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Comment

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.

B. G. Rawlins et al.

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We would like to thank both anonymous referees for their thorough and valuable comments on the content of our manuscript, and their suggestions for improving the paper.

Anonymous Referee 1

Major comment 1: Empirical model for PCO_2 .

You combined two different data sets: One data set with single measurement from 2643 headwater catchments throughout England and Wales, all samples taken during

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summer months, excluding PCO_2 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 PCO_2 . 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 PCO_2 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 PCO_2 values, comprising single samples taken during summer months, you excluded samples taken at above average flows. In the combined data set, stream PCO_2 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 PCO_2 values AND concentration of free dissolved CO_2 . 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 PCO_2 throughout the year (hypothetical assumption), you would still have a seasonality in concentration of free dissolved CO_2 following the seasonality of water temperature, with high concentrations in summer when water temperature is elevated and low con-

centrations 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.

Author comment: There are a number of issues to address here:

1. **statistically significant predictors:** Although on initial assessment it appears that there are non statistically significant predictors retained in the linear regression model (Table 4; IG, LM and Elev.Urban) with *P*-values >0.05, these must be included because they also occur in the model as statistically significant interactions (e.g. as Elev:IG and Elev:LM – IG denotes the land use term improved grassland and LM denotes less managed land). We must include the main effect when its inclusion has a statistically significant interaction (based on stepwise selection as described in the MS), if we are to be able to give a simple interpretation to the interaction. One cannot simply remove the main effects. The interaction between Elevation and Land Use has, as one of its interaction terms, Elev:Urban – the interaction between elevation and urban land. The interaction between Elevation and Land Use is statistically significant and so all the interaction terms must be included in the model. We have explained this

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point in revised version of the MS and retained the model in its original form.

2. **Formation of separate models for spatial and temporal data:** In exploring the temporal and spatial datasets, we had originally undertaken separate analyses of each, forming separate models with differing predictors. We felt that including these separate analyses in the main paper could detract from the central message and lead to confusion; for example we would need to present and discuss three independent linear regression models. The study already comprises a set of complex components (land cover contrasts, geomorphic and seasonal predictors) and analyses which needed to be brought together (as depicted by Figure 2 in the original version of the discussion paper) in a coherent way. However, we can see why it would be useful to present separate analyses in this way. We have therefore included separate models for the spatial and temporal data in two separate appendices in the revised version of the manuscript and refer to these in the main text when we form the full spatio-temporal model. We think this is the most effective way to address this concern. The model relating solely to the temporal data from the three headwater catchments includes two statistically significant temporal coefficients (sine and cosine of year day). The model relating solely to the headwater survey data for the summer months also includes statistically significant temporal coefficients for this restricted period.

3. **Seasonality in *PCO2* and free C for headwater catchments:** We know from our exploratory analysis of the year round data for the three headwater catchments that there is a very clear seasonal signal in *PCO2*. The datasets we have access to for these headwater catchments have different sets of associated measurements; in all cases there is stream temperature data, but there is discharge for only one (Black burn). In this case, the *PCO2* concentration-discharge relationships have already been explored for the catchment in a

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previous publication (Dinsmore and Billett, 2008) and we do not wish to repeat the full interpretation in our manuscript, but we have added a summary of it to our revision. We have collated the data as suggested for PCO_2 , free-C and temperature for all three catchments and produced a single plot depicting this (see Figure 1). The caption associated with this figure is: ‘Seasonal variations in stream water PCO_2 (μatm), temperature ($^{\circ}C$) and Free C concentrations ($mg\ l^{-1}$) for three headwater catchments: a) Blackwater, b) Pow and c) Black burn’. This figure demonstrates the seasonality in PCO_2 and free C; greater PCO_2 values and free C concentrations occur in the warm summer months by contrast to the cool winter months, whilst spring and autumn (fall) are intermediate. Note, the temporal data for the Pow catchment (plot b in the linked Figure 1) is limited to monthly samples, whilst there is much more frequent data for the other two sites. This plot also highlights the change in the relationship of PCO_2 to free C; a greater proportion of free C relative to PCO_2 at colder by contrast to warmer temperatures. We have included this Figure and an accompanying interpretation in the revised version of the manuscript. We consider that it may be difficult to draw wider conclusions from the temporal data (in relation to catchment properties and altitude; as suggested by the reviewer) because we only have a single catchment in each case (lowland arable, moderate elevation grassland and upland bog) and such interpretations would therefore be somewhat speculative. Hence, we do not think it appropriate to extend the interpretation in this way in our revised version.

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 $< 8 \text{ km}^2$ 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. Then 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.

Author comment: We have explored our original data and also data from gauging stations in England and Wales where there are records of stream flow which span the period 1961–1990. We found 8 stations with daily flow throughout this period, but these did not extend across the entire landscape of E&W, but were in areas of south Wales and northern England and so did not extend across the full range of rainfall-runoff landscape types. Monthly flow at these 8 stations varied by a maximum factor of 5 (January–July) and this made us question whether the 30-fold difference we computed and presented in our original manuscript. After considering the various options we decided the optimum solution would be to use the global runoff data at 0.5° resolution published by Fekete et al. 2002; suggested by reviewer 1. We have used these data to determine runoff at 1 km resolution for England and Wales and also to compute potential CO₂ evasion fluxes. We

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have updated our manuscript based on application of these data. Based on these data the maximum difference in monthly runoff is a factor of 14 (runoff in January $14\times$ runoff in August) and the new total runoff is 53806 Gt, which is 93% of the previous total (57840 Gt). The main effect is to slightly enhance runoff during the summer months (compared to winter), resulting in small positive runoff values in southern and eastern England (where many of these had been set to zero based on the approach taken in the original manuscript). We consider these changes address the (valid) criticisms raised by reviewer 1. The overall impact leads to an increase in total potential CO₂ evasion because of the larger runoff values for the summer months when the largest free CO₂ values occur. Another effect of this change is that the images of monthly potential flux estimates now appear blocky, due to the blocky nature of the runoff values.

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).

Author comment: We have added this to the revised version.

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.

Author comment: We have added this to the revised version.

Page 16459, 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

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pH observed later?

Author comment: The reviewer is correct and we would have liked to make instantaneous measurements of stream pH at the time of the sampling but this was not feasible given the sampling procedures adopted in the survey. We know that the general pattern of headwater stream pH from our sampling and analysis (see Figure 2) is consistent with the expected pattern across the UK landscape (low pH in base poor upland areas with little buffering capacity and higher pH values in lowland areas with greater base cation buffering capacity). However, we cannot rule out some change in pH; we do not have data where both instantaneous and delayed measurements were made.

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?

Author comment: Yes, dominance means that land cover which has the largest areal proportion, so in some catchments it may be that the dominant land cover class does not necessarily cover more than half of the stream catchment. We have clarified this in the revised version of the MS.

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.

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Author comment: We picked the nearest gauging station even if it was situated on another stream - we have made this clear in the revised version of the MS.

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

Author comment: We have modified this in the revised version.

Page 16467, Lines 7-10: You exclude catchments larger than 8km² 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 km². 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.

Author comment: We had to make an exception for the slightly large catchment area for the Pow because it was the only one that had data available which was sufficient to compute *PCO₂*, and with an intermediate elevation (between the lower elevation Blackwater (Wensum) and the higher elevation Black burn) catchments, and grassland land cover that contrasts with the other two temporal catchments. We have explained this in the revised version within the section on seasonal variations in stream water *PCO₂*.

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.

Author comment: We have discussed this in the revised version.

Page 16469, Line 26 – Page 16470, Line 2: Here you describe spatial differences
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in soil pH. Do you expect soil pH to be a control on stream PCO_2 ? Do have a data set on soil pH? If yes, do you see a correlation to PCO_2 ? Is soil pH correlated with land cover?

Author comment: Good suggestion and we have amended the discussion to include this in the revised version. Here we suggested that in agricultural soils, where the pH is maintained around neutral and fertilisers to maximize productivity have correspondingly large rates of soil respiration leading to greater production of CO_2 . This may lead to large fluxes of dissolved CO_2 , but it depends on the balance between losses to percolating water as dissolved CO_2 and gaseous CO_2 emissions from the soil surface, for which we do not have quantitative data. Referee 2 states that in their opinion dissolved CO_2 losses (through leaching) from agricultural soils should be minimal because they are well aerated and atmospheric losses are dominant. We have modified our original text to reflect this complexity. We do not have soil pH data at a sufficient resolution to examine the correlation as suggested. We would certainly expect some correlation of pH with land cover due to: i) liming of arable fields where acidity reduces crop growth, and ii) liming of improved grassland.

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.

Author comment: We have made this modification in the revised version. Our model predicts a mean annual flux of $0.44 \text{ tC km}^{-2} \text{ yr}^{-1}$ or $1.6 \text{ g CO}_2 \text{ m}^{-2} \text{ yr}^{-1}$ (expressed on the basis of total land area). This latter value is twenty-five times smaller than the figure of $40.4 \text{ g CO}_2 \text{ m}^{-2} \text{ yr}^{-1}$ for this region published by Raymond et al. (2013). We have commented on the possible reasons for this difference which we suspect are because many of the studies on PCO_2 from the UK have focussed on upland, organic rich catchments where PCO_2 fluxes are

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substantially larger than for lowland settings; the latter constitute a far greater proportion of the landscape of England and Wales.

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

Author comment: We have made this modification in the revised version.

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*.

Author comment: We have added a comment related to this point.

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.

Author comment: Although no specific guidance is provided by the journal, the conclusion section of papers (in our experience) should contain a simple summary of the findings, and should not be re-iterating the points in the discussion or future research questions (which may also have been addressed in the discussion). We have not changed the style of the conclusion.

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

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in pH and alkalinity and high in dissolved organic matter which might contribute to the titrable alkalinity.

Author comment: No, unfortunately we do not have these measurements.

Table 2: It does not get clear what contrasts^{1, 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.

Author comment: We have added the details of the contrasts as footnotes to Table 2; these contrasts were already stipulated in the text in the section headed '2.4.2 Land cover: orthogonal contrasts'.

Anonymous Referee 2

General Comment

1. The authors present a model containing 10 variables which predicts 24% of the spatial/temporal variation in *PCO2*. This suggests it has limited value. I believe that one of the main problems with this approach is that the model is predicting *PCO2* values which have been modelled themselves.

Author comment: Of course we would prefer to use direct measurements of *PCO2* but such data are rarely available across large scales, and such data are necessary if we are to build models. Many other large scale studies have used approaches for predicting *PCO2* based on measured stream water parameters (e.g. Butman and Raymond, 2013) - see further references and comments below. We consider that a model where the objective is to predict spatial (landscape scale) and temporal (year-round) variation of *PCO2* in headwater streams from widely available landscape data is actually doing a reasonable job

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if it accounts for 24% of the variation given that it so variable. We show that each of the predictors is statistically significant and is therefore worthy of inclusion in our model.

2. There is a significant N American, European (inc. UK) literature on *PCO₂* and CO₂ evasion, which is poorly represented in the manuscript.

Author comment: Throughout our introduction and discussion we cite a series of papers that we considered were important or relevant, given the approach we adopted in our paper based on analyses from a unique, large dataset of head-water stream geochemical analyses. We did not consider it necessary in our manuscript to represent more general studies on freshwater CO₂ (and its evasion) from either Europe or N. America because this could detract from a concise presentation of our approach. We do not believe a general representation of the CO₂ evasion literature would enhance our manuscript, unless there are specific studies which we have omitted that are pertinent (e.g. based on large headwater surveys?). We have not modified our original manuscript in this regard.

16455, L1: Several papers (see Kling et al. 1991 Science; Hope et al. 2001 L&O) already show that CO₂ evasion is likely to account for much, much more than 10% of NEE.

Author comment: We have added a citation to address this point demonstrating the extent to which freshwater CO₂ evasion can account for much a greater proportion of catchment/ landscape NEE.

16456, L16-17: it would be better to turn this into a testable hypothesis.

Author comment: We thank the referee for this comment. We have reconsidered how we express the distinction between Catchment Area and Stream Order in the original manuscript, highlighting the difference between the two; continuous and

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categorical data, respectively. The main purpose of using such features (channel order or catchment area) was to examine the effects of ‘scale’ on PCO_2 . By using catchment area (0.01 to 254 km²), it is possible to examine a broader range of scales – with finer divisions between them – than stream order (predominantly classes 1 to 4). We have modified the manuscript to make this clear and removed the comparison between catchment area and stream order which confused matters unnecessarily.

16457, L3-6: what is the justification for this statement or assumption? These are the areas of the catchment (headwaters) where evasion rates are known (and have been measured) to be highest.

Author comment: The point we are making here, which perhaps was not as clear as it could have been in the original manuscript, is that in general headwater streams will have larger PCO_2 values than those of greater stream order (there is strong evidence for this from the literature e.g. Butman and Raymond (2011) and in our dataset) because the former typically have short pathways connecting the channel to local soils (sometimes via shallow groundwater). The processes which lead to this are that runoff and shallow groundwater from these headwater soils entering channels will be enriched in PCO_2 because there has been limited potential for these waters to exchange CO_2 with the atmosphere. Even though headwater streams have greater potential for CO_2 evasion (compared to the higher order channels) due to the larger gas transfer coefficients associated with larger velocities and turbulent flow, the *net* loss is restricted because shallow groundwater water entering the headwaters (e.g. within a distance of a few km downstream of the point at which the water table meets the land surface to form the channel) also have the larger PCO_2 values. Further downstream, the flow paths connecting channels to soils (and the associated PCO_2) are much longer, and in all but the most permeable lithologies the total contributions to flow are considerably smaller. So downstream of headwater channels, in general the bal-

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ance shifts towards a net loss of PCO_2 . On this basis, the quantity of free CO_2 in headwater streams are an effective way to estimate the magnitude of potential CO_2 evasion. The evidence for the combination of these processes (sources, pathways and evasion losses of CO_2) is that in most larger scale datasets, PCO_2 values are larger in the headwaters than those further downstream (Butman and Raymond, 2011) and that the vast majority of CO_2 evades from the headwaters; Johnson et al. (2008) suggest up to 90% evades from headwater reaches of the Amazon basin. We have edited the revised version to make this clearer.

16457, L11-14: the authors are making a huge assumption here, that all free CO_2 evades downstream so there is no need to calculate k values. There is a significant body of literature to show that CO_2 concentrations (even in many large rivers systems) never reach equilibrium with the atmosphere. It is also unclear what the authors mean by ‘limited downstream changes in water chemistry’. The statement needs to be clarified, particularly as rivers typically show significant spatial changes in water chemistry.

Author comment: We have made a significant assumption that all CO_2 evades. However, we were careful to specify that the aim of our model was to predict ‘potential’, not ‘actual’ CO_2 evasion fluxes, so we believe our study is clear in its objectives and the associated limitations. A more complex model (beyond the scope of this study) and considerable validation measurements would be required to predict actual evasion at this scale. In terms of downstream changes in chemistry, we mean that in combining flows from a range of headwater catchments, stream chemistry becomes a mixture of these contributions so any local variations tend to be smoothed/averaged rather than accentuated. The significant changes in streamwater pH, largely due to CO_2 evasion, occur predominantly in headwater reaches of channels rather than in higher order sections. We have added a comment to clarify this.

16457, L21: this is a misrepresentation of Dinsmore et al. (2010) as I believe
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their work is based on one headwater site only.

Author comment: We have modified the ms to make it clear that we are referring to the single catchment monitored by Dinsmore et al. (2010), but also two other catchments un-related to the work referred to in Dinsmore et al. (2010).

16459, L19: “theoretical *PCO2*” is being modeled by the authors, from several variables, but it is unclear which ones (pH? temperature? DIC?). The authors need to clearly state how they are doing this in their model, so readers can evaluate it’s usefulness for themselves. It would also be appropriate (like most models) to validate it against real *PCO2* data.

Author comment: We have modified the MS to make it clear which of the measured stream water variables are being used to predict *PCO2* (pH, alkalinity and the major anions and cations plus DOC where it is available). We used the speciation code PHREEQC to compute *PCO2*; this technique is widely used (e.g. Butmann and Raymond, 2011) and has been thoroughly validated elsewhere (Neal et al., 1998; Hunt et al., 2001). We do not consider it necessary to undertake another validation exercise for our dataset.

16461, L6: the authors need to define ‘dominant’ land cover class. Does this mean >50% coverage?

Author comment: This was commented on by referee 1 and we have addressed this in our response to their comment and in the revised MS.

16461, L16: what is the BFIHOST value?

Author comment: The BFIHOST value is an index value (between 0 and 1) relating to hydrological source of river flow. It is a dataset that was derived for the UK from a combination of information on catchment baseflow index (BFI) and associated maps classified by the hydrology of their soil types and substrates (HOST).

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A BFIHOST value of one implies that river flow is entirely related to groundwater sources (no runoff contributions), whilst a value of zero implies all flow is from shallow runoff. We have added a description of the BFIHOST value to the revised MS.

16464, L8-10: It's not clear why the authors expect to find higher PCO_2 in agricultural streams; PCO_2 is not just based on soil productivity. These systems typically contain well-aerated, highly managed soils, which lose soil CO_2 rapidly to the atmosphere. Poorly drained, organic-rich natural systems are where highest PCO_2 occur because of their poor drainage and their ability to accumulate significant sub-surface CO_2 stores which connect to the aquatic pathway.

Author comment: We neglected to include further reasons why we expect PCO_2 values are greatest in streams of areas lowland agricultural areas. There are two reasons; these are areas where mean annual rainfall is substantially lower than in upland regions, so water:soil contact time in these lowland areas is longer and there is also less dilution of gaseous CO_2 . We have modified the manuscript to make this clear.

16467, L2-3: CO_2 evasion = $PCO_2 \times \text{flow}$ is a gross over-simplification, because there are so many factors which influence CO_2 concentration in the aquatic system.

Author comment: We agree that this is a simplification, but we consider that headwater stream PCO_2 provides an integrated value of a range of catchment and in-stream processes that can be used to predict the 'potential' evasion flux from the aquatic system when combined with runoff data.

Figure 7: Is the data presented in this figure realistic? The suggestion is that the highest evasion rates occur in the higher pH soils and not in the organic-rich upland areas of the UK. High pH soils produce circum-neutral or high pH streamwater, which based on the carbonate equilibrium, contains little or no free

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CO₂. I suggest the authors revisit their model as it appears to calculate PCO_2 incorrectly. Further underlying data or variables like pH and DIC, would help the reader sense-check these regional differences.

Author comment: Figure 7 does *not* suggest that the highest evasion rates occur in the higher pH, lowland soils of the England and Wales - it shows that PCO_2 values are greatest in streams of areas with higher pH soils, but these are also the areas where mean annual rainfall is substantially lower than in upland regions, so both water:soil contact time in these lowland areas is longer and there is less dilution of gaseous CO₂, which in combination account for the larger PCO_2 values. Figure 8 *does* show that the highest 'potential' CO₂ evasion fluxes ($PCO_2 \times \text{flow}$) in both winter and summer occur in upland regions (according with expectation). We do not believe our model computes PCO_2 incorrectly. The statement that 'High pH soils produce circum-neutral or high pH streamwater, which based on the carbonate equilibrium, contains little or no free CO₂' is simply incorrect. Alkalinity is independent of PCO_2 because neither PCO_2 nor the uncharged species H₂CO₃ is involved directly in charge balance. Total dissolved carbonate species, ΣCO_2 , is a conservative quantity assuming the solution cannot exchange with a gas phase. In our study stream waters are generally over saturated with CO₂ indicating that these waters are not in equilibrium with the atmosphere (i.e. although stream water at sampling is open to exchange, the waters have recently been in a closed or quasi-closed system). There are many examples from the UK where carbonate-rich groundwaters have large PCO_2 values (see Worrall et al., 2007). We do not believe there is any basis for suggesting our model-based predictions of PCO_2 are incorrect and we do not feel it necessary to provide summaries for the other regional variables as suggested.

References:

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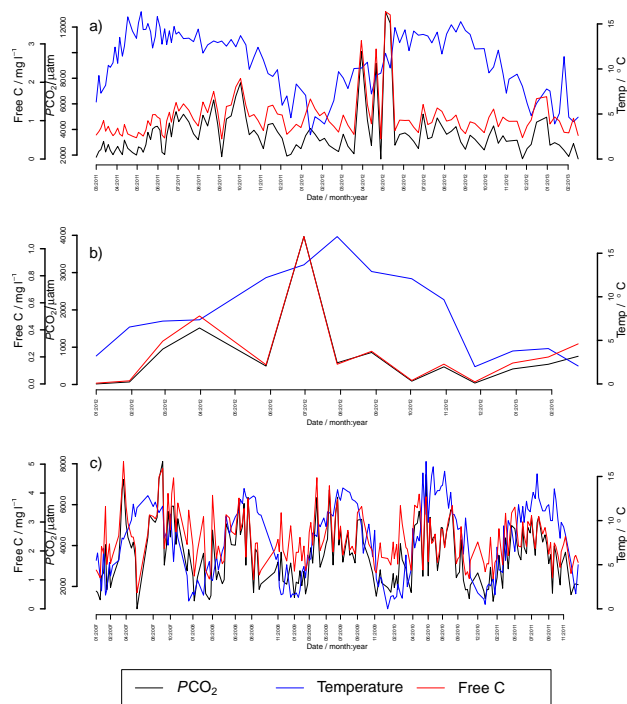


Fig. 1. Seasonal variations in stream water PCO_2 (μatm), temperature ($^{\circ}\text{C}$) and Free C concentrations (mg l^{-1}) for three headwater catchments: a) Black-water, b) Pow and c) Black burn

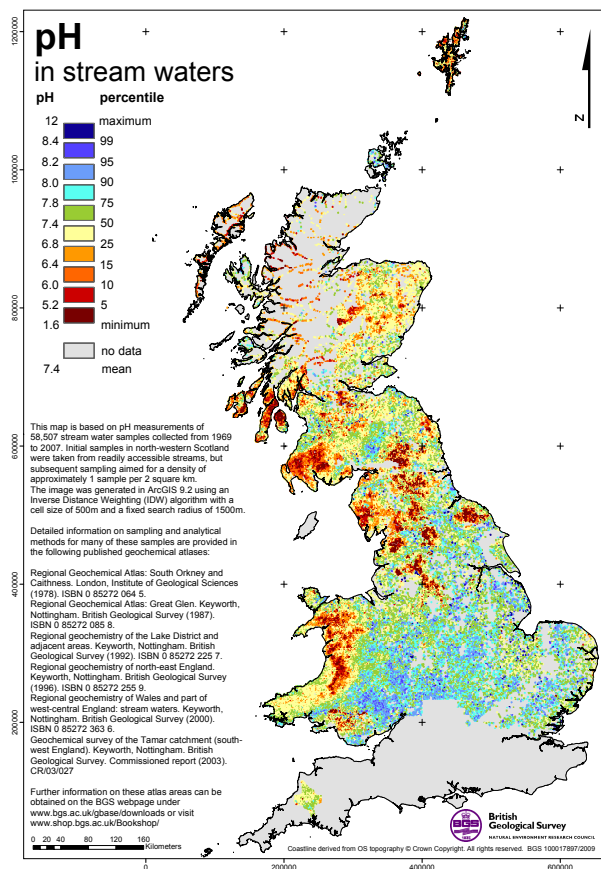


Fig. 2. Headwater stream pH across England and Wales