

*Setting the baseline for shale gas -  
establishing effective sentinels for water  
quality impacts of unconventional  
hydrocarbon development*

Article

Accepted Version

Creative Commons: Attribution-Noncommercial-No Derivative Works 4.0

Worrall, F., Wade, A. ORCID: <https://orcid.org/0000-0002-5296-8350>, Davies, R. J. and Hart, A. (2019) Setting the baseline for shale gas - establishing effective sentinels for water quality impacts of unconventional hydrocarbon development. *Journal of Hydrology*, 571. pp. 516-527. ISSN 0022-1694 doi: <https://doi.org/10.1016/j.jhydrol.2019.01.075> Available at <https://centaur.reading.ac.uk/82258/>

It is advisable to refer to the publisher's version if you intend to cite from the work. See [Guidance on citing](#).

To link to this article DOI: <http://dx.doi.org/10.1016/j.jhydrol.2019.01.075>

Publisher: Elsevier

All outputs in CentAUR are protected by Intellectual Property Rights law, including copyright law. Copyright and IPR is retained by the creators or other copyright holders. Terms and conditions for use of this material are defined in the [End User Agreement](#).

[www.reading.ac.uk/centaur](http://www.reading.ac.uk/centaur)

**CentAUR**

Central Archive at the University of Reading

Reading's research outputs online

1 **SETTING THE BASELINE FOR SHALE GAS – ESTABLISHING EFFECTIVE SENTINELS FOR WATER**  
2 **QUALITY IMPACTS OF UNCONVENTIONAL HYDROCARBON DEVELOPMENT**

3

4 Fred Worrall<sup>1\*</sup>, Andrew J. Wade<sup>2</sup>, Richard J. Davies<sup>3</sup> and Alwyn Hart<sup>4</sup>

5 1. Department of Earth Sciences, Durham University, Science Labs, Durham DH1 3LE, UK.

6 2. Department of Geography and Environmental Science, University of Reading,  
7 Whiteknights, Reading, RG6 6AB, UK.

8 3. School of Natural and Environmental Sciences, Newcastle University, Newcastle, NE1  
9 7RU, UK.

10 4. Environment Agency, Research Assessment and Evaluation, Sapphire East,  
11 Streetsbrook Road, Solihull, B91 1QT, UK

12

13 **ABSTRACT**

14 There is a need for the development of effective baselines against which the water quality  
15 impacts of industry in general, and shale gas extraction specifically, can be assessed. The  
16 salinity, and hence the specific conductance, of fluids associated with shale gas extraction is  
17 typically many times higher than that of river water. The contrast between these two water types  
18 means that testing for salinity (specific conductance) could provide an ideal sentinel for  
19 detecting environmental impact of shale gas extraction. Here, Bayesian generalised linear  
20 modelling was used to predict specific conductance across English surface waters. The  
21 modelling used existing, spot-sampled data from 2005 to 2015 from 123 sites to assess

---

\* Corresponding author: [Fred.Worrall@durham.ac.uk](mailto:Fred.Worrall@durham.ac.uk); tel. no: +44 (0)191 334 2295; fax no: +44 (0)191 334 2301

22 whether this approach could predict variation for subsequent years or for a new site (data  
23 from 2002 to 2015). We show that the results were readily projected in to subsequent years  
24 for sites included in the initial analysis. The use of covariates (land-use, hydroclimatic and soil  
25 descriptors) did not prove useful in predicting specific conductance at further sites not  
26 previously included in the analysis. The extension of the approach to 6833 English river  
27 monitoring sites with 10 or more observations from more than one year over the period 2005  
28 to 2015 showed that it was possible to reproduce the seasonal variation in river water specific  
29 conductance. The approach taken here shows that it is possible to use low-frequency but  
30 widespread monitoring data to predict natural variation at monitoring sites to give a  
31 probabilistic assessment of whether or not a pollution incident has occurred and the seasonal  
32 variation, expressed as uncertainty bounds around the observations, at a specific site has  
33 been exceeded.

34

35 **Keywords:** shale gas; Bayesian statistics; generalised linear modelling

36

## 37 **1. Introduction**

38 To assess and indeed demonstrate an impact of any activity, it is necessary to show, within a  
39 reasonable level of certainty, that the industry has changed an environmental state over and  
40 above either that which was true without the activity present or beyond some accepted  
41 minimum level of harm. The need for demonstrating impact or indeed the ability to confirm  
42 the absence of an impact means that a baseline, or pre-intervention control, needs to be  
43 established for comparison with subsequent observations. The United Kingdom has a nascent  
44 shale gas industry and, given experience from the United States shale gas industry, one

45 concern is the impact upon water quality of ground and surface water (eg. Kahrilas et al.,  
46 2014; Vengosh et al., 2014). To reassure the public and ensure protection of the UK water  
47 resource it is important that techniques exist for the detection, identification and attribution  
48 of pollution for possible impacts of unconventional hydrocarbon resource development. A  
49 number of technologies are used for water quality monitoring and several have been  
50 proposed for rapid, even continuous monitoring to detect any the water quality impacts of  
51 shale gas developments (eg. CH<sub>4</sub> – Teasdale et al., 2014; Radium – Lagace et al., 2018; Barium  
52 and Sulphate - Niu et al., 2018; Strontium isotopes – Kohl et al., 2014). However, here we  
53 propose a sentinel approach in which a single key parameter can be used as a rapid and early  
54 warning. However, to be an effective and robust sentinel of change the parameter monitored  
55 should have four properties. Firstly, any water quality parameter should be a lead, and not a  
56 lag, indicator of change, i.e. it should occur at the beginning of any impact to provide early  
57 warning and so that mitigation could be rapidly deployed. Second, the parameter must be  
58 sufficiently sensitive having a high contrast with the normal or background activity and so that  
59 any change cannot be mistaken for background or natural variation. Thirdly, the parameter  
60 should show a high specificity for the activity of concern and not normally be associated with  
61 or mistaken for, other activities; i.e. in this case it should be specific to a shale gas industry  
62 and not to other industries for example, conventional hydrocarbon extraction. Finally, the  
63 measurement technology should be cheap and readily deployable so that it can be used  
64 widely used and provide a large sample size.

65 By far the greatest difference between the waters arising from a shale gas well pad  
66 (those waters could be the fracking fluid, the flowback water or the produced water), and  
67 surface waters is salinity or its associated determinands, eg. total dissolved solids (TDS) or  
68 electrical conductivity (in this study, specific conductance which is the electrical conductivity

69 of water standardised to a fixed temperature). The salinity of flowback water and deep  
70 formation water, as determined by TDS is often greater than seawater let alone greater than  
71 the salinity of river waters. Rowan et al. (2011) reviewed the total dissolved solids (TDS) of  
72 shale gas flowback water from US shale gas formations and showed that the flowback fluids  
73 were between two thirds and 10 times the seawater TDS (log TDS of seawater < 4.6) and much  
74 larger still than freshwater TDS (log TDS of freshwater ~ 2.6). Equally, the salinity of fracking  
75 fluids is far higher than that of surface waters and so salinity can also be used as a parameter  
76 for detecting fracking fluids as well as flowback water in surface and groundwater. For  
77 example, the only shale gas well so far fracked in the UK was at Preese Hall in Lancashire  
78 (Environment Agency, 2011, as cited in Almond et al., 2014). In this case, the flowback fluid  
79 salinity was between 3 and 5 times higher that of seawater; in contrast freshwater salinity is  
80 typically only 0.2% of seawater, i.e. only a 0.07% addition of such flowback water would cause  
81 a doubling of salinity in an English surface water. Yet rather than being expensive or requiring  
82 specialist equipment salinity, or specific conductance or TDS, are regularly and routinely  
83 measured in surface and ground waters and there are long term records of freshwater specific  
84 conductance measurements whereas there are no long term measurements across multiple  
85 sites of dissolved CH<sub>4</sub> (eg. Teasdale et al., 2013). These properties mean that salinity, and its  
86 allied measures specific conductance and TDS, make an ideal sentinel of change for detecting  
87 water quality impacts of a developing shale gas industry as it readily measured; shows a high  
88 contrast against a background of freshwater environments; is highly specific for shale gas  
89 development; and its high specificity and contrast with background mean that it could be a  
90 lead indicator of any incident. Furthermore, high salinity water from hydrocarbon exploitation  
91 has been observed to be a major cause of toxicity in exposed organisms (He et al., 2017;

92 Blewett et al., 2017) and in the Canadian province of Alberta in 2015 there were 113  
93 documented incidents of spills of flowback and produced water (Alessi et al., 2016).

94         However, although there are considerable numbers of measurements of specific  
95 conductance available, these measurements have not been collected for the purpose of  
96 creating a baseline against which impacts of a new industry can be judged. The Environment  
97 Agency have identified a range of statistical tools for use with monitoring data for specific  
98 sites and are currently trialling these at two sites in the north of England. However, there is  
99 no coherent and consistent means of handling existing data to make the assessment of any  
100 impact; a coherent method is needed for objectivity and transparency and therefore, this  
101 study proposes a new method to use existing specific conductance data to assess the impact  
102 of fracking on surface and groundwater quality based upon generalised linear modelling. This  
103 approach is entirely data driven and uses all the existing data without the need for the  
104 parameterisation required in physical models; it is flexible with respect to the distribution  
105 chosen to represent the specific conductance data; and can include existing factorial (eg.  
106 location) and covariate information (eg. river flow or land use). The model was developed  
107 within a Bayesian framework. The Bayesian framework means that the approach creates a  
108 structure whereby all information has some value, i.e. information from monitoring sites not  
109 in a catchment of interest help inform the distribution of data within the catchment of  
110 interest. Furthermore, new information can be directly added to update estimates; and all  
111 model outputs come with a probability which means that risk and uncertainty are considered  
112 at all stages. The approach creates a dynamic baseline for assessment of water quality effects  
113 of a shale gas industry. Such a baseline is dynamic in both time and space, i.e., generating a  
114 time series of expected results that would be different for different catchments. Estimated  
115 and predicted baseline results are both specific to a given location and develop over time in

116 response to natural changes meaning that it will improve with ongoing monitoring at shale  
117 gas or other infrastructure sites. Therefore, the approach of this study was to construct a  
118 dynamic baseline for surface water specific conductance using Bayesian generalised linear  
119 modelling such the outputs of the model give a probability of an unusual event, i.e. a pollution  
120 incident. The approach used the extensive, low frequency (generally monthly) monitoring of  
121 specific conductance across English surface waters as this gave access to many years of data  
122 (data between 2002 and 2015 were used in this study) from many sites and rivers while  
123 including catchments where shale gas development is planned.

124

## 125 **2. Methodology**

### 126 *2.1. Study sites*

127 The study initially used specific conductance data from the 123 Harmonised Monitoring  
128 Scheme sites across England (HMS - Bellamy and Wilkinson, 2001 – Fig. 1). HMS monitoring  
129 sites were selected for inclusion into the original monitoring programme if they were at the  
130 tidal limit of rivers with an average annual discharge greater than  $2 \text{ m}^3\text{s}^{-1}$ , or any tributaries  
131 with a mean annual discharge above  $2 \text{ m}^3\text{s}^{-1}$  (Bellamy and Wilkinson, 2001). The specific  
132 conductance of natural waters increases with temperature. This study used data for specific  
133 conductance – specific conductance is the electrical conductivity of the water sample at a set  
134 temperature, in the case of this study  $25 \text{ }^\circ\text{C}$ . Records of specific conductance for HMS sites  
135 can be paired with records of either instantaneous or average daily flow for these sites. For  
136 the purpose of this study records from 2002 to 2015 were considered. Although the main  
137 study period for this study was the decade 2003 – 2014 as records from 2002 were used to  
138 construct prior information for the statistical model and for 2015 there were incomplete flow



139 records available meaning that data for 2015 were used for testing and validating the models  
140 developed.

141 On the basis of the result from the HMS sites the study was extended to include all  
142 river sites in the England sampled between 2003 and 2015 where there were 10 or more  
143 samples with the measurements made in more than one year. The sampling constraints were  
144 included to ensure that interaction terms could be estimated and to limit the quantity of data  
145 to be analysed. Only measurements from routine river monitoring and not pollution incidents  
146 were considered.

147

## 148 *2.2. Bayesian generalised linear modelling*

149 The statistical modelling was based the Bayesian approach to generalised linear modelling.  
150 Each data point (specific conductance measurement -  $\kappa$ ) is assumed to be generated from a  
151 particular distribution in the exponential family of distributions, the mean,  $\mu$ , of the distribution  
152 depends on the independent variables,  $\mathbf{X}$ , through:

153

$$154 \quad E(\kappa) = \mu = g(\mathbf{X}\beta) \quad (i)$$

155

156 where  $E(\kappa)$  is the expected value of  $\kappa$  – the specific conductance;  $\mathbf{X}\beta$  is the linear predictor, a  
157 linear combination of unknown parameters  $\beta$ ; and  $g$  is the link function. The link function is  
158 often defined by the choice of distribution and in this case a gamma distribution was chosen.  
159 A priori, a gamma distribution has a number of advantages over other distributions, firstly, it  
160 readily approximates normal, log normal, exponential and Weibull distributions. This  
161 flexibility means that no adjustment for values close to the limit of detection is required.

162 Second, the gamma distribution is only defined for positive numbers and so there is no  
163 possibility that physically impossible negative values would be predicted as would be case  
164 with a normal distribution. Evidence from high frequency sampling has supported the use of  
165 a gamma distribution (Worrall et al., 2015). However, to test the appropriateness of the use  
166 of a gamma distribution the analysis of the HMS data was repeated using Weibull, normal,  
167 log normal and exponential distributions.

168 The form of the gamma distribution is defined as  $\Gamma(\alpha, \beta)$  where  $\alpha$  is commonly known  
169 as the shape factor and  $\beta$  is the rate factor, and:

170

171  $E(x) = \frac{\alpha}{\beta}$  (ii)

172  $\sigma^2 = \frac{\alpha}{\beta^2}$  (iii)

173

174 Linear predictors included factors and covariates. The factors considered in this study  
175 were Site, Month and Year. The Site factor is the difference between all the monitoring sites  
176 from the HMS for which specific conductance data were available – this factor had 123 levels  
177 one for each site. The Year factor had 12 levels for each year from 2003 to 2014. The Month  
178 factor had 12 levels one for each calendar month. The two-way interactions between factors  
179 were included.

180 The Bayesian approach was achieved by Markov Chain Monte Carlo (MCMC)  
181 simulation to estimate the posterior distribution of the specific conductance using WinBUGS  
182 version 14 (Lunn et al., 2013). The length of the MCMC chain was 30000 cycles after a 10000  
183 burn in cycles with samples saved every 10 cycles and with 1 chain. Model fit was tested using  
184 a number of approaches. First, that the 95% credible interval for any factor does not include

185 zero, this is henceforward referred to as being significantly different from zero at a probability  
186 of 95%. Second, that inclusion of the factor, interaction, or covariate caused the total model  
187 deviance to decrease, and third, that the inclusion of an additional factor, interaction or  
188 covariate decreased the deviance information criterion (DIC). It is generally true that inclusion  
189 of factors, interactions or covariates will decrease the total deviance of a model as the  
190 inclusion means greater degrees of freedom for fitting and so the DIC accounts for the  
191 inclusion of more fitting parameters against the additional fit of the model.

192 In the Bayesian analysis a weak uninformative Jeffrey prior distribution was used  
193 whereby the expected value was set as the mean of all specific conductance from the year  
194 2002 and the standard deviation was set as 100 times the coefficient of variation of the  
195 dataset, i.e. the prior was centred on the expected value of the data and was almost uniform  
196 in distribution. Given the size of the dataset and its spatial and temporal coverage it was  
197 deemed unnecessary or reasonable to develop a stronger prior distribution.

198

### 199 *2.3. Covariate information*

200 Covariate information was defined and developed as for Worrall et al. (2014). The CEH  
201 Wallingford digital terrain model (Morris and Flavin, 1994) was used to calculate the  
202 catchment area to each monitoring point. The CEH digital terrain model has a 50 m grid  
203 interval and a 0.1 m altitude interval. Secondly, the dominant soil-type of each 1 km<sup>2</sup> grid  
204 square classified into one of three types (mineral, organo-mineral or organic soils) based upon  
205 the system of Hodgson (1997) using nationally-available data (Smith et al., 2007). In this  
206 classification system, peat soils are classed as organic soils. Thirdly, Land use for each 1 km<sup>2</sup>  
207 of England was classified into three land uses: arable, grass and urban from the June  
208 Agricultural Census for 2004 (Defra, 2005). The June Agricultural Census also records the

209 number of cattle and sheep in each 1 km<sup>2</sup> and so as to provide a single measure for livestock,  
210 the equivalent sheep per hectare were calculated based on published nitrogen export values  
211 (Johnes et al., 1996) which gives a ratio of 3.1 sheep per cow. The soil and land-use  
212 characteristics for each 1 km<sup>2</sup> were summed across the catchment to each of the monitoring  
213 points and the relative proportion of different soil and land-use properties was determined.

214 For each of the HMS catchments for which specific conductance data were available,  
215 hydrological characteristics were available from the UK's National River Flow Archive  
216 ([www.ceh.ac.uk/data/nrfa/](http://www.ceh.ac.uk/data/nrfa/)). The characteristics used were: the base flow index (BFI), the  
217 average actual evaporation (AET) and the average annual rainfall (SAAR). The average annual  
218 total river flow for each catchment was taken as the difference between average annual  
219 rainfall and the average actual evaporation for each catchment.

220 The river flow at the time of sampling was available from the HMS records and was  
221 paired with the specific conductance data. Flow data, even instantaneous flow data, will be  
222 co-linear with catchment area, i.e. river flows are more likely to be larger for larger  
223 catchments and so as an alternative approach, flow records for each site were converted to  
224 the percentile flow for that site.

225 All covariate information was tested for normality using the Anderson-Darling test  
226 (Anderson and Darling, 1952) and log-transformed if required. To understand the importance  
227 of covariates a simple sensitivity analysis was conducted whereby a 10% increase in the  
228 average value of each significant covariate was imposed and the change in the specific  
229 conductance noted.

230

231 *2.4. Model application*

232 The model was considered in two stages. Firstly, to predict the specific conductance at an  
233 HMS site, i.e. a monitoring site included in the analysis. In this case the model was developed  
234 including the Site factor but without those covariates that are specific to each site and  
235 therefore would be co-linear with the Site factor. Secondly, the model was applied to predict  
236 conductance at a non-HMS site whose monitoring records were available but because the  
237 monitoring site is not part of the HMS it was not included in the first stage analysis, ie. a site  
238 not included in the original Site factor. This second analysis, therefore could not include the  
239 Site factor and so this second analysis used Year and Month as factors but considered the  
240 entire range of covariates defined for the new site.

241 On the basis of the results of the above a subsequent analysis included all the English  
242 sites with 10 or more data over at least two years in the period 2003 to 2015. In this third  
243 analysis the Site, Year and Month factors were used and their two-way interactions also  
244 included.

245 Given outputs and fit of the model were developed to consider the impact of shale  
246 gas developments and so for application and comparison sites were chosen within the one of  
247 the developing shale gas basins of the UK. Both chosen sites were selected to be the nearest  
248 available to the development sites in the Vale of Pickering (Fig. 1). The first site is an HMS  
249 monitoring site on the River Derwent at Loftsome Bridge and was included in the 123 sites in  
250 the Site factor of the initial analysis. The predicted specific conductance at this site was  
251 compared to observed conductance and then predicted for the year 2015, i.e. the  
252 subsequent. The second site of application was to a site not in the HMS monitoring network  
253 and therefore not included in the first analysis with the Site factor. The site chosen was on  
254 the Costa Beck (Fig. 1), chosen because it the monitoring site nearest to the proposed shale  
255 gas extraction site.

256 The purpose of this study was to create a dynamic baseline against which any influx of  
257 highly saline waters from fracking operations could be detected, therefore, the real question  
258 is what volume of fracking fluid could this approach detect at a given probability. There has  
259 only been one fracking operation conducted in the UK at Preese Hall in Lancashire (Fig. 1) and  
260 the conductivity of flowback fluid from the Preese Hall well varied from 133730 and 150614  
261  $\mu\text{S}/\text{cm}$  (Broderick et al., 2011).

262 No salinity or total dissolved solids (TDS) is reported within the available databases  
263 but standard relationships between salinity and specific conductance exist (Weyl, 1964)

264

$$265 \text{ Salinity} = 0.000004\kappa^2 + 0.53\kappa - 201 \quad (\text{iv})$$

266

267 Where Salinity is in  $\text{mg}/\text{l}$ . Equation (iv) was used to convert specific conductance to values,  
268 but it should be remembered that Equation (iv) was only defined for salinity  $> 1000 \text{ mg}/\text{l}$   
269 which is equivalent to a conductance of  $2200 \mu\text{S}/\text{cm}$ .

270

### 271 **3. Results**

#### 272 *3.1. Model development*

273 Between 2003 and 2014 there were 14495 measurements of specific conductance at 123 sites  
274 across England which could be paired with flow records and matched with catchment  
275 characteristics. Preliminary examination of the data showed one site should be removed  
276 (River Weaver at Frodsham) as it regularly had specific conductance over  $10000 \mu\text{S}/\text{cm}$  which  
277 was not seen at any other site – the high values could simply be due to the site being too close  
278 to the tidal limit. The distribution of all results shows a bimodal distribution with peaks at 200

279  $\mu\text{S}/\text{cm}$  and at  $550 \mu\text{S}/\text{cm}$ . Fitting single gamma distribution to all the data gives  $\Gamma(2.2, 282)$   
280 which gives an expected value of specific conductance,  $E(\kappa) = 633.5 \mu\text{S}/\text{cm}$ , with the 95%  
281 interval being 95 to  $1117 \mu\text{S}/\text{cm}$  and given a freshwater limit of  $1000 \text{ mg}/\text{l}$  salinity then 0.2%  
282 of conductivity measurements exceeded this limit. The fit of this single distribution represents  
283 a base case for the prediction of specific conductance at any one site against which it is  
284 possible to judge the benefit of more complex models.

285         The model using only known factors (Site, Month and Year) shows that all three factors  
286 were significant (where significance is as defined above that the 95% credible interval does  
287 not contain zero) and so to were the interactions of the three factors (Table 1). It should be  
288 noted that at this stage of modelling that the deviance for models fitted using normal, log  
289 normal, exponential and Weibull distributions each lead to tot total deviance  $> 200000$ , i.e. a  
290 gamma distribution provided the best-fit. The percentile flow, when included, was significant  
291 and showed that specific conductance decreased with increasing flow which is a dilution  
292 effect with new, more rainwater-like and lower conductivity water coming in with higher  
293 flows. The inclusion of the covariates decreased the credible interval and the deviance of the  
294 model, however, the DIC did not decrease suggesting that inclusion of this additional  
295 covariate may not be justified.

296         Given the inclusion of all the factors and the percentile flow covariate it is now  
297 reasonable to calculate and plot the expected value of the specific conductance ( $\kappa$ ) for each  
298 site (Fig. 2). The expected value so calculated allows for the differences in sampling times and  
299 conditions. The values do show regional differences with the lowest values in the north and  
300 the west of England and the highest values in the east and centre of the country. These  
301 regional differences may reflect underlying geology or climate differences.

302           When catchment covariates were included the Site factor was removed. The best-fit  
303 model is detailed in Table 2 and shows that a range of catchment characteristics are not  
304 significant in the prediction of conductivity and these are: BFI, AET, and the area of organic  
305 soils. Amongst the significant terms by far the most important was the change in flow and as  
306 flow increases the specific conductance of river water decreases and the term in flow is very  
307 close to, but still significantly different from,  $-Q^{1/4}$ . However, it should be noted that flow is co-  
308 linear with catchment area and rainfall, i.e. flow increases with both increased average rainfall  
309 and catchment area. River water specific conductance decreases with increasing catchment  
310 size and increasing average rainfall. The effect of flow and rainfall can be ascribed to dilution  
311 from rainfall, however, the impact of increasing catchment area is less straight forward as it  
312 might be expected that increased catchment size in the UK means that increased influence of  
313 groundwater rather than rainwater but this term may be co-linear with the river flow. The  
314 most important of the soil terms was the area of organo-mineral soils and while increasing  
315 the area of the mineral soils leads to decreased conductivity the presence of organo-mineral  
316 soils increases river water conductivity. As for land-use, the area of grassland decreased the  
317 conductivity, while increasing urban area increased conductivity; urban areas are sources of  
318 salt from roads and wastewater inputs can also increase salinity. The map in Fig. 2 cannot  
319 show the catchment area contributing to each site but the significant covariates could help  
320 explain the pattern of expected values observed in Fig. 2. Relatively low expected values of  $\kappa$   
321 are observed in the north and west of England where rainfall is higher and river flows might  
322 also be expected to be higher. The pattern with respect to land use and soil type is more  
323 complex as mineral soils dominate to the east and south and so to do arable and urban land  
324 use, i.e. competing effects of soil and land use effects on the specific conductance.



325           When no covariates were included, the Month factor did show a significant seasonal  
326 cycle although only three months are significantly different from zero – October, November  
327 and December - and all three led to lower specific conductance. When the covariates were  
328 included then four months were significantly different from zero; during April and July the  
329 specific conductance was significantly higher than the annual mean, while for November and  
330 December the specific conductance was significantly lower. The month factor appears to  
331 follow river flow rather than following road salt applications which would peak in the winter  
332 months.

333           The Year factor was significant but for most years there is no significant difference  
334 from zero and only 2007 and 2008 showing significantly lower values and 2014 showing  
335 significantly higher values. The difference between levels of the Year factor are clearly  
336 explained by including covariates which when included showed that 2004, 2005, 2007, 2008  
337 and 2012 all show significantly lower values and only 2013 showed significantly higher values.  
338 When Year was included as a covariate rather than a factor then there was a significant role  
339 for Year as a covariate with specific conductance increasing over the time period across all  
340 sites but only by  $0.01 \mu\text{S}/\text{cm}/\text{yr}$ , i.e. although significantly different from zero the trend is very  
341 small compared to other changes due to the other covariates, factors, or interactions.

342

### 343 *3.2. Model Application*

344 First, the approach was applied to the River Derwent at Loftsome Bridge, a site included in  
345 the dataset for analysis. There were 151 observations of specific conductance at Loftsome  
346 Bridge between 2002 and 2014, and the best-fit gamma distribution across all years and  
347 months gives  $E(\kappa) = 544 \mu\text{S}/\text{cm}$  and 95% credible interval of 405 to  $735 \mu\text{S}/\text{cm}$ . In comparison  
348 to the observations for 2014 at Loftsome Bridge (Fig. 3) shows that all but one observation is

349 within the credible interval suggesting that this one observation could be considered as an  
350 unusual observation. When prediction at the included site was performed, prediction for  
351 specific conductance ( $\kappa$ ) at Loftsome Bridge for 2015, i.e. for a site included in the analysis  
352 but for a year beyond that included in the data, then the observed data was within the  
353 predicted credible interval (Fig. 4) – note that there were only 9 measurements of  $\kappa$  at  
354 Loftsome Bridge in 2015. Of course, as an alternative approach to assessing the performance  
355 of the modelling the predicted values of the expected value for Loftsome Bridge in 2014  
356 between difference models with their varying inclusion of factors, interactions and to  
357 compare to prediction of the model for specific conductance (Table 3). The comparison of  
358 models shows that it is the inclusion of all three factors with their two-way interactions that  
359 brings the results to include those observed, but the further inclusion of covariates does not  
360 improve the model prediction.

361         Second, the model was applied to the site at Costa Beck, i.e. a site never included in  
362 the analysis. Over the period 2002 to 2015 there were 65 observations of specific  
363 conductance with an expected value of specific conductance,  $E(k) = 621 \mu\text{S}/\text{cm}$  and 95%  
364 credible interval of 568 to 684  $\mu\text{S}/\text{cm}$ . The results show that the model overpredicts  $\kappa$  (Fig.  
365 5), of the 20 observations at Costa Beck measured 11 were within the range predicted but of  
366 the remaining 9 observations all were lower than predicted. So whereas the model approach  
367 works well for modelling and prediction at sites which are included in the original dataset any  
368 extension to other, not previously considered, sites was not as effective. Therefore, the study  
369 extended the application to all monitoring sites in England.

370

371 *3.3. Model of all English monitoring sites*

372 In total there were 6833 river monitoring sites which met the criteria (Fig. 6) and plotting the  
 373 calculated expected values ( $E(\kappa)$ ) shows a tendency of increasing  $E(\kappa)$  from west to east across  
 374 England and perhaps also from north to south, but the largest values of  $E(\kappa)$  are not in the  
 375 south east corner of England but in more central areas of England and especially rivers  
 376 entering the Wash. This tendency across England perhaps follows gradients in climate from  
 377 the wetter western and more mountainous areas of the west and north towards drier,  
 378 lowland areas of eastern England. Furthermore, the tendency for higher  $E(\kappa)$  to eastern  
 379 England also seems to follow geology with more permeable and younger geology occurring  
 380 in east compared to the west. The map in Fig. 6 also shows that other potential sources of  
 381 high salinity water are not important. For example, it might be expected that urban conurbations  
 382 with their high density of major roads, which would be salted in winter, would represent  
 383 “hot spots” of specific conductance, but the major English conurbations are not visually  
 384 obvious in Fig. 6. Furthermore, areas of the UK with worked salt deposits (Cheshire, north-  
 385 west England) do not show up as “hot spots” of specific conductance in Fig. 6.

386 Application of the model from all English monitoring sites to the specific conductance  
 387 data for Costa Beck shows that rather than a systematic overprediction the results now show  
 388 only three observations were overpredicted but none were underpredicted (Fig. 7).

389

### 390 *3.4. Model sensitivity*

391 With respect to sensitivity then it is true for a volume of incoming high salinity water could  
 392 be detected if:

393

$$394 \frac{Q_f}{Q_r} = \frac{(\kappa_r^{max} - \kappa_r)}{(\kappa_f - \kappa_r^{max})} \approx \frac{(\kappa_r^{max} - \kappa_r)}{\kappa_f} \quad (iv)$$

395

396 Where:  $Q_x$  = the discharge due to the river (r) or from fracking (f) –  $m^3/day$ ;  $\kappa_x$  = specific  
397 conductance for the river (r) and for the fluid from the fracking operation (f) –  $\mu S/cm$ ; and  
398  $\kappa_r^{max}$  = the maximum specific conductance predicted for the river –  $\mu S/cm$ . Given that  $\kappa_f \gg \kappa_r^{max}$   
399 the denominator simplifies. For the Preese Hall well flowback fluid and the river  
400 discharge recorded at Loftsme Bridge in 2014 shows that in this case there was a 95%  
401 probability of being able to detect as little as 272  $m^3/day$  in February 2014 but this rose in  
402 wetter winter months to as high as 745  $m^3/day$  (Fig. 8). The volume of fracturing fluid used  
403 varies depending on the shale-play, the operator, well depth, the number of fracturing stages  
404 and the length of the wells (Nicot and Scanlon, 2012). The European Parliament summarised  
405 the US literature on the volume of water required per well and found the volume ranged from  
406 1500 to 45000  $m^3$  (Clancy et al., 2018), whilst Jiang et al. (2014) note that the average  
407 Marcellus well consumes 20000  $m^3$  (with a range from 6700 to 33000  $m^3$ ) of freshwater per  
408 well over its lifetime. The single well drilled in the UK at Preese Hall (Lancashire) required  
409 8400  $m^3$  of water. Taylor et al. (2013) when considering the scenarios for the development of  
410 a UK shale gas industry considered the development of a 10-well pad of 10 laterals which  
411 would require 136000  $m^3$  of water per well. Initially it is likely that the water required will be  
412 trucked to the site rather than piped, thus requiring between 2856 and 7890 trucks over a 20  
413 year period with truck movements concentrated in to the first two years at between 3.9 –  
414 10.8 truck movements per day during phases of site development and production. Given the  
415 volume that a single truck can transport (30  $m^3$ ) means that a site might need storage for  
416 approximately 600  $m^3$  of water, i.e. two days worth of truck movements at maximum  
417 predicted number of trucks. Therefore, the alternative question to ask is how small a river  
418 would need to be monitored in order to give a defined chance of detecting a leak or spill?

419 Applying Equation (iv) to calculate  $Q_r$  given the values of  $\kappa_r$  for Loftsome Bridge in 2014 and  
420 the range of values of  $\kappa_f$  observed for Preese Hall flowback fluid and a  $Q_f$  of between 30 and  
421  $600 \text{ m}^3/\text{day}$  means that for a 97.5% probability of detecting leaks with river flow of 0.6 and 1  
422  $\text{m}^3/\text{s}$  (Fig. 9). Given the catchment characteristics used as covariates in this study an average  
423 flow of  $1 \text{ m}^3/\text{s}$  would be true in the UK for catchments of less than  $9 \text{ km}^2$ .

424 The approach above assumes the water quality problem arises from an acute incident  
425 of spill or leakage to surface water and not a chronic seepage of contaminated fluids from  
426 depth to surface. Osborn et al. (2011) reported that contamination of shallow groundwater  
427 overlying the Marcellus shale resulted from poor well integrity in the shale gasfields, while  
428 Warner et al. (2014) reported no such contamination for shallow groundwater overlying the  
429 Fayetteville shale in Arkansas and Wilson et al. (2017) showed that contamination from the  
430 shale layers was extremely unlikely for the UK's Bowland shale.

431

#### 432 **4. Discussion**

433 This study has developed a consistent and coherent approach to the use of conductivity  
434 monitoring data. The Bayesian approach uses all available data to predict distributions at sites  
435 of interest. For determinands with defined environmental quality standards (eg. water  
436 framework directive – EC Directive, 2000) individual results are viewed relative to these  
437 standards while for other determinands (eg. specific conductance) even such comparisons  
438 may not occur as no legal standard exists. Furthermore, the review period for water quality  
439 monitoring is not always clear, under an operators permit the operator should review  
440 continuously, i.e. data reviewed each time new data is produced and the regulator informed  
441 if there is an issue. The regulator in the UK may be asked to report at anytime to the Secretary

442 of State at the highest government level, but how often this occurs is not clear. In the  
443 approach used here each datum can be viewed against a prediction that is based upon all  
444 available information and this can be viewed in a probabilistic framework, i.e. what is the  
445 probability that a new observation is exceptional and not what should be expected. In the  
446 case of used here measured specific conductance was judged against a predicted distribution  
447 as a means of testing whether an exceptional has or has not occurred. But equally we can use  
448 the predicted distribution to assess the probability that an environmental standard has been  
449 breached, for example in the case of specific conductance what would be the probability that  
450 the stream has a salinity  $> 1000$  mg/l ( $\kappa > 2270$   $\mu\text{S}/\text{cm}$ ).

451 In effect this approach has built up a method to improve assessment at any one site.  
452 At the simplest level one could examine the distribution of observed data at any site and  
453 compare the latest observation with that distribution. But that would not be a fair comparison  
454 because a local interannual variation might mean that comparing one observation with data  
455 from all years would be inappropriate, i.e. there is a interannual trend at site which values in  
456 the current year would tend to be lower than those in a previous year; thus a distribution for  
457 the given year would be better than comparing with data from all years. Equally there could  
458 be expected to be an intra-annual cycle in values and so even grouping observation by year  
459 would be misleading as some months would naturally be expected to have higher values than  
460 others. So including a measure of intra-annual cycle (eg. month) would improve the  
461 distribution for comparison. But of course it is unlikely that there will be sufficient  
462 observations to give such a reasonable distribution for any month for any year and any one  
463 site or indeed enough observations for any site and so it would be if information from other  
464 sites could be drawn open: this then is what this approach has achieved. By using all available  
465 information the approach here estimate a distribution of observations for every month, for

466 every year at each site. An analogous, non-Bayesian approach might be that of weighted  
467 regression analysis (Hirsch et al., 2010, 2015),

468 The approach could improve with the use of further covariates. The study has considered  
469 a range of covariates but in most cases covariates were surrogates for site information (eg.  
470 catchment area or land use). Within the HMS dataset it was possible to include river flow but  
471 this was not possible at all sites simply because in this dataset there are only 677 sites which  
472 are co-located with river flow gauging stations. However, as data has been chosen from water  
473 quality monitoring sites there would be other water quality parameters measured at these  
474 sites which may provide additional, covariate information. Specific conductance could be  
475 expected to co-vary with some cations and anions but equally the compositions of hydraulic  
476 fracking fluid may lead to use of other water quality parameters with a reasonably high degree  
477 of specificity for pollution incidents from unconventional hydrocarbon operations. Further,  
478 the analysis could become multi-dimensional, i.e. a further determinand could be to the  
479 analysis. Johnson et al. (2015) have suggested that sources of brine in areas of unconventional  
480 hydrocarbon extraction could be distinguished by use of Cl/Br ratio; Sr isotopes or the ratio  
481  $(Ba + Sr)/Mg$ . Indeed, Wilson and Van Briesen (2013) used Cl/Br ratios to detect shale gas  
482 fluids in surface waters of the Mononghela river in Pennsylvania. However, all three of these  
483 fail the criteria outlined in this study for a good being a good sentinel if for no other reason  
484 than they are not regularly measured.

485 The approach proposed here could be applied to the majority of data from water quality  
486 monitoring. Even in a focused network of monitoring sites such as may be used within the  
487 context of a developing shale gas industry there is no criteria for assessing whether pollution  
488 has or is occurring. For example, Krogulec and Sawicka (2015) discuss groundwater  
489 monitoring in Poland for the impacts of shale gas development but at no point suggest

490 numbers of monitoring points or frequency of sampling. Niu et al. (2018) proposed a change  
491 point analysis upon water quality time series in streams from areas of unconventional  
492 hydrocarbon exploitation. Loomer et al. (2018) used a higher frequency sampling of  
493 groundwater in area of Canada to determine the appropriate sampling frequency for  
494 monitoring unconventional hydrocarbon exploitation. Austen et al. (2017) suggest that  
495 unconventional hydrocarbon operations in the Fayetteville Shale had no impact on surface  
496 water quality on the basis of trends solely recorded after the unconventional hydrocarbon  
497 well pads had been installed and did not formally compare to any control. Down et al. (2015)  
498 have published a baseline geochemical assessment of the Triassic basin of North Carolina, a  
499 prospective shale gas basin at the time of the study, however the study provides no  
500 suggestion as to how these results might be used to assess any impact of a shale gas industry.  
501 Alternatively, Werner et al. (2013), Darrah et al. (2014) and Hildenbrand et al. (2015) have  
502 provide extensive water quality surveys of Arkansas' Fayetteville shale; Marcellus shale and  
503 the Barnett shale of Texas respectively, but in each case the surveys were after shale gas had  
504 been exploited in the area for many years. However, Hildenbrand et al. (2016) did consider  
505 the change in groundwater quality with the development of unconventional hydrocarbon  
506 resources in the Permian Basin of Texas and the sampling started before shale gas had been  
507 extracted in the majority of the area.

508 The approach developed and tested provides a number of clear advances over the current  
509 situation:

- 510 i) This is a systematic transparent approach to analysing data and provides a probability, with  
511 uncertainty, as to the nature of any observed data. Thus in turn the probability that any  
512 pollution has, or has not, happened can be assessed.



- 513 ii) The approach makes use of all available information and so the approach gains value from  
514 the whole monitoring network, i.e. maximum information is gained from the current, past  
515 and ongoing monitoring. This approach, therefore, gives good value for the money  
516 invested in environmental monitoring.
- 517 iii) All risk assessment is actual a probability statement and the tools here use Bayesian  
518 approaches so all results will be a probability and with an uncertainty.
- 519 iv) The Bayesian framework means that the tool automatically updates and so contributes to  
520 the development of a dynamic baseline in time and space.
- 521 v) The approach proposed can be used to assess information content and informational  
522 efficiency of the current monitoring network monitoring.

523

524 In regions of especial interest or concern with respect to shale gas extraction it would be  
525 easy for industry or regulators to place a water quality sonde in a local waterway to produce  
526 quasi continuous records of water quality and especially conductivity. Indeed, conductivity is  
527 the most commonly measured water quality parameter on such sondes (Halliday et al., 2012).  
528 Unlike for spot sampling in-situ water quality sondes are subject to damage and vandalism  
529 and must be maintained and calibrated in-situ. Son et al. (2015, 2018) have proposed the use  
530 of in-situ water quality sondes down borehole in areas of active hydraulic fracturing in  
531 northern Colorado to monitor for pollution events. The problem of interpretation would be  
532 equally true for high frequency as for low frequency data obtained from spot sampling, i.e. a  
533 coherent framework for assessing the probability that a pollution event had or was happening  
534 would still be required and an expectation of what baseline conditions represent natural  
535 would still need to be constructed. The United States Environmental Protection Agency have

536 developed a system for working with real-time, quasi-continuous data for the detection of  
537 pollution events (CANARY - USEPA 2012b). Quasi-continuous data could be readily  
538 incorporated into the approach presented here and analysis with the network of existing data  
539 providing informative prior information within the Bayesian framework proposed.  
540 Furthermore, such quasi-continuous records have been viewed by many authors as perfect  
541 information and so in comparison to results from less frequent spot sampling it would be  
542 possible to judge the value of perfect information relative to low frequency sampling (Worrall  
543 et al.,2013).

544

## 545 **5. Conclusions**

546 The study has developed a Bayesian generalised linear modelling approach to understanding  
547 specific conductance in English river waters. We could model specific conductance at river  
548 sites down to the natural variation at the monthly time step. The model could predict at sites  
549 included in the analysis but did not work well within the currently available covariates to  
550 predict at unknown sites. The model was extended to 6883 sites across England and this  
551 enabled our approach to predict a monthly distribution at any of these sites. The approach  
552 can be used to assess whether an observation is unusual against a regulatory standard or by  
553 predicting a distribution at each point of time at a point of interest the regulator could set  
554 their own criteria more appropriate for the local activity being monitored. The model shows  
555 that most rivers could readily absorb leaks of fracking fluids due to low volume of daily use  
556 on a single well pad. We propose that this approach could provide a coherent and consistent  
557 approach to analyzing water quality data while enhanced use of all available data.

558

559 **Acknowledgements**

560 The data for this study was all taken from the Environment Agency's WIMS database and all  
561 of which is available freely from the UK government. This research was carried out as part of  
562 the ReFINE research consortium led by Newcastle and Durham Universities. ReFINE has been  
563 funded by Ineos, Shell, Chevron, Total, GDF Suez, Centrica and NERC. We thank the ReFINE  
564 Independent Science Board for prioritising the research projects undertaken by ReFINE.

565

566 **References**

567 Alessi, D.S., Zlofarghari, A., Kletke, S., Gehman, J., Allen, D.M., Goss G.G., 2016. Comparative  
568 analysis of hydraulic fracturing wastewater practices in unconventional shale  
569 development: water sourcing, treatment and disposal practices. *Canadian Water  
570 Resources Journal* 42(2), 122-137.

571 Almond, S., Clancy, S.A., Davies, R.J., Worrall, F., 2014. The flux of radionuclides in flowback  
572 fluid from shale gas exploitation. *Environmental Science & Pollution Research* 21(21),  
573 12316-12324.

574 Anderson, T. W., Darling, D.A., 1952. Asymptotic theory of certain "goodness-of-fit" criteria  
575 based on stochastic processes. *Annals of Mathematical Statistics* 23, 193–212.

576 Austin, B.J., Scott, E., Massey, L., Evans-White, M.A., Entekin, S., Haggard, B.E., 2017.  
577 Unconventional natural gas development did not result in detectable changes in water  
578 chemistry (within the South Fork Little Red River). *Environmental Monitoring and  
579 Assessment* 189(5), Art. No. 209

580 Bellamy, D., Wilkinson, P., 2001. OSPAR 98/3: an environmental turning point or a flawed  
581 decision? *Marine Pollution Bulletin* 49, 87-90.

582 Blewett, T.A., Delompre, P.L.M., He, Y.H., Folkerts, E.J., Flynn, S.L., Alessi, D.S., Goss, G.G.,  
583 2017. Sublethal and Reproductive Effects of Acute and Chronic Exposure to Flowback and  
584 Produced Water from Hydraulic Fracturing on the Water Flea *Daphnia magna*.  
585 *Environmental Science & Technology* 51(5), 3032-3039.

586 Broderick, J., Wood, R., Gilbert, P., Sharmina, M., Anderson, K., Footitt, A., Glynn, S., Nicholls,  
587 F., 2011. Shale gas: an updated assessment of environmental and climate change  
588 impacts. A report commissioned by The Co-operative and undertaken by researchers at  
589 the Tyndall Centre, University of Manchester.

590 Clancy, S.A., Worrall, F., Davies, R.J., Gluyas, J.G., 2018. The potential for spills and leaks of  
591 contaminated liquids from shale gas developments. *Science of the Total Environment*  
592 626, 1463 – 1473.

593 Darrah, T.H., Vengosh, A., Jackson, R.B., Warner, N.R., Poreda, R.J., 2014. Noble gases identify the  
594 mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus  
595 and Barnett Shales. *Proceedings of the National Academy of Sciences of the United States of*  
596 *America* 111(39), 14076-14081

597 DEFRA, 2005. *Agriculture in the United Kingdom - 2004*. Department of Environment, Food  
598 and Rural Affairs, HMSO, London, 2005.

599 Down, A., Schreglmann, K., Plata, D.L., Elsner, M., Warner, N.R., Vengosh, A., Moore, K.,  
600 Coleman, D., Jackson, R.B., 2015. Pre-drilling background groundwater quality in the  
601 Deep River Triassic Basin of central North Carolina, USA. *Applied Geochemistry* 60, 3-13.

602 EC Directive, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23  
603 October 2000 establishing a framework for Community action in the field of water  
604 policy. *Official Journal L 327* , 22/12/2000 P. 0001 – 0073

605 Environment Agency, 2011. Shale Gas. North West – Monitoring of Flow back water.  
606 [webarchive.nationalarchives.gov.uk/20140328145127](http://webarchive.nationalarchives.gov.uk/20140328145127)

607 Halliday, S. J., Wade, A.J., Skeffington, R.A., Neal, C., Reynolds, B., Rowland, P., Neal, M.,  
608 Norris, D., 2012. An analysis of long-term trends, seasonality and short-term dynamics in  
609 water quality data from Plynlimon, Wales. *Science of the Total Environment*, 434, 186-  
610 200.

611 He, Y., Flynn, S.L., Folkerts, E.J., Zhang, Y., Ruan, D.L., Alessi, D.S., Martin, J.W., Goss, G.G.,  
612 2017. Chemical and toxicological characterizations of hydraulic fracturing flowback and  
613 produced water. *Water Research* 114, 78-87.

614 Hildenbrand, Z.L., Carlton, D.D., Fontenot, B.E., Meik, J.M., Walton, J.L., Taylor, J.T., Thacker,  
615 J.B., Korlie, S., Shelor, C.P., Henderson, D., Kadjo, A.F., Roelke, C.E., Hudak, P.F., Burton,  
616 T., Rifai, H.S., Schug, K.A., 2015. A Comprehensive Analysis of Groundwater Quality in The  
617 Barnett Shale Region. *Environmental Science & Technology* 49(13), 8254-8262.

618 Hildenbrand, Z.L., Carlton, D.D., Fontenot, B.E., Meik, J.M., Walton, J.L., Thacker, J.B., Korlie, S., Shelor,  
619 C.P., Kadjo, A.F., Clark, A., Usenko, S., Hamilton, J.S., Mach, P.M., Verbeck, G.F., Hudak, P.,  
620 Schug, K.A., 2016. Temporal variation in groundwater quality in the Permian Basin of Texas,  
621 a region of increasing unconventional oil and gas development *Science of the Total*  
622 *Environment* 562, 906-913.

623 Hirsch, R.M., Moyer, D.L., Archfield, S.A., 2010. Weighted regression on time, discharge and  
624 season (WRTDS), with application to Chesapeake Bay river inputs. *Journal of the*  
625 *American Water Resources Association* 46(5), 857-880

626 Hirsch, R.M., Archfield, S.A., De Cicco, L.A., 2015. A bootstrap method for estimating  
627 uncertainty of water quality trends. *Environmental Modelling & Software* 73, 148-166.

628 Hodgson, J.M., 1997. Soil Survey Field Handbook: Describing and Sampling Soil Profiles. Soil  
629 survey Technical Monograph No. 5. Soil Survey and Land Research Centre, Silsoe.  
630 England.

631 Jiang, M., Hendrickson, C.T., VanBriesen, J.M., 2014. Life cycle water consumption and  
632 wastewater generation impacts of a Marcellus shale gas well. Environmental Science &  
633 Technology 48(4), 1911-1920.

634 Johnes, P., Moss, B., Phillips, G., 1996. The determination of total nitrogen and total  
635 phosphorus concentrations in freshwaters from land use, stock headage and population  
636 data: testing of a model for use in conservation and water quality management.  
637 Freshwater Biology 36, 451-473.

638 Johnson, J.D., Graney, J.R., Capo, R.C., Stewart, B.W., 2015. Identification and quantification  
639 of regional brine and road salt sources in watersheds along the New York/Pennsylvania  
640 border, USA. Applied Geochemistry 60, 37-50.

641 Kahrilas, G. A., Blotevogel, J., Stewart, P.S., Borch, T., 2014. Biocides in hydraulic fracturing  
642 fluids: A critical review of their usage, mobility, degradation, and toxicity. Environmental  
643 Science & Technology 49(1), 16-32.

644 Kohl, C.A.K., Capo, R.C., Stewart, B.W., Wall, A.J., Schroeder, K.T., Hammack, R.W., Guthrie,  
645 G.D., 2014. Strontium Isotopes Test Long-Term Zonal Isolation of Injected and Marcellus  
646 Formation Water after Hydraulic Fracturing. Environmental Science & Technology 48(16),  
647 9867-9873.

648 Krogulec, E., Sawicka, K., 2015. Groundwater protection in shale gas exploration areas - a  
649 Polish perspective. Episodes 38(1), 9-20.

650 Lagace, F., Foucher, D., Surette, C., Clarisse, O., 2018. Radium geochemical monitoring in well  
651 waters at regional and local scales: an environmental impact indicator-based approach.  
652 *Chemosphere* 205, 627-634.

653 Loomer, D.B., MacQuarrie, K.T.B., Al, T.A., Bragdon, I.K., Loomer, H.A., 2018. Temporal  
654 variability of dissolved methane and inorganic water chemistry in private well water in  
655 New Brunswick, Canada. *Applied Geochemistry* 94, 53-66.

656 Lunn, D., Jackson, C., Best, N., Thomas, A., Spiegelhalter, D., 2013. The BUGS book – A practical  
657 introduction to Bayesian analysis. CRC Press, Abingdon, UK.

658 Morris, D.G., Flavin, R.W., 1994. Sub-set of UK 50m by 50m hydrological digital terrain model  
659 grids. NERC, Institute of Hydrology, Wallingford.

660 Nicot, J.P., Scanlon, B.R., 2012. Water use for shale-gas production in Texas, US.  
661 *Environmental Science & Technology* 46(6), 3580-3586.

662 Niu, X.Z., Wendt, A., Li, Z.H., Agarwal, A., Xue, L.Z., Gonzales, M., Brantley, S.L., 2018.  
663 Detecting the effects of coal mining, acid rain, and natural gas extraction in Appalachian  
664 basin streams in Pennsylvania (USA) through analysis of barium and sulfate  
665 concentrations. *Environmental Geochemistry and Health* 40(2), 865-885.

666 Osborn, S.G., Vengosh, A., Warner, N.R., Jackson, R.B., 2011. Methane contamination of  
667 drinking water accompanying gas-well drilling and hydraulic fracturing. *Proceedings of  
668 the National Academy of Sciences of the United States of America* 108(20), 8172-8176

669 Rowan, E.L., et al. (2011). Radium Content of Oil- and Gas-Field Produced Waters in the  
670 Northern Appalachian Basin (USA): Summary and Discussion of Data. *Scientific  
671 Investigations Report*, US Geological Survey 2011-5135.

672 Son, J.H., Carlson, K.H., 2015. Real-time surrogate analysis for potential oil and gas  
673 contamination of drinking water resources. *Applied Water Science* 5(3), 283-289.

674 Son, J.H., Hanif, A., Dhanasekar, A., Carlson, K.H., 2018. Colorado Water Watch: real-time  
675 groundwater monitoring for possible contamination from oil and gas activities.  
676 Environmental Monitoring and Assessment 190(3), Art. No 138

677 Taylor, C., Lewis, D., Byles, D., 2013. Institute of Directors (Infrastructure for Business) report:  
678 Getting shale gas working. Institute of Director, London, UK.

679 Teasdale, C.J., Hall, J.A., Martin, J.P., Manning, D.A.C., 2014. Ground Gas Monitoring:  
680 Implications for Hydraulic Fracturing and CO<sub>2</sub> Storage. Environmental Science &  
681 Technology 48(23), 13610-13616.

682 United States Environmental Protection Agency, 2012. CANARY user's manual version 4.3.2.  
683 EPA 600/R-08/040B.

684 Vengosh, A., Jackson, R. B., Warner, N., Darrah, T. H., Kondash, A., 2014. A critical review of  
685 the risks to water resources from unconventional shale gas development and hydraulic  
686 fracturing in the United States. Environmental Science & Technology 48(15), 8334-8348.

687 Warner, N.R., Kresse, T.M., Hays, P.D., Down, A., Karr, J.D., Jackson, R.B., Vengosh, A., 2013.  
688 Geochemical and isotopic variations in shallow groundwater in areas of the Fayetteville  
689 Shale development, north-central Arkansas. Applied Geochemistry 35, 207-220.

690 Weyl, P.K., 1964. On the change in electrical conductance of seawater with temperature.  
691 Limnology & Oceanography 9(1), 75–78.

692 Wilson, J.M., Van Briesen, J.M., 2013. Source Water Changes and Energy Extraction Activities  
693 in the Monongahela River, 2009-2012. Environmental Science & Technology 47(21),  
694 12575-12582.

695 Wilson, M.P., Worrall, F., Davies, R.J., Hart, A., 2017. Shallow Aquifer Vulnerability From  
696 Subsurface Fluid Injection at a Proposed Shale Gas Hydraulic Fracturing Site. Water  
697 Resources Research 53(11), 9922-9940



698 Worrall, F., Howden, N.J.K., Burt, T.P., 2013. Assessment of sample frequency bias and  
699 precision in fluvial flux calculations – an improved low bias estimation method. Journal  
700 of Hydrology 503, 101-110.

701 Worrall, F., Burt, T.P., Howden, N.J.K., 2014. The fluvial flux of particulate organic matter from  
702 the UK: Quantifying in-stream losses and carbon sinks. Journal of Hydrology 519, 611-  
703 625.

704 Worrall, F., Howden, N.J.K., Burt, T.P., 2015. Understanding the diurnal cycle in fluvial  
705 dissolved organic carbon - The interplay of in-stream residence time, day length and  
706 organic matter turnover. Journal of Hydrology 523, 830-838.

707

708 Fig. 1. Location of the Harmonised monitoring scheme (HMS) sampling sites used in this  
709 study including the chosen sites within The Vale of Pickering (River Derwent at Loftsome  
710 Bridge; and Costa Beck) as well as the site at Preese Hall.

711

712 Fig. 2. Maps of: a) the expected mean ( $E(\kappa)$ ); b) the 97.5<sup>th</sup> percentile; and c) the 2.5<sup>th</sup>  
713 percentile of the specific conductance ( $\kappa$ ).

714

715 Fig. 3. The comparison of the predicted and observed specific conductance for Loftsome  
716 Bridge (River Derwent) in 2014.

717

718 Fig. 4. The comparison of the predicted and observed specific conductance for Loftsome  
719 Bridge (River Derwent) in 2015.

720

721 Fig. 5. The comparison of the predicted and observed specific conductance for Costa Beck  
722 based upon model from HMS data.

723

724 Fig. 6. Maps of: a) All English stream and river water sites with sufficient data to be included  
725 in this study; and b) the expected mean ( $E(\kappa)$ ).

726

727 Fig. 7. The comparison of the predicted and observed specific conductance for Costa Beck  
728 using the model based upon data from all English monitoring sites.

729

730 Fig. 8. The detectable volume of fracking discharge (a leak of any of the possible high salinity  
731 fluid from the well pad) predicted at Loftsome Bridge.

732

733 Fig. 9. The flow required to detect a typical volume stored within a single well pad.

734 Table 1. The details of model fit with increasing introduction of factors, their interactions and  
 735 inclusion of Year and percentile flow (%flow) as covariates.

| Factors  |       | Interactions |   | Covariates |            | Deviance | DIC   |
|----------|-------|--------------|---|------------|------------|----------|-------|
| Site     | Month | Year         |   | Year       | Log(%flow) |          |       |
| Observed |       |              |   |            |            |          |       |
| x        |       |              |   |            |            | 17772    | 17773 |
| x        | x     |              |   |            |            | 17690    | 17770 |
| x        | x     |              | x |            |            | 17590    | 17773 |
| x        | x     | x            |   |            |            | 17650    | 17470 |
| x        | x     | x            | x |            |            | 17373    | 17630 |
| x        | x     | x            | x |            | x          | 17270    | 17530 |
| x        | x     |              | x | x          | x          | 17200    | 15500 |

736

737 Table 2. The coefficient of those covariates found to be significant and the sensitivity of the  
 738 prediction of specific conductance to a 10% increase in the average value.

| Covariate            | Mean     | 2.5%     | 97.5%    | Average                | Sensitivity ( $\mu\text{S}/\text{cm}$ ) |
|----------------------|----------|----------|----------|------------------------|---|
| LogQ                 | -0.23    | -0.24    | -0.22    | 4.46 m <sup>3</sup> /s | -14.4                                   |
| Area                 | -0.00016 | -0.0002  | -0.00011 | 146 km <sup>2</sup>    | -0.95                                   |
| Aver. rainfall       | -0.0016  | 0.0018   | -0.0014  | 1369 mm                | -8.7                                    |
| Mineral soil         | -0.00016 | 0.0022   | 0.00009  | 28.2 km <sup>2</sup>   | -0.18                                   |
| Organo-mineral soils | 0.0007   | 0.0046   | 0.00088  | 95.4 km <sup>2</sup>   | 2.95                                    |
| Arable               | 0.00029  | 0.00012  | 0.00047  | 10.4 km <sup>2</sup>   | 0.12                                    |
| Grass                | -0.0003  | -0.00047 | -0.00014 | 78.5 km <sup>2</sup>   | -1.0                                    |
| Urban                | 0.026    | 0.0022   | 0.003    | 5.5 km <sup>2</sup>    | 0.6                                     |
| Constant             | 6.02     | 5.97     | 6.07     |                        |   |

739

740

741 Table 3. The application of the derived models to predict the distribution of specific  
 742 conductance at Loftsome Bridge, River, Derwent, 2015.

| Factors  |       | Interactions |   | Covariates |            | Predicted |      |       |
|----------|-------|--------------|---|------------|------------|-----------|------|-------|
| Site     | Month | Year         |   | Year       | Log(%flow) | Mean      | 2.5% | 97.5% |
| x        |       |              |   |            |            | 633       | 95   | 1117  |
| x        | x     |              |   |            |            | 543       | 526  | 568   |
| x        | x     |              | x |            |            | 546       | 523  | 571   |
| x        | x     |              |   |            |            | 545       | 474  | 629   |
| x        | x     | x            |   |            |            | 535       | 510  | 562   |
| x        | x     | x            | x |            |            | 616       | 508  | 744   |
| x        | x     | x            | x |            | x          | 617       | 513  | 739   |
| x        | x     | x            | x | x          | x          | 612       | 510  | 732   |
| Observed |       |              |   |            |            | 606       | 571  | 643   |

743

744

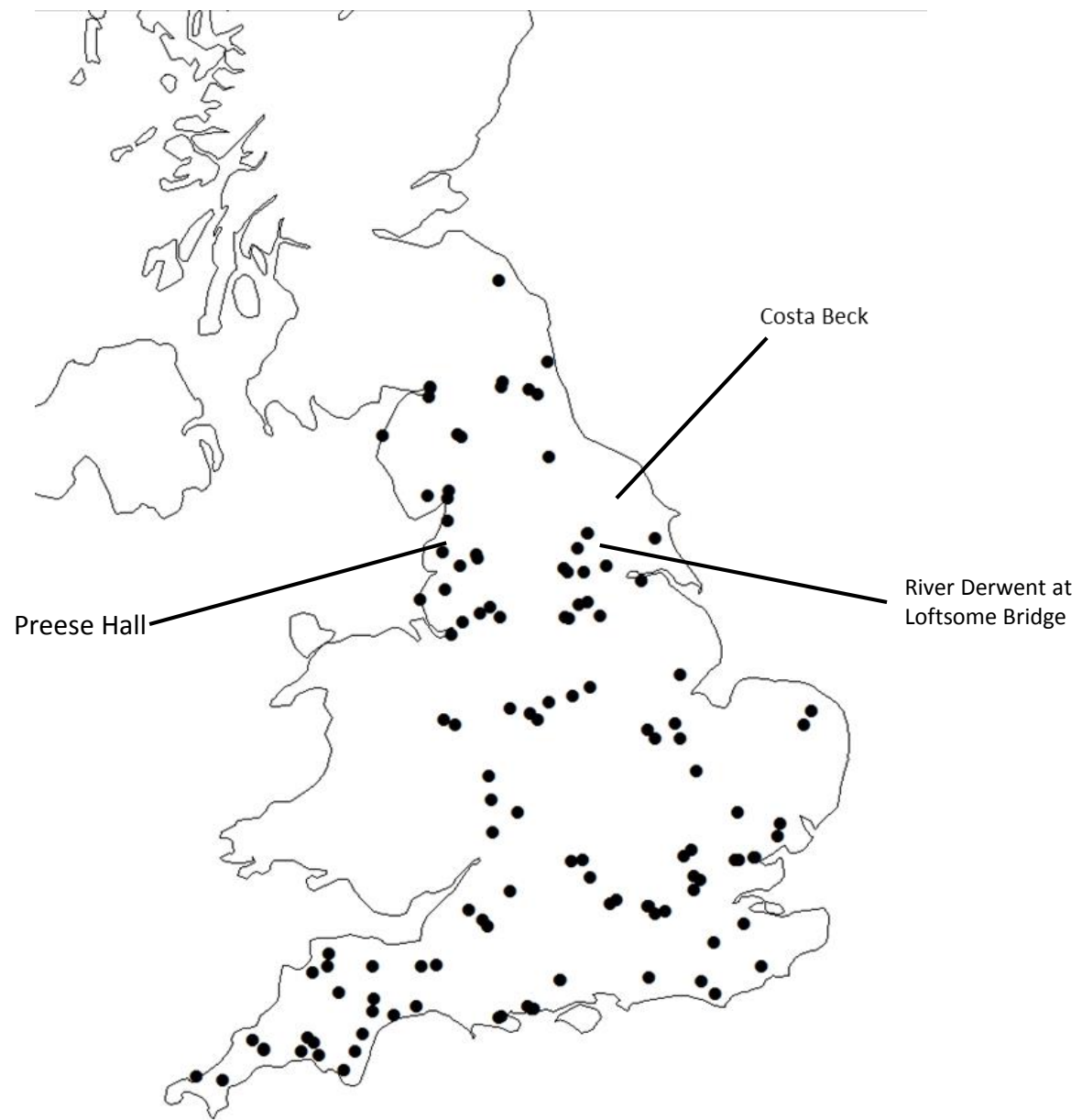


Fig. 1

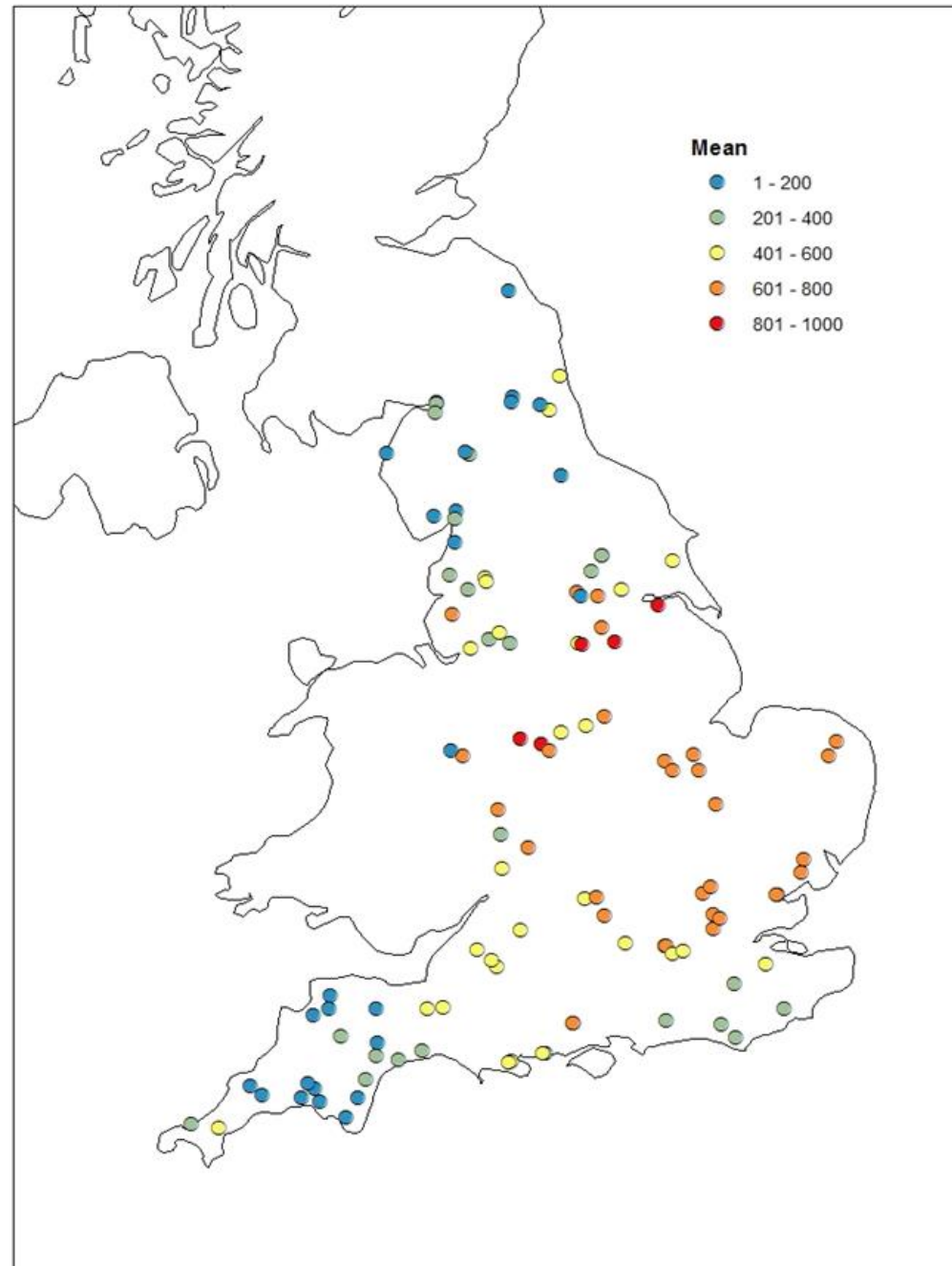


Fig.2

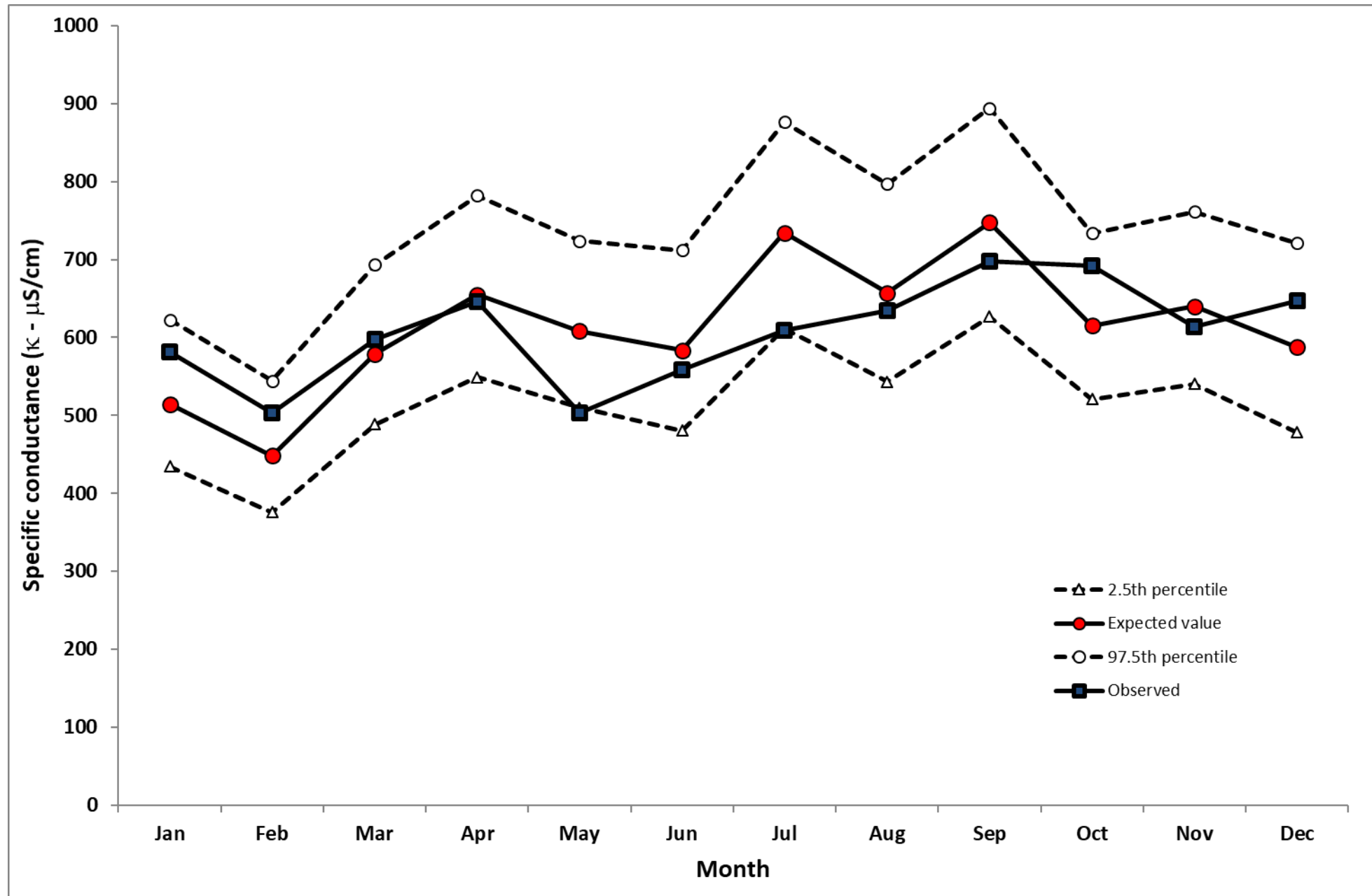


Fig.3

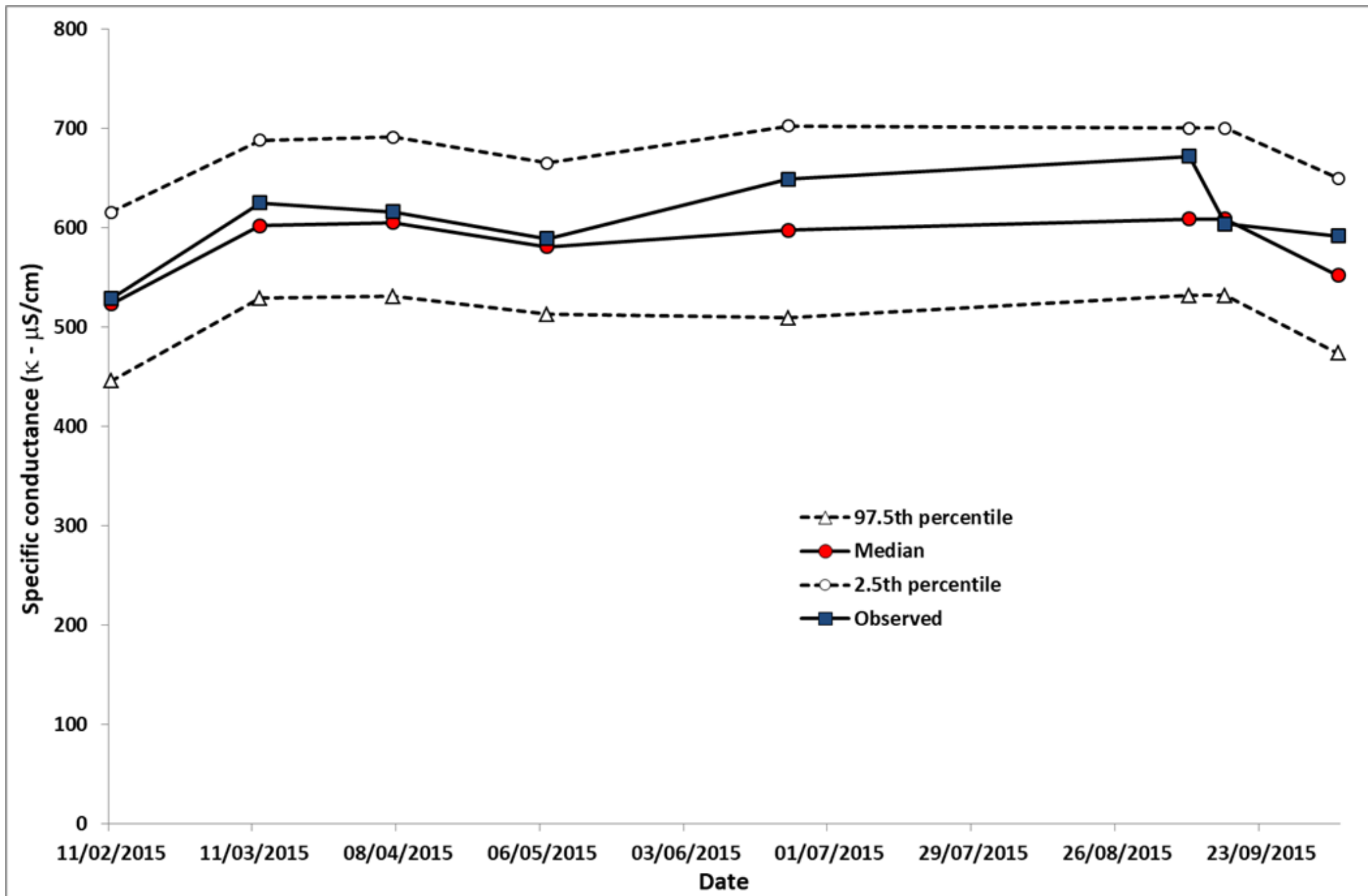


Fig.4



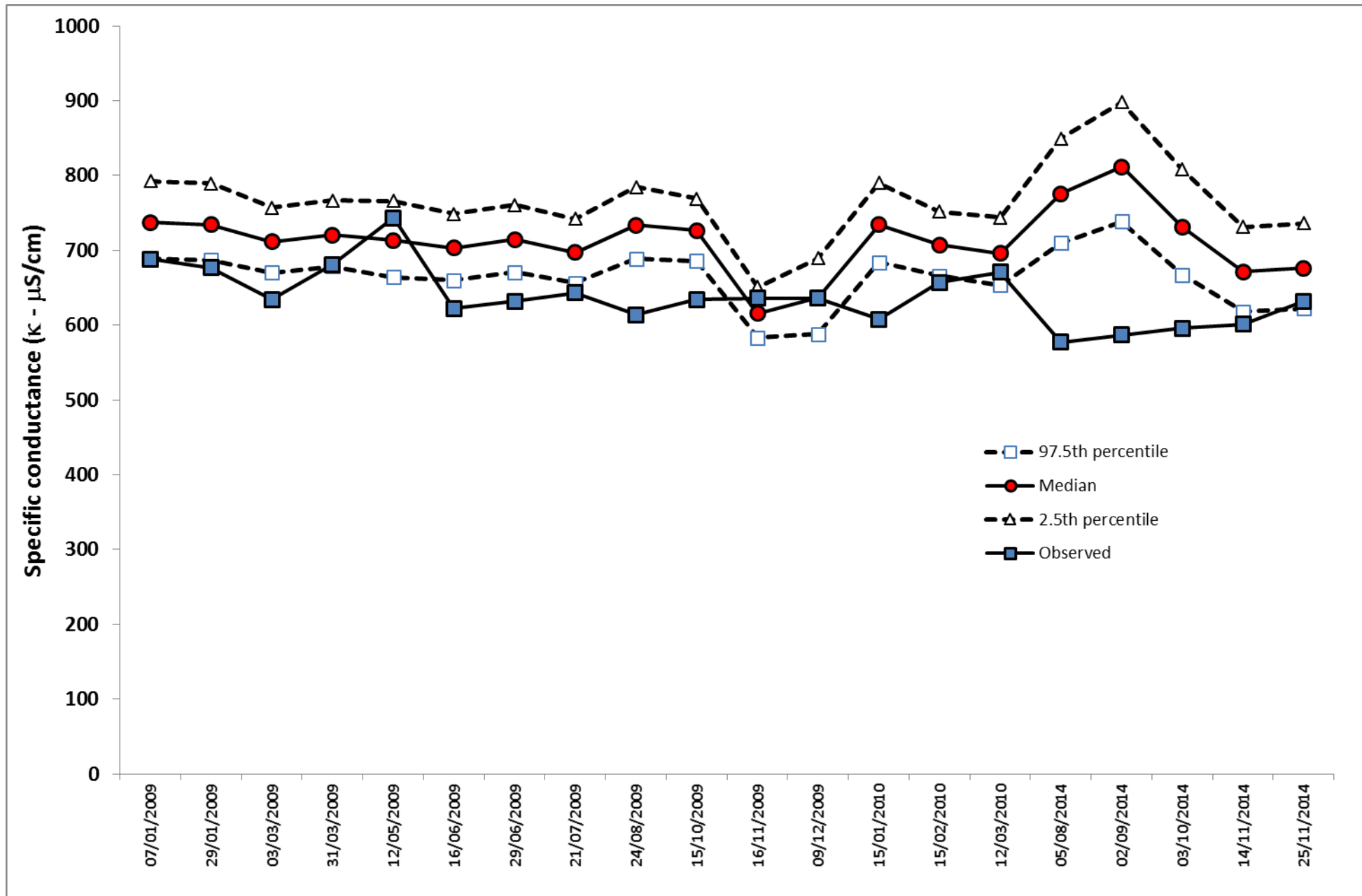


Fig. 5

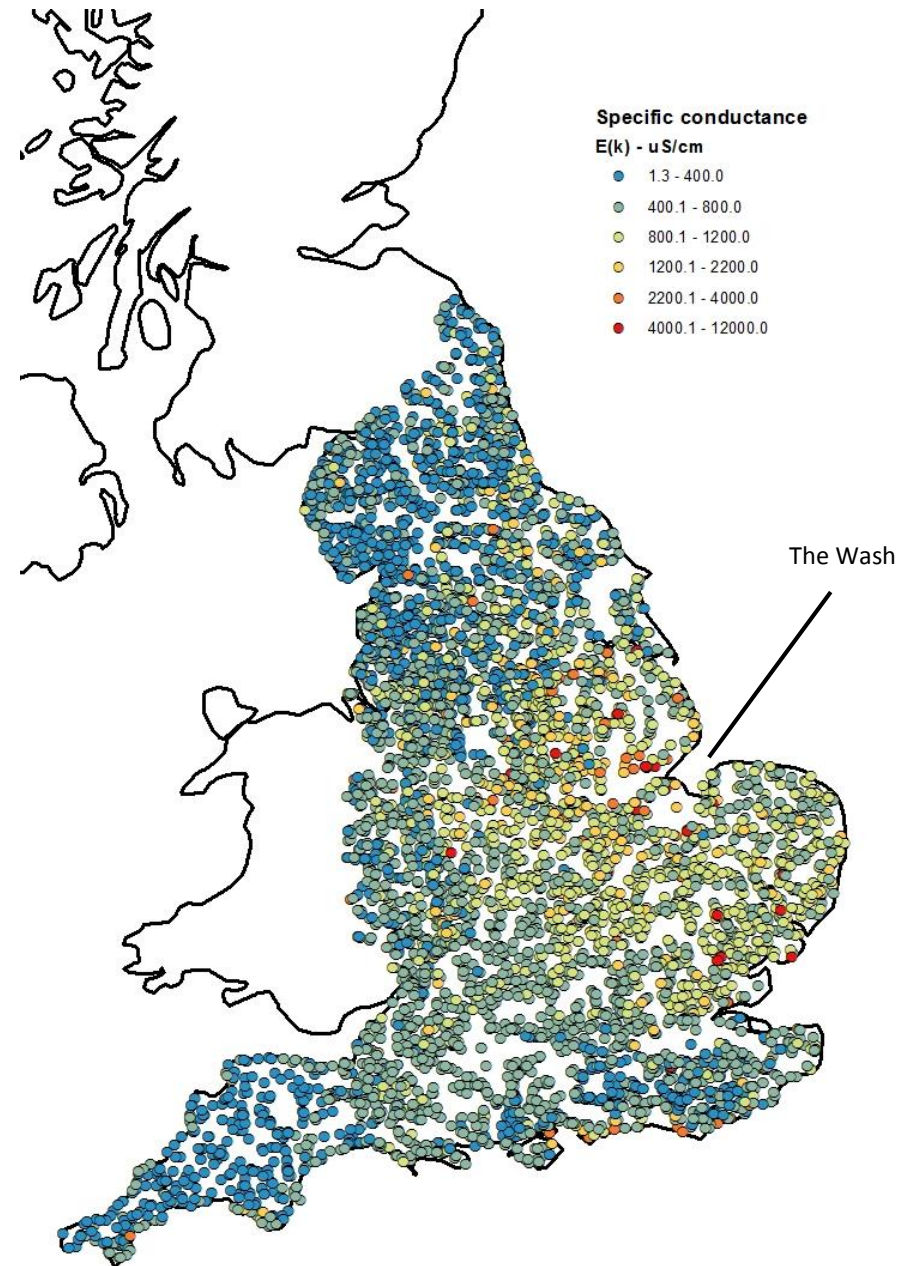


Fig. 6

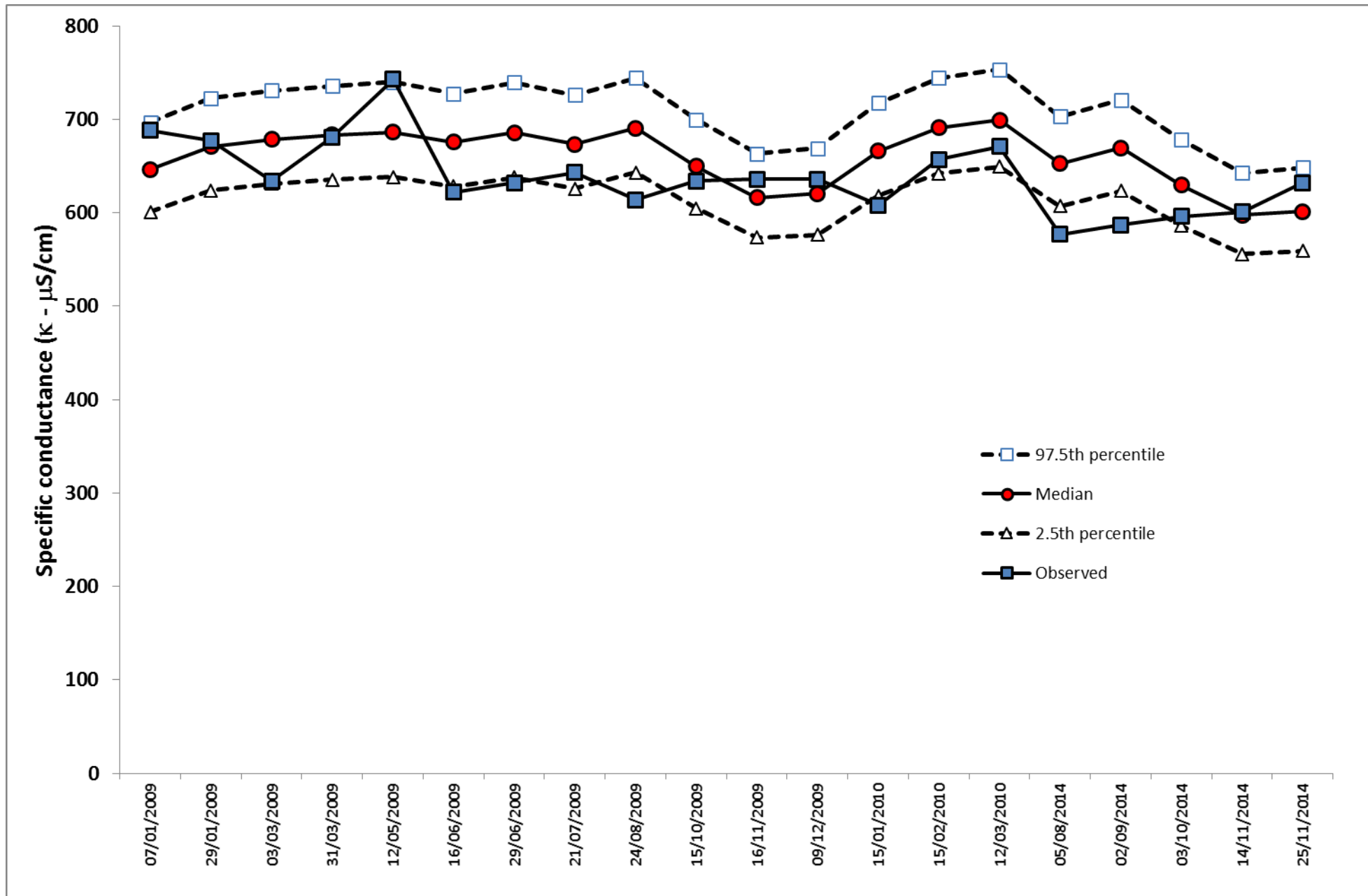


Fig. 7

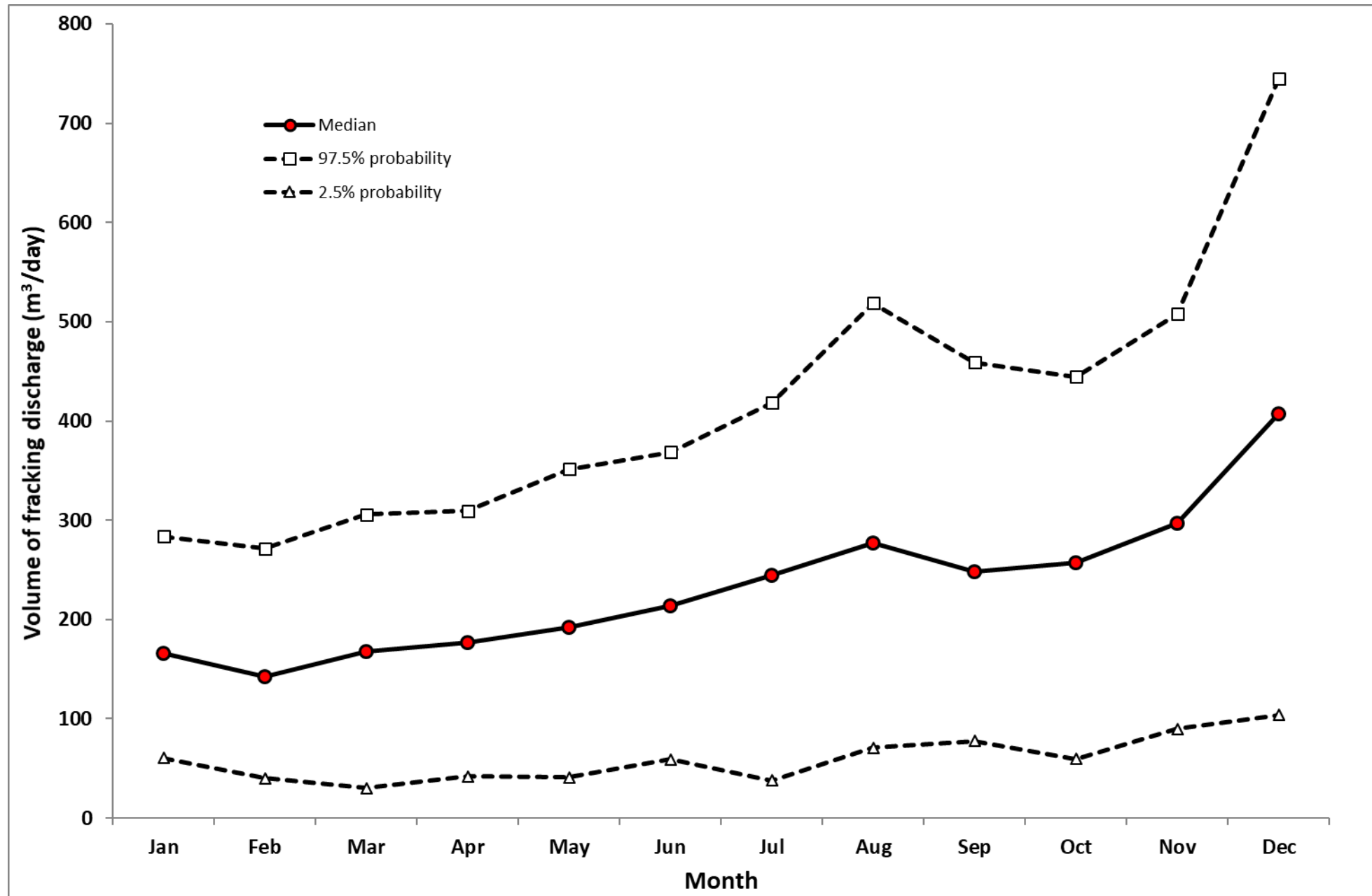


Fig. 8

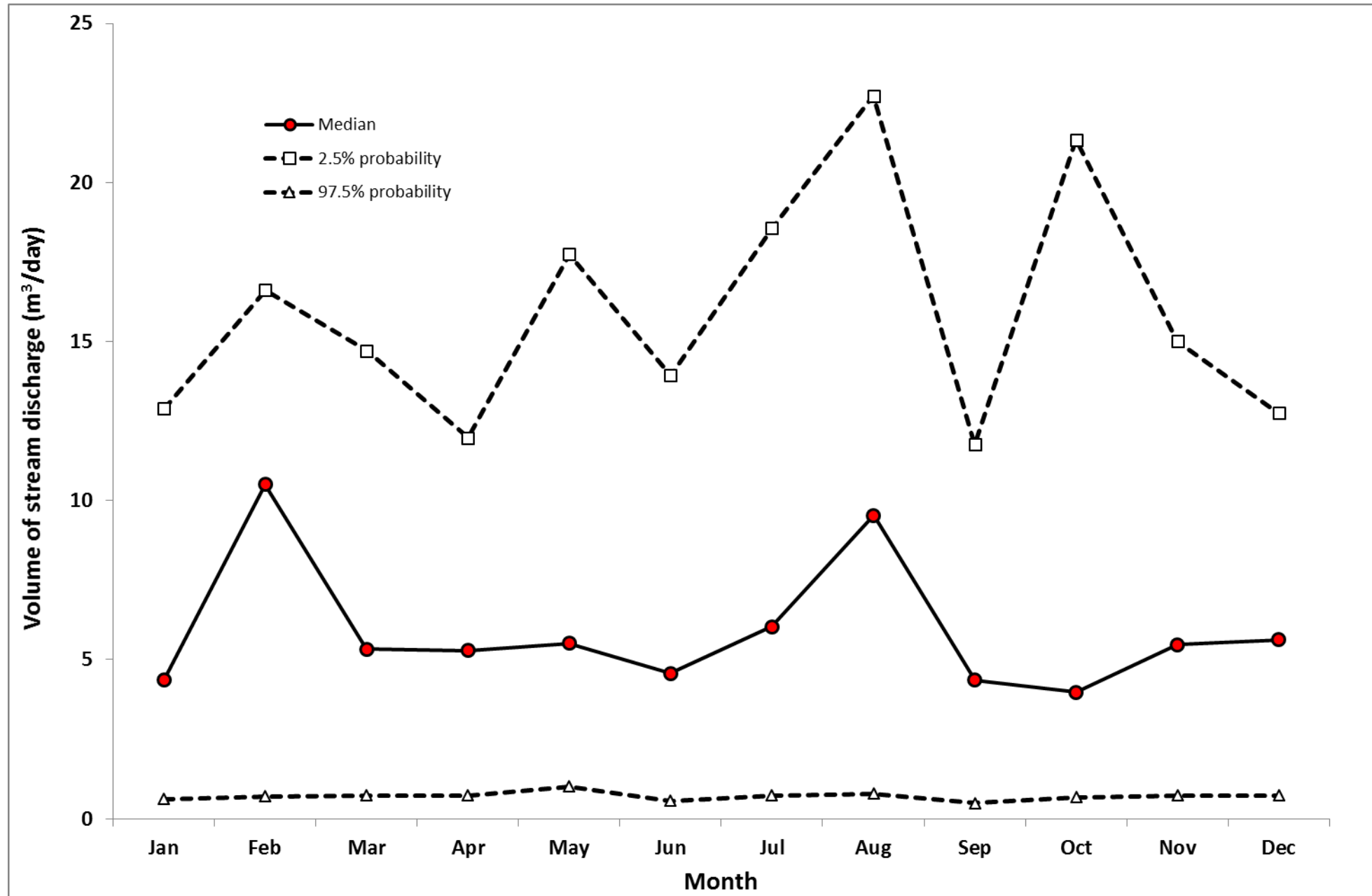


Fig. 9