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Interactive comment on "A model of potential carbon dioxide efflux from surface water across England and Wales using headwater stream survey data and landscape predictors" *by* B. G. Rawlins et al.

Anonymous Referee #1

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The MS by Rawlins et al. presents an empirical model of seasonal and spatial patters in headwater stream CO2 partial pressures (pCO2). They trained this model on a sampling data set of headwater streams throughout England and Wales. For this, they make use 1) of an extensive data set of single measurements from a wide variety of headwater stream systems and 2) weekly to monthly time series of pCO2 values from three catchments. From the first mentioned data set, they select a set of catchments with catchment areas smaller than 8 km^2, after they found that for catchments up to this size pCO2 is not significantly correlated to catchment area. Larger catchments are

excluded because they show a tendency for lower pCO2 values, likely due to evasion of CO2, which would introduce a negative bias in their empirical model. Then, they combine these two data sets, i.e. the data set of single measurements from 2634 sampling locations, and the three local time series. They use a multiple linear regression to derive an empirical equation predicting headwater stream pCO2 from catchment properties and parameters describing the time within the seasonal cycle. This empirical model explains 24% in the variation of pCO2. They use this model to derive a map of headwater stream pCO2 for each month of the annual cycle throughout England and Wales in a 1km^2 spatial resolution. They combine these estimates with modelled stream flow and water temperature to derive the amount of dissolved CO2 in excess to atmospheric concentrations and by this the potential amount of CO2 evading to the atmosphere.

The subject of the MS, CO2 evasion from headwater streams, is timely and of interest for a broad readership in Biogeosciences, particularly for those interested in reconciling terrestrial C budgets. The overall methodological approach presented here is original and interesting. However, I have some concerns regarding the statistics and the empirical prediction equation as they are presented in the MS and I would like to ask for some clarifications and some major revisions (see major comments). For the rest of the MS I have only minor comments. The MS is well written and in most parts the methodology and the results are clearly presented. I suggest publication of the MS after major revisions.

Major comment:

Major comment #1: Empirical model for pCO2

You combined two different data sets:

One data set with single measurement from 2643 headwater catchments throughout England and Wales, all samples taken during summer months, excluding pCO2 values for which the instantaneous discharge was higher than the mean monthly flow; and one data set comprising three catchments with time-series of weekly to monthly samples covering the whole annual cycle.

Then you used the combined data set to derive an empirical model predicting spatial as well as seasonal patterns in head water stream pCO2. This is some-how problematic as:

1) The seasonal trends are only derived from the three catchments within the data set, for which you have time-series of pCO2 values. You report that for England and Wales a predicted stream flow, which reaches its maximum in December and its minimum in June, with the December flow being about 30 times as high as the flow in June. For the first data set of stream pCO2 values, comprising single samples taken during summer months, you excluded samples taken at above average flows. In the combined data set, stream pCO2 values for summer months with low flows dominate your statistics, whereas for the rest of the year, when stream flow is higher, you have data from only three catchments.

2) You use 11 predictors for your empirical model. That is a very high number considering the low r^2=0.24. Three of the predictors are not statistically significant and should thus not be used as predictors

I suggest following procedure for your revision: Before you combine the data sets with single measurements and with time-series, you should analyze the two data sets separately:

1) First, you should use the data set with single measurements to analyze the spatial variations during summer months and set up an empirical model of these spatial variations during summer. Then you should discuss the identified predictors.

2) Then you should describe the observed seasonality for the three catchments with time-series of pCO2 values AND concentration of free dissolved CO2. Showing the seasonality of these both variables would be interesting as the relation between both

depends on the Henry-constant and thus water temperature. Even if you would have constant pCO2 throughout the year (hypothetical assumption), you would still have a seasonality in concentration of free dissolved CO2 following the seasonality of water temperature, with high concentrations in summer when water temperature is elevated and low concentrations during winter when water temperature is low. To rule out this effect of the water temperature, you should describe the seasonality of both variables.

You should describe the seasonality per catchment and analyze the correlations to the parameters describing the time in the year but also, if available, to other parameters like water temperature or air temperature and discharge. Then you should compare these three time-series and discuss if you see differences in the seasonality and, if so, what could be the cause of these differences (like different seasonality in temperature or stream flow, differences in altitude and catchment properties). This would be really interesting and it would be nice if you discussed these differences with regard to your predictions.

A very important question here is whether or not you can confirm the seasonality in stream flow with about 30 times higher stream flow during December than during June.

When setting up the final empirical model for seasonal and spatial variations in stream pCO2, you should discard all predictors which are not statistically significant.

Major comment #2: Modelling monthly stream flow

You model monthly stream flow as effective precipitation that you derive from rainfall data in 1km resolution and data of potential evapotranspiration in 40km resolution (Page 16465, Line 18-25). You calculate the effective precipitation in the high resolution of 1km, which is problematic as the potential evapotranspiration data are in a much coarser resolution. Theoretically, it is not valid to produce geospatial output in a resolution which is higher than that of the coarsest input data set. This can cause high uncertainty in the estimated effective rainfall, particularly if you address small headwater catchments < 8 km^2 as you do in your study. You should at least discuss that problem. Another problem: the potential evapotranspiration is likely higher than the actual evapotranspiration. You should rather derive the effective rainfall by subtracting the actual evapotranspiration from precipitation. Otherwise you underestimate the total amount of effective rainfall.

To overcome this problem, I see two possibilities:

1) You should compare your modelled monthly flow with that derived from stream gauges. Than you can derive the uncertainty related to your modelled stream flow and maybe a correction factor which you could apply to your modelled monthly flows.

2) There is the data set of runoff fields in half degree resolution by Fekete et al. (2002) (for the latitudes of the UK this would roughly be about the 40 km resolution of the potential evapotranspiration data). Using these data would be the easiest option.

Generally, you should analyze some time-series of discharge from stream gauges and validate if these support the predicted seasonality with stream flow in December being 30 times that of June.

Minor comments:

Page 16455, Line 1-5: Here you can add the new global study by Raymond et al. (2013), which use a methodology which is very similar to the study by Butman and Raymond (2011).

Page 16455, Line 5-7: Here you could add the reference Regnier et al. (2013), which present a global map of river pCO2 data availability.

Page 1649, Line 8-11: If you measure the pH at the evening of the day of sampling, i.e. some hours after the sampling, how does this might affect the pH values? Can you rule out that the pH changes e.g. due to change in water temperature? Do you have instantaneous observation of pH, i.e. taken at the time of sampling? If yes, do you get differences in pH values if you compare to pH observed later?

Page 16461: Line 6-10: How is dominance of one land cover class defined? Is that simply the land cover class that takes the highest areal proportion? If yes, does this mean that the dominant land cover class does not necessarily cover more than half of the stream catchment?

Page 16461, Line 13 – Page 16462, Line 13: I do not completely understand how you assigned a nearest neighbor gauging station and transferred the information on average flow. Did you choose a gauging station that lies directly upstream or downstream, so that the discharge is about the same? Or did you pick the nearest gauging station, even if it was situated on another stream, and then considered the flow per area, so that you just can assume the same flow per area for the stream and date for which you have a pCO2 value? That should be clarified in the MS.

Page 16466, Line 2: Replace ‘free C’ by ‘free CO2’.

Page 16467, Lines 7-10: You exclude catchments larger than 8km^2 from your statistical analyses because you argue that for larger catchments pCO2 is lower due to CO2 evasion being higher than CO2 inputs from ground water and in-stream production of CO2. Among the three catchments with weekly to monthly time-series (which you also include in your statistics) there is one catchment (Eden, Pow) with an area of 10 km^2. Of course, it would not be a good idea to remove it from the statistics. But please explain that and why you make an exception for this catchment.

Page 16467, Line 20-22: The finding that non-forested area: wetter vs. dryer does not give a statistically significant contrast is very interesting. Does wetter non-forested area comprise wetlands? One would suspect wetland proportions within a catchment to be an important control on organic C and dissolved CO2 exports from the soils. Please, shortly discuss this point.

Page 16469, Line 26 – Page 16470, Line 2: Here you describe spatial differences in soil pH. Do you expect soil pH to be a control on stream pCO2? Do have a data set on soil pH? If yes, do you see a correlation to pCO2? Is soil pH correlated with land cover?

Page 16470, Line 21: Please compare this flux per total area with those given by Raymond et al. (2013) for that area. Tables with values from this publication can be downloaded from the online version of that article.

Page 16471, Line 2-3: There might be a word missing in this sentence.

Page 16471: Line 15-18: Careful with this conclusion. There should be correlations between soil properties and land use. Even if you use land use as a predictor, it is not necessarily the only control. Some soil properties found in combination with some land use classes might also have an effect on stream pCO2.

Page 16472-16473: The conclusion is written as a simple summary of the study. The conclusion should summarize the answers to the research questions and the main points from the discussion and then synthesize these main points, conclude what these findings mean for the research field and then give an outlook what future studies should take into account and which research gaps should be filled next. Please rewrite the conclusion accordingly.

Table 1: For the catchment of the Black burn you had pCO2 values from direct measurements. Do you also have observation of alkalinity and pH for this catchment? If yes, please compare calculated values vs. direct observations. You would likely get different values because this stream is draining a bog, likely low in pH and alkalinity and high in dissolved organic matter which might contribute to the titrable alkalinity.

Table 2: It does not get clear what contrats1, 2,... stand for. Neither from that table nor from Figure 5. You should either write in the table to which land cover classes the contrasts refer to, or add the numbering of contrasts to figure 5.

References

Fekete, B. M. et al. (2002), High-resolution fields of global runoff combining observed river discharge and simulated water balances, Global Biogeochemical Cycles, 16(3).

Raymond, P. A. et al. (2013), Global carbon dioxide emissions from inland waters, Nature, 503(7476), 355–359.

Regnier, P. et al. (2013), Anthropogenic perturbation of the carbon fluxes from land to ocean, Nature Geoscience, 6(8), 597–607.

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