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Characterization and comparison of groundwater quality and redox conditions in the Arakawa Lowland and Musashino Upland, southern Kanto Plain of the Tokyo Metropolitan area, Japan

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ABSTRACT

Groundwater is essential for the Earth biosphere but is often contaminated by harmful chemical compounds due to both anthropogenic and natural causes. A key factor controlling the fate of harmful chemicals in groundwater is the reduction/oxidation (redox) conditions. The formation factors for the groundwater redox conditions are insufficiently understood. In this study, long-term groundwater quality beneath one of the world megacities was monitored and evaluated. We measured and compared hydrogeochemical conditions including groundwater quality (35 chemical parameters) and redox conditions of five aquifers in the Arakawa Lowland and Musashino Upland, southern Kanto Plain of the Tokyo Metropolitan area, Japan. Monitoring results suggested the following: The main origin of groundwater is precipitation in both the Lowland and Upland areas. The three aquifers in the Arakawa Lowland are likely fully separated, with one unconfined and two confined aquifers under iron reducing and methanogenic conditions, respectively. Oppositely, in the Musashino Upland, the water masses in the two aquifers are likely partly connected, under aerobic conditions, and undergoing the same groundwater recharge and flow processes under similar hydrogeological conditions. The different groundwater redox conditions observed are likely caused by the very different groundwater residence times for the Arakawa Lowland and Musashino Upland.

Keywords: Groundwater quality, Groundwater redox conditions, Hydrogeochemical processes,

Long-term monitoring, Tokyo Metropolitan area of Japan

1. Introduction

Fresh water such as river water and groundwater constitute only around 2.5% out of the water on the Earth. The abundance of river water is quite small and is estimated to be approximately 0.006% of freshwater while around 30% of freshwater is groundwater (Shiklomanov, 1998). At least half of the global population depends on groundwater as the source of drinking water (Appelo and Postma, 2005). The usage of groundwater is very diverse and includes agricultural, industrial, and domestic water purposes. Around 2.5 billion people depend only on groundwater for their daily water usage (WWAP, 2015). In Japan, approximately 9 billion m^3 of groundwater is annually used for agricultural, industrial, and domestic water purposes, corresponding to 11% of the total water usage in 2015 (Official website of Ministry of Land, Infrastructure, Transport and Tourism, Government of Japan). In Tokyo, the daily amount of groundwater extracted for agricultural, industrial, and domestic use is approximately 0.38 million m^3, almost all extracted from western Tokyo except for special wards of Tokyo (Bureau of Environment, Tokyo Metropolitan Government, Japan, 2019a).

Groundwater is basically characterized by markedly lower flow rate and longer residence time (approximately 1500 years as a mean value) compared to other fresh water resources including river water which shows an averaged residence time of around 16 days (Shiklomanov, 1998). During the flow processes from recharge area to discharge area, groundwater can be contaminated by harmful chemical compounds due to both anthropogenic and natural factors. One of the most important conditions controlling the fate (solubility, chemical speciation, toxicity, bioavailability, and mobility) of harmful chemical compounds is the reduction/oxidation (redox) conditions in the groundwater. For instance, the fate of arsenic, chromium, inorganic nitrogen (NO_3^-, NO_2^-, and NH_4^+), chlorinated volatile organic compounds (e.g., tetrachloroethene and trichloroethene), and BTEX (benzene, toluene, ethylbenzene, and xylene) is significantly affected by groundwater redox conditions (Blowes et al., 1997; Wiedemeier et al., 1998; Tesoriero et al., 2001; Islam et al., 2004; Aelion et al., 2010; Puckett et al., 2011; Grießmeier et al., 2017). Groundwater redox conditions are created during microbially induced redox processes. Dissolved oxygen is normally first to be used as electron acceptor. In absence of oxygen, the order of utilization of electron acceptors is generally NO_3^-, Mn (IV), Fe (III), SO_4^{2-}, and CO_2, resulting in simultaneous production of N_2, Mn (II), Fe (II), Sulfide (H_2S, HS^-, and S^{2-}), and CH_4, respectively. Predominant microorganisms significantly change with the progression of these processes and groundwater redox conditions become more reductive (Christensen et al., 2000; Naudet et al., 2004; Appelo and Postma, 2005; McMahon and Chapelle, 2007; Tesoriero et al., 2015).

In the southern Kanto Plain of the Tokyo Metropolitan area of Japan, decrease in hydraulic heads and land subsidence were recognized as serious problems due to excessive pumping of groundwater after the 1950s. The problems were reported previously, however, they became more serious after the 1950s. Increases in hydraulic heads occurred after regulation of groundwater pumping (Endo and Ishii, 1984; Hachinohe et al., 2006; Hayashi et al., 2007; Monyrath et al., 2010). In recent years, contamination by harmful chemical compounds is often considered as one of the most serious groundwater issues. For example, arsenic, lead, NO_3^- and NO_2^-, and chlorinated volatile organic compounds including tetrachloroethene and trichloroethene are currently observed in the groundwater of the Tokyo area (Bureau of Environment, Tokyo Metropolitan Government, Japan, 2019b; Saitama Prefectural Government, Japan, 2019). To evaluate the fate of harmful chemical compounds and design effective groundwater protection and remediation strategies, fundamental knowledge about groundwater redox conditions and the formation factors for redox conditions in the area is necessary but previous studies regarding groundwater quality in especially the Arakawa Lowland of the southern Kanto Plain are lacking.

Further, subsurface warming with temperature increase in the subsurface and groundwater environments has been observed in many areas of the world (Harris and Chapman, 1997; Pollack et al., 1998; Huang et al., 2000; Taniguchi et al., 2003; Perrier et al., 2005; Taniguchi et al., 2007; Kooi, 2008). In the Tokyo Metropolitan area as one of megacities in the world, subsurface warming has already been reported by Taniguchi et al. (2007). This phenomenon has also been recognized at depths shallower than 40 m in the Arakawa Lowland (Miyakoshi et al., 2018). Subsurface warming, also regarded as subsurface thermal pollution, is caused by surface warming effects such as global warming and urbanization (Huang et al., 2000; Taniguchi et al., 2003). This potentially negative phenomenon may be accelerated by additional and excess exhaust heat from larger underground infrastructures including subways, shopping malls, and sewage systems, especially in the megacities. Subsurface warming can affect physical, chemical, and biological processes in the subsurface and groundwater environments (Banks, 2008; Bonte et al., 2011; Hähnlein et al., 2013) and thereby accelerate changes in groundwater quality. Therefore, the acquisition of long-term monitoring data for groundwater quality as baseline data prior to escalation of subsurface warming is highly essential.

The objectives of this study were therefore: (i) to acquire long-term groundwater quality data including 35 chemical parameters for five aquifers in the Arakawa Lowland and Musashino Upland, southern Kanto Plain of the Tokyo Metropolitan area of Japan, representing one of the megacities in the world, (ii) to characterize hydrogeochemistry including the basic interpretation of groundwater quality in each study area based on the acquired long-term monitoring data, and (iii) to compare groundwater redox conditions and discuss the factors creating the difference of redox conditions in both Lowland and Upland areas.

2. Materials and methods

2.1. Site description

The groundwater monitoring sites were established at the campuses of Saitama University (35^{o}51′44.0″N, 139^{o}36′34.0″E) and Tokyo University of Agriculture and Technology (35^{o}41′03.1″N, 139^{o}29′07.9″E) in the southern Kanto Plain of the Tokyo Metropolitan area, Japan (Fig. 1a). At both monitoring sites, boreholes were dug by an excavation machine using water containing bentonite and calcium hydroxide with continuously injected micro bubble. Stainless steel and vinyl chloride pipes with rubber as sealing material were used together with bentonite and silica sand as backfill materials for installing the groundwater monitoring wells. A manual drilling technique and vinyl chloride pipes were used for the installation of monitoring wells in the unconfined aquifer of the Arakawa Lowland.

The Saitama University site is located in the Arakawa Lowland (hereafter, Lowland site) and the altitude at the site is approximately 6.0 m above mean sea level of Tokyo Bay as the reference place in Japan (Fig. 1a). Groundwater monitoring wells were installed in one unconfined (strainer depth: 1.5-2.5 m below the surface) and two confined (strainer depths: 15.5-18.4 m below the surface (hereafter, confined upper aquifer) and 37.7-40.0 m below the surface (hereafter, confined lower aquifer)) aquifers (Fig. 1b). A previous study for the stratigraphy and transitions of sedimentary environments in the latest Pleistocene to Holocene sediment core was carried out in very close proximity to the Lowland site (Komatsubara et al., 2010). The unconfined aquifer (Holocene) consists of back marsh deposits with non-marine clayey to silty sediments. In the confined upper aquifer (Holocene), inner bay to delta front deposits are distributed and it consists of silty to sandy marine sediments. The particle size of the sediment in the confined lower aquifer (Pleistocene) is markedly coarser than those of the unconfined and confined upper aquifers and consists of sandy to gravelly fluvial (non-marine) sediments. Further information on the hydrogeological conditions at the Lowland site is given in previous studies (Saito et al. 2014; 2016; Brunetti et al. 2017; Ueshima et al. 2017). Around the Lowland site, subsurface warming has already been observed at 20 m, 30 m, and 40 m depths (Miyakoshi et al., 2018). Rates of increase in the temperature between April 2007 and December 2015 were estimated to be 0.034°C/year, 0.023°C/year, and 0.193°C/year at 20 m, 30 m, and 40 m depth, respectively. Shallower depths showed higher rates of the increase and based on simple one-dimensional heat transport analysis, subsurface warming was suggested to be induced by recent surface warming in the area.

The Tokyo University of Agriculture and Technology site is located near the border of the Tachikawa Terrace and the Musashino Terrace on the Musashino Upland (hereafter, Upland site) and the altitude at the site is approximately 60 m above mean sea level of Tokyo Bay (Fig. 1a). Two confined (strainer depths: around 38 m below the surface (hereafter, confined upper aquifer) and 50 m below the surface (hereafter, confined lower aquifer)) aquifers were targeted in the long-term groundwater quality monitoring (Fig. 1b). Two monitoring wells were installed in each aquifer and are located within several meters distance to each other. Consequently, the acquired data in two wells of each aquifer showed almost the same chemical concentration and characteristics for groundwater quality. Therefore, only the data acquired in one monitoring well of each aquifer is used and discussed in this study. Based on a previous study focusing on analyses of sedimentary facies and depositional environment for sediment cores obtained at the Upland site (Funabiki et al., 2014), both upper and lower aquifers consist of sandy gravels of river channels. Those sediments were formed under non-marine environment during Pleistocene. Additional information on the hydrogeological properties at the Upland site is given in previous studies (Saito et al. 2014; Thuyet et al. 2016; Brunetti et al. 2017; Ueshima et al. 2017). In Tokyo, subsurface warming has also been observed up to approximately 140 m depth based on monitoring in 29 boreholes (Taniguchi et al., 2007). Several of the monitoring wells are located in the Musashino Upland, suggesting a high possibility of subsurface warming around the Upland site.

2.2. Field works and laboratory analyses

At both monitoring sites, groundwater was periodically sampled from all five aquifers using a sampling bailer (custom-made by ASANO TAISEIKISO ENGINEERING Co., Ltd., Japan) after purging the groundwater of at least two well volumes. The monitoring was started from June 2011 in the confined upper and lower aquifers and July 2016 in the unconfined aquifer at the Lowland site.

At the Upland site, monitoring was conducted from November 2011 to October 2015 in both confined upper and lower aquifers. Approximately 160, 180, and 80 samples were obtained in the confined upper and lower aquifers and the unconfined aquifer at the Lowland site, respectively. At the Upland site, approximately 100 samples were taken from each monitoring well in the confined upper and lower aquifers.

After groundwater sampling, on-site measurements of water temperature, pH, electric conductivity (EC), dissolved oxygen (DO), and oxidation-reduction potential (ORP) were immediately carried out using portable analyzers (DKK-TOA CORPORATION, Japan) calibrated precisely at each sampling event. The obtained groundwater was immediately filtered using a 0.20 μm membrane filter (DISMIC-25CS, Toyo Roshi Kaisha, Ltd., Japan). For the measurement of heavy metals and trace elements, nitric acid was added to the filtered groundwater to prevent the precipitation of metal compounds. Chemical analyses described below were carried out in the following days. Major cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) and anions (Cl^-, NO_2^-, Br^-, NO_3^-, and SO_4^{2-}), dissolved organic and inorganic carbon (DOC and DIC), and heavy metals and trace elements (Li, B, Al, Si, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Sr, Cd, Sb, and Pb) were analyzed using an ion chromatograph (HIC-NS, SHIMADZU CORPORATION, Japan or ICS-1500, Nippon Dionex K.K., Japan), TOC analyzer (TOC-V CSH, SHIMADZU CORPORATION, Japan), and ICP-MS (ICPM-8500, SHIMADZU CORPORATION, Japan), respectively. Single measurement was performed for each chemical component analyzed by ion chromatograph and TOC analyzer. The analytical precision for both these instruments is estimated to be within 10% based on numerous measurements on water samples. For heavy metals and trace elements measured by the ICP-MS, the analysis for each groundwater sample was conducted three times and the analytical precision was within 10%. For the DIC, there are three main chemical forms of H_2CO_3, HCO_3^-, and CO_3^{2-} and their relative abundance ratios are depending on the pH values in water environment (Weathers et al., 2013). In this study, the concentration of HCO_3^- was basically calculated using pH, ionic strength, activity coefficient, and equilibrium constant. For some groundwater samples, semi-quantitative dissolved CH_4 measurements (except for the sample from the unconfined aquifer at the Lowland site) and determination of stable oxygen ($^{18}O/^{16}O$) and hydrogen (D (i.e. ^{2}H)/^{1}H) isotope ratios were conducted using a gas chromatograph (GC-2014, SHIMADZU CORPORATION, Japan) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) and water isotope analyzer (L2130-i, Picarro Inc., USA) based on cavity ring-down spectroscopy, respectively. The measurement of stable oxygen and hydrogen isotope ratios was performed six to eight times for each groundwater sample, with an analytical precision within 0.1‰. The dissolved CH_4 concentration in groundwater was determined once. All chemical instruments are installed at Saitama University, except for the water isotope analyzer managed by Research Institute for Humanity and Nature, Japan.

Another sampling bailer (custom-made by ASANO TAISEIKISO ENGINEERING Co., Ltd., Japan) allowed for taking out the groundwater without exposure to the air and was used for dissolved CH_4 measurement. Groundwater samples were directly put into analytical vials with approximately 60% of the vial volume occupied by the samples. The obtained groundwater in the analytical vials was stored at constant room temperature (20°C) and humidity (60%) for a day to achieve gas-liquid equilibrium inside the vials and was used for measurement of the gas phase in the headspace using a GC-TCD/FID. For stable oxygen and hydrogen isotope ratios, their values are expressed as $\delta^{18}O$ and δD, respectively, which are the relative deviations in per mil (‰, parts per thousand) to Vienna Standard Mean Ocean Water (V-SMOW) as standard solutions. The $\delta^{18}O$ and δD values are given as:

$$\delta^{18}O, \delta D = \left(\frac{R_{Sample}}{R_{Standard}} - 1\right) \times 1000\ (‰) \quad [1]$$

where R is the ratio of the heavy to light isotope ($^{18}O/^{16}O$ or $D/^{1}H$) for groundwater and analytical standards. In addition to the determination of the $\delta^{18}O$ and δD values for some groundwater samples, precipitation was periodically sampled at the Lowland site using a hand-made precipitation collector with anti-evaporation system. The $\delta^{18}O$ and δD values in the precipitation samples were determined based on the same analytical method for revealing the local meteoric water line (discussed below) around the monitoring sites. The precipitation monitoring was carried out every 2 weeks (averaged sampling frequency) from December 2012 to April 2015 and a total of 49 samples were obtained.

3. Results and discussion

3.1. Origin of the groundwater in the Arakawa Lowland and Musashino Upland

Figure 2 illustrates relations between δ^{18}O and δD for the precipitation collected at the Lowland site and groundwater in all five aquifers at both Lowland and Upland sites. For the precipitation data monitored from December 2012 to April 2015, the δ^{18}O and δD values were markedly variable and ranged from -15.2‰ to -1.9‰ and -101.4‰ to -7.3‰, respectively. Linear regression was applied to these plotted data and the obtained equation as the local meteoric water line for the monitoring sites was found to be $\delta D = 7.2\delta^{18}O + 7.7$ ($R^2 = 0.93$). A previous study reported the local meteoric water lines in Ogawa town, Utsunomiya city, Kumagaya city, Kashiwa city, and Tsukuba city which are located relatively close to the monitoring sites in this study and all inside the Kanto Plain, Japan. Their local meteoric water lines were found to be $\delta D = 7.6\delta^{18}O + 10.3$ ($R^2 = 0.92$), $\delta D = 8.3\delta^{18}O + 7.3$ ($R^2 = 0.87$), $\delta D = 7.5\delta^{18}O + 10.9$ ($R^2 = 0.93$), $\delta D = 7.4\delta^{18}O + 8.6$ ($R^2 = 0.98$), and $\delta D = 7.6\delta^{18}O + 10.5$ ($R^2 = 0.86$), respectively (Yabusaki et al., 2016). Thus, the equation of the regression line obtained at the Lowland site was quite similar to those of the previous study.

Generally, in precipitation formation processes from ocean water evaporation to raindrops formation through condensation, changes in δ^{18}O and δD values (i.e. isotopic fractionation) are mainly controlled by the kinetic isotope effect due to different behaviors between lighter isotopes (^{1}H and ^{16}O) and heavier isotopes (D and ^{18}O). During the evaporation process, lighter isotopes tend to be found in water vapor due to their high vapor pressure, while heavier isotopes are relatively rich in the remaining water. The degree of isotopic fractionation during the evaporation is generally affected by atmospheric humidity and temperature. Oppositely, heavier isotopes tend to be rich in raindrops and the water vapor is simultaneously enriched with lighter isotopes during raindrop formation after condensation. The δ^{18}O and δD values in precipitation also change depending on temperature, latitude, altitude, and terrain in the areas where the precipitation occurs (Hoefs, 2004).

Craig (1961) found a significant relation between δ^{18}O and δD values in 400 samples of water from rivers, lakes, and precipitation as below:

$$\delta D = 8\delta^{18}O + 10 \quad [2]$$

The equation is known as the global meteoric water line and is frequently used in Earth and environmental sciences. Since 1961, the International Atomic Energy Agency (IAEA) has investigated monthly δ^{18}O and δD values in precipitation with a global-scale observation network. Based on these long-term monitoring results, Rozanski et al. (1993) gave a global meteoric water line with arithmetic means as below:

$$\delta D = (8.17 \pm 0.06)\delta^{18}O + (10.35 \pm 0.65), r^2 = 0.99, n = 206 \quad [3]$$

The equations of the local meteoric water lines in the Kanto Plain of Japan are similar to the global meteoric water lines, Eqs. [2] and [3].

Generally, the δ^{18}O and δD values in precipitation vary markedly while in groundwater, they show almost constant values throughout the year due to sufficient mixing of water inside aquifers during infiltration and flowing processes. For the δ^{18}O and δD composition in all five aquifers at the monitoring sites, approximately 60 groundwater samples were analyzed. The averaged δ^{18}O, δD, and deuterium excess (d-excess) values in each aquifer are shown in Table 1, with standard deviation (1σ). The d-excess value was calculated by the equation $d = \delta D - 8\delta^{18}O$ proposed by Dansgaard (1964). The δ^{18}O and δD composition in groundwater showed almost constant values compared to those of the precipitation (Fig. 2). The groundwater data from all five aquifers at both Lowland and Upland sites were placed very close to the local meteoric water line around the monitoring sites (Fig. 2). We note that the mixing of water with different history such as seawater, fossil water, pore water, formation water, and other water affected by evapotranspiration and high degree of reactions with the surrounding geology should be considered when δ^{18}O and δD values in groundwater are not placed near the local meteoric water line (Hoefs, 2004). The results suggest that main origin of the groundwater at these study sites is precipitation. Moreover, most of the data at both monitoring sites were similar (Fig. 2 and Table 1), suggesting a similar groundwater recharge areas if water source and mixing history is otherwise similar.

3.2. Characterization of hydrogeochemistry in the Arakawa Lowland and Musashino Upland

Figure 3 presents temporal variations of major cations and anions (meq/L) in the groundwater from both the unconfined and the confined upper and lower aquifers at the Lowland site and the confined upper and lower aquifers at the Upland site. As mentioned, at least 80 groundwater samples were obtained based on the periodic monitoring and highly valuable long-term and high-resolution groundwater quality data were acquired in each aquifer of the monitoring sites. All five aquifers showed almost constant groundwater quality during the long-term monitoring period over several years. In the unconfined aquifer of the Lowland site, however, the concentration of HCO_3^- was fluctuating and also the electrical balance between the cations and anions within the groundwater was slightly biased toward a negative charge. The electrical balance is given as:

$$Electrical\ Balance\ (\%) = \frac{(Sum\ of\ cations + Sum\ of\ anions)}{(Sum\ of\ cations - Sum\ of\ anions)} \times 100 \quad [4]$$

where both cations and anions are expressed in concentration unit of meq/L (Appelo and Postma, 2005). According to Appelo and Postma (2005), the accuracy of the chemical analysis for major cations and anions in groundwater can be estimated from the calculated electrical balance since the sum of positive and negative charges in groundwater should balance. The electrical balance in the unconfined aquifer at the Lowland site was -14.5% as an averaged value. Also, the mean values of the electrical balance were +4.40%, +3.59%, +3.09%, and +3.15% in the confined upper and lower aquifers at both Lowland and Upland sites, respectively. The electrical balance values in all aquifers except the unconfined aquifer at the Lowland site are less than ±5%. Therefore, the relatively larger averaged value of the electrical balance in the unconfined aquifer at the Lowland site is likely not related to any analytical problems and needs further investigation. At the beginning of the monitoring in the confined lower aquifer of the Lowland site, decreasing trends for major cations and anions were observed (Fig. 3). This may be associated with the effect of installation of the monitoring wells. A previous study suggested that rapid dissolution of newly exposed mineral surfaces and fine particles of minerals generated during well drilling caused significant increase in alkalinity and concentrations of Ca^{2+} and Mg^{2+} (Kim, 2003). However, study by Kim (2003) was carried out in a sandy silicate aquifer and the groundwater chemistry was dominated by silicate weathering. Since the hydrogeological conditions in the confined lower aquifer at the Lowland site are different, the findings by Kim (2003) may not directly relate to the present study. At the Upland site, the experiment of heated groundwater injection was shortly carried out during 2 months from October to November 2014. The pumped-up groundwater heated to 30°C was continuously injected into the confined lower aquifer at the flow rate of 20 L/min. Even during the experiment period, groundwater quality was almost the same with constant trends compared to the period before starting the experiment. Therefore, to facilitate correct data interpretation, data representing start-up of monitoring in the confined lower aquifer at the Lowland site and during the in-situ thermal experiment at the Upland site are removed for the discussion.

All acquired data for major cations and anions in all five aquifers are plotted as a Piper diagram (Fig. 4). A relatively large fluctuating trend was observed for the HCO_3^- concentration in the unconfined aquifer of the Lowland site (Fig. 3). According to Fig. 4, however, the fluctuation seems to be not crucial compared to that of other four aquifers in this study. The averaged chemical concentrations in all five aquifers calculated from the monitoring data in Fig. 4 are shown in Table 2, with standard deviation (1σ). Also, a Schoeller plot and a Stiff diagram were produced based on the mean chemical concentrations (Figs. 5 and 6).

At the Lowland site, there was almost no NO_3^- with clear SO_4^{2-} detection in the unconfined aquifer, while for the confined upper and lower aquifers, the chemical components of NH_4^+ and CH_4 (Fig. 8) were clearly detected with almost no NO_3^- and SO_4^{2-} present (Figs. 3, 4, 5, and 6 and Table 2). The groundwater in the unconfined and confined lower aquifers consisting of non-marine sediments was a $Ca-HCO_3$ dominated type (Fig. 6), which is a typical shallow groundwater quality. The confined upper aquifer formed under marine environment showed a completely different trend and was a Na, K, and $Mg-HCO_3$ dominated type groundwater. Based on these results, all three aquifers indicated significantly different characteristics of water quality, clearly suggesting that these aquifers are completely separate and distinct aquifers. On the other hand, at the Upland site, the chemical components of NO_3^- and SO_4^{2-} were clearly detected with almost no presence of NH_4^+. Both the confined upper and lower aquifers, which consist of non-marine sediments, showed a $Ca-HCO_3$ dominated type groundwater. All plotted monitoring data for both aquifers in the Piper diagram (Fig. 4) clearly overlapped. Further, the figure shapes in the Schoeller plot (Fig. 5) and Stiff diagram (Fig. 6) are not significantly different between both aquifers. Thus, the groundwater quality in both aquifers is markedly similar and these aquifers likely represent a unique water circulation system, i.e. the water masses are not fully separated. The groundwater in both aquifers is likely undergoing the same groundwater recharge and flowing processes under very similar hydrogeological conditions such as sedimentary facies and depositional environments.

3.3. Comparison of groundwater redox conditions in the Arakawa Lowland and Musashino Upland

In this section, to achieve precise data interpretation, groundwater redox conditions are discussed mainly based on behaviors of redox sensitive chemical species instead of just DO and ORP values. Figure 7 illustrates a modified Piper diagram for SO_4^{2-}-NH_4^+-NO_3^- as groundwater redox sensitive species in all five aquifers at both Lowland and Upland sites. Also, a modified Stiff diagram for the averaged concentration of groundwater redox sensitive chemical species plotted using the unit of meq/L (except for CH_4) is shown in Fig. 8. The CH_4 was analyzed based on the semi-quantitative method and the measured data were plotted as % in the headspace gas of analytical vials (see Materials and methods). The Fe concentration was quantified as total dissolved Fe using ICP-MS. Only the chemical form of Fe (II) is possible to be soluble with much less solubility of Fe (III) especially under circumneutral pH conditions. Since the groundwater in all five aquifers showed neutral pH (from 6.5 to 7.6), the concentration of total dissolved Fe is assumed to be nearly equal to Fe (II) concentration. Also, under aerobic groundwater conditions, Fe (II) is generally easy to be oxidized and transformed to the Fe (III) form. Because of the much lower solubility of Fe (III) under neutral range pH conditions, Fe (III)-hydroxides are produced and precipitate under aerobic groundwater conditions (Appelo and Postma, 2005). In this study, the notation of Fe (II) is therefore used instead of total dissolved Fe.

At the Lowland site, a much higher abundance ratio of SO_4^{2-} (more than 90%) was observed (Fig. 7) with a very low abundance ratio of NH_4^+ and almost no NO_3^- presence in the unconfined aquifer. Relatively high concentration of Fe (II) was detected (Fig. 8), up to around 10 mg/L. The concomitant presence of these three redox sensitive species (NH_4^+, Fe (II), and SO_4^{2-}) with almost no NO_3^- existence suggests that the groundwater was under intermediate anaerobic and iron reducing condition. The groundwater from the confined upper and lower aquifers is characterized by the high NH_4^+ abundance ratio > 90%, almost no NO_3^- and SO_4^{2-} existence, and a clear CH_4 detection (0.7% and 1.6% as mean values in the upper and lower aquifers, respectively). Because of the evidence for both almost no SO_4^{2-} detection (instead of sulfide) and CH_4 detection, the groundwater is suggested to be under strong (complete) anaerobic and methanogenic conditions. Sometimes (not systematically analyzed), the concentration of sulfide was measured at low concentration levels in both aquifers, based on the simple and semi-quantitative colorimetric method. The sulfide concentration was slightly higher in the confined upper aquifer than that in the confined lower aquifer. Almost no SO_4^{2-} detection indicates complete sulfate (SO_4^{2-}) reduction to sulfide (H_2S and HS^-). Sulfide is well known to be a strongly complexing transition metal and one of the most common metal complexes found is iron sulfide and the hereby formed insoluble minerals (e.g. Pyrite, Marcasite, Mackinawite, and Troilite). The groundwater in both aquifers is suggested to be under methanogenic (strong anaerobic) condition with less sulfide (H_2S and HS^-) and Fe (II) (approximately 35 μg/L and 60 μg/L as average in the confined upper and lower aquifers, respectively). Hence, the dissolved iron and sulfide aqueous concentrations may be limited from mineral iron sulfide precipitation in these aquifers. At the Upland site, the groundwater in the confined upper and lower aquifers showed completely different trends, especially for the behaviors of redox sensitive species compared to the results at the Lowland site. The combined abundance ratios of NO_3^- and SO_4^{2-} reached more than 90% with a very low abundance ratio of NH_4^+ (Fig. 7). Also, there was no detectable CH_4 (Fig. 8). These results suggest that the groundwater in both aquifers is under aerobic condition with much lower Fe (II) concentration in the groundwater, approximately 25 μg/L as a mean value.

Groundwater redox conditions were highly different at the Lowland and Upland sites. Generally, groundwater redox conditions are controlled by several hydrogeochemical and microbial factors, including the mineral composition, the concentration of redox sensitive chemical species, and the type and activity of microorganisms. Also, the difference of groundwater flow systems such as groundwater recharge area or discharge area can affect the formation of groundwater redox conditions (Gascoyne, 1997; Gómez et al., 2006). The groundwater in recharge areas may be under aerobic conditions due to less progress of microbially induced redox processes with relatively short groundwater residence time, while for groundwater in discharge areas, there is a possibility of the existence of anaerobic conditions. Around the monitoring sites, the groundwater is basically originating from mountainous, hilly, and upland areas in the western Kanto Plain (corresponding to the western areas marked with red and yellow in Fig. 1), being groundwater recharge areas, and moving to the lowland areas in the center of Kanto Plain, being groundwater discharge areas

(Ministry of Land, Infrastructure, Transport and Tourism, Government of Japan, 1996; Miyakoshi and Uchida, 2001; Hachinohe et al., 2006; Hisatomi et al., 2015) (Fig. 1). Especially, the Lowland site is located at the left bank of the Arakawa river and fairly close to the river (only around 1 km). Thus, the unconfined aquifer may be partly recharged by the Arakawa river and, also, mixed with groundwater from the Omiya Upland located in the eastern part of the monitoring site (corresponding to the eastern area marked with green in Fig. 1).

The Lowland site is located in the Arakawa Lowland and the area is generally considered as a groundwater discharge area in terms of broad groundwater flow systems. The groundwater in the unconfined and the two confined aquifers was probably under iron reducing and methanogenic conditions, respectively, because microbially induced redox processes were likely evolved sufficiently during groundwater flow having longer residence time. On the other hand, the Upland site is located in the Musashino Upland and the groundwater in confined aquifers is likely recharged by the precipitation, river water, and the unconfined aquifer in the Upland area (Sindou, 1968). The Musashino Upland is located close to groundwater recharge areas and the groundwater has relatively short residence time (Yasuhara et al., 2014). Therefore, aerobic groundwater conditions in the two confined aquifers may be maintained at the Upland site. Considering the different groundwater flow systems around the monitoring sites together with the $\delta^{18}O$ and δD results, the groundwater recharge areas at both sites may be relatively similar. The different groundwater redox conditions were likely caused by different groundwater residence time for the Arakawa Lowland and Musashino Upland, being predominantly groundwater discharge and recharge areas respectively. Further investigation on mineral composition and type and activity of microorganisms is needed together with high-resolution groundwater monitoring for further clarifying the formation factors behind the very different groundwater redox conditions at the investigated sites.

4. Conclusions

Long-term groundwater quality including 35 chemical parameters for five aquifers in the Arakawa Lowland and Musashino Upland, southern Kanto Plain of the Tokyo Metropolitan area of Japan, representing one of the megacities in the world was monitored. Based on these data, hydrogeochemistry including groundwater quality and redox conditions was characterized and compared for both Lowland and Upland areas. The factors creating the difference of groundwater redox conditions were discussed.

The monitoring of stable oxygen and hydrogen isotope ratios for groundwater in five aquifers as well as precipitation in the Arakawa Lowland suggested that the main origin of groundwater is the precipitation in both Lowland and Upland areas. The acquired long-term and high-resolution groundwater quality data with at least 80 groundwater samples obtained in each aquifer showed almost constant groundwater quality during the monitoring period over several years. According to the acquired data, the three aquifers in the Arakawa Lowland are likely completely separate and distinct aquifers, while the two aquifers in the Musashino Upland, are not fully separated and the groundwater in the two aquifers are undergoing the same groundwater recharge and flow processes under very similar hydrogeological conditions.

The behavior of the groundwater redox sensitive chemical species revealed that an unconfined aquifer in the Arakawa Lowland was probably under intermediate anaerobic and iron reducing conditions. Strong anaerobic and methanogenic conditions were found in other two confined aquifers in the Arakawa Lowland. Oppositely, in the Musashino Upland, the groundwater in two confined aquifers was found to be under aerobic conditions. The different groundwater redox conditions were likely due to very different groundwater residence time in the Arakawa Lowland and Musashino Upland. The degree of progress in microbially induced redox processes evolved with groundwater flow was likely different in the Lowland and Upland areas with the processes markedly more pronounced in the Arakawa Lowland.

Current research status on relationships between groundwater flow systems including recharge area or discharge area and groundwater redox conditions is still insufficient and more research is needed based on long-term and comprehensive investigation of groundwater quality and redox conditions in different parts of the world and, also, representing other megacities.

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References

Aelion, C.M., Höhener, P., Hunkeler, D., Aravena, R., 2010. Environmental Isotopes in Biodegradation and Bioremediation. CRC Press, Boca Raton, USA.

Appelo, C.A.J., Postma, D., 2005. Geochemistry, Groundwater and Pollution, 2nd Edition. A.A. Balkema Publishers, Leiden, the Netherlands.

Banks, D., 2008. An Introduction to Thermogeology: Ground Source Heating and Cooling.

Blackwell Publishing Ltd., Oxford, UK. https://doi.org/10.1002/9781118447512

Blows, D.W., Ptacek, C.J., Jambor, J.L., 1997. In-situ remediation of Cr (IV)-contaminated groundwater using permeable reactive walls: Laboratory studies. Environmental Science & Technology 31 (12), 3348-3357. https://doi.org/10.1021/es960844b

Bonte, M., Stuyfzand, P.J., Hulsmann, A., van Beelen, P., 2011. Underground thermal energy storage: Environmental risks and policy developments in the Netherlands and European Union. Ecology and Society 16 (1), 22.

Brunetti, G., Saito, H., Saito, T., Šimůnek, J., 2017. A computationally efficient pseudo-3D model for the numerical analysis of borehole heat exchangers. Applied Energy 208, 1113-1127. https://doi.org/10.1016/j.apenergy.2017.09.042

Bureau of Environment, Tokyo Metropolitan Government, Japan, 2019a. Monitoring results of groundwater pumping in FY 2017. https://www.kankyo.metro.tokyo.lg.jp/water/groundwater/pumping_regulations/outline.html (accessed 29 January 2020) (in Japanese)

Bureau of Environment, Tokyo Metropolitan Government, Japan, 2019b. Monitoring results of groundwater quality in FY 2018. https://www.kankyo.metro.tokyo.lg.jp/water/groundwater/investigation.html (accessed 28 January 2020) (in Japanese)

Christensen, T.H., Bjerg, P.L., Banwart, S.A., Jakobsen, R., Heron, G., Albrechtsen, H.J., 2000. Characterization of redox conditions in groundwater contaminant plumes. Journal of Contaminant Hydrology 45 (3-4), 165-241. https://doi.org/10.1016/S0169-7722(00)00109-1

Craig, H., 1961. Isotopic variations in meteoric waters. Science 133, 1702-1703. https://doi.org/10.1126/science.133.3465.1702

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus 16 (4), 436-468. https://doi.org/10.3402/tellusa.v16i4.8993

Endo, T., Ishii, M., 1984. Hydrogeology and Subjects Caused by Recovering of Groundwater Level in Tokyo. Journal of the Japan Society of Engineering Geology 25 (3), 111-120 (in Japanese with English abstract). https://doi.org/10.5110/jjseg.25.111

Funabiki, A., Naya, T., Saito, H., Takemura, T., 2014. Sedimentary facies and depositional environment of CRE-TAT-1 and CRE-TAT-2 drilling core in Fuchu-city, Tokyo, central Japan. Journal of the Sedimentological Society of Japan 73 (2), 137-152 (in Japanese with English abstract). https://doi.org/10.4096/jssj.73.137

Gascoyne, M., 1997. Evolution of redox conditions and groundwater composition in recharge-discharge environments on the Canadian Shield. Hydrogeology Journal 5 (3), 4-18. https://doi.org/10.1007/s100400050253

Gómez, P., Turrero, M.J., Garralón, A., Peña, J., Buil, B., Cruz, B. de la, Sánchez, M., Sánchez, D.M., Quejido, A., Bajos, C., Sánchez, L., 2006. Hydrogeochemical characteristics of deep groundwaters of the Hesperian Massif (Spain). Journal of Iberian Geology 32 (1), 113-131.

Grießmeier, V., Bremges, A., McHardy, A.C., Gescher, J., 2017. Investigation of different nitrogen reduction routes and their key microbial players in wood chip-driven denitrification beds. Scientific Reports 7, 17028. https://doi.org/10.1038/s41598-017-17312-2

Hachinohe, S., Takahashi, M., Ishiyama, T., Sasaka, K., Shiraishi, H., Matsuoka, T., 2006. Geo-environment in Saitama Prefecture. Annual Report from the Center for Environmental Science in Saitama 6, 114-131 (in Japanese with English abstract).

Hähnlein, S., Bayer, P., Ferguson, G., Blum, P., 2013. Sustainability and policy for the thermal use of shallow geothermal energy. Energy Policy 59, 914-925. https://doi.org/10.1016/j.enpol.2013.04.040

Harris, R.N., Chapman, D.S., 1997. Borehole temperatures and a baseline for 20th-century global warming estimates. Science 275, 1618-1621. https://doi.org/10.1126/science.275.5306.1618

Hayashi, T., Miyakoshi, A., Yasuhara, M., 2007. Change of groundwater environment and problems in large urban areas in Japan. Journal of Japanese Association of Hydrological Sciences 37 (4), 271-285 (in Japanese with English abstract). https://doi.org/10.4145/jahs.37.271

Hisatomi, Y., Nakayama, D., Matsuyama, H., 2015. Long Term Variation and Future Projection of Shallow Groundwater Flow in Musashino Terrace as Simulated by MODFLOW. Journal of Japan

Society of Hydrology and Water Resources 28 (3), 109-123 (in Japanese with English abstract). https://doi.org/10.3178/jjshwr.28.109

Hoefs, J., 2004. Stable Isotope Geochemistry. Springer-Verlag, Berlin Heidelberg, Germany. https://doi.org/10.1007/978-3-662-05406-2

Huang, S., Pollack, H.N., Shen, P.-Y., 2000. Temperature trends over the past five centuries reconstructed from borehole temperatures. Nature 403, 756-758. https://doi.org/10.1038/35001556

Islam, F.S., Gault, A.G., Boothman, C., Polya, D.A., Charnock, J.M., Chatterjee, D., Lloyd, J.R., 2004. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. Nature 430, 68-71. https://doi.org/10.1038/nature02638

Kim, K., 2003. Long-Term Disturbance of Ground Water Chemistry Following Well Installation. Ground Water 41 (6), 780-789. https://doi.org/10.1111/j.1745-6584.2003.tb02419.x

Komatsubara, J., Kimura, K., Fukuoka, S., Ishihara, Y., 2010. Sedimentary facies and physical properties of the latest Pleistocene to Holocene sediment core (GS-SSS-1) in the Arakawa Lowland, Saitama City, central Japan. Journal of the Sedimentological Society of Japan 69 (1), 3-15 (in Japanese with English abstract). https://doi.org/10.4096/jssj.69.3

Kooi, H., 2008. Spatial variability in subsurface warming over the last three decades; Insight from repeated borehole temperature measurements in The Netherlands. Earth and Planetary Science Letters 270 (1-2), 86-94. https://doi.org/10.1016/j.epsl.2008.03.015

McMahon, P.B., Chapelle, F.H., 2008. Redox processes and water quality of selected principal aquifer systems. Ground Water 46 (2), 259-271. https://doi.org/10.1111/j.1745-6584.2007.00385.x

Ministry of Land, Infrastructure, Transport and Tourism, Government of Japan, 1996. Groundwater map in Saitama and Gunma areas. http://nrb-www.mlit.go.jp/kokjo/inspect/landclassification/water/w_national_map_cw.html (accessed 30 January 2020) (in Japanese)

Miyakoshi, A., Hayashi, T., Hamamoto, H., Hachinohe, S., 2018. Evaluation of subsurface warming recognized in long-term observation of subsurface temperature in southeastern Saitama Prefecture, Japan. Journal of Groundwater Hydrology 60 (4), 495-510 (in Japanese with English abstract). https://doi.org/10.5917/jagh.60.495

Miyakoshi, A., Uchida, Y., 2001. Distribution of subsurface temperature and groundwater flow system in the Kanto Plain. Bulletin of the Geological Survey of Japan 52 (6-7), 253-290 (in Japanese with English abstract). https://doi.org/10.9795/bullgsj.52.253

Monyrath, V., Sakura, Y., Miyakoshi, A., Hayashi, T., 2010. Subsurface thermal environment and groundwater flow around Tokyo Bay, Japan. Environmental Earth Sciences 60 (5), 923-932. https://doi.org/10.1007/s12665-009-0228-9

Naudet, V., Revil, A., Rizzo, E., Bottero, J.-Y., Bégassat, P., 2004. Groundwater redox conditions and conductivity in a contaminant plume from geoelectrical investigations. Hydrology and Earth System Sciences 8 (1), 8-22. https://doi.org/10.5194/hess-8-8-2004

Official website of Ministry of Land, Infrastructure, Transport and Tourism, Government of Japan. https://www.mlit.go.jp/mizukokudo/mizsei/mizukokudo_mizsei_tk1_000062.html (accessed 29 January 2020) (in Japanese)

Perrier, F., Le Mouel, J.-L., Poirier, J.-P., Shnirman, M.G., 2005. Long-term climate change and surface versus underground temperature measurement in Paris. International Journal of Climatology 25 (12), 1619-1631. https://doi.org/10.1002/joc.1211

Pollack, H.N., Huang, S., Shen, P.-Y., 1998. Climate change record in subsurface temperatures: A global perspective. Science 282, 279-281. https://doi.org/10.1126/science.282.5387.279

Puckett, L.J., Tesoriero, A.J., Dubrovsky, N.M., Nitrogen contamination of surficial aquifers - A growing legacy. Environmental Science & Technology 45 (3), 839-844. https://doi.org/10.1021/es1038358

Rozanski, K., Araguás-Araguás, L., Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. In: Climate change in continental isotopic records. Geophysical Monograph 78, 1-36. https://doi.org/10.1029/GM078p0001

Saitama Prefectural Government, Japan, 2019. Monitoring results of groundwater quality in FY 2018. https://www.pref.saitama.lg.jp/a0505/h30chikasuijyoujikansikekkagaiyou.html#gaikyou (accessed

28 January 2020) (in Japanese)

Saito, T., Hamamoto, S., Mon, E.E., Takemura, T., Saito, H., Komatsu, T., Moldrup, P., 2014. Thermal properties of boring core samples from the Kanto area, Japan: Development of predictive models for thermal conductivity and diffusivity. Soils and Foundations 54 (2), 116-125. https://doi.org/10.1016/j.sandf.2014.02.004

Saito, T., Hamamoto, S., Ueki, T., Ohkubo, S., Moldrup, P., Kawamoto, K., Komatsu, T., 2016. Temperature change affected groundwater quality in a confined marine aquifer during long-term heating and cooling. Water Research 94, 120-127. https://doi.org/10.1016/j.watres.2016.01.043

Shiklomanov, I.A., 1998. World Water Resources: A New Appraisal and Assessment for the 21st Century. UNESCO International Hydrological Programme (IHP), Paris, France.

Shindou, S., 1968. Hydrogeology of the Musashino Terrace. Journal of Geography 77 (4), 223-246 (in Japanese with English Abstract). https://doi.org/10.5026/jgeography.77.4_223

Taniguchi, M., Shimada, J., Uemura, T., 2003. Transient effects of surface temperature and groundwater flow on subsurface temperature in Kumamoto Plain, Japan. Physics and Chemistry of the Earth A/B/C 28 (9-11), 477-486. https://doi.org/10.1016/S1474-7065(03)00067-6

Taniguchi, M., Uemura, T., Jago-on, K., 2007. Combined effects of urbanization and global warming on subsurface temperature in four Asian cities. Vadose Zone Journal 6 (3), 591-596. https://doi.org/10.2136/vzj2006.0094

Tesoriero, A.J., Löffler, F.E., Liebscher, H., 2001. Fate of origin of 1,2-Dichloropropane in an unconfined shallow aquifer. Environmental Science & Technology 35 (3), 455-461. https://doi.org/10.1021/es001289n

Tesoriero, A.J., Terziotti, S., Abrams, D.B., 2015. Predicting redox conditions in groundwater at a regional scale. Environmental Science & Technology 49 (16), 9657-9664. https://doi.org/10.1021/acs.est.5b01869

Thuyet, D.Q., Saito, H., Saito, T., Moritani, S., Kohgo, Y., Komatsu, T., 2016. Multivariate analysis of trace elements in shallow groundwater in Fuchu in western Tokyo Metropolis, Japan. Environmental Earth Sciences 75: 559. https://doi.org/10.1007/s12665-015-5170-4

Ueshima, M., Takemura, T., Saito, T., Ito, Y., Hamamoto, S., Saito, H., Komatsu, T., 2017. Relationship between trace elements and depositional environments in shallow sediments: A case study from Southern Kanto Plain, Central Japan. Environmental Earth Sciences 76: 633. https://doi.org/10.1007/s12665-017-6968-z

Weathers, K.C., Strayer, D.L., Likens, G.E., 2013. Fundamentals of Ecosystem Science. Academic Press, New York, USA. https://doi.org/10.1016/C2009-0-03622-8

Wiedemeier, T.H., Swanson, M.A., Moutoux, D.E., Gordon, E.K., Wilson, J.T., Wilson, B.H., Kampbell, D.H., Haas, P.E., Miller, R.N., Hansen, J.E., Chapelle, F.H., 1998. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water. United States

Environmental Protection Agency, Cincinnati, USA.

WWAP (United Nations World Water Assessment Programme), 2015. The United Nations World Water Development Report 2015: Water for a Sustainable World. UNESCO, Paris, France.

Yabusaki, S., Shimano, Y., Suzuki, Y., 2016. Characteristics of stable isotopes in precipitation at Kanto district, Fukushima City, Matsumoto City and Kyoto City-Variation of stable isotopes in precipitation due to climate change and prediction of its future-. Journal of Japanese Association of Hydrological Sciences 46 (2), 139-155 (in Japanese with English Abstract). https://doi.org/10.4145/jahs.46.139

Yasuhara, M., Inamura, A., Morikawa, N., Takahashi, M., Suzuki, H., Gingerich, S.B., Takahashi, H., Kazahaya, K., Ohwada, M., Tosaki, Y., Makino, M., Hayashi, T., Miyakoshi, A., Suzuki, Y., Yabusaki, S., Miyashita, Y., Nakamura, T., Ohta, T., 2014. Groundwater system in the central Kanto plain. Integral research and application of the subsurface geology “the central Kanto Plain” Miscellaneous Map Series 40, 231-254 (in Japanese with English Abstract).

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 1 Averaged $\delta^{18}O$, δD, and deuterium excess (d-excess) values (‰) in the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and two aquifers (CUA and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined aquifer, confined upper aquifer, and confined lower aquifer, respectively. Values in parentheses express standard deviation (1σ).

Component	Unit	UCA–Lowland		CUA–Lowland		CLA–Lowland		CUA–Upland		CLA–
$\delta^{18}O$	‰	−7.9	(0.2)	−6.9	(0.1)	−7.7	(0.1)	−8.1	(0.1)	−8.2
δD	‰	−50.6	(0.9)	−46.2	(0.7)	−50.6	(0.6)	−52.5	(0.8)	−53.4
d−excess	‰	12.4	(1.1)	8.8	(0.5)	11.0	(0.6)	12.1	(0.6)	12.5

Table 2 Averaged concentration of major cations (Na^+, NH_4^+, Mg^{2+}, K^+, and Ca^{2+}) and anions (Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^-) (meq/L) in the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and two aquifers (CUA and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined aquifer, confined upper aquifer, and confined lower aquifer, respectively. Values in parentheses express coefficient of variation.

Component	Concentration unit	UCA–Lowland	CUA–Lowland	CLA–Lowland	CUA–Uplan

Na^+	mg/L	18.07	(10.4)	27.93	(5.2)	18.88	(7.8)	13.85	(
NH_4^+	mg/L	0.59	(107.2)	11.54	(8.3)	3.56	(40.2)	0.36	(15
K^+	mg/L	1.24	(53.7)	19.84	(4.7)	5.65	(25.8)	3.42	(1
Mg^{2+}	mg/L	18.69	(9.4)	17.71	(3.5)	8.34	(9.4)	13.74	(
Ca^{2+}	mg/L	37.83	(9.6)	25.29	(4.0)	25.41	(10.7)	40.53	(
Cl^-	mg/L	28.52	(15.9)	32.37	(7.3)	10.71	(10.1)	17.03	(
NO_3^-	mg/L	0.26	(119.2)	0.12	(204.2)	0.18	(155.8)	13.12	(4
SO_4^{2-}	mg/L	24.95	(11.8)	0.23	(178.0)	0.05	(278.0)	56.15	(1
HCO_3^-	mg/L	265.80	(19.3)	228.16	(5.3)	159.57	(5.4)	108.73	(1

Fig. 1 (a) Location of established groundwater monitoring sites at the campuses of Saitama University and Tokyo University of Agriculture and Technology in the Arakawa Lowland (Lowland site) and Musashino Upland (Upland site), respectively, in the southern Kanto Plain of the Tokyo Metropolitan area of Japan (the base map was taken from Geospatial Information Authority of Japan), and (b) geological columns with monitored three aquifers (UCA, CUA, and CLA) at the Lowland site and two aquifers (CUA and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined aquifer, confined upper aquifer, and confined lower aquifer, respectively.

Fig. 2 Relationships between $d^{18}O$ and dD (‰, V-SMOW) for the precipitation at the Lowland site, and the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and two aquifers (CUA and CLA) at the Upland site. LMWL, UCA, CUA, and CLA stand for local meteoric water line, unconfined aquifer, confined upper aquifer, and confined lower aquifer, respectively.

Fig. 3 Temporal variations of the concentration of major cations (Na^+, NH_4^+, Mg^{2+}, K^+, and Ca^{2+}) and anions (Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^-) (meq/L) in the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and two aquifers (CUA and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined aquifer, confined upper aquifer, and confined lower aquifer, respectively.

Fig. 4 A Piper diagram for the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and two aquifers (CUA and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined aquifer, confined upper aquifer, and confined lower aquifer, respectively.

Fig. 5 A Schoeller plot for averaged concentration of major cations (Na^+, NH_4^+, Mg^{2+}, K^+, and Ca^{2+}) and anions (Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^-) (meq/L) in the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and two aquifers (CUA and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined aquifer, confined upper aquifer, and confined lower aquifer, respectively.

Fig. 6 A Stiff diagram for averaged concentration of major cations (Na^+, NH_4^+, Mg^{2+}, K^+, and Ca^{2+}) and anions (Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^-) (meq/L) in the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and two aquifers (CUA and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined aquifer, confined upper aquifer, and confined lower aquifer, respectively.

Fig. 7 A modified Piper diagram for SO_4^{2-}, NH_4^+, and NO_3^- as groundwater redox sensitive chemical species in the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and two aquifers (CUA and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined aquifer, confined upper aquifer, and confined lower aquifer, respectively.

Fig. 8 A modified Stiff diagram for averaged concentration of groundwater redox sensitive chemical species (NO_3^-, SO_4^{2-}, NH_4^+, and Fe (II): meq/L and CH_4: %) in the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and two aquifers (CUA and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined aquifer, confined upper aquifer, and confined lower aquifer, respectively. The Fe (II) concentration is modified with 10 times.

Highlights (3 to 5 bullet points, maximum 85 characters including spaces per bullet point):

Long-term groundwater quality including 35 chemical parameters was monitored.

Five aquifers in the Arakawa Lowland and Musashino Upland of Japan were targeted.

Completely different groundwater redox conditions were observed for both study areas.

Three aquifers in the Lowland were under iron reducing to methanogenic conditions.

Two aquifers in the Upland were under aerobic conditions.

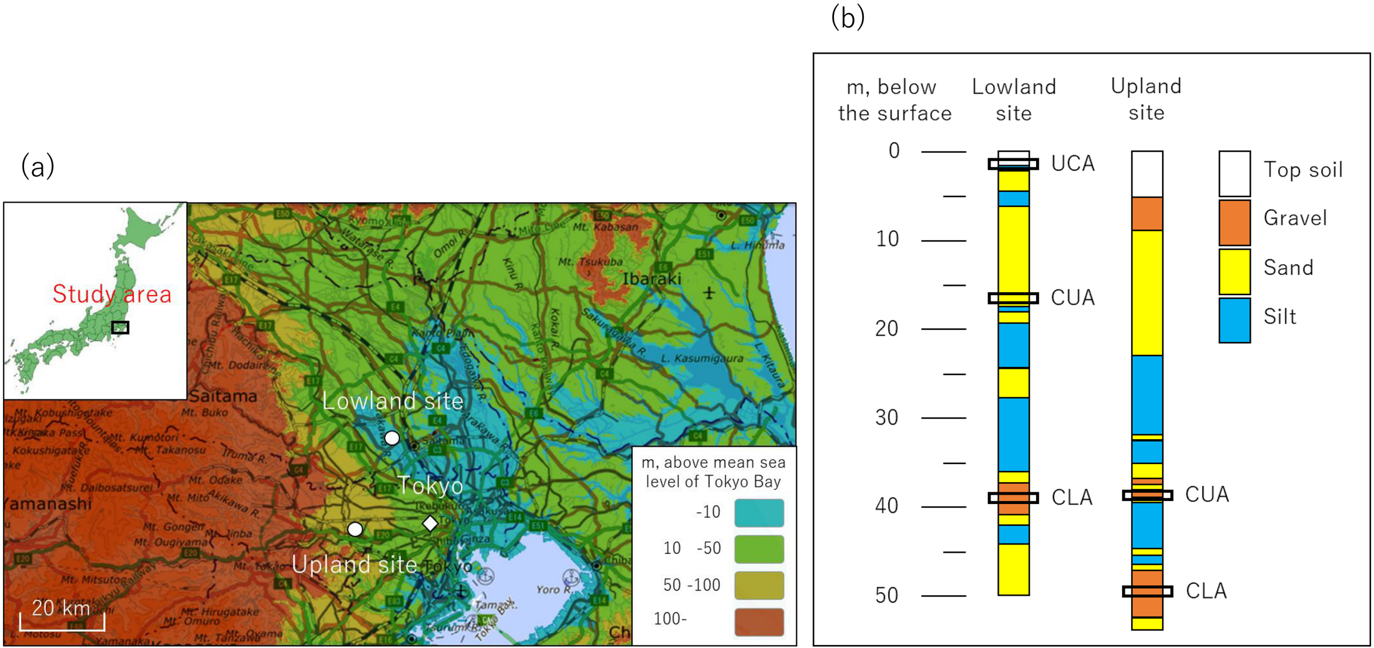

(a)
Study area
Saitama
Ibaraki
Yamanashi
Lowland site
Tokyo
Upland site
L. Kasumigaura
Tokyo Bay
20 km
m, above mean sea level of Tokyo Bay
-10
10 -50
50 -100
100-
(b)
m, below the surface
0
10
20
30
40
50
Lowland site
Upland site
UCA
CUA
CLA
CUA
CLA
Top soil
Gravel
Sand
Silt

Figure 1

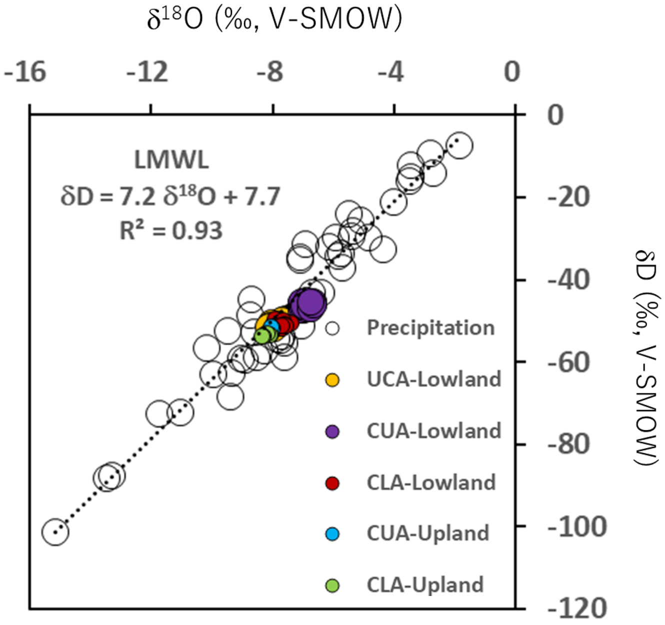

δ18O (‰, V-SMOW)
-16
-12
-8
-4
0
δD (‰, V-SMOW)
0
-20
-40
-60
-80
-100
-120
LMWL
δD = 7.2 δ18O + 7.7
R² = 0.93
Precipitation
UCA-Lowland
CUA-Lowland
CLA-Lowland
CUA-Upland
CLA-Upland

Figure 2

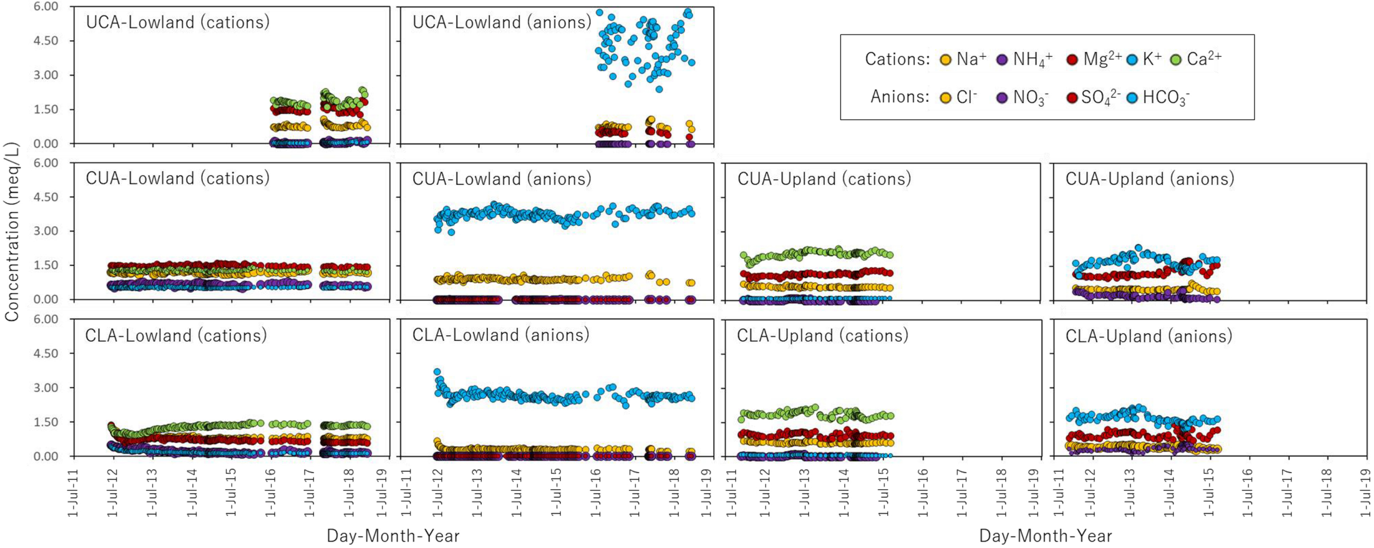

UCA-Lowland (cations)
UCA-Lowland (anions)
CUA-Lowland (cations)
CUA-Lowland (anions)
CUA-Upland (cations)
CUA-Upland (anions)
CLA-Lowland (cations)
CLA-Lowland (anions)
CLA-Upland (cations)
CLA-Upland (anions)
Cations: Na+ NH4+ Mg2+ K+ Ca2+
Anions: Cl- NO3- SO42- HCO3-
Concentration (meq/L)
0.00
1.50
3.00
4.50
6.00
1-Jul-11
1-Jul-12
1-Jul-13
1-Jul-14
1-Jul-15
1-Jul-16
1-Jul-17
1-Jul-18
1-Jul-19
Day-Month-Year

Figure 3

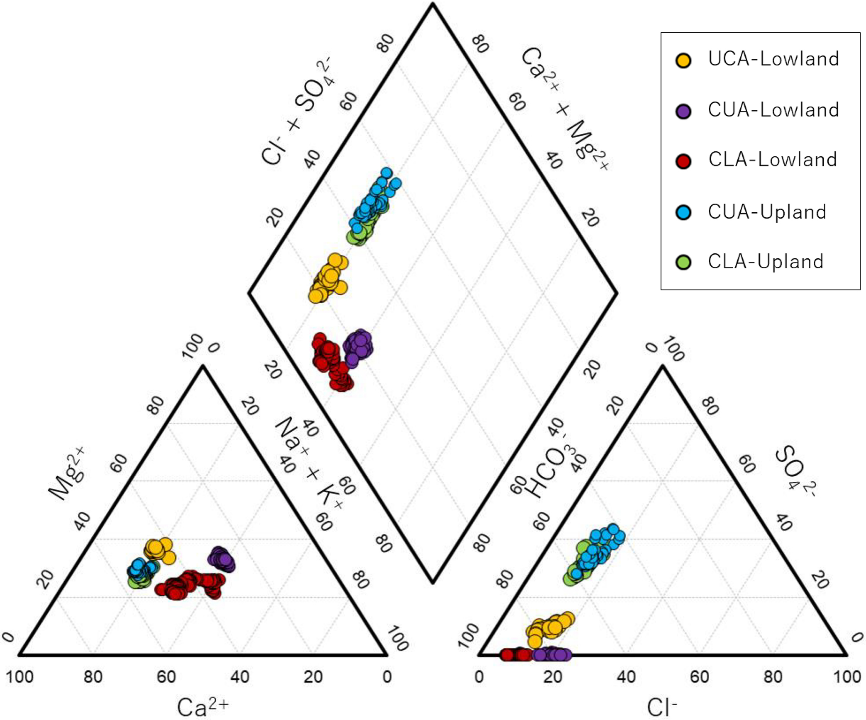

UCA-Lowland
CUA-Lowland
CLA-Lowland
CUA-Upland
CLA-Upland
$Cl^- + SO_4^{2-}$
$Ca^{2+} + Mg^{2+}$
Mg^{2+}
$Na^+ + K^+$
HCO_3^-
SO_4^{2-}
Ca^{2+}
Cl^-
0
20
40
60
80
100

Figure 4

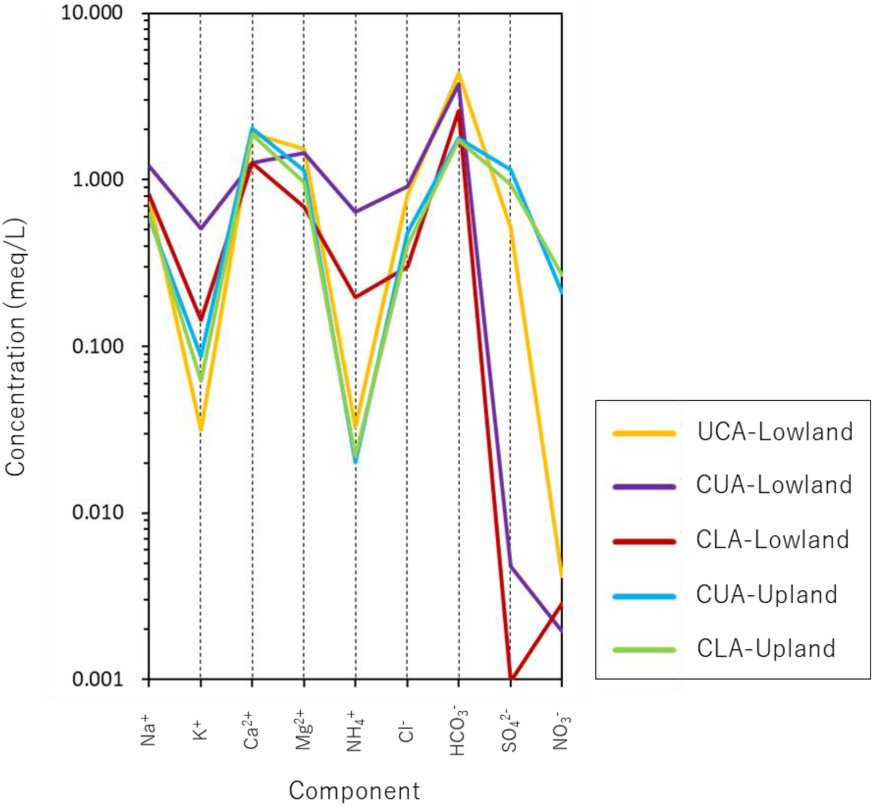

10.000
1.000
0.100
0.010
0.001
Concentration (meq/L)
Na^+
K^+
Ca^{2+}
Mg^{2+}
NH_4^+
Cl^-
HCO_3^-
SO_4^{2-}
NO_3^-
Component
UCA-Lowland
CUA-Lowland
CLA-Lowland
CUA-Upland
CLA-Upland

Figure 5

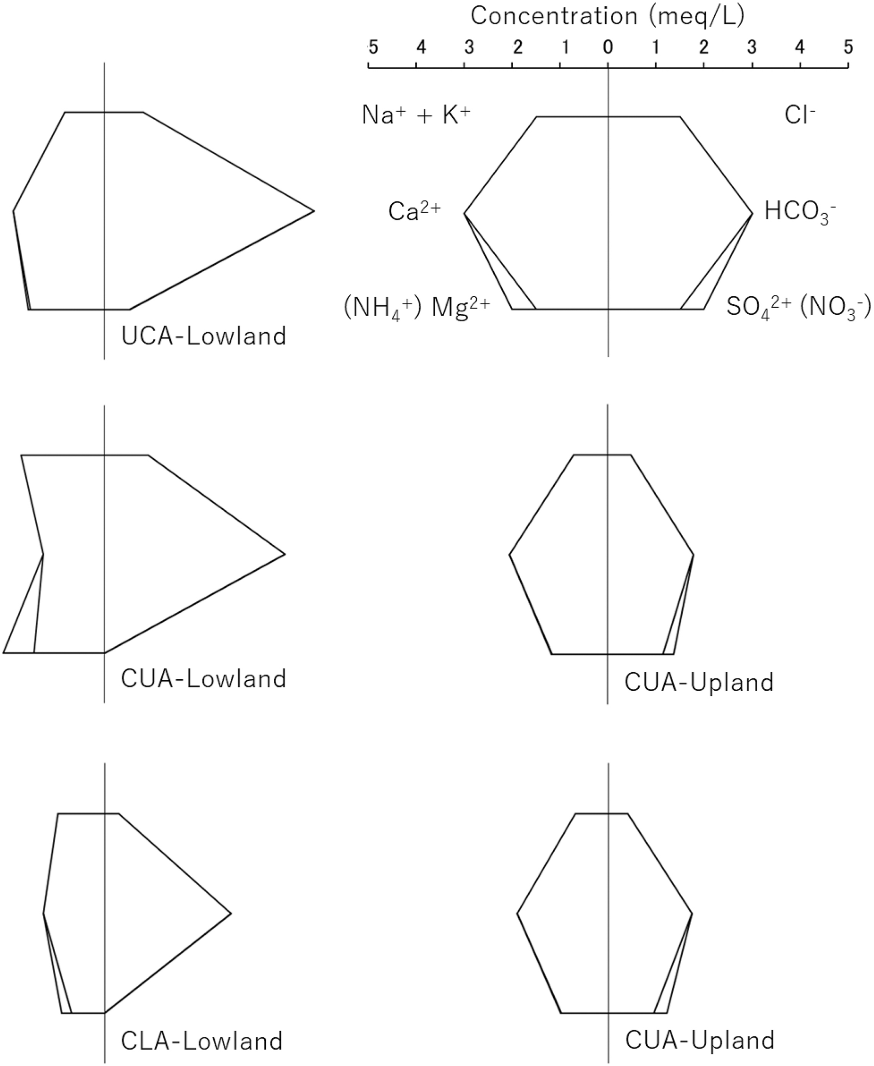
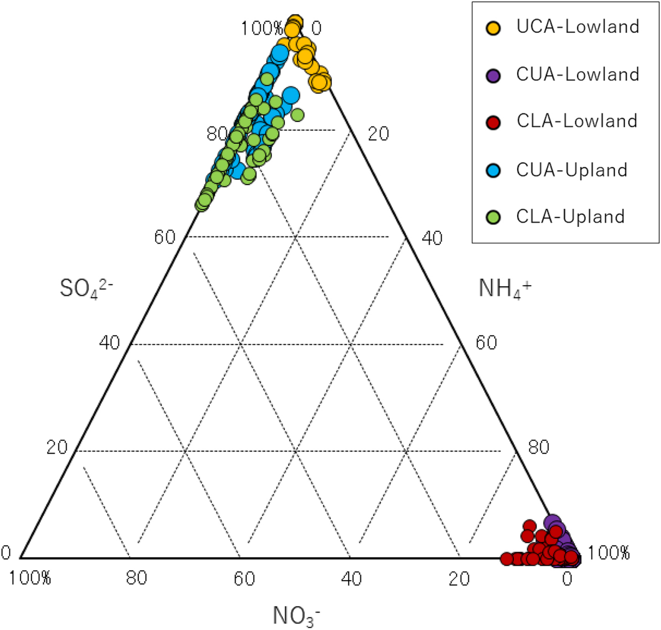

Concentration (meq/L)
5 4 3 2 1 0 1 2 3 4 5
Na+ + K+
Cl-
Ca2+
HCO3-
(NH4+) Mg2+
SO42+ (NO3-)
UCA-Lowland
CUA-Lowland
CUA-Upland
CLA-Lowland
CUA-Upland

Figure 6



100%
0
20
40
60
80
100%
SO$_4^{2-}$
NH$_4^+$
NO$_3^-$
100%
80
60
40
20
0
UCA-Lowland
CUA-Lowland
CLA-Lowland
CUA-Upland
CLA-Upland

Figure 7

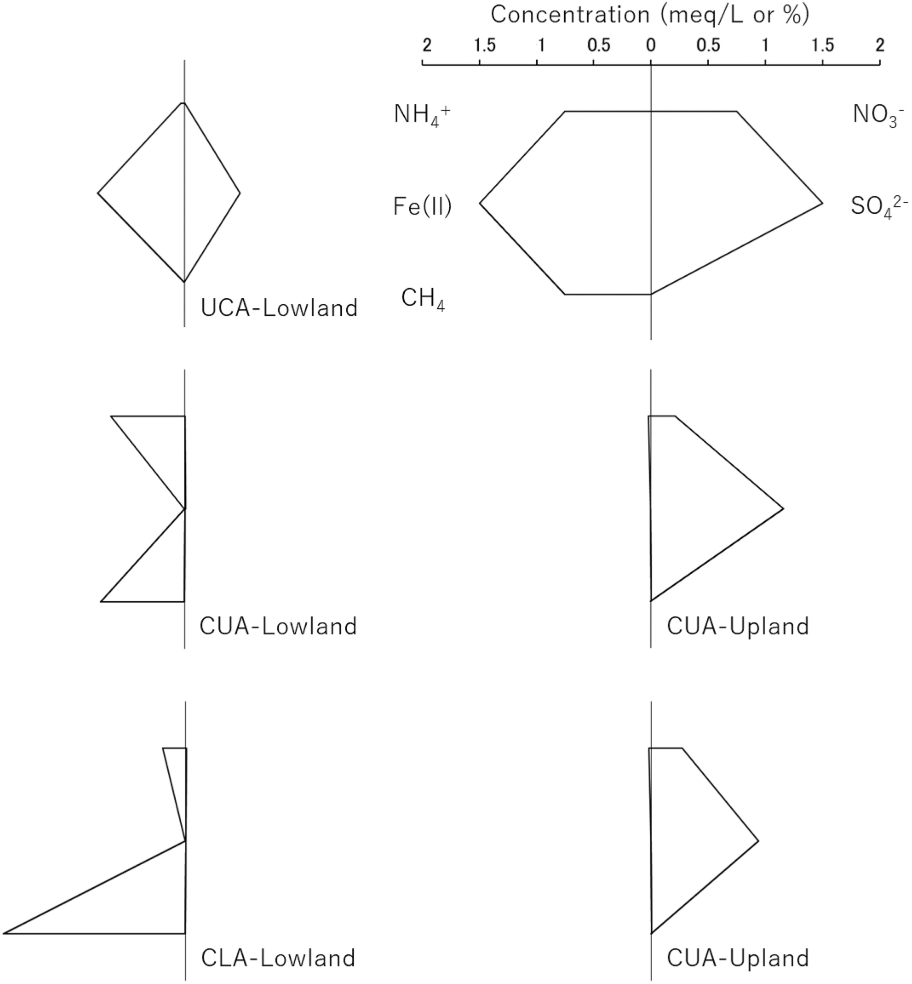

Concentration (meq/L or %)
2
1.5
1
0.5
0
0.5
1
1.5
2
NH_4^+
NO_3^-
Fe(II)
SO_4^{2-}
CH_4
UCA-Lowland
CUA-Lowland
CUA-Upland
CLA-Lowland
CUA-Upland

Figure 8