

## Response to reviewers

**The authors would like to thank both reviewers for their expert assessment of our manuscript. We have now duly addressed all comments and suggestions to the best of our knowledge. Please find our answers to reviewers' requests below in bold, with page and line numbers referring to the revised manuscript.**

### Anonymous Referee #1

Received and published: 15 October 2020

#### I) General comments

This technical note conveys a solution for field surveys of trace gas fluxes in remote locations requiring the collection of discrete gas samples that are stored for subsequent laboratory analyses. For H<sub>2</sub> and CO in particular, the storage of small volume gas samples in glass vials is impeded by H<sub>2</sub> and CO emissions from butyl rubber septum fitted to caps.

In a first series of experiments, the authors have carefully tested H<sub>2</sub>, CO and CH<sub>4</sub> emissions from different materials and conditioning protocols. Replacement of conventional butyl rubber septum by silicone plug was proven the most efficient approach to reduce background contamination of H<sub>2</sub> and CO. A second experiment has been undertaken to demonstrate performance for long-term (92 days) storage of gas mixtures in modified vials. Stored gas diffusion through silicone was substantially reduced by replacing septum of screwed caps by a stainless-steel bolt and gasket.

Experiments were well conceived, including relevant controls and adequate number of repetitions.

**We thank the reviewer for their positive general assessment of our work. We agree that among the many potential applications, modified Exetainers may be particularly useful for measuring trace-gas fluxes in remote locations.**

#### II) Specific comments

- Comparison of H<sub>2</sub>, CO and CH<sub>4</sub> emission rates reported in Figure 2 should be supported by statistical analyses.

**Thank you for this helpful suggestion. We have conducted a linear regression analysis to compare the slopes of each gas and treatment to the control and reference gas. Results are summarised in a new Table S1 in the supporting information.**

- Slope integrating concentration times series in vials presented in figure S1 should be accompanied with standard error to explicitly show variability of reduction or enhancement of trace gas concentration during long-term storage.

**We agree with the reviewer. The respective standard errors of the regression slope have now been added to Fig. S1.**

- I wonder whether stainless-steel should be replaced with nylon bolt in applications involving survey of marine environments (sea brines cause H<sub>2</sub> emissions originating from metal corrosion).

**This is an excellent suggestion, which we have incorporated in the revised manuscript on p12 l237-240. In our specific application of SEs in marine environments, stainless steel was suitable as gas samples could be kept dry and separate from water samples, but this may not always be possible.**

III) Technical corrections

- L91: References are missing.

**Thank you for pointing this out, the missing references have now been included (p5, l99).**

- L221-223: No data is available to support the statement – better to remove the sentence.

**We agree with the reviewer and have removed the statement in question.**

## Anonymous Referee #2

Received and published: 10 November 2020

This is a valuable piece of work, well suited for a technical report. The authors produce and test a modified version of commercial Exetainer, that will be useful for many scientists taking gas samples in the field.

H<sub>2</sub> and CO are sometimes difficult to preserve in gas samples stored in common containers. Two main processes can modify the mole fraction of H<sub>2</sub> and CO: emission from materials in contact with gas (e.g. container walls or septa), and diffusion through container wall or seal. This paper presents a modification of commercial Exetainers in which both these processes are minimized, resulting in an improved gas stability performance.

The paper is well written and to the point. I have only few minor comments as listed below.

**We thank the reviewer for the positive assessment, and are grateful for the detailed and thorough comments listed below, which will greatly improve the manuscript.**

### General comments

- from line 36: The authors compare the convenience of large glass flasks with the small glass vials, but we should be aware that these are used by partly different communities with different requirements. The (1-L and larger) glass flasks are widely used in the atmospheric science community (e.g. NOAA), where often a large air sample is needed. The stability requirements are also much stricter - there, a change in the mole fraction of e.g. CH<sub>4</sub> of 2 ppb (0.1%) over several months is already not acceptable (see for examples the WMO compatibility goals - the sample stability should fit well within these limits) (Table 1 in WMO, 2018). The modified Exetainers are useful in situations where signals are large thus precision requirements are more relaxed. Stating this more clearly would be useful.

**We thank the reviewer for highlighting these important points, which we have now included in the revised manuscript on p2 138-48:**

**“...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...”**

**“... Although these systems represent the ‘gold standard’ for gas-sample storage, they have two major disadvantages: ...”**

**“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 (...) are widely used containers to store trace-gas samples.**

**We fully agree that for certain applications such as atmospheric monitoring there are much stricter requirements which SEs cannot meet. Our SEs are meant to complement, rather than compete against, established and proven gas-sample storage systems customary in certain research fields with stricter criteria.**

- some materials emit CO under light. How were the samples stored, in light or dark? Please specify in the method section.

**All samples were stored in the dark between measurements, and the respective method sections have been amended.**

- a short discussion of possible phenomena, and on why these materials were chosen (SS to minimize diffusion through the cap, silicone to minimize the emissions ) may be useful for other scientists trying to make similar experiments for other containers or other gases.

**We appreciate the reviewers suggestion for an additional discussion paragraph on “possible phenomena” (we assume this means possible degradation mechanisms of the various rubber materials), and the choice of materials. However, we do not have sufficient data on the specific composition of the rubbers to speculate on potential degradation pathways leading to H<sub>2</sub> or CO emissions. We also think this would extend far beyond the purpose of this technical note.**

**We have now better emphasised the reasoning behind the choice of materials for the SEs throughout the manuscript (see below), and provided suggestions for some alternative materials. We hope this will satisfy what we believe was the essence of the reviewer’s request, to provide better guidance for scientists wanting to prepare and adapt SEs for their own use.**

**p1 l17-18: “...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.”**

**p11 l195-198: “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.”**

**p12 l212: “...stainless steel bolt and O-ring as secondary diffusion barrier provided stable storage...”**

Specific comments

- line 23: compared to many other gases in atmosphere, CO and H<sub>2</sub> are actually not “highly reactive”, as they have lifetimes of several months and 2 years resp. I suggest removing these words.

**We agree with the reviewer, the respective words have been removed.**

- lines 36 - 39: glass flask are widely used for atmospheric samples for mole fraction measurements as well, see also general comment

**Thank you, this has been amended according to the suggestions above.**

- line 63: the materials were washed and treated, which I assume passivate the surface, but then they were cut into pieces. Does this not counteract the passivation, since it exposes fresh emission surfaces?

**We agree with the reviewer that cutting was not ideal for the treated materials Tex, Tgr and Tbl. This was however a necessary step to be able to use an autosampler and 12 mL Exetainers for repeated, controlled measurements of the same sample. It also appears that the number of cuts was of minor importance compared to the source/brand of septum. For example Tgr and Tex were both treated grey chlorobutyl rubbers, with Tex cut once and Tgr several times, but the latter showed lower H<sub>2</sub> and CO release. Given the relatively poor performance of treated butyl stoppers in general, we believe the small uncertainty introduced by the cutting is justifiable.**

- line 80: consider adding the info that the silicone purpose is to keep emissions inside container low

**Thank you for this valuable suggestion, we have now included this information in the following sentence (p4 l87-88):**

**“...short-term sample handling, but minimises contamination during long-term storage; and ii) ...**

- lines 79-81: consider stating that the silicone and oring were chosen as the best options based on the tests at 2.1? Also, mention the type of oring, and whether it was tested in the previous experiment

**Thank you, we have now included a brief reference to the materials test at the beginning of the paragraph (p4 l85):**

**“Based on the materials test, two simple modifications of Exetainers...”**

- line 92: why did the authors use bolts, and not e.g. a simple round piece of stainless steel?

**A valid question and likely of general interest; we have thus included this information in the revised manuscript on p5 l102-105:**

**“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.”**

- lines 182 – 183: unclear, the 0.2 ppm increase in CO cannot be equal to the contamination with a small amount of ambient air as introduced by a needle, since the ambient air is normally around 0.1 to 0.2 ppm.

**We thank the reviewer for pointing this out. The comparison with contamination from piercing was referring to H<sub>2</sub> only. The text has now been amended accordingly (p11 l193):**

**“For H<sub>2</sub>, this is close to the contamination introduced by ...”**

- lines 188 – 189: the indication of an underlying zero order reaction is interesting, maybe important enough to mention in the abstract? Also, such a zero order (degradation) reaction may be temperature and light dependent – does this suggest that exetainers stored in cold and dark will be more stable?

**We thank the reviewer for emphasising our observation of a zero-order degradation reaction, which we have now incorporated in a sentence in the abstract (p1 l14-15):**

**“All tested materials showed a near-linear increase in H<sub>2</sub> and CO mixing ratios, indicating a zero-order reaction and material degradation as the underlying cause.”**

**As for light dependency, we believe gas samples are routinely stored in the dark, and not much improvement could be gained from further tests. Temperature on the other hand may indeed play an important role for potentially minimizing contamination, and samples stored at lower temperatures could be more stable. However, rubber materials could also become brittle or stiff at low temperatures, which could have adverse effects. A formal investigation of temperature effects on sample contamination was beyond the scope of this study, provided that sufficient results were achieved with SEs stored at room temperature. However, we have mentioned this aspect in the discussion (p11 l208-209) as a recommendation for further investigations.**

**“Temperature may also play an important role for any degradation reaction, and thus merits further investigations for potentially reducing contamination.”**

Technical comments

- line 56: 2.2 should be 2.1

**Thank you, this has been corrected.**

- line 91: reference(s) missing

**Thank you, the correct references have been added.**

- “concentration” usually refers to mass/volume. The units “ppm”, “ppb” normally mean mol/mol (or volume/volume), thus refer to mole fractions or mixing ratios.

**We agree with the reviewer; the terminology has now been adapted throughout the manuscript.**

- Table 1, caption: part of the text missing?

**Many thanks for highlighting this obvious omission. The missing text has now been added to the caption of Table 1:**

**“Table 1: Treatments for testing rubber materials for H<sub>2</sub> 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.”**

- Fig. 2: I suggest indicating in the figure caption that the y-axes are different

**Thank you for this suggestion, which has now been added to the caption of Fig. 2.**

- line 151: "0.18 ppb" should be "0.18 ppm"

**Thank you, this has been corrected.**

- Figure 4, caption: I think the figure does not show the relative differences (rel dif would be (stored – fresh) / fresh), but the absolute values of fresh and stored gas.

**Indeed, the figure shows measured mixing ratios. The caption has not been updated from a previous version showing relative differences. Thank you for highlighting this error, which has now been corrected:**

**"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."**

- Supplement figure: I think the "fresh" and stored" are reversed, the stored gas is the one changing.

**Thank you, this has now been corrected.**

#### References

NOAA Cooperative Air Sampling Network, <https://www.esrl.noaa.gov/gmd/ccgg/flask.html>

WMO, 2018: [https://library.wmo.int/index.php?lvl=notice\\_display&id=20698](https://library.wmo.int/index.php?lvl=notice_display&id=20698)

# 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<sub>2</sub>), carbon monoxide (CO) and methane (CH<sub>4</sub>) 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<sub>4</sub> and other greenhouse gases, no information on reliable storage is available for H<sub>2</sub> and CO. We show that vials sealed with butyl rubber stoppers are not suitable for storing H<sub>2</sub> 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<sub>2</sub> and CO ~~concentration~~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<sub>2</sub> 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<sub>2</sub> 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 ~~concentration~~mixing ratios of H<sub>2</sub> and CH<sub>4</sub> exceeding 60 days of storage at atmospheric and elevated (10 ppm) ~~concentration~~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<sub>2</sub>) 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 ~~highly reactive and thus 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<sub>2</sub> 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



30 and consumed abiotically in 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<sub>2</sub> 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~~), (~~Rothe et al., 40 2005; Thrun et al., 1979~~). ~~and They~~ are routinely 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<sub>2</sub> (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). ~~However, Although~~ these systems represent the ‘gold standard’ for gas-sample storage, they have 45 two major ~~downsides~~disadvantages: they require the collection of large sample volumes of >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~~For these reasons~~, glass vials of a few mL volume closed with butyl rubber septa (either crimp-capped or screw-capped, e.g. Exetainers®) are ~~among the most~~ widely used containers to store trace-gas samples, in various scientific fields. They are 50 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 from a reference gas) of trace gases such as methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) 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, 55 2003).

To our knowledge, storage of H<sub>2</sub> and CO at trace levels in Exetainers or crimp-cap vials have not been investigated. However, anecdotal reports of rapid sample contamination with H<sub>2</sub> 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 60 and a stainless steel bolt, and confirm the long-term stability of H<sub>2</sub>, CH<sub>4</sub> and, to a lesser extent, CO concentration mixing ratios.

## 2 Materials and Methods

### 2.2-1 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<sub>2</sub>, CO and CH<sub>4</sub> 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<sup>-1</sup>) with pressure regulated to 1.8 bar at closure. The reference gas consisted of pre-calibrated industrial-grade pressurized air with concentration mixing ratios of 0.568 ppm H<sub>2</sub>, 0.665 ppm CO and 1.96 ppm CH<sub>4</sub>. Samples were stored in the dark and then 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<sub>2</sub>, CO and CH<sub>4</sub> 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<sub>2</sub>, 10 ppb for CO and 170 ppb for CH<sub>4</sub> as determined by replicate samples (n=7) of zero-grade air zero -(BOC Australia, North Ryde NSW, Australia).

**Table 1: Treatments for testing rubber materials for H<sub>2</sub> 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	Exetainer septum	Labco <sup>a</sup>	NaOH	(0.6)	12
Con3				NaOH	(0.6)	3
UT2	Butyl septum	chlorobutyl	Sigma-Aldrich <sup>b</sup>	Untreated	2	10
UT4				Untreated	4	8
Tex					NaOH	2
Tgr		Grey chlorobutyl		NaOH	2	10
Tbl		Black non-halogenated	Rubber BV <sup>c</sup>	Washing + autoclave	2	10

SPA		Parfix All-Purpose			2	10
SPB	Silicone sealant	Parfix Bathroom	Selleys <sup>d</sup>	Curing for 3 weeks	2	10
SSW		Selleys Wet Area				
FKM	O-ring	Viton™	RS Pro <sup>e</sup>	Untreated	2	10
NBR		Nitrile		Untreated	2	10

<sup>a</sup> Labco Limited, Lampeter, Ceredigion, SA48 7HH United Kingdom

<sup>b</sup> Rubber BV, 1211 JG Hilversum, Netherlands

<sup>c</sup> Sigma-Aldrich Pty Ltd (A Subsidiary of Merck), Macquarie Park, NSW 2113. Australia

<sup>d</sup> Selleys, a division of DuluxGroup (Australia) Pty Ltd, Clayton VIC 3168, Australia

<sup>e</sup> RS Components Pty Ltd, Smithfield. NSW. 2164, Australia

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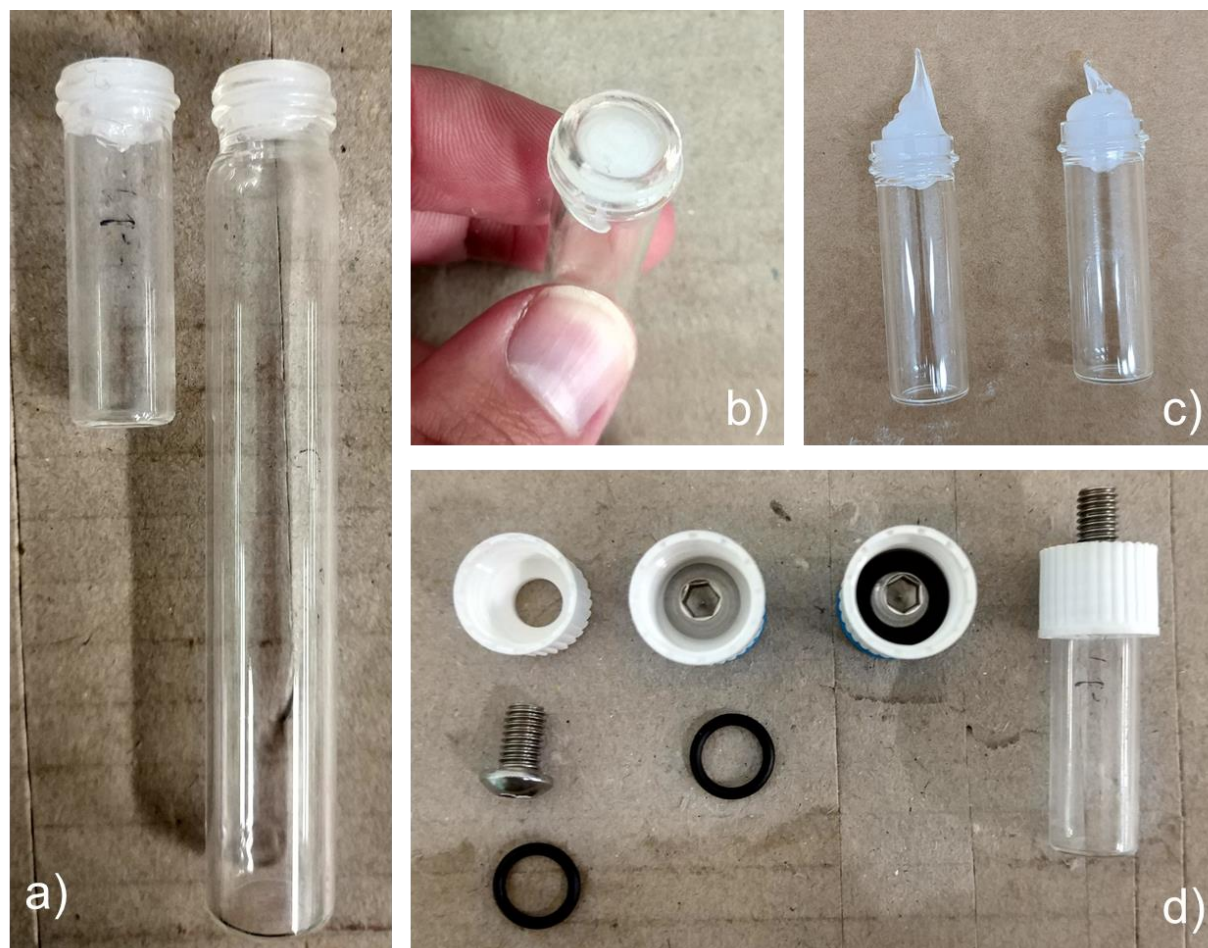
## 2.2 Exetainer modifications

Based on the materials test, two simple modifications of Exetainers (silicone-sealed Exetainers, SEs) are proposed to minimise contamination of gas samples containing H<sub>2</sub> 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 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<sub>2</sub> 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<sub>2</sub> 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)(refs), 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

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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.



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**Fig. 1: Simple and inexpensive modification of Exetainers for minimising contamination of gas samples with  $H_2$  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

115 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  
120 with calibration gas, and a batch of 12 mL conventional Exetainers was capped with NaOH treated septa and flushed with

pressurised air. ~~Samples~~ 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

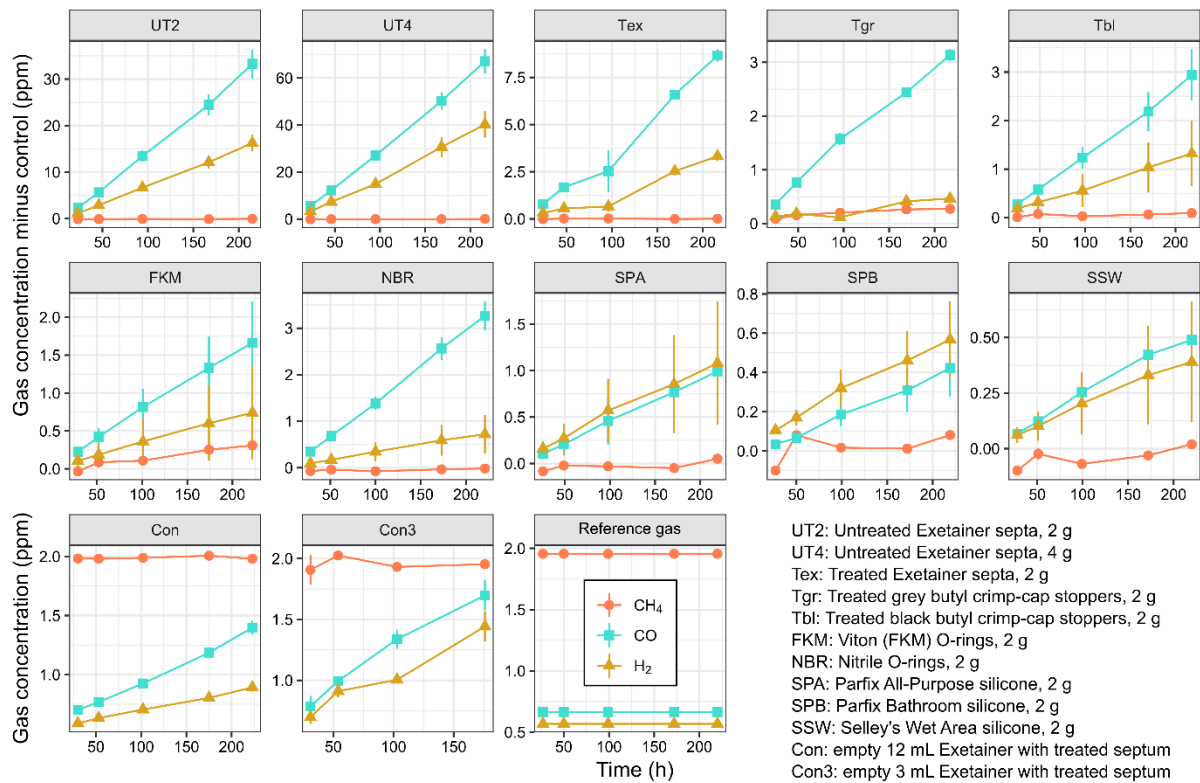
#### 3.1 Hydrogen and carbon monoxide release from rubber materials

125 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<sub>2</sub> and CO during short storage times of a few hours or days, with ~~orders of~~  
~~magnitudes significant~~ differences between materials (Figs. 2 and 3; Table S1). Untreated Exetainer septa released the highest  
amounts of both H<sub>2</sub> and CO; control-corrected mean ~~concentration~~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  
130 to 20 times higher than empty control Exetainers. The ~~concentration~~-increase was linear and roughly proportional to mass,  
with double the material (4 g) approximately doubling the ~~concentration~~mixing ratios of H<sub>2</sub> and CO (UT4, Fig. 2). Rates of H<sub>2</sub>  
and CO release were 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<sub>2</sub> and CO release by a  
factor of 4 (Tex; Fig. 2); however, corrected ~~concentration~~mixing ratios still reached 3 ppm and 8 ppm at the end of the  
135 experiment, with an increase of 3 pmol H<sub>2</sub> 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<sub>2</sub> and CO ~~concentration~~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 ~~concentrations~~. Smaller 3 mL Exetainers showed an even  
higher contamination with 1.4 ppm H<sub>2</sub> and 1.7 ppm CO after 7 days.

Grey crimp-cap stoppers treated in the same way performed slightly better, with little H<sub>2</sub> release and lower CO release than  
140 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<sub>2</sub> (Tbl; Figs. 2 and 3). Untreated O-ring materials performed better than all butyl rubbers;  
Viton O-rings showed lower H<sub>2</sub> and CO release, and nitrile O-rings lower H<sub>2</sub> release than butyl rubbers (FKM and NBR; Figs.  
2 and 3). Silicone sealants showed the lowest potential for H<sub>2</sub> and CO release (SPA, SPB and SSW; Fig. 2), with SSW  
performing best. Interestingly, H<sub>2</sub> and CO release rates were similar for both gases for silicones, while nearly twice as high for  
145 CO than H<sub>2</sub> for all butyl and O-ring rubbers (Figs. 2 and 3).

None of the tested rubber materials caused increasing CH<sub>4</sub> ~~concentration~~mixing ratios (Fig. 2), except Viton O-rings with a  
small release of approximately 0.3 pmol g<sup>-1</sup> h<sup>-1</sup> (Fig. 3). Most treatments showed similar CH<sub>4</sub> ~~concentration~~mixing ratios than  
controls, which occasionally led to negative ~~concentration~~mixing ratios when corrected (Fig. 2).



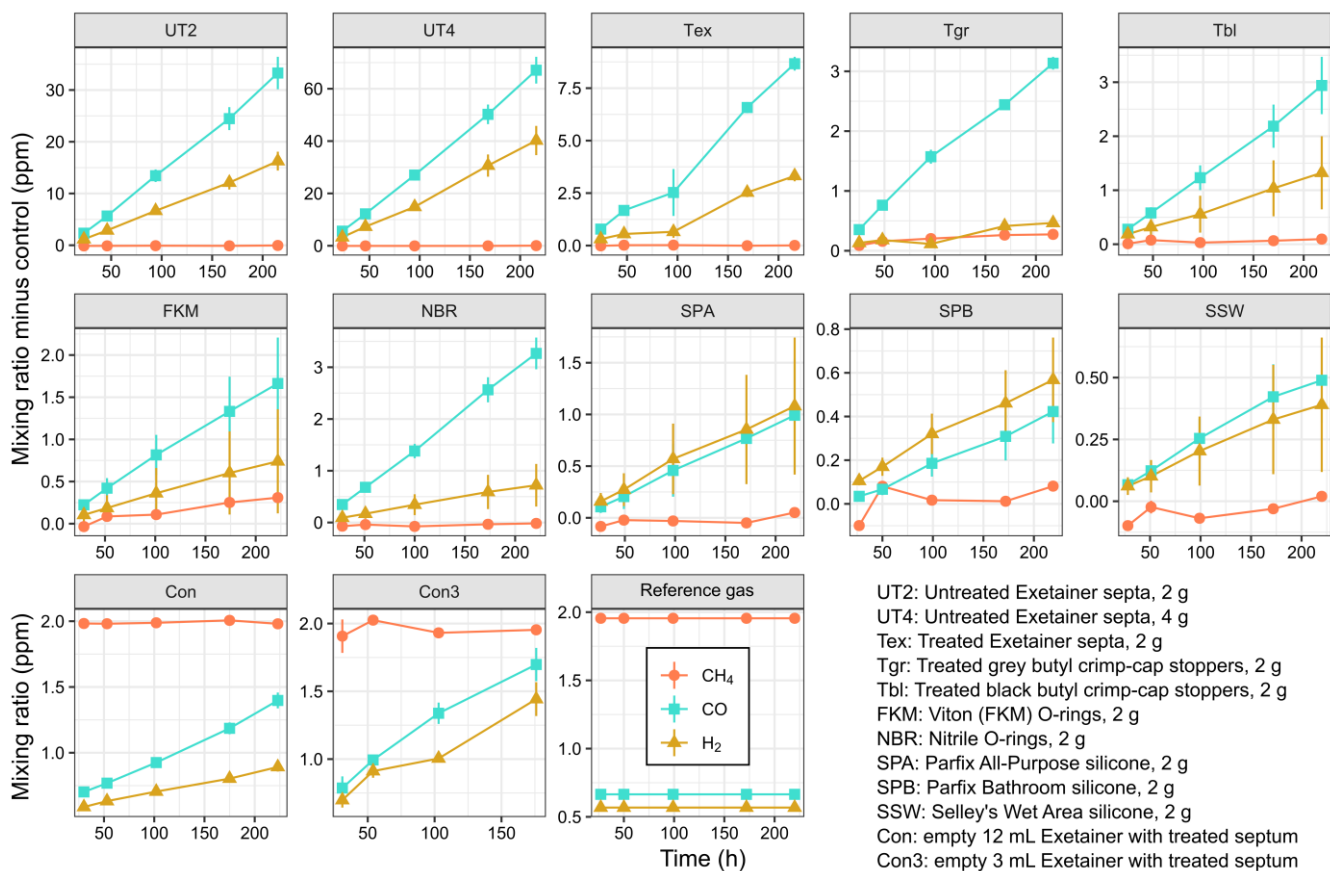


Fig. 2: Hydrogen (H<sub>2</sub>), carbon monoxide (CO) and methane (CH<sub>4</sub>) release from various sealing rubbers, corrected for release in empty control vials. Replicate samples (n=4) of 2 g or 4 g of rubber material were prepared in 12 mL Exetainers sealed with a treated Exetainer septum, and 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.**

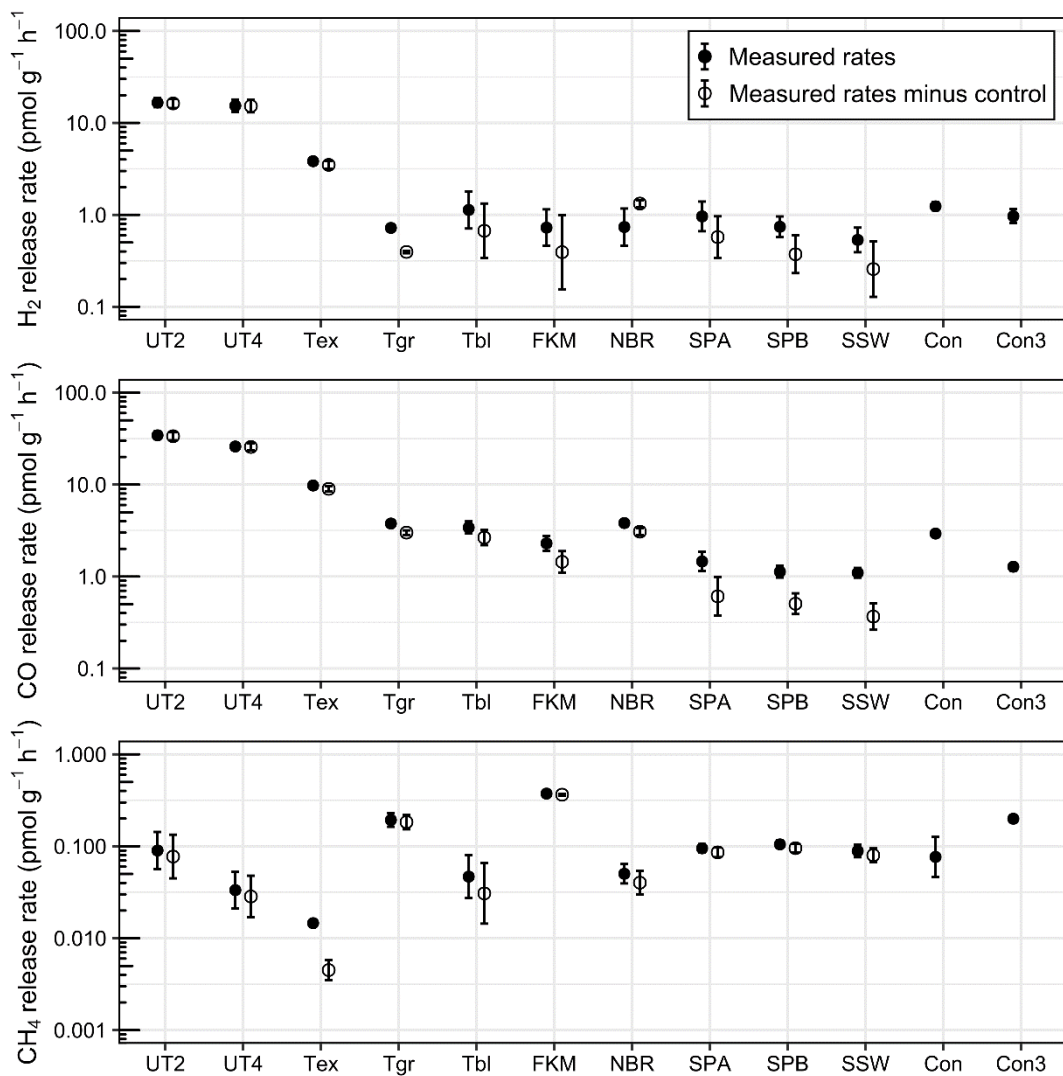


Fig. 3: Rates of trace gas release from various rubber materials in 3 mL (Con3) and 12 mL (all other treatments) Exetainers, normalised to mass. Please refer to Fig. 2 for treatments legend.

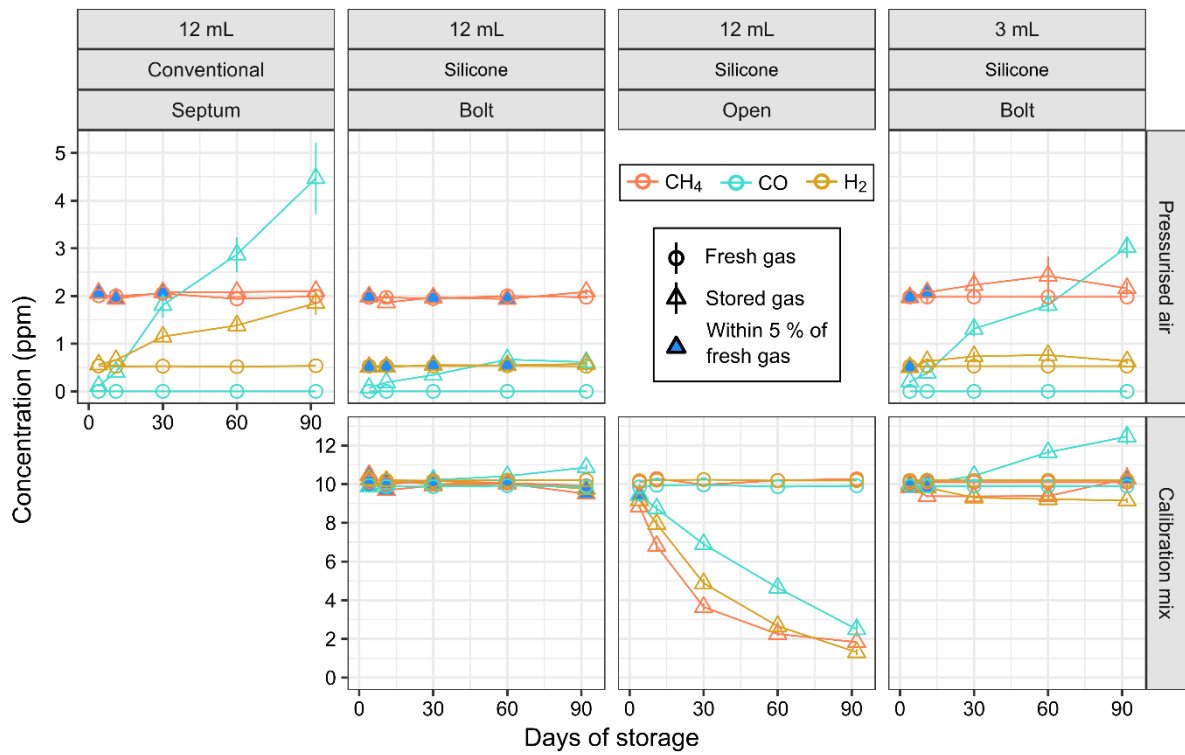
### 3.2 Stability of trace gas samples in silicone-sealed Exetainers

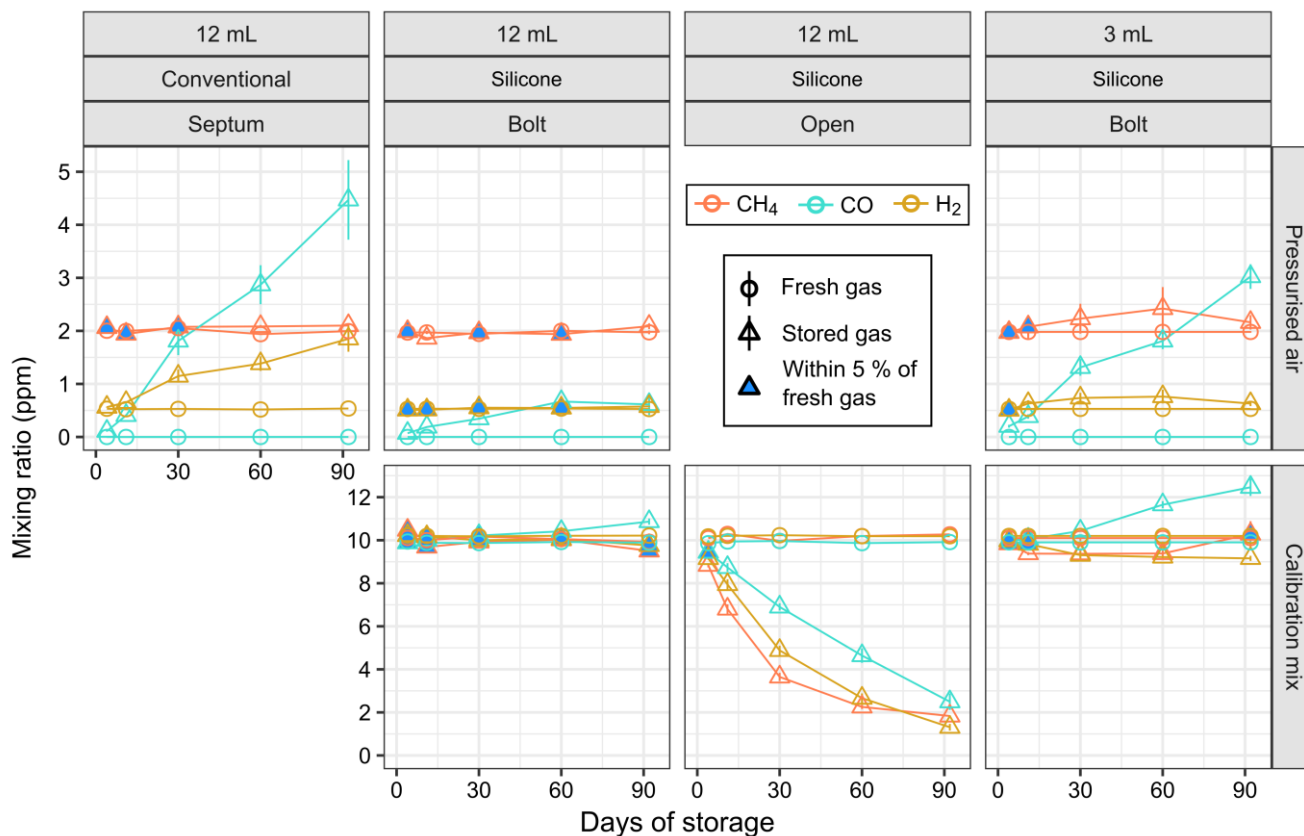
160 Gas samples of two reference gases (pressurised air and a 10 ppm calibration mix) were stored up to three months in Exetainers with different seals, and compared against fresh reference gas (Fig. 4 and Fig. S1). Conventional 12 mL Exetainers with treated septa showed a significant increase in H<sub>2</sub> and CO concentration mixing ratios during storage of pressurised air, with deviations from fresh gas larger than 5 % after 3 days of storage (Fig. 4); CH<sub>4</sub> concentration 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

165 bolt remained stable (deviation < 5 %) for more than 60 days for both CH<sub>4</sub> and H<sub>2</sub>. Concentration Mixing ratios of CO increased



from below detection limit (~70 ppb) to 0.18 ~~ppb~~-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 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<sub>4</sub> and H<sub>2</sub> stable for up to 10 days (Fig. 4). Both CH<sub>4</sub> and H<sub>2</sub> ~~concentration~~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 ~~concentrations~~they equilibrated with air.





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Fig 4: ~~Relative difference in m~~Measured ~~concentration~~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 ~~concentration~~the mixing ratio is plotted as zero.

#### 180 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<sub>2</sub> and CO. Among tested rubber materials, butyl rubbers exhibited the highest rates of H<sub>2</sub> and particularly CO release, regardless of any pre-treatment. Untreated Exetainer septa performed particularly poorly; measured rates indicate that ~~concentration~~mixing ratios of H<sub>2</sub> and CO in air samples stored in conventional 12 mL  
 185 Exetainers could essentially double and quadruple every 24h. Treatment of septa with NaOH greatly reduced potential contamination, but ~~concentration~~mixing ratios in air samples could still double approximately every two weeks for H<sub>2</sub> 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

190 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<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> and 0.2 ppm CO in vials sealed with silicone. ~~This For H<sub>2</sub>, 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.

205 ~~However, diffusive exchange through silicone rubber is rapid and requires an impermeable second barrier to prevent this, as proposed with our SEs.~~

Specific mechanisms for H<sub>2</sub> 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<sub>2</sub> and CO in all rubber materials, regardless of pre-treatment and ~~concentration~~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 ~~concentration~~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<sub>4</sub>. 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<sub>2</sub> to CO release of 1:1 for silicones and at least 1:2 for other rubbers.

215 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<sub>2</sub> 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<sub>2</sub> and CO at trace levels for longer than a few days.

220 Our modified SEs ~~sealed~~ with a stainless steel bolt and O-ring as secondary diffusion barrier provided stable storage under ambient temperatures for gas samples with H<sub>2</sub> and CH<sub>4</sub> 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<sub>2</sub> samples, and extend reliable storage times for CH<sub>4</sub> 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  
225 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<sub>2</sub> and CH<sub>4</sub>, and showed deviations thereafter. Yet, for these gases  
~~concentration mixing ratios~~ stabilised within 10 to 30 days to a slightly higher level with pressurised air, and a slightly lower  
230 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<sub>2</sub> and CH<sub>4</sub> ~~concentration mixing ratios~~ than pressurised air, and lower  
~~concentration mixing ratios~~ than the calibration mix. Therefore, 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  
235 with high-purity N<sub>2</sub> after measurement, and storing them in an atmosphere of known composition, ideally similar to future  
samples.

Surprisingly, ~~concentration mixing ratios~~ of H<sub>2</sub> were much less affected than CO during storage in SEs, unlike in emission  
experiments where silicones showed similar rates of H<sub>2</sub> and CO release (Fig. 2 and 3). However, we also observed high  
variability in H<sub>2</sub> emissions from silicones, with some replicates showing H<sub>2</sub> increase comparable to CH<sub>4</sub>, others to CO. We  
240 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<sub>2</sub> only during curing, while CO  
appears to be released by a degradation reaction at a consistent rate.

We have now employed 12 mL SEs for several projects in terrestrial and marine environments with 400 to 600 samples and  
245 storage times of up to one month. Once prepared, SEs could be pierced numerous times without compromising tightness,  
~~while Although not explicitly tested, we observed less contamination when piercing the silicone plug with needles compared  
to thinner butyl septa, particularly when the needle was withdrawn slowly and the silicone was allowed to seal before the  
needle was fully out.~~ Stainless steel bolts, O-rings and Exetainer plastic caps have been repeatedly used ~~numerous times~~  
without ~~any compromise signs of degradation.~~ We have not observed any corrosion of bolts in marine applications, as SEs  
250 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 use nylon bolts (after testing for H<sub>2</sub> 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

255 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 availability

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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