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Lichens As Indicators of Pollution

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ABSTRACT: Lichens are sensitive to atmospheric pollution such as nitrogen (N) because they receive all their nutrients and water from wet and dry atmospheric deposition (fall out). Nitrogen deposition can increase the load of nutrients.

KEYWORDS-lichens, indicators, pollution, atmosphere, nitrogen

I.INTRODUCTION

An indicator species is any biological species that defines a trait or characteristic of the environment.

A conservation practitioner can use an indicator species as a surrogate for overall biodiversity, monitoring the outcomes of management practices by measuring the rise or fall of the population of the indicator species.[1,2,3]

What are Lichens? They are a symbiotic relationship between algae and fungi. The fungus provides shelter for the algae and the algae provides food for the fungi. Lichens do not have roots; instead they receive all their nutrients from the atmosphere.

Lichens as Bio-Indicators Lichens are sensitive to atmospheric pollution such as nitrogen (N) because they receive all their nutrients and water from wet and dry atmospheric deposition (fall out). Nitrogen deposition can increase the load of nutrients. Too much N can harm and kill the algae's chlorophyll which is used to produce sugars feeding it and the fungi.

Certain species of lichen are more tolerant of N than others. Scientists monitor lichen communities. If an increase in N tolerant species in combination with a decrease in N sensitive species occurs this may indicate an increase in atmospheric N deposition.

Lichens are the "canaries in the coal mine" of N deposition. A shift in their species composition and/or their health exemplifies the potential beginning of ecosystem decline due to N deposition.

Total inorganic (reactive) wet nitrogen deposition across the United States in 2012. Data collected by the National and Atmospheric Deposition Program (NADP).

nadp.isws.illinois.edu/nadp/

Scientists who monitor the health of the lichens and pair this bio-monitoring data with atmospheric deposition data from the National Atmospheric Deposition Association (NADP) (http://nadp.sws.uiuc.edu/) can determine the sources and levels of pollution causing detrimental effects.

Since nitrogen deposition occurs as both wet and dry measurements two collecting systems are used. The NADP National Trends Network (NTN) (http://nadp.sws.uiuc.edu/ntn/) measure nitrate (NO_3^-) and ammonium (NH_4^+) weekly in rain and snow samples over 250 U.S. sites.

The US Environmental Protection Agency Clean Air Status and Trends Network (CASTNET) (https://www.epa.gov/castnet) measures gaseous HNO₃ and dry deposition particulate NH_4^+ and NO_3^- across 94 U.S. sites.

The	critical	loads	of	atmospheric	deposition	science	committee
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(CLAD) http://nadp.sws.uiuc.edu/committees/clad/ works across science, management, and government. It meets twice yearly at the spring and fall NADP meetings with goals to:

- Facilitate technical information sharing on critical loads topics within a broad multi-agency/entity audience;
- Fill gaps in critical loads development in the US;[4,5,6]
- Provide consistency in development and use of critical loads in the US;
- Promote understanding of critical loads approaches through development of outreach and communications materials.

The NPS acts as an ideal entity to monitor the effects of anthropogenic pollution on natural systems. In collaboration with NADP and EPA critical loads are being identified. Total annual N deposition has decreased from 2002 to 2015 thanks to policies put in place based on the collected data. Continued monitoring will help to access nitrogen deposition effects and protect sensitive ecosystems and ecosystem services.

II.DISCUSSION

The fungal part is called a mycobiont and the non-fungal part is called a photobiont which contains chlorophyll.

Many lichen partners also include one photobiont & one mycobiont that is not universal & there are lichens with more than one photobiont partner.

Lichens also produce pigments and other secondary compounds which can be used as dyes.

In some parts, they are also used as delicacies & also in traditional medicine. Some of the lichens can also degrade polyester resins and pollutants like lead and copper.

Lichens usually grow in a wide range of environmental conditions. But they are quite sensitive to atmospheric pollutants like sulfur and nitrogen.

Air pollution also leads to a decline in the lichen population and thus, they can be used as indicator organisms.

Lichens are organisms consisting of a symbiotic relationship between a fungus and a chlorophyll-containing partner, either algae or cyanobacteria. Fungi are incapable of photosynthesis as they do not possess chlorophyll, but algae and cyanobacteria do. By forming a symbiotic relationship, the fungus gains constant access to nourishment, and can thus thrive. Lichens are found in both nature and in human-made environments, including rocks, trees, barren earth, metal and concrete. They are sensitive to air pollution because they receive all nutrients from the atmosphere, which makes them valuable as indicator species. In particular, the two pollutants that mostly affect lichens are nitrogen (N) and sulfur dioxide (SO_2).

How does nitrogen affect lichens?

Lichens need nitrogen to survive as it supports them to produce necessary proteins and organic acids. Additionally, cyanobacteria engage in what is called nitrogen fixation, where the element is converted to ammonia, a more stable and easier-to-use form. The nitrogen used by lichens can be gaseous (N_2) , or come in the form of nitric oxide (NO) or nitrogen dioxide (NO_2) . Certain lichen species are sensitive to ammonia, while others are not. Too much nitrogen can in fact over-fertilize certain lichen species and cause them to die. Excess nitrogen can also kill the chlorophyll of the alga, which deprives the fungi of the necessary sugars for survival.

How does sulfur dioxide affect lichens?

Lichens are sensitive to sulfur dioxide. The compound easily dissolves in water, which the organism can then absorb, and is prevalent in the air in its gaseous state as well. Sulfur dioxide interferes with the cyanobacteria's ability to fix nitrogen, and destroys the chlorophyll of the alga, thus inhibiting photosynthesis. The compound also impedes lichen reproduction and spore germination across certain species.

How are lichens used to indicate air quality?

In the United States, the health of various lichen species are monitored and paired with atmospheric deposition data to identify critical sources and overall levels of air pollution. Atmospheric deposition is the process of gases and particles

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from the atmosphere being transferred to earth.[7,8,9] In this case, scientists are looking at nitrogen deposition levels to protect sensitive ecological systems.

Lichens have also been used in Germany as a bioindicator for air pollution, as they are sensitive to a number of air pollutants. Specifically, lichens are the most sensitive to sulfur dioxide, but other acidic pollutant gases as well as heavy metals and photo oxidants. In Germany, two methods existed that used lichens as indicators: exposure of lichens and recording of lichen growth on trees under natural conditions. The recording of the trees follows a certain standard:

- Must have a minimum circumference of 60 cm
- Must be self-supporting
- Must not be shaded or only slightly shaded

It is also important to note that different lichen species have different sensitivities to air pollutants. Thus the variety in lichen species are taken into account when calculated and represented to the air quality index. This is done by determining the degree of cover and vitality.

The Dutch developed a method of classifying lichens: "nitrophyte" lichen species thrive in high-nitrogen environments and on tree bark with high pH, while "acidophyte" lichen species prefer the opposite. Bark pH has been found to be affected by sulfur dioxide concentrations. This method has been used to map and monitor nitrogen and ammonia pollution patterns across countries in Europe, and has also helped discover that lichens respond to global warming. The Dutch method should not be mixed up with the Ellenberg method, which uses "Ellenberg N Values" that estimate the position along a productivity/macro-nutrient availability gradient at which a species reaches peak abundance. The method consists of an "Ellenberg N Index" determined by allocating an N score to each plant species, so that the overall mean score for the community is on a scale of nutrient poor to nutrient rich, rated 1 to 10 respectively. This method is also suitable to indicate environmental impacts, as it has been used to indicate species change and colonization across time.

Lichens are also being used to monitor nitrogen levels at tea farms in Sri Lanka and the Himalayan forests. The growers use fertilizer that contains nitrogen in the form of ammonia, and as such are conducting research to see how the element would affect the ecology of the area.

What's the best way to measure air quality?

While there is no doubt that lichens are certainly a useful indicator species, the information they provide is limited — they can only be used to monitor nitrogen and sulfur dioxide levels when in fact there are many more pollutants that serve as ecological and health threats. Moreover, indicator species are unable to give you immediate feedback of exact pollution levels, only averages over a longer period of time – similar to data you would be getting from a long-term passive collector. This makes sourcing, control, management, and improvement of air quality difficult. It is far more useful to have real-time data available in order to monitor the direct impact of changing pollution sources, such as traffic throughout a day. Doing so also helps track the effectiveness and success of implemented clean air actions.

Today's technology has allowed for the creation and production of lower-cost IoT air quality sensors. Breeze Technologies is a leading provider of these sensors, alongside cutting-edge data and analytics.

III.RESULTS

Lichens are considered the result of a symbiotic association of a fungus and an alga. More precisely the term "alga" indicates either a Cyanobacteriae or a Chlorophyceae; the fungus is usually an Ascomycetes, although on rare occasions it may be either a Basidiomycetes or a Phycomycetes.

In this association, the alga is the part that is occupied with the formation of nutrients, since it contains chlorophyll, while the fungus supplies the alga with water and minerals.

The compositional changes in lichen communities are correlated with changes in levels of atmospheric pollution. The application of method A allows the elaboration of an IAP. This method (LeBlanc and De Sloover, 1970) makes it possible to map out the quality of the air in a determined area. The IAP gives an evaluation of the level of atmospheric pollution,[10,11,12] which is based on the number (n), frequency (F) and tolerance of the lichens present in the area under study.

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In areas where lichens are not killed by contaminants, it is possible to make biomonitoring studies through the direct analysis of contaminants in the thallus. Method B, which consists of transplanting lichen thalli, has the great advantage of being applicable even in "lichen desert" areas (in areas that are unsuited to lichen survival due to high pollution levels), or it can be used in areas where there are no suitable substrata [88, 89]. The lichen thalli used are taken from tree bark in areas of low pollution and then fixed to suitable surfaces (e.g. cork) and exposed in monitoring areas where samples are taken periodically in order to evaluate the health of the thalli and their degree of damage. Lichen damage is expressed as a percentage of necrotised lichen surface. The main problem with this method is that found in the difficulty in providing a valid interpretation of transplanted thalli damage percentages. There are also methods that allow identification of necrotic areas, defining them on photographs of lichen thalli. A certain error margin, due to the subjective interpretation of the images, has also been found for this procedure. Possible tendencies to over- or underestimate may be corrected through use of statistics tests (2, t student). The transplant method is also used in classical bioaccumulation studies that analyse contaminants in tissue. Numerous works regarding this method are concerned with trace elements and in particular, bioaccumulation, absorption, retention, localisation and release, tolerance and toxicity

The accumulation of metals in plants depends upon many factors, such as the availability of elements; the characteristics of the plants, such as species, age, state of health, type of reproduction, etc.; and other such parameters as temperature, available moisture, substratum characteristics, etc. [3, 119]. Contaminants deposit on lichens through normal and indirect (occult) precipitation. This latter includes mist, dew, dry sedimentation and gaseous absorption [120]. Indirect precipitation occurs in highly stable atmospheric conditions and contains higher nutriment and contaminant concentrations of different orders of size when compared to normal precipitation [121]. In general, three mechanisms have been put forward with regard to the absorption of metals in lichens [103]: 1. intracellular absorption through an exchange process; 2. intracellular accumulation; 3. entrapment of particles that contain metals. Many experts have attempted to increase knowledge of these bonding processes - that is, the interaction between lichen and metal - using various analytical techniques, such as nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR) and luminescence. It should, however, be noted that knowledge regarding the understanding of the entire process that is responsible for metal absorption and accumulation in lichens is still scarce. A new approach has been attempted [122], where metal-lichen interaction is studied by applying microcalorimetric techniques with the aim of obtaining enthalpic measurement data. To carry out these tests and to process the microcalorimetric data, the metallichen complex is considered as an overall co-ordinating agent, given that it is not possible at this time to know which particular molecule is responsible for co-ordination with the metal. [13,14,15]Considering the constant towards equilibrium and the enthalpy trend for Evernia prunastri, the following trend has been found: Pb Zn Cd Cu Cr; which indicates a good correlation between the metal bond and the enthalpy values in the absorption process (metal uptake). Lichens are also excellent bioaccumulators of elements and trace elements, since the concentrations found in their thalli can be directly correlated with those in the environment

Studies made of transplanted Evernia prunastri highlight the fact that the capacity for Pb accumulation expressed as the relationship between the concentration in the latest sample and the initial concentration value, is 10.2 in the Fontainbleau site (France), 3.7 for the Würzburg site (Germany) [101] and 4.4 for the city of Rome (Italy) [134]. Recently, Conti et al. [88] also employed Evernia prunastri for biomonitoring the atmospheric deposition of heavy metals at urban, rural and industrial sites in Central Italy. Lichen samples were collected in a control site 1500 m a. s. l. (Parco Nazionale d'Abruzzo, Central Italy) and subsequently transplanted at urban site (Cassino city centre), at rural location (7 km away from Cassino city) and at industrial location (Piedimonte S. Germano) surrounding an automobile factory. Lichen samples were transplanted at the four cardinal points of each site. Studies of bioaccumulation of Pb, Cd, Cr, Cu and Zn in lichen samples were performed five times at regular intervals between November 2000–December 2001. Results showed the good ability of Evernia prunastri to accumulate the heavy metals under study. As expected, the area chosen as control site showed significantly (Friedman test, cluster analysis) lower impact in comparison to the other sites and the rural site showed smaller impact than the urban and the industrial sites. More recently, a study dealing with nuclear microprobe analysis of an E. prunastri transplanted thallus in thin cross-sections [118], concluded that trace elements are mainly concentrated on the cortex of the thallus, with the exception of Zn, Ca and K. In Italy, different biomonitoring studies carried out using lichens have shown that Pb is still very widespread in spite of the introduction of lead-free petrol. This indicates that high levels of this metal are still released (and/or re-suspended) by vehicle traffic [16,17,18]. Vehicle traffic seems to be the main source of atmospheric Cr, Cu and Pb in the central Italian sites [71]. Climatic factors most probably play an important role in the bioaccumulation of heavy metals, even if this role is as yet unclear. The direction in which pollutants are transported by the wind is most surely fundamental in

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determining their main fallout points. Nimis et al. [6] correlates pollution from an industrial pole (northern Italy) with that at a distant agricultural centre, situated in the predominant wind direction. It is well known that heavy metal content in lichen thalli tends to alternate over time in phases of accumulation and subsequent release. The causes of these differences may lie in the incidence on this phenomenon of acid rain. Deruelle [101] indicates that the periodic releases of Pb that occur in lichens may depend upon lixiviation induced by acid precipitation. Indeed, laboratory experiments show that lixiviation does not occur at pH 7 [6]. Heavy metals do, in any case, influence water loss in lichen thalli, and the accumulative effect of Pb, Cu and Zn on water loss, after absorption of a mix of metals in solution, has been observed in the laboratory [137]. Moreover, laboratory studies showed that the number of mobile hydrogen ions bonded in lichens (Hypogymnia physodes) depends on the concentration of hydrogen ions in the precipitation with which the lichens are in contact

The number of hydrogen ions accumulated in lichens is proportional to the level of atmospheric precipitation acidification and the pH of precipitation should be determined by the assessment of mobile cations bonded in exposed or naturally grown lichens [138, 139]. Altitude seems to play an important role in Pb and Cd concentrations, as studied on Hypogymnia physodes [140]. In particular, Pb concentration increases in a linear fashion as altitude increases, while Cd increases in the same way up to altitudes of 900-1100 m. For higher altitudes, Cd concentrations follow a decreasing trend. What is more, H. physodes is one of the most suitable bioindicators in the study of the bioaccumulation of trace elements [141] in view of its high-tolerance capacities. In general, the higher accumulation of heavy metals in the thallus found after the summer period, may be due to the increased hydration that results from autumn rainfall [91]. In Mediterranean climates, the trace element content in lichens as they are (unwashed), is strongly influenced by soil dust contamination [142]. Loppi et al. [143] in spite of high correlation levels of Al, Fe and Ti in Parmelia sulcata does not find any linear correlation for these elements with their concentration levels in the soil. This would lead to the supposition that contamination through dust is highly variable and probably depends upon the local characteristics of the sites under study. Cd is considered to be particularly toxic for various lichen species [144, 145]. Concentration intervals of 1.26-5.05 and 1.56-6.40 µg g1 have been found for A. ciliaris and L. pulmonaria, respectively. These values (considering average values) are considered to be close to the appearance of toxicity symptoms. Furthermore, Cd has a high negative correlation with protein and reducing sugar content [19,20]. Lichens from the Usnea species have been used to evaluate heavy metal deposition patterns in the Antarctic [147]. The activities carried out in the different scientific stations could be potential sources of pollution and contribute to the circulation of trace metals in this site. The relationship between cationic concentrations in lichens, as shown for Cladonia portentosa, can be used as an index of acid precipitation. In particular, the K+/Mg2+ ratio and the (extracellular) Mg2+/(intracellular) Mg2+ in lichen apexes is strongly correlated to H+ concentrations in precipitation. High concentrations of H+ that are found in acid rain cause increases in extracellular Mg2+. In general, the variation in Mg2+ concentration in lichens can be considered to be a good indicator of acid rainfall [3, 148, 149]. Acid-moisture depositions containing heavy metals can significantly reduce lichen survival in affected geographical areas. In lichens (Bryoria fuscescens) exposed to simulated acid rainfall containing two levels of Cu2+ and Ni2+ only or combined with acid rain (H2SO4) at pH 3 for 2 months in addition to environmental rainfall, it was observed that the alga and fungus components respond in different ways to pH levels and that they have a specific interaction that is correlated to the toxicity of the metals. In particular, the alga component is the more sensitive to acid rain and to the mix of heavy metals

Critical concentrations of heavy metals in alga thalli were > 50 μ g g1 for Cu and > 7 μ g g1 for Ni in the presence of acidity and > 20 μ g g1 for Ni in absence of acidity [150, 151]. Another recently developed field of application for biomonitoring with lichens is that of indoor pollution and in particular, the analysis of air particulates. Rossbach et al. [152] found a high ratio between the concentrations of Cr, Zn and Fe in air particulate samples taken from the filters of air conditioning systems in different hotels in different cities and in Usnea spp. samples found in the conditioned environments.

IV.CONCLUSION

In general, lichen distribution in northern Italy seems mainly to be regulated by SO2 pollution [68, 69, 302]. As far as regards central Italy, a study of Parmelia caperata made by Ref. [21] found a strong correlation (r2 = 0.93; p < 0.05) between IAP values and the total heavy metal content (Cd, Cr, Cu, Hg, Ni, Pb, Zn). Techniques for drawing up air quality maps using lichens, or the use of the transplant method, allow us to obtain information about a vast area in a short amount of time and at contained costs. These methodological approaches, although they cannot be considered as replacements for standard atmospheric pollution monitoring carried out using control stations, are without a doubt valid environmental biomonitoring instruments in different cases: 1. as a preliminary evaluation, or rather as an estimate of

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the base impact in a set area, with the aim of preventing future human-derived impact; 2. to monitor an alreadycompromised environmental situation; 3. to control the quality of reclamation efforts already carried out. Application of the system approach to the solving of problems regarding atmospheric pollution is doubtless valid and fundamentally requires an evaluation of the progress made in the areas of study considered, the identification of pollution sources and the cause/effect correlation of the same [298]. Of course, from that mentioned in the above points 1, 2 and 3, it can be seen that for this reason, necessary interventions must have three main objectives: 1. environmental prevention: with the aim of intervening at the impact source and thus in advance of the pollutant event; 2. environmental protection: to eliminate the effects of pollutant actions or to tend to minimise these effects; 3. environmental restoration: with the aim of removing damages caused by previous actions. The necessity to increase our knowledge of bioindication studies using lichens remains a fundamental point in the development of research. It is possible to say that for a large majority of pollutants and their effects upon lichens, our knowledge is at an advanced stage in its development in terms of both the quantity and quality of information. Nonetheless, it is possible to point out that in a significant part of bioindication studies of lichens, there is a tendency to study the environmental effects of situations that have already been compromised. This signifies a scarce propensity to carry out studies that fundamentally have an eye to aspects of environmental prevention.[20]

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