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PHYSICOCHEMICAL CHARACTERISTICS AND SURFACE SEDIMENTARY DIATOMS AS INDICATORS OF TROPHIC STATUS OF THE DARNA RESERVOIR, NASHIK, MAHARASHTRA, INDIA

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ABSTRACT

The physicochemical characteristics and surface sedimentary diatoms of the Darna Reservoir for the pre and the post monsoon seasons were investigated during May 2010 and February 2011 respectively. The pH value indicates alkaline nature of the Darna Reservoir. The calcium content of the reservoir was below 25 mg/l and therefore considered as less rich water bodies. The decline in silica content may be due to absorption of silica by bottom vegetation. The higher values of the phosphorous indicate very poor quality and mesotrophic - eutrophic water of the Darna Reservoir. The concentrations of Na, Fe, Cl, SO₄, K and Zn are well within the desirable limits. The increased concentration of Mg, Ti and K indicates the enhanced soil erosion in the watershed. The higher K content may also be due to excessive use of fertilizers in the adjoing agricultural lands and grape farms. The higher Mg content in the reservoir may be attributed to the developmental activities around reservoir such as dam concretization using cement etc. The high Fe and Si content during pre monsoon season may be due to erosion of magnetite and silica rich soils and the enrichment of iron at the deepest part of the reservoir. The surface sediments (pre and post monsoon seasons) of the Darna Reservoir divulged maximum abundance of *Aulacoseira granulata*, *Discostella stelligera and Cyclotella ocellata*. Thus, these diatom taxa indicate alkaline, mesotrophiceutrophic water quality of the Darna Reservoir.

Keywords: Hydrochemistry, Surface Sediments, Diatoms, Darna Reservoir, Nashik

INTRODUCTION

Reservoirs are artificial structures designed mainly to preserve water for agriculture, flood control, municipal drinking water or to generate hydroelectric power (Liu et al., 2012). The reservoirs are more like an artificial lake and the thing that made them different from the lakes is that they may contain pumps and discharge gates, which can influence their limnological conditions (Liu et al., 2012). The reservoir can be divided into three zones: a shallow, upstream riverine zone, a transitional zone and a deep lacustrine zone close to the dam on the basis of their distinct longitudinal gradients in their morphology and hydrodynamics (Metre and Callender, 1997). These longitudinal gradients influence the physical, chemical and biological processes that affect sedimentation as well as the diatom assemblages that accumulate in the sediments (Liu et al., 2012). Reservoir sediments are rarely used as environmental archives because of the potential for sediment disturbance by fluctuating water levels. However, rapid rates of sedimentation, proximity to urban centres and often the existence of management records may make them potentially important resources for reconstructing recent, anthropogenically derived environmental change (Shotbolt et al., 2006). The bottom sediments from the reservoir are not very common due to the differences in hydrodynamics of the lakes and reservoirs. Some workers have studied the various ecological aspects of the reservoirs using diatoms and geochemistry (Wang et al., 2008, Liu et al., 2012, Shotbolt et al., 2006).

The Darna Reservoir falls under the toposheet no 46 H/12 and situated in the Nashik district on the North West part of the Maharashtra state (Figure 1). The Nashik district covers an area of about 15530 sq. Km. The entire area of the Nashik district falls in latitude 19° 35′ and 20° 50′N and longitude 73°30′ and 74° 55′E in the Survey of India toposheets no 47 E, I and 46 H, L. The Darna reservoir is present at about 20 km from the village Wadivarhe on the Nashik -Mumbai highway and 15 km from the Nashik city. A

Research Article

masonary dam was constructed by British Government in 1916. The total length of reservoir is 1634m and the maximum height of the dam is 28 m. Physiographically, the western part of the district is represented by highly rugged and dissected terrain of the Western Ghats. The bathymetric variation in the Darna Reservoir is shown in figure 1. The land use pattern helps in interpretation of the possible source of pollution in the reservoirs. The land use pattern of the watershed of the Darna Reservoir clearly shows the dominance of agricultural land and grass land around the reservoir. The agricultural activity is dominated by sugarcane cropping. The fallow land is also associated with the grass land and agricultural land around the reservoir is a matter of great concern from ecological and environmental point of view since the modern agricultural practices involves use of synthetic fertilizers which may lead to early or rapid eutrophication of the reservoirs.



Figure 1: a) Map of India showing location of the Maharashtra State, b) Map of Maharashtra state showing Nashik District, c) Map of Nashik District, d) Ouline map of the Darna Reservoir, e) Bathymetric map of Darna Reservoir

The hydrochemical analysis of the Darna Reservoir revealed the present water quality during the pre and the post monsoon seasons and the extent of the anthropogenic impact on the reservoir. The physicochemical characteristics of many lakes of the Vidarbha region have been extensively studied by various workers (Humane *et al.*, 2009, 2010a, 2010b; 2012a, 2012b; Humane and Humane, 2015; Aprajit, 2013; Badge *et al.*, 2014; Bante, 2014, Bawanwade, 2014, Bihade, 2011; Bramhankar, 2011; Borkar, 2011a; Borkar 2011b, Chalakh, 2014; Chopkar, 2009; Dhargave, 2012; Fadanvis, 2014; Ingewar, 2012; Juare *et al.*, 2014; Kamble *et al.*, 2014). Kumar *et al.*, (2008) have worked on physicochemical characteristics and diatoms as indicator of trophic status of the Kishore Sagar Lake, Rajasthan. Singh *et al.*, (2010) have studied the seasonal diatom variations with reference to physico-chemical properties of water of Mansagar Lake of Jaipur, Rajasthan. Physicochemical parameters of water particularly DO, pH, TH, BOD, COD, TDS, and EC were followed after Trivedi and Goel (1986), APHA (1985) and Sharma and Saini (2003). Bradbury and Metre (1997) have studied a land-use and water-quality history of White Rock Lake reservoir, Dallas, Texas. Sarwar and Wazir (1991) have studied physicochemical characteristics of freshwater ponds of Srinagar, Kashmir.

The geochemical analysis of the bottom sediments from the lakes and reservoirs are mostly carried out to know the source and variation in the sediment input and to prepare the database of the present day input

Research Article

of sediments. The reservoir sediments are good archived for the paleoecological study in particular because rapid rates of sedimentation, proximity to urban centres and often the existence of management records, make them potentially important resources for reconstructing recent, anthropogenically derived environmental change (Shotbolt *et al.*, 2006; Xu *et al.*, 2006, 2007). The quantity and quality of geochemical variables helps to understand which anthropogenic activity have highest impact on the reservoir.

Water quality evaluation using diatoms has become a new tool for environmental implications. The diatoms are microscopic unicellular algae that built complex, beautiful cell wall of silica and have the size $2-500 \mu m$ (John, 2014).

Diatoms are used as an indicator of reconstruction of the past and present ecological status due to their high sensitivity to limnological variables such as nutrient concentration, pH, conductivity and well preservation in fossil deposits. Diatoms play an important role for evaluating past and recent water quality and environmental conditions.

The deterioration of lake water quality has been a common environmental concern throughout the world during the later half of the 19^{th} Century (Valpola, 2006). Reservoir sediments are used as important environmental archives and provide temporal records of inputs from both the drainage basin and the atmosphere (Foster *et al.*, 1991; Lees *et al.*, 1997; Callender, 2000; Smol *et al.*, 2005; Audry *et al.*, 2004 and Yeloff *et al.*, 2005).

Several workers have correlated the lake trophic status with the distribution of diatom taxa in the surface sediments (Christie and Smol, 1993; Fritz *et al.*, 1993; Hall and Smol, 1999; Battarbee, 1997; Kelly, 1999; Dixit and Smol, 1994 and John, 2014).

Gonzalves (1947) was the pioneering worker on diatoms from the Maharashtra State. Thomas and Gonzalves (1965) recorded 98 diatoms from the eight hot springs of Maharashtra. Sarode and Kamat (1979, 1980a, b, c, 1983a, b, c) gave detailed description of 227 species of diatoms for the first time from Vidarbha and Marathwada regions of the Maharashtra state.

Nandkar *et al.*, (1983) described diatoms from sewage and oxidation ponds of Nagpur. Barahate and Tarar (1981, 1983) have recorded a few diatoms from Khandesh (Now Jalgaon region of Maharashtra). Sarode and Kamat (1984) described freshwater diatoms of Maharashtra. Gandhi (1998) reported 129 species of freshwater diatoms from the Chandola Lake of Gujarat. Misra and Shukla (2006) reported some freshwater diatoms from Uttaranchal state. Some species of diatoms from the hot spring of Ladakh was studied by Prasad *et al.*, (1984). Recently, Venkatachalapathy *et al.*, 2013 and 2014 have investigated diatoms and water quality assessment of Yercaud Lake in Tamil Naidu and Waishen River and Loktak Lake of Manipur.

Logannathan *et al.*, (2014) have studied distribution of fresh water diatoms of the Perumal Lake, Tamil Naidu. The polluted and unpolluted zones of river Gomati using diatoms was demarkated by Verma *et al.*, (1996, 2000).

A lot of work has been done to study the past environment using lake sediments. However, there is a lack of work related to the past and present ecological developments on the reservoirs in India especially the the Darna reservoirs of the Nashik district since the construction of the dams. Similarly, there is no record of sediment geochemistry and hydrochemistry of this reservoir. Therefore, the present work is a maiden attempt to investigate the Darna Reservoir of the Nashik District, Maharashtra to understand water quality status and its relationship with diatoms of surface sediments.

MATERIALS AND METHODS

Methodology

The surface sediment (grab) samples (DRG₁₋₃) and water samples (DRW₁₋₃) were collected at the same place from where the water samples of the Darna Reservoir during pre and post monsoon seasons of May 2010 and February 2011 respectively and numbered as DRG₁ and DRW₁ (Lat: N 19° 48' 52" N; Long: E 73° 45' 14" E), DRG₂ and DRW₂ (Lat: N 19°32' 92" N; Long: E 73° 44' 40" E) and DRG₃ and DRW₃ (Lat: N 19° 48'4.40" N; Long: E 73° 44' 35" E).

Research Article

Water Samples: A systematic sampling of the water samples from the Darna Reservoir was done during two seasons i.e. Pre-Monsoon and Post- Monsoon. The water samples were collected in the plastic bottles from the Darna Reservoir. The geographic positions of sample locations were specifically noted with the help of GPS. Temperature, pH, Conductivity and DO of the water was measured at the time of sampling. Then, the collected water samples were sent to the laboratory for hydrochemical analysis. The various physicochemical parameters of the water samples such as pH, Electrical Conductivity, Alkalinity, Chloride, Calcium, Magnesium, Nitrate-Nitrogen, Iron, Phosphorous, Aluminium, Manganese, Silica, Sodium, Potassium were measured using several equipment as given below: pH meter (model- 101E), Digital conductivity meter (Model-601), Titrimetric analysis, UV spectrophotometer (make- Systronics, model no. 118), UV-visible spectrophotometer from the Water Quality Envirocare Laboratory, Nashik.

Grab Sediments: The surface sediment (grab) samples were collected from the Darna Reservoir using a heavy stainless steel bucket and kept in a polythene zip-lock bag with proper labels. The X-ray Fluoroscence analysis (XRF) of the powdered surface sediment samples (-170 mesh size) of the Darna Reservoir were analyzed from Wadia Institute of Himalayan Geology, Dehradun, (WIHG) for major major oxides and trace elements (Model: Brucker 58 Tiger) for the post monsoon surface sediments. The pre monsoon surface sediments of the Darna Reservoir were analyzed from Indian Bureau of Mine (IBM), Pilot Plant Nagpur using XRF spectrometry for mjor oxides and trace elements (PW2403-MAGIX, PANlytical).

Maceration of Grab Sediments

Maceration of surface sediments of both the seasons was done using standard procedure of Batterbee (1986). The diatom slides were studied under Biological Research Microscope (Leica DM 350) at 40x, 63x and 100x (oil immersion) magnifications. Microphotography and identification of diatoms were done followed by their enumeration to understand their response to changing water quality.

Geological Setting

The catchment area surrounding the Darna Reservoir consists of basalt of the Deccan volcanic province. The Darna Reservoir is mostly surrounded by 6-7 Pahoehoe and Megacryst basaltic lava flows of the Ratangarh Formation of the Sahyadri Group belonging to the Upper Cretaceous to Lower Eocene age and also associated with the Alluvium in the form of discontinuous patches along the banks and flood plains of major rivers like Godavari, Girna and their tributaries (DRM, 2001). Basaltic lava flows occupies about 90% of the area of the district. These flows are normally horizontally disposed over a wide stretch and give rise to table land type of topography also known a plateau. These flows occur in layered sequences and represented by massive unit at the bottom and vesicular unit at the top of the flow. These flows are separated from each other by marker bed known as 'bole bed'. The ground water in the Deccan Trap Basalt occurs mostly in the upper weathered and fractured parts down to 20-25 m depth. At places, these potential zones are encountered at deeper levels in the form of fractures and inter-flow zones (Dhonde, 2009).

RESULTS AND DISCUSSION

Hydrochemistry: The water samples collected from the Darna Reservoir during Pre and Post monsoon seasons from three different locations have been analyzed for various parameters such as pH, conductivity, alkalinity calcium, magnesium, sulphate, nitrate, chloride, sodium, potassium, aluminum, silica, iron, and total phosphorous and total nitrogen (Table 1, Figures 2a - o). The physicochemical characteristics of the Darna Reservoir water show deviations during pre and post monsoon seasons. The calculations of the pair of linear correlation coefficients and the construction of hierarchic dendograms were prepared to know the relationship of the physico-chemical characters, during pre and post monsoon seasons of the Darna Reservoir (Tables 2, 3; Figure 3). The physicochemical characters during pre-monsoon season (Figure 3a) are separated into seven main groups: (I) Zn-N₂, (II) K-PO₄, (III)SiO₂-NO₃, (IV) SO₄-Cl, (V) Fe-Na-Mg-Ca, (VI) EC-TH-TA and (VII) pH-TDD-NH₃ and during the post-monsoon season (Figure 3b) are distinguished into six main groups: (I) Fe-Mg, (II) TDD-NH₃-Zn-N₂-K, (III) SiO₂-NO₃, (IV) SO₄-Cl-Na, (V) EC-Ca-TH-TA and (VI) pH-PO₄.

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Figures 2: a – o, Physico-chemical parameters of Darna Reservoir (Pre-Monsoon; Post- Monsoon)

Table 1: Water chemistry of the Darna Reservoir (Pre-Monsoon and Post-Monsoon) (r	ig/l for all the	parameters except	pH and EC
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Sample	nН	EC	ТА	тн	Ca	Ma	Na	Fo	CI	50	\mathbf{NO} (\mathbf{N})	SiO	$\mathbf{PO}(\mathbf{P})$	K	7n
No.	pm	(umhos/cm)	IA	111	Ca	wig	114	re	CI	504	1103(11)	5102	104(1)	K	2.11
D1Pre	7.98	232	52	100	12.8	16.3	4.34	0.11	24	6.8	1.06 (0.239)	4.56	0.59(0.188)	1.72	0.08
D2Pre	7.88	216	48	92	12.8	14.4	3.18	0.1	20	5.52	0.83 (0.187)	3.26	0.59 (0.183)	1.6	0.07
D3Pre	7.83	213	46	84	11.2	13.4	3.08	0.09	19	4.21	0.8 0.180)	3.09	0.59 (0.192)	1.52	0.063
Mean	7.83	220	46.1	84	11	13.4	3.1	0.1	19	4.21	0.8 (0.202)	3.09	0.59 (0.1872)	1.5	0.06
D1 Post	7.25	174	38	64	11.2	8.64	3.98	0.09	18	5.12	1.12 (0.252)	4.6	0.53 (0.172)	1.64	0.1
D2Post	7.19	170	37	62	7.6	10.3	3.6	0.08	17	5.04	0.98 (0.221)	3.94	0.58 (0.189)	1.56	0.08
D3Post	7.14	164	36	60	7.2	10.1	3.08	0.09	17	4.98	0.96 (0216)	3.09	0.59 (0.192)	1.52	0.063
Mean	7.14	169	36	60	7.2	8.64	3.08	0.08	17	4.98	0.96 0.230)	3.09	0.53 (0.184)	1.64	0.08

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Table 2: Correlation coefficient matrices of various physicochemical parameters in Pre-monsoon water samples of Darna Reservoir															
	РН	Ec	Alk	Cl	SO4	Ca	Mg	NO3	ТР	Fe	Na	К	Si	TDD	Zn
РН	1.0000	-0.5439	-0.6897	-0.5792	-0.8180	-0.9954	-0.9954	-0.6990	-0.5084	0.9954	-0.8142	-0.4787	-0.7422	- 0.3273	0.996078
EC		1.0000	0.9827	0.9991	0.9276	0.6218	0.6218	0.9803	0.9991	-0.6218	0.9301	0.9971	0.9661	- 0.1469	0.962512
Alk			1.0000	0.9897	0.9807	0.7559	0.9999	0.9742	-0.7559	0.9659	0.9659	0.9972	0.9742	- 0.3273	0.996078
Cl				1.0000	0.9427	0.6547	0.9878	0.9964	-0.6547	0.9449	0.9930	0.9762	0.9965	- 0.5000	0.973223
SO4					1.0000	0.8693	0.9831	0.9112	-0.8693	1.0000	0.8966	0.9926	0.9113	- 0.8660	0.99415
Ca						1.0000	0.7643	0.5885	-1.0000	0.8660	0.5605	0.8030	0.5887	- 0.8660	0.810885
Mg							1.0000	0.9712	-0.7643	0.9843	0.9625	0.9981	0.9712	- 0.0714	0.997131
NO3								1.0000	-0.5885	0.9139	0.9994	0.9544	1.0000	- 0.0714	0.87266
ТР									1.0000	-0.8660	-0.5605	-0.8030	-0.5887	0.5000	-0.3504
Fe										1.0000	0.8995	0.9934	0.9140	- 0.5000	0.99485
Na											1.0000	0.9437	0.9994	- 0.0714	0.939162
K												1.0000	0.9545	- 0.3974	0.99991
Si													1.0000	- 0.1057	0.950436
TDD														1.00	-0.40964
Zn															1

(TDD: Total Diatom Density of Surface Sediments)

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	PH	Ec	Alk	Cl	SO4	Ca	Mg	NO3	TP	Fe	Na	K	Si	TDD	Zn
PH	1.000	0.986	0.998	0.891	0.999	0.928	-		-	-		-		0.693	0.99998
	0	0	6	0	6	6	0.8355	0.9372	0.9508	0.6141	0.9899	0.8805	0.9922	4	4
EC		1.000	0.993	0.803	0.980	0.853	-		-	-		-		0.563	0.98694
		0	4	0	6	8	0.7323	0.8660	0.8859	0.7370	0.9997	0.7892	0.9991	6	9
Alk			1.000	0.866	0.996	0.907	-		-	-		-		0.654	0.99890
			0	0	6	8	0.8056	0.9177	0.9333	0.6547	0.9960	0.8544	0.9974	7	6
Cl				1.000	0.904	0.995	-		-	-		-		0.944	0.88845
				0	2	9	0.9939	0.9934	0.9878	0.1890	0.8178	0.9997	0.8751	9	9
SO4					1.000	0.939	-		-	-		-		0.714	0.99936
					0	2	0.8515	0.9472	0.9596	0.5903	0.9853	0.8943	0.9880	6	9
Ca						1.000	-		-	-		-		0.911	0.92645
						0	0.9798	0.9997	0.9979	0.2774	0.8667	0.9935	0.8751	3	6
Mg														-	
								-			-		-	0.975	-
							1.0000	0.9747	0.9646	0.0795	0.7493	0.9961	0.7605	3	0.83239
NO3									-	-		-		0.901	0.93996
								1.0000	0.9992	0.3004	0.8784	0.9905	0.8865	1	2
TP														-	
											-		-	0.882	-
									1.0000	0.3394	0.8974	0.9840	0.9048	5	0.94365
Fe											-		-	0.755	0.04676
										1.0000	0.7196	0.1666	0.7077	9	1
Na														0.584	0.99071
											1.0000	0.9999	0.9999	4	9
K													-	0.584	0.98974
~ .												1.0000	0.8145	4	3
Si													1 0000	0.598	0.68928
													1.0000	2	6
TD														1.000	0.68928
D														0	6
Zn															1

Table 3: Correlation coefficient matrices of various physicochemical arameters in Post-monsoon water samples of Darna Reservoir

(TDD: Total Diatom Density of Surface Sediments)

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The surface water temperature of the Darna Reservoir ranges from 29°C (Pre-monsoon) and 22°C (post monsoon) respectively. Thus, this reservoir belongs to the typical water body of the tropical latitude, where temperature ranges between 25° C to 30° C in summer and 16° C to 20° C in winter (Das, 1989). The pH of the water sample in pre monsoon season ranges from 7.8 to 7.9 with a mean value of 7.87, whereas it ranges from 7.14 to 7.25 with a mean value of 7.19 in the post monsoon season. The pH of the Darna Reservoir indicates its alkaline nature. The increased pH in the Darna Reservoir may be owed to the breakdown of the organic matter and augmented photosynthetic activity (Kumar et al., 2008; Singh and Mahajan, 1987). The pH of the water also depends upon relative quantity of calcium, carbonate and bicarbonates (Pearsall, 1930 and Zafar, 1966). The alkalinity of the water depends upon the carbonates and bicarbonates content (WLS, 2007). The total alkalinity (Alk mg CaCO₃/l) (Figure 2i) of the Darna Reservoir varies from 46-52 mg/l (Pre-monsoon) and 36-38 mg/l (Post-monsoon) (Figure 2i). The alkalinity values more than 100 mg/l indicate nutrititionally rich water (Phillipose, 1960 in Kumar et al., 2008). Thus, the Darna Reservoir indicates moderate trophic status. The electrical Conductivity ranges from 213µmhos/cm to 232 µmhos / cm with a mean value of 220µmhos / cm in pre monsoon and 164µmhos/cm to 174µmhos/cm with a mean value of 169.33µmhos/cm in post monsoon seasons. The pre monsoon water samples of this reservoir show higher EC than the post monsoon waters. The higher values during the pre-monsoon season may be due to the discharge of ions from the decayed organic matter. The electrical conductance above 0.20mS in water is regarded as eutrophic (Rawson, 1960 in Kumar et al., 2008). Thus, the water samples of the Darna Reservoir during pre monsoon seasons were more eutrophic. The alkalinity ranges from 46mg/l to 52mg/l with a mean value of 48.66 mg/l in the pre monsoon samples and ranges from 36 mg/l to 38 mg/l with mean value of 37 mg/l in the post monsoon season. The higher concentration of carbonates may lead to rise in the alkalinity of the water. On the contrary, the high level of calcium, carbondioxides and bicarbonates makes the water less alkaline (Kumar et al., 2008). The hardness of the water depends upon the calcium and magnesium content along with carbonates and bicarbonates (Singh et al., 2010). The hardness of water is controlled by the level of calcium, magnesium, carbonates and bicarbonates associated with chlorides, sulphate and anions of minerals (Kumar et al., 2008). The total hardness of the Darna Reservoir was 84-100mg/l (pre-monsoon) and 60 - 64 mg/l (post-monsoon). The 'nutrients rich' water will have more than 60 ppm hardness (Spence, 1964 in Kumar et al., 2008). Thus, the Darna Reservoir may be classified as 'nutrient rich'. The concentrations Calcium (Ca) and Magnesium (Mg) in the pre-monsoon water samples ranges from 11.2 mg/l to 12.8 mg/l and 13.44 mg/l to 16.32 mg/l with a mean value of are 11.73 mg/l and 14.72 mg/l respectively, whereas the concentrations of Ca and Mg have declined in the post monsoon samples and ranges from 7.2 mg/l to 11.2 mg/l and 8.64 mg/l to 10.32 mg/l with a mean value of 8.6 mg/l and 9.68 mg/l respectively. The average Ca content of the Darna Reservoir ranges from 11 mg/l to 7.2 mg/l during pre and post monsoon seasons respectively (Figure 2h). The calcium concentration above 25 mg/l is considered as "rich" water body (Ohle, 1934). The Ca content of the Darna Reservoir during both the seasons was less than the Mg content. Organic matter and magnesium are having close association with each other (Zafar, 1964). The higher concentration of calcium as compare to magnesium may be due to quicker reaction of CO₂ with calcium salt altering large amount of calcium into dissolved bicarbonates (Kumar et al., 2008). The calcium content of this reservoir was below 25 mg/l and therefore considered as less rich water bodies (Ohle, 1934). The Chloride content in water ranges from 19mg/l to 24mg/l with average value occurs to be 21 mg/l in pre monsoon season and varies from 17mg/l to 18mg/l to with average value of 17.33 mg/l in post monsoon season. The SO₄ ranges from 4.21mg/l to 6.80mg/l with mean value of 5.51 mg/l in pre-monsoon samples with decreased values ranging from 4.98 mg/l to 5.12 mg/l with mean value of 5.04 mg/l in post monsoon season. The silica content of the Darna Reservoir ranges from 3.09 to 4.56 mg/l (pre-monsoon) and 3.09 to 4.6 (post-monsoon) (Figure 21). The weathering of rocks and soils in the respective watersheds of the reservoirs may be responsible for the increased silica content along with the disintegration of the diatom frustules (Kumar et al., 2008). The silica content of the Darna Reservoir during the pre and post monsoon seasons was lower. Thus, the decrease in the silica content may be due to absorption of silica by bottom vegetation i.e. phytolith like grasses, sponge

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spicules, cysts and diatoms (Ahl, 1966 in Kumar *et al.*, 2008; Figures 4). The concentration of sodium and potassium content in water was 3.08 mg/l to 4.34 mg/l and 1.52 mg/l to 1.72 mg/l in the pre monsoon water samples with mean value of 3.53 mg/l and 1.61 mg/l, and 3.08 mg/l to 3.98 mg/l and 1.57 to 1.61 mg/l in the post monsoon season with mean value of 3.55 mg/l and 1.57 mg/l respectively. The phosphorus is often the limiting nutrient in water bodies and essential for the aquatic plant and animal growth (Kumar *et al.*, 2008). The common total phosphorous values for the Wisconsin, USA is given in table 4 (WLS, 2007). The total phosphorus content of the Darna Reservoir ranges from 0.1859 to 0.1924 mg/l during pre monsoon and 0.1728 to 0.1924 mg/l during the post monsoon seasons. The higher values of the phosphorous indicate very poor quality of the Darna Reservoir water (Table 4, WLS, 2007). The augmentation in phosphorous content of the water body may be due to the faster decomposion of the organic matter (Kumar *et al.*, 2008; Meena *et al.*, 2007).



Figure 3: (a – b) Hierarchic Dendograms of correlation matrix of physicochemical parameters in water samples of the Darna Reservoir. a) Premonsoon; b) Post monsoon





Figures 4 a- f: Geochemistry of surface sediments of Darna Reservoir

Table 4: Common total	nhosnhorous	values for the	Wisconsin.	USA (WLS.	2007)
	phosphorous	values for the	vv isconsing			200 1)

Water Quality	Total Phosporous values (mg/l)	
Good	< 0.020	
Fair	0.020 - 0.050	
Poor	0.050 - 0.150	
Very Poor	> 0.150	

The nitrogen is also a crucial nutrient for the growth of the aquatic plants and organism (Prakash, 1994). The common total nitrogen values for the Wisconsin, USA is given in table 5 (WLS, 2007). The nitrogen

Research Article

content of the Darna Reservoir ranges from 0.1807 to 0.2394 mg/l in (Pre-monsoon) and 0.2168 to 0.2529 mg/l (Post- monsoon). The nitrogen concentrations show oligotrophic status of the Darna Reservoir during pre-monsoon and the post monsoon seasons (Table 5, WLS, 2007). The concentrations of Na, Fe, Cl, SO₄, K and Zn are well within the desirable limits (WHO, 1984; BIS, 2003) in the reservoir (Figures 2 b, d, e, m, j, o). This suggests that water of the Darna Reservoir can be safely used for the domestic purspose and also for drinking purpose after filtering.

The overall hydrochemical investigation suggests the enhanced concentration of the majority of the water parameter at the sample location DRW_1 and shows decreasing trend at DRW_2 and DRW_3 . The similar trend was observed during the post monsoon season as well.

Tuble 5. Common total phosphorous v	andes for the wisconshi, Corr (wills, 2007)
Water Quality	Total Nitrogen values (mg/l)
Oligotrophic	< 0.4
Mesotrophic	0.4 - 0.6
Eutrophic	0.6 – 1.5
Hyper-eutrophic	> 1.5

 Table 5: Common total phosphorous values for the Wisconsin, USA (WLS, 2007)

Geochemistry: The geochemical analysis of the surface sediment samples of the Darna Reservoir shows increased values of P_2O_5 , Fe_2O_3 and MnO in the post monsoon samples than the pre monsoon samples (Figures 5a-f). A significant increase in the TiO₂ concentration is noted in pre monsoon season (0.62 to 1.49 mg/gm). The post monsoon season indicates enhanced soil erosion and weathering of adjacent rocks and their supply to the reservoir due to increased rainfall. The geochemical elements like SiO₂, Al₂O₃, MgO, K₂O, Cr₂O₃, NiO, ZnO, Rb₂O, SrO, ZrO and BaO show significant increase in the post monsoon sediment samples in the Darna Reservoir. The pair of linear correlation coefficients were computed and hierarchic dendograms were arranged to recognize the association of the major elements and the trace elements (Tables 6 and Figures 6 a - b). These dendograms exibit the relationship of the major and trace elements in the major groups and within the groups as well. For the Darna Reservoir (Figure 6a), the geochemical elements of the surface sediments (pre monsoon) are separated into three main groups: (I) Na – Mg, (II) Fe- Ti and (II) K – Ca – Mn-P-Zn-Cu, while the post monsoon surface sediments (Figure 6b) are categorized in to four main groups: (I) Ti-Pb-Zn-Cu, (II) Fe – Mn, (III) Ca-K-Mg and (IV) Na-P.

Table 6: Major elemental cond	centrations of Darna Rea	servoir ((Pre-Monsoon a	and Post-Monsoon)
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Sample No.	Na %	Mg%	P %	K %	Ca %	Ti %	Mn %	Fe %	Cu %	Zn %	Pb %	Si %
D1Pre	0.26	0.46	0.28	0.26	2.72	0.37	0.8	10.49	0.02	0.05	ND*	NA*
D2Pre	0.24	1.04	0.26	0.24	2.32	0.46	0.64	10.34	0.01	0.04	ND*	NA*
D3Pre	0.24	1.07	0.21	0.26	2.11	0.77	0.64	10.67	0.01	0.03	ND*	NA*
Mean	0.25	0.86	0.25	0.25	2.38	0.53	0.69	10.5	0.01	0.04	ND*	NA*
D1 Post	0.54	1.63	0.05	0.77	3.32	0.92	0.16	0.11	3.05	0.53	0.37	21.18
D2Post	0.27	1.45	0.07	0.70	1.16	0.89	0.14	0.10	1.03	0.16	0.11	21.59
D3Post	0.24	1.36	0.07	0.71	1.03	0.89	0.13	0.09	0.92	0.13	0.09	21.57
Mean	0.35	1.48	0.06	0.73	1.84	0.90	0.14	0.10	1.67	0.27	0.19	21.45

(Note: NA: Not Analyzed; ND: Not Detected)



Figure 5 (a – b): Hierarchic dendograms of correlation matrix of geochemical elements of the surface sediments of Darna Reservoir a) the Pre monsoon and b) Post Monsoon

Research Article

Pre-Monsoon (DR) Genera	Diatoms species	Post-Monsoon (DR) Genera	Diatoms species			
1)Aulacoseira	1) Aulacoseira granulata	1)Aulacoseira	1)Aulacoseira granulata			
1 /1 /1 /1 /1 /1 /1 /1 /1 /1 /1 /1 /1 /1	2) Aulacoseira ambigua	1)11000050000	2)Aulacoseira ambigua			
	3) Aulacoseria islandica		3)Aulacoseria islandica			
	4) Aulacoseria distans		4)Aulacoseria distans			
2)Amphora	5) Amphora ovalis	2)Amphora	5)Amphora ovalis			
2)11111111010	6) Amphora obtusa	2)/111/2/10/14	6)Amphora obtusa			
	7) Amphora australiensis		7)Amphora australienesis			
3)Achnanthes	8) A chranthes brevines	3)Achnanthes	8) A chronthes brevines			
4)Racillaria	9) Recillaria pavillifer	4)Racillaria	9)Bacillaria paxillifer			
5)Calonais	10) Caloneis ventricosa	5)Caloneis	10)Caloneis ventricosa			
5)Culonels	11) Calonais bacillum	5)Calolicis	11)Calonais bacillum			
6)Cyclotella	12) Cyclotella meneabiniana	6)Cyclotella	12)Cyclotella managhiniana			
0)Cyclolellu	12)Cyclotella ocellata	0)Cyclolellu	12)Cyclotella ocellata			
7)Cocconcis	14) Cocconais placentula	7)Coccorreis	14)Coccorreis placentula			
7)Cocconets	14) Cocconeis piacentula	/)Cocconets	14)Cocconeis piacentula			
8)Cymbella	15) Cymbella lanceolata	8)Cymbella	15)Cymbella lanceolata			
9)Discostella	16) Discostella stelligera	9)Discostella	16)Discostella stelligera			
10)Diploneis	17) Diploneis ovalis	10)Diploneis	17) Diploneis ovalis			
· •	18) Diploneis smithii	· •	18) Diploneis smithii			
11)Epithemia	19)Epithemia turgida	11Epithemia	19) Epithemia turgida			
12)Encyonema	20)Encyonema minutum	12)Encyonema	20) Encyonema minutum			
13)Fragilaria	21)Fragilaria rumpens	13)Fragilaria	21) Fragilaria rumpens			
14)Fragilariforma	22)Fragilari forma constricta	14)Fragilariforma	22) Fragilariforma constricta			
15)Gomphonema	23)Gomphonema minutum	15)Gomphonema	23) Gomphonema minutum			
16)Gyrosigma	24)Gyrosigma kützingii	16)Gyrosigma	24)Gyrosigma kützingii			
	25)Gyrosigma spencerii		25)Gyrosigma spencerii			
17)Nitzschia	26)Nitzschia sp.	17)Nitzschia	26)Nitzschia amphibian			
18)Navicula	27)Navicula viridula	18)Navicula	27)Navicula viridula			
	28) Navicula radiosa		28)Navicula radiosa			
			29)Navicula cryptocephala			
19)Pinnularia	29)Pinnularia borealis	19)Pinnularia	30)Pinnularia borealis			
	30)Pinnularia gibburalia		31)Pinnularia gibburalia			
	31)Pinnularia gibba		32)Pinnularia gibba			
20)Planothidium	32)Planothidium delicatum	20)Planothidium	33)Planothidium delicatum			
21)Rhopaloidia	33)Rhopaloidia gibbularia	21)Rhopaloidia	34)Rhopaloidia gibbularia			

Research Article

	34)Rhopaloidia gibba		35)Rhopaloidia gibba
	35)Rhopalodia musculus		36)Rhopalodia musculus
22)Stephanodiscus	36)Stephanodiscus niagarae	22)Stephanodiscus	37)Stephanodiscus niagarae
23)Synedra	37)Synedra ulna	23)Synedra	38)Synedra ulna
24)Surirella	38)Surirella ovalis	24)Surirella	39)Surirella ovalis
	39)Surirella tenera		40)Surirella tenera
	40)Surirella angusta		41)Surirella angusta
25)Sellaphora	41)Sellaphora pupilla	25)Sellaphora	42)Sellaphora pupula
26)Tryblionella	42)Tryblionella levidensis	26)Tryblionella	43)Tryblionella levidensis
	43)Tryblionella victoriae		44)Tryblionella victoria
-	-	27)Eunotia	45)Eunotia sp.

Figure 6: Checklist of diatoms recovered from Surface sediments (Pre and Post monsoon) Darna Reservoir (DR)

The surface sediments of the Darna Reservoir clearly show the abundance of Mg, Ti and K (Figures 5 ac) during the Post monsoon season. On the contrary, the pre monsoon season exhibit high Fe content (Figures 5 d-f). Ca content was comparatively low with its higher values during pre monsoon season (Figures 5 d-f). Ti is the indicator of soil erosion (Garrison and Laliberte, 2010). The Ti content has derived from the soils associated with the dykes belonging to low Ti- tholeiites (Jain and Gupta, 2013). The flows in the Nashik area are mainly composed of plagioclase feldspar, pyroxene, olivine, ilmenite, magnetite, palagonite glass, zeolites, chlorite, chlorophaite and secondary glass (Jain and Gupta, 2013). The Darna Reservoir is mostly surrounded by the agricultural lands and lava flows. Thus, the increased concentration of Mg, Ti and K indicates the enhanced soil erosion in the watershed of the Darna Reservoir. The higher K content may also be due to excessive use of fertilizers in the adjoing agricultural lands and grape farms. The higher Mg content in the reservoir may be attributed to the developmental activities around reservoir such as dam concretization using cement etc. The post monsoon season shows the significantly high content of Si (Figures 5 d-f). The high value of Si may have derived from erosion of soils rich in silica. The flows of the Nashik region contains about 48- 50.25% of SiO₂ (Jain and Gupta, 2013). The P concentrations were higher during pre monsoon season owing to use of fertilizers in the surrounding agricultural lands. The higher Fe content in the reservoir during pre monsoon season may be due to erosion of magnetite rich soils and the enrichment of iron at the deepest part of the reservoir. The decline in the Fe conent may be due to dilution during the post monsoon season.

Diatom analysis: The systematic classifications of diatoms proposed by Round et al., (1990) and John (2014) havw been used in the present research work. The systematic description of diatoms is completely depending on the distinctiveness of frustules i.e. size, shape, structure, symmetry and nature of raphae and density of striae. The sedimentary diatoms recovered from the surface (grab) sediments (Pre and Post monsoon seasons) of the Darna Reservoir are described systematically. The taxonomic work and classification of Mann (1999) have also been exercised in this work. The pre monsoon surface sediments of the Darna Reservoir shows the presence of total 43 species belonging to 26 genera, while the Postmonsoon surface sediments revealed 45 species belonging to 27 genera (Figure 6). The surface (grab) sediments (Pre and Post monsoon seasons) of the Darna Reservoir were studied to recognize the diatom diversity (Figures 7) and the related water quality was compared with the relatively most abundant species. The surface sediments (pre and post monsoon seasons) of the Darna Reservoir divulged maximum abundance of Aulacoseira granulata, Discostella stelligera and Cyclotella ocellata (Table 7) Thus, these diatom taxa can be used as the indicators of average values of physicochemical parameters to interpret diatom inferred past water quality status after comaring with other lakes and reservoirs of the region. The average values of physicochemical parameters of the Darna Reservoir and associated dominant sedimentary diatom taxa during the pre and post monsoon seasons are shown in Table 7.

Research Article

 Table 7: Most abundant diatoms from the surface sediments (PM: Pre Monsoon and PoM: Post Monsoon) of the Darna Reservoir and their preferred range of Physico-chemical parameters

	Most	Phys	sicochen	nical pa	ramet	rnysicocnemical parameters												
Season s	abundant Diatom species	pН	EC µmho s/cm	Alk mg CaCO ₃ /L	Cl mg/l	SO4 mg/l	Ca mg/l	Mg mg/l	NO ₃ mg/l	TP mg/l	Fe mg/l	Na mg/l	K mg/l	Zn mg/l	Si mg/l			
PM	Aulacoseira granulata																	
	Cyclotella meneghinia na	7.83	220.00	46.1	19	4.21	18.1 3	13.4	0.8	0.59	0.09	3.1	1.5	0.06	3.09			
	Navicula viridula																	
PoM	Aulacoseira granulata																	
	Cyclotella meneghinia na	7.14	169.00	36	17	4.98	13.3 3	8.64	0.96	0.53	0.08	3.08	1.64	0.08	3.09			
	Navicula viridula																	
Averag e	-	7.48	194.5	41.05	18	4.59	15.7 3	11.02	0.88	0.56	0.085	3.09	1.57	0.07	3.09			



Figure 7: Percent (%) Diatom abundance in surface sediments (grab) of the Darna Reservior

Conclusions

The Darna Reservoir is alkaline nature and the increased pH in the reservoir owed to the breakdown of the organic matter and augmented photosynthetic activity with the relative amount of calcium, carbonate and bicarbonates. It is more eutrophic during pre monsoon season and less rich water body with very poor water quality with reference to calcium content. The low silica content may be due to absorption of silica by bottom vegetation i.e. phytolith like grasses, sponge spicules, cysts and diatoms. The higher values of the phosphorous indicate very poor quality of the Darna Reservoir. The high phosphorous content of the

Research Article

water body may be due to the faster decomposion of the organic matter. The water of this reservoir can be safely used for the domestic purspose and also for drinking purpose after filtering.

The increased concentration of Si, Mg, Ti and K indicates the enhanced soil erosion in the watershed of the Darna Reservoir. The higher K and P content may also be due to excessive use of fertilizers in the adjoing agricultural lands and grape farms. The higher Mg content in the reservoir may be attributed to the developmental activities around reservoir such as dam concretization using cement etc. The higher Fe content in the reservoir during pre monsoon season may be due to erosion of magnetite rich soils and the enrichment of iron at the deepest part of the reservoir.

The surface sediments (pre and post monsoon seasons) of the Darna Reservoir divulged maximum abundance of *Aulacoseira granulata, Discostella stelligera and Cyclotella ocellata*. These diatom taxa indicate alkaline, mesotrophic- eutrophic water quality of the Darna Reservoir. Thus, these diatom taxa can be used as the indicators of average values of physicochemical parameters to interpret diatom inferred past water quality status after comparing with other lakes and reservoirs of the region.

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Repository

All the studied specimens have been kept in the Applied Micropaleontology Laboratory, Department of Geology, RTM Nagpur University, Nagpur. The slides are numbered as DRC1-DRC 70 and DRG1-DRG3 Pre-monsoon DRG1-DRG3 Post-monsoon, GRC1-GRC92, GRG1-GRG3 Pre-monsoon and GRG1-GRG3 Post-monsoon.

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