

Occurrence and fate of chlorofluorocarbon plumes in groundwater

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Abstract Chlorofluorocarbons (CFCs) are stable volatile organic compounds that have been manufactured since about 1930 and appeared thereafter in the atmos- and hydrospheres. Oceanographers use CFC analyses in the pg l^{-1} range as tracers for ocean mixing processes. In hydrogeology, it has been suggested that CFCs may be used similarly for age-dating of groundwater. We reviewed studies that report on CFCs in groundwater from 16 porous and fractured aquifers on three different continents. In 12 aquifers, groundwater was found to be locally contaminated with CFCs in concentrations exceeding equilibrium with respect to modern air. Reported sources of contaminants include direct industrial solvent spills, river water infiltration, and landfills. Natural attenuation of CFCs in aerobic aquifers is limited. Evidence that reductive dechlorination of CFCs is occurring in anaerobic aquifers is provided. Possible degradation products known to be toxic (HCFC-21) or even carcinogenic (HCFC-31) are rarely studied. In order to assess the vulnerability of aquifers, there is a need to better identify these compounds.

Key words age-dating; aquifer vulnerability; attenuation; CFC; dechlorination; fate; freons; tracers

INTRODUCTION

Chlorofluorocarbons (CFCs) are synthetic organic chemicals fully substituted with chlorine and fluorine atoms that were first manufactured in the 1930s (Busenberg & Plummer, 1992). They were used worldwide as aerosol propellants, refrigerants, foam blowing agents, solvents and intermediates for synthesis of fluorinated polymers. World production peaked in 1986 with about 10^6 metric tons per year (Key *et al.*, 1998). The two chlorofluoromethanes, dichlorodifluoromethane (CCl_2F_2 , CFC-12) and trichlorofluoromethane (CCl_3F , CFC-11) made up to 77% of the total global market of CFCs in 1994. Due to their release into the environment, and due to their volatility and excellent chemical stability, CFCs accumulated in the atmosphere and were proven to be involved in the depletion of the stratospheric ozone. Consequently, many governments signed the Montreal protocol on substances that deplete the ozone layer (UNEP, 1987) and decreased the production of CFCs in the 1990s coming to a complete ban in 1996. It is predicted, however, that CFC concentrations in the atmosphere will be significant for at least this century because of the long atmospheric lifetimes and continuing sources (Watson *et al.*, 1990). The known increases of worldwide atmospheric concentrations of CFC-11 and CFC-12 and their low detection limits make them a tool for the dating of water. Since the mid-1970s, these CFCs have been routinely used for dating and tracing water masses in oceanographic studies (Bullister & Weiss, 1983). Later, hydrogeologists started to use CFCs as an age-dating

tool for groundwater (Thompson & Hayes, 1979). The presence of detectable concentrations of CFCs in groundwater indicates recharge after the late 1930s (Ekwurzel *et al.*, 1994), or mixing of older water with younger water. The successful use of CFCs as an age-dating tool has been reported in a number of studies since then, but in an even larger number of studies, measured CFC concentrations were super-saturated relative to air phase concentrations. Also, frequently the ratio of individual CFCs was not explicable using atmospheric ratios and solubilities. Thus, many CFC measurements could not be used for age-dating. This article will review 25 years of CFC measurements in groundwater and discusses the implications with a focus on the following questions:

- How frequently are CFC plumes encountered in groundwater?
- Which sources lead to contamination of groundwater by CFCs?
- What is the fate (and risk) of CFC plumes in groundwater?

DATABASE

Peer-reviewed data on CFC-11 and CFC-12 concentrations in 16 porous and fractured aquifers, measured by well-experienced laboratories, have been included in this study (Table 1). Reported detection limits for the CFCs in groundwater range from 0.5 to 2 g l⁻¹ (Bullister & Weiss, 1988; Hofer & Imboden, 1998). The analytical techniques normally used measure the CFCs in a concentration range below equilibrium with respect to air. We estimated the equilibrium concentrations based on reported recharge temperatures for each aquifer in Table 1 according to Busenberg & Plummer (1992). All samples with concentrations exceeding equilibrium concentrations were defined as contaminated. Thus, contamination is not defined here relative to a scale linked to human health risk, since CFCs are not toxic. In a study by Squillace *et al.* (1999), the reporting limit for CFCs in ambient groundwater was 0.2 µg l⁻¹, and the analytical technique was not aimed at detection of CFCs in the pg l⁻¹ range. The percentage of samples exceeding air equilibrium is not presented in that study.

RESULTS

In only four aquifers, all water samples had CFC concentrations at or below expected air equilibrium concentrations. These four aquifers included volcanic hot springs, and porous aquifers in rural areas in Canada and Germany. In most other aquifers, a small percentage of between 5 and 30% of the samples contain at least one CFC in a concentration exceeding air equilibrium. No clear trend as to whether CFC-11 or CFC-12 contamination is more frequent is evident. In one Swiss aquifer influenced by river water infiltration, all samples were contaminated with CFC-11. There is only one article using the term *CFC plume* when reporting data, i.e. in the Edwards aquifer in Texas (Thompson & Hayes, 1979), a 72 km long anomaly with elevated concentrations of CFC-11 was found in 1979. The origin of the spill was not known. It was calculated that the total amount of CFC-11 involved to create this plume could have been as small as 21 kg (Thompson & Hayes, 1979).

DISCUSSION

Occurrence of CFCs in groundwater

Although the number of aquifers in which CFC concentrations have been carefully measured (Table 1) is small, a few general features can be seen from the data. Volcanic hot springs did not contain CFCs. This agrees with measurements of CFCs in volcanic gases (Jordan *et al.*, 2000). Volcanism can thus be excluded as CFC contamination source, and CFCs are proven to be of anthropogenic origin. Below we discuss a few mechanisms by which CFCs may enter groundwater.

Equilibrium with modern air The solubilities of CFC-11 and CFC-12 in water and seawater were determined by Warner & Weiss (1985) for the temperature range of

Table 1 Reported peer-reviewed data on CFC-11 and CFC-12 concentrations in various aquifers.

Aquifer: Location, geology, thickness	Re- charge temp.(°C)	No. of samples	% cont.*	Max. CFC-11 (pg l ⁻¹)	Max. CFC-12 (pg l ⁻¹)	Reference
Hot Springs (Arkansas, USA), volcanic rocks	n.m.	2	none	3	n.m.	(Thompson & Hayes, 1979)
Wharton Tract (New Jersey, USA), unconsolidated sandy sediments, 30 m	3.7	8	none	910	n.m.	(Thompson & Hayes, 1979)
Sturgeon Falls (Ontario, Canada), silty sands, 21 m	3	20	none	937	553	(Cook <i>et al.</i> , 1995)
Rhine Valley (Bocholt, Germany), sand, 0–50 m	10.1	15 2 wells	none	261	350	(Oster <i>et al.</i> , 1996)
Delmarva Peninsula (Delaware, USA), sand and gravel, <30 m	9	173	5	55624	397	(Dunkle <i>et al.</i> , 1993)
New Jersey Coastal Plane (USA), sand, 50 m	13	15	6	2525	598	(Szabo <i>et al.</i> , 1996)
Rhine Valley (Schwetzinger Hardt, Germany) sand, 30–40 m	10.1	14 1 well	7	1099	374	(Oster <i>et al.</i> , 1996)
Central Oklahoma Aquifer (USA), terrace deposits, shales, sandstones, 230 m	9	58	16	39500	1.1 × 10 ⁶	(Busenberg & Plummer, 1992)
Valdosta (Georgia, USA), karstic limestone, 13–167 m, river infiltration	17.5	85	20	540	64600	(Plummer <i>et al.</i> , 1998)
Taurus Mountains (Turkey), karstified, 1000 m	5–15	11	27	1717	1153	(Nativ <i>et al.</i> , 1999)
Edwards Aquifer (Texas, USA), limestone, CFC-11 spill	n.m.	18	33	36000	n.m.	(Thompson & Hayes, 1979)
Mirror Lake (New Hampshire, USA), fractured crystalline bedrock, 250 m	6	21	33	88830	2300	(Goode, 1998)
Waterloo Moraine (Ontario, Canada), sand silt, gravel, 60 m	6	14	36	1090	6665	(Johnston <i>et al.</i> , 1998)
Little Hungarian Plain (Danube, Hungary), coarse sands, 100 m, river infiltration	10–14	18	56	2006	1252	(Böhlke <i>et al.</i> , 1998)
Linsental (Switzerland), gravel, 25 m, river infiltration	8.6	39 + 7	100	4100	730	(Hofer & Imboden, 1998; Beyerle <i>et al.</i> , 1999)
Whole USA, public drinking water wells	var.	2948	0.8 [†]	1.5 × 10 ⁶	3.0 × 10 ⁶	(Squillace <i>et al.</i> , 1999)

* Exceeding equilibrium with respect to air in 1990.

† Percentage of samples exceeding reporting limit of 0.2 µg l⁻¹.

n.m.: not measured.

0–40°C and 0–40 parts per thousand salinity. Since the 1970s, the atmospheric concentrations of CFCs have been monitored (Busenberg & Plummer, 1992) and reconstructions of atmospheric concentrations for the period before have been calculated based on manufacturers' data and rates of photolysis in the stratosphere. Busenberg & Plummer (1992) present the concentrations of CFC-11 and CFC-12 at equilibrium with the atmosphere in selected years in natural waters at different temperatures. Groundwater with a temperature of 10°C and in equilibrium with the atmosphere in 1990 contained 810 and 320 pg l⁻¹ of CFC-11 and CFC-12, respectively. Local and temporal excesses of CFC concentrations in the atmosphere of up to 160% have been found in the air at Heidelberg, Germany (Oster *et al.*, 1996), at Taipei City (Wang *et al.*, 2000) and also in the New York metropolitan area (Ho *et al.*, 1998). Oster *et al.* (1996) show that this variability is significantly dampened by molecular diffusion in the vadose zone, and that local excesses in groundwater therefore do not exceed 60% (CFC-11) and 100% (CFC-12). Maximum CFC-11 and CFC-12 concentrations in soil air in 1990 near Heidelberg were expected to be 700 and 500 pptv (Oster *et al.*, 1996). This would lead to equilibrium concentrations in groundwater at 10°C of 1430 and 466 pg l⁻¹ and explains all values found in the studies in the two German aquifers reported in Table 1.

Sampling artefacts Several authors report that the origin of CFC contaminated samples is due to sampling artefacts. These include sampling equipment such as tubing (Busenberg & Plummer, 1992) and well-construction materials such as sand installed at well screens, grout used to seal the borehole annulus and PVC adhesives (Goode, 1998). Note that samples with CFC contamination several orders of magnitude higher than air equilibrium can often not be quantified properly by the sensitive analytical techniques applied in many laboratories, and reported data tend to underestimate the number of contaminated samples as well as the highest measured concentrations.

Infiltration of contaminated river water River water has been clearly identified as a CFC source for groundwater (Busenberg & Plummer, 1992; Clark *et al.*, 1995; Böhlke *et al.*, 1998; Plummer *et al.*, 1998). A 40-year record of historic CFC contamination in the Danube River is preserved in the aquifer underlying the little Hungarian Plain (Böhlke *et al.*, 1998) and could be described using independent ³H and He isotope techniques for groundwater age-dating. Surface waters in Oklahoma had unusually large CFC concentrations especially near Oklahoma City, and treated sewage discharged into rivers was suspected of being the origin for CFCs in the aquifer (Busenberg & Plummer, 1992).

Landfills Significant amounts of CFCs have been dumped in landfills containing municipal and industrial wastes. It has been shown that gaseous emissions from landfills containing municipal wastes (including old spray cans (Laugwitz *et al.*, 1990; Deipser & Stegmann, 1994) or shredded insulation foams and plastics (Haderlein & Pecher, 1988) contain significant CFC concentrations in the range 0.1–200 mg m⁻³ for CFC-11, and 35–600 mg m⁻³ for CFC-12 (Gendebien *et al.*, 1992; Allen *et al.*, 1997). Soil gas surveys at up to 130 m away from a landfill at Foxhall in Suffolk, UK, revealed measurable amounts of CFCs and lead to the conclusion that CFCs can migrate as gaseous pollutants through the vadose zone to groundwater (Ward *et al.*,

1996). Groundwater in equilibrium with typical landfill gas concentrations would contain CFCs in the 10^7 pg l⁻¹ range.

Solvent spills CFC-11 and CFC-12 have boiling temperatures of 23°C and -30°C, respectively. They were thus not very practical solvents, but CFC-11 may have been used occasionally. Industry used CFC-113 as a degreasing solvent, and groundwater plumes with CFC-113 have been reported (Lesage *et al.*, 1990). Similar to trichloroethene wastes, CFC solvents may have been dumped into the vadose zone as DNAPL.

Thermal heat pumps In Switzerland, more than 10 000 pumps were operated in 1992 to extract heat from the ground. Some of these installations use the geothermal heat gradient in the vadose zone, others are using the heat in groundwater. Primary and secondary heat-conducting fluids such as glycols or refrigerants are pumped through closed circuits. No studies are available concerning the impact of such heat circuits on groundwater quality. A leak in such a circuit may, however, create a DNAPL spill of CFCs into the ground. Since 1994, only HCFCs are permitted in new installations in Switzerland.

Fate of CFCs in groundwater

Volatilization Gaseous loss to the vadose zone and the atmosphere is a potential mechanism leading to natural attenuation of CFC plumes in groundwater. As discussed in Werner & Höhener (2002), losses of volatile pollutants through a stagnant groundwater table are limited by diffusion and are therefore very small. These losses, however, are expected to increase in the case of a frequently oscillating groundwater table.

Biotransformation Transformations of CFCs and HCFCs in the subsurface were observed only after 1990. Previously, CFC-11 and CFC-12 were “expected to be almost totally unreactive biologically” (Rowland & Molina, 1975). Under aerobic conditions such as in seawater, no transformations are known. Lovley & Woodward (1992) first demonstrated bacterial removal of near-atmospheric concentrations of CFC-11 and CFC-12 during incubation of anoxic soils, sediments, and bacterial cultures. In bioreactors simulating landfill conditions with elevated CFC concentrations, Deipser (1998) and Ejlerthsson *et al.* (1996) showed biologically catalysed dechlorination of CFC-11 to HCFC-21 and HCFC-31 (as illustrated in Fig. 1), and of CFC-12 to HCFC-22.

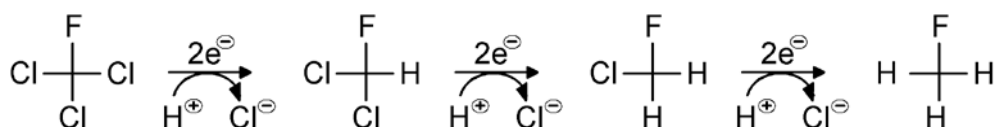


Fig. 1 Dechlorination of CFC-11 to HCFC-21, HCFC-31 and HFC-41.

Reductive defluorination of CFCs and HCFCs has never been observed at ambient temperatures since the fluorine-carbon bond is extremely stable. HCFC-21, -22, and -31 are regularly found as major trace compounds in landfill gases (Allen *et al.*, 1997).

HCFC-21 is reported to be toxic, having an exposure limit (MAK-value) of 10 mg m^{-3} (DFG, 1997). Due to this toxicity, HCFC-21 was not produced by industry as a refrigerant or aerosol. HCFC-31 is suspected to be carcinogenic. Hydrogeologists using the CFCs for age-dating frequently find recent groundwater samples with CFC-11 and/or CFC-12 concentrations below detection limit. Oster *et al.* (1996) report that in various anaerobic environments such as groundwater, lake water or composts, the rate of dechlorination of CFC-11 is always roughly ten times larger than the rate of dechlorination of CFC-12. Degradation rates are large enough to prevent migration of CFC plumes in anaerobic aquifers. However, the HCFC degradation products are equally mobile, more toxic and may persist in anaerobic aquifers. A plume of CFC-11 in an anaerobic aquifer is thus likely to exhibit similar features to a plume of tetrachloroethene, being transformed to a more toxic transformation product vinyl-chloride. No field studies can be found at present on the fate of HCFC-21 or HCFC-31 in aquifers.

CONCLUSIONS

Contamination of groundwater with CFCs in concentrations above equilibrium with modern air is a widespread phenomenon. In many geological settings, CFC measurements cannot be used as an age-dating tool but rather as a tool for aquifer vulnerability assessments. However, sampling techniques and monitoring installations are critical in attaining accurate assessments of CFC contamination in groundwater. CFCs are candidates to remain for very long time periods in aquifers. Whereas in aerobic groundwater they persist as CFCs, they are transformed to stable and toxic HCFCs in anaerobic groundwater. More work is needed to accurately analyse and better understand the fate of HCFCs in groundwater.

REFERENCES

- Allen, M., Braithwaite, A. & Hills, C. C. (1997) Trace organic compounds in landfill gas at seven UK waste disposal sites. *Environ. Sci. Technol.* **31**, 1054–1061.
- Beyerle, U., Aeschbach-Hertig, W., Hofer, M., Imboden, D. M., Baur, H. & Kipfer, R. (1999) Infiltration of river water to a shallow aquifer investigated with $^3\text{H}/^3\text{He}$, noble gases and CFC. *J. Hydrol.* **220**, 169–185.
- Böhlke, J. K., Revesz, K., Busenberg, E., Deak, J., Deseé, E. & Stute, M. (1998) Groundwater record of halocarbon transport by the Danube River. *Environ. Sci. Technol.* **31**, 3293–3299.
- Bullister, J. L. & Weiss, R. F. (1983) Atmospheric chlorofluoromethanes in the Greenland and Norwegian seas. *Science* **221**, 265–268.
- Bullister, J. L. & Weiss, R. F. (1988) Determination of CCl_3F and CCl_2F_2 in seawater and air. *Deep-Sea Res.* **35**, 839–853.
- Busenberg, E. & Plummer, L. N. (1992) Use of chlorofluorocarbons (CCl_3F and CCl_2F_2) as hydrologic tracers and age-dating tools: the alluvium and terrace system of central Oklahoma. *Wat. Resour. Res.* **28**, 2257–2283.
- Clark, J. F., Smethie, W. M. & Simpson, H. J. (1995) Chlorofluorocarbons in the Hudson estuary during summer months. *Wat. Resour. Res.* **31**, 2553–2560.
- Cook, P. G., Solomon, D. K., Plummer, L. N., Busenberg, E. & Schiff, S. L. (1995) Chlorofluorocarbons as tracers of groundwater transport processes in a shallow, silty sand aquifer. *Wat. Resour. Res.* **31**, 425–434.
- Deipser, A. (1998) Biodegradation of volatile CFCs, HCFCs and VC in compost and marl. *Waste Manage. Res.* **16**, 330–341.
- Deipser, A. & Stegmann, R. (1994) The origin and fate of volatile trace components in municipal solid waste landfills. *Waste Manage. Res.* **12**, 129–139.
- DFG (Deutsche Forschungsgemeinschaft) (1997) *List of MAK and BAT Values 1997. Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Report no. 33.* Wiley-VCH Verlag GmbH, Weinheim, Germany.

- Dunkle, S. A., Plummer, L. N., Busenberg, E., Philips, P. J., Denver, J. M., Hamilton, P. A., Michel, R. L. & Coplen, T. B. (1993) Chlorofluorocarbons (CCl_3F and CCl_2F_2) as dating tools and hydrologic tracers in shallow groundwater of the Delmarva Peninsula, Atlantic Coastal Plain, United States. *Wat. Resour. Res.* **29**, 3837–3860.
- Ejlertsson, J., Johansson, E., Karlsson, A. & Svensson, B. H. (1996) Anaerobic degradation of xenobiotics by organisms from municipal solid waste landfilling conditions. *Antonie van Leeuwenhoek* **69**, 67–74.
- Ekwurzel, B., Schlosser, P., Smethie, W. M., Plummer, L. N., Busenberg, E., Michel, R. L., Weppernig, R. & Stute, M. (1994) Dating of shallow groundwater: comparison of the transient tracers $^3\text{H}/^4\text{H}$, chlorofluorocarbons, and ^{85}Kr . *Wat. Resour. Res.* **30**, 1693–1708.
- Gendebien, A. et al. (1992) *Landfill Gas: From Environment to Energy*. EC, Directorate General Energy, Luxembourg.
- Goode, D. J. (1998) Ground-water age and atmospheric tracers: simulation studies and analysis of field data from the Mirror Lake Site, New Hampshire. PhD Thesis, Princeton University, USA.
- Haderlein, S. & Pecher, K. (1988) Mobility of chlorofluorocarbons in deposits of shredder wastes from plastic and metal utilizing industries. *Wat. Air Soil Pollut.* **37**, 459–464.
- Ho, D. T., Schlosser, P., Smethie, W. M. & Simpson, H. J. (1998) Variability in atmospheric chlorofluorocarbons (CCl_3F and CCl_2F_2) near a large urban area: implications for groundwater dating. *Environ. Sci. Technol.* **32**, 2377–2382.
- Hofer, M. & Imboden, D. (1998) Simultaneous determination of CFC-11, CFC-12, and Ar in water. *Anal. Chem.* **70**, 724–729.
- Johnston, C. T., Cook, P. G., Frape, S. K., Plummer, L. N., Busenberg, E. & Blackport, R. J. (1998) Ground water age and nitrate distribution within a glacial aquifer beneath a thick unsaturated zone. *Ground Water* **36**, 171–180.
- Jordan, A., Harnisch, J., Borchers, R., LeGuern, F. & Shinoharta, H. (2000) Volcanogenic hydrocarbons. *Environ. Sci. Technol.* **34**, 1122–1124.
- Key, B. D., Howell, R. D. & Criddle, C. S. (1998) Fluorinated organics in the biosphere. *Environ. Sci. Technol.* **31**, 2245–2254.
- Laugwitz, R., Poller, T. & Deipser, A. (1990) Der Beitrag von Hausmülldeponien zum Stoffkreislauf der Fluorchlor-kohlenwasserstoffe. (The contribution of domestic waste landfills to the chlorofluorocarbon cycle). *Muell Abfall* **22**, 316–318.
- Lesage, S., Jackson, R. E., Priddle, M. W. & Riemann, P. G. (1990) Occurrence and fate of organic solvent residues in anoxic groundwater at the Gloucester landfill, Canada. *Environ. Sci. Technol.* **24**, 559–566.
- Lovley, D. & Woodward, J. C. (1992) Consumption of freons CFC-11 and CFC-12 by anaerobic sediments and soils. *Environ. Sci. Technol.* **26**, 925–929.
- Nativ, R., Gunay, G., Hotzl, H., Reichert, B., Solomon, D. K. & Tezcan, L. (1999) Separation of groundwater-flow components in a karstified aquifer using environmental tracers. *Appl. Geochem.* **14**, 1001–1014.
- Oster, H., Sonntag, C. & Munnich, K. O. (1996) Groundwater age dating with chlorofluorocarbons. *Wat. Resour. Res.* **32**, 2989–3001.
- Plummer, L. N., Busenberg, E., McConnell, J. B., Drenkard, S., Schlosser, P. & Michel, R. L. (1998) Flow of river water into a karstic limestone aquifer. 1. Tracing the young fraction in groundwater mixtures in the Upper Floridan Aquifer near Valdosta, Georgia. *Appl. Geochem.* **13**, 995–1015.
- Rowland, F. S. & Molina, M. J. (1975) *J. Rev. Geophys. Space Phys.* **13**, 1–35.
- Squillace, P., Moran, M. J., Lapham, W. W., Proce, C. V., Clawges, R. M. & Zogorski, J. S. (1999) Volatile organic compounds in untreated ambient groundwater of the United States, 1985–1995. *Environ. Sci. Technol.* **33**, 4176–4187.
- Szabo, Z., Rice, D. E., Plummer, L. N., Busenberg, E. & Drenkard, S. (1996) Age dating of shallow groundwater with chlorofluorocarbons, tritium/helium-3 and flow path analysis, Southern New Jersey Coastal Plain. *Wat. Resour. Res.* **32**, 1023–1038.
- Thompson, G. M. & Hayes, J. M. (1979) Trichlorofluoromethane in groundwater—a possible tracer and indicator of groundwater age. *Wat. Resour. Res.* **15**, 547–554.
- UNEP (1987) Montreal protocol on substances that deplete the ozone layer. United Nations Environment Program.
- Wang, J. L., Chew, C., Chen, S. W. & Kuo, S. R. (2000) Concentration variability of anthropogenic halocarbons and applications as internal reference in volatile organic compound measurements. *Environ. Sci. Technol.* **34**, 2243–2248.
- Ward, R. S., Williams, G. M. & Hills, C. C. (1996) Changes in major and trace components of landfill gas during subsurface migration. *Waste Manage. Res.* **14**, 243–261.
- Warner, J. & Weiss, R. F. (1985) Solubilities of chlorofluorocarbons 11 and 12 in water and seawater. *Deep-Sea Res.* **32**, 1485–1497.
- Watson, R. T., Rodhe, H., Oeschger, H. & Siegenthaler, U. (1990). Greenhouse gases and aerosols. In: *Climate Change—the IPCC Scientific Assessment* (ed. by J. T. Houghton, G. J. Jenkins & J. J. Ephraums), 4–40. Cambridge University Press, Cambridge, UK.
- Werner, D. & Höhener, P. (2002) The influence of water table fluctuations on the volatilisation of contaminants from groundwater. In: *Groundwater Quality: Natural and Enhanced Restoration of Groundwater Pollution* (ed. by S. F. Thornton & S. E. Oswald), IAHS Publ. no. 275 (this volume).