

## Experimental tests of natural gas samplers prior to mercury concentration analysis

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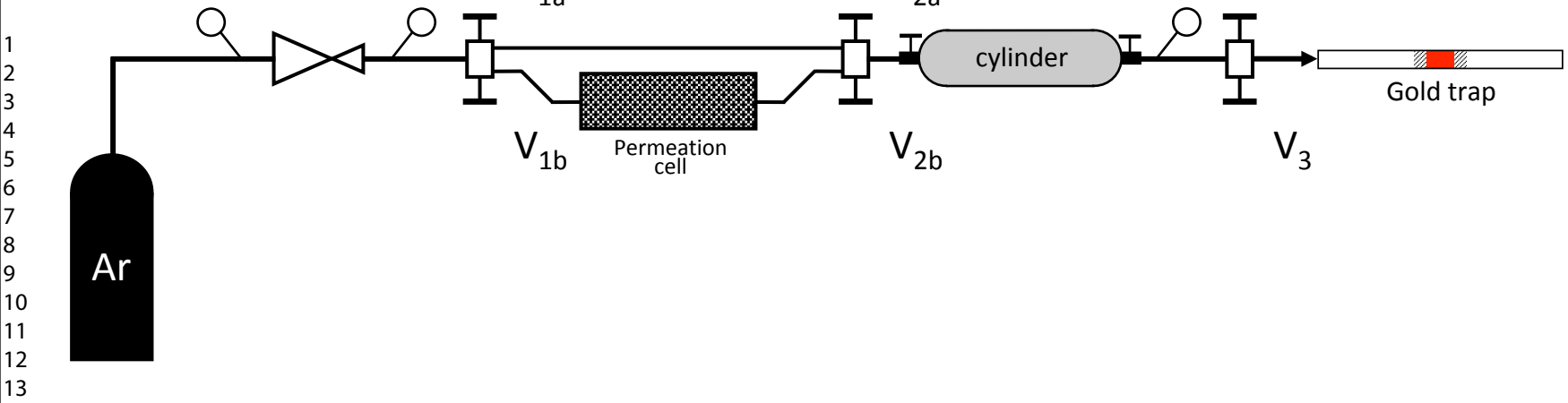
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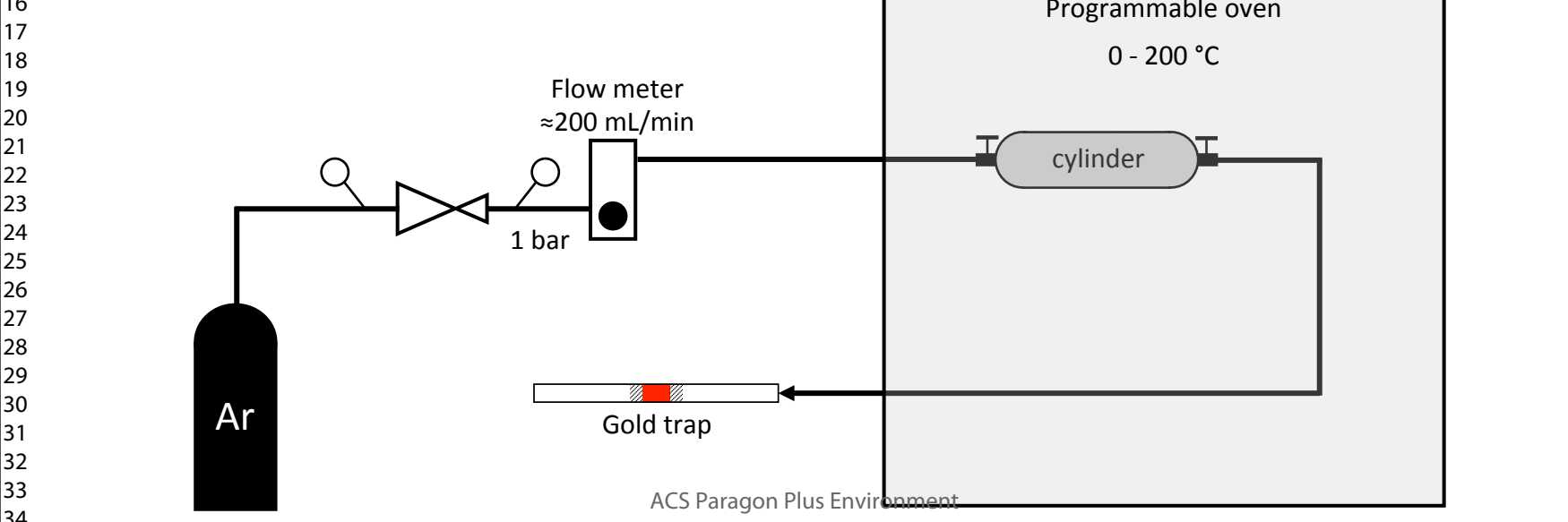
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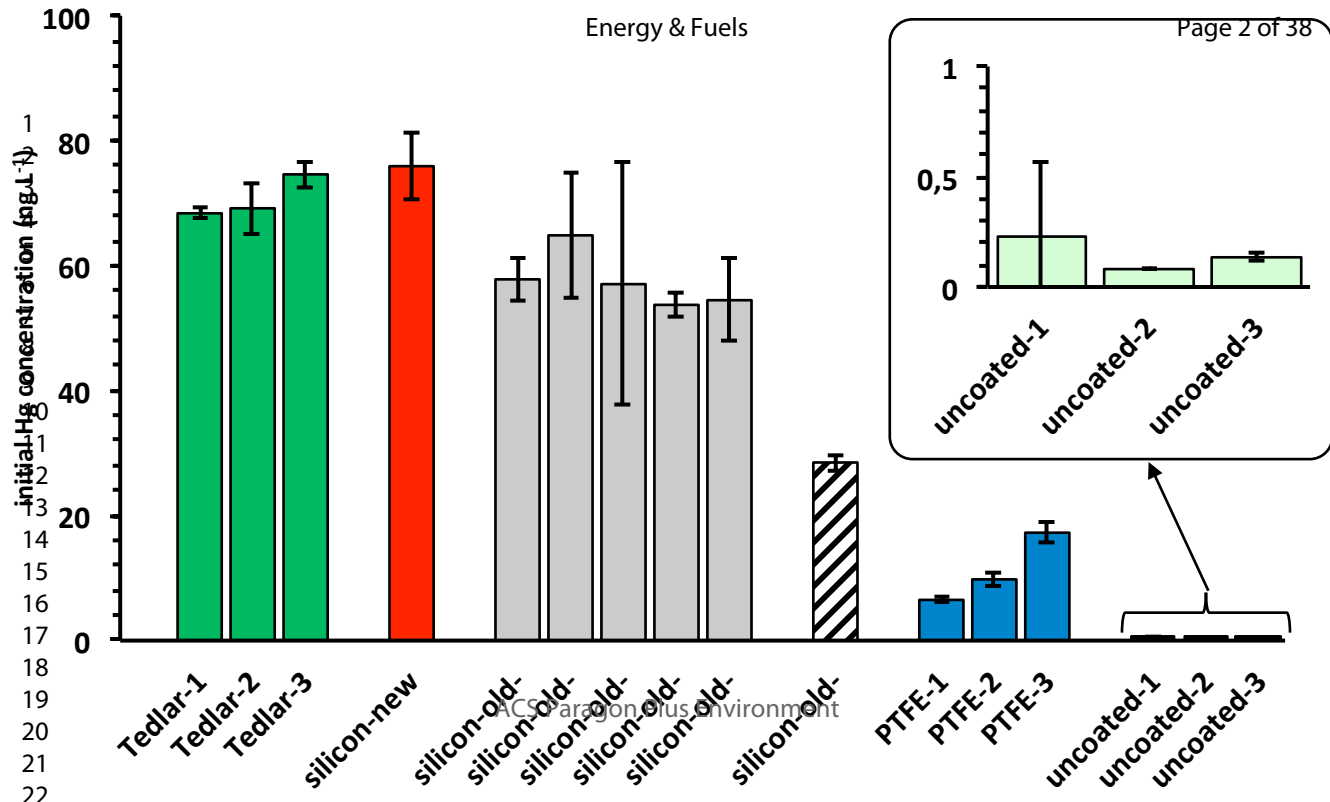
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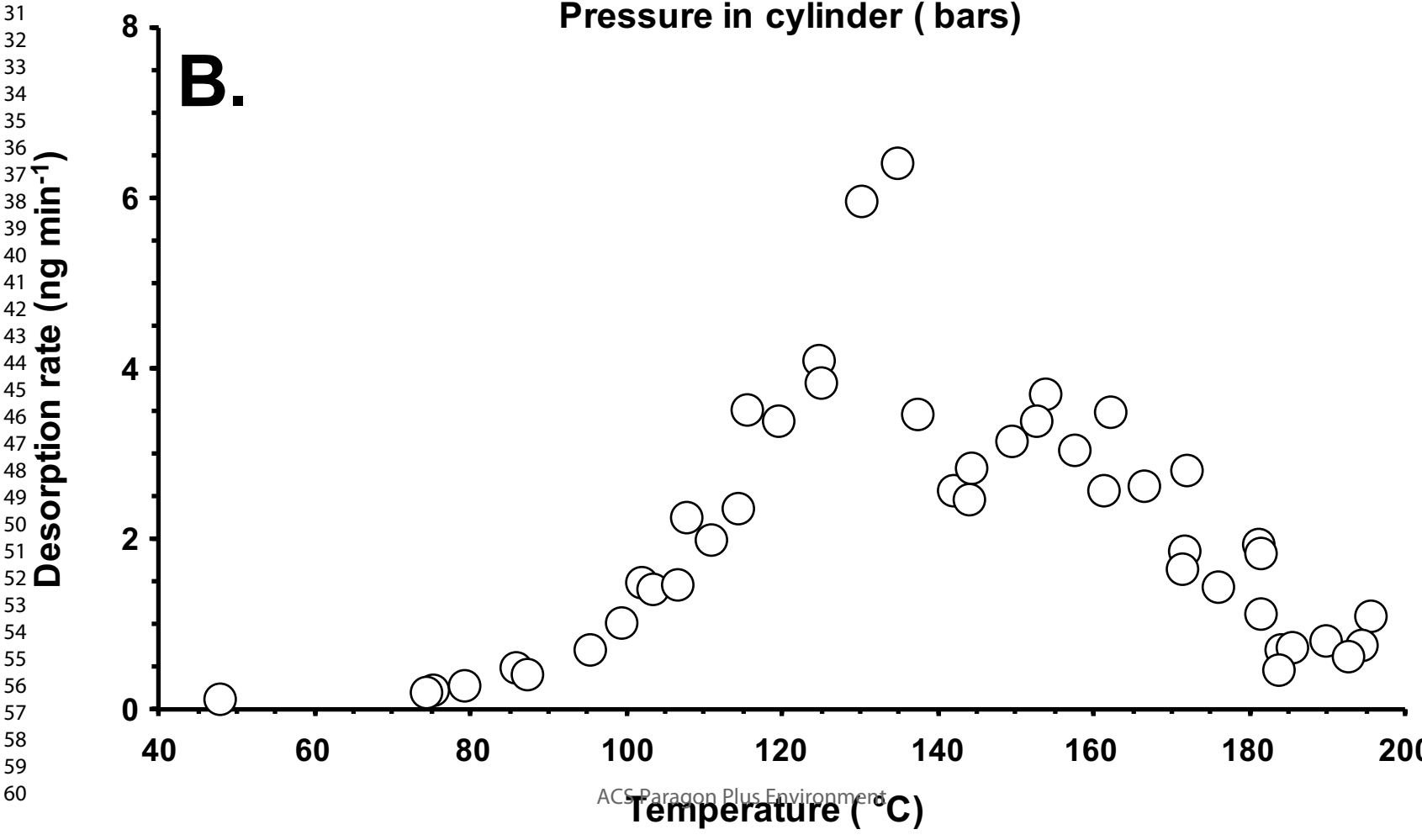
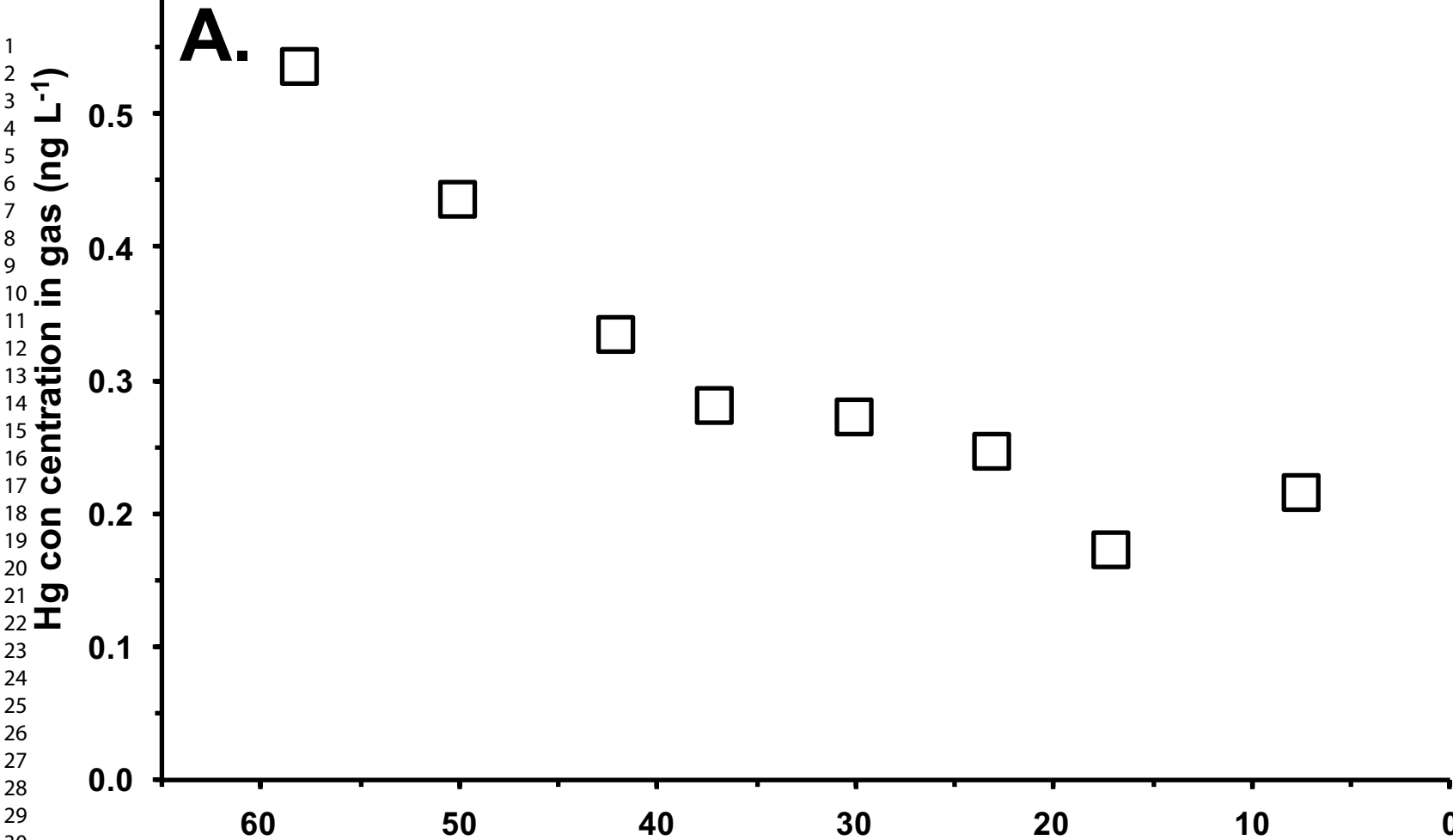
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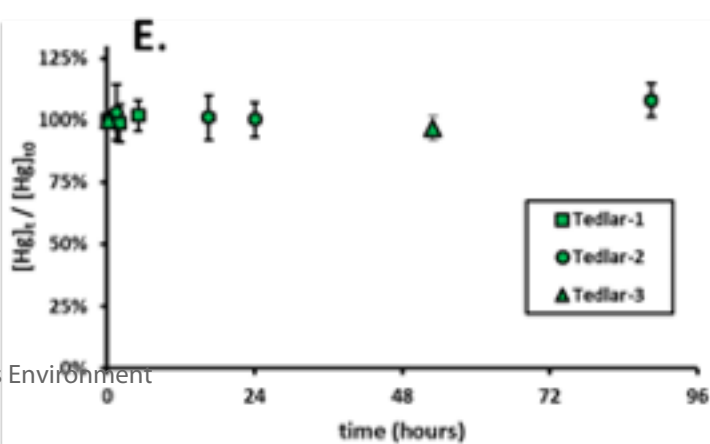
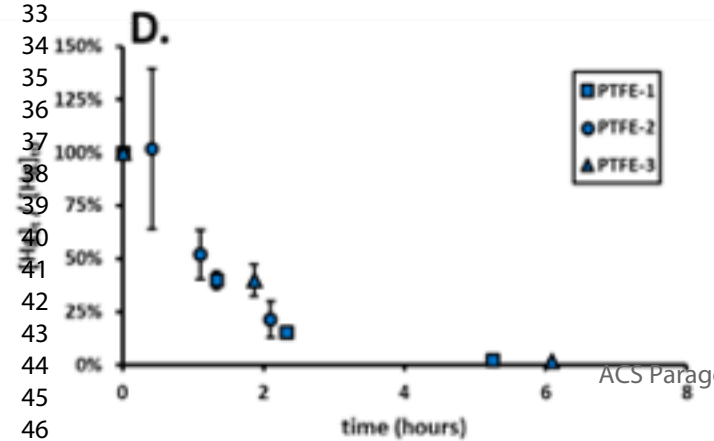
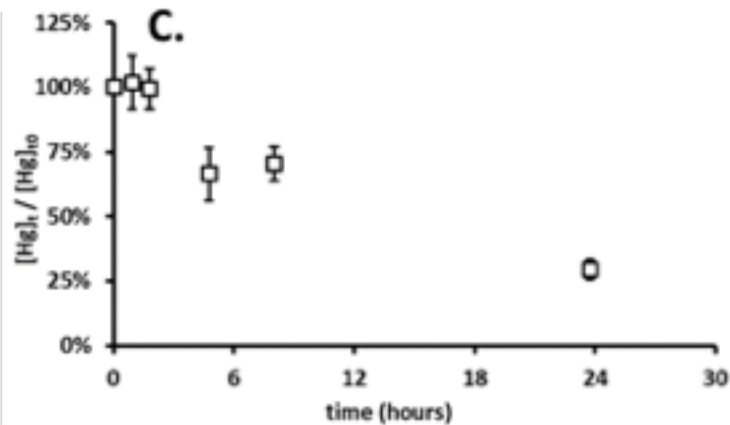
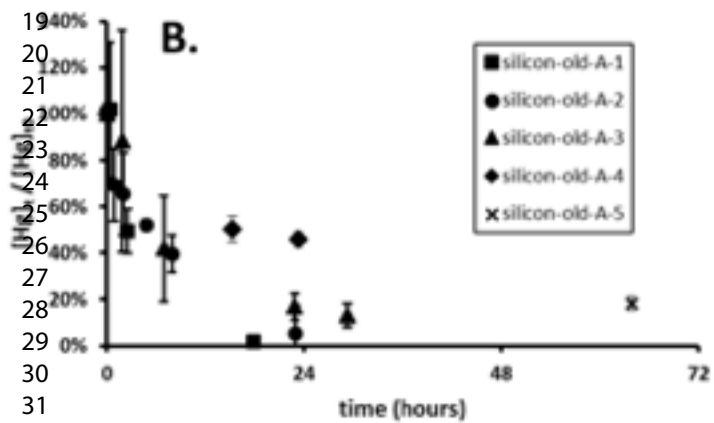
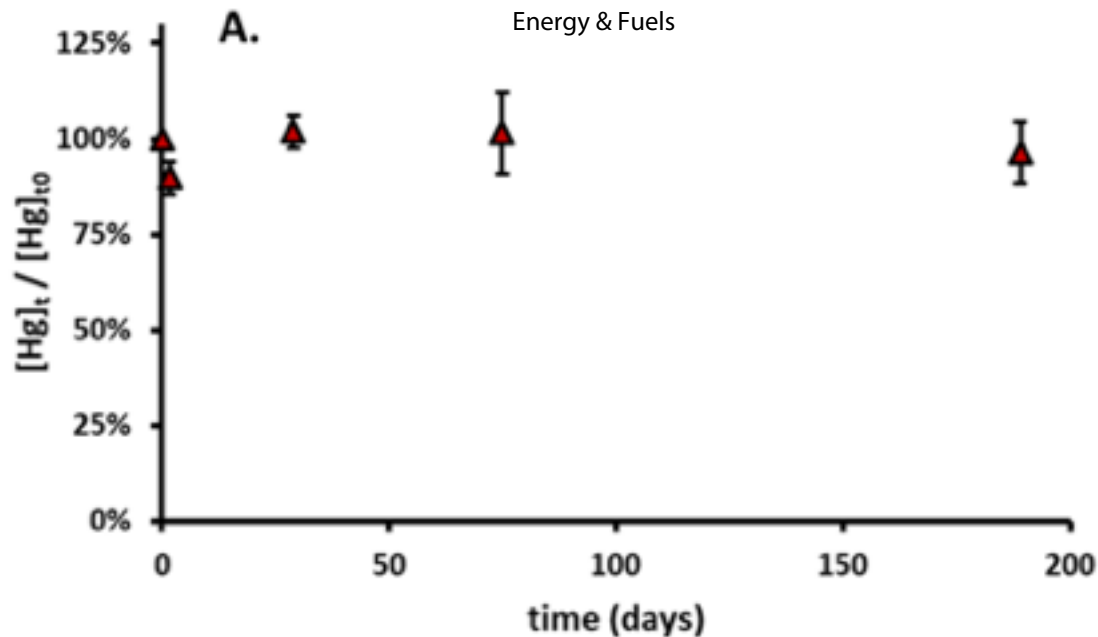


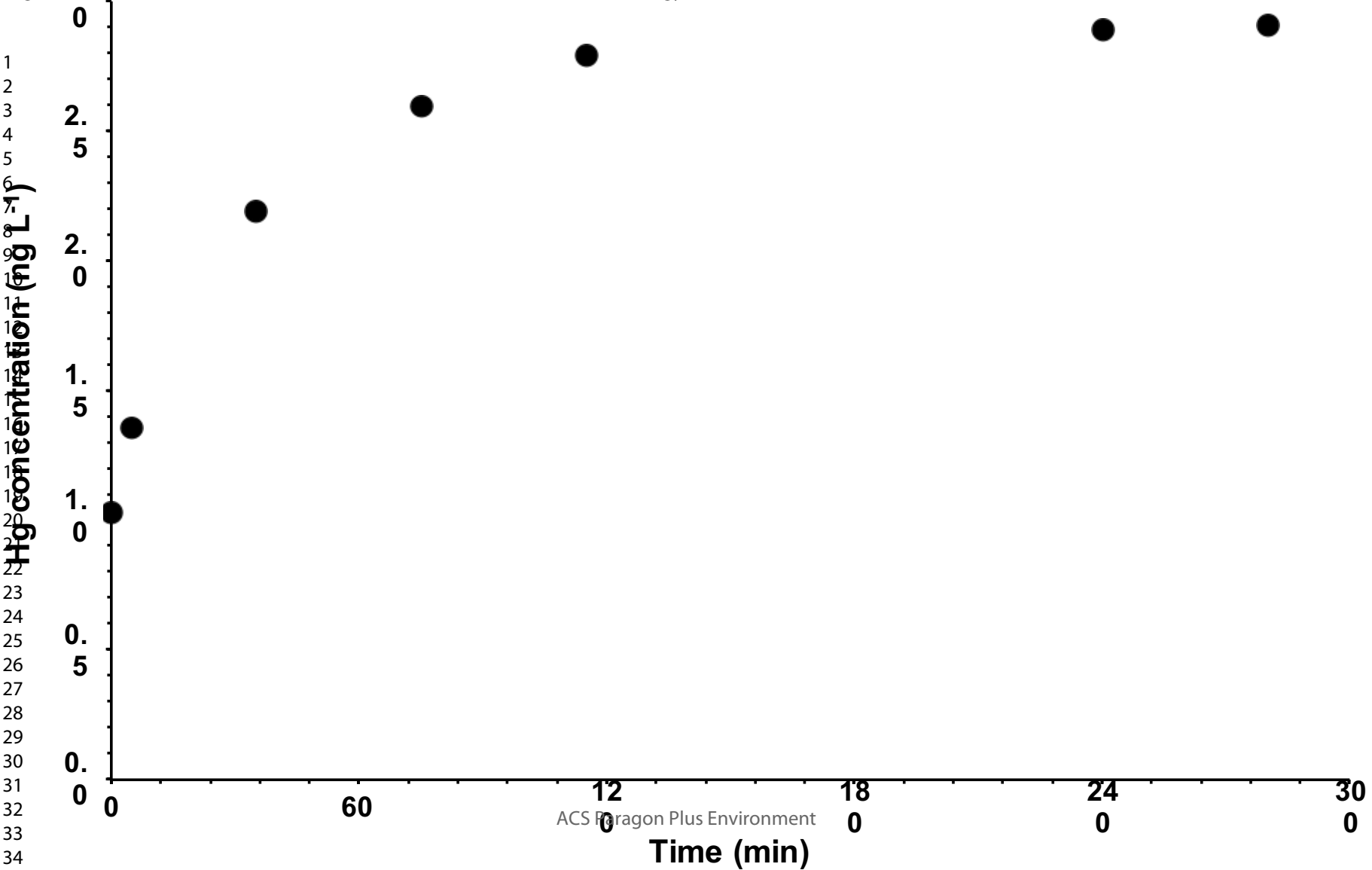
**B.**











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# Experimental tests of natural gas samplers prior to mercury concentration analysis

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**ABSTRACT**

Mercury (Hg) is a natural, trace component of natural gas. Corrosion of aluminum heat exchangers by liquid metallic Hg can lead to dramatic issues. The quantification of gaseous Hg concentration in natural gas streams is therefore crucial prior to the implementation of Hg removal units for preventing the formation of liquid Hg. Different methodologies exist for the determination of Hg concentration in natural gas, one of which relies on the sampling of natural gas at high pressure using stainless-steel cylinders prior to off-site Hg measurement. An inert internal coating is supposed to hamper Hg adsorption, presumably making the Hg analysis reliable. Here, we challenge this statement by showing that even silicon-coated cylinders are inefficient for preventing Hg adsorption on internal walls. Different cylinders were tested for gaseous Hg concentration stability over time in a clean Argon matrix. We find that gaseous Hg concentration sharply declines in almost all tested cylinders (uncoated, PTFE-coated and silicon-coated) to reach undetectable levels within a day or two due to adsorption, with the notable exception of a brand new silicon-coated cylinder. Heating cylinders up to 190 °C allowed the recovery of most of the adsorbed Hg and revealed the occurrence of two distinct Hg species with distinct release temperatures. Our results suggest

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3 Hg<sup>0</sup> is first physically adsorbed and further oxidized, presumably  
4  
5 in relation to sulfur compounds covering the internal walls of  
6  
7 the cylinders. The newly purchased silicon-coated cylinder kept  
8  
9 a constant gaseous Hg concentration over 6 months because it  
10  
11 never interacted with any real Natural Gas sample containing  
12  
13 substantial sulfur concentrations relative to Hg.  
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## INTRODUCTION

The occurrence of mercury (Hg) in natural gas is of great concern for the petroleum industry. Hg occurs naturally in petroleum and natural gas, with reported concentrations covering several orders of magnitude (from ng Nm<sup>-3</sup> to mg Nm<sup>-3</sup> ranges in natural gas).<sup>1</sup> The Hg in petroleum reservoirs undergoes reduction and is therefore mostly present as Hg<sup>0</sup>,<sup>2</sup> a highly volatile species. In hydrocarbon extraction and processing, Hg therefore likely goes to the light natural gas phase, although variations towards lower temperatures might allow some oxidation.<sup>3</sup>

In addition to health and environmental problematics, the petroleum industry adds another issue concerning Hg. Specifically, the large drop in temperature during liquefied natural gas (LNG) production tends to lower the gaseous Hg saturation value, potentially leading to the formation of liquid metallic Hg.<sup>4</sup> The action of metallic mercury as a corrosion catalyst for aluminum heat exchangers is well illustrated by two accidents that occurred in 1973 and 2004 in Skikda (Algeria). The corrosion of aluminum heat exchangers due to liquid Hg formation led to a dramatic failure, causing numerous deaths. Hg-induced corrosion can occur via two pathways: amalgam corrosion and liquid-metal embrittlement.<sup>5,6</sup> Both pathways

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3 require a breach in the surface aluminum oxide layer to allow  
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5 direct contact between metallic aluminum and liquid Hg.  
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8 The implementation of Hg removal units upstream of sensitive  
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10 operations avoids such failure. These Hg removal units are,  
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12 however, efficient up to a maximum amount of Hg treated after  
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14 which they have to be either regenerated or replaced. The  
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16 knowledge of Hg concentration in the natural gas treated is  
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18 therefore a prerequisite for establishing appropriate operation  
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20 procedures. Different methodologies exist for the quantification  
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22 of Hg concentration in natural gas. The sampling step can be  
23  
24 performed by preconcentrating Hg on solid sorbents or gold traps  
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26 (amalgamation)<sup>7</sup> or by bubbling in oxidizing solutions.<sup>8</sup> All these  
27  
28 sampling techniques have disadvantages related to sampling  
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30 conditions (flow rate, pressure)<sup>8,9</sup> that can lead to long  
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32 sampling periods depending on the Hg concentration.  
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37 As an alternative, natural gas sampling at high pressure can be  
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39 performed using cylinders. This efficiently reduces the sampling  
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41 time, and large amounts of gas can be stored. Although a  
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43 subsequent amalgamation step is required prior to Hg  
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45 quantification, this step is more conveniently done off-site in  
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47 a laboratory. Hg adsorption issues on metallic surfaces are,  
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49 however, well known, including potential amalgamation with other  
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51 metals,<sup>10</sup> precipitation of Hg sulfides<sup>11,12</sup> or simply by physical  
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53 adsorption. The efficiency of cylinders as natural gas samplers  
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3 prior to Hg quantification is therefore doubtful, with the  
4 possibility of adsorption issues. Cylinders internally coated  
5 with inert materials (silicon, PTFE) were developed to overcome  
6 adsorption issues for sulfur and Hg. Stability tests from the  
7 manufacturer,<sup>13</sup> as well as another independent test,<sup>11</sup> showed the  
8 efficiency of a silicon coating in preventing Hg losses from the  
9 gas phase.

10  
11 To understand some positive and negative results that were  
12 highlighted in the laboratory during recent Hg sampling and  
13 measurement campaigns, we decided to perform our own experiments  
14 on different cylinders to confirm their efficiency prior to  
15 their use on the field. Moreover, none of the latter two studies  
16 investigated the efficiency of a silicon-coated cylinder that  
17 was previously used on the field (and might already contain  
18 adsorbed compounds or have been modified by the sampling or the  
19 transportation). The influence of a hydrocarbon gas with a  
20 complex matrix therefore remains poorly understood. Our tests  
21 thus focus on the comparison of new and used silicon-coated  
22 cylinders. We also included a PTFE-coated cylinder, an uncoated  
23 cylinder and a Tedlar bag to obtain a full overview.

## 24 **EXPERIMENTAL SECTION**

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26 **Samplers.** We purchased a new silicon-coated cylinder from  
27 Restek® (Lisses, France). This cylinder had therefore never  
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3 interacted with any hydrocarbon gas, and we could evaluate the  
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5 initial inertness of the coating material.  
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8 Two other silicon-coated cylinders (hereafter referred to as  
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10 silicon-old-A and B) purchased from Restek (Lisses, France) were  
11  
12 used for our tests. These cylinders were both used approximately  
13  
14 ten times for sampling processed of commercial natural gas. The  
15  
16 major sulfur compound that was present in the sampled gas is  
17  
18 tetrahydrothiophene (THT), an additive for detecting natural gas  
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20 leaks (odorant).  
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24 We obtained one PTFE-coated and one uncoated cylinder from the  
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26 Total Exploration Production Research Center (CSTJF, Pau,  
27  
28 France). Both were used for natural gas sampling at production  
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30 sites in the past, but the precise sampling history is unknown.  
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32 However, the presence of gas components such as H<sub>2</sub>S or thiophenic  
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34 compounds is highly probable.  
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38 Another sampling option is the use of Tedlar® bags (Lisses,  
39  
40 France). These bags made of a fluoropolymer are supposed to be  
41  
42 inert and this material is commonly used in Hg research. Our  
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44 tests therefore include experiments with a new Tedlar bag for  
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46 comparison with cylinders.  
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49 **Generation of Hg-Contaminated Gas.** For loading, a cylinder was  
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51 first connected to the previously developed system presented in  
52  
53 Figure 1A.<sup>8</sup> Argon (5.0 from Linde) was delivered to the system at  
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55 70 bars, passing through first a permeation cell containing  
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3 liquid Hg and then through the cylinder. Argon is contaminated  
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5 in Hg when passing through the permeation cell. The Hg  
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7 concentration depends on the argon flow rate and system  
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9 pressure. To generate reproducible Hg concentrations in  
10  
11 cylinders, we adopted a procedure that used a 30 min flushing  
12  
13 period with Hg-contaminated Argon at 500 mL min<sup>-1</sup> prior to  
14  
15 cylinder closure. All experiments, except when stated otherwise,  
16  
17 were conducted using this procedure at a pressure of 70 bars.  
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21 A similar method was used for loading the Tedlar bag, except  
22  
23 that the flow meter was installed upstream of the bag (no outlet  
24  
25 on Tedlar bags). The Tedlar bag was connected after the 30 min  
26  
27 flushing procedure and filled with 15 L of argon. The system  
28  
29 with the permeation cell was further kept at 70 Bars to ensure  
30  
31 comparability of the cylinder results.  
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35 For blank evaluation, argon was delivered directly to a gold  
36  
37 trap using a bypass (Figure 1A). The system blank was relatively  
38  
39 high (1 ng L<sup>-1</sup>), representing the repeated uses of this system  
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41 for experimental work on Hg over the past decade.  
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44 **Subsampling for Hg Concentration Measurement.** The gaseous Hg  
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46 concentration was determined at several time steps for each  
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48 test, including the evaluation of the initial Hg concentration.  
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50 One valve of the cylinder was opened, and the stream out was  
51  
52 adjusted to 150 - 200 mL min<sup>-1</sup>. A gold trap was then connected to  
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54 sample the desired gas volume. Gas flow rate and sampled volume  
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3 were controlled and measured by a gas counter (Mass-View MV-102,  
4  
5 Bronkhorst).

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7 As the reliability of a single measurement is doubtful, every  
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9 sampling used 4 distinct gold traps. The four subsampling  
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11 replicates were performed successively by replacing gold traps.  
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13 A volumetric gradient approach was adopted for reliable Hg  
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15 quantification (see supporting information section 1, Figure  
16  
17 S1). The slope between the volume sampled and the amount of Hg  
18  
19 recovered was used as the Hg concentration.  
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23 **Thermal Desorption Experiments.** Following the gaseous Hg  
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25 stability experiments, thermal desorption was attempted on  
26  
27 several cylinders. The cylinder was placed in a programmable  
28  
29 oven under an argon flow of approximately 200 L min<sup>-1</sup>. Desorbed  
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31 Hg was sampled using a gold trap installed downstream of the  
32  
33 cylinder, outside the oven (Figure 1B).  
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37 Initial experimental temperature was 70°C. In addition to the  
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39 control panel, the temperature was monitored using 2 independent  
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41 sensors. The gold trap was left for 10 min (approximately 2 L of  
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43 gas sampled) before being replaced. This was repeated three  
44  
45 times to provide three different estimates for desorption rates  
46  
47 at each temperature. The oven temperature was then increased by  
48  
49 10°C, and the procedure was repeated until 190°C. Because we  
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51 used PTFE tape on screws to prevent gas leaks, we did not  
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3 perform experiments at higher temperatures (PTFE melts at  
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5 205°C).

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7 **Hg Analysis.** We used an automated double amalgamation system  
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9 with atomic fluorescence spectrometry (Sir Galahad, PS  
10  
11 Analytical, UK) for Hg analysis. Briefly, Hg from the gold traps  
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13 was thermally desorbed by heating at 500°C for 50 s and carried  
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15 to an analytical gold trap by an argon flow. The analytical gold  
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17 trap is then heated at 500°C for 15 s and an argon flow carries  
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19 the released gaseous Hg to the atomic fluorescence detector. The  
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21 instrumental detection limit is 10 pg. Considering that our  
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23 system blank was 1 ng L<sup>-1</sup>, we had no issues related to the  
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25 instrumental detection limit.  
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## 30 **RESULTS AND DISCUSSION**

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32 **Initial Gaseous Hg Concentration and Temporal Stability.** The  
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34 loading procedure led to different initial Hg concentrations  
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36 depending on the cylinder we tested. Three successive tests with  
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38 the Tedlar bag gave consistent values of approximately  
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40 71 ± 3 ng L<sup>-1</sup> (n = 3, Figure 2), which compares well with a test  
41  
42 performed on the new silicon-coated cylinder (76 ± 6 ng L<sup>-1</sup>). Two  
43  
44 other tests were conducted on the silicon-coated cylinder, but  
45  
46 we adopted a different peanut butter-based loading strategy. For  
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48 these two tests (2 and 3), the 30 min flushing step was avoided,  
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50 which led to initial gaseous Hg concentrations of 29 ± 1 and  
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52 33 ± 1 ng L<sup>-1</sup>, respectively. This lower concentration is related  
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3 to the variable flow rates through the permeation cell during  
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5 the loading, leading to different gas/liquid fractionation  
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7 values.  
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10 The old silicon-coated cylinder A was successively tested 5  
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12 times with comparable initial Hg concentrations (average value  
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14  $58 \pm 4 \text{ ng L}^{-1}$ ,  $n = 5$ ). This is slightly lower than the new  
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16 silicon-coated cylinder and Tedlar bag. We acknowledge that  
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18 small differences in the loading procedure (exact flushing flow  
19  
20 rate in particular) might be responsible for small differences  
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22 in the initial gaseous Hg concentration. The old silicon-coated  
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24 cylinder B, however, gave a low initial Hg concentration of  
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26  $29 \pm 1 \text{ ng L}^{-1}$ . This low Hg concentration relative to the new  
27  
28 silicon-coated cylinder is unlikely to be derived from the  
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30 procedure itself, and likely reveals adsorption already occurred  
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32 during our loading procedure.  
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37 The three experiments conducted on the PTFE-coated cylinder  
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39 gave three different initial Hg concentrations, with an  
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41 increasing trend from  $6.5 \pm 0.3$  to  $17.3 \pm 1.6 \text{ ng L}^{-1}$ . Compared to  
42  
43 the results obtained for the silicon-coated cylinders, these  
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45 values are rather low and likely indicate that adsorption  
46  
47 occurred. The results for the uncoated cylinder were even worse,  
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49 with initial Hg concentrations evaluated to be an order of  
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51 magnitude below the system blank (approximately  $0.07 \text{ ng L}^{-1}$ ,  
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53 average of three tests). This clearly shows that uncoated  
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3 cylinders efficiently adsorb Hg. In fact, even a test performed  
4 during the flushing procedure by sampling at the outlet of the  
5 uncoated cylinder reflected negligible gaseous Hg concentration.  
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7 Further stability tests were not conducted on uncoated  
8 cylinders, as all Hg seemed to be initially rapidly adsorbed.  
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10 All other cylinders were tested for Hg concentration stability  
11 over time.  
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15 The newly purchased silicon-coated cylinder efficiently  
16 maintained a constant Hg concentration during short-term  
17 experiments (a few hours, see Figure S2 in supporting  
18 information). A longer-term experiment showed that gaseous Hg  
19 concentration is stable over at least 6 months, supporting  
20 previous tests performed by the manufacturer (Figure 3A). The  
21 old silicon-coated cylinders, however, behaved differently, with  
22 a clear decrease in gaseous Hg concentration, visible after only  
23 a few hours (Figure 3B and C). Despite the lower initial Hg  
24 concentration in the old silicon-coated cylinder B (Figure 2),  
25 the decline seems to be slower than for cylinder A (Figure 3B  
26 and C). The PTFE-coated cylinder showed a fast decline in  
27 gaseous Hg concentration, reaching undetectable levels after  
28 only 3 h. Despite the differences in initial Hg concentration  
29 among the three tests, we observe a surprisingly identical  
30 declining trend.  
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3     **Adsorption of Gaseous Hg and Equilibrium.** Only the new silicon-  
4 coated cylinder and the Tedlar bag were able to maintain a  
5 constant gaseous Hg concentration (Figure 3A and E). From all  
6 these observations, we conclude that gaseous Hg is progressively  
7 adsorbed on the internal cylinder walls, at least in the old  
8 cylinders (silicon and PTFE-coated). The five successive tests  
9 on the old silicon-coated cylinder A revealed different rates of  
10 decrease (Figure 3B), with faster decline for the first tests  
11 (no Hg detected after 20 h) than the last (20 % of Hg remaining  
12 after 60 h). Following these experiments, an empty cylinder was  
13 filled with uncontaminated argon (bypass shown in Figure 1) at  
14 70 bars without flushing the system. The gaseous Hg  
15 concentration was then monitored for 5 h. It increased from an  
16 initial Hg concentration of 1 ng L<sup>-1</sup> (similar to the system  
17 blank) to stabilize at approximately 2.9 ng L<sup>-1</sup> (Figure 4). This  
18 demonstrates that Hg adsorption is ruled at least partly by an  
19 equilibrium relationship with gaseous Hg.  
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41     All our stability tests consisted of measurements performed on  
42 very small gas samples compared to the amount of gas stored in  
43 the cylinder, which is not informative regarding the behavior of  
44 Hg during cylinder purge. The old silicon-coated cylinder B was  
45 left filled with Hg-contaminated gas for 15 more days. The gas  
46 was then entirely flushed through gold traps at 150-200 mL min<sup>-1</sup>.  
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3 We determined that the gaseous Hg concentration at the beginning  
4 of the procedure was approximately 0.5 ng L<sup>-1</sup>. It progressively  
5 decreased with pressure during the cylinder purge (Figure 5A).  
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7 This finding shows that pressure influences the equilibrium  
8 relationship between adsorbed Hg and gaseous Hg.  
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14 **Thermal Desorption Results.** We tested the possibility of  
15 recovering adsorbed Hg by heating the cylinder. The cylinder was  
16 flushed with argon and heated from 70 to 190°C. A gold trap  
17 recovered desorbed Hg for 10 minutes before being replaced. We  
18 found that desorption rates generally increased with temperature  
19 (Figure 5B). However, we also noted a double-peak shape,  
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21 indicating two optimal desorption temperatures. The desorption  
22 rates first increased when the temperature was increased from 70  
23 to 130°C. Desorption rates then stabilized or decreased,  
24 followed by a further increase.  
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37 The double-peak shape we obtained during the thermal desorption  
38 experiment is likely indicative of the occurrence of two  
39 distinct forms of adsorbed Hg species, as the volatilization  
40 temperature indicates Hg species.<sup>14,17, 18</sup> Adsorbed Hg<sup>0</sup> is  
41 classically released at low temperatures due to its volatility  
42 (from 70 degC, peak around 80 - 150 deg C depending on the  
43 procedure)<sup>17</sup>. This is consistent with the first peak we observe,  
44 with desorption starting around 80 degC and increasing until 130  
45 degC. Other Hg forms, consisting of oxidized Hg (either as  
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3 particulate, Hg salts or Hg complexes), are released at higher  
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5 temperatures that vary depending on the species.  
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8 This is well illustrated by a study showing that GC injector  
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10 temperature is critical for the evaluation of Hg<sup>0</sup> levels in  
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12 liquid hydrocarbon samples. Thermal decomposition of Hg  
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14 particles into Hg<sup>0</sup> might lead to overestimation of Hg<sup>0</sup>  
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16 concentration<sup>19</sup>. Our procedure does not allow the identification  
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18 of this species but the double peak shape unambiguously suggests  
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20 the presence of both physically adsorbed Hg<sup>0</sup> and an oxidized Hg  
21  
22 form into the cylinder. The decomposition of Hg compounds to  
23  
24 gaseous Hg<sup>0</sup> is also the principle of a Hg quantification method  
25  
26 in liquid hydrocarbon samples consisting in heating at 200 degC  
27  
28 and measuring headspace gaseous Hg, in equilibrium with  
29  
30 dissolved Hg<sup>0</sup>.<sup>20</sup> Similarly, a Hg removal technique suggests  
31  
32 heating liquid hydrocarbons at temperatures higher than 175 degC  
33  
34 in order to transform all Hg species to Hg<sup>0</sup>, easier to remove  
35  
36 from hydrocarbon streams <sup>21</sup>.  
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41  
42 During our experiments, only Hg<sup>0</sup> and Argon were delivered to  
43  
44 the cylinder. Therefore, Hg oxidation obviously occurred in the  
45  
46 cylinder. Sulfur species, especially H<sub>2</sub>S, are known to indirectly  
47  
48 cause depletion in gaseous Hg<sup>12,15</sup> by first reacting with metallic  
49  
50 oxide surfaces. The sampling history of this cylinder (old  
51  
52 silicon-coated cylinder B) indicated that its use was limited to  
53  
54 the sampling of a natural gas containing very low amounts of Hg  
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3 (on the  $\text{ng Nm}^{-3}$  level, measured independently by the amalgamation  
4 method). Sulfur species should have been present at very low  
5 levels as well, with the notable exception of THT, which is  
6 injected upstream for leak detection. As  $\text{H}_2\text{S}$ , THT contains  
7 reduced sulfur that might interact with Hg. The most likely  
8 explanation for our observations involves the adsorption of THT  
9 or other reduced sulfur compound on internal cylinder walls,  
10 providing binding sites for  $\text{Hg}^0$ . The oxidation of Hg from  
11 physically adsorbed  $\text{Hg}^0$ , followed by complexation with reduced  
12 sulfur, was already observed in solution.<sup>16</sup> We propose that a  
13 similar sorption and oxidation pathway also affects gaseous Hg.  
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28 We note that silicon coating is also expected to be inert to  
29 sulfur compounds. This is probably true to some extent, but the  
30 inertness is not perfect, as shown by tests from the  
31 manufacturer itself (From Restek Technical Resources). The main  
32 problem here is that typical sulfur and Hg concentrations differ  
33 by several orders of magnitude. In other words, although less  
34 than 1% sulfur adsorption is not problematic for sulfur  
35 measurement and speciation, it can affect Hg adsorption and lead  
36 to the complete depletion of Hg from the gas phase.  
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48 The thermal desorption procedure was also applied to the  
49 uncoated cylinder and the PTFE-coated cylinder (see supporting  
50 information section 3, Figure S3). In contrast to the silicon-  
51 coated cylinder B, however, the procedure was applied several  
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3 months after the cylinder purge. Both revealed a very high  
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5 content of adsorbed Hg, although exact quantification was not  
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7 attempted. The results for the PTFE-coated cylinder also suggest  
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9 two Hg species, although the oxidized Hg seems to be very high  
10  
11 compared to the physically adsorbed Hg. This might derive from  
12  
13 faster oxidation, which is supported by the fast depletion of  
14  
15 gaseous Hg concentration during our experiments (all Hg lost  
16  
17 within 3 h). It could also be related to the lag between the  
18  
19 gaseous Hg stability and thermal desorption experiments (2  
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21 months).  
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26 **Mass Balance and Reaction Rates.** The initial gaseous Hg  
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28 concentration in the old silicon-coated cylinder B suggested  
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30 that 600 ng of gaseous Hg was present inside the cylinder at the  
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32 initial stage of the experiment. As already mentioned, this is  
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34 quite different from the new silicon-coated cylinder, for which  
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36 the same loading procedure led to an initial gaseous Hg amount  
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38 of about 1500 ng. We already discussed this difference and  
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40 attributed it to fast adsorption occurring during the loading  
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42 procedure. The initial gaseous Hg amount in the silicon-coated  
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44 cylinder B does not account for Hg adsorbed during the loading  
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46 and therefore underestimate the initial Hg budget.  
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51 During the purge of silicon-coated cylinder B, we recovered a  
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53 total of 5 ng of Hg (Figure 5A) which is somewhat negligible  
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55 compared to the initial Hg budget. The thermal desorption  
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3 procedure allowed us to recover 1100 ng of Hg (Figure 5B),  
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5 almost twice the initial Hg budget. The 500 ng excess is  
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7 unlikely to originate from the natural gas previously sampled  
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9 using this cylinder, as the Hg concentration was four orders of  
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11 magnitude lower than that of the contaminated gas we generated.  
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13 It more likely derives from Hg that was adsorbed during the  
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15 loading of the cylinder, prior to the evaluation of the initial  
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17 gaseous Hg concentration. The total amount of Hg we retrieve  
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19 during the purge and thermal desorption is comparable to the  
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21 1500 ng that are present in the new silicon-coated cylinder when  
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23 using the same loading procedure. The slight difference might be  
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25 caused by minor differences during the loading procedure, or to  
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27 the formation of another Hg species that is released at higher  
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29 temperature. Considering that we have two Hg species in the  
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31 cylinder, fast adsorption might be related to the physical  
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33 adsorption of  $\text{Hg}^0$ . Adsorption rates during the initial stage of  
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35 the experiments (including during the loading procedure) are  
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37 therefore controlled by sorption sites for  $\text{Hg}^0$ . The reaction  
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39 scheme with subsequent oxidation, together with the slower  
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41 adsorption rates observed during our experiments (Figure 3C),  
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43 suggests that the oxidation step is the limiting factor when  
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45 equilibrium is reached between physically adsorbed and gaseous  
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47  $\text{Hg}^0$ .  
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3 The reaction scheme we inferred excludes the direct oxidation  
4 of gaseous  $\text{Hg}^0$ , as we speculated that  $\text{Hg}^0$  first requires physical  
5 adsorption. The observation of Larsson et al.<sup>12</sup> is, however, in  
6  
7 good agreement with this hypothesis, as no Hg loss was observed  
8  
9 at 75°C and 100°C from a gas containing  $\text{Hg}^0$  and  $\text{H}_2\text{S}$ . At such low  
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11 temperatures, only the physical adsorption of  $\text{Hg}^0$  should be  
12  
13 inhibited, thus direct oxidation of gaseous  $\text{Hg}^0$  would induce  
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15 losses of Hg even at 75 - 100 degC. Additional indirect evidence  
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17 derives from a previous test of a silicon-coated cylinder. The  
18  
19 authors showed no evolution of gaseous Hg concentration in their  
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21 cylinder upon heating at 100°C throughout the experiment,<sup>11</sup>  
22  
23 although this study did not show any results for a similar  
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25 cylinder kept at ambient temperature.  
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32 **Conclusion and Recommendations.** We provided experimental  
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34 evidence showing the inefficiency of silicon coatings for  
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36 natural gas sampling prior to Hg analysis (as well as PTFE  
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38 coatings). The inertness of the coating regarding Hg adsorption  
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40 is initially efficient but does not last in time. We suggest  
41  
42 that the adsorption of sulfur species on the coated surfaces  
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44 provides sorption sites for Hg and can ultimately lead to the  
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46 transformation of  $\text{Hg}^0$  into less volatile oxidized forms. Tedlar  
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48 bags might be inert to Hg. However, our tests used only a new  
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50 Tedlar bag, so that the fluoropolymer surfaces never experienced  
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52 any contact with sulfur species. Further experiments are  
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3 required for evaluating Tedlar bags as a sampling alternative  
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5 prior to Hg analysis in natural gas, but the fragility and the  
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7 size of this sampler system are also negative points that might  
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9 be considered when the sample has to travel.  
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12 We acknowledge that appropriate sampling procedures using  
13  
14 cylinders might be imagined (sampling at 100degC to avoid  
15  
16 adsorption), but adsorption needs to be considered even in the  
17  
18 case of silicon-coated cylinders. The repeated use of cylinders  
19  
20 for sampling different natural gas samples might lead to both  
21  
22 adsorption and desorption, as the partition is ruled by an  
23  
24 equilibrium relation and depends on the total Hg budget and  
25  
26 pressure. Alternative standard methodologies involving Hg  
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28 preconcentration by amalgamation or oxidation in acidic  
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30 solutions ( $\text{KMnO}_4/\text{H}_2\text{SO}_4$ )<sup>8</sup> might be preferable, despite flow rate  
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32 limitations.<sup>9</sup>  
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40 ASSOCIATED CONTENT

#### 41 42 43 **Supporting Information**

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47 Additional methodology explanation and thermal release tests performed on PTFE-coated and  
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49 uncoated cylinders are given in supporting information.  
50

51 AUTHOR INFORMATION

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35 cylinders.  
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## CAPTIONS TO FIGURES

**Figure 1.** Schemes of the systems used for (A) the loading of Hg-contaminated gas in the cylinders and (B) thermal desorption experiments.

**Figure 2.** Initial Hg concentration measured after sampler loading with Hg-contaminated argon. Are shown only the initial Hg concentration for experiments including a 30 min preliminary flushing step during the loading experiment. The results for 6 different samplers are shown, as well as for the different tests conducted on each sampler.

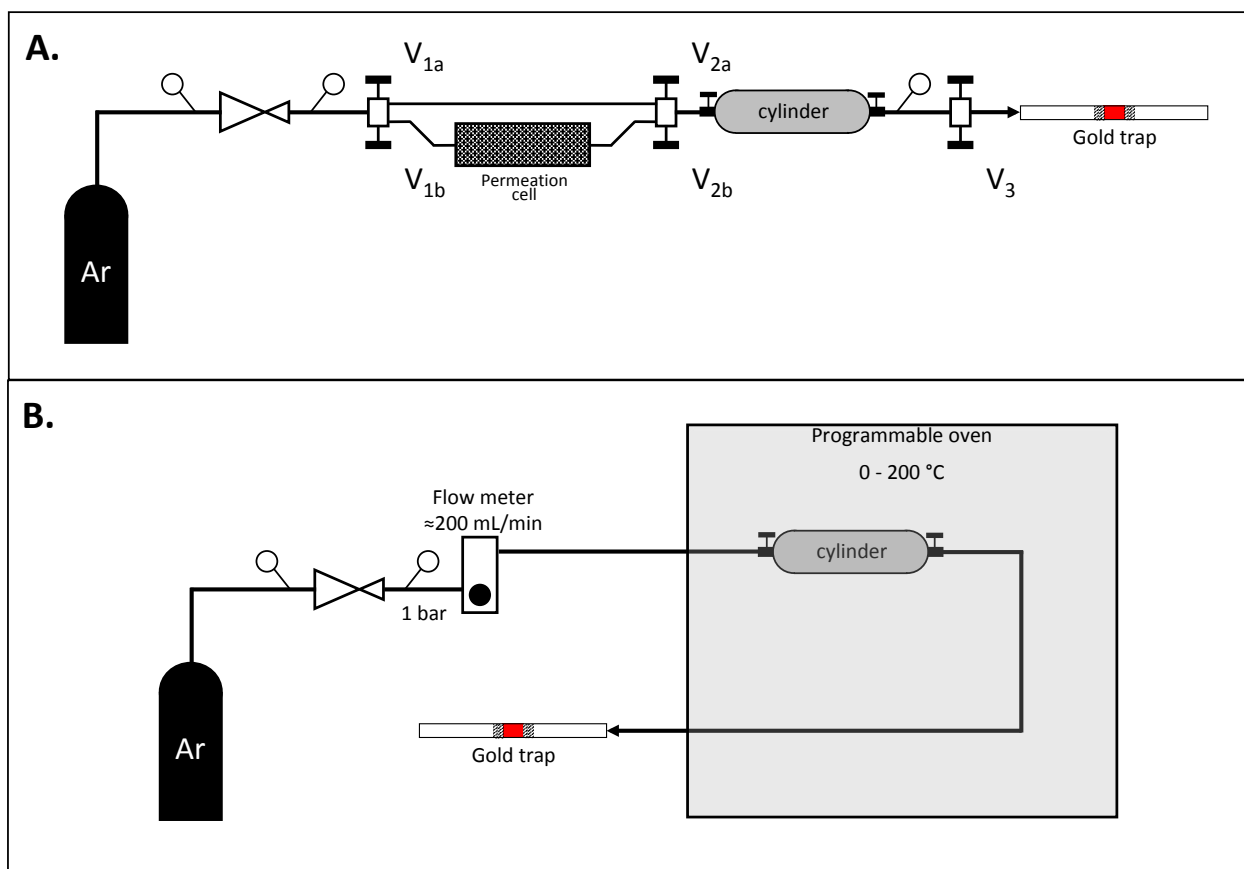
**Figure 3.** Gaseous Hg concentration variations over time during stability experiments conducted on (A) a new silicon-coated cylinder, (B) the old silicon-coated cylinders A and (C) B, (D) the PTFE-coated cylinder and (E) the Tedlar bag. Note the differences in the x-axis scale, especially for panel A (days unit compared to other panels in hours). Only the long-term test is shown for the new silicon-coated cylinder (panel A), and the results of the short-term tests (1 and 2) can be found in supporting information Figure S2.

**Figure 4.** Evolution of gaseous Hg concentration in the old silicon-coated cylinder A after loading with uncontaminated argon. This test was conducted after the five tests with contaminated argon (Figure 3 B). The initial gaseous Hg

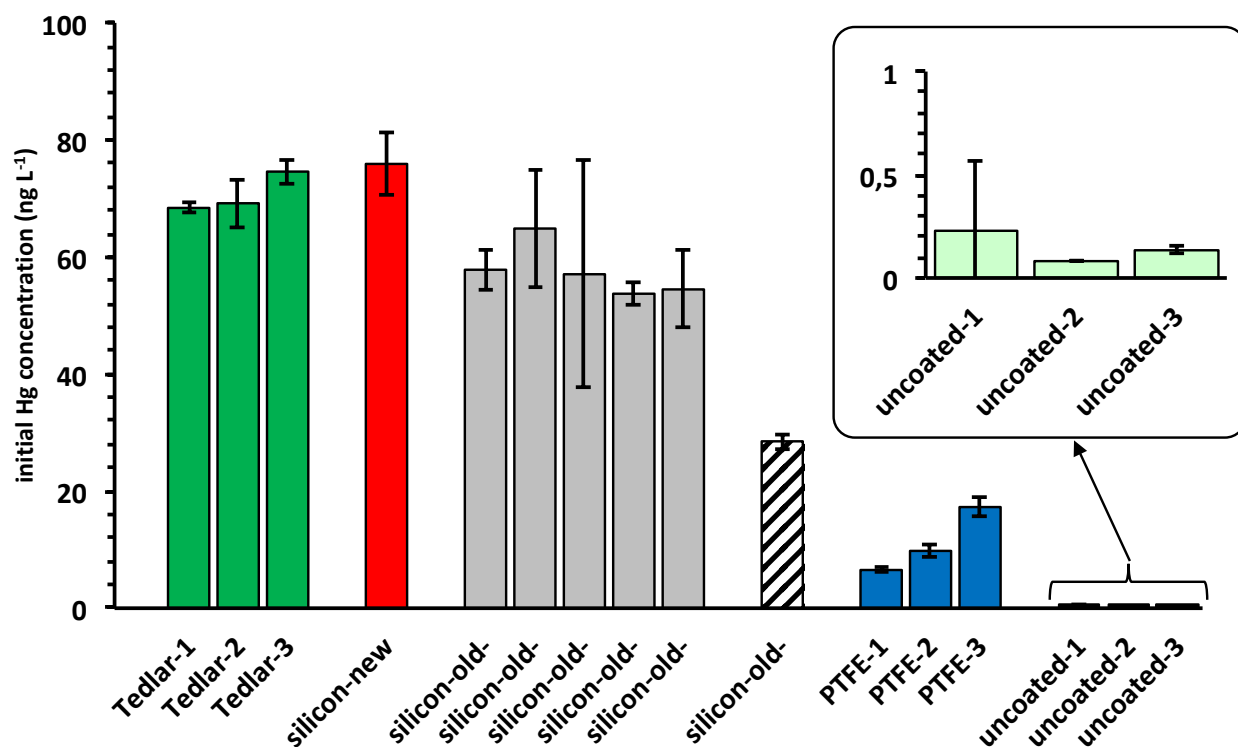
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3 concentration of  $1 \text{ ng L}^{-1}$  is consistent with the system blank  
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5 value.  
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8 **Figure 5.** Hg recovery during (A) purge and (B) heating of the  
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10 old silicon-coated cylinder B. Panel A shows the variations in  
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12 gaseous Hg concentration during silicon-coated cylinder B purge,  
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14 shown as gaseous Hg concentration as a function of pressure left  
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16 in the cylinder. Panel B illustrates the temperature dependence  
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18 of Hg desorption rates.  
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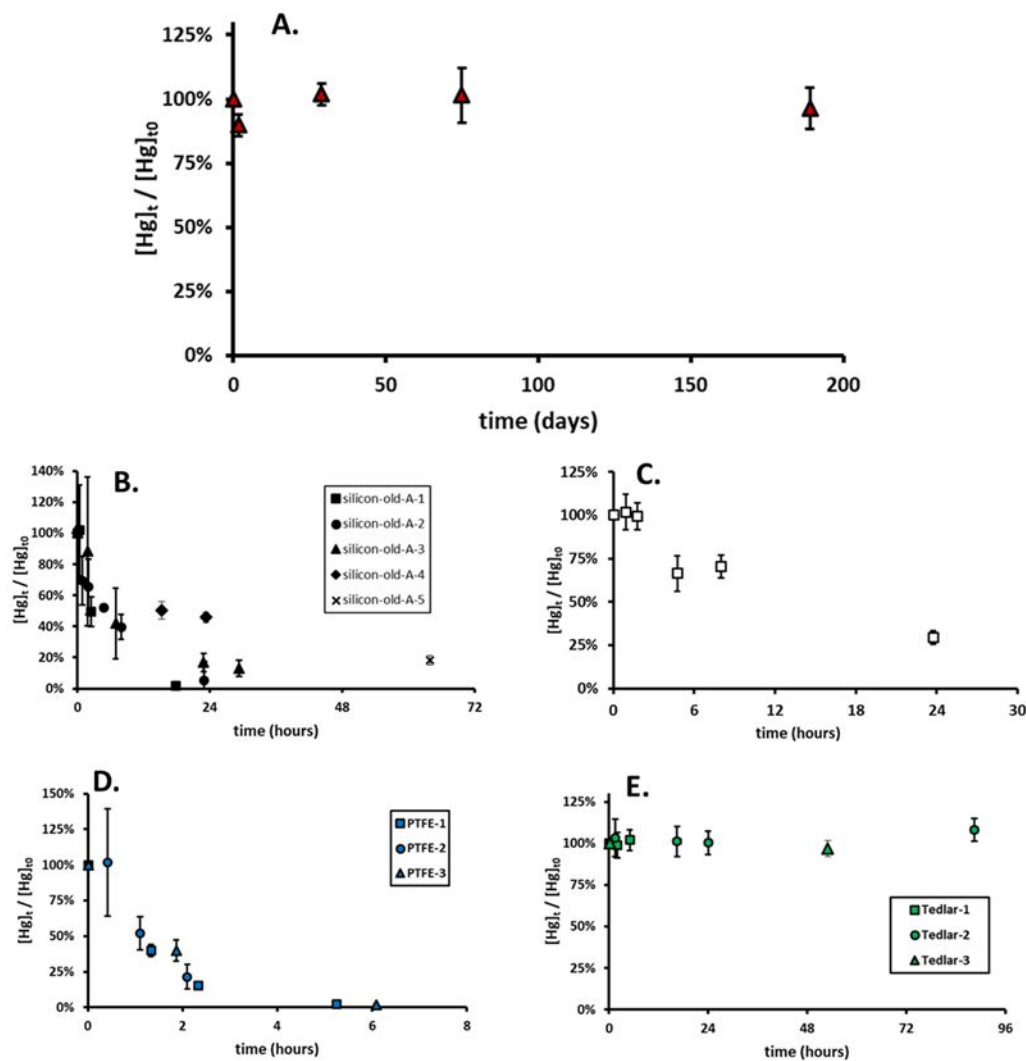
## FIGURES



**Figure 1.** Schemes of the systems used for (A) loading of Hg-contaminated gas in the cylinders and (B) thermal desorption experiments.

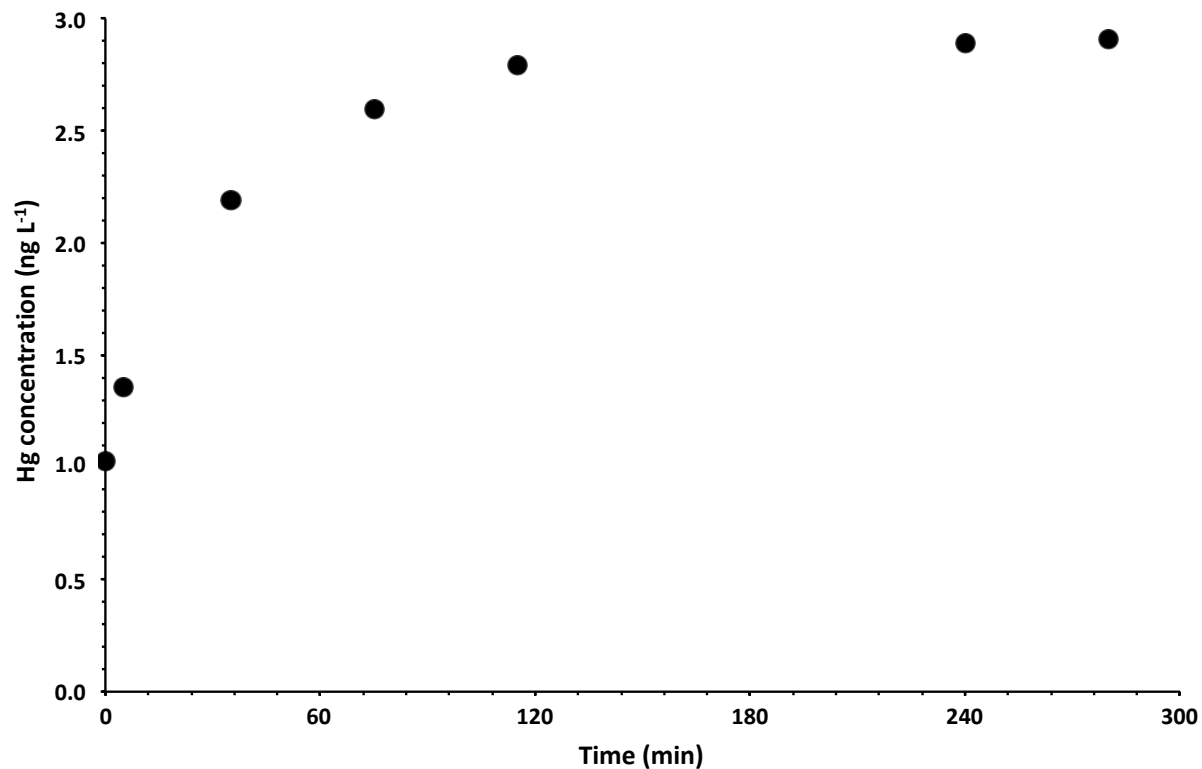


**Figure 2.** Initial Hg concentration measured after sampler loading with Hg-contaminated argon. Are shown only the initial Hg concentration for experiments including a 30 min preliminary flushing step during the loading experiment. The results for 6 different samplers are shown, as well as for the different tests conducted on each sampler.

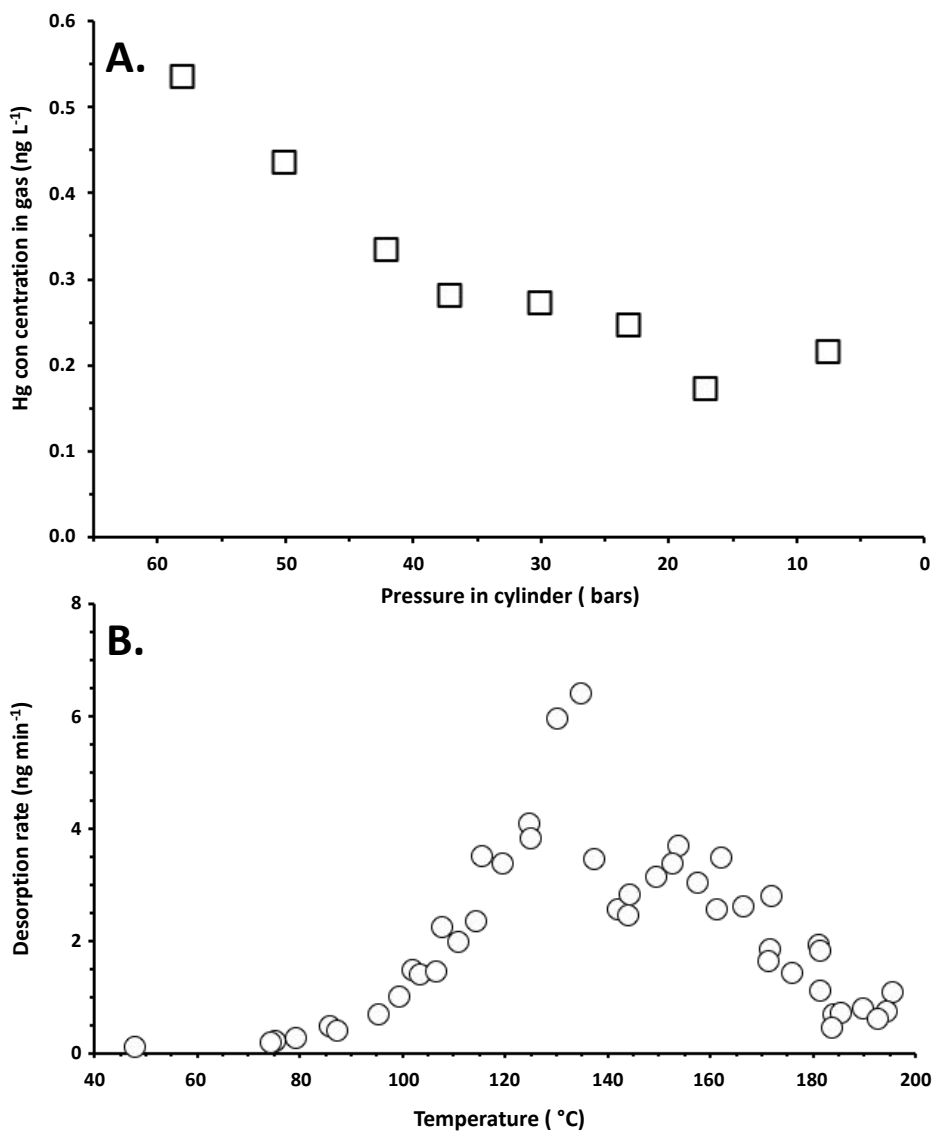


**Figure 3.** Gaseous Hg concentration variations over time during stability experiments conducted on (A) a new silicon-coated cylinder, (B) the old silicon-coated cylinders A and (C) B, (D) the PTFE-coated cylinder and (E) the Tedlar bag. Note the differences in the x-axis scale, especially for panel A (days unit compared to other panels in hours). Only the long-term test is shown for the new silicon-coated cylinder (panel A), and the

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3 results of short-term tests (1 and 2) can be found in supporting  
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5 information Figure S2.  
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**Figure 4.** Evolution of gaseous Hg concentration in the old silicon-coated cylinder A after loading with uncontaminated argon. This test was conducted after the five tests with contaminated argon (Figure 3B). The initial gaseous Hg concentration of 1 ng L<sup>-1</sup> is consistent with the system blank value.



**Figure 5.** Hg recovery during (A) purge and (B) heating the old silicon-coated cylinder B. Panel A shows the variations in gaseous Hg concentration during the purge of the silicon-coated cylinder B, shown as a gaseous Hg concentration as a function of the pressure left in the cylinder. Panel B illustrates the temperature dependence of Hg desorption rates.