CHLOROFLUOROCARBONS
NEW TRANSIT TRACERS FOR GROUNDWATER DATING

Liang-Feng HAN and Manfred Gröning

Isotope Hydrology Section, IAEA

What are CFCs?

Chlorofluorocarbons (CFCs), specifically CFC-11 (CCl_3F), CFC-12 (CCl_2F_2) and CFC-113 ($C_2Cl_3F_3$), are chemically stable, entirely man-made compounds. CFCs have been manufactured for a variety of purposes and released on a large scale into the atmosphere and hydrosphere since 1940's.

Because of their rapid accumulation in the atmosphere, their contribution to ozone destruction in the lower stratosphere, and their contribution as atmospheric greenhouse gases, CFCs have received widespread attention in recent years. Since the 1970s, in addition to many individual monitoring efforts, regular measurements of atmospheric CFC concentrations have been carried out at stations throughout the world. Based on the production records and release data prior to 1977 and world-wide atmospheric measurements thereafter, growth curves of atmospheric concentrations of CFCs from 1940 to the present have been reconstructed (Fig.1).

Recent studies have confirmed that CFCs, like other global transient tracers such as ^{3}H and ^{85}Kr, can be used as a tool for dating groundwater. The basic assumption in dating groundwater is that the concentrations of CFCs in a particular water mass are at equilibrium with the CFC partial pressures in the atmosphere at the time when the water reaches the groundwater table and is further on isolated from the atmosphere. Thus, by measuring CFC concentrations in groundwater, together with the known "input functions" and solubility data it is possible to determine the residence time ("age") of the groundwater.

Advantages of CFCs as Dating Tools

CFCs present several advantages over the other transient tracers:

- The analysis is easy, inexpensive and rapid. CFC concentrations are determined by a gas chromatographic method. A single determination requires less than 30 ml of water and 30 minutes of time.
- ^{3}H "bomb" peaks will continue to fade. Thus, in the decades ahead the easy detection of CFCs will allow them to be used in hydrological studies in cases where it is difficult or impossible to achieve results with ^{3}H. CFCs are globally distributed, their atmospheric concentrations are not strongly dependent on latitude. This makes them especially useful in studies in the southern hemisphere, which received much fewer bomb HTO than the northern hemisphere in the mid-1960's.
- CFCs are very sensitive indicators to contamination of groundwater by modern surface water. The detection limit of CFCs is about 0.01pmol/kg. Therefore, less than 0.1% modern surface water in pre-1940 groundwater is detectable.
- CFC concentration ratios can be used to estimate the age of the groundwater (Fig.2). From the relative concentrations of two CFCs in a water sample one can determine the atmospheric CFC concentration ratio at the time when the water was isolated from the atmosphere. This may provide additional and more precise information about the groundwater age, is an independent plausibility check and avoid erroneous conclusions eventually drawn from concentration measurements. It should be noted that although the CFC concentrations in the water depend strongly on the temperature, the concentration ratios are almost temperature-independent (Fig.3). Consequently, in cases where the recharge temperature is uncertain, the age of the ground water can still be determined. As seen in Fig.3, in general, a 5°C error in estimation of the recharge temperature would result in an error of more than 20% in the calculated atmospheric CFC concentrations, causing an uncertainty of several years, particularly for water recharged after 1975. On the other hand, a 5°C error in recharge temperature would result in only a slight difference in the calculated atmospheric CFC concentration ratios (<6%). The annual increase rate of atmospheric CFC concentration ratios is so rapid (>6% between 1950 and 1990), that a 5°C error in the recharge temperature would only cause an uncertainty in the age estimation of 1 year or less. Additionally, it is even possible, based on the age determined by the CFC ratios to estimate further the recharge temperature, e.g., if the CFC concentrations in the water are lower than expected from the recharge year, the recharge temperature must be higher than assumed, and vice versa.

Limitations of CFCs

Possible limitations of the use of CFC dating technique are:

- Compared to other tracers, CFC concentrations in groundwater are more sensitive to contamination from ur-

(Continued on page 14)

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TECHNICAL

(Continued from page 13)
ban and industrial sources.

• The samples, particularly the older waters, can be easily contaminated by trace levels of CFCs introduced during sampling, storage and analysis.

• Generally, the non-local CFC input functions are used for groundwater dating. However, because CFCs are released into the atmosphere from anthropogenic sources, the CFC input functions in densely-inhabited regions might be different from the non-local trends and might even be much more variable with time.

• Other processes that can modify CFC concentrations in groundwater, such as sorption on soil and organic matter, microbial degradation, entertainment of excess air can contribute to uncertainties in age estimation of groundwater.

Due to all these limitations mentioned above, CFC analyses may not replace other tracers such as ^{3}H and ^{85}Kr completely; but instead, they provide important information that will supplement the other tracers in dating groundwater. The different shape of the input functions for CFCs and ^{3}H provides possibilities to derive water admixtures more precisely and improve water dating (the CFC input functions are relatively smooth and steadily increasing, while ^{3}H is dominated by the 1963 bomb peak). This can be demonstrated by the following two examples: 1) In the case where an "old" groundwater (age of several decades) is contaminated by a small portion of "young" water, ^{3}H and CFCs provide quantitatively different information: whereas ^{3}H is most sensitive to water formed in the 1960's, CFCs pronounce any contribution of recent groundwater. 2) Due to the shape of the input functions hydrodynamic dispersion may have a small effect on CFC-based ages, whereas dispersion of the bomb peak typically results in increased $^{3}H/^{3}He$ ages in post-bomb peakwaters and reduced ages in pre-bomb peak waters.

In these two cases, the combined use of CFCs and $^{3}H/^{3}He$ dating techniques can help to eliminate some of the uncertainties in modern groundwater dating.

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Contributions may be addressed to:

Water and Environment News, Isotope Hydrology Section, International Atomic Energy Agency, P.O. Box 100, Wagramerstrasse 5, A-1400, Vienna, AUSTRIA
Tel. +43-1-2060-21741;
Fax:+43-1-20607;
E-Mail: z.h.pang@iaea.org

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