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Assessment of Hydrochemical Characteristics and Water Quality as Monitoring of Environmental Conditions in Shallow Groundwater and Kinokawa River, Wakayama Prefecture, Japan

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Abstract

Shallow groundwater and river water problems in each country are caused by various factors such as natural factors such as natural disasters, human activity factors such as waste pollution, and others. In this study, we analysed the hydrochemical characteristics of river water to determine the water quality of shallow groundwater and Kinokawa river in Wakayama region of Japan. Shallow groundwater and river water samples were taken along the Kinokawa river at a total of 86 points. The water samples were analysed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). In this case, we investigated physicochemical parameters such as total dissolved solids which mainly depend on the concentration of major ions such as Ca, Mg, Na, K, Cl, Li, HCO_3, NO_3 and S04 which are used to characterise river water quality. The results of this study show that the calculated values of SAR, PI, Na%, MH and RSC indicate good groundwater use for irrigation purposes. Comparison of geochemical data showed that more than 75% SAR, 94% PI, 80% %Na, and 97% MH indicated a good environmental condition category and the river water can be used for irrigation purposes. The water quality information presented in this paper will be useful for sustainable management of water resources in the study area.

Keywords: river water, hydrochemistry, shallow groundwater, water quality, geochemical characterization, inductively coupled plasma-mass spectrometry

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INTRODUCTION

Monitoring environmental conditions in water is crucial for several reasons, each contributing to the health of ecosystems, human communities, and the overall environment. Healthy water bodies support a wide variety of aquatic species (Al-Khashman et al., 2017; Ighalo et al., 2021; Pasika & Gandla, 2020). Monitoring helps ensure that the water quality supports the life and reproductive cycles of organisms. Aquatic habitats can be sensitive to changes in water quality. Regular monitoring helps maintain the natural conditions needed for these habitats to thrive. In ensuring human health and safety, many communities rely on natural water bodies for drinking water. Monitoring ensures that water sources are free from harmful contaminants. Water quality is essential for safe recreational activities like swimming, boating, and fishing. Monitoring prevents health risks associated with polluted water (Jha et al., 2020; Kumar et al., 2009; Yu et al., 2018).

In the area of economic benefits, clean water is vital for the health of fish populations, which are essential for commercial and subsistence fishing industries. Pristine water bodies attract tourists, supporting local economies. Monitoring helps maintain the appeal of these natural attractions. Monitoring provides the data needed for informed environmental management and policy decisions. It helps identify pollution sources and evaluate the effectiveness of regulations. On the other hand, in sustainable resource management, it is ensured that water use is sustainable and does not compromise the needs of future generations (Kasayanond et al., 2019).

In the climate change adaptation, monitoring helps detect changes in water conditions that may result from climate change, such as altered precipitation patterns, temperature fluctuations, and extreme weather events (Jalili et al., 2019; Moustafa El Baba, Prabin Kayastha, Marijke Huysmans, 2020; Pazand & Pazand, 2020). This monitoring also provides the information needed to adapt water management strategies to changing environmental conditions. In early warning and disaster prevention, timely detection of pollution events allows for quick response to mitigate impacts on ecosystems and human health. Not only that, monitoring in flood and drought management also helps manage data on water levels and flows, but flood and drought management monitoring also helps prevent or mitigate floods and droughts (Hong et al., 2021; Paper, n.d.; Sujitapan et al., 2024).

One of the important monitoring is in the river water. River water monitoring is crucial for several reasons, and it plays a vital role in maintaining the health of aquatic ecosystems and human populations. Many communities rely on rivers for their drinking water supply. Monitoring ensures that the water is safe for consumption and free from harmful contaminants. Regular monitoring helps detect pathogens that can cause diseases, ensuring timely action to protect public health.

Monitoring data can reveal trends in water quality over time, helping to understand the impact of human activities and natural processes. Data from monitoring programs also inform environmental policies and regulations aimed at protecting water resources. Monitoring can provide early warning of pollution events or environmental disasters, allowing for prompt response and mitigation (Haerudin et al., 2019; Ighalo et al., 2021; Sujitapan et al., 2024). It helps in managing river flows and water levels, which is essential for flood control and drought management. Effective monitoring ensures sustainable management of water resources, balancing the needs of different users and preserving water for future generations. Healthy rivers provide various ecosystem services such as water purification, climate regulation, and recreational opportunities. Monitoring helps maintain these services (Calligaris et al., 2018; Jan et al., 2021; Mutri et al., 2024).

In the habitat preservation, monitoring water quality helps maintain the conditions necessary for the survival of fish, invertebrates, and other aquatic organisms (Adejumo et al., 2018; Jalili et al., 2019; Jan et al., 2021; Paital, 2015; Umar Kura et al., 2013). On the other hand, it also helps identify sources of pollution, which can then be managed to prevent harm to aquatic ecosystems. Clean water is essential for the fishing industry and aquaculture. Monitoring ensures that water quality meets the standards required for these activities. Rivers are often used for recreational activities such as swimming, boating, and fishing. Good water quality is essential to attract tourists and ensure their safety (Chafa et al., 2022; Hong et al., 2021; Ighalo et al., 2021; Lakshmikantha et al., 2021; Mutri et al., 2024; Yu et al., 2018).

In summary, river water monitoring is essential for safeguarding human health, protecting the environment, supporting economic activities, and ensuring sustainable development (Al-Khashman et al., 2017; Luo et al., 2018; Moustafa El Baba, Prabin Kayastha, Marijke Huysmans, 2020; Mutri et al., 2024; O. et al., 2014; Parrone et al., 2020). It provides the necessary data for informed decision-making and effective management of water resources. In scientific research, continuous monitoring provides valuable data for scientific research, enhancing our understanding of aquatic ecosystems and environmental processes (Bartram & Ballance, 1996). On the other hand, scientific research in monitoring the state of the environment can also promote public awareness and education about the importance of water quality and environmental stewardship.

Therefore, monitoring of environmental conditions in the environment, especially river water, is carried out to obtain information on the state of the environment based on Drinking Water Quality Standards (DWQS) of Japan and World Health Organization (WHO) standards. In this study, we used assessment of hydrochemical characteristics as a research method to determine water quality.

METHOD

Shallow groundwater and river water samples were obtained from open data in previous research by Ii et al., (2019)which had been collected from 86 points along the Kinokawa River, Wakayama, Japan. Each water sample was analyzed for primary cations and anions. All chemical analyses was performed from April 2012 to November 2016 using water analysis techniques such as Ion Chromatography for chlorine (Cl), Inductively Coupled Plasma-Atomic Emission Spectroscopy for (Li), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for (Ca and Mg, Na, K, Ca and SiO_2), the concentration of NO_3 and HCO_3^- for the sampled water was measured with a TOC analyzer.

All water samples were taken from shallow groundwater and river water along the Kinokawa river for about 136 km, which flows from east to west. The average flow rate of the river is estimated to be about 37.4 m^3/s. It is known that the Kinokawa River is crossed by the largest fault in the Kii Peninsula region, the Median Tectonic Line (MTL) (**Figure 1**). The suspected changes in concentration and chemical components in shallow groundwater and Kinokawa river water are the reason for the water quality study. The geological structure of the Kinokawa River basin is composed of alluvial sediments in sambagawa metamorphic rocks. In the north and south of the Kinokawa River basin, Izumi sedimentary rocks and sambagawa metamorphic rocks are present **(Figure 2)**. It is also known that the MTL fault is the boundary between the Izumi group and the alluvial sediments and most of the hot springs appear in this alluvial sedimentary area (de Jong et al., 2009).

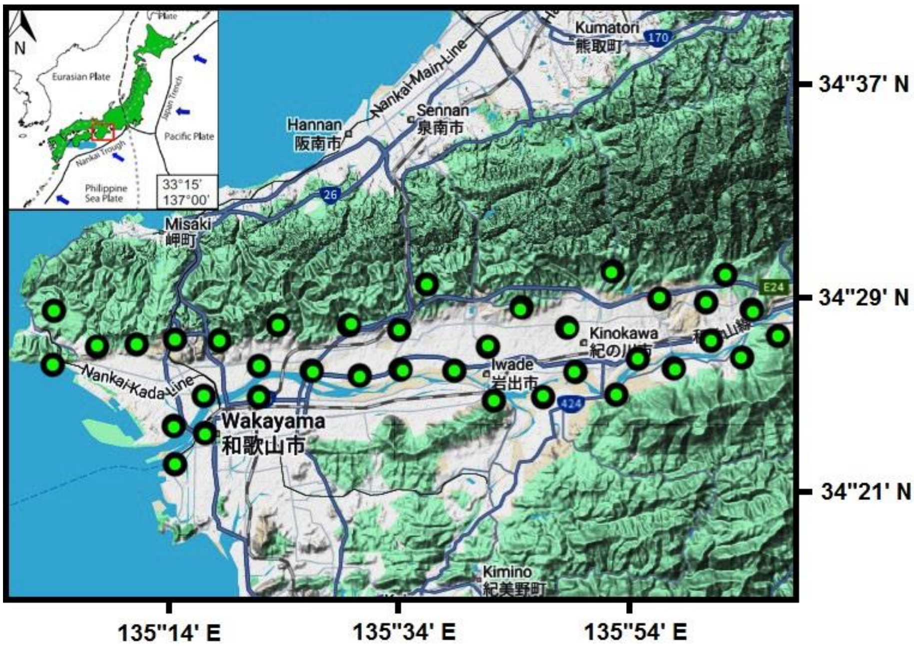

Figure 1. The location of sampling point on shallow groundwater and Kinokawa river water in northern Wakayama Prefecture, Southwest, Japan.

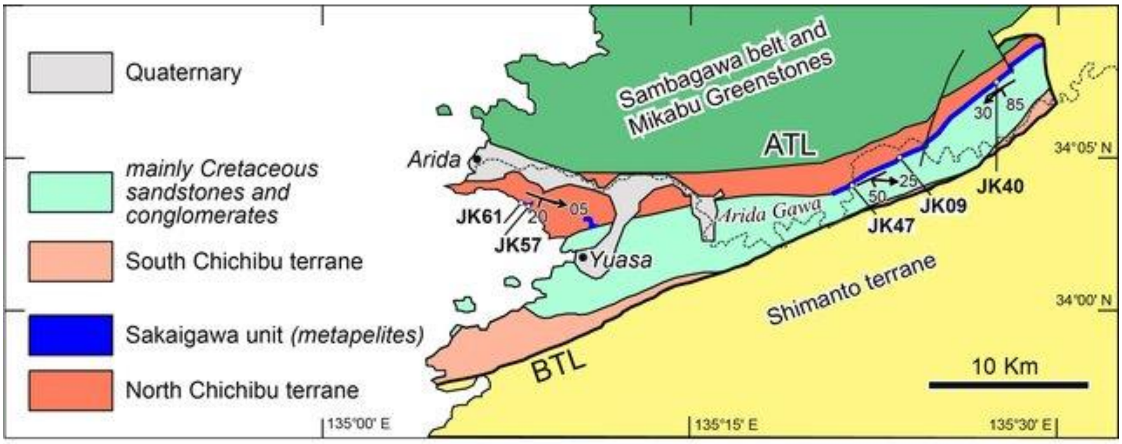

Figure 2. The geological of northern Wakayama Prefecture, Southwest, Japan (de Jong et al., 2009).

Evaluation of water hydrogeochemical qualities for irrigation use

The chemical characterization of groundwater schemes developed is primarily based on the concentrations of various dominant cations and anions (Al-ahmadi & El-Fiky, 2009). Six indices [Electrical conductivity (EC), percentage of sodium (Na%), sodium adsorption ratio (SAR), permeability index (PI), magnesium hazard (MH), and residual sodium carbonate (RSC)] (Chandrasekar et al., 2014) were used to determine the suitability of groundwater for irrigation/agricultural activities (Adimalla & Venkatayogi, 2018).

Percent sodium (%Na)

The suitability of ground water for irrigation depends on the mineralization of water and its effects on plants and soils. The concentrations of EC and Na are important in classifying irrigation water (de Andrade et al., 2008). If the high salt content (high EC) in ground water will cause the formation of saline soil. A very high salinity, on irrigated land is one of the main causes of loss of production. Sodium concentration is also very important in classifying irrigation water. If the concentration of high sodium in groundwater soil permeability will be reduced and eventually produce the soil with poor internal drainage. The incorporation of sodium with carbonate forms an alkaline soil, while the sodium combined with chloride forms saline soil (Adimalla, 2013).

$$\%Na = \frac{Na^{+} + K^{+}}{(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})} x100$$

Sodium adsorption ratio (SAR)

The relative activity of sodium ions in the exchange reaction with the soil is expressed in terms of the ratio of sodium adsorption (SAR). Calculation of SAR value can indicate the effect of cation concentration relative to the amount of Na^{+} in the soil, used to evaluate the sodicity of irrigation water (Wilcox, 1955).

$$SAR = \frac{Na}{\sqrt{(Ca + Mg)/2}}$$

Permeability index (PI)

Permeability is influenced by sodium, calcium, magnesium, chloride, and soil bicarbonate contents (Hwang et al., 2017). Based on the PI, the suitability of groundwater for irrigation use can be classified into grades 1.(Excellent), 2.(Good), and 3.(Unsuitable) based on the Doneen permeability index (1964) (Hwang et al., 2017).

$$PI = Na + \left\{ \left(\frac{\sqrt{HCO_3}}{(Ca + Mg + Na)} \right) \times 100\% \right\}$$

Magnesium hazard (MH)

One element that can maintain the most balance in the waters is calcium and magnesium, but this balance does not apply in ground water. Magnesium can be reduced to groundwater, especially ground water that contains high levels of sodium and salt (Adimalla & Venkatayogi, 2018). However, excessive Mg^{2+} in water will also adversely affect the soil quality, make it alkaline, and damage the farming system. Based on previous research by Szabolcs and Darab (1964) in (Hwang et al., 2017) proposed magnesium hazard (MH) values for irrigation water and MH was calculated by the following equation.

$$MH = \frac{Mg}{(Ca + Mg)} x100$$

The MH values in the study area ranged from 5.2% to 23.6%, all samples were considered appropriate for irrigation (<50%), but high salinity by percent sodium, making groundwater less good for agriculture.

Residual sodium carbonate (RSC)

Magnesium and calcium are the most enduring elements in equilibrium in waters, but the excess amount of magnesium and calcium ions that precipitate can become carbonate (Adimalla & Venkatayogi, 2018). Increased sodium concentrations in ground water can reduce the concentration of magnesium and calcium, but very high sodium concentrations can reduce soil permeability. One of the factors causing increased sodium absorbs is the high residual value of sodium carbonate RSC (Keith David Todd, 2005). Sodium carbonate residue (RSC) also affects the suitability of ground water for *irrigation* use. When the amount of carbonate exceeds calcium and magnesium, there is the possibility of precipitation that gives a lot of calcium and magnesium. Consequently, the relative proportion of sodium in water increases in the form of sodium carbonate, and this surplus, shown by RSC, is calculated as follows (Hwang et al., 2017).

$$RSC = \left(CO_3{}^{2-} + HCO_3{}^{-}\right) - \left(Ca^{2+} + Mg^{2+}\right)$$

RESULTS AND DISCUSSION

Descriptive statistics of the physicochemical parameters of analytical data and the permissible constraints of various organizations such as the World Health Organization (WHO) and Drinking Water Quality Standards (DWQS) of Japan are presented in **Table 1**. Total Dissolved Solid (TDS) is an inorganic salt compound comprising calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), chloride (Cl), and sulfate (SO_4) as well as small amounts of organic matter dissolved in water. TDS in drinking water comes from natural sources, sewage, urban runoff and industrial wastewater. The MTL fault and the occurrence of hot springs around the Kinokawa river may also contribute to the TDS content in the river water. Differences in TDS concentration in water vary greatly depending on different geological structures due to differences in mineral solubility (Gordon et al., 2008; Selvakumar et al., 2017). In this study, the TDS values vary between 31.70 to 365.80 mg/L with an average value of 99.79 mg/L; for drinking purpose the maximum allowable TDS guideline value prescribed by the WHO (2004) is 1,000 mg/L. High TDS values in this study, caused by high concentration of chlorine (Cl) and calcium (Ca).

Calcium (Ca) concentrations ranged from 2.90 to 63.40 mg/L with an average value of 24.22 mg/L and magnesium (Mg) ranged from 1.10 to 24.10 mg/L with an average value of 7.26 mg/L. From the data in this study, the average concentrations of calcium (Ca) and magnesium (Mg) did not exceed the WHO water quality standards and DWQS. High calcium (Ca) levels in river water are primarily due to the natural weathering of calcium-rich rocks such as limestone, dolomite, and gypsum. When these rocks come into contact with water, especially rainwater that is slightly acidic due to dissolved carbon dioxide (CO_2), calcium is leached out and enters the river system. This process is known as chemical weathering. The primary source of calcium in river water is the natural weathering of calcium-containing rocks. While the rainwater, which is slightly acidic, enhances the dissolution of calcium from rocks. Areas with a high concentration of calcium-rich rocks will naturally have higher calcium levels in their rivers (Gordon et al., 2008).

Sodium (Na) is one of the most important elements of river water, but if its concentration exceeds 200 mg/L makes water unsuitable for domestic use, as it can lead to severe health problems such as hypertension, congenital disease, kidney disorders and neurological disorders in the human body (Adimalla, 2013; Adimalla & Venkatayogi, 2018). The concentration of sodium (Na) ions varies from 3.20 to 94.60 mg/L with an average value of 4.79 mg/L. The sodium (Na) value in this study did not exceed the WHO's desired limit of 200 mg/L. The concentration of sodium (Na) is usually influenced by the natural cation exchange mechanism due to the interaction of water and rocks (Selvakumar et al., 2017).

Table 1. Drinking water standard specifications and statistical information of ionic concentration

Parameters	Minimum	Maximum	Mean	*WHO 2004	**DWQSs
TDS (mg/L)	31.70	365.80	99.79	1000	500
Ca (mg/L)	2.90	63.40	24.22	200	300

Mg (mg/L)	1.10	24.10	7.26	150	300
Na (mg/L)	3.20	94.60	20.17	200	200
K (mg/L)	0.20	20.00	4.79	12	-
Cl (mg/L)	2.70	120.40	16.41	600	200
SO_2 (mg/L)	4.10	94.60	26.92	250	-
Li (mg/L)	0	0.054	0.005	0.01	-
HCO_3 (mg/L)	15	253	87.86	-	-
NO_3 (mg/L)	0	59.4	12.26	50	10

*World Health Organization (*WHO*) standards
**Water Quality Standards (DWQSs) of Japan

Potassium (K) concentrations vary between 0.20 and 20.00 mg/L with an average grade of 4.79 mg/L. High potassium levels in river water can result from a combination of natural processes and human activities. Out of a total of 86 river water samples, 5 exceeded the maximum limit set by WHO 2004 of 12 mg/L. Similar to calcium, potassium is naturally released into water through the weathering of potassium-rich minerals like feldspars and micas found in rocks and soils. Erosion of soil, especially agricultural soil rich in fertilizers, can carry potassium into rivers. On the other hand, potassium is a common component of fertilizers. Runoff from agricultural lands can introduce significant amounts of potassium into rivers. Some industries release potassium as a byproduct, which can enter river systems through discharge. Wastewater from residential areas and treatment plants can contain potassium from household products and human waste. The breakdown of plant and animal matter releases potassium into the soil, which can then be washed into rivers during rain events. High potassium levels can contribute to nutrient imbalances in aquatic ecosystems, potentially affecting plant and animal life. Elevated potassium can influence the overall chemical composition of the water, affecting its suitability for various uses (Al-ahmadi & El-Fiky, 2009).

Chloride (Cl) concentrations ranged from 2.70 to 120.40 mg/L, and with an average grade of 16.41 mg/L. High calcium levels in river water are primarily caused by the natural weathering of calcium-rich rocks such as limestone, dolomite, and gypsum. When rainwater, which is slightly acidic due to dissolved carbon dioxide, interacts with these rocks, it dissolves the calcium minerals and carries them into the river. This process is known as chemical weathering (Adimalla & Venkatayogi, 2018). The concentration of chloride (Cl) in river water in the study area does not exceed the allowable limit of 600 mg/L by WHO and 200 mg/L by DWQS.

The sulfate (SO_4) concentration ranged from 4.10 to 94.60 mg/L with an average value of 26.92 mg/L. High sulfate levels in river water can result from both natural processes and human activities. Sulfate is naturally released into water through the weathering of minerals like gypsum ($CaSO_4$) and pyrite (FeS_2). When these minerals come into contact with water, they dissolve and release sulfate ions into the river. Based on human activities, Fertilizers and pesticides often contain sulfate compounds. Runoff from agricultural lands can introduce these sulfates into rivers (Selvakumar et al., 2017; Adimalla & Venkatayogi, 2018). However, The concentration of sulfate (SO_4) ions in river water in the study area does not exceed the allowable limit of 250 mg/L by WHO.

The concentration of Lithium (Li) in river water varies from 0 to 0.054 mg/L with an average value of 0.005 mg/L. Lithium (Li) is commonly found in the earth's mantle. The geographical location of the Kinokawa River is close to the MTL and there are many hot springs that may originate from the earth (Umam et al., 2022). Therefore, some river water that has Li values exceeding the standard limit is caused by the contribution of hot springs that enter the river (Ii et al., 2019).

Bicarbonate (HCO_3) in this study has a high enough concentration value with a minimum value of 15 mg/L, a maximum of 253 mg/L and an average of 87.86 mg/L. The most significant source of bicarbonate in river water is the weathering of carbonate rocks such as limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). When rainwater, which contains dissolved carbon dioxide (CO_2), comes into contact with these rocks, a chemical reaction occurs, producing bicarbonate (HCO_3^-). The weathering of silicate minerals also contributes to bicarbonate production, although to a lesser extent compared to carbonate rocks. Rainwater absorbs CO_2 from the atmosphere, forming weak carbonic acid (H_2CO_3). When this acidic water infiltrates the ground and interacts with carbonate rocks, bicarbonate ions are formed (Chae et al., 2006; Kimura, 1990).

Representation of hydrochemical data

The relationship between TDS (as an indicator of anthropogenic contamination) and major ions serves to understand the spatial control of the major ion concentrations **(Figure 3)** and **(Figure 4)**. For all the major ions examined, their concentrations tended to increase with increasing TDS. However, it should be noted that the steep sloping line is the highest contributing element such as HCO_3 **(Figure 3)**. However, if we look at the standard limits, the elements that have higher values are K and Li **(Figure 4)**. This proves that shallow groundwater and Kinokawa river water has contributions from environmental influences both natural and human activities in the area. The geographical location close to major faults such as the MTL is one of the reasons for the contribution of deep groundwater that comes out as hot springs around the river.

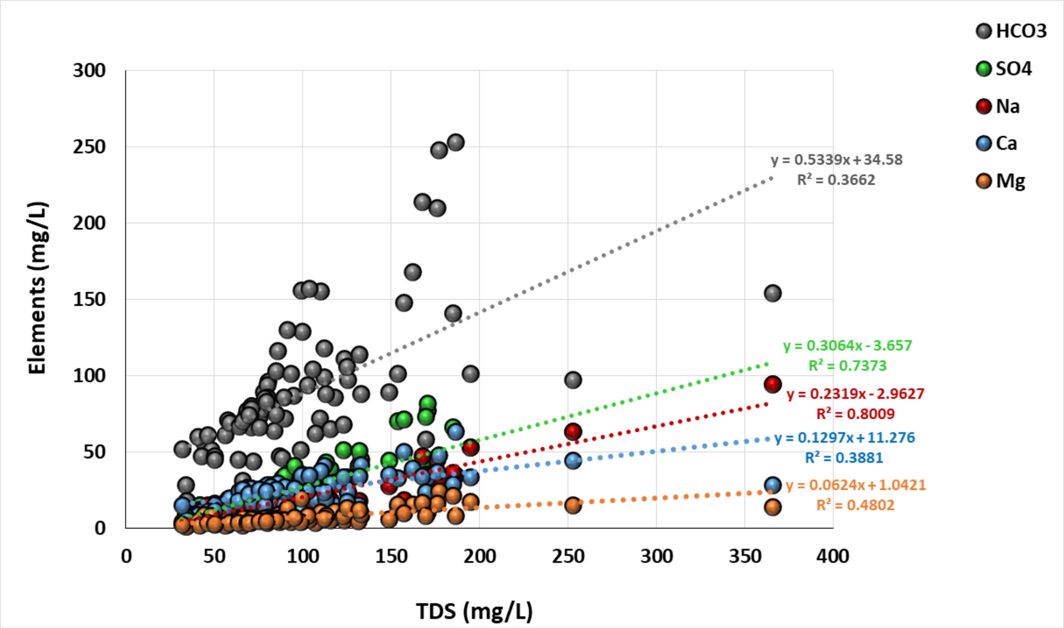

Figure 3. Interpretation between TDS and some elements (HCO_3, SO_4, Na, Ca, and Mg)

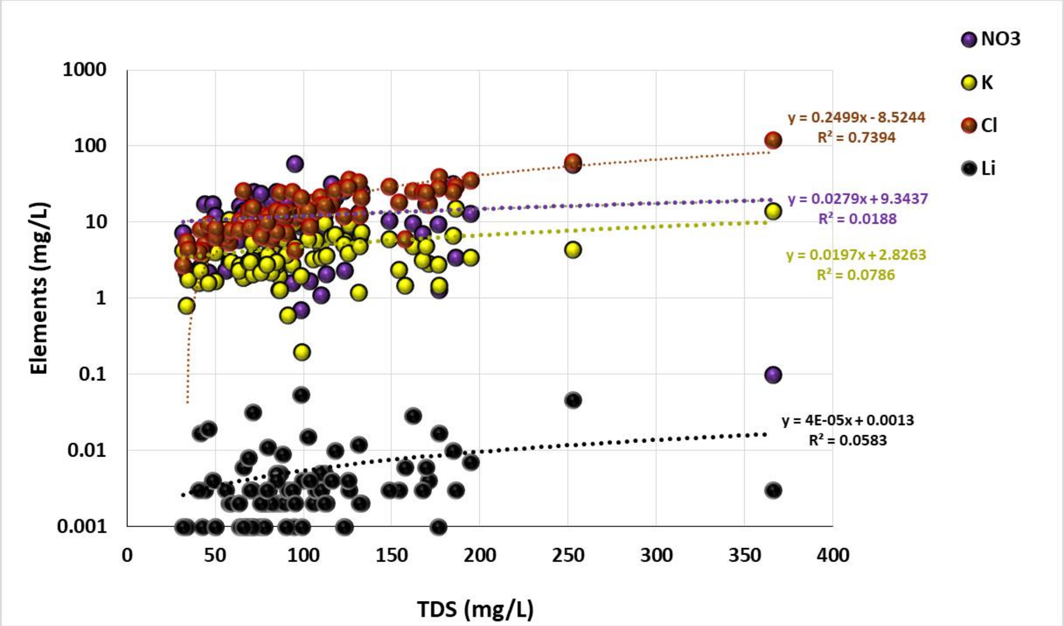

Figure 4. Interpretation between TDS and some elements (NO_3, K, Cl, and Li)

Geochemical diagrams/classification of groundwater

Based on the Ternary diagram shown in **Figure 5** that almost all river water samples in this study have dominant elements of both basic soil elements (Na + K) or alkaline elements (Ca + Mg). While in the triangle with bicarbonate and strong acid elements ($Cl+SO_4$) almost all samples are dominated by sulfate and cloride while the other 3 samples are dominated by bicarbonate. In the overall piper plot section, almost all river water samples fall into the calcium cloride type category which may be influenced by the presence of a large fault, namely MTL (Amita et al., 2014, 2014; Doğan et al., 2006; Ii et al., 2019; Jomori et al., 2013; Morikawa et al., 2016; Tabei et al., 2002). While some samples fall into the magnesium bicarbonate type.

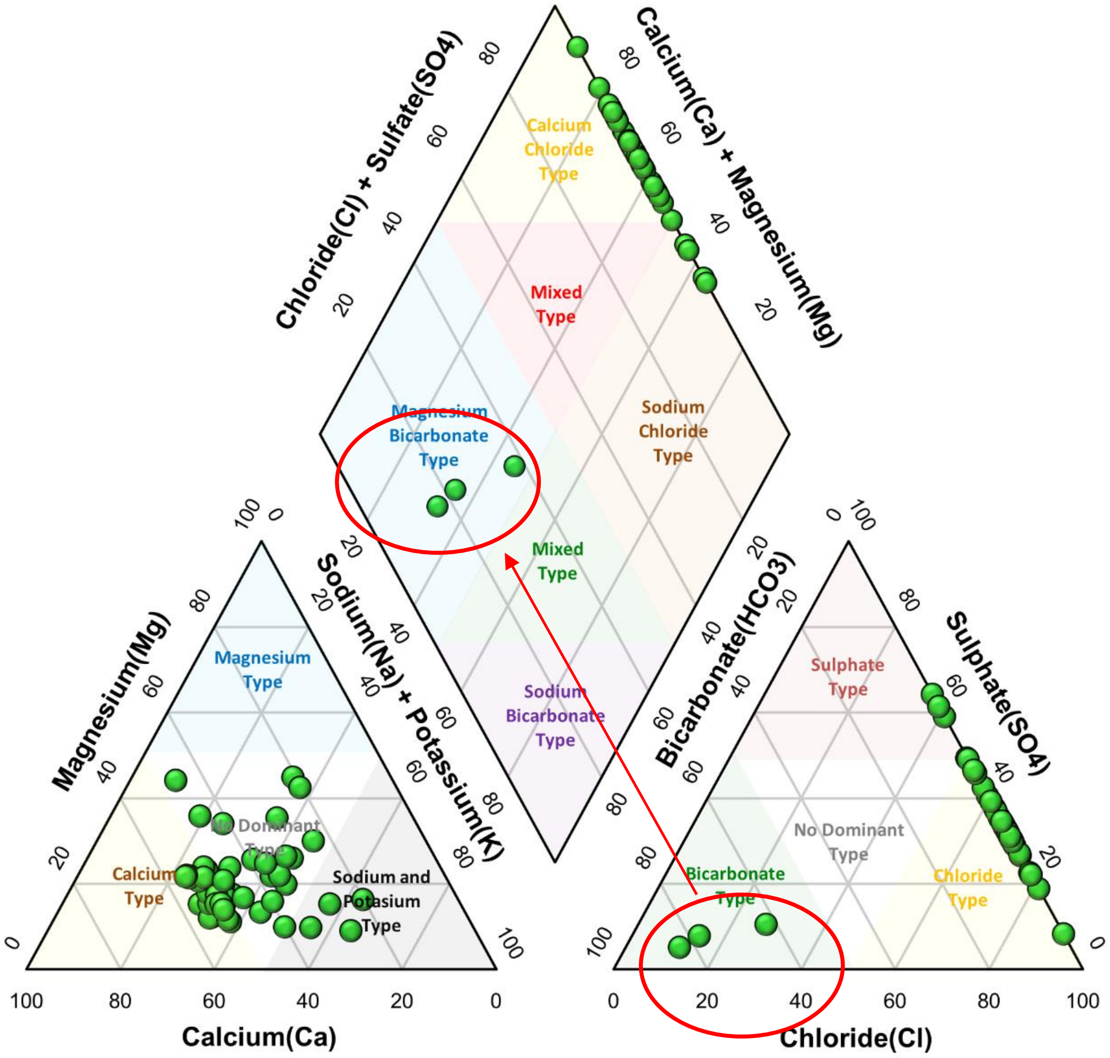

Figure 5. Tenary diagram of water samples from shallow groundwater and Kinokawa river water.

Classification of water quality

Based on **Table 2** shows the quality parameters. For SAR values, 65 samples or 75.58% fall into the 'no problem' category, while 12 samples or about 13.95% fall into the 'increasing problem' category. A total of 9 samples or about 10.46% fall into the 'severe problem' category. In addition, the quality value of other parameters such as PI has a 'suitable' category of 94.18%. While the remaining 5.81% are included in the 'unsuitable' category. For NA%, as many as 1.16% are in the 'excellent' category, while 39.53% are in the 'good' category, as many as 48.83% are in the 'permissible' category, and another 10.46 are in the 'doubtful' category (Keith David Todd, 2005). According to the classification, the MH results showed that 97.67% of the river water samples in this study fell into the 'suitable' category and the remaining 2.32% fell into the 'unsuitable' category (Hwang et al., 2017).

Table 2. Quality parameters results in groundwater samples in the study area (Wilcox, 1955; Al-ahmadi & El-Fiky, 2009; Hwang et al., 2017; Adimalla & Venkatayogi, 2018).

Parameters	Range	Water Quality Class (Irrigation uses)	Samples (n = 86)	
			Total of sample	Percentage (%)
Sodium adsorption ratio (SAR)	<6	No Problem	65	75.58
	6-9	Increasing problem	12	13.95
	>9	Severe problem	9	10.46
Permeability index (PI)	<60	Suitable	81	94.18
	>60	Unsuitable	5	5.81
Percent sodium (%Na)	<20	Excellent	1	1.16
	20-40	Good	34	39.53
	40-60	Permissible	42	48.83
	60-80	Doubtful	9	10.46
	>80	Unsuitable	0	0
Magnesium hazard (MH)	<50	Suitable	84	97.67
	>50	Unsuitable	2	2.32
Residual sodium carbonate (RSC)	<1.25	Suitable	-	-
	1.25-2.5	Marginal	-	-
	>2.5	Not suitable	-	-

*In (no.) indicates number of the samples fall in particular category
**In (%) indicates percentage of the samples out of 86, were fall in the particular category

CONCLUSION

Based on analyses of water samples taken in the shallow groundwater and Kinokawa river water of Wakayama Japan, it has been possible to understand the geochemical quality of the river water and evaluate its suitability for drinking and irrigation/agricultural purposes. The study concluded that the river water in the study area is suitable for use as agricultural irrigation water. In this context, the environmental conditions along the Kinokawa river are favourable. The groundwater chemistry in the ternary diagram shows that there is no dominant cation in the hydrochemical facies. While the dominant anions are cloride and sulfate. Although some samples are in the bicarbonate dominant type. The high concentration of Cl is typical of anthropogenically contaminated groundwater and has a contribution from deep groundwater entering streams. This result correlates with the fact that the study site is close to a major fault, the MTL, and there are hot springs around the river. The groundwater quality table shows that most of the water samples fall into the safe category. The calculated values of SAR, PI, Na%, MH and RSC indicate good groundwater use for irrigation purposes. Comparison of geochemical data showed that more than 75% SAR, 94% PI, 80% %Na, and 97% MH indicated a good environmental condition category and the river water can be used for irrigation purposes. The results of this study suggest that proper control of specific pollutant sources associated with land use characteristics, which should be based on monitoring the spatial variation of large long-term ions, would be the most effective for groundwater treatment in Wakayama region, Japan. The water quality information presented in this paper will be useful for sustainable management of water resources in the study area.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest concerning the publication of this article. The authors also confirm that the data and the article are free of plagiarism.

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