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Assessment of Physico-Chemical Characteristics and Heavy Metal Content of Mangrove Water and Sediment from Selected Sites, Gulf of Khambhat, Gujarat, India

Dhara Tuteja, Rita Kumar, Neel Talati, Nirmal Kumar

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ABSTRACT

Due to their function in averting catastrophic weather occurrences like tsunamis and cyclones, mangrove forests are of paramount importance. The current study sought to determine the heavy metal content in water and sediment as well as the physico-chemical quality of mangrove water and sediment. Physico-chemical parameters and edaphic characteristics were studied for different sites i.e. Vadgam, Tada Talav and Kantiajal of the Gulf of Khambhat having mangrove vegetation. Physico-chemical parameters and heavy metals were higher at Kantiajal which is situated in Hansot tehsil of Bharuch district. This might be because it is adjacent to the industrial area of Ankleshwar and Panoli. Some of the physico-chemical parameters studied were turbidity, salinity, dissolved oxygen, COD, sulphate, phosphate, ammonical nitrogen, Iron (Fe), Manganese (Mn), Zinc (Zn), Copper (Cu), Cobalt (Co) and Lead (Pb) were the metal selected for the study. In order to develop conservation and management plans, a thorough research of the mangrove species in the Gulf of Khambhat, Gujarat, is required. The current study gives the baseline data for these species.

Keywords Mangrove water sediment, Physico-chemical, Heavy metal.

INTRODUCTION

Mangrove forests are by far the most prolific ecosystems, growing on protected coasts and in estuaries across the tropics, as well as in certain subtropical areas (Das *et al*. 2022). Many of the coastal marine creatures in the mangrove environment are natural sources of protein, and they are significant for coastal protection and as a supply of firewood and charcoal (Macintosh and Ashton 2002). With their roots, mangroves trap silt while also absorbing wave energy and delaying the hydrological flow of storm surges (Valiela *et al*. 2001, Chong 2005). Mangrove forests are significant tropical coastal tidal ecosystems that thrive on nutrient-rich muddy bottoms with low oxygen levels, fluctuating tides and a varying amount of salinity. It is rated one of the most prolific terrestrials, and as a result, it plays an important role as a primary producer in estuary systems, providing food for inhabitants (fauna populations) as well as

Dhara Tuteja[1*], Dr Rita Kumar[2], Neel Talati[3], Dr Nirmal Kumar[4]

[2,4]Head of the Department, [1,2,3]Department of Biological and Environmental Science, Natubhai V. Patel College of Pure and Applied Sciences (NVPAS), Vallabh Vidyanagar 388120, Gujarat, India

[4]Department of Environmental Science and Technology, Institute of Science and Technology for Advanced Studies and Research (ISTAR), Vallabh Vidyanagar, Gujarat, India

Email: dharadesai0110@gmail.com
*Corresponding author

the adjoining coastal food web (Zulkifli *et al*. 2012, Marchand *et al*. 2011, Zulkifli *et al*. 2014). Mangroves are bio-indicators for a variety of contaminants in the environment, including heavy metals, organic pollutants, and hydrocarbons. Heavy metals, like the earth's crust, are naturally occurring compounded elements that exist in different proportions in the environment. They are non-biodegradable contaminants that take a long time to collapse through biological or chemical processes (Singare 2012). When the acceptable value is exceeded, it becomes hazardous and carcinogenic.

Mangroves cover less than 1% of the total land area on the planet (Singh *et al*. 2012). The range of mangroves is quite broad along the eastern coastlines of America and Africa. The largest land cover of Mangroves globally is possessed by Asia with a percentage of about 42%. Indonesia and Malaysia contribute the highest mangroves among the Asian countries. India ranks the fourth largest country with mangrove coverage of 6749 km^2. The mangrove area being 80% on the coast is larger than the west coast being 20%. Around 25 species of mangroves have been limited to the eastern coast of India, whereas 34 species are present along the western coast, with eight species located solely on the west coast. Mangrove species namely *Sonneratia caseolaris, Suaeda fruticose, Urocnhondra setulose*, and certain others are exclusively found on the western coast of India. The Gulf of Khambhat, along India's west coast, is the most important marine environment. *Avicennia marina (forssk*.) is the mangrove species that alone accounts for 90% of the total mangrove coverage in Gujarat. It is a global plant that may thrive in a variety of coastal settings.

As a result of coastal development activities including industries, harbors, jetties, quarrying, and other human activities, pollution of marine zones has become a global problem. A number of point and non-point sources, including sewage, industrial effluents, solid waste, silt, petroleum hydrocarbons, agricultural chemicals runoff, fertilizers, and pesticides, are among the sources of pollution that reach the beach. Marine sediments are one of the most important reservoirs for heavy metals in coastal areas. Heavy metal contamination in maritime water and sediments has risen in recent years due to its potential impact on the biosphere. (Kumar *et al*. 2011, Tripathi *et al*. 2016, Tang *et al*. 2019, Singh *et al*. 2020).

Study area

The research was conducted at three locations in Gujarat: Vadgam, Tadatalav, and Kantiyajal (Fig. 1). The physico chemical parameters of water, the heavy metal accumulated in the water and sediments were analyzed in all three respective sites.

Vadgam (VGM) is situated in the Khambhat taluka, Anand district of Gujarat. It is located 35 km to the west of Anand. The latitude and longitude position for the site is 22º19'04"N and 72º22'45"E, respectively. It is at a height of 19 meters above sea level. The mangroves present in this village are short in height, giving shrubs appearance. Tadatalav (TTM) is a village positioned in the Khambhat taluka of Anand district, Gujarat. It is located 40 km towards the west of Anand. The latitude and longitude position for the site is 22º15'18"N and 72º27'11"E, respectively. Tadatalav is situated 19 meters in height beyond sea level. The estuaries formed near Tadatalav receive water from the Gulf of Khambhat. The mangroves present in Tadatalav are mostly small and stunted in height with limited growth and a basal area of approximately 1 m^2. Kantiyajal (KJM) is positioned in the Hansot tehsil of Bharuch district, Gujarat. Kanityajal has located 60 km from the district headquarters in Bharuch. The latitude and longitude position for the site is 21º28'38"N and 72º39'25"E, respectively. The total area of Kantiyajal is approximated to be

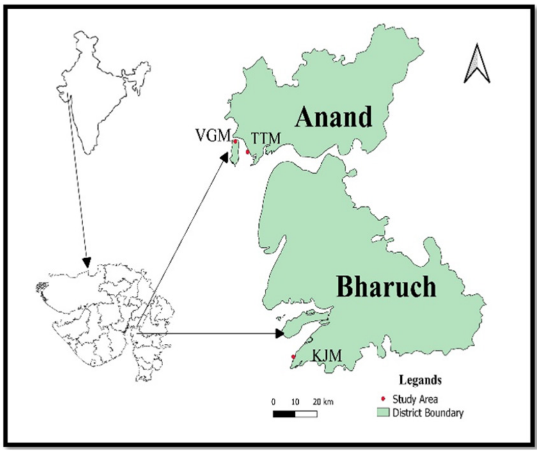

Fig. 1. Mangrove sites of Gujarat selected for study.

2594.91 (hectares) with an estimated population of 1218 people. It is located 22 km above sea level. The mangroves present in this region are moderately dense and open mangrove types. Mangroves in this region have grown naturally. The size of the mangroves is small and appears like a shrub nearly 2-3 m tall.

MATERIALS AND METHODS

The investigation was completed in December, January, and February of 2022. The period corresponds to low water levels. According to the American Public Health Association (APHA 2017), all of the analyses were based on conventional methodologies that were adequate for each water quality indicator. Samples were collected using clean plastic containers and sediment samples were picked up in clean zip-lock bags. pH, EC, temperature, acidity, alkalinity, DO, BOD, COD, TSS, TDS, Ca hardness, total hardness, Mg hardness, sulfate, phosphate, salinity, turbidity, Na, K, ammonical nitrogen, Fe, Mn, Zn, Cu, Co, Cr, Pb, S are the parameters to be studied for water samples and organic carbon, available phosphorus, available potassium, soil pH, soil EC are to analyzed for sediment samples. Temperature, electrical conductivity, salinity, turbidity, and pH of the water determine the survival rate of plants and animals in the aquatic ecosystem. These parameters were determined onsite with the help of instruments namely pH meter, thermometer, salinity meter, turbidimeter, conductivity meter, Do was fixed onsite and later estimated in the laboratory by the azide modification method. COD is estimated by the reflux digestion method. The turbidimetric method was used for the estimation of sulfate in surface water. Inorganic phosphate was estimated by the stannous chloride colourimetric method. Emission spectroscopy, which deals with the excitation of electrons from the ground state to a higher energy level and then returning to their original state with the emission of light, is used to estimate sodium and potassium. Nesslerization was used to calculate ammonical nitrogen levels (colourimetric method). For the estimation of heavy metals like Fe, Zn, Mn, Cu, Co, Cr, Pb, and S, the preserved sample has to be acid digested with concentrated acid. The soil surrounding the mangrove plants was collected in plastic bags and later dried in the sun. After drying, the water soil samples were tested for heavy metals using ICP at Anand Agricultural University's micronutrient department (AAU).

RESULTS AND DISCUSSION

Physico-chemical characteristics of water

Extreme hydroclimatic conditions, which are generally regulated by a sequence of meteorological events, are constantly present in the coastal zone including the mangrove biotope. Tides, which are by far the most significant biological variables sewing as a significant energy input, have an impact on the mangrove environment. The continuous mixing of water masses with different physical-chemical qualities complicates the hydrography and nutrient cycling in mangrove areas. Saraya (1984) established that two fundamental variables impact the environmental conditions of mangrove waterways: Short-term changes produced by tidal inundation and seasonal changes induced by monsoonal cycles. Analytical results of physico-chemical parameters are shown in Table 1.

Table 1. Physico-chemical analysis of mangrove water.

Parameter	VGM	TTM	KJM	Unit
pH	9.6	9.8	10.3	-
EC	1410	1740	1620	µs/cm
Temperature	18.5	19.3	18.9	C
Acidity	147	160	153	mg/l
Alkalinity	260	152	100	mg/l
DO	5.05	4.5	5.24	mg/l
BOD	0.5	0.3	0.7	mg/l
COD	158	220	192	mg/l
TSS	58	65	67	mg/l
TDS	143	160	193	mg/l
Total hardness	61	57	63	mg/l
Sulphate	11.3	16	12.3	mg/l
Phosphate	12.9	17.5	11.1	mg/l
Salinity	47.6	53	55.6	Ppt
Turbidity	17.6	19	27.2	NTU
Na	4530	3800	4400	mg/l
K	1380	1441	1530	mg/l
Ammonical nitrogen	10.13	18.6	19.8	mg/l

It shows the results of a laboratory investigation of many water quality indicators such as DO, BOD, minerals, and macronutrients.

The water temperature remained between 18.5 to 19.3 degrees Celsius, while the pH was 9.6 to 10.3. At VGM pH measured was 9.6, at TTM it was 9.8 and at KJM pH recorded was 10.3.

Electric conductivity indicates the amount of salt dissolved in water. In VGM, EC reported for the sampling period was 1530 µs/cm whereas in the case of TTM recorded EC was 1650 µs/cm. At KJM which receives much more industrial effluent from Ankleshwar and Panoli GIDC EC was 1720 µs/cm. The results were per Dattatreya *et al*. (2018).

Dissolved and particulate organic materials, dissolved inorganic compounds (excluding dissolved gases), and suspended inorganic substances are all included in total solids in a water sample. Total solids are the combination of total suspended solids and total dissolved solids. During the study at VGM, TTM and KJM TDS (total dissolved solids) detected were 301, 373, and 495 mg/l respectively. Total suspended solids measured as VGM, TTM, and KJM were 237, 261, and 398 mg/l, respectively, at all three sample locations. Pawar (2013) measured average TS of 43-47 mg/l while working on the mangrove habitat at Uran, Navi Mumbai, which confirms the current TS estimate.

The presence of residential waste and the lack of regular tidal action, which would have flushed and diluted dissolved elements as well as bicarbonates, which might enhance alkalinity levels, may have affected the higher total alkalinity values found in pre-monsoon irrespective of the season. Alkalinity levels were 415, 368, and 463 mg/l at VGM, TTM, and KJM, correspondingly.

The quantity of dissolved oxygen in water is an indication of current water quality, trophic state, and hence the ability of water to maintain a well-balanced aquatic life. It's necessary for the respiratory metabolism of the mangrove ecosystem's whole aerobic aquatic life. The chemical and biological oxygen demands of water are reduced when the dissolved oxygen level of water rises. As a result, it's critical to have a tolerable level of dissolved oxygen in the water to keep living creatures alive. 03 mg/l was the DO content recorded at VGM, 2.8 mg/l was at TTM and at KJM dissolved oxygen content was low compared to other sites at 2.5 mg/l. BOD content of VGM in the selected study period was 0.5 mg/l and COD recorded was 278 mg/l at TTM recorded BOD and COD were 0.3 mg/l and 305 mg/l respectively. At KJM, BOD amount was 0.3 mg/l and COD was 347 mg/l.

The presence of divalent cations, particularly calcium (Ca) and magnesium (Mg), imparts hardness, with magnesium dominating in saltwater and accounting for the greater hardness levels reported. Due to the dominance of neritic water (which is rich in divalent cations, notably of 'Mg') during this season, Dattatreya *et al*. (2018) discovered higher summer values of total hardness in the mangrove zone within the Krishnapatnam coast. Total hardness concentration was highest at KJM, 247 mg/l, and lowest at TTM, 197 mg/l. Total hardness concentration was highest at VGM, 203 mg/l.

Salinity is the important and deciding factor that determines the composition of the biological component within the mangrove environment for distributions of living organisms. The biological characteristics of the environment are littered with fluctuations in salinity. Salinity was high compared to monsoon and less in relationship with the pre-monsoon season. Salinity recorded at VGM, TTM and KJM are 49 ppt, 86 ppt and 53 ppt respectively.

Because mangroves are found in shallow locations vulnerable to the effects of tides, waves, and currents, their waterways are typically murky. These cause the sediments packed with organic matter to be resuspended regularly, enriching the underlying water column with organic matter (Kumar *et al*. 2006). Turbidity measured for VGM was 17.5 NTU, at TTM it was 15.1 NTU and at KJM it was 14.9 NTU.

Na and K content varied at all the sampling sites. At VGM Na was 4763 mg/l and K content was 2245 mg/l. At TTM Na measured was 6497 mg/l and K was 3047 mg/l. Na noted at KJM was 7018 mg/l and K was 3441 mg/l.

Table 2. Physico-chemical analysis of mangrove sediment.

Parameter	VGM	TTM	KJM
Soil pH	8.13	8.12	8.22
Organic carbon (%)	0.52	0.76	0.69
Available phosphorus (kg/ha)	7.67	7.01	7.42
Soil EC (dS/m)	31.3	15.5	17.5
Available potassium (kg/ha)	2063	2478	5440

Ammonical Nitrogen is an important factor in the mangrove ecosystem was measured. At VGM it was 2.47 mg/l, at TTM it was 15.87 mg/l and at KJM it was 1.5 mg/l.

Physico-chemical characteristic of sediment

The result of the sediment quality studied is shown in Table 2. Soil texture studies represent the dominance of Clay at all three sites. That means the sediments were clayey.

Table 3 shows the association found between the various physico-chemical parameters of mangrove water. pH shows a positive correlation with EC, acidity, alkalinity, TSS, TDS, Total hardness, sulphate, and phosphate. Salinity shows a positive correlation between pH and EC. Here COD is negatively correlated with DO and BOD.

A positive correlation indicates that when one parameter's concentration rises, the other parameter's concentration rises as well, whereas a negative correlation asserts that as one parameter's concentration falls, the negatively associated parameter's concentration or value rises. The correlation value ranges from +1 to -1; values close to 0 indicate no connection between the parameters, while values closer to +1 indicate significant correlation, and values closer to -1 indicate a strong negative correlation.

ANOVA: Single factor

There was a significant difference between the mangrove water parameters collected from sites in the post-monsoon season at $p < 0.05$ during the sampling period. Here p-value calculated was 1.9 × 10^-22 (Table 4).

Table 3. Correlation between physico-chemical parameters of mangrove water.

	pH	EC	Temp	Acidity	Alka	DO	BOD	COD	TSS
pH	1								
EC	0.989	1.000							
Temp	0.839	0.747	1.000						
Acidity	0.906	0.832	0.990	1.000					
Alkalinity	0.505	0.370	0.894	0.823	1.000				
DO	-0.993	-0.965	-0.896	-0.948	-0.601	1.000			
BOD	-0.866	-0.931	-0.454	-0.573	-0.006	0.803	1.000		
COD	0.992	0.962	0.900	0.952	0.609	-1.000	-0.797	1.000	
TSS	0.927	0.860	0.982	0.999	0.792	-0.964	-0.615	0.966	1.000
TDS	0.989	0.956	0.910	0.958	0.627	-0.999	-0.783	1.000	0.972
TH	0.806	0.708	0.998	0.981	0.918	-0.868	-0.402	0.873	0.969
Sulphate	0.789	0.688	0.996	0.975	0.929	-0.854	-0.376	0.859	0.962
Phosphate	0.999	0.994	0.814	0.886	0.466	-0.987	-0.887	0.986	0.909
Salinity	0.098	0.247	-0.459	-0.332	-0.809	0.016	-0.583	-0.026	-0.282
Turbidity	-0.899	-0.954	-0.514	-0.628	-0.075	0.842	0.998	-0.837	-0.668
Na	0.955	0.989	0.639	0.739	0.227	-0.915	-0.975	0.911	0.774
K	0.976	0.998	0.700	0.792	0.305	-0.945	-0.954	0.941	0.823
Amm Nit	-0.060	0.090	-0.594	-0.478	-0.892	0.174	-0.447	-0.184	-0.431

Table 3. Continued.

	TDS	TH	Sulphate	Phosphate	Salinity	Turbidity	Na	K	Amm Nit
pH									
EC									
Temp									
Acidity									
Alkalinity									
DO									
BOD									
COD									
TSS									
TDS	1.000								
TH	0.884	1.000							
Sulphate	0.871	1.000	1.000						
Phosphate	0.982	0.779	0.761	1.000					
Salinity	-0.049	-0.510	-0.534	0.143	1.000				
Turbidity	-0.824	-0.464	-0.439	-0.917	-0.525	1.000			
Na	0.901	0.594	0.571	0.967	0.389	-0.988	1.000		
K	0.933	0.658	0.636	0.985	0.313	-0.973	0.997	1.000	
Amm. Nit	-0.207	-0.640	-0.661	-0.016	0.987	-0.384	0.238	0.158	1.000

Heavy metal concentration in mangrove water and sediment

Heavy metal contamination affects mangroves as a result of man-made activities such as mining, metal smelting, fossil fuel combustion, agricultural pesticide manufacture, as well as home and industrial sewing. Because mangrove sediments are anaerobic and have high sulphide content, they have a high metal-binding capacity, which allows them to quickly

Table 4. One way ANOVA of physico-chemical parameter of mangrove water.

Summary				
Groups	Count	Sum	Average	Variance
pH	3	27.3	9.1	0.09
EC	3	4900	1633.333333	9233.333333
Temperature	3	79.2	26.4	0.91
Acidity	3	2091	697	5719
Alkalinity	3	1246	415.3333333	2256.333333
DO	3	8.3	2.766666667	0.063333333
BOD	3	1.1	0.366666667	0.013333333
COD	3	930	310	1209
TSS	3	896	298.6666667	7544.333333
TDS	3	1169	389.6666667	9617.333333
Total hardness	3	647	215.6666667	745.3333333
Sulphate	3	110.4	36.8	8.4268

Table 4. Continued.

Summary groups	Count	Sum	Average	Variance		
Phosphate	3	23.3	7.76666667	6.773333333		
Salinity	3	188	62.66666667	412.3333333		
Turbidity	3	47.5	15.83333333	2.093333333		
Na	3	18278	6092.666667	1393870.333		
K	3	8760	2920	375391		
Ammonical nitrogen	3	19.84	6.613333333	64.49963333		
Anova						
Source of variation	SS	df	MS	F	P-value	F crit
Between groups	119310027.5	17	7018236.913	69.94606013	1.90E-22	1.915321
Within groups	3612162.406	36	100337.8446			
	Total	122922189.9	53			

collect metals and raise their concentration in the sediments. This increased metal concentration leads to bioaccumulation in plant tissues (Kannan *et al*. 2016).

On the other side, heavy metal pollution has the potential to disrupt ecosystems and biodiversity since it can enter the food chain in the marine biota. Metal concentrations in the immediate environment, such as water and sediments, as well as the amount of time exposed, are related to heavy metal bioaccumulation. Other elements that contribute to accumulation include salinity, pH, hardness, and temperature. Because they are located in intertidal sections of the coastal zone, mangrove wetlands are frequently vulnerable to heavy metal contamination from anthropogenic sources (Abohassan 2013).

Table 5 shows prescribed standards for heavy metal content of mangrove water and sediment. Fe content of water was highest at KJM (2.15 ppm), followed by VGM (1.6 ppm) and TTM (0.36 ppm). Mn concentration was also high at KJM (0.56 ppm), followed by VGM (0.095 ppm) and TTM (0.36 ppm). Zn content of KJM was 0.87 ppm, at VGM it was 0.225 and 0.42 was at TTM. Cu content was highest at TTM (0.847 ppm), followed by KJM (0.41 ppm) and VGM (0.082). Co concentration of VGM water was 0.0094 ppm, at TTM it was 0.0099 ppm and 0.0079 ppm was recorded at KJM. Cr recorded highest at TTM (0.0083 ppm), followed by KJM (0.0064 ppm) and VGM (0.0057 ppm). Pb content was recorded in following order KJM (0.37 ppm) > TTM (0.092 ppm)

Table 5. Heavy metal content of mangrove water and sediment.

Sl No.	Parameters	Units	Prescribed standards
1	Chloride	mg/L	1000.0*
2	Boron	mg/L	0.7****
3	Phosphate	mg/L	0.001-0.01**
4	Sulfate	mg/L	250***
5	Silicate	mg/L	2.8**
6	Ammonium	mg/L	2.2*****
7	Zinc	mg/L	0.5**
8	Aluminium	mg/L	0.1*****
9	Manganese	mg/L	0.1***
10	Iron	mg/L	0.3***

* Water Quality Standards for Coastal Waters Marine Outfalls. SW-II Standard. Central Pollution Control Board, New Delhi. ** South African Water Quality Guidelines for Coastal Marine Waters, 1996. International Target Values for the Natural Marine Environment, Vol.1, pp B-1-B-3. and Chap. 4.2. pp 31.; *** KepMenKes No. 51/MENKES/SK/VII/2004. quality standards of the Environment Decree No. 51 in 2004 on Marine water quality standards for marine biotas.; **** UK Marine Standards.; ***** Canadian Water quality standards for Marine fisheries and aquatic life, Environment Canada, 1987 CEC, 1978, 1980 committee for fisheries, 1993.

Table 6. Heavy metal content of mangrove water and sediment.

Parameter		VGM	TTM	KJM
Fe	Water	1.6	0.36	2.15
	Sediment	23.24	16.9	24.87
Mn	Water	0.095	0.037	0.56
	Sediment	18.91	14.56	29.24
Zn	Water	0.225	0.42	0.87
	Sediment	0.74	0.53	3.01
Cu	Water	0.082	0.847	0.41
	Sediment	6.37	3.38	13.57
Co	Water	0.0094	0.0099	0.0079
	Sediment	2.7	2.19	16.24
Cr	Water	0.0057	0.0083	0.0064
	Sediment	0.4	2.07	0.73
Pb	Water	0.084	0.092	0.37
	Sediment	1.12	1.4	3.35
S	Water	92	1557	3519
	Sediment	1307	2357	5169

> VGM (0.084 ppm). S was higher at KJM (3519 ppm), followed by TTM (1557 ppm) and VGM (92 ppm). Table 6 displays the findings from the study of the heavy metal content of mangrove water and sediment at the sampling sites.

Because sediments have the potential to trap heavy metals from water, mangrove sediments operate as a sink for heavy metal buildup (Tang *et al*. 2019). Metal concentration was found higher in sediment compared to water at all the sites. Fe content was found in order of KJM (24.87 ppm) > VGM (23.24 ppm) > TTM (16.9 ppm). Mn, Zn, Cu and Co content also followed the same trend. KJM (Mn - 29.24 ppm, Zn – 3.01 ppm, Cu – 13.57 ppm, Co – 16.24 ppm) > VGM (Mn - 18.91 ppm, Zn – 0.74 ppm, Cu – 6.37 ppm, Co – 2.7 ppm) > TTM (Mn - 14.56 ppm, Zn – 0.53 ppm, Cu – 3.38 ppm, Co – 2.19 ppm). Pb content at VGM was 1.12 ppm, at TTM it was 1.4 ppm and at KJM it was 3.35 ppm. S content of sediment was also higher than water. At KJM it was 5169 ppm, at TTM it was 2357 ppm and at VGM 1307 ppm.

CONCLUSION

Based on the analysis results, it appears that the water sample contains excessive amounts of phosphate and heavy metals, including Fe, Mn, and Zn, which are beyond the acceptable range. The highest concentration of heavy metals was found at KJM, while the lowest was detected at TTM, followed by VGM.

Furthermore, the water quality test conducted in the Gulf of Khambhat indicates that the ecosystem is degrading. Due to the high levels of heavy metals present in the water and sediment, there is a risk of bioaccumulation in plants present at the site, as well as biomagnification in grazing cattle that consume these contaminated plants. Therefore, it is critical to minimize the amount of industrial effluent that is directly released into the environment in order to reduce pollution.

To address this issue, measures such as implementing more stringent regulations for the discharge of industrial effluent and ensuring that effluent is treated before being released into the environment may be necessary. Additionally, monitoring of the water and sediment quality should be conducted on a regular basis to assess the effectiveness of these measures in reducing pollution and preventing further damage to the ecosystem.

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