

An Analytical Method Development for the Study of Chemical Species of Mercury in the Atmosphere

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ABSTRACT

Introduction: Both natural and anthropogenic activities add mercury (Hg) to the atmosphere. The speciation and chemical transformation of mercury in the atmosphere can significantly influence how it is deposited on the Earth's surface. **Methods:** To better understand the impact of urban emissions on global mercury cycling, we developed an inexpensive technique for the reliable measurement of gaseous oxidized mercury (GOM) in air. This simple technique is based on a thermal decomposition-difference method previously developed by others for aircraft studies of GOM in the remote troposphere. Measurements of total atmospheric mercury (TAM) were made by decomposing all forms of mercury in ambient air to gaseous elemental mercury (GEM) at 500°C prior to detection using cold vapour atomic fluorescence spectroscopy (CVAFS). The amount of GOM was determined through the difference between TAM and GEM values.

Results and Discussion: A diurnal pattern was found for GEM, with the highest concentrations of Hg species found ranging from 2:00 to 5:00 PM and the lowest and most stable values from 9:00 PM to 6:00 AM. The amount of GOM was estimated on the 5th floor balcony of Pavillon Président-Kennedy at Université de Québec à Montréal to be $14.7 \pm 10.3 \text{ ng}\cdot\text{m}^{-3}$ (arithmetic mean from eight groups of TAM-GEM differences in the afternoons of July 12 and 14, 2011 and 95% confidence interval). The inconsistent GOM result, in addition to a large error value, suggests the need for further investigation, and to compare the efficiency of this method to previously established methods to identify and quantify the mercury species in urban GOM.

KEYWORDS

*Gaseous elemental mercury (GEM);
Total atmospheric mercury (TAM);
Mercury Speciation; Thermal decomposition;
Gaseous oxidized mercury (GOM)
measurements*

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INTRODUCTION

Mercury is a toxic pollutant that poses danger to both humans and ecosystems. Bioaccumulation in the aquatic food chain and human body can potentially lead to serious health problems such as permanent brain damage (1, 2). Mercury participates in a number of complex environmental processes, best described as a series of chemical, biological and physical transformations. These govern the distribution of Hg in and between different compartments of the environment (3), which are illustrated in Fig. 1 (4). Both natural and anthropogenic (human) activities have been found to contribute to mercury emission to the atmosphere (5). While natural sources include volcanoes, soil, forests, lakes and open oceans, the anthropogenic sources are mainly industrial activities such as coal-burning power generation and municipal

and biomedical solid waste incineration (6). As the observed increase in Hg concentration following industrialization has been extensively documented (3), it is generally accepted that the anthropogenic emissions, concentrated in urban areas, have greatly increased relative to natural sources (6-7). There are several Hg species known to occur in the environment, three of which are most important (5). GEM [Hg^0 or $\text{Hg}(0)$] has a high vapor pressure and a relatively low solubility in water, making it the most stable atmospheric mercury species and subject to long-range transport. GOM (also referred to as reactive gaseous mercury or RGM) or divalent inorganic mercury [Hg^{2+} or $\text{Hg}(\text{II})$] includes the mercury halides (e.g. HgCl_2 , HgBr_2 , etc.). GOM is thought to be the principle form in wet deposition, as it has higher solubility than GEM and strong affinity for many inorganic and organic ligands. Particulate mercury (P-Hg) is the mercury bound to airborne particles whose lifetime in air is typically less than 10 days, though it depends on the size of the carrier particle. Elemental mercury vapor can circulate for up to a year, dispersing widely, during which a small portion may undergo photochemical oxidation to inorganic mercury. Inorganic mercury is easily scavenged by precipitation travelling to the Earth's surface. This mercury in rain is then deposited to soils and bodies of water. Once in soil or lake/river sediments, the mercury accumulates until a physical event causes it to be released again. Although Hg^0 is the predominant form with only a few percent of the total present as GOM and Hg (8-9), GOM is particularly important because it can be readily scavenged by precipitation and has a much higher dry deposition velocity than Hg_0 and P-Hg.

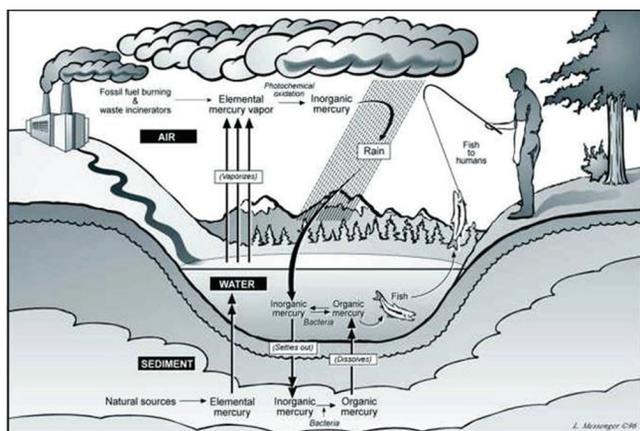


Fig 1. A Simplified Schematic of the Mercury Cycle in the Environment (3)

It is known that mercury oxidation is the main mechanism of removal of GEM from the atmosphere (5). Thus, in order to better understand Hg cycling in the environment and the impact of point-source atmospheric emissions, it becomes critical to develop instrumentation for determining the chemical speciation of Hg (3). While techniques for GEM sampling and measure-

ment are now quite mature (8), methods for GOM measurements are still under development. Therefore, the development of a highly sensitive detector of GOM for atmospherically relevant concentrations (i.e. low picograms per cubic meter, pg/m^3) is a high priority research topic (6, 8-10). Three common methods for measuring ambient GOM (8, 10-12) have been developed: i) refluxing mist chambers; ii) ion-exchange membranes behind particulate filters, and iii) potassium chloride (KCl)-coated tubular denuders. The advantages and disadvantages of these methods have also been reported previously (10). The annular denuder method has so far been the most widely employed among these methods being developed because of the high-time resolution achieved and its relative simplicity (8). Recently, the KCl denuder technique has come under fire for the susceptibility to trap GOM to other atmospheric constituents (e.g. ozone) (12). Thus, a denuder-based aircraft instrument with a higher temporal resolution (15 min) measurement of GOM was deployed alongside a new difference technique for aircraft measurements of GEM and GOM (13). This difference technique determines GOM concentrations as total atmospheric mercury (TAM) minus GEM. While TAM was measured by a Tekran 2537 CVAFS that pulled sample air through a pyrolyzer at 500°C , GEM was measured with another Tekran 2537 CVAFS that pulled sample air through a KCl denuder and a particulate filter. This difference method is a relatively fast technique for measurement of GOM, compared to other methods such as KCl denuder. The results obtained from the difference method have shown a linear consistent correlation with GOM concentrations determined by KCl denuder. Nevertheless, 15% ($\pm 13\%$) discrepancy was found between the two methods, suggesting the difference technique typically measures higher GOM than the KCl denuder method (13). Given the success of the difference technique for measurement of oxidized mercury in the remote troposphere (13), it holds significant promise for measurement of GOM and/or Hg-P in other regions of the atmosphere.

Several studies have shown that urban/industrial areas can be subject to greater deposition of mercury from local anthropogenic Hg sources than regional/global sources (10, 14). Nevertheless, mercury measurements in the urban atmosphere are quite limited compared with those in the remote and rural areas (6). Mercury speciation in the urban atmosphere is even less frequently studied (6), and to our current knowledge, no studies have been based on the difference technique proposed herein. Therefore, the objectives of this research project are: 1) to develop an efficient difference technique based on the aircraft experiment for the accurate measurements of GOM and GOM+Hg-P in the urban areas of Montreal; 2) to study the diurnal, seasonal and temporal variability of urban atmospheric mercury species; 3) to verify the efficiency of this method by comparing with the KCl denuder method; and 4) to identify and quantify the

main mercury species in GOM using the thermal decomposition method by comparison with the known mercury standards such as HgCl_2 and HgBr_2 . Mercury speciation information from this study will be used to estimate mercury emissions from Montreal to the troposphere, and will be used to assess the impact of these emissions on the cycling of this element on the local, regional, and global scale.

METHODS

GENERAL METHOD FOR THE MEASUREMENTS OF GOM

Simultaneous measurements of RGM and Hg-P (and GEM) were performed by conversion to Hg^0 for detection using a Tekran 2600 CVAFS automated Hg measurement system (Tekran Inc., Toronto, Ontario, Canada). The principle implies that passing an air stream through a thermal oven heated at 500°C decomposes GOM and Hg-P to Hg^0 ; and GEM is measured by bypassing the oven and introducing the air stream directly into the CVAFS. The Tekran 2600 was set to measure Hg^0 every four minutes using EPA method 1631 (15), which is the method associated with the CVAFS Tekran 2600 software for determination of Hg in the range of 0.5–100 ng/L (15). The EPA 1631 method has been widely used in our laboratory as we have used this method and revised versions during the last decade. The method detection limit (MDL) for Hg is three times the standard deviations of blank measurements, which are presented in the results section.

By determining the difference of hot versus ambient air measurements, we are expected to obtain reliable measurements of the amount of GOM in the urban air, which is described by equations (1) to (3):

$$\text{Hg}_{500\text{C}}^0 = \text{Hg}_{\text{air}}^0 + \text{Hg}_{\text{OxHg}}^0 \quad (1)$$

$$\text{Hg}_{\text{AT}}^0 = \text{Hg}_{\text{air}}^0 \quad (2)$$

$$\text{Hg}_{500\text{C}}^0 - \text{Hg}_{\text{AT}}^0 = \text{Hg}_{\text{OxHg}}^0 \quad (3)$$

where:

$\text{Hg}_{500\text{C}}^0$ is the quantity of elemental mercury measured by passing air through the thermal oven at 500°C ($\text{ng}\cdot\text{m}^{-3}$);

Hg_{AT}^0 is the quantity of elemental mercury in air at ambient temperature ($\text{ng}\cdot\text{m}^{-3}$);

$\text{Hg}_{\text{OxHg}}^0$ is the amount of mercury present in air as oxidized mercury ($\text{ng}\cdot\text{m}^{-3}$).

INSTRUMENT SETUP

THERMAL DECOMPOSITION UNIT

The unit for thermal decomposition of oxidized mercury consists of 1/4" (0.635 cm) borosilicate glass inlet surrounded by an Omegaux brand oven that is capable of reaching temperatures up to 1800°F (982°C). However, for the purpose of this study, we kept the temperature of the oven consistently at 500°C . The temperature of the glass inlet is continuously measured with a type K thermocouple. A simplified schematic diagram of the instrument setup is illustrated in Fig. 2. The outlet of the decomposition unit is connected to a brass two-way valve that connects directly to the CVAFS. The flowmeter has been set to $300\text{ mL}\cdot\text{min}^{-1}$ to control the flow of the sample into the instrument by regulating the pump flow. The valve is also connected to a Teflon tube, which draws air directly from the ambient environment. By toggling the two-way valve manually, ambient air may thus be sampled either directly at ambient temperature or at elevated temperature through the decomposition unit.

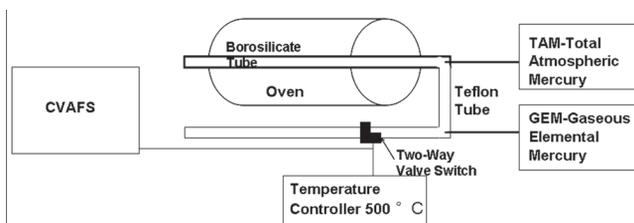


Fig 2. A Simplified Schematic Diagram of the Experimental Setup: Thermal Decomposition Unit and CVAFS

CVAFS

The Tekran model 2600 CVAFS is a very stable, sensitive ultra-trace mercury analyzer, and has been recognized for its high sensitivity, low noise and stability (18). The technique differs from the more conventional atomic absorption (AA) and mass spectrometric (MS) techniques in that it is more sensitive (levels in the low parts per quadrillion (ppq) range) (19), more selective, inexpensive, and is linear over a wide range of concentrations (15). In addition, CVAFS is used in the measurement of trace amounts of volatile mercury and makes use of the unique characteristic of mercury that allows vapor measurement at ambient temperature.

CALIBRATION

The Tekran 2600 mercury analyzer was calibrated in the laboratory room using manual Hg_0 injections. The manual Hg_0 injections were done by injecting a series of known volumes (2 μL , 10 μL , 25 μL , 50 μL , 75 μL and 100 μL) of mercury-saturated air withdrawn from a reservoir headspace into the Tekran 2600 analyzer injection port. The calibration unit reservoir temperature

was kept at ambient temperature (23 °C). At this temperature, the vapor pressure of mercury is 16.879 pg / μL according to the mercury saturation table (20).

VERIFICATION OF THE THERMAL DECOMPOSITION EFFICIENCY

To estimate the thermal decomposition efficiency of this developed analytical technique at converting GOM to Hg^0 , two methods were used. Ontario Hydro Method (OHM) and insertion of a glass wool tube were employed for direct comparisons, which are illustrated in Figs. 3 and 4 respectively. HgCl_2 and HgBr_2 diffusion sources were connected to the inlet of the thermal decomposition unit to introduce GOM-rich gas streams into the thermal decomposition unit.

ONTARIO HYDRO METHOD (OHM)

This method was used to monitor oxidized (and elemental) mercury fluxes from industrial sources (21). A 1 Normal KCl solution was prepared by dissolving 7g KCl crystals into an impinger flask containing 100 mL Milli-Q water. A 20% SnCl_2 solution was prepared by adding 20 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 10 mL concentrated HCl to 100 mL Milli-Q water. The solutions were purged overnight with mercury-free argon to remove all traces of Hg, and then stored by covering with parafilm. Air was drawn by the CVAFS through the HgCl_2 source and KCl solution for several samplings, followed by injection of 1 mL of SnCl_2 into the impinger, and analysis of the impinge headspace by CVAFS. After 20 minutes, another 0.5 mL of SnCl_2 was injected into the impinger, and the headspace was again analyzed for Hg^0 . Injection of SnCl_2 and monitoring of Hg^0 produced was repeated several times for each HgCl_2 collection.

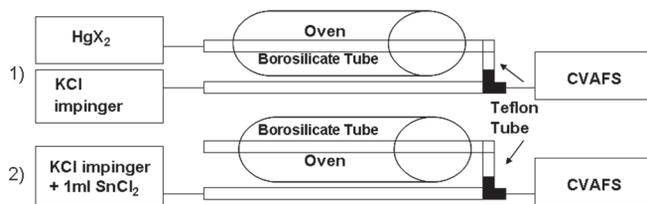


Fig 3. A Simplified Schematic Diagram of the Ontario Hydro Method (OHM) for Efficiency Test

INSERTION OF A GLASS WOOL TUBE

As the Ontario Hydro method does not provide a quick check of the efficiency of the thermal decomposition unit due to various contaminations, a simpler method was pursued by introducing a glass wool tube into the thermal decomposition instrumental unit. This method works due to the principle that GOM sticks to glass wool while GEM does not. This efficiency method was deployed in two steps. Firstly, a glass wool tube was added between the oven unit and the CVAFS, and a mercury

halide standard (HgCl_2 or HgBr_2) was connected to the oven to measure the amount of GOM into the thermal decomposition unit along with most of the GOM stuck to the glass wool. Secondly, the glass wool tube was directly inserted inside the thermal decomposition unit and without the mercury halide standard; the amount of GOM stuck to the glass wool from the previous run was measured by running with the CVAFS a second time. The sum of these two-step measurements can be then used to estimate the thermal decomposition efficiency.

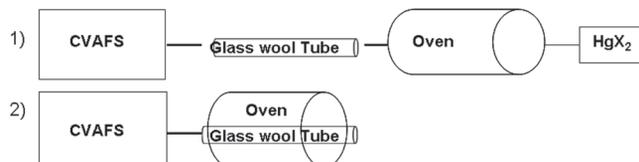


Fig 4. A Simplified Schematic Diagram of the Efficiency Test Using the Method of the Glass Wool Tube Insertion

ATMOSPHERIC GOM MEASUREMENTS IN DOWNTOWN MONTREAL

The study site was moved from the indoor laboratory to an open area on the 5th floor terrace of the science building, Pavillon Président-Kennedy at UQAM. This was done to truly investigate the amount of oxidized mercury in atmosphere as this would better reflect regional anthropogenic activities involving mercury use (22). Ambient air GEM concentrations were also measured overnight in order to get a diurnal cycle of mercury in the urban area.

RESULTS AND DISCUSSION

CALIBRATION CURVE

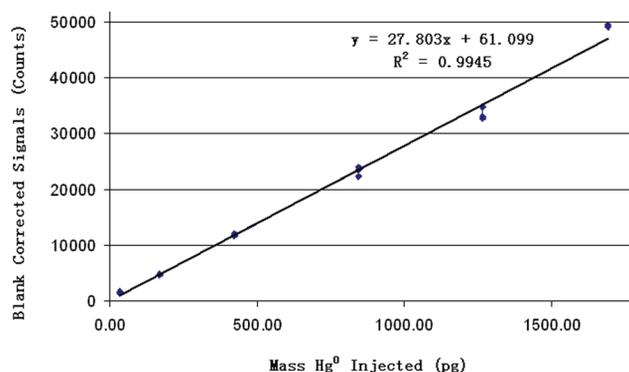


Fig 5. Calibration Curve for the Determination of the Amount of Hg^0 Injected into CVAFS

The slope from this calibration curve (Fig. 5) was found to be 27.803 counts/pg, from which the amount of Hg^0 injected can be calculated by following equations (4)-(6):

$$\frac{C}{m} = \text{Hg}^0 \quad (4)$$

$$\frac{t_{\text{sampling}}}{60 \text{ sec/min}} Q = \text{Vol.}_{\text{Hg}^0} \quad (5)$$

$$\frac{\text{Hg}^0}{\text{Vol.}_{\text{Hg}^0}} = \text{Hg}^0 \quad (6)$$

where:

C is the number of peak area counts per run (counts)
m is the slope of the calibration curve in counts per picogram (counts/pg)

Hg^0 is the amount of Hg in picogram (pg)

t_{sampling} is the method sampling time in seconds (sec)

Q is the sampling flow rate in liters per minutes (L/min)

$\text{Vol.}_{\text{Hg}^0}$ is the volume of Hg in liters (L)

Deviations of the analyzer between calibrations were less than 15%, which suggested that this calibration was well done according to the EPA 1631 manual (15). The variability of most of the data in this study was around 3% and had an average counts/room air run of 880 counts/run, which corresponds to 31.6 pg Hg^0 using equation (4). Then, using the 70 second sampling time at 0.3 L/min; this gives a concentration of Hg^0 in room air of 90.4 $\text{ng}\cdot\text{m}^{-3}$ Hg^0 . This value is larger than the average of GEM measurements found in downtown Montreal over 24 hours, 65.3 $\text{ng}\cdot\text{m}^{-3}$ Hg^0 . However, this value can still be considered within the big range, and shows how the laboratory is filled with a significant amount of mercury versus outside areas. Mercury concentrations posing human health risks are in the range 0.7–4.2 $\times 10^7$ $\text{ng}\cdot\text{m}^{-3}$; thus, this shows the mercury levels in our laboratory and in the present atmosphere are still acceptable (16, 17).

TEMPORAL VARIABILITY OF ATMOSPHERIC GEM IN DOWNTOWN MONTREAL

The reliability of measuring GEM in air limits the capability to detect oxidized mercury as a difference between TAM and GEM. Air measurements had varied stability over short time-periods. This variability can be described with the diurnal cycle (Fig. 6) recorded over 24 hours on July 27 and 28, 2011. The concentrations of elemental Hg (GEM) species tended to be low and stable in the late night time and early morning (between 9:00 PM to 6:00 AM). GEM then started increasing around 6:00 AM until reached its maximum in the afternoon (between

2:00 PM to 5:00 PM), and tended to decrease in the late afternoon and even more from evening time before stabilizing again and reached its minimum at 9 pm. This diurnal pattern indicated that significant temporal variations in concentrations of GEM were observed in the daytime ranging from 21–276 $\text{ng}\cdot\text{m}^{-3}$, especially in the afternoon. In addition, this diurnal cycle could also reflect highly variable emission patterns from anthropogenic mercury sources during the daytime and the lower emissions at night, when human activity is less. Hence, these results indicate that local anthropogenic sources have significant influence on the levels of the Hg species in the urban atmosphere.

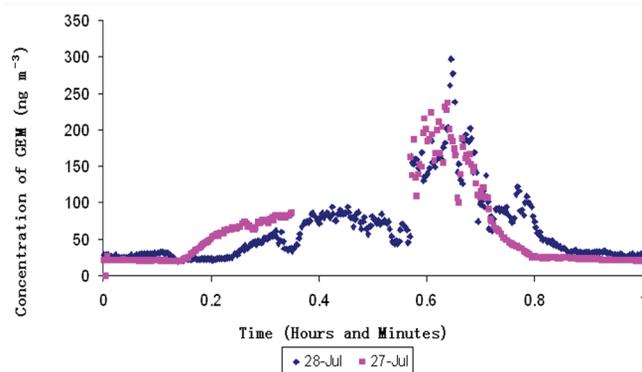


Fig 6. Diurnal Pattern of GEM in Ambient Atmosphere Mercury Species On July 27–28, 2011 for 24 Hours

Moreover, no consistent pattern was observed between fluctuations in TAM hot air measurements and observed variable concentrations of GEM during the afternoon time. This made the determination of GOM difficult during the daytime and could suggest that TAM levels are unrelated to GOM fluctuations, or that variable atmospheric conditions are differentially affecting the various mercury species.

The method detection limit (MDL) for the difference technique according to the results in Fig. 6 is at least 6–50 $\text{ng}\cdot\text{m}^{-3}$, depending on the variability. This MDL with CVAFS is very high compared to the MDLs found in other related studies using CVAFS, 0.04 and 0.06 $\text{ng}\cdot\text{m}^{-3}$ (6, 13). This suggests that other systematic errors might present that need to be identified and accounted for.

ATMOSPHERIC GOM MEASUREMENTS IN DOWNTOWN MONTREAL

The average TAM-GEM difference, based on the data collected with significant variations in the afternoons on July 12 and 14, 2011 from noon to 6:30 PM was estimated to be 14.7 ± 10.3 $\text{ng}\cdot\text{m}^{-3}$ (arithmetic mean from eight groups of TAM-GEM differences and 95% confidence intervals). The relatively large error value suggested that further method investigation is required.

VERIFY THERMAL DECOMPOSITION EFFICIENCY

The Ontario Hydro Method (OHM) was employed at first, and failed to check its efficiency as much higher peak area values were observed when room air was passed through either the KCl or SnCl₂ impinger. This suggests that the solutions themselves might have been contaminated by mercury. As preparation of the new sample standards and solutions is a very time consuming process, we chose to employ a simpler method using a glass wool tube. This new efficiency test was not successfully done at present due to the fact that the incoming flux of GOM was significantly higher than that found in a similar source tested by others (27 pg·min⁻¹ (8)). However, we believe the latter is a better method since only further decrease of the fluxes from the diffusion sources prior to testing is needed to make this method of efficiency a success.

CONCLUSION

In conclusion, the difference-thermal decomposition technique has been successfully developed and applied partly to measure GOM in downtown Montreal. Although GOM results were very limited, they have indicated that an urban area is a continuous source of Hg species that potentially impact local and regional TAM levels. Also, local and regional anthropogenic sources contributed significantly to the levels and the distributions of the Hg species in the urban atmosphere (6). Due to the significant fluctuations observed in the afternoon, a clear relationship between atmospheric TAM and GOM has not been established. Thus, the contribution of urban areas to atmospheric Hg budget remains unknown at this point (6), due to lack of experimental data and the large uncertainty on the limited measurements made so far. This suggests more systematic approaches are needed for quantifying the contribution of urban areas to atmospheric Hg.

Future work in the short term could establish an association between TAM and GEM by collecting TAM data overnight, in order to accurately measure the difference GOM results. Moreover, the MDL could be decreased by increasing the flow rate and the method sampling time. In the long term, as the manual switching complicates evaluation of the diurnal variability in GOM over a long period of time and limits the number of measurements, an automated valve could be employed to facilitate the switch and increase the number of measurements. In addition, due to the high incoming flux of GOM, testing the method efficiency using the glass wool tube and investigating the decomposition profiles of different Hg species with varying temperature are difficult at this point. Since the cooling process should in principle decrease the vapor pressure of mercury halides above the source crystals; and therefore, the incoming

flux of GOM, the problem could be resolved by further cooling the sources in a dry-ice ethanol/liquid-nitrogen bath. Furthermore, Hg air sampling should be done not only in downtown Montreal, but also in other areas to investigate and compare the results. Finally, reasons for temporal variations are not apparent. This suggests a need for further investigation and a need to prove the efficiency of the thermal decomposition unit by comparing with the KCl denuder method with ambient air replaced by nitrogen gas during collection, in order to prevent interference by ozone (12).

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