

# Seasonal Variation of Heavy Metals in the Surface Water of Gahirmatha Estuary, Kendrapara, Odisha

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**Abstract**— The coastal stretch of Kendrapada district of Odisha is also known as Gahirmatha; located at eastern region of Odisha, these regions are known for estuary of the rivers Dhamra, Baitarani and Brahmani. Gahirmatha Beach located in Bhitarkanika providing a large base for millions of Olive Ridley Turtles, which is known to be one of most important nesting beaches for turtles in the world. In recent years, heavy metals pollution of the aquatic environment has become a worldwide problem due to materialistic behaviours, intrinsic tenacity, toxicity and non-biodegradable in nature. The study area is situated between the latitude 20° 25' 00"N to 20° 32' 00"N & longitude 86° 45' 00"E to 86° 48' 00"E. This study aimed to determine the concentrations of the heavy metals (Mercury as Hg, Vanadium as V, Chromium as Cr, Manganese as Mn, Iron as Fe, Cobalt as Co, Nickel as Ni, Copper as Cu, Zinc as Zn, Arsenic as As, Lead as Pb, Molybdenum as Mo, Cadmium as Cd) and also their distribution in the water collected from the eastern part of Bay of Bengal from four different estuary locations of Gahirmatha coast, Odisha. The concentrations of heavy metals was measured using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The heavy metals concentrations were found in decreasing sequence of Zn > Fe > Cu > Cr > V > Co > Mn > Ni > Pb > As > Mo > Hg > Cd. The variation of relative concentrations of some of the heavy metals may be affected basically by two reasons; the first one is the riverine influence through both Dhamra and Brahmani river. The second reason behind it may be the anthropogenic liberation through local activities; that are may responsible for the change of water quality.

**Keywords:** Heavy metals, ICP-MS, Estuary, Riverine influence, Gahirmatha coast, Aquatic environment.

## 1 INTRODUCTION

INDIA has a coastal stretch about 7500 k.m. which is 18<sup>th</sup> longest coastline and second largest peninsula in the world.

Exclusive Economic Zones (EEZs) of India covers an area of about 2.3 million km<sup>2</sup>. Most of the economic sensitive zones like Mangroves, tidal flats, coral reefs, Wild life sanctuaries, Turtle breeding grounds and Salt Lake are presented at the coastal areas. India is having 9 coastal states and 4 coastal UT's which nearly occupying 43,230 km<sup>2</sup> of coastal wetlands, 97 major estuaries, 34 major lagoons, 5403 km<sup>2</sup> of mangrove areas, 1401 km<sup>2</sup> coral reef area and 6271 k.m.<sup>2</sup> marine protected areas. Activities around the coast like Port & Harbour, Fisheries & Aquaculture, Coastal industry, Power plants, Renewable energy, Oil & Gas, Tourism, Shipping, Mining and Desalination are situated near the coastal areas due to the water requirement.

In recent years, heavy metals pollution of the aquatic environment has become a worldwide problem due to materialistic

behaviours, intrinsic tenacity, toxicity and non-biodegradable in nature. Due to the possible toxic effect of the heavy metals and capability to bioaccumulate in aquatic ecosystems [1, 2,20], recently the study of distribution and pollution degree of heavy metals in coastal zone has fascinated more public concerns [3-5]. In the aquatic environment the probable sources of heavy metal pollution are mining and industrial wastes [6,16]. These metals differ from other toxic materials in a way that they are neither created nor destroyed by human. They are inert in the environment and are often considered to be conservative pollutants if left undisturbed [7]. However, the rapid industrialization, urbanization, population growth, agricultural and other human activities have resulted in severe pollution by heavy metals globally, especially in developing countries [8,18].

Freshwater runoff, the atmosphere, and point source of human activities are the main sources of metal input to estuaries and coastal water [9]. Although some metals commonly called Heavy Metals (with atomic weight ranging from 63.546 to 200.590 and having similar electrons in its outermost shell) have been seen to have high toxic potential to aquatic organisms when they are above the natural environmental threshold [10], many of them are essential to proper biota metabolism when they exist within the threshold concentrations. Some examples of these essential metals are; cobalt, copper, iron, magnesium, molybdenum, vanadium, strontium, and zinc etc. [11,19].

Heavy metals are generally defined as metals that have high densities and cause water contamination and environmental problems. Metals like arsenic, cadmium, chromium, mercury, nickel, and lead are repeatedly considered as indicators of anthropogenic influence in marine environment and are themselves of potential risk to the natural environment

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[12,15,17]. Several researchers have demonstrated that the evaluation of metal distribution in marine surface water is important due to high pollution with heavy metals [13,14].

Water quality monitoring is essential to control physical, chemical and biological characteristics of water bodies and helps pollution detection. Especially, estuarine water body are facing more risk to contaminants through riverine system. From this point of view, water quality monitoring in many estuaries around the world has been under taken since more than three decades. Gahirmatha stretch is nearest to Bhitarkanika. Gahirmatha is a popular tourist attraction of Odisha. It is also world's largest nesting beach for Olive Ridley sea turtles [21,22]. It ranges from Dhamra river mouth in north to Brahmani river mouth in south. Bhitarkanika regions is located at East-coast region of Odisha. It is second largest mangrove ecosystem of India after the Sunderbans, West Bengal [22].

Bhitarkanika located at the confluence of Brahmani and Baitarani river deltas in the district of Kendrapara in Orissa and is the second largest viable mangrove ecosystem in India (after Sunderbans). Bhitarkanika Wildlife Sanctuary stretched from 20°30' N to 20°50' N latitude and 86°30' E and 87°06' E longitude. Out of the total environmental area, the mangrove forests found nearly 130 km<sup>2</sup>. The rest area covers water bodies, agriculture land, revenue lands and villages respectively. Bhitarkanika of Odisha offerings a variability of habitats and climatic conditions. The Sanctuary is circumscribed by river Dhamara in the north, the river Hansua to the west and Bay of Bengal on the eastern and southern sides respectively [23].

The Sanctuary is home to the numbers of Estuarine Crocodiles in the Indian sub-continent, with a population of more than 1650 crocodiles. It is the only major mangrove patch of the State of Odisha which is legally and administratively well protected and has a long-term role in protecting the life and property of the people of the hinterland from cyclones, and other natural calamities [24-26]. The National park is essentially a network of creeks and canals which are inundated with waters from rivers Brahmani, Baitarani, Dhamra and Patasala forming a unique ecosystem.

The objective of our study was to determine the concentrations of the heavy metals (Mercury as Hg, Vanadium as V, Chromium as Cr, Manganese as Mn, Iron as Fe, Cobalt as Co, Nickel as Ni, Copper as Cu, Zinc as Zn, Arsenic as As, Lead as Pb, Molybdenum as Mo, Cadmium as Cd) and also their distribution in the water collected from the eastern part of Bay of Bengal from four different estuary locations of Gahirmatha coast, Odisha. It was intended to appraise the contamination status of different metals in surface water our study area during the months of March & April (pre-monsoon) and November & December (post-monsoon) of the year 2019.

## 2 MATERIALS AND METHODS

### 2.1 Study area

Coastal stretch of Gahirmatha regions is located at East-coast region of Odisha, these regions are known for estuary of the rivers Dhamra, Baitarani and Brahmani. Gahirmatha marine Sanctuary is a marine wildlife sanctuary located in the estuarial region of Bramhani & Baitaran, eastern region of Odisha.

Bhitarkanika is also known for second largest mangrove ecosystem in India, which providing home to saltwater crocodile (*Crocodylus porosus*), Indian python, king cobra, black ibis, darters and many other species of flora and fauna. Gahirmatha Beach located in Bhitarkanika providing a large base for millions of Olive Ridley Turtles, which is known to be one of most important nesting beaches for turtles in the world. The study area is situated between the latitude 20° 25' 00''N to 20° 32' 00''N & longitude 86° 45' 00''E to 86° 48' 00''E. The details of longitude and latitude values of sampling points are shown in Table-1. The sampling points are selected starting from upstream of river near shore up to 2.8 km toward sea. (Table 1 and Figure1).



Figure 1. Map of water sampling sites along the coast of Bay of Bengal.

Table-1: Geographical locations of the sample collecting points

Sampling Point	Name of Sampling Point	Coordinates	Distance from shore in k.m
G1	Hansua Mouth Up	20°32'10.41''N / 86°47'30.95''E	0.5
G2	Hansua Mouth	20°29'53.08''N / 86°46'49.88''E	2.0 from mouth
G3	Jambu Up	20°27'43.14''N / 86°41'38.68''E	2.2 from mouth
G4	Jambu	20°25'29.60''N / 86°45'31.72''E	2.5

### 2.2 Surface water sample collection

Three surface water samples were collected from about 10 cm below the water surface from each sampling site or point of Gahirmatha coastal area, eastern part of Bay of Bengal. Niskin water sampler was used to collect the water Samples. One litre of water sample was being transferred to the pre-cleaned sampling bottles (HDPE bottle) from the collected water [27]. To avoid further contamination Nearly 2 to 3 drops of 1N nitric acid (HNO<sub>3</sub>) added to the water samples to fix and keep the pH level below 2. The water samples were kept in chill condition (i.e., refrigerator or ice box) till the samples arrive up to laboratory for extraction and further analysis.

## 2.3 Extraction of samples and Instrumentation

The water samples were filtered through 0.45µm GF/C filter paper, from the 1lt samples. The pH is being balanced from 4 to 6 by adding acid (Acetic acid) and alkali (Ammonia) buffer as required. Then transfer the water sample to a cleaned separating funnel. Then 10ml 1% APDA solution was added followed by 50ml MIBK solution to the water sample. The chemical mixed sample was being shaken for 10 minutes, then allowed to stand for 30 minutes. After the phase separation, two layers were being formed. The aqueous layer was discarded and 50ml 4N HNO<sub>3</sub> was added to the organic phase. After that, it was shaken vigorously for next 10 minutes. After phase separation, the lower aqueous layer containing desired metal ions were collected and stored for further analysis by Inductively Coupled Plasma-Mass Spectrometry (Perkin Elmer; Model: Nexion300x).

## 3 RESULTS AND DISCUSSIONS

### 3.1 Results

The seasonal variations in the concentration of the heavy metals of Gahirmatha estuarine region were well marked. The seasonal variations of thirteen heavy metals (Hg, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Pb, Mo and Cd) in all four sampling points (G1, G2, G3 and G4) with both low tide (LT) and high tide (HT) of sea during pre-monsoon and post-monsoon seasons are described as follows.

During dry season or pre-monsoon season at sampling point G1; the average concentration of mercury in low tide 0.323 ± 0.015 µg/l, while in high tide the average concentration is 0.383 ± 0.015 µg/l, Vanadium in low tide 2.718 ± 0.020 µg/l, while in high tide 2.980 ± 0.010 µg/l, Chromium in low tide 2.235 ± 0.022 µg/l, while in high tide 4.596 ± 0.015µg/l, Manganese in low tide 0.514 ± 0.005µg/l, while in high tide 0.536 ± 0.029 µg/l, Iron in low tide 12.472 ± 0.016 µg/l, while in high tide 21.975 ± 0.057 µg/l, Cobalt in low tide 0.567 ± 0.016 µg/l, while in high tide 0.867 ± 0.006 µg/l, Nickel in low tide 0.832 ± 0.020 µg/l, while in high tide 1.117 ± 0.015 µg/l, Copper in low tide 17.219 ± 0.322 µg/l, while in high tide 17.881 ± 0.020 µg/l, Zinc in low tide 32.061 ± 0.046 µg/l, while in high tide 20.237 ± 0.015 µg/l, Arsenic in low tide 0.313 ± 0.006 µg/l, while in high tide 0.777 ± 0.015 µg/l, Lead in low tide 0.892 ± 0.020 µg/l, while in high tide 0.740 ± 0.010 µg/l, Molybdenum in low tide 0.300 ± 0.010 µg/l, while in high tide 0.240 ± 0.010 µg/l, Cadmium in low tide 0.256 ± 0.015 µg/l, while in high tide 0.120 ± 0.010 µg/l.

In case of wet season or post-monsoon season at sampling point G1; the average concentration of mercury in low tide 0.623 ± 0.015 µg/l, while in high tide the average concentration is 0.723 ± 0.012 µg/l, Vanadium in low tide 1.270 ± 0.010 µg/l, while in high tide 1.397 ± 0.012 µg/l, Chromium in low tide 2.920 ± 0.020 µg/l, while in high tide 5.613± 0.021 µg/l, Manganese in low tide 1.237 ± 0.012 µg/l, while in high tide 1.293 ± 0.015 µg/l, Iron in low tide 18.247 ± 0.015 µg/l, while in high tide 18.460 ± 0.010 µg/l, Cobalt in low tide 0.577 ± 0.015 µg/l, while in high tide 0.890 ± 0.010 µg/l, Nickel in low tide 0.468 ± 0.020 µg/l, while in high tide 0.587 ± 0.012 µg/l

,Copper in low tide 18.813 ± 0.015 µg/l, while in high tide 19.030± 0.026 µg/l, Zinc in low tide 17.650 ± 0.030 µg/l, while in high tide 16.710± 0.010 µg/l, Arsenic in low tide 0.533± 0.025 µg/l, while in high tide 0.670± 0.010 µg/l, Lead in low tide 0.407 ± 0.015 µg/l, while in high tide 0.493 ± 0.015 µg/l, Molybdenum in low tide 0.343 ± 0.021 µg/l, while in high tide 0.427 ± 0.015 µg/l, Cadmium in low tide 0.173 ± 0.015 µg/l, while in high tide 0.223 ± 0.010 µg/l.

During dry season or pre-monsoon season at sampling point G2; the average concentration of mercury in low tide 0.13 ± 0.010 µg/l, while in high tide the average concentration is 0.057 ± 0.006 µg/l, the average concentration of Vanadium in low tide 2.57 ± 0.010µg/l, while in high tide the average concentration is 3.031 ± 0.015µg/l, the average concentration of Chromium in low tide 0.323 ± 0.012µg/l, while in high tide the average concentration is 2.07± 0.024µg/l, the average concentration of Manganese in low tide 2.503 ± 0.038µg/l,while in high tide the average concentration is 0.399 ± 0.01 µg/l, the average concentration of Iron in low tide 18.48 ± 0.01 µg/l, while in high tide the average concentration is 18.477 ± 0.016 µg/l, the average concentration of Cobalt in low tide 0.923 ± 0.04 µg/l, while in high tide the average concentration is 1.142 ± 0.02 µg/l, the average concentration of Nickel in low tide 1.689 ± 0.305µg/l, while in high tide the average concentration is 0.761 ± 0.01 µg/l, the average concentration of Copper in low tide 17.637 ± 0.015µg/l, while in high tide the average concentration is 20.697 ± 0.012 µg/l, the average concentration of Zinc in low tide 25.641 ± 0.01µg/l, while in high tide the average concentration is 32.14 ± 0.026µg/l, the average concentration of Arsenic in low tide 0.19 ± 0.02µg/l, while in high tide the average concentration is 0.469 ± 0.014 µg/l, the average concentration of Lead in low tide 0.223 ± 0.015µg/l, while in high tide the average concentration is 0.704 ± 0.006 µg/l, the average concentration of Molybdenum in low tide 0.863 ± 0.015µg/l, while in high tide the average concentration is 0.223 ± 0.006 µg/l, the average concentration of Cadmium in low tide 0.303 ± 0.015µg/l, while in high tide the average concentration is 0.086 ± 0.006 µg/l.

In wet season or post-monsoon season at sampling point G2; the average concentration of mercury in low tide 0.435 ± 0.013µg/l, while in high tide the average concentration is 0.509± 0.01 µg/l, Vanadium in low tide 0.847±0.016µg/l, while in high tide 1.062±0.004µg/l, Chromium in low tide 1.969 ± 0.011µg/l, while in high tide 4.512 ± 0.013µg/l, Manganese in low tide 0.426 ± 0.006µg/l, while in high tide 0.509 ± 0.009 µg/l, Iron in low tide 16.668± 0.017µg/l, while in high tide 16.662 ± 0.071 µg/l, Cobalt in low tide 0.211 ± 0.012µg/l, while in high tide 0.436± 0.021µg/l, Nickel in low tide 0.541± 0.009µg/l, while in high tide 1.04± 0.043µg/l, Copper in low tide 15.319 ± 0.009µg/l, while in high tide 17.82 1± 0.055µg/l, Zinc in low tide 33.341± 0.027µg/l, while in high tide 26.311 ± 0.036 µg/l, the average concentration of Arsenic in low tide 0.341 ± 0.028µg/l,while in high tide 0.411 ± 0.011µg/l, Lead in low tide 0.152± 0.01µg/l, while in high tide 0.192 ± 0.016µg/l, Molybdenum in low tide 0.3 ± 0.01µg/l, while in high tide 0.536± 0.015 µg/l, Cadmium in low tide 0.136 ± 0.01 µg/l, while in high tide 0.075 ± 0.013 µg/l.

During dry season or pre-monsoon season at sampling point

G3; the average concentration of mercury in low tide  $0.36 \pm 0.072 \mu\text{g/l}$ , while in high tide the average concentration is  $0.062 \pm 0.018 \mu\text{g/l}$ , Vanadium in low tide  $2.463 \pm 0.143 \mu\text{g/l}$ , while in high tide  $2.511 \pm 0.135 \mu\text{g/l}$ , Chromium in low tide  $2.701 \pm 0.168 \mu\text{g/l}$ , while in high tide  $2.769 \pm 0.12 \mu\text{g/l}$ , Manganese in low tide  $0.229 \pm 0.151 \mu\text{g/l}$ , while in high tide  $0.247 \pm 0.066 \mu\text{g/l}$ , Iron in low tide  $15.492 \pm 0.328 \mu\text{g/l}$ , while in high tide  $17.357 \pm 5.679 \mu\text{g/l}$ , Cobalt in low tide  $2.66 \pm 0.125 \mu\text{g/l}$ , while in high tide  $2.053 \pm 0.07 \mu\text{g/l}$ , Nickel in low tide  $0.438 \pm 0.055 \mu\text{g/l}$ , while in high tide  $0.475 \pm 0.061 \mu\text{g/l}$ , Copper in low tide  $2.68 \pm 0.201 \mu\text{g/l}$ , while in high tide  $3.282 \pm 0.101 \mu\text{g/l}$ , Zinc in low tide  $4.941 \pm 0.096 \mu\text{g/l}$ , while in high tide  $16.144 \pm 0.106 \mu\text{g/l}$ , the average concentration of Arsenic in low tide  $0.071 \pm 0.02 \mu\text{g/l}$ , while in high tide  $0.519 \pm 0.141 \mu\text{g/l}$ , Lead in low tide  $0.064 \pm 0.055 \mu\text{g/l}$ , while in high tide  $1.856 \pm 0.056 \mu\text{g/l}$ , Molybdenum in low tide  $0.134 \pm 0.075 \mu\text{g/l}$ , while in high tide  $0.078 \pm 0.055 \mu\text{g/l}$ , Cadmium in low tide  $0.043 \pm 0.035 \mu\text{g/l}$ , while in high tide  $0.066 \pm 0.025 \mu\text{g/l}$ .

In case of wet season or post-monsoon season at sampling point G3; the average concentration of mercury in low tide  $0.2 \pm 0.046 \mu\text{g/l}$ , while in high tide the average concentration is  $0.2 \pm 0.046 \mu\text{g/l}$ , the average concentration of Vanadium in low tide  $2.207 \pm 0.210 \mu\text{g/l}$ , while in high tide the average concentration is  $2.967 \pm 0.087 \mu\text{g/l}$ , the average concentration of Chromium in low tide  $0.347 \pm 0.126 \mu\text{g/l}$ , while in high tide the average concentration is  $4.6 \pm 0.12 \mu\text{g/l}$ , the average concentration of Manganese in low tide  $3.428 \pm 0.046 \mu\text{g/l}$ , while in high tide the average concentration is  $0.523 \pm 0.045 \mu\text{g/l}$ , the average concentration of Iron in low tide  $10.46 \pm 0.075 \mu\text{g/l}$ , while in high tide the average concentration is  $22.025 \pm 0.051 \mu\text{g/l}$ , the average concentration of Cobalt in low tide  $0.657 \pm 0.07 \mu\text{g/l}$ , while in high tide the average concentration is  $0.863 \pm 0.07 \mu\text{g/l}$ , the average concentration of Nickel in low tide  $0.27 \pm 0.60 \mu\text{g/l}$ , while in high tide the average concentration is  $1.13 \pm 0.046 \mu\text{g/l}$ , the average concentration of Copper in low tide  $17.65 \pm 0.07 \mu\text{g/l}$ , while in high tide the average concentration is  $17.871 \pm 0.076 \mu\text{g/l}$ , the average concentration of Zinc in low tide  $0.46 \pm 0.089 \mu\text{g/l}$ , while in high tide the average concentration is  $20.247 \pm 0.06 \mu\text{g/l}$ , the average concentration of Arsenic in low tide  $0.183 \pm 0.09 \mu\text{g/l}$ , while in high tide the average concentration is  $0.773 \pm 0.08 \mu\text{g/l}$ , the average concentration of Lead in low tide  $0.847 \pm 0.091 \mu\text{g/l}$ , while in high tide the average concentration is  $0.747 \pm 0.07 \mu\text{g/l}$ , the average concentration of Molybdenum in low tide  $0.223 \pm 0.045 \mu\text{g/l}$ , while in high tide the average concentration is  $0.237 \pm 0.05 \mu\text{g/l}$ , the average concentration of Cadmium in low tide  $0.32 \pm 0.053 \mu\text{g/l}$ , while in high tide the average concentration is  $0.14 \pm 0.062 \mu\text{g/l}$ .

During dry season or pre-monsoon season at sampling point G4; the average concentration of mercury in low tide  $0.337 \pm 0.086 \mu\text{g/l}$ , while in high tide the average concentration is  $0.183 \pm 0.1 \mu\text{g/l}$ , the average concentration of Vanadium in low tide  $2.542 \pm 0.127 \mu\text{g/l}$ , while in high tide the average concentration is  $3.27 \pm 0.105 \mu\text{g/l}$ , the average concentration of Chromium in low tide  $2.238 \pm 0.055 \mu\text{g/l}$ , while in high tide the average concentration is  $1.92 \pm 0.145 \mu\text{g/l}$ , the average concentration of Manganese in low tide  $0.541 \pm 0.07 \mu\text{g/l}$ , while in high tide the average concentration is  $0.349 \pm 0.098 \mu\text{g/l}$ , the

average concentration of Iron in low tide  $12.475 \pm 0.1 \mu\text{g/l}$ , while in high tide the average concentration is  $18.254 \pm 0.055 \mu\text{g/l}$ , the average concentration of Cobalt in low tide  $0.557 \pm 0.061 \mu\text{g/l}$ , while in high tide the average concentration is  $1.071 \pm 0.105 \mu\text{g/l}$ , the average concentration of Nickel in low tide  $0.852 \pm 0.081 \mu\text{g/l}$ , while in high tide the average concentration is  $0.727 \pm 0.1 \mu\text{g/l}$ , the average concentration of Copper in low tide  $18.069 \pm 1.639 \mu\text{g/l}$ , while in high tide the average concentration is  $18.836 \pm 0.065 \mu\text{g/l}$ , the average concentration of Zinc in low tide  $32.091 \pm 0.091 \mu\text{g/l}$ , while in high tide the average concentration is  $7.301 \pm 0.01 \mu\text{g/l}$ , the average concentration of Arsenic in low tide  $0.32 \pm 0.056 \mu\text{g/l}$ , while in high tide the average concentration is  $0.622 \pm 0.05 \mu\text{g/l}$ , the average concentration of Lead in low tide  $0.902 \pm 0.015 \mu\text{g/l}$ , while in high tide the average concentration is  $1.029 \pm 0.05 \mu\text{g/l}$ , the average concentration of Molybdenum in low tide  $0.313 \pm 0.071 \mu\text{g/l}$ , while in high tide the average concentration is  $0.315 \pm 0.055 \mu\text{g/l}$ , the average concentration of Cadmium in low tide  $0.246 \pm 0.051 \mu\text{g/l}$ , while in high tide the average concentration is  $0.238 \pm 0.066 \mu\text{g/l}$ .

In post-monsoon season at sampling point G4; the average concentration of mercury in low tide  $0.19 \pm 0.02 \mu\text{g/l}$ , while in high tide the average concentration is  $0.077 \pm 0.05 \mu\text{g/l}$ , Vanadium in low tide  $2.173 \pm 0.091 \mu\text{g/l}$ , while in high tide  $2.735 \pm 0.067 \mu\text{g/l}$ , Chromium in low tide  $4.449 \pm 0.08 \mu\text{g/l}$ , while in high tide  $2.245 \pm 0.065 \mu\text{g/l}$ , Manganese in low tide  $0.568 \pm 0.081 \mu\text{g/l}$ , while in high tide  $0.517 \pm 0.05 \mu\text{g/l}$ , Iron in low tide  $25.826 \pm 0.105 \mu\text{g/l}$ , but in high tide  $12.452 \pm 0.066 \mu\text{g/l}$ , Cobalt in low tide  $1.134 \pm 0.107 \mu\text{g/l}$ , while in high tide  $0.551 \pm 0.082 \mu\text{g/l}$ , Nickel in low tide  $1.089 \pm 0.05 \mu\text{g/l}$ , while in high tide  $0.832 \pm 0.04 \mu\text{g/l}$ , Copper in low tide  $21.048 \pm 0.075 \mu\text{g/l}$ , while in high tide  $17.069 \pm 0.056 \mu\text{g/l}$ , Zinc in low tide  $18.045 \pm 0.065 \mu\text{g/l}$ , while in high tide  $32.084 \pm 0.02 \mu\text{g/l}$ , Arsenic in low tide  $1.252 \pm 0.06 \mu\text{g/l}$ , while in high tide  $0.316 \pm 0.05 \mu\text{g/l}$ , Lead in low tide  $0.342 \pm 0.07 \mu\text{g/l}$ , while in high tide  $0.303 \pm 0.025 \mu\text{g/l}$ , Molybdenum in low tide  $0.162 \pm 0.025 \mu\text{g/l}$ , while in high tide  $0.908 \pm 0.026 \mu\text{g/l}$ , The average concentration of Cadmium in low tide  $0.132 \pm 0.027 \mu\text{g/l}$ , while in high tide  $0.126 \pm 0.075 \mu\text{g/l}$ .

### 3.2 Discussions

Bioactive trace metals in seawater, including Cd, Co, Cu, Fe, Mn, Ni, and Zn, play important roles in influencing global biogeochemical cycles and Estuary-oceanic ecosystem dynamics. The environmental conditions with respect to heavy metals (Zn, As, Cu, Fe, Co, Ni, Cr, Mn, Mo, V, Pb, Hg and Cd) were found to be in good conditions due to the low concentrations of these metals in the stretch. There were obvious seasonal variations in their concentrations. The distribution patterns of some metals indicated the potential influence of terrestrial inputs. The analysis results indicated that both terrestrial inputs and biological processes regulated the distributions and seasonal variations in metals in the three different phases. Dissolved Fe and Mn were mainly influenced by terrestrial inputs, while dissolved Ni, Cu, Zn and Cd by biological processes. For metals in the particulate phase, biological processes become the main factor that control the behaviours of most of the metals.

### 3.2.1 Bar Graph Analysis

There are two axis (X-axis and Y-axis) in bar graphs. In most bar graphs, the x-axis runs horizontally and y-axis runs vertically. In this study pie charts used to show the concentration of all thirteen heavy metals at each sampling point during pre-monsoon and post-monsoon seasons in both tides (Low tide & High tide) respectively.

#### 1. Mercury (Hg):

The below present mercury graph describes about the variability of concentration at different sampling sites. In both G1 and G2 site the mercury concentration during both pre- & post-monsoon shows continuous increase from low tide to high tide. In case of pre-monsoon the concentration is low but during post-monsoon the concentration is increasing. It may be due to the increase of the effluent from the industry present in catchment area of river. The concentration G3 site is not much altering during pre-monsoon to post-monsoon. During low tide of pre-monsoon is having more concentration then post-monsoon. The concentration of high tide in pre-monsoon is less compared to high tide of post-monsoon. In G4 site the concentration of pre-monsoon is more than post-monsoon during both low and high tide.

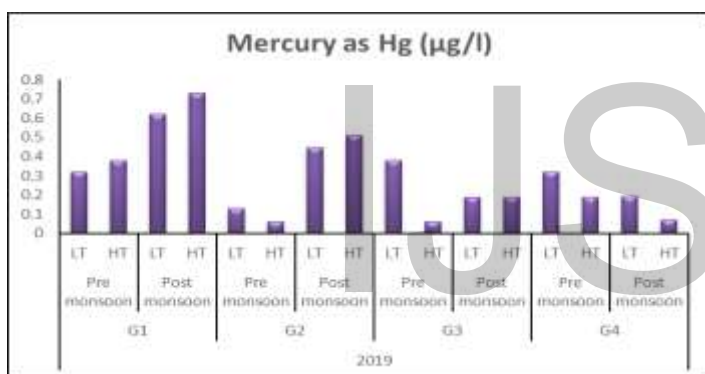


Figure 2. Bar Graph of concentration of Mercury (Hg) in Gahirmatha during pre- and post-monsoon

#### 2. Vanadium (V):

The results we get from below vanadium bar graph are described here. In Both G1 and G2 site the concentration was higher in pre-monsoon of both low & high tide then the Post-monsoon.

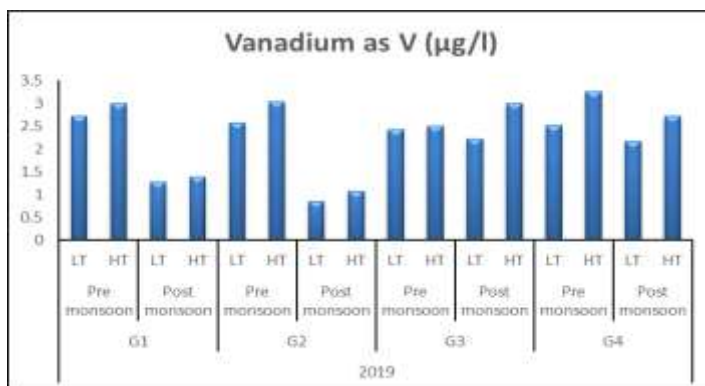


Figure 3. Bar Graph of concentration of Vanadium (V) in Gahirmatha during pre- and post-monsoon

In the G3 site the concentration during both the pre-monsoon and post-monsoon season shows similar concentration; but the high tide concentration is slightly increasing during post-monsoon. In G4 site the concentration of pre-monsoon is slightly decreases toward post-monsoon.

#### 3. Zinc (Zn):

The below graph describes the concentration of zinc in 4 different sites. In G1 site the low tide of pre-monsoon is drastically decrease during post-monsoon season, but the high tide during pre-monsoon concentration is slightly decreasing toward post-monsoon. In G2 site the Low tide of pre-monsoon is increasing toward post-monsoon and the high tide is decreasing toward post-monsoon. In G3 site, pre-monsoon concentration is increasing toward post-monsoon. In G4 site the low tide concentration is decreasing highly from pre-monsoon to post-monsoon and in case of high tide the concentration is extremely increases from pre-monsoon to post-monsoon.

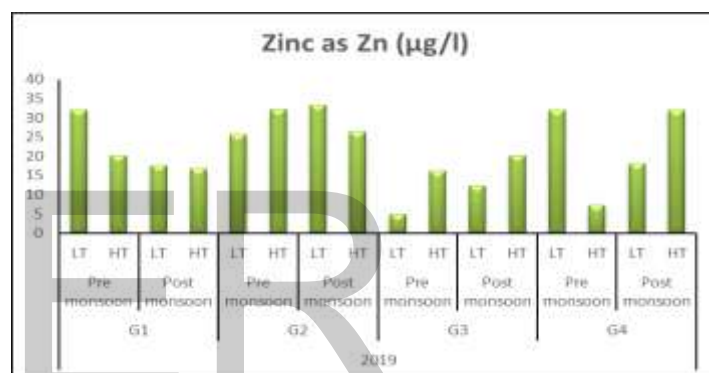


Figure 4. Bar Graph of concentration of Zinc (Zn) in Gahirmatha during pre- and post-monsoon

#### 4. Arsenic (As):

Arsenic concentration of all the sites are given in the below graph. In G1 site the concentration of low tide in pre-monsoon is slightly increasing toward post-monsoon and the high tide in pre-monsoon is slightly decreasing toward post-monsoon.

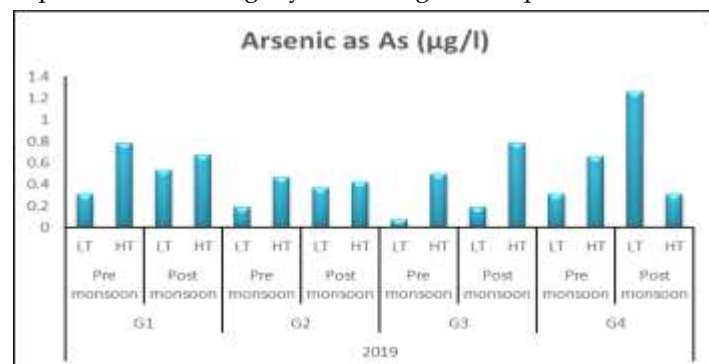


Figure 5. Bar Graph of concentration of Arsenic (As) in Gahirmatha during pre- and post-monsoon

In G2 site the low tide concentration of pre-monsoon is increasing in post-monsoon and the high tide concentration is similar in both pre & post-monsoon. In G3 site both the low

and high tide concentration is moderately increasing from pre-monsoon to post-monsoon. In G4 site the low tide concentration is drastically increasing from pre to post-monsoon, but the high tide concentration is decreasing slightly toward post-monsoon.

**5. Lead (Pb):**

Lead concentration of all the sites are given in the below graph. In G1 site the concentration is decreasing from pre-monsoon to post-monsoon. In G2 site the low tide of pre-monsoon is slightly decreasing toward post-monsoon, but the concentration in high tide is decreasing extremely from pre-monsoon to post-monsoon. In G3 site the low tide concentration terribly increasing from pre-monsoon to post-monsoon and the high tide concentration is exceedingly is decreasing from pre-monsoon to post-monsoon. In G4 site the concentration is showing decreasing trend from pre-monsoon to post-monsoon.

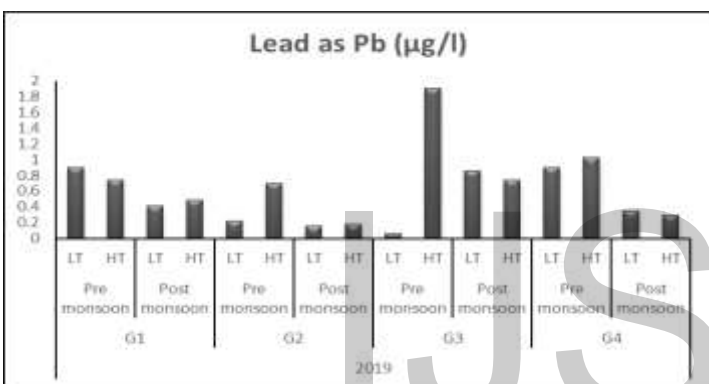


Figure 6. Bar Graph of concentration of Lead (Pb) in Gahirmatha during pre- and post-monsoon

**6. Molybdenum (Mo):**

The concentrations of 4 different sites are prescribed below the graph. In G1, G3 and G4 sites the concentration of pre-monsoon is increasing toward post-monsoon season.

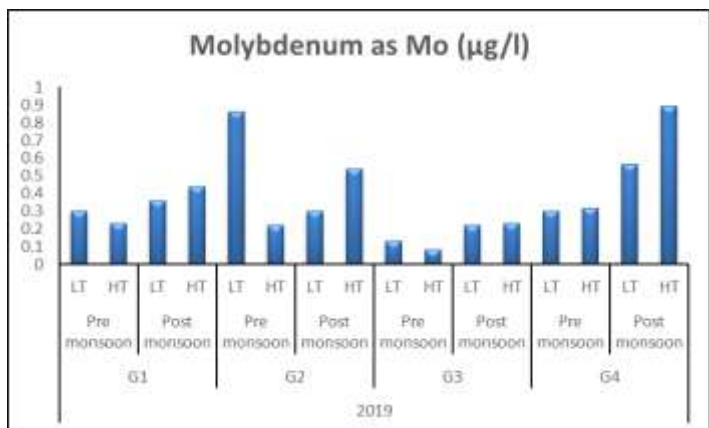


Figure 7. Bar Graph of concentration of Molybdenum (Mo) in Gahirmatha during pre- and post-monsoon

In G2 site the low tide concentration of pre-monsoon is

thoroughly decreasing in post-monsoon season, but the high tide concentration is increasing toward post-monsoon.

**7. Cadmium (Cd):**

Cadmium concentration of all the sites are given in the below graph. In G1 site the low tide concentration in pre-monsoon is decreasing toward post-monsoon and the high tide concentration is increasing. In G2 site low tide concentration is decreasing from pre-monsoon to post-monsoon, but in case of the high tide the concentration is remains same in both the season. In G3 site low tide concentration from pre-monsoon to post-monsoon is extremely increasing, but in case of high tide the concentration is slightly increasing. In G4 site low tide concentration is highly is decreasing from pre-monsoon to post-monsoon, but the high tide concentration is slightly increasing toward post-monsoon.

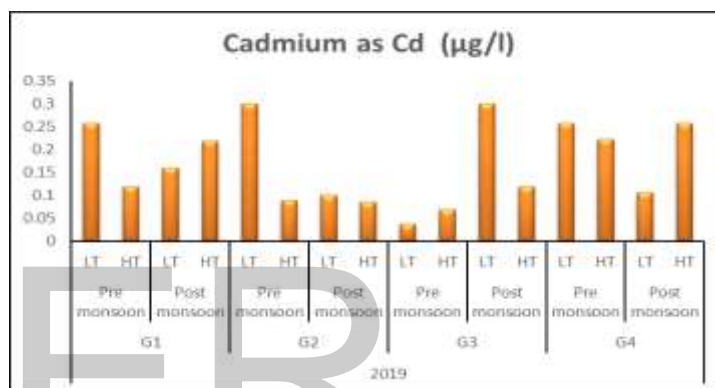


Figure 8. Bar Graph of concentration of Cadmium (Cd) in Gahirmatha during pre- and post-monsoon

**8. Chromium (Cr):**

The chromium concentration is showing in below graph. In G1 and G2 sites the concentration of both low tide and high tide are highly increasing from pre-monsoon to post-monsoon. In G3 site low tide in pre-monsoon is extremely decreasing toward post-monsoon, but the high tide concentration is highly increasing from pre-monsoon to post-monsoon. In G4 site both the low tide and post-monsoon are increasing from pre-monsoon to post-monsoon.

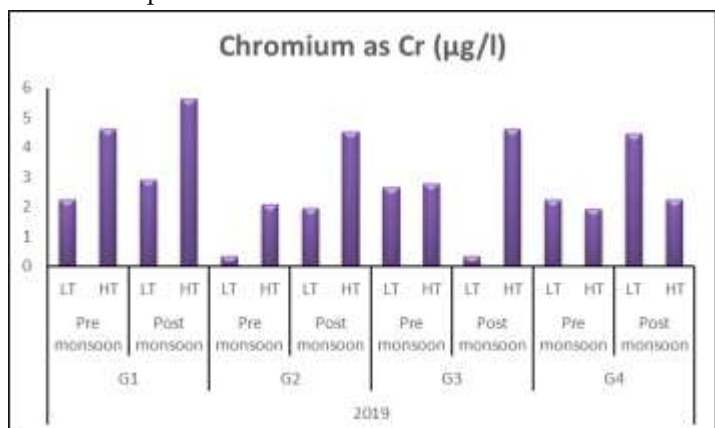


Figure 9. Bar Graph of concentration of Chromium (Cr) in Gahirmatha during pre- and post-monsoon

**9. Manganese (Mn):**

The results we get from below manganese bar graph are described here. In G1 site the concentration of both low and high tides are increasing from pre-monsoon season to post-monsoon. In G2 site the low tide in pre-monsoon is highly decreasing toward post-monsoon season, but high tide concentration is similar to post-monsoon. In G3 site low tide concentration is tremendously increasing from pre-monsoon to post-monsoon season, but in case of high tide the concentration is slightly increasing toward post-monsoon. In G4 site the concentrations are approximately similar for both low tide and high tide.

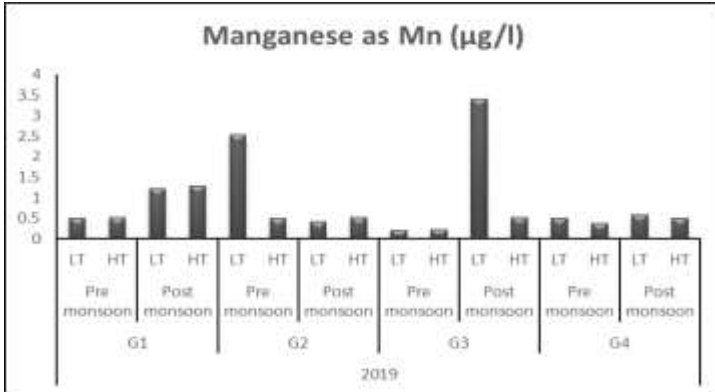


Figure 10. Bar Graph of concentration of Manganese (Mn) in Gahirmatha during pre- and post- monsoon

**10. Iron (Fe):**

The below present iron graph describes about the unevenness of concentration at different sampling sites. In G1 low tide is slightly increasing from pre-monsoon to post-monsoon, but in the high tide the concentration is slightly decreasing toward post-monsoon. In G2 site both the low tide and high tide concentrations are decreasing in post-monsoon season with respect to pre-monsoon. In G3 site the low tide is slightly decreasing, but high tide concentration is increasing from pre-monsoon to post-monsoon. In G4 site the low tide concentration is extremely increasing from pre-monsoon to post-monsoon, but high tide concentration is slightly decreasing in post-monsoon.

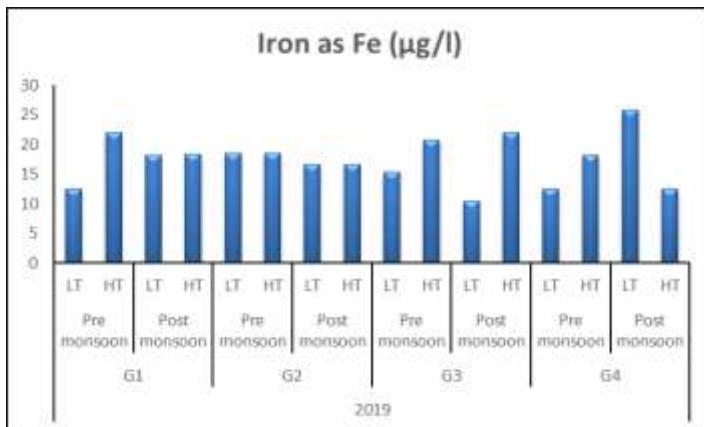


Figure 11. Bar Graph of concentration of Iron (Fe) in Gahirmatha during pre- and post- monsoon

**11. Cobalt (Co):**

The below graph describes the concentration of cobalt in 4 different sites. In G1 site the concentration of both low tide and high tide is similar in pre-monsoon as post-monsoon season. In G2 and G3 sites the concentration of low tide and high tide are decreasing from pre-monsoon to post-monsoon. In G4 site low tide concentration is increasing from pre-monsoon to post-monsoon, but high tide is decreasing from pre-monsoon to post-monsoon.

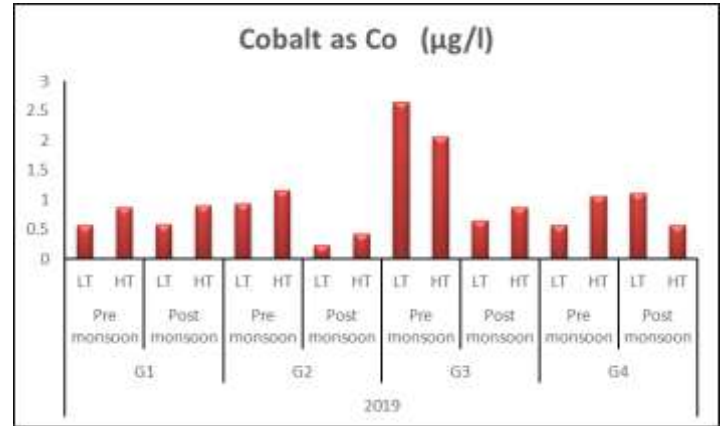


Figure 12. Bar Graph of concentration of Cobalt (Co) in Gahirmatha during pre- and post- monsoon

**12. Nickel (Ni):**

Nickel concentration of all the sites are given in the below graph. In G1 site both the concentration of low tide and high tide are decreasing from pre-monsoon to post-monsoon. In G2 site concentration of low tide is decreasing from pre-monsoon to post-monsoon, but the high tide concentration is increasing toward post-monsoon. In G3 site the low tide concentration is decreasing from pre-monsoon to post-monsoon and the high tide concentration is increasing toward post-monsoon season. In G4 site low tide concentration is increasing from pre-monsoon to post-monsoon, but the high tide is similar in both pre- and post-monsoon season.

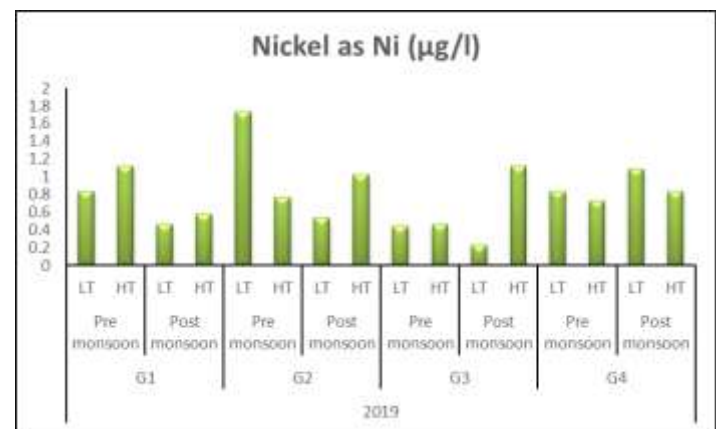


Figure 13. Bar Graph of concentration of Nickel (Ni) in Gahirmatha during pre- and post- monsoon

**13. Copper (Cu):**

The copper concentration is showing in below graph. In G1 site both low tide and high tide concentration are similar in pre-monsoon as post-monsoon. In G2 site both low tide and high tide concentrations are slightly decreasing from pre-monsoon to post-monsoon. In G3 site both low tide and high tide concentration are increasing highly from pre-monsoon to post-monsoon. In G4 site low tide concentration is increasing from pre-monsoon to post-monsoon and the high tide concentration is slightly decreasing.

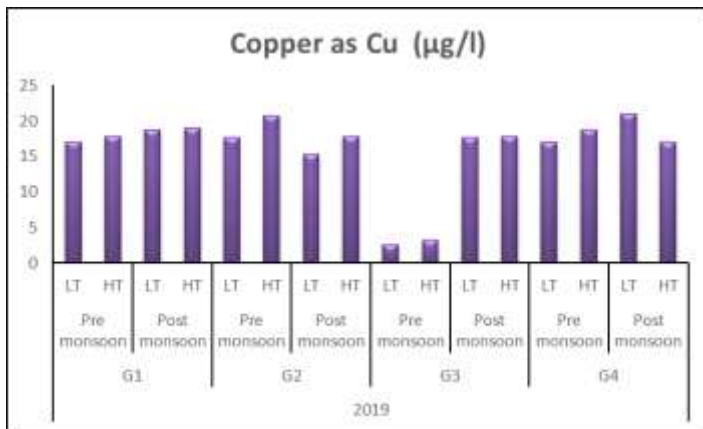


Figure 14. Bar Graph of concentration of Copper (Cu) in Gairimatha during pre- and post- monsoon

**3.2.2 Pie chart Analysis**

A pie chart is a round outline or chart that shows the relative involvement that various classes add to a general aggregate. A wedge of the circle speaks to each category's contribution, with the end goal that the diagram takes after a pie that has been cut into various estimated cuts. Pie chart can be used as an import tool for analysis of various types of data. In this study pie charts used to show the concentration percentages (%) of all thirteen heavy metals at each sampling point during pre-monsoon and post-monsoon seasons in both tides (Low tide & High tide) respectively.

Following two figures (Figure-15 & Figure-16) shows that the percentage of concentration of Zinc (25.1% to 45.5%),

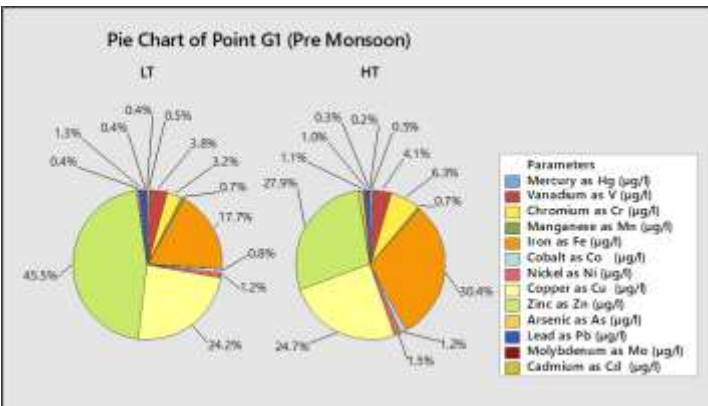


Figure 15. Pie Chart of sampling point G1 in low and high tide during pre-monsoon

During post-monsoon the concentration percentage of manganese (1.9%) is equal in both the tides. At high tide the concentration percentage of chromium (8.4%) which is nearly double of the concentration at low tide (4.6%). The concentration percentage of Vanadium are nearly equal; i.e. 2.0% in low tide and 2.1% in high tide. The concentration percentages of other heavy metals like mercury, Cobalt, Nickel, Arsenic, Lead etc. are minimum in both pre-monsoon and post-monsoon seasons. The relative average seasonal concentrations of the heavy metals in Point G1 may be arranged in the order: Zn>Cu>Fe>Cr>V>Mn>Ni> Co> Pb>As>Hg>Mo>Cd.

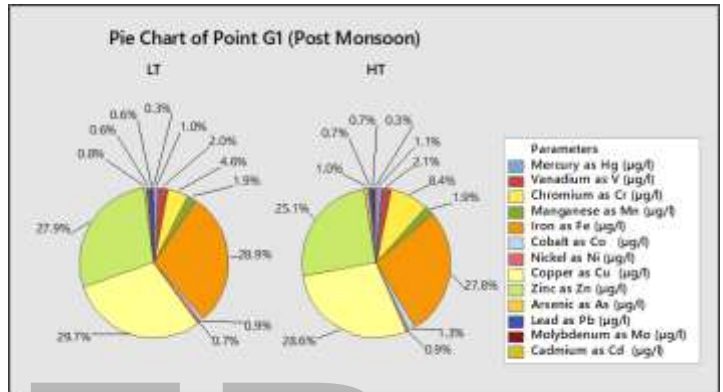


Figure 16. Pie Chart of sampling point G1 in low and high tide during post-monsoon

The figures (Figure-17 & Figure-18) shows that the percentage of concentration of Zinc (35.8% to 47.2%), Copper (21.7% to 25.7%) and Iron (23.0% to 25.8%) are higher than other heavy metals in both the seasons. At sampling point G2 during pre-monsoon in low tide the concentration percentage of Nickel (2.4%) is nearly three times of high tide concentrations percentages (0.9%). The concentration percentages of Vanadium, Cobalt and Copper are nearly equal in both the tides; i.e., 3.6%,1.3% and 24.7% in low tide and 3.8%,1.4% and 25.7% in high tide respectively. The concentration percentage of Manganese at low tide (3.5%) is nearly 6 times of the concentration % of high tide (0.6%) and the concentration percentage of Chromium in high tide (2.6%) is nearly 5 times of the concentration percentage in low tide (0.5%).

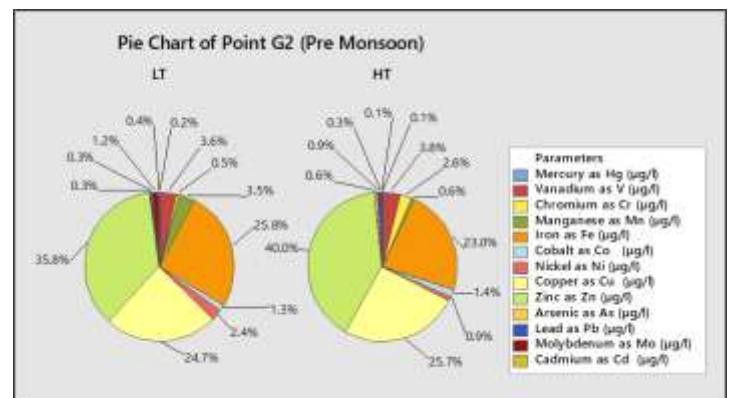


Figure 17. Pie Chart of sampling point G2 in low and high tide during pre-monsoon



In post-monsoon the concentration percentage of Manganese (0.6% in low tide & 0.7% in high tide), Vanadium (1.2% in low tide & 1.5% in high tide) and Iron (23.6% in low tide & 23.8% in high tide) are nearly equal in both the tides. The concentration percentage of Nickel (1.5%) and Chromium (6.4%) in high tide which are nearly two times of the concentration of low tide (0.8% & 2.8% respectively). The concentration percentages of other heavy metals like mercury, Molybdenum, Cadmium, Arsenic, Lead etc. are minimum in both pre-monsoon and post-monsoon seasons. The relative average seasonal concentrations of the heavy metals in Point G2 may be arranged in the order: Zn>Cu>Fe>Cr> V > Ni> Mn> Co> Mo> As>Pb>Hg>Cd.

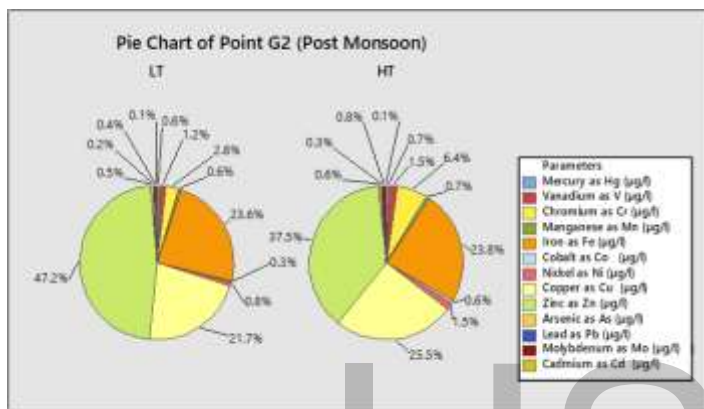


Figure 18. Pie Chart of sampling point G2 in low and high tide during post-monsoon

Following two figures (Figure-19 & Figure-20) shows that the percentage of concentration of Zinc (15.5% to 31.8%), and Iron (21.3% to 47.9%) are higher than other heavy metals in both the seasons.

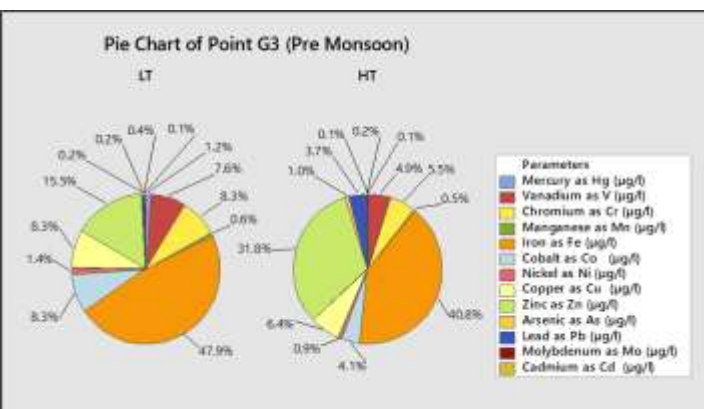


Figure 19. Pie Chart of sampling point G3 in low and high tide during pre-monsoon

During pre-monsoon in low tide at sampling point G3 the concentrations of Chromium (8.3%), Copper (8.3%), Nickel (1.4%), Vanadium (7.6%) and Iron (47.9%) are higher than at high tide concentrations percentages of Chromium (5.5%), Copper (6.4%), Nickel (0.9%), Vanadium (4.9%) and Iron (40.8%). The concentration percentage of Arsenic in high tide (1.0%) is nearly five times of the concentration percentage in

low tide (0.2%). The concentration percentages of Cobalt (8.3%) in low tide is nearly two times of the high tide concentration (4.1%). The concentration percentage of zinc in high tide (31.8%) is nearly double of the concentration percentage in low tide (15.5%) but, in case of Lead the concentration in high tide (3.7%) is nearly 18 times of the concentration percentage in low tide (0.2%); i.e., the concentration of Lead is drastically increase during tide change.

During post-monsoon the concentration percentage of Cobalt (1.3% in low tide and 1.2% in high tide) is nearly equal in both the tides. At high tide the concentration percentage of chromium (6.4%) which is nearly 9 times of the concentration in low tide (0.7%). The concentration percentage of Nickel (1.6%) in high tide which is 3 times of the concentration in low tide (0.5%). The concentration percentage of copper (35.9%) in low tide is greater than the percentage of concentration(24.7%) in high tide. The relative average seasonal concentrations of the heavy metals in Point G3 may be arranged in the order: Fe>Zn>Cu> Cr> V > Co> Mn> Pb>Ni> As>Hg>Mo>Cd.

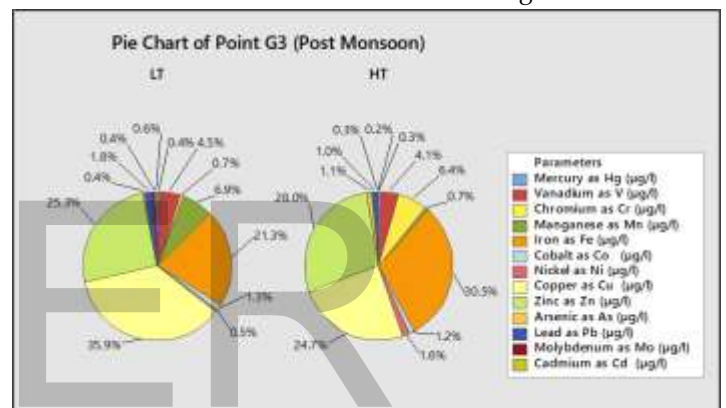


Figure 20. Pie Chart of sampling point G3 in low and high tide during post-monsoon

In the following two figures (Figure-21 & Figure-22) the percentage of concentration of Zinc (13.5% to 45.6%), Copper (24.2% to 34.8%) and Iron (17.7% to 33.7%) are higher than other heavy metals in both the seasons.

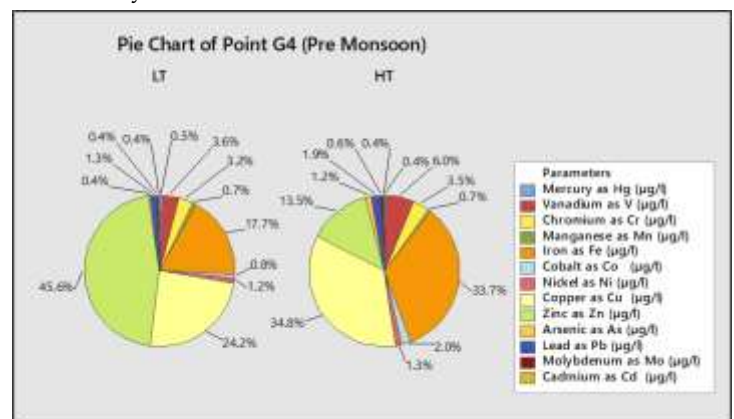


Figure 21. Pie Chart of sampling point G4 in low and high tide during pre-monsoon

During pre-monsoon at sampling point G4 in low tide the

concentration percentage of Lead (0.4%), Arsenic (0.4%), Cobalt (0.8%) and Vanadium (3.6%); which are lesser than the concentration percentage of Lead (1.9%), Arsenic (1.2%), Cobalt (2.0%) and Vanadium (6.0%) in high tide. The concentration percentage of Nickel is nearly equal; i.e. 1.2% in low tide and 1.3% in high tide.

In post-monsoon the concentration percentage of Mercury is very less in low tide (0.2%) and high tide(0.1%).At low tide the percentage of concentration of Arsenic(1.6%);which is 4 times of the concentration of concentration of Arsenic in low tide(0.4%).The percentage of concentration of manganese is nearly equal 0.8% in low tide and 0.7% in high tide. The relative average seasonal concentrations of the heavy metals in Point G4 may be arranged in the order: Zn>Cu>Fe>Cr> V > Ni> Co> Pb> As>Mn> Mo> Cd >Hg.

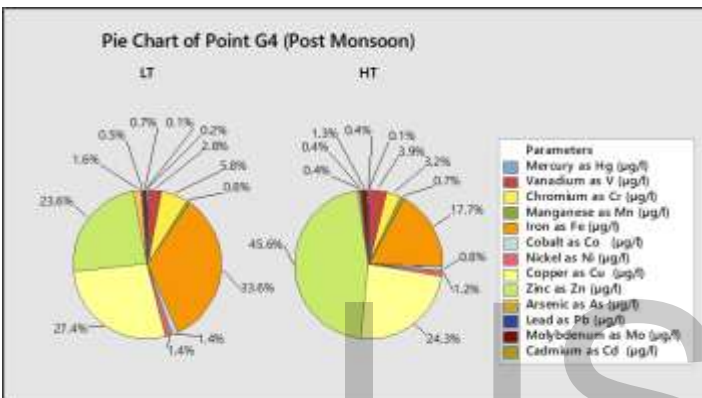


Figure 22. Pie Chart of sampling point G4 in low and high tide during post-monsoon

#### 4 CONCLUSION

From this study it was observed that the some of heavy metals are found to be higher in the surface water of Gahirmatha estuary region. During pre-monsoon season the relative average concentrations of the heavy metals in low tide of Bay of Bengal may be arranged in the order: Zn> Fe> Cu> V> Cr> Co> Ni>Mn>Pb> Mo> Hg> As> Cd and in high tide the relative average concentrations of the heavy metals may be arranged in the order: Fe> Zn> Cu> V> Cr> Co> Pb> Ni> As> Mn> Mo> Hg> Cd. Similarly, during post-monsoon season the relative average concentrations of the heavy metals in low tide of sea may be arranged in the order: Zn> Cu> Fe> Cr> V> Ni> Mn>Co> As> Mo> Pb> Hg> Cd; while in case of high tide the relative average concentrations may be arrange in the order: Zn> Cu> Fe> Cr> V> Co> As> Ni> Pb> Mn> Hg> Mo> Cd. The overall relative average concentrations of heavy metals may be arranged in the order: Zn> Fe> Cu> Cr> V> Co> Mn>Ni> Pb> As>Mo> Hg> Cd. The variation of relative concentrations of some of the heavy metals may be affected basically by two reasons; the first one is the riverine influence through both Dhamra and Brahmani river. This could be the main reason behind the variation of concentration of metals. The second reason behind it may be the anthropogenic liberation through local activities; that are may responsible for the change of water quality.

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