

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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Individual scientific issues: I benefit from having seen the previous interactive comments and some of what I would have said has been voiced in other reviews and responded to by the authors, so I will not focus on these. I too consider that the interpretation is hypothetical as this is a study sampled over several significant gradients (scale, time, lithology) with one the of most important being the least-well constrained: the soil C composition and relative contribution of C3 or C4 derived CO₂ to run-off. To unravel this properly the authors need data on land-use and soil isotopic composi-

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tions proportionally in each catchment and this appears from a response to a previous reviewer, problematical. However, I would urge the authors to try and find this data or sub-samples soils to see how the distribution varies. This is important to properly assess soil CO₂ budgets: mixing of C4 in carbonate catchments will provide a very different range to C3 in carbonate catchments.

Reply: We agree on the referee's comment regarding the uncertainties in isotope compositions of soil carbon which was also pointed out by other reviewers. To resolve this problem, we conducted a survey on the carbon isotope composition of soil organic materials in both catchments. Soil samples were collected near the springs and from the deposits near the river outlets to obtain representative soil organic carbon for catchments. $\delta^{13}\text{C}$ of soil organic carbon ranged from -27.1 to -22.1 permil. $\delta^{13}\text{C}$ tends to increase with the soil depth and no distinction in $\delta^{13}\text{C}$ of soil organic carbon was observed between two catchments. The litter layers (relatively recent organic components) have similar $\delta^{13}\text{C}$ values in both catchments ranging from -31.1 to -29.3 permil. Although detailed soil carbon dynamics may not be constrained by this survey, the similar $\delta^{13}\text{C}$ of soil organic carbon in both catchments suggest that the distinct carbon isotope ratios of DIC in each catchment are not the result of different organic carbon input into the hydrologic systems. This new isotope result will be added in the revised manuscript.

In addition to the C3/C4 issue compromising clear interpretation I would like to see an expansion in the uncertainties section of discussion acknowledging the uncertainty associated with bi-weekly sampling in terms of the budget calculations of export and CO₂ outgassing. I refer the authors here to Jarvie et al, 2001, Tetzlaff et al, 2007 and Waldron et al., 2007 as examples of detail generated by semi-continuous covarying logged parameters. Of particular relevance here is Waldron et al 2007, which reconstructs semi-continuous profiles from isotopic end-member mixing models and, details the amount of local variation that can take place under changing hydrographic conditions such as event flow. Bi-weekly sampling does not capture significant shorter detail

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that if included may significantly change budget and source estimations. The plotting of the rainfall profile is useful but more incisive would be the hydrographs. They often scale with catchment size – but I can accept in a karst landscape this may be less straightforward – so although not measured at sampling points may provide more detail on flow influences that the rainfall profile which will only be reflected in flow (including at springs) after influence by the degree of catchment saturation / recharge. There is a suggestion of the plot against rainfall of hydrological response by control of source of DIC to the catchment but could this be explored in more depths with hydrographs for each stream sampling point that rainfall? It may even allow end member mixing models (suggested by Figure 4a).

Reply: As the referee pointed out, a continuous monitoring of river chemistry along with hydrograph will provide a better insight for riverine carbon dynamics. Especially, carbon exchanges associated with rapid hydrological changes can be better monitored. For the study sites, the remote location hampered the implementation of on-site continuous hydrological monitoring. Therefore, it is not possible to quantitatively analyze concentration and carbon isotope ratios of DIC in the context of detailed water regime changes (e.g., discharge), as the referee suggested. At the later part of section 4.4, we will add discussions on the uncertainties associated with our 'spot sampling' by comparing with the type research design from Waldron et al. (2007).

Specific comments: 1. Some of the references used could be additionally more recent e.g. I think there may be a more up-to-date reference than Maybeck 1987 of C export by rivers that the authors should seek to cite, similarly I would also refer the authors to Cole et al (Plumbing the Global Carbon Cycle, Ecology, 2003?) for global C reprocessing and outgassing.

Reply: We will add total C flux of 0.9 Peta gC reported by Cole et al. (2007) along with inorganic carbon flux of 0.43 Peta gC from Meybeck (1987).

Cole, J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G.,

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Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J. and Melack, J. (2007) Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget. *Ecosystems*, 10, 171–184, DOI: 10.1007/s10021-006-9013-8

2. Page 1082, lines 18: 'Based on stoichiometric considerations, the proportion of soil CO₂ in rivers ranges from 50% in carbonate catchments (another 50% is from the carbonate minerals) to 100% in silicate catchments' I think this is a considerable oversimplification only applicable where there is no soil cover: in silicate catchment headwaters overlain by considerable peat depth for example, a large proportion of DIC in the river is soil-derived, as identified by isotopic composition (see for example, Waldron et al 2007).

Reply: In general, soil layers are less developed in mountainous Korean watersheds and accumulation of peats are also uncommon. While the assumed ratios may be simplified, the numbers are still meaningful for theoretical stoichiometric calculations. We will modify the expression regarding the ratios such that the ratios can be oversimplification in natural conditions.

3. I think in addition to a geology map a crop/soil map is needed as there is a mix of C₃/C₄ vegetation (-27/-14) and this could compromise isotopic interpretation. Currently there is insufficient info to assess the relative contributions of C₃/C₄ soil CO₂ contribution

Reply: Reliable crop maps are not available in the study area. In this mountainous region, the cropland occupies relatively small proportion and the type of crops changes seasonally and annually. We tried to resolve the uncertainties associated with C₄ distribution by measuring carbon isotope composition of soil organic carbon for both catchments. As explained in the earlier part of this reply letter, $\delta^{13}\text{C}$ of soil organic carbon was from -27.1 to -22.1‰ and tends to increase with the soil depth. Importantly, no distinction in $\delta^{13}\text{C}$ of soil organic carbon was observed between two catchments.

4. Section 2.2: did water always discharge at 37 m³/day and if so how was this mea-

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sured? How quickly after sample collection was alkalinity measured? Isotopic analytical reproducibility was measured on what (a DIC samples, a lab carbonate?) and calculated from how many samples?

Reply: The spring discharge was measured manually at the field for four times in 2005 to cover the seasonal changes in water regime. Alkalinity was measured on site along with other variables. Reproducibility was determined by (1) duplicate sampling and analyses of water samples, (2) analyses of lab. carbonate standard and NBS standards.

5. Sections 3.1 and 3.2 effectively repeat of the content of Table 2 bar the conversion of DO to % saturation and the temperature data. but if there is no page limitation as an on-line journal then useful to have both

Reply: In the revised manuscript, the repetition of numbers will be removed and characteristics of the data will be explained.

Technical corrections and typing errors: 1. The word 'values' is not needed after a measurement category e.g. $\delta^{13}\text{CDIC}$, pH. We not use it after length; it is sufficient to use just 'pH ranged from. . .' or ' $\delta^{13}\text{CDIC}$ ranged from. . .'. We would not say length values, or weight values for example.

Reply: 'values' will be removed unless if there is a clear need to use it.

Re Table 2: Font size in table 2 is far too small – this will not be legible in a printed version. Data has been justified around decimal point but looks strange: centre justification may be better. The number of measurements also needs to be included to allow to the reader to gauge the sample size. I do not find DO in mg/L a useful measurements as the solubility is temperature dependent. I think this data should also be presented as % dissolved oxygen saturation - the river may always be at full saturation but absolute concentration can vary due to temperature; presenting the data as a concentration alone masks this. I appreciate this is given in 2.

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Reply: The font sizes will be increased and dissolved oxygen will be reported as saturation index.

Legend in Figure 3: no need for the phrase 'and normalised to catchment area' as this is apparent from the units (m^2)

Reply: 'normalized' will be removed.

3. Fig 1. As this paper depends so heavily on the geology I think it would be useful to also have a cross-section of the geology e.g. does the sandstone underlie the limestone or vice versa. This is needed to provide support that the spring waters represent the lithology of sampling alone.

Reply: Instead of adding cross section, the following sentence will be added to help clarify geology of the study area.

"The lower reaches of the carbonate catchment consist of Ordovician limestones and both spring and stream water samples were collected from the same rock formation. The siliceous (meta-) sedimentary rocks that constitute silicate catchment and part of carbonate catchment unconformably overlie Ordovician limestones. In the silicate catchment, the thickness of (meta-) sedimentary rocks is known to be greater than ~500m and both spring and stream water samples were collected on the silicate basement."

4. Figures 4 are also too small. The data cloud boundary on the lower diagram is off the figure so the scale on the figure needs adjusted to accommodate this. The r^2 values need to be accompanied by p values to show how significant the regression is.

Reply: The figure will be re-drafted.

5. Notation is incorrect in Fig5 and earlier in the text: when using capital delta to show a different then small delta is not needed additionally.

Reply: The small delta will be removed.

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6. I also noted Doctor et al 2007 paper is not in the reference list, yet this a key paper to the manuscript as discusses enrichment during degassing.

Reply: The reference will be added correctly. Doctor, D. H., Kendall, C., Sebestyen, S. D., Shanley, J. B., Ohte, N. and Boyer, E. W. (2008), Carbon isotope fractionation of dissolved inorganic carbon (DIC) due to outgassing of carbon dioxide from a headwater stream. *Hydrological Processes*, 22: 2410–2423. doi: 10.1002/hyp.6833

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