Environ Monit Assess (2011) 181:225–241
DOI 10.1007/s10661-010-1825-5

Biomonitoring with epiphytic lichens as a complementary method for the study of mercury contamination near a cement plant

Tanja Ljubič Mlakar · Milena Horvat · Jože Kotnik · Zvonka Jeran · Tomaž Vuk · Tanja Mrak · Vesna Fajon

Received: 2 December 2009 / Accepted: 24 November 2010 / Published online: 17 December 2010

Abstract The study was focused on understanding the mercury contamination caused by a cement plant. Active and passive biomonitoring with epiphytic lichens was combined with other instrumental measurements of mercury emissions, mercury concentrations in raw materials, elemental mercury concentrations in air, quantities of dust deposits, temperatures, precipitation and other measurements from the cement plant's regular monitoring programme. Active biomonitoring with transplanted lichens *Pseudevernia furfuracea* (L.) Zopf was performed at seven of the most representative sites around the cement plant and one distant reference site for periods of 3, 6 and 12 months. In situ lichens of different species were collected at the beginning of the monitoring period at the same sites. Mercury speciation of the plant exhaust gas showed that the main form of emitted mercury is reactive gaseous mercury Hg^{2+}, which is specific for cement plants. Elemental mercury in air was measured in different meteorological conditions using a portable mercury detector. Concentrations in air were relatively low (on average below 10 ng m^{-3}). In situ lichens showed Hg concentrations comparable to lichens taken from the background area for transplantation, indicating that the local pollution is not severe. Transplanted lichens showed an increase of mercury, especially at one site near the cement plant. A correlation between precipitation and Hg uptake was not found probably due to a rather uniform rainfall in individual periods. Dust deposits did not influence Hg uptake significantly. Lichens vitality was affected over longer biomonitoring periods, probably due to some elements in dust particles, their alkalinity and the influence of other emissions. Mercury uptake measured in vital transplanted lichens was in a good correlation with the working hours (i.e. emitted Hg quantity) of the kiln. The study showed that selected lichens could be used to detect low to moderate Hg emissions from a cement plant and that the biomonitoring procedure could be further standardized and used as part of an environmental monitoring programme.

Keywords Mercury · Emission · Biomonitoring · Epiphytic lichens · Cement plant

T. Ljubič Mlakar (✉) · T. Vuk
Salonit Anhovo, Building Materials, Joint-Stock Co., Anhovo 1, 5210 Deskle, Slovenia
e-mail: tanja.ljubic-mlakar@salonit.si

M. Horvat · J. Kotnik · Z. Jeran · T. Mrak · V. Fajon
Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

Introduction

The cement clinker production process involves specific behaviour of mercury due to the counter flow of materials and gases and recycling of filter dust in high temperature, several staged processes, which cause several mercury loops. Due to the cycling procedures Hg mass flows within the process are multiplied several times in comparison to the Hg mass flow into the process and the Hg mass flow emitted from the plant (Ljubič Mlakar et al. 2008, 2009, 2010). Mercury enters the process with raw materials and fuels and is transformed into a gaseous form at elevated temperatures between 200°C and 700°C. Mercury in the exhaust gas bound on particles is mostly removed by dust filters and recycled with the raw materials. The rest of the mercury is emitted through the main chimney with exhaust gases. The specific feature to cement plants is the high share of reactive gaseous Hg^{2+} in emitted gas (Bhatty 1995; Schneider and Oerter 2000; Schäfer and Hoenig 2001; VDZ 2006; Ljubič Mlakar et al. 2008, 2009, 2010).

Beside different parameters, e.g. the height of the stack, temperature of gases, plume height, meteorology, terrain, etc., mercury deposition processes strongly depend on the mercury species emitted. Hg^0 is practically not deposited locally and it predominantly contributes to the global cycle. For mercury bound on particles (Hg(p)) wet deposition is the most significant process and for Hg^{2+} both processes (dry and wet deposition) are important mechanisms for entry into the local environment (US EPA 1997). We also assumed that in the case study and other cement plants with a high share of Hg^{2+} emission the local deposition of mercury is important and also connected with accumulation processes in biomonitoring lichens (Balarama et al. 2004).

There are two main possibilities to study the influence of mercury emissions from a cement plant: to measure the emissions from the stack and model the dispersion into the environment or, alternatively, to use biomonitoring or other direct measurements in the environment. There are numerous models for modelling of atmospheric pollution processes, but there are still some limitations on the models used, especially in very complex terrain, which is also the case with the cement plant studied. In general, both measurements and the modelling approach are connected with high uncertainty. Compliance monitoring of mercury mainly includes only information on total Hg emissions through stack flue gases. In some cement plants, continuous monitoring of mercury in exhaust gases has already been introduced using various measuring devices, but in many cases, such systems have some problems regarding accurate detection of Hg concentrations (Schneider and Oerter 2000; Johansen and Hawkins 2003; VDZ 2006).

Biomonitoring methods reflect processes in living organisms and could indirectly indicate some possible health effects in the area, e.g. in connection with food chain effects (Bargagli 1998; Conti and Ceccheti 2001), and in view of several limitations of other (instrumental and modelling) monitoring techniques, biomonitoring could be used in integral monitoring approaches to fill the gaps. In terms of reliability and cost-effectiveness, lichens are very appropriate biomonitoring plants for short- and long-term environmental monitoring of mercury due to their specific properties and absorptive capacity for gaseous forms (especially of reactive Hg^{2+}) or Hg bound to particles (Garty 1993; Jeran et al. 1995; Bargagli 1998; Horvat et al. 2000; Wolterbeek 2002; Szczepaniak and Biziuk 2003; Balarama et al. 2004). Because of these benefits, we chose this technique combined with other direct measurements as the main methodology of the study. One of the major reasons that biomonitoring methods have not been widely used in official monitoring programmes and have not been adopted by regulators as yet is the problem of variability and the lack of quantification (Bargagli 1998; Wolterbeek 2002; Wolterbeek and Verburg 2002; Szczepaniak and Biziuk 2003). In this study, special attention was given to the possibility of quantification.

The influence of different industrial and urban activities has been studied intensively by several authors using biomonitoring methods. An overview of biomonitoring methods, the use of lichens, statistical methods for interpreting results and other important aspects of biomonitoring was given by Garty (1993), Tuba and Csintalan

(1993), Sloof (1995), Bargagli (1998), Conti and Ceccheti (2001), Wolterbeek (2002) and Szczepaniak and Biziuk (2003). The effects of environmental pollution on lichen vitality, cell integrity, metabolic processes and the damage caused by deficiency or excess of specific pollutants and elements were studied by Garty et al. (1993) and Vingiani et al. (2004). The effects of local variations on biomonitoring quality were studied in detail by Wolterbeek and Verburg (2002). Seasonal and climatic effects on bioaccumulation of individual elements by lichens and mosses were studied by Fernández et al. (2000), Adamo et al. (2003), Garty et al. (1993) and Vingiani et al. (2004). The process of uptake and bioaccumulation as well as the vitality and growth of lichens depend on different parameters, e.g. lichen type, age and sorption characteristics, mercury species, solubility of elements and compounds, pH, bond type and strength, leaching, lichen vitality, characteristics of the micro location, precipitation level and humidity, temperature, altitude, ambient elemental occurrences, seasonal effects (elemental leaching and increased availability by rainfall), variations in growth rates, availability of calcium ions and other factors connected to local variability (Garty 1993; Bargagli 1998; Fernández et al. 2000; Conti and Ceccheti 2001; Wolterbeek 2002; Ikigura and Akagi 2002; Adamo et al. 2003; Garty et al. 1993; Balarama et al. 2004; Vingiani et al. 2004; Bergamaschi et al. 2007; Branquinho et al. 2008). In Hg uptake by lichens, gaseous rather than particulate forms are involved (Bargagli 1998). Some trace elements e.g. Zn, Cr, Cu, As, Cd, Se, Ni, Tl, etc. and emissions of NO_x, SO_2, halogen compounds, ozone, organic compounds, dioxins, furans, etc. from the cement plant could influence lichen metabolism and uptake (Garty et al. 1993; Bargagli 1998; Wolterbeek and Verburg 2002; Wolterbeek 2002).

Biomonitoring of trace elements and mercury near power plants was performed by (Bargagli et al. 1997), using native plants. Active biomonitoring of mercury near waste incinerators was performed by Carpi et al. (1994), using moss and grass for 14 days of active biomonitoring at relatively low mercury concentrations. Hg emissions from chlor-alkali plants were studied by (Fernández et al. 2000), using transplanted (30 days) and native mosses in different seasons. (Fernández et al. 2004) also performed statistical analysis of the variability of active biomonitoring of Hg and other elements near a chlor-alkali plant and a concrete plant. Calasans and Malm (1997) used transplanted lichens and Lodenius (1998) used transplanted mosses to study dry and wet atmospheric deposition of Hg^0 near a chlor-alkali plant with very high concentrations. In Slovenia, active and passive biomonitoring with lichens has been successfully used to evaluate the spatial and temporal impacts of former mercury and uranium mines (Lupšina et al. 1992; Jeran et al. 1995). Similar methods were used around natural gas processing facilities in Croatia (Horvat et al. 2000) and also by Tuba and Csintalan (1993).

Mercury emissions from cement plants are not as high as emissions from e.g. coal-fired power plants, but they still represent a significant part of total anthropogenic emissions. In 2008, they were estimated to comprise about 5.6% of total mercury emissions from global anthropogenic sources and to about 12.6% in Europe (without Russia) (Pirrone et al. 2008) based on a cement plant emission inventory for 2000 (Pacyna et al. 2006). However, only a limited number of papers were published about the nature and behaviour of mercury emissions from cement plants (Fukuzaki et al. 1986; Johansen and Hawkins 2003; Schuhmacher et al. 2004; Ljubič Mlakar et al. 2006). Among industrial facilities, power plants and waste incinerators could be the most similar to cement plants, but both have different speciation of Hg in their exhaust gases and a larger share of Hg^0 (US EPA 1997). The presented study formed part of an integral study which was focused on the behaviour and mass flows of mercury in the cement production process (Ljubič Mlakar et al. 2006, 2008, 2009, 2010). The Salonit Anhovo, Joint-Stock Co. cement plant in Slovenia (Fig. 1) was selected as the case study.

The main aim of the study was to evaluate the type and quantity of mercury emissions from the cement plant, to check the severity of mercury contamination in the local environment and to determine the relationships between the quantity of mercury emitted from the plant and mercury

Fig. 1 Location of the cement plant of Salonit Anhovo in Slovenia

concentrations in transplanted lichens and thus to indicate the possibility of quantification of this biomonitoring methodology.

Experimental

Study site

The cement plant is located in the western part of Slovenia, in the narrow Soča valley, an area with naturally elevated mercury concentrations (Fig. 1).

The river is the natural transport system for mercury from the former mercury mining area of Idrija (Horvat et al. 2002, 2003; Hines et al. 2000; Grönlund et al. 2005). The climate in this area is sub-Mediterranean, showing the influence of the Adriatic Sea. According to measurements between 1961 and 1990 at the nearest meteorological measuring station (Bilje, about 30 km from Anhovo), the average annual precipitation is 1,456 mm/year and the average yearly temperature is 11.8°C. Precipitation is also measured regularly by the Salonit Anhovo internal measuring network and the data are collected in the plant database. The area (height above sea level is about 90 m) is surrounded by steep mountain slopes (up to 787 m a.s.l.). The high peaks and steep mountain slopes prevent free air circulation in the valley, but the area is in general quite windy. Wind roses in the location of the cement plant were determined in previous studies and were used to help explain the results of this study (Ministry of the Environment and Spatial Planning of Republic of Slovenia 1995, 2004). The predominant wind directions are indicated in Fig. 2. The most common winds follow the topography of the valley. Prevailing wind directions are on average from N to NNE and SSW. Stronger winds follow

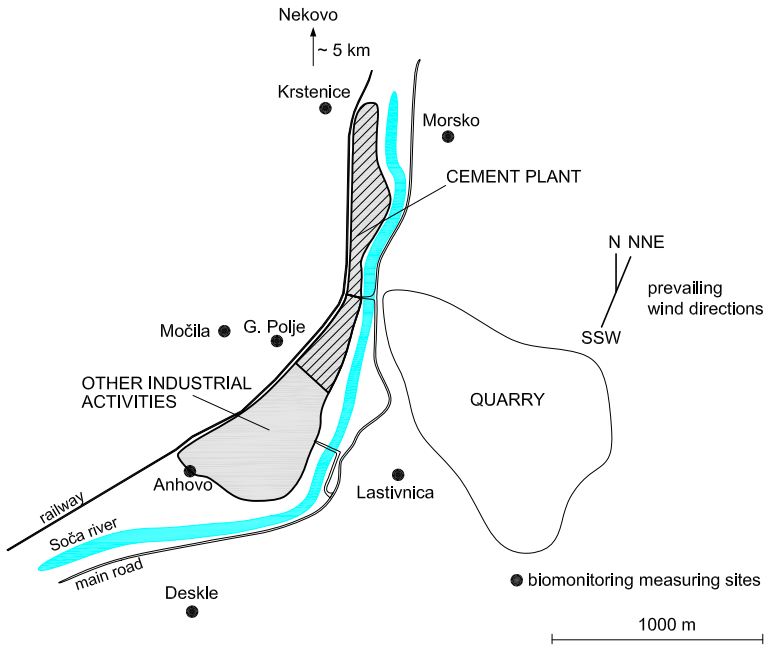

Fig. 2 Sampling locations for lichen biomonitoring near the cement plant and prevailing wind directions. The direction of local reference location (Nekovo) is marked by an arrow (site off map)

the same directions. Winds in other directions across the valley, e.g. E and W, blow mostly at night and in colder periods of the year and are less typical. There is a significant difference between day and night, as well as between summer and winter wind conditions. During the winter and at nights, more winds are directed up the valley (SSW direction).

Beside emissions from the main kiln chimney, there are several other dust emission sources in the cement plant region based on dust from background materials in the local area e.g. grinding mills, packing devices, silos, dispersed sources (internal transport, a quarry, manipulation of outdoor materials, etc.) and other industrial activities like the manufacture of concrete and fibre-cement products, etc. (Fig. 2). The only important source of Hg in the area is the cement plant and the main release of mercury is from the kiln stack.

Measuring concept, sampling, sample preparation and transplantation of lichens

Different species of in situ lichens and the transplanted epiphytic lichen *Pseudevernia furfuracea* (L.) Zopf in combination with other instrumental measurements were used to evaluate the influence of mercury emissions from the cement plant on the environment caused by atmospheric dry and wet deposition. Beside passive and active biomonitoring at the selected measuring sites around the cement plant, the following measurements and analysis were also performed: mercury emissions from the stack, mercury concentrations in raw materials and materials from the cement plant, elemental mercury concentrations in air, dust deposits, temperatures, precipitation and some other measurements of the regular cement plant monitoring programme. Passive and active biomonitoring was planned on the basis of experience with the existing emission measuring network (Fig. 2) in the surroundings of the cement plant, which has been used for a period of two decades for collecting dust depositions, inhalable particulates and some heavy metals in dust depositions (Košuta and Bizjak 2000). An additional benefit of the existing measuring network was the possibility to collect some other data that could help to interpret the results.

Sampling of lichens and transplantation

P. furfuracea (L.) Zopf, a fruticose epiphytic lichen, was selected as the biomonitoring organ-

ism for the experiment with transplanted lichens due to its (a) specific morphology which enables easy collection and cleaning and (b) its moderate sensitivity to air pollution (Hawksworth and Rose 1976; Bargagli 1998) with the ability to grow on acidic and acidified substrates. It has also often been employed for bioaccumulation surveys (Bari et al. 2001; Vingiani et al. 2004; Bergamaschi et al. 2007; Adamo et al. 2003). Background lichen thalli were collected from a single European larch, *Larix decidua* Mill., on the Pokljuka plateau (1,200 m a.s.l.), a remote mountain area in the Eastern Julian Alps on 21st May, 2005. In the laboratory, they were cleaned (according to the procedure for lichen preparation described below) and packed in nylon net bags (~4 mm mesh): one large (~4 g) or two to three smaller thalli (~1.5–2 g) were packed in each bag.

The experiment with transplanted lichens was performed in the period from 26th May 2005 for 3, 6 and 12 months at eight locations (Fig. 2) in the surroundings of the cement plant. Seven locations were chosen in its close vicinity within 2 km. The location of Nekovo lying about 5 km N from the cement plant chimney in an area above the Soča river valley was selected as the local reference (background) site, not directly influenced by the cement plant. The length of the period of exposure of transplanted lichens is one of the very important aspects of active biomonitoring. Lichens can show changes in a very short period of a few weeks in severely polluted areas. In moderate or low pollution areas, changes could be slow, taking decades. Residence times could also be different (i.e. 1–5 years), but the activity of lichens could also be influenced by other factors affecting their vitality, as described in introduction and section on lichen vitality below. Periods of active biomonitoring were selected in accordance with the knowledge that mercury emissions from the cement plant are low and that general pollution in the area is moderate to low. Other studies, performed mostly in areas with higher mercury pollution (e.g. Calasans and Malm 1997; Lodenius 1998; Fernandez et al. 2004) used shorter periods, but in this case study very short periods might not show sufficient changes in mercury concentrations.

At each location, nine bags containing lichen thalli were tied with plastic string on branches of local fruit trees at a height of 1.5 to 2 m above the ground and left for 3, 6 or 12 months. After the end of each exposure period three sample bags (subsamples) were collected from each location and transferred to the laboratory. The collection of samples at each location was performed on 25th August 2005, the second on 23th November 2005 and the third on 25th May 2006. The cement production was running without special problems in the whole period of biomonitoring; only in March and April 2006 was the kiln stopped due to major maintenance work. In this period the electrostatic precipitator for cleaning flue gases from the kiln was exchanged with a modern filter bag cleaning device. More details about local specifics in the individual sampling periods are given in Table 4.

Sampling of in situ lichens near the cement plant

On 26th May 2005 in situ lichens were also collected from the same locations as chosen for exposure of transplanted lichens. In general the lichen flora was relatively poor and sufficient quantities of macrolichens (*Xanthoria parietina* (L.) Th. Fr., *Punctelia subrudecta* s.lat. and *Flavoparmelia caperata* (L). Hale) were found only at four out of eight sampling locations (Table 4). At the most exposed sites in the near vicinity of the cement plant only *X. parietina*, a typical neutrophytic species, which favours basic substrates, was found. This species is known from the literature to be tolerant to higher calcium deposition (Armstrong 1990) and was reported to be abundant in the close vicinity of cement plants even on acidic pine and birch substrates (Jalkanen et al. 2000).

Preparation of lichen samples

In the laboratory, in situ lichen samples were carefully separated from bark. Samples were not washed, as our aim was to measure particles that were physically trapped on the surface of the thallus as well as chemically bound to the cell wall or present intercellularly. Transplants of *P. furfuracea* were cleaned, dead parts removed and only healthy and undamaged thalli were processed

further. For analysis, all lichen samples were made brittle by immersion in liquid nitrogen and then crushed and homogenized by grinding in an agate ball mill (Jeran et al. 1996, 2002; Horvat et al. 2000).

Analytical and measuring methods

Determination of elemental gaseous mercury concentrations in air

Elemental gaseous mercury concentrations in air were measured using a Lumex RA-915+ Zeeman Mercury Analyzer (Sholupov et al. 2004). The analyzer operation is based on differential atomic absorption spectrometry using high frequency modulation of light polarization. The detection limit of the instrument for ambient air, industrial and natural gases is 2 ng m^{-3} at a flow rate through the instrument of 20 L min^{-1}. The precision of the method at low mercury concentrations expressed as the relative standard deviation is about 10% to 15%. Measurements of elemental gaseous mercury were made at or near the same sampling sites (Fig. 2) used for exposure of transplanted lichens. Measurements were made about 1.5 m above the ground in May 2005, January 2006 and October 2006. Sampling times lasted from 2 to 7 h. Air temperatures were between 6°C and 15°C at the time of sampling.

Sampling of mercury speciation in flue gas

Gaseous Hg species in flue gases were determined by the MESA method principle (Prestbo and Bloom 1995; Prestbo and Tokos 1997). The MESA sampling system for gas phase Hg species employs a series of heated, solid phase absorbent traps. The flue gas is drawn through a heated quartz tube followed by a series of two KCl/soda lime traps and two iodinated carbon traps. Oxidised Hg species (Hg^{2+}, MeHg) are absorbed by the KCl/soda lime sorbent, while Hg^0 passes through and is collected by the iodinated carbon sorbent. Flue gas flow rates through the traps were 0.5 ± 0.1 L min^{-1} for a 1-h (±10 min) period. The traps were heated at 95 ± 5°C. The traps were stored in special plastic containers at approximately 0°C. Flue gas was extracted from the stack through a previously acid-washed quartz tube to the heated system of traps. To prevent any contamination with outside air, a gold trap was placed between the last trap and the vacuum pump. Each sampling procedure was performed three times.

Sampling of solid particles in the flue gas

Solid particles from the flue gas were sampled by the manual gravimetric method for determination of the concentration and mass flow in the stack (performed by RACI, d.o.o.). The method is appropriate for concentrations between 0.005 and 10 g m^{-3}. The measurement uncertainty was greater than 10% with concentrations below 0.05 g m^{-3}. The method complies with the standard ISO 9066:1992. In the last sampling period the sampling was performed by the manual gravimetric method according to standard EN 13284–1:2002 Stationary source emissions—Determination of low range mass concentration of dust: the manual gravimetric method (Institute for Health Protection, Institute for Environmental Protection, Maribor) is appropriate for dust concentrations between 0.0005 and 5 g m^{-3} with a declared measurement uncertainty below 30%. The dust from the flue gas was collected on a previously dried and weighed filter. The sampling device was placed in the gas flow under isokinetic conditions. The concentration of particles in the gas was calculated from the mass of dust and the flow through the filter.

Determination of total mercury concentration in solid samples

Total Hg in lichens and solid samples from the process was analysed by CV AAS (cold vapour atomic absorption spectrometry) after wet digestion. Samples from the process collected in the last sampling period were analysed mostly by combustion and CV AAS detection (DMA analyser). The two methods were inter-compared on a number of samples in order to assure comparability of results. In the wet digestion method about 200 mg of powdered sample was weighed directly in a

teflon digestion vessel, and after adding 4 ml of concentrated HNO_3 (lichens) or 5 ml of HNO_3 and HF in the proportion 2:1 and 1 ml HCl (materials from the process), the vessel was closed and the mixture was left to react at room temperature for an hour. Digestion was finished by heating at 100°C for 12 h on a hot plate. When cool, the sample was diluted with Milli-Q water to the mark (25.8 ml). An aliquot of the digest was added to the reduction cell and after reduction with $SnCl_2$, mercury was swept from the solution by aeration and concentrated on a gold trap. Mercury was then released from the gold trap by heating and detected by CV AAS. Applying the above analytical procedure, the limit of detection (LOD) for the determination of total Hg was 0.2 ng g^{-1}. The estimated uncertainty with a coverage factor of 2 was 14% (Horvat et al. 1986, 1991).

The second approach was performed by a commercially available DMA-80 system (Milestone Srl) which was found to be very suitable for accurate and precise determination of total mercury in solid samples from the cement plant production process. The method combines thermal decomposition of the sample, amalgamation and atomic absorption detection. In principle, approximately 100 mg of solid sample is weighed in a metal boat and placed in the auto-sampler. Controlled heating in an oxygenated decomposition furnace is used to liberate mercury from solid and aqueous samples in the instrument. The sample is dried and then thermally and chemically decomposed within the decomposition furnace at 650–850°C, depending on the sample matrix. An oxygen stream passing through the tube carries the remaining decomposition products through the amalgamator that selectively traps mercury vapour. Then flowing oxygen carries the mercury vapour through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. The absorbance (peak height) was measured at 254 nm as a function of mercury concentration. The method is described in detail by EPA – Method 7473 [5-SW-846]. Applying the above analytical procedure, the LOD for determination of total Hg was 0.1 ng g^{-1}. The estimated uncertainty with a coverage factor of 2 was 12%.

Determination of quantities of dust depositions

Dust depositions were regularly determined at the measuring locations in the surroundings of the cement plant with the method VDI 2119 Part 2: Measurement of Particulate Precipitations; Determination of Dust Precipitation with Collecting Pots Made of Glass (Bergerhoff Method). The principle of the method is capturing dust particles in a plastic pot of defined diameter filled with water, for a defined period of time. After that the pot is transported into the laboratory where the dust is dried and heated to obtain the solid dry fraction, which is weighed. The result is given as the quantity of particles per m^2 per day. The method is a good indicator of pollution of the environment with particles larger than 10 μm, but it could be somewhat affected by contamination (e.g. insects, leaves, etc.).

Analytical quality control

Possible limitations of the methodology used could be related to the selection and density of measuring sites, methods of sample collection, preparation and the analysis protocol, beside local and natural variability. To minimize these possible effects, we used the experience of the existing measuring network and strict procedures of sampling and analytical methods. All lichen samples were treated and analysed in accordance with quality assurance principles and standards requirements. Hg was determined in each sample by three successive measurements. Measurements of gases were performed with calibrated devices and in accordance with the principles of measurement protocols and standards. Solid and liquid samples were analysed in accordance with quality assurance principles. In all cases, there were at least two or three (n) independent analyses. The accuracy of the results was also verified by the regular use of the Certified Reference Materials (CRMs) – IAEA-405 (Sediment), NBS-1630 (Coal) and IAEA-336 (Trace and minor elements in lichens). Data obtained were recorded on data quality control charts and no deviations outside the acceptable range were observed.

Results and discussion

Mercury emissions from the cement plant

Mercury measurements of exhaust gas and materials and in different operational regimes were performed systematically in three measuring campaigns and additionally regular monitoring of total mercury was performed twice a year. Total mercury emissions from the cement plant were always far below the limit value of 0.05 mg Nm^{-3} (Directive 2000/76/EC). The maximum value of about 0.01 mg Nm^{-3} was measured on 14th February 2006. The average annual mercury emission from the main chimney, according to all the measurements, was about 10 kg. According to the last set of measurements the share of particulate mercury Hg(p) was only 0.3% and the share of gaseous mercury Hg(g) was 99.7% on average, but this measurement series was performed after the installation of the new bag filter, which is also much more efficient in dust cleaning than the previously used electrofilter. In the previous system (the first two measurement campaigns) Hg(p) was about 10% and Hg(g) about 90% and the temperature of the exhaust gas was about 30°C lower. The majority of gaseous mercury emission Hg(g) in the last set of measurements was in the reactive Hg^{2+} form. The share of Hg^{2+} depended on the operating regime and was much higher (about 83%) when the system operated in the so-called direct mode than in the combined mode of operation (about 51%). According to the results of all measuring sets, we could estimate the approximate shares of mercury species in the emitted gas stream during the biomonioring period as 10% Hg(p), 60% Hg^{2+} and 30% Hg^{0} on average (all regimes of operation).

Effects of background, local variability, dust deposition and seasonal effects on lichen vitality and mercury uptake

Representative samples from the quarry were collected and analyzed to obtain an overview of Hg concentrations in the natural background of the cement plant. Results are given in Table 1. The concentrations of mercury in raw materials are low. Concentrations of Hg in lichens were several magnitudes higher and thus we can exclude the influence of background materials and particulate forms on the uptake of mercury by lichens. The main influence comes from the cement plant, which is the only source of gaseous mercury emissions in this area.

Table 1 Results of Hg analysis in selected samples of raw materials from the main quarry of Rodež near the cement plant

Component	Hg (ng g^{-1})	Relative standard deviation (%)	No. of samples
AL	9.62	22.6	4
AS	13.24	8.7	3
AD	18.92	7.6	4
FR	43.65	79.0	4

Relative standard deviation between three successive analyses of Hg in the single sample was in the range of 0–9%

AL limestone, left; *AS* limestone, middle; *AD* limestone, right; *FR* flysch

The main characteristics of successive periods of biomonitoring with transplanted lichens are given in Table 2. Table 3 shows the results of measurements of dust deposition in individual measuring sites. The periods of biomonitoring were 3, 6 and 12 months from the initial date (26th May 2005) and thus lichens transplanted for longer periods were exposed to all the listed conditions and to sum of dust depositions in individual periods.

It was observed that natural lichens were absent in the sampling sites of Deskle, Močila, Lastivnica and Morsko. This could be partly the consequence of the lack of suitable trees and other substrates or also the consequences of air pollution and other environmental effects. Transplanted lichens collected after individual sampling periods were examined visually by eye. It was found that some of the exposed thalli were affected during exposure, especially during winter. They became partly or completely fragile and mouldy. The most effected site was Morsko with two samples affected after 6 months and three samples after 12 months. At Močila, one sample was affected after 6 and three samples after 12 months; in Deskle, two of three samples were affected after 12 months and in

Table 2 Characteristics of individual periods of active biomonitoring with transplanted lichens

Period of exposal		Precipitation (mm)	Avg. temperature (°C)	Working hours kiln (h)
26.5.05–25.8.05	Summer	469	20.2	1881
25.8.05–23.11.05	Autumn	497	13.7	1807
23.11.05–25.5.06	Winter and Spring	772	7.2	2803

Anhovo, Lastivnica, Krstenice and Nekovo one of three samples was harmed after 12 months.

According to the nature of the materials involved in the process of cement production, the most relevant dust emissions are related to materials with a high content of Ca and other elements like Fe, Al and Si. Calcium compounds (e.g. limestone, cement, clinker) have basic pH properties (Jalkanen et al. 2000) and the alkaline hydration reaction of cement or clinker dust particles in aqueous media (rain). The harmful effect on transplanted *P. furfuracea* could be explained by the acidophilic nature of this species which is not able to tolerate the alkalinity caused by dust of calcium-based cement particles reacting with water (rain, moisture).

Mercury uptake by surviving lichens was the highest in the first period of exposal (Summer) in most cases. Dust deposits had no particular influence on Hg uptake. A correlation between precipitation and Hg uptake was also not found.

Measurements of elemental gaseous mercury in air

Concentrations of elemental gaseous Hg were measured with a transportable Lumex RA-915+ Zeeman Mercury Spectrometer three times in different meteorological conditions: May 2005—sunny, moderate wind blowing SSW to NNE; January 2006—cloudy, practically no wind; October 2006—cloudy, very weak wind blowing SSW to NNE.

Elemental gaseous mercury concentrations emitted from the cement production plant were spread over a relatively large range (1–103 ng m^{-3}) but were, in most cases, below 10 ng m^{-3}. The only exception was the elemental gaseous Hg mean concentration of about 80 ng m^{-3}measured on May 2005 at the Morsko site, which was significantly higher. During the measurement, the wind was blowing in a SSW direction from the main cement plant chimneys of height 75 m. We can assume that this measurement showed the influence of the cement clinker production process. Two other series of measurements were performed under conditions with weak or no wind, and they showed a more uniform mercury distribution in the cement plant surroundings. Evidently, elemental gaseous mercury from the stack, which represents only a minor part of the total Hg emitted, was diluted by several order of magnitude at a distance of a few hundred metres from the plant.

A slight decreasing trend of Hg^0 concentrations with distance was observed. The whole area around the plant showed quite low Hg^0 concentrations. Correlations between Hg^0 in air and the distance from the chimney were not very good as the terrain and meteorology in this area are complex; measurements of Hg^0 in air were limited to only three periods and not all possible meteorological conditions were included. To obtain better correlations more measurements in all the representative meteorological conditions would be necessary, but according to the difficult terrain, wind specifics and the rise of the hot plume from

Table 3 Quantities of cumulative dust deposition in g m^{-2} in individual successive periods of biomonitoring

Location: Unit:	Nekovo g m^{-2}	Krstenice g m^{-2}	Morsko g m^{-2}	Močila g m^{-2}	G. Polje g m^{-2}	Deskle g m^{-2}	Anhovo g m^{-2}	Lastivnica g m^{-2}
26.5.05–25.8.05	6.3	8.4	13.1	11.0	16.7	9.6	17.2	10.2
25.8.05–23.11.05	7.0	8.7	13.5	7.6	10.9	6.6	9.9	9.0
23.11.05–25.5.06	12.6	18.3	15.8	12.5	27.0	15.8	22.1	14.9

Table 4 In situ lichen samples

Lichen species	Location	Substrate
Xanthoria parietina	Anhovo	*Prunus domestica*, *Prunus avium*
Xanthoria parietina	Gorenje Polje	*Fraxinus* sp.
Xanthoria parietina		*Prunus avium*
Punctelia subrudecta	Krstenice	*Prunus domestica*
Punctelia subrudecta	Nekovo	*Prunus domestica*
Flavoparmelia caperata		*Prunus domestica*

the stack, such a correlation would be probably difficult to obtain.

Mercury in in situ lichens

Mercury concentrations in in situ lichens collected near the cement plant (Table 4) at the beginning of biomonitoring with transplanted lichens are presented in Fig. 3. In situ lichens could not be collected from the sampling locations of Deskle, Lastvnica, Morsko and Močila due to absence of adequate amounts of macrolichens. Re-sampling after the period of exposure of the transplanted lichens was not performed, as we wished only to record the state of in situ lichens in the observed region.

Concentrations of Hg in different lichen species at all sampling locations near Salonit Anhovo were comparable and in agreement with the results of in situ *Hypogymnia physodes* collected at remote sites all over Slovenia where values between 50-170 ng g^{-1} were obtained (Jeran et al. 1996 and 2002) and also with initial concentrations in *P. furfuracea* lichens collected in Pokljuka and used for transplantation. Small differences in Hg between different species can be related to interspecies variations, host trees, age and characteristics of the micro location and other effects of local variability described in the previous section. Concentrations were also in accordance with other literature data about ranges of concentrations in in situ fruticose epyphitic lichen (Bargagli 1998), thus showing that the contamination caused by mercury emission from the cement plant is not severe. For comparison, concentrations of Hg in lichens from one of the most contaminated places in Slovenia, the former Idrija mercury mine area, was a factor of 1,000 times higher, in the range of up to 25–188 μg g^{-1}(Kotnik and Horvat 2000; Lupšina et al. 1992).

Mercury in transplanted lichens

Only healthy transplanted lichens were used for the analysis of mercury with the CVAAS method. At all sampling locations Hg levels in exposed lichens increased with time (Table 5).

Relative standard deviations of three successive measurements on the same sample (bag) were between 0–9% of average value, while relative standard deviations between average Hg concentrations in three parallel samples (bags) of lichens in the same sampling periods were between 3–20%, taking into account only the cases with

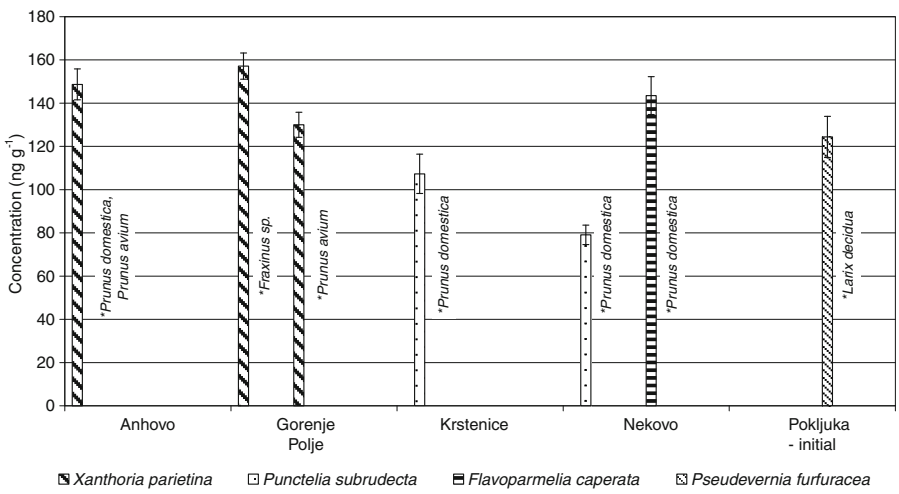

Fig. 3 Concentrations and standard deviations of measurements ($n = 3$) of total mercury by CV AAS in in situ lichens near the cement plant and in initial background (initial) lichens from Pokljuka (average value of selected representative lichens). Host tree species are marked with an *asterisk*, lichen species are represented by *different patterns of bars*

Table 5 Total mercury concentrations measured by CV AAS in transplanted lichens after 3, 6 and 12 months of exposure

Location	Nekovo	Krstenice	Morsko	Močila	G. Polje	Lastivnica	Deske	Anhovo
3 months	170	151	137	179	181	156	159	162
6 months	208	175	175	189	222	162	172	180
12 months	198	199	–	–	259	200	151	235

Results are expressed in ng g^{-1} dw as an arithmetic mean calculated from all available measurements. The initial value was 124 ng g^{-1}

three representative results (samples of surviving lichens). For easier interpretation, the results were normalized to the average initial concentration of Hg in *P. furfuracea* (124 ng g^{-1}) and are presented as concentration ratios (CR) after 3, 6 and 12 months of exposure in Fig. 4.

Evidently, CR above 1 was observed at all locations. The highest concentration ratios were found at G. Polje and Anhovo, which lie in the predominant wind directions with respect to the position of the main stack. Surprisingly, mercury enrichment in lichens exposed at the reference site of Nekovo was higher than expected and could be ascribed either to atmospheric transport from the cement plant or long-range transport from other more distant sources (Idrija or continental). Concentrations of Hg in transplanted lichens showed higher Hg concentrations than in the in situ lichens *P. subrudecta and F. caperata* collected at the beginning of the exposure period, which could be due to differences between lichens species but also due to adaptation processes (Fernández et al. 2000).

Concentration ratios in *H. physodes* (L.) Nyl. exposed in a previous study (Horvat et al. 2000) in areas close to the former mercury mine site in Idrija were many times higher (up to a factor of 40). In areas near the gas treatment plant Molve, Croatia, the factor was up to 5. According to the above mentioned paper, concentration ratios and values reported in our study would then correspond to air values of Hg in the range between 5 to 10 ng m^{-3}. In Fig. 5 some results from all three areas are plotted and compared.

In Fig. 5, vertical lines represent the mean and concentration ranges (min–max) of elemental Hg in air; horizontal lines represent mean ± standard deviation ($n = 3$) of total Hg concentrations in lichens. The reference site represents the average total Hg concentration in in situ lichens at Pokljuka and the average elemental gaseous Hg concentration in uncontaminated areas (Kotnik and Horvat 2000). Last two series of measurements of Hg^0 in air around the cement plant were included in the picture.

Although the lichen species were different, it can easily be observed that at all three study areas (Molve, Idrija and Anhovo) mean total mercury concentrations in lichens and elemental mercury in air follow the same trend. Such finding shows potential for their practical use in biomonitoring

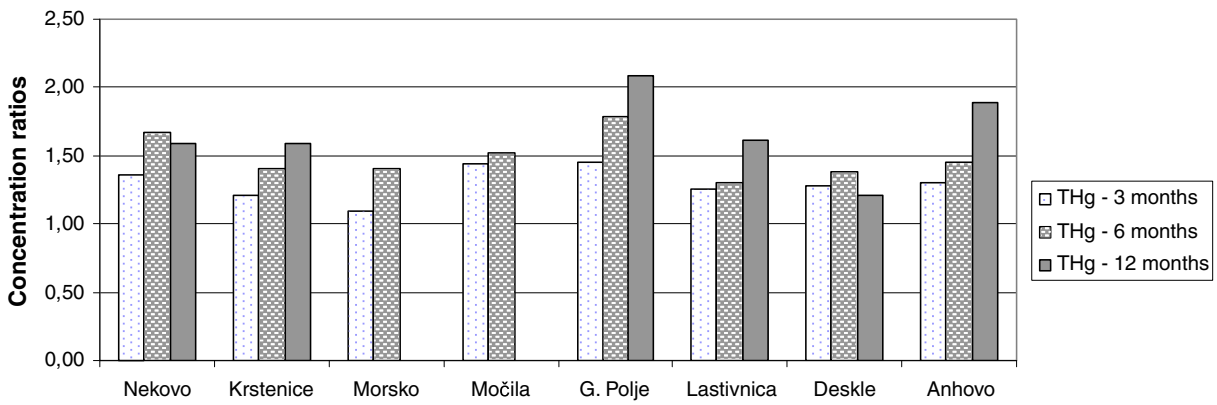

Fig. 4 Concentration ratios for total Hg in transplanted lichens after 3, 6 and 12 months of exposure

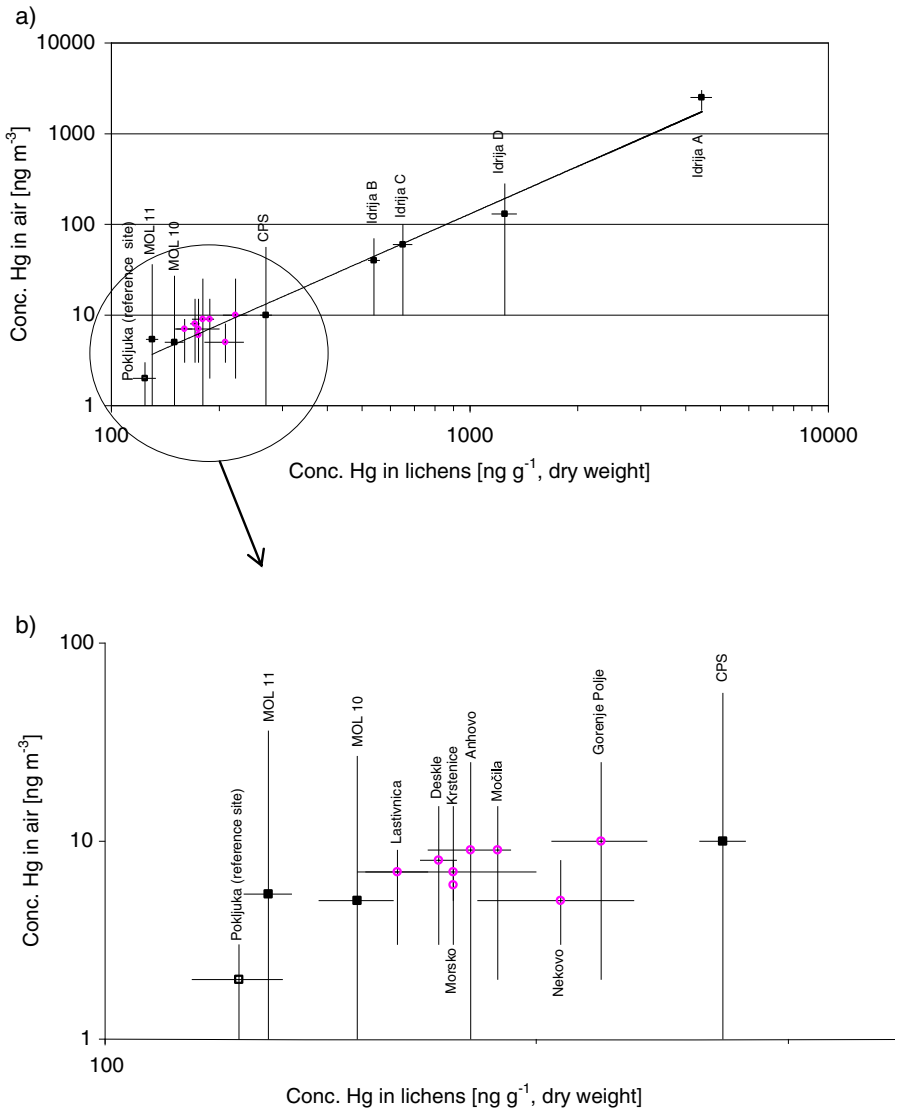

Fig. 5 Comparison of correlation between **a** mercury concentrations in transplanted *H. physodes* at Molve (natural gas treatment facility – MOL, CPS) and Idrija (Horvat et al. 2000 *black*, *rectangular symbols*) and **b** *P. furfuracea* around the cement plant Anhovo (present study, *open round symbols*) after 6 months of exposure vs. Hg^0 in air

for regular monitoring programmes, though further optimization and validation of the methodology would be necessary.

Correlations of mercury biomonitoring results and emissions

The production process is relatively constant (except in the period of the major maintenance period) and the combination of raw materials and fuels in the period of biomonitoring was unchanged so that Hg emissions could be supposed to be steady with only some short-term oscillations due to Hg cycling and changes in operational regimes of the process (Ljubič Mlakar et al. 2008, 2009, 2010; Schäfer and Hoenig 2001). Because of this special feature, we could approximate that Hg emissions are linearly proportional to the working hours of the cement kiln. An example of this relationship for the most representative sites according to the surviving lichens, the distance from the chimney and the directions of predominant winds (G. Polje, Anhovo, Krstenice) is presented in Fig. 6.

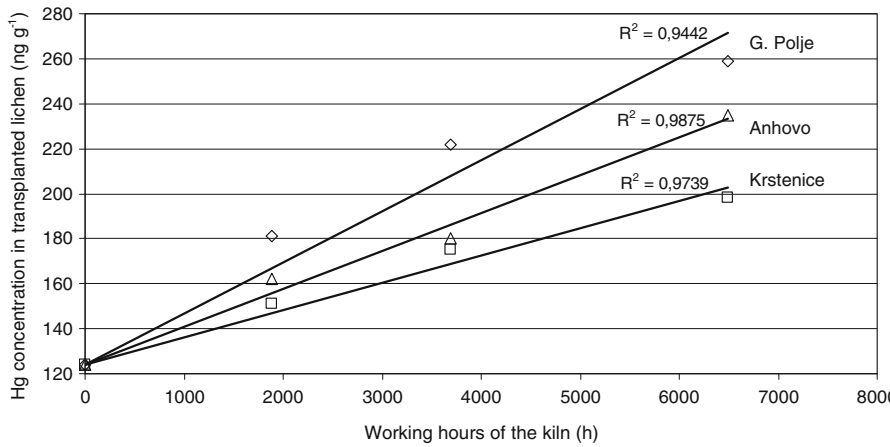

Fig. 6 Relation between Hg concentrations in transplanted lichens at the three most representative sites (G. Polje, Anhovo, Krstenice) and working hours of the kiln. The initial point is set to the initial Hg concentration (124 ng g^{-1})

All sites presented show a good relationship between working hours and the concentration of mercury in transplanted lichens. Correlation functions were derived for all locations with at least one surviving lichen sample after 12 months of exposure (Morsko and Močila were excluded).

The R^2 values indicate which sites are best correlated with the working hours of the kiln (quantity of mercury emitted from the cement plant). G. Polje, Krstenice, Lastivnica and Anhovo have the best fitted linear regression lines. Concentrations of Hg in Deskle and Nekovo are less correlated with working hours of the kiln and showed a decrease after 12 months. The Hg concentration increase was the highest in G. Polje, followed by Anhovo. Krstenice and Lastivnica (Lastivnica is not presented in Fig. 6) showed lower but similar rates. The results are in accordance with the meteorological conditions (winds) and geographical characteristics (distance from the chimney). Figure 6 indicates that the methodology of biomonitoring with transplanted lichens has the potential to be developed as a complementary quantitative monitoring methodology for facilities like cement plants.

Conclusions

Emission of mercury from the case study cement production plant is relatively low but according to the high share of emitted gaseous Hg^{2+} the local deposition is evaluated to be significant. The total annual mercury emissions from the observed cement plant were estimated to be about 10 kg on average and a maximum of 24 kg. The annual anthropogenic emission of mercury in Slovenia in 2005 was estimated to 413.8 kg with 17.6 kg emitted from cement plants (AMAP/UNEP 2008). Based on these data the approximate share of the cement industry in Slovenia was 4.3% and in this share 2.4% was from the case study cement plant.

Elemental mercury concentrations in air were low (below 10 ng m^{-3}) at all measuring sites and there was a slight falling trend with distance from the emission point source. Rainfall, temperature and dust deposition were followed, but a direct relationship between Hg accumulation and precipitation was not detected during the transplantation experiment probably due to a rather uniform rainfall in individual periods. Hg is absorbed mainly from the gaseous phase and dust loads had no specific influence on Hg absorption. Consequently mercury concentrations in in situ lichens were low and comparable with concentrations in lichens from the background area. As the cement plant is the only important source of mercury in the area and the natural background raw materials have very low mercury concentrations, it can be concluded that the contamination caused by the cement plant is low.

It was shown that active biomonitoring with transplanted lichen *P. furfuracea* can be successfully used for temporal and spatial assessment of mercury deposition near the cement plant even in

the conditions specific of the cement plant – i.e. relatively low mercury emissions, predominance of the gaseous reactive form (Hg^{2+}), low Hg^0 concentrations in air, complex terrain and specific wind conditions. The sensitivity of the methodology was good enough to record and detect a significant response, differences between individual measuring sites and temporal–spatial trends, but for future monitoring programmes probably lichens species with higher resistance to alkalinity would be more suitable.

The sites most influenced were determined according to the concentration ratios and trend lines between working hours and concentrations in transplanted lichens. These sites are located near the stack and in the direction of the predominant winds. Linear regression lines between the working hours of the kiln and mercury concentrations at the most influenced sites showed high R^2 coefficients and the most important finding was that the quantities of emitted mercury were in good linear correlation with mercury concentrations in the transplanted lichens exposed for 3, 6 and 12 months.

Correlations between mercury uptake by lichens and the working hours of the kiln (emission) confirmed that the methodology used has the potential to be utilised and further developed as a monitoring system complementary to instrumental methods (Fig. 6). The uncertainty could be minimised by programmed and exact sampling and analytical procedures, as well as with other elements of quality control.

As high temperature industrial processes could contribute significantly to toxic element air pollution, the results of this study are also very important for the Salonit Anhovo cement plant. Each change in the use of fuels, raw materials or technology could cause changes of emissions and it is extremely important to control emissions by simple and cost-effective methodologies. In the future this will become even more important due to the increased use of alternative fuels and secondary raw materials in cement production plants.

Acknowledgements The authors acknowledge the help of the management and technical co-workers of the Salonit Anhovo Joint-Stock Co. as well colleagues from the Jožef Stefan Institute and the International Jožef Stefan Postgraduate School for support and help. The authors would like to express their gratitude to Prof. Dr. Aleksandra Kornhouser Frasier for encouraging us to start this study and in connecting people from industry and research institutes. The study was financed by the Salonit Anhovo Joint-Stock Co.

References

Adamo, P., Giordano, S., Vingiani, S., Castaldo Cobianchi, R., & Violante, P. (2003). Trace element accumulation by moss and lichen exposed in bags in the city of Naples (Italy). *Environmental Pollution, 122*(1), 91–103.

AMAP/UNEP. (2008). *Technical background report to the global atmospheric mercury assessment* (pp. 164). Oslo: AMAP, UNEP Chemicals.

Armstrong, R. A. (1990). The influence of calcium and magnesium on the growth of the lichens Parmelia saxatilis and Xanthoria parietina on slate substrates. *Environmental and Experimental Botany, 30*(1), 51–57.

Balarama, M. V., Krishna, D., Karunasagar, D., & Arunachalam, J. (2004). Sorption characteristics of inorganic, methyl and elemental mercury of lichens and mosses: Implication of biogeochmical cycling of mercury. *Journal of Atmospheric Chemistry, 49*(1–3), 317–328.

Bargagli, R. (1998). *Trace elements in terrestrial plants. An ecophysiological approach to biomonitoring and biorecovery*. Berlin: Springer.

Bargagli, R., Cateni, D., Nelli, L., Olmastroni, S., & Zagarese, B. (1997). Environmental impact of trace element emissions from geothermal power plants. *Archives of Environmental Contamination and Toxicology, 33*(2), 172–181.

Bari, A., Rosso, A., Minciardi, M. R., Troiani, F., & Piervittori, R. (2001). Analysis of heavy metals in atmospheric particulates in relation to their bioaccumulation in explanted Pseudovernia furfuracea thalli. *Environmental Monitoring and Assessment, 69*(3), 205–220.

Bergamaschi, L., Rizzio, E., Giaveri, G., Loppi, S., & Gallorini, M. (2007). Comparison between the accumulation capacity of four lichen species transplanted to a urban site. *Environmental Pollution, 148*, 468–476.

Bhatty J. I. (1995). *Role of minor elements in cement manufacture and use*. Research and Development Bulletin RD109T: Portland Cement Association.

Branquinho, C., Gaio-Oliveira, G., Augusto, S., Pinho, P., Maguas, C., & Correia, O. (2008). Biomonitoring spatial and temporal impact of atmospheric dust from a cement industry. *Environmental Pollution, 151*(2), 292–299.

Calasans, C., & Malm, O. (1997). Elemental mercury contamination survey in a chlor-alkali plant by the use of transplanted Spanish moss, Tillandsia usneoides (L.). *Science of the Total Environment, 208*(3), 165–177.

Carpi, A., Weinstein, L. H., & Ditz, D. W. (1994). Bioaccumulation of mercury by Sphagnum moss near a municipal solid waste incinerator. *Air Waste, 44*(5), 669–672.

Conti, M. E., & Ceccheti, G. (2001). Biological monitoring: Lichens as bioindicators of air pollution assessment – a review. *Environmental Pollution, 114*(3), 471–492.

Councile Directive 2000/76/EC on the incineration of waste.

Fernández, J. A., Aboal, J. R., & Carballeira, A. (2000). Use of native and transplanted mosses as complementary techniques for biomonitoring mercury around an industrial facility. *Science of the Total Environment, 256*(2–3), 151–161.

Fernández, J. A., Aboal, J. R., & Carballeira, A. (2004). Identification of pollution sources by means of moss bags. *Ecotoxicology and Environmental Safety, 59*(1), 76–83.

Fukuzaki, N., Tamura, R., Hiranom, Y., & Mizushima, Y. (1986). Mercury emission from a cement factory and its influence on the environment. *Atmospheric Environment, 20*(12), 2291–2299.

Garty, J. (1993). Lichens as biomonitors for heavy metal pollution. In B. Markert (Ed.), *Plants as biomonitors: Indicators for heavy metals in the terrestrial environment* (pp. 193–263). Weinheim: VCH.

Garty, J., Karary, Y., & Harel, J. (1993). The impact of air pollution on the integrity of cell membranes and chlorophyll in the lichen Ramalina duriaei (De Not.) Bagl. transplanted to industrial sites in Israel. *Archives of Environmental Contamination and Toxicology, 24*(4), 455–460.

Grönlund, R., Edner, H., Svanberg, S., Kotnik, J., & Horvat, M. (2005). Mercury emissions from the Idria mercury mine measured by differential absorption lidar techniques and a point monitoring spectrometer. *Atmospheric Environment, 39*(22), 4067–4074.

Hawksworth, D., & Rose, F. (1976). *Lichens as air pollution monitors*. London: Edward Arnold.

Hines, M. E., Horvat, M., Faganeli, J. (2000). Mercury biogeochemistry in the Idrija river, Slovenia from above the mine into the Gulf Trieste. *Environtal Research, 83*(2), 129–139. *sec A*.

Horvat, M., Jeran, Z., Špirič, Z., Jaćimović, R., & Miklavčič, V. (2000). Mercury and other elements in lichens near the INA Naftaplin gas treatment plant, Molve, Croatia. *Journal of Environmental Monitoring, 2*(2), 139–144.

Horvat, M., Jereb, V., Fajon, V., Logar, M., Kotnik, J., Faganeli, J., et al. (2002). Mercury distribution in water, sediment and soil in the Idrijca and Soča river systems. *Geochemistry: Exploration, Environment, Analysis, 2*(3), 287–296.

Horvat, M., Kontić, B., Kotnik, J., Ogrinc, N., Jereb, V., Logar, M., et al. (2003). Remediation of mercury polluted sites due to mining activities. *Critical Reviews in Analytical Chemistry, 33*(4), 291–296.

Horvat, M., Lupšina, V., & Pihlar, B. (1991). Determination of total mercury in coal fly ash by gold amalgamation cols vapour atomic absorption spectrometry. *Analytica Chimica Acta, 243*, 71–79.

Horvat, M., Zvonarič, T., & Stegnar, P. (1986). Optimization of a wet digestion method for the determination of mercury in blood by cold vapour absorption spectrometry (CV AAS). *Vestnik Slovenskega Kemijskga Društva, 33*(4), 475–486.

Ikigura, J. R., & Akagi, H. (2002). Lichens as a good bioindicator of air pollution by mercury in small-scale gold mining areas, Tanzania. *Bulletin on Environtal Contamination Toxicology, 68*(5), 699–704.

Jalkanen, L., Mäkinen, A., Häsänen, E., & Juanoja, J. (2000). The effect of large anthropogenic particulate emissions on atmospheric aerosols, deposition and bioindicators in the eastern Gulf of Finland region. *Science of the Total Environment, 262*(1–2), 123–136.

Jeran, Z., Byrne, A. R. , & Batič, F. (1995). Transplanted epiphytic lichens as biomonitors of air-contamination by natural radionuclides around the Žirovski vrh uranium mine, Slovenia. *Lichenologist, 27*(5), 375–385.

Jeran, Z., Jaćimović, R., Batič, F., & Mavsar, R. (2002). Lichens as integrated air pollution monitors. *Environmental Pollution, 120*(1), 107–113.

Jeran, Z., Jaćimović, R., Batič, F., Smodiš, B., & Wolterbeek, H. Th. (1996). Atmospheric heavy metal pollution in Slovenia derived from results for epiphytic lichens. Fresenius. *Journal of Analytical Chemistry, 354*(5–6), 681–687.

Johansen, V. C., & Hawkins, G. J. (2003). *Mercury speciation in cement kilns: A literature review*. PCA R&D Serial No. 2567, Portland Cement Association.

Košuta, M., & Bizjak, M. (2000). Air quality in the surrounding of Salonit Anhovo. In *Air protection in Slovenia, 15–17 November, ZTI, Ljubljana* (pp. 111–119). in Slovenian.

Kotnik, J., & Horvat, M. (2000). Izhodišča za izdelavo analize onesnaženosti z živim srebrom in predlog ukrepov na podlagi direktiv Evropske Unije: IJS-DP-8290. Ljubljana: Jožef Stefan Institute. In Slovenian.

Ljubič Mlakar, T., Horvat, M., Kotnik, J., Jeran, Z., Vuk, T., Mrak, T., et al. (2006). Mercury in the system of cement clinker production and emissions control. In *8th International conference on mercury as a global pollutant, Madison, Wisconsin, USA*. poster (abstract).

Ljubič Mlakar, T., Horvat, M., Vuk, T., Stergaršek, A., Kotnik, J., Tratnik, J., et al. (2008). A Study of mercury species and mass balance in the process of cement clinker production indicating potentials for mercury emission control. In *GCHT-7, Gas Cleanning at High Temperatures, Newcastle, Shoal Bay, Australia*.

Ljubič Mlakar, T., Horvat, M., Vuk, T., Stergaršek, A., Kotnik, J., Tratnik, J., et al. (2009). The role of fules on mercury mass flows in the process of cement clinker production, In *Mercury emissions from coal 6th workshop MEC6, Ljubljana, Slovenia*.

Ljubič Mlakar, T., Horvat, M., Vuk, T., Stergaršek, A., Kotnik, J., Tratnik, J., et al. (2010). Mercury species, mass flows and processes in a cement plant. *Fuel, 89*(8), 1936–1945.

Lodenius, M. (1998). Dry and wet deposition of mercury near a chlor-alkali plant. *Science of The Total Environment, 213*(1–3), 53–56.

Lupšina, V., Horvat, M., Jeran, Z., & Stegnar, P. (1992). Investigation of mercury speciation in lichens. *Analyst, 117*(3), 673–675.

Ministry of the Environment and Spatial Planning of Republic of Slovenia (1995). *Report on measurements and evaluation of air pollution in the surrounding of Salonit Anhovo*. in Slovenian.

Ministry of the Environment and Spatial Planning of Republic of Slovenia (2004). *Report on measurements of air pollution in Morsko*. in Slovenian.

Pacyna, E. G., Pacyna, J. M., Steenhuisen, F., & Wilson, S. (2006). Global anthropogenic mercury emission inventory for 2000. *Atmospheric Environment, 40*(22), 4048–4063.

Pirrone, N., Cinnirella, S., Streets, D. G., Feng, X., Mukherjee, A. B. , Leaner, J., et al (2008). Overview of global mercury emissions from natural and anthropogenic sources. In N. Pirrone, R. Mason (Eds.), *Mercury fate and transport in the global atmosphere: Measurements, models and policy implications*. Nairobi: UNEP.

Prestbo, E. M., & Bloom, N. (1995). Mercury speciation adsorption (MESA) method for combustion flue gas: Methodology, artifacts, intercomparison, and atmospheric implications. *Water, Air and Soil Pollution, 80*(1–4), 145–158.

Prestbo, E. M., & Tokos, J. J. S, (1997). Mercury speciation in coal combustion flue gas: MESA method. In *Air & Waste Management Association's 90th Annual Meeting & Exhibition*, June 8–13, 1997. Toronto, Ontario, Canada.

Schäfer, S., & Hoenig, V. (2001). Operational factors affecting the mercury emissions from rotary kilns in the cement industry. *ZKG International, 54*(11), 591–600.

Schneider, M., & Oerter, M. (2000). Limiting and determining mercury emissions in the cement industry. *ZKG International, 53*(3), 121–130.

Schuhmacher, M., Domingo, J. L. J. L., & Garreta, J. (2004). Pollutants emitted by a cement plant: Health risks for the population living in the neighborhood. *Environmental Research, 95*, 198–206.

Sholupov, S., Pogarev, S., Ryzho, V., Mashyanov, N., & Stroganov, A. (2004). Zeeman atomic absorption spectrometer RA-915+ for direct determination of mercury in air and complex matrix samples. *Fuel Processing Technology, 85*(6–7), 473–485.

Sloof, J. E. (1995). Lichens as quantitative biomonitors for atmospheric trace-element deposition, using transplants. *Atmospheric Environment, 29*(1), 11–20.

Szczepaniak, K., & Biziuk, M. (2003). Aspects of the biomonitoring studies using mosses and lichens as indicators of metal pollution. *Environmental Research, 93*(3), 221–230.

Tuba, Z., & Csintalan, Z. (1993). The use of the moss transplantation technique for bioindication of heavy metal pollution. In B. Markert (Ed.), *Plants as biomonitors: Indicators for heavy metals in the terrestrial environment* (pp. 403–411). Weinheim: VCH Publishers.

US EPA-452/R-97–005 (1997). Fate and transport of mercury in the environment. In *Mercury Study Report to Congress, Volume 3*.

VDZ (2006). *Activity report* 2003–2005.

Vingiani, S., Adamo, P., & Giordano, S. (2004). Sulphur, nitrogen and carbon content of Sphagnum capillifolium and Pseudevernia furfuracea exposed in bags in the Naples urban area. *Environmental Pollution, 129*(1), 145–158.

Wolterbeek, B. (2002). Biomonitoring of trace element air pollution: Principles, possibilities and perspectives. *Environmental Pollution, 120*(1), 11–21.

Wolterbeek, H. Th., & Verburg, T. G. (2002). Judging survey quality: Local variances. *Environmental Monitoring and Assessment, 73*(1), 7–16.