

## THE RELATIONSHIP BETWEEN INTENSITY OF VEHICLE TRAFFIC AND ACCUMULATION OF CHEMICAL ELEMENTS IN LICHEN *Xanthoria parietina*

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**Abstract.** *Xanthoria parietina* (L.) Th. Fr. (1860) was used to monitor the pollution with chemical elements caused by car traffic. In this study, in 8 counties in Romania, both the central and peripheral parts of *X. parietina* were used to indicate accumulation of chemical elements over time. The results indicated that the vehicle number was significantly correlated to Al, Zn, Cu, and Mn concentrations accumulated in the central parts of *X. parietina*. In addition, Zn and Fe accumulated in peripheral parts of *X. parietina* were also correlated with the number of vehicles. The two parts of *X. parietina* accumulate the chemical elements at different rates due to their ripeness degree. The central parts are old and accumulate high metal concentrations whilst the peripheral ones are young and accumulate low metal concentrations. In conclusion, the long-time exposure of central parts is well defined through the accumulation of more metals, compared to the short-time exposure of peripheral parts characterized by the accumulation of two metals. Also, *X. parietina* could be used as monitor of metal pollution caused by car traffic.

**Keywords:** biomonitoring, lichens, metal accumulation, number of vehicles, atmospheric pollution, Romania.

**Rezumat. Relațiile dintre intensitatea traficului rutier și acumularea elementelor chimice în *Xanthoria parietina*.** *Xanthoria parietina* (L.) Th. Fr. (1860) a fost utilizată pentru monitorizarea poluării cu elemente chimice cauzată de traficul rutier. În acest studiu atât părțile centrale cât și cele periferice ale speciei *X. parietina* au fost utilizate pentru a indica acumularea elementelor chimice de-a lungul timpului. Rezultatele au indicat că numărul vehiculelor a fost semnificativ corelat cu concentrațiile Al, Zn, Cu și Mn acumulate în părțile centrale ale speciei *X. parietina*. De asemenea Zn și Fe acumulate în părțile periferice ale speciei *X. parietina* au fost corelate cu numărul de vehicule. Cele două părți ale speciei *X. parietina* acumulează diferit elemente chimice datorită gradului acestora de maturitate. Părțile centrale sunt mature și acumulează concentrații mari de metale în timp ce părțile periferice sunt juvenile și acumulează concentrații reduse de metale. În concluzie expunerea pe termen lung a părților centrale este bine definită prin acumularea mai multor metale în comparație cu expunerea pe termen scurt a părților periferice caracterizată prin acumularea a două metale. De asemenea, *X. parietina* poate fi utilizată ca monitor al poluării cu metale cauzată de traficul rutier.

**Cuvinte cheie:** biomonitorizare, licheni, acumularea metalelor, numărul de vehicule, poluare atmosferică, România.

### INTRODUCTION

On a global scale, human activities have altered natural resources and as a consequence have affected biodiversity at multiple spatial scales (BRETAGNOLLE et al., 2018); therefore, new technologies have been developed for the evaluation of environmental problems (CONTI & CECCHETTI, 2001; DYTŁOW & GÓRKA-KOSTRUBIEC, 2019).

There is a wide range of monitors of environmental quality (STERZYŃSKA et al., 2018), but lichen species have a high capacity to accumulate metals so as to reflect the level of the contaminants dispersed in different compartments of the environment. Therefore, these cryptogamic organisms are successfully used in environmental monitoring studies (CONTI & CECCHETTI, 2001; ASLAN et al., 2011; DOĞRUL-DEMIRAY et al., 2012; PARZYCH et al., 2016; PEREIRA et al., 2018). Human activities, climatic conditions, the geographical morphology of the land, mineral resources and earth erosion influence the metal accumulation in cryptogamic organisms (BARGAGLI et al., 2002; PARZYCH et al., 2016).

One of the main pollution sources is vehicular traffic that releases a wide range of pollutants into the environment, such as compounds of nitrogen, sulphur, carbon (SUJETOVIENÉ, 2010), metals (CONTI & CECCHETTI, 2001; ITE et al., 2014; JI et al., 2019; PAOLI et al., 2019), phosphorus compounds, fluorides, chlorides, radionuclides, and ozone that are uptaken by lichens (CONTI & CECCHETTI, 2001; FENN et al., 2007). Studies on human health in relation to environmental pollution have revealed that some of the chemical elements such as Be, B, Li, Al, Ti, V, Cr, Mn, Co, Ni, Cu, As, Se, Sr, Mo, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, W, Pt, Au, Hg, Pb, and Bi are harmful for humans (MORAIS et al., 2012).

Heavy metals affect human health (MORAIS et al., 2012; JAN et al., 2015; WANG et al., 2019); for this reason, the control of the pollutants in atmosphere should be performed by responsible agencies directly implied in the environmental protection (WANG et al., 2019). Many countries worldwide still have serious environmental problems related to vehicles that are responsible for the non-exhaust metal contamination of the environment (ADAMIEC et al., 2016).

The aim of the study is based on the assessment of the relationship between car traffic and metal concentrations accumulated in the central and peripheral parts of the *Xanthoria parietina* lichen. The main objective is based on the effect of car traffic intensity on atmospheric quality assessed by metal deposition in the central and peripheral parts of *X. parietina*.

## MATERIALS AND METHODS

Research activity was performed along alignments and at distance from alignments during July and December 2015. The studied area includes 8 counties as follows: Bacău, Brăila, București, Călărași, Constanța, Cluj, Galați, and Hunedoara (Fig. 1). The sampling design consists in the selection of 8 alignment segments represented by two trees located along the roadsides at a considerable distance from one another and 1 tree far away from the roadsides. On each selected tree along the alignments and at distance from these, thalli of *Xanthoria parietina* (L.) Th. Fr. (1860) were collected. A total of 24 trees were sampled of which 16 trees along the alignments and 8 trees at distance from alignments. Along each selected alignment segment, the cars in motion were counted for 10 minutes to reveal the intensity of vehicle traffic (VICOL, 2014). Lichen thalli were collected using a knife at 1 m height above the soil to avoid eutrophication. As an important criterion, only healthy thalli with entire central and peripheral parts, were collected.



Figure 1. The location of sampling sites in different counties from Romania (Source: Google Earth Pro V 7.3.2.5776. (December 14, 2015). Romania. 45° 52' 22.05"N, 26° 08' 58.69"E, Eye alt 1141.41 km. SIO, NOAA, U.S. Navy, NGA, GEBCO. US Dept of State Geographer. Landsat/Copernicus 2018. <http://www.earth.google.com> [April 23, 2019].

In the laboratory, lichen thalli were cleaned by impurities with tweezers. Afterwards, all lichen thalli were separated into central and peripheral parts. Lichen thalli were not washed to avoid the loss of chemical elements. Further, lichen thalli were dried at 50°C for 48 hours and then were milled using a mortar and pestle. The chemical analysis of the elements was performed using 0.5 g of granulated material mixed in 9 mL of Suprapur concentrate 65% HNO<sub>3</sub> and 0.2 mL of Suprapur concentrate 37% HCl.

The samples were digested, after which were filtered in a 50 mL volumetric flask, then made up with distilled water. The digestion was performed using a furnace (MARS Expres SN/Mars 24050). The determination of chemical elements was performed by means of an inductively coupled plasma mass spectrometer (Agilent 7700 Series ICP-MS with ASX500 autosampler). The element concentrations were expressed in μg/g of dry weight.

The statistical analysis was performed based on three variables such as the number of vehicles in motion along the alignments, the distance from alignments and the concentration of chemical elements.

The dataset was primarily subjected to univariate statistics used to calculate the mean, standard deviation (Table 1) and the coefficient of variation (Table 2). As regard the coefficient of variation, both one-tailed and two-tailed *p* values of Fligner-Killeen test *T* have been considered particularly to highlight whether the variation in metals is higher in the central parts unlike to peripheral parts of the thalli and whether there are significant variations in metals among the central and peripheral parts of the *Xanthoria parietina*, respectively (HAMMER et al., 2001).

Table 1. The univariate statistics mean and standard deviation (M±SD) for accumulated metals in both central and peripheral parts of *Xanthoria parietina*.

| Metals | M±SD                    |                            |
|--------|-------------------------|----------------------------|
|        | Central parts of thalli | Peripheral parts of thalli |
| Pb     | 12.17±7.00              | 10.56±5.33                 |
| Cd     | 0.54±0.30               | 0.63±0.36                  |
| Ni     | 4.1±1.77                | 4.45±2.52                  |
| As     | 1.59±1.25               | 1.49±1.26                  |
| Hg     | 0.41±0.10               | 0.35±0.14                  |
| Al     | 1005.24±998.82          | 810.63±430.54              |
| Cs     | 0.37±0.02               | 0.33±0.09                  |
| Cr     | 4.64±2.11               | 4.51±2.11                  |
| Zn     | 83.99±47.42             | 90.60±60.31                |
| Co     | 0.98±0.57               | 0.95±0.59                  |
| Cu     | 2.93±6.24               | 3.16±6.64                  |
| Fe     | 1840.81±1414.82         | 1528.39±900.10             |
| Mn     | 121.01±110.33           | 91.10±52.33                |

Table 2. The coefficient of variation and Fligner-Killeen test calculated for accumulated metals in both central and peripheral parts of *Xanthoria parietina*.

| Metals | Coefficient of variation (%) |                            | Fligner-Killeen test (T) | p one-tailed | p two-tailed |
|--------|------------------------------|----------------------------|--------------------------|--------------|--------------|
|        | Central parts of thalli      | Peripheral parts of thalli |                          |              |              |
| Pb     | 57.56                        | 52.39                      | 21.77                    | 0.45         | 0.91         |
| Cd     | 56.37                        | 58.08                      | 6.12                     | 0.25         | 0.51         |
| Ni     | 43.26                        | 56.65                      | 25.55                    | 0.14         | 0.29         |
| As     | 74.29                        | 84.94                      | 17.41                    | 0.22         | 0.45         |
| Hg     | 26.28                        | 26.85                      | 18.57                    | 0.41         | 0.82         |
| Al     | 99.36                        | 53.11                      | 22.35                    | 0.40         | 0.80         |
| Cs*    | n/a                          | n/a                        | n/a                      | n/a          | n/a          |
| Cr     | 43.00                        | 46.88                      | 24.12                    | 0.24         | 0.49         |
| Zn     | 56.46                        | 66.57                      | 27.88                    | 0.05         | 0.10         |
| Co     | 58.65                        | 62.36                      | 17.19                    | 0.31         | 0.62         |
| Cu     | 48.27                        | 50.48                      | 21.08                    | 0.47         | 0.94         |
| Fe     | 76.85                        | 58.89                      | 20.57                    | 0.42         | 0.84         |
| Mn     | 91.17                        | 57.44                      | 17.42                    | 0.16         | 0.32         |

Legend: n/a not available data; \*statistical program require at least 3 values for each column

The Shapiro-Wilk ( $W$ ) test was used to check the data normality. The results of this test have indicated a non-normal distribution of the data ( $p < 0.05$ ); therefore, the dataset was log transformed ( $x+1$ ) to improve the data normality. The log transformed data did not indicate a normal distribution of the dataset. Thus, non-parametric correlation was selected for data analysis (HAMMER et al., 2001).

The Kendall rank order correlation coefficient ( $\tau$ ) was used to identify significant relationships between the number of cars along the alignments and metal concentrations. Also, the metal concentrations were analysed with distance from alignments (DYTHAM, 2011). The relationships were performed between the metal concentrations in the central and peripheral parts of *X. parietina* detected along the alignments and the number of running vehicles. At distance from alignments, the metal concentrations in the central and peripheral parts of *X. parietina* were analysed in relation to the distance from alignments. The central and peripheral parts of *X. parietina* were used as indicators of long time (central parts) and short time (peripheral parts) of accumulation of metals.

The statistical analyses were performed using PAST software (HAMMER et al., 2001).

## RESULTS

A total of 13 metals (Pb, Cd, Ni, As, Hg, Al, Cs, Cr, Zn, Co, Cu, Fe, and Mn) were determined in both the central and peripheral parts of *Xanthoria parietina* (Table 1). As regards the variation of metal concentrations accumulated in the central and peripheral parts of *Xanthoria parietina*, no significant results were obtained (Table 2).

A total of 760 cars were counted for the selected alignment segments. The results indicated that metals such as Al, Zn, Cu, Mn accumulated in the central parts of *Xanthoria parietina* were significantly correlated to the number of cars in motion whilst only Zn and Fe accumulated in peripheral parts of *X. parietina* were significantly related to the number of cars (Table 3).

At distance from roadsides, the metals accumulated in the central and peripheral parts of *Xanthoria parietina* decreased in concentrations (Table 4).

Table 3. Relationships between the metals accumulated in central and peripheral parts of *Xanthoria parietina* and the number of cars in motion along alignments.

| The number of cars in motion | Metal concentrations |       |       |        |        |       |
|------------------------------|----------------------|-------|-------|--------|--------|-------|
|                              | AlC                  | ZnC   | CuC   | MnC    | ZnP    | FeP   |
|                              | 0.38*                | 0.45* | 0.40* | 0.53** | 0.55** | 0.40* |

Legend: C-central parts of *Xanthoria parietina*; P-peripheral parts of *Xanthoria parietina* \*p < 0.05; \*\*p < 0.01

Table 4. Relationships between the metals accumulated in central and peripheral parts of *Xanthoria parietina* far away from alignments.

| Distance from roads | Metal concentrations |        |        |         |        |        |        |
|---------------------|----------------------|--------|--------|---------|--------|--------|--------|
|                     | NiC                  | HgC    | AlC    | FeC     | NiP    | AlP    | FeP    |
|                     | -0.71*               | -0.80* | -0.57* | -0.78** | -0.57* | -0.71* | -0.71* |

Legend: see the legend of Table 5

## DISCUSSIONS

Vehicle exhausts represent an important source of pollution along the alignments (ASLAN et al., 2011; LIU et al., 2012). Also, other anthropogenic sources such as different industrial branches, agricultural technologies, farming, domestic heating, urban emissions and development of human population alter the environmental conditions and affect human health (BARGAGLI et al., 2002; ASLAN et al., 2011; PARZYCH et al., 2016; PEREIRA et al., 2018).

In the present study, the concentrations of Al, Zn, Cu, Mn, and Fe were highest near the roadsides. According to other similar studies Fe, Mn, Zn, Cu, Pb, Ni, Se, Cr, and Cd are present in higher concentrations near roads with intensive vehicular traffic (ASLAN et al., 2011; PARZYCH et al., 2016; PAOLI et al., 2019).

The particularity of Cu, Hg, and Zn consists in long distance transport; furthermore, their impact on the environment is enhanced by multiple local emissions (BARGAGLI et al., 2002). Soil particles are the main source of Cu and its dynamics is greatly supported by vehicular traffic (ASLAN et al., 2011; PEREIRA et al., 2018); finally, they are uptaken by biota components (BARGAGLI et al., 2002; ASLAN et al., 2011). The high level of Fe and Zn in environment could be caused by a high intensity of vehicular traffic. Furthermore, high concentrations of Cu and Zn were found near industrial sources such as mines and smelting plants (BARGAGLI et al., 2002). Zinc could be released into the environment by the wearing of tires, lubricating oils, diesel oil, unleaded petrol, and brake pads (ASLAN et al., 2011; PARZYCH et al., 2016; PEREIRA et al., 2018). Agricultural practices are important sources of Zn emission, especially farming and application of fertilizers (ASLAN et al., 2011).

The functional components of cars and fossil products such as diesel oil and unleaded petrol are important sources of iron and manganese. Also, soil along the roads is significantly enriched in these elements (ASLAN et al., 2011). The nickel is released into the atmosphere by combustion of fossil products used by non-industrial buildings (PARZYCH et al., 2016). Lithophile (Al, Fe, Ni) and atmophile (Hg) metals decreased in concentrations at distance from alignments. The decreasing concentrations of Al, Hg, Ni, and Fe far away from alignments could be due to environmental conditions from traditional landscapes represented by cleaner air (PAOLI et al., 2018). Another study revealed a decrease in heavy metal concentrations far away from roads (ASLAN et al., 2011).

Some elements, such as Fe, Mn, Cu, and Zn, are essential for organisms; for this reason, their optimal presence in lichens is normal (ASLAN et al., 2011). New car technologies have provided performant models such as electrical cars but these are focused especially on the mitigation of exhaust emissions and therefore non-exhaust emissions remain a crucial problem worldwide which can act synergistically to other pollution sources (AMATO et al., 2014; TIMMERS & ACHTEN, 2016).

## CONCLUSIONS

Although there is approved a legislative framework focused on the mitigation of vehicular exhaust emissions, the environment is still polluted with metals that could be released by non-exhaust emissions. Far away from roads Ni, Hg, Al, and Fe have decreased in their concentrations in the central parts of *X. parietina* whilst the concentrations of Ni, Al, and Fe have decreased in the peripheral parts of *X. parietina*. The long and short term monitoring of *X. parietina* has indicated a clear reduction of metals far away from alignments.

## ACKNOWLEDGEMENTS

The author is indebted to Vicol Ioana and Costache Florina-Cristina for assistance in the field and laboratory activities. Also, the author thanks Andreea Dumitru (Buturuga) for the chemical analysis of elements. The primary idea and methodology of the researches are parts of the author's Doctoral Thesis presented at the University of Bucharest, Faculty of Geography, 2012. The study was performed within the project "Long-term National Monitoring System of Bioaccumulation of Airborne Heavy Metals" (RO04-66074 - BioMonRo) financed through the EEA Grants Financial

Mechanism run by Iceland, Liechtenstein and Norway under the Programme RO04 - "Reduction of hazardous substances" conducted by the Bucharest Institute of Biology of the Romanian Academy [grant number no. 3452/19.05.2015].

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Received: April 12, 2020  
Accepted: July 08, 2020