P2 Continuous DIAL measurement of atmospheric trace Hg

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Continuous DIAL measurement of atmospheric trace Hg is presented. The measurement was performed using a DIAL system with a dye laser pumped by the second harmonic of a Nd:YAG laser. The third harmonic of the dye laser output was used for the “on” and “off” wavelengths, which were set to 253.65 nm and 253.67 nm, with 0.02 nm separation. A Hg concentration of 0-1 ppt was measured at 450-520 m altitude. The errors from O_3 and aerosol effect are about 0.045 and 0.001 ppt, and the total error is about 0.15 ppt, which includes instrumental error, statistical error and the error due to change in atmospheric conditions.

1. Introduction

Mercury is the only pollutant that is present in the troposphere in elemental form. Atomic mercury is also an interesting geophysical tracer gas associated with certain ore deposits, as well as geothermal, seismic, and volcanic activities. Therefore, measurement of mercury concentration in the atmosphere is of considerable interest and importance. Differential absorption lidar (DIAL) has been used for monitoring mercury concentration in atmosphere[1]. However, most measurements were used for point monitoring of high mercury concentration such as mercury emission from industrial plants which use mercury in the process. When mercury concentration in ambient atmosphere is measured, the error from other species effect is more important.

Continuous 16 hour mercury measurement was performed using our DIAL system[2,3], In the following sections, measurement results and error analysis are presented.

2. Experimental system

The laser transmitter of the DIAL system consists of a Nd: YAG pumped dye laser, operating at a repetition rate of 10 Hz. The second harmonic of Nd: YAG laser (532 nm) was used to pump the dye laser with LDS dye. The dye laser can emit two wavelengths, λ_a and λ_b, on alternate pulses, which are tunable within the oscillation range of LDS765 dye. The output of LDS765 dye, 760.95 nm and 761.01 nm, were converted to 253.65 nm and 253.67 nm which correspond to the “on” and ”off” wavelengths by a third harmonic generator composed of a pair of KDP(KH_2PO_4) crystals. The laser beams of the “on” and ”off” wavelengths are transmitted into sky, whose backscatter radiation is collected by a coaxial telescope system of 500 mm diameter. An interference filter (center wavelength: 261.76 nm, FWHM: 33.5 nm) selects the appropriate wavelength range for the detection performed with a photomultiplier tube (PMT), which is gated by a high voltage gate pulse with about 250 μs width. The PMT signal is digitized by a transient digitizer with 20 MHz time resolution corresponding to a range resolution of 7.5 m. The digitized signal is transferred to an computer where data are averaged and stored for later analysis. The DIAL system is permanently installed on the ground at Komae Research Laboratory, Central Research Institute of Electric Power Industry, in Komae city, Japan ($35^0 38'$ N, $139^0 35'$ E), about 20 km west of downtown Tokyo.

3. **Continuous mercury monitoring at low altitude**

Continuous 16 hour mercury measurement was performed from 17:30 July 27 to 09:30 July 28, 2001. The integration time was set to 10 minutes for one profile, for a total of 96 profiles during the measurement. Before DIAL measurement, a null profile (two laser wavelengths were both set to the "off" wavelength) was measured in order to prove that all laser beams were in the field of view (FOV) of telescope.

The range-resolved mercury concentration was obtained by DIAL equation(1):

$$N(R) = \frac{1}{2\Delta R \Delta\sigma} \ln[\frac{P_{on}(R)}{P_{off}(R)} \frac{P_{off}(R+\Delta R)}{P_{on}(R+\Delta R)}] \qquad (1)$$

where $\Delta\sigma$ is differential absorption cross section, which is 3.3×10^{-18} m^2 for mercury measurement [1], and ΔR is the range resolution. $P_{on}(R)$ and $P_{off}(R)$ are the return signals at the "on" and "off" wavelengths, respectively. Before calculation using equation (1), the obtained signals were processed as follows: the background data was subtracted from the return signal, and all signals were averaged over 10 time bins corresponding to range resolution of $\Delta R = 75$ m.

The measurement results at 450 m and 525 m altitude are shown in Fig.1. The measured Hg concentration value varied with altitude and time, but was stable during the time interval from 01:30 to 05:30 July 28, 2001.

An example of the obtained range-corrected signal $P(R)\times R^2$ is shown in Fig.2. Figure 2 is the mean value of range-corrected signals from 01:30 to 05:30 July 28, for a total of 4 hours, which corresponds to the concentration stable range in Fig.1. This indicates that complete overlap between the transmitted beam and telescope FOV was achieved for $R > 400$ m.

4. **Evaluation of measurement error**

In this mercury measurement, we consider the following errors: the null error whose value shows

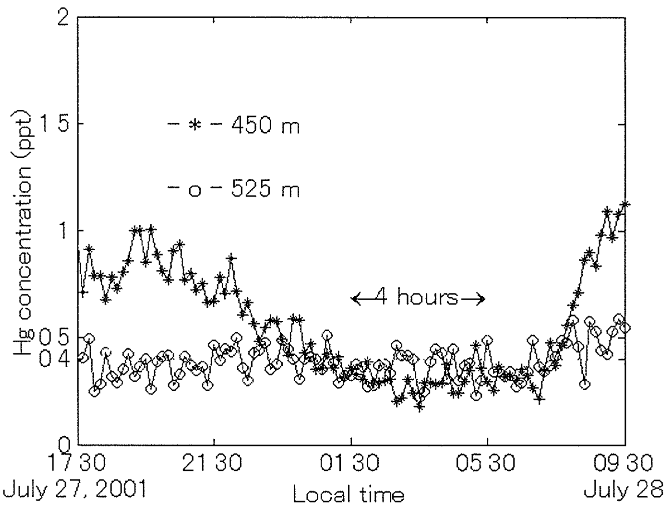

Fig.1: Hg concentration obtained from 17:30 July 27 to 09:30 July 28, 2001

how precisely the laser beam was aligned to FOV,

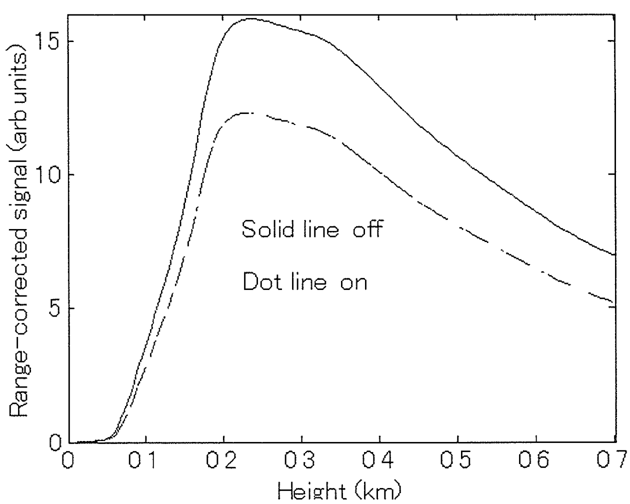

Fig.2: Range-corrected signal averaged from 01:30 to 05:30 July 28

statistical error including error due to the atmospheric condition variation obtained from standard deviation of 48 profiles during the stable 4 hours of measurement, backscatter error, and effect of O_3.

Fig.3 shows the DIAL and null profiles obtained from the data in Fig. 2. The statistical error is also shown as error bars on the DIAL results in Fig.3. The statistical error is larger at higher altitude, because of weaker return signal intensity.

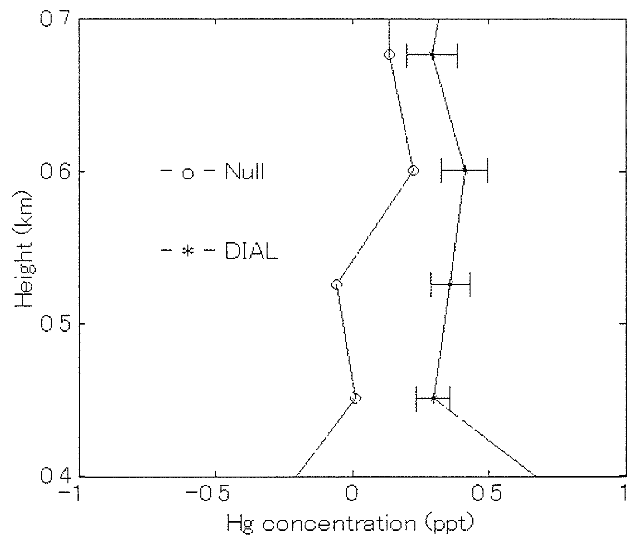

Fig.3: Null profile and Hg concentration profile with statistical error

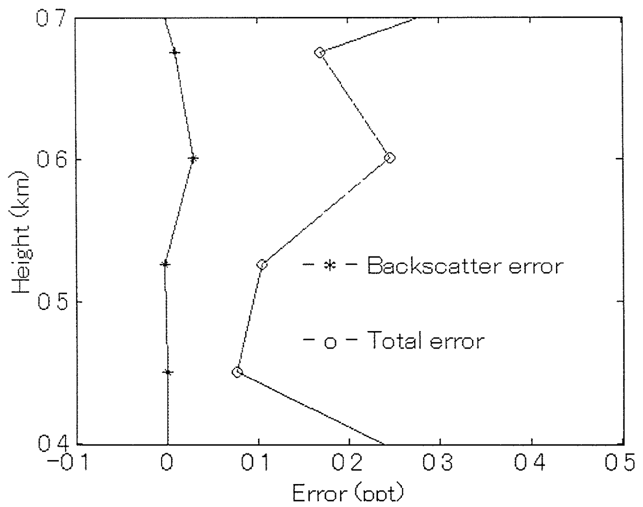

Fig.4: Backscatter error and total measurement error

Figure 4 shows the backscatter error which was calculated by equation

$$\varepsilon_B = \frac{\lambda_{off} - \lambda_{on}}{\lambda_{off}} \times \frac{d}{dz} \frac{3 \times \left(R_{\lambda_{off}}(z) - 1\right)}{R_{\lambda_{off}}(z)} \qquad (2)$$

discussed in reference[4], where

$$R_{\lambda_{off}}(z) = \frac{\beta_{Mie} + \beta_{Rayleigh}}{\beta_{Rayleigh}} .$$

Aerosol wavelength dependence law is assumed as $\alpha \propto \lambda^{-\kappa}$ with $\kappa = 1$. Calculation result shows that the backscatter error is very small, about 1×10^{-3} ppt, which shown in Fig.4.

Regarding the effect of O_3, we consider the O_3 differential absorption cross section between the "on" and "off" wavelength, 3×10^{-21} m^2, and assume a typical O_3 concentration of 50 ppb. The effect is calculated as 0.045 ppt.

After considering the above errors, the total measurement error shown in Fig.4 can be obtained. The measurement error at higher altitude is larger because null errors and statistical errors become larger.

5. Conclusion

Continuous mercury measurement for 16 hours was performed and a concentration of 0 ~1 ppt was obtained at around 500 m. The main errors are null error and statistical error including the error due to the atmospheric condition variation. Backscatter error is very small, in the order of 10^{-3} ppt. The total measurement error averaged from 400 m to 700 m.was obtained to be about 0.15 ppt. Measurement of the absorption cross section of mercury using our laser and the interference due to O_2 are of future study.

Reference:

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