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A multi-disciplinary investigation of the provenance, pathways and geothermal potential of Irish thermal springs

A thesis submitted to the School of Natural Sciences, National University of Ireland, Galway, for the degree of

Doctor of Philosophy

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February 2016

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IRETHERM

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Summary

The geothermal energy of thermal groundwater is currently being exploited for district-scale heating in many locations world-wide. The Carboniferous bedrock in the south and east of Ireland hosts a number of thermal springs with temperatures ranging from 12 – 25 °C. These temperatures are elevated with respect to average Irish groundwater temperatures (9.5 – 10.5 °C), and represent a geothermal energy potential, which is currently under evaluation. This thesis furthers our understanding of the sources, circulation pathways and temporal variations of the Irish thermal springs, by using a multi-disciplinary methodology (including audio-magnetotelluric (AMT) geophysical surveying, time-lapse temperature and chemistry measurements, and hydrochemical analysis) to develop hydrogeological conceptual models for several of these springs.

A sub-set of six springs in the Carboniferous limestones of the Dublin Basin were examined. Seasonal hydrochemical data were explored using multivariate statistical analysis to investigate the source aquifers of the thermal groundwaters. The analysis indicates that the thermal waters flow within the limestones of the Dublin Basin, and there is evidence that some springs receive a contribution from deep-basinal, saline fluids. Three-dimensional electrical resistivity models of the subsurface were constructed from AMT data collected at Kilbrook spring (maximum of 25.0 °C) and St. Gorman’s Well (maximum of 21.8 °C). These models revealed two types of geological structure beneath the springs; (1) Carboniferous normal faults, and (2) Cenozoic strike-slip faults. The karstification of these vertically-persistent structures, particularly where they intersect, has provided conduits that facilitate the operation of a relatively deep hydrothermal circulation pattern (likely estimated depths between 240 and 1,000 m) within the Dublin Basin. The thermal maximum and simultaneous increased discharge observed at several of the springs each winter must be the result of rapid infiltration, heating and re-circulation of meteoric waters within a structurally- and recharge-controlled hydrothermal circulation system.
Declaration

This work has not previously been submitted for a degree in any university. To the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the thesis itself.

_____________________
Sarah Blake

Dublin, February 2016
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But it's hark! the whistle's blowing with a wild, exultant blast,
And the boys are madly cheering, for they've struck the flow at last:
And it's rushing up the tubing from four thousand feet below,
Till it spouts above the casing in a million-gallon flow.
And it's down, deeper down-
Oh, it comes from deeper down:
It is flowing, ever flowing, in a free, unstinted measure
From the silent hidden places where the old earth hides her treasure-
Where the old earth hides her treasures deeper down.

‘Song of the Artesian Water’ by Banjo Paterson (1896)
1. Introduction

1.1. Key concepts

The geothermal energy of deep, thermal groundwater is currently being exploited for a range of applications in many locations world-wide, and its potential is now being explored in Ireland as part of the IREETHERM project (www.iretherm.ie). Ireland is situated in a low-enthalpy geothermal setting, far from any tectonic plate boundaries or active volcanism. Nevertheless, there exist at least forty-two occurrences of thermal springs and thermal shallow groundwater in the south and east of the island (Goodman et al., 2004; Figure 1-1). The aim of this thesis is to investigate the provenance and the geothermal energy potential of the heated groundwater using a multi-disciplinary approach.

Figure 1-1: Irish thermal spring and thermal shallow groundwater locations (after Goodman et al., 2004), with the approximate trace of the Iapetus Suture Zone (after Wilkinson, 2010) and Carboniferous strata (from www.gsi.ie).
A spring is defined as a location on the Earth’s surface where groundwater visibly discharges from an aquifer (Kresic, 2010). This discharge is due to a difference in elevation between the hydraulic head in the aquifer and the land surface (hydraulic head is measured in metres and expresses the energy in a fluid as the height of a column of the fluid). This difference in elevation can arise in a number of ways, and springs can be broadly divided into two groups based upon the hydraulic head conditions in the source aquifer; (1) gravity, or descending, springs occur where the water table of an unconfined aquifer intersects the land surface, and (2) artesian, or ascending, springs occur where water discharges at the land surface under pressure from the confined conditions in the aquifer. The emergence or occurrence of a spring in a particular location is dependent upon the geological characteristics, the topography of the land surface, and the hydrogeological recharge pattern. Intermittent springs are those that discharge periodically at certain times of the year, in response to groundwater recharge patterns. The nature of karst aquifers make intermittent springs a common feature of the karst landscape, as karst conduits can rapidly transmit large volumes of recharge waters to a previously dry spring orifice. Faults can play a major role in the emergence of springs, particularly in fractured bedrock and karst aquifers (Figure 1-2). If the permeability of the bedrock is increased in a fault zone, the fault may provide conduits for groundwater storage and flow, and provide a barrier to flow across the fault (Bense et al., 2013), forcing groundwater to circulate in the plane of the fault.

A thermal spring is often defined as a spring with a mean annual temperature that is above the mean annual air temperature at the spring’s location (e.g., Drew, 2001; Kresic, 2010), however there is no universally accepted classification for a thermal spring. Thermal springs can be broadly divided into “warm” and “hot” springs depending upon their temperature (“hot” springs have a higher temperature than “warm” springs). “Hot” thermal springs are associated with areas of high-enthalpy geothermal activity, where the near-surface geothermal gradient is high. The geothermal gradient describes how the temperature of the Earth increases with depth at a particular location, and is measured using detailed downhole temperature measurements in boreholes. The near-surface geothermal gradient is higher near tectonic boundaries where the Earth’s heat escapes from the interior of the planet. The global average geothermal gradient is estimated to be 30 °C/km (Kresic, 2010).
Geothermal systems are commonly described as being either high- or low-enthalpy (see e.g., Xydis et al., 2013); this is a qualitative description of the amount of heat energy available in the system. A low-enthalpy, or low-temperature geothermal system is defined as one in which the temperature of the groundwater is generally below 150 °C at a depth of one kilometre (Axelsson et al., 2010).

Thermal springs with very high temperatures occur around the world in active volcanic areas, and can erupt as geysers and fumaroles where the pressures and temperatures are sufficient to boil the groundwater (e.g., Geysir, Iceland; Suwa Geyser, Nagano, Japan; Old Faithful Geyser, Wyoming, U.S.A.). The highest temperatures measured at the surface of these geysers tend to hover around the boiling point of water (100 °C at sea level), although they may be super-heated by a few degrees (Kresic, 2010). Even higher temperatures exist at depth beneath the springs. High-temperature thermal springs can also occur in extensional rift settings, such as the European Cenozoic Rift System in central Europe (Rajchl et al., 2009). This rift system is the cause of many famous high-temperature thermal springs in the Upper Rhine Graben (e.g., Wiesbaden, Germany; springs with temperatures up to 70 °C (Loges et al., 2012)) and the Eger Rift (e.g., Karlovy Vary, Czech Republic; temperatures up to 73 °C (Vrba, 1996)), among other areas. The geothermal gradient in these high-enthalpy settings is enhanced, and, when coupled with a significant permeability along fractures and faults in the bedrock, may allow for the circulation and storage of large amounts of heated groundwater at relatively shallow depths beneath the surface. Lower-temperature thermal springs and even cold springs can also be found in active volcanic areas and extensional rift settings, where they may be a result of hot groundwater mixing with cold groundwater (e.g., Figure 1-2).

Thermal springs can also be found in low-enthalpy settings, (such as Ireland) where there is no appreciable enhancement of the near-surface geothermal gradient. Vertical or sub-vertical fault zones can provide permeable pathways parallel to the fault core (Bense et al., 2013) through otherwise impermeable bedrock, and can facilitate the rapid movement of heated water from a deep, warm aquifer to discharge at the land surface as an artesian thermal spring. These fault-controlled features can be spatially limited to very discrete areas, and may occur adjacent to cold spring features, depending upon the geological complexity of the area. Low-temperature thermal springs with temperatures between 20 and 50 °C (defined as “warm” by the
U.S. NOAA, www.ngdc.noaa.gov) exist in the sedimentary rocks of the Appalachian area of the eastern U.S.A., and the occurrence of these springs is governed by structural and lithological controls (Hobba et al., 1979).

Figure 1-2: Schematic representation of an example of upwelling of thermal groundwater along a fault zone. From Kresic (2010).

1.1.1. The Irish thermal springs

In Ireland, average groundwater temperatures typically range from 9.5 to 10.5 °C (Aldwell and Burdon, 1980). As defined by Aldwell and Burdon (1980), and Goodman et al. (2004), thermal springs are considered to be those natural groundwater springs where the mean annual temperature is appreciably warmer than average groundwater temperatures. In this study springs with a mean annual temperature above 12 °C are considered thermal (this threshold between “warm” and “cold” Irish groundwater is also used by Aldwell (1996), Goodman et al. (2004) and Mooney et al. (2010)). The average annual air temperature for the south and east of Ireland (where the thermal springs occur, Figure 1-1) is between 9 and 10 °C (data from Met Éireann, www.met.ie), so a lower limit of 12 °C also satisfies the widely used criteria that a thermal spring should have a higher temperature than the average annual air temperature at its location.

The thermal springs and thermal shallow groundwater occurrences recorded to date in Ireland range in temperature from 12 °C to 25 °C, and three of these are known to have maximum temperatures in excess of 20 °C. The thermal springs issue from limestone bedrock of Carboniferous age (Figure 1-1) and follow a NE – SW distribution pattern that is broadly coincident with the Iapetus Suture Zone, a major Caledonian tectonic structure in Irish geology. Some of the thermal springs have
been utilised in the past as therapeutic spa wells (e.g., Lady's Well, Mallow, Co. Cork, average temperature of 19.5 °C; Louisa Bridge Spa Well, Leixlip, Co. Kildare, maximum of 17.5 °C), and many more have religious and cultural significance, as “holy wells”, as is evident from their names (e.g., St. Brigid's Well, Co. Dublin, maximum of 19 °C; St. Gorman's Well, Co. Meath, maximum of 21.8 °C). The thermal spring waters at Lady’s Well in Mallow have also been used to partially heat a municipal swimming pool (Goodman et al., 2004). This is the only example recorded to date of an Irish thermal spring being utilised as a source of geothermal energy.

The stable isotopic ratios of the warm springs indicate that they are predominantly meteoric in origin (Burdon, 1983; Mooney et al., 2010), which suggests that, despite their elevated temperatures, the major component of the thermal spring water comes from relatively shallow, relatively recent recharge events. The Irish thermal springs are therefore expected to comprise a mixture of groundwaters from different sources and different recharge areas. These groundwaters are expected to have different depths of circulation and different residence times within the host bedrock. Understanding the interactions of these hydrochemical elements is critical for characterising the springs as a geothermal energy resource.

1.1.2. Geothermal energy potential of the Irish thermal springs

Thermal springs and their associated hydrothermal systems are used worldwide for energy, heating and recreational purposes. Their use and energy potential depends largely upon the amount of heat available (dependent on temperature and volume of water). If the hydrothermal circulation system is large enough, high-temperature springs and super-heated groundwater in volcanic areas can be used for large-scale heating projects and even electricity production (e.g., in 2014, Iceland fulfilled 28.9 % of its total electricity requirements from geothermal power plants (National Energy Authority of Iceland, www.nea.is)). Lower-temperature thermal groundwater from low-enthalpy geothermal settings may also be exploited for local and district-scale heating projects, e.g., Paris, France (Castillo et al., 2011), and Southampton, United Kingdom (Busby, 2010).

The geothermal energy potential of Ireland is currently being explored as part of the IREHERM project, funded by Science Foundation Ireland, one aim of which is to
determine the suitability of Irish thermal springs as a geothermal energy resource. The Irish thermal springs are undoubtedly a low-enthalpy resource, given their relatively low temperatures coupled with Ireland’s aseismic and non-volcanic geological setting. Notwithstanding the low temperatures, there are three ways in which Irish thermal groundwater may have geothermal energy potential.

i) **Local-scale heating requirements**
At their present temperatures, heat energy could be abstracted from the spring waters as they emerge at the surface, or the thermal groundwater could be intercepted in the subsurface with shallow boreholes. This energy could be supplemented with a heat pump to provide the desired end-temperatures (e.g., Sparacino et al., 2007). Applications could include local-scale heating projects such as greenhousing, aquaculture, domestic and industrial central heating, and recreational purposes such as spas or swimming pools (e.g., Xydis et al., 2013). The municipal swimming pool at Mallow, Co. Cork is partially heated by thermal groundwater (19 °C) abstracted from the hydrothermal feeder structures supplying Lady’s Well thermal spring (Goodman et al., 2004).

ii) **District-scale space heating**
If groundwaters with higher temperatures (in excess of 30 °C) can be abstracted from deeper boreholes in the vicinity of one of the springs, this could facilitate large-scale heating projects in nearby building infrastructure, such as apartment blocks and large public or industrial buildings. Low-enthalpy, district-scale heating by thermal groundwater is in operation in many locations worldwide, including, e.g.; Paris, France (Castillo et al., 2011), where water between 57 and 85 °C is abstracted from between 1.5 and 2 km depth; Southampton, United Kingdom (Busby, 2010), where brine with a temperature of 76 °C rises naturally from 1.8 km depth to 100 m below the surface; and the Minewater project in Heerlen, the Netherlands (Verhoeven et al., 2013), which abstracts thermal waters of 31 °C from flooded coal mine shafts at a depth of around 700 m. The installation of such a system commonly involves a series of doublets, which facilitates the abstraction of heated waters and the re-injection of the relatively cooled wastewaters. Figure 1-3 shows a schematic of such an operation from Heerlen. The success of such a heating system largely depends upon the location of the thermal aquifer in an urban environment, close to endusers.
iii) Electricity production

The geothermal gradient in Ireland is poorly understood due to a paucity of deep borehole temperature measurements, but is estimated at 25 °C/km for the Irish Midlands (Goodman et al., 2004). Technological advances in using intermediate-temperature (110 – 160 °C) groundwaters in binary-cycle power-plants (Franco and Villani, 2009) provide real potential for electricity generation within the range of geothermal gradients observed in Ireland, provided deep (4 – 5 km) source regions can be identified. Permeability and the volume of water available for abstraction is also a critical factor in determining the viability of deep geothermal systems. Franco and Villani (2009) conclude: “Geothermal binary plants can be competitive with other energy conversion technologies if and only if acceptable brine consumption levels (kg/s per net MW of electricity (MWe) generated) can be attained”. The results of their study showed that a source temperature of 110 °C may require up to 120 kg/s/MWe of input fluids, which could render the geothermal plant economically infeasible. By contrast, a higher temperature input fluid of 160 °C could only require 20 kg/s/MWe of fluid.
Higher observed geothermal gradients in the Rathlin Basin, Antrim, Northern Ireland (42 °C/km; Goodman et al., 2004) and in Newcastle, Co. Dublin (33 °C/km; Allen and Burgess, 2010) indicate the presence of temperatures in excess of 100 °C at depths of between 2.5 and 3 km. The geothermal gradients in Rathlin and Newcastle were calculated from detailed temperature measurements in deep boreholes (1,482 and 1,337 m respectively). Care must be taken when extrapolating a geothermal gradient measured at shallow depths to deeper regions, as a linear extrapolation of the gradient does not take into account the decrease in porosity with depth, which can cause a decrease in the geothermal gradient due to the increase in bulk thermal conductivity. Sharp breaks in the geothermal gradient can occur as a result of thermal advection (i.e., fluid movement through fractures) or at the top of over-pressured reservoirs, where the increased water content in over-pressured shales results in an increase in geothermal gradient. Thermal springs are likely to be indicators of deep-seated hydrothermal circulation patterns (i.e., indicators of the presence of deep, permeable reservoirs of heated waters), and in some areas it may prove possible for these hydrothermal systems to be intercepted at significant depths to obtain temperatures in excess of 110 °C.

1.2. Research questions

This thesis describes the investigation of the Irish thermal springs as carried out within the IRETHERM project. The broad aims, or research “questions”, driving this work were to (1) identify the source aquifer(s) for the thermal waters, (2) characterise the circulatory system, and (3) assess the potential for the existence of deeper, higher-temperature circulation patterns for future geothermal exploitation. A brief background to each of these research questions is provided below.

What is the source of the thermal water?

The Irish thermal spring waters are mainly composed of waters that are recently recharged from rainfall events. From previous studies (Burdon, 1983; Mooney et al., 2010), it is recognised that most of the thermal springs have major ion hydrochemistry that is comparable to the calcium-bicarbonate signal that is typical of many Irish groundwaters circulating in limestones. However, there are hydrochemical traits in some of the thermal springs that, along with their elevated
temperatures, hint at longer residence times and deeper circulation patterns (e.g., the high electrical conductivities seen in St. Edmundsbury spring and Louisa Bridge Spa Well). Dissolved inert gas and stable isotopic analyses carried out by Burdon (1983) suggest that Louisa Bridge Spa Well has a component of long-residence-time water with a residence time in excess of 30,000 years. Thus, water samples recovered from the Leinster thermal springs are likely to be a mixture of at least two groundwater components of different residence times, and from different sources and different recharge areas (e.g., the deeper-circulating, older waters and the recent recharge waters). Aside from any geothermal utilization where the spring water is taken “as is” from the surface or shallow subsurface, pinpointing the source aquifer for the thermal water is crucial if the springs’ hydrothermal systems are to be exploited.

**How does the thermal water circulate in the subsurface?**

The Irish thermal springs occur in Carboniferous limestone bedrock, which has a poor primary porosity. The majority of the transmission of groundwater in this bedrock is likely to occur in secondary porosity joints, fractures and conduits. The karstic presentation of some of the springs (issuing from conduits; ephemeral ponds; rapid onset of artesian flow) suggests that the thermal waters ascend to the surface through dissolutionally enhanced fissures and fractures in the limestone bedrock. Characterising these feeder structures (orientation, vertical extent, hydraulic capabilities) is of crucial importance for targeting drillholes for future geothermal exploration.

**Do deeper, higher temperature waters exist at greater depths beneath the springs?**

The promising geothermal gradients in the Rathlin Basin, Antrim, and in Newcastle, Dublin, indicate that there is the potential for high temperatures (necessary for electricity production) at accessible depths in Ireland. However, no thermal springs exist in these areas of enhanced geothermal gradients. In the absence of enhanced geothermal gradients, is it possible for significant reservoirs of high-temperature groundwaters to be found relatively close to the surface, if they are able to exploit major, vertical tectonic structures and ascend quickly? Are the thermal springs a “smoking gun” indicating the presence of a regional-scale hydrothermal circulation pattern along the deep-seated NE – SW faults associated with the Iapetus Suture Zone (Figure 1-1; and Chapter 2, section 2.2.1)? Primary and secondary porosity
generally decrease with depth, even though relatively deep karst features (caves, conduits) can be formed at depths in excess of 500 m (Kaufmann et al., 2014). The significant NE – SW tectonic fabric associated with the Iapetus Suture Zone is likely to be pervasive through the entire crust, so is the most likely candidate for facilitating deep circulation patterns of thermal waters.

1.3. Scope of thesis

IRETHERM is an academic-government-industry collaborative project to develop a strategic and holistic understanding of Ireland’s geothermal energy potential through integrated modelling of new and existing geophysical and geological data. Eight “targets” for further investigation, primarily using electromagnetic geophysics, were identified; the Irish thermal springs constitute one of these targets, and are explored in this thesis. The thermal springs are the surface expression of highly complex, and largely inaccessible, natural systems. A multi-disciplinary approach was adopted, including electromagnetic geophysical surveys, hydrochemical analysis and detailed temperature and chemistry measurements, in order to address the specific research aims of this thesis (section 1.2 above).

This work incorporates knowledge and methods from many related fields in the Earth sciences (geology, hydrogeology, geophysics, geochemistry), and utilises two complex disciplines in particular – multivariate statistical analysis and magnetotellurics (a natural source electromagnetic geophysical prospecting technique). The innovation of this work was to apply these developed techniques in their most up-to-date formats in an efficient way on new data from the thermal springs, to gain the maximum amount of information from these complex, and potentially economically valuable, natural systems. This work is the first time that multivariate statistical analysis has been used on thermal groundwaters in Ireland, and it is the first time that a compositional data analysis approach has been used on Irish groundwater samples. It is also the first time that audio-magnetotellurics has been used to create three-dimensional (3-D) electrical resistivity images of the subsurface beneath the springs. This thesis does not dwell on an in-depth exposition of the theory behind any of the methods used, but rather aims to give the reader a firm grounding in the basics of each method, the practicalities of their application to real data, and the benefits of integrating information from different disciplines. This
thesis will also provide the reader with references, should they wish to gain a more detailed understanding of the techniques. The strong focus of each of the research papers that constitute this thesis is the joint application of several lines of enquiry to develop a hydrogeological conceptual model of a real-world, “black box”, natural system.

A sub-selection of six thermal springs in Leinster was chosen for detailed investigation in this work (Figure 1-4). These springs were chosen both for their individual hydrogeological attributes, and for their proximity to urban centres in the east of Ireland, which could make them suitable for geothermal use. The detailed geological and hydrogeological background for these springs is discussed in Chapter 2, section 2.2. For scientific and logistical reasons, it was deemed a better use of resources if a deep understanding of a small number of springs was obtained; rather than a more superficial study of a larger number of springs. Some cost- and time-saving compromises were made: historical groundwater chemistry data from the Hydrometric and Groundwater Section of the Environmental Protection Agency were used as a cold groundwater comparison; loggers to measure only temperature and electrical conductivity were purchased as they were less expensive than those with water level recorders; and spring discharges were not measured in any systematic way during this project as the maintenance and construction of weirs would have been too costly. Isotopic and gas measurements and analysis were also unfortunately beyond the scope of this project. Two of the six thermal springs were selected for geophysical surveying and modelling (see Figure 1-4).

The specific aims of this thesis have been formulated in order to address the research questions described in section 1.2, and they are as follows:

1. Investigate the source of the thermal waters using multivariate statistical analysis of new hydrochemical data from the thermal springs (Chapter 2);
2. Compare the hydrochemistry of the thermal spring waters to “average” cold groundwaters from limestone bedrock (Chapter 2);
3. Characterise the temporal behaviour of the springs and how they relate to seasonal recharge (Chapters 2, 3 and 4);
4. Characterise the conduits or pathways supplying the thermal waters to the surface using a passive, deep-reaching, geophysical method (audio-magnetotellurics) (Chapters 3 and 4); and
5. Explore the possibility or evidence for deeper circulation patterns, which may offer higher temperature waters (Chapter 5).

Figure 1-4: Leinster thermal springs selected for further investigation. AMT surveys and modelling carried out at St. Gorman’s Well and Kilbrook spring. Geological map from www.gsi.ie.

1.4. Methodology

A multi-disciplinary approach has been adopted in this investigation, including the use of the following tools: 1) audio-magnetotelluric (AMT) geophysical surveys; 2) time-lapse logger measurements of temperature, electrical conductivity and (in one instance) water level; and 3) multivariate statistical analysis of hydrochemical data. These tools are described in detail in the papers that constitute Chapters 2, 3 and 4. The aims of this section are to briefly introduce each method, provide supplementary information not included in the papers, and to provide references for the reader who requires more detail.

1.4.1. AMT surveys

AMT measurements were collected at Kilbrook spring, Co. Kildare (July 2012), St. Edmundsbury spring, Lucan, Co. Dublin (December 2012), and St. Gorman’s Well, Enfield, Co. Meath (October 2013). For Kilbrook spring and St. Gorman’s Well, the data quality was generally good, and further details of the data collection, processing, modelling and interpretation of the results for these springs are provided in Chapters 3 (Kilbrook spring) and 4 (St. Gorman’s Well) of this thesis. The AMT data quality was poor for St. Edmundsbury spring due to the proximity of the survey
area to Dublin city centre (approximately 10 km) and resulting cultural interference. These data are not useful in their current state, and cannot be used for the generation of reliable resistivity models; more sophisticated time series analysis is required to remove the excessive cultural noise contamination. The AMT data for St. Edmundsbury spring was therefore not included in this thesis.

**AMT theory**

The AMT method is an electromagnetic geophysical technique that determines the distribution of the electrical properties of the subsurface, and is widely used for exploring geothermal resources (for a recent review see, e.g., Muñoz, 2012) and hydrogeological targets (e.g., Falgàs et al., 2011; Kalscheuer et al., 2015) due to its ability to detect low-resistivity, water-bearing rocks in the subsurface. AMT surveys were conducted at the thermal springs to target the geological structures and (electrically conductive) water-bearing conduits occurring beneath the springs. AMT is a branch of the magnetotelluric method (MT), and recent comprehensive reviews of MT (including AMT) are provided in textbooks by Simpson and Bahr (2005), Berdichevsky and Dmitriev (2008), and Chave and Jones (2012). MT can be used for very deep, crustal- or lithospheric-scale studies, and AMT is useful for shallower studies. The depth of penetration of AMT can be several hundred metres and even greater than a kilometre below the surface, depending on the resistivity of the bedrock. Natural electromagnetic fields that are utilised as source fields in MT studies range in frequency from approximately $10^{-5}$ to $10^5$ Hz. AMT studies use higher frequency (>8 Hz) electromagnetic waves that are generated by “distant” electric lightning discharge during lightning storms, and propagate around the globe in the Earth-ionosphere waveguide. Commonly, a frequency interval with poor signal-to-noise ratio is found between 1,000 Hz and 5,000 Hz, which is called the AMT “dead-band”. In these surveys, AMT soundings were recorded overnight to maximise the data quality, as night-time signals are usually strong enough to provide good estimates of the transfer functions of AMT dead-band frequencies (García and Jones, 2005).

The AMT method determines the distribution of electrical resistivity in the subsurface by relating simultaneous measurements of the naturally occurring fluctuations of the electric and magnetic fields at the Earth's surface. As an
electromagnetic wave interacts with the Earth, its amplitude will decay at a rate dependent on the conductivity of the medium and the frequency of the wave, such that information about the near-surface is obtained from high-frequency variations and information about deep structure is obtained from low-frequency variations. In a half-space of uniform resistivity, the depth at which an electromagnetic wave decays to 1/e of its original value is known as the “skin depth”, δ, and is an approximate measure for the depth of penetration of the wave,

$$\delta = \sqrt{\frac{1}{\omega \mu_0 \sigma}}$$  \hspace{1cm} (Eq. 1-1)

where \( \omega \) is the angular frequency of the electromagnetic field, \( \mu_0 \) is the magnetic permeability of free space, and \( \sigma \) is the electrical conductivity of an equivalent homogeneous half-space.

![Figure 1-5: Typical AMT station configuration, as deployed in this study. All electrodes and magnetometers were buried at depths greater than 20 cm. The central electrode was used to ground the recording device.](image)

At sufficiently large distances from their source (lightning discharges in the case of AMT studies), the electromagnetic fields can be considered as plane (i.e., laterally uniform) waves. At the Earth’s surface, the horizontal electric fields \( E_x \) and \( E_y \) (in V/m) and the horizontal and vertical magnetic fields \( B_x, B_y \) and \( B_z \) (in nT) are measured. Subsequently, the magnetic fields are converted to horizontal and vertical magnetic field intensities \( H_x, H_y \) and \( H_z \) (in A/m) (Figure 1-5). These
electromagnetic field components are connected through transfer functions in the frequency domain, i.e., through the impedance tensor $Z$ and the vertical magnetic transfer function (or “tipper”) $T$. $Z$ and $T$ are frequency dependent; they relate different components of the electric and magnetic fields at a given frequency, and are dependent upon the electrical properties of the material the fields propagate through. These tensors are complex, and so each matrix element is a complex number containing real and imaginary parts, i.e., each component has a magnitude and a phase.

The impedance tensor, $Z$, relates the horizontal magnetic and the horizontal electric fields:

$$\begin{bmatrix} E_x \\ E_y \end{bmatrix} = Z \begin{bmatrix} H_x \\ H_y \end{bmatrix}$$

(Eq. 1-2)

where

$$Z = \begin{bmatrix} Z_{xx} & Z_{xy} \\ Z_{yx} & Z_{yy} \end{bmatrix}$$

(Eq. 1-3)

The vertical magnetic transfer function, $T$, relates the horizontal and the vertical magnetic fields:

$$H_z = T \begin{bmatrix} H_x \\ H_y \end{bmatrix}$$

(Eq. 1-4)

where

$$T = [T_x \quad T_y]$$

(Eq. 1-5)

$T$ is usually represented by the real and imaginary induction arrows defined on the $xy$ plane, and these can be used to provide information about the dimensionality of the structure in the subsurface. The amplitude of the vertical magnetic field increases with lateral resistivity gradients (Simpson and Bahr, 2005), and the real induction arrows usually indicate significant lateral contrasts in the resistivity, by pointing either towards (Parkinson, 1959), or away from (Wiese, 1962) the anomalous current concentration characterised by the presence of a conductive anomaly. Parkinson’s convention, with the real arrows pointing towards the conductive anomalies, is usually preferred (Simpson and Bahr, 2005).
To provide a link to the resistivity distribution of the subsurface, impedance tensor elements $Z_{ij}$ can be transformed to apparent resistivities, $\rho_{a,ij}$, and phases, $\phi_{ij}$. The apparent resistivity, $\rho_a$, is defined as the average resistivity of an equivalent homogeneous half-space model at a particular frequency:

$$\rho_{a,ij} = \left(\frac{1}{\omega \mu_0}\right) |Z_{ij}|^2 ; \quad (\text{Eq. 1-6})$$

$$\phi_{ij} = \tan^{-1}\left(\frac{\text{Im}(Z_{ij})}{\text{Re}(Z_{ij})}\right) . \quad (\text{Eq. 1-7})$$

In this way, the raw time series components can be converted into an apparent resistivity curve for the subsurface beneath each station (Figure 1-6).
Figure 1-6: Raw AMT time series and apparent resistivity and phase curves for station 6 near St. Gorman’s Well, Enfield Co. Meath. Note the inconsistencies and large error bars in the AMT dead-band (around 1 kHz in particular). The 50 Hz signal and associated harmonics from power lines were removed during acquisition by a filter within the Phoenix instrumentation.
**Data modelling and inversion**

Typically, AMT data from a number of stations are modelled together (using an inversion process) to produce an electrical resistivity model of the subsurface. To obtain the resistivity model, we must use the observed AMT data to make inferences about the physical properties of the subsurface. Given a realistic model of the subsurface, $m$, we should be able to use the laws of physics to compute the observed AMT data values, $d$; this is termed the “forward problem”. Its inverse, i.e., reconstructing the model from a set of measurements, is called the “inverse problem” (Figure 1-7).

![Cartoon representation of the inverse problem.](image)

**Figure 1-7:** Cartoon representation of the inverse problem.

In the ideal case, an exact physical theory would exist to describe how the data should be transformed in order to produce the model. In reality, even processed data from real-world observations contain noise that can have a variety of sources, e.g., un-modelled influences on instrument readings, or numerical round-off (Aster et al., 2013). Inversion describes the almost “trial-and-error” approach that is used to find the optimal model solution that best fits the data. The forward operator of the inversion process, $f$, can be described as

$$f(m) = d$$  \hspace{1cm} (Eq. 1-8)

and leads to the inverse operator

$$m = f^{-1}(d)$$  \hspace{1cm} (Eq. 1-9)

where $m$ and $d$ represent model parameters and observed data respectively. The inverse operator as defined in Equation 1-9 exists only in very rare cases. Even if a linear relationship holds between the parameters of interest and the calculated data, the matrix relating the simulated data to the parameters may not be invertible as the
system may be over- or under-determined (Menke, 2012). In general, this non-inversion indicates that the matrix is not square, or is not full-rank. Where inherently non-linear relationships between the parameters and the data exist, as in electromagnetic field problems (Aster et al., 2013), inversion is even less practicable. In these cases, the corresponding forward models have to be solved by numerical methods, and considerable efforts must be taken to make the solution possible at all (Aster et al., 2013). The non-linear scenario is by far the most common case in geophysics. There are several problems inherent in the inverse modelling of geophysical data that need to be borne in mind when attempting to interpret a model (these problems are discussed in detail in Aster et al. (2013)): (1) there may be no model that exactly fits the data due to noise or an inaccurate physical approximation of the problem; (2) there may be more than one model which adequately fits the data; this is called “non-uniqueness”; and (3) the process of computing the solutions to an inverse problem may become unstable, i.e., a small change in a measurement can lead to a large change in the estimated model (this instability can be counteracted by regularization - introducing additional constraints to bias the solution).

In practice, the inverse modelling of AMT is an iterative process that begins with a simple, estimated model of the subsurface. This “a priori” model is discretized into cells that form the model mesh, and the forward operator solves a system of equations for each cell to produce synthetic data (this equation system includes the basic equations of MT along with appropriate boundary conditions). This synthetic data is compared to the observed data, and their difference is usually presented as a root-mean-squared (RMS) misfit. To reduce the RMS, the starting model is modified and the forward calculations begin again. The aim of the inversion is to find the optimal values of the model parameters that fit the observed data by minimising the misfit between the predicted subsurface model and the actual observations. A common approach is to seek the minimum of an “objective function”, Φ, to minimise a combination of the data misfit and the model complexity:

$$\Phi = \Phi_d + \beta \Phi_m$$ \hspace{1cm} (Eq. 1-10)

where $\Phi_d$ is a measure of data misfit, $\Phi_m$ represents the model complexity or roughness, and $\beta$ is a regularization parameter that balances the effects of $\Phi_d$ and $\Phi_m$. For this thesis, 3-D modelling of AMT data using the ModEM code (Egbert and
Once a satisfactory resistivity model has been obtained (i.e., a model with a low overall RMS that also has well-fitting data for each frequency for each site), an understanding of the electrical properties of various Earth materials allows structural and lithological interpretations of the model to be made (Figure 1-8). Usually, more competent, unfractured, crystalline rocks have high resistivity, and regions of low resistivity can be attributed to the presence of interconnected conductive material that is, typically, a minor component of the whole rock. Ionic conduction may occur due to saline water filling pore space or intruding along fracture zones, and can result in a lowering of the bulk resistivity of the rock, provided there are sufficient interconnected pathways for the saline fluids; this is likely to be an important process in hydrothermal scenarios. The resistivity values of sedimentary rocks and limestones (such as are found in the Dublin Basin) can depend upon a variety of factors, such as clay content and porosity. Unweathered limestone can generally have high resistivity values of between 1,000 and 100,000 Ωm. However, shale horizons can reduce the bulk resistivity to values as low as 10 Ωm (Palacky, 1988), and the amount of fluid contained in the rock (in pores or fractures) will also reduce its bulk resistivity (Telford et al., 1990). Due to the diffusive character of the AMT method, and the smearing effects inherent in the use of regularized modelling solutions, the application of AMT to the Irish thermal spring targets is unlikely to resolve in detail the individual conduits or fractures transmitting the thermal waters. However, the presence of water-bearing conduits in a volume of limestone bedrock will reduce the bulk resistivity of the rock as a whole, and this should be evident in the model.
1.4.2. Time-lapse logger measurements

Detailed long-term (two years) observations of temperature and chemistry were carried out in order to assess the temporal variation of the springs. As the geothermal energy potential of a hydrothermal system is largely dependent upon the temperature and volume of the available thermal waters, establishing a thorough understanding of the spring’s behaviour through time was a valuable exercise. Burdon (1983) provides relatively detailed discharge data for Kilbrook spring and St. Gorman’s Well, which suggest that the temperature of each spring increases when the discharge increases (in the winter recharge period). Due to the relative expense of constructing and maintaining weirs, and the problematic morphologies of some of the springs, it was decided that for this project, temperature (T) and electrical conductivity (EC) would be monitored long-term, and would suffice as a proxy for discharge (e.g., Anderson, 2005; Sebok et al., 2013). For the last year of measurements, the T and EC measurements at St. Gorman’s Well were supplemented with water level measurements, confirming the close relationship between temperature and discharge at this location (see Chapter 4).
HOBO U24-001 temperature and electrical conductivity loggers were installed at each of the six thermal spring locations in Figure 1-3 in July and August 2013 and recorded T (°C) and EC (µS/cm) at 15-minute intervals (Table 1-1). Data from four of these loggers are presented in this thesis: St. Edmunds bury spring and Louisa Bridge Spa Well in Chapter 2 (Figure 2-4); St.Gorman’s Well in Chapter 2 and Chapter 4 (Figures 2-4 and 4-6); and Kilbrook spring in Chapter 3 (Figure 3-8). The loggers were calibrated before installation and cross-checked against the field measurements of T and EC each time the data were collected. Summary statistics for the data were calculated using the Onset HOBOWare® software (Version 3.4.1) and are discussed in Chapter 2 (Table 2-3). The logger data is presented alongside daily effective rainfall data for the region, calculated from daily rainfall and potential evapotranspiration data from Dunsany synoptic station (Met Éireann), situated 10 km north of Kemmins Mill spring.

Water level data were collected for St. Gorman’s Well only, from 26th April 2014 until 21st September 2015. These measurements were made using a Solinst Levelogger LT unit, which was suspended in the borehole at St. Gorman’s Well at a depth of approximately 6 m below ground level. The measurements were compensated for barometric pressure using measurements from a Solinst Barologger LT unit positioned in a nearby barn. This data is discussed in Chapter 4 (Figure 4-6).

<table>
<thead>
<tr>
<th>Spring</th>
<th>Start of records</th>
<th>End of records</th>
<th>Any gaps?</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. Edmundsbury spring</td>
<td>02/07/2013</td>
<td>08/07/2015</td>
<td>Feb - May 2014, instrument repairs</td>
</tr>
<tr>
<td>St. Gorman’s Well</td>
<td>03/07/2013</td>
<td>09/08/2015</td>
<td>28/7/13 - 6/8/13, instrument failure</td>
</tr>
<tr>
<td>Huntstown Fault spring</td>
<td>03/07/2013</td>
<td>23/10/2014</td>
<td>No</td>
</tr>
<tr>
<td>Kemmins Mill spring</td>
<td>03/07/2013</td>
<td>23/01/2014</td>
<td>No</td>
</tr>
<tr>
<td>Kilbrook spring</td>
<td>04/07/2013</td>
<td>08/04/2015</td>
<td>No</td>
</tr>
<tr>
<td>Louisa Bridge Spa Well</td>
<td>07/08/2013</td>
<td>08/09/2015</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 1-1: Length of time-lapse temperature and electrical conductivity records for the six Leinster thermal springs.

1.4.3. Multivariate statistical analysis of hydrochemical data

The hydrochemical data were analysed in order to identify the source of the thermal waters. The chemical composition of groundwater frequently reflects the chemical composition of the host bedrock, and can provide valuable information on inputs to the hydrogeological system that further influence the hydrochemistry (Güler et al., 2012). Simple groundwater provenance studies involving hydrochemical data tend to
assume that the hydrochemical composition recorded in the groundwater sample is representative of the composition of the source, with no modification of the hydrochemistry en-route to the surface. More complex models may take into account mixing of different types of groundwater in the subsurface, and even the action of different hydrochemical processes on the groundwater composition. Hydrochemical analysis is especially useful in karstified areas, as are often found in the Carboniferous limestones of Ireland, where hydrochemical data can be equally or more important than traditional hydrodynamic data when attempting to understand and model groundwater flow (Pavlovskiy and Selle, 2015).

**Hydrochemical data collection**

Hydrochemical data were recovered from the six Leinster thermal springs shown in Figure 1-4, along with two cold seepages in the vicinity of Huntstown Fault spring. The springs were sampled and analysed over five seasons to assess any temporal variation in the spring chemistry and to provide some seasonal overlap for a more robust analysis. Major, minor and trace element concentrations were measured, and blank samples were used to ensure the quality of the laboratory analyses. The data collection and lab analysis protocol is discussed in detail in Chapter 2, and some additional details are provided here. A total of 78 samples (including duplicate samples, but not including blanks) were collected and analysed.

Each of the chosen sampling locations has a different morphology, from deep open ponds (e.g., Louisa Bridge Spa Well) to boreholes (e.g., St. Gorman’s Well) to slow seepages (the Huntstown cold seepages). A single sampling protocol was designed to be applied in these different scenarios, in an attempt to eliminate any bias that may have arisen from the use of different methods. A “clean hands, dirty hands” protocol was adopted in the field (US EPA, 1996) in order to recover the best water samples possible that were truly representative of the formation waters. The sampling apparatus is illustrated in Figure 1-9. Each of the eight sampling locations was assigned their own sampling kit, consisting of HDPE tubing, silicone connectors, a valve and a 0.45 µm filter (cellulose nitrate), to avoid cross-contamination between the sites. Unfiltered water from the spring was pumped slowly using a peristaltic pump to a cleaned and rinsed bucket, where the physico-chemical parameters (temperature, pH, electrical conductivity, TDS) were measured every few minutes. Once these parameters had stabilised, the spring water was pumped through a filter
for several minutes (in order to flush out any precipitates that may have formed in the filter), and then collected in pre-cleaned sample bottles. A flow-through cell was not used, as the majority of the sampling locations were open to the air and therefore already oxygenated. For the cold seepages, a slight deviation from the protocol was necessary because the flow was low (sometimes dripping) and diffuse; the seepage waters were first collected in another clean receptacle before being pumped.

All spring samples were duplicated for each round and a system of blanks using ultrapure water (from a Milli-Q® water purification system) was used to ensure the accuracy of the laboratory analyses (as recommended by USGS, 2006). For each sampling round, each laboratory was sent three blanks of ultrapure water; these were the “lab”, “trip” and “field” blanks. The “lab” blank was prepared before sampling commenced and left in a cool place for the duration of the sampling programme. The “trip” blank was prepared with the “lab” blank, then transported into the field and back again. The “field” blank was prepared in the field using the field apparatus and then transported with the rest of the samples (for each round, the field blank was taken at Kilbrook spring, using that spring’s designated sampling apparatus). The blanks were treated in exactly the same way as the spring water samples, i.e., they were also acidified if necessary. In this way, potential sources of contamination could be identified and traced either to i) the data collection method; ii) sample transport; or iii) the laboratory analysis. Happily, in this study the blanks indicated no contamination of the samples.

Figure 1-9: Cartoon of hydrochemical sampling apparatus used at each sampling location.
Historical groundwater quality data provided by the EPA were also used in the analysis for comparative purposes (see Chapter 2). The cold groundwater samples were collected from three monitoring boreholes at Ryewater, Co. Kildare (RW1, RW2 and RW3; see Figure 1-4 and Figure 2-3) between June 2009 and July 2012. The location for this cluster of monitoring boreholes was selected on the basis that the geology (limestones of the Lucan Formation) was representative of the typical bedrock geology for east-central Ireland (Moe et al., 2010). These boreholes are located in the centre of the Leinster thermal spring survey area.

**Multivariate statistical analysis**

King et al. (2014) noted that studies focusing on the groundwater chemistry to assess interactions between different types of groundwater are only useful if their chemistries are sufficiently different. Similar observations have led to the increasing use of more objective, discriminative approaches, such as multivariate statistical analysis (MSA), which can identify subtleties and complexities that are often overlooked by more traditional methods of analysis (e.g., Cloutier et al., 2008; Page et al., 2012; Raiber et al., 2012; Daughney et al., 2012; Menció et al., 2012; Hu et al., 2013; Engle and Rowan, 2014; Giménez-Forcada and Vega-Alegre, 2015). Data mining techniques are used to explore large amounts of data, and uncover consistent patterns or structures within the data. Data mining usually involves a series of processes such as: detection of outliers; discerning relationships between variables; grouping similar sub-sets of data in an unbiased way; classification of groups of data; and predictive modelling. Multivariate statistical analysis is the application of a series of statistical tools to study variability within a multi-dimensional dataset. Two such tools are hierarchical cluster analysis (HCA) and principal component analysis (PCA). HCA is useful for finding and grouping similar data points, and PCA is useful for effectively reducing the number of dimensions in the data set so the operator can sensibly interpret the data.

Hydrochemical data from a single sample consist of a series of measurements of analytes, commonly expressed in proportions such as mg/L, ppm or ppb. A change in one component of the solution modifies the relative amount of every other component; the data are compositional. Compositional data are intrinsically constrained, and do not follow the traditional rules of Euclidean geometry, in which most statistical tools operate. Problems can arise when standard statistical tools are
applied to investigate compositional data unless the data are properly processed beforehand. The application of compositional data analysis (CoDa) techniques prior to the MSA deconstrains the compositional data, and results in a more realistic and insightful analysis, as compared to a more standard statistical analysis of the data (e.g., Otero et al., 2005; Wang et al., 2014). The basic principles of CoDa techniques, and practical ways to implement them, are outlined in Chapter 2 (section 2.4). The reader is referred to Aitchison (1986), Pawlovsky-Glahn and Olea (2004) and Buccianti and Grunsky (2014) for a more detailed introduction to the development of the mathematical theory and concepts behind CoDa.

A compositional MSA including PCA and HCA was used on the hydrochemical data from the Leinster thermal springs to highlight differences in the hydrochemistry within the thermal spring dataset and also to distinguish between the thermal springs and typical cold groundwater in the area (from the historical Ryewater data set). A brief introduction to the theory behind HCA and PCA is outlined here, and more detailed information is provided in Chapter 2, section 2.4.3.

HCA is a method of cluster analysis which seeks to build a hierarchy of clusters within a data set, which are then interpreted by the operator. Agglomerative HCA (used in this study) is the “bottom up” approach to HCA, with each data point beginning as its own cluster, and pairs of clusters merging as the hierarchy is established. The classical output of a HCA is the dendrogram (e.g., Figure 2-6). In order to decide which clusters should be combined, a measure of dissimilarity between sets of data points is required. In most methods of hierarchical clustering this is achieved by use of an appropriate metric (a measure of distance between pairs of observations), and a linkage criterion which specifies the dissimilarity of sets as a function of the pairwise distances of observations in the sets (Hastie et al., 2013). There are a variety of options for both the metric and the linkage criterion. In this study, the classic Euclidean distance, \( d \), was used:

\[
d(a, b) = \sqrt{\sum_{i}^{n} (a_i - b_i)^2},
\]

(Eq. 1-11)

where \( a \) and \( b \) are two samples or observations, and \( n \) is the number of dimensions in the data set (in this case corresponding to the number of chemical analytes measured). In this study, Ward’s linkage criterion was used, also known as Ward’s
Chapter 1: Introduction

minimum variance method; it minimises the total within-cluster variance by using the error sum of squares as its objective function. Ward’s linkage can be implemented recursively by using the Lance-Williams formula. For three clusters \( C_i, C_j \) and \( C_k \), having \( n_i, n_j \) and \( n_k \) points in each cluster respectively, the distance between clusters can be computed as:

\[
d(C_i \cup C_j, C_k) = \frac{n_i + n_k}{n_i + n_j + n_k} d(C_i, C_k) + \frac{n_j + n_k}{n_i + n_j + n_k} d(C_j, C_k) - \frac{n_k}{n_i + n_j + n_k} d(C_i, C_j)
\]

(Eq. 1-12)

PCA is a multivariate data analysis technique that attempts to uncover the underlying structure to a dataset (Davis, 1986). It is particularly useful for exploring large datasets as it effectively reduces the number of dimensions in the data, but core details or patterns in the data are not lost (Page et al., 2012). It extracts the major components that control the chemical variability in the dataset (Güler et al., 2012) and is a well-proven technique for hydrochemical scenarios, including the investigation of thermal spring water provenance (Helena et al., 2000; Tanaskovic et al., 2012). In mathematical terms, PCA can be carried out in two ways; by eigendecomposition or by singular value decomposition (SVD). SVD is generally preferred for numerical accuracy. PCA by SVD is an interpretation of the SVD of a data matrix. The SVD expresses any data matrix, \( X \), as the product of three matrices:

\[
X = U \cdot D \cdot V^T
\]

(Eq. 1-13)

where:

- the rows of \( V \) identify the variables, and its columns represent the loadings or principal components;
- \( D \) is a diagonal matrix containing the singular values in decreasing order (the standard deviations of the new “principal components” coordinates of the dataset); and
- the rows of \( U \) identify the samples in the new coordinates of the dataset, called the scores (Van den Boogaart and Tolosana-Delgado, 2013).

The results of a PCA are usually interpreted with a biplot – the joint graphical representation of the variable loadings and sample scores (Gabriel, 1971). This allows information from samples and variables to be assessed together for any two
principal components (usually the first two components as these represent the majority of the total variance in the dataset).

1.5. **Summary of papers**

This thesis is structured around the following three research papers.

<table>
<thead>
<tr>
<th>Paper 1 (Chapter 2): Lead author – major role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blake, S., Henry, T., Murray, J., Flood, R., Muller, M., Jones, A.G., Rath, V.</td>
</tr>
<tr>
<td>Investigating the provenance of thermal groundwater using compositional multivariate statistical analysis: a hydrogeochemical study from Ireland.</td>
</tr>
<tr>
<td>Under review at Applied Geochemistry (Special Issue).</td>
</tr>
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</table>

MSA of hydrochemical data from the thermal springs, within the CoDa framework, was used to investigate the provenance of the thermal groundwater. The CoDa approach to MSA is a relatively recent addition to the field, and most studies of compositional data still tend to ignore methods developed to manage the constrained data (Buccianti and Grunsky, 2014). As it considers the compositional nature of hydrochemical data, and avoids potentially spurious results found frequently by the more conventional use of log-ratio transformations, the results of a compositional MSA are more reliable, and in this case allow for more realistic interpretations of the hydrogeological processes governing the hydrochemistry. The advantages of using a CoDa approach to MSA are fully demonstrated in the supplementary material of this paper.

The results of the MSA were examined alongside detailed time-lapse temperature and chemistry measurements from several of the springs, and indicate the influence of three important hydrogeological processes controlling the hydrochemistry of the thermal waters: 1) salinity and increased water-rock-interaction; 2) dissolution of carbonates; and 3) dissolution of metal sulfides and oxides associated with mineral deposits. The analysis also identified subtle temporal variations in the hydrochemistry of the thermal springs, which could not be identified with more traditional graphing methods. This study has highlighted the influence of at least two different aquifer types (one deep, one shallow) on several of the Irish thermal springs.
The author was responsible for data acquisition, quality control and preparation of hydrochemical data for the statistical analysis, calibration and processing of the time-lapse temperature and electrical conductivity data, all statistical analyses with R and Python, interpretation of the results, preparation of tables and figures, and the majority of the writing.

**Paper 2 (Chapter 3): Lead author – major role**

**Understanding hydrothermal circulation patterns at a low-enthalpy thermal spring using audio-magnetotelluric data: a case study from Ireland.**

Under review at Journal of Applied Geophysics.

This paper combines the results of AMT modelling and time-lapse temperature and electrical conductivity measurements for Ireland’s warmest thermal spring (Kilbrook spring, Co. Kildare) to characterise the hydrothermal circulation pattern and image any conduits or pathways supplying the thermal waters to the surface. The ModEM 3-D code (Egbert and Kelbert, 2012; Kelbert et al., 2014) was used to invert the AMT data and generate a 3-D electrical resistivity model of the subsurface beneath the spring. The model revealed a prominent NNW-aligned structure within a highly resistive limestone lithology that is interpreted as a dissolutionally-enhanced, water-bearing, strike-slip fault, of probable Cenozoic age. The karstification of this structure, which extends to depths of at least 500 m directly beneath the spring, has provided conduits that facilitate the operation of a relatively deep hydrothermal circulation pattern (likely estimated depths between 560 and 1,000 m) within the limestone succession of the Dublin Basin. This paper illustrates how the AMT method can be used in a multi-disciplinary investigation of an intermediate-depth (100 – 1,000 m), low-enthalpy, geothermal target, and shows how the different strands of inquiry from a multi-disciplinary investigation may be woven together to gain a deeper understanding of a complex hydrothermal system.

The author was responsible for: AMT data collection, processing, 3-D modelling and interpretation; calibration, processing and interpretation of the time-lapse temperature and electrical conductivity measurements; development of the
conceptual model; preparation of all tables and figures; and the majority of the writing.

**Paper 3 (Chapter 4): Lead author – major role**


**Understanding hydrothermal circulation patterns at a low-enthalpy thermal spring using audio-magnetotelluric and time-lapse temperature data: St. Gorman’s Well, Ireland.**

In preparation for submission to Geothermics.

This paper follows the same approach as Paper 2 and combines the results of 3-D AMT modelling and time-lapse temperature and electrical conductivity measurements for St. Gorman’s Well, to characterise the hydrothermal circulation pattern at the spring. The addition of detailed water-level measurements at this spring enabled the development of a more detailed conceptual model than for Kilbrook spring in Paper 2. As in Paper 2, the same procedure for the 3-D inversion was followed, and revealed the intersection of a NW trending Carboniferous normal fault with a N-trending Cenozoic strike-slip fault very near to the spring. The intersection of these structures, and subsequent enhanced dissolution of the bedrock, has provided a network of conduits that is a likely location for the hydrothermal circulation pattern feeding the spring. The likely depth of circulation for this hydrothermal system is estimated between 240 and 1,000 m within the limestone succession of the Dublin Basin.

The author was responsible for: AMT data collection, processing, 3-D modelling and interpretation; calibration, processing and interpretation of the time-lapse temperature and electrical conductivity measurements; development of the conceptual model; preparation of all tables and figures; and the majority of the writing.
Chapter 2: Multivariate statistical analysis

2. Investigating the provenance of thermal groundwater using compositional multivariate statistical analysis: a hydrogeochemical study from Ireland

Abstract
The geothermal energy of thermal groundwater is currently being exploited for district-scale heating in many locations world-wide. The chemical compositions of these thermal waters reflect the provenance and circulation patterns of the groundwater, which are controlled by recharge, rock type and geological structure. Exploring the provenance of these waters using multivariate statistical analysis (MSA) techniques increases our understanding of the hydrothermal circulation systems, and provides a reliable tool for assessing these resources.

Hydrochemical data from thermal springs situated in the Carboniferous Dublin Basin in east-central Ireland were explored using MSA, including hierarchical cluster analysis (HCA) and principal component analysis (PCA), to investigate the source aquifers of the thermal groundwaters. To take into account the compositional nature of the hydrochemical data, compositional data analysis (CoDa) techniques were used to process the data prior to the MSA.

The results of the MSA were examined alongside detailed time-lapse temperature measurements from several of the springs, and indicate the influence of three important hydrogeological processes on the hydrochemistry of the thermal waters: 1) salinity and increased water-rock-interaction; 2) dissolution of carbonates; and 3) dissolution of metal sulfides and oxides associated with mineral deposits. The use of MSA within the CoDa framework identified subtle temporal variations in the hydrochemistry of the thermal springs, which could not be identified with more traditional graphing methods (e.g., Piper diagrams), or with a standard statistical approach. The MSA was successful in distinguishing different geological settings and different annual behaviours within the group of springs. This study demonstrates the usefulness of the application of MSA within the CoDa framework in order to
better understand the underlying controlling processes governing the hydrochemistry of a group of thermal springs in a low-enthalpy setting.

2.1. Introduction
The geothermal energy of deep, thermal groundwater is currently being exploited for district-scale heating in many locations world-wide, such as Paris, France (Castillo et al., 2011), Milan, Italy (Sparacino et al., 2007), and Southampton, United Kingdom (Busby, 2010). It is now being explored in Ireland as part of the IRETERM project, one aim of which is to determine the suitability of Irish thermal springs as a geothermal energy resource. The hydrochemical signatures of the thermal springs are indicative of a meteoric origin (Burdon et al., 1983; Mooney et al., 2010); given this hydrochemistry and their elevated temperatures, the thermal springs are expected to comprise a mixture of groundwaters from different sources and different recharge areas. These groundwaters are expected to have different depths of circulation and different residence times within the host bedrock. Understanding the interactions of these hydrochemical elements is critical for characterising the springs as a geothermal energy resource.

In Ireland, average groundwater temperatures typically range from 9.5 to 10.5 °C (Aldwell and Burdon, 1980). As defined by Aldwell and Burdon (1980), and Goodman et al. (2004), thermal springs are considered to be those natural groundwater springs where the mean annual temperature is appreciably warmer than average groundwater temperatures. In this study springs with a mean annual temperature above 12 °C are considered thermal. Forty-two thermal springs and thermal shallow groundwater occurrences have been recorded to date in Ireland (Goodman et al., 2004) (Figure 2-1 c)). These springs range in temperature from 12 °C to 25 °C, and three have maximum temperatures in excess of 20 °C. The thermal springs issue from limestone bedrock of Carboniferous age. Some of the springs have been utilised in the past as therapeutic spa wells (e.g., Lady's Well, Mallow, Co. Cork (average temperature of 19.5 °C); Louisa Bridge Spa Well, Leixlip, Co. Kildare (maximum of 17.5 °C)), and many more have religious and cultural significance, as holy wells, as is evident from their names (e.g., St. Brigid's Well, Co. Dublin (maximum of 19 °C); St. Gorman's Well, Co. Meath (maximum of 21.8 °C)). The thermal spring waters at Lady’s Well in Mallow have also been used to
partially heat a municipal swimming pool (Goodman et al., 2004). To date, this is the only recorded example of an Irish thermal spring being utilised as a source of geothermal energy.

![Image](image.jpg)

**Figure 2-1:** Location and geological setting of Irish thermal groundwaters: (a) general location of Irish thermal spring and thermal shallow groundwater locations (after Goodman et al., 2004) along with mineral deposits and the approximate trace of the Iapetus Suture Zone (after Wilkinson, 2010); (b) generalised palaeogeographic map of the Dublin Basin during the Viséan Stage (modified from Sevastopulo and Wyse Jackson (2009)); and (c) detailed geological map of the study area, within the Carboniferous Dublin Basin, showing thermal springs included in the hydrochemical sampling programme (red circles), and the location of the Ryewater monitoring wells. The maximum temperature (red) and electrical conductivity in µS/cm (blue) are given for each thermal spring (data from HOBO loggers). Coloured triangles in each of the thermal spring labels refer to colour coding used for these locations in subsequent figures. Geology map from the Geological Survey of Ireland (www.gsi.ie).
The IREThERM investigation of Irish thermal springs aims to (1) identify the source aquifer(s) for the thermal waters, (2) characterise the circulatory system, and (3) assess the potential for the existence of deeper, higher-temperature circulation patterns for future geothermal exploitation. A multi-disciplinary approach has been adopted in this endeavour, including the use of geophysical surveys (to be discussed in future publications), time-lapse measurements of temperature and electrical conductivity, and detailed hydrochemical analysis. In this paper, new hydrochemical data from a small sub-set of the thermal springs are analysed using a compositional data analysis (CoDa) approach to multivariate statistical analysis (MSA), and interpreted alongside the high-resolution, time-lapse temperature and electrical conductivity measurements to better characterise the source of the thermal waters.

Six springs in the east-central region of Ireland were selected for detailed investigation (the Leinster thermal springs, Figure 2-1 c)). These springs were chosen for both their proximity to urban centres, which could make them suitable for geothermal use, and for their individual hydrogeological attributes. Waters from St. Gorman's Well and Kilbrook spring exhibit some of the highest spring water temperatures in Ireland (maxima of 21.8 °C for St. Gorman’s Well and 25.0 °C for Kilbrook spring were recorded in this study). Waters from St. Edmundsbury spring in Co. Dublin and Louisa Bridge Spa Well in Co. Kildare have the highest electrical conductivities measured in thermal springs in Ireland (maxima of 1664 μS/cm and 1644 μS/cm respectively), and a chemical composition distinct from the calcium-bicarbonate signal that is typical of many Irish groundwaters circulating in limestones.

In the absence of good quality hydrodynamic data (e.g., groundwater discharge information, regional groundwater levels) for the Leinster thermal springs, the results presented here represent the first detailed exploratory analysis of hydrochemical data from these springs. Hydrochemical analysis is especially useful in karstified areas, where hydrochemical data is often equally or more important than traditional hydrodynamic data when attempting to understand and model groundwater flow (Pavlovskiy and Selle, 2015). The chemical composition of groundwater frequently reflects the chemical composition of the host bedrock, and can provide valuable information on inputs to the hydrogeological system that further influence the hydrochemistry (Güler et al., 2012). King et al. (2014) noted that studies focusing on
the groundwater chemistry to assess interactions between different types of groundwater were only useful if their chemistries were sufficiently different. Similar observations have led to the increasing use of more objective, discriminative approaches, such as multivariate statistical analysis (MSA), which can identify subtleties and complexities that are often overlooked by more traditional methods of analysis (e.g., Cloutier et al., 2008; Page et al., 2012; Raiber et al., 2012; Daughney et al., 2012; Menció et al., 2012; Hu et al., 2013; Engle and Rowan, 2014; Gimenéz-Forcada and Vega-Alegre, 2015).

Hydrochemical data from a single sample consist of a series of measurements of analytes, commonly expressed in proportions such as mg/L, ppm or ppb. A change in one component of the solution modifies the relative amount of every other component; the data are compositional. Compositional data are intrinsically constrained, and do not follow the traditional rules of Euclidean geometry, in which most statistical tools operate. Problems can arise when standard statistical tools are applied to investigate compositional data unless the data are properly processed beforehand. In this paper, we show how the application of CoDa techniques to the data prior to the MSA results in a more realistic and insightful analysis, as compared to a more standard statistical analysis of the data. The compositional MSA is used here to highlight differences in the hydrochemistry within the dataset, and also to distinguish between the thermal springs and typical cold groundwater in the area. The compositional MSA also sheds light on the temporal variation in the behaviour of the springs.

2.2. Study area in context

2.2.1. Geological setting of the Irish thermal springs

The Irish thermal springs occur in Carboniferous limestone bedrock along a wide lineament that traverses the centre of Ireland from NE to SW, broadly coincident with the putative trend of the Iapetus Suture Zone (ISZ) (Figure 2-1 a)). The ISZ is a major tectonic structure in Irish geology and separates two former continents, Laurentia and Avalonia, which converged during the Caledonian orogenic cycle approximately 475 to 405 Ma (e.g., Chew and Strachan, 2014). Terrestrial, red-bed, clastic facies were deposited on the resulting landmass during the Devonian period.
(e.g., Graham, 2009), followed by a shift to predominantly carbonate deposition as a result of a regional marine transgression during earliest Carboniferous times (MacDermot and Sevastopulo, 1972). The infilling of Carboniferous basins in Ireland was probably mostly accommodated by movement on NE-SW oriented structures, whose orientation was inherited from Caledonian orogenic events (Worthington and Walsh, 2011). Extensive carbonate production continued in Ireland for much of the Mississippian epoch (e.g., Somerville 2008), which was followed by a switch to non-calcareous facies during the upper Mississippian and lower Pennsylvanian epochs (e.g., Fallon and Murray, 2015).

The Carboniferous (Mississippian: Tournaisian to Viséan) limestones that host the thermal springs tend to exhibit poor primary porosity. Permeability is greatly improved by karst and fracture development, which provide important conduits and fissures for groundwater flow. The thermal springs are frequently associated with deep-seated, high-angle faults, which transport the warm waters to the surface (Mooney et al., 2010). The Carboniferous limestones in the Irish Midlands are also host to significant (world-class) massive sulfide deposits (Wilkinson and Hitzman, 2015). These mineral deposits also have a close spatial relationship with the ISZ (Figure 2-1 a)), and their extensive development attests to the presence and operation of very large hydrothermal systems in the past (Wilkinson, 2010). Both the thermal springs and the major mineral deposits are associated with the dominant NE-SW structural lineaments. These deep-seated, pervasive faults, although no longer active, may still provide fluid pathways enhanced by dissolutional processes in places (karstification), allowing water to flow from deeper units up to the surface, and are probably very important in controlling regional groundwater flow (Henry, 2014).

The six springs chosen for further study are situated in the Carboniferous Dublin Basin, which contains c. 2,000 m of sedimentary infill. This depocentre was one of several to develop across Ireland during the early Mississippian; these depocentres were connected via shallow intervening shelf areas (e.g., Murray 2010). The Dublin Basin is largely fault-bounded and floored by a basement of Precambrian crystalline rocks and Lower Palaeozoic metasediments, which are unconformably overlain by Devonian terrestrial sandstones and conglomerates. A phase of ramp sedimentation during Tournaisian times produced carbonate facies of predominantly argillaceous bioclastic limestones and shales (Jones et al., 1988). During Viséan times, active
faulting within the basin led to the development of distinct shallow platforms and contrasting deeper regions. The platform facies are typically represented by clean, thickly bedded, and generally shale-free, limestones, whereas the deeper basinal facies are characterised by thinly inter-bedded, cherty limestones and shales (mapped regionally as the Lucan Formation or ‘Calp’; see Marchant and Sevastopulo 1980). The interface between the initial phase of ramp sedimentation and subsequent development of shelf platforms in the Dublin Basin is marked by a widespread phase of Waulsortian carbonate mudbank ('reef') development (Lees and Miller 1995). These fine-grained limestones commonly contain infilled, sparry cavities and are quite pure (in terms of carbonate content). This purity makes them susceptible to karstification. Bedding is often indistinct, particularly towards the centres of individual carbonate mounds. These mudbanks commonly coalesced or formed aggregates with intervening, laterally equivalent, off-bank facies, which are typically represented by thin, nodular, chert-rich shales.

Four out of the six Leinster thermal springs studied here discharge from mapped Waulsortian limestone localities. It is therefore important to consider the structural controls on fluid flow within the Waulsortian facies. Due to the commonly unbedded nature of Waulsortian limestones, any karstic dissolution will tend to exploit areas of fissured and faulted rock, rather than bedding planes. Additionally, the chert-rich, off-mound deposits are much less soluble by comparison, and may provide an impermeable seal, which can further focus the direction of groundwater flow and dissolution of the carbonate. This can allow for flow within discrete Waulsortian mounds to become concentrated along vertical or sub-vertical pathways with relatively little lateral dissipation of flow into bedding planes (Moore et al., 2015). The thickest developments of Waulsortian limestones in the Dublin Basin are over 500 m thick (Strogen et al., 1996); a thickness of Waulsortian limestone in excess of 450 m has been recorded at the site of St. Gorman’s Well, in the Dublin Basin (Murphy and Brück, 1989). In carbonates, the existence of deep dissolitional features (depths of at least 500 m) is likely to be controlled by prominent fault structures (Kaufmann et al., 2014). Dissolitional features in the Waulsortian limestones within the survey area for this study have been reported at depths of 250 - 300 m (borehole reports from www.mineralsireland.ie) and may possibly exist at 510 m in one reported instance (Murphy and Brück, 1989). It is highly likely that these
features in the Waulsortian limestone play an important role in the operation of deep groundwater circulation patterns and facilitate the ascent of the thermal spring waters to the surface.

### 2.2.2. Hydrogeological setting

The six warm springs and two cold seepages studied in this work are situated in a relatively flat and low-lying landscape, predominantly used for agricultural purposes, in the eastern part of Ireland (Leinster), in the Eastern River Basin District. Local hilly features reach a maximum of c. 130 m above ordnance datum (mAOD), and a slight topographic gradient is evident towards the eastern coast of Ireland. The spring elevations range from approximately 20 to 90 mAOD. The 30-year (1981-2010) average annual rainfall in the area is 868 mm/yr (Walsh, 2012), and during the sampling period the annual rainfall was 863 mm in 2013 and 922 mm in 2014 (data from Met Éireann). Evaporative losses for the region are estimated at 450 mm/yr (Met Éireann). The bedrock in the study area is broadly classified by the Geological Survey of Ireland (GSI) as “locally important, moderately productive” limestone aquifer. Most recharge to aquifers in Ireland occurs in the period between October and April, and typical estimated recharge rates for this area are 101-200 mm/yr (Hunter Williams et al., 2011). The Leinster thermal springs surveyed in this study generally have their maximum discharges in the winter, when recharge rates are highest, and, where known, these discharge values are presented in Table 2-1. No detailed hydrodynamic data was available for this study.

The hydrochemical signatures of Irish thermal springs imply that they are mainly composed of meteoric waters that are recently recharged from rainfall events (Burdon, 1983; Mooney et al., 2010). Most of the warm springs have major ion compositions that are comparable to Irish carbonate groundwaters (Ca-HCO$_3$-type). For a better interpretation, the results of the hydrochemical analysis of the Leinster thermal spring waters are compared here with observations from “typical” Irish carbonate groundwaters. Figure 2-2 is a (non-compositional) Piper diagram comparing the six thermal springs and two cold seepages from this study with historical monitoring well data collected by the Irish Environmental Protection Agency (EPA) at Ryewater between 2009 and 2012 (the location of the Ryewater sampling points can be seen in Figure 2-1 c)). With the exception of the cold seepages, and Louisa Bridge Spa Well and St. Edmundsbury spring (saline, or NaCl-
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type groundwater), the majority of the data plot in the normal range for Ca-HCO$_3$-type waters.

As noted by Burdon (1983), there are hydrochemical traits in some of the thermal springs that, along with their elevated temperatures, suggest longer residence times and deeper circulation patterns (e.g., the high electrical conductivities seen in St. Edmundsbury spring and Louisa Bridge Spa Well). Dissolved inert gas and isotopic analyses carried out by Burdon (1983) suggest that Louisa Bridge Spa Well has a component of water with a residence time in excess of 30,000 years. Thus, water samples recovered from the Leinster thermal springs are likely to be a mixture of groundwaters from different sources and different recharge areas (e.g., a thermal spring water could be composed of a mixture of a deeper-circulating, older groundwater, and more recent recharge from a shallow groundwater system).

![Piper diagram of hydrochemical analyses from the Leinster thermal spring dataset (triangles) and cold groundwater samples from the Ryewater monitoring boreholes between June 2009 and July 2012 (crosses). Samples from the deep Ryewater boreholes form distinct clusters that are labelled.](image)

Figure 2-2: Piper diagram of hydrochemical analyses from the Leinster thermal spring dataset (triangles) and cold groundwater samples from the Ryewater monitoring boreholes between June 2009 and July 2012 (crosses). Samples from the deep Ryewater boreholes form distinct clusters that are labelled.
Analogous thermal and saline springs can be found in the Carboniferous limestones of northern England. Intermediate-temperature thermal springs (with a similar range of temperatures to the Irish thermal springs) are located in Derbyshire; the warmest of these is located in Buxton and has a temperature of 27.2 °C (Gunn et al., 2006). The mineral waters of Harrogate in North Yorkshire are cool but contain components of sulphurous and saline waters; the saline component of the groundwater is associated with migration of brines of meteoric origin through a major fault system called the Harrogate anticline (Bottrell et al., 1996; Murphy et al., 2014). It is possible that a similar combination of lithological and structural controls are in operation in both Irish and British Carboniferous limestone localities to produce hydrothermal and mineral groundwater circulation patterns through deep faults.

<table>
<thead>
<tr>
<th>Spring</th>
<th>Location</th>
<th>Geological setting</th>
<th>Max. T (°C)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. Edmundsbury spring</td>
<td>53°21'58.59&quot;N 6°25'35.42&quot;W</td>
<td>Waulsortian Limestone Fm.</td>
<td>17.0</td>
<td>Discharges from bedrock on south bank of River Liffey. Flooded periodically (minimum temperature not representative of thermal groundwater). Conspicuous iron staining from spring waters.</td>
</tr>
<tr>
<td>St. Gorman's Well spring</td>
<td>53°26'34.57&quot;N 6°53'9.68&quot;W</td>
<td>Adjacent to faulted contact between Waulsortian Limestone Fm. and Lucan Fm.</td>
<td>21.8</td>
<td>Ephemeral pond, adjacent borehole used for sampling - drilled in 1980s. Normal flow pattern is artesian in winter (max. ~ 1,000 m³/d) when pond is full. Maximum temperatures in winter.</td>
</tr>
<tr>
<td>Huntstown Fault spring</td>
<td>53°24'11.44&quot;N 6°19'54.29&quot;W</td>
<td>Strike-slip fault of Cenozoic age in Boston Hill Fm. limestone</td>
<td>16.3</td>
<td>Discharges from 1 m wide cavity along fault. Steady temperature and maximum discharges of ~ 5,000 m³/d reported.</td>
</tr>
<tr>
<td>Kemmins Mill spring</td>
<td>53°25'47.13&quot;N 6°38'35.16&quot;W</td>
<td>Gravelly till deposits overlying faulted contact between Lucan Fm. and older limestones</td>
<td>14.9</td>
<td>Shallow abstraction well in gravel deposits used for domestic and farming purposes. Steady temperature and &quot;slow boil&quot; bubbling.</td>
</tr>
<tr>
<td>Kilbrook spring</td>
<td>53°25'24.23&quot;N 6°46'31.63&quot;W</td>
<td>Gravel and sand glacial till over faulted contact between Lucan Fm. and younger Namurian deposits</td>
<td>25.0</td>
<td>Discharges from old gravel quarry excavations. Depth to bedrock estimated at 25 - 30 m. Discharge (max. ~ 850 m³/d) greatest in winter. Fairly steady, high temperature throughout the year.</td>
</tr>
<tr>
<td>Louisa Bridge Spa Well</td>
<td>53°22'14.44&quot;N 6°30'23.42&quot;W</td>
<td>Gravel deposits overlying Lucan Fm. limestone</td>
<td>17.5</td>
<td>Historical spa well and pond with engineered surrounds built in early-19th century. Steady temperature, yellowish-orange deposits left by spring water.</td>
</tr>
</tbody>
</table>
Table 2-1: (previous page) Morphological and geological setting of the Leinster thermal springs and cold seepages surveyed in this study. Temperature data for the two cold seepages measured with a Hanna Combo meter. Other temperature data measured by HOBO temperature loggers.

2.3. Materials and methods

2.3.1. Sample collection and analysis – new data

New samples from the six thermal springs and two cold seepages in Figure 2-1 c) are the focus of this study. Geographical coordinates, geological setting, temperature range and a brief description of each spring is provided in Table 2-1. Data were recovered for analysis over five seasons to assess the temporal variation in the spring chemistry and to provide some seasonal overlap for a more robust analysis. The springs were sampled in July/August and October 2013, and in January, May and August 2014. Samples were not collected from St. Edmundsbury spring in January 2014 as the spring was flooded by the River Liffey at that time. Each sample was duplicated, i.e., there are ten samples for each sampling point collected at five different times (with the exception of St. Edmundsbury spring, which has eight samples collected over four seasons). Temperature (°C) and electrical conductivity (μS/cm) were recorded at each spring prior to sampling using a calibrated YSI 556 portable multi-probe. The pH was recorded using a Hanna HI 98130 Combo meter (use of both instruments facilitated cross-checking of results).

A total of 78 water samples (not including blanks) were analysed for major and minor ions by ELS Ltd., Cork, Ireland, and also for a suite of 70 trace elements by Acme Ltd. (now trading as Bureau Veritas Ltd.), Vancouver, Canada. Samples were collected using a low-flow peristaltic pump and an in-line 0.45 μm filter to obtain samples that were most representative of the formation water (see Henry, 2014). The method used was based upon the technical standards ASTM D6452-99 and ISO5667-11, and the methods of Barcelona et al. (1994) and Puls and Barcelona (1996). For the two seepages, the waters were first collected in clean plastic containers before being pumped through the filtration system into pre-cleaned bottles for transport. Samples for trace element analysis were acidified to a pH of < 2 with trace metal grade nitric acid (John, 2000; Huang et al., 2013) prior to transport. All spring samples were duplicated for each round and a system of blanks using ultrapure water (from a Milli-Q® water purification system) was analysed by each
laboratory for each round (as recommended by USGS, 2006). The blanks showed no contamination of the samples. The samples were stored in a cool box during transport and storage prior to shipment to the laboratories for analysis.

At ELS Ltd. the analyses for total concentrations of major ions were measured using inductively coupled plasma mass spectrometry (EM130 ICP-MS), total alkalinity was measured using a Titralab EW153, and sulfate and chloride concentrations were determined using EW154M-1 AQ2-UP2 EW015/016 Autoanalyser Spectrophotometry. At Acme Ltd. trace element concentrations were determined using ICP-MS. Details of the analytes retained for the final analysis, including limits of detection (LOQ) and the percentage of observations below the LOQ for each sample, are presented in Table 2-2.

2.3.2. Historical data

Historical groundwater quality data provided by the EPA were also used in the multivariate analysis for comparative purposes. The cold groundwater samples were collected from three monitoring boreholes at Ryewater, Co. Kildare (RW1, RW2 and RW3; see Figure 2-1 c) and Figure 2-3) between June 2009 and July 2012. The location for the monitoring boreholes was selected on the basis that the geology (limestones of the Lucan Fm.) was representative of the typical bedrock geology for east-central Ireland (Moe et al., 2010). These boreholes were chosen for this study as they are located in the centre of the thermal spring survey area. Three different sampling horizons were used in each borehole:

- T – transition zone between subsoils and underlying bedrock (location of intake section varies between 2 and 14 m below ground level (mbgl));
- S – shallow bedrock (intake varies between 5 and 30 mbgl); and
- D – deep bedrock (intake varies between 34 and 82 mbgl).

Data from the subsoil horizon (RW3sub) and nearby surface water (SW1 – from the River Ryewater) were also included in the dataset. Temperatures in the bedrock wells ranged from 8.7 to 12.6 °C, with an average of 10.5 °C. The average electrical conductivity of the bedrock groundwater was 585 μS/cm.
### Table 2-2: Major, minor and trace analytes, limits of quantification and methods of analysis.

For each analyte, the number of samples with levels below the LOQ is given as a percentage (calculated for the new hydrochemical dataset; total number of samples, including duplicates, is 78).

#### Major ions (> 1 ppm)

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Measured units</th>
<th>LOQ</th>
<th>Method of analysis</th>
<th>% LOQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>ppm</td>
<td>0.05</td>
<td>ICP-MS</td>
<td>0.005</td>
</tr>
<tr>
<td>Cl</td>
<td>ppm</td>
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<td>ICP-MS</td>
<td>0.005</td>
</tr>
<tr>
<td>K</td>
<td>ppm</td>
<td>0.05</td>
<td>ICP-MS</td>
<td>0.005</td>
</tr>
<tr>
<td>Mg</td>
<td>ppm</td>
<td>0.05</td>
<td>ICP-MS</td>
<td>0.005</td>
</tr>
<tr>
<td>Na</td>
<td>ppm</td>
<td>0.05</td>
<td>ICP-MS</td>
<td>0.005</td>
</tr>
<tr>
<td>Sr</td>
<td>ppb</td>
<td>0.01</td>
<td>ICP-MS</td>
<td>0.005</td>
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<tr>
<td>HCO$_3$</td>
<td>ppm CaCO$_3$</td>
<td>10</td>
<td>Titralab</td>
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<tr>
<td>SO$_4$</td>
<td>ppm</td>
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<td>Spectrophotometry</td>
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</table>

#### Minor & trace ions

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Measured units</th>
<th>LOQ</th>
<th>Method of analysis</th>
<th>% LOQ</th>
</tr>
</thead>
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<tr>
<td>NH$_3$</td>
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<td>Spectrophotometry</td>
<td>19.23</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>ppm</td>
<td>0.009</td>
<td>Spectrophotometry</td>
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<td>F</td>
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<td>ppb</td>
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<td>ICP-MS</td>
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<td>ICP-MS</td>
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<td>ICP-MS</td>
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<td>ICP-MS</td>
<td>0.01</td>
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<tr>
<td>Sb</td>
<td>ppb</td>
<td>0.05</td>
<td>ICP-MS</td>
<td>25.64</td>
</tr>
<tr>
<td>Se</td>
<td>ppb</td>
<td>0.5</td>
<td>ICP-MS</td>
<td>5.13</td>
</tr>
<tr>
<td>Tl</td>
<td>ppb</td>
<td>0.01</td>
<td>ICP-MS</td>
<td>12.82</td>
</tr>
<tr>
<td>U</td>
<td>ppb</td>
<td>0.02</td>
<td>ICP-MS</td>
<td>0.02</td>
</tr>
<tr>
<td>Zn</td>
<td>ppb</td>
<td>0.5</td>
<td>ICP-MS</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**2.3.3. Time-lapse temperature measurements**

HOBO U24-001 temperature and conductivity loggers were installed at each of the six thermal spring locations in July and August 2013 to record temperature and electrical conductivity (EC, µS/cm) at 15-minute intervals for the duration of the hydrochemical sampling programme and beyond (data from three of the thermal springs along with daily effective rainfall data for the region are presented in Figure
Daily rainfall and potential evapotranspiration data from Dunsany synoptic station (Met Éireann), situated 10 km to the N of Kemmins Mill spring (Figure 2-1c), were used to calculate the effective rainfall according to the formula used by Hunter Williams et al. (2011):

\[
\text{Effective rainfall} = \text{Rainfall} - 0.82(\text{Potential Evapotranspiration}).
\]  

(Eq. 2-1)

The loggers were calibrated before installation and cross-checked against the field measurements of temperature and EC each time the data were collected. Summary statistics for the data were calculated using the Onset HOBOWare® software (Version 3.4.1) (Table 2-3). For St. Gorman’s Well, data are missing for the period between July 28th and August 6th 2013 due to instrument failure. For St. Edmundsbury spring, the period between July 2013 and February 2014 shows the influence of instrument drift on the temperature readings (gradual increase in temperature during this period). The logger was repaired and redeployed in May 2014. In general, the temperature readings were more reliable than the EC readings. Due to the aerated nature of the spring waters, the EC measurements were susceptible in most cases to the influence of fouling by bacterial growths on the sensors. Those questionable EC readings that may have been affected by fouling have been indicated in Figure 2-4 where appropriate. The quality of the EC data for St. Edmundsbury spring was particularly poor due to build-up of iron-oxide deposits on the sensor, but these data have been included here for completeness.

<table>
<thead>
<tr>
<th>Spring</th>
<th>pH range</th>
<th>Max EC (μS/cm)</th>
<th>Max T (°C)</th>
<th>Min T (°C)</th>
<th>Mean T (°C)</th>
<th>σ T</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. Edmundsbury spring</td>
<td>7.37 - 7.67</td>
<td>1664</td>
<td>17.0</td>
<td>8.5*</td>
<td>16.2*</td>
<td>1.01*</td>
</tr>
<tr>
<td>St. Gorman's Well</td>
<td>6.7 - 7.8</td>
<td>790</td>
<td>21.8</td>
<td>10.5</td>
<td>17.2</td>
<td>3.1</td>
</tr>
<tr>
<td>Huntstown Fault spring</td>
<td>6.68 - 7.7</td>
<td>1049</td>
<td>16.3</td>
<td>15.0</td>
<td>15.5</td>
<td>0.35</td>
</tr>
<tr>
<td>Kemmins Mill spring</td>
<td>6.9 - 7.56</td>
<td>520</td>
<td>14.9</td>
<td>14.1</td>
<td>14.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Kilbrook spring</td>
<td>6.71 - 7.8</td>
<td>723</td>
<td>25.0</td>
<td>19.5</td>
<td>23.9</td>
<td>0.65</td>
</tr>
<tr>
<td>Louisa Bridge Spa Well</td>
<td>6.95 - 7.77</td>
<td>1644</td>
<td>17.5</td>
<td>13.9</td>
<td>16.8</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Table 2-3: Summary statistics for non-compositional data from the thermal springs. Temperature (T) and electrical conductivity (EC) data from time-lapse logger measurements. *St. Edmundsbury temperature minimum due to flooding – not representative of thermal groundwater.
Figure 2-3: Sketch of the EPA monitoring borehole installation at Ryewater, Co. Kildare: a) Photo of RW1, RW2 and RW3 boreholes from Moe et al. (2010); b) Schematic diagram of RW1 installation, with subsurface geology after Moe et al. (2010). Cold groundwater samples (from 2009 – 2012) were collected from three horizons in each of the three boreholes. The intake of the Transition horizon piezometers (suffix T) varies between 2 – 14 mbgl, the intake of the Shallow bedrock horizon piezometers (S) varies between 5 – 30 mbgl, and the intake of the Deep bedrock horizon piezometers (D) varies between 34 – 82 mbgl.

2.4. Statistical procedures

The procedure followed in this study for compositional MSA of the hydrochemical data is illustrated in Figure 2-5. This procedure consisted of preparation of the input data matrices, application of CoDa techniques, and the MSA (hierarchical cluster analysis (HCA) and principal component analysis (PCA)). A standard statistical
Chapter 2: Multivariate statistical analysis

analysis was also carried out using the raw, new data for comparison with the CoDa approach (see section 2.8).

2.4.1. Data preparation

As a check on the accuracy of the analytical results, ionic balance errors for the new data were calculated using PhreeqC (version 2.18) (Parkhurst and Appelo, 1999) with the minteq.dat database. The majority of samples had calculated ionic balance errors below the recommended standard of ±5% (Freeze and Cherry, 1979), and 11 out of a total of 78 samples had elevated errors of between ±5% and ±10%. All 78 water samples were retained for further analysis as the ionic balance error of 10% was deemed acceptable (e.g., Güler et al., 2002; Cloutier et al., 2008; King et al., 2014).

Only compositional hydrochemical data, i.e., ionic concentrations in mg/L or ppm, were included for the statistical analysis. Non-compositional data, such as temperature, pH and electrical conductivity, were not included. Any variables with an elevated number of samples below the LOQ (> 33% of samples below the LOQ) were discarded. The discarded variables included NO₃, Fe, Ni, Cr and Pb. The data matrix for the Leinster thermal springs and cold seepages (including trace element data – called Matrix (3)) consisted of 78 observations and 30 variables (see Table 2-2 for a list of variables).

The historical groundwater quality data from the Ryewater boreholes were examined alongside the new thermal spring data, and any overlapping variables were chosen to create a new combined dataset. Again, those variables with a large number of observations below the LOQ (> 33%) were discarded. As defined by Krešić (2007), a major constituent element of groundwater is one with a concentration greater than 1 mg/L. On this basis, a subset of eight major ions (Ca, K, Mg, Na, Cl, HCO₃, SO₄ and Si) was chosen from the combined thermal and historical datasets. Sr was also included, as for many samples it has a value > 1 mg/L. Two matrices using major ion data were compiled; the first, for the new thermal spring data only (called Matrix (1)), contained 78 observations and 9 variables; and the second, for both the new and the historical data combined (Matrix (2)), contained 214 observations and 9 variables.
Figure 2-4: Time-lapse temperature (blue) and electrical conductivity (black) measurements. a) St. Edmundsbury spring. b) St. Gorman’s Well (inset shows semi-diurnal fluctuations over two days in August 2013). c) Louisa Bridge Spa Well. d) Daily effective rainfall data calculated from Met Éireann data (Dunsany synoptic station, Meath). Hydrochemical sampling seasons are indicated in red (A = July/August 2013, B = October 2013, C = January 2014, D = May 2014, E = August 2014). Data is missing for St. Edmundsbury spring between February and May 2014 due to failure of the data logger; likewise for St. Gorman’s Well in August 2013. Evidence of fouling (growth on sensor) as a result of incorrect positioning of the logger is indicated for Louisa Bridge Spa Well.

Figure 2-5: Methodological flow-chart illustrating steps taken in compositional data analysis and MSA.

2.4.2. Compositional data analysis (CoDa)

It is critically important that the compositional nature of environmental data be taken into consideration for practically any aspect of statistical data analysis (Filzmoser et al., 2009a), as a failure to do so has been shown to generate misleading results (e.g., Otero et al., 2005; Wang et al., 2014). Non-compositional data are not constrained and exist in a sub-set of real space, $U^D$, in which the rules of Euclidean geometry apply. Compositional data, such as hydrochemical measurements, are inherently multivariate and exist within their own sample space (referred to as the simplex, $S^D$, where $D$ is the number of dimensions of the sample space), which does not follow the rules of Euclidean geometry. The use of standard statistical tools on compositional data can thus lead to spurious correlations, which can produce unrealistic results (see, e.g., Flood et al., 2015). Since the 1980s, and particularly following the work of Aitchison (1986), statisticians and geochemists have made significant progress in developing methods to treat compositional data to overcome this problem of spurious correlation. These improvements have been achieved by
using a family of log-ratio transforms (Aitchison, 1986; Egozcue et al., 2003) to convert the original compositional data into new coordinates, which follow the rules of Euclidean geometry in real space. This transformation forms the basis of CoDa, and allows all of the relative information in a compositional sample to be conveyed into a real space where ordinary statistical analysis may be validly carried out. CoDa tools for the processing and transformation of compositional data are freely available through the R statistical environment (version 3.10.1) (R Development Core Team, 2015). Some of these tools have been used in this work (Figure 2-5), in particular the packages “compositions” (Van den Boogaart and Tolosana-Delgado, 2008) and “zCompositions” (Palarea-Albaladejo and Martin-Fernández, 2015). These tools allow the data to be analysed in such a way that an insight into the variability of the geochemical processes influencing the data can be obtained without geometric distortion or bias. The reader is referred to Aitchison (1986), Pawlovsky-Glahn and Olea (2004) and Buccianti and Grunsky (2014) for an introduction to the development of the mathematical theory and concepts behind CoDa, and Van den Boogaart and Tolosana-Delgado (2013) for details on how to implement CoDa procedures in R.

To examine the compositional data, it is inadvisable to calculate raw correlations or covariances due to the spurious effects mentioned above. Instead, the use of the variation matrix is advocated (Aitchison, 1986), estimated here for the thermal spring data (Table 2-4). Each component of the variation matrix, $\tau$, describes the log-relationship between two variables $x_i$ and $x_j$ (in this case chemical analytes), and is defined as

$$\tau_{ij} = \text{var} \left( \ln \left( \frac{x_i}{x_j} \right) \right),$$  \hspace{1cm} (Eq. 2-2)

and estimated by

$$\tau_{ij} = \frac{1}{N-1} \sum_{n=1}^{N} \ln \left( \frac{x_{ni}}{x_{nj}} \right)^2 - \ln \left( \frac{\bar{g}_i}{\bar{g}_j} \right)^2,$$  \hspace{1cm} (Eq. 2-3)

where $N$ is the number of observations and $\bar{g}_i$, $\bar{g}_j$ are the geometric mean values for the two variables in question. A small value of $\tau_{ij} = \tau_{ji}$ implies a good proportionality between the two variables. This allows the identification of strongly co-dependent variable pairs in the dataset. An index of proportionality (first
introduced as an “approximate correlation coefficient” by Aitchison, \( \rho \), for any pair of variables, \( i \) and \( j \), can be estimated using the following transformation:

\[
\rho_{ij} = \exp\left( -\frac{r^2_{ij}}{2} \right),
\]  

(Eq. 2-4)

(Van den Boogaart and Tolosana-Delgado, 2013) (Table 2-4). Strong relationships between pairs of variables have an index close to 1. The indices reveal a perfectly proportional relationship between \( \text{NH}_3 \) and \( \text{NH}_4 \) (\( \rho = 1 \)) which is sensible as the \( \text{NH}_4 \) values were calculated from the measured ammonia values by the analytical laboratory (\( \text{NH}_3 \) measured as N in mg/L). Proportional relationships (\( \rho > 0.99 \)) also exist for the major ion pairs Na/Cl and Ca/HCO\(_3\).

Since CoDa techniques treat all components of the composition simultaneously, the absence of data or the presence of censored values in a compositional dataset can prevent the application of the log-transformation approach (Palarea-Albaladejo et al., 2014; Buccianti et al., 2014). The censored values demand careful treatment in order to avoid the introduction of serious bias to the results. In hydrochemical datasets it is not uncommon to have observations with non-detectable levels of one or more components. A detection limit (DL) is the threshold below which measured values of a particular analyte cannot be distinguished from a blank signal. Laboratories regard values near the DL as less precise than values further away, and account for this uncertainty by introducing a LOQ that is usually a multiple of the DL. The LOQ can be considered as a threshold for reliable measurements (Palarea-Albaladejo et al., 2015). A simple and common approach, which is standard in environmental studies using MSA, is to address censored data by replacement with a non-zero value equal to half the LOQ for that particular variable (e.g., Farnham et al., 2002; Güler et al., 2002; Raiber et al., 2012). However, this and similar approaches do not take into account the inherent multivariate structure of the data and are incompatible with CoDa. A superior approach, and one that is employed here, is to replace censored data points based on the log-ratio Expectation-Maximisation algorithm of Palarea-Albaladejo and Martín-Fernández (2008). This replacement procedure uses the information in the covariance structure to produce a conditional estimate of the censored values whilst preserving the ratios between those observations or components without censored values (Palarea-Albaladejo et al., 2014).
| As  | B   | Ba  | Br  | Ca  | Cl  | Co  | Cr  | Cu  | Fe  | Ga  | Ge  | Hg  | In  | I   | K   | La  | Mg  | Mn  | Mo  | Nb  | Ni  | Pb  | Sb  | Se  | Si  | Sn  | Sr  | TI  | Tl  | U   | V   | W   | Xe | Xe | Zn  | Al  | Cd  | Co  | Cr  | Cu  | Fe  | Ga  | Ge  | Hg  | In  | I   | K   | La  | Mg  | Mn  | Mo  | Nb  | Ni  | Pb  | Sb  | Se  | Si  | Sn  | Sr  | TI  | Tl  | U   | V   | W   | Xe | Xe | Zn  | Al  | Cd  | Co  | Cr  | Cu  | Fe  | Ga  | Ge  | Hg  | In  | I   | K   | La  | Mg  | Mn  | Mo  | Nb  | Ni  | Pb  | Sb  | Se  | Si  | Sn  | Sr  | TI  | Tl  | U   | V   | W   | Xe | Xe | Zn  | Al  | Cd  | Co  | Cr  | Cu  | Fe  | Ga  | Ge  | Hg  | In  | I   | K   | La  | Mg  | Mn  | Mo  | Nb  | Ni  | Pb  | Sb  | Se  | Si  | Sn  | Sr  | TI  | Tl  | U   | V   | W   | Xe | Xe | Zn  | Al  | Cd  | Co  | Cr  | Cu  | Fe  | Ga  | Ge  | Hg  | In  | I   | K   | La  | Mg  | Mn  | Mo  | Nb  | Ni  | Pb  | Sb  | Se  | Si  | Sn  | Sr  | TI  | Tl  | U   | V   | W   | Xe | Xe | Zn  | Al  | Cd  | Co  | Cr  | Cu  | Fe  | Ga  | Ge  | Hg  | In  | I   | K   | La  | Mg  | Mn  | Mo  | Nb  | Ni  | Pb  | Sb  | Se  | Si  | Sn  | Sr  | TI  | Tl  | U   | V   | W   | Xe | Xe | Zn  | Al  | Cd  | Co  | Cr  | Cu  | Fe  | Ga  | Ge  | Hg  | In  | I   | K   | La  | Mg  | Mn  | Mo  | Nb  | Ni  | Pb  | Sb  | Se  | Si  | Sn  | Sr  | TI  | Tl  | U   | V   | W   | Xe | Xe | Zn  | Al  | Cd  | Co  | Cr  | Cu  | Fe  | Ga  | Ge  | Hg  | In  | I   | K   | La  | Mg  | Mn  | Mo  | Nb  | Ni  | Pb  | Sb  | Se  | Si  | Sn  | Sr  | TI  | Tl  | U   | V   | W   | Xe | Xe | Zn  | Al  | Cd  | Co  | Cr  | Cu  | Fe  | Ga  | Ge  | Hg  | In  | I   | K   | La  | Mg  | Mn  | Mo  | Nb  | Ni  | Pb  | Sb  | Se  | Si  | Sn  | Sr  | TI  | Tl  | U   | V   | W   | Xe | Xe | Zn  | Al  | Cd  | Co  | Cr  | Cu  | Fe  | Ga  | Ge  | Hg  | In  | I   | K   | La  | Mg  | Mn  | Mo  | Nb  | Ni  | Pb  | Sb  | Se  | Si  | Sn  | Sr  | TI  | Tl  | U   | V   | W   | Xe | Xe | Zn  | Al  | Cd  | Co  | Cr  | Cu  | Fe  | Ga  | Ge  | Hg  | In  | I   | K   | La  | Mg  | Mn  | Mo  | Nb  | Ni  | Pb  | Sb  | Se  | Si  | Sn  | Sr  | TI  | Tl  | U   | V   | W   | Xe | Xe | Zn  | Al  | Cd  | Co  | Cr  | Cu  | Fe  | Ga  | Ge  | Hg  | In  | I   | K   | La  | Mg  | Mn  | Mo  | Nb  | Ni  | Pb  | Sb  | Se  | Si  | Sn  | Sr  | TI  | Tl |
Table 2-4: (previous page) Variation matrix for thermal spring hydrochemistry dataset (30 variables). The lower triangle provides the variation element ($\tau_{ij}$) for all variable pairs – the smaller the variation element, the greater the proportionality between the two variables. The upper triangle contains a transformation of each variation element, which provides an approximate index of proportionality for each variable pair. Those proportionality indices indicating very strong relationships (> 0.8) are highlighted in bold text.

In this study, the centred-log-ratio (clr) transformation was applied to each of the raw data matrices. The clr-transformation uses the geometric mean of the data as a denominator to represent compositional data as a real vector. For a matrix, $x$, of $D$ parts:

$$\text{clr}(x) = \left(\ln \frac{x_i}{g(x)}\right)_{i=1,...,D}, \text{ where } g(x) = \sqrt[0]{x_1 \cdot x_2 \cdot ... \cdot x_D}.$$  \hfill (Eq. 2-5)

This transformation was developed by Aitchison (1986) and is commonly used for covariance-based PCA (Drew et al., 2008; Engle and Blondes, 2014: see also Filzmoser et al., 2009b). By log-transforming the data, two key principles of CoDa are met - scale invariance and sub-compositional coherence. Scale invariance implies that the data are unitless and the focus is now upon the relative relationships between the various components. Sub-compositional coherence means that results from a subset of components and results from the full composition are not contradictory, i.e., results do not depend upon whether the data are closed to a common constant or not (Palarea-Albaladejo and Martín-Fernández, 2015). In this analysis, no closure operation was applied to the data.

2.4.3. Multivariate statistical analysis (MSA)

MSA tools, such as HCA and PCA, are proven techniques for the exploration of large hydrochemical datasets (recent examples using CoDa techniques include Buccianti et al. (2014), and Engle and Rowan (2014)). In this work, MSA was applied to reduce the number of parts (or variables) of the dataset and to decipher the underlying processes affecting the hydrochemistry (in particular, to distinguish between the hydrochemical processes at work in the deep, thermal aquifer and those processes typical of shallow, cold, Irish groundwater). It is important to note that while MSA allows for samples to be grouped by similar physical and chemical properties, it does not immediately identify which trends or processes may be important in controlling the composition of the groundwater (Güler et al., 2002). It is therefore important to consider the results of MSA in conjunction with other
available hydrogeological and geological data to interpret the underlying structure in the dataset in a meaningful way. Here, the results are interpreted alongside more traditional graphing methods (Figure 2-2) and time-lapse temperature and electrical conductivity measurements (Figure 2-4).

**Hierarchical cluster analysis (HCA)**
Cluster analysis is a family of multivariate techniques designed to uncover and classify naturally occurring subgroups within a dataset based upon similarities between the observations. HCA is one such technique that seeks to build a hierarchy of clusters, and can also be applied to compositional data that are log-transformed (Van den Boogaart and Tolosana-Delgado, 2013). Agglomerative HCA was employed to group the water samples based upon similarities in their hydrochemistry, and was applied to clr-transformed data from the Leinster thermal springs and cold seepages (Matrix (3)). The Euclidean distance and Ward’s linkage method were used. Euclidean distance of clr-transformed data is equivalent to the Aitchison distance (e.g., Aitchison et al., 2000). Visual examination of the dendrogram suggested the presence of six strongly distinct clusters (boxes A to F in Figure 2-6).

**Principal component analysis (PCA)**
PCA is a multivariate data analysis technique that attempts to elucidate an underlying structure to a dataset (Davis, 1986). It is particularly useful for exploring large datasets as it effectively reduces the number of parts (or variables) in the data, but core details or patterns in the data are not lost (Page et al., 2012). It extracts the major components that control the chemical variability in the dataset (Güler et al., 2012) and is a well-proven technique for hydrochemical scenarios, including the investigation of thermal spring water provenance (Helena et al., 2000; Tanaskovic et al., 2012), although the usual approach, as exemplified by the examples cited, is to use a classical PCA on raw hydrochemical data, i.e., the data are treated as non-compositional. Here, the PCA was performed on appropriately log-transformed data following the CoDa approaches of Otero et al. (2005), Engle and Rowan (2014) and Engle et al. (2014).

Standardization and normalization of the raw data is commonly performed prior to a PCA (Davis, 1986; Cloutier et al., 2008; Page et al., 2012). For the CoDa approach,
the data are centred once the clr-transformation is applied. The PCA operation extracts the principal components, or loadings, by singular value decomposition (SVD) of the (clr-transformed) data matrix. SVD is generally the preferred method for PCA for numerical accuracy and stability (R Development Core Team, 2015). The SVD produces a new matrix of standardized coordinates for each sample, called the scores, and a new matrix of variable loadings with columns representing the principal components.

The results of a PCA are usually interpreted with a biplot – the joint graphical representation of the variable loadings and sample scores (Gabriel, 1971). The samples are represented as points and the variables as arrows, or rays. The transformation of compositional data using log-ratios has an effect on how the biplot may be interpreted – after transformation, meaningful statements may only be made involving ratios of components (Buccianti and Grunsky, 2014). The interpretation of the covariance biplot has been adapted for compositional data (Aitchison and Greenacre, 2002) to explore the compositional structure of codependence of the variables. In a compositional covariance biplot, the rays of the biplot cannot be directly interpreted as each has a complex relationship to all of the original variables, so the links between ray vertices are more important for interpretation. The length of a ray generally represents the communality of the variable, i.e., how much of the total variance is represented by that variable (Otero et al., 2005). The higher the proportion of the total variance in the dataset represented by the biplot, the better and more trustworthy the representation of the variables involved. For the compositional covariance biplots used in this paper, the following rules of interpretation apply (subject to the proportion of total variance explained by the biplot): 1) if two vertices are coincident or situated close to each other, they are proportional; 2) the length of a link between two vertices is proportional to the log ratio of those two variables; 3) if three or more vertices lie on the same link, they may represent a sub-composition with one single degree of freedom; and 4) if two links between four separate clr-variables are orthogonal then the corresponding pairs of variables may vary independently of each other (this also applies for two orthogonal links describing sub-compositions).
Figure 2-6: Cluster analysis dendrogram for compositional agglomerative HCA of Matrix (3). The HCA has clustered the samples into six distinct groups according to their chemical similarities, labelled A to F. Samples are numbered according to spring: 1) St. Edmundsbury spring; 2) St. Gorman’s Well; 3) Huntstown Fault spring; 4) Huntstown Fe₂O₃ cold seepage; 5) Huntstown CaCO₃ cold seepage; 6) Kemmins Mill spring; 7) Kilbrook spring; and 8) Louisa Bridge Spa Well. They are also labelled according to the season in which the sample was collected: a. August 2013; b. October 2013; c. January 2014; d. May 2014; and e. August 2014. Duplicate samples for each spring were collected.
2.5. Compositional MSA results

2.5.1. HCA

The HCA of the thermal spring data (Matrix (3)) identified six main clusters of samples (Figure 2-6). These clusters mostly correspond to individual springs, but with some exceptions. St. Edmundsbury spring and Louisa Bridge Spa Well are grouped into one cluster (C), indicating a very close similarity between the two. The remaining five clusters, A, B, D, E and F contain samples from Kemmins Mill spring, Huntstown “CaCO$_3$” cold seepage, Huntstown “Fe$_2$O$_3$” cold seepage, Kilbrook spring and Huntstown Fault spring respectively. Samples from St. Gorman’s Well are distributed between three clusters (A, B and F). The samples collected from St. Gorman’s Well in July/August and October 2013 are most similar to the warm spring from Huntstown Fault (F); samples collected in January 2014 are grouped with Huntstown “CaCO$_3$” cold seepage (B); and the samples from May and August 2014 are grouped with the warm spring at Kemmins Mill (A). The HCA suggests that St. Gorman’s Well had the largest variation in hydrochemistry throughout the sampling period; this is corroborated by the time-lapse temperature and electrical conductivity measurements (Table 3 and Figure 3), which show that St. Gorman’s Well also has the largest variation in temperature throughout the year. The nature of this temporal variation and what it might imply about the provenance of the warm component of the spring water is discussed further in section 2.6.4.

2.5.2. PCA

PCA was applied to the three different data matrices described in section 2.4.1 and Figure 2-5 above. The number of observations for the thermal spring data included duplicate measurements, and these are indicated clearly in Figure 2-7. The inclusion of these duplicates in the PCA does not appreciably affect the outcomes or interpretation, but illustrates the reliability and quality of the measurements. The PCA of Matrix (1) investigated the hydrogeological processes controlling the major ion concentrations and overall hydrochemistry within the group of thermal springs; PCA of Matrix (2) explored any differences or similarities between the thermal springs and cold groundwater from the same area; and PCA of Matrix (3) investigated the more subtle effects of any hydrogeological processes impacting the trace element hydrochemistry of the thermal waters.
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![Two principal component plots with various data points labeled for different thermal springs and Ryewater wells, and seasons indicated.]

<table>
<thead>
<tr>
<th>Thermal springs:</th>
<th>Ryewater wells:</th>
<th>Seasons:</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. Edmundsbury</td>
<td>Deep</td>
<td>a August 2013</td>
</tr>
<tr>
<td>St. Gorman’s Well</td>
<td>Shallow</td>
<td>b October 2013</td>
</tr>
<tr>
<td>Huntstown Fault</td>
<td>Transition</td>
<td>c January 2014</td>
</tr>
<tr>
<td>Huntstown Fe2O3 seep</td>
<td>Subsoil</td>
<td>d May 2014</td>
</tr>
<tr>
<td>Huntstown CaCO3 seep</td>
<td>Surface water</td>
<td>e August 2014</td>
</tr>
<tr>
<td>Kemnans Mill spring</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kilbrook spring</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Louisa Bridge Spa Well</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Figure 2-7:** (see previous page for a) and b)) Compositional PCA biplots: a) Matrix (1) (see section 2.4.1), orthogonal links $S$ and $C$ are indicated; b) Matrix (2); c) Matrix (3), orthogonal links $M$, and $S - C$ are indicated. Hydrochemical sampling seasons for the thermal data are indicated as follows: a = Jul/Aug 2013, b = Oct 2013, c = Jan 2014, d = May 2014, e = Aug 2014. Duplicate samples for each spring were collected. For the historical cold groundwater data, samples were collected at various times between 2009 and 2012. The season in which these samples were collected is indicated as follows: a = Jun – Aug, b = Sept – Nov, c = Dec – Feb, d = Mar – May.
Matrix (1): Major ions – Leinster thermal spring dataset (9 variables)

The scree plot of variance in Figure 2-8 a) “breaks” after the second component (i.e., there is a sudden and marked change in slope), indicating that a compositional biplot of the first two PCs will provide a trustworthy representation of the data. The first two PCs represent 91.1 % of the total log-ratio (clr) variance in this dataset. The compositional covariance biplot (Figure 2-7 a)) shows the highest clr-variances for SO$_4$ and Si, followed by Cl and Na, and the lowest clr-variances for K, Sr and Mg.

The PCA has grouped the samples from Louisa Bridge Spa Well, St. Edmundsbury spring and Kilbrook spring separately in the western quadrants of the biplot. This is in agreement with the HCA, where samples from these springs were clustered with the highest p-values. Samples from the remaining springs and cold seepages are located in the eastern quadrants of the biplot and appear to be more disperse. There is overlap between samples from St. Gorman’s Well and Kemmins Mill spring in the NE quadrant and the three sampling points from Huntstown plot near to each other in the SE quadrant. Samples from St. Gorman’s Well have the largest dispersion in the biplot, indicating that it has the highest clr-variance of all the springs. On the basis of this plot, which explores the major ion chemistry only, St. Gorman’s Well does not follow the temporal variation pattern revealed by the HCA, but appears to behave similarly to Kemmins Mill spring for all sampling seasons.

The main inferences arising from the biplot in Figure 2-7 a) are:

- The vertices for Na and Cl lie close to each other; this indicates their proportionality (verified by the very low clr-variance of [Na, Cl]; 0.35 % of total clr-variance). The samples from Louisa Bridge Spa Well and St. Edmundsbury spring are strongly associated with Na and Cl.
- It is possible to draw a link between the vertices of Cl, Na, K, and Sr, indicating that these variables may form a sub-composition with a single degree of freedom.
- The vertices of SO$_4$, Ca, HCO$_3$ and Si lie on a common link, forming a sub-composition with one degree of freedom. This link is almost orthogonal to the link drawn between Cl, Na, K, and Sr, suggesting that these two sub-compositions may vary independently of each other. Ca could lie on either link, however, the sub-compositions are more orthogonal to each other, and therefore more independent of each other, when the variables are distributed
between them as [Cl, Na, K, Sr] and [SO$_4$, Ca, HCO$_3$, Si] (this was checked by calculating the correlation between the first singular vectors for each sub-composition – see Van den Boogaart and Tolosana-Delgado, 2013).

- The two links can be interpreted as two independent influencing processes, or sets of processes, on the hydrochemistry of the springs: the “water-rock interaction” link $S$ [Cl, Na, K, Sr] representing the increased association with saline, Na-Cl-type waters towards the Na/Cl end of the link, and perhaps increased residence times towards the K/Sr end of the link; and the “carbonate” link $C$ [SO$_4$, Ca, HCO$_3$, Si] representing the dissolution of different types of carbonate bedrock (HCO$_3$ at one end of the link and SO$_4$ at the other end).

- St. Edmundsbury spring and Louisa Bridge Spa Well have a strong association with the Na/Cl end of link $S$. Samples in the eastern quadrants of the biplot are more disperse and have a stronger association with the $C$ link; they range from having an association with the SO$_4$ end of the link (the Huntstown sampling locations) to being more strongly associated with HCO$_3$ and Si (St. Gorman’s Well and Kemmins Mill).

![Figure 2-8](image_url)

**Figure 2-8:** Scree plots of the variance represented by each principal component for each data matrix: a) Matrix (1); b) Matrix (2); and c) Matrix (3).

**Matrix (2): Major ions – thermal spring and Ryewater datasets (9 variables)**

The scree plot “breaks” after the third PC (Figure 2-8 b)), indicating that the majority of the clr-variance in the dataset should be represented by these three PCs (77.6 %). The total clr-variance described by the first two PCs (and hence by the covariance biplot) is 64.9 %, making any initial interpretation less reliable than for the previous PCA. The biplot (Figure 2-7 b) reveals that the inclusion of the
historical cold groundwater data has produced a noticeably different distribution of the variable vertices. Cl has the highest clr-variance in the biplot, followed by Sr, Na, Ca and SO₄. In terms of the distribution of the samples, the PCA has again successfully, and rather tightly, grouped the clusters of thermal springs identified in the HCA. St. Edmundsbury spring and Louisa Bridge Spa Well are located in the NW quadrant, Kilbrook spring is rather close to the origin in the SW quadrant, while the remaining springs and cold seepages lie in the eastern quadrants. St. Gorman’s Well again exhibits the largest dispersion of all the thermal springs and plots close to the vertices for HCO₃ and Si. Examining the distribution of samples from the Ryewater dataset, there is a clear distinction between samples from the deep bedrock boreholes, which lie in the SW quadrant, and samples from shallow bedrock, the transition zone and subsoil horizons, which generally lie east of centre and close to the origin. Samples from the transition zone in boreholes RW1 and RW2 form a disperse cloud of points in the NW quadrant near the Cl vertex indicating that the very shallow groundwater from the transition zone at these two locations has a hydrochemistry that is dominated by Cl.

The main inferences arising from the biplot in Figure 2-7 b) are:

- The NW quadrant is dominated by Cl and Na; the clr-variance for Cl and Na is equal to 5.84% of the total variance, indicating that they have a high degree of proportionality in this data set. Shallow cold groundwater from the transition zone (RW1T and RW2T) has a large variation in Cl but little association with Na suggesting possible extraneous chloride contamination of this shallow groundwater. St. Edmundsbury spring and Louisa Bridge Spa Well show an association with both Na and Cl and are the only thermal waters in this particular quadrant, as expected.

- The vertices for Ca and SO₄ are almost coincident; their clr-variance is 7.24% of the total, suggesting that these variables are proportional. Likewise, the link between Si and HCO₃ is very short; their clr-variance is 6.46% of the total, indicating that these variables are proportional.

- A common link may be drawn between Ca, SO₄, Si and HCO₃, indicating a sub-composition with one degree of freedom (clr-variance for the sub-composition is 24.76% of the total clr-variance in the data set). The thermal springs and cold seepages from St. Gorman’s Well, Kemmins Mill and
Huntstown are located along this link. Similar to Figure 2-7 a), St. Gorman’s Well and Kemmins Mill spring have a closer association with the Si and HCO$_3$ end of this link whereas the Huntstown samples have a closer association with the Ca and SO$_4$ end.

- The deep, cold groundwaters from RW1D, RW2D and RW3D lie in the SW quadrant, along with Kilbrook thermal spring, and show an association with Sr and, to a lesser degree, K.

**Matrix (3): thermal spring dataset including minor and trace ions (30 variables)**

The scree plot appears to “break” after the fourth PC (Figure 2-8 c)), after which a total of 85.6 % of the total clr-variance of the dataset is represented. A biplot of the first two PCs accounts for just 61 % of the total variance. The hydrochemistry of this dataset is quite complex and cannot be adequately represented by just two PCs. However, the biplot (Figure 2-7 c)) has some interesting features. The total variance of the dataset is dominated by Mn which has the highest communality, followed by Co (23.09 and 10.47 % of the total clr-variance respectively). These two variables lie in the NW quadrant. The sub-composition [Li, Cs, Na, Cl] is situated in the SW quadrant and represents just 1.52 % of the total clr-variance, indicating a proportional relationship. The sub-composition [SO$_4$, Ca, HCO$_3$, Si] is situated in the NE quadrant and represents 3.39 % of the total clr-variance, indicating a proportional relationship. The clusters from Figure 2-6 are once again clearly defined in terms of the distribution of the samples in Figure 2-7 c). Samples from St. Edmundsbury spring and Louisa Bridge Spa Well lie further away from each other than in the other biplots in the SW quadrant, indicating subtle differences in hydrochemistry, which are evident upon comparison of their trace element chemistries. The samples from Huntstown are also more disperse: samples from Huntstown “Fe$_2$O$_3$” cold seepage and the Huntstown Fault spring are mainly in the NW quadrant whereas samples from Huntstown “CaCO$_3$” cold seepage lie in the opposite corner of the biplot. Samples from St. Gorman’s Well show a remarkably large, almost linear dispersion from NW to SE of the biplot, which is more consistent with the results of the HCA.

The main inferences that may be discerned from the biplot in Figure 2-7 c) are:

- There appears to be a common link between the following variables from southwest to northeast on the biplot: Li, Cs, Cl, Na, Rb, Br, K, Sr, Mg, Si, HCO$_3$, Ca, and SO$_4$. The link between them represents a continuum between
the two independent hydrogeological processes identified in Figure 6 a), and processes \( S \) [Na, Cl, K, Sr] and \( C \) [Si, HCO\(_3\), Ca, SO\(_4\)] form endmembers of an axis (the link \( S – C \)) representing the trade-off between saline and calcium-bicarbonate groundwaters in the dataset.

- As expected, St, Edmundsbury spring and Louisa Bridge Spa Well have the greatest association with the \( S \) end of the link \( S – C \), and their hydrochemistry is clearly governed by increased salinity. Moving along the \( S – C \) link, Kemmins Mill spring, St. Gorman’s Well and the samples from Huntstown are shown to have an association with the \( C \) end of the link.

- The link between Mn and Ba is orthogonal to the link \( S – C \); this orthogonality was checked by calculating the correlation between the first singular vectors for each sub-composition (Van den Boogaart and Tolosana-Delgado, 2013), which was found to be very low (a value of 0.07), thus the links are independent. This new link is called \( M \) and is independent of processes \( S \) and \( C \). Link \( M \) represents the processes of mineralisation and the dissolution of mineral sulfides, sulfates and oxides hosted in the carbonate bedrock, particularly those containing Mn at one end of the link, and Ba at the other. Barite and manganese are sometimes associated with the massive sulfide deposits found in Irish Lower Carboniferous limestones (e.g., Cole, 1922; Boyce et al., 2003).

- Samples in the northwest quadrant of the biplot have a stronger association with the Mn end of link \( M \), such as samples from Huntstown “Fe\(_2\)O\(_3\)” cold seepage and Huntstown Fault spring, which also have the highest Fe content.

- Data from St. Gorman’s Well is widely dispersed in the biplot. At all times, the data from St. Gorman’s Well has a stronger association with the \( C \) end of the \( S – C \) link. The greatest seasonal variation in chemistry occurs along the axis of link \( M \). The spring has the closest association with the Mn end of link \( M \) in the low-recharge period (seasons “a” and “b”).

2.6. Discussion

For this provenance study of the thermal springs, it is largely assumed that the compositions measured at the springs represent the compositions of their respective sources, i.e., there has been no further modification of the groundwater chemistry en-
route to the surface. The compositional approach to MSA provides a deeper insight into the hidden structure of the data set than a standard statistical approach. The results of the three compositional PCAs were used to identify three underlying processes that are likely to control the hydrochemistry of the thermal springs (“salinity” \((S)\), “carbonate” \((C)\) and “mineralisation” \((M)\)), and to examine the covariance behaviour of the springs alongside several cold groundwater samples from the same locality. The two most important processes that govern the major ion hydrochemistry, \(S\) and \(C\), are independent and define the major ion hydrochemistry of the thermal springs (Figure 2-7 a)). When data from the Ryewater boreholes are introduced, or more variables are added to the thermal dataset, the picture becomes less clear with less of the total variance represented by the biplot (Figure 2-7 b)). This is because for compositional data, trace element concentrations typically exhibit large log-ratio variances but low Euclidean variances (the concentrations are small by definition) (see: Otero et al., 2005; Engle et al., 2014). In Figure 2-7 c) processes \(S\) and \(C\) form endmembers of an axis (the link \(S – C\)), which is orthogonal to link \(M\), indicating that process \(M\) is independent of processes \(S\) and \(C\). Here, we discuss each of the processes in detail, and discuss how the compositional MSA has added to the understanding of the temporal variation of St.Edmundsbury spring, St. Gorman’s Well and Louisa Bridge Spa Well (Figure 2-4).

2.6.1. \(S\), the “water-rock-interaction” link

\(S\) joins the major ions \([\text{Na, Cl, K, Sr}]\) (and possibly Mg and Ca). This link represents the difference between saline, NaCl-type waters at the Na/Cl end, and more typical Ca-HCO\(_3\)-type waters at the other end, a difference that is probably governed by a combination of hydrogeological processes. In Figure 2-7 c), \(S\) also includes the minor and trace ions Li, Cs, Rb and Br. Fluid-mobile trace elements, such as Li, Rb and Cs, are generally considered as residence-time indicators as they are progressively released from carbonate, silicate or oxide minerals in the aquifer, even during periods of low-flow (Aquilina et al., 1997; Edmunds and Smedley, 2000; Reyes and Trompetter, 2012). Likewise, K in groundwater is controlled by the amount and duration of progressive water-rock interactions (Edmunds et al., 2003). K comes principally from the weathering of feldspars and clay minerals, and is not typically abundant in pure carbonate bedrock. This may indicate an extra source of K to the groundwater, such as a non-carbonate lithology situated deeper in the basinal
sequence, or in the basement beneath it. The most likely potential contributors of extra K to the thermal springs are the terrestrial Devonian sandstones, mudstones and conglomerates beneath the Dublin Basin. These sediments are commonly arkosic and contain detrital clastic materials from erosion and un-roofing of the Caledonian granites. (The Lucan Fm. overlying the Waulsortian Limestone Fm. also contains shales and is quite rich in clay materials. The deep Ryewater boreholes were all drilled in this particular unit, and this may explain the observed association between the deep, cold groundwater in these boreholes and K and Sr in Figure 2-7 b.) In general, an association with the Na/Cl end of link \( S \) represents the influence of salinity and increased water-rock interaction times (and increased residence times) on the groundwater chemistry, and possibly the influence of non-carbonate lithologies.

St. Edmundsbury spring and Louisa Bridge Spa Well have the highest electrical conductivities of the Leinster thermal springs (maxima of 1664 \( \mu \text{s/cm} \) and 1644 \( \mu \text{s/cm} \) respectively) and the highest chloride concentrations (means of 487 mg/L and 481 mg/L respectively). They form their own cluster in the HCA (Figure 2-6) with a very high \( p \)-value. Their representation in the Piper diagram in Figure 2-2 indicates how different they are from the other thermal waters and cold groundwaters. They also contain high concentrations of K (means of 5.7 mg/L and 8.0 mg/L respectively). Their strong relationship with \( S \) suggests they are the most influenced by salinity and have the longest residence times. This is supported by other available data, such as legacy isotopic and inert gas measurements (Burdon, 1983) that suggest a groundwater residence time in excess of 30,000 years for Louisa Bridge Spa Well.

The relationship between Na, Cl and Br is used to provide information about the provenance and evolution of saline waters (e.g., Davis et al., 1998), and can help to assess the source of extra chloride in the groundwater. The extra chloride may be from either: natural dissolution of chloride evaporites, such as halite (\( \text{NaCl} \)) or sylvite (\( \text{KCl} \)); or anthropogenic contamination (e.g., the addition of fertilizers to land, de-icing of roads or industrial practices) (Davis et al. 2001). This relationship has traditionally been investigated by plotting the variables in a scatter-plot, or by plotting a combination of ratios of the variables, and there are many examples available in the literature with which to compare new data. However, these approaches do not fully account for the compositional nature of the data, and have
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the potential to cause spurious correlations and misleading results. A newer, and less used, approach using the isometric log-ratio (ilr) transformation developed by Egozcue et al. (2003) can be used to avoid potential problems. This method was applied in Engle and Rowan (2013) and is discussed in detail therein. The method uses the ilr-transformation to convert the compositional data (expressed here as molar concentrations) to a new coordinate system, where each point is represented by \((z_2, z_1)\).

\[
\begin{align*}
  z_1 &= \frac{1}{\sqrt{2}} \ln \frac{[Na]}{[Cl]} ; \\
  z_2 &= \frac{\sqrt{2}}{\sqrt{3}} \ln \sqrt[3]{\frac{[Na][Cl]}{[Br]}} .
\end{align*}
\]

Eq. (2-6) Eq. (2-7)

In the first coordinate, \(z_1\), Br is excluded so this provides insight into the relative gain/loss of Na compared to Cl. In \(z_2\), Br is included and this can be used to assess the degree of evaporite dissolution by the groundwater, as Br is usually excluded from the lattices of evaporite crystals, and is thus depleted in waters that gain their chloride from the dissolution of evaporites. Figure 2-9 a) shows the ilr-coordinates for the thermal spring data from this study (Na-Br-Cl), and these data are compared to the geochemically modelled pathway for the progressive dissolution of halite by seawater from Engle and Rowan (2013). Their geochemical model tested the process of halite dissolution versus the evaporation of seawater; the model assumes no major input of Na, Cl, or Br other than seawater or halite dissolution. Samples containing Na and Cl derived from the evaporation of seawater should plot down and to the left of the value for modern seawater, while meteoric waters which have dissolved halite should plot up and to the right.

The samples from St. Edmundsbury spring and Louisa Bridge Spa Well are distinguished from the other thermal springs as having higher \(z_2\) values, indicating less Br and suggesting that the Cl comes from the dissolution of evaporites (probably halite). The lower values for \(z_1\) for these two springs indicate that the Na/Cl ratio is reduced in these springs. The samples plot below the pathway for halite dissolution but to the right of modern seawater, so the samples from St. Edmundsbury spring and Louisa Bridge Spa Well could represent a mixture between water that dissolved evaporites, and water that has not been accounted for by the simple geochemical model.
Figure 2-9: a) Plot of ilr-coordinates $z_1$ and $z_2$ for the Na-Cl-Br system for all thermal spring data. An increase in $z_2$ due to a lower relative amount of Br suggests the addition of chloride through the dissolution of evaporites (halite). Geochemically modelled pathway for the progressive dissolution of halite by seawater, and modern seawater measurements after Engle and Rowan (2013). b) Relationship between the proportion of Ca to Na in thermal spring waters and the origin of their salinity (as indicated by Cl/Br molar ratios). St. Edmundsbury spring and Louisa Bridge Spa Well lie in the “redissolved evaporites” range of values for Cl/Br (after Yardley and Bodnar, 2014), but contain excess Ca which is probably due to an increased interaction with carbonate bedrock.

Although the use of ratios of raw concentrations has been shown to be problematic (Engle and Rowan, 2013), the Cl/Br mass ratios for the spring waters were examined and compared to existing values in the literature; Cl/Br was found to exceed 200 for Kilbrook spring, St. Edmundsbury spring and Louisa Bridge Spa Well, which suggests that additional chloride is available to the groundwater aside from normal
concentrations that may be expected from meteoric recharge and shallow groundwater (Davis et al., 1998; Freeman, 2007). Waters affected by the dissolution of halite commonly have Cl/Br mass ratios of between 1,000 and 10,000 (Davis et al., 1998). St. Edmundsbury and Louisa Bridge Spa springs lie at the lower end of this range (840 to 1,314). The excess chloride is not likely to have an anthropogenic source given that no other common indicators of pollution (such as nitrates or phosphates) were detected in these spring waters, and waters contaminated by sewage generally have lower Cl/Br mass ratios of between 300 and 600 (Davis et al., 1998). The lack of seasonal variation in chloride rules out the application of salt to roads in winter as a source. The origin of the salinity was further investigated by using the relationship between the proportion of Ca to Na in the warm springs and their Cl/Br molar ratios (Figure 2-9 b)). These results were compared to those for brines from sedimentary basins (Yardley and Bodnar, 2014). St. Edmundsbury spring and Louisa Bridge Spa Well were found to plot in the Cl/Br range for a “redissolved evaporite” source, but to contain higher levels of Ca than redissolved evaporite brines from sedimentary basins (Figure 2-9 b)). These values of Cl/Br and Ca suggest that these thermal spring waters from the Dublin Basin have derived their excess Cl from the dissolution of an evaporite source, followed by a phase of interaction with carbonate rocks, which has led to an elevated Ca signature compared to the sedimentary basinal brines of Yardley and Bodnar (2014).

The use of both ilr-ratios and conventional molar ratios in Figure 2-9 strongly suggest that the waters of St. Edmundsbury spring and Louisa Bridge Spa Well have gained their high chloride concentrations from the dissolution of evaporites. Evaporite deposits are not known at present from the vicinity of the Dublin Basin, but it is feasible that they could have precipitated during the deposition of the (basal) terrestrial part of the Devonian sequence, particularly during more arid intervals. For comparison, the Cl/Br mass ratios (345 to 556) for thermal springs in Bockfjord, Svalbard, Norway (maximum temperature of 25.6 °C) suggest that these springs derived at least part of their excess chloride from evaporitic deposits in Devonian sandstones (Banks et al., 1998). Evaporites could also have formed as a result of fluctuations in sea level during the later Viséan leading to exposure of limestone shelf areas (e.g., Cózar and Somerville 2005; see also Barham et al., 2012).
Clear evidence to support the existence of either Devonian or Viséan evaporites in or beneath the central Dublin Basin is admittedly lacking. Evaporites are documented in the lower Tournaisian strata of the northwestern part of the Dublin Basin, and on the margins of the Leinster Massif in the southeast of Ireland (Nagy et al., 2005). Dense brines formed by the dissolution of these evaporites could possibly have infiltrated and become trapped in deeper stratigraphic horizons, and these brines may have migrated to the central part of the Dublin Basin. Looking further afield, substantial Viséan-aged evaporites (anhydrites) are documented in the Solway Basin in Cumbria, England (Crowley et al., 1997); similar evaporite deposits may have formed closer to the Dublin Basin in the central and eastern Irish Sea (e.g., Hendry et al., 2015). Another potential source for evaporite brines in the Dublin Basin could be the migration of hyper-saline brines from post-Carboniferous evaporite deposits in adjacent offshore basins. In this respect, the halite-dominant facies in the Triassic Mercia Mudstone group of the Kish Bank Basin (e.g., Dunford et al., 2001) could be a possible candidate.

Johnson et al. (2009) investigated the fluids responsible for regional dolomitisation (related to base metal mineralisation) in the Irish Midlands, and included part of the Dublin Basin. From the study of fluid inclusions in minerals, they identified

- a widespread high-salinity, low-temperature fluid type, which on the basis of enrichment of Cl to Br, they interpreted as most likely being the product of dissolution of halite, and

- elevated levels of K in some of the fluids, which were attributed to interaction with either arkosic Devonian sandstones, or interaction with felsic basement rocks, including the Leinster Granite.

Although the circulation system that emplaced these fluid inclusions was in operation millions of years ago, it is still interesting to note that the hydrochemical results of Johnson et al. (2009) point to dissolution of evaporites and arkosic sandstones, which are both found within the Devonian sequence of the Irish Midlands.

2.6.2. \( C \), the “carbonate” link

The carbonate link, \( C \), can be considered as representing the influence of carbonate bedrock dissolution on the major ion groundwater hydrochemistry. All of the
thermal springs and cold seepages in the dataset are hosted in carbonate bedrock, yet some are more heavily influenced by carbonate dissolution than others. Figures 2-7 a) and 2-7 b) show a general division between HCO₃ and Si at one end of the C link, and SO₄ at the other, representing a trade-off between HCO₃ and SO₄ in their relationships with Ca. The samples that are most affected by C are distributed so that samples from St. Gorman’s Well and Kemmins Mill springs have a greater association with HCO₃, and samples from Huntstown Fault warm spring and the two nearby cold seepages (“Fe₂O₃” and “CaCO₃”) have a greater association with SO₄.

The addition of sulfate ions to the groundwater may be due to the oxidation of sulfides, such as pyrite (FeS₂). Pyrite is widely present in many lithostratigraphic units in the Dublin Basin. Oxidation of pyrite by the introduction of water in an oxidising environment proceeds as follows:

\[ 2\text{FeS}_2 + 2\text{H}_2\text{O} + 7\text{O}_2 \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \]  

(Eq. 2-8)

The iron sulfate (Fe₂SO₄) can then be converted to ferric iron oxide (Fe₂O₃) in the presence of bacteria (Sutton et al., 2013). The sulfuric acid produced then dissolves the calcium carbonate in the limestone to produce secondary gypsum (CaSO₄.2H₂O):

\[ \text{H}_2\text{SO}_4 + \text{CaCO}_3 \rightarrow \text{CaSO}_4 + \text{CO}_2 + \text{H}_2\text{O} \]  

(Eq. 2-9)

The increased SO₄ in the groundwater comes from the dissolution of the secondary gypsum, with some extra Ca also contributed. However, most of the Ca is likely to come from the interaction of groundwater with the carbonate bedrock itself (with the addition of Mg resulting from dissolution of dolomitised limestone). Thus the sulfate end of link C is best interpreted as representing the influence of the dissolution of pyrite-hosting carbonates, and in particular, those limestone formations within the Dublin Basin that contain widespread disseminated and vein pyrite. This is a shallow process requiring well-oxygenated input fluids.

The samples most strongly affected by C are from the two cold seepages from Huntstown, which have concentrations of Mg and Ca that increase linearly with SO₄. This suggests a similar source for both of these groundwaters, even though their physical appearances are very different (the “Fe₂O₃” seepage is characterised by a conspicuous iron-oxide staining whereas the “CaCO₃” seepage is so-called because of its tufa-like deposits). Pyrite is evident in bedrock sampled near to the seepages,
so it is highly likely that the SO$_4$ comes from the dissolution of secondary gypsum caused by the oxidation of pyrite and dissolution of carbonate. However, Fe occurs above the LOQ in only one of these seepages, “Fe$_2$O$_3$”. The levels of Fe in this seepage vary considerably throughout the year (from 97 in January 2014 to 3,494 ppb in August 2014) with the largest values occurring in October 2013 (2,198 ppb) and August 2014 (3,494 ppb) after two episodes of heavy rainfall. This indicates a strong connection and rapid response to recharge inputs, and suggests that there is a short-term increase in pyrite oxidation after periods of intense recharge. It is possible that the “Fe$_2$O$_3$” and “CaCO$_3$” seepages are hydraulically connected, as they both issue from the same lithological horizon.

Springs that are most closely associated with HCO$_3$ and Si, at the other end of the C link, include St. Gorman’s Well and Kemmins Mill spring. Both of these springs are thermal and have a close (proximal) association with Waulsortian limestones. The elevated HCO$_3$ may be a result of dissolution of the relatively pure carbonate belonging to this particular facies, whereas the elevated Si may be the result of dissolution of the enclosing, off-mound, chert-rich limestones and shales.

2.6.3. $M$, the “mineralisation” link

The mineralisation link, $M$, represents the effect of the dissolution of minerals on the hydrochemistry, particularly metal sulfides and oxides. As a process, $M$ is apparently independent of $S$ and $C$ but less important in terms of controlling the overall hydrochemistry of the samples. It controls the minor and trace element hydrochemistry, specifically the metals Mn, Co and Ba. However, $M$ can also be considered as representing other metals not included in the final dataset, such as Fe; there were too many observations with Fe below the LOQ to include it as a variable in the final MSA. Those samples with a high association with the Mn end of link $M$ generally have higher Fe too. This is not surprising, as Mn and Fe commonly occur together in hydrothermal mineral deposits in carbonate host rocks (e.g., Wilkinson et al., 2011; Fusswinkel et al., 2014).

As mentioned previously, hydrothermal base metal (Pb-Zn) mineral deposits are a significant feature of the Carboniferous limestones in the Irish Midlands (Figure 2-1a). Barite is commonly associated with these deposits (e.g., Tynagh mine, Co. Galway) and dissolution of this mineral phase could be a contributor of Ba to
groundwater. The clr-variance of Ba represents a rather small proportion of the total clr-variance of the dataset (under 2%), so any interpretation regarding Ba is tentative at best. Kilbrook spring has an association with the Ba end of link $M$, perhaps indicating a relative abundance in Ba from the dissolution of barite in the source aquifer beneath Kilbrook.

The springs with the closest association to the Mn end of link $M$ are Huntstown “Fe$_2$O$_3$” cold seepage and Huntstown Fault thermal spring. These springs have consistently high Mn concentrations and Huntstown Fault spring is the only sampling point in the survey area to consistently show Pb concentrations above the LOQ. Huntstown Fault spring also has the highest Zn levels with concentrations one order of magnitude higher than samples from any other sampling point. Manganese ore could feasibly occur in the same stratigraphic horizons as the Pb-Zn mineral deposits, and was historically mined in the Dublin Basin, in Sutton. Huntstown Fault spring discharges from a large Cenozoic strike-slip fault (Moore and Walsh, 2013) in sub-Waulsortian, argillaceous bioclastic strata. Mineralisation is commonly hosted towards the top of these argillaceous bioclastic strata. Given the stratigraphic position of the Huntstown Fault spring, and its proximity to another significant fault of Carboniferous age (Moore and Walsh, 2013), it is possible that the fault from which it springs, or some connecting fault, contains some Pb-Zn mineralisation along its length that is being re-mobilised (dissolved) by the slightly warm water (15.5 °C on average). Samples from the end of the low-recharge period from St. Gorman’s Well also lie close to the Mn end of link $M$, indicating a relative enrichment in Mn that is possibly due to the dissolution of Mn-bearing minerals during this period.

The interpretation of the MSA assumes that the chemistry of the groundwater is faithfully representative of the groundwater in the source aquifer. However, in reality it is likely that redox-sensitive components such as Fe and Mn that are present in deep, reduced waters may be lost by precipitation as these reduced waters interact with oxygenated shallow groundwater. The precipitation of metal-(hydr)oxides may also “scavenge” other redox-sensitive metals from solution. These types of redox reactions may contribute to the seasonal variability of these metals in some of the thermal springs.
2.6.4. Temporal variations of the spring waters

The discharge, temperature and hydrochemistry of the thermal springs vary throughout the year. In general, traditional hydrochemical graphing methods use only a portion of the available information and neglect the minor constituents (Güler et al., 2002). The Piper diagram in Figure 2-2, which plots the data in terms of the major ion content of each sample, fails to provide an adequate sense of any temporal variation of the springs. MSA can include more variables and so capture subtle temporal changes in hydrochemistry that may be missed by more traditional techniques (e.g., Helena et al., 2000; King et al., 2014). The PCA results are examined here alongside the time-lapse temperature records (Figure 2-4). The PCA biplots (Figure 2-7) show the PCA sample scores are most tightly grouped for St. Edmundsbury spring, indicating little annual variation in hydrochemistry. The sample scores for St. Gorman’s Well consistently show the greatest dispersion, indicating the most annual variation in hydrochemistry for this spring. This is an expected result as these springs show the least and the greatest annual variation in temperature - ignoring the obvious flooding by river water of St. Edmundsbury spring (see minimum values in Table 2-3 - the water is released periodically from a dam further upstream).

S reflects the influence of increased water-rock interaction on groundwater hydrochemistry, particularly for St. Edmundsbury spring and Louisa Bridge Spa Well. The implication that these particular springs have longer residence times is further supported by the stable temperature measurements made at both locations. The tight clustering of PCA sample scores from St. Edmundsbury spring suggests little seasonal variability in the spring, and this is supported by the steady temperature profile in Figure 2-4 a). Apart from the effects of flooding on St. Edmundsbury spring, the temperature remains relatively constant throughout the year (~16 °C), and does not seem to have a flashy response to rainfall. This steady temperature shows that St. Edmundsbury spring is not periodically influenced by shallow, cool, groundwater recharge processes; therefore the warm spring waters must have a longer residence time and a deeper circulation pattern that is insulated from surface and near-surface processes. Louisa Bridge Spa Well (Figure 2-4 c)) behaves somewhat differently to St. Edmundsbury spring; the water temperature between April and September is relatively stable (~17 °C), but there is greater
variation in temperature between October and April, which is when groundwater recharge is greatest and groundwater levels are highest. The PCA sample scores from Louisa Bridge Spa Well have a greater dispersion than for St. Edmundsbury spring. From Figure 2-4 c) it appears that Louisa Bridge Spa Well is influenced by mixing with cooler recharge waters during the winter recharge period. The stable temperatures recorded during the low recharge period (April to October) suggest a direct connection at this time between the spring and the source of the warm water without any mixing with cooler waters.

The observed seasonal differences between Louisa Bridge Spa Well and St. Edmundsbury spring are probably due to differences in their geological settings. Louisa Bridge Spa Well issues from a gravelly till deposit and was discovered in 1794 during the construction of the Royal Canal (Aldwell and Burdon, 1980). Depth to the limestone bedrock is 8.6 m at the site (data from the GSI). This layer of unconsolidated Quaternary overburden may provide a mixing zone for the warm waters to become diluted by shallow, cooler waters in winter. In contrast, St. Edmundsbury spring issues directly from a fissure in the limestone bedrock on the banks of the River Liffey.

St. Gorman’s Well has a very complex temperature and EC profile (Figure 2-4 b)), which is suggestive of a non-linear response to recharge, and of turbulent, conduit flow in karstic apertures. The spring has its natural expression as an ephemeral pond, so measurements and samples were collected from a borehole next to the spring. The discharge of the spring becomes artesian in winter when the pond fills and the temperature of the water increases very rapidly from cold (< 11 °C) to a maximum of 21.8 °C. When the flow is not artesian, semi-diurnal fluctuations in water level (Burdon, 1983), temperature and EC (this work) are attributed to the influence of earth tides upon the confined or semi-confined bedrock aquifer (Figure 2-4 b) inset).

The PCA sample scores for St. Gorman’s Well have the largest dispersion in the biplots, and especially in Figure 2-7 c), when trace element data are included in the PCA. In Figures 2-7 a) and 2-7 b), St. Gorman’s Well appears to have a strong association with the Si and HCO₃ end of link C, as opposed to the SO₄ end. Indeed, from the Piper diagram (Figure 2-2) the hydrochemistry seems to be strongly of the Ca-HCO₃-type. In Figure 2-7 c) the hydrochemistry of St. Gorman’s Well varies
along link $M$, with warmer samples from the winter recharge period (seasons “c” and “d”) showing the least influence from the dissolution of metal-oxides. Samples from the low-recharge period (seasons “a”, “b” and “e”) show a stronger association with the Mn end of link $M$ and a higher dissolved metal content. This seasonal difference suggests that the winter thermal water system has a different and less evolved hydrochemistry than the mid-temperature summer water system. This hydrochemical difference is corroborated by lower EC measurements for the winter flow system (Figure 2-4 b)), which suggest greater dilution with fresh recharge waters in winter. The seasonal differences in hydrochemistry support the hypothesis that the influx of cooler recharge waters to the karstic flow system in winter facilitates the operation of a relatively deep circulation pattern within the limestone succession which allows cool water to infiltrate quickly to depth, become heated and mixed, and then rapidly ascend to the surface where it issues with a temperature in excess of 20 °C. The waters issuing in the low recharge period have a lower temperature, so have not circulated as deeply as the warmer winter waters, but their greater association with the Mn end of link $M$ suggests a longer residence time and greater interaction with the bedrock in a confined aquifer (as evidenced by the semi-diurnal fluctuation in temperature and water level).

2.7. Conclusion

This study has demonstrated the usefulness of the application of MSA within the CoDa framework in order to better understand the underlying controlling processes governing the hydrochemistry of a group of thermal springs in a low-enthalpy setting, each with different geological and hydrogeological settings, and with distinctive and differing patterns of annual behaviour.

Assessment of major ion data (Figure 2-7 a)) clearly suggests two distinct processes controlling the hydrochemistry of the thermal springs dataset The “salinity” link, $S$, represents the influence of increased water-rock-interaction processes and implies that the springs associated with the Na/Cl end of the link are not typical Ca-HCO$_3$-type groundwaters, which would normally be expected in a limestone aquifer such as the Carboniferous bedrock of the Dublin Basin. The “carbonate” link, $C$, represents the effect of the dissolution of different types of limestone bedrock on the hydrochemistry (simplified as a trade-off between SO$_4$ and HCO$_3$). When data from
cold groundwater and surface water in the area are included in the PCA (Figure 2-7 b)), the distinction between these two links becomes less clearly defined, especially as the biplot represents less of the total variance in the dataset. The inclusion of all available data for the thermal springs (30 variables) into the PCA identified a third distinct process controlling the hydrochemistry (Figure 2-7 c)). The “mineralisation” link, $M$, represents the influence of the dissolution of mineral deposits associated with the carbonate bedrock, particularly Mn at one end of the link, and Ba at the other. It is less important in the control of the total hydrochemistry as it affects only minor and trace ions, and metals in particular.

Springs associated with the Na/Cl end of link $S$ are likely to have a moderate to high temperature with very little annual variation. They are characterised by higher salinity and EC due to an increased water-rock-interaction and residence time. The source aquifer is likely to be deep, confined and well-insulated from fluctuating near-surface hydrogeological processes. The excess Na and Cl observed in these springs are not due to any anthropogenic contamination but instead possibly derive from the dissolution of evaporites. The precise origin of the evaporites required to facilitate this process remains cryptic at present, and the source lithology may be either intra- or extra-basinal. The hydrochemistry of St. Edmundsbury spring and Louisa Bridge Spa Well is closely associated with the Na/Cl end of link $S$, and they appear to be fed from the same aquifer (or two very similar aquifers). In comparison to the cold, Ca-HCO$_3$-type groundwater from the Ryewater boreholes, which circulates within the limestones of the Lucan Fm., St. Edmundsbury spring and Louisa Bridge Spa Well must have their source in a deeper stratigraphic horizon, perhaps within the Devonian terrestrial strata. Springs associated with link $C$ are likely to be cold, or cooler thermal springs (with the exception of St. Gorman’s Well, which has extremely variable moderate to high temperatures). Depending upon their location along the link, they have either a higher SO$_4$ content (with increased Ca and Mg) controlled by the oxidation of sulfides such as pyrite, or a higher HCO$_3$ and Si content controlled by the dissolution of pure Waulsortian limestones and associated chert layers. They are likely to have an unconfined or semi-confined source and a good supply of fresh, infiltrating, recharge waters. It is likely that the source is a relatively shallow one, as oxidising waters are required for both pyrite and carbonate dissolution. Springs associated with the Mn end of link $M$ are also likely to be
associated with high Fe content and dissolution of pyrites hosted in the carbonate bedrock. These springs are most similar to cold groundwater from the shallow bedrock boreholes at Ryewater in terms of their major ion hydrochemistry.

The compositional MSA has greatly facilitated the investigation of a large hydrochemical dataset and has highlighted the influence of at least two different aquifer types (one deep, one shallow) on several of the Irish thermal springs examined. The results of the compositional MSA also facilitate assessment of the temporal variations in the hydrochemistry of the thermal springs. This temporal variation is not apparent if a standard statistical approach is used (see Supplementary Material). The sample scores for St. Edmundsbury spring are tightly clustered, indicating stable hydrochemical conditions. This is supported by very stable water temperatures and reflects a deep source for the spring with minimal influence from shallow recharge processes. The temperature profile for Louisa Bridge Spa Well shows a slight influence from shallow, cooler waters during the winter recharge period. The MSA has also provided an insight into the seasonal variations of St. Gorman’s Well, with the complex temperature and EC profile of this spring due to conduit flow within karstified bedrock.

2.8. Supplementary material

2.8.1. Standard (non-compositional) MSA

A standard, or non-compositional, approach to MSA has been applied in many recent hydrochemical studies. In a standard MSA, the compositional nature of the data is not addressed prior to the analysis (common analysis techniques are HCA and PCA). Two of the raw data matrices described above were used for a comparative standard statistical analysis. The first, for the major ion data from the new thermal springs data set, contained 78 observations and 9 variables (Matrix (1)). The second, for the major, minor and trace element data from the new thermal springs data set, contained 78 observations and 30 variables (Matrix (3)).

In a standard analysis, censored data are usually dealt with by replacement with a non-zero value equal to some multiple of the LOQ for that particular variable (Güler et al., 2002). For this comparative study, the censored data were replaced with a value equal to half of the LOQ. The data were log-normalized (Cloutier et al., 2008)
and standardized by subtracting the mean of the distribution from each data point and dividing by the standard deviation of the distribution (Davis, 1986), resulting in a new set of values with a mean of zero and a standard deviation of 1. HCA and PCA were then carried out on each data set using the same methodology as described above for the CoDa analysis.

The standard (non-compositional) PCA biplot is interpreted as follows: (1) if the angle between sample vectors (points) is small, they have a similar association with, or response to, the variables; (2) if the angle between two variable vectors is small, they are strongly associated; (3) the cosine of the angle between any two variables approximates their correlation coefficient; and (4) the length of a variable vector is approximately equal to the standard deviation of the variable (Kroonenberg, 2007).

### 2.8.2. Comparison of standard MSA to CoDa approach

**HCA**

As with the CoDa approach, the standard HCA of the thermal spring data (30 variables including major, minor and trace ions) identified six main clusters of samples (Figure 2-10). The following similarities exist between the CoDa and standard approaches:

- St. Edmundsbury spring and Louisa Bridge Spa Well are grouped into one cluster (A) with a high p-value (p = 1);
- samples from Kilbrook spring are grouped together in one cluster (E) with a high p-value (p = 1); and
- samples from Huntstown “CaCO₃” cold seepage, Huntstown “Fe₂O₃” cold seepage, and Huntstown Fault spring occupy their own clusters (clusters B, C and D, respectively). Several striking dissimilarities between the CoDa and standard approaches to HCA exist (comparing Figure 2-6 to Figure 2-10). Huntstown “CaCO₃” cold seepage, Huntstown “Fe₂O₃” cold seepage, and Huntstown Fault spring are grouped closely together in the standard HCA, suggesting a greater degree of hydrochemical similarity between the waters at these locations, despite their obvious differences as is evident from the nature of the deposits left by the seepages (see Table 2-1). The standard HCA groups all samples from St. Gorman’s Well and Kemmins Mill spring in one cluster with a high p-value (p = 0.97) (F), and fails to recognise the large seasonal variations in hydrochemistry of St. Gorman’s Well.
Figure 2-10: Cluster analysis dendrogram for non-compositional agglomerative HCA of Leinster thermal springs dataset - Matrix (3). Samples are labelled as in Figure 2-6.
Figure 2-11: Non-compositional PCA biplots: a) Matrix (1) - thermal springs dataset (9 variables); b) Matrix (3) - thermal spring dataset including minor and trace ions (30 variables). Samples are labelled as in Figure 2-6.
PCA

Figure 2-11 shows the scree plots and biplots for the non-compositional PCA. The data set containing major ion data only (Figure 2-11 a)) has a PCA scree plot that "breaks" after the third PC, and the biplot represents a total of 76.7 % of the total variance of the data set. This compares unfavourably to the compositional covariance biplot for major ion data in Figure 2-7 a), which represents over 90 % of the total variance. The relative positions of the variable vectors and sample scores is similar in both the CoDa and standard approaches, although the standard PCA assigns more importance to the variables K, Sr and Mg, and less importance to Si. The first PC of the standard biplot suggests a strong correlation between Na, Cl, Sr, Mg and K, and the association of St. Edmundsbury spring and Louisa Bridge Spa Well with these variables. The second PC indicates a strong correlation between SO\textsubscript{4} and Ca and a negative correlation between these two ions and HCO\textsubscript{3}, with the remaining samples distributed along this axis.

The data set containing major, minor and trace ion data (Figure 2-11 b)) has a PCA scree plot that “breaks” after the second PC, and the biplot represents a total of 58.3 % of the total variance of the data set. This is similar to the compositional covariance biplot for major ion data in Figure 2-7 c) (61 %). The CoDa and standard approaches produce very different biplots for these data. The standard PCA retains a similar distribution for the variables and samples. Again, the first PC of the standard biplot suggests a strong correlation between Na, Cl, Sr, Mg and K, with the addition of Rb, Cs and Li, and the association of St. Edmundsbury spring and Louisa Bridge Spa Well with these variables. The second PC indicates a strong correlation between SO\textsubscript{4}, Ca, Sb and Cu and the association of samples from the three Huntstown sampling locations, and a negative correlation with HCO\textsubscript{3} and P, which appear to be associated with Kilbrook spring.

Model comparison

Given the PCA results, it would appear that for major ion data, the compositional covariance biplot is more reliable as it represents a higher proportion of the total variance. In general, separate interpretations of the standard and CoDa biplots for major ion data yield similar conclusions, at least for Na, Cl, Ca, SO\textsubscript{4} and HCO\textsubscript{3}. When the number of variables is increased to include minor and trace ions, the compositional covariance biplot is marginally more reliable than the standard biplot.
(61% compared to 58.3% of the total variance represented), and these two biplots are very different in terms of variable and sample distributions. For the standard biplots, the addition of more variables does not alter the distribution of the major ions or the samples, with the result that the addition of more variables does not increase our insight into the data set. In contrast, with the addition of more variables the compositional covariance biplot reveals more subtle structure in the data, as can be seen from the relative positions of the samples from the Huntstown sampling locations, and in the large variation of samples from St. Gorman’s Well. As discussed in section 2.6, this difference is due to the fact that as compositional data, trace element concentrations typically exhibit large log-ratio variances but low Euclidean variances (the concentrations are small by definition) (see: Otero et al., 2005; Engle et al., 2014).

A model comparison was made by plotting the sample scores for the first principal components of both the standard and compositional PCAs (Figure 2-12) and performing a simple least-squares regression (Andrews and Vogt, 2014; Flood et al., 2015). For the major ion data, the two models are significantly negatively correlated ($R^2 = 0.88$, $p = 0.001$), this similarity facilitates the similar general interpretations of these models. When more variables are added, the two models are positively correlated and the overall difference between the two models increases ($R^2 = 0.66$, $p = 0.001$), which results in different interpretations for the two models. The negative and positive nature of the correlations is mathematically insignificant and is the result of the arbitrary assignment of sign to the scores during the singular value decomposition of the PCA (Bro et al., 2008).
Figure 2-12: Comparison of sample scores from compositional and standard PCA by least squares regression. a) Sample scores from Matrix (1). b) Sample scores from Matrix (3).
3. Understanding hydrothermal circulation patterns at a low-enthalpy thermal spring using audio-magnetotelluric data: a case study from Ireland (Kilbrook spring)

Abstract

Kilbrook spring is a thermal spring in east-central Ireland. The temperatures in the spring are the highest recorded for any Irish thermal spring in (maximum of 25.0 °C). The temperature is elevated with respect to average Irish groundwater temperatures (9.5 – 10.5 °C), and represents a geothermal energy potential, which is currently under evaluation. A multi-disciplinary investigation based upon an audio-magnetotelluric (AMT) survey, and including time-lapse temperature and chemistry measurements, and hydrochemical analysis, has been undertaken with the aims of investigating the provenance of the thermal groundwater and characterising the geological structures facilitating groundwater circulation in the bedrock.

A three-dimensional (3-D) electrical resistivity model of the subsurface at Kilbrook spring was obtained by the inversion of AMT impedances and vertical magnetic transfer functions. The model is interpreted alongside high resolution temperature and electrical conductivity measurements, and a previous hydrochemical analysis.

The hydrochemical analysis and time-lapse measurements suggest that the thermal waters have a relatively stable temperature and major ion hydrochemistry, and flow within the limestones of the Carboniferous Dublin Basin at all times. The 3-D resistivity model of the subsurface reveals a prominent NNW-aligned structure within a highly resistive limestone lithology that is interpreted as a dissolutionally enhanced strike-slip fault, of probable Cenozoic age. The karstification of this structure, which extends to depths of at least 500 m directly beneath the spring, has provided conduits that facilitate the operation of a relatively deep hydrothermal circulation pattern (likely estimated depths between 560 and 1,000 m) within the limestone succession of the Dublin Basin. The results of this study support the hypothesis that the winter thermal maximum and simultaneous increased discharge
Chapter 3: Detailed study of Kilbrook spring

at Kilbrook spring is the result of rapid infiltration, heating and re-circulation of meteoric waters within this structurally-controlled hydrothermal circulation system.

This paper illustrates how AMT may be useful in a multi-disciplinary investigation of an intermediate-depth (100 – 1,000 m), low-enthalpy, geothermal target, and shows how the different strands of inquiry from a multi-disciplinary investigation may be woven together to gain a deeper understanding of a complex hydrothermal system.

3.1. Introduction

Deep hydrothermal systems are well-established geothermal exploration targets. The potential of these systems is now being investigated in Ireland as part of the SFI-funded IRETHERM project. A multi-disciplinary approach has been adopted, integrating geophysical surveys and hydrochemical analysis with the aims of (1) identifying the source aquifer(s) for the thermal groundwater, (2) characterising the circulatory systems, and (3) assessing the potential for the existence of deeper, higher temperature, circulation patterns for future geothermal exploitation. A number of thermal springs have been identified that are currently being investigated. This paper presents a case study of one of these, Kilbrook spring, which has the highest recorded temperatures of any thermal spring in Ireland (maximum of 25.0 °C recorded during this study). This study shows how the use of geophysics as part of a multi-disciplinary investigation can result in a better understanding of the operation of a low-enthalpy hydrothermal system.

In Ireland, average groundwater temperatures typically range from 9.5 to 10.5 °C (Aldwell and Burdon, 1980) and thermal springs are considered to be those natural groundwater springs where the mean annual temperature is appreciably warmer than average groundwater temperatures (Aldwell and Burdon, 1980; Goodman et al., 2004). The spring is located in east-central Ireland (Figure 3-1) and was first discovered in the late 19th century when the nearby Royal Canal was constructed (Burdon, 1983). The spring discharges from a glaciofluvial sand and gravel deposit in a disused quarry, which is located between the urban centres of Enfield, Co. Meath, and Kilcock, Co. Kildare. The temperature profile of Kilbrook spring is consistently high and varies little throughout the year, with a mean temperature of
24.0 °C. The maximum discharge occurs in winter (857 m³/d measured in January 1982; see Burdon, 1983) with a mean discharge of 472 m³/d. This combination of relatively high discharge and high temperature is an encouraging indicator of the geothermal energy potential of the spring.

**Figure 3-1**: Geological setting of Irish thermal groundwaters: (a) Irish thermal spring and thermal shallow groundwater locations (after Goodman et al., 2004), with significant mineral deposits and the approximate trace of the Iapetus Suture Zone (after Wilkinson, 2010); (b) palaeogeographic map of the Dublin Basin during the Viséan Stage (modified from Sevastopulo and Wyse Jackson (2009)); and (c) geological map of the study area (from www.gsi.ie) showing thermal springs included in the hydrochemical sampling programme. Maximum temperatures (red) and electrical conductivities in µS/cm (blue) are given for each thermal spring. Coloured triangles in each of the thermal spring labels refer to colour coding used for these locations in subsequent figures.
The AMT method is an electromagnetic geophysical technique that is widely used for exploring geothermal resources (e.g., Arango et al., 2009; Barcelona et al., 2013; Piña-Varas et al., 2014; Zhang et al., 2015) and hydrogeological targets (e.g., Falgàs et al., 2011; Kalscheuer et al., 2015) due to its ability to detect low-resistivity, water-bearing rocks in the subsurface. AMT is a passive technique that uses high-frequency, natural source fields generated by worldwide lightning activity. It is useful for characterising the shallow subsurface. The depth of penetration can be up to several hundred metres and even greater than a kilometre, depending on the resistivity of the bedrock. When used as part of a multi-disciplinary approach (incorporating geological, hydrogeological, and other geophysical data), AMT is an efficient and relatively inexpensive method for improving the characterisation of a geothermal resource (compared to other methods of geophysical exploration or to drilling).

In this paper we present a new model from an AMT survey at Kilbrook spring. The twin overarching goals of the AMT survey were (1) to identify any (electrically conductive) fluid conduit systems associated with the thermal spring, and (2) to assess the nature and extent of the hydrothermal circulation pattern. The results are discussed alongside detailed time-lapse measurements of temperature and electrical conductivity, and hydrochemical data collected seasonally at the spring.

3.2. Kilbrook spring in context

3.2.1. Geology and hydrogeology

Irish thermal springs occur in Carboniferous limestone bedrock along a wide band that traverses the centre of Ireland from NE to SW, broadly coincident with the putative trend of the Lower Palaeozoic Iapetus Suture Zone (ISZ) (Figure 3-1 a)). The ISZ was produced by the final closure of the Iapetus Ocean in late Silurian times, during the later stages of the Caledonian Orogenic cycle (e.g., Chew and Strachan, 2014). Following collision, terrestrial sediments were deposited during the Devonian period (e.g., Graham, 2009), before a shift to predominantly carbonate deposition as a result of a regional marine transgression during earliest Carboniferous (Tournaisian) times (MacDermot and Sevastopulo, 1972). During the Tournaisian and Viséan, several intra-cratic basins developed across Ireland as a
result of tectonism and subsidence (e.g., de Morton et al., 2015; Somerville, 2008; Strogen et al., 1996), principally controlled by movement on NE-SW oriented structures, whose orientation was inherited from underlying Caledonian trending features (Worthington and Walsh, 2011). Extensive carbonate production continued in Ireland for much of the Mississippian, before a switch to terrigenous mud and sand deposition in the Serpukhovian and Bashkirian (formerly regionally termed the Namurian in northwest Europe: see Sevastopulo and Wyse Jackson, 2009; Barham et al., 2015).

Kilbrook spring is situated in the Carboniferous Dublin Basin (Figure 3-1 b)), which contains c. 2,000 m of sedimentary infill and saw the widespread development of carbonate buildups (‘reefs’) during late Tournaisian to early Viséan times (Somerville et al. 1992). This particular facies, commonly termed the Waulsortian Limestone Formation (Fm.), is characterised by very fine-grained, pure carbonates containing sparry masses. Bedding within the carbonate buildups is often indistinct: these buildups commonly formed aggregates, and intervening, off-mound facies are typically represented by thin, nodular, chert-rich shales (Lees and Miller 1995). The relative purity of this carbonate facies results in it being prone to chemical dissolution and the development of karst features, which is an important consideration for modern groundwater circulation. Active tectonism during the Viséan age led to the development of shallow shelf platforms and contrasting deeper regions in the Dublin Basin. The deeper basinal facies is characterised by thinly inter-bedded, cherty limestones and shales (mapped regionally as the Lucan Fm., or “Calp”; see Marchant and Sevastopulo 1980). Kilbrook spring itself discharges from the Lucan Fm. near its lithostratigraphic contact with overlying Namurian non-carbonate sediments (Figures 3-1 c) and 3-2). The spring issues from a surficial glaciofluvial deposit consisting of coarse sands and gravels. This deposit covers an area of 0.32 km², has an oblate shape oriented NW to SE, and may infill a depression in the surface of the underlying bedrock. Bedrock exposure in the area is generally poor, and there are limited borehole records available. Two boreholes were completed in 1983 by the Geological Survey of Ireland (GSI) (Figure 3-2):

- extremely weathered bedrock was encountered at a depth of 23 m in one borehole adjacent to the spring pond; this material resembled a fault breccia (Burdon, 1983), indicating the proximity of the spring to a significant
Kilbrook spring is situated 35 km west of Dublin, in a relatively flat and low-lying landscape in the Eastern River Basin District. The elevation in the survey area (Figure 3-2) ranges from approximately 80 to 100 mAOD. The 30-year (1981-2010) average annual rainfall in the area is 868 mm/yr (Walsh, 2012); during the sampling period (for the hydrochemical sampling and time-lapse measurements) the annual rainfall was 863 mm in 2013 and 922 mm in 2014 (data from Met Éireann, www.met.ie). Evaporative losses for the region are estimated at 450 mm/yr (Met Éireann). The main use of land is agricultural, and the spring itself is situated in a disused gravel pit. The Lucan Fm. is classified by the GSI as “locally important, moderately productive” aquifer, and the Namurian shales and sandstones are classified as “poor aquifer, generally unproductive”. Most recharge to aquifers in Ireland occurs in the period between October and April, and typical estimated recharge rates for this area are between 101 and 200 mm/yr (Hunter Williams et al., 2011).

The pond at Kilbrook spring is largest during winter, in the high recharge period between October and April, when its surface area is approximately 100 m². In the summer, the discharge decreases and the area of the pond is reduced. Water flows northward from this pond to a larger pool, then discharges to a land drain 150 m north of the spring. The discharge of the spring was monitored on a monthly basis between 1981 and 1983 (Burdon, 1983), and from these data the discharge is estimated to be approximately 860 m³/d during the winter, with a yearly average of 470 m³/d. No detailed hydrodynamic data were available for this study area.

The water from Kilbrook spring has a calcium-bicarbonate (Ca-HCO₃-type) hydrochemical signature, typical of many recently infiltrated, cold, Irish groundwaters circulating in limestones, and also typical of the majority of the Irish thermal springs. The hydrochemical signatures of the thermal springs imply that they are mainly composed of meteoric waters that are recently recharged from rainfall events (Burdon, 1983; Mooney et al., 2010). Burdon (1983) showed that Kilbrook spring contained lower tritium levels and higher radiogenic ⁴He levels than cold
groundwater. These low tritium levels, along with the elevated temperatures, are suggestive of longer residence times and a deeper circulation pattern for the thermal groundwater. Water samples recovered from Kilbrook spring are likely to be a blend of groundwaters from different sources and different recharge areas. The thermal water could be composed of a mixture of a deeper-circulating, older groundwater, and more recent, meteoric recharge water from a shallow groundwater system.

Figure 3-2: AMT station locations and local geology (from www.gsi.ie) at Kilbrook spring.

With regards to regional geophysics, gravity surveys in the Leinster region have highlighted the importance of NE-trending alignments in the tectonic fabric of the crust (e.g., O’Reilly et al., 1996), which are visible due to reactivation of Caledonian thrust faults in the early Carboniferous causing density variations in the Carboniferous cover. Airborne electromagnetic data, recently collected in northern
Leinster by the TELLUS programme (www.tellus.ie) have also highlighted a regional NE structural trend. On a more local scale, the TELLUS data appears to show a NNW structural trend at shallow depths (10 – 40 m). Figure 3-3 shows the apparent conductivity values calculated for a depth of 20 m as provided by TELLUS. Within the AMT survey area at Kilbrook, there appears to be little conductivity variation at these shallow depths; this may be attributed to the presence of the gravel deposit shown in Figure 3-2.

![Figure 3-3: Apparent conductivity distribution at 20 m depth as modelled from Tellus airborne electromagnetic data (from the Tellus data viewer at www.tellus.ie).](image)

3.2.2. Structural geology

The Carboniferous limestones in Ireland that host the thermal springs generally tend to exhibit poor primary porosity. Secondary porosity and permeability are greatly improved by both fracture and karst development, providing discrete pathways for groundwater flow; it is therefore important to consider structural controls on fluid flow within these limestones. In carbonates, the development of deep dissolutional features (at depths of at least 500 m) is likely to be controlled and facilitated by prominent fault structures (Kaufmann et al., 2014). Irish thermal springs are frequently associated with deep-seated, high-angle faults, which facilitate the movement of warm waters towards the surface (Mooney et al., 2010), and they appear to be associated with the dominant NE-SW structural lineaments apparent in Ireland’s bedrock (Figure 3-1 a)). These deep-seated, pervasive faults, although no longer tectonically active, may still provide fluid pathways enhanced by
dissolutional processes in discrete zones (through karstification), allowing water to flow from deeper units up to the surface, and are probably very important in controlling regional groundwater flow (Henry, 2014).

The development of secondary porosity in the Waulsortian Limestone Fm. is likely to contribute to the development of thermal springs in the Dublin Basin, as four out of six thermal springs studied in detail during the IRETHERM project issue from, or have a close spatial association with, mapped surface outcrop of Waulsortian strata, as can be seen in Figure 3-1 c). While Kilbrook spring issues from supra-Waulsortian strata, the Waulsortian Limestone Fm. may exist beneath these strata. The centres of Waulsortian buildups are typically massive (see Lees and Miller, 1995), so any karstic dissolution will tend to exploit areas of fissured and fractured rock. By comparison, the chert-rich, off-mound facies are much less soluble, and may thus act to constrain or focus groundwater flow. Flow within discrete Waulsortian mounds can become concentrated along vertical or sub-vertical pathways with relatively little lateral dissipation of flow (Moore et al., 2015).

Dissolutional features in the Waulsortian limestones in the Dublin Basin near St. Gorman’s Well (Figure 3-1 c)) have been reported at depths of 250 - 300 m (borehole reports from www.mineralsireland.ie) and may possibly exist at 510 m in one reported instance (Murphy and Brück, 1989). These features play an important role in the operation of deep groundwater circulation patterns and facilitate the movement of the thermal spring waters to the surface.

A significant (28 km) NE – SW oriented normal fault is present close to Kilbrook spring on the geological map (Figures 3-1 and 3-2), juxtaposing downthrown Namurian sediments to the east and upthrown Lucan Fm. limestones to the west. The trend on this fault is Caledonian and it is likely that it is deep-seated, and of Carboniferous age. These Carboniferous normal faults were subsequently reactivated as thrust faults during later compressional tectonic events (e.g., Hitzman, 1999), leading them to act as impermeable barriers to groundwater flow; this occurs mainly because they are enriched with incorporated host-rock clays and shales by a combination of fault rock attenuation and smearing, and by dissolution-related restite formation (Moore and Walsh 2013). In certain locations, particularly where they are intersected by N-oriented, Cenozoic, strike-slip faults, they can become karstified
and have their permeability greatly increased (Moore and Walsh 2013). A local example of such an intersection of structures can be seen at Rathcore Quarry, six kilometres west of Kilbrook spring. Here, the intersection of a Carboniferous normal fault and a N-oriented Cenozoic strike-slip fault has resulted in the development of a large karstic depression (20 metres wide), which has been subsequently filled with unconsolidated materials.

3.3. AMT survey

The AMT method determines the distribution of the electrical properties of the subsurface and the results can be expressed in terms of electrical conductivity (S/m) or electrical resistivity (Ωm). Conductivity and resistivity are inversely related so that a body with high resistivity will have a low conductivity, and vice versa. Here, the results of the AMT survey are expressed in terms of resistivity, with equivalent conductivity values supplied for context.

3.3.1. AMT method

The magnetotelluric (MT) method is a geophysical technique that determines the distribution of electrical resistivity in the subsurface by relating simultaneous measurements of the naturally occurring fluctuations of the electric and magnetic fields at the Earth's surface. Recent comprehensive reviews of the MT method are provided by Simpson and Bahr (2005), and Chave and Jones (2012). Natural electromagnetic fields that are utilised as source fields in MT studies range in frequency from approximately $10^{-5}$ to $10^{5}$ Hz. AMT studies utilise higher frequency (>8 Hz) electromagnetic waves that are generated by electric lightning discharge during lightning storms and propagate around the globe in the Earth-ionosphere waveguide. Commonly, a frequency interval with poor signal-to-noise ratio is found between 1,000 Hz and 5,000 Hz, which is called the AMT “dead-band”. Garcia and Jones (2005) demonstrated that night-time signals are usually strong enough to provide good estimates of the transfer functions of AMT dead-band frequencies, with maximum signal strength occurring around local midnight. For this reason, the AMT soundings for this survey were carried out overnight to maximise the data quality.
3.3.2. AMT dataset

The AMT survey was designed to target any karstified conduits occurring beneath the thermal spring at Kilbrook. Forty-one AMT measurement locations (stations) were laid out in an approximate grid pattern, centred on the spring itself, with approximately 200 m between sites (Figure 3-2). The grid covered a total area of 2.7 km². This layout was chosen to investigate depths in excess of 100 m beneath the spring (with a separation of 200 m between stations at the surface, the volumes of measurement beneath each of the stations first overlap at a depth of around 100 m, thus providing a more reliable estimation of the properties of the subsurface at depths greater than 100 m). The survey was carried out in July 2012. Overnight AMT measurements were made using Phoenix MTU-5 systems with an electrode array and horizontal magnetic coil configuration oriented to geomagnetic north-south-east-west, combined with a vertical magnetic recording at each station. Data were acquired in the frequency range between 1 Hz and 10,000 Hz. As the data quality in populated areas is often affected by man-made (“cultural”) electrical noise, one system was deployed as a remote magnetic reference station in a culturally quiet location approximately 4.6 km NE of the spring. This extra station allowed for remote reference processing (Gamble et al., 1979). The AMT time series were processed using Phoenix SSMT2000 software, which employs a robust variant of a remote reference processing algorithm based on Jones and Jödike (1984), and Jones et al. (1989). Aside from the aforementioned AMT dead-band, the data quality was generally good between 10 Hz and 10,000 Hz. The impedance tensors ($Z$) and the vertical magnetic transfer functions ($T$) were estimated for each frequency for each station. Each curve was manually edited to remove excessively noisy data in the AMT dead-band.
Figure 3-4: Phase tensor dimensionality analysis using $Z$ responses. White-grey colours indicate frequencies affected by the presence of 1-D or 2-D structures. Other colours represent frequencies affected by 3-D structures. The stations are arranged from W to E in three panels to correspond with the boxes outlined in the map of the survey area.
Figure 3-5: Induction arrow dimensionality analysis using T responses, following the Parkinson criteria. The stations are arranged from W to E in three panels to correspond with the boxes outlined in the map of the survey area.
3.3.3. Dimensionality analysis

The dimensionality of the data was analysed by investigating the Z and T responses independently of each other. For the Z responses, the dimensionality analysis was performed by examining the phase tensors (Caldwell et al., 2004), which have the advantage of being unaffected by galvanic distortion of the electric fields. Figure 3-4 shows the calculated phase tensor for each frequency for each station, depicted as an ellipse. For a 1-D scenario the phase tensor will be represented by a circle, and for a 2-D case the phase tensor will be represented by a symmetrical ellipse, with the orientation of the major axis aligned either parallel or perpendicular to the regional geo-electrical strike direction. For 3-D cases the phase tensor will be non-symmetrical, necessitating the use of an additional angle, β, to characterise the tensor. Caldwell et al. (2004) suggest that a value of the skew angle, β, greater than 3° indicates a 3-D scenario. Theoretically, if β exists (i.e. β > 0°) then the scenario is 3-D. The review paper by Booker (2014) recommended taking the errors in β into account when determining dimensionality. In this thesis, the approach as suggested by Campanyà et al. (in review) is used, and this takes the errors on β into account. Figure 3-4 shows the calculated value of β divided by the error in determining β. Thus \( \frac{\beta}{\text{error skew } \beta} > 1 \) indicates a 3-D scenario. For example, a skew angle β of 2° that was calculated with an error of 0.5° would indicate a 3-D scenario, as it proves that β is greater than 0°. In Figure 3-4, the ellipses representing 3-D conditions are coloured depending upon the magnitude of β normalized by the corresponding error. All stations in Figure 3-4 show coloured ellipses for some frequencies, indicating 3-D conditions for the survey area. For the T responses, induction arrows (Schmucker, 1970) following the Parkinson criteria (i.e., the real arrows tend to point towards current concentrations in conductive anomalies (Jones, 1986)) were used. Figure 3-5 shows the induction arrows for each station and each frequency (station 33 has no induction arrows because the T data quality was poor for this station). For a 1-D scenario the length of the induction arrows will be less than the threshold length of the assumed errors as there is no induced vertical magnetic field. For a 2-D scenario the induction arrows will point in the same or exactly opposite directions for all periods and stations. In a 3-D scenario, real and imaginary induction arrows will point in different (oblique) directions at any one frequency for any station (as can be
seen in Figure 3-5). The results from Figures 3-4 and 3-5 indicate the existence of a 3-D scenario beneath the survey area.

3.3.4. 3-D inversion
Based upon the results of the dimensionality analysis, 3-D inversion was adopted as the most appropriate course of action. AMT data from 28 frequencies (excluding frequencies in the dead-band, particularly between 800 Hz and 2,000 Hz) were prepared for the inversion; these data were subsequently re-edited on a station-by-station basis to remove particularly noisy frequencies. The data were inverted using the ModEM 3-D inversion code (Egbert and Kelbert, 2012; Kelbert et al., 2014). The vertical magnetic transfer functions (T) were inverted alongside the four components of the impedance tensors (Z) to improve the resolution of the subsurface resistivity values (e.g., Siripunvaraporn and Egbert, 2009). The mesh for the resistivity model consisted of 90 × 90 × 90 cells, with square cells with sides 50 m long in the horizontal plane of the central region of interest. This central region was a square with sides 3 km long. Padding cells were added in the x and y directions with an incremental factor of 1.3. In the z direction, 10 air layers were added above the resistivity model. The first (surface) layer of the model was 10 m thick; these layers were incrementally increased by a factor of 1.025 until a thickness of 60 m was achieved. The layers were then increased by a factor of 1.1. The final model dimensions were 8 km × 8 km × 5 km. Several preliminary models were assigned a homogeneous half space with varying resistivity values as their starting and prior models; the best results (i.e., with the least extreme values and resolving the most structure) were obtained with half-spaces of 300 and 500 Ωm (0.003 and 0.002 S/m). An average of four models (two starting models with homogeneous half-spaces of 300 Ωm and 500 Ωm, and the two resultant models from those inversions) was calculated and set as the prior model for the final inversion. The model mesh was not rotated, as advocated by Kiyan et al. (2014), as preliminary models showed the subsurface to have 3-D structure with no one predominant geoelectrical strike direction evident. An error floor of 5 % was imposed for all components of Z (calculated from the modulus of the off-diagonal components Z_{xy} and Z_{yx}), and an absolute error of 0.03 was used for T. Variation of the smoothing parameters was investigated for the model; values between 0.1 and 0.5 were tested, and an
intermediate value of 0.3 (in all directions) for the smoothing parameter gave the minimum root mean square (RMS) misfit for the data.

No correction or compensation was applied to the data to account for galvanic distortion, which is a tractable problem in 2-D cases, but far less practicable in 3-D (see Jones, 2011). An examination of the apparent resistivity curves revealed no particular “problem areas” for galvanic distortion. As a 3-D modelling approach was used, with a fine parameterization in the uppermost part of the model, it was expected that the model would not be greatly affected by near-surface galvanic distortion effects at our target depths (e.g., Sasaki and Meju, 2006; Farquharson and Craven, 2009; Meqbel et al., 2014). Galvanic distortion may affect the very shallowest layers of the model, but at depth, particularly beneath 100 m where every part of the model is sampled by numerous stations, the conductivity shows a smooth and consistent distribution and any unresolved features near to the surface appear to have been assimilated by the model. Hence, at depths greater than 100 m the effects of galvanic distortion in the model should be negligible. Also, the inversion of $T$ alongside $Z$ should decrease the susceptibility of the model to the effects of galvanic distortion. As $T$ does not involve the electric field directly (see Eq. 1-4), it is not subject to the same galvanic distortion as $Z$. However, it can become distorted if the deflection of electric currents by in-phase electric fields alters the vertical magnetic fields (Booker, 2014). The resulting models do not show obvious artefacts (i.e., site-correlated model structures), which commonly indicate the presence of static shifts.

3.3.5. Final model

The final resistivity model converged after 38 iterations with a RMS misfit of 2.05. Figure 3-6 shows the residual misfit of the data to the model responses for each period and each station. In general, the fit to $Z_{yx}$ is better than to $Z_{xy}$, and the lower frequencies show a poorer fit. Upon examination of the model, and given that the space between stations is approximately 200 m, the model results are more reliable from approximately 100 m depth. Resolution of fine structure decreases with depth, and the total depth of resolution of the model is defined by the presence of a low resistivity body (with a slightly lower resistivity value than the initial model), which plots between 1,500 m and 3,000 m depth.
The model shows a large region of high resistivity in the centre of the survey area (Figure 3-7). At shallower depths, the spring is located on the NW edge of this resistive body, with more conductive material to the NW. There are two highly resistive cores within this high resistivity region with apparent resistivity values in excess of 5,000 Ωm (< 0.0002 S/m). The spring is situated on the linear boundary between these two resistive cores. This linear boundary is evident from depths of around 100 m to 800 m, has a lower resistivity than the surrounding material, and is oriented NNW. This feature is vertical or sub-vertical when viewed in profile (Figure 3-11 b)). There is a region of low-resistivity material of between 10 and 500 Ωm (0.1 to 0.002 S/m) in the NW portion of the survey area. The boundary between this region and the resistive region is irregular with an approximate NE-SW trend. There is a large low resistivity pocket directly to the north of the spring, and this can be seen to extend to a depth of approximately 200 m (Figure 3-8, P1). There is also a region of less resistive material east of the spring, on the edge of and to the east of the survey area; as there are no stations directly above this feature, it is not possible to properly resolve it, and so it is not discussed further here.
Figure 3-6: (cont. overleaf) Representation of the data fit to the model responses from the final 3-D inversion. Data from both components of T and all four components of Z are represented (real and imaginary parts). The stations are grouped to reflect the three boxes in the inset: the stations are arranged in order of their appearance from W to E. The coloured scale represents the difference between the data and the model response divided by the error for each frequency at each station.
Chapter 3: Detailed study of Kilbrook spring
Chapter 3: Detailed study of Kilbrook spring
Figure 3-7: (previous page) Horizontal slices through the final 3-D resistivity model. The depth of each slice is indicated. The spring is located at 53°25'24.23"N 6°46'31.63"W.

Figure 3-8: Vertical profiles (P1, P2 and P3) through the final resistivity model. The profile locations are indicated in the plan view of the survey area. The locations of the AMT stations are indicated by inverted triangles.
3.4. Discussion

The results from time-lapse temperature measurements, hydrochemical analysis and the AMT survey are discussed here to develop an integrated conceptual model for the hydrothermal circulation pattern at Kilbrook thermal spring.

3.4.1. Time-lapse temperature measurements

Continuous temperature and electrical conductivity (EC) measurements were collected at Kilbrook spring between July 2013 and April 2015 (Figure 3-9). The EC data are presented in µS/cm (1 µS/cm is equivalent to 0.0001 S/m). Further information regarding data collection is available in Chapter 2, section 2.3.3. In general, the temperature readings proved to be reliable, but the EC readings appear to have been adversely affected by the influence of fouling by bacterial growths on the sensors. This is evident in Figure 3-9, where the EC readings appear very unstable after any re-installation of the logger. From seasonal field measurements using a Hanna HI 98130 Combo meter (measurements indicated in Figure 3-9 and Table 3-1), the EC of Kilbrook spring appears to be fairly stable (maximum of 652 µS/cm and a mean of 634 µS/cm).

The temperature profile for the first year (July 2013 – June 2014; Figure 3-9) shows remarkably stable temperatures that are lower at the end of the summer (specifically between August and November), and slightly higher in winter (after December), which initially appears counterintuitive. This general profile is repeated in the second year (July 2014 – April 2015). The summer period in the first year has slightly lower temperatures than in the subsequent year (approximately 23.5°C compared to 24.5 °C for the second year). The period between August and November is characterised by a flashy signature with short-lived decreases in temperature to as little as 19.5 °C (October 2014). This flashy period has a longer duration in the first year. The month of November is marked by a gradual increase in temperature; higher temperatures are sustained throughout the winter and spring, with temperatures dipping again in August. The onset of the high-temperature, winter phase in November/December is gradual. A maximum temperature of 24.8 °C was recorded in the first year in June 2014, and a maximum of 25 °C was recorded in the second year at the end of January 2015.
Figure 3.9: Time-lapse temperature (black) and electrical conductivity (grey) for Kilbrook spring. Daily effective rainfall (blue) calculated from Met Éireann data (Dunsany synoptic station, Meath). First two panels show data from 2013 – 2014; second two panels show data from 2014 – 2015. Insets show enhanced fluctuations in temperature over two seven-day periods following the new moon on July 8th 2013 and the super full moon on August 10th 2014. Numbers in red indicate field measurements of electrical conductivity and dashed red lines indicate hydrochemical sampling rounds.
Table 3-1: Summary statistics for Kilbrook spring. Temperature (T) data from logger measurements. EC and pH measured in field with Hanna Combo meter during data collection rounds.

<table>
<thead>
<tr>
<th>pH range</th>
<th>Max EC (μS/cm)</th>
<th>Min EC (μS/cm)</th>
<th>Mean EC (μS/cm)</th>
<th>Max T (°C)</th>
<th>Min T (°C)</th>
<th>Mean T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.71–7.8</td>
<td>652</td>
<td>616</td>
<td>634</td>
<td>25.0</td>
<td>19.5</td>
<td>24.0</td>
</tr>
</tbody>
</table>

Data from monthly discharge measurements made in 1982 (Burdon, 1983) show the discharge of the spring to be greatest in winter (particularly between December and April), and very low in summer (particularly between July and November). This suggests that the (hydrothermal) circulation pattern is controlled by annual recharge, and that the spring has a hydraulic connection to meteoric recharge processes occurring at the surface and in the shallow subsurface.

Despite an obvious connection to meteoric recharge processes, for most of the year the temperature profile (and the EC profile, Table 3-1) is steady and does not show direct influence from rainfall events (Figure 3-9); this supports the presence of, and influence from, a deeper aquifer with a degree of insulation from near-surface recharge processes. Towards the end of the summer, between August and November, the profile becomes flashy with local drops in temperature, presumably as a response to input of cooler recharge waters. However, this flashy signature does not continue beyond December into the winter period. It is possible that the increase in the regional water table due to the increase in recharge at the end of the summer period puts into operation a higher-temperature, higher-discharge circulation pattern at Kilbrook spring. This winter circulation pattern must be deep-seated, as it does not show any influence (delayed or otherwise) from rainfall events.

In both years the temperature profile exhibits diurnal and semi-diurnal fluctuations at certain times (see insets in Figure 3-9), which are more pronounced in the summer when water levels are low. The diurnal fluctuations are partly influenced by the daily changes in temperature at the open pond surface. Semi-diurnal fluctuations in water level were first identified in 1982 (Burdon, 1983) and compared to gravity-tide-corrected data. The close correlation of the two signals confirmed the strong influence of the Earth’s gravity tides upon the water levels in Kilbrook spring, with maximum variations occurring around the times of the new and the full moon (Burdon, 1983). The relative movements of the Earth, Sun and Moon cause a
periodic distortion in the shape of the Earth that causes groundwater to be expelled from confined or semi-confined aquifers. The presence of these semi-diurnal fluctuations in water level (Burdon, 1983) and temperature (this study) is evidence that both water level and temperature are controlled by tidal forces, and that the thermal groundwater is stored under confined (or semi-confined) aquifer conditions. The semi-diurnal fluctuations still exist in the winter, but are less pronounced due to the increase in discharge, which indicates the interaction and mixing of the thermal waters with a shallow, unconfined aquifer during the winter.

3.4.2. Hydrochemical analysis

Several of the Irish thermal springs were sampled in July/August and October 2013, and in January, May and August 2014 (sampling times indicated on Figure 3-9). This hydrochemical analysis is the subject of Chapter 2, and details of the sample collection and analysis are provided in section 2.3.1.

The major ion chemistry of Kilbrook spring during the sampling period (2013 to 2014) is comparable to Irish Ca-HCO$_3$-type groundwaters and reflects the findings of previous studies (Burdon, 1983). It is clear from Figure 3-10 a) that the major ion hydrochemistry of the spring varies little throughout the year. Therefore, the majority of the groundwater supplying the spring must circulate in limestone bedrock. Two of the other springs have a notably saline hydrochemistry (St. Edmundsbury spring and Louisa Bridge Spa Well).

Previous work has suggested that Kilbrook spring (along with most Irish thermal springs) has a predominantly meteoric hydrochemistry; however, some indicators of a deeper circulation and a longer residence time exist ($^4$He and tritium analyses from Burdon (1983)). These indicators, along with slightly elevated levels of chloride, sodium and potassium, suggest that Kilbrook spring represents a mixture of shallow, recently recharged meteoric waters, and deeper, older, and more saline waters. From borehole records, it is estimated that the glaciofluvial deposit from which the spring emerges extends to a depth of at least 23 m. The higher Na concentrations at Kilbrook spring could be due to the buffering effect of this thickness of glaciofluvial sands and gravels, or it could be due to the interaction of the thermal waters with the Namurian non-calcareous shales, which are not present at any of the other thermal spring sites.
The relative amounts of sodium, chloride and bromide (the Na-Cl-Br system) were examined to assess the source of the excess chloride in the groundwater. The Cl/Br mass ratios were found to exceed 200 for Kilbrook spring, St. Edmundsbury spring and Louisa Bridge Spa Well; this suggests that additional chloride is available to the groundwater aside from normal concentrations that may be expected from meteoric recharge and shallow groundwater (Davis et al., 1998; Freeman, 2007). This excess chloride may be from either: i) natural dissolution of evaporites, such as halite (NaCl) or sylvite (KCl); or ii) anthropogenic contamination such as the addition of fertilizers to land, de-icing of roads or industrial practices (Davis et al., 2001). Waters influenced by the dissolution of halite commonly have Cl/Br mass ratios of between 1,000 and 10,000 (Davis et al., 1998). The values for Kilbrook spring are too low for this range. The excess chloride could therefore have an anthropogenic source given that waters contaminated by sewage generally have lower Cl/Br mass ratios of between 300 and 600 (Davis et al., 1998). However, no other common indicators of pollution (such as nitrates or phosphates) were routinely detected in the spring. The lack of seasonal variation in chloride argues against the application of salt to roads in winter as a source.

The origin of the salinity was further investigated by using a compositional data analysis technique to assess the relationship between Na, Cl and Br (see Chapter 2, sections 2.4.2 and 2.6.1). This method, from Engle and Rowan (2013), uses the isometric log-ratio (ilr) transformation developed by Egozcue et al. (2003) to convert the compositional data (expressed as molar concentrations) to a new coordinate system, where each point is represented by \((z_2, z_1)\):

\[
z_1 = \frac{1}{\sqrt{2}} \ln \frac{[Na]}{[Cl]} \quad \text{and} \quad \text{Eq. (3-1)}
\]

\[
z_2 = \frac{\sqrt{2}}{\sqrt[3]{3}} \ln \sqrt{\frac{[Na][Cl]}{[Br]}} \quad \text{Eq. (3-2)}
\]

In the first coordinate, \(z_1\), Br is excluded so this provides insight into the relative gain/loss of Na compared to Cl. In \(z_2\), Br is included and this can be used to assess the degree of evaporite dissolution by the groundwater, as Br is usually excluded from the lattices of evaporite crystals, and is thus depleted in waters that gain their chloride from the dissolution of evaporites. Figure 3-10 b) shows the ilr-coordinates for Na-Cl-Br for the Leinster thermal springs.
Figure 3-10: a) Piper diagram of hydrochemical analyses from the Leinster thermal springs. b) Plot of ilr-coordinates ($z_1$, $z_2$) for the Na-Cl-Br system for Leinster thermal springs. An increase in $z_2$ due to a lower relative amount of Br suggests the addition of chloride through the dissolution of evaporites (halite). Geochemically modelled pathway for the progressive dissolution of halite by seawater, and modern seawater measurements after Engle and Rowan (2013).
These data are compared to the geochemically modelled pathway for the progressive dissolution of halite by seawater from Engle and Rowan (2013). Samples containing Na and Cl derived from the evaporation of seawater should plot down and to the left (in the negative x and y directions) of the value for modern seawater, while meteoric waters which have dissolved halite should plot up and to the right (in the positive x and y directions). The saline thermal springs (St. Edmundsbury spring and Louisa Bridge Spa Well) probably owe their excess chloride to the dissolution of evaporites (Chapter 2). Kilbrook spring has an intermediate chemical composition between the Ca-HCO₃-type thermal springs and the more saline springs, and contains a higher relative proportion of sodium to chloride than even the saline springs. The Kilbrook spring samples collected in the summer appear to contain more Na and less Br than samples from the winter, and could be more influenced by evaporite dissolution.

The hydrochemical composition of Kilbrook spring probably represents the mixing of more dilute, shallower groundwaters of the Ca-HCO₃-type, and deeper, more saline, basinal fluids derived from the dissolution of chloride evaporites. The warmer waters from the winter recharge period overlap with the other Ca-HCO₃-type thermal springs in Figure 3-10 b); this suggests that the winter discharges are the result of a greater degree of mixing with more dilute, shallow recharge groundwaters. The spring discharge in summer, although slightly cooler, exhibits a greater hydrochemical influence from deep, saline groundwater.

3.4.3. AMT model

The published geological map of the survey area (McConnell et al., 2001) shows limestone throughout the region (Figures 3-1 and 3-2). The resistivity values of limestone can depend upon a variety of factors, such as clay content and porosity. Unweathered limestone can generally have high resistivity values of between 1,000 and 100,000 Ωm (conductivity of between 10⁻³ and 10⁻⁵ S/m). However, shale horizons can reduce the bulk resistivity to values as low as 10 Ωm (0.1 S/m) (Palacky, 1988). The amount of fluid contained in the rock will also reduce its bulk resistivity (Telford et al., 1990). Seawater has a low resistivity of less than 1 Ωm (> 1 S/m), whereas fresh water has higher resistivities of up to 100 Ωm (0.01 S/m) (Palacky, 1988).
Even in heavily karstified regions, large cavities in limestones (caves) tend to range in size up to 10 m (Kaufmann et al., 2014), and the cavities formed in the limestones of the Dublin Basin are not expected to exceed widths of a few metres. Given the size of the cells in the AMT model mesh (50 m × 50 m in the central region of interest) the resolution is unlikely to resolve the details of the water-bearing conduits precisely. However, the presence of water-bearing conduits in a volume of limestone bedrock will reduce the bulk resistivity of the rock as a whole, and this should be evident in the model. Faults can also contain clays as well as fluids, and these will reduce the bulk resistivity of the model in the region of the fault. It is worth noting that the survey was carried out in July 2012, when regional groundwater levels were low.

The main features of the AMT geophysical model are highlighted in Figure 3-11. The orientations of the structures visible in the 3-D model are broadly similar to the published geological map of the survey area, however some differences are evident. The most compelling feature in the AMT model is the NNW-trending linear feature that runs through the resistive core of the model directly beneath the spring, and can be distinguished to depths of approximately 500 m. This feature runs through almost the entire survey area, and is therefore imaged by several stations at every point; it is not likely to be an artefact of the modelling process. The location and orientation of this feature corresponds closely to the inferred contact between the boundary between the Namurian shales and the Lucan Fm.; however, in the geophysical model, the feature appears to have exactly the same material on either side of it. The orientation of the NNW feature is consistent with the pattern of regionally identified Cenozoic strike-slip faults. These faults are typical throughout the area of the Dublin Basin, and are known to produce very high discharges in other locations (Moore and Walsh, 2013) (e.g., Huntstown thermal spring, Figure 3-1 c): see also Chapter 2, Table 2-1). The NNW feature beneath Kilbrook spring must represent the main water-bearing conduit (or a series of interconnected conduits) in the bedrock, and probably formed as a result of preferential dissolution of the limestone along a vertically pervasive Cenozoic strike-slip fault.

The resistive core in the centre of the model has resistivity values in excess of 1,000 Ωm. These resistivity values are similar to values obtained for the Waulsortian Limestone Fm. elsewhere in the Dublin Basin (personal observations, made at the
site of St. Gorman’s Well thermal spring (Figure 3-1 c)). The Waulsortian Limestone Fm. is resistive due to the relative purity of its carbonate and its crystalline nature. It is lithostratigraphically feasible for the Waulsortian Limestone Fm. to underlie Kilbrook spring, but there is no nearby outcrop or borehole information to support this.

At shallower horizons (to depths of approximately 300 m), the NW region of the model appears to have a lower resistivity than the central resistive region and could possibly represent the mapped Lucan Fm., which is expected to have a lower resistivity than the underlying Waulsortian Limestone Fm. due to its higher clay content and interbedded shale-rich nature. This less resistive region appears to have a NE – SW trend, which is coincident with the regional geophysical gravity and TELLUS surveys, and also with the orientation of the mapped geological fault that runs through the survey area. This region could also owe its lower electrical resistivity to the development of water-bearing conduits in proximity to the geological fault.

A large pocket of low-resistivity material is present just north of Kilbrook spring, which extends to a depth of approximately 200 m (see Figure 3-7 and Figure 3-8, P1). This could represent a karstic depression in the bedrock that has been subsequently filled with unconsolidated sediments of lower resistivity that are possibly also more permeable. Large, infilled, karstic depressions have been documented in the area where Carboniferous normal faults intersect Cenozoic strike-slip faults (Moore and Walsh, 2013), albeit on a smaller scale. This depression is located where the NNW fault meets the mapped, shallow, NE-oriented fault. This configuration could represent the intersection of a Cenozoic strike-slip fault and a Carboniferous normal fault, and subsequent karst development of high permeability zones along the structures (Figure 3-11), as conceptualised from observations in quarries and mines in the region in Moore and Walsh (2013).

Although the resolution of the model lessens with increasing depth, the base of the resistive limestone appears to be located at a depth of approximately 1000 m (Figure 3-11), which probably represents the extent of the Dublin Basin in this particular location, and the top of the more conductive basement. This conductive basement is likely to comprise Silurian and Ordovician metasediments.
3.4.4. Conceptual model

Information from several different strands of enquiry presented here converge on the consensus that although the thermal spring at Kilbrook does contain a deep groundwater component, the hydrothermal circulation pattern is influenced by the availability of fresh recharge waters and structurally controlled by the presence of karstified faults in the limestone bedrock.

Figure 3-11: Schematic diagram of the main features in the interpretation of the final 3-D AMT model.
Towards the end of the summer the temperature profile of Kilbrook spring becomes less stable with local minor drops in temperature as the regional water table rises and cooler recharge waters are made available to the hydrothermal system. With the establishment of the winter season (in November), the temperature rises slightly (to a maximum of 25.0 °C) and stabilises once more. This is probably caused by an enhanced activation of the hydrothermal circulation pattern, which occurs once the regional water table reaches some critical level. The seasonal differences in temperature support the hypothesis that the influx of cooler recharge waters to a karstic flow system in winter facilitates the operation of a relatively deep and fast circulation pattern within the bedrock, which allows cool water to infiltrate quickly to depth, become heated and mixed, and then rapidly ascend to the surface where it issues with a temperature in excess of 24 °C. In the summer the thermal waters have a lower temperature, so must not have circulated as deeply as the warmer winter waters, but their more saline hydrochemistry (Figure 3-10) suggests a longer residence time and greater degree of interaction with the bedrock aquifer.

Our model has identified for the first time a significant, NNW oriented fault, of probable Cenozoic age, beneath Kilbrook spring. Given that NNW Cenozoic strike-slip faults have been identified as the main structures controlling groundwater flow in the region (Moore and Walsh, 2013), and that elsewhere in the Dublin Basin such structures have been shown to be a source of thermal groundwater (e.g., Huntstown spring in Figure 3-1 c)), it is likely that the hydrothermal circulation pattern for Kilbrook spring is operating along the plane of this NNW structure (Figure 3-11), although our model fails to resolve it at depths in excess of 500 m.

The intrinsically massive nature of the Waulsortian Limestone Fm. allows for the development of vertical or sub-vertical dissolutional flow features, with little lateral dissipation of flow, which can facilitate the rapid transport of recharge fluids to depth, or the rapid ascent of thermal fluids to the surface. Although there is as yet no unequivocal evidence to groundtruth our AMT model, based upon the electrical resistivity values obtained for the faulted bedrock directly beneath the spring, it is possible that this could represent the Waulsortian Limestone Fm. The properties of the Waulsortian strata would allow for the formation of a deeply pervasive, vertical structure such as is imaged in our model.
Chapter 3: Detailed study of Kilbrook spring

The geothermal gradient of Ireland is generally poorly understood, however an average near-surface value of 25 °C/km has been suggested for the Irish Midlands by Goodman et al. (2004). In the summer, the slightly lower-temperature thermal waters (23.5 °C in 2013 and 24.5 °C in 2014) derive from a confined limestone aquifer and have a temperature that is approximately 14°C above average. The confined source aquifer for this flow system is likely to be situated at depths in excess of 560 m, suggesting regional rather than local recharge. The high-temperature fluids from the deep, confined aquifer are mixed with and diluted by cool, shallow recharge waters of meteoric origin during their ascent, so this aquifer is likely to be situated at depths much greater than 560 m.

Overall, the chemistry of the thermal spring waters indicates that the major contribution comes from a limestone source, and the hydrothermal circulation pattern must operate in limestone bedrock. Since our resistivity model suggests an approximate thickness of limestone of between 800 m and 1,000m, a deep hydrothermal circulation pattern in excess of 560 m within limestone is entirely feasible.

Deep groundwater circulation in limestones must occur along dissolutionally enhanced fractures and faults, as primary porosity is usually very low. The density of fractures is expected to decrease with depth and so the transmission of water will occur in highly localised zones within the rock. Fluids will be more likely to flow along open fractures, i.e., those that are opened by tectonic forces. It is therefore possible to speculate that any regional, deep, groundwater circulation in the Dublin Basin will occur in karstified zones, along vertically-pervasive, NNW Cenozoic strike-slip faults and older Carboniferous normal faults. Gunn et al. (2006) carried out isotopic studies on deep groundwater circulation in a carbonate aquifer in Derbyshire, England, and calculated that deep, thermal, groundwater flow constitutes 5% of total groundwater discharge from the Peak District limestone aquifer. A similar study for the wider Dublin Basin would be a valuable addition to our understanding of regional thermal groundwater flow, and perhaps enable quantification of thermal flow in the region.
3.5. Conclusions

AMT is a proven method for investigating geothermal scenarios, and we have shown here how it may be successfully utilised as part of a cost-effective, multi-disciplinary approach to characterise a small-scale, low-enthalpy, hydrothermal system at intermediate depths (100 m to 1,000 m). The interpretation of the AMT results alongside inexpensive data obtained from time-lapse temperature, chemistry and water level measurements have allowed for a better understanding of the hydrothermal circulation pattern at Kilbrook spring. Although the relatively stable and high temperatures of the spring make it an attractive candidate for geothermal energy abstraction, an important consideration for its energy potential is the large seasonal differences in discharge. Higher discharges and temperatures occur simultaneously during the winter season, when thermal energy requirements in the Northern Hemisphere are at their maximum.

The AMT 3-D inversion results have revealed a NNW-oriented region of reduced resistivity, extending to depths of at least 500 m, which is interpreted as a water-bearing Cenozoic strike-slip fault. This structure, in combination with a shallower, NE–SW, Carboniferous normal fault in the NW region of the model, is likely to be the main facilitator of a relatively deep hydrothermal circulatory system.

Our resulting conceptual model positions the structurally controlled hydrothermal system entirely in limestone bedrock. Given the known thicknesses of the Carboniferous sediments in this area (> 1000 m), this is unsurprising. In the summer, the thermal groundwater is provided by a deep, confined aquifer situated at depths in excess of 560 m. These thermal waters show evidence of mixing with deep, highly evolved saline waters. In the winter, the slightly higher temperatures, higher discharges, and slightly less evolved hydrochemistry (lower Na and higher Br) are provided by seasonal input of fresh recharge waters and the activation of a deep hydrothermal circulation pattern in the limestone, at depths well in excess of 560 m.

It is evident that karstification of intersecting geological structures within the limestone bedrock has been the main factor in the development of a thermal spring at Kilbrook. If the Irish thermal springs are to be exploited in the future for geothermal energy purposes, it is crucial to gain a thorough understanding of the local and regional structural geology at shallow and deep levels, in order to effectively target
this geothermal energy resource. This paper has demonstrated how an electromagnetic geophysical technique such as AMT can greatly help in this regard. Since the Irish thermal springs occur in limestone bedrock, their hydrothermal circulation patterns are likely to be centred on the intersection of geological structures, and therefore a 3-D deployment of AMT stations followed by 3-D inversion could be an optimal strategy for similar surveys in the future.
4. Characterising the hydrothermal circulation pattern beneath a low-temperature thermal spring using a multi-disciplinary approach: a case study from Ireland (St. Gorman’s Well)

Abstract

A hydrogeological conceptual model of the source, circulation pathways and temporal variation of a low-enthalpy thermal spring is derived from a multi-disciplinary approach. St. Gorman’s Well is a thermal spring in east-central Ireland with a complex and variable temperature profile (maximum of 21.8 °C). New geophysical data from a three-dimensional (3-D) audio-magnetotelluric (AMT) survey are combined with new time-lapse hydrogeological data, and a previous hydrochemical analysis to investigate the operation of the hydrothermal system. This paper is an example of how different strands of inquiry from a multi-disciplinary investigation may be woven together to gain a deeper understanding of the geothermal potential of a complex hydrothermal system.

The hydrochemical analysis and the time-lapse temperature, electrical conductivity and water level records suggest that the thermal waters are temporally variable but flow within the limestones of the Carboniferous Dublin Basin at all times. The 3-D electrical resistivity model of the subsurface revealed two prominent structures: 1) a NW-aligned faulted contact between two limestone lithologies; and 2) a dissolutionally-enhanced, N-aligned, strike-slip fault, of probable Cenozoic age. The intersection of these two structures, and subsequent karstification of the limestone bedrock, has provided conduits that facilitate the operation of a relatively deep hydrothermal circulation pattern (likely estimated depths between 240 and 1,000 m) within the limestone succession of the Dublin Basin. The results of this study support a hypothesis that the winter thermal maximum and simultaneous increased discharge at St. Gorman’s Well each winter is the result of rapid infiltration, heating and re-circulation of meteoric waters within a structurally controlled hydrothermal circulation system.
4.1. Introduction

The potential to exploit the geothermal energy of deep, thermal groundwater is currently being explored in Ireland as part of the SFI-funded IRETHERM project. A number of thermal springs have been identified that are currently under investigation. A multi-disciplinary approach has been adopted, integrating geophysical surveys, time-lapse measurements of hydrogeological parameters, and detailed hydrochemical analysis, with the aims of (1) identifying the source aquifer(s) for the thermal groundwater, (2) characterising the circulatory systems, and (3) assessing the potential for the existence of deeper, higher temperature, circulation patterns for future geothermal exploitation. This paper presents a case study of one of the springs, St. Gorman’s Well, and shows how different strands of inquiry from a multi-disciplinary investigation may be woven together to develop a hydrogeological conceptual model of the source, circulation pathways and temporal variation of a low-enthalpy thermal spring.

In Ireland, average groundwater temperatures typically range from 9.5 to 10.5 °C (Aldwell and Burdon, 1980) and thermal springs are considered to be those natural groundwater springs where the mean annual temperature is appreciably warmer than average groundwater temperatures (Aldwell and Burdon, 1980; Goodman et al., 2004). St. Gorman’s Well is located in east-central Ireland (Figure 4-1) close to the urban centre of Enfield, Co. Meath, and has historical and cultural significance as a “holy well”. There is evidence that this spring was originally dedicated to St. Ultan (Conway, 2010), and the current name of the spring probably derives from an anglicisation of the Irish word goradh, which means heat. St. Gorman’s Well discharges naturally as an ephemeral pond, and is typically dry during the summer months. Waters from St. Gorman's Well exhibit some of the highest spring water temperatures in Ireland (maximum of 21.8 °C recorded during this study). The temperature and discharge profile of St. Gorman’s Well is complex and varies throughout the year. Temperatures are highest in winter, and ranged between 10.5 and 21.8 °C during this study. The maximum discharge occurs in winter (1018 m³/d measured in January 1982 (Burdon, 1983); Table 4-1) with a mean annual discharge of 398 m³/d. This variation adds further complexity to the characterisation of the spring as a geothermal resource, as the amount of thermal energy available for exploitation varies throughout the year.
In this paper, we present a new 3-D model from an AMT survey at St. Gorman’s Well. The AMT method is an electromagnetic geophysical technique that is widely used for exploring geothermal resources (e.g., Arango et al., 2009; Barcelona et al., 2013; Piña-Varas et al., 2014; Zhang et al., 2015) and hydrogeological targets (e.g., Falgás et al., 2011; Kalscheuer et al., 2015) due to its ability to detect low-resistivity, water-bearing rocks in the subsurface. AMT is a passive technique that is useful for characterising the shallow subsurface. The depth of penetration can be several hundred metres and even greater than a kilometre below the surface, depending on the resistivity of the bedrock. When used as part of a multi-disciplinary approach (incorporating geological, hydrogeological, and other geophysical data), AMT is an efficient and relatively inexpensive method for improving the characterisation of a geothermal resource (see also Chapter 3).

<table>
<thead>
<tr>
<th>Month</th>
<th>Rainfall (mm)</th>
<th>Discharge (m³/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan-82</td>
<td>84</td>
<td>1017.6</td>
</tr>
<tr>
<td>Feb-82</td>
<td>58</td>
<td>616.8</td>
</tr>
<tr>
<td>Mar-82</td>
<td>80</td>
<td>746.4</td>
</tr>
<tr>
<td>Apr-82</td>
<td>25</td>
<td>549.6</td>
</tr>
<tr>
<td>May-82</td>
<td>67</td>
<td>177.6</td>
</tr>
<tr>
<td>Jun-82</td>
<td>120</td>
<td>81.6</td>
</tr>
<tr>
<td>Jul-82</td>
<td>19</td>
<td>26.4</td>
</tr>
<tr>
<td>Aug-82</td>
<td>81</td>
<td>4.8</td>
</tr>
<tr>
<td>Sep-82</td>
<td>77</td>
<td>0.0</td>
</tr>
<tr>
<td>Oct-82</td>
<td>106</td>
<td>4.8</td>
</tr>
<tr>
<td>Nov-82</td>
<td>119</td>
<td>768.0</td>
</tr>
<tr>
<td>Dec-82</td>
<td>87</td>
<td>780.0</td>
</tr>
</tbody>
</table>


The overarching goals of this investigation were: (1) to identify any (electrically conductive) fluid conduit systems associated with the thermal spring; (2) to assess the temporal variability of the spring; and (3) to assess the nature and extent of the hydrothermal circulation pattern. The 3-D AMT model and detailed time-lapse hydrogeological measurements (temperature, electrical conductivity and water level) are discussed alongside a previous analysis of seasonal hydrochemical data from the spring (Chapter 2).
Chapter 4: Detailed study of St. Gorman’s Well

4.2. St. Gorman’s Well in context

4.2.1. Geology and hydrogeology

Irish thermal springs occur in Carboniferous limestone bedrock along a wide band that traverses the centre of Ireland from NE to SW, broadly coincident with the putative trend of the Lower Palaeozoic Iapetus Suture Zone (ISZ) (Figure 4-1 a)).
The ISZ was produced by the final closure of the Iapetus Ocean in late Silurian times, during the later stages of the Caledonian Orogenic cycle (e.g., Chew and Strachan, 2014). Following collision, terrestrial sediments were deposited during the Devonian period (e.g., Graham, 2009), before a shift to predominantly carbonate deposition as a result of a regional marine transgression during earliest Carboniferous (Tournaisian) times (MacDermot and Sevastopulo, 1972). During the Tournaisian and Viséan, several intra-cratic basins developed across Ireland as a result of tectonism and subsidence (e.g., Strogen et al., 1996; Somerville, 2008; de Morton et al., 2015), principally controlled by movement on NE-SW oriented structures, whose orientation was inherited from underlying Caledonian trending features (Worthington and Walsh, 2011). Extensive carbonate production continued in Ireland for much of the Mississippian, before a switch to terrigenous mud and sand deposition in the Serpukhovian and Bashkirian (formerly regionally termed the Namurian in northwest Europe: see Sevastopulo and Wyse Jackson, 2009; Barham et al., 2015).

St. Gorman’s Well is situated in the Carboniferous Dublin Basin (Figure 4-1 b)), which contains c. 2,000 m of sedimentary infill and saw the widespread development of carbonate buildups (‘reefs’) during late Tournaisian to early Viséan times (Somerville et al. 1992). This particular facies, commonly termed the Waulsortian Limestone Formation (Fm.), is characterized by very fine-grained, pure carbonates containing sparry masses. Bedding within the carbonate buildups is often indistinct; these buildups commonly formed aggregates, and intervening, off-mound facies are typically represented by thin, nodular, chert-rich shales (Lees and Miller 1995). The relative purity of this carbonate facies results in it being prone to chemical dissolution and the development of karst features, which is an important consideration for modern groundwater circulation. Active tectonism during the Viséan age led to the development of shallow shelf platforms and contrasting deeper regions in the Dublin Basin. The deeper basinal facies is characterized by thinly inter-bedded, cherty limestones and shales (mapped regionally as the Lucan Fm., or “Calp”; see Marchant and Sevastopulo 1980).
St. Gorman’s Well discharges from the Waulsortian Limestone Fm. near to its faulted contact with the younger Lucan Fm. (Figure 4-2). While bedrock exposure in the area is generally poor, the SG8 geothermal borehole (Figure 4-2), was drilled very near to St. Gorman’s Well (Murphy and Brück, 1989). The data from SG8 suggests that: (1) the spring is situated on or very close to a westward dipping, faulted contact between Waulsortian limestones and Calp limestones; (2) significant cavities in the Waulsortian limestones are present between 68-74 m, 257-263 m, and possibly at 510 m depth; and (3) the downhole groundwater temperatures peak at 21.7 °C in the cavity zone between 68-74 m. This suggests that the high groundwater temperatures observed at St. Gorman’s Well are the result of deep circulation
patterns, controlled by the presence of permeable structures and conduits within the Waulsortian limestones. The Waulsortian limestones are therefore expected to be locally or zonally karstified in the area near St. Gorman’s Well. Developments of Waulsortian limestones in the Dublin Basin can exceed thicknesses of 500 m (Somerville et al., 1996; Strogen et al., 1996), and a thickness of Waulsortian limestone in excess of 460 m was recorded in SG8 (Murphy and Brück, 1989).

St. Gorman’s Well is situated 40 km west of Dublin, in a relatively flat and low-lying landscape in the Eastern River Basin District. The elevation in the survey area (Figure 4-2) ranges from approx. 70 to 90 mAOD, and the spring is situated at an elevation of 80 mAOD. The 30-year (1981-2010) average annual rainfall in the area is 868 mm/yr (Walsh, 2012); during the sampling period (for the hydrochemical sampling and time-lapse measurements) the annual rainfall was 863 mm in 2013 and 922 mm in 2014 (data from Met Éireann, www.met.ie). Evaporative losses for the region are estimated at 450 mm/yr (Met Éireann). The main use of land is agricultural, and the spring and its surroundings have been proposed as a National Heritage Area by the Geological Survey of Ireland (GSI). Depth to bedrock at the spring is 3 m and the overburden consists of limestone till (Burdon, 1983). The Lucan Fm. is classified by the GSI as “locally important, generally moderately productive” aquifer, and the Waulsortian Limestone Fm. is classified as “locally important, moderately productive in local zones only”. Most recharge to aquifers in Ireland occurs in the period between October and April, and typical estimated recharge rates for this area are between 101 and 200 mm/yr (Hunter Williams et al., 2011).

The pond at St. Gorman’s Well is typically filled during winter, in the high recharge period (October to April), when its surface area is approximately 40 m². In the summer, the discharge decreases and the pond is typically dry by September (Table 4-1). A nearby borehole (described in Murphy and Brück (1989) as SG4) situated 20 m to the west of the pond was used for year-round sampling and measurements in this study. The borehole is a 48 m deep, open hole in the limestone bedrock. The borehole has its maximum discharge January, when the water level is artesian; this is when the water temperature is at its maximum (21.8 °C recorded during this study). The borehole discharges to a land drain, which joins a small stream 0.8 km northwest of the borehole. This small stream flows northward and eventually joins up with the
River Blackwater. No detailed hydrodynamic data were available for this study. For the duration of this investigation (2013 – 2015), the maximum winter discharge from the borehole was estimated to be approximately 1,000 m$^3$/d; this is concurrent with the monthly discharge measurements for the spring pond in 1982 (Table 4-1). These historical discharge measurements indicate that the spring has a mean annual discharge of approximately 400 m$^3$/d.

The water from St. Gorman’s Well has a Ca-HCO$_3$-type hydrochemical signature, typical of many recently infiltrated, cold, Irish groundwaters circulating in limestones, and also typical of the majority of the Irish thermal springs. The hydrochemical signatures of the thermal springs imply that they are mainly composed of meteoric waters that are recently recharged from rainfall events (Burdon, 1983; Mooney et al., 2010). Burdon (1983) showed that St. Gorman’s Well contained lower tritium levels than cold groundwater (samples collected in August 1982). These low tritium levels, along with the elevated temperatures, are suggestive of longer residence times and deeper circulation patterns for the thermal groundwater. Water samples recovered from St. Gorman’s Well are likely to be a blend of groundwaters from different sources and different recharge areas. The thermal water could be composed of a mixture of a deeper-circulating, older groundwater, and more recent, meteoric recharge water from a shallow groundwater system.

4.2.2. Structural geology
Gravity surveys in the Leinster region have highlighted the importance of NE-trending alignments in the tectonic fabric of the crust (e.g., O’Reilly et al., 1996), which are visible due to reactivation of Caledonian thrust faults in the early Carboniferous causing density variations in the Carboniferous cover. Airborne electromagnetic data, recently collected in northern Leinster by the TELLUS programme (www.tellus.ie) have also highlighted a regional NE structural trend. On a more local scale, the TELLUS data appears to show a NW structural trend at shallow depths (10 – 40 m). Figure 4-3 shows the apparent conductivity values calculated for a depth of 20 m as provided by TELLUS. Within the AMT survey area at St. Gorman’s Well, there appears to be a resistive body to the NE of the spring.
Chapter 4: Detailed study of St. Gorman’s Well

Figure 4-3: Apparent conductivity at 20 m depth as modelled from Tellus airborne electromagnetic data (from the Tellus data viewer at www.tellus.ie).

The Carboniferous limestones in Ireland that host the thermal springs generally tend to exhibit poor primary porosity. Secondary porosity and permeability are greatly improved by both fracture and karst development, providing discrete pathways for groundwater flow; it is therefore important to consider structural controls on fluid flow within these limestones. In carbonates, the development of deep dissolutional features (at depths of at least 500 m) is likely to be controlled and facilitated by prominent fault structures (Kaufmann et al., 2014). Irish thermal springs are frequently associated with deep-seated, high-angle faults, which facilitate the movement of warm waters towards the surface (Mooney et al., 2010), and they appear to be associated with the dominant, Caledonian, NE – SW structural lineaments apparent in Ireland’s bedrock (Figure 4-1 a)). These deep-seated, pervasive faults, although no longer tectonically active, may still provide fluid pathways enhanced by dissolutional processes in discrete zones (through karstification), allowing water to flow from deeper units up to the surface, and are probably very important in controlling regional groundwater flow (Henry, 2014).

The development of secondary porosity in the Waulsortian Limestone Formation is likely to contribute to the development of thermal springs in the Dublin Basin, as four out of six thermal springs studied in detail during the IREThERM project issue from, or have a close spatial association with, mapped surface outcrop of Waulsortian strata, as can be seen in Figure 4-1 c). The centres of Waulsortian
buildups are typically massive (see Lees and Miller, 1995), so any karstic dissolution will tend to exploit areas of fissured and fractured rock. By comparison, the chert-rich, off-mound facies are much less soluble, and may thus act to constrain or focus groundwater flow. Flow within discrete Waulsortian mounds can become concentrated along vertical or sub-vertical pathways with relatively little lateral dissipation of flow (Moore et al., 2015).

Dissolutional features in the Waulsortian limestones in the Dublin Basin near St. Gorman’s Well (Figure 4-1 c)) have been reported at depths of 250 - 300 m (borehole reports from www.mineralsireland.ie) and may possibly exist at 510 m in one reported instance (Murphy and Brück, 1989). These features play an important role in the operation of deep groundwater circulation patterns and facilitate the movement of the thermal spring waters to the surface.

Large Carboniferous faults in the Irish Midlands tend to have an inherited Caledonian alignment (NE – SW), and can be geometrically linked to contemporaneous NW-oriented cross faults, relay faults and splays that controlled Carboniferous basin bathymetry and patterns of sediment deposition throughout the region. These Carboniferous normal faults were subsequently reactivated as thrust faults during later compressional tectonic events (e.g., Hitzman, 1999), leading them to act as impermeable barriers to groundwater flow; this occurs mainly because they are enriched with incorporated host-rock clays and shales by a combination of fault rock attenuation and smearing, and by dissolution-related restite formation (Moore and Walsh 2013). Carboniferous and Variscan structures in the Irish Midlands are offset by NW- and NE-oriented conjugate Cenozoic strike-slip faults, which are the main groundwater-controlling structures in quarries and mines in the region, and can be identified by their distinct iron-oxide staining due to groundwater flow (Moore and Walsh, 2013). The Cenozoic strike-slip faults were formed by sub-horizontal N – S Alpine compression (Cooper et al., 2012), under low confining pressures, and have been identified in Irish mines at depths in excess of a kilometre (Moore et al., 2015). In certain locations, particularly where they are intersected by Cenozoic strike-slip faults, the Carboniferous normal faults can become karstified and have their permeability greatly increased (Moore and Walsh 2013). A local example of such an intersection of structures can be seen at Rathcore Quarry, two kilometres east of St. Gorman’s Well. Here, the intersection of a Carboniferous normal fault and
a N-oriented Cenozoic strike-slip fault has resulted in the development of a large karstic depression (20 metres wide), which has been subsequently filled with unconsolidated materials.

St. Gorman’s Well is situated on a normal-fault-bounded inlier of Waulsortian Limestone Fm. in the western part of the Dublin Basin (Moore et al., 2015). A NW oriented, normal fault is mapped close to St. Gorman’s Well (Figures 4-1 and 4-2), juxtaposing downthrown Lucan Fm. sediments to the west (hanging wall) and upthrown Waulsortian Limestone Fm. to the east (foot wall). On the basis of borehole records, Murphy and Brück (1989) estimated the dip of the fault to be approx. 60 ° W. The fault has a minimum vertical displacement of 750 m, and is likely to be deep-seated, and of Carboniferous age.

4.2.3. Previous hydrochemical analysis

During the course of the IRETERHERM project, samples were collected and analysed from the six thermal springs in Figure 4-1 c). These hydrochemical analyses are the subject of Chapter 2; the analyses and results pertaining to St. Gorman’s Well are discussed here. Geographical coordinates, geological setting, maximum temperatures and a brief description of each spring is provided in Chapter 2, Table 2-1. Data were recovered for analysis over five seasons to assess the temporal variation in the spring chemistry and to provide some seasonal overlap for a more robust analysis. The springs were sampled in July/August and October 2013, and in January, May and August 2014 (see Figure 4-8).

The major ion chemistry of St. Gorman’s Well, as measured during the sampling period from July 2013 to August 2014, is comparable to Irish Ca-HCO₃-type groundwaters and reflects the findings of previous studies (Burdon, 1983). It is clear from Figure 4-4 that the major ion hydrochemistry of St. Gorman’s Well varies little throughout the year, despite its large variations in temperature. Chapter 2 describes the statistical analysis of the hydrochemical dataset; this analysis revealed nothing in the hydrochemistry of St. Gorman’s Well to suggest the presence or influence of deep-basinal fluids. In other words, the major ion chemistry of St. Gorman’s Well is typical of Ca-HCO₃-type groundwater at all times, even when the temperatures and discharges are simultaneously at their maxima. The chemistry of St. Gorman’s Well was distinguished from other Ca-HCO₃-type groundwaters in the dataset as having a
stronger association with Si and HCO₃ and a weaker association with SO₄; this was interpreted as the influence of the dissolution of the pure carbonate and associated chert layers of the Waulsortian facies on St. Gorman’s Well. The statistical analysis also revealed that St. Gorman’s Well has the largest temporal variations in trace element hydrochemistry of all the thermal springs sampled. The concentration of dissolved metals (Mn and Co in particular) in the groundwater increases during the summer (May to October); this increase in dissolved material is reflected by a general increase in electrical conductivity during the same period (Figure 4-8). This seasonal difference could suggest that the winter thermal water system has a different and less evolved hydrochemistry to the summer thermal water system due to greater dilution with fresh recharge waters in winter.

![Piper diagram of hydrochemical analyses from the Leinster thermal springs including St. Gorman’s Well.](image)

**Figure 4-4:** Piper diagram of hydrochemical analyses from the Leinster thermal springs including St. Gorman’s Well.

4.3. Methodology

4.3.1. AMT survey

The AMT method determines the distribution of the electrical properties of the subsurface and the results can be expressed in terms of electrical conductivity (S/m) or electrical resistivity (Ωm). Conductivity and resistivity are inversely related so that a body with high resistivity will have a low conductivity, and vice versa. Here, the results of the AMT survey are expressed in terms of resistivity. The
magnetotelluric (MT) method is a geophysical technique that determines the distribution of electrical resistivity in the subsurface by relating simultaneous measurements of the naturally occurring fluctuations of the electric and magnetic fields at the Earth's surface. Recent comprehensive reviews of the MT method are provided by Simpson and Bahr (2005), and Chave and Jones (2012). Natural electromagnetic fields that are utilised as source fields in MT studies range in frequency from approximately $10^{-5}$ to $10^5$ Hz. Audio-magnetotelluric (AMT) studies utilise higher frequency (>8 Hz) electromagnetic waves that are generated by electric lightning discharge during lightning storms and propagate around the globe in the Earth-ionosphere waveguide.

The AMT survey was designed to target any karstic conduits occurring beneath St. Gorman’s Well. Thirty-eight AMT measurement locations (stations) were laid out in an approximate grid pattern, centred on the spring itself, with approximately 200 m between sites (Figure 4-2). The grid covered a total area of 2.6 km$^2$. This layout was chosen to investigate depths in excess of 100 m beneath the spring (with a separation of 200 m between stations at the surface, the volumes of measurement beneath each of the stations first overlap at a depth of around 100 m, thus providing a more reliable estimation of the properties of the subsurface at depths greater than 100 m). The survey was carried out in October 2013 to take advantage of cleared fields that had been harvested. Overnight AMT measurements were made using Phoenix MTU-5 systems with an electrode array and horizontal magnetic coil configuration oriented to geomagnetic north-south-east-west, combined with a vertical magnetic recording at each station. Data were acquired in the frequency range between 1 Hz and 10,000 Hz. As the data quality in populated areas is often affected by man-made (“cultural”) electrical noise, one system was deployed as a remote magnetic reference station in a culturally quiet location approximately 9.5 km north of the spring. This extra station allowed for remote reference processing (Gamble et al., 1979). The AMT time series were processed using Phoenix SSMT2000 software, which employs a robust variant of a remote reference processing algorithm based on Jones and Jödicke (1984), and Jones et al. (1989). Aside from the AMT dead-band (a frequency interval with poor signal-to-noise ratio that is found between 1,000 Hz and 5,000 Hz), the data quality was generally good between 10 Hz and 10,000 Hz. The impedance tensors ($Z$) and the vertical magnetic transfer functions ($T$) were
estimated for each frequency for each station. Each curve was manually edited to remove excessively noisy data in the AMT dead-band.

The dimensionality of the data was analysed by investigating the Z and T responses independently of each other (see supplementary material, section A), and the results indicate the existence of a 3-D scenario beneath the survey area. A 3-D inversion was adopted as the most appropriate course of action. The data were inverted using the ModEM 3-D inversion code (Egbert and Kelbert, 2012; Kelbert et al., 2014), and further details of the inversion process are provided in the supplementary material (section 4.6).

4.3.2. Time-lapse hydrogeological measurements

Continuous temperature and electrical conductivity (EC) measurements were collected at St. Gorman’s Well between July 2013 and July 2015, and are presented along with effective rainfall data in Figure 4-8. Daily rainfall and potential evapotranspiration data from Dunsany synoptic station (Met Éireann), situated 14 kilometres to the northeast of the spring, were used to estimate the effective rainfall. Data from July 2013 to December 2014 were featured in Chapter 2, and data from January 2015 to July 2015 are presented here for the first time. New water level data from St. Gorman’s Well are presented from late April 2014 to July 2015.

A HOBO U24-001 temperature and conductivity logger was installed in the borehole at St. Gorman’s Well in July 2013 and recorded temperature (°C) and EC (µS/cm) at 15-minute intervals. The logger was calibrated before installation and cross-checked against field measurements of temperature and EC each time the data was collected. Raw, unadjusted EC measurements are presented in Figure 4-8. In general, the temperature and EC readings were reliable and seemed unaffected by the influence of fouling by bacterial growths on the sensors. Temperature and EC data are missing for the period between July 28th and August 6th 2013 due to instrument failure. Summary statistics for the data were calculated using Onset HOBOWare® software (Version 3.4.1) (Table 4-2). Water level measurements were also recorded every 15 minutes from late April 2014 using a Solinst Levelogger LT unit, which was suspended downhole at a depth of approximately 6 m below ground level. The measurements were compensated for barometric pressure using measurements from a Solinst Barologger LT unit positioned in a nearby barn. Water level measurements
Table 4-2: Summary statistics for St. Gorman’s Well. Temperature (T) and electrical conductivity (EC) data from logger measurements. pH measured in field with Hanna Combo meter during data collection rounds.

<table>
<thead>
<tr>
<th>pH range (μS/cm)</th>
<th>Max EC (μS/cm)</th>
<th>Min EC (μS/cm)</th>
<th>Mean EC (μS/cm)</th>
<th>Max T (°C)</th>
<th>Min T (°C)</th>
<th>Mean T (°C)</th>
<th>σ T</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7 - 7.8</td>
<td>790</td>
<td>544</td>
<td>631</td>
<td>21.8</td>
<td>10.5</td>
<td>17.7</td>
<td>3.0</td>
</tr>
</tbody>
</table>

4.4. Results and discussion

The combined results from the AMT survey, time-lapse hydrogeological measurements and the hydrochemical analysis are discussed and interpreted here to develop a conceptual model for the hydrothermal circulation pattern at St. Gorman’s Well thermal spring site.

4.4.1. 3-D AMT model

The published geological map of the region (McConnell et al., 2001) shows limestone throughout the survey area (Figures 4-1 and 4-2). The resistivity values of limestone can depend upon a variety of factors, such as clay content and porosity. Unweathered limestone can generally have high resistivity values of between 1,000 and 100,000 Ωm. However, shale horizons can reduce the bulk resistivity to values as low as 10 Ωm (Palacky, 1988). The amount of fluid contained in the rock will also reduce its bulk resistivity (Telford et al., 1990). Seawater has a low resistivity of less than 1 Ωm, whereas fresh water has higher resistivities of up to 100 Ωm (Palacky, 1988).

Even in heavily karstified regions, large cavities in limestones (caves) tend to range in size up to 10 m (Kaufmann et al., 2014), and the cavities formed in the limestones of the Dublin Basin are not expected to exceed widths of a few metres. Cavities from the SG8 borehole next to St. Gorman’s Well range in size up to 3.8 m (Murphy and Brück, 1989). Given the size of the cells in the AMT model mesh (50 m × 50 m in the central region of interest) the resolution is unlikely to resolve the details of the water-bearing conduits precisely. However, the presence of water-bearing conduits in a volume of limestone bedrock will reduce the bulk resistivity of the rock as a
whole, and this should be evident in the model. Faults can also contain clays as well as fluids, and these will reduce the bulk resistivity of the model in the region of the fault. It is worth noting that the survey was carried out in October 2013, when water levels were probably at their lowest (see Figure 4-8).

The final resistivity model converged after 60 iterations with a root mean square (RMS) misfit of 1.93. Figure 4-12 shows the residual misfit of the data to the model responses for each period and each station. Upon examination of the model, and given that the space between stations is approximately 200 m, the model results are more reliable from approximately 100 m depth. Resolution of fine structure decreases with depth, and is poor below 500 m. The absolute extent of the sensitivity of the data is defined by the presence of a low resistivity body (with a slightly lower resistivity value than the initial model), which plots between 1,200 m and 1,700 m depth. Beneath this low-resistivity horizon, the values are the same as the a priori model. The shallowest point where the data no longer detects any variation in resistivity is located beneath the conductive body. Figure 4-5 shows that the apparent resistivity curve for each station tends to show a change to conductive conditions at lower frequencies; this is corroborated by phases greater than 45° at lower frequencies. The resolution is too poor at these depths so we have refrained from over-interpreting this structure. However, in shallower parts of the model, the core resistive block (interpreted as limestone) appears to peter out between 800 and 1,000 m (Figure 4-8). Although the resolution is too poor for us to pinpoint this boundary precisely, this conductor exists, and could potentially represent the limit of the Dublin Basin and the (relatively electrically conductive) metamorphic Silurian and Ordovician rocks of the basement.

The model shows a large region of high resistivity in the centre and NE of the survey area with the spring located at its centre (Figure 4-7). There is a highly resistive core to this region with apparent resistivity values in excess of 5,000 Ωm. There is a smaller region of low resistivity material in the SW corner of the survey area, with minimum resistivities lower than 100 Ωm. The boundary between the low resistivity and high resistivity regions is a relatively sharp, linear feature, which is oriented NW – SE. This boundary appears to have a dip of approximately 40° to the SW when viewed in profile (Figure 4-6). Between this boundary and the spring, there are pockets of lower resistivity material (100 – 1,000 Ωm), which appear to have the
same orientation as the boundary, from NW – SE. The largest of these pockets, to the NW of the spring, is a quasi-conical body that is 300 m wide and 300 m long at a depth of 100 m below the surface, and extends to a depth of approximately 250 m (Figure 4-6). The sides of this body are oriented N – S, and it aligns with a low-resistivity bulge in the boundary between the low resistivity and high resistivity regions.

**Figure 4-5**: Apparent resistivity and phase curves for all AMT soundings (xy and yx modes).
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Figure 4-6: Vertical profiles (P1 and P2) through the final resistivity model, and close-up view of top 200 m of P2 (bottom). The profile locations are indicated in the plan view of the survey area. The locations of the AMT stations are indicated by inverted triangles.

Figure 4-7: (overleaf) Horizontal slices through the final 3-D resistivity model. The depth of each slice is indicated. The area of each plot corresponds to the extent of the survey area indicated in Figures 4-1 and 4-2. The spring is located at 53°26'34.57"N 6°53'9.68"W.
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The main features of the interpreted geophysical model are highlighted in Figure 4-9. The results from the model are generally consistent with the published geological map of the survey area, and with the airborne electromagnetic data from the locality (see Figure 4-3). The resistive region in the NE of the model is interpreted as the Waulsortian Limestone Fm., which is expected to be resistive due to the purity of the carbonate and its crystalline nature. The less resistive region in the SW corner of the model is interpreted as the Lucan Fm., which is expected to have a lower resistivity than the Waulsortian Limestone Fm. due to its higher clay content and shale-rich nature. The contact between these two units dips to the SW at approximately 40°, which is comparable to the dip estimates of Murphy and Brück (1989). This model shows that the contact between the two lithologies lies further south than the contact on the geological map (Figure 4-2), and also has a slightly different orientation (the fault on the map is oriented WNW). The vertical extent of the resistive Waulsortian Limestone Fm. appears to be approximately 800 m, although the model loses resolution with depth. The 3-D model is in agreement with records from the borehole SG8, which reached a final depth of 510 m in Waulsortian limestones (Figure 4-9).

The spring is situated on the SW edge of the zone of highest resistivity within the Waulsortian limestones. Between the spring and the boundary with the Lucan Fm., there is a mottled zone with pockets of lower resistivity material trending from NW to SE in the same alignment as the faulted contact, which probably represents a water-bearing zone of higher permeability. It is likely that the highly resistive Waulsortian limestones have become karstified due to their proximity to the normal faulted contact.

The large, 250 m deep, area of low resistivity, to the NW of the spring, could represent a karstic depression that has subsequently been filled with sediments of lower resistivity (e.g., tills from the last glacial maximum) that are possibly also permeable. The sides of the depression are oriented N-S and the depression itself is directly north of a significant bulge in the faulted contact (Figure 4-9). This configuration could represent the intersection of a Cenozoic strike-slip fault and a Carboniferous normal fault and subsequent karst development of high permeability zones along the structures. A large, infilled, karstic depression has been documented 2 km east of the spring (section 4.2.2 above) where a Carboniferous normal fault is intersected by a Cenozoic strike-slip fault. Cenozoic strike-slip faults in particular
are known to produce very high flow rates in other locations in the Dublin Basin (e.g., Huntstown thermal spring, Figure 4-1 c) and Table 2-1). Borehole evidence from Murphy and Brück (1989) suggest that in boreholes adjacent the spring, maximum temperatures were encountered in cavities in Waulsortian limestones at a depth of 70 m. A slice through the AMT model at 75 m depth (Figure 4-7) shows a linear area of reduced resistivity trending NE-SW from the faulted contact to the spring. This is possibly the feeder conduit for the thermal waters, although the size of the cells in the model mesh are probably too large to resolve the conduit accurately.

4.4.2. Time-lapse hydrogeological measurements

The spring exhibits a distinctive pattern of high-temperature, high-volume, winter discharges and intermediate-temperature, steady, summer behaviour (Figure 4-8). This pattern is repeated annually, although with slight differences; this suggests that the hydrothermal circulation pattern is controlled by annual recharge, and that the spring has a direct hydraulic connection to meteoric recharge processes. The summer period is characterised by a stable, intermediate temperature (approximately 16 °C) and increased EC (approximately 700 µS/cm) in both years, although the EC in the second year shows a more flashy profile with localised peaks. The onset of the winter recharge period in October is marked by a decrease in temperature (a minimum temperature of 10.5 °C was recorded in 2013, and 12.6 °C was recorded in 2014). The minimum temperatures reached in 2013 are similar to average cold groundwater temperatures. In both years, there is a sudden and dramatic increase in temperature and simultaneous decrease in EC at a point early in the winter recharge period. This increase in temperature occurred in December 2013, and in November 2014. On December 23rd 2013, the temperature of the spring increased by 6 °C in six hours. On November 14th 2014, the temperature increased by 4 °C in twelve hours. In both years, after this sudden increase, there was a more steady increase in temperature until the spring reached its annual maximum (these maxima occurred in February 2014 (21.8 °C) and January 2015 (21.4 °C)). During these periods of sustained high temperatures, steadily low EC values were observed (values between 550 and 600 µS/cm in both years). In the summer period of each year, the temperature of the spring falls back quite rapidly to intermediate temperatures, while the EC has a more dramatic, sudden increase to approximately 700 µS/cm, thus completing the annual cycle.
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It appears that the spring responds in a non-linear way to large inputs of recharge waters to the system. The decrease in temperature after the onset of the winter recharge period in October occurs after the first period of heavy rainfall of the season. In both years, there is a sudden increase in the temperature of the spring a few days after local maxima in the rainfall records (intense rainfall occurred on December 18th 2013 and November 13th 2014). The difference between the temperature profiles for the two years is probably due to the amount of recharge input to the system. In winter 2013-2014, the profile is a little more extreme than in the subsequent year, with lower minima and slightly higher maxima. The switch from low to high temperatures in December 2013 is faster and the high temperatures are also more stable throughout the winter recharge period. The total rainfall for the period between October and April (inclusive) is 614 mm for the first year and 518 mm for the second year; this seems to suggest that higher recharge input to the system can result in higher and more sustained winter temperatures for the spring. It is interesting that during the drier summer period, particularly in the first year, localised increases in rainfall do not appear to have any effect on the temperature of the spring.

The water level records (measured in metres above a datum; i.e., as the relative height of a column of water above the logging unit) began in late April 2014. The water level profile generally follows the same pattern as the temperature profile; i.e., when the water level is increasing, so is the temperature. The maximum water level measured is 6.7 m; this represents the height of the water column above the logger when the flow is artesian in the winter. The transition from intermediate/cold temperatures to high temperatures, which is marked by a sudden change in the temperature and EC profiles, corresponds to a more gradual increasing trend for the water level. The water level decouples from temperature in November 2014 and begins to rise while the temperature continues to fall; this marks a change in the behaviour of the spring as the effects of the warm aquifer are obscured by the rising local and regional groundwater levels with the onset of winter. It can be surmised that the local groundwater level must reach a critical threshold before the temperature increases rapidly (the temperature increase occurred in 2014 when the water level was 5.05 m above the datum, or 1.65 m below the surface). However, both the water level and the temperature reach their maxima around the same time.
The temperature, EC and water level measurements exhibit semi-diurnal fluctuations (see insets in Figure 4-8), which are more pronounced in the summer period, when water levels are low. Semi-diurnal fluctuations in water level for St. Gorman’s Well were identified by Burdon (1983) and compared to gravity tide correction data for a period in 1981. The close correlation of the two signals confirmed the strong influence of the Earth’s gravity tides upon the water levels in the spring, with maximum variations occurring around the times of the new and the full moon. The relative movements of the Earth, Sun and Moon cause a periodic distortion in the shape of the Earth that causes groundwater to be expelled from confined or semi-confined aquifers. These fluctuations are evidence that the intermediate-temperature thermal groundwater is stored under confined or semi-confined bedrock aquifer conditions during the summer. It is possible that the groundwater is still subject to confined aquifer conditions during the winter, but the artesian flow of the spring obscures the semi-diurnal signal. Data from this study shows that the water level fluctuations mirror those of the temperature and EC; i.e., when temperature and EC are at a local maximum, the water level is at a local maximum (Figure 4-8). This implies that the water being periodically expelled from the confined aquifer by the action of the gravity tides is warmer with a higher EC, and this water is being mixed with cooler, less evolved waters, probably in a closed system. The nature of this water is in contrast to the high-temperature, winter waters, which have a lower EC.

The unusual, rapid onset of the high-temperature phase is suggestive of non-linear, piston flow in karstic conduits. Periodic and intermittent springs are a well-documented feature of some karst aquifers (e.g., a periodic, non-linear flow pattern was identified in a karstic spring in Derbyshire, England, and attributed to an unstable sediment blockage in the system (Bottrell and Gunn, 1991)). The lower EC values in winter could be suggestive of dilution by fresh recharge waters. However, the solubility of calcium carbonate is strongly influenced by the presence and availability of CO2. It is possible that the thermal component that comes to the surface in winter is stored in an aquifer with little influx of “fresh” CO2-carrying waters, for example, a deep aquifer, with a large catchment area and long residence times. An increase in temperature will decrease the solubility of CO2 and hence decrease the solubility of CaCO3, along with other carbonates and sulfates, resulting in a lower EC. In this way, a low EC may not necessarily indicate a younger
recharge water, and the residence times of the thermal waters at St. Gorman’s Well may be long.

St. Gorman’s Well is temporally variable, and its non-linear response to rainfall suggests a karstic conduit system of transport for the thermal waters. Given the geological setting of the spring it is feasible to envisage a network of karstic conduits interacting at different times of the year, under the influence of seasonal recharge conditions. Figure 4-8 identifies three distinct hydrogeological flow systems in operation at different times of the year. Each of these flow systems represents a groundwater with a distinct chemistry and temperature pattern.

- **System I** is steady: it has an intermediate temperature (approximately 16 °C) and likely has a confined or semi-confined, deep, warm source that mixes with shallower, cooler groundwater.
- **System II** is cooler: it occurs at the beginning of the winter recharge season when the influence of cooler waters becomes stronger and overwhelms the steady, intermediate temperatures.
- **System III** is warm: it has a high, steady temperature (> 20 °C) and slightly lower (and more stable) EC; the flow is artesian with a discharge of approximately 1,000 m³/d, and semi-diurnal fluctuations in temperature are largely obscured by the artesian flow.

The switch-over between System II and System III occurs early in the winter, and occurs suddenly and non-linearly; this strongly suggests the presence of conduit flow in karst as the mechanism by which these flow patterns occur. The switch-over from System III back to System I is more gradual, and the temperature decreases as the drier summer season progresses.

**Figure 4-8:** (overleaf) Time-lapse temperature (red), electrical conductivity (black), and water level (blue) measurements for St. Gorman's Well. Water level is presented in metres above an arbitrary datum. Daily effective rainfall data (grey) is from the Met Éireann synoptic station in Dunsany, Co. Meath. First two panels show data from 2013 – 2014; second two panels show data from 2014 – 2015. Insets for August 2013 and July 2014 show three days of semi-diurnal fluctuations in temperature and EC (and water level for 2014 only). Dashed red lines indicate hydrochemical sampling rounds. Roman numerals indicate interacting hydrogeological flow systems. Dashed black arrows indicate sudden switch from flow system II to III in 2014, and corresponding water level.
4.4.3. Previous hydrochemical analysis

The year-round Ca-HCO3-type signature of the waters suggest that the hydrothermal circulation pattern occurs exclusively in limestone bedrock, i.e., within the Carboniferous Dublin Basin. The seasonal differences in trace element hydrochemistry (an increase in dissolved metals in the summer) indicate that the high-temperature thermal waters of System III (Figure 4-6) have a different hydrochemistry than the intermediate-temperature System I. These seasonal differences could be due to the influx of recharge waters to the karstic flow system, which facilitates the operation of a relatively deep circulation pattern within the limestone succession. Two possible explanations for the intricate temporal pattern of St. Gorman’s Well are posited here: 1) cool, dilute, winter recharge waters infiltrate quickly to depth, become heated and mixed, and then rapidly ascend to the surface where they issue with a high temperature in excess of 20 °C and a low EC; or 2) recharge waters infiltrate slowly over a large catchment area and are stored at depth in a thermal aquifer with limited CO2 availability, which limits the solubility of carbonates and sulfates in the aquifer and provides a high temperature, yet low EC spring water.

4.4.4. Conceptual model

Information from several different strands of enquiry converge on the consensus that the hydrothermal circulation pattern beneath St. Gorman’s Well is governed by the availability of fresh recharge waters and structurally controlled by the presence of conduits in karstified limestones of the Waulsortian Limestone Fm.. These limestones, by their nature, allow for the development of vertical or sub-vertical dissolitional flow features, with little lateral dissipation of flow, which can facilitate the rapid transport of recharge fluids to depth, or facilitate the rapid ascent of thermal fluids to the surface. Evidence of these structures beneath the spring has been provided by the 3-D resistivity model. Given the proven efficiency of the Cenozoic strike-slip faults at transmitting large quantities of thermal groundwater, it is likely that this hydrothermal circulation pattern is operating along the plane of the N-S structure indicated in Figure 4-9, although our model fails to resolve this structure at depths in excess of 400 m.
The geothermal gradient of Ireland is generally poorly understood, however an average near-surface value of 25 °C/km has been suggested for the Irish Midlands by Goodman et al. (2004). In the summer (System I in Figure 4-8), the intermediate-temperature thermal waters come from a confined or semi-confined limestone aquifer and have a temperature that is approx. 6 °C above average. Using a simple calculation, and assuming no mixing and no loss of heat as the fluids ascend to the surface, the confined source aquifer for this flow system is likely to be situated at a minimum depth of 240 m. System II in Figure 4-8 represents the mixing of these intermediate-temperature waters with cool, fresh, recharge waters as the regional water table rises and activates shallow, cold, flow systems with the onset of winter. In the winter, the high-temperature thermal waters of System III are approx. 12 °C above average, which represents a minimum depth of circulation of 500 m (again assuming no mixing and no loss of heat). The rapid onset of the high-temperature winter thermal system is probably caused by piston flow in karst conduits as the winter hydrothermal circulation pattern is activated by a large influx of recharge waters. The hydrochemistry of these waters suggests that all flow systems in Figure 4-8 operate in limestone bedrock. Since the resistivity model suggests a thickness of limestone of approximately 1,000 m, a deep hydrothermal circulation pattern within limestone to depths in excess of 500 m is feasible.

Deep groundwater circulation in limestone must occur along dissolutionally enhanced fractures and faults, as primary porosity is usually very low. The density of fractures is expected to decrease with depth and so the transmission of water will occur in highly localised zones within the rock. Fluids will be more likely to flow along open fractures, i.e., those that are opened by tectonic forces. It is therefore possible to speculate that any regional, deep, groundwater circulation in the Dublin Basin will occur in karstified zones, along vertically-pervasive, NNW Cenozoic strike-slip faults and older Carboniferous normal faults. Gunn et al. (2006) carried out isotopic studies on deep groundwater circulation in a carbonate aquifer in Derbyshire, England, and calculated that deep, thermal, groundwater flow constitutes 5% of total groundwater discharge from the Peak District limestone aquifer. A similar study for the wider Dublin Basin would be a valuable addition to our understanding of regional thermal groundwater flow, and perhaps enable quantification of thermal flow in the region.
Figure 4-9: Top: Horizontal slice through final resistivity model at 150 m depth showing the main intersecting geological structures and potential water-bearing zones of karstified bedrock. Bottom: Vertical profile through the model (P2 in Figure 4-6) showing main features of the hydrothermal flow system. SG8 indicates the extent of the 500 m geothermal borehole from Murphy and Brück (1989).

4.5. Conclusions
A hydrogeological conceptual model of the source, circulation pathways and seasonal variation of a low-enthalpy thermal spring was deduced from a multi-disciplinary approach. St. Gorman’s Well has an extremely variable temperature profile which ranges from 10.5 °C to 21.8 °C. For the geothermal energy potential of the spring, it is important to consider that the large annual variations in temperature
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will control how much geothermal energy is available for abstraction at any particular time, and also that the temperatures in the spring can vary from year to year. Three distinct patterns of behaviour have been identified from detailed temperature and EC profiles; these patterns have annual repeatability and represent the interaction of three different flow systems within the overall hydrothermal circulation pattern. They indicate a non-linear hydrogeological system with rapid changes from one pattern of behaviour to another, and little direct influence from rainfall. This suggests a degree of storage in the flow system, and insulation from shallow recharge processes during the summer when the regional water table is lower. The semi-diurnal signature in temperature, EC and water level indicates confined conditions in the thermal aquifer for at least part of the year. The results of a previous hydrochemical analysis suggest that the thermal waters flow entirely in limestone bedrock, and subtle variations in the minor and trace element chemistry are due to the interaction of different flow systems, as identified from the time-lapse temperature profile.

The results of a 3-D inversion of AMT data from St. Gorman’s Well have revealed a compelling N – S oriented region of reduced resistivity, which is interpreted as a water-bearing Cenozoic strike-slip fault. This structure, in combination with the NW – SE Carboniferous normal fault to the southwest of the spring, is likely to be the main facilitator of a relatively deep hydrothermal circulatory system. The results of the 3-D model are corroborated by borehole records from the area. The resulting conceptual model positions the structurally- and recharge-controlled hydrothermal system entirely in limestone bedrock. In the summer, the intermediate temperatures are provided by a deep, confined aquifer at a minimum depth of 240 m. In winter, the high temperatures and high discharges are provided by the seasonal activation of a deep hydrothermal circulation pattern in the limestone, at a minimum depth of 500 m. This circulation pattern may extend within the limestone to depths of approximately 1,000 m.

It is evident that the karstification of intersecting structures within the Waulsortian Limestone Fm. has been the main factor in the development of a thermal spring at St. Gorman’s Well. It is likely that the particular properties of these limestones, when they are intersected by major geological structures, have played an important role in the development of thermal springs elsewhere in Ireland. If the thermal springs are to
be exploited in the future for geothermal energy purposes, it is vital to gain a thorough understanding of the structural geology of the spring sites, at shallow and deep levels, in order to effectively target this geothermal energy resource. We have shown here how a geophysical technique such as AMT can greatly help in this regard. Since the hydrothermal circulation patterns are likely to be centred on the intersection of geological structures, a 3-D deployment of stations followed by 3-D inversion could be an optimal strategy for future surveys.

4.6. Supplementary information

4.6.1. Dimensionality analysis of AMT data

The dimensionality of the data was analysed by investigating the \( Z \) and \( T \) responses independently of each other. For the \( Z \) responses, the dimensionality analysis was performed by examining the phase tensors (Caldwell et al., 2004), which have the advantage of being unaffected by galvanic distortion of the electric fields. Figure 4-10 shows the calculated phase tensor for each frequency for each station, depicted as an ellipse. For a 1-D scenario the phase tensor is represented by a circle, and for a 2-D case the phase tensor is represented by a symmetrical ellipse, with the orientation of the major axis aligned either parallel or perpendicular to the regional geoelectrical strike direction. For 3-D cases the phase tensor will be non-symmetrical, necessitating the use of an additional angle, \( \beta \), to characterise the tensor. Caldwell et al. (2004) suggest that a value of the skew angle, \( \beta \), greater than 3° indicates a 3-D scenario. Theoretically, if \( \beta \) exists (i.e. \( \beta > 0^\circ \)) then the scenario is 3-D. The review paper by Booker (2014) recommended taking the errors in \( \beta \) into account when determining dimensionality. In this thesis, the approach as suggested by Campanyà et al. (in review) is used, and this takes the errors on \( \beta \) into account. Figure 4-10 shows the calculated value of \( \beta \) divided by the error in determining \( \beta \). Thus \( \left| \frac{\text{skew } \beta}{\text{error skew } \beta} \right| > 1 \) indicates a 3-D scenario. For example, a skew angle \( \beta \) of 2° that was calculated with an error of 0.5° would indicate a 3-D scenario, as it proves that \( \beta \) is greater than 0°. In Figure 4-10, the ellipses representing 3-D conditions are coloured depending upon the magnitude of \( \beta \) normalized by the corresponding error, following the approach of Campanyà et al. (in review). All stations in Figure 4-10 show coloured ellipses for some frequencies, indicating 3-D conditions for the
survey area. For the $T$ responses, induction arrows (Schmucker, 1970) following the Parkinson criteria (i.e., the real arrows tend to point towards current concentrations in conductive anomalies (Jones, 1986)) were used. Figure 4-11 shows the induction arrows for each station and each frequency (stations 4, 33, 35 and 38 have no induction arrows because the $T$ data quality was poor for these stations). For a 1-D scenario the length of the induction arrows is less than the threshold length of the assumed errors as there is no induced vertical magnetic field. For a 2-D scenario the induction arrows point in the same or exactly opposite directions for all periods and stations. In a 3-D scenario, real and imaginary induction arrows point in different (oblique) directions at any one frequency for any station (as can be seen in Figure 4-11). The results from Figures 4-10 and 4-11 indicate the existence of a 3-D scenario beneath the survey area.

4.6.2. 3-D inversion of AMT data

AMT data from 28 frequencies (excluding frequencies in the dead-band, particularly between 800 Hz and 2,000 Hz) were prepared for the inversion; these data were subsequently re-edited on a station-by-station basis to remove particularly noisy frequencies. The data were inverted using the ModEM 3-D inversion code (Egbert and Kelbert, 2012; Kelbert et al., 2014). The vertical magnetic transfer functions ($T$) were inverted alongside the four components of the impedance tensors ($Z$) to improve the resolution of the subsurface resistivity values (e.g., Siripunvaraporn and Egbert, 2009). The mesh for the resistivity model consisted of $90 \times 90 \times 90$ cells, with square cells with sides 50 m long in the horizontal plane of the central region of interest. This central region was a square with sides 3 km long. Padding cells were added in the $x$ and $y$ directions with an incremental factor of 1.3. In the $z$ direction, 10 air layers were added above the resistivity model. The first (surface) layer of the model was 10 m thick; these layers were incrementally increased by a factor of 1.025 until a thickness of 60 m was achieved. The layers were then increased by a factor of 1.1. The final model dimensions were $8 \text{ km} \times 8 \text{ km} \times 5 \text{ km}$. Several preliminary models were assigned a homogeneous half space with varying resistivity values as their starting and prior models; the best results (i.e., with the least extreme values and resolving the most structure) were obtained with half-spaces of 300 and 500 $\Omega$m (0.003 and 0.002 S/m). An average of four models (two starting models with homogeneous half-spaces of 300 $\Omega$m and 500 $\Omega$m, and the two resultant models
from those inversions) was calculated and set as the prior model for the final inversion. The model mesh was not rotated, as advocated by Kiyan et al. (2014), as preliminary models showed the subsurface to have 3-D structure with no one predominant geoelectrical strike direction evident. An error floor of 5 % was imposed for all components of $Z$ (calculated from the modulus of the off-diagonal components $Z_{xy}$ and $Z_{yx}$), and an absolute error of 0.03 was used for $T$. Variation of the smoothing parameters was investigated for the model; values between 0.1 and 0.5 were tested, and an intermediate value of 0.3 (in all directions) for the smoothing parameter gave the minimum root mean square (RMS) misfit for the data.

No correction or compensation was applied to the data to account for galvanic distortion, which is a tractable problem in 2D cases, but far less practicable in 3D (see Jones, 2011). An examination of the apparent resistivity curves revealed no particular “problem areas” for galvanic distortion. As a 3-D modelling approach was used, with a fine parameterization in the uppermost part of the model, it was expected that the model would not be greatly affected by near-surface galvanic distortion effects at our target depths (e.g., Sasaki and Meju, 2006; Farquharson and Craven, 2009; Meqbel et al., 2014). Galvanic distortion may affect the very shallowest layers of the model, but at depth, particularly beneath 100 m where every part of the model is sampled by numerous stations, the conductivity shows a smooth and consistent distribution and any unresolved features near to the surface appear to have been assimilated by the model. Hence, at depths greater than 100 m the effects of galvanic distortion in the model should be negligible. Also, the inversion of $T$ alongside $Z$ should decrease the susceptibility of the model to the effects of galvanic distortion. As $T$ does not involve the electric field directly (see Eq. 1-4), it is not subject to the same galvanic distortion as $Z$. However, it can become distorted if the deflection of electric currents by in-phase electric fields alters the vertical magnetic fields (Booker, 2014). The resulting models do not show obvious artefacts (i.e., site-correlated model structures), which commonly indicate the presence of static shifts.
Figure 4-10: Phase tensor dimensionality analysis using Z responses. White-grey colours indicate frequencies affected by the presence of 1-D or 2-D structures. Other colours represent frequencies affected by 3-D structures. Stations are arranged from W to E in three panels to correspond with the boxes outlined in the map of the survey area (Figure 4-2).
Figure 4-11: Induction arrow dimensionality analysis using T responses, following the Parkinson criteria. Stations are arranged from W to E in three panels to correspond with the boxes outlined in the map of the survey area (see Figure 4-2).
Chapter 4: Detailed study of St. Gorman’s Well

Figure 4-12: (cont. overleaf) Representation of the data fit to the model responses from the final 3-D inversion of AMT data (section 4.1.). Data from both components of T and all four components of Z are represented (real and imaginary parts). The stations are grouped to reflect the three boxes in the inset: the stations are arranged in order of their appearance from W to E. The coloured scale represents the difference between the data and the model response divided by the error for each frequency at each station.
Chapter 4: Detailed study of St. Gorman's Well

\[ Z_{xx} \text{ (real)} \]
\[ Z_{yy} \text{ (real)} \]

\[ Z_{xx} \text{ (imag.)} \]
\[ Z_{yy} \text{ (imag.)} \]

\[ Z_{xy} \text{ (imag.)} \]
\[ Z_{yx} \text{ (imag.)} \]
5. Discussion and conclusions

This thesis investigates the source, circulation pathways and seasonal variations of a sub-set of the Irish thermal springs, in a broad assessment of their geothermal energy potential. A combination of techniques, including audio-magnetotelluric (AMT) electromagnetic geophysical surveys and multivariate statistical analysis (MSA) of hydrochemical data, has been applied to derive hydrogeological conceptual models at two specific spring sites (Chapters 3 and 4). MSA was also used to investigate the hydrochemical relationships between six thermal springs in Leinster (Chapter 2). The results have enhanced our understanding of these complex natural systems, and have identified geological structures common to both springs that play major roles in the hydrothermal circulation of thermal groundwater. In a methodological sense, the thesis also demonstrates: (1) the suitability of AMT for the characterisation of small-scale, intermediate-depth (100 m to 1,000 m), hydrothermal circulation systems in fissured and fractured bedrock (Chapters 3 and 4); and (2) the benefits of using a compositional approach to MSA as compared to a standard, non-compositional approach (Chapter 2). The methodologies outlined in each of the three papers that constitute this thesis provide a transferable work-flow that may be applied to other similar thermal spring sites in future investigations.

5.1. The potential for deeper, higher-temperature groundwater

The thermal springs of Ireland have relatively low temperatures compared to other geothermal settings. In Chapters 3 and 4, the approximate depth of circulation of the thermal waters was estimated based upon an average geothermal gradient of 25 °C/km for the Irish Midlands (Goodman et al., 2004). For Kilbrook, the circulation pattern was estimated to extend to a minimum depth of 560 m; for St. Gorman’s Well the minimum depth was estimated to be 240 m in the summer, and 500 m in the winter. The thickness of Carboniferous sediments in this part of the Dublin Basin is expected to exceed 1,000 m (this minimum thickness is corroborated by the AMT results), so a hydrothermal circulation pattern entirely in carbonate rocks is feasible for both Kilbrook spring and St. Gorman’s Well, as corroborated by their
hydrochemistry. The increased temperatures observed at the thermal springs can therefore be explained without the invocation of an enhanced geothermal gradient, or a deep and hot aquifer. As some heat loss must occur as the fluids ascend to the surface, it is possible that slightly higher temperatures than those observed at the spring orifices may be obtained if the hydrothermal conduits were intercepted at depth (between approximately 500 m and 1,000 m depth, for either of the springs studied). This would require extremely precise, or lucky, drilling, but may provide waters of sufficient temperatures for large-scale space heating (Section 1.1.2).

It is clear from the hydrogeological conceptual models developed in Chapters 2, 3 and 4 that karstification of intersecting geological structures is likely to be an important influence on the occurrence and location of the thermal springs; in other words, the springs are structurally controlled. The locations of thermal springs across the country along the putative Iapetus Suture Zone is not likely to be due to coincidence, as it represents a tectonic zone of Caledonian alignment, where the geological structures are likely to be large and vertically persistent. The springs are also lithologically controlled; they always occur in Carboniferous bedrock, and in most cases have a close association with the Waulsortian Limestone Fm. The lithology controls the occurrence of the thermal springs because the carbonate sedimentary rocks facilitate the formation of karstified, transmissive structures that can rapidly transport the thermal waters to the surface.

As the springs are dependent upon karstification of geological structures, their circulation patterns are probably limited to carbonate strata for the most part, and therefore limited to the Carboniferous basin fill in the Irish Midlands. A further constraint on the depth of circulation is the availability of karst conduits, which must become scarce at depths in excess of 500 m (Kaufmann et al., 2014). In the absence of a high geothermal gradient in the Irish Midlands, it is therefore unlikely that high-temperature groundwaters such as are required for geothermal electricity generation will be found in Ireland.

5.2. Answering the research questions

Five specific aims of this thesis are laid out in Section 1.3, and repeated here:
1. Investigate the source of the thermal waters using MSA of new hydrochemical data from the thermal springs;
2. Compare the hydrochemistry of the thermal spring waters to “average” cold groundwaters from limestone bedrock;
3. Characterise the temporal behaviour of the springs and how they relate to seasonal recharge;
4. Characterise the conduits or pathways supplying the thermal waters to the surface using a passive, deep-reaching, geophysical method (AMT); and
5. Explore the possibility or evidence for deeper circulation patterns, which may offer higher temperature waters.

The first four aims are addressed by Chapters 2, 3 and 4, and the fifth aim is addressed in section 5.1 above.

Chapter 2 investigates the provenance of the thermal groundwater for a group of springs using MSA, and compares the seasonal hydrochemistry of the thermal waters to typical cold groundwater from limestone bedrock (Aims 1, 2 and 3). Three significant hydrogeological processes that influence the hydrochemistry of the thermal springs are identified from the analysis. The springs can be broadly grouped according to chemistry, into either Ca-HCO$_3$-type or NaCl-type groundwaters (Kilbrook spring has an intermediate chemistry between the two groups). The saline springs (St. Edmundsbury spring and Louisa Bridge Spa Well) have very similar profiles with intermediate temperatures and little temporal variability, which suggests a common source aquifer for these springs. An analysis of the trace element hydrochemistry strongly suggests an evaporite source for the chloride concentrations in both saline springs, although the precise stratigraphic origin of these evaporites is unknown. In contrast, the group of calcium-bicarbonate-type springs exhibits a wide range of temperatures, and seasonal behaviours, the most striking of which is the complex case of St. Gorman’s Well.

Chapter 3 explores the efficacy of the AMT method as part of a multi-disciplinary investigation of Kilbrook spring in an attempt to define the nature of the hydrothermal circulation pattern beneath it (Aim 4). The 3-D resistivity model of the subsurface revealed a prominent NNW-oriented strike-slip fault in the limestone
bedrock directly beneath the spring, of probable Cenozoic age, which probably provides the pathway for the circulation of the thermal waters. It appears that this structure intersects a NE-oriented Carboniferous normal fault at shallow depths. In conjunction with the geophysical model, hydrochemical and temperature data were examined to assess the source of the thermal water and the temporal variations in the behaviour of the spring (Aims 1 and 3). Kilbrook spring is found to have stable and high temperatures. Slightly higher temperatures and discharges in the winter indicate that the hydrothermal circulation pattern is driven and controlled by the availability of fresh recharge waters. These winter discharges are hydrochemically more dilute than in summer when the regional water table is lower. The hydrochemistry data also indicate that Kilbrook spring receives a contribution from a deep, saline source.

Chapter 4 investigates St. Gorman’s Well by following a similar line of enquiry to Chapter 3, with the addition of detailed water level measurements to examine the complex temporal variations and enhance the hydrogeological conceptual model (Aims 3 and 4). The temperature, electrical conductivity and water level measurements indicate a highly non-linear response to effective rainfall, which is suggestive of fluid flow in karst conduits. Hydrochemical data indicate a limestone source for the predominantly calcium-bicarbonate waters (Aim 1); this is corroborated by local borehole evidence. Three distinct patterns of behaviour are identified for St. Gorman’s Well, which represent the interaction of different hydrogeological flow systems within the karstified Waulsortian Limestone Fm. at different times of the year. The pathway for the hydrothermal circulation is provided by a N-oriented Cenozoic strike-slip fault that intersects a NW-oriented Carboniferous normal fault, as indicated by the 3-D resistivity model. Echoing the pattern observed for Kilbrook spring, St. Gorman’s Well has higher temperatures and discharges of more diluted waters in the winter; indicating a recharge-driven hydrothermal circulation pattern.

There are several striking similarities between the conceptual models for Kilbrook spring and St. Gorman’s Well, despite their rather different temporal behaviours. Temperature profiles for both springs indicate the seasonal activation of a deep-seated hydrothermal circulation pattern; each winter, fresh recharge circulates rapidly
to depth, is heated and then discharged at the springs. The 3-D geophysical models highlight N or NNW trending structures intersected by NE or NW trending structures. Cenozoic strike-slip faults proliferate in the Dublin Basin, have orientations from NNE to NNW, and are highly transmissive. The NE Carboniferous normal faults and contemporaneous NW cross-faults are usually sealing faults except where they are intersected by Cenozoic strike-slip faults (Moore and Walsh, 2013). The structural configuration that exists beneath both Kilbrook spring and St. Gorman’s Well has the capacity to transmit large volumes of water, and is an ideal pathway for a seasonally-activated, deep-seated hydrothermal circulation system. The 3-D resistivity models show both springs to be situated on high-resistivity bedrock; in the case of St. Gorman’s Well, this is proven to be a significant thickness of Waulsortian Limestone Fm. The properties of the Waulsortian limestones are conducive to the formation of vertically persistent structures, and they are prone to karst formation along fissures and fractures, making these rocks an ideal host for a structurally-controlled hydrothermal circulation system. There is no bedrock exposure or borehole record at Kilbrook, but based upon the electrical resistivity values obtained from the AMT model, there is the possibility that the Waulsortian Limestone Fm. may exist beneath the spring.

5.3. Recommendations and outlook

Based upon the findings of this thesis, and in order to further increase our understanding of the Irish thermal springs, the following suggestions for future work on this topic are provided:

General recommendations

i. The geothermal gradient in Ireland is poorly known, and as a result, only simple calculations of likely reservoir depths were used in this study. Superior estimates for the geothermal gradient would necessitate a costly drilling programme, but, if carried out properly, would provide definitive information about the deep geothermal potential of Ireland.

ii. A parallel study of the Munster thermal springs in the southwest of Ireland (a similar combination of hydrochemical and deep electromagnetic surveys)
would provide a direct comparison to this work on the Leinster thermal springs.

iii. Further investigation is required to examine the apparent link between Waulsortian Limestone Fm. deposits and thermal spring occurrence across the whole of Ireland. Optimally, this would include a drilling programme.

iv. An investigation into the similarities between Irish and U.K. thermal springs could yield interesting results, as (intermediate-temperature) thermal springs in both countries are found in similar bedrock deposits with similar temperature ranges (e.g., Taffs Well, Wales (Farr and Bottrell, 2013); Buxton spring, Derbyshire (Gunn et al., 2006)).

**Hydrochemistry**

i. Collation and analysis of hydrodynamic data for the thermal springs (including e.g., local well surveys for seasonal groundwater head levels) would enable hydrological recharge balances to be calculated. This information could be used to inform numerical mixing models, particularly in the case of St. Gorman’s Well, where three interacting flow systems have been identified.

ii. Collection of new cold groundwater chemistry data from a variety of stratigraphic targets in the Dublin Basin, including trace elements (particularly Br), would be useful to further investigate the evaporite source of the saline thermal springs. $^{36}$Cl isotopic measurements would also provide more information on the source and mixing of the saline groundwater component (e.g., Rao et al., 2005).

iii. Sr isotope measurements could be used as a tracer to investigate whether the source of the thermal waters is intra- or extra-basinal. A pilot study is currently underway at UCD (unpublished report completed by Elliott Mueller, 2015); early results suggest a more radiogenic source for the saline thermal springs (St. Edmundsbury spring and Louisa Bridge Spa Well) (pers. comm. Stephen Daly, 2016), suggestive of terrigenous rather than carbonate source rocks.

iv. Stable isotopic measurements of the thermal groundwaters were last carried out in the early 1980s. An updated survey would enhance our understanding
of how the thermal springs are recharged, and would enable comparison of thermal groundwaters to stable isotope contour maps (e.g., Darling et al., 2003).

v. The measurement of helium isotopic ratios at thermal springs along the Iapetus Suture Zone could identify the contribution of mantle $^3$He to the groundwater, and therefore possibly infer the presence of crustal-penetrating faults (e.g., Newell et al., 2015).

**Geophysics**

i. In collaboration with ETH, Zurich, controlled source electromagnetic (CSEM) measurements were made at St. Edmundsbury spring in April 2012 (Wagner et al., 2013), and followed by AMT measurements in December 2012, with the intention of simultaneously interpreting the data from these surveys. Despite remote reference processing, the AMT data quality is very poor due to cultural interference, and no further modelling has been carried out. Future work could comprise re-processing of the data using advanced processing techniques to extract useful resistivity models of the subsurface. As St. Edmundsbury is a saline thermal spring, with a deep-seated source aquifer, a reliable characterisation of the feeder structures would be very interesting.

ii. In early 2016, the Tellus project (www.tellus.ie) will publicly release new airborne electromagnetic data collected over the Irish Midlands (including Counties Meath and Kildare). Integration of this data with existing AMT data could provide improved resolution of electrically-conductive, water-bearing conduits in the first 100 m of the subsurface (where the AMT results are less reliable). A country-wide, southward extension of the Tellus survey is likely to occur in the next few years, so this data could also be useful to study the Munster thermal springs in the future.

iii. Alternatively, a complementary, shallow, electromagnetic technique, such as DC resistivity, could be used in conjunction with AMT at thermal spring sites to improve the resolution in the first 100 m below the surface, and thus enhance our knowledge of the subsurface.
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