

CFCs and SF₆ for groundwater dating: a SWOT analysis

W.G. Darling, D.C. Gooddy & B.L. Morris
British Geological Survey, Wallingford, UK
A.M. MacDonald
British Geological Survey, Edinburgh, UK

ABSTRACT: A knowledge of the residence time of groundwater is of importance in understanding key issues in the evolution of water quality. Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF₆) offer a convenient way of dating waters up to ~60 yrs old. In contrast to tritium, these gases are well-mixed in the atmosphere so their input functions are much less problematic. While any one of these 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. Mainly for SF₆, the phenomenon of ‘excess air’ also requires consideration. Mainly for the CFCs, local sources of contamination need to be considered, as do redox conditions. For both SF₆ and the CFCs, the nature and thickness of the unsaturated zone need to be factored into residence time calculations. This paper attempts a balanced look at the pros and cons of the trace-gas dating method.

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 or close to 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 CFC-11, CFC-12, CFC-113 and SF₆ (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. SF₆, another industry-derived gas, has been detectable in the atmosphere since the early 1960s and is still rising strongly in concentration.

Theoretically the concentrations of these gases in a groundwater can be matched to a particular year of recharge. In practice there may be complications, either with the tracers themselves, or 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. This review takes a ‘SWOT’ (Strengths–Weaknesses–Opportunities–Threats) approach to this and other aspects of CFC and SF₆ dating.

2 PRINCIPLES OF THE METHOD

The use of CFCs and SF₆ as indicators of residence time is based on the known rise of their atmospheric concentrations 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). Figure 1 shows the concentrations of CFC 11, CFC-12, CFC 113 and SF₆ to be expected in groundwater recharged between 1950 and 2010 at a temperature of 10°C, typical of much of the UK. Higher or lower recharge temperatures would tend towards lower or higher concentrations respectively.

3 STRENGTHS

3.1 Sampling and analysis

Sampling 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 SF₆ 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 SF₆ it is 0.1 fmol/L. Both CFC and SF₆ analyses should ideally be calibrated to a bulk air standard from an AGAGE atmospheric monitoring station (<http://agage.eas.gatech.edu/>). Analysis is rapid and cost-effective compared to tritium and other radio-isotope techniques.

3.2 Interpretation

Measured CFC and SF₆ concentrations can be interpreted in terms of age simply by reading off the year of recharge from the curves in Figure 1 (adjusted if necessary for local recharge temperature (RT)). However, this presupposes that the measured water is the result of piston flow, i.e. as if along a simple tubular flowline from recharge to discharge. In reality, groundwaters are just as likely to be mixtures of young and older waters, or to be the result of mixing of waters arriving along flowlines of different lengths and therefore different ages. This last category in particular may be a consequence of mixing in the wellbore when a borehole is unlined.

Two basic ways of resolving this exist. One is to plot one CFC versus another. Figure 2a shows a plot of CFC-11 vs CFC-12, with the piston flow curve and the modern–old binary mixing line. Given the error on the analysis, not to mention fairly ubiquitous small enhancements due to contamination (see 4.4 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. 2b) 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 SF₆ versus CFC-12 (Fig. 2c). The resulting 'bow-shape' 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 SF₆–CFC bow are really opposite extremes of groundwater behaviour. In reality, most groundwater flow may be more complicated, which is why some intermediate lumped-parameter flow models such as the exponential mixing (EMM) and exponential piston flow (EPM) models have been proposed (Maloszewski & Zuber 1982). Figure 3 compares the concentration curves for the three 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).

4 WEAKNESSES

4.1 Unsaturated zone

The vadose or unsaturated zone (USZ) poses certain problems for the interpretation of CFCs and SF₆. The movement of atmospheric trace gases through the USZ occurs both in the dissolved and gas phases. When the USZ is thin, the trace-gas composition of moisture maps on to that of the atmosphere (Cook & Solomon 1995; Engesgaard et al., 2004). In the deeper USZ of simple porous aquifers there is a time lag for the diffusive transport of CFCs and SF₆, a function of the tracer diffusion coefficients, tracer solubility in water, and moisture content (Weeks et al., 1982; Cook and Solomon, 1995). In the deepest USZs this suggests the tracer age could be greater than the mean advection time of recharge. In fractured aquifers however, the situation would be reversed meaning that CFC or SF₆ ages obtained from groundwaters effectively represent residence time only since recharge reached the water table, i.e. within the saturated zone (Darling et al. 2005). However, whatever the type of aquifer, provided there is some knowledge of rock properties the effect of the USZ can be factored in to age calculations.

4.2 Elevation effects

Atmospheric pressure falls almost linearly with rise in altitude, so that at ~5000 m above sea level it has declined to half the value. Therefore 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 SF₆ 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, 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, with the latter exceeding the former, and therefore tend to cancel out rather than reinforce each other.

Strictly speaking pressure and temperature are simply factors that require correcting for, rather than weaknesses. They only tend to become so in mountainous terrain where recharge elevation is poorly constrained.

4.3 Excess air

Excess air (EA) arises from the forcible dissolution of air bubbles that inevitably occurs during the recharge process. 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. 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 cc/L (STP) but may be higher, sometimes significantly so, in fractured aquifers (Wilson & McNeill 1997). For 'normal' groundwaters with an EA component of up to ~5 cc/L, there is a need to correct measured SF₆ concentration but not CFC-12 as other uncertainties are of the same order. At greater concentrations of EA, both SF₆ and CFC-12 should be corrected. Recharge temperature affects the correction, which increases with temperature (Fig. 4). Figure 4 strictly only applies 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 (e.g. Wilson & McNeill 1997) or derived from measuring N₂, Ar or other noble gases on a representative suite of samples. The correction can be accomplished by a simple iterative procedure that takes account of various factors (Busenberg & Plummer 2000).

4.4 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 (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. Owing to their extremely low atmospheric equilibrium levels, CFC concentrations can reach several hundred times modern values but still be below drinking water guideline concentrations. But even very low amounts of contamination can be problematic to groundwater dating: with reference to Figure 3 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.

SF₆ reaches contaminated values only rarely. Anthropogenic sources include high-voltage electricity supply equipment, Mg and Al smelting, and landfills (e.g. Fulda & Kinzelbach 2000; Santella et al 2007). Terrigenous sources include rocks containing fluorite, fine grained volcanic rocks such as rhyolite, and areas of metallic mineralisation (e.g. Harnish and Eisenhauer, 1998; Koh et al, 2007).

4.5 Microbial degradation

There is ample evidence that CFCs are affected by microbial breakdown under low-O₂ 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 1989; Oster et al. 1996; Sebol et al. 2007;

Horneman et al. 2008). Figure 5 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.

While not bacterially mediated, sorption 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 matter content (IAEA 2006).

4.6 Temperature

Whereas CFC-12 is the most robust CFC under low-O₂ conditions (see previous section), there is some limited evidence that it may be more subject to temperature effects. Table 1 gives results obtained from two warm springs, in Belgium and the UK. Two different laboratories found CFC-12 below detection whereas CFC-11, CFC-113 and SF₆ were all present at detectable concentrations. The mechanism by which CFC-12 would be affected in preference to the other trace gases remains to be established, and indeed a larger database is required to determine whether the effect is real or a contamination-related artefact.

5 OPPORTUNITIES

5.1 CFCs as flow tracers

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).

Three CFCs are commonly measured on groundwater samples, which allows the use of trilinear plots. Such plots are commonly 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 of such a plot is shown in Figure 6, which is based on a quarried and landfilled area in the southern UK (Darling et al. 2010).

In this case, neighbouring groundwaters have different CFC fingerprints so that probable flowpaths can be identified. The observed contrast between the proportions of individual CFCs presumably arises from the disposal of different kinds of waste material in the various landfills now occupying the several small scale excavations remaining as a legacy of chalk quarrying operations.

5.2 Waters of mixed age

When CFCs and SF₆ are unaffected by contamination, they are as outlined earlier 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 component is present, and in what proportion. This can help to decide whether or not to have the water dated by radiocarbon or other costly long-term age indicator.

The sensitivity of CFC and SF₆ 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 past, tritium has performed this role but the CFCs and SF₆ can give more quantitative information and provide a degree of 'redundancy' that a single tracer cannot. Table 2 shows the results of CFC and 14C measurements on groundwaters from a block-faulted, till-covered Triassic sandstone aquifer in the Lagan Valley of Northern Ireland. This shows firstly good agreement between the small percentages of modern water calculated from CFC-11 and CFC-12 concentrations in individual boreholes, and secondly the heterogeneity of this type of faulted aquifer both in terms of the proportion of modern water present and the calculated model age of the old component.

5.3 New tracers

Other atmospheric trace gases have been proposed as residence time indicators (Busenberg & Plummer 2008). CFC-13 (CF₃Cl), currently present in the atmosphere at about the same concentration as SF₆, has been rising steadily presumably because at this very low concentration it is not yet seen 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 (SF₅CF₃) is also increasing in the atmosphere. Its advantage over SF₆ appears to be a lack of terrigenous production. To date it has reached only a few percent of the current SF₆ value so analytical precision is problematic. Both these new tracers seem likely to start featuring over the next few decades if atmospheric concentrations keep rising.

6 THREATS

It is clear from Figure 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 (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 SF₆ co-plot approach (Figs 2c & 3) is used, because the rise of SF₆ so far shows no sign of significant slowing. Clearly for the next few decades the effect of lower CFCs will merely cause the CFC–SF₆ 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.

7 CONCLUSIONS

Like all groundwater dating methods, the CFCs and SF₆ have advantages and disadvantages. A SWOT analysis reveals the following.

Sampling and analysis is reasonably straightforward. Under ideal conditions the gases can be used to date groundwaters up to ~60 yrs old and resolve piston flow from simple mixing.

Excess air is more of an issue than recharge elevation, though normally only for SF₆. Degradation of CFCs generally occurs only under low-oxygen conditions, but possibly also under thermal conditions. Contamination of CFCs (anthropogenic) or SF₆ (terrigenic) may occur, but then be usable as a flow rather than age tracer.

The 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.

ACKNOWLEDGMENTS

We thank Eurybiades Busenberg and Werner Aeschbach-Hertig for helpful reviews of the original manuscript.

REFERENCES

Aeschbach-Hertig, W., Peeters, F., Beyerle, U., & Kipfer, R. 2000. Paleotemperature reconstruction from noble gases in ground water taking into account equilibrium with entrapped air. *Nature* 405: 1040–1044.

Böhlke, J.K., Revesz, K., Busenberg, E., Deak, J., Deseo, E., & Stute, M., 1997, A groundwater record of halocarbon transport by the Danube River. *Environmental Science and Technology* 31: 3293–3299.

Busenberg, E. & Plummer, L.N. 1992. Use of Chlorofluorocarbons (CCl₃F and CCl₂F₂) as hydrologic tracers and age dating tools: the alluvium and terrace system of central Oklahoma. *Water Resources Research* 28: 2257–83.

Busenberg, E. & Plummer, L.N. 2000. Dating young groundwater with sulfur hexafluoride: Natural and anthropogenic sources of sulfur hexafluoride. *Water Resources Research* 36: 3011–3030.

Busenberg, E. & Plummer, L.N., 2008, Dating groundwater with trifluoromethyl sulfurpentafluoride (SF₅CF₃), sulfur hexafluoride (SF₆), CF₃Cl (CFC-13), and CF₂Cl₂ (CFC-12), *Water Resources Research*, 44: W02431, doi:10.1029/2007WR006150.

Cook, P.G. & Solomon, D.K., 1995. Transport of trace gases to the water table: Implications for groundwater dating with chlorofluorocarbons and krypton-85. *Water Resources Research* 31: 263–270.

Darling, W.G., Morris, B.L., Stuart, M.E. & Goody, D.C. 2005. Groundwater age indicators from public supplies tapping the Chalk aquifer of Southern England. *Water and Environment Journal* 19: 30–40.

Darling, W.G., Goody, D.C., Riches, J. & Wallis, I. 2010. Using environmental tracers to assess the extent of river–groundwater interaction in a quarried area of the English Chalk. *Applied Geochemistry* doi: 10.1016/j.apgeochem. 2010.01.019.

Engesgaard, P., Højberg, A.L., Hinsby, K., Jensen, K.H., Laier, T., Larsen, F., Busenberg, E. & Plummer, L.N., 2004. Transport and time lag of chlorofluorocarbon gases in the unsaturated zone, Rabis Creek, Denmark. *Vadose Zone Journal* 3: 1249–1261.

Fulda, C. & Kinzelbach, W. 2000. Sulphur hexafluoride (SF₆) as a new age-dating tool for shallow groundwater: methods and first results. *Proc. International Conference on Tracers and Modelling in Hydrogeology, Liège, Belgium*. IAHS Publication no. 262. IAHS Press, Wallingford, Oxfordshire, UK, 181–185.

Goody, D.C, Darling, W.G., Abesser, C. & Lapworth, D.J. 2006. Using chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF₆) to characterize groundwater movement and residence time in a lowland Chalk catchment. *Journal of Hydrology* 330: 44–52.

Harnish, J. & Eisenhauer, A. Natural CF₄ and SF₆ on Earth. *Geophysical Research Letters* 25: 2401–2404.

Hem, J.D. 1992. Study and interpretation of the chemical characteristics of natural water. United States Geological Survey Water-Supply Paper 2254, 3rd edn, 263 pp.

Höhener, P., Werner, D., Balsiger, C. & Pasteris, G. 2003. Worldwide occurrence and fate of chlorofluorocarbons in groundwater. *Critical Reviews in Environmental Science and Technology* 33: 1–29.

Horneman, A., Stute, M., Schlosser, P., Smethie, W., Santella, N., Ho, D.T., Mailloux, B., Gorman, E., Zheng, Y. & van Geen, A. 2008. Degradation rates of CFC-11, CFC-12 and CFC-113 in anoxic shallow aquifers of Araihasar, Bangladesh. *Journal of Contaminant Hydrology* 97: 27–41.

IAEA (International Atomic Energy Agency), 2006. Use of Chlorofluorocarbons in Hydrology: A Guidebook, STI/PUB/1238, 277 pp. Obtainable from http://www-pub.iaea.org/MTCD/publications/PDF/Pub1238_web.pdf.

Khalil, M.A.K. & Rasmussen, R. 1989. The potential of soils as a sink of chlorofluorocarbons and other man-made chlorocarbons. *Geophysical Research Letters* 16: 679–682.

Koh, D.C., Plummer, L.N., Busenberg, E. & Kim, Y. 2007. Evidence for terrigenous SF₆ in groundwater from basaltic aquifers, Jeju Island, Korea: implications for groundwater dating. *Journal of Hydrology* 339: 93–104.

Maloszewski, P. & Zuber, A. 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers. 1, Models and their applicability. *Journal of Hydrology* 57: 207–231.

Morris, B.L., Darling, W.G., Cronin, A.A., Rueedi, J., Whitehead, E.J. & Goddy, D.C. 2006. Assessing the impact of modern recharge on a sandstone aquifer beneath a suburb of Doncaster, UK. *Hydrogeology Journal* 14: 979–997.

Oster, H. 1994. Datierung von Grundwasser mittels FCKW: Voraussetzungen, Möglichkeiten und Grenzen. Dissertation, Universität Heidelberg.

Oster, H., Sonntag, C. & Münnich, K.O. 1996. Groundwater age dating with chlorofluorocarbons. *Water Resources Research* 37: 2989–3001.

Plummer, L.N. & Busenberg, E. 1999. Chlorofluorocarbons. In: P.G. Cook & A.L. Herczeg (eds), *Environmental Tracers in Subsurface Hydrology*, Kluwer, Dordrecht, 441–478.

Santella, N., Ho, D.T., Schlosser, P. & Stute, M. 2007. Widespread elevated atmospheric SF₆ mixing ratios in the Northeastern United States: Implications for groundwater dating. *Journal of Hydrology* 349: 139–146.

Sebol, L.A., Robertson, W.D., Busenberg, E., Plummer, L.N., Ryan, M.C. & Schiff, S.L. 2007. Evidence of CFC degradation in groundwater under pyrite-oxidizing conditions. *Journal of Hydrology* 347: 1–12.

Weeks, E.P., Earp, D.E. & Thompson, G.M. 1982. Use of atmospheric fluorocarbons F-11 and F-12 to determine the diffusion parameters of the unsaturated zone in the southern high plains of Texas, *Water Resources Research* 18: 1365–1378.

Wilson, G.B. & McNeill, G.W., 1997. Noble gas recharge temperatures and the excess air component. *Applied Geochemistry* 12: 747–762.

FIGURE CAPTIONS

Figure 1. Variation over time of the concentrations in groundwater of the CFCs and SF₆ assuming equilibrium with the Northern Hemisphere atmospheric mixing ratios at a recharge temperature of 10°C (typical of the UK). Based on data from http://water.usgs.gov/lab/software/air_curve/.

Figure 2. Plots of (a) CFC-11 vs CFC-12, (b) CFC-113 vs CFC-12, and SF₆ vs CFC-12 showing the piston flow curve (PFM) and the binary mixing line (BM) between modern and old groundwater. RT = 10°C. Year of recharge shown for PFM.

Figure 3. Example plot of SF₆ 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 4. The effect of recharge temperature (RT) on the excess air (EA) correction that sample analyses require to give reliable ages. Owing to its lower solubility, SF₆ needs correction at all levels of EA while for CFC-12 only at >5 cc/L (STP).

Figure 5. The effect of redox conditions on the bacterial degradation of the CFCs (after Sebol et al. 2007).

Figure 6. Trilinear plot of the CFCs using over-modern groundwater concentrations to determine flow/dilution trends in a landfilled area of the Chalk, southern UK. From Darling et al. (2010).

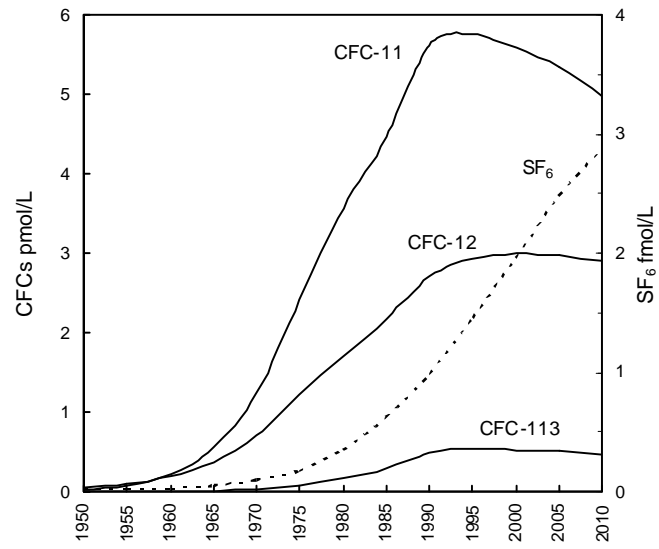


Figure 1

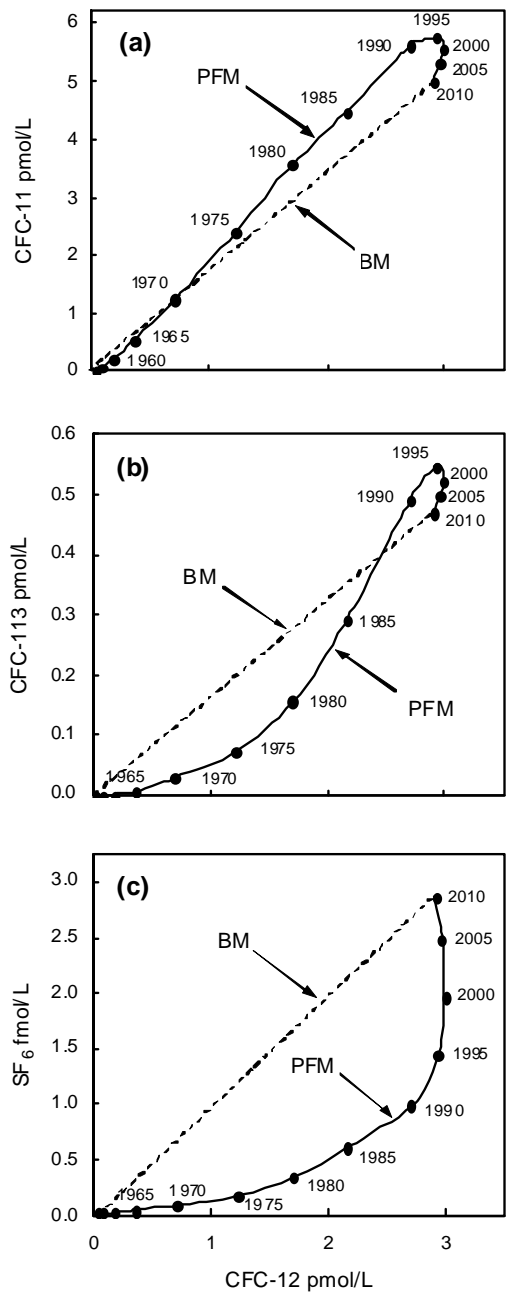


Figure 2

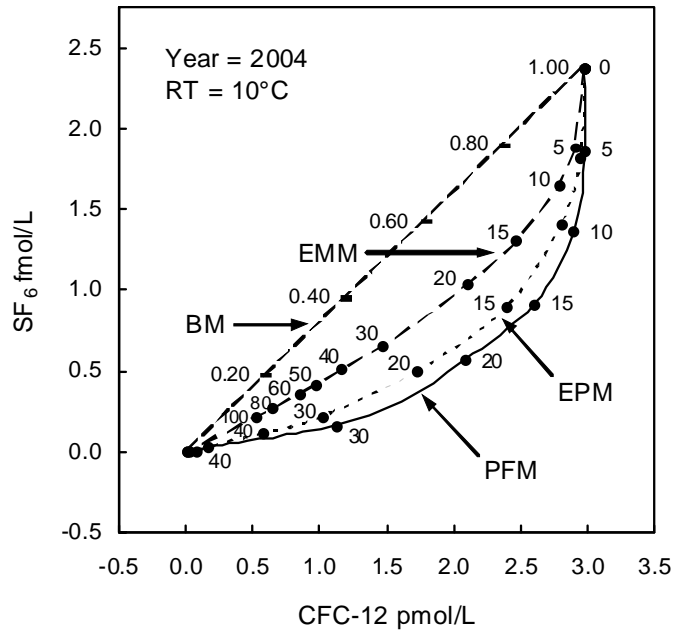


Figure 3

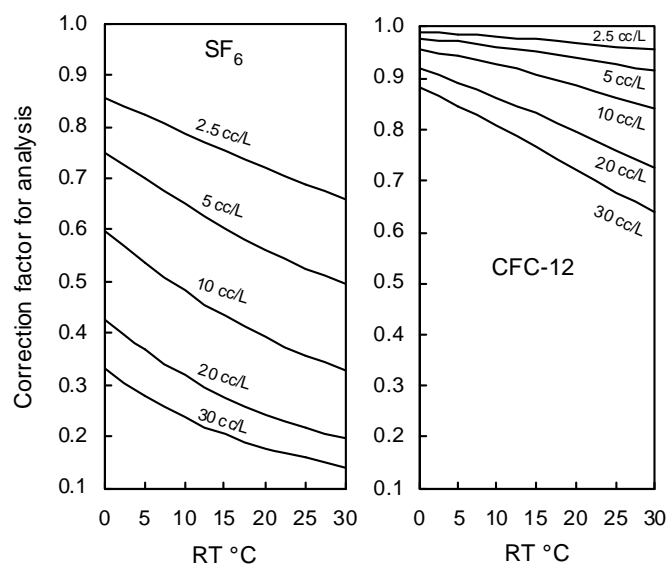


Figure 4

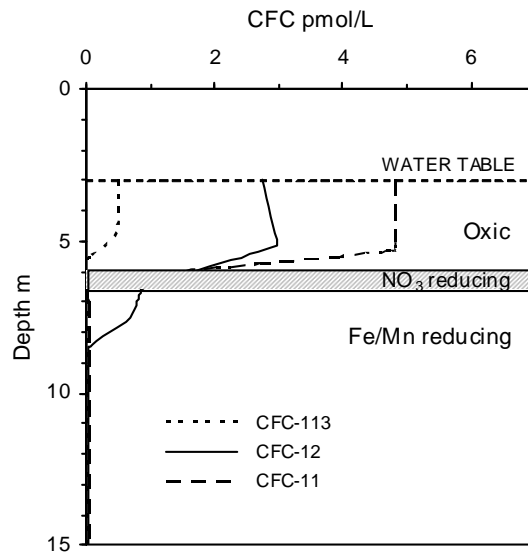
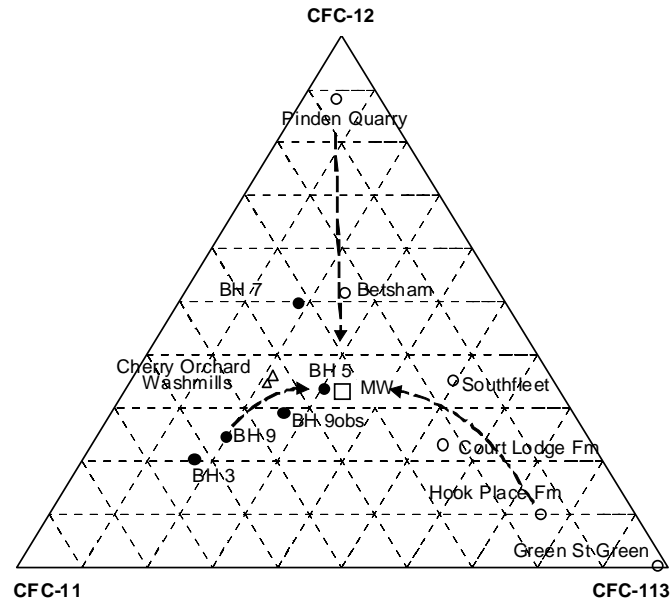


Figure 5



Figure

Table 1. Evidence for a possible thermal effect on CFC-12, which is below detection while other species remain detectable.

Site	CFC-12 pmol/L	CFC-11 pmol/L	CFC-113 pmol/L	SF ₆ fmol/L
<i>Bath, UK, temp 47°C, analysis by Spurenstofflabor</i>				
Cross Spring	<0.01	0.26	0.04	-
Stall Street BH	<0.01	0.17	0.02	-
<i>Chaufontaine, Belgium, temp 37°C, analysis by BGS</i>				
Chaud A	<0.02	0.55	-	0.18
Chaud B	<0.02	0.54	-	0.13

Table 2. Small amounts of modern water detected in Lagan Valley (Northern Ireland) groundwaters with Holocene bulk radiocarbon ages, showing the good agreement between CFC 11 and CFC-12. The right-hand column gives the model age for the old components.

Borehole	CFC av.			¹⁴ C model age in yrs	
	CFC-12	CFC-11	CFC av.	Bulk	Old comp.
CH	0.07	0.05	0.06	4450	5200
CL	0.00	0.02	0.01	1950	2000
E3	0.00	0.01	0.01	300	350
KH	0.04	0.04	0.04	1100	1300
LB	0.09	0.04	0.07	4200	5150
LC	0.07	0.02	0.04	2500	2990
LP1	0.13	0.11	0.12	390	1550
LP2	0.08	0.03	0.06	3900	4600
ML	0.06	0.05	0.05	7850	9200
MO	0.00	0.04	0.02	4700	4950
MV	0.03	0.03	0.03	3150	3400