Aquifers Interaction in the Southwestern Foot of Mt. Fuji, Japan, Examined through Hydrochemistry and Statistical Analyses

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Abstract:

Major ion chemistry, oxygen isotope and multivariate statistical method were used to investigate aquifers interaction in the southwestern foot of Mt. Fuji, the largest Quaternary stratovolcano in Japan. Groundwater samples were taken from different aquifers which are in descending order: the superficial aquifer, aquifers residing in the New Fuji Lava and the Old Fuji Aquifer. The geochemical signatures of groundwaters, notably the molar Na/Cl and Na/Ca ratios, oxygen stable isotope and the nitrate contents evolution, in conjunction with the hierarchical cluster analysis allowed to highlight three groundwater systems differing by their hydrochemical facies and residence time: 1) The shallow and highly polluted groundwaters of the superficial aquifer, 2) Groundwaters of the New Fuji Lava moderately mineralized and polluted, 3) The non-polluted groundwaters of the Old Fuji Aquifer. Waters of these systems are interacting. In fact, nitrate contamination, in provenance from the superficial aquifer, was detected in the New Fuji Lava layers and the deep groundwaters of the Old Fuji. Furthermore, many samples taken from the Old Fuji Aquifer were characterized by a relatively enriched δ¹⁸O. These results prove that groundwaters of the New Fuji layers could be mixed with groundwaters of the overlying superficial aquifer and that these groundwaters, supposed to flow only horizontally, can flow vertically through the cracks, causing the mixing of deep and old groundwater of the Old Fuji with groundwaters recently recharged and polluted.

KEYWORDS Hydrochemistry; Hierarchical cluster analysis; Groundwater; Mixing; Mt. Fuji

INTRODUCTION

Volcanic rocks are considerably known by their complex hydraulic features due to their great textural and lithological variabilities, their different level of weathering and their complex spatio-temporal distribution (Vernier, 1993). These characteristics make the understanding of groundwater flow system in volcanic terrains extremely difficult notably when the rocks are fractured or in case of the presence of multiple aquifers. To manage groundwater resources in such flow systems, hydrologists have recourse to stable isotopes and major ions geochemistry that have been widely used for the comprehension of groundwater flow and/or inter-aquifer mixing in volcanic areas (Asai et al., 2009; Demlie et al., 2007; Suzuki, 2003; Tweed et al., 2005).

Mt. Fuji, the highest mountain in Japan with an elevation of 3776 m, is one of a few large composite volcanoes made of basalt in the world. The investigation of groundwater flow in the southwestern foot of this mountain has been carried out by many researchers. In fact, the recharge elevations were identified by the use of stables isotopes (Yasuhara et al., 2007). Ikeda (1989) estimated the direction of groundwater flow in the New Fuji Lava and the deep Old Fuji Aquifers by using the spatial distribution of bicarbonate concentrations. Tsuchi (2007) proposed a conceptual model (Figure 1) explaining most of the springs surrounding the foot of Mt. Fuji. He reported that spring waters derived from precipitation falling at an altitude of more than 1000 m are stored in the crushed parts between the New Fuji Lava layers. These groundwaters, subjected to the pressure exerted by the overlying volcanic rocks, are flowing throughout the clinkers before springing out in their end at the foot. Accordingly, the previously cited studies (Yasuhara et al., 2007; Ikeda, 1989; Tsuchi, 2007), which have been conducted under the assumption that groundwater is moving in a continuous and lithologically homogeneous aquifers, led to the assessment of groundwater flow system horizontally. However, in view of the geological structure complexity of volcanic aquifers and the high permeability caused by the multiple joints and fractures of volcanic rocks, it can be hypothesized that a vertical connection between different aquifer-units is occurring notably within the overlapping New Fuji Lava flow beds. Therefore, this paper discusses the possibility of interaction existing among Mt. Fuji’s aquifers by using major dissolved components, nitrate as an indicator of surface contamination and oxygen stable isotope coupled with a multivariate statistical method.

STUDY AREA

The following study was conducted in the southwestern foot of Mt. Fuji, a dormant stratovolcano situating on Pacific coast of central Japan. The climate of Mt. Fuji area is humid temperate with an annual precipitation ranges from 2750 to 3000 mm on the wettest east slope and from 1500 to 2000 mm on the north slope (Kizawa et al., 1969). The study area consists of a gentle slope which is broadly bordered by Mt. Ashitaka on the east, the lowland facing Suruga Bay on the

Received 13 October, 2010
Accepted 14 August, 2011

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However, the central or middle part of the lava flow gets cold slowly. The crushed and permeable parts, so called clinkers, existing between the lava layers present the “route” through which the groundwaters flow and they may constitute “the water-bearing horizons”. Because basaltic rocks, constituted by many overlapping lava flows with various length and width, are well known by their high permeability and the abundance of joints and fractures (Demlie et al., 2007; Koh et al., 2005), a vertical interconnection may occur between the water-bearing horizons of the New Fuji Lava and 3) The Old Fuji Aquifer residing the pyroclastic mudflow deposits of the Old Fuji.

**MATERIAL AND METHODS**

**Sampling and analytical techniques**

Sixty three samples were collected during five sampling campaigns carried out in July and November 2008, July and September 2009, and January 2010. Seven samples were taken from the superficial aquifer, twelve from springs draining the New Fuji Lava and the others from wells reaching the Old Fuji Aquifer. Figure 1 shows the location of the sampling points. Measurement of electric conductivity (EC), pH and water temperature were made in the field using portable electronic instruments. The concentration of $\text{HCO}_3^-$ was determined by titration with standard sulfuric acid 0.01 M. The hydrochemical samples were filtered through a 0.22 $\mu$m membrane filter immediately after sampling. The $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ and $\text{SiO}_2$ were analyzed by the inductively coupled argon plasma atomic emission spectrophotometer (Jarrel-Ash, ICAP-757V, Japan). The $\text{Na}^+$, $\text{K}^+$, $\text{Cl}^-$, $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ were analyzed by ion chromatography. The total dissolved solid (TDS) are calculated as the sum of major ions. The $\delta^{18} \text{O}$ was measured by using a Finnigan MAT-252 mass spectrometer. The results
were expressed in the conventional δ-notations representing as per mil deviations from the V-SMOW.

Hierarchical cluster analysis (HCA)

It has been proved that the hierarchical cluster analysis (HCA) serves as a suitable tool for understanding groundwater hydrochemical regimes through the discretization of the study area into groundwater zones (Hussein, 2004; Mahlknecht et al., 2004; Demlie et al., 2007). This technique aims to classify a set of samples into two or more coherent groups that share almost common properties. These groups might be interpreted in terms of aquifer types, residence times and the degree of pollution effect on water chemistry.

The hydrochemical variables that have been chosen in this study are: pH, EC, Ca\(^{2+}\), Mg\(^{2+}\), K\(^{+}\), Na\(^{+}\), HCO\(_3\)\(^{-}\), SO\(_4\)\(^{2-}\), NO\(_3\)\(^{-}\) and SiO\(_2\). The transformation and the standardization of all the data is the first step to be performed, so that each variable measured via different units was standardized in order to have equal weight for the HCA. The measurement of the similarity between the different hydrochemical variables was realized by selecting the squared Euclidean distance. The clustering was performed by using the Ward’s Method which linked iteratively nearby samples. The result of the HCA is represented under the form of graph known as ‘dendrogram’.

RESULTS AND DISCUSSION

The hydrochemical facies of groundwater was determined by the use of Piper triangular Diagram (Figure 3). Two main facies were distinguished: the first facies corresponds to groundwater enriched in calcium, nitrate and sulfate. This facies characterizes groundwater of the superficial aquifer and some samples originating from groundwater flowing within the permeable units of the New Fuji Lava flows. These waters would be affected by the ammonium-sulfate fertilizer ((NH\(_4\))\(_2\)SO\(_4\)) applied in tea plantation fields distributed largely around 100 to 500 m altitude in the area. Most of the groundwater sampled from the Old Fuji Aquifer represents the second facies of which the chemical composition was characterized as calciumbicarbonate type. Piper diagram also demonstrates that numerous samples of the Old Fuji Aquifer, as well as some springs derived from the confined groundwater draining the deepest permeable New Fuji Lava layers lying in intermediate compositional field notably with respect to the anion composition. In fact, these samples are more enriched in chloride and nitrate and this character might be regarded as a witness of inter-aquifer mixing. It is also interesting to note that some samples of the Old Fuji Aquifer are more enriched in sodium (location nos. 66, 10, and 72). This trend might result from cation exchange reactions between calcium in groundwater and sodium in the aquifer matrix material and/or volcanic rock weathering particularly the dissolution of plagioclase minerals and therefore it might point out groundwater of longer residence time (Ikeda, 1989).

Figure 4 shows the result of the hierarchical cluster analysis. The simple visual examination of the dendrogram clearly highlights two main groups of groundwater quality. The group A corresponds to non-contaminated groundwater and the group B can be divided into three subgroups differing by the degree of contamination. Mean values of hydrochemistry and isotopes for each group are presented in Table I.

Almost all samples clustered in group A are of alkaline nature (Mean pH value equal to = 8.3). These samples, taken from deep wells exceeding 100 m depth, show the lowest chemical composition (the mean total dissolved solids, TDS = 73.9 mg/L and EC = 93.7 μS/cm). Their mean nitrate content is about 2.7 mg/L. They are also characterized by the lowest isotopic composition (~8.8%).

Groundwaters of the subgroup B II-1 are moderately mineralized with a mean TDS and EC equal to 101.7 mg/L and 142.2 μS/cm, respectively. This cluster comprises groundwater deriving from different aquifers. A slight contamination of the groundwater can be revealed by the increase of NO\(_3\)\(^{-}\) and SO\(_4\)\(^{2-}\) concentrations when comparing with the previous set. These groundwaters are also characterized by a depleted isotopic composition (~8.3%). The molar Na/Cl ratio in both clusters described above is widely higher than 0.8 which is the typical value for mean global precipitation (Langmuir, 1997) suggesting that Na\(^+\) is derived from water-rock interaction most likely the plagioclase dissolution (Supplement 1). Further, the Na/Cl ratios recorded in the Old Fuji Aquifer are ranging between 2.4 and 8.9 with an average of 4.8. The mean value is almost two times greater than that for spring waters classified into the subgroup B II-1 (2.5 with variation range from 1.8 to 3). Ikeda (1989) stated that the most important rock-forming mineral in the volcanic ejecta in this area is the plagioclase and it is assumed that the water-rock interaction is a water-plagioclase reaction leading to the change of the chemical composition of the moving groundwater that will be characterized by the increase in the quantity of Na\(^+\). Thus, the high Na/Cl ratio of samples grouped within the Group A may testify the relative longer residence time of the Old Fuji groundwater compared with groundwater draining the New Fuji Lava Aquifers. The longer residence times of groundwaters originating from the mudflow deposits of the
Old Fuji Aquifer by comparison to these originating from the New Fuji Aquifer have been reported in previous studies (Ochiai and Kawasaki, 1970; Tosaki et al., 2011). Tosaki et al. (2011) estimated the residence times of spring waters located around Mt. Fuji by using the $^{36}$Cl Bomb Pulse. Spring waters of the southwestern foot of the mountain, were found to possess residence times of decades (0 to 32 years). In contrast, groundwaters originating from the mudflow deposits of the Old Fuji Aquifer were characterized by low $^{36}$Cl/Cl ratio with estimated residence times of more than 55 years. These groundwaters, considered of old age, are also enriched in Na+ and have the lowest K/Na. Hence, the interpretation of the great residence times of groundwaters of the Old Fuji Aquifer on the basis of high sodium contents may be reliable.

The highest bicarbonate and silicate concentrations discriminate groundwater of the subgroup B II-2. This subgroup has relatively high EC and TDS values (210 $\mu$S/cm and 146.5 mg/L, respectively). The $^{\delta}$18O of this cluster varies widely. The effect of the anthropogenic influences on groundwater quality is clearly discernible through the high nitrate and sulfate mean concentrations which are around 20 and 14 mg/L, respectively. The high bicarbonate, sodium, silicate and calcium contents observed in this group suggest groundwater having traveled through long flow paths promoting rock weathering. However, some contaminated samples (location nos. 1, 14 and 48), characterized by an elevated nitrate concentration (23, 29 and 47 mg/L, respectively), show an isotopic enrichment ($^{\delta}$18O > −8.3‰) and low pH (< 7.3) (Supplement 2). Thus, the enrichment of these samples by the above mentioned ions is most probably caused by the mixing with groundwater of the overlying superficial aquifer. For the remaining samples of this cluster (location nos.16, 66 and 78), although their emplacement in the down-gradient area, they are characterized by low $^{\delta}$18O (−9.4, −8.9 and −9.7‰, respectively). Moreover, Yoshimaike spring (location no. 16) and groundwater taken from the location no. 66 were distinguishable by the most elevated molar Na/Ca ratio equal to 1.8 and 2.2, respectively, while this ratio does not exceed 1.8 in the remaining samples of the Old Fuji Aquifer. Thus, the highly evolved chemical character of these samples may infer longer flow paths and therefore longer residence time. Likewise, a moderate nitrate contamination was noticed in these groundwaters with a concentration of 9.6 mg/L and 17.9 mg/L in Yoshimaike and location no. 66, respectively (Supplement 2). Consequently, given the detection of nitrate pollution in the most evolved and thus oldest groundwaters, the possibility of mixing of deep groundwater with modern contaminated sources becomes very probable.

The subgroup B I comprises principally the samples taken around Sugita area either from springs or shallow wells (location nos. 20, 21, 22, 31 and 44) (Supplement 3). Groundwaters of this group have the highest EC and TDS.

Table I. Mean hydrochemical and isotopic compositions of groundwater cluster groups

| Cluster Group | pH  | EC $\mu$S/cm | TDS mg/L | Na mg/L | K mg/L | Mg mg/L | Ca mg/L | Cl mg/L | NO3 mg/L | SO4 mg/L | HCO3 mg/L | SiO2 mg/L | $^{\delta}$18O % |
|---------------|-----|--------------|----------|---------|--------|---------|---------|--------|---------|---------|-----------|---------|---------------|
| A (29)        | 8.3 | 93.7         | 73.9     | 6.3     | 0.7    | 3.0     | 8.6     | 2.2    | 2.7     | 4.5     | 45.9      | 35.4    | −8.8         |
| B II-1 (21)   | 7.3 | 142.2        | 101.7    | 7.3     | 1.5    | 4.5     | 13.3    | 4.9    | 12.1    | 10.7    | 47.4      | 41.5    | −8.3         |
| B II-2 (7)    | 7.7 | 210.1        | 146.5    | 11.4    | 2.6    | 6.7     | 16.6    | 5.8    | 20.9    | 14.8    | 67.8      | 44.2    | −8.5         |
| B I (6)       | 6.7 | 246.7        | 152.0    | 6.3     | 2.9    | 6.9     | 23.6    | 7.4    | 30.3    | 30.1    | 34.4      | 39.6    | −7.8         |

Number in parentheses corresponds to the number of samples clustering in the group.
and the most elevated nitrate and sulfate contents revealing a pronounced pollution state. The mean pH value is slightly acidic. On the other side, the $\delta^{18}O$ is the most enriched and the bicarbonate and silicate contents are low. These features play in favor of a shallow flow system prevailing most probably the superficial aquifer and the upper aquifer horizons of the New Fuji Lava. Nitrate is a potentially useful tracer of recently recharged water. Thus, the high nitrate content accompanied by the relatively highly enriched isotopic composition could indicate the recent recharge of these aquifers at lower altitude.

Both, Piper Diagram and the hierarchical cluster analysis, highlight the contamination of groundwaters of the New Fuji Lava Aquifer. This contamination might be in provenance from the highly polluted superficial aquifer. In addition, the detection of nitrate with a relatively important contents in some samples of the Old Fuji Aquifer, may testify the vertical leakages of groundwaters from the water-bearing horizons of the New Fuji Lava toward the Old Fuji Aquifer. This vertical leakage of groundwater is occurring probably thanks to the clinkers existing between the lava layers and enormously depends on the three dimensional structures of lava flows. Figure 5 illustrates a representative conceptual diagram on the mechanism of the aquifers interaction. The proposed diagram shows that besides the horizontal clinkers responsible of the horizontal groundwater flow, lateral clinkers separating the lava blocks of different and limited lateral extents could play an important role in the percolation of groundwaters downward causing thus groundwaters mixing.

**CONCLUSION**

Using groundwater geochemical signatures and hierarchical cluster analysis, it was possible to highlight the complex interaction between aquifers in the southwestern foot of Mt. Fuji. In fact, the results of both hydrochemical and multivariate statistical technique are mutually supportive and allowed to reveal three interacting groundwater systems: 1) Shallow flow system locally and recently recharged and prevailing the superficial aquifer. 2) Deep flow system of the Old Fuji Aquifer. Groundwaters draining this aquifer are of great residence time and recharged at higher altitudes as it was indicated by the molar Na/Cl ratio and the depleted oxygen stable isotope. 3) The flow system draining the New Fuji Lava layers acting as a connector between the above mentioned systems. Indeed, groundwater flow in the New Fuji layers which is assumed to be dominantly horizontal along the individual and laterally extensive water-bearing horizons, might flow vertically through the existing cracks or lateral clinkers causing the pollution of the oldest groundwater draining the deepest New Fuji layers as well as groundwater of the Old Fuji Aquifer. Thus, the application of environmental tracers should be performed carefully since aquifers mixing could cause the underestimation of groundwater residence time. That is, an estimated residence time under non-mixing assumption may be shorter than the actual residence time.

On the other hand, this study demonstrates that nitrate contamination have impacted the shallow groundwater system and the risk of deep groundwater pollution from surficial sources is increasing because of the intensive fertilization practices, the high rainfall that infiltrates soils and the high hydraulic conductivity of underlying rocks.
Therefore, some measures should be taken in advance in order to adequately protect groundwater resources against further deterioration in the future.

ACKNOWLEDGEMENTS

Authors are grateful to Ms. Sayako Ueno for her help in groundwater sampling and chemical analysis. This work was partly supported by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (No. 19300304). On sampling groundwater or springs, support from Shizuoka Prefecture, Fuji City, and well owners is really appreciated.

SUPPLEMENTS

Supplement 1: Na/Ca versus Na/Cl.
Supplement 2: Table of major ion concentrations and oxygen stable isotope contents of groundwater.
Supplement 3: HCA classification of groundwater samples.

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