Supporting Information

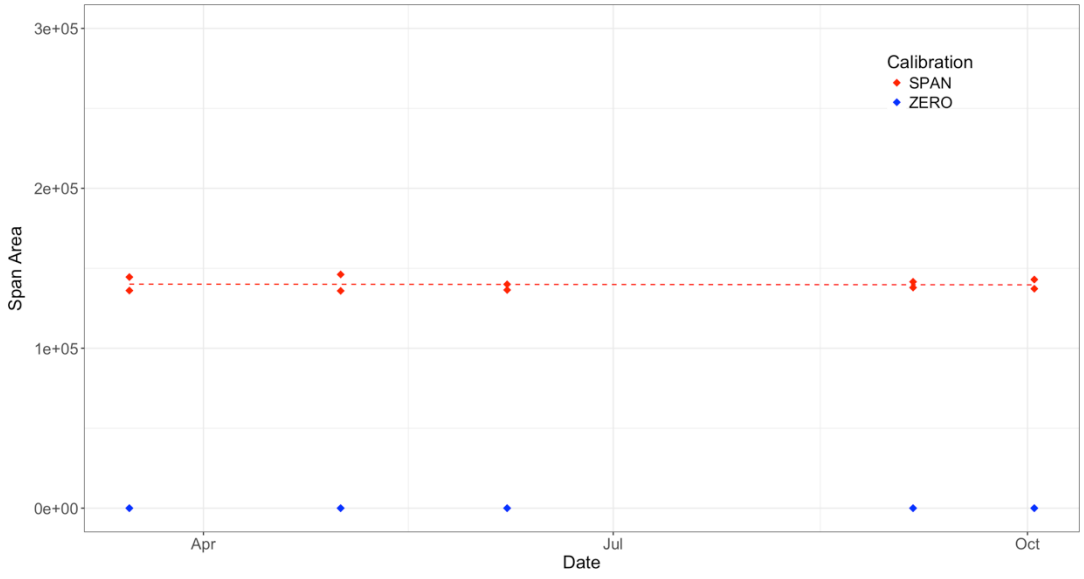
Evaluation of cation exchange membrane performance under exposure to high Hg^0 and $HgBr_2$ concentrations

Matthieu B. Miller[1*], Mae S. Gustin[2], Sarrah Dunham-Cheatham[2], Grant C. Edwards[1]

[1]Faculty of Science and Engineering, Department of Environmental Science, Macquarie University, Sydney, NSW, 2113, Australia
[2]Department of Natural Resources and Environmental Science, University of Nevada, Reno NV, 89557, United States

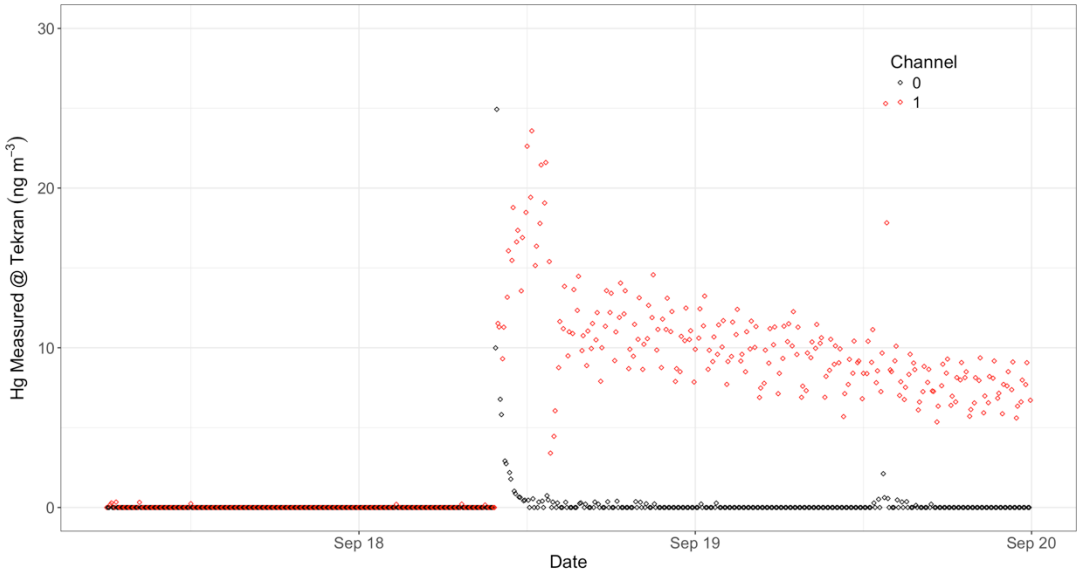
Tekran QA/QC

The Tekran 2537A unit operated consistently over the duration of study. All internal calibrations showed good analyzer zeros, and stable span areas (139875 ± 2.7%) with no drift (SI Fig. 1). The calibration data indicates that: 1) there was no Hg contamination within the 2537A unit, and 2) there was no passivation of the gold traps. Every calibration was also checked by external Hg vapor source injections. The system was not operated with a recurring automatic internal calibration, due to the variable timing of the experimental work.



SI Figure 1. Tekran 2537A internal calibration data for the duration of the study.

System blanks were performed by flowing scrubbed zero air through the entire path of the permeation system, which produced blank values below the Tekran® 2537A detection limit (< 0.1 ng m^{-3}, SI Fig. 2 as example). In addition, the system routinely zeroed out when deploying CEM filters on both sample lines during $HgBr_2$ permeations.



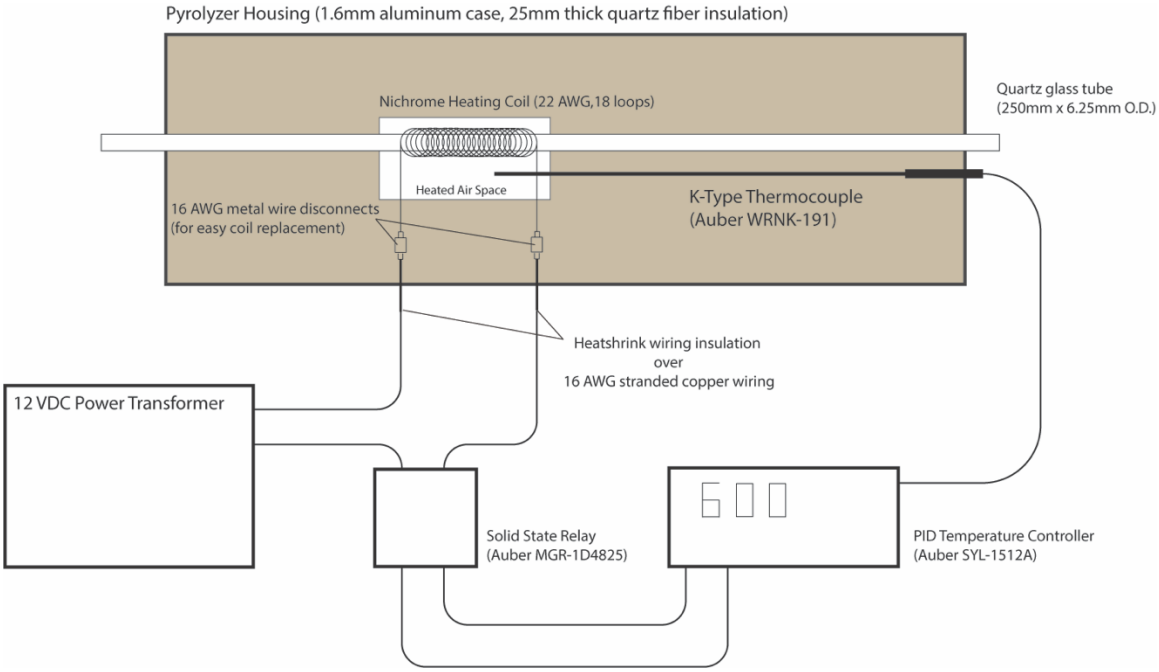
SI Figure 2. Example of system zero check prior to turning on $HgBr_2$ permeation source.

Pyrolyzer Design

The pyrolyzer used in the study (SI Fig. 3) consisted of a 25.4 cm long quartz glass tube of 0.625 cm diameter (custom, URG Corporation). A loosely packed 3 cm section of quartz wool was lodged in the mid-section of the tube, and this 3 cm section was wrapped with 22 gauge Nichrome wire (18 loops). The quartz tube was closely contained within 2.5 cm thick quartz fiber insulation within a 1.6 mm aluminum casing, except for an enclosed air space around the heated Nichrome coil section. The coil wire was connected to 16 AWG stranded copper wire with all metal disconnects, which were buried within the quartz fiber insulation to reduce thermal fatigue on the connections. The copper wire insulation was stripped and replaced with higher

temperature heat-shrink insulation where the wiring passed through the pyrolyzer case to the external power supply. The tip of a 150 mm long K-type thermocouple (Auber WRNK-191) was inserted through the insulation into the heated air space next to the coil to provide a temperature feedback for a PID controller (Auber SYL-1512A). Power to the Nichrome coil was supplied by a 12 VDC transformer through a solid-state relay (Auber MGR-1D4825) switched by the PID controller.

It was found that the position of the feedback thermocouple in the airspace outside of the heating coil caused a large discrepancy between nominal temperature setpoint and actual temperature inside the heated section of pyrolyzer tube. In general, much higher temperatures are achieved inside the coil than outside. To compensate for this, actual temperature at the heated coil section was verified to 600 °C by external IR sensor and internal thermocouple probe.

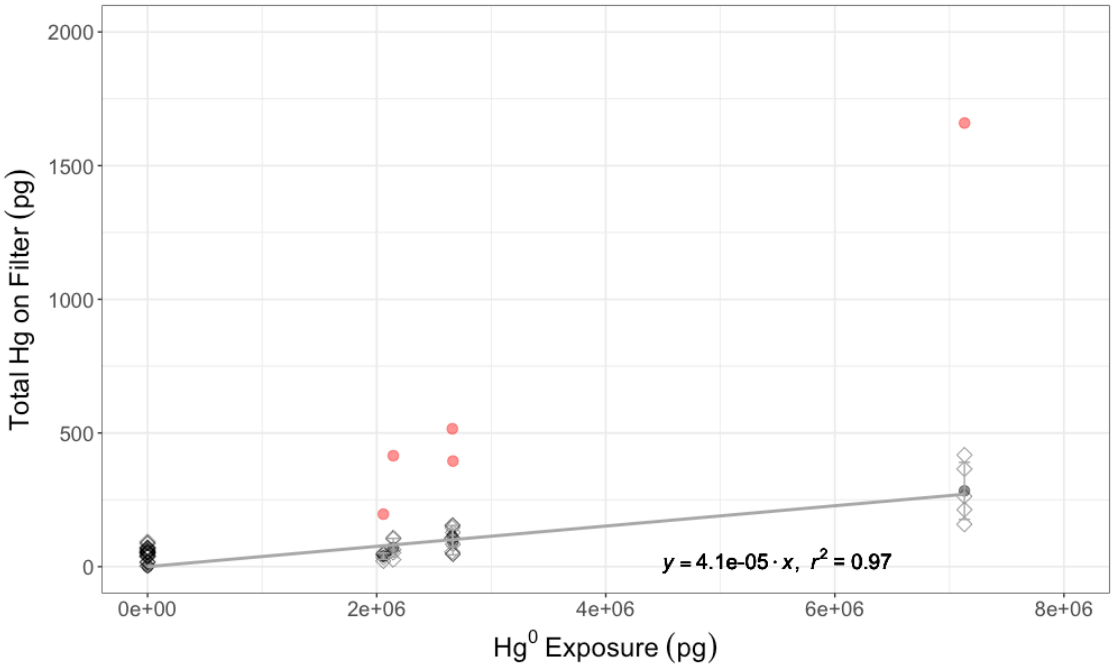


SI Figure 3. Detailed schematic of pyrolyzer design.

The pyrolyzer design used in this study was not 100% efficient at thermally reducing $HgBr_2$ to Hg^0, based on the higher total Hg recoveries on the CEM filters versus total Hg measured through the pyrolyzer on the Tekran 2537. A larger heated section, and higher temperatures than 600 °C would likely improve pyrolyzer efficiency.

GEM Permeation

The first CEM filter in line during the GEM permeations always showed more total Hg than the following 5 downstream filters, which were not significantly different from each other (SI Fig. 4). We believe it is unlikely that the Hg observed on the first CEM filters results from GEM uptake. Even at the highest GEM permeation level, the first filter captured only ~1700 pg of Hg, out of a total permeated amount of over 7.3 *million* pg (a 0.02 % uptake rate). This means that the downstream CEM filters were still exposed to about 7.2985 *million* pg of GEM but captured less total Hg. The most likely explanation is that the first CEM filters were scrubbing a small component of residual RM that was coming off the system, possibly minor oxidation of the Hg^0 bead. Therefore, the first in-line filters were not included in calculation of GEM uptake rates.



SI Figure 4. Hg on first in-line CEM filters (red circles) versus following downstream filters (open diamonds and regression line), during the 5 GEM permeations. These first filters were not used in calculations of GEM uptake, on the strong suspicion they were capturing a small component of residual RM.