

Developing a passive trap for diffusive atmospheric ^{14}C sampling



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ABSTRACT

^{14}C - CO_2 measurement is a unique tool to quantify source-based emissions of CO_2 for both the urban and natural environments. Acquiring a sample that temporally integrates the atmospheric ^{14}C - CO_2 signature that allows for precise ^{14}C analysis is often necessary, but can require complex sampling devices, which can be difficult to deploy and maintain, especially for multiple locations. Here we describe our progress in developing a diffusive atmospheric CO_2 molecular sieve trap, which requires no power to operate. We present results from various cleaning procedures, and rigorously tested for blank and memory effects. Traps were tested in the environment along-side conventional sampling flasks for accuracy. Results show that blank and memory effects can be minimized with thorough cleaning and by avoiding overheating, and that diffusively collected air samples agree well with traditionally canister-sampled air.

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1. Introduction

With tropospheric mixing ratios of CO_2 surpassing 400 ppm, the highest ratio in 800,000 years [1], there is a crucial need to better understand the dynamics of the global carbon (C) cycle. To mitigate potential changes in the global carbon cycle, we need a better understanding of climate feedbacks and their drivers, which requires improved quantifications of the magnitude and timing of individual CO_2 emission sources. Particularly important are better constraints on (1) the magnitude of regional emissions of anthropogenic CO_2 from fossil fuel burning in urban environments [2] and (2) how pools of old C stored in soils can be re-mineralized to CO_2 and released back to the atmosphere, as this can act as a positive feedback for climate change [3]. In both the urban and natural setting, the radiocarbon content of CO_2 (^{14}C) provides a unique tracer of C cycling, allowing us to ascertain sources to C emissions [4].

^{14}C is a radionuclide produced by cosmic rays interacting with the Earth's atmosphere. It decays into ^{14}N by a β^- decay and has a half-life of 5730 years. The rates of production and radioactive decay, combined with atmospheric mixing and absorption into the ocean and global biomass, determines the ratio of $^{14}\text{C}/^{12}\text{C}$ in the atmosphere. Upon sequestration through photosynthesis, C enters living matter with the ratio of $^{14}\text{C}/^{12}\text{C}$ of that of the atmosphere at the time it was fixed. However, after death, without further inputs of C from photosynthesis or consumption, the ratio of

$^{14}\text{C}/^{12}\text{C}$ in organic matter will decrease with time due to radioactive decay of the ^{14}C isotope.

Since the industrial revolution in the mid-19th century, the ^{14}C content of the atmospheric CO_2 had been decreasing due to large inputs of ^{14}C -deplete CO_2 derived from fossil fuel (ff) [5]. In 1955, the depletion of atmospheric $\Delta^{14}\text{C}$ due to ff was estimated to be -15% to -25% compared to natural levels [6]. However, this decreasing trend was interrupted by aboveground thermonuclear weapons testing that occurred between 1950 and the mid 1960s. As a result, in 1963–1964, the ^{14}C content of CO_2 of the Northern Hemisphere reached a peak of nearly double the natural abundance. It has thereafter been decreasing due to the ban of aboveground testing in 1963 and mixing of the ^{14}C enriched CO_2 into the global biosphere and ocean, as well as the continual addition of ^{14}C free ff CO_2 . However this large pulse of ^{14}C , followed by accurate atmospheric monitoring, created a unique setting, allowing for the use of atmospheric ^{14}C as a tracer of C cycling on annual to decadal timescales [3].

Precise ^{14}C - CO_2 measurements are a powerful tool for determining emission sources (e.g. [7–11]). However, establishing a regional estimate of emission sources can be challenging in both urban and natural environments. When sampling, it is often difficult to integrate a multitude of gas sources that vary in both time and space. In urban areas, precautions need to be taken to ensure that temporally changing emissions (such as traffic and plant and soil respiration) are fully integrated and that sampling is not over-influenced by pinpoint sources (i.e. emissions from one factory) [12]. The same applies in the natural environments, where

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emissions change both diurnally and seasonally, and can be sporadic due to their dependence on physical factors, such as temperature (e.g. degassing from lakes during ice break-up [13]), or soil freezing [14], or precipitation [15], as well as plant phenology [16,17]. In addition, sampling sites are often remote and at times inaccessible, making routine and year round sampling difficult.

As a consequence, there is a growing interest in developing a passive diffusive atmospheric and/or soil CO₂ trap, with particular interest in using zeolite molecular sieve as a CO₂ absorbent. The benefit of a passive diffusive trap is that it requires no electricity and slowly absorbs CO₂ into the sieve, integrating a period of days to weeks. CO₂ collected by the zeolite trap can be released by heating upon returning to the laboratory. Zeolites have been successfully used to pre-concentrate CO₂ from the gas-stream of purification lines for accelerator mass spectrometry (AMS) analysis [18–20].

For atmospheric ¹⁴C-CO₂ measurements, zeolites have proven to be potentially useful for sampling periods greater than a one month [23]. However, use for short term sampling (<2 weeks) has proven difficult due to the low CO₂ content in air, high water moisture, and evidence of C blanks [21,22]. In this paper we present our progress in developing a high precision, low blank and low memory, passive diffusive atmospheric CO₂ zeolite trap to be used for ambient CO₂ environmental sampling.

2. Materials and methods

Our prototype trap (Fig. 1) is constructed from parts already available in our lab. The zeolite is placed inside a 6 in. long × 1/2 in. o.d. quartz tube connected to a valve assembly via a Swagelok 1/4 or 1/2 in. Ultra-Torr Tee fitting (SS-4-UT-3 for 1/4 in. fitting or SS-8-UT-3 for 1/2 in. fitting, Swagelok, Torrance, California, USA). The valve assembly has two openings. One opening is fitted with a 1/2 in. plug valve (SS-8P6T2, Swagelok, Torrance, California, USA) that allows for sample collection. For cleaning, a second needle valve (SS-1KS4, Swagelok, Torrance, California, USA) controls the flow of ultra high purity (UHP), Grade 5.0 helium (He UHP300, Airgas Inc., Santa Ana, California, USA) into the trap. This valve is connected to a 1/16 in. stainless steel capillary (using an assortment of available reduction fittings) that extends to the bottom of the quartz tube directing UHP He flow directly into the zeolite.

Two grain sizes of 13X zeolite were tested: 8/12 beads (208647, Sigma Aldrich, St. Louis, Missouri, USA) and 45/60 mesh (20304, Supelco Analytical, St. Louis, Missouri, USA). As an initial cleaning, prior to trap assembly, zeolite is baked at 700 °C for 3 h in an oven open to atmosphere. The zeolite is then placed either directly into the quartz tube or into a stainless steel mesh envelope. The envelope is made by taking a 6 in. × 1.5 in. piece of 316 stainless steel mesh with 0.114 mm diameter mesh opening (9419T39, McMaster-Carr, Santa Fe Springs, California, USA), folding in half lengthwise and folding the sides to create a pouch. The pouch is pre-cleaned by baking it in an oven at 800 °C for 2 h. A weighed amount of zeolite is spread evenly inside, the pouch top is folded closed, rolled into a spiral and inserted into the quartz tube. Once the trap is assembled, the quartz tube portion of the trap is heated to 700 °C overnight under vacuum, followed by a flow-through of He for a thorough cleaning.

Several cleaning procedures were tested by heating the quartz section of the traps in a tubular heater (discontinued, Watlow, Riverside, California, USA) controlled using a variable transformer (3PN1010B, Staco Energy Products Co., Dayton, Ohio, USA), while connected to a vacuum line and purging with UHP He under various conditions. First, a quick pulse of He was passed over the zeolite by closing the vacuum line, pressurizing the line to 1 atm with UHP He, opening the line to quickly pump the He away and repeating two more times. In subsequent tests, the zeolite was flushed with UHP He continuously at a rate of roughly 30 ml/min,

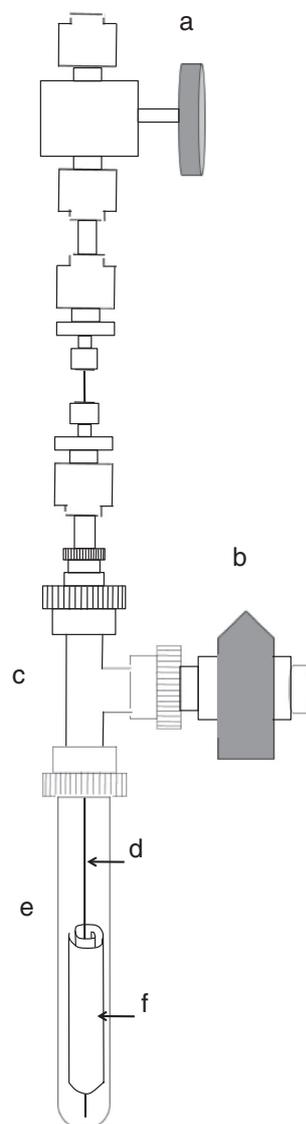


Fig. 1. Trap design – (a) needle valve controls He flow to trap; (b) 1/2 in. Swagelok Ultra-Torr valve opens and closes trap for sampling; (c) Swagelok Ultra-Torr Tee fitting; (d) 1/16 in. stainless steel capillary for UHP He delivery; (e) 6 in. long × 1/2 in. o.d. quartz tube; (f) stainless steel mesh envelope with zeolite.

passing through to the pump. This was tested at intervals of 3, 10 and 30 min. Results were compared using UHP He directly from the cylinder versus He scrubbed with a CO₂ molecular absorbent, (Carbosorb Granular 0.7–1.2 mm, B1018, Elemental Microanalysis Limited, Okehampton, Devon, UK). Cleaning temperatures of 500 and 700 °C were both tested.

To test cleaning efficiency, modern and dead (¹⁴C free) standards were consecutively trapped and released from the same trap. Gas standards were made following the standard procedures of Keck Carbon Cycle facility (KCCAMS) at UC Irvine, i.e. combusting solid standards material in a closed quartz tube at 900 °C with CuO for 2 h. Modern gas standards were made by combusting OX1 standard (NBS oxalic acid, [24]), while ¹⁴C-dead standard gas was made by combusting coal that had been pretreated with an acid/base wash [25]. After combustion, sealed tubes were cracked on the vacuum line and the amount of gas was measured using a calibrated pressure gauge. A pre-cleaned trap was attached to the vacuum line and the standard gas was allowed to absorb to the trap. Monitoring the pressure gauge showed that the CO₂ pressure dropped to 0 torr within 5 s, however the CO₂ was allowed to

absorb to the zeolite for 15 min to ensure all of the standard gas was absorbed. To recover the captured CO₂ gas, the quartz tube of the trap was heated for 45 min, without He flow-through, while connected to a vacuum line. Desorption temperature of 450 and 700 °C were both tested. Released CO₂ was purified cryogenically and graphitized via a sealed tube zinc reduction method [26]. Between each standard, traps were cleaned using the various methods described above.

As a test of accuracy for diffusive sampling in the environment, trap samples were collected alongside air canisters. Both samplers were placed outside on a 3rd floor balcony of Croul Hall, a campus building at the UC Irvine, and placed within 0.5 m of each other to ensure they were collecting the same air. Prior to sampling, traps were cleaned and filled with 1 atm of UHP N₂ gas that had been scrubbed through a CO₂ molecular absorbent (Carbosorb Granular 0.7–1.2 mm) to match/mimic atmospheric pressure. The sampling opening was also fitted with a glass tube filled with Mg(ClO₄)₂ to avoid absorption of water vapor by the zeolite. Samples were collected with both 1/2 and 1/4 in. sampling openings. The 45 L air canisters were evacuated on a vacuum line and fitted with a pressure gauge and a 2 m long × 0.125 mm i.d. stainless steel capillary through which sample gas was slowly drawn into the canister. The pressure of the canister was monitored and the collection rate was estimated based on the percent vacuum pressure lost.

Both samplers passively collected atmospheric air for a period of several days up to one month, during a two-month period from May to July 2014. Air CO₂ was purified and graphitized as previously described, using a desorption temperature of 400–450 °C for 45 min to collect the sample CO₂. After extraction, the trap was stored, either with or without cleaning, for a period of several days to several months. To ensure that over a month long period trapped air was being collected in a consistent manner, several trap/canisters sets were used, one set to sample the entire month, another set to sample the first 2-week period, and a final set to sample the second 2-week period. Meanwhile, atmospheric CO₂ concentration was measured by building CO₂ monitors and used for estimating average CO₂ concentration during sampling period.

All ¹⁴C analyses were performed at UC Irvine's KCCAMS, on a compact AMS from National Electrostatics Corporation (NEC 0.5MV 1.5SDH-2 AMS system) with a modified NEC MC-SNICS ion-source [27,28]. A simultaneous AMS δ¹³C measurement in this system allows for the correction of fractionation that could occur both during the sampling, graphitization process and inside the AMS system. The relative percent error of day-to-day analysis, including extraction, graphitization and AMS measurement, is between 2.5‰ and 3.0‰ based on our secondary standards measured in the past. Radiocarbon concentrations are given as Δ¹⁴C, following the conventions of Stuiver and Polach [29].

3. Results and discussion

3.1. Blank and memory assessment

Tests of trapped standard gases show that the zeolite exhibits a significant blank if not thoroughly cleaned. Initial tests with minimal cleaning (either 3 purges or 3 min of UHP He flow-through) showed that OX1-CO₂ ¹⁴C Fm (fraction modern) values became increasingly depleted with decreasing sample size when sample size is <0.1 mg C (although dead C blank from regular combustion, graphitization and AMS machine had already been corrected using matching sizes of non-trapped OX1). The modern C blank was corrected based on matching sizes ¹⁴C dead standard, such as a coal, following the approach by Santos et al. [30].

Here we use *R*, the measured sample-to-standard ratio defined in Eq. (1) below to assess blank and memory effect of all zeolite traps. No dead or modern C blanks were applied in *R* calculation.

$$R = \frac{({}^{14}\text{C}/{}^{12}\text{C})_{\text{sample}}}{({}^{14}\text{C}/{}^{12}\text{C})_{\text{OX1}}} \quad (1)$$

When processed OX1 has a *R* value of 1, it indicates that the sample's ¹⁴C ratio agrees with the consensus value of OX1 of 1.0398 Fm.

Regardless of the size of sieve used, the observed average *R* is 0.975 ± 0.021 (*n* = 9) for the minimal cleaning traps (Fig. 2a and b). Using 0.25 g of 45/60-mesh sieve and increasing He flow-through time to 10 min, improved OX-1-¹⁴CO₂ values (average *R* = 0.9937 ± 0.0063, *n* = 9, Fig. 2c). While decreasing the amount of zeolite (from 1 to 0.25 g) reduced the amount of contamination, it also decreases the total maximum CO₂ absorption capacity of the trap. Initial tests estimated the capacity of the zeolite to be approximately 12 mg C/g sieve (data not shown). Using greater amounts of zeolite will be advantageous during field sampling, as the trap would be less susceptible to saturation by water vapor, which could limit absorption of CO₂. Therefore we continued our experiments with traps built with 1 g 45/60 mesh zeolite.

In order to increase the amount of surface area exposed to sample and cleaning gases, which increases sample absorption and cleaning efficiency, respectively, the original grain size (8/12 mesh) was replaced with smaller size zeolite sieve (45/60 mesh) and the zeolite grains were spread apart inside the trap using a mesh envelope (see Section 2). The total He volume was also increased, by increasing the flow-through time to 30 min. Results showed that the dead C blank increased slightly (average *R* = 0.9879 ± 0.0072, *n* = 4) which we attributed to impurities in the UHP He and the increased amount of flow-through volume. Repetition of the test using UHP He scrubbed with CO₂ molecular absorbent further improved the dead C blank. OX1 values showed no significant deviation from the consensus value (*R* = 0.9970 ± 0.0071, *n* = 7, Fig. 2e), even on small samples of less than 0.1 mg C, suggesting that the UHP He directly from a cylinder indeed contained small amounts of depleted CO₂ and requires pre-scrubbing.

Due to problems encountered with dead blanks occurring after the storage (see discussion below), we also tested modern OX1 standard gas using lower cleaning and desorption temperatures. After cleaning at a temperature of 500 °C with 30 min of scrubbed UHP He flow through, measured OX1 values again showed no significant deviation from the consensus values (average *R* = 0.9953 ± 0.0037, *n* = 7, for sample size from 0.084 to 0.5 mg C, Fig. 2f).

In all tests, the OX1-CO₂ standards that were trapped after coal-CO₂ standards did not show significant differences from other OX1-CO₂ standards, suggesting very little to no memory effect for the zeolite. Tests also showed that the modern C blank was very small, typically between 1 and 2 μg C (Fig. 2g–i). Our blanks compare well with those found by Garnett and Murray [20].

Although reasonable blanks were obtained in vacuum line tests, where standard gas was absorbed to the zeolite and quickly desorbed and collected, we noted that traps that had been sampling or stored for several weeks released ¹⁴C depleted C when cleaned at 700 °C with He flow-through. The C blank from the cleaning process varied greatly in ¹⁴C value and size (Δ¹⁴C range = 37‰ to –920‰, size range 8–160 μg C). The variation is most likely caused by several factors including variability in cleaning procedures and a wide range in the ¹⁴C value of samples collected on the trap prior to cleaning. Although no strong correlations could be found to sampling/storage time, storage conditions (i.e. under vacuum or filled with N₂) or number of times the trap had been sampled or cleaned, ¹⁴C values generally decreased with increasing C blank size suggesting the presence of a slowly degassing of ¹⁴C depleted C. When the traps were heated to 700 °C without He flow-through,

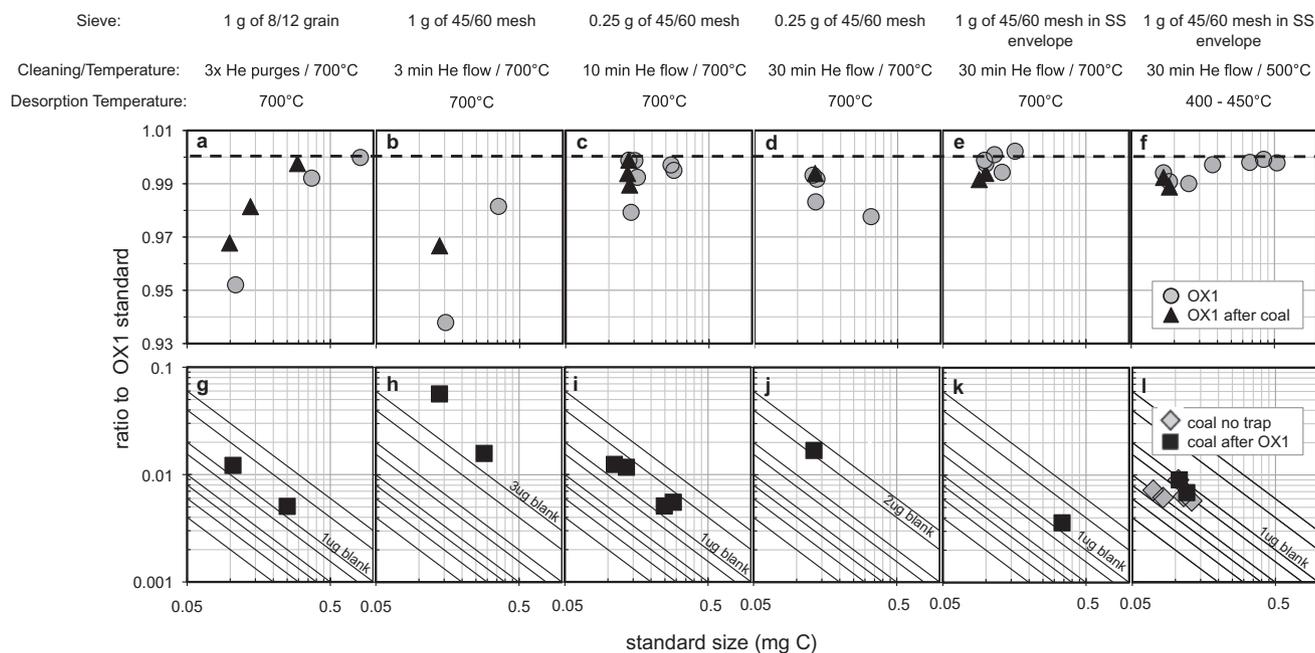


Fig. 2. Blank and memory assessment – upper panels (a–f) show tests of the dead C blank using OX1-CO₂ standard. Dashed line of 1 represents measured OX1 is the same as the defined value of OX1. Gray circles show OX1-CO₂ when it was the first sample to the trap or after another OX1-CO₂ standard. Black triangles represent OX1-CO₂ standards released from cleaned traps after a coal standard. The lower panels (g–l) show tests of the modern C blank using coal-CO₂ standard following the approach by Santos et al. [30]. Gray diamonds show coal-CO₂ processed only on the vacuum line (i.e. not trapped). Black squares represent coal-CO₂ standards released from cleaned traps after OX1-CO₂ standard. No blank corrections were applied in ratios shown in these plots. Above the panels described the size of molecular sieve used and the trap configuration (i.e. with or without SS envelope), the cleaning conditions (He flow and cleaning temperature) and the sample desorption temperature.

any collected gas was below the detection limit of our pressure gauge (<0.1 µg C). To ensure the CO₂ was not coming from the cleaning He gas, scrubbed He was flowed through a liquid nitrogen trap for 2 h. However, no detectable amount of CO₂ was collected. Also, trapped sample gas released at 400–450 °C and collected without He flow-through showed no sign of contamination (see below Section 3.3). These observations suggest that the release of the ¹⁴C-depleted CO₂ requires both high temperature (≥700 °C) and He flow. It is unclear whether this C blank is coming from the zeolite itself, or from another part of the trap, such as the silicone grease used to lubricate the valves or the o-rings in the Ultra-Torr fittings, both of which may degas volatile organic C under elevated temperature. However, due to similar blank issues observed by other research groups using different 13× zeolite trap designs [20] [22], this may be a property inherent to the zeolite, possibly the binding compound used to manufacture it. Overheating (>700 °C, and/or prolonged heating) may degrade the binding material and cause the release of ¹⁴C-depleted C that can be carried out by He flow. One trap that was accidentally overheated to >700 °C consistently showed more ¹⁴C-depleted C blank during cleaning than other traps, which supports the above binding material break down hypothesis.

Based on all test results, we finalize our trap pretreatment and cleaning procedure as the following: (1) Prior to trap assembly, bake 1 g of 45/60 mesh zeolite at 700 °C for 3 h in an oven open to atmosphere; (2) place zeolite into a stainless steel mesh envelope that is pre-baked in an oven at 800 °C for 2 h; (3) heat trap portion of the assembled quartz tube to 700 °C overnight under vacuum, followed by 30 min flow-through of CO₂-scrubbed He. For desorbing sample CO₂ from the trap, heat it at 450 °C for 45 min (CO₂ collected), followed by cleaning at 500 °C for 30 min with flow-through of CO₂-scrubbed He (not collected). Trap is stored with He atmosphere between samples. The ambient air samples presented below were collected and desorbed using traps prepared with the above procedure.

3.2. Absorption rate tests in ambient air CO₂ concentration

The absorption rate of the traps is positively correlated to the size of the sampling opening and negatively correlated to the length of the pathway based on Fick's first law. This was well demonstrated in a barium hydroxide solution passive CO₂ trap device developed by Bertoni et al. [31]. The pathway length of our trap is ~28 cm, which is mainly determined by the safe length between the valve of the trap and our heating oven for CO₂ desorption. Traps with a 1/4 in. opening absorbed CO₂ at an average rate of 0.021 mg C/day and remained linear up to 31 days (Fig. 3). Tests of several traps, with a 1/2 in. opening over different sampling periods gave a linear absorption rate of 0.042 mg C/day up to 28 days (Fig. 3). At 28 days they had collected approximately 0.7 mg C. Samples collected over 14 days would likely give >0.3 mg C which is a reasonable size for ¹⁴C analysis in our AMS system. As expected from Fick's first law, the diffusion rate, and thus absorption rate, would increase with increasing CO₂ concentration as well (such as in soil gas), which we plan directly to test with our traps in the future.

Monitoring of the vacuum pressure showed that the sampling rate of the 45 L canister with the capillary setup was linear up to 28 days. They were measured to collect ~5 mg of C over this period, resulting in a relatively constant flow rate of approximately 0.19 mg C/day. With this linear sampling rate, we were able to evaluate the zeolite-trapped samples against the canister-collected samples side by side.

3.3. Atmospheric ¹⁴CO₂ results

In each sample collection comparison, the ¹⁴C-CO₂ collected from the trap did not differ from that collected from the canister within analytical error ($1\sigma = 1.5\text{--}2.2\%$, Fig. 4). Over the 2-month period from May to July 2014, the ¹⁴C signature of air samples did not change significantly. The average $\Delta^{14}\text{C}$ of air collected by

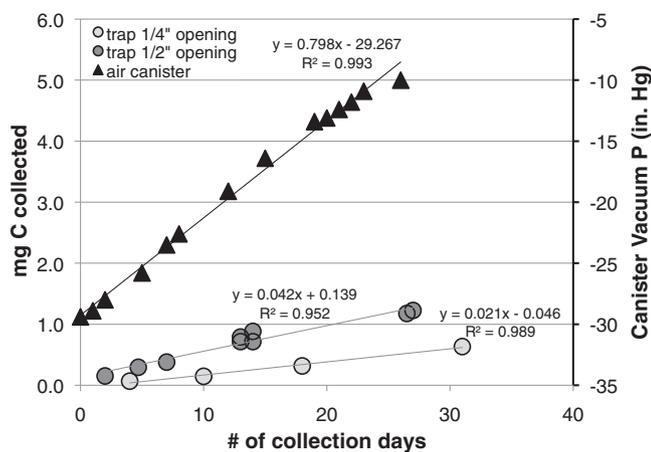


Fig. 3. Absorption rates – amount of CO₂ absorbed vs. the number of collection days. Absorption rate of the canister (triangles) was estimated by drop in vacuum pressure (in. Hg). Absorption rate of the trap shown for 1/4 in. sampling opening (light gray circles) and 1/2 in. sampling opening (dark gray circles). Linear regression relations are shown next to each line.

canisters was $10.6 \pm 1.7\%$ ($n = 4$), while the average trapped air $\Delta^{14}\text{C}$ was $10.1 \pm 1.7\%$ ($n = 4$). The average $\Delta^{14}\text{C}$ of all air measurements together was $10.4 \pm 1.7\%$ ($n = 8$, canister and trap measurements). The absorption rates of the traps ranged from 0.044 to 0.065 mg C/day. Traps that sampled longer periods (i.e. month-long periods) exhibited lower average sampling rates compared to the traps that only sampled two-week intervals. We believe this variation is likely due to hydration of the $\text{Mg}(\text{ClO}_4)_2$ water trap, which would partially block the diffusion of air into the trap, leading to decreased average sampling rates over time.

We used the collected air samples from the UC Irvine campus (May to July of 2014) to quantify how much anthropogenic emissions contributed to the total CO₂ concentrations as an example for tracing sources of emissions through ¹⁴C measurements. To calculate the fraction of ff derived CO₂ (f_f), we used the following mass balance equation (Eq. (2)):

$$\Delta^{14}\text{C}_m = \Delta^{14}\text{C}_f f_f + \Delta^{14}\text{C}_b f_b \quad (2)$$

where $\Delta^{14}\text{C}_m$ is the ¹⁴C signature measured, $\Delta^{14}\text{C}_f$ is the ¹⁴C signature of CO₂ derived from ff, $\Delta^{14}\text{C}_b$ is the ¹⁴C signature in background air; f_f and f_b are the fractions of ff derived CO₂ and background air

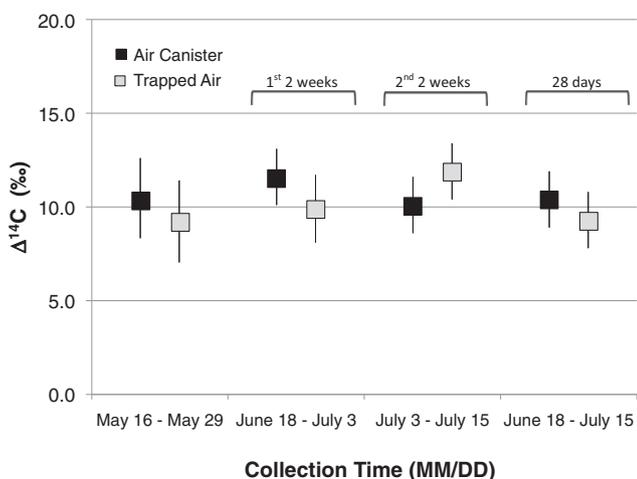


Fig. 4. Environmental test – $\Delta^{14}\text{C}$ -CO₂ (‰) of air samples collected using canister (black) and trap (light gray) samplers.

CO₂, respectively. We made the assumption that the entirety of the CO₂ collected consisted solely of background air CO₂ and ff derived CO₂, therefore:

$$f_f + f_b = 1 \quad (3)$$

The equation can be substituted and rearranged to solve for the f_f (Eq. (4)):

$$f_f = \frac{\Delta^{14}\text{C}_m - \Delta^{14}\text{C}_b}{\Delta^{14}\text{C}_f - \Delta^{14}\text{C}_b} \quad (4)$$

We used a value of -960% for $\Delta^{14}\text{C}_f$ according to a study of California gasoline [32] and a value of 19.6% as a value $\Delta^{14}\text{C}_b$, the average $\Delta^{14}\text{C}$ value measured at Point Barrow, Alaska during our sampling period (Xu, unpublished data). We assumed that the error of both measurements is 2.5% , the average measurement error of our facility (see Section 2). Following this calculation, the f_f was estimated to be approximately 0.0094 ± 0.0031 . To express this in units of ppm, the atmospheric CO₂ concentration was estimated from the university's building air monitors which measure CO₂ concentrations every 15 min. The average outside CO₂ concentration during our sampling period was 408.4 ± 6.6 ppm, thereby giving estimated f_f contribution of approximately 3.8 ± 1.3 ppm.

4. Conclusions

Our work here demonstrates the challenges of utilizing zeolites for ¹⁴C-CO₂ environmental sampling. We demonstrated that it is possible to make reproducible and accurate ¹⁴C measurements on standard gases after the zeolite is thoroughly cleaned to remove ¹⁴C-deplete C. Environmental gas samples collected diffusively were shown to be comparable to samples collected by canisters. Through diffusive sampling, the zeolite absorbs CO₂ in a linear manner, making it ideal for collecting time integrated CO₂ samples. We confirmed that the rate of CO₂ absorption is greatly determined by the area of the sampling opening where diffusion occurs, as expected from Fick's first law. With a 1/2 in. opening we found that 2-week long sampling periods collect a sufficient amount of ambient CO₂ for ¹⁴C analysis. Although stored traps showed a measurable amount of blank, this did not appear to affect results of samples collected from the environment.

Future work will include changing the design of the trap to make it more durable for extended field sampling and shipping and improving the method to exclude water vapor as this will saturate the zeolite and reduce CO₂ absorption. Tests are needed to show how absorption rates differ for different atmospheric CO₂ concentrations and to determine the source and physical conditions that facilitate release of the ¹⁴C-depleted C blank we observed during cleaning. This will decrease the likelihood of sample contamination.

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