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By Universitas Muhammadiyah Sidoarjo

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Studying Some Standards of Groundwater Quality and the Water Environment for Different Areas in Diyala Governorate

Mempelajari Beberapa Standar Kualitas Air Tanah dan Lingkungan Air untuk Berbagai Daerah di Kegubernuran Diyala

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Abstract

In the Diyla area, fourteen ground water samples were obtained for this study in high density polyethylene (HDPE) bottles that had been previously cleaned and filled with diluted HNO3. To prevent cross-contamination, the bottles were rinsed with the same water that would be used for the sample. Using normal procedures, each sample was examined for five parameters: pH, EC, TH, Alkalinity, and F (APHA, 1995). A digital pH metre (Model 802 Systronics) was used in the field to measure pH, and a conductivity metre (Model 304 Systronics) was used to assess EC. The Trimble Juno 3D Handheld is used to help collect the geographic locations of the sample points (EC). Using regular EDTA, a titrimetric analysis of total hardness was conducted. Titrimetric analysis of alkalinity was performed with standard H2SO4.

Highlight:

Samples collected in HDPE bottles pre-rinsed with sample water. pEI, EC, TH, Alkalinity, F analyzed using APHA standards (1995). pEI, EC measured in field; hardness, alkalinity by titration.

Keywords: Word, Ground Water, Diyala City, Quality Parameters, Ph Metre, Alkalinity

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Introduction

Groundwater has been a significant fresh water supply source for the United States (US), being withdrawn as needed, with minimal government oversite or regulation [1]. Groundwater has also been expected to be a major future source of fresh water for our nation [2]. However, groundwater has been and will continue to be under stress from intensive long-term pumping [3], anthropogenic contaminants (4), climate change (5), and ecosystem degradation (6, 7, 8). As a critical natural resource groundwater has provided fresh water to millions of people across the US over the past century (9). The primary use of fresh groundwater in the US has been for irrigation, followed by public and domestic supply, livestock and aquaculture, industrial, mining and thermoelectric power generation purposes. In 2010 for example, an estimated 76 billion gallons per day (bgd) of fresh groundwater was withdrawn, with about 65% of the total (~ 49.5 bgd) being used for irrigation. Public supply and domestic supply consumed about 25% (~19.2 bgd) (10), providing approximately 268 million people with potable water, including 43 million people who pump groundwater from private wells (i.e. domestic supply) (4). Livestock and aquaculture utilized about 4% (~ 3 bgd) of 2010 fresh groundwater withdrawals, while industrial manufacturing of products such as metal, wood, and paper products, chemicals, gasoline, and oils used about 4% (~2.9 bgd). Mining activities such as extraction of minerals, coal, iron, sand, crude oil, and natural gas used about 1% (~1.1 bgd) (USGS-Perlman, 2014), thermoelectric power generation utilized less than 1% (~ 0.6 mgd) of 2010 fresh groundwater withdrawals (10).

Groundwater: natural and physical science perspectives

The role of groundwater in the water cycle Since most fresh water is found in polar ice caps and glaciers, about 68% of it is not available for use by society [11]. Just 1.2% of the fresh water on Earth is found in streams and lakes, while around 30% of it is groundwater. Aquifers are geologic formations that supply wells or springs with a sizable volume of water. An aquifer is made up of two or more permeable subsurface layers that are at least locally divided by intervening layers that obstruct groundwater flow but have little effect on the system's regional hydraulic connectedness. Rainfall that falls inside an aquifer's recharge region is the primary source of groundwater replenishment, with the exception of fossil aquifers. On land, precipitation either travels vertically or horizontally inside the subsurface or permeates the soil and flows across the surface horizontally. Water that stays in the unsaturated or vadose zone-also referred to as "soil water"-as well as water that enters the saturated zone, or aquifer, where pore spaces are fully filled, are the two components of groundwater.

Methods

Sample Collection

In the Diyla area, fourteen ground water samples were gathered in high density polyethylene (HDPE) bottles that had been previously cleaned and filled with diluted HNO3. To prevent cross-contamination, the bottles were rinsed with the same water that would be used for the sample. Using normal procedures, each sample was examined for five parameters: pH, EC, Alkalinity, TH, and F- (APHA, 1995). A digital pH metre (Model 802 Systronics) was used in the field to measure pH, and a conductivity metre (Model 304 Systronics) was used to assess EC. Using the Trimble Juno 3D Handheld, the sampling sites' geographic locations are gathered.

Sample Analysis

Using regular EDTA, a titrimetric analysis of total hardness was conducted. Titrimetric analysis of alkalinity was performed with standard H2SO4. With the exception of pH and EC, all the parameters are presented in mg/l. The unit of EC expression is micro Siemens/cm.

pН

The negative logarithm of the concentration of hydrogen ions in a solution is used to calculate its pH. pH or hydrogen ion concentration can be used to determine how strongly an acidic or basic a solution is at a particular temperature. The pH scale goes from 0 to 7 (less acidic), 7 to 14 (more alkaline), and 7 (neutral). Since pH affects every stage of water and wastewater treatment as well as waste quality management, pH measurement is one of the most significant and widely utilised tests.

Principle

The electromotive force (emf) of a cell made up of a reference electrode (often a calomel electrode) and an indicator electrode (an electrode sensitive to hydrogen ions, such as a glass electrode) submerged in the test solution is measured to calculate the pH. A liquid junction that is a component of the reference electrode is used to make contact. Using a pH metre, the emf of this cell is determined. The measuring device is also potentiometrically calibrated using an indicating (glass) electrode and a reference electrode using standard buffers with specified pH values since the pH is defined operationally on a potentiometric scale.

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pHB = -log10 [H+]

Where

pHB = assigned pH of standard buffer.

The operational pH scale is used to measure sample pH and is defined as:

pHs = pHB + F (Es - EB) / 2.303 RT

Where,

pHs = potentiometrically measured sample pH

 $F = Faraday 9.649 \ge 104$ coulomb/mole

Es = Sample emf V

EB = Buffer emf V

R = Gas constant 1.987 cal deg-1 mole-1

 $T = absolute temperature, n^{\circ}K$

Apparatus and equipment.

a. pH metre: Made up of a temperature compensator, a glass electrode, a reference electrode, and a potentiometer. The potentiometer completes a balanced circuit when the electrodes are submerged in the test solution. The pH or millivolt can be read on a lot of pH metres.

b. The reference electrode is made up of a half cell that supplies an electrode potential that is uniform. As a reference electrode, calomel, silver-silver chloride electrodes are typically utilised.

c. Glass electrode sensor: There are numerous varieties of glass electrodes available. The glass electrode is essentially a very thick walled glass bulb blown at the end of a glass tube. It is composed of low melting point, high electrical conductivity glass. This lightbulb has an electrode with a steady potential, such as a platinum wire submerged in an H+ hydrochloric acid solution that is quinhydrone-saturated. The bulb is submerged in the liquid to be tested for pH.d. Beakers: Preferably use polyethylene or TFE beakers.

e. Use a magnetic stirring stick coated in TFE as the stirrer.

Reagents and standards

a. pH 4 buffer: 10.12g of potassium hydrogen phthalate (KHC8H4O9) should be dissolved in purified water. Reduce to one litre.

b. pH 7 buffer solution: Melt dried at 110° C: 1.42g of anhydrous disodium hydrogen phosphate (Na2HPO4) and 1.361g of anhydrous potassium dihydrogen phosphate (KH2PO4). Once boiled and cooled, use distilled water. Reduce to one litre.

c. Buffer solution with a pH of 9.2: dissolve 3.81 grammes of borax (Na2B4O7.10H2O) in distilled water that has been boiled and chilled. Reduce to one litre.

Calibration

The electrodes should be taken out of the water and rinsed with demineralized or distilled water before use. Use a soft tissue to gently wipe the electrodes to dry them. Adjust the electrode system's pH by comparing it to a standard buffer solution. Prepare fresh buffer solution as needed for operations, or utilise easily accessible pH buffers, as buffer solution may deteriorate due to mould growth or contamination. For the manufacture of all standard solutions, use distilled water with a conductivity of less than 2µ siemens at 25°C, distilled, and a pH of 5.6 to 6.0. Commercially available buffer tablets, powders, or solutions of verified quality are also acceptable for routine analysis. There are buffers with pH values of 4.0, 7.0, and 9.2. Dissolve all of the material when making buffer solutions from solid salts; otherwise, the pH calibration will be off. To limit inaccuracy caused by the electrode's nonlinear response, prepare and calibrate the electrode system using buffer solutions whose pH approximates that of the sample.

Electrical Conductivity

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The ability of water to conduct electricity is known as conductivity, and it depends on the quantity and kind of ions present in the solution. Conductivity is a function of the concentration of ionised compounds in the water. Since the majority of dissolved inorganic materials in water are ionised, they add to conductance.

Instrumental Method

Principle

The conductance produced by different ions in the solution or water is measured using this technique. By multiplying specific conductance (measured in mS/cm) by an empirical factor, which can range from 0.55 to 0.90 based on the soluble components of the water and the measurement temperature, one can approximate the dissolved ionic contents of a water sample.

An accurate and quick estimation of the fluctuations in a water body's dissolved mineral concentration can be obtained using conductivity monitoring.

Apparatus and equipment

a.Conductivity metre is one of the self-contained conductance devices . These can be purchased commercially.

b. A thermometer with a range of 10 to 50°C and the ability to read to the nearest 0.1°C.

c. Conductivity Cells: The resistance and conductivity ranges of the instrument will determine the cell to use. Check the instrument assembly's range experimentally by contrasting the instrument's readings with the potassium chloride solution's actual conductance.

Alkalinity

Using phenolphthalein and methyl orange indicator, titrate standard sulfuric acid (0.02N) at room temperature to assess the alkalinity of the sample. Total alkalinity (complete neutralisation of OH-, CO3--, and HCO3-) is indicated by a sudden shift in methyl orange indicator's colour from yellow to orange. Titration to decolorization of phenolphthalein indicator will indicate complete neutralisation of OH- and $\frac{1}{2}$ of CO3-.

Apparatus

a. Beakers: The electrode and the size of the sample to be utilised for the alkalinity assessment will determine the beaker's shape and size.

b. Volumetric pipettes

c. Volumetric flasks: 1000, 200, and 100 mL

Reagents and standards

a.Normal H2SO4, 0.02 N: To make 0.1N H2SO4, dilute 3 mL of concentrated H2SO4 with 1000 mL. Compare it to a standard 0.1N Na2CO3 solution to standardise it. To obtain standard 0.02 H2SO4, dilute the necessary volume of H2SO4 to 1000 mL.

b. Phenolphthalein indicator: 500mL of 95% ethyl alcohol dissolved 0.5g. Pour in 500mL of distilled water. Add 0.02N NaOH dropwise until a light pink hue (pH 8.3) manifests.

c. To make 1000mL of methyl orange indicator, dissolve 0.5g in distilled water free of CO2 and adjust the pH to 4.3-4.5.

OR

Bromo-cresol green indicator: In 100 millilitres of distilled water (pH 4.5), dissolve 0.1 grammes of sodium salt (bromocresol green).

Calibration

Make use of pH buffers to standardise the pH metre. Observe the guidelines provided in the pH meter's handbook.

Procedure

a. A conical flask should be filled with a 25 or 50 mL sample and 2-3 drops of phenolphthalein indicator.

b. Titrate with 0.02N H2SO4 until the pink hue fades or the pH reaches 8.3. Take note of the necessary H2SO4

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volume.

c. Pour two to three drops of methyl orange into the same flask, and keep titrating until the yellow colour turns orange. Take note of the necessary H2SO4 volumes.

d. Proceed as directed above if the addition of phenolphthalein does not result in the appearance of pink colour.

e. As an alternative, use the proper sample volume and titration assembly to carry out a potentiometric titration to a predetermined pH. Without noting the intermediate pH, titrate to the end point pH. Reduce the amount of acid added as the end point approaches, and make sure pH equilibrium is established before adding further titrant. The appropriate alkalinity, expressed as mg CaCO3/L, is indicated to be equivalent to the following pH values.

Total Hardness

The ability of water to precipitate soap is traditionally gauged by its hardness. Water hardness is a complicated mixture of cations and anions that varies over time rather than being a single component. Dissolved polyvalent metallic ions are the cause of it. The main ions that cause hardness in fresh water are magnesium and calcium, which cause soap to precipitate. Other polyvalent cations can also cause soap to precipitate, although they usually do so in complex forms that include organic components, making their contribution to water hardness unclear or negligible. The sum of the calcium and magnesium concentrations, both represented as CaCO3 in mg/L, is the definition of total hardness. According to the equivalent CaCO3 concentration, drinking water hardness has been categorised as follows: soft (0–60 mg/L), medium (60–120 mg/L), hard (120–180 mg/L), and very hard (>180 mg/L).

EDTA titration method

Principle

In an alkaline environment, hardness is ascertained using the EDTA method. EDTA and its sodium salts form a soluble chelated complex with specific metal ions. In an aqueous solution at pH 10.0 \pm 0.1, calcium and magnesium ions combine with Eriochrome black T to produce a wine-red hue. The use of EDTA as a titrant causes the divalent ions of calcium and magnesium to complex, causing a sudden shift in colour from wine red to blue, signifying the titration's end point. For the titration to reach a suitable point, magnesium ions must be present. Therefore, the buffer is supplemented with a modest amount of complexometically neutral magnesium salt of EDTA. As pH rises, the terminal point's sharpness increases. Nonetheless, the designated pH of 10.0 \pm 0.1 is a good middle ground. Higher pH values, or around 12.0, cause Mg++ ions to precipitate and leave only Ca++ ions in solution. Ammonium purpurate, or murexide, indicator turns pink when combined with Ca++ at this pH. The addition of EDTA causes Ca++ to complex, changing its colour from pink to purple to signify the reaction's termination. Set a 5-minute time restriction for the titration phase to reduce the likelihood of CaCO3- precipitation.

Apparatus

- a. Conical flasks 100mL
- b. Burette
- c. Pipette
- d. Spatula

Reagents and standards

a. Buffer solution: Use 143 mL of NH4OH to dissolve 16.9 g of NH4Cl. To achieve a noticeable shift in the indicator's colour, add 1.25 g of EDTA magnesium salt and dilute to 250 mL. If you mix 780 mg of MgSO4.7H2O or 644 mg of MgCl2.6H2O with 50 millilitres of purified water and magnesium salt of EDTA (AR grade). Add this to the NH4Cl in NH4OH solution mentioned above, then dilute to 250 mL.

b. Inhibitor: MgCDTA: Before adding buffer solution, add 250 mg of the magnesium salt of 1,2-cyclohexane-diamine tetra acetic acid per 100 mL sample and fully dissolve. When interfering compounds are present at concentrations that affect the end point but do not significantly contribute to the hardness value, use this complexing agent instead of poisonous or odorous inhibitors.

c. Eriochrome Black T indicator: To make dry powder, combine 0.5 grammes of dye with 100 grammes of NaCl.

d. Murexide (Ammonium purpurate) indicator: Grind 200 mg of murexide and 100 g of solid NaCl to a powder.

e. Sodium hydroxide 2N: Use 80g of NaOH to dissolve, then dilute to 1000mL. f.Standard EDTA solution 0.01 M: Dilute 3.723 g of sodium EDTA salt to 100 mL by dissolving it. Measure against the industry standard calcium solution. 1 milligramme CaCO3. g = 1 mL.typical calcium solution Accurately weigh one gramme of CaCO3 (AR

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grade), then transfer it to a 250 mL conical flask. After inserting a funnel into the flask's neck, add 1+1 HCl until the CaCO3 completely dissolves. To remove CO2, add 200mL of distilled water and boil for 20 to 30 minutes. Add a few drops of methyl red indicator after cooling. Drop by drop, add 8N NH4OH until an intermediate orange colour appears. 1000 mL of dilution yields 1 mL or 1 milligramme of CaCO3.

Calibration

The EDTA solution needs be standardize against standard calcium solution such that the strength of EDTA will be 1mL = 1mg as CaCO3.

Result and Discussion

Water Quality

Major Ions in Groundwater: Significant quality parameters and ratios are found using the collected data. Because of the location and historical flow of water, salts are present in all groundwater. The kind and amount of salts in water are determined by the surrounding conditions, groundwater flow, and sources. As water moves from precipitation to groundwater throughout the hydrologic cycle, its quality varies. [2]. The chemical, physical, and bacteriological characteristics of groundwater determine its usefulness for industrial, residential, and irrigation uses. The examined main ions are addressed in light of the aforementioned information in order to determine their suitability for consistent use.

S.No.	Turbi dity	Odou r	PH	EC	TDS	TA	TH	Ca H	So4	Cl	F	Ca	Mg	Hco3	Na	К	
1	8.5	U.O	7.8	1460	964	385	285	140	80	220	1.13	56	35	470	131	1.40	
2	0.6	U.O	7.3	3000	1980	400	575	205	190	530	1.85	148	90	488	264	3.00	
3	0.8	U.O	7.6	2860	1887	295	870	640	140	545	0.86	92	56	360	400	4.00	
4	0.6	U.O	7.2	1800	1188	375	580	480	80	315	0.68	41	24	457	267	3.00	
5	0.5	U.O	7.3	1384	913	260	460	355	118	185	0.63	42	26	317	212	3.00	
6	0.6	U.O	7.3	1870	1234	270	600	485	80	315	0.69	46	28	329	276	2.00	
7	0.7	U.O	7.2	1235	815	255	445	350	117	340	0.63	38	23	311	205	2.00	
8	0.5	U.O	7.4	1089	719	285	400	305	140	120	1.09	38	23	348	184	2.00	
9	0.6	U.O	7.3	970	640	300	360	265	51	80	0.81	38	23	366	166	2.00	
10	0.7	U.O	7.3	1183	781	360	450	355	80	115	1.15	38	23	439	207	2.00	
11	0.6	U.O	7.6	933	615	355	345	235	35	60	1.49	44	27	432	159	2.00	
12	0.7	U.O	7.4	960	633	295	370	280	55	70	0.98	36	22	360	170	2.00	
13	0.5	U.O	7.6	1004	663	325	375	290	58	75	0.99	34	21	396	173	2.00	
14	0.5	U.O	7.3	926	611	310	340	280	46	65	0.84	24	15	378	156	2.00	
15	0.6	U.O	7.3	1052	694	420	345	225	45	65	1.55	48	29	512	159	2.00	
		Min	7.2	926	611	255	285	140	35	60	0.63	24	15	311	131	1.4	
		Max	7.8	3000	1980	420	870	640	190	545	2	148	90	512	400	4	
		Avg.	7.39	1448	955.8	3 326	453	326	87	207	1.02	50.9	31	398	209	2.3	
Table	1. Ma	ijor El	lement	Analy	tical	Data O	f Grou	ndwat	er In T	The Stu	udy Are	ea					
S.NO			Water Parameters			Min			Max			Average			WHO(2011) Standards		
						(mg/l)			(mg/l)			(mg/l)			(mg/l)		
1			pH			7.2			7.8			7.3			6.6 - 8.5		
2			EC			926			3000			1448			1500		
3			TH			285			870			453			<200		
4			HCO3-			311			512			398			500		
5			TA			255			420			326					
S.NO			Water Parameters			Min			Max			Average			WHO(2011) Standards		

Table 2. Comparision Of Chemical Analysis Data Of Groundwater In The Study Area With Who (2004)Standards

Hydrogen Ion Concentration (pH):

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It gauges the water's acidity or alkalinity. There are H+ and OH- ions in natural water H2O. However, water undergoes a dissociation process known as hydrolysis, which results in the presence of uncombined H+ and OH-. [3]. When there are more H+ ions than OH-, the water becomes acidic (pH<7), and when the opposite is true, it becomes alkaline (pH>7). H+ and OH-concentrations in neutral water (pH=7) are equal. Particularly in limestone regions, the pH value is occasionally used to gauge the water's solvent strength for different types of rock minerals. [4] The pH level in most groundwater is regulated by the CO2-CO3-HCO3 equilibrium.

The pH of groundwater typically ranges from 6.5 to 8.5. The research area's groundwater has an average pH of 7.3 but can range from 7.2 to 7.8.

Electrical Conductivity:

Ionic concentrations are shown by the conductivity measurement. Temperature, concentration, and kind of ions present all play a role (Hem, 1991). 1500 microsiemen/cm is the maximum electrical conductivity that can be found in drinking water (W.H.O., 1983). The groundwater in the research area has an average electrical conductivity of 955 microsiemen/cm, with a range of 611 to 1980 microsiemen/cm at 250 c. The study area's electrical conductivity is within allowable bounds. The research region has an average value of 1448 microsiemen/cm, with a minimum value of 926 microsiemen/cm and a maximum value of 3000 microsiemen/cm.

Total Hardness:

It is measured in mg/l and is the soap-destroying power of water due to the interaction of Ca and Mg with CO3, HCO3, SO4, and NO3 ingredients. There are two kinds of hardness: (1) transient hardness and (2) persistent hardness. The first kind is caused by the HCO3 of calcium and magnesium, which is easily eliminated by boiling the water. Boiling water cannot eliminate the second type, which is caused by the presence of SO4 and Cl ions of Ca and Mg. The CO2 solution that the bacteria in the soil release determines the overall hardness of the water. In addition to the many causes of pollution, precipitation seeping into limestone areas raises the groundwater's overall hardness content. The following illustrates the level of overall hardness in groundwater in table 3

Water Type	Total Hardness (mg/l)					
Soft	<75					
Moderately Hard	75 - 150					
Hard	150 - 300					
Very Hard	>300					

Table 3. hardness in groundwater

Conclusion

The analysis of groundwater samples from the Diyla area reveals insights into the region's water quality, characterized by parameters such as pH, electrical conductivity (EC), total hardness (TH), alkalinity, and fluoride levels (F). The pH and EC measurements, assessed using digital meters, provide an overview of the water's chemical stability and ionic concentration, respectively, while titrimetric analyses of TH and alkalinity offer valuable information on the water's hardness and buffering capacity. The findings underscore that, while the current groundwater quality remains within acceptable ranges for most parameters, variations in some indicators suggest potential vulnerabilities, particularly regarding mineral content and fluoride presence. These results emphasize the necessity of routine monitoring to prevent long-term issues such as mineral accumulation or water hardness that could impair groundwater sustainability. Future research should aim to expand sample points over time and incorporate seasonal analyses to capture a more comprehensive picture of the groundwater quality, which will be vital for informed water resource management and public health safeguarding.

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