Anal. Chem. **1998,** *70,* 724−729

Simultaneous Determination of CFC-11, CFC-12, N_2, and Ar in Water

Markus Hofer* and Dieter M. Imboden

Swiss Federal Institute of Technology (ETH) and Swiss Federal Institute of Environmental Science and Technology (EAWAG), CH-8600 Dübendorf, Switzerland

We have developed a new method for the simultaneous analysis of CFC-11, CFC-12, N_2, and Ar in water that allows field samples, collected in copper tubes and locked gas-tight, to be transported and stored for several weeks. In the laboratory the gases are extracted in a vacuum system and frozen onto cold traps. CFCs are measured with a GC-ECD, and N_2 and Ar are measured with a GC-TCD. Detection limits are 0.007 pmol kg^{-1} for CFC-11, 0.017 pmol kg^{-1} for CFC-12, and 0.89 μmol kg^{-1} for N_2 and Ar. The reproducibility of replicate samples with modern CFC concentrations (1σ) lies within ±1.8% for CFC-11, ±1.5% for CFC-12, ±0.6% for N_2, and ±0.8% for Ar. The oxygen demand and anoxic degradation rates of CFCs in the copper tube samplers were determined with lake water. At room temperature (22 °C), the oxygen demand is 14.3 ± 7.6 μmol kg^{-1} d^{-1}, and the CFC-11 anoxic degradation rate is 0.0026 ± 0.0006 pmol kg^{-1} d^{-1}. For CFC-12, no anoxic degradation was detected within 200 days.

Chlorofluorocarbons (CFCs) have been used as tracers to study mixing processes in the ocean since the late 1970s. In the early 1980s, Gammon et al.[1] constructed a device, later modified by Bullister and Weiss,[2] for the analysis of dissolved CFCs in seawater. This device is based on the purge-and-trap method. To avoid contamination, measurements on the water samples, which are stored in glass syringes, must be conducted within a few hours. This equipment, therefore, had to be designed for shipboard operation.

Analysis in the field may be appropriate in oceanography, where large numbers of samples must be dealt with. However, for small series of samples taken from various different water bodies, e.g., lakes or groundwater, a stationary laboratory system is more suitable. In the literature, different possibilities of storing CFC samples have been described. Busenberg and Plummer[3] suggested flame-sealing groundwater samples in glass ampules, whereas Jean-Baptiste et al.[4] proposed collecting oceanic samples in situ using specially cleaned and treated copper tubes and then analyzing them in the laboratory using the purge-and-trap method described by Bullister and Weiss.[2]

Since our group is experienced in analyzing tritium and helium samples,[5,6] the decision was made to use an analogous method for the CFCs. In the method described here, water samples are transferred to copper tubes without coming into contact with air and then locked gas-tight in the tubes. In the laboratory, the gases are extracted from the water sample using a vacuum system. After removal of water vapor, O_2, N_2, and Ar in cold traps, the CFCs are analyzed in a gas chromatograph (GC).

The advantages of the device described here are that N_2 and Ar can be measured parallel to the CFCs in the same sample. This offers the possibility of detecting gas supersaturation, particularly common in groundwater,[7,8] and of making corrections to water age calculations. Although O_2 can also be measured with this method, it is not considered as a tracer since it is not conservative. The measurement of O_2 is, however, important to check whether anaerobic CFC degradation could already have occurred during storage. Because the system is closed, CFCs and other gases are adsorbed quantitatively. Uncertainties with respect to the efficiency of the traps, typical for purge-and-trap methods,[4] do not exist. As a further advantage, the same copper tube samplers can be used to sample both $^3H/^3He$ and CFCs. In the case of sample loss, the samplers, which do not require special cleaning, can easily be swapped over.

EXPERIMENTAL SECTION

Sampling. Water samples for CFC analysis are taken in the same copper tubes ($^3/_8$ in., soft quality) already employed in our laboratory for sampling rare gases.[5,6] These copper tubes require no additional cleaning for CFC sampling. Sampling in lakes is conducted using 5-L Niskin bottles. The copper tube is connected to the Niskin bottle with a short silicon tube and flushed well with sample water. For groundwater sampling, a submersible pump with PVC tubing is used. Before sampling, the borehole is first pumped out until it has been flushed through at least twice. The copper tube is then connected to the pump and also flushed well. Finally, the copper tube is clamped off at both ends, sealing off the sample (of about 45 g of water) gas-tight. In this way, samples can be obtained quickly and safely even under difficult conditions.

---

(1) Gammon, R. H.; Cline, J.; Wisegarver, D. *J. Geophys. Res.* **1982**, *87*, 9441−9454.
(2) Bullister, J. L.; Weiss, R. F. *Deep-Sea Res.* **1988**, *35*, 839−853.
(3) Busenberg, E.; Plummer, L. N. *Water Resour. Res.* **1992**, *28*, 2257−2283.
(4) Jean-Baptiste, P.; Messias, M. J.; Alba, C.; Charlou, J. L.; Bougault, H. *Deep-Sea Res.* **1994**, *41*, 1361−1372.
(5) Kipfer, R. Ph.D. dissertation no. 9463, ETH Zürich, 1991.
(6) Aeschbach-Hertig, W. Ph.D. dissertation no. 10714, ETH Zürich, 1994.
(7) Heaton, T. H. E.; Vogel, J. C. *J. Hydrol.* **1981**, *50*, 201−216.
(8) Dunkle, S. A.; Plummer, L. N.; Busenberg, E.; Phillips, P. J.; Denver, J. M.; Hamilton, P. A.; Michel, R. L.; Coplen, T. B. *Water Resour. Res.* **1993**, *29*, 3837−3860.

S0003-2700(97)00499-X CCC: $15.00

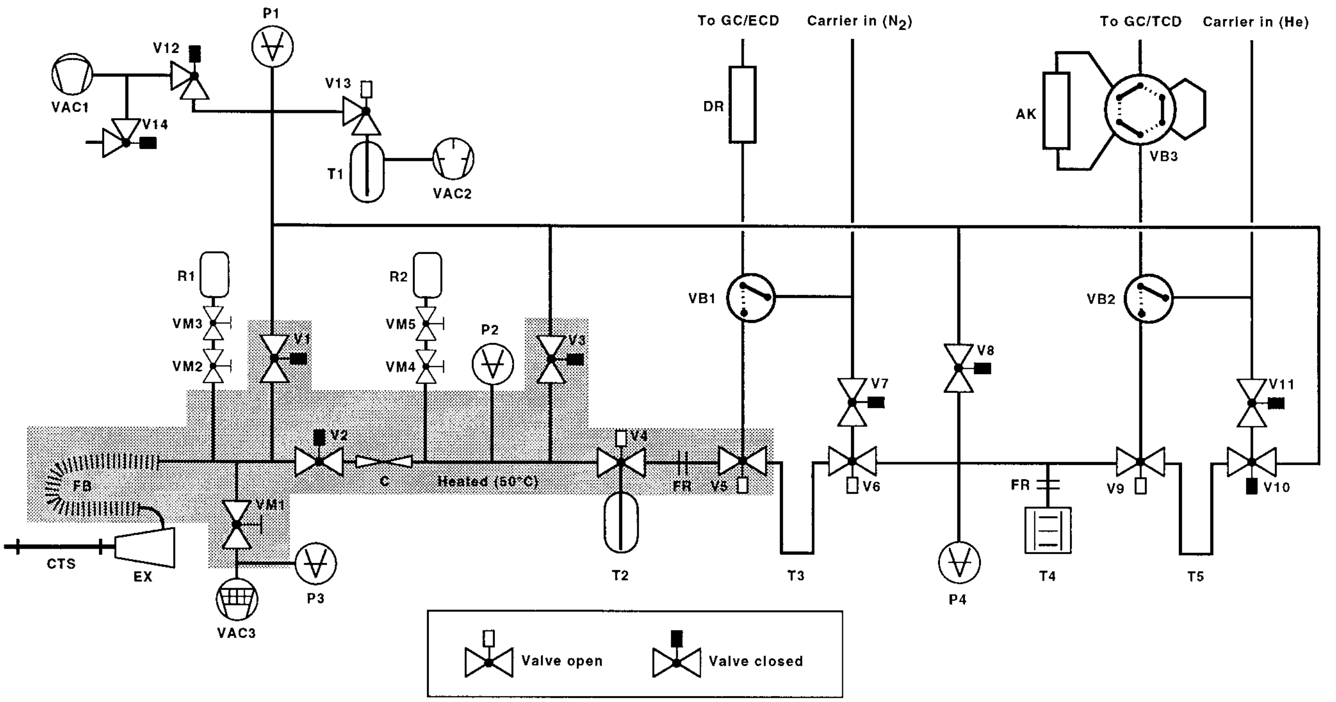

Figure 1. Schematic diagram of the vacuum extraction line. The shaded area represents plumbing and valves heated to 50 °C to prevent condensation. Abbreviations: see text.

Because the rate of leakage of gases from the atmosphere to the water sample through the copper tube is low ($<9 \times 10^{-22}$ mol s^{-1} for ^4He,[5,6] i.e., <0.02% of the total ^4He in the sample per year), samples can be stored and transported without contamination.

Extraction Line. The setup of the extraction line is illustrated schematically in Figure 1. The extraction line consists mainly of commercially available components, some of which had to be modified.

The copper tube CTS is connected to the extraction vessel EX (volume ~500 mL) by means of a fastening device which presses the front of the copper tube UHV-tight onto a metal cutting edge.[5] The extraction vessel is connected to the extraction line by means of flexible tubing FB (length 1 m).

Valves V1–V11 are pneumatically activated fold-bellows valves (Nupro SS-4BK-TW) and are normally closed. The spindle tips of these valves, which are made of Kel-F, were heated overnight at 150 °C in a vacuum (2×10^{-2} mbar). The threads of the spindle tips were drilled so as to leave no nonflushable dead volume. Valve V4 is modified so that the cold trap T2 can be closed against the capillary C (length 1 cm, diameter 0.8 mm), leaving no dead volume. Between trap T2 and valve V5, filter gasket FR (Cajon Ni-4-VCR-2-GR 60M), with a pore width of 60 μm, is installed to reduce the cross-sectional area. Valves V5, V6, V7, V9, V10, and V11 are modified so that the carrier gas flow can wash the sample gases from traps T3 and T5 into the GC with no dead volume and without broadening the peaks unnecessarily or causing peak-tailing. To protect the GC from water vapor coming from trap T3, a drying column DR (length 20 cm, diameter $^1/_4$ in.), filled with magnesium perchlorate (Merck, Darmstadt, Germany), is installed. Those individual valves that are not directly welded are connected with $^1/_4$-in. Cajon fittings (Arbor Inc.) and $^1/_4$-in. stainless steel tubing.

VM1 is a manually operated fold-bellows valve with steel spindle tips (Nupro SS-4H-TW). VM2 is welded to VM3, and VM4 to VM5, with $^1/_4$-in. steel tubes so that they can be used as gas pipets with volumes of about 0.9 cm^3. VM2, VM3, VM4, and VM5 are manually operated fold-bellows valves (Nupro SS-4H-TSW) modified with copper spindle tips in our workshop. R1 and R2 are electropolished standard reservoirs (each with a volume of approximately 2 L) connected to each of the gas pipets. Aliquots from these reservoirs are used for calibration purposes and for air measurements.

The extraction line is evacuated in three stages using the following pumps: (i) membrane pump VAC1 (Vacuumbrand MZ4) to pump water vapor out of the system (pressure about 5 mbar), (ii) rotary vacuum pump VAC2 (Edwards E2M5; to about 2×10^{-2} mbar), and (iii) adsorption pump VAC3 (molecular sieve, 5 Å, at −196 °C; 10^{-3} mbar). Valves V12–V14 are electropneumatic angle valves (Balzers EVA 016P) which are normally in the closed position.

The vacuum is monitored using four Pirani gauge heads P1 (Balzers TPR 010) and P2–P4 (Balzers TPR 018) connected to a total pressure controller (Balzers TPG 300).

T1–T3 are empty cold traps cooled to −196 °C using liquid nitrogen. T4 is a sorption trap filled with 0.3 g of activated charcoal at a temperature of −196 °C. Trap T5 is held at room temperature and serves as a sample loop. VB1 and VB2 are pneumatically operated three-way ball valves (Whitey, SS-41XS2, Arbor Inc.) that allow the supply of carrier gas to be led to the GC either directly or through traps T3 and T5. VB3 is a pneumatically operated six-way ball valve (Whitey, SS-43Y6FS2, Arbor Inc.) that allows the gases to be admitted to the GC either directly or via column AK (length 10 cm, diameter $^1/_8$ in.), which is filled with activated charcoal and held at 450 °C. In the hot activated charcoal, any O_2 present is reduced to CO_2. Consequently, Ar, whose retention time at room temperature is the same as that of O_2, can be analyzed without cooling the GC column.

Table 1. Gas Chromatograph Parameters

	CFCs	O_2, N_2, Ar
column	Supelco 5% Fluorcol 60/80 mesh Carbopack B 10 ft × $^1/_8$ in.	Alltech molecular sieves, 5-Å 80/100 mesh 6 ft × $^1/_8$ in.
carrier gas	N_2 (99.9990%)	He (99.9990%)
carrier gas flow	30 mL min^{-1}	40 mL min^{-1}
column temperature	12 min at 80 °C 30 °C min^{-1} to 180 °C 17 min at 180 °C	25 °C
detector	Shimadzu ECD-9A ^{63}Ni	Shimadzu TCD
detector temperature	300 °C	100 °C
current	2 nA	190 mA

By injecting the gases directly, the sum of O_2 and Ar can be measured.

The tube diameters of the GC part are $^1/_8$ in. (Swagelok fittings). All plumbing and valves within the shaded area of Figure 1 are heated to 50 °C with electrical heating tape to prevent condensation of water vapor. After setup, the entire device was evacuated to 2×10^{-2} mbar and heated to 90 °C for several days.

Gas Chromatograph (GC). The analyses are conducted using a gas chromatograph (Shimadzu GC-14 A, Kyoto, Japan) equipped with an electron capture detector (ECD) for the determination of CFCs and a thermal conductivity detector (TCD) for the determination of O_2, N_2, and Ar. The exact GC parameters are shown in Table 1. The retention times of the peaks are 7.9 (CFC-11), 3.0 (CFC-12), 1.9 (N_2), and 1.3 min (Ar and O_2).

Valve Control and Data Processing. The pneumatic valves are controlled by a personal computer (Apple Macintosh II) equipped with a multifunction card (National Instruments NB-MIO-16XL-42). The signals from the Pirani gauge heads (0−10 V) are recorded by this card, are digitized, and appear in the control field of the computer. Both output signals from the GC detectors (0−1 V) are sampled at 100 Hz. To reduce the volume of data, only the five-point mean is stored on the computer hard disk (data bunching). Control and data acquisition programs were written exclusively for this system in PASCAL, utilizing a commercially available software library (National Instruments, NIDAQ). The same computer is used to control the GC system via an RS-232 interface.

The chromatograms are evaluated using programs written in MatLab (The MathWorks Inc.); this software allows the baselines of the peaks to be determined and the areas under the peaks to be calculated.

RESULTS AND DISCUSSION

Extraction and Analysis of Water Samples. After a new copper tube sampler CTS (see Figure 1) is connected to the extraction vessel EX, the system is evacuated. The pneumatic valves V1−V14 are set as shown in Figure 1. All manual valves VM1−VM5 are closed. The cold traps T2−T4 are cooled with liquid nitrogen. The connected copper tube sampler is opened, allowing the sample water to flow into the extraction vessel. Valve V2 is opened for 4 min, and the gases are extracted from the water sample. By shaking the extraction vessel EX, all transient materials degas and, together with the water vapor, stream through the capillary C, thus preventing back-diffusion of the gases. In trap T2, CFCs and water freeze out. O_2, N_2, and Ar are held back in trap T4 at the cold activated charcoal.[9] After 4 min, valve V2 is closed, and the procedure is halted for 6 min to allow all gases to be adsorbed. Valve V4 is then closed and trap T2 thawed with water. During 4 min, CFCs, along with some water vapor, stream through the filter gasket FR and freeze in trap T3. Valves V5 and V6 are then closed, and trap T3 is thawed with water. By opening valve V7 and switching over valve VB1, the CFC mixture is dried in column DR and injected into the gas chromatograph. Simultaneously, trap T4 is thawed. An aliquot of the gas mixture, containing predominantly N_2, Ar, and remnants of O_2, is admitted into trap T5. The valve V9 is then closed, and, by opening valve V11 and switching over valve VB2, the gases are transferred to the GC column over the activated charcoal AK. The sample throughput rate of this method is 1 sample/h.

Wet Blank. The blank value of a sample is determined by measuring a so-called wet blank as follows. After the gases have been extracted from a sample and their concentrations measured, the water is returned from the apparatus to the copper tube, which is then closed off and disconnected from the apparatus. The wet blank is measured by reconnecting the tube to the apparatus (this time using the other end of the tube) and following exactly the same extraction and measuring procedure as that employed when dealing with a normal water sample. The wet blanks determined in this way lie within 0.014 ± 0.007 pmol kg^{-1} for CFC-11 and 0.025 ± 0.008 pmol kg^{-1} for CFC-12. These values barely exceed the detection limits of the method. The blanks for O_2, N_2, and Ar lie below their respective detection limits.

Standard Gas Mixture. For calibration purposes, purified air—as a standard for O_2, N_2, and Ar—is spiked with a commercially available CFC mixture (Carbagas) containing 3.27 ppm ± 0.7% CFC-11, 1.70 ppm ± 1.1% CFC-12, and 0.72 ppm ± 1.7% CFC-113 (1 σ error) diluted with nitrogen (99.9990%). Three gas pipet aliquots of this gas mixture (2.831 cm^3 ± 0.2%) are allowed into the evacuated reservoir R2 (2011.6 cm^3 ± 0.1%), and then the reservoir is filled to atmospheric pressure with air which has been purified over a 10-Å molecular sieve. The gas amounts in such a standard reservoir are known to a precision of ±1.0% for CFC-11, ±1.3% for CFC-12, ±0.9% for O_2, ±0.9% for N_2, and ±0.9% for Ar.

All pipet aliquots taken from the standard reservoir must be corrected as follows using the dilution factor $F = 0.999\,5311$:

$$C_n = C_1 F^n \tag{1}$$

where n is the number of pipet aliquots taken from the reservoir,

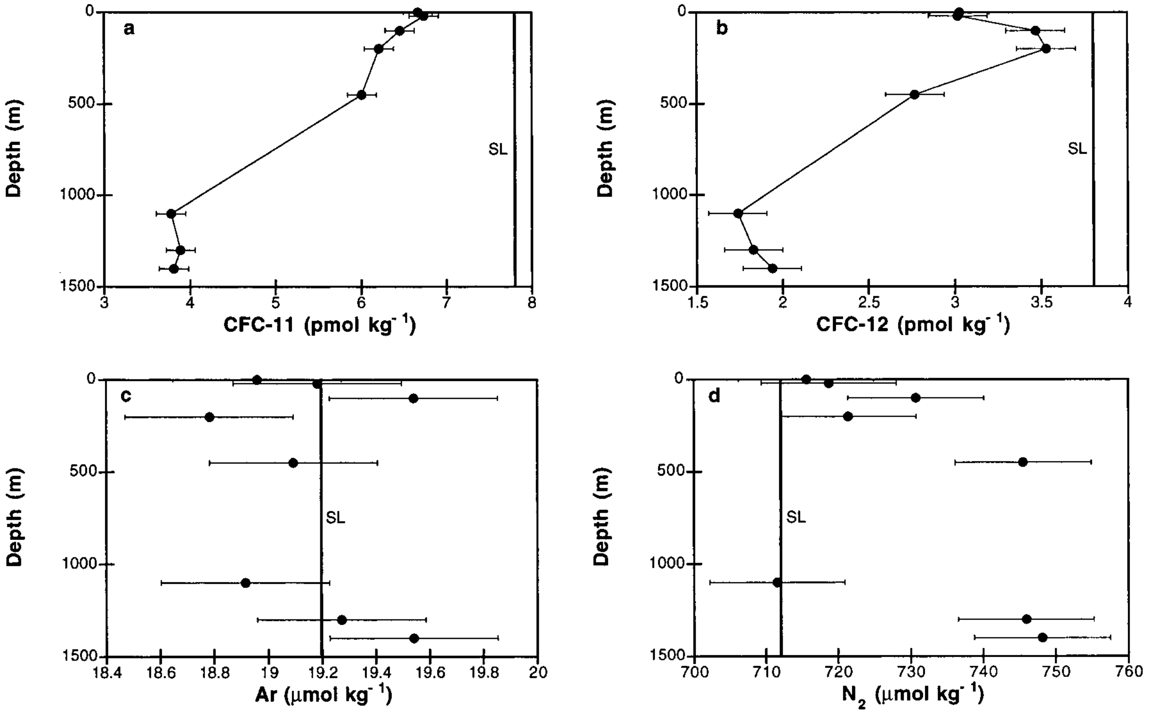

Figure 2. Measurements from the South Basin of Lake Baikal. (a,b) The saturation line (SL) shows the expected CFC concentration at a water temperature of 3.5 °C and at the current atmospheric concentrations of 270 pptv for CFC-11 and 530 pptv for CFC-12.[15,16] (c,d) SL shows the equilibrium gas concentration at a water temperature of 3.5 °C.[17]

C_1 the concentration in the first pipet aliquot, and C_n the concentration in the nth pipet aliquot. Several hundred pipet aliquots can be taken from the standard reservoir. The standard remains stable for several months.

Measurement of Standards. Two or three standards are measured in the course of 1 day between water sample measurements. From the gas mixture in reservoir R2, 1−3 gas pipet aliquots are admitted to the extraction system. For this procedure, the valves' positions are as shown in Figure 1, traps T3 and T4 are cooled with liquid nitrogen to −196 °C, and traps T2 and T5 are at room temperature. After 10 min, the traps are closed and thawed with water, and CFCs and other gases are quantified in the GC.

The reproducibility of the standards determined from pairs of standard measurements performed on the same day is ±1.3% for CFC-11, ±0.9% for CFC-12, ±0.5% for N_2, and ±0.9% for Ar.

The addition of standard gas to a wet blank extraction of a water sample shows that no difference can be ascertained between wet and dry standard measurements. Hence, dry standard measurement is preferred to save time.

Dry Blank. To determine the blank value of a standard, we measure a so-called dry blank. This is achieved using the same procedure used for a standard measurement, but without admitting gas. These blanks correspond to 0.007 ± 0.007 pmol kg^{-1} for CFC-11 and 0.04 ± 0.008 pmol kg^{-1} for CFC-12. The blanks for O_2, N_2, and Ar lie beneath the limit of detection.

Detection Limits and Uncertainty. The detection limit, expressed as the double peak height of the measured noise, lies within 0.007 pmol kg^{-1} for CFC-11, 0.017 pmol kg^{-1} for CFC-12, and 0.89 μmol kg^{-1} for N_2 and Ar. Reproducibility between water samples, determined using double samples from Swiss lakes with modern CFC concentrations, is ±1.8% for CFC-11, ±1.5% for CFC-12, ±0.6% for N_2, and ±0.8% for Ar. Total measurement uncertainty, estimated from the errors of all single steps, is ±2.5% for CFC-11, ±2.3% for CFC-12, ±1.3% for N_2, and ±1.6% for Ar. The extraction efficiency, determined at the CFC-11 peak, is better than 99.9%.

Calculations and Interpretation. Calculations of sample concentrations are based on calibration curves prepared from the standards obtained during 1 day of measurements. CFC-11 standards can be fitted by a second-order polynomial, whereas linear fits suffice for CFC-12, N_2, and Ar. Since wet and dry blanks have practically the same values, for samples with high CFC concentrations no blank correction was considered necessary. The calibration curves are not, however, forced to run through the origin; for small CFC concentrations blank corrections are made.

Sample Contamination. The danger of contamination during sampling has been pointed out in the literature.[3,10] Our method of sampling groundwater was tested by sampling a known, old groundwater at several boreholes. In these samples, no CFC concentrations higher than the blank value were found. The use of Niskin bottles to sample lake water was tested by sampling the anaerobic deep water of Lac Pavin (France); again, no CFC concentrations exceeding the blank level were found.

Stability of Samples during Storage. It is known that CFC-11 and CFC-12 degrade under anoxic conditions.[11−13] The

---

(9) Kipfer, R.; Aeschbach-Hertig, W.; Baur, H.; Hofer, M.; Imboden, D. M.; Signer, P. *Earth Planet. Sci. Lett.* **1994**, *125*, 357−370.

(10) Weiss, R. F.; Carmack, E. C.; Koropalov, V. M. *Nature* **1991**, *349*, 665−669.

(11) Lovley, D. R.; Woodward, J. C. *Environ. Sci. Technol.* **1992**, *26*, 925−929.

(12) Denovan, B., A.; Strand, S. A. *Chemosphere* **1992**, *24*, 935−940.

Table 2. Groundwater Linsental, 24 November 1995

sample	distance[a] (m)	temp (°C)	CFC-11 (pmol kg^{-1})	ΔCFC-11[b] (%)	CFC-12 (pmol kg^{-1})	ΔCFC-12[c] (%)	N_2 (μmol kg^{-1})	ΔN_2[d] (%)	Ar (μmol kg^{-1})	ΔAr[d] (%)
Töss	0.0	5.1	9.76 ± 0.17	37	4.56 ± 0.07	30	688 ± 9	0.7	18.0 ± 0.3	−1.7
CS10L	3.8	10.6	20.79 ± 0.17	303	4.93 ± 0.07	88	717 ± 9	18.9	16.9 ± 0.3	5.6
CS10U	5.4	8.7	18.06 ± 0.17	215	4.98 ± 0.07	72	731 ± 9	16.3	17.5 ± 0.3	4.4
C11L	9.5	10.7	24.70 ± 0.17	381	5.37 ± 0.07	105	721 ± 9	19.8	17.1 ± 0.3	6.9
C12L	18.5	10.7	24.23 ± 0.17	372	5.46 ± 0.07	109	728 ± 9	20.9	17.7 ± 0.3	10.4
C13U	28.0	10.6	18.61 ± 0.17	261	5.21 ± 0.07	98	705 ± 9	16.8	17.3 ± 0.3	7.7
C13L	28.0	10.7	25.24 ± 0.17	392	5.60 ± 0.07	114	722 ± 9	19.9	17.3 ± 0.3	8.3
C14L	135.0	9.7	29.95 ± 0.17	452	6.04 ± 0.07	120	656 ± 9	6.7	16.3 ± 0.3	−0.5

[a] Distance from the River Töss. [b,c] Supersaturation relative to the concentration expected in equilibrium with a modern atmospheric concentration of 270 pptv for CFC-11 and 530 pptv for CFC-12.[15,16] [d] Supersaturation relative to the equilibrium concentration with the atmosphere.[17]

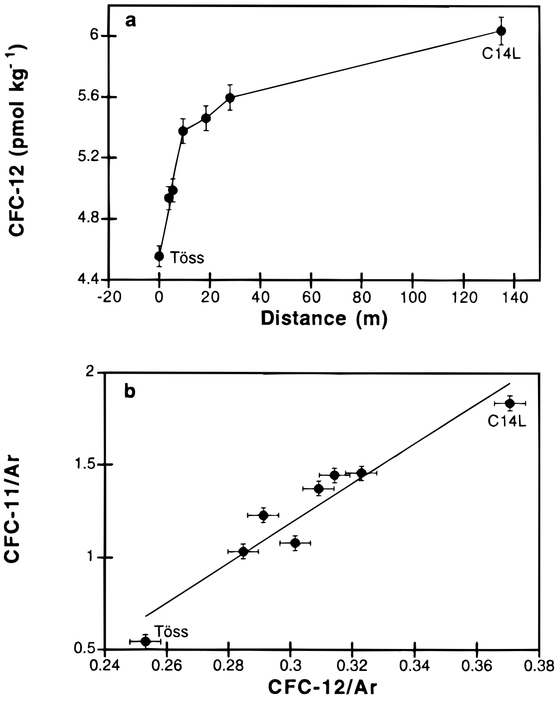

Figure 3. Groundwater samples from Linsental. (a) The River Töss infiltrates into the aquifer, diluting the high CFC-12 concentration in the groundwater, represented by sample C14L. (b) Provided the measurements represent simple binary mixtures between two types of water (end members), e.g., water from the River Töss and from borehole C14L, these concentration ratios must lie on a straight line.

degradation rate of CFC-12 in water is described as being about 10 times smaller than that of CFC-11.[13]

To test the stability of water samples in copper tube samplers, six duplicate samples from Lake Biel, a 74-m-deep, well-mixed Swiss lake, were measured. O_2 concentrations were determined directly on-board a ship using the Winkler method. The first sample of each pair was measured 10 days after sampling and the second after 200 days of storage at room temperature (22 °C). The zero-order O_2 degradation rate derived from the first set of samples was 14.3 ± 7.6 μmol kg^{-1} d^{-1}, implying that the samples were oxygen-free after about 1 month, which is about the maximum time during which samples can be stored safely. After 200 days, the zero-order degradation rate for CFC-11 was 0.0026 ± 0.0006 pmol kg^{-1} d^{-1}, while for CFC-12 no significant change in concentration could be detected.

In order to slow down the degradation of O_2 and the subsequent anoxic degradation of CFC-11 in copper tube samplers during long periods of storage, it is advisable to cool the samples or even to freeze them, which is easily possible in copper tubes, as leakage tests in our laboratory have shown.

APPLICATIONS

Lake Baikal. As part of an international expedition to Lake Baikal conducted under the auspices of BICER (Baikal International Center of Environmental Research), a sampling profile for the determination of CFC concentrations was taken on 8 December 1995 at the deepest point (1430 m) of the South Basin of the lake (51°42′07″ N, 105°01′49″ E, Figure 2). The actual measuring was commenced about 2 months later, in February 1996. The samples became partially frozen during transport but were stored at room temperature in our laboratory. In none of the samples could any O_2 be detected after 2 months, and so anoxic degradation of CFC-11 must be presumed. However, according to our estimates, this degradation lies within the limits of error of our method and, hence, could be neglected.

Our measurements are in good agreement with published data.[10,14] Ar concentrations correspond to the expected saturation concentrations at ambient pressures and temperatures; however, N_2 seems to be oversaturated, especially in the deeper part of the lake. An interpretation of these data has been published elsewhere.[14]

Groundwater. In Linsental (460 m above sea level), a part of the valley of the River Töss close to the city of Winterthur, Switzerland, several boreholes were drilled in direct proximity to the river. Our results (Figure 3) show that river water infiltrates into the aquifer at this location.

In Table 2, the data resulting from the sampling conducted on 24 November 1995 are assembled. "Töss" refers to samples taken directly from the river. The boreholes have screens 1 m long at a defined depth in the aquifer. A "U" in the sample name implies that the screen of this borehole lies in the upper part of the aquifer, and an "L" implies that it lies in the lower part.

---

(13) Oster, H.; Sonntag, C.; Munnich, K. O. *Water Resour. Res.* **1996**, *32*, 2989−3001.

(14) Peeters, F.; Kipfer, R.; Hohmann, R.; Hofer, M.; Imboden, D. M.; Kodenev; Khozder, T. *Environ. Sci. Technol.* **1997**.

(15) Warner, M. J.; Weiss, R. F. *Deep-Sea Res.* **1985**, *32*, 1485−1497.

(16) Montzka, S. A.; Butler, J. H.; Myers, R. C.; Thompson, T. M.; Swanson, T. H.; Clarke, A. D.; Lock, L. T.; Elkins, J. W. *Science* **1996**, *272*, 1318−1322.

(17) Weiss, R. F. *Deep-Sea Res.* **1970**, *17*, 721−735.

Gas concentrations were measured 2 months after the sampling date. Although O_2 concentrations in all samples lay between 5 and 12 mg L^{-1} at the time of sampling, no O_2 could be detected after 2 months storage at approximately 22 °C. No correction for possible CFC-11 degradation was made. All groundwater samples show supersaturation compared with the river water for CFCs and for the other dissolved gases. The high degree of supersaturation with respect to the CFCs is due either to continental excesses compared to the global background[13] or to contamination of the investigation area from other sources. Contamination during sampling is very unlikely, based on tests performed with a known, CFC-free groundwater.

The above results confirm the utility of the method described here for measuring concentrations of CFCs, N_2, and Ar in the same sample. Especially in the case of groundwater samples, the additional information on dissolved gases obtained using this method can be very helpful in determining supersaturation levels or in detecting binary mixtures.

ACKNOWLEDGMENT

We thank Urs Menet and Heiri Baur for helping to build the extraction line and for the use of their workshop; Oliver Seifert for helping to write the integration software; Wisi Zwissig, Michael Schurter, Rolf Kipfer, Roland Hohmann, and Mike Sturm for sampling; Philippe Périsset for building the electronic hardware and for his programming help; and David Livingstone for linguistic improvements to the text.

Received for review May, 13, 1997. Accepted November 17, 1997.

AC970499O