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Mercury speciation in natural waters: Measurement of dissolved gaseous mercury with a field analyzer

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Abstract. Mercury evasion from water is commonly modeled using measurements of dissolved gaseous mercury (DGM). We developed a method using a recently available automated field-ready mercury vapor analyzer to rapidly measure the concentrations of DGM in surface waters. We summarize here results of laboratory tests of the method, field intercomparisons with a manual method, and selected data from recent sampling campaigns in Florida and Michigan. The method uses the 1.5 lpm flow of a Tekran® Model 2537A mercury analyzer to purge and analyze discrete water samples, generating near real time (5-min) data on DGM in samples and blanks. Application of the Tekran allowed for detailed analysis of DGM removal kinetics and short-term diel studies characterizing the influence of sunlight and precipitation on DGM production in surface waters. Gas removal kinetics for dozens of samples indicates a first-order rate constant, and supports a 20-min. purge time for surface water samples from Florida (40-min for Michigan samples). Blanks are measured during a second such purge. Our results indicate that DGMs determined by both automated and manual methods are generally comparable, and that DGM in Florida samples is unstable during storage (loss rate constant $\sim$0.1–0.2 h^{-1}), probably due to oxidation. This suggests that rapid in-field analysis is preferred to storage with delayed analysis. Our data indicate that DGM at the Florida site is influenced by inputs of reactive Hg in rainwater, and by production of surface DGM during photoreduction of oxidized Hg in the water column.

Introduction

Atmospheric mercury is deposited by wet and dry processes to environmental surfaces, and the importance of air/surface exchange processes in the cycling

of Hg in aquatic ecosystems is well known (e.g. Expert Panel 1994). Because of its volatility, mercury is unique among the trace metals in its cycling in the environment, and we now understand its ability to be emitted (or re-emitted) from surfaces once deposited. This can significantly influence its persistence in both terrestrial and aquatic systems, and Hg emission from surface waters could limit the formation of methylmercury (Fitzgerald et al. 1994). Mercury emissions have been widely reported from surface waters in both marine and freshwater systems (e.g. Baeyens et al. 1991; Vandal et al. 1991). The mechanism of Hg emission from water (termed evasion) may be biologically mediated, but recent evidence suggests an important role for direct photochemical reduction of Hg^{2+} species to dissolved elemental mercury vapor (Hg°) (Xiao et al. 1995; Amyot et al. 1994). Dissolved gaseous mercury (DGM) measurements are important in estimating mercury evasion rates from water (Gill & Fitzgerald 1987). Some models suggest that evasion could be a major source of mercury to the troposphere on the global scale (Mason et al. 1994).

Evasion is commonly estimated using a stagnant film model (a two-layer gas transfer approach) with measurements of DGM (e.g., Fitzgerald et al. 1994). Fluxes are then derived by application of a simple equilibrium partitioning model based on the Henry's Law constant, or by a two-layer gas exchange model based on the measured concentration gradient across the air/water interface (e.g., Kim & Fitzgerald 1986; Schroeder & Fanaki 1988). Surface fluxes have also been directly measured with dynamic chambers (e.g., Xiao et al. 1991) and micrometeorological techniques (Lindberg et al. 1996). Using field measurements, Xiao et al. (1991) and Lindberg et al. (1996) found that midsummer evasion rates are of the same order as deposition rates for Swedish oligotrophic forest lakes including Lake Gardsjön. Estimates of longer term fluxes by these authors suggested that evasion could equal or exceed total deposition over time periods from a month (Lindberg) to a year (Xiao). Schroeder et al. (1995) recently suggested that annual evasion rates could range from $\sim$40 to 90% of deposition rates in Lakes Ontario and Superior. Earlier whole-lake estimates of Hg evasion from the Great Lakes varied from $\sim$0.2 t/y to $\sim$8 t/y for Lakes Superior and Erie, respectively (as summarized in Shannon & Voldner 1995). More recently, these authors modeled evasion from the five Great Lakes and reported fluxes ranging from $\sim$50 to $>$200% of atmospheric loading to the overall water surface (Shannon & Voldner 1995). It is clearly important to verify the scale of these flux estimates, and measurements of DGM are critical in this regard.

The commonly used manual method for DGM involves purging water samples with Hg-free nitrogen gas under pressure, and collection of the removed DGM on gold-coated sand amalgamation traps for subsequent

laboratory analysis (e.g., Vandal 1991). In some previous studies, samples were routinely collected in the field, stored for some hours in Teflon bottles in the dark under sub-ambient temperature, transferred to the laboratory, and then purged under pressure onto gold traps to remove DGM (Krabbenhoft et al. 1998). In addition to potential speciation changes in stored samples, other disadvantages of published methods include slow turnaround of the data, delayed detection of contamination, and longer purging times, leading to a lower time resolution for experimental studies. In addition, with the pressurized purge and trap method it is possible for some loss of DGM to occur without detection, leading to data which are biased low.

In 1995, we initiated measurements of Hg fluxes over waters near the Florida Everglades using flux chamber (FC), micrometeorological, and thin-film modeling approaches. As part of this work, we developed new methods for rapid in-field flux (Lindberg et al. 1999) and aqueous speciation measurements utilizing a recently available near-real time mercury monitoring device. We report here tests and applications of a method for analysis of DGM in surface waters using a Tekran® Mercury Vapor Analyzer which has several advantages over commonly used manual sampling methods. Our tests of the method in Florida suggest that DGM may not be stable in samples stored in Teflon bottles over periods of several hours, due to either oxidation, adsorption, or degassing of the DGM through the teflon, and that automated in-field methods of DGM analysis are preferred. A detailed presentation of the complete DGM data set collected from the Florida site with these methods is available (Lindberg et al. 1999).

Methods and sites

Rationale. We developed the Tekran Automated Purging System (TAPS) to alleviate the need for extended storage, and to allow for the relatively "rapid" (<1 h) analysis of sequential samples needed for diel studies, and studies of the effects of solar radiation and precipitation events on DGM production in surface waters. By providing "near-real-time" concentration data (<1 h for sample plus blank), the TAPS method also affords the important advantages of in-field blank determinations, and immediate feedback on the vacuum integrity of the purging apparatus. With the vacuum-based TAPS method, a leak in the purging vessel is quickly detectable in the instrument readout by the presence of elevated Hg° introduced into the sample from ambient air (while this works well in low-DGM systems such as those studied here, it may be less useful where the DGM and ambient air signals are comparable; however, leaks will always be immediately apparent in the purge blanks). The ability to quantify field blanks can also preclude the loss of data from

contaminated purging and sampling vessels which might otherwise remain undetected until a later time during analysis.

The Tekran Mercury Vapor Analyzer was introduced in 1993 and has gained wide use as a field and laboratory monitoring device (e.g., Schroeder et al. 1995). The device uses now-routine gold-trap and cold-vapor atomic fluorescence spectroscopic (CVAFS) analytical methods to analyze Hg vapor in ambient air, providing continuous sequential analyses of samples collected over periods of ~5 min. The advantages of applying the Tekran to more sophisticated studies has become clear, and several groups have published such approaches for direct measurement of Hg° fluxes over surfaces (e.g., Poissant & Casimir 1998; Lindberg & Price 1999). To our knowledge, this paper is the first published application of the Tekran to aquatic speciation analyses such as DGM.

Sites. We collected surface water samples for these tests at sites in Florida and Michigan during August 1996 and 1997 (MI) and April–November, 1996 (FL) [some FL data from March 1998 was added in press]. Samples in Florida were collected upflow from wooden platforms anchored in the sediment at the site of the Everglades Nutrient Removal (ENR) Project. The ENR is adjacent to the Loxahatchee Wildlife Refuge on the northern perimeter of Florida's Everglades, and was developed as an experimental wetlands by the South Florida Water Management District for use as a storm water treatment area (Guardo et al. 1995). For reasons not yet completely clear, DGM levels in the ENR are among the lowest reported in the literature (Lindberg et al. 1999; c.f. Vandal et al. 1991), providing a challenging test of the methods described here. In Michigan, surface water samples were collected on Burt Lake from a wooden platform 50 m offshore. Burt Lake is a clear, oligotrophic inland lake located in northern Michigan. Samples were also collected from Lakes Michigan and Superior at depths of 1–10 meters below the surface. The EPA R/V Lake Guardian was stationed 2–50 km offshore while a small boat was deployed ~1 km from the R/V to avoid contamination. The DGM levels in freshwater lakes in the Great Lakes region (e.g., Vandal et al. 1991) are consistent with those reported in the literature, and allowed for detailed analysis of DGM removal kinetics using the TAPS method.

Approach. All materials used for Hg sampling or storage were cleaned in the laboratory prior to deployment in the field either by rigorous acid washing (UM glass and all teflon) or acid washing plus high-temperature firing (ORNL glass bottles) as described elsewhere (Landis & Keeler 1997; Lindberg 1996). Surface water samples were manually collected in the field

using clean handling methods (e.g., Cleckner 1995). In Florida, surface water samples for DGM were collected by completely filling the 2.2 L Teflon bottle (no headspace) and sealing with a solid Teflon cap (the bottle was rinsed three times with site water before filling the final time). The bottle was filled by gently dipping it directly into the water column, or by using a well-rinsed peristaltic pump system to transfer the sample from depth. We used blank-tested replicate bottles to collect side-by-side samples for storage tests. One of the pair was connected to the TAPs and purged immediately, while the other was stored in an ice cooler kept in the dark at ambient water temperature for several hours. Water samples in Michigan were similarly collected as surface grab samples (Burt Lake, MI) or by using a peristaltic pump (Lakes Michigan and Superior).

After collection, all sample bottles were wrapped in black plastic to eliminate photolytic reactions, and were immediately transferred to the onsite field laboratory (trailers or vans; we also developed an air-conditioned container to house a Tekran at remote sampling platforms) for analysis by methods described below. Samples were generally purged within 10–30 minutes. Working in minimal light, the sample volume was adjusted by removing water to a pre-determined line on the Teflon or glass bottle, the vessels were sealed as illustrated below, placed in an ambient temperature water bath, and protected from light before DGM purging was initiated. In both methods, the DGM concentration is computed from the difference between the two successive sample and blank purges.

The purging apparatus initially used with both approaches consisted of a 2.2 L bottle with a cover with two, 1/4" ID transfer port fittings (illustrated in Figure 1a) and was completely constructed of PFA Teflon®. A gas dispersion tube with a coarse glass frit was attached to Teflon tubing (the MI apparatus used Teflon tubing with pin-holes in place of the glass frit). The tubing was sealed in the inlet transfer port such that the frit was near the bottom of the bottle and a short portion extended above the fitting to attach to the Hg-free purge gas (N_2 or air). An iodated, activated carbon trap (e.g., Lindberg 1981) was attached to the inlet port to supply Hg-free air in TAPS mode, while a gold coated sand or bead trap was used to supply Hg-free N_2 in the manual purge mode. Teflon tubing extended through the outlet port fitting for attachment either to the Tekran or to a gold sampling trap. The bottle was sealed by hand-tightening followed by clamping with a high-pressure, stainless steel clamp. We have since determined using the Tekran to "sniff" the sample that the bottle cover can be sealed positively by hand tightening (this holds for vacuum purging with TAPS only).

For purging with the *Tekran Automated Purge System (TAPS)*, the inlet line to the Tekran analyzer was connected directly to the outlet line from

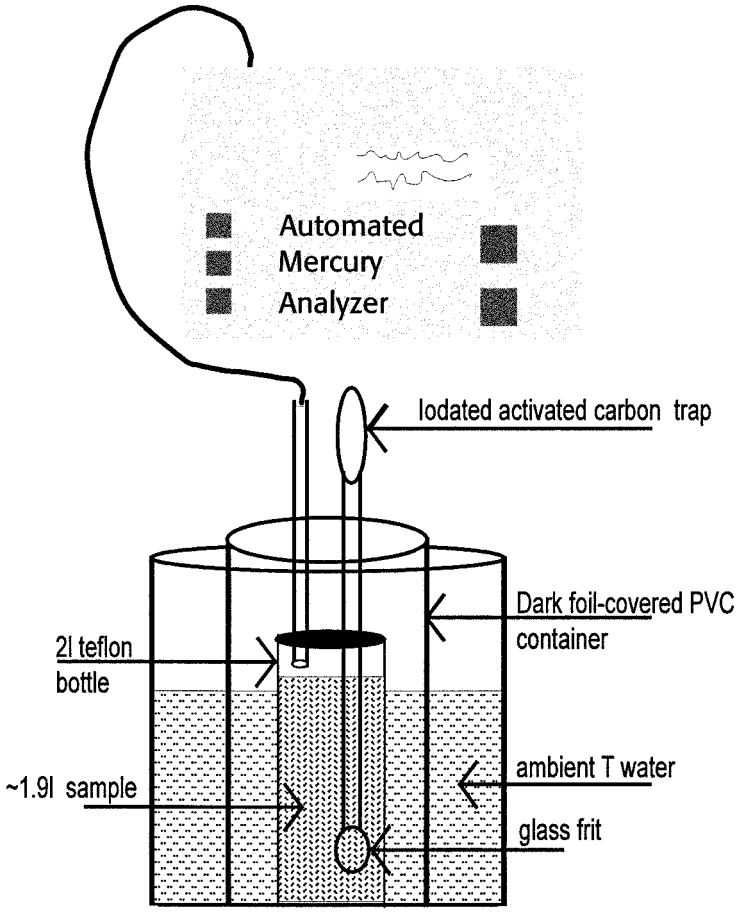

Figure 1. (a) Schematic of the Tekran Automated Purge System (TAPS) developed for in-field determination of mercury speciation in water. Operation is described in the text. The dimensions of the teflon purging vessel are 10×24 cm.

the purge bottle (Figure 1(a)) at the beginning of a discrete air sampling sequence. The Tekran mercury vapor analyzer was operated in the normal 5-min sample collection mode (see below). For the Florida samples eight, 5 min purge samples at a flow rate of 1.5 L/min were collected for a total 40 min run time (20-min sample, 20-min blank for a total of 60 L gas flow, yielding a purge gas/water volume ratio $\sim$30). Longer purge times were necessary for the samples collected in Michigan for which the DGM levels were much higher than those collected in Florida. Twelve, 5 min. purge samples were collected for a total 60 min. run time or 90 L total gas (40-min. sample, 20-min. blank, gas/water volume ratio $\sim$45). The iodated activated carbon trap

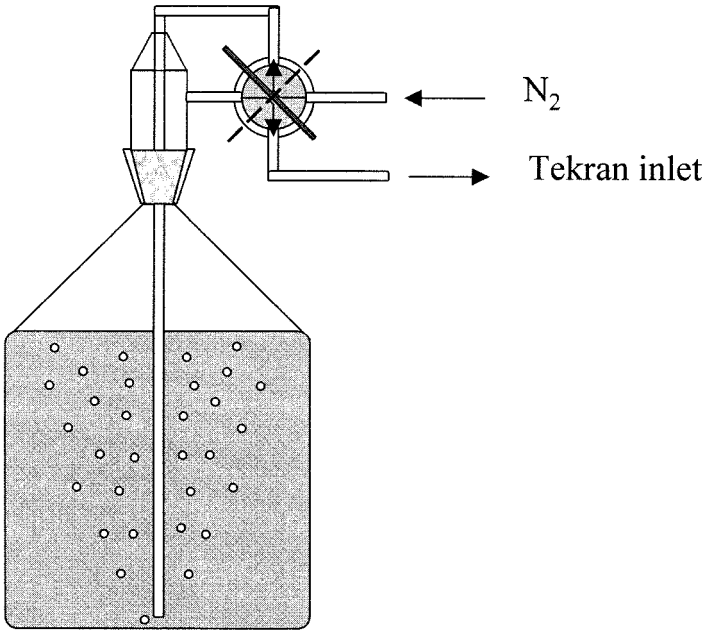

Figure 1. (b) Glass purging apparatus used with the TAPS shown in sample purge mode. The dashed line indicates the position of the stopcock in tubing flush mode.

connected to the purge bottle inlet supplied clean ambient air for purging (the blank value is readily tested prior to sampling by purging the dry sample bottle into the Tekran; the values are often below detection, ∼0.5 pg, and generally <2 pg, e.g., see Figure 3 below).

The TAPS method was also used in Michigan to evaluate an all glass sampling and analysis design. The apparatus shown in Figure 1b included a 2 L glass bottle and impinger with ground glass joints. Samples were purged with Hg-free N_2 supplied through a 0.5 psi regulator (part of the Tekran zero gas supply). A glass impinger with a 4-way Teflon stopcock and long glass tube was attached to the bottle with the tube ∼1 cm from the bottom. The stopcock allowed N_2 to flow to the Tekran inlet in either sample purge mode or tubing flush mode. In sample purge mode (Figure 1(b)) Hg-free N_2 flowed into the sample through the top of the stopcock and down the long glass tube. The DGM was removed from solution by N_2, and flushed through the bottom of the stopcock into the Tekran. In tubing flush mode Hg-free N_2 flowed through the stopcock directly into the Tekran bypassing the sample (indicated in Figure 1(b) by a dashed line). This flushing of the inlet tubing eliminated the signal from ambient air before a sample was purged. This mode also

provided a quantitative leak check before sampling, yielding generally lower system blanks than other approaches.

For purging with the *manual pressure method*, nitrogen gas was supplied through silicone tubing into the Teflon or glass bottle through a gold-coated sand/bead trap. A gold-coated sand/bead trap was connected to the outlet with Teflon tubing to collect the purged DGM. In Florida, samples were purged onto gold-coated traps at 0.75 L N_2/min for 40 min followed by another 40 min for a blank sample (60 L total gas). Samples from Lake Michigan were purged onto gold-coated bead traps at 0.5 L N_2/min for 90 min followed by another 90 min for blanks (90 L total gas).

In the manual method, the reusable gold-coated quartz sand or bead traps (a quartz tube with Teflon tubing on both ends) were pre-blanked by heating to ∼450 °C prior to use and sealed with Teflon plugs. The traps efficiently collect known forms of gaseous mercury by amalgamation and adsorption on the gold coating. After return to our primary laboratory (usually within 5 d) the gold traps were analyzed for Hg° by dual-amalgamation cold vapor atomic fluorescence spectrometry (CVAFS) using methods modified for the ORNL lab (Lindberg et al. 1995). The CVAFS system was calibrated using a gas-tight microsyringe to inject Hg°-saturated air from a constant temperature bath onto a gold trap. This procedure yielded very high precision (<0.5% relative standard error based on 6 replicate injections over 6h, using peak-area integration). The absolute detection limit for Hg° (three times the instrumental noise) is ∼0.2 pg, and the working limit in our lab based on gold trap blanks is ∼1–2 pg (compared to typical DGM sample signals of 10–100 pg). All handling and analysis of gold traps in our laboratory was done in class 100 laminar flow clean air benches (particulate Hg <0.001 ng/m^3, Hg° ∼5–8 ng/m^3). Similar details on the UMAQL laboratory are available (Vette 1998).

Tekran operation. The Tekran Model 2537A Mercury Vapor Analyzer provides an automated implementation of the gold preconcentration/CVAFS analysis method (Fitzgerald et al. 1979). The analyzer has been commercially available since 1993 (Ng et al. 1993) and has been subject to a number of intercomparison studies (Schroeder et al. 1994; Schroeder et al. 1995; Ebinghaus et al. 1999). The analyzer utilizes a pure gold trap rather than coated sand and uses single stage rather than two stage preconcentration. Figure 2 shows a simplified flow diagram. The Tekran normally can be operated for several hours on a 12v battery/inverter system, and with lecture bottles of Ar and activated carbon scrubbers to provide zero air, the unit can be made relatively portable (e.g., Lindberg & Price 1999).

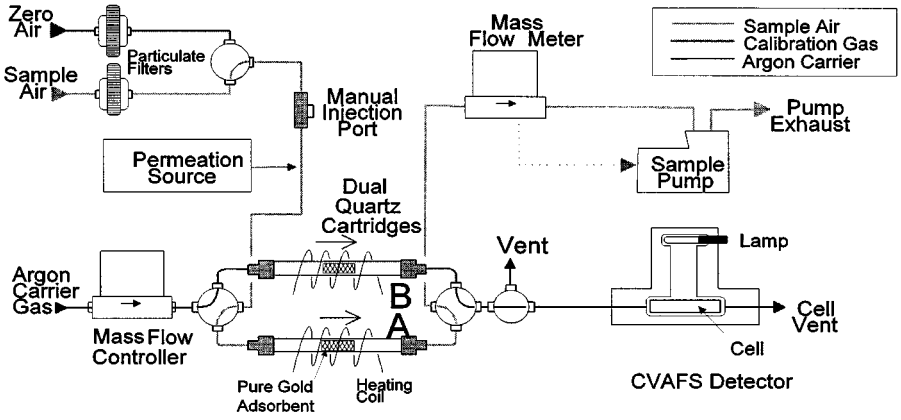

Figure 2. Schematic flow diagram of Tekran® automated mercury analyzer.

Sample air is drawn through a 47 mm dia., 0.2 μm poresize Teflon® particulate filter membrane (Cole Parmer). A teflon solenoid valve is used to select either the sample air stream, or zero air for calibration purposes. A dual cartridge arrangement is provided to allow for simultaneous sampling and analysis on alternate traps, yielding continuous monitoring of the sample stream (e.g., while one trap samples the purged DGM, the other trap is desorbed and analyzed as outlined below). Each cartridge contains a proprietary arrangement of solid gold adsorbent within a 0.6 by 13 cm quartz tube. Unlike gold coated traps, this design is capable of withstanding hundreds of thousands of collection/thermal desorption cycles. Two four-way teflon solenoid valves are switched together to alternately feed sample air or UHP argon carrier gas into the sampling cartridges. A mass flow meter (Tylan) monitors the sample flow rate. A feedback circuit controls the pump speed to maintain a preset flow rate of 1.5 lpm. All volumes are referenced to 0 °C, 760 mm Hg.

A mass flow controller (Tylan) is used to set the carrier flow to optimal values for the various stages of each desorption cycle. The carrier gas is passed through the cartridge undergoing analysis and into a teflon bypass solenoid valve. The carrier gas is vented to atmosphere during the initial "HiFlush" period of analysis. During this period, the cartridge still contains appreciable amounts of sample air and venting this mixture to atmosphere greatly reduces contamination of the detector surfaces. Once the cartridge undergoing analysis has been purged of air, the solenoid is turned off and the carrier gas passes through to the detector. Captured mercury is thermally desorbed from the cartridge by a resistive heater. The response of the detector is integrated to provide a quantitative measure of the amount of mercury that

Table 1. Timing parameters for the Tekran sampling and desorption cycle used for this study.

Step name	Duration (sec)	Flow ml/min	Notes
Sample	300	1500, Air	Sampling on one cartridge occurs in parallel with desorption of the other cartridge. The roles of the cartridges are then reversed. The desorption stages are shown below.
HiFlush	60	100, Argon	Removes air from cartridge. The vent solenoid is **ON** during this period only.
Baseline	10	80, Argon	Measures baseline during a quiescent period to determine instrument background noise level.
Heating	28	80, Argon	Ballistic heating of cartridge to >500 °C.
Peak delay	35	80, Argon	This period allows time for the peak to elute completely after heating has terminated. The peak is integrated by the instrument and calculations performed to yield total pg or ng/m^3.
Cool down	80	80, Argon	This enforced delay ensures that the cartridge has cooled sufficiently to trap mercury when it is called upon to sample again.
Idle	Balance	5, Argon	After the desorption cycle is complete, the cartridge idles until the sampling period on the other cartridge has elapsed.

was desorbed. Table 1 summarizes the operational parameters for the Tekran as used in this study.

Automated periodic recalibrations are provided using an internal permeation source. Two point calibrations (zero and span) are performed separately for each cartridge. The permeation tube (VICI Metronics) provides approximately 1 pg/sec at +50.0 °C. It is not practical to certify these low rates gravimetrically, so manual injections are used to initially calibrate the tube against a saturated mercury vapor standard (Dumarey 1985).

Preparation and storage of sample bottles Between sampling, collection bottles were stored in the field with purged sample water. We discovered that bottles which had been initially cleaned by treatment in an ambient temperature or boiling acid bath, stored in the lab, and then filled with sample water were found to yield unusually high DGM concentrations. Presumably, mercury vapor from indoor air permeated the thick Teflon bottle material and

was released during purging. However, after extended purging during which a few samples were processed in these bottles, typical and reproducible data could be obtained with these same bottles. Thus, bottles were stored with purged onsite water between sampling events and were pre-purged to remove accumulated mercury vapor at the start of a sampling day (for ~15 min). With the Tekran method it was a rapid process to detect contaminated bottles, and this was done routinely before each new site was sampled. When bottles began to show noticeable surface residue, they were cleaned by acid bathing and then reconditioned for use.

Results and discussion

DGM purging kinetics, blanks, and TAPS operation. The collection of 5-min DGM purge concentrations by the TAPS method provides useful data with which to evaluate the efficiency of this purging approach, as well as information on the kinetics of DGM removal from various samples. The method may also be used to measure DGM production rates under controlled conditions, as discussed below. Figures 3a and b show typical examples of the purging curve for DGM removal from surface waters at each site. To date, we have seen this same behavior in >99% of ~200 samples from FL and MI analyzed with the TAPS method. The initial portion of Figure 3a and b (time < 0) illustrates the purge jar blank, generated by sampling charcoal-filtered air through the empty purge jar (the initial peak represents the air within the empty bottle which is not part of the actual blank). As soon as good zeros are achieved, the sample is introduced, and DGM purging is initiated (T_0). The resulting curves clearly show that DGM has been completely purged from the Florida sample by 20 min., while 40 min. was required to purge DGM from the Michigan sample. After the sample was purged free of DGM, an additional 20 (or 40) min purge was done to quantify the whole-system blank. The original sample DGM is then computed from the difference between the sample and blank purge, and expressed on a water volume basis. Continued purges rarely generate any signal above the initial blank (last portion of Figure 3a).

We believe that the blank probably represents a generally small "system" blank (e.g. comparable to that signal before T_0) plus insitu dark production of DGM. It must be noted that this second "blank" signal can be large, and is sometimes related to the initial sample purge signal. For example, in ~70 samples collected during the spring and fall of 1996 at the FL site, the blank signal was about 40% of the overall sample signal (mean sample ~8 pg/L, mean blank ~3 pg/L). The blank was significantly correlated with the sample signal (e.g. for the 70 FL samples, $r = 0.83$, $P < 0.01$). By its nature, this

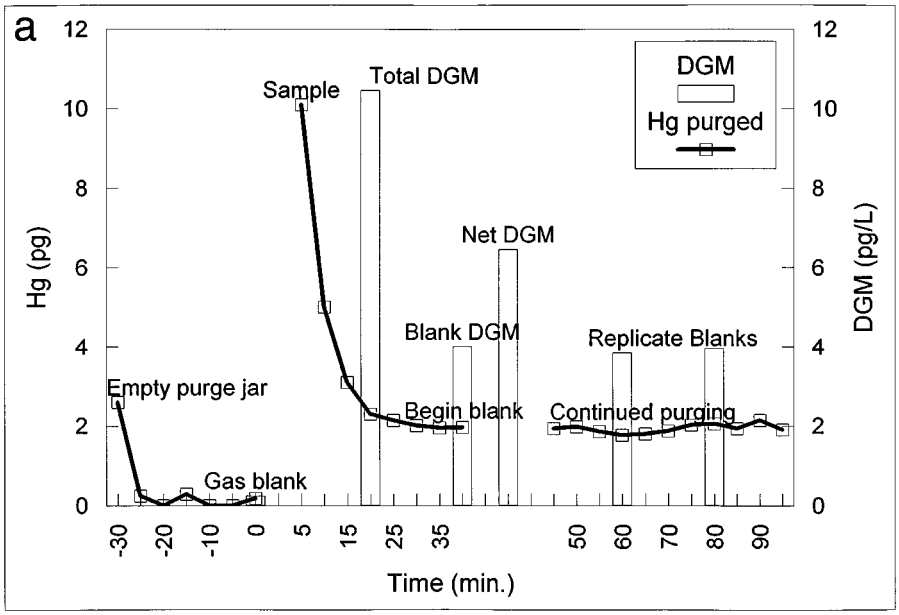

Figure 3. Example DGM purge curves generated with TAPS using water from the Florida Everglades Nutrient Removal Project site (a) and Burt Lake, MI (b), showing zero-gas blank, sample signal, and system blank signal, and results of continued purging of the FL sample. Note different scales. 3(b) is on following page.

second TAPS system "blank" signal itself may provide useful information on the sample. The relationship for the MI site (Figure 3b) is more favorable due to the higher DGM concentrations in those waters (mean sample ~25 pg/L, mean blank ~4 pg/L for the teflon purge system) combined with lower system blanks. Interestingly, blanks for the UMAQL all-glass system are typically <1 pg, suggesting that the teflon purge bottles do "store" some elemental Hg vapor internally.

A detailed analysis of the purging kinetics of DGM from samples collected in Michigan revealed that the removal of DGM followed first order kinetics. Samples were collected in both Teflon (n = 33) and glass (n = 35) bottles from Burt Lake (n = 17) and Lake Superior (n = 51) and analyzed using the TAPS method. The first order removal curves plotted in Figure 4 show strong linearity for both materials ($r^2 > 0.98$) and confirm that at 40 min ~99% of the DGM initially present in the samples was removed. It was expected that the DGM removal efficiency (indicated by the removal constant, k) would be greater for the Teflon vessel because its dimensions favored a longer gas bubble residence time in solution. Despite the different dimensions of the Teflon (10×24 cm) and glass (15×15 cm) purging vessels, the removal

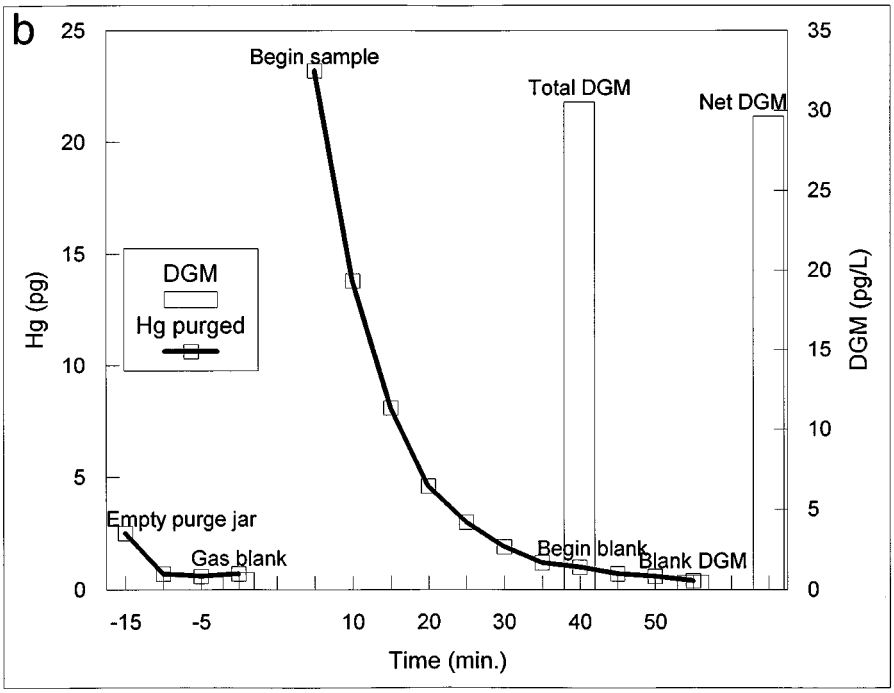

Figure 3. Continued.

constants were not significantly different ($p < 0.35$), indicating little effect of bottle geometry.

Because of this well defined purging behavior, it may be possible to rapidly approximate sample DGM concentrations using the initial purge data. The DGM purged from solution during the first 10 min. was used to derive site dependent correction factors, and applied to predict final DGM concentrations. The correction factors were determined by regressing the measured, field-blank corrected DGM concentrations and the DGM concentrations estimated using purge data from the first 10 min. The slope and intercept from the regression were used to predict the final DGM concentrations from the estimated DGM concentrations. A comparison between the predicted and measured DGM concentrations indicated a strong positive correlation for samples collected from Lake Superior ($r^2 = 0.95$; $p < 0.01$). While this method assumes these characteristics apply to all samples at a given site, the shorter analysis time would allow the high resolution sampling intervals useful for rapid screening studies.

Method intercomparisons and sample storage tests. Several tests of the purging methods were performed at each site. Among the questions of interest

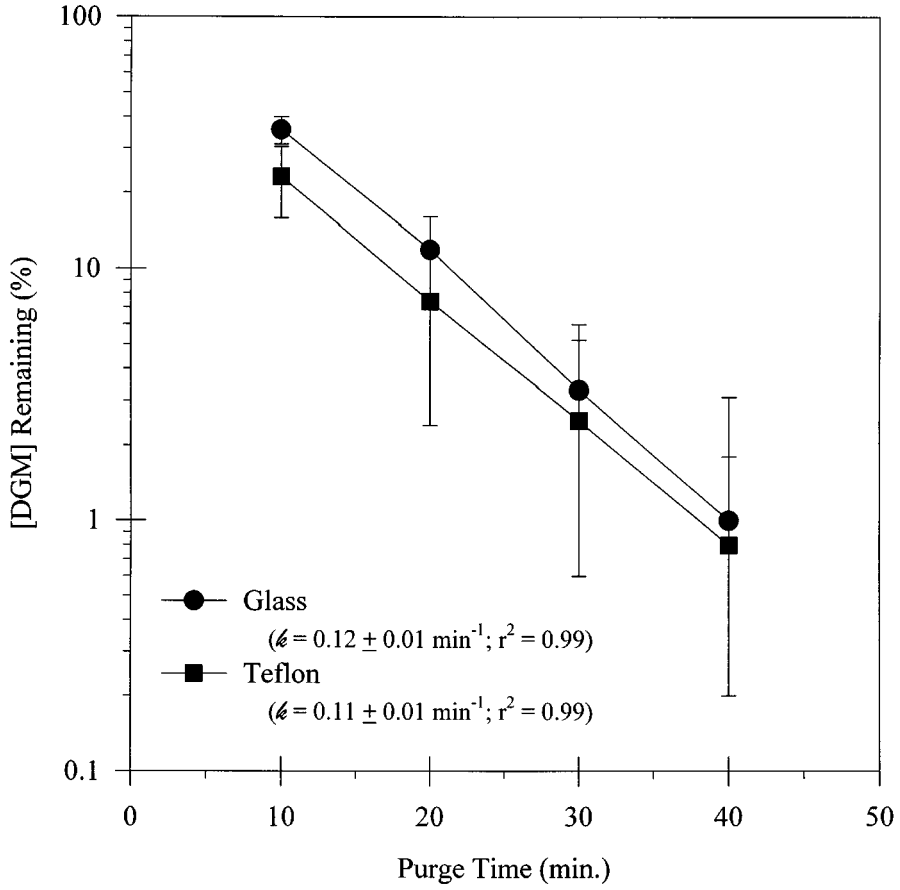

Figure 4. Kinetics of DGM removal from Teflon and glass purging vessels for samples collected in Michigan.

were comparability of the manual and TAPS methods, and the precision of each, as well as the stability of stored samples. Duplicate samples were collected from Lake Michigan in July, 1994 and purged simultaneously to determine the precision of the manual pressure purge method. In general, the results from many duplicate samples (n = 21) showed relatively good agreement overall (regression slope = 0.98 ± 0.16). Although the data indicated no significant differences between duplicate samples ($p < 0.40$) the results were quite scattered (r^2 = 0.65). The variability in the data appears to be random and may have been caused by an incomplete seal in the purge vessels. Because the samples were purged under pressure, the DGM lost due to leakage cannot be quantified.

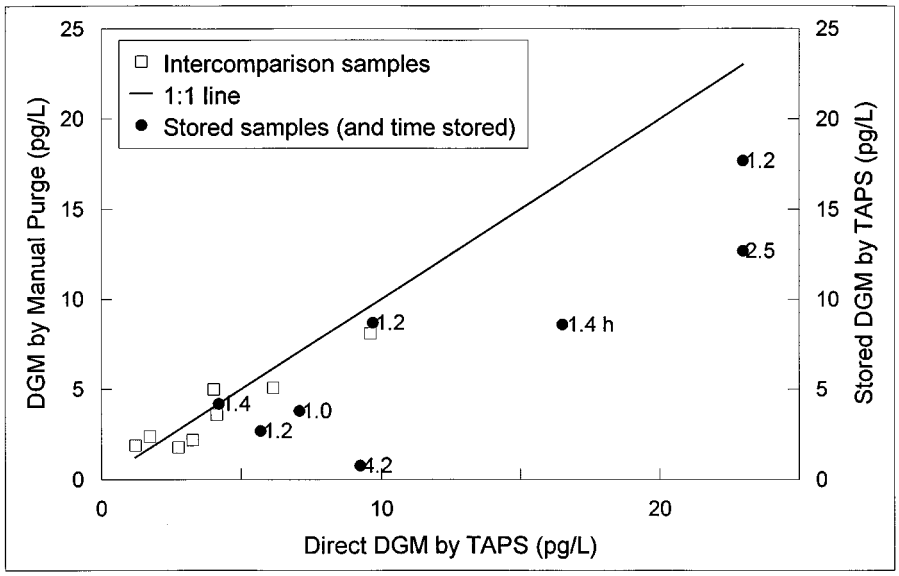

Figure 5. Intercomparison of manual and TAPS results for DGM in Everglades waters, and results of purging paired stored and fresh samples.

A direct intercomparison of the two purge methods was performed at the Florida site, using duplicate purge jars with each purging method. As part of this, we also determined the precision of replicate TAPS purges. However, with only one field Tekran instrument, we could not run simultaneous replicates, and we assumed that paired samples collected simultaneously but analyzed in sequence could be used (one being stored in Teflon or glass with zero headspace for ~1 h under cool, dry conditions, while the other was being purged). It was during these measurements that we generated data suggesting that samples for DGM collected at the Florida site were not necessarily stable in storage, even over short periods, although this had been generally assumed.

Figure 5 summarizes two data sets showing both the intercomparison of the manual pressure and automated TAPS purge methods for DGM, as well as the results of purging stored replicate samples using TAPS. As shown in the lower portion of the plot, the manual and TAPS methods generated comparable results on fresh samples, even at quite low levels of DGM (mean manual DGM = 3.8 ± 2.2 pg/L, mean TAPS = 4.1 ± 2.7 pg/L). The results were strongly correlated ($r = 0.93$, $p < 0.01$), but were biased ~10% low for the manual method (regression slope = 0.87 ± 0.06), certainly within the level of uncertainty at these levels of DGM (*t*-test showed no significant difference in mean DGM, $p > 0.17$).

Table 2. Results of sample storage tests using surface waters from the Florida Everglades Nutrient Removal (ENR) project. The duplicate samples were stored with zero headspace in either sealed glass bottles (the original collection bottles, for samples prior to 7/25) or sealed Teflon jars (same as those used for TAPS purging, for samples 7/25–12/5). All bottles were stored in the dark at ambient temperature in ice chests. These measurements were made during the 1996 sampling year.

			DGM in sample (pg/L)				
Date	Time	Site	Original	Stored	Storage (h)	Total loss	K(loss rate, h^{-1})[a]
4/18	1200	Cell 4	4.0	2.1	4	48%	0.2
6/27	835	Cell 4	7.1	3.8	1	46%	0.6
"	1030	Cell 4	4.2	4.2	1.4	0%	0
7/17	825	Cell 2U	23	17.7	1.2	23%	0.2
"	825	Cell 2U	23	12.7	2.5	45%	0.2
"	1215	Cell 2U	9.7	8.7	1.2	10%	0.1
7/25	810	Cell 2L	16.5	8.6	1.4	48%	0.5
"	1045	Cell 2L	5.7	2.7	1.2	53%	0.6
12/5	830	Cell 2U	37.1	25.9	2.3	30%	0.2
"	830	Cell 2U	37.1	8.9	6.2	76%	0.2

[a] Loss rate constant assuming first order kinetics.

The results of purging stored samples were less encouraging. There was a clear indication of DGM loss in samples collected at the Florida site across a wide range of DGM levels (∼5–20 pg/L; Figure 5). Losses occurred in nearly all Florida samples stored for periods ranging from ∼1–20 h, regardless of the initial DGM concentration. The overall losses were highly variable, ranging from ∼0–80% (Table 2). On average, DGM levels in samples stored for 1–3 h decreased by about 30% (from 16 ± 11 pg/L for immediate purges, to 11 ± 8 for stored samples). The DGM concentrations of fresh vs. stored samples were strongly correlated ($r = 0.80$, $p < 0.01$), but significantly biased (regression slope = 0.46 ± 0.11). The sequential data from 7/17 and 12/5 [and two more recent periods added in press, Figure 6] suggest that the loss rates are first order, and the median half life of stored DGM in these samples was on the order of 3 h. Half of the estimated loss rate constants fall between ∼0.10–0.20 h^{-1}.

The instability of DGM in these waters is not surprising, and Hg speciation measurements of any kind are subject to this problem. Interestingly, a very limited test of samples collected in Michigan indicated no significant losses when stored for less than 3 h. The fate of the lost DGM is unknown, but could include adsorption to walls or particles, oxidation of Hg°, degassing as a result of an incomplete seal during storage (unlikely), or diffusion into or through the lattice structure of the Teflon storage jar (but not the glass jars).

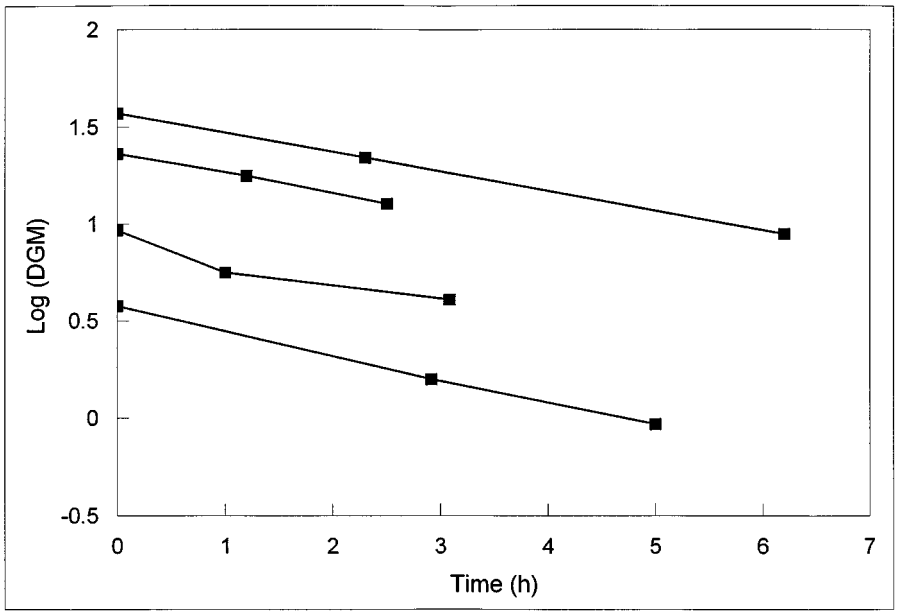

Figure 6. Losses of DGM from stored replicate samples analyzed by TAPS. The upper curves are the sequential data from 7/17/96 and 12/5/96 in Table 2; the lower curves are for recent tests from samples collected in March 1998 (Lindberg et al. 1999).

Mean loss rates for samples stored in teflon jars are moderately larger than those from glass jars (Table 2). Little is known about the oxidation of DGM in natural waters, although first order rate constants for DGM "oxidation" of 0.1 h^{-1} have been observed in seawater (based on measured net losses of DGM in closed bottles stored under both dark and light conditions; Amyot et al. 1997a). However, losses of DGM from stored freshwater samples have not previously been observed (Amyot et al. 1997b), although several more recent examples of this behavior are now available (Lindberg et al. 1999).

Factors influencing DGM in surface waters. The purge/removal kinetics shown in Figures 3–4 were exhibited by all but a few samples from FL and MI. The few exceptions revealed interesting information regarding potential sources of DGM in Florida waters. Figure 7 shows two exceptions and two more typical curves for comparison. The unusual sample from 10:05 on 11/5 was collected during a rain event, and represented surface water which had received 2.2 cm of rainfall in a 60-min period. To date this remains the only sample which exhibited such a curve, showing significant dark production of DGM during the initial 20-min. purge, an actual increase in the DGM signal during purging, and continued dark production beyond the normal 40-min

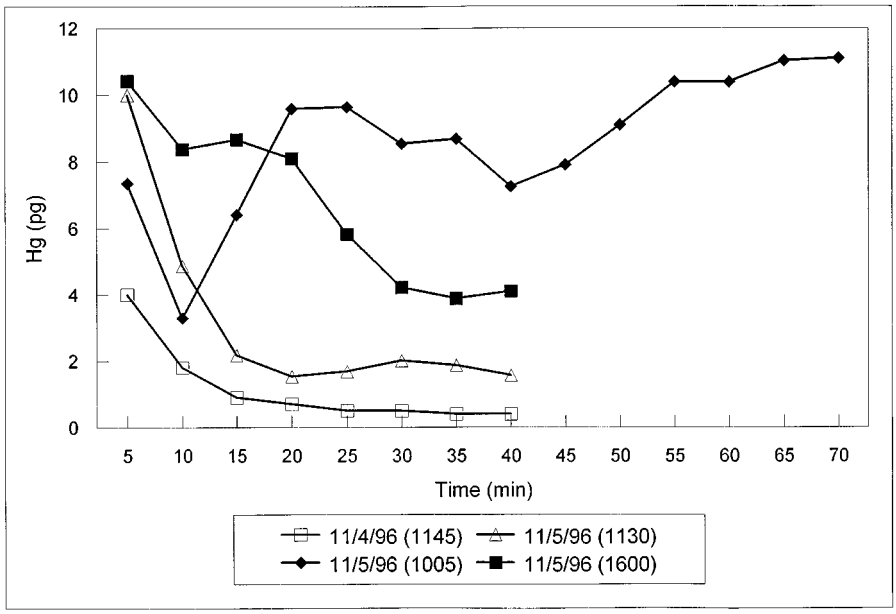

Figure 7. Results of purging several Everglades samples using the TAPS method, including one collected during a rain event (11/5/96 at 1005) and after a second larger rain event (11/5/96 at 1600; see text for details).

purge. We suspect that the sample itself may have been influenced by direct precipitation during collection. In comparison, the samples collected prior to and following the rain event (at 11:45 on 11/4, and 11:30 on 11/5) both exhibited typical purge curves while that collected at 16:00 after a second rain event had ended (4.7 cm at 14:30–15:00) also exhibited an unusual behavior (Figure 7), suggesting some dark production of DGM. This unusual sample suggests an important role of rainwater in contributing reducible Hg to these surface waters which are normally low in DGM. Because of its behavior, DGM could not be computed for this sample (blank>sample); however, using the mean blank that was measured for the 5 samples collected before and after this rain event ($\sim 4 \pm 2$ pg/L) yields a DGM for the rain-affected sample of 34 pg/L, which would be the highest DGM we have measured in this system. Such rain events have a clear influence on surface water DGM at this site, which increased by $\sim$40% from an average of 3.9 ± 0.9 pg/L on 11/4 (the day prior to the rain) to 5.5 ± 2.5 pg/L in the 6-h period following this and the second event. A crude mass balance on the system suggests that only a small fraction (<1%) of the added Hg in rainfall would need to be reduced to produce these increases in DGM.

Precipitation in the Everglades is known to contain significant concentrations of total and reactive Hg, especially during the summer (Dvonch et al. 1995, 1998), and the first rain event on 11/5 exhibited a total Hg concentration of 10.2 ng/L (compared to a typical mid-ENR surface water concentration of ∼1 ng/L). Dissolved reactive mercury (DRM, as $SnCl_2$-reducible Hg) was also measured during this period (Bloom pers. comm.). DRM in surface water increased from an average of 280 ± 190 pg/L in the days before the event to 680 ± 180 pg/L in 3 samples collected from 1 to 3 h after the event. The rainfall itself contained 1200 pg/L DRM (∼10% of the total Hg). Generally lower levels of DRM have been measured in the Everglades during the dry winter period (Hurley et al. 1998), as expected. Although their actual speciation is unknown, we assume the DRM species are a precursor to DGM which may be reduced insitu by biotic and abiotic processes (e.g., photoreduction, Xiao et al. 1995). This has been demonstrated in the field by Amyot et al. (1997b). We have also observed an increase in DGM across the ENR following major rain events after extended dry periods, and overall levels of DGM in the ENR are highest during the summer wet season (Lindberg et al. 1999) further supporting precipitation as one source of reducible Hg.

The ability of the TAPS approach to measure short-term changes in DGM suggest it could be used to quantify the DGM produced during solar irradiation of water samples. This experiment yielded the other example of an atypical DGM purge curve which occurred when we exposed the TAPS purge jar to direct sunlight. The production of DGM from Hg^{2+} species by photolytic processes is well known, and has been shown in the laboratory to be enhanced by dissolved organic matter (e.g. Xiao et al. 1995). Because of these reactions, DGM purges are carefully protected from light. However, for irradiated samples the TAPS method provides the opportunity to directly observe the kinetics of DGM production under sunlight (related insitu measurements using manual methods with submerged bottles and extended exposure times have been published by Amyot et al. 1994). Figure 8 shows the results of one such experiment. The sample was first purged normally, showing typical behavior (DGM = 7.7 pg/L), then immediately carried outside and exposed to direct sunlight for ∼2 h while continuously purged. The response was immediate, with the Tekran Hg signal increasing more than 3-fold in 20 min. at which point production leveled off. The average production rate under these nonequilibrium conditions was ∼200 fM/h, near the upper end of the range of average rates measured in boreal lakes by Amyot et al. (1994). Although the Teflon jar attenuates little of the incoming radiation, these waters absorb strongly in the UV due to high DOC levels, and these production rates would not be expected insitu, except near the water surface. Regardless, the potential for DGM production is clear. Assuming typical levels of Hg in this sample

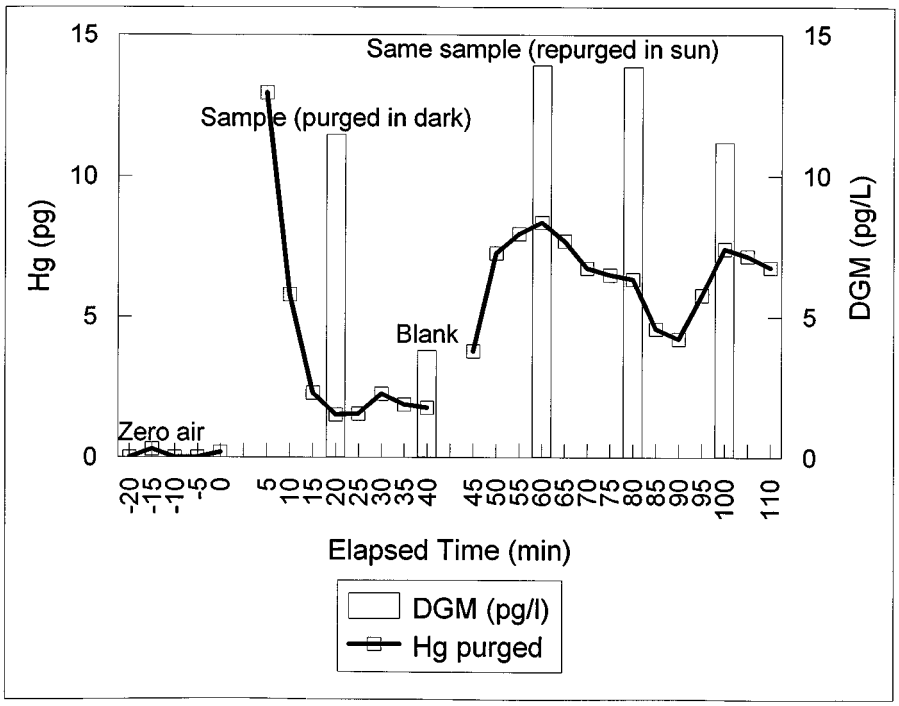

Figure 8. Results of sequentially purging an Everglades sample in the dark and in direct sunlight, showing production of DGM during irradiation.

(∼1 ng/L, Miles & Fink 1998) with ∼10–30% in reactive form, we estimate that DGM production could continue at this rate for several hours. It is common for DGM levels in Florida to reach a maximum at midday during non-rain periods (e.g. Krabbenhoft et al. 1998), suggesting a response to solar radiation (e.g., Amyot et al. 1994). This same pattern is strongly reflected in our measurements of DGM and Hg evasion at our Florida site (Lindberg et al. 1999).

Note added in press. The TAPS method may also be modified to measure reactive mercury in solution. We have modified this approach to analyze solutions used to measure reactive gaseous mercury in air (Lindberg & Stratton 1998). This method originally involved collection of the soluble gas in a liquid mist, followed by analysis of the acidified water for Hg-II compounds by $SnCl_2$ reduction in the laboratory and gas stripping onto gold sand traps. Our recent success with performing this analysis in the field in near-real-time using the Tekran analyzer suggests that a simple modification of the TAPS method could also be used with a DGM sample to measure reactive

mercury in surface waters in parallel with or following analysis for DGM. Some applications of this approach in the Great Lakes have been described (Vette 1998).

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