Technical Note: Inexpensive modification of Exetainers for the reliable storage of trace-level hydrogen and carbon monoxide gas samples

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Abstract. Atmospheric trace gases such as dihydrogen (H_2), carbon monoxide (CO) and methane (CH_4) play important roles in microbial metabolism and biogeochemical cycles. Analysis of these gases at trace levels requires reliable storage of discrete samples of low volume. While commercial sampling vials such as Exetainers® have been tested for CH_4 and other greenhouse gases, no information on reliable storage is available for H_2 and CO. We show that vials sealed with butyl rubber stoppers are not suitable for storing H_2 and CO due to release of these gases from rubber material. Treating butyl septa with NaOH reduced trace gas release, but contamination was still substantial, with H_2 and CO mixing ratios in air samples increasing by a factor of 3 and 10 after 30 days of storage in conventional 12 mL Exetainers. All tested materials showed a near-linear increase in H_2 and CO mixing ratios, indicating a zero-order reaction and material degradation as the underlying cause. Among the rubber materials tested, silicone showed the lowest potential for H_2 and CO release. We thus propose to modify Exetainers by closing them with a silicone plug to minimise contamination, and sealing them with a stainless steel bolt and O-ring as secondary diffusion barrier for long-term storage. Such modified Exetainers exhibited stable mixing ratios of H_2 and CH_4 exceeding 60 days of storage at atmospheric and elevated (10 ppm) mixing ratios. The increase of CO was still measurable, but nine times lower than in conventional Exetainers with treated septa, and can be corrected for due to its linearity by storing a standard gas alongside the samples. The proposed modification is inexpensive, scalable and robust, and thus enables reliable storage of large numbers of low-volume gas samples from remote field locations.

1 Introduction

Dihydrogen (H_2) and carbon monoxide (CO) are trace gases present in the atmosphere at 0.53 ppm and approximately 0.15 ppm (Ehhalt and Rohrer, 2009; Petrenko et al., 2013). They are important intermediates in numerous biogeochemical reactions, with environmental equilibrium concentrations kept at trace levels by tightly controlled production and consumption reactions (Hoehler et al., 1998; Khalil and Rasmussen, 1990). Atmospheric H_2 and CO play an important role in microbial sustenance for soil bacteria, and soils consist an important sink in the global atmospheric budget (Constant et al., 2009; Cordero et al., 2019; Greening et al., 2015; Liu et al., 2018). In addition, both gases can be produced and consumed abiotically in

30   photochemical or naturally occurring redox reactions (Conrad and Seller, 1985; Fraser et al., 2015; Hoehler, 2005; Lee et al., 2012).

Investigating the turnover of environmental H_2 and CO at trace concentrations generally requires the collection of discrete samples for analysis with a sensitive gas chromatography system (GC). Ideally, the GC is field-deployable and measurements can be conducted in situ, which eliminates the problem of gas storage altogether (King and Weber, 2008; Meredith et al.,

35   2017). Alternatively, a field-laboratory or shipboard setup may allow for short-term (minutes to hours) storage of samples in syringes or gas-tight sampling bags (Conrad and Seiler, 1988). However, such arrangements are not always feasible (e.g. at remote or inaccessible field sites), and samples have to be stored for longer periods (days to months).

Glass flasks or bulbs of 0.5 – 1 L volume sealed with hoses or O-rings have been found to provide stable, long-term storage of a variety of atmospheric trace gases and their stable isotope ratios (Rothe et al., 2005; Thrun et al., 1979). They are routinely

40   used in applications with strict stability requirements of less than a few ppb deviation after many months of storage, e.g. for cooperative atmospheric trace-gas monitoring (https://www.esrl.noaa.gov/gmd/ccgg/flask.html; last accessed 18/11/2020), or sampling campaigns involving isotopic ratios of H_2 (Chen et al., 2015; Schmitt et al., 2009). Other similar designs include stainless steel flasks and cylinders (Khalil et al., 1990; Sulyok et al., 2001). Although these systems represent the 'gold standard' for gas-sample storage, they have two major disadvantages: they require the collection of large sample volumes of

45   >1 L, and they are often prohibitively expensive for large-scale field campaigns with hundreds or thousands of samples.

In applications where signals are large and thus precision criteria less stringent, e.g. for measuring environmental gas fluxes, glass vials of a few mL volume closed with butyl rubber septa (either crimp-capped or screw-capped, e.g. Exetainers®) are widely used containers to store trace-gas samples. They are relatively inexpensive and fit many GC autosamplers, thus making them ideally suitable for large measurement campaigns. In particular, Exetainers have shown good stability (<5% deviation

50   from a reference gas) of trace gases such as methane (CH_4), nitrous oxide (N_2O) and carbon dioxide (CO_2) of up to one month, regardless of temperature (Faust and Liebig, 2018; Glatzel and Well, 2008; Rochette and Bertrand, 2003). Longer storage times induced deviations of up to 30% from the reference gas, but could be corrected for by storing a standard gas together with the samples (Faust and Liebig, 2018; Laughlin and Stevens, 2003).

To our knowledge, storage of H_2 and CO at trace levels in Exetainers or crimp-cap vials have not been investigated. However,

55   anecdotal reports of rapid sample contamination with H_2 and CO from butyl stoppers has been an ongoing concern. Here we demonstrate that various butyl rubber septa commonly used for sealing glass vials release significant amounts of hydrogen and carbon monoxide over short periods of time. We then propose a simple modification to seal Exetainers with silicone sealant and a stainless steel bolt, and confirm the long-term stability of H_2, CH_4 and, to a lesser extent, CO mixing ratios.

2 Materials and Methods

2.1 Demonstration of trace-gas release from rubber materials

A selection of typical rubber materials used for sealing gas-sampling containers were tested for release of H_2, CO and CH_4 by incubating them for several days in closed containers. Exetainers of 12 mL volume were chosen for containers as they fitted the autosampler of the GC, thus minimising variability due to manual sample injection. Twelve different treatments were prepared in quadruplicates; details of the treatments and rubber materials are summarised in Table 1. Some treatments involved pre-treating butyl rubber by i) boiling for 2 h in 0.1 M NaOH and then twice in Milli-Q water (Lin et al., 2012); and ii) washing with a surfactant (Tween 20) followed by rinsing and autoclaving twice (Ruth Henneberger, personal communication). After pre-treatments, rubber materials were weighed to 2 g or 4 g depending on treatment, then cut to smaller pieces to fit into Exetainers. Five control Exetainers were prepared empty. All samples were closed with a NaOH pre-treated Exetainer septum (typical weight 0.6 g); thus, all treatments including controls were equally exposed to this septum in the lid. In addition, empty 3 mL control Exetainers were prepared in triplicates for each timepoint to investigate the effect of a smaller sample volume. At the start of the experiment, all samples were flushed with a reference gas for at least 5 min at high flow (> 1 L min^{-1}) with pressure regulated to 1.8 bar at closure. The reference gas consisted of pre-calibrated industrial-grade pressurized air with mixing ratios of 0.568 ppm H_2, 0.665 ppm CO and 1.96 ppm CH_4. Samples were stored in the dark and measured 5 times over the course of 9 days; samples were measured repeatedly, except for 3 mL control Exetainers which were discarded after measurements due to insufficient volume for repeated sampling. Measurements of H_2, CO and CH_4 were performed on a VICI TGA 6k equipped with an autosampler and a sample-injection loop of 1 mL, using a pulse-discharge helium ionisation detector as described earlier (Islam et al., 2019). The detection limits for the three gases were 61 ppb for H_2, 10 ppb for CO and 170 ppb for CH_4 as determined by replicate samples (n=7) of zero-grade air zero (BOC Australia, North Ryde NSW, Australia).

80 **Table 1: Treatments for testing rubber materials for H$_2$ and CO release. The control treatments consisted of empty Exetainers; the other treatments contained the listed amount of material, excluding the approximately 0.6 g of pre-treated Exetainer septa used for sealing all treatments and controls.**

Treatment	Type	Product	Supplier	Pre-treatment	Mass (g)	Residual volume (mL)
Con	Control			NaOH	(0.6)	12
Con3		Exetainer septum chlorobutyl	Labco [a]	NaOH	(0.6)	3
UT2				Untreated	2	10
UT4				Untreated	4	8
Tex	Butyl septum			NaOH	2	10
Tgr		Grey chlorobutyl	Sigma-Aldrich [b]	NaOH	2	10
Tbl		Black non-halogenated	Rubber BV [c]	Washing + autoclave	2	10
SPA		Parfix All-Purpose			2	10
SPB	Silicone sealant	Parfix Bathroom	Selleys [d]	Curing for 3 weeks	2	10
SSW		Selleys Wet Area			2	10
FKM	O-ring	Viton™	RS Pro [e]	Untreated	2	10
NBR		Nitrile		Untreated	2	10

[a] Labco Limited, Lampeter, Ceredigion, SA48 7HH United Kingdom
[b] Rubber BV, 1211 JG Hilversum, Netherlands
[c] Sigma-Aldrich Pty Ltd (A Subsidiary of Merck), Macquarie Park, NSW 2113. Australia
[d] Selleys, a division of DuluxGroup (Australia) Pty Ltd, Clayton VIC 3168, Australia
[e] RS Components Pty Ltd, Smithfield. NSW. 2164, Australia

2.2 Exetainer modifications

85 Based on the materials test, two simple modifications of Exetainers (silicone-sealed Exetainers, SEs) are proposed to minimise contamination of gas samples containing H$_2$ and CO at trace levels. The modifications consist of i) a small, permanent plug of silicone sealant that can be pierced with needles during short-term sample handling, but minimises contamination during long-term storage; and ii) a stainless-steel bolt and Viton (FKM) O-ring instead of a butyl septum to provide a long-term seal blocking diffusive gas exchange. Selleys Wet Area silicone sealant was used to fill the inside top 5 – 10 mm of the Exetainer

90 glass vials (Fig. 1a and 1b). The sealant was administered with a 10 mL plastic syringe for finer handling. First, a thin layer was applied to close the bottom end of the plug, then the plug was filled upwards, to avoid slow expulsion of sealant due to overpressure in the Exetainer. A surplus of about the same amount of sealant was administered at the top to account for potential contraction during curing (Fig. 1c). After curing for 1 – 2 weeks, the surplus was cut at the rim of the glass thread

with a scalpel, while also scraping off any residual silicone from the rim. Newly prepared SEs were then flushed with high-purity N_2 at slight overpressure and placed in a vacuum chamber for 2 weeks to extract residual gases entrapped in the silicone. However, this vacuum step is not strictly necessary, as good results were also achieved with silicone Exetainers flushed with N_2 and left in ambient air for several weeks.

Well-prepared SEs should be gas-tight in the short term (minutes to hours) and hold overpressure for several days or weeks. However, gas diffusion through silicone is rapid compared to butyl rubber (Bhide and Stern, 1991; Van Amerongen, 1946), thus SEs require a second seal for long-term storage. For this purpose, commercially available buttonhead stainless-steel bolts (M6 x 10 mm, grade 304) were inserted into empty Exetainer plastic lids, and a Viton O-ring (9.25 mm ID, 12.7 mm OD) was added to seal the bolt against the Exetainer glass rim (Fig. 1d). In principle, any disk of an impermeable and inert material fitting into the Exetainer cap may serve as secondary diffusion barrier. In our case, using commercial M6 bolts was the most inexpensive and most readily available option, with the rounded buttonhead having the additional benefit of reducing the air cavity between bolt and silicone plug. For sample access or analysis, the bolt and O-ring can simply be removed, with the pierceable silicone plug containing the sample. For analysis times of several hours, e.g. when using an autosampler, SEs can be closed with a conventional treated septum to minimise diffusive exchange.
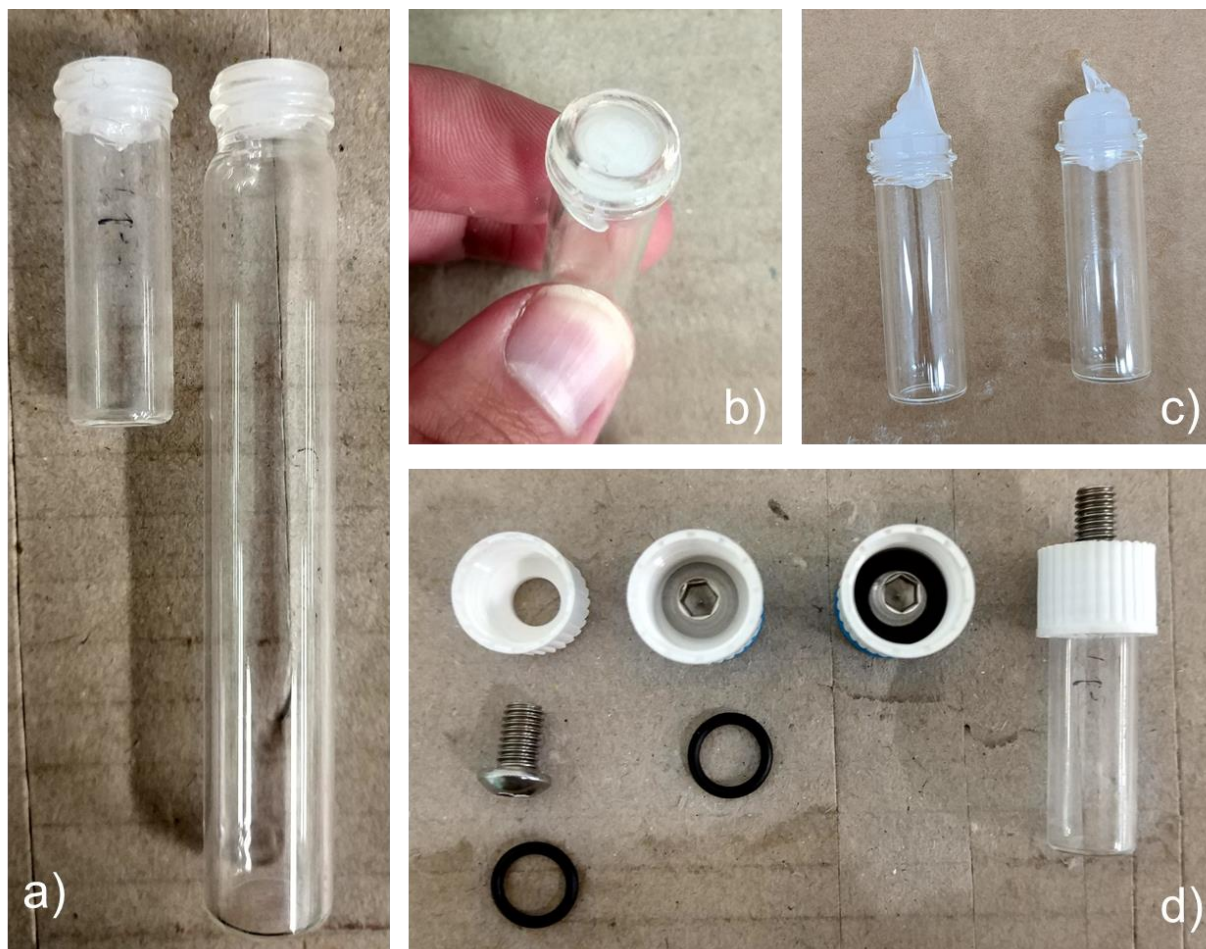
Fig. 1: Simple and inexpensive modification of Exetainers for minimising contamination of gas samples with H₂ and CO at trace levels. a and b) Finished silicone-sealed Exetainers (SEs); c) SE after curing, before cutting the excess; d) replacing the septum with a stainless steel bolt and O-ring for long-term storage.

2.3 Long-term storage test of silicone-sealed Exetainers

Long-term storage tests were conducted with 3 mL and 12 mL SEs containing different reference gases, to test sample stability and tightness of SEs. Quadruplicate SEs of both volumes were prepared for each of the 5 timepoints by flushing with either pre-calibrated pressurised air (0.643 ppm H_2 and 1.99 ppm CH_4; CO not detected) to test for gas release from materials, or a calibration gas (10.2 ppm H_2, 9.90 ppm CO and 10.1 ppm CH_4) to test for tightness of the seal. The SEs were prepared eight months prior to flushing and set to 1.8 bar final pressure. For comparison, a batch of 12 mL SEs was left uncapped and flushed with calibration gas, and a batch of 12 mL conventional Exetainers was capped with NaOH treated septa and flushed with pressurised air. All samples were stored in the dark, and analysed alongside the reference gases after 3, 10, 30, 60 and 92 days of storage.

3 Results

3.1 Hydrogen and carbon monoxide release from rubber materials

A short-term storage test using pre-calibrated pressurised air as reference gas was conducted with various sealing rubbers. All tested rubber materials released H_2 and CO during short storage times of a few hours or days, with significant differences between materials (Figs. 2 and 3; Table S1). Untreated Exetainer septa released the highest amounts of both H_2 and CO; control-corrected mean mixing ratios in 12 mL exetainers reached 16 ppm and 33 ppm from 2 g of material after 9 days (UT2, Fig. 2). This was 30 and 50 times higher than the initial reference gas, and close to 20 times higher than empty control Exetainers. The increase was linear and roughly proportional to mass, with double the material (4 g) approximately doubling the mixing ratios of H_2 and CO (UT4, Fig. 2). Rates of H_2 and CO release where thus nearly identical for UT2 and UT4 treatments when normalised to mass (Fig. 3).

Treated materials performed significantly better. Boiling Exetainer septa with 0.1 M NaOH reduced H_2 and CO release by a factor of 4 (Tex; Fig. 2); however, corrected mixing ratios still reached 3 ppm and 8 ppm at the end of the experiment, with an increase of 3 pmol H_2 and 10 pmol CO every h per g material (Fig. 3). Empty control Exetainers of 12 mL volume closed with a treated septum showed mean H_2 and CO mixing ratios of 0.89 ppm and 1.4 ppm after 9 days, 1.6 and 2.1 times higher than initial mixing ratios in air. Smaller 3 mL Exetainers showed an even higher contamination with 1.4 ppm H_2 and 1.7 ppm CO after 7 days.

Grey crimp-cap stoppers treated in the same way performed slightly better, with little H_2 release and lower CO release than treated Exetainer septa (Tgr, Figs. 2 and 3). Washed and autoclaved black crimp-cap stoppers were comparable to grey stoppers for CO, but released slightly more H_2 (Tbl; Figs. 2 and 3). Untreated O-ring materials performed better than all butyl rubbers; Viton O-rings showed lower H_2 and CO release, and nitrile O-rings lower H_2 release than butyl rubbers (FKM and NBR; Figs. 2 and 3). Silicone sealants showed the lowest potential for H_2 and CO release (SPA, SPB and SSW; Fig. 2), with SSW performing best. Interestingly, H_2 and CO release rates were similar for both gases for silicones, while nearly twice as high for CO than H_2 for all butyl and O-ring rubbers (Figs. 2 and 3).

None of the tested rubber materials caused increasing CH_4 mixing ratios (Fig. 2), except Viton O-rings with a small release of approximately 0.3 pmol g^{-1} h^{-1} (Fig. 3). Most treatments showed similar CH_4 mixing ratios than controls, which occasionally led to negative mixing ratios when corrected (Fig. 2).
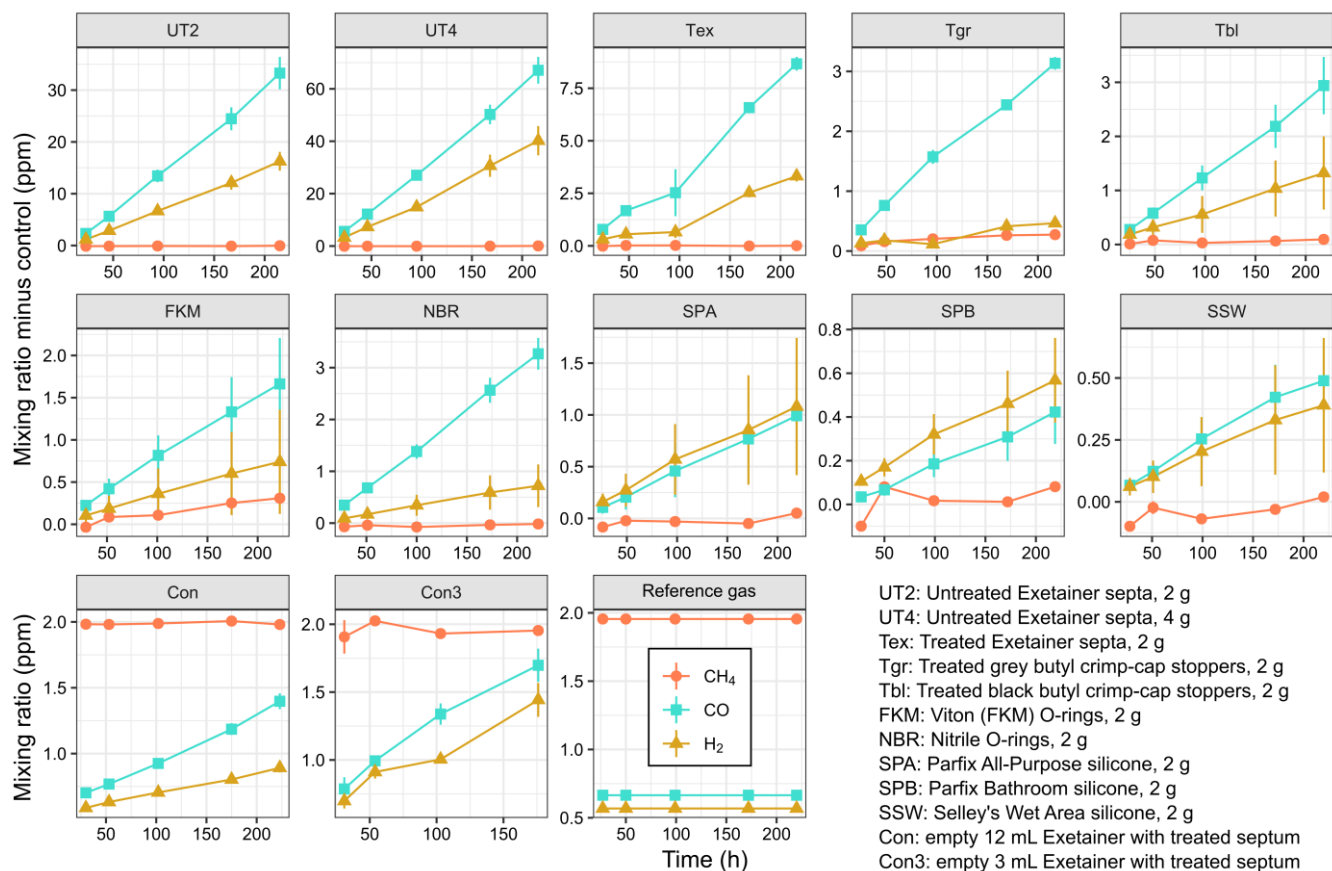
Fig. 2: Hydrogen (H₂), carbon monoxide (CO) and methane (CH₄) release from various sealing rubbers, corrected for release in empty control vials. Replicate samples (n=4) of 2 g or 4 g of rubber material were prepared in 12 mL Exetainers sealed with a treated Exetainer septum, and flushed with pressurised air as reference gas. Controls consisted of empty Exetainers (n=6) sealed with a treated Exetainer septum. Samples were measured repeatedly except for Con3 samples where n=3 replicates were sacrificed for each measurement, due to low gas volume. Please note the different scales of the y-axes.

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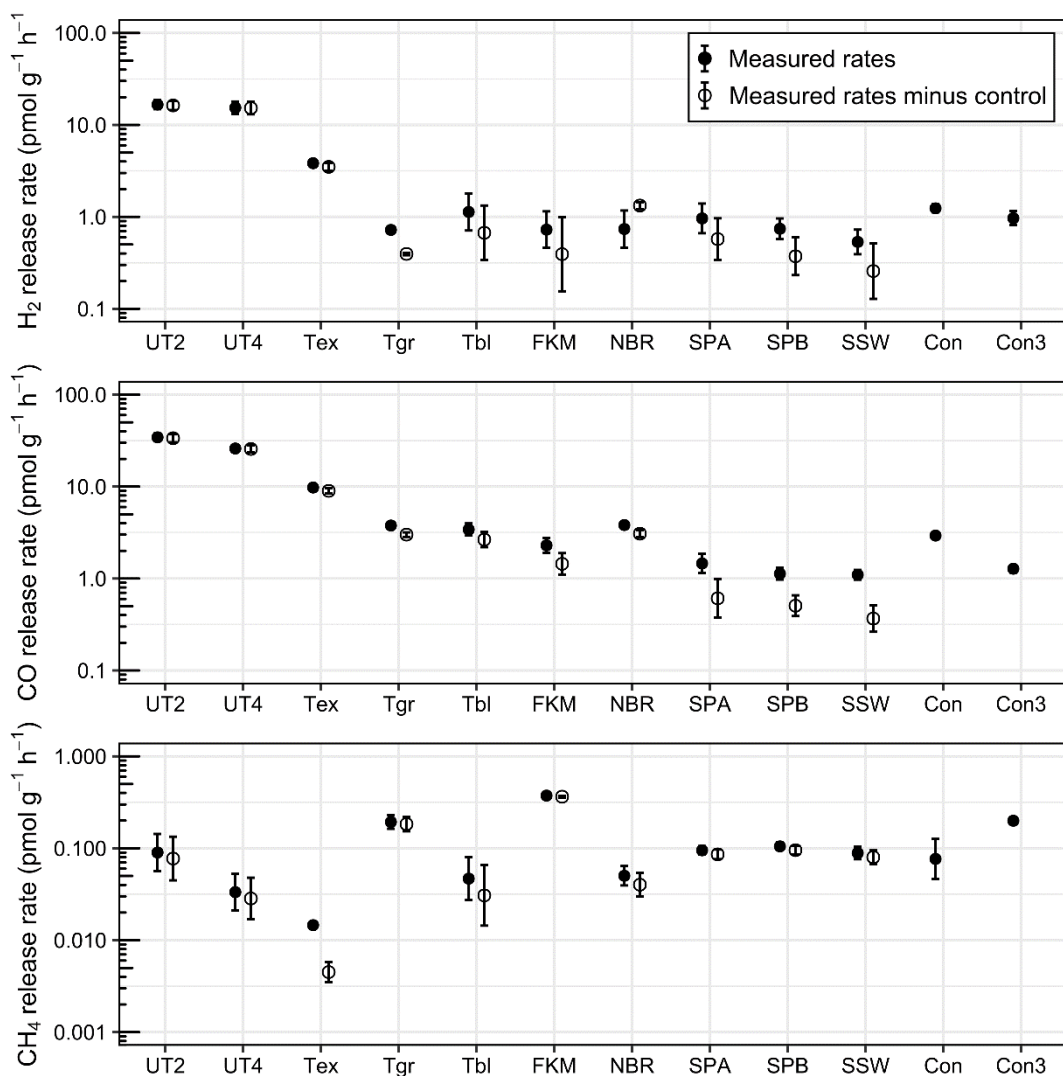


Fig. 3: Rates of trace gas release from various rubber materials in 3 mL (Con3) and 12 mL (all other treatments) Exetainers, normalised to mass. Please refer to Fig. 2 for treatments legend.

3.2 Stability of trace gas samples in silicone-sealed Exetainers

Gas samples of two reference gases (pressurised air and a 10 ppm calibration mix) were stored up to three months in Exetainers with different seals, and compared against fresh reference gas (Fig. 4 and Fig. S1). Conventional 12 mL Exetainers with treated septa showed a significant increase in H_2 and CO mixing ratios during storage of pressurised air, with deviations from fresh gas larger than 5 % after 3 days of storage (Fig. 4); CH_4 mixing ratios were within 5 % of fresh gas for at least 30 days, and slightly higher afterwards. In contrast, pressurised air stored in 12 mL SEs sealed with a stainless steel bolt remained stable (deviation < 5 %) for more than 60 days for both CH_4 and H_2. Mixing ratios of CO increased from below detection limit (~70

ppb) to 0.18 ppm in 3 days and around 0.6 ppm in 92 days of storage; however, the rate of increase was approximately linear and nearly an order of magnitude lower compared to conventional Exetainers (Fig. S1). The 10 ppm calibration gas remained

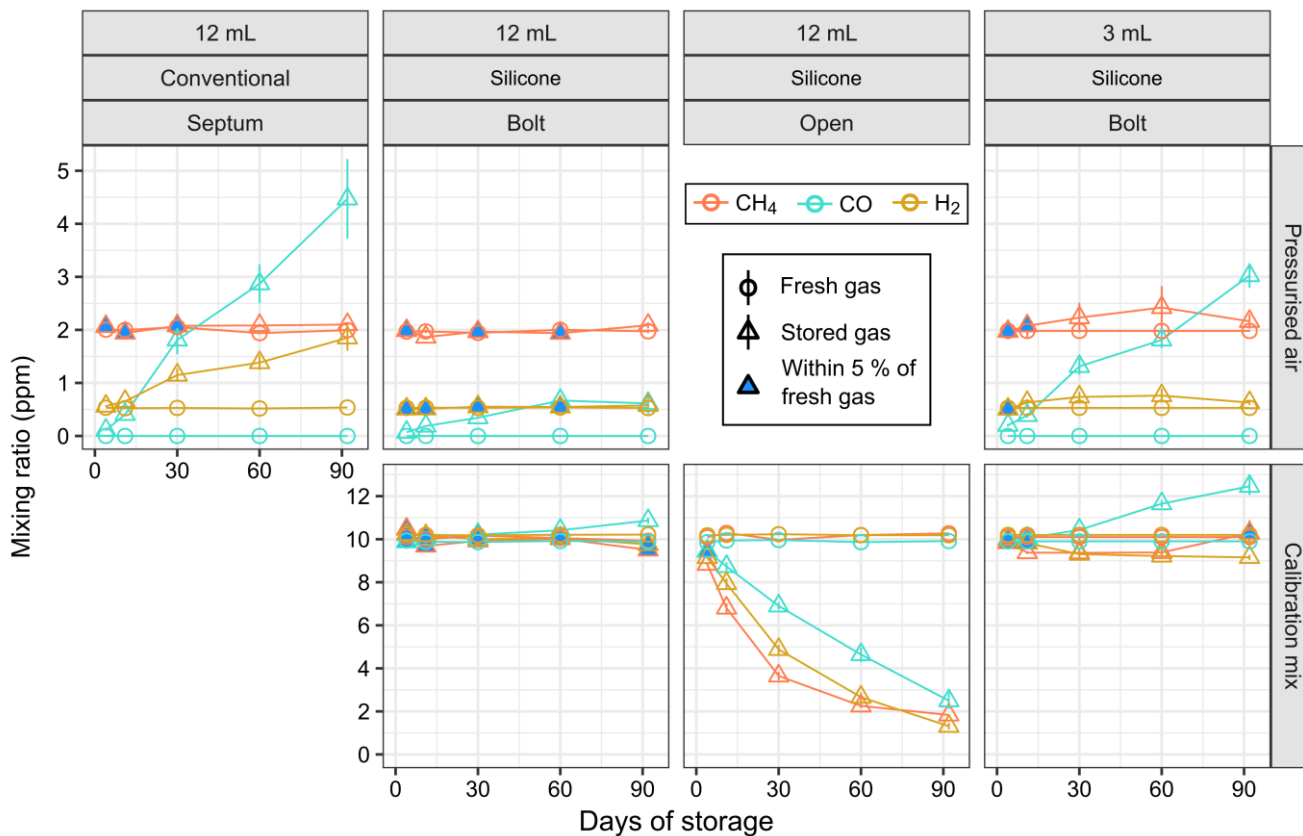
165   stable in bolt-sealed 12 mL SEs for all three gases for at least 60 days, and deviations were less than 10 % after 92 days of storage (Fig. 4). The smaller 3mL SEs showed higher variability in both fresh and stored gases, with CH_4 and H_2 stable for up to 10 days (Fig. 4). Both CH_4 and H_2 mixing ratios increased with storage in pressurised air, and decreased in the calibration mixture; for CO we observed a clear increase in both reference gases. We also tested the calibration mix in SEs with the silicone left open to lab air, and observed the expected exponential decrease for all three gases as they equilibrated with air.

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Fig 4: Measured mixing ratio of reference gases (pressurised air and calibration mix) freshly flushed from cylinder, versus stored for up to three months in Exetainers with different seals. Error bars indicate standard error of the mean. The blue fill indicates the difference between freshly flushed and stored gas is within 5 % of fresh gas. Note that CO was not detected in fresh pressurised air, and the mixing ratio is plotted as zero.

175   **4 Discussion**

Our results clearly demonstrate that commercially available gas-sample vials sealed with butyl rubber are not suited for the storage of gas samples with trace levels of H_2 and CO. Among tested rubber materials, butyl rubbers exhibited the highest rates of H_2 and particularly CO release, regardless of any pre-treatment. Untreated Exetainer septa performed particularly

poorly; measured rates indicate that mixing ratios of H_2 and CO in air samples stored in conventional 12 mL Exetainers could essentially double and quadruple every 24h. Treatment of septa with NaOH greatly reduced potential contamination, but mixing ratios in air samples could still double approximately every two weeks for H_2 and every week for CO. The level of contamination was proportional to the volume of the vial and the mass of rubber (a proxy for the specific surface area in contact with the enclosed gas phase); therefore, form factor and volume of vials have to be considered. For example, serum vials with an increased volume of >100 mL and thus lower exposed surface area relative to volume may still be suitable for gas storage or incubation experiments lasting a few weeks, if treated stoppers are used (Islam et al., 2019, 2020; Kessler et al., 2019).

Viton and nitrile rubbers performed much better than butyl septa for H_2, though CO release was still substantial. In principle, butyl septa could be replaced with Viton or nitrile; some commercial products are available for crimp-cap vials and may be an alternative for laboratories with an existing stock of such vials. We have not tested septa made from these materials however, and tightness, possible treatments and resistance to multiple piercings will need to be evaluated alongside potential contamination. Particularly for CO, Viton and nitrile may not be much better than treated butyl rubber.

Silicone sealants showed the lowest potential for H_2 and CO release. Assuming a second barrier to control diffusion (discussed below) and a typical septum weight of 0.5 g, contamination after one month of storage would theoretically accumulate to 0.1 ppm H_2 and 0.2 ppm CO in vials sealed with silicone. For H_2, this is close to the contamination introduced by piercing the septum with a needle, which inevitably introduces a small amount of ambient air (Lin et al., 2012). Such a rate can be acceptable for many projects, particularly when investigating relative changes. In addition, our selection of silicone sealants was based on local availability and thus rather limited. Although all three products performed reasonably well, there may be better or worse among the multitude of commercially available silicone-based sealants. We thus strongly recommend to test some locally available products for gas release before preparing SEs.

Specific mechanisms for H_2 and CO release from different rubbers have not been investigated here. We can however highlight some common patterns among the different rubbers tested. First, a near-linear increase in H_2 and CO in all rubber materials, regardless of pre-treatment and mixing ratio, indicates a zero-order reaction and thus points towards degradation of material as underlying cause, rather than release of entrapped or dissolved gas. Entrapped or dissolved gases would slowly equilibrate with the gas phase, thus rates would show an inverse correlation with mixing ratios. Silicones showed slightly reduced rates towards the end of the release experiment (Fig. 2), but the trend was weak. We cannot exclude the possibility of entrapped or dissolved gases at higher concentrations in the materials, but this appears less realistic when considering negligible release of CH_4. Chemical degradation of rubbers can occur via multiple and complex reactions and strongly depend on its composition and polymer structure (Dubey et al., 1995). Likely, silicones degrade differently to butyl and O-ring rubbers, as indicated by the ratio of H_2 to CO release of 1:1 for silicones and at least 1:2 for other rubbers. Temperature may also play an important role for any degradation reaction, and thus merits further investigations for potentially reducing contamination. Regardless of the cause of H_2 and CO release however, among the rubbers tested here, only silicones and possibly Viton seem to be suitable for storing small gas samples with H_2 and CO at trace levels for longer than a few days.

Our modified SEs with a stainless steel bolt and O-ring as secondary diffusion barrier provided stable storage under ambient temperatures for gas samples with H_2 and CH_4 at ambient levels, and with all three gases at elevated levels, for up to two months (Fig. 4). The SEs thus allow long-term storage of small volumes of trace-level H_2 samples, and extend reliable storage

215   times for CH_4 samples by one month compared to conventional Exetainers (Faust and Liebig, 2018). There was still significant contamination of gas samples with CO at ambient levels, likely released from the silicone plug. Yet, the increase was nine times lower than in conventional Exetainers with treated septa. Most importantly, the increase appeared to be linear, and thus offers the potential to correct for this bias by storing a reference gas alongside the samples (Laughlin and Stevens, 2003). The 3 mL SEs were stable for 3 to 10 days for H_2 and CH_4, and showed deviations thereafter. Yet, for these gases mixing ratios

220   stabilised within 10 to 30 days to a slightly higher level with pressurised air, and a slightly lower level with calibration mix. We suspect this to be a result of equilibrium partitioning between silicone and gas phase, which is much more pronounced in the 3 mL vials with a higher silicone-gas ratio. This may lead to a "memory" effect when gases from previous samples can partition into the silicone, then back into the gas phase in the new sample. In our case, 3 mL SEs were stored in lab air with slightly higher H_2 and CH_4 mixing ratios than pressurised air, and lower mixing ratios than the calibration mix. Therefore,

225   partitioning between gas and silicone could explain the observed pattern in 3 mL SEs, but seemed largely negligible in 12 mL SEs. To minimise this effect, we suggest purging SEs with high-purity N_2 after measurement, and storing them in an atmosphere of known composition, ideally similar to future samples.

Surprisingly, mixing ratios of H_2 were much less affected than CO during storage in SEs, unlike in emission experiments where silicones showed similar rates of H_2 and CO release (Fig. 2 and 3). However, we also observed high variability in H_2

230   emissions from silicones, with some replicates showing H_2 increase comparable to CH_4, others to CO. We suspect this was an effect of heterogeneous curing of the large silicone plugs we prepared for the emission experiment, which cured for three weeks before cutting to smaller pieces. In contrast, the SEs used in the long-term storage test were made 8 months prior to the test and were fully cured. We therefore speculate that silicones emit H_2 only during curing, while CO appears to be released by a degradation reaction at a consistent rate.

235   We have now employed 12 mL SEs for several projects in terrestrial and marine environments with 400 to 600 samples and storage times of up to one month. Once prepared, SEs could be pierced numerous times without compromising tightness, while stainless steel bolts, O-rings and Exetainer plastic caps have been repeatedly used without any signs of degradation. We have not observed any corrosion of bolts in marine applications, as SEs were kept dry and separate from water samples at all times. However, for certain applications where contact with seawater is inevitable, we recommend marine-grade stainless steel, or to

240   use nylon bolts (after testing for H_2 and CO release). Overall, the proposed system is simple to implement, inexpensive, adaptable, robust and reliable, and can be integrated in many existing sampling and processing pipelines.

Author contributions

PAN, EC and PLMC designed the experiments, and PAN, EC and TJ carried them out. CG and PLMC provided logistical and technical support. PAN prepared the manuscript with contributions from all co-authors.

Data availiability

All data can be made available by the authors upon request.

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Competing interests

The authors declare that they have no conflicts of interest.

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