## Authors' response to:

***Interactive comment on "Detection and attribution of global change effects on river nutrient dynamics in a large Mediterranean basin" by R. Aguilera et al.***

***Anonymous Referee #1***

*Received and published: 29 April 2015*

*The manuscript by Aguilera et al. deals with spatio-temporal patterns of nitrate and phosphate concentration in the Ebro river basin and tries to explain them by climate variability (seasonality, NAO) and anthropogenic impacts (land use, fertilizers, irrigation, river damming, waste water inputs). For that, they use 31yr time-series data (1980-2011) from 50 sampling location distributed over the Ebro river and its tributaries. For 37 sampling locations, they additionally analyze time series of stream flow. They use dynamic factor analyses to extract common temporal patterns of all the time series. The identified seasonal cycles, multi-annual cycles, and long-term trends. However, these patterns have a different weight at each sampling location and a substantial proportion of sampling locations shows opposite trends. Then, the authors use multivariate statistics to analyze the relation between the factor loadings associated to each pattern at each sampling location and the differences in catchment properties and other environmental drivers. Overall, the manuscript is of potential interest for the readership of Biogeosciences. I would suggest the publication of the manuscript after some moderate revisions. In most of its parts, the manuscript is well written and the methods are clearly enough described. At some points, some clarifications are needed. In the following, I give some specific comments on methodology and results followed by more general comments on the text.*

We thank Referee #1 for their constructive criticism and detailed comments and suggestions. We addressed these in the revised version of the manuscript and provide here the corresponding specific answers to each of the Referee's suggestions. The original Referee's comments are indicated in italics.

***#1 In-stream/in-reservoir processes – catchment area***

*The authors analyze different potential drivers of the spatial-temporal patterns of fluvial nitrate and phosphate concentrations. Most of the identified drivers relate to the catchment properties and the sources of nitrate and phosphate. For the temporal patterns, in-stream and in-reservoir processes (in particular nutrient uptake by algae growth) play an important role as well. Consequently, the authors analyze reservoir capacity and location as potential environmental drivers. A potential driver of spatial differences in temporal patterns which could easily be addressed as well would be catchment area. This might not be a driver which changes over short time-spans, but, as a surrogate measure for average water traveling time, an important explanatory variable for the different identified patterns. The cluster analysis in section 4.3 and the related figures 3 and 4 suggest an upstream-downstream pattern and catchment area as explanatory variable seems thus promising. For instance, the pattern 3 identified for nitrates seem to become more important in upstream direction (clusters 4->1->2->3).As I get it from the methods section (section 3.7), land use (i.e. different no-point sources of nutrients) is calculated once for the whole catchment and once for a buffer area around the sampling location. This provides the possibility to distinguish between non-point sources (i.e. agricultural areas) that are more upstream and those not far from the sampling location. For the latter, in-stream transformation and retention processes play less a role than for the nutrient loads coming from farther upstream, due to the shorter traveling time. The catchment area could maybe add valuable information. With increasing catchment area, on the one hand, the average traveling time of the water coming from upstream increases, and, on the other hand, the relative contribution from the 10 km buffer area decreases.*

We agree that catchment area plays a role in shaping spatial differences in temporal patterns of nutrient concentration in river basins. For this reason, we originally included the total upstream catchment area in the land use explanatory variables. In other words, we used the areas of the upstream catchments to specific monitoring points for each of the land uses we considered; Industrial, Urban, Dryland and Irrigated agriculture, Forest, Grassland, and Water, all of which were expressed in $km^2$. In addition, in order to depict more local conditions, these land uses were also included as explanatory variables with values obtained within a 10 km radius of each sampling point.

Additionally, meteorological variables such as precipitation and air temperature, as well as water and land management variables such as reservoir capacity and fertilizer application were also introduced as the sum of the values in upstream catchments to each specific sampling point, reflecting in this way the catchment area factor.

The use of catchment area as a separate explanatory variable added a high degree of collinearity with the relevant above mentioned variables. Catchment area was therefore excluded in our analysis. This is now specified in the Methods section in Page 9 of the revised manuscript.

*In section 3.7, the authors write that they consider "reservoir capacity and location, waste water treatment plants (WWTP) discharge and location". From the manuscript, it does not get clear to me how they consider the location of reservoirs and WWTPs. This would be important to know, because the location (immediately upstream or farther upstream?) would likely have an effect.*

We considered the total capacity of reservoirs and the total discharge from upstream catchments for each sampling point as the farther upstream component. By separately considering the capacity and discharge of these explanatory variables (reservoirs and WWTP) immediately upstream the sampling point within the 10km buffer, we differentiated between more local effects and regional effects. An additional sentence was introduced in this Section to clarify this point (Page 9, Lines220-222 of the revised manuscript).

***#2 Instream/reservoir processes part 2 N vs P***

*The spatio-temporal patterns of nitrate and phosphate concentrations might influence each other. With regard to algae uptake of nitrate and phosphate, it would be interesting to know what is the limiting factor of algae growth in the basin. Is it either nitrate or phosphate, or another factor (like light limitation)? Nitrate and phosphate show different long-term trends, with phosphate decreasing in the 1990s and nitrate somewhat later (large rivers). Does this have an effect on in-stream/reservoir algae growth and nutrient uptake/retention?*

A very significant decrease in the concentration of the dissolved phosphorus was observed after the mid 90s. This decrease coincides with the improvement of urban sewage treatment in the most important cities of the Ebro basin. According to a study carried out by Ibañez et al., (2008) there was a significant positive correlation between the concentration of dissolved phosphorus and the concentration of total chlorophyll between the 1987-2004 period (Page 19 of the revised manuscript). Here, low flow conditions together with decreasing dissolved phosphorous and decreasing phytoplankton were likely the main factors causing the increase of water transparency, which improved the eutrophy condition. The results of this study suggest that the observed changes in chlorophyll (first increasing and then decreasing) in the lower Ebro River were a direct consequence of the changes in phosphorus and the DIN/DIP ratio.

**#3 Land use change**

*The authors analyze time-series of nitrate and phosphate over the 31 yr period 1980 to 2011. They explain differences in increasing and decreasing trends by the areal proportion of different land use types. What time is represented by the used land use data? Was there a significant change in land use in the Ebro Basin over the last three decades?*

Re-vegetation is the most significant catchment change that has occurred in the mountainous areas of the Ebro basin during the 20th century. The onset of farmland abandonment and re-vegetation is set between 1950 and 1960 (Garcia-Ruiz et al., 1996). The land use conditions included in our study represent the average conditions between the period 1980 to 2011, where no other significant or drastic land use changes occur, other that management practices related to the improvement of industrial and urban wastewater, which is reflected in the decrease of phosphate in the mid 1990s. The latter sentence was included Section 3.7 for further clarification (Page 9, Lines 213-216 of the revised manuscript).

**#4 Climate change**

*The authors argue that climate change would have an effect on nutrient and phosphate concentration. They identify, however, only effects of climate on the seasonality and multi-annual cycles of phosphate and nitrate concentration which could be related to climatic seasons and the NAO. To show the effect of CLIMATE CHANGE on nitrate and phosphate concentration, they would need to identify a correlation between long-term trends in nutrient concentrations and climatic variables.*

We wanted to reflect the effect of climatic variables in the spatio-temporal distribution of dissolved nutrients in the Ebro basin. We found that streamflow and air temperature shaped nitrate patterns, and that regional and global climatic modes influenced the variability of nutrients at the basin scale. In a sense, the changes in these climatic modes within the 31 years included in our study could indicate the potential role of climate change in in-stream nutrient variability. Regarding long term trends, we did not find a significant correlation between nutrients and climatic variables. This is now discussed in Section 5.1 of the revised manuscript (Pages 17-18)

***#5 Nutrient fluxes from land to sea***

*The lateral fluxes of nitrate and phosphate would be more interesting than the concentrations, because they directly describe the inputs of nutrients to the river or the exports of nutrients to the coast. The fluxes could be easily compared if they were reported relative to the catchment area (e.g. t N km-2yr-1 or moles m-2yr-1). It would be interesting for the readers what the spatio-temporal patterns of nutrient fluxes would be. Also for the long-term trend it would be more interesting to see if the flux of nutrients increased/decreased, in particular for the sampling location which is farthest downstream (because this sums up all the changes upstream and represents the final export to the coast).*

We mainly dealt with nutrient concentration as we wanted to study the temporal and spatial distribution of nutrients in the river network of the Ebro basin and to relate these in-stream concentrations to potential sources of impact related to global change phenomena. Nevertheless, exploring the fluxes that ultimately reach coastal waters is also interesting. For this reason, and as suggested in this comment, we have included the fluxes in two key stations: Downstream-Tortosa and Upstream-Mendavia, both on the Ebro River (Supplementary Material in the revised manuscript). We however did not perform DFA for these fluxes due to computational difficulties related to the complexity of these analyses and the time restrictions for the revision of this manuscript.

Regarding the long-term trends, the overall decrease of phosphate flux is reflected in both upstream and downstream sampling points shown in the Supplementary Material (Section S.1). Significant long-term trends in nitrate flux were not identified.

***#General Comments***

***<u>Introduction</u>***

*Page 5261*

*L 6: You should try to find a more suitable word for "action". Maybe "impact"?*

The word action is in the original definition of global change by the US Global Change Research Act, we therefore maintain this word in this particular line. Impacts of global change phenomena on freshwater resources are mentioned in the following lines (Page 2 in the revised manuscript).

*L12-15: Please, shortly explain here why this would be a fundamental concern.*

Nutrient pollution derived from anthropogenic activities impacts inland and coastal waters, resulting in serious environmental and human health issues, and impacting the economy. A brief referenced explanation has been added to the text (Page 2, Lines 40-42 in the revised manuscript).

*L22-24: I don't really understand this sentence. Are you talking about the eutrophication of the rivers themselves (then the concentrations of nitrate and phosphate in the water would be important) or about the eutrophication of the coastal waters (then the fluvial nitrate and phosphate fluxes would be important).*

In this context, we are mainly referring ot the eutrophication of rivers and inland waters themselves, which is also why we work with nutrient concentration values instead of fluxes. The sentence has been rewritten (Page 2 in the revised manuscript).

*Page 5262*
*L1-3: Do you really mean "insight of the physical, biological, or socioeconomical events"? Or rather the impacts of these events?*

By extracting the key properties of time-series one can obtain evidence of changes and hints of potential causes behind such changes, which are later corroborated with comprehensive analyses. In a sense, one thus obtains information about the potential events that might have caused the observed impacts on the time-series being analyzed. This sentence has been nonetheless slightly modified to clarify our point (Page 3 in the revised manuscript).

*L13-19: Maybe you should shortly explain and evaluate (strengths, shortcomings) of all of each methods.*

Although the evaluation of these methods is out of the scope of this paper, we emphasize some strengths and shortcomings of the different methods in the following lines (Page 3, Lines 75-83 in the revised manuscript), such as the inability of extracting common patterns from sets of time-series and not being able to deal with missing observations.

*L20: "Spectral analysis" was not mentioned before. What do you mean by "methods like spectral analyses"? Does this include all the methods named above?*

We meant that spectral analysis methods, such as Singular Spectral Analysis, as well as the previously mentioned methods related to trend analysis and time-series analysis in general, are not able to simultaneously extract common patterns from a set of time-series. The sentence in the previous manuscript has been modified to exemplify spectral analysis methods (Page 3 in the revised manuscript).

*L24-28: The meaning of this sentence is not clear to me. As I get it from the text, you need a good data coverage to identify local stressors and disentangle their effect from the effects of global stressors. Thus, you try to avoid discarding time-series from your data pool and rather opt for an advanced method which can get valuable information out of less-consistent time series. If that is the case, you should clarify this here and write it in a more comprehensible way.*

Yes, we wanted to avoid discarding time-series in our dataset and therefore chose a method that could simultaneously deal with sets of time-series and cope with data gaps. The sentence has been modified to emphasize this idea (Page 4 in the revised manuscript).

***<u>3 Methods</u>***

*Page 5264*

*L14-15: How do you defined patterns? Are these the temporal patterns, i.e. seasonality, long-term trends and multi-annual cycles? Please, clarify here.*

We make reference to the temporal patterns, such as cycles and trends. This line has been modified to make this clearer (Page 5 in the revised manuscript).

*L16: The abbreviation 'DFA' should be defined. It appears here for the first time.*

The abbreviation and its definition first appears on Page 5263 (Introduction), and are also included in the abstract. We however have defined DFA also in this line (Page 5 in the revised manuscript).

*Page 5266*

*L12-13: "significant trends that are not necessarily a straight line". Better use formulations like "non-linear trend".*

The line has been changed to the suggested formulation (Page 7 in the revised manuscript).

Page 5268

L3-4: Do you have a reference for this?

A reference has been included to support the idea that generalized least squares for regression modeling is advisable when neighboring values of the response variable tend to be spatially correlated (Page 9 in the revised manuscript).

*L5-8: What is a "spatial error structure"? What are the other 5 options for error structures? Why is the Gaussian structure (=" Gaussian distribution" ?) the best option?*

This sentence has been modified to clarify the implementation of the Gaussian distribution as the spatial error structure, which was the best option for our generalized least squares (gls) models fitted by means of the nlme R-Package (Pinheiro et al., 2012) (Page 9 in the revised manuscript).

***<u>4 Results</u>***

*Page 5270*

*L1-3: How significant is that trend, when 20 of the 50 stations show an opposite trend? Also in Fig. 1c, this trend is not visible.*

The trend is not visible as nitrate pattern 3 was not the dominant pattern (i.e., it had a negligible factor loading magnitude) in this particular sampling point (Miranda de Ebro), located in the upstream section of the basin. The significance or relevance of this opposite decreasing trend in nitrate concentration is indicated by the magnitude of the factor loadings in those 20 stations, shown in Figure 2.

*In Table 2, the authors list the identified potential drivers of all identified patterns, also for pattern 3. For pattern three, they make the distinction between stations with a positive factor loading and stations with a negative factor loading. Interestingly, for both they identified 'Industrial area (%) UPSTREAM' as explanatory variable with the same positive coefficient. What does that mean? Please, discuss.*

The role of the Industrial area (%) UPSTREAM explanatory variable and the same sign for nitrate Pattern 3 with positive factor loadings (decreasing long-term trend) and with negative factor loadings (increasing ling-term trend) could be explained by the fact that Pattern 3 was particularly relevant (i.e., factor loading magnitudes were higher, regardless of their sign) in areas with little industrial activity. What made the difference between the decreasing versus the increasing trends, in addition to the other significant explanatory variables identified, could have been the varying types of industrial activities present in the vicinities of particular sampling points. The information on specific types and impacts of industrial activities in the basin was not available.

Page 5271

*L3-17: Here, it would be interesting to see a similar pattern analysis for stream flow, because the authors identified a clear relation of nitrate pattern 1 to stream flow (Fig. 1e). Next, it would be interesting to see if stations with different factor for nitrate pattern 1 would also show different factor loadings for any identified pattern of stream flow.*

We extracted common patterns from streamflow time-series in 37 sampling points in the basin. The relevant results related to the coherent cycles of streamflow with nutrient concentration and climatic variables are presented in the paper. However, carrying out a full analysis of the DFA streamflow patters, including all the steps outlined in the Methods section, would have considerably extended the length of the manuscript and potentially hindered the interpretability and the main scope of this paper. For this reason, these more specific analyses are not included here.

Also, there was no factor loading sign switching among the extracted patterns for streamflow.

*Table 2: For nitrate pattern 1 – positive factor loadings, Mean air temperature (upstream) was identified as an important explanatory variable. This variable was also identified to show a strong negative correlation to nitrate pattern two (Fig. 1e). In Fig 1e,f, the nitrate patterns 1 and 2 do not seem that different, with a minimum in late summer, when average air temperature is highest. This is an issue that would have to be discussed.*

The significance of mean air temperature as an important explanatory variable for nitrate pattern 1 (positive factor loadings) has to do with the spatial distribution of the mean temperature values and the (negative) relationship between these two, identified by means of gls regression models.

The relationship between temperature and Pattern 2 in Fig 1e. is based on averaged temperature values for the Ebro basin.

Furthermore, although there is a common minimum in late summer between nitrate patterns 1 and 2, there two patterns are overall very different from each other and were clearly and significantly related to two different variables, as shown in Table 2 and Figures 1e and 1f.

Page 5272

*L19-21: The authors showed that nitrate pattern 2 can be correlated to temperature and this might be due to biological activity, or phenology like the authors expressed it. While reading 'phenology', I think about terrestrial vegetation and, in this context here, the control of terrestrial nutrient cycling on the exports of* *nutrients to streams. Here, the authors show that this pattern (pattern two) is most dominant in the far downstream part of the Ebro. If a terrestrial control was the cause of this temporal pattern, it would be interesting to know why this pattern is less dominant in more upstream parts. Might it be that this pattern is due to in-stream uptake of N and P by aquatic autotrophic production? Then, 'phenology' might be a bit misleading.*

As stated in the case of nitrate concentration, assimilation by freshwater primary producers during summer and the seasonal evolution of leaf fall and decomposition could have taken a major role. These factors are grouped in the term phenology, which is not restricted to terrestrial ecosystems, but can also include the activity of freshwater algae.

Nevertheless we have stated that the nitrate pattern 2 related to temperature in the Ebro basin gained more relevance in the downstream rivers and streams due to the presence and control of large reservoirs and the biogeochemical processes occurring therein and immediately downstream (Page 14 in the revised manuscript).

We include a discussion of the potential downstream shift from terrestrial phenology to biogeochemical reservoir processes as biological control of pattern 2 in the Discussion section of the revised manuscript (Page 15), as suggested by the Referee in the following comment.

***5 Discussion***

*Page 5273, L21-Page5274, L4: See comment before. The nitrate pattern 2 seems to be most dominant in the downstream part. Could this indicate that algae growth has a more dominant effect than phenology of terrestrial ecosystems? Or is this due to the fact that pattern 1 is lower (due to retention in reservoirs) and thus the relative contribution of pattern 2 is higher? But then, the pattern 2 driven by terrestrial ecosystem phenology would also be attenuated due to water retention in reservoirs and, thus, algae growth would be left as the driver for pattern 2 in the downstream section of the Ebro. Maybe you should discuss the potential downstream shift from terrestrial phenology to algae growth as biological control of pattern 2.*

Terrestrial phenological processes such as those involved in leaf fall and decomposition would potentially be more important in upstream sections of the basin, where the biogeochemical activity in large reservoirs is not present. Based on this and the previous Referee's comment, we have specified the effect of downstream reservoir biogeochemical control on nitrate pattern 2 in the Discussion of the revised manuscript (Page 15).

*Page 5275: If the authors also showed their results from the DFA for stream flow, like they did for nitrate and phosphate in Fig 1, this could help interpreting and discussing the effects of NAO and ENSO on the patterns of nitrate and phosphate. So far, from figure 1, only the average 12 month cycle of stream flow is visible. In table 1, they also state stream flow oscillations at 1.5, 2.2, 3.2, and 4.2 yrs. It would be interesting to have these identified patterns for stream flow as a plot which could be directly compared to those for phosphate and nitrate. It would also be interesting to see if there is a longterm trend for stream flow, in particular at the site farthest downstream.*

As stated earlier in this document, we extracted common patterns from streamflow time-series in 37 sampling points in the basin. Adding all this information in the manuscript would detriment its current flow and its main scope. For this reason, we have added the DFA results for streamflow in Section S.2 of the Supplementary Material.

No significant correlation was found between long-term trends for streamflow and nutrients in the Ebro basin, and this is indicated in Table 1 for each pattern with a significant long-term trend identified by the Kendall tau and p-values in the yue-Pilon trend analyses. In fact, we did not identify any significant trend in streamflow common patterns identified by means of DFA.

*Section 5.2, first paragraph: Here, I got a bit confused and had to read through the text several times. From Page 5272, L27 to Page 5276, L4: Do you refer to the sampling locations with increasing trends? If yes, please clarify that in the text.*

We refer to all significant trends identified for both nitrate and phosphate; we have clarified this idea in the revised manuscript.

*You should try to restructure the whole paragraph and make it more logical. For the explanation of decreasing vs. increasing trends, you should start with the terrestrial sources: what human activities might have decreased nitrate concentrations (e.g. more rational application of synthetic fertilizers, improved sewage water treatment) and what might have increased nitrate concentrations at other sampling locations. Then you should come to the differences related to upstream-downstream patterns. Of course, head water streams might show stronger increasing trends if the sources increased, and decreasing trends when the sources decreased. Smaller catchments are likely more homogenous than larger catchments, that means that it is more likely that either decreasing or increasing terrestrial inputs prevail. Larger catchments, in particular because the catchments here are nested and large catchment contain multiple small sub-catchments considered here, will more likely contain a mix of increasing and decreasing terrestrial sources. Further, due to longer traveling times of the water, and additionally the impact of reservoirs, increasing nitrate inputs might also cause increased algae uptake (and denitrification?) that might attenuate increasing trends at downstream locations.*

We have re-structured the first paragraph in Section 5.2 in the revised manuscript to include the suggestions stated above.

**Author's response to:**

***Interactive comment on "Detection and attribution of global change effects on river nutrient dynamics in a large Mediterranean basin" by R. Aguilera et al.***

***Anonymous Referee #2***
*Received and published: 30 April 2015*

*This manuscript deals with river nutrient dynamics in the Ebro basin, and attempts to link nutrient variations in the river and its tributaries to a number of environmental and anthropogenic factors. For this study, the authors use data from public databases, from which they extracted nitrate and phosphate concentrations, and are using the data from 50 sampling locations where they were able to construct a 31-year time series.*

*They are also using water discharge time series for 37 of these 50 sampling locations.They are using a number of statistical tools, in conjunction, to highlight trends and patterns, in order to identify interannual or seasonal cycles, and to associate them with the external factors considered. I appreciated the fact that the authors do point out that public databases and time series often are poorly maintained and lack data.*

*Overall, the manuscript is well written, the description of the tools used, and why, is helpful and clear. The topic is within the Biogeosciences scope. I would only suggest minor revisions, mostly clarifications on some points I will go over below.*

We thank Referee #2 for their constructive criticism and for providing specific comments below, these are dealt with in the revised version of the manuscript and we provide here the corresponding specific answers to each of the Referee's suggestions.

*The main issue for me here is the use of the term "global change". We are all aware that global change does not exclusively mean climate change, and I understand that the external factors taken into account in this study can fall within the "global change" category. However, I would like to see a short paragraph defining what exactly the authors mean by global change in this instance, and why these particular factors were chosen and relate to that definition. The reason why I mention this is that the notion of global change appears early in the manuscript, and then in the conclusions, but we lack insight so as to what it really means here. "Global change effects" or "global change impacts" is an extremely broad notion.*

Global change in our paper includes anthropogenic activities such as land use and water management practices, as well as changes in climatic conditions. There is a brief description of the concept of global change in Page 2 of the revised manuscript.

*The spatial component of the variability studied also could benefit from extra space in the manuscript. In section 3.7 it is said that for each sampling point, mean values and percent areas were calculated considering 2 regions: is this for all potential explanatory variable listed above between lines 17 and 25, or only some of them? Were you able to get complete time series for ALL these variables? And what of their location (reservoirs, WWTPs: : :), this could be useful to know. If I understand correctly, the spatial distribution of patterns/explanatory variables is computed from the patterns themselves found though DFA? I had a hard time picturing spatial distribution from the manuscript alone, even though the figures are good. Figure 5 is a good attempt at putting together explanatory variable and affected clusters, but if the colored circles refer to clusters in Fig. 3 and Fig 4., how can we know if red circles are Cluster 1 from fig. 3 or Cluster 1 from fig. 4. Same thing with blue circles (Cluster 4 from fig. 3 or cluster 2 from fig. 4?). The clustering and conclusions drawn from explanatory variables identified should be discussed more in depth in section 5. All in all the "spatial" talk is very technical, and adding a paragraph in the discussion regarding this would make it easier to understand.*

The spatial distribution of the relevant patterns was identified by the magnitude of the factor loading for each pattern, and these magnitudes are defined by DFA results. The values for explanatory variables represented averages at each particular sampling point location. The main objective here was to find any relationship between the factor loading magnitude distribution and the relevant explanatory variables identified by regression models. The average values for explanatory variables for the two regions (total upstream and local buffer) were computed for all variables. Further clarification is now provided in Section 3.7 in the revised manuscript.

Regarding Fig. 5, the clustering colors belong to the corresponding nutrient, i.e, Fig.3 cluster colors for nitrate appear in Figure 5 in the NO3 sub-figure and Fig.4 cluster colors for phosphate belong in the PO4 sub-figure in Fig. 5. Nevertheless, to avoid confusion, we have clarified the origin of the cluster coloring in Fig. 5 in the revised version of the manuscript by assigning capital letters to the nutrient sub-figures (A for nitrates and B for phosphates), and by explicitly specifying their link to clusters Figs. 3 and 4.

The clustering and conclusions drawn from explanatory variables have been further discussed in Section 5 of the revised manuscript.

*Section 4.1: Are the 3 extracted patterns common to all 50 times series?*

Yes, the 3 extracted patterns are common to the set of 50 time-series, and this has been emphasized in the revised manuscript (Page XXX). The relevance of each pattern at each monitoring point is indicated by the magnitude of the factor loading obtained at that point.

*Section 3.1: - “collected from public databases”: did you use multiple different databases to construct the time series? If so, were the measurements made the same way at each sampling site, maybe they were automated? Were they all comparable? - “some unreasonable values were manually removed”: did you try to link these values with land use data? How unreasonable? Were they measurement errors?*

The 50 time-series for nitrate and phosphate concentration, as well as streamflow values, were obtained from the same database of water quality monitoring carried out by the Ebro Basin Authority (CHE; http://www.chebro.es/). The same measurement methodology, specific to each variable, was applied throughout the entire network of monitoring points.

Unreasonable values were mainly outliers and those derived from the inappropriate use of characters such as decimal commas instead of decimal points, which could be grouped as recording errors. The sentence has been modified to include this information in the revised manuscript (Page 5).

*Streamflow time series: I was a bit confused with the streamflow time series. Were you able to get complete streamflow time series for 37 sampling sites? Why reconstruct it? Maybe a sentence could be added in section 3.3 explaining this further?*

As stated in the text (Pages 5-6 of the revised manuscript), we used the DFA resulting streamflow patterns to enhance the signal to noise ratio of the measured streamflow time-series, which in turn facilitated the identification of characteristic oscillations and potential relationships between streamflow and other variables.

The 37 streamflow time-series contained data gaps, for this reason we obtained the reconstructed continuous streamflow time-series based on DFA resulting patterns and factor loadings. This information has been added to this section to provide further clarification.

*References: In the manuscript you cite (Caille, 2009) but in the reference list we find Caille et al., 2012. Please correct. P 5274, line 2: Gonzalez et al., 2012 does not appear in the reference list*

The reference should read (Caille, 2012), this has been corrected in the revised manuscript. Also, the reference related to González (2012) has been included in the reference list.

*p. 5275, section 5.1, lines 1-13: ENSO discussion/oscillation pattern: Is there also a similar pattern affecting precipitation? Or air temperatures? Could this further link your findings with ENSO? On the same page, line 15, I would replace "in our view", maybe with "in our opinion"?*

We observed that both nutrient and streamflow patterns in the basin showed oscillations coherent with those of the ENSO and NAO, which are known to modify the magnitude and frequency of precipitation. In this case, we used streamflow as a surrogate variable for precipitation. Looking at the air temperature patterns in the Ebro basin, we can add that they also present the supra-annual frequencies characteristics of the above mentioned climatic modes. Specifically, air temperature patterns had significant frequencies of 2.2, 2.7, 3.3 and 5.7 yr. This information has been added to Section 5.1 (Page 17) in order to provide further evidence of the link to ENSO and NAO.

Line 438 in Page 17 of the revised manuscript now starts with the phrase "in our opinion".

*Typos: P 5272, line 18 "showed the largest relevance of pattern 1": please replace "of" with "for"*

The typo has been corrected. The line 350 (Page 14) now reads "showed the largest relevance for Pattern 1".

## Detection and attribution of global change effects on river nutrient dynamics in a large Mediterranean basin

R. Aguilera, R. Marcé, and S. Sabater

**<u>Revised Manuscript – List of relevant changes</u>**

The reference to specific relevant changes in the revised manuscript (including reference to page/line numbers) is included in the authors' point-by-point response to referees 1 and 2. Here we present a general summary of the most significant changes in the revised version of the manuscript:

- Clarification sentences on the issues of catchment area, instream and reservoir processes, land use and climate changes, and nutrient fluxes have been included following the suggestions of Referee #1.

- Clearer definitions for specific terms and concepts have been provided as suggested by both referees.

- The Methods and Discussion sections have been particularly expanded to include further explanation and discussion on key issues of the methodology and the implications of our findings.

- A Supplement Material has been added to include the estimation of nutrient fluxes in two key locations in the basin, as well as the resulting common patterns for potential drivers of nutrient variability in our basin (e.g., streamflow and air temperature).

- New references were added when needed in order to provide support to new concepts introduced based on the questions and comments of the referees.

# Detection and attribution of global change effects on river nutrient dynamics in a large Mediterranean basin

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**Abstract**

Attributing changes in river water quality to specific factors is challenging because multiple factors act at different temporal and spatial scales, and it often requires examining long-term series of continuous data. But data consistency is sometimes hindered by the lack of observations of relevant water quality variables and the low and uneven sampling frequency that characterize many water quality monitoring schemes. Nitrate and dissolved phosphate concentration time-series (1980–2011) from 50 sampling stations across a large Mediterranean river basin were analyzed to disentangle the role of hydrology, land-use practices, and global climatic phenomena on the observed nutrient patterns, with the final aim of understanding how the different aspects of global change affected nutrient dynamics in the basin. Dynamic Factor Analysis (DFA) provided the methodological framework to extract underlying common patterns in nutrient time-series with missing observations. Using complementary methods such as frequency and trend analyses, we sought to further characterize the common patterns and identify the drivers behind their variability across time and space. Seasonal and other cyclic patterns were identified, as well as trends of increase or decrease of nutrient concentration in particular areas of the basin. Overall, the impact of global change, which includes both climate change and anthropogenic impacts, on the dynamics of nitrate concentration across the study basin was found to be a multifaceted process including regional and global factors, such as climatic oscillations and agricultural irrigation practices, whereas impacts on phosphate concentration seemed to depend more on local impacts, such as urban and industrial activities, and less on large-scale factors.

## 1. Introduction

The Earth system is intrinsically dynamic but the intensity and rate of recent environmental changes are overall unprecedented (Meybeck, 2003; García-Ruiz et al., 2011). Land-use change and management practices, pollution, human demography shifts, and climate change are components of global environmental change (Rosenzweig et al., 2008), understood as the synergy between climate change and direct action of human activities on the territory (U.S. Global Change Research Act, 1990). Freshwaters are at the forefront of the phenomena associated to global change (Vörösmarty et al., 2010), and impacts on water resources availability as well as on their quality are extensive (Parmesan and Yohe, 2003; Milly et al., 2005; Grimm et al., 2008; Rabalais et al., 2009; Gallart et al., 2011).

Nutrient pollution derived from anthropogenic activities impacts inland and coastal waters, resulting in serious environmental and human health issues, and impacting the economy (Howarth et al., 2002; Woodward et al., 2012). A fundamental concern in river ecology is therefore to understand the spatial patterns of nutrient concentration and loading in rivers, their variation during the last decades, and whether these are promoted by the increasing human activities (Grizzetti et al., 2011), or associated to climate change (Marcé et al., 2010). This is particularly relevant in Mediterranean regions where the imbalance between available water resources and increased demands has become a growing problem (Milly et al., 2005; Bovolo et al., 2011), and where streams and rivers bear concurrent additional pressures such as damming, water extraction, and urbanization (Sabater and Tockner, 2010). In Spain, for instance, the construction rate of large dams peaked during the 1960s and 1970s, whereas human population density and urban area in the Mediterranean region increased during the 1990s (Cooper et al., 2013). Furthermore, nutrient pollution ~~export~~ in Mediterranean rivers contributes to eutrophication because of the co-existence of naturally-occurring low flows and high water demand (Caille, 2012). However, it is challenging to attribute changes in nutrient concentration dynamics to specific factors, because factors of change exist and act at different temporal and spatial scales (Kundzewicz and Krysanova, 2010). Identifying factors and causes often requires examining long-term series of data, which should be consistent and of good quality. Such detailed analysis, which aims to extract the key properties enclosed in time-series, is essential to obtain insight of the physical, biological, or socioeconomical events and associated impacts that originally shaped these time-series (Ghil et al., 2002). It is realistic to consider that temporal trends and spatial patterns reveal emerging environmental problems (Lane et al., 1994; Lovett et al., 2007; Marcé et al., 2010; Estrada et al., 2013). Data consistency can be however affected by the lack of observations of relevant water quality variables and the low or uneven sampling frequency, which are common characteristics of many water quality monitoring schemes worldwide. These impede the appropriate analysis of the time-series available from long-term monitoring, eventually affecting management decisions on the minimization of effects of global change, and particularly in Mediterranean regions, where there is a dearth of knowledge compared to other temperate regions (Benítez-Gilabert et al., 2010). The vast majority of studies of global change impact based on the analysis of longterm data use time-series methods like the Mann–Kendall and the Seasonal Kendall analyses for trend detection (Chang, 2008; Bouza-Deaño et al., 2008; Argerich et al., 2013); wavelet analysis for temporal patterns (Kang and Lin, 2007); and combinations of statistical models such as univariate and multivariate regressions (Tilman et al., 2001); and analysis of variance and variography (i.e., spatial dependence measured as a function of the distance and direction separating two locations; Bernal et al., 2013). ~~However, methods like s~~Spectral analysis (e.g., Singular Spectrum Analysis), is limited to characterizing the spectral density to detect any periodicities in the data and does not necessarily allow the identification of common patterns embedded in a collection of time-series (Zuur et al., 2003). Furthermore, most of the above mentioned ~~se~~ methods do not easily accommodate missing observations, which are extremely abundant in most public environmental databases. The~~se~~ ~~limitations –~~restrictions on the number of time-series that can be analyzed and the requirements of continuous time-series needed to implement such methods make the analysis of water quality datasets in large regions difficult and cumbersome~~, compromising the spatial and temporal coverage of the analyses, while~~. Since in most occasions the impact of global change on a given ecosystem consists in the overlap of multiple stressors acting at both regional and local scales~~. Therefore~~, it is necessary using methodologies that explicitly consider the inextricable link between temporal and spatial patterns of change and that are able to accommodate missing values. We use a combination of Dynamic Factor Analysis (DFA), classical time-series methods, and spatial regression models to extract underlying common patterns in a set of time-series and to depict their relationships with local and global scale phenomena. We apply the above to a set of river nutrient concentration time-series within a Mediterranean basin in order to identify temporal and spatial patterns at the basin-wide scale, and to understand how global change shapes these patterns. Both nitrate and dissolved phosphate dynamics were analyzed in order to disentangle the role of hydrology, land-use practices, and climate phenomena on the observed patterns, with the final aim of understanding how the different aspects of global change may affect nutrient variability (and hence water quality) in the basin.

## 2. Study area

The Ebro River is one of the main tributaries of the Mediterranean Sea. The mean annual runoff at the outlet is 13 408 hm3. The basin covers a highly heterogeneous area of ca. 85 500 km2, which extends from the southern-facing side of the Cantabrian range and Pyrenees and the northern-facing side of the Iberian Massif until the river reaches the Mediterranean Sea (Sabater et al., 2009). The geographical setting of the Ebro River determines a large range of climatic conditions (Sabater et al., 2009). Mean annual precipitation varies from over 2000mm in the Pyrenees to less than 400mm in the arid interior. Overall, silicic materials are located in the uppermost altitudes while calcareous materials occur at lower elevations (Lassaletta et al., 2009). The water biogeochemical characteristics are highly influenced by anthropogenic activities. The main effects are those due to water discharge regulation (i.e., the construction of large reservoirs) and agriculture (determining increases in nitrate concentration) (Romaní et al., 2010). The intense use of water throughout the basin (Boithias et al., 2014) puts the Ebro River under strong pressure particularly in the most downstream sections during dry annual periods, when irrigation is widespread. The basin started a sanitation plan during the 90s that progressively covered most of the local inputs.

## 3 Materials and methods

### 3.1 Time-series data

Existing nitrate and phosphate concentration as well as water discharge data of the Ebro River Basin were collected from public databases (Ebro Basin Authority (CHE)). The frequency of sampling was monthly. We selected 50 monitoring points distributed all across the basin that showed the longest time-series, consisting in 31 year-long (1980–2011) monthly data. Thus, these time-series had a maximum length of 372 data points, although most of the stations contained observation gaps. ~~Some unreasonable values~~Outliers, related mainly to recording errors, were manually removed considering expected ranges of values for each nutrient. Discharge time-series were available in 37 of the sampling sites.

### 3.2 Detection and attribution of global change effects: methodological steps

The first step in defining global change effects on nutrient time-series was to detect common temporal patterns (i.e., cycles and trends) (Sect. 3.3) in the 50 nutrient time series (nitrate or phosphate) using Dynamic Factor Analysis (DFA) (Zuur et al., 2003). Once the common patterns for nitrate and phosphate were identified, we described the significant cycles and trends present in those patterns with classical frequency (Sect. 3.4) and trend (Sect. 3.5) analyses. Subsequently, the potential dependence on hydrological variability was sought by exploring any significant association between patterns and water discharge time-series (Sect. 3.6). We finally assessed the spatial variability of these patterns and their relationship to environmental change drivers in the region by means of spatial regression models (Sect. 3.7) and clustering (Sect. 3.8).

**3.3 Extraction of common nutrient concentration patterns**

Dynamic Factor Analysis (DFA; Zuur et al., 2003) is a dimension-reduction method that estimates underlying common patterns in a set of time-series. It is based in the so-called state-space model, which treats each observed time-series as a linear combination of multiple state processes (Holmes et al., 2012). A considerable advantage of the state-space approach is the ease with which missing observations can be dealt with. The main disadvantage of DFA is that it can be computationally expensive. DFA decomposes the observed time-series from all sampling points included in the analysis into common patterns and their associated error terms (Holmes et al., 2012). The resulting patterns are in turn related to factor loadings, which indicate the weight that each pattern has at every monitoring point included in the analysis. In other words, DFA models the different time-series as a linear combination of common temporal patterns, in a similar way a Principal Component Analysis reduces an *n*-dimensional problem into a few manageable axes. Both the identified common patterns and their relevance at each sampling point (i.e., the factor loadings) were subsequently analyzed using additional time-series and regression techniques. DFA was applied to our database by means of the MARSS v3.4 R-package (Holmes et al., 2013). We also used DFA to enhance the signal to noise ratio of the measured streamflow time-series which in turn facilitated the identification of characteristic oscillations and potential relationships between streamflow and other variables. After DFA, we reconstructed the streamflow time-series at each sampling point (since the original time-series contained missing observations) using the best linear combination of the common patterns identified during DFA. This procedure is equivalent to other signal to noise ratio enhancement methods, like reconstruction using Singular Spectrum Analysis (Ghil et al., 2002), with the difference that our approach enhances the features shared by the different time-series.

**3.4 Identification of significant oscillations in the common nutrient concentration patterns**

We analyzed all significant frequencies present in the common patterns identified by DFA using frequency analysis. We specifically aimed to identify frequencies that could be linked to seasonal cycles (6 and 12 months period) and climatic interannual oscillations. We chose the Multitaper Method (MTM) due to its reduced variance of spectral estimates compared to classical methods (Ghil et al., 2002). Frequencies significantly different from noise at the $p < 0.05$ level were identified using the $F$ test for spectral frequencies. MTM was applied using the Multitaper R-Package (Rahim and Burr, 2013).

**3.5 Identification of significant temporal trends in the common nutrient concentration patterns**

Since the common patterns are allowed to be stochastic in DFA, they can also contain significant trends that are ~~not necessarily a straight line~~non-linear (Zuur et al., 2007). We therefore sought to identify the significant trends present in individual patterns and to characterize such trends as increasing or decreasing over time. We used the implementation of the Yue–Pilon's (Yue et al., 2002) prewhitening approach included in the zyp R-package (Rahim and Burr, 2013) to determine the trends in data that are serially correlated. The method computes both the Kendall's tau statistic and the Kendall's *p* value.

**3.6 Relationships between streamflow and the common nutrient concentration patterns**

The relationships between streamflow and nitrate and phosphate concentration patterns from the DFA analysis were assessed with the Maximal Information Coefficient (MIC) method

(Reshef et al., 2011), which belongs to a larger family of statistics called Maximal Information-based Nonparametric Exploration (MINE; http://www.exploredata.net/). MIC captures a wide range of associations which are not restricted to be linear, and without the need to define a model a priori. MIC provides a score that roughly corresponds to the coefficient of determination of the data relative to the regression function, and a significance level. In our case, we calculated MIC scores and significance levels for each paired combination of common nutrient concentration patterns and the DFA reconstructed streamflow series measured at each sampling station. We used these filtered streamflow time-series instead of the original ones due to the continuity of the resulting filtered series and in order to enhance the signal to noise ratio.

### 3.7 Attribution of drivers for spatio-temporal variabilility of the common nutrient concentration patterns

Factor loadings are the multiplication factors that determine the linear combination of the common patterns to produce a best-fit nutrient concentration time-series (Zuur et al., 2003). Factor loadings can take positive or negative values when specific time-series behave in an opposite way to that described by the extracted pattern. Therefore, the geographical distribution of factor loading values across monitoring points inform about the spatial development of the processes responsible for the extracted patterns. To evaluate the relationship between the relevance (i.e., factor loading) of the extracted patterns at each sampling point and the environmental change drivers, we selected a set of potential explanatory variables that were spatially distributed. These included meteorological variables (mean annual air temperature and precipitation), reservoir capacity and location, wastewater treatment plants (WWTP) discharge and location, specific streamflow (runoff index), mean river nutrient concentration in the sampling point, land use distribution, and five variables related to nitrogen loads and their sources obtained by (Lassaletta et al., 2012): application of synthetic fertilizers, application of manure, inputs by biological fixation, total exported N, and point sources. The land use conditions included in our study represent the average conditions between the period 1980 to 2011, where no other significant or drastic land use changes occur, other that management practices related to the improvement of industrial and urban wastewater, which is reflected in the decrease of phosphate in 1990s.

For each sampling point we calculated mean values or percent areas of all the above explanatory variables considering two different regions. The first included: a buffer area of 10 km surrounding the point, aimed at capturing the more local conditions. In the case of reservoirs and WWTP, this represented the immediate upstream potential effects of these variables on individual sampling points. The second region included the total basin upstream from the sampling point. The total basin area per se was excluded from the explanatory variables analyses as it was highly collinear with the variables calculated for the basin upstream area of each sampling point.

The potential explanatory variables were related to factor loadings measured at each sampling site by the Generalized Least Squares (GLS) regression model (Pinheiro and Bates, 2000). The use of generalized least squares for regression modeling is advisable when neighboring values of the response variable tend to be spatially correlated (Pinheiro and Bates, 2000). The GLS models were fitted using the nlme R-Package (Pinheiro et al., 2012). In our case, we assumed a spatial error structure using , the Gaussian structure distribution being the most appropriate among the (six) available options available in nlme, since it provided the best model results based on Akaike Information Criterion (AIC) values. A combination of forward and backward selection was used to identify the significant explanatory variables, using the AIC criterion to identify the best model. We fitted different GLS models for sampling stations showing opposite signs of the factor loading for a given Pattern (e.g., stations showing positive and negative factor loadings for Pattern 1 of nitrate concentration were treated separately). The rationale of this procedure is that many fundamental features of the patterns (phase of the time-series, relationships with streamflow and other variables, direction of the trends) change when the pattern is flipped due to a change of the factor loading sign, potentially implying different generating mechanisms. ~~The GLS models were fitted using the nlme R-Package (Pinheiro et al., 2012)~~. In order to assess the model fit and the variance explained, we calculated a Generalized R-Squared based on (Cox and Snell, 1989) using the r.squaredLR function included in the MuMIn R-Package (Barton, 2014).

### 3.8 Spatial aggregation of common nutrient concentration patterns and explanatory variables

We assessed the clustering of the spatial distribution of nutrient concentration patterns and the significant explanatory variables found in GLS regression models. We used the clustering analysis to portray homogeneous regions in terms of the presence of concrete nutrient concentration patterns and their likely drivers. Our final aim was to highlight the most relevant cause-effect mechanisms that define vulnerable regions to the effects of global change. We used the implementation of the unsupervised *k*-Means algorithm in the open source data visualization and analysis tool Orange 2.7 (http://new.orange.biolab.si/), which uses the between-cluster-distances score to assess the most effective grouping. The method looks for a solution where all the features (in our case, the value of all factor loadings and significant explanatory variables found during GLS modeling) within each group are as similar as possible, and all the groups themselves are as different as possible. Thus, it is not necessary to define the number of desired cluster beforehand. We applied the *k*-means algorithm without any spatial constraints. Although explicit spatial relationships actually exist between sampling points along a river network, our aim was to identify clusters exclusively based on the information contained in the factor loadings and explanatory variables.

## 4 Results

### 4.1 Common nutrient concentration patterns in the basin

The DFA analysis for nitrate concentration extracted 3 common patterns from the set of 50 time-series (Fig. 1a), where the order of the extracted patterns has no implication on the importance or weight of a particular pattern. Patterns 1 and 2 identified in nitrate time-series had a marked seasonal component appreciated visually (Fig. 1a) and further confirmed by the significant 12 month cycles found in the frequency analysis (Table 1). The seasonal evolution of Pattern 1 was clearly associated with the seasonal streamflow pattern (Fig. 1e), suggesting that it was hydrology-driven. The MINE analysis also detected significant associations between Pattern 1 of nitrate concentration and the DFA reconstructed streamflow series in almost all sites across the basin (Table 1). Nitrate concentration increased with streamflow (sites showing positive factor loadings), and was affected by a dilution dynamics (negative factor loadings). In contrast, Pattern 2 was strongly associated with the seasonal evolution of the mean air temperature in the basin (Fig. 1f), suggesting its connection to phenological processes (lower values during the growing season). Pattern 1 of nitrate concentration was also associated to a ca. 2.6 year periodicity according to the MTM analysis, and Pattern 3 showed a significant 3.5 yr oscillation period (Table 1). Pattern 3 also included a significant decreasing trend (Table 1). The signs associated to DFA factor loadings of Pattern 3 indicated that 20 of the 50 stations were in fact following the opposite trend. The significance or relevance of this opposite decreasing trend in nitrate concentration is indicated by the magnitude of the factor loadings in those 20 stations (shown in Figure 2)

DFA extracted four common patterns from the 50 dissolved phosphate concentration time-series included in the analysis (Fig. 1b). The 1990s represented a shift-time point for phosphate patterns. In all four patterns, a sharp decrease in the phosphate concentration occurred in the early 1990s, and shifted to a steady behavior till the end of the study period, but the four patterns differed in peak timing before the 1990s. Despite the overall decrease (also observed in phosphate flux in upstream and downstream locations; Section S.1. of Supplementary Material), only Pattern 2 had a highly significant trend while trend in Pattern 4 was only marginally significant (Table 1). Pattern 1 had a marked seasonal cycle, potentially driven by streamflow (suggested by the significant relationship between the seasonal evolution of the pattern and streamflow; Fig. 1b). However, the MINE algorithm detected just 2 significant associations between this pattern and the DFA reconstructed streamflow time-series from the sampling sites (Table 1). Pattern 3 showed cycles of ca. 4.3 and 1.6 yr (Table 1). The frequency analysis of the 37 DFA reconstructed streamflow series revealed several characteristic oscillations. Apart from the strong seasonal signal, there were significant oscillations at 1.5, 2.2, 3.2, 4.2, and 9 years in several sampling stations. Periods from 1.5 to 4.2 years were highly coherent with the oscillations found in the common patterns of nitrate and phosphate concentration (Table 1), suggesting that multi-year oscillations in nutrients concentration were related to streamflow variability. Interestingly, nitrate and phosphate patterns showing at least one significant oscillation with period longer than one year also showed many significant MINE associations with streamflow across sites (Table 1). No significant trend was detected in the streamflow series (extracted common DFA patterns shown in Section S.2 of the Supplementary Material).

**4.2 Factors explaining the distribution of the different nutrient concentration patterns**

The GLS regression models for the distribution of factor loadings for each Pattern identified several significant explanatory variables (Tables 2 and 3). Since nitrate concentration Patterns 1 and 2 showed contrasted positive and negative factor loadings across sites, we considered different models for sites showing positive and negative factor loadings. The distribution of positive factor loadings for Pattern 1 strongly related to the total area of water (mainly reservoirs). The higher the total area occupied by water upstream, the higher the weight of Pattern 1. Other associations were also significant, although their prediction weights on the model were less important: a negative relationship with mean annual air temperature upstream from the sampling point; a positive relationship with dryland farming area around the sampling point; and a negative association with the industrial areas upstream from the sampling point (Table 2). Negative factor loadings of Pattern 1 were related to the presence of irrigated agricultural lands and to the mean annual precipitation received upstream. The reservoir water capacity upstream the sampling point had a small and marginally significant effect.

Factor loadings for Pattern 2 of nitrate were strongly associated to sites with irrigated agricultural areas upstream from the sampling point. The distribution of Pattern 2 was also weakly related to the annual mean precipitation and the presence of irrigated lands. Finally, the distribution of factor loading values for Pattern 3 was spatially associated to industrial areas. The main difference between models for negative and positive factor loadings for this pattern was dictated by the relevance of distinct sources of nitrogen being used in the area, namely, synthetic fertilizers and manure (Table 2). Globally, the explanatory power of the GLS models for the distribution of phosphate patterns was much lower than for nitrate concentration models (Table 3). Pseudo-$R^2$ values were one third of those found in nitrate models, except for Pattern 1 that reached similar explanatory power. The distribution of the factor loadings of Pattern 1 was explained by a complex combination of synthetic fertilizer load and industrial area upstream from the sampling point, the runoff index associated to it, and the mean river phosphate concentration in the site. Overall, the distribution of the phosphate patterns was hardly explained by the set of explanatory variables considered in this study, and was mainly explained by the presence of industrial areas upstream of the sampling points (Table 3).

## 4.3 The joint spatial distribution of the nutrient concentration patterns and explanatory factors

The clustering analysis for the spatial distribution of the nitrate patterns and the significant explanatory variables found 4 aggregations among the 50 sampling sites (Fig. 3a). Cluster 1 contained sampling points located mainly in downstream sections of major tributaries of the Ebro River (particularly along the Segre River); Cluster 2 included points in upstream locations of tributaries and in the main Ebro; Cluster 3 comprised points located even more upstream; and Cluster 4 collected the downstream sites of the main stem of the Ebro River. These clusters were characterized by significant differences in the absolute values of the factor loadings for Pattern 1 (Fig. 3b, non parametric Wilcoxon test for mean comparison, $p = 0.011$), and Pattern 2 ($p = 0.017$). Cluster 1 showed the largest relevance ~~of~~ for Pattern 1, Cluster 4 for Pattern 2, and Cluster 3 for Pattern 3. Therefore the most fundamental regional difference in the dynamics of nitrate concentration in the basin was a switch from a streamflow-dominated dynamics in Cluster 1 to a ~~phenology~~reservoir biogeochemistry-dominated of Cluster 4. The preeminence of Pattern 3 in Cluster 3 was also a significant spatial pattern extracted from the clustering analysis.

These differences between clustering groups were coincident with significant differences for many explanatory variables, particularly the extension of irrigated agriculture ($p < 0.0001$), the presence of reservoirs upstream the sampling point ($p < 0.0001$), and the application of synthetic fertilizers ($p < 0.0001$). Cluster 3 showed the minimum values for these variables, followed by Cluster 2 and Cluster 1, whereas Cluster 4 showed the largest values. Contrastingly, the clustering analysis for the phosphate concentration resulted in a poor regionalization with only 2 different aggregations (Fig. 4a), one including just 5 sampling points. There were no obvious spatial clusters beyond Cluster 2, which included points with higher values for Pattern 4 ($p$ = 0.006). This coincided with very high phosphate concentrations ($p$ = 0.002) and extensive industrial areas ($p$ = 0.001) related to the sampling points. The poor regionalization in the phosphate case stressed again the apparently idiosyncratic behavior of phosphate concentration across sampling sites.

## 5 Discussion

### 5.1 The nature of nutrient concentration patterns in the Ebro basin

The analysis of the impacts of global change on freshwater ecosystems requires the use of appropriate tools to identify the main regional trends and modes present in hydrological and water quality variables. Results of this study show that the combination of DFA, traditional time-series analysis, and regression methods is a convenient approach and several features of the time series shared by many sampling points across the Ebro basin can be detected.

The analysis of the nutrient concentration time-series detected the existence of seasonal patterns related to hydrology. Although the common hydrological relation with nutrient dynamics (Donner et al., 2002) may hide the detection of other seasonal cycles not related to streamflow, our analysis also detected seasonality that was unrelated to hydrology. While Pattern 1 of nitrate concentration was related to streamflow, the nitrate dynamics in the basin was also related to the phenological cycles of the adjacent terrestrial ecosystems or other water bodies upstream of each sampling point (Pattern 2). Terrestrial phenological processes such as those involved in leaf fall and decomposition would potentially be more important in upstream sections of the basin, where the biogeochemical activity in large reservoirs is not present. In the downstream section, in turn, the reservoir biogeochemical control on rivers and streams shaped Pattern 2 for nitrate concentration. The actual mechanism behind the association between nitrate concentration and air temperature may be complex, and in fact it may differ at different sampling points, since air temperature can co-vary with many other factors. In the case of nitrate concentration, assimilation by freshwater primary producers during summer (Carpenter and Dunham, 1985) and the seasonal evolution of leaf fall and decomposition (González, 2012) could have taken a major role. However, other factors may contribute to lower concentrations, like the seasonal cycle of denitrification in the adjacent terrestrial ecosystems and upstream water bodies during summer months (Tatariw et al., 2013).

Nutrient concentrations showed multiple associations with streamflow spanning from the seasonal to the interannual scale. One of the most prominent features of nitrate concentration time-series was the existence of a switching relationship with streamflow (expressed by the changing sign of factor loadings for Pattern 1). This implies a fundamental change of the dynamics of nitrate concentration and suggests a major change in the sources of nitrogen to freshwaters. The positive relationship between nutrient concentration and streamflow suggest the preponderance of diffusive inputs from the terrestrial ecosystems and non-irrigated agricultural fields, whereas the negative relationshippointed to a dilution mechanism typical of locations having point sources. The GLS models further identified the land fraction occupied by irrigated agriculture as the main factor associated to the presence of negative factors loadings for Pattern 1 of nitrate concentration. Summer irrigation is a common agricultural practice in Mediterranean areas that can disrupt the relationship with the natural flow regime as well as the nitrate dynamics. This has been already observed in the Ebro basin where the intra-annual N export differed among rainfed and irrigated crops, the former following the flow regime, the latter modifying it (Lassaletta et al., 2012). In addition, irrigation has the capability of altering local and regional precipitation behavior through changes in soil moisture and heat budgets (Boucher et al., 2004), particularly in downstream areas (Huber et al., 2014). However, none of these regional climate effects has been 25 confirmed in the Ebro basin. The absence of seasonal relationships between nitrate concentration and streamflow (i.e., very low absolute values for Pattern 1) can also be related to the proximity to large reservoirs in the lower section of the basin, where the seasonal nitrate concentration cycles seem to be highly influenced by the water released from the reservoirs.

The supra-annual frequencies detected in the nitrate and phosphate concentration patterns in the Ebro point out to associations with climatic oscillations identified in the Mediterranean region. The North Atlantic Oscillation (NAO) has multiple modes starting at 1.4 years, while the El Niño–Southern Oscillation (ENSO) has modes between 2.4 and 5.2 years (Rodó et al., 1997). Both the nutrient patterns and the streamflow series showed oscillations coherent with those from the ENSO and NAO, which are known to modify, through teleconnections, the magnitude and frequency of precipitation in a heterogeneous manner (Rodó et al., 1997). Furthermore, air temperature common patterns (shown in Section S.3. of Supplementary Material) in the basin also showed significant frequencies between 2.2 and 5.7 ys, which further confirmed the relationship of meteorological conditions in the basin to the above mentioned climatic modes.

The impact of ENSO on nitrate river concentrations is, in fact, not uncommon in areas under indirect ENSO effects, such as the SE United States (Keener et al., 2010). Moreover, the associations of ENSO with streamflow modifications (Marcé et al., 2010) and nitrate concentration dynamics (Vegas-Vilarrúbia et al., 2012) in the Iberian Peninsula have been unambiguously stated. Indeed, all nutrient concentration patterns showing significant supra-annual frequencies also showed significant relationships with streamflow in many sites across the basin. In our ~~view~~ opinion, this indicates that the effect of atmospheric teleconnections on nitrate and phosphate concentrations was driven by modifications in the streamflow. Since streamflow relies on both precipitation and evapotranspiration, extreme events such as droughts and heat waves promoted by global atmospheric teleconnections can have significant effects on river water quality in the basin. Indeed, the relationship between the partially predictable global climate modes and the occurrence and frequency of extreme events is a very active topic in the literature (Coumou and Rahmstorf, 2012), and their links with water quality crisis episodes should be further investigated, especially in the Mediterranean region, where climate extreme events are predicted to increase (García-Ruiz et al., 2011). Overall, the changes in these climatic modes within the 31 years included in our study could indicate the potential role of climate change in in-stream nutrient variability. Regarding long term trends, no significant correlation was found between nutrients and climatic modes.

**5.2 Nutrient trends and local management practices**

The spatial distribution of the relevant patterns was identified by the magnitude of the factor loading for each pattern, and both results are obtained by means of DFA. Further cluster analyses including factor loadings as well as the corresponding significant explanatory variables provided further information about the spatial distribution and the dynamics of nutrient concentration patterns in the Ebro basin. The most remarkable spatial difference was the switch between streamflow-dominated nitrate concentrations in upstream sections of the basin (Cluster 1) to nitrate concentrations being controlled by the biogeochemical activity of large reservoirs in downstream sections of the Ebro (Cluster 4). This switching dynamics was not evident in the phosphate analyses.

In the case of ~~N~~nitrate concentration, both ~~showed~~ decreasing and increasing trends were observed~~in areas across~~ the basin. The association of the trends with sampling points affected by large loads of synthetic fertilizer (decreasing trend) and manure (increasing trend) indicates that nitrate trends were possibly promoted by the application of agricultural practices that, in the last three decades, can be associated with a more rational fertilizer application (Lassaletta et al., 2012). Also, the implementation of sewage treatment schemes in the basin can be partly invoked to justify this decrease (Romaní et al., 2010). The dominant role of nitrate concentration trends in the more upstream locations of the basin (mostly included in Cluster 3) suggest that the impact of human activities upstream sampling points were higher in headwater and small streams, and that these water courses and corresponding sub-basins were the most vulnerable to increasing nitrate trends. On the other hand, decreasing trends also dominated the time-series in some of the sampling points included in Cluster 3, suggesting that upstream locations are also prone to improvement due to remediation measures and best management practices. Particularly, our analysis suggests that the application of synthetic fertilizers precluded the existence of a decreasing trend in some areas of the basin, but the application of manure as a fertilizer actively promoted increasing nitrate concentration trends. This increasing nitrate trend was mainly observed in sampling points related to Cluster 1, particularly along the Segre River (NE of the basin). Overall, ~~W~~while ~~during the last decades~~ manure application has dramatically grown in some specific areas during the last decades (Terrado et al., 2010), there has been a more rational application of synthetic fertilizers in the basin (Lassaletta et al., 2012).

The overall decrease of phosphate concentration in the Ebro basin since the early 1990s was highlighted by all four extracted patterns. This decreasing trend coincides with the improvement of urban sewage treatment in the most important cities of the Ebro basin (Ibáñez et al., 2008), since most patterns of phosphate dynamics derive from point sources. Furthermore, according to the same study by Ibañez et al., (2008), there was a significant positive correlation between the decreasing phosphate concentration and decreasing total chlorophyll in the lower Ebro basin between the 1987-2004 period. The reduction of phosphate fertilizers in the agriculture could have also resulted in the reduction of phosphate loads exported to rivers and streams (Bouza-Deaño et al., 2008). A similar pattern has been observed in the Loire River (France), where the wastewater treatment plants and the concurrent ban on phosphorus content in washing powders (Floury et al., 2012) were highly effective. Severe reductions of riverine phosphorus loads were common in Europe during the 1990s, while nitrate concentrations decrease has been limited to recent years (Ludwig et al., 2009). Overall, the significant trends identified in nitrate and phosphate concentration, whether increasing or decreasing, across the Ebro basin appear to be modulated by local management practices associated to the different anthropogenic activities that have co-existed in the basin during the study period, but no climatic factor seemed to play any relevant role in shaping decreasing or increasing trends of nutrient concentration.

## 6. Conclusions

Our results imply that the impact of global change on the dynamics of nitrate concentration across the Ebro basin is a multifaceted process that includes regional and global factors while impacts on phosphate concentration depend more on local impacts and less on large-scale factors (Fig. 5). In the case of nitrate, our analyses have identified the presence of irrigated agriculture and its corresponding fertilization management practices (synthetic fertilizers or manure), the presence of industrial activities in the basin, and damming as the main global change factors. Other climatic processes linked to streamflow variability were also identified, but the impact of climate changes on these processes is uncertain and could not be disentangled in this study. These factors shape a complex dynamics including temporal trends, and interannual and seasonal cycles, with either strong or vanishing relationships with streamflow, and links with phenological processes in upstream terrestrial ecosystems and downstream reservoirs. Interestingly, the impact of identified factors on this rich dynamics was not homogenous across the basin, but clustered in 4 regions not entirely coherent from a geographic perspective (Fig. 3). In contrast, phosphate concentration showed a more idiosyncratic behavior. The only relevant global change mechanism acting at large scales is the presence of industrial activities and the application of synthetic fertilizers, which defines higher phosphate concentrations in Cluster 2. The explanatory power of our models was low in the case of phosphate concentration dynamics, meaning that most variability was accounted by factors not considered in our models. Although these factors may include some relevant regional drivers, the contrasting results from the nitrate analysis imply that the ultimate reason of the lower performance of the phosphate models is the absence of the more local factors, such as the different timing of implementation of wastewater treatment technologies.

Overall, our analysis shows that nitrate concentration dynamics is more responsive to regional and global factors, while global change impacts on phosphate concentration dynamics operate at the small scales of point sources. Anthropogenic land uses seem to play the most relevant role, and appropriate fertilization management may aid in stabilizing temporal trends, thus avoiding future nitrate concentration increases. The relevance of the inter-annual signals in our nutrient concentration series suggest that any impact of climate change on the intensity and timing of global climate phenomena driving inter-annual streamflow oscillations can also exert a significant impact on river nutrient dynamics. This would be expressed more likely in variations of the prevalence of extreme events in streamflow that would impact nutrient dynamics. This may add to a multi-stressor situation typical from freshwaters in Mediterranean countries, guaranteeing future research on this topic.

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## Tables

| Nutrient | Trend (Kendall tau) | Significant oscillations (years) | Significant MINE relationships with streamflow (number of sites out of 37) | Other relationships with streamflow |
|---|---|---|---|---|
| ***Nitrate*** | | | | |
| Pattern 1 | ns | 1 and 2.6 | 34 | • Strong seasonal coherence (Fig. 1e)<br>• Coincident and significant streamflow oscillation at 2.2 years |
| Pattern 2 | ns | 1 | 12 | • Nothing to remark |
| Pattern 3 | -0.53*** | 3.5 | 22 | • Trend NOT related to streamflow<br>• Coincident and significant streamflow oscillation at 3.2 years |
| ***Phosphate*** | | | | |
| Pattern 1 | ns | 1 | 2 | • Moderate seasonal coherence (Fig. 1g) |
| Pattern 2 | -0.09** | ns | 4 | • Trend NOT related to streamflow |
| Pattern 3 | ns | 1.6 and 4.3 | 25 | • Coincident and significant streamflow oscillations at 1.5 and 4.2 years |
| Pattern 4 | -0.08* | ns | 10 | • Trend NOT related to streamflow |

Table 1: Characterization of the temporal variability and relationships with streamflow of nutrient patterns detected with DFA in the Ebro basin.

| Nitrate Patterns | Pseudo $R^2$ | Explanatory Variable | Coefficient | Std. Error | t-value | p-value |
|---|---|---|---|---|---|---|
| Pattern 1 - Positive Factor Loadings | 0.65 | Mean Air Temperature (°C) UPSTREAM | -1.42 | 0.30 | -4.66 | 0.0001 |
| | | Water area ($km^2$) UPSTREAM | 0.06 | 0.00 | 13.75 | 0.0000 |
| | | Dryland Farming (%) LOCAL | 0.00 | 0.00 | 3.23 | 0.0035 |
| | | Industrial area (%) UPSTREAM | -0.12 | 0.04 | -2.91 | 0.0074 |
| Pattern 1 - Negative Factor Loadings | 0.61 | Reservoir Capacity ($hm^3$) LOCAL | -0.05 | 0.02 | -2.64 | 0.0166 |
| | | Irrigated agriculture area (%)UPSTREAM | 0.30 | 0.05 | 6.37 | 0.0000 |
| | | Mean Annual Precipitation (m) UPSTREAM | 0.48 | 0.11 | 4.42 | 0.0003 |
| Pattern 2 | 0.59 | Irrigated agriculture area ($km^2$) UPSTREAM | 0.11 | 0.01 | 19.06 | 0.0000 |
| | | Irrigated agriculture area (%) LOCAL | 0.00 | 0.00 | -2.59 | 0.0127 |
| | | Mean Daily Precipitation (m) LOCAL | 0.16 | 0.07 | 2.29 | 0.0269 |
| Pattern 3 - Positive Factor Loadings | 0.57 | Industrial area (%) UPSTREAM | 0.04 | 0.01 | 6.53 | 0.0000 |
| | | Synthetic Fertilizer Load UPSTREAM | -0.01 | 0.00 | -3.45 | 0.0018 |
| Pattern 3 - Negative Factor Loadings | 0.56 | Industrial area (%) UPSTREAM | 0.04 | 0.01 | 4.81 | 0.0001 |
| | | Areal Manure Load UPSTREAM | 0.04 | 0.01 | 3.01 | 0.0063 |
| | | Water area (%) UPSTREAM | 0.01 | 0.01 | 2.14 | 0.0428 |

Table 2: GLS resulting potential drivers involved in the spatiotemporal variability of nitrate patterns in the Ebro basin.

| Phosphate Patterns | Pseudo $R^2$ | Explanatory Variable | Coefficient | Std.Error | t-value | p-value |
|---|---|---|---|---|---|---|
| Pattern 1 | 0.62 | Synthetic Fertilizer Load UPSTREAM | 0.46 | 0.08 | 6.18 | 0.0000 |
| | | Mean river phosphate concentration | -0.07 | 0.02 | -3.97 | 0.0003 |
| | | Runoff Index UPSTREAM | -0.03 | 0.01 | -3.69 | 0.0006 |
| | | Industrial area (%) UPSTREAM | 0.19 | 0.05 | 4.02 | 0.0002 |
| Pattern 2 – Positive Factor Loadings | 0.20 | Industrial area ($km^2$) UPSTREAM | 0.03 | 0.02 | 2.22 | 0.0384 |
| Pattern 2 – Negative Factor Loadings | 0.17 | Grass and shrubland area (%) LOCAL | 0.01 | 0.00 | 2.24 | 0.0339 |
| Pattern 3 | 0.21 | Industrial area ($km^2$) UPSTREAM | 0.05 | 0.01 | 3.60 | 0.0008 |
| Pattern 4 | 0.14 | Industrial area (%) UPSTREAM | 0.05 | 0.02 | 2.75 | 0.0083 |

Table 3: GLS resulting potential drivers explaining the spatiotemporal variability of phosphate patterns in the Ebro basin.

# Figures

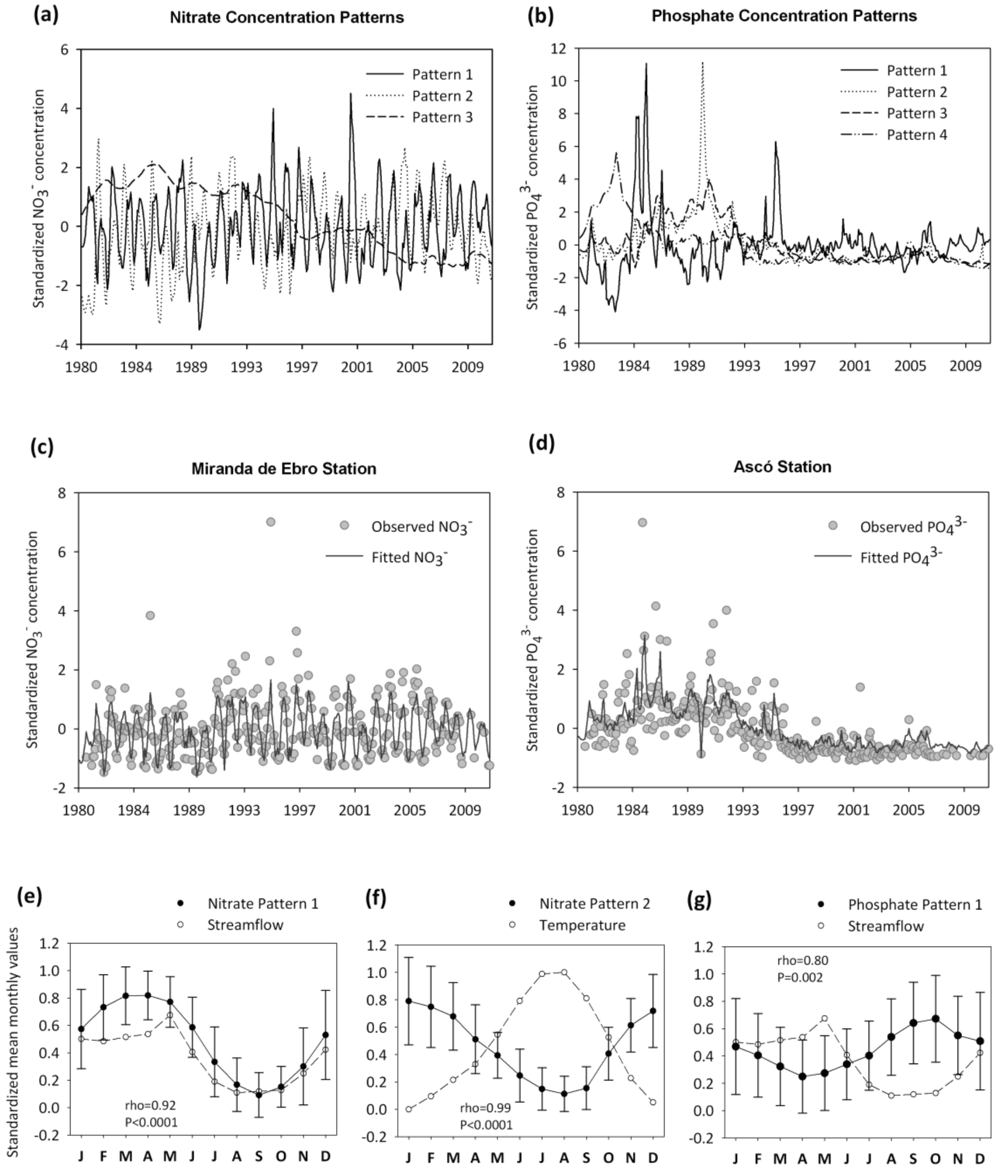



Figure 1: *Top:* DFA resulting patterns for nitrate (a) and phosphate (b) concentration. *Middle:* Examples of observed time-series and fitted DFA models at two selected monitoring points for nitrate (c) and phosphate (d) concentration. The DFA models in panels (c) and (d) are the result of a linear combination of the patterns in panels (a) and (b), respectively. *Bottom:* Seasonal variation for nitrate Pattern 1 and streamflow (e), nitrate Pattern 2 and Temperature (f), and phosphate Pattern 1 and streamflow (g). Points depict monthly averages for the entire 31 year time-series. For temperature and streamflow, the average is for all time-series available. We only included standard deviations as error bars for the nutrient patterns to enhance readability.

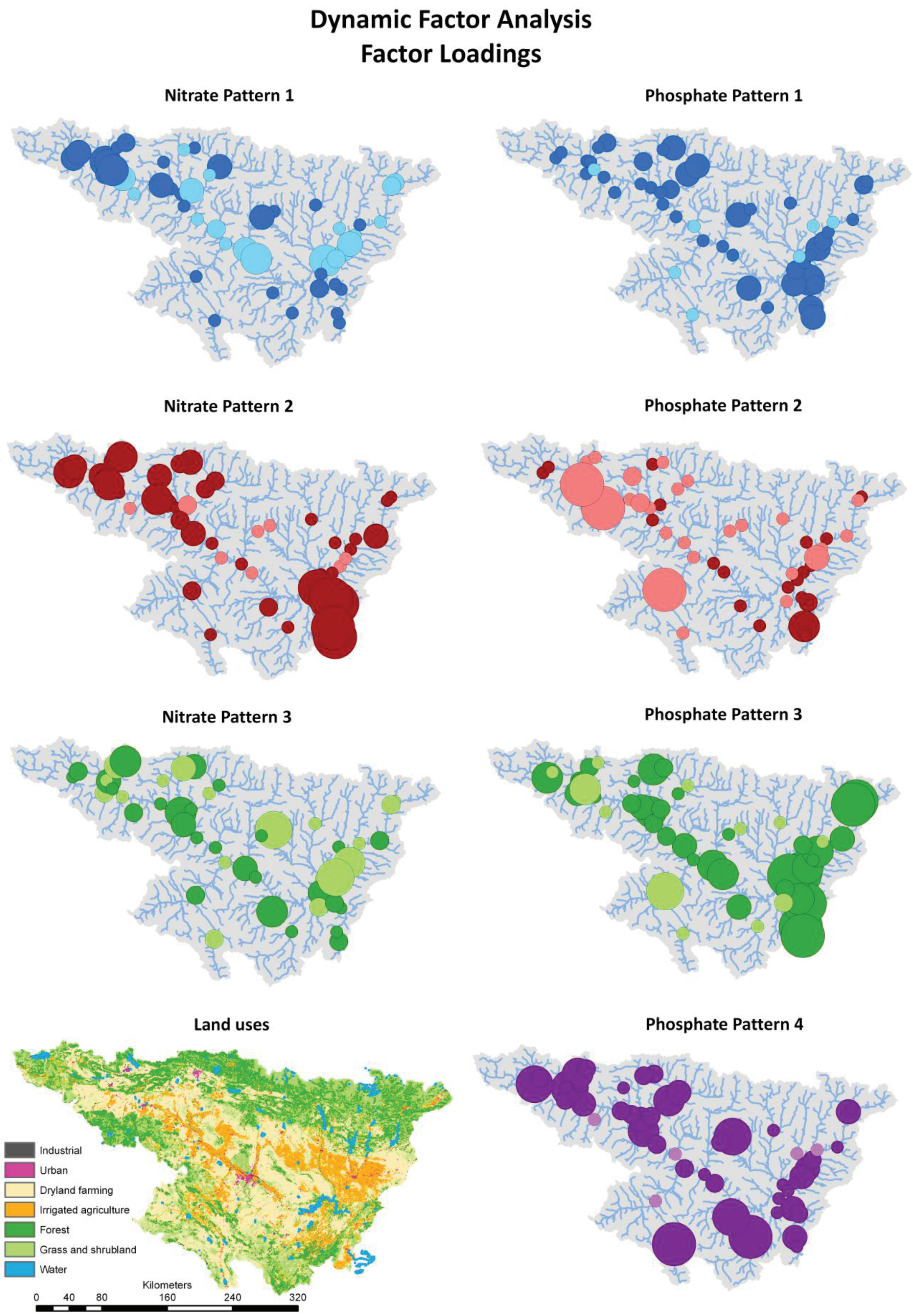
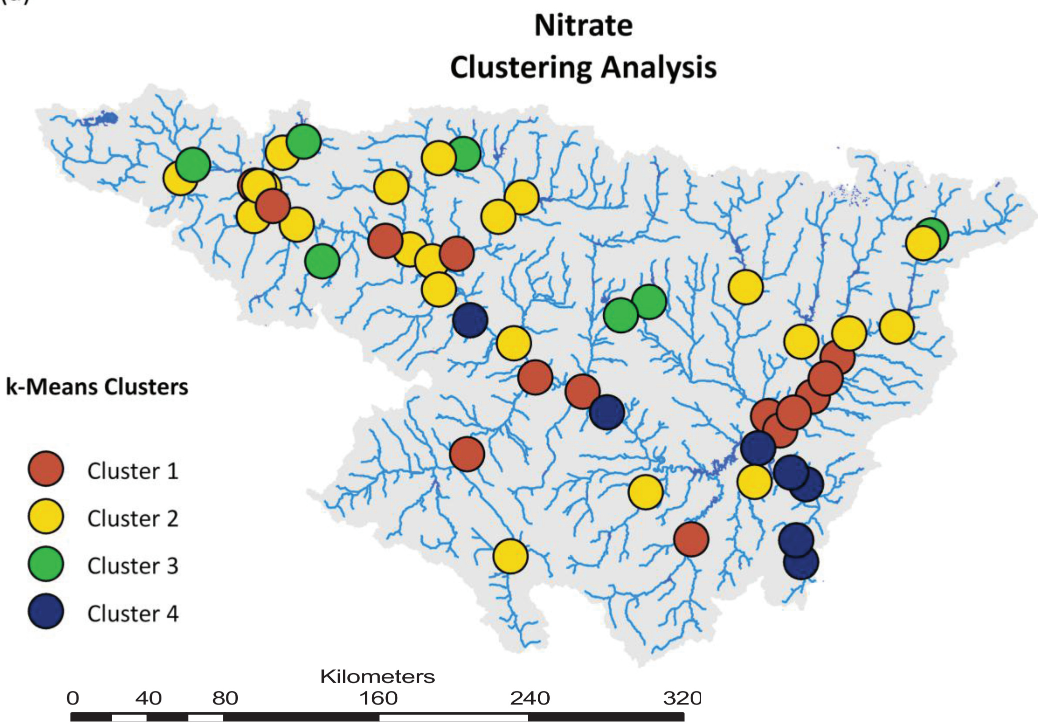



Figure 2: Factor loadings associated to nitrate patterns (left column) and phosphate patterns (right column). Dark circles indicate positive factor loadings and light-colored circles represent negative factor loadings. The size of the circles represents the magnitude of the Factor Loading at each monitoring point. A map with major land uses in the Ebro basin is enclosed in the lower left corner.

(a)




(b)

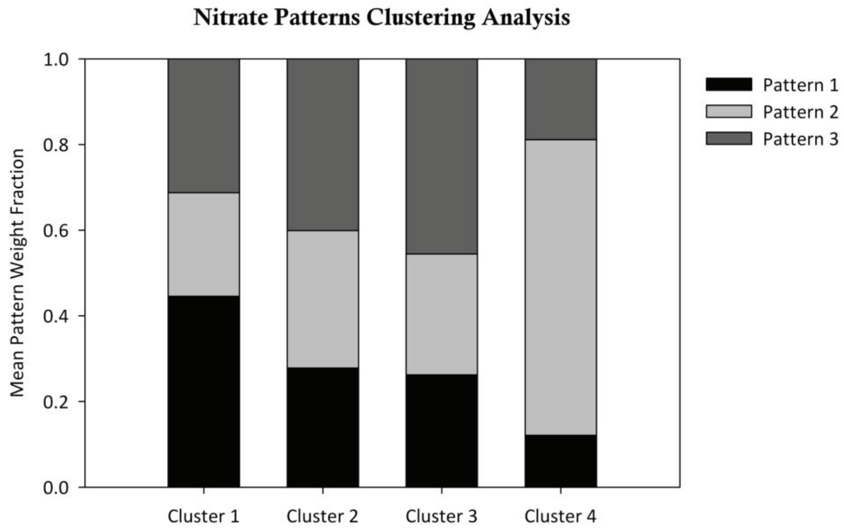
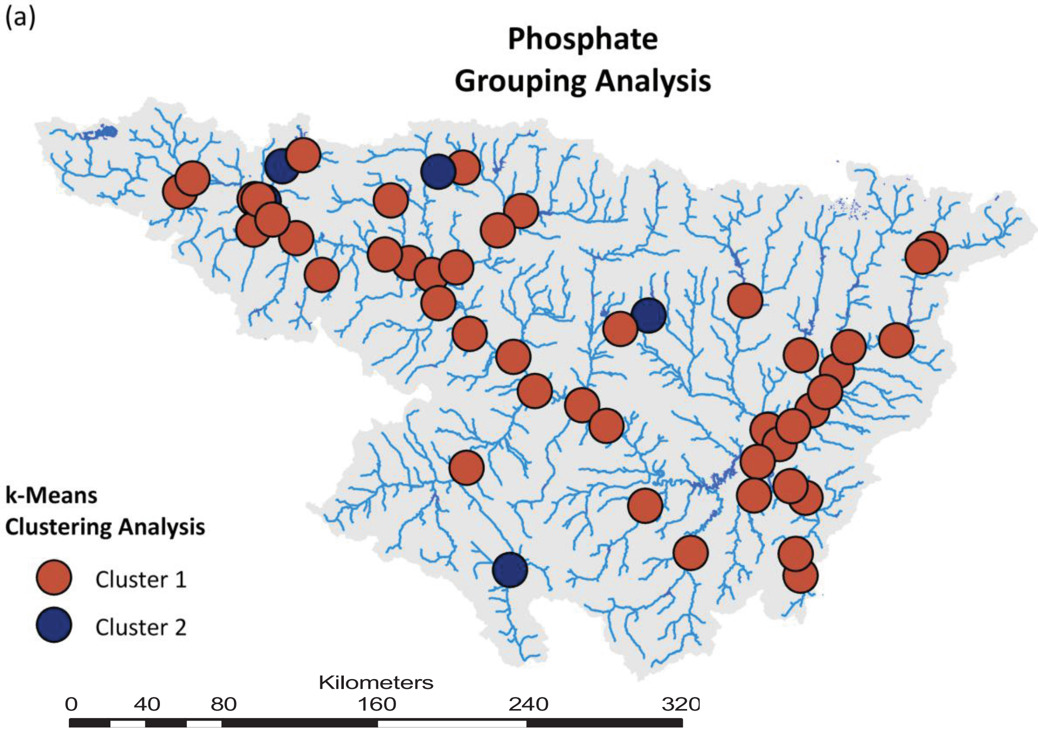



Figure 3: (a) Clustering analysis results for the spatial distribution of nitrate concentration patterns and associated explanatory variables. (b) Mean fraction of Factor Loadings (i.e., the overall weight of a specific pattern) found in each of the 4 clusters identified in the analysis.

(a)




(b)

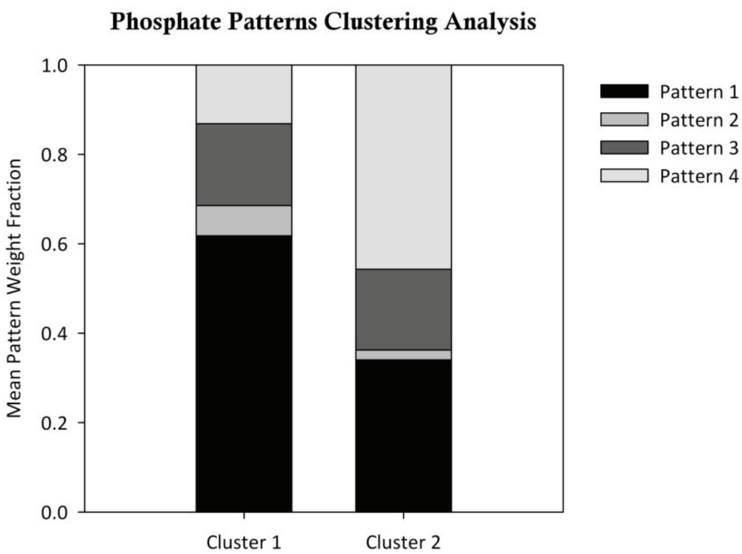
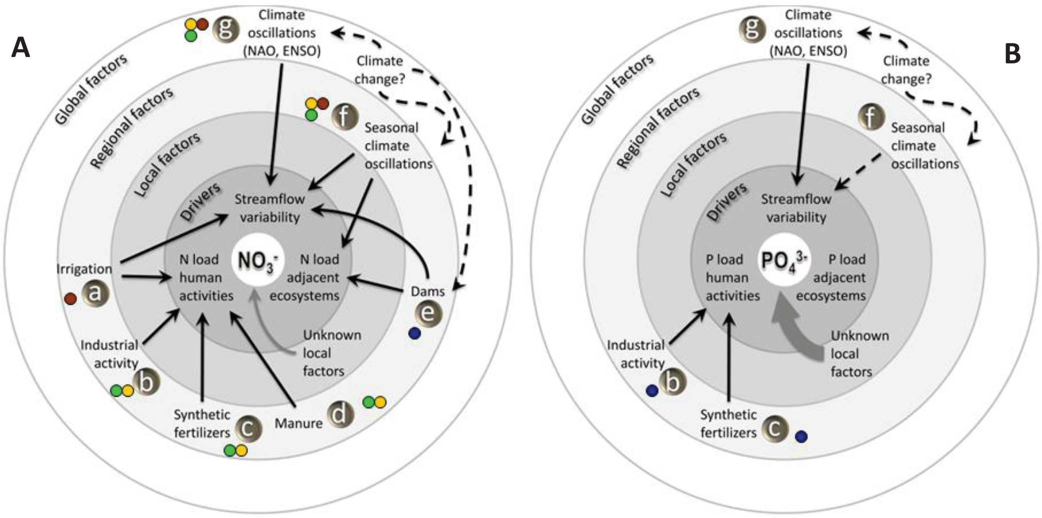



Figure 4: (a) Clustering analysis results for the spatial distribution of phosphate concentration patterns and associated explanatory variables. (b) Mean fraction of Factor Loadings (i.e., the overall weight of a specific pattern) found in each of the 4 clusters identified in the analysis.




(a) Nitrate concentration switches from a concentration to a dilution dynamics with streamflow.

(b) Contributes to process (a) and favors the nitrate trends in the basin.
Helps defining the basic dilution dynamics explaining phosphate concentration patterns across the basin.

(c) The application of synthetic fertilizers hampers a background decreasing trend in nitrate concentration.
One of the main contributors to phosphorus loading at the regional scale.

(d) Areas with significant application of manure are prone to increasing trends in nitrate concentration.

(e) Nitrate delivered by dams overrides the nitrate dynamics associated to seasonal streamflow in downstream locations

(f) Climate seasonality define the basic annual pattern of nitrate related to streamflow and inputs from terrestrial ecosystems.
The association with phosphate concentration is weaker.

(g) Low frequency oscillations in streamflow impact the dynamics of nitrate and phosphate concentration

Figure 5: Global change factors that, acting at different scales, contribute to shaping the spatio-temporal variability of nitrate and phosphate concentration in the Ebro basin. Lettered circles describe the relationship between nutrient concentration patterns and the identified factors and drivers of change. Colored circles in A: Nitrate and B: Phosphate link types of relationship to corresponding clusters (if applicable) displayed in Figures 3 (nitrate) and 4 (phosphate), respectively.