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Abstract

Based on the physicochemical characteristics, metals emitted from the source (both natural and anthropogenic) contributes towards spatial continuity at regional scale. Apart from intrinsic properties of metals, meteorological conditions and topography of the region is also known to contribute towards the spatial continuity. In the present study comparative spatial assessment of twelve metals in lichen *Phaeophyscia hispidula* collected from mountains and plains of north western India was carried out with the help of indicator kriging method. In plains and mountains the total metal concentration varies between 25.38 - 429.24 $\mu\text{g g}^{-1}$ and 22.77- 506.95 $\mu\text{g g}^{-1}$ dry weight respectively. Geospatial mapping provided insight into the spatial behavior of different metals in plain and mountain regions. In plains, Cr, Cd, Cu and Pb had higher concentration having higher coverage area, while metals like Cd and Hg had highest localized distribution indicating point sources. Observations indicated that apart from local sources, meteorological conditions specially wind direction also plays important role in spatial behavior of the metals, which has been verified by the bioaccumulation pattern of metals in lichen samples from mountainous region. Among which three mountainous states of North Western India, Uttarakhand has higher concentration of metals which may be attributed to the wind direction together with local anthropogenic sources.

Key Words: Lichens; topography; GIS mapping, interpolation technique, biomonitoring

Introduction

Heavy metals pose serious threat to the ecosystem due to its bioaccumulation and biomagnification properties. Both anthropogenic and geogenic (lithogenic) sources result in environmental contamination at local/regional/global scale. The diversity and distribution of various metals is known to be mainly influenced by emission source and climatic condition (Serelis et al. 2010). Quantification of metals merely provides the variation in the metal concentration at different locations. In order to understand the dispersal of metals and its ecotoxicological potential, spatial behaviour of metal requires to be investigated. Spatial interpolation technique visualizes the continuity and variability of sample data by creating continuous prediction surface onto a geographical space. As an effective tool of Geographical Information System (GIS), interpolation techniques compile and analyze

widespread data for precise regional representation of the variables from multiple sources as well as locales. The statistical interpolation methods illustrate spatial prediction at unknown points and can be used for diverse mapping applications for assessment of 'spatial risk' in health science, geochemistry, pollution modeling or climatic phenomenon at regional as well as global scale (Lam 1983; Watson 1992).

Spatial prediction of the above phenomenon's can be approximated by a function depending on the spatial heterogeneity and location of irregularly distributed sample points in geographical space (Mitas and Mitasova 1999). *Kriging*, one of the widely accepted interpolation techniques, has the advantage of considering the spatial structure of the variable, i.e., known spatially correlated distance or direction biases in the data points (Cattle et al. 2002; Raju et al. 2019). In recent years, a non-parametric approach based geostatistical kriging or cokriging estimator has been widely experienced to predict the probabilistic evidence of an unsampled point $Z[x,y]$ from unconditional data (Juang and Lee 2000; Passarella et al. 2002; Goovaerts et al. 2005, Adhikary et al. 2011).

The use of lichens in estimating the quality of the air, from different parts of the world are available and well studied more than four decades and published >2000 account on the lichen and environmental studies (Garty 2001, Shukla et al. 2014; Liu et al. 2016). However, the lichen biomonitoring data has been well utilized to predict the air quality of the area of interest, yet very few studies have been conducted in the country to investigate the regional pattern of metal pollution and its dispersal (Bajpai et al. 2010, 2014).

In the present study effort has been made to utilize spatial interpolation technique to compare the metal accumulation pattern at regional scale in plain and mountainous regions of North western India using lichen biomonitoring data to investigate the spatial behavior of metals studied and identify the pollution in disturbed areas and for framing regulatory policies.

Materials and methods

Study area and sample collection: The samples of a common foliose lichen *Phaeophyscia hispidula* (Ach.) Essl, was collected from different parts of the north central India by the authors RB and VS during 2016-2019 (Fig 1). The voucher (duplicate) specimens are deposited in CSIR-National Botanical Research Institute, Herbarium (LWG). At least three lichen samples with 3 replicate each (n=9) from each site was used for the analysis.

Elemental analysis: The oven-dried (70°C) lichen samples were grounded to fine powder and digested (0.5 g) in HNO₃: H₂O₂ (3:1 v/v). After digestion the volume was made to 5 ml by Milli Q water. Prior to analysis the samples were diluted 10 times and the concentration of elements (Fe, Zn, Co, Ni, Cu, Se, Mn, Mo, Cd, Hg, Cr and Pb) was analysed using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Agilent 7500 CE) following method by Dwivedi et al. (2010), internal standardization of all the samples was done by adding Rhodium (4 µg l⁻¹).

The standard reference materials of metals/metalloids (E-Merck, Germany) were used for the calibration and quality assurance for each analytical batch. Analytical data quality of metals/metalloids was ensured with repeated analysis (n=3) of quality control samples, and the results were found within (±2.82) the certified values. Recovery of Fe, Zn, Mn, Cu, Co, Se, Cr, Pb and As from the samples were found to be more than 98%, as

determined by spiking of samples with a known amount of elements. The detection limit for each element was 1 µg⁻¹.

Kriging for spatial interpolation: The spatial distribution of the random variable in space is the function of structural component showing the spatial trend of the variables $[m(x_i)]$, stationary regionalized component defining the local variation between the variable in space $[\varepsilon(x_i)]$, and random noise independent on location (ε') within the framework of a linear model. Spatial interpolation considers spatial autocorrelation between the random variables $[Z(x_i); i \in \{1 \dots n\}]$ to transform a regional database (elemental concentration in lichen *Phaeophyscia hispidula*) on to a smooth continuous surface. Spatial autocorrelation specifies the spatial dependency between the random variables and estimated through semivariogram (Berke 2004). Semivariogram defined as the half variance of the average square difference between points $[Z(x_i)]$ and $[Z(x_i + h)]$ separated at lag distance (h) and represented by Eq. 1 where, $\gamma(h)$ is semivariance, Z is the known variable at the location (x_i), n is the number of pairs of sample point $Z(x_i)$ and h is the lag width or distance between the pair of points (x_i) and ($x_i + h$) (Matheron 1963).

$$\gamma(h) = \frac{1}{2n(h)} \sum_{i=1}^{n(h)} \{Z(x_i) - Z(x_i + h)\}^2 \# \quad (\text{Eq. 1})$$

The 'semivariogram function' best fitted to the theoretical model is used to generate semivariogram parameters i.e. nugget (C_0), sill ($C_0 + C_1$) and range (C_2) using weighted least square technique. The best fitted semivariogram model allows predicting the variables (Z') at unknown locales (x_o) (Hohn 1999).

Indicator Kriging

Indicator kriging assumes a model where regionalized spatial autocorrelation between the random variable is a function of binary variable. The binary values are the indicator codes $[I(x_i) = 0 \text{ or } 1]$ transformed from the random variables $[Z(x_i); i \in \{1 \dots n\}]$ through the use of desirable threshold (Z_{th}) for continuous data (Hohn 1999). The indicator codes are estimates as 1 if $Z(x_i) \geq Z_{th}$, otherwise considered as 0. Spatial autocorrelation between the indicator codes (binary variables) is calculated using semivariogram function (Eq. 2) and best fit model is used to derive the semivariogram parameters. Sill gives the maximum value of semivariance $[\gamma_i(h)]$ of indicator codes and nugget (ε'') measure the variance of non-spatially autocorrelated noise of indicator codes.

$$\gamma_i(h) = \frac{1}{2n(h)} \sum_{i=1}^{n(h)} \{I(x_i; z_{th}) - I(x_i + h; z_{th})\}^2 \# \quad (\text{Eq. 2})$$

The derived value of semivariance $[\gamma_i(h)]$ of the indicator codes and Lagrange multiplier (L_m) is used to obtain weighted coefficient (λ_i) (Eq. 3) and spatial prediction (I') at an unknown point (x_o) is calculated using indicator kriging estimator using Eq. 4. As the value of indicator codes $I(x_i)$ are 0 or 1, the predicted probability variable also range in class 0 to 1.

$$\sum_{i=1}^n \lambda_i \gamma(x_i) + (L_m) = \gamma(x_i) \quad (Eq. 3)$$

$$I'(x_0; z_{th}) = \sum_{i=1}^n \lambda_i I(x_0; z_{th}) \quad (Eq. 4)$$

The suitability of exponential semivariogram models for prediction of indicator values are validated using Cross validation technique.

Results and Discussion

Twelve metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Mo, Cd, Pb and Hg) of geogenic as well as anthropogenic origin were analyzed in lichen, *Phaeophyscia hispidula* collected from different locations of northern plains (Uttar Pradesh, Madhya Pradesh, some parts of Chhattisgarh) and mountainous states (Jammu & Kashmir, Himachal Pradesh and Uttarakhand) of India. Result revealed substantial variation in the concentration of different metals in the two regions; in plains and mountains; the total metal concentration varied between 25.38 - 429.24 μgg^{-1} and 22.77 - 506.95 μgg^{-1} dry weight respectively (Table 1). Among all the localities highest concentration was observed for iron (345.6 μgg^{-1}) followed by manganese (341 μgg^{-1}) and zinc (179.66 μgg^{-1} dry weight) in lichen samples from Uttarakhand. Results shows that in plains metals are having wider distribution, while in mountains among the three states considered, Uttarakhand and Himachal Pradesh also has substantial presence of anthropogenic metals like Mercury (1.57 μgg^{-1} dry weight), Lead (228.08 μgg^{-1} dry weight) and Chromium (75.46 μgg^{-1} dry weight).

Among the various metals analyzed in lichen samples, from both plains and mountainous regions of India, showed variation in concentration of metals which may be due to local emissions or long range transport. The concentration of various metals analyzed in lichen *Phaeophyscia hispidula* samples from both plains and mountainous regions of India have used as point data (random variable) to generate a regional database for spatial interpolation. The concentration values of all twelve metals have transformed into indicator codes and spatial autocorrelation between them have been estimated from empirical semivariogram. The exponential semivariogram model has found best fitted to the experimental semivariogram of indicator codes and optimized values of nugget, sill and range of influence for each metal concentration has noted (Table 2). The semivariogram models for all metal concentration has explained and illustrated with an example of Cd.

The best fit exponential semivariogram model for indicator codes of Cd, shown as an example, indicates a nugget variance, C_0 of 0.039 with the sill, $C_0 + C_1$ (maximum elemental concentration in Lichen)² and the range of influence, C_2 as 20.72 and 27.75 km, respectively. Semivariogram parameters indicated that indicator codes of Cd have high spatial autocorrelation within the range of 27.75 km radius. The model indicated that the nugget variance is quite low (0.039) as compared to its corresponding maximum value of semivariance (sill) i.e. 2.072 (Table 2). A small value of nugget indicates the low non-spatially auto correlated variance of indicator codes. The quality of semivariogram model is explained by the semivariance percentage calculated using Eq. 5 which indicated that

~95.89% of the semivariance of the indicator codes is modeled by the semivariogram over a range of 27.75 km radius.

$$\text{Maximum Semivariance \%} = \frac{[\gamma_i(h)] - [(\varepsilon''x_i)]}{[\gamma_i(h)]} \times 100\# \quad (\text{Eq. 5})$$

The resultant semivariogram model and corresponding optimized semivariogram parameters for all elements are cross-validated. The cross-validation result of Cd concentration for an example is shown in Fig 2. The semivariogram models and cross validation for all twelve metal concentrations have been interpreted and explained in a similar way as Cd (Table 2 and Fig.3). Mean error and average standard error for exponential semivariogram models of all elemental concentration are within a range of 0.0042-0.067 and 0.44-0.51, respectively. Finally, predicted probability distribution maps of the corresponding element are later generated from indicator kriging estimator using Eq. 4. The predicted probability maps show a variable degree of all twelve metal concentrations at a scale of 0 to 1 both plain and mountainous regions of India.

The predicted probability maps of individual metals showed that spatial continuity of metals is more in plains while mountainous sites showed local hot spots, only mercury and cadmium showed highest spatial continuity in mountainous region (Fig 4 and Fig 5). Mercury is known to be emitted to the atmosphere from both natural and anthropogenic sources. The coal combustion, waste incineration, mining, refining and manufacturing and chlorine-alkali production are the major sources of Hg in the atmosphere. The human activities emit both elemental Hg with long life in the atmosphere and reactive gaseous mercury (RGM) and particulate Hg, which has short resident life in the air and are deposited near the emission source. It has been observed that natural sources are believed to be rich in elemental mercury (Li et al. 2009; Munteanu and Munteanu 2007). Spatial continuity of mercury shows wider distribution of mercury, indicating existence of elemental Hg. Since mercury sources are scanty in the mountains and shows long range transport in the area, yet the conclusion requires extensive monitoring of Hg in near future.

High spatial continuity of cadmium may be attributed to heavy tourist activity in mountain region due to location of pilgrimage centers in the mountains of north western India. Cadmium is released into the atmosphere by wear and tear of motorcar tires. Both anthropogenic and geogenic sources result in the emission of metals to the environment. Anthropogenic sources of metals are mostly related to vehicular activity as lubricating oil often contains metals like Cd, Cu, and Zn. Automobile tires and brake pads are potential source of Zn, while car metal plating in welded plates and in tires emit Ni to the environment (Shukla and Upreti 2007; Bajpai et al. 2004). Cd and Zn are very mobile and highly bioavailable metals which may be the main factor controlling its bioaccumulation in plants including lichens. Geogenic sources mainly include processes like leaching and weathering of rocks. Metals like Co and Ni known to found in organic matter and clays its mobility increases in acidic condition

The relative variation in rate of dispersion is known to be a controlling factor for the spatial continuity of the metals. It has been observed that metals like Ni and V reflect the particulate nature, which results in relative low rate of dispersion, while metals like Cu and Cr are dispersed in small particles resulting in higher spatial continuity of the metals, which is in conformity with the present observation.

Influence of topography and wind direction may well be understood by the variation in the metal concentration in the three hilly states of North western Himalayas. Of the three states, metal concentration is highest in Uttarakhand, as due to westerly winds the state is directly exposed to pollution load of northern India and dominant vehicular activity due to pilgrimage.

The present observations reveals the application of lichen biomonitoring data together with GIS tools to record the variation in the metal concentration and its probable correlation with other abiotic and biotic factors provides valuable information regarding its influence in controlling dispersal of pollutants at regional scale.

Conclusion

The study shows that metal profile is influenced by both anthropogenic and natural sources. The topography also plays an important role in the spatial distribution of metal in different region therefore, an integrated approach is required to understand the environmental consequence of metal and associated health effects. Though the study has been conducted taking few sites representative from various states but it presents the applicability of lichen biomonitoring data for regional mapping. Interpolation requires point data to be distributed normally in space. The study could be more reliable in future if proceed with a large number of samples data. However, the topographical constrain of mountainous region of northern India allow only limited data to collect. The study demonstrates that geographic information system may be predicting the probable zones of high risk. The study could help in planning sustainable environmental development of the concern region on a long term basis.

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Consent to Publish: All authors given his/her consent for publication and authors have no conflicts of interest.

Authors Contributions: Author RB collected samples, metal estimation and writing first draft of manuscript, VS also collected samples and assist in metals estimation and AR perform kriging analysis of data. Authors CPS and DKU provide fruitful discussions and comments for improving the manuscript.

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Availability of data and materials: The lichen voucher specimen was deposited in the herbarium of the CSIR-National Botanical Research Institute, Lucknow (LWG), India.

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286 **Legends:**

287 Figure 1: Map showing different localities in North Central India from where lichen samples were collected

288 Figure 2: Exponential semivariogram model best fitted to the experimental semivariogram of indicator values
289 transformed from Cd concentration of lichen *Phaeophyscia hispidula*. The best fit indicates that nugget
290 variance, C_0 is 0.039; sill, C_0+C_1 is 20.72 (elemental concentration in lichen)²; the range of influence, C_2
291 is 27.75 km

292 Figure 3: Cross validation showing relationship between measured and predicted indicator values of Cd
293 concentration.

294 Figure 4: Predicted probability maps showing distribution of elemental concentration in lichen, *Phaeophyscia*
295 *hispidula* in plains of north central India

296 Figure 5: Predicted probability maps showing distribution of elemental concentration in lichen, *Phaeophyscia*
297 *hispidula* in mountains of northern India.