

**Altitude effect on deuterium isotopic composition of lakes and hydrogeochemical parameters of groundwater in humid and semi arid regions**Arya Satheesan^a, P Jegathambal^{a,*}, Blessy Thomas^a, P. Sundarambal^b^aWater Institute, Karunya University, Coimbatore, India^bCSG Engineers Pte Ltd, Block 53, #05-317, Lengkok Bahru, 150053, Singapore

ABSTRACT:- Lakes are bodies of water, where flow from one or several rivers is impounded by a natural obstacle. Groundwater is an important component of lake budgets. In this study, isotope footprint compositions and analysis of hydrogeochemical parameters of Ooty lake (2,220m above MSL), Pookode lake (770m above MSL), Mananchira lake (20m above MSL) and Kollam Chira lake (1m below MSL) are carried out. The impacts of altitude effect on the isotopic composition in lakes are assessed. The water type and water mixing patterns of lakes and wells were identified from the hydrogeochemical data. The stable hydrogen isotope composition of the lakes and ground waters was determined. The isotopic results show a vivid relationship with altitude which closely approaches a linear correlation. The precipitation and surface waters become increasingly depleted in deuterium with increasing altitude and decreasing temperature. The lake waters at high elevations on the leeward side of mountain ranges are strongly depleted in deuterium as compared to waters on the windward side. Continental effect is also clearly visible in this study. There is observed a higher depletion of isotopes in water samples from Ooty lake, which is farthest from the Calicut coast.

Keywords: Lakes, Hydrogeochemistry, Stable Isotopes, deuterium, Altitude effects, India

I. Introduction

Lakes are water bodies which lie on land and are larger and deeper than ponds. They are a good source of groundwater recharge. They are a heterogeneous mixture of various water sources like surface runoff, streams and precipitation. Input sources to the lake are precipitation, runoff carried by streams and channels, groundwater channels and aquifers, and some artificial sources. Output sources are evaporation from the lake, surface and groundwater flows, and any extraction by humans. Lakes can be classified based on zones, types and even stratification. The study of physical, chemical and biological parameters of lake waters helps us in understanding the lake water structure and functions of the ecosystem. The lakes are affected by various environmental changes. Various factors like changes in land use patterns, alterations to the natural vegetation, population increase, industrial development and other anthropogenic activities can adversely affect the lake ecosystem. This may decrease the quality of water and thereby lead to the extinction of fishes and other aquatic organisms. The analysis of physical and chemical parameters plays a vital role in assessing the water quality of the lakes [6]. The hydrogeochemical parameters of the lake waters and the groundwater are affected by the natural and human activities. The variation of dissolved ions concentration in the lake waters and the nearby groundwater are dependent on lithology, velocity of flow, nature of geochemical reactions, solubility of salts and anthropogenic activities. The geochemical interactions can be a reason for the changes in water chemistry [4]. The interpretation of geochemical analysis helps in classification of lake water type. The hydrofacies of the lakes and the nearby wells helps to find the origin or source of the water [5]. In lakes, the major isotope effects found are due to evaporation. During evaporation, fractionation of lake water takes place. The evaporating moisture will be isotopically depleted and the lake waters are enriched with heavier isotopes [2]. The main objective of this study is to identify the significance of altitude effect on the lakes using isotopic footprints and hydrogeochemical parameters

A. Study Area

Four lakes at different altitudes were selected for the study. Kollam Chira (1m below M.S.L), Mananchira (20m above M.S.L), Pookode lake (770m above M.S.L), Ooty lake (2,220 m above M.S.L). Kollam Chira is a man-made lake near Koyilandi, Kozhikode district in Kerala. The co-ordinates of the lake are 11°27'37"N 75°40'31"E. It is spread across an area of 10.45 acres. It is situated at 25 km's away from the Kozhikode city. Kollam Chira is near to the Coastal area and this lake is below the Mean Sea Level. It is a historical lake belonging to a few temples in the region. Mananchira is a man-made lake situated in the centre of the city of Kozhikode in Kerala at the co-ordinates of

11° 15' 15.9" N, 75° 46' 47.9" E. It is a fresh water lake enclosed by laterite on all sides. This lake is an important source of drinking water for the Calicut City. The lake is rectangular in shape and 3.49 acres (130m x 109m) in area at an elevation of 20 m. The average temperature and rainfall in the region is 27°C and 3500 mm respectively. The South West Monsoon and North East Monsoon mainly contribute rainfall in the area. The lake stratum is lime stone. Pookode lake is a perennial, natural freshwater lake in the Vythiri taluk of Wayanad district in Kerala. It is located between 11° 34' 0" and 11° 32' 24" latitude and between 76° 1' 34" longitude. Watershed of Pookode Lake lies on the western side of western ghats which is the eastern high land zone of Kerala. The altitude of the lake is 770 meters above sea level. The lake area is spread across 8.5 hectares. Maximum depth of the lake is 6.5 metres. The average temperature and rainfall of the region is 23.3°C and 4433 mm respectively. 60% of rainy days are in South West Monsoon, 30% during North East Monsoon & remaining in dry period. Orography is an important reason for high rainfall values in the Western ghats region. The chief rock type of Pookode area is Biotite Gneiss. Horn blend is also present in very less amount. Ooty lake is located in Ooty in the Nilgiris district, Tamil Nadu at the co-ordinates of 11.4061° N and 76.6882° E. It is an artificial lake which covers an area of 23 hectares. The maximum length and width of the lake is 2.5 km x 140 m respectively. The Surface area of the lake is 3.885 km². The lake is situated at an elevation of 2,220 m from the Mean sea level. The temperature ranges from 10°C to 25°C during summer and 0°C to 21°C during winter. The average annual rainfall in the region is observed as 1920 mm. The amount of rainfall received in South West Monsoon is slightly more (Since, Ooty location is in western ghats) or almost equal to North East Monsoon. The main source of lake is the rain water from the catchment area and also the city sewage. This water overflow through Kodappanmundu Channel and finally reaches the lake. Ooty lake is highly eutrophied and polluted due to heavy weed infestation in the lake is visible

II. Materials and Method

A. Field Data Collection

Water samples were collected from Mananchira, Kollam Chira, Pookode lake and Ooty lake. A few water samples were collected from the wells nearby each lakes and also from Calicut Beach. Sampling was carried out in Mananchira and Calicut beach on 1st February 2014, Pookode Lake on 2nd February 2014, Ooty lake on 21st February 2014 and Kollam Chira on 23rd February 2014. Pre sterilised plastic cans of 1 liter capacity with stopper were used for collecting samples for hydrochemical parameters. Water samples were collected in 120 ml acidified plastic bottles for heavy metal analysis and 60 ml torsion bottles for stable isotope analysis. All details were clearly labeled on the isotope bottles and were tightly capped to avoid evaporation of the samples. Water samples from the lakes were collected from 0.5 m from the surface. The water level measurements and the depth from which water samples collected in wells were also measured using measuring tapes. The co-ordinates of the sampling locations were recorded accurately as possible using a Global Positioning System (GPS).

B. Hydrogeochemical Analysis

The water samples collected were analyzed in the Water Institute of Karunya University. The various hydrogeochemical parameters were analyzed for the water samples based on APHA standard procedures. Various parameters like pH, turbidity, electrical conductivity, hardness, chloride, alkalinity, calcium, magnesium, sulphates, nitrates, sodium and potassium were analyzed using analytical, colorimetric and instrumental methods. The pH of all the samples were measured using a Eutec pH meter 1500. Electrical conductivity is the ability of an aqueous solution to conduct electric current. It is the measurement of the concentration of dissolved solids ionized in water in μS or mS using EUTEC CON 2700 conductivity meter. Turbidity is an optical characteristic of water in NTU which is determined using HACH 2100Q Portable Turbidimeter. All samples were analysed using JASCO V-650 UV-Vis spectrophotometer to find out nitrate and fluoride concentration. Ultraviolet-Visible Spectrophotometry uses light in the visible and adjacent near-UV and near-infrared ranges and works on the principle of Beer-Lambert law. The water samples were analysed for heavy metals using Agilent 240 Atomic absorption spectrophotometer. ELICO Flame photometer is used to find the sodium and potassium ion concentrations in the water samples.

C. Interpretation of Hydrogeochemical Parameters

Aquachem software was used for graphical and numerical analysis of water quality data. Piper diagram helps to determine the chemical relationships among the waters and thereby classify them into different water types. Mixing of waters can also be found out from these tri-linear plots. Two triangles are used to plot cations and anions. Major cations (Ca^{2+} , Mg^{2+} , $\text{Na}^+ + \text{K}^+$) are plotted on one triangular diagram and major anions ($\text{CO}_3^{3-} + \text{HCO}_3^-$, Cl^- , SO_4^{2-}) on another triangle. The cations and anions on the triangles are projected up until they intersect on the diamond portion which in

turn indicates the water type. Piper diagram mainly helps to indicate the samples that have similar composition. The Stiff diagrams are plotted for individual samples. They are used to compare the concentration of selected anions and cations. Shape of the plot in the stiff diagram indicates the 'relative proportions of the various ions'. Size of the plot in the stiff diagram indicates the 'total ionic concentration'. They can be plotted on maps to show the location of different water types and also to show the regional variation of ion chemistry. Schoeller diagram helps to compare the log concentration of fluid components, with the components connected with a line (of many samples). A wide range of concentrations can be shown in this plot as the concentrations are plotted on log scale. When many samples are represented on the same plot, individual patterns may be lost, but the mixing patterns will be clearly visible. The main advantage of Schoeller diagram compared to the piper diagram is that the actual sample concentrations are displayed and compared.

D. Stable Isotope Analysis

The water samples were analyzed for stable isotope of Hydrogen (Deuterium). Isotope Analysis was done using Thermo Fisher scientific IRMS at Physical Research Laboratory, Ahmedabad. Isotopic compositions are normally expressed in δ - notation, as deviation of heavy to light isotope ratios relative to an international standard of known composition (in parts per thousand or per mil). In case of deuterium $dD = (R_{sp} - R_{Std} / R_{Std}) * 10^3$ where R_{SP} is the ratio of heavier to lighter isotope of sample and R_{Std} is the ratio of heavier to lighter isotope of standard. Positive values of 'dD' indicate enrichment of rare isotopes while the negative values of 'dD' indicate depletion of rare isotopes. The standard used is V-SMOW (Vienna-Standard Mean Oceanic Water). Stable isotopes are measured using an Isotope Ratio Mass Spectrometer (Thermo Fisher scientific IRMS). The isotopic ratio mass spectrometer has a typically low resolution in the order of organic mass spectrometer.

III Results and Discussions

A. Hydrogeochemical Analysis:

Various hydrogeochemical parameters were analyzed for the water samples from the lakes and the nearby wells using APHA standard procedures. The Minimum, average, and Maximum values of each parameter in each of the lake-nearby wells are summarized in the Table1.

[Table 1]

TABLE I. HYDROGEOCHEMICAL PARAMETERS OF LAKES IN KERALA AND TAMIL NADU

Place	Kollam Chira lake, Kerala			Mannachira lake, Kerala		
Parameters	Min	Avg	Max	Min	Avg	Max
pH	5.60	6.23	7.30	6.50	7.07	7.90
TDS	61.8	80.1	141	155.	416.2	1312.
Cl-	0.00	2.37	7.10	7.10	82.24	546.
Ca	20.0	27.5	45.0	55.0	86.67	175.0
Mg	5.00	19.1	30.0	10.0	403.3	2630.
NO ₃ -				0.63	2.27	6.83
(SO ₄) ²⁻	9.66	12.	15.3	11.9	89.52	489.0
HCO ₃ ³⁻	2.50	2.50	2.50	50.0	195.	300.0
Na	9.70	10.7	13.5	13.7	60.2	314.3
K	5.90	6.80	8.50	9.50	15.77	19.80

Comparing the obtained results for hydrogeochemical parameters with the CPCB standards, it is clearly visible that almost all the parameters are within the permissible limits in all lakes with a few exceptions. The concentration of Mg

ions is very high in Ooty lake which is due to the discharge of city sewage into the lake. Even after treating the sewage water, the Mg ion concentrations are high.

B. Piper Diagram

The major water types of the four lake systems are found out by plotting it separately on the trilinear plots. The major water type in the Kollam Chira is found out to be Mg-Ca-Na. The water type found in the nearby wells of Kollam Chira is Mg-Ca and Ca-Na-Mg-SO₄. Majority of water samples show mixed type cations. But a few shows dominance of Mg ions and another sample shows the influence of Ca. Among the major ions, most of them are plotted within the SO₄. The influence of mixed type anions are seen in a very few samples. Kollam Chira used for bathing and washing by the local people. Due to the continuous use of soaps and detergents, Mg & Ca ions can be higher in the lake water. The Major water type of Mananchira is found out to be Ca-Mg and Ca-Mg-HCO₃. The water types found out in the nearby Wells are Ca-Mg-HCO₃ and Ca-Mg. The water from the beaches shows the dominance of Mg-Na-Cl water type. Majority of the Mananchira and the nearby ground water samples show the dominance of Ca in the cations. But Mg cations are seen more in the water samples collected from the Calicut beach. In the case of anions, Bicarbonates are more for the lake water and the nearby ground water samples. But the beach water samples show the dominance of Cl ions. A Mananchira Lake stratum is composed of lime stone (CaCO₃). The solubility of lime stone in the lake strata can be the reason of Ca and HCO₃ in the lake water. Increasing urbanization and certain industries near the lake add to pollute this water. Chemical industries add Mg to plastics and other materials, which can be the reason for the traces of Mg ions present in the lake waters. It is clearly evident that no much influence of sea water occurs in the lake even though the Calicut beach is nearby. The Pookode lake has a major water type of Mg- Ca-HCO₃. The nearby ground waters show Ca-Mg-HCO₃ water type. Many water samples show mixed type Cations. But many other samples show the clear dominance of Mg ions followed by an influence of Ca. The majority of the water samples have bicarbonates as dominant Anions. Main underlying rocks of the Pookode lake are Biotite Gneises (Quartz, Feldspar, Biotite) and Hornblende. This geology may be the reason of the dominance of Mg and Ca in this fresh water lake. From the Piper diagram, the major water type of the Ooty lake is found out to be Ca-Mg-Na-HCO₃. The water types of the nearby wells are found out to be Ca- Mg-Na-HCO₃ and Ca-Mg-HCO₃. Majority of the water samples show 'mixed' type Cations. But many samples show the influence of Ca. The waste water entering the Sewage treatment plant and even the treated water coming out, which is discharged into the Ooty lake shows the dominance of Mg ions. In case of anions, the majority of the water samples show the dominance of bicarbonates. The main reason for the Mg, Ca, HCO₃ ions in the lake water can be the discharge of city sewage into the lake. The used water which joins the lake may have soap and detergent contents and can pollute the lake.

B. Stiff Diagram

From the Shape analysis of the stiff diagram, it is found out that Na-Cl is least present in Kollam Chira waters. CaHCO₃ is more in the lake water compared to NaCl and MgSO₄ is most dominant in Kollam Chira. In case of Mananchira lake water sample it is found out that CaHCO₃ is dominant there. MgSO₄ is comparatively less and NaCl is the least present ratio. It is visible that CaHCO₃ ratio is dominant in the Pookode lake water sample. MgSO₄ is comparatively less in many samples whereas in a few samples MgSO₄ is higher than CaHCO₃ ratio. NaCl is least present in Pookode lake. The dominant ion proportion in Ooty lake is found as CaHCO₃. MgSO₄ is comparatively less present proportion and NaCl is least present in Ooty lake waters. From the Size analysis of the Stiff diagrams, it is clearly visible that the Ooty lake has much higher concentration of all ionic species than the other lakes. Total Ionic Concentration pattern of the different lakes are Ooty lake > Mananchira > Kollam Chira > Pookode lake.

C. Schoeller Diagram

In case of Kollam Chira, the relative tendency of ions (mg/l) in lake water is Mg > Ca > Na and SO₄ > HCO₃. In Ground waters it shows a trend of Ca ≥ Mg > Na. From the Schoeller diagram, it is visible that the proportion of ionic concentration of Groundwaters in the Manachira lake region is higher than that of the lake waters. The relative tendency of ions (mg/l) in both lakes and ground waters are Ca > Mg > Na in case of Cations and HCO₃ > Cl > SO₄ in case of Anions. In Pookode lake the mixing of lake water with ground water is clearly visible. In the lake waters the relative tendency of ions (mg/l) are Mg > Ca > Na and HCO₃ > Cl > SO₄. In ground waters, the Cations show a relative tendency of Ca > Mg > Na and anions show a trend of HCO₃ > Cl > SO₄. In case of Ooty lake water, both the lakes and the ground water samples show a relative tendency of ions (mg/l) as Ca > Mg > Na for cations and HCO₃ > Cl > SO₄ for anions.

TABLE II. HYDROGEOCHEMICAL ANALYSIS OF LAKE AND GROUNDWATER SAMPLES USING PIPER DIAGRAM, STIFF DIAGRAM AND SCHOELLER DIAGRAM

Place	Piper Diagram	Stiff Diagram	Schoeller Diagram
Kollam Chira, Kerala	Major Water type : Mg-Ca-Na Near by Wells : Mg-Ca & Ca-Na-Mg-SO ₄	Na-Cl = least Ca-HCO ₃ = less Mg-SO ₄ = dominant	Lakes Mg > Ca > Na & SO ₄ > HCO ₃ Ground waters Ca >= Mg > Na
Mananchira, Kerala	Major water type: Ca-Mg Ca-Mg-HCO ₃ Near by Wells : Ca-Mg-HCO ₃ Ca-Mg	Ca-HCO ₃ = Dominant Mg-SO ₄ = less dominant Na-Cl = least	Lakes & GW Ca > Mg > Na HCO ₃ > Cl > SO ₄
Pookode lake, Kerala	Major water type : Mg- Ca-HCO ₃ Near by wells : Ca-Mg-HCO ₃	Ca-HCO ₃ = Dominant Mg-SO ₄ = less Na-Cl = least	Lakes Mg > Ca > Na HCO ₃ > Cl > SO ₄ Ground waters Ca > Mg > Na HCO ₃ > Cl > SO ₄
Ooty lake, Tamil Nadu	Major water type : Ca-Mg-Na-HCO ₃ Near by wells : Ca- Mg-Na-HCO ₃ Ca-Mg-HCO ₃ Outlet STP : Mg	Ca-HCO ₃ = dominant Mg – SO ₄ = less dominant Na – Cl = least	Lakes & GW Ca > Mg > Na HCO ₃ > Cl > SO ₄

D. Stable Isotope Analysis (dD)

Out of the four lakes studied, three lakes are in Kerala and the other lake is in Tamil Nadu. Kerala is closer to the equator, compared to Tamil Nadu. Kerala lies in between Arabian Sea (west) and Western Ghats (east). The Western Ghats prevent the dry winds blowing from the north from entering Kerala, and therefore Kerala receives copious South west monsoon. Due to that Kerala coast receives the first precipitation, which results in enriched isotope value here. Then the vapour travels diagonally into Tamil Nadu and shows comparatively lesser isotopic values in the Western Ghats of Nilgiris. The isotopic composition of surface water is similar to that of precipitation. Same isotopic trend is observed in the cases of the four lakes studied, in which two lakes are near by the Kerala coast (the Pookode lake on the western side of the Western Ghats and the Ooty lake on the other extreme of Western Ghats). North East Monsoon travels over large land masses before reaching kerala coast which results in large continental effect. Evaporation is the reason for the most

significant isotope effects found in lakes which results in the enrichment of rare isotope, there by producing higher isotopic values. Kollam Chira, Mananchira, Pookode lake, and Ooty lake have higher dD values compared to the nearby ground water sources which indicates evaporation in lakes is high. In case of Kollam Chira, the dD values are ranging from 2.54 per mil to 11.54 per mil. Around Mananchira lake region the isotopic values of D is varying from -7.16 per mil to 11.47 per mil. dD values of Pookode lake is varying from -2.87 per mil to -10.51 per mil. In Ooty lake, highest depletion of heavier hydrogen isotope was observed compared to all other lakes. dD values of Ooty lake is varying from -27.56 per mil to -30.26 per mil. Isotopic composition of precipitation becomes progressively lighter (dD value decrease) with decreasing temperature. The same isotopic trend is found in the case of lake waters. Isotopic composition of lake waters are getting depleted with the decrease in temperature. A trend for temperature follows a line regression of $y = 1.516 - 44.78 (R^2 = 0.833)$. At higher altitude, the isotopic composition of precipitation gets depleted compared to that at lower altitude. This isotopic effect is termed as Altitude Effect or Elevation Effect or Alpine Effect. Isotopic depletion of deuterium is from -1 to -4 per mil per 100m rise in altitude. When vapour leaves the coastal area and reaches the continental area, vapour mass rises over the land and cools adiabatically causing orographic precipitation. A trend for elevation follows a line regression of $y = -0.015x + 4.532 (R^2 = 0.908)$. Event lapse rates (dD versus altitude) calculated by linear regression show that the concentration of heavy isotopes in the lake water samples generally decreases with altitude. The decrease in dD values with increasing altitudes reflects a decrease in condensation temperature as air masses are uplifted by topography over high mountains. Isotopic composition decreases

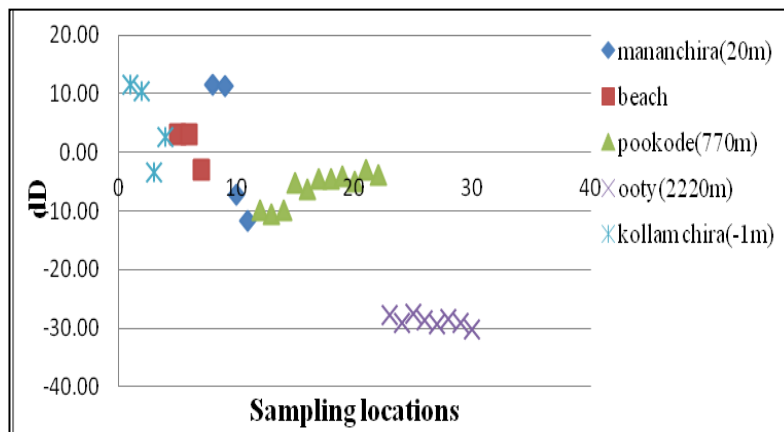


Figure 1. Sampling locations Vs deuterium (dD)

enriched. Colder inner regions receive isotopically depleted precipitation. Calculated trends for the (dD values decrease) with increasing in-land distance from coast. Coastal precipitations are isotopically distance to the Calicut beach follows the regression model $y = -0.208x + 6.207 (R^2 = 0.884)$ for dD (Fig. 1 to Fig. 5)

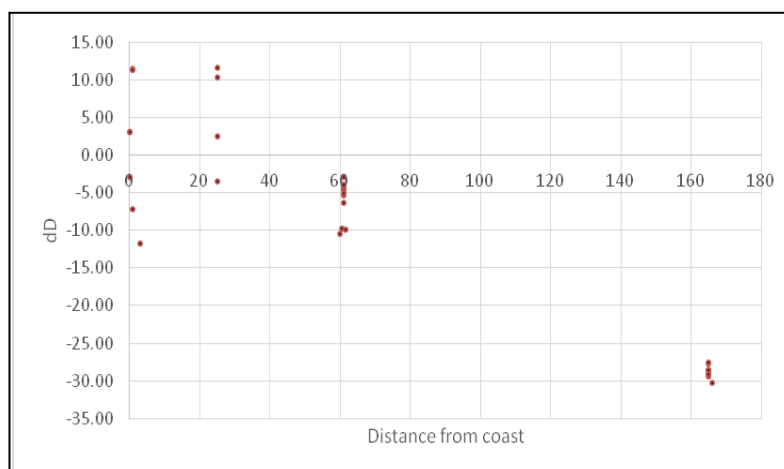


Figure 2. Distance of the sample locations from the coast

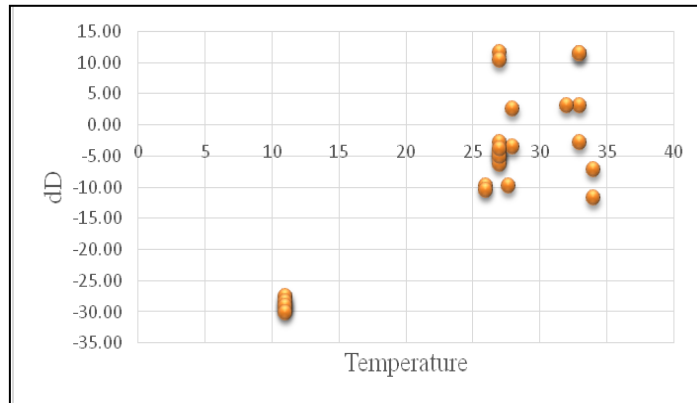


Figure 3: Temperature of the sample locations Vs dD

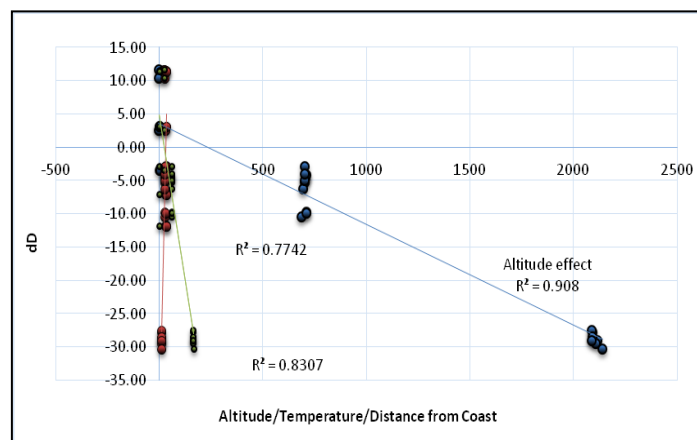


Figure 4: Altitude of the sample location Vs dD

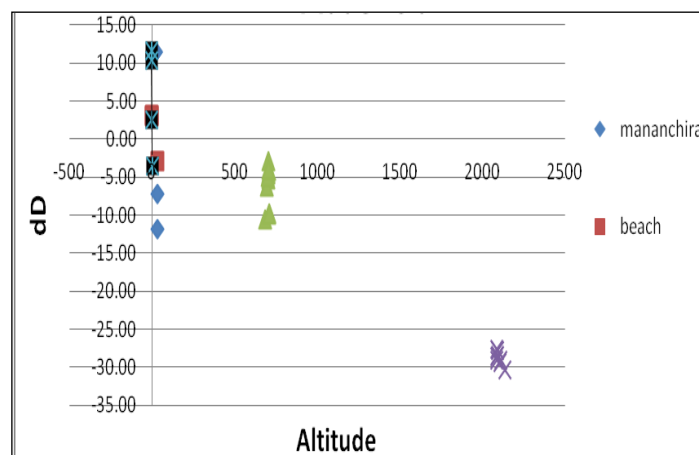


Figure 5: . Comparison of altitude effect, temperature effect and continental effect Vs deuterium (dD)

IV Conclusion

The various hydrogeochemical parameters were analyzed for the water samples from the lakes and the nearby wells. In all the lakes, almost all parameters were within the permissible limits except a few exceptions. The reason for too high concentration of Mg in Ooty lake may be due to the overflow of city sewage into the lake waters. From the Hydrogeochemical data, Piper diagram, Stiff diagram and Schoeller diagram was plotted. The water type, mixing patterns of water, proportion of ions and total ionic concentration is found out. The stable Hydrogen isotope composition

of the lakes and Ground waters were found out. The significant isotope effects in lakes are due to the enrichment of rare isotopes produced by evaporation. In case of Kollam chira, the dD values are ranging from 2.54 per mil to 11.54 per mil. Around mananchira lake region the isotopic values of D is varying from -7.16 per mil to 11.47 per mil. dD values of Ooty lake is varying from -27.56 per mil to -30.26 per mil. The lakes have higher dD values compared to the nearby ground water source which indicates evaporation in lakes is high. The decrease in dD values with increasing altitudes primarily reflects a decrease in condensation temperature as air masses are uplifted by topography over high mountains. Isotopic composition becomes progressively lighter (dD values decrease) with increasing inland distance from coast.

V References

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