hydrology

Article

Influence of Dissolved Oxygen, Water Level and Temperature on Dissolved Organic Carbon in Coastal Groundwater

Thilagavathi Rajendiran [1,*], Chidambaram Sabarathinam [2], Banajarani Panda [3] and Vetrimurugan Elumalai [4]

[1] Department of Geology, V.O. Chidambaram College, Tuticorin 628008, India
[2] Water Research Center, Kuwait Institute for Scientific Research, Kuwait City 13109, Kuwait; csabarathinam@kisr.edu.kw
[3] Department of Geology, Ravenshaw University, Cuttack 753003, India; banajapanda@ravenshawuniversity.ac.in
[4] Department of Hydrology, University of Zululand, Kwa Dlangezwa 3886, South Africa; elumalaiv@unizulu.ac.za
* Correspondence: thilagavathir1987@gmail.com

Abstract: The quality of groundwater has been severely impacted by urbanization around coasts. The change in climate and land use patterns has deteriorated the quality and availability of groundwater. One of the main issues in contemporary groundwater quality research is dissolved organic carbon (DOC) in the water. The influence of DO, water level and water temperature on DOC in groundwater was identified in the current study by sampling 68 groundwater samples. The analytical results revealed that ~18% of total samples have DOC > 5 mg/L. The groundwater samples represented in the urban regions show high DOC. The samples with higher DOC correlated positively with dissolved inorganic ions, such as Ca, K, NO_3, Fe and DO. Domestic wastewater, agricultural runoff and local geology all have an impact on the DOC of groundwater. Groundwater chemistry is shown to be controlled by both aerobic and anaerobic conditions based on the DOC's interactions with other ions. The study interrelates various sources, such as land use, geology, water level and temperature, to the DOC in groundwater and infers that the levels are higher in shallow groundwater, predominantly around the built-up region followed by the agricultural region. The temperature changes enhance the DOC in groundwater due to the variation in microbial activity. The shallow water level with a lower temperature shows the maximum DOC. Apart from the sediment organic matter and microbes, the study also attributes land use pattern to the source of DOC in groundwater.

Keywords: groundwater; dissolved organic carbon; inorganic ions; water level; temperature

check for updates

Citation: Rajendiran, T.; Sabarathinam, C.; Panda, B.; Elumalai, V. Influence of Dissolved Oxygen, Water Level and Temperature on Dissolved Organic Carbon in Coastal Groundwater. *Hydrology* **2023**, *10*, 85. https://doi.org/10.3390/hydrology10040085

Academic Editors: Monzur Imteaz and Roohollah Noori

Received: 21 January 2023
Revised: 30 March 2023
Accepted: 4 April 2023
Published: 6 April 2023

1. Introduction

The suitability of groundwater is greatly reliant on dissolved organic carbon (DOC) concentration, owing to its capability to modify aquatic chemistry and bacterial loads. An enormous ratio of the recognized threat is related by the occurrence of decontaminated by-products (DBPs) [1], which are intensely associated with DOC [2–6]. The concentration of higher DOC can increase the portability of additional pollutants in groundwater, containing heavy metal nutrients and other compounds connected with organic matter (OM) and dissolved substances. The groundwater contains copious DOC [7–9], which varies the redox values, disturbing the nature of groundwater in provincial aquifers [10,11]. Studies [12,13] have inferred that the significant contribution of DOC to the local ecosystem is mainly governed by the transport of DOC from shallow groundwater. Further, DOC plays a key role in the geochemical variations in shallow/perched and deeper/regional groundwater in the aquifers [14,15]

Bacterial activity in an ecosystem is fundamentally triggered by the availability of DOC from the degradation of plant matter [16,17]. Due to population expansion and urbanization, pollution levels in groundwater may rise [18,19] and the resulting DOC levels are expected to rise further [20,21]. While numerous studies [2–6,20] have looked into the sensitivities, existences, causes and transport of regular DOC, few have looked at groundwater DOC in tandem with temporal and spatial factors [22,23]. The microbiological and geochemical processes occurring deep below the Earth's surface are reflected in DOC, making it both evocative and prolific. While some of these activities, such as denitrification [20,24], are deliberate, DOC augmentation directly disrupts bacterial survival and flexibility [25,26]. There is between 1 and 5 mg of dissolved organic carbon (DOC) per mL (mg/L) in the clean groundwater that lies beneath cultivated areas that have been harvested. However, specific animal and farming organizations note that the end product has DOC > 5 mg/L [27].

It has been found that the DOC content in the vast majority of the world's subsurface water supplies is less than 5 mg/L [28]. Changing climate conditions and urban land use are both associated with DOC shifts in groundwater aquifers. Increasing dissolved organic carbon (DOC) levels in an aquifer can be achieved via a number of different methods [24,29]. However, DOC composition is controlled by certain proteins, carbohydrates and contaminated water such as sewage effluents, which is why higher levels of DOC coincide with fulvic and humic acids [30]. This is likely due to the reluctance of molecular laboratory investigations, the most remarkably enriched pollutant movement and polymerase chain reaction (PCR) [31].

People in the Pondicherry region rely heavily on groundwater for their daily activities. Research into groundwater geochemistry was spurred on by factors, including excessive groundwater depletion, harsh agricultural methods and the underlying geological background. As a result of pumping water from the coastal aquifer, salt water is now infiltrating inland. Several scientists have investigated the saltwater that enters the Puducherry coastal aquifer [32,33]. The Pondicherry area is home to a complex aquifer, and alterations to the interaction and environmental activity of aquatic systems can be encouraged by increasing DOC levels. Previous research in the area has attempted to identify the various factors that contribute to the unique chemistry in the region's groundwater [33–39], including investigations into microbial contamination [40] and arsenic mobilization in groundwater [33,41]. The many risks posed by DOC necessitate an understanding of the factors that contribute to its presence in groundwater. Prior research on DOC in the area has considered the impact of formation [38,42]. Groundwater DOC is suggestive and/or causative of several subsurface microbial and geochemical processes because a subset of biomolecular components is reactive [9]. However, DOC enrichment directly affects microbial oxygen availability and subterranean microbial survival and movement [26]. Higher amounts of dissolved organic matter (DOM) in groundwater can decrease optical clarity (or increase turbidity), which can affect the efficacy of certain treatment techniques (e.g., irradiation) and cause problems with DOC by-products after disinfection [43]. In polluted waters, such as sewage effluent, proteins and carbohydrates may dominate DOC composition [30]. Groundwater was contaminated because of dissolved organic carbon (DOC) from landfill leachate, which combined with the metals to produce complexes. The presence of DOC accelerated the metals' movement [44]. Dissolved organic carbon (DOC) was studied to determine its properties and markers of wastewater origin in both reclaimed wastewaters and groundwater. Hydrophilic DOC made up more than half of the total in activated carbon and RO effluents, and no humic acid was identified [45]. Dissolved organic carbon (DOC) in the shallow groundwater of Sri Lanka was mapped according to seasonal risk zones for chronic kidney disease of unknown etiology (CKDu). The results suggested that a significant impact on CKDu was exerted by the interplay between DOC and Ca, Mg and the metabolites of certain pesticides [46]. To further investigate the potential link between CKDu incidence and the DOC in drinking water, the authors later investigated the interactions of Ca and SO_4 with a model organic fraction of humic acid (SHA) [47]. The literature review summarizes the fact that DOC in groundwater is derived from multiple sources, due to different geological settings, domestic and agricultural discharge, water table fluctuations, temperature, DO conditions, etc. An attempt was made in this study to determine the predominant DOC-contributing sources to groundwater. The novelty stems from the determination of the sources in groundwater with major ions from a layered geological sequence, with multiple land use patterns adjoining the coastal region. This investigation takes place in Southern India, an area characterized by high temperatures, high humidity and variable precipitation patterns that are replenished, in large part, by local rivers and tanks, such as the Gingee and Ponnaiyar. Human activities are responsible for a significant amount of the decline in groundwater levels in this area. Therefore, research is required for the analysis of water quality trends as well as to derive the long-term management of its groundwater resources. Insights from the study may be transferable to other parts of India where water shortage is a problem due to overuse, poor water quality and climate-change-related variations in rainfall. Considering the above facts, the study on DOC in the groundwater is significant; in addition, studying the interrelationship of physical parameters, such as temperature, water level fluctuation and the relation with land use patterns, in the coastal urban groundwaters is a novel approach.

2. Study Area

The Puducherry region is situated in the southeastern part of India (293 km^2), which extends between 79°37′ and 79°50′ E and 11°45′and 12°0′ N (Figure 1a). It comprises five communes, including Bahour, Ariyankuppam, Nettapakkam, Villiyanur and Mannadipet. As per the Census of India (2011), Puducherry has a total population of 950,289, of which 69% live in urban areas and 31% in rural areas. Further, 27 °C and 37 °C are the average temperatures during summer and 22 °C to 28 °C during winter. The humidity fluctuates from 70% to 85% with respect to season. The precipitation is from dual monsoons, such as northeast (October and November) and southwest monsoon (June–September), in the study area. Additionally, 1250 mm is noted as the average annual rainfall in this region. The Northeast Monsoon (NEM) contributes 63% (October to December) and Southwest Monsoon (SWM) contributes 29% (June to September) of the rainfall. Topographically, the region is a plain, with an average altitude of 15 m above the mean sea level (msl), with major geomorphological units of coastal plain, uplands and alluvial plain [48–50].

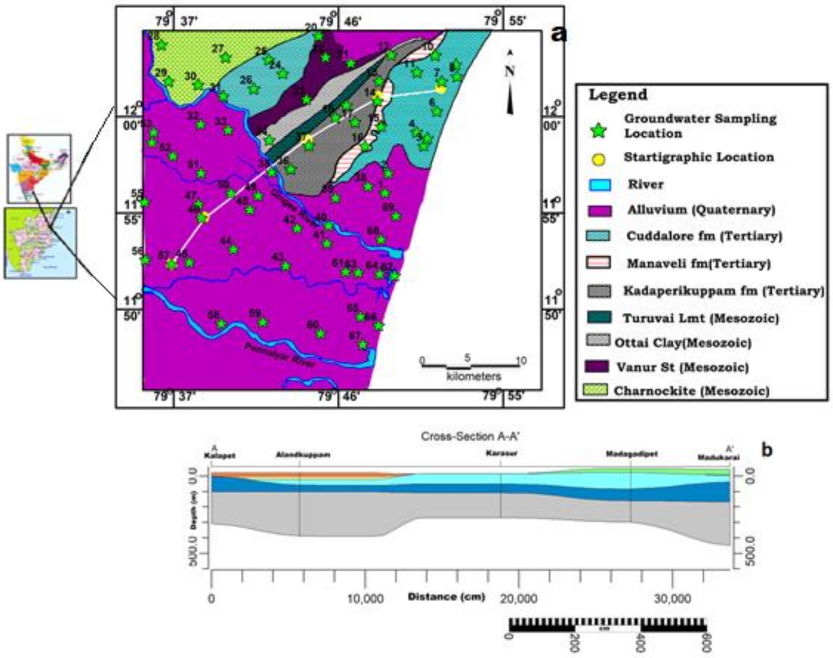

Figure 1. (**a**) Location of the study area with monitoring locations, (**b**) cross-section along A-A′.

Land Use Land Cover (LULC) of the study region shows that the agricultural lands are predominant, occupying nearly 62% of the study area followed by build-up land (26.7%) and water bodies (8.9%). Compared to the land use patterns of 2005 and 2015, it is observed that the agriculture land reduced by 2.2%, build-up area increased by 3.2% and water bodies reduced by 0.7% [51]. The most common crops are paddy rice and sugarcane. Millets, legumes, oil seeds, cotton, vegetables and tapioca are some of the other crops grown. The industrial estates in Pondicherry are well known for being highly reliant on groundwater.

Gingee and Ponnaiyar River are the two major rivers that flow from northwest to southeast. The drainage patterns are dendritic and sub-dendritic. Sedimentary formations, stretching in age from cretaceous (Mesozoic era) to recent (Quaternary), are represented. The Mesozoic formations are exposed in the Northwestern part, with a minor representation of Archean formations. The tertiary formation is composed of lower and upper tertiary, characterized by the Cuddalore, Manaveli and Kadaperikkuppam formations. The recent (Quaternary) formation in this zone is signified by alluvium and laterites. Laterites ensue as a tinny cap above the Cuddalore establishment. Kankar and Shale are observed in Alluvium. The subsurface stratigraphy (Figure 1b) and lithological cross-section reflect the vertical variations and the nature of the aquifers [52] with a peripheral marine ailment in the Cuddalore formation. Clay underlying lignite in this sequence was reported by [53]. The common trend in the Tertiary and Cretaceous formations is NE-SW through mild dip towards the southeast. However, the similar strike indicates a dip with a maximum of 10° in the Cuddalore formations.

Within the research region, the two most important water-bearing formations are Sedimentary rocks, such as the Cuddalore and Vanur sandstones, and crystalline rocks such as the Archeans, which are both prone to cracking and fractures. Throughout most of the area, there are sedimentary strata that are particularly permeable. Topographically, the region is a plain with an average altitude of 15 m above the mean sea level (msl) (Figure 2). The gradient of land is dipping towards the east and, thus, the groundwater also regionally flows toward the east (towards the coast). There are three primary potential aquifer systems in the region, all of which are based on porous sedimentary rock: The Vanur—Ramanathapuram Sandstone (Cretaceous), the Cuddalore sandstone (Tertiary) and the shallow alluvial (Quaternary) aquifers. The CGWB can be seen in Table 1 [54]. The research region has a depth range of 19.5–601.5 mbgl, a discharge of 1–60 lps, a storativity (S) of 8.9×10^{-4} to 4.3×10^{-3} psi^{-1} and a transmissivity (K) of 50–2000 m^2/day.

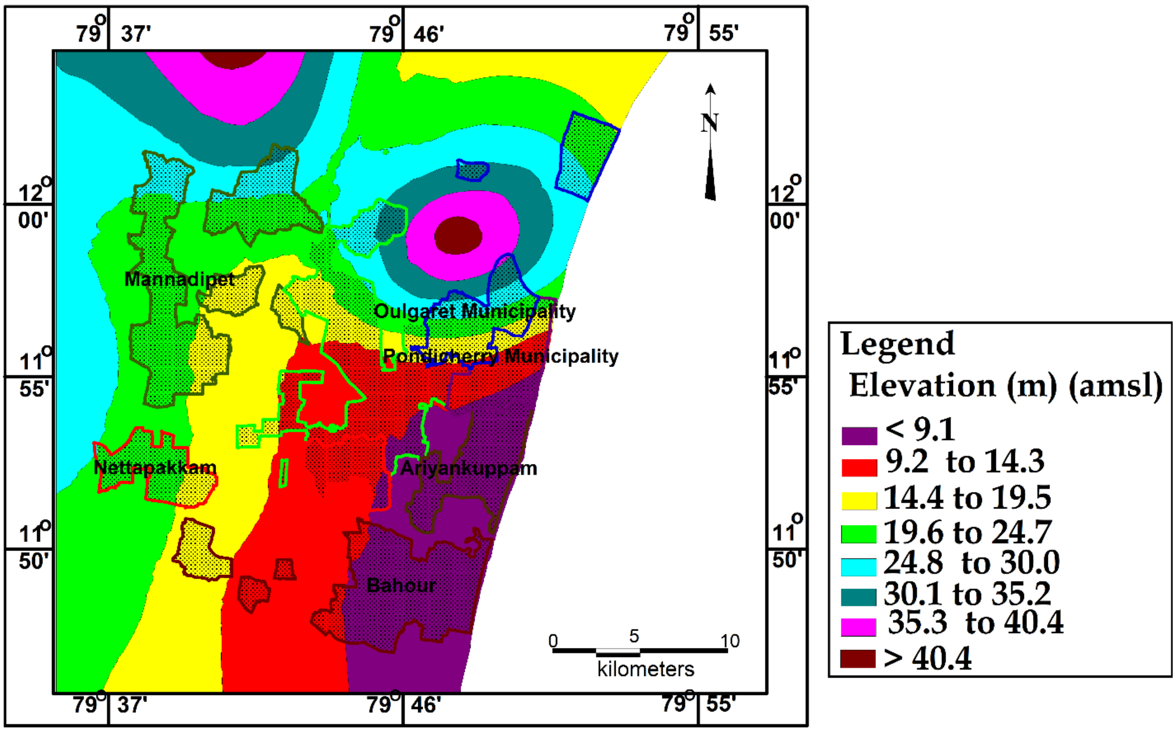

Figure 2. Elevation map of the study area with communes.

Table 1. The geological succession along with their aquifer parameters in the study area [53,54].

Era	Period	Transmissivity Value (m^2/day)	Storage Coefficient	Specific Yield Prospects (CU.M/D)	The Depth of Tube Wells (mbgl)	Thickness of These Aquifers (m)	Groundwater Condition
Cenozoic	Quaternary	275–770	-	<200	25–50	5 to 34	Unconsolidated, Unconfined
	Tertiary	1000–2000	9.58×10^{-5} and $8.9 \times 10^{-4.}$	1000–2000	25–350	20 to 245	Unconsolidated, Mainly Confined some patches as unconfined
Mesozoic	Cretaceous	100–2000	2.93×10^{-5} to 1.36×10^{-4}	700–800	65–400	38 to 92	Unconsolidated, Mainly Confined some patches as unconfined
	Archaean	<1–15		100–200	10–15		Consolidated, Occur as unconfined aquifer in weathered mantle and semi confined to confined aquifer in fractures

3. Materials and Methods

In order to account for variations in water depth, lithology, geomorphology, the impact of seepage and other anthropogenic or natural variables, 68 borewell samples were collected during SWM in August (2016). In situ measurements included pH, EC and DO (Table 2). After collection, the samples were filtered through 0.45-micron filter paper, stored them in one-liter polyethylene containers and then 250 mL of sample was used to analyze dissolved organic carbon. Cations and anions were analyzed using standard techniques [55]. The ion balance error was used to estimate the analytical precision of the ion measurements, which was found to be within 10% of the stated value (Table S1).

Table 2. Summary of groundwater chemical constitutions from different locations in the study area (*n* = 68 samples).

Parameters	Minimum	Maximum	Average
Well Depth (m)	13.5	150.00	57.93
pH	5.2	9.5	6.79
Temp (°C)	29.1	33.6	31.01
Ca (mg/L)	16	124	63.12
Mg (mg/L)	2.4	84	22.72
Na (mg/L)	42.7	394.3	189.33
K (mg/L)	1.7	247.8	28.02
HCO_3 (mg/L)	73.2	597.8	320.49
Cl (mg/L)	68.63	514.03	249.64
SO_4 (mg/L)	0.03	0.99	0.52
NO_3 (mg/L)	BDL *	184.16	16.2
PO_4 (mg/L)	BDL	17.98	0.79
Si (mg/L)	33	258	143.15
DO (mg/L)	1.55	5.21	3.59
DOC (mg/L)	0.49	28.92	3.29
Fe (mg/L)	BDL	5.02	0.36
Mn (mg/L)	BDL	0.37	0.06

* below detection limit.

Statistical analysis of the data was performed using SPSS v.10. Pearson's correlation coefficient was established for the correlation matrix among the ion pairs. The values lie from +1 to −1, the values near to +1 are considered to be perfect correlation and the high and low degrees of correlation are in values ranging from +0.75 to +1 and from 0 to + 0.25. A "Total Organic Carbon Analyzer TOC-VCSH" (Shimadzu model of ASI-V/TOC-VCSH) was used to measure the DOC in water samples after acidifying them with a small amount of hydrochloric acid and purging them with gas. As a result, the inorganic carbon (IC) and expelled CO_2 from the sample solution combine to generate carbon dioxide gas. By using acidification and sparging (the elimination of inorganic carbon), NPOC measurements are similar to TOC measurements. It is possible for purgeable organic compounds to be removed from a sample when using the sparging method; as a result, TOC measurement is also known as NPOC [56,57]. DOC is measured using a 680 °C combustion catalytic oxidation/NDIR method (Figure S1), TC is measured from 0 to 25,000 mg/L and TOC CSH has a CV of 1.5% at most for reproducibility. In order to validate THM readings, a single sample (raw water, treated water with reducing agent, treated water with HCL) was chosen. This includes a liquid–liquid extraction process for THMs (LLE). A gas chromatograph equipped with an electron capture detector was used for THM analysis (ECD). Using inductively coupled plasma mass spectrometry (ICPMS), the ionic concentrations of manganese and iron were determined (ICP-MS ELAN DRC II, Perkin Elmer Sciex Instrument). For QA/QC and precision, tests were also conducted with blanks and with standards.

4. Results and Discussion

The physicochemical parameter values of the groundwater are given in Table 2. The quantity of the dissolved salts and salinity is determined by measuring electrical conductivity (EC), the most significant indices for water quality. Higher values of EC in the groundwater reflect leaking or mixture of the aquifer material or mixing of saltwater [58]. The groundwater samples have EC values ranging between 751 and 2343 µS/cm (Table 2). The order of major ion concentrations was Na > K > Ca > Mg and HCO_3 > Cl > NO_3 > PO_4 > $SO_{4.}$ The predominant ion in the groundwater is Na, and HCO_3 is the dominant cation and anion, with an average concentration of 189.33 and 320.49 mg/L, respectively.

4.1. DOC in Groundwater

DOC varies with respect to location; the maximum, minimum and average values are 29, 0.5 and 3.6 mg/L, respectively (Table 2). The DOC concentrations were observed to be maximum in Nallavadu: (Sample no. 61) with 29 mg/L (Figure 3), predominantly 82% of samples fall between 0 and 5 mg/L, 10.2% of samples fall between 5 and 10 mg/L of DOC and 7.3% of samples have a value >10 mg/L. Spatially, the higher concentration in the study area is noted in the Northwestern and Southeastern region (Figure 3). Dissolved organic carbon (DOC) in drinking water must be less than 5 mg/L or it would have an undesirable effect on water distribution and/or be considered an aesthetic irritation to consumers [59]. The greater concentration of DOC is roughly > 5 mg/L and will produce challenges for the water treatment, and it leads to disinfection by-products, including trihalomethanes, and the DOC will also affect the color of the water. Sample 61, located near Nallavadu, was chosen because it had the highest DOC among the samples taken. More than 600 disinfection by-products (DBPs) are known worldwide. In this context, the trihalomethanes (THMs) have been generally documented in potable water supply [60], including chloroform ($CHCl_3O$), bromoform (CHBr) and dibromochloromethane (CH_2Cl_2). Considering health hazards, a sample from Nallavadu with DOC was tested for THMs, i.e., $CHCl_3$, $CHBr_2Cl$ and CHBr. From the preliminary concentration, it was noted as 0.275 µg/L of bromoform, 0.166 µg/L of dibrmochloromethane and 0.187 µg/L of bromodichloromethane + chloroform in the groundwater. The THMs were in the following order: CHBr > $CHCl_3$ > $CHBr_2Cl$. Bromoform is the most abundant of the studied compounds [61,62], perhaps due to the higher concentration of Bromide in the samples. This is followed by chloroform and dibromochloromethane.

4.2. Relationship between DO and DOC

The degree of microbial oxygen consumption in the aquifer matrix determines the DOC concentration. Statistical investigation reveals a relationship between dissolved organic carbon (DOC) and dissolved oxygen (DO) in aquifers, with the strength of this relationship mostly determined by DOC's bioavailability [63]. Groundwater samples typically show a negative relationship between dissolved organic carbon (DOC) and dissolved oxygen

(DO). The correlation between DOC and DO [64] seen in these samples demonstrates the presence of aerobic respiration. When DOC is present in water with no dissolved oxygen, denitrification might occur due to low sulphur levels [65,66]. While oxygen deficiency is maintained, electron donors, such as Mn^{2+} and Fe^{2+}, can accumulate next to a transport route. In addition, estimating low DOC alongside high DO reveals an extraneous source of bioavailable DOC (Figure 4).

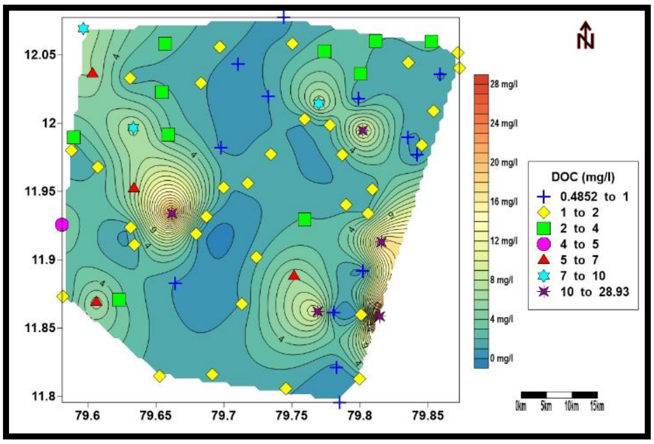

Figure 3. Spatial representation of DOC concentration in groundwater samples.

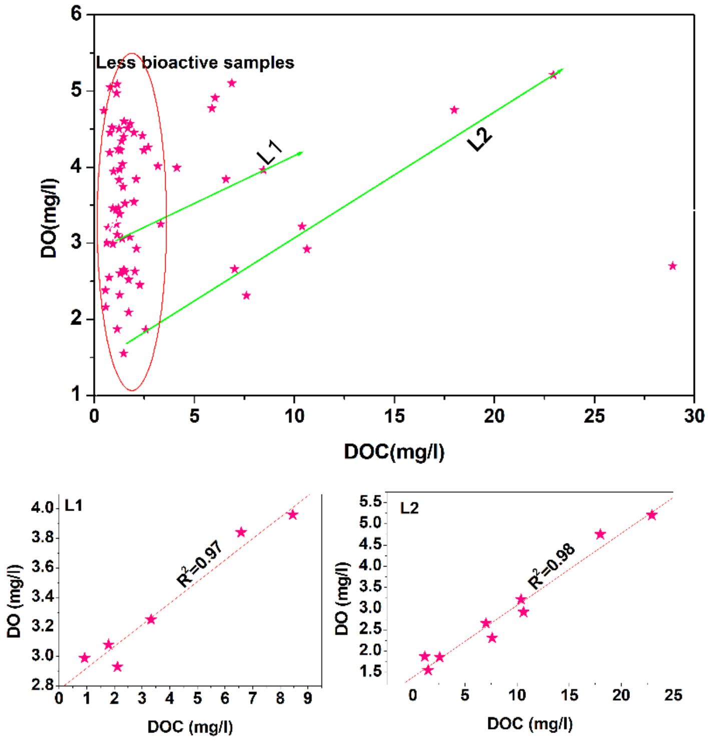

Figure 4. Representation of groundwater sample in the plots of DOC vs. DO.

The samples have a scattered distribution of low DOC and high DO. Due to the fact that DOC and DO levels are both low (as they were calculated in a low-carbon aquifer), this indicates that DOC is not bioavailable. In addition, some samples exhibit a rising trend of DOC with rising DO, suggesting greater bioavailability of DOC at higher DO concentrations (Figure 4 L1 and L2). There was a strong relationship between the DOC and DO concentrations in the groundwater. Microbial reduction processes involving manganese, iron and pH are responsible for the rising DOC. DOC was found to have a positive association with Fe and Mn and a negative association with DO and pH. The idea that samples with DOC < 5 mg/L are less bioavailable than those with DOC > 5 mg/L is supported by interpretations from the correlation matrix.

Bioavailable DOC is indicated in samples with concentrations of 5 mg/L or higher. Hydrogen ions, manganese and iron all respond to rising DOC-DO linear/hyperbolic performance [67]. Groundwater [13,68] with high concentrations of DOC and DO may originate in irrigated areas, which are a major source of bioavailable [69] (bioactive or biologically active) carbon. In contrast to the low bacterial activity elsewhere, the high DO in the research area indicates that oxygen is being used by microbes. Therefore, it is reasonable to conclude that oxidation, deep within the aquifer, is negligible, as anaerobic oxidation requires one of these pathways to occur. Therefore, comparing the bioavailability of DOC in various samples can be conducted qualitatively with the use of the DO and DOC interaction study. Only one sample (showing rising DOC and falling DO) was found to have a near-anoxic condition in the region under study.

4.3. Temperature and Water Level

The temperatures of the groundwater samples varied from 29.1 to 33.6 °C. DOC concentrations drop as temperature rises, while some samples show the opposite trend up to 30 °C. Due to variations in microbial activity, DOC is not uniformly distributed throughout the research area. Increased DOM [70] and an increase in groundwater DOC may stimulate biological activities in regions with high soil moisture and high ambient temperatures. The availability of water is crucial to the DOC cause. Concentrations of dissolved organic carbon (DOC) in groundwater are much higher at shallow water depths and lower at deeper water depths. Sedimentary sequence groundwater DOC may be predictably correlated with water table depth. Figure 5 shows the temperature and water level dependence of low and high DOC in the groundwater. There is a wide range of depths from which groundwater is sampled, from 13.7 to 152.4 mbgl. Nallavadu has a shallow depth of 13.7 mbgl, while Madukarai has a deeper depth of 152.4 mbgl. Figure 5 shows that the concentration of DOC is greatest in samples collected from shallow depths (i.e., 60 mbgl) and diminishes in samples collected from greater depths. In shallow groundwater zones, DOC is discovered to be affected by the soil's surface as a result of vertical recharge caused by increased amounts of precipitation. Sorption with high pH increases DOC in a few deeper samples. Figure 6 shows the cross-section of the water with a DOC concentration of more than 5 mg/L. It follows that the regions of shallow depth and lower temperature have higher DOC.

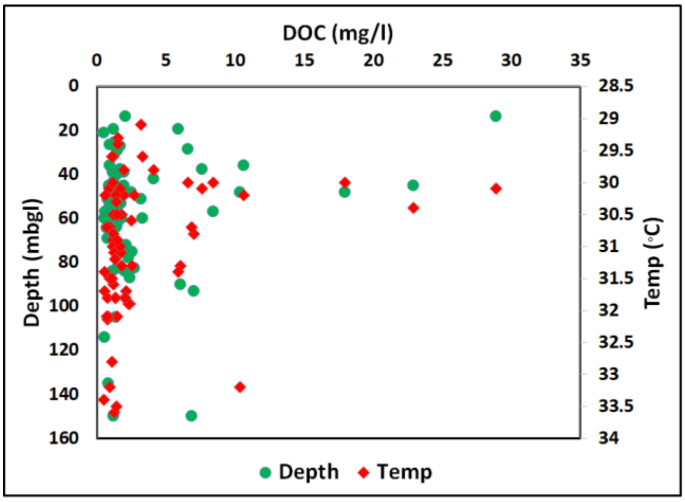

Figure 5. Comparison of the depth, temperature and DOC in groundwater.

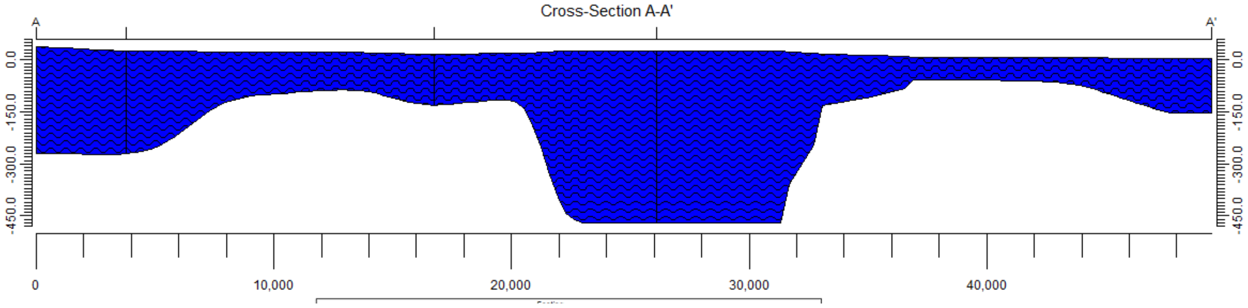

Figure 6. The depth profile of DOC (>5mg/L) in groundwater along the cross-section A-A′ (indicated in Figure 1).

4.4. Other Observed Groundwater Constituents

The pH of the groundwater ranges from 5.2% to 9.5%. It was found that greater DOC values observed in samples are associated with lower pH values, but this is only the case for a subset of samples (Figure 7). Due to the supersaturation with CO_2, the mineralization of DOC consumes DO, making most samples slightly acidic [71]. Precipitation at neutral pH is demonstrated by the complexation of DOC with metal ions [72]. At increasing pH, both anaerobic conditions and biodegradation slow down, leading to samples with lower DOC contents.

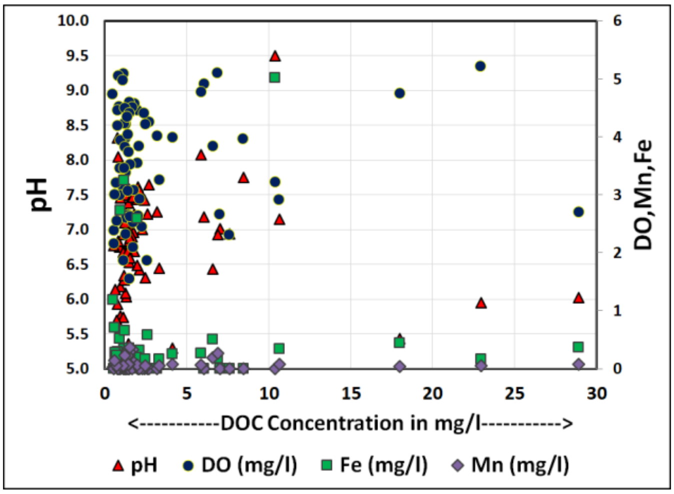

Figure 7. Water quality parameters and DOC.

Manganese levels in the samples range from background levels (BDLs) to 0.37 mg/L. Fe^{2+} levels as high as 5.02 mg/L were recorded. Twenty-three percent of the samples above the maximum allowable concentration (0.3mg/L) [73] and 10% of the samples showed concentrations of Mn^{2+} more than the recommended threshold (0.1mg/L) (Figure 7). There was a weaker positive connection between DOC, Fe^{2+} and Mn^{2+} in anaerobic groundwater samples [74–76]. Organic pollution [77] caused by dissolved iron in groundwater caused by agricultural land usage can be detrimental to mechanical irrigation systems and artificially constructed water supply bores [78,79]. The necessity for DO limits DOC biodegradation because aerobic circumstances cause organisms to consume carbon at a faster rate than anaerobic organisms. The relevance of iron and manganese organic molecules appears to be minimal. Groundwater with a lower pH may be caused by the consumption of dissolved oxygen due to the presence of higher DOC, which is detected in a small percentage of samples.

As the number of human-made sources rises, nitrate (NO_3^-) has emerged as a major groundwater pollutant. NO_3^- levels in groundwater can be found anywhere from BDL to 184mg/l. In excess of the allowable level, i.e., 45 mg/L [73], 8.9 percent of samples were found. Some of the groundwater samples in the study show a negative connection between NO_3 and DOC concentrations (Figure 8), which is consistent with microbial changes with denitrification. However, in a few instances, NO_3 levels were quite low. The lack of nitrate (NO_3) in groundwater with elevated DOC indicates that there are not enough electron acceptors in these sources. NO_3 is the most effective electron acceptor for microbial uptake in low DO conditions. Energy sources contain solid stage C, Mn^{2+} and Fe^{2+} dissolved under anaerobic conditions in terrestrial DOC [26]. The oxidation of DOC leads to higher DO and lower DOC, suggesting that carbon is used before denitrification [80]. The anaerobic environment required for denitrification is not feasible in highly oxygenated water. Hence, due to this fact, DOC accessibility varies depending on hydrogeological conditions [81].

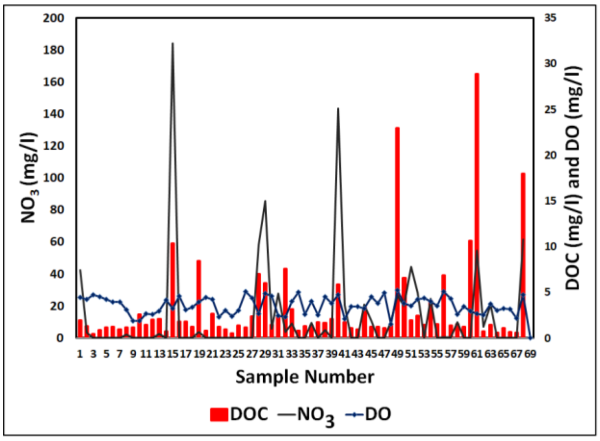

Figure 8. Relationship of DOC, DO and NO_3.

4.5. Geology and Groundwater Evolution

Dissolved organic carbon concentration in groundwater is mostly governed by geology. The geologic formations represented in the area under study range from the Mesozoic (Cretaceous) to the Cenozoic (Quaternary and Tertiary). Thus, 24 percent of higher DOC is observed in Quaternary samples (12 percent are from 5–10 mg/L and 12 percent are from > 10 mg/L of DOC), followed by 15 percent of higher DOC noted in the Tertiary samples, and, finally, a few samples of high older aquifers of the Mesozoic era (i.e., Cretaceous) contain 13.6 percent of high DOC. Younger aquifers (shown in Figure 9) [26] had greater DOC contents in their matrix than older formation samples. The Cenozoic epoch, from which the majority of higher DOC samples originate, is characterized by a shorter residence time [82] and a biogeochemical regime in which DOC is rapidly created and consumed.

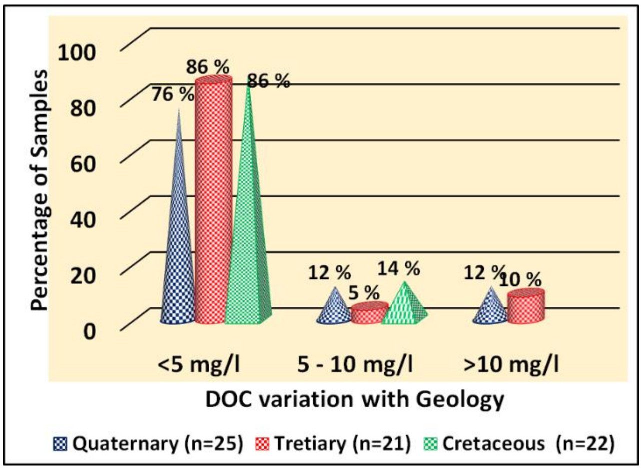

Figure 9. Spatial representation of DOC with respect to geology.

Older formations have lower DOC levels because of aquifer mineral oxidation, adsorption and biodegradation [83]. The natural source of DOC in tertiary samples may be pinpointed because of the prevalence of tertiary lignite in the research area and the shallow marine depositional environment [42,84]. The residence time of groundwater often increases with age [85]. We found that DOC decreased as Silica increased, suggesting that environmental factors play a significant role in the latter's elevation. The dissolution of silicate minerals is the primary source of dissolved Silica in samples [75]. More DOC can be absorbed by the aquifer matrix if it contains silicate minerals [86,87]. Depleted DOC is more likely to be in older formation groundwater as a result of oxidation and also adsorption processes to the surfaces of aquifer minerals, as evidenced by the negative connection between DOC with Si in the dissolved solids.

4.6. Representation of DOC on Land Use

The dataset confirms that urban land use is associated with elevated levels of DOC in the subsurface. Low DOC concentrations were more common in agricultural areas. From 2005 to 2015, there were shifts in land use that indicated a net loss of agricultural land of up to 2.2% while the amount of urban land grew by 3.2%. About 23% of the samples have DOC levels that are unsafe (i.e., >5 mg/L). The majority of higher DOC samples are found in urban areas (Figure 10), while most of the remaining samples are associated with agricultural land use. Leaching from landfills, animal waste and even human and household waste [88–93] are mechanisms by which DOC enters into groundwater in urban areas. The greater (>5 mg/L) groundwater DOC in agricultural areas may be primarily controlled by fertilizer run-off, but the complexation via Fe may also play a substantial role in this increase. Nitrate and chloride are the most commonly utilized water quality markers of anthropogenic contamination. Nitrate levels in groundwater samples were highest around the site where DOC levels were also highest. Although DOC had a good link with NO_3, a higher concentration of DOC in the built-up region is the impact of domestic sewage and industry effluents, which are diluted and most likely leached into the underlying aquifers. As a result, climate change is also linked to an increase in dissolved organic carbon in relation to diverse land use patterns, which will impact groundwater quality and, by extension, human health.

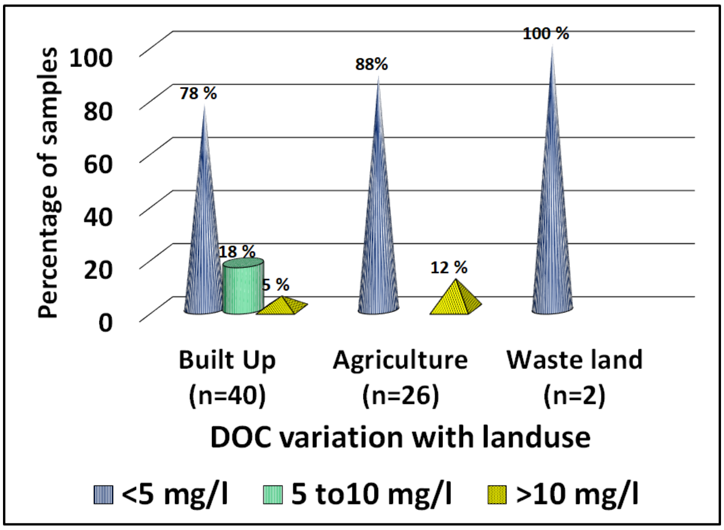

Figure 10. Dominance of DOC with respect to Land use.

4.7. Groundwater-Dissolved Organic Carbon Controls

Figure 11 shows that there is a positive association between DOC and DO, calcium, potassium, nitrate and iron through the use of factor analysis and correlation studies among the ions found in groundwater samples (Figure 11). DOC is moderately positively correlated with manganese and magnesium. Groundwater temperature, water depth, Silica and pH were also found to have a negative correlation with DOC (Figure 11). Urban samples are consistently found to have greater DOC levels than their rural counterparts. Based on the correlations between DOC and other variables, we can infer that geology, climate, land use and associated water chemistry are the four primary determinants of DOC distribution (Figure 11). Cumulatively, 54.9 percent of the entire variance may be accounted for. Two principal component analysis (PCA) factors describe DOC loading, with PCA 2 containing 14.5 percent of the variance and positively loading K, NO_3 and Fe (Figure 12). Nitrate production and metal load both result from agricultural pollution reflected by the positive loading of NO_3, Fe and K with DOC. Complexation, sorption and precipitation processes, as well as the representation of these samples in the landfill region, are indicative of heavy metal activity. PCA 3 includes DOC with 12.3% variance, positively loading on Ca, DO and SO_4. Anaerobic waters have been found to have greater concentrations of DOC, DO and SO_4 [94]. Anaerobic microorganisms use metal electron acceptors to consume dissolved O_2 and produce sulfate [23,94]. The presence of marcasite is strongly suggested by the large quantity of readily extractable sulphate in the lignite layer [38,95]. The dissolution of calcite from the cretaceous formation is triggered by the positive loading of Ca, DO and DOC with a negative pH, which reflects an increase in DOC with DO that causes a fall in pH. Changes in pH occur once an anoxic state has been established and biodegradation rates have decreased [96–98]. Therefore, the by-products of microbial respiration can be seen in the relationship between Ca and DOC [15].

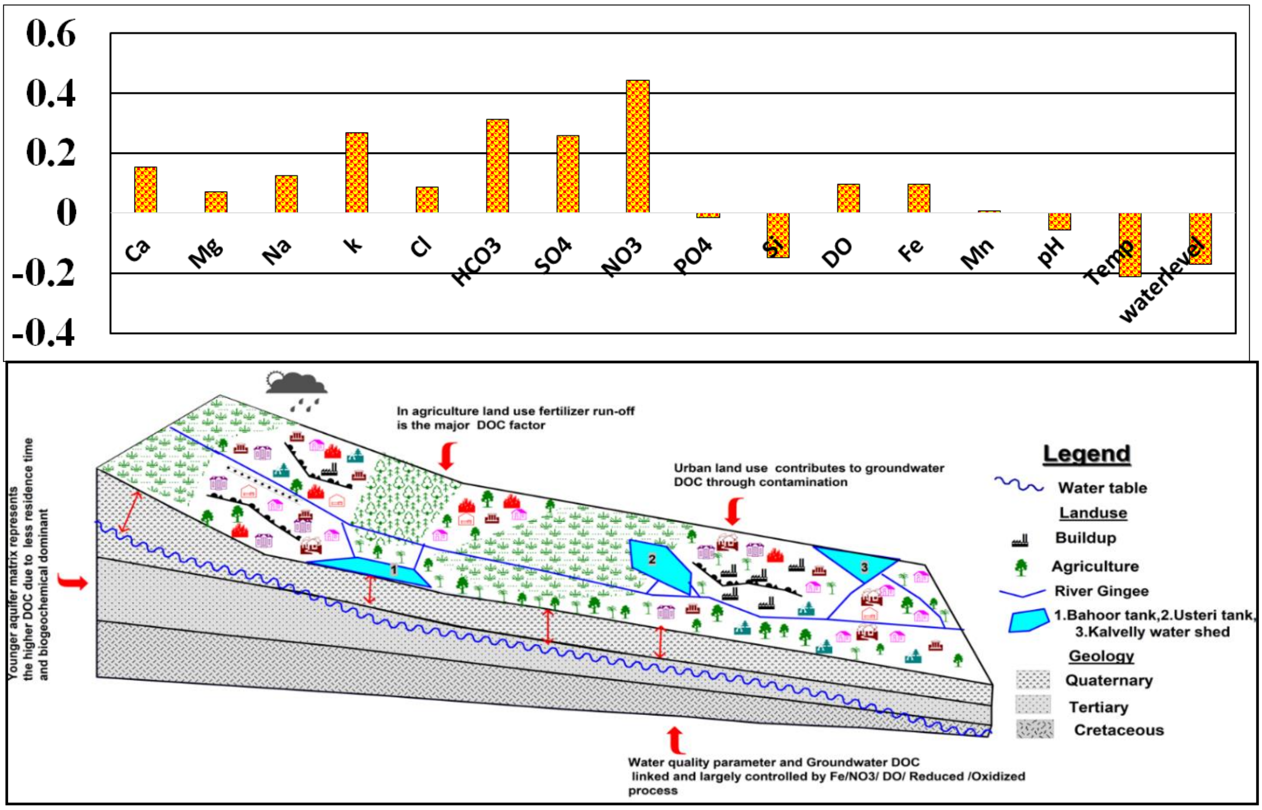

Figure 11. Pictorial representation of drivers and correlation of change in groundwater DOC concentration.

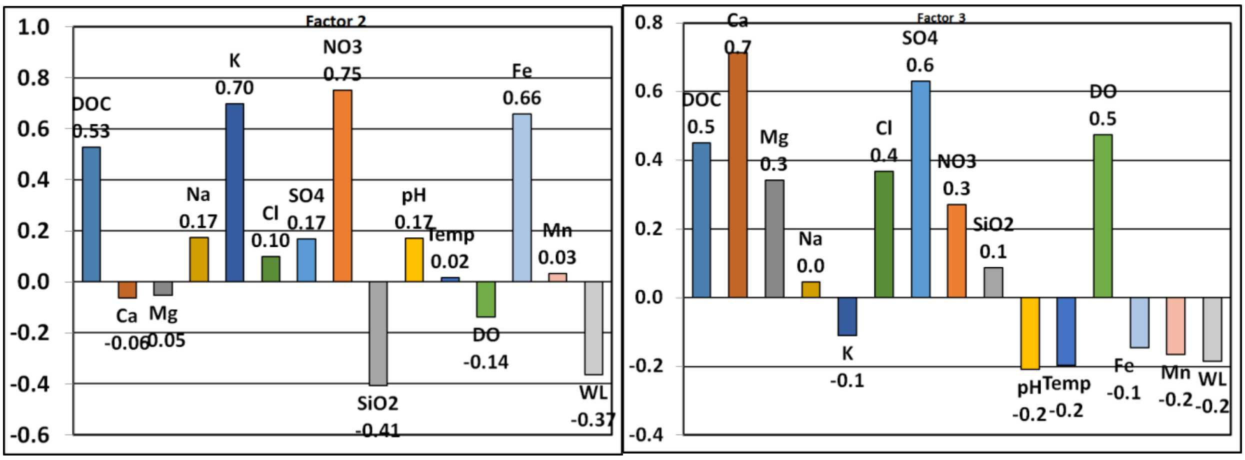

Figure 12. Component matrix comparison of DOC in groundwater samples (since Factor 2 and Factor 3 had positive loadings of DOC, these two factors were considered).

5. Conclusions

The supply of DOC depends on the rate of many biogeochemical processes in groundwater, including aerobic respiration, nitrification and denitrification, and might also constrain the abundance and diversity of invertebrate assemblages. The variation in nitrate concentration in the number of aquifers shows the water mixing rather than the denitrification. The study brings out the novel findings that recharge the shallow alluvial aquifers, identified through higher DOC values and also the fact that the temperature variation due to the geothermal gradience lowers the DOC values in the deeper groundwater. The study also identifies that both the urban and agricultural regions contribute DOC to the groundwater and the urban influence predominates. Further, earlier studies have identified the influence of temperature and water level on DOC. The current study has brought out the interrelationship of these parameters along with DO on the DOC of groundwater.

Dissolved organic carbon in groundwater samples of the study area ranged from 0.5 to 29 mg/L, which is influenced by fluctuations in water level and its temperature. The inference shows vertical variation in DOC and it is inferred due to the anaerobic condition in deeper aquifers. Shallow water levels have high DOC compared to other samples from wells with deeper water table. Tertiary and Quaternary samples show higher DOC. Based upon the land use pattern, 75% of samples from built-up land have more DOC than the agricultural land. The continuous increase in built-up land leads to an increase in domestic sewage, landfill leachates and industrial effluents in the study area, enhancing the DOC concentration in built-up land areas. Possible sources for elevated DOC in agricultural land include the use of organic-rich fertilizers. Higher groundwater DO indicate that the microbial activity has consumed the oxygen where the minimal biological activity occurred. The occurrence of an elevated DOC concentration along with electron acceptors and metals, showing the positivity of denitrification and negativity of enhancing the metal mobility, is interestingly noted, in that converse drift exists in the circumstance of groundwater from Tertiary and Alluvium development. However, the elevated concentrations of DOC can have favorable results for agricultural nitrate such as denitrification. It also has harmful effects on the health of lower stream locations.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/hydrology10040085/s1, Figure S1: Flow chart for DOC analysis in TOC–VCSH (after user manual TOC –VCSH/CPN); Table S1: Analytical methods for all parameters.

Author Contributions: T.R.—Conceptualization, Methodology, Data Curation, Writing—Original Draft Preparation, Funding Acquisition; C.S.—Writing—Review and Editing, Validation, Supervision; B.P.—Formal Analysis, Software, Validation. V.E.—Investigation, Supervision. All authors have read and agreed to the published version of the manuscript.

Funding: The authors wish to express thanks to University Grants Commission (UGC) No. F.15-1/201617/PDFWM201517TAM34825(SAII) for providing the necessary financial support to carry out this study.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: This article includes all the data used in this study. Original data can be obtained upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Evans, S.; Campbell, C.; Naidenko, O.V. Cumulative risk analysis of carcinogenic contaminants in United States drinking water. *Heliyon* **2019**, *5*, e02314. [CrossRef] [PubMed]
2. Findlay, S.; Sinsabaugh, R.L. Unravelling the sources and bioavailability of dissolved organic matter in lotic aquatic ecosystems. *Mar. Freshw. Res.* **1999**, *50*, 781–790. [CrossRef]
3. Sadiq, R.; Rodriguez, M.J. Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: A review. *Sci. Total Environ.* **2004**, *321*, 21–46. [CrossRef] [PubMed]
4. Lawson, M.; Polya, D.A.; Boyce, A.J.; Bryant, C.; Ballentine, C.J. Tracing organic matter composition and distribution and its role on arsenic release in shallow Cambodian groundwaters. *Geochim. Cosmochim. Acta* **2016**, *178*, 160–177. [CrossRef]
5. Fleck, J.A.; Bossio, D.A.; Fujii, R. Dissolved organic carbon and disinfection by-product precursor release from managed peat soils. *J. Environ. Qual.* **2004**, *33*, 465–475. [CrossRef]
6. Bauer, M.; Blodau, C. Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. *Sci. Total Environ.* **2006**, *354*, 179–190. [CrossRef]
7. Leenheer, J.A. Occurrence of dissolved organic carbon in selected groundwater samples in the United States. *U.S. Geol. Surv. J. Res.* **1974**, *2*, 361–369.
8. Thurman, E.M. *Organic Geochemistry of Natural Waters*; Martinus Nijhoff/DR W. Junk Publishers: Dordrecht, The Netherlands, 1985; p. 497.
9. Aiken, G. Organic matter in ground water. In *U.S. Geological Survey Open File*; Report 02–89; USGS: Reston, VA, USA, 1989; p. 7.
10. McMahon, P.B.; Chapelle, F.H. Redox processes and the water quality of selected principal aquifer systems. *Groundwater* **2008**, *46*, 259–285. [CrossRef]
11. Tesoriero, A.J.; Puckett, L.J. O_2 reduction and denitrification rates in shallow aquifers. *Water Resour. Res.* **2011**, *47*, W12522. [CrossRef]
12. Boyer, E.W.; Hornberger, G.M.; Bencala, K.E.; McKnight, D.M. Response characteristics of DOC flushing in an alpine catchment. *Hydrol. Process.* **1998**, *11*, 1635–1647. [CrossRef]
13. Baker, M.A.; Valett, H.M.; Dahm, C.N. Organic carbon supply and metabolism in a shallow groundwater ecosystem. *Ecology* **2000**, *81*, 3133–3148. [CrossRef]
14. McMahon, P.B.; Chapelle, F.H. Microbial production of organic acids in aquitard sediments and its role in aquifer geochemistry. *Nature* **1991**, *349*, 233–235. [CrossRef]
15. Chapelle, F.H. *Dissolved Organic Carbon in Groundwater Systems*; The Groundwater Project: Guelph, ON, Canada, 2022. [CrossRef]
16. Davidson, E.A.; Janssens, I.A. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature* **2006**, *440*, 165–173. [CrossRef]
17. Jenkinson, D.S.; Adams, D.E.; Wild, A. Model estimates of CO_2 emissions from soil in response to global warming. *Nature* **1991**, *351*, 304–306. [CrossRef]
18. Maghrebi, M.; Noori, R.; Partani, S.; Araghi, A.; Barati, R.; Farnoush, H.; Haghighi, A.T. Iran's Groundwater Hydrochemistry. *Earth Space Sci.* **2021**, *8*, 8. [CrossRef]
19. Maghrebi, M.; Noori, R.; Sadegh, M.; Sarvarzadeh, F.; Akbarzadeh, A.E.; Karandish, F.; Barati, R.; Taherpour, H. Anthropogenic Decline of Ancient, Sustainable Water Systems: Qanats. *Ground Water* **2022**, *61*, 1. [CrossRef]
20. Foster, S.S.D.; Chilton, P.J. Groundwater: The processes and global significance of aquifer degradation. *Philos. Trans. R. Soc. Lond. Ser. B* **2003**, *358*, 1957–1972. [CrossRef]
21. Harvey, C.F.; Swartz, C.H.; Badruzzaman, A.B.M.; Keon-Blute, N.; Yu, W.; Ali, M.A.; Jay, J.; Beckie, R.; Niedan, V.; Ahmed, M.F.; et al. Arsenic mobility and groundwater extraction in Bangladesh. *Science* **2002**, *298*, 1602. [CrossRef]
22. Goñi, M.A.; Gardner, I.R. Seasonal dynamics in dissolved organic carbon concentrations in a coastal water-table aquifer at the forest marsh interface. *Aquat. Geochem.* **2003**, *9*, 209–232. [CrossRef]
23. Shen, Y.; Hetal, C.F. Origins and bioavailability of dissolved organic matter in groundwater. *Biogeochemistry* **2015**, *122*, 61–78. [CrossRef]
24. Thayalakumaran, T.; Bristow, K.L.; Charlesworth, P.B.; Fass, T. Geochemical conditions in groundwater systems: Implications for the attenuation of agricultural nitrate. *Agric. Water Manag.* **2008**, *95*, 103–115. [CrossRef]

25. Chapelle, F.H.; Bradley, P.M.; Journey, C.A.; McMahon, P.B. Assessing the relative bioavailability of DOC in regional groundwater systems. *Groundwater* **2013**, *51*, 363–372. [CrossRef] [PubMed]
26. Thayalakumaran, T.; Lenahan, M.J.; Bristow, K.L. Dissolved organic carbon in groundwater overlain by irrigated sugarcane. *Groundwater* **2015**, *53*, 525–530. [CrossRef] [PubMed]
27. Rivett, M.O.; Buss, S.R.; Morgan, P.; Smith, J.W.N.; Bemment, D.C. Nitrate attenuation in groundwater: A review of biogeochemical controlling processes. *Water Res.* **2008**, *42*, 4215–4232. [CrossRef] [PubMed]
28. McDonough, L.K.; Santos, I.R.; Andersen, M.S.; O'Carroll, D.M.; Rutlidge, H.; Meredith, K.; Oudone, P.; Bridgeman, J.; Gooddy, D.C.; Sorensen, J.P.R.; et al. Changes in global groundwater organic carbon driven by climate change and urbanization. *Nat. Commun.* **2020**, *11*, 1–10. [CrossRef] [PubMed]
29. Kalbitz, K.; Solinger, J.H.; Park, B.; Michalzik, B.; Matzner, E. Controls on the dynamics of dissolved organic matter in soils: A review. *Soil Sci.* **2000**, *165*, 277–304. [CrossRef]
30. Blondin, F.; Simon, L.; Maazouzi, C.; Foulquier, A.; Delolme, C.; Marmonier, P. Dynamics of dissolved organic carbon (DOC) through stormwater basins designed for groundwater recharge in urban area: Assessment of retention efficiency. *Water Res.* **2015**, *81*, 27–37. [CrossRef]
31. Artinger, R.; Buckau, G.; Geyer, S.; Fritz, P.; Wolf, M.; Kim, J.I. Characterization of groundwater humic substances: Influence of sedimentary organic carbon. *Appl. Geochem.* **2000**, *15*, 97–116. [CrossRef]
32. Raymond, M.F.; Mallèn, G.; Engel, M.; Ahmed, A.; Rossi, P. Characterizing aquifer heterogeneity using bacterial and bacteriophage tracers. *J. Environ. Qual.* **2015**, *44*, 1448–1458.
33. Thilagavathi, R.; Chidambaram, S.; Prasanna, M.V.; Thivya, C.; Singaraja, C. A study on groundwater geochemistry and water quality in layered aquifers system of Pondicherry region, southeast India. *Appl. Water Sci.* **2012**, *2*, 253–269. [CrossRef]
34. Sridharan, M.; Senthil Nathan, D. Hydrochemical Facies and Ionic Exchange in Coastal Aquifers of Puducherry Region, India: Implications for Seawater Intrusion. *Earth Syst. Environ.* **2017**, *1*, 5. [CrossRef]
35. Thilagavathi, R.; Chidambaram, S.; Thivya, C.; Tirumalesh, K.; Venkatramanan, S.; Pethaperumal, S.; Prasanna, M.V.; Ganesh, N. Influence of variations in rainfall pattern on the hydrogeochemistry of coastal groundwater—An outcome of periodic observation. *Environ. Sci. Pollut. Res.* **2019**, *26*, 29173–29190. [CrossRef]
36. Thilagavathi, R.; Chidambaram, S.; Thivya, C.; Prasanna, M.V.; Tirumalesh, K.; Pethaperumal, S. Assessment of groundwater chemistry in layered coastal aquifers using multivariate statistical analysis. *Sustain. Water Resour. Manag.* **2017**, *3*, 55–69. [CrossRef]
37. Chidambaram, S.; Prasanna, M.V.; Karmegam, U.; Singaraja, C.; Pethaperumal, S.; Manivannan, R.; Anandhan, P.; Tirumalesh, K. Significance of pCO_2 values in determining carbonate chemistry in groundwater of Pondicherry region, India. *Front. Earth Sci.* **2011**, *5*, 197–206. [CrossRef]
38. Thilagavathi, R.; Chidambaram, S.; Thivya, C.; Prasanna, M.V.; Singaraja, C.; Tirumalesh, K.; Pethaperumal, S. Delineation of natural and anthropogenic process controlling hydrogeochemistry of layered aquifer sequence. *Proc. Natl. Acad. Sci. USA* **2014**, *84*, 95–108. [CrossRef]
39. Thilagavathi, R.; Chidambaram, S.; Thivya, C.; Prasanna, M.V.; Pethaperuamal, S.; Tirumalesh, K. A Study on the Behaviour of Total Carbon and Dissolved Organic Carbon in Groundwaters of Pondicherry Region, India. *Int. J. Earth Sci. Eng.* **2014**, *7*, 1537–1550.
40. Pethaperumal, S.; Chidambaram, S.; Prasanna, M.V.; Verma, V.N.; Balaji, K.; Ramesh, R.; Karmegam, P.; Paramaguru, U. A study on groundwater quality in the Pondicherry region. *EcoChronicle* **2008**, *3*, 85–90.
41. Tirumalesh, K.; Ramakumar, K.L.; Prasad, M.B.K.; Chidambaram, S.; PethaPerumal, S.; Prakash, D.; Nawani, N. Microbial evaluation of groundwater and its implications on redox condition of a multi-layer sedimentary aquifer system. *Environ. Process.* **2015**, *2*, 331.e346. [CrossRef]
42. Pethaperumal, S. Study on Groundwater Chemistry in the Pondicherry Region. Ph.D. Thesis, Annamalai University, Tamil Nadu, India, October 2010.
43. Thilagavathi, R.; Chidambaram, S.; Thivya, C.; Prasanna, M.V.; Tirumalesh, K.; Pethaperuamal, S. Dissolved Organic Carbon in Multilayered Aquifers of Pondicherry Region (India): Spatial and Temporal Variability and Relationships to Major Ion Chemistry. *Nat. Resour. Res.* **2017**, *26*, 119–135. [CrossRef]
44. Regan, S.; Hynds, P.; Flynn, R. An overview of dissolved organic carbon in groundwater and implications for drinking water safety. *Hydrogeol. J.* **2017**, *25*, 959–967. [CrossRef]
45. Christensen, J.B.; Jensen, D.L.; Christensen, T.H. Effect of dissolved organic carbon on the mobility of cadmium, nickel and zinc in leachate polluted groundwater. *Water Res.* **1996**, *30*, 3037–3049. [CrossRef]
46. Fujita, Y.; Ding, W.-H.; Reinhard, M. Identification of wastewater dissolved organic carbon characteristics in reclaimed wastewater and recharged groundwater. *Water Environ. Res.* **1996**, *68*, 867–876. [CrossRef]
47. Makehelwala, M.; Wei, Y.; Weragoda, S.K.; Weerasooriya, R.; Zheng, L. Characterization of dissolved organic carbon in shallow groundwater of chronic kidney disease affected regions in Sri Lanka. *Sci. Total Environ.* **2018**, *660*, 865–875. [CrossRef] [PubMed]
48. Makehelwala, M.; Wei, Y.; Weragoda, S.K.; Weerasooriya, R. Ca^{2+} and $SO_4{}^{2-}$ interactions with dissolved organic matter: Implications of groundwater quality for CKDu incidence in Sri Lanka. *J. Environ. Sci.* **2020**, *88*, 326–337. [CrossRef] [PubMed]
49. Ramesh, R.; Purvaja, R.; Senthilvel, A. National assessment of shoreline change: Puducherry coast. In *NCSCM/MoEF Report*; NCSCM: Chennai, India, 2011; pp. 1–57.

50. Mani Murali, R.; Ankita, M.; Amrita, S.; Vethamony, P. Coastal vulnerability assessment of Puducherry coast, India using analytical hierarchical process. *Nat. Hazards Earth Syst. Sci.* **2013**, *1*, 509–555. [CrossRef]
51. Thilagavathi, R.; Chidambaram, S.; Ramanatahan, A.L.; Rao, M.S.; Prasanna, M.V.; Tirumalesh, K.; Pethaperumal, S. An attempt to evaluate the influence of geomorphology on the hydrogeology of coastal aquifer. *Ind. J. Geomorphol.* **2013**, *18*, 103–114.
52. Bhuvan Statistical Data WMS. Available online: https://bhuvan-ras2.nrsc.gov.in/cgi-bin/LULC250K.exe (accessed on 25 March 2019).
53. Thilagavathi, R.; Chidambaram, S.; Prasanna, M.V.; Pethaperumal, S. A study on the interpretation of spontaneous potential and resistivity logs in layered aquifer sequence of Pondicherry Region, South India. *Arab. J. Geosci.* **2013**, *7*, 3715–3729. [CrossRef]
54. CGWB. *Ground Water Resources and Development Prospects in Pondicherry Region*; CGWB: Pondicherry, India, 1993.
55. American Public Health Associated—APHA. *Standard Methods for the Examination of Water and Wastewater*, 19th ed.; APHA: Washington, DC, USA, 1998.
56. Chan, C.C.; Lam, H.; Zhang, X.-M. *Practical Approaches to Method Validation and Essential Instrument Qualification*; Wiley: Hoboken, NJ, USA, 2010.
57. Reckhow, D.A. *Analysis of Total Organic Carbon TOC SOP ver3*; University of Massachusetts, Environmental Engineering Research Laboratory: Amherst, MA, USA, 2012.
58. Hounslow, A.W. *Water Quality Data: Analysis and Interpretation*; CRC Lewis: Boca Raton, FL, USA, 1995; p. 397.
59. Technical support document for ontario drinking water standards. In *Objectives and Guidelines*; Ministry of the Environment: Ottawa, ON, Canada, 2003; ISBN 4449e01.
60. Richardson, S.D. *Encyclopedia of Environmental Analysis and Remediation*; Wiley: New York, NY, USA, 1998; pp. 1398–1421.
61. Amy, G.L.; Tan, L.; Davis, M.K. The effects of ozonation and activated carbon adsorption on trihalomethane speciation. *Water Res.* **1991**, *25*, 191–202. [CrossRef]
62. Pan, Y.; Zhang, X. Four groups of new aromatic halogenated disinfection byproducts: Effect of bromide concentration on their formation and speciation in chlorinated drinking water. *Environ. Sci. Technol.* **2013**, *47*, 1265–1273. [CrossRef]
63. Chapelle, F.H.; Bradley, P.B.; Kaiser, M.K.; Benner, R. Dissolved oxygen as an indicator of bioavailable dissolved organic carbon in groundwater. *Groundwater* **2012**, *50*, 230–241. [CrossRef]
64. Foulquier, A.; Malard, F.; Mermillod-Blondin, F.; Datry, T.; Simon, L.; Montuelle, B.; Gilbert, J. Vertical change in dissolved organic carbon and oxygen at the water table region of an aquifer recharged with storm water: Biological uptake or mixing? *Biogeochemistry* **2010**, *99*, 31–47. [CrossRef]
65. Hinke, S.R.; Tesoriero, A.J. Nitrogen speciation and trends, and prediction of denitrification extent, in shallow US groundwater. *J. Hydrol.* **2013**, *509*, 343–353. [CrossRef]
66. Hunt, C.D., Jr. Ground-water quality and its relation to land use on Oahu, Hawaii, 2000–2001. In *Water-Resources Investigations Report 2004, 03-4305*; USGS: Reston, VA, USA, 2004; p. 76.
67. McMahon, P.B.; Chapelle, F.H.; Bradley, P.M. Evolution of redox processes in groundwater. In *Aquatic Redox Processes*; Tratnyek, P.G., Grundl, T.J., Haderlein, S.B., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, USA, 2011; Volume 1071.6.
68. Weymann, D.; Well, R.; Flessa, H.; von der Heide, C.; Deurer, M.; Meyer, K.; Konrad, C.; Walther, W. Groundwater N_2O emission factors of nitrate-contaminated aquifers as derived from denitrification progress and N_2O accumulation. *Biogeosciences* **2008**, *5*, 1215–1226. [CrossRef]
69. Chapelle, F.H.; Bradley, P.M.; Dan, J.G.; Tiedeman, P.J.; Lacombe, K.; Kaiser, K.; Benner, R. Biochemical indicators for the bioavailability of organic carbon in ground water. *Groundwater* **2008**, *47*, 108–121. [CrossRef]
70. Grieve, I.C. Seasonal, hydrological, and land management factors controlling dissolved organic carbon concentrations in the loch fleet catchments, Southwest Scotland. *Hydrol. Process* **1990**, *4*, 231–239. [CrossRef]
71. Harvey, J.W.; Fuller, C.C. Effect of enhanced manganese oxidation in the hyporheic zone on basin-scale geochemical mass balance. *Water Resour. Res.* **1998**, *34*, 623–636. [CrossRef]
72. Tipping, E.; Reddy, M.M.; Hurley, M.A. Modeling electrostatic and heterogeneity effects on proton dissociation from humic substances. *Environ. Sci. Technol.* **1990**, *24*, 1700–1705. [CrossRef]
73. BIS. *Indian Standard Specifications for Drinking Water 2012*; BIS: New Delhi, India, 2012.
74. Bone, S.E.; Charette, M.A.; Lamborg, C.H.; Gonneea, M.E. Has submarine groundwater discharge been overlooked as a source of mercury to coastal waters. *Environ. Sci. Technol.* **2012**, *41*, 3090–3095. [CrossRef]
75. Black, F.J.; Paytan, A.; Knee, K.L.; Sieyes, N.R.; Gangull, P.M.; Gray, E.; Flegal, R. Submarine groundwater discharge of total mercury and monomethyl mercury to central California coastal waters. *Environ. Sci. Technol.* **2009**, *43*, 5652–5659. [CrossRef]
76. Appelo, C.; Postma, D. Geochemistry. In *Groundwater and Pollution*, 2nd ed.; Balkema: Rotterdam, The Netherlands, 2005.
77. Nakayama, F.S.; Bucks, D.A. Water quality in drip/trickle irrigation: A review. *Irrig. Sci.* **1991**, *12*, 187–192. [CrossRef]
78. Chapelle, F.H. *Ground-Water Microbiology and Geochemistry*; John Wiley & Sons: New York, NY, USA, 2001; p. 496.
79. Hamilton, W.A. Microbially influenced corrosion as a model system for the study of metal microbe interactions: A unifying electron transfer hypothesis. *Biofouling* **2003**, *19*, 65–76. [CrossRef] [PubMed]
80. Buss, S.R.; Rivett, M.O.; Morgan, P.; Bemment, C.D. Attenuation of nitrate in the subsurface environment. In *Environment Agency Science Group Report*; Environment Agency of England and Water Science: Bristol, UK, 2005; Report SC030155/2.

81. Jacinthe, P.A.; Groffman, P.M.; Gold, A.J. Landscape and watershed processes—Dissolved organic carbon dynamics in a riparian aquifer: Effects of hydrology and nitrate enrichment. *J. Environ. Qual.* **2003**, *32*, 1365–1374. [CrossRef] [PubMed]
82. Evans, C.; Futter, M.; Moldan, F.; Valinia, S.; Frogbrook, Z.; Kothawala, D. Variability in organic carbon reactivity across lake residence time and trophic gradients. *Nat. Geosci.* **2017**, *10*, 832. [CrossRef]
83. Shen, Y.H. Sorption of natural dissolved organic matter on soil. *Chemosphere* **1999**, *38*, 1505–1515. [CrossRef]
84. MacDonald, A.M.; Dochartaigh, B.E.; Smedley, P.L. *Baseline Groundwater Chemistry in Scotland's Aquifers (OR/17/030)*; British Geological Survey: London, UK, 2017; pp. 1–77.
85. Weissmann, G.S.; Zhang, Y.; LaBolle, E.M.; Fogg, G.E. Dispersion of groundwater age in an alluvial aquifer system. *Water Resour. Res.* **2002**, *38*, 16–1116-13. [CrossRef]
86. Lilienfein, J.; Qualls, R.G.; Uselman, S.M.; Bridgham, S.D. Adsorption of dissolved organic carbon and nitrogen in soils of a weathering chronosequence. *Soil Sci.* **2004**, *68*, 292–305. [CrossRef]
87. Jardine, P.M.; Mayes, M.A.; Mulholland, P.J.; Hanson, P.J.; Tarver, J.R.; Luxmore, R.J.; McCarthy, J.F.; Wilson, G.V. Vadose zone flow and transport of dissolved organic carbon at multiple scales in humid regions. *Vadose Zone J.* **2006**, *5*, 140–152. [CrossRef]
88. Lapworth, D.; Nkhuwa, D.; Okotto-Okotto, J.; Pedley, S.; Stuart, M.; Tijani, M.; Wright, J. Urban groundwater quality in sub-Saharan Africa: Current status and implications for water security and public health. *Hydrogeol. J.* **2017**, *25*, 1093–1116. [CrossRef]
89. Lapworth, D.J.; Gooddy, D.C.; Butcher, A.S.; Morris, B.L. Tracing groundwater flow and sources of organic carbon in sandstone aquifers using fluorescence properties of dissolved organic matter (DOM). *Appl. Geochem.* **2008**, *23*, 3384–3390. [CrossRef]
90. Utton, A.E. The development of international groundwater law. *Nat. Resour. J.* **1982**, *22*, 95–118.
91. Johnson, L.; Richards, C.; Host, G.; Arthur, J. Landscape influences on water chemistry in Midwestern stream ecosystems. *Freshw. Biol.* **1997**, *37*, 193–208. [CrossRef]
92. Meierdiercks, K.L.; Kolozsvary, M.B.; Rhoads, K.P.; Golden, M.; McCloskey, N.F. The role of land surface versus drainage network characteristics in controlling water quality and quantity in a small urban watershed. *Hydrol. Process.* **2017**, *31*, 4384–4397. [CrossRef]
93. Lawrence, A.; Gooddy, D.; Kanatharana, P.; Meesilp, W.; Ramnarong, V.J.H.J. Groundwater evolution beneath Hat Yai, a rapidly developing city in Thailand. *Hydrogeol. J.* **2000**, *8*, 564–575.
94. Chapelle, F.H. *Groundwater Microbiology and Biochemistry*; Wiley: New York, NY, USA, 1993.
95. Anandhan, P.; Ramanathan, A.L.; Chidambaram, S.; Manivannan, R.; Ganesh, N.; Srinivasamoorthy, K. A study on the seasonal variation in the geochemistry of the groundwater in and around Neyveli region, Tamilnadu. In Proceedings of the International Conference on Hydrogeochemistry, Tamil Nadu, India; 2000.
96. Noori, R.; Maghrebi, M.; Jessen, S.; Bateni, S.M.; Heggy, E.; Javadi, S.; Nouri, M.; Pistre, S.; Abolfathi, S.; AghaKouchak, A. Decline in Iran's Groundwater Recharge—Preprint (Version 1), Research Square. 2023. Available online: https://doi.org/10.21203/rs.3.rs-2608948/v1 (accessed on 5 April 2020).
97. Singaraja, C.; Chidambaram, S.; Jacob, N.; Selvam, S.; Prasanna, M.V. Tidal effects on groundwater dynamics in shallow coastal aquifers—Southeast coast of Tamilnadu, India. *Arab. J. Geosci.* **2016**, *6*, 1–19. [CrossRef]
98. Salmani, H.; Javadi, S.; Eini, M.R.; Golmohammadi, G. Compilation simulation of surface water and groundwater resources using the SWAT-MODFLOW model for a karstic basin in Iran. *Hydrogeol. J.* **2023**. [CrossRef]