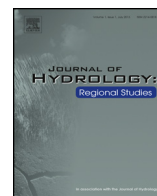




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## Groundwater recharge and flow on Montserrat, West Indies: Insights from groundwater dating



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### ABSTRACT

*Study region:* Montserrat, Lesser Antilles, Caribbean.

*Study focus:* Analysis of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  isotopes, and chlorofluorocarbon (CFC) anthropogenic tracers in Montserrat groundwater provides insights into the age and provenance of the spring waters.

*New hydrological insights:*  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  analysis indicates uniform recharge elevations for groundwaters on Montserrat. CFC-11 and CFC-12 analysis reveals age differences between isotopically similar, high elevation springs and low elevation aquifer waters. Low CFC concentrations within a confined low elevation aquifer suggest water ages of ~45 years. High CFC concentrations in the northern and western springs are explained by rapid infiltration of cool (high CFC concentration) rainfall into saturated compartments, with flow through the vadose zone to the phreatic zone dominated by compartment flow. Lower CFC concentrations in a number of aligned warmer springs suggest a contribution from older, warmer waters from depth. Temperatures and CFC concentrations indicate older component supply rates of up to 8 L/s to the highest yielding spring on Centre Hills, with contributions of up to 75% in the warmest spring waters.

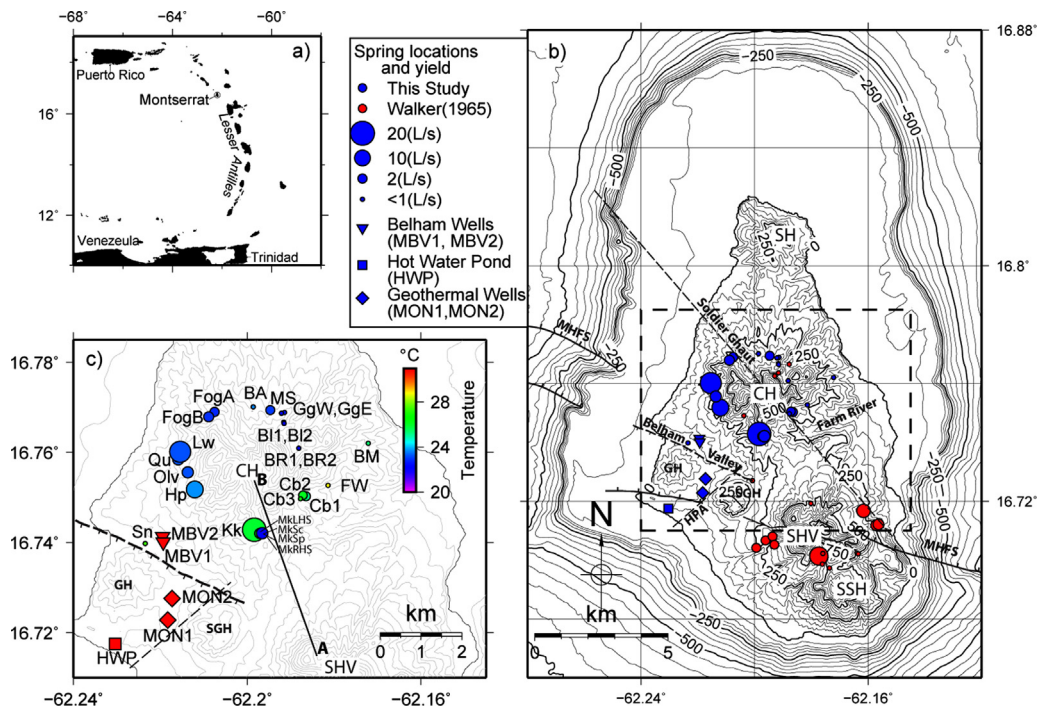
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## 1. Introduction

Despite high rainfall on the tropical, volcanic island of Montserrat, Lesser Antilles (Fig. 1a), surface water is limited and the deeply incised drainage channels (known locally as ghauts) are largely ephemeral. The only permanent streams are sourced from springs which emerge at elevations ranging from 200 and 400 m (amsl) (Hemmings et al., 2014). The freshwater demands of the entire island are met by potable supply from six productive springs on the flanks of the extinct volcanic complex of Centre Hills (CH) (Fig. 1b). In 2013 the combined discharge from the six supply springs was in excess of 50 L/s (Montserrat Utilities Ltd. (MUL), unpublished data). Supply at this rate easily meets the current demands of the population, (~19 L/s). However, consumption rates are expected to rise as population and agriculture recover, during a period of relative quiescence, after >15 years of destructive and disruptive volcanic activity at Soufrière Hills Volcano. An expected increase in future freshwater demands, together with historical fluctuations in spring discharge (Hemmings et al., 2014), demonstrates the fragility of the freshwater resource on Montserrat.

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**Fig. 1.** (a) Location of Montserrat within the Lesser Antilles arc. (b) Spring locations and discharge with major volcanic complexes (SH, Silver Hills; CH, Centre Hills; SHV, Soufrière Hills Volcano; SSH, South Soufrière Hills.) Also marked are GH, Garibaldi Hill; SGH, St George's Hill and the major active (solid lines) and inferred (dashed lines) fault systems: MHFS, Montserrat-Havers Fault System and Belham Valley fault, from [Feuillet et al. \(2010\)](#); Soldier Ghaut fault, inferred by [Hautmann et al. \(2010\)](#); HPA, the NE trending fault inferred by [Ryan et al. \(2013\)](#) from earthquake hypo-centres. (c) Temperatures of spring waters and Belham Valley artesian well waters (inverted triangles) [Hemmings et al. \(2014\)](#). Also marked is Hot Water Pond (HWP, square) at 56 °C and the locations of the two geothermal boreholes (MON1 and MON2, diamonds). Spring codes relate to springs in [Table 1](#). Circle radius is proportional to spring discharge. The line A–B is the surface trace of the schematic cross-section presented in [Fig. 8](#).

Fragile water resources are familiar to many island populations, particularly on volcanic islands where high surface permeabilities are typical and groundwater flow is critical to supply. Understanding the complex groundwater systems that exist in these settings is essential for effective and sustainable resource management. The results of this study highlight and illuminate the complexity that exists in volcanic island hydrology, particularly volcanic arc islands. The methods we describe will be useful for study of groundwater systems in other volcanic island settings. In a recent study on the basaltic ocean island of Hawaii, [Kelly and Glenn \(2015\)](#) combined anthropogenic tracers (Chlorofluorocarbons, CFCs) and isotope analysis to explore the residence times and recharge areas of groundwater in coastal drinking water aquifers. Here, we analyse CFCs and stable isotopes  $\delta^{2}\text{H}$  and  $\delta^{18}\text{O}$ , in Montserrat groundwater, aiming to provide insights into the age and provenance of the island's vital spring waters.

### 1.1. CFCs as groundwater tracers

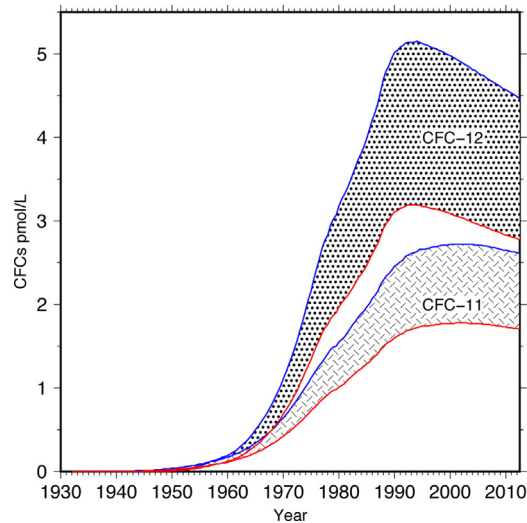
Chlorofluorocarbon (CFC) analysis, particularly CFC-11 and CFC-12, have proven to be a valuable tool for dating groundwater younger than 60 years ([Stuart et al., 2010](#)). It also has the potential to provide insights into the extent of mixing between groundwater components of different age ([Goody et al., 2006](#)). The use of CFCs for dating of groundwater is based on known concentrations in the atmosphere over the last 60 years, together with observations that they are globally well-mixed, and the assumption that their solubility in water follows Henry's Law at the temperature of recharge ([Darling et al., 2012](#)). CFC concentrations in groundwater are assumed to be proportional to the partial pressure,  $p_i$ , of the gas in the atmosphere at the time of recharge ([Dunkle et al., 1993](#); [Plummer et al., 2006](#)):

$$C_i = K_{H_i} p_i, \quad (1)$$

where  $C_i$  is the concentration of a particular CFC compound in water, and  $K_{H_i}$  is the Henry's Law coefficient for that CFC compound.  $K_H$  is a function of both temperature and salinity and has the form ([Warner and Weiss, 1985](#)),

$$\ln K_H = a_1 + a_2 \left( \frac{100}{T} \right) + a_3 \ln \left( \frac{T}{100} \right) + S \left[ b_1 + b_2 \left( \frac{T}{100} \right) + b_3 \left( \frac{T}{100} \right)^2 \right], \quad (2)$$

where  $T$  is temperature in degrees kelvin and  $S$  is salinity in parts per thousand by weight.  $a_1$ ,  $a_2$ ,  $a_3$ ,  $b_1$ ,  $b_2$  and  $b_3$  are least squares fitting parameters, determined by and detailed in [Warner and Weiss \(1985\)](#).



**Fig. 2.** Groundwater concentration ranges for CFC-11 (hatched) and CFC-12 (dotted) at recharge temperatures between 12 °C (blue lines) and 22 °C (red lines), due to changes in atmospheric concentration over time. CFC concentrations in the atmosphere have declined as a result of the Montreal Protocol on Substances that Deplete the Ozone Layer. Based on data from [water.usgs.gov/lab/software/air\\_curve](http://water.usgs.gov/lab/software/air_curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Eq. (2) demonstrates the temperature and salinity dependence of Henry's Law coefficient,  $K_H$ . For groundwater dating application the salinity correction is often omitted (Plummer et al., 2006). Partial pressure,  $p_i$ , of CFC gases in the atmosphere is also dependent on temperature, due to the variation of water vapour pressure with temperature.  $p_i$  is also a function of atmospheric pressure which is usually approximated using an estimate for recharge elevation (Plummer et al., 2006). Fig. 2 illustrates the effect that recharge temperature has on CFC-11 and CFC-12 concentrations in water recharged since 1930. CFC concentrations are higher when recharge occurs at lower temperatures. If recharge temperature, and to a lesser extent the recharge elevation, is well known, analysis of CFC concentration can be used to date groundwater. Fig. 2 highlights that well constrained recharge temperature is particularly important for dating groundwater younger than 20 years.

Combined CFC and Sulphur hexafluoride ( $\text{SF}_6$ ), analysis of groundwater on Maltese islands of Malta and Gozo provided groundwater ages and saturated zone travel-time estimates of between 15 and 60 years (Stuart et al., 2010). On the volcanic island of Jeju, Korea, Koh et al. (2007) combined CFC-12, CFC-11,  $\text{SF}_6$  and  $\text{H}^3$  analysis to distinguish groundwater ages in basaltic aquifers. They established that groundwaters followed a binary mixing model between young (~10 years) and old (~50 years) end members.

Koh et al. (2007) also highlight issues with contamination of groundwater samples leading to potential tracer excess in volcanic settings. In Jeju they suggest that granitic basement rocks provide a terrigenous source of  $\text{SF}_6$  that bias groundwater dating estimates towards younger ages, by up to 20 years. Elevated concentrations of  $\text{SF}_6$  are potentially due to chemical interaction of groundwaters with rocks containing fluorite or sulphide minerals (Harnisch and Eisenhauer, 1998; Darling et al., 2012; Roques et al., 2014). Possibly as a consequence of such contamination,  $\text{SF}_6$  analysis on groundwater samples from Montserrat did not produce coherent or reliable results. Therefore, only results from CFC analysis are present here.

CFC concentrations in groundwater are also susceptible to contamination. Potential contamination sources include local anthropogenic variations in atmospheric levels (Ho et al., 1998), and environmental contamination, particularly from leaching from landfill (Höhener et al., 2003), and mixing with waste water (Kralik et al., 2014). It has also been speculated that volcanoes can produce chlorofluorocarbons (Gribble, 1994), thus disrupting both CFC and  $\text{SF}_6$  analysis on samples from active volcanic environments. Frische et al. (2006) measured CFCs and  $\text{SF}_6$  above detection limits in volcanic gases from Nicaraguan subduction volcanoes. However, they found that levels were in relative proportions characteristic of the ambient atmosphere, concluding that the levels were due to varied amounts of air entrainment into the volcanic edifice, with no significant additional CFC or  $\text{SF}_6$  production by the volcanic activity.

## 1.2. Hydrological and hydrogeological background

In addition to the six tapped springs on Centre Hills, Montserrat, there are a further 19 springs which are untapped or abandoned, due to low yields or limited access. The springs are generally situated on the edges of steep and deeply incised drainage valleys or ghauts. Long-term spring yield monitoring (MUL, unpublished data), combined with one-off flow gauging during field visits in 2010–2013, provides a total spring discharge estimate of ~78 L/s. Individual springs discharge water at up to 19 L/s. Such high discharge rate at relatively high elevation (300 m amsl for Killiekrankie spring, the highest order spring), on an island with only ephemeral river flow and no other surface water, requires the presence of reasonably laterally continuous low permeability units. In Hemmings et al. (2014) we proposed two potential conceptual hydrological models

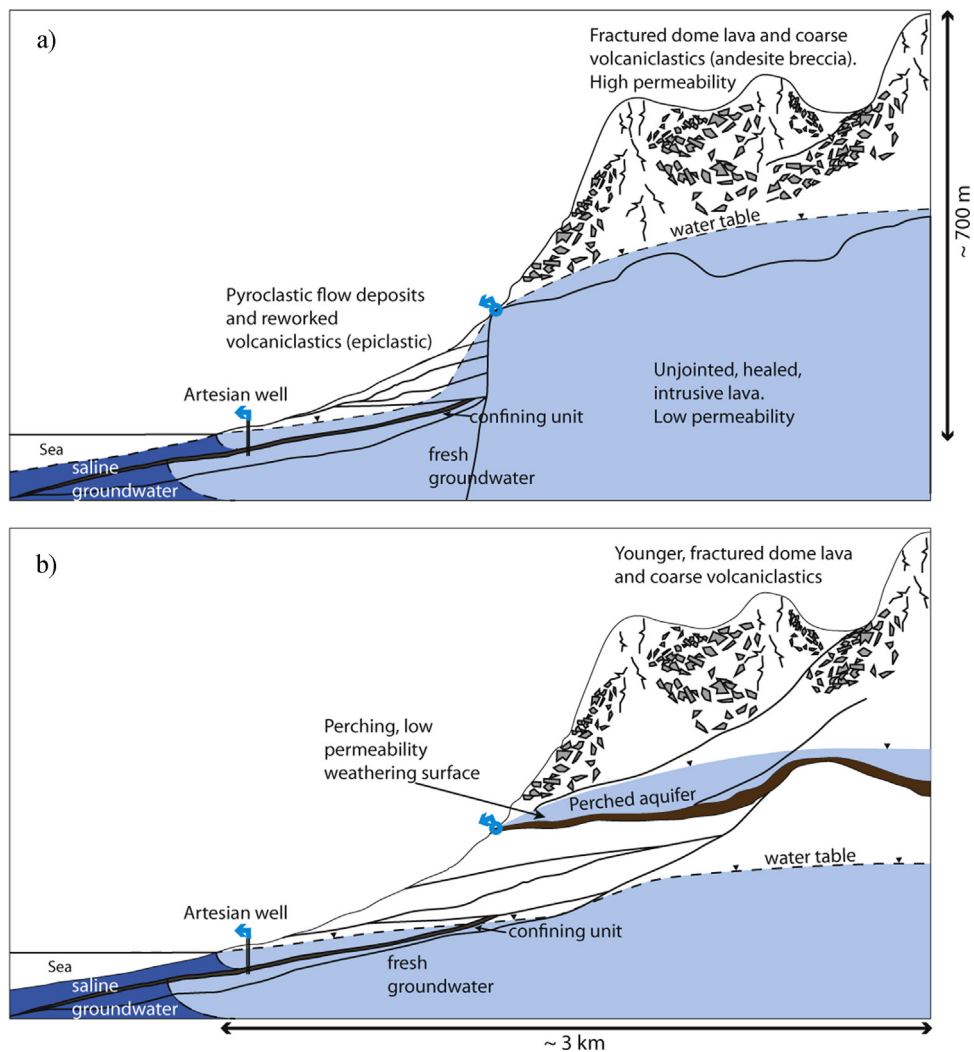


Fig. 3. Type 1 conceptual model (a) and the Type 2 conceptual model (b) of the hydrology on Montserrat, after Hemmings et al. (2014)

describing Montserrat springs. Type 1 (Fig. 3a), based on models developed on volcanic islands such as the Canaries (Cabrera and Custodio, 2004; Custodio, 2007), describes a low permeability intrusive and (hydro)thermally altered core, overlain by fractured and jointed extrusive andesitic lava breccia and talus (autoclastic) and flanked by volcaniclastic and reworked material. Relatively high permeability autoclastic, volcaniclastic and reworked deposits host aquifers which, when exposed by erosion, form springs, normally located on the slopes of incised ghauts. In Type 2 scenario (Fig. 3b), low permeability fine ash and/or weathered palaeosol layers perch aquifers at high elevation. Again, springs occur where the aquifers are exposed by erosion.

The temperature of Centre Hills spring waters are temporally stable but vary spatially, from 22 °C to 29 °C (Hemmings et al., 2014, Fig. 1c). Warmer springs, with temperatures greater than 25 °C, are located in a line extending north-east from the highest yielding Killiekrankie spring (Fig. 1c). Specific electrical conductivity (SEC<sub>25</sub>), referenced to 25 °C, is also elevated in the warmer springs (Table 1). To explain the systematic temperature variation, Hemmings et al. (2014) suggest a contribution of warmer waters from an aquifer at depth, possibly supplied through faults to the high elevation spring aquifers. Previous studies have not identified significant chemical differences between the Centre Hills spring waters (Chiodini et al., 1996; Davies and Peart, 2003; Jones et al., 2010). Jones et al. (2010) attributed high SO<sub>2</sub>/Cl in a few untrapped Centre Hills springs in 2008 to a contribution from run-off influenced by volcanically derived SO<sub>4</sub>.

Additional and notable hydrological features include two artesian wells within the Belham Valley: MBV1 and the flowing artesian MBV2 (triangles on Fig. 1b and c). These wells tap a confined aquifer, 15–38 m below mean sea level (bmsl), beneath one of the islands larger, though still ephemeral, drainage channels. Drilling well logs from 2004 (HydroSource, 2004) describe a thin (1 m) clay cap, beneath a thicker (12 m) lahar deposit, overlying the Belham Valley aquifer which is confined in reworked alluvial and channel deposits. These units are beneath a further ~35 m lahar deposits, alternating with volcanic

**Table 1**

Groundwater CFC concentrations, and  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  results from springs and wells surveyed in February 2013. Also displayed are temperature and specific electrical conductivity ( $\text{SEC}_{25}$ , referenced to 25 °C) data, initially presented in Hemmings et al. (2014).

Spring code	Spring name	Elev. (m amsl)	Date	Temp. (°C)	$\text{SEC}_{25}$ ( $\mu\text{S}/\text{cm}$ )	CFC-12 ( $\text{pmol}/\text{L}$ )	CFC-11 ( $\text{pmol}/\text{L}$ )	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
BA	Blackwood Allen	315	10/02/13	23.6	458	1.89	3.16	-2.95	-11.3
Bl1	Bottomless Ghaut 1	332	04/02/13	22.1	554	2.63	4.85	-3.3	-13.7
Bl2	Bottomless Ghaut 2	356	04/02/13	22.1	255	2.23	5.27	-3.23	-12.3
BM	Bessy Mack	190	11/02/13	25.4	1288	1.98	2.53	-3.3	-13.6
BR1	Big River 1	398	04/02/13	22.7	331	2.17	4.52	-2.99	-10.5
BR2	Big River 2	398	04/02/13	22.1	353	2.37	5.24	-2.9	-9.9
Cb1	Corbett 1	306	02/02/13	25.2	467	1.90	4.01	-3.09	-11.3
Cb2	Corbett 2	325	02/02/13	26.1	423	1.34	2.32	-3.11	-11.8
Cb3	Corbett 3	327	11/02/13	26.9	419	1.55	2.42	-3.12	-11.3
FogA	Fogarty A	309	18/02/13	22.8	287	2.10	4.62	-3.01	-10.0
FogB	Fogarty B	306	18/02/13	22.9	283	2.24	3.87	-3.06	-10.9
FW	Fairy Walk	248	11/02/13	28.8	555	1.14	2.05	-3.48	-14.9
Hp	Hope	306	08/02/13	23.7	306	2.28	4.45	-2.98	-10.2
Kk	Killiekrankie	297	31/01/13	25.9	308	1.99	3.25	-3.05	-10.0
Kk	Killiekrankie	297	14/02/13	25.7	309	1.71	2.94		
Lw	Lawyers	188	30/01/13	23.2	281	2.04	8.27	-3.00	-9.6
Lw	Lawyers	188	10/02/13	23.2	279	2.49	6.02		
MS	Mongo/ Underwood	345	09/02/13	23.0	588	2.11	5.55	-3.13	-12.1
Olv	Olveston	240	01/02/13	23.2	282	2.12	4.51	-2.91	-10.7
Qu	Quashie	231	30/01/13	23.2	285	1.88	4.16	-2.95	-10.0
Qu	Quashie	231	10/02/13	23.1	285	2.11	3.50		
Sn	Sunny	15	06/02/13	27.4	1703	1.04	2.15	-2.89	-11.0
HWP1	Hot Water Pond seaward	1.0	07/02/13	40.4	49,100	0.79	1.41	2.47	-0.9
HWP2	Hot Water Pond up-valley	1.5	07/02/13	56.1	38,600	0.88	0.56	1.09	-6.5
MBV1	Belham Well 1	34	06/02/13	31.0	663	0.38	0.56	-2.92	-10.9
MBV2	Belham Well 2	29	06/02/13	31.0	630	0.56	0.97	-2.95	-11.2

breccia deposits (between 1.5 and 12 m thick), with occasional, thin (~1 m) lapilli fall and channel units. The remaining ~10 m to the 2004 drilling surface is composed of block, pumice and ash flow deposits. Since the onset of volcanic activity in 1995 the Belham valley has been inundated and infilled by remobilised pyroclastic flow and lahar deposits (Barclay et al., 2007), raising the channel surface by 10–15 m (Donnelly, 2007). This process has continued since the completion of the wells in 2004, raising the ground surface around the well housings by 0.5–1 m. The most recent deposits are composed of unconsolidated volcanic sand, with boulders and cobbles, and occasional clay and silt interbeds (Donnelly, 2007). Waters produced by the Belham wells are at 31 °C with  $\text{SEC}_{25}$  of 663 and 630  $\mu\text{S}/\text{cm}$ , respectively; the wells are maintained for back-up supply. In other respects, the Belham well waters and the springs are chemically similar (Jones et al., 2010). Jones et al. (2010) suggest that the well waters were sourced from a deeper, longer residence time aquifer than the Centre Hills springs, based on detection of a slight enrichment in Na, Mg, Si, Cl, K, Ca, Fe Rb and Sr. Jones et al. (2010) also suggest that an enrichment in  $\delta^{13}\text{C}$  may represent some hydrothermal contribution to the Belham aquifer.

A definite manifestation of the hydrothermal system exists at the coast, just north of the destroyed former capital Plymouth; the now buried Hot Water Pond (HWP). Previous studies identified seeps supplying HWP waters close to 90 °C (Chiodini et al., 1996). Chiodini et al. (1996) characterised these waters as “neutral Na-Cl type”, enriched in Ca, K, Li, B  $\text{NH}_4$ , and  $\text{SiO}_2$  and depleted in Mg and  $\text{SO}_4$  relative to sea water. The hydrothermal system on Montserrat has been the subject of some recent interest regarding geothermal energy development (Younger, 2010; Ryan et al., 2013; Poux and Brophy, 2012). HWP is considered to be a surface expression of hot upflow of the Soufrière Hills Volcano (SHV) geothermal system, concentrated at the intersection of the NW-WNW trending zone of weakness identified by Wadge and Isaacs (1988) – the Belham Valley fault system (Feuillet et al., 2010) – and a NE trending fault inferred by earthquake hypo centres (Ryan et al., 2013; HPA in Fig. 1). Recent seismological studies support the presence of such a NE-SW open fracture system in this location (Baird et al., 2015). Geothermal boreholes MON1 and MON2 (Figure 1), drilled in 2013, target this feature with reported temperatures of 230 °C and 265 °C at 2300 and 2800 m depth, respectively (Ryan et al., 2013; Ryan and Shalev, 2014).

With the analysis of CFC-11 and CFC-12 concentrations and  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  of Montserrat groundwater samples, this study adds to temperature and  $\text{SEC}_{25}$  data published in Hemmings et al. (2014). This tracer analysis allows us to distinguish different groundwater components in otherwise chemically similar waters.

## 2. Methods

Twenty-six groundwater samples from Montserrat were collected for analysis of CFC and SF6 for age dating, during a February 2013 field campaign when spring temperature and specific electrical conductivity ( $\text{SEC}_{25}$ ) were also recorded (see Hemmings et al., 2014 for  $\text{SEC}_{25}$  and temperature observations). Groundwater samples were also collected for analysis of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotopes. Twenty-two samples are from 19 springs on and around Centre Hills; two samples are from wells that

tap a confined aquifer in the Belham Valley (MBV); two further samples are from shallow (50 cm) pits dug to intercept the now buried coastal Hot Water Pond (HWP), where geothermal groundwater is expected to mix with seawater (Hemmings et al., 2014).

For reliable CFC analysis careful sample collection is essential, to avoid contamination by atmospheric air (Plummer et al., 2006). Groundwater from springs and HWP were collected through PVC tubing using a battery powered impeller pump. To minimise contact with the air, samples were collected as close to the spring emanation point as possible and upstream of any water treatment (chlorination). A motor speed controller was devised to allow pumping at reduced flow rates in the low flow springs and also to prevent turbulence. Three times the tubing volume was pumped before sampling at each spring site. Sample collection followed the USGS single bottle method (Plummer et al., 2006). Glass, 125 mL sample bottles with foil-lined caps were rinsed three times in the spring waters, then filled inside a 10 L bucket. The sample bottles were filled, from the base, until the bucket overflowed. Critically, the bottles were capped underwater to prevent any air contamination. An extra seal of tape was then wrapped around the caps to prevent air contamination during transit.

For sampling of the Belham Valley well waters, the procedure was modified. The MBV1 sample was taken during a pumping test; the well was pumped continuously for 30 min at  $\sim 30$  L/s before the sample was collected from the medium density polyethylene (MDPE) outflow pipe. Due to the very high discharge rate it was not possible to fill the sample bottle from the base. However, care was still taken to over fill the sample bottle and seal underwater, as above, to limit contact with the air. MBV2 is an artesian well, flowing at  $\sim 3.5$  L/s, and is piped through an MDPE pipe to a discharge point  $\sim 10$  m from the wellhead. The discharging pipe is too wide to fill the sample bottle from the base; once again care was taken to over-fill the bottle in the bucket to minimise air contact and exclude air from the sample.

Isotope samples were collected concurrently in 10 mL glass vials, and capped immediately to prevent evaporation. Waters were prepared for stable isotope analysis on an Isoprime 100 mass spectrometer using standard methods (CO<sub>2</sub> equilibration for  $\delta^{18}\text{O}$ , on-line chromium reduction for  $\delta^2\text{H}$ ). Values are expressed as permil (‰) with respect to VSMOW2 (Vienna Standard Mean Ocean Water2). Analytical precisions are  $\pm 0.1\%$  for  $\delta^{18}\text{O}$  and  $\pm 1\%$  for  $\delta^2\text{H}$ .

Bubble formation due to dissolved air in CFC samples is normal and can be corrected for during analysis (Plummer et al., 2006). However, as no significant bubbles formed in the samples collected from Monserrat, such correction was not necessary. The CFC samples were analysed at the BGS GeoEnvironmental Laboratories using gas chromatography with cryogenic preconditioning (Oster et al., 1996; Gooddy et al., 2006). The anticipated analytical precision of the technique is on the order of  $\pm 5\%$  (Gooddy et al., 2006). Duplicate samples were collected for three springs: Lawyers, Quashie and Killiekrankie. Duplicate samples were taken between 11 and 14 days apart and show percentage differences of between  $\pm 10$  and  $\pm 20\%$ . There is large discrepancy in CFC-11 concentration for the two samples from Lawyers. CFC-11 concentration in the first sample from Lawyers is significantly elevated above modern CFC-11 levels; it is therefore considered contaminated and removed from further analysis. Although the results from the duplicate samples may genuinely represent different waters at different sampling times, the other field parameters (temperature, SEC<sub>25</sub> and discharge) are the same at both sampling times. For the purposes of this study, differences between duplicate samples are assumed to represent potential sampling error.

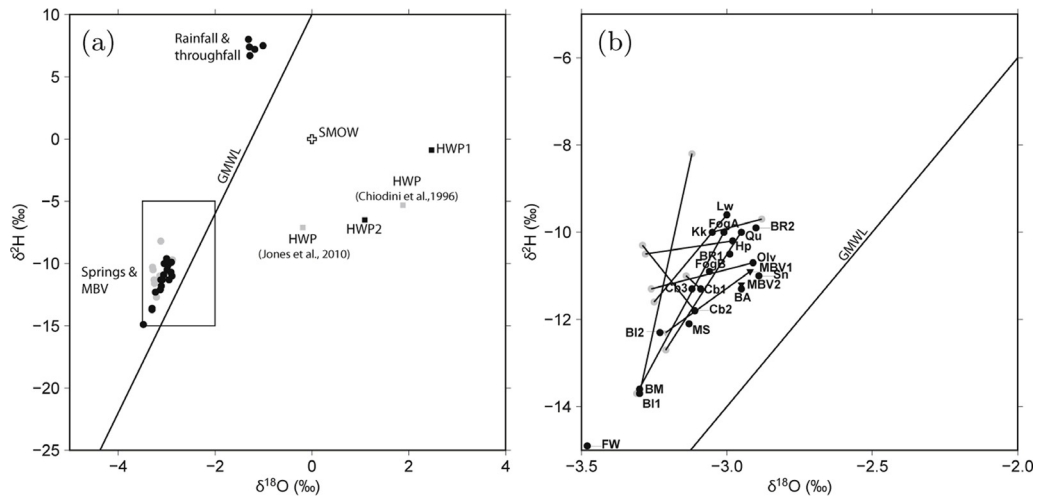
### 3. Results

The results of the CFC and  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  analysis are presented in Table 1, together with additional field parameters (temperature and SEC<sub>25</sub>).  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values for springs and the Belham Valley aquifer sampled in the two Belham Wells (MBV1 and MBV2) are tightly distributed around means of  $-3.08\%$   $\delta^{18}\text{O}$  and  $-11.3\%$   $\delta^2\text{H}$ , with standard deviations a little outside measurement precision (0.16‰ and 1.5‰, respectively). The springs lie offset from the meteoric water line, consistent with the offset of analysed rainfall and through fall samples, and also with previous analysis of spring samples collected in June 2008 (Jones et al., 2010; Fig. 4a). Fairy Walk (FW), the warmest of the springs (28.8 °C) is marginally depleted in  $^{18}\text{O}$  and  $^2\text{H}$ , relative to the other springs and the well waters (Fig. 4b), with  $-3.48\%$   $\delta^{18}\text{O}$  and  $-14.9\%$   $\delta^2\text{H}$ . All the spring and well waters are noticeably depleted relative to means of  $-1.21\%$   $\delta^{18}\text{O}$  and  $-7.36\%$   $\delta^2\text{H}$  for rainfall and throughfall samples collected during the same campaign. HWP samples are significantly enriched in both  $^{18}\text{O}$  and  $^2\text{H}$  relative to the springs (Fig. 4a, Table 1).

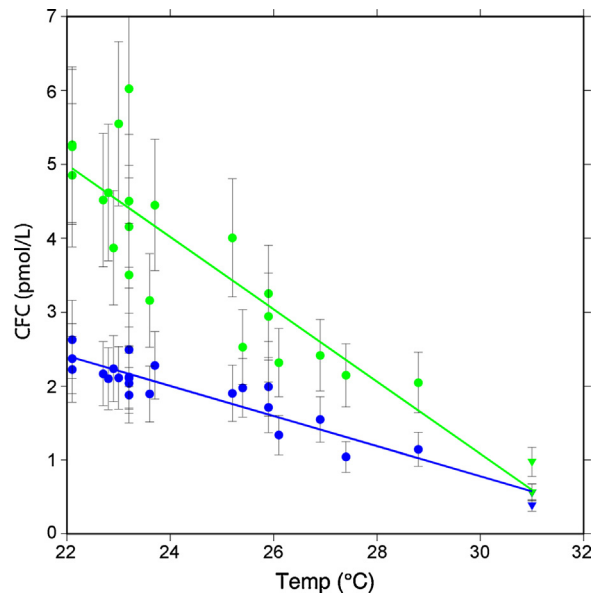
The springs and well waters all have similar isotopic signatures. However, the results from CFC analysis reveal differences, previously unrecognised. Groundwaters from the confined aquifer beneath the Belham Valley (MBV1 and MBV2) have the lowest CFC concentrations, generally indicative of older water.

There is also a clear relationship between the CFC concentrations and the temperature of the springs (Fig. 5). This relationship cannot be accounted for by simple temperature dependence of CFC solubility. CFC solubility is inversely related to temperature. However, Henry's Law predicts CFC concentrations to be just 0.55 pmol/L lower for CFC-12, and 1 pmol/L lower for CFC-11, in water equilibrated with the atmosphere at 30 °C, compared to equilibration at 20 °C. The CFC data suggests that the warmer springs on the south side of Centre Hills produce older water than the cooler springs on the west and north, with the oldest waters sampled in the artesian Belham Valley aquifer.

HWP samples also exhibit low CFC concentrations. However, these values are consistent with modern groundwater at HWP field temperatures, suggesting that sampled waters were free to exchange with atmospheric CFC, albeit at elevated temperature.



**Fig. 4.** (a)  $\delta^{18}\text{O}$  vs  $\delta^2\text{H}$  for all Montserrat water samples. Isotopic values of springs, rainfall and throughfall (black dots), collected during the same campaign, lie offset from the global meteoric water line (GMWL, black line). Values for springs and Belham Valley well waters (MBV, inverted triangles) are consistent with observations of Jones et al. (2010) (grey dots and inverted triangles). Waters sampled from Hot Water Pond (HWP, black squares) are significantly enriched relative to the springs. HWP data from Chiodini et al. (1996) and Jones et al. (2010) are also plotted as grey squares in (a). The cross marks Standard Mean Ocean Water (SMOW). The box in (a) demarks the limits for (b). (b) is focussed on the data range covered by the springs and Belham Valley well waters. Symbol format is the same as (a).



**Fig. 5.** Relationship between spring CFC concentration and temperature in Montserrat groundwater. CFC-11 data (green) follows the linear regression trend  $y = -0.49x + 15.75$ , with  $R^2 = 0.82$  ( $n = 23$ ). CFC-12 concentrations (blue) follow linear regression trend  $y = -0.21x + 6.93$ , with  $R^2 = 0.89$  ( $n = 23$ ). Triangles represent data from Belham Valley wells (MBV1, MBV2). Error bars represent an conservative error estimate of  $\pm 20\%$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

## 4. Discussion

### 4.1. Hot Water Pond

The enrichment of stable isotopes in Hot Water Pond samples, relative to the springs is expected; a positive  $\delta^{18}\text{O}$  offset from the global meteoric water line is consistent with the observations of Chiodini et al. (1996) and Jones et al. (2010), although the absolute values vary (Fig. 4a). Chiodini et al. (1996), who sampled near 90 °C thermal spring water, prior to the onset of the 1995 volcanic eruption, suggest that the offset may be the result of water–rock interaction within a high enthalpy geothermal system, or mixing with arc-type magmatic water. However, Jones et al. (2010) conclude that HWP waters, including those sampled by Chiodini et al. (1996), lie on a mixing line between seawater, with a slight  $^{18}\text{O}$  shift

due to interaction with hot rock at depth, and Belham Valley aquifer-type waters. They propose that a lack of pronounced enrichment in volcanic volatiles in HWP samples suggests negligible magmatic fluid contribution. The variation in HWP  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values between previous studies (Chiodini et al., 1996; Jones et al., 2010) and those presented here may represent temporal evolution or behavioural changes of the thermal spring. However, consistent sampling of the waters at this site is difficult due to dynamic geomorphology associated with its coastal location and recent deposition of volcanic material (Hemmings et al., 2014). Relative enrichment of the seaward sample (HWP1), with higher  $\text{SEC}_{25}$  and presumably higher seawater content compared to the hotter HWP2, suggest favour for the model of Jones et al. (2010): water on a mixing line between  $^{18}\text{O}$  rich seawater and Belham Valley aquifer-type waters. The seawater end-member in this model requires  $\delta^{18}\text{O}$  enrichment beyond the measured levels for seawater in this region ( $\delta^{18}\text{O} \approx 1.0\text{‰}$ , Schmidt et al., 1999; Sanjuan et al., 2005), supporting the hypothesis for interaction with hot-rocks at depth. However, the presence of additional geothermal or magmatic fluid components cannot be ruled-out based on this data alone; detection of such a fluid component requires a more comprehensive chemical analysis.

## 4.2. Springs and Belham Valley wells

### 4.2.1. $\delta^2\text{H}$ and $\delta^{18}\text{O}$

The isotopic composition of groundwater can be strongly affected by recharge elevation.  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotope depletion on the order of  $-0.15$  and  $-1.0\text{‰}$  per 100 m, respectively, have been recorded in a number of island settings (see compilation in Scholl et al., 1996). Scholl et al. (1996) use  $\delta^{18}\text{O}$  composition variations between  $-6$  and  $-2\text{‰}$  to estimate recharge elevation for well and spring waters on Hawaii. The relative consistency in isotopic composition of the springs and the Belham Valley aquifer waters, presented here, suggest that these waters are derived from recharge at consistent elevations, presumably above the elevation of the springs (400 m amsl). The spring and well waters are depleted in  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  compared to rainfall and throughfall samples, collected from elevations below 250 m, during the same sampling campaign (Fig. 4a). This discrepancy is not unexpected; the isotopic composition of groundwater generally reflects the average isotopic composition of recharge. Although the relative depletion of spring waters may result from the groundwater being derived from recharge at higher elevations, this would imply an unusually high lapse rate. It is more likely that the discrepancies between isotopic signatures of groundwater and rainwater are due to temporal variations in the isotopic balance of rainfall and recharge (Clark and Fritz, 1997). Schol et al. (2009) identified different isotopic signatures for different rainfall types in Puerto Rico. Wet season rainfall, delivered largely by tropical easterly waves and low pressure systems, including tropical storms, was isotopically depleted compared to the predominantly orographic showers occurring in the dry season.

Spring and well waters, rainfall and throughfall samples plot offset from the global meteoric water line (Fig. 4a). A tentative local meteoric water line based on the relatively depleted springs and well waters, and the rainfall sample is defined by a gradient of 9 and an intercept around 16 ‰. This is similar to the local meteoric water line defined for Puerto Rican GNIP stations above 300 m elevation (slope of 8.5, intercept around 16 ‰, IAEA/WMO, 2015; Schol et al., 2009). It is also comparable to local meteoric water line suggested for the island of Martinique (slope of 8 and intercept of 16 ‰, Sanjuan et al., 2005).

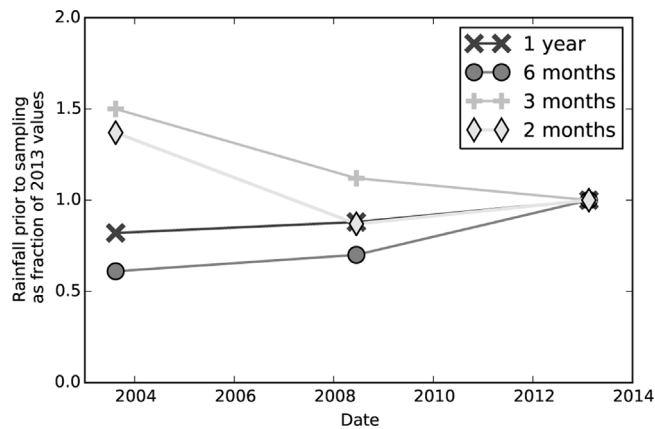
$\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values from spring and Belham Valley well samples, collected in February 2013, are consistent with the values obtained by Jones et al. (2010) in June 2008 (Fig. 4b). Jones et al. (2010) attributed differences between waters sampled in June 2008 and August 2003 (Davies and Peart, 2003) to secular or seasonal variations. Rainfall data from Monserrat (provided by Monserrat Utilities Ltd., MUL) reveal that the depth of precipitation was slightly reduced in the year and six months prior to the August 2003 sampling by Davies and Peart (2003) compared to the respective time periods prior to the 2008 sampling by Jones et al. (2010), which itself was drier than prior to the 2013 sampling in this study. However, the quarter-year, and two-month period immediately preceding the 2003 sampling was significantly wetter than the respective periods prior to both the 2008 and 2013 sampling (Fig. 6). From the isotope surveys of Davies and Peart (2003) and Jones et al. (2010) it was not clear if the isotopic variations in groundwater are seasonal or related to longer term changes. The addition of the new  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  data presented here suggest that consideration also needs to be given to shorter timescale variations in the isotopic balance of groundwater, on the order of 2–3 months.

The relative depletion in isotopic values of the spring waters, compared to the dry season point samples of rainfall and throughfall presented here, may represent a recharge bias towards wet season recharge. However, confirmation of this would require further regular isotope sampling of rainfall and spring discharges.

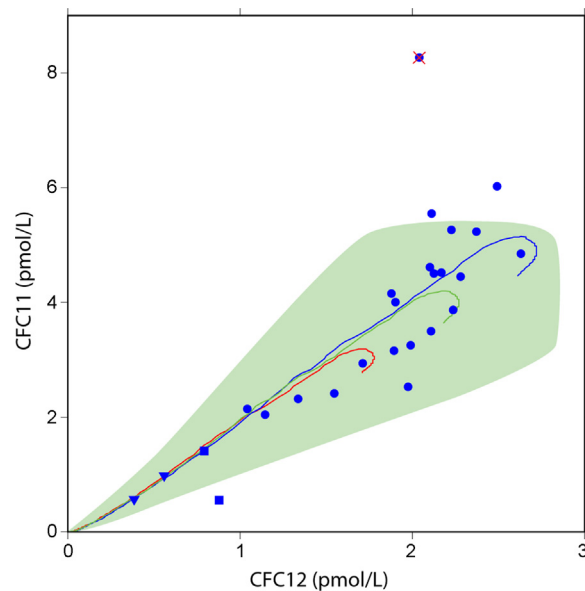
### 4.2.2. CFC-11 and CFC-12

As discussed in (Hemmings et al., 2014), recharge at elevation may occur at temperatures below the apparent ambient annual average air temperature at sea level ( $\sim 26^\circ\text{C}$ ). A maximum recharge temperature of  $22^\circ\text{C}$  can be estimated from the temperature of the springs in the northwest of Centre Hills. This is in-line with estimated air temperatures, due to adiabatic cooling, at  $\sim 600$  m (amsl) (Blume, 1974). Assuming a recharge temperature of  $22^\circ\text{C}$  the majority of the samples contain CFC concentrations higher than the current atmospheric CFC level (17 samples for CFC-12, 16 samples for CFC-11). Sixteen samples for CFC-12 and 14 samples for CFC-11 are still higher than would be expected for peak atmospheric concentrations in the early 1990 and the early 2000, respectively. Three major scenarios can produce CFC concentrations that are apparently higher than modern atmospheric concentrations:



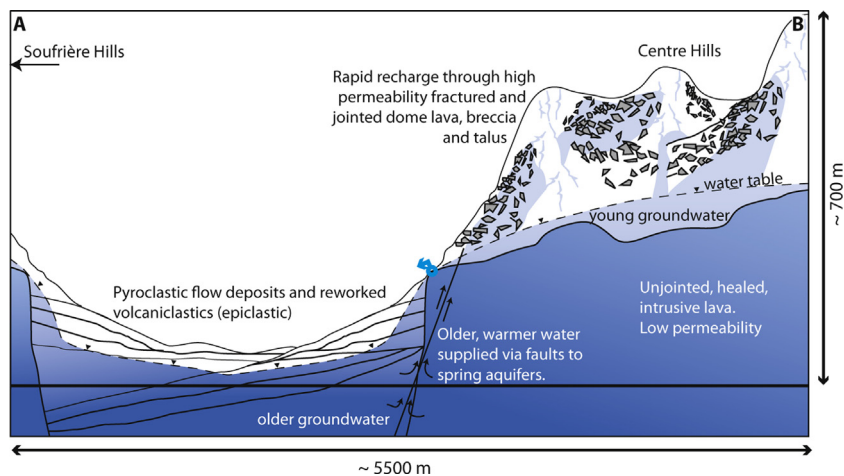


**Fig. 6.** Rainfall for the one year, six, three and two months prior to 2003 and 2008 surveys of [Davies and Peart \(2003\)](#) and [Jones et al. \(2010\)](#) as a fraction of the rainfall over the same period prior to the 2013 sampling.



**Fig. 7.** Cross-plot of CFC-12 vs CFC-11. Blue dots are results from Montserrat springs, triangles are from Belham Valley wells, and squares from Hot Water Pond. The red crossed dot is the suspected contaminated Lawyers sample. The red line represents the historical equilibrium curve for groundwater CFC concentration at recharge temperature of 22 °C blue at 12 °C and green at 16 °C. The shaded green area marks the range CFC concentrations that are within error ( $\pm 20\%$ ) of the equilibrium curve at 16 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

1. Sample contamination from local CFC source. Contamination often results in an excess of one CFC relative to the other ([Höhener et al., 2003](#); [Darling et al., 2012](#)). An example of a potentially contaminated sample is the first sample from Lawyers spring, with a markedly elevated CFC-11 concentration ([Fig. 7](#)). However, the contamination source is unclear. There are no settlements and very little human activity around or above the springs. The other samples do not appear to demonstrate significant contamination.
2. Significant excess air within groundwater. Excess air ([Heaton and Vogel, 1981](#)) is caused by the trapping of air within pore spaces below the water table due to fluctuations in water level. Excess air concentrations in most aquifer environments are  $< 5 \text{ cm}^3/\text{L}$  (Standard Pressure and Temperature, STP) but may be significantly higher in fractured hard-rock aquifers ([Wilson and McNeill, 1997](#); [Manning and Caine, 2007](#)). The relative concentration changes in dissolved gases due to excess air are in inverse proportion to their solubility. The CFCs, which are relatively soluble, would for example require an excess air contribution of  $\sim 10 \text{ cm}^3/\text{L}$  (STP) to raise concentrations by 10% ([Darling et al., 2012](#)).
3. Overestimation of recharge temperatures. The solubility of CFC in water is inversely proportional to temperature. For example the CFC concentration in water in equilibrium with the atmosphere at 10 °C is 4.98 pmol/L for CFC-11 and 2.85 pmol/L for CFC-12; at 20 °C the concentrations are 3.02 and 1.83 pmol/L, respectively. Clearly, overestimating the recharge temperature can lead to systematic misinterpretation of CFC concentrations.



**Fig. 8.** An update of Type 1 conceptual model (Fig. 3a). A schematic cross-section between A and B, with a southern Centre Hills spring supplied by both young cool meteoric waters (light blue), and older warmer waters (dark blue) from depth. White regions represent the unsaturated material. Sea level is marked by a thick horizontal black line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The cross-plot of CFC-11 versus CFC-12 (Fig. 7) demonstrates that both CFC-11 and CFC-12 concentrations are “over modern” for a number of samples, for recharge temperatures of 22 °C, assuming no excess air correction is required. If lower recharge temperatures are assumed, the CFC concentrations of these “over modern” samples are closer to current or peak atmospheric concentrations. For example, a recharge temperature of 12 °C could explain the CFC-12 concentrations in all the samples, although a few of the CFC-11 values are still high, but within error. Allowing for errors in the analysis of  $\pm 20\%$  a recharge temperature of 16 °C can fit the CFC data. Sixteen degrees celsius is significantly lower than the apparent ambient air temperature, even with elevation adjustment.

A potential hypothesis for recharge occurring at such low temperatures is rapid infiltration to a saturated zone before rainwater reaches thermal equilibrium. With a thick vadose zone, as is expected on Montserrat, such a saturated zone may be represented by shallow saturated compartments. Cascade and saturated channel flow between sequential compartments could potentially buffer the recharging water from CFC re-equilibration with the unsaturated zone, preserving the low temperature concentrations in the waters that recharge the regional aquifer, and eventually emanate from the springs. Although this mechanism is not tested here, in terms of the relative equilibration and diffusion times for temperature and CFCs in infiltrating rainwater, the notion of saturated compartmental flow in volcanic settings has been suggested before (Ecker, 1976).

By comparing CFC-11, CFC-12 and SF6 concentrations it can be possible to distinguish between piston flow mechanism and mixing of different aged groundwaters (Goody et al., 2006). In the absence of SF6 data and with the uncertainties in recharge temperature and excess air described above, it is not possible to ascribe a definitive flow mechanism or age to the Montserrat spring waters. Assuming piston flow, a recharge temperature of 16 °C, and recharge elevation above the elevation of the springs, for example, 500 m amsl, the CFC concentrations in the oldest waters (Belham Valley, MBV1 and MBV2) provide recharge date estimates of 1970 and 1967, respectively, assuming no old CFC-free water is admixed. Uncertainties in recharge temperatures shifts these estimates by a maximum of  $\pm 2$  years, for temperature ranges between 12 °C and 22 °C. Recharge elevation uncertainty has a negligible effect on the estimated groundwater age.

The working hypothesis presented in Hemmings et al. (2014) suggested a contribution of deeper warmer water to explain the anomalously high temperatures in the southern Centre Hills springs. The CFC analysis presented here supports this hypothesis; the warm spring waters represent mixtures of deeper older groundwater and the young meteoric water that supplies the western and northern springs. The SW-NE alignment of the warmer and older southern Centre Hills springs is suggestive of upflow from depth along a permeable fault and fracture network. Such a network may be an extension of, or related to, the NE trending fault alignment associated with HWP and the geothermal targets (HPA in Fig. 1), as described by Ryan et al. (2013).

If one assumes linear binary mixing between end-members, Belham well-type waters (~45 ya) and Bottomless Ghaut waters (modern), the relative contributions of young (cold) and old (warm) waters suggested by temperature, and CFC-11 and CFC-12 are in reasonable agreement. The estimated contribution of older, warmer water at the high discharge Killiekrankie spring is between 40 and 45%. At Fairy Walk, the warmest Centre Hills spring, up to 65–75% may be from the deeper, older and warmer water source. The relative depletion in  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  at Fairy Walk compared to the other groundwater samples may indicate some steam contribution to this spring. However, a complete geochemical survey would be required to definitively elucidate any signature of a steam component.

The assumption here is that the older, warmer end-member is represented by the Belham Valley well-type water. Although the CFC data reveals that the oldest sampled groundwaters on Montserrat were from the confined Belham Valley

aquifer, we cannot rule-out the possibility that these waters are themselves intermediate. If the warmer groundwater end-member contributing to the southern Centre Hills springs is even older and warmer than the Belham Valley well waters, a lower volume contribution would be needed to produce the temperature and CFC results highlighted above.

An updated conceptual model, based on Fig. 3a, incorporating the additional constraints provided by combined temperature,  $\text{SEC}_{25}$ , CFC and isotope data is illustrated in Fig. 8. This model describes flow of recharging meteoric water through saturated fractures and breccia compartments within the high permeability vadose zone in the central portion of the Centre Hills complex. These cool, young waters feed the springs at elevations between 200 and 400 m amsl, on the flanks of Centre Hills. Aquifers associated with the southern warmer springs receive additional contributions of older waters from deeper warmer aquifers, supplied via high permeability fault or fracture networks.

## 5. Conclusions

The consistency of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values for Montserrat's Centre Hills springs and the Belham Valley confined aquifer waters indicates groundwaters are derived from similar recharge elevations. However, CFC-11 and CFC-12 analysis reveals age differences in otherwise similar groundwaters. Low CFC concentrations in warm ( $31^\circ\text{C}$ ) waters from within the confined Belham Valley well aquifer are suggestive of water ages of  $\sim 45$  years, if no old, CFC-free water is present. While CFC concentrations springs are indicative of predominantly young, modern groundwater. Lower CFC concentrations in the warmer springs, identified in Hemmings et al. (2014), suggest a contribution from older, warmer waters, probably supplied via faults and fractures from deeper aquifers. Temperatures and CFC concentrations indicate potential contributions of up to 75% for the warmest spring on Centre Hills and supply rates of up to 8 L/s to the highest yielding spring.

The CFC and  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  data also provide insights into the groundwater recharge regime on the island. High CFC concentrations in the northern and western springs can be explained by rapid infiltration of cool (high CFC concentration) rainfall into saturated compartments, with transport through the vadose zone to the phreatic zone dominated by compartment flow. Transport within saturated compartments reduces CFC equilibration with vadose zone air and allows relatively rapid movement through the unsaturated zone, providing young water to the springs. Groundwaters are depleted in  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  relative to rainfall and throughfall samples. High frequency isotopic analysis of groundwaters and rainfall is necessary to explore potential spatial and temporal variations of groundwater recharge. Such a study would reveal more detail of the residence time of the young spring waters, as well as the likely response to changes in recharge patterns.

## Conflict of interest statement

None declared.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ejrh.2015.08.003> These data include Google maps of the most important areas described in this article.

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