Available online at www.sciencedirect.com
ScienceDirect
Science of the Total Environment 387 (2007) 353–362
Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind
www.elsevier.com/locate/scitotenv

Technical note

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

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Received 23 February 2007; received in revised form 6 June 2007; accepted 8 June 2007
Available online 12 July 2007

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, 2000; Cook et al., 1996; Oster et al., 1996). 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

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0048-9697/$ - see front matter.
doi:10.1016/j.scitotenv.2007.06.015

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. Fig. 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.

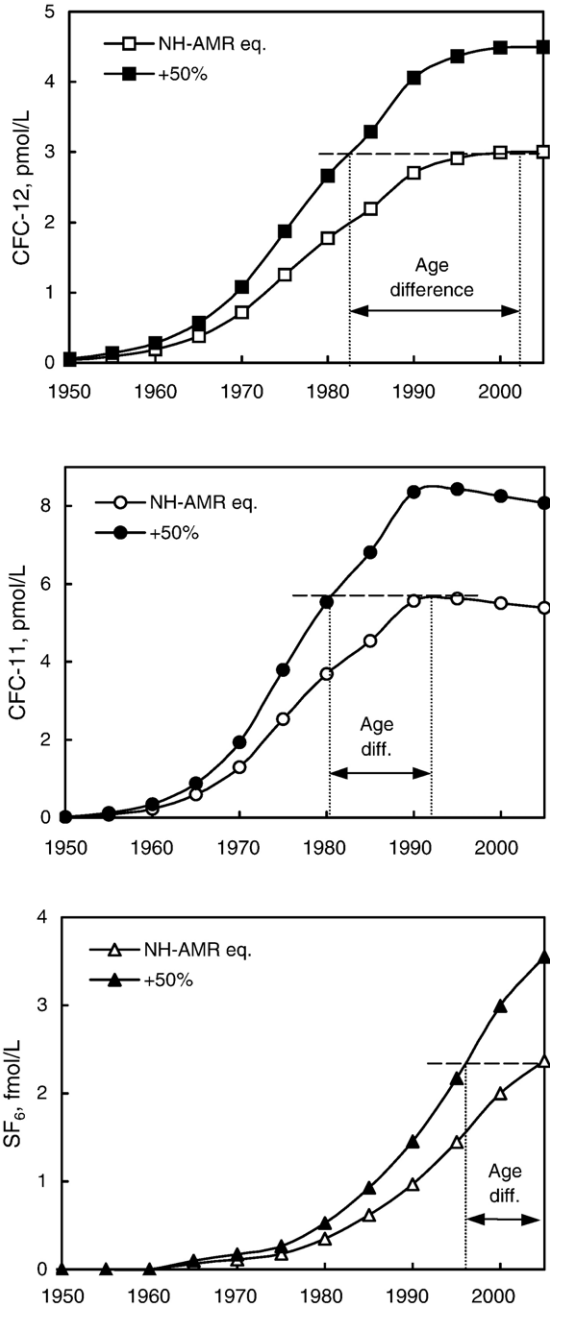

Fig. 1. Plots showing the concentration of CFC-12, CFC-11 and SF_6 in air-equilibrated water at 10 °C, based on the respective NH-AMR (northern hemisphere atmospheric mixing ratio) curves over the past half-century (from http://water.usgs.gov/lab/software/air_curve/). Also shown is the concentration curve for a notional 50% local atmospheric excess, and the resulting maximum difference in interpretation of water age.

2.2. Approach of the present study

Presumably the areas most likely to suffer from regional LAEs are to be found within urban boundaries.