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

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Abstract

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, primarily associated with urbanisation and thereby affecting the interpretation of data derived from groundwater studies. Since the soil acts as a low-pass filter for atmospheric trace gas fluctuations, the possible existence of LAEs in the UK has been investigated by measuring the mixing ratios of CFC-11, CFC-12 and SF_6 in soil gases from sites within the UK's two largest cities (London and Birmingham) and a smaller 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 short-term archives of trace-gas information but were much less consistent in performance.

While the lack of significant current LAEs for SF_6 can justifiably be extrapolated to past decades, different global emission patterns mean that this is much harder to justify for the CFCs. Nevertheless, in the absence of further evidence it is concluded that the use of CFC and SF_6 input functions based on the NH-AMR curves is generally justified for the UK, with the proviso that urban groundwater investigations should not rely on the CFCs as age tracers.

Keywords: CFCs; SF_6; urban atmospheric mixing ratios; groundwater dating

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 (largely based on the five long-term ALE/GAGE/AGAGE collection stations – see http://agage.eas.gatech.edu) indicate that the gases are well-mixed in the atmosphere (Maiss and Brenninkmeier, 1998), and therefore a single input function for each gas should in theory suffice for groundwater investigations in the northern hemisphere (there is a slight lag in the southern hemisphere inputs).

However, local atmospheric excesses (LAEs) due largely to urbanisation and its associated industrial activity have been observed by some researchers. For example, Oster et al. (1996) and Ho et al. (1998) found significant CFC excesses in Germany and the New York metropolitan area respectively, while significant SF_6 excesses have since been measured in the same regions (Fulda and Kinzelbach, 2000; Bauer et al., 2001; Santella et al., 2003). On the basis of these measurements, the use of input functions raised by up to 60% above the global average has been proposed. Clearly 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 current 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., 2006; Morris et al., 2006).

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 50% increase 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 (stable isotope balances indicate no significant seasonal bias to groundwater recharge in the UK – Darling et al, 2003).

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 atmospheric monitoring which would otherwise be required to determine the magnitude of a present-day 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), typically integrating over timescales in excess of one month.

2.2 Approach of the present study

Presumably the areas most likely to suffer from regional LAEs are to be found within urban boundaries. 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 mainly to the NW 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 (although Bristol tends towards this condition – Rivett et al, 2003). 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 constitute a comparably valid archive. 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.

3. Sampling and analysis

3.1 Sampling

Grassed parkland sites were chosen as being likely to share the air quality of the general urban area while being least likely to have suffered from industrial activities which might have given rise to contamination in the soil zone.

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.

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 $\delta^{13}C_{CO2}$ 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 the AGAGE network.

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 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 *‰).* (It is considered that LN-EF(ii) may have intercepted a fracture or parting in the stiff over-consolidated London Clay at this locality.)

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 temperature 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-10 concentration, in one case (LN-HP) down to 58%.

5. Discussion

5.1 General observations

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 (Table 2). On each of the sampling days there were breezy or windy conditions, which would tend to disperse any plumes containing elevated proportions of one or more of the three trace gases. The Birmingham site BM-KL stands out in having had CFC-11 and SF_6 values more than twice as high as the NH-AMR values. However, in the context of urban atmospheric measurements, Rivett et al. (2003) found transient CFC-11 peaks of up to eight times the normal urban background, which itself was close to that measured contemporaneously at Mace Head. Although their monitoring was carried out in Bristol, it is reasonable to assume that such transients could equally well occur in Birmingham, and that therefore their significance is limited.

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 (Figure 3). CFC-11 was more variable but there was only one very high value, from BL-TP. This was 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. (The monitoring work in Bristol of Rivett et al. (2003) referred to above also found the CFC-12 urban background to be similar to the Mace Head record.) There was little evidence from the BM-KL site for the elevated values found in the atmosphere.

Nevertheless, it appears that CFC-11 is the most variable of the three trace gases in both the atmosphere and soil zone. While the reasons for this remain speculative, it is consistent with the observation that CFC-11 is usually the least consistent of the three in groundwater studies (e.g. Dunkle et al., 1993; MacDonald et al., 2003: Gooddy et al. 2006).

Consideration of prevailing wind direction and industrial history leads 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, the percentages 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 preceding the time of sampling. Since SF_6 is not known to undergo decomposition in lake waters, this implies either long residence (of the order of years), air equilibration at significantly higher temperatures, or a combination of both. Considering the month of sampling (March), the effect of elevated temperatures seems unlikely. While the relatively small volume of the lakes would also appear to preclude long residence, it is possible that resource management is a factor: for example, the most SF_6-depeleted lake, the Serpentine in Hyde Park, is partially maintained from borehole sources abstracting from the Chalk aquifer, which in this area is likely to contain old, SF_6-dead groundwater.

5.2 Implications for urban groundwater studies

5.2.1 The CFCs

Studies of urban and peri-urban groundwaters have quite often reported 'over-modern' concentrations of the CFCs (Hohener et al., 2003; Morris et al., 2005; Morris et al. 2006) and, as mentioned in the introduction, some researchers have justified using the LAE concept to extract dates from waters which they regard as otherwise uncontaminated (e.g. Oster et al., 1996). The alternative interpretation, that CFC excesses are the results of variable point-source contamination, inevitably hinders the understanding of urban groundwater systems in terms of 'true' residence time.

However, while this study has found little evidence of a consistent CFC-12 or CFC-11 LAE in the year 2006, it is not necessarily the case that "the present is the key to the past" as is suggested by Figure 1. The simple running 50% excess depicted is probably not very realistic given the decline in CFC emissions since 1994 owing to the implementation of the Montreal Protocol (Montzska et al., 1999). Using the approach of Bauer et al. (2001), whereby the time dependence of the local excess is proportional to the global emission rate, trends for equilibrium groundwater concentrations of the two gases would be of the type depicted in Figure 6. Three observations can be made about the time-dependent LAEs: maximum age differences for a given dissolved concentration could conceivably exceed those for the fixed model; there would be no fixed LAE in percentage terms; and the present would be a poor guide to the past.

Of course, a local atmospheric excess might be to varying degrees independent of the global emissions, but without long-term observations there is no way of knowing this. Therefore, even if point-source groundwater contamination is discounted, the use of CFCs as age tracers in many urban/industrial environments is likely to be of limited value, unless an LAE for them can be reconstructed from indicators such as $^{3}H/^{3}He$ or ^{85}Kr, which would rather defeat the object of using CFCs as dating agents in the first place. On the other hand, the use of CFCs as simple hydrogeological indicators is largely unaffected by this limitation (e.g. Morris et al., 2005; Morris et al., 2006).

5.2.2 SF_6

In contrast to the CFCs, the continuing rise in atmospheric SF_6 means that the present is much more likely to be a guide to the past, with the fixed percentage excess depicted in Figure 1 being probably the most appropriate model to consider: indeed, this was the approach adopted by Fulda and Kinzelbach (2000).

Therefore, the absence of evidence for any significant LAE in the UK cities studied here suggests that SF_6 can be used in urban groundwater studies on the basis of its unmodified NH-AMR curve, with over-modern concentrations being the consequence of local point-source contamination rather than an atmospheric excess.

Does the lack of evidence for current and therefore probably past SF_6 excesses have any bearing on the situation for the CFCs? Only in terms of speculation that urban/industrial activity would be unlikely to give rise to a major excess of one type of compound over the other, or that British meteorological conditions are not generally conducive to the existence of LAEs.

5.3 Implications for non-urban groundwater studies

Since the unmodified NH-AMR curve for SF_6 appears to be justifiable for urban areas, there seems little reason not to apply it in the wider UK. The situation for the CFCs is, as has been demonstrated, more complex. Nevertheless, in the absence of evidence to the contrary, it is proposed here that the default position for the wider UK should be the use of the NH-AMR curves for the CFCs also. This approach has for example been tested with some success in rural areas of England (Gooddy et al, 2006) and Scotland (MacDonald et al, 2003). This is not to say that contamination never occurs in rural groundwaters, but it can often be traced to subsurface point sources such as landfills or factories, or to interaction with surface waters.

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, averaging out short-term 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 up to 60% 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.

For SF_6, 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 an input function based on the northern hemisphere atmospheric mixing ratio curve appears to be justified for the UK. For the CFCs, however, their emissions history means that though their current LAEs are mostly low, they may have been of more significance in the past. Therefore the CFCs need to be used with considerable caution in urban groundwater investigations.

While this study has found little evidence for current LAEs, it does suggest that determining soil-gas compositions from several parkland or similar undisturbed sites in a prospective urban investigation area would be a worthwhile precaution, from the point of view of SF_6 if not the CFCs. (To avoid air contamination, stiff clay soils may be better avoided.) Lake water samples, on the other hand, are very much less precise guides to the possible existence of an LAE.

Acknowledgments

We thank our colleague David Jones (BGS Keyworth) for equipment loan and advice on soil-gas sampling. We are also grateful to the referees (Dr S Bauer and two anonymous) for their detailed comments. This paper is published with the permission of the Executive Director, British Geological Survey (NERC).

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