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Hiroshiro, Yoshinari
Urban and Environmental Engineering, Graduate School of Engineering, Kyushu University

Jinno, Kenji
Institute of Environmental Systems, Graduate School of Engineering, Kyushu University

Berndtsson, Ronny
Department of Water Resources Engineering, Lund University

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HYDROGEOCHEMICAL PROPERTIES OF A SALINITY-AFFECTED COASTAL AQUIFER IN WESTERN JAPAN

Yoshinari Hiroshiro,[1*] Kenji Jinno,[2] and Ronny Berndtsson[3]

[1]*Urban and Environmental Engineering, Graduate School of Engineering, Kyushu University, 6-10-1, Hakozaki, Fukuoka812-8581, Japan*
[2]*Institute of Environmental Systems, Graduate School of Engineering, Kyushu University, 6-10-1, Hakozaki, Fukuoka812-8581, Japan*
[3]*Department of Water Resources Engineering, Lund University, Box 118, S-221 00 Lund, Sweden*

Abstract:

Coastal groundwater aquifers are often exposed to heavy pumping and consequently to risks of saltwater intrusion. In many cases however, the observed increase in groundwater salinity can only be partly explained by actual saltwater intrusion from the sea. Other salinity-increasing processes may also significantly contribute to the total salt content of the groundwater. This paper describes a geochemical investigation that was carried out to investigate recent salinity increases in groundwater for the Motooka coastal area in Fukuoka, Japan. A strong increase in electrical conductivity (EC) at 15-20 m depth was observed, corresponding to the fresh- and saltwater interface. Oxidation-reduction potentials (ORP) observed in deeper groundwater was low, indicating long residence time for the groundwater. These results together with hydrogen-oxygen isotope ratio analysis indicated that the deeper groundwater is affected by seawater. Consequently, observed tritium concentration in the shallow groundwater system was higher than that of the deeper groundwater system, and a ^{14}C isotope dating of shell samples collected at 2-m depth indicated an age of about 2000 years. The overall results suggest that the aquifer was originally below the current sea floor and that deeper saline groundwater is not mixed with the shallower fresh groundwater. The deeper groundwater is therefore mainly affected by old seawater. In other words, modern saltwater intrusion has not yet occurred even if some wells contain saline water. The study shows that even though coastal aquifers are heavily pumped, the reason for the rise in groundwater salinity may not necessarily be due to seawater intrusion. Further geochemical and hydrological investigations will be necessary to identify the underlying mechanisms.

KEYWORDS Salinity-affected coastal groundwater aquifer; Groundwater quality; Redox conditions; Electrical conductivity; Environmental isotope analysis

INTRODUCTION

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* Corresponding to: Yoshinari Hiroshiro, Urban and Environmental Engineering, Graduate School of Engineering, Kyushu University, 6-10-1, Hakozaki, Fukuoka812-8581, Japan. E-mail: hirosiro@civil.kyushu-u.ac.jp

Saltwater intrusion is a common phenomenon in coastal aquifers. The total saltwater content of coastal aquifers however, can only be partially explained by direct seawater intrusion. Generally, the flow rate of freshwater in shallow groundwater is faster than that of saline groundwater at larger depths. The salt content of the groundwater also depends on the geological matrix material in the aquifer and the contact time between the matrix and groundwater. In order to determine the causes of groundwater salinity and the extent of seawater intrusion due to overpumping, it is necessary to understand all salinization processes and the mechanisms contributing to groundwater salinity.

Ikeda (1989) showed that qualitative changes in saline groundwater could be explained by ion exchange reactions due to exchangeable cations in the soil matrix. On the other hand, Wicks *et al*. (1995) indicated that the evolving processes determining saline groundwater quality with changing depths could be explained by dissolution/precipitation reactions and diagenesis of the water-rock interaction of calcite, dolomite, and gypsum. Price *et al*. (1991) performed a geochemical investigation of the chemical species change at different mixing rates of seawater to groundwater and examined the dissolution/precipitation reactions of the carbonate minerals in saline groundwater. Smedley and Edmunds (2002) described sequential changes of chemical species occurring along groundwater flow lines and investigated these in relation to the changing redox conditions in the aquifer.

As seen from the above, research on groundwater salinization processes has covered a broad range of factors that can influence groundwater salinity. . In general however, studies on the quality of groundwater in coastal areas often fail to grasp the vertical distribution of redox conditions and the gradually changing spatial chemical evolution in the aquifer. This is an important issue affecting the salinity process, which can significantly influence interpretation of the cause of salinity and therefore possible remedies.

According to the above, we present herein a geochemical investigation involving the vertical distribution of redox conditions in a salinity-affected coastal groundwater aquifer at Motooka, Fukuoka City, Japan. Besides the redox investigation, we use chemical species and environmental isotope analysis as the primary tools of investigation. The paper concludes with discussion and interpretation of the results and offers possible solutions for remediation.

METHODS AND EXPERIMENTAL OBSERVATIONS

The investigated area for saline groundwater is located in Motooka, west of Fukuoka City, Japan. The site for groundwater sampling is shown in Fig. 1 and well depths where groundwater was sampled are shown in Table 1. Land uses for the site include industrial greenhouses, paddy fields and field farms. Groundwater is mainly utilized for agricultural purposes, particularly for industrial greenhouses. A part of the study site is also intended as a new campus area for Kyushu University, which is likely to place increased stress on the groundwater supply. Together with decreasing groundwater recharge, concerns regarding saltwater intrusion have risen. In order to present a thorough analysis of all relevant processes that can contribute to the total salt content of the groundwater, sampling and chemical analysis was prepared together with an analysis of the geological strata in the area. A detailed description of the applied methodology is presented below.

Figure 2 shows the geological structure of each observation well. The geological properties of the 17-m deep B2 well display a mafic schist. Wells B2, B3, and B4 are all deeper than 10 m and also display inclusions of granodiorite. Proximity to the sea is in the order from B1 to B4 (see Fig. 1). Groundwater sampling was carried out using a cylindrical clear acrylic sampler furnished with a 50 m calibrated line. The diameter of the sampler is 40 mm and its length 580 mm. The sampling volume was about 0.4 L at each sampling occasion. Groundwater passes through the sampler as a rubber valve is opened during lowering of the sampler through the groundwater. The sampler is lowered until the desired sampling depth is reached, upon which the rubber valve is closed and the groundwater sample is obtained.

For each well, groundwater samples were analyzed for water temperature, pH, electric conductivity (EC), dissolved oxygen, oxidation reduction potential (ORP), Cl^-, NO_3^-, SO_4^{2-}, Na, K, Mg, Ca, Mn, Fe, ^3H, δD, $\delta^{18}O$, $\delta^{13}C$, and ^{14}C. Furthermore, we measured cation concentrations of Na, K, Mg, Ca, Mn, and Fe using atomic absorption spectrometry and anion concentrations of Cl^-, NO_3^-, and SO_4^{2-} using ion chromatography. The ^3H was analyzed by a combined use of the electrolysis condensing method and a liquid scintillation measuring method, δD and $\delta^{18}O$ was measured according to the uranium reduction balance method and H_2O-CO_2 balance was obtained by atomic absorption spectrometry. In addition, ^{14}C in selected shell samples were analyzed from the B2 boring cores to determine the age of stratum deposit. The ^{14}C measurements were undertaken by JNC (Japan Nuclear Fuel Cycle Development Institute), Tono Geoscience Center. The Japan tandem type acceleration machine was used for mass analysis measurement. For ^{14}C measurement accuracy reference is made to Sheng *et al*. (2000). The isotope ratio δ was calculated as

$$\delta = [(Rx - Rs)/Rs] \times 1000 \quad (‰) \qquad (1)$$

where *R* expresses ratios (D/H, $^{18}O/^{16}O$, and $^{13}C/^{12}C$), and subscripts *x* and *s* refer to the sample and the quality of a standard (standard mean ocean water, SMOW), respectively. The accuracy and reproducibility of isotopic values are $\pm$1‰ for hydrogen, $\pm$0.1‰ for oxygen, and $\pm$0.2‰ for carbon. With regard to analyses of chemical species by atomic absorption spectrometry and ion chromatography, large dilution (5000 times) was required to measure the concentrations due to high concentration of samples. The HCO_3^- concentration was calculated from the balance of equivalent concentrations between cations and anions.

RESULTS AND DISCUSSION

Vertical distribution of EC and ORP

Figure 3 shows the vertical distribution of EC and ORP. The EC and ORP were carefully measured at 1 m intervals from the water surface in the observation wells. Rapid increase of EC is seen at depth 20 m in B1, 15 m in B2, and 15 m in B3. These depths represent the interface between fresh- and saltwater. At B4 the EC shows a constant value of about 11000 μS cm^{-1} until 23 m. Also at B4 there is a gradual increase in EC from a depth of 23 to about 35 m. For shallow depths, B1, B2, and B3 have EC values of 2000-10000 μS cm^{-1}. These EC concentrations indicate salt content that is extremely high to be used for agricultural purposes. Land uses around utilized wells include industrial greenhouses, paddy fields, and private farm fields. In some areas, inappropriate fertilizers have been applied that may have contributed to the high EC values.

Figure 3 also reveals the redox conditions of the aquifer. The ORP at B1, B2, B3, and B4 displays a corresponding decrease for each rapid increase of EC. Generally, the flow velocity of the saline part of the groundwater is extremely small compared to that of the corresponding freshwater in the shallow groundwater. In other words, small groundwater flow velocity in the saline zone results in long residence time for the water. Long residence time gives rise to reducing conditions in the saline zone due to anaerobic bacteria that may be activated by the presence of organic material. Since the observed ORP is small for deeper groundwater, it is assumed that low ORP is closely connected to biogeochemical mechanisms due to the long residence time.

Hydrogen-oxygen isotope ratio

Figure 4 shows the relation between the hydrogen-oxygen isotope ratio at all sampling points. Groundwater sampled at 10 m depths for all points were found to originate from precipitation because of their location on the meteoric water line ($\delta D=8\delta^{18}O+10$; e.g., Craig, 1961). On the other hand, samples in B2, B3, and B4 at 30 m depths were found to be on the mixing line of meteoric water and seawater. It is therefore inferred that the deeper groundwater is affected by saltwater from the sea. The δD and $\delta^{18}O$ generally increased with increasing Cl^- concentration (Fig. 5).

Piper diagram and water quality characteristics

Water quality characteristics at B1-30 m as shown by the Piper diagram in Fig. 6, is classified as alkaline carbonate type ($Ca(HCO_3)_2$ freshwater). Other samples (at B1-10 m, B2-10 m, B2-30 m, B3-10 m, B3-30 m, B4-10 m, and B4-30 m) can be classified as alkaline non-carbonate type (Na_2SO_4 or NaCl). Here, the Cl^- is the dominant anion compared to $SO_4^{2-}+NO_3^-$. As shown in Fig. 3, deep groundwater at B1 to B4 is saline. Unlike the chemical properties at B2 to B4, the B1-30 m samples have a high Ca^{2+} content. The geology at B1-30 m is schist and at other points it is weathered granite. Generally, when schist forms, it is assumed that cation exchange capacity is larger than weathered granite. This is because more Ca^{2+} is released due to cation exchange between Na^+ and Ca^{2+} than at other points (e.g., Appelo and Postma, 1994; Ikeda, 1989).

Mixing rate of sea water intrusion

The chemical reaction during fresh/salt water displacement can be evaluated more accurately by calculating their composition based on conservative mixing of saltwater and freshwater, and then comparing the conservative concentration with the actual samples found in the groundwater (e.g., Appelo and Postma, 1994). The concentration of an ion *i* by conservative mixing of seawater and fresh water is:

$$m_{i,mix} = f_{sea} \cdot m_{i,sea} + (1 - f_{sea}) \cdot m_{i,fresh} \qquad (2)$$

where m_i is the concentration of *i* (meq/L), f_{sea} is the fraction of seawater in mixed water, and subscripts *mix*, *sea*, and *fresh* indicate conservative mixture of seawater and fresh water.
Any change in concentration $m_{i,react}$ as a result of chemical reaction (not mixing) then becomes:

$$m_{react} = m_{i,sample} - m_{i,mix} = m_{i,sample} - \left(f_{sea} \cdot m_{i,sea} + (1 - f_{sea}) \cdot m_{i,fresh} \right) \quad (3)$$

where $m_{i,sample}$ is the actual observed concentration in the sample.

The fraction of seawater is normally based on Cl^- concentration of the sample. Chloride is assumed to be a conservative element. The Cl^- based fraction of seawater is:

$$f_{sea} = \frac{m_{Cl^=,sample} - m_{Cl^-,fresh}}{m_{Cl^-,sea} - m_{Cl^=,fresh}} \qquad (4)$$

If there is no source of Cl^- but seawater and $m_{Cl^-,fresh}=0$ then (4) is simplified to:

$$f_{sea} = \frac{m_{Cl^-,sample}}{566} \qquad (5)$$

where Cl^- concentration is expressed in meq/L, and the Cl^- concentration of 35 for seawater is set to 566 meq/L. The Cl^- concentration of ocean water is assumed to be constant everywhere on earth.

The resulting seawater fraction in all observation wells using Eqs. (2)-(5) is shown in Table 2. The concentrations at 10 m depth for all observation wells were adopted as background freshwater concentration for each well. The mixing rate of seawater intrusion in all observation wells, B1-30 m (53%), B2-30 m (42%), B3-30 m (29%), and B4-30 m (7%) are shown in decreasing order. The downward trend in seawater mixing rate from B1 to B4 is clearly related to their distance from the sea.

Tritium concentration

The approximate age of groundwater can be determined by the tritium content, assuming that groundwater is moving according to assumed piston flow without mixing of new and old groundwater. However, this assumption is complicated by the fact that the actual groundwater may be composed of water from many different origins. As deep groundwater in the observation wells may be assumed to be mixed with seawater, estimating the age of groundwater according to tritium content should consider the influence of seawater.

Table 3 shows the tritium concentration in observation wells. Kakiuchi *et al*. (1999) reported that the tritium concentration of surface ocean water is 0.3-3.4 TR in the east Pacific and Indian Ocean. Their seawater samples were collected between 19th December 1996 and 18th February 1997, whereas groundwater sampling for the study area was conducted on 18th February 2000, a difference in sampling date of about 3 years. Any correction of tritium concentration due to the time lag of 3 years was not considered. However, by using both the mixing rate of seawater and the measured concentration of tritium for deep well samples, the tritium concentration in the saline groundwater adjusted by seawater tritium can be calculated by the following equation:

$$TR_{calc} = \frac{TR_{meas.} - T_{sea} f_{sea}}{1 - f_{sea}} \qquad (6)$$

where T_{sea} is the tritium concentration in the seawater, $TR_{meas.}$ is the tritium concentration at B1-30 m, B2-30 m, B3-30 m and B4-30 m, and $TR_{calc.}$ is the tritium concentration in the salinized groundwater adjusted for the effect of seawater tritium in deep well samples.

The results according to Eq. (6) show that T_{sea}=1.85TR, where 1.85TR is the arithmetic average of 0.3TR and 3.4TR. In the case of B3-30 m, $TR_{meas.}$=0.5TR, T_{sea}=1.85TR, f_{sea}=0.295, $TR_{calc.}$=-0.065. Negative tritium concentrations ($TR_{calc.}$) were calculated for samples B1-30 m, B2-30 m, and B4-30 m. This indicates that T_{sea}=1.85TR may be overestimated. It therefore seems reasonable to assume zero tritium concentration of seawater in the saline groundwater (i.e., T_{sea}=0 TR). Results calculated according to this value show that deep groundwater at B1 - B4 does not mix with the shallow groundwater.

Age estimation of stratum formation by ^{14}C dating method

Generally, the ^{14}C content in dead organisms decreases with time due to the termination of new ^{14}C supply. The ^{14}C dating of shells that were collected at 2-10 m depth at B2 is shown in Table 4. Shells could only be found at 2-10 m below the soil surface, where the geological feature is predominantly alluvium (sandy silt). The results suggest that the study area may have been a part of the seabed 2000 years ago. For depths ranging from 4-10 m, it was found that the stratum was formed between 6000-7000 years ago. The deposits at about 8 m was, on average, formed approximately 5000 years ago (2000~7000 years ago), which coincides with the period of last transgression (Holocene transgression) fairly well. Following this period, it is assumed that the surface deposits (to 2 m depth) were formed by sedimentation from river deposits and artificial reclamation. Subsequently, the shallow fresh groundwater was produced by excess rainfall.

According to the above analyses, it may be concluded that deeper saline groundwater does not mix with the shallower fresh groundwater, and that the source of the shallow groundwater results from precipitation, as evidenced by the hydrogen-oxygen isotope ratio. Deeper groundwater on the other hand, was seen to be affected by old seawater as seen from the ^{14}C isotope dating. Ultimately, it may be assumed that no saltwater intrusion has yet occurred, even though some wells displayed saline water due to the presence of fossil groundwater in the area.

CONCLUSIONS

The mixing zone between fresh- and saltwater was clearly observed from the electrical conductivity profile in the investigated area. The low ORP values for deeper saline groundwater in all observation wells indicated reducing conditions. Specifically, it was seen that ORP decreased with rapid increase in electrical conductivity. The mixing rate of sea water at B1-30 m showed the highest value for all sampling points, however according to the Piper diagram, water located in this area was classified as CaCl-type and not NaCl-type. On the other hand, hydrogen-oxygen isotope analysis revealed that the groundwater at B1-30 m was salinity-affected. Consequently, it is recommended that in order to investigate the qualitative characteristics of groundwater, stable isotopes should be utilized as an index of geochemical properties in addition to characterization of the water quality using a Piper diagram. Although the tritium concentration was generally low so that the age of groundwater could not be determined, it was found that deeper saline groundwater at B1, B2, B3, and B4 did not mix with the shallower fresh groundwater. The results of the hydrogen-oxygen isotope ratio indicated that the source of shallow groundwater originated from precipitation. In contrast, it was found that the deeper groundwater was affected by old seawater. ^{14}C isotope dating was used to show that the present area was originally below sea level. In conclusion, saltwater intrusion has not yet occurred even though some wells display saline water. Excessive pumping of groundwater for irrigation of industrial green houses and paddy fields are likely to cause upconing of the saltwater which will further add to the fossil salinity already at hand. Possible remedies may include the construction of artificial rainfall infiltration facilities on the new campus area of Kyushu University, management of groundwater pumping discharge for agricultural purposes and maintenance of areas for paddy fields.

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