Biomonitoring of mercury in air by transplanted lichens

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Abstract: Mercury biomonitoring in air using transplanted lichens specie *Hypogymnia physodes* was used at natural gas treatment facilities, reference stations and former mercury mining areas. The results indicated excellent agreement between predicted Hg concentrations in air and Hg concentrations in transplanted lichens.

Keywords: mercury, air, biomonitoring, lichens, gas and oil industry, mercury mining

INTRODUCTION

It is well known that lichens continuously accumulate Hg and other elements from the atmosphere, and therefore concentrations depend on ambient levels of these elements, the age of the lichens and their physiological conditions (HORVAT ET AL., 2000; LOPPI, 2001; CONTI AND CECCHETI, 2001). Concentrations of mercury in lichens represent the average long-term Hg status in air, while Hg measurements in air represent only the average value during the sampling period (e.g. from several minutes to the maximum daily average concentrations). Natural gas contains various forms of inorganic and organic Hg species which have to be removed from the gas due to technological and environmental reasons. Legislation requires regular monitoring of mercury emissions into the atmosphere where various techniques could be used. Biomonitoring investigated in this study represents cost-effective means to assess the level of contamination of ambient mercury around hot spots of mercury pollution.

Sampling, transplantation of lichens and sample preparation

In the present study various geographical areas were studied: (a) the INA Naftaplin Gas Treatment Plants in Croatia, where the efficiency of an industrial facility for removal of Hg from natural gas was investigated, and (b) Zutica and Etan, (c) the mercury mining area, Idrija, Slovenia, and (d) Reactor center wich represents clean area close to Ljubljana. Experimental sites are presented in Figure 1.

As the first step, the lichen species *H. physodes* was collected from orchard trees at a pristine area in Slovenia approximately one week before transplantation. In the laboratory, lichens were carefully cleaned from the branches and collected within polyethylene nets. Three nets were fastened to branches or on an artificial rod about 1.5-2 m above the ground at each location in Croatia, as well as at three reference locations, one in Ljubljana at the Reactor Center (no mercury source) and two in Idrija (known elevated mercury concentrations in the air

due to previous mining activity). Some lichen material was kept in the laboratory for determination of the initial concentration of Hg and other trace elements. Samples were then further prepared according to the procedure described elsewhere (HORVAT ET AL., 2000). At the same time, as lichens were transplanted, soil samples were collected at same locations. For determination of elements in soil we collected approximately 2 kg of composite soil sample to polyethylene bags. One soil sample was composed from at least four sub-samples collected in the radius of 10 to 20 m.

Date	Molve/ Vinkovci/ Idrija	Žutica/ Idrija
Transplantation starting date	25.10.2000	24.04.2002
3 months	29.01.2001	22.08.2002
6 months	10.05.2001	19.12.2002
12 months	30.11.2001	13.05.2003

Figure 1. Dates of transplantation and sampling of lichens and locations in Croatia and Slovenia

ANALYTICAL METHODS

Determination of total mercury was performed by CV AAS (Cold Vapor Atomic Absorption Analysis) (HORVAT ET AL., 1986; HORVAT ET AL., 1991). The accuracy of the results was checked by the use of the certified reference material: IAEA-336, Trace and Minor Elements in Lichens. Scandium and other elements (not discussed in this presentation) were determined by instrumental neutron activation analysis (INAA) (JAČIMOVIČ ET AL., 2003).

The data was treated to account for geological background the results for lichens and soil samples were normalized to the concentration of scandium (Sc) and enrichment factors were calculated (Equation 1).

$$EF = \frac{\frac{concEl_x}{concSc} LICHEN}{\frac{concEl_x}{concSc} SOIL} \quad (1)$$

Where: EF = enrichment factor, $concEl_x$ = concentration of element (in mg kg^{-1}), $concSc$ = concentration of scandium (in mg kg^{-1})/

RESULTS AND DISCUSSION

Mercury concentration in lichens before transplantation was relatively low (about 0.12 mg/kg). After 3 and 6 months of exposure Hg increased significantly at MOLVE stations CPS-1 and CPS-2, as well as at one station in Idrija. (Figure 2, left) Very step increase was observed at station CPS-2 from 6 to 12 months of exposure. Due to the well known volatility of elemental Hg these concentrations are probably directly correlated with the average elevated concentrations at two CPS stations . After 12 months of exposure slight increase of Hg was also observed at stations MOL-11 and MOL-12, while at Đurđevac and Etan-2 the increase was less than 20%. The same applies for the second experiment, where mercury was elevated only Idrija, which means that at other gas and oil treatment facilities mercury is not emitted into the atmosphere.

Highest Hg concentrations were found at the station CPS 1 and CPS-2 after 12 months of exposure (up to 12,9 mg.kg^{-1} dry weight). This is related to the emission of Hg from the technological facility for natural gas treatment including elimination of Hg from the original gas. These results are in agreement with the results of a similar experiment performed in 1997 and 1999 (HORVAT ET. AL., 1997, 1998, 2000).

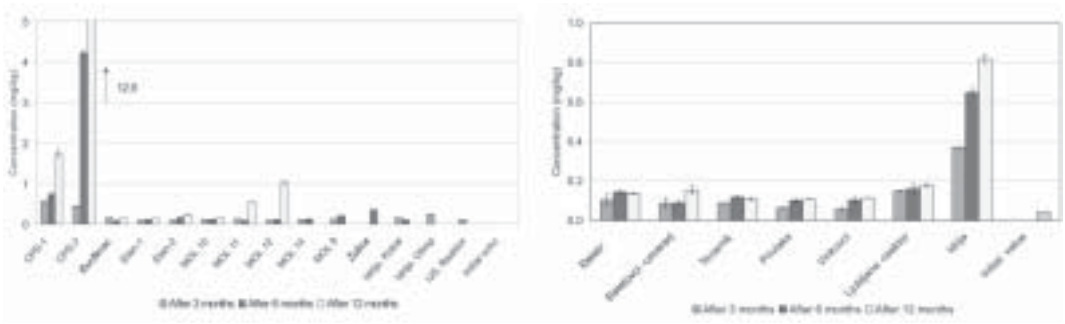

Figure 2. Mercury concentration in transplanted lichens

Based on the previous work conducted at similar locations a relationship with average Hg concentration in air and in lichens was established (HORVAT ET. AL., 2000). The relationship is shown in Figure 3. Therefore after 6 months of exposure of lichens, it can be estimated that the average concentrations of Hg in air at CPS-1 ion the first 6 months of exposure was in the range between 10 to 100 ng/m^3, and at CPS-2 in the range between 2000 to 3000 ng/m^3 and at Idrija Olimp of up to about 70 ng/m^3. Concentrations of

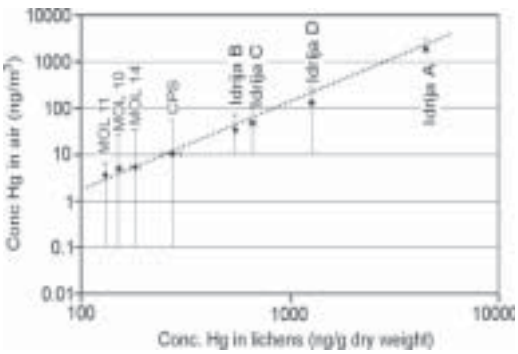

Figure 3. Correlation between mercury concentrations in air and in transplanted lichens (*H. physodes*) after 6 month of exposure

Hg in air in Idrija at Olimp was continuously measured and it was in the range between 30 to 90 ng/m^3 with an average of 65 ng/m^3, which is in excellent agreement with predicted value from Figure 3 and serve as the validation of the relationship previously established. As the concentrations of Hg in lichens significantly increased at CPS-2 during the last 6 months of exposure (from 5 to 12 months) the average concentration of Hg during this period must have been much higher, exceeding 10 000 ng/m^3.

Geochemical normalization with Sc and calculation of enrichment factors is presented in Figure 4, which confirms the increased Hg concentration affected by anthropogenic sources at MOLVE and Idrija..

CONCLUSIONS

In conclusion, the results show that mercury concentrations at the gas treatment and pumping stations have been elevated only at MOLVE while at other stations it has not been increased significantly. At the Reactor center in Ljubljana, mercury concentrations in lichens remained the

same throughout the year in response to the stable and low concentrations of Hg in the air (average concentration in the air is between 2-3 ng. m^{-3}). In Idrija, where mercury concentrations are significantly elevated in the air due to mercury mining, mercury levels in lichens significantly increased. The results of this study again confirmed the suitability of epyphitic lichens as biomonitors of air pollution with Hg.

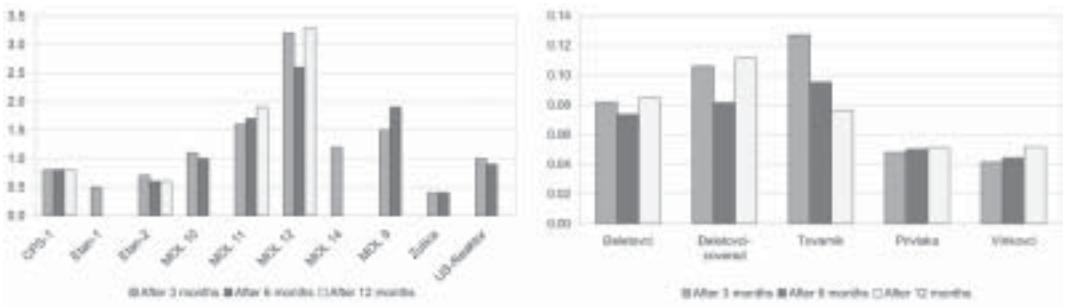

Figure 4. Enrichment factors

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