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An assessment of the applicability of global CFC and SF_6 input functions to groundwater dating in the UK

Groundwater Management Programme

Internal Report IR/06/085

BRITISH GEOLOGICAL SURVEY

GROUNDWATER MANAGEMENT PROGRAMME
INTERNAL REPORT IR/06/085

An assessment of the applicability of global CFC and SF_6 input functions to groundwater dating in the UK

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Keywords

CFCs, SF_6, groundwater dating.

Bibliographical reference

DARLING W G AND GOODDY D C. 2006. An assessment of the applicability of global CFC and SF_6 input functions to groundwater dating in the UK. *British Geological Survey Internal Report*, IR/06/085. 21pp.

Keyworth, Nottingham British Geological Survey 2006

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Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6) are increasingly being used to date recent groundwater components. While these trace gases are generally well-mixed in the atmosphere, there is evidence that local atmospheric excesses (LAEs) exist in some areas of the world, associated with urbanisation and thereby complicating the interpretation of data derived from groundwater studies. Previous research has shown that the soil acts as a low-pass filter for short-term atmospheric trace gas fluctuations, so that soil gases should yield integrated evidence for LAEs if present. To investigate the possible existence of LAEs in the UK, mixing ratios of CFC-11, CFC-12 and SF_6 have been measured in soil gases from sites within the UK's two largest cities (London and Birmingham) and a third urban area, Bristol. While there was some evidence of excesses, most of the measured mixing ratios for CFC-12 and SF_6 were less than 10% above the current northern hemisphere atmospheric mixing ratio (NH-AMR) values. CFC-11 was more variable, but usually less than 20% above the NH-AMR value. Surface waters were also investigated as possible trace-gas archives but were much less consistent in performance. Overall, given the errors associated with trace-gas groundwater dating (e.g. precision of measurement, assumptions about recharge temperature, excess air, contamination or degradation in the subsurface), there is little justification for factoring in the minor LAEs found in this study to urban or peri-urban groundwater investigations, and accordingly the use of CFC and SF_6 input functions based on the NH-AMR curves appears to be justified for the UK.

1 Introduction

Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6) are increasingly being used to date recent groundwater components (Busenberg and Plummer, 1992; Cook et al. 1996; Oster et al., 1996: Busenberg and Plummer, 2000). Their use in this role depends critically on the input function, i.e. the atmospheric mixing ratio over time for the individual gases (Plummer and Busenberg, 1999). Observations by the worldwide network of atmospheric monitoring stations indicate that the gases are well-mixed in the atmosphere (Maiss and Brenninkmeier, 1998), and therefore a single set of input functions for each gas should in theory suffice for groundwater investigations worldwide.

However, local atmospheric excesses (LAEs) due presumably to industrial activity have been observed by some researchers. For example, Oster et al. (1996) and Ho et al. (1998) found CFC excesses in south-west Germany and the New York metropolitan area respectively, while SF_6 excesses have since been measured in the same areas (Fulda and Kinzelbach, 2000; Santella et al., 2003). On the basis of these measurements, several studies have proposed using input functions raised by up to 60 % above the global average. Clearly, then, it is important for groundwater dating studies in the more-populated areas of the world to be aware of this possibility, and if possible to address it. The work reported here is concerned with the situation in southern Britain, an area with a relatively high population density where CFCs and SF_6 are increasingly being used for groundwater dating (Bateman 1998; Darling et al., 2005; Gooddy et al., in press; Morris et al., in press).

2 Background

2.1 THE IMPORTANCE OF ASSESSING LOCAL ATMOSPHERIC MIXING RATIOS

The effects of LAEs on water dating vary with each of the gases, but can have a major impact. Figure 1 shows plots of the groundwater concentrations calculated from the northern hemisphere atmospheric mixing ratio (NH-AMR) curves (http://water.usgs.gov/lab/software/air_curve/), and a notional 50% excess from the beginning of emissions. Both assume a recharge temperature of 10°C, which is close to the annual average air temperature for lowland Britain.

It is apparent that while age differences are very small in waters recharged around 50 years ago, in recent waters they are profound. Taking the highest point on each of the NH-AMR curves, the same groundwater concentration would be indicating differences of about 9 yr (SF_6), 12 yr (CFC-11), and 20 yr (CFC-12). Thus if an LAE is present in an area, it must be taken into consideration for groundwater dating purposes. Not only can it help to correct the water age, but can also be used to extract useful information from waters that would be regarded as ‘over modern’ — i.e. contaminated — using the NH-AMR.

The intensive long-term atmospheric monitoring which would otherwise be required to determine the magnitude of an LAE can be avoided by sampling soil air. Studies have shown that the soil acts as a low-pass filter for variations in atmospheric gas mixing ratios (Dörr and Münnich, 1990; Oster et al., 1996; Santella et al.; 2003), meaning that it preserves within certain limits the average atmospheric signal in the sampling area.

2.2 APPROACH OF THE PRESENT STUDY

Southern Britain contains the UK’s two largest cities, London (population 7 million for Greater London) and Birmingham (1 million, though the remainder of the West Midlands Conurbation extending to the NW and SE of the city contributes a further 4 million people). As such, they are obvious areas to seek evidence of atmospheric excesses. A third city, Bristol (0.4 million) was chosen for comparison. The location of each city is shown in Figure 2.

While there are some variations in topography across each city, none of the areas is in a pronounced basin where stagnant atmospheric conditions might prevail. The predominant wind direction for each of the urban areas is SW to WSW (Chandler and Gregory, 1976). This means that Bristol is most ‘upwind’, while Birmingham and London are at comparable ‘effective distances’ from the ocean of approximately 200 km. In neither case are there major industrial areas supervening.

In this study, the approach to quantifying possible atmospheric excesses has focused mainly on the soil atmosphere. However, standing surface water bodies have also been sampled to investigate whether they are comparably valid archives. The rationale for this is that hydrogeological surveys using water dating techniques would find it more convenient to sample waters than soil gases.

Table 1 gives the locations of the sites chosen for sampling. BGS Wallingford was included as a semi-rural control site.

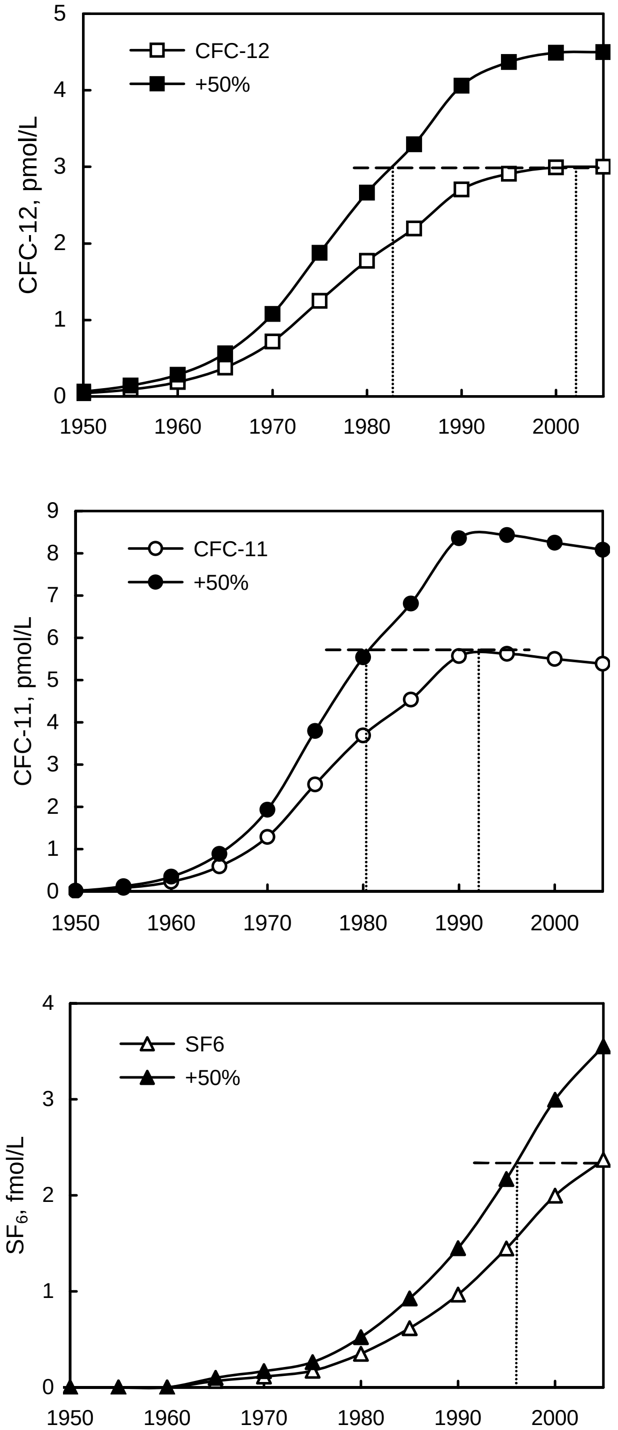

Figure 1. Plots showing the concentration of CFC-12, CFC-11 and SF_6 in air-equilibrated water at 10ºC, based on the respective NH-AMR (northern hemisphere atmospheric mixing ratio) curves over the past half-century. Also shown is the concentration curve for a 50% local atmospheric excess, and the resulting maximum difference in interpretation of water age for a particular dissolved concentration.

Table 1. Locations of sites selected for soil gas sampling in London, Birmingham and Bristol, plus the control site at Wallingford. NGR – National Grid Reference.

Site	**Site code**	**Details**	**NGR**		**Soil geology**
			E	N	
LONDON					
Chislehurst	LN-PW	Adjacent Petts Wood NT area	545380	169285	Palaeogene sands
Epping Forest	LN-EF	Connaught Water	540515	195050	Palaeogene clay
Harrow-on-the-Hill	LN-HH	Sports ground E side of Hill	515385	187145	Palaeogene clay
Hyde Park	LN-HP	The Serpentine	527120	180250	Quaternary sands
Richmond Park	LN-RP	Pen Ponds	520535	172740	Quaternary sands
BIRMINGHAM					
Edgbaston	BM-ER	Edgbaston Reservoir	404005	286955	Quaternary sands
Kingshurst	BM-KL	Lake, Cole Valley	416550	287755	Quaternary alluvium
Sandwell	BM-SP	Swan Pool	402510	292110	Carboniferous mudstone
Shirley	BM-NR	S of Northbrook Road	412330	280080	Quaternary till
BRISTOL					
Clifton Down	BL-CD	W of Clifton Down Road	356500	173775	Carboniferous Limestone
Fishponds	BL-OP	Oldbury Park	363605	176640	Carboniferous sandstone
Hanham Common	BL-HC	Football field	363835	171275	Carboniferous sandstone
Southmead	BL-TP	Trymside Park	358185	177920	Carboniferous Limestone
WALLINGFORD					
CEH Met Site	W	Grounds of Maclean Building	461715	189800	Quaternary alluvium

3 Sampling and analysis

3.1 SAMPLING

Mature grassed parkland areas were chosen as being least likely to have suffered from industrial activities which might have given rise to contamination in the subsurface.

A stainless steel tube of approximately 8 mm o.d. and 4 mm i.d. was fitted with a disposable tip and driven into the ground by a sliding hammer to a depth where significant resistance was encountered (this varied with the nature of the soil conditions). The tube was then extracted by 20–30 mm to create a small void into which soil gas could diffuse. After purging atmospheric air from the steel tube and the connecting flexible tubing with a hand vacuum pump, the soil gas was sampled into a pre-evacuated 300 ml glass bulb. At each site two or more tubes were driven in 1–2 m apart to assess how representative the individual samplings might be.

Lake waters were sampled by pumping with a 12 V ‘caravan’ type pump immersed to a depth of at least 0.5 m below surface. The sample water was collected and stored using the bottle-within-can method described by Oster (1994).

Atmospheric spot samples were also taken at most sites, using the same type of 300 ml pre-evacuated glass bulbs as were used for the soil gas sampling.

Details of the sampled sites are provided in Table 1, while locations are shown in Figure 2.

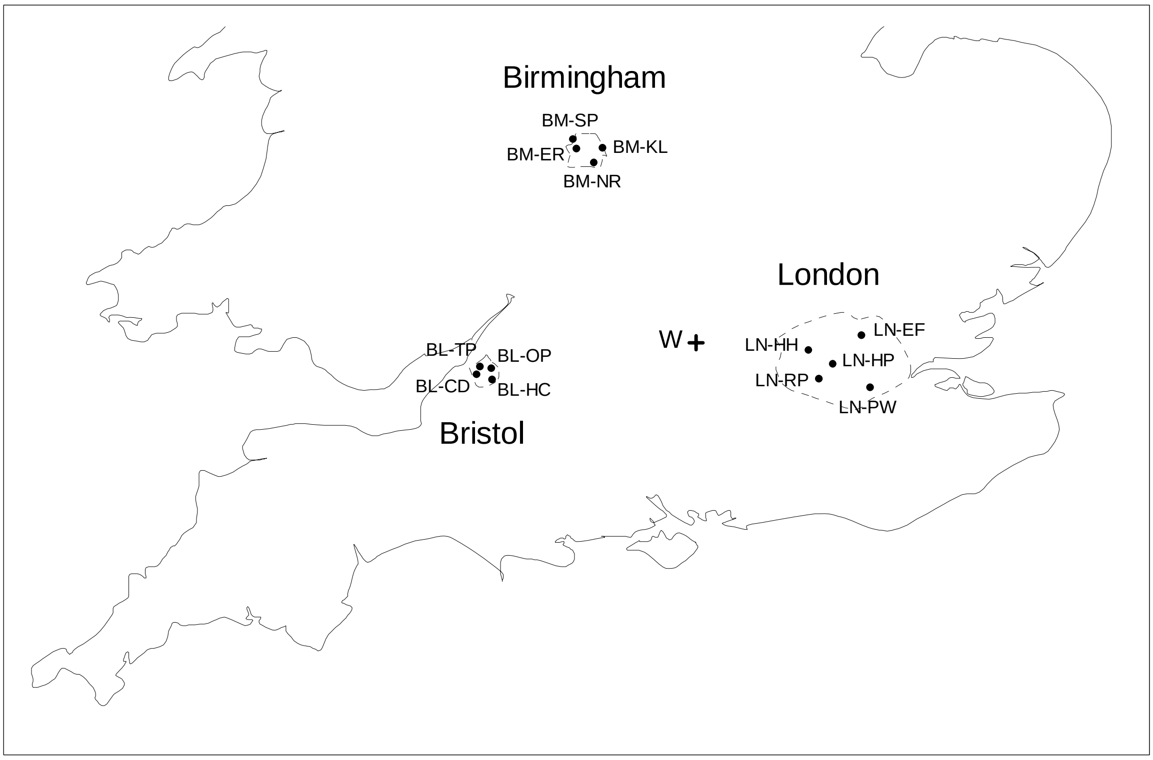

Figure 2. Map of southern Britain showing the approximate location of the sampling sites in relation to urban boundaries (see Table 1 for fuller site information). W – location of BGS Wallingford. Site codes as in Table 1.

3.2 ANALYSIS

Soil gas samples were analysed for CFCs and SF_6 by cryotrapping onto porous-polymer-packed sample loops followed by quantification by gas chromatography using an electron capture detector (ECD). The method used was based largely on the approach of Bullister and Weiss (1988). To check how representative the samples were of the soil atmosphere, CO_2 concentrations were measured by gas chromatography using a thermal conductivity detector (TCD), and $\delta^{13}C$-CO_2 values were determined by isotope ratio mass spectrometry.

Waters were measured for CFC and SF_6 concentrations by stripping out the dissolved gases using an N_2 purge before cryotrapping as described above, again based on the methods of Bullister and Weiss (1988).

Both CFC and SF_6 analyses were calibrated back to an air standard collected at the Mace Head Atmospheric Research Station of NUI Galway, Ireland.

4 Results

4.1 ATMOSPHERIC GASES

Results for atmospheric gases are given in Table 2, together with the end-2005 NH-AMR values (http://water.usgs.gov/lab/software/air_curve/). All the CFC-12 values lie between 100 and 114% of the NH-AMR value of 539 pptv (parts per trillion by volume). Most CFC-11 values fall in the range 101–119%, but two Birmingham sites (BM-KL and BM-NR) are approximately twice as high as the NH-AMR value of 250 pptv. Most SF_6 values are between 96 and 112% of the NH-AMR value of 6.1 pptv, but two sites exceed this by one-third (LN-RP) and one-and-a-half times (BM-KL). The BM-KL atmospheric sample was therefore the only site where two of the three trace gases were significantly elevated above NH-AMR values.

4.2 SOIL GASES

The results of the soil gas sampling are also given in Table 2. The CO_2 concentrations (0.4 to 5.3 %) and $\delta^{13}C$ values (–25 to –30 ‰) indicate that in all cases except one, LN-EF (ii), the gas extracted consists predominantly of soil air rather than a mixture with inadvertent atmospheric contamination (CO_2 <0.04 %, $\delta^{13}C$ ~8 ‰).

Intra-site trace gas measurements were generally in good agreement. For CFC-12, 13 out of 14 sites yielded measurements within 5%, the exception being BL-TP (6.2%). For CFC-11, seven out of 14 sites were within 5%, and a further 5 within 10%. One of the two remaining sites was within 13% (LN-HH), though BL-TP was very poor. For SF_6, nine out of 14 sites were within 5%, a further three sites within 10%, and one site (LN-EF) at 11%.

The measured values for CFC-12, CFC-11 and SF_6 are shown in graphic form in Figure 3. As a result of the usually good intra-site agreement, the results from each site have been averaged and are shown in relation to the end-2005 NH-AMR. On each plot the +10% value is also shown, with an additional +20% for CFC-11 only. For CFC-12, one site is just below atmospheric, 12 out of 14 sites lie within the +10% band, and one is elevated at +33% (BL-TP). For CFC-11, two sites are just below atmospheric, six sites are within +10%, and another three within about +20%. A further three sites are elevated by approximately one-third, while there is an extreme enrichment of over four times for BL-TP. For SF_6, 13 out of 14 sites are within ±10% of atmospheric, the remaining site (LN-EF) being just in excess at +10.5%.

4.3 SURFACE WATERS

Results from the surface water sampling are provided in Table 3. No samples were obtained from Bristol because topographic and geological conditions preclude the existence of sizeable lakes within the city. However, all Birmingham and London soil sampling sites have adjacent water samples except for LN-PW in SE London (Figure 2). Also provided in the table are the theoretical concentrations of the CFCs and SF_6 in air-equilibrated water at 10°C (AEW-10), the approximate annual average temp for southern Britain, based on the NH-AMR values for end-2005.

Each of the eight surface water sites has CFC compositions in excess of AEW-10. All CFC-12 values fall within +50%, as do three-quarters of the CFC-11 values. By contrast, three-quarters of the SF_6 values are below the AEW concentration, in one case (LN-HP) down to 58%.

Table 2. Results of soil gas sampling at the studied sites, including analyses of CFC-12, CFC-11, SF_6, CO_2 and $\delta^{13}C$-CO_2. Also included are values for the CFCs and SF_6 from atmospheric samples collected at the same site.

Site	**Site code**	**Date**	**Atmosphere**			**Soil sample**					
			CFC-12	**CFC-11**	**SF_6**	**Depth**	**CFC-12**	**CFC-11**	**SF_6**	**CO_2**	**$\delta^{13}C_{CO2}$**
			pptv	**pptv**	**pptv**	**mbgl**	**pptv**	**pptv**	**pptv**	**% vol**	**‰ PDB**
LONDON											
Chislehurst	LN-PW	15-Mar-06	550	253	6.58	0.60	539	251	6.25	0.39	-26.5
						0.65	532	242	6.13	0.71	-27.2
Epping Forest	LN-EF	15-Mar-06	550	253	6.87	0.25	570	342	6.36	0.62	-27.8
						0.30	547	335	7.14	0.07	-
Harrow-on-the-Hill	LN-HH	10-Mar-06	-	-	-	0.70	577	350	6.21	0.82	-27.5
						0.70	584	309	6.16	0.70	-27.1
Hyde Park	LN-HP	10-Mar-06	539	254	6.40	0.70	546	269	6.07	0.62	-27.8
						0.70	555	261	6.21	0.78	-25.3
						0.70	571	271	6.08	0.83	-25.0
Richmond Park	LN-RP	15-Mar-06	544	267	8.34	0.80	548	232	6.93	1.94	-27.1
						0.75	552	254	6.37	2.03	-26.5
BIRMINGHAM											
Edgbaston	BM-ER	28-Mar-06	557	269	6.35	0.65	574	279	6.02	2.50	-25.9
						0.50	577	287	6.63	2.49	-26.5
Kingshurst	BM-KL	28-Mar-06	594	548	15.72	0.65	577	304	6.17	4.15	-29.2
						0.35	584	301	5.96	3.98	-29.1
Sandwell	BM-SP	28-Mar-06	562	297	6.09	0.30	561	349	6.68	3.28	-30.2
						0.35	566	330	6.24	0.47	-29.1
Shirley	BM-NR	28-Mar-06	581	477	6.61	0.65	562	276	6.39	0.89	-28.1
						0.50	567	252	6.45	0.51	-28.9
						0.75	553	254	6.46	0.41	-27.6
BRISTOL											
Clifton Down	BL-CD	23-Mar-06	611	281	5.89	0.35	598	275	6.07	0.45	-25.2
						0.45	587	257	6.03	0.51	-25.2
Fishponds	BL-OP	23-Mar-06	602	253	6.04	0.35	585	220	6.03	3.16	-28.5
						0.50	578	235	5.97	1.14	-28.2
Hanham Common	BL-HC	23-Mar-06	614	289	6.28	0.55	570	285	5.73	1.92	-26.4
						0.70	587	292	5.80	0.38	-24.6
Southmead	BL-TP	23-Mar-06	596	252	6.11	0.55	735	2251	6.43	5.28	-29.3
						0.65	692	458	6.20	2.67	-29.3
WALLINGFORD											
CEH Met Site	W	06-Feb-06	547	262	6.41	0.70	538.5	249.5	6.76	0.60	-26.7
						0.70	548.2	259.6	6.29	0.68	-26.6

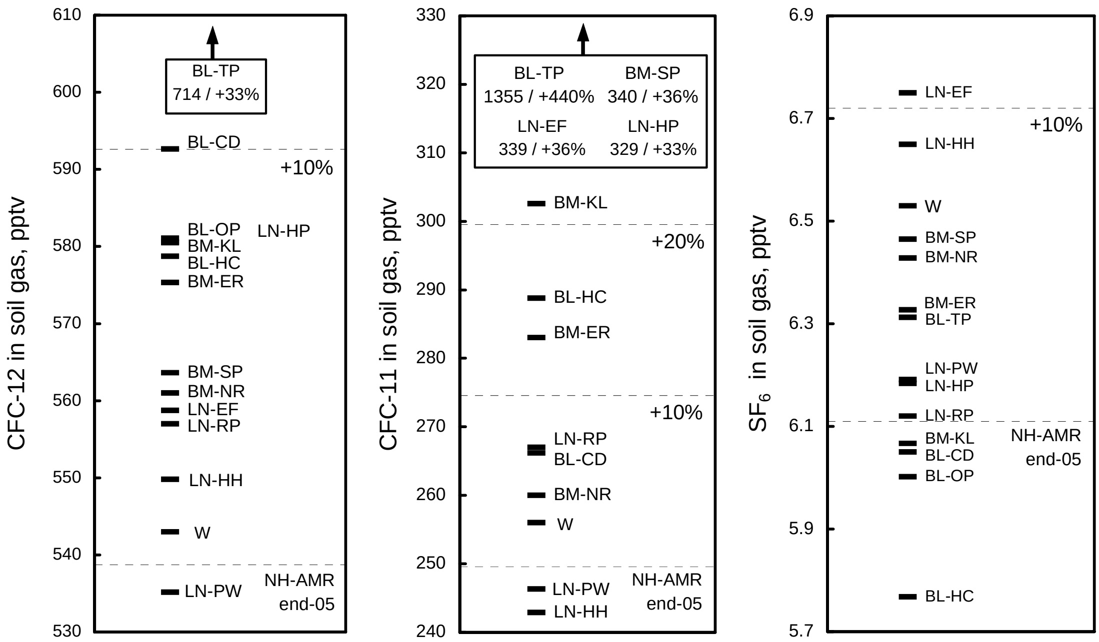

Figure 3. CFC and SF_6 compositions of soil gas samples from the studied sites. Also shown are the NH-AMR (northern hemisphere atmospheric mixing ratio) values for the end of 2005, with 10 and 20% additions as appropriate. Site codes as in Table 1.

Table 3. Concentrations of the CFCs and SF_6 dissolved in lake waters adjacent to the soil sampling sites in London and Birmingham. Also shown is the calculated composition of air-equilibrated water (AEW) at 10°C based on the NH-AMR (northern hemisphere atmospheric mixing ratio) for end-2005.

Site	Site code	Surface area	Temp	CFC-12	CFC-11	SF_6
		ha	°C	pmol/l	pmol/l	fmol/l
LONDON						
Epping Forest	LN-EF	5	6.2	3.82	5.81	3.03
Harrow-on-the-Hill	LN-HH	2	6.2	3.14	5.40	2.33
Hyde Park	LN-HP	16	6.0	4.11	7.56	1.48
Richmond Park	LN-RP	5	6.0	3.79	6.32	1.75
BIRMINGHAM						
Edgbaston	BM-ER	25	7.7	3.66	14.70	2.36
Kingshurst	BM-KL	5	10.0	4.08	7.30	6.74
Sandwell	BM-SP	5	8.5	3.79	6.27	2.14
Shirley (Olton Res.)	BM-NR	10	9.2	4.47	8.90	2.19
WATER IN EQUILIBRIUM WITH THE ATMOSPHERE						
NH-AMR end-2005	AEW		10	2.97	5.27	2.57

5 Discussion

The atmospheric gas samples, though necessarily only a ‘snapshot’ of conditions on the day of sampling, were for the most part close to the current NH-AMR figures. On each of the sampling days there were breezy or windy conditions, which would tend to dilute and disperse any plumes containing elevated proportions of one or more of the three trace gases. It is noteworthy therefore that the Birmingham site BM-KL had CFC-11 and SF_6 values more than twice as high as the NH-AMR values.

The soil gases were generally consistent, particularly for CFC-12 and SF_6 where nearly all values were within 10% of the current NH-AMR value. CFC-11 was more wayward but there was only one very high value, from BL-TP, also the only site with significantly raised CFC-12, suggesting that in this single instance the site selection was flawed, e.g. there may have been landfilling or creation of made ground in the vicinity which has contributed to the elevated CFCs. There was little or no evidence from the BM-KL site for the elevated values found in the atmosphere.

Prevailing wind direction and industrial history lead to the empirical prediction that LAEs should be developed least in Bristol and most in Birmingham. Figure 4 shows plots of measured atmospheric versus soil gas compositions for each of the three gases, with the cities differentiated. For CFC-12, London is least enriched and Bristol the most. For CFC-11, the picture is less clear but London shows the least excesses in atmospheric or soil gas. For SF_6 Bristol is lowest, while London is highest in soil gases. Thus no overall pattern emerges; the data in Table 2 suggest no pattern either within the individual cities, although the sampling density clearly cannot be definitive in this regard. The semi-rural control site (Wallingford) as might be expected gives results close to the NH-AMR values for the CFCs, with SF_6 being only slightly elevated by comparison.

Consideration of the surface water data from London and Birmingham reveals that the variation exceeds that of the soil gases from neighbouring sites (Figure 5). While dissolved CFC-12 gives the most consistent results, they are almost always enriched relative to soil gases. This is perhaps not especially surprising; different residence times, temperature cycling effects and surface or subsurface ingress of small amounts of pollution may all combine to invalidate the use of a single set of AEW values. Perhaps the most notable feature of the water samples is that SF_6 tends to be significantly below the AEW-10 value. The reason for this remains problematic, for instance, SF_6 is not known to suffer decomposition in lake waters.

Studies of urban and peri-urban groundwaters have often encountered ‘over-modern’ concentrations of the CFCs (e.g. Hohener et al., 2003; Morris et al., 2005: Morris et al. in press) and, as mentioned in the introduction, some researchers use the LAE concept to extract dates from waters which they regard as otherwise uncontaminated. While there may conceivably be regions of the world where this is a valid approach, the results reported here lead to the conclusion that it cannot be justified in present-day Britain, and that it is therefore more prudent to regard CFC excesses as the results of variable point-source contamination. Although this inevitably hinders the understanding of urban groundwater systems in terms of ‘true’ residence time, the CFCs still have some value as tracers. SF_6 tends to suffer very much less than the CFCs from contamination, so remains a potential dating agent.

A caveat to the above view is that LAEs may have existed in the past when the use of CFCs was uncontrolled. However, in the absence of any historical data for the cities concerned, this can only be speculation.

While this research finds little evidence that LAEs are a useful concept for urban groundwater studies in Britain, it does suggest that checking soil gas samples from several parkland or similar undisturbed sites in a prospective investigation area would be a worthwhile precaution. Lake water samples, on the other hand, are very much less precise guides to the possible existence of an LAE.

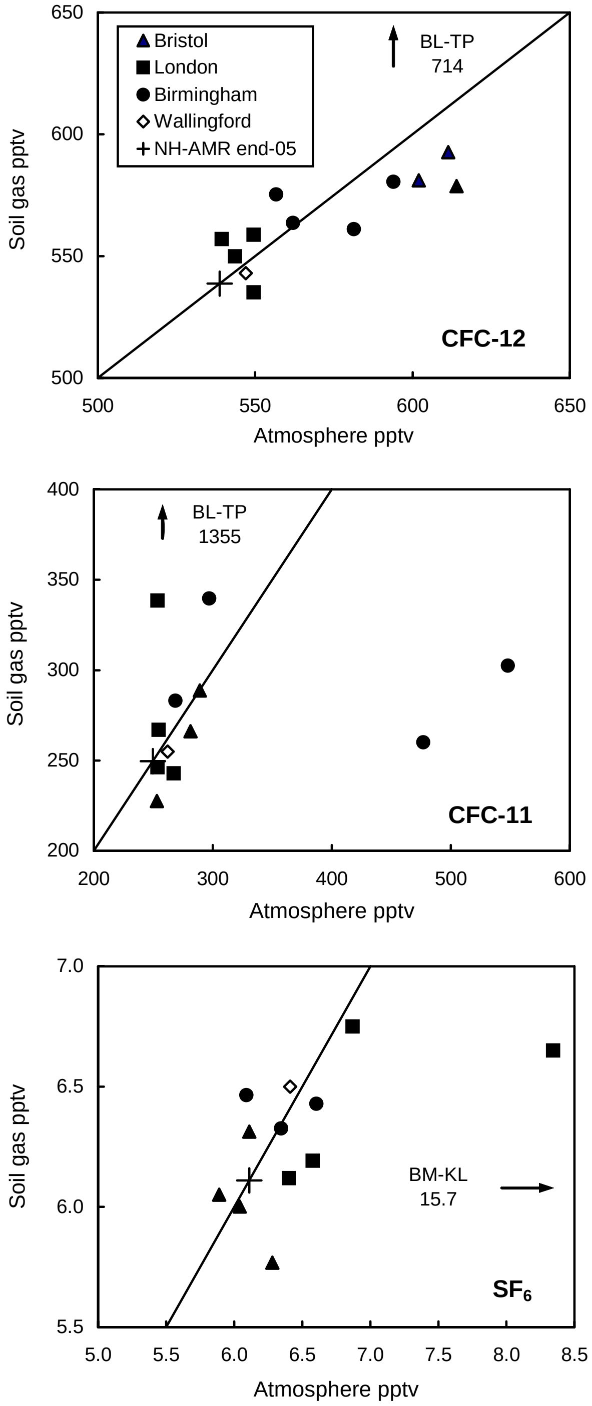

Figure 4. Averaged soil gas versus atmospheric composition for the studied sites. Also shown are the 1:1 ratio lines and the NH-AMR (northern hemisphere atmospheric mixing ratio) values for end-2005.

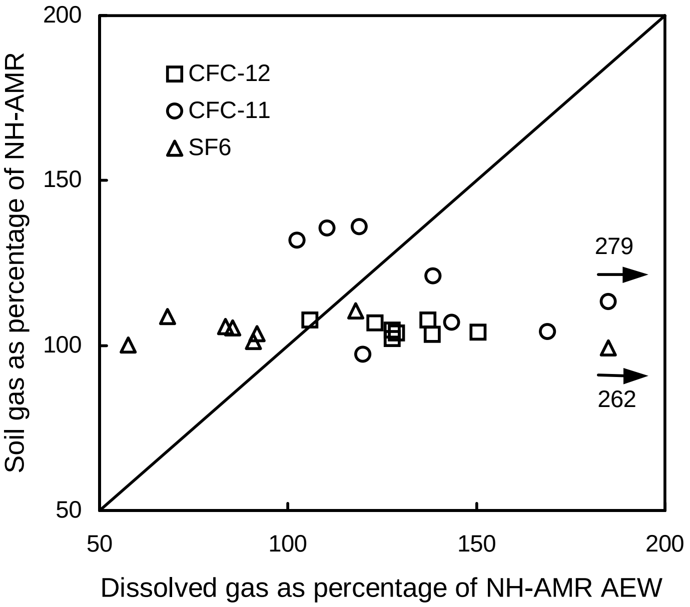

Figure 5. Soil gas versus lake water excesses in the CFCs and SF_6 for sites in London and Birmingham, based on NH-AMR (northern hemisphere atmospheric mixing ratio) values for end-2005 and assuming air-equilibrated water (AEW) at 10°C.

6 Conclusions

The possible existence of local atmospheric excesses (LAEs) has been investigated in three major British cities (London, Birmingham, Bristol) in connection with the use of CFCs and SF_6 as groundwater dating agents.

The primary approach was to measure soil gases because previous research has shown that the soil acts as a low-pass filter for atmospheric fluctuations. A secondary approach was to measure the concentration of the CFCs and SF_6 in lake waters, relating these back to notional atmospheric compositions.

In the soil gases, CFC-12 and SF_6 were nearly always close to the current northern hemisphere average mixing ratios, i.e. with excesses of less than 10%. CFC-11 was more variable, with excesses usually <20%. There was no consistent evidence for the LAE values of ≥50% proposed for some other urbanised regions of the world. In the waters, concentrations of all three gases were much more variable, rendering the interpretation of results problematic.

Overall, given the errors associated with trace-gas groundwater dating (e.g. precision of measurement, assumptions about recharge temperature, excess air, contamination or degradation in the subsurface), there is little justification for factoring in the minor LAEs found in this study to urban or peri-urban groundwater investigations, and accordingly the use of CFC and SF_6 input functions based on the northern hemisphere atmospheric mixing ratio curves appears to be justified for the UK. However, the precautionary principle suggests that a basic soil survey across any other urban area to be investigated with these dating agents would be worthwhile.

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