

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: I consider this to be an interesting paper that combines isotopic insight with concentration and efflux measurements in two contrasting catchments. The number of papers that exist that combine these data sets is still low and thus this represents an important contribution. The paper is generally very-well written and the approach the authors taken to the interpretation is clear – it may have been useful to have had more supplementary information detailing how flux estimates have been calculated as very difficult to check these. The measured tone of the paper represents

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a hypothetical interpretation, bar in the abstract where the text is too definite and needs clarification this is interpretation, not fact. By virtue of scale and sampling intensity there is some uncertainty associated with this research, but it moves our understanding on and builds a basis for more detailed studies. Further, the geographic location of the data set further expands our global knowledge and presents the opportunity for assessing the generic nature or otherwise and fluvial isotope dynamics and CO₂ efflux budgets. For example the silicate groundwater end-member if similar to that observed in other studies (e.g. Waldron et al, 2007) and increasing this database allows future hypothesis testing studies to be formulated with more direction. For all these reasons, this paper offers a welcomed contribution. I have some comments re the soil end member sources and on confidence of upscaling of budgets, that I will address under the individual scientific issues.

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 compositions 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. 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 rel-

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evance 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 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). Jarvie et al (2001) Use of continuous water quality records for hydrograph separation and to assess short-term variability and extremes in acidity and dissolved carbon dioxide for the River Dee, Scotland *The Science of the Total Environment* 265 , 85-98 Tetzlaff et al (2007). Assessing nested hydrological and hydrochemical behaviour of a mesoscale catchment using continuous tracer data. *J. Hydrol.* 336, 430-443. Waldron, Scott and Soulsby (2007) Stable Isotope Analysis Reveals Lower-Order River Dissolved Inorganic Carbon Pools Are Highly Dynamic: *Environ. Sci. Technol.* 41, 6156-6162

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. 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

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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). 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 4. Section 2.2: did water always discharge at 37 m³day⁻¹ and if so how was this measured? 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? 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

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. 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⁻¹ 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. Legend in Figure 3: no need for the phrase ‘and normalised to catchment area’ as this is apparent from the units (m²) 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. 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

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needs adjusted to accommodate this. The r^2 values need to be accompanied by p values to show how significant the regression is. 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. 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.

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Discussion Paper

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