±0.04

Table 2: Mean concentrations of Chromium (mg/kg) in the sediment samples of 15 sites of Kollidam estuary

Site/ Month	January	March	May	July	September	November
KS-I	11.23±0.68	12.23±0.72	12.23±0.72	17.03±1.9	18.4±1.14	20.26±1.79
KS-II	24.46±1.45	25.5±1.52	25.5±1.52	29.6±1.82	31.73±1.97	34.33±2.8
KS-III	36.66±2.14	37.86±2.38	37.86±2.38	42±3.04	44±3.04	46±3.04
KS-IV	49.93±2.94	53±3.12	53±3.12	55.73±3.7	60.7±4.2	64.46±6.71
KS-V	65.26±3.88	67.13±4.03	67.13±4.03	73.53±4.5	76.03±5.11	77.56±4.83
KS-VI	80.4±5.7	80.86±5.14	80.86±5.14	84.66±5.3	88.4±7.23	88.66±5.35
KS-VII	85.26±5.1	87.13±5.35	87.13±5.35	96.13±12.3	95.4±11.45	94.83±12.8
KS-VIII	86.41±7.23	87.7±6.37	87.7±6.37	91.5±6.08	94.07±10.4	91.5±8.53
KS-IX	81.38±9.32	83.74±8.96	83.74±8.96	91.97±8.1	89.11±7.76	91.86±9.07
KS-X	75.81±8.66	76.13±8.87	76.13±8.87	80.23±8.9	82.49±8.96	85.9±7.99
KS-XI	62.2±7.12	67.83±5.92	67.83±5.92	71.46±6.7	72.03±8.15	73.49±8.61
KS-XII	47.03±4.88	48.67±8.75	48.67±8.75	57.86±5.4	62±7.01	61.04±5.56
KS-XIII	35.08±3.95	36±4.09	36±4.09	43.3±5.43	42.6±4.26	43.62±5.06
KS-XIV	23.31±2.66	24.62±2.75	24.62±2.75	28.26±2.7	30.06±3.5	32±3.73
KS-XV	10.7±1.22	11.59±1.33	11.59±1.33	18.7±4.75	19.16±2.51	19.62±2.06

Table 3: Mean concentrations of Copper (mg/kg) in the sediment samples of 15 sites of Kollidam estuary

Site/ Month	January	March	May	July	September	November
KS-I	13.25±0.82	9.17±0.54	10.73±0.66	12.9±0.78	14.2±0.79	15.9±0.87
KS-II	18.36±1.10	11.24±0.69	11.83±0.64	18.77±1.12	19.63±1.12	20.99±1.26
KS-III	23.46±1.36	19.4±1.17	20.63±1.56	23.97±1.36	28.78±1.59	27.43±1.70
KS-IV	31.7±1.92	27.5±1.60	29.84±1.83	32.03±1.85	33.72±2.04	33.4±1.90
KS-V	34.73±2.12	32.16±1.94	36.06±2.05	37.96±2.13	39.16±2.31	41.93±2.57
KS-VI	45.56±2.76	43.96±2.68	42.96±2.68	47±2.879	48.83±2.81	50.16±2.92
KS-VII	51.5±3.04	48±2.87	51.91±3.07	52.26±3.78	52±3.25	53±3.12
KS-VIII	48.9±5.71	46.66±5.32	47.5±7.3	49.4±5.63	49.36±5.83	50.6±5.81
KS-IX	43.13±4.96	40.79±4.73	39.87±0.45	44.64±5.14	47.36±4.89	50.4±5.2
KS-X	35.98±4.13	32.96±3.84	32.16±3.75	37.06±4.20	37.96±4.29	39.7±4.67
KS-XI	29.03±3.26	27.16±3.15	27.46±2.57	29.76±3.40	29.82±3.40	31.83±3.61
KS-XII	22.3±2.6	18.43±2.13	19.57±2.71	23.17±2.66	26.03±2.91	27±3.03
KS-XIII	18.31±1.72	14.56±1.67	11.5±1.47	18.76±2.11	19.86±2.28	26.09±2.91
KS-XIV	12.32±1.43	8.72±1.02	9.11±1.06	10.96±1.26	15.2±1.65	13.5±1.47
KS-XV	12.7±1.21	9.27±0.83	10.79±0.87	9.68±0.87	13.91±0.89	16.8±1.13

Table 4: Mean concentrations of Iron (mg/kg) in the sediment samples of 15 sites of Kollidam estuary

Site/ Month	January	March	May	July	September	November
KS-I	64.3±3.87	22.5±1.4	35.74±2.05	84.65±5.01	84.65±5.01	112.37±6.82
KS-II	450.12±1.7	259±16.64	298±18.24	387.47±23.1	387.47±23.1	634.25±20.7
KS-III	1002±59.0	917±16.82	889.67±5.3	1023.33±6.4	1023.33±6.4	1221.67±7.5
KS-IV	1326.6±7.0	1236.17±7.5	1350±78.9	1503±91.24	1503±91.24	1731.31±1.0
KS-V	1842.3±1.0	1672±103.06	1726.43±1	1967±121.6	1967±121.6	2234±134.8
KS-VI	2160±12.6	2103±125.79	2074.7±1.2	2234±140	2234±140	2395.67±1.4
KS-VII	2503±15.2.	2379±147.98	2436.1±1.4	2669.67±1.6	2669.67±1.6	2589±166.4
KS-VIII	2422.33±2	2341.45±2.6	2268.3±2.5	2452.33±2.8	2452.33±2.8	2647.22±3.0
KS-IX	2163.3±2.0	2059.67±2.3	2016.4±2.2	1973±225.3	1973±225.3	2202.53±2.4
KS-X	1833±19.9	1719±190.78	1645.8±1.8	1928±208.8	1928±208.8	2122.33±2.4
KS-XI	1346.3±1.4	1261.67±1.4	1224.6±1.3	1433±15.6	1433±15.6	1651.33±17
KS-XII	1353±11.2	1270±97.86	1233±95.3	1385±112.6	1385±112.6	1586.33±1.4
KS-XIII	970±112.6	938.17±10.1	886.63±6.6	820.97±89.6	820.97±89.6	1161.67±1.2
KS-XIV	368.66±4.2	279.37±31.5	283.61±3.2	422.31±45.6	422.31±45.6	580±60.82
KS-XV	53.34±6.21	21.42±2.48	61.27±6.65	80.27±8.96	80.27±8.96	136±15.62

Table 5 Mean concentrations of Lead (mg/kg) in the sediment samples of 15 sites of Kollidam estuary

Site/ Month	January	March	May	July	September	November
KS-I	20.63±1.80	19.43±1.93	18.27±1.23	20.5±1.56	21.7±2.25	22.06±2.09
KS-II	31.36±1.79	24.04±1.86	23.51±2.41	27.9±2.79	33.77±3.23	34.86±2.845
KS-III	39.0±3.15	36.1±1.81	32.4±3.92	43.67±4.81	46.71±4.31	45.53±4.110
KS-IV	52.9±5.21	46.29±2.81	41.06±4.9	53.83±5.44	57.19±5.92	55.9±4.1
KS-V	64.16±4.12	62.7±3.65	55.17±3.37	76.97±4.74	69.24±4.14	65.33±3.95
KS-VI	81.8±5.07	77.35±4.54	64.63±3.91	91.51±5.53	89.47±5.21	84.86±5.22
KS-VII	92.73±5.41	90.18±5.53	90.84±5.26	93.27±5.44	94.31±5.80	95.4±5.46
KS-VIII	89.16±10.43	87.23±10.20	86.46±9.92	88.87±10.31	91.77±10.96	89.5±10.50
KS-IX	77.7±8.49	77.0±8.1	68.86±8.00	79.4±9.73	85.18±9.04	80.73±9.33
KS-X	61.08±6.31	59.19±6.82	53.43±6.13	62.1±7.19	67.62±7.92	65.18±5.78
KS-XI	49.53±5.71	44.6±5.2	41.47±4.90	50.28±5.80	66.59±7.42	53.95±4.56
KS-XII	40.81±4.80	35±4.11	34±3.91	41.967±4.80	46.75±5.24	45.16±3.96
KS-XIII	30.67±2.10	26.27±2.20	23.6±2.30	26.47±2.20	32.56±3.41	30.9±2.89
KS-XIV	29.87±2.02	26.52±2.39	23.18±2.09	30.13±2.84	34.39±2.75	31.9±3.12
KS-XV	20.17±2.11	19.1±2.1	19.23±1.93	23.83±3.40	22.6±2.34	21.26±2.84

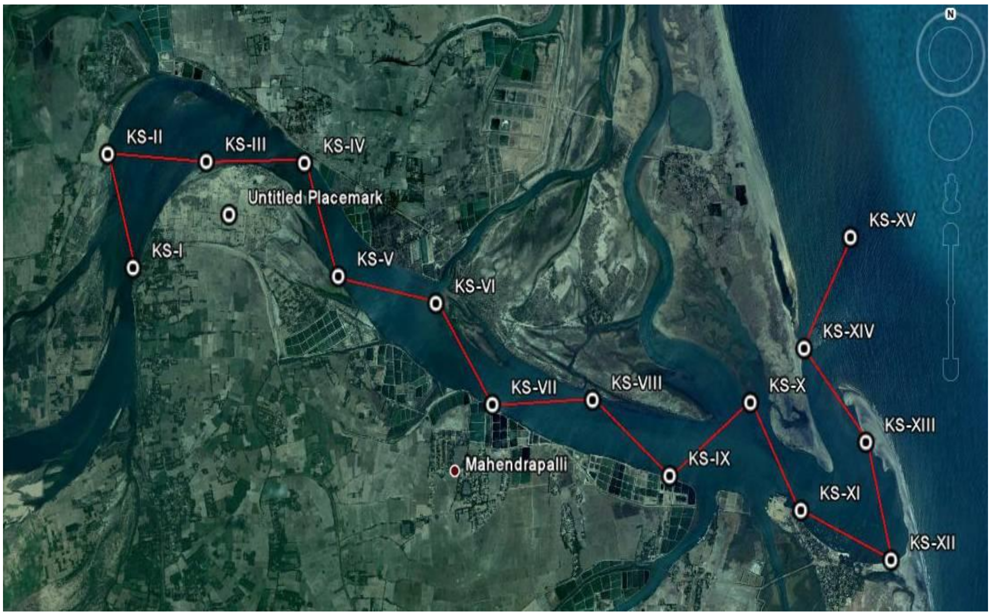

Figure 1: The study area and sediment sampling sites in Kollidam estuary locations

5. Acknowledgement

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