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Influence of Physical, Chemical and Biological Parameters on Distribution of Dissolved Carbon dioxide in Ground Waters of Visakhapatnam, Andhra Pradesh, India

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Abstract

The present study was carried out in order to understand the influence of biological, physical and chemical parameter on the distribution of dissolved carbon dioxide in four different regions Such as Coastal, Residential, Commercial, and Industrial regions ground waters of Visakhapatnam during winter season. This study revealed physical, chemical and biological properties of Coastal and Residential regions and Commercial and Industrial regions are seems to show similar behaviour. The bio available total dissolved carbohydrate (TDCHO) and total dissolved proteins (TDPRO) found to be high in the coastal and residential regions than commercial and industrial regions ground waters. High heterotrophic respiration rates are found in the commercial and industrial regions than coastal and residential region ground waters. Ground water pCO₂ levels (~ 15000 µ atm) in Visakhapatnam are 50 times higher than atmospheric carbon dioxide levels. Dissolved carbon dioxide (pCO₂) doesn't show much variability in among these four regions, but the sources for the CO2 are different from coastal and residential to the commercial and industrial region ground waters.

Keywords

Groundwater; Carbon Dioxide; DO; Carbohydrates; Proteins; pH; Alkalinity; Visakhapatnam.

Introduction

The nonstop increasing in temperature of the planet is really a great disappointment. The main reason for increasing temperature is because of global warming. Global warming begins when sunlight reaches the Earth, the atmospheric particles, clouds, reflective ground surfaces and surface of oceans then sends back about 30 % of sunlight back into the space, at the same time as the remaining is absorbed by oceans, air, and land, as a result heats up the surface of the planet and atmosphere, making life viable [1]. As the Earth warms up, this solar energy is radiated by infrared rays and thermal radiation, propagating directly out to space thereby cooling the Earth. However, some of the outgoing radiation is re-absorbed by carbon dioxide, methane, ozone, water vapours, and other gases in the atmosphere and is radiated back to the Earth. These gases are generally known as greenhouse gases due

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to their heat-trapping capacity [1].

Increasing emissions of greenhouse gases either by naturally or by human activities led to a substantial rise in atmospheric concentrations of greenhouse gases [2-4]. From the last 40 years, global emissions of all major greenhouse gases increased.Net emissions of carbon dioxide increased by 42%, which is particularly important because carbon dioxide accounts for about three-fourths of total global emissions. Carbon dioxide emissions, are increasing faster in some parts of the world than in others [5]. The majority of emissions come from three regions: Asia, Europe, and the United States, which together account for 88% of total global emissions [2].

The global carbon cycle is the flux of carbon (C) among reservoirs where C has short or long residence time. The major reservoirs are inorganic and organic carbon in rocks, dissolved inorganic carbon in seawater, soil inorganic and organic carbon, marine, terrestrial and atmosphere [6]. Human contributions to the global C cycle result from oxidation of fossil fuel (organic C in rock), manufacturing, and alteration of the terrestrial biosphere through deforestation and other landscape alterations that interrupt carbon cycling or release formerly stored carbon.

These authors postulated that these fluxes were supported largely by terrestrial carbon entering into rivers and streams, either as terrestrial organic matter or groundwater CO_2 as that was subsequently mineralized by the aquatic environment. They further suggested that this could be a major pathway for return of terrestrially fixed C to the atmosphere, and one that is not considered or measured in terrestrial C balance studies [7], carbon budgets for terrestrial ecosystems could be imperfect if hydrologic export of evaded CO_2 , dissolved organic and inorganic carbon (DOC and DIC) and particulate organic carbon are not considered [8-10].

Production of carbon dioxide (CO_2) in soils can lead to super saturation of dissolved partial pressure of carbon dioxide (pCO_2) in groundwater [11]. Davidson et al. [12-14] found that concentrations of CO_2 within deep soil air profiles in Amazon forests and pastures often exceed 50,000 ppm indicating that supersaturated groundwater may be common. As groundwater enters rivers and streams, much of the pCO_2 rapidly evade to the atmosphere, thus transferring C that was fixed in terrestrial ecosystems to the atmosphere via an aquatic pathway. The objective of our study is to estimate the dissolved carbon dioxide concentrations in ground waters of Visakhapatnam with respective to physical, chemical, and biological influence.

Materials and Methods

Study area and sampling locations

Visakhapatnam is one of the districts located on the North East of Andhra Pradesh. It is situated between 17°15', 18°32' North latitude and 18°54', 83°30' Eastern longitude. It is covered by Eastern Ghats on the North and West and the other end is covered by coastline. The current population of the district is 48,75,496 as 2018. The Geographical area



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of the district is 11161 Sq. Km. It has different climatic conditions which vary in various parts. The climate near coast is moist, becomes warmer towards the interior regions and cools down at hilly areas. The district receives a normal annual rainfall of 1202 mm, 72% of which is contributed by South-West monsoon and 13% by North-East monsoon, rest is shared by winter and summer showers, which are the main sources for groundwater recharge.

Ground water samples are collected in four different regions where living conditions are completely different from one another such as, coastal area, commercial area, industrial and residential areas. Sampling locations in coastal area were selected which extend up to 1km from the coast line, an area of 5.75 sq.km was covered. Places where extensive commercial activities took place were categorized into commercial zones, an area of 2.65 sq.km was covered. Majority of the industries like Hindustan Petroleum Corporation Limited, Bharat Heavy Plates and Vessels, Visakhapatnam Steel Plant where widespread industrial activities take place were considered under industrial area, an area of 11.4 sq.km was covered. Places with excess residential population are considered under residential areas, an area of 5.97sq.km was covered (Figure 1).



Samples were collected from bore wells, open wells and also from deep hand pumps at different locations from October-2017 to January-2018 (4 months) at 40 sampling locations. Temperature readings were taken on site by using mercury-thermometer. Chloride concentration was estimated by Argentometric titration method [15,16]. Dissolved Oxygen (DO) was measured using Winkler's titration method of Carritt and Carpenter [17]. The analytical precision, expressed as standard deviation, was 0.07% for DO. Heterotrophic respiration (HR) was measured by following the method [18]. The pH and total alkalinity (TA) were measured by potentiometric (Metrohm, Switzerland) Gran titration methods following Standard Operating Procedures (SOP) suggested by the Department of Energy [19]. The precision for pH, TA were 0.002, 2.0 µmol l-1 respectively. The pCO₂ was computed using measured salinity (Chloride x 0.0018066), temperature, nutrients (phosphate and silicate; data is not included), pH and alkalinity using dissociation constants [20] for 0 to 40 salinity ranges using CO₂ sys program [21].

Total dissolved carbohydrates (TDCHO), about 1 ml of filtered water sample (with GF/F filter) was taken in a clean dry glass test tube and 1 ml of 5% phenol and 5 ml of 96% sulphuric acid was added. At the hot (exothermic) condition, resulted from addition of sulphuric acid to sample, polysaccharides, di-saccharides and oligissaharides are converted to monossacharides, which are then dehydrated to hydroxyl methyl furfural. This forms an orange-yellow colored complex with phenol. The reaction test tube kept in a water bath having temperature of 25°C for 20-30 min and the absorbance of the solution was measured at 490 nm using UV-Visible spectrophotometer method [22]. The detection limit for carbohydrates is from 1 - 120 mg/l of glucose. In the case of total dissolved proteins (TDPRO), about 2 ml of filtered sea water samples were heated at 80°C for 30 min in

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alkaline medium (0.5 ml of 1N NaOH) to dissolve proteins. After cooling, aliquot of 2.0 ml was transferred into test tube and 5.0 ml of carbonate-tartrate-copper solution was added and mixed. After 10 min, 1.0 ml of Folin-Ciocalteu reagent was added and absorbance of the complex was measured at 650 nm using spectrophotometer [23]. The detection limit for proteins is 0.01-1 mg/l protein (Bovine Serum Albumin). Samples were analyzed in duplicate and reported as mean values. Precisions for TDCHO and TDPRO were \pm 0.11, and \pm 0.2 μ M respectively based on standard deviation of analysis of 10 aliquots of same sample.

Graphical representation and statistical analyses of data

The software "Grapher" and "Surfer" was used for graphical representation of 2 Dimensional and 3 Dimensional to our data and for statistical analysis, the Rank Correlation matrix (Spearman's; r²), and student t-test, PRIMER was used for drawing dendrogram and SPSS was used for Principal component analysis (PCA) and for VENN diagram Interacting Venn – Unions by tree was used [24].

Results and Discussion

The seasonal changes in the atmospheric temperature have significant impact on the variability of water temperature. The change in the temperature in the ground water has influence on aquatic life and concentration of dissolved gases such as CO2, O2 and chemical solutes. During our study period temperature varied from 24°C to 27.5°C with an average 25.8 \pm 0.78°C (Table 1). A higher temperature was noticed in Industrial and Commercial station (26.0 ± 0.74°C) than Coastal and Residential stations (25.5 ± 0.76°C; Table 1). Chloride concentration varied from 36.4 mg/l to 253.7 mg/l with an average (145.7 \pm 49.6 mg/l; Table 1) and a bit higher concentrations are noticed in coastal and residential station (147.5 \pm 52.5 mg/l) than Industrial and Commercial stations (144.5 \pm 48.5 mg/l). Water with chloride concentration <500 mg/l are normally presumed to be excellent for drinking according to WHO [25]. These measurements are higher than that of chloride concentration reported at the same study region by (~ 77 mg/l; 18) and lower than that of (199.5 mg/l, [26]; 197.5mg/l, [27]; 330 mg/l, [28]; 250 mg/l, [29]). The variability in concentration of our data with the earlier reported data may be because of difference in the sampling station and as well as difference in the sampling period. pH has significant impact on the bio-geochemistry of the ground water, chemical composition, acidification of ground water and, trace gases accumulations rates depend on the pH variability in ground water [30]. In present study pH varied from 5.94 to 7.96 (7.06 \pm 0.33) (Figure 2a) and a bit higher pH values are found in Coastal and Residential regions (7.08 \pm 0.08) than Industrial and Commercial regions (6.99 ± 0.07; Table 1), our pH values are concurrent with the other reports by Kiranmai et al. [32,26,28]. Even though the averages seems to be close, but these two regions are significantly differed with statistical analysis-student t-test p<0.1 and t=1.32 (Table 1).





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Table 1: Mean (± SD) of physical chemical and biological properties andANOVA statistical significance of variation is given between Coastal &Residential and Commercial & Industrial region ground waters. *, **, ***indicates p<0.1, 0.05 and 0.001 respectively, and ns- no significance.</td>

Parameter	Coastal and Residential regions	Industrial and Commercial regions	t -value
Temperature (°C)	25.8 ± 0.78	26.0 ± 0.74	-2.1**
Chloride (mg/l)	147.5 ± 52.5	144.4 ± 48.5	0.17
рН	7.18 ± 0.08	6.99 ± 0.07	1.32*
Alkalinity (mg/l)	744.78 ± 47.2	592.81 ± 59.54	1.69**
DO(mg/l)	4.26 ± 1.1	4.01 ± 0.24	1.01*
HR(mg/l/d)	1.11 ± 0.04	1.69 ± 0.31	1.72**
TCHO (µ MC)	9.12 ± 0.23	7.93 ± 0.30	3.04***
TPRO(µ MC)	2.46 ± 0.18	1.82 ± 0.11	1.6**
pCO _₂ (μ atm)	13729.04 ± 1265.20	14292.69 ± 1507.10	ns

Alkalinity of water is a measure of weak acid present in it and of the cations balanced against them and alkalinity plays an important role in controlling enzyme activities [33]. Alkalinity of water is mainly caused by cations combined either as carbonate and/or bicarbonate or occasionally as hydroxide [34]. Alkalinity concentration in present study varied from 110.57 to 1185.5 mg/l (679.9 ± 259.5 mg/l; Figure 2b). Higher alkaline waters are found in the Costal and Residential region (774.78 ± 47.25 mg/l, Table 1) than Industrial and Commercial region (592.80 ± 59.54 mg/l, Table 1), and these two regions are statistically differ from one another with respective to student t-test (p<0.05, t=0.69; Table 1). Our values are higher than that of earlier reports 550.2 mg/l [28], 369.7 mg/l [35] and 190 mg/l [29]. Higher alkalinity values in the ground water of Tirrupur, Tamilnadu that was may be because of contamination with domestic and industrial wastes [36]. High values of alkalinity in the water samples indicate pollution of organic nature and give an unpleasant taste to the water. In addition to this enhancement of alkalinity in ground water may also because of increasing in the carbonates rock re mineralization [37,38].

Oxygen is the regulator of metabolic process of animals and plant communities and indicator of water condition [39]. DO is a highly

fluctuating factor and this value changes depending upon water depth, temperature and the oxygen partial pressure at the location [40]. Dissolved oxygen concentration in our study region varied from 1.18 to 5.45 mg/l (3.10 ± 1.09 mg/l; Figure 2c) and higher DO concentrations were found in the Coastal and Residential regions $(4.41 \pm 1.1 \text{ mg/l}; \text{ Table 1})$ than Industrial and Commercial regions $(4.01 \pm 0.24 \text{ mg/l})$ wrt statistical analysis- student t-test (p<0.1, t=1.01; Table 1). Our study values are consistent with the values reported by Madhusudan et al. [34], 4.3 mg/l, while lower than that of Rameeza et al. [28] 6.2 mg/l and sheen et al. [32] 6.5 mg/l in Visakhapatnam ground water. DO displays a positive linear relation with TDCHO (r^2 =0.77, p<0.001) (Table 2) and inverse relation with HR (r^2 =0.82, p<0.001; Table 2), pCO₂ (r²=0.75, p<0.001; Table 2) in Coastal and Residential regions and inverse relation with HR (r²=0.89, p<0.001; Table 2), pCO₂ (r²=0.42, p<0.1; Table 2) in Industrial and Commercial regions, suggesting that DO significantly consumed by heterotrophic organisms. Heterotrophic and their activities are responsible for the dissolve gas concentrations in the water bodies. In our study region HR varied from 1.11 to 3.65 (mg O2 consumption/l/d) with mean (2.89±1.18 mg O_2 consumption/l/d; Figure 2d) and we found more respiration rates in Industrial and Commercial regions $(1.69 \pm 0.31 \text{ mg O}_2 \text{ consumption/l/d})$ than Coastal and Residential regions (1.11 \pm 0.04 mg O₂ consumption/l/d) and the respiration rates in both the regions are significantly differ from one another with p<0.05, t=1.72 (Table 1). HR shows a linear inverse correlation with TDCHO (r²=0.81, p<0.001; Table 2) in Coastal and Industrial regions and with TDPRO (r²=0.91, p<0.001; Table 2) in Industrial and Commercial regions. Suggesting that in Coastal and Residential region heterotrophs are preferably consuming TDCHO where as in Industrial and Commercial regions they are preferring TDPRO, the change in the food preference by heterotrophs may be because of the variability in the community structure of the heterotrophs in the both the regions. In both the regions HR shows a positive linear relation with pCO₂ (r²=0.86, p<0.001; r²=0.92, p<0.001; Table 2) and inverse relation with TDCHO and TDPRO, suggesting that consumption TDCHO and TDPRO are the main source of pCO₂ in the ground waters at the study regions, which is further supported by an inverse relation between DO and HR in the both the regions (Table2) (Figure 3d and 4d).

Table 2: Rank and correlation matrix (Spearman's; r) of different properties in the ground waters of Visakhapatnam (*, **, *** indicates p<0.1, 0.05 and 0.001 respectively).

Coastal and Residential regions									
Parameters	Alkalinity	рН	DO	HR	TDCHO	TDPRO	pCO2		
Alkalinity		0.65**	0.15	-0.50**	0.13	0.43*	-0.48*		
рН			0.70***	-0.70***	0.60**	0.37*	-0.73***		
DO				-0.82***	0.77***	0.26	-0.75***		
HR					-0.81***	-0.33	0.86***		
TDCHO						0.16	-0.90***		
TDPRO							-0.25		
pCO ₂									
Industrial and Commercial regions									
Parameters	Alkalinity	рН	DO	HR	TDCHO	TDPRO	pCO2		
Alkalinity		0.42*	0.19	0.13	0.03	-0.25	0.17		
рН			0.31	-0.40*	-0.41*	0.49**	-0.51**		
DO				-0.89***	-0.17	0.29	-0.42*		
HR					0.23	-0.91***	0.92***		
трсно						-0.1	0.16		
TDPRO							-0.92***		
pCO2									

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Dissolved and Particulate bio available organic compounds (Carbohydrates, Amino acids, Proteins, Fatty acids and Lipids) are the main food sources to the heterotrophic organisms in the aquatic system [41,42]. In present study TDCHO varied from 6.35 to 11.19 μ MC (8.39±1.28 μ MC; Figure 2e), higher concentrations were found in the Coastal and Residential regions (9.12±0.03 µMC; Table 1) than Industrial and Commercial regions (7.93±0.3 µMC; Table 1) and these two regions significantly differ with respective to TDCHO concentrations with student t-test (p<0.001, t=3.04; Table 1). TDCHO displays, significant inverse relation with HR and pCO₂ at Coastal and Residential regions (r²=0.81, p<0.001; r²=0.90, p<0.001; Table 2; Figure 3a&c), where as in Industrial and Commercial regions, TDCHO is not showing any significant relation with HR and pCO₂, suggesting that TDCHO was being consumed by heterotrophs in farmer regions than lateral regions (Table 2). TDPRO varied from 1.27 to 4.0 µMC $(2.15 \pm 0.58 \,\mu\text{MC}; Figure 2f)$ and higher concentrations were noticed Coastal and residential regions (2.46 \pm 0.18 μ MC) than Industrial and Commercial regions (1.82 \pm 0.11 μ MC) and the concentration of TDPRO in these both the regions were significantly differ w.r.t student t-test (p<0.05, t=1.6). TDPRO shows a significant negative linear relation with HR (r²=0.91, p<0.001; Table 2; Figure 4c) and pCO₂ (r²=0.92, p<0.001; Table 2; Figure 4a) in Industrial and Commercial regions and no such relation was found in the Coastal and Residential regions (Table 2). Suggesting that, heterotrophic organisms are preferred to consume TDPRO in Industrial and Commercial regions. CO₂ is one of the key parameter which alters the pH of the aquatic system. The main sources of CO₂ in aquatic system are dissolution of the CO₂ from atmosphere and heterotrophic respiration. Where as in the case of ground, as it is closed system dissolution of CO₂ from atmosphere is not possible then the only source of CO₂ is heterotrophic respiration and the variability of CO₂ concretions depending on the heterotrophic activity. Present study pCO₂ concentrations are varied from 1944.9 to 25530.8 μ atm (micro atmosphere) with a mean 15011.4±6590.8 µatm. Higher concentrations of CO₂ found in Industrial and Commercial regions (14292.69±1507.1 μ atm; Figure 2g) than Costal and Residential regions (13729.04±1265.2 μ atm), statistical analysis with student t-test raveled that CO₂ concentration in these two region are not significantly different (Table 1). pCO₂ showed a significant negative relation with TDCHO in Coastal and Residential regions (r²=0.90, p<0.001; Table 2; Figure 3a) and with TDPRO in Industrial and Commercial regions (r²=0.92, p<0.001; Table 2; Figure 4a). It also showed a significant linear positive correlation with HR (Figure 4b and 3b) and inverse relation with DO in both industrial and Commercial regions (r²=0.86, p<0.001; r²=0.75, p<0.001; Table 2) and Coastal and Residential regions (r²=0.92, p<0.001; r²=0.41, p<0.05; Table 2) respectively. Suggesting that, the main source of pCO₂ into this region may be due to heterotrophic consumption of TDCHO and TDPRO compounds, which is further supported by the inverse relation of pCO₂ with DO.

In order to understand the relation among physical, chemical and biological parameter of ground waters at Visakhapatnam, dendogram was drawn based on measured parameters (Temperature, Chlorinity, pH, Alkalinity, DO, HR, TDCHO, TDPRO, pCO₂). Two clusters have been formed at 70% level with reference to physical and chemical parameters along with the different station at different regions (Coastal and Residential, Industrial and Commercial) in Visakhapatnam ground water. Again in that two cluster, one is dived into two groups at 85% level representing one group with Coastal and Residential regions and other Industrial and Commercial regions. Few stations of Coastal and Residential regions (5, 8, 10, 16, and 18) have shown similarity with Industrial and Commercial region stations and stations 35, 36, 39, and 40 which belongs to Industrial and Commercial regions were showed similarity with Coastal and Industrial regions stations (Figure 5a). Figure 5b Venn diagram clearly explains that the stations 6 and 7 of Costal and Residential regions have similar concentration of pH, HR and pCO, with station 38 of Industrial and Commercial regions. Stations 35, 36, and 39 of Industrial and Commercial have similar concentrations with 8, 10, and 16 in Costal and Residential regions; the intermixing of these may be because of having similar concentrations with respective to parameters HR. Stations 35, 36, 39, 40 of Industrial and Commercial regions have similar concentrations of pCO, with 8, 10, 16, and 18 of Coastal and Residential regions respectively followed by 39 and 40 with 5 and 18 with respective to pH values (Figure 5b). This suggests that the concentration of total measured physical and chemical parameters displayed similarity with reference regions.



Principal Component Analysis (PCA) showed that water chemistry conditions in the both the regions were significantly differs from one another. The principal component analysis of physical , biological and chemical data revealed that the source of pCO_2 in Coastal and Residential regions was mainly because of heterotrophic respiration, and which was mainly because of consumption of TDCHO, which is

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further supported by a inverse relation of pCO_2 with DO and TDCHO in this region (Figure 6a). Where as in the Industrial and Commercial regions pCO_2 mainly contributed by consumption of TDPRO by heterotrophic organisms (Figure 6b).





Conclusion

In order to examine the spatial variability of physical, chemical and biological parameters and their influence on the distribution of pCO₂ concentrations, a study was conducted during core winter season from October-2017 to January-2018 in Visakhapatnam ground waters. Warm, less alkaline and slight acidified waters are noticed in Industrial and Commercial regions. Higher bio available TDCHO, TDPRO are found in Coastal and Residential region ground waters. pCO₂ Concentrations are found to be more or less same in the both the regions but the pCO₂ concentrations controlling factors are different, in Coastal and Residential regions the pCO₂ is because of consumption of TDCHO and in Industrial and Commercial region it was because of consumption of TDPRO. This was a small regional study on distribution of pCO₂ concentrations in ground waters of Visakhapatnam, but intensive studies are needed on variability in pCO₂ concentration in ground waters and their flexes to the atmosphere.

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