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Geospatial drivers of the groundwater $\delta^{18}O$ isoscape in a temperate maritime climate (Republic of Ireland)

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Research papers

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ABSTRACT

In recent years, the concept of “isoscapes” has been used to describe spatiotemporal stable isotope distributions within natural environments including groundwater systems at multiple scales. This study presents an updated groundwater $\delta^{18}\text{O}$ isoscape for the Republic of Ireland and describes the climatic and geological drivers influencing $\delta^{18}\text{O}$ composition. In all, 142 geographically and geologically representative groundwater installations were sampled and analysed, in addition to 35 samples from six nested boreholes. Geospatially, Irish groundwater exhibits high $\delta^{18}\text{O}$ values in southern and western coastal regions, becoming progressively depleted inland before reaching lowest measured values along the eastern coast, equating to a national groundwater $\delta^{18}\text{O}$ profile range of approximately 3‰. Groundwater $\delta^{18}\text{O}$ composition is primarily driven by location with respect to orographically influenced rainfall deposition and annual precipitation volume, with a bias towards winter recharge. Results also demonstrate that local/regional (hydro)geological setting exerts a secondary influence on $\delta^{18}\text{O}$ composition via infiltration and recharge mechanisms. “Flashy” groundwater systems (e.g. karst limestones) are more likely to exhibit seasonal groundwater $\delta^{18}\text{O}$ patterns, whereas low productivity systems with high residence times (e.g. granites), tend to display a dampened composition to groundwater recharge and exhibit more temporally constant $\delta^{18}\text{O}$ values. The derived $\delta^{18}\text{O}$ isoscape enhances current understanding of what is a geologically distinct groundwater setting, whilst also potentially serving as a $\delta^{18}\text{O}$ “sentinel” for continental Europe, with respect to both groundwater and precipitation, due to Ireland’s geographic location.

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1. Introduction

Isotope hydrology represents a well-established and increasingly-employed approach to elucidating local and regional hydrodynamic regimes (Gat, 1996; Jasechko and Taylor, 2015; Sprenger et al., 2016). Systematic variations in the isotopic composition of natural water bodies provide evidence of spatiotemporal water movement and associated hydrological fluxes, both above and below ground (Craig, 1961; Kendall and McDonnell, 2012). $\delta^{18}\text{O}$ is the ratio of the stable isotopes of oxygen-18 (^{18}O) and oxygen-16 (^{16}O) and has been shown to function as a reliable indicator of previous climatic flux (Craig, 1961; Rozanski, 1985; Clark and Fritz, 1997). The composition of $\delta^{18}\text{O}$ is only affected by physical processes (Craig, 1961; Dansgaard, 1964), thus, classification of

the stable groundwater isotopic composition is particularly useful for interpreting subsurface flow pathways and source identification (e.g. groundwater-surface water interactions) (Davisson and Criss, 1993; Gat, 1996; Ma et al., 2017), processes which are frequently difficult to describe or predict via hydro-chemical characterisation or (chemical) hydrograph separation alone (Hunt et al., 2005).

In recent years, the concept of “isoscapes” (i.e. isotopic landscapes) has been used to describe mapping of large-scale spatiotemporal distributions of stable isotope ratios in myriad environmental matrices including rainfall, the oceans, rocks, flora, and fauna (Wassenaar et al., 2009; Bowen and Good, 2015). The concept aids understanding of the interactions between the hydrological and biogeochemical cycles (Bowen and Good, 2015; Sánchez-Murillo and Birkel, 2016), with precipitation isoscapes typically driving $\delta^{18}\text{O}$ patterns in surficial waters (Wassenaar et al., 2009). Previous hydrological investigations have found that

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the isotopic composition of annual precipitation is similar to that of groundwater (e.g. Darling et al., 2003; Wassenaar et al., 2009; Filippini et al., 2015; Ma et al., 2017), suggesting that the proportion of recharge to precipitation is temporally constant (Jasechko et al., 2014). This is attributed to the homogenisation of seasonal rainfall compositions that typically occurs within the unsaturated zone (Darling and Bath, 1988), meaning the stable isotopic composition of groundwater tends to mirror the volume-weighted long-term isotopic mean of precipitation (Darling, 2004). Accordingly, recent studies have presented isoscapes pertaining to shallow regional groundwater systems as an isotopic integrator of long-term seasonally weighted precipitation inputs (Darling et al., 2003; Kortelainen and Karhu, 2004; Wassenaar et al., 2009; West et al., 2014; Raidla et al., 2016; Sánchez-Murillo and Birkel, 2016). However, not all studies have reported this correlation (Jasechko et al., 2014), with recharge found to be biased towards seasonal and/or intensive monthly rainfall (Jasechko and Taylor, 2015; Sánchez-Murillo and Birkel, 2016). The annual variation of $\delta^{18}\text{O}$ in groundwater can also depend on the level of heterogeneity associated with recharge areas, variations in the type of precipitation (e.g. snowmelt), and physical catchment characteristics (i.e. vegetation cover, rock type and soil depth), which can represent important drivers of the groundwater isoscape during interception and infiltration processes (Gat, 1996; Darling, 2004; Gleeson et al., 2009; Raidla et al., 2016).

Darling et al. (2003) have previously presented a baseline groundwater $\delta^{18}\text{O}$ isoscape for Ireland, with the current study building on this by sampling an increased number of monitoring wells covering a wider spatial area. The objective of this study was to investigate in more detail the relative influence of local climate (precipitation and temperature) on the spatial variation of groundwater $\delta^{18}\text{O}$, and whether processes affecting groundwater recharge (and infiltration) rates (e.g. hydrogeological setting, land use) significantly influence spatially distributed groundwater $\delta^{18}\text{O}$. The developed isoscape may be used to inform future monitoring of climatic and anthropogenic change at multiple scales, whilst presented findings will also enhance current understanding of what is a geologically distinct groundwater system. Furthermore, the groundwater $\delta^{18}\text{O}$ data presented in this study may serve as a “sentinel” for continental Europe due to Ireland’s location on the eastern fringes of the Atlantic Ocean.

2. The Republic of Ireland

This study was undertaken in the Republic of Ireland (70,273 km²), hereafter referred to as Ireland, a mid-latitude country located on the Atlantic seaboard of Western Europe (Fig. 1). The Irish climate is described as “temperate maritime”, influenced both by the warm waters of the North Atlantic Drift and the prevailing westerly winds of the Atlantic Ocean. Average annual rainfall (1981–2010) is approximately 1230 mm (Walsh, 2012), decreasing from western (1000–1400 mm) to eastern (700–1000 mm) seaboard, with up to 3000 mm in elevated areas (Fig. 2). Driest periods typically occur from April to July (Walsh, 2012). Mean annual air temperatures (1981–2010) typically occur within the range 9–10 °C, with highest temperatures during the summer period (Mean Seasonal Maxima: 18–20 °C) (Walsh, 2012). Annual actual evapotranspiration ranges from 400 to 500 mm (Hunter-Williams et al., 2013), with most recharge occurring during the period October–April (Misstear et al., 2009).

The geology of Ireland is characteristically diverse; upland landscapes, which dominate a majority of the Irish coastline (Fig. 1), comprise Precambrian to Lower Palaeozoic metamorphic, igneous and sedimentary rocks, whilst midland and western regions are dominated by flatter Upper Palaeozoic (Carboniferous) rocks, and

particularly karstified and dolomitised limestones. Classification of bedrock formations is based primarily on overall aquifer productivity, (potential) yield, and areal extent, in addition to the predominant subsurface flow mechanisms, which in Irish bedrock systems is typically via fracture pathways (solutionally enhanced fissures and karst conduits) (Hunter-Williams et al., 2013). Irish groundwater is typically un-confined, and as water storage is a function of fissure permeability (secondary porosity), a majority of Irish aquifers are not considered significant by international standards with regard to storage, yields, or areal extent. However, they are important for local supplies and have been delineated into three primary classifications, namely *regionally important*, *locally important* and *poor* (Fig. 3). The Precambrian and lower Palaeozoic bedrock formations are typically fractured hard rocks, the majority of which are classified as Poor aquifers (lower, less sustainable yields), whilst Carboniferous limestones are typically more productive (i.e. Regionally Important), due to secondary and tertiary porosity. “Locally important” aquifers include sandstones and limestones within the Devonian and Carboniferous successions and are neither as productive, nor as spatially extensive as regionally important aquifers (Misstear et al., 2009).

An overburden (subsoil) of glacial deposits (typically 5–15 m thickness) covers most of the important bedrock aquifers in Ireland (Misstear et al., 2009). These are dominated by tills, typically characterised by ‘moderate’ to ‘low’ hydraulic conductivities. Superficial deposits also include fluvial and glacio-fluvial sand and gravel deposits (Misstear et al., 2009), as well as significant areas of peat cover (approximately 14% of the national area) (Connolly and Holden, 2009). Percolation through these deposits typically occurs as diffuse recharge; conversely, point recharge is characteristic of karstified limestone areas (Hunter-Williams et al., 2013). The main hydrogeological controls on groundwater recharge are subsoil permeability and subsoil thickness, with both of these used to categorise groundwater ‘vulnerability’ (Hunter-Williams et al., 2013). Five groundwater vulnerability categories have been identified, namely extreme (X, outcrop, shallow rock or karst), extreme (E), high (H), moderate (M) and low (L) (DOELG, 1999). Grassland represents the dominant land-use in Ireland, accounting for 60.7% of total land area, with cropland (9.5%), forestry (10.6%), wetland (16%) and urban settlements (1.7%) accounting for the majority of the remainder (www.cso.ie).

3. Methodology

3.1. Groundwater sampling

Groundwater samples were obtained from the national groundwater monitoring network operated by the Irish Environmental Protection Agency (EPA). This network comprises 289 instrumented boreholes and springs representative of the variable hydrogeological conditions and pressures typically encountered in Irish groundwater (<http://www.epa.ie/water/wm/groundwater/programme/>). Spatially representative groundwater samples accounting for climate, geology and topography, were taken from 142 network points (Fig. 1), and analysed for $\delta^{18}\text{O}$ during June/July 2013, with 65% (n = 92) and 35% (n = 50) sampled from deep boreholes and shallow groundwater springs, respectively. Additionally, 35 samples were taken from 3 nested borehole clusters at 6 locations (Fig. 1) used to investigate groundwater recharge mechanisms in poorly productive aquifer systems (CDM, 2010). Borehole nests were employed to sample groundwater from (1) subsoil deposits close to the surface (0.5–2.0 m below ground level [mbGL]) (2) the weathered bedrock ‘transition’ zone (0.8–4.3 mbGL), (3) shallow groundwater within the bedrock system (5.8–20.5 m mbGL) and (4) deeper in the bedrock column where

Fig. 1. Map of study area showing location of groundwater monitoring sites and IAEA GNIP stations. The Elevation range is in meters above sea level. Dominant prevailing trade wind directions are represented by arrows (<https://www.met.ie/climate/wind.asp>). Inset shows the location of Ireland in relation to Europe.

significant water-bearing fractures or faults occur (17.0–57.0 mbGL) (CDM, 2010).

The employed sampling methodology adhered with standard aquifer sampling protocols whereby boreholes were purged to at least three well volumes based upon the calculated internal borehole volume, ensuring a representative aquifer sample (IAEA, 2017a). Samples were stored unfiltered and unpreserved in 10 ml polyethylene containers (IAEA, 2017a), and refrigerated (<4 °C)

prior to laboratory analysis, which was undertaken within 4 weeks of sampling.

3.2. Laboratory analysis

$\delta^{18}\text{O}$ analysis was performed using Continuous Flow-Isotope Ratio Mass Spectrometry (Thermo Delta^{plus} CF-IRMS) and Gas Chromatography (GC) (Klein Gebbinck et al., 2014). Samples were

Fig. 2. Groundwater monitoring stations in relation to spatial distribution of 30-year mean annual precipitation (1980–2010).

transferred to 12.5 ml glass Exetainers® which had been double washed in milliQ deionised water and dried at 70 °C for 12 h prior to use. 0.5 ml sub-samples were pipetted into 12 ml flat-bottomed Exetainers, capped and flushed (80 ml/min) with 0.3% CO₂ in a pure He gas mix for 500 s, and subsequently equilibrated in a thermostatically controlled sample block at 23 °C for 21 h. The equilibrated headspace gas was sampled by a CTC auto sampler before entering a Thermo Gas Bench, comprising an 8-port Valco valve for analyte loading/filling; a 100 µl sample loop, and two Nafion

(C7HF13O5 S.C2F4 sulfonated tetrafluoroethylene-based fluoropolymer co-polymer membrane) traps for moisture removal. Ten 100 µl aliquots per sample were taken and sent to the CF-IRMS via the GC.

Reference standards characterised by known δ values were run with each block of unknown samples. The first peak was discarded for each sample to condition the GC and reduce potential carry-over. Calculated standard deviations for the remaining peaks from each sample were used to assess IRMS stability during sample

Fig. 3. Groundwater monitoring stations and the primary Geological Survey of Ireland aquifer classifications.

runs. Measurements of $\delta^{18}\text{O}$ are expressed in permil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW) according to the relationship in Eq. (1):

$$\delta_{\text{sample}}(\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) * 1000 \quad (1)$$

where δ_{sample} is the isotope ratio of sample relative to the V-SMOW and R is the $^{18}\text{O}/^{16}\text{O}$ atomic ratio. Measurement precisions are estimated to be $\pm 0.4\text{‰}$.

3.3. Isotopes in precipitation

Two stations of the International Atomic Energy Agency (IAEA)-World Meteorological Organisation (WMO) Global Network of Isotopes in Precipitation (GNIP) are located in Ireland, at Valentia ($51^{\circ}93'\text{N}$, $10^{\circ}25'\text{W}$) and Armagh ($54^{\circ}35'\text{N}$, $6^{\circ}64'\text{W}$) (Fig. 1). Monthly monitoring $\delta^{18}\text{O}$ data is available for each station from 1961 and 2012, respectively (IAEA, 2017b). To compare shallow

groundwater to local precipitation, two groundwater wells sampled close to the IAEA stations were utilised. Groundwater sites at 'Portmagee' and 'The Wood' were sampled c. 9 km west and c. 22 km west of Valentia and Armagh, respectively (Fig. 1), and compared with corresponding long-term annual and monthly weighted isotope $\delta^{18}\text{O}$ composition and precipitation amount patterns.

3.4. GIS analysis

Long-term mean monthly (1981–2010) precipitation and air temperature were sourced from Ireland's National Meteorological Service (Met Éireann), across a grid cell network of 1 km (<http://www.met.ie/climate-ireland/30-year-averages.asp>). To account for short-term temporal recharge variation and associated mechanisms (i.e. rapid recharge, preferential flow), nine antecedent precipitation periods were calculated and spatially attributed to all sample points, as previously employed by Hynds et al. (2012). Elevation data were retrieved from a Digital Elevation Model developed for Ireland by the NASA Shuttle Radar Topography Mission (<http://dublin-tet.routetopa.eu:8080/lv/dataset/digital-elevation-model-of-ireland-from-nasas-shuttle-radar-topography-mission-srtm>). Spatial data relating to local/regional bedrock lithology, Quaternary deposits and aquifer units were sourced from the GSI (<http://www.dccae.gov.ie/en-ie/natural-resources/topics/Geological-Survey-of-Ireland/data/Pages/Data-Downloads.aspx>), in addition to groundwater vulnerability, estimated and measured recharge, and subsoil thickness and permeability data layers. Land-use/land cover data were accessed from the EPA CORINE (Co-Ordinated INformation on the Environment) data series (<http://gis.epa.ie/GetData>). All geographical information system processing was carried out in ArcGIS ArcMap v.10.3. The $\delta^{18}\text{O}$ groundwater isoscape was developed using a 1 km² grid resolution and interpolations based on a thin plate algorithm (Franke, 1982), following the methods described in Sánchez-Murillo and Birkel, 2016.

3.5. Statistical analysis

Variables were classified for statistical analysis based upon data type (Table 1). Variables considered over-parameterised (≥ 10 measurement levels) were generalised via aggregation (e.g. aquifer type, bedrock type, land cover). The Kolmogorov-Smirnov test and Q-Q plots were used to assess data normality; measured groundwater $\delta^{18}\text{O}$ was not normally distributed, thus non-parametric tests were employed. Spearman's rank correlation coefficient (ρ , R_{sp}) was used to test for correlations between continuous variables. The Mann-Whitney U Test with a standardised test

statistic and asymptotic significance was used to test for association between groundwater $\delta^{18}\text{O}$ and categorical variables with two levels of measurement (e.g. sample source). Kruskal-Wallis One-Way Analysis of Variance (ANOVA on ranks) was employed to test for associations between groundwater $\delta^{18}\text{O}$ and categorical variables with >2 measurement levels (e.g. subsoil thickness).

Outline analyses (not presented here) indicate that several climatic and geological variables exhibit significantly multicollinear relationships across the country, for example, from west to east, annual rainfall mean and bedrock geology type are significantly correlated ($F = 8.070$; $p = 0.004$). Accordingly, in order to determine the concurrent influence of climate and geology, a multivariate modelling approach encompassing statistical classification (spatial cluster analysis) and multivariate logit modelling based upon the resulting statistical clusters (categories) was employed. Thus, diagnostics could be used to corroborate that climate and geology exert a concurrent influence on groundwater $\delta^{18}\text{O}$ in the Republic of Ireland, as opposed to one or other category being simply associated with the actual driver via univariate analyses. Hynds et al. (2014) have previously employed a similar statistical design to demonstrate diverse parallel bacterial transport mechanisms within the Irish subsurface.

Cluster analyses were carried out to i) determine whether definable subgroups exist with respect to groundwater $\delta^{18}\text{O}$ and geographical location, and ii) employ subgroups for multinomial logit regression. Spatial clustering was undertaken using an agglomerative hierarchical approach with an Unweighted Pair Group Method with Arithmetic Mean (UPGMA) linkage criterion and the squared Euclidean distance (similarity) metric. Clusters were developed and mapped based upon geographical location (latitude, longitude), thus developed clusters represent sampling location relative to measured groundwater $\delta^{18}\text{O}$. It was considered that inclusion of unitless continuous variables for multinomial logit regression would result in overly complicated models with a low level of interpretability.

Multinomial logit regression was used to model and predict individual sample membership of developed spatial clusters, (Hosmer and Lemeshow, 2000; Twarakavi and Kaluarachchi, 2005), and thus attribute specific geological and climatic drivers (Tables 2 and 3) to spatial $\delta^{18}\text{O}$ cluster membership. As locational variables (Latitude, Longitude) were used to develop spatial clusters, these variables were excluded, with all other collated variables included for model development. Variable inclusion ordering (i.e. most significant univariate drivers included first) was based upon univariate factor analysis (Tables 2 and 3), with all potential predictor variables diagnosed for (multi)collinearity prior to modelling. Due to high levels of collinearity encountered

Table 1
Variable classification for analysis.

Continuous Data		Categorical Data	
Variable	Measurement Unit	Variable	Measurement Level
Positional Coordinate (Lat/Long)	N/A	Sample Source	2
Elevation	m ¹	Subsoil Thickness (DTB ²)	5
Seasonal Mean Precipitation	mm	Aquifer Type	10
Annual Mean Precipitation	mm	Generalised Aquifer Type	3
Antecedent Precipitation	mm	Groundwater Vulnerability	5
Seasonal Mean Air Temperature	°C	Recharge Capacity (Y/N)	2
Annual Mean Air Temperature	°C	Drainage	3
Mean Wind Direction	%	Bedrock Type	20
Recharge Coefficient	mm/year	Generalised Bedrock Type	6
Recharge Capacity	mm	Subsoil Type	22
Estimated Recharge	mm	Generalised Subsoil Type	6
		CORINE Land Cover	11
		Generalised Land Cover	6

¹ Above ordnance datum;

² Depth to bedrock.

Table 2

Univariate association analyses between measured groundwater $\delta^{18}\text{O}$ and continuous (scale) variables; Non-parametric Spearman R_{sp} . Two-tailed tests of significance with cases excluded on pair-wise basis.

	N	R_{sp}	p
<i>Location:</i>			
X-Coordinate	142	−0.438	<0.001
Y-Coordinate	142	−0.408	<0.001
Elevation (m)	142	−0.052	0.540
<i>Recharge:</i>			
Recharge Coefficient (mm/year)	141	0.153	0.053
Recharge Capacity (mm)	141	0.046	0.590
Estimated Recharge (mm)	141	0.167	0.048
<i>Seasonal Climate:</i>			
Mean Annual Precipitation	142	0.530	<0.001
Spring Mean Precipitation	142	0.483	<0.001
Summer Mean Precipitation	142	0.425	<0.001
Autumn Mean Precipitation	142	0.561	<0.001
Winter Mean Precipitation	142	0.519	<0.001
Mean Annual Temperature	142	0.414	<0.001
Spring Mean Temperature	142	0.372	<0.001
Summer Mean Temperature	142	0.156	0.063
Autumn Mean Temperature	142	0.449	<0.001
Winter Mean Temperature	142	0.536	<0.001
<i>Antecedent Precipitation</i>			
24-h	142	0.110	0.223
48-h	142	0.171	0.019
120-h	142	−0.033	0.617
10-day	142	−0.078	0.321
30-day	142	0.265	0.002
60-day	142	0.211	0.011
90-day	142	0.349	<0.001
120-day	142	0.470	<0.001
150-day	142	0.250	0.001

Note: Spring – March, April, May; Summer – June, July, August; Autumn – September, October, November; Winter – December, January, February.

Table 3

Results of categorical univariate association analyses between groundwater $\delta^{18}\text{O}$ and hydrogeological variables.

Variable	Sample Number	Test Statistic	p
Sample Source ¹	142	1.643	0.200
Subsoil Thickness ²	142	12.410	0.015
Aquifer Type ²	142	21.088	0.007
Groundwater Vulnerability ²	142	7.770	0.100
Recharge Cap. Applied (Y/N) ¹	141	0.808	0.369
Drainage ²	142	5.083	0.079
Bedrock Type ²	142	45.487	<0.001
Subsoil Type ²	142	8.098	0.151
Landuse/Land Cover ²	142	3.458	0.630

¹ Mann-Whitney U Test with standardised test statistic and asymptotic significance (Median Comparison);

² Kruskal-Wallis One-Way Analysis of Variance (ANOVA).

between mean (annual and seasonal) precipitation and temperature, interaction variables were developed. Pearson goodness of fit ($p > 0.05$), likelihood ratio ($p < 0.05$), and Nagelkerke's pseudo R^2 were used to evaluate model fit. All data analyses were undertaken within the R statistical environment.

4. Results

4.1. Groundwater $\delta^{18}\text{O}$ and climate

The groundwater isoscape of $\delta^{18}\text{O}$ (‰) is presented in Fig. 4. Overall, 142 geographically diverse groundwater sources were sampled with a mean $\delta^{18}\text{O}$ value of -6.31‰ (Std. Dev. 0.61) found over a measurement range of 3.4‰ (Min: -7.53‰ ; Max: -4.13‰)

(excluding shallow and transitional samples from nested wells). An additional 9 $\delta^{18}\text{O}$ values (McCormack, et al., 2014) from groundwater wells sampled in June–July 2011 in an under-represented area of west Ireland, the karst landscape of The Burren, were included to improve isoscape interpolation; however, this data is not used in statistical analysis.

Distinct depletion gradients are observed across Ireland, with enriched $\delta^{18}\text{O}$ values encountered in southern and western coastal areas and a progressive decrease towards inland regions, with the most depleted $\delta^{18}\text{O}$ values occurring along the eastern coast. Most annual and seasonal climatic variables (total precipitation, mean air temperature) exhibited significant positive correlations with groundwater $\delta^{18}\text{O}$, although a lack of significance was noted between $\delta^{18}\text{O}$ and mean air temperature during summer months ($p = 0.063$) (Table 2). Both latitude and longitude exhibit statistically significant associations with measured $\delta^{18}\text{O}$ ($p < 0.001$) (Table 2). The high level of association attributed to east–west location (X coordinate), concurs with a highly significant negative correlation between X-coordinate and total annual precipitation ($r = -0.690$, $p < 0.001$), thus indicating that groundwater $\delta^{18}\text{O}$ in the Republic of Ireland is driven by regional precipitation. Groundwater $\delta^{18}\text{O}$ was significantly associated with six of nine examined antecedent periods, most notably the 30-day ($p = 0.002$), 90-day ($p < 0.001$), 120-day ($p < 0.001$), and 150-day ($p = 0.001$) periods prior to sampling, with significance shown to peak at 120-days (Table 2).

4.2. Groundwater $\delta^{18}\text{O}$, geology and land-use

Highest mean groundwater $\delta^{18}\text{O}$ was associated with samples from regionally important aquifers (Mean -6.26‰); whilst generally unproductive bedrocks (Mean: -7.15‰) were associated with a significantly lower mean $\delta^{18}\text{O}$ than other aquifer productivity types ($p = 0.007$; Table 3). Contrasting $\delta^{18}\text{O}$ distributions were also associated with differing bedrock categories (Table 3, Fig. 5), with means ranging from -7.19‰ (Silurian volcanics and metasediments) to -5.37‰ (granites) ($p < 0.001$). A relatively narrow mean $\delta^{18}\text{O}$ composition range was encountered within varying limestone bedrock lithologies (-6.68‰ to -6.16‰), with a lower and narrower mean range found among sandstone types (-6.13‰ to -6.06‰).

Groundwater $\delta^{18}\text{O}$ exhibited limited variability with respect to subsoil type, ranging from -6.63‰ in areas dominated by well drained sands and gravels, to -6.22‰ in areas overlain by tills (Fig. 6a). Contrary to expectation, a statistically significant association was not found at the 95% CI between $\delta^{18}\text{O}$ and groundwater vulnerability category ($p = 0.100$) (Table 3). Overall, a lower $\delta^{18}\text{O}$ range and mean were associated with samples from Low vulnerability (thick overlying subsoil layers and/or low permeability subsoils) regions, with ranges and means exhibiting an overall increase in concurrence with increasing groundwater vulnerability. This pattern was not observed within X-Extreme zones (zones characterised by Extreme vulnerability classification, and located in karst areas or areas with sand/gravel aquifers), with the $\delta^{18}\text{O}$ mean rising from -6.05‰ (Extreme) to -6.29‰ (X-Extreme) (Fig. 6c). Similarly, measured $\delta^{18}\text{O}$ increased relatively linearly with decreasing subsoil thickness from $>10\text{ m}$ to 1 m (depth to bedrock). However, regions with $<1\text{ m}$ subsoil cover did not conform to this trend, instead exhibiting a marked mean increase (Fig. 6b). With respect to landuse/land cover classification (Fig. 6d), $\delta^{18}\text{O}$ means ranged from -5.81‰ (inland marsh) to -6.51‰ (urban/urban fringe), with no statistically significant difference found ($p = 0.63$; Table 3). Some level of association was noted between categorical drainage classification and measured $\delta^{18}\text{O}$ ($p = 0.079$), with means ranging from -6.21‰ in categorically

Fig. 4. Interpolated groundwater isoscape of $\delta^{18}\text{O}$ (‰) for the Republic of Ireland. Note, 'additional samples' sourced from [McCormack, et al. \(2014\)](#).

“dry” areas, to -6.49‰ in areas characterised by the presence of made ground.

4.3. Precipitation

Long-term weighted means of $-5.50 \pm 0.55\text{‰}$ (2012–2015) and $-8.27 \pm 0.46\text{‰}$ (2012–2015) were associated with Valentia and Armagh, respectively, resulting in a national precipitation gradient

of -2.5‰ to -3.0‰ over an approximate 400 km south-western to north-eastern profile.

The $\delta^{18}\text{O}$ composition of precipitation displays a marked seasonal trend, with high $\delta^{18}\text{O}$ during summer and low $\delta^{18}\text{O}$ during winter over the 1988–2015 period, with a notable annual decrease from September to October ([Fig. 7](#)). The groundwater sampling points at Portmagee and The Wood measured groundwater $\delta^{18}\text{O}$ compositions of -4.44‰ and -7.37‰ respectively. The

Fig. 5. Box-plot of $\delta^{18}\text{O}$ Stable Isotope Compositions ($n = 142$) delineated by aggregated bedrock type; cross wire represents outlier within 10% of IQR, star represents outlier >25% from IQR.

Fig. 6. (A) Groundwater $\delta^{18}\text{O}$ mean and aggregated subsoil type, (B) Groundwater $\delta^{18}\text{O}$ mean and categorical subsoil depth, (C) Groundwater $\delta^{18}\text{O}$ mean and vulnerability category, and (D) Groundwater $\delta^{18}\text{O}$ mean and land cover.

groundwater $\delta^{18}\text{O}$ composition measured at Portmagee overlaps with the mean $\pm$ SD of precipitation for the months between October and March from Valentia (Fig. 7a); whilst the groundwater $\delta^{18}\text{O}$ composition measured at The Wood overlaps with the mean $\pm$ SD of precipitation for the months between November and April from Armagh (Fig. 7b). The groundwater $\delta^{18}\text{O}$ composition at The Wood is closer to the mean of the long-term weighted annual precipitation mean.

4.4. Nested boreholes

Nested boreholes ($n = 35$) exhibited a mean $\delta^{18}\text{O}$ value of -6.23‰ (Std. Dev. 0.85) over a measurement range of 3.14 (Min: -7.53‰ ; Max: -4.38‰). Results indicate that groundwater becomes increasingly enriched with depth (Fig. 8; Table 5); significant correlations were found between $\delta^{18}\text{O}$ concentrations measured in subsoil and deep groundwater ($n = 7$; $R_{sp} = 0.88$; $p = 0.001$), transition and deep groundwater ($n = 13$; $R_{sp} = 0.81$; $p < 0.001$), and shallow and deep groundwater ($n = 14$; $R_{sp} = 0.73$; $p < 0.001$) profiles. In general, depleted values were found in layers

closest to the surface and enriched values encountered in deep groundwater at 10 of the 17 borehole nests.

4.5. Spatial cluster modelling

Four distinct clusters were found (1 – Coastal South; 2 – East/Midlands, 3 – Western Inland and 4 – Coastal West) (Fig. 9), with an associated silhouette measure of cluster adhesion and separation of 0.67 (i.e. well defined cluster membership). In terms of predictor importance, all clusters were characterised by the following predictor order: $\delta^{18}\text{O} \gg \text{X-coordinate} \gg \text{Y-coordinate}$. The largest cluster (Cluster-1; Coastal South; $N = 62$, 43.7%) was associated with a mean groundwater $\delta^{18}\text{O}$ of -6.10‰ , whilst clusters 2 (East/Midlands; $N = 40$), 3 (Western Inland; $N = 33$), and 4 (Coastal West; $N = 7$) had representative $\delta^{18}\text{O}$ means of -6.88‰ , -6.37‰ , and -4.69‰ , respectively.

Cluster-3 (Western Inland) was used as the reference category (i.e. models predict cluster membership based upon comparison with reference cluster) for multinomial logit modelling as the cluster mean was most comparable with the overall mean. The final

Fig. 7. Comparison of the $\delta^{18}\text{O}$ isotopic groundwater composition to mean weighted annual and seasonal averages of precipitation IAEA data from (a) Valentia and (b) Armagh and monthly precipitation amounts.

optimised multinomial logit model is presented in Table 4. Overall, the model had a high Pearson goodness of fit ($\chi^2 = 378.021$, $p = 0.698$), likelihood ratio ($\chi^2 = 142.934$, $p < 0.001$), a moderate/high pseudo R^2 value (Nagelkerke $R^2 = 0.697$ i.e. 69.7% of system variability described), and correctly classified 76.1% of sample points to the appropriate spatial cluster ranging from 71.4% (Cluster-4) to 80% (Cluster 2). As shown (Table 4), the optimised model includes mean annual rainfall and mean annual temperature (interaction variable), source type (borehole/spring), aggregated aquifer type, and a dichotomised drainage variable (Dry/Not Dry). Due to the expected relationship between recharge and

groundwater $\delta^{18}\text{O}$, models were developed with forced entry of both recharge coefficient (mm/year) and estimated recharge rate (mm), with an improved model not found in either case.

5. Discussion

5.1. Climatic drivers

A direct relationship was found between measured groundwater $\delta^{18}\text{O}$ and long-term (1980–2010) mean annual precipitation,

Fig. 8. Relationship between $\delta^{18}\text{O}$ isotopic composition in deep groundwater and groundwater $\delta^{18}\text{O}$ isotopic composition in (a) subsoil (b) transition and (c) shallow groundwater zones in nested boreholes from poorly productive bedrock aquifer systems.

Table 4

Multinomial Logit model for developed groundwater $\delta^{18}\text{O}$ clusters.

Effect	–2 Log Likelihood of Reduced Model	Chi-Square*	df	Sig.
Model Intercept	196.861	0.000	0	
AnnRainfall*AnnTemp	270.960	74.099	3	<0.001
Sample Source	217.526	20.664	3	<0.001
Gen_Aquifer_Type	214.097	17.236	6	0.008
Drainage (Dry/Not Dry)	205.847	8.986	3	0.029

* The chi-square statistic is the difference in –2 log-likelihoods between the final model and a reduced model. The reduced model is formed by omitting an effect (variable) from the final model.

Table 5

Average groundwater $\delta^{18}\text{O}$ from monitoring units in borehole nests.

Site	Subsoil	Transition	Shallow groundwater	Deep groundwater	Aquifer vulnerability
Dripsey	n/a	–6.42 (2)	–6.1 (3)	–5.94 (3)	High
Glencastle	–5.21 (3)	–5.87 (2)	–5.51 (3)	–4.76 (3)	High/Extreme
Gortinlieve	–7.16 (1)	–6.72 (3)	–6.52 (2)	–6.58 (3)	High
Mattock	–6.77 (2)	n/a	–7 (2)	–7.17 (2)	Low
New Village	n/a	–5.42 (3)	–5.04 (3)	–5.03 (3)	Extreme
Ryewater	–6.83 (1)	–7.2 (3)	–7.37 (1)	–7.22 (3)	Medium

* n/a implies the monitoring unit is not present at respective location.

similar to that reported in previous studies (e.g. Darling et al., 2003; Wassenaar et al., 2009); whilst wind direction was also considered, it was omitted due to multi-collinearity with rainfall; however, wind movement in Ireland is known to be dominated by south-westerly prevailing winds (<http://www.met.ie/climate/climate-of-ireland.asp>). Seasonal analysis reveals that statistical correlations become stronger during autumn and winter months, i.e. primary recharge periods in humid-temperate climates (Darling et al., 2003). Winter recharge is also reflected via associations with air temperature; significant correlations were observed between long-term mean annual winter temperatures, whilst no significant relationship was found with mean annual summer temperatures over the same period. Previous studies have shown that the $\delta^{18}\text{O}$ composition of shallow groundwater may become enriched by soil evaporation, albeit more so in arid and Mediterranean regions with irrigated soils (e.g. Davisson and Criss, 1993; Ma et al., 2017), than in temperate regions (Sprenger et al., 2016). However, whilst the mean annual temperature gradi-

ent across Ireland is relatively uniform, it is unknown whether soil evaporation is a driving process influencing the temporal $\delta^{18}\text{O}$ composition of groundwater.

The relative timing of recharge was investigated via development and analysis of local antecedent rainfall periods (Table 2); significant $\delta^{18}\text{O}$ relationships were associated with longer (>90 days) periods, with levels of association decreasing beyond 150 days, thus implying most effective recharge occurs within 3–5 months following rain deposition. However, the association with antecedent rainfall conditions is complicated somewhat by the observed association between shorter periods (48 h) of antecedent rainfall and groundwater $\delta^{18}\text{O}$. The authors consider that this is suggestive of rapid bypass/recharge or localised preferential flow into deeper groundwater systems as a secondary mechanism at some sources, resulting in short-term (1–5 days) variations in $\delta^{18}\text{O}$. These processes have been previously reported in fractured hard rock aquifer systems in Ireland (Cai and Ofterdinger, 2016) and further afield (e.g. Gleeson et al., 2009; Sánchez-Murillo and

Fig. 9. The Republic of Ireland with developed spatial cluster members.

Birkel, 2016; Ma et al., 2017). These relatively rapid recharge rates thus provide further evidence of the (expected) high hydrological turnover of groundwater in Irish aquifer systems.

5.2. Geological drivers

Whilst results indicate that precipitation is the predominant driver of groundwater $\delta^{18}\text{O}$ composition in Ireland, multinomial logit modelling indicates that local/regional geological setting

exerts a parallel (albeit lesser) influence. Mean groundwater $\delta^{18}\text{O}$ differences may reasonably be ascribed to the geographical position of the sampling point, however the contrasting ranges in variance indicate likely differences in groundwater residence time, signifying that differing groundwater flow systems will be more sensitive to characteristic infiltration and recharge rates. Thus, findings indicate that systems with generally low residence times, such as limestone karst systems, will likely exhibit seasonal patterns in groundwater $\delta^{18}\text{O}$ composition, whereas low productivity

systems with high residence times (e.g. granites) will likely display a dampened $\delta^{18}\text{O}$ composition to groundwater recharge and therefore exhibit more temporally constant $\delta^{18}\text{O}$ values (Fig. 5). However, no univariate relationship was found between groundwater $\delta^{18}\text{O}$ and aquifer type. The aquifer classification scheme entails grouping different bedrock lithological types and therefore does not necessarily account for the geological heterogeneities influencing recharge rates and $\delta^{18}\text{O}$ composition. This likely explains why significant correlation are found between bedrock type and groundwater $\delta^{18}\text{O}$, but not the broader aquifer classification type.

Previous studies have shown that the characteristics of subsoil overlying a bedrock aquifer will influence the groundwater $\delta^{18}\text{O}$ composition (e.g. Gleeson et al., 2009; Ma et al., 2017). Whilst no significant relationship was found between overlying sediment type and groundwater $\delta^{18}\text{O}$ in the current study, significant associations were found between both subsoil depth and groundwater 'vulnerability'. Highest $\delta^{18}\text{O}$ mean values were associated with categorically *Extreme* areas, with means progressively decreasing in parallel with subsoil depth (i.e. *Low* vulnerability) (Fig. 6c), suggesting seasonal isotopic composition is dampened with increasing soil depth. Conversely, non-significant associations were observed within *X-Extreme* zones i.e. areas with little or no soil cover, indicating that attenuation of temporal precipitation compositions are limited in these areas.

5.3. Precipitation $\delta^{18}\text{O}$ gradient and groundwater interaction

The estimated precipitation $\delta^{18}\text{O}$ gradient ($<-3.0\text{‰}$) across Ireland is significantly greater than that previously reported by Rozanski et al. (1993) and Bowen and Revenaugh (2003), who estimated a precipitation gradient of -2.0‰ , per 1000 km across continental Europe. This finding indicates rapid rainfall deposition from air masses moving inland from the southern and western coastal regions of Ireland.

The results of $\delta^{18}\text{O}$ measured in groundwater sampling locations close to the IAEA precipitation stations gives further detail on the influence of geological factors on groundwater $\delta^{18}\text{O}$ composition. The groundwater sampling point at 'Portmagee' is located in a categorically *Extreme* vulnerability area and within a poorly productive bedrock region; whilst 'The Wood' is located in a categorically *Low* vulnerability that is underlain by a karstified bedrock aquifer. Though definitive conclusions cannot be made in the absence of inter-annual groundwater $\delta^{18}\text{O}$ data, results from the current study suggest that where overlying subsoil layers are thin (i.e. *High* and *Extreme* vulnerability), groundwater $\delta^{18}\text{O}$ will generally be reflective of the seasonal precipitation content (e.g. 'Portmagee'), and respond more readily to recharge events, whereas *Low* vulnerability areas are more representative of the long term precipitation $\delta^{18}\text{O}$ mean due to slower recharge rates (e.g. 'The Wood'). Groundwater $\delta^{18}\text{O}$ content will also be influenced by the hydrogeological properties of the bedrock, likely explaining why the selected groundwater installation near Armagh exhibited a higher level of enrichment compared with the annual precipitation mean i.e. due to the karstified nature of this groundwater system, and the likelihood that groundwater in the area is recharged, and transported, from other areas in the catchment.

5.4. Groundwater depth profiles

Analysis of nested boreholes located in poorly productive aquifer systems reveal a relatively consistent progressive depletion of groundwater $\delta^{18}\text{O}$ in concurrence with increasing depth (Fig. 8; Table 5). Measured $\delta^{18}\text{O}$ values in deep groundwater are more likely representative of the long term groundwater $\delta^{18}\text{O}$ mean, whilst groundwater $\delta^{18}\text{O}$ content in shallower samples are derived from recent recharge and thus exhibit a more seasonally variable

$\delta^{18}\text{O}$ composition, similar to those observed in precipitation (Fig. 7). Previous studies have found that soil depth exhibits a direct correlation with isotopic enrichment of groundwaters (Darling and Bath, 1988; Davisson and Criss, 1993; Ma et al., 2017). Gradient profiles may thus potentially be used to indicate when recharge from recent rainfall events influences deeper groundwater $\delta^{18}\text{O}$ composition. A previous study (Cai and Ofterdinger, 2016) at two of the nested boreholes sites (Glencastle and Gortlinlieve) (Fig. 1), both of which are located in hard metamorphic bedrock regions, found that recharge processes at Gortlinlieve were dominated by fast infiltration pathways, whilst recharge at Glencastle was dominated by slower matrix flow. The measured $\delta^{18}\text{O}$ values appear to confirm these findings with similar shallow and deep groundwater $\delta^{18}\text{O}$ values at Gortlinlieve indicating rapid mixing and decreased temporal attenuation in shallow groundwater, whereas the observed downward enrichment gradient in $\delta^{18}\text{O}$ at Glencastle indicates slower rates of water movement.

5.5. Limitations

Whilst the current study presents and analyses a significant spatial dataset of groundwater $\delta^{18}\text{O}$ from the geologically diverse Republic of Ireland, it is important to note that groundwater isotope measurements were attained during one relatively short (8 weeks) sampling period, and therefore do not account for within- and inter-annual variation. Seasonal patterns in precipitation $\delta^{18}\text{O}$ are evident from Irish IAEA monitoring stations, with results indicating that seasonal precipitation patterns are reflected in groundwater, and particularly in *High/Extreme* vulnerability areas. In order to confidently discern temporal disparities, seasonal monitoring is necessary, and therefore recommended. There are also areas of Ireland, such as in the southwest, that are poorly represented on the presented isoscape and should be included for future study. Moreover, $\delta^{18}\text{O}$ studies are typically undertaken in conjunction with the measurement of stable hydrogen isotopes, deuterium (δD). Whilst the relationship between $\delta^{18}\text{O}$ and δD is typically linear (e.g. Wassenaar et al., 2009; Raidla et al., 2016), δD measurement is primarily used to quantify evapotranspiration (δD excess; and the global and local meteoric water lines). Accordingly, future studies should include δD in order to better indicate precipitation origin and evaporative effects. Recent studies (e.g. Sánchez-Murillo and Birkel, 2016) have employed both precipitation and groundwater isoscapes to calculate $\delta^{18}\text{O}$ ratios and estimate recharge rates. An isotopic precipitation network would therefore greatly aid the understanding of oftentimes complex recharge process in Ireland.

6. Conclusions

This study presents an updated groundwater $\delta^{18}\text{O}$ isoscape for Ireland and examines the geo-climatic drivers controlling these isotopic compositions. Although it was not possible to effectively characterise temporal isotopic variation within the scope of this research, results are considered to represent the geospatial $\delta^{18}\text{O}$ condition with respect to Irish groundwaters. Overall, groundwater $\delta^{18}\text{O}$ was confirmed to vary by more than 3‰ (Min: -7.53‰ ; Max: -4.13‰ ; $n = 142$), characterised by high $\delta^{18}\text{O}$ values in southern and western coastal regions, becoming progressively depleted towards the eastern coast. Location with respect to orographically influenced rainfall deposition and annual precipitation volume are the primary determinants of groundwater $\delta^{18}\text{O}$ content in the Republic of Ireland, thus indicating relatively modern groundwater recharge as the primary isotopic source. This is further substantiated by antecedent rainfall analysis, with significant associations observed for rainfall volumes from 1 to 5 months (and particularly

3–5 months) prior to groundwater sampling, with a clear dominance displayed by winter recharge.

Logit modelling of locational clusters shows that local/regional (hydro)geological setting exerts an additional influence on groundwater $\delta^{18}\text{O}$ composition, with high productivity bedrocks (e.g. karst limestone), bedrock aquifers with little or no soil/subsoil cover, and regions characterised by *High/Extreme* groundwater vulnerability, found to be more likely to attenuate the seasonal precipitation $\delta^{18}\text{O}$ composition. Conversely, groundwater from poorly productive bedrocks, regions with high groundwater residence times (e.g. bedrocks capped with significant subsoil depths), and *Low/Moderate* aquifer vulnerability areas, were more likely to reflect the long-term mean annual precipitation composition. However, differences between seasonal and annual groundwater $\delta^{18}\text{O}$ compositions are likely to be relatively minor, with the presented groundwater $\delta^{18}\text{O}$ isoscape reflecting the nature of hydrogeology in Ireland being characterised by shallow groundwater conditions and high (hydrological) turnover.

Study findings are considered informative with regard to other practical applications. The observed variation of $\delta^{18}\text{O}$ with depth through the groundwater column, and the measured short-term (48 h) response to rain-events at some sources, suggests that a geologically focused, temporal monitoring programme be employed to better understand and thus improve local and regional groundwater recharge estimation, and particularly in hard rock systems. Additionally, based upon study findings, the authors advise caution be employed when using $\delta^{18}\text{O}$ as an environmental tracer in hydrograph separation studies (i.e. delineation of surface water-groundwater interactions); the spatial $\delta^{18}\text{O}$ distributions of precipitation and groundwater, as well as inter-annual temporal variation, tend to be locally or regionally specific. Finally, considering the strong association between the $\delta^{18}\text{O}$ composition in precipitation and groundwater, the $\delta^{18}\text{O}$ composition of groundwater may be useful as a proxy for the long term fluctuation in key climatic parameters, such as temperature and precipitation, and therefore changes related to climate and groundwater resources, however more research is required to bear this out.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhydrol.2017.09.017>.

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