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Characterization of surface water isotope spatial patterns of Scotland

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ABSTRACT

The extended National Waters Inventory of Scotland (NWIS) monitoring network in combination with an extensive, supplementary low flow sampling campaign was used to create isoscapes of surface water for management purposes at high spatial resolution (100 m grid) across Scotland. The δ^2H isoscape shows a strong isotopic separation along a north-south and east-west topographic (mountainous to the north and west and lowlands to the east) and climatic (wetter west, drier east) gradients. Isotopes were enriched in the western domain and depleted in the east and central Highland domains. The surface water *d*-excess isoscape show more complex spatial variability mainly related to contrasting moisture sources (sub-tropical North Atlantic Ocean, the North Sea, Polar Continental, and the Arctic) as well as secondary evaporation processes. The two-year NWIS isotope record exhibited a significant seasonal evaporative effect on surface water isotopes that progresses from winter through to a maximum in autumn as indicated by Local Evaporation Lines (LELs). The surface water isoscapes can be efficiently reproduced with geographically weighted regression (GWR) models using gridded annual precipitation, remotely sensed actual evapotranspiration, land cover, soil wetness, catchment area, and mean elevation. The GWR models showed potential to assess isotopic changes under future climate and land use change.

1. Introduction

The concept of “isotopic landscapes” or “isoscapes” (West et al., 2010) has become a valuable tool to understand hydro-climatic processes and their effect on water resources across different spatial scales (Bowen and Revenaugh, 2003; Terzer et al., 2013; Jasechko et al., 2013; Evaristo et al., 2015; Good et al., 2015). Historically, the use of stable water isotopes in the environmental sciences was dependent on analytical capability. Fortunately, the development of inexpensive instrumentation based on laser spectroscopy has greatly enhanced our ability to characterise the temporal and spatial variability of isoscapes at high resolution (Gupta et al., 2009; Good et al., 2014; Munksgaard et al., 2014). Recently, isoscapes have emerged as a low-cost and effective tracer visualization technique to understand precipitation dynamics (Lachniet and Paterson, 2009; Sánchez-Murillo et al., 2016a, 2016b), groundwater recharge mechanisms (Heilweil et al., 2009; Jasechko and Taylor, 2015; Sánchez-Murillo et al., 2016a, 2016b), paleoclimate (Vimeux et al., 2005; Lachniet, 2009; Risi et al., 2010), and ultimately, enhance water resources management (Bowen and Good, 2015). However, to use isoscapes as a physically-based management tool - as advocated by Bowen and Good (2015) - the spatial resolution needs to cover regional as well as local scales. The latter requires sampling efforts able to generate a complete spatial representation of complex terrain. A sufficiently high density of observations is particularly important in mountainous landscapes due to the complex interaction of hydro-meteorological processes and small scale landscape heterogeneity (Yamanaka et al., 2015).

In addition to characterising spatial variation with the highest possible density monitoring network, the geostatistical method used for spatial interpolation is also critical. There are several algorithms available and all have advantages or disadvantages, but there is little guidance as to which algorithm is the most suitable for isoscape

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applications. Common approaches use a) relatively simple nearest neighbour-related interpolations (such as spline and inverse distance weighting) or b) linear regression, taking explanatory variables such as elevation, latitude, distance to the ocean, slope, and stream network into account (Bowen and Revenaugh, 2003; Wassenaar et al., 2009; Kaseke et al., 2016). Newer network-related algorithms, tailored to take, for example, stream networks into account are also available (Bowen et al., 2011). However, few isotope studies look to incorporate the most basic features of spatial heterogeneity for interpolation. The class of "geographically weighted regression" (Fotheringham et al., 2002) explicitly allows a comprehensive assessment of different explanatory variables that are potentially related to isotopes, their spatial patterns and the physical processes governing water isotope fractionation.

Oxygen-18 ($\delta^{18}O$) or deuterium (δ^2H) isoscapes have been used as a potential indicator to explain moisture origin and evaporative fractionation processes which lead to observed isoscapes and their potential practical application to water management (Sánchez-Murillo et al., 2016a, 2016b). More recently, isotopes are increasingly analysed together with the deuterium excess (*d*-excess = δ^2H-8·$\delta^{18}O$; originally proposed by Dansgaard, 1964). The *d*-excess is the y-intercept of the global meteoric water regression line (GMWL) with a value of +10‰. If the *d*-excess departs from +10‰, particularly for lower values, this is a potential indication of land surface evaporation that affects the isotopic composition. Jouzel et al. (2013) mentions that precipitation *d*-excess values may deviate from +10‰ due to a combination of three factors: a) a relative humidity (RH) increase in the precipitation source, b) a decrease in sea surface temperature (SST), and c) greater wind speeds ($>7\,\mathrm{ms}^{-1}$) affecting the evaporation regime and subsequent kinetic fractionation. Furthermore, the recycling of transpiration fluxes, which could represent up to 80–90% of terrestrial evapotranspiration (Jasechko et al., 2013), may affect the parental isotope composition of precipitation. Such changes, may in combination with catchment specific characteristics, ultimately affect surface water isotopes. Similarly, indices such as the *lc*-excess based on the deviation from the Local Meteoric Water Line (LMWL) rather than the GMWL proved a useful indicator of evaporative fractionation mainly at smaller catchment scales (Sprenger et al., 2016). Therefore, the composition of stable isotopes in combination with derivatives such as the *d*-excess can be powerful tools to explain spatial variation of the components of the hydrological cycle (e.g. precipitation, evapotranspiration and surface waters) and any deviation from the observed and interpolated average conditions caused by environmental changes including climate and land use changes.

Isoscapes and their physical drivers are particularly useful in areas with marked precipitation, temperature and topographical gradients. Scotland represents a heterogeneous environment and we, therefore, build on previous work by Darling and Talbot (2003) and Tyler et al. (2016) who first constructed precipitation isoscapes for the British Isles. In this study, we focus on surface water isotope data and analyse spatial variability at a national (Scottish) scale, interpolated to relatively high spatial resolution (100 m grid), to inform management decisions from regional to local scale. Inferences on moisture sources covering Scotland could be made from surface water isotopes, even in absence of precipitation isotope records, providing that catchment characteristics are accounted for. To relate isoscapes to environmental characteristics as explanatory variables of their average spatial variability, we constructed geographically weighted regression (GWR) models. The GWR models can capture such spatial heterogeneity explaining important drivers on surface water isoscapes and can serve as a learning tool for potential future isotopic changes driven by environmental (climate and land use) change.

The specific objectives were:

a) To analyse and complement the National Waters Inventory of Scotland (NWIS) stable isotope data base for spatial patterns using regression and interpolation techniques.
b) To relate the surface water isotopes to environmental variables to identify important drivers of spatial patterns using GWR models across Scotland.
c) To evaluate GWR models for construction of surface water isoscapes and the relationship to precipitation source moisture.

2. Background, monitoring and methods

2.1. Site description and precipitation, surface water and groundwater monitoring

Surface water sites (rivers) for stable water isotope analysis (number of sites (n) = 90) across Scotland were sampled at approximately monthly intervals using a standard protocol for two years from 2011 to 2013. The monitoring sites were mostly established as part of the National Water Inventory for Scotland project (NWIS) to systematically assess the environmental state of Scottish water bodies as required by the European Union Water Framework Directive (Dawson et al., 2012). The sites corresponded to the Harmonised Monitoring Scheme (HMS – Ferrier et al., 2001) that is managed by the Scottish Environmental Protection Agency (SEPA) (Fig. 1A–C) and was recently used by Spezia et al. (2017) for water quality classification. The NWIS sites were complemented with research sites of at least monthly sampling from the University of Aberdeen to improve spatial coverage (n = 14; Soulsby et al., 2014, 2015). The monitoring network covers catchments from $<1\,\mathrm{km}^2$ to the largest Scottish catchment (River Tay) with $\sim4900\,\mathrm{km}^2$ (Table S1). The sites also span a wide range of elevations (from lowlands to highlands with a maximum altitude of ~1300 m a.s.l.) (Fig. 1A), land uses (intense agriculture, forested, urban, and heather moorland), and the observed marked west-east Scottish climate gradient (high rainfall up to $\sim3\,\mathrm{myr}^{-1}$ in the west compared to the much drier east coast with annual rainfall of $\sim800\,\mathrm{mm\,yr}^{-1}$) (Fig. 1B) (Birkel et al., 2013). Air temperature (mean annual temperature across Scotland, MAT = 6.3 °C) decreases with altitude in correspondence to an environmental lapse rate of close to −0.6 °C/100 m (Fig. 1C) and the southwest is milder compared to a cooler east. Soils range from intensively farmed brown earth soils along the east coast to podzolic soils over much of the Highlands with less developed inceptisols on the steeper hillslopes. The valley bottoms and hilltop areas are frequently dominated by organic rich histosols. The soil cover importantly affects recharge and runoff generation processes across Scotland (Soulsby et al., 2006).

In addition, 29 groundwater wells were monitored over the same period, but sites are concentrated on the east coast and are located mostly within Scottish Monitored Priority Catchments identified as Nitrate Vulnerable Zones (NVZ). The wells cover a range of depths from 10 m to 50 m of mostly sedimentary rocks (old red sandstone), glacial (till, sand, and gravel), and alluvial (sand, gravel) deposits. As a reference, we included data from five precipitation monitoring sites compiled from the published literature concentrated on the east coast and the highlands (Soulsby et al., 2014, 2015). Apart from the high-temporal resolution (daily) and localised precipitation data collected by Soulsby et al. (2014, 2015), the coverage of precipitation isotope information over the whole of Scotland, is scarce for the period 2011–2013 and only one historic Global Network of Isotopes in Precipitation (GNIP) station existed with data for 1965 (Eskdalemuir). Due to insufficient NWIS sample coverage in the west of Scotland and the northern (Shetlands, Orkneys) and western islands (Inner and Outer Hebrides), we conducted an additional surface water spot sampling campaign (n = 56) under low flow conditions to eliminate the effect of high flow events with more depleted or enriched isotopes over spring and early summer 2016. The complete data set of surface water samples (n = 146) was used to construct isoscapes and to assess spatial patterns. Only the 90 longer-term sites with monthly sampling from 2011 to 2013 were used for temporal pattern analysis. All samples were