# BIOLOGICAL EFFECTS OF AIRBORNE POLLUTANTS RELEASED DURING CEMENT PRODUCTION ASSESSED WITH LICHENS (SW SLOVAKIA)

Luca Paoli[1], Anna Guttová[2], Alice Grassi[1], Anna Lackovičová[2], Dušan Senko[2], Stefano Loppi[1,*]

[1] Department of Life Science, University of Siena, via Mattioli 4, 53100 Siena, Italy;
[2] Institute of Botany, Slovak Academy of Sciences, Dúbravská cesta 9, 84523 Bratislava, Slovakia

## Abstract

In this paper we investigated the biological effects of airborne pollutants released during cement production by means of epiphytic lichens (SW Slovakia). We assessed the effects of dust pollution on lichen diversity around a limestone quarry (on the quarry-facing and the opposite side of *Fagus sylvatica* boles) and the content of selected elements in samples of the lichen *Xanthoria parietina* collected around a cement mill, two quarries and urban and rural sites at increasing distance from the sources of pollution. Dust contamination from limestone quarrying affected lichen diversity within a distance of 350 m from the source. ~~The analysis of the functional traits of the lichen diversity was particularly helpful as indicator of dust pollution.~~ Approaching the quarry, the diffusion of basi-nitrophilous species, the decrease of acidophilous species and the asymmetrical distribution of lichens on the tree boles, with a higher coverage of basiphilous species in the side facing the source of dust were observed. These responses, based on the functional traits of the lichen diversity, are helpful in monitoring studies around similar sources of pollution. In samples of *X. parietina* collected around the quarries and the cement mill, Ca, Ti, Fe, V, Al and Ni were significantly higher than in the surrounding environment. Calcium was a good tracer for dust contamination around the quarries and the cement plant and a clear decrease in its content with increasing distance from the source was found, with normal values reached within 1,700 m from the cement mill. Lichens can be successfully used as indicators to integrate instrumental monitoring networks, when air pollution from cement factories is concerned.

**Keywords:** ~~Air pollution~~, Bioindicators, Bioaccumulation, Cement, Dust, Lichens, *Xanthoria parietina*

* Corresponding author. E-mail address: stefano.loppi@unisi.it (S. Loppi)

## 1. Introduction

Global cement production in 2012 has been estimated at 3.6 billion tonnes, translating into a +3% increase compared to 2011, with China representing 59.3% of the world's total cement production (Cembureau, 2012). During cement production, pollutants may be released to the environment from quarrying and grinding of the raw material, kiln operations, transportation, power generation and packing and dispatch of the cement from the industry. Rock quarrying, grinding and kiln operations are source of coarse and fine particulate matter, which, transported by the wind, may deposit in the surroundings (Bluvshtein et al., 2011) and may have an environmental impact on local vegetation and productivity, affecting crops, grasslands, trees, bryophytes and lichens, via physical or chemical effects (Farmer, 1993; Loppi and Pirintsos, 2000). Power generation from combustion processes can be a source of airborne pollutants from the cement mill that affects the surrounding environment. Such pollutants include $SO_2$, $NO_x$, $CO_2$, particulate matter and heavy metals and potentially, dioxins and furans in case of waste burning (Ali et al., 2011; Schuhmacher et al., 2004).

Lichens are suitable bioindicators of the effects of air pollution, providing reliable information on the quality and characteristics of the environment (Nimis et al., 2002). Lichens are perennial, slow-growing organisms that maintain a fairly uniform morphology in time, are highly dependent on the atmosphere for nutrients, and do not shed parts as readily as vascular plants. The lack of a waxy cuticle and stomata allows many contaminants to be absorbed over the whole lichen surface (Ferry et al., 1973). Bioaccumulation involves the absorption and release of molecules with the surrounding environment, as a result of the balance between biotic and abiotic components of ecosystems and biogeochemical cycles (Bačkor and Loppi, 2009; Garty, 2001). Lichen monitoring can be used as a complementary system that integrates instrumental monitoring around point sources of atmospheric pollution. Consequently, epiphytic lichens can be profitably used for monitoring dust fallout and the effects of dust contamination (Loppi and Pirintsos, 2000). Dust pollution was shown to influence lichen diversity (Loppi and Pirintsos, 2000; Marmor et al., 2010), element accumulation (Branquinho et al., 2008) and physiological processes of lichen thalli (Zaharopoulou et al., 1993). In general, alkaline dust pollution increases bark pH and consequently enhances the diffusion of basiphilous species (Marmor et al., 2010) at the expense of acidophilous ones (Loppi and Pirintsos, 2000). Calcium content of lichens exposed to dust pollution near a cement industry is considered the foremost cement-dust indicator (Branquinho et al., 2008). Several studies associated cement production to the release of high loads of Ca into the atmosphere (see e.g. the review of Garty and Garty-Spitz, 2011). Furthermore, heavy metals released from cement industries powered by means of fossil fuels and/or waste burning (Schuhmacher et al., 2004) can be detected in topsoils (Bermudez et al., 2010) and in native and transplanted lichens (Demiray et al., 2012; Ljubič Mlakar et al., 2011).

The presence of a cement mill near Bratislava (SW Slovakia), offered the opportunity to investigate in the field the biological and chemical effects of airborne pollutants released during cement production, with an emphasis on dust pollution.

This work was carried out to investigate: i) the impact of dust pollution from limestone rock quarrying on epiphytic lichen diversity in relation to angular exposure and distance from the source; and ii) the impact of airborne pollutants from the cement production in the surrounding environment, analysing the accumulation of selected elements in native lichens.

## 2. Material and Methods

### 2.1 Study area

The study area extends over ca. 32 km$^2$ (Fig. 1). The cement plant, operating since the 1970s, is located ca. 40 km NE of Bratislava (SW Slovakia), on the foot of the Malé Karpaty Mts, surrounding it to the S and E. The landscape is rural, characterized by arable land, pastures and forests (beech and mixed oak, hornbeam, linden and maple). Elevation ranges between 200 and 450 m asl. The climate is continental, with an average annual rainfall of ca. 700 mm. ~~Prevailing winds flow towards SE (ca. 40%) or NW (ca. 20%) with an average speed intensity of 3.7 m/s in both directions (Lapin et al., 2002).~~ The closest town (3,500 inhabitants) is located 1.5 km W of the cement mill.

Currently, the average capacity of the cement mill is 150,000 t/y of clinker and 160,000 t/y of cement  The raw material is extracted in a limestone ($CaCO_3$) quarry with an operating capacity of 1 750 000 t/y. The material has a fraction of MgO ranging from 2.2% to 10.9% (dolomitic limestone) (www.enviroportal.sk). Nearby, a paleobasalt quarry is situated, with an operating capacity of 600,000 t/y; the material extracted here is chiefly addressed to the market and is characterized by a share of $SiO_2$ (52–57%), MgO (5–12%), CaO (ca. 10%), FeO and $Fe_2O_3$ (5–14%), $Al_2O_3$ (<14%), $TiO_2$ (0.5–2%) and traces of $Na_2O$ and $K_2O$. The production of grey cement is powered by waste (68%), coal (21%), petroleum coke and gas burning (11%), while the production of white cement by petroleum coke (51%), waste (28%) and gas burning (21%); with increasing trend regarding the share of waste (Anonymous, 2011). Airborne emissions from the cement mill are available through continuous instrumental monitoring (yearly average [legal limit]) (www.holcim.sk):

- grey cement line $NO_x$ (475 mg/Nm$^3$ [800]), PM (3 mg/Nm$^3$ [30]), $SO_2$ (30 mg/Nm$^3$ [50]), TOC (31 mg/Nm$^3$ [60]), HCl (4 mg/Nm$^3$ [10]);
- white cement line $NO_x$ (732 mg/Nm$^3$ [800]), PM (3 mg/Nm$^3$ [30]), $SO_2$ (188 mg/Nm$^3$ [300]), TOC (6 mg/Nm$^3$ [10]), HCl (7 mg/Nm$^3$ [10]).

### 2.2 Lichen diversity

To investigate the impact of dust deposition around the limestone quarry, the diversity of epiphytic lichens on *Fagus sylvatica* trees was measured, being the site surrounded by a mature *Fagus* forest, where suitable trees are available. Thirty trees, randomly selected along a belt surrounding the border of the quarry (15) and along a belt at a distance of ca. 350 m from the border of the quarry (15) were sampled (Fig. 1). The latter was selected after a preliminary assessment of lichen distribution, being also the spatial limit of the spontaneous *Fagus* forest directly surrounding the quarry.

The diversity of epiphytic lichens was scored using the index of lichen diversity (ILD) suggested by Pišút and Pišút (2006). The ILD was calculated as the sum of vitality and abundance of epiphytic lichens on the bole (girth >90 cm) at 0–2 m above ground of isolated trees or on trees distant at least 10 m from the closest one. Vitality and abundance of each lichen species were expressed using a specific scale combining both parameters (Lackovičová, 1982; Pišút and Lisická–Jelínková, 1974): 1 = one or a few normally developed thalli, or scattered dying out thalli; 3 = numerous damaged thalli, or scattered healthy thalli; 5 = frequent healthy thalli. The ILD of each monitoring site was taken as the arithmetic mean of the ILD measured for each sampled tree.

The dataset collected for this study was supplemented with relevés collected with the same methodology in 1970s by A. Lackovičová. Eight sampling sites were studied on natural *Fagus* stands within the same area (Vajarská – Veľký Petrklín, Fig. 1) before the opening of the quarry (unpublished data).

To investigate the influence of angular exposure to the quarry, the lichen diversity was sampled separately on the quarry-facing side of the bole and the sheltered side, by dividing the tree circumference into two semi-circumferences and expressing the diversity as the sum of ILD values per each side. To avoid any effect of subjectivity and ensure data quality, each measurement was carried out and double-checked by at least two skilled operators.

Besides total lichen diversity, for data interpretation, ILD values were calculated grouping the species according to their functional value: from previous studies it was reported that dust pollution from limestone quarries and cement works had a neutralizing effect on tree barks, promoting lichen assemblages typical of trees with alkaline barks (Gilbert, 1976; Jürging, 1975; Recchia and Polidoro, 1988). Therefore, we compared ILD values determined by basiphilous species *vs* ILD values of acidophilous species. Species were assigned to their functional group according to the ecological indicator values reported in the database by Nimis and Martellos (2008); concerning pH of the substratum, species with the score 4–5 were evaluated as basiphilous (slightly basic substrata, i.e. loving dust-covered barks), species with the score 1–2 were evaluated as acidophilous. Species nomenclature follows Guttová et al. (2013). In case of identification problems during field sampling, specimens were collected and identified later in the laboratory. Species belonging to the genus *Lepraria* and juvenile (undeveloped) thalli of *Physcia* and *Lecanora* have been determined up to the genus level.

### 2.3 Element accumulation

To investigate element accumulation in native samples of the lichen *Xanthoria parietina*, several sites were selected (see Fig. 1), corresponding to potential pollution sources, namely a cement mill (1), a limestone quarry (2) and a paleobasalt quarry (3) and potential target sites, namely inhabited (4) and agricultural areas (5, 6). Within each site, lichen thalli were collected (July 19th, 2011, after 2 weeks of sunny days) at 50–200 cm from the ground, from 3–5 different sampling points, each corresponding to a tree (mainly *Acer, Fagus* or *Prunus*). At least 30 different lichen thalli were collected at each site, placed in paper bags, air-dried and stored.

In the laboratory, *Xanthoria* samples were carefully cleaned under a binocular microscope to remove extraneous material deposited onto the surface, such as remnants of mosses, bark and soil particles. Only the peripheral parts of the lobes (up to 5 mm from lobe tips) were selected for the analysis; this part roughly corresponds to the biomass produced during the last year. Samples were not washed since there is evidence that washing may unpredictably alter the chemical composition of the thalli (Bettinelli et al., 1996).

Unwashed samples were pulverized and homogenized with a ceramic mortar and pestle. About 200 mg of powdered lichen material was mineralized with a mixture of 6 mL of 70% $HNO_3$, 0.2 mL of 60% HF and 1 mL of 30% $H_2O_2$ in a microwave digestion system (Milestone Ethos 900) at 280°C and 55 bars. The concentrations of selected elements (As, Cd, Cr, Fe, Hg, Mn, Ni, Pb, V) were determined by ICP–MS (Perkin Elmer – Sciex, Elan 6100) or alternatively (Al, Ca, Cu, S, Ti, Zn) by ICP–OES. Results were expressed on a dry weight basis (µg/g dw). Analytical quality was checked with the Standard Reference Material IAEA–336 'lichen' and GBW–07601 'tobacco'. Precision of analysis was within 18% for Al, Cu, Fe and Hg and within 10% for the remaining elements.

### 2.4 Bark pH

The pH of *Fagus sylvatica* bark was measured following a standard method by Härtel and Grill, as reported in Farmer et al. (1990). Pieces of bark from 10 trees were collected and the upper layer, ca. 3 mm thick, was cut into pieces and mixed, then 4 g were put into 30 mL distilled water. After extraction for 24 h (n = 3), the pH of the extract was measured with a pH–meter (Eutech Instruments pH 510).

### 2.5 Statistics

The significance of differences between ILD at the limestone quarry and 350 away and between the exposed and sheltered side of the boles were checked using the Kolmogorov–Smirnov test ($p<0.05$). Differences in species composition of epiphytic lichen communities were analysed by detrended correspondence analysis (DCA), programme package CANOCO 4.5 (ter Braak and Šmilauer, 2002).

The Kolmogorov–Smirnov test ($P<0.05$) was used to check whether element depositions in *Xanthoria parietina* at the limestone quarry, the paleobasalt quarry, the cement mill and the closest urban area are significantly higher respect to the agricultural sites of the surrounding environment. After normalization of the data, Pearson correlation coefficient was used to find significant relationships ($p<0.05$) between pairs of elements.

A GIS model of Ca depositions in *X. parietina* was created using GRASS GIS v6.4, released under the GNU/GPL license. In the first step, a sum of measured values (concentration in µg/g dw) for each element was calculated. Then these sums were normalized, in such a way that the resulting value for the element with the lowest count of occurrence was equal to one. The coefficient was used to divide each table row for each element. The output were normalized theoretical values for each element and locality that we would have measured in the case that every element was equally present at all localities. A Digital Terrain Model was used to calculate the initial derivations of elevation, slope angle and slope aspect, for the development of a geographically weighted regression, using Ca as leading factor. The model also accounted for wind direction and intensity, based on data from the national meteorological service (Slovak Hydrometeorological Institute, www.shmu.sk). The model was calculated using Regularized Spline with Tension (RST) (Mitášová and Mitáš, 1993) implemented as a *v.surf.rst* and *v.vol.rst* modules. RST allows local spatial prediction to be performed in a flexible and robust way. The *v.vol.rst* interpolates values to a 3-dimensional raster map from 3-dimensional point data given in a 3-D vector point.

## 3. Results

### 3.1 Lichen diversity

Twenty-five lichen species were recorded on *F. sylvatica* trunks (Tab. 1). Owing to natural bark properties, lichen communities on beech are typically characterized by the dominance of acidophilous species. Within the study area, at a distance of 350 m from the limestone-quarry, acidophilous species dominated lichen communities (12 out of 15 species) and basi-nitrophilous species contributed only 5% to the overall ILD value. The proximity to the quarry enhanced the occurrence of basi-nitrophilous lichens (10 out of 18 species). The average ILD value increased from 17±5 to 30±10 and the share of basi-nitrophilous lichens rose from 5% to 60%. The average pH of beech bark increased from 5.3±0.3 to 5.9±0.3 approaching the quarry (Tab. 1).

DCA arranged the relevés measured during the present study into two well defined groups, reflecting the share of basi-nitrophilous and acidophilous species in connection with distance from the quarry (Fig. 2). The relevés on the trees surrounding the quarry form a compact cluster characterized by the dominance of basi-nitrophilous species (e.g. *X. parietina*, *Physcia adscendens*, *Phaeophyscia orbicularis*). The relevés on the trees at 350 m from the limestone-quarry are characterized by the prevalence of acidophilous species, e.g. *Pyrenula nitida*, *Porina aenea*, *Arthonia radiata*. The latter are similar to the relevés carried out in the past in natural beech forests, which form a distinct group with additional dominating acidophilous species e.g. *Hypogymnia physodes*, *Cladonia* spp. (only basal squamules), *Pertusaria amara*. Comparing present and past (1970s) relevés, basiphilous species are clearly spread in the surroundings of the quarry.

In addition, an asymmetrical distribution of the lichens around the bole was observed on the border of the quarry, where the side of the trees directly facing the quarry was strongly colonized by basi-nitrophilous lichens respect to the sheltered side (Fig. 3).

### 3.2 Element accumulation

In samples of *X. parietina* collected around the quarries and the cement mill, Ca, Ti, Fe, V, Al and Ni were significantly higher than in the surrounding environment (Tab. 2). In particular, the highest levels of Al, Fe, Hg, Mn, Ti and V were measured around the paleobasalt quarry. The highest concentration of Ca (2 460 μg/g) was measured at the cement mill and was 2.4 fold higher than the background value of the study area (1 070 μg/g). A model of Ca depositions in the area is shown in Figure 4. Lichens from the inhabited area had the lowest content of Al, Fe, Mn, Ni, Ti and V, but were enriched in Ca (1 450 μg/g).

Positive correlations were found between Al–Ti, Al–Fe, Al–Mn, Al–V, Ti–Fe, Ti–Mn, Ti–V, Fe–Mn, Fe–V, Mn–V and also Hg–Ti, Hg–Fe, Hg–Mn, Hg–V, suggesting their common terrigenous origin (Tab. 3). The concentrations of the other elements (As, Cd, Cr, Cu, Pb, Zn) suggested a low contamination by airborne pollutants from combustion processes (Bargagli and Nimis, 2002), exceptions being S and Ni. In fact, all sampling sites were affected by a high level of S in the lichens (2 940–5 720 μg/g). The content of Ni indicated a condition of moderate pollution (>3 μg/g) around the cement mill and the quarries, and of low pollution (≤3 μg/g) at the other sites.

## 4. Discussion

### 4.1 Lichen diversity

The results of the present study indicated a strong influence of dust on epiphytic lichen communities in the surroundings of the limestone quarry and the functional traits of the lichen diversity have been particularly helpful as indicators of dust pollution. Alkaline dust from limestone quarries and cement works has a neutralizing effect on tree barks, promoting lichen assemblages typical of trees with alkaline barks (e.g., *Physcia* spp. and *Xanthoria* spp.). Previous studies showed that alkaline dust causes a rise in bark pH, leading to hypertrophication and replacement of acidophilous lichens with xero-nitrophilous ones. This phenomenon is particularly relevant approaching cement mills (Recchia and Polidoro, 1988), quarries (Gilbert, 1976; Loppi and Pirintsos, 2000), dirt roads (Loppi, 1996) and agricultural areas (Loppi and De Dominicis, 1996), especially in arid environments (Paoli et al., 2006). In the proximity of quarries, independently whether alkaline or acid dust is deposited, epiphytic lichens seems to be influenced directly by the physical effect of the deposited dust, and up to 50 m from the quarries, all species can be regarded as nitrophilous (Loppi and Pirintsos, 2000). Branquinho et al. (2008) estimated that the direct impact of dust around a cement factory (in Portugal) was in the range 250 – 1000 m from the source. Cement dust had a hygroscopic effect (Branquinho et al. 2008), which may contribute to the increase of xerophilous lichens approaching the source of dust (Loppi and Pirintsos, 2000; Recchia and Polidoro, 1988). Dust deposition around limestone quarries was found to raise bark pH of

*Fraxinus excelsior* from 3.5 to 6.5 (Gilbert, 1976) and correlations among species diversity, bark pH and distance from the quarry were reported. Alkaline dust around alkaline waste dump and magnesite works was found to increase bark pH of *Malus domestica* and stimulate the diffusion of nitrophilous lichen communities with dominating *X. parietina* (Pišút and Pišút, 2006). Alkaline dust pollution may increase bark pH and the proportion of dust indicator species both according to the distance from the source and the vertical gradient in the tree canopy, wherever the highest and exposed part of the canopy correspond to the highest share of basiphilous species (Marmor et al., 2010). Similarly, in our study bark pH of *F. sylvatica* rose from 4.9 (min) to 6.3 (max) approaching the limestone quarry and the lichen vegetation was clearly enriched in basi-nitrophilous species. According to Loppi and Pirintsos (2000), wind-blown dust can create xeric microclimatic conditions and high deposition of alkaline dust leads to a shift of lichen communities dominated by meso-acidophilous species of weakly eutrophicated environments, such as *Flavoparmelia caperata* and *Parmotrema perlatum*, to communities dominated by basi-nitrophilous and xerophilous species, such as *Physcia* spp. and *X. parietina* (Loppi, 1996).

Other studies showed that approaching cement factories the lichen vegetation is enriched in basiphilous and xerophilous species, but in the close proximity to the factories an area devoid of any lichen could be found (Recchia and Polidoro, 1988; Recchia et al., 1991). In fact, extreme loads of alkaline dust may heavily affect also basiphilous and nitrophilous lichens, leading to a condition of lichen desert approaching the source of pollution (Loppi and Pirintsos, 2000; Pišút and Pišút, 2006). Gilbert (1976) found a zonation of lichens around a lime dust source in England. Heavily dusted trees had few lichens and this zone was followed by a zone containing lichens that are normally saxicolous together with species typical of highly eutrophicated habitats. Lichen diversity and coverage both increase with the distance from cement mills (Recchia and Polidoro, 1988). Jürging (1975) reported that dust from cement factories has the same effect of ammonia emissions on nearby lichen communities, promoting nitrophilous species. However, at least in the present study, the strongest impact of quarrying operations extends up to a maximum of 350 m from the source. Likely owing to the buffering capacity of the forest belt surrounding the quarry, at this distance the lichen vegetation is much less influenced by dust and resembles natural assemblages, but is still lacking several species which are typically found on *Fagus* trunks at remote areas and were present in the study area in the past.

Our data revealed an asymmetrical distribution of lichens on the boles near the quarry, where the diffusion of dust from the quarry clearly promoted the functional group of basiphilous species and reduced acidophilous ones. Studies on the distribution of lichens on road lining trees influenced by car traffic suggested that the more/less turbulent diffusion of pollutants may be the cause for similarities/differences in angular distribution of lichen thalli and their element contents around the bole (Del Guasta, 2000; Paoli et al., 2013). In the case of the quarry, with particles of higher dimensions and a less turbulent dust diffusion, the sampling aspect becomes more critical in the design of a sampling procedure, as suggested by Adams and Gottardo (2012).

The study of the lichen diversity indicated that in the assessment of the biological effects of dust pollution around quarries and cement mills with lichens, functional response groups are particularly helpful. The signals to be searched gradually approaching the source of dust pollution are: increase of basi-nitrophilous and xerophilous species; decrease of acidophilous species; higher share of basiphilous lichens in the side facing the source of dust; and, lastly, the disappearance of lichens at heavily dusted sites.

### 4.2 Element accumulation

All stages of cement production, from extraction of the raw material to the production itself, can be a source of dust pollution (Branquinho et al., 2008; Carreras and Pignata, 2002; Jalkanen et al., 2000; Pignata et al., 2007).

In our study, the high correlations among soil/rock related elements in the lichen *X. parietina* and the high content of Ca in native lichens around the cement mill and the quarries suggest a common source, namely dust released during quarrying, grinding of the raw material, transportation, and kiln operations for the production of cement. We found out that Ca in lichens is a good tracer for dust contamination around the quarries and the cement plant, as suggested by Branquinho et al. (2008). In their study, dust pollution around a cement industry was investigated by means of native (*X. parietina*) and transplanted (*Ramalina canariensis*) lichens. A marked decrease in Ca content in *X. parietina* with increasing distance from the cement mill was found. At approximately 250 m from the source, Ca reached a background value of 1,377 µg/g, whereas at the cement mill, Ca was up to 20 times higher (Branquinho et al., 2008). In our study, according to the model of Ca depositions, the concentrations of this element reach normal values in lichen thalli within 1,700 m from the cement mill.

In lichens, Ca is generally present for the vast majority in extracellular form, whereas only a little part occurs intracellularly (Garty and Garty-Spitz, 2011) and SEM observations revealed that cement dust particles can be also included within the thallus (Recchia et al., 1991).

Calcium dust may react differently depending on the wet or dry period (Garty and Garty-Spitz, 2011). In fact, according to Branquinho et al. (2008), two kinds of dust can be observed in relation to cement production. One kind is a cement/clinker dust which produces a thick layer and accumulates in the lichens in wet periods: in this case the increase of Ca from cement/clinker dust is coincident with an increasing volume of precipitation whereas a decrease may coincide with an increasing number of dry days. On the other hand, Ca-dust derived from small and lose particles of limestone may accumulate in dry periods, being washed off with increasing volumes of rain (Branquinho et al., 2008). It is therefore suggested that lichens are very helpful to detect the spatial impact of Ca-containing dust, whereas when interpreting the temporal impact it is important to account for wet and dry periods differently affecting the accumulation of this element.

The decrease of contamination occurring with distance from cement plants can be detected also analysing soil samples: soil contamination drops with distance and with increasing depth from surface (Asubiojo et al., 1991; Bermudez et al., 2010). Soils monitored around a cement factory in Nigeria were enriched in Ca, S, Ni, Zn and Cu. The enrichment of S was supposed to originate from $CuSO_4$ component of cement rather than from fuel burning (Asubiojo et al., 1991). We found out a significant correlation between S and Cu in our lichens. Carreras and Pignata (2002) reported that S levels in transplanted lichens were not associated with emissions from a cement industry in Cordoba (Argentina). Also Branquinho and co-workers (2008) did not find relationships between S concentrations in lichens and potential sources of pollution in their study area.

Sulphur is an element typically associated with fossil fuels combustion and epiphytic lichens are extremely effective as biomonitors of S contamination, e.g. around geothermal sources (Loppi, 1996; Loppi et al., 1998). In the study area all sites were concerned by a high level of S in *X. parietina* (2,940–5,720 µg/g). Richardson (1981) reported background levels of S in lichens generally below 1 000 µg/g, with enhanced levels above this threshold. Nieboer et al. (1978) indicated values above 2,000 µg/g as enhanced. In Slovakia, Bačkor et al. (2003) measured S content in natural populations of lichens near a steel factory in the town of Košice by EDX microanalysis, reporting an average content of 3,900 µg/g S in the crustose species *Lecanora chlarotera*, and 1,400 µg/g S in the foliose species *Physcia tenella*. In moss samples from Slovakia, the content of S is generally within the range 700–3,400 µg/g, corresponding to an average deposition of ca. 500 $mg/m^2/y$ (Maňkovská and Oszlányi, 2009). As documented by instrumental monitoring, in Slovakia atmospheric $SO_2$ production decreased from 33,400 t/y in 1990 to 9,800 t/y in 2005, and a response of sensitive lichens to this improvement was evident (Guttová et al., 2011; Lackovičová et al., 2013). However, Maňkovská and Oszlányi (2010) suspect that the main source of atmospheric S deposited in moss samples is the use in heavy oil combustion and the long-range transboundary pollution from Austria and the Czech Republic.

Our data do not allow to infer whether the source of S is local or whether contamination originates from long range transport, since also additional measurements of S in a natural population of *X. parietina* from a remote site 35 km W of the study area were similar (5 700 ± 211 µg/g) to those found around the cement mill. However, in a parallel experiment, samples of the lichen *Evernia prunastri* taken from an unpolluted background area and exposed in the study sites progressively accumulated S, suggesting that this element may originate from ongoing processes (unpublished data).

Nevertheless, despite the high values of S in *X. parietina* samples, the low levels of other atmospheric pollutants typically associated with industrial processes (As, Cd, Cr, Hg, Pb) suggest a low contamination from combustion processes (Bargagli, 1998). Concerning Ni, the levels measured around the cement mill and the quarries (3.2–4.1 µg/g) indicate a moderate contamination (Bargagli and Nimis, 2002). Nickel is naturally present in fuel oils and coal (Adriano, 1986) and its concentration in lichens can be considered a good tracer of pollution from fossil fuels, power plants and metallurgical industries (Garty, 1993; Minganti et al., 2003). Cement mills are often equipped with a furnace for power generation by waste burning, therefore Hg can be considered an element of potential toxicological interest around this kind of source. Mercury can be released during the incineration of municipal solid waste and lichens are very efficient accumulators of Hg (Loppi et al., 2006; Tretiach et al., 2011). A study carried out near a cement mill in Slovenia showed a clear accumulation of this element in thalli of the lichen *Pseudevernia furfuracea* exposed in the surrounding environment (Ljubič Mlakar et al., 2011). In our study area, Hg contamination near the cement plant was not found in *X. parietina*. Similar indications have been reached in a parallel experiment with transplanted *E. prunastri* (unpublished data). The transplants of *E. prunastri* confirmed the results of native *X. parietina,* that the main source of contamination in the area is dust released during extraction, transportation and processing of raw materials during cement production.

Several studies deduced the occurrence of trapped particulates in lichen thalli from the similarity of Fe/Ti ratios in lichens and soil/rock material (Garty, 2001; Loppi et al., 1999). In our study, an average Fe/Ti ratio of 12.2±0.9 was found throughout the sampling sites. The small coefficient of variation within the whole area (7%) witnesses the common soil/rock origin of Fe, Ti and related elements (Al, Hg, Mn and V; Tab. 3), except for the closest urban area, where the low levels of such elements and the high Fe/Ti ratio (15.9) indicated a low rock/soil contribution to the elemental content of the lichens. However, a significant Ca load in native lichens showed that the closest urban area was concerned by dust depositions from the cement mill.

## 5. Conclusions

This study outlined the effects of dust contamination from a limestone quarry on the lichen diversity within a distance of 350 m from the source. Approaching a limestone quarry, the diffusion of basi-nitrophilous species, the decrease of acidophilous species and the asymmetrical distribution of the lichens on the tree boles, with a higher coverage of basiphilous species in the side facing the source were identified as the main signals of the effects induced by dust contamination. These responses, based on the functional traits of the lichen diversity, are helpful in monitoring studies around similar sources of pollution. In samples of *X. parietina* collected around the quarries and the cement mill, Ca, Ti, Fe, V, Al and Ni were significantly higher than in the surrounding environment. Accumulation of Ca was very useful to trace the area of high impact of the cement mill, which according to the model was within 1,700 m from the source. The low levels of As, Cd, Cr, Cu, Hg, Mn, Pb, Zn suggested a reduced contamination by airborne pollutants originating from combustion processes, except for S and Ni.

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Figure 1. Study area with formal localization of the sampling sites: 1) cement mill (48°27’23”N, 17°11’43”E); 2) limestone quarry (48°26’46”N, 17°12’41”E); 3) paleobasalt quarry (48°26’39”N, 17°13’51”E); 4) urban area (48°27’51”N, 17°09’58”E); 5) agricultural area (sampling points from 3 (48°28’09”N, 17°13’13”E) to 5 km (48°28’46”N, 17°15’04”E) from the cement mill); 6) agricultural area (48°30’12”N, 17°17’42”E; 10 km from the cement mill).

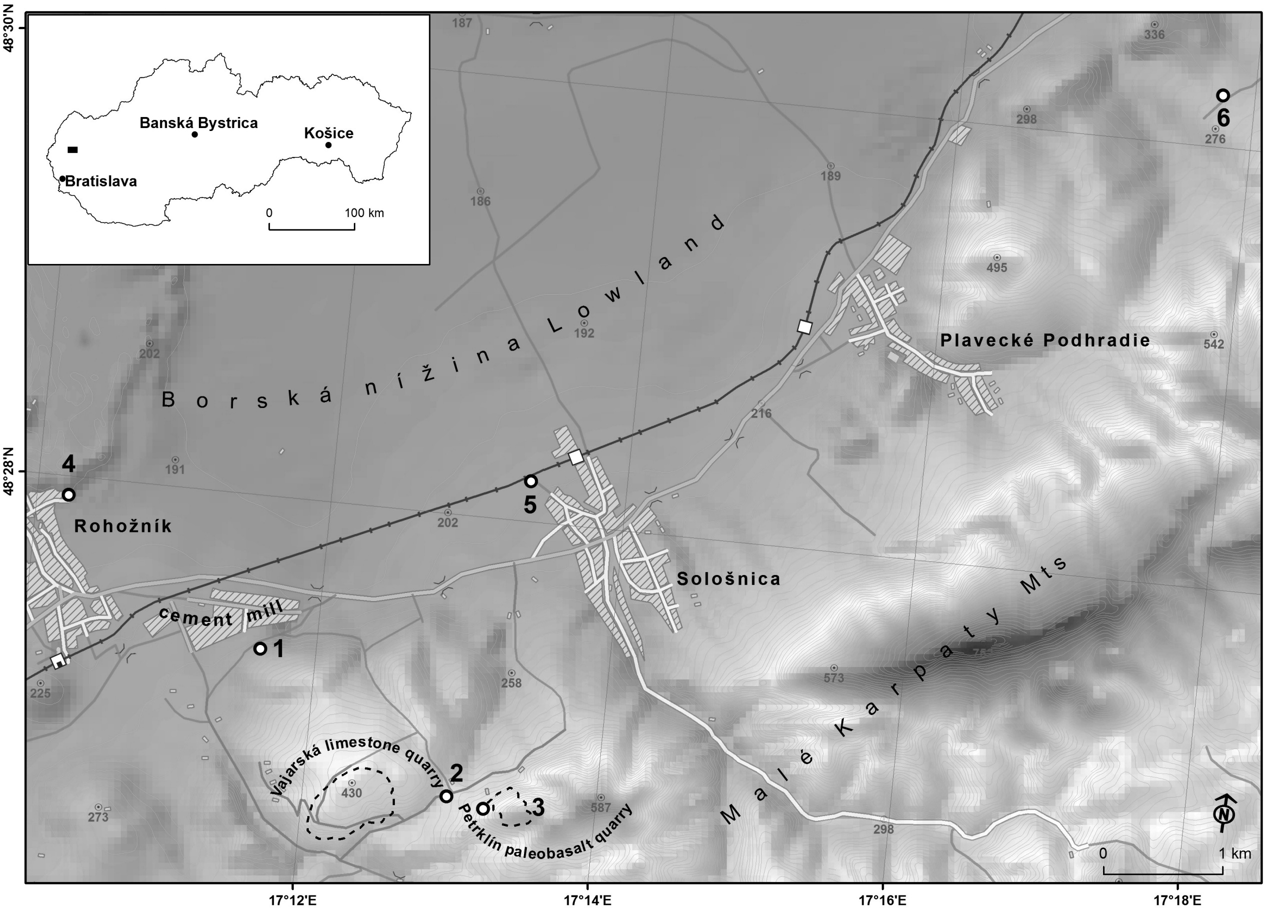
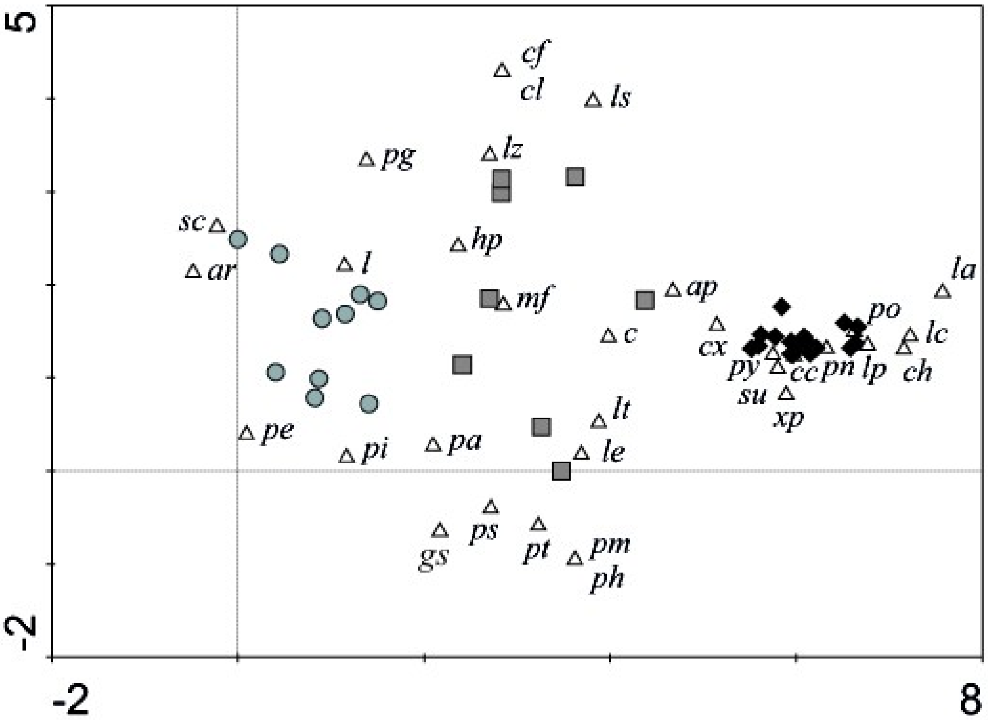


Table 1. Index of lichen diversity (ILD) combining vitality-abundance of the lichens on the border of the limestone quarry and at a distance of 350 m, on the exposed and sheltered side of the boles. Acidophilous ($^{a}$), basiphilous ($^{b}$) and nitrophilous ($^{n}$) species; percentage of relevés where the species was present over total relevés (P%). In brackets abbreviations used in detrended correspondence analysis. * Significant difference (Kolmogorov–Smirnov test, $p<0.05$).

| **Species** | **P%** | **ILD at the limestone quarry** | | **ILD at 350 m from the quarry** | |
|---|---|---|---|---|---|
| | | **Exposed side** | **Sheltered side** | **Exposed side** | **Sheltered side** |
| *Phaeophyscia orbicularis* (Neck.) Moberg (po) $^{b, n}$ | 45 | 5 | 3 | | |
| *Xanthoria parietina* (L.) Th.Fr. (xp) $^{b, n}$ | 48 | 3 | 3 | | |
| *Phaeophyscia nigricans* (Flörke) Moberg (pn) $^{b, n}$ | 42 | 3 | 1 | | |
| *Caloplaca pyracea* (Ach.) Th.Fr. (ch) $^{b, n}$ | 29 | 3 | 1 | | |
| *Physcia adscendens* (Fr.) H.Olivier (py) $^{b}$ | 52 | 3 | 5 | 1 | |
| *Lecanora chlarotera* Nyl. (lt) $^{a, n}$ | 26 | 3 | 3 | | |
| *Amandinea punctata* (Hoffm.) Coppins & Scheid. (ap) $^{a, n}$ | 26 | 3 | | | |
| *Lecania cyrtella* (Ach.) Th.Fr. (lc) $^{a}$ | 29 | 3 | 1 | 1 | |
| *Caloplaca cerinelloides* (Erichsen) Poelt (cc) $^{b, n}$ | 19 | 1 | 1 | | |
| *Scoliciosporum umbrinum* (Ach.) Arnold (su) $^{a}$ | 10 | 1 | 1 | 1 | |
| *Candelariella xanthostigma* (Ach.) Lettau (cx) $^{a}$ | 52 | 3 | 1 | 1 | 1 |
| *Phlyctis argena* (Spreng.) Flot. (pg) $^{a}$ | 10 | 3 | 1 | 1 | 1 |
| *Lecidella elaeochroma* (Ach.) M.Choisy (le) $^{a, b, n}$ | 16 | 1 | | 1 | 1 |
| *Lepraria* sp. (ls) $^{a}$ | 10 | | 1 | | 1 |
| *Scoliciosporum chlorococcum* (Stenh.) Vězda (sc) $^{a}$ | 6 | | | 3 | 1 |
| *Graphis scripta* (L.) Ach. (gs) $^{a}$ | 3 | | | | 1 |
| *Physcia* sp. juv. | 3 | | | | 1 |
| *Lecanora carpinea* (L.) Vain. (lp) $^{a, b}$ | 19 | 3 | 1 | 1 | 3 |
| *Porina aenea* (Wallr.) Zahlbr. (pe) $^{a}$ | 39 | 1 | 3 | 3 | 3 |
| *Lecanora subcarpinea* Szatala (la) $^{a}$ | 32 | 1 | 3 | 3 | 3 |
| *Pyrenula nitida* (Weigel) Ach. (pi) $^{a}$ | 26 | | | 1 | 3 |
| *Arthonia radiata* (Pers.) Ach. (ar) $^{a}$ | 23 | | | 1 | 3 |
| *Lecanora* sp. (l) | 16 | 1 | 1 | 1 | 5 |
| **ILD per side of the bole** | | 20 ± 6 * | 10 ± 6 * | 7 ± 3 | 10 ± 4 |
| **pH of the bark per side of the bole** | | 6.1 ± 0.2 * | 5.7 ± 0.1 * | 5.3 ± 0.3 | 5.3 ± 0.3 |
| **Total ILD per site** | | 30 ± 10 * | | 17 ± 5 * | |
| **pH of the bark per site** | | 5.9 ± 0.3 * | | 5.3 ± 0.3 * | |

Figure 2. Detrended correspondence analysis (DCA): ordination diagram of the relevés. Black diamonds – relevés scored along the limestone quarry and grey circles – relevés at a distance of 350 m (present study); grey squares – relevés in natural *Fagus sylvatica* stands in 1970s. White triangles – lichen species.



For abbreviations of species scored in this study and in 1970s see Tab. 1; species recorded only in 1970s: *Cladonia coniocraea* (cl), *C. fimbriata* (cf), *Cladonia* sp. (c), *Hypogymnia physodes* (hp), *Lecanora conizaeoides* (lz), *Melanelixia fuliginosa* (mf), *Parmelia sulcata* (ps), *Parmelina tiliacea* (pt), *Pertusaria amara* (pm), *Physconia grisea* (ph). Cumulative percentage variance of species data on first two axes 23.2%; eigenvalues for first two axes 0.900 and 0.335 respectively; lengths of gradients for first two axes 6.663 and 3.160 respectively.

Figure 3. Functional traits of lichen diversity expressed as Index of Lichen Diversity (ILD, acidophilous *vs* basiphilous species) on the boles of *Fagus sylvatica* at the limestone quarry and 350 m from the border of the quarry.

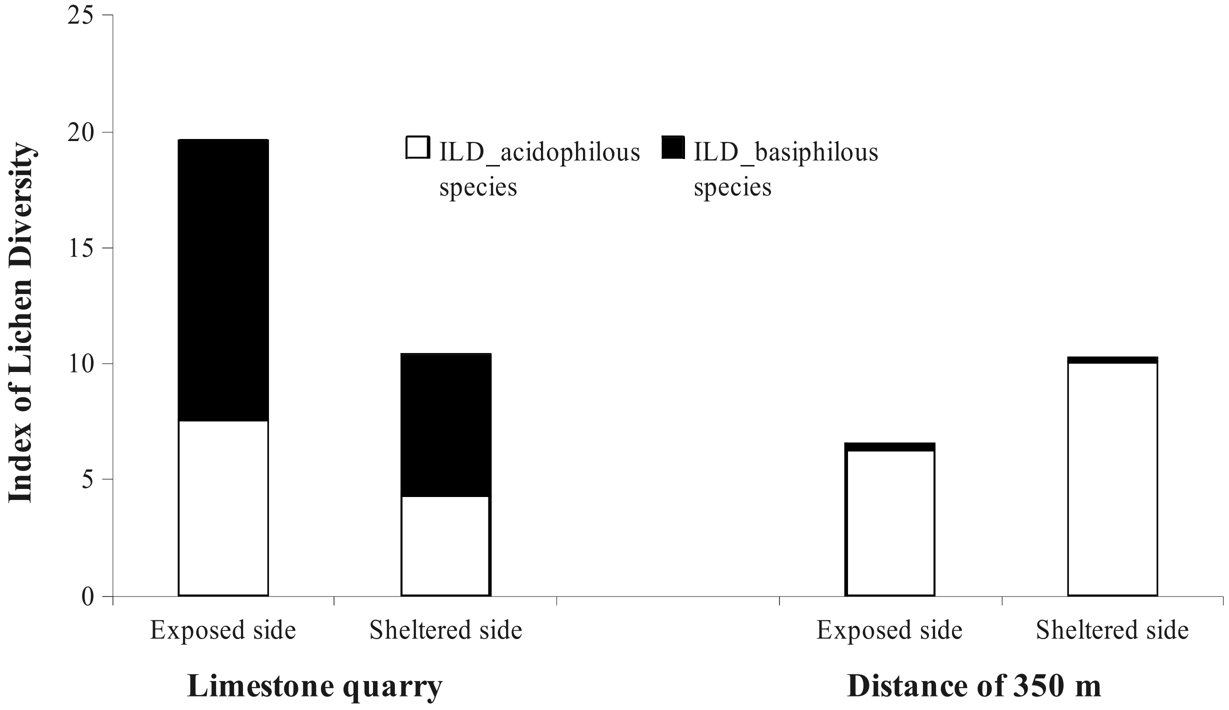


Table 2. Average of element concentrations ± SD (μg/g) measured in native *Xanthoria parietina*. Distances refer to the cement mill. Values in bold are significantly higher respect to the agricultural sites (3 – 10 km of distance) (Kolmogorov–Smirnov test, $p<0.05$).

| **Sampling sites** | **Element concentrations** | | | | |
|---|---|---|---|---|---|
| | **Ca** | **Ti** | **Fe** | **V** | **Al** |
| Cement mill | **2,460 ± 123** | **48 ± 5** | **604 ± 109** | **1.9 ± 0.1** | **295 ± 53** |
| Limestone quarry | **1,630 ± 82** | **48 ± 5** | **555 ± 100** | **1.5 ± 0.1** | **300 ± 54** |
| Paleobasalt quarry | **2,020 ± 101** | **296 ± 30** | **3,460 ± 623** | **6.4 ± 0.4** | **829 ± 149** |
| Urban (1.5 km) | **1,450 ± 73** | 18 ± 2 | 287 ± 52 | 0.7 ± 0.1 | 131 ± 24 |
| Agricultural (3 km) | 1,097 ± 25 | 29 ± 13 | 349 ± 145 | 1 ± 0.4 | 182 ± 75 |
| Agricultural (10 km) | 1,110 ± 56 | 24 ± 3 | 329 ± 59 | 1 ± 0.1 | 202 ± 36 |

| | **Ni** | **Mn** | **Hg** | **S** | **Cu** |
|---|---|---|---|---|---|
| Cement mill | **4.1 ± 0.4** | **27 ± 1** | 0.02 ± 0.01 | 5,110 ± 256 | 4.6 ± 0.9 |
| Limestone quarry | **3.2 ± 0.3** | 23 ± 1 | 0.02 ± 0.01 | 2,940 ± 147 | 3.0 ± 0.6 |
| Paleobasalt quarry | **3.3 ± 0.3** | **89 ± 4** | **0.07 ± 0.01** | 4,220 ± 211 | 4.0 ± 0.8 |
| Urban (1.5 km) | 1.9 ± 0.2 | 17 ± 1 | **0.05 ± 0.01** | 4,310 ± 216 | 3.3 ± 0.7 |
| Agricultural (3 km) | 2.1 ± 0.7 | 20 ± 2 | 0.02 ± 0.01 | 5,207 ± 878 | 4.5 ± 1.1 |
| Agricultural (10 km) | 2.1 ± 0.4 | 23 ± 1 | 0.02 ± 0.01 | 5,720 ± 286 | 4.6 ± 0.9 |

| | **As** | **Cd** | **Pb** | **Cr** | **Zn** |
|---|---|---|---|---|---|
| Cement mill | **0.83 ± 0.04** | **0.28 ± 0.03** | **3.2 ± 0.1** | **2.8 ± 0.1** | 46 ± 3 |
| Limestone quarry | 0.50 ± 0.03 | **0.28 ± 0.03** | **3.4 ± 0.1** | 2.0 ± 0.1 | 34 ± 2 |
| Paleobasalt quarry | **0.80 ± 0.04** | **0.30 ± 0.03** | **2.4 ± 0.1** | 1.6 ± 0.1 | 43 ± 3 |
| Urban (1.5 km) | 0.37 ± 0.02 | 0.24 ± 0.02 | 2.0 ± 0.1 | 2.1 ± 0.1 | 30 ± 2 |
| Agricultural (3 km) | 0.56 ± 0.19 | 0.21 ± 0.04 | 1.8 ± 0.3 | 1.7 ± 0.4 | 33 ± 8 |
| Agricultural (10 km) | 0.47 ± 0.02 | 0.20 ± 0.02 | 1.6 ± 0.1 | 1.6 ± 0.1 | 39 ± 3 |

Table 3. Pearson correlation coefficients between pairs of elements in native *Xanthoria parietina.* Only significant values are given (*$p$<0.05; **$p$<0.01; ***$p$<0.001).

| | Al | S | Ca | Ti | V | Cr | Mn | Fe | Ni | Cu | Zn | As | Cd | Hg | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | - | | | | | | | | | | | | | | |
| S | - | - | | | | | | | | | | | | | |
| Ca | - | - | - | | | | | | | | | | | | |
| Ti | 0.98*** | - | - | - | | | | | | | | | | | |
| V | 0.99*** | - | - | 0.99*** | - | | | | | | | | | | |
| Cr | - | - | - | - | - | - | | | | | | | | | |
| Mn | 0.98*** | - | - | 1.00*** | 0.99*** | - | - | | | | | | | | |
| Fe | 0.98*** | - | - | 1.00*** | 0.99*** | - | 1.00*** | - | | | | | | | |
| Ni | - | - | - | - | - | - | - | - | - | | | | | | |
| Cu | - | 0.91** | - | - | - | - | - | - | - | - | | | | | |
| Zn | - | - | - | - | - | - | - | - | - | - | - | | | | |
| As | - | - | - | - | - | - | - | - | - | - | - | - | | | |
| Cd | 0.72* | - | - | - | - | - | - | - | - | - | - | - | - | | |
| Hg | - | - | - | 0.76* | 0.71* | - | 0.76* | 0.76* | - | - | - | - | - | - | |
| Pb | - | - | 0.73* | - | - | - | - | - | - | - | - | - | - | - | - |

Figure 4. GIS model of Ca depositions in native thalli of the lichen *Xanthoria parietina*.