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Grain Size Distribution and Its Relation to the Geochemical Parameters in the Chemical and Petrochemical Complex of Vadodara District of Gujarat, India

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Abstract

Grain size of sediments has an important relationship with the infiltration rate of water and rate of surface run off. Hence, it is essential to analyze the connection between different textures and geochemical parameters. In the present study, numbers of shallow cores of soil samples were taken along the river Mini flowing in the northern part of Vadodara district of Gujarat, India. Ground water samples were also acquired from the same region. Parameters like iron and nitrite were analysed both in different layers of the shallow cores and groundwater. It was inferred from the analysis that location of industries and the path of river Mini had important contribution in the pattern of the concentration of parameters both horizontally and vertically.

Keywords: Grain size, geochemical parameter, correlation.

Introduction

The grain size of the sediments is an important aspect because it determines the rate of runoff and capacity of infiltration of water. With the increasing grain size, the rate of infiltration increases and rate of surface runoff decreases, while decreasing grain size restricts higher rate of infiltration and supports greater surface runoff. The concentration of different parameters in the grains depends upon their size apart from the depositional environment, anthropogenic and lithologic sources and mineralogical composition of the sediment[1]. The infiltration rate is particularly affected by grain size of the sediments, amount of rainfall and aquifer condition[2,3]. Surface, subsurface water and soil quality is much susceptible to solid wastes and effluents in the industrial region which is also controlled by sediment size distribution to a great extent. Grain size distribution and its impact on the concentration of elements have been undertaken by many scientists. Heavy metals like Zn, Cd, Al, Mg, Ba, Pb, Mo, Fe, Cu, Co, Ni, Cr and As were analysed in surface sediment of the Ismit Bay, Turkey and it was found that, the northern coast was heavily polluted by industrial and domestic wastes[4]. Study on level of major elements in sediments of Ria de Vigo in Galice in north western Spain showed that, particle size as well as industrial, urban and rural waste dumping sites plays an important role in the level of metal concentration in the sediment[5]. The effect of grain size distribution on heavy metal content in the soil through factor analysis and correlation in Chebachji Lake in south of western Siberia of Russia depicted an inverse relationship between the sediment particle size and element content in the soil[6]. In the study of concentration of toxic heavy metals (Ni, Cu, Cd, and Pb) in the sediments of Dongping Lake in China it was found that the absorption of substances increased with the decrease in grain size[7]. The study on the concentration of the Cu, Cr, Pb, Zn and Ni in <63 µm grain size in urban areas of southern Brazil inferred that heavy metals could be transferred quite rapidly on the impermeable surfaces[8]. Suspended material concentration in grain size distribution and their association with heavy metal concentration on the left bank of Kojour River, Iran was analysed by using multivariate regression analysis and bivariate[9]. High concentration of Pb, Cd, Zn and Cr were observed in coastal sediments of the Bay of Bengal, India[10]. The concentration of trace metals in sediments was analysed in Ennore Creek of Chennai, India and high level of Fe, Cr, Cu, N, Pb and Zn was noted in finer sediment [11]. Si, Al, Fe, Mn, Cu, Zn and Cr concentration in the sediments of Damodar River, India were analysed and it was observed that the level of heavy metals tended to increase as the size of the grains got finer[12]. The core sediment in Achankovil river basin of India showed that concentration of heavy metal increases with an increase in depth[13]. Geochemical parameters of groundwater like pH, conductivity, TDS, total hardness, alkalinity, Na, K, Ca, Mg, Cl, Cu, Zn, Fe and As were analysed in the Budhi Gandak belt in Muzaffarpur district, India. It was found that iron and arsenic were found above the permissible limit of WHO[14]. Similar kind of studies showed concentration of different parameters was above the permissible limit[15-18].

Vadodara district of Gujarat, India, has a number of chemical and petrochemical industries. A number of such chemical industries are located in the northern part of Vadodara City and on the south of river Mini which is a tributary of river Mahi. These chemical and petrochemical industries encompass Nandesari Gujarat Industrial Development Corporation (GIDC), Indian Petro Chemical Complex Limited (IPCL), Jawahar Nagar and Gujarat State Fertilisers and Chemical Limited (GSFC). The industrial wastes generated by these industries, is dumped in the open space and the effluents are released in the effluent channels from IPCL and Nandesari GIDC to river Mini which finally find its path to Gulf of Cambay[19]. Thus, it is necessary to evaluate the relationship between the grain size distribution and concentration of chemical parameters in groundwater and soil. In the present study, such attempt has been made and the relationship is evaluated near the chemical and petro chemical complex of Vadodara district of Guajrat.

Material and Methods

Study Area: The present study focuses upon a selected part along the river Mini which is nearer to the industrialized belt of Vadodara district of Gujarat, India. The area encompasses many chemical and petrochemical industries. In the north, it is bounded by Savli taluka of Vadodara district while Vadodara Urban Agglomeration is towards the south. In the west, the area extends upto river Mahi. Nandesari GIDC is spread over an area of 2.06 sq. km[20]. There are about 250 small and medium units which largely produce a number of chemicals, pharmaceuticals, dyes, pesticides, plastics etc.[21]. Deepak Nitrite Limited in Nandesari produces sodium nitrate, sodium nitrite, calcium nitrate, calcium nitrite, potassium nitrate and potassium nitrite etc.[22]. GSFC is another major complex and is spread over 3.21 sq. km.[20]. Rock phosphate, sulphur and liquid sulphur, ammonia, phosphoric acid, benzene, methyl, ketones, sulphuric acid, hydrochloric acid, potassium nitrate and sodium nitrate etc. are some of the other finished products produced by GSFC[23]. IPCL (now owned by Reliance Industries) produces benzene, carbon fiber, caustic soda, chlorine etc.[24]. Gujarat Refinery in Jawaharnagar is the largest refinery of IOCL and generates liquefied petroleum gas, auto and natural gas, petrol, gasoline, gas oil, jet and marine fuel, bitumen, petrochemical special product and crude oil[25].

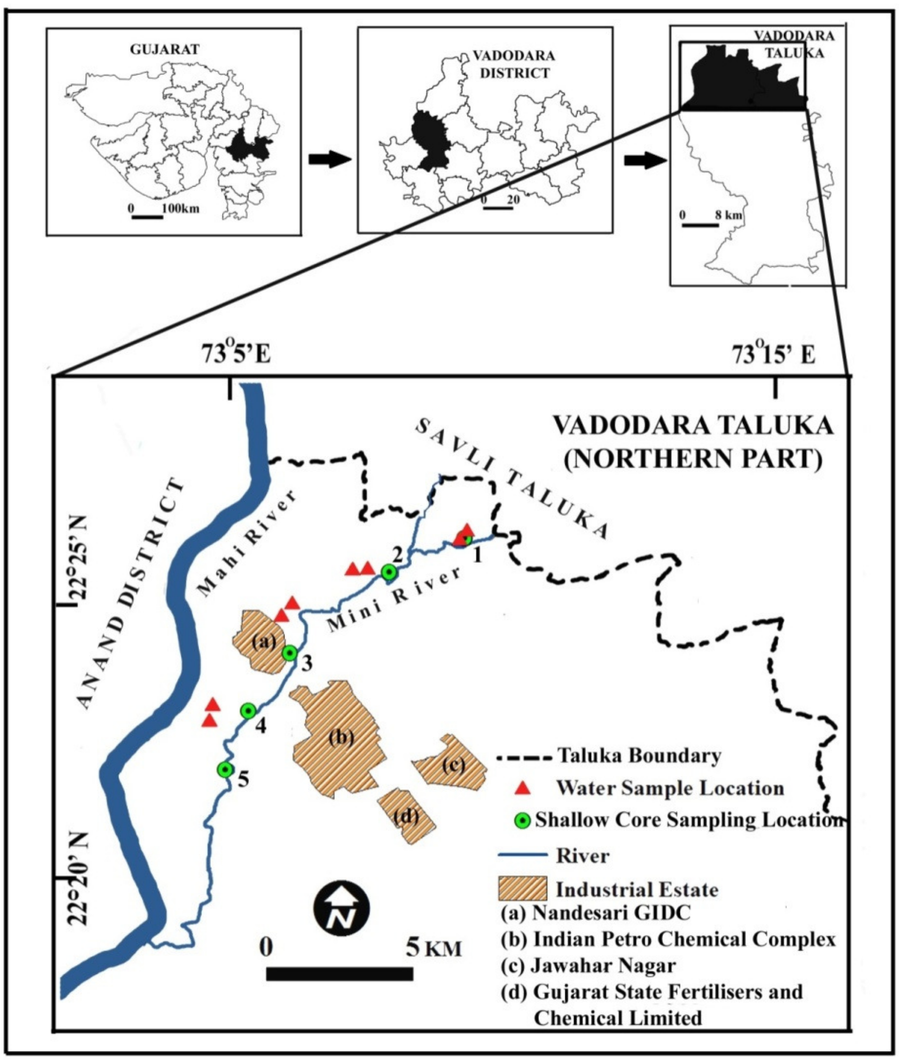

Figure-1
Study Area

Methodology: Sample collection and analysis: Five sampling locations were selected along the path of river Mini. During the selection of the sampling locations, equal distance between the samples was taken into consideration. The sampling locations were marked by using handheld GPS (Garmin eTrex Vista). PVC (Polyvinyl Chloride) pipes with 3 inch diameter were used for coring (figure-2). Initially, the surface area was cleared and the pipe was held vertically. At the top of the pipe, a thick piece of wood was kept and continuous hammering has been done on it so that the pipe can penetrate into the subsurface. After collection of the sample, the pipe was capped from both the sides to restrict its contact with the air. The pipe was cut longitudinally along with the core by using stainless steel saw. One portion of the core was kept along with the pipe by wrapping it tightly using high grade clean film under low temperature for future purpose. Other portion was sub-sampled by using stainless steel saw latitudinally at 1 inch interval. Each of the portions of the sub-samples was retained in the zipped polytheline bag. The sample of 0-1 inch, 4-5 inch and 8-9 inch of depth were selected for grain size analysis through the standard wet sieving method[26]. Groundwater samples were collected from the open tube well (table-4). 500 ml polyethelene bottle tied with weight on one end and a rope on the other end was used to collect the samples from the wells. After the collection of the samples, it was acidified with HCl and kept in the capped polyethelene bottles. Iron and nitrite were analysed by standard colourimetric technique through the 1,10 Phenanthroline method[27] and Cadmium Reduction Methods[28] using Elico Double beam UV/Vis spectrophotometer (Sl-210) in the laboratory of Department of Geography, Faculty of Science, The M. S. University of Baroda. The results obtained from the analysis were used in the statistical software of Origin for diagrammatic representation and ARC GIS 10 was used for the mapping.

Figure-2
Coring for soil sample collection

Results and Discussion

Grain size Distribution: On an average, clay comprised of more than 50% of the total quantity of samples. However, the average percentage of clay was slightly less (44.90%) in the intermediate zone. Thus, clay was found dominantly in the entire region (table-1). One-third of the sediments consisted of silt (36.53 %). But the zone between 4-5 inch, where the percentage of clay was low, the proportion of silt was higher (41.26%). Clay and silt together contributed to more than 90% of the total sediments. The percentage of the sand was least (~10%). Spatial variations were observed in the characteristics of sediments. The percentage of clay in the immediate layer (0-1 inch of depth) increased from 60-76 % downstream (table-1. a). A volte-face was observed with silt where a decrease in the percentage (31.87% to 13.85%) was evident downstream. In this direction, point 2 was the only exception where the proportion of the clay (27.35%) was much lower than that of the silt (65.55 %). Although dominance of clay was evident in the intermediate layer but some variations were spotted. The average clay percentage was lower (44.90%) and decreased downstream from 65.37% to 56.43% (table- 1.b). However, some fluctuations were observed in the intermediate parts. The average silt amount increased (41.26%) in the intermediate layer. Never the less, fluctuations were observed in the proportion of silt (table-1b). The maximum intensity of clay (80.58%) was noted in sampling location 2 and the minimum (11.84%) at the adjacent point (sampling location 3). Later, it again increased to 55.91% in sampling location 4. The lowest layer of the soil (8-9 inch of depth) was characterised by higher percentage of clay (56.28%) while silt and sand percentages were lesser (34.86% and 8.86%) (table-1.c). The maximum clay percentage (85.18%) of the lowest layer was observed downstream while the percentage of silt was lowest in this layer. The highest percentage of silt (56.69%) was noted in sampling location 3. Its percentage decreased from this point both downstream and upstream. The sand percentage was least (~10%) in all the layers of the region with middle layer of the sampling location 3 being the only exception.

Distribution of Iron in Subsoil: In all the three layers the concentration of iron in subsoil along the river increased downstream (table-2). In the upper most layer (0-1 inch of depth) the level of iron gradually increased from 2.13 to 55.64 mg/kg with the average concentration of 43.39 mg/kg. The concentration of iron ranged between 5.87 mg/kg to 43.14 mg/kg in the intermediate layer (4-5 inch of depth).While the average iron level (24.75 mg/kg) in this layer was lower than average iron level of upper layer (0-1 inch depth) as well as bottom layer (8-9 inch of depth). In the deepest layer, the level of iron varied between 3 mg/kg to 21 mg/kg with an average concentration of 29.18 mg/kg.

Table-1a
Distribution of grain size immediate layer (0-1 inch)

Sample Location	Sand%	Silt%	Clay%
1	8.10	31.87	60.03
2	7.10	65.55	27.35
3	6.22	29.35	64.43
4	5.16	26.81	68.03
5	10.11	13.85	76.04
Average	7.34	33.49	59.18

Table-1b
Distribution of grain size intermediate Layer (4-5 inch)

Sand%	Silt%	Clay%
7.22	27.41	65.37
6.08	80.58	13.34
34.80	11.84	53.36
8.07	55.91	36.02
13.03	30.54	56.43
13.84	41.26	44.90

Table-1c
Distribution of grain size Bottom (8-9 inch)

Sand%	Silt%	Clay%
10.29	29.01	60.70
6.23	48.41	45.36
11.29	56.69	32.02
2.83	39.01	58.16
13.67	1.15	85.18
8.86	34.86	56.28

Source: Computed

In sampling locations 2, 4 and 5, the maximum level of iron in subsoil was observed at the upper most layer (0-1 in of depth). Here, the concentration of iron was 21.83 mg/kg, 52.64 mg/kg and 55.64 mg/kg respectively (table-2). Lowest concentration was found at the deepest layer except sampling location 3 with concentration of 101.15 mg/kg at 8-9 inch of depth. In the entire region sampling location 1 had the least concentration of iron but comparatively higher concentration was observed at the intermediate layer while bottom layers had lower concentration of iron except sampling location 3.

Table-2
Concentration of iron in sediments

Sample Location	Immediate Layer	Intermediate Layer	Bottom Layer	Average
1	2.13	5.87	3.16	3.72
2	21.83	7.71	4.43	11.32
3	84.44	50.51	101.15	78.70
4	52.93	16.53	15.58	28.35
5	55.64	43.14	21.6	40.13
Average	43.39	24.75	29.18	32.44

Source: Computed

Distribution of Nitrite in Subsoil: Among all the sampling locations, average concentration of nitrite was noted in the immediate layer (table-3). In the upper most layer (0-1 inch of depth) the highest average concentration of nitrite was 62.67 mg/kg and lowest 27.67 mg/L was observed at the bottom most layer. The concentration of nitrite in immediate and the bottom most layer of subsoil increased downstream along the river (table-3). The average concentration of nitrite in the intermediate layer was 36.96 mg/kg.

Table-3
Concentration of nitrite in sediments

Sample Location	Immediate Layer	Intermediate Layer	Bottom Layer	Average
1	56.25	50	12.5	39.58
2	63.39	31.25	16.07	36.90
3	51.78	36.6	39.28	42.55
4	77.67	50.89	33.03	53.86
5	64.28	16.07	37.5	39.28
Average	62.674	36.962	27.676	42.44

Source: Computed

Sampling location wise concentration of nitrite depicted that sampling location 4 had highest average concentration (53.86 mg/kg). In all the sampling locations, immediate layer showed highest concentration of nitrite while in the bottom most layer, concentration was less except in the sampling locations 3 and 5.

Concentration of Iron and Nitrite in Groundwater: The dilution of nitrite in ground water ranged between 20.54 mg/l to 113.3 mg/l with an average concentration of 57.56 mg/l and standard deviation of 44.18. Highest absorption of nitrite was observed (113.30 mg/l) at sampling location 2 while the lowest level was recorded at sampling location 3 (20.54 mg/l). The level of iron in groundwater ranged between 0.34 mg/l to 2.33 mg/l (table-4). 1.10 mg/l was the average concentration with high standard deviation of 0.89. Sampling location 3 had maximum level of iron (2.33 mg/l) in groundwater whereas least was noted in sampling location 2 (0.34 mg/l).

Correlation between Grain size Distribution and Groundwater Parameters: Karl Pearson correlation was used to calculate the relationship between the parameters (iron and nitrite) and grain size distribution. Strong positive correlation existed between the iron and nitrite concentration in the subsoil (table-5). Sampling location 2 and 4 depicted correlation values of +0.99 and +0.93 respectively. While sampling locations 1, 3 and 5 showed relatively lower positive correlation (+0.12, +0.35, and +0.42 respectively). Negative correlation existed between percentage of sand and concentration of iron in all the sampling locations except sampling location 2 (table-6.a). Nitrite concentration had strong negative relationship with sand percentage particularly at 1, 3 and 5 sampling locations (-0.92, -0.76 and -0.81 respectively). On the other hand, positive correlation was noted at sampling locations 2 and 4. No specific pattern was observed between the groundwater parameters and silt percentage (table-9). At sampling location 3 (near Nandesari) the correlation between silt percentage and iron concentration was strong and positive (+0.95). On the other hand, soil sample location 1 and 4 showed negative relationship between silt percentage and iron concentration viz. -0.91 and -0.80. A reverse pattern was observed between iron concentration and clay percentage. The concentration of nitrite and silt percentage from sampling locations 4 and 5 depicted negative correlation (-0.51 and -0.52) whereas, the sample location 1, 2 and 3 had positive correlation (+0.28, +0.34 and +0.04). A positive relationship existed between clay percentage and nitrite concentration except for the sampling location 2 with correlation value of -0.38 (table-7c). Layer wise correlation between grain size and concentration of parameters in the sediments depicted some of the important facts. In the immediate layer, correlation between sand percentage and concentration of iron and nitrite was negative and weak (-0.24 and -0.28). In the layer of 4-5 inch, the sand fraction and iron concentration showed strong positive relation with the value of +0.83 while at the same depth the value was weak and negative (-0.16) between sand fraction and nitrite. In the other two layers, the correlation values of sand fraction with sand nitrite was positive (+0.35 and +0.24 respectively). The correlation between silt and parameters (iron and nitrite) in all the layers were negative and weak except between silt percentage and iron content at 4-5 inch depth which is negative but strong (-0.66) Silt and iron content correlation value at 8-9 inch depth was positive (+0.45). The correlation between clay percentage and both the parameters was positive in all the layers (table-8).

Table-4
Concentration of water parameters in ground water

Sample Location	**Concentration**				**Clay % in sediment**	**Geographical Location**
	Iron	Iron (Average)	Nitrite	Nitrite (Average)		
1	0.97	0.95	58.03	72.77	62.03	N22.44078 E73.15444
1	0.92		87.5			N22.44153 E73.15482
2	0.34	0.34	113.3	113.30	28.68	N22.43244 E73.12254
2	Nil		Nil			N22.43166 E73.12439
3	1.2	2.33	22.32	20.54	49.94	N22.41758 E73.09970
3	3.45		18.75			N22.41910 E73.10239
5	1.26	0.79	21.42	23.66	72.55	N22.38728 E73.07896
5	0.23		25.89			N22.38658 E73.07603

Source: Computed

Table-5
Correlation between iron and nitrite level in sediments

	Location 1		Location 2		Location 3		Location 4		Location 5	
	Iron Level	Nitrite Level	Iron Level	Nitrite Level	Iron Level	Nitrite Level	Iron Level	Nitrite Level	Iron Level	Nitrite Level
Iron Level	1	N.A.	1	N.A.	1	N.A.	1	N.A.	1	N.A.
Nitrite Level	+0.12	1	+0.99	1	+0.35	1	+0.93	1	+0.42	1

Source: Computed, N.A.-Not Applicable

Table-6
Correlation of grain size and concentration (conc.) of iron in sediments

		Location 1		Location 2		Location 3		Location 4		Location 5	
Table 6.a		Sand %	Iron Conc.	Sand %	Iron Conc.	Sand %	Iron Conc.	Sand %	Iron Conc.	Sand %	Iron Conc.
	Sand %	1	N.A.	1	N.A.	1	N.A.	1	N.A.	1	N.A.
	Iron Conc.	-0.51	1	+0.95	1	-0.88	1	-0.04	1	-0.87	1
Table 6.b		Silt %	Iron Conc.	Silt %	Iron Conc.	Silt %	Iron Conc.	Silt %	Iron Conc.	Silt %	Iron Conc.
	Silt %	1	N.A.	1	N.A.	1	N.A.	1	N.A.	1	N.A.
	Iron Conc.	-0.91	1	+0.21	1	+0.95	1	-0.80	1	+0.56	1
Table 6.c		Clay %	Iron Conc.	Clay %	Iron Conc.	Clay %	Iron Conc.	Clay %	Iron Conc.	Clay %	Iron Conc.
	Clay %	1	N.A.	1	N.A.	1	N.A.	1	N.A.	1	N.A.
	Iron Conc.	+0.99	1	-0.25	1	-0.49	1	+0.72	1	-0.45	1

Source: Computed, N.A.-Not Applicable

Table-7
Correlation between grain size and concentration (conc.) of nitrite in sediment

		Loction 1		Loction 2		Loction 3		Loction 4		Loction 5	
Table 7.a		Sand%	Nitrite Conc.	Sand%	Nitrite Conc.	Sand%	Nitrite Conc.	Sand%	Nitrite Conc.	Sand%	Nitrite Conc.
	Sand%	1	N.A.	1	N.A.	1	N.A.	1	N.A.	1	N.A.
	Nitrite Conc.	-0.92	1	+0.90	1	-0.76	1	+0.34	1	-0.81	1
Table 7.b		Silt%	Nitrite Conc.	Silt%	Nitrite Conc.	Silt%	Nitrite Conc.	Silt%	Nitrite Conc.	Silt%	Nitrite Conc.
	Silt%	1	N.A.	1	N.A.	1	N.A.	1	N.A.	1	N.A.
	Nitrite Conc.	+0.29	1	+0.35	1	+0.04	1	-0.52	1	-0.51	1
Table 7.c		Clay%	Nitrite Conc.	Clay%	Nitrite Conc.	Clay%	Nitrite Conc.	Clay%	Nitrite Conc.	Clay%	Nitrite Conc.
	Clay%	1	N.A.	1	N.A.	1	N.A.	1	N.A.	1	N.A.
	Nitrite Conc.	+0.27	1	-0.38	1	+0.64	1	+0.41	1	+0.62	1

Source: Computed, N.A.-Not Applicable

Table-8
Depth wise correlation between grain size and concentration of parameters in sediment

0-1 Inch Depth		0-1 Inch Depth		4-5 Inch Depth		4-5 Inch Depth		8-9 Inch Depth		8-9 Inch Depth	
Sand%	Iron Conc.	Sand%	Nitrite Conc.	Sand%	Iron Conc.	Sand %	Nitrite Conc.	Sand%	Iron Conc.	Sand%	Nitrite Conc.
1		1	N.A.	1	N.A.	1	N.A.	1	N.A.	1	N.A.
-0.24	1	-0.28	1	+0.83	1	-0.16	1	+0.35	1	+0.24	1
Silt	Iron Conc.	Silt	Nitrite Conc.	Silt %	Iron Conc.	Silt	Nitrite Conc.	Silt%	Iron Conc.	Silt%	Nitrite Conc.
1	N.A.	1	N.A.	1	N.A.	1	N.A.	1	N.A.	1	N.A.
-0.45	1	-0.07	1	-0.66	1	+0.02	1	+0.45	1	-0.12	1
Clay%	Iron Conc.	Clay %	Nitrite Conc.	Clay	Iron Conc.	Clay	Nitrite Conc.	Clay%	Iron Conc.	Clay%	Nitrite Conc.
1	N.A.	1	N.A.	1	N.A.	1	N.A.	1	N.A.	1	N.A.
0.48	1	+0.10	1	+0.38	1	+0.07	1	+0.38	1	+0.07	1

Source: Computed, N.A.-Not Applicable

Table-9
Correlation between grain size and concentration of parameters in ground water

Sand %	Iron Conc.	sand%	Nitrite Conc.
1	N.A.	1	N.A.
+0.91	1	-0.90	1
Silt%	Iron Conc.	silt%	Nitrite Conc.
1	N.A.	1	N.A.
-0.35	1	+0.84	1
Clay%	Iron Conc.	clay%	Nitrite Conc.
1	N.A.	1	N.A.
+0.15	1	-0.71	1

Source: Computed, N.A.-Not Applicable

Discussion: Clay was dominantly found in the immediate layer (figure-3) followed by silt and sand, that constituted the least percentage. Thus, it can be said that the clayey type of soil is dominant along the river Mini which comes under alluvial soil category. The presence of such type of soil in the north-western part of the district is mainly due to the fluvial processes[29]. The concentration of nitrite was higher in the immediate layer which decreased with the increasing depth (figure-4). Significant concentration of iron was also observed in the immediate layers where the clay percentage was maximum (figure-5). As the percentage of grain size gets finer the infiltration rate decreases significantly. Thus, the rate of infiltration from the surface to the subsurface also decreases and concentrates mainly in the upper most layers[2,30]. Sampling location 3 showed the maximum concentration of iron in all the layers (figure-5). Nandesari is an Industrial Notified Area and many chemicals are used which are related to iron and nitrite in the industries. The solid industrial wastes generated from the industries are also dumped in the nearby areas (figure-6). These ongoing industrial activities may be one of the reason for higher concentration of iron. Sampling location 1 or upstream point had lowest concentration of iron which is far away from the industrial estate (table-2). But, at sampling location 5 (downstream) which is also far from the industries the concentration was higher. It may be due to the downstream flow of river Mini. When the river is crossing the industrial estate (sampling location 3) the level of iron and nitrite in the sediment increase (table-2 and 3). Therefore, the downstream points showed higher concentration than the upstream ones. Consequently, the significance of river Mini is clearly observed in the study area. During the rainy season, the wastes get mixed with rainwater and flow southwards resulting into the high level of iron and nitrite in the sediment particularly in the downstream. The concentration of nitrite in groundwater is negatively correlated with the clay percentage in the sediment (-0.70). A considerably higher concentration of nitrite was observed at sampling location 2 where the silt percentage is high with lowest percentage of clay (table-4) whereas, lowest level of nitrite was noted at sampling location 4 where the clay percentage is highest. The level of iron in ground water and the percentage of clay in the sediment did not show any specific correlation (+0.15) which indicated the natural occurrence of iron in the surface and subsurface soil.

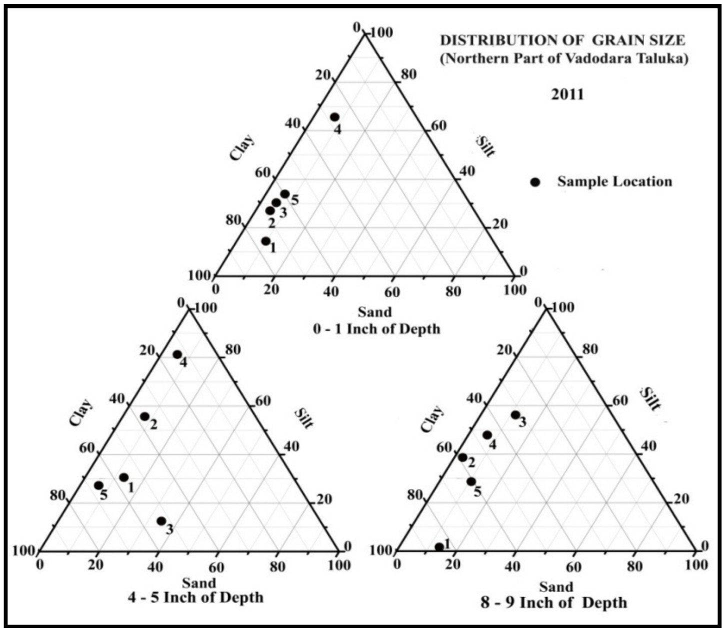

Figure-3

Ternary diagram showing distribution of grain size

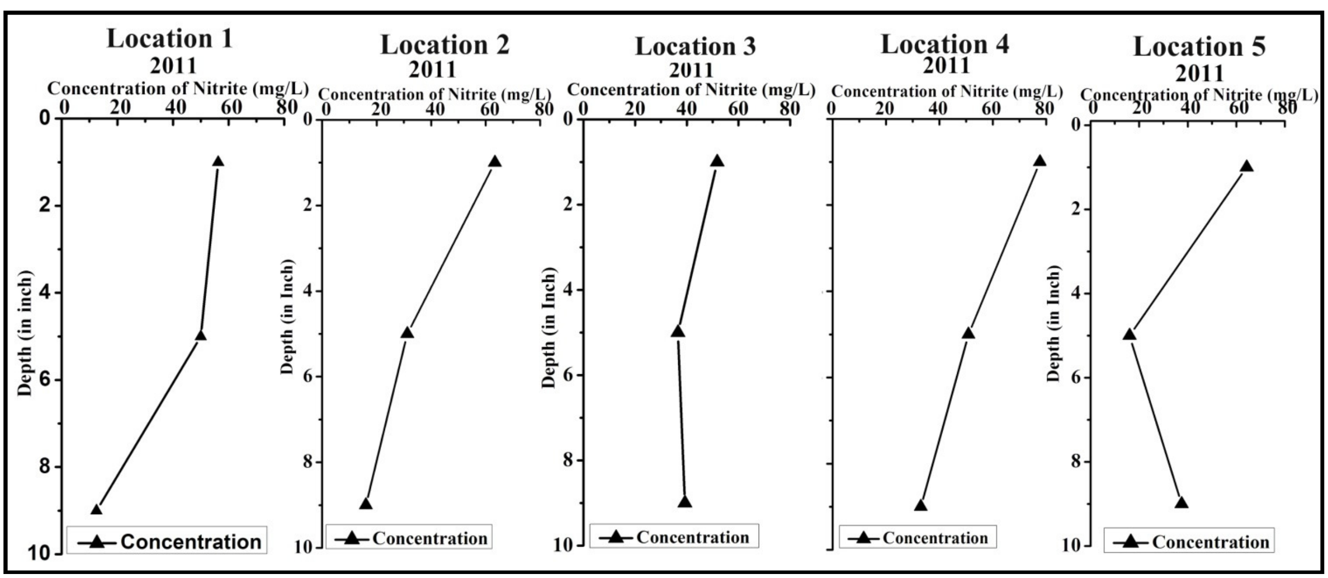

Figure-4

Concentration of nitrite in sediment

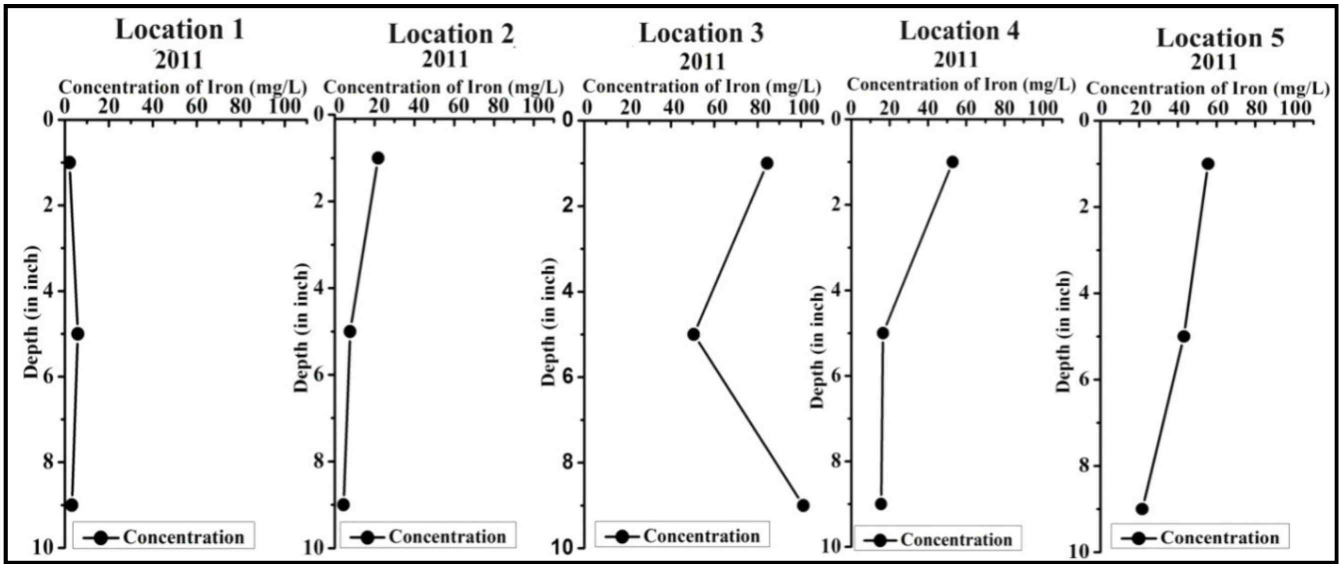

Figure-5
Concentration of iron in sediment

Figure-6
Dumping of industrial waste in Nandesari GIDC

Conclusion

In the entire study area, the percentage of percentage of clay in the sediment was maximum and helped in restricting the percolation rate of water in association with the parameters of iron and nitrite from the surface to the subsurface. The concentration of iron and nitrite in subsurface soil significantly augmented after passing through the industrial region which clearly indicated the contribution of the industries. River Mini played an important role and worked as a vector in this concern. Both the parameters had positive relationship which also indicated the importance of grain size distribution of the region both in surface and subsurface.

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