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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*Title Page

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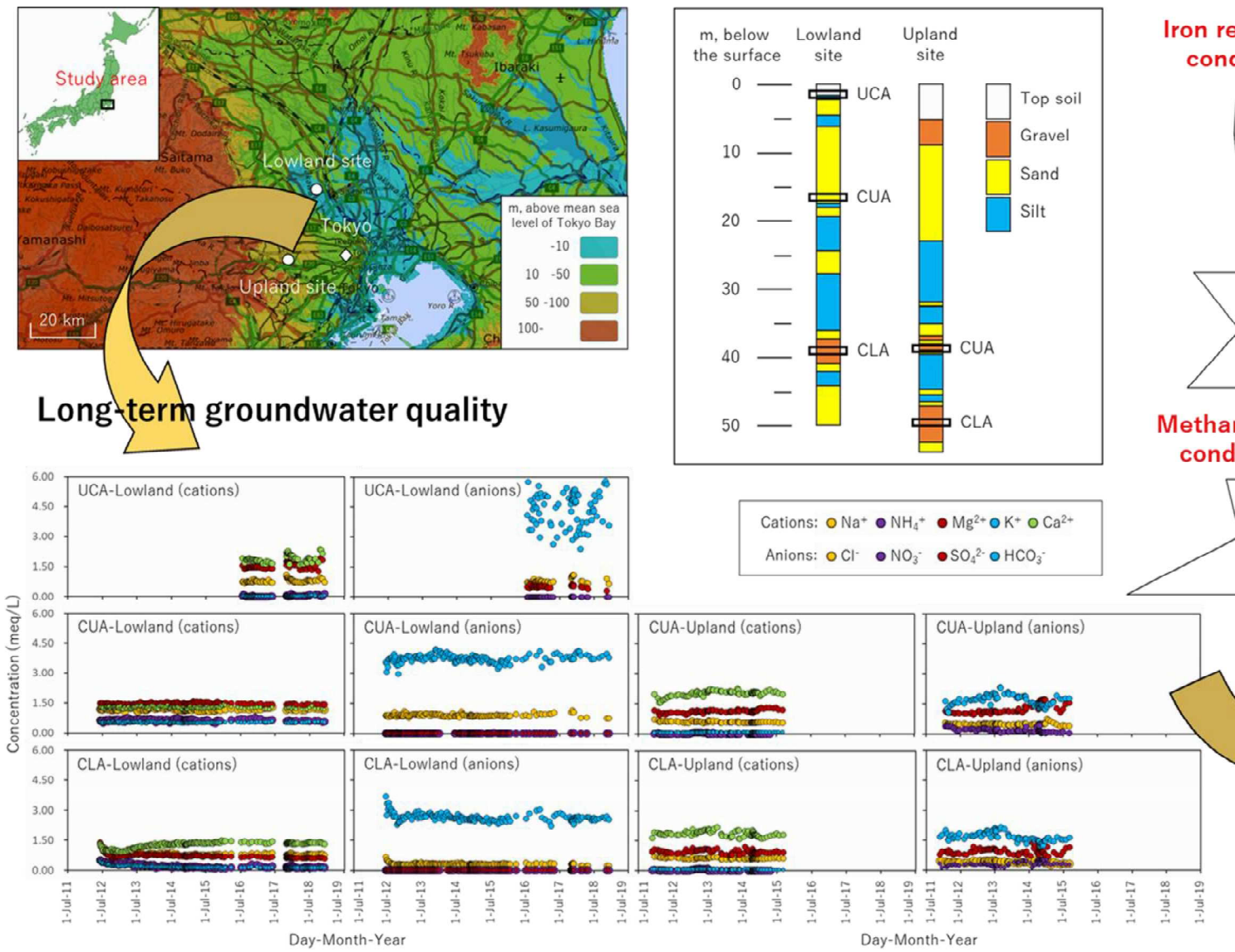
*Graphical Abstract



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

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.

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 observed very different groundwater redox conditions were likely caused by the difference between groundwater recharge and discharge areas of the Musashino Upland and Arakawa Lowland.

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 drinking water purposes. Around 2.5 billion people depend only on groundwater for their daily water usage (WWAP, 2015). Therefore, groundwater is highly essential for the Earth biosphere from not only qualitative but also quantitative aspects.

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, groundwater contamination by harmful chemical compounds often occurs due to the extremely high and dense population. 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). 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°51′44.0″N, 139°36′34.0″E) and Tokyo University of Agriculture and Technology (35°41′03.1″N, 139°29′07.9″E) in the southern Kanto Plain of the Tokyo Metropolitan area, Japan (Fig. 1a).

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 presented in Saito et al. (2014); Saito et al. (2016); Brunetti et al. (2017); Ueshima et al. (2017).

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 of the hydrogeological environments at the Upland site is reported in Saito et al. (2014); Thuyet et al. (2016); Brunetti et al. (2017); Ueshima et al. (2017).

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) and 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. 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. ^2H)/^1H) 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.

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 41 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 $\delta^{18}O$ 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 $\delta^{18}O$ and δD values were markedly variable and ranged from -15.16 to -1.85‰ and -101.38 to -7.32‰, 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 $\delta D = 7.19\delta^{18}O + 7.73$ ($R^2 = 0.93$). 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ and δD composition in the confined upper and lower aquifers at the Lowland site, more than 40 groundwater samples were analyzed and showed almost constant values compared to those of the precipitation, Fig. 2. In the other three aquifers at the monitoring sites, approximately 20 groundwater samples were measured and the $\delta^{18}O$ and δD values were also almost constant. 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). The results suggest that main origin of the groundwater at these study sites is precipitation. 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/or high degree of reactions with surrounding geology should be considered when $\delta^{18}O$ and δD values in groundwater are not placed near the local meteoric water line (Hoefs, 2004).

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%, +4.21%, +3.12%, and +3.15% in the confined upper and lower aquifers at both Lowland and Upland sites, respectively. Because the electrical balance values in all aquifers except for the unconfined aquifer at the Lowland site are less than ±5%, the relatively larger averaged value of the electrical balance in the unconfined aquifer at the Lowland site can be explained from the existence of other ionic components and, hence, may be not related to analytical problems. 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 creating a possibility for the mixing of groundwater from upper aquifers. 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 1, with standard deviation (1σ). Also, a Schoeller plot and a Stiff diagram were produced based on the mean chemical concentrations (meq/L), 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 1). 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

Figure 7 illustrates a modified Piper diagram for SO_4^{2-}-NH_4^+-NO_3^- as groundwater redox sensitive chemical 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 the following section, 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

303 common metal complexes found is iron sulfide and the hereby formed insoluble minerals (e.g. Pyrite,
304 Marcasite, Mackinawite, and Troilite). The groundwater in both aquifers is suggested to be under
305 methanogenic (strong anaerobic) condition with less sulfide (H_2S and HS^-) and Fe (II)
306 (approximately 35 μg/L and 60 μg/L as average in the confined upper and lower aquifers,
307 respectively). Hence, the dissolved iron and sulfide aqueous concentrations may be limited from
308 mineral iron sulfide precipitation in these aquifers.

309 The groundwater in the confined upper and lower aquifers at the Upland site showed completely
310 different trends, especially for the behaviors of redox sensitive species compared to the results at the
311 Lowland site. The combined abundance ratios of NO_3^- and SO_4^{2-} reached more than 90% with a very
312 low abundance ratio of NH_4^+ (Fig. 7). Also, there was no CH_4 (under the detection limit), Fig. 8.
313 These results suggest that the groundwater in both aquifers is under aerobic condition with much
314 lower Fe (II) concentration in the groundwater, approximately 25 μg/L as a mean value.

315 Groundwater redox conditions were highly different at the Upland and Lowland sites. Generally,
316 groundwater redox conditions are controlled by several hydrogeochemical and microbial factors,
317 including the mineral composition, the concentration of redox sensitive species, and the type and
318 activity of microorganisms. Also, the difference of groundwater flow systems such as groundwater
319 recharge area or discharge area can affect the formation of groundwater redox conditions (Gascoyne,
320 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. At the Lowland site, the monitoring 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 due to markedly low altitude only several meters above sea level, Fig. 1a. 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.

At the Upland site, the monitoring 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). Therefore, the Upland site may be located relatively close to the groundwater recharge areas compared to the Lowland site and thus aerobic groundwater conditions in two confined aquifers are maintained at the Upland site. Further investigation on mineral composition and type and activity of microorganisms is needed for sufficiently clarifying formation factors of these completely different groundwater redox conditions at both 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 completely different groundwater redox conditions are suggested due to the difference of groundwater flow systems including the groundwater recharge and discharge areas. The degree of progress in microbially induced redox processes evolved with groundwater flow was likely different in the Upland and Lowland 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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Table
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Table 1 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 standard deviation (1σ).

Component	Concentration unit	UCA-Lowland		CUA-Lowland		CLA-Lowland		CUA-Upland		CLA-Upland	
Na^+	mg/L	18.07	(1.89)	27.93	(1.44)	18.88	(1.48)	13.85	(0.90)	14.30	(1.21)
NH_4^+	mg/L	0.59	(0.63)	11.54	(0.95)	3.56	(1.43)	0.36	(0.57)	0.40	(0.63)
K^+	mg/L	1.24	(0.67)	19.84	(0.93)	5.65	(1.46)	3.42	(0.39)	2.42	(0.61)
Mg^{2+}	mg/L	18.69	(1.76)	17.71	(0.62)	8.34	(0.78)	13.74	(0.93)	11.67	(1.17)
Ca^{2+}	mg/L	37.83	(3.63)	25.29	(1.01)	25.41	(2.72)	40.53	(3.09)	37.58	(2.65)
Cl^-	mg/L	28.52	(4.54)	32.37	(2.35)	10.71	(1.08)	17.03	(1.16)	14.40	(1.70)
NO_3^-	mg/L	0.26	(0.31)	0.12	(0.25)	0.18	(0.28)	13.12	(5.29)	16.65	(4.96)
SO_4^{2-}	mg/L	24.95	(2.94)	0.23	(0.41)	0.05	(0.13)	56.15	(6.52)	44.96	(6.21)
HCO_3^-	mg/L	265.80	(51.30)	228.16	(12.09)	159.57	(8.57)	108.73	(14.64)	104.90	(11.73)

Figure
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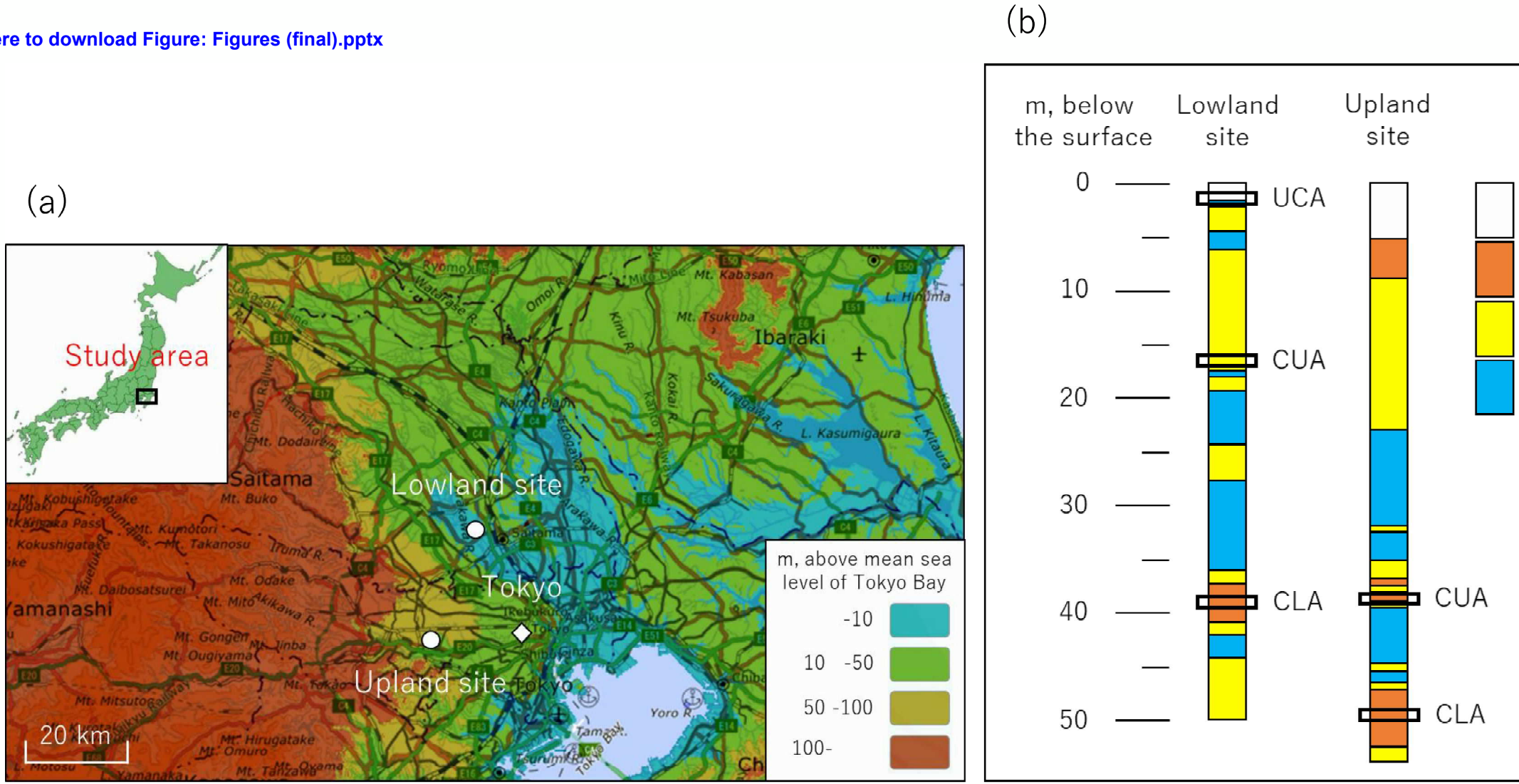

Fig. 1 (a) Location of established groundwater monitoring sites at the campuses of Saitama University and Toky of Agriculture and Technology in the Arakawa Lowland (Lowland site) and Musashino Upland (Upland site), resp the southern Kanto Plain of the Tokyo Metropolitan area of Japan (the base map was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

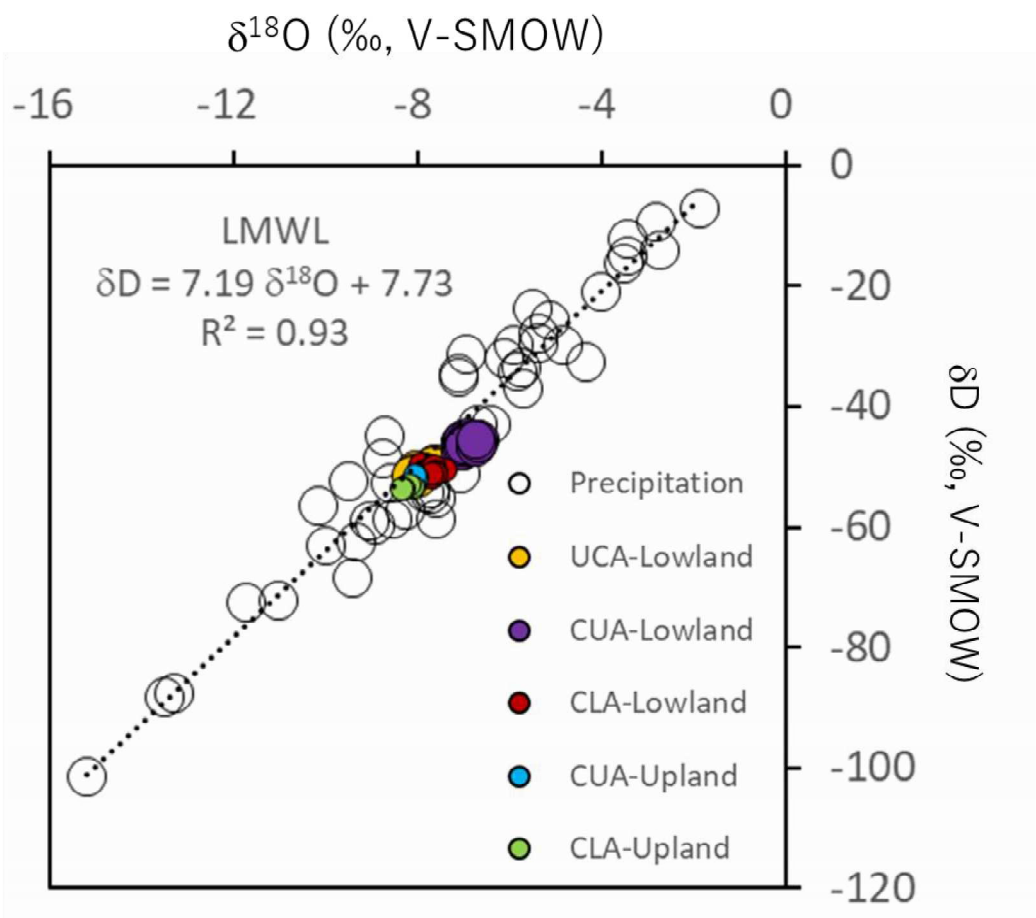

Fig. 2 Relationships between d^{18}O and dD (‰, V-SMOW) for the precipitation at the Lowland site, and the groun three aquifers (UCA, CUA, and CLA) at the Lowland site and two aquifers (CUA and CLA) at the Upland site. LM CUA, and CLA stand for local meteoric water line, unconfined aquifer, confined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

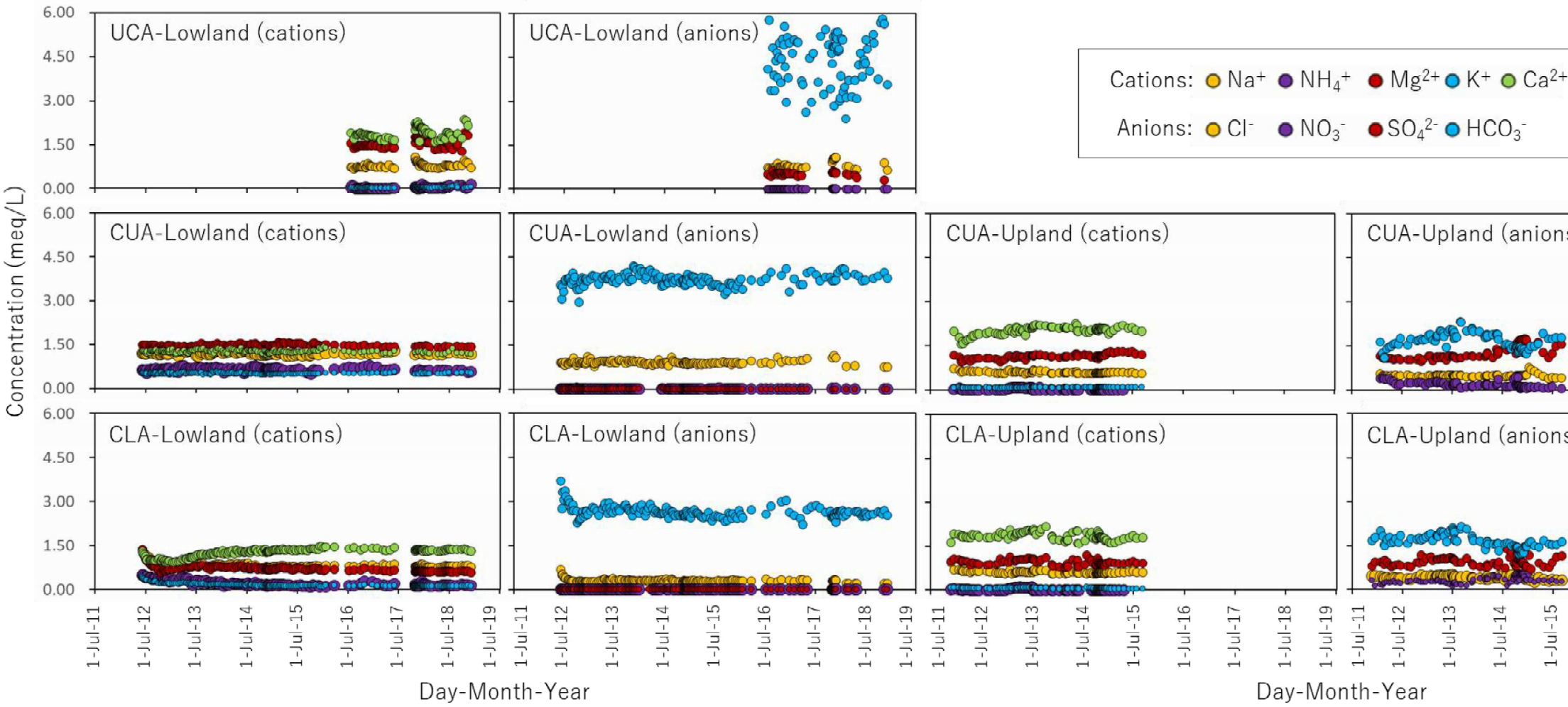

Fig. 3 Temporal variations of the concentration of major cations (Na^+, NH_4^+, Mg^{2+}, K^+, and Ca^{2+}) and anions (Cl^- and HCO_3^-) (meq/L) in the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and two a and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined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

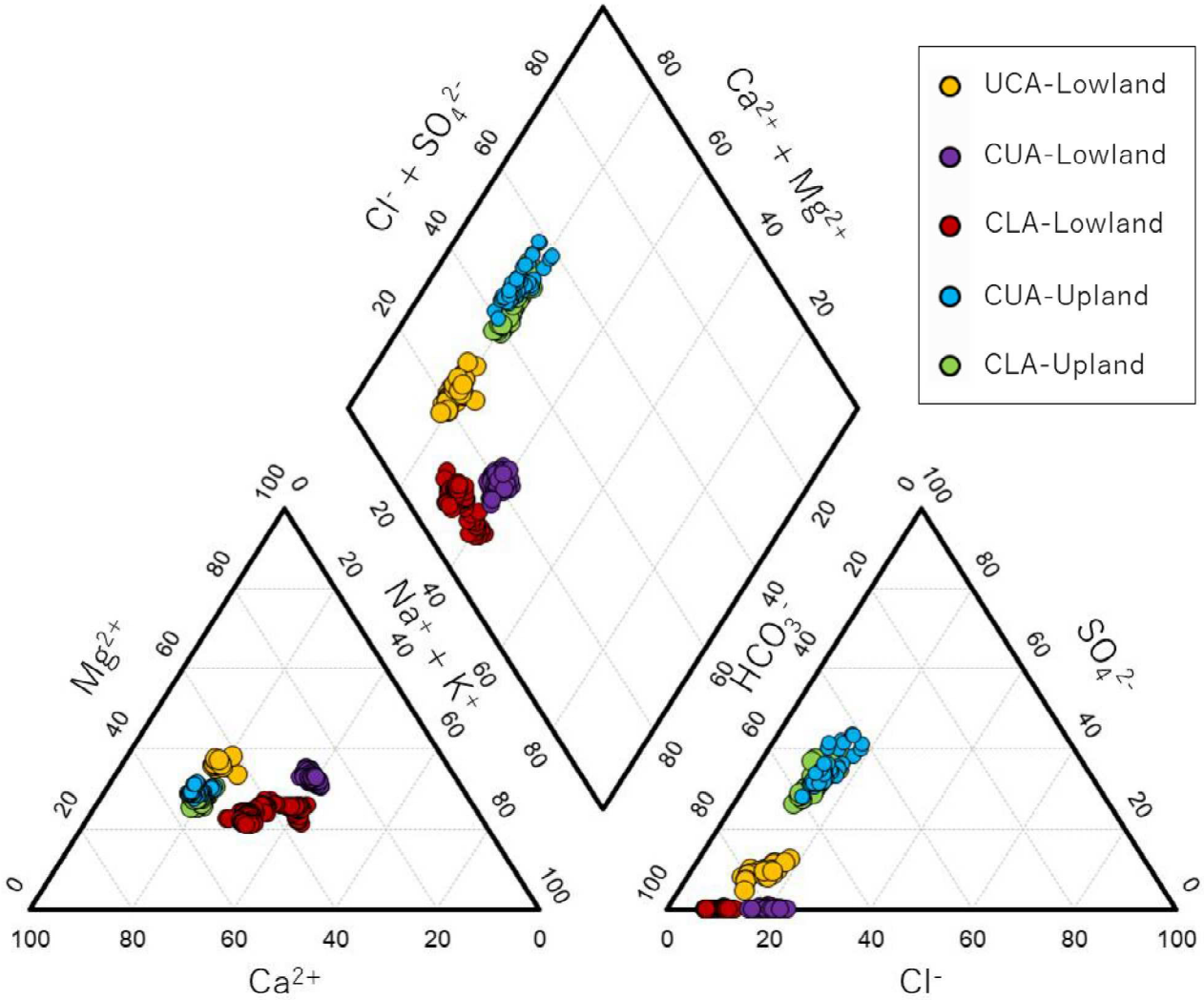

Fig. 4 A Piper diagram for the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and tw
(CUA and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined aquifer, confined upper aquifer, and
lower aquifer, respectively.

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

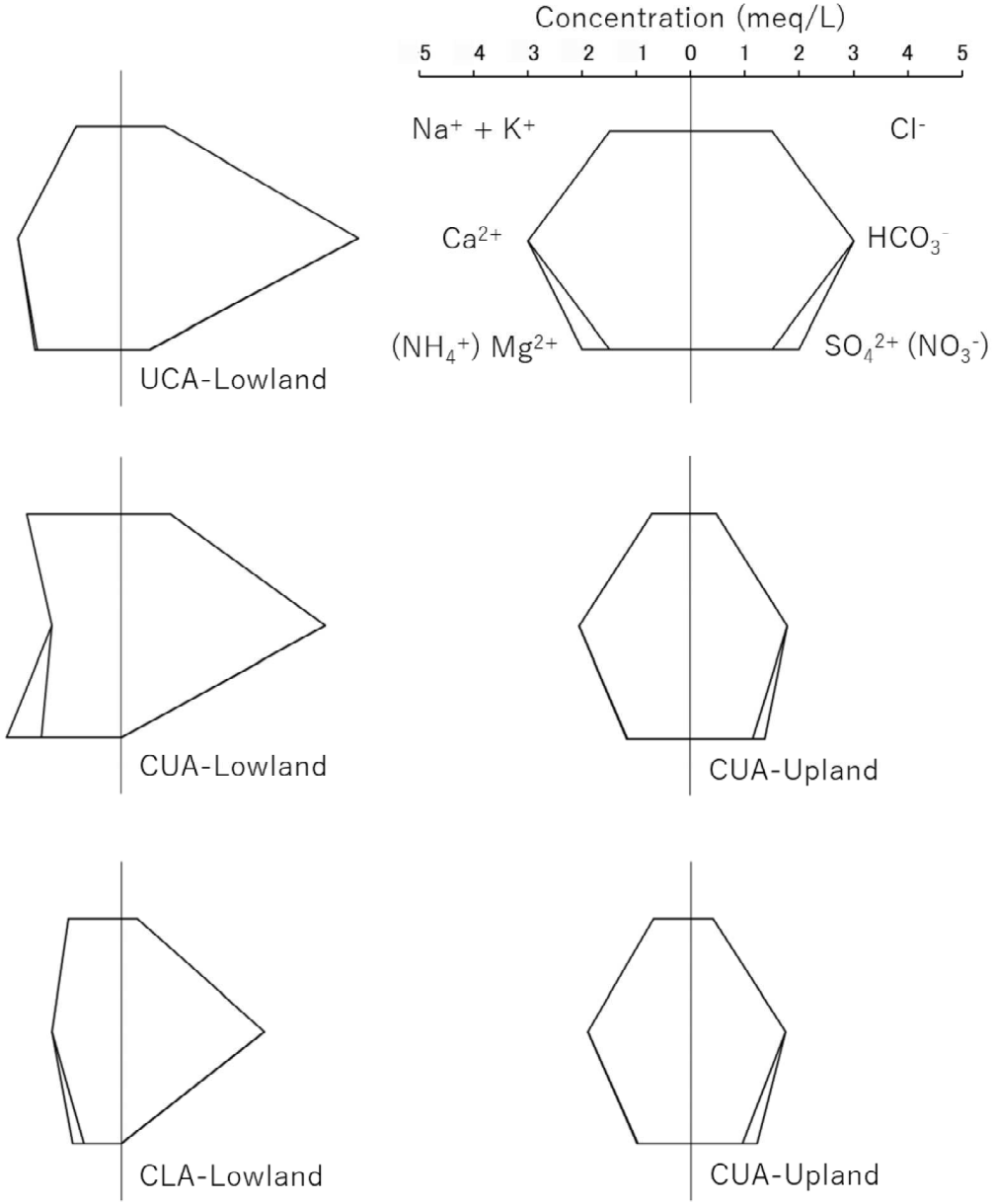

Fig. 6 A Stiff diagram for averaged concentration of major cations (Na^+, NH_4^+, Mg^{2+}, K^+, and Ca^{2+}) and anions (C and HCO_3^-) (meq/L) in the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and two a and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined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

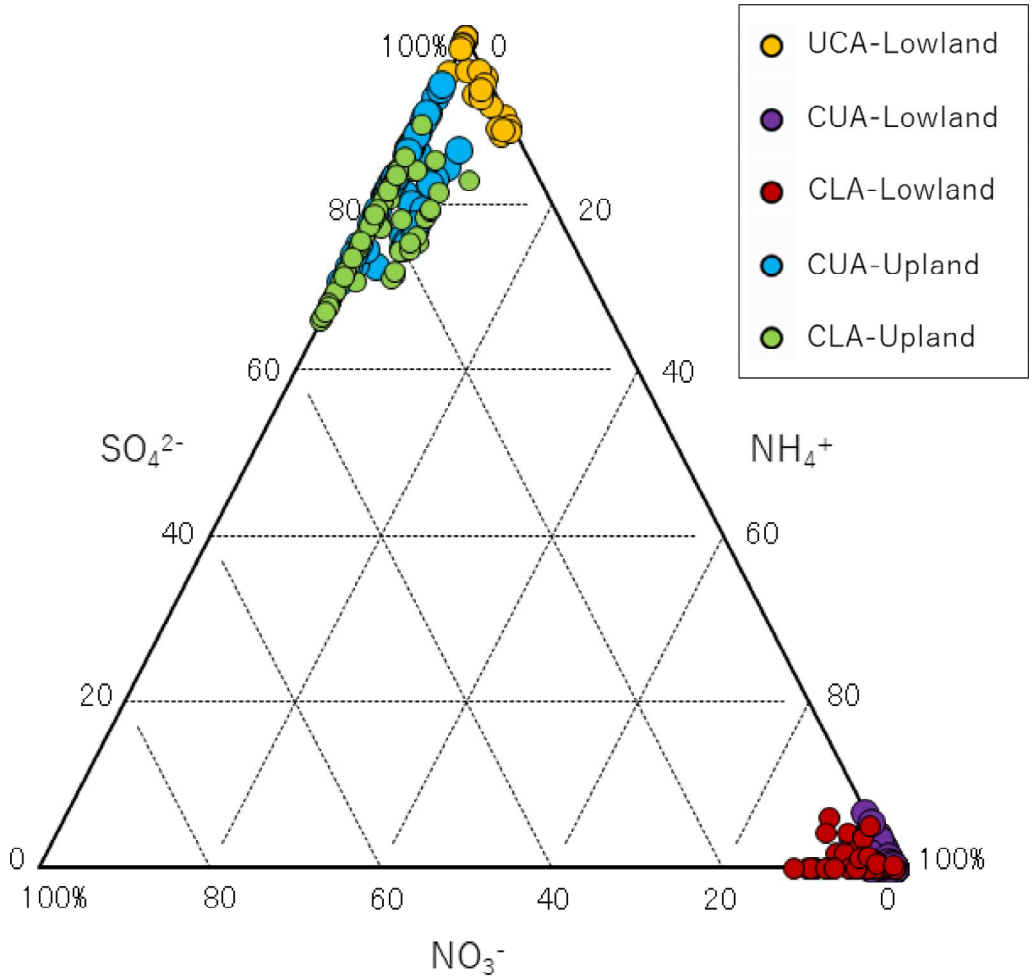

Fig. 7 A modified Piper diagram for SO_4^{2-}, NH_4^+, and NO_3^- as groundwater redox sensitive chemical species in the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowland site and two aquifers (CUA and CLA) at tl site. UCA, CUA, and CLA stand for unconfined aquifer, confined upper aquifer,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

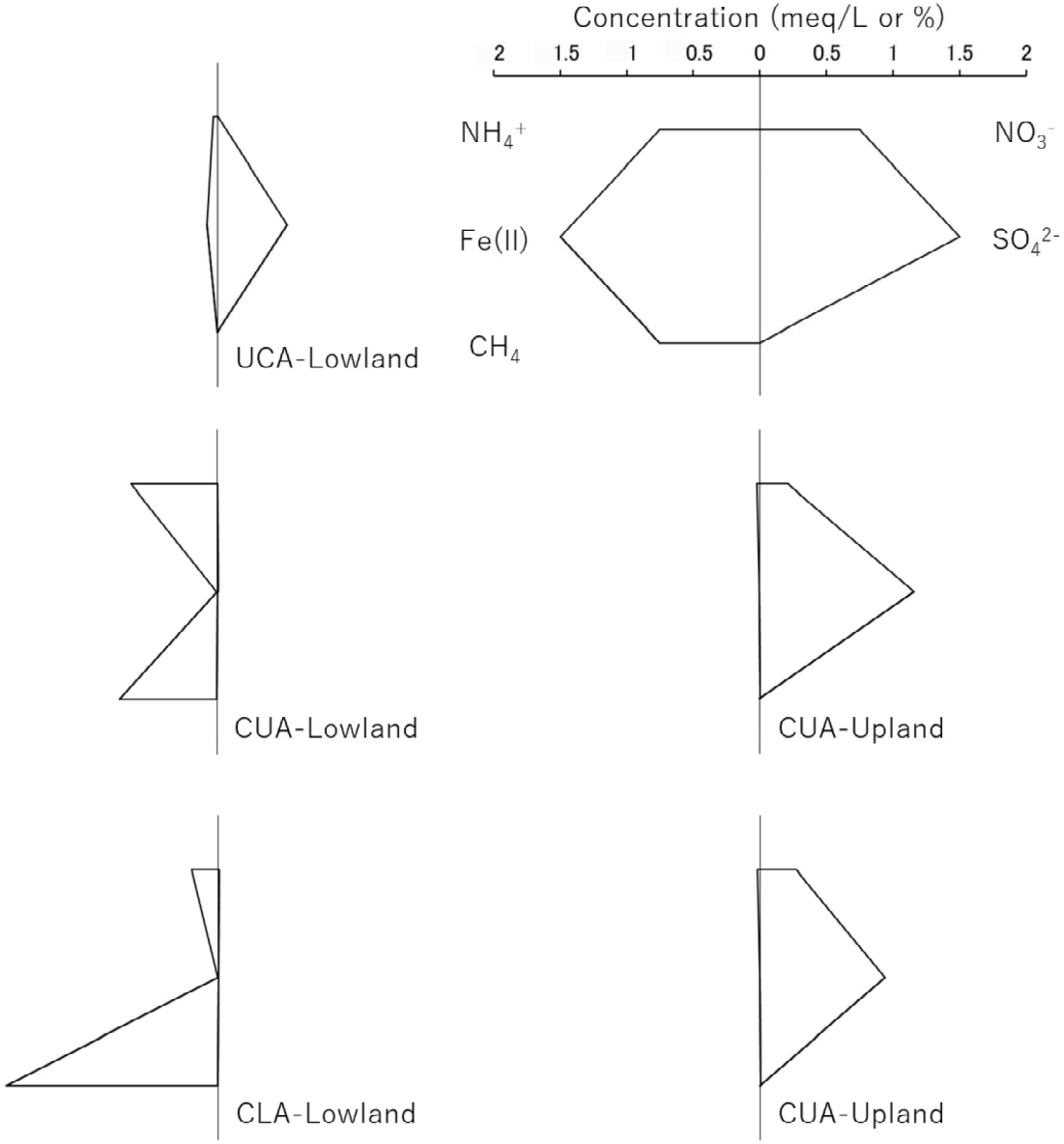

Fig. 8 A modified Stiff diagram for averaged concentration of groundwater redox sensitive chemical species (NO_3 NH_4^+, and Fe (II): meq/L and CH_4: %) in the groundwater from three aquifers (UCA, CUA, and CLA) at the Lowla two aquifers (CUA and CLA) at the Upland site. UCA, CUA, and CLA stand for unconfined aquifer, confined uppe confined lower aquifer, respectively.