

***Interactive comment on “Dissolved inorganic carbon export from carbonate and silicate catchments estimated from carbonate chemistry and  $\delta^{13}\text{C}_{\text{DIC}}$ ” by W. J. Shin et al.***

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General comments:

1. Presented data and descriptions include several interesting and important information. The document itself is valuable as a report of a case study on isotopic characteristics of DIC of groundwater and streamwaters in headwater catchments, but the conclusion is not new. It might be true that case studies on this type of topic have not been appeared frequently, and is understandable of the importance of data set of this study. However, to answer the question of whether the DIC dynamics and amount in the

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headwater catchments are important for the global carbon budget estimation, precise estimation of its contribution to global scale carbon budget. The authors concluded that “the importance of dynamic carbon exchange occurring at headwater regions and its variability with catchment lithology for a more reliable carbon budget in river systems”. Second half of this sentence is grammatically confusing. Should write “importance of evaluation of variability with catchment lithology for a more reliable carbon budget in river systems. I do not believe that sufficient data sets and discussions have been made in the paper.

Reply: As the referee pointed out, the implication of this study (and dataset) for global carbon budget may not be generalized and quantified due to the possible heterogeneity of the headwater settings depending on hydro-geological, vegetation and climatic factors. We’ll make this point clear in the ‘Conclusion’ section in the revised manuscript.

“...its variability with catchment lithology...” will be rephrased as “...the evaluation of its variability with catchment lithology...”.

2. There are several questions on results and discussion. In the carbonate catchment, the alkalinity of streamwater is lower than that in spring water, although the EC of streamwater is higher than that of spring. Usually, alkalinity changes closely with EC, because that is often altered by the amounts of mineral cations. What kind of mechanisms could explain this disagreement? Or, weren’t these differences of Alk, and EC significant?

Reply: Alkalinity and EC generally correlate positively if mineral weathering is the major control. However, Hill and Neal (1997) reported decoupled variations between Alkalinity and EC in stream waters of small headwater catchments. In their study, EC increases were often associated with Alkalinity decreases when soil- and surface-derived water components (with nutrients and organic acids) increased in the stream waters. Since cation and anion compositions of the studied waters were not analyzed, we cannot determine the major control of EC variation. We assume a comparable condition

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to Hill and Neal (1997) study, i.e., the higher Alkalinity in the carbonate groundwater was the result of carbonate basement weathering, while the lower alkalinity with the higher EC in the carbonate stream water was caused by the variable input of soil water component. We will mention Hill and Neal (1997) study as an example of decoupled EC and Alkalinity variation in the revised manuscript.

Hill T. and Neal C. (1997) Spatial and temporal variation in pH, alkalinity and conductivity in surface runoff and groundwater for the Upper River Severn catchment. *Hydrology and Earth System Sciences*, 1(3), 697-715.

3. It is reasonable that pCO<sub>2</sub> of the spring waters were higher than those in stream waters both at the silicate catchment and carbonate catchment. However, pCO<sub>2</sub> of spring water (meaning, groundwater) in the silicate catchment was much higher than that of the carbonate catchment. The difference of those was larger than the difference between spring and stream. Additionally, seasonal variation with high in summer was significant in the pCO<sub>2</sub> of the spring water of the silicate catchment. As the authors mentioned, increase of pCO<sub>2</sub> in the spring water was caused by the soil gas CO<sub>2</sub> supplied through the decay process of soil organic matters by the microbes and roots respiration. This indicates that there was a significant difference in the CO<sub>2</sub> supply by root respiration and degradation of soil organic matters in soils between the silicate and carbonate catchment. If there is this difference, it is not ideal comparison between these two catchments, because the conditional differences were multiple.

Reply: As the referee pointed out, there may be possible difference in organic decomposition processes in soils between two catchments. Our assumption of similar soil decomposition processes is based on the fact that vegetation, climatic and hydrological conditions in both catchments are not dissimilar. We agree on the referee's point that the possible variability in soil carbon dynamics may exist with basement lithology but, at this point, supporting evidence is limited due to the paucity of relevant studies. We will add this discussion in the 'conclusion' section in the revised manuscript.

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As was explained in the manuscript, the difference in pCO<sub>2</sub> and its seasonality in spring waters between silicate and carbonate catchments is, by itself, the reflection of the disparate carbon exchange processes occurring at soil and groundwater reservoirs in each catchment. We assume that the difference mentioned above was not caused by the difference in soil microbial and root respiration processes, but by the difference in the subsurface weathering processes (weathering of carbonates vs. silicates) which were unique in each catchment. For example, the lower pCO<sub>2</sub> and reduced seasonality in pCO<sub>2</sub> in the carbonate catchment was caused by the weathering of carbonates and associated changes in pH and the ratio of CO<sub>2</sub>/HCO<sub>3</sub><sup>-</sup>. Therefore, the studied setting is assumed to be adequate to examine the variability in carbon exchange processes with catchment lithology.

Individual comments:

See the attached PDF file with my comments added directly on the PDF document.

Reply:

p. 1802 line 27: Doctor et al. (2008) will be listed in the reference with correct year of publication.

p. 1803 line 2~4: '...to investigate factors controlling d13CDIC. ....' will be rephrased to '...to investigate the effect of catchment lithology on d13CDIC. ...'.

p. 1803 line 10~11: 'at upstream catchments' will be rephrased to 'in the studied catchments'.

p. 1803 line 23: The distribution of C4 plants in the study area and its possible difference between two catchments are not clear due to the lack of quantitative studies on this subject. We take this as a part of uncertainties in our estimation of d13C of soil organic material and will be mentioned in the revised manuscript.

p. 1804 line 5~10: Map will be re-drafted to indicate the catchment boundaries and lithology more clearly, and also to clarify the association between spring and stream

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waters in each catchment.

p. 1804 line 12: The manufacturer of the equipment will be indicated in the revised manuscript.

p. 1806 line 22: '...may have retained the pristine characteristics of the groundwaters..' will be rephrased to '...may represent the characteristics of the groundwaters..'

p. 1807 line 1: The citation indicates the source of the ratio and will be specified in the revised manuscript.

p. 1807 line 12: As discussed previously, the effect of C4 plants cannot be quantified.

p. 1807 line 23: By taking the referee's comment, we will specify the physiology of the degassing from the spring water. Degassing is assumed to occur mainly during discharge of groundwaters. We also consider that the lower pCO<sub>2</sub> during non-growing season (e.g., winter) was related to the reduced production of soil CO<sub>2</sub> as the referee pointed out.

p. 1808 line 3~4: The possibility of different soil processes will be discussed in the revised manuscript.

p. 1808 line 13: Since the stream water pCO<sub>2</sub> was mostly greater than the atmospheric equilibrium, the process is more likely 'CO<sub>2</sub> degassing' rather than 'CO<sub>2</sub> exchange'.

p. 1808 line 20~25: Saturation state of dissolved oxygen is the only parameter that can indicate the effect of aquatic photosynthesis in our dataset. As we discussed in the text, the stream water was dominantly photosynthetic, but our interpretation was that aquatic photosynthesis (as indicated by dissolved oxygen contents) was not a major control of d13CDIC variations as manifested in Fig. 5.

p. 1809 line 17: Reply to this comment is the same as above.

p. 1809 line 20~21: The references were chosen as examples of soil CO<sub>2</sub> input into the stream waters. We'll clarify the meaning of references in the revised manuscript.

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p. 1810 line 2~3: EC can increase as a result of the input of mineral weathering products and/or the input of soil water with nutrients and organic acids/bases. In this study setting, we assume the second possibility as a cause of EC increase and simultaneous Alkalinity decrease in carbonate stream waters as compared to carbonate spring waters.

p. 1810 line 5: The citation is an example of EC decrease associated with rapid turnover of soil waters due to seasonally concentrated precipitation.

p. 1810 line 5~7: As the referee indicated, the same hydrologic and climatic conditions exist for both catchments. However, due to different basement lithology and associated water chemistry, the effect was more pronounced in pCO<sub>2</sub> variation in silicate catchment, while the effect was manifested in EC variation in carbonate catchment.

p. 1810 line 22~24: By adopting the referee's comment, '...produced by soil respiration..' will be changed to '...produced by increased soil respiration..'

p. 1810 line 24~25: Weathering of carbonate minerals increases pH of water thereby decreasing the ratio of CO<sub>2</sub>/HCO<sub>3</sub><sup>-</sup>. This is why the pCO<sub>2</sub> was lower in the carbonate catchment and its variability was not notable.

Fig. 1: will be re-drafted.

Fig. 4: We assume that EC varied mainly by the input of soil water with varying residence time in relation to water regime change.

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