

# LUND UNIVERSITY

# Differential Absorption Lidar Mapping of Atmospheric Atomic Mercury In Italian **Geothermal Fields**

Edner, H; Ragnarson, P; Svanberg, Sune; Wallinder, E; Deliso, A; Ferrara, R; Maserti, B. E

Published in: Journal of Geophysical Research

DOI: 10.1029/91JD03108

1992

Link to publication

Citation for published version (APA): Edner, H., Ragnarson, P., Svanberg, S., Wallinder, E., Deliso, A., Ferrara, R., & Maserti, B. E. (1992). Differential Absorption Lidar Mapping of Atmospheric Atomic Mercury In Italian Geothermal Fields. *Journal of Geophysical Research*, *97*(D4), 3779-3786. https://doi.org/10.1029/91JD03108

Total number of authors:

#### **General rights**

Unless other specific re-use rights are stated the following general rights apply:

- Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the
- legal requirements associated with these rights

· Users may download and print one copy of any publication from the public portal for the purpose of private study or research.

- You may not further distribute the material or use it for any profit-making activity or commercial gain
  You may freely distribute the URL identifying the publication in the public portal

Read more about Creative commons licenses: https://creativecommons.org/licenses/

#### Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

LUND UNIVERSITY

**PO Box 117** 221 00 Lund +46 46-222 00 00

# Differential Absorption Lidar Mapping of Atmospheric Atomic Mercury in Italian Geothermal Fields

H. Edner, P. Ragnarson, S. Svanberg, E. Wallinder

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

A. De Liso, R. Ferrara, and B.E. Maserti

CNR - Istituto di Biofisica Via S. Lorenzo 26, I-56127 Pisa, Italy

Revised manuscript, Dec. 1991

To appear in Journal of Geophysical Research

# Differential Absorption Lidar Mapping of Atmospheric Atomic Mercury in Italian Geothermal Fields

H. Edner, P. Ragnarson, S. Svanberg, E. Wallinder

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

A. De Liso, R. Ferrara, and B.E. Maserti

CNR - Istituto di Biofisica Via S. Lorenzo 26, I-56127 Pisa, Italy

#### Abstract

Results from extensive lidar measurements on atmospheric atomic mercury in Italian geothermal fields are reported. A mobile differential absorption lidar system operating on the 254 nm mercury resonance line with a measuring range of about 1 km was used in mineralized as well as non-mineralized areas. Measurements were performed at geothermal power stations and in an unexploited field with natural surface geothermic manifestations. Atomic mercury concentrations ranging from 2-1000 ng/m<sup>3</sup> were mapped. The high Italian geothermal mercury concentrations are in strong contrast to the recent lidar finding of the absence of atomic mercury in Icelandic geothermal fields.

#### INTRODUCTION

Atomic mercury is frequently found at elevated concentrations in geothermal fields. This can constitute a pollution problem but can also provide an interesting possibility for prospecting for geothermal energy [*Varekamp and Buseck, 1983*]. Previous studies with mercury point monitors at the Geysers geothermal plant in California and at the Cerro Prieto plant in Mexico reveiled high concentrations of atomic mercury in the tower exhaust air [Robertson et al., 1977]. In independent cooling measurements at Geysers geothermal plant a multi-pass the atomic atomic mercury was used absorption spectrometer sensitive only to [Jepsen, 1973]. In one geothermal plume more than  $28 \ \mu g/m^3$  was detected while the concentration in ambient air at the field site was of the order of hundreds of ng/m<sup>3</sup>. Also in Italian geothermal fields such as Larderello and Piancastagnaio (Tuscany) high concentrations have been measured [Ferrara et al., 1991]. Generally mercury appears in its atomic form (90 %) while chemical compounds are more rare in the atmosphere form (90 %) while chemical compounds are more rare in the atmosphere.

The contribution of the geothermal sources to the worldwide mercury flux is actually poorly investigated. Values for mercury flux from volcances and associated natural geothermal sources have been estimated to  $10^{-}10^{8}$  g/y by various authors [Anderson, 1975; Unni et al., 1978]. These values are less than a per cent of the estimation of  $\sim 2 \cdot 10^{6}$  g/y for total natural and anthropogenic sources of atmospheric mercury [Matheson, 1979]. More recently, Varekamp and Buseck proposed a value of  $1-7 \cdot 10^{6}$  g/y for volcanic flux [Varekamp and Buseck, 1980], but it is probably still underestimated. In fact, Siegel and Siegel found for the Kilauea main vent an annual flux of of  $2.6 \cdot 10^{8}$  g/y and reported a value of  $3.5 \cdot 10^{6}$  g/y for six Central American volcances [Siegel and Siegel, 1984]. Mercury is also known to be present in Icelandic geothermal fields [Kristmannsdóttir, 1984] but the methods used did not allow any assessment of the speciation of the element. Recently, field experiments using differential absorption lidar (DIAL) techniques [Measures, 1984] were performed in Icelandic geothermal fields in an attempt to map atomic mercury distributions [Edner et al., 1991]. The lidar technique is only sensitive to atomic mercury and not to chemical compounds since it relies on the differential absorption of the atmosphere at the mercury resonance line at 253.6 nm. It was surprisingly found that elevated values of atomic mercury could not be found in any of the three geothermal fields investigated. In view of the extensive information available on mercury in Italian geothermal fields and in order to make a comparison with the Icelandic findings we decided to perform the lidar field experiments reported on in the present paper.

Geothermal energy plays an important part in Italian energy supply presently accounting for about 3 percent of the total electricity production and with a strong developmental plan. Major geothermal exploration areas in Italy are indicated on the map given in Fig. 1. High enthalpy (with a vapor temperature > 200 °C) and low enthalpy (with a vapor temperature < 200 °C) geothermal fields are distributed in the entire territory. Out of these the Larderello and the Mt. Amiata endogenous fluids are well suited for direct electricity production. These two fields differ in that the Larderello geothermal field, one of the two deposits of dry vapour known in the world, is situated in a nonmineralized region, while the Mt. Amiata hydrothermal system is situated in a strongly mineralized region, rich in cinnabar ore. A comparison between the atmospheric mercury contents in these areas is therefore of special interest. The stratigraphic sequence in the Larderello and Mt. Amiata geothermal fields are characteristic of Central-Southern Tuscany (*Atkinson et al., 1977*). Starting with the deepest terrains known in this area, we have:

a) a basal terrigenous complex, consisting mainly of phyllites and quartzites of the Paleozoic-Triassic ("basement" and lower part of the Tuscan series);

b) a mainly carbonate complex (Tuscan series) with at the base dolomites and anhydrites (upper Triassic), massive limestones and cherty stratified limestones (Lower Jurassic), marls and radiolarites (Middle-Upper Jurassic);

c) an upper terrigenous complex (Tuscan series), with at its base, a shaly formation (Scaglia), overlain by Nummulite- bearing calcarenites and, in some places, sandstones (Macigno) (Eocene-Oligocene);

d) a mainly shaly flysch facies complex, containing marly and arenaceous formation ("Alberese-Pietra-forte" group) (Cretaceous-Eocene);

e) a mainly clay complex of the Lower-Middle Pliocene, lying unconformably over all the lower complexes.

The presence of a volcanic body distinguishes the Mt. Amiata geothermal area from the other Tuscan ones. The Mt. Amiata massif (1738 m) is constituted by a volcanic complex, formed by lava and lava domes of a mainly quartz-latitic composition.

The volcanic region of Mount Amiata has an extension of about 400 km<sup>2</sup> and is one of the most important cinnabar (HgS) deposits in the world. The cinnabar mines were intensely exploited from the beginning of

the last century till 1980. Even now the widespread roasted cinnabar deposits and the mine ventilation outlets are a noticeable source of atmospheric mercury pollution.

In the Mt. Amiata region there are three known small geothermal fields (each one of no more than  $10 \text{ km}^2$  of area), in which energy extraction has been performed since 1959; actually, three power plants are operating. In this region three important thermal stations are also present.

Because of these pecularities the Mt. Amiata region has been intensely studied since the beginning of the 20th century. The first studies on the metal pollution consequences on the health of the mercury miners date back to 1909 [Giglioni, 1909]. Later, studies on mercury concentrations in fresh-water mussels [Renzoni and Bacci, 1976; Bacci et al., 1978] and on mercury levels in the environment [Bombace et al., 1973] were performed. After the end of the mercury mining period substantial research efforts on the mercury levels in both the abiotic and the biotic compartments were carried out by several authors [Ferrara et al., 1982; Breder and Flucht, 1984; Bargagli and Baldi, 1984; Ferrara et al., 1986; Bargagli et al., 1986; Ferrara et al., 1988; Barghigiani et al., 1988; Ferrara et al., 1991]. In this literature data on atmospheric mercury levels related to soil degassing processes are given. No information is available on atmospheric mercury emissions from geothermal fields.

The geothermal area of Larderello is located in the central part of Tuscany 100 km SW from Firenze. It is characterized by the presence of "soffioni" (vapor dominated hot steam jets), "lagoni" (pools of boiling mud and water) and "thermal springs" (warm water used as thermal baths since the Etruscan time). The exploration of the vapor for electric power production dates back to 1904. Till now 27 geothermal power plants, each with an extracted power from 20 to 118 MW, are present. For the next few years the installation of 20 standardized geothermal plants with a power of 20 MW are scheduled.

The health hazard of the geothermal emissions as atmospheric mercury sources has been hypothesized since 1973 [Siegel and Siegel, 1975]. Preliminary studies [Ferrara et al., unpublished data] in abiotic and biotic compartments reveal a small increase of the mercury levels with respect to the background values in Tuscany. Mercury concentration values are instead high close to the geothermal plants, probably because of the fall out of the emitted mercury.

Extensive field experiments using the lidar techique supported by analytical point monitoring were performed in the Mt. Amiata and Larderello geothermal areas during 3 weeks of September 1990. In the next section we give a brief description of the lidar system used and of the point monitors. Then measurements and results are reported with an estimation of the total mercury flux from a particular geothermal plant. Finally, we discuss the result of the present work.

#### DESCRIPTION OF MERCURY LIDAR SYSTEM AND POINT MONITORS

The remote atomic mercury mapping was performed with a mobile laser radar system with a basic construction as has been described by *Edner et al.* [1987]. The system was further developed to allow atomic mercury measurements, particulary what regards achieving a sufficient laser pulse power and a sufficiently low laser linewidth at the 253.6 nm mercury resonance line [*Edner et al., 1989*]. The system was later used in Icelandic geothermal fields, as discussed above [*Edner et al., 1991*].

The lidar equipment is housed in the laboratory space of a Volvo F610 truck, towing a 20 kVA diesel electric generator making the system self-supporting in field work. A photograph of the lidar van at the Castelnuovo di Val di Cecina geothermal power plant is shown in Fig. 2. The pulsed laser lidar transmitter is a tunable dye laser, pumped by the third harmonic of a powerful Nd:YAG laser. With about 200 mJ pumping energy the dye laser produced pulses at about 507 nm of up to 30 mJ energy at 10 Hz. The green dye laser pulses are frequency-doubled in a beta-barium borate (BBO) crystal to reach the mercury resonance line at 253.6 nm with pulse energies up to 5 mJ. The frequency of the laser is controlled by observing the absorption in a cell with saturated mercury vapor. Every second pulse the laser is tuned just off the line for recording reference signals.

The laser beam is directed out into the atmosphere via a large, computer-controlled mirror on top of the lidar van. In this way the measurement direction can be chosen. Back-scattered light from the atmosphere is reflected via the same large mirror down into a vertical Newtonian telescope with a diameter of 40 cm. The telescope field-of-view is selected by a small aperture in the image plane, where a metal mirror reflects off all light into a TV camera, except that in the solid angle covering the propagating laser beam. The lidar signal is detected by a photomultiplier tube preceded by an interference filter selecting the mercury resonance line. In order to reduce the requirements of dynamic range of the detection electronics the photomultiplier voltage, determining the gain, is ramped up to reach its full value at a time corresponding to a measurement range of about 300 m.

The signal from the photomultiplier tube is fed to a transient recorder where an A/D conversion is performed. Lidar signals from on- and off-resonance laser pulses are then averaged in separate memories to reach the required signal-to-noise ratio. By using the ratio of the on and off signals, the absorption from Hg at a certain distance can be monitored, and the concentration as a function of distance can be calculated without a knowledge of the atmospheric aerosol distribution, since the wavelength difference is only 10 pm. The off-resonance wavelength is positioned on the high-wavelength side of the mercury line to avoid interference due to molecular oxygen absorption [Edner et al., 1989]. By measuring in several adjacent directions data for constructing a horizontal or a vertical map of the atmospheric Hg concentration can be obtained. Integration of the concentration in a vertical plane downwind from the source can be combined with wind data to measure the flux of mercury.

The on-resonance lidar signal from a mercury plume will contain some contribution from resonance fluorescence, which will slightly affect the concentration evaluation [Edner et al., 1989]. The main effect is a displacement of the calculated concentration profile to a position further from the lidar system. Since the displacement normally is smaller than the evaluation interval and does not affect the total concentration in a flux measurement, no attempts to correct for this effect were made in the present measurements. The effects of Doppler broadening and rotational Raman lines in the backscattered light, producing unabsorbed components in the on-resonance lidar signal [Ismail and Browell, 1988; Ismail and Browell 1989], were also found to be negligible.

For the point measurements supporting the lidar data monitors based on collection of mercury on a gold trap followed by flameless atomic absorption-spectrometry were used. Air is sucked at a flow rate of 0.5-2litres/minute by means of a membrane pump. The absorption collector is made by a quartz tube (length 15 cm, internal diameter 0.3 cm) containing a coil of pure gold (0.2 g). The agreement between lidar and point monitoring data was established in an industrial area, where the atmospheric mercury was known to be in atomic form because of the metallic mercury source (chlor-alkali plant) [*Ferrara et al., 1991*].

#### MEASUREMENTS AND RESULTS

Measurements were performed at four places, located in two different geothermal fields: at Piancastagnaio in the Mt. Amiata region, and at Larderello, Castelnuovo di Val di Cecina and Lagoni Rossi in the region of the Larderello geothermal fields. At the first three places measurements were made at geothermal power plants while the natural emissions from the largely unexploited field at Lagoni Rossi were studied.

#### Piancastagnaio

The studied geothermal power plant is one of several in the Mt. Amiata region. The electricity production is about 20 MW. Raw lidar signal intensities for on- and off-resonance wavelengths as recorded in a direction through the plume close to the plant are shown in Fig. 3. The ratio differential absorption lidar curve is also included in the figure. The effect of the ramping of the photomultiplier voltage can clearly be seen with a strong resulting reduction in the near field region. At distances larger than 300 m the true fall-off of the curves can be seen. In the ratio curve a horizontal part corresponds to the absence of mercury, which is the case for distances up till 150 m and beyond 500 m. The strong reduction in the ratio curve between these two distances corresponds to the presence of a mercury plume. By making a scan across the plume direction a vertical map as shown in Fig. 4 can be obtained. Here the averaged result from 3 individual vertical scans during a total measuring time of 50 minutes is shown. The mapping was made from a different position further away from the plant and the plume was captured about 100 m downwind from the plant.

Values measured with point monitors at 2 m above the ground upwind the power plant were of the order of 3-4 ng/m<sup>3</sup> at a distance of 30 m, while downwind values of 900-1000 ng/m<sup>3</sup> were attained at a distance of 10 m.

Integrating the mercury concentration over the plume cross section and multiplying with the wind velocity perpendicular to the measurement direction a value for the total atomic mercury flux from the plant could be obtained. With an estimated wind velocity of 3-4 m/s we arrive at the value 18-24 g/h, corresponding to an annual atmospheric mercury discharge of 160 - 210 kg.

#### Larderello

The geothermal electric power stations at Larderello are the largest ones in Europe. Our studies in Larderello were confined to the older of the two stations, built in 1948 and later modernized and with a maximum output power of 118 MW. Three "soffioni" originating in geothermal reservoirs situated at 700, 1500 and 3500 m depth are conducted to the power plant. The station has four cooling towers.

During the measurement period in Larderello there was almost no wind, and thus determinations of the total flux of mercury from the station could not be made. Lidar measurements were performed in different directions for assessing the mercury concentrations. Point measurements were performed at different locations from the ground level up to 15 meter elevation around the four cooling towers.

The result of a vertical scan close to and downwind the northernmost cooling tower is shown in Fig. 5. The silhouette of a cooling tower (to scale) is included as are some results from our point monitors.

#### Castelnuovo di Val di Cecina

The electric power plant at Castelnuovo di Val di Cecina has an output power of 30 MW. A view of the plant was given in Fig. 2. The concentration of atomic mercury was mapped by the lidar and the result is given in Fig. 6. The figure is a composite of vertical and horizontal scans as indicated by the dots. From this charting it is evident that the main part of the mercury is not emerging together with the visible water vapor plume from the top of the cooling tower but rather it escapes from the openings in the lower part of the tower.

the openings in the lower part of the tower. With the aim of explaining these findings we think a brief description of the functioning of the cooling towers is necessary. The cooling water coming from the turbine, with a temperature of about 45°C, is pumped into the top of the cooling tower, from where it trickles towards the bottom from a height of about 15 m. External air enters the tower by the lower openings with a flow of 12·10° m<sup>3</sup>/h to cool the trickling water, which is then sent back again to the turbine, with a temperature of about 30°C. A determination of the mercury levels in the water sampled at the lower openings has shown concentrations (400 ng/l) higher than that observed in condensed vapor (10-80 ng/l). The high levels of atmospheric mercury might come from a process of collection and release of the mercury contained in the cooling air by the water that trickles inside the tower. The cooling tower then behaves like a scrubber system for the atmospheric mercury.

Mercury values in the air measured with point monitors at 0.5 m above, the ground and at a distance of 200 m around the plant, are about 3 ng/m<sup>2</sup>, except in the downwind direction, where values of 20 ng/m<sup>2</sup> were observed.

# Lagoni Rossi

In the Lagoni Rossi area only two small geothermal power plants with output powers of 7 and 1 MW, respectively, are operating. There are many natural emissions of endogenous vapor ("putizze") in this area and our measurements were confined to the natural emission areas. The lidar system was placed close to an area of open geothermal manifestations. A map showing the measurement paths and the localization of our point monitors is shown in Fig. 7. There also our mean mercury concentrations data for the study period are included. Several measurements with point monitors were performed in the area with open geothermal manifestations with readings ranging from 5-15 ng/m<sup>3</sup> close to the ground. It was hard to measure close to the ground with the lidar system because of strongly scattering plumes of condensed water vapor. As can be seen in Fig. 7 the average value in the path crossing the jet plume area was just 6 ng/m<sup>3</sup> for the beam traversing the atmosphere at 3-8 m distance above the ground. For the same direction a point monitor measurement of 15 ng/m<sup>3</sup> is indicated. The higher values towards the north and north-east of the lidar system are probably related to emissions from one of the two geothermal power plants.

Towards the south we performed measurements over the valley of the river Cornia terminating the laser beam against the slope on the other side of the river at a distance of 1610 m (as measured with the lidar

"range finder"). In these measurements the atmospheric backscattering was strong enough to allow an evaluation out to a distance of 750 m. Two range intervals were evaluated showing а decrease mercury in concentration at higher heights above the ground. For evaluating the concentration at larger distances the echo from the grass slope was used. It was noticed that there were much larger fluctuations in the signals from the ground-echo than from the atmosphere. This is due to beam steering in the atmosphere due to turbulence. For the atmosphere this has a minor importance since the signal is derived from the atmosphere present everywhere whereas the spatially unstable beam may hit the ground at different places. Thus, in order to obtain reliable data using topographic targets or retro-reflectors it is necessary to perform a substantial signal averaging, when using a DIAL system with alternating on and off-resonance wavelengths. The lidar measured concentration south of the river is therefore more uncertain.

#### DISCUSSION

In the present measurements it was established that geothermal energy extraction is connected with substantial emissions to the atmosphere of atomic mercury. This is particularly evident in the geothermal field in the mineralized area of Mt. Amiata, where fluxes of mercury of 18-24 g/h have been measured from a geothermal plant. The good agreement between lidar and point measurements on occasions when measurements were possible to intercompare also shows, that the Italian geothermal mercury emissions are mainly in the atomic form. This is in strong contrast to the recent findings of zero atomic mercury atmospheric emission in Icelandic geothermal fields [*Edner et al., 1991*]. Mercury is present also in Iceland [*Kristmannsdottir, 1984*], but in a speciation not containing elemental mercury.

It is difficult to draw far-reaching conclusions regarding the amount of mercury emission from the different geothermal areas studied, due to the limited time for the measurements with typically a few days on each location. A comparison of mercury fluxes was also hampered by the lack of wind during the experiments in Larderello. However, it should be noted that the estimated annual mercury discharge to the atmosphere from a plant like the one studied in Piancastagnaio producing 20 MW is typically 1/3 of the one of the major chlor-alkali plant at Rosignano-Solvay (Livorno) producing 120,000 tons of chlorine annually [*Ferrara et al., 1991*]. Further studies over a longer time period are needed for a more quantitative comparison of the mercury emission from different geothermal areas. The present measurements have shown that lidar can be a very useful technique in this context, with its ability to cover a large area and to make mesurements of the mercury flux from different sources.

#### ACKNOWLEDGEMENTS

The authors gratefully acknowledge assistance in the measurements by P. Olsson. This work was supported by the Swedish Natural Science Research Council and the Swedish Board for Space Activities.

#### REFERENCES

Anderson, A.T., Some basaltic and andesitic gases, Rev. Geophys. Space Phys., 13, 37-55, 1975.

Atkinson, P., R. Celati, R. Corsi, and H. Ramey, Thermodynamic behavior of the Bagnore geothermal field, in Proc. *Geothermal Resource Assessment and Reservoir Engineering*, Larderello, Sept. 12-16, pp 78-130, ENEL-ERDA (eds), Roma, 1977.

Bacci, E., C. Leonzio, and A. Renzoni, Mercury decontamination in a river of Mount Amiata, Bull. Environ, Contam. Toxicol., 20, 577-581, 1978.

Bargagli, R., and F. Baldi, Mercury and methilmercury in higher fungi and their relation with the substrata in a cinnabar mining area, *Chemosphere*, 13, 1059-1071, 1984.

Bargagli, R., C. Barghigiani, and B.E. Maserti, Mercury in vegetation of the Mount Amiata area, *Chemosphere*, 15, 1035-1042, 1986.

Barghigiani, C., R. Bargagli, B.Z. Siegel, and S.M. Siegel, Source and selectivity in the accumulation of mercury and other metals by the plants of M. Etna, *Water, Air and Soil Pollut.*, *39*, 395-408, 1988.

Bombace, M.A., L. Cigna Rossi, G.F. Clementi, G. Zuccaro Labellarte, M. Allegrini, E. Lanzola, and L. Gatti, Ricerca ecologica sulle zone mercurifere del Monte Amiata, *Igiene e Sanitá Pubblica, 20,* 191-237, 1973.

Breder, R., and R. Flucht, Mercury levels in the atmosphere of various regions and locations in Italy, Sci. Total Env., 40, 231-244, 1984.

Edner, H., K. Fredriksson, A. Sunesson, S. Svanberg, L. Unéus, and W. Wendt, Mobile remote sensing system for environmental monitoring, *Appl. Opt.* 26, 4330-4338, 1987.

Edner, H., G.W. Faris, A. Sunesson, and S. Svanberg, Atmospheric atomic mercury monitoring using differential absorption lidar techniques, *Appl. Opt.*, 28, 921-930, 1989.

Edner, H., G.W. Faris, A. Sunesson S. Svanberg, J. Ö. Bjarnason, H. Kristmannsdóttir, and K. H. Sigurdsson, Lidar search for atmospheric atomic mercury in Iceland geothermal fields, *J. Geophys. Res.*, 96, 2977-2985, 1991.

Ferrara, R., A. Petrosino, B.E. Maserti, A. Seritti, and C. Barghigiani, The biogeochemical cycle of mercury in the Mediterranean, *Env. Technol. Lett.*, 3, 449-456, 1982.

Ferrara, R., B.E. Maserti, A. Petrosino, and R. Bargagli, Mercury levels in rain, air and subsequent washout mechanism in a central Italian region, *Atmos. Environ.*, 20, 125-128, 1986.

Ferrara, R., B.E. Maserti, and R. Bargagli, Mercury in the atmosphere and in lichens in a region affected by a geochemical anomaly, *Environ. Technol. Lett.*, 9, 689-694, 1988.

Ferrara, R., B.E. Maserti, H. Edner, P. Ragnarson, S. Svanberg, and E. Wallinder, Mercury emissions to the atmosphere from a chlor-alkali plant measured by the lidar technique, Submitted to Atmospheric Environment.

Ferrara, R., B.E. Maserti, H. Edner, P. Ragnarson, S. Svanberg, and E. Wallinder, Atmospheric mercury detections by lidar and point monitors in environmental studies, in *Environmental Geochemistry and Health*, 1991 (in press).

Ferrara, R., B.E. Maserti, and R. Breder, Mercury in abiotic and biotic compartments of an area affected by a geochemical anomaly (Mt. Amiata, Italy), *Water, Air and Soil Pollution*, 1991, in press.

Giglioni, G.Y., Contributo allo studio dell'idrargirismo professionale nel bacino del Monte Amiata (Sirena), *Il Ramazzini, 3*, 230-396, 1909.

Ismail, S., and E.V. Browell, Influence of rotational Raman scattering in DIAL measurements, *Proc. 14th International Laser Radar Conference*, Innichen - San Candido, Italy, June 20-24, 1988.

Ismail, S., and E.V. Browell, Airborne and spaceborne lidar measurements of water vapor profiles: a sensitivity analysis, *Appl. Opt.*, 28, 3603-3615, 1989.

Jepsen, A.F., Measurements of mercury vapor in the atmosphere, Chapter 5 in *Trace Elements in the Environment, Adv. in Chem. Ser.*, vol. 123, pp. 80-94, American Chemical Society, Washington, D.C., 1973.

Kristmannsdóttir, H., Chemical evidence from Icelandic geothermal systems, in *Hydrothermal Processes at Seafloor Spreading Centers*, edited by P.A. Rona, K. Bostrom, L. Laubier and K.L. Smith, Jr., pp. 291-320, Plenum, New York, 1984.

Matheson, D.H., Mercury in the atmosphere and in precipitation, in *The Biogeochemistry of Mercury in the Environment*, edited by J.O. Nriagu, pp.113-129, Elsevier/North-Holland Biomedical Press, Amsterdam, 1979.

Measures, R.M., Laser Remote Sensing, Wiley Interscience, New York, 1984.

Renzoni, A., and E. Bacci, Bodily distribution, accumulation and excretion of mercury in a freshwater mussel, *Bull. Environ. Contam. Toxicol.*, 15, 366-373, 1976.

Robertson, D.E., E.A. Crecelius, J.S. Fruchter, and J.D. Ludwick, Mercury emissions from geothermal power plants, *Science 196*, 1094-1097 (1977)

Siegel, S.M., and B.Z. Siegel, Geothermal hazards. Mercury emission, *Environ. Sci. Technol.*, 9, 473-474, 1975.

Siegel, S.M., and B.Z. Siegel, First estimate of annual mercury flux at the Kilauea main vent, *Nature, 309*, 146-147, 1984.

Unni, C., W. Fitzgerald, D. Settle, G. Gill, B. Ray, C. Patterson, and R. Duce, The impact of volcanic emission on the global atmospheric cycles of sulfur, mercury and lead (abstract), *Eos Trans. AGU*, 59, 1223, 1978.

Varekamp, J.C., and P.R. Buseck, Mercury emissions from Mount St Helens during September 1980, *Nature*, 293, 555-556, 1981.

Varekamp, J.C., and P.R. Buseck, Hg anomalies in soils: a geochemical exploration method for geothermal areas, *Geothermics 12*, 29-47, 1983.

ł

# FIGURE CAPTIONS

Fig. 1. Map of Italy with major geothermal exploration fields indicated.

Fig. 2. Photograph of the lidar system at the geothermal power plant at Castelnuovo di Val di Cecina.

Fig. 3. Lidar signals on and off the Hg resonance line near the geothermal power plant at Piancastagnaio.

Fig. 4. Charting of the mercury concentration distribution in a vertical plane downwind from the Piancastagnaio plant.

Fig. 5. Vertical lidar scan of mercury concentration close to a cooling tower at Larderello. Concentration results from point monitor measurements are also inserted.

Fig. 6. Distribution of mercury in the vicinity of cooling towers at Castelnuovo di Val di Cecina deduced from vertical and horizontal lidar scans as indicated by the dots.

Fig. 7. Schematic map of the Lagoni Rossi geothermal area with averaged mercury concentrations as assessed by lidar and point monitors.













