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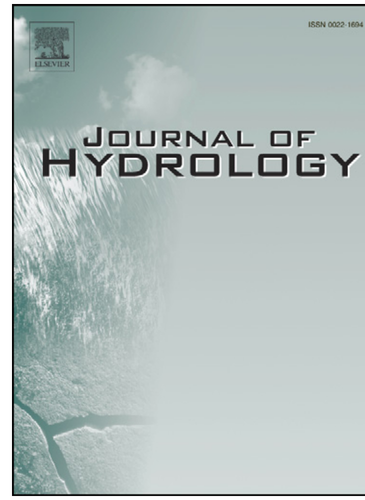

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Predicting river water quality across North West England using catchment characteristics

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Abstract

Linear relationships between regional water quality and catchment characteristics (terrain, land cover, geology, base flow index and rainfall) are examined for rivers in North West England using a GIS-based approach and an extensive Environment Agency water quality database. The study considers the role of diffuse and distal point sources on river water quality. The results show that base cation concentrations are strongly linked to catchment terrain and land cover, while pH is linked to bedrock geology and land cover. Mean nitrate concentrations are most strongly related to arable cover, although distal point sources in urban and rural catchments appear to have a significant effect on river nitrate concentrations in the region. Orthophosphate and suspended sediment concentrations are most closely related to the percentage urban development. Linear models are tested on a large independent water quality dataset, resulting in maps showing predicted water quality across the region. The approach works well for the prediction of nitrate concentrations and other constituents which have predominantly diffuse sources. In contrast, the linear approach to predicting orthophosphate concentrations in North West rivers using catchment characteristics is problematic. The major influence of point sources may mask the effect of wider basin attributes on orthophosphate concentrations. Within-river processing of phosphorus may also explain why the relationship breaks down. Further work is needed to explain phosphorus contributions and variability in North West rivers, especially in the context of effective catchment management.

Key words: Rivers; Nitrate; Phosphate; Base cations; pH; Sediments; Modelling; GIS

1. Introduction

Excessive inputs of nutrients (nitrogen and phosphorus) to fluvial systems can lead to adverse biological effects including algal growth and changes in ecosystem function and diversity (Mason, 1996; Carpenter et al., 1998; Mainstone and Parr, 2002; Withers and Lord, 2002). High loadings of fine sediment to rivers and the subsequent accumulation on the channel bed can impact fish and invertebrates which rely on benthic habitats (Heany et al., 2001; Mainstone et al., 2008). Runoff from agricultural land and effluents from urban and industrial areas are major sources of nutrients and fine sediment in river systems (Vitousek et al., 1997; Hart et al., 2004; Jarvie et al., 2006; Ulen et al., 2007; Edwards and Withers, 2008; Neal et al. 2010). The relative contributions from these diverse sources can vary significantly in space (e.g. Nedwell et al., 2002; Neal et al., 2008; Mainstone et al., 2008; White and Hammond, 2009) and in time (e.g. Stutter et al., 2008; Bowes et al., 2009).

The importance of water quality deterioration due to enhanced nutrient and contaminant inputs, and the need for effective targeting of mitigation approaches and river catchment management, has led to the development of a variety of water quality models. Several broad types of models exist depending upon requirements such as the spatial and temporal scale of application (Johnes and Heathwaite, 1997). Process-based nutrient export models, such as INCA (Integrated Nitrogen in Catchments; Whitehead et al., 1998), PSYCHIC (Phosphorus and Sediment Yield Characterisation In Catchments; Davidson et al., 2008; Stromqvist et al., 2008) and SWAT (Soil and Water Assessment Tool; Arnold et al., 1998) are useful for retrospective evaluation and scenario analysis, but often need detailed parameterisation and extensive calibration (Merritt et al., 2003; Cherry et al., 2008). An alternative to these often complex models are simple 'black box' empirical approaches, such as those based on nutrient export coefficients (Johnes, 1996; Jordan and Smith, 2005) and PIT (Phosphorus Indicators

Tool; Heathwaite et al., 2003). These models can be particularly useful for large-scale extrapolation, and for exploring how future changes in land use and/or fertiliser application may impact river water quality (e.g. Johnes et al., 2007). However, since they operate by applying an empirically-derived export value to each hypothesised source they do not lend themselves to new inferences about potential processes.

A hybrid of these two approaches links river water quality to catchment characteristics or attributes, and employs statistical techniques for up-scaling. These models can shed light on potentially important drivers via the catchment characteristics incorporated in the model, but since they do not include complex and heterogeneous processes they can be applied over large spatial areas (Wade et al., 2004; Cherry et al., 2008). Developing water quality models based on the percentage surface area of a catchment covered by a particular characteristic was traditionally undertaken using mapping techniques (e.g. Lynch and Dise, 1985), but with the advent of GIS, the approach is much faster and has seen considerable development in recent years. GIS-regression based approaches have been used to explore controls on the distributions of riverine nutrient and sediment concentrations across varied geographical regions (e.g. Smith et al., 1997; Clark et al., 2004; Donohue et al. 2005; 2006; van de Perk et al., 2007; Siakeu et al., 2004; Davies and Neal, 2004; 2007; Helliwell et al., 2007; Alexander et al., 2008). It has also been used to investigate controls on surface water acidification (e.g. Hornung et al., 1995; Thornton and Dise, 1998; Vuoeuema and Forsius, 2008) and linkages between river metal and sediment levels and catchment attributes (e.g. Jarvie et al., 2002; Saikau et al., 2004). Although the GIS-regression approach has been widely used for producing statistical models of water quality, fewer studies have used the approach to generate spatial predictions of water quality at unmonitored points along the river network, especially in regions with mixed catchment settings. A variety of important legislative drivers have been introduced to help mitigate surface water pollution, primarily the European Water Framework Directive (WFD) (European Parliament, 2000). Simple GIS-based statistical models of river water quality and associated spatial predictions are potentially highly useful for identifying river reaches at risk of failing to meet environmental objectives set by such legislation. This approach may provide a useful complement or alternative to those process-based models currently in use for informing decisions regarding the targeting of measures to reduce river pollution.

This paper explores empirical relationships between river water quality and a suite of catchment characteristics in North West England. This region is characterised by a wide range of land uses and catchment settings. It represents a mix from the urban heartlands of the industrial North West to upland rural areas of outstanding natural beauty, and consequently there is considerable variability in water quality. Within a GIS framework, linear relationships are used to predict river water pH and the concentrations of calcium, magnesium, nitrate-N, orthophosphate-P and suspended solids across the North West. Model outputs are validated using a large independent dataset. The aims of the study are to (1) identify broad-scale controls on river water quality, (2) provide insights into the relative importance of diffuse and distal point sources for chemical constituents of water quality, and (3) investigate the utility of GIS-regression based approaches for predicting river water quality in the North West.

2. Study area

North West England (Figure 1) is typified by the industrial cities of Manchester and Liverpool; the heartland of the 19th century English Industrial Revolution. Although these urban and highly populated areas dominate large portions of the south of the region, large parts of the North West are rural. These include The Lake District located in Cumbria (Britain's largest national park), the Forest of Bowland in Lancashire, the Pennine fringe to the east of the region, and intensive agricultural areas on the North West coast. Much of the bedrock geology is characterised by a variety of Carboniferous and Permian-Triassic sedimentary rocks. An exception to this is the Lower Palaeozoic metamorphic and volcanic rocks in the uplands of The Lake District. Steep slopes are typical of this upland region. Major rivers in the North West include the Irwell and Mersey in Greater Manchester, the Lune, Ribble and Wyre in Lancashire and the Eden and Duddon in Cumbria (Figure 1). These rivers provide major freshwater inputs to the Irish Sea.

3. Methods

3.1. Water quality data

Calcium (Ca^{2+}); magnesium (Mg^{2+}); nitrate (NO_3^{-}-N); orthophosphate (PO_4^{3-}-P); and suspended solid (SS) concentrations, together with pH measurements, were acquired using databases of the Environment Agency (EA) of England and Wales. The EA sample rivers and streams at monthly intervals. Further details of the methods used by the EA are described by Neal et al. (1999). River monitoring data from the EA's routine monitoring programme for the period 1995 to 2001 were used in the study. This period was selected to ensure harmonisation with spatial datasets and to ensure that the monitoring period was the same across the North West region. Monitoring sites were only selected where more than 60 readings were available for each determinand. Point sources (e.g. effluents from waste water treatment works) can have a major effect on river water chemistry at sites in close proximity to these inputs (Neal et al., 2008). At these locations there is potential for these inputs to mask relationships between river water chemistry and basin-wide attributes (Davies and Neal, 2004). Therefore, monitoring stations located immediately downstream (within 500m) of Environment Agency consent to discharge sites (i.e. known point sources on the river network) were not included in the selection. Catchments with a strong urban-industrial base and a high number of point sources were still included in the analysis, but these distal point sources are diffuse in nature ('diffuse-point', c.f. Neal et al., 2004; 2008). From approximately 1500 EA monitoring sites across the North West region, the number of sites for each determinand that met the criteria was: 318 (Ca^{2+}), 264 (Mg^{2+}), 530 (NO_3^{-}-N), 566 (PO_4^{3-}-P), 562 (SS) and 620 (pH) (Figure 1). The sites used in the analysis cover a wide range of catchment sizes, land uses, geology, rainfall, and water quality. For each of the determinands the arithmetic mean was calculated.

3.2. Spatial datasets

This study uses five spatial datasets. A description of each is provided below.

3.2.1. Centre for Ecology and Hydrology (CEH) Wallingford Digital Terrain Model (DTM). Available as a 50 m (horizontal) and 0.1 m (vertical) resolution grid (Morris and Flavin, 1990).

3.2.2. Centre for Ecology and Hydrology (CEH) Land Cover Map 2000 (LCM2000). Available as a 25 m UK-wide grid. There are 26 land cover classes available in the LCM2000. These were aggregated into 12 new classes: Arable, Acid grassland, Bracken, Calcareous grassland, Exposed rock, Heathland, Improved grassland, Neutral grassland, Urban, Water, Wetland and Woodland.

3.2.3. British Geological Survey (BGS) Bedrock Geology. Available as 1:625,000 scale data via the British Geological Survey Digital Geological Map of Great Britain (DiGMapGB). The large number of bedrock classes were aggregated to form 8 new bedrock classes: coal measures, conglomerates, granites and lavas, limestones, shales, siltstones, sandstones and shales, and sandstones and mudstones.

3.2.4. Base Flow Index (BFI). Available as a 1 km UK-wide grid of BFI values. BFI values range between 0 and 1 and indicate the ratio of base flow to total flow volume (Gustard et al., 1992).

3.2.5. Met Office Standard Annual Average Rainfall (SAAR). Available as a 1 km grid based on the average annual rainfall for the period 1961-1990.

3.3. Spatial data analyses

Catchments upstream of each of the selected monitoring sites were delineated using the DTM and the Deterministic Eight-Direction (D8) flow routing algorithm. This was performed in the Terrain Analysis System (TAS), a software package for performing spatial analysis operations for environmental applications (Lindsay, 2005). To ensure that catchment outlets were positioned correctly on the digital stream network, the advanced outlet repositioning approach (AORA) was used (Lindsay et al., 2008). Using the raster calculator function in TAS, the mean elevation, slope, aspect, BFI and rainfall were derived for entire extent of each catchment. The percentage of each of the land cover and bedrock classes were derived in the same way.

3.4. Statistical methods

To assess potential controls on mean river water quality, stepwise multiple linear regression (SMLR) analyses were performed. SMLR analysis identifies a subset of predictors (Table 1) that statistically contribute to explained variance on the response variable. Monitoring sites were randomly separated into two groups, the first for model derivation, and the second for model validation. Given the greater uncertainty in model predictions at the catchment scale it is important to test model outputs on large independent validation datasets (Cherry et al., 2008). Therefore, model development and validation datasets were split into two equal sized groups (see section 3.1 for the number of sites for each determinand). In both groups a wide range of catchment characteristics and sizes were included, as well as a good spatial distribution of sites (Figure 1). Error was assessed for each set of values of the independent variables by visual examination of residuals and by diagnostic indices. Plots of the estimates of the dependent and standardised residuals were also constructed to test for homoscedasticity. To assess multivariate collinearity, tolerance and variance-inflation factor (VIF) statistics were also assessed. These build in the regressing of each independent variable on all others. Regression models for the determinands were tested by comparing observed mean values with the predicted mean values for the second independent group of sites. All statistical analyses were performed in JMP v8 (SAS).

3.5. Spatial predictions of water quality

There are a variety of GIS-based methods for interpolating and visualising the value of an attribute at un-sampled locations (Burrough and McDonnel, 1998). Visualisation of model outputs for large regions requires spatial aggregation. Approaches for aggregation include: regular grid sizes (e.g. Jordan et al., 1994; Daly et al., 2002; Brazier et al., 2004; Stromqvist et al., 2008); regular intervals on the stream network (e.g. Davies and Neal, 2004); hydrological response units (e.g. Cooper et al., 2000; 2004); and catchments/sub-catchments (e.g. Kernan et al., 2001; Wade et al., 2001; Evans et al., 2006). Visualisation of water quality predictions at the scale of major catchments in the North West region was initially considered, but rejected since these large-scale catchments would mask small-scale variations in catchment characteristics. Predicted water quality was calculated and mapped for isobasins (similar sized sub-catchments; Lindsay et al., 2006) within the North West region. Isobasins were created using the DTM and the digital stream network. Within a GIS framework, the regression equations and spatial datasets were used to predict river water quality for each isobasin.

4. Results

4.1. River water quality and the geography of the North West

There is considerable variability in land cover across the North West region (Table 2). River basins containing monitoring sites with >40% cover of arable land include the Mersey, Ribble, Wyre and Kent. The Mersey and Wyre basins also have sites with >60% urban cover. Within the Ribble and Eden basins there are monitoring sites with >80% improved grassland. There is a wide range of BFI values across the North West region. Values range from 0.22 (Mersey) to 0.84 (Eden): low values of BFI represent high "flashiness" of the catchment and low permeability of the system; higher values of BFI result in greater dampening of the rainfall signal and greater within-catchment storage.

River basins with the highest overall mean Ca^{2+} and Mg^{2+} concentrations (>40 mg l^{-1} and >7.5 mg l^{-1} respectively) are the Mersey, Ribble, Wyre and Eden. The Esk and Irt basins have overall mean Ca^{2+} and Mg^{2+} concentrations <2.5 mg l^{-1} and <1.2 mg l^{-1} respectively. pH values across the region are generally circumneutral, with the exception of low values (<4.5) at several monitoring sites within the Mersey basin. Nitrate concentrations at individual monitoring sites range from 0.19 mg-N l^{-1} at a site in the Eden basin to 48.9 mg-N l^{-1} at a site in the Mersey basin. The river basins with the highest overall mean NO_3^- concentrations (>2 mg-N l^{-1}) are the Mersey, Ribble, Wyre, Kent, Wampool and Eden. The Leven, Esk and Irt have overall mean NO_3^- concentrations <1 mg-N l^{-1}. The highest mean PO_4^{3-} concentration recorded at an EA monitoring site is 4.62 mg-P l^{-1} (within the Mersey basin). The lowest PO_4^{3-} concentration (0.002 mg-P l^{-1}) occurs in the Eden and Leven basins. There is a wide range of suspended solid concentrations across the North West. Values at individual sites range from 2.87 mg l^{-1} in the Derwent basin to 110 mg l^{-1} at a site in the Mersey basin.

4.2. Linkages between water quality and catchment characteristics

Stepwise multiple linear regression (SMLR) analyses show that mean Ca^{2+} concentrations are negatively related to mean catchment slope and positively related to the percentage of improved grassland cover in the catchment, percentage urban cover, and percentage limestone bedrock (Table 3). Slope explains ~55% of the variance in mean Ca^{2+} concentrations, with an additional ~20% from improved grassland and limestone bedrock. Mean Mg^{2+} concentrations are also related to land cover and catchment geology. Magnesium concentrations are positively related to arable and urban cover, and negatively related to siltstone bedrock and rainfall. River water pH is related to catchment geology (hard weathering lithologies and limestone) and land cover (wetland and heathland). These geological and land cover variables explain 60% of the variance in mean pH values. Mean NO_3^- concentrations are positively related to the cover of arable land, improved grassland and urban. Arable land explains ~40% of the variability in mean NO_3^- concentrations across the North West. Orthophosphate concentrations are positively related to urban cover, arable cover, and catchment area. Only 23% of the variance in PO_4^{3-} concentrations can be explained by these characteristics, with urban cover contributing to ~15% of the variance. Suspended solid concentrations are related to urban cover, catchment terrain (slope and altitude) and bedrock geology (shales). Urban cover explains ~40% of the variance in mean suspended solid concentrations.

4.3. Model testing

Overall, there is good agreement between observed and predicted Mg^{2+} and pH values (R^2 = 0.65 and 0.60 respectively; Figure 2). Predicted Ca^{2+} concentrations are generally in good agreement with observed concentrations, but the model under-predicts Ca^{2+} concentrations for a limited number of sites with observed concentrations between 60 and 90 mg l^{-1} (Figure 2a). The results reveal that the model for NO_3^--N is reasonable, but there is under-prediction of mean NO_3^--N for those sites with observed values >5 mg-N l^{-1} (Figure 2d). The results show that PO_4^{3-} concentrations are significantly under-predicted for many sites (Figure 2e). For some sites there is an order-of-magnitude difference between observed and predicted PO_4^{3-} concentrations. There is also some over-prediction for some low P sites. Comparison of observed and predicted SS concentrations also shows under- and over- prediction (Figure 2f).

4.4. Spatial predictions

The regression equations (Table 3) were used to predict the river water quality of the isobasins created for the North West. Mapping the results (Figure 3) shows that the upland areas of Cumbria, the Forest of Bowland, and the Pennine fringe to the north and east of Manchester, and the east of the Eden, have low predicted mean concentrations of Ca^{2+} (<10 mg l^{-1}), Mg^{2+} (<5 mg l^{-1}), NO_3^- (<0.5 mg-N l^{-1}), PO_4^{3-} (<0.05 mg-P l^{-1}), SS (<0.05 mg l^{-1}), and pH (<5.5). The predictions show that the lowlands of the North West have varied water quality. Elevated mean Ca^{2+}, PO_4^{3-} and SS concentrations (>80 mg l^{-1}, >0.8 mg-P l^{-1} and >50 mg l^{-1}, respectively) are predicted for some coastal areas of the Mersey, Ribble and Wyre basins, especially Liverpool and Preston (Figure 3). High mean Ca^{2+}, PO_4^{3-} and SS concentrations are also predicted for the Greater Manchester conurbation. Low Ca^{2+} and SS concentrations are predicted for parts of the Lancashire Plain, which is located in the lower reaches of the Ribble and Wyre. Predicted mean PO_4^{3-} concentrations for this region range between 0.5 and 0.9 mg-

P l^{-1}. The Lancashire Plain has predicted high concentrations of Mg^{2+} and NO_3^- (>50 mg l^{-1} and >7 mg-N l^{-1} respectively; Figure 3). Much of the lower reaches of the Mersey and Eden basins have predicted mean NO_3^- concentrations >3 mg-N l^{-1}.

5. Discussion

5.1. Catchment drivers and pressures on water quality

This analysis provides an assessment of the linkages between river water quality and catchment characteristics across North West England. For the major cations (Ca^{2+} and Mg^{2+}) and river water pH there is considerable variability across the North West (Table 2). Previous studies have found the distribution of Ca^{2+} and Mg^{2+} concentrations in rivers and streams to depend strongly upon weathering of soil and bedrock geology (e.g. Robson and Neal, 1997; Thornton and Dise, 1998; Smart et al., 1998; Oguchi et al. 2000; Jarvie et al., 2002). In our study mean Ca^{2+} concentrations are mainly linked to slope (Table 2). Slope probably represents an aggregation of rainfall, soils, geology, vegetation and temperature (weathering). The lowest Ca^{2+} concentrations occur at sites with steeper slopes. Higher precipitation, thinner soils and predominantly base-poor geologies at these locations explain the low mean Ca^{2+} concentrations. The SMLR identified a link between mean Ca^{2+} concentrations and the cover of improved grassland. This may be due to leaching of Ca^{2+} from fertilised pastures where liming has been used to offset soil acidification (Cuttle and James 1995; Price, 2003). Sites where mean Ca^{2+} concentrations are under-predicted (Figure 2) generally occur in river basins containing intensive agriculture (Figure 4, Table 1). High fertiliser application and leaching of Ca^{2+} from these soils (Goulding and Blake, 1998) are a possible explanation for the elevated Ca^{2+} concentrations at these sites. Mean Mg^{2+} concentrations are linked to the percentage of arable and urban land cover (Table 3), both of which occur in the lowlands. Permian-Triassic sedimentary rocks dominate much of the North West lowlands, especially in the southern part of the region. It is likely that the elevated Mg^{2+} concentrations in the lowlands are due to underlying geology, rather than urban or arable land cover (Table 3). The model for pH performs well and the findings are consistent with similar studies (e.g. Smart et al., 1998; Thornton and Dise, 1998). The spatial prediction of pH (Figure 3) highlights low pH levels in the high altitude areas of the Lake District and the Pennines, and high pH in the lowland areas and the river valleys in the north of the region.

The results of the analysis reveal that NO_3^--N is related to arable cover and, to a lesser extent, the cover of improved grassland and urban (Table 3). This is in agreement with other studies (e.g. Thornton and Dise, 1998; Ferrier et al., 2001; Jarvie et al., 2002; Davies and Neal, 2007; Neal et al., 2008). Although the analysis reveals that mean NO_3^- concentrations are mainly related to the extent of arable land, the highest observed NO_3^- concentrations in the North West region occur in the urban and highly industrialised Mersey basin (Table 1). This area is characterised by a large number of waste water treatment works and other effluent discharges (Rothwell et al., 2010). Point sources have been shown to be major contributors to river NO_3^--N in urban environments (e.g. Davies and Neal, 2004; Meynendonckx et al., 2006). Sites where there is significant under-prediction of mean NO_3^- concentrations (Figure 2) tend to occur in the low lying urbanised southern part of the region (Figure 4, Table 1). Point source inputs of sewage effluent may be significant and explain the elevated concentrations in these urban catchments. Interestingly, under-prediction of mean NO_3^- concentrations also occurs in rural areas (Figure 4, Table 1). Point sources associated with rural settlement may explain the elevated observed NO_3^- concentrations at these sites (Neal et al. 2006).

The results indicate that mean SS concentrations are most strongly linked to urban cover, suggesting that anthropogenic sources are the major contributor to fine sediment delivery in the North West. Ferrier et al. (2001) also found a strong link between urban catchments and suspended solids in Scottish rivers. Collins et al. (2008) show that sediment loss from point and diffuse urban sources can be significant, especially in heavily urbanised regions. Urban suspended sediment within the North West is likely to represent a mix of point (sewage or industrial effluent) and diffuse (runoff from roads, industrial areas or residential housing) sources. The challenge therefore is to evaluate the relative contributions from these diverse sources in the urban sector. Although the SMLR did not identify agriculture as a predictor of SS concentrations, it did identify slope and altitude as predictors (Table 3). In low-relief coastal locations in the North West, particularly the Ribble and Wyre (Figure 1), intensive agriculture is common. The spatial prediction identifies this zone as having elevated SS concentrations (Figure 3).

Observed PO_4^{3-} concentrations are highly variable across the North West (Table 1), but comparison of observed and predicted PO_4^{3-} values reveals that the model fails to predict the very high PO_4^{3-} concentrations (Figure 2). In a similar study, Davies and Neal (2007) also reported under-prediction of PO_4^{3-} concentrations for locations immediately downstream of waste water treatment works. In our study, data from EA monitoring stations immediately downstream of known point source inputs were not included in the analysis in an attempt to avoid the potential for sewage effluent inputs to mask relationships between water quality and the catchment attributes. Sites where there is significant under-prediction of mean PO_4^{-} concentrations (Figure 2) occur in urban and rural areas of the region (Figure 4, Table 1). The results of this study suggest that ‘diffuse-point’ source inputs (c.f. Neal et al., 2004; 2008), i.e. point sources at distal locations in a catchment, can still have a significant influence on river PO_4^{3-} concentrations further downstream. Point sources in the North West appear to be of major importance with respect to PO_4^{3-}-P enrichment in rivers and streams. This is consistent with previous studies in other regions around the UK (e.g. Neal and Jarvie, 2005; Neal et al., 2005; Jarvie et al., 2006; Neal et al. 2008; Jarvie et al., 2008). Despite the continued control of point source discharges associated with sewage effluent and improvements in treatment processes, this study clearly highlights that point sources still have a major effect of river nutrient levels in urban and rural catchments in the North West. The linear regression model also over-predicts PO_4^{3-} concentrations at a large number of sites in the North West (Figure 2), especially in the southern part of the region (Figure 4). Variation in within-river processing of PO_4^{3-}-N (House, 2003; Withers and Jarvie, 2008), may also determine PO_4^{3-} concentrations in North West rivers. Linkages between PO_4^{3-}-N and catchment characteristics start to break down when there are within-river losses.

5.2. The utility of the catchment characteristic approach

Water quality models using the catchment characteristic approach have been developed for many different environments and have proved to be highly successful in predicting variation in catchment water quality (e.g. Donohue et al. 2005; 2006; van de Perk et al., 2007; Davies and Neal, 2004; 2007; Helliwell et al., 2007). In this study it is clear that the approach works well for those water constituents derived from diffuse sources. Predicted NO_3^- concentrations across the North West region highlight agricultural diffuse sources in coastal areas and nutrient poor locations in the uplands (Figure 3). Although a reasonable estimate of NO_3^--N is obtained, contributions from urban and rural point sources are likely to be under-represented in the spatial prediction. The overwhelming influence of point sources on river PO_4^{3-} concentrations makes it difficult to identify strong relationships with the catchment characteristics investigated. The empirical approach could be refined by combining the physical catchment characteristics with information on discharge consents and population density, and by combining PO_4^{3-} concentration data with river discharge. Non-linear approaches could also be used to identify sites with different controls on PO_4^{3-} concentrations. Albeit, the spatial prediction of mean PO_4^{3-} concentrations in North West rivers (Figure 3) serves as a broad indication of areas at risk of elevated PO_4^{3-} concentrations. A combination of the catchment characteristic approach together with models such as PSYCHIC (Davidson et al., 2008; Stromqvist et al., 2008) or the Load Apportionment Model (Bowes et al., 2008; 2009) may provide a better understanding of phosphorus variability in North West rivers.

6. Conclusion

This study indicates that models based on catchment characteristics can be very useful for regional prediction of pH and the concentrations of Ca^{2+} and Mg^{2+} in rivers, and appear a reasonable first approach for predicting mean NO_3^--N and suspended solids concentrations. The results show that mean NO_3^- concentrations in North West river basins are mainly linked to diffuse agricultural inputs, but that point source inputs are also significant in urban and rural catchments. The results show that distal point sources within a catchment can play a major role in influencing river PO_4^{3-} concentrations further down the river network. High concentrations of PO_4^{3-} at some sites associated with point sources may disproportionately influence underlying relationships with catchment characteristics. More work is needed to fully evaluate nutrient sources and dynamics in North West rivers, especially in the context of catchment management and the growing pressure for increased housing and associated requirements for sewage treatment.

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Figure captions

Figure 1. Environment Agency river water sampling sites across North West England used in the study. Inset indicates the location of the North West region in Great Britain.

Figure 2. Comparisons between observed and predicted river water quality for the independent validation dataset. (a) Ca^{2+} (mg l^{-1}); (b) Mg^{2+} (mg l^{-1}); (c) pH; (d) NO_3^{-} (mg-N l^{-1}); (e) PO_4^{3-} (mg-P l^{-1}); (f) suspended solids (mg l^{-1}). The plot shows the regression line (solid red), 95% confidence limits (dashed red) and the 1:1 line (solid black).

Figure 3. Maps of predicted river water quality for sub-catchments across North West England. Predictions are based on the regression models in Table 3. (a) Ca^{2+} (mg l^{-1}); (b) Mg^{2+} (mg l^{-1}); (c) pH; (d) NO_3^{-} (mg-N l^{-1}); (e) PO_4^{3-} (mg-P l^{-1}); (f) suspended solids (mg l^{-1}).

Figure 4. Maps showing the location of monitoring sites where linear models (Table 3) over- and under- predict mean chemical concentration. Values are the difference between observed and predicted concentrations. (a) Ca^{2+} (mg l^{-1}); (b) NO_3^{-} (mg-N l^{-1}); (C) PO_4^{3-} (mg-P l^{-1}).

	Predictor variable
Terrain	Altitude, Aspect, Slope,
Land cover	Arable, Acid grassland, Bracken, Calcareous grassland, Exposed rock, Heathland, Improved grassland, Neutral grassland, Urban, Water, Wetland and Woodland
Bedrock geology	Coal measures, Conglomerates, Granites and lavas, Limestone, Shales, Siltstones, Sandstones and shales, Sandstones and mudstones
Ground water recharge	Base Flow Index
Meteorology	Rainfall

Table 1. Predictor variables used in the stepwise multiple linear regression.

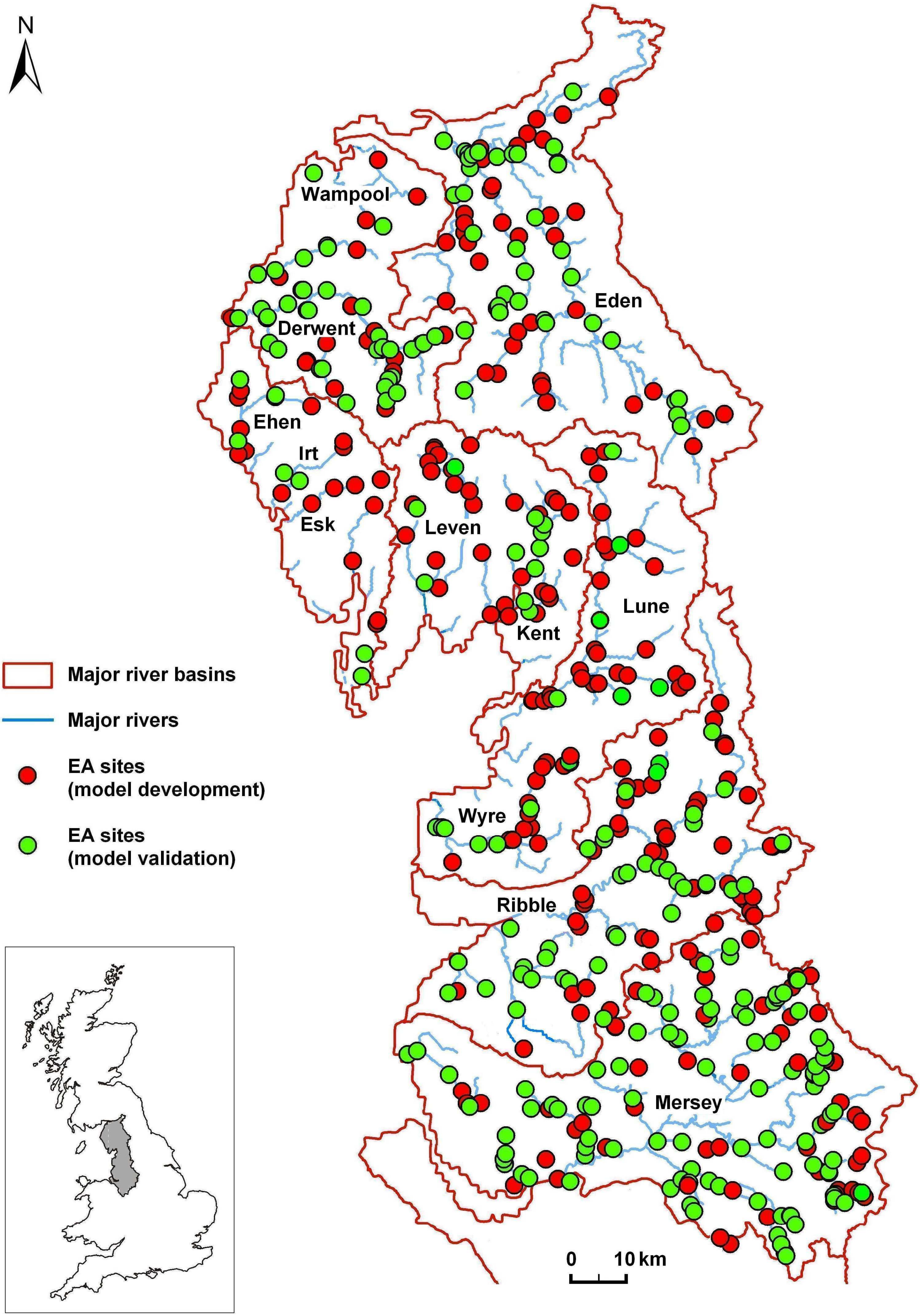
Basin	Arable	Urban	Improved grassland	BFI	Ca^{2+}	Mg^{2+}	pH	NO_3^-	PO_4^{3-}	SS
	%	%	%		mg l^{-1}	mg l^{-1}		mg-N l^{-1}	mg-P l^{-1}	mg l^{-1}
Mersey	10.2	16.8	18.7	0.45	50.1	12.7	7.61	3.19	0.30	17.3
	(0 - 56.9)	(0 - 67.5)	(0 - 65.0)	(0.22 - 0.81)	(4.18 - 199)	(2.49 - 46.3)	(4.36 - 8.43)	(0.47 - 48.9)	(0.03 - 4.62)	(5.06 - 110)
Ribble	4.56	7.76	31.9	0.37	44.2	8.15	7.86	2.41	0.34	15.5
	(0 - 36.2)	(0 - 37.1)	(0 - 81.5)	(0.27 - 0.61)	(15.3 - 84.2)	(1.90 - 33.3)	(6.54 - 8.26)	(0.39 - 14.5)	(0.03 - 3.79)	(3.60 - 82.7)
Wyre	6.94	15.2	29.9	0.36	41.8	11.7	7.49	2.21	0.22	26.6
	(0 - 42.3)	(0 - 74.5)	(5.06 - 64.7)	(0.30 - 0.53)	(5.54 - 122)	(1.55 - 53.9)	(6.67 - 7.98)	(0.58 - 6.72)	(0.03 - 0.63)	(8.55 - 86.6)
Lune	1.03	1.07	32.1	0.39	34.3	3.22	7.85	1.25	0.05	5.74
	(0.03 - 3.92)	(0 - 3.85)	(4.69 - 68.5)	(0.26 - 0.72)	(8.91 - 80.3)	(1.95 - 7.02)	(7.31 - 8.25)	(0.44 - 4.17)	(0.02 - 0.24)	(3.46 - 12.6)
Kent	9.14	2.61	48.3	0.53	28.8	7.10	7.69	2.89	0.07	7.05
	(1.38 - 51.2)	(0.07 - 8.74)	(18.1 - 73.1)	(0.34 - 0.74)	(9.55 - 59.7)	(1.76 - 48.1)	(7.40 - 8.21)	(0.86 - 5.05)	(0.02 - 0.28)	(3.56 - 18.35)
Leven	3.50	2.00	14.8	0.41	8.41	1.23	7.23	0.99	0.07	3.96
	(0.35 - 17.3)	(0.11 - 10.1)	(2.85 - 51.1)	(0.25 - 0.56)	(4.31 - 18.3)	(0.71 - 2.28)	(6.89 - 7.83)	(0.24 - 2.72)	(0.002 - 0.24)	(2.98 - 6.13)
Esk	1.01	0.62	2.70	0.36	2.21	0.83	6.51	0.43	0.02	3.15
	(0.42 - 1.52)	(0.02 - 1.32)	(1.35 - 4.82)	(0.30 - 0.40)	(1.58 - 2.77)	(0.59 - 0.99)	(6.15 - 6.76)	(0.38 - 0.50)	(0.015 - 0.016)	(3.01 - 3.39)
Irt	0.53	0.80	7.78	0.34	2.23	1.16	6.83	0.61	0.03	7.68
	(0.11 - 4.48)	(0 - 1.12)	(1.95 - 20.0)	(0.33 - 0.49)	(2.04 - 6.24)	(0.73 - 1.61)	(6.64 - 7.23)	(0.49 - 0.79)	(0.018 - 0.023)	(3.17 - 18.3)
Ehen	8.40	1.19	29.5	0.46	21.4	2.78	7.44	1.43	0.05	15.07
	(0.03 - 16.8)	(0.26 - 2.48)	(1.11 - 56.9)	(0.34 - 0.69)	(2.36 - 44.6)	(0.84 - 5.16)	(6.55 - 7.75)	(0.42 - 3.05)	(0.02 - 0.1)	(3.55 - 31.8)
Derwent	3.91	0.74	24.1	0.44	12.9	1.47	7.08	1.18	0.06	8.02
	(0 - 14.9)	(0 - 3.16)	(0.52 - 72.8)	(0.28 - 0.61)	(1.49 - 93.2)	(0.55 - 4.05)	(6.36 - 8.08)	(0.33 - 3.59)	(0.004 - 1.4)	(2.87 - 39.8)
Wampool	13.1	1.19	68.8	0.41	n.a	n.a	7.94	4.16	0.16	13.0
	(5.54 - 17.7)	(0.56 - 2.14)	(64.5 - 78.5)	(0.34 - 0.48)			(7.53 - 8.19)	(2.50 - 6.30)	(0.1 - 0.29)	(11.59 - 15.0)
Eden	7.57	1.41	46.7	0.47	43.6	7.53	7.89	3.04	0.11	8.12
	(0 - 25.4)	(0 - 7.10)	(2.17 - 84.6)	(0.23 - 0.84)	(1.67 - 171)	(1.04 - 17.0)	(6.92 - 8.25)	(0.19 - 9.74)	(0.002 - 0.39)	(3.12 - 17.6)

Table 2. Mean values for selected catchment characteristics and water quality for Environment Agency monitoring sites in North West river basins. Values in parenthesis are the range of catchment characteristics and water quality for individual sites within each basin. The river basins are shown in Figure 1.

Response variable	**Regression equation**
Ca^{2+}	14.5 − 0.73*Slope + 0.51*Improved Grassland + 0.92*Urban + 0.16*Limestone; *p* = <0.001, SEE = 10.2, n = 159; R^2 = 0.77 (where *S* = 0.56; *S, IG* = 0.65; *S, IG, U* = 0.74; *S, IG, U, L* = 0.77)
Mg^{2+}	5.18 + 0.48*Arable + 0.31*Urban − 0.57*Siltstone − 0.002*Rainfall; *p* = <0.001, SEE = 4.45, n = 132; R^2 = 0.55 (where *A* = 0.34; *A, U* = 0.49; *A, U, Si* = 0.53; *A, U, Si, R* = 0.55)
pH	7.71 − 0.01*Granites and lavas − 0.02*Wetland + 0.004*Limestone − 0.009*Heathland *p* = <0.001, SEE = 0.34, n = 310; R^2 = 0.60 (where *G* = 0.37; *G, W* = 0.53; *G, W, L* = 0.58; *G, W, L, H* = 0.60)
NO_3^--N	0.24 + 0.11*Arable + 0.04*Improved Grassland + 0.02*Urban *p* = <0.001, SEE = 1.45, n = 265; R^2 = 0.52 (where *A* = 0.39; *A, IG* = 0.50; *A, IG, U* = 0.52)
PO_4^{3-}-P	0.02 + 0.01*Urban + 0.01*Arable + 0.0003*Area; *p* = 0.001, SEE = 0.3, n = 283; R^2 = 0.23 (where *U* = 0.17; *U, A* = 0.21; *U, A, Ar* = 0.23)
SS	15.5 + 0.38*Urban − 0.17*Slope − 0.06*Shales − 0.02*Altitude; *p* = <0.001, SEE = 8.25, n = 281; R^2 = 0.50 (where *U* = 0.43; *U, S* = 0.47; *U, A, Sh* = 0.48; *U, A, Sh, Al* = 0.50)

Table 3. Regression equations describing relations between river water quality and catchment characteristics across North West England. The R^2 value for each model is shown together with the variance explained by each predictor variable. *S* Slope; *IG* Improved Grassland; *U* Urban; *L* Limestone; *A* Arable; *Si* Siltstone; *R* Rainfall; *G* Granites and lavas; *W* Wetland; *H* Heathland; *Ar* Area; *Sh* Shales; *Al* Altitude.

Figure 1


N
Wampool
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Major river basins
Major rivers
EA sites
(model development)
EA sites
(model validation)

Figure 2

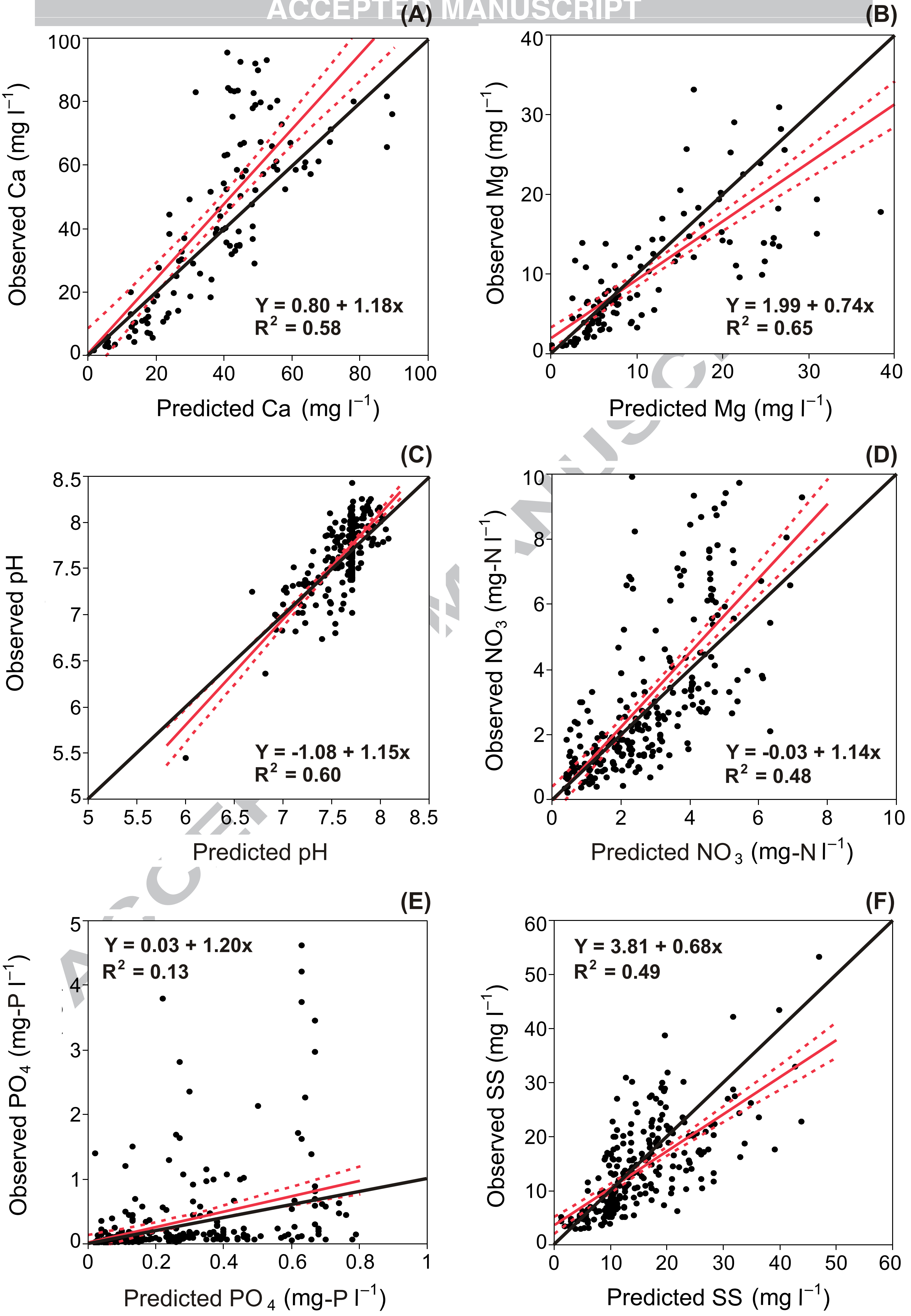

(A)
Y = 0.80 + 1.18x
R² = 0.58
Observed Ca (mg l⁻¹)
Predicted Ca (mg l⁻¹)
(B)
Y = 1.99 + 0.74x
R² = 0.65
Observed Mg (mg l⁻¹)
Predicted Mg (mg l⁻¹)
(C)
Y = -1.08 + 1.15x
R² = 0.60
Observed pH
Predicted pH
(D)
Y = -0.03 + 1.14x
R² = 0.48
Observed NO3 (mg-N l⁻¹)
Predicted NO3 (mg-N l⁻¹)
(E)
Y = 0.03 + 1.20x
R² = 0.13
Observed PO4 (mg-P l⁻¹)
Predicted PO4 (mg-P l⁻¹)
(F)
Y = 3.81 + 0.68x
R² = 0.49
Observed SS (mg l⁻¹)
Predicted SS (mg l⁻¹)

Figure 3

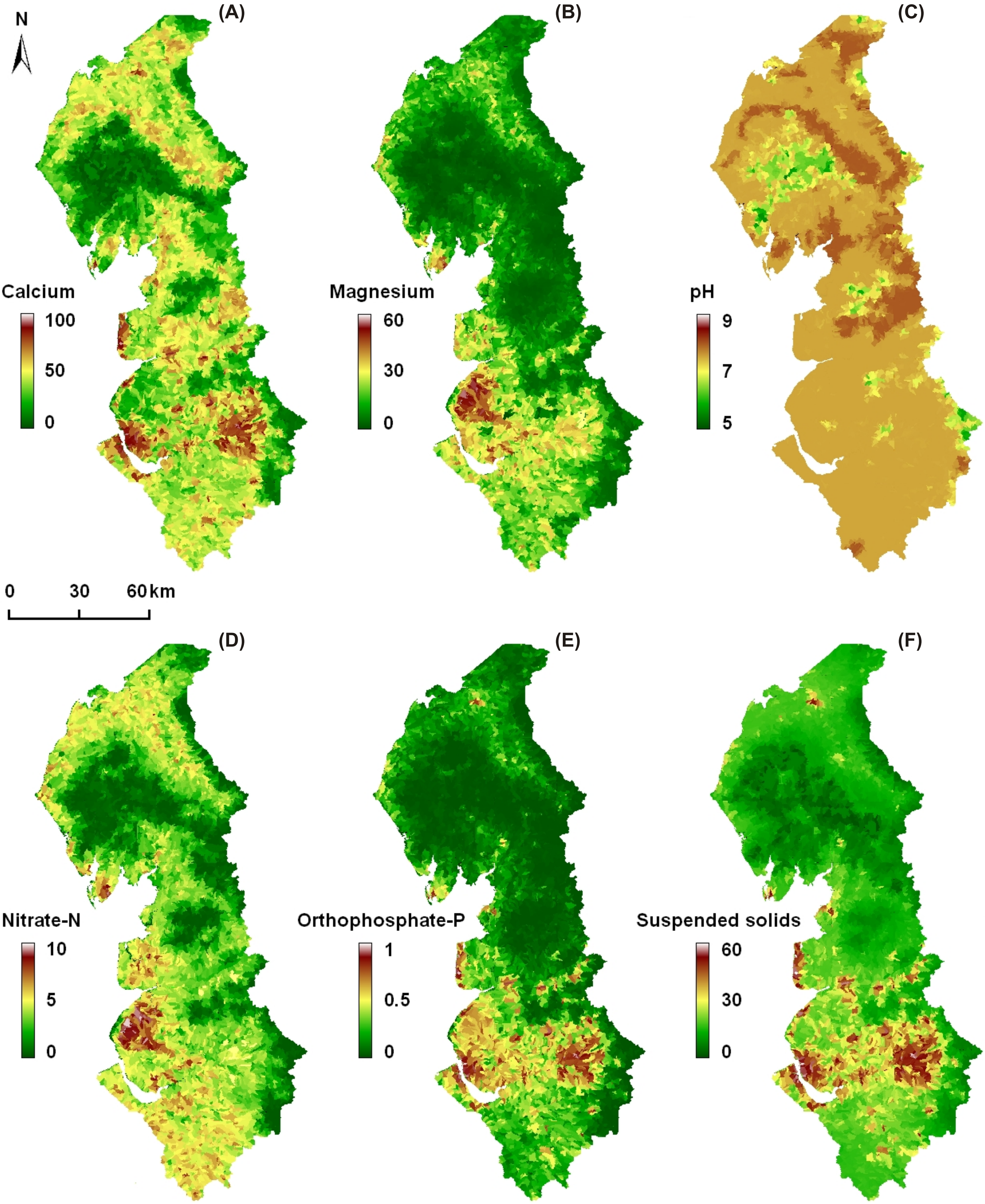
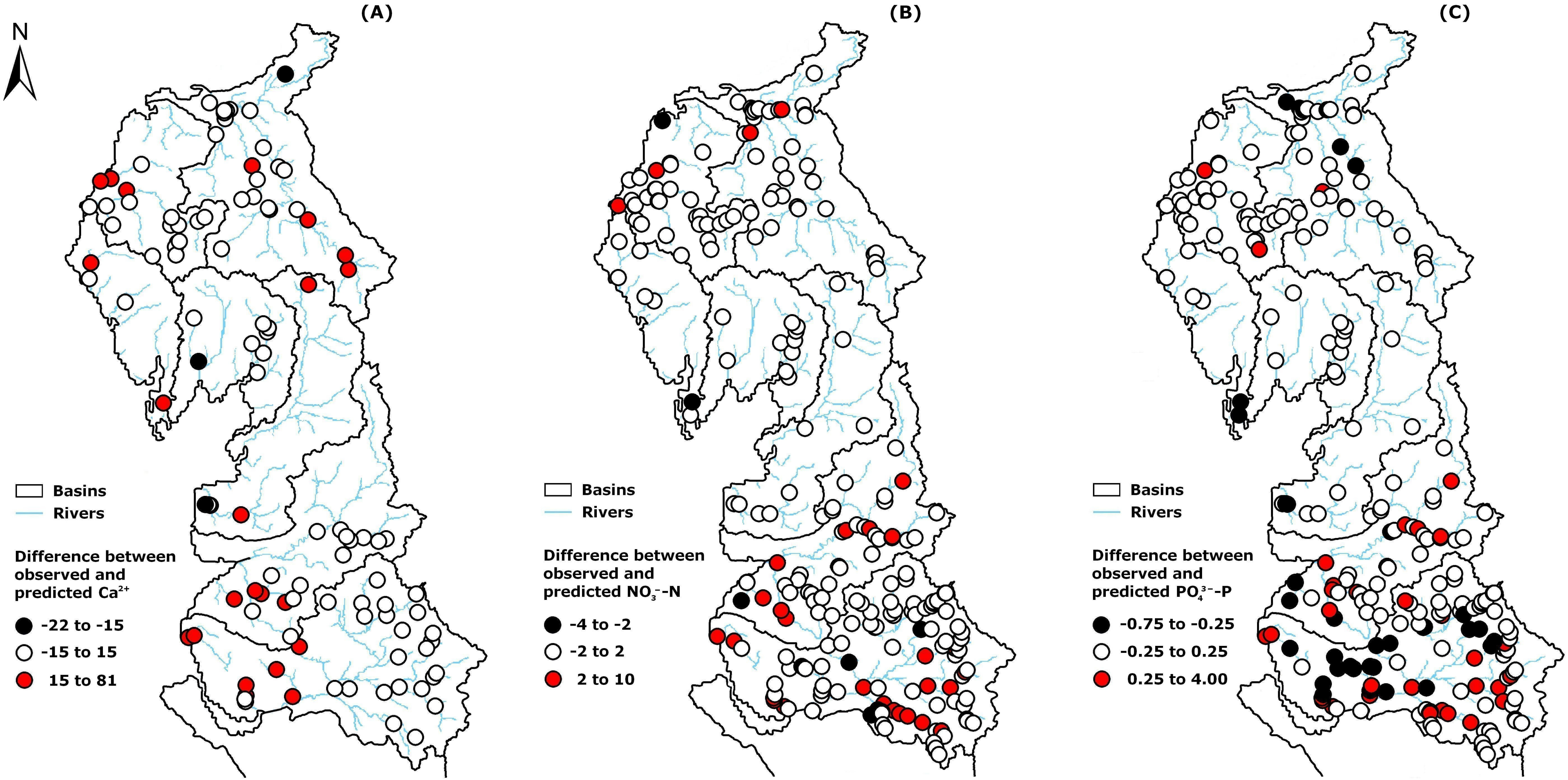

N
(A)
(B)
(C)
Calcium
100
50
0
Magnesium
60
30
0
pH
9
7
5
0
30
60 km
(D)
(E)
(F)
Nitrate-N
10
5
0
Orthophosphate-P
1
0.5
0
Suspended solids
60
30
0

Figure 4


(A)
N
Basins
Rivers
Difference between observed and predicted Ca²⁺
-22 to -15
-15 to 15
15 to 81
(B)
Basins
Rivers
Difference between observed and predicted NO₃⁻-N
-4 to -2
-2 to 2
2 to 10
(C)
Basins
Rivers
Difference between observed and predicted PO₄³⁻-P
-0.75 to -0.25
-0.25 to 0.25
0.25 to 4.00