



Geochemical techniques to define deep thermal spring protection zones

Chief Scientist's Group report

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Professor Doug Wilson
Chief Scientist

Executive summary

Deep thermal springs occur where groundwater rises from deep within the Earth's crust at a rate that preserves elevated water temperatures. Thermal springs are important natural resources. In the past, the mineral-rich waters were believed to have powerful medicinal properties. Nowadays, thermal spring waters in the UK feed luxury thermal spas, are the sites of historical bath remains and are bottled as mineral drinking water. Despite their socio-economic value, no national-scale regulations are currently in place to manage or protect thermal springs. This lack of protection could put this resource at risk from over-exploitation, pollution and hydrological change.

Several previous reports from the Environment Agency have covered the topic of thermal springs, along with brackish, or deep groundwater in general. In terms of deep thermal springs, SC180009 focused on identifying and mapping deep-sourced spring resources. SC180015 highlighted the need to constrain the provenance and flow pathways and outlined guidance for spring protection zones, similar to the framework applied to protect shallow groundwater systems. Both reports stress that thermal springs are valuable and potentially vulnerable resources and that the Environment Agency should consider implementing environmental legislation to protect thermal springs against future change.

However, quantifying vulnerability and effectively defining spring protection zones requires a robust understanding of the hydrogeological controls on thermal springs. Unresolved sub-surface flow pathways, distal recharge zones and large storage capacities make thermal springs highly complex systems that are difficult to constrain. Geochemical tools can be used to understand deep thermal groundwater origins and flowpaths.

The aims of this report are to:

- Inform the Environment Agency about the use of geochemical techniques to understand the origin, age and flow paths of deep thermal springs.

- Summarise previous geochemical research on deep thermal springs in the UK.
- Identify research gaps and make recommendations for future research to predict change and protect deep thermal springs.

This report highlights the wide range of geochemical proxies that are available to understand thermal groundwater, as well as the wealth of existing geochemical data about thermal springs in the UK. Over the last 40 years, geochemical research has been conducted on the five major thermal springs in the UK. Methods such as stable and radioactive isotopes, noble gases, geothermometry and anthropogenic marker detection have been applied. These data have provided valuable insights into the origin, transport pathways (and depth) and age of thermal spring waters.

There are still several critical uncertainties. Some thermal springs lack important geochemical data that could help to refine our understanding of hydrogeological processes. Many proxy methods, such as geothermometric techniques and radiocarbon dating, include large assumptions or uncertainties, which could produce misleading information if not calibrated by other proxy evidence. Additionally, most geochemical data are taken from where the spring emerges, and there are no deep boreholes to sample thermal groundwater along sub-surface flow pathways. Finally, most data represent spot samples, and there are currently no routine monitoring protocols in place to understand geochemical variability. Opportunities for future geochemical research to address these gaps in our knowledge are identified.

More broadly, this report highlights the need to integrate geochemical data into 3-dimensional hydrogeological models of deep thermal groundwater storage and spring emergence. This will help to refine understanding of flow-pathways and identify areas that could be most at risk from subsurface developments. It is recommended that information on how other countries monitor and protect their thermal springs is compiled, helping to inform future policy decisions.

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1 Introduction

Thermal springs occur where geothermally heated groundwater rises from deep within the Earth's crust and emerges at the surface with water temperatures that are significantly higher than the mean annual air temperature. These thermal springs are invaluable natural resources, with important historical and socio-economic relevance. The mineral-rich thermal spring waters were long believed to have medicinal properties, with the potential to alleviate a wide variety of diseases including leprosy, infertility and rheumatism. During the Roman Age, important settlements were built around thermal springs, and people travelled long distances to bathe or drink the waters in search of healing. Nowadays, thermal springs are tourist attractions, associated with historical bath remains and active thermal spas, or bottled and sold as mineral drinking water.

In order for thermal springs to form, several hydrogeological conditions need to co-occur. First, groundwater needs to circulate to adequate depths within the crust to allow for geothermal heating by the Earth's interior. This geothermal heat is produced by the radioactive decay of unstable elements and residual heat from planetary accretion, with temperatures in the crust increasing by an average of 28°C per km depth in the UK (Busby and others, 2011). Second, the aquifer storing deep thermal groundwater needs to be sufficiently permeable and have a well-connected network of fractures, allowing for deep waters to rapidly rise to the surface without extensive heat loss to surrounding bedrock or from dilution by cold, shallow groundwater. There is currently no commonly accepted definition of a thermal spring, with various temperature thresholds and terminology of hot versus warm thermal springs. Here, we discuss thermal springs with temperatures exceeding 20°C, following Darling (2019), where water temperatures are significantly higher than mean annual air temperatures and shallow groundwater systems – between 9 and 11°C in the UK.

In the UK, there are only five locations where geothermally heated waters emerge as springs with temperatures exceeding 20°C. These are the Bath hot springs, the Hotwells system in Bristol, the Matlock and Buxton hot springs in the Peak District and

Taff's Well in south Wales. All of these deep thermal spring systems are associated with Carboniferous Limestone aquifers, which were deposited during the Tournaisian - Visean age from 358.9 - 330.9 million years ago. Within this formation, groundwater is circulated to depths of 600 - 3000m below the Earth's surface along deep basinal folds and confined by overlying low permeability strata (Burgess and others, 1980).

The range of depths and variable dilution by cold, shallow groundwater results in spring temperatures ranging from 21-47°C. The locations of deep thermal springs in the UK are shown in Figure 1. There are other springs in the UK with slightly elevated temperatures between 11-20°C or with highly mineralised waters, that are not considered in this report. These springs may also have a deep thermal origin, but experience extensive dilution by cold, shallower groundwater.

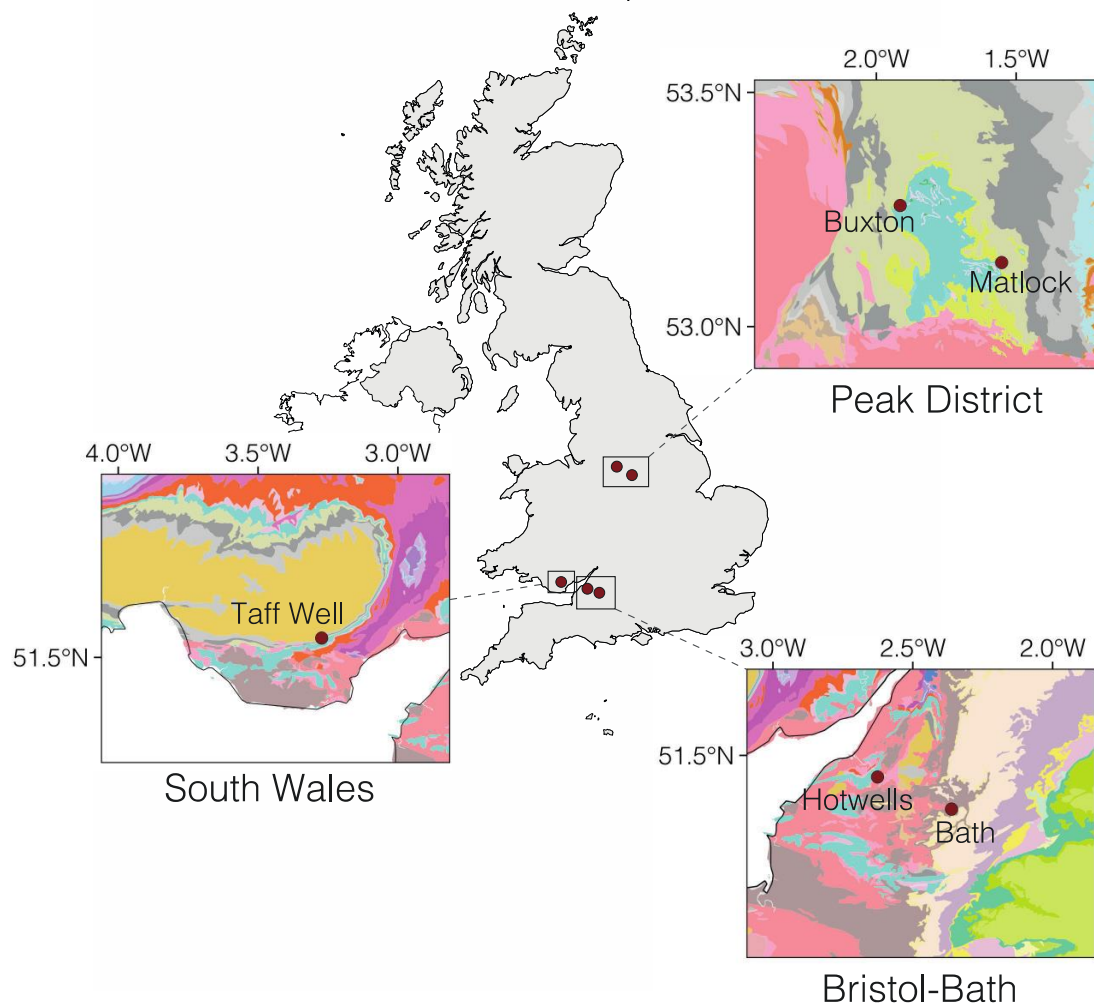


Figure 1. Map showing the locations of the five deep thermal springs in the UK that have water temperatures above 20°C. The close-up maps show the surface geology, with Carboniferous Limestone in blue. Geological maps contain British Geological Survey materials ©2020, 1:625,000 scale.

The most famous thermal springs in the UK are located in the city of Bath in north-east Somerset. This city is a UNESCO World Heritage Site due to the Roman Bath remains and the region attracted 6.25 million tourists in 2018, contributing £470 million to the

local economy (B&NES, 2018). The thermal springs currently emerge with temperatures of around 45 ° C and feed the luxury Thermae Bath Spa. The other thermal springs in the UK emerge at temperatures from 20 - 28 ° C and have variable histories and current socio-economic importance. The Buxton spring waters are currently bottled and sold as mineral drinking water, and a luxury thermal spa opened in 2020 after investments of roughly £70 million (Bisknell, 2019). In contrast, some thermal springs in the UK are not currently used. For example, the Hotwells thermal waters in Bristol discharge directly into the River Avon, after reductions in spring temperature and flow led to the decline of this region as a spa destination in the mid-19th century (Stamper, 2013).

Despite the historical and socio-economic importance of thermal springs in the UK, the potential vulnerability of this natural resource is currently not well-established. Potential problems that could affect thermal springs include reduced flow due to over-exploitation or natural hydrological change, increased dilution by shallow groundwater, changes in geochemical composition, the growth of harmful bacteria, contamination of local groundwater supplies and disturbances caused by extractive operations such as drilling wells or onshore oil and gas exploration (Darling, 2019). In Bath, several of these issues have affected the thermal springs in the past, including a severe reduction of flow due to deepening of a brewery well in 1836 (Kellaway, 1993) and the growth of harmful thermophilic amoebae due to increased oxygenation of the spring waters (Gallois, 2006). The presence of these amoebae led to the death of a young girl in 1978, and public use of the Bath thermal waters ceased for almost 30 years while new spa facilities were constructed.

Currently, there are no national scale legal protections for deep thermal springs. Local councils have regulations to protect a small radius around where the spring emerges, but there are no distal protections in place specifically relating to the thermal springs. As such, the spring recharge zone and sub-surface flow paths may be vulnerable to change, with potential socio-economic and environmental implications. Previous reports commissioned by the Environment Agency highlighted the need to define spring protection zones, similar to source protection zones of shallow groundwater systems (SC180009, Environment Agency 2020a & SC180015, Environment Agency 2020b).

These zones would include protection of land near to where the spring emerges, segments of deep flow paths that could be at risk from deep sub-surface use and the spring recharge zone (Figure 2). However, there are currently many challenges to defining deep thermal spring protection zones. In particular, the recharge areas, water residence times and sub-surface flow paths are difficult to constrain, leading to large uncertainties about potential risks. Additionally, the sources of deep thermal groundwater are often far from where the spring emerges and involve huge storage capacities, meaning that spring protection zones could cover impracticably large areas.

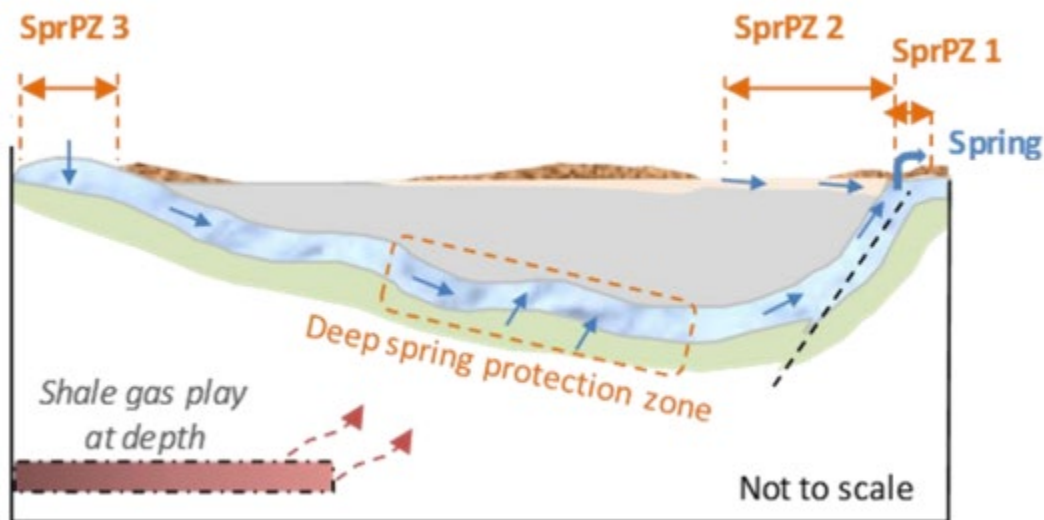


Figure 2. Schematic of spring protection zones (SprZ), as recommended in EA report SC180015 (Environment Agency 2020b).

Geochemical methods offer tools to understand, map and protect deep thermal springs. A variety of geochemical tracers are available, which can provide valuable information about the source, age, depth, pathways and mixing of deep thermal spring water. This geochemical information can help to define the recharge zone, sub-surface flow paths and critical controls on thermal spring emergence, allowing for better assessments of potential vulnerabilities and accurate delineation of spring protection zones. This report summarises the application of geochemical methods to understand deep thermal spring

waters. It presents previous geochemical research on deep thermal springs in the UK and highlights potential avenues for future research.

2 Geochemical methods to understand deep thermal springs

2.1 Introduction to geochemical proxies

Geochemical analysis can give valuable information about the sources, age and flow paths of groundwater. Potential geochemical tools include ratios of stable or radioactive isotopes, the presence of geothermometer compounds and the concentrations of noble gases, trace metals, or anthropogenic markers. Here, the focus is on applications to understand thermal springs. However, many of these techniques can be applied to understand shallow, brackish or deep groundwater.

2.2 Major ion and trace-metal concentrations

Interactions between groundwater and the surrounding bedrock cause dissolution of minerals, meaning that the geochemical signature of the host aquifer is incorporated into groundwater. As such, the concentrations and relative proportions of dissolved major ions such as bicarbonate (HCO_3), sulphate (SO_4), calcium (Ca) and sodium (Na), as well as trace-metal elements, act as a geochemical fingerprint of groundwater. These data can be used to infer important information about water-rock interactions, helping to define flow-pathways, dominant weathering processes and groundwater evolution. In particular, the major ion/trace metal concentrations can be used to identify the dominant host aquifer rock type, potentially exclude inputs from surrounding strata and disentangle mixing between different groundwater sources.

Thermal spring water often contains elevated concentrations of dissolved major ion and trace metal species due to enhanced water-rock interactions and long residence times. Where the thermal spring water is used commercially, several geochemical species are routinely measured to check for water quality. These data can provide long-term records of the geochemical stability of spring waters. Major ion data are often combined with

physio-chemical parameters such as pH and inputted into geochemical models such as PHREEQ-C to understand equilibrium conditions, redox state and chemical weathering processes. This approach can help to inform other geochemical interpretations, such as dating techniques or stable isotope ratios.

Both major ion and trace metal analyses are relatively basic techniques, which use only small volumes of water and do not require specialist interpretations. As such, major ions and trace metals are routinely measured, and data are widely available for groundwater systems across the UK, including compilations from EA baseline aquifer reports.

2.3 Stable isotopes

Stable isotopes of a specific element are non-radioactive atoms with the same number of protons, but variable numbers of neutrons. Within the environment, the relative proportions of different stable isotopes are present in fixed, known proportions referred to as the natural abundance ratio. For example, oxygen has three stable isotopes, ^{16}O , ^{17}O and ^{18}O with natural abundances of 99.76, 0.04 and 0.2% respectively. Due to the slight mass differences between different isotopes, physical and biogeochemical processes affecting a particular element can cause often subtle, but measurable shifts away from these natural abundance ratios. The relative shifts are known as isotopic fractionation and can provide important information about the processes controlling elemental cycling, or provide clues about the environmental history of a sample.

The ratio of stable isotopes is reported using delta (δ) notation. This is a ratio of the isotopic composition of a sample, relative to the ratio of a reference standard. Delta notation is defined in equation 2.1 below, where x and y represent stable isotopes of element E.

$$\delta^x E = \frac{(^x E / ^y E)_{\text{sample}}}{(^x E / ^y E)_{\text{standard}}} - 1 \quad (2.1)$$

As the resulting values are usually very small, delta values are multiplied by 1000 and expressed in parts per mille (‰). Standards are isotopic reference materials with well-defined isotope ratios, allowing for comparisons of results between different research groups. Examples of reference standards are Vienna Peedee Belemnite (VPDB) for carbon isotopes and Vienna Standard Mean Ocean Water (VSMOW) for aqueous oxygen and hydrogen isotopes. Several key isotope systems that can give valuable information about the origin, age and flow paths of thermal spring water are discussed in the following section.

2.3.1 Water isotopes

The isotopes of hydrogen (H) and oxygen (O) in water act as powerful tracers of the hydrological cycle. Fractionation of water initially occurs during evaporation from the ocean or surface waters. Isotopically-heavy water molecules (i.e. ^{18}O and ^2H) evaporate less readily than lighter isotopes, especially at low temperatures, causing depletion of ^{18}O and ^2H in water vapour. The heavier isotopes of water also condense more quickly, meaning that water vapour becomes gradually more depleted in ^2H and ^{18}O with increased time/transport and the isotopic signature of precipitation can depend on the temperature, altitude and relative distance inland. As a result of these fractionation processes, waters have unique isotopic compositions that can be used to infer information about their source and the processes that formed them. Within meteoric water, isotopes of H and O fractionate in proportion to one another along the global meteoric water line (GMWL). Definitions of δ -notations for H and O-isotopes are given in equation 2.2 below.

$$\delta^2H = \frac{(^2H/^1H)_{\text{sample}}}{(^2H/^1H)_{\text{VSMOW}}} - 1 \quad \delta^{18}O = \frac{(^{18}O/^{16}O)_{\text{sample}}}{(^{18}O/^{16}O)_{\text{VSMOW}}} - 1 \quad (2.2)$$

When applied to deep thermal groundwater, water isotope values can provide valuable information about the origin, recharge zone, broad age and mixing of deep thermal spring waters. The most common use of water isotopes is to clarify whether groundwater is of meteoric, marine or mixed origin. All deep thermal spring waters in the UK fall close to the global meteoric water line (GMWL of Craig, 1961), meaning they are ultimately of meteoric origin. Water isotopes can also be used to define physical and chemical parameters within groundwater systems, such as mixing ratios or the occurrence of critical water-rock exchange reactions. Schematics summarising key processes that can affect water isotopes within groundwater are shown in Figure 3 below.

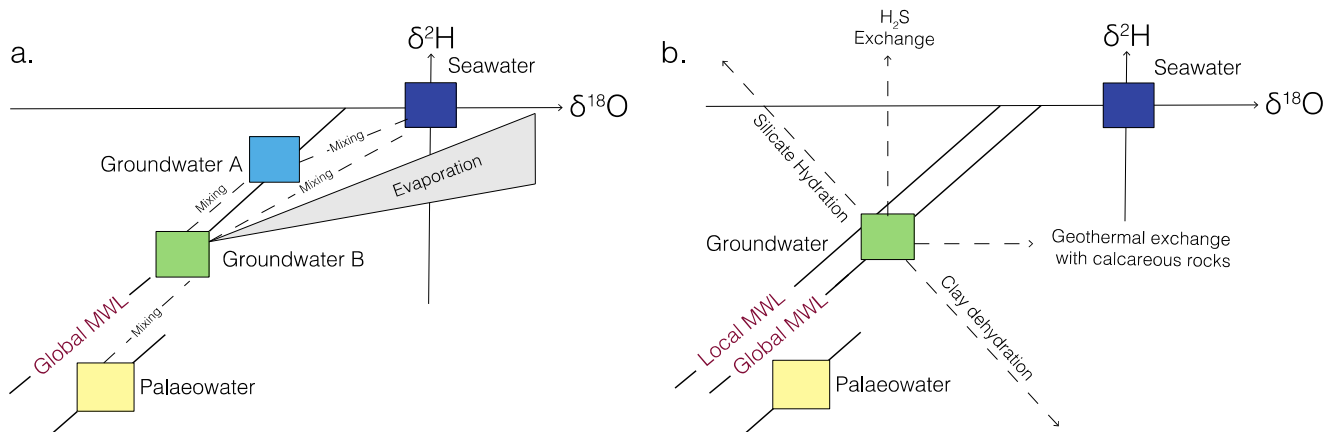


Figure 3. Schematic of processes affecting water-isotopes in groundwater; (a) shows the global MWL and mixing-lines between different groundwater components, seawater and palaeowater. In the UK and other humid temperate climates palaeowaters lie further down the global MWL; (b) shows processes within groundwater systems that can fractionate O/H isotope ratios. Figure adapted from Gehl and others (2000).

Furthermore, water isotopes can be used to determine whether meteoric groundwater was recharged during warmer or cooler climates, often correlating to the Pleistocene or Holocene epochs in the UK, giving a very broad estimate of water age. This is primarily

due to the strong temperature dependence of the isotopic composition of precipitation. During the glacial Pleistocene epoch, lower temperatures meant that rainfall was more isotopically light compared to equivalent Holocene age waters. For example, across Europe, the $\delta^{18}\text{O}$ values of groundwater recharged during these epochs differed by 1.5 to 2.0 ‰, as shown in Figure 4. Far more accurate groundwater dating methods exist, as discussed in the following sections. However, this is still a potentially important factor to consider when interpreting long residence groundwater $\delta^{18}\text{O}$ values.

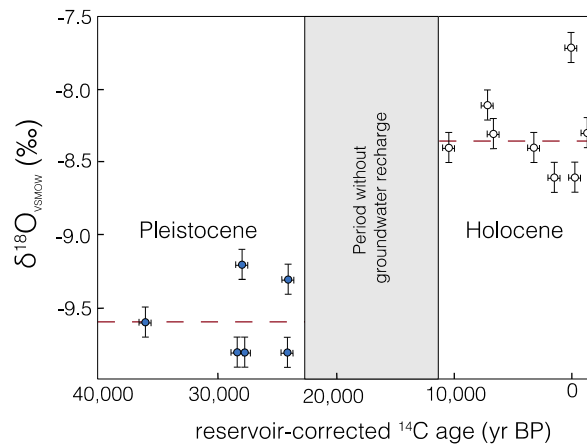


Figure 4. Comparison between Pleistocene and Holocene age groundwaters. The $\delta^{18}\text{O}$ values of groundwaters recharged during glacial epochs is significantly more negative than Holocene aged groundwaters. Figure adapted from Geyl and others (2000) and references therein.

2.3.2 Carbon isotopes

Carbon (C) has two stable isotopes; ^{12}C and ^{13}C with natural abundances of 98.9% and 1.1% respectively. $\delta^{13}\text{C}$ values are reported relative to the VPDB standard, as defined in equation 2.3.

$$\delta^{13}\text{C} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}} - 1 \quad (2.3)$$

The $\delta^{13}\text{C}$ values of groundwater can have a wide range, reflecting multiple sources and variable relative proportions of carbon components, each with a different C-isotope signature. Examples of sources of dissolved carbon in groundwater include soil CO_2 , dissolution of carbonate minerals and organic matter from soils, vegetation or rocks. As such, $\delta^{13}\text{C}$ values can be used to trace the key sources and cycling processes of carbon within groundwater systems. The $\delta^{13}\text{C}$ of deep thermal groundwater is primarily used to calibrate ^{14}C dating models to give radiocarbon ages, but can also be used as an index of the amount of water–rock interaction. These models require a robust understanding of how the sources, sink and feedback processes affect carbon. This is discussed in more detail in Section 2.7 below.

2.3.3 Strontium isotopes

Strontium (Sr) is an alkaline earth metal with four naturally occurring stable isotopes: ^{84}Sr (0.56%), ^{86}Sr (9.86%), ^{87}Sr (7.0%) and ^{88}Sr (82.58%). Despite being classed as a trace metal, Sr is present in measurable concentrations in most bedrock, rivers and groundwater. Sr isotopes are measured using thermal ionisation mass spectrometry (TIMS) and values are commonly reported as a ratio of $^{87}\text{Sr}/^{86}\text{Sr}$, rather than in δ -notation. Sr isotope analysis by TIMS is an established and cost-effective technique that has been applied to a variety of hydrogeological problems.

Sr can act as a useful tracer because Sr isotopes do not experience measurable fractionation during geochemical cycling. Therefore, groundwater Sr derived from chemical weathering processes have the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as the source minerals of

the bedrock. Differences in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of groundwater can either reflect mineralogical variability along different groundwater flow paths or variable weathering congruency approaching chemical equilibrium. As such, if the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of surrounding bedrock are known, then Sr isotope ratios can be used to infer information about the pathway of groundwater and the extent of water-rock interactions. This information can exclude groundwater flow through lithologies with distinctly different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, helping to define 3-dimensional flow pathways. When combined with additional data, such as dissolved major ion or trace metal concentrations, Sr isotope ratios can be used to deconvolve mixing between different groundwater components. The fact that seawater Sr isotopes vary over geological time may be helpful in attributing the involvement or otherwise of a particular sedimentary formation, as the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio will be preserved in rock matrix or cement.

2.3.4 Non-traditional stable isotopes

Analytical advances of multi-collector inductively-coupled mass spectrometry (MC-ICPMS) have allowed for the development of non-traditional stable isotope measurements. These data can provide insights to understand the cycling of a particular element, such as a trace metal. Applied to groundwater, these can help to deconvolve a specific process, that could be critical to understand the controls of a system. Future work should consider investigating non-traditional stable isotope systems to constrain unknowns in conceptual models or refine assumptions involved in other proxy methods. Examples may include using calcium isotopes to infer information about water-rock interactions for ^{14}C age models (Section 2.7) or developing silicon isotopes to aid in silica geothermometer calculations (Section 2.4.1).

Information about stable isotope techniques in groundwater systems were primarily compiled from Gehl and others (2000), Kendell (2004) and references therein.

2.4 Geothermometric proxies

Geothermometric proxies are used to infer the highest temperature that a body of groundwater has been exposed to, allowing for estimates of geothermal groundwater temperatures without having to drill deep wells. These temperature estimates can then be used to infer the maximum circulation depths of groundwater based on geothermal gradients, giving inference of deep flow pathways. Applications of geothermometer proxies are based on the solubility of different minerals under variable temperature and pressure conditions. These relationships are empirically derived and involve several key assumptions when applied to groundwater. First, the aquifer must be at chemical equilibrium, with stable rates of precipitation and dissolution between mineral and solute. Secondly, it is assumed that the chemical composition of the groundwater is not significantly modified as it rises to form a thermal spring and that the maximum exposure temperature is geochemically preserved (Fournier, 1977).

2.4.1 Silica geothermometers

Silica geothermometry is based on the principle that the dissolution of silicate minerals in geothermal groundwater varies primarily as a function of temperature. Two empirical relationships are commonly applied, depending on whether the dissolution of quartz or chalcedony polymorphs control silica concentrations (equations 2.4 & 2.5; (Fournier, 1977, Arnorsson, 1983)). Other equations exist to account for steam loss or pressure conditions in high-temperature geothermal systems, but these are not relevant to thermal springs in the UK. In geothermal systems with temperatures < 100°C, amorphous (non-crystalline) silica phases are likely to control solubility (Founier, 1977).

$$\text{Quartz : } t^{\circ}\text{C} = \frac{1309}{5.19 - \log(\text{SiO}_2)} - 273.15 \quad (2.4)$$

$$\text{Chalcedony : } t^{\circ}\text{C} = \frac{1112}{4.91 - \log(\text{SiO}_2)} - 273.15 \quad (2.5)$$

2.4.2 Cation geothermometers

The ratio of several other dissolved cations can be used to infer the maximum temperature a body of groundwater has been exposed to, based on thermal transformations of feldspar and clay minerals. These proxies include sodium-potassium (Na-K), sodium-lithium (Na-Li) and sodium-potassium-calcium (Na-K-Ca) ratios (Fournier and Truesdell, 1973, Fournier, 1979). However, all of these cation geothermometers are only applicable to silicate host rocks, with water temperatures exceeding 100°C (Karingithi, 2009). As all thermal springs in the UK are located in carbonate aquifers and probably have temperatures lower than 100°C, cation geothermometer methods cannot be used for these systems. However, these proxies may be useful to understand other deep geothermal groundwater resources.

Information about geothermometer techniques was compiled from Karingithi (2009) and Ferguson and others (2009).

2.5 Noble gases

Due to their chemical stability, noble gases can be ideal tracers of environmental processes. Applied to investigate deep groundwater, the radioactivity of certain noble gas isotopes can give valuable information about water residence times. Simple dissolved concentration measurements of helium (He), neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe) can inform on recharge temperatures and conditions.

2.5.1 ⁴Helium

⁴He is a stable isotope of helium, primarily produced from the decay of radioactive U-Th series elements within the Earth's crust. Within closed systems, such as confined aquifers, water-rock interactions cause ⁴He concentrations to increase within groundwater as a function of uranium concentrations and age. Measurable concentrations of ⁴He are typically present after roughly 1000 years and may continue to accumulate for millions of years. As such, the concentration of ⁴He in groundwater

can ideally be used as a dating tool and to locate areas of deep or old groundwater discharge. However, ^4He is a complex tracer with multiple sources, sinks and controls that must be accounted for when estimating ^4He model ages.

Interpretations of ^4He data depend on several key assumptions. Firstly, the recharge temperature which controls the potential for excess air and initial solubility of ^4He from the atmosphere must be well-constrained and corrected for to quantify radiogenic ^4He formed within an aquifer. Secondly, the in-situ production rates from local bedrock need to be calculated. These production rates can vary as a complex function of the rock type, uranium concentrations, fracturing, porosity, grain-size and degree of weathering. Systems are often simplified to assume homogeneous bedrock-type and porosity along a groundwater flow path, which may not represent real conditions. Finally, as aquifers do not represent perfect closed-system models, the relative sources and sinks of ^4He must all be accounted for. These sources and sinks may include degassing of ^4He to the atmosphere, fluxes across aquifer/aquitard boundaries with differing ^4He compositions and potential magmatic sources (Torgersen and Stute, 2013). Assuming the errors of all controls are estimated, ^4He can serve as a useful tool to understand groundwater with residence times of >1000 years. Comparisons of ^4He and ^{14}C methods are useful to corroborate age models and give more robust estimates of groundwater age.

^4He has also been postulated as a potential tracer for younger groundwater. Some aquifers with rocks >100 Ma may release ancient ^4He trapped within crystal lattice structures, controlled by rates of solid-state diffusion rather than radioactive decay. If these diffusion rates can be quantified within an aquifer, ^4He concentrations can be used to date groundwater with ages from tens to hundreds of years. As few other groundwater dating tools are accurate for waters with ages of 60 to 1000 years, this can provide valuable information to understand groundwater residence times or detect moderately aged components within thermal springs (Solomon and others, 1996)

Sampling and analysis of ^4He is logistically challenging, with the potential for gas loss or atmospheric contamination during sample collection. Investigations of ^4He is often

combined with a suite of other noble gas measurements, including ^3He , Ne, Ar, Kr and Xe. Constraining the concentrations of these other noble gases can help to define initial conditions, recharge temperatures/elevations and U-Th decay rates, giving more confidence in ^4He model ages (Torgersen and Stute, 2013).

2.5.2 ^{39}Ar

^{39}Ar is produced through the interaction of cosmic rays with nuclides of potassium (K) and argon in the atmosphere. ^{39}Ar then decays to ^{39}K with a half-life of 269 years. Within groundwater, measurements of the rate of ^{39}Ar radioactive decay fill the dating gap between young residence time indicators such as CFCs and the radiocarbon method. This can be useful to detect the presence of water components with age ranges of 50-1000 years. At present roughly 2000L of water needs to be degassed in the field and ^{39}Ar is measured by low level counting methods in a high-pressure ultra-low background environment, making analysis logistically challenging. There is also potential for additional underground production of ^{39}Ar that can obscure age signals, as well analytical interferences from ^{39}Cl .

2.5.3 ^{81}Kr

^{81}Kr is a radiogenic isotope of the noble gas krypton, primarily formed as the product of atmospheric reactions with other Kr-isotopes. This isotope is radioactive, decaying to ^{81}Br with a half-life of $\sim 250,000$ years. When isolated from the atmosphere, the radioactive decay of $^{81}\text{Krypton}$ can be used to infer the residence times of groundwater. Due to the long half-life, $^{81}\text{Krypton}$ can give age estimates for long residence time groundwater, with ages from 50,000 - 1,000,000 years. This range means that ^{81}Kr isotopes are not applicable to thermal spring systems in the UK, but this proxy may be useful for dating isolated, deep groundwater for geothermal use in the future. However, only a few laboratories worldwide can measure ^{81}Kr , and there are problematic interferences with ^{85}Kr , which decays with a much shorter half-life of 10.76 years (Section 2.6.2).

Information about ^4He and other noble gas dating techniques was compiled primarily from Torgersen and Stute (2013) and Gehl and others (2000).

2.6 Anthropogenic Tracers

The detection and relative concentration of various anthropogenic marker compounds can be used to infer the presence and proportions of shallow, modern groundwater within thermal springs. This information can help to disentangle proportions of deep-thermal and shallow-cold groundwater components, aiding interpretations of deep groundwater geochemistry, flow pathways and mixing processes (Darling and others, 2012, Chambers and others, 2019).

2.6.1 Chlorofluorocarbons & Sulphur hexafluoride

Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6) are trace gases, primarily released into the atmosphere by anthropogenic activities. CFCs are produced by aerosols and the refrigeration industry, with no known natural sources. The production of CFCs was regulated by the Montreal Protocol in 1987 after the gases were found to have a potent greenhouse effect and destroy the ozone layer. SF_6 is primarily used for electrical applications and is a potent greenhouse gas with a global warming potential 23,900 times higher than CO_2 . SF_6 was banned by the EU in 2014, but this legislation excludes the electrical industry, which is the primary source. Concentrations of SF_6 have been increasing continuously since the 1970s, whereas concentrations of most CFCs began increasing in the 1950s, but began to level off or decrease since the 1990s, as shown in Figure 5. Despite being banned for over 30 years. Research found increasing concentrations of CFC-11 being emitted from north eastern China, potentially complicating age estimates (Rigby and others, 2019).

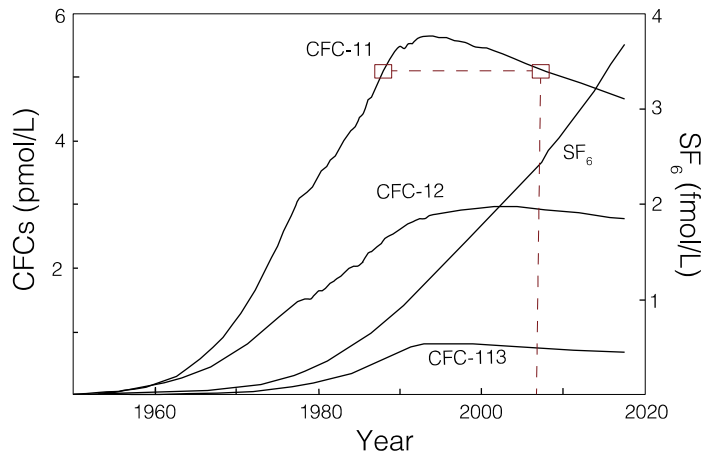


Figure 5. Variability of CFC and SF₆ concentrations of groundwaters in equilibrium with the atmosphere at 10°C. Figure sourced from Chambers and others (2019), using data from the US Geological Survey. The dashed red line shows how CFC-11 gives non-unique dates for certain concentrations, caused by decreasing atmospheric levels since ~1990.

CFCs and SF₆ dissolve in groundwater to give concentrations that are proportional to the atmospheric concentration at the time of recharge. As such, the concentrations of these anthropogenic trace gases can be used as a convenient and inexpensive method to date groundwater with ages of up to ~60 years. Multiple gases need to be measured, as decreasing concentrations of some CFCs mean that a particular concentration does not give a unique groundwater age. The recharge altitude and temperature also need to be known and corrected for in order to get accurate ages. Potential complications of using CFC and SF₆ concentrations include variability caused by the unsaturated zone, piston flow versus binary mixing, excess air, degassing, contamination and the possibility of microbial degradation of marker compounds (Darling and others, 2012).

Applied to thermal spring waters, the presence and concentration of CFCs and SF₆ can be used to quantify the mixing of shallow, modern groundwater with deep thermal groundwater. Disentangling these different components is vital to understand the true

signature of deep thermal groundwater, model connectivity with shallow groundwater and to correct other proxies such as ^{14}C dating for modern dilution.

As the atmospheric concentrations of some anthropogenic gases continue to decrease, new tracers are likely to emerge to date young groundwater components. These may include trifluoromethyl sulphurpentafluoride (SF_5CF_3), nitrogen trifluoride (NF_3), bromotrifluoromethane (Halon-1301, CF_3Br) and CFC-13, although their controls within groundwater systems are not fully understood (Weiss and others, 2008, Darling and others, 2012). The detection and potential implications of these emerging anthropogenic contaminants should be considered when monitoring thermal spring waters in the future.

2.6.2 Nuclear markers

Several radioactive markers are also used to date/detect modern groundwater in thermal spring systems, including isotopes of hydrogen (tritium; ^3H) and krypton (^{85}Kr). Tritium is a radioactive isotope of hydrogen, which decays to form ^3He with a half-life of 12.43 years. Tritium naturally occurs at very low levels in the atmosphere, formed by the interactions of cosmic rays with atmospheric gases. Between 1953-1963, concentrations of tritium peaked due to numerous nuclear weapons tests by the United States and the Soviet Union but decreased rapidly since atmospheric bomb tests were banned in 1963.

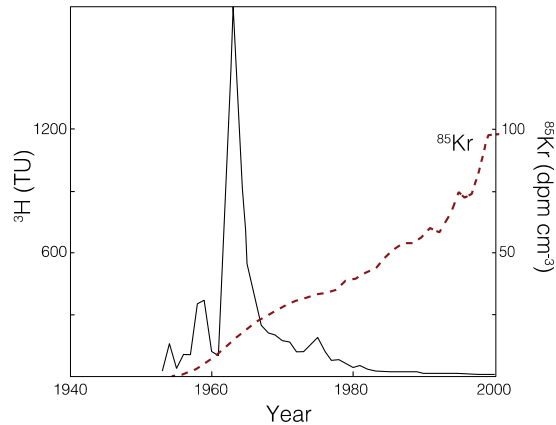


Figure 6. Variability in ^3H and ^{85}Kr concentrations in precipitation from Odense, Denmark. ^3H concentrations (black-solid) peaked during the early 1960's compared to ^{85}Kr (red dotted), which have continued to increase since the 1950s. Figure adapted from Alvarado and others (2005), using data from the global network of isotopes in precipitation database (GNIP).

The concentrations of tritium in groundwater have been used to infer information about the timescales for mixing and flow of groundwater, with recharge ages of less than ~ 100 years. However, interpretations of ^3H are complex as concentrations in precipitation (and therefore groundwater) vary as a function of multiple parameters including the distance from the ocean, latitude and season. Furthermore, the decreasing concentrations of ^3H due to radioactive decay and decreasing atmospheric levels mean that non-unique dates are inferred. The most straightforward and most robust application of tritium to deep thermal springs is to ascertain whether detectable concentrations are present. If so, this indicates that some fraction of the thermal spring water must have been recharged after nuclear testing in 1953, indicating mixing with shallow, young groundwater. While the many complicated controls, make it difficult to derive the exact age, measurement of the decay product ^3He as well would enable the 'mass balance' of ^3H decay to be calculated.

$^{85}\text{Krypton}$ is a radioactive noble gas, produced by the fission of uranium and plutonium and has a half-life of 10.76 years. Sources of ^{85}Kr include nuclear bomb tests and nuclear power stations. As opposed to ^3H , atmospheric concentrations of ^{85}Kr are

steadily increasing (Figure 6) and do not vary on seasonal timescales. However, concentrations do show considerable spatial variability, linked to point sources such as nuclear power plants, which needs to be accounted for. Similar to CFCs and SF₆, the concentrations of ⁸⁵Kr can act as a useful age marker and environmental tracer for groundwaters with ages of up to ~60 years. As a noble gas, ⁸⁵Kr behaves conservatively, with no chemical interactions or microbial degradation that can modify the concentrations of other tracer compounds. However, ⁸⁵Kr is not commonly used as a groundwater tracer. At present, only a few laboratories worldwide can measure ⁸⁵Kr, and in excess of 100L of water are required due to trace-level concentrations.

Information about nuclear marker techniques in groundwater systems were primarily compiled from Gehl and others (2000), Kendell (2004) and references therein.

2.7 Radiocarbon dating

Radiocarbon dating is the most widely applied method used to date deep groundwater resources with ages from 1000 - 30,000 years. Radioactive carbon (¹⁴C) is continuously produced by reactions of cosmic ray neutrons with atmospheric nitrogen and decays with a half-life of 5730 years. This ¹⁴C then oxidises to form ¹⁴CO₂, mixes with the atmosphere, is taken up by plants during photosynthesis and becomes incorporated in the Earth's biogeochemical cycles. Microbially-produced soil CO₂ dissolves in groundwater to form dissolved inorganic carbon (DIC). Using the radioactive decay rate of ¹⁴C this can then be used as a dating tool. However, due to the complexity of carbon cycling with groundwater systems, the application of radiocarbon dating methods is limited by many uncertainties. These uncertainties relate to three key topics:

1. Determination of the initial ¹⁴C content of groundwater at the point of isolation from the unsaturated- zone. This value can be complicated by reactions between dissolved CO₂ and minerals in soils and sediments, as well as assumptions that solar activities were similar to modern activities when groundwater was recharged.

2. Assessment of how geochemical reactions within the aquifer could affect the ^{14}C content of groundwater. These reactions can pertain to the presence of dissolved organic carbon (DOC) in recharge waters, oxidation of organic carbon from aquifer sediments or methanogenesis reactions which can add to the DIC pool. Furthermore, cation exchange reactions and the weathering of feldspars or carbonates can also influence both the ^{13}C and ^{14}C signatures, complicating interpretations.
3. Evaluation of the extent to which physical processes alter the ^{14}C content of groundwater. These processes could include variable mixing of old and young waters, diffusive exchange with confining bedrock or hydrodynamic dispersion along flow paths.

All of these processes can obscure interpretations of ^{14}C data and lead to large uncertainties in groundwater ages. Various models attempt to quantify these processes, usually requiring $\delta^{13}\text{C}$ values to constrain dominant carbon cycling feedbacks using additional proxies to understand the mixing of different groundwater components or modern dilution, and integration into geochemical reaction path models. When applied to deep thermal groundwater systems, ^{14}C model ages often have uncertainties of ~ 5000 years, representing a significant unknown and limiting conceptual models about storage capacities and resource sustainability. For more detailed information on groundwater radiocarbon methods, we refer the reader to Plummer and Glynn (2013).

Radiocarbon dating methods can also be applied to the DOC fraction of some groundwater systems, although this is also problematic. Roughly 100-200 L of groundwater has been required for analysis, and it is necessary to separate low and high molecular weight DOC species. Furthermore, the initial ^{14}C value of DOC should be adjusted for additional sources such as from the dissolution of particulate organic carbon and sedimentary organic matter, which have similar uncertainties as ^{14}C DIC. However, many researchers use modern activity levels, in the absence of compelling evidence to the contrary, Comparisons of ^{14}C ages inferred from DOC can help to refine and check the validity of DIC models. Future research will likely involve the

development of compound-specific ^{14}C analyses, but this has not yet been applied to date groundwater systems.

Information about radiocarbon dating techniques was compiled primarily from Plummer and Glynn (2013) and Gehl and others (2000).

2.8 Summary of information from geochemical tracers

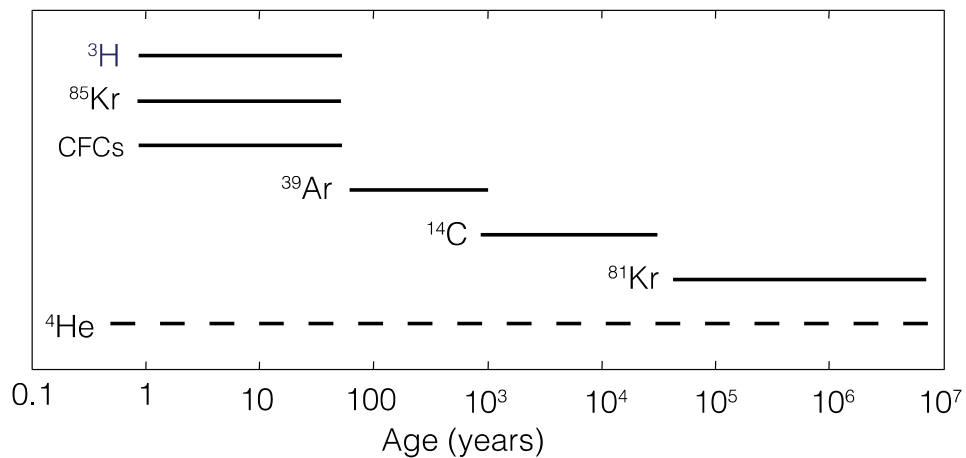


Figure 7. Comparison of the temporal range of residence-time indicator compounds. Figure adapted from Darling and others (2019).

Table 1. Summary of the primary information that can be inferred from a geochemical proxy

Geochemical proxy	Examples/notation	Summary of use
Major ions	Na, Ca, SO ₄ etc.	Cation geothermometry, mineral weathering/equilibrium and flow pathways
Silica	SiO ₂	Silica geothermometry to estimate peak equilibrium temperatures and max flow depths
Nitrogen	NO ₃	Indication of near surface contamination/dilution
Trace metals	Sr, Li, Ba etc	Possible indicators of source aquifer, water-rock interactions and flow pathways
Stable water isotopes	δ ¹⁸ O and δ ² H	Origin of groundwater (e.g. meteoric, marine, glacial, Holocene/Pleistocene) and mixing ratios
Carbon stable isotopes	δ ¹³ C	Inference of controls on carbon cycling within aquifer. Necessary for radiocarbon dating correction
Strontium isotopes	⁸⁷ Sr/ ⁸⁶ Sr	Inference of flow pathways, water-rock interactions and mixing of different water compounds
Noble gases	⁴ He, ³⁹ Ar, ⁸¹ Kr	Estimates of groundwater age where ¹⁴ C or anthropogenic marker methods are not applicable
Noble gases	Ne, Ar, Kr, Xe	Inform recharge temperatures and conditions
Anthropogenic markers	CFCs, SF ₆	Indicates presence/ relative dilution by/ age of modern groundwater
Tritium	³ H	Indicates presence of a post-1953 water component
Radiocarbon dating	¹⁴ C	Indication of groundwater age/residence time. Range from 1000-50,000 years.

Table 2. Summary and comparison of key geochemical methods used to understand deep thermal spring waters. Ticked boxes show the potential applications of a geochemical proxy. Data primarily compiled from Geyh and others (2000) and references therein.

Geochemical proxy	Analytical method	Applications						Age range (years)
		Source	Mixing	Pathway	Temp.	Dating	Recharge temperature	
Major ions and trace metals	IC/ICP-OES	✓	✓	✓				n/a
Water stable isotopes	IRMS	✓	✓			*		*
Carbon stable isotopes	IRMS					**		n/a
Strontium isotopes	TIMS	✓	✓	✓				n/a
Silica geothermometer Cation	IC/ICP-OES				✓			n/a
geothermometer	IC/ICP-OES				✓			n/a
⁴ Helium	QMS					✓		variable
³⁹ Argon	LLC/AMS/ATTA					✓		50-1000
⁸¹ Krypton	LLC/AMS/ATTA					✓		50,000-1,000,000
Neon, Argon, Krypton, Xenon	QMS						✓	n/a
CFCs and SF ₆	GC-ECD		✓			✓		< 60
Radiocarbon dating	AMS					✓	.	1000- 50,000

* = Oxygen stable isotopes can be used to distinguish between Holocene and Pleistocene Epoch groundwaters

** = Carbon stable isotope data is essential to calibrate ¹⁴C age data

IRMS = Isotope ratio mass spectrometry; TIMS = Thermal ionisation mass spectrometry; IC = Ion chromatography; ICP-OES = Inductively coupled plasma optical emission spectroscopy; QMS = Quadrupole mass spectrometry; LLC = Low level counting; AMS = Acceleration mass spectrometry; ATTA = Atom trap trace analysis; GC-ECD = Gas chromatography using electron capture detector

3 Geochemical evidence from deep thermal springs in the UK

3.1 The Bath Thermal Springs

Officially, the Bath thermal springs were discovered by the Romans who founded the city of Aqua Sulis in 75AD and built a religious temple around the thermal springs. This developed into a bathing and socialising complex, with the thermal water channelled through pipes to feed a series of pools and heated rooms. People made pilgrimages from far and wide to bathe in the waters and worship at the temple. When the Romans withdrew in the 5th century, the baths fell into disrepair and were partially destroyed by flooding. However, use of the thermal waters continued, and Bath developed as an important city. Particularly during the 17th and 18th century, the thermal waters were believed to be the cure for a wide variety of diseases and Bath grew as a popular Spa destination. During the 19th century, the spa waters were even bottled as medicine for rheumatism, gout, lumbago and neuritis (Davis and Bonsall, 2006).

Bath is now a World Heritage Site because of its historical significance, ancient Roman bath remains, Georgian and Victorian architecture and thermal springs. The Roman Baths are one of the most visited tourist attractions in the UK, receiving 1.3 million tourists in 2018 (ALVA, 2019). In 2006, the luxury Thermae Bath Spa was opened following £45 million of investment, allowing the public to bathe in the waters. Both the Roman Baths and Thermae Spa indirectly contribute millions to the local economy.

3.1.1 Key Geochemical Data

- Bath has 3 thermal springs, which have temperatures from 41 to 48°C (Burgess and others, 1980; Green 1992).
- $\delta^{2}\text{H}$ and $\delta^{18}\text{O}$ values indicate the thermal springs waters are of meteoric origin and were recharged during the early Holocene (Burgess and others, 1980).
- Major ion geochemistry shows transport through carboniferous limestone, with elevated concentrations of Ca, HCO_3 and SO_4 .
- $\delta^{13}\text{C}$ values are close to zero, indicating extensive interaction with carbonate bedrock, on timescales of thousands rather than hundreds of years.
- The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the spring waters are significantly higher than the carboniferous limestone, indicating an additional source of Sr (Burgess and others, 1980; Edmunds and others, 2014).
- Noble gas concentrations give a recharge temperature of $10.3 \pm 0.5^\circ\text{C}$, reinforcing interpretations of Holocene recharge conditions from water-isotope signatures (Edmunds and others, 2014).
- The Bath spring waters have been ^{14}C dated. Burgess and others (1980) calculated a mean age of 19,200 years and depending on modern mixing ratios, could contain a component with ages $>50,000$ years. However, there are many assumptions included in this calculation, and the authors concluded that the majority of geochemical evidence, such as recharge temperatures and $\delta^{18}\text{O}$, indicate bulk recharge during the last 10,000 years.
- Analyses of the ^{14}C of the springs were repeated by Edmunds and others (2014) who concluded that values are unlikely to be meaningful due to the extensive interactions with the carbonate limestone that overprint ^{14}C signatures.
- ^{39}Ar values of a potential residual atmospheric component are low and within the range estimated for in-situ production. These data were interpreted to mean that the groundwater age is over 1000 years (and potentially much older, though this can't be inferred from ^{39}Ar methods) (Edmunds and others, 2014).
- High ^4He concentrations indicate either long-residence times or an enriched radiogenic source such as very old waters from the underlying Devonian

Sandstones. An age model for ^4He gave bulk ages of 5000 years, but included large assumptions (Edmunds and others, 2014).

- The chalcedony geothermometer gives a maximum temperature of 64°C while the quartz geothermometer gives a maximum temperature of 96°C (Edmunds and others, 2014), though it is unlikely that quartz is the controlling phase for SiO_2 concentration. These temperature estimates limit the circulation of water to a maximum depth of ~ 3 km.
- Low (but detectable) concentrations of CFCs in groundwaters sampled in the year 2000 indicate mixing of thermal waters with a maximum of 5% of modern groundwater (Edmunds and others, 2014).
- ^{85}Kr and ^3H concentrations indicate that 2-8% of the thermal spring waters have ages of less than 30 years (Edmunds and others, 2014).
- Age estimates ranging from 1000 - 12,000 years create large uncertainties in thermal spring storage capacities and flow pathways, limiting our ability to accurately model these systems (Edmunds and others, 2014).

3.1.2 Current Protections

The Bath thermal springs are protected by the Public Health Bath Act of 1925 and Section 33 of the County of Avon Act of 1982. These acts gave Bath and North East Somerset Council powers to protect the thermal springs, defining three concentric risk zones where permission is needed for wells, boreholes and other excavation work. These zones require permission for work greater than 5m below ground level in the centre of the city, below 15m along the Avon river valley and 50m in the wider area surrounding Bath. These restricted zones are highlighted in Figure 8 below. No protections are in place for the recharge zone or deep flow pathways. A report from the British Geological Survey summarises the potential problems and vulnerability of thermal spring resources with respect to hydrocarbon or geothermal exploration in the

future (Smith and Darling, 2012). This report will act as a useful foundation to inform the Environment Agency on future legislation.

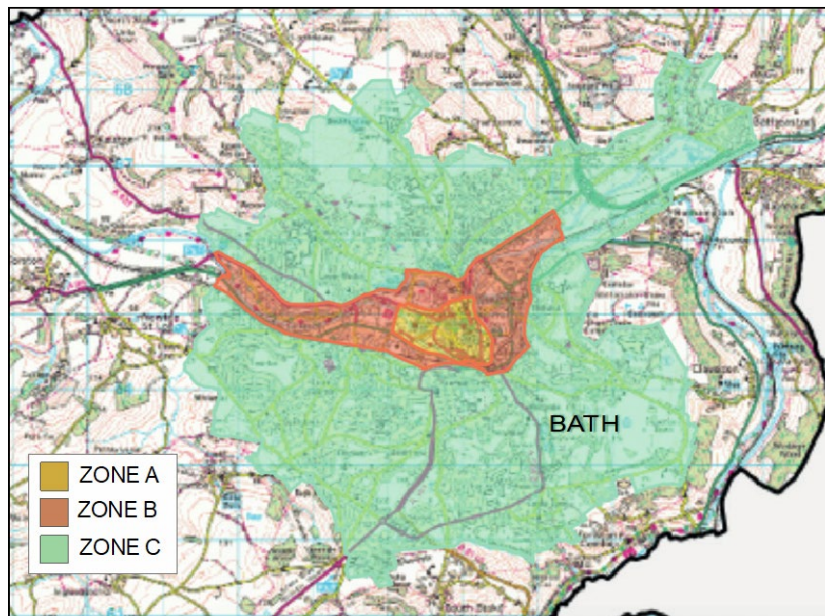


Figure 8. Map showing the three concentric zones where permissions are required for excavation work below a certain depth and defined by the County of Avon Act of 1982. Map adapted from Bath and North East Somerset Council (2021).

3.2 The Bristol Hotwells Spring

The first documents referring to the thermal springs at Hotwells date from the 15th century and the springs began to gain popularity during the 17th and 18th centuries, when the Hotwells House spa, entertainment complexes and genteel housing were constructed (Figure 9a). The milky white thermal waters were believed to have curative properties, helping to alleviate hot livers, feeble brains, venereal disease, tuberculosis and cancer. However, the distance from Bristol city centre and inaccessibility down the steep Avon gorge limited the spa's success. In the 1780s, an ambitious engineering project drilled 250ft through the carboniferous limestone to tap and pump the thermal waters to a hotel in Clifton. Following this work, both springs began to cool significantly and the popularity

of thermal spas declined. The Hotwells House complex was demolished in 1822 to allow for the widening of the River Avon. During the 19th century, there were several unsuccessful attempts to revive the spring. At present, the spring has no commercial use and is only visible at low tide as small discharges on the muddy banks of the River Avon (Figure 9b). Many residents of Bristol are unaware of its existence.

Information and images about the history of the Hotwells springs was compiled from Reid (1992) and Stamper (2013).

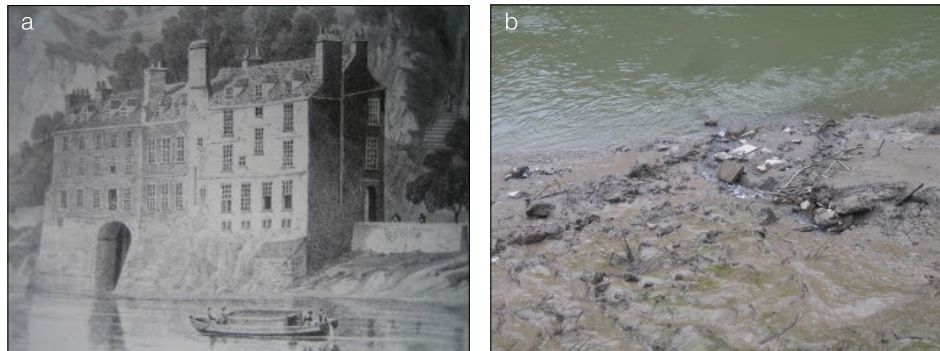


Figure 9. Past and present images of the Hotwells spring (a) shows the Georgian Era Hotwells House spa complex; (b) shows the present outlet of the thermal springs through the muddy banks of the River Avon.

3.2.1 Key Geochemical Data

- The thermal springs at Hotwells discharge into the River Avon with temperatures of 24°C (Burgess and others, 1980; Green, 1992).
- Major ion ratios, trace-metal concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Hotwells thermal spring are very similar to the Bath thermal waters, indicating they are likely to share the same thermal source (Burgess and others, 1980).
- Silica geothermometers show maximum temperatures of 49°C for a chalcedony control and maximum temperatures of 72°C for a quartz control, with a best overall estimate of 60°C (Burgess and others, 1980), although, as discussed previously, quartz is unlikely to be the main control on Si.

- Tritium concentrations of 34.0 TU in 1977, and high nitrate levels, indicate considerable dilution of thermal waters with a modern, near-surface groundwater component. Ratios are roughly 1:2.3 thermal to non-thermal (Burgess and others, 1980).
- No geochemical data has been analysed since 1980, and so it is uncertain how the geochemistry of the Hotwells thermal springs may have changed over the last 40 years.
- Applications of more advanced geochemical techniques would help to provide more evidence to confirm if the Bath and Hotwells thermal springs have the same origin.

3.2.2 Current Protections

There are no local protections in place to protect the Hotwells thermal springs.

3.3 The Buxton Spring

Similar to Bath, the thermal springs in Buxton were first developed during Roman times. The town was known as Aquae Arnemetiae, meaning 'the baths of the goddess of the grove'. In the late 18th and 19th century the town became a fashionable spa destination, with the Crescent Hotel attracting affluent members of society to bathe in the healing waters. The thermal baths closed to the public in 1981, due to structural problems and public health notices by the local authorities.

In 1992, the Crescent Hotel was purchased by the Buxton council, with the plan to restore and transform the building into a 5* spa hotel. The Buxton Thermal Spa and hotel were due to open in 2007, with the aim to boost the local economy by over £4.5 million a year. However, the project suffered multiple setbacks and unexpected costs, finally opening in October 2020 at a cost of around £70 million, funded from a variety of public and private sources.

In addition to the thermal baths, the thermal spring waters are used for drinking water. The St. Anne fountain was built in the 1940s, allowing public consumption of the thermal waters and is still used in the town. Since 1992, Nestle has had the rights to bottle and sell the thermal spring water as Buxton Mineral water. In 2012, over £35

million was invested in the new state-of-the-art bottling factory. Buxton mineral water is currently the best-selling British water brand in the UK.

Information about the history of the Buxton springs was compiled from Gunn and others (2006) and VisitBuxton (2021).

3.3.1 Key Geochemical Data

- The Buxton Spring has a constant temperature of $27.5 \pm 0.5^\circ\text{C}$ (Brassington, 2007).
- The Buxton thermal waters contain relatively dilute concentrations of dissolved major ions with low Ca and SO_4 and high Mg/Ca ratios compared to other spring waters (Gunn and others, 2006).
- $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values indicate the thermal springs waters are of meteoric origin and were recharged during the Holocene (Edmunds, 1971).
- The Buxton thermal springs are enriched in ^{87}Sr compared to other waters in the region. This implies transport in a locally-confined deep sandstone aquifer to the west of Buxton (Gunn and others, 2006).
- The Buxton thermal water has been dated using ^{14}C , giving an age of 3900 - 6400 years. The best estimate for the age of the thermal spring water is probably ~5000 years (Barker and others, 2000).
- Tritium concentrations of 1.8 TU in 1969 (Edmunds, 1971) and 0.8 TU in 1998 (Barker and others, 2000) imply almost negligible mixing with modern groundwater. This finding is supported by below detection levels of nitrate (Gunn and others, 2006).
- Very low CFC concentrations indicate <2% mixing with modern waters (Brassington, 2007).
- Thermal spring discharge rates correlate to changes in the level of the water table, with a lag of several days (Barker and others, 2000; Brassington, 2007). This correlation is believed to be due to a loading effect, transferring a pressure wave through to deeper aquifer systems (Brassington, 2007). As such, the Buxton spring may be vulnerable to declining discharge in the future if the water table falls due to anthropogenic activity or droughts.

3.3.2 Current Protections

There are several separate spring sources in Buxton with separate abstraction licences used for bottling and the spa hotel. These licences control the abstraction rights and there is no competition between them. High Peak Borough Council hold the rights to the abstractions, which Nestle then use for water bottling and the hotel use for the spa. It is our understanding that there is an obligation to maintain flow to the lion's mouth fountain, St. Ann's Well, for public use. The Environment Agency carry out routine water quality monitoring on the water at the fountain.

The Buxton sources are protected by a Source Protection Zone 1 and supplementary planning policy produced by High Peak Borough Council. There are no specific local laws protecting the springs, although the High Peak Borough Council planning policy does afford some protection by imposing controls on development locally.

3.4 The Matlock Spring

The Matlock thermal spring was discovered in 1698, and a small bathing pool called 'Woolleys Well' was built from wood and lead. A second spring was found, and several pools were built in the 1850s offering hydropathic treatments for a wide variety of illnesses. The Matlock lido opened in 1934, attached to the New Bath Hotel. This hotel closed in 2013 but was reopened in June 2019 as part of a £3 million project to rejuvenate the area. The thermal waters are also used by the Matlock aquarium.



Figure 10. Past and present images of the Matlock thermal lido. (a) shows Matlock lido in the 1930s; (b) shows the modern day lido, which was reopened in 2019.

Information and images about the history of the Matlock springs was compiled from Andrews (2019) and references therein.

2.4.1 Key Geochemical Data

- The major ion geochemistry of Matlock spring waters is significantly different from Buxton, with far higher concentrations of dissolved Ca and SO₄ (Gunn and others, 2006).
- $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values indicate the thermal springs waters are of meteoric origin and were recharged during the Holocene (Edmunds, 1971).
- $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Matlock thermal spring waters are significantly different from the Buxton waters and show no Sr-isotope evidence of interactions with Namurian Sandstones (Gunn and others, 2006).
- The $\delta^{13}\text{C}$ values are isotopically heavy compared to non-thermal spring waters in this region showing extensive dissolution/re-precipitation of carbonate minerals (Gunn and others, 2006).
- Tritium concentrations were 4.4 TU in 1969, showing very minimal inputs of modern groundwaters (Edmunds, 1971). As far as we are aware, no other anthropogenic marker analyses have been conducted since 1969.
- The Matlock spring waters have not yet been dated by ^{14}C methods and do not have a well-constrained age.

2.4.2 Current Protections

There are currently no local protections to protect the Matlock thermal springs.

3.5 Taffs Well Spring

The Taff's Well thermal spring is the only deep-thermal spring in Wales, emerging roughly 10 km north of Cardiff city centre in the town of Taffs Well. The first document referring to the Taffs Well spring dates from the 1760s, when a German chemist prescribed drinking several pints of the spring water as a cure for rheumatism (Farr, 2014). Popularity peaked during the 1800s, with reports of long queues of people waiting to bathe in the thermal waters. From 1930, the thermal waters fed a popular local

outdoor swimming pool. However, this pool closed in the 1950s after extensive flooding (Farr, 2014). Over the last 30 years, various unsuccessful attempts have been made to reopen the Taffs Well thermal spring to the public and in 2014, following works to stabilise the roof of the well, reinstate drainage and clean out the building, the spring was opened once again for visitors (Farr and Huish, 2015). The thermal waters are now the focus of a low carbon heat recovery scheme led by Rhondda Cynnon Taf Council. Water from the thermal spring will be passed through heat exchangers with the recovered heat used to supply space heating to the nearby Ffynnon Taf primary school.

Information and images about the Taff's Well spring was compiled from Farr and Bottrell (2013) and Farr (2014).



Figure 11. Past and present images of Taffs Well thermal spring; left, in 1861 (Hall and Hall, 1977) and right, in 2013, photograph by Gareth Farr.

3.5.1 Key Geochemical Data

- Mean water temperature = $21.6 \pm 0.5^{\circ}\text{C}$ (August 2008 - September 2009) (Farr and Bottrell, 2013).
- Depending on local geothermal gradients, the minimum flow depths estimated for the thermal waters range from 400 - 700 m (Farr and Bottrell, 2013; Thomas and others, 1983).
- $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values indicate the thermal springs waters are of meteoric origin and recharged during the Holocene (Farr and Bottrell, 2013).

- Dissolved concentrations of noble gases indicate a recharge temperature of $8.1 \pm 1.8^\circ\text{C}$ and recharge elevations several hundred meters above sea-level (Farr and Bottrell, 2013).
- $^{14}\text{C}_{\text{DIC}}$ analysis, using a simple $\delta^{13}\text{C}$ correction, gives a bulk age of 11,250 years but likely has a large error due to uncertainties regarding the input of 'dead' mineral carbon from the Carboniferous Limestone under elevated temperatures. As such, a conservative bulk age of 5000 years was assigned (Farr and Bottrell, 2013).
- Dissolved oxygen concentrations range from 4% to 15.5% (Farr and Bottrell, 2013).
- High dissolved $^{87}\text{Sr}/^{86}\text{Sr}$ ratios relative to values of carboniferous limestone indicate significant water-rock interactions with sandstone strata of the Marros group (Farr and Bottrell, 2013).
- High dissolved ^4He concentrations suggest inputs of old groundwater from the Devonian Red Sandstone that underlie the Carboniferous limestone aquifer (Burgess and others, 1980).
- Concentrations of the nutrients nitrate, nitrite and phosphate are below detection level, indicating that little or no surface runoff enters the spring (Farr and Bottrell, 2013).
- Tritium activities are below detection indicating limited mixing with modern surface waters (Farr and Bottrell, 2013).
- CFC and SF_6 concentrations are low and indicate mixing with 3-6% modern groundwaters (Farr and Bottrell, 2013).

3.5.2 Current Protections

There are no local protections in place for the Taff's Well spring. The spring is owned and managed by Rhondda Cynnon Taf Council and falls in the regulatory area of Natural Resources Wales.

Table 3. Summary of existing geochemical data from the thermal springs in the UK

Location	Ref.	Major ions	TM	$\delta^{18}\text{O}/\delta^2\text{H}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$	^4He	^{39}Ar	CFC	SF_6	^3H	^{85}Kr	^{14}C	SiO_2
Bath	a,b,c	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓
Hotwells	a,b	✓	✓	✓	✓	✓	✓				✓			✓
Buxton	d,e,f	✓	✓	✓	✓	✓	✓		✓		✓		✓	
Matlock	e,f	✓	✓	✓	✓	✓	✓				✓			
Taff's Well	a,g	✓	✓	✓	✓	✓	✓		✓	✓	✓		✓	

References: (a) Burgess and others (1980) (b) Barker and others (2000) (c) Edmunds and others (2014) (d) Evans and others (1979) (e) Brassington (2007) (f) Gunn and others (2006) (g) Farr and Bottrell (2013).

Table 4. Summary of the locations and key characteristics of deep thermal springs in the UK.

Location	Latitude	Longitude	Spring names	Temp °C	pH	E.C. $\mu\text{S cm}^{-1}$	Discharge litres/day	Water age kya	Current uses
Bath	51.381	-2.362	The King's Bath	45 ^a	6.7 [*]	2560 [*]			Thermal waters feed Bath Spa and public drinking fountains
			Cross Bath	41 ^a	6.7 [*]	2830 [*]	1.25x10 ^{6#}	5-10 ⁺	
			The Hetling Spring	47 ^a	-				
Bristol	51.452	-2.627	Hotwells	24 ^a	-	-	0.41x10 ^{6#}	5-10 ⁺	No commercial use
Buxton	53.259	-1.915	St Anne's Well	27.2 ^b	7.06 ^b	509 ^b	1.0x10 ^{6b}	~5 ⁺	Thermal waters bottled/sold and feeding Buxton Spa
Matlock	53.137	-1.552	East Bank Rising	21.0 ^b	6.48 ^b	819 ^b	0.041x10 ^{6b}	-	Thermal waters feed lido
			New Bath Hotel	20.5 ^b	7.56 ^b	850 ^b			
Taff's Well	51.543	-3.273	Taff's Well	21.6 ^c	7.6 ^c	539 ^c	0.008x10 ^{6c}	~5 ^c	No commercial use

References: (a) Green (1992) (b) Gunn and others (2006) (c) Farr and Bottrell (2013) (*) Edmunds and others (2014) (#) Kellaway (1993) (+) Darling (2019) and references therein

4 Discussion

4.1 Summary

This report highlights the wealth of geochemical tools that can be applied to understand the origin, age and flow pathways of deep thermal springs. Methods range from major ion and trace metal concentrations to understand water-rock interactions, water isotopes to understand groundwater sources, and radiocarbon and noble gas isotope activities to estimate water residence times. The report provides outlines of the geochemical proxies that can be applied to understand thermal springs and other groundwater systems, the key information they provide, and the assumptions involved.

The geochemistry of all five thermal spring groups in the UK has been analysed, providing valuable insight into the origin, flow pathways and residence time of these systems. These insights would not be possible without geochemical proxies and have greatly enhanced our understanding of the controls on thermal spring systems. Bath thermal springs are the most well studied, and a comprehensive suite of geochemical tools have been applied. Despite this wealth of data, the age estimates of groundwater at Bath springs currently ranges from 1,000 - 12,000 years and there is considerable ongoing debate about the size/location of the recharge zone. Large uncertainties also exist for other thermal spring systems in the UK. For example, the Hotwells springs lack critical data and the geochemistry of these waters have not been revisited since the 1970s, resulting in uncertainty in any changes over the last 40 years.

Overall, geochemical analysis of the thermal springs in the UK has provided a wealth of information but there are still critical unknowns that would make defining spring protection zones problematic. In particular, the recharge zones of thermal springs are not well constrained, there are no geological or hydrogeological data from deep boreholes available to inform geological models and calibrate flow paths, and age estimates are either non-existent or have large ranges. Furthermore, the potential risks and vulnerabilities of thermal spring systems are not well understood. More research is needed to address these knowledge gaps and uncertainties before deep thermal spring protection zones can be implemented effectively.

4.2 Suggestions for future-work

Following from this report, future research to better understand and protect thermal springs in the UK includes:

- Create formal definitions for deep thermal springs to guide future research.
- Improve understanding of the thermal spring recharge zones, sub-surface flow pathways and residence times using 3-dimensional hydrogeological models. These models should be based on improved geological (borehole) and geophysical data and use geochemical data for calibration. This information would help to identify areas that could be most vulnerable to hydrological change and predict the fate of potential pollutants along the flow paths.
- Conduct additional analyses to fill gaps in the geochemical data for some springs such as applying dating methods to the Matlock thermal waters, and explore the possibility of re-analysing waters that have not been measured for the last 20-40 years to investigate whether the geochemistry of springs may have changed.
- Analyse long term monitoring data from the Bath and Buxton thermal springs, as the variability in flow rates or geochemistry could help to refine hydrological models and understand subtle controls on the thermal springs.
- Widen investigations to compile existing geochemical/hydrological data for other springs that may originate from depth, but where dilution by cold groundwater might overwrite a thermal signature. If these springs have a commercial or ecosystem value, they may need similar protections to the thermal springs outlined in this report.
- Use a Natural Capital approach to understand the value and importance of deep thermal springs, both currently and with potential developments in the future. This information will help with decision making related to protecting springs.
- Investigate ways in which potential risks and vulnerability of thermal springs can be understood and/or managed, for example using spring protection zones. It could be helpful to consider the ways deep thermal springs are monitored and protected in other countries, for example in Hungary or Croatia.

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