

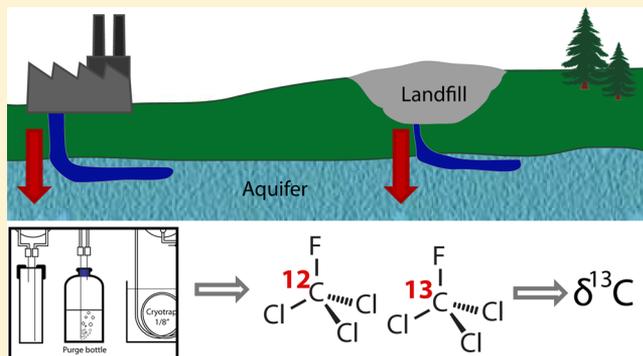
# Compound-Specific Stable Carbon Isotope Analysis of Chlorofluorocarbons in Groundwater

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**ABSTRACT:** Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), controlled substances due to their role in stratospheric ozone loss, also occur as dissolved contaminants in groundwaters. Stable carbon isotopic signatures may provide valuable new information on the fate of these compounds as has been seen for other priority hydrocarbon contaminants, but to date no method for extraction and isotopic analysis of dissolved CFCs from groundwaters has been developed. Here we describe a cryogenic purge and trap system coupled to continuous flow compound-specific stable carbon isotope analysis mass spectrometry for concentrations as low as 35  $\mu\text{g/L}$ . The method is validated by comparing isotopic signatures from

water extracted CFCs against a new suite of isotopic CFC standards. Fractionation of CFCs in volatilization experiments from pure-phase CFC-11 and CFC-113 resulted in enrichment factors ( $\epsilon$ ) of  $+1.7 \pm 0.1\%$  and  $+1.1 \pm 0.1\%$ , respectively, indicating that such volatile loss, if significant, would produce a more  $^{13}\text{C}$  depleted signature in the remaining CFCs. Importantly, no significant fractionation was observed during volatile extraction of dissolved CFCs from aqueous solutions.  $\delta^{13}\text{C}$  values for groundwaters from a CFC-contaminated site were, on average, more enriched than  $\delta^{13}\text{C}$  values for pure compounds. Such enriched  $\delta^{13}\text{C}$  values have been seen in other hydrocarbon contaminants such as chlorinated ethenes and ethanes due to in situ degradation, but definitive interpretation of such enriched signatures in field samples requires additional experiments to characterize fractionation of CFCs during biodegradation. The establishment of a robust and sensitive method of extraction and analysis, as described here, provides the foundation for such future directions.



Chlorofluorocarbons (CFCs) are anthropogenically produced volatile, long-lived, and nontoxic compounds. They have been used as refrigerants, propellants, foaming agents, and solvents and are important intermediates in the production of anesthetics and other fluorinated compounds.<sup>1</sup> CFC loss into the environment and their long atmospheric lifetimes have contributed to stratospheric ozone destruction. Consequently, production of these compounds was banned under the Montreal Protocol (1987) and its amendments, and since that time atmospheric mixing ratios have started to decrease.<sup>2</sup>

CFCs have also been detected in groundwater, and contamination of aquifers is an issue throughout North America.<sup>3</sup> Emission of CFCs into groundwater from various legacy sources such as landfills, spills of industrial solvents and foam materials, leaking equipment, and improper disposal presents a continuing challenge for control and remediation.<sup>4–6</sup> Even excluding wells with known point sources of volatile organic compounds (VOCs), Squillace et al. found more than 0.2  $\mu\text{g/L}$  in 3% of 2354 tested wells for CFC-11 and CFC-12 with concentrations reaching up to 20 and 40  $\mu\text{g/L}$ , respectively.<sup>7</sup> Although relatively nontoxic, degradation products of CFCs such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are problematic due to their global warming potential, carcinogenicity, and toxicity.<sup>2</sup> HCFCs and

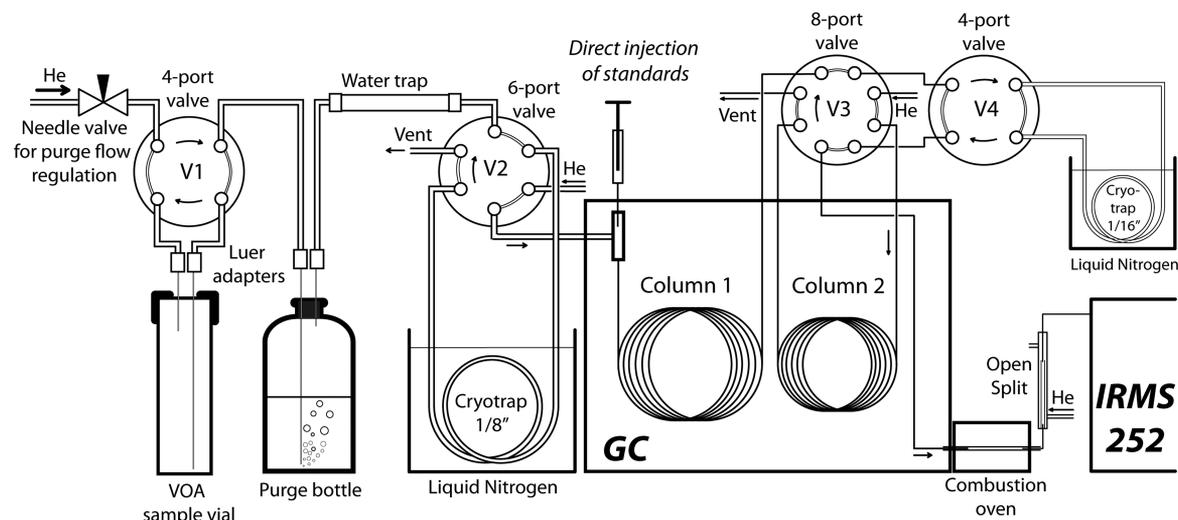
HFCs were used as replacements for CFCs and therefore also occur at some sites as primary contaminants.

Isotope studies of CFCs and HCFCs in atmospheric samples have focused to date on source apportionment in the atmosphere using stable carbon isotope analysis.<sup>8–12</sup> One study also applied stable chlorine isotope analysis ( $\delta^{37}\text{Cl}$ ) and showed the potential for large enrichment factors due to photolysis in the stratosphere.<sup>13</sup> In soils and waters CFCs are relatively stable compounds but may degrade due to biotic and abiotic processes such as microbial dechlorination<sup>14,15</sup> and reaction with zerovalent iron (ZVI).<sup>16,17</sup> Isotope analysis of CFCs in water, however, has only been reported once in a laboratory study demonstrating the viability of  $\delta^{13}\text{C}$  analysis of headspace for laboratory samples produced via abiotic degradation experiments with ZVI and for air samples collected near landfills.<sup>17</sup> To date, no method exists to extract and isotopically analyze CFCs or HCFCs from groundwater. Compound-specific isotope analysis (CSIA) has become a valuable tool to identify and quantify degradation of contaminants such as aliphatic and aromatic chlorinated compounds in groundwaters, but the potential to apply a

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**Figure 1.** Schematic drawing of the cryogenic purge and trap system coupled to a GC–C–IRMS setup. The P&T system is shown in purge mode. VOA vials are connected to V1 and samples transferred to the purge bottle. Helium carrier gas purges VOC from the water sample and carries the purge gas phase through the water trap to remove water vapor prior to cryogenic trapping. For transfer of trapped VOCs to the GC valve, V2 is turned and liquid nitrogen replaced with a hot water bath ( $>60\text{ }^{\circ}\text{C}$ ). Released compounds are separated on column 1 and transferred to the IRMS instrument directly if valves V3 and V4 are in the position shown. This setup also allows for direct injection of CFC working standards to monitor the day-to-day performance of the GC–C–IRMS system. For peak cutting, V4 is turned and the target compound collected in the 1/16 in. cryotrap. For final separation and analysis, valve V3 is turned and the compounds are released onto column 2 and sent to the IRMS instrument.

similar approach to CFCs and HCFCs has yet to be explored in any detail.<sup>18–21</sup>

Here we present a new method combining purge and trap (P&T) extraction and CSIA of carbon applicable for CFCs and HCFCs based on the standard 40 mL VOA (volatile organic analyses) vial method, which is the standard protocol for groundwater sample collection. Conservation of  $\delta^{13}\text{C}$  signatures during the entire extraction procedure is tested to ensure no isotopic fractionation is associated with the sample extraction and handling. A suite of in-house CFC isotopic working standards were characterized by both CSIA and measurement by offline sealed tube combustion analysis via dual-inlet mass spectrometry.<sup>22</sup> Enrichment factors for volatilization of two CFCs are determined to investigate isotopic fractionation due to phase partitioning. Finally, we present the first isotopic measurements of CFCs and HCFCs in groundwater samples from a contaminated site to establish the proof of principle for this new method.

## EXPERIMENTAL SECTION

### CFC and HCFC Reference Gases and Water Solutions.

Pure-phase trichlorofluoromethane (CFC-11), trichlorofluoroethane (CFC-113), and chlorodifluoromethane (HCFC-22) were purchased from SynQuest Laboratories, United States, for testing of the extraction method and to establish a set of in-house isotopic working standards. An additional pure-phase sample of CFC-11 was obtained from a recycler. Before offline analysis, all compounds were archived in glass ampules after the method of Hunkeler et al.<sup>22</sup> Gaseous standards were stored in pressurized metal canisters equipped with a brass integral bonnet needle valve (HCFC-22). Sealed ampules of liquid standards (CFC-11, CFC-113) were stored at  $5\text{ }^{\circ}\text{C}$ .

Aqueous-phase stock solutions of dissolved CFCs (usually  $15\text{ mg/L}$ ) were prepared by adding liquid compound (CFC-11, CFC-113) to deionized water in a 500 mL bottle sealed with a Mininert screw cap. These solutions were stirred for at least 2 h until all CFC was dissolved. For the HCFC-22 stock solution, a

275 mL bottle was filled with 270 mL of deionized water and crimp-sealed with a gray Wheaton poly(tetrafluoroethylene) (PTFE) stopper. A 1 mL volume of headspace was replaced by HCFC-22 gas and the bottle shaken overnight until equilibrium was reached.

**Offline Preparation of Pure-Phase Compounds and Dual-Inlet Measurement.** Isotopic characterization of working standards was performed by sealed combustion tube offline preparation of  $\text{CO}_2$  from each compound and subsequent dual-inlet (DI)  $\delta^{13}\text{C}$  measurement. This routine and well-established method is briefly described below. A more detailed description is provided in the literature.<sup>23</sup>

For combustion of HCFCs/CFCs to  $\text{CO}_2$  for isotopic analysis, quartz glass tubes were sealed at one end and filled with  $\text{CuO}$  and  $\text{Cu}$  (1.5 and 1 g, respectively). After evacuation on a vacuum line,  $5\text{ }\mu\text{L}$  of compound was added via a side-injection port, and the tubes were flame-sealed. Combustion was carried out for 1 h at  $850\text{ }^{\circ}\text{C}$  in a muffle furnace to convert all carbon to  $\text{CO}_2$ . A further hour at  $600\text{ }^{\circ}\text{C}$  transformed all nitrogen species to  $\text{N}_2$ . During subsequent cleanup,  $\text{CO}_2$  was separated from any traces of remaining gases and water and sealed in Pyrex glass tubes (e.g., break seals).

Stable carbon isotope analysis was performed on a Finnigan MAT 252 isotope ratio mass spectrometer equipped with a DI system. The sealed Pyrex tubes were cleaned with ethanol and loaded into the tube cracker connected to the inlet port of the DI system. After evacuation (to  $5 \times 10^{-5}$  mbar), the tube was broken and  $\text{CO}_2$  transferred into the left bellow of the inlet system. The right bellow was filled with a  $\text{CO}_2$  working standard cross-calibrated against the international standards NIST-17 and NIST-18. The pressure in the two bellows was adjusted in a way that the signal sizes ranged from 3 to 4 V and with a less than 0.1 V difference between the sample and standard. The results are reported as  $\delta$ , which is the relative deviation of a sample from the international IAEA standard V-PDB (Vienna Pee-Dee-Belemnite) expressed in per mil:

$$\delta^{13}\text{C} (\text{‰}) = \left( \frac{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}}}{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{standard}}} - 1 \right) \quad (1)$$

**Purge and Trap Preconcentration System.** A cryogenic purge and trap system was developed to extract dissolved CFCs and HCFCs from water, and conservation of carbon isotopic values was tested (Figure 1). The purge and trap system consists of a 1/8 in. (3.2 mm) stainless steel cryotrap, a needle valve for purge flow regulation, 1/16 in. (1.6 mm) stainless steel tubing for sample transfer, a Drierite water trap, and a four-port (V1) and a six-port (V2) valve (Valco). Stainless steel syringe needles with Opti Lok connectors were used to connect the sample vials with the purge bottle. The extraction system allows the installation of differently sized purge bottles and quantitative transfer of sample water from standard VOA vials into the extraction line via a septum. The GC injector connects to the six-port (V2) valve and the cryotrap for sample transfer to the GC after extraction from the water (Figure 1).

Before a purge and trap cycle was started, a flow meter was connected to the vent at valve V2, and the helium purge flow rate was adjusted. Valve V1 was switched into bypass position, and an empty purge bottle, crimped with a gray Wheaton PTFE stopper, was attached. Thereafter the cryotrap was immersed in liquid nitrogen and a VOA vial connected by perforating the septum with both needles. As soon as valve V1 was switched into transfer mode, the water sample was pumped into the purge bottle (V2 in the purge position as in Figure 1). Purge gas flowed through the sample vial over the entire P&T cycle to ensure quantitative transfer of any volatilized compounds. Before being cryotrapped, the CFC-enriched purge gas passed through a Drierite-filled glass tube ( $L = 250$  mm, i.d. = 5 mm) for water vapor removal. When trapping was completed, V2 was turned and the liquid nitrogen trap replaced by a hot-water bath ( $>60$  °C) for rapid release of the cryo-trapped  $\text{CO}_2$  and a focused pulse transfer into the split/splitless injector of the GC–C–IRMS (gas chromatography–combustion–isotope ratio mass spectrometry) setup.

Prior to isotope fractionation tests, cryotrapping and purge efficiencies were evaluated. For this purpose the setup was connected to the injector of a gas chromatograph (Varian 3400, 30 m  $\times$  0.52 mm GSQ column) equipped with a flame ionization detector. First, cryotrapping efficiencies were compared for purge flow rates of 10–100 mL/min of helium. Once optimum flow rates were determined that allow for quantitative collection of CFCs in the cryotrap, the purge efficiencies were tested. Samples of 40, 100, and 500 mL were prepared all containing the same absolute amount of compound (i.e., 15, 150, and 300  $\mu\text{g}$  for HCFC-22, CFC-11, and CFC-113, respectively). Recovery rates after P&T were calculated by comparison to directly injected CFC standards. For purging, a He-to-water ratio of 5:1 was used for all sample volumes, resulting in purge times of 10, 25, and 125 min.

Isotope fractionation due to extraction of CFCs from water samples was evaluated by preparing test samples similar to those for purge efficiency testing, i.e., 40, 100, and 250 mL containing the same amount of compound each. Samples were extracted and cryotrapped according to the procedure described above. Typically at least two replicate analyses were performed for each volume and compound.

**CSIA of Carbon in CFCs/HCFCs.** Separation of extracted VOCs was carried out via gas chromatography in two different ways: (a) the VOCs were separated on column 1 only, and all eluting compounds were directly transferred to the IRMS instrument, or (b) the peak of one target compound was directed into the 1/16 in. cryotrap (“peakcut”) and refocused, and thereafter, the trap was heated to send the trapped compound onto column 2 prior to isotope analysis. Procedure b was necessary to improve the peak shapes and therewith the isotopic detection limits (see the Results and Discussion).

Most of the analyses were executed in single-column mode (a) as shown in Figure 1 and followed closely the well-established laboratory procedure for  $\delta^{13}\text{C}$  CSIA.<sup>22,24</sup> The GC–C–IRMS system consists of a Varian 3300 with a split/splitless injector interfaced with the Finnigan MAT 252 mass spectrometer via a microcombustion furnace. CFCs or HCFCs transferred from the P&T system into the injector were then separated on column 1 (GSQ plot column,  $L = 60$  m, i.d. = 0.32 mm) before directly entering the furnace for combustion of separated compounds to  $\text{CO}_2$ . For pure-phase analysis, the gas chromatograph was operated isothermally to shorten the measurement times. For groundwater samples a temperature program was applied to achieve baseline separation of the eluting peaks (start at 120 °C, ramp to 220 °C at 4 °C/min, hold for 20 min; column head pressure 32 psi). The  $\text{CO}_2$  peaks entering the mass spectrometer were referenced against the external  $\text{CO}_2$  working standard, which was injected twice via the dual inlet prior to every run.  $\delta^{13}\text{C}$  values were calculated according to eq 1. Compound-specific CFC in-house working standards and, additionally, an isotopically characterized methane standard were injected daily to ensure measurement accuracy.

For procedure b, valve V4 was turned ca. 5 s before peak elution and the compound collected cryogenically. The peak start and end times had been determined beforehand. After trapping, V4 was switched back and valve V3 turned. This engaged column 2 (Agilent DB-624,  $L = 25$  m, i.d. = 0.25 mm) and transferred all subsequently eluting compounds from column 1 to the vent. For column 2 an isothermal temperature was chosen (CFC-113, 100 °C; CFC-11, 140 °C; column head pressure 18 psi). To release the trapped compounds onto column 2, valve V4 was turned and the 1/16 in. cryotrap rapidly heated.

**Volatilization Experiments.** Experiments were carried out to investigate isotope effects due to volatilization, also called vapor pressure isotope effects (VPIEs). Masses of 1 mg each of pure-phase liquid CFC-11 and CFC-113 were injected into 1 mL vials and allowed to volatilize at room temperature. After a partial vaporization of each compound estimated by volume, the vial was closed, the remaining fraction of liquid CFC determined by weight, and the isotopic composition measured by GC–C–IRMS. Enrichment factors ( $\epsilon_C$ , ‰) were calculated using the Rayleigh equation<sup>25</sup>

$$\ln \left( \frac{\delta^{13}\text{C} + 1000}{\delta^{13}\text{C}_0 + 1000} \right) \approx \ln(f) \epsilon_C \quad (2)$$

where  $\delta^{13}\text{C}_0$  indicates the initial  $\delta$  value of the pure-phase liquid CFC before volatilization and  $f$  is the fraction of liquid compound remaining in the vial.

## RESULTS AND DISCUSSION

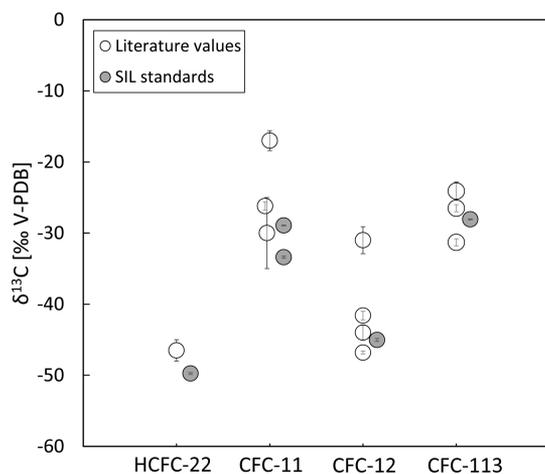
**Offline/Dual-Inlet Characterization of Working Standards.** Offline conversion of CFCs to CO<sub>2</sub> in sealed combustion tubes and consecutive dual-inlet measurements were carried out to establish isotopic working standards for use in a day-to-day laboratory routine.<sup>22</sup> The results are summarized in Table 1.

**Table 1. Offline Dual-Inlet Characterization of Pure-Phase CFCs/HCFs<sup>a</sup>**

compd	lab ID	type	$\delta^{13}\text{C}$ (‰)	$\sigma$	<i>n</i>
HCFC-22	SIL-63	gas	-49.71	0.13	12
CFC-11	SIL-64	solvent	-28.93	0.05	8
CFC-11	SIL-65	solvent	-33.34	0.08	8
CFC-113	SIL-66	solvent	-28.07	0.07	10

<sup>a</sup>The standard deviation refers to external reproducibility on *n* individually prepared combustion tube samples. The internal measurement precision is usually better than 0.03‰.

Different compounds showed different isotopic signatures ranging from -28.1‰ for CFC-113 to -49.7‰ for HCFC-22, probably due to different production mechanisms and precursor materials as has been noted for other anthropogenic compounds.<sup>26</sup> Generally, Stable Isotope Laboratory at the University of Toronto (Earth Sciences) (SIL) working standards were in agreement with previously published ranges of  $\delta^{13}\text{C}$  values of pure-phase CFCs and HCFCs from different sources (Figure 2). Even though the database for pure-phase



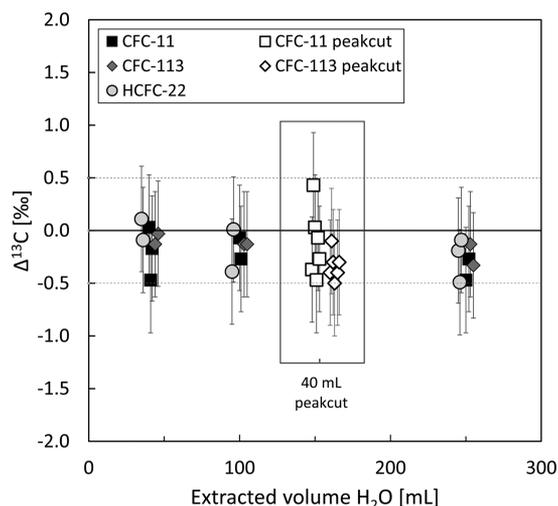
**Figure 2.** Carbon isotope values for SIL working standards (gray symbols) compared to  $\delta^{13}\text{C}$  values of pure compounds CFCs and HCFCs from the literature (white symbols).<sup>8–12</sup> In the current study pure compound CFC-12 was only measured via continuous flow (*n* = 5), while the three other isotopic working standards were characterized offline (Table 1). Error bars shown are based on external reproducibility on replicates.

CFCs and HCFCs is still relatively small, this comparison suggests that the overall range of  $\delta^{13}\text{C}$  values is consistent with the range of petroleum hydrocarbon feedstock used to produce these chemicals, which are typically in the range of -58‰ to -20‰.<sup>27</sup>

**Accuracy and Sensitivity.** Initially, the purge flow rates, He-to-water purge ratios, and purge times were varied to determine the optimal settings to maximize the purging and extraction efficiencies for sample volumes of 40–250 mL. Hence, a purge flow rate of 20 mL/min and a He-to-water ratio

of 5:1 were used for all samples in this study. The purge times varied from 10 to 65 min for 40–250 mL, respectively. The P&T extraction efficiencies for HCFC-22, CFC-11, and CFC-113 varied from 65% to 85% under these conditions. As described below, and as has been previously observed in various studies for aromatic hydrocarbon extraction and chlorinated ethenes, even extraction efficiencies substantially less than 100% do not result in isotopic fractionation (see below).<sup>18,28</sup> Longer purge times are a possible approach to purge larger volumes of water. However, 500 mL samples required 2 h purge times, which, while technically possible, are unlikely to be a feasible routine for day-to-day laboratory procedures. Therefore, this study focused on 40 mL VOA vial volumes typically used at field sites, as well as 100 and 250 mL bottles.

After purge efficiency tests, isotope fractionation due to P&T was evaluated. As noted above, the P&T extraction of dissolved CFCs caused no isotopic fractionation even with extraction efficiencies of 65–85%. The method was tested by comparing offline standards characterized by the dual inlet against CFCs extracted from water by the P&T system and analyzed by continuous flow GC-C-IRMS (Figure 3). For water volumes



**Figure 3.** Values of  $\delta^{13}\text{C}$  determined for HCFC-22, CFC-11, and CFC-113 extracted from water by the P&T system. Values are expressed in parts per thousand deviation from offline-characterized isotopic in-house working standards (see the text). Sample volumes of 40, 100, and 250 mL were tested for direct separation on column 1 (filled symbols), and additionally, 40 mL samples of CFC-11 and CFC-113 were tested with peak cutting (empty symbols, inset). All dissolved and extracted samples had  $\delta^{13}\text{C}$  values in agreement with the known  $\delta^{13}\text{C}$  values within  $\pm 0.5$ ‰.

of 40–250 mL the isotopic signature deviated by less than 0.5‰ from the  $\delta^{13}\text{C}$  values determined by offline/dual-inlet-characterized pure-phase liquids, confirming that no significant isotope fractionation is caused during the P&T extraction procedure within the typical measure of total uncertainty for CSIA incorporating both accuracy and reproducibility.<sup>22,24</sup> This finding is also important as it may suggest that volatilization from groundwaters at field sites is also unlikely to cause significant changes in the  $\delta^{13}\text{C}$  values.

Isotopic detection limits, presented as concentrations for given sample volumes in Table 2, were estimated using the data in Figure 3. The concentrations are calculated on the basis of a split flow rate of 6 mL/min and a minimum signal size of 0.5 V necessary to maintain an overall uncertainty in  $\delta^{13}\text{C}$  of  $\pm 0.5$ ‰.

Table 2. Isotopic Detection Limits ( $\mu\text{g/L}$ ) for HCFC-22, CFC-11, and CFC-113 Based on Data Shown in Figure 3<sup>a</sup>

sample vol (mL)	HCFC-22		CFC-11		CFC-113	
	no peak cut	no peak cut	no peak cut	peak cut	no peak cut	peak cut
40	230 $\pm$ 0	1450 $\pm$ 450	190 $\pm$ 30		2165 $\pm$ 835	270 $\pm$ 130
100	110 $\pm$ 20	940 $\pm$ 0			800 $\pm$ 200	
250	35 $\pm$ 5	115 $\pm$ 5			640 $\pm$ 0	

<sup>a</sup>The detection limits represent the theoretical minimum concentrations for given sample volumes required to achieve a 0.5 V signal in the mass spectrometer at a split flow rate of 6 mL/min. The detection limits are improved, on average, by a factor of 5 (CFC-11) to 10 (CFC-113) if peak cutting is applied. Uncertainties in these theoretical detection limits result from slight differences in the peak heights and purge efficiencies.

On this basis, isotopic detection limits for HCFC-22 ranged from 230 to 35  $\mu\text{g/L}$  for 40 and 250 mL samples, respectively, corresponding approximately to 7–12 nmol of carbon injected on-column.

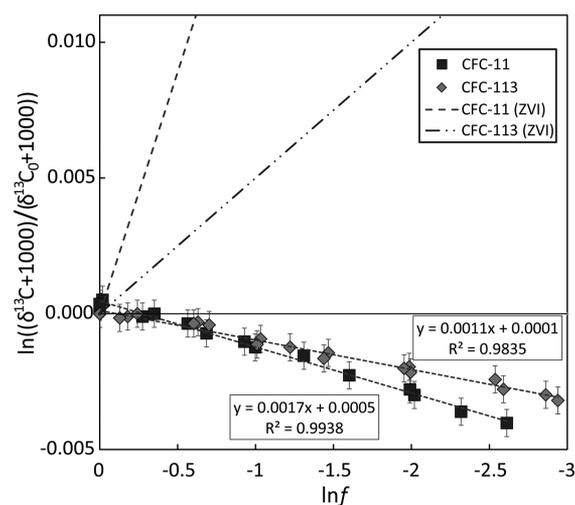
Comparing the detection limits of P&T-extracted CFC-11, CFC-113, and HCFC-22 without peak cutting, for CFC-11 and CFC-113 the injected amounts of carbon required to achieve a 0.5 V signal are 4–20 times higher than that for HCFC-22, corresponding to 40–220 nmol. The difference is due to broader chromatographic peaks for these two CFCs, resulting in lower signal sizes for the same number of moles injected. In comparative tests a peak area of 12 V s produced an HCFC-22 signal of 1.7 V, whereas for CFC-11 a signal size of only 0.17 V was achieved. This reduced sensitivity is not a problem for laboratory experiments, but it limits the applicability of the method for field samples with lower concentrations, underlining the importance of the peak cutting approach to improve chromatography and hence the determination limits.

As demonstrated (Figure 3), the peak cutting and cryo-refocusing technique achieves the same overall uncertainty in  $\delta^{13}\text{C}$  analysis, but due to better chromatography, the signal sizes improved by an order of magnitude for CFC-11 and CFC-113 (Table 2). Isotopic detection limits similar to that of HCFC-22 (P&T) could thereby be achieved, specifically concentrations of 190–270  $\mu\text{g/L}$  for typical 40 mL VOA vial samples. This is higher than typically achieved for other contaminants such as CF and chlorinated ethenes,<sup>29</sup> but sufficient for CFC and HCFC concentrations typically found in groundwater at many contaminated field sites.

The methods presented demonstrate that no isotopic fractionation is associated with P&T extraction and CSIA analysis for three different test compounds for volumes up to 250 mL and concentrations as low as 35  $\mu\text{g/L}$ —a range well within the typical concentrations found at contaminated field sites. This was a necessary step to establish the feasibility of measuring carbon isotope signatures for CFCs and HCFCs in environmental samples at concentrations typical of contaminated field sites.

**Inverse Isotope Effects Due to Volatilization from Pure-Phase CFCs.** Volatilization experiments were carried out with pure-phase liquids CFC-11 and CFC-113 to determine the magnitude of VPIEs under kinetic conditions. During volatilization of both CFCs, we observed an inverse isotope effect with  $^{13}\text{C}$  becoming more depleted in the remaining liquid as volatile loss proceeds. The data fit a Rayleigh model with  $r^2$  values of 0.98 and 0.99 for CFC-113 and CFC-11 respectively. The corresponding enrichment factors obtained from Rayleigh plots were  $+1.7 \pm 0.1\%$  for CFC-11 and  $+1.1 \pm 0.1\%$  for CFC-113 (Figure 4).

Inverse VPIEs of carbon have been reported for chlorinated aliphatic and cyclic hydrocarbons dissolved in water and under equilibrium (closed system)<sup>18,30,31</sup> as well as for kinetic



**Figure 4.** Rayleigh plots for pure-phase volatilization of CFC-11 and CFC-113 compared to the slopes of abiotic degradation experiments with ZVI as reported by Archbold et al.<sup>17</sup> Data for pure-phase volatilization represent three individual experiments for each compound. Each point represents the  $\delta^{13}\text{C}$  value (normalized against the initial  $\delta^{13}\text{C}_0$ ) of the remaining liquid, expressed as the fraction  $f$  remaining on a logarithmic scale. Error bars designate the overall uncertainty of  $\pm 0.5\%$ . The analytical precision ( $1\sigma$ ) of quantitative measurements is  $<0.5\%$  (gravimetric determination of  $f$ ). The slopes of the regression lines correspond to enrichment factors ( $\epsilon$  with a 95% confidence interval) of  $+1.7 \pm 0.1\%$  for CFC-11 and  $+1.1 \pm 0.1\%$  for CFC-113. The positive  $\epsilon$  indicates inverse isotope effects for volatilization of each compound; i.e., the remaining liquid becomes progressively depleted in  $^{13}\text{C}$ . Enrichment factors reported by Archbold et al. for reactions with ZVI correspond to  $-17.8 \pm 4.8\%$  for CFC-11 and  $-5.0 \pm 0.3\%$  for CFC-113, indicating normal isotope effects.<sup>17</sup>

volatilization (open system) of pure-phase liquids.<sup>32–34</sup> The reason for these inverse effects is supposedly a change in the vibrational frequency of molecules containing a  $^{13}\text{C}$  isotope which influences the intermolecular bonding forces.<sup>35</sup> In most previous studies VPIEs were smaller than the total uncertainty for  $\delta^{13}\text{C}$  continuous flow analysis ( $\pm 0.5\%$ ).<sup>22</sup> The extent of equilibrium and kinetic VPIEs for chlorinated aliphatic compounds generally seems to be small in magnitude in both cases and does not differ significantly between closed system equilibrium isotope effects (EIEs) and open system kinetic isotope effects (KIEs). For example, Hunkeler and Aravena determined  $\epsilon$  values (EIEs) of  $+1.3\%$  for dichloromethane (DCM) and  $+0.6\%$  for trichloroethene (TCE) dissolved in water.<sup>31</sup> Huang and co-workers reported  $\epsilon$  values (KIEs) of  $+0.65\%$  and  $+0.31\%$  for volatilization of pure-phase DCM and TCE, respectively.<sup>33</sup>

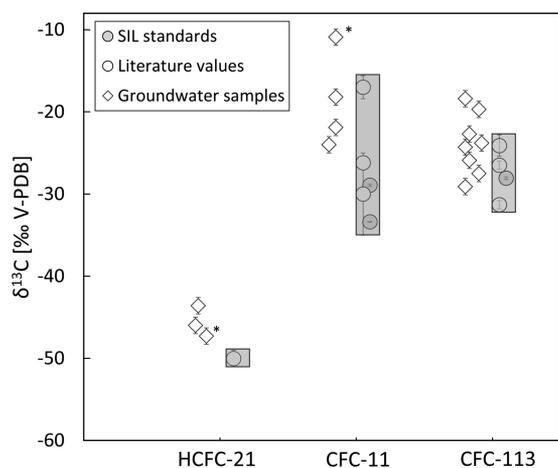
To date, no enrichment factors have been published showing open system volatilization (KIEs) of water-dissolved chlori-

nated compounds. In our own experiments, volatilization of water-dissolved CFCs by purging (P&T) did not cause measurable carbon isotope fractionation. Hence, conditions at the field site may be crucial for the occurrence of VPIEs, e.g. confined/free aquifer causing open/closed system conditions or volatilization from water/non-aqueous-phase liquids. Generally, VPIEs are relatively small, and as shown in previous cited studies, their maximum extent may be in a range of  $\delta^{13}\text{C}$  values similar to that found for pure compound volatilization.

In addition to the overall magnitude of possible KIEs associated with volatilization, it is important to consider the implications of these inverse isotope effects. While experiments have yet to be carried out to determine the carbon isotope effects associated with biodegradation of CFCs, such effects are likely to be normal isotope effects and larger in magnitude than volatilization, as has been demonstrated for all other hydrocarbon contaminants to date.<sup>22</sup> Hence, even if VPIEs occurred at a field site, they would not be mistaken for biodegradation effects. If an enrichment in  $\delta^{13}\text{C}$  values for CFCs were discovered, VPIEs would only have had the impact of diminishing the size of that enrichment signal, leading to a conservative (minimum) estimate of the effects of biodegradation.

#### Groundwater Samples from a Contaminated Site.

Groundwater samples from a contaminated site were measured to demonstrate the applicability of the methods described in this paper and to provide the first determination of  $\delta^{13}\text{C}$  values of CFCs in groundwater. The isotopic composition of 10 individual samples with 120–8900  $\mu\text{g/L}$  concentrations of CFC-11, CFC-113, and HCFC-21 was characterized. Both direct single-column and peak cutting techniques were used for CFC-11 and CFC-113, depending on the concentrations in the samples. HCFC-21 was only analyzed in direct mode due to the high concentrations at this site. The results are summarized in Figure 5 and are compared to pure compound  $\delta^{13}\text{C}$  values from our own laboratory and previous studies.



**Figure 5.** Groundwater samples (open tilted squares) compared to pure compound CFC/HCFC ranges (circles in shaded rectangles) from the literature<sup>8,10–12</sup> and from SIL in-house isotopic working standards. For HCFC-21 no isotopic measurements have been reported previously. The range shown here represents characterization of one pure-phase compound using the continuous flow technique ( $n = 5$ ) in our own laboratory. Symbols marked with an asterisk were measured in the same groundwater sample.

Compared to the pure compound  $\delta^{13}\text{C}$  values reported to date, the isotopic signatures of groundwater samples generally showed a tendency toward more enriched values. Several groundwater samples had  $\delta^{13}\text{C}$  values that are more enriched than observed to date for any pure-phase CFCs. Experiments investigating carbon isotope fractionation during abiotic degradation of CFC-11 and CFC-113 on ZVI have shown large isotope enrichment factors associated with the C–Cl bond cleavage.<sup>17</sup> To date no comparable experiments have been carried out to establish fractionation factors during microbial reductive dechlorination, but a similar large fractionation is likely associated with the enzymatic dechlorination as well. The enriched  $\delta^{13}\text{C}$  values observed in one of the groundwater samples at the site could be consistent with either abiotic degradation or biodegradation. Notably, the sample with the most  $^{13}\text{C}$  enriched value for CFC-11 (denoted by an asterisk in Figure 5) contains HCFC-21, a possible product of degradation of CFC-11. Pure HCFC-21 has a much more depleted  $\delta^{13}\text{C}$  value, but a pattern of  $^{13}\text{C}$ -enriched parent and  $^{13}\text{C}$ -depleted daughter product could also be consistent with isotopic fractionation due to biodegradation. That said, these samples were run first and foremost to test the new analytical technique on realistic field samples. A conclusive interpretation of these results requires additional work, specifically experiments to characterize fractionation factors associated with biodegradation and likely further experiments on ZVI to better constrain the fractionation factors published to date. In addition, more work to characterize the range of values associated with pure compound HCFC-21 is required as HCFC-21 can also be present at field sites as a primary contaminant.

## CONCLUSIONS

In this paper we present, to our knowledge, the first ground-truthed direct and compound-specific P&T–GC–C–IRMS method to measure stable carbon isotopic signatures of CFCs and HCFCs in waters. The P&T approach allows for the stable carbon isotope analysis of large water samples with CFC concentrations in the lower microgram per liter range, which makes it applicable to investigate contaminated groundwaters at many sites. Volatilization experiments with pure-phase CFCs showed small inverse VPIEs, whereas volatilization from water due to purging did not result in any measurable isotope effects. Further investigations are necessary to be able to predict the volatilization isotope effects of CFCs in different phases and in different systems. However, if compared to the only published isotope effects to date, conducted for abiotic degradation, the maximum measured volatilization isotope effects for CFCs are still small and inverse and therefore cannot be mistaken for normal degradation isotope effects. The first measured groundwater samples indicate, overall, more enriched  $\delta^{13}\text{C}$  values than those of pure compounds analyzed to date, and degradation may be a possible scenario at this site. More specific information may be obtained once enrichment factors for microbial degradation are established. Finally, the method demonstrated here may be appropriate not only for other CFCs and HCFCs but also for a large variety of highly volatile organic compounds with similar boiling points and air–water partitioning behavior such as haloforms and methyl halides. Our method is therefore not limited to the investigation of degradation processes in groundwater but may, for instance, also be used for isotope analysis and source apportionment of these naturally produced compounds in lake and ocean water.

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## Notes

The authors declare no competing financial interest.

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