# 5 Ecosystem Monitoring

Monitoring the quality and sustainability of the ecosystem with lichens has been studied worldwide. Three major categories of assessment that have been identified so far for the role of lichens in ecosystem monitoring include air quality, climate and biodiversity. Both natural and man-made disturbances/disasters are responsible for imbalance in the ecosystem.

With increasing economic growth, environmental contamination, especially air pollution, is resulting in environmental degradation in the developing nations of Asia, especially India. In order to attain sustainable economic development, monitoring and eradication of environmental problems is important. The highest priority issues include monitoring of the quality of air, water and soil, deforestation and degradation of the natural environment.

Lichens are very useful for monitoring spatial and/or temporal deposition patterns of pollutants as they allow accumulation of pollutant throughout its thalli, and concentrations of pollutants in lichen thalli may be directly correlated with environmental levels of these elements. Lichens also meet other characteristics of the ideal sentinel organism: they are long lived, having wide geographical distribution, and accumulate and retain many trace elements to concentrations that highly exceed their physiological requirements. The details of the factors affecting the ecosystem, natural as well as anthropogenic, and role of lichens in ecosystem monitoring have been discussed.

## 5.1 Introdcution

Monitoring the ecological effects of contaminants released as a result of natural and/or man-made processes in the ecosystems, to detect changes in environmental quality, is best referred as *ecological monitoring*, as pollutants are not only localised to their source of origin but also contaminate global environment. The widespread dispersing nature of pollutants makes spatio-temporal monitoring of pollutants pertinent to ensure sustainable development either using air samplers or bioindicator species (Seaward 1974).

Natural sources of atmospheric pollutants generally include dust emissions, living and dead organisms, lightning and volcanoes. Over Asia, mineral dust is the major natural aerosol because of the vast desert regions. Other gases and aerosols are mainly the result of anthropogenic emissions, or airborne in situ production, rather than natural emissions. As the most important natural pollutant, dust aerosols play an important role in the climate system by affecting the radiation budget (Tegen and Lacis 1996; Sokolik et al. 1998), biogeochemical cycles (Martin and Fitzwater 1988; Martin 1991; Archer and Johnson 2000) and atmospheric chemistry (Dentener et al. 1996; Dickerson et al. 1997; Martin et al. 2003). Moreover, they have important consequences on surface air quality (Prospero 1999). Dust aerosols originating from East Asia, one of the major dust emission regions in the world, may influence the

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**Table 5.1** Methods for ecosystem monitoring utilising lichens

| | Techniques | |
|---|---|---|
| 1 | Transplant | Transplanting healthy lichens into a polluted area and measuring changes in thallus physiology and elemental composition |
| 2 | Lichen zone mapping | To indicate the severity of pollution with reference to distance from the source, as reflected by change in composition of lichen diversity |
| 3 | Sampling individual species | Measurement of contaminants accumulated within the thallus |

After Garty (2001)

ecological cycle of the North Pacific Ocean and the air quality over North America (Prospero 1999; Wuebbles et al. 2007).

A number of traditional studies dealing with atmospheric contamination are available but most of them have been limited to problems of high cost and the difficulty of carrying out extensive sampling, in terms of both time and space. There is, thus, an ever-increasing interest in using indirect monitoring methods such as analysis of organisms that are biomonitoring (Garty 2001). Biomonitoring involves the use of organisms and biomaterials to obtain information on certain characteristics of the ecosystem. According to Markert et al. (2003), biomonitoring is a composite phenomenon comprised of several interrelated terms.

| | |
|---|---|
| Bioindicator | provides information on the environment or the quality of environmental changes |
| Biomonitor | provides quantitative information on the quality of the environment |
| Reaction indicators | are organisms which are sensitive to air pollutants and are utilised in studying the effects of pollutants on species composition and on physiological and ecological functioning |
| Accumulation indicators | are organisms which readily accumulate a range of pollutants without being harmed by the excessive concentration of the pollutants |
| Passive biomonitors | occurs naturally in the area |
| Active biomonitors | are transplanted into the research area for a specific period of time |

Lichens are undoubted reliable bioindicators in the monitoring of ecosystem changes as Litmus test for ecosystem health (Hawksworth 1971). Biomonitoring provides relevant information about ecosystem health either from changes in the behaviour of the monitor organism (species composition and/or richness, physiological and/or ecological performance, morphology) or from the concentrations of specific substances in the monitoring organisms (Table 5.1). Thus, lichens can be used for the quantitative and qualitative determination of natural and human-generated environmental factors.

Biomonitors which are mainly used for qualitative determination of contaminants can be classified as being sensitive or accumulative. Sensitive biomonitors may be of the optical type and are used as integrators of the stress caused by contaminants and as preventive alarm systems. They are based upon either optical effect as morphological changes in abundance behaviour related to the environment and/or physical and chemical aspects as alteration in the activity of different enzymes systems as well as in photosynthetic or respiratory activities, while accumulative bioindicators have the ability to store contaminants in their tissues and are used for the integrated measurement of concentration for such contaminants in the environment, and those species involved are called accumulator (indicator) species. According to Wolterbeek et al. (2003), indicator species are recognised as 'Universal' and 'Local'. The term Universal is restricted to those species which are found exclusively on substrates containing high concentrations of pollutants for which the species is proposed as an indicator species. Local indicators are species which are associated with pollutant-bearing substrates in certain geographical areas but which also grow elsewhere in non-mineralised areas.

Various monitor materials have been applied in trace element air monitoring programmes, such as lichens, mosses, ferns, grasses, tree and pine needles. The mechanisms of trace element uptake and retention are still not sufficiently known. It is necessary to select out appropriate organisms which are suitable for the study purposes.

Lichens are natural sensors of our changing environment: the sensitivity of particular species and communities to a very board spectrum of environmental condition, both natural and unnatural, is widely acknowledged. Nevertheless, lichens undoubtedly represent one of the most successful forms of symbiosis in nature. They are to be found worldwide, exploiting not only all manner of natural, usually stable, micro- and macro-environments, but in many cases adapting to extreme conditions, including some brought about by human disturbance. Lichens are therefore used increasingly in evaluating threatened habitats, in environmental impact assessment and in monitoring environmental alterations, particularly those resulting from a disturbingly large and growing number of anthropogenic pollutants.

That lichens are sensitive to air pollution is, of course, a generalisation that requires cautious interpretation and limited extrapolation. The distribution patterns of a lichen species may well reflect varying levels of an air pollutant, but variation in its distribution may also be caused by a variety of abiotic or biotic factors as well. Furthermore, all lichens are not equally sensitive to all air pollutants; rather, different lichen species exhibit differential sensitivity to specific air pollutants. Sensitive species may become locally extirpated when a pollutant is present, but at least some tolerant species are likely to persist. This differential sensitivity is, however, very useful when interpreting air pollution effects. The absorption of metals in lichens involves some mechanisms like intercellular absorption through an exchange process, intracellular accumulation and entrapment of particles that contain metals.

Thus, lichens have a long history of use as monitoring of environmental pollution (Nimis 1990). A number of authors have advocated the use of biological monitoring to assess and understand the status of trends within natural ecosystem and focused on heavy metals, PAHs accumulation and their interactions due to natural and man-made disturbances/disasters (Nriagu and Pacyna 1988; Jeran et al. 2002; Godinho et al. 2008; Upreti and Pandey 2000; Shukla and Upreti 2007a, b). In areas that lack naturally growing lichens due to high levels of air contamination, lichen transplantation method, first introduced by Brodo (1961), is being applied as a standard method to study airborne metal and sulphur pollutants (Conti and Cecchetti 2001; Budka et al. 2004; Baptista et al. 2008).

There are large amounts of studies with respect to the effects of air pollution to epiphytic lichens and the use of lichens as bioindicators (Geebelen and Hoffman 2001; Paoli et al. 2011; Davies et al. 2007; Giordani 2007) as well as biomonitors (Nash 1976; Herzig et al. 1989; Gombert et al. 2002; Frati et al. 2006; Tretiach et al. 2007; Guidotti et al. 2009). Most of the studies have been carried out in urban areas where air pollution is caused by a number of factors. However, comparatively little comprehensive and precise data about biomonitoring with lichens from India is available.

## 5.2 Natural and Human Disturbances/Disasters

Nature is the major source of elements of inorganic and organic origin. Various categories of pollutants having natural and man-made origin include heavy metals, metalloids, polycyclic aromatic hydrocarbons (PAHs) and radionuclides. Natural processes (volcanic eruption) result in release of elements but nature has sinks which consume those elements via mineral cycling as in the case of metals. In lower concentration, especially metals except few are not toxic, they facilitate physiological functioning of the organism, but when its concentration exceeds permitted levels and shows phytotoxicity, then it is considered as pollutant. Radioactive substances have biological half-life which facilitates decay of these chemicals. Best example of source and sink is

$CO_2$ emission (potential greenhouse gas); in natural conditions $CO_2$ emitted by plants is consumed by other organisms maintaining the environmental levels roughly constant, but when human activity also releases these chemicals in the atmosphere, it results in imbalance in the natural cycling of the elements which enter either food chain via biomagnification and gases released remain in the atmosphere and act as potential greenhouse gases, resulting in elevation of global temperature and glacier retreat phenomenon.

Nitrogen oxides (NOx), volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), particles and metals are some of the pollutants considered to be of ecological significance (Bignal et al. 2007, 2008). In addition, effects of ammonia ($NH_3$) on vegetation at roadside verges (Truscott et al. 2005) and on bark pH that influences lichen vegetation around a pig stock farm in Italy (Frati et al. 2006) and toxicity of nitric acid ($HNO_3$) to the lichen *Ramalina menziesii* have been recognised. Sulphur dioxide ($SO_2$) was once regarded as the most notorious pollutant affecting lichens, but the rapid reduction in $SO_2$ has been remarkable in the industrialised world today (Nieboer et al. 1977).

The relation of sulphur dioxide ($SO_2$) to lichens has been broadly studied throughout the world as this pollutant was once regarded as the most harmful compound to lichens. A wide range of methods is used to analyse the physical properties of lichens such as chlorophyll, sulphur isotope composition, sugar content, spectral reflectance, membrane proteins, moisture content and ethylene content (Conti and Cecchetti 2001). These studies have proved the deterioration of physical structures of lichens being exposed to sulphur compounds (LeBlanc et al. 1974; Shirazi et al. 1996).

Many recent studies relating to the effects of air pollution on lichens focus on NOx and there are numerous results showing the significant correlation between lichens and the pollutant. Nitrogen is an essential element for life, being involved in the synthesis of protein and nucleic acids (Nash 2008). However, an excess amount of nitrate deposition can deteriorate the symbiotic relationship. For instance, NOx has a strong effect on (Davies et al. 2007; Aragón et al. 2010), its community composition, frequency and dispersal (Larsen et al. 2007). In addition, lichen population declines in high NOx content (van Dobben et al. 2001; Giordani 2007). At the molecular level, Tretiach et al. (2007) showed that a large amount of NOx can damage the photobionts of transplanted *Flavoparmelia caperata*, hindering photosynthesis. This is probably due to the increased reactive oxygen species (ROS). They reported that a high concentration of $NO_2$ in the cells forms nitrous and nitric acids, which acidifies the cytoplasm and results in protein denaturation and deamination of amino acids and nucleic acid.

Despite those negative effects, some lichen species such as *Lecanora dispersa* and *Phaeophyscia orbicularis* are NOx tolerant (Davies et al. 2007). Even though Nash (1976) confirmed in a laboratory experiment the phytotoxic effect of $NO_2$ on lichens that were fumigated with 4 ppm (7,520 μg $m^{-3}$) for 6 h, he suggested that the pollutant would probably not be harmful to lichens since the $NO_2$ concentration detected in natural environment was usually less than 1 ppm. Thus, the effect of NOx on lichens seems controversial and unclear.

### 5.2.1 Heavy Metal

Heavy metals are chemical elements that exhibit metallic properties. Many different definitions of the term heavy metal have been proposed, based on density, atomic number, atomic weight, chemical properties or toxicity (Prasad 1997). Toxicity of metal is mainly dependent on the oxidation state of the element which is responsible for its bioavailability to the plants (Table 5.2).

Heavy metals are natural constituents of the earth's crust. Most of the metals are toxic in nature; their stable and non-biodegradable character allows their entry into the food chain and pose harmful effects to the organism in contact. Anthropogenic activities have drastically altered the biochemical and geochemical cycles and balance of some heavy metals. The principal man-made sources of heavy metals are point sources related mainly to industrial activities, e.g.

**Table 5.2** Oxidation state, toxicity and bioavailability of various metals present in the ecosystem due to natural and/or anthropogenic processes

| Elements | Redox state | Major sources | Toxicity and bioavailability |
|---|---|---|---|
| Arsenic (As) | III, V | Natural | Arsenite (III) is commonly the dominant species in moderate to strongly anoxic soil environments and is much more toxic, soluble and mobile than the oxidised form, arsenate (V) (Aide 2005) |
| Nitrogen (N) | III, 0, III, V | Natural | An essential nutrient but odd nitrogen compounds like PAN are toxic. Bioavailability to the food chain is facilitated by nitrogen-fixing bacteria in lichens and root nodules of higher plants |
| Carbon (C) | IV to IV | Natural/anthropogenic | Carbocatenation properties makes them main constituents of hydrocarbons |
| Chromium (Cr) | III, VI | Anthropogenic | Only +3 and +6 states are stable under most conditions of the surface environment. Cr(VI) is both highly soluble and toxic to plants and animals, yet Cr(III) is relatively insoluble and an essential micronutrient (Fendorf 1995; Negra et al. 2005) |
| Copper (Cu) | I, II | Anthropogenic | Copper mobility is decreased by sorption to mineral surfaces. Cu 2+ sorbs strongly to mineral surfaces over a wide range of pH values (Gasparatos 2012) |
| Sulphur (S) | II to VI | Anthropogenic | In II oxidation state it forms phytotoxic gas $SO_2$ and in VI state it forms $SF_6$ a potential green house gas |
| Iron (Fe) | II, III | Natural | |
| Manganese (Mn) | II, IV | Natural | Mn (IV), which is the most stable in neutral to slightly alkaline conditions, and Mn (II), which is stable in reducing conditions (Post 1999) |
| Nickel (Ni) | | Anthropogenic | Various oxidation states but only Ni (II) is stable in the pH and redox conditions found in the soil environment (Essington 2004; McGrath 1995) |
| Lead (Pb) | II | Anthropogenic | Lead is a widespread pollutant in the soil environment with a long residence time compared with most other inorganic pollutants (Gasparatos 2012) |

mines, foundries and smelters, and combustion byproducts and traffic, etc. Relatively volatile heavy metals and having lower density get associated with the particulate matter which may be widely dispersed throughout to longer distances, often being deposited thousands of miles from the site of initial release (Bari et al. 2001; Goyal and Seaward 1982). In general, the smaller and lighter a particle is, the longer it will stay in the air. Larger particles, greater than 10 μm in diameter tend to settle to the ground by gravity in a matter of hours, whereas the smallest particles (less than 1 μm in diameter) can stay in the atmosphere for weeks and are mostly removed by precipitation (Buccolieri et al. 2006).

A dynamic equilibrium exists between atmospheric nutrient/pollutant accumulation and loss that can make lichen tissue analysis a sensitive tool for the detection of changes in air quality of many pollutants (Farmer et al. 1991; Baddeley et al. 1972). In an entire lifespan, lichens undergo multiple wetting and drying cycles during a day. When hydrated, nutrients and contaminants are absorbed over the entire surface of the lichen. During dehydration, nutrients and many contaminants concentrate by absorption to cell walls, cloistering inside organelles or crystallising between cells (Nieboer et al. 1978). Lichens posses an ability to accumulate sulphur, nitrogen and metals from atmospheric sources better than plants (Berry and Wallace 1981; Brown et al. 1994; Beckett and Brown 1984). Macronutrients, such as nitrogen, sulphur, potassium, magnesium and calcium, are comparatively mobile and easily leached, and therefore, measurable changes in tissue concentrations can occur over weeks or months with seasonal changes in deposition (Bargagli 1998; Boonpragob et al. 1989), while trace and toxic metals such as cadmium, lead, and zinc are more tightly bound or sequestered within lichens and therefore more slowly released (Garty 2001). However, metals can stay in the environment for 20 years or more after their deposition, and elevated levels in lichens reveal this. If air quality improves, levels of metals will decrease over time, and changes in air quality can be detected in lichen tissue over a period of years (Bargagli and Nimis 2002). While it may take decades to return to background levels, changes may be observable from 1 year to the next as new growth takes place and metals are leached from older tissues. For spatio and temporal air quality assessment purposes, collection of a large-enough sample size, comprised of many individuals, should be sufficient to determine the average tissue concentration for that population.

As both natural and anthropogenic sources contribute to the bioaccumulation of metals in an organism, identifying the relative contribution from each source becomes a complex task. Puckett (1988) reported a method of calculating enrichment factors (EFs) to compare the concentration of metal within a plant with potential sources in the environment. The equation EF calculation is:

$$\mathrm{EF} = \frac{x\,/\,\text{reference element in lichen}}{x\,/\,\text{reference element in crustal rock}}$$

Enrichment factors (EFs) are calculated to know the origin of metal either lithogenic and/or airborne. EFs studies indicate that Fe and Mn have a significant crustal origin and that the lower-concentration heavy metals Cd, Cu, Pb and Zn are mainly of anthropogenic origin. Accordingly to geochemical calculations, Al, Fe, and Mn have a significant crustal origin, while, Cd, Cu, Pb and Zn are of anthropogenic origin. Moreover, Fe resulted predominant in the coarse particle fraction, while Ni, Pb, V and Zn were predominant in the fine particle fraction (Buccolieri et al. 2006).

The major sources of heavy metal pollution in urban areas of India are anthropogenic, while contamination from natural sources predominates in the rural areas. Anthropogenic sources of pollution include those associated with fossil fuel (vehicular activity) and coal combustion, industrial effluents, solid waste disposal, fertilisers and mining and metal processing. At present, the impact of these pollutants is confined mostly to the urban centres with large populations, high traffic density and consumer-oriented industries. Natural sources of pollution include weathering of mineral deposits, forest/bush fires and windblown dusts. The heavy metals which are monitored by lichens include: aluminium

(Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), manganese (Mn), strontium (Sr), tin (Sn), titanium (Ti), vanadium (V) and zinc (Zn).

As developing countries of Asia become industrialised and urbanised, heavy metal pollution is likely to reach disturbing levels. Lichens are frequently exposed to excess metals which they may tolerate as a result of detoxification mechanisms. Considerable amounts of heavy metals are immobilised by cell wall components, and the main processes for maintaining metal homeostasis in lichens, including transport of heavy metals across membranes, are chelation and sequestration (Backor and Loppi 2009). There is a conspicuous lack of data on the nature and extent of metal pollution either at local or regional levels, particularly to assist in the understanding of metal cycling in the environment. No systematic studies are being carried out to examine the dynamics of tropical ecosystems.

Although most countries in the sub-region recognise the need to combat pollution, environmental controls are either non-existent or inadequate. Most industries discharge effluents into the environment without any prior treatment, and the manufacture of 'pollution-intensive' products is being shifted to the developing countries where strict controls do not exist. The establishment of comprehensive monitoring systems and information gathering should be given priority by governments of the developing countries (for lichen biomonitoring data, see Sect. 5.2.1.5).

### 5.2.2 Arsenic (Metalloids)

Arsenic is a naturally occurring toxic element and its toxicity, mobility and bioavailability in soil are highly dependent on pH and redox potential (Aide 2005). Arsenic in air is found in particulate forms as inorganic As, and the dust of industrial periphery contains huge amount of As element (Menard et al. 1987). Methylated arsenic is a minor component in the air of suburban, urban and industrial areas and that the major inorganic portion is a variable mixture of the trivalent As(III) and pentavalent As(V) forms, the latter being predominant. From both biological and toxicological aspects, arsenic compounds can be classified into three major groups: inorganic arsenic compounds, organic arsenic compounds and arsenic gas. Two inorganic forms of As, arsenite ($As[OH]_3$) and arsenate ($H_2{\cdot}AsO_4^-$ and $HAsO_4^{2-}$), are the main species in soils. Arsenite is commonly the dominant species in moderate to strongly anoxic soil environments and is much more toxic, soluble and mobile than the oxidised form, arsenate (Aide 2005). Common organic arsenic compounds are arsanilic acid, methylarsonic acid, dimethylarsinic acid and arsenobetaine.

Arsenic is released in the atmosphere from both natural and anthropogenic sources. The dominance of the anthropogenic factors is made obvious by high levels of As recorded near coal-based power plant and other industrial sites. The principal natural source is volcanic activity with minor contributions by exudates from vegetation and windblown dusts. Man-made emissions to air arise from the smelting of metals; the combustion of fuels, especially of low-grade brown coal; and the use of pesticides. According to Niriagu and Azcue (1990), arsenic is widely used in agriculture (manufacturing of pesticides), livestock (preservatives), medicines, electronic industries and mostly metallurgy. It is also released unintentionally as a result of many human activities such as smelting or roasting of any sulphide-containing mineral and, with combustion of fossil fuels, releases due to rapid leaching of exposed wastes from mining and ore processing activities, due to the manufacture of arsenicals and due to the greatly accelerated erosion of the land. The areas in the neighbourhood of the industrial complex, mining and vehicular activities exhibit significant increase in the concentration of arsenic. According to US EPA, the mean level of As ranges from <1 to 3 ng/$m^3$ in remote areas and from 20 to 30 ng/$m^3$ in urban areas.

Asia, especially Southeast Asia, has problem of As contamination of ground water as serious threat to human health. Recent studies show that more than 100 million people in Bangladesh, West Bengal (India), Vietnam, China and other South Asian countries drink and cook with

**Table 5.3** Arsenic concentration (in μg $g^{-1}$) in different lichen species collected from diverse regions of India

| S. No. | Species | Sites | Conc. (mini-max) | References |
|---|---|---|---|---|
| 1. | *Caloplaca subsoluta* (Nyl.) Zahlbr. | Mandav, Madhya Pradesh | 0.46–19 | Bajpai et al. (2009a, b, 2010b) |
| 2. | *Diploschistes candidissimus* (Kr.) Zahlbr. | Mandav, Madhya Pradesh | 1.24–17.34 | Bajpai et al. (2009a, b, 2010b) |
| 3. | *Lepraria lobificans* Nyl. | Mandav, Madhya Pradesh | 28.63–51.20 | Bajpai et al. (2009a, b, 2010b) |
| 4. | *P. praesorediosum* (Nyl.) Hale | Mandav, Madhya Pradesh | 12.2–42.12 | Bajpai et al. (2009a, b, 2010b) |
| 5. | *P. euploca* (Ach.) *Poelt in pisut* | Mandav, Madhya Pradesh | 5.87–10.52 | Bajpai et al. (2009a, b, 2010b) |
| 6. | *P. hispidula* (Ach.) Essl. | Mandav, Madhya Pradesh | 10.98–51.95 | Bajpai et al. (2009a, b) |
| 7. | *P. hispidula* (Ach.) Essl. | Rewa, Madhya Pradesh | 0.00–19.60 | Bajpai et al. (2011) |
| 8. | *Phylliscum indicum* Upreti | Mandav, Madhya Pradesh | 8.11–20.99 | Bajpai et al. (2009a, b, 2010b) |
| 9. | *P. cocoes* (Sw.) Nyl. | NTPC, Uttar Pradesh | 8.9–77 | Bajpai et al. (2010a, b) |
| 10. | *P. cocoes* (Sw.) Nyl. | Katni, Madhya Pradesh | BDL–33.4 | Bajpai et al. (2011) |
| 11. | *P. cocoes* (Sw.) Nyl. | West Bengal | 5.20–48.10 | Bajpai and Upreti (2012) |
| 12. | *Remototrachyna awasthii* | Mahabaleshwar city, Maharashtra (2011) | 0.18–3.96 | Bajpai et al. (2013) |
| 13. | *R. awasthii* | Mahabaleshwar city, Maharashtra (2012) | 0.36–4.11 | Bajpai et al. (2013) |

arsenic-contaminated water, which can cause skin lesions, internal cancers, respiratory illnesses, cardiovascular diseases and neurological problems (Cheng et al. 2005). In Bangladesh, about one-third of the wells among nearly five million tested are considered unsafe (van Geen et al. 2005). This is due to the excessive use of tube wells as safe surface waters become scarce. When the tube wells pump ground water through geological layers rich with arsenic, the toxic metal is leached and accumulates in the wells, especially when the infiltrated waters become polluted (Cheng et al. 2005).

In India the states of West Bengal, Madhya Pradesh, Bihar and some parts of Uttar Pradesh are facing a lot of skin problem due to arsenic in water pollution. Few studies of arsenic accumulation in hydrophytes and ferns are available. Singh et al. (2006) examined the metabolic adaptation of *Pteris vittata* L., an arsenic hyperaccumulator fern, in different concentrations of arsenic solution and evaluated their tolerance capacity. Srivastava et al. (2007) reported metabolic adaptations at >315 μg $g^{-1}$ dry weight of *Hydrilla verticillata* (L.f.) Royle, exposed to different concentrations of arsenic. Mishra et al. (2008) studied the phytochelating activities of *Ceratophyllum demersum* L., against 76 μg $g^{-1}$ dry weight of arsenic concentration. In India most of the studies of heavy metal accumulation in lichens are focused on metals originating from vehicular and industrial activities like Pb, Cu, Fe and Zn, and little attention is being paid on other trace elements such as Hg, Mn and Ag as well as metalloids (Shukla and Upreti 2012).

Biomonitoring of As content in lichens has been carried out in Europe and in America, but in India recently biomonitoring studies employing lichens have been carried out to study the arsenic accumulation in lichen species having different growth form and growing naturally at different parts of India as well as explore a suitable As accumulator species (Table 5.3).

From the levels of As estimated in lichens of different parts of the country, it is clear that As represents one of the most abundant metalloid in the air and easily accumulated by different growth forms of lichens. The lichen thallus exhibits significant increase in the concentration of arsenic than their substrates.

Rate of absorption and accumulation of heavy metals is dependent on morphological feature of lichen thalli in addition to the kind and intensity of emission sources. The uptake of arsenic by a particular organism depends on the bioavailability of arsenic (which depends on its chemical form and environmental conditions) and the characteristics of the organism itself and of its substratum (Garty 2001; Loppi and Pirintsos 2003).

West Bengal is widely known for higher arsenic-contaminated state in India. As has been found accumulated in higher concentration in lichen thallus and lesser in substratum. Accumulation of pollutants is a continous process for lichens, as in the pollutants accumulate pollutants cummulatively over the year with least possibilities of leaching out from the thallus. However, pollutants deposited on substratum can be washed out with rainwater or blown off by wind. According to Deb et al. (2002), the concentrations of As in different areas shows the accumulation sequences as industrial > heavy traffic > commercial > residential.

Wind and its direction are probable agents for dispersion of elements, away from the source. Dispersion of metals depends on the gravity of a particular metal along with speed and direction of wind. Correlation coefficient indicated the dispersion of As in all the directions, however poor towards south and east affirmed the role of prevailing wind in bioaccumulation (Garty 2001).

A foliose lichen (*Pyxine cocoes*) growing luxuriantly in As-contaminated sites of W. B. in Hooghly and Nadia was analysed for arsenic. The mean arsenic concentration in lichen thallus ranged between $6.3 \pm 1.5$ and $48.1 \pm 2.1$ μg $g^{-1}$ dry weight, whereas in substratum it was quite low and ranged between $0.8 \pm 0.1$ and $2.3 \pm 0.9$ μg $g^{-1}$ dry weight. Maximum As was observed in samples collected from the immediate surroundings of Regional Rice Research Station. The higher concentration of As in thallus as compared to substrates clearly indicates that the As accumulation is airborne and not taken up from the substratum.

Arsenic is widely used in manufacturing of pesticides, weedicides and fertilisers which are capable to contaminate the atmosphere (Al and Blowes 1999). The agricultural land exhibited maximum As concentration ($48.1 \pm 2.1$ μg $g^{-1}$ dry weight) probably due to the frequent use of pesticides and fertiliser in the paddy fields.

Detailed studies on effect of As on transplanted lichen thalli of *P. cocoes* were carried out with different arsenate concentrations of 10, 25, 50, 75, 100 and 200 μM. The thalli were sprayed every alternate days. The thalli harvested on 10, 20, 30 and 45 days exhibit changes in photosynthetic pigments, chlorophyll fluorescence, protein content and antioxidant enzymes. The quantity of photosynthetic pigments exhibited a decreasing trend till 20 days but increased from 30 days onwards. Concomitantly, chlorophyll fluorescence also showed a decreasing trend with increasing arsenic treatment duration as well as concentration. The higher concentration of arsenate was found to be deleterious to the photosynthesis of lichen as the chlorophyll fluorescence and the amount of pigments decreased significantly. The protein content of lichen increased uninterruptedly as the concentration of arsenate as well as duration of treatment increased. The enzymatic activities of superoxide dismutase and ascorbate peroxide increased initially at lower concentration of arsenate but declined at higher concentrations and longer duration of treatment. The catalase activity was found to be most susceptible to arsenate stress as its activity started declining from the very beginning of the experiment (Bajpai et al. 2012).

It is evident that most of the As metalloid associated with anthropogenic sources deposited directly over the lichen surface. The recorded significant difference in As concentrations among exposure areas may further emphasise the acceptance of lichen to monitor As from the atmosphere. In Indian context more studies are required to determine the concentration of As in lichens around pollution sources in different phytogeographical areas of the country. It is also evident that past mining records in the area, vehicular emission and use of agricultural pesticides played a significant role in the release of As in the environment (Bajpai et al. 2009a).

Among the different growth forms of lichens, the foliose lichen *Pyxine cocoes* appears more suitable species for carrying out arsenic accumulation studies in India. The data obtained on various parameters in transplant study and passive biomonitoring studies clearly shows the effectiveness of *P. cocoes* as biomonitor.

### 5.2.3 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs and their homologues are synthesised by the incomplete combustion of organic material arising, partly, from natural combustion and majority due to anthropogenic emissions. In nature, PAHs may be formed three ways: (a) high temperature pyrolysis of organic materials, (b) low to moderate temperature diagenesis of sedimentary organic material to form fossil fuel, and (c) direct biosynthesis by microbes and plants (Ravindra et al. 2008). Forest fires, prairie fires and agricultural burning contribute the largest volumes of PAHs from a natural source to the atmosphere. The actual amount of PAHs and particulates emitted from these sources varies with the type of organic material burned, type of fire (heading fire vs. backing fire), nature of the blaze (wild vs. prescribed; flaming vs. smouldering) and intensity of the fire. PAHs from fires tend to sorb to suspended particulates and eventually enter the terrestrial and aquatic ecosystems as atmospheric fallout (Baumard et al. 1998). Incomplete combustion of organic matter at high temperature is one of the major anthropogenic sources of environmental PAHs. The production of PAHs during pyrolysis (i.e. partial breakdown of complex organic molecules during combustion to lower molecular weight) is the major anthropogenic contribution of PAHs to an ecosystem (Xu et al. 2006; Baek et al. 1991; Zhang and Tao 2008). As the efficiency of energy utilisation has improved, emissions of PAHs in developed countries have decreased significantly in the past decades (Pacyna et al. 2003). However, PAH deposition on the Greenland ice sheet indicates that global PAH emissions have been constant from the beginning of the industrial period up to the early 1990s (Masclet et al. 1995), suggesting that PAH emissions from developing countries have been increasing due to rapid population growth and the associated energy demand. Because of this close relationship between PAH emissions and energy consumption, a strong correlation is anticipated between PAH emissions and some social and economic parameters. Moreover, a strong correlation exists between atmospheric PAH concentrations and population (Hafner et al. 2005). PAH emission inventories have been developed for several countries (the US and UK) and regions (the former USSR, Europe and North America) (Pacyna et al. 2003; Tsibulsky et al. 2001; US EPA 1998; Wenborn et al. 1999; Galarneau et al. 2007; Van der Gon et al. 2007). China has the only PAH emission inventory for a developing country, with $km^2$ resolution and dynamic PAH emission changes from 1950 to 2004 (Zhang and Tao 2008, 2009).

Srogi (2007) has discussed in detail the effect of PAHs exposure on different components of the ecosystem together with assessment of the risks and hazards of PAH concentrations for the ecosystem (Figs. 5.1 and 5.2) as well as on its limitations. Being semivolatile organic pollutants, PAHs exists in gas and/or particulate phase depending upon the vapour pressure of the individual PAHs remaining gas and particulate phase (Table 5.4).

The PAH concentration varies significantly in various rural and urban environments and is mainly influenced by vehicular and domestic emissions. Due to the persistent nature of PAHs, they have an ability to get transported to long distances far away from their origin mainly in polar regions via regular process of volatilisation and condensation termed as 'Hoping' (Fernandez et al. 1999).

In recent years, PAHs studies have attracted attention in air quality monitoring studies mainly due to its carcinogenic and mutagenic properties (Table 5.4). Among the different PAHs, 5- and 6-ringed PAHs are known to be potential carcinogens (Fig. 5.1); benzo(*a*)

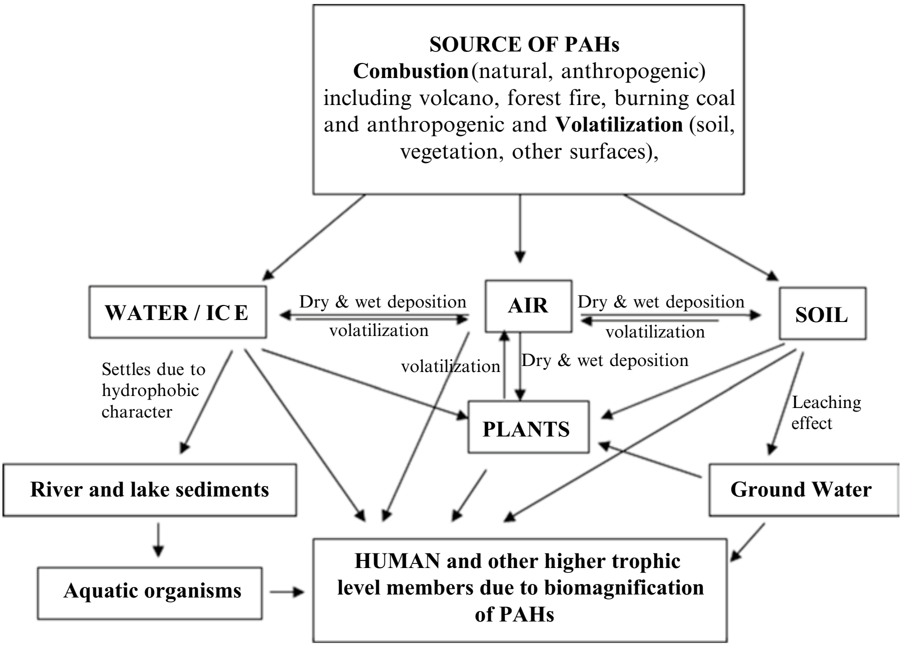


**Fig. 5.1** Fate of organic pollutants after being emitted from the source resulting in the contamination of the entire ecosystem

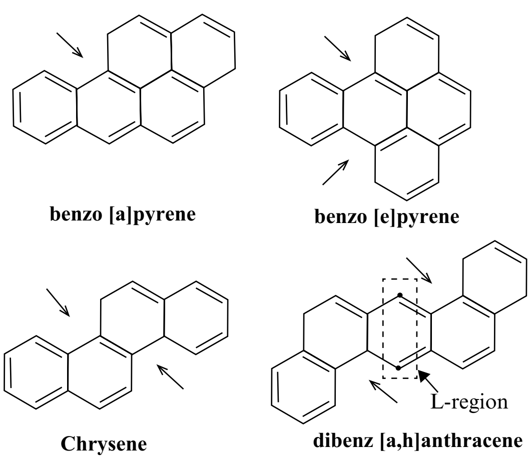


**Fig. 5.2** Mechanism of gas phase degradation of naphthalene resulting in the formation of 2-nitronaphthalene; reaction is being initiated by a hydroxyl radical (Adapted from Bunce et al. 1997 and Sasaki et al. 1997)

pyrene (B(a)P) has been identified as being highly carcinogenic (Park et al. 2002). In view of health concern, monitoring the level of particle-bound PAHs in urban areas needs urgent attention (Chetwittayachan et al. 2002). Both petrol- and diesel-fuelled vehicles produce PAHs and nitro-PAHs (Ravindra et al. 2006). Nitro-PAHs are more potent carcinogen which are being produced by gas phase degradation of naphthalene resulting in the formation of 2-nitronaphthalene (Fig. 5.3).

It has been observed that 70–75 % of the carbon in coal is in aromatic form; the 6-membered ring aromatics are dominant with a small 5-membered ring fraction present as well and dominance of particular PAHs indicates its source of origin (Table 5.5) (Ravindra et al. 2008). PAHs such as benz(*a*)anthracene, benzo(*a*)pyrene, benzo(*e*) pyrene, dibenzo(*c*,*d*,*m*)pyrene, perylene and phenanthrene have been identified in coal samples.

Terrestrial sources of PAHs include the non-anthropogenic burning of forests, woodland and moorland due to lightning strikes. In nature, PAHs may be formed in three ways: (1) high-temperature pyrolysis of organic materials, (2) low to moderate temperature diagenesis of sedimentary organic material to form fossil fuels and (3) direct biosynthesis by microbes and plants (Ravindra et al. 2008).

In the last decade there has been increased interest in quantification of organic contaminants

**Table 5.4** PAHs monitored using lichens including 16 US EPA priority PAHs, their phase distribution and related health risk

| S. No. | PAHs | Particle/gas phase distribution | Carcinogenicity |
|---|---|---|---|
| 1 | Naphthalene | Gas phase | Nitro substituted form potential carcinogen |
| 2 | Acenaphthylene | Gas phase | |
| 3 | Acenaphthene | Gas phase | |
| 4 | Fluorene | Gas phase | |
| 5 | Phenanthrene | Particle gas phase | |
| 6 | Anthracene | Particle gas phase | |
| 7 | Fluoranthene | Particle gas phase | |
| 8 | Pyrene | Particle gas phase | |
| 9 | Benz[*a*]anthracene | Particle phase | √ |
| 10 | Chrysene | Particle phase | √ |
| 11 | Benzo[*b*]fluoranthene | Particle phase | √ |
| 12 | Benzo[*k*]fluoranthene | Particle phase | |
| 13 | Benzo[*a*]pyrene | Particle phase | √√ |
| 14 | Benzo[*e*]pyrene | Particle phase | |
| 15 | Dibenz[*a*,*h*]anthracene | Particle phase | √ |
| 16 | Benzo[*g*,*h*,*i*]perylene | Particle phase | |
| 17 | Indeno[1,2,3-*c*,*d*]pyrene | Particle phase | √ |

√√ Potential carcinogen

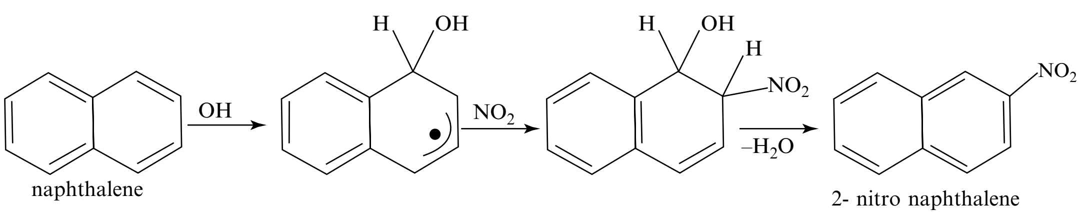


**Fig. 5.3** Molecular structures of some PAHs having bay region (depicted with *arrows*) along with L-region having location of highest electron density (depicted by *dots*) in dibenz[*a*,*h*]anthracene, responsible for carcinogenicity in PAHs (Modified from Jerina et al. 1978 and Flesher et al. 2002)

in mountain regions, especially in Europe and America (Daly and Wania 2005). Several studies in Europe have demonstrated that chemicals emitted in low latitudes may be transported to higher latitudes as part of the moving air mass, where due to cooler temperatures they condense resulting in deposition of PAHs in high-altitude ecosystems and on ice (Mackay and Wania 1995), while few studies have been conducted in the Indian Himalayas. Detailed effect of PAHs on ecosystem and health risk requires extensive sampling and modelling for interpretation of the results.

Apart from assessment of PAHs and its influence around source of pollution, long-range atmospheric transport and deposition of PAHs is another area of concern, particularly biosphere reserves which sustain high endemism of species and high-altitude ecosystems, especially snow-capped peak, glaciers and pristine alpine forest in the Himalayan region, which are exposed to long-range dispersal of pollutants, as persistent organic pollutants are volatile and can evaporate into atmosphere and are transported to high-altitude regions.

Globally various studies have been conducted using indicator species including lichens (Table 5.6) as a reliable environmental tool for spatio-temporal monitoring of PAHs to identify

**Table 5.5** Individual PAHs and their source of origin

| S. No. | PAHs | Source of origin | References |
|---|---|---|---|
| 1 | Chrysene and benzo[*k*] fluoranthene | Coal combustion | Khalili et al. (1995) and Smith and Harrison (1998) |
| 2 | Benzo[*g*,*h*,*i*]pyrene, coronene and phenanthrene | Motor vehicle emission | Smith and Harrison (1998) |
| 3 | Low-molecular-weight PAHs; fluoranthene and pyrene | Diesel trucks | Miguel et al. (1998) |
| 4 | High-molecular-weight PAHs especially B[a]P and dibenz[*a*,*h*]anthracene | Light duty vehicle | Miguel et al. (1998) |
| 5 | Phenanthrene, fluoranthene and pyrene | Vehicular activity (Salting of road during winter) | Harrison et al. (1996) |
| 6 | Phenanthrene, fluoranthene and pyrene | Emission from incineration | Smith and Harrison (1998) |
| 7 | Fluorine, fluoranthene and pyrene along with moderate level of benzo[*b*]fluoranthene and indeno[1,2,3]pyrene | Oil combustion | Harrison et al. (1996) |

emission sources, dispersal and atmospheric deposition (Augusto et al. 2009, 2010; Guidotti et al. 2003; Garćia et al. 2009; Shukla et al. 2012a).

In India PAHs accumulation studies (Table 5.7) with lichens have been recently initiated in the Himalayan region of Uttarakhand (Shukla and Upreti 2009). The PAHs accumulation in lichens of different localities of Dehradun city and on the way to Badrinath was estimated recently (Shukla and Upreti 2009; Shukla et al. 2010). The first baseline data on the distribution and origin of polycyclic aromatic hydrocarbons (PAHs) in *Phaeophyscia hispidula* collected from Dehradun city and other urban settlements of Uttarakhand exhibit the presence of 13 types of PAHs (naphthalene (0.14–5.65 ppm), acenaphthylene (0.89–22.13 ppm), fluorene + acenaphthylene (0.07–3.38 ppm), phenanthrene (0.06–6.47 ppm), anthracene (0.01–0.38 ppm), fluoranthene (0.01–3.58 ppm), pyrene (0.13–14.46 ppm), benzo(*a*)anthracene + chrysene (0.01–0.13 ppm), benzo(*k*)fluoranthene (0.01–0.03 ppm), benzo(*b*)fluoranthene (0.02–0.09 ppm), benzo(*a*)pyrene (0.00–0.03 ppm), dibenzo(*a*, *h*)anthracene (0.17–0.31 ppm), indino (1,2,3–cd ppm) and pyrene + benzo(ghi)perylene (0.00–0.20 ppm). The PAHs were of mixed origin, a major characteristic of urban environment. Significantly higher concentration of phenanthrene, pyrene and acenaphthylene indicates road traffic as major source of PAH pollution. Probable mechanism of bioaccumulation may be attributed to the donor–acceptor complex and has been reported to be formed between polycyclic aromatic hydrocarbons (carcinogenic and noncarcinogenic) and compounds of biological importance (Harvey and Halonen 1968). Therefore, PAHs (hydrophobic in nature) readily combine with these organic moiety to form adduct. The higher accumulation of 2- and 3-ring PAH in lichens may be because most of the species contains depsides and depsidones with active –OH sites, which facilitate adduct formation. *Phaeophyscia* and *Pyxine* have skyrin triterpine and lichenoxanthone (having hydroxyl group) which readily combine with most of the PAHs.

According to Domeňo et al. (2006) lichens could be used as good bioindicators for air PAHs quantification. Twelve out of the sixteen PAHs studied were found in lichen *Xanthoria parietina* samples with concentration ranging from 25 to 40 ng $g^{-1}$. The highest concentrations in lichens *Xanthoria parietina* were found for dibenzo(*a*,*h*) anthracene and benzo(*k*)fluoranthene, followed by benzo(*a*)anthracene, chrysene and fluorene. The reason of non-detection in lichens of other PAHs (five or more rings in their structure)

**Table 5.6** Studies reporting concentration of PAHs contaminants in different parts of the world

| S. No. | Chemical | Sample | Location | Date | Concentration | References |
|---|---|---|---|---|---|---|
| 1. | PAHs associated with PM | Air sample | São Paulo city, Brazil (S.A.) | Aug.–Sep. 2000 | 0.065–31.2 ng $m^{-3}$ | Vasconcellos et al. (2003) |
| 2. | PAHs associated with PM | Air sample | Hong Kong | 1993–1995 | 0.41–48 ng $m^{-3}$ | Zheng and Fang (2000) |
| 3. | PAHs | Lichen biomonitoring *Pseudevernia furfuracea* | Rieti, Italy | Nov. 1999–July 2001 | 36–375 μg $kg^{-1}$ | Guidotti et al. (2003) |
| 4. | PAHs | *Poa trivialis* (grass) and soil | Nancy (France) | March 1998 | | Bryselbout et al. (2000) |
| 5. | PAHs | Salt marsh plant, *Spartina alterniflora* | Dover, New Hampshire (U.S.A) | 2003 | BDL–71 μg $g^{-1}$ | Watts et al. (2006) |
| 6. | PAHs | SPM | Yangtze estuarine (China) | Feb. 2006–Aug. 2006 | 3- and 4-ring PAH in higher concentration | Ou et al. (2010) |
| | | Sediment | | | | |
| | | Road dust | | | | |
| 7. | PAHs | Soil | Tokushima (Japan) | NM | 1–147 μg $kg^{-1}$ | Korenaga et al. (2000) |
| 8. | PAHs | Air | Tehran (Iran) | Apr. 2004–Mar. 2005 | 18.71–3085 ng $m^{-3}$ | Halek et al. (2010) |
| 9. | PAHs | Lichen (*Parmelia sulcata*, *Evernia prunastri*, *Ramalina farinacea*, *Pseudevernia*, *Usnea* sp. *Lobaria pulmonaria*, *Xanthoria parietina*, *Hypogymnia physodes*) | Aragón valley | 2004 | 692–6,420 ng $g^{-1}$ | Blasco et al. (2008) |

**Table 5.7** Total PAHs concentration and individual PAH concentration in different lichen species collected from different regions of India

| Species | PAH | Naph | Acy | Fl and Ace | Phen | Anthr | Fluo | Pyr | B(a)A & Chry | B(k)F | B(b)F | B(a)P | D(a, h)A | IP & B (g, h, i) P | ΣPAH | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Acarospora bullata* | Mana (Uttarakhand) | 9.42 | 4.42 | BDL | 16.18 | BDL | BDL | BDL | 0.05 | BDL | BDL | BDL | BDL | BDL | 30.07 | Shukla et al. (2010) |
| *Acarospora praeradiosa* | Mana (Uttarakhand) | 2.91 | 0.21 | BDL | 16.75 | BDL | BDL | BDL | BDL | BDL | BDL | 0.05 | BDL | 0.09 | 22.98 | Shukla et al. (2010) |
| *Dermatocarpon vellereum* | Joshimath (Uttarakhand) | 10.55 | 16.31 | BDL | 6.4 | BDL | 0.36 | BDL | 0.05 | BDL | BDL | BDL | BDL | 0.05 | 33.72 | Shukla et al. (2010) |
| *D. vellereum* | Rudraprayag (Uttarakhand) | BDL–4.74 | BDL–0.29 | BDL–0.3 | BDL–0.2 | BDL–0.06 | BDL–0.16 | BDL–0.009 | 0.002–0.68 | BDL–0.013 | BDL–0.002 | BDL–0.03 | BDL–0.09 | BDL–0.04 | 0.14–4.96 | Shukla et al. (2013b) |
| *Dimelaena oreina* | Mana (Uttarakhand) | 18 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 18 | Shukla et al. (2010) |
| *Heterodermia angustiloba* | Badrinath (Uttarakhand) | 6.65 | 18.6 | BDL | 7.73 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 32.98 | Shukla et al. (2010) |
| *Lepraria lobificans* | Rishikesh (Uttarakhand) | 0.2–41.97 | BDL–1.98 | BDL–0.29 | BDL–0.11 | 0.003–1.06 | BDL–8.67 | BDL–0.04 | BDL–0.013 | 0.006–0.012 | BDL–0.009 | BDL–0.003 | BDL–0.09 | BDL–0.17 | 0.5–43.1 | Shukla (2012) |
| *Phaeophyscia. Hispidula* | Badrinath (Uttarakhand) | 0.01–2.5 | 0.26–1.51 | BDL–2.16 | BDL–2.08 | BDL–0.08 | BDL–1.2 | BDL | 0.008–2.6 | BDL | BDL–0.01 | BDL–0.06 | BDL–0.16 | BDL–0.01 | 0.68–7.7 | Shukla et al. (2010) |
| *P. hispidula* | Dehradun (Uttarakhand) | BDL–5.66 | BDL–22.14 | BDL–3.38 | BDL–6.47 | BDL–0.38 | 0.009–3.59 | 0.09–14.47 | BDL–0.132 | BDL–0.03 | BDL–0.08 | BDL–0.04 | BDL–0.18 | BDL–0.2 | 3.38–25.01 | Shukla and Upreti (2009) |
| *P. hispidula* | Dehradun (Uttarakhand) | BDL–0.24 | BDL–0.94 | 1.57–1.69 | 0.26–0.39 | BDL–0.01 | 0.4–1.85 | 0.15–2.6 | 0.14–0.18 | 0.01–0.02 | 0.02 | BDL–0.003 | BDL | BDL | 5.1–5.3 | Shukla et al. (2010) |
| *Phaeophyscia orbicularis* | Srinagar (Uttarakhand) | 0.42 | ND | 0.9 | 0.56 | 0.01 | 0.47 | ND | ND | 0.11 | 0.13 | ND | 0.04 | 0.013 | 2.653 | Shukla et al. (2010) |
| *Pyxine subcinerea* | Haridwar (Uttarakhand) | 0.025–2.9 | 0.03–42.0 | BDL–0.63 | 0.01–0.75 | BDL–0.19 | 0.043–185.8 | BDL–0.009 | BDL–0.0012 | BDL–0.002 | BDL–0.02 | BDL–0.01 | BDL–0.01 | BDL–0.009 | **1.25–187.3** | Shukla et al. (2013a) |
| *Remototrchyna awasthii* | Mahabaleshwar (Maharashtra) | BDL–5.67 | 0.07–14.47 | BDL–3.75 | BDL–4.34 | BDL–0.16 | 0.05–3.21 | 0.06–10.48 | BDL–0.32 | BDL–1.39 | BDL–1.37 | BDL–1.97 | BDL–0.59 | BDL–0.35 | 0.193–54.78 | Bajpai et al. (2013) |
| *Rinodina sophodes* | Kanpur city (Uttar Pradesh) | BDL–0.32 | 0.01–0.099 | BDL–0.16 | 0.027–0.06 | BDL–0.07 | BDL–0.06 | BDL–0.05 | BDL–0.13 | ND | ND | ND | ND | ND | 0.19–0.49 | Satya et al. (2012) |

present in the atmosphere in high concentrations may be of being almost exclusively adsorbed on suspended particulate matter. Concerning the origin of the PAHs found in the lichen, benzo(*a*) pyrene is usually emitted from catalyst and non-catalyst automobiles. Benzo(*a*)anthracene and chrysene are often resulted from the combustion of both diesel and natural gas. In both cases the origin suggests the traffic road as a major source of these compounds, which fits to other studies in which benzo(*a*)pyrene and dibenzo(*a*,*h*)anthracene indicate traffic emission and identify traffic as the main source of urban PAH emission.

Apart from quantification of PAHs (Table 5.7) lichen biomonitoring has been successfully employed to monitor the spatial behaviour of PAHs along with changes in the PAHs in the land use class and related health risk has been estimated (Augusto et al. 2009, 2010; Shukla et al. 2010, 2012a, b; Bajpai et al. 2013). In the high-altitude Himalayan ecosystem, impact of air PAHs fraction has been observed which widely influence the spatial behaviour of PAHs in the area. In a study carried out in Central Garhwal Himalayas, it was observed that the bioaccumulation of 2- and 3-ringed PAHs was higher in samples from higher altitude, while bioaccumulation of fluoranthene (4 ringed PAH), having high spatial continuity, showed higher concentration in samples from higher altitude, while PAHs with 5 and 6 rings were confined to the lower altitude at the base of the valley justifying its particulate bound nature (Shukla et al. 2012a, b).

In India PAHs profile in lichens considerably varies from site to site. Diagnostic molecular ratio has been applied to the biomonitoring data and the results were found to be in conformity with the pollution source, dominant mode of transport. As in Haridwar city, commercial and tourist activity encourages more and more diesel-driven vehicles and has been affirmed by diagnostic ratios at industrial and city centre, an important holy pilgrimage, having combustion being predominant source (Shukla et al. 2012a).

Metallic content (originating mainly due to vehicular activity) bioaccumulated in lichen correlated with its PAH concentration to trace the source of PAH in the air of Haridwar city. Lichen thalli of *Pyxine subcinerea*, collected from 12 different localities of Haridwar city were analysed. The total metal concentration of four metals (chromium, copper, lead and cadmium) ranged between 369.05 and 78.3 μg $g^{-1}$, while concentration of 16 PAHs ranged between 1.25 and 187.3 μg $g^{-1}$.

Statistical correlation studies revealed significant positive correlation between anthracene and chromium ($r = 0.6413$, $P < 0.05$) and cadmium with pyrene ($r = 0.6542$, $P < 0.05$). Naphthalene, acenaphthene, fluorene, acenaphthylene, anthracene and fluoranthene are reported to be main constituent of diesel vehicle exhaust which is in conformity with the present analysis as lead (indicator of petrol engine exhaust) had negative correlation with all these PAHs (Shukla and Upreti 2011a, b).

Growth from of lichens may also play a significant role in the accumulation of PAHs. The saxicolous, crustose and squamulose species growing on rocks mostly accumulated uniform concentration of low-molecular-weight 2- and 3-ringed compounds. The higher vehicular activities or excessive usage of wood and coal in a particular area is responsible for higher concentration of PAHs (Blasco et al. 2011).

Studies carried out till now in India establishes the utility of *Phaeophyscia hispidula* as an excellent biomonitoring organism in monitoring of PAHs from foothill to the sub-temperate area of Garhwal Himalayas and may be effectively utilised in the other part of the country with transplant studies.

### 5.2.4 Radionuclides

Radionuclides occur naturally as trace elements in rocks and due to radioactive decay of Uranium-238 and Thorium-232 resulting in release of large amount of energy in the form of ionising radiation which may be alpha, beta or gamma radiations (Table 5.8). When these ionising radiations strike a living organism, it may injure cellular integrity of the organism. Consequently it may lead to cancer and other health problems.

**Table 5.8** Common radionuclides, its sources and related health impact

| Contaminant | Sources | Health impact |
|---|---|---|
| Radium-226 | Natural | Carcinogen |
| Radium-228 | Natural | Carcinogen |
| Radon-222 | Natural | Carcinogen |
| Uranium | Natural | Kidney toxicity, carcinogen |
| Adjusted gross alpha emitters | Natural and man made | Carcinogen |
| Gross beta and photon emitter | Natural and man made | Carcinogen |

Natural radioactivity arises mainly from primordial radionuclides, like 40-K, and the radionuclides 238-U and 232-Th and their fission products. These radionuclides are present at trace levels in all rocks and ground formations with concentrations varying within a wide range in different geological settings. Soils will have concentration of natural radionuclides determined by their concentrations in the parent rock from which the soils originate and also by various geological processes. Physicochemical properties of soils also have an important role to play in the concentration, distribution and behaviour of radionuclide in soils (Baeza et al. 1995; Belvermis et al. 2010). Silicic igneous rocks like granites are considered to be important sources of uranium mobilisation as they contain higher uranium and thorium content. They are also associated with uranium deposits and contain significant amounts of labile uranium (Ivanovich and Harmon 1982). Hence, the levels of natural environmental radioactivity and the associated external exposure due to gamma radiation are observed to be at different levels in the soils of different regions in the world (UNSCEAR 1993; Patra et al. 2013).

Man-made source including the exploitation of nuclear energy for military and peaceful purposes has considerably increased the risks of higher doses of ionising radiations being received by different components of the ecosystem. The release and effect of nuclear radiation has received particular attention after the tragic accident in April 26, 1986, at the Chernobyl Nuclear Power Plant (NPP) in Ukraine, and another large-scale accident, explosion of the deposit of nuclear wastes in Kyshtym in Eastern Urals in 1957, has also been investigated (Nikipelov et al. 1990; Sawidis 1988). The Fukushima nuclear disaster in the year 2011 was a result of the location of the NPP in the high seismic zone in Japan which resulted in the release of a large amount of nuclear radiation.

It has been observed that the impact of nuclear accident is maximum within the radius of 6–8 km; the fallout of products of nuclear fuel is more or less homogenous and rather dense. At greater distances the fallout of radioactive particles of nuclear fuel was influenced by atmospheric processes and by physical peculiarities of thrown-out particles; their sedimentation was patchy and accumulation in lichens is heterogenous (Biazrov 1994).

As nuclear accidents result in considerable release of fission products of the nuclear fuel into the atmosphere in the area, therefore, application of lichen biomonitoring related with the ecological consequences of nuclear catastrophes is related to the understanding of the spatial distribution of a number of radionuclides in the thalli of different lichen species and elucidation of both general patterns and regional features of the accumulation of radionuclides in the thalli of lichens from the nuclear accidents both spatially and temporally (Biazrov 1994).

A number of studies carried out before and after the Chernobyl accident, have demonstrated that lichens and mosses can accumulate high amounts of radioactivity (Hviden and Lillegraven 1961; Eckl et al. 1986; Papastefanou et al. 1988, 1992; Seaward et al. 1988; Hanson 1967). Interest in the behaviour of radionuclides in natural ecosystems was first developed during the 1960s, at the time of weapons testing in the atmosphere, because of the observed transfer of Cs-137 along the lichen–reindeer–man food chain (Hanson 1967).

The most critical food chain in the world for concentrating airborne radionuclides is the lichen–caribou–human food chain. Lichens accumulate atmospheric radionuclides more efficiently than other vegetation due to their lack of roots, large surface area and longevity. Uptake from the substrate is minimal compared with the uptake from wet or dry deposition. Lichens are the main winter forage for caribou, which in turn, are a main dietary staple for many northern Canadians. Thus, airborne radionuclides, particularly cesium-137 (137Cs), lead-210 (210Pb) and polonium-210 (210Po), are transferred efficiently through this simple food chain to people, elevating their radiological dose (Thomas and Gate 1999).

Lichens have been frequently used to monitor spatial patterns in radioactive deposition over wide areas (Feige et al. 1990). Terricolous lichens as well as epiphytic lichens may be effectively utilised as biomonitors (Sloof and Wolterbeek 1992). Radiocesium content in Finnish lichens was 5–10 times higher than in higher plants before 1960, but after 1965, there was a rapid decrease of nuclear weapon tests and subsequently radionuclide fall out. There was no apparent decrease in concentration in lichens (Salo and Miettinen 1964; Tuominen and Jaakkola 1973).

Radiocesium uptake is generally highest in terricolous and lowest in epiphytic lichens, epilithic species ranging in between which depends on several factors, such as the inclination of the thallus and its hydration physiology (Kwapulinski et al. 1985a, b). Guillitte et al. (1994) found that lichens with a horizontal thallus occurring on tree branches were twice as contaminated as those with a vertical thallus growing on tree trunks. Most of the radiocesium is deposited at the thallus surface, whereas uptake from the soil seems to be negligible; only 2 % of the soil radiocesium can penetrate into terricolous lichen thalli. Hanson and Eberhardt (1971) found a seasonal cycle of radiocesium in lichens, with maximum values in summer and a minimum in midwinter. The distribution of radiocesium in lichen thalli was the object of several studies, starting from the early 1960s. In fruticose lichens the apical parts of the thalli contain 2–14 times more cesium than the basal parts (Paakola and Miettinen 1963; Hanson 1967). The mobility of radiocesium inside the thallus was studied by Nevstrueva et al. (1967); results indicate that Cs and Sr are rather mobile within the thallus, Cs being less leachable. *Cladonia stellaris* was periodically monitored in Sweden from 1986 to 1990 which showed that there was a slight downward movement of radiocesium through the lichen carpets; however, some 70–80 % of radiocesium still resided in the upper 3 cm (Kreuzer and Schauer 1972; Mattsson 1974). According to Hanson and Eberhardt (1971), the concentrations of radiocesium are relatively stable in the upper parts of terricolous lichens, but the radionuclide is apparently cycled between the lower portions of the lichen mats and the humus layer. Feige et al. (1990) studied the radionuclide profile of *Cetraria islandica* and *Cladonia arbuscula*: the radionuclides are almost uniformly distributed throughout the thalli, although the upper parts of *Cladonia arbuscula* appear to be more radioactive than the lower parts. In *Cetraria islandica*, the apothecia tend to accumulate more radionuclides than the rest of the thallus. Some of the pictures show also the presence of locations with higher concentration corresponding to products of nuclear fusion or to highly radioactive particles deriving from the Chernobyl accident and trapped inside the thalli. The same authors have also tried to wash the lichens in deionised water: after a week only 8 % of the radionuclides were removed, and after 2 weeks the removal interested only 3 % of the remaining radioactivity (Nimis 1996).

Morphological differences between species may play an important role in their capacity to intercept and retain radiocesium. Kwapulinski et al. (1985a, b) found species-specific differences in four species of *Umbilicaria* collected in Poland. Sloof and Wolterbeek (1992) studied radiocesium accumulation in a foliose lichen, *Xanthoria parietina*, and expressed the activity on a weight and on an area basis and found large variations between parts of the thallus with and without fruit bodies, whereas the average radiocesium activity expressed per surface area was almost constant. In general, lichens, especially foliose and fruticose species, have a high surface area to mass ratio; this property is often reported as one of the main reasons for their relatively high capacity to accumulate heavy metals and radionuclides (Seaward et al. 1988; Nimis et al. 1993). Like in higher plants, uptake and release of cesium in lichens may be affected by the chemically related and physiologically important elements, potassium, sodium and, in a lesser degree, calcium (Tuominen and Jaakkola 1973). This factor, however, seems to be important only on a physiological level. Much less studied are the physiological mechanisms underlying radiocesium uptake by lichens. According to Tuominen and Jaakkola (1973) some process of cationic exchange should be involved. However, Handley and Overstreet (1968) demonstrated that the fixation of radiocesium in lichen thalli does not depend on their physiological activity, being mostly a passive phenomenon.

According to Subbotina and Timofeeff (1961), however, radiocesium ions were still strongly bound and difficult to remove from partially decomposed thalli. This would suggest that the ions are transported into the thallus and bound to cytoplasmic molecules through processes of active translocation. There is some evidence that lichens are more resistant than other organisms to high radioactivity: according to Biazrov (1994), lichen thalli measured near Chernobyl showed extremely high radioactivity values, but these did not cause any visually discernible anomalies in the development of lichen thalli, confirming the data on the high resistance of lichens to radioactive irradiation earlier presented by Brodo (1964). The biological half-time of radiocesium in lichens is very variable, depending on the species and especially on precipitation (Tuominen and Jaakkola 1973). The literature values range from 2.7 to 17 years. The effective half-life of radiocesium in carpets of *Cladonia* was estimated differently by different authors: from 5 to 8 years, to 17+4 years, and 7–8 years in the upper 3 cm and about 8–10 years in the whole carpet (Ellis and Smith 1987; Lidén and Gustavsson 1967). Martin and Koranda (1971) gave a biological half-time of ca. 8 years in interior Alaska and of 3–3.7 years in coastal areas. These differences might be due to differences in precipitation between the humid coastal areas and the relatively dry internal regions. Lidén and Gustavsson (1967) suggested that as time elapses from the moment of deposition, the effective half-life of radiocesium for lichens will increase. In Canada, after the cessation of nuclear weapons' testing in 1962, the cesium deposited as fallout was available to agricultural plants for only a few years (Bird 1966, 1968); further north, the fallout was not lost as quickly; lichens, mosses and vascular cushion plants between 60° and 70°N demonstrated significant available Cs-137 in the 1980s, long after it had disappeared from the more contaminated regions further south (Hutchinson-Benson et al. 1985; Meyerhof and Marshall 1990). According to Hanson (1967), the biological half-life period in *Cladonia stellaris* is of 3–6 years when deposition has happened in the liquid form, of 1–13 years when it has occurred in the gaseous form. Different formulas to calculate the removal half-times in lichens were proposed (e.g. Gaare 1990; Sloof and Wolterbeek 1992). However, a generalisation is probably difficult: different factors affect the actual half-life of radiocesium in lichens; some of them depend on features of the lichen itself, such as growth rates, genetic variability and density of fructifications; others depend on characteristics of the station, such as microclimatic variability, leaching of the substrata and geographic situation. The sampling techniques, as well, may have an influence on the estimates: different values might be obtained if sampling the upper vs. the lower parts of the thalli.

The estimation of the residence time of long-lived radionuclides in lichens and mosses is important for mineral cycling studies in natural ecosystems, especially in case of edible species, because of their important role in the food chain (Iurian et al. 2011).

Biological half-life, also termed as ecological half-life, residence time or environmental half-life, refers to the time it takes to reduce the amount of a deposited element to half its initial value by natural processes. The effective half-life is the time taken for the amount of a specified radionuclide in the body to decrease to half of its initial value as a result of both radioactive decay and natural elimination.

Lichens are living accumulators of natural and man-made radionuclides and heavy metals (Table 5.9) (Eckl et al. 1986; Seaward 1992; Jeran et al. 1995; Boileau et al. 1982). Gorham (1959) reported for the first time that lichens are

**Table 5.9** Levels of radionuclide content in different lichen species

| S. No | Lichen | | Radionuclide content | | | | | | | | References |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Ra-226 | Pb-210 | Mn-54 | Zn-65 | Sr-90 | Cs-137 | Ce-Pr-144 | U-238 | |
| 1 | *Cetraria nivalis* (pCi $gm^{-1}$ dry weight) | Greenland | – | – | 0.8 | 1.0 | 4.9 | 12.0 | 13.2 | – | Hanson (1971) |
| 2 | *Alectoria ochroleuca* | Greenland | – | – | 0.07 | 2.3 | 2.6 | 13.3 | 17.6 | – | |
| 3 | *Cetraria delisei* | Greenland | – | – | 1.9 | 0.9 | 1.4 | 25.0 | 11.5 | – | |
| 4 | *Stereocaulon paschale* | Greenland | – | – | N.D. | 1.6 | 4.7 | 20.0 | 14.9 | – | |
| 5 | *Cladina stellaris* (Bq $kg^{-1}$ dry weight) | Polar Urals | – | – | – | – | 90–150 | 190–450 | – | – | Nifontova (2000) |
| 6 | *Cladina stellaris* | Northern Urals | – | – | – | – | 50–100 | 120–310 | – | – | |
| 7 | *Flavocetraria nivalis* | Polar Urals | – | – | – | – | 50–160 | 100–430 | – | – | |
| 8 | *Flavocetraria nivalis* | Northern Urals | – | – | – | – | 70–90 | 220–230 | – | – | |
| 9 | *Hypogymnia physodes* (Bq $kg^{-1}$ dry weight) | Slovenia | 6–279 | 175–1904 | – | – | – | – | – | 0.14–6.16 | Jeran et al. (1995) |

much more efficient in accumulating radiocesium than higher plants, hence representing suitable bioindicators of the radioactive fallout. A good correlation is known to exist between total radiocesium content in lichens and total estimated deposition, which led to the use of these organisms as biomonitors of radioactive compounds (Hanson 1967; Nimis 1996). The large surface area of lichens, relative to their mass, is one of the main reasons for their relatively high capacity to accumulate radionuclides or other elements, like heavy metals. Handley and Overstreet (1968) demonstrated that the fixation of radiocesium in lichen thallium does not depend on their physiological activity, being mostly a passive phenomenon. In general, epigeic lichens accumulated higher Cs-137 concentrations than epiphytic lichens. The cesium content in the epiphytic lichens is mostly due to the absorption of the airborne radionuclides, unlike the epigeic lichens which can accumulate the Cs-137 from air but also through the exchange of cesium atoms between the lithogenic substrate and lichen thallus. Moreover, epiphytic lichens are somehow protected from any kind of contamination, by the crown of the tree on which they grow.

Radionuclide concentrations, e. g. in the thalli of lichens, exceed by far the content of the same substances in various organs of vascular plants (Biazrov and Adamova 1990; Adamova and Biazrov 1991). As was revealed experimentally, these organisms are capable of retaining high dosages of ionising radiation (1,000 R/24 h during 22 months) without detrimental effects (Brodo 1964).

Cesium-137 concentrations in lichen and moss samples have been studied for calculations of natural depuration rates. The natural depuration rates are estimated at biological half-lives. The biological half-lives of 137Cs in a lichen and moss samples (*Xanthoria parietina* and *Leucodon immersus*) are estimated to be 58.6 and 10.9 months, respectively. The result supports the view that radioactivity monitoring in lichens can be a more useful monitor than mosses to determine the lasting effect of radioactive fallout (Topcuoğlu et al. 1995).

It has been studied that high nuclear irradiation does not cause any visually discernable anomalies in the development of lichen thalli which imparts high resistance to lichens to radioactive irradiation and makes them a bioindicator of nuclear fallout (Brodo 1964).

Specific activity of Cs-137, K-40 and Be-7 in four lichen species were chosen for the calculation of biological half-times: the epiphytic lichens *Pseudevernia furfuracea* (from *Betula pubescens*) and *Hypogymnia physodes* (from *Betula verrucosa*), specific for the mountainous and subalpine regions, and the epigeic lichens *Cladonia squamosa* and *Cladonia fimbriata.*

Natural samples of lichen *Peltigera membranacea* were tested for uranium sorption mechanism. Thalli were incubated in solutions containing 100 ppm U for up to 24 h at pH values from 2 to 10. U the pH range 4–5. Maximum U uptake by *P. membranacea* averaged nearly 42,000 ppm which represented the highest concentration of biosorbed U of any lichen reported. Electron probe microanalysis (EPM) revealed that U uptake is spatially heterogeneous within the lichen body, and U attains very high local concentrations on scattered areas of the upper cortex. Energy dispersive spectroscopic (EDS) analysis revealed that strong U uptake correlates with phosphate signal intensity, suggesting involvement of biomass-derived phosphate ligands or surface functional groups in the uptake process (Haas et al. 1998).

Differences in radionuclide content have been observed between the lichen species growing on different mountain rocks and slopes and at different elevations. These differences depend both on the structural and functional characteristics of lichen species and on specific climatic and ecological conditions at the site of their growth (Seaward 1988; Nifontova 2000).

However, in India no such study has been carried out yet but it has prospects as India has large deposits of thorium in the southern coast of the country as well as use of nuclear energy in power generation is also starting. Therefore, in view of the studies carried out worldwide, study of the spatio-temporal behaviour of these radionuclides, lichen biomonitoring may be explored in India as sentinels of radionuclides.

### 5.2.5 Climate Change

Many chemical compounds present in the earth's atmosphere act as greenhouse gases. Some of them occur in nature (water vapour, carbon dioxide, methane and nitrous oxide), while others are exclusively human-made (like gases used for aerosols). These gases allow sunlight to enter the atmosphere freely. When sunlight strikes the earth's surface, some of it is reflected back towards space as infrared radiation (heat); it gets trapped by these compounds. In order to maintain temperature equilibrium over time, the amount of energy sent from the sun to the earth's surface should be about the same as the amount of energy radiated back into space, leaving the temperature of the earth's surface roughly constant. But the presence of greenhouse gases which absorb this infrared radiation and trap the heat in the atmosphere causes imbalance resulting in global temperature rise. Levels of several important greenhouse gases have increased by about 25 % since large-scale industrialisation began around 150 years ago. During the past 20 years, burning of fossil fuel is the source of anthropogenic carbon dioxide emissions. Concentrations of carbon dioxide in the atmosphere are naturally regulated by carbon cycle. The movement (flux) of carbon between the atmosphere, land and oceans is dominated by natural processes via plant photosynthesis. These natural processes can absorb net 6.1 billion metric tonnes of anthropogenic carbon dioxide emissions produced each year (measured in carbon equivalent terms); an estimated 3.2 billion metric tonnes is added to the atmosphere annually. The earth's positive imbalance between emission and absorption results due to continuing increase in greenhouse gases in the atmosphere due to excessive anthropogenic contribution. World carbon dioxide emissions was expected to increase by 1.9 % annually between 2001 and 2025 mainly in the developing world where emerging economies, such as China and India, where fossil fuel is used for energy generation. In the developing countries emissions are expected to grow at 2.7 % annually between 2001 and 2025 and surpass emissions of industrialised countries near 2018 (http://www.eia.gov/environment.html; US Energy Information Administration 1998).

Global-warming potential (GWP) is a relative measure of how much heat a greenhouse gas traps in the atmosphere. It compares the amount of heat trapped by a certain mass of the gas to the amount of heat trapped by a similar mass of carbon dioxide. A GWP is calculated over a specific time interval, commonly 20, 100 or 500 years. GWP is expressed as a factor of carbon dioxide (whose GWP is standardised to 1). For example, the 20-year GWP of methane is 72 (IPCC 2007). The GWP depends on the following factors:

1. The absorption of irradiation by the compound
2. The spectral location of its absorbing wavelengths
3. The atmospheric lifetime of the compound

The combustion of fuels mainly releases $SO_2$, NOx, CO and ozone. NOx is easily oxidised to $HNO_3$ (the resulting lifetime of NOx is approximately 1 day); it cannot be directly transported over long distances. Additionally, $HNO_3$ in the troposphere is removed quickly by deposition and is not an effective reservoir for NOx. However, research in the past decades has shown that peroxyacetyl nitrate (PAN) is a more efficient reservoir for NOx in long-range transport (Hov 1984; Staudt et al. 2003).

Ozone is a major pollutant in the intercontinental transport research not only due to its adverse effects on air quality and climate over the downwind regions but also because of the complexity in the photochemistry involved in its production and destruction along the transport process. Recent surface ozone measurements in Asia in comparison with earlier measurements indicate that Asian ozone concentrations have increased significantly in the last few decades (Intergovernmental Panel on Climate Change IPCC 2001), due to increases in anthropogenic emissions of ozone precursors in Asia (for details see in Sect. 5.2.5).

Carbon monoxide (CO) a product of incomplete combustion, can be effectively transported globally due to its long lifetime of 1–3 months in the troposphere (Staudt et al. 2001; Liu et al. 2003). A major source of the springtime Asian CO outflow is biomass burning in Southeast Asia, extending from northeast India to southern China and maximising in Burma and Thailand (Heald et al.

2003). The air plumes from biomass burning are transported over the Pacific at lower latitudes than typical of other Asian anthropogenic pollutants (Heald et al. 2006). The CO, however, oxidises very fast and forms $CO_2$, which though is not noxious but is one of the major contributors of greenhouse effect. This implies a reduction of CO, hence $CO_2$ emissions, can only be achieved by improving the engine efficiency or by using fuels containing lower concentration of carbon such as natural gas.

The compressed natural gas (CNG) is a clean-burning alternative fuel for vehicles (Kathuria 2002) with a significant potential for reducing harmful emissions especially fine particles. It has been observed that diesel combustion emits 84 gram per kilometre (g/km) of such components as compared to only 11 g/km in CNG. The levels of greenhouse gases emitted from natural gas exhaust are 12 % lower than diesel engine exhaust when the entire life cycle of the fuel is considered. It has also been found that one CNG bus achieves emission reduction equivalent to removing 85–94 cars from the road. The emission benefits of replacing conventional diesel with CNG in buses lies on the fact that it results in reduction (%) of CO, NOx and PM to 84, 58 and 97 %, respectively (Kathuria 2004).

Another potential greenhouse gas (GHG), methane ($CH_4$) is involved in a number of chemical and physical processes in the earth's atmosphere. In the global $CH_4$ cycle, substantial amount of $CH_4$ is consumed by biological processes. The only known biological sink for atmospheric $CH_4$ is its oxidation in aerobic soils by methanotrophs or methane-oxidising bacteria (MOB), which can contribute up to 15 % to the total global $CH_4$ reduction. Methanotrophs, Gram-negative bacteria that utilise $CH_4$ as their sole source of carbon and energy, play a crucial role in reducing global $CH_4$ load due its $CH_4$ consumption characteristics (Singh 2011).

Although the complexity of the natural system sets fundamental limits to predictive modelling, the approach is useful in obtaining a first approximate estimate for the potentially dramatic impact of climate change on biodiversity. Models that can elucidate the correlations between climate and biophysical processes and thus increase ability to predict the consequences of the effects of climate change on distribution of species and their habitats should be developed (Sutherland et al. 2006). Better information on the climate sensitivity of species is essential to be able to detect responses of individual species to climate change, to assess critical levels and to develop anticipatory strategies. Thus, there is a need to find appropriate indicators to identify the effects of climate change, to verify results of modelling and to determine the response of species (Sutherland et al. 2006; Bässler et al. 2010).

The effects of climate change can be best monitored in alpine and montane ecosystems, as clearly described by Grabherr et al. (1994). Mountain species are unusually sensitive to the climate and are threatened by climate change (Pauli et al. 2007; Thuiller et al. 2005) because they lose parts of their range. The effects of warming are worsened by the disproportionately rapid decrease in available land surface area with increasing altitude. Species in low mountain ranges are limited in how they can adjust their ranges in response to increasing temperature. Currently, the most relevant physical and temporal scales of ecological investigation are local (Walther et al. 2002). At this local scale, there is a need to consider a variety of taxonomic groups (Ellis et al. 2007). At a regional scale, a strong impact of global warming on various taxonomic groups is expected, with some species becoming extinct. The species–environment relationship for high-montane species is expected to be less complex and seems to be dominated mainly by the effect of low temperatures for several taxonomic groups. Thus, it is assumed that climate warming will lead to a sensitive behaviour, specifically to changes in distribution in the form of decreasing probability of occurrence. These selected species are hence good indicators at a regional scale, suitable for long-term monitoring designed to validate results from modelling and to determine the response of species to climate change. It is assumed that all high-montane species will have the same response driven by the same environmental factors, which would make most of these species suitable as cross-taxon climate-sensitive indicators. Such indicator species might reduce the potentially high costs of climate change monitoring of species inhabiting more complex systems at lower altitudes (Chapin and Körner 1994).

Lichens are considered as sensitive indicators of global warming, as the spread of several thermophilous epiphytes in north-western Central Europe has been attributed to late twentieth-century warming (Hauck 2009). Occurrence of range expansions especially in the western-most parts of temperate Europe with its mild climate supports the hypothesis that these recent changes in the distribution or regional frequency of lichen species are driven by rising temperatures. In the recent years some thermophilous lichen species strongly increased in frequency, such as *Candelaria concolor*, *Flavoparmelia caperata*, *Hyperphyscia adglutinata*, *Hypotrachyna* sp., *Parmotrema perlatum* and *Punctelia borreri* (Søchting 2004; Aptroot and van Herk 2007). Others lichen species have invaded Western Europe from outside (*Heterodermia obscurata*, *Physcia tribacioides*) (Wolfskeel and van Herk 2000). Some lichens from cold environments with arctic alpine or boreal-montane distribution patterns have declined at lowland sites and on isolated mountains of temperate Western and Central Europe (Aptroot and van Herk 2007).

Biological monitoring (with epilithic lichens) of the local consequences of anticipated global climate change has been studied in Israel. The study was based on standardised protocol which included sampling scheme, including lichen measurement along transects on flat calcareous rocks, and construction of a trend detection index (TDI). TDI is a sum of lichen species cover with coefficients chosen so as to ensure maximum ability to detect global climate trends. Coefficients were estimated along an altitudinal gradient from 500 to 1,000 MSL. The gradient study demonstrated that the TDI index is performed better than other integrated indices. Measuring, for instance, a 100 transects in 50 plots (two-transect-per-plot scheme) allows one to detect a climate-driven change in the epilithic lichen community corresponding to a 0.8 C shift in annual mean temperature. Such resolution appears sufficient in view of global warming of 2.5 C considered by the Intergovernmental Panel on Climate Change as a realistic prediction for the end of the next century (Insarov et al. 1999; Insarov 2010).

Change in the lichen diversity in relation to climate change has been well worked out (Hauck 2009; Aptroot and van Herk 2007), but in India few such studies have been carried out (Joshi et al. 2011, 2008) which revealed terricolous lichens respond to global warming as their distribution has been restricted due to warming phenomenon. In the Himalayas (Pindari region) green algae-containing lichens exhibit an increase in number than cyanolichen based on comparison of the past published account of lichens three decades earlier as well as there has been increase in trentepohiliod lichen species and decrease in soil- and rock-inhabiting lichens (Joshi and Upreti 2008).

Another aspect related with climate change is increased UV-B radiation due to ozone depletion caused by Chloro Fluoro Carbons (CFCs). This phenomenon is quite pronounced in the polar region. Spring time ozone depletion in the polar region is due to release of chlorofluorocarbons in the earth atmosphere and is a serious cause of concern among environmentalists. Flora of Antarctic is mostly dominated by cryptogamic plants with limited distribution mostly confined to Sub-Antarctic region. Cryptogams being photoautotrophic plant, for light requirements, are exposed to extreme seasonal fluctuation in photosynthetically active radiation (PAR) and ultraviolet (UV) radiation. Antarctic cryptogams are known to withstand the enhanced UV radiation by synthesis of screening compounds (UV-B-absorbing pigments and anthocyanin compounds). A major part of the UV-absorbing compounds appeared to be constitutive in lichens which are usnic acid, perlatolic acid and fumarphotocetraric acid which is particularly induced by UV-B. Secondary metabolites such as phenolics, parietin and melanin also enhance the plant defence, by different molecular targets in specific solar irradiance and potential for increased anti-oxidative protection to UV-induced vulnerability (Singh et al. 2011).

Photoprotective potential of desiccation-induced curling in the light-susceptible old forest lichen, *Lobaria pulmonaria,* also provides evidence for morphological adaptations in lichens to tolerate high incident radiation (Barták et al. 2006).

Although the use of indicator species remains contentious, it can be useful if some requirements are fulfilled (Carignan and Villard 2002; Niemi and McDonald 2004). Correlation of changes at community or individual levels of lichens correlates better with changes in the land-use class and air quality rather than rising temperature. Therefore, these aspects need special consideration while utilising changes in lichen diversity in predicting the impact of climate change on biodiversity (Hauck 2009).

### 5.2.6 Assessment of Paleoclimatic Conditions (Lichenometry)

Quantitative estimation of paleoclimate is fundamental to the reconstruction of past environmental and biotic change and provides a baseline for predicting the effects of future regional and global climate change (Liu and Colinvaux 1988; Wilf 1997; Behling 1998). Some of the most widely used methods employ biological proxies such as pollen, diatoms or plant megafossils.

Accelerated rate of melting of glaciers due to global warming is a worldwide phenomenon, especially in tropical region. Due to temperature rise glaciers are melting rapidly causing the shrinking, subsidence and retreating of glaciers with the result of expansion and formation of glacial lakes to the stage of potential glacial lake outburst floods (GLOFs). The glacier retreat phenomena has been taking place rapidly in recent decades, with the common and widespread fear of too much water (GLOFs) and too little water (glacier retreat). Temperature, precipitation and humidity have changed significantly over the last half century (Vuille et al. 2008). Studies show a temperature increase of around 0.6–0.2 °C since 1900 (Lozan et al. 2001). In a study carried out in Northern Pakistan, increased seismic activity has been correlated with rise in temperature which results due to isostatic rebound of earth caused by loss in mass of glaciers, termed as 'unloading phenomenon' (Usman et al. 2011).

Himalayan region is one of the most dynamic, fragile and complex mountain ranges in the world due to tectonic activity and a rich diversity of climates, hydrology and ecology. The high Himalayan region is the fresh water source of largest river systems in Asia, on which over 1.3 billion peoples are dependent. The melting of snow and ice from these glaciers and snowmelt runoff from the mountains is of course just a part of the water supplies of these rivers. The instabilities can impact people severely, especially those residing within or near the mountains (Kulkarni 2007).

Lichenometric techniques is very useful in dating moraine ridges on recent glacier forelands in alpine regions, as once attached to substratum, the position of lichen thallus during the entire lifespan does not change; therefore, the age of lichen is an alternate for the minimum exposure time of a substrate to the atmosphere and sunlight. Lord William Hamilton (1730–1803), a naturalist, first applied botany on geological dating problems and tried to relate the density and type of vegetation cover with the age of lava flows of Vesuvius. The basic concept of lichenometry is based on the similar approach. The use of lichens growth for relative dating of the surfaces was first proposed by the botanist Knut Faegri in the 1930s which was further expanded by the Austrian botanist Roland Beschel in the 1950s (Beschel 1950; Joshi and Upreti 2008). Lichenometry has majority of applications from dating glacier moraines, landslides and fluvial deposits to calibrating the age through the formation of old monuments, buildings and other archaeological structures (Innes 1985). The applications of lichenometry based on different palaeoclimatic events, reconstructions and man-made artefacts used lichenometry in reconstructing the Holocene environment from deltaic deposits in northeast Greenland. Gob et al. (2003) used the technique in Figarella river catchment in France. The dating was performed on lichens present on terrace pebbles to determine the period of their deposition or terrace formation and incision of the river. According to the study the Figarella underwent three major incision phases. The highest level of 20–25 m did not have any

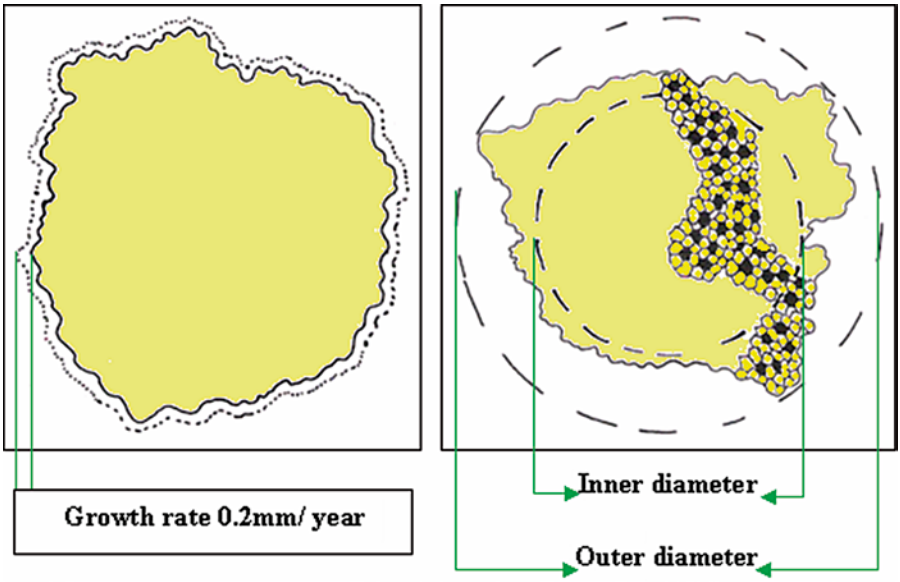


**Fig. 5.4** Lichenometric studies are based on annual growth rate of radially growing lichens as in *Rhizocarpon geographicum*

lichen colonisation and was inhabited by high, dense scrub. The maximum lichen size below 12 m of terrace was 11 cm that envisaged the age of the terrace formation about 1,800 years. This leads us to conclude that the river began to incise and transform the pebble sheets in the terrace about 2,000 years ago. The third level was at 3 m and represented by largest thalli size of 7 cm that indicates 400 years old terrace level. The study also highlighted the relation of boulder transportation with palaeofloods. The presence of largest lichen thalli on riverbed boulders indicated the longevity of their stable conditions. That in turns gave an idea of the last or ancient flood occurrences (Joshi et al. 2012).

An interesting and rather unnoticeable application of lichenometry is to date the prehistoric eruption of volcanoes in a particular landscape. On account of high tolerance, lichens can survive in extreme conditions of heat. Many lichens such as *Caloplaca crosbyae, Dirinaria aegialita, D. applanata, Candelaria concolor, Ramalina umbilicata, Hyperphyscia adglutinata, Syncesia* and *Xanthoparmelia* sp. are known to grow on magma (Jorge-Villar and Edwards 2009).

Dating range depends on the specific species and environmental factors. In temperate environments foliose form is expected to survive about 150 years, while crustose forms can provide dating 400–600 years, and at high latitudes, dating may exceed 1,000 years (Winchester 2004). Absolute dating is based on the size of the largest surviving lichen. Therefore, reference to their specific details should be taken as minimum approximations only. Other factors leading to lichen mortality and renewed colonisation are competition for growing space on the rock surface, vegetation rate, weathering and geomorphic changes (Joshi 2009). In alpine environments, growth of *Rhizocarpon geographicum* is very slow, i.e. 0.2 mm year$^{-1}$ (Hansen 2008).

In India, lichenometry has been initiated in the initial years of the last decade. But lack of valuable information in the study sites in favour of palaeoclimatic conditions and surfaces to date is the major problem in the application of the technique in India (Joshi and Upreti 2008). In a study carried out in Pindari glacier, lichen, *Rhizocarpon geographicum,* with a known growth rate of 0.2 mm year$^{-1}$ was selected to date recent glaciations activity in the area (Fig. 5.4).

Advantage of applying lichenometry in reconstruction of paleoclimate with some restrains lies on simple methodology, where the other surface dating tools such as radiocarbon dating, dendrochronology and weathering techniques face difficulties. Species identification in the field, influence of environmental factors on growth rate, nature and timing of colonisation (colonisation delay), absence of reproducibility in many published sampling designs, the supposed inadequacy of a single parameter as an index of age and difficulties associated with the methodology of growth rate determination are some of the drawbacks in the implementation of lichenometry. However, as the technique is widely used in relative or approximate dating, its role in tectonic, geomorphic, geo-chronological studies and in other landform evolutions underlies the importance of the technique.

### 5.2.7 Loss of Biodiversity

Both natural and man-made disasters are responsible for the loss of biodiversity. Natural catastrophes include volcanic eruptions, hurricanes, heavy rains and floods, while economic growth is also causing decline in biodiversity. In most of South Asia, the percentage of land area in which nature is protected is low compared to that in the developed world. Most of the protected areas in India and Pakistan are only partially protected. Of all the major South Asian countries, as far as the area afforded nature protection is concerned, Sri Lanka is most environmentally protected. In the case of China, a much higher proportion of its land area than in India is protected and more than 80 % of its protected area is totally protected compared to India's 24 % (Alauddin 2004).

Rapid loss of forest area results in loss of flora and fauna and leads to loss of carbon sequestration potential. Tropical forest ecosystems contain the world's greatest diversity of flora and fauna (Sporn et al. 2010). The world's tropical forests disappeared at the rate of 15 million hectares per year (equivalent to 40 % of the Japanese archipelago) during the latter half of the twentieth century. During the 10-year period from 1990 to 2000, Indonesia's forest decreased by 1.2 % (from 118.1 million to 105 million ha), Malaysia's by 1.2 % (from 21.7 to 19.3 million ha), Myanmar's by 1.5 % (from 39.6 to 34.4 million ha), the Philippines' by 1.5 % (from 6.7 to 5.8 million ha) and Thailand's by 0.7 % (from 15.9 to 14.8 million ha). The deforestation in northern China and Mongolia is mainly due to overgrazing, which is aggravating the yellow dust storm phenomenon, while deforestation in Siberia is due to commercial logging (Japan Environmental Council 2005).

Increasing demand for wood and hence commercial logging is the main cause of the forest fires as burning is the cheapest way to clear land for agricultural and construction purposes (Fig. 5.5). In Southeast Asian countries like Indonesia, Malaysia, Singapore, Brunei and Thailand, forest fires are executed to expand palm oil plantations. Since 1977 Indonesian forest fire smoke has become a regular environmental event. The smoke gets worse in dry weather, especially when coupled with the *El Niño* phenomenon (Japan Environmental Council 2005).

Boreal forest fires also result in emissions of NOx and PAN which can enhance the formation of $O_3$ in the Arctic. Current estimates of the emission ratios for NOx and PAN (relative to CO) from boreal forest fires are highly uncertain and based on few studies (Singh et al. 1996, 2000a, b).

Another negative aspect of urbanisation and population rise is increase in demand of food grains which ultimately leads to conversion of forest area into cropland. Throughout most of Asia, the area under cropland has increased. Cropland area in Bangladesh and China has decreased in the early 1990s compared to the early 1980s. In South Asia, Pakistan has experienced the highest increases in cropland, while among the countries of East and Southeast Asia, Malaysia recorded the highest increase (~47 %) followed by Indonesia (20 %). Developed countries with the exception of Australia and Germany have recorded declines in cropland area. Land under permanent pasture has virtually remained unchanged for Indian subcontinent, while India and Nepal have recorded declines in their respec-


**Fig. 5.5** Clearing of forest for construction, preparation of crop land and selective logging of trees has resulted in forest decline and loss of biodiversity

tive areas. All the Asian countries have experienced decline in the natural forest cover. Pakistan, Philippines and Thailand have registered much faster decline (more than 3 % per annum) than the rest (Alauddin 2004).

Naturally growing plant communities are reported to provide useful information regarding ambient air quality. Reduction in species diversity, selective disappearance of sensitive species and visible injury to the plant structure are some of the circumstantial evidences which indicate deterioration in the air quality of the area (Rai et al. 2011).

Secondary forest and plantations have lower lichen species richness compared with the primary forest as secondary rain forests lack the Thelotremataceae flora of the virgin forests. The lack of old stands and monospecific character of the plantations has led to a strong depletion and alteration of the lichen flora, with some species becoming dominant as Physciaceae members are predominant on *Mangifera indica* plantation in the majority of locations in India. Terricolous lichen (lichen growing on soil) indicates undisturbed area, Usneoid community indicates pollution-free area, while Physcioid lichen communities indicate polluted or highly polluted areas. Reduction in the thallus with closeness to the pollution source is also an indicator which can be utilised to understand the effect of point source (especially thermal power plants and industrial set ups) on air quality of the area (Chaphekar 2000; Singh et al. 1994). Changes due to forest destruction have severe impact at community level but it has rarely been documented. Among the different communities, foliicolous communities are more prone to microclimatic changes based on their substrate specificity and sensitivity. Sipman (1997) observed that clearing of forest caused foliicolous lichen species to become discoloured and moribund. Some foliicolous lichens reappear in secondary/regenerated forest but its frequency is lower as compared to primary forests.

Epigeic moss (*Hypnum cupressiforme* Hedw.) and epigeic lichen (*Cladonia rangiformis* Hoffm.) samples were collected simultaneously in the Thrace region, Turkey, where mosses were found at all sampling sites; the lichen could be collected only at 25 of the sites, presumably because lichens are more sensitive than mosses with respect to air pollution and climatic variations. All elements showed higher accumulation in the moss than in the lichen, whereas element intercorrelations were generally higher in the lichen (Coskun et al. 2009).

Lichens have been used for monitoring local hot spots of pollution, and regional patterns of pollutants which indicates the uptake of metals from the substrates, interspecies differences, and a comparison of the data with other bioindicator species provides the effectiveness of lichens as biomonitors (Garty 2001; Gombert et al. 2004).

Cyanolichens (blue-green algae-containing lichens) are useful as an indicator of forest ecosystem function in temperate and boreal forests. Cyanolichens are important in forest nutrient cycle, as these species are sensitive to both pollution and forest age continuity (Mc Cune 1993; Neitlich and Will-Wolf 2000; Sillett and Neitlich 1996). In India in an ecologically studied area of Pindari, glacier area exhibits less cyanophycean lichens than Milan glacier area. *Lobaria* and *Sticta* are sensitive to air quality as well as reliable indicators of species-rich old forest with long forest continuity (Kondratyuk and Coppins 1998; Kuusianen 1996a, b; Sillett et al. 2000; Joshi 2009).

Lichens are recognised as being very sensitive to air pollution, and in recent decades, several qualitative or quantitative methods have been proposed for assessing environmental quality of urban areas on the basis of lichen data (Seaward 1989). The correlation between $SO_2$ emissions and the nature of lichen communities led Hawksworth and Rose (1970) to develop a bioindication scale for the qualitative estimation of mean winter sulphur dioxide levels in England and Wales using epiphytic lichens. Two separate scales were prepared, one for lichens on moderately acid bark and the other for lichens on basic or nutrient-enriched bark. Several mapping studies based on this method were established (Hawksworth 1973; Belandria and Asta 1986).

Van Haluwyn and Lerond (1986) proposed a qualitative method based on lichenosociology with a 7-point scale based on easily recognisable species. Quantitative methods permit the calculation of a pollution index with a mathematical formula based on different parameters relative to the epiphytic flora. One of these is the Index of Poleotolerance (IP) proposed by Trass (1973):

$$\mathrm{IP} = \sum_{1}^{n} a \times \frac{c}{C}$$

where $n$ = the number of species, $a$ = the degree of tolerance of each species on a scale of 1–10 determined by field experience, $c$ = the corresponding level of covering and $C$ = the overall degree of cover of all species. However, the best known is the method of De Sloover and Le Blanc (1968) or IAP (Index of Atmospheric Purity):

$$\mathrm{IP} = \frac{1}{10} \sum_{1}^{n} Q \times f$$

$Q$ = the resistance factor or ecological index of each species, and $f$ = the frequency coverage score of each species.

Ammann et al. (1987); Herzig et al. (1989); Herzig and Urech (1991) tested 20 different IAP formulas, comparing IAP values with direct measurements of eight air pollutants ($SO_2$, $NO_2$, Pb, Cu, Cd, Zn, Cl and dust), and found the best correlation with the formula

$$\mathrm{IP} = \sum_{1}^{n} F$$

(model based on the sum of the lichen species frequencies). The IAP approach to bioindication has recently been reviewed by Kricke and Loppi (2002). Asta and Rolley (1999) reviewed the formula of IAP, where f represents a cover value ranked from 1 to 5 only. Other quantitative methods have been established in different countries. In Germany the VDI (1995) method is based on the calculation of the frequency of species within a sampling ladder of 10 quadrats (each 10 = 10 cm) placed against the trunk. In Italy, the methodology proposed for monitoring the effects of air pollution by phytotoxic gases ($SO_2$ and NOx) based on a measure of biodiversity calculated as the sum of frequencies of epiphytic species within a sampling ladder of 10 quadrats (each 15 = 10 cm) (Nimis et al. 1990; Nimis 1999) has been widely applied there (Giordani et al. 2002; Loppi et al. 2002). The most recent methodology, strongly standardised to provide easier comparisons throughout Europe, is not related to any pollutant, but can be considered as an indicator of general environmental quality is LDV (Lichen Diversity Value (Asta et al. 2002)).

The LDV method determines the actual state of lichen diversity before or after long-term exposure to air pollution and/or to other types of environmental stress. The interpretation of geographic patterns and temporal trends of lichen diversity in terms of pollution, eutrophication, climatic change, etc. may be assisted by using ecological indicator values and a numerical analysis of a matrix of species and relevés (Asta et al. 2002).

LDV provides a rapid, low-cost method to define zones of different environmental qualities. It provides information on the long-term effects of air pollutants, eutrophication, anthropisation and climatic change on sensitive organisms. It can be applied in the vicinity of an emission source to prove the existence of air pollution and to identify its impact, or, on a larger scale, to detect hot spots of environmental stress. Repeated monitoring at the same sites enables assessment of the effects of environmental change. Data quality largely depends on the uniformity of growth conditions: the more uniform, the more reliable are the results. A high degree of standardisation in sampling procedures is therefore necessary.

The Lichen Diversity Value (LDV) involves two steps: the first step in calculating the LDV of a sampling unit (*j*) is to sum the frequencies of all lichen species found on each tree (*i*) within the unit. Since substantial differences in lichen growth may be expected in different sides of the trunks, the frequencies have to be summed separately for each aspect. Thus, for each tree there are four Sums of Frequencies (tree *i*: SFiN, SFiE, SFis, SFiiw).

Next, for each aspect the arithmetic mean of the Sums of Frequencies (MSF) for sampling unit *j* is calculated

$$\mathrm{MSFNj} = \frac{\begin{pmatrix}\mathrm{SF1Nj} + \mathrm{SF2Nj} + \mathrm{SF3Nj} \\ + \mathrm{SF4Nj} + \cdots + \mathrm{SFnNj}\end{pmatrix}}{n}$$

where MSF is the mean of the Sums of Frequencies of all the sampled trees of unit *j*; SF is the Sum of Frequencies of all lichen species found at one aspect of tree *i*; N, E, S and W are north, east, south and west; *n* is the number of trees sampled in unit and *j* = the Lichen Diversity Value of a sampling unit *j*, LDVj is the sum of the MSFs of each aspect

$$\mathrm{LDVj} = \left(\mathrm{MSFNj} + \mathrm{MSFEj} + \mathrm{MSFSj} + \mathrm{MSFWj}\right)$$

Study on the diversity and distribution of lichens in and around Nainital city (Kumaun Himalayas) has been carried out by Kholia et al. (2011) and enumerated 105 species of lichens belonging to 48 genera and 21 families. The distribution pattern of lichens distinctly differentiated three zones (core: high pollution, intermediate: struggling zone and normal zone: good for lichen growth (Fig. 5.6)).

As lichens are well-documented indicators of air pollution, it was expected that lichen distribution and abundance would be negatively affected by air pollution (Hauck 2008). The results showed a gradient of increasing lichen cover and diversity with increasing distance from pollution discharge points. Transects upwind of these points also showed greater cover, diversity and height than those downwind of the pollution points. Comparisons between the sites revealed significantly higher cover, diversity and height at one control site. In the other control site only cover was significantly higher than that of the polluted area (Loppi and Frati 2006).

The analysis of air pollution level with metals using lichens and further statistical analysis includes calculation of the background concentrations and the contamination factors indicate extreme contaminations in the surroundings of

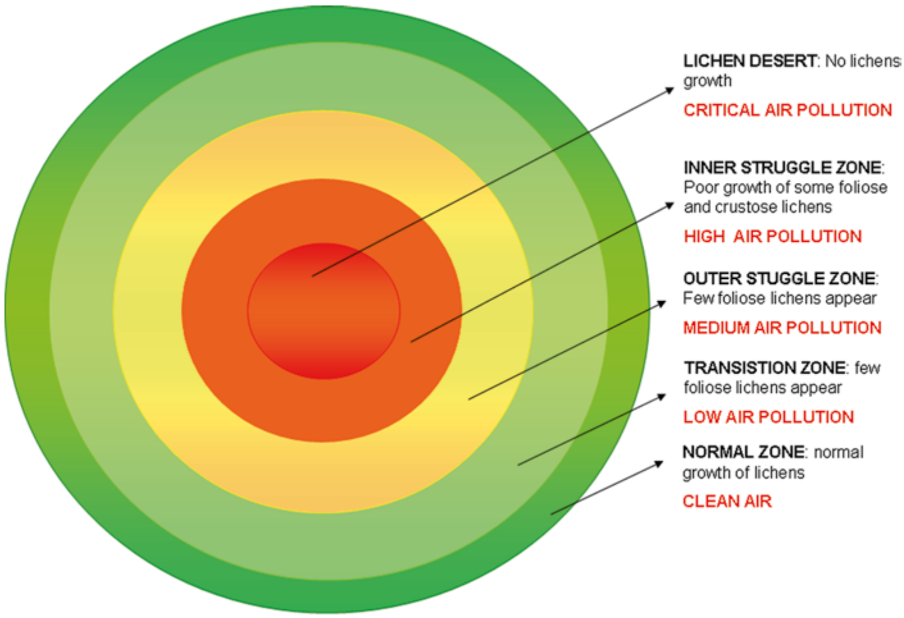


**Fig. 5.6** Five classification zones corresponding to degree of injury to lichen flora and level of total air pollution (Herzig et al. 1989)

point sources. The comparison of the distribution maps for metal concentrations enables the identification of the pollution sources (State et al. 2012).

Epiphytic lichen diversity is impaired by air pollution and environmental stress. The frequency of occurrence of lichen species on a defined portion of tree bark is used as an estimate of diversity and as a parameter to estimate the degree of environmental stress. Lichen biomonitoring provides a rapid, low-cost method to define zones of different environmental qualities. It provides information on the long-term effects of air pollutants, eutrophication and climatic change on sensitive organisms. It can be applied in the vicinity of an emission source to prove the existence of air pollution and to identify its impact, or, on a larger scale, to detect hot spots of environmental stress. Repeated monitoring at the same sites enables assessment of the effects of environmental change. Data quality largely depends on the uniformity of growth conditions: the more uniform, the more reliable are the results. A high degree of standardisation in sampling procedures is therefore necessary (Pinho et al. 2004).

Sernander (1926) recognised the disappearance of lichens from cities due to increasing pollution and conducted the systematic mapping and recognised three distinct zonations in which ‘Lichen desert’ is the city centre where the tree trunks were devoid of lichens. Struggle zone is comprised of areas outside the city centre with tree trunks poorly colonised with lichens followed by the ‘normal zone’ where lichen communities on the tree trunks were well established. Subsequently, the large number of similar city maps showed that these zonations were well correlated with the degree of pollution, the size of the urbanisation area and the prevailing winds.

Lichen diversity is adversely affected by point source. Lichen thallus size, thallus number and frequency of occurrence, along with diversity of lichens at three levels (species, generic and family) are considered as variables to see the community composition across the distance from a point source (paper mill) in Assam. Result showed that the number of lichen thallus per tree in study area ranged from 3 to 16, while thallus area per tree varied from 20 to 256.48 $cm^2$. The number of species showed high positive correlation with the number of genera, families, thalli and thallus area. The number of thalli showed high positive correlation with area covered, number of thallus and thallus area per tree. Distance from the paper mill exhibited no significant correlation with either variable. Multivariate analysis showed two major groups and two subgroups of communities. Sites which are more polluted showed a decrease in the community variables. Fifteen out of seventeen sites were the most affected ones. Epiphytic lichen community study thus can be used to study levels of pollution impact around a source of pollution (Pulak et al. 2012).

The use of lichen in mapping lichen community changes with respect to changes in air quality has been carried out employing standardised protocols in Europe and America, where lichen biomonitoring is an integral part of environmental impact assessment programme (Pinho et al. 2004). But no such protocols are standardised in Asia; majority of the biomonitoring studies carried out till date is based on random sampling of lichens from an area of interest.

Foliose and fruticose epiphytic lichens are best suited for biomonitoring studies (Seaward 1993; van Dobben and ter Braak 1999). In urban environment, sulphur dioxide along with the $NO_X$ gases (resulting from vehicular emissions) has antagonistic effect on lichen community at relatively high doses of gases in the environment (Balaguer et al. 1997). Changes in the composition of lichen diversity including frequency, density and abundance provide first-hand evidence on the alterations in air quality of an area due to air pollution or microclimatic changes (van Herk et al. 2002; Aptroot and van Herk 2007).

Since the last century there has been a considerable change/decline in the lichen biodiversity all around the world (Hauck 2009). It has been observed that rate of decline of lichen biodiversity in the Himalayan region, especially Garhwal Himalayas, is quite faster (Upreti and Nayaka 2008). There is a considerable increase in the abundance of thermophilous and poleotolerant lichens in the temperate climate of Garhwal Himalayas. (Shukla and Upreti 2011a, b; Shukla 2007). PCA analysis revealed that sites influenced with anthropogenic activity negatively contribute towards lichen diversity of the area (Shukla and Upreti 2011a, b).

In India grid plotting technique has been utilised to map lichen diversity in Lucknow city. In this study distribution of each species was plotted in 1 × 1 km grid in all direction. The distribution data of lichens collected from all the four areas, viz. north, east, west and south, provided four distinct zones, viz. Zone A, with no lichen growth, was the area within the centre of the city up to 5 km all around, Zone B showed presence of some calcareous lichens mostly in the areas with old historical buildings, Zone C had scarce growth of few crustose and foliose lichen in the localities with scattered mango trees, and Zone D showed normal growth of different epiphytic lichen taxa together with same foliicolous (leaf inhabiting) lichens, an indication of a more or less pollution-free environment (Saxena 2004).

Presence or absence of lichens has invariably been linked with environmental pollution and is used to estimate the range of pollution and pollutants from the source of emission. High or low lichen diversity is the result of various factors like certain types of air pollution, changes in forest management or stand structure, diversity of plant substrates available for colonisation, climate favourability and periodicity of fire (Jovan 2008). The widely used Shannon Index of general diversity or H index is a mimic of the so-called information theory formula that is hard to calculate factorials and combines the variety and evenness of components as one overall index of diversity (Odum 1996). It is calculated using the following formula:

$$H = -\sum\left(\frac{\mathrm{ni}}{N}\right)\log\left(\frac{\mathrm{ni}}{N}\right) \quad \text{or} \quad -\sum(\mathrm{Pi})\log(\mathrm{Pi}),$$

where ni = importance value for each species, $N$ = total of importance values and Pi = importance probability for each species.

Giordano et al. (2004) studied the relation of Shannon Index with pollution in Italy and correlated biodiversity to the total number of species ($r = 0.88$). According to Odum (1996), species diversity tends to be low in physically controlled ecosystems (i.e. subjected to strong physicochemical limiting factors) and high in biologically controlled ecosystems. Wilhm (1967) demonstrated the changes in Shannon index of diversity (*H*) of the benthos downstream from a pollution outfall. Trivedi (1981) in a number of surveys has demonstrated that pollution produces striking changes in biotic community. Some species may be unable to survive and others may persist in reduced locations and certain other species may be able to attain greater abundance. Zullini and Peretti (1986) observed the significant decrease in Shannon diversity index of moss-inhabiting nematodes on an increase of the Pb content in the moss growing near the industrial area in Italy. Junshum et al. (2008) applied three biological indices, namely, algal genus pollution index, Saprobic index and Shannon index, to classify the water quality around a power plant in Thailand and concluded that the Shannon Index of diversity appeared to be much more applicable and interpretable for the classification of water quality into three categories (clean, moderately polluted, heavily polluted) in comparison to the other two.

In a study carried out in a paper mill area in Assam (India), Shannon diversity index (*H*) of lichen community around an industry has been used to determine the effect of air pollution in the surrounding areas. The Shannon index was mapped by plotting it with the help of kriging (interpolation technique) and a pollution gradient model was prepared. It was observed that higher polluted areas with low values of Shannon index are the regions around and nearer to the paper mill and town area and around stone crusher units. It is concluded that the Shannon index is a potential indicator to measure the effect of air pollution and can be used to delineate the pollution zones around any industrial area (Pulak et al. 2012).

The comparison of the lichen diversity with an earlier study carried out during 1960–1980s exhibits a distinct change in the Lucknow. In and around the city of Lucknow out of the 18 species recorded in the past, 14 species are common to the present study. It seems that the remaining 4 species (*Julella* sp., *Opergrapha herpetica*, *Peltula euploca* and *Phylliscum macrosporum*) of the former study might have become totally extinct from the area. The change in lichen communities in the district is mainly due to change in the environmental condition during the last 25 years. This indicates the replacement of the sensitive species of lichens with tolerant ones in the district (Saxena 2004).

Lichen flora of Kolkata revealed the exclusive occurrence of pollution-resistant species, *Parmelia caperata* (=*Flavoparmelia caperata*), on the roadside trees of Kolkata. The most probable reason for existence of resistant species was long-range dispersal of pollutants (caused by nearby factories) with wind (Das et al. 1986; Shukla and Upreti 2012).

In another study, Das et al. (2013) studied the impact of anthropogenic factors on abundance variability among lichen species in southern Assam. It was observed that the area with least anthropogenic pressure shows a general universal pattern of natural communities, i.e. a J-curve pattern, where majority of the species are rare and few are abundant. With a small change in anthropogenic pressure, there is little effect on rare species but the abundant species increased. With major changes both the rare and the abundant species decrease changing the overall community composition. The J-curve changes to a uni-modal curve; the moderately abundant species are found to be resilient against anthropogenic pressure levels. The community ecology of organisms has its root in evolutionary history, succession and biogeography. The studies on community ecology, therefore, may help in throwing significant light on these important aspects and can also be used as indicators of ecosystem health.

Lichen flora of Garden city, Bangalore, was explored by Nayaka et al. (2003). Significant change in the lichen diversity was observed in comparison to earlier study conducted 18 years ago. There were only four species common between two studies. Air quality of Pune city in Maharashtra Province was assessed by distribution of lichens in the city. It was observed that out of the 20 streets/sites of the Pune city surveyed, only 11 sites showed the presence of lichens Nayaka and Upreti (2005a).

An earlier enumeration of lichens of Indian Botanical Garden collected by Kurz in 1865 and described by Nylander in 1867 was compared by Upreti et al. (2005). It is interesting to note that in the last more than 140 years, the lichen flora of the area has been changed significantly as only 3 species out of 50 species (recorded earlier) were common between the two studies.

More systematic and standardised lichen diversity studies are required to be conducted in India in order to monitor the air quality and establish lichen biomonitoring, an integral part of environmental assessment programmes.

## 5.3 Solely Human Disturbances/ Disasters

With increasing economic growth (industrialisation and urbanisation) (Fig. 5.7), environmental contamination, especially air pollution, is resulting in environmental degradation in the developing nations of Asia. In many Asian countries including India, environmental component of sustainable development is virtually ignored compared with economic benefits, resulting in deterioration of ecosystem affecting quality of air, water and soil. In the quest of rapid economic development, political and business support for environmental impact assessment (EIA) is given low priority (Foster 1993; Curran 2000). Countries that have achieved rapid industrialisation and economic development have done so at the cost of extensive environmental damage (Alauddin 2003; Li et al. 2009).

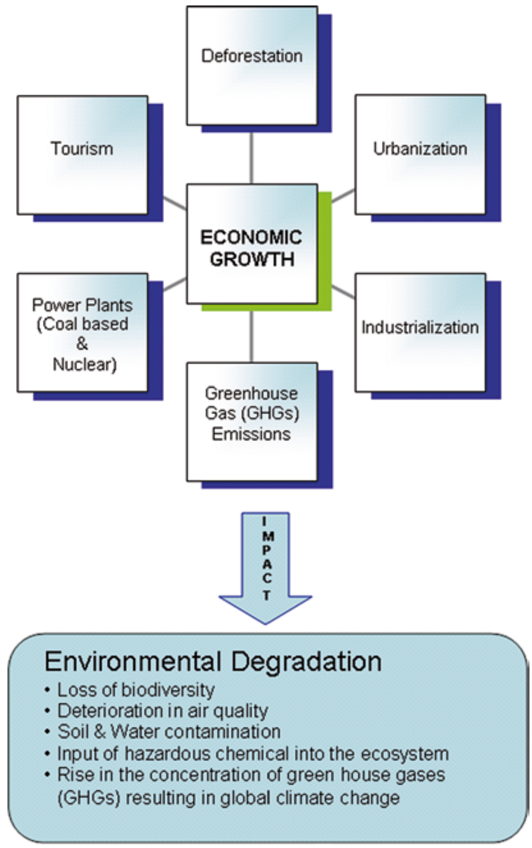


**Fig. 5.7** Conceptual diagram showing the impact of various types of developmental activities resulting in environmental degradation

The relationship between economic growth and the environment has been controversial. Classical economic theory always indicated negative relation between economic growth and environmental quality. The empirical and theoretical literature on the Environmental Kuznets Curve (EKC) has suggested that the relationship between economic growth and the environment could be positive and hence growth is a prerequisite for environmental improvement (Fig. 5.8). The EKC depicts the empirical pattern that at relatively low levels of income per capita, pollution level (and intensity) initially increases with rising income but then reaches a maximum and falls thereafter. The dominant theoretical explanation is that when GDP increases, the greater scale of production leads directly to more pollution, but, at a higher level of income per capita, the demand for health and environmental quality rises with income which can translate into environmental regulation, in which case there tend to be favourable shifts in the composition of output and in the eco-friendly techniques of production (Panayotou 2003). For example, the air in London, Tokyo and New York was far more polluted in the 1960s than it is today. This theoretical assumption has been proved by several lichen biomonitoring studies carried out in advanced countries of Europe, according to which the present levels of pollutants are lower in comparison to earlier data (Lisowska 2011; Crespo et al. 2004; Seaward 1997).

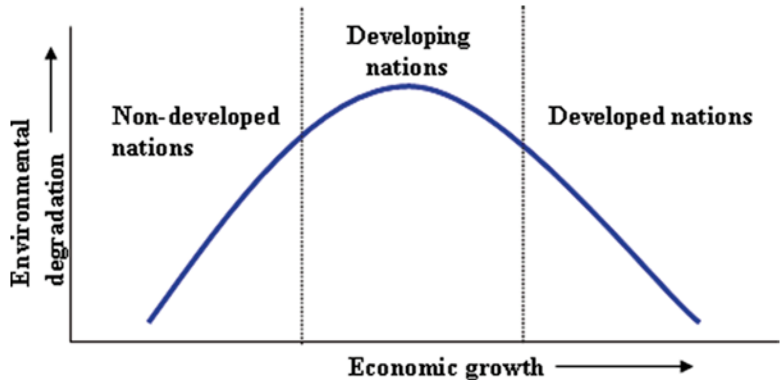


**Fig. 5.8** Environmental Kuznets Curve (EKC) showing relation between environmental and economic developments (Modified from Panayotou 2003)

Asia is the world's largest and most populous continent and covers 8.6 % of the earth's total surface area (or 29.4 % of its land area). With over four billion people, it has more than 60 % of the world's current human population. As evident and measured by annual percentage change in GDP, many Asian countries, especially in East Asia, have experienced rapid economic growth (Alauddin 2003; Li et al. 2009).

In developing countries unplanned rapid expansion of economic activities, consideration for environmental conservation and many problems resulting due to degradation in quality of ambient environment such as clean air, safe drinking water and quality of food are being given low priority (Japan environmental council 2005). Statistical data provided by various international organisations, including the World Bank, have indicated that the annual cost of all aspects of air quality degradation is substantial and could constitute up to around 2 % of GDP in developed countries and more than 5 % in developing countries. These costs include mortality, chronic illness, hospital admissions, lower worker and agricultural productivity, IQ loss and reduction of visibility. Up to 800,000 premature deaths and up to one million prenatal deaths have been estimated as one consequence of air pollution globally (Abdalla 2006).

In the developing countries a causal relationship between air pollution and health effects has been reported. Increased cases of respiratory problems and low pulmonary function is due to exposure to respirable suspended particulate matter (RSPM) which remains suspended in the urban air and easily inhaled. Asthmatic populations are also susceptible to the impact of particulate and $SO_2$ exposure. Most evidence suggests that populations living in cities with high levels of air pollution in developing countries experience similar or greater adverse effects of air pollution. According to Smith et al. (1999) around 40–60 % of acute respiratory infection is due to environmental causes.

Association between mortality rate and particulate air pollution has long been studied. Dockery et al. (1993) related excess daily mortality from cancer and cardiopulmonary disease to several air pollutants, especially fine particulate matter ($PM_{2.5}$, particulate matter with aerodynamic diameter of equal to or less than 2.5 μm), in their prospective cohort study. Since then, many other epidemiological studies on the adverse human effects of air pollutants have been carried out, ranging from variations in physiological functions and subclinical symptoms (heart rate variability, peak expiratory flow rate, etc.) to manifest clinical diseases (asthma, chronic obstructive pulmonary disease, stroke, lung cancer, leukaemia, etc.), premature births and deaths (Delfino et al. 1998; Naeher et al. 1999; Laden et al. 2000; Suresh et al. 2000; Janssen et al. 2002; Calderón-Garcidueňas et al. 2003; Wilhelm and Ritz 2003; O'Neill et al. 2004; Preutthipan et al. 2004; Han and Naeher 2006).

Even though the current fossil fuel use in developing countries is half that of the developed countries, it was expected to increase by 120 % by the year 2010. If control measures are not implemented, it has been estimated that by the year 2020 more than 6.34 million deaths will occur in developing countries due to ambient concentrations of particulate air pollution (Mukhopadhyaya and Forssel 2005).

Present environmental crisis in Asia is mainly because of non-standardised environmental parameters for environmental regulation, and moreover environmental impact assessment (EIA) is overpowered by economic gains in terms of GDP. In absence of standardised EIA protocol, newly developing countries are susceptible to accumulate more pollution-emitting industries. As a result many countries in the East Asian region are very likely to accumulate pollution emitting industries as rich countries filter out such industries and transfer them to newly developing countries (Kim 1990). According to Kim (2006) without strict environmental control, it is very likely that East Asia will accumulate the worst pollution in the world.

Variation in the extent, regulatory form and practical application of EIA in different developing countries is dependent on resources, political and administrative systems, social systems as well as the level and nature of economic development (George 2000). Other than problem in the system, there are several prominent difficulties in developing countries in relation to EIA report preparation, prominent being the lack of trained human resources and of financial resources which often leads to the preparation of inadequate and irrelevant EIA reports in developing countries (Clark 1999) as well as baseline socio-economic and environmental data being inaccurate, difficult to obtain or non-existent in developing countries (Wilbanks et al. 1993). Lohani et al. (1997) attributed lack of attention and commitment to follow-up as a serious shortcoming in Asian EIA practice. Projects in developing countries may change substantially between authorisation and implementation, and environmental controls may not be observed or monitored. There is relatively little information about the accuracy of developing country EIA predictions. The major limiting factors concerning the development of Asian EIA practice is the lack of effective communication of EIA results and recommendations to decision makers. In some eastern Asian countries, EIA begins after the construction commences and is used only to confirm that the environmental consequences of the project are acceptable (Brifett 1999; Wood 2003).

The worst impact of non-standardised economic development is the increasing global temperature and increased frequency of natural disasters.

Anthropogenic activities resulting due to human settlements result in three main sources of air pollution: (1) stationary or point, (2) mobile and (3) indoor. In developing countries, especially in the rural area, indoor air pollution from using open fires for cooking and heating is a serious problem, while industries, power plants, etc. are the cause of stationary air pollution. In urban areas, both developing and developed countries, it is predominantly mobile or vehicular pollution that contributes to overall air quality problem. Air pollutants emitting due to vehicular activity has local–regional–global impact, viz. local (e.g. smoke affecting visibility, ambient air, noise), regional (such as smog, acidification) and global (i.e. global warming) (Faiz et al. 1996).

## 5.3.1 Urbanisation, Expanding Cities and Industrialisation

### 5.3.1.1 Urbanisation and Expanding Cities

Many metropolitan cities in developing countries located in the Asia face serious air pollution problem. Asian megacities cover <2 % of the land area but emit >16 % of the total anthropogenic sulphur emissions of Asia. It has been estimated that urban sulphur emissions contribute over 30 % to the regional pollution levels in large parts of Asia. The average sulphur contribution of megacities over the western Pacific increased from <5 % in 1975 to >10 % in 2000 (Guttikunda et al. 2003). Urban air has high concentrations of sulphur dioxide and suspended particulate matter (SPM). In large cities where traffic is concentrated, air pollution is reaching serious levels, mainly caused by vehicles. The health impacts of airborne fine particulate matter (known as $PM_{2.5}$), and diesel exhaust particles (DEP), are matters of particular concern (Zhang et al. 2007).

The pollution from vehicles are due to discharges like CO, unburned hydrocarbons (HC), Pb compounds, NOx, soot and suspended particulate matter (SPM) mainly from exhaust pipes. A study reports that in Delhi one out of every ten school children suffers from asthma that is worsening due to vehicular pollution (CPCB 1999; Cropper et al. 1997).

The rapid urbanisation of many cities in South and Southeast Asia has increased the demand for bricks, which are typically supplied from brick kilns in peri-urban areas. Brick kilns, along with aluminium smelters, ceramic manufacture and phosphorus fertiliser factories, are the major sources responsible for atmospheric fluoride pollution (Weinstein and Davison 2003). Bricks are produced from soil (usually clay) that may contain fluoride at concentrations up to 500 ppm in brick kilns at temperatures ranging from 900 to 1,150 °C. At these temperatures, fluoride compounds are released into the atmosphere in the form of gaseous HF, silicon fluoride and particulate calcium fluoride, along with other pollutants such as sulphur dioxide ($SO_2$) (Ahmad et al. 2012)

As India and China develop into the world's manufacturing centre, air quality in this region is also deteriorating rapidly. The amount of air pollutants generated in the region is the world's largest. As the air pollution becomes regionalised, the soils and waters of the entire Northeast Asian region will also be affected (Kim 1993). China in particular, because of its rapid push to industrialise, is experiencing dramatic levels of aerosol pollution over a large portion of the country (Liu and Diamond 2005; Kim 1993, 2006).

By 1992, China was producing an estimated 14.4 million tonnes of dust a year and 16.85 million tonnes of sulphur dioxide; and solid wastes were increasing by 20 million tonnes annually. Many of the fastest-growing enterprises are based on high energy and high material consumption, while rural enterprises are among the heaviest polluters.

There has been exponential increase in anthropogenic NOx air pollution in Asia between the years 1975 and 2000 from ~10,000 to ~30,000 kt/year (Akimoto 2003). In India, air quality in national capital Delhi, data shows that of the total 3,000 metric tonnes of pollutants (Blackman and Harrington 2000) bleached out every day, close to two-third (66 %) is from vehicles. Similarly, the contribution of vehicles to urban air pollution is 52 % in Bombay and close to one-third in Calcutta (Button and Rietveld 1999). The worst thing about vehicular pollution is that it cannot be avoided as the emissions are emitted at the near-ground level where we breathe. Pollution from vehicles gets reflected in increased mortality and morbidity and is revealed through symptoms like cough, headache, nausea, irritation of eyes, various bronchial problems and visibility.

Anthropogenic aerosols, mainly black carbon soot, alter the regional atmospheric circulation, contributing to regional as well as global climate change (Dutkiewicz et al. 2009). Menon et al. (2002) and Rosenfeld et al. (2007) have suggested that reducing the amount of anthropogenic black carbon aerosols, in addition to having human health benefits, may help diminish the intensity of floods in south China and droughts and dust storms in north China. Similar considerations apply to India. India's air pollution, because it is also rich in black carbon, has reached the point where scientists fear it may have already altered the seasonal climate cycle of the monsoons.

#### 5.3.1.2 Industrial Development

More than 80 % of energy is produced from coal, a fuel that emits a high amount of carbon and greenhouse gases and other toxic inorganic and organic pollutants. Fine particles or microscopic dust from coal or wood fires and unfiltered diesel engines are rated as one of the most lethal forms or air pollution caused by industry and ageing coal or oil-fired power stations. Industrial processes also release chemicals known as halocarbons and other long-lived gases, some of which trap heat in the atmosphere and lead to global warming.

India, a faster developing economy, is among the ten most industrialised countries in the world. It has the world's eighth largest economy. Since economic liberalisation beginning in 1991, India's economy grew by 5 % a year, on average, during 1992–1997 and at a higher rate after that. However, rapid economic and industrial growth is causing severe urban and industrial pollution. India's per capita carbon dioxide emissions were roughly 3,000 lb (1,360 kg) in 2007, which is less as compared to China and the USA, with 10,500 lb (4,763 kg) and 42,500 lb (19,278 kg), respectively. India has been ranked as the seventh most environmentally hazardous country in the world by a new ranking released recently. Brazil was found to be the worst on environmental indicators, whereas Singapore was the best. The USA was rated second worst and China was ranked third. According to Time magazine's list of most polluted cities in the world, New Delhi and Mumbai figure in top 10. Heavy reliance on coal for power generation has exacerbated India's environmental problems.

The burning of fossil fuels is the main cause of atmospheric air pollution and the main source of anthropogenic $CO_2$ emissions (IEA 1999).

About 90 % of total emissions of carbon monoxide (CO) in Gulf countries are due to transportation activities. In the Gulf Cooperation Council (GCC) countries total atmospheric emission loads are about 3.85 million tonnes per year, made of 28 % CO, 27 % $SO_2$ and 23 % particulates (UNEP, 1999). Recent studies have indicated that the Gulf countries emit about 50 % of the total of Arab countries' (254 million metric tonnes of carbon) emissions of $CO_2$.

#### 5.3.1.3 Mercury Emission

Industrial and allied activities like coal combustion, waste incineration, metal mining, refining and manufacturing and chlorine-alkali production are the major anthropogenic sources of highly toxic metal, Mercury (Hg). Due to long residence time of $Hg^0$ in the atmosphere from 0.5 to 2 years and being able to travel long distances and deposited in remote places even 1,000 km away from the sources, mercury (Hg) is considered as a global pollutant. Anthropogenic activities emit both elemental Hg ($Hg^0$) with a long life in the atmosphere and reactive gaseous mercury (RGM) and particulate Hg, which are short lived in the air and deposited near the emission source. Natural processes, including volcanoes and geothermal activities; evasion from surficial soils, waterbodies, and vegetation surfaces; and wild fires, as well as the reemission of deposited mercury also result in the release of substantial amount of mercury in the atmosphere mainly in the form of $Hg^0$. Global oceanic emission is estimated to be 800–2,600 tonnes/a and global natural terrestrial emission is estimated to be 1,000–3,200 tonnes/a. Thus, through all sources there is a total natural mercury emission of 1,800–5,800 tonnes/a. The global anthropogenic Hg emission to the atmosphere was estimated to be 2,190 tonnes in 2000, of which two-thirds of the total emission of ca. 2,190 tonne of Hg came from combustion of fossil fuels. Asian countries contributed about 54 % (1,179 tonnes) to the global Hg emission from all anthropogenic sources worldwide in 2000. China leads the list of the ten countries with the highest Hg emissions from anthropogenic activities followed by India, Japan, Kazakhstan and Democratic People's Republic of North Korea. With more than 600 tonnes of Hg, China contributes about 28 % to the global mercury emission (Li et al. 2009).

Hg can be converted to toxic methylmercury (Me–Hg) and gets accumulated in the food chain. The outbreaks of severe mercury poisoning in Minamata, Japan, and Iraq in the last centaury had posed threat to the eco-environment system and human beings. In Japan, Mercury-contaminated effluent discharged into Minamata Bay from an acetaldehyde-producing factory. Me–Hg got bioaccumulated by fish and shellfish which when consumed by humans caused Minamata disease. Mercury poisoning killed more than 100 people and paralysed several thousands of people around Minamata Bay and the adjacent Yatsushiro

**Table 5.10** Hg concentrations (in μg $g^{-1}$ dry weight) in lichen thallus of different species from India

| S. No. | Lichen species | Locality | Concentration | References |
|---|---|---|---|---|
| 1 | *Phaeophyscia hispidula* (Ach.) Essl. | Dehradun, Uttarakhand | 0.00–47.00 | Rani et al. (2011) |
| 2 | *Pyxine cocoes* (Sw.) Nyl. | North side Lucknow city | 2.10–5.90 | Saxena et al. (2007) |
| 3 | *Phaeophyscia orbicularis* | North side Lucknow city | 3.4 | Saxena et al. (2007) |
| 4 | *Lecanora leprosa* | North side Lucknow city | 1.10–3.10 | Saxena et al. (2007) |
| 5 | *Arthopyrenia nidulans* | North side Lucknow city | 5.90 | Saxena et al. (2007) |
| 6 | *Sphinctrina anglica* | North side Lucknow city | 3.90 | Saxena et al. (2007) |
| 7 | *Bacidia submedialis* | North side Lucknow city | 7.50 | Saxena et al. (2007) |

Sea since 1956. In the early 1970s in Iraq, a major methylmercury poisoning resulted due to consumption of seed grain treated with a Me-Hg fungicide, which resulted in the death of 10,000 people and 100,000 had permanently brain damaged (Li et al. 2009). Some lichen biomonitoring related with Hg pollution has been carried out in India (Table 5.10).

#### 5.3.1.4 Fluoride Emission

Hydrogen fluoride (HF) is one of the most phytotoxic air pollutants (Weinstein and Davison 2003). HF and other fluoride compounds in the atmosphere are deposited onto the vegetated surfaces either in gaseous or particulate form, while airborne gaseous fluorides can enter directly into the leaf through stomata. This fluoride then dissolves in the apoplast, altering the photosynthetic process, causing visible injury and ultimately affecting growth and yield. The impact of atmospheric fluoride pollution from various sources on crops has also been well documented (Brewer 1960; Mason et al. 1987; Moraes et al. 2002). Lee et al. (2003) reported damage to vegetation around brick and ceramic factories in Taiwan, and local effects on vegetation of fluoride emissions from aluminium factories and thermal power plants have been reported in India (Lal and Ambasht 1981; Pandey 1981, 1985; Narayan et al. 1994; Ahmad et al. 2012).

Other than fluoride emission the poorly regulated brick kilns also contribute significantly to local sulphur and black carbon emissions (Emberson et al. 2003; Iqbal and Oanh 2011).

#### 5.3.1.5 Assessment of Urban and Industrial Pollution with Lichens

Lichens have been recognised and successfully utilised as biological indicators of air quality. They are among the most valuable and reliable biomonitors of atmospheric pollution. Primarily lichens were utilised to monitor gaseous pollution, namely, sulphur ($SO_2$) and nitrogen ($NO_x$, $NH_3$, $NO_3$, etc.) (Rao and LeBlanc 1967; Vestergaard et al. 1986). Lichens show high sensitivity towards sulphur dioxide because their efficient absorption systems result in rapid accumulation of sulphur when exposed to high levels of sulphur dioxide pollution (Wadleigh and Blake 1999). The algal partner (5–10 % of total thallus structure) is most affected by the sulphur dioxide as chlorophyll is irreversibly converted to phaeophytin, and thus, photosynthesis is inhibited (Upreti 1994). Lichens also absorb sulphur dioxide dissolved in water (Hawksworth and Rose 1970). Excessive levels of pollutants in the atmosphere, especially $SO_2$, have detrimental effect on the physiology and morphology of sensitive species and causes extinction of the species, which ultimately results in changed lichen diversity pattern (Haffner et al. 2001; Purvis 2000).

Photosynthesis is the core physiological function of an autotrophic organism and its functional state has been considered as an ideal tool to monitor the health and vitality of plants (Clark et al. 2000). Between gas exchange and chlorophyll fluorescence methods for measuring the photosynthetic performance in a plant, the latter technique has become more popular in the recent years. Introduction of highly user-friendly portable fluorometers further widened the scope of photosynthesis research, especially in in situ conditions. The technique was also found to be useful for studying samples such as lichens and bryophytes, whose structure otherwise makes them difficult to study with conventional gas exchange systems (Maxwell and Johnson 2000; Genty et al. 1989). The chlorophyll fluorescence technique provides a large amount of data with a minimum of expertise and time and without injury to the plants. The technique most frequently utilises the parameter Fv/Fm as a reliable indicator of the maximum photochemical quantum efficiency of photosystem II or photosynthetic performance of organism under investigation (Butler and Kitajima 1975). It is the only parameter that is not temperature sensitive and measured in dark-adapted samples. Fv/Fm is calculated from F0, the fluorescence when the reaction centre of PSII is fully open, and Fm, the maximum fluorescence when all the reaction centres are closed following a flash of saturation light. Fv (i.e. Fm – F0) is the maximum variable fluorescence in the state when all nonphotochemical processes are at a minimum (van Kooten and Snel 1990).

Photosynthetic performances of 82 lichens occurring in Western Himalayas were determined using chlorophyll fluorescence. Fv/Fm ranged from 0.023 to 0.655, with terricolous Cladonia subconistea at alpine region having maximum value. Photosynthetic performances of alpine lichens were found to be better than those of temperate due to the influence of favourable climate, wet soil and rock in the region. As the study was carried out during early summer, most of the lichens started experiencing stress which is evident by their Fv/Fm values. As many as ten chlorolichens (with green alga as photobiont) growing in temperate region are severely stressed and have values <0.1. The stress components in the study area are mostly water availability and high-intensity light. The cyanolichens (with blue-green alga as photobiont) have relatively lower Fv/Fm ranging from 0.075 to 0.315. On the basis of their Fv/Fm values, the lichens in the present study are classified into three categories: normal, moderate and severely stressed with values ranging from 0.5 to 0.76, 0.3 to 0.49 and 0.01 to 0.29, respectively (Nayaka et al. 2009).

In recent times, sensitivity to other pollutants has been explored. Lichens are adversely affected by short-term exposure to nitrogen oxides as low as 564 μg $m^{-3}$ (0.3 ppm; Holopainen and Kärenlampi 1985). Most reports regarding lichen sensitivity to fluorine relate the physical damage of lichens to tissue concentrations or a specific point source of emissions rather than ambient levels. In general, visible damage to lichens begins when 30–80 ppm fluorine has been accumulated in lichen tissues (Perkins 1992; Gilbert 1971). In one fumigation study (Nash 1971), lichens exposed to ambient F at 4 mg $m^{-3}$ (0.0049 ppm) accumulated F within their thalli and eventually surpassed the critical concentration of 30–80 ppm. Fluorine is associated with aluminium production and concentrations in vegetation may be elevated near this type of industrial facility. In addition to gaseous pollutants, lichens are sensitive to depositional compounds, particularly sulphuric and nitric acids, sulphites and bisulphites and other fertilising, acidifying or alkalinising pollutants such as $H^+$, $NH_3$ and $NH_4^+$. While sulphites, nitrites and bisulphites are directly toxic to lichens, acidic compounds affect lichens in three ways: direct toxicity of the $H^+$ ion, fertilisation by $NO_3^-$ and acidification of bark substrates (Farmer et al. 1992).

Effect of simulated acid rain and heavy metal deposition on the ultrastructure of the lichen *Bryoria fuscescens* (Gyeln.) Brodo and Hawksw. was studied. Algal and fungal components responded differently to pH, and there was an interaction with metal toxicity. The algal partner was the most sensitive to acid rain and heavy metal combinations and had more degenerate cells than the fungal partner. Damage was apparent in chloroplasts and mitochondria, where thylakoid and mitochondrial cristae were swollen. The fungal partner was the more sensitive to high concentrations of metal ions in non-acidic conditions, suggesting a synergistic interaction between the metals and acidity. The results suggest that acid wet deposition containing metal ions may reduce survival of lichens (Tarhanen 1998).

Lichen partners differ in the ability to sequester the heavy metals; mycobiont, comprising more than 90 % of total lichen biomass, accumulates most of the heavy metals from the environment. Sanità di Toppi et al. (2005) found that mycobiont hyphae, especially those forming the upper cortex of lichen thalli, were the main site of Cd accumulation which may be attributed to the presence of extracellular lichen substances produced by fungal hyphae. Significant positive correlation of Cd and Cr content and lichaxanthone has been observed in *Pyxine subcinerea* (Shukla 2012).

In the Netherlands, a number of studies have demonstrated that ammonia-based fertilisers alkalinise and enrich lichen substrates that in turn strongly influence lichen community composition and element content (van Herk and Aptroot 1999; van Dobben et al. 2001; van Dobben and ter Braak 1998, 1999).

In a mixed urban environment, pollutant mixes can have synergistic, additive or antagonistic effects on lichens, and individual species differ in their sensitivity to these pollutants and their response to pollutant mixes (Hyvärinen et al. 2000; Farmer et al. 1992). During the past 20 years, much data have been collected concerning metal tolerance and toxicity in lichens (Garty 2001).

Metals can be classified into three groups relative to their toxicity in lichens (Nieboer and Richardson 1981):

1. Class A metals: $K^+$, $Ca^{2+}$ and $Sr^{2+}$ are characterised by a strong preference for $O_2$-containing binding sites and are not toxic.
2. Ions in the B metals class: $Ag^+$, $Hg^+$ and $Cu^+$ tend to bind with N- and S-containing molecules and are extremely toxic to lichens even at low levels.
3. Borderline metals: $Zn^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and $Pb^{2+}$ are intermediate to Class A and B metals. Borderline metals, especially those with class B properties (e.g. $Pb^{2+}$, $Cu^{2+}$), may be both detrimental by themselves and in combination with sulphur dioxide.

This provides a good rationale to monitor both metal- and sulphur/nitrogen-containing pollutants simultaneously if possible.

Adverse effects of metals include decreases in thallus size and fertility, bleaching and convolution of the thallus, restriction of lichens to the base of vegetation (Sigal and Nash 1983) and mortality of sensitive species. Microscopic and molecular effects include reduction in the number of algal cells in the thallus (Holopainen 1984), ultrastructural changes of the thallus (Hale 1983; Holopainen 1984), changes in chlorophyll fluorescence parameters (Gries et al. 1995), degradation of photosynthetic pigments (Garty 1993) and altered photosynthesis and respiration rates (Sanz et al. 1992). The first indications of air pollution damage from $SO_2$ are the inhibition of nitrogen fixation, increased electrolyte leakage and decreased photosynthesis and respiration followed by discoloration and death of the algae (Fields 1988). More resistant species tolerate regions with higher concentrations of these pollutants but may exhibit changes in internal and/or external morphology (Nash and Gries 1991). Elevation in the content of heavy metals in the thallus has also been documented in many cases (Garty 2001), but it is not always easy to establish what specific effect these elevated levels will have on lichen condition or viability. Tolerance to metals may be phenotypically acquired, but sensitivity of lichens to elevated tissue concentrations of metals varies greatly among species, populations and elements (Tyler 1989). The toxicity of metal ions in lichen tissue is the result of three main mechanisms: the blocking, modification or displacement of ions or molecules essential for plant function. Metal toxicity in lichens is evidenced by adverse effects on cell membrane integrity, chlorophyll content and integrity, photosynthesis and respiration, potential quantum yield of photosystem II, stress ethylene production, ultrastructure, spectral reflectance responses, drought resistance and synthesis of various enzymes, secondary metabolites and energy transfer molecules (Garty 2001).

The influence of pollution sources on the presence of trace elements and on lichen species community composition in the natural area has been carried out which revealed that lichen diversity negatively correlated with Cu, Pb and V. The study also underlined the value of combining the use of biomonitors, enrichment factors and lichen diversity for pollution assessment to reach a better overview of both trace elements' impact and the localisation of their sources (Achotegui-Castells et al. 2012).

In India lichen biomonitoring has been successfully employed for air quality monitoring in different regions of the country employing different bioindicator species (Table 5.11). Accumulation of metal (Al, Cd, Cu, Cr, Fe, Pb, Ni, Zn) pollutants in lichen thallus by passive as well as active principals are well known from different cities of the country such as Uttar Pradesh (Faizabad, Lucknow, Kanpur and Raebareli district), Madhya Pradesh (Dhar, Katni and Rewa district) and West Bengal (Hooghly and Nadia district), Maharashtra (Pune and Satara district) and Uttarakhand (Dehradun, Pauri district). The accumulation of different metals decrease with increasing distance from the city centre. The metals Cr, Cu and Pb were more at the higher vertical position (20–25 ft), whereas other metals (Zn, Fe) accumulated maximum at lower vertical position (4–5 ft).

Accumulation rate of heavy metals depends to a large extent on physical aspects such as thallus type and their morphological features (Garty et al. 1979). A number of atmospheric pollutants are recognised as a significant factor in the deterioration of cultural properties. Atmospheric deposition of heavy metals such as As, Al, Cd, Cr, Cu, Fe, Ni and Zn in four different growth forms of lichens exhibit diverse quantitative variations. The difference in metal concentrations were tested using an ANOVA test ($p<5$ %) between the species and between the sites. Among the different growth forms, most of the heavy metal exhibits their higher level of accumulation. The competitive uptake studies revealed the selectivity sequence as foliose > leprose > squamulose > crustose. In calcium and magnesium these selectivity sequence represented as crustose > squamulose > foliose > leprose forms. The morphology and anatomy of the thallus may play an important role in accumulation of pollutants.

All the sites in the city exhibited an enhanced level of metals, as most of the metals analysed except Ca and Mg have anthropogenic origin due to vehicular activities.

The *Phaeophyscia hispidula*, *Diploschistes candidissimum*, *Phylliscum indicum* and *Lepraria lobificans* belonging to foliose, crustose, squamulose and leprose growth forms, respectively, seem to be efficient bioaccumulators of inorganic pollutants. These species are good mitigator of atmospheric fallouts and can be utilised for air quality monitoring in the area.

The bioaccumulation factor (BAFs) was maximum in *Lepraria lobificans* for Ca, Mg and Al, whereas *Diploschistes candidissimum* has maximum BAF for As. Both the foliose lichens (*P. hispidula* and *P. praesorediosum*) have maximum BAFs for Fe. The bioaccumulation factor was zero for Zn, Ni, Cd and Cr because these metals were not detected in substratum.

The damage caused by the metallic pollutants in the lichen *Pyxine subcinerea* Stirton, by measurements of Chl a, Chl b, total Chl, carotenoid and protein and OD 435/415 ratio significantly, exhibits the changes in physiology. It was observed that Cu, Pb and Zn significantly affect the physiology of the lichen *P. subcinerea*. Multiple correlation analysis revealed significant correlation (<0.001) among the Fe, Ni, Cu, Zn and Pb metals analysed. Cd did not correlate with any other metals except Fe ($p<0.05$). Cu, Pb and Zn are the main constituents of the vehicular emissions and had significant positive correlation ($p<0.001$) with protein content, while the OD 435/415 ratio values decreased statistically ($p<0.001$) with increase in amount of Cu, Pb and Zn (Shukla and Upreti 2008).

According to Beckett and Brown (1983), Cd and Zn compete with one another for sites holding bivalent cations, which is consistent with the observation that the correlation coefficients between Cd and Zn, although not statistically significant, exhibit negative trends (Shukla et al. 2012a, b). Usually Zn, Cu and Fe are supposed to act antagonistically against Cd. Zn, Fe and Cu are negatively correlated with Cd. The significant positive correlation of protein with Cd indicates the synthesis of protein under Cd-stressed condition similar to expression of stress protein 70 (hsp 70) in the lichen photobiont *Trebouxia erici*

**Table 5.11** Concentration (in μg g$^{-1}$ dry weight) of various lichens collected from different phytogeographical regions of India

| | Species | Sites | Ni | Al | Ca | Cd | Cr | Cu | Fe | Pb | Mg | Mn | Zn | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | *Acarospora gwynii* | Maitri Station (East Antarctica) | | | | 19.28–97.87 | 36.36–124.84 | 6,420–8,560 | | | | | 12.4–69 | Upreti and Pandey (1999) |
| 2. | *Arthopyrenia nidulans* | Lucknow city (North) (Uttar Pradesh) | BDL | | | BDL | 137.5 | 21.7 | 5,183 | 15.6 | | | 219.7 | Saxena et al. (2007) |
| 3. | *Bacidia submedialis* | Lucknow city (North) (Uttar Pradesh) | BDL | | | BDL | 127.4 | 66.6 | 5,283 | 5.9 | | | 96.7 | Saxena et al. (2007) |
| 4. | *Buellia grimmae* | Maitri Station (East Antarctica) | | | | 57.75 | 395 | 11,290 | | | | | 71.8 | Upreti and Pandey (1999) |
| 5. | *B. isidiza* (Nyl.) Hale | Bangalore city (Karnataka) | | | | | 12.99 | 86.02 | 22,721 | 22 | | | 102.7 | Nayaka et al. (2003) |
| 6. | *B. pallida* | Maitri Station (East Antarctica) | | | | 54.76 | 138.88 | 10,070 | | | | | 51 | Upreti and Pandey (1999) |
| 7. | *Caloplaca subsoluta* (Nyl.) Zahlbr. | Mandav (Madhya Pradesh) | 0.60–10 | 17.7–176 | 147.9–195 | 0.2–0.9 | 0.5–6.5 | 1.0–16 | 6.2–14.2 | | 210–376.8 | | 48.5–81.6 | Bajpai et al. (2009a, b, 2010a) |
| 8. | *Chrysothrix candelaria* (L.) Laundon | Bangalore city (Karnataka) | | | | | 5.18–95.3 | 19.66–23.7 | 748–7,556 | 0.00–623.95 | | | 95.76–157.49 | Nayaka et al. (2003) |
| 9. | *Cryptothecia punctulata* | Fungicidal, South India | | | 100 | | | 575.4 | 2,226 | | | | | Nayaka et al. (2005) |
| 10. | *Dimelaena oreina* | Badrinath (Uttarakhand) | 6.9–13.3 | | | 0.67–2 | BDL | BDL | 8,348–21,780 | 7.9–158.5 | | | 22.1–48.6 | Shukla (2007) |
| 11. | *Diploschistes candidissimus* (Kr.) Zahlbr. | Mandav (Madhya Pradesh) | 1.2–10.6 | 16.5–181.6 | 150.68–314.45 | 0.10–0.80 | 0.50–5.80 | 0.9–12.5 | 8.3–19.0 | | 283.4–415.39 | | 45.9–94.9 | Bajpai et al. (2009a, b, 2010a) |
| 12. | *D. gypsaceus* | Bhimbetka (Madhya Pradesh) | | | 77.45 | | | | | | | | | Bajpai et al. (2010c) |
| 13. | | | | | 87.66 | | | | | | | | | Bajpai et al. (2010c) |
| 14. | *Dirinaria aegialita* (Afz. In Ach.) Moore | Bangalore city (Karnataka) | | | | | 0.00–34.57 | 8.99–16.06 | 6,887–7,358 | BDL–46.4 | | | 98.60–122.39 | Nayaka et al. (2003) |
| 15. | *D. confluens* (Fr.) Awasthi | Faizabad city (High Way) (Uttar Pradesh) | | | | | | | | 0.17–6.0 | | | | Dubey et al. (1999) |
| | *D. papillulifera* (Nyl.) Awasthi | | | | | | | | | | | | | |

(continued)

**Table 5.11** (continued)

| | Species | Sites | Ni | Al | Ca | Cd | Cr | Cu | Fe | Pb | Mg | Mn | Zn | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 16. | *D. consimilis* (Stirton) Awasthi | Bangalore city (Karnataka) | | | | | 35.59 | 22.22 | 7081.00 | 149.15 | | | 198.14 | Nayaka et al. (2003) |
| 17. | *D. consimilis* (Stirton) Awasthi | Lucknow city (commercial/ industrial) (Uttar Pradesh) | | | | | BDL–1740 | BDL–13.65 | BDL | BDL | | | BDL–36.60 | Mishra et al. (2003) |
| 18. | *D. consimilis* (Stirton) Awasthi | Lucknow city (residential sites) (Uttar Pradesh) | | | | | 89.1–1,920 | BDL–12.45 | | | | | BDL–8.70 | Bajpai et al. (2004) |
| 19. | *Dermatocarpon vellereum* | Badrinath (Uttarakhand) | 1.58–4.96 | | | 0.42–0.94 | BDL–7.5 | BDL–1.56 | 1,331–5,464 | 9.68–16.98 | | | 18–36.9 | Shukla (2007) |
| 20. | *Endocarpon subrosettum* | | | | 99.41 | | | | | | | | | Bajpai et al. (2010c) |
| 21. | *Graphis scripta* (L.) Ach. | Bangalore city (Karnataka) | | | | | BDL | 10.06 | 863.00 | BDL | | | 384.55 | Nayaka et al. (2003) |
| 22. | *Heterodermia diademata* (Taylor) Awasthi | Bangalore city (Karnataka) | | | | | 6.62–6.82 | 1.71–11.02 | 3,020–4,402 | 0.00–30.49 | | | 126.54–160.0 | Nayaka et al. (2003) |
| 23. | *Lecanora muralis* | Badrinath (Uttarakhand) | 3.6–15.2 | | | 2.0–8.1 | BDL–6.6 | BDL–5.3 | 5,487–7,720 | 58.8–171 | | | 20.3–113.4 | Shukla (2007) |
| 24. | *Lecanora fuscobrunnea* | Maitri Station (East Antarctica) | | | | 25.35 | 59.95 | 9,820 | | | | | 15.86 | Upreti and Pandey (1999) |
| 25. | *L. cinereofusca* H. Magn. | Faizabad city (crowded places) (Uttar Pradesh) | | | | | | | | BDL–1.05 | | | | Dubey et al. (1999) |
| 26. | *L. expectans* | Maitri Station (East Antarctica) | | | | 60.38 | 53.29 | 9,420 | | | | | 37.44 | Upreti and Pandey (1999) |
| 27. | *L. leprosa* | Lucknow city (Uttar Pradesh) | 2.20–5.40 | | | 0.30 | 0.00–25.60 | 8.30–13.20 | 1573.00–1748 | 6.0–12.80 | | | 53.2-66 | Saxena et al. (2007) |
| 28. | *L. leprosa* Fee | Bangalore city (Karnataka) | | | | | 29.92 | 9.84 | 3,121 | 154 | | | 128.15 | Nayaka et al. (2003) |
| 29. | *L. perplexa* Brodo | Bangalore city (Karnataka) | | | | | 7.96 | 7.37 | 265 | 199.32 | | | 531.5 | Nayaka et al. (2003) |
| 30. | *Lecidea cancriformis* | Maitri Station (East Antarctica) | | | | 20.72 | 75.41 | 4,950 | | | | | 44.71 | Upreti and Pandey (1999) |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 31. *L. siplei* | Maitri Station (East Antarctica) | | | | 56.12 | 237.41 | 17,510 | | | | | 55.44 | Upreti and Pandey (1999) |
| 32. *Lepraria lobificans* Nyl. | Mandav (Madhya Pradesh) | 1.53–17.05 | 2.15–124.82 | 11.68–23.87 | BDL–3.05 | 17.12–978.99 | 12.46–41.4 | 319.8–3,196 | | 6.0–17.79 | | 110.49–165.67 | Bajpai et al. (2009a, b) |
| 33. *Parmotrema austrosinensis* (Zahlbr.) Hale | Bangalore city (Karnataka) | | | | | BDL | 20.26–158.32 | 586–4,530 | BDL | | | 100.67–153.9 | Nayaka et al. (2003) |
| 34. *Parmotrema praesorediosa* (Nyl.) *Hale* | Bangalore city (Karnataka) | | | | | 8.39–28.2 | 15.65–16.06 | 2,040–7,389 | 164.4–233.3 | | | 126.9–321.2 | Nayaka et al. (2003) |
| 35. *P. praesorediosum* (Nyl.) Hale | | | | 41.27 | | | | | | | | | Bajpai et al. (2010c) |
| 36. *P. praesorediosum* (Nyl.) Hale | Mandav (Madhya Pradesh) | 0.70–10.50 | 25.4–285.1 | 98.57–109.31 | 0.30–2.0 | 15.50–1136.9 | 0.00–56.5 | 361.20–8172.5 | | 27.85–61.3 | | 140.20–218.50 | Bajpai et al. (2009a, b, 2010a, b, c) |
| 37. *Peltula euploca* | | | | 95.89 | | | | | | | | | Bajpai et al. (2010c) |
| 38. *P. euploca* (Ach.) Poelt in pisut | Mandav (Madhya Pradesh) | 1.20–12.70 | 14.1–101.2 | 163.3–190.52 | 0.10–0.50 | 1.00–9.20 | 3.90–38.80 | 195.10–279.30 | | 154.84–195.16 | | 18.70–47.00 | Bajpai et al. (2009a, b, 2010a, b, c) |
| 39. *Pertusaria leucosorodes* Nyl. | Bangalore city (Karnataka) | | | | | 3.04 | 5.84 | 570.00 | 31.92 | | | 79.86 | Nayaka et al. (2003) |
| 40. *Phaeophyscia hispidula* (Ach.) Essl. | Dehradun city (Uttarakhand) | 7.22–17.39 | | | | 103.79–1189.56 | 19.96–31.36 | 8348.37–12543.40 | 0.01–17.42 | | | 116.97–198.78 | Shukla et al. (2006) |
| 41. *P. hispidula* (Ach.) Essl. | Pauri and Srinagar (Uttarakhand) | 54.00–67.90 | | | | 79.65–151.89 | 24.02–35.76 | 4505.00–10923.00 | 231.90–425.90 | | | 84.99–141.80 | Shukla and Upreti (2007b) |
| 42. *P. hispidula* (Ach.) Essl. | (Mandav (Madhya Pradesh) | 1.30–19.30 | 21.20–302.40 | 97.30–115.13 | 0.60–2.80 | 19.50–1091.80 | 14.70–88.90 | 985.10–7891.90 | | 20.00–54.76 | | 44.60–170.70 | Bajpai et al. (2009a, b) |
| 43. *P. hispidula* (Ach.) Essl. | Rewa (Madhya Pradesh) | | 92.70–561.80 | | 0.00–6.80 | 0.00–35.20 | | 176.50–419.40 | 0.00–11.70 | | | 103.10–214.60 | Bajpai et al. (2011) |
| 44. *P. hispidula* (Ach.) Essl. | Dehradun, (Uttarakhand) | 52.50–1230.00 | | | 2.00–875.00 | 193.00–4410.00 | 42.20–780.00 | 1135.00–29456.00 | 66.60–1336.60 | | 124.00–6412.50 | 119.00–5910.00 | Rani et al. (2011) |
| 45. *P. hispidula* (Ach.) Essl. | Dehradun, (Uttarakhand) | 7.90–24.20 | | | 0.06–33.60 | 2.68–22.00 | 0.90–21.30 | 136.00–234.00 | 6.35–52.40 | | | 16.10–69.60 | Shukla et al. (2012a, b) |

(continued)

**Table 5.11** (continued)

| | Species | Sites | Ni | Al | Ca | Cd | Cr | Cu | Fe | Pb | Mg | Mn | Zn | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 46. | *P. hispidula* (Ach.) Essl. | Badrinath (Uttarakhand) | 11.1–18.1 | | | 0.5–1.9 | BDL–5.5 | BDL–5.3 | 4783–14335 | 38.8–52.2 | | | 43.5–70.5 | Shukla (2007) |
| 47. | *P. orbicularis* | Lucknow city (Uttar Pradesh) | 10.70 | | | 0.00 | 62.20 | 18.30 | 19374.00 | 4.80 | | | 70.90 | Saxena et al. (2007) |
| 48. | *Phylliscum indicum* Upreti | Mandav (Madhya Pradesh) | 0.60–9.40 | 2.50–103.10 | 229.86–320.70 | 0.10–0.60 | 0.90–7.30 | 5.30–33.10 | 196.70–306.70 | | 102.70–168.78 | | 16.80–37.50 | Bajpai et al. (2009a, b, 2010a, b, c) |
| 49. | *Physcia caesia* | Maitri Station (East Antarctica) | | | | 106.66 | 100.00 | 10350.00 | | | | | 74.66 | Upreti and Pandey (1999) |
| 50. | *P. tribacia* (Ach.) Nyl. | Bangalore city (Karnataka) | | | | | 0.00 | 33.32 | 6683.00 | 191.12 | | | 276.47 | Nayaka et al. (2003) |
| 51. | *Pyrenula nanospora* (A. Singh) Upreti | Bangalore city (Karnataka) | | | | | 36.43 | 18.28 | 1506.00 | 175.90 | | | 231.01 | Nayaka et al. (2003) |
| 52. | *Pyxine cocoes* (Sw.) Nyl. | Bangalore city (Karnataka) | | | | | 9.53–10.31 | 16.30–19.32 | 9795–12,056 | 0.00–63.63 | | | 103.30–224.60 | Nayaka et al. (2003) |
| 53. | *P. cocoes* (Sw.) Nyl. | Lucknow city (Uttar Pradesh) | 0.00–9.60 | | | 0.00–0.40 | 0.00–34.40 | 10.20–21.70 | 3,255–5,183 | 3.30–10.60 | | | 57.60–63.40 | Saxena et al. (2007) |
| 54. | *P. cocoes* (Sw.) Nyl. | Raebareli, NTPC, Uttar Pradesh | 0.60–18.30 | 297–1,631 | | | 0.90–12.10 | 2.50–12.10 | 58.60–1498.40 | 0.50–9.30 | | | 7.80–59.60 | Bajpai et al. (2010a, b) |
| 55. | *P. cocoes* (Sw.) Nyl. | Katni (Madhya Pradesh) | | 78.2–365.10 | | 0.00–6.30 | 0.80–26.20 | | 103.0–689.40 | 0.00–13.30 | | | 57.30–194.40 | Bajpai et al. (2011) |
| 56. | *P. cocoes* (Sw.) Nyl. | Hooghly and Nadia (West Bengal) | | 98.80–1376.10 | | 0.00–4.50 | 0.00–40.30 | 0.00–10.20 | 69.30–730.10 | 0.00–89.10 | | | 0.00–118.10 | Bajpai and Upreti (2012) |
| 57. | *P. petricola* Nyl. In crombie | Bangalore city (Karnataka) | | | | | 18.47–19.00 | 115.19–338.12 | 5538.00–9202.00 | 83.33–101.40 | | | 105.38–133.05 | Nayaka et al. (2003) |
| 58. | *Pyxine subcinerea* Stirton | Haridwar city (Uttarakhand) | 13.50–719.25 | | | 4.20–51.45 | 16.40–94.40 | 19.65–144.10 | 795.00–17280.00 | 17.25–157.80 | | | 158.00–1178.00 | Shukla et al. (2013a, b) |
| 59. | *P. subcinerea* Stirton | Srinagar, Garhwal (Uttarakhand) | 0.02–0.14 | | | 0.00–0.14 | 0.06–0.19 | 0.27–0.84 | 43.08–55.93 | 0.26–0.62 | | | 1.76–4.69 | Shukla and Upreti (2008) |
| 60. | *P. subcinerea* Stirton | Rudraprayag (Uttarakhand) | | 66.7–369.1 | | BDL-56.5 | 30.1–246.9 | 18.4–101.8 | 38.4–150.5 | 8.4–44.7 | | BDL–274.9 | 27.2–189.4 | Shukla (2012) |
| 61. | *Remototrachyna awasthii* | Mahabaleshwar city, Maharashtra | | 125.00–1295.00 | | 0.11–1.83 | 0.92–3.01 | 89.1–966.40 | 0.00–18.80 | | | 7.30–31.00 | 15.06–45.90 | Bajpai et al. (2013a) |
| 62. | *R. awasthii* | Mahabaleshwar city, Maharashtra | | 335.80–1295.16 | | 0.16–1.90 | 0.97–3.53 | | 334.97–989.83 | 0.38–19.57 | | 4.62–37.00 | 16.60–49.46 | Bajpai et al. (2013b) |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 63. *Rhizocarpon flavum* | Maitri Station (East Antarctica) | | | 51.08 | 96.56 | 10040.00 | | | | 67.12 | Upreti and Pandey (1999) |
| 64. *Rinodina olivaceobrunnea* | Maitri Station (East Antarctica) | | | 46.01 | 82.33 | 14240.00 | | | | 71.44 | Upreti and Pandey (1999) |
| 65. *Sphinctrina anglica* | Lucknow city (Uttar Pradesh) | 3.80 | | 0.00 | 50.70 | 25.80 | 3251.00 | 3.10 | | 49.40 | Saxena et al. (2007) |
| 66. *Umbilicaria aprina* Nyl. | Maitri Station (East Antarctica) | | | | 7.40–15.63 | 55.00–138.00 | 5386.00–11386.00 | 6.33–25.75 | | | Upreti and Pandey (1994) |
| 67. *U. decussata* (Vill.) Zahlbr. | Maitri Station (East Antarctica) | | | | 3.36–4.20 | 45.00–93.00 | 4966.00–12760.00 | 5.66–19.80 | | | Upreti and Pandey (1994) |
| 68. *Usnea antarctica* | Maitri Station (East Antarctica) | | | 122.39 | 166.66 | 8840.00 | | | | 111.97 | Upreti and Pandey (1999) |
| 69. *Xanthoria elegans* | Badrinath (Uttarakhand) | 2.84–8.04 | | 0.09–0.33 | BDL | 5.06–8.01 | 3.3–3.7 | 2.87–7.49 | | 33.87–50.3 | Shukla (2007) |

(Bačkor et al. 2006). Metal tolerance in animal and plants (vascular and non-vascular) is known to be conferred by production of a special class of proteins called metallothioneins and phytochelatins (PCs). The PCs play a central role in the detoxification of several heavy metals, especially Cd (Prasad 1997).

The higher resistance of chlorolichens to heavy metals compared with cyanolichens may be attributed to the phytochelatin synthesis in lichens with *Trebouxia* algae (Branquinho et al. 1997). Similarly in the present study, *P. hispidula*, a trebouxioid lichen, may gain an ecological advantage from their ability to counter heavy metal with prompt phytochelatin synthesis. However, there are few researches on the biosynthesis and function of phytochelatins in lichens in response to heavy metal exposure (Branquinho 2001; Pawlik-Skowrońska et al. 2002). Heavy metals are known to induce 'hsc' synthesis (heat shock proteins) which ultimately prevents damage of the membranes against sublethal and lethal temperatures. In plants, thermo protection by heavy metals via heat-shock cognates and the role of heat-shock proteins in protecting membrane damage by functioning as molecular chaperones is a manifestation of co-stress (Prasad 1997), which seems to be true for *Phaeophyscia hispidula* (Shukla et al. 2012a, b).

Lichens take up nutrients from (a) the substratum on which it is attached (bark, as in the case of epiphytic lichens) and (b) the metal-enriched ambient atmosphere (particulates and dissolved ions) (Nieboer and Richardson 1981). The concentrations of trace elements in lichen thalli may be directly correlated with environmental levels of these elements (Loppi et al. 1998; Purvis et al. 2008; Shukla and Upreti 2007a). Therefore, lichen biomonitoring can be applied to assess the air quality of an area. However, bioaccumulation is dependent on various factors, one of them being the contribution of the substratum on which lichen colonises (Lodenius et al. 2010; Thormann 2006; Baker 1983; Markert et al. 2003; St. Clair et al. 2002a, b). In a study carried out for assessing metal contents of a lichen species (*Pyxine subcinerea* Stirton) and mango bark collected from Haridwar city (Uttarakhand), were compared with soil, sampled from beneath the tree from which lichens were collected. The metal content in lichen, bark and soil ranged from 1,573 to 18,793, 256 to 590 and 684 to 801 μg $g^{-1}$, respectively. This clearly indicates that lichens accumulated higher amounts of metal compared to bark or soil. Statistical analysis revealed that metal concentration in lichens did not show significant linear correlation with the bark or soil. Pearson's correlation coefficients revealed negative correlation of Pb ($r=-0.2245$) and Ni ($r=-0.0480$) contents between lichen and soil, which indicate direct atmospheric input of metals from ambient environment. Quantification and comparison of elemental concentration in lichens, its substratum and soil can provide valuable information about air quality in the collection area (Shukla et al. 2013a, b).

Assessment of concentration variation of heavy metal provides vital information on the spatial behaviour of those metals affecting the air quality. In a study, samples of *Pyxine subcinerea* Stirton (a lichen species) were collected from Rudraprayag valley (Uttarakhand) to investigate the metal profile accumulated in lichens. Multivariate statistical analysis was carried out to elucidate possible contribution of various sources of pollution, including the anthropogenic sources as well, on the heavy metal profile in lichens. Cluster analysis successfully grouped geogenic and anthropogenic inputs represented by Al and Mn and Cu, Cd, Pb and Zn, respectively. Principal component analysis did segregate sites based on the origin (major contributors): PC1 corresponds to major contribution of geogenic metals, while PC2 corresponds to anthropogenic loadings. PC1 is dominated by highly significant positive loadings of Al and Mn, and PC2 is dominated by significant loadings of Cr, Pb, Zn and Cd. The study shows that lichen biomonitoring data may be effectively utilised to distinguish source of heavy metals in air which bioaccumulates in lichens (anthropogenic and/or natural sources) (Shukla unpublished) .

The origin of PAHs was also assessed using the Phe/Ant, Flu/Pyr, Ant/Ant + Phe, Flu/Flu + Pyr and Naph/Phen concentration ratios. The total concentration of 16 PAHs ranged from 3.38 to

25.01 μg $g^{-1}$ with an average concentration of 12.09 ± 9.38 (SD). The PAH ratios clearly indicate that PAHs were of mixed origin, a major characteristic of urban environment. Significantly higher concentration of phenanthrene, pyrene and acenaphthylene indicates road traffic as major source of PAH pollution in the city. The study establishes the utility of *P. hispidula* as an excellent biomonitoring organism in monitoring both PAH and metals from foothill to subtemperate area of the Garhwal Himalayas (Shukla and Upreti 2009).

In a long-term biomonitoring study carried out in Dehradun, capital city of Uttarakhand, it was observed that the total metal concentration was the highest at sites heavily affected by traffic like Mohkampur Railway Crossing, Haridwar Road (42,505 μg $g^{-1}$). Dela Ram Chowk, located in the centre of the city, also had higher metal concentration, 34,317 μg $g^{-1}$, with maximum concentration of Pb at 12,433 μg $g^{-1}$, while Nalapani forest area had minimum total metal concentration (1,873 μg $g^{-1}$) as well as minimum Pb level at 66.6 μg $g^{-1}$, indicating anthropogenic activity, mainly vehicular activity, responsible for the increase in metal concentration in the ambient environment. In comparison with the earlier years 2004 and 2006, air pollution as indicated by similar lichen shows a considerable increase in the total metal concentration (especially Pb) in the ambient air of Dehradun city, which may be attributed to exponential rise in the traffic activity in the last 5 years (Rani et al. 2011).

*Phaeophyscia hispidula*, a common foliose lichen, growing in its natural habitat, was analysed for the concentration of six heavy metals (Fe, Ni, Zn, Cr, Cu and Pb) from five different sites of Pauri city, Garhwal Himalayas, Uttaranchal, India. The concentration of metals is correlated with the vehicular activity and urbanisation. The total metal concentration is highest at Circuit House on Pauri-Devprayag Road, followed by Malli on Pauri-Srinagar Road, which experience heavy traffic throughout the year, while Kiyonkaleshwar area, having less vehicular activity, had minimum accumulation of metal. The statistical parameter, coefficient of variation % showed higher CV% for Fe and Cr but lower for Cu and Ni. The concentrations of most of the metals at different sites were statistically significant (0.01 level). There was high spatial variability in the total metal concentrations, at different sites, that ranged from 5,087.1 to 11,500.44 μg $g^{-1}$ with an average concentration of 8,220.966 ± 2,991.467 (SD) (Shukla and Upreti 2007b).

*Pyxine cocoes* a foliose lichen commonly growing on Mango trees in tropical regions of India is an excellent organism for determining the pollutants emitted from coal-based thermal power plant and accumulated in lichens after prolonged exposure. The diversity and distribution of lichens in and around such power plant act as useful tool to measure the extent of pollution in the area. The distributions of heavy metals from power plant showed positive correlation with distance for all directions. The speed of wind and direction plays a major role in dispersion of the metals. The accumulation of Al, Cr, Fe, Pb and Zn in the thallus suppressed the concentration of pigments (chlorophyll a, chlorophyll b, total chlorophyll); however, it enhanced the level of protein. Further the concentration of chlorophyll content in *P. cocoes* increased with decreasing the distance from the power plant, while protein carotenoid and phaeophytisation exhibit significant decrease.

The morphology, chemistry and anatomy of lichens play important role in accumulation of metals. Another common tropical lichen species *Phaeophyscia hispidula* belonging to the same lichen family (Physciaceae) as of *Pyxine* has distinct morphology and chemistry. A thick tuft of rhizinae (hair like structure) on the lower surface of the thallus in *Phaeophyscia hispidula* acts as a metal reservoir and thus exhibits higher accumulation of most of the metals than *Pyxine.* The crust-forming lichens attached tightly to the substrates through their whole lower surface have the highest accumulation of Al in the metal sequence, while the squamulose and foliose forms show Fe in the higher concentrations. The lichens have special affinity with iron and they accumulate iron in greater amount than other metals.

Chlorophyll degradation value is considered to be an appropriate index for evaluating the effects of heavy metal pollution in lichens. In the present investigation the value of chlorophyll degradation ranges between 0.579 and 0.995 and 1.4 and 0.80 for control site and a site with high levels of vehicular traffic, respectively, as reported by Kardish et al. (1987).

Coefficient of correlation between different physiological parameters shows that chlorophyll content is significantly correlated ($p < 0.01$) with carotenoid content, while protein content is negatively correlated with all other physiological parameters (with Chl. b $r = -0.5491$, carotenoid $r = -0.5809$, OD $r = -0.5034$).

In many studies from different regions of the world, concentration of total chlorophyll was affected by traffic level (Kauppi 1980; Arb et al. 1990; Carreras et al. 1998; Shukla and Upreti 2007a). Specifically, lichen located at sampling sites with high traffic level had increased chlorophyll concentration. It might be inferred that the content of chlorophylls increased parallel to the level of pollutant emitted by traffic.

According to Beckett and Brown (1983), Cd and Zn compete with one another for sites holding bivalent cations. It is consistent with the observation that the correlation coefficients between Cd and Zn, although not statistically significant, exhibit negative trends. Usually Zn, Cu and Fe are supposed to act antagonistically against Cd. Zn, Fe and Cu are negatively correlated with Cd. The significant positive correlation of protein with Cd indicates the synthesis of protein under Cd-stressed condition similar to expression of stress protein 70 (hsp 70) in the lichen photobiont *Trebouxia erici* (Bačkor et al. 2006). Metal tolerance in animal and plants (vascular and non vascular) is known to be conferred by production of a special class of proteins called metallothioneins and phytochelatins (PCs). The PCs play a central role in the detoxification of several heavy metals, especially Cd (Prasad 1997).

The higher resistance of chlorolichens to heavy metals compared with cyanolichens may be attributed to the phytochelatin synthesis in lichens with *Trebouxia* algae (Branquinho et al. 1997). Similarly in the present study, *P. hispidula,* a trebouxioid lichen, may gain an ecological advantage from their ability to counter heavy metal with prompt phytochelatin synthesis. However, there are few researches on the biosynthesis and function of phytochelatins in lichens in response to heavy metal exposure (Branquinho 2001; Pawlik-Skowrońska et al. 2002). Heavy metals are known to induce 'hsc' synthesis (heat shock proteins) which ultimately prevents damage of the membranes against sublethal and lethal temperatures. In plants, thermo protection by heavy metals via heat-shock cognates and the role of heat-shock proteins in protecting membrane damage by functioning as molecular chaperones are a manifestation of co-stress (Prasad 1997), which seems to be true for *P. hispidula.*

The assessment of lichen diversity in Dehra Dun city clearly indicates that the members of lichen family Physciaceae, especially *P. hispidula,* grows luxuriantly in both busy sites in the centre of the city and periurban rural areas (Shukla and Upreti 2007b). Increase in Physciaceae in temperate regions has been associated with both increasing temperature and increasing availability of nutrients (Loppi and Pirintsos 2000; Saipunkaew et al. 2007; van Herk et al. 2002).

More than 70 % of the population of India lives in rural areas and agriculture is their major livelihood. In the recent years diesel, being cheaper than petrol, is the predominant fuel used (>70 % consumption) for various agriculture practices and automobiles. Diesel exhaust is known to produce higher concentration of carcinogenic nitro-PAHs in comparison to petrol-fuelled vehicles along with low-toxicity 2-, 3- and 4-ringed PAHs. Petrol engine exhaust gases tend to have higher concentrations of the 5- and 6-ringed PAHs (benzo(*a*)pyrene, benzo(*g*,*h*,*i*) perylene, indeno(1,2,3-*cd*)pyrene, coronene) which are more carcinogenic than the 2- and 3-ringed PAHs. Nitro-PAHs are known to be potential health hazardous compounds even if its concentration in diesel exhaust is quite lower. Further, non-toxic simple PAHs like naphthalene may undergo photochemical reactions to form highly toxic nitro-PAHs such 1-nitronaphthalene (C.P.C.B 2005). Thus, diesel in India is the major contributor of PAH emissions into the environment (C.P.C.B 2005).

In a study carried out in Haridwar city, metallic contents (originating mainly due to vehicular activity) bioaccumulated in lichens were correlated with their PAH concentration to trace the source of PAH in air. The total metal concentration of four metals (chromium, copper, lead and cadmium) ranged between 369.05 and 78.3 μg $g^{-1}$, while concentration of 16 PAHs ranged between 1.25 and 187.3 μg $g^{-1}$. Statistical correlation studies revealed significant positive correlation between anthracene and chromium ($r=0.6413$, $p<0.05$) and cadmium with pyrene ($r=0.6542$, $p<0.05$). Naphthalene, acenaphthene, fluorene, acenaphthylene, anthracene and fluoranthene are reported to be main constituent of diesel vehicle exhaust which is in conformity with the present analysis as lead (indicator of petrol engine exhaust) had negative correlation with all these PAHs. The results indicate that diesel-driven vehicles contribute more towards ambient PAHs level.

Gas-particulate phase partitioning of PAHs may be monitored by studying the PAH profile in lichens. Anthropogenic sources at large are responsible for the release of PAHs, which gets bioaccumulated in plants along various spatial scales, based on their physicochemical properties. Atmospheric PAHs are distributed both in gaseous and particulate forms. In the present study a lichen species, *Dermatocarpon vellereum* Zschacke, has been collected from different altitudes in and around Rudraprayag valley, located in Central Himalayan region of India to investigate the spatial distribution of PAHs in the valley. PAHs concentration recorded ranged from 0.136 to 4.96 μg $g^{-1}$. Variation in PAHs concentration (based on ring profile) at different altitudes in comparison to centre of the town (Rudraprayag) at an altitude of 760 m provided vital information regarding spatial behaviour of PAHs. Result revealed that the bioaccumulation of 2- and 3-ringed PAHs was higher in samples from higher altitude, while bioaccumulation of fluoranthene (4 ringed PAH), having high spatial continuity, showed higher concentration in samples from localities away from town centre. The result verifies association of fluoranthene with particulate matter resulting in its wider distribution as suspended particulate matter and thus remains in gas phase as well. PAHs with 5 and 6 rings were confined to the lower altitude at the base of the valley justifying its particulate bound nature (Shukla et al. 2013).

It is clear from the studies that of all the studies carried out till date, members of the Physciaceae family are hyperaccumulators of metals and few species are established bioindicator species like *Pyxine cocoes*, *Phaeophyscia hispidula* and *Rinodina sophodes*.

### 5.3.2 Power Plants

Extensive use of coal in the thermal power plants causes some of the worst air pollution and has been linked to respiratory diseases and lung cancer. The burning of low-quality coal that contains high levels of fluorides and heavy metals is the main source of air pollution in China. A study reported that the IQs of children aged 8–13 in villages with high occurrences of fluorosis from burning this coal were about ten points lower than those in other areas (Li et al. 1995). It is reported that more than 40 million Chinese people suffer from symptoms of fluorosis caused by burning coal, making it the most widespread epidemic in China (Lee 2005).

Fossil fuels are a source of sulphur dioxide ($SO_2$) and carbon dioxide ($CO_2$). These compounds contribute to acidification and climate change. As a result of rapid economic growth, the use of fossil fuels, and the consequent emission of air pollutants, has been increasing in Asia and may do so in the coming decades. As a result, $SO_2$ emissions may increase fast in the future, and critical loads for acidifying deposition may be exceeded for a range of ecosystems in large parts of Asia (Foell et al. 1995). In Europe and North America, countries have developed strategies to reduce acidification by emission control. In Asia, such policies have only recently received attention and focus mainly on technologies to control $SO_2$ emissions like fuel and fuel gas desulphurisation. Replacing fossil fuels by renewable energy sources may be an alternative to these technical measures. This may also reduce $CO_2$ emissions (Boudri et al. 2002).

Recent literature referring to lichen biomonitoring of power plants has dealt mostly with airborne elements emitted by power plants using fossil fuels. The majority of the investigations of power plant emissions, airborne pollutants and lichens as monitors were performed in temperate zones. Lichens applied as monitors near coal-fired power stations in Portugal, for example, were found to accumulate heavy metals such as Fe, Co, Cr and Sb originating from coal and ash particles drifting through the air and positioned on the thallus (Freitas 1994). Freitas (1995) analysed the comparative accumulation of Cr, Fe, Co, Zn, Se, Sb and Hg in two vascular plants and in the epiphytic lichen *Parmelia sulcata* in an industrial region occupied by a thermal coal-fired power station, a chemical plant and an oil refinery. Of the three organisms, the lichen was found to be the most effective bioaccumulator. The technique of biomonitoring with lichens was also applied to estimate the air quality in the La Spezia district, Italy, in relation to a coal-fired power plant and other industrial activities (Nimis et al. 1990). The lichen *Parmelia caperata* collected from *Olea sativa* trees was meant to biomonitor the $SO_2$ pollution in the study area. The applied index, based on the frequency of species within a sampling grid, showed a high statistical correlation with pollution data measured by recording gauges. The distribution of the lichen *P. caperata* was found to correspond best with the lichen index. The lichen *P. caperata* was used again as a bioindicator of heavy metal pollution in an additional study in La Spezia (Nimis et al. 1993). Data on the amounts of 13 metals in lichen thalli in 30 stations were compared with the data of lichens collected in other parts of Italy. Mn and Zn did not coincide with substantial pollution-related phenomena, whereas extreme pollution-related phenomena coincided with high levels of Pb and Cd in an area adjacent to an industrial zone. Within the industrial zone, phenomena related to evident deposition referred to Al, As, Cr, Fe, Ni, Ti and V. Additional studies reported on the use of lichens around coal-fired power stations in arid and semiarid areas. Nash and Sommerfield (1981) found, within a radius of a few kilometres of a power station in New Mexico, that lichens contained elevated concentrations of B, F, Li and Se relative to lichens in more remote sites. One lichen species was found to contain elevated concentrations of Ba, Cu, Mn and Mo in sites located in the vicinity of the station. Few studies have been conducted in India involving lichen, only heavy metals (Bajpai et al. 2010a, b, c).

Effect of coal mining on frequency, density and abundance has been studied around Moghla coal mines, Kalakote area of Jammu and Kashmir (Charak et al. 2009). Study revealed that pollutants released from open coal mining activities not only effected quantitative distribution but also have effect on the quantitative parameters.

Levels of arsenic (As) and fluoride (F) were determined in an epiphytic lichen *Pyxine cocoes* (Sw.) Nyl., collected from the vicinity of a coal-based thermal power plant of Raebareli, India. Both elements are abundant in lichen thallus, while their substratum contained negligible amount. The As ranged between $8.9 \pm 0.7$ and $77.3 \pm 2.0$ μg $g^{-1}$ dry weight in thallus and $1.0 \pm 0.0$ and $9.7 \pm 0.2$ μg $g^{-1}$ dry weight in substratum, whereas F ranged between $9.3 \pm 0.52$ and $105.8 \pm 2.3$ μg $g^{-1}$ dry weight in thallus; however, it was not detected in the substratum. The quantities of As in thallus increased with decreasing distance from the power plant, but F showed an opposite trend. The distribution of As and F around the power plant showed positive correlation with distance in all directions with better dispersion in western side as indicated by the concentration coefficient ($R2$). The F accumulation patterns in lichens clearly indicate that the coal burning in power plant is the major contributor and has its maximum levels on the downwind side. The analysis of variance and LSD indicated that the As/F concentrations among lichen thallus is significant at $p < 0.01$ % level (Bajpai et al. 2010a, b, c).

The lichen diversity assessment carried out around a coal-based thermal power plant indicated the increase in lichen abundance with the increase in distance from the power plant in general. The photosynthetic pigments, protein and heavy metals were estimated in *Pyxine cocoes* (Sw.) Nyl., a common lichen growing around a thermal power plant for further inference. Distributions of heavy metals from the power plant showed positive correlation with distance for all directions; however, western direction has received better dispersion as indicated by the concentration coefficient *R*2 . Least significant difference analysis showed that speed of wind and its direction plays a major role in dispersion of heavy metals. Accumulation of Al, Cr, Fe, Pb and Zn in the thallus suppressed the concentrations of pigments like chlorophyll a, chlorophyll b and total chlorophyll; however, it enhanced the level of protein. Further, the concentrations of chlorophyll contents in *P. cocoes* increased with decreasing the distance from the power plant, while protein, carotenoid and phaeophytisation exhibited significant decrease.

### 5.3.3 Persistent Organic Pollutants (POPs)

POPs possess toxic properties and resist degradation. POPs bioaccumulate and are transported, through air, water and migratory species, across international boundaries, and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems (Stockholm Convention 2001) (Table 5.12). The Stockholm Convention on Persistent Organic Pollutants (POPs) was adopted in 2001 and revised in 2009 in response to the urgent need for global action to protect human health and the environment from chemicals that are highly toxic and persistent and bioaccumulate and move long distance in the environment. The Convention seeks the elimination or restriction of production and use of all intentionally produced POPs (i.e. industrial chemicals and pesticides). It also seeks the continuing minimisation and, where feasible, ultimate elimination of the releases unintentionally produced POPs such as dioxins and furans (http://www.pops.int/documents/convtext/convtext_en.pdf).

Over the last three decades, organic contaminants have been of increasing importance in environmental monitoring. For the last decades, persistent organic pollutants (POPs) have been found in large concentrations in Arctic areas. These substances accumulate in living organisms and are enriched throughout the food chain (Harmens et al. 2013).

Polychlorinated biphenyl (PCB) is one of the most important environmental toxins of this type. PCB is a group of synthetically produced persistent toxic chlororganic compounds. PCB is stored in the fatty parts of the organism and accumulates in the food chain. Humans, fatty fish and carnivores (such as polar bears) can therefore accumulate concentrations in their bodies that are so high that they are poisoned.

HCB is an interesting chemical in the category of POPs and has long half-lives in air, water and sediment (Mackay et al. 1992) and is extremely persistent in the environment. HCB had several uses in industry and agriculture. HCB was first introduced in 1933 as a fungicide on the seeds of onions, sorghum and crops such as wheat, barley, oats and rye. It is believed that agricultural use of HCB dominated its emissions during the 1950s and 1960s. Its octanol/air and octanol/water partition coefficients are lower than for many other POPs, which indicate it is more likely to undergo environmental re-cycling than for PCBs. Atmospheric degradation of HCB is extremely slow and is not an efficient removal process. In air, HCB is found almost exclusively in the gas phase, with less than 5 % associated with particles in all seasons except winter, where levels are still less than 10 % particle bound (Cortes et al. 1998; Cortes and Hites 2000). Gas phase partitioning results in its transport to great distance in the atmosphere before being removed by deposition or degradation. Van Pul et al. (1998) modelled the atmospheric residence time of HCB. The transport distance (the distance over which 50 % of the chemical is removed) for HCB was calculated to be $10^5$ km. Due to this long atmospheric residence time, it is distributed widely on national, regional or global scales. HCB in the troposphere can be removed from the air phase via atmospheric deposition to water and soil (Bidleman et al. 1986; Ballschmitter and Wittlinger 1991; Lane et al. 1992a, b). The hydrophobic nature of HCB results in its preferential partitioning into sediment, soil and plant surfaces (Barber et al. 2005).

**Table 5.12** List of Persistent Organic Pollutants (POPs) (according to Stockholm Convention 2001 and 2009 and LRTAP convention 1998 and 2009) and their sources

| Persistent Organic Pollutants (POPs) | LRTAP convention | Stockholm convention | Sources |
|---|---|---|---|
| Aldrin | 1998 | 2001 | Used as ectoparasiticide, pesticide |
| Chlordane | 1998 | 2001 | Used as ectoparasiticide, insecticide, termiticide and additive in plywood adhesives |
| DDT (1,1,1-trichloro-2,2-bis (4-chlorophenyl)ethane) | 1998 | 2001 | Disease vector control agents for malaria and intermediate in production of dicofol intermediate |
| Dieldrin | 1998 | 2001 | Pesticide |
| Endrin | 1998 | 2001 | None |
| Heptachlor | 1998 | 2001 | Termiticide |
| Hexachlorobenzene (HCB) | 1998 | 2001 | Solvent in pesticide |
| Mirex | 1998 | 2001 | Termiticide |
| Toxaphene | 1998 | 2001 | None |
| Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) | 1998 | 2001 | Unintentionally formed and released from thermal processes involving organic matter and chlorine as a result of incomplete combustion or chemical reactions |
| Polychlorinated biphenyls (PCB) | 1998 | 2001 | Unintentionally formed and released from thermal processes involving organic matter and chlorine as a result of incomplete combustion or chemical reactions |
| Chlordecone | 1998 | 2009 | Pesticide |
| Hexachlorohexane (HCH) including Lindane | 1998 | 2009 | Pesticide |
| Hexabromobiphenyl (HBB) | 1998 | 2009 | Industrial |
| PAHs | 1998 | 2009 | Unintentionally formed and released due to incomplete combustion of organic matter |
| Hexachlorobutadiene | 2009 | 2009 | Unintentionally formed and released due to incomplete combustion of organic matter |
| Pentachlorobenzene | 2009 | 2009 | Pesticide |
| Polybrominated diphenyl ethers (PBDEs) | 2009 | 2009 | Unintentionally formed and released due to industrial processes |
| Perfluorooctane sulfonic acid, its salts | 2009 | 2009 | Unintentionally formed and released due to industrial processes |
| Perfluorooctane sulfonyl fluorides (PFOs) | 2009 | 2009 | Unintentionally formed and released due to industrial processes |
| Polychlorinated naphthalenes | 2009 | NI | Unintentionally formed and released due to industrial processes |
| Short-chain paraffins (SCPs) | 2009 | NI | Unintentionally formed and released due to industrial processes |

*NI* not included

γ-HCH (gamma-hexachlorocyclohexane), also known as the insecticide Lindane, is a chlororganic compound that has been used both as an insecticide in agriculture and as pharmaceutical treatment for head lice and scabies. Lindane is a neurotoxin that primarily affects the nervous system, liver and kidneys in humans. It can also have a carcinogenic effect.

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) constitute a family of toxic, persistent and hydrophobic environmental pollutants, which have been shown to accumulate in biota. In Europe, environmental concentrations have increased slowly throughout this century until the late 1980s. These organic compounds have been shown to be carcinogenic in animals and humans. Sources inventories suggest that there are two main sources of PCDD/Fs in the environment: (1) combustion processes and (2) the occurrence as impurities in the manufacture of chlorinated aromatic products. A large number of combustion processes that generate PCDD/Fs occur in urban environments such as burning of coal, wood and petroleum, burning of municipal wastes, domestic burning and metal smelting. Food, especially products that originate from animals, is usually the main source of exposure for PCDD/Fs in humans. Uptake of persistent atmospheric PCDD/Fs in vegetation is the first step in the multi-pathway through the food chain resulting in the contamination of animals and humans.

In order to ensure temporal and spatial representation of pollution measurements, long-term continuous sampling at a large number of sites on broad scale is required. Measurements of PCDD/Fs atmospheric deposition with technical equipment at a regional and national scale are rarely available. Atmospheric analysis of PCDD/Fs is almost restricted to emission sources. Generally, articles concerning PCDD/Fs measurements are made in soil, water or biological organisms.

Lichens have a wide geographical distribution, occurring in rural areas as well as in urban and industrial areas, thus allowing comparison of pollutant concentrations from diverse regions. The morphology of lichens does not vary with seasons and therefore, accumulation can occur throughout the year. Furthermore, they depend mostly on the atmospheric deposition for their nutrition because 'root structures' do not function as in higher plants.

Different lichen species in places with different emission sources were collected at different times of the year in order to test the efficiency of lichens as PCDD/Fs biomonitors and the results showed that total concentration of PCDD/Fs in lichens was more similar to the concentrations reported for animals (top of the food chain) and soils (act as sinks) than those reported for plants. In general, the congeners and homologue profile observed in lichens resemble that of the atmosphere more that of the soil showing that lichens are potential good biomonitors of PCDD/Fs (Augusto et al. 2007).

India has extensive production and usage of organochlorine pesticides (OCPs) for agriculture and vector control. Despite this, few data are available on the levels and distribution of OCPs in the urban atmosphere of India. Passive and active air sampling conducted in seven metropolitan cities, New Delhi, Kolkata, Mumbai, Chennai, Bangalore, Goa and Agra, revealed concentrations (in pg·m$^{-3}$) ranged between 890 and 17,000 (HCHs), 250 and 6,110 (DDTs), 290 and 5,260 (chlordanes), 240 and 4,650 (endosulfans) and 120 and 2,890 (hexachlorobenzene). HCHs observed in India are highest reported across the globe. Chlordanes and endosulfans are lower than levels reported from southern China. Comparisons with studies conducted in 1989 suggested general decline of HCHs and DDTs in most regions. γ-HCH dominated the HCH signal, reflecting widespread use of Lindane in India. High *o,p′*-/*p,p′*-DDT ratios in northern India indicate recent DDT usage. Endosulfan sulphate generally dominated the endosulfan signal, but high values of α/β-endosulfan at Chennai, Mumbai and Goa suggest ongoing usage. Result shows local/regional sources of OCPs within India (Chakraborty et al. 2010).

No data is available on use of lichens for biomonitoring POPs in India except for PAHs (which has been discussed in detail in Sect. 5.1.3).

### 5.3.4 Peroxyacyl Nitrates (PAN)

Peroxyacyl nitrates ($RC(O)OONO_2$) is generated in air masses polluted by fuel emissions or by biomass burning. They are generally secondary pollutants produced by the photoinduced reactions initiated by the presence of volatile organic pollutants, ozone in atmosphere. They are toxic to the environment and phytotoxic in nature (Teklemariam and Sparks 2004), irritate human eyes and lead to genetic mutation (Kleindienst 1994). PAN act as reservoirs for odd nitrogen compounds, becoming involved in atmospheric circulation and influencing air quality (Singh et al. 1992a, b) on local, regional and global scales. PAN plays an important role in tropospheric chemistry and is a better indicator of photochemical smog than ozone (Zhang et al. 2011). Thermal decomposition rate of PAN is highly temperature dependent, resulting in lifetimes between 1 h at 298 K and about 5 months at 250 K. Thus, PAN can be transported over intercontinental distances in the cold upper troposphere (Singh 1987).

PAN was first detected in the Los Angeles area during smog episodes, exhibiting values of several ppbv (Stephens 1973). PAN amounts in clean air areas are generally much lower, namely, between 50 and 100 pptv only. Widespread southern hemispheric PAN pollution extending from South America to East and South Africa and as well as above the South Pacific has been observed during the annual biomass burning period in South America and South Africa in September and October (Singh et al. 1996, 2000a, b).

Only a few studies have reported PAN in Asia (Lee et al. 2008; Zhang and Tang 1994). More comprehensive studies have been carried out in North America and ambient PAN have been studied in southern California since 1960 (Grosjean 2003).

### 5.3.5 Ozone ($O_3$)

Ozone ($O_3$) is currently assumed worldwide as the most important air pollutant. Ozone is produced by photochemical reactions of the primary precursors such as hydrocarbons and nitrogen oxides (NOx). Emissions of these precursors are increased by industrialisation and the growing numbers of motor vehicles. Furthermore, $O_3$-producing photochemical reactions are favoured by high temperatures and high light intensities (Lefohn 1991). In many developing countries, urbanisation and industrialisation are increasing (Madkour and Laurence 2002).

Along the past decades, there has been a global increase in the lower tropospheric $O_3$ levels (Emberson et al. 2001) attributed primarily to increases in anthropogenic $O_3$ precursors (Derwent et al. 2002). Concentrations in rural or forested areas are generally as high as or higher than in urban regions (Millán et al. 1992). The identification and characterisation of $O_3$-induced foliar injury symptoms in well-adapted plant species by means of controlled field experiments are of major interest for assessing the risks imposed by air pollutants on local plant species. Such investigations assist in defining areas with phytotoxic concentrations and detecting levels of chronic pollution (Furlan et al. 2008).

In fact, bioindicator organisms must react to both atmospheric concentrations of pollutants and climatic conditions during exposures, the intensity of responses depending on the biological characteristics of each species, enabling the determination of the real amplitude of stress to which the plants and vegetation are exposed (Smith et al. 2003). Field surveys have recorded $O_3$-like injury symptoms on numerous tree, shrub and forbs species in Europe and North America (Furlan et al. 2008). However, little information is available on the effects of ozone on the multitude of native plant species throughout Europe or even North America and much less in tropical regions where $O_3$ concentrations have been increasing.

The effects of $O_3$ on lichens are poorly studied, compared with $SO_2$ and $NO_2$. The studies of toxicity of $O_3$ to lichens seem controversial. $O_3$ causes oxidative damage of cell membranes in lichens as a result of peroxidation of lipid membrane (Conti and Cecchetti 2001). Moreover, a field study with transplanted *Hypogymnia* *physodes* by Egger et al. (1994a, b) showed a high amount of end products of peroxidation in lichens exposed to a high concentration of $O_3$. However, Riddell et al. (2010) found no negative response of *Ramalina menziesii* to $O_3$ fumigations.

Few ozone studies have included bryophytes. Gagnon and Karnosky (1992) have shown that *Sphagnum* species are especially susceptible to ozone, having reduced photosynthesis, reduced growth, loss of colour and symptoms of desiccation, but that there are some remarkable reactive differences among species. Elevated ozone had no effect on germination of *Polytrichum commune* spores at concentrations of 11, 50, 100 and 150 ppb (Bosley et al. 1998), but it stimulated protonematal growth at 50 ppb and gametophore area increased to 189, 173 and 125 % of the controls at 50, 100 and 150 ppb, respectively, compared to that at ambient concentrations (Petersen et al. 1999).

Lichens are adversely affected by peak ozone concentrations as low as 20–60 μg $m^{-3}$ (0.01–0.03 ppm; Egger et al. 1994a, b; Eversman and Sigal 1987). With regard to ozone, most reports of adverse effects on lichens have been in areas where peak ozone concentrations were at least 180–240 μg $m^{-3}$ (0.09–0.12 ppm; Scheidegger and Schroeter 1995; Ross and Nash 1983; Sigal and Nash 1983; Zambrano et al. 2000). Although ozone can, in some cases, damage dry lichens, lichens are generally considered to be less susceptible to ozone damage when dry. Ruoss and Vonarburg (1995), for example, found no adverse effects on lichens in areas of Switzerland with daily summer peaks of 180–200 μg $m^{-3}$ (0.09–0.10 ppm) $O_3$. They attributed this lack of response to the fact that ozone concentrations never rose above 120 μg $m^{-3}$ (0.06 ppm) when the relative humidity was over 75 %.

Physical and chemical monitoring of air quality is still scarce in the country, even in the more developed south and southeast regions. Alternative methods, such as biomonitoring with sensitive plant species, are expected to offer effective means for identifying ozone-laden areas. Relatively little is known about the ambient levels of $O_3$ in lichens, especially in India, due to the high cost of using monitoring instruments to assess $O_3$ levels in urban and rural areas.

### 5.3.6 Increasing Tourism

Tourism is one of the fastest-growing economic sectors in the world. Similarly, in India, tourism has become one of the major sectors of the economy, contributing to a large proportion of the National Income (up to 6.23 % to the national GDP) and generating huge employment opportunities (8.78 % of the total employment). India witness more than five million annual foreign tourist arrivals and 562 million domestic tourism visits. The 'Incredible India' campaign launched by the Ministry of Tourism highlights natural and culture-rich areas of India, and location of Hindu holy pilgrimages, especially in the Himalayas, also attracts pilgrims (www.incredibleindia.org; www.itopc.org/travel-requisite/tourism-statistics.html).

No doubt tourist activity generates economy but there are pros and cons involved with the development of tourism industry in the country. One of the most important adverse effects of tourism on the environment is increased pressure on the carrying capacity of the ecosystem in each tourist locality. Increased infrastructural developments lead to large scale deforestation and destabilisation of natural landforms. Increased tourist flow leads to increased dumping of solid waste in the vicinity area resulting in disturbances as well as depletion of water and fuel resources. Flow of tourists to ecologically sensitive areas resulted in destruction of rare and endangered species due to trampling, disturbing of natural habitats which directly affect biodiversity, ambient environment and air quality profile of the tourist spot (Lalnunmawia 2010; Shukla 2007).

Lichen biomonitoring studies carried in the Himalayas and Western Ghats (biodiversity-rich areas) indicate that tourist activity has serious impact on the air quality of the area (Nayaka and Upreti 2005a, b). Changing lichen diversity due to infrastructural development is quite evident in urban settlements of Garhwal Himalayas

(Shukla and Upreti 2011a, b). In the holy pilgrimage centre of Badrinath, lichen diversity is dominated by toxitolerant lichens. The lichen family Physciaceae with 10 species is dominant in the area followed by Acarosporaceae and Parmeliaceae with 7 species each. *Lecanora muralis*, *Rhizoplaca chrysoleuca*, species of *Xanthoria* (*X. ulophyllodes, X. elegans* and *X. sorediata*) and *Dimelaena oreina* are abundant in the area.

In Gangotri, Gomukh (origin of holy river Ganga) and Badrinath areas, the occurrence of Physciaceae as the dominant family in these areas indicates nitrophilous conditions prevailing in the holy pilgrimages, which may be due to heavy tourist activity during the holy voyage (Upreti et al. 2004; Shukla and Upreti 2007c).

In the Badrinath area surface coverage of *Xanthoria elegans* and *Lecanora muralis*, known nitrophilous species, is very high. It has been reported by van Herk, (2001) that the presence and dominance of these nitrophilous species indicates the effect of human activity and animal rearing on lichen vegetation. The total absence of fruticose lichens in the area, highly sensitive to environmental alterations, also reflects the deteriorated air quality due to heavy vehicular activity and human activity as a result of pilgrimage.

In a study to observe the PAHs profile in different settlement of Garhwal Himalayas, it was found that out of the four localities the concentration of PAHs and the total carcinogenic PAH percentage (ΣcPAH%) was highest in lichens from Badrinath area, which is located in the inner Himalayas and experienced heavy vehicular and human activity during the 'holy voyage'. PAHs diagnostic ratios utilised to elucidate the probable source of origin of the PAHs indicated pyrolytic origin which is being attributed to cold climate and heavy usage of wood for cooking purpose (Shukla et al. 2010).

Vehicular activity resulting due to tourism adds on to the normal levels of emission due to daily anthropogenic activities (Shukla et al. 2012b). Vehicular activities not only emit significant quantity of metallic pollutant but also are major source of health hazardous compounds, PAHs. In an attempt to characterise, simultaneously, inorganic as well as organic pollutants in a biodiversity-rich area which is heavily influenced by tourist activity and, thus, assess the impact of tourist activity on the ecosystem, the study was carried out with an aim to assess the heavy metal (HM) and polycyclic aromatic hydrocarbons (PAHs) in the air of a biodiversity as well as tourist-rich area of Western Ghats by applying a most frequent-growing lichen *Remototrachyna awasthii* (Hale and Patw.) Divakar and A. Crespo, as biomonitor. Thalli of *R. awasthii* were collected from eight sites of Mahabaleshwar area located in Western Ghats. Total metal concentration (HM) ranged from 644 to 2,277.5 μg $g^{-1}$ while PAHs concentration between 0.193 and 54.78 μg $g^{-1}$. HM and PAHs concentrations were the highest at Bus stand, while control site (Lingmala Fall) exhibited the lowest concentration of HM as well as PAHs followed by samples from site with little or no vehicular activity (both these sites are having trekking route). It was also evident from this study that vehicular emission played a significant role in the release of HM and PAHs as pollutants in the environment.

B(a)P, the classical chemical carcinogen, is considered to be the useful indicator for cancer risk assessment. The average concentration of B(a)P in Mahabaleshwar ranged from BDL to 1.97. According to the World Health Organization (WHO), B(a)P is considered to be a reliable index for the assessment of total PAHs carcinogenicity. Since B(a)P is easily oxidised and photodegraded, therefore, the PAHs carcinogenic character could be underestimated. For better quantification of carcinogenicity related to the whole PAH factor, BaP equivalent potency (BaPE) index after Yassaa et al. (2001), Mastral et al. (2003) and Cheng et al. (2007) has been calculated. BaPE is quite high at bus stand and Venna Lake, whereas the control sites Lingmala Fall and Wilson Point have 0 values. BaPE index (Fig. 5.3), thus, indicates that the cancer risk is associated with high vehicular activity. Thus, urban population appears to be exposed to significantly higher cancer risk (Bajpai et al. 2013).

## 5.4 Conclusion

Environmental problems have been aggravated by the rapid expansion of human and industrial activities. In order to solve environmental problems and achieve sustainable development, an integrated effort has to be made to deal with a broad range of environmental issues, from identification of source, managing locally, regionally as well as globally. Biomonitoring is one such cost-effective and reliable method to keep a watch on the environmental problems persisting today.

The present discussion shows that biomonitoring studies not only provide data on the present air quality data but an integrated approach involving physicochemical analysis could establish bioindicators as an integral part of air quality regulatory practices in Asian countries, especially in India, as in the western countries. Biomonitoring data may be effectively utilised in regulatory management practices to reduce emissions of a wide array of toxic pollutants either at local level or by regulatory agencies, making use of natural resources as sentinels of sustainable development.

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