Swedish University of Agricultural Sciences

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Dear Editor,

Please find a new version of the enclosed manuscript 'Map-based prediction of organic carbon in headwater streams improved by downstream observations from the river outlet', which we would like to be considered for publication in Biogeosciences. We have done our best to address the concerns of the comments provided during the discussion phase. In particular we have made use of their constructive suggestions to highlight the novelty of this manuscript which demonstrates the value of river outlet chemistry in modelling the water chemistry of individual headwater streams, and the advantages of hierarchical mixed models that allow for differences between different catchment networks when using map information to model stream chemistry. We have also made use of the referee suggestions to simplify the presentation.

Below you can find our detailed point-by-point response to all referee comments, followed by a marked-up manuscript version. We hope that the manuscript is now acceptable for publication in Biogeosciences.

Yours Sincerely,

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Anonymous Referee #1

The study addresses the scientifically relevant question on how to predict water chemistry of small headwater catchments that are not regularly monitored. The study combines two different approaches on how to predict headwater stream total organic carbon (TOC): (1) A map/GIS based approach including mainly land use, soil and geological data in combination with (2) river outlet TOC data of intermediate catchments that include the headwater catchments. The study is within the scope of BG and the combination of the two above mentioned approaches is clearly novel. Nevertheless, the manuscript suffers from several major shortcomings that make it difficult to judge about the quality of the results and the conclusions. Following, I will outline my concerns that I think need to be addressed before I might recommend the manuscript for publication:

Major concerns:

i) Loosing scope of what is promised in the title and the hypothesis. The title clearly states, that the study shows how downstream organic carbon observations can improve map-based predictions of organic carbon in headwater streams. One sentence in the abstract and two paragraphs in the text outline the goal of the study: (1) Testing whether river outlet chemistry can be used as an additional source of information to improve the prediction of the chemistry of upstream headwaters, relative to models based on map information alone (P007L3ff – Abstract); (2) finding out whether the combination of map and river outlet chemistry give better prediction than either one used separately (P9008L29f - Introduction); (3) determining whether models based on geographical data can be improved by adding concentrations measured at the river outlet (P9014L7ff). It is more or less clear, what the focus of the study should be. Unfortunately the focus of the study gets lost in the course of the manuscript. One of my major concerns is that only a small paragraph in the results sections (3.3.4 Evaluation of river outlets) is dedicated to the focus of the study. Moreover, the tables and figures (Table 5 and Figures 3-5) that are linked to this paragraph are too detailed and are not able to direct the reader to the focus of the study / the results of the study. Additionally, the above mentioned table and figures are not well described in the text. I would suggest a table or figure with reduced details and a clear emphasis on the focus of the study, that outlet measurements can improve map based predictions. Unfortunately the result that outlet TOC measurements can improve map predictions is not adequately discussed in the discussion section. The first two paragraphs in the discussion section (P9021L6-18) should be rather shifted to the results section. In the discussion section, the result that the OutMap version gave 5-15% better prediction than Map only, should have been put in a broader context. What is the interpretation of this improvement? Additionally, it should have been discussed in more detail, what are potential explanations that including OutletTOC is leading to an improvement. In contrast to that, the major part of the discussion is about how the unexplained variance could be explained; this is important to be discussed, but not to such an extent that the discussion about the focus of the study is marginalised.

Thank you for these valuable comments. We understand that the referee is concerned that the discussion spends too little time on the main focus of the paper – the ability to improve predictions of headwater TOC by combining GIS information from the headwaters with outlet TOC. Furthermore, the complexity of the figures and tables made it unclear as to how they related to the main goals. We have used these concerns to guide our revision of the text.

The discussion now starts immediately with this as the subject of the first paragraph (lines 442-450 in the track changes active version) and the entire discussion deals more thoroughly with the overall goals of the paper as announced in the title. This includes

exploration of why the outlet information can lead to improvement of headwater predictions. The figures and tables have also been given more pedagogical captions that are better integrated into the text.

With regards to specifically why the outlet can provide information to improve headwater predictions, we have presented the reasoning for this in new text for Section 2.5.2 (lines 268-275) and come back to this explanation in the conclusion (lines 517-534). In this response to the reviewer we will also summarize the reasoning more thoroughly: There is a great deal of variability in TOC between headwaters (km^2 scale) in the same mesoscale catchment (10s of km^2). Many studies have shown that map info can go a long way to describing that TOC variability, but these studies are generally of many sites within one small area (10-100 km^2), or single sites spread across very large areas (100-1000 km between sites). Here we are trying to achieve a model that captures small-scale landscape variability (numerous sites in a mesoscale catchment) across a large scale region (100s of km between the mesoscale catchments). The catchment outlet is a summary of a particular mesoscale catchment. As such the outlets "normalize" the overall average TOC from one particular region to another. While this can seem intuitively correct, finding a way to achieve this is not easy using many common approaches. But this is just what mixed models (MM) are well adapted for, and why they have found use in a variety of applications. This paper has adapted the mixed model approach to the issue of predicting headwater chemistry, in this case TOC and found that the outlet does add useful information. It should be born in mind that when using landscape information together with outlet chemistry to predict headwater chemistry, TOC was the chemical parameter for headwaters that was least well modelled (Temnerud et al., 2010). Therefore applying the MM approach here to other parameters is likely to yield greater improvements.

The conclusion section contains an additional major shortcoming: It is concluded that the mixed models approach is improving predictions compared to the predictions that are solely based on outlet TOC (which was done by the author in a previous study). This is contrary to what is written in the title and the abstract (OutletTOC is improving map based predictions).

We appreciate that the reviewer noted that our conclusion was stated ambiguously, making it possible to interpret it the wrong way. As the reviewer noted from the title and abstract, what we intended to say in the conclusion was that the PLS/mixed model approach for predicting individual headwaters using both OutletTOC and map information, gave better performance than the attempt by Temnerud et al. (2010) which used only OutletTOC on headwater median TOC and TOC IQR. This is now stated more clearly in the revised conclusion (lines 517-534) so that it does not contradict what we wrote in the title and the abstract.

Moderate concerns:

ii) The experimental setup and the environmental conditions during the sampling are not well described.

We have thoroughly revised the methods section to better describe the experimental setup by including information on sampling strategies and we have also been more explicit about the experimental conditions during sampling. The new text (lines 128-142) now begins: "The synoptic surveys of mesoscale catchments used in this study were designed to provide a snapshot of the water chemistry in stream networks (Table 1, Fig. 1),

with a strategy of sampling most watercourse junctions, lake inlets and outlets as well as the river outlets from each mesoscale catchment. In total there were data from 17 synoptic surveys conducted between 2000 and 2008 in nine catchments distributed across Sweden, spanning a north-south gradient of 800 km through the north-temperate and boreal zones (Fig. 1).”

In the methods section, it is not well described, how many headwater catchments were tested.

We have revised the Method section to be more clear about the numbers of tested headwaters. This can be found in the last two paragraphs of Section 2.5.1 (lines 252-266), and in the second paragraph of Section 2.5.2 (lines 295-316). In the Results section we also clarified the cross-references to Table 5 where the numbers of tested headwaters are also stated explicitly.

How many headwater catchments are within each of the 9 larger catchments?

The number of sampled headwaters differs slightly between the different synoptic surveys for each river, and the numbers (n_{HW}) are presented in Table 2. In the original manuscript we did not cross-reference to this table in Section 2.1 Sampling Approach. We have now added that cross reference to the text (line 137).

How do the headwater catchments differ from each other in land use, soil, topography and geology?

Thank you for a great idea. In Table S1 median values of map information for each river are now stated. We have also added box-plots of map information as well as TOC for each synoptic survey, see Fig. S2-S8.

Moreover, the naming of the larger catchments is not consistent.

We have checked the manuscript thoroughly and we could not detect where the naming of the rivers (the largest catchments) is not consistent. But we can see, however, that there was a possibility to be clearer about the naming conventions. In the text the abbreviations for each river were not added, but were stated in Table 1. In Table 2 the same abbreviations are used with a suffix to designate the sampling year. What could be experienced as inconsistent is that Cluster A has the abbreviation as River Anråse å (A). We have now renamed the clusters from A, B, C to c1, c2, c3 to remove the risk for confusing “Cluster A” with “River A”.

Are intermediate sites/catchments congruent with the nine investigated catchments in figure 1?

The last paragraph in the Method section (line 339-341) reads: “As an additional step in the evaluation of the models the most successful MM from the nine MM calibrations was tested on the sites between the headwaters and the river outlets, the intermediate sites (n = 501).” So yes, the intermediate sites are congruent with the nine investigated catchments.

Additionally, information of the meteorological conditions shortly before the sampling and discharge information during the sampling would be helpful in the interpretation of the results. I am aware, that it is not possible to get detailed information about discharge anymore (although it could be of great importance to have discharge information, as TOC variations are often closely linked to discharge variations). Nevertheless, it would be helpful to have at least the information, whether there was rainfall before the sampling or whether we have high flow or low flow conditions.

Records of river flow are maintained by the Swedish Meteorological and Hydrological Institute (SMHI). So it is in fact possible to recover this antecedent flow information. At this scale much of these flow records are modelled, but the modelling has been shown to be reliable. In Fig. S1 we now add weather and flow conditions 30 days before, and during, each sampling occasion for each river outlet and synoptic survey. Information about these data are now included in Section 2.2 Study sites (lines 168-170). For each headwater upstream from one of those outlets, we expect that the antecedent patterns are reasonably similar as the weather is similar at that scale, with the possibility that individual convective storm events may vary at the scale of a few km. The lack of detailed flow data for the individual headwaters are discussed in the Discussion section (lines 460-468).

iii) Figures are not self-explanatory, not clearly laid out and not well explained. Figures 2 to 5 are not directly able to show the message that they should transport. This is a combination of several points: They are not clearly laid out and the labels are too small. Moreover, figures 3 to 5 (including their captions) are not self-explanatory or just understandable after studying them for a long time (at least when it comes to the point of understanding the message they want to transport regarding the focus of the study).

We have now increased the size of the labels. While the layout is harder to improve, there is indeed much information in the figures, especially figures 3-5. The layout is hard to simplify, but we have expanded the captions considerably to better explain the information in the figures.

For example the caption for Figure 3 now reads: "Scatterplots of measured headwaters with total organic carbon (TOC in mg L^{-1}) on the x-axis, and the three different versions of the mixed models $Cal_{MM}00_{c1}$ on the y-axis: Out version on the left panel, OutMap version on the right panel and Map in-between. Data for year 2000 ($Cal_{MM}00_{c1}$) on the top row in red text, followed by Test data; second row 2002 & 2005 data, third row is 2007 data and the last row is 2008 data. R. Anråse å indicated by circles, R. Danshytteån by diamonds, R. Getryggsån by rectangles, R. Krycklan by triangles (winter 2005 by upside-down triangles), R. Lugnån by squares, R. Mangslidsälven by multiplication sign, R. Ottervattsbäcken by up-side-down triangles, R. Vänjaurbäcken by right tilted triangles and R. Viggan by plus sign. The black line is the 1:1-line."

Minor concerns:

P9007L25f: Structure of the sentence: "The headwaters also combine to provide..."

The new sentence (lines 57-59) reads: "The headwaters also provide much of the water and solutes to downstream locations (Person et al., 1936; Leopold et al., 1964)."

P9008L10-16: These two sentences are contradictory to a certain extent; much of the small-scale heterogeneity is averaged out at larger spatial scales vs. monitoring of downstream sites might provide information about headwaters upstream. This needs further explanation and would be also an interesting question to be discussed in the discussion section.

We appreciate that there was an apparent contradiction in saying that downstream sites could provide useful information about individual headwaters even though the variation is averaged out at the downstream sties. We developed our presentation of the modelling approach (Section 2.5.2, lines 268-275) to point out that while much of the small-scale heterogeneity is averaged out at larger spatial scales, the downstream sites still might provide information about headwaters. The measurements at the river outlet proved necessary to reproduce more correct average headwater TOC levels. Excluding the OutletTOC measurements leads to the assumption that average TOC levels in the headwaters were similar in different catchment stream networks if the map information is similar, which is not always true (cf. sampling 2007 and 2008) when looking at networks that are spread out across a large landscape. It might sound contradictory that the large small-scale heterogeneity was correlated with river outlets, but the mixture of all headwaters ends up in the river outlets, and the transition time from when the water enter headwaters until it reaches the river outlet is rather small (hours to a day) in many of these systems, allowing conservative mixing of headwaters to be reflected in the river outlet chemistry.

While we wrote in the Discussion about how well this approach worked, we overlooked highlighting the value of coupling it to the scale issue of small-scale heterogeneity. We do this now by starting the Discussion section with this point (lines 443-451): ”In 25 of 27 tests, including river outlet chemistry (OutletTOC) resulted in lower errors in the mixed models predictions of the TOC for individual headwaters, and intermediate sites, compared to using map information alone. The measurements at the river outlet were necessary to reproduce more correct average headwater TOC levels (Table 5). Excluding the OutletTOC measurements leads to the assumption that average TOC levels in the headwaters were similar in different catchment stream networks if the map information is similar, which is not always true (cf. sampling 2007 and 2008). This is the first article to test how to include river outlet chemistry with map information for modelling headwaters, and how well the river outlet chemistry improved the models.”

P9009L27: “kNN”: needs explanation when firstly introduced.

We have removed the term kNN from the Introduction.

P9009L27: Wasn’t also TOC_Outlet used to derive TOC median and IQR values?

That is correct, we missed the most obvious candidate! We have now added that to the sentence (line 112).

P9011L4: I would not call spruce the dominant tree species. In several catchments, pine is the tree species with the largest volume and in most of the other catchments, spruce is not dominating but has just moderately higher volumes then pine.

That is correct. We have now rephrased the sentence (lines 152-155) to: “All sampled catchments (including headwaters, intermediate watercourses and river outlets)

consisted mainly of forest (>80%) with a dominance of coniferous forest made up of Norway 146 spruce (Picea abies) and Scots pine (Pinus silvestris) (Table S1).”

P9011L2: “All catchments”: all headwater catchments? Is this paragraph only about the headwaters?

All catchments mean both headwaters, intermediate and river outlets, in other words all 938 sampled catchments. The sentence has been revised to read (line 152): “All sampled catchments (including headwaters, intermediate watercourses and river outlets)…”

P9011L5: “Mires and small lakes made up most of the remaining parts”: Clear-felled areas are larger than the sum of mires and lakes in many catchments. I would not consider clear-felled areas as forests, especially when it comes to a study about TOC.

It is true that clear-felled areas could have another impact on TOC than the land-use class forest. In this sentence we consider clear-felled areas as part of the forest, since specific data on recently clear-felled areas was not included in the map data available to us. In the future it would be worthwhile treating recently clear-felled areas as a separate class, but in this study clear-felled areas have been treated as forest, since management practices require regeneration of the forest, meaning that what has been clear-felled is at some stage of regeneration.

P9014L25: Abbreviations like Cal_PLS_00_A are not helpful to read the manuscript in a fluent way. Maybe you can come up with a better solution, although it might be difficult to find a better solution.

As the reviewer points out, these are long abbreviations. We have considered this, and have not found a better solution, even though we have considered different approaches. We consider the one we have in the manuscript as the best way to include all necessary information, even if it is a bit long.

P9014L27: Were the mesoscale catchments sampled or the headwater catchments?

All 938 catchments were sampled, both headwaters, intermediate and river outlets (the mesoscale catchments). OutletTOC is based on the measurements at the outlet.

P9015L11ff: The assumption, that headwaters within the same catchment are more similar to each other than to headwater from other catchment, needs further explanation. I guess this depends on the similarity are heterogeneity of headwaters within a catchment and on the driving factors that control TOC behaviour.

Good point. We have tried to clarify the basis for this assumption in Section 2.5.2 Modelling individual headwaters. The start of this section (lines 268-275) now reads: When modelling individual headwaters we want to predict specific values for each of the different headwaters in all catchments. As an effort to improve these simulations, we make an assumption that headwaters within the same mesoscale catchment are more similar to each other than to headwaters from other mesoscale catchments due to subtle combinations of physiographic, weather and other factors which combine to influence the TOC levels in ways which are not readily apparent from the available map information, but might be

reflected in differences between the average TOC levels in the different mesoscale catchments. This assumption leads to a new data structure. To model this data structure we use hierarchical linear mixed models (MM; Littell et al., 2006), which allow the estimation of the correlation between headwaters within the same mesoscale catchment and adjusts the analysis accordingly.

P9018L4f: Sentence structure needs to be revised.

The sentence was changed (lines 353-354) to: "The first principal component (PC) of the PLS-model of median headwater TOC was significant for both PLS calibration sets year 2007 and 2008, but not the second PC."

P9018L19: "that is all other data than 2007": Sentence structure needs to be revised

The sentence was changed (lines 359-362) to: "The calibration of the model using the CalPLS07$_{c2}$ data was evaluated by using the test data. This yielded a PRESS for TOC IQR that was lower than when the model was calibrated using CalPLS08$_{c2}$ (Table 3)."

P9020L24: "Out of 27 different combinations": Isn't there something missing? Perhaps: In 25 out of 27 different combinations.

The sentence was changed (lines 430-435) to: "In 25 out of 27 different combinations of MM (three different calibration data sets, three versions of each calibration (Out, Map, OutMap) and three different test data sets), the OutMap version gave the best performance with the lowest PRESS, while two Map versions (map information only, no OutletTOC included) gave the lowest PRESS (Table 5 and Fig. 3-5)."

Table S1: What is the difference between no value and 0.00? Is 0.00 just a rounding effect or does it also mean no value?

"0.00" is just a rounding effect. To clarify this, the title of Table S1 now includes the sentence: "0.00 is a rounding effect, while no value means that the median value is null."

References

Temnerud, J., Fölster, J., Buffam, I., Laudon, H., Erlandsson, M., and Bishop, K.: Can the distribution of headwater stream chemistry be predicted from downstream observations?, Hydrol. Process., 24, 2269-2276, doi:10.1002/hyp.7615, 2010.

Anonymous Referee #2

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Review of the manuscript “Map-based prediction of organic carbon in headwaters streams improved by downstream observations from the river outlet” by Temnerud and colleagues. This manuscript describes an attempt to model the DOC concentration in headwaters (catchments smaller than 2 km2) from nine boreal catchments (from 30 to 235 km2) combining GIS-landscape information with DOC observations from the downriver outlet of each catchment. Authors consider this study a step forward with respect to a previous similar study (Temnerud et al., 2010). In this new manuscript the step forward consist to: i) integrate into the analysis the landscape catchment properties and; ii) the implementation of complex statistic tools. Finally, the modeling effort helps to explain up to the 52% of the TOC variance in headwaters. Authors recognize that the proportion of the explained variance is not satisfactory. However also they remark that it is better than the previous work (Temnerud 2010). Therefore the main conclusions are that: i) DOC information from outlet alone is insufficient for predicting DOC (median and variability) in headwaters and ii) that, at least in these systems, GIS based catchment data is useful to improve partially the DOC prediction in headwaters. The manuscript is well written and objectives are well stated. Tables are appropriates however figures are difficult to understand. In any case, it is extremely arduous to follow and understand the modeling approach and results description. Overall, this contribution is interesting especially in a context of water quality monitoring and management. In a scientific context this study reveals that, although the GIS provide valuable information, it is a limited tool to model accurately DOC in small catchments. This suggests that important potential explanatory variables are missing in the analysis.

My most relevant comment pivots around the selection of the potential explanatory variables. Without being and expert on PLS and mixed model and being conscious of my limitation in understanding these sophisticated approaches, it surprises to me that some explanatory variable that does not emerge in the PLS are, a posteriori, included ad hoc in the mixed model. This is the case of the “proportion of lake surface”. As point out by authors, this variable is considered important for DOC in boreal rivers (see references in the manuscript). Authors reveal that some explanatory variables are not included in the PLS analysis as “consequence of ” large number of zero values” (pag 9015). Is this the situation of “proportion of lake surface”? According to figure 1 and Table S1 most of the catchments have lakes in their drainage network. Therefore this variable should not have a “large number of zero values". Then the question is: Why the "proportion of lake surface" disappear from PLS output? If this apparently important variable cannot be included into the PLS analysis does it suggests that the PLS is an inappropriate tool? If Lake surface coverage is important and it emerges as significant variable in MM I wonder if the model calibration should to include an additional fourth version: "OutLsc": DOC outlet + lake surface coverage but no map information. This additional model run might help to weight the effective importance of the landscape parameters included in table S1. Is the GIS information overrated? Moreover, the importance of the "proportion of lake surface" also suggests that morphological structure of the river network (and the terrestrial zones surrounding the river network as well, i.e. riparian strips) might have some importance on DOC in headwaters. This comment leads inevitably to wonder why the list of potential explanatory variables do not include any parameter that might incorporate the hydro-geomorphology properties of the study streams/rivers (average main stem longitudinal slopes, river length of confluences, drainage densities).

Finally, I found anomalous the absence of some basic hydro-climatic parameter. At the discussion the authors affirm that sets Cal07 and Cal08 are measured during "different flow situations and seasons". It exists a very rich and abundant literature form the authors that explicitly explore the importance of discharge, winter climate/snowmelt and antecedent hydro-climatic biogeochemical conditions on DOC variability at the Vastrabacken catchment (see Agren et al., 2010 for an example). This headwater stream drains into the larger Nyanget catchment which is included in the present manuscript. In these studies it appears clear the importance of these hydroclimatic parameters on DOC concentration in these boreal headwaters. Therefore, having in mind this knowledge, I strongly suggest that some hidro-climatic parameter (although approximate and coarse) should be included in the analysis otherwise it will be really improbable to obtain satisfactory DOC estimation with GIS information only.

Reference cited: Ågren, A., Haei, M., Köhler, S. J., Bishop, K., and Laudon, H.: Regulation of stream water dissolved organic carbon (DOC) concentrations during snowmelt; the role of discharge, winter climate and memory effects, Biogeosciences, 7, 2901–2913, doi:10.5194/bg-7-2901-2010, 2010. Temnerud, J., Fölster, J., Bu_am, I., Laudon, H., Erlandsson, M., and Bishop, K.: Can the distribution of headwater stream chemistry be predicted from downstream observations? Hydrol. Process., 24, 2269– 2276, doi:10.1002/hyp.7615, 2010.

We appreciate both the queries in this review, as well as the finding that this paper is of interest in the context of water quality monitoring and management. For indeed it is just the challenge of living up to the EU Water Directive of protecting all water, which includes a myriad of headwaters with relatively little systematic monitoring, that is the motivation for our overall objective of finding ways to predict the situation in individual headwaters from more readily available GIS data, supported by water monitoring data from downstream sites. We note several concerns in the reviewer comments that we will reply to:

1. **Why isn't lake surface area included as a factor in PLS models: Our focus was on predicting the headwaters, and few of these headwaters have any lake area. Figure 1 shows that most headwaters lack lakes. The lakes are usually found a little bit further downstream in the investigated catchments. In the updated Table S1 the median lake surface coverage is stated, please note that this is not the number of lakes in headwaters. So including lake area would not be of much use in predicting the water quality of most (median) headwaters. And precisely as the reviewer understood from our text, it is the issue of many zero values in a PLS that led us to leave this variable out of that statistical analysis.**
2. **Morphology and catchment structure: A second concern is that information on the morphology and structure of the catchment was not included. There are indeed great possibilities for constructing map information from maps. In the spirit of objectively choosing map information we have worked through the map information directly available from public data bases. The digital network of watercourses in Sweden are in scale 1:100000, which means that most headwaters are not found on this map and are not correctly drawn. If others find the hierarchical linear mixed modelling approach useful, then the possibility is open to explore other sources of information. But given the focus on presenting a relatively sophisticated modelling approach, we have chosen not to add a new dimension of complexity in the construction of map information that may be helpful.**
3. **Complexity of the figures and model presentation: This brings us to another point of the referee, and that is the difficulty of following the tables and figures, even though the referee found the text as a whole generally well written with**

clear objectives. In this revision we have sought to be more pedagogical in integrating the tables and figures into the text. We have also rewritten the captions to better explain the figures and link them to the relevant sections in the text.

4. **The influence of hydroclimatic factors: It is true that weather conditions do influence TOC, with both season and flow rate exerting different combinations of influence on different waters (Winterdahl et al., 2015). More intriguingly, “memory effects” from the antecedent conditions in the preceding year have been identified by Ågren et al. (2010) as noted by the reviewer. However, these climatic memory effects were of secondary importance to the flow conditions and season at the time of sampling. Ågren et al. (2010) required a focused modelling effort to bring forth these memory effects. We did not seek to incorporate hydroclimatic data into our analysis due to the need for more accurate flow and weather related data (hourly-daily) for each headwater (<2 km^2) for it to be scientifically sound to include weather related data in the modelling. Recent work from the boreal region has quantified the great variability of specific discharge in the boreal landscape (Lyon et al., 2012). Even without weather data, but with river outlet TOC, we could explain up to 52% of the variation in headwater TOC. We think this is satisfactory considering the small size of the catchments. The revised manuscript discusses the difficulty of knowing the hydroclimatic conditions of the headwaters in the Discussion (lines 461-468 in the track changes active version): “In our approach we did not include the weather related data (temperature, precipitation, flow) in the models (PLS and MM) since it was not available for headwaters, but only for the river outlet. Presumably discharge for each headwater could benefit the models, but measuring discharge at all individual headwaters would have been very time consuming (and was not performed). To model discharge with appropriate accuracy at all these headwaters (size<2 km^2) is so far too difficult to perform due to large heterogeneity at these small scales (Lyon et al., 2012), and lack of precipitation data for all these headwaters.”**

References

Ågren, A., Haei, M., Köhler, S. J., Bishop, K., and Laudon, H.: Regulation of stream water dissolved organic carbon (DOC) concentrations during snowmelt; the role of discharge, winter climate and memory effects, Biogeosciences, 7, 2901-2913, doi:10.5194/bg-7-2901-2010, 2010.

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Map-based prediction of organic carbon in headwaters streams improved by downstream observations from the river outlet

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Journal: Biogeosciences
Running title: Modelling TOC in headwater streams

Abstract

In spite of the great abundance and ecological importance of headwater streams, managers are usually limited by a lack of information about water chemistry in these headwaters. In this study we test whether river outlet chemistry can be used as an additional source of information to improve the prediction of the chemistry of upstream headwaters (size <2 km^2), relative to models based on map information alone. We use the concentration of total organic carbon (TOC), an important stream ecosystem parameter, as the target for our study. Between 2000 and 2008, we carried out~~conducted~~ 17 synoptic surveys ~~of streams within~~in 9 mesoscale catchments (size 32-235 km^2). Over 900 water samples were collected in total, primarily from headwater streams but also including each catchment's river outlet during every survey~~from catchments ranging in size from 0.03 to 235 km²~~. First we used partial least square regression (PLS) to model the distribution (median, interquartile range (IQR)) of headwater stream ~~total organic carbon (~~TOC~~) median and interquartile values~~ for a given catchment, based on a large number of candidate variables including sub-catchment characteristics from GIS, and measured river chemistry at the catchment outlet. The best candidate variables from the PLS models were then used in hierarchical linear mixed models (MM) to model TOC in individual headwater streams. Three predictor variables were consistently selected for the MM calibration sets: (1) proportion of forested wetlands in the sub-catchment (positively correlated with headwater stream TOC), (2) proportion of lake surface cover in the sub-catchment (negatively correlated with headwater stream TOC), and (3) ~~whole-catchment~~ river outlet TOC (positively correlated with headwater stream TOC). Including river outlet TOC improved predictions, with~~as a predictor in the models gave~~ 5-15% lower prediction errors than when using map information alone. Thus, data on water chemistry measured at river outlets offers information which can complement GIS-based modelling of headwater stream chemistry.

Keywords: mixed model, partial least square, organic carbon, headwater, stream

1 Introduction

Headwaters make up most of the watercourse length and hence provide a large proportion of the lotic habitat in a landscape (Meyer et al., 2007). The headwaters also ~~combine to~~ provide much of the water and solutes to downstream locations (Person et al., 1936; Leopold et al., 1964). It is widely known that variability in water chemistry changes with catchment size, typically with small watercourses showing the highest variability in space (Wolock et al., 1997; Temnerud and Bishop, 2005) and time (Nagorski et al., 2003; Buffam et al., 2007). Significant field sampling efforts (Hutchins et al., 1999; Smart et al., 2001; Likens and Buso, 2006; McGuire et al., 2014) have been made to quantify the variability of headwaters in individual catchments. Readily derived GIS data from maps and satellite images have been used to model some chemical constituents in larger rivers (Alexander et al., 2007), but are seldom effective at predicting the chemistry of individual headwater streams (Strayer et al., 2003b; Strayer et al., 2003a; Temnerud et al., 2010). This is presumably in large part due to the greater importance of small-scale heterogeneity in headwater catchment characteristics, as compared to riverine catchments where much of the variability averages out at larger spatial scales (Gomi et al., 2002; MacDonald and Coe, 2007).

Since aquatic monitoring activities are generally located at downstream sites (Evans et al., 2010), this might provide information about the headwaters upstream from the monitoring sites. In an attempt to use environmental monitoring data to predict seldom assessed headwater streams, the chemistry at the river outlet was used by Temnerud et al. (2010) to predict the median and interquartile range (IQR) of several environmentally relevant stream chemistry parameters, including total organic carbon (TOC), acid neutralizing capacity (ANC) and pH. This demonstrated that the river outlets were correlated to statistical features of the upstream population of headwaters. In that study significant relationships were found for ANC, pH and TOC between headwaters median and IQR vs the river outlets, with the strongest relationships for ANC, and the weakest for TOC. Of seven different leave-one-out attempts one model was significant for headwater median TOC and none for headwater TOC IQR (Temnerud et al., 2010). No map information was employed in that study.

In this study the goal was to test whether map information can be combined with river outlet chemistry to predict TOC in individual headwaters. More specifically, would~~did~~ the combination of map and river outlet chemistry ~~gave~~ give a better prediction than either one used separately. In this follow-up study we have chosen to focus solely on the prediction of TOC, for two main reasons. First, TOC is of great ecological importance for boreal and ~~many north temperate~~other watercourses because of its influence on pH, buffering capacity, ~~bioavailability of~~ nutrient~~s~~ bioavailability, metal~~s~~ and pollutants transport, ~~as well as~~ light climate, microbial productivity,~~energy available to micro-organisms~~ and ~~of course impacts on~~ carbon cycling (Wetzel, 2001; Schwarzenbach et al., 2003). Secondly, the statistical distribution of headwater TOC was not well predicted in the previous study using only downstream chemistry as the predictor (Temnerud et al., 2010). If the approach succeeds with TOC, then there is reason to hope that it would be even more effective in predicting other aspects of water chemistry.

An important aspect of modelling headwaters is that the spatial variation is largely dependent on temporal factors, often flow-related (Buffam et al., 2007), but also season (temperature and precipitation) and even long-term trends (Hytteborn et al., 2015). This temporal variation within a single headwater can be greater than the variation of TOC between catchments in the same biome. We want to make the reader aware that it could be easier to model headwaters in different catchments (at the same time) than headwaters in the same catchments that are sampled at different times.

Thus we modelled headwater~~s~~ TOC-concentration's on several occasions in different stream networks ~~by combining~~using catchment map information (Andersson and Nyberg, 2009)~~, to~~ complemented by data on the river outlet TOC-concentration.

While this may seem straight-forward, there are in fact some theoretical challenges; the method must deal with both strong correlations between observations and between explanatory variables. We used a two-step modelling approach to handle these challenges. First we used partial least square regression (PLS), which can deal with strong correlations between explanatory variables, to model headwater stream TOC median and IQR-values for the mesoscale catchments from information ~~derived from~~on catchment land cover, geology, soil type maps, ~~and~~ vegetation and river outlet chemistry ~~(kNN)~~. The best~~Candidate~~ explanatory variables from the PLS models were then used as candidate variables for ~~in~~ hierarchical linear mixed models (MM). Such MM have the advantage of being able to deal with strong correlations between observations (such as within a mesoscale catchment stream network), but MM are not appropriate for large numbers of explanatory variables. So PLS modelling was used first to narrow the number of explanatory variables, and then ~~so~~ MM ~~were~~ was used in the next step to model individual headwater streams. Thus, MM can account for the clustered data structure of catchment properties in a drainage network (Littell et al., 2006). Mixed models have been used rather successfully in related types of data evaluation (Jager et al., 2011; Sakamaki and Richardson, 2013). Two ~~major~~ distinguishing features of our study~~what we present here~~ are that ~~we~~ i) we test~~ed~~ a combination of information from maps (GIS) with direct measurements of chemistry at the river outlet~~,~~ to create models of individual headwaters and ii) we test~~ed~~ our models on data that ~~was~~ were not used in ~~the~~ model calibrations.

2 Methods

2.1 Sampling approach

The synoptic surveys of mesoscale catchments used in this study were designed to provide a snapshot of the water chemistry in stream networks (Table 1,~~ and~~ Fig. 1), with a strategy of sampling most watercourse junctions, lake inlets and outlets as well as the river outlets from each mesoscale catchment. In total there were data from 17 synoptic surveys conducted between 2000 and 2008 in nine catchments distributed across Sweden, spanning a north-south gradient of 800 km through the north-temperate and boreal zones (Fig. 1). This data set amounted to 938 stream samples of which 420 were from headwaters. Headwaters are defined as first order streams with catchments smaller than 2 km^2 in each of the nine drainage networks sampled (Table 1). The number of sampled headwaters differs between surveys (n_{HW} in Table 2). ~~The catchments span a north-south gradient of 800 km through the north-temperate and boreal zones.~~ All sampling during a given survey was carried out during a one to three day period (Table 2 and Fig. S1), except for R. Krycklan in winter 2005, which took ~~(~~two weeks due to cold weather and difficulties finding the streams in deep snow~~,~~. Stable base flow discharge was maintained throughout that winter sampling period, so that survey was still effectively a snapshot in time.~~but discharge was stable winter base flow).~~

Five of the nine catchments contain~~have~~ at least one headwater stream site that has been monitored for runoff and chemistry regularly for a decade or more (Edström and Rystam, 1994; Temnerud et al., 2009; Köhler et al., 2008; Löfgren et al., 2011; Laudon et al., 2013). Of the other four catchments, R. Ottervattsbäcken was sampled twice and R. Vänjaurbäcken sampled once (the name R. Sörbäcken ~~are~~ was used in the references, as this~~which~~ is a tributary in R. Vänjaurbäcken, Temnerud and Bishop, 2005; Temnerud et al., 2007) while R. Viggan and R. Mangslidsälven were sampled once, for this study.

2.2 Study sites

~~Headwaters are defined as first order streams with catchments smaller than 2 km^2 in each of the nine drainage networks sampled (Table 1).~~ All sampled catchments (including headwaters, intermediate watercourses and river outlets) consisted mainly of forest (>80%) with a dominance of coniferous forest made up of Norway spruce (*Picea abies*) and Scots pine (*Pinus silvestris*) (Table S1). Mires and small humic lakes made up most of the remaining parts of the catchments, while the proportion of agricultural and developed areas were minimal (<1%). The mean annual air temperature in the river catchments (1990-2010) ranged from 7.8 °C in the southernmost river, R. Anråse å, to 2.6 °C in the northernmost, Krycklan. Mean annual precipitation (1990-2010) ranged from 980 mm at R. Anråse å, to 649 mm at R. Vänjaurbäcken.

Daily mean air temperature, daily precipitation and daily runoff for 1961-2010 at each river outlet were~~as~~ modelled by the Swedish Meteorological and Hydrological Institute (SMHI) (Johansson, 2000; Johansson and Chen, 2003), data received 20th of June 2013 from http://luftweb.smhi.se. Daily runoff for 1990-2010 at each river outlet was modelled based on Hydrological Predictions for the Environment program (HYPE) (Lindström et al., 2010), data received 20th of June 2013 from http://vattenweb.smhi.se. Typical accuracy in the HYPE modelling for small catchments (<200 km^2) is 10% (Strömqvist et al., 2012; Arheimer and Lindström, 2013). Catchment-specific daily mean air temperature, total precipitation and mean specific discharge are illustrated ~~in~~ (Fig. S1) for the period of 30 days up to and including each sampling.

2.3 Map information

To relate headwater TOC to catchment characteristics, we began with 34 catchment parameters (Table S1, Fig. S3-S8) taken from the Swedish land cover data map (SMD), year 2000, version 2.1, which is based on the CORINE database (Bossard et al., 2000) as well as Geology and Quaternary deposits from the Geological Survey of Sweden (SGU) map, scale 1.1 million. The kNN-database of vegetation that has forestry variables estimated from LANDSAT 5 and LANDSAT 7 satellite photos (version year 2000, Reese et al., 2003; Reese et al., 2002), provided data about the average age and height of the forest as well as volume of the biomass for different tree species. All catchment map information uses the same version, year and scale of the maps so that the map data are commensurate between catchments (Table S1 in the Supplement).

2.4 Chemical analyses

After collection, all water samples were kept dark and cool until they were analysed. Total organic carbon (TOC) was measured by combustion and analysis as CO_2 using a Shimadzu TOC-VPCH analyser after acidification and sparging to remove inorganic carbon. Dissolved organic carbon (DOC) is the concentration of organic carbon in a filtered water sample (common cut-off is 0.45 µm~~ filter~~)~~ water sample~~. It has previously been shown that DOC and TOC differ on average by less than 5% (Ivarsson and Jansson, 1994; Köhler, 1999), so TOC is essentially identical to DOC in the large majority of the Swedish surface waters (see also Gadmar et al., 2002; Laudon et al., 2011).

2.5 Statistical analysis

The main objective of this article is to model the TOC of individual headwaters based on map information and river outlet TOC. We use the following two-step approach where~~To be able to reproduce correct TOC levels in the headwaters~~ we first ~~need to be able to i)~~ find the best map variables for predicting the average level and distribution around that level using PLS.~~for~~

~~each catchment and ii)~~ Secondly, we use MM to predict individual headwaters within each catchments~~describe variation within the catchments~~. ~~We use the following two-step approach:~~

~~First we describe the distribution of the response variable, headwater's TOC, on a catchment level using map information and river outlet TOC. For this we model the median of headwater TOC using PLS on median values of available explanatory variables. We also predict the variation within each catchment, expressed as interquartile range (IQR), using the same explanatory variables. PLS is in both cases used since we have many potentially correlated candidate variables.~~

~~In the next step we model the TOC of individual headwaters by hierarchical linear mixed models (MM), which can account for the clustered data structure of our dataset, i.e. can account for correlations between headwaters within the same catchment. For this model the explanatory variables that were identified as important in step i) are used. To further be able to describe within-catchment variation additional explanatory variables were also tested.~~

We are particularly interested in determining whether models based on geographical data, like lake surface coverage, forest coverage or altitude can be improved by adding data on TOC concentrations measured at the river outlet.

2.5.1 Modelling headwater median and interquartile range

To model the median and interquartile range of TOC in headwaters in different catchments we use partial least squares regression (PLS). Variables included in this model are TOC at the river outlet (OutletTOC) and a number of variables describing information derived from land cover, geology, soil type maps and vegetation (kNN) (Table S1). The main purpose of PLS was to narrow down the number of explanatory variables for subsequent use in the mixed models approach.

All data, both explanatory and response variables, were centred by mean normalisation and weighted by dividing the variables with the standard deviation prior to PLS analysis in SIMCA for Windows v13.0 (Umetrics). PLS identifies the relationship between explanatory variables and response variables through a linear model, and is less sensitive to correlated explanatory variables (so-called multicollinearity) when compared to multiple linear regression approaches (Geladi and Kowalski, 1986), since the explanatory variables are combined to factors. ~~For the same reason PLS also allows the inclusion of more explanatory variables than there are observations.~~

In the PLS analyses, the goodness-of-fit parameter Q^2 was used to quantify the model performance, which is the average (n = 7, default value in SIMCA) explained variance of a randomly selected fraction (1/7 of the data) of the validation data not used to fit the model. In robust models, R^2 and Q^2 are often similar, but the latter will decline as models become increasingly over-fit. Even though PLS models work by defining factors, i.e. combinations of explanatory variables, it is also possible to compute coefficients and weights that describe the direction and relative strength of the individual explanatory variables on the response variable; weights with larger absolute values indicate greater importance to a given latent component. All PLS-models were refined by iteratively removing variables that had non-significant coefficients. This procedure served to minimize the difference between R^2 and Q^2 values while retaining high explanatory power, i.e. to find a model that can be generalized to new data, while retaining good explanatory power. The relative importance of each explanatory variable is ranked using 'variable importance on the projection' (VIP) scores, derived as the sum of square of the PLS weights across all components. VIP values greater than one are considered to indicate variables that are most important to the overall model (Eriksson et al., 2006).

PLS allows for more explanatory variables than observations and gives us ~~therefore~~ the possibility to include many candidate variables. Still, some of the variables available needed to be excluded for the following reasons:

- Some variables, e.g. volume of oak, had zero value for all observations or only few observations different from zero. These variables could not be included due to the lack of variation ~~in them~~.

- Geographical variables for the river outlet were not included, since they correlate highly with the median of the corresponding variable at the headwater scale. The latter is considered to bear more information and was therefore included.

The analysis was run on three calibration data sets: One with data from year 2000 where headwaters within four mesoscale catchments (these catchments are called ~~A~~c1) were sampled $\text{Cal}_{\text{PLS}}00_{\cancel{\text{A}}\text{c1}}$ (n = 4; M0, O0, Vä0, Vi0). In $\text{Cal}_{\text{PLS}}07_{\cancel{\text{B}}\text{c2}}$ the headwaters of five mesoscale catchments (catchments c2~~B~~) were sampled in 2007 (n = 5; A7, D7, G7, K7, L7) and in $\text{Cal}_{\text{PLS}}08_{\cancel{\text{B}}\text{c2}}$, the same five mesoscale catchments as in $\text{Cal}_{\text{PLS}}07$, were sampled in 2008 (n = 5; A8, D8, G8, K8, L8). The test data sets consist of the same groupings, but were not used in the calibrations ($\text{Test}_{\text{PLS}}00_{\cancel{\text{A}}\text{c1}}$, $\text{Test}_{\text{PLS}}07_{\cancel{\text{B}}\text{c2}}$, $\text{Test}_{\text{PLS}}08_{\cancel{\text{B}}\text{c2}}$).

After running the three different PLS models we determined whether the same variables appeared to be important (VIP>1) in the model fittings. These variables were taken as good candidates to reproduce the ~~general~~ TOC level of the headwaters and therefore included in the mixed modelling of the individual headwaters in the next step (Section 2.5.2). An additional test set was created, $\text{Test}_{\text{PLS}}02\&05_{\cancel{\text{C}}\text{c3}}$, which was comprised of data from the two catchments sampled once in 2002 and twice in 2005 (catchments ~~C~~c3, n=3; O2, K5s, K5w, where s stands for summer and w for winter). No calibration was done on this data set, but was used for testing robustness of the models with respect to seasonality.

2.5.2 Modelling individual headwaters

When modelling individual headwaters we want to predict specific values for each of the different headwaters in all catchments. As an effort to improve these simulations, we make an assumption that headwaters within the same mesoscale catchment are more similar to each other than to headwaters from other mesoscale catchments due to subtle combinations of physiographic, weather and other factors which combine to influence the TOC levels in ways which are not readily apparent from the available map information, but might be reflected in differences between the average TOC levels in the different mesoscale catchments. This assumption leads to a new data structure. ~~When modelling individual headwaters we want to reproduce individual values for the different headwaters in all catchments, which leads to a new data structure, where we need to assume that headwaters within the same catchment are more similar to each other than to headwaters from other catchments.~~ To model this data structure we use hierarchical linear mixed models (MM; Littell et al., 2006), which allow the estimation of the correlation between headwaters within the same mesoscale catchment and adjusts the analysis accordingly. A MM does not allow for highly correlated explanatory variables, so the number of explanatory variables must be substantially smaller than the number of observations. To fit these models we use candidate explanatory variables from the PLS approach described in 2.5.1. In the PLS analysis some explanatory variables were excluded due to a large number of zero values giving rise to a median sub-catchment value of zero for all catchments. One of these parameters, lake surface area,~~Some of these variables~~ may still be important for~~can still be interesting in~~ modelling individual headwaters~~, for example lake surface coverage~~. If lakes have a moderately large volume (appreciable residence time) they are known to influence the organic content (Eriksson, 1929; Birge and Juday, 1926). Therefore lake cover surface is expected to have an influence on the prediction of individual ~~headwater~~ TOC_{HW}, and thus this variable was included as a potential predictor in the MM models even though this variable was not~~could not be~~ important in the PLS modelling~~used in the PLS (median value was zero) to explain the median TOC of several headwaters~~.

MMs were performed using package lme4 (version 1.1-7) in the software R (version 3.1.2) (R Development Core Team, 2014). Headwater data from year 2000 (numbers of headwaters = 69; M0, O0, Vä0, Vi0), 2007 (n_{HW} = 138; A7, D7, G7, K7, L7) or 2008 (n_{HW} = 148; A8, D8, G8, K8, L8) were used as calibration data sets (denoted $Cal_{MM}00_{Ac1}$, $Cal_{MM}07_{Bc2}$ and $Cal_{MM}08_{Bc2}$, respectively), one set at a time. We have two objectives in this approach:

i) To make predictions on the same headwaters but at different time points. For this observations for 2008 ($Test_{MM}08_{Bc2}$) ~~are~~ were predicted by the model ~~calibration~~ calibrated with data from 2007 ($Cal_{MM}07_{Bc2}$~~,~~). ~~and~~ The observations ~~for~~ from 2007 ($Test_{MM}07_{Bc2}$) were also ~~are~~ predicted ~~by~~ based on a model calibrated using the 2008 data ($Cal_{MM}08_{Bc2}$).

ii) To make predictions on a new set of headwaters at a different time point. For this:

- observations from 2002 and 2005 ($Test_{MM}02\&05_{Cc3}$), 2007 ($Test_{MM}07_{Bc2}$) and - 2008 ($Test_{MM}08_{Bc2}$) respectively were predicted by models calibrated using data from 2000 on an entirely different set of catchments ($Cal_{MM}00_{Ac1}$) and
- observations from 2000 ($Test_{MM}00_{Ac1}$), 2002 and 2005 ($Test_{MM}02\&05_{Cc3}$) -were predicted by models calibrated using data from 2007 or 2008 on an entirely different set of catchments ($Cal_{MM}07_{Bc2}$ and $Cal_{MM}08_{Bc2}$, respectively).

$Test_{MM}02\&05$ is sampled in one catchment 2002 and two times in another catchment in 2005 (n_{HW} = 65; O2, K5s, K5w, where s stands for summer and w for winter), no calibration was done on this data set. We used the testing to see if the calibrations worked on other data sets which were not included in the calibration.

To test the impact of including TOC at river outlet (OutletTOC) on the MM performance, three model versions were made from~~of~~ each calibration data set~~were run~~:

- version Out includes OutletTOC but no map information,
- version Map includes map information but not OutletTOC while
- version OutMap includes both OutletTOC and map information.

In total nine different MM were calibrated.

For ~~model~~ fitting of the MM, Akaike information criterion (AIC) (Akaike, 1974) and p-values were used. AIC is a goodness-of fit measure, which is corrected for the complexity of the model, similar to the adjusted R^2. The p-values in regression models determine if parameter estimates are significantly different from zero, i.e. if there is a significant relationship between an explanatory variable and the response variable. The p-values were calculated according to Kenward and Roger (1997) using ‘krmodcomp’ in R package ‘pbkrtest’ (version 0.4-1). During the model fitting, added variables were checked to see if they increased the predictive ability of the model by computing the prediction error sum of squares (PRESS). The smaller the PRESS value the closer ~~is~~ the prediction is to the observed values. Kenward and Roger (1997) version of R^2 for predictions is called P^2 (similar to Q^2 for PLS). The P^2 were calculated according to Méndez Mediavilla et al. (2008), with the modification that instead of leave-one-out validation we compute P^2 on the evaluation test sets: P^2 = 1-PRESS/TSS where

TSS is the total sum of squared differences between modelled values and the mean of observations in the evaluation set. Median absolute errors (MedAE) and median relative errors (MedRE%) were also calculated.

As an additional step in the evaluation of the models the most successful MM from the nine MM calibrations was tested on the sites between the headwaters and the river outlets, the intermediate sites (n = 501).

3 Results

For all synoptic surveys the median TOC_{HW}~~headwater median TOCs~~ values were higher than the values at the respective outlets (Table 2), with large differences (>20%) for 14 of 17 synoptic surveys. The median TOC_{HW}~~headwater median TOC~~ for all surveys together (12 mg L^{-1}) was also higher than the median outlet TOC of 10 mg L^{-1} (Fig. 2 and Table 2). For all synoptic surveys, except A8, there was a funnel-shape in the TOC concentration with larger variation in smaller catchments that attenuates with increasing catchment size (Fig. 2). Reproducing this variation in the headwaters (Fig. S2), and assigning individual headwaters to the proper value within that large variation, is one of the challenges of modelling water chemistry in a landscape perspective.

3.1 Modelling headwater median

The first principal component (PC) of the PLS-model of median headwater TOC was significant for both PLS calibration sets year 2007 and 2008~~For both PLS calibration sets year 2007 and 2008 the first principal component (PC) was significant in the PLS-models for median headwater TOC~~, but not the second PC. No significant PLS-model was established using calibration set year 2000 ($\mathrm{Cal_{PLS}00_{\cancel{A}c1}}$). Calibration using data set 2007 ($\mathrm{Cal_{PLS}07_{\cancel{B}c2}}$) gave higher R^2 and Q^2 than using the data set for 2008 calibration ($\mathrm{Cal_{PLS}08_{\cancel{B}c2}}$) (Table 3). The calibration of the model using the ~~Verification based on the evaluation data of~~ $\mathrm{Cal_{PLS}08_{\cancel{B}c2}}$~~,~~ data was evaluated by using the test data.~~that is all other data than 2008,~~ This yielded a~~had lower~~ PRESS for the median TOC that was lower than when the model was calibrated using~~similar data for~~ $\mathrm{Cal_{PLS}07_{\cancel{B}c2}}$ (Table 3). Based on PLS-modelling of median headwater TOC, suitable candidates for the mixed models (MM) of individual headwaters were: altitude of sampling sites, OutletTOC, proportion of clear-felled, coniferous forest, mixed forest, wet mires, coniferous forest on mires as well as the volume of birch-, spruce- and total forest volume.

3.2 Modelling headwater interquartile range (IQR)

For both PLS calibration sets year 2007 and 2008 the first principal component (PC) was significant in the PLS-models for IQR headwater TOC, but not the second PC. No significant PLS-model was established using calibration set year 2000 ($\mathrm{Cal_{PLS}00_{\cancel{A}c1}}$). The calibration of the model using the~~Verification based on the evaluation data of~~ $\mathrm{Cal_{PLS}07_{\cancel{B}c2}}$~~,~~ data was evaluated by using the test data.~~that is all other data than 2007,~~ This yielded a~~had lower~~ PRESS for TOC IQR that was lower than when the model was calibrated using~~similar data for~~ $\mathrm{Cal_{PLS}08_{\cancel{B}c2}}$ (Table 3). Headwaters TOC IQR ~~of TOC~~ modelled by PLS indicates three variables as suitable candidates for the MM: OutletTOC, proportion of clear-felled area and birch volume.

3.3 Modelling individual headwaters

The PLS approach from Section 3.1 identified the variables that can determine the median level of TOC, and the variation around that median, on a range of different catchments. In the following analysis we seek models to predict the TOC of individual watercourses at different locations and points in time~~variables to reproduce both the median levels as well as describe the within-catchment variability~~. ~~We did this with two separate approaches:~~

~~We determine which variables best can capture the within-catchment variation in headwater TOC. To do this we fit a model to Cal$_{MM}$07$_{B}$ and Cal$_{MM}$08$_{B}$ respectively and predict the observations from 2007 (Test$_{MM}$07$_{B}$) and 2008 (Test$_{MM}$08$_{B}$).~~

~~We examined which variables can determine the correct overall level of TOC as well as capture the within-catchment variation. To do this we fit a model to Cal$_{MM}$00$_{A}$, one model for all these catchments, and predict observations from 2002 and 2005 (Test$_{MM}$02&05$_{C}$), 2007 (Test$_{MM}$07$_{B}$) and 2008 (Test$_{MM}$08$_{B}$). A model for Cal$_{MM}$07$_{B}$ and Cal$_{MM}$08$_{B}$ was used to predict values from 2000 (Test$_{MM}$00$_{A}$), 2002 and 2005 (Test$_{MM}$02&05$_{C}$).~~

3.3.1 Modelling individual headwaters and predicting those same headwaters at other points in time

When we fit the models to a calibration set, e.g. headwaters measured in 2007, we start with a base model consisting of the variables identified by the PLS model for the interquartile range, i.e. OutletTOC on the catchment scale and proportion wet mires as well as volume birch, with different values for different headwaters. The base model was fitted with a MM using catchment as the random factor describing the hierarchical structure. Other variables were included in a forward selection procedure always adding the most significant variable of the remaining set of variables. Candidate variables used in this were all land use variables (including lake surface coverage) and all variables giving the volume of different tree species with exception of the volume of oak and beech, since these volumes are generally very low and zero for many headwaters. After fitting the model the ability to predict new data was tested and non-significant variables in the model were individually removed to check if their removal also worsened the predictive ability of the model.

The models created by~~gained from~~ this procedure are listed in Table 4. The models produced by Cal$_{MM}$07$_{\cancel{B}c2}$ and Cal$_{MM}$08$_{\cancel{B}c2}$ were very similar and can predict the data at the same sites quite well, i.e. the Cal$_{MM}$07$_{\cancel{B}c2}$ model can predict the Test$_{MM}$08$_{\cancel{B}c2}$ data set well and the other way round (Fig. 4-5 and Table 5).

3.3.2 Modelling individual headwaters and predicting new headwaters at other time points

When we use the calibration set Cal$_{MM}$00$_{\cancel{A}c1}$ to fit a model, the variables selected (same procedure as in 3.3.1) were OutletTOC, lake surface coverage and coniferous forest on mires. We evaluate this model by predicting values in the test sets Test$_{MM}$07$_{\cancel{B}c2}$ and Test$_{MM}$08$_{\cancel{B}c2}$ (Fig. 3). The best prediction model parameters are given in Table 4, with model performance in Fig. 3 and error results in Table 5. Predictions for new sites in the test set Test$_{MM}$00$_{\cancel{A}c1}$ and Test$_{MM}$02&05$_{\cancel{C}c3}$ are less satisfactory and indicate that the models might be over fitting the data.

3.3.3 Evaluation on intermediate sites

The headwater models were also tested on the sites of intermediate size (i.e. >2 km^2) but excluding the river outlet (lower parts of Table 5). In general the intermediate sites were modelled as successfully as the headwaters (Table 5). Cal$_{MM}$07$_{\cancel{B}c2}$ gave predictions for the intermediate sites which were not as good as for the other data sets, i.e. higher MedRE%, than Cal$_{MM}$08$_{\cancel{B}c2}$ and Cal$_{MM}$00$_{\cancel{A}c1}$.

3.3.4 Evaluation of river outlets

~~In an attempt t~~To test the effect of including the river outlet TOC on the performance of MM predictions for individual headwaters, three versions of each calibration data set ~~were~~ was used to create three different models, one using outlet TOC alone (Out), one using map information alone (Map), and one using both the outlet and map information (OutMap). ~~with~~ The ~~same~~ map variables were the same for each calibration data set but with different calibrated coefficients (Table 4). In 25 o~~O~~ut of 27 different combinations of MM (three different calibration data sets, three versions of each calibration (Out, Map, OutMap) and three different test data sets), the OutMap version ~~(OutletTOC and map information combined)~~ gave the best performance with the lowest PRESS, while two Map versions (map information only, no OutletTOC included) gave the lowest PRESS (Table 5 and Fig. 3-5). Similar results were observed for the intermediate sites (Table 5 and Fig. 3-5). The OutMap version gave 5-15% better predictions than Map only.

4 Discussion

~~With the approach in this study we were able to achieve P^2-values around 50%, indicating that about 50% of the variation in the individual headwater test sets can be explained with a model including the explanatory variables OutletTOC, lake surface coverage and proportion of coniferous forests on mires. In two of the three calibrations, the proportion of broad-leaved forest and elevation were also significant.~~

In 25 of 27 tests, including river outlet chemistry (OutletTOC) resulted in lower errors in the mixed models predictions of the TOC for individual headwaters, and intermediate sites, compared to using map information alone. The measurements at the river outlet were necessary to reproduce more correct average headwater TOC levels (Table 5). Excluding the OutletTOC measurements leads to the assumption that average TOC levels in the headwaters were similar in different catchment stream networks if the map information is similar, which is not always true (cf. sampling 2007 and 2008). This is the first article to test how to include river outlet chemistry with map information for modelling headwaters, and how well the river outlet chemistry improved the models.

To predict the correct mean values for headwater TOC is still a challenge in our application of mixed models, since the calibration sets consist of 4-5 catchment systems, and these were sampled only a few times for each calibration. This clearly makes generalisations to new catchments or flow-situations difficult and uncertain. Calibration sets Cal07 and Cal08 share most of the catchments, but are measured during different years and perhaps more importantly, during different flow situations and seasons. Even if most headwaters are the same in $\text{Cal}_{\text{MM}}07_{\cancel{\text{Bc2}}}$ and $\text{Cal}_{\text{MM}}08_{\cancel{\text{Bc2}}}$, and the models produced were similar, it was still not possible to account for more than about 50% of the variation in the other set of data, indicating that there is large variability in time. Weather is a factor that varies with time (and space) and influences stream water chemistry. In our approach we did not include the weather related data (temperature, precipitation, flow) in the models (PLS and MM) since it was not available for headwaters, but only for the river outlet. Presumably discharge for each headwater could benefit the models, but measuring discharge at all individual headwaters would have been very time consuming (and ~~were~~ was not performed). To model discharge with appropriate accuracy at all these headwaters (size<2 km^2) is so far too difficult to perform due to large heterogeneity at these small scales (Lyon et al., 2012), and lack of precipitation data for all these headwaters.

With the approach in this study we were able to achieve P^2-values around 50%, indicating that about 50% of the variation in the individual headwater test sets can be explained with a model including the explanatory variables OutletTOC, lake surface coverage and proportion of coniferous forests on mires. In two of the three calibrations, the proportion of broad-leaved forest and elevation were also significant.

Most lakes in these catchments are dimictic (mixing of the lake from the surface to bottom twice each year). Some of the data used in this study (year 2007 and 2008) has been used to evaluate the impact of lakes on stream water chemistry and there were indications that lake influence differs as a function of season, catchment and constituent (Lyon et al., 2011). The presence of lakes had a stronger influence on stream water TOC levels in October 2007 than in April 2008. Thus the presence of lakes could influence the impact of river outlet TOC on headwater TOC in MM. Lakes are known to often decrease TOC concentration (Müller et al., 2013; Weyhenmeyer et al., 2012), although this effect is not always visible at a landscape scale (Lottig et al., 2013) and lakes can also delay pulses of TOC within river networks, which is a complicating factor (Hytteborn et al., 2015).

The proportion of coniferous forest on mires had a positive sign and proportion of lake surface coverage had a negative sign for all calibration sets~~,~~. ~~which~~ This is plausible based on earlier studies (Andersson and Nyberg, 2009; Pers et al., 2001; Oni et al., 2013; Lottig et al., 2013; Clark et al., 2010). Ågren et al. (2014), Hope et al. (1997), Löfgren et al. (2014), Mattsson et al. (2003) and Walker et al. (2012) have also found that the amount of organic matter in the catchment soils (mire, wet- or peat land proportion) is often positively correlated with stream TOC concentration (e.g. Mulholland et al., 2001), even if the extent of organic soils can be hard to estimate from maps (Creed et al., 2003; Johnston et al., 2008).

That broad-leaved forest had a negative coefficient for Cal07~~Bc2~~ and Cal08~~Bc2~~ (Table 4-5) could be related to several factors. In these systems most of the broad-leaved forest is made up of birch (*Betula pendula*). The negative coefficient of broad-leaved/birch could be a direct effect of birch on water chemistry; i.e. more birch in a coniferous landscape could give runoff with lower organic carbon (Brandtberg et al., 2000; Fröberg et al., 2011). However, in a set of explanatory variables like this, with a large amount of geographical information, many of the variables are correlated. This results in the fact that similarly good models could be found with other sets of explanatory variables. For instance, in our data set we found high correlations among volume of various tree species, furthermore volume of Pine also had high correlation with these variables: proportion of coniferous forest, site altitude, volume of birch, broad-leaved forest and volume of spruce.

In this work we use calibration sets and test sets rather than the popular leave-one-out cross-validation method, since we have dependent, clustered data. Shao (1993) showed that leave-one-out cross-validation tends to select unnecessarily large models if observations are correlated. Libiseller and Grimvall (2003) showed that this is true for data that are serially correlated, since a single removed observation can be reproduced easily by observations in the temporal vicinity of the left-out observation. The same should hold for clustered data, where a single left-out headwater would be reasonably predicted by other headwaters in the same catchment.

~~In Temnerud et al. (2010) data from A7, D7, G7, K5, L7, O0 and S0 (S is a tributary in Vä0 and most data are the same) were used in leave-one-out cross-validation linear models on median and IQR TOC. In that study, one model of seven gave a significant median TOC model. In the current data set with nine catchments we observed that the differences between catchments were quite large and could partly (P^2 around 50%; Table 5) be described by the included variables for individual headwaters.~~

5 Conclusion

Our modelling approach, using both river outlet TOC and map information from the headwater catchments, could explain up to 52% of the variance in TOC among individual headwater streams. This is much better performance than an earlier attempt using river outlet TOC without map information (Temnerud et al., 2010) , in which only one of seven models were significant for predicting headwater median TOC and none were significant for predicting headwater TOC IQR.~~The mixed models approach, using river outlets TOC and map information, could explain up to 52% of the variance in TOC among individual headwater streams. This is far better performance than the attempt by Temnerud et al. (2010) in which only one of seven different leave-one-out attempts gave a significant model for headwater median TOC and none gave significant models for headwater TOC IQR.~~ The key factor in our approach here is the use of mixed models which allow the same headwaters to have different TOC depending on weather and flow etc. Since MM cannot use large numbers of correlated explanatory variables, PLS was used to identify a set of candidate explanatory variables for the MM. Since our combined approach~~the used method~~ increased the predictability for TOC, it would be interesting to evaluate ~~if~~ whether the method could improve prediction of headwater~~s~~ pH and ANC, for which models using outlet catchment chemistry were already fairly successful~~that worked better than TOC in~~ (Temnerud et al., 2010).

In order to have the same map resolution for all catchments, due to lack of universal availability of fine-scale data, a rather coarse resolution was used (e.g. 50 meter grid data for altitude and soil map of scale 1.1 million). The Swedish authorities are LiDAR scanning all of Sweden to build a 2 meter grid digital elevation model and are generating maps connecting all watercourses up to the headwaters (through lakes and wetlands), which by 2017 will provide new data that could help in modelling the headwaters. This improved map information might further improve the mixed model approach demonstrated here ~~that~~ which includes river outlet chemistry. This will hopefully get us closer to the ability to predict individual headwaters that are such vital building blocks of aquatic ecosystems, but remain so very difficult to model.

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Tables

Table 1. Characteristics of the rivers. Cluster is the grouping of~~different~~ calibration and test sets used in the modelling. Air temperature (T °C) and specific discharge (q mm day^{-1}) are the medians of daily values for 1990-2010, precipitation (P mm) is the median of the yearly sum. P, T and q are modelled by SMHI, see Methods for more details.

Cluster	River	Lat. N & Long E	Size (km^2)	T	P	q
~~B~~c2	Anråse å[a] (A)	58º01'; 11º51'	74	7.8	983	0.95
~~B~~c2	Danshytteån[a] (D)	59º42'; 15º05'	72	6.1	774	0.70
~~B~~c2	Getryggsån[a] (G)	59º48'; 15º17'	32	5.9	800	0.84
~~B~~c2~~ and~~, ~~C~~c3	Krycklan[b] (K)	64°14'; 19°46'	61	2.6	659	0.51
~~B~~c2	Lugnån[a] (L)	57º06'; 14º48'	122	6.1	831	0.60
~~A~~c1	Mangslidsälven (M)	60°23', 12°54'	235	4.9	823	0.75
~~A~~c1~~ and~~, ~~C~~c3	Ottervattsbäcken[c] (O)	64°02'; 19°06'	71	2.6	659	0.50
~~A~~c1	Vänjaurbäcken[c] (Vä)	64°19', 18°43'	200	2.2	649	0.47
~~A~~c1	Viggan (Vi)	60°21', 12°46'	116	3.9	870	0.85

[a] Temnerud *et al.* (2009)
[b] Laudon et al. (2013)
[c] Temnerud and Bishop (2005)

Table 2. Median concentration~~values~~ of total organic carbon (TOC, mg L^{-1}), with 25th and 75th~~-~~ percentiles in brackets, plus weather parameters (T, P, q) using the median value from the 30 days prior to sampling as modelled by SMHI (See Methods for more details). ~~see Table 1 for river names.~~ Clusters ~~is~~ are the different groups of calibration and test sets used in the modelling~~,~~. ~~set~~ Sets ~~is~~ are the different data sets used, with acronyms corresponding to river names (Table **Error! Reference source not found.**) and the last digit of the sampling year. ~~HW is headwaters.~~ M = Month of sampling, ~~(M)~~ HW is headwaters and n_{HW} = number of sampled HW ~~(n_{HW})~~. ~~Median of 30 Julian days before sampling, for the outlet, of modelled air temperature (T °C), precipitation (P mm) and specific discharge (q mm day^{-1}).~~

Cluster	Set	Year	M	n_{HW}	TOC_{HW}	OutletTOC	T	P	q
~~B~~c2	A7	2007	10	45	8.6 (5.8-12)	6.7	11	4.3	1.3
~~B~~c2	A8	2008	4	45	7.7 (6.6-9.9)	6.9	3.9	2.8	4.4
~~B~~c2	D7	2007	10	34	16 (13-29)	11	9.9	2.0	0.41
~~B~~c2	D8	2008	4	33	12 (9.6-17)	10	1.7	1.2	1.2
~~B~~c2	G7	2007	10	21	27 (18-36)	12	9.1	3.2	0.63
~~B~~c2	G8	2008	4	22	18 (13-20)	8.9	1.3	0.95	1.2
~~C~~c3	K5s	2005	6	24	15 (12-18)	10	13	1.8	0.69
~~C~~c3	K5w	2005	2	17	12 (6.9-17)	5.0	-5.1	0.75	0.16
~~B~~c2	K7	2007	7	12	12 (9.7-15)	4.3	14	2.1	0.26
~~B~~c2	K8	2008	9	22	20 (16-25)	15	11	4.7	1.6
~~B~~c2	L7	2007	10	26	20 (16-32)	15	7.9	1.9	0.91
~~B~~c2	L8	2008	4	26	15 (10-20)	12	0.7	1.2	1.3
~~A~~c1	M0	2000	8	7	19 (13-22)	14	15	1.8	1.3
~~A~~c1	O0	2000	6	31	20 (16-27)	15	9.7	1.4	1.3
~~C~~c3	O2	2002	8	24	20 (14-32)	15	17	3.0	0.21
c1~~A~~	Vä0	2000	6	18	12 (10-15)	9.5	9.9	2.2	1.8
~~A~~c1	Vi0	2000	8	13	16 (9.0-19)	15	14	2.2	1.5

Table 3. Partial least square regression (PLS) results indicating the goodness of fit for the prediction of~~predicting the~~ median ~~(Med)~~ and the interquartile range (IQR) of headwater total organic carbon (TOC) concentration (mg L^{-1}). Cal is calibrated and 00, 07 and 08 refer to sampling year (2000, 2007 and 2008) of catchment (number=n). PRESS is the prediction error sum of squares.

Cal	Var	n	R^2	Q^2	PRESS
00~~A~~c1	Median	4	ns	ns	ns
	IQR	4	ns	ns	ns
07~~B~~c2	Median	5	96	94	581
	IQR	5	96	92	346
08~~B~~c2	Median	5	90	83	192
	IQR	5	54	17	530

Table 4. Coefficients for the best-fit ~~Hierarchical~~ hierarchical linear mixed models (MM) ~~different coefficients~~, where ~~headwaters~~ Log_{10} (TOC_{HW}) is the response variable. See the Method section for more details.

MM model	Version	Intercept	OutletTOC (mg L^{-1})	Lake surface coverage[p]	Coniferous forest on mires[p]	Broad-leaved forest[p]	Sites altitude (m a.s.l.)
Cal00~~Ac1~~	Out	0.861	0.0245				
	Map	1.156		-1.509	0.592		
	OutMap	0.885	0.0201	-1.479	0.568		
Cal07~~Bc2~~	Out	0.822	0.0380				
	Map	1.074		-1.867	1.022	-0.900	0.000619
	OutMap	0.736	0.0363	-1.863	0.956	-0.970	0.000554
Cal08~~Bc2~~	Out	0.671	0.0439				
	Map	0.913		-0.675	1.303	-0.697	0.000903
	OutMap	0.700	0.0199	-0.684	1.243	-0.740	0.000940

[p] is the proportion of the entire catchment area covered by this particular feature.

Table 5. Hierarchical linear mixed models (MM) results predicting headwater (HW) organic carbon (TOC) concentration in Log10. Cal is calibrated and 00, 07 and 08 refer to sampling year (2000, 2007 and 2008). The different coefficients are found in Table **Error! Reference source not found.**. Each calibration has three versions (intercept is always included): Out, Map and OutMap. The Out version includes OutletTOC, the Map version includes the map information, while OutMap includes both OutletTOC and map information. The prediction error sum of squares (PRESS) is the squared differences between observed and predicted values for the Y-data kept out of the model fitting ~~of~~ in the Test sets (00 stands for year 2000, 02&05 for 2002 and 2005, 07 for 2007 and 08 for 2008). The bold values show the lowest PRESS of the three versions for that Test data, bold PRESS per test sites are the lowest for that version. Intermediate sites (is) stands for sites between headwaters and the river outlet. R^2 for predictions is called P^2 (similar to Q^2 for PLS): P^2 = 1-PRESS/TSS where TSS is the total sum of squared differences between modelled and the mean of observations. AE is absolute error and RE is relative error, calculated on TOC in mg L^{-1}.

Cal	Version	00 ~~A~~c1	00 ~~A~~c1	00 ~~A~~c1	07 ~~B~~c2	07 ~~B~~c2	07 ~~B~~c2	08 ~~B~~c2	08 ~~B~~c2	08 ~~B~~c2
Cal n_{HW}			69			138			148	
$Test_{HW}$		02&05 ~~C~~ c3	07 ~~B~~c2	08 ~~B~~c2	00 ~~A~~c1	02&05 ~~C~~ c3	08 ~~B~~c2	00 ~~A~~c1	02&05 ~~C~~ c3	07 ~~B~~c2
n $Test_{HW}$		65	138	148	69	65	148	69	65	138
$PRESS_{HW}$	Out	3.42	8.71	4.78	2.28	3.68	5.98	3.10	4.58	7.92
	Map	2.79	8.51	5.35	**2.24**	**2.70**	3.97	3.17	3.57	7.63
	OutMap	**2.47**	**7.82**	**4.00**	2.26	2.88	**3.92**	**3.01**	**3.45**	**6.26**
P^2_{HW}	Out	13.5	19.8	42.9	9.2	8.5	20.6	5.0	3.3	31.5
	Map	29.4	21.7	36.1	10.8	32.9	47.3	2.7	24.5	34.0
	OutMap	37.6	28.0	52.0	10.1	28.3	48.0	7.5	27.1	45.9
$MedAE_{HW}$	Out	6.85	8.00	4.99	3.30	4.61	4.89	6.30	6.85	7.52
	Map	4.54	7.24	5.56	7.67	5.79	4.91	7.84	5.43	7.34
	OutMap	6.32	6.59	5.03	8.29	7.51	4.57	7.14	6.84	5.80
$MedRE\%_{HW}$	Out	45.9	53.4	45.9	47.1	26.8	60.8	33.1	46.6	55.5
	Map	42.1	56.3	52.2	52.2	66.8	39.3	50.6	65.3	53.1
	OutMap	42.1	56.3	52.2	98.1	44.2	35.7	58.6	54.3	48.0
n_{is}		129	155	135	82	129	135	82	129	155
$PRESS_{is}$	Out	5.59	5.35	3.19	3.24	4.92	6.24	3.30	5.18	5.28
	Map	5.95	7.92	2.98	**2.42**	4.44	**1.71**	2.50	4.17	7.26
	OutMap	**4.45**	**3.93**	**1.41**	2.52	**3.15**	1.92	**2.46**	**3.31**	**4.59**
P^2_{is}	Out	20.3	47.9	52.4	-11.2	19.8	-46.8	-17.8	14.7	26.8
	Map	15.3	22.9	55.5	17.0	27.6	59.6	10.7	31.3	-0.46
	OutMap	36.6	61.8	78.9	13.6	48.6	54.9	12.1	45.4	36.4
$MedAE_{is}$	Out	3.97	4.22	2.08	5.89	5.10	2.27	5.65	5.22	3.81
	Map	3.74	4.69	3.57	2.90	3.99	2.22	3.29	3.64	4.78
	OutMap	3.63	3.00	2.42	4.18	4.48	2.62	2.66	3.60	3.78
$MedRE\%_{is}$	Out	40.9	43.0	43.2	69.9	53.6	84.0	41.4	38.9	34.9
	Map	68.2	59.0	36.8	40.6	94.6	23.1	37.3	72.2	50.3
	OutMap	38.2	33.5	23.5	88.4	73.6	25.0	41.6	52.0	40.3

Figures legend

Fig. 1. Map of Sweden with the nine investigated catchments, see Table **Error! Reference source not found.** for coordinates. Labels in brackets are the abbreviated names of the catchments and year of sampling.

Fig. 2. Total organic carbon (TOC in mg L^{-1}) as a function of catchment size (~~km^2 in~~note Log_{10} scale) for ~~the nine mesoscale catchments, in total~~ 17 synoptic~~al~~ surveys of 9 catchments~~studies~~; a) is A7, b) is A8, c) is D7, d) is D8, e) is G7, f) is G8, g) is K5s, h) is K5w, i) is K7, j) is K8, k) is L7, l) is L8, m) is M0, n) is O0, o) is O2, p) is Vä0 and q) is Vi0. See Table 1 and Table 2 for description of surveys~~the full catchment names~~.

Fig. 3. Scatterplots of measured headwaters with total organic carbon (TOC in mg L^{-1}) on the x-axis, and the three different versions of the mixed models $Cal_{MM}00_{Ac1}$ on the y-axis: Out version on the left panel, OutMap version on the right panel and Map in-between. Data for year 2000 ($Cal_{MM}00_{Ac1}$) on the top row in red text, followed by Test data; second row 2002 & 2005 data, third row is 2007 data and the last row is 2008 data. R. Anråse å indicated by circles, R. Danshytteån by diamonds, R. Getryggsån by rectangles, R. Krycklan by triangles (winter 2005 by upside-down triangles), R. Lugnån by squares, R. Mangslidsälven by multiplication sign, R. Ottervattsbäcken by up-side-down triangles, R. Vänjaurbäcken by right tilted triangles and R. Viggan by plus sign. The black line is the 1:1-line.

Fig. 4. Scatterplots of measured headwaters with total organic carbon (TOC in mg L^{-1}) on the x-axis, and the three different versions of the mixed models $Cal_{MM}07_{Bc2}$ on the y-axis: Out version on the left panel, OutMap version on the right panel and Map in-between. Data for year 2007 ($Cal_{MM}07_{c2}$) on the third row in red text, followed by Test data; first row 2000 data, second row 2002 & 2005 data and the last row is 2008 data. R. Anråse å indicated by circles, R. Danshytteån by diamonds, R. Getryggsån by rectangles, R. Krycklan by triangles (winter 2005 by upside-down triangles), R. Lugnån by squares, R. Mangslidsälven by multiplication sign, R. Ottervattsbäcken by up-side-down triangles, R. Vänjaurbäcken by right tilted triangles and R. Viggan by plus sign. The black line is the 1:1-line.

Fig. 5. Scatterplots of measured headwaters with total organic carbon (TOC in mg L^{-1}) on the x-axis, and the three different versions of the mixed models Cal08 on the y-axis: Out version on the left panel, OutMap version on the right panel and Map in-between. Data for year 2008 ($Cal_{MM}08_{Bc2}$) on the last row in red text, followed by Test data; first row 2000 data, second row 2002 & 2005 data and the third row is 2007 data. R. Anråse å indicated by circles, R. Danshytteån by diamonds, R. Getryggsån by rectangles, R. Krycklan by triangles (winter 2005 by upside-down triangles), R. Lugnån by squares, R. Mangslidsälven by multiplication sign, R. Ottervattsbäcken by up-side-down triangles, R. Vänjaurbäcken by right tilted triangles and R. Viggan by plus sign. The black line is the 1:1-line.

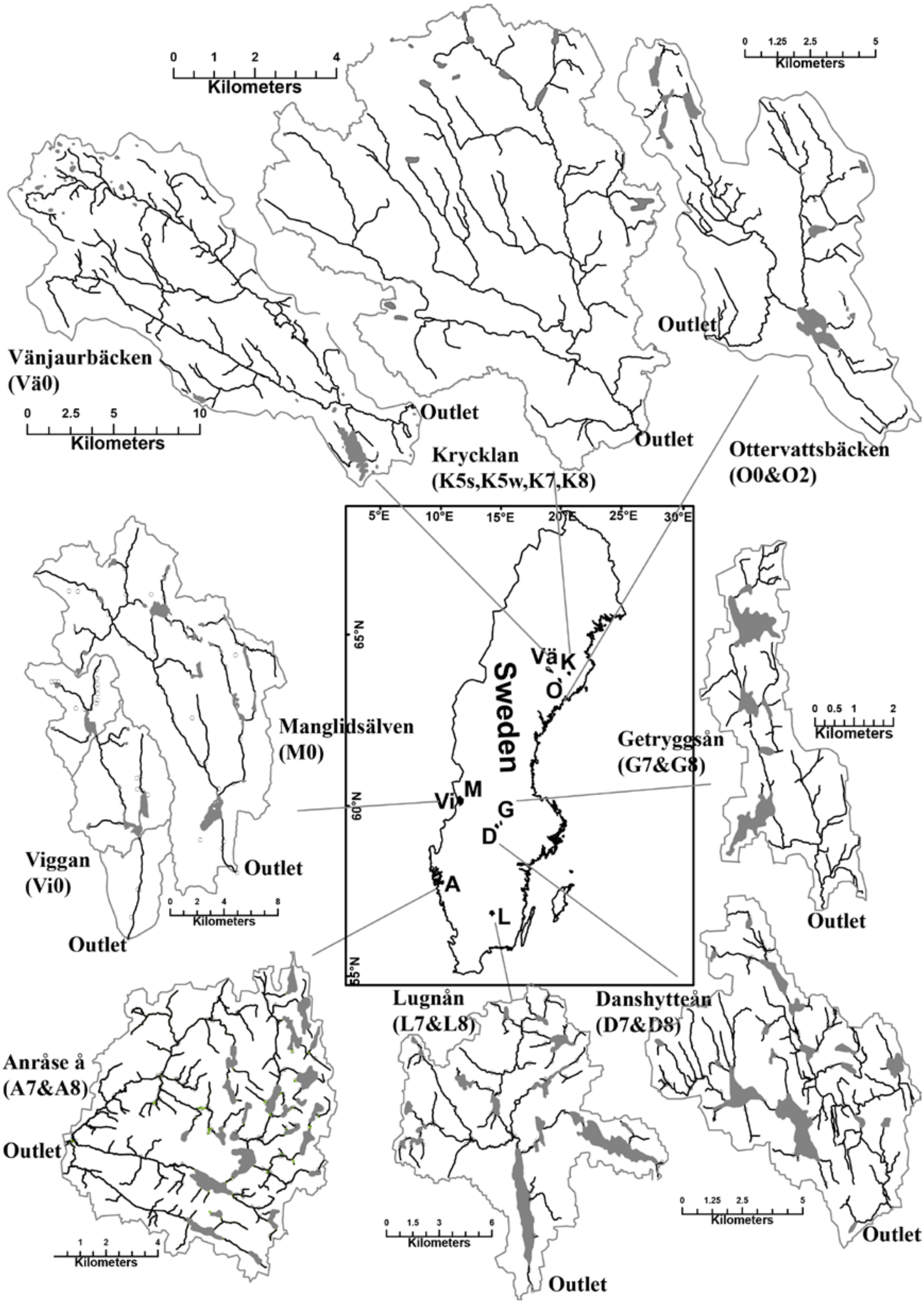
Vänjaurbäcken
(Vä0)
Kilometers
Outlet
Krycklan
(K5s,K5w,K7,K8)
Outlet
Ottervattsbäcken
(O0&O2)
Outlet
Kilometers
Kilometers
Sweden
Vä
K
O
M
Vi
G
D
A
L
5°E
10°E
15°E
20°E
25°E
30°E
65°N
60°N
55°N
Manglidsälven
(M0)
Outlet
Viggan
(Vi0)
Outlet
Kilometers
Getryggsån
(G7&G8)
Kilometers
Outlet
Anråse å
(A7&A8)
Outlet
Kilometers
Lugnån
(L7&L8)
Kilometers
Outlet
Danshytteån
(D7&D8)
Kilometers
Outlet

Fig. 1

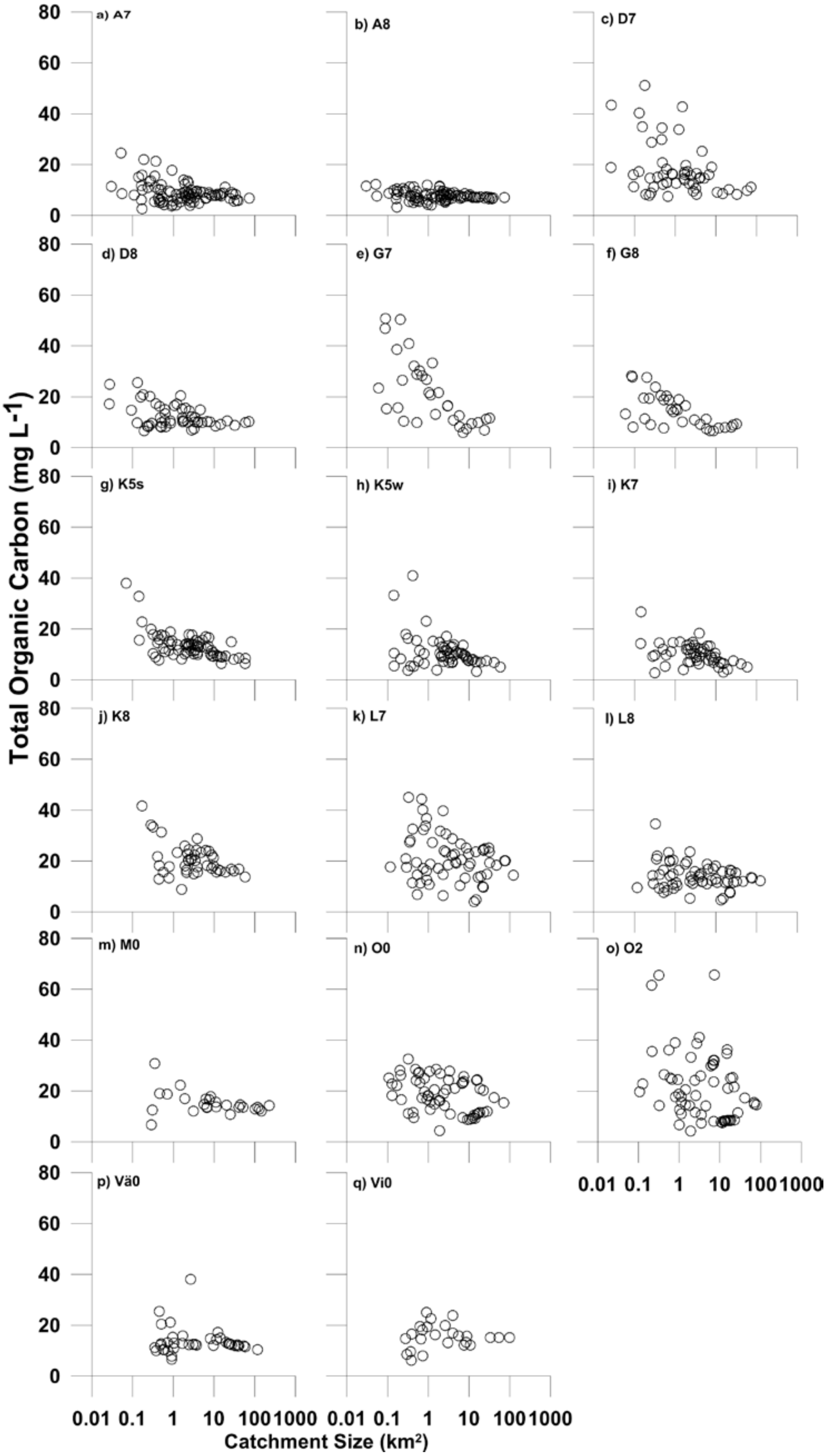
a) A7
b) A8
c) D7
d) D8
e) G7
f) G8
g) K5s
h) K5w
i) K7
j) K8
k) L7
l) L8
m) M0
n) O0
o) O2
p) Vä0
q) Vi0
Total Organic Carbon (mg L-1)
Catchment Size (km2)
0
20
40
60
80
0.01
0.1
1
10
100
1000

Fig. 2

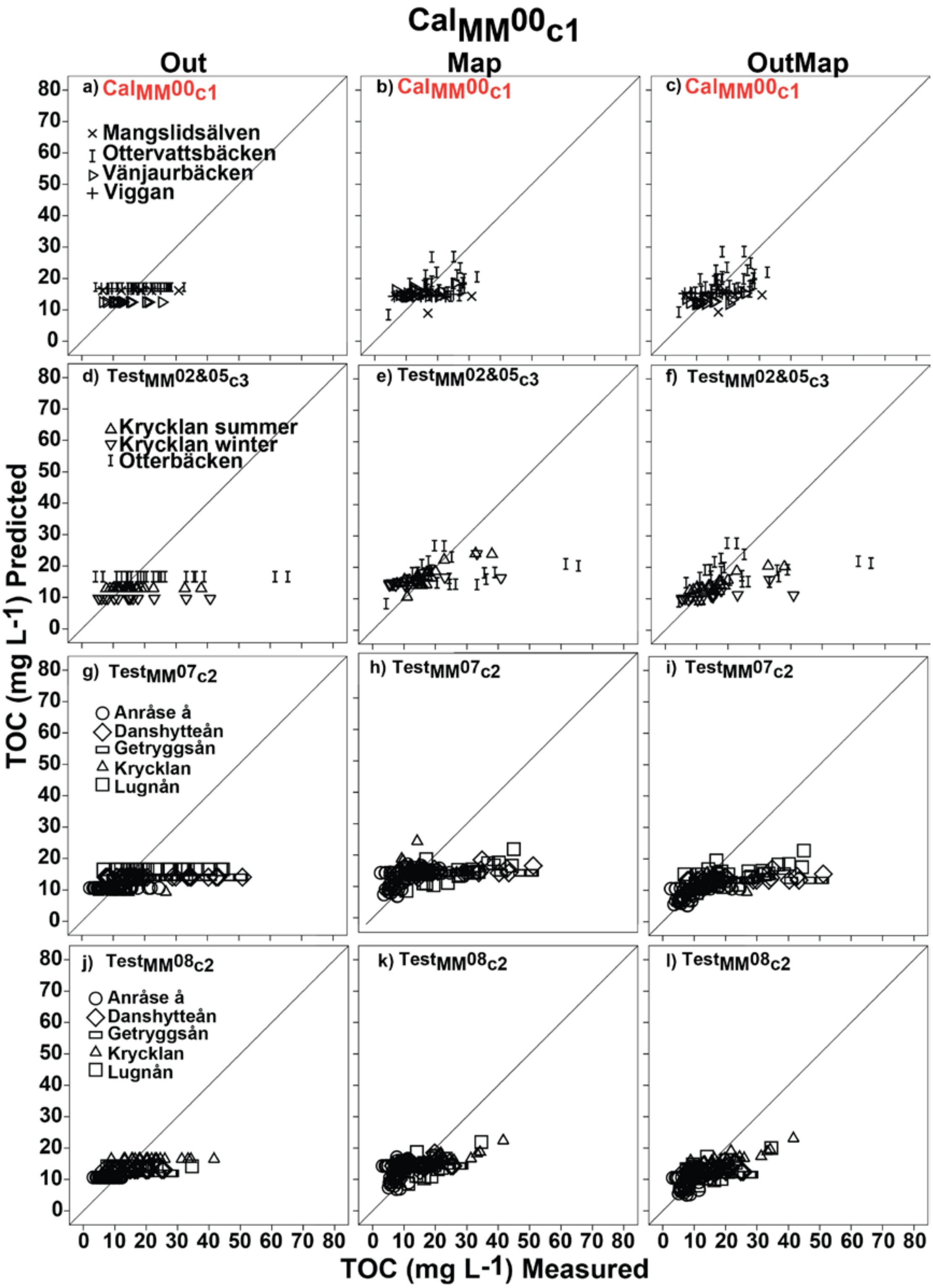
CalMM00c1
Out
Map
OutMap
a) CalMM00c1
b) CalMM00c1
c) CalMM00c1
× Mangslidsälven
I Ottervattsbäcken
▷ Vänjaurbäcken
+ Viggan
d) TestMM02&05c3
e) TestMM02&05c3
f) TestMM02&05c3
△ Krycklan summer
▽ Krycklan winter
I Otterbäcken
g) TestMM07c2
h) TestMM07c2
i) TestMM07c2
○ Anråse å
◇ Danshytteån
▭ Getryggsån
△ Krycklan
□ Lugnån
j) TestMM08c2
k) TestMM08c2
l) TestMM08c2
TOC (mg L-1) Predicted
TOC (mg L-1) Measured
0 10 20 30 40 50 60 70 80

Fig. 3

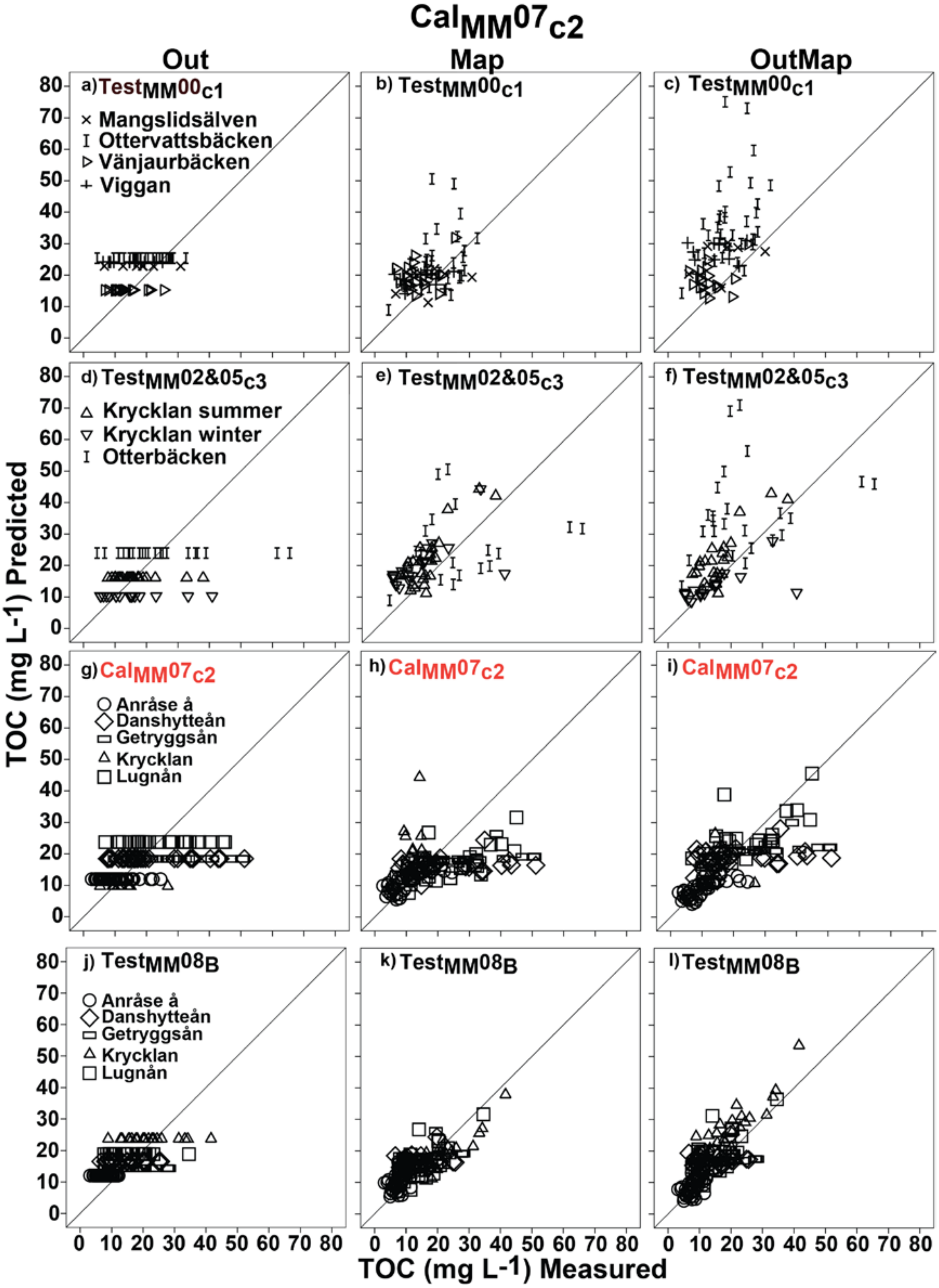
CalMM07c2
Out
Map
OutMap
a) TestMM00c1
× Mangslidsälven
I Ottervattsbäcken
▷ Vänjaurbäcken
+ Viggan
b) TestMM00c1
c) TestMM00c1
d) TestMM02&05c3
△ Krycklan summer
▽ Krycklan winter
I Otterbäcken
e) TestMM02&05c3
f) TestMM02&05c3
g) CalMM07c2
○ Anråse å
◇ Danshytteån
Getryggsån
△ Krycklan
□ Lugnån
h) CalMM07c2
i) CalMM07c2
j) TestMM08B
○ Anråse å
◇ Danshytteån
Getryggsån
△ Krycklan
□ Lugnån
k) TestMM08B
l) TestMM08B
TOC (mg L-1) Predicted
TOC (mg L-1) Measured

Fig. 4

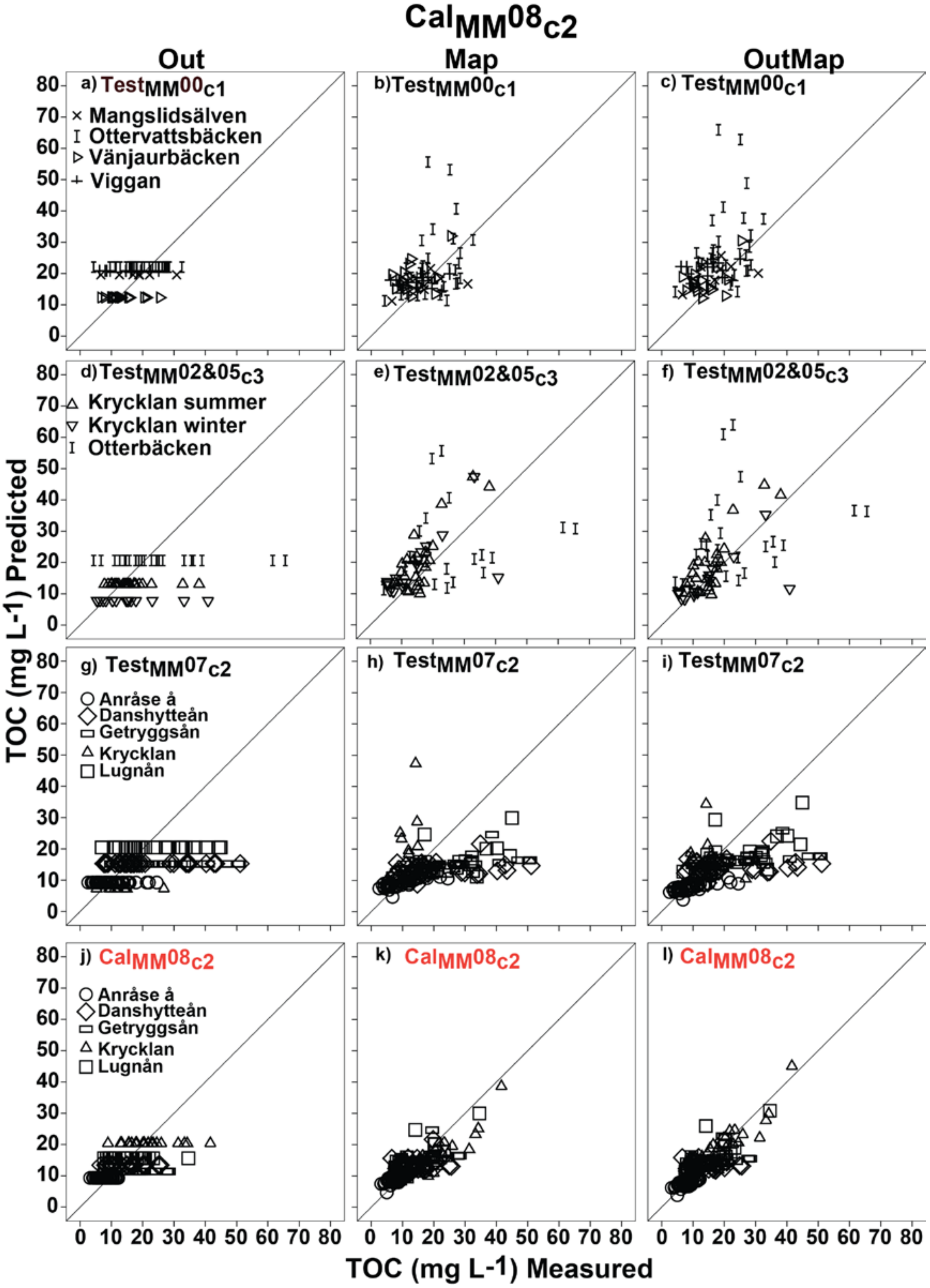
CalMM08c2
Out
Map
OutMap
a) TestMM00c1
× Mangslidsälven
I Ottervattsbäcken
▷ Vänjaurbäcken
+ Viggan
b)TestMM00c1
c) TestMM00c1
d)TestMM02&05c3
△ Krycklan summer
▽ Krycklan winter
I Otterbäcken
e) TestMM02&05c3
f) TestMM02&05c3
g) TestMM07c2
○ Anråse å
◇ Danshytteån
▭ Getryggsån
△ Krycklan
□ Lugnån
h) TestMM07c2
i) TestMM07c2
j) CalMM08c2
○ Anråse å
◇ Danshytteån
▭ Getryggsån
△ Krycklan
□ Lugnån
k) CalMM08c2
l) CalMM08c2
TOC (mg L-1) Predicted
TOC (mg L-1) Measured
0 10 20 30 40 50 60 70 80

Fig. 5