Lidar Monitoring of Atmospheric Atomic Mercury and Sulfur Dioxide in Guangzhou, China

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Abstract— A Differential Absorption Lidar (DIAL) system based on a dye laser pumped by a 20 Hz Nd:YAG laser was constructed and used for range-resolved atomic mercury and sulfur dioxide monitoring. These gases are both severe pollutants in China, and there is a considerable interest to map such gases. Measurements were performed from a fixed laboratory, with the eye-safe laser beam pointing upwards at a 15° angle, to assess the vertical distribution of the gases. Long term quasi-continuous monitoring of background mercury and sulfur dioxide concentrations is presented. In particular, the influence of weather conditions was studied during prolonged measurement sequences. We have now studied prominent wash-out effects on mercury due to rainfall. For sulfur dioxide, a pollutant that causes acid rain quite high concentrations measured in Guangzhou were observed to fall drastically at rainfall due to wash-out.

1. INTRODUCTION

Today, due to the Chinese rapid industrialization and urbanization, one area of growing concern is the mercury emissions, and the adverse effect of mercury on human health and the ecosystem is well-known. Man-made mercury emissions are the main cause of global mercury pollution [1]. Waste incineration, coal-fired power plants, and other industrial processes which are powered with fossil fuels such as cement plants and metallurgic industries are the important sources of global man-made mercury pollution [2]. Mercury is a high abundance and widespread element in the earth crust. Mercury mostly exists as cinnabar, HgS. Volcanic, geothermal, and other geogas emissions cause gaseous mercury release. For example; geogas emissions cause the abnormally high soil mercury concentrations in the Chengdu area of the Sichuan province, China [3]. Mercury is also an important tracing gas in geophysics with potential for prospecting [4].

Acid rain is mainly due to dilute sulfuric acid and dilute nitric acid formation. The combustion of fossil fuels produces oxides of sulfur and nitrogen which are released to the atmosphere. Sulfur dioxide reacts with water to generate sulfuric acid [5]. Acid rain is a severe environmental issue with impact on human health, soil acidification, buildings and statues. According to estimates, the annual mean concentration of SO_2 in major Chinese cities was 60 $\mu g/m^3$ in 1993 [6].

Differential Absorption Lidar (DIAL) applied in remote sensing of atmospheric gaseous pollutants has been an effective method to acquire range-resolved concentration information in real-time measurement (see, e.g., [7]). A first version of a DIAL system constructed by our group is described in [8], where also initial studies of atomic mercury (the only air pollutant present in atomic form) are reported. The system is constructed with a 30 cm diameter receiving telescope and is equipped with a narrow-band dye laser pumped by a 20 Hz Nd:YAG laser. We now describe further measurements of background atomic mercury and also sulfur dioxide measurements, as well as the concentration reduction at rainfall due to wash-out. The results were performed with the DIAL system located at the South China Normal University, University City Campus in Guangzhou, China.

2. MERCURY MONITORING

The DIAL technique uses pulsed laser emission at on- and off-wavelengths matched to a peak of an absorption line and slightly off the absorption peak of the gas interest, respectively. The slope of the ratio of the recorded on-wavelength and off-wavelength lidar signal intensities gives information on the gas concentration. We have [7]:

$$\frac{I(\lambda_{on}, R)}{I(\lambda_{off}, R)} = \exp\left\{-2\int_0^R N_{(r)}\left[\sigma\left(\lambda_{on}\right) - \sigma\left(\lambda_{off}\right)\right]dr\right\} \tag{1}$$

Here $I(\lambda_{on}, R)$ and $I(\lambda_{off}, R)$ are the backscattering light intensities for the on- and off-wavelengths, respectively; $\sigma(\lambda_{on})$ and $\sigma(\lambda_{off})$ are the absorption cross-sections for the on- and off-wavelengths, respectively; $N(r)$ is the gas concentration at distance r, and R is the detection distance. The absorption line parameters of the gas of interest can generally be found from HITRAN [9].

The on- and off-wavelengths of mercury, as employed in our study are 253.729 nm and 253.744 nm (vacuum), respectively. The dye laser is set around 5 mJ per pulse. Figure 1 shows the variation of the background mercury concentration for a period of quasi-continuous monitoring, from 00 : 00, November 5th, 2013 to 9 : 00, November 6th, 2013. There was rainfall from 7 : 35 until 10 : 00, November 4th, 2013 with an integrated rain level is 3.8 mm. The mean temperature during the monitoring period was 20 ± 1°C; the mean temperature when it was raining was about 1°C lower than when it was not raining. The figure shows a 60–110 m altitude measurement which resulted in an average mercury concentration of 6 ± 1 ng/m^3 from 0 : 00 to 7 : 00, November 5th, 2013. From 8 : 00 to 10 : 00 on the 5th the average mercury concentration is 1 ± 1 ng/m^3. Generally speaking, for this period sometimes the mercury concentration is lower than the DIAL system resolution. We note that there is a prominent wash-out effect on mercury due to the rainfall with strong reduction of the background concentration. The mercury concentrations are also sensitive to temperature, especially in industrial areas with deposited mercury, since the metal is very volatile. Since the variation of temperature between the period of rainfall and no rain is only slight; the reduction of mercury concentration is mainly caused by the rainfall effect. The average mercury concentration from 12 : 00 in 5th to 9 : 00 in 6th is 4 ± 1 ng/m^3. It indicates that the mercury concentration rises again quite rapidly after the rainfall.

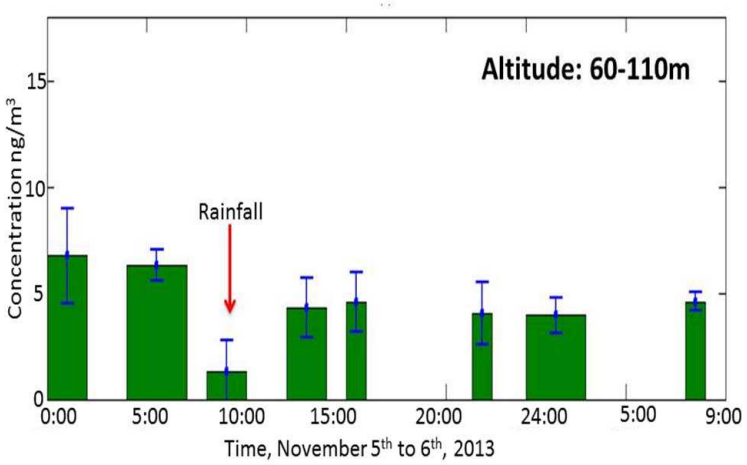

Figure 1: A 35-hour quasi-continuous mercury concentration measurement; the error bars give the evaluated errors of the mercury concentrations; Rain was falling from 7 : 35 until 10 : 00; during this time the rainfall was 3.8 mm.

3. SULFUR DIOXIDE MONITORING

The on- and off-wavelengths for sulfur dioxide are 300.03 nm and 299.3 nm (vacuum), respectively. Compared to mercury, sulfur dioxide measurements are less demanding due to broader absorptive features. The dye laser is set around 5 mJ/pulse. Figure 2 gives a typical DIAL curve of sulfur dioxide monitoring; the insert figure is the curve of the backscattering signal of on- and off- wavelengths, also showing the interception of a cloud by the beam. The figure shows obvious sulfur dioxide absorption from 150 m up to 1500 m, corresponding to the altitude interval from 50 m to 40 m. We could observe that the ratio is almost flat from 150 m to 2000 m corresponding to the altitude between 400 m and 550 m, which indicates that the concentration is much lower at high altitude. For sulfur dioxide around 300 nm, longer measurement ranges than for mercury, up to 3 km, are possible, related to reduced atmospheric scattering and higher available output pulse energies. In our experiments, the cloud base frequently limited the measurement range.

Figure 3 gives the concentration distribution for different altitudes (50–10 m, 10–20 m, 200–400 m and 400–550 m). In Figure 3, the white areas represent absence of data due to weather conditions and low-lying clouds. For the 50–100 m altitude, the highest concentration (203 µg/m^3) is obtained around 18 : 00. From 18 : 00 to 19 : 00, the concentration of SO_2 remains high; the

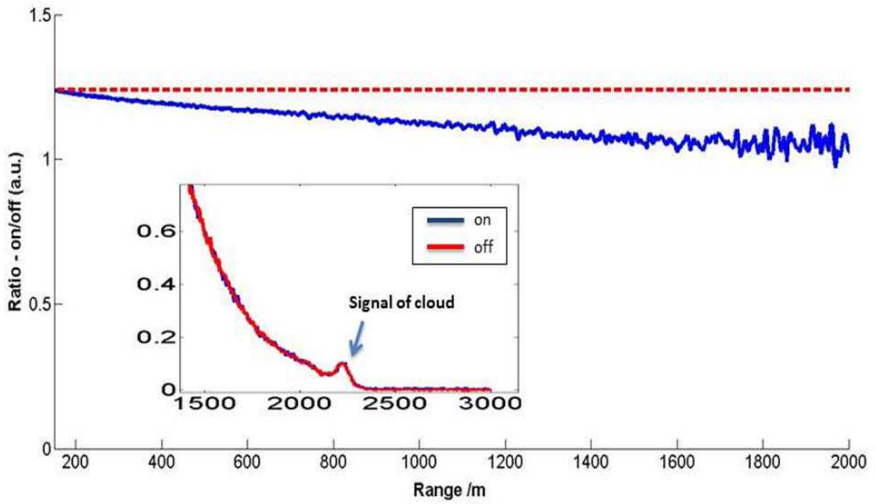

Figure 2: Differential absorption curve of sulfur dioxide. The insert figure shows the curves for on- and off-wavelengths, with termination in a cloud at 2200 m range.

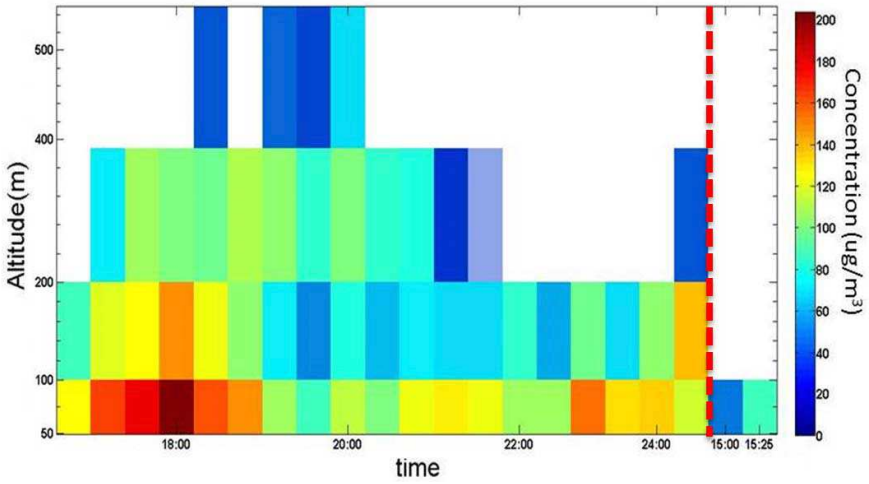

Figure 3: Sulfur dioxide data from 24 hours of DIAL measurements, from 16 : 15, March 5th, 2014 to 15 : 25, March 6th, 2014.

average concentration is 177 $\mu g/m^3$. From 100 m up to 200 m, the concentration distribution is similar as for 50–100 m, but showed a trend of decrease. For the higher altitude (200–400 m), the concentration continues to decline. For the 400–550 m altitude, the average concentration from 19 : 00 to 20 : 30 is 41 $\mu g/m^3$. Measurements were performed quasi-continuously under dry weather conditions until shortly after midnight. Then, during the night it started to rain, with an integrated rainfall for March 6 of 4.5 mm. Measurements were then resumed in the afternoon. As show in the figure (15 : 00–15 : 25) the observed SO_2 concentrations and also the measurement range are much lower than before. We observe drastic SO_2 wash-out due to the rainfall.

4. CONCLUSIONS

A 35-hour quasi-continuous DIAL mercury concentration measurement and a 24-hours quasi-continuous measurement for sulfur dioxide were performed in Guangzhou, China. The wash-out effects on mercury due to rainfall have been studied. Likewise, the concentration of SO_2 falls drastically at rainfall due to wash-out and associated acid rain formation. Our lidar system is now being integrated into a fully mobile facility, capable to be deployed into the field for remote sensing measurements in the atmospheric, aquatic, agricultural and cultural heritage sectors. Besides DIAL, fluorescence and Raman lidar, remote laser-induced break-down spectroscopy (LIBS) lidar studies will be pursued.

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