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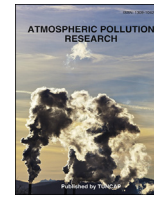

Effect of the interaction between transplants of the epiphytic lichen *Pseudevernia furfuracea* L. (Zopf) and rainfall on the variation of element concentrations associated with the water-soluble part of atmospheric depositions

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Water Soluble Bulk Deposition (WSBD) and Water Soluble Leaching (WSL) from *Pseudevernia furfuracea* thalli transplanted in a anthropized zone were separately collected in four locations where weather stations were set up for monitoring rainfalls rate and daily temperature.

The thalli were exposed for three months during which 13 major rainfalls took place. The concentrations of 15 elements (Al, V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Pb, As, Cd, Ti, Sn, Sb) were measured as well in WSBD and WSL as in the lichen thalli at the end of the exposure period. The total bioaccumulation of each element was significantly correlated with its % representation in both the lichen input (WSBD) and output (WSL). Elements with a small water-soluble input-pool were mostly taken up by the thalli (output/input < 1). Among the elements with a high input-pool, Zn was nearly systematically taken up while Al and Mn were lost (output/input > 1). Al showed a significant direct correlation with the increase in mm and hours of rainfall (i.e. transition from net loss to net uptake) while Mn showed an inverse correlation (transition from net uptake to net loss), which may be due to element competition modulated by water-stimulated lichen physiology. Al was strongly bioaccumulated while Mn showed a slight increase in exposed thalli. This suggests that rainfall-induced loss can result in an underestimation by lichen biomonitoring of element concentrations in atmospheric deposition and an increase in the bioavailability of potential toxic elements for other environmental compartments.

1. Introduction

Due to their lack of roots and rhizomes, epiphytic lichens must take up most of their micro- and macro-nutrients from the atmospheric pool (Bargagli and Mikhailova, 2002) following both wet depositions, like fog, dew (Nash III, 2008) and rainfall, and dry depositions (Garty and Garty-Spitz, 2015) which are effectively captured by foliose and fruticose lichens by means of their high surface/biomass ratio (Tretiach et al., 2007). Depending on their association with the solid phase (particulate) or liquid phase (water), elements can contribute to the formation of four different lichen pools: particulate-associated elements adsorbed on the thallus surface, particulate-associated elements entrapped within the intercellular spaces, water-soluble elements linked to exchange sites of the fungal cell wall and intracellular pool elements. The turnover of the first and last pool are respectively very short and long, while that of the other two will depend on their water solubility, the amount in atmospheric depositions and the affinity for exchange sites (Nieboer and Richardson, 1980). Due to their capacity for very high extracellular element accumulation, lichens have been successfully used in biomonitoring to evaluate anthropogenic atmospheric contamination (Tommasini et al., 1976; Sloof and Wolterbeek, 1991). When environmental conditions impede long-term lichen colonization, a transplantation technique can be performed by transferring epiphytic lichens from a pristine area

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where they show plentiful growth to an area to be monitored (Kauppi, 1976; Bajpai et al., 2004). However many factors can affect the detection of atmospheric element enrichment by transplants: the lichen species, intensity of emission sources, remembrance time (Reis et al., 1999), and climatic parameters of the exposure area such as wind velocity and frequency, temperature, humidity and rainfall (Nimis et al., 1989; Bačkor and Loppi, 2009). The role of rainfall seems quite controversial; although an increase of thalli hydration can promote metabolic activities and result in tissue uptake of captured elements (Kershaw, 1972), intense rainfalls can displace and leach externally accumulated elements (Deruelle, 1992; Lawrey and Hale, 1981). When this occurs repeatedly and shortly before transplant removal from the exposure area, the extracellular pool can be seriously underestimated (Corapi et al., 2014).

Most experimental approaches aimed at evaluating the effect of the lichen-rainfall interaction on variation of the water-soluble part of elements in bulk deposition have been carried out in controlled (lab) conditions, while there have been very few field studies and most of them involved native populations (Pike, 1978; Blett and Geiser, 2003). The present study, with a complete field-based approach, had two goals:

a) to evaluate the number and type of elements respectively taken up or lost from the lichen water-soluble pool following rainfall events during the three-month exposure period,
b) to search for correlations between mm and hours of rainfall and the element input (WSBD)/element output (WSL) ratio during the three months of exposure.

The results could be useful for a better understanding of the effect of rainfall on the outcomes of lichen biomonitoring, i.e. the extent to which the extracellular pool of elements (with different degrees of water solubility) of transplanted thalli can be affected by the duration and amount of rainfall.

2. Materials and methods

Because of the lack of lichen colonization in the study area, thalli of the epiphytic lichen *Pseudevernia furfuracea* were transplanted to four monitoring sites from a nearly pristine area in the Sila National Park whose mean annual climatic parameters are: temperature = 10.1 °C, relative humidity = 76.8%, rainfall = 1 644 mm (ARPACAL, 2016).

Within the study area (27 km^2, Fig. 1), anthropization consists of a dense road network (including the A3 motorway), the urban areas of Rende and Settimo di Montalto and a biomass power plant with an output of 13.3 MWh/h. Mean annual temperature, relative humidity and rainfall are respectively: 16.4 °C, 65.1% and 1 247 mm (ARPACAL, 2016).

Four multi-collector systems (MCS) with meteorological stations were set up in locations all around the biomass power plant, one per geographical side and, above all, safe from vandalism. Each MCS consisted of a metal rod, inserted into a concrete base, holding three wooden shelves at a height of two metres above ground. Each shelf supported a HPDE (high-density polyethylene) bucket. A metal ring tightly enveloped with an HPDE film protruded from the metal rod 1 cm above the bucket opening. An HPDE double net (with a 0.5 cm mesh) was stretched over two of the three rings. One of these double nets was completely filled with a monolayer of thalli of the epiphytic lichen *P. furfuracea* for a total amount of 11 g d.w. Based on the relationship between dry weight and surface area in *P. furfuracea* (personal communication: Prof. Stefano Loppi, University of Siena), the biomass corresponded to a lichen surface of 0.0957 m^2. In this way, wet and dry depositions were effectively intercepted (maximization of lichen contact surface with the atmosphere) and the exposure modality was standardized through the four monitoring sites (Canha et al., 2013). The second double net (without lichen thalli) was used as a “blank” for interception of atmospheric depositions. A Davis Vantage Vue meteorological station, equipped with a Weather Link data logger (recording time once every 15 min) to monitor the mm and hours of rainfall and the temperature, was placed near each MCS. All were located far enough from any building or reliefs to avoid their effect on the flux and composition of atmospheric depositions (AASC, 1985; EPA, 1987). Thalli were exposed from February 20 to May 20, 2013.

Collection of the three different water-soluble parts (treatment a) Only Bucket (OB), treatment b) Bucket + Double Net (BDN), treatment c) Bucket + Double Net + Lichen (BDNL) was carried out after the end of each of the 13 major rainfalls (episodes with a different and discontinuous duration) that took place during the three-month exposure period. Water pH was measured before the sample collection. The water sample amounted to a volume of 25 mL that was filtered (IC-Millex Millipore 0.45 μm).

The concentrations of Al, V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Pb, As, Cd, Ti, Sn and Sb were measured in the lichen thalli (expressed as μg/g d.w.) and in the water sample (expressed as mg/L). These elements were selected based on literature data on biomass power plant and traffic atmospheric emissions. Three lichen subsamples were selected for each monitoring site, immersed in liquid nitrogen until brittle and pulverized in a ceramic pestle. An aliquot of 100 mg was added to 12 mL of ultrapure nitric acid and mineralized in a microwave oven (Milestone Ethos 900) for 30 min. In total, 138 water samples were collected and 100 μl of ultrapure nitric acid were added to 10 mL of each of them before mineralization. Accuracy and precision were evaluated by means of the reference material BCR 482 (*Pseudevernia furfuracea* lichen) for the thalli analyses and the NIST 1 643 standard for the water sample analyses. Element concentrations were measured by ICP-MS (PerkinElmer SCIEX Elan DRC) at the Mass Spectroscopy Laboratory of the Department of Biology, Ecology and Earth Sciences (University of Calabria). The water concentrations of elements relative to treatment OB were considered as water-soluble bulk deposition (WSBD), i.e. the water-soluble element input to lichen biomass (11 g d.w.), while the water concentrations of elements relative to treatment BDNL were considered as water-soluble leaching (WSL), i.e. the water-soluble element output from lichen biomass (11 g d.w.). Due to the different interception surfaces between treatments OB and BDNL, their element water concentrations were corrected by their relative surface and expressed as mg/L/m^2. Moreover, to avoid bias in temporal trends of element concentrations in water samples due to a dilution effect caused by rainfalls of different intensity and duration, the results were expressed as the ratio WSL/WSBD, i.e. the output per input unit. Thalli bioaccumulation was calculated as the difference between the concentration of each element before exposure and the concentration at the end of the three-month exposure period. Regression analyses were performed using the statistical software MINITAB 16.0 release.

3. Results

Table 1 shows the mm and hours of rainfall for each station at the end of each of the major rainfalls during the thalli exposure period, their sum per station and the general mean, the pH of the corresponding WSBD and WSL (with median and inter-quartiles) and the parameters ΔT/mm of rainfall and ΔT/hours of rainfall, i.e. the sum of each daily Tmax - Tmin relative to the time between a pair of water collections (including the duration of the second rainfall) divided by the amount of rain of the second rainfall