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1 Application of a simple multiplicative spatio-
2 temporal stream water quality model to the river
3 Conwy, North Wales

4

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12 **Abstract**

13 We use a simple multiplicative spatio-temporal model to describe variability in a
14 sequence of water quality monitoring data from headwater streams in the Conwy
15 catchment, North Wales. The spatial component of the model treats concentrations as
16 due to simple mixing of a small number of distinct source types, each associated with
17 particular upstream catchment characteristics. The temporal component allows
18 concentration variability due to seasonal or hydrological change. We apply the model
19 using three candidate catchment characteristic classifications to generate mixing

1

1 concentrations, and a seasonal component to describe temporal variability, and test a
2 range of sub-models. We identify a cross-classification of soil and land cover as
3 providing the best spatial indicator of water quality of the classifications considered.
4 The spatial model based on a selected grouped cross-classification was shown to
5 account for between 35% and 90% of the spatial variability and the seasonal model
6 accounted for between 45% and 100% of the temporal variability in the data.
7 Analysis of residuals showed an inverse relationship between DOC and sulphate and
8 between hydrogen ion concentration and calcium and magnesium. We also found
9 residual correlations between sites which are strongly related to landscape class. These
10 are attributed to landscape class by time interactions which are not accounted for in the
11 simple multiplicative model.
12 *Key words:* stream water quality; landscape; classification; multiplicative;

13 **1 Introduction**

14 Stream water quality is measured to determine whether acceptable ecological
15 standards are being met, and to support investigations into the source and fate of
16 material in solution and suspension. Water quality management through contaminant
17 source control is based on the interpretation of the data generated by monitoring
18 programmes. Data collected commonly include repeated measurement of water quality
19 variables at fixed sampling locations, generating spatio-temporal datasets. These give
2

1 useful but limited information on the contaminant budget of a catchment, and a fuller
2 spatio-temporal description of water quality variability can be provided by models
3 representing sources and their fates at a range of scales, supported by water quality
4 measurements and other features of the catchment.

5 Stream water quality models may rely on the known distribution of sources and source
6 characteristics to track material in solution or suspension through a stream network.

7 The application of these models does not require stream water quality measurements,
8 though they may be useful for calibration. Alternatively, models may use river water
9 quality measurements to infer source magnitudes given the upstream distribution of
10 source locations, and extrapolate locally based on known source locations upstream of
11 unmonitored stream sites. This approach tailors loss estimation to local conditions, but
12 if used without other knowledge may neglect useful information. For local use, a hybrid
13 approach is to start with a model which includes initial numerical estimates of
14 magnitudes of known source types, and calibrate the model from stream water quality
15 measurements.

16 There are a number of models which use accumulated knowledge of source magnitudes
17 to estimate water quality at new sites. These have been developed largely to account
18 for agricultural diffuse source pollution by the nutrients nitrogen and phosphorus.
19 Losses of these nutrients have been modelled by nutrient budgeting based on farm

1 management including details of livestock, crop management and drainage
2 characteristics. Losses are estimated by a simple accounting procedure, and are often
3 expressed on an annual basis. Johnes¹ presents a simple annual loss accounting model,
4 and this approach has been widely adopted^{2,3}. Other models estimate losses at a finer
5 timescale and include a component allowing losses to vary according to hydrological
6 conditions. Catchment scale models of this type generally include a delivery component
7 describing transfers to the larger river network, and a routing component describing
8 transfer through the river network, possibly allowing for point sources. These models
9 include AGNPS⁴, SWAT⁵, HSPF⁶, MAGPIE⁷, and are reviewed by Borah and Bera^{8,9}.

10 Models which use stream water quality to infer source magnitudes are generally of
11 regression structure, and may be partially constrained to give some natural mixing
12 interpretation. The simplest such model uses unstructured regression of concentrations
13 on a range of catchment characteristics^{10,11}. Unconstrained models of this form may
14 include negative coefficients which have no natural interpretation and which may
15 generate negative concentrations. If logged concentration data are used as response
16 variables, then additive terms imply a multiplicative model of the raw data, which is not
17 compatible with additive contributions from a number of sources. These considerations
18 suggest that the spatial component of a model should be interpretable as a sum of
19 (positive) contributing sources. These simple nutrient accounting models commonly rely

1 on a landscape classification, with characteristic nutrient or other loss from each class¹²⁻
2 ¹⁷. Apart from individual studies, a modelling framework, SPARROW, has been
3 developed for estimation of contributing pollutant sources from stream water quality
4 monitoring data using a constrained regression approach^{18,19}. Where there is temporal
5 variability in water quality this may be seasonal or driven by hydrological variability
6 which may be due to a dilution effect of relatively uncontaminated precipitation. A
7 simple dilution effect is multiplicative, affecting all concentrations derived from fixed
8 sources equally. In practice, a hydrological response may mobilise new sources, and
9 precipitation does contain some contaminants. Nevertheless, the dilution argument
10 does suggest a multiplicative term may be appropriate for the temporal component of a
11 simple water quality model. If precipitation is uniform over a wide area, then dilution
12 may be regionally similar. An extension of the SPARROW modelling framework to
13 include a multiplicative temporal effect has been described by Wellen *et al.*²⁰.

14

15 We apply a simplified version of Wellan *et al.*'s²⁰ spatio-temporal model in which the
16 spatial component is additive and the temporal component a seasonal multiplier of the
17 spatial component. We examine the performance of the model in describing the
18 variability in concentration changes measured in headwater subcatchments of the
19 Conwy catchment, North Wales. Our model excludes point sources, which are largely

5

1 absent from the headwater subcatchments sampled. The influence of any instream
2 processes is assumed to be accounted for through their influence on the estimated
3 drainage concentrations from the landscape classes used at the scale of the headwater
4 subcatchments. The model can be interpreted as assuming simple mixing of end-
5 members generated by a small number of landscape classes, with equal dilution or
6 proportionate generation at equal times, for all end-member sources.

7 We consider three different landscape classification schemes as potential end-member
8 sources for the spatial component of the model. Each scheme is derived from national
9 UK databases. On any sampling occasion, each landscape class is assumed to generate
10 an end-member runoff component with characteristic water quality. Downstream water
11 quality is taken to be a mixture of end members, according to the upstream proportion
12 of each class under the selected classification scheme. The model does not allow
13 interaction between time and space, so that concentrations may not stay fixed for one
14 landscape class while varying in another class. Interaction between landscape classes
15 and temporal effects may be tested through residual analysis. The model is applied
16 individually to a range of variables, so that proportional changes in concentration over
17 time may vary between water quality variables.

18

1 In our application of the model to the Conwy catchment, water quality is measured
2 quarterly through two years, and given this limited number of sampling occasions, we
3 estimate a seasonal effect only, recognising that this will be influenced by hydrological
4 and other conditions at the time of sampling.

5 **2 Methods**

6 The spatio-temporal model expresses concentration of a single water quality variable as
7 the product:

$$8 \quad y_{s,t} \lambda = c_s \lambda_t \quad (1)$$

9 In equation (1), $y_{s,t}$ is a concentration measurement at location $s = 1, \dots, n_s$ and field
10 excursion $t = 1, \dots, n_t$. The parameters c_s and λ_t represent the spatial and temporal
11 components of the model. The time parameter λ_t adjusts simulated concentrations c_s
12 as they are influenced by such factors as hydrological conditions and season at the time
13 of sampling.

14

15 We extend the model of equation (1) to allow c_s to be a function of the configuration of
16 landscape classes within the catchment, which are assumed to be available as a
17 complete fine-scale spatial coverage. In particular, where a catchment property is

7

1 distributed upstream of a sampling point, we assume simple mixing of upstream
 2 contributions by landscape class, so that

$$3 \quad c_s \vartheta = \sum_j p_{s,j} \vartheta_j \quad (2)$$

4 where in equation (2) $p_{s,j}$ is the proportion of the headwater subcatchment covered by
 5 landscape class $j=1,\dots,m$ and ϑ_j is the concentration in water draining landscape
 6 class j at the defined reference sampling time. This is the functional form of the spatial
 7 representation used by Cooper *et al.*¹³ and in terms of fluxes assumes simple mixing of
 8 contributions from each class, under the condition that the flow from each class is area-
 9 proportional.

10 We further extend the model to allow λ_t in equation (1) to be a function of time-varying
 11 covariates, so

$$12 \quad \lambda_t = f_t(\varphi) \quad (3)$$

13 In equation (3), $f(\varphi)$ is some function whose value at any point in time depends on the
 14 parameter array φ . Combining equations (1), (2) and (3) gives

$$15 \quad y_{s,t} \vartheta = \left(\sum_j p_{s,j} \vartheta_j \right) \left(\lambda_t \right) \quad (4)$$

$$\log(y_{s,t} \vartheta) = \log \left(\sum_j p_{s,j} \vartheta_j \right) + \log(\lambda_t)$$

1 Our hypothesis is that equation (4) explains sufficient of the variability in concentrations
 2 to be useful for estimating of water quality in headwater streams at large temporal and
 3 spatial scales. We include random terms in the logarithmic form of equation (4), giving

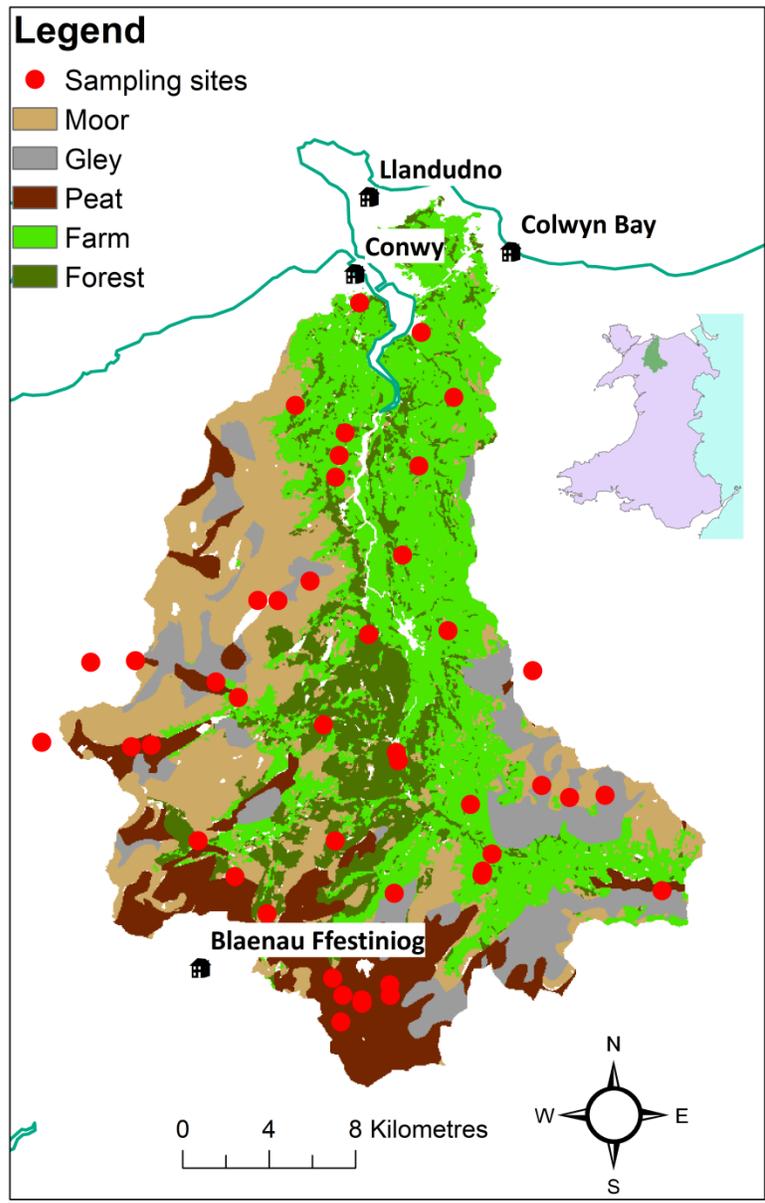
$$\begin{aligned}
 \log(y_{s,t}) &= \eta_{s,t} + \lambda_t + \zeta_s \\
 &+ \log\left(\sum_j p_{s,j} \vartheta_j\right) + \lambda_t \\
 &+ \log(f_k) + \xi_t
 \end{aligned}
 \tag{5}$$

5 In equation (5) ζ_s is a random site effect, ξ_t a random sampling occasion effect, and
 6 $\eta_{s,t}$ a residual error term assumed uncorrelated in time and space. Wellen *et al.*²⁰ also
 7 include temporal correlation in their model through a random walk structure for the
 8 temporal parameters. Because we apply the model only to independent headwater
 9 subcatchments for we ignore instream losses (Wellen *et al.*²⁰ $H_{i,j}^S$ and $H_{i,j}^R$). While
 10 equation (5) is the most complete form of the model used, we also consider sub-models
 11 which excluding the fixed effects ϑ_j and φ_k .
 12 The models are applied to a number of measured water quality variables, and
 13 inferences made on the relationship between these variables through studying both
 14 estimated model parameters and residual series.

15 **3 Application**

1 **3.1 Spatio-temporal survey**

- 2 We sampled stream water from 39 independent headwater subcatchments of the
- 3 Conwy catchment in North Wales (Fig 1).



1

2

Figure 1. The Conwy catchment, North Wales

11

1 The Conwy catchment (3°50W 53°N) includes a range of common upland UK landscapes
2 (73% of the catchment is above 200m compared with 28% of the UK) with the main
3 components being the mountains and moorland of Snowdonia, plantation forestry with
4 non-native coniferous species, and enclosed improved grazing land for sheep and cattle.
5 There are smaller areas of broadleaved woodland and little urbanisation. Elevation
6 varies from sea level to 1060m, with rainfall between 600 and 3000 mm yr⁻¹. The
7 catchment above the tidal limit is described in detail by Evans *et al.*¹⁴.

8 The subcatchments monitored are upstream of registered point sources such as sewage
9 treatment works or industrial effluent discharge, most draining uninhabited moorland
10 or forest. A small number of farmed subcatchments included farm buildings where
11 washings from yards or seepage from septic tanks. Such indeterminate sources are
12 taken as contributing to the overall diffuse source contribution for the purposes of this
13 analysis. Samples were collected at each subcatchment site on eight occasions at three-
14 monthly intervals between September 2008 and June 2010.

15 Headwater subcatchments were chosen with the aim of providing good estimates of
16 model parameters rather than to estimate population values of variables. To this end
17 they were selected where possible to be dominated by a single landscape class expected
18 to strongly influence water quality as defined and identified from maps and a field visit.
19 Simple random sampling of first order streams would include numerous very mixed

1 subcatchments with little information for the estimation of parameters associated with
2 landscape differences in drainage water quality. The purpose here is to demonstrate a
3 modelling approach at an example catchment, rather than to attempt to provide a fully
4 parametrised model which can be applied without modification throughout the United
5 Kingdom. The modelling approach may be applied elsewhere, with estimation of local
6 parameters. If used elsewhere with the parameter values estimated for the Conwy,
7 residual analysis would provide some insight into differences between the study
8 catchment and the Conwy. eThe three landscape classifications used in modelling were
9 based on:

- 10 1. Soil class
- 11 2. Land cover
- 12 3. Dual soil/land cover (“landscape”, cf Evans *et al.*¹⁴)

13

14 ***Soil class***

15 We use the England and Wales National Soil Resources Institute (NSRI) LandIS soil
16 classification <http://www.landis.org.uk/index.cfm>, combining some soil classes which
17 are either poorly represented or distributed in the catchment. The final classes used are
18 shown in Table 1.

19

Table 1. Soil classification

13

Soil class	LandIS soil association
Humic ranker	311
Brown soil	541, 561
Brown podzolic soil	611, 612
Stagnopodzol	654
Stagnogley	713
Stagnohumic Gley	721
Peat	1013

1

2

3 **Land cover (LCM)**

4 The UK 2007 Land Cover Map (LCM2007,

5 <http://www.ceh.ac.uk/LandCoverMap2007.html>) includes 23 classes at UK scale. After

6 some consolidation of major land cover groups in to account for poor representation in

7 the Conwy catchment, we use the classes shown in Table 2.

8

9 **Table 2. Land cover class**

Land cover class	LCM 2007 class
Broadleaved Woodland	1
Coniferous Woodland	2
Arable and Horticulture	3
Improved Grassland	4
Unimproved Grassland	5,6

14

Acid Grassland	8
Heather	10
Heather Grassland	11
Bog	12
Montane and Rock	13,14
Fresh water	16
Built up	22, 23

1

2 **Dual soil/land cover (“landscape”)**

3 In a previous study of the Conwy catchment, Evans *et al*¹⁴ identified five major
 4 landscape classes, defined by combining soil and land cover classes. They started from a
 5 landscape division based on all soil and land cover combinations present and clustered
 6 these into five classes based on available stream water quality data. The grouped
 7 landscapes are defined as “Mountain”, “Peat”, plantation coniferous forestry (“Forest”),
 8 gley moorland (“Gley”) and enclosed farmland (“Farm”), and used these to model water
 9 quality in the catchment. The combination of class groups used in the landscape
 10 definition is shown in Table 3.

11

Table 3. Combined landscape classification

LandIS soil association	LCM2007 land cover class	Combined landscape class
	1,2	“Forest”
	3,4,5,23	“Farm”
1013		“Peat”
721		“Gley”

15

All present except 721 and 1013	8,10,11,13,14	“Mountain”
---------------------------------	---------------	------------

1

2 This choice of grouping is also supported by evidence from other studies of enhanced
3 atmospheric deposition of some water quality variables, differences in soil processes in
4 different soil types, particularly between peat and mineral soils, and the strong
5 association between water quality and farming, where the fertility of the soil is
6 artificially influenced by farming practices^{12,21,11}.

7

8 The three classifications do not explicitly include a number of covariates which are likely
9 to influence water quality, including topography, slope and precipitation. However,
10 these covariates are highly correlated with catchment characteristics and their influence
11 is therefore partly accounted for within the classification schemes.

12 **3.2 Sample collection and chemical analysis**

13 Field samples of stream water were collected in polypropylene bottles and stored at 4⁰C
14 prior to analysis. Major ions sodium, potassium, calcium, magnesium were analysed
15 using ICP-OES; chloride and sulphate using ion chromatography; nitrate colorimetrically
16 using a SEAL AQ2 discrete analyzer; pH by pH electrode and non-purgeable organic
17 carbon (NPOC), taken to be equivalent to dissolved organic carbon (DOC), using a Skalar

16

1 Formacs analyser. The data and details of the chemical analysis methods used may be
 2 accessed at Cooper *et al.*²².

3 **3.3 Model implementation**

4 We used the `nlmer` routine in the R package (<http://www.r-project.org/>) `lme4` for
 5 non-linear model fitting. We fitted seven models of increasing complexity. We used the
 6 model shown by equation (5) as the most complex, with sub-models as shown in Table
 7 6.

8 **Table 6. Model components (cf. Equation (5))**

Model no.	Model	Spatial effect C_s	Temporal effect λ_t
1	Simple mean	-	-
2	Random spatial only	ζ_s	-
3	Random temporal only	-	ξ_t
4	Random spatial and temporal	ζ_s	ξ_t
5	Random and fixed spatial; random temporal	$\log\left(\sum_j p_{s,j} \vartheta_j\right) \zeta_s$	ξ_t
6	Random and fixed temporal; random spatial	ζ_s	$\log(f_{t,k}) \xi_t$
7	Random and fixed temporal and spatial	$\log\left(\sum_j p_{s,j} \vartheta_j\right) \zeta_s$	$\log(f_{t,k}) \xi_t$

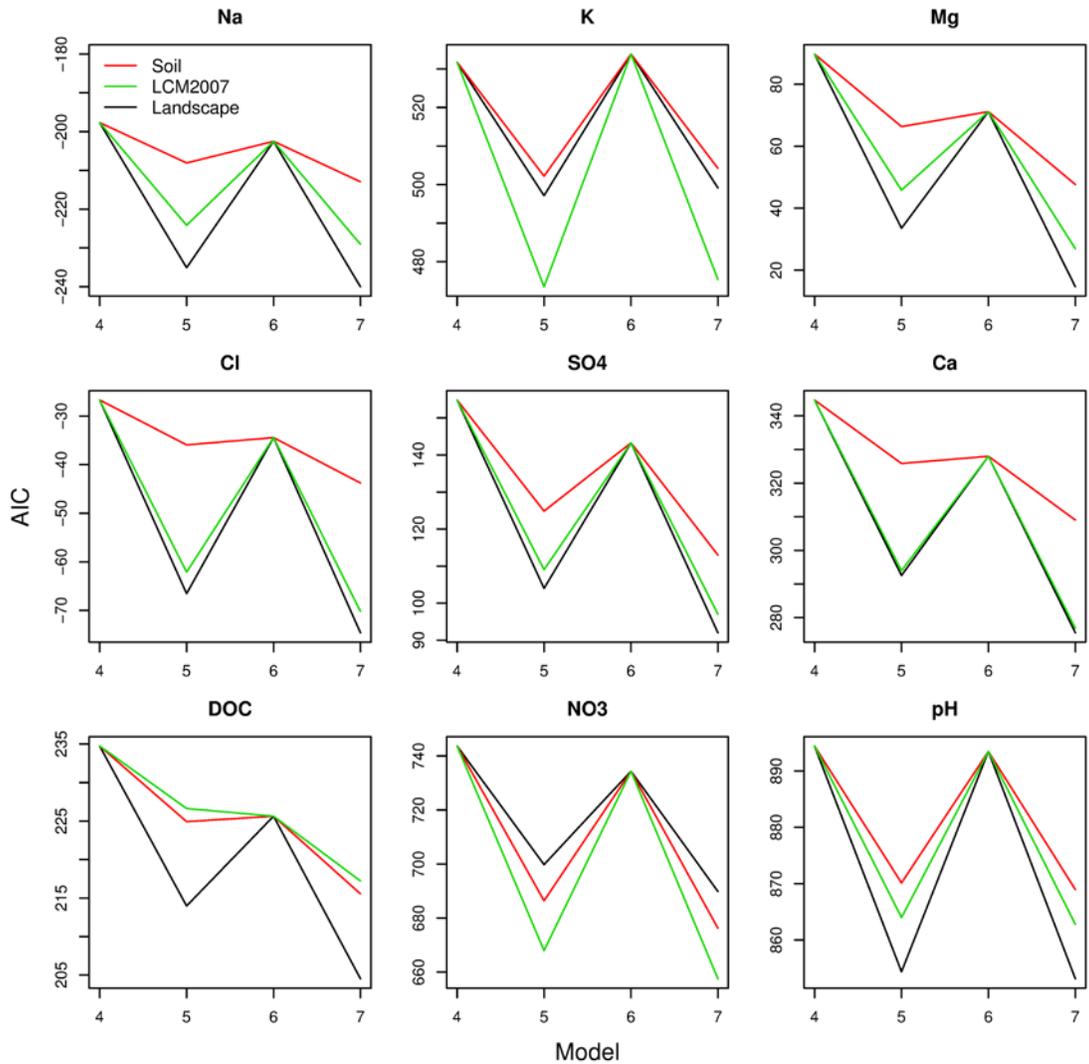
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1 **4 Results**

2 **4.1 Differences between models and choice of spatial covariates**

3 Model performance is first assessed using AIC (Akaike Information Criterion) values. The
4 lowest AICs for the 3 spatial classifications were given by model 7 for most water quality
5 variables, with the combined landscape classification in most cases giving the lowest
6 AIC. Exceptions were potassium, for which model 5 was preferred. For both nitrate and
7 potassium, the land cover classification gave lower AIC than the combined landscape.
8 This is thought due to greater resolution of agricultural land using LCM2007 land cover,
9 where the leaching of these two nutrients varies considerably within different crop and
10 grazing regimes. The apparent superiority of Model 5 for potassium is due to the lack of
11 a consistent seasonal pattern in measured concentrations. With the exception of DOC
12 and nitrate, the poorest model fit in terms of AIC was for the soil classification. For the
13 major cations Na, K, Mg, Ca fitting a random temporal effect (Model 3) gives an
14 estimated variance of the random effect of zero, indicating that there is no detected
15 seasonal variability between sites. With the exception of K, a seasonal effect is
16 detectable for these variables when explicitly parametrised (Models 6 and 7). DOC, NO₃
17 and pH show both seasonal effects and differences between classes within classification
18 schemes. Results are summarised graphically in Figure 2 for models 4 to 7. Note that

- 1 models 4 and 6 include no spatial component, so their AIC is the same for all choices of
- 2 spatial classification.



3

4

Figure 2. AIC values by determinand and model

5

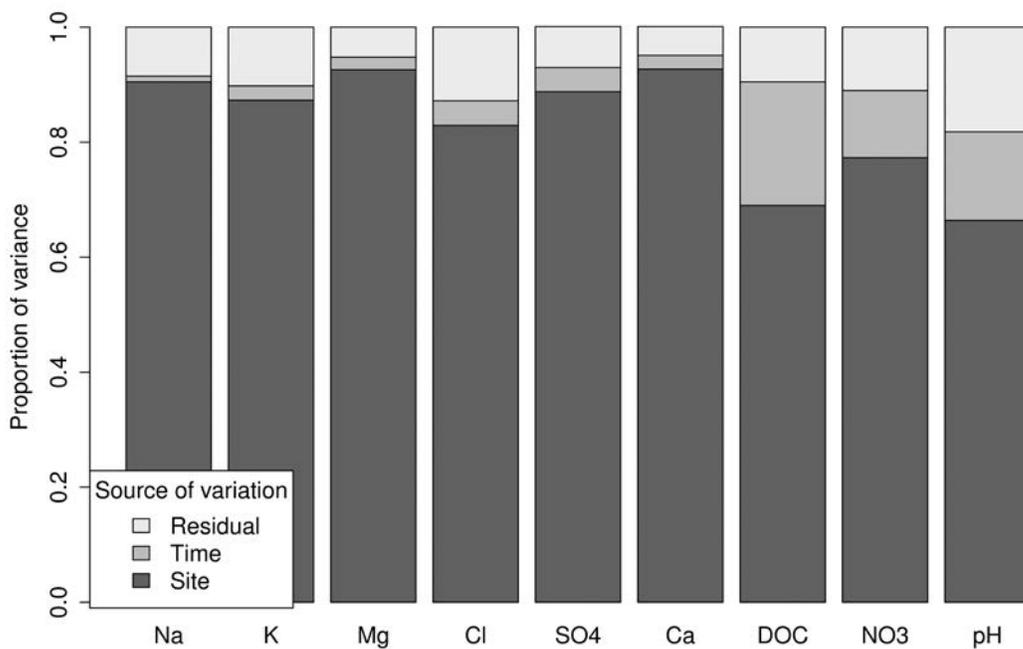
Model 4 includes spatial and temporal effects as random only. For models 5 to 7, some

6

of this variability is accounted for by fixed effects and some by random effects, but the

19

1 total spatial and temporal variability accounted for remains the same as for model 4.
2 The variance proportions associated with the application of model 4 to each water
3 quality variable are shown in Figure 3. The dominant source of variability is spatial
4 rather than temporal for all variables. The seasonal effect is greatest for DOC, nitrate
5 and pH.



6

7 **Figure 3. Proportions of variance accounted for by site, sampling time and**
8 **residual for Model 4**

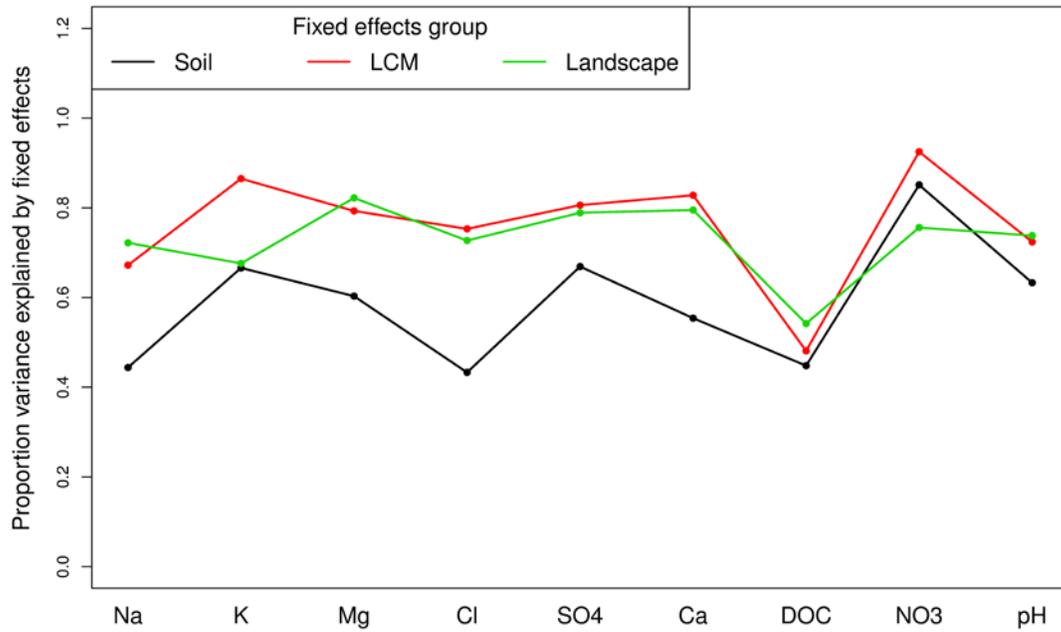
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20

1 **4.2 Differences between choice of spatial and temporal covariates**

2 Figures 4 and 5 show the spatial and temporal variability accounted for by the fixed
3 effects model, as a proportion of the variability accounted for by a random effect alone.
4 The figures suggest that the quality of fit between variables is quite consistent within
5 landscape classifications. Both the land cover and the landscape classification give
6 similarly high explanatory power. However, the landscape classification has fewer
7 parameters and therefore tends to have lower AIC values. Figure 5 shows the very high
8 proportion of the temporal variability which is accounted for by the seasonal model. The
9 data for these variables suggest that spatial class influences concentrations, but that
10 there is consistency between sampling times at individual sampling points. That is to
11 say, site effects within spatial classes are significant and persistent. Differences between
12 sampling occasions tend to be consistent regardless of site or spatial class.

13



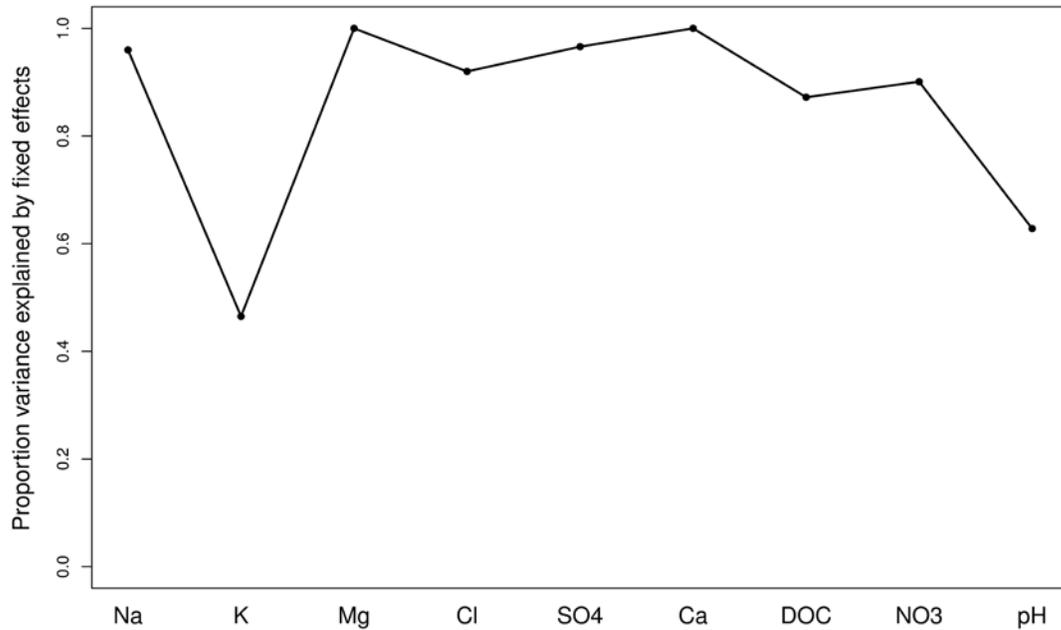
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2 **Figure 4. Performance of fixed effects groups in terms of site variance**

3

accounted for

4



1

2 **Figure 5. Performance of seasonal fixed effect in terms of time variance**

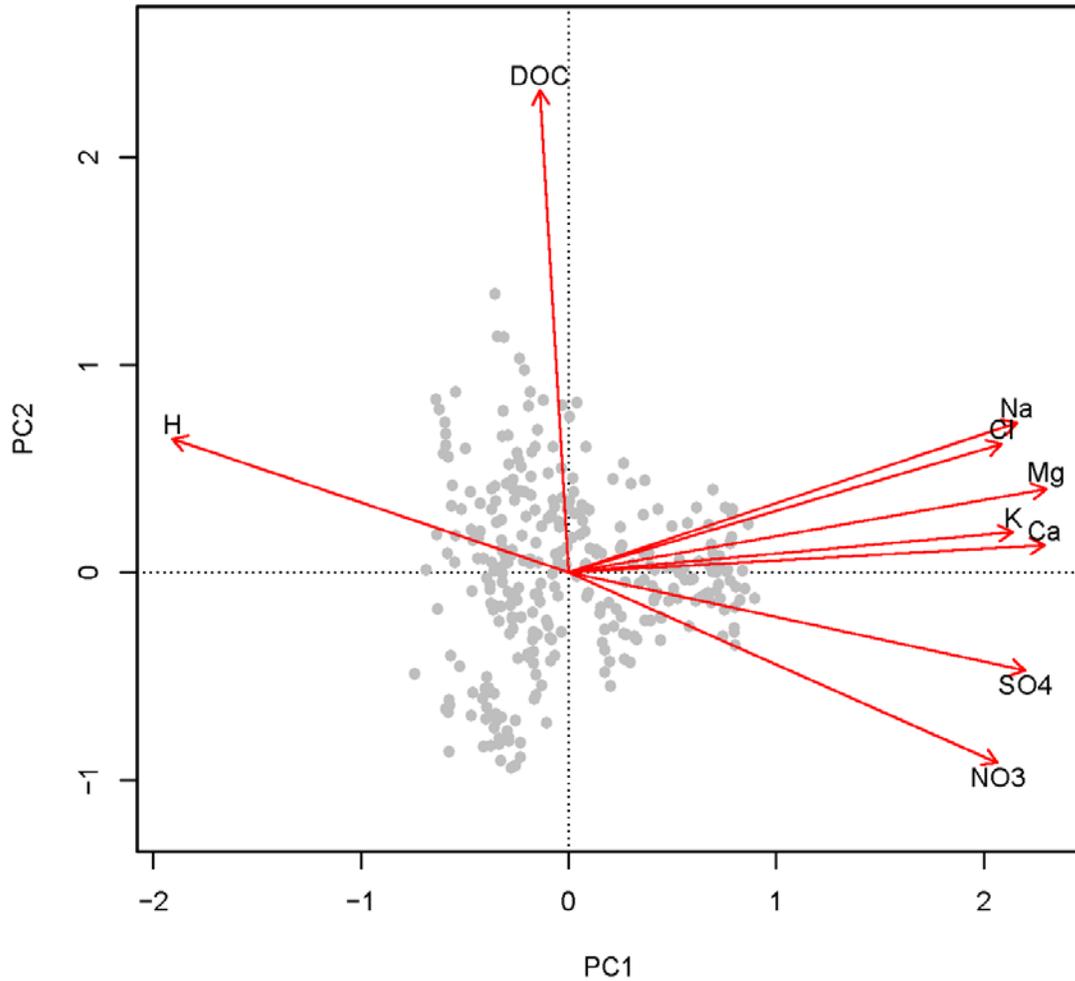
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accounted for

4 **4.3 Residual analysis**

5 Our analysis has been applied to individual water quality variables without accounting
 6 for any correlation structure between them. Even if the model gives an excellent fit for
 7 individual variables, the residual sequences for variables which are strongly related may
 8 still show strong correlation. First ignoring between-site correlation we consider the

- 1 residual between-variable relationships. Returning to the logged raw data, the first two
- 2 scaled principal components are plotted in Figure 6.

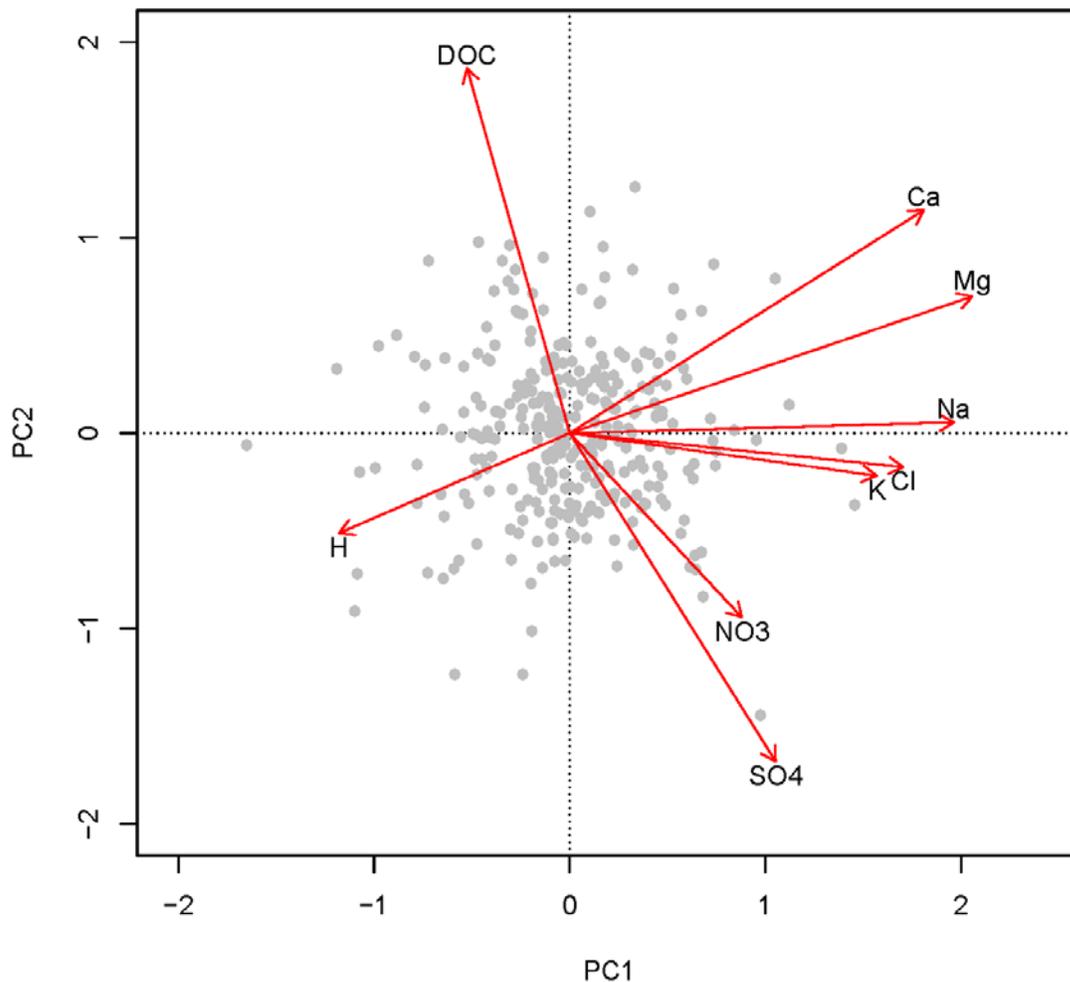


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4 **Figure 6. Scaled principal components plot for log(raw data)**

24

1 Figure 6 is strongly influenced by the agricultural component of water quality, which
2 tends to show high concentrations of all major ions apart from hydrogen and dissolved
3 organic carbon. Sulphate and nitrate are included amongst these major ions, and appear
4 to be inversely related to hydrogen ion concentration, despite being acid anions. These
5 two major anions are associated with the major cations rather than hydrogen in
6 satisfying a charge balance in stream water.



1

2

Figure 7. Scaled principal components plot for residuals

3

Figure 7 shows scaled principal components of the residual series. One of the main

4

effects of model fitting is to reduce the strong influence of agriculture. The remaining

5

variability shows the strongest inverse relationships between DOC and sulphate/nitrate

26

1 and between hydrogen and calcium/magnesium. Plots of DOC against sulphate residuals
2 for individual sites suggest that the relationship is strongest for those sites with high
3 concentrations of peat. The inverse relationship between DOC and sulphate in upland
4 waters has been noted and explained elsewhere²³. Our results show that the inverse
5 relationship holds at catchment scale. The inverse relationship with nitrate is believed to
6 be related to an unaccounted site by time interaction associated with seasonal
7 differences between these two variables. In peat subcatchments, high DOC is measured
8 during summer when nitrate concentrations are low due to plant uptake.

9

10 To examine clustering of residual behaviour by site, we first take principal components
11 of the (39 site x 8 field excursion) row x (9 determinand) column matrix of residuals.
12 Each principal component then represents an independent linear combination of
13 determinands having diminishing influence on the overall variance of the residuals. We
14 then reconfigure the principal components matrix to give a 72 x 39 matrix, each column
15 of which comprises 8 values over time x 9 principal components. We can then cluster
16 the sites using these data to investigate relationships between sites, associated with
17 interaction terms related to site and time. We use the `hclust` routine of R to generate
18 clusters.

19

27

1 Cluster analysis of the transformed residuals generates 7 natural clusters of sites. The
 2 interpretation of these clusters is that the chemistry of cluster members has similar site
 3 by time interactions unaccounted for by the model. A comparison of the locations of
 4 cluster members with the original dominant landscape classes suggests some
 5 correspondence (Table 7).

6

7 **Table 7. Relationship between residual clusters and landscape**
 8 **classes – allocation by site**

		Residual cluster						
		Farm 1	Farm 2	Margi -nal farm	Peat/ Gley	Mountain	Outlier 1	Outlier 2
Dominant Landscape	Farm	7	6	0	0	0	0	0
	Forest	2	0	2	0	2	0	0
	Gley	0	0	1	3	0	0	1
	Mountain	0	0	3	0	5	0	0
	Peat	0	0	1	3	1	2	0

9

10 Two clusters of residuals correspond approximately to the single original “farm”
 11 landscape classification. A comparison of the raw data suggests that this split is based
 12 on higher Na, Mg and SO₄, and lower DOC in one group. Of the remaining clusters, it is
 13 not possible to identify one associated with forest, though mountain and peat clusters

28

1 are identifiable, and an additional cluster associated with subcatchments at the upper
2 extreme of enclosed agriculture (marginal farm). Three outlier sites are identified, two
3 of which are adjacent subcatchments. Within clusters, there is some evidence that
4 nearby sites (on a 1km scale) have more similar chemistry than more distant sites within
5 the same cluster. Table 7 indicates that the simple spatio-temporal model fails to
6 capture some interactions between season and landscape class, particularly associated
7 with agricultural land use. This suggests that there would be benefit in modelling these
8 landscapes separately.

9

10 **5 Discussion**

11 The analysis confirms that most of the variability in water quality can be described by
12 the spatial component of the model. This is no doubt partly because of the wide range
13 of landscapes present in the catchment, and the absence of hydrological extremes from
14 the limited sequence of measurements made. Clearly longer time series of data would
15 provide greater opportunities for identifying temporal relationships between water
16 quality variables and covariates. For base cations there is either little seasonal
17 variability, or it is not consistent across landscapes. The greater seasonal variability in
18 pH, nitrate and DOC is interpretable in terms of known biogeochemical processes. DOC
19 concentrations are higher in summer when there is greater microbial activity, while
29

1 nitrate is higher in winter when there is less uptake. The pH is higher in summer when
2 flow is lower and weathering effects on stream water quality are greater.

3 The principal components analysis of residuals between variables shows how the
4 remaining interactions between variables splits into an inverse relationship between
5 DOC and sulphate and nitrate, and an inverse relationship between hydrogen ion
6 concentration and calcium and magnesium, with sodium, potassium and chloride
7 grouped together. These relationships are interpretable as due to differential
8 weathering in deeper soils, and an interchange between sulphate and DOC particularly
9 in peaty soils.

10 Cluster analysis of residuals by site suggests that many of the original landscape
11 classification units are still distinguishable. This is consistent with there being important
12 landscape by time interactions which are unaccounted for by the model. The lack of an
13 apparent forest cluster suggests the model has successfully accounted for any
14 distinguishing characteristics of this landscape. The subcatchments formerly classified as
15 forest are now grouped according to the pre-forest landscape. The cluster analysis also
16 suggests peat and gley residuals are not distinguishable. There are close field similarities
17 between these two landscapes; both are upland and poorly drained, with the gley
18 generally having less development of peat. Both are nutrient poor with high DOC
19 concentrations. The suggested new cluster of marginal farmland corresponds to a

1 recognised landscape in upland Wales named ffridd. This is a region characterised by
2 bracken, coarser grasses and scattered bushes between the enclosed fields and the
3 open hill. The two separate clusters for farmland suggest a need for a further split based
4 on DOC concentrations. Of the three outliers, two show unusually high sodium and
5 chloride concentrations. The sodium to chloride ratio is consistent with a sodium
6 chloride source in the subcatchment. A marine source would be indicated by raised
7 concentrations of magnesium, which are not observed. Since both subcatchments
8 receive drainage from a road which is salted in winter, we assume that road salt is the
9 source of the elevated sodium and chloride concentrations. The third outlier is believed
10 to be both misclassified and to include an unidentified point source. While the mapped
11 soil classification is gley, field evidence suggests the soil is largely peat. Elevated
12 concentrations of Ca and Mg at this site at low flows suggest the existence of a point or
13 geological source of base-rich weathering.

14

15 Water quality monitoring programmes generate large volumes of multivariate spatio-
16 temporal data. While these can be used to calibrate models, a relatively simple
17 statistical analysis of the data can aid in the interpretation of such data by identifying
18 common features between sites, between sampling occasions and between variables.
19 The framework used here is an example of how such a model can be used to identify

31

1 proportions of variability attributable to various sources; identify outlier sampling sites;
2 identify likely additional diffuse or point sources and identify features common to
3 particular landscapes.

4

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