The practicalities of using CFCs and SF_6 for groundwater dating and tracing

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Abstract Knowledge of groundwater residence time is important in understanding key issues in the evolution of water quality, whether this occurs due to water–rock interaction or simply by mixing or contamination. The build-up in the atmosphere of the trace gases chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6) from the middle of the last century offers a convenient way of dating waters up to ~60 yrs old. The gases are well-mixed in the atmosphere so their input functions are not area-specific as is the case with tritium. While any one of these trace gases can in principle provide a groundwater age, when two or more are measured on water samples the potential exists to distinguish between different modes of flow including piston flow, exponential flow and simple end-member mixing. As with all groundwater dating methods, caveats apply. Factors such as recharge temperature and elevation must be reasonably well-constrained. Primarily for SF_6, the phenomenon of 'excess air' also requires consideration. Primarily for the CFCs, local sources of contamination need to be considered, as do redox conditions. For both SF_6 and the CFCs, the nature and thickness of the unsaturated zone need to be factored into residence time calculations. However, as an inexpensive dating method, the trace gases can be applied to a wide range of groundwater problems where traditional age indicators might once have been used more sparingly. Examples include tracing flowlines, detecting small modern inputs in 'old' waters, and pollution risk assessment. In the future, with the main CFCs are already declining in the atmosphere, new anthropogenic trace gases are likely to take their place.

Keywords: chlorofluorocarbons; sulphur hexafluoride; groundwater residence time; flow tracing; groundwater mixing

1. Introduction

Important hydrogeochemical issues such as the effects of climate change on water quality, or the origin of high-arsenic groundwater, involve the study of water–rock interaction processes occurring effectively at the present day. As part of such investigations, it is important to have a readily-available way of dating young (i.e. up to decades old) waters. The atmospheric trace gases CCl_3F (CFC-11), CCl_2F_2 (CFC-12), $C_2Cl_3F_3$ (CFC-113) and SF_6 (sulphur hexafluoride) are increasingly being used as tracers of groundwater residence time (IAEA 2006). Large-scale production of CFC-12 began in the early 1940s, followed by CFC-11 in the 1950s and by CFC-113 in the 1960s. CFC-11 and CFC-12 were used mainly for refrigeration and air-conditioning, while CFC-113 was used as a solvent. Inevitably they leaked into the environment, with atmospheric concentrations rising until the 1990s, when production was cut back to protect the ozone layer as a result of the Montreal Protocol. SF_6, another industry-derived gas largely used for its electrical and thermal insulation properties, has been detectable in the atmosphere since the early 1960s and is still rising steadily in concentration.

Theoretically the concentrations of these gases in a groundwater can be matched to a particular year of recharge, but in practice there may be complications. Some of these have to do with the tracers themselves, while others are related to the fact that groundwater as sampled is probably rather rarely of a single recharge age, owing to a combination of wellbore and within-aquifer mixing processes. Nevertheless, even where age quantification is not possible the CFCs and SF_6 may be useable as flow tracers.

This paper focuses on the practicalities of dating and tracing groundwater movement using these trace gases, much of it based on the authors' experiences over past decade. In doing so it builds on previous reviews, notably those of Cook and Solomon (1997), Plummer and Busenberg (1999), Busenberg and Plummer (2000) and the IAEA handbook on CFCs in hydrology (IAEA, 2006).

2. Background

2.1. Fundamentals of the method

The use of anthropogenic trace gases in groundwater as indicators of residence time is based on the known rise of their concentrations in the atmosphere over the past 60 yrs, the observation that they are well-mixed in the atmosphere (unlike tritium), and the assumption that they dissolve in water according to their Henry's Law solubilities at the temperature of recharge (Plummer & Busenberg 1999). Fig. 1 shows the concentrations of CFC-11, CFC-12, CFC-113 and SF_6 to be expected in northern hemisphere groundwater recharged between 1950 and 2010 at a temperature of 10°C and elevation near sea level. Higher or lower recharge temperatures would tend towards lower or higher concentrations respectively. It should be noted that southern hemisphere trace gas concentrations lag those of the northern hemisphere by 1–2 years.

2.2. Sampling and analysis

Precautions should be taken to avoid contamination (particularly of the CFCs) from sampling equipment such as pumps and tubing (Dunkle et al., 1993; Cook et al., 1995). This is best tested by using proposed new equipment to sample old waters in which the anthropogenic tracers are known to be below detection. Sample collection by the bottle-in-can method of Oster (1994), or more recently the single bottle method of the USGS (IAEA 2006), is straightforward and requires no specialist expertise. CFCs and SF_6 are measured by gas chromatography using an electron capture detector (GC- ECD) following cryogenic pre-concentration (IAEA 2006). The detection limit for CFC concentrations in water is 0.01 pmol/L, while for SF_6 it is 0.1 fmol/L. Both CFC and SF_6 analysis should ideally be calibrated to a bulk air standard collected at an atmospheric monitoring station, preferably one of the AGAGE network (http://agage.eas.gatech.edu/). Analysis is rapid and cost-effective compared to tritium and other radio-isotope techniques where weeks to months may be required for counting or ingrowth.

2.3.Data interpretation

Measured CFC and SF_6 concentrations can be interpreted in terms of age simply by reading off the year of recharge from the curves in Fig. 1 (adjusted if necessary for local recharge temperature). However, this presupposes that the measured water is the result of simple piston flow, i.e. as if along a tubular flowline from recharge to discharge (Fig. 2a). In reality, groundwaters are just as likely to be mixtures of waters of different ages (Fig. 2b), either mixing within the aquifer or, probably more likely, within the wellbore when a borehole is unlined (Plummer and Busenberg, 1999). Where aquifers are fractured there may be potential for mixing between older, slow-moving waters and much more recent recharge moving through the fracture network (Fig. 2c), as described for example by Cook et al. (2005).

Two basic ways of resolving flow processes exist. One is to plot one CFC versus another. Fig. 3a shows a plot of CFC-11 vs CFC-12, with the piston flow curve and the modern—old binary mixing line. Given that the error on the analysis, not to mention fairly ubiquitous small enhancements due to contamination (see Section 3.5 below), it is clear that that resolving piston flow from mixing will usually be difficult. The situation is somewhat improved by plotting CFC-113 versus CFC-12 (Fig. 3b) but there is still room for some ambiguity, particularly around the crossover in the late 1980s. An effective way of resolving this is to plot SF_6 versus CFC-12 (Fig. 3c). The resulting 'bow-shape' due to the significantly different input functions has good separation over most of the field, and no crossover. The other CFCs can substitute for CFC-12.

The simple piston flow and binary mixing model (PFM and BM) scenarios outlined by the SF_6–CFC bow are really opposite extremes of groundwater behaviour. In reality, most groundwater flow may be more complicated, which is why various intermediate lumped-parameter flow models such as the exponential mixing (EMM) and exponential piston flow (EPM) models have been proposed (Maloszewski & Zuber, 1982). Figure 4 compares the concentration curves for the four types of model, with residence times on the PFM, EPM and EMM curves, and amount of modern water expressed in fractional terms ('modern fraction') on the BM line. It is important to note that information derived from plotting analyses on this type of diagram must be considered in relation to hydrogeological information, not least regarding borehole construction. This is because groundwater mixing may occur just as readily (if not more so) in boreholes as in aquifers, giving misleading information if interpreted in isolation.

It will be noted that the EMM line actually extends back beyond the ~60 yr limit of the PFM. This is a consequence of the exponential nature of the putative mixing and is the reason why tracers of the post-war period can under appropriate conditions be used to infer groundwater residence times of up to ~100 yrs (Maloszewski & Zuber, 1982).

3. Factors requiring consideration

3.1. The unsaturated zone

The unsaturated (vadose) zone poses certain problems for the interpretation of CFCs and SF_6. The movement of atmospheric trace gases through the unsaturated zone may occur both in the dissolved and gas phases. When the unsaturated zone is relatively thin, the trace-gas composition of moisture maps on to that of the atmosphere (Cook & Solomon 1995; Engesgaard et al., 2004). In the deeper unsaturated zone of simple porous aquifers, there is a time lag for the diffusive transport of CFCs and SF_6 through the unsaturated zone. This is a function of the tracer diffusion coefficients, tracer solubility in water, and moisture content (Weeks et al., 1982; Cook and Solomon, 1995). In a deep unsaturated zone this suggests the tracer age will be older than the mean advection time of recharge. In fractured aquifers, however, the time lag may be much shorter (see e.g. Darling et al., 2005) meaning that CFC or SF_6 ages obtained from groundwaters effectively represent residence time since recharge reached the water table, i.e. within the saturated zone only. However, whatever the type of aquifer, provided there is some knowledge of rock properties the effect of the unsaturated zone can be factored into age calculations.

3.2. Elevation effects

In mountainous areas there may be significant differences in atmospheric pressure and temperature between the recharge and discharge zones of a particular groundwater system. Where differences are large, corrections are necessary.

Atmospheric pressure decreases exponentially with rise in altitude so that (for example) at ~5000 m above sea level it has declined to half the value (ICAO, 1964). This affects the partial pressures of all atmospheric gases, including the CFCs and SF_6. In practical terms, some knowledge of the average elevation of recharge is desirable if relief of the study area exceeds approximately 1000 m. In very high-altitude areas, such as the Altiplano of the Andes, the elevation of the discharge area would also have to be factored in. Taking a simple case of recharge at 1000 m and discharge at sea level (0 m), a correction factor of 1.13 would need to be applied to the measured CFC and SF_6 data to allow comparison with a calibration curve based on sea-level atmospheric pressure of approximately 1000 mb.

Temperature typically falls with rise in altitude, with an average ‘lapse rate’ of 6.5°C per 1000 m (ICAO, 1964), though this is highly dependent on local factors. For the 1000 m to 0 m scenario considered above, this would introduce a correction factor of approximately 0.7 (it would vary slightly for the different gases). Thus the altitude-based pressure and temperature correction factors work in opposite directions (Fig. 5), with the latter only slightly exceeding the former and, therefore, tend to cancel out rather than reinforce each other at around average lapse rates.

3.3. Excess air

Excess air (EA) arises from the forcible dissolution of air bubbles that inevitably occurs during recharge. This is a process which supplements the dissolved gas content due to simple atmospheric equilibration, on which trace gas dating depends, and therefore requires correction, otherwise waters will appear too young. The impact of EA on a particular gas is in inverse proportion to the solubility of that gas.

EA is present in all groundwaters to some extent, related to factors such as the nature of matrix porosity, amount of fracturing, and size of seasonal fluctuations in water table elevation. It is usually present to the extent of a few cm^3/L (at STP) in sedimentary aquifers: for example, average values of 2.8 ± 1.2 (sd) and 2.6 ± 0.9 (sd) were found for groundwaters abstracted from the two main water supply aquifers of England, the Chalk and the Sherwood Sandstone (Gooddy et al., 2006; Wilson et al., 1994). Such consistency would appear to justify the assumption of a standard amount of EA in a specific aquifer without the need to measure EA in every sample (e.g. Zuber et al., 2005). However, EA values may be higher and more variable, sometimes significantly so, in fractured hard-rock aquifers (Wilson and McNeill 1997), making the use of a standard EA value less justifiable.

Fig. 6 shows the effect of EA on the correction factor for trace-gas measurements at a recharge temperature of 10°C. For temperate-climate groundwaters with an EA component of up to ~5 cm^3/L, there is a need to correct measured SF_6 concentration but not CFC-12 since other uncertainties are of the same order. At greater concentrations of EA, both SF_6 and CFC-12 should be corrected. Recharge temperature affects the correction, which increases with temperature (Fig. 7). This is because while equilibrium gas solubilities diminish with rising temperature, the volume of incorporated EA per litre remains the same. Figs 6 and 7 strictly only apply to simple unfractionated EA; partial or closed-system equilibration of EA can also occur and may need to be considered (Aeschbach-Hertig et al., 2000).

Likely EA values for particular aquifers can be found in the literature, or derived from measuring the neon excess on a representative suite of samples, or simply the N_2/Ar ratio if denitrification can either be ruled out or accounted for (Heaton and Vogel, 1981; Wilson and McNeill, 1997). However, before applying any correction to trace gas concentrations based on EA, some consideration of its age is required. EA is primarily derived from water-table fluctuations forcing gas bubbles into solution, and there is therefore the possibility that it is somewhat younger than the recharge age of the water in which it is dissolved. Bauer et al (2001) have described an iterative routine to account for this. In general, however, a simple correction based on the assumption that EA is contemporaneous with recharge is likely to suffice given the other uncertainties in the application of trace-gas groundwater dating.

3.4. Degassing

An opposite problem to the incorporation of excess air is the partitioning of the trace gases into gas bubbles arising from processes such as the formation of methane in anoxic groundwaters (Fortuin and Willemsen, 2005) or the production of nitrogen gas from denitrification beneath agricultural areas (Visser et al., 2007). As with EA, the low solubility of SF_6 makes it particularly susceptible to degassing (Visser et al., 2009), potentially leading to a significant overestimate of groundwater age in an environment where CFCs are subject to degradation and therefore themselves of doubtful use as age indicators.

3.5. Additions from contamination

At a basic level, the concentrations in groundwater of likely anthropogenic contaminants such as nitrate are often seen to rise with the proportion of young groundwater (Böhlke and Denver, 1995; MacDonald et al., 2003; Koh et al., 2006; Kennedy et al., 2009). However, the trace gases themselves may suffer from contamination. The CFCs in particular are likely to reach values in excess of atmospheric equilibrium owing to inputs from sources such as industrial activities and leaking landfills. Contamination may be atmospheric or in-ground (Ho et al., 1998; Höhener et al., 2003) and is not too surprising: for example it has been calculated that less than one-tenth of the amount of CFC-12 present in a single domestic refrigerator (of older design) could theoretically contaminate a moderately sized aquifer to more than ten times current atmospheric equilibrium levels (Morris et al., 2006), i.e. giving the water a modern fraction value of 10. Contamination tends to affect urban/peri-urban and fractured aquifers the most (Morris et al., 2005a, 2006). Owing to their extremely low atmospheric equilibrium levels, dissolved CFC concentrations can reach several hundred times modern values but still be below drinking water guideline concentrations (Darling et al., 2010). But even very low amounts of contamination can be problematic: with reference to Fig. 4 it is clear that a small enhancement in CFC-12 could make a binary-mixed water appear to be the product of exponential mixing or piston flow.

SF_6 less commonly reaches contaminated values. Sources include high-voltage electricity supply equipment, Mg and Al smelting, and landfills (e.g. Fulda & Kinzelbach, 2000; Santella et al., 2007). The use of SF_6 as an injected tracer for hydrological purposes (e.g. Harden et al., 2003) could also result in local contamination.

Some groundwater dating studies using CFCs or SF_6 have measured or assumed a ‘local atmospheric excess’ (LAE). For example, in western Germany Oster et al. (1996) and Bauer et al., (2001) proposed input functions raised by up to 65%. Where an LAE is suspected, this can be checked by sampling soil gases which should give a mixing ratio similar to that of the current local atmosphere with any short-term fluctuations damped out (Oster et al., 1996). However, because of the decline in CFC emissions over the past twenty years this approach is now only likely to work well for SF_6 (Darling and Gooddy, 2007).

3.6. Additions from terrigenic sources

Although volcanoes have been linked to CFC production, Frische et al. (2006) found the CFCs in volcanic emissions to be present in the same ratios as in the atmosphere, suggesting that the source was atmospheric gas drawn into the relatively porous volcanic edifices. Evidence from gases trapped in ice cores has to some extent been complicated by the possibility of contamination from the refrigeration equipment necessary for core handling, but at least some values measured in ice of pre-industrial age have been below the then detection limit of 5 pptv (Khalil and Rasmussen, 1989a). This suggests that terrigenic CFC production is insignificant.

For SF_6, terrigenic production is much more significant. Sources include rocks containing fluorite, and areas of metallic sulphide mineralisation (e.g. Harnisch and Eisenhauer, 1998; Koh et al., 2007). Anomalously high concentrations of SF_6 have also been noted in some sedimentary rocks (von Rohden et al., 2010) and from granitic terrain (Fig. 8).

3.7. Microbial breakdown

There is ample evidence that CFCs are affected by microbial breakdown under anoxic conditions. This tends to affect CFC-11 and CFC-113 more rapidly than CFC-12, as reported in a number of studies (e.g. Khalil & Rasmussen, 1989b; Oster et al., 1996; Hinsby et al., 2007; Sebol et al., 2007; Horneman et al., 2008). Fig. 9 shows an example of this in relation to a groundwater with redox layering. Typically reduction effects are revealed by major differences in apparent age between the different CFCs. However, if conditions are highly reducing it is possible that all three CFCs will have been reduced to concentrations below the detection limit, thus showing a measure of agreement while not reflecting the true age. It is therefore important to be aware of redox conditions when interpreting CFC data. However, this is not necessarily as simple as recording whether or not dissolved O_2 was below detection limit (typically 0.1 mg/L) at the time of sampling. Mixing between different inflows in or near the wellbore, already mentioned earlier, has the potential to mix waters with different dissolved O_2 concentrations. Therefore it cannot be assumed that detectable dissolved O_2 rules out any possibility of CFC reduction effects.

3.8. Sorption

While unlike the redox-related breakdown sorption is not bacterially mediated, it will also have the effect of lowering CFC concentrations. It is only likely to be a problem in aquifers where the matrix has a high organic content (IAEA, 2006). Where sorption does occur, it is likely the effect increases in magnitude from CFC-12 to CFC-11 to CFC-113 (Ciccioli et al., 1980).

3.9. Thermal effects

Whereas CFC-12 is the most robust CFC under low-O_2 conditions (see previous section), there is some limited evidence that it may be more subject to thermal effects. Table 1 gives results obtained from two warm springs issuing from limestones in Belgium and the UK. Two different laboratories found CFC-12 below detection whereas CFC-11, CFC-113 or SF_6 were present at detectable concentrations, suggesting the addition of small proportions of modern cold water at a late stage in the flow system. The robustness of this phenomenon and the mechanism by which CFC-12 could be removed in preference to the other trace gases remains to be established. A recent study of mixing between thermal and shallow groundwaters in Yellowstone National Park (Gardner et al., 2011) showed no consistent evidence for CFC-12 removal at higher concentrations, so the phenomenon may be restricted in occurrence to very low concentrations and/or type of thermal system.

3.10. Effect of the factors on groundwater age

From the curves in Fig.1 it is apparent that the correction due to any particular effect will have least impact on age where the individual curve is rising most quickly with time, and vice versa . In the earlier days of CFC and SF_6 use, it could be confidently stated that an under- or over-estimate of the original trace gas concentration resulted in a water appearing to be respectively older or younger than its true age (Plummer and Busenberg, 1999). While at the present time this remains the case for SF_6, the Montreal Protocol-related reduction in atmospheric emissions has resulted in a more complex situation for the CFCs, with gradient reversal resulting in non-unique ages for certain concentration ranges. Thus for the CFCs it is no longer possible to generalise on the age direction of effect-based corrections.

4. **Applications beyond simple water dating**

4.1. Combined Tracer and Hydraulic Modelling

The use of CFCs and SF_6 in groundwater dating partly relies on the assumption that the age distribution can be analytically described (Varni and Carrera, 1998). In the simplest homogeneous systems with a few assumptions this is straightforward. However, in more complex heterogeneous systems, processes such as of dispersion, diffusion and mixing due to well screen length, this can have a significant bearing on the interpretation of age dates (Weissman et al., 2002). To address this issue, a number of researchers have combined environmental tracer techniques and hydraulic analyses such as particle tracking (Cook et al., 2005, Reilly et al., 1994; Szabo et al., 1996; Troldborg et al., 2008). These methods provide a feedback that refines the model. This improves the quantification of the flow system and has been shown to give better understanding of flow patterns, travel times, dispersion and recharge processes.

4.2. Waters of mixed age

When CFCs and SF_6 are unaffected by contamination, they are as outlined earlier (2.3) capable of discriminating between piston flow and mixed waters. This makes them a rapid and cost-effective way of screening to determine if an old groundwater component is present, and in what proportion. This can help to decide whether or not to have the water dated by radiocarbon or other long-term age indicator.

The high sensitivity of CFC and SF_6 analysis also offers a way of testing apparently old groundwaters for modern inputs which, though small in volume may have water-quality implications in the sense that anthropogenic contaminants could reach the water table in decades or less. In the past, tritium has performed this role but the CFCs and SF_6 can give more quantitative information and provide a degree of 'redundancy' that a single tracer cannot. Table 2 shows the results of CFC and ^{14}C measurements on groundwaters from a block-faulted, till-covered Triassic sandstone aquifer in the Lagan Valley in Northern Ireland. This shows generally good agreement between the small percentages of modern water calculated from CFC-11 and CFC-12 concentrations in individual boreholes.

The small amount of modern recharge indicated by the CFCs is likely to have added some radiocarbon with an activity much closer to modern values. In principle this small amount of higher ^{14}C activity can be subtracted from the measured activity to give the 'true' age of the old water component, based on the proportion of modern water as measured by the CFCs. However, the ^{14}C activity of the modern recharge needs to be estimated. The highest published radiocarbon activity measured in Lagan Valley groundwaters is approximately 90 pmc (Cronin et al., 2005), so this value has been used to correct the original ^{14}C ages by subtracting the modern input (Table 2). Other assumptions are that the dissolved inorganic carbon concentrations are similar in both young and old waters, and that there is simple binary mixing. These are fairly large assumptions and therefore Table 2 is at best indicative.

Other studies which report and consider the presence of CFCs or SF_6 in waters with relatively low ^{14}C activity are those of Cook et al. (2005) and Solomon et al. (2010).

4.3. Flow tracing

Low concentrations of the CFCs, SF_6 or other anthropogenic tracers may be used to indicate cross-flow and short-circuiting in multi-screen or poorly-constructed wells, especially if used in conjunction with geophysical logging techniques (Buckley et al., 2001).

When groundwaters contain ‘over-modern’ concentrations of the CFCs (i.e. modern fraction values >1) clearly no quantitative residence-time information can be obtained from them, beyond the fact that they must contain at least a proportion of post-war recharge. However, over-modern concentrations can sometimes be used to fingerprint water bodies and therefore shed light on processes such as infiltration, mixing and dilution (Busenberg & Plummer, 1992; Böhlke et al., 1997; Bateman, 1998).

Three CFCs are commonly measured on groundwater samples, which allows the use of trilinear plots. Such plots are often used in the interpretation of inorganic hydrochemical data as a way of detecting patterns of groundwater mixing or evolution (e.g. Hem, 1992), though they require a certain amount of care in interpretation since they depict ratios rather than absolute concentrations. As with all such plots, concentrations of the three CFCs need to be converted to percentages. It is most convenient to do this using modern fraction values (see above), which are themselves directly proportional to the originally-measured concentrations. On this basis, modern air-equilibrated water sits in the centre of the plot. An example is shown in Fig. 10, which is based on a quarried and landfilled area in the southern UK (Darling et al., 2010). In this case, groundwaters have different CFC fingerprints as a result of differences in the type of waste material filling individual quarries, and can be followed along the flowline towards discharge.

4.4. Risk assessment

A study carried out to investigate the risk from *Cryptosporidium* in public supply water from the Chalk aquifer of southern England also measured CFCs (Morris et al., 2005b). In some cases these waters had over-modern concentrations. Table 3 shows CFC-12 excesses as being rather better at predicting the presence of *Cryptosporidium* than a standard hydrogeological risk assessment. While it is not suggested that such assessments should be abandoned, CFC excess as an indication of the existence of contaminant pathways may be a useful screening tool in certain types of aquifer.

5. The future

5.1. Decline of the CFCs

It is clear from Fig. 1 that CFC concentrations in the atmosphere have started to decline. Study of that figure shows that concentrations similar to those of the present day (c. 2010) also occurred 16–23 yrs ago, depending on the CFC. In theory, because the ratios between the CFCs are slightly different now from what they were in the 1987–94 period, it should still be possible to use CFCs to resolve the different ages (at least until they reach pre-industrial baseline values). In practice, measurement precision is unlikely to be high enough to do this unambiguously.

The lowering of atmospheric CFC concentrations is however much less of an issue if the SF_6 co-plot approach (Fig. 11) is used (the rise of SF_6 so far shows no sign of slowing). Clearly for the next few decades the effect of lower CFCs will merely cause the CFC-SF_6 piston flow line to become more curved – with the benefit that it will become easier to distinguish between mixed and PFM or EPM groundwaters over much of the age range (see Fig. 11).

5.2. New tracers

Other atmospheric trace gases have been proposed as residence time indicators (Busenberg & Plummer, 2008) or appear to have that potential (Weiss et al., 2008). CFC-13 (CF_3Cl), currently present in the atmosphere at about the same concentration as SF_6, has been rising steadily presumably because at the current very low concentration it is not yet regarded as a threat to the ozone layer. It also has the advantage that it has not been widely used industrially and therefore groundwaters are less likely to be contaminated with it than the conventional CFCs. Trifluoromethyl sulphurpentafluoride (SF_5CF_3) is also increasing in the atmosphere. Since it is not immune to anthropogenic contamination (Knowles et al., 2010), its main advantage over SF_6 may lie in the apparent lack of terrigenic production. Nitrogen trifluoride (NF_3) is accumulating at a similar rate. Currently SF_5CF_3 and NF_3 have reached only a few percent of the current SF_6 value so analytical precision is problematic, but both these new tracers could start featuring over the next several decades as their atmospheric mixing ratios rise.

5. Conclusions

Like all groundwater dating methods, the CFCs and SF_6 have advantages and disadvantages. This paper has considered the following aspects:

– Sampling and analysis is straightforward. Under ideal conditions the gases can be used to date groundwaters up to ~60 yrs old and resolve piston flow from simple mixing, but understanding trace gas behaviour in the unsaturated zone can be challenging.

– Correcting for recharge temperature and altitude inevitably involves some uncertainty but the corrections tend to cancel each other out. The effects of excess air need to be considered, though normally only for SF_6.

– Non-correctible factors include the contamination of CFCs (predominantly anthropogenic in origin) and SF_6 (mainly terrigenic), and the degradation of CFCs, generally occurring only under low-oxygen conditions but possibly also under thermal conditions.

– In the absence of contamination or other non-correctible effects, the CFCs and SF_6 can (like other age tracers) be used to calculate recharge rates and flow velocities, to calibrate numerical flow models, and to reveal the presence of small amounts of modern water in otherwise pristine resources.

– Even when contamination is present, distinctive CFC fingerprints may allow the tracing of groundwater flow paths or provide a potential screening tool for risk assessment – indeed, the comparatively rapid and inexpensive analysis for both SF_6 and the CFCs should promote more innovative use of the gases as environmental tracers.

- The three conventional CFC tracers are declining in the atmosphere and will be unusable for dating in several decades' time. However, new trace gases are likely to replace them in this role.

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Table 1. Results of trace gas analysis on the Bath (UK) and Chaudfontaine (Belgium) thermal waters, showing the below-detection concentrations of CFC-12 compared to CFC-11 and CFC-113 or SF_6.

Site	CFC-12 pmol/L	CFC-11 pmol/L	CFC-113 pmol/L	SF_6 fmol/L
Bath, UK, emergence temp 47°C, measured by Spurenstofflabor				
Cross Spring	<0.01	0.26	0.04	-
Stall Street BH	<0.01	0.17	0.02	-
Chaudfontaine, Belgium, emergence temp 37°C, meas. by BGS				
Chaud A	<0.02	0.55	-	0.18
Chaud B	<0.02	0.54	-	0.13

Table 2. Example of CFCs indicating the presence of small amounts of modern water in the Triassic aquifer of the Lagan Valley, Northern Ireland, showing generally good agreement between CFC-11 and CFC-12 as indices of the proportion of modern water present. Measured bulk radiocarbon activities $A^{14}C_m$ have been corrected for modern inputs to give the activity of the old component $A^{14}C_o$ (see text). Both measured and re-calculated activities have been converted into ages using the $\delta^{13}C$-based approach of Clark and Fritz (1997), and assuming a soil carbonate value of –3‰ and a soil CO_2 value of –26‰.

Borehole	CFC-12	CFC-11	CFC av.	$\delta^{13}C$-DIC	$A^{14}C_m$	$A^{14}C_o$	^{14}C model age in yrs	
	Modern Fraction			‰	pmc		Bulk	Old comp.
CH	0.07	0.05	0.06	-17.9	37.7	34.3	4450	5200
CL	0.00	0.02	0.01	-18.2	52.3	52.0	1950	2000
E3	0.00	0.01	0.01	-17.1	58.8	58.6	300	350
KH	0.04	0.04	0.04	-17.3	54.4	52.9	1100	1300
LB	0.09	0.04	0.07	-16.3	34.7	30.8	4200	5150
LC	0.07	0.02	0.04	-15.2	39.3	37.1	2500	2990
LP1	0.13	0.11	0.12	-14.1	45.9	39.9	390	1550
LP2	0.08	0.03	0.06	-16.8	37.4	34.3	3900	4600
ML	0.06	0.05	0.05	-17.6	24.5	20.7	7850	9200
MO	0.00	0.04	0.02	-16.7	33.9	32.8	4700	4950
MV	0.03	0.03	0.03	-16.6	40.4	39.0	3150	3400

Table 3. Standard risk assessment vs CFC-12 excess as a guide to the presence of *Cryptosporidium* in waters from public supply springs and boreholes in the Chalk aquifer of the Portsmouth area, S England. Data from Morris et al. (2005b).

Original hydrogeology-based *Cryptosporidium* risk assessment	**Subsequent bacterial detection**	**CFC-12 >modern**
'At risk'		
Bedhampton Spr	✓	✓
Fishbourne	✓	✓
Havant Spr	✓	✓
Hoe		
Lovedean	✓	✓
Maindell	✓	✓
Northbrook		
Soberton	✓	
West Street		
Worlds End		✓
'Little risk'		
Aldingbourne		
Brickkiln		
Eastergate	✓	✓
Funtington		
Lavant	✓	✓
Lower Upham		
Newtown		
Slindon		
Walderton		
West Meon		
Westergate		✓
Woodmancote		✓

Figure captions

Figure 1. Variation over time of the concentrations in ground-water of the CFCs and SF_6 assuming equilibrium with the Northern Hemisphere atmospheric mixing ratios at a recharge temperature of 10°C (typical of the UK). Note the difference in axial scales between SF_6 and the CFCs. Based on data from http://water.usgs.gov/lab/software/air_curve/.

Figure 2. Schematic cross-sections illustrating types of groundwater flow to a borehole: (a) a thin porous sandstone aquifer unit, with a borehole sampling water with a tight age distribution; (b) a more complex aquifer with a fully-penetrating unlined borehole sampling a mixture of different flow path lengths; (c) a limestone aquifer with a borehole sampling a mixture of older, slow-moving water with young water moving rapidly down the fracture network from the surface.

Figure 3. Plots of (a) CFC-11 vs CFC-12, (b) CFC-113 vs CFC-12, and SF_6 vs CFC-12 showing the piston flow curve (PFM) and the binary mixing line (BM) between modern and old groundwater. Year of recharge shown for PFM.

Figure 4. Example plot of SF_6 vs CFC-12 showing the PFM, EPM and EMM age curves, with groundwater residence times in years. Also shown is the binary mixing line BM with amounts of modern water expressed as a fraction of unity. Based on Gooddy et al. (2006).

Figure 5. Graphs showing the corrections to be applied to trace gas data to bring them to sea-level conditions of temperature and pressure. Temperature correction based on a 6.5°C lapse rate. Altitude in metres above sea level (m asl).

Figure 6. Graph showing the corrections required for SF_6 and the CFCs to account for the presence of differing amounts of excess air. The curves assume recharge at 10°C.

Figure 7. Graphs showing the effect of recharge temperature (RT) on the magnitude of the excess air correction for CFC-12 and SF_6 at temperatures from 0 to 30°C.

Figure 8. Concentrations of SF_6 measured in groundwaters sampled in Nigeria, (a) from Mesozoic sediments, (b) from the granitic basement aquifer. The dashed line shows the expected value for recharge for the year of sampling (2010). Based on data from Lapworth et al. (in rev.).

Figure 9. The effect of redox conditions on the bacterial degradation of the CFCs (after Sebol et al. 2007).

Figure 10. (a) Trilinear plot of CFC-11, CFC-12 and CFC-113 from boreholes in a quarried area of the Chalk in north Kent, UK. The plot is based on modern fraction values, with arrows showing apparent dilution trends towards the ratios in atmospherically-equilibrated modern water (MW); (b) map showing the borehole locations and likely flowlines based on the trilinear plot, with known areas of landfill outlined. Based on Darling et al. (2010).

Figure 11. Although the decline in the atmospheric mixing ratios of the CFCs is already leading to non-unique CFC ages, the continuing rise in SF_6 means that the co-plot approach can resolve these.

Figure 12. CFC-13, SF_5CF_3 and NF_3 atmospheric mixing ratios compared to that of SF_6. Unlike CFC-11 and CFC-12, these trace gases are not declining in the atmosphere. Data from Busenberg and Plummer (2008), Weiss et al. (2008) and http://water.usgs.gov/lab/software/ air_ curve/.

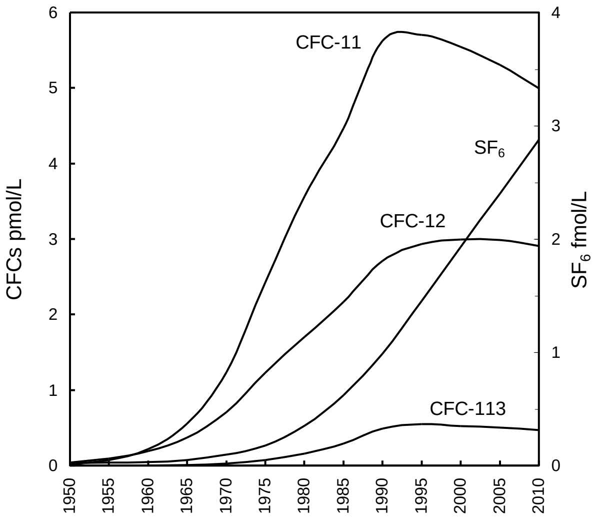
CFC-11
SF$_6$
CFC-12
CFC-113
CFCs pmol/L
SF$_6$ fmol/L
0
1
2
3
4
5
6
0
1
2
3
4
1950
1955
1960
1965
1970
1975
1980
1985
1990
1995
2000
2005
2010

Figure 1

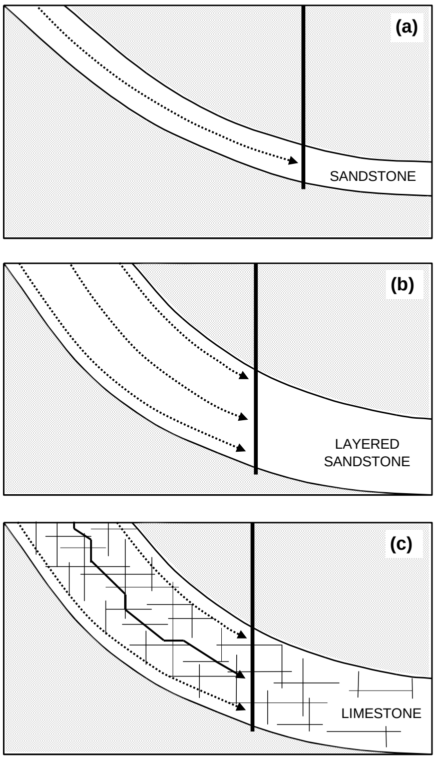

Figure 2

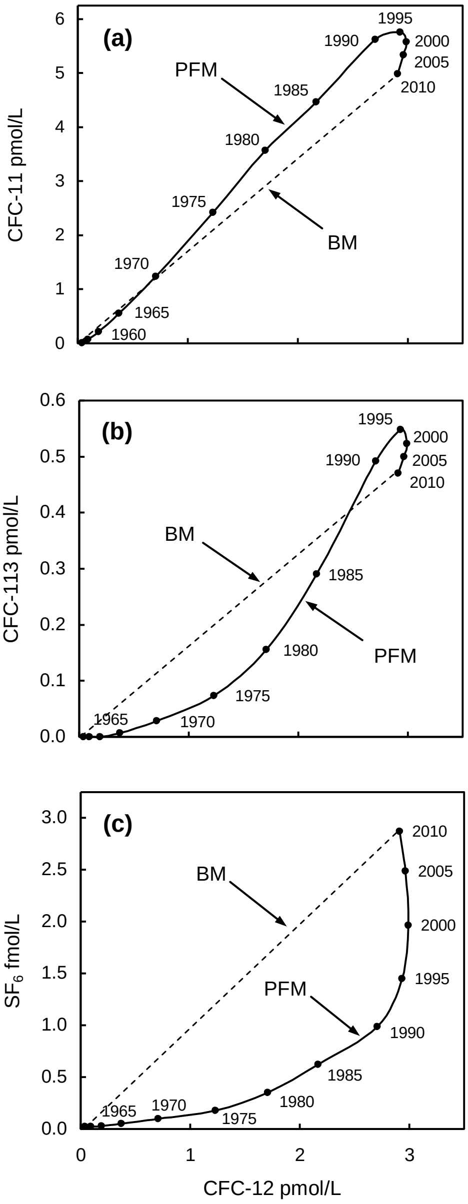
(a)
CFC-11 pmol/L
0
1
2
3
4
5
6
PFM
BM
1960
1965
1970
1975
1980
1985
1990
1995
2000
2005
2010
(b)
CFC-113 pmol/L
0.0
0.1
0.2
0.3
0.4
0.5
0.6
BM
PFM
1965
1970
1975
1980
1985
1990
1995
2000
2005
2010
(c)
SF$_6$ fmol/L
0.0
0.5
1.0
1.5
2.0
2.5
3.0
BM
PFM
1965
1970
1975
1980
1985
1990
1995
2000
2005
2010
0
1
2
3
CFC-12 pmol/L

Figure 3.

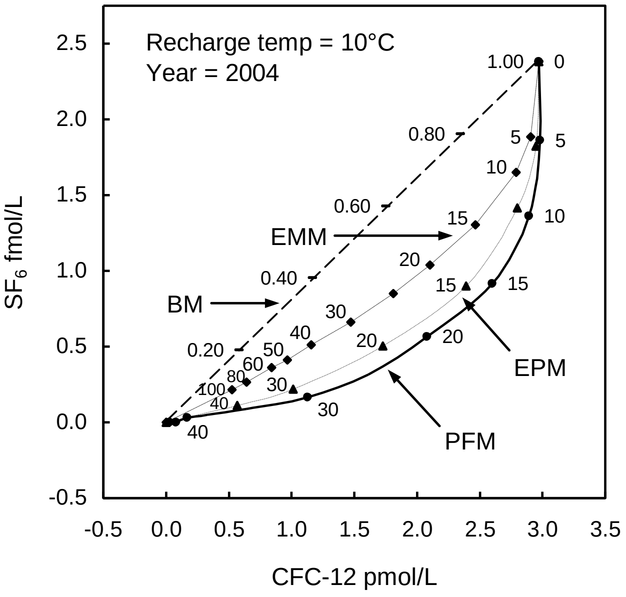
Recharge temp = 10°C
Year = 2004
1.00
0
0.80
5
5
10
0.60
15
10
EMM
20
0.40
15
15
BM
30
40
20
20
0.20
50
60
EPM
80
30
100
40
30
40
PFM
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
SF_6 fmol/L
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
CFC-12 pmol/L

Figure 4.

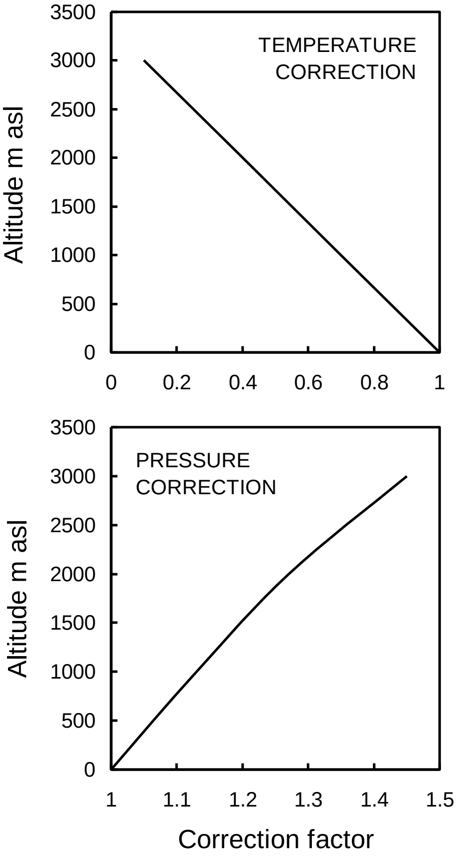
3500
3000
2500
2000
1500
1000
500
0
Altitude m asl
TEMPERATURE
CORRECTION
0
0.2
0.4
0.6
0.8
1
3500
3000
2500
2000
1500
1000
500
0
Altitude m asl
PRESSURE
CORRECTION
1
1.1
1.2
1.3
1.4
1.5
Correction factor

Figure 5.

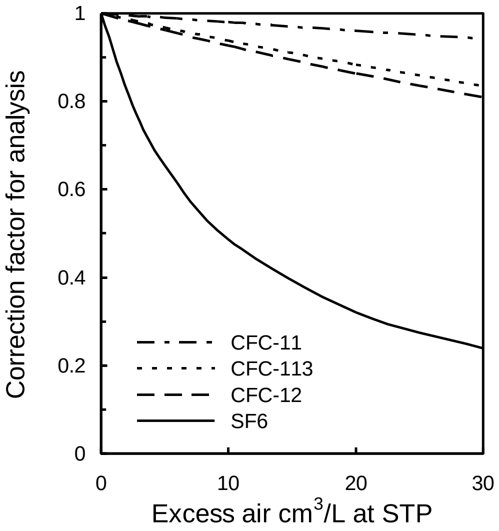
Correction factor for analysis
1
0.8
0.6
0.4
0.2
0
0
10
20
30
Excess air cm3/L at STP
CFC-11
CFC-113
CFC-12
SF6

Figure 6

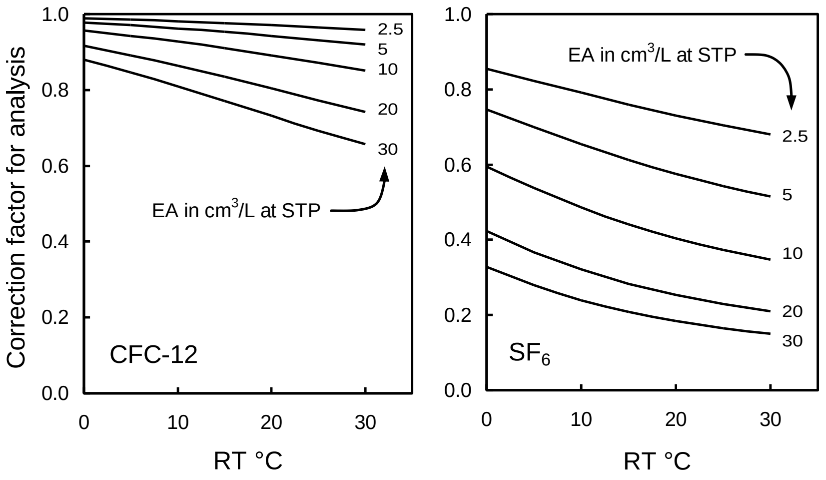
Correction factor for analysis
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
RT °C
2.5
5
10
20
30
EA in cm^3/L at STP
CFC-12
SF$_6$

Figure 7

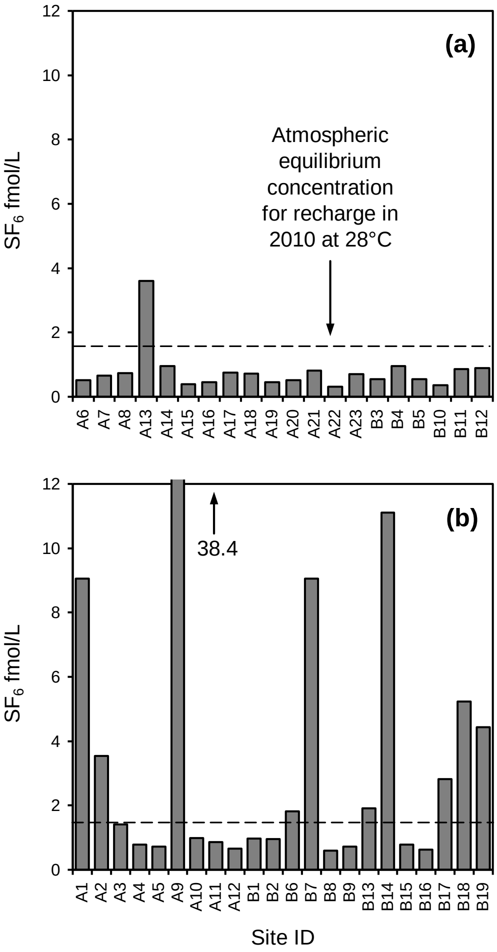
(a)
SF$_6$ fmol/L
Atmospheric equilibrium concentration for recharge in 2010 at 28°C
0
2
4
6
8
10
12
A6
A7
A8
A13
A14
A15
A16
A17
A18
A19
A20
A21
A22
A23
B3
B4
B5
B10
B11
B12
(b)
38.4
A1
A2
A3
A4
A5
A9
A10
A11
A12
B1
B2
B6
B7
B8
B9
B13
B14
B15
B16
B17
B18
B19
Site ID

Figure 8

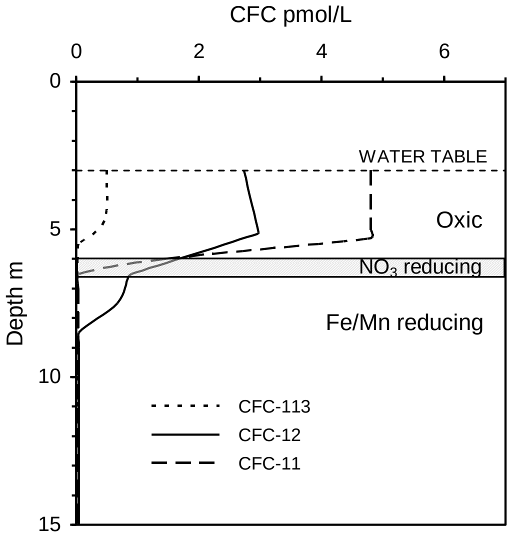
CFC pmol/L
0
2
4
6
0
5
10
15
Depth m
WATER TABLE
Oxic
NO_3 reducing
Fe/Mn reducing
CFC-113
CFC-12
CFC-11

Figure 9.

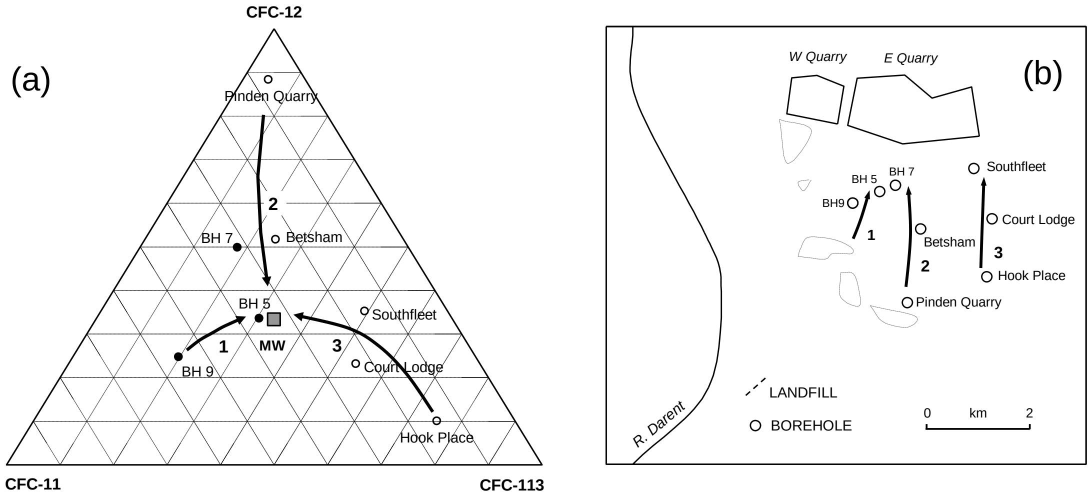
(a)
CFC-12
CFC-11
CFC-113
Pinden Quarry
2
BH 7
Betsham
BH 5
Southfleet
1
MW
3
BH 9
Court Lodge
Hook Place
(b)
W Quarry
E Quarry
Southfleet
BH 5
BH 7
BH9
Court Lodge
1
Betsham
3
2
Hook Place
Pinden Quarry
LANDFILL
BOREHOLE
0
km
2
R. Darent

Figure 10.

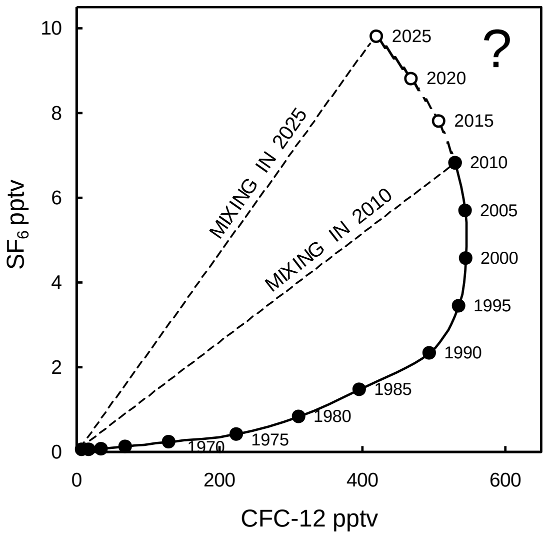
10
8
6
4
2
0
0
200
400
600
CFC-12 pptv
SF_6 pptv
MIXING IN 2025
MIXING IN 2010
?
2025
2020
2015
2010
2005
2000
1995
1990
1985
1980
1975
1970

Figure 11

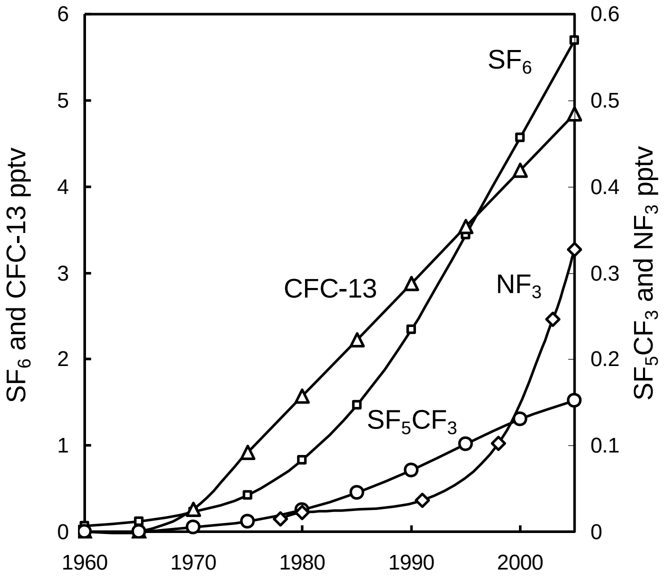
6
5
4
3
2
1
0
0.6
0.5
0.4
0.3
0.2
0.1
0
1960
1970
1980
1990
2000
SF6 and CFC-13 pptv
SF5CF3 and NF3 pptv
SF6
CFC-13
NF3
SF5CF3

Figure 12