Available online at www.sciencedirect.com

SCIENCE DIRECT

Atmospheric Environment 39 (2005) 7474–7480

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Elemental mercury emissions from chlor-alkali plants measured by lidar techniques

Rasmus Grönlund*, Mikael Sjöholm, Petter Weibring, Hans Edner, Sune Svanberg

Department of Physics, Lund Institute of Technology, P.O. Box 118, SE-221 00 Lund, Sweden

Received 15 October 2004; accepted 23 June 2005

Abstract

Differential absorption lidar (DIAL) techniques have been utilized to measure elemental gaseous mercury fluxes from mercury cell chlor-alkali (MCCA) plants as a part of the European Union funded European mercury emissions from chlor-alkali plants (EMECAP) project. Three plants have been selected as study objects and a total of six measurement campaigns have been performed, one intercalibration campaign and five flux evaluation campaigns, in both winter and summer. The measurements were carried out using the Swedish optical parametric oscillator- (OPO) based mobile lidar system developed at Lund Institute of Technology. The study shows large differences in the mercury emissions measured in winter or summer and at the different plants. The average values for the campaigns ranged from 6 g h^{-1} in the winter campaign at the Swedish plant to 54 g h^{-1} in the summer campaign at the Italian plant.

Keywords: DIAL; Atmospheric mercury flux; EMECAP; Chlor-alkali plant; OPO

1. Introduction

Mercury cell chlor-alkali (MCCA) plants use liquid mercury as a cathode in electrolytic cells to produce chlorine, sodium hydroxide and hydrogen by electrolysis of brine solution. In this process, very large quantities of mercury are handled and because of the high-vapor pressure of mercury already at low temperatures, considerable amounts of mercury is emitted to the atmosphere, due to spills, leakage from mercury cells or pumps, maintenance activities, etc. (Southworth et al., 2004). Although the MCCA technique is in many places being replaced by alternatives, it is still the most commonly used in Europe.

Over the last decades, increased awareness of the environmental and human health impacts of mercury has led to stronger regulations against mercury emissions, leading to decreased emissions (Schroeder and Munthe, 1998). However, the chlor-alkali industry still constitutes a large mercury polluter, in 1995 responsible for about 12% (41.3 tonnes year^{-1}) of the anthropogenic total mercury emissions in Europe (Pacyna et al., 2001). More recent estimates reports emissions from the chlor-alkali industry to be responsible for about 17% (40.4 tonnes year^{-1}) of anthropogenic total mercury emissions in the year 2000 (Pacyna, 2003). A report from the Euro-Chlor Association (Anon, 2001) shows constantly decreasing, but still significant, emissions from chlor-alkali plants.

In this context a large cross-disciplinary project, financed by the European Union, concerning the European mercury emission from chlor-alkali plants

*Corresponding author. Tel.: +46 46 222 41 38; fax: +46 46 222 42 50.
E-mail address: rasmus.gronlund@fysik.lth.se (R. Grönlund).

1352-2310/$ - see front matter
doi:10.1016/j.atmosenv.2005.06.060

(EMECAP) has been pursued. 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 MCCA plants (Mazzolai et al. 2004; http://www.emecap.com). Within the project, epidemiological studies of people living in the vicinity of MCCA industries are performed (Barregård et al., to appear) and linked to the levels of mercury in the environment, which are assessed by point monitoring of mercury in air, soil and living organisms around the mercury emitters (Wängberg et al., 2003). These data are managed by a data mining-based software (Fayyad et al., 1996) which, interrogating dedicated epidemiological and environmental data bases, provides high-level information in terms of health risk.

For understanding the regional atmospheric dispersion of mercury a mathematical model is being developed (Munthe et al., 2001). Two key inputs in this model 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 Differential absorption lidar (DIAL) technique (Svanberg, 1994), are treated in the present paper. The model also needs input on the chemical composition of the emitted mercury, i.e. elemental mercury (Hg^0) versus reactive gaseous mercury (RGM, Hg^{2+}), etc. Such measurements were also performed and are presented in Wängberg et al. (2005).

Although flux estimation is an important issue, few techniques for flux measurements exist. Recently, Differential optical absorption spectroscopy (DOAS) measurements in the air vent from a US MCCA plant combined with wind measurements were used to assess mercury flux from the cell house (Kinsey et al., 2004). Here, the concentration is integrated over the measured path between the light-source and the detector. Using the DIAL technique, range-resolved measurements of atomic mercury concentrations and fluxes can be measured. Our group has previously reported on this kind of measurements from MCCA plants, employing different laser systems, but the same mercury absorption line at 253.65 nm (Edner et al., 1989; Ferrara et al., 1992; Edner et al., 1995; Wängberg et al., 2003; Sjöholm et al., 2004). In the present report mercury fluxes from summer and winter campaigns at three different European MCCA plants, Eka Nobel in Bohus, Sweden, Solvay in Rosignano Solvay, Italy and Zakłady Azotowe in Tarnów, Poland, are presented.

2. Measurement technique

DIAL measurements were performed on atomic mercury, using two wavelengths, one *on* the absorption line (253.65 nm) and the other slightly *off*. The *off* wavelength was chosen at a longer wavelength than the *on* wavelength to avoid interference with a close-lying, weak oxygen absorption line (Edner et al., 1989). Some unsaturated hydrocarbons and aromatic compounds absorbs light in the same wavelength region, but these elements have quite slow absorption features compared to the *on*/*off*-wavelengths and are not considered to be abundant enough to affect the signal. This was verified by measurements outside the plume not showing elevated mercury concentrations. The lidar signal was collected time-resolved to obtain a range-resolved measurement. By forming the ratio between the *on* and *off* signals, the DIAL curve is obtained, being flat where no mercury is present and sloping downwards in the presence of mercury. Since the *on* and *off* wavelengths are chosen close to each other, no other differences than the mercury absorption are expected. The output energy may be slightly different for the two wavelengths; however, this does not matter since the slope of the normalized DIAL curve is the only pertinent factor when analyzing the mercury concentrations. Particulate mercury and different Hg(II) species do not have any absorption of light at 253.65 nm, thus not being detected by the technique presented.

Each DIAL measurement, in a certain direction, gives the range-resolved mercury concentration along the laser beam. By vertical scanning of the laser beam downwind from a pollution source, in this case a chlor-alkali plant, a concentration cross-section of the mercury plume is found. The mercury flux is estimated by area integration of the concentration and multiplication by the wind speed component perpendicular to the cross-section surface.

The measurements were performed using the Swedish optical parametric oscillator- (OPO) based mobile lidar system, built inside a Volvo F610 truck (Weibring et al., 2003). The OPO (Spectra-Physics MOPO-730) is pumped by a pulsed (20 Hz) frequency-tripled Nd:YAG laser at 355 nm and gives output in the wavelength range 440–1800 nm which can be frequency doubled to reach wavelengths down to 220 nm. The OPO is modified with piezo-electric elements so that the wavelength can be switched within a range of $160\,cm^{-1}$ between consecutive shots. The average linewidth of the transmitter is normally better than $0.2\,cm^{-1}$ and the pulse length is typically 3–4 ns. An absorption cell system is used to compensate for fluctuations in wavelength and linewidth of the emitted laser light pulses.

The laser radiation is sent into the air through the dome, hoisted to the roof of the truck, which can be rotated 360° and by using a folding mirror the beam can be tilted vertically from −10° to 55°. The backscattered radiation is collected using the on-axis, 40-cm-diameter Newtonian telescope and focused onto a photomultiplier tube. An interference filter is used to suppress background light, since only elastic scattering is of interest. The retrieved signal is then digitized at a