

Lichens as effective bioindicators for monitoring environmental changes: A comprehensive review

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ABSTRACT

Lichens, due to their unique biology and sensitivity to contaminants, have emerged as valuable tools for bio-monitoring. Their ability to respond to climatic and air quality variations makes them reliable indicators of environmental shifts. This mini review critically evaluates lichen characteristics and their potential as predictive indicators of environmental changes when coupled with precise research methodologies. Our findings highlight lichens as organisms capable of responding to ecological toxins, thus functioning as bioindicators. Their gradual growth rate allows them to accumulate substances, surpassing even *Tracheophyta* in survival. Moreover, lichens exhibit exceptional nutrient cycling, contributing to ecosystems from a local to regional scale. Given the global significance of environmental alterations and contamination, lichens serve as natural indicators of heat and pollution effects, particularly in mountainous regions. We explore various approaches, including biological strategies, employed to assess atmospheric conditions and contamination susceptibility. Notably, lichens have been identified as significant contributors to particulate matter trapping, revealing a previously unexplored yet vital research avenue. In conclusion, this review underscores the pivotal role of lichens in morphological features and their capacity to capture particulate matter, shedding light on a promising area for further investigation.

1. Introduction

In recent years, the utilization of cosmopolitan organisms as indicators to assess atmospheric quality has seen a noteworthy upsurge (Abas and Awang, 2020). These organisms exhibit the capacity to respond, react, and adapt to shifts in ecological conditions, whether at an individual or community level. Notably, the activity and productivity of ants are heavily influenced by soil humidity (Šestinová et al., 2019), while the resilience of catfish in low-quality water makes them valuable for evaluating water quality (Standen et al., 2018). Employing biological markers for biomonitoring offers a distinct advantage as it signifies the vitality of life forms or processes, diverging from conventional analyses that merely reflect observable quality (Rodrigo-Comino and Cerdà, 2018; Abas et al., 2018). Furthermore, cosmopolitan organism indicators demonstrate an ability to detect a broad spectrum of pollutants, enhancing biomonitoring capabilities by facilitating assessments of prior exposures and identifying specific vulnerabilities. A pivotal

characteristic of an effective biological marker for biomonitoring is the dual capability of acting as both a sensitive responder and an accumulator (Abas and Awang, 2017).

Sensitive biomonitoring is characterized by spatial manifestations encompassing physiological and morphological variations, often serving as indicators of pollutant stress and detection systems (Abas and Awang, 2020). On the other hand, accumulative biomonitoring involves the storage of pollutant residues within their tissues, allowing for the quantification of environmental pollutants. Certain bioindicators exhibit dual characteristics, functioning as both sensitive and accumulative biomonitoring tools; a prime example is lichens (Nash, 2008; Abas et al., 2019).

Lichens, in particular, hold significant importance in environmental monitoring and assessment, especially in relation to industrial emissions (Shukla et al., 2012b). Comprising a fungal-algal/cyanobacterial symbiotic association, lichens are small perennial plants with the algae providing nutrients to the fungus in exchange for shelter within the

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thalli (Sujetovienė, 2017). Operating without defensive tissues, lichens have the capacity to absorb moisture, vital minerals, and gases from their surroundings (Nash, 2008). They exhibit sensitivity to a range of anthropogenic factors, with physiological variations linked to air quality, climate fluctuations, and forest preservation (Giordani, 2019). Lichens enable us to monitor the long-term accumulation of contaminants as pollutants accumulate within them. They are the most susceptible bioindicators of environmental contamination and are also utilized as markers of polluted air at the regional level. This employment aids in mapping the contribution of lichen species within a particular zone, facilitating the transplantation of healthy lichens, assessing thalli degradation, and evaluating the accumulation of pollutants within the lichen thallus (Sujetovienė, 2015).

Lichens have served as valuable biomonitoring tools for many years due to their direct absorption of components from the air and their resilience against them. The deposition of various contaminants significantly impacts lichen compositions, leading to alterations in their structure. In urban and industrial regions, susceptible species tend to disappear, while resilient species persist in less contaminated areas (Abas and Awang, 2020). Processes such as the inhibition of visible radiation, organic processes, pigment material, respiration, membrane damage, and the over-accumulation of free radicals have been consistently emphasized in individual-scale bioaccumulation studies to assess the physiological effects of contamination (Majumder et al., 2013). Lichens possess the remarkable ability to absorb compounds across their entire surface, often surpassing their metabolic requirements. The absorbed constituents remain retained for extended periods and can be utilized in bioaccumulation experiments to quantify the varying levels of accumulated components amid changing climatic conditions.

Primarily, lichens have been utilized as accumulation markers and sensitive indicators of ecological quality, attributed to their proficiency in accumulating and their resistance against various pollutants (Sujetovienė, 2015). Gupta et al. (2016) employed thirteen bioindicator communities of lichen to assess the environmental status of Badrinath, Uttarakhand. Their study revealed that sites with lower anthropogenic activities demonstrated lower pollution levels compared to sites with high anthropogenic activities, which exhibited elevated pollution levels.

Furthermore, Protano et al. (2017) assessed the bioindication and bioaccumulation potential of transplanted lichen *Pseudovernia* (*P. furfuracea*) in urban indoor environments. *P. furfuracea* was evaluated as a bioindicator for metals and polycyclic aromatic hydrocarbons (PAHs) in indoor settings, employing elements such as As, Cd, Cr, Cu, Hg, Ni, and Pb, alongside twelve selected PAHs. The successful application of *P. furfuracea* for indoor monitoring represents a significant finding that could serve as a pivotal tool for enhancing air quality monitoring programs within educational settings. This approach could also play a crucial role in focusing on health prevention interventions for youth, who constitute one of the most vulnerable populations.

Singh et al. (2018) conducted a study on the accumulation of six heavy metals, namely iron (Fe), chromium (Cr), copper (Cu), zinc (Zn), lead (Pb), and nickel (Ni), within epiphytic foliose lichen species (*Canoparmelia texana*, *Pyxine subcineria*, and *P. hispidula*) in a polluted area of Srinagar city and its surroundings in the Garhwal hills of the Western Himalaya. The results showed that *C. texana* exhibited lower accumulation of Fe, Zn, Cr, and Cu compared to *P. subcineria* and *P. hispidula*. The latter two species demonstrated significant increases in heavy metal accumulation due to pollutant exposure, with *P. subcineria* exhibiting the highest accumulation. The observed heavy metal concentrations in the studied lichen species followed this order: Fe > Zn > Cu > Cr > Pb > Ni. In a separate study by Singh et al. (2019), heavy metal deposition by the foliose lichen *P. coccinea* (Sw.) Nyl. was documented. As the distance from the paper mill decreased, concentrations of Fe, Cr, and Zn exhibited a significant increase, whereas Pb and Ni showed non-significant enhancements, except for Cu, which decreased. Notably, Fe displayed a strong positive relationship with Cr, Zn, and Ni, but a weak negative correlation with Cu. Pb and Ni exhibited a notable positive association

with Zn. Similarly, Cr displayed positive correlations with Zn, Pb, and Ni, but a strong negative correlation with Cu. Daimari et al. (2021) conducted an assessment of the influence of environmental factors on the anatomy, physiology, and deposition of contaminants on the lichen *Parmotrema tinctorum* (Nyl.) Hale. The study involved transplanting this lichen species into two cities in the Brahmaputra Valley: Tezpur (small) and Guwahati (large). The experiments unveiled significant anatomical damage, with a greater extent of harm observed in transplants from the larger city. The lichen transplants from high-traffic areas exhibited lower maximum chlorophyll content, while higher electrical conductivity was reported. Notably, all transplants indicated a substantial deposition of Cd. Both Cd, Pb, and Zn were found to be abundant in lichen samples collected from both Guwahati and Tezpur. Additionally, slight elevations were observed for Cr, Cu, K, and Ni. The correlations among pairs of indicator metal species clearly demonstrated the anthropogenic impact. This study sheds light on the intricate relationship between environmental factors, contaminants, and lichen health, highlighting the need for continued monitoring and mitigation strategies in urban environments.

2. Lichens as bioindicators and techniques to assess them

Lichens demonstrate mutualistic relationships between phycobionts and mycobionts. The term 'phycobiont' encompasses blue-green algae or chlorophyceae, while 'mycobiont' includes ascomycetes, and rarely basidiomycetes (Conti and Cecchetti, 2001). These perennial species share morphological similarities and are highly reliant on mineral nutrients present on the thalli's surface, influenced by both wet and arid deposition. In addition to their surface characteristics, the roughness and structure of lichens contribute to particle interception and prevention (Szczepaniak and Biziuk, 2003). Lichens exhibit various growth forms, including fruticose, foliose, and crustose types. Fruticose lichens are particularly susceptible to contamination, followed by foliose or crustose types. Notably, within this evaluation, foliose lichens emerge as superior absorbers compared to fruticose lichens (Clair et al., 2002a, b) (see Fig. 1).

The evaluation of lichen species prominently considers susceptibility to sulfur dioxide, forming a significant aspect of primary classification. An alternative classification approach emphasizes semi-quantitative characteristics or aligns with sulfur dioxide vulnerability, which varies across acid and eutrophic bark conditions (Conti and Cecchetti, 2001). Three techniques relevant to the accumulation of metals in lichens are commonly recommended: accumulation through cell membrane redemption, intercellular amassing, and defense of particles with metal endurance. As metals accumulate and are subsequently released over time, the concentration of heavy metals within the lichen thallus tends to change. Geological changes (altitude), temporal variations (periodic changes), soil particles, local emission sources, long-range transport, and acid precipitation influence metal absorption in lichens (Szczepaniak and Biziuk, 2003). These methods can present certain challenges in environmental quality investigations: spatial variations may lead to sampling errors; minimal amounts of several micropollutants (which can cumulatively change over time) could introduce methodological discrepancies; the distinction is determined by alternating or appropriate emission of contaminants (Conti and Cecchetti, 2001).

3. Monitoring of atmosphere alteration and air pollution

3.1. Physical variables

Physical variables such as temperature and precipitation play a pivotal role in monitoring atmospheric changes. Temperature serves as a crucial indicator and the ultimate outcome of environmental processes linked to energy resources and their dynamics. Examples include derived soil heat flux, evapotranspiration, solar radiation, and convection (Xu et al., 2002; Hore and Uniyal, 2008). Numerous studies across

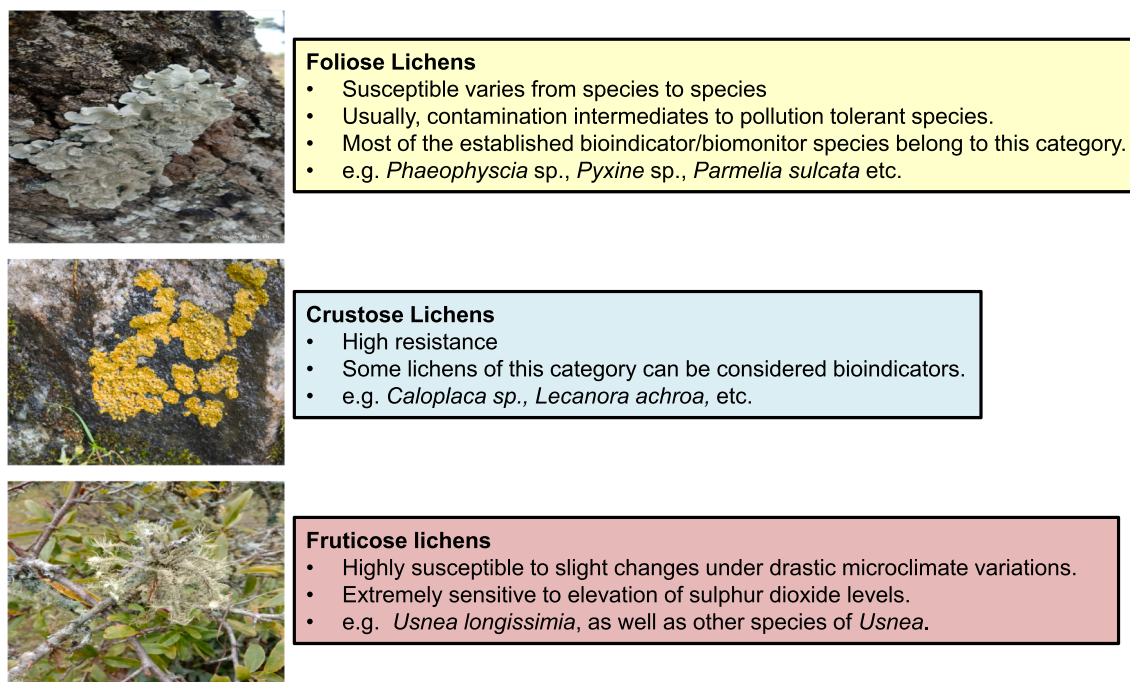


Fig. 1. Growth forms of lichen, their sensitivity and biomonitoring potential.

different regions of the world demonstrate that the global mean temperature and occurrences of intense precipitation have significantly increased in recent times (Keggenhoff et al., 2014).

3.2. Chemical variables

Compound variables used for contamination monitoring encompass the determination of potential toxic elements such as mercury (Hg), zinc (Zn), lead (Pb), magnesium (Mg), manganese (Mn), chromium (Cr), aluminum (Al), copper (Cu), iron (Fe), cadmium (Cd), nickel (Ni), and others. Additionally, contaminant gases such as SO_x, NO_x, etc., are monitored. Researchers study the monitoring of heavy metals through plant species and assess atmospheric quality under various conditions (Kumar et al., 2015).

3.3. Biological variables

Numerous investigations have assessed the quality of the atmosphere through the utilization of microorganisms (viruses, bacteria), plants (moss, lichen), and animals (spiders, fish, firefly larvae, dragonflies) as biological indicators. It has been determined that variations in the biological processes of animals and plants are profoundly influenced by environmental variables and contamination levels in the region. The responses of plants and animals to changes in the environment can serve as indicators of these alterations (Parmesan and Yohe, 2003; Inouye, 2008). The impact of environmental change on plant phenology is substantial, affecting growth, flowering times, seed production, reproductive capacity, and the frequency of reproductive events within a growing season. These changes can potentially lead to shifts in diversity, abundance, physiological and morphological variations, species richness, pollutant accumulation, and mutualism (Inouye, 2008). The natural consequences of these alterations in ecological processes ultimately influence the equilibrium of species, symbiotic relationships, distribution, and the diversity of both plants and animals within the region (Dahlgren et al., 2007; Miller-Rushing and Primack, 2008).

4. Global warming and climate change

Global warming may lead to a higher frequency of extremely hot days while causing a decrease in the number of highly frozen days (McCune, 2000). This warming trend could result in increased concentrations of rainfall and extreme precipitation events in some regions, causing both intensified droughts and floods in various areas (Gombert et al., 2003). In high latitudes, winter weather could see elevated levels of precipitation and soil moisture. Although the majority of surface warming is anticipated in the Arctic and Antarctica during winter, minimal warming is projected on hot days (Van Herk et al., 2002). The shift of winter conditions northward by 5-10° latitude in the northern hemisphere may lead to shortened snow seasons, varying based on snow depths for durations of one month or more (Bates et al., 2001). In mountainous regions, the snowline could rise between 140 and 170 m within the Temperate Zone for every one-degree Celsius increase in temperature, potentially causing the retreat and exposure of clean soil as snow patches or glacier ice masses withdraw (Purvis et al., 2003). Projections suggest that 30 to 50 percent of the current ice mass could collapse by 2100. Furthermore, permafrost areas are expected to diminish by 16 percent in the northern hemisphere (Brunialti and Giordani, 2003).

Elevated mountains with abrupt slopes could become more unstable due to ground melting or changes in the geophysical system, potentially resulting in increased occurrences of landslides or avalanches with varying frequencies (Pisani et al., 2007). The effects of global warming have both direct and indirect impacts on lichens, causing changes in habitats and shifts in interactions among species within lichen communities and with other organisms (Insarov and Schroeter, 2002).

4.1. Biodiversity alterations

Environmental alterations can directly impact species diversity through physiological responses of species or indirectly by altering interactions among species. Biodiversity is adversely affected when environmental degradation combines with disruption; this combination may result in significant or irreversible species loss (Nimis and Purvis, 2002). Factors such as temperature change, as well as alterations in surface

usage and forestation, could lead to regional declines in species diversity (Insarov and Schroeter, 2002). Opportunistic or highly adaptable organisms may thrive, potentially outcompeting slower-growing species and those requiring more stable conditions (Hughes, 2000). Species could face permanent extinction if native populations cannot recover through re-immigration from surrounding areas, particularly in marine regions impacted by rising water levels. Additionally, the upper slopes of low hills that were once within alpine zones and could support forest canopies due to ascending tree lines are now exposed due to the retreat of alpine glaciers. Species that require cooler environments for survival may become regionally extinct. Conversely, areas exposed by snow or ice melting could become available for colonization by lichens and plants (Insarov and Schroeter, 2002).

4.2. Effects of climate changes on lichens

Lichen growth and ecology are influenced by primary physiological processes, precipitation, haze, dew, and steam stress, which govern thallus water content, as well as ecological components (Nimis and Purvis, 2002; Bacelar et al., 2004). Several metabolic processes, including gas exchange, organic reactions, and chemical conversions between photobiont and mycobiont, have been observed to benefit from thallus water infiltration (Oztetik and Cicek, 2011; Majumder et al., 2013). Maximum hot days, minimum cold periods, or average annual temperature significantly impact the net photosynthetic rate of lichens, pigment degradation, thallus water content, and mineral nutrient levels. These factors contribute to the overall effect of temperature on lichen biomass (Sujetovienė, 2015). Changes in ecological temperature alterations can trigger physiological modifications within the thallus, potentially leading to the development of novel ecotypes or shifts within species diversity over time.

Due to their poikilohydrous environment, lichens exhibit significant physiological differences compared to larger plants. Most lichen species exhibit resistance to environmental stressors such as high and low temperatures, extreme illumination (including ultraviolet radiation), drought, and dormancy (Weissman et al., 2006). Moreover, many lichen species demonstrate resilience in harsh ecological conditions while hydrated (Armstrong, 2017). Consequently, lichens exhibit slower growth rates compared to taller vegetation (Insarov and Schroeter, 2002).

Numerous studies have explored the effects of global warming and environmental changes on lichens, examining aspects such as pigment composition, pigment degradation, and cytomembrane integrity to assess the impact of elevated temperatures on epiphytic lichens (Pisani et al., 2007). Lichens serve as cost-effective bioindicators in environmental monitoring, frequently utilized to gauge the effects of global warming, contamination, shifts in land use patterns, and various phylogenetic stressors on habitats (Rai et al., 2011). Some lichen species demonstrate the potential to adapt their habitats, as evident by the presence of a few sub-tropical species in relatively temperate regions (Van Herk et al., 2002). Many lichen species are highly sensitive to atmospheric conditions and are significantly influenced by subtle fluctuations in climatic variables. Consequently, global climate change has a profound impact on the distribution of lichen species (Watson, 2004).

The habitats of vulnerable lichens, especially in elevated areas of tropical mountains, represent potential locations for lichen disappearance due to rising temperatures, highlighting the estimated, determined, and uncertain impacts of lichen-environment interactions (Aptroot, 2009). In high-latitude regions where global environmental changes have occurred rapidly and extensively, bryophytes and lichens contribute more to biodiversity than vascular plants (Matveyeva and Chernov, 2000). A study conducted on the Chorabari glacier in the Garhwal Himalaya, India, facilitated the qualitative analysis of lichens to investigate global environmental variations and their effects on the Himalayan Mountains (Chaujar, 2009). This study traces the period when the Chorabari glacier began retreating from its maximum advancement point in this part of the Himalaya. Earlier research on the

Dokriani Bamak glacier revealed a retreat period of approximately 314 years in that specific region of the Himalaya. Studies on glaciers across both the northern and southern hemispheres indicate that many of them initiated retreat during the mid-eighteenth century, signaling the end of the maximum extent of the Little Ice Age. These findings imply that global climatic changes commenced during the early to mid-eighteenth century, though further research is required to confirm this. It is possible that the impact was initially felt in equatorial zones, as demonstrated by the north-facing Himalayan glaciers like the Dokriani Bamak.

5. Response of lichens to air pollutants

In studies focusing on atmospheric quality, lichens are commonly employed as receptor-based bio-monitors (Sett and Kundu, 2016). Numerous research endeavors have explored the morphology and physiology of lichens in relation to sulfur dioxide, component compounds, ozone, major metals, and various atmospheric contaminants (Lalley and Viles, 2005; Lalley and Viles, 2008) (refer to Table 1). Lichens have been recognized and employed by many investigators as auxiliary tools for assessing atmospheric quality (Garty, 2001). The properties of lichens used for quantifying contamination encompass morphological, physiological, and ecological characteristics. Multiple studies have emphasized the significance of lichen morphology and physiology in the selection of indicator species (Port et al., 2018). The effectiveness of microscopic and molecular analyses, encompassing Protocista cell arrays within thallus organization, has been explored for assessing atmospheric quality. These analyses involve quantification of reduction efficacy, ultrastructural alterations of the thallus, changes in pigment emission variables, degradation of complex pigments, and modified chemical activity alongside respiration rates (Sett and Kundu, 2016).

5.1. Polycyclic aromatic hydrocarbons

These substances are classified as having individual physical condition risks, some of which possess notable carcinogenic and mutagenic characteristics (Shukla and Upreti, 2012). The ignition process and oil spills serve as sources of polycyclic aromatic hydrocarbons. Polycyclic aromatic hydrocarbons (PAHs) are released into the atmosphere in the nation of Asia due to historical fuel usage as well as the utilization of wood for cooking and other purposes (Shukla et al., 2010b).

To assess the quantification of polycyclic aromatic hydrocarbons within the Garhwal Himalayas, Shukla and Upreti (2011) examined lichens collected from various sites in the initiation of the Garhwal Himalayas, Uttaranchal. This study revealed the origin of metabolism for polycyclic aromatic hydrocarbons within the lichen *Phaeophyscia hispidula* from Dehradun, a metropolitan region of Uttaranchal. The investigation identified diverse sources, highlighting a significant feature of metropolitan atmosphere. The research recognized the effectiveness of *P. hispidula* as an exceptional bioaccumulation organism in studying each polycyclic aromatic hydrocarbon and metal in the moderate zones of the nation of Asia (Shukla and Upreti, 2009). In metropolitan cities, transportation appears commonplace, serving as a notable source of contamination. The urban environment's secure setting primarily favors the growth of nitrophilous lichens, with *P. hispidula* being highly exposed to external contamination and capable of accumulating elevated quantities of heavy metals on polluted surfaces (Shukla and Upreti, 2007).

5.2. Potential toxic elements

These sources originate from both natural and phylogenetic factors within the environment. Natural contributors include volcanic eruptions, soil emissions, fires, and saline spray. Phylogenetic sources encompass emissions from various anthropogenic activities such as

Table 1

Lichens mediated mechanism for the assessment of different pollutants in the environment.

Lichens Species	Metals/other pollutants	Results/ Mechanism	References
<i>Canoparmelia texana</i> (Tuck.) Elix & Hale, <i>Pyxine subcineria</i> Stirt. and <i>P. hispidula</i> (Ach.) Essl.	Fe, Zn, Cr, and Cu	The accumulation of six heavy metals e.g., iron (Fe), chromium (Cr), copper (Cu), zinc (Zn), lead (Pb), and nickel (Ni) by epiphytic foliose lichen species (<i>Canoparmelia texana</i> , <i>Pyxine subcineria</i> , and <i>P. hispidula</i>) in a polluted area of Srinagar city and its surroundings in the Garhwal hills of the Western Himalaya in which <i>C. texana</i> was least accumulated to Fe, Zn, Cr, and Cu than the <i>P. subcineria</i> and <i>P. hispidula</i> where heavy metals were significantly increased due to exposure of pollutants while <i>P. subcineria</i> showed maximum accumulation.	Singh et al., (2018)
<i>Lepraria lobificans</i> Nyl	Cd, Cr, Ni, Al, Fe, Cu, and Zn	To efficiently regulate environmental metals, leprose lichen grows naturally on buildings and monuments throughout the city of Mandav, Central India. Fe displayed high absorption in both the thallus as well as the surface of seven metals with an average value of 2195.63 µg/g.	Bajpai et al. (2010d)
<i>Parmotrema tinctorum</i> (Nyl.)	Cd, Pb, Zn, Cr, Cu, K, and Ni	The impact of environmental factors on the anatomy and physiology, as well as the deposition of contaminants on the lichen <i>Parmotrema tinctorum</i> (Nyl.) Hale which was transplanted in two cities of the Brahmaputra Valley: Tezpur (small) and Guwahati (large). The maximum chlorophyll content of lichen transplants from high-traffic areas was found to be lower; on the other hand, electrical conductivity was reported to be greater.	Daimari et al. (2021)
<i>Parmotrema reticulatum</i> (Taylor) M. Choisy	Cr, Cu, Pb and Zn	Across two years, three classes of lichens were tracked utilizing active and passive biomonitoring to determine levels of heavy metals “on thallus” and “in-thallus”. Overall, the research indicates that the lichens absorb contaminants from the air consistently before the balance is restored and <i>P. reticulatum</i> was the active species to track concentrations of spatiotemporal emissions.	Kularatne and De Freitas (2013)
<i>Phaeophyscia hispidula</i> (Ach.) Essl	Cd, Cu, Fe and Zn	Protein was significantly and negatively associated with pigment quantities between the biological variables ($r = -0.3838$, Chl. b); -0.5809 (Carotenoid); -0.5034 (OD), but was highly associated significantly with Cd ($r = -0.6822$, $P < 0.01$). Among pollutants, Cu ($r = -0.4639$), Fe ($r = -0.2676$) and Zn ($r = -0.0549$) were negatively associated with Cd. It was also noticed that the amount of chlorophyll, as well as protein, raised proportional to the number of metallic contaminants, suggesting the stress responses pathway in <i>P. hispidula</i> (Himalayan region).	Shukla et al. (2012b)
<i>Pyxine cocoes</i> (Sw.) Nyl and <i>Phaeophyscia hispidula</i> (Ach.) Essl	Fe, Al, Zn, As, Cr, Pb, Cd	In Katni and Rewa cities of Madhya Pradesh, Central India, the extent of environmental heavy metal emission was evaluated. <i>Pyxine cocoes</i> and <i>Phaeophyscia hispidula</i> were assessed to be used as indicator species towards seven contaminants. The metal efficacy arrays were Fe > Al > Zn > As > Cr > Pb > Cd in the city of Katni and Al > Fe > Zn > Cr > As > Pb > Cd in the city of Rewa.	Bajpai et al., (2011)
<i>Pyxine cocoes</i> (Sw.) Nyl	Al, As, Cd, Cr, Cu, Pb, Fe, and Zn	species was investigated as a bioindicator marker as well as the influence of environmental contaminants on physiological integrity. Fv/Fm, the proportion of chlorophyll degradation, and the Al, As, Cd, Cr, Cu, Pb, Fe, and Zn dimensional estimates found in the thallus were calculated. The report's data analysis showed important associations among Fv/Fm as well as the quality of elements (Al and Cr).	Karakoti et al. (2014)
<i>Bulbothrix setschwanensis</i> (Zahlbr.) Hale, <i>Everniastrum cirrhatum</i> (Fr.) Hale, and <i>Parmotrema reticulatum</i> (Taylor)	atranorin and salazinic acid	The altitudinal gradient influenced the quantitative profile of atranorin and salazinic acid in Parmelioid lichens. <i>Bulbothrix setschwanensis</i> (Zahlbr.) Hale, <i>Everniastrum cirrhatum</i> (Fr.) Hale, and <i>Parmotrema reticulatum</i> (Taylor) Choisy were expected to have significant concentrations of chemical substances as the altitude increased.	Shukla et al. (2016)
<i>Remototrachyna awasthii</i> (Hale & Patw.) Divakar & A. Crespo	heavy metal (HM) and polycyclic aromatic hydrocarbons (PAHs)	By applying the most common lichen <i>Remototrachyna awasthii</i> as a bioindicator, the heavy metal and PAHs in the atmosphere and also the tourist-rich region of Western Ghats was evaluated. The overall metal concentrations varied from 644 to 2277.5 µg/g while the amount of PAHs varied from 0.193 to 54.78 µg/g.	Bajpai et al. (2013a)

industrial output (oil refineries, smelters, organic compounds, and chemical industries), as well as raw sewage, landfill sites, coal combustion, and vehicular traffic (LeGalley et al., 2013).

The absorption and concentration of heavy metals through lichen thalli are made evident through lichen life and stress (Szczeplaniak and Biziuk, 2003; Baćkor and Loppi, 2009). A method of detecting contamination through pollutants with lichens involves the absorption of metals within lichen thalli. This absorption process is influenced by several atmospheric conditions, including temperature, moisture, air density, lichen morphology, and the availability of toxic metals in the atmosphere (Sujetovienė, 2015). Given that lichens serve as excellent bioaccumulators of toxic substances, the quantity of these substances contained within their thalli is directly linked to the climate conditions (Aprile et al., 2010; LeGalley et al., 2013; Hauck et al., 2013). The metal concentrations within lichens primarily depend on the specific metal present in the environment, as well as the physical and chemical characteristics of the metal-containing molecules (size and acidity) (Sujetovienė, 2015).

Various rates of lichen metal uptake have been discovered for certain toxic substances, indicating a phenomenon of selective metal uptake. The observed variations in metal uptake are attributed to the arrangement and binding sites on plasma membranes, leading to differential assimilation or ion substitution (Carreearas and Pignata, 2007). Metals with a stronger affinity for binding sites than less reactive cations may saturate the assimilation capacity of lichen thalli, thereby impeding the absorption of other cations. Certain lichen species can be classified as “rigorous accumulators” (Dighton and White, 2017). Transplantation studies have highlighted the capacity of lichens to accumulate metals over multiple periods of examination within their thalli. The E/C ratios analyzed across various locations demonstrate “rigorous accumulation” for *Xanthoria caperata*, whereas *Parmotrema chinense* shows “accumulation” (Aprile et al., 2010). *H. physodes*, *P. furfuracea*, and *Usnea hirta* transplanted to a metropolitan area in Italy exhibit similar absorption capacities, while *P. sulcata* shows a lower absorption capacity (Bergamaschi et al., 2007). The absorption capacity may vary for certain constituents. For instance, the absorption ability of *X. parietina* and

Parmelia tiliacea species differs only for calcium, chlorine, copper, and lead (Yenisoy Karakaş and Tuncel, 2004). An elevated proportion of potassium, iron, magnesium, zinc, manganese, and copper was found within the thalli of *H. physodes*, while magnesium, zinc, lead, copper, and cadmium were detected in *Usnea hirta* transplanted to traffic sites (Sujetovienė, 2015). On the other hand, certain species may exhibit minimal absorption capability and could be considered weak accumulators. The absorption of toxic substances in thalli of the genus *Cladonia* spp. was comparatively low, likely due to the frequent substrate pollution. Consequently, only a few species may hold environmental significance even when competing with pioneering species in anthropogenically influenced regions (Osyczka and Rola, 2013).

Several lichen species have been identified as suitable candidates for transplantation and heavy metal accumulation. Lichen species characterized by delicately separated and densely sorediate thalli generally exhibit a stronger tendency for metal accumulation, relatively speaking (Aprile et al., 2010). External growth conditions play a significant role in influencing the bioaccumulation capability (Adamo et al., 2007). The reduced assimilation of specific metallic cations could be attributed to the formation of weak complexes with cytomembrane ligands, making them easily displaced and replaceable by cations with a higher affinity for the binding sites on the plasma membrane (Carreras and Pignata, 2007).

5.3. Sulphur compounds

The susceptibility of lichens to sulfur compounds has been measured over an extended period, underpinning their use as effective biomonitors. Lichens' heightened susceptibility to sulfur compounds is influenced by the alkaline nature of sulfur dioxide, which represents the primary source of sulfur in the atmosphere (Batić, 2002). The deleterious impact of sulfur compounds involves nucleon configuration and the oxidation of sulfur to sulfate, along with the generation of radicals during the oxidation process. Additionally, changes in allocation rates and alterations in physiological variables serve as key indicators for assessing lichens' response to sulfur pollution. Lichens are highly suitable biomonitors due to their sensitivity to environmental sulfur dioxide, a significant concern leading to the decline of lichen populations, particularly in urban or industrial areas (Giordani, 2007). Shrub-like species tend to be more susceptible to sulfur compounds than many foliose or crustose species.

Heavily contaminated regions may not support typical species recolonization, leading to the emergence of toxotolerant organisms within these areas (Upreti et al., 2005). Modest quantities of sulfur dioxide, reacting with low bark pH, continue to hinder the recolonization of susceptible lichens in urban areas (Bates et al., 2001; Batty et al., 2003). The severity of sulfur dioxide damage is directly linked to the amount of sulfur dioxide present: higher quantities correlate with more severe damage. Lichens can exhibit sensitivity to sulfur dioxide, resulting in morphological alterations such as smaller and more compact thalli, as well as reduced coverage (Massara et al., 2009). Sulfur dioxide primarily affects cellular activity, influencing enzyme reactions (Grube, 2010). The acidification susceptibility of lichens may be influenced by the emulsifying ability of bioactive compounds they produce. Species that produce usnic acid, for example, are associated with higher acidity and are less common in areas with high contamination levels (Hauck and Jürgens, 2008). An increase in sulfur dioxide levels in the environment has been directly linked to higher conductivity values in *P. sulcata* (Marques et al., 2005). The most significant plasma membrane damage was observed in lichen thalli from areas with the highest sulfur dioxide levels (Alebić-Juretić and Arko-Pijevac, 2005). As a result, lichens serve as valuable bioindicators of sulfur contamination, as they can absorb and accumulate toxic sulfur compounds or exhibit varying susceptibilities to them.

5.4. Nitrogen compounds

A substantial amount of nitrogen (N) is naturally generated, leading to increased phylogenetic emissions. A discontinuous equilibrium exists for the contribution of phylogenies to energy generation, industrial activity, transportation, and agriculture. Nitrogen returns from non-combustion processes are facilitated by distinct pathways. For example, aqua fortis are used in the production of explosives and fastening methods. The three most commonly found nitrogen compounds in the form of ammonia are ionized nitric oxide, nitrogen dioxide, and the reduced form of nitrogen. Accumulations of nitrogen acidify and eutrophicate habitats (Stevens et al., 2011). The influence of nitrogen deprivation affects species' reliance on various factors, including the duration of exposure, the total quantity or variety of nitrogen, and the susceptibility of organisms (Bobbink et al., 2010; Erisman et al., 2013). To observe nitrogen contamination using lichens, three approaches are employed (Sujetovienė, 2015): (1) alterations in lichen species composition, (2) variations in physiological variables, and (3) nitrogen accumulation within lichens. The accumulation of nitrogen in the atmosphere appears to be altering lichen community composition. Lichen's interactions with nitrogen are highly diverse due to their susceptibility to their ionic environment.

The stratum is acidified by nitrate-nitrogen, while an increase in the ammonium ion concentration leads to higher hydrogen ion levels. NOx has a significant impact on lichen diversity, community composition, growth rate, and distribution (Davies et al., 2007). Additionally, lichen abundance decreases under high levels of NOx (Giordani, 2007). Certain nitrogen-tolerant species thrive with nitrogen addition, enhancing their physiological status and increasing their nitrogen consumption (Ochoa-Hueso and Manrique, 2011). The resistant lichen *Cladonia foliacea* can serve as an indicator of nitrogen responses. Moreover, numerous species suited for nutrient-poor habitats with abundant and dispersed acid-sensitive (susceptible to eutrophication) organisms are negatively affected by nitrogen enrichment (Gaio-Oliveira et al., 2004; Pilkington et al., 2007; Pinho et al., 2008). High nitrogen levels lead to a reduction in the abundance of many lichen species, resulting in a general homogenization of lichen communities with a dominance of resistant species (Liska and Herben, 2008). A study assessing the impact of eutrophication in pine forests over a period of forty-five years revealed changes in the decline of ground lichen species adapted to nutrient-poor conditions (Reinecke et al., 2014).

At a molecular scale, Tretiach et al., (2007b) reported that a large amount of NOx can damage an alga-transplanted *Flavoparmelia caperata*, likely due to increased free radicals as a result of higher nitrogen dioxide levels within the cells, forming nitric oxide or nitric acid. This acidification of the protoplasm leads to biomolecule damage and degradation, affecting the chemical integrity of macromolecules. When exposed to extreme nitrogen levels, fungi exhibited greater damage than algae (Dahlman et al., 2002; Gaio-Oliveira et al., 2004). Ergosterol, a component of the fungal cell membrane, is used as an indicator of fungal respiration. Noticeable reductions in ergosterol were observed with increasing nitrogen uptake in *Evernia prunastri*, suggesting that higher nitrogen absorption can inflict more harm on the fungal partner compared to the algae (Gaio-Oliveira et al., 2005).

Chitin, a component of the mycobiont's semipermeable membrane, is associated with the amount of fungal biomass. The increase in algal resources was accompanied by a corresponding decrease in fungal resources, as indicated by changes in the pigment-to-chlorophyll ratio, polysaccharide content, and ergosterol levels (Dahlman et al., 2003). The reduction of essential cations within the lichen thallus serves as a general indicator of the nitrogen component's toxicity. Ammonia production led to a decrease in cytoplasmic K⁺ and Mg²⁺ in *Xanthoria parietina* (Munzi et al., 2011). Severe ammonium loading can compromise cytoplasmic integrity, potentially causing protoplasmic damage characterized by intracellular K⁺ leakage. Electrical conduction measurements revealed cytoplasmic membrane damage during periods of

high nitrogen stress (Munzi et al., 2009), though no significant differences were observed over the four-week experimental period (Munzi et al., 2012). Under non-toxic increases in nitrogen availability, lichens responded by investing more nitrogen in their metabolism and carbon assimilation capacity, resulting in enhanced growth rates (Palmqvist et al., 2002). Elevated nitrogen supply favors metabolism up to around twenty metric tons of nitrogen per hectare per year (Ochoa-Hueso and Manrique, 2011). Beyond this point, increased photosynthesis was not observed. Therefore, it is evident that excessive nitrogen may adversely affect nitrogen pathways and the photosynthesis process in lichens. Elevated NO_x levels lead to reduced efficiency in the photosynthetic apparatus of algal partners within lichens (Tretiach et al., 2007b). It is suggested that nitrogen oxides disrupt trans-thylakoid proton gradient structures, while non-photochemical heating is also significantly affected.

5.5. Ozone

Ozone at the Earth-scale is not emitted directly into the environment; rather, it forms through chemical reactions involving nitrogen oxides and volatile organic compounds. Ozone is the most significant atmospheric oxidant responsible for causing damage to plants (Führer, 2002). Generally, lichens are not considered as susceptible to ozone compared to vascular plants (Bertuzzi et al., 2013). However, in both historical and recent lichen species records, varying susceptibility to ozone's adverse effects on lichens has been documented. Species sensitive to ozone, such as *Evernia prunastri*, *Peltigera* spp., *Pseudocyphellaria* spp., and *Ramalina* spp., have disappeared due to the impact of this oxidizing agent in areas like Los Angeles. Susceptible organisms like *Usnea* spp. and *Collema nigrescens* are found in restricted regions, while even the somewhat tolerant *Hypogymnia enteromorpha* has reduced in quantity and exhibits morphological anomalies such as thallus bleaching and decay (Sujetovienė, 2015). Physiological studies have revealed a range of outcomes from ozone exposure.

Numerous recent experiments involving ozone provide evidence supporting the claim that it has a harmful impact on lichens. Experimental exposure to ozone resulted in a significant decrease in the efficiency of photosystem two (PSII) reaction kinetics, the breakdown of several algal cells, and consequent thallus bleaching. Additionally, a reduction in photosynthetic rates was observed (Zambrano and Nash, 2000). Under field conditions encompassing various potential variables, the ozone levels present during the course of the study were sufficiently high to have led to adverse effects on lichens, including reduced chlorophyll degradation and photosynthesis (Zambrano and Nash, 2000). Ozone directly exerts damaging effects on lichens through the rapid generation of free radicals. The ozone intensity displayed a direct correlation with malondialdehyde and superoxide dismutase levels in *Hypogymnia physodes*, indicating oxidative damage and cell stress in membrane and enzyme systems that protect against oxidation. However, exposing five lichen species to ozone for four hours a day over a fourteen-day period did not induce any changes in PSII efficiency as assessed by ultraviolet rays (Calatayud et al., 2000).

Furthermore, neither the chemical change in greenhouse gas incorporation nor the xanthophyll cycle activity was affected by an increased level of ozone. The results of the applied studies suggest that the functionality of the photosystem was not influenced by ozone (Calatayud et al., 2000; Riddell et al., 2010, 2012). It is quite evident that the effects of ozone under investigational and real-world conditions encompassed biophysical, physiological, and structural damage within the studied lichens. Despite the evidence of ozone impacts, several researchers suggest that lichens may not be a reliable indicator of ozone, as no significant effect of ozone exposure was detected (Riddell et al., 2010; Bertuzzi et al., 2013). It is proposed that lichens possess remarkable capabilities to withstand the myriad generations of reactive oxygen species induced by elevated ozone concentrations (Calatayud et al., 2000; Bertuzzi et al., 2013).

6. Conclusions

Lichens play a vital role in ecosystems, displaying significant diversity and abundance despite challenging ecological conditions. They have adeptly adapted to various environments around the world, serving as key indicators for long-term monitoring of global climate change and environmental contamination. Lichens are regarded as excellent indicators of various emissions and serve as sensitive bio-monitors of environmental quality due to their responses to atmospheric pollutants. To date, the observed changes have been evident in ongoing monitoring efforts. However, limited research has explored the relationship between lichens and global warming. Developing countries need to establish suitable methods for lichen studies, including the bio-accumulation of emissions. The capacity of lichens to accumulate pollutants, heavy metals, and harmful substances has contributed to our understanding of worldwide air pollution patterns. Nonetheless, in this era of rapid industrial progress, it is crucial to expand these investigations globally and across a broader spectrum of species. Identifying additional species of interest that can adapt to ongoing chemical changes in our environment is imperative. Furthermore, comprehending the role of morphological features in different lichen species for trapping particulate matter, a previously unexplored but vital research domain, is essential. In today's world, lichens offer multifaceted benefits as bio-indicators. One noteworthy advantage is their versatility in assessing changes occurring within specific ecosystems at various scales.

Authors' contributions

MT and SB write the initial draft of the manuscript, VK and JR-C edited the manuscript, figures and table. All authors have read and approved the final manuscript.

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Declaration of competing interest

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