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The hydrogeology and hydrochemistry of the thermal waters at Taffs Well, South Wales, UK.

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Abstract: Taffs Well is the only thermal spring in Wales, with an average temperature of 21.6°C ± 0.5°C. The River Taff is adjacent to the spring and removal of a weir and work on flood defences has reduced mixing with flood water from the river. This has enabled data to be gathered that more closely represent the thermal water end-member than previously possible. Limited interaction with modern waters is confirmed by tritium, nitrate, CFC and SF_6 concentrations below or close to lower detection limits, showing at most 6% mixing with modern waters. ^{14}C dating suggests a conservative age estimate of at least 5000 years.

Values for dissolved noble gases suggest that the waters originate as rainfall at an altitude several hundred metres higher than the spring. The northern Carboniferous Limestone outcrop is proposed, which would then require recharged waters to flow to a depth of 400m and distance of 25km, following the synclinal structure of the South Wales Coalfield, to discharge at the spring. Sr isotope data suggest interaction with the Marros Group (formerly known as the Millstone Grit), the waters flowing within or close to the contact between the Carboniferous Limestone and Marros Group before rising via the Tongwynlais Fault.

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Taffs Well spring lies north of Cardiff in southern Wales, UK, at National Grid Reference ST 11925 83639 and at an elevation of 30m aOD (Fig.1). The spring emerges on the eastern bank of the River Taff, where the Taff valley forms a steep-sided gorge. Spring water is contained inside a 4m-deep brick-lined well within an associated well-building, constructed during the 1800s.

In England springs with average temperatures that exceed 20°C include those near the Mendip Hills at Bath and Bristol (Gallois, 2006) and those at Buxton in the Derbyshire Peak District (Gunn *et al*., 2006; Brassington, 2007). In Ireland the only spring-water temperature exceeding 20°C is found at Mallow in County Cork (Brück *et al*., 1986). All of these springs lie in or adjacent to relatively deep basinal fold structures that incorporate Carboniferous rock successions dominated by limestone. As a reflection of the effects of the geothermal gradient, meteoric water penetrating permeable strata within such deep structures can be heated by contact with hot rock at depth, and may then return to the surface without significant loss of temperature (Gallois, 2006). Taffs Well spring occupies a similar structural setting, on the southern limb of the South Wales Coalfield Syncline (Fig.1).

History

Details of the early history and use of Taffs Well spring are only patchily documented. Whereas Roman settlements and roads occur throughout the Taff Valley, there is no evidence of any Roman use of the waters. The first-known chemical analysis of the water, recorded by Linden (1760), includes the comment that he has, *"…no doubt it will prove a great efficacy in all kind of consumptions"*.

Before artificial flood banks were created, frequent river flooding destroyed any temporary well-housing emplaced to give privacy to bathers. During the 19th century a weir was built across the Taff, widening the river and diverting it eastwards towards the spring. Several 19th-century books and guides (Hall, 1861; Anon, 1868; Worralls, 1875) report visitors bathing in the waters, which were thought to aid the cure of rheumatism. Increasing popularity of the spring among tourists was reported by the chemist J W Thomas (1877), who noted that, *"…the well waters have long since obtained some celebrity, especially … as a curative agent for rheumatism"*. He also concluded, *"…we do not feel encouraged by this story (which, by the way, we rather fancy we have heard before) to insist very much upon the curative properties of the Water of Taffs Well."*

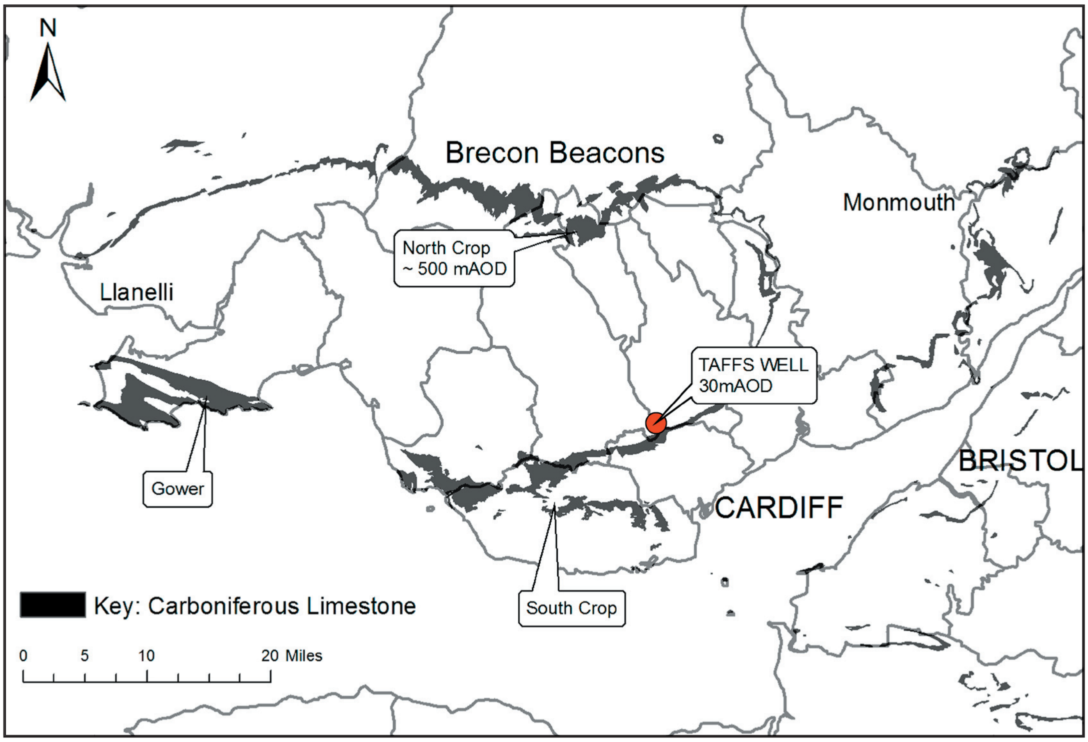


__Figure 1:__ The location of Taffs Well. Generalized outcrops of rocks belonging to the Carboniferous Limestone Supergroup are shown, including those around the basin of the South Wales Coalfield Syncline, emphasizing the separation of the proposed springwater source area on the North Crop and the spring location on the southeastern side of the basin.

Figure 2: Recent (August 2012) view of the Taffs Well spring's well-house.

The well-house fell into disrepair around the beginning of the First World War and after renovation by the villagers of Taffs Well in 1929 the site, now including a small swimming pool,re-opened in 1930. A description of the restored site was provided by the celebrated travel writer H V Morton (1932) in his *'In Search of Wales'*. Both pool and well-house fell into disuse again during the 1950s following a high flood. In contrast, during a drought in 1978, the well's output was used to water the village bowling greens. When research into the UK's thermal waters was renewed during the late 1970s, results of detailed analyses of the Taffs Well water were provided by Burgess *et al*. (1980) and the British Geological Survey (BGS) again drew attention to Taffs Well when it was mentioned by Buckley *et al*. (1988).

During the 1990s partial redevelopment of the area was embarked upon by the Rhondda Cynon Taff Council. Engineering works in 2011 included installation of a dual-level overflow to the River Taff, which was designed to maintain the level of the well and reduce flooding from the spring water into the adjacent park. Currently the Taffs Well spring is not used for public water supply or recreation, in contrast with some other UK thermal water sources, such as St Ann's Well at Buxton in the Peak District and the Bath Springs.

River Taff flood defences

Parkland surrounding Taff Well spring has been designated a fluvial flood plain by Environment Agency Wales. The River Taff is approximately 29.5m wide and can reach 2 to 2.5m depth in the Taffs Well area. In the early 1970s a major improvement scheme carried out on the River Taff involved the removal of a weir, re-sectioning of the river channel and the construction of a flood defence embankment along the river's eastern bank. The embankment is about 3m high and it is likely that it was constructed from river gravels dredged from the River Taff when its channel was re-sectioned in the early 1970s. Reflecting the use of river gravels in its construction, the flood bank is a semi-permeable barrier and flooding has occurred due to seepage and backflow from nearby culverts. Major flooding in 1979 extended behind the River Taff embankment. Further engineering work was carried out on the flood defences from 1989 to 1990, during which the riverside embankment was armoured with gabions and blockstone, and the landward face was supported and retained by 'porcupine' concrete block walling.

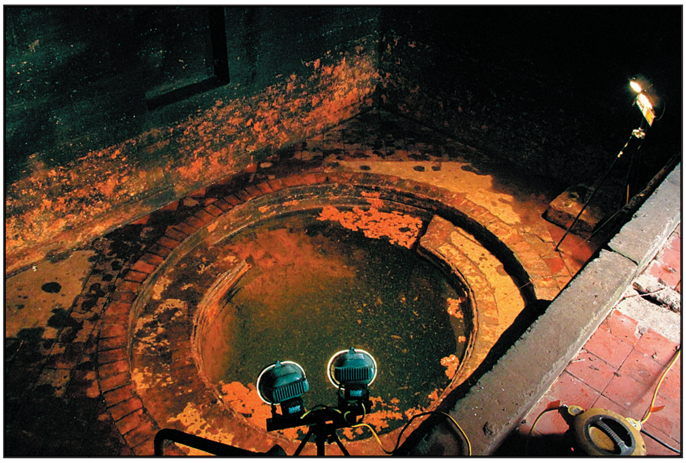


Figure 3: The brick-lined well within the Taffs Well spring's well-house.

Geology

In the Taffs Well area (Fig.4) Westphalian rocks of the South Wales Coal Measures Group overlie clastic rocks of the Namurian Marros Group, which was previously referred to as the Millstone Grit (Waters *et al.,* 2009). Beneath the Marros Group The highest beds of the Carboniferous Limestone Supergroup are Visean limestones belonging to the Hunts Bay Subgroup (part of the Pembroke Limestone Group). These limestones overlie older, dolomitized, Visean beds of the undifferentiated Pembroke Limestone Group (Waters *et al.,* 2009), which in turn overlie the Cwmyniscoy Mudstone, Castell Coch Limestone and Tongwynlais formations, of Tournaisian age, which belong to the Avon Group. The Avon Group beds encompass a conformable lithological transition from the dominantly continental red sandstones, conglomerates and mudstones of the Devonian Upper Old Red Sandstone (Squirrel and Downing, 1969) into the dominantly marine succession of the overlying Carboniferous Limestone.

The superficial geology at the Taffs Well spring comprises river alluvium and river terrace deposits. Alluvial deposits reaching 28m depth are reported in a drilling log on the western side of the River Taff. A borehole log from the eastern side of the Taff (BGS ST18SW320) reports an unknown thickness of sands overlying weathered limestone before terminating at 85m below ground level.

The bedrock succession, including the Carboniferous limestone beds, forms part of the southern limb of the South Wales Coalfield Syncline, and locally the rocks dip at 40°, generally towards the northwest, in the vicinity of the Taffs Well spring. With its trace crossing the River Taff, the north–south Tongwynlais or Taffs Well Fault passes very close to the site of the Taffs Well spring (Fig.4). This fault is a continuation of the Daren-ddu Fault, which is a major fracture that trends northwest–southeast in the Westphalian (Coal Measures) rocks of the South Wales Coalfield (Aldous, 1988). The Tongwynlais section of the fracture is a normal fault with a local downthrow in the Taffs Well area of about 85m towards the west, and it affects both the Carboniferous beds and the underlying Devonian Upper Old Red Sandstone succession (Squirrell and Downing, 1969).

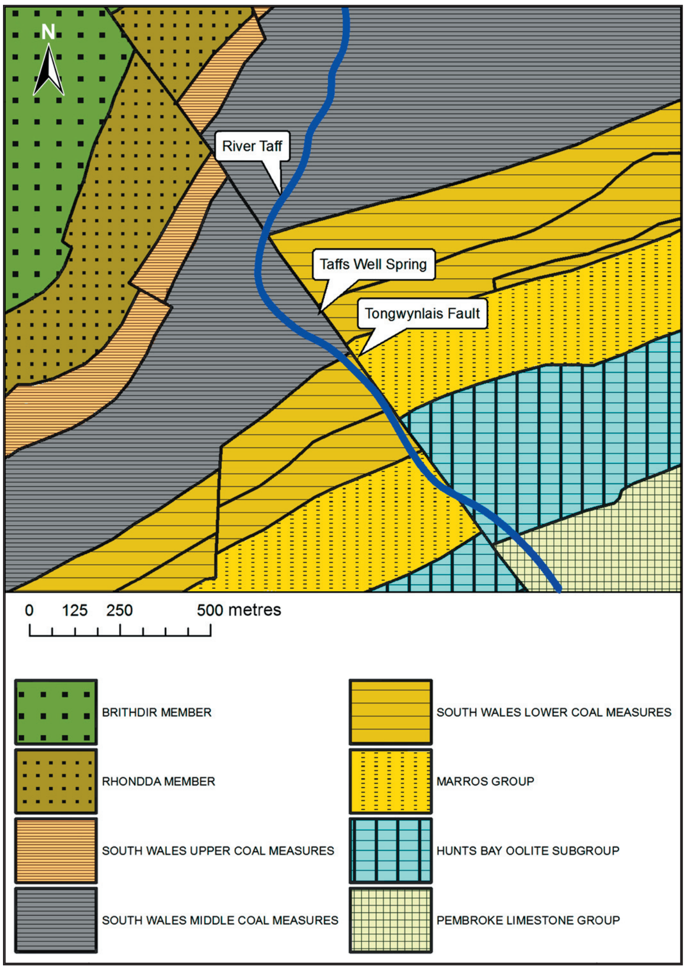


Figure 4: Generalized bedrock geology of the area around the Taffs Well thermal spring, showing also the mapped surface trace of the Tongwynlais Fault.

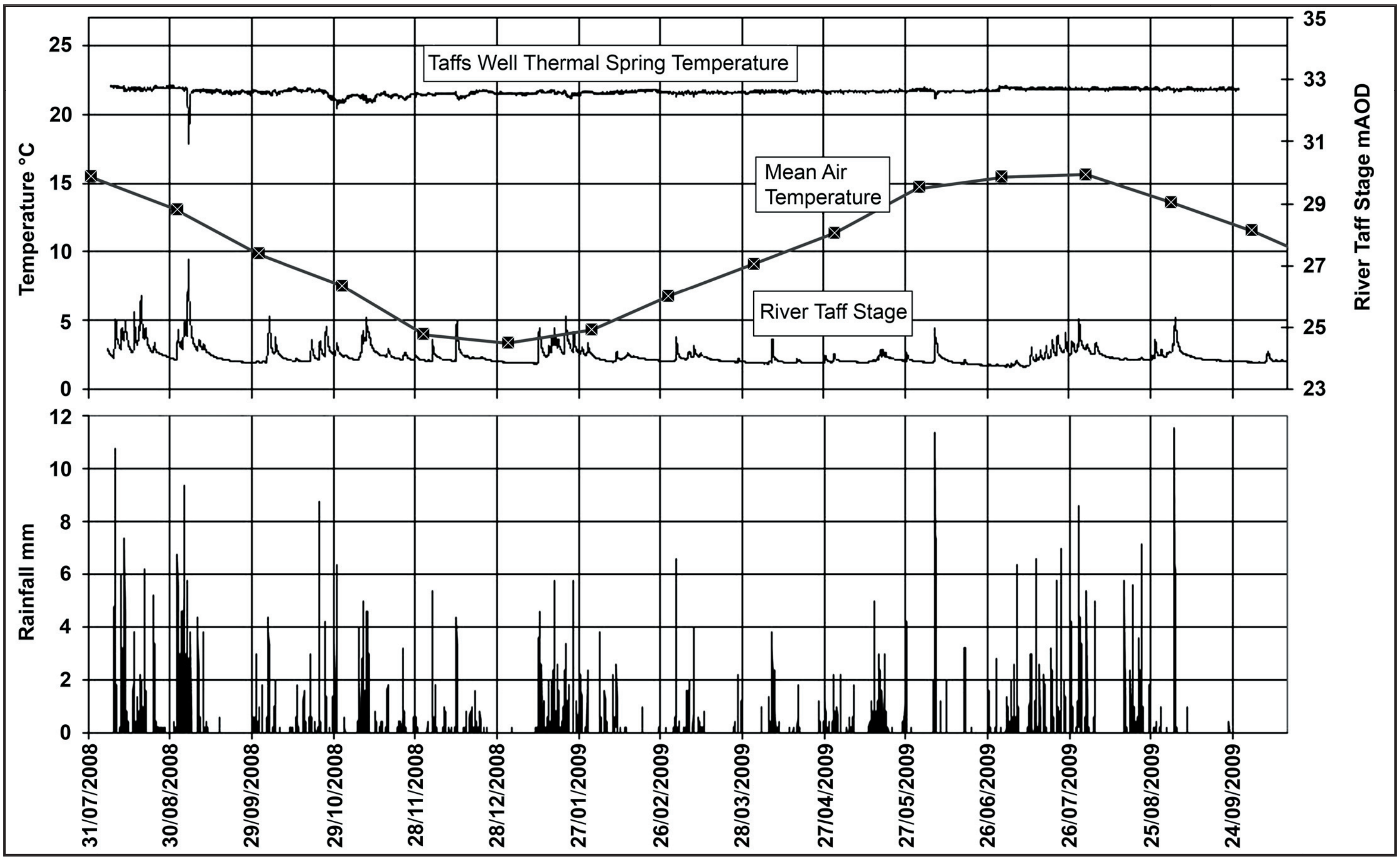


Figure 5: *Taffs Well thermal spring temperature, mean air temperature, River Taff stage data and rainfall.*

Data collection, sampling and analytical procedures

A Solinst LTC 3001 logger was used to record the temperature in Taffs Well spring. The logger has a temperature accuracy of ±0.2°C, resolution of 0.01°C and range of −20°C to +80°C. Data were collected every 30 minutes and about 20,000 temperature readings were collected during the monitoring period between August 2008 and September 2009. The logger was suspended 2.85m below the surface of the water by attaching a wire onto a float. This method ensured that the logger was always submerged and that water flowing into the base of the well was being monitored.

Water quality samples were collected on site from both the existing overflow pipe and directly from the well using a submersible 12V pump. Field readings for pH, temperature, dissolved oxygen and electrical conductivity were measured on a YSI 556 multi-parameter field meter. Only inorganic substances were determined, with analysis undertaken at the Environment Agency national laboratory (accredited by UKAS to the current EN ISO 17025 standard).

Analysis of water samples for chlorofluorocarbon (CFC) and sulphur hexafluoride (SF_6) levels provides a means of dating groundwater up to 50 years old. When used together CFCs and SF_6 can help to resolve details of the extent to which groundwater mixing occurs (Gooddy *et al.,* 2006). Samples for CFC and SF_6 analysis were collected using a submersible 12v pump installed 2m below the water's surface. The samples were collected in a glass jar and were allowed to overfill whilst submerged in a larger bucket of water. This ensured there was no modern atmospheric contamination of the waters. The BGS analysed the samples using gas chromatography with a cryogenic purge-and-trap system. Dissolved noble gas samples were also analysed by the BGS. Samples for tritium and ^{14}C analysis were also collected using a submersible pump 2m below the water's surface.

The isotopes $^{87}Sr/^{86}Sr$ were analysed at the James Hutton Institute, Aberdeen. An approximately 20 ml sample was evaporated to dryness, re-dissolved and the Sr isolated using chromatography; isotopic composition was then determined by thermal ionisation mass spectrometry.

Stage data for the River Taff were recorded at the Tongwynlais Gauging Station (ST 13165 81810), which lies some 2km downstream. Water quality samples from the River Taff were collected from Taffs Well bridge (ST 11736 83795), about 250m upstream from the Taffs Well spring.

Results

Physical parameters

A maximum temperature of 22.1°C and mean temperature of 21.6°C ± 0.5°C (Fig.5) were recorded using an *in situ* Solinst data logger. Higher temperatures were recorded on the YSI 556 field meter with a mean of 22° from five separate readings. This may be due to the field readings being taken at the outflow pipe where surrounding air temperature or sunlight could have raised the temperature, especially in the summer. Although these field readings are reported (Table 1b), only the temperature data from the *in situ* Solinst data logger were used for the temperature analysis. The *in situ* temperature is twice that of many groundwater readings from springs, wells and boreholes across Wales, which average 11.3°C within the Carboniferous Limestone (Environment Agency Wales 2008a-d). Temperature readings were taken every 0.5m from the surface to 4m depth using a Solinst temperature dipper.

The data show that the vertical temperature within the well was constant. Reduction below 20°C is rare, having occurred only once during the study period. The decrease in temperature was short-lived, lasting only several hours with a minimum recorded temperature of 17.9°C. Several smaller changes of less than 1°C from the mean were observed and may, under further statistical analysis, show correlation with elevated river levels.

The earliest reference to the discharge of Taffs Well was made by J W Thomas (1877), who stated that, *"The spring is very powerful, and appears from rough calculation to afford about 800 gallons per hour."* [0.001 m^3/s or 87.24 m^3/d]. These estimates agree with the flow measurements made during the present study. Dissolved oxygen concentrations within the thermal waters are notably low and range from 4% to 15.5%. The measured electrical conductivity was relatively stable, varying between 500 µs/cm and 558 µs/cm (Tables 1a–c).

Thomas *et al.,* (1983) calculate a minimum depth for the origin of the thermal water at 600m, and suggest the actual depth is around 700m, within the Carboniferous Limestone succession. This calculation assumed a geothermal gradient of 20°C/km. Recent studies (Busby *et al.*, 2011) suggest the geothermal gradient within the upper 1km of sedimentary crust in the UK may be closer to 28°C/km. If this is the case then it might suggest a more shallow origin for the waters at Taffs Well, of about 400m.

Reference	Thomas, 1877	Thomas, 1877	Squirrell and Downing, 1969	Burgess et al., 1980
Date	1875	1877	1969	1980
Temp °C	—	18.61	13 – 22	19.7
pH *in situ*	—	—	—	—
Conductivity 25°C µS/cm	—	—	—	—
Dissolved oxygen %	—	—	—	—
Ca mg/l	44.5	43.7	44	40
Mg mg/l	18.3	17.9	18	22.5
Mg-Filt mg/l	—	—	—	—
Na mg	31	—	31	15
K mg/l	1.3	—	—	1.3
Fe µg/l	—	—	—	—
Fe-Filt µg/l	—	—	—	—
Mn µg/l	—	—	—	—
Mn-Filt µg/l	—	—	—	—
Sr µg/l	—	—	—	270
HCO_3 mg/l	—	—	—	—
Cl mg/l	36	36	35	36
SO_4 mg/l	23.8	23.1	23.8	23
Nitrate N mg/l	—	—	—	0.9
F mg/l	—	—	—	—

Table 1a: *Historical water quality data from the Taffs Well thermal spring (see also tables 1b and 1c).*

Chemistry

The inorganic chemical data include those from historical analyses (Table 1a) and modern analyses (Table 1b) of the Taffs Well spring water. Only data from the recent analyses are used to calculate mean values for the inorganic chemistry, although the historical data are consistent with the more recent results. The results are compared with baseline data from Carboniferous Limestone aquifers across Wales (Table 1c) and also to data from local abstractions in the Taffs Well area (Table 1b). The baseline data presented in Table 1c are mean values for six separate Carboniferous Limestone study areas in Wales (Environment Agency Wales, 2008 a-e).

The dominant ions in all samples are Ca and HCO_3 and total mineralization at Taffs Well averages 427 mg/l. The major ion chemistry is very stable with Ca, Mg, Na, K, HCO_3, Cl and SO_4 showing very little variation in all known analyses. HCO_3 ranges from 248 mg/l to 275 mg/l and SiO_2 is elevated with a mean value of 16.5 mg/l compared to mean baseline values of 6.5 mg/l. Uranium is low at 0.6 µg/l when compared to the local groundwater in superficial deposits (1.1 µg/l) but similar to baseline data for water abstracted from the limestone (0.69 µg/l). The water is also devoid of the main nutrients; nitrate, nitrite and orthophosphate are all below the limits of detection (0.196 mg/l, 0.004 mg/l and 0.2 mg/l respectively). Nitrate (N) in the River Taff has a mean value of 1.3 mg/l, with 1.6 mg/l N in local water samples from superficial deposits and the Carboniferous Limestone.

Reference	*Current study*	*Current study*	*Current study*	*Current study*	*Current study*	*Current study*	*Local Groundwater*
Date	08/08/2008	04/02/2010	04/02/2010	02/07/2010	28/07/2010	MEAN	MEAN
Temp °C (YSI field meter)	22.3	21.7	21.7	22.2	22.1	22.0	15.4
pH *in situ*	—	—	7.6	—	7.6	7.6	7.6
Conductivity 25°C µS/cm	500	557	558	554	527	539	667
Dissolved oxygen %	6.0	15.5	11.8	—	4.0	9.3	91.7
Ca mg/l	42.2	41.2	41.4	41.2	41.4	41.5	79.2
Mg mg/l	23.8	23.1	23.3	23.2	23.4	23.4	23.4
Mg-Filt mg/l	23.5	23.5	23.6	—	23.7	23.6	23.3
Na mg	38.3	38.0	38.8	38.7	39.2	38.6	34.6
K mg/l	2.9	3.0	3.1	3.1	3.1	3.0	2.6
Fe µg/l	45	122	663	53	77	192	759
Fe-Filt µg/l	30	30	102	—	34	49	<30
Mn µg/l	135	157	416	167	172	209	41
Mn-Filt µg/l	134	120	167	—	143	141	41
Sr µg/l	325	317	319	321	323	321	160
HCO_3 mg/l	275	261	261	248	260	261	296
Cl mg/l	37.3	36.1	35.9	36.4	35.8	36.3	61.8
SO_4 mg/l	19.0	19.0	19.0	18.7	19.1	19.0	23.2
Nitrate N mg/l	<0.196	<0.196	<0.196	<0.196	<0.196	<0.196	1.6
F mg/l	0.54	0.53	0.51	0.52	0.54	0.53	0.07

Table 1b: *Water quality data from the Taffs Well thermal spring collected during the current study, compared with mean values for local groundwater (see also tables 1a and 1c). Temperature data are from a YSI556 field meter and not the in situ Solinst logger.*

Reference	*BASELINE Carboniferous Limestone Porthcawl Schwyl*	*BASELINE Carboniferous Limestone North Crop West*	*BASELINE Carboniferous Limestone North Crop Central*	*BASELINE Carboniferous Limestone Anglesey*	*BASELINE Carboniferous Limestone Gower*	*BASELINE Carboniferous Limestone Pembrokeshire*	*Baseline ALL Carboniferous Limestone Wales*
Date	MEAN	MEAN	MEAN	MEAN	MEAN	MEAN	MEAN
Temp °C	12.0	11.0	11.0	10.9	12.0	11.0	11.3
pH *in situ*	7.2	7.2	7.7	7.1	7.1	7.1	7.2
Conductivity 25°C µS/cm	497	418	200	683	514	546	476
Dissolved oxygen %	58.0	56.0	—	53.1	—	—	55.7
Ca mg/l	96.0	85.0	42.0	103.6	71.0	113.0	85.1
Mg mg/l	8.3	3.9	1.7	9.3	12.0	9.2	7.4
Mg-Filt mg/l	9.1	—	—	9.2	—	7.7	8.7
Na mg	23.0	7.1	3.7	26.7	21.0	19.0	16.8
K mg/l	2.1	1.1	0.4	4.1	1.8	2.5	2.0
Fe µg/l	180	110	190	106	327	503	236
Fe-Filt µg/l	26	8	52	48	43	17	32
Mn µg/l	59	7	29	36	56	98	48
Mn-Filt µg/l	4	6	13	20	22	9	12
Sr µg/l	195	125	46	217	86	135	134
HCO_3 mg/l	276	248	117	327	209	344	254
Cl mg/l	40.0	15.0	6.3	41.7	41.0	38.0	30.3
SO_4 mg/l	27.0	15.0	6.6	18.8	21.0	20.0	18.1
Nitrate N mg/l	3.2	1.7	0.8	3.5	6.2	4.5	3.3
F mg/l	0.09	0.07	0.03	0.15	0.05	0.04	0.1

Table 1c: *Welsh regional baseline water quality averages (compare with tables 1a and 1b).*

Table 2: *Tracers and gases in the water of the Taffs Well thermal spring.*

		Result	Unit
	Tritium	< 1	TU
Gas	Temperature	21.73	°C
	N_2	93.63	%
	O_2	4.72	%
	Ar	n/a	%
	CO_2	0.53	%
	CH_4	n/a	%
	He	0.066	%
Aerosols	CFC-11	0.26	pmol/L
	CFC-12	0.18	pmol/L
	SF_6	<0.1	pmol/L
Noble gases	He	6.07×10^{-3}	ccSTP/L
	Ne	2.26×10^{-4}	ccSTP/L
	Ar	4.12×10^{-1}	ccSTP/L
	Kr	9.6×10^{-5}	ccSTP/L
	Xe	1.5×10^{-5}	ccSTP/L

Barium is elevated, at 283 µg/l, compared to baseline data for the Carboniferous Limestone aquifers in Wales, which have a mean of 47.2 µg/l. Fluoride is elevated at 0.53 µg/l, and this is not reflected in the local groundwater (0.07 µg/l) or the Carboniferous Limestone baseline (0.1 µg/l). Strontium is elevated, averaging 321 µg/l, which is twice as high as in the local superficial deposit groundwater (159.6 µg/l) and over twice the recorded level in the Carboniferous Limestone (134 µg/l). Iron is the most variable element, with results ranging between 45 µg/l and 663 µg/l. Manganese is elevated, with a mean of 209.4 µg/l, compared to a mean value of 41µg/l for local water abstractions from superficial deposits and the Carboniferous Limestone.

The following determinands were all below the limit of detection; aluminium, ammonia, antimony, copper, nickel, lithium, beryllium, boron, cadmium, chromium, cobalt, lead, nitrate, nitrite, orthophosphate, silver, thallium, tin, titanium, vanadium and zinc. No organic analyses have been undertaken at Taffs Well spring.

Gas species

Gas was first collected and analysed by Thomas (1877), who reported the composition as being 95.84% nitrogen, 1.16% carbonic acid with traces of hydrocarbon gases. Thomas also estimated the volume of gas released from the well at 4.5 cubic feet per/ hour and suggested that the only possible source of nitrogen could be from shale or coal strata.

For this study gas was sampled using a submerged, water-filled plastic bottle with which 350 ml of gas was collected during a 30-minute period. Rising gas displaced the water in the submerged bottle and was then decanted via a thin pipe into a sealed gas-sample bag. Analyses (Table 2) confirm that the sample is composed almost entirely of nitrogen, with small amounts of oxygen, carbon dioxide and helium, which could be an artefact of the sampling process, reflect a small error margin, or be due to mixing with more recent waters. At the laboratory argon could not be separated from oxygen; hence they are reported together (4.72%). The helium in Taffs Well is composed mainly of alpha particles. Dissolved concentrations of the noble gases He, Ne, Ar, Kr and Xe were determined at the BGS. The Ne, Ar, Kr and Xe results convert to indicate a recharge temperature of 8.1 ± 1.8°C, which is consistent with the age-dating evidence for Holocene recharge, and indicates that recharge occurred several hundred metres above sea level.

Tracers and isotopes

Tritium, chlorofluorocarbons (CFC) and sulphur hexafluoride (SF_6) were used as tracers to identify mixing with modern waters. Tritium was below the detection limit of 1TU and suggests limited mixing with modern waters. CFC and SF_6 results show that there is between <3 and 6% mixing with modern groundwater. This can be broken down into CFC-12 (0.18 pmol/L), equivalent to 6% modern water; CFC-11 (0.26 pmol/L) equivalent to 5% modern water; and SF_6 which was <0.1 fmol/L, equivalent to <3% modern water.

The isotopes $^{87}Sr/^{86}Sr$ were analysed, with an isotopic ratio of $^{87}Sr/^{86}Sr$ 0.711508 ± 0.000011 determined, enabling comparisons with other thermal spring waters such as those at Buxton.

Analysis for ^{14}C shows the radiocarbon activity is 9.63 ± 0.2 percent modern. A bulk age of 11,250 years is produced using a simple $\delta^{13}C$ based correction $\delta 13C_{TDIC} = -9.76‰$. The oxygen and hydrogen stable isotopes, $\delta^{18}O$ −6.63‰, $\delta^{2}H$ −42.1‰, look very similar to what would be expected at present, and suggest that recharge occurred within the Holocene (i.e. up to c.10,000 years old). Due to the slightly ambiguous results a conservative estimate of 5,000 years is proposed as the age of the water.

Summary of key features

The most notable feature of the Taffs Well thermal spring is a relatively stable temperature generally only showing a small variation around 21.6°C ± 0.5°C. Low dissolved oxygen and only small variations within the electrical conductivity are complemented by a stable major ion chemistry of Ca – HCO_3 type. Water quality analyses have shown there is an absence of main nutrients N, NO_3, P and OP and that the minor ions are dominated by Ba, F and Sr. Trace elements dominated by Fe and Mn and the absence of Al, NH_3, Sb, Cu, Ni, Li, Be, B, Cd, Cr, Co and Pb all help to distinguish the inorganic chemistry. Gas released in the well is almost entirely made up of nitrogen.

Environmental tracer analyses show that tritium is below the detection limit and an $^{87}Sr/^{86}Sr$ ratio of 0.711508 ± 0.000011 was recorded. CFC and SF_6 values suggest at most 6% mixing with modern waters and the noble gases indicate a recharge temperature of 8.1°C ± 1.8°C and elevation of several hundred metres above sea level. ^{14}C levels indicates recharge within the Holocene, consistent with water stable-isotope composition, and a conservative estimate of its age is 5,000 years.

Local Conceptual Model

The local conceptual model is shown diagrammatically in Figure 6. Water temperature of the Taffs Well spring is not affected by changes in the ambient air temperature or changes within the temperature of the River Taff. There is some evidence of limited mixing (3–6%) with more modern waters, supported by CFC/SF_6 results. The absence of nitrates, ammonia and tritium further confirm that the water has undergone only very limited mixing with modern waters. During 05 September 2008, 41mm of rainfall was recorded, and the River Taff stage at Tongwynlais (2km downstream) measured 27.2m aOD, the highest level met during the monitoring period (Fig.5). During this event the spring temperature dropped to 17.9°C. This is the lowest temperature reading collected during the monitoring period and might reflect limited mixing of more modern water. Cooling of the water may occur due to two main factors:

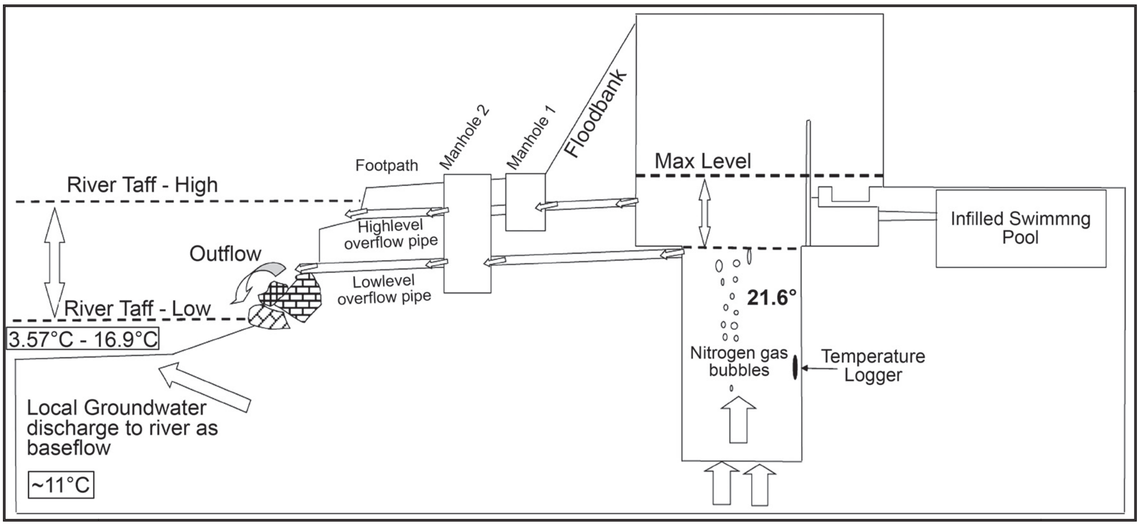


Figure 6: *Local conceptual model of Taffs Well thermal spring.*

Author(s)/Study	*Date*	*Temperature*
Current Study	2008	**22.12°C**
Buckley *et al.*	1988	**20.60°C**
Burgess *et al.*	1980	**19.60°C**
River Taff re-sectioned and flood embankment created in early 1970s		
Edmunds *et al*.	1969	**18.50°C**
Squirrell and Downing	1969	**22.00°C**
Squirrell and Downing	1969	**13.00°C**
Aubrey Strahan	1895	**19.00°C**
Aubrey Strahan	1895	**12.70°C**
J W Thomas	1877	**18.61°C**

Table 3: *Temperature measurements at Taffs Well thermal spring, 1877–2008.*

1) very local recharge from groundwater within the superficial deposits and 2) high river levels causing the ingress of surface water through the semi-permeable flood wall into the well. The actual explanation is likely to be a combination of both factors. Once the river level subsided the thermal water was able to return to a temperature close to the average of 21.6°C within a few hours. Currently it is unclear whether there is any correlation between the magnitude of river-level change and groundwater temperature variation in the Taffs Well spring. Some increases in river stage appear to have a lowering effect on water temperature whereas others do not.

It is possible that the spring was more likely to mix with colder waters from the River Taff prior to the construction of the flood embankment in the early 1970s. Further flood defence work in the 1990s allowed more separation of the spring from mixing with river water. Mixing with river water prior to flood bank defence works could explain the more variable, mostly lower, temperatures measured historically at Taffs Well spring (Table 3).

It can be concluded from these observations that heavy rainfall, coupled with high river water levels, has the ability to reduce the temperature of the water in the spring temporarily. Decreases to temperatures below 20°C are rare, and associated only with large precipitation events and elevated river stages.

Regional Conceptual Model

Groundwater flow is gravity driven, caused by the difference in topographical and hydraulic heads. Head could be created between the Carboniferous Limestone along the North Crop of the South Wales Coalfield Basin, as suggested by Burgess *et al.,* (1980), at an altitude of some 500m aOD and the Taffs Well spring at 30m aOD. The altitude of the North Crop corresponds to a recharge temperature of 8.1 ± 1.8°C, as derived from consideration of the noble gas data. The ^{4}He content of groundwater at Taffs Well is large and cannot be generated through local transit through limestone alone; this suggests a deeper origin, perhaps within the underlying Devonian strata (Burgess *et al.,* 1980).

Recharge is derived from direct precipitation passing into the ground via surface karst features and by swallowing of rivers on the limestone or adjacent formations. Surface water from springs flowing out of Devonian or other Carboniferous strata may also contribute to recharge if subsequently entering the limestone. Only a very small amount of the total recharge on the North Crop will contribute to the flow at Taffs Well, with the majority discharging at local springs and as baseflow to rivers. Noble gas data suggest that recharge of water occurred several hundred metres above sea level – a broad altitude that is consistent with that of the Carboniferous Limestone along the North Crop. Recharged water would then need to flow a minimum distance of 25km and reach a depth of at least 400m, flowing beneath the Coal Measures within fractures, fissures or bedding planes of the Marros Group and the Carboniferous Limestone Supergroup to discharge at the Taffs Well spring (Fig.7).

It is assumed that beneath the South Wales Coalfield Basin there is limited porosity/permeability within the Carboniferous Limestone Supergroup as a whole, due to the overburden pressure decreasing the size of pores, fractures or fissures. As such the movement of water at depth must be related to, and limited to, selected enlarged fractures (fault planes or joint fissures) and dissolutional voids related to primitive dissolutional permeability imprints along major inception horizons (e.g. Lowe, 2004). Sr isotope data suggest that there is significant exchange and interaction between waters within the Carboniferous Limestone Supergroup, principally the Pembroke Limestone Group, and the overlying Marros Group.

Having passed beneath the coalfield, in order to return to the surface the water must find favourable pathways. Temperature-induced density gradients can act to facilitate the upward movement of groundwater (e.g. Brassington, 2007) and reduction in viscosity at higher temperature also accelerates thermal water circulation (Goldscheider *et al*., 2010). Faults such as the Tongwynlais Fault, may act as guides to the establishment of conduit flow or might act as local barriers to groundwater movement, depending upon interplay of various factors. The Tongwynlais Fault penetrates both the Carboniferous and Devonian sequences (Squirrell and Downing, 1969) and could provide pathways for deep thermal water to move upwards towards the surface.

Evolution of water quality

In tables 1a–c the chemistry of the Taffs Well spring water is compared to that of local groundwater abstractions and to baseline groundwater quality from the Carboniferous Limestone (Environment Agency, 2008a–d). Recent samples are also compared to data obtained during the latter part of the 19th century (Thomas, 1877) and, more recently, by Downing (1958), Edmunds *et al.* (1969) and Burgess *et al.* (1980). The dominant ions in all samples are Ca and HCO_3, and alkalinity is more-or-less constant, averaging 218 mg/l. A Ca–HCO_3 water-type is consistent with that of other Carboniferous Limestone aquifers in Wales, but the Taffs Well waters contain a number of other components that are elevated in concentration above baseline values for other south Wales Carboniferous Limestone groundwater. These include SiO_2, Mn, Ba, F and Sr.

The concentration of major ions at Taffs Well in1877 was similar to that in 2010. Compared to the Carboniferous Limestone baseline data, Mg and Na are elevated and the water is devoid of the main nutrients, nitrate, nitrite and orthophosphate, which are all below the limits of detection. Nitrate (N) in the River Taff averages 1.3 mg/l, and is 1.6 mg/l in the local superficial deposits and weathered Carboniferous Limestone. Thus the absence of detectable nitrate in the Taffs Well waters is consistent with the theory that there is limited mixing with modern water. Low oxygen levels are not reflected in local groundwater and river water, which has between 90–100% dissolved oxygen. Dissolved oxygen can be severely depleted by the effects of biological activity and/or chemical reduction processes during rock–water interaction.

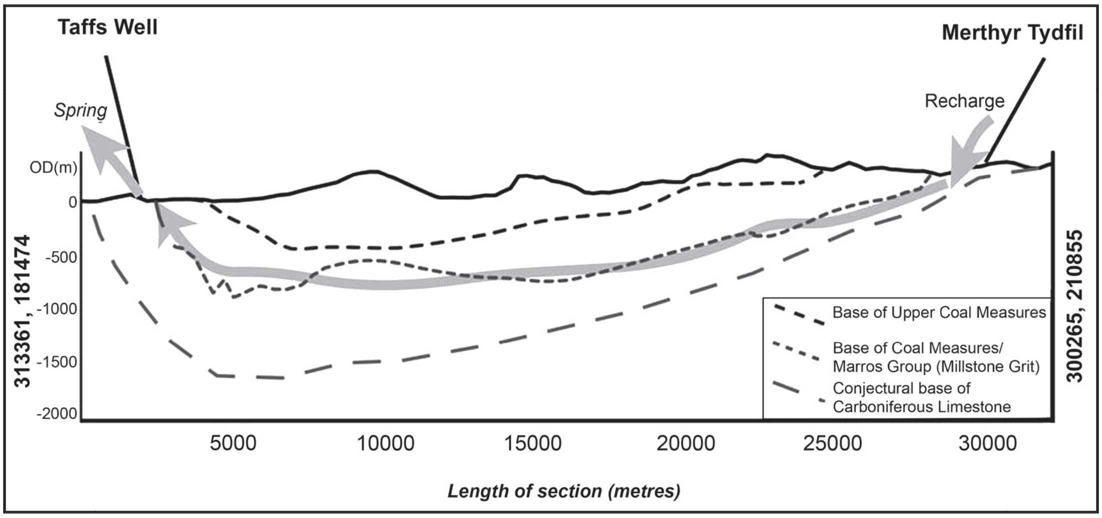
Barium and fluoride values are elevated compared to the Carboniferous Limestone baseline groundwater quality data. It is likely that the water's fluoride content has originated from contact and interaction with a source rock such as the Carboniferous Limestone over a long timescale. Fluoride can be derived from dissolution of trace quantities of fluorite (CaF_2), ion exchange on mineral species such as fluorapatite ($Ca_5(PO_4)_3F$) or by ion exchange on sheet silicates such as various types of mica that could be present in the Marros Group.

Iron has proved one of the most variable elements giving readings of 45 ug/l to 663 ug/l l. Fe (2+) is soluble under reducing conditions, which must occur along the deep flow-path of the thermal waters. As the waters rise towards the surface, limited mixing with local groundwater and interaction with atmospheric oxygen may cause varying amounts of iron to precipitate.

Manganese is elevated with a mean value of 209 µg/l compared to 41 µg/l for water abstracted from the local superficial deposits and Carboniferous Limestone. Oxidation has led to precipitation of manganese deposits on the inside of the well building and the spring's overflow pipe. Elevated levels of manganese were interpreted by Gunn *et al*. (2006) as an indicator of interaction of deep groundwater with Namurian sandstones before rising at the Buxton thermal springs.

SiO_2 values in the Taffs Well spring water are elevated, with an average of 16.6 mg/l, which is higher than in waters abstracted from the local superficial deposits (5.9 mg/l) and Carboniferous Limestone (5.3 mg/l). A likely origin for dissolved SiO_2 would be weathering reactions of silicate minerals within the quartzose sandstones in the adjacent Marros Group. Uranium content is low at 0.6 ug/l, compared to values of 1.1 ug/l in the local superficial deposits and 1.2 ug/l in the Carboniferous Limestone.

Figure 7: Regional conceptual model of the Taffs Well thermal spring.



Prior to the impact of anthropogenic influences, rainfall sulphate in the UK was dominated by marine aerosol input (Coulson *et al*., 2005), which would have had SO_4/Cl of 0.14. However, rock weathering adds sulphate through oxidation of sulphide minerals, and can readily increase SO_4/Cl values to c.0.5 (Robinson and Bottrell, 1997), a level similar to that in the Taff's Well water. The slightly elevated sulphate at Taffs Well could therefore simply represent the composition of allogenic recharge to the karst (e.g. from catchments on the overlying Marros Group or the underlying Devonian Old Red Sandstone), rather than sulphate added during subsurface flow. However, Bottrell (1991) found that sulphate within evaporite mineral deposits in abandoned phreatic caves in south Wales was derived from the overlying Marros Group. This indicates that subsurface hydraulic connections exist between the Marros Group and underlying beds of the Pembroke Limestone Group, a relationship borne out by the widespread presence of interstratal karst dolines across much of the Marros Group outcrop in south Wales (e.g. Thomas, 1974).

Strontium in Carboniferous Limestone has an isotopic composition close to that of Early Carboniferous sea-water, and limestone groundwaters contain Sr with a similar isotopic composition (0.7085 to 0.7088; Gunn *et al.,* 2006). The Buxton thermal waters contain Sr enriched in radiogenic 87Sr (87Sr/86Sr = 0.7102), which was attributed by Gunn *et al.,* (2006) to a significant component of Sr (and other solutes) being derived from interaction of groundwater with Millstone Grit Group strata. The analyzed 87Sr/86Sr of 0.711508 at Taffs Well is significantly more radiogenic than at Buxton, which might imply a more significant component from sandstone weathering. The Sr isotope composition of waters from the Millstone Grit Group in northern England and from the coeval Marros Group in South Wales varies, reflecting the source-areas and respective source-rocks of the sandstones in different depositional basins (Montgomery *et al.,* 2006). Thus in Yorkshire and northeastern England it is lowest (0.7110 to 0.7114), higher in the Peak District in central England (0.7119) and highest in Millstone Grit facies rocks in Devon (southwest England) at 0.7125 and 0.7126. Unfortunately there are no data for Marros Group waters from South Wales, but whole-rock Sr isotopic compositions of water from Carboniferous sandstones in South Wales are similar to those in the Peak District (Leng *et al.,* 1999). If 0.7119 represents a South Wales Marros Group source compared with 0.7085 for Carboniferous Limestone water, a composition of 0.7115 at Taffs Well implies that 80% of the dissolved Sr is derived from the Marros Group. This supports the suggestion that sandstone weathering is the source for the essentially non-limestone components (SiO_2, etc) as discussed above.

The components indicative of sandstone weathering in the Taffs Well water could be:

1) derived entirely on the flow path from the deep limestone aquifer to the present spring;
2) derived by interaction with sandstone, implying that at least a part of the deep flow path must be at the limestone–sandstone boundary, or within sandstone beds;
3) mixing of old groundwaters derived from Pembroke Limestone Group (plus or minus Avon Group) and Marros Group aquifers in closely similar proportions over the history of observations at Taffs Well;
4) derived from allogenic recharge from surface catchments with sandstone bedrock (Marros Group or to a lesser extent the Devonian Old Red Sandstone depending upon catchment).

Sr cannot be attributed to a flow path entirely within the Carboniferous Limestone (Case 1) as the waters rise and discharge through the Marros Group. Given the position of the spring above the upper boundary of the buried limestone, then in cases 2 and 3 the sandstone involved would again be part of the Marros Group; this seems to be the most likely source of Sr. It is also possible that, if recharge occurred from Devonian Old Red Sandstone and the Marros Group, then Sr could potentially be sourced from both of these rocks during recharge.

Age of water

^{14}C was analysed and radiocarbon activity for the Taffs Well sample reported at 9.63 ± 0.2 percent modern. A bulk age of 11,250 years is produced using a $\delta^{13}C$ based correction. Bulk age is also subject to other factors, such as an unknown amount of dissolved inorganic carbon (DIC) from underlying Devonian sandstones or overlying Carboniferous sandstones, oxygen and hydrogen isotopes and increased reaction rates in thermal waters. The unknown contribution of DIC from sandstone units makes it difficult to assign a value for the $\delta^{13}C$ rock when carrying out the correction. Terrestrial sandstones normally have a $\delta^{13}C$ more negative than the zero value assigned to limestone. This would have the effect of reducing the age by up to a few thousand years from the bulk age (*pers comm,* Dr George Darling, 15/12/2010).

The oxygen and hydrogen stable isotopes are consistent with present-day recharge within the Holocene. Reaction rate increases caused by thermal waters tend to make such waters appear older than they actually are and other data to support development of more advanced correction models are unavailable. Taking these unknown factors into account a conservative estimate of 5,000 years as the age of the water at Taffs Well is proposed here. Such an age suggests that this is among the oldest groundwater in Wales; however, residence times at the saline springs in Llandrindod Wells may contain even older water from the late Pleistocene (Edmunds *et al*., 1998).

The confined deep and slow regional flow of groundwater that is represented by the output of the Taffs Well spring is certainly contrary to the general hydrogeological setting of most springs in the south Wales area. Many of the springs on the North Crop source younger water within more local catchments than that of Taffs Well. Recharge is a combination of direct effective precipitation and also input from allogenic streams, sinks and cave systems; their flow paths and flow times vary greatly from those of the Taffs Well waters. Tracer tests are a common method for defining the source of water and travel time to limestone springs. Groundwater velocities in multi-injection tracer tests at Ogof Draenen reached 4km/day and connected areas 8km apart (Maurice and Guilford, 2011). Both the potentially rapid flow velocities and young age of the water in other springs on the North Crop limestones are key differences between the water at Taffs Well and that at other springs in the same recharge area. Assuming an age of 5000 years and distance from recharge to discharge of about 25km the flow velocity of the water emerging at Taffs Well spring might be only about 0.005 km/year.

Conclusions

Taffs Well is the only thermal spring in Wales. Temperatures are stable with only relatively small fluctuations at about 21.6°C ± 0.5°C. Variations in historical temperature readings are attributed to local mixing with modern waters, mainly from the adjacent River Taff, prior to more substantial flood defence works that helped to reduce mixing of the water.

The water quality shows a stable major ion chemistry of a Ca–HCO_3 type. The main nutrients, N, NO_3, P and OP are absent. Minor ions are dominated by Ba, F and Sr with key trace elements represented by Fe and Mn. Dissolved oxygen is low (4–15.5%) and electrical conductivity is relatively stable with an average of 540 µs/cm.

Presence of low levels of tracers suggests only limited mixing with modern waters. Tritium is below the limit of detection and CFC / SF_6 are also low suggesting, at most, 6% mixing with modern waters. Mixing of modern water can occur during very high river stage levels in the adjacent River Taff. The $^{87}Sr/^{86}Sr$ ratio of 0.711508 +/- 0.000011 suggests a strong interaction with sandstones of the Marros Group. Values of ^{14}C indicate recharge within the Holocene, and a conservative estimate of the age of recharge is suggested at 5,000 years. Gas produced in the well is almost entirely made up of nitrogen.

Dissolved noble gases indicate that recharge occurred at a greater topographical elevation, possibly in the area of the limestone outcrop along the North Crop of the South Wales Coalfield Basin, with recharge via sinking streams and via dolines. Sr isotopes suggest that flow is likely to be primarily within the Marros Group, although flow through the Carboniferous Limestone is probable and interaction with the Devonian Old Red Sandstone is not impossible. The waters flow some 25km, reaching depths of at least 400m before meeting the Tongwynlais Fault and rising through the Carboniferous strata to surface in Taffs Well.

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