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An investigation of water quality status in Gebeng industrial estate, Pahang, Malaysia

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Abstract

Gebeng is a rapidly growing industrial area in Pahang, Malaysia. The study was conducted to explore the pollution level and to find out the human interference on surface water quality. The highly polluted parameters were BOD, COD, DO, ammonical nitrogen, phosphate, Pb, Cu, Cd, Co and As and most of the stations categorized as polluted (Class III and IV). Heavy metals like Pb, Cu, Co, Cd and As were higher at upstream river zone and highly polluted nevertheless the downstream zone and surface water were comparatively less polluted. Industrial wastes and effluents increased the contamination levels of the studied water.

Keywords: Contamination, Effluent, Gebeng, Human activities, Heavy metals, Surface water, Water quality

Introduction

Now a day, it is necessary to monitor the change of water status cautiously and prudently, as the civilization is dependent on water resources for versatile needs. In spite of its substantial necessity, it is very much neglected. Surface water plays an important contribution in agriculture, industrial and drinking purposes. Industrial activity is one of the main factors for water pollution.

Industrial practices have been made a huge pressure on sweet water Hu *et al.* (2013). In addition, due to lack of effective treatments and management, the industrial effluents and wastes are degrading the water quality throughout the world. The concentrations of biological oxygen demand (BOD), ammonia-Cal nitrogen (NH3-N), suspended solids (SS), As, Hg, Cd, Cr, Pd and Zn of Malaysian surface water are higher than the permissible limits (My Water, Malaysian Water 2011). A huge industrial dumping is going on in Malaysia which is deteriorating the surface water as well as ground water quality Syukor *et al*. (2013). It is reported that a lot of industries are active in Gebeng industrial estate, Malaysia, that promoting contamination by industrial processes. Therefore, a detailed study was done to identify the pollutants, pollution level and the sources of water pollution in the study area.

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Material and Methods

The sampling stations are situated between 03°56'34"N 103°22'30"E and 03º 59' 1" N 103º22' 40"E. Figure.1 depicts the area and the sampling stations of Gebeng industrial region. A large number of industries are active in Gebeng area, such as metal works factories, steel industries, petro-chemicals, chemicals, palm oil mills, polymer, energy, oil and gas industries, coal mining, concrete industries, concrete ducting and pipe coating facility, chicken food, wood processing, detergent and air product. On the basis of type of industries, topography and discharge points, surface water, upstream river and downstream river sampling stations were selected from the Tungguk River and from the low lying locations of the industrial estate.

Sampling and Preservation

Water samples were collected from July 2012 to June 2013 from three zones. Total of 15 sampling points were selected from 3 zones, where five replications of each sample were taken. There were

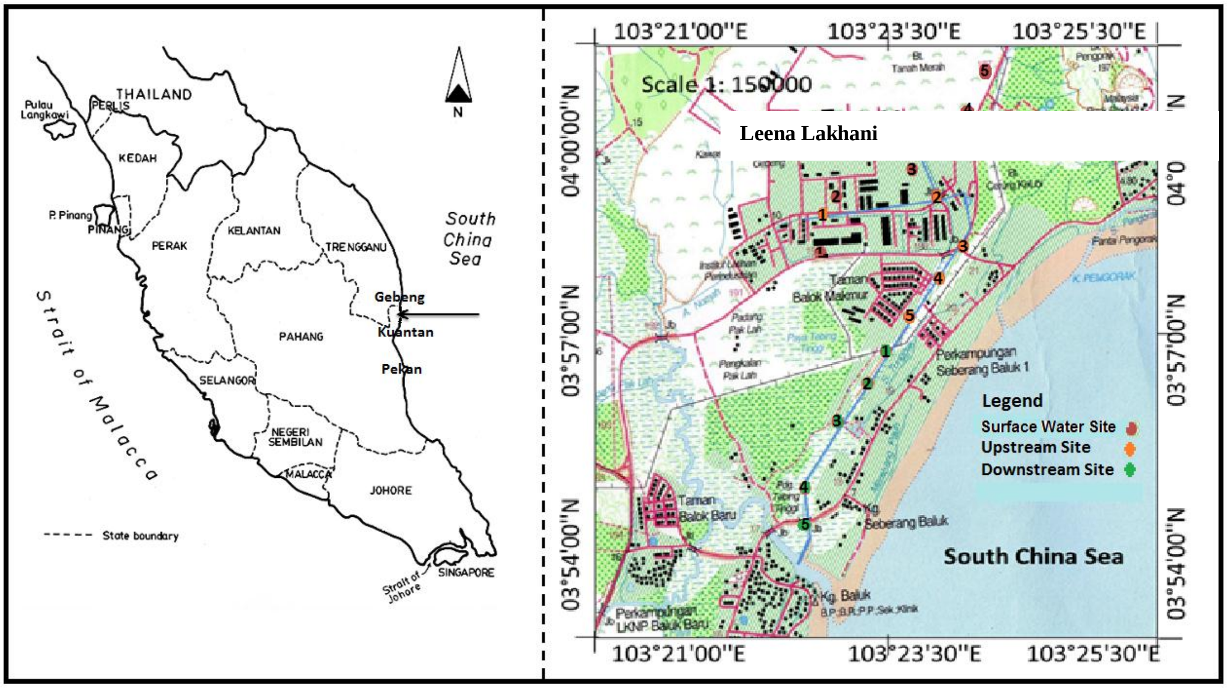

Fig.1 Map of the study area and sampling sites

five stations at surface water (SW), five stations from upstream river water (USRW) and another five stations from downstream river water (DSRW). Water sampling was made according to the standard procedure. Samples were collected approximately from the 10 cm under the surface using 500 ml HDPE bottles. Immediately after sampling, the collected samples were inundated with icebox and later transferred to the laboratory and preserved in a refrigerator at below 4^{o}c temperature. The water samples were collected for BOD determination at dark bottles (300 ml). Campaigns for the collection of surface water were performed on dry (February to August) and wet seasons (October to January). Some parameters such as temperature, dissolved oxygen (DO), electrical conductivity (EC), pH, turbidity and total dissolved solids (TDS) were determined in situ.

Laboratory Analysis

The BOD, COD, TSS, TDS, ammonia Cal-nitrogen, nitrate, sulfate, and phosphate were analyzed by standard methods. The spectrophotometer model HACH DR2500 at specific wave lengths were used for the determination of COD, ammonia Cal-nitrogen, nitrate, sulfate and phosphate (APHA, 2013). Selected heavy metals were determined by using ICP-MS. Furthermore, TSS was analyzed gravimetrically after filtration with an adequate sample through a glass fiber filter and drying at 105^{o}C. BOD was measured as the difference between initial and 5-day readings. All the water samples were analyzed within 7 days of sampling.

Statistical Analyses

Statistical analysis was done by using SPSS software version16.0. Standard deviation and Mean and Correlation analysis (Pearson, 2 tailed) was also made to determine significant correlation among parameters by SPSS software.

Contamination Intensity

Contamination Intensity was calculated to compare with the standard values of different parameters recommended by WHO and Malaysia. The following equation was used to calculate Contamination Intensity (Rao, 2012).

$$CI = \frac{C, S\tan dard}{C, Analysed}$$

The parameter like dissolved oxygen (DO), where the low value indicates the poor water quality. For this, we could named it as the contamination intensity modified (CIm) and can expressed by the following equation.

$$CI(m)=\frac{C,Analysed}{C,Standard}$$

,Where CI(m) refers contamination intensity (modified) and C represents concentration.

Water quality index (WQI):

By water quality is meant as a phenomenon where water quality parameters are compared with the respective standard value. In this study, water quality index was calculated on the basis of the concentrations of DO, BOD, COD, ammonical nitrogen, SS and pH (Haque *et al.* 2010).

WQI= 0.22 × SIDO+ 0.19 × SIBOD+0.16× SICOD+ 0.15 × SIAN+ 0.16 × SISS +0.12 × SI PH, where, SI explains sub index function of the parameters.

Results and Discussion

The concentration of studied parameters and contamination assessment by standard limits (In-Situ Parameters). The studied surface water temperature in dry season varied from 26.53 to 38.34 ^{o}C and the overall mean was 32.62 ^{o}C (Table 1) while in wet season the temperature ranged from 25.70 to 28.79 ^{o}C. The highest average temperature (34.79 ^{o}C) was recorded at upstream river zone in dry season due to the discharge of hot water, effluents from surrounding industries and for climatic conditions.The lowest average temperature was found at downstream river zones (25.70). Saad *et al.* (2008) revealed that the normal water temperatures of Malaysia ranged from 27.00 to 31.00°C. The temperature of studied surface water showed a decline trend from dry season to wet season because of high rainfall. However the average temperature at dry season was recorded

Table 1: Concentrations of water quality parameters in dry seasons with the perspectives of three zones

Parameters	Standard Limits	Surface Water Mean (Range)	Contamination Intensity/Contamination intensity modified	River Upstream Water Mean (Range)	Contamination Intensity	River Downstream Water ,Mean (Range)	Contamination Intensity	Overall Mean (Three zones), (Range)
Temp. ^{o}C	25(WHO)	32.06±2.32 (28.11-38.34)	1.28	34.79±2.06 (28.40-37.39)	1.39	28.02±0.77 (26.53-29.97)	1.12	32.62±5.36 (26.53-38.34)
pH	6.5-8.5 (WHO)	6.59±0.64 (4.28-7.76)	0.88	6.67±0.96 (4.67-7.40)	0.89	7.19±0.56 (6.25-7.76)	0.96	6.59±0.64 (4.28-7.76)
Conductivity (m S/cm)	1 (INWQS)	0.41±0.13 (0.03-0.74)	0.41	2.02±0.40 (1.74-2.48)	2.02	15.26±2.13 (9.25-25.22)	15.26	5.91±2.01 (0.03-14.28)
Turbidity (NTU)	5 (INWQS)	6.8±0.10 (6.70-6.90)	1.36	15.40±1.68 (14.30-17.90)	3.08	9.62±0.93 (8.70-10.60)	1.92	10.61±4.38 (6.70-17.90)
DO (mg/L)	5 (WHO)	3.27±0.10 (3.16-3.35	1.53	1.81±0.29 (1.52-2.10	2.76	2.68±0.30 (2.37-2.84)	1.87	2.59±0.73 (1.52-3.35)
BOD_5 (mg/L)	1 (INWQS)	22.45±1.71 (20.70-24.41)	22.45	28.50±6.52 (20.46-34.25)	28.50	6.37±0.46 (5.90-6.88)	6.37	19.11±11.43 (5.90-34.25)
COD (mg/L)	10 (INWQS)	52.17±10.29 (40.60-60.30)	5.22	102.43±20.73 (87.00-126.00)	10.24	56.5±4.45 (51.6-60.30)	5.65	70.37±27.85 (52.17-102.43)
TSS(mg/L)	25 (INWQS)	15.67±3.51 (12.00-17.00)	0.63	67.33±3.52 (64.00-71.00)	2.69	12.00±2.00 (10.00-14.00)	0.48	31.67±20 (12-67.33)
Ammoniacal-N(mg/L)	0.10 (INWQS)	2.41±0.08 (2.29-2.47)	24.1	2.73±0.07 (2.68-2.80)	27.30	3.64±0.28 (3.26-3.90)	36.40	2.93±0.64 (2.29-3.90)
Nitrate (mg/l)	45 (WHO)	0.15±0.04 (0.11-0.19)	$3.33*10^{-3}$	1.10±0.32 (0.39-1.40)	0.02	0.42±0.16 (0.32-0.66)	$9.33*10^{-03}$	0.56±0.19 (0.15-1.10)
Phosphate (mg/l)	0.20 (INWQS)	4.931±2.11 (1.72-8.80)	24.65	1.76±0.28 (1.48-2.27)	8.8	0.31±0.08 (0.20-0.42)	1.55	2.33±1.27 (0.20-8.80)
Sulphate (mg/l)	250 (WHO)	38.33±2.08 (36-40)	0.15	414±10.82 (402-423)	1.66	666.67±25.14 (560-840)	2.67	373±102.27 (36-840)

above the recommended limits of Malaysia (DOE, 2000).Temperature had a moderate positive correlation with BOD (r=0.676, p=0.025) (Table.7). The pH of the studied surface water varied from 4.28 to 7.76. The average pH value in dry season was recorded at 6.59 whereas it was measured 6.00 at wet season. It was observed that the average pH values rose from rainy season to dry season (Table 1 and Table 2). The pH of the studied surface water varied from 4.28 to 7.76. The studied water was categorized into class V, in accordance with Interim National Water Quality Standards, Malaysia. Etesin *et al*. (2013) worked at Iko River, Nigeria and reported similar findings in their studies. Table 3 illustrates that pH positively correlated with BOD (r=0.748, p=0.013) and Cr (r=0.648, p=0.043). On the other hand, it showed negative correlation with Pb (r=-0.667, p=0.035).

The EC concentration ranged from 0.03-25.22 µS/cm. The average EC was recorded at 5.91 and 0.76 µS/cm in dry season and wet season respectively. The highest average value 15.26 µS/cm was recorded in dry season at downstream river zone due to tidal influence, as the zone was adjacent to the South China Sea (Haris *et al*. 2008). In contrast, the lowest average concentration 0.21 µS/cm was measured at upstream river zone in wet season because the zone was free from tidal intrusion and the availability of rain water. The EC values of downstream river zone belonged to Class IV, while the remaining others zones were within the permissible ranges of INWQS (Interim National Water Quality Standards). EC was observed strong positive co-relation with TDS (r=0.999, p=0.000) and statistically significant at 1% level and a moderate positive co-relation with Sulfate (r=0.664, p=0.036) and Ni (r=0.777, p=0.008). The average turbidity of the studied surface water was determined 10.61 and 169.55 NTU in dry and wet seasons respectively. However it ranged from 6.70-405.40 NTU. The higher average turbidity was found at the downstream river stations because of new industrial developments and subsequently due to highly weathered clayey soils being washed

Table 2: Concentrations of water quality parameters at different zones during wet season

Parameters	Standard Limits	Surface Water Mean (Range)	Contamination Intensity	River Upstream Water Mean (Range)	Contamination Intensity	River Downstream Water ,Mean (Range)	Contamination Intensity	Overall Mean(Three zones), (Range)
Temp. ^{o} C	25 (WHO)	27.26±0.14 (26.39-28.79)	1.09	27.95±0.23 (27.69-28.26)	1.12	27.07±0.71 (25.70-27.93)	1.08	27.43±0.46 (25.70-28.79)
pH	6.5 -8.5 (WHO)	4.92±0.27 (4.41-5.12)	0.66	6.10±0.38 (5.70-6.40)	0.81	6.99±0.54 (6.39-7.46)	0.93	6.001±1.04 (4.41-7.46)
Conductivity (m S/cm)	1 (INWQS)	0.55±0.06 (0.52-0.58)	0.55	0.21±0.04 (0.16-0.24)	0.21	1.52±0.04 (1.49-1.56)	1.52	0.76±0.42 (0.16-1.56)
TSS (mg/L)	25 (INWQS)	15.35± 4.12 (10-23)	0.61	32.00±5.00 (25.00-39.00)	1.28	17.33± 5.13 (13-23)	0.69	28.22± 8.47 (10-39)
Turbidity (NTU)	5 (INWQS)	28.57±1.40 (27.1-29.9)	4.08	93.00±2.00 (91.00-95.00)	18.60	387.07± 15.95 (376.3-405.4)	77.41	169.55± 191.12 (27.1-405.4)
DO (mg/L)	5(WHO)	4.56±0.11 (4.45-4.67)	1.10	3.34±0.55 (2.93-3.97)	1.50	6.30±0.05 (6.25-6.35)	0.79	4.73±1.49 (2.93-6.35)
BOD_5 (mg/L)	1 (INWQS)	11.76±1.21 (10.45-12.86)	1.96	15.01±4.48 (10.08-18.85)	2.50	7.93±0.41 (7.50-8.31)	1.32	11.56±3.54 (0.01-0.27)
COD (mg/L)	10 (INWQS)	19.72±5.78 (10.00-24.00)	1.97	45.10±3.56 (41.30-49.60)	4.51	27.63±7.85 (22.00-36.60)	2.76	30.82±12.98 (19.72-45.10)
Sulphate (mg/L)	250 (INWQS)	41±5.57 (35-46)	0.16	58±3.68 (55-62)	0.23	1213.33±70.24 (1140-1280)	4.85	437±65.27 (35-1280)
Phosphate (mg/L)	0.20 (INWQS)	0.34±0.03 (0.31-0.37)	1.70	2.17±0.48 (1.87-2.73)	10.85	0.24±0.03 (0.21-0.27)	1.20	0.91±0.51 (0.21-2.73)
Ammonium (mg/L)	< 1.0 (INWQS)	1.93±0.46 (1.42-2.50)	1.93	2.03±0.54(1.25-2.70)	2.03	1.70±0.81(0.71-2.50)	1.70	1.89±0.17(1.25-2.70)
Nitrate (mg/L)	>7 (INWQS)	0.21±0.02 (0.19-0.23)	0.03	3.03±0.46 (2.70-3.70)	0.43	1.68±0.43 (1..40-2.30)	0.24	1.64±0.23 (0.21-3.03)

Table 3: Pearson correlation coefficient matrix of studied parameters

	pH	EC	Tem.	TSS	Tur.	COD	BOD	NO3	SO4	PO4	DO	As	Pb	Cd	Co	Cr	Cu	Zn	Ba	NH3-N
pH	1																			
EC	0.86	1																		
Tem.	0.334	-0.228	1																	
TSS	-0.117	-0.148	0.09	1																
Tur.	0.332	-0.047	0.064	0.647	1															
COD	0.421	-0.219	0.412	0.661*	0.715	1														
BOD	0.748	-0.268	0.696*	0.052	0.288	0.714*	1													
NO3	0.445	-0.018	-0.063	-0.572	0.076	-0.329	0.101	1												
SO4	0.459	0.664*	0.373	0.247	0.323	0.286	0.259	-0.09	1											
PO4	-0.324	-0.129	-0.121	-0.286	-0.14	-0.547	-0.471	0.466	-0.274	1										
DO	-0.517	-0.235	-0.392	0.426	-0.238	-0.022	-0.411	-0.748*	-0.364	-0.239	1									
As	-0.378	-0.294	-0.109	-0.178	-0.047	-0.425	-0.44	0.368	-0.384	0.970**	-0.138	1								
Pb	-0.667*	0.222	0.154	-0.143	-0.487	-0.32	-0.341	-0.37	-0.027	0.349	0.061	0.313	1							
Cd	0.229	-0.17	0.513	-0.74	-0.195	0.426	0.615	-0.3	0.007	0.176	-0.036	-0.13	0.32	1						
Co	0.126	-0.29	0.504	0.798**	0.593	0.772**	0.464	-0.39	0.368	-0.175	0.021	-0.073	-0.01	0.309	1					
Cr	0.648*	0.046	-0.091	-0.295	-0.02	-0.119	0.228	0.517	0.09	-0.25	-0.174	-0.354	-0.756*	-0.332	-0.402	1				
Cu	-0.045	0.477	0.161	-0.327	-0.293	-0.166	-0.046	-0.03	0.257	0.38	-0.275	0.295	0.679*	0.551	-0.091	-0.43	1			
Zn	-0.061	0.339	0.309	0.287	0.187	-0.078	-0.218	-0.04	0.621	0.388	-0.159	0.298	0.27	-0.23	0.321	-0.11	0.294	1		
Ba	-0.388	0.536	0.04	-0.008	-0.115	-0.1	-0.233	-0.21	0.291	0.289	-0.209	0.221	0.837**	0.294	0.117	-0.717*	.798**	0.341	1	
NH_3-N	0.619	0.108	-0.06	-0.572	0.074	-0.18	0.292	.901**	0.032	0.051	-0.732*	-0.058	-0.52	-0.242	-0.147	0.674	-0.16	-0.263	-0.315	1

away and mixed with surrounding water bodies (Wilson,2010). According to INWQS, the upstream river water and downstream river water values of wet season contain higher turbidity and categorized in class III while the remaining zones of two seasons were included into class I. Turbidity was positively correlated with TSS (r=0.647, p=0.043) and COD (r=0.715, p=0.020). Dissolved oxygen (DO) content of the studied water was found to be ranging from 1.52 to 6.35 mg/L while the overall average values were 2.59 and 4.73 mg/L in dry and wet seasons respectively. The highest average value (6.30 mg/L) was recorded at downstream river zone in rainy season whereas the least average value (1.81 mg/L) was measured in upstream rive zone in dry season which was grouped into class IV. The result exhibited that the overall mean values of DO ranged from 2.59 to 4.73 mg/L. It's an alarming data for the area. The data denoted that the surface water of the Gebeng industrial estate was heavily enriched with contaminants and organic wastes which were incorporated through industrial dumping and caused high deoxygenation. The similar findings were revealed by Yisa *et al*. (2010) in their studies on Water Quality of River Landzu, Nigeria. DO had moderate negative correlation with nitrate (r=-0.748, p=0.013). The concentrations of studied parameters and contamination assessment by standard limits (Ex situ parameters) High mean biological oxygen demand (BOD) was found at 28.50 mg/L at upper stream stations in dry season, while the lowest mean BOD value was recorded (6.37 mg/L) at downstream river stations. The higher BOD was found due to higher industrial discharges Walakira *et al*. (2011). In dry season comparatively higher BOD was observed than from wet season. Higher temperature and lower precipitation resulted in high BOD, at dry season. The average BOD values of upper river zone and wetlands zone in dry season were recorded above 12.00 mg/L, indicating the zones belonged to class V. Furthermore, downstream river zone in dry season and all zones of wet season were recorded 1.32 to 6.37 mg/L. The overall mean values of two seasons were determined above Malaysian threshold level. BOD exhibited a moderate positive correlation with pH (r=0.748, p=0.013), temperature (r=0.696, p=0.025) and COD (r=0.714, p=0.020). Chemical oxygen demand (COD) concentrations of studied water varied from 10.00 to 126.00 mg/L. The overall mean of COD concentrations were 70.37 mg/L and 30.82 mg/L in dry and wet seasons respectively. During dry season, the high COD was determined at upper stream river zone (102.43mg/L), which gone in class V, while other two zones were belonged to class IV (INWQS). Moreover, it was observed that only the average COD of the surface water zone in wet season was categorized into class II, whereas rest two zones of wet season were classified under class III. The results exhibited that COD increased for middle stations compared to others due to industrial interference.From the correlation analysis it was found that COD had a moderate positive relation with TSS (r=0.661, p=0.037), turbidity (r=0.715, p=0.020), BOD (r=0.714, p=0.020) and Co (r=0.772, p=0.009). The total suspended solids (TSS) of studied water were found to vary from 15.35 to 67.33 mg/L (Table 1 & Table 2). The average TSS of the studied water found 31.67 and 28.22 mg/L in dry and wet season respectively. The highest average TSS (67.33 mg/L) was observed at dry season in upper stream river zone, none the less the lowest average value was found (12.00 mg/L) at downstream river zone in dry season. According to the INWQS the critical level of TSS values for the surface water of Malaysia varies from 25 to 50 mg/L. The average TSS contents of upper river zone were above Malaysian critical limits. Water having high TSS is not suitable for drink as well as it is harmful for health (Vinod & Chopra 2012). It was found from the study that TSS was positively correlated with Turbidity (r=0.647, p=0.043), COD (r=0.661, p=0.037) and Co (r=0.798, p=0.006).The ammonical-nitrogen were found to range from 1.42 to 3.90 mg/L (Table 1 and Table 2). The average values were 2.93 mg/L and 1.89 mg/L for dry and wet season respectively. The high average concentration 3.64 mg/L was recorded at downstream river water in dry season while the least average value was recorded at downstream river zone in wet season. In dry season, the upstream and downstream river zone was categorized into class V while rests of the other zones in both seasons were classified under class IV (in accordance with INWQS). For supporting aquatic life, the threshold value of ammonical nitrogen for Malaysian surface water is 0.90 mg/L. From the statistical analysis it was found that ammonical N was positively correlated with dissolved oxygen (r=0.668, p=0.0350), but negatively correlated with pH (r=-0.760, p=0.011) and nitrate (r=-0.761, p=0.0110). In general, nitrateis derived from the decomposition of organic matter by bacterial activity. It was found to be ranging from 0.11 to 3.70 mg/L. The average nitrate value was determined at 0.56 mg/L and 1.64 mg/L in dry and wet season respectively (Table 1 and Table 2). The highest average value 3.03 mg/L was found at upstream river zone in wet season whereas the lowest average value was detected 0.15 mg/L at surface water in dry season. The nitrate contents of all zones in two seasons were categorized under class V. Das *et al*. (2003) studied the lotic water quality in Cuttack, India and found nitrate content were above permissible level. Nitrate of the studied samples negatively correlated with DO (r=-0.748, p=0.013). The phosphate (PO_4^{3-}) levels of studied water varied from 0.21 to 8.80 mg/L and the overall mean values were 2.33 mg/L and 0.91 mg/L in dry and wet season respectively (Table 1 & Table 2). The highest mean value was recorded for surface water (4.931 mg/L) in dry season while the least average value was determined at upper river zone in wet season. The phosphate concentrations in the upstream river were found to be higher due to waste of detergent industries (Goltman, 1975). Excess phosphate in water may cause eutrophication and can reduce DO content. Correlation analysis showed that phosphate has a significant positive relationship with As (r=0.970, p=0.000). The sulfate ($SO_4^{=}$) concentrations of present study varied from 35.00 to 1280.00 mg/L. The overall mean concentrations were 373.00 mg/L and 437.00 mg/L in dry and wet seasons respectively. The average highest sulfate content 1213.33 mg/L was found in downstream river zone in wet season. In the study area, sulfate was contaminated through waste discharges; coal burning, fossil fuel and combustion processes. Meays *et al*. (2012) worked in British Colombia, Canada and stated that sulfate incorporated in water by anthropogenic activities such as melting, coal mining, pulp and paper industries. According to

INWQS guideline, 250 mg/L concentration of sulfate is suitable for the lives of water bodies. The average sulfate values of all zones in both seasons were recorded above INWQS guideline value. Sulfate was positively correlated with EC (r=0.664, p=0.036) and TDS (r=0.665, p=0.036).

Heavy Metal Status

The heavy metals concentrations are presented at Table 4 and Table 5. The average arsenic (As) content of the studied water samples were 0.0617 mg/L and 0.0208 µg/g in dry and wet season respectively. The highest average of As was observed at 0.0745 µg/g in upstream river water in dry season (Table 5). Arsenic pollution was caused due to metal melting, burning fossil fuel and timber treatment. Rosario & Paula (2012) studied on surface and ground water in Portugal and found the industrial activities were responsible for As pollution. It showed that As concentrations of surface water and upstream river water in dry season were above Malaysian permissible limits while the downstream river stations and the all stations of wet seasons were recorded within the Malaysian limit. Arsenic was found to have a strong positive correlation with phosphate (r=0.970, p=0.000) and significant at 1% level. The average Barium (Ba) concentrations of the studied water sample were 0.0753 µg/g and 0.3193 µg/g in dry and wet season respectively and it was found to be ranging from 0.0427 to 0.4921 µg/g. The highest result 0.1938 µg/g was determined at wet season in downstream river water, because the industrial wastes having Ba accumulated at this zone, while the lowest value 00.0359 µg/g was observed at surface water stations in wet season. From the data it was observed that the Ba contents of all stations were in natural levels that included in class I of INWQS. In the study, correlation analysis showed that Ba had a positive relationship with Pb (r=0.837, p=0.003), Cu (r=0.798, p=0.006) and negative relationship with Cr (r=-0.717, p=0.020).The average cadmium (Cd) content of the water of the study area was 0.0283 µg/g and 0.0093 µg/g in dry and wet season respectively. The highest average value 0.0308 µg/g recorded at downstream river zone in dry season, while the lowest value 0.0016 µg/g was observed in downstream water in wet season. From the results it was found that the Cd concentrations of all stations were higher at dry season especially in upstream river water samples. Due to dry condition and the lesser precipitation, industrial activities and especially with the availability of the inflow of effluents had caused the contamination of Cd Wogu and Okaka (2011). According to INWQS, the Cd values of all zones in dry season and the surface water sites at rainy season were categorized into class V. However, the Cd showed no correlation with studied parameters.The Cobalt (Co) concentration of the studied water varied from 0.1508 to 0.8251 µg/g. The average concentrations were 0.5007 and 0.4034 µg/g in dry and wet season respectively. The highest average 0.7179 µg/g Co content was recorded at upstream river zone in dry season. Co concentrations increased due to wastes of catalyst used in industries, alloy, paints, power plants, grinding and cutting tool factories. According to INWQS, the Co content of all zones was determined above permissible limits. From the correlation analysis it showed that Co had a positive relation on TSS(r=0.798, p = 0,006) and COD (r=0.772, p=0.009). The chromium (Cr) content of water samples ranged from 0.0296 to 0.1805 µg/g. The average Cr (Table 4 and Table 5) concentrations were determined at 0.0538 and 0.0949 µg/g at dry and wet seasons respectively. The heaviest Cr concentration was measured in upstream river zone in wet season. The Cr content of upstream river water in both seasons was detected above INWQS standard limit of Malaysia. Nadeem-ul-Haque *et al*. (2009) recorded extremely higher Cr content in surface and ground water of the industrial areas of Karachi, Pakistan. Cr was positively related with pH (r=0.648, p=0.043), and negatively correlated with Pb (r=-0.756, p=0.011) and Ba (r=-0.717, p=0.020). The average Cupper (Cu) concentrations of present study were 0.2523 µg/g and 0.2044 µg/g at dry and wet seasons respectively. It varied from 0.0124 to 0.6419 µg/g. The higher Cu value was observed in upstream river zone due to dumping of industrial wastes like coal. Wogu & Okaka (2011) observed higher Cu pollution was due to industrial activities, in surface water of Warri River, Nigeria. In accordance with INWQS, the average Cu concentration was recorded higher in upstream river zone in dry season.

Table 4: Contents of selected heavy metals in dry seasons

Parameters	INWQS	Surface Water Mean (Range)	Contamination Intensity	River Upstream Water Mean (Range)	Contamination Intensity	River Downstream Water ,Mean (Range)	Contamination Intensity	Overall Mean (Range)
As (µg/gm)	0.0500	0.0601±0.0137 (0.0544-0.0618)	1.20	0.0745±0.01 (0.0688-0.0893)	1.49	0.0423±0.0138 (0.0339-0.0451)	0.85	0.0617±0.0172 (0.0339-0.0893)
Ba (µg/gm)	1.0000	0.0691±0.0058 (0.0634-0.0749)	0.06	0.0427±0.0078 (0.0431-0.0503)	0.04	0.1140±0.1459 (0.0294-0.2825)	0.11	0.0753±0.0361 (0.0427-0.114
Cd (µg/gm)	0.0100	0.0271±0.0053 (0.0212-0.0316)	2.71	0.0308±0.0018 (0.0293-0.0329)	3.08	0.0269±0.0052 (0.0208-0.0303)	2.69	0.0283±0.0022 (0.0212-0.0329)
Co (µg/gm)	0.1100	0.5446±0.1634 (0.3572-0.7168)	4.95	0.7179±0.0910 (0.6191-0.8251)	6.53	0.0585±0.0585 (0.1803-0.3201)	0.53	0.5007±0.2422 (0.1803-0.8251)
Cr (µg/gm)	0.0500	0.0466±0.0166 (0.0296-0.0644)	0.93	0.0713±0.0111 (0.0575-0.0814)	1.43	0.0456±0.0065 (0.0393-0.0532)	0.91	0.0538±0.0151 (0.0296-0.0814)
Cu (µg/gm)	0.0500	0.0266±0.014756 (0.0133-0.0437)	0.53	0.5218±0.084736 (0.4496-0.6419)	10.44	0.3583±0.0272 (0.1729-0.5982)	7.17	0.2523±0.2523 (0.0133-0.6419)
Pb (µg/gm)	0.0499	0.4879±0.1527 (0.3561-0.7756)	9.78	0.6904±0.1588 (0.4898-0.8475)	13.84	0.4402±0.1590 (0.2561-0.6847)	8.82	0.5395± 0.1328 (0.2561-0.7756)
Zn (µg/gm)	5.0000 mg/L (Canada)	0.8981±0.0977 (0.8097-1.003)	0.18	1.2614±0.3956 (0.8404-1.943)	0.25	0.9612±0.1034 (0.8675-1.0721)	0.19	1.0402±0.1942 (0.8981-1.2615)

Table 5: Concentration of selected heavy metals at different zones during wet seasons

Parameters	INWQS	Surface Water Mean (Range)	Contamination Intensity	River Upstream Water Mean (Range)	Contamination Intensity	Downstream River Water ,Mean (Range)	Contamination Intensity	Overall Mean (Range)
As (µg/gm)	0.0500	0.0204±0.0173 (0.0156-0.0395)	0.41	0.0359±0.0182 (0.0217-0.0407)	0.72	0.0203±0.0104 (0.0162-0.0218)	0.41	0.0208±0.0173 (0.0161-0.0475)
Ba (µg/gm)	1.0000	0.0359±0.0083 (0.0269-0.0433)	0.04	0.0516±0.0494 (0.0214-0.1087)	0.05	0.1938±0.2587 (0.0297-0.4921)	0.19	0.3193±0.0869 (0.0214-0.4921)
Cd (µg/gm)	0.0100	0.0224±0.0039 (0.0198-0.0269)	2.24	0.0041±0.0017 (0.0024-0.0058)	0.41	0.0016±0.0005 (0.0011-0.0021)	0.16	0.0093±0.0114 (0.0016-0.0224)
Co (µg/gm)	0.1100	0.4501±0.0489 (0.4304-0.5227)	4.09	0.5723±0.1065 (0.4181-0.6625)	5.20	0.1876±0.0272 (0.1508-0.2149)	1.71	0.4034±0.1967 (0.1508-0.6625)
Cr (µg/gm)	0.0500	0.0357±0.0068 (0.0264-0.0421)	0.71	0.1320±0.0327 (0.1095-0.1805)	2.64	0.1171±0.0129 (0.1044-0.1313)	2.34	0.0949±0.0518 (0.0264-0.1805)
Cu (µg/gm)	0.0500	0.0226±0.0087 (0.0124-0.0337)	0.45	0.3449±0.0438 (0.3126-0.4078)	6.89	0.2458±0.0968 (0.1329-0.3496)	4.92	0.2044±0.1651 (0.0124-0.4078)
Pb (µg/gm)	0.0499	0.1306±0.0151 (0.1234-0.1479)	2.62	0.3017±0.0278 (0.2713-0.3298)	6.05	0.1235±0.0049 (0.1199-0.1291)	2.47	0.1852±0.1009 (0.1199-0.3298)
Zn (µg/gm)	5.0000	0.1095±0.0297 (0.0874-0.1433)	0.02	0.1485±0.0266 (0.1187-0.1698)	0.03	0.1604±0.0676 (0.0892-0.2237)	0.03	0.1394±0.0266 (0.1095-0.1604)

The statistical analysis showed that Cu was positively correlated with Pb (r=0.679, p=0.031) and Ba (r=0.798, p=0.006). Lead (Pb) content of the studied water samples was found to vary from 0.1199 to 0.8475 µg/g. The mean value was 0.5395 µg/g and 0.1852 µg/g in dry and wet seasons respectively. The high average Pb value 0.6904 µg/g was recorded at upstream river zone due to industrial activities, while the lowest result 0.1235 µg/g was observed at downstream river zone in wet season. Nadeem-ul-Haque *et al*. (2009) studied on water of the industrial areas of Karachi, Pakistan and detected high Pb. The concentration of Pb for all stations was categorized as class IV in accordance with INWQS. The study exhibited that Pb content of studied surface water was positively correlated with Ba (r=0.837, p=0.003) and Cu (r=0.679, p=0.031) and negatively correlated with pH (r=-0.667, p=0.035) and Cr (r=-0.756, p=0.011). Zinc (Zn) concentration of studied water samples ranged from 0.0874 to 1.943 µg/g. The average values were at 1.0402 µg/g and 0.1394 µg/g in dry and wet season respectively. The data showed that Zn content of all stations was within the permissible limit and the studied surface water was not polluted with Zn. It was categorized as class II and I, in accordance with INWQS. In this study, Zn exhibited no correlation with any other parameters.

Contamination Intensity of the studied parameters comparison with standard values: Contamination intensity of different parameters is presented at Table 1, Table 2, Table 4 and Table 5. In dry season, the contamination intensity was comparatively higher than the rainy season. It was found that temperature; turbidity, BOD, COD, ammonical nitrogen and phosphate showed the value higher than 1 in both dry and wet seasons for surface water samples. For upstream river water, it has exhibited that the temperature, turbidity, TSS, BOD, COD, ammonical nitrogen and phosphate were recorded above 1 in both seasons. At downstream river water temperature, electrical conductivity, turbidity, BOD, COD, ammonical nitrogen, phosphate and sulfate were measured higher than 1 while in wet season the contamination intensity of pH, TSS and nitrate were observed below 1. Never the less, all other studied parameters were found higher than 1.In this study, Phosphate, ammonical nitrogen, BOD, COD were observed as having high pollution intensity. In dry season, contamination intensity of As and Co was illustrated more than 1 for wetland water and upstream river water but less than 1 in downstream river water. In addition, Ba and Zn were found to have a lower pollution intensity that indicated the studied waters were not contaminated by those metals at both seasons. Pb was detected to be badly contaminated as the intensity value showed above standard limit in all three zones in both seasons. Cd exhibited the contamination intensity value higher than 1 in all three zones in dry season, but for wet season it showed higher than 1 for wet land surface water while the other two zones determined lower than 1 in pollution intensity. Cr contamination intensity value indicated that upward river zone was above the recommended level while the other two zones were found near the standard value for dry season; whereas Cr contamination intensity was detected below 1 at wet land water. Only in the surface water zone, Cu intensity was below 1 whereas other two zones were above 1 for both seasons. For DO, having low value indicates bad water quality. So for DO, we used the second equation for contamination intensity calculation. The ontamination intensity (modified) values for DO was found higher than 1 for all zones in both seasons except at downstream river water in wet season.

Water quality parameters and Water quality index

Average water quality parameters such as pH, DO, BOD, COD, ammonical nitrogen and total uspended solids were used for WQI calculation. The studied waters were classified on the basis of DOE-WQI values. Table 6 and Table 7 represent water quality parameters for water quality index and water quality classification of the studied water. It was illustrated that all stations of surface water zone were categorized into class III (polluted).

Table 6: Average water quality parameters for WQI at different stations

Station	Location	pH	DO (%)	BOD (mg/L)	COD (mg/L)	Ammonical Nitrogen (mg/L)	SS (mg/L)
SW1	03º 59' 1" N 103º22' 40"E	6.19	41.86	19.71	39.99	2.51	16.88
SW2	03º 59' 11" N 103º22' 47"E	5.87	46.54	20.57	48.09	2.37	14.97
SW3	03º 59' 37" N 103º24' 46"E	6.09	44.20	22.17	55.02	2.39	16.22
SW4	03º59'10.92"N 103º47.28"E	5.69	46.28	20.02	40.62	2.40	15.43
SW5	03º59 '16"N -103º 23' 18"E	5.51	41.71	17.62	35.91	2.31	14.98
USRW1	03°88' 55" N 103° 19' 20"E	5.28	25.35	29.22	107.51	2.76	61.58
USRW2	03º 58'34" N 103º23' 17" E	5.87	36.79	25.08	89.93	2.55	54.16
USRW3	03º 58' 33" N 103º23' 24"E	6.02	38.48	26.02	76.09	2.51	50.71
USRW4	03º58'13"N-103º23'23E	6.75	50.83	27.49	70.55	2.38	49.83
USRW5	03º57'54"N 103º23'23"E	6.95	53.04	26.77	63.99	2.43	51.09
DSRW1	03º57'40" N103º23'15"E	7.02	71.89	6.92	51.84	3.63	20.34
DSRW2	03º57'33.5" N103°21'52"E	6.96	80.34	9.17	48.92	2.79	22.69
DSRW3	03º57'19 "N 103°22'59"E	6.78	75.27	7.04	46.18	3.07	19.42
DSRW4	03°56'55" N -103°22'19.7"E	6.62	80.99	6.94	37.57	2.85	12.97
DSRW5	03°56'34"N 103°22'30"E	6.57	76.57	10.06	40.52	2.93	13.81

Table 7: Studied water classification based on DOE-WQI

Monitoring station	Calculated WQI value	Water Class	Monitoring station	Calculated WQI value	Water Class
SW1	58.28371	III	USRW4	56.19393	III
SW2	59.19362	III	USRW5	57.18834	III
SW3	57.88067	III	DSRW1	72.69117	III
SW4	59.02838	III	DSRW2	74.63294	III
SW5	58.54253	III	DSRW3	74.6998	III
USRW1	42.49405	IV	DSRW4	77.26208	II
USRW2	49.8384	IV	DSRW5	73.62601	III
USRW3	51.1117	IV			

Moreover, among the five sites of upward river zone, first three (USRW1, USRW2, USRW3) belonged to class IV (highly polluted), because these stations were affected by industrial dumping, whereas the remaining two stations were categorized into class III (polluted). In addition, for downstream river waters all stations except DSRW4 were classified in group III, while DSRW4 belonged to class II.

Conclusion

From the study it was revealed that the pH of studied surface water was neutral to extremely acidic. EC was included within the recommended standard. It showed that the studied water having higher BOD, COD, NH_3-N, NO_3^-, PO_4, Pb, Cd, Cu, Co and lower DO. Moreover, higher TSS and turbidity were found at upper river zone, due to industrial dumping. Furthermore, the amount of BOD and COD were determined comparatively high in river upward zone. Considering all results and data it could be said that the sites and zone located at the vicinity of industries contain higher contaminants and the concerned surface water were contaminated by industrial pollutants. However, the results differed on the basis of season, types of industries and sea water intrusion. The physico-chemical parameters and the studied results indicated that the industries such as catalyst using industries, petrochemicals, chemicals, metal builders and others had been caused by heavy metals contamination. The study also revealed that emphasis should be given on proper treatment of industrial effluents and wastes to reduce the pollution status. In addition, sustainable industrialization approaches have to be taken for preservation and protection of surface water.

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