Atomic mercury flux monitoring using an optical parametric oscillator based lidar system

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Abstract A newly developed optical parametric oscillator (OPO) based differential absorption lidar (DIAL) system has been applied to the monitoring of atomic mercury emissions at several chlor-alkali plants in Europe. The versatility of the system is illustrated by measured time series of mercury flux and movies of vertical and horizontal concentration distributions, which yield important input parameters for the environmental community. Long term measurements of the resonance absorption of mercury at 253.65 nm poses special demands, i.e. long term stability, on the light source that often have been hard to fulfill, in different respects, for standard OPO and dye laser based systems. Here, approaches to meet these demands are presented.

OCIS codes: (280.1120) Air pollution monitoring; (280.1910) DIAL, differential absorption lidar; (300.6210) Spectroscopy, atomic; (190.4970) Parametric oscillators and amplifiers; (140.3580) Lasers, solid state; (280.3640) Lidar; (010.3640) Lidar; (010.1120) Air pollution monitoring.

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1. Introduction

The increased awareness of the impact of mercury on the environment and human health has caused stronger regulations against mercury emissions [1,2]. This calls for more powerful measurement techniques for surveillance of the emissions from different sources and for monitoring the local dispersion of the mercury released. In the most commonly employed chlor-alkali production scheme in Europe, mercury is still used as a liquid cathode in the electrolytic cells where chlorine, sodium hydroxide and hydrogen are formed in the electrolysis of sodium chloride. Due to the high vapor pressure of mercury already at low temperatures, considerable amounts of mercury are released into the atmosphere in the process. Thus, the chlor-alkali industry constitutes a large mercury polluter, responsible for about 12% (41 tonnes/year) of the anthropogenic total mercury emissions in Europe [3]. In this context a large cross-disciplinary project, financed by the European Union, concerning the **E**uropean **m**ercury **e**mission from **c**hlor-**a**lkali **p**lants (EMECAP) has been initiated. The goal of the project is to provide decision-makers with an improved tool for evaluating the risk to the human health and the environment around mercury cell chlor-alkali (MCCA) plants [4]. Two key inputs in this assessment are the initial plume extension and the emitted flux of gaseous elemental mercury at the source industries. Such measurements, performed within the EMECAP project, utilizing the DIAL (DIfferential Absorption Lidar) technique [5], are treated in the present paper.

DIAL measurements of mercury have been performed for a long time using dye laser systems [6,7], that have the disadvantage of having a fast degrading gain medium needing frequent service. A more convenient alternative in this respect is an all-solid-state laser system. However, the drawback of such systems is that they generally have problem producing light with stable and narrow linewidth, which is important for measurements of spectrally sharp absorption features like the one in atomic mercury. One way of dealing with this problem is by injection seeding with a narrow-banded light source, e.g. a diode laser, at the desired wavelength [8]. Unfortunately, the availability of such narrow-banded laser sources is limited to certain wavelength regions, which makes that solution not always feasible. However, a general approach to deal with the linewidth problem was recently implemented in an all-solid-state lidar system in Lund. The new system, developed on the same mobile platform as an earlier dye laser based lidar system, employs a Nd:YAG pumped Optical Parametric Oscillator (OPO) that, combined with frequency doubling and mixing stages, can generate pulsed radiation ranging from the deep-UV to the mid-IR regions [9]. The system has the possibility to present concentration maps and flux in real time during the measurement. Movies of the concentration distribution are easily made to study the temporal variation of the emission pattern during long times.

Fig. 1. The mobile lidar system in a field campaign in Rosignano Solvay, Italy.

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2. The system

The measurements presented in this paper were performed with the newly developed mobile lidar system, Fig.1, at Lund University [9]. A key component of the system is the light source, which is a modified Optical Parametric Oscillator laser system (Spectra Physics MOPO-730) that is pumped by a frequency-tripled injection seeded Nd:YAG laser (Spectra Physics Model GCR-290) and equipped with doubling and mixing crystal units.

The main modification of the OPO is the introduction of piezo-electric control of all nonlinear crystals and the mirror in the Littman cavity master oscillator, as illustrated in Fig. 2. This modification makes it possible to tune the wavelength up to 160 cm^{-1} between each shot, i.e. within a period of 50 ms, in the wavelength ranges 220-690 nm, 730-1800 nm and 2600-4300 nm [10].

Although the average spectral linewidth of the generated pulses is better than 0.2 cm^{-1}, the linewidth can reach 0.4 cm^{-1} due to fluctuations in the Littman cavity, which allows several modes to be simultaneously amplified. If the linewidth becomes broad compared to the width of the spectral feature under study the measurement is impaired. Therefore, the system is equipped with two on-line surveillance systems for monitoring the spectral quality of the emitted light. One Fabry-Pérot based system monitors the wavelength, linewidth and power in real time. Based on the linewidth measured, the backscattered light pulse from the atmosphere can be sorted into an appropriate linewidth category, which can be individually evaluated with an appropriate absorption cross-section, and if the pulse is too broad the corresponding data is not used in the evaluation process.

Moderate linewidth and wavelength fluctuations can also be handled by splitting off a small fraction of the UV pulse to an internal gas cell system, where the light is divided into two paths. One beam is passing through an absorption cell with a drop of mercury at atmospheric pressure, and the other one is passed through a cell without mercury. By measuring the mercury cell temperature, the internal mercury vapor concentration can be calculated [11]. This, together with the length of the cell and the mercury cell absorption detected gives, in real time during the DIAL measurement, the effective absorption cross section, which compensates for fluctuations in wavelength and linewidth.

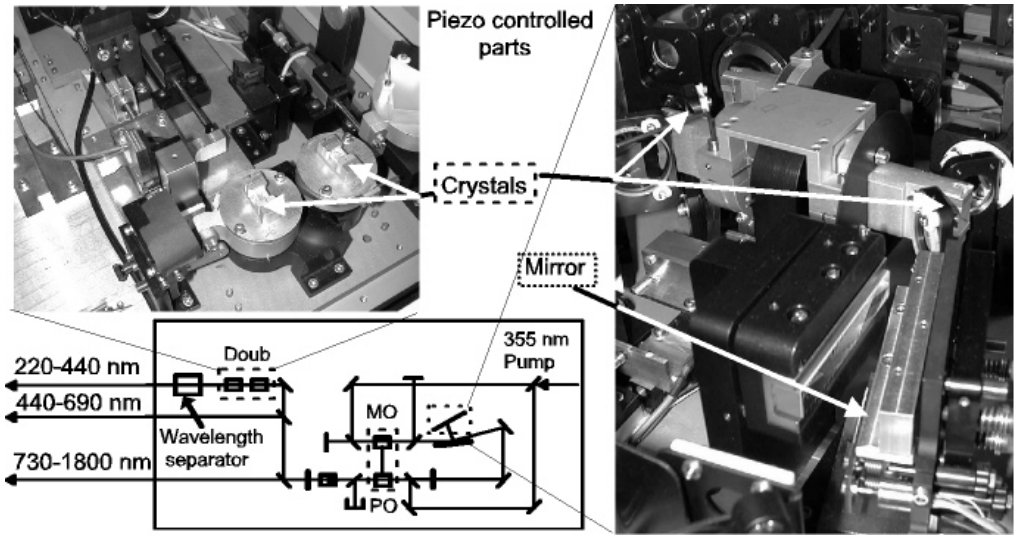

Fig. 2. Schematic overview of the master oscillator (MO) and power oscillator (PO) transmitter.

The mercury probing UV-light pulse duration is about 3-4 ns and the typical pulse energy is 12 mJ. However, the energy is normally lowered to about 5 mJ and a comparatively large

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beam divergence of about 2 mrad (full angle) of the transmitted light is set by a variable Galileian beam expander to avoid stimulated emission on the atomic line, which would result in a different effective absorption cross-section. Proper operation conditions were determined in a separate investigation [7]. The laser pulses are directed into the atmosphere by the use of a computer controlled optical dome, and a coaxial receiving Newtonian telescope collects the back-scattered photons. Before the received probing light enters a photo multiplier tube (PMT), an interference filter attenuates the background light. Furthermore, the gain of the PMT is modulated in order to suppress the signal due to intense light coming from closer distances. A 12-bit analogue digitizer unit (Licel) operating at 20 MHz, corresponding to a 7.5-m spatial resolution, then digitizes the signal from the PMT.

The mobile lidar system is accompanied by a 45 kVA diesel powered electrical generator, which makes it possible to select the appropriate measurement positions during field campaigns without being limited by stationary electrical supply facilities.

3. Measurements and results

DIAL measurements at the resonance absorption line at 253.65 nm of gaseous elemental mercury were performed with the mobile lidar system, during several field campaigns at different MCCA plants in Europe. The purposes of the measurement campaigns were to estimate the total emission of elemental mercury into the atmosphere and to make an inter-calibration with other mercury monitoring techniques as well as to provide input for the modeling of mercury dispersion. To achieve this the lidar light beam was scanned in 7-15 directions in a vertical plane, down wind of the mercury emitting cell houses, and in a horizontal plane, resulting in 2-D concentration maps. The detection range was limited to about 800 m or less depending on the scattering and absorption properties of the local atmosphere at the UV wavelengths used. Each map was, in most cases, acquired during 3-5 minutes in order to obtain a good signal to noise ratio. The radial concentration distributions were evaluated by locally weighted polynomial regression [12] using a global bandwidth [13]. The resulting radial concentration distributions for different angles of direction was then transformed into a Cartesian (x,y) coordinate system and interpolated to give 2-D concentration maps.

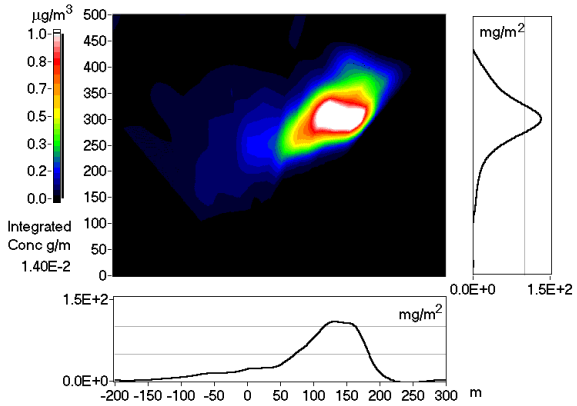

Fig. 3. (417 KB) Movie of horizontal concentration maps from the MCCA plant in Rosignano Solvay 2002-02-03, 12:11-12:38.

As an example of a concentration map, a horizontal mercury plume distribution at the MCCA plant in Rosignano Solvay (Italy) is given in Fig. 3, where a movie based on three horizontal concentration maps, recorded within half an hour with interpolated maps in between, is presented. It can be seen that the peak concentration in the plume is in the order of µg/m^3 and that the concentration level decreases a whole order of magnitude within a few hundred meters.

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An insight into the mercury plume dynamics is given in Fig. 4 and Fig. 5, where movies of consecutive vertical concentration maps, without time interpolation, from the MCCA plants in Bohus (Sweden) and Rosignano Solvay (Italy), respectively, are presented for measurements of a few hours. The concentration ($\mu g/m^3$) was integrated to give an area-integrated concentration ($\mu g/m$), which was multiplied by the wind component orthogonal to the measured plane to render the flux (g/h).

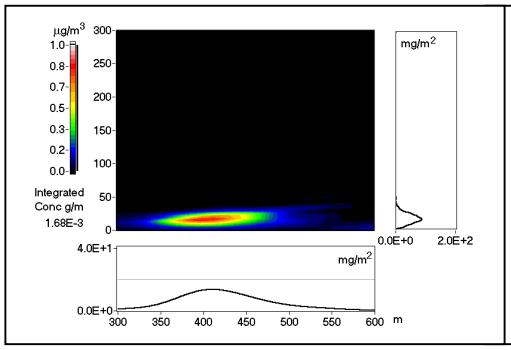

Fig. 4. (611 KB) Movie of vertical concentration maps from the MCCA plant in Bohus 2002-01-18, 12:00-15:27.

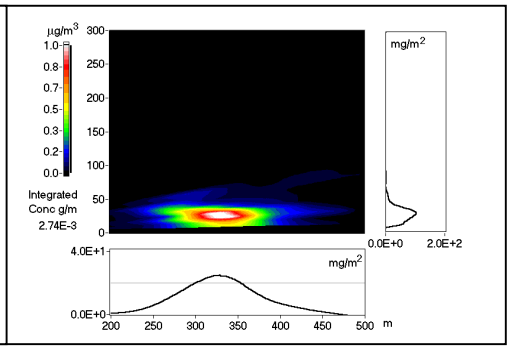

Fig. 5. (467 KB) Movie of vertical concentration maps from the MCCA plant in Rosignano Solvay 2002-02-04, 14:35-17:57.

The over-all accuracy in the flux measurements is limited by the accuracy of the wind measurements [14]. Since the accuracy is decreased for wind directions nearly parallel with the direction measured, the system was moved to the most appropriate positions regarding the mercury source and the prevailing wind directions. However, the wind direction unavoidably is changing and because there is a certain set up time after the system has been moved there are still flux data from less favorable wind conditions. For this reason, the results of measurements during wind directions more parallel to the scan direction than 25 deg was excluded from the final flux compilation. A wind vane and anemometer, placed on the roof of the cell house, monitored the wind at approximately the center height of the mercury plume with a time resolution of 30 s. Due to the lower accuracy of this instrument at lower wind speeds, data obtained at wind speeds less than 1 m/s was excluded from the final compilation also.

As examples, time series of mercury flux, evaluated as mentioned above, from Bohus and Rosignano Solvay, respectively, are presented in Fig. 6. In the lower part of the figure hourly mean values are presented. The mean values were only calculated if there were more than three accepted flux measurements during the period, since it is important that the wind conditions is fairly stable during the averaging period. The influence of wind fluctuations can be seen in the large variation in the flux during the first half of the measurement period on January 30. Later that day, the wind became more stable and also more perpendicular to the laser beam, resulting in more stable flux data. During the winter campaigns average fluxes of 6 g/h and 20 g/h were measured at the two MCCA plants in Bohus and Rosignano Solvay, respectively.

An inter-calibration between the lidar system and two point-monitoring systems was performed during an initial autumn campaign at the MCCA plant in Bohus [15]. The two point monitors were based on gold amalgamation of the mercury followed by thermal desorption and atomic fluorescence spectrophotometry (TEKRAN) and atomic absorption spectrophotometry (GARDIS), respectively. During the inter-comparison the GARDIS and TEKRAN instrument were sampling air in a point located 3 m above ground, while the lidar sampling volume (~40m *0.5m^2 , in this particular case) was placed as near (6 m above ground) that sampling point as obstructing building elements made possible. Remembering the slight difference in sampling volumes, an excellent agreement between the instruments could be seen [15].

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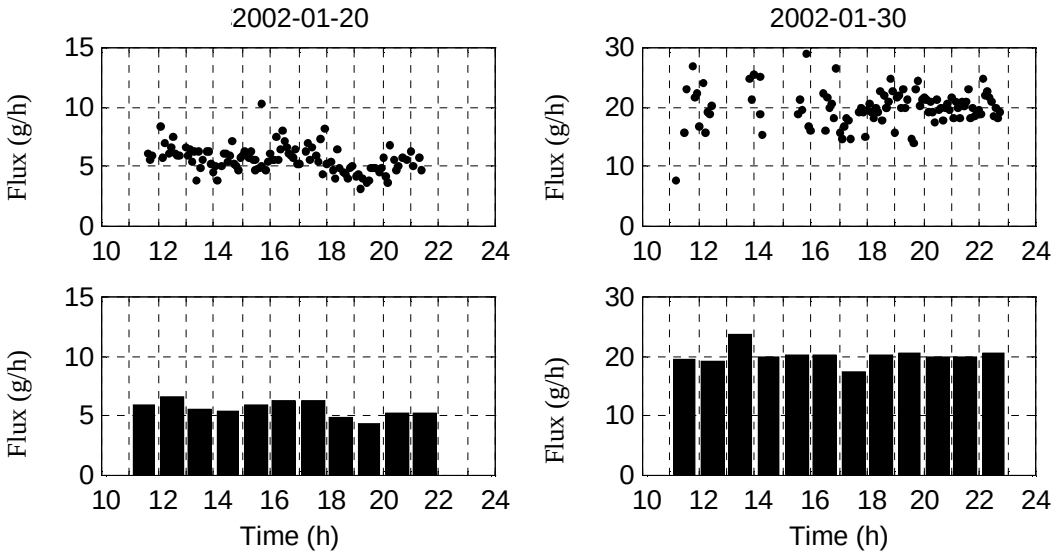

Fig. 6. Typical mercury fluxes from Bohus (left) and Rosignano Solvay (right), respectively.

4. Conclusions

The OPO based lidar system has proven to be an efficient tool for measurements of mercury in the field. Long time series of flux and concentration distributions can readily be obtained, constituting an essential input for dispersion modeling of the pollutant. The concentration values measured by the lidar system are in good agreement with corresponding values obtained by standard point monitoring systems and the accuracy in the flux measurements is normally limited by the accuracy of the wind field measurements.

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