Chlorofluorcarbon (CFC) Analysis of Groundwater

CFC analysis of groundwater provides a method for determining the age of groundwater that has recharged the aquifer during the last 40 years.

Sampling and Submitting Samples

It is always difficult when sampling groundwater for CFC analysis to find a method that is practical and easy to use without the potential of contamination of the sample. When the CFC laboratory was first developed at CSIRO Land and Water, sampling required the use of a stainless steel bailer, ultra-high purity nitrogen and glass ampoules sealed by blowtorch. Over the years, the glass ampoules have been replaced with glass bottles with screw top metal lids (available from the CLW laboratory) and, more recently, certain types of submersible pumps have been tested and are now used instead of the stainless steel bailer in some applications.

CFC analyses are a very useful way of getting recharge information on water that is up to 4 or 5 decades old. Unfortunately, there are contaminants both in some groundwater bodies and potentially in the sample collection process that can limit the application. When sampling, it is advisable to stay clear of plastic material as much as possible and where plastic has to be used, it is best to use nylon and limit the contact time with the water. Hence, nylon tubing is usually used attached to stainless pumps when sampling groundwater. Groundwater that has been in contact with PVC casing and has not been sufficiently flushed can cause problems. Hence, ensure 3 or more bore volumes of water are removed before collecting samples of groundwater for CFC analysis.

The groundwater being sampled should have minimal contact with air. A pump rate of at least a few litres per minute will help ensure this. However, if the pump rate is too high, then it may be possible for the pump to cavitate and cause problems. The groundwater being sampled should flow directly into the sample bottle via the nylon hose and displace water into a larger metal or glass container (as per figure below). Water is allowed to flow out of the larger container. The container should be large enough to allow the lid to be placed on the bottle whilst under water. A container with a capacity of several litres is ideal for this. After the bottles are filled, and sealed, remove from the container, dry and label. The best way to label is using plastic, electrical tape which is easily removed after analysis so that the bottles can be reused. Please ensure the lids are tight by giving the caps a “tweak” using a pair of multigrips after they have been hand-tightened. Be careful not to over-tighten and strip the thread or break the bottle.

Ensure that there are no air bubbles in the sample bottle immediately after collection and then, if OK, send the samples to the laboratory. Please note that air bubbles often develop several minutes to days after sampling for a variety of reasons. These do not cause a problem.

Please note that, because of potential problems during sampling and analysis, groundwater samples should be collected in triplicate. Reports will only be given where there is good reproducibility in with at least 2 of the replicates.

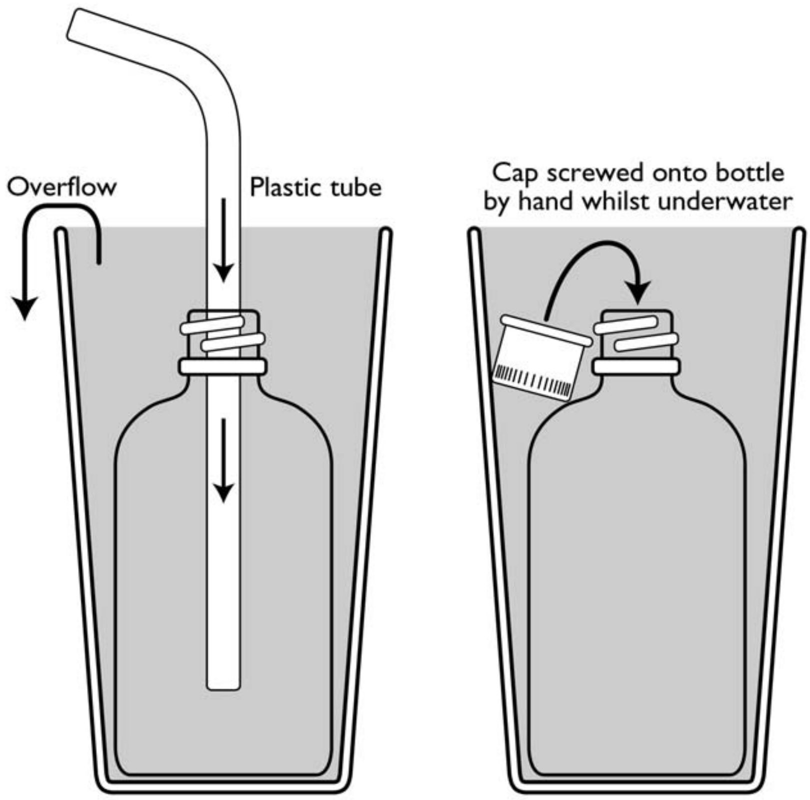

Figure 1 Dispensing water from the bailer to the sample bottle

Analysis Methodology

CFC-11 and CFC-12 concentrations in groundwater are measured by firstly stripping the CFC gas from the water sample under a stream of ultra-high purity nitrogen gas. The CFC gas/nitrogen is the passed through a gas chromatograph where the CFC-11 and CFC-12 peaks are identified and measured separately. The set up at CSIRO CLW closely follows that described by Bussenberg and Plummer, 1992.

The CFC-11 and CFC-12 concentrations measured are those of the water (pg kg^{-1}). To convert these to an age, we then determine the equivalent concentration in the atmosphere (pp by vol). To do this, we require information on the salinity of the water, the recharge temperature of the water (mean annual temperature usually) and the surface elevation. This value is then matched to measured atmospheric data to give a CFC-11 and CFC-12 age.

CFC Analytical Errors

Analytical precision for CFC-11 is approximately ± 2% at 500 pg kg^{-1}, ± 5% at 100 pg kg^{-1}, and ± 20% at 20 pg kg-1. Analytical precision for CFC-12 is ± 2% at 500 pg kg^{-1}, ± 10% at 100 pg kg^{-1}, and ± 30% at 20 pg kg^{-1}. Corresponding errors in apparent CFC ages are approximately ± 2 years for ages less than 20 years, increasing to ± 4 years for ages of 30 years. The detection limit for both CFCs is usually approximately 5 pg kg-1, which equates to an age of ~ 1961 although potential errors in sampling means that we usually do not quote CFC-11 and CFC-12 ages older than 1965. It is not possible to determine ages prior to that date. Where large peaks interfere with CFC peaks in the chromatograms, detection limits may be higher than this. The sampling blank is estimated to be approximately 10 pg kg-1 for CFC-12 and 20 pg kg-1 for CFC-11.

Where concentrations are not given, it is due to either interference on the chromatogram, or to poor reproducibility of replicate samples.

Please note that CFC-11 degrades under anoxic conditions. This is often seen as the CFC-11 age >> CFC-12 age. If this is the case, the CFC-12 age better reflects the groundwater age.

Further information on CFC dating can be found in:

Busenberg, E. and 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. Water Resources Research, 28(9):2257-2283.

Cook, P.G. and Solomon, D.K. (1997) Recent advances in dating young groundwater : 3H/3He, chlorofluorocarbons and 85Kr. J. Hydrol., 191:245-265.

Cook, P.G. and Herczeg, A.L. (1998) Groundwater Chemical Methods for Recharge Studies. Part 2 of The Basics of Recharge and Discharge. CSIRO Publishing.

Plummer, L.N., Michel, R.L., Thurman, E.M. and Glynn, P.D. (1993) Environmental tracers for age-dating young groundwater. In Regional Ground-Water Quality, Van Nostrand Reinhold, New York, pp.255-294.

Plummer, L.N. and Busenberg, E. (1999) Chlorofluorocarbons. In P.G. Cook and A.L. Herczeg (1999) Environmental Tracers in Subsurface Hydrology. Kluwer Academic Press, p.441-478.

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