

Emissions of Trace Elements from Motor Vehicles Monitored by Active Biomonitoring: a tunnel study in the Western Cape, South Africa using ICP-MS and neutron activation

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Abstract. Application of mosses and lichens as biomonitors, analyzed by nuclear and related techniques, has been extensively used to provide information about air quality. These plants possess efficient accumulation capacity for many air pollutants from atmospheric deposition. Studying air pollution with plants, instead of the commercial air filters is a simple, low-cost, effective method to estimate levels of air pollutants and their impact on humans and animals. A steady global increase of the use of active biomonitoring, whereby biomonitors are collected from relatively pristine habitats and transplanted to different environments, is due to scarcity or total absence of native biomonitors in certain environments e.g. large cities with heavy technogenic load and industrial regions as well as in arid areas. Biomonitoring of trace elements resulting from road traffic, specifically from tunnels, has not yet received adequate attention in the research world. In our pilot study in the Western Cape, moss and lichen species were deployed inside Huguenot tunnel and the results are presented in this work. Samples were analysed by the multi-elemental Inductively-Coupled Mass Spectrometry (ICP-MS). Moreover, samples will later be subjected to the non-destructive instrumental epithermal neutron activation analysis (ENAA), thus facilitating an intercomparison of results obtained by ENAA and ICP-MS.

1. Introduction

Air quality assessment is one of the necessary procedures implemented by countries in order to manage their air quality. This is because air pollution is a serious environmental health problem. Anthropogenic pollutants produced by industrialization, urban growth and vehicle emissions are major causes of atmospheric pollution [1] Biomonitoring of air pollution, whereby mosses and lichens are used as biomonitors, is a widely used technique world-wide although it has not yet been fully utilized in South Africa. Evaluating air pollution using this method is considerably simpler and cheaper than using ordinary aerosol filters [2]. Biomonitoring may generally be defined as the use of biological material to acquire information about the condition of the environment. Due to the absence of a root system in mosses and lichens, these organisms predominantly rely on the environment to which they

are exposed to for their nutrient uptake and they possess high capacities of retaining many ions [3, 4]. Hence they were found suitable to monitor atmospheric deposition of heavy metals and other trace elements, either by *in situ* (passive biomonitoring) or by the use of transplants (active biomonitoring) [5, 6]. Active biomonitoring is an alternative and a valuable tool of evaluating air pollution levels in large cities with heavy technogenic load and industrial regions as well as in arid areas where mosses of lichen do not grow [2]. However, active biomonitoring of trace elements emitted by vehicles, especially using biomonitors in tunnels, has not yet received adequate attention in the research world [7]. Here we report first (preliminary) results of element concentrations measured inside Huguenot tunnel using lichen and moss. Two bags of lichen species; *Usnea subfloridana* and *Parmotrema perlatum*, were deployed next to each other to study their effectiveness in the uptake of a series of trace elements from air inside the tunnel over a defined time period. In addition, two bags with a mixture of two moss species (*Leptodon smithii* and *Pterogonium gracile*) were deployed and used to investigate the uptake rate of trace elements from vehicle emissions by using biomonitors. Lichen and moss samples were analysed using the multi-elemental analytical technique, Inductively-Coupled Mass Spectrometry (ICP-MS), and the results are presented here. At a later stage, these samples will be analysed using the non-destructive instrumental epithermal neutron activation analysis (ENAA) method at the IBR-2 pulsed fast reactor of Frank Laboratory of Neutron Physics (FLNP) - Joint Institute for Nuclear Research (JINR), Dubna, Russia. This will facilitate an intercomparison of results obtained by ENAA and ICP-MS.

2. Materials and Methods

2.1. Study Area

This study was conducted inside the Huguenot tunnel, a toll tunnel near Cape Town in the Western Cape Province, South Africa (SA). The tunnel is 3.9 kilometres long. It is an extension of the national road (N1) through the Du Toitskloof mountains that separate Paarl from Worcester (Figure 1). Huguenot tunnel is maintained by a subsidiary of the Murray & Roberts construction company called Tolcon. It currently provides one lane of traffic in each direction. At least 12 000 vehicles; including both light and heavy-duty vehicles using both diesel and petrol, pass through the tunnel daily.

The samples were deployed at the first vehicle cross cutting (VCC1), which is about 1 km from the western entrance (in the direction Cape Town to Worcester) of the tunnel.

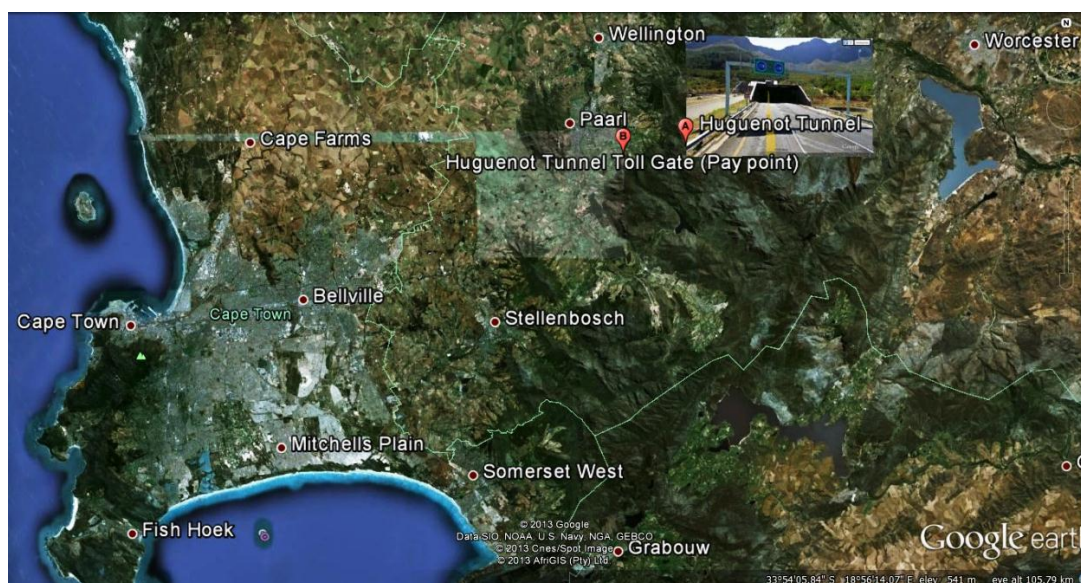


Figure 1. Google earth map of the Western Cape showing location of Huguenot tunnel.

2.2. Preparation of Lichen and Moss Bags and their Exposure

Lichens and mosses were collected from a pristine area (mountainous area near Montagu) in the Western Cape. In the laboratory, lichen and moss species were not washed but cleaned from foreign plant material and soil particles. About 3 g dry-weight of lichens and mosses was loosely packed in a 10 × 10 cm² nylon mesh bags, with 1 mm mesh size. The lichen and moss bags were deployed on a railing attached to the wall of the tunnel, about 4 m above the ground. Table 1 below shows a summary of exposure and collection dates for our lichen and moss bags.

Table 1. Exposure and collection dates for our lichen and moss bags.

Date	Lichens		Mosses	
5-April-2013	Both bags exposed			
17-April-2013		Both bags collected	Both bags exposed	
24-April-2013				1 st bag collected
5-May-2013				2 nd bag collected

Lichen bags were both exposed on 5th of April 2013, prior to moss bags, and were both collected on the 17th of April 2013 (12 days exposure time). Moss bags were both exposed on the 17th of April 2013. The first one was collected on the 24th of April 2013 (7 days exposure time) and the second one was collected on the 5th of May 2013 (19 days exposure time).

2.3. Sample preparations and measurements for ICP-MS method

To determine the initial (background) concentrations of trace elements in the biomonitors, 2 replicates of non-exposed samples for each biomonitor were analysed by ICP-MS before being exposed in the tunnel. After exposure, lichens and mosses were removed from the nylon mesh bags and manually homogenized. Concentrations of a series of trace elements in them were determined by ICP-MS method. ICP-MS measurements were performed at the Central Analytical Facilities (CAF), Stellenbosch University, Stellenbosch, South Africa, using an Agilent 7700x ICP-MS with Octupole Reaction System.

Samples were dried at 40 °C in a laboratory oven for 3 days. After the drying process, samples were milled in IKA A10 analytical mill. About 0.3 g of each sample was weighed and transferred into a microwave vessel and about 10 ml HNO₃ was added into each vessel. Samples were left to stand open for 20 minutes to predigest before the vessels were sealed and commencing with the microwave heating process. About 40 g of deionised water was weighed and added in a sample bottle that was cleaned in 1% HNO₃ and then added to the digest sample in the microwave vessel to make up 50 ml. Samples were stirred in the microwave vessel, transferred to the sample bottle and then subjected to the ICP-MS.

3. Results and Discussion

The amounts of trace elements found in lichens and mosses after exposure in the tunnel were compared with the initial values that were measured from the unexposed samples. In order to evaluate the accumulated content of trace elements, concentration of each element measured before exposure ($C_{initial}$) was subtracted from the one measured after exposure ($C_{exposed}$);

$$C_{final} = C_{exposed} - C_{initial}$$

Comparing the results of elemental concentrations obtained in three tunnel studies from; Lisbon (Portugal) traffic tunnel, Laaer Berg tunnel in Vienna, Austria and highway tunnel in Houston (USA), the following elements Zn, V, Ba, Cr, Pb, Ni, Cd, As, Cu, and Sb were identified and linked to

vehicular emissions inside traffic tunnels while Fe was mostly associated with road dust [7, 8, 9, 10]. Hence in this study, the relative high concentrations of Fe were excluded for further discussions. Furthermore, those authors agree on Zn, Ba, Cr and Cu as the major marker elements for vehicle emissions inside traffic tunnels.

In addition, using various species of biomonitors, in this study their accumulation rates were investigated. The mean concentrations of Zn, Ba, Cu, Pb and Fe increased after exposure (of 12 days) for *Usnea subfloridana* (lichen) and the mixture of *Leptodon smithii* and *Pterogonium gracile* (both mosses) but not for the *Parmotrema perlatum* species (lichen). This trend did not occur in the case of V, Ni, and Cr. This includes a decrease in concentrations of V, Ni, and Cr in both lichen species (see Table 1 and Figures 1 and 2). Results for Cd, As and Sb were also excluded due to their relatively low concentration levels.

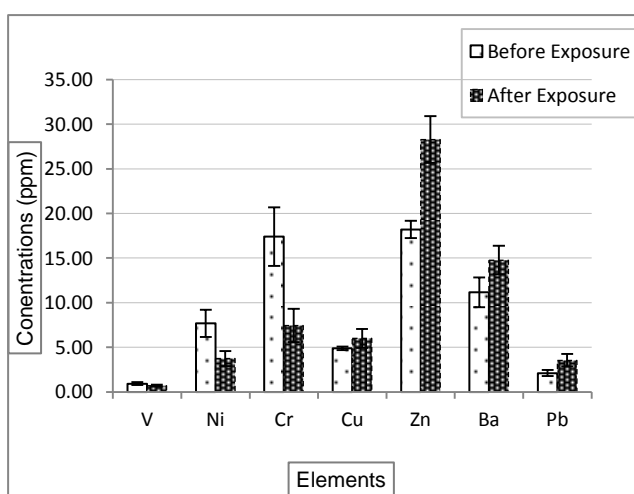


Figure 2. Figure showing accumulation of elements in *Usnea subfloridana* after 12 days of exposure.

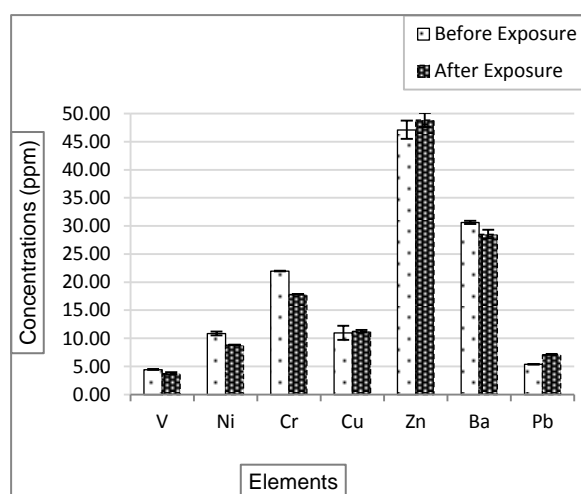


Figure 3. Figure showing accumulation of elements in *Parmotrema perlatum* after 12 days of exposure.

For both species, concentrations of V, Ni, and Cr are higher before exposure than after exposure. For *Usnea subfloridana*, there is a slight increase observed in concentrations of Cu, Ba, Pb while a large increase is found in Zn. For *Parmotrema perlatum*, the differences in concentrations for Cu, Zn, Ba and Pb are within uncertainties. In a study by Gailey and Lloyd in 1986, specifically looking at “The Effects of Length of Exposure on Metal Concentrations”, they stated that some trace elements (more especially heavy metals) entrapped by biomonitors can be leached/volatilized out of the nylon net of the suspended bag and this will lead to a decrease in the contents of some trace elements in biomonitors. This usually happens when biomonitors are still trying to adjust under toxic conditions of the new environment in which they have been trans-located to. However, once they reach equilibrium with the new environment, then they accumulate metals most efficiently. Moreover, the leaching of those metals is likely to also occur when biomonitors approach their saturation level [11]. Therefore, the decrease in concentrations of V, Ni, Cu observed in our results in both lichen species, as well as of Ba in *Parmotrema perlatum*, is likely to be caused by leaching. That means 12 days exposure time was not enough for our lichens to reach equilibrium with the harsh conditions inside the tunnel. Zn and Pb were accumulated in both species, i.e. their mean concentrations increased within 12 days period of exposure. However, *Usnea subfloridana* shows extra effectiveness in absorbing and accumulating Zn.

In figure 4, we observe an increase in average concentration levels as the exposure time increases for the elements shown.

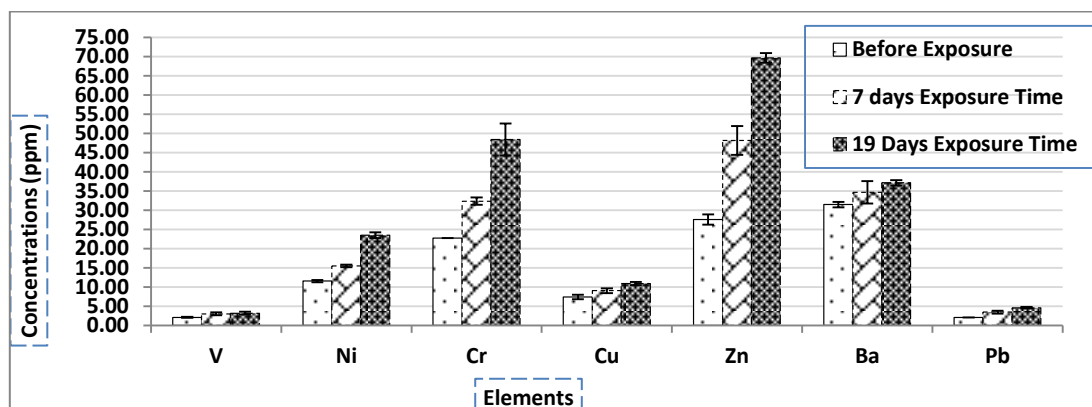


Figure 4. Figure showing accumulation of elements in a mixture of two moss species (*Leptodon smithii* and *Pterogonium gracile*) over different exposure times.

Most of biomonitoring investigative work has always been done using mosses as they are regarded as analogues of air filters. This is due to their well-known exceptional ability to absorb, accumulate and retain heavy metals through wet and dry atmospheric deposition [2, 7]. In this study, the moss species also behaved in similar manner. In this respect, we can deduce that the increase in the elemental content in the exposed mosses is directly proportional to the length of exposure even for our shortest length of exposure (i.e. 7 days).

In Figure 5 we show results of cluster analysis (CA) for indicators of road traffic emissions in tunnels, presenting three clusters. Our results are consistent with the results from fairly comparable studies [7, 8, 9, 10].

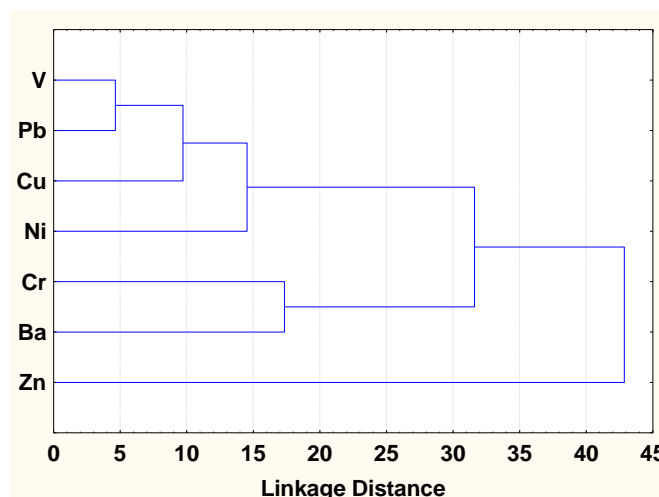


Figure 5. Dendrogram resulting from hierarchical cluster analysis of trace elements associated with road traffic emissions.

Variables (V, Pb, Cu and Ni) contained in the first cluster are linked to different road traffic related source; road dust containing traffic related particles, auto exhausts, oil combustion, as well as brake and tire wear. The second cluster with Cr and Ba represents diesel fuel and tire wear. The third cluster also represents a number of traffic related sources; auto exhausts, motor oil, as well as break and tire wear. The fact that all groups are connected at a certain distance demonstrates that all the main sources

of those elements are emissions from motor vehicles. According to [12], the application of multivariate statistical analysis (e.g. cluster analysis) to datasets assists in revealing the character and the origin of pollution sources within a particular study area.

4. Summary and Conclusion

Our results show *Usnea subfloridana* to be more efficient in accumulating trace elements from vehicle emission in tunnels, compared to the other lichen species *Parmotrema perlatum*. Lichens are likely to initially undergo leaching of trace elements when exposed to unfavourable conditions like tunnels. Thus, a longer exposure time is essential for them to reach equilibrium with their new environment before they can appropriately accumulate trace elements. All determined elements associated with vehicle emissions in tunnels were considerably accumulated by mosses even after a short exposure time of 7 days, which is 5 days shorter than that of lichens. Hence biomonitoring with mosses is generally ideal. The outcomes of this study demonstrate mosses to be more efficient than lichens in monitoring road traffic emission even under enhanced polluted conditions of a traffic tunnel. Cluster analysis of our results for the considered elements confirms the linkage of those trace to emissions from vehicles.

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