

# Physicochemical and Heavy Metal Contamination in Surface Water, Sediment, and Benthic Organisms of Bile, Rivers State

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## ABSTRACT

This study investigates the impact of crude oil contamination on the physicochemical properties and heavy metal concentrations in surface water, sediment, and benthic organisms (*Callinectesamnicola*) at Bille Creek, Rivers State, Nigeria. Samples were collected bi-monthly from March 2023 to January 2024 from three stations in the creek. The study assessed the presence of Total Petroleum Hydrocarbons (TPH), Polycyclic Aromatic Hydrocarbons (PAH), heavy metals (Cobalt, Zinc, Nickel, Cadmium, Iron, Chromium), and physicochemical parameters including pH, turbidity, dissolved oxygen (DO), total dissolved solids (TDS), and chloride concentrations. The results revealed fluctuating TPH and PAH concentrations, with elevated levels in certain months, indicating crude oil spill events. Heavy metals such as Cobalt, Zinc, Nickel, and Cadmium showed significant variations across stations, with higher concentrations at Station 3, suggesting localized pollution. TPH and PAH levels in benthic organisms showed a similar trend, indicating bioaccumulation of contaminants. Elevated heavy metal concentrations in the benthic community pose risks to aquatic life and human health. The study highlights the need for continuous monitoring and remediation efforts to mitigate the long-term impacts of crude oil contamination in the ecosystem.

**Keywords:** Crude Oil, Heavy Metal, Pollution, Benthic Organisms, Ecosystem

## I. INTRODUCTION

Water is a key part of human existence; it plays an important role in sustaining life. Its major functions are the manufacturing and distribution of food, the functioning of companies, and the

transportation of goods and services. Water plays a crucial role in promoting human development; however, its management is often inadequate[1]. Anthropogenic and natural sources are contributing to a steady increase in the level of water deterioration. The examination of different water contamination sources, the matching remediation techniques used, and the economic consequences coming from human activities are serious global issues.

The combined effects of human activities and natural events present a considerable threat to the welfare of plant and animal species [2][3]. The physicochemical properties of water have a major influence on the ecological processes of the ecosystem, which can affect the overall well-being of the water system [4]. Human interference can alter the chemical composition of the aquatic ecosystem, hence possibly causing alterations in migratory patterns, habitat displacement, and overall feeding behaviours[5]. Contaminants that come from effluents from homes, agricultural waste, and industrial discharge are discharged daily into the aquatic environment, and this gives rise to the overall increase in the total contaminant burden of the environment.

Additionally, the degree and nature of the contaminants are dependent on the characteristics of the source and the environment receiving the contaminant [6][7]. The major ways through which water is polluted are through the discharge of effluents or wastewater, heavy metal pollution from crude oil, and pollution. To effectively solve the issues of pollution in the environment, the origin and nature of the pollutant must be known. This will allow generality in the application mode and the type of treatment method to be used [8].

The advancement of crude oil transportation and exploration has intensified in recent years, resulting in a rise in oil spill occurrences. Heavy metal contamination is one of the main environmental contaminants in the world and has increased as a result [9]. Among the most frequently found pollutants in effluent discharge are heavy metals, which are toxic and can accumulate in living organisms. Heavy metals do not decompose readily and undergo biological reactions slowly. They tend to produce negative results in the environment and are part of the food chain of living organisms. When humans consume these organisms eventually, they become poisonous and, in the long run, cause different types of disease[10].

Heavy metals are connected to different health issues such as dwarfism, developmental conditions, cancer, organ failure, nervous system damage, and, in some cases, death [11]. Exposure to some heavy metals, such as mercury and lead, even at low levels, can cause damage and breakdown of the human immune system.

## II. MATERIALS AND METHODS

### 2.1 Sampling methodology

Samples were collected from three (3) different locations from Bille Creek, Bille, in Degema L.G.A. The samples were collected bi-monthly for a period of 11 months from March 2023 to January 2024, and the samples obtained were analyzed in triplicate.

### 2.2 Surface Water Samples

Standard precautions were adopted according to [12] during surface water collection, and the sterile bottle container used was submerged into the water while being closed, and then immediately opened to collect the water samples then capped back while still being in the subsurface water.

### 2.3 Sediment Samples

The sediment samples were collected using eckman grab sampler after collecting the surface water samples, and precautions were taken according to [13]. The sediment sample was collected facing upstream and scooped in the direction of the upstream while carefully removing the excess water from the scoop.

### 2.4 Biota Samples

The crab samples were carefully collected from fisherfolk and stored in an ice box before being taken to the lab for analysis.

### 2.4 Physicochemical parameters analysis

All physicochemical properties of collected samples from Bille Creek were determined based on the procedure explained by the American Public Health Association [14]. All parameters, except otherwise stated, were measured in mg/L, and data obtained were compared with World Health Organisation (WHO) standards for environmental acceptability.

### 2.5 Determination of Heavy Metals

An atomic absorption spectrophotometer (AAS) was used to estimate Co, Zn, Ni, Ca, Cr, and Fe concentrations. As specified by the manufacturers, the instrument was set up and operated.

### 2.6. Sample Preparation

Sediment samples were air dried; fish samples were granulated in a blender; and water was digested with 20 ml conc. H<sub>2</sub>SO<sub>4</sub>.

## III. RESULTS AND ANALYSIS

The results from the different analyses of the Sediment Samples, Surface water samples, and Benthic Organism samples are divided into three main sections, namely: Analysis of Variance results.

### 3.1. Concentration of Physicochemical and heavy metal parameters of Surface water, Sediment, and Callinectes amnicola

The results from the analysis of the surface water, sediment, and biota samples are presented graphically from Fig. 4.1 to Fig

In the results for Physicochemical Parameters for Surface Water, Total Petroleum Hydrocarbons (TPH): In the Surface Water samples, Station 1 recorded very low to undetectable levels of TPH throughout the study, except for May 2023 (1.53 mg/kg). Station 2 displayed extremely high concentrations in July and September 2023 (6128.00 mg/L and 5858.00 mg/L, respectively). Similarly, Station 3 reached a peak of 8146.00 mg/L in July 2023, declining afterward. Total Petroleum Hydrocarbons (TPH) in the Sediment sample showed that Station 1 recorded a peak in TPH concentration in May 2023 (2466.42 mg/kg), which subsequently dropped to a consistent range between 12.18 and 20.86 mg/kg across other months. Station 2 had the highest TPH concentrations in March 2023 (3057.94 mg/kg) and May 2023 (2654.74 mg/kg), followed by a significant decline in later months. Station 3 showed moderately high values, peaking in March

2023 at 2066.00 mg/kg, followed by a decline over the year.

In Benthic Samples, Station 1 had the lowest TPH levels across all stations, ranging from 0.01 to 12.92 mg/kg. In contrast, Station 2 and Station 3 showed elevated levels in March 2023 (15.35 mg/kg and 19.32 mg/kg, respectively) with a decline in subsequent months. Indicating potential contamination events during these periods. In *Callinectes amnicola*, the recorded Total

Petroleum Hydrocarbons (TPH) levels varied significantly across the stations and months. Station 1 had a peak TPH concentration in March 2023 (12.92 mg/kg) and then drastically decreased to minimal values (0.01-0.02 mg/kg) in subsequent months. Stations 2 and 3 also showed higher TPH levels in March 2023 (15.35 mg/kg and 19.32 mg/kg, respectively) with secondary peaks in July and September 2023, indicating a potential contamination event during this period.

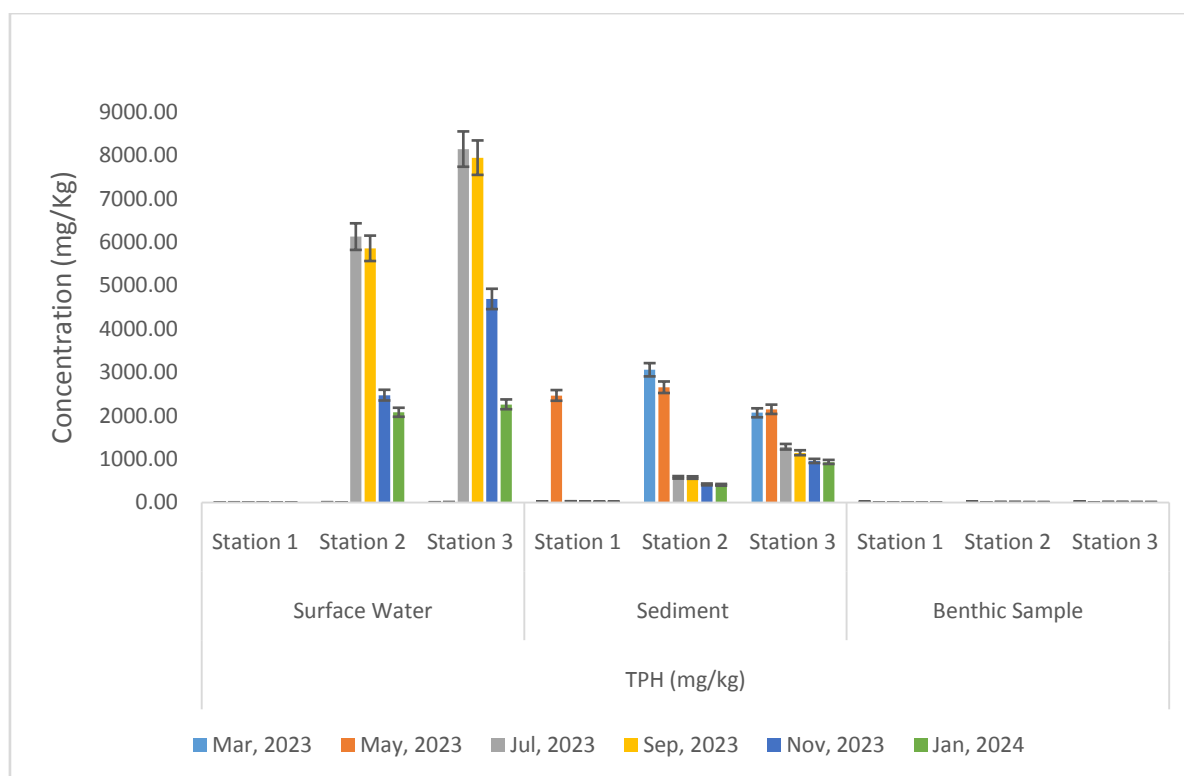


Fig 4.1: Mean concentration of Total Petroleum Hydrocarbon (TPH) in surface water, sediment and *C. amnicola* across the stations

In July 2023, surface water showed minor Polycyclic Aromatic Hydrocarbon (PAH) concentrations at Station 2 (0.05 mg/L) and Station 3 (0.04 mg/L), with no detection at Station 1. Sediment samples revealed consistent PAH levels at Station 1 (2.72-4.15 mg/kg), while Stations 2 and 3 experienced pronounced PAH peaks in March 2023 (39.46 mg/kg and 30.27 mg/kg, respectively),

with Station 3 showing subsequent fluctuations. For *Callinectes amnicola* in March 2023, PAH levels were minimal, with Station 3 recording the highest concentration (0.67 mg/kg), followed by Station 2 (0.59 mg/kg) and Station 1 (0.52 mg/kg). No PAH data were recorded for other months in this organism.

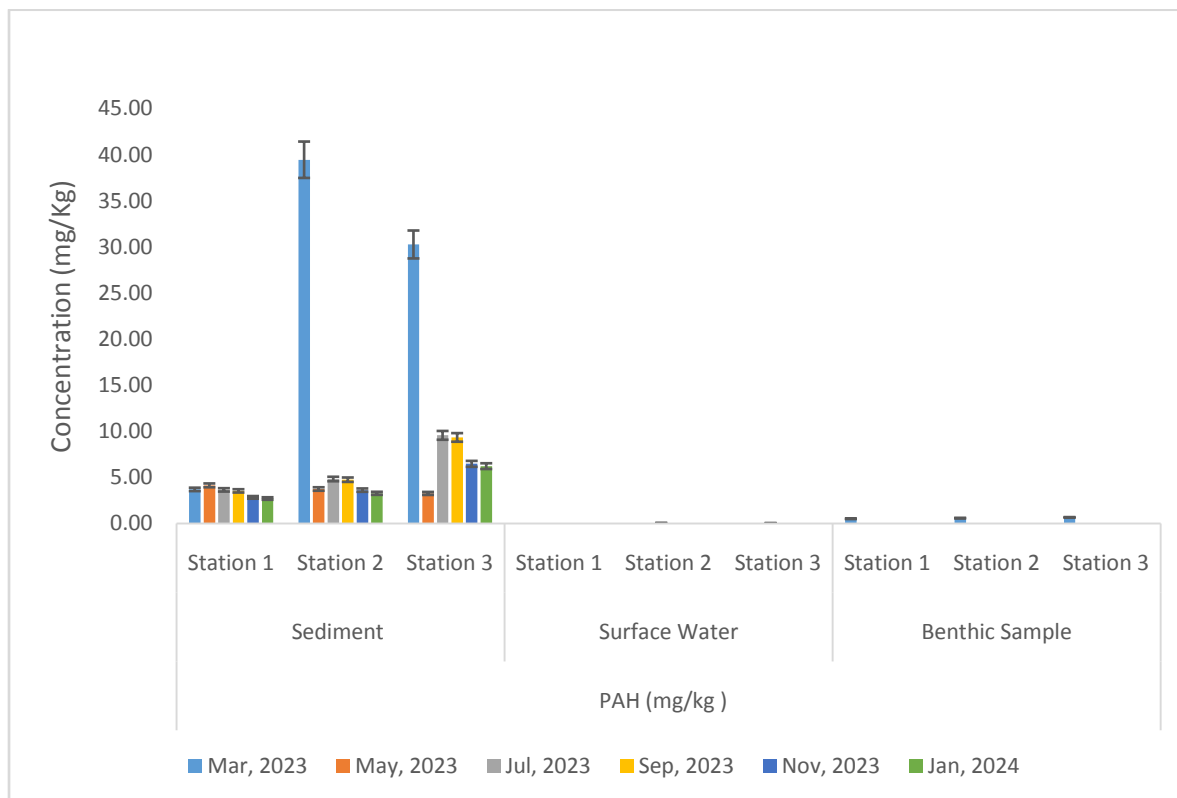


Fig 4.2: Mean concentration of Polycyclic Aromatic Hydrocarbon (PAH) in surface water, sediment and C. amnicola across the station

The turbidity varied across stations and months, with the highest recorded at Station 3 in September 2023 (22.22 FNU)

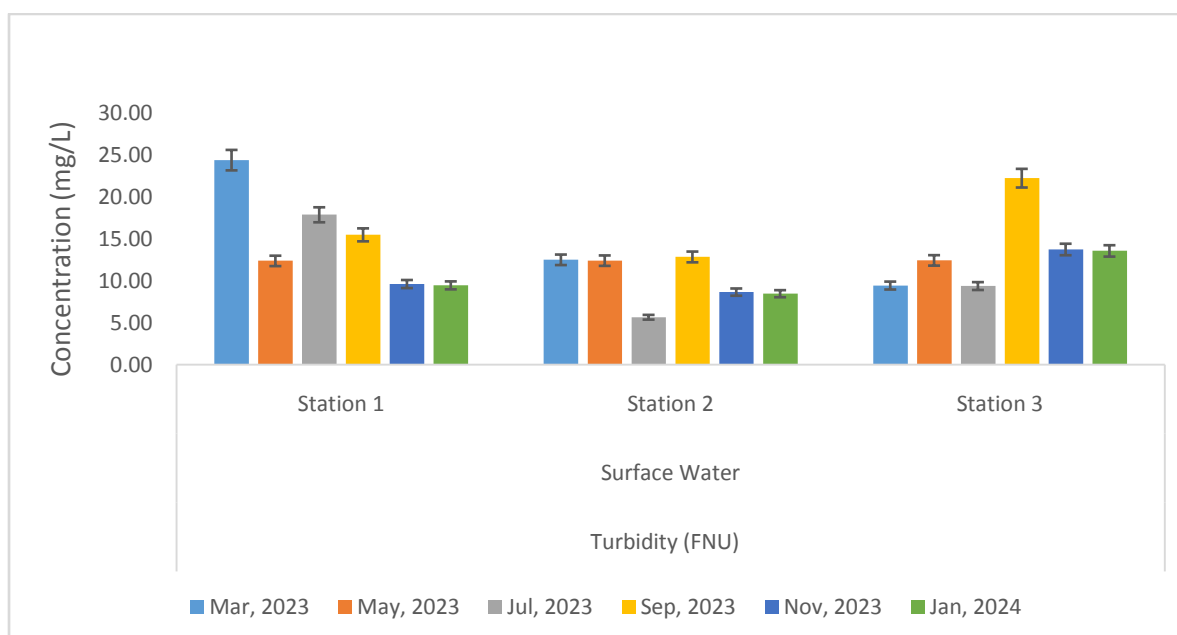


Fig 4.3: Mean concentration of Turbidity in surface water across the stations

TDS values ranged from 7222 mg/L (Station 2, July 2023) to 11431 mg/L (Station 1, March 2023), In the results for Total Dissolved Solids (TDS) and Chloride (Cl<sup>-</sup>), Surface Water

TDS concentrations were highest at Station 1 in March 2023 (11431 mg/L), decreasing gradually

over the following months.

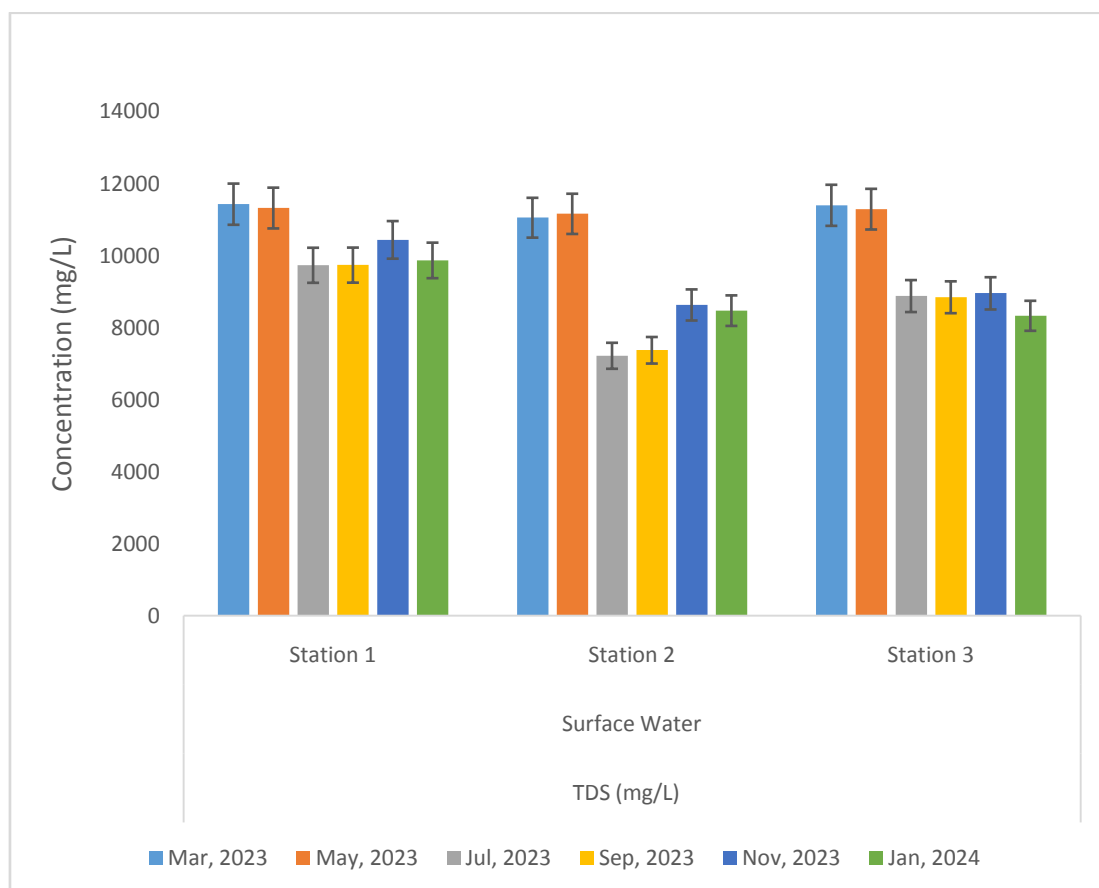


Fig 4.4: Mean concentration of Total Dissolved Solute in surface water across the stations  
Phosphate levels were slightly higher, with Station 1 recording a maximum of 2.83 mg/L in March 2023.

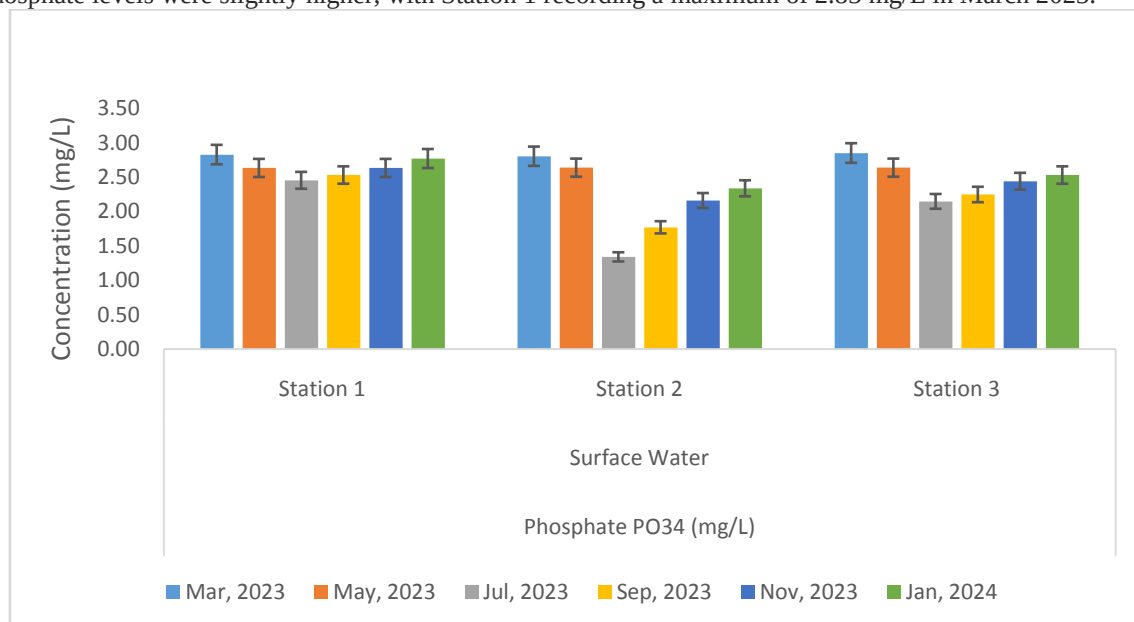


Fig 4.8: Mean concentration of Phosphate in surface water across the stations

In Total Alkalinity and Total Hardness: Alkalinity and hardness were highest at Station 3 in January 2024 (43.67 mg/L for alkalinity and 64.67 mg/L for hardness).

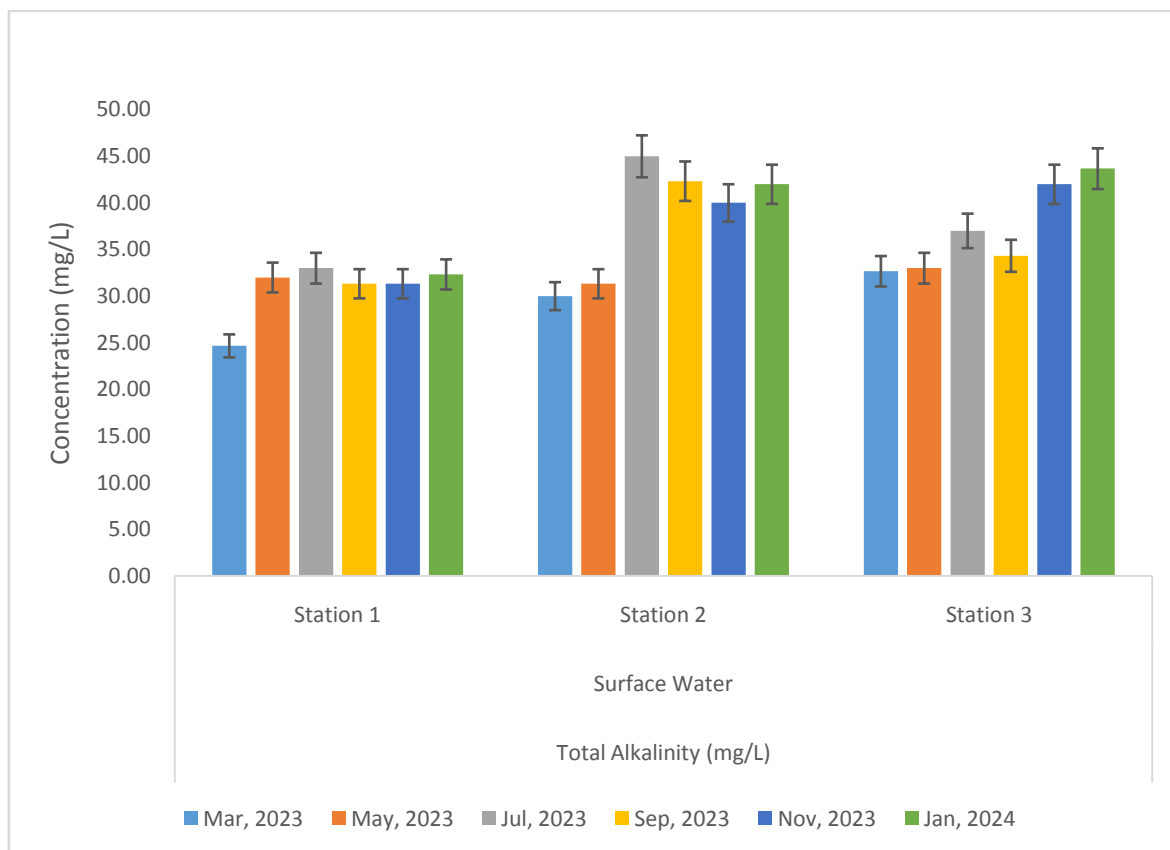


Fig 4.9: Mean concentration of Alkalinity in surface water across the stations

DO concentrations remained fairly consistent, with slight variations, ranging between 4.70 mg/L to 5.90 mg/L.

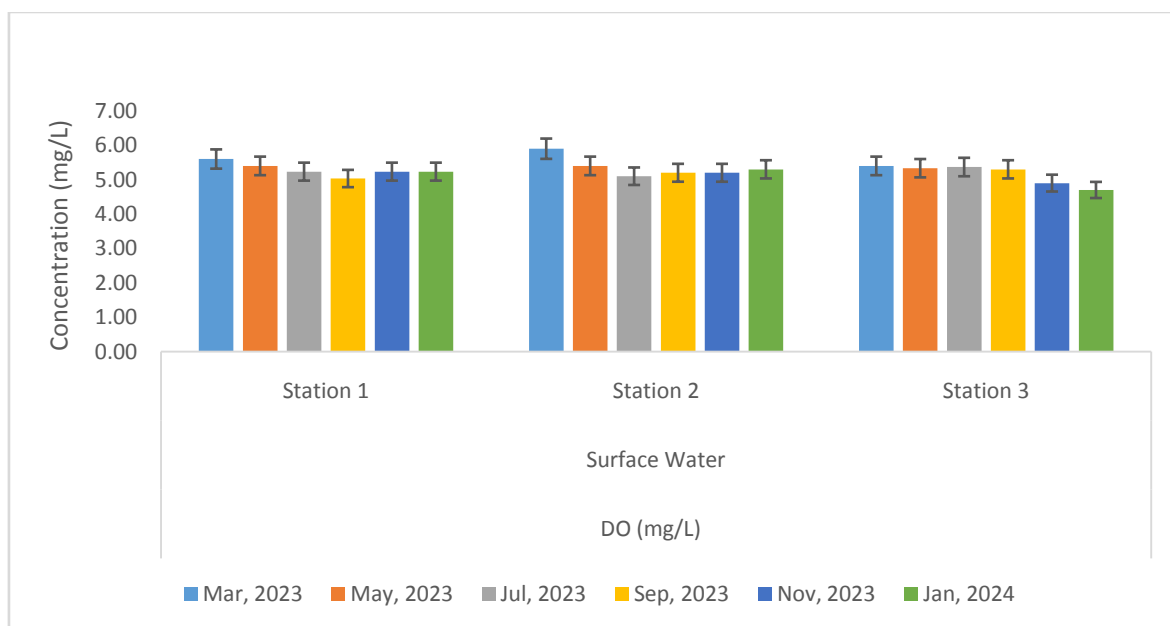


Fig 4.11: Mean concentration of Dissolved Oxygen in surface water across the stations

The pH in surface water ranged from slightly acidic to neutral, with specific values recorded between 6.42 at Station 3 in July 2023 and 7.54 at Station 1 in September 2023. Station 1 exhibited consistently neutral to slightly alkaline

pH (7.32-7.54), while Stations 2 and 3 showed slightly lower levels. In contrast, sediment pH was consistently slightly acidic across all stations, with values ranging from 5.50 to 5.97, and the lowest recorded pH of 4.57 at Station 2 in July 2023.

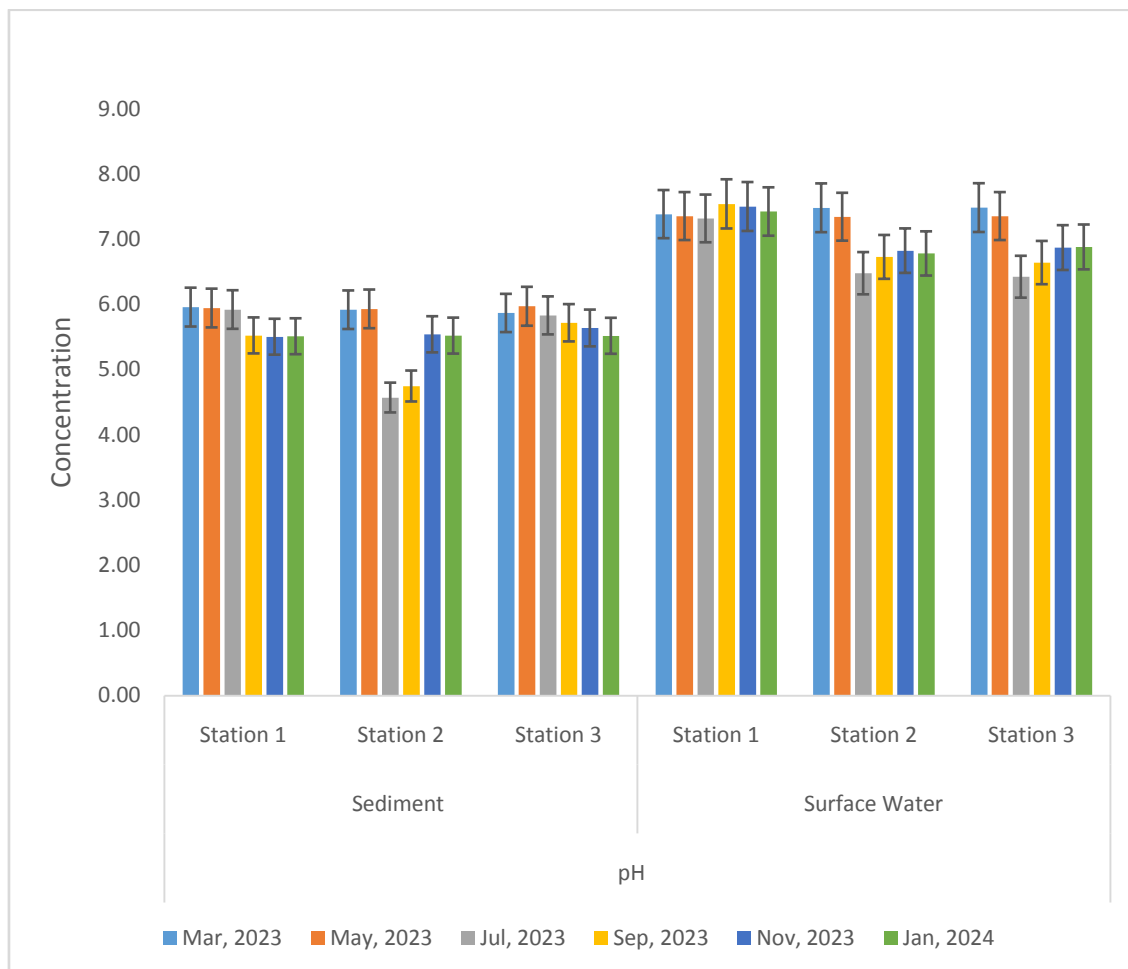


Fig 4.12: Mean concentration of pH in sediment and surface water across the stations

Surface water pH ranged from slightly acidic to slightly alkaline (6.42-7.54), whereas sediment pH was consistently slightly acidic (5.50-5.97). In surface water heavy metal concentrations, Cobalt (Co) showed the highest level at Station 1 in March 2023 (0.49 mg/L) with a decreasing trend, Zinc was generally low with a peak of 0.33 mg/L at Station 3 in September 2023, and Nickel

concentrations were consistent across stations (0.20-0.29 mg/L). Cadmium (Cd) data was minimal with low concentrations, Iron fluctuated with a peak at Station 2 in November 2023 (0.49 mg/L), and Chromium (Cr) was detected sporadically, with the highest concentration at Station 1 in May 2023 (0.27 mg/L).

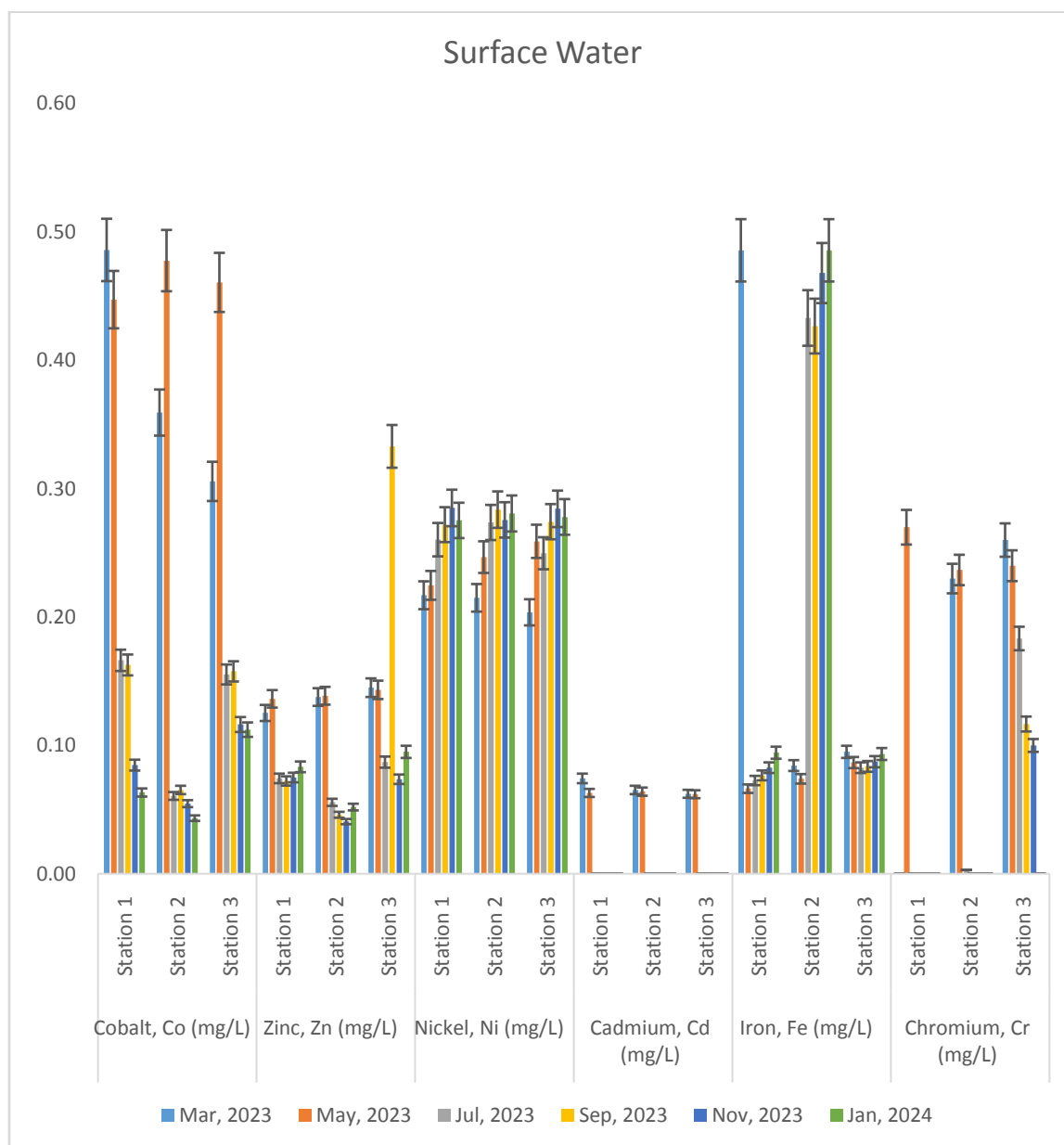


Fig 4.13: Mean concentration of heavy metals (Co, Zn, Ni, Cd, Fe, Cr) in surface water across the stations.

Heavy Metals analysis in Sediment indicated stable Cobalt (Co) concentrations (4.69-11.68 mg/kg) across all stations. Zinc (Zn) fluctuated, with Station 2 showing a significant decrease from March 2023 (49.86 mg/kg) to January 2024 (22.41 mg/kg). Nickel (Ni) and

Cadmium (Cd) levels were low with minor variations. Iron (Fe) concentrations notably decreased between March 2023 and January 2024, especially at Station 2 (3925.54 to 2054.78 mg/kg). Chromium (Cr) remained relatively low, with a peak of 12.75 mg/kg at Station 2 in May 2023.



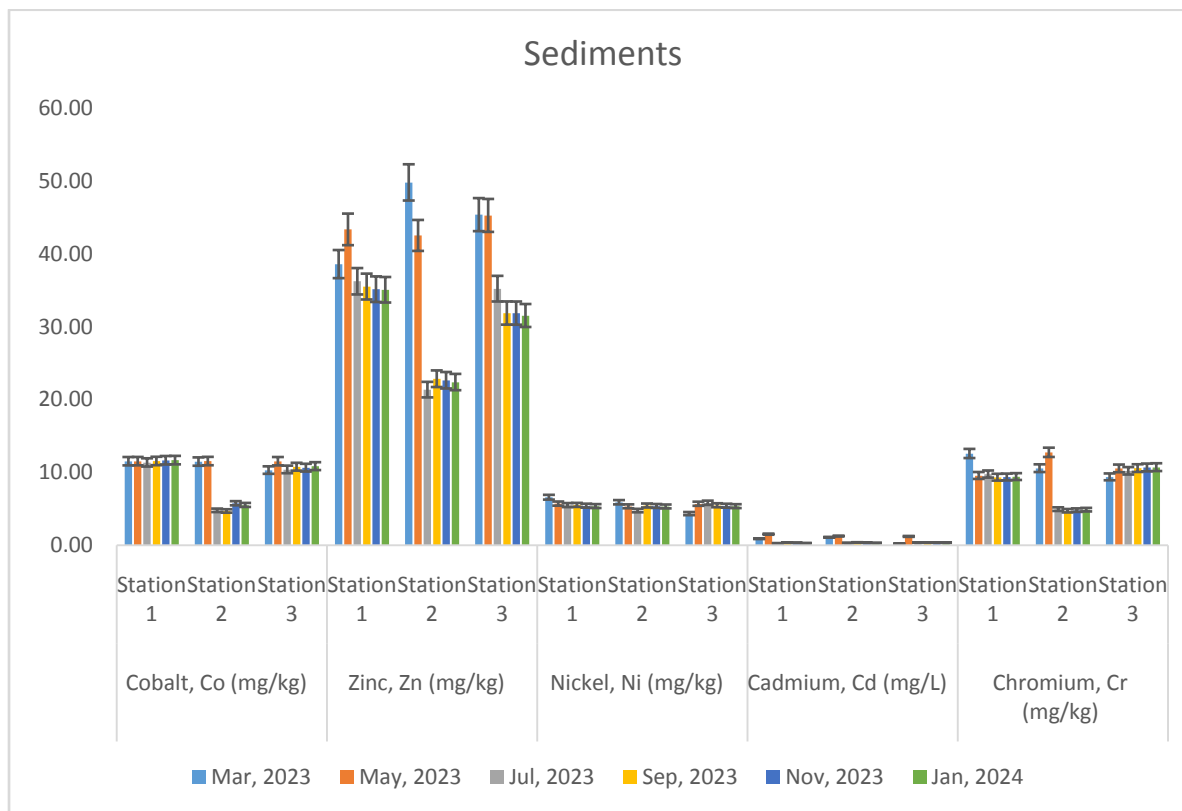


Fig 4.17: Mean concentration for heavy metals (Co, Zn, Ni, Ca, Cr) in sediment across the stations (part 1)

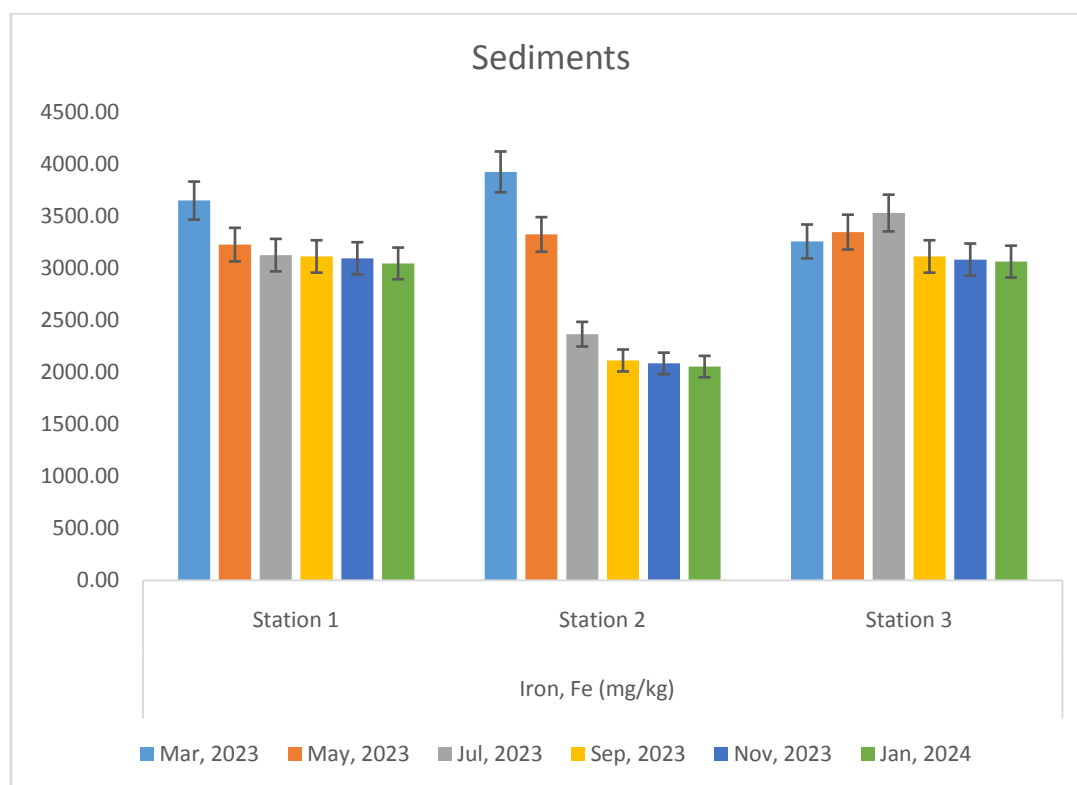


Fig 4.18: Mean concentration for heavy metals (Fe) in sediment across the stations (part 2)

The heavy metal analysis revealed varying concentrations across stations and months. Cobalt (Co) ranged from 4.20 to 11.28 mg/kg, with Station 3 showing the highest level in July 2023. Zinc (Zn) levels fluctuated, peaking at Station 1 in July 2023 (63.68 mg/kg), with elevated levels observed from July to January 2024 across all stations. Nickel (Ni) showed significant peaks in July 2023, notably at Station 3 (13.45 mg/kg), followed by a decline. Cadmium (Cd) concentrations were consistently higher at Station 3, peaking in July 2023 (3.45

mg/kg), with zero readings recorded at all stations in May 2023. Manganese (Mn) was detected only at Station 2 in March 2023 (0.01 mg/kg). Iron (Fe) concentrations were generally high, with peaks at Station 1 in March 2023 (646.10 mg/kg) and Station 3 in September 2023 (479.50 mg/kg), followed by a decreasing trend. Chromium (Cr) levels remained stable, ranging from 4.45 to 5.38 mg/kg, with the highest reading at Station 2 in March 2023 (5.38 mg/kg).

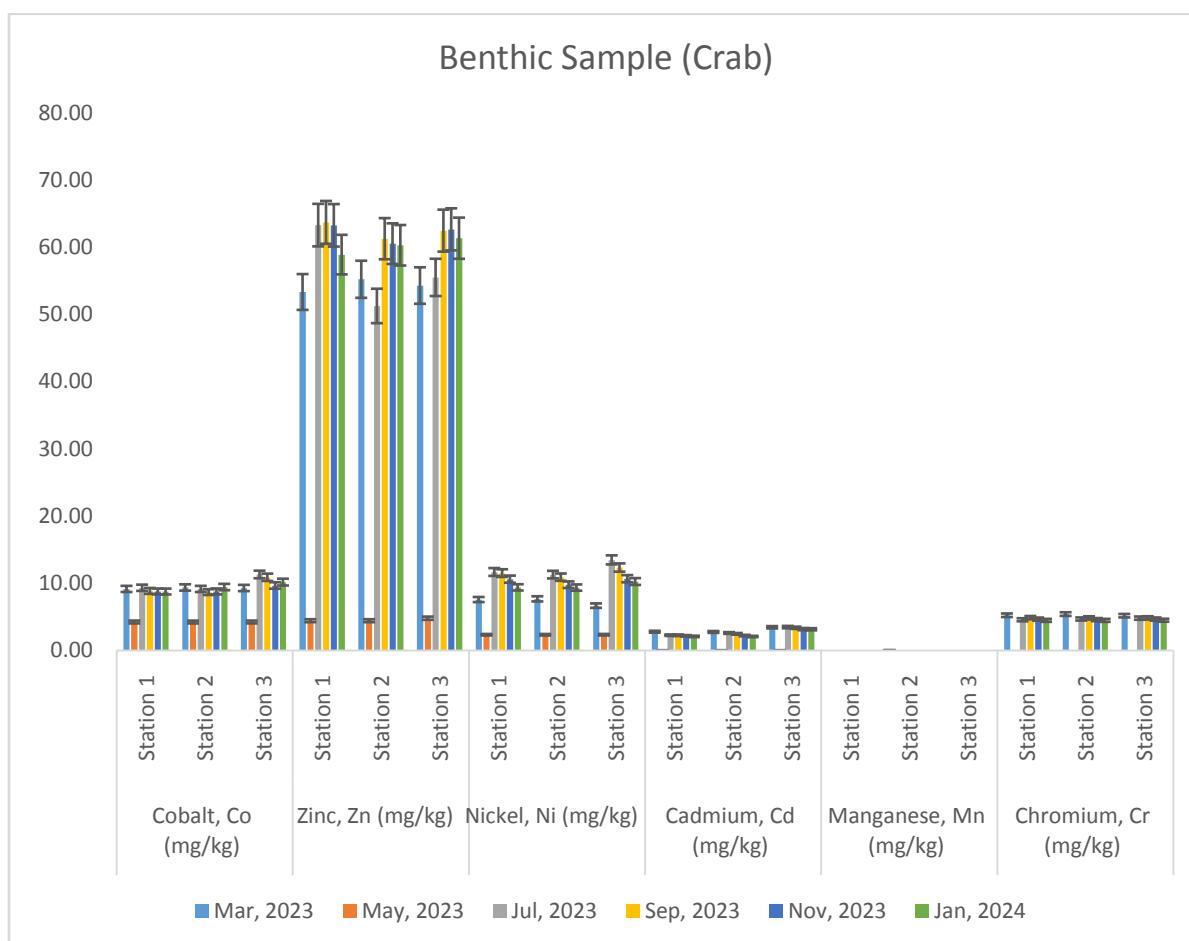


Fig 4.19: Show the mean concentration for heavy metals of *C. amnicola* in sediment across the stations (part 2).

## IV. DISCUSSION

### 4.1 Effect of Oil Spill on Physicochemical Parameters and Heavy Metal Parameters of Surface Water Samples

Contaminated drinking water is a primary route for human exposure to crude oil contaminants. Oil spills, leaks, or effluent discharge into freshwater sources introduce toxic substances like hydrocarbons and heavy metals, which pose health risks when ingested. Chemicals in crude oil, such as polycyclic aromatic

hydrocarbons (PAHs) and heavy metals, have toxicological effects on human health, causing respiratory issues, neurological disorders, and an increased cancer risk [15][16]. This highlights the need for thorough assessments of water bodies, as seen in Bille Creek after an oil spill.

In Table 4.3, Total Petroleum Hydrocarbon (TPH) results show interesting patterns. At Station 1, TPH was below detectable limits except for May 2023 ( $1.531 \pm 0.002$  mg/L). At Station 2, May 2023 recorded below detectable

limits, but other months showed significant variations ( $P < 0.05$ ), with the highest in July 2023 ( $6128.00 \pm 3.055$  mg/L). Station 3 saw a peak in TPH in July 2023 ( $8146.00 \pm 11.533$  mg/L), with a decrease by January 2024 ( $2261.00 \pm 7.506$  mg/L). High TPH levels in Stations 2 and 3 indicate severe pollution, which can harm aquatic life and water quality. The pollution's localized source is confirmed by spatial variation between stations. Continuous exposure to hydrocarbons like benzene, toluene, and xylene affects the central nervous system [17][18]. Immediate remediation is necessary for Stations 2 and 3.

The Polycyclic Aromatic Hydrocarbons (PAH) results indicate consistent levels below detection limits ( $< 0.001$  mg/L) across all stations and time points, except in July 2023 at Station 2 ( $0.052 \pm 0.001$  mg/L) and Station 3 ( $0.043 \pm 0.003$  mg/L). This suggests that the crude oil spill may contain oil low in PAH but high in other Total Petroleum Hydrocarbons (TPH). PAHs are toxic, persistent environmental pollutants that pose significant risks to aquatic life and human health [19][20].

Turbidity (FNU) results show varying trends across stations. At Station 1, turbidity decreased from  $24.37 \pm 0.252$  FNU in March 2023 to  $9.457 \pm 0.047$  FNU in January 2024, with significant differences ( $P < 0.05$ ). Station 2 showed a high of  $12.84 \pm 0.020$  FNU in September 2023 and a low of  $5.657 \pm 0.012$  FNU in July 2023. The July 2023 reading was within the WHO recommended limit of 5 FNU. Station 3 peaked at  $22.22 \pm 0.108$  FNU in September 2023. High turbidity levels, which reduce light penetration, can negatively impact aquatic ecosystems by affecting photosynthetic processes [21][22].

For Total Dissolved Solids (TDS), Station 1 showed values ranging from  $9735.00 \pm 4.00$  mg/L in July 2023 to  $11431.00 \pm 4.041$  mg/L in March 2023. Station 2 exhibited significant reductions in TDS, from  $11163.00 \pm 41.199$  mg/L in May 2023 to  $7222.00 \pm 1.528$  mg/L in July 2023, followed by increases. Station 3 had the highest TDS of  $11400.00 \pm 55.770$  mg/L in March 2023. The WHO recommended limit for TDS is  $\leq 1000$  mg/L, and these elevated TDS levels suggest significant pollution, potentially from agricultural runoff or wastewater discharge. The high TDS in the study area indicates serious pollution, necessitating a comprehensive remediation strategy.

Chloride ( $\text{Cl}^-$ ) concentrations in Station 1 decreased from  $5215.00 \pm 17.010$  mg/L in May 2023 to  $2590.00 \pm 3.055$  mg/L in January 2024, with significant differences between months. In

Station 2, chloride levels dropped from  $5257.00 \pm 2.517$  mg/L in May 2023 to  $1683.00 \pm 5.00$  mg/L in January 2024. Station 3 recorded the highest chloride level in May 2023 ( $5435.00 \pm 2.517$  mg/L) and the lowest in January 2024 ( $2433.00 \pm 4.619$  mg/L). The recorded levels significantly exceed the WHO recommended limit of  $\leq 250$  mg/L, indicating high pollution from industrial or urban runoff. Elevated chloride concentrations can harm aquatic life, particularly fish [13].

For Nitrate ( $\text{NO}_3^-$ ) concentrations, Station 1 showed values ranging from  $1.367 \pm 0.058$  mg/L in July 2023 to  $2.367 \pm 0.153$  mg/L in May 2023. Station 2 showed the lowest concentration in July 2023 ( $1.10 \pm 0.10$  mg/L) and the highest in May 2023 ( $2.367 \pm 0.058$  mg/L). Station 3 peaked at  $2.467 \pm 0.058$  mg/L in January 2024. Although within WHO limits ( $\leq 50$  mg/L), high nitrate levels suggest nutrient pollution, likely from agricultural runoff, which can lead to eutrophication and harmful algal blooms [23].

Phosphate ( $\text{PO}_4^{3-}$ ) levels in Station 1 were relatively stable, ranging from  $2.453 \pm 0.021$  mg/L in July 2023 to  $2.827 \pm 0.085$  mg/L in March 2023. In Station 2, phosphate decreased from  $2.637 \pm 0.104$  mg/L in May 2023 to  $1.340 \pm 0.026$  mg/L in July 2023. Station 3 showed the highest phosphate level in March 2023 ( $2.850 \pm 0.020$  mg/L) and the lowest in July 2023 ( $2.147 \pm 0.021$  mg/L). High levels of phosphate, particularly from sewage and agricultural runoff, promote eutrophication and affect aquatic plant life by encouraging the growth of phytoplankton and algae [24].

The conductivity results ( $\mu\text{S}/\text{cm}$ ) at Station 1 ranged from  $16166.00 \pm 3.512$   $\mu\text{S}/\text{cm}$  in July 2023 and January 2024 to  $20762.00 \pm 25.865$   $\mu\text{S}/\text{cm}$  in March 2023. Significant differences ( $P < 0.05$ ) were observed for all months except July and September 2023. At Station 2, conductivity varied from  $13127.00 \pm 3.055$   $\mu\text{S}/\text{cm}$  in July 2023 to  $20529.00 \pm 8.622$   $\mu\text{S}/\text{cm}$  in May 2023, with significant differences across months. In Station 3, conductivity decreased from  $20252.00 \pm 39.209$   $\mu\text{S}/\text{cm}$  in March 2023 to  $15244.00 \pm 5.686$   $\mu\text{S}/\text{cm}$  in January 2024, with significant differences observed except for July and September 2023. High conductivity in Station 1 suggests the presence of dissolved salts, which can negatively affect water quality and aquatic life. The WHO recommends conductivity levels  $\leq 2500$   $\mu\text{S}/\text{cm}$  [25], but the values recorded exceed this limit, indicating pollution from agricultural runoff or sewage [26]. Elevated conductivity can be detrimental to aquatic ecosystems, especially fish populations [27][28].

Chloride ( $\text{Cl}^-$ ) concentrations in Station 1 decreased from  $5215.00 \pm 17.010$  mg/L in May 2023 to  $2590.00 \pm 3.055$  mg/L in January 2024, with significant differences across months. In Station 2, chloride levels dropped from  $5257.00 \pm 2.517$  mg/L in May 2023 to  $1683.00 \pm 5.00$  mg/L in January 2024. Station 3 recorded the highest chloride level in May 2023 ( $5435.00 \pm 2.517$  mg/L) and the lowest in January 2024 ( $2433.00 \pm 4.619$  mg/L). These levels exceed the WHO recommended limit of  $\leq 250$  mg/L [25], suggesting pollution from industrial or urban runoff, which can harm aquatic life [13].

Phosphate ( $\text{PO}_4$ ) concentrations in Station 1 ranged from  $2.453 \pm 0.021$  mg/L in July 2023 to  $2.827 \pm 0.085$  mg/L in March 2023. In Station 2, phosphate decreased from  $2.637 \pm 0.104$  mg/L in May 2023 to  $1.340 \pm 0.026$  mg/L in July 2023. Station 3 showed the highest phosphate level in March 2023 ( $2.850 \pm 0.020$  mg/L) and the lowest in July 2023 ( $2.147 \pm 0.021$  mg/L). High phosphate levels from sewage and agricultural runoff can promote eutrophication, affecting aquatic plant life by encouraging phytoplankton and algae growth [24].

The results for Dissolved Oxygen (DO) at Station 1 ranged from  $5.033 \pm 0.058$  mg/L in September 2023 to  $5.60 \pm 0.00$  mg/L in March 2023. In Station 2, DO varied from  $5.10 \pm 0.00$  mg/L in July 2023 to  $5.90 \pm 0.00$  mg/L in March 2023, while in Station 3, DO was lowest in January 2024 ( $4.70 \pm 0.00$  mg/L) and highest in March 2023 ( $5.40 \pm 0.00$  mg/L). The USEPA recommends a minimum DO level of 6 mg/L, and the recorded levels across all stations were below this threshold [13]. Low DO levels in Station 3, particularly in January 2024, suggest pollution or higher organic matter decomposition rates, leading to hypoxic conditions that are detrimental to aquatic life.

The pH values in Station 1 ranged from  $7.317 \pm 0.006$  in July 2023 to  $7.54 \pm 0.010$  in September 2023, while in Station 2, the lowest pH was  $6.477 \pm 0.032$  in July 2023 and the highest was  $7.48 \pm 0.000$  in March 2023. Station 3 exhibited the lowest pH in July 2023 ( $6.423 \pm 0.006$ ) and the highest in March 2023 ( $7.483 \pm 0.006$ ). All pH values were within the recommended limits of 6.5–8.5 by WHO and 6.5–9.0 by USEPA [13][25]. pH is a critical indicator of water quality, and these values suggest that the water quality in the study area remains within acceptable limits.

For heavy metals, Copper, Manganese, and Arsenic were below detectable limits across all stations. However, the concentration of Cobalt (Co) showed significant variations. At Station 1, Co decreased from 0.486 mg/L in March 2023 to 0.063

mg/L in January 2024. In Station 2, Co peaked at 0.478 mg/L in May 2023 and dropped to 0.043 mg/L in January 2024. Similarly, Station 3 recorded a high of 0.461 mg/L in May 2023 and a low of 0.112 mg/L in January 2024. The general decrease in Co concentrations over time suggests a reduction in pollution sources, potentially due to changes in industrial activity or seasonal variations. Heavy metals like Co, when accumulated in aquatic organisms, can cause gill epithelial damage, fish mortality, and stress [29].

Zinc (Zn) concentrations in Station 1 decreased from 0.125 mg/L in March 2023 to 0.083 mg/L in January 2024. Station 2 showed fluctuations, with the lowest concentration of 0.041 mg/L in November 2023. Station 3 recorded an anomaly in July 2023 (0.333 mg/L), followed by a decrease to 0.095 mg/L in January 2024. The variations in Zn concentrations could be due to episodic events like heavy rainfall causing increased runoff, though no concentrations exceeded the USEPA's recommended limit of 2,000  $\mu\text{g/L}$  [13].

Nickel (Ni) concentrations in Station 1 increased from 0.217 mg/L in March 2023 to 0.275 mg/L in January 2024. In Station 2, Ni increased from 0.215 mg/L to 0.281 mg/L, and Station 3 saw a similar trend from 0.204 mg/L to 0.278 mg/L. These increasing trends suggest persistent pollution from industrial effluents or urban runoff. The recorded Ni concentrations exceed the WHO recommended limit of  $\leq 70$   $\mu\text{g/L}$  [25] and are approximately two times higher than the USEPA limit of 100  $\mu\text{g/L}$ . Chronic exposure to high levels of Ni can lead to cancer, DNA damage, and other health issues [30]. This poses a significant risk to both aquatic life and human health, especially in areas where people rely on water sources for daily activities [31].

The results for Copper, Manganese, and Arsenic were consistently below detectable levels ( $<0.001$  mg/L) across all stations and time points. However, Cadmium (Cd) was detectable in Station 1 and 2 only in March and May 2023, with concentrations decreasing from 0.074 mg/L to undetectable levels ( $<0.001$  mg/L) from July 2023 onwards. Station 3 showed a similar trend, with detectable Cd only in March and May 2023. The rapid reduction suggests natural attenuation, with initial detections possibly linked to specific pollution events. Although Cd concentrations exceeded the recommended limits by WHO ( $\leq 3$   $\mu\text{g/L}$ ) and USEPA (0.005  $\mu\text{g/L}$ ) in March and May 2023, they later dropped below detectable levels, posing no immediate concern. However, further investigation into the pollution source is necessary

to prevent recurrence. High Cd accumulation in the kidneys is toxic, causing vomiting, diarrhea, headaches, and even death at high concentrations [30][32][33].

Iron (Fe) concentrations in Station 1 decreased significantly from 0.486 mg/L in March 2023 to 0.094 mg/L in January 2024. Station 2 showed an increase from 0.084 mg/L in March 2023 to 0.486 mg/L in January 2024. Station 3 had fluctuations, peaking at 0.087 mg/L in May 2023. The varying concentrations suggest dynamic sources, likely influenced by industrial discharge or natural processes like sediment resuspension. The recorded values remained below the USEPA recommended limit of 1.0 mg/L [13].

Chromium (Cr) was detectable in Station 1 only in May 2023 (0.27 mg/L). In Station 2 and 3, Cr was detectable from March (0.23±0.02 mg/L and 0.26±0.017 mg/L) to July 2023, with a significant decrease in Station 3 to 0.10±0.000 mg/L in November 2023. The early presence of Cr may be linked to industrial discharge, with a decrease suggesting the cessation of pollution sources. The concentrations exceeded the WHO ( $\leq 50$  µg/L) and USEPA (100 µg/L) limits in March and May 2023, but later fell below detectable limits. Chromium is toxic to aquatic life and can accumulate in fish, posing health risks to humans consuming contaminated fish [34]. Monitoring and preventive measures are essential to mitigate these risks.

#### 4.2 Effect of Oil spill on Physicochemical Parameters and Heavy metal of Sediment Samples

Sediments act as sinks for pollutants, absorbing a variety of contaminants through processes such as river hydrodynamics, biogeochemical processes, and environmental conditions. Heavy metals in sediments serve as key indicators of environmental changes in aquatic ecosystems [35]. Due to the increasing focus on environmental protection, there has been growing interest in studying the levels of heavy metals in water, sediments, and benthos [35]. In this study, Bille Creek was exposed to an oil spill, a significant environmental hazard, making the analysis of crude oil and associated heavy metals in sediment essential for assessing the ecological impact.

The Total Petroleum Hydrocarbons (TPH) analysis showed that in Station 1, TPH peaked in May 2023 (2466.00 ± 2.875 mg/kg) and significantly decreased by January 2024 (12.18 ± 0.009 mg/kg), with varying levels over the months, indicating fluctuating pollution events. In Station 2,

TPH levels were generally higher than in Station 1, with the highest concentration recorded in March 2023 (3058.00 ± 16.997 mg/kg), and a significant reduction to 405.20 ± 2.042 mg/kg by January 2024. Station 3 exhibited a steady decline in TPH from March 2023 (2066.00 ± 0.478 mg/kg) to January 2024 (933.10 ± 6.495 mg/kg), with the last two months showing no significant difference. This suggests varying exposure to crude oil discharge, with Station 3 showing the highest pollution levels. Prolonged exposure to TPH can harm human health and aquatic ecosystems, particularly affecting the central nervous system [17][18].

Polycyclic Aromatic Hydrocarbons (PAH) levels in the sediments also fluctuated. In Station 1, PAH peaked in May 2023 (4.145 ± 0.001 mg/kg) and decreased by January 2024 (2.718 ± 0.008 mg/kg). Station 2 recorded the highest PAH concentration in March 2023 (39.46 ± 0.280 mg/kg), dropping sharply thereafter. In Station 3, PAH levels peaked in March 2023 (30.27 ± 0.092 mg/kg), and decreased to 6.229 ± 0.012 mg/kg by January 2024. The fluctuations and significant reductions in PAH levels highlight the persistence of these pollutants and their harmful impact on benthic organisms, which are immobile and exposed to pollutants for prolonged periods [19][20].

Conductivity measurements in Station 1 spiked in May 2023 (7331.00 ± 4.726 µS/cm), then stabilized between 1427.00 ± 1.155 µS/cm and 1539.00 ± 2.517 µS/cm through January 2024. Station 2 showed a higher conductivity peak in March 2023 (8885.00 ± 4.726 µS/cm), with fluctuations continuing until January 2024 (6452.00 ± 2.000 µS/cm). Station 3 recorded its highest conductivity in July 2023 (7326.00 ± 4.163 µS/cm) and remained consistently high through January 2024 (6543.00 ± 3.055 µS/cm). Elevated conductivity indicates high levels of dissolved ions and salts, suggesting pollution, and has a correlation with total dissolved solids and chloride ions. Elevated conductivity can negatively affect water quality and aquatic life, especially if it remains high over extended periods [27][28].

Phosphorus (P) concentrations in sediments showed a slight decrease over time. In Station 1, phosphorus decreased from 0.270 ± 0.000 mg/kg in March 2023 to 0.180 ± 0.000 mg/kg in January 2024. Station 2 saw a similar decrease, from 0.360 ± 0.010 mg/kg in March 2023 to 0.180 ± 0.000 mg/kg in January 2024. Station 3 showed a decline from 0.353 ± 0.032 mg/kg in March 2023 to 0.160 ± 0.000 mg/kg in January 2024. Phosphorus, a key contributor to nutrient pollution, can lead to eutrophication in water



bodies, exacerbating the effects of the oil spill and other pollutants.

Total Organic Carbon (TOC) in Station 1 remained relatively stable, fluctuating between  $6.894 \pm 0.004\%$  in March 2023 and  $6.129 \pm 0.004\%$  in January 2024. Station 2 showed a more significant decrease in TOC, from  $6.827 \pm 0.002\%$  in March 2023 to  $4.213 \pm 0.003\%$  in January 2024, indicating a reduction in organic pollution. Station 3 also recorded a decrease, from  $8.956 \pm 0.004\%$  in March 2023 to  $5.273 \pm 0.005\%$  in January 2024. The higher TOC values in Station 1 suggest persistent organic pollution, whereas the decreasing values in Stations 2 and 3 may indicate a reduction in organic contamination over time.

Overall, the findings highlight significant spatial and temporal variations in the concentration of pollutants across the stations, with the highest pollution levels observed in Station 3. Continuous monitoring and remediation efforts are necessary to mitigate the long-term impacts of the oil spill and other pollutants in the Bille Creek ecosystem.

Total Organic Nitrogen (TON) levels in Station 1 varied slightly from  $0.563 \pm 0.002\%$  in March 2023 to  $0.515 \pm 0.001\%$  in January 2024. Station 2 recorded a decline from  $0.568 \pm 0.007\%$  in March 2023 to  $0.313 \pm 0.001\%$  in January 2024. Station 3 had fluctuations, with a peak in March 2023 ( $0.777 \pm 0.010\%$ ) and a decrease to  $0.624 \pm 0.001\%$  by January 2024. Significant differences ( $P < 0.05$ ) were observed between the months, particularly between March and January. TON is a primary limiting nutrient in marine ecosystems [36], and at high concentrations, it can lead to algal blooms, eutrophication, hypoxia, and ocean acidification. Although no specific WHO standard exists, elevated TON levels indicate increased nitrogen enrichment, which can significantly impact aquatic environments.

The pH of sediment samples in Station 1 decreased slightly from  $5.957 \pm 0.021$  in March 2023 to  $5.510 \pm 0.000$  in January 2024. Station 2 experienced more significant variation, with a drop to  $4.570 \pm 0.000$  in July 2023 before rising again to  $5.520 \pm 0.000$  in January 2024. Station 3 showed a minor decline from  $5.867 \pm 0.021$  in March 2023 to  $5.517 \pm 0.006$  in January 2024. All stations recorded pH values lower than the [25] and [13] recommended limits for aquatic ecosystems. Low pH levels in Station 2 during July and September 2023 indicated acidification, leading to negative effects on the water's chemistry, such as the loss of exchangeable bases and mobilization of toxic metal ions. Acidification adversely affects aquatic organisms at all trophic levels, causing productivity

and biomass shifts and the loss of sensitive species [37].

Heavy metal contamination in sediments, particularly from crude oil, is a key concern. The study revealed that Cobalt, Zinc, Nickel, Cadmium, Iron, and Chromium had high concentrations, while Copper, Manganese, and Arsenic were below detectable limits ( $<0.001$ ). The increased heavy metal concentrations are indicative of anthropogenic pollution rather than natural enrichment [35]. Remobilization of these metals can occur due to environmental changes such as acidification or redox processes, further impacting aquatic organisms [35].

Cobalt (Co) concentrations in Station 1 were relatively stable, ranging from  $11.530 \pm 0.081$  mg/kg in March 2023 to  $11.680 \pm 0.006$  mg/kg in January 2024. In Station 2, Co levels dropped significantly from  $11.550 \pm 0.015$  mg/kg in May 2023 to  $4.773 \pm 0.021$  mg/kg in July 2023, before slightly fluctuating and stabilizing at  $5.517 \pm 0.099$  mg/kg in January 2024. Station 3 exhibited a similar pattern with fluctuations, from  $10.310 \pm 0.208$  mg/kg in March 2023 to  $10.850 \pm 0.025$  mg/kg in January 2024. Cobalt is toxic to aquatic life, causing mortality, gill epithelial damage, and overall stress [29]. Chronic exposure to Co in humans can lead to conditions similar to chronic hypoxia and may also cause cardiomyopathy, elevated hemoglobin levels, and polycythemia.

Zinc (Zn) concentrations varied across stations. In Station 1, Zn levels peaked in May 2023 at  $43.40 \pm 0.108$  mg/kg, then decreased to  $35.10 \pm 0.015$  mg/kg by January 2024. Station 2 showed the highest concentration in March 2023 ( $49.86 \pm 0.031$  mg/kg) and decreased to  $22.41 \pm 0.017$  mg/kg in January 2024. Station 3 had its highest Zn concentration in March 2023 ( $45.43 \pm 0.162$  mg/kg) and lowest in January 2024 ( $31.56 \pm 0.569$  mg/kg). All concentrations were below the threshold effect level (TEL) of 124 mg/kg and the probable effect level (PEL) of 271 mg/kg [38], suggesting no immediate environmental concerns from zinc. However, high zinc exposure can lead to adverse health effects such as nausea, vomiting, and abdominal discomfort [39].

Nickel (Ni) concentrations were high across all stations. In Station 1, Ni levels ranged from  $6.577 \pm 0.270$  mg/kg in March 2023 to  $5.360 \pm 0.030$  mg/kg in January 2024. Station 2 recorded a decrease from  $5.887 \pm 0.045$  mg/kg in March 2023 to  $5.307 \pm 0.012$  mg/kg in January 2024, while Station 3 showed an increase from  $4.327 \pm 0.143$  mg/kg in March 2023 to  $5.350 \pm 0.017$  mg/kg in January 2024. While these values were below the TEL and PEL, long-term exposure could

lead to bioaccumulation in benthic organisms, causing long-term ecological effects [38]. Nickel is a toxic heavy metal that can be absorbed through inhalation, ingestion, and dermal exposure, with long-term exposure linked to serious health effects such as cancer and organ toxicity.

The analysis of heavy metals in the sediment samples showed that Copper, Manganese, and Arsenic levels were consistently below detection limits ( $<0.001$  mg/kg) across all stations and time points. This is a positive result as Copper, Manganese, and Arsenic are highly toxic in elevated concentrations. Copper, in particular, is required in trace amounts by the body, but excessive exposure can lead to liver buildup, hemolysis, and damage to red blood cells, causing anaemia and organ dysfunction. Manganese exposure has been linked to oxidative stress, mitochondrial dysfunction, and neurotoxicity [40]. Arsenic is a known carcinogen, with severe health impacts including skin cancer, liver damage, and lung cancer. The absence of detectable Copper, Manganese, and Arsenic significantly reduces the environmental risks associated with these metals and allows for a greater focus on other pollutants.

Cadmium (Cd) levels in the sediment samples fluctuated across the stations. In Station 1, Cd peaked in May 2023 at  $1.497 \pm 0.137$  mg/kg, before dropping to  $0.267 \pm 0.012$  mg/kg by January 2024. Station 2 showed similar fluctuations, with a peak in May 2023 ( $1.233 \pm 0.101$  mg/kg) and a decrease to  $0.283 \pm 0.006$  mg/kg by January 2024. Station 3 experienced an increase in Cd levels from  $0.190 \pm 0.020$  mg/kg in March 2023 to  $1.190 \pm 0.020$  mg/kg in May 2023, followed by a decline to  $0.310 \pm 0.000$  mg/kg in January 2024. The peak concentrations of Cd in May 2023 exceeded the threshold effect level (0.68 mg/kg) and approached the probable effect level (1.5 mg/kg), indicating cadmium contamination in the sediment [38]. Cd is a potent endocrine disruptor and can lead to serious health issues, including nausea, vomiting, liver and kidney damage, and death at high concentrations [32].

Iron (Fe) concentrations varied across the stations, with Station 1 showing a significant decrease from  $3650.00 \pm 5.879$  mg/kg in March 2023 to  $3046.00 \pm 0.849$  mg/kg in January 2024. In Station 2, Fe levels decreased from  $3926.00 \pm 1.977$  mg/kg in March 2023 to  $2055.00 \pm 0.047$  mg/kg in January 2024. Station 3 showed fluctuations but remained high compared to Station 2, decreasing from  $3257.00 \pm 2.717$  mg/kg in March 2023 to  $3063.00 \pm 0.525$  mg/kg in January 2024. Although the high concentrations of Iron may not be directly related to the oil spill,

sediment-bound metals like Fe can become remobilized and released into the water under certain environmental conditions, such as changes in pH or redox conditions [30].

Chromium (Cr) concentrations varied across the stations, with Station 1 recording the highest in March 2023 ( $12.59 \pm 0.172$  mg/kg) and a decrease to  $9.417 \pm 0.015$  mg/kg by January 2024. In Station 2, Cr levels peaked in May 2023 ( $12.75 \pm 0.025$  mg/kg), followed by a decrease to  $4.867 \pm 0.021$  mg/kg by January 2024. Station 3 exhibited a slight increase from  $9.377 \pm 0.136$  mg/kg in March 2023 to  $10.71 \pm 0.006$  mg/kg in January 2024. These concentrations remained below the threshold effect level (52.3 mg/kg) and the probable effect level (160 mg/kg), suggesting that chromium levels were not high enough to cause significant ecological disruption [38]. However, chromium can accumulate in aquatic organisms, causing toxicity when consumed by humans [34]. Its presence in the sediment is still a concern due to its toxic effects on aquatic life and potential human health risks.

The deposition of heavy metals in sediments is a key issue during oil spills, as these metals accumulate in the sediment, further exacerbating the environmental risks. Metals like Cd, Cr, and Co can be remobilized due to changes in environmental conditions such as acidification and redox processes, leading to further contamination of the water and affecting aquatic organisms. Heavy metal pollution in sediments can pose long-term risks to both the aquatic ecosystem and human health, especially as these metals accumulate in the food chain [30][41]. Continuous monitoring and remediation efforts are essential to mitigate the impact of these pollutants and protect the health of aquatic ecosystems and communities dependent on the creek.

### 4.3 Effect of Oil Spill on Petroleum Contaminants and Heavy Metal Parameters of Benthic Sample

Metals in aquatic ecosystems can be absorbed by organisms from the surrounding water or ingested through food. Once absorbed, metals tend to accumulate in specific tissues rather than distribute uniformly throughout the body. In the context of a crude oil spill, it is essential to assess the impact of heavy metals on aquatic organisms, particularly benthic communities, to understand how these metals accumulate and the potential ecological risks. This analysis helps evaluate how crabs, as benthic organisms, accumulate metals from both water and sediment, offering insights into environmental contamination.

The results for Total Petroleum Hydrocarbons (TPH) in the benthic organisms showed significant changes across stations. In Station 1, TPH levels decreased drastically from 12.92 mg/kg in March 2023 to 0.011 mg/kg in January 2024. Station 2 showed an initial high concentration of 15.35 mg/kg in March 2023, followed by a sharp decrease to 0.017 mg/kg in May 2023. TPH levels then rose again, peaking at 7.548 mg/kg in September 2023, before decreasing to 5.357 mg/kg by January 2024. Station 3 followed a similar trend with an initial drop to 0.018 mg/kg in May 2023 and a rise from July 2023 to January 2024. These fluctuations indicate ongoing or episodic crude oil contamination, with Station 1 showing a reduction in pollution sources, while Stations 2 and 3 experienced elevated levels over time. The persistence of these pollutants in benthic organisms highlights the need for further intervention and remediation [18].

For Polycyclic Aromatic Hydrocarbons (PAH), concentrations were detectable in March 2023 (0.516 mg/kg in Station 1, 0.593 mg/kg in Station 2, and 0.668 mg/kg in Station 3). However, PAH levels fell below detection limits (<0.001 mg/kg) in the subsequent months across all stations. This rapid decrease may indicate that natural degradation processes reduced PAH availability in the environment, making it less accessible for accumulation in organisms. PAHs can have harmful sublethal effects on aquatic species, impairing reproduction and causing physiological stress [42]. Crude oil exposure to benthic organisms can occur both via ingestion and through the gills, presenting significant risks to their health and reproduction [18].

Cobalt (Co) concentrations in the benthic organisms showed variability. In Station 1, Co decreased from 9.130 mg/kg in March 2023 to 8.74 mg/kg in January 2024. Station 2 recorded a drop to 4.20 mg/kg in May 2023, followed by a slight increase to 9.407 mg/kg in January 2024. In Station 3, Co concentrations initially decreased to 4.207 mg/kg in May 2023 but peaked at 11.28 mg/kg in July 2023, before decreasing to 10.14 mg/kg in January 2024. The fluctuations in Co concentrations suggest episodic pollution events, with Station 3 showing a higher accumulation of cobalt over time. Cobalt exposure in aquatic organisms can lead to various health issues, including stress, gill epithelial damage, and overall toxicity [29]. Chronic exposure to Co can also lead to cardiomyopathy and other severe health problems in humans consuming contaminated seafood.

Zinc (Zn) concentrations in the benthic organisms followed a fluctuating trend. Station 1 showed an increase from 53.32 mg/kg in March 2023 to 63.68 mg/kg in September 2023, before decreasing slightly to 58.88 mg/kg in January 2024. Station 2 exhibited an increase from 60.51 mg/kg in November 2023, stabilizing at 60.27 mg/kg in January 2024. Station 3 had fluctuations, peaking at 62.64 mg/kg in November 2023. These fluctuations suggest ongoing pollution sources, possibly from industrial discharges or the oil spill event. Zinc toxicity can cause adverse health effects, including nausea, vomiting, and gastrointestinal distress [39]. While the concentrations of Zn were below the threshold for acute toxicity, continuous exposure could still lead to long-term ecological impacts.

Nickel (Ni) concentrations showed an increasing trend across all stations. In Station 1, Ni increased from 7.547 mg/kg in March 2023 to 11.65 mg/kg in July 2023, then decreased slightly to 9.36 mg/kg in January 2024. Station 2 also showed a rise from 5.887 mg/kg in March 2023 to 11.26 mg/kg in July 2023. Station 3 had the highest peak in July 2023 at 13.45 mg/kg, decreasing to 10.23 mg/kg by January 2024. Nickel concentrations remained below the threshold effect level (TEL) of 15.9 mg/kg but posed a risk of bioaccumulation in benthic organisms, which could lead to long-term adverse effects such as cancer, DNA damage, and cellular disruption [30].

Cadmium (Cd) levels in the benthic organisms showed an initial increase in March 2023 (2.757 mg/kg in Station 1) before decreasing to 2.060 mg/kg in January 2024. Station 2 showed a similar trend, with the highest concentration recorded in March 2023 and a decrease in the following months. Station 3 had the highest concentration of 3.45 mg/kg in July 2023. The presence of high Cd concentrations, especially in Station 3, suggests localized pollution, potentially linked to the oil spill. Cd is a known toxin that accumulates in the kidneys and can cause nausea, vomiting, and kidney damage [33]. Chronic exposure to Cd can also lead to severe health complications in humans consuming contaminated crabs [30].

Overall, the findings from this study underscore the significant impacts of crude oil contamination on the benthic community in Bille Creek. The fluctuating concentrations of TPH, PAH, and heavy metals such as Cobalt, Zinc, Nickel, and Cadmium in benthic organisms indicate ongoing or episodic pollution events. The accumulation of these contaminants in the benthic community poses substantial ecological and health risks. Continued monitoring and remediation



efforts are critical to mitigate the long-term effects of oil spills and other pollutants in the ecosystem.

## V. CONCLUSION

The analysis of Bille Creek's surface water, sediment, and benthic organisms reveals significant contamination due to crude oil spills. The physicochemical parameters, such as TPH, PAH, and heavy metals fluctuated across stations, with Station 3 experiencing the highest contamination levels. TPH concentrations in benthic organisms demonstrated bioaccumulation, suggesting persistent pollution from oil spills. The presence of elevated levels of heavy metals, including Cobalt, Zinc, Nickel, and Cadmium, poses substantial risks to aquatic life and human health, as these metals can accumulate in organisms, leading to toxic effects. The findings underscore the need for immediate remediation and continuous monitoring of the ecosystem to prevent further contamination and mitigate long-term environmental and health risks. The study serves as a crucial assessment of the ecological impacts of crude oil pollution, highlighting the need for proactive measures to safeguard aquatic ecosystems and human populations relying on these water sources.

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