The Reston Chlorofluorocarbon Laboratory

CFC Sampling Method - Bottles

A procedure that involves filling and capping simple glass bottles with special foil-lined caps under water has been tested. Samples analyzed after storage over 6 months demonstrate the validity of the new method. This document describes the sampling procedure and presents results of tests with the CFC bottle method.

CFC bottle method

If archival of water samples for CFC or other VOC analysis for periods of more than 6 months is required, then it is recommended that water samples be collected in fused borosilicate ampoules, as before (Busenberg and Plummer, 1992). Otherwise, water samples for CFC analysis can be collected in glass bottles capped with a special foil-lined cap, as described below.

Source of bottles and caps

Bottles and caps can be obtained from the Scientific Specialties company at 800-648-7800. The bottles are 125ml (4 oz) boston round clear glass and have a cap size 22-400.

Item No. B73504 is a case of 24 bottles with teflon lined caps. **These bottles have the wrong caps!** Discard these caps and replace them with the caps below.

Bottles are also available from any Wheaton glass supplier as Wheaton part number 217112, which is a case of 24 bottles with no caps.

The caps are sold as Scientific Specialties item no. A69522, white plastic caps with aluminum foil liner in a bag of 72. **Use only these aluminum lined caps! This cap is the key to the method.** Discard any caps, if the foil liner appears scratched, dented, or altered in any way.

Filling procedure

Instruction given below must be followed to the letter to obtain good results with the bottle sampling method for CFCs in ground water.

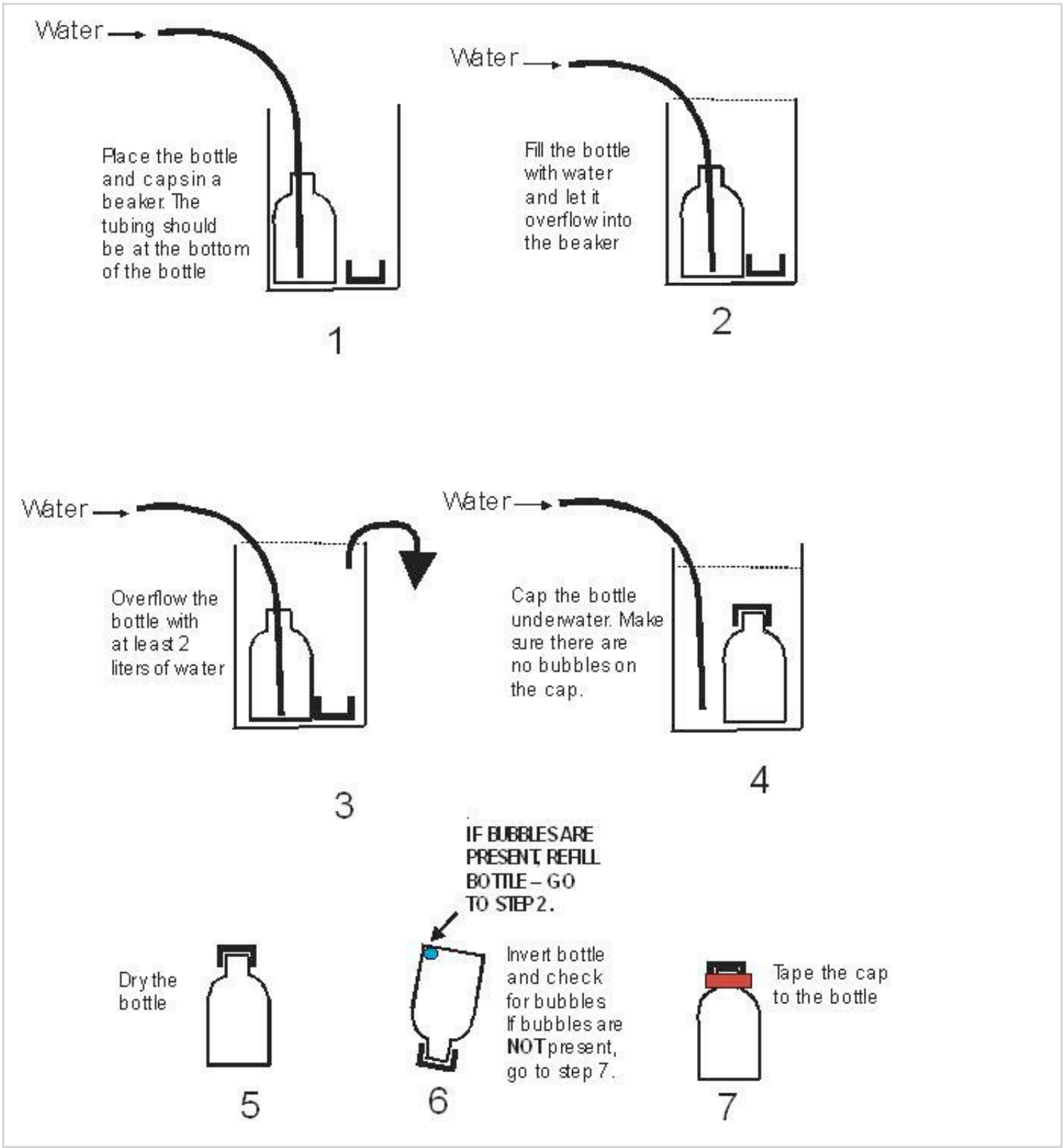
We are receiving too many samples with loose caps and caps that are not properly taped (see below for examples).

The bottles and caps should be **thoroughly** rinsed with the ground water. The bottles are filled **underwater in a beaker and capped underwater**. Refrigeration-grade copper tubing is required. The filling procedure is carried out within a two to four liter beaker. A plastic beaker is fine. Collect 5 bottles per well or spring.

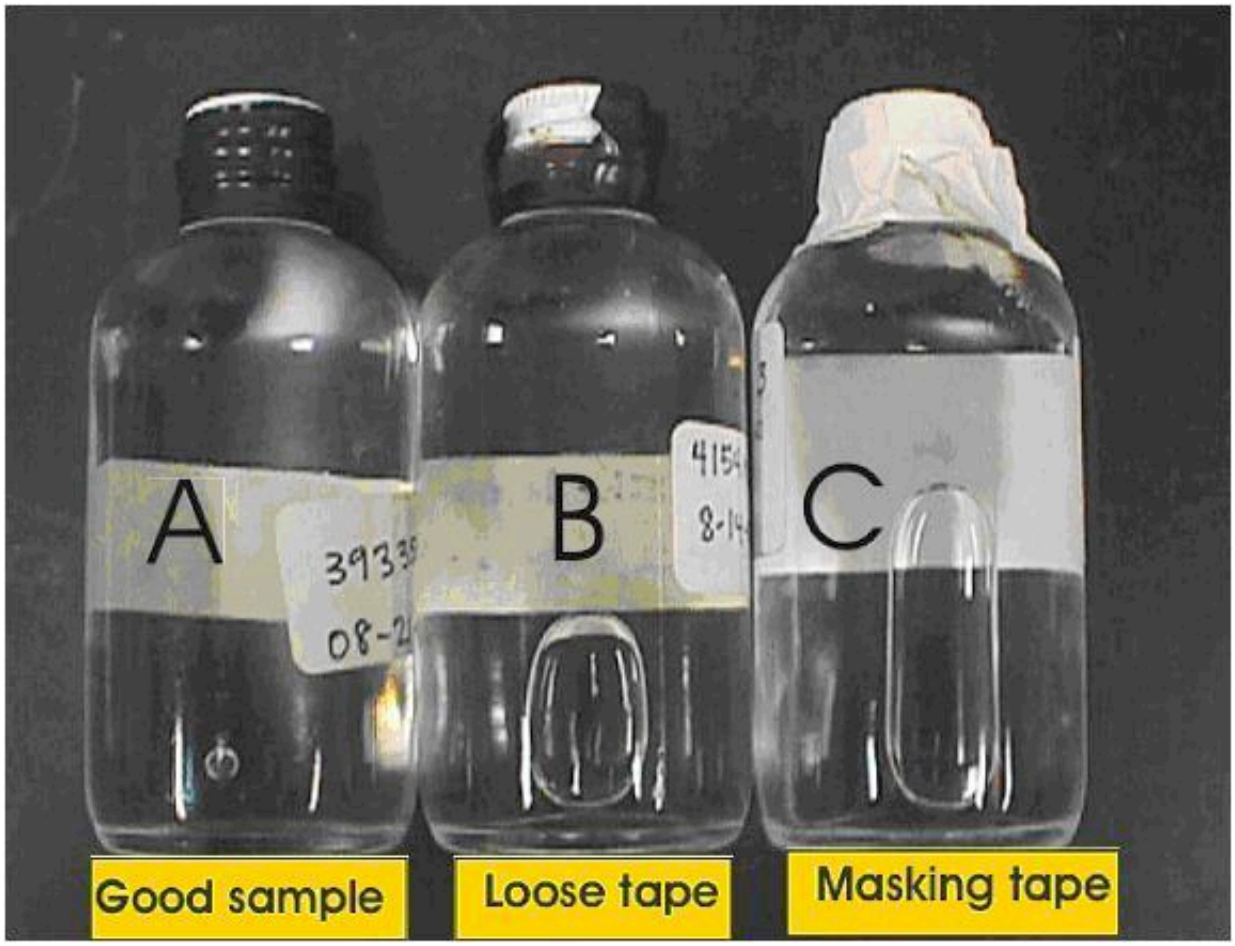
The procedure is shown below:

1. After the well has been purged, place the bottle in the beaker and then insert the end of the copper tubing from the pump all the way into the **bottom** of the bottle.
2. Fill the bottle as shown with well water until it overflows.
3. Continue to overflow the bottle until the beaker overflows. Allow at least 2 liters of water to flow through the bottle and out of the beaker.
4. Select a cap and tap it under water to dislodge air bubbles. Remove the copper tube from the bottle and **tightly cap the bottle underwater** without allowing the water in the bottle to come in contact with air. Flushing the bottle with more water is far better than with less water.
5. Remove the capped bottle from the beaker, dry the bottle and **RE-tighten** the cap. The tighter the cap the better.
6. Invert the bottle, tap it and check it for air bubbles. If there are bubbles, repeat the procedure from step 2 above. If it is necessary to refill the bottle, you must use a **new** cap.

7. If there are no bubbles present, tape the cap **securely** to the bottle with **electrical tape**. Wrap the tape in a clockwise direction looking down from the bottle top. Two rounds of electrical tape are needed. Do not forget to label each bottle with the well name, date, and time of sampling and the sequence number of each bottle as it was collected, one through five, in the order of collection.
8. Store bottles upside down until shipment. A bubble will form in most samples. This is normal.



Examples of properly and improperly sealed bottles



A. Good example. Very tiny bubble formed.
B. Poorly taped cap, air leak - note the large bubble that formed.
C. Cap taped with masking tape, poor seal and large air bubble formed.

Results of tests comparing CFC analyses of waters collected in ampoules and in bottles

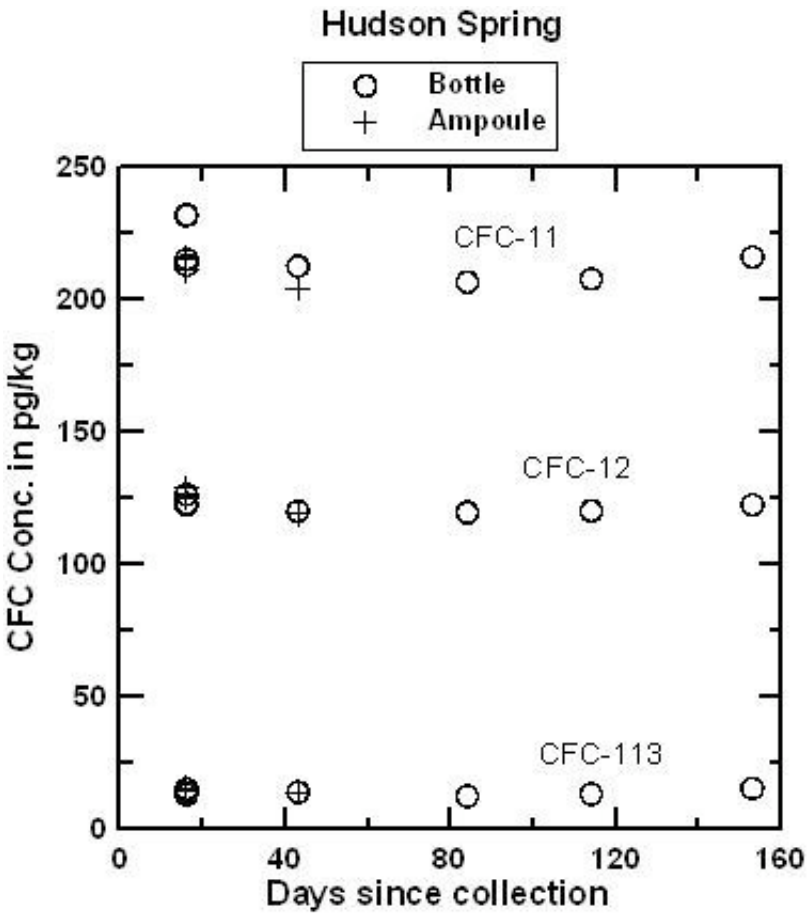
A large number of ampoules and bottles were collected from two sources--

(1) water from Hudson Spring which discharges from a limestone karst near the base of the Blue Ridge Mountains at Luray, Virginia, and

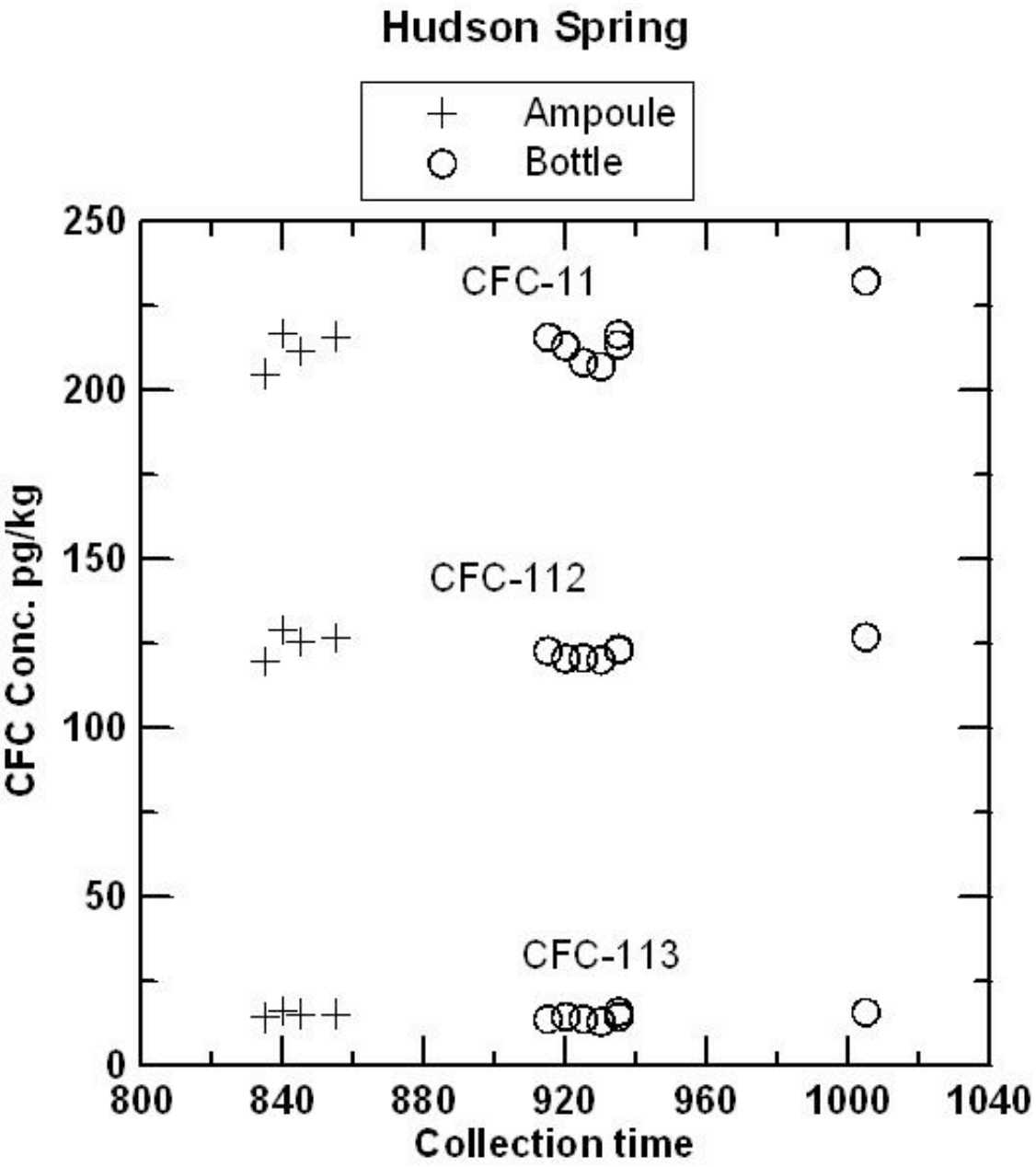
(2) water from a deep well in Coastal Plain sands near Milford, Virginia.

Hudson Spring has been sampled for CFCs and $^{3}H/^{3}He$ over a period of several years and has consistently yielded water with mid-1970s apparent age. Water from the Milford well was expected to be at or near the detection limit for all CFCs. The comparison of ampoules and bottles has continued for 153 days for water from Hudson Spring and 98 days for water from the Milford well. CFC concentrations in water from the Milford well were near or below the detection limit of 2 pg/kg in both ampoules and bottles. In a few cases, water from the Milford well contained detectible CFC-12 but pairs of ampoules and bottles agreed within ± 1 pg/kg in a range of 0 to 10 pg/kg (pre-1954 water). Apparently, there was some small variation in the CFC composition of water discharged from the well. CFC-113 was not detected in either ampoule or bottle, which eliminated the possibility of air contamination during storage. There was an

interference of an unknown VOC that gave the appearance of 4-5 pg/kg of CFC-11. Even with the trace interference. The interpreted apparent CFC-11 recharge date was be pre-1950 for CFC-11 which is near the detection limit of the dating method. The figures below compare concentrations of CFC-11, CFC-12, and CFC-113 measured in water from ampoules and bottles from Hudson Spring, as a function of storage time and as a function of collection time. The tests are being continued, but preliminary results indicate that blanks can be collected and stored using the bottle method. It is anticipated that water samples collected in bottles will be analyzed within 4 months of the date they are received at the Reston Chlorofluorocarbon Laboratory. Samples should be shipped promptly to the Reston Chlorofluorocarbon Laboratory following collection.



Plot comparing CFC-11, CFC-12 and CFC-113 concentrations in water from Hudson Spring analyzed after storage of more than 40 days in fused borosilicate ampoules and more than 150 days in glass bottles. In the apparent recharge age of the water. The small variations in CFC concentrations are equivalent to differences of less than 0.5 years. And as shown below, the small differences in likely reflect differences in concentrations in discharge from the spring over the period of collection of ampoules and bottles (several hours), rather than changes on storage.



Comparison of CFC-11, CFC-12, and CFC-113 measured in ampoules and bottles plotted in sequence of field collection. The plot suggests that at least some of the very small variations observed represent real variations in water composition discharging from the spring, rather than changes occurring during storage.

Photos