

Reply to comments from Anonymous Referee #1.

General comment:

The authors present a study about quantification of groundwater discharge in a river in an extensive irrigation watershed in Japan. Their study used three methods to estimate the groundwater impact: flow measurements and 2 isotopic approaches (stable isotopes of the water molecules and Sr isotopes). The global approach and the sampling strategy is good and appropriate to answer the question (the raw data are not provided and should be added as supplementary material). This study is of interest for the scientific community and also as potential tools in terms of water management. The text is relatively short considering the work presented and the various approaches applied. Thus, the detail reasoning especially concerning the groundwater contribution estimated through the 3 approaches is hard to follow and thus the main conclusions are too weakly supported by the main text. The manuscript would benefit to have a more detailed text, and to remove at least one or two figures (e.g. figures 6 and 12).

[Response]

We appreciate the reviewer for his/her time and effort in reviewing our manuscript as well as the corresponding thoughtful comments.

As suggested by the reviewer, we will present raw data as supplementary material; however, the detailed analysis on the principal component was out of the scope of this study. We are currently working on multiple geochemical tracers to understand the hydrological processes in this watershed and it will be reported in our following paper.

In the previous version of the manuscript, the method of determining the endmembers was not clearly described, and there was an inconsistency between the endmember described in the manuscript (i.e., the values of the irrigation water and the spring, ODK) and depicted in Fig 7 of the previous manuscript (i.e., the plot of the endmember indicated by the open and black circles). In the previous manuscript, we calculated the ratio of groundwater to the stream water using the former (the values described in the manuscript), instead of the latter (the values depicted in the figure). This inconsistency induced confusion in the readers.

Therefore, we created a new section (3.3.1) describing the endmember determination and recalculated the ratio of groundwater in the stream (3.3.2) and the quantified groundwater discharge (3.3.3). More specifically, we determined the groundwater endmember of Sr isotope from the crossing point of the regression line of the stream water samples and the horizontal line

departing from the spring, ODK in Fig 4 (b) (in the revised manuscript). We describe the response in more detail in the following specific comment.

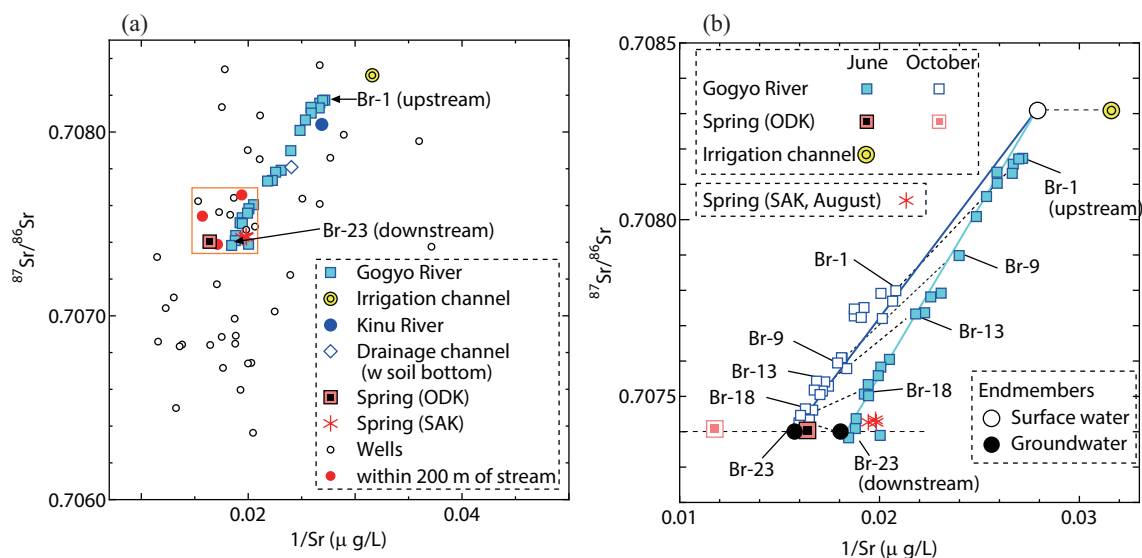


Figure 4: Sr isotope obtained from the watershed-scale survey: (a) all samples obtained during the irrigation period, and (b) comparison of Sr isotopic compositions in stream water during irrigation and non-irrigation periods.

Figure 12 (in the previous manuscript) is an important figure showing that the spatial and temporal variations in Sr isotopes was less than those of water isotopes. These figures support part of our conclusion that Sr isotopes are more appropriate than water isotopes in terms of the consistency for representing the groundwater endmember; thus, we would like to retain these figures in the revised manuscript.

The discussion section should be more detailed and argued with a solid comparison of both isotopic approaches considering their discriminating power. Sr is a WRI marker and thus will translate the lithological variations and water circulations, to be useful, contrasted signatures of the considered end-members are required; while stable isotopes of the water molecule, will mainly trace (in this context) the evaporation effect and could highlight variations along the hydrological cycle. For these reasons, and comments below, I recommend this work to be published in HESS with major revisions.

[Response]

We updated sections 4.1 and 4.2 to describe the testing of the robustness of the endmembers and the consistency of estimated groundwater ratios in the stream using two isotopes. We also added chloride concentration to corroborate our conclusion as described below.

By using the abovementioned endmembers consistently throughout the manuscript, the estimated values of groundwater ratios in the stream in the previous manuscript have been revised (see figures below). In the previous manuscript, the estimated ratios from Sr and water isotopes were in good agreement in the non-irrigation period, while they differed in the irrigation period (see updated version of the Figures 13 and 14). However, in the revised manuscript, they show good agreement during the irrigation period, whereas discrepancies were observed during the non-irrigation period. The groundwater ratios in the stream, estimated from Sr isotopes, increased over the river course: 6–93% during the irrigation period and 46–99% in the non-irrigation period. Stable isotopes of water provided similar estimates during the irrigation period (7–83%), but discrepancies were observed during the non-irrigation period (41–69%).

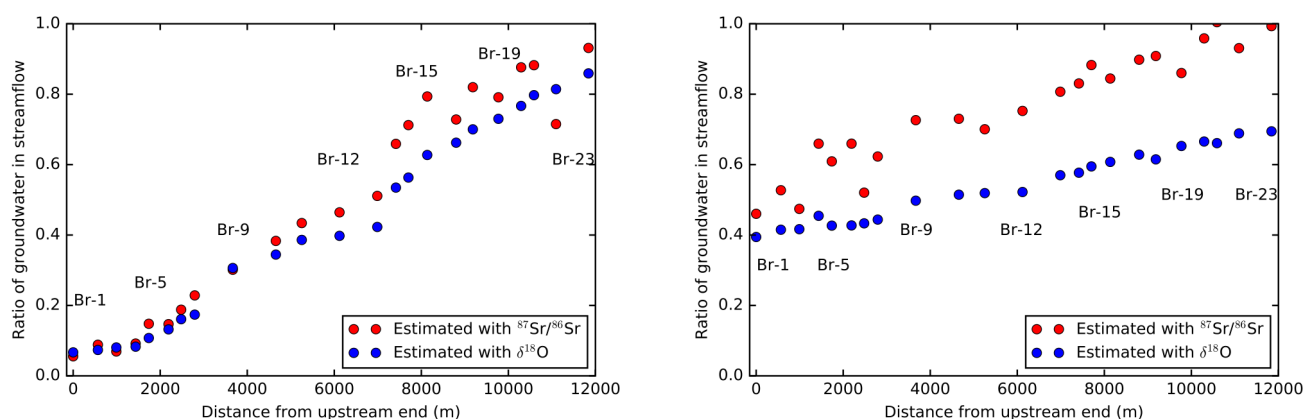


Figure 13 and 14 [Updated version] Ratios of groundwater in the streamflow based on $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ during irrigation period (left) and non-irrigation period (right).

To elucidate the causes of the differences in the estimates from both isotopes, we used the chloride concentration of stream water. Chloride concentration at the upstream end was 5.24 mg/l (irrigation) and 5.09 mg/l (non-irrigation) and showed a similar increasing trend up to the middle reach of the stream. However, the concentration differed at the downstream end: 7.23 mg/l (irrigation) and 6.25 mg/l (non-irrigation). The chloride concentration of the spring ODK, located near the downstream end, was 7.47 mg/l and 7.62 mg/l during the irrigation and non-irrigation

periods, respectively.

The higher chloride concentration at the downstream water and its similarity to the spring ODK in the irrigation periods suggests that the stream water was highly affected by groundwater, which was consistent with the estimated groundwater ratios in the stream using either Sr or water isotopes. On the other hand, the lower chloride concentration at the downstream end in the non-irrigation period suggested that the stream water was less affected by groundwater discharge. This observation was consistent with the estimates of groundwater ratio using water isotopes, corroborating the overestimation by Sr isotopes.

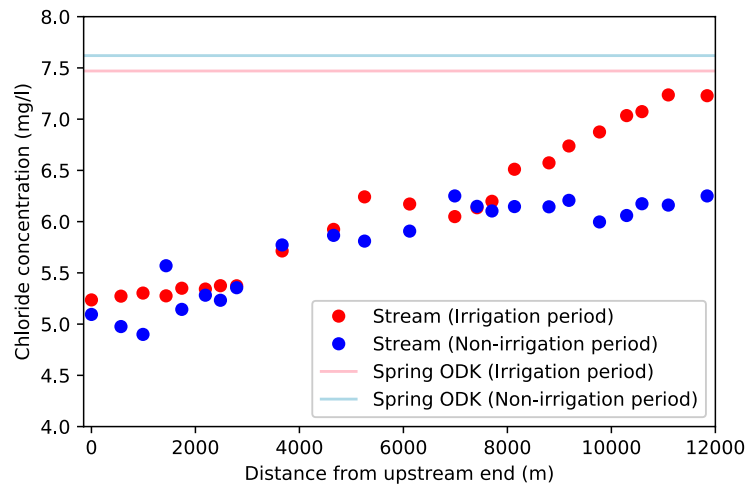


Figure 6 [added to the revised manuscript] Chloride concentration in stream water and the spring, ODK.

Attention should be paid to distinguishing groundwater discharge and hyporheic exchange (Kalbus et al., 2006). In streams, the ratio of groundwater discharge estimated using Sr isotopes might not entirely be attributed to groundwater discharge, but include water-rock interaction (WRI) in hyporheic zones. During the non-irrigation period when the groundwater discharge was not dominant due to low groundwater level, the hyporheic exchange increases the probability of stream water interacting with subsurface water in the hyporheic zone. Thus the surface water receives more exchangeable Sr isotopes that have lower $^{87}\text{Sr}/^{86}\text{Sr}$ values from the sediments in the river bed and bank. This process can explain higher groundwater ratios in the stream using Sr isotopes during the non-irrigation period, compared with those estimated using water isotopes. This influence was relatively larger during the non-irrigation period because groundwater discharge was not sufficient, while during the irrigation period, the effects of WRI can be

negligible because of the higher rate in groundwater discharge from the regional aquifer.

In the previous manuscript, we concluded that Sr isotope is more stable in terms of space and time than water isotopes and has higher discriminating power for quantifying groundwater discharge compared with the water isotopes. However, in addition to this advantage, it should be noted that Sr isotopes can vary through WRI and might overestimate the groundwater contribution to streams, especially when the groundwater discharge does not dominate the hyporheic exchange rate. We would, therefore, conclude that the combined use of multiple tracers, including Sr and water isotopes and geochemical tracers, is recommended for examining the water mixture.

[Changes in the manuscript]

To reflect all these changes, we moved all the results regarding the endmember analysis from the discussion in the previous manuscript. In the revised manuscript, we also expanded the discussion, describing the use of multiple isotopes and geochemical tracer for understanding the hydrological cycle.

Specific comments:

Almost all the references are cited in the introduction. The main text, and especially the discussion, should refer to appropriate references. Note that only 23 references are cited, which is not enough considering the 3 applied approaches and the abundant available literature available for each approach.

[Response]

As described in the response to the general comment, we have expanded the discussion section on the contribution of groundwater discharge and hyporheic exchange from multiple tracers. We have also added several references accordingly.

Samples dedicated to Sr isotopes analysis must be filtered and acidified to pH 2 with suprapure HNO₃. Authors probably do it this way and this should be specified. Sr isotopes analysis: change $^{87}\text{Sr}/^{86}\text{Sr}$ of 8.37. . . . to $^{88}\text{Sr}/^{86}\text{Sr}$ (page 4, line 17).

[Response]

The description has been corrected as follows.

[Changes in the manuscript]

(previous manuscript) we collected two bottles of water (50 mL), one for Sr isotopes and the other for stable isotopes of water. Both samples were filtered through 0.20 μm membrane filters.

(revised manuscript) we collected two 50-mL polyethylene bottles of water, one for Sr isotopes and the other for stable isotopes of water. Both samples were filtered through a disposable cellulose acetate filter (pore size, 0.2 μm ; DISMIC 25CS020A5, Advantec, Tokyo, Japan).

(previous manuscript) The values of $^{87}\text{Sr}/^{86}\text{Sr}$ were normalized to a $^{87}\text{Sr}/^{86}\text{Sr}$ of 8.375209.

(revised manuscript) The values of $^{87}\text{Sr}/^{86}\text{Sr}$ were normalized to a $^{88}\text{Sr}/^{86}\text{Sr}$ of 8.375209.

Sr concentration analysis method is not reported: please add it with the uncertainty.

Water isotopes analysis too poorly explained: especially using laser method, the salinity effect of the samples should carefully considered. Here we have no idea of the electric conductivity or TDS of the samples to evaluate a potential impact. More generally, the manuscript would benefit to have a brief overview of the major elements concentration.

[Response]

Sr concentration and other rare elements were analyzed with ICP-MS, and the major elements were analyzed with ion chromatography. While we are currently working on the analysis of the principal component among these elements, which will be published in our next paper, we will add a table that describes the concentrations of the major and rare elements and water and Sr isotope ratios in the supplement of the revised paper.

The chloride concentration in the groundwater samples ranged from 2.83 to 13.18 mg/l during the irrigation period, and from 0.99 to 15.13 mg/l during the non-irrigation period. This low chloride concentration indicated that there have been little effects of salinity on the analysis water isotopes.

For water isotopes, the uncertainty for both O and H measurements should be added.

[Response]

We added the measurement errors for O and H in the revised manuscript. The relative errors of the standard material during the analysis for all the samples were less than 0.02‰ for $\delta^{18}\text{O}$ and 0.15‰ for $\delta^2\text{H}$.

Section 2.2.1: specify the measurements period, over a same day, week, . . . ? what as the weather during that period ?

[Response]

We have added a description about the weather and the measurement period. We also added a figure that depicts the seasonal variations in precipitation and groundwater table of the watershed.

[Changes in the manuscript]

The groundwater and surface water sampling were conducted during three consecutive days in each of the irrigation and non-irrigation period (21–23 June 2016 and 12–14 October 2016). To minimize the effect of precipitation on surface water sampling, we determined the sampling date in which cumulative precipitation for one week before the sampling periods were less than 20 mm. The average temperature during the surveys were 22 and 15°C for the irrigation and non-irrigation periods, respectively.

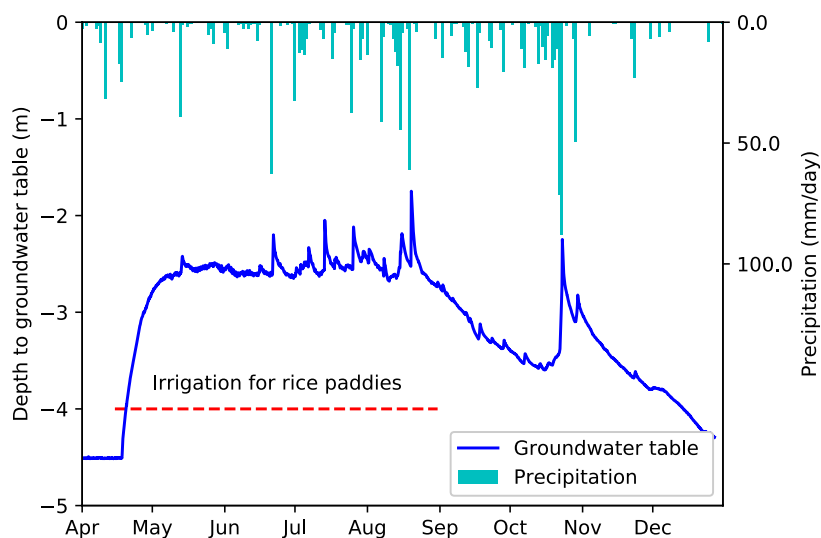


Figure 2 Seasonal variations in precipitation and depth of the groundwater table.

Section 2.2.2: Equation 3 is not very clear, why not simply using for [Sr] and Sr isotopes (with $R = 87\text{Sr}/86\text{Sr}$, $C = \text{Sr concentration}$, $f = \text{fraction of endmember 1}$) : $R_m = [f(R_1 \cdot C_1) + (1-f)(R_2 \cdot C_2)] / C_m$ and $C_m = f C_1 + (1-f) C_2$ Specify that equation 4 is only true for stable isotopes of the water molecule.

[Response]

Equation (3) was directly derived from the reference (Faure and Mensing, 2009), and it was used for explaining ‘the $87\text{Sr}/86\text{Sr}$ of a mixture of two water samples A and B is a linear function of the inverse of the Sr concentration in the mixture’. For the estimation of the mixing ratio of water A and B, equation (4) in the previous manuscript can only be used for water isotope. We added the equation for the mixing ratio using Sr isotopes: $f_a(\text{Sr}) = (C_m R_m - C_b R_b) / (C_a R_a - C_b R_b)$. This equation is also derived from Faure and Mensing (2009).

[Changes in the manuscript]

The existing ratio of water sample A in the mixture, f_a , can be calculated using two isotopes: $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$. The existing ratio of A estimated with $^{87}\text{Sr}/^{86}\text{Sr}$, $f_a(\text{Sr})$, can be calculated with Eq. (4):

$$f_a(\text{Sr}) = (C_m R_m - C_b R_b) / (C_a R_a - C_b R_b) \quad (4)$$

The existing ratio estimated with $\delta^{18}\text{O}$, $f_a(\text{O})$, can be calculated with Eq. (5):

$$f_a(\text{O}) = (R_m - R_b) / (R_a - R_b) \quad (5)$$

where R_a , R_b and R_m are the values of $\delta^{18}\text{O}$ in the sample A, B and the mixture.

Section 3.1.2: line 9: . . . because of mixing with fractionated water . . . Could we also consider that water has undergone direct evaporation and not only a mixing with an “older” evaporated water?

[Response]

The concentration of Sr in the paddy with slower irrigation rate was 1.6 times higher than that with the higher rate, suggesting that 38% of ponded water was evaporated in the slower rate paddy. Changes in $\delta^{18}\text{O}$ due to evaporation can be estimated with the Craig-Gordon model; and the model indicates $\delta^{18}\text{O}$ increase by 3‰ from 38% of evaporation from the water surface. This is consistent with the difference in $\delta^{18}\text{O}$ between the paddies with slower and faster irrigation rate, 3.8‰. Thus, we would argue that the increase in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in both slower rate paddy was simply owing to the evaporation from the water surface, not owing to the mixing with the fractionated water in the paddy.

[Changes in the manuscript]

(previous manuscript) water at the lower rate outlet was depleted in light isotopes, likely because of **mixing with fractionated water in the paddy**.

(revised manuscript) water at the lower rate outlet was depleted in light isotopes. Considering the Sr isotope result mentioned above, this result is **likely due isotope fractionation by the evaporation of paddy water**, which is derived from irrigation water and rain water.

Section 3.2.1: in this section, the choice of the groundwater end-member (ODK / SAK) need to be better explained and argued as we note that the local wells present great variations for Sr isotopic signatures (figure 6).

In the same way in figure 7 and the text referring to this figure, the end-members “surface water” derived from the irrigation channel and the “groundwater end-member(s)” derived from the springs SAK and ODK should be explained.

[Response]

As described in the response to the general comment, we created a new section (3.3.1) to explain how we determined the endmembers. Figures 6 in the previous manuscript that illustrated variations in Sr isotopic compositions of all the samples helps to highlight the groundwater sampled near the stream (within 200 m of the stream; red circles) is concentrated near the samples from the spring, ODK, while other sampling wells were highly scattered in the figure. We highlighted that the points presumably interact with the stream in a box with orange line.

We determined the endmember of the groundwater at the crossing of the two lines in Figure 7 (previous manuscript): the regression line of the stream water samples and the horizontal line from the plot of ODK ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7074$). For the surface water endmember, we also used the regression lines. The regression lines for the irrigation and non-irrigation periods crossed near the plot for the irrigation water; and we chose this crossing as the surface water endmember.

It is also worth noting that $^{87}\text{Sr}/^{86}\text{Sr}$ of the two springs in the upstream (SAK) and in the downstream (ODK) exhibited similar values, whereas $\delta^{18}\text{O}$ of them were totally different.

Section 3.2.2:

lines 25-30: data plotting below the LMWL have an explanation, the studies cited give this explanation, it's not only an observation.

[Response]

Thank you for bringing this to our attention. The cited references indicate that seasonal variations exist in deuterium excess (d-excess) in precipitation over large part of the East Asia. We have revised the expression accordingly.

[Changes in the manuscript]

(previous manuscript) ... was consistent with the **observation** that ...

(revised manuscript) ... was consistent with the **explanation** that ...

Line13 page 9: data from the paddy define a line with a slope of 5.1, is this value in agreement with local annual humidity?

[Response]

The relative humidity in this region is approximately 75% in summer (from June through to August) at the Utsunomiya meteorological station, located 20 km from the watershed. The

observed slope for the rice paddy water in this study, 5.1, was less steep than the estimated slope from the Craig-Gordon model (approximately 6) but consistent with the observed slope (ranging from 4 to 6) in other rice paddies in Japan (Hamada et al., 2004; Tsuchihara et al., 2011, Tsuchihara et al., 2016).

[Changes in the manuscript]

(previous manuscript) the measured $\delta^{18}\text{O}$ at the outlet suggests that the effects of kinetic fractionation resulted in different $\delta^{18}\text{O}$ values that depended on the rate of irrigation

(revised manuscript) the measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ at the outlet suggests that the effects of kinetic fractionation mainly due to evaporation resulted in different $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values that depended on the rate of irrigation.

Tsuchihara, T., Yoshimoto, S., Shirahata, K., and Ishida, S. (2016): ^{17}O -excess and stable isotope compositions of rainwater, surface water and groundwater in paddy areas in Ibaraki, Japan, Transactions of The Japanese Society of Irrigation, Drainage and Rural Engineering, 84 (2), I_185-I_194.

Tsuchihara, T., Yoshimoto, S., Ishida S., and Imaizumi, M. (2011): Classification of recharge sources of groundwater in a paddy dominant alluvial fan based on geochemical and isotopic analyses, Technical report of the National Institute for Rural Engineering, 211, 21-34.

Hamada, Y., Yabusaki, S., Tase, N., and Taniyama, I. (2004): Stable isotope ratios of Hydrogen and Oxygen in paddy water affected by evaporation, Journal of Japanese Association of Hydrological Sciences, 34(4), 209-216.

Section 4.1:

line 17 : specify why percolation has no effect on stable isotopes of water molecule.

Lines 23-24: not clear, do you mean that spring (ODK) water reflect the buffering effect of the aquifer?

[Response]

Gehrels et al. (1998) observed $\delta^{18}\text{O}$ in soil water at different depths and found that the values near the ground surface varied in time, reflecting temporal variations in recharged water, while it converged with depth to the average of the variation. Water isotopes obtained at depths of 1.0 and 1.5 m were almost similar and close to the values of the average of two water samples obtained

in the paddy fields with different irrigation rates. This observation suggests that the water isotopes in the soil can average the variations in the isotopic compositions from rice paddies.

The values of the water isotopes obtained at the soil water sampling plot, which is close to the apex of the fan, were similar with the values obtained at the spring, ODK, which is located at the toe of the fan. This can be explained by the buffering effect of the aquifer.

[Changes in the manuscript]

(previous manuscript) While the stable isotopes in ponded water changed in many ways, percolation appeared to have little effect on water isotopes in subsurface flow, ...

(revised manuscript) While the stable isotopes in ponded water changed in many ways, the isotopic composition appeared to converge to the average of the surface water variation through percolation.

(previous manuscript) This lower variability suggests that spring water isotopes were spatial and temporal averages.

(revised manuscript) This lower variability suggests that spring water isotopes reflected the buffering effects of the regional aquifer.

Gehrels, J.C., Peeters, J.E.M., De Vries, J.J., Dekkers, M. (1998) The mechanism of soil water movement as inferred from ^{18}O stable isotope studies, Hydrological Sciences Journal, 43(4), 579-594.

Section 4.2.1:

lines 6 to 16: this part can be shortened (too descriptive in the discussion section).

Figure 12 can also be removed.

[Response]

As described above, we would like to retain these figures because they support our argument.

Line 31 and followings: How is calculated the fraction of groundwater estimated from Sr isotopes in Br 1 and Br 23? from figure 7, Br1 is constituted of less than 10% of groundwater and Br23 has the signature of the groundwater end-member, i.e. almost 100% of groundwater . . . Please clarify.

Same thing for the global calculations in figure 13 and 14. In figure 14, colors are inversed compared to figure 13, to be checked.

[Response]

As described in the response to the general comment, we have clarified the endmember determination and corrected the inconsistency in the calculated groundwater ratios in Figures 13 and 14 (previous manuscript). The groundwater ratios at Br-23 constituted more than 90% of groundwater for both the irrigation and non-irrigation periods. We examined the similarity and discrepancies of the estimated groundwater ratios using Sr and water isotopes and discussed it, incorporating the chloride concentration of the stream. We also corrected the use of colors in these figures (see above response to general comment).