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TECHNICAL NOTE

Analytical artifacts produced by a polycarbonate chamber compared to a Teflon chamber for measuring surface mercury fluxes

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Abstract We found significant differences in mercury fluxes measured with a dynamic surface mercury flux chamber made of Teflon versus one made of polycarbonate. While both materials responded reasonably well when virgin materials were used, the polycarbonate chamber was found to exhibit significant chamber blanks under light after it was exposed to surface mercury fluxes of >100 ng/m^2/h. Most significantly, the polycarbonate chamber blocked all wavelengths of light below ~320 nm. Given that ultraviolet radiation plays an important role in soil mercury flux, the polycarbonate chamber was found to significantly underestimate observed fluxes from background soil in both high light conditions (by 1–4-fold) and under diffuse, low light conditions (by ~10-fold). These results suggest that Teflon produces fewer analytical artifacts in the surface emission of mercury measured with a flux chamber than polycarbonate.

Keywords Atmosphere · Elemental mercury · Emission · Atomic fluorescence

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Introduction

The dynamic flux chamber is an accepted method for measuring mercury emissions from surfaces [1–4]. Early designs utilized Teflon as a chamber material due to its low blank values and resistance to contamination with mercury [1, 2, 4, 5]. However, in recent years, polycarbonate has gained acceptance as a chamber material as it also exhibits low blank values, is significantly less expensive than Teflon, and is a rigid polymer that allows for a much simpler chamber design than flexible Teflon sheets [6–13]. Polycarbonate chambers have been used in field studies to assess the effect of rainfall on surface emissions of mercury, to quantify mercury emissions from naturally enriched surfaces, to examine mercury fluxes in polar regions, and to study soil mercury flux in urban areas [6, 7, 9–11]. These chambers have also been used in laboratory studies to examine the effect of flushing flow rate on measured flux rates, the role of light wavelength in surface mercury emissions, and the effect of moisture on soil mercury flux [8, 12, 13].

Recent research suggests that ultraviolet light plays a significant role in the soil mercury emissions process [12, 14, 15]. Further, UV-B radiation has been implicated as the UV wavelength band that is most significant in the soil emissions process [15, 16]. UV-B radiation is a natural component of the solar spectrum and its role in the soil mercury flux process would be most significant in day-time field studies under full light conditions. However, polycarbonate is not transparent to all wavelengths of UV light, and transmits UV-B light poorly. Thus we examined the role that chamber material plays in producing analytical artifacts during the measurement of soil mercury emissions.

Methods

Surface mercury fluxes were measured with two similar dynamic flux chambers, one constructed of polycarbonate (Carlisle, Oklahoma City, OK, USA) and one of Teflon (Welch Fluorocarbon, Dover, NH, USA). Both chambers had a bottom surface area of 0.013 m^2, and similar internal volumes, with the Teflon funnel containing 0.58 l and the polycarbonate chamber 0.49 l. The two chambers had four inlet holes (0.1 cm^2 each) drilled in their side, and air was pulled through the chambers at a rate of 1.5 l/min through a 0.3 cm^2 outlet hole in the tops of the conical chambers. Surface fluxes were estimated by measuring both inlet and outlet total gaseous mercury concentrations for both chambers with a Tekran (Knoxville, TN, USA) mercury vapor analyzer (model 2537A) unit (sample flow rate = 1.5 l/min, sample time = 5 min) in conjunction with a Tekran automated sampling (TADS) system [17, 18]. In this method, mercury is monitored continually for five-minute increments, alternating between the inlet and outlet ports of the chamber. Fluxes are then estimated using the steady state flux calculation:

$$F = (C_o - C_i)Q/A \tag{1}$$

where C_o and C_i are the mercury vapor concentrations (ng/m^3) at the outlet and inlet, Q is the flushing flow rate (m^3/h), A is the surface area (m^2) of the base of the chamber, and F is the steady state flux ($ng/m^2/h$) [14]. All flux values are reported with a 95% confidence interval and the number of replicate measurements made (n). The minimum detectable flux based on the reproducibility of measurements between the gold traps was 0.04±0.03 $ng/m^2/h$ (n=21).

Daily calibration tests of the Tekran 2537A unit with an internal mercury source remained consistent during the sampling period, with the 95% confidence interval of all calibration measurements equaling approximately 1.5% of the mean calibration value. Monthly calibrations against an external mercury source confirmed that the Tekran readings remained consistent during the study; the difference between the external and internal sources equaled less than 2.48% of the mean calibration and was not significant at the 95% confidence level.

Incident radiation was measured with two instruments to obtain both PAR and UV-B intensity readings. PAR radiation (400–700 nm) was measured with a Li-Cor model LI-250 light meter connected to a Li-Cor pyranometer with an accuracy of ±5% (Li-Cor, Lincoln, NE, USA). This instrument has a broad range response; however, it does not effectively respond to radiation below 400 nm. As such, UV-B radiation was measured with a Multi-Sense MS100 optical radiometer with a MP-131 UV-B Sensor (UVP, Cambridge, UK). Surface temperature was measured with an infrared thermometer (Control Company, Friendswood, TX, USA) with an accuracy of ±2 °C.

Experiments were conducted under both controlled laboratory conditions and at a field location. Laboratory experiments were conducted under three conditions: dark, PAR lighting, and UV-B lighting. PAR lighting was supplied by a 250 W broad-spectrum metal halide grow lamp placed 30 cm above the samples (Garden Light III; Sun System, Vancouver, WA, USA). The lamp produced a PAR intensity (measured with the pyranometer) of 41.1 W/m^2 at the soil surface, and a UV-B intensity (measured with the radiometer) of 60 mW/m^2. UV-B lighting was supplied by a 2×15 W Spectroline model xx-15B UV-B lamp (Spectronics, Westbury, NY, USA). The UV-B lamp produced a PAR intensity (measured with the pyranometer) of 0.6 W/m^2 at the soil surface, and a UV-B intensity (measured with the radiometer) of 1180 mW/m^2.

As described below, fluxes were taken over three types of surfaces. Chamber blanks were conducted by placing the chambers over a clean piece of Teflon. Both chambers initially exhibited low blank contamination, and chamber blanks averaged 0.3±0.4 $ng/m^2/h$ (n=8) for the Teflon chamber and 1.1±1.4 $ng/m^2/h$ (n=10) for the polycarbonate chamber. The difference between the two chamber blanks was not significant at the 95% confidence level.

Laboratory measurements were also made over a mercury-sand sample that was created by mixing 20 g of laboratory-grade silicon dioxide sand with a particle size range of 0.5–10 μm (>90%, and ~80% 1–5 μm) (Sigma-Aldrich, St. Louis, MO, USA) with 5 ml of high-purity Milli-Q water (prepared with a Millipore Elix system, Bedford, MA, USA) to which 3×10^{-7} g of mercury as the $HgCl_2$ salt had been added. This mixture was spread to a depth of approximately 1 mm and an area of ~0.01 m^2 on a clean sheet of Teflon and allowed to air-dry. The final concentration of mercury in the sand sample was calculated to be 0.015 ppm. Sand samples were sent out for confirmatory mercury analysis for which the average total Hg concentration was found to be 0.014±0.001 ppm (Studio Geochimica, Seattle, WA, USA). Sand samples were also analyzed by headspace analysis for elemental mercury (Hg^0) and all samples were below detection limits for Hg^0.

Field measurements were made over an open-field soil plot from which surface vegetation had been removed at the Blackrock Research Forest in Cornwall, NY, USA, located in the Hudson River valley approximately 50 miles north of New York City. Soil at the site was sampled and analyzed for mercury at two depths: surface soil was a composite of soil from 0–5 cm and below-surface soil was a composite from 5–10 cm. Four soil cores were analyzed for mercury (Studio Geochimica) and total mercury in surface soil averaged 0.064±0.01 ppm while below-surface soil averaged 0.051±0.003 ppm. The difference between mercury concentrations in the surface and below-surface samples was not significant at the 90% confidence level. All soil

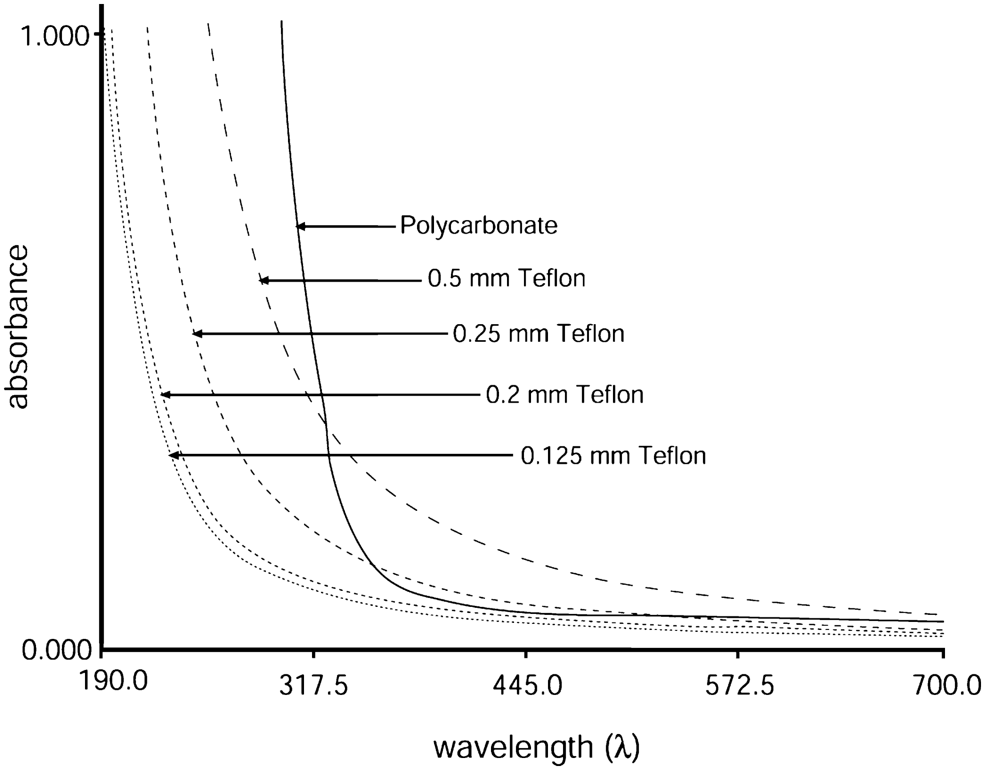

Fig. 1 Absorbance spectra for polycarbonate and four different thicknesses of Teflon film

samples were analyzed by headspace analysis for Hg^0 and all samples were below detection limits for Hg^0.

Results

To determine the spectral transmissions of the different chamber polymers, we measured light absorbance in the wavelength range of 190–700 nm using a UV 2100 U UV-Vis dual-beam recording spectrophotometer (Shimadzu, Columbia, MD, USA). Because the transmission of light through Teflon varies with polymer thickness, we tested several samples of Teflon film (Fig. 1; personal communication, E. Welch from Welch Fluorocarbon, Dover, NH, USA, October 2006). As seen in Fig. 1, polycarbonate blocks all wavelengths of light below ~320 nm. While light

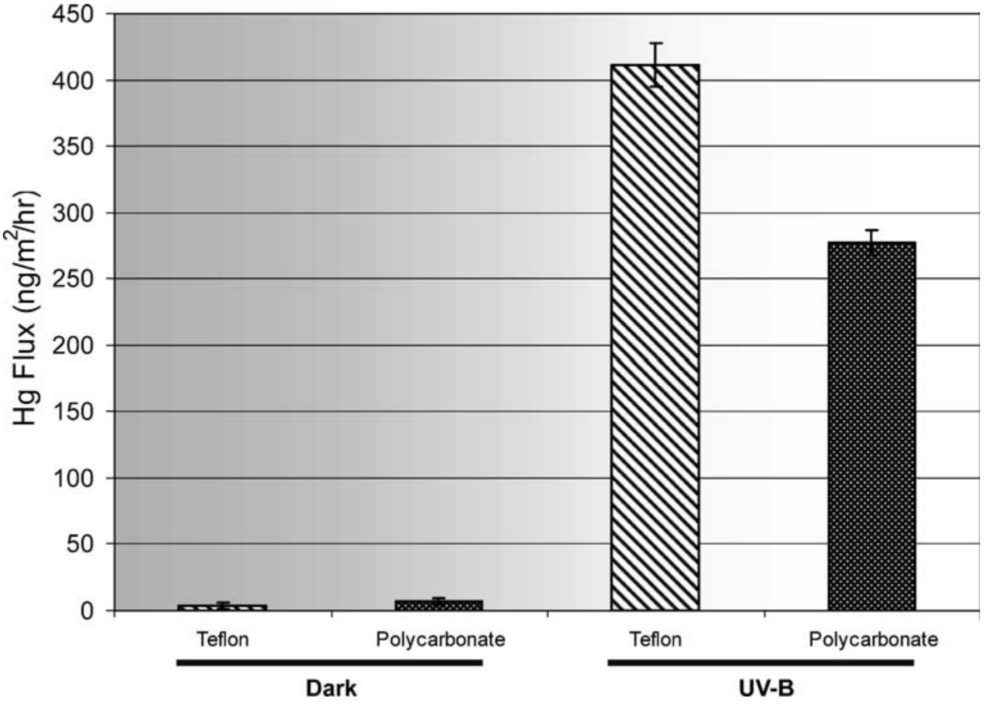

Fig. 2 Mean mercury fluxes ±95% CI ($n \geq 12$) measured using a Teflon and polycarbonate chamber in the dark and under UV-B light over a sand sample treated with 0.015 ppm Hg as the $HgCl_2$ salt

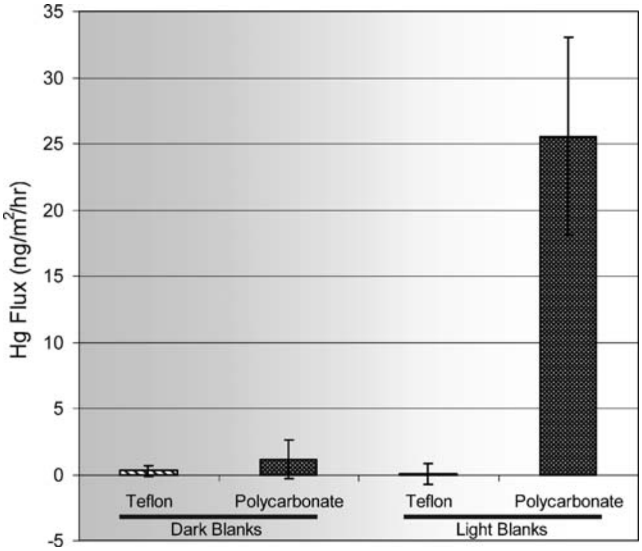

Fig. 3 Mean mercury fluxes ±95% CI ($n \geq 8$) for chamber blanks run in the dark and light with the Teflon and polycarbonate chambers following exposure to high mercury levels shown in Fig. 2

transmission through Teflon varied, the 0.5-mm-thick film proved at least partially transparent to wavelengths below 300 nm, the 0.25-mm film transmitted well down to 250 nm, and the 0.125- and 0.2-mm films showed transparency down to 190-nm wavelengths.

For the purpose of this study, we used a Teflon chamber with a wall thickness of ~0.5 mm. Both the polycarbonate (~2.5 mm thick) and Teflon chambers transmitted a large percentage of the PAR radiation (92% and 96%, respectively). However, the chambers differed significantly in their transmission of UV-B light, with the polycarbonate transmitting <26% of measured UV-B radiation and Teflon transmitting >73%.

We conducted sequential laboratory comparisons of our Teflon chamber with the polycarbonate chamber. Fluxes of mercury from sand treated with 0.015 ppm Hg as the $HgCl_2$ salt were measured in the dark and under UV-B lighting. As seen in Fig. 2, surface fluxes measured under the Teflon and polycarbonate chambers were similar in the dark [4.1±2.4 (n=16) and 7.1±2.2 (n=12) ng/m^2/h Hg, respectively, not significant at the 95% confidence level]; however, fluxes measured under UV-B light were significantly higher with the Teflon chamber [411±17 (n=12) versus 277±9 (n=16) ng/m^2/h Hg, significant at the 99.9% confidence level].

Further problems were seen with the polycarbonate chamber following the experiment just described. Subsequent to the exposure of the chambers to high levels of mercury, when chamber blanks were run under dark conditions, both polymers showed low blank values that were not significantly different from zero. However, when exposed to light, the polycarbonate exhibited high blank contamination, while the Teflon continued to exhibit a blank that was not significantly different from zero (Fig. 3).

To examine the effect of the chamber material on real field surface emissions, we then conducted side-by-side measurements with a clean Teflon chamber and a polycarbonate chamber over a field soil plot. As seen in Fig. 4, the polycarbonate chamber underestimated surface mercury

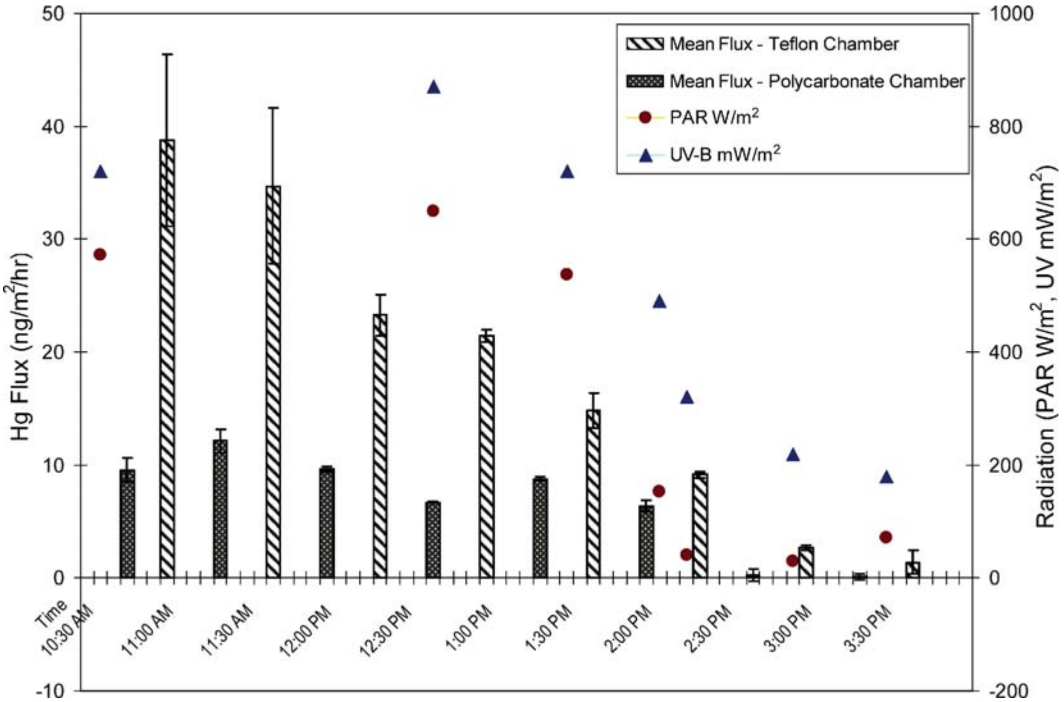

Fig. 4 Mean soil mercury flux± 95% CI (n=2) at a field research site in Cornwall, NY, USA, measured on 27 October 2006 (EDT) with side-by-side polycarbonate (*gray dot*) and Teflon (*diagonal stripe*) surface chambers (*left axis*). PAR radiation intensity (W/m^2, *solid circles*) and UV-B radiation intensity (mW/m^2, *solid triangles*) are plotted according to the *right side axis*

fluxes at all times throughout the day. Under high light conditions between 10:30 am and 1:30 pm (Eastern Daylight Time), the polycarbonate chamber gave a flat response of mercury flux to light, whereas the Teflon chamber recorded fluxes that were proportional to incident radiation, as has been reported in other studies [5, 19]. At approximately 2 pm, cloud cover increased significantly in the area and incident radiation fell precipitously (Fig. 4). Fluxes measured with the polycarbonate chamber decreased in a single step and remained nonsignificantly different to zero under full cloud cover (95% confidence). Conversely, fluxes measured with the Teflon chamber decreased in proportion to light intensity (and UV-B intensity) and remained significantly greater than zero at all times (95% confidence).

Discussion

An ideal surface flux chamber affects the microenvironment within that chamber as little as possible. This work demonstrates that polycarbonate significantly affects both the spectrum of light reaching the surface below the chamber (in particular UV) and the emission of mercury from surfaces both in the laboratory and in real field settings. In other work that compared polycarbonate to Teflon chambers, only average site flux values were compared, and diel measurements made by different chambers, each at different locations with different substrate mercury concentrations, were compared [7]. Thus, it may be that the subtle differences seen between the chambers in this study were not identified.

This work implies that polycarbonate chambers in high light conditions may underestimate surface soil fluxes by 100–400%. This work also suggests that under low, diffuse light conditions, such as below a forest canopy, the polycarbonate chamber may erroneously measure soil fluxes that are not significantly different from zero even when naturally occurring fluxes are significantly greater than zero.

This work demonstrates that all surface flux chamber measurements should be conducted with a chamber that is transparent to UV radiation. While any material that is UV-transparent and exhibits low blank contamination would be appropriate, given the transparency of Teflon to a wide range of radiation wavelengths, we are currently working to design a Teflon surface chamber with walls ≤0.25 mm for surface mercury flux measurements (Welch Fluorocarbon, Dover, NH, USA). Research with this redesigned surface mercury flux chamber is currently underway.

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