DIFFERENTIAL ABSORPTION LIDAR MEASUREMENTS OF MERCURY FLUXES

Rasmus Grönlund[(1)], Mikael Sjöholm[(1)], Petter Weibring[(1,2)], Hans Edner[(1)], Sune Svanberg[(1)]

[(1)] Atomic Physics Division, Lund Institute of Technology, P.O. Box 118, SE-22100 Lund, Sweden,
E-mail: rasmus.gronlund@fysik.lth.se, sune.svanberg@fysik.lth.se
[(2)]National Center for Atmospheric Research, Boulder, Colorado, USA

ABSTRACT

Differential absorption lidar (DIAL) has been used to measure elemental mercury fluxes. The measurements have been performed by using the optical parametric oscillator-based mobile lidar system developed at Lund Institute of Technology, employing the mercury absorption line at 254 nm. By mapping the mercury concentration over an area downwind from the emission area and combining with wind data from a vane and anemometer the flux can be calculated. Here, we report on measurements from European chlor-alkali plants and the Idrija mercury mine, Slovenia.

1. INTRODUCTION

Elemental mercury is emitted from both natural and anthropogenic sources. Differential absorption lidar (DIAL) for measurement of elemental mercury was developed in our group from 1982 [1]. Recent measurements performed include chlor-alkali plants in Sweden, Italy and Poland [2-4] and the Idrija mercury mine in Slovenia [5].

At mercury cell chlor-alkali plants, sodium hydroxide and chlorine gas are produced by electrolysis of brine solution with mercury cells serving as one of the electrodes. Thus, large amounts of mercury are handled in the process, and inevitably mercury is emitted to the atmosphere – due to leaks in the system, maintenance procedures and gassing from spills.

In a mercury mine, mercury is present as elemental liquid mercury and as cinnabar ore (HgS). Mercury is released to the air from the natural deposits. In mining operations, the cinnabar ore is burned in a furnace to extract the elemental mercury. In this process, large amounts of mercury are released to the air.

2. MEASUREMENT SYSTEM

The measurements were performed using the mobile lidar system developed at the Lund Institute of Technology [6]. 20 Hz laser radiation is generated by a modified Nd:YAG-pumped optical parametric oscillator (OPO) system (Spectra Physics MOPO-730). The OPO consists of a master oscillator, with a BBO-crystal in an external cavity and a power oscillator as an amplifier part. The external cavity ensures a narrow linewidth. In the OPO laser radiation in the wavelength range 440-1700 nm can be produced and by a frequency doubling unit, UV wavelengths down to 220 nm can be produced. The OPO is modified with piezo-electric elements that can tilt the crystals to switch between the on- and the off-wavelength on a shot-to-shot basis. Wavelength stability is ensured by an absorption cell calibration system. The radiation is directed to the air through a roof-top dome, via a computer controlled folding mirror, such that the radiation can be directed as desired. The back-scattered radiation is collected by an on-axis Newtonian telescope with 40 cm diameter and detected using a photomultiplier tube. Typically, the signal is averaged over 100 shots on each wavelength and from the raw data, the concentration along the direction can be found. By scanning the measurement direction and interpolating between directions, the concentration over an area can be mapped.

3. MEASUREMENTS

A measurement is typically performed as a vertical scan down-wind from the pollution source. Then, a cross-section of the pollutant plume is achieved and the flux can be calculated by multiplying the area-integrated concentration with the wind speed perpendicular to the measurement plane. One such scan, giving a flux value, is taken in about 5 minutes. A measurement campaign is typically 1-2 weeks and measurements are repeated during this period to yield a representative value. Also, horizontal scans can be performed to locate the sources of pollution.

Wind data are continuously logged using a wind vane and anemometer. This instrumentation is placed as close to the measurement plane as possible, to measure the wind speed and direction in the region of interest. In one measurement campaign, tests were performed with a wind Doppler lidar system, to measure the wind field in the area of interest and to compare the results with the anemometer [7]. The study showed that the error in the anemometer measurement is relatively small.

4. RESULTS

Every scan gives a concentration map as the one seen in Fig. 1. The lidar system is placed in the origin in the coordinate system and the axes are the distances horizontally and vertically from the system. The grayscale shows the concentration in each point. The measurement is performed in a few directions and interpolated to give the result.

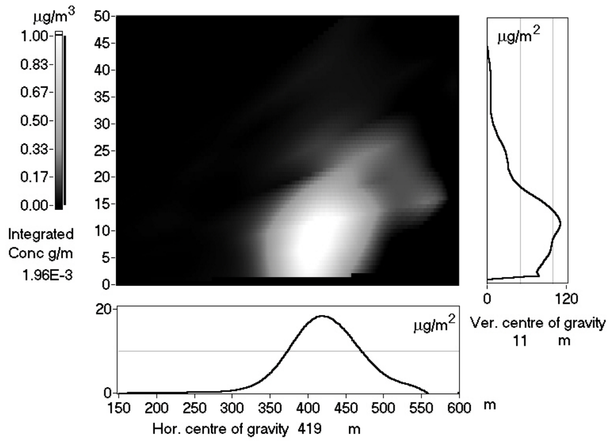

Fig. 1. Concentration map for a vertical scan.

4.1 Chlor-Alkali Industries

The mercury emission from chlor-alkali plants and its effects on workers and people living near-by were studied in a large EU-funded project (EMECAP) where our part was to measure the flux of elemental mercury from the test sites. Measurements were performed both in summer and winter and it was noted that the summer campaigns showed higher emission values. The plants in Sweden (Bohus), Italy (Rosignano Solvay) and Poland (Tarnów) showed different emission values [2-4]. The results from the different campaigns can be seen in Fig. 2.

4.2 The Idrija Mercury Mine

Measurements at the Idrija mercury mine in Slovenia were performed in a late October campaign, with quite cold weather and at many times heavy rainfall. Mining operations have been stopped, but still elevated levels of mercury can be seen [8]. Especially elevated levels could be found by the old refinery oven, where the mercury was extracted from the cinnabar ore [5]. Fluxes of about 2 g/h were measured from this area.

5. DISCUSSION

Our measurements show that the DIAL technique can efficiently be employed for measurements of elemental mercury using an OPO as radiation source. The collaborations show that lidar data are useful to scientists in other branches.

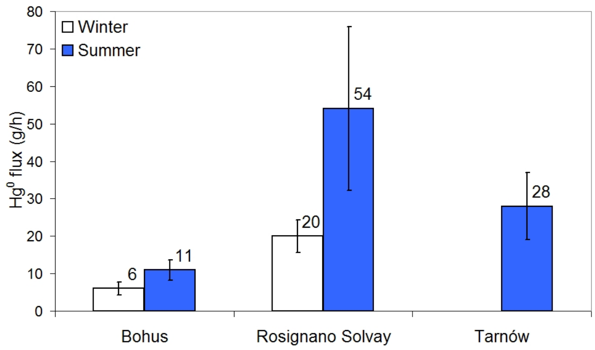

Fig. 2. Mercury emissions from the three different European chlor-alkali plants.

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