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How does temporal variation affect the value of stream water as a medium for regional geochemical survey?

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ABSTRACT

Stream water is a key medium for regional geochemical survey for mineral exploration and environmental protection. However, stream waters are transient, and measurements are susceptible to various sources of temporal variation. In a regional geochemical survey stream water data comprise 'snapshots' of the state of the medium at a sample time. For this reason the British Geological Survey (BGS) has included monitoring streams in its regional geochemical baseline surveys (G-BASE) at which daily stream water samples are collected, over variable time intervals, to supplement the spatial data collected in once-off sampling events.

In this study we present results from spatio-temporal analysis of spatial stream water surveys and the associated monitoring stream data. We show that the variability of monitoring stream data from the G-BASE surveys has a temporally correlated component which can be treated as independent between streams, and therefore as a component of the nugget (spatially uncorrelated variance) of the spatial variograms of stream water survey data. For the variables examined this component was small relative to the spatial variability, which indicates that the value of stream water data to provide spatial geochemical information is not compromised by temporal variability. However, these conclusions are conditioned on the particular data set which was collected only in the summer months, specifically to limit temporal variability. Temporal variation in stream water analyses may be less tractable in wetter conditions. We show how the spatial data from stream water surveys can be mapped by ordinary kriging, with the predictions interpreted as an estimate of the temporal (summer months) mean, and the kriging variance reflecting the partition of the nugget variance of the spatial variogram between spatial and temporal components.

1. Introduction

Geochemical mapping entails the sampling of surface materials, notably soils, stream sediments and stream waters. It is generally recognized that regional scale survey of all these media can provide information on both geogenic and anthropogenic sources of geochemical variability (De Vivo et al., 2008), and this information can be useful for the investigation of mineral resources and for managing potentially harmful elements whether these arise from naturally occurring mineralizations or pollution (Cocker, 1999; Simpson et al., 1993). For this reason geochemical surveys at regional and national scale have included sampling of all three media (De Vivo et al., 2008; Birke et al., 2015). The Geochemical Baseline Survey of the Environment (G-BASE), conducted in the United Kingdom by the British Geological Survey (BGS), included sampling of stream waters for a limited set of determinands at its inception, and since 1988 routine sampling of both stream sediments and stream waters for multi-element analysis (Johnson et al., 2005).

Surveys of stream waters provide general geochemical information, and are also informative about issues of water quality of direct relevance for policy, management and regulation. For example, G-BASE stream water data have been used to estimate exposure of non-human species to naturally occurring radionuclides (Jones et al., 2009), to understand the significance of geogenic sources of arsenic (Breward, 2007) and to estimate carbon dioxide fluxes from surface waters (Rawlins et al., 2014). Geochemical surveys of stream waters have been used to investigate pollution associated with industrial activity (Vaisanen et al., 1998) and to investigate the combined effects of geology and anthropogenic factors on water quality (Reimann et al., 2009).

While data on stream water are useful, it is, at least potentially, more transient than soil or sediment. In a regional survey a stream is visited once, and the sample that is collected represents a snapshot of its geochemical composition at a particular time. The water chemistry of a particular stream is subject to variation over time over a range of temporal scales. Kirchner and Neal (2013) report studies on detailed analysis of the streamwater chemistry from two headwater catchments at Plynlimon in Wales. These showed fractal scaling of solute concentrations consistent with a model of randomly varying inputs across the catchment followed by dispersion driven by water transport across the landscape (Kirchner et al., 2001). The concentration of an analyte in stream water may vary in response to flow rate. One reason for this is a dilution effect. An increase in flow rate may also be associated

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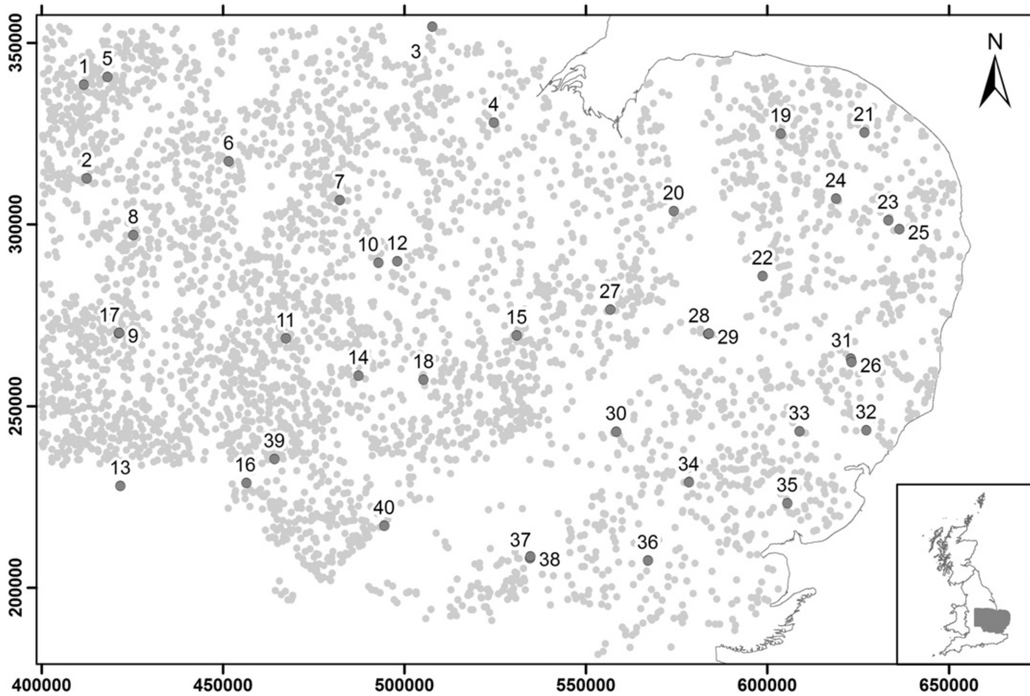

Fig. 1. First order stream sample sites (small light grey symbols) and monitoring stream sites (large dark grey symbols with numbers). Coordinates are in metres relative to the origin of the British National Grid. The location of the sampled region is seen in an inset map of Great Britain.

with an increase in the influence of the distinctive chemistry of rainwater on the composition of the stream (Appelo and Postma, 2007; Drever, 1997), contributions from overland flow or increased leaching of solutes into shallow groundwater. Over longer periods stream water composition may respond to seasonal differences in rainfall and to anthropogenic inputs, such as artificial fertilizers, which may include various trace elements along with the principal nutrients, and slurries and manures which may contribute both organic components, macronutrients such as P and trace elements such as Cu.

These sources of temporal variation must be accounted for when stream water geochemical data are interpreted to understand regional spatial variation. Hutchins et al. (1999) compared the spatial variability of stream water data from G-BASE sampling in Wales with temporal observations made in a single catchment within the country at 2- to 4-week intervals. They did not attempt any spatio-temporal statistical modelling of these data, but noted that geological, meteorological and anthropogenic effects could be seen in the spatial variation. They concluded that more observations on temporal variability of stream water data were needed in combination with the spatial sampling for robust inference. In 1997 BGS modified the field sampling procedures of the G-BASE survey to include repeated sampling from a small number of monitoring sites, sampled daily while the regional survey was conducted nearby. As a result the monitoring-site data consist of relatively short local time series, from a few days up to 30 or 40. This provides information on the short-scale temporal variability of the variables measured on stream water in the G-BASE survey.

While there have been detailed studies on the temporal variation of streamwater chemistry within one or two associated catchments (e.g. Neal et al., 2013; Kirchner and Neal, 2013) we require a more extensive study of spatio-temporal variability in order to understand how temporal variation affects the interpretation of data from spatial surveys with one-off sampling of individual streams. In this paper we analyse the data on some key variables from monitoring stream sites in the G-BASE survey of part of the English Midlands and the East Anglia region. We use a linear mixed model to examine the within-stream variation over time, including the extent to which this variation is temporally correlated over short intervals. We then analyse the survey sample data (restricted to first-order streams) using statistical models for spatio-temporal variability to examine how the temporal variation, examined at the monitoring sites, and the spatial variation interact. On the basis of this we can quantify the implications of temporal variation of stream water properties for the spatial interpretation of data from the regional survey which comprises only spot samples from any given stream.

2. Materials and methods

2.1. Sampling and data

The data used in this study were collected in part of the East Midlands and the East Anglia region of England from 1996 to 2007, with no sampling in 2001 due to an outbreak of foot and mouth disease. In each year sampling was undertaken during the period from June through to September, that is to say in summer months. This was a deliberate decision to avoid wetter periods of the year and so to sample, as far as possible, when base flows dominate the stream flow. We used the stream water survey data and the data from monitoring sites collected in this period. Fig. 1 shows the spatial distribution of both data sets. The sampled region is a lowland area, predominantly under agriculture but with some urban centres. Figure S1 in the supplementary material (journal website) shows the solid geology according to a generalized lithological classification. The aquifers are almost exclusively sedimentary, with Triassic and Jurassic mudstones, Cretaceous chalk, Palaeogene clays and poorly consolidated Pleistocene sediments dominating the area. These give rise to a generally subdued topography and so streams are relatively slow-flowing. Figure S9 shows the stream water survey sample sites collected in each year

The data were collected according to the standard G-BASE procedures (Johnson et al., 2005). Drainage sample sites, at which both sediment and water specimens were collected, were identified in advance on small streams (first or second order). The target sample density was one sample per 1.5–2.0 km ^{2}, but sample density varied in accordance with drainage density. Fig. 1 shows, for example, that samples were absent or very sparse in a band running approximately south-west–north-east where the bedrock is Cretaceous chalk. Filtered samples for major- and trace-element analysis were collected from mid-