Agropedology 2016, 26 (01), 87-93

Spatial distribution of Fe and Mn in paper mill effluent affected agricultural soils in Morigaon, Assam

S.K. Reza[1]*, Utpal Baruah[2] and S.K. Singh[3]

[1]*ICAR- National Bureau of Soil Survey and Land Use Planning, Sector-II, DK-Block, Salt Lake, Kolkata, West, India*
[2]*ICAR- National Bureau of Soil Survey and Land Use Planning, Jorhat, India*
[3]*ICAR-National Bureau of Soil Survey and Land Use Planning, Nagpur-440033, India*

Abstract: The spatial distribution of Fe and Mn in the paper mill effluent contaminated area of Jagiroad, Assam, India were investigated using statistics, geostatistics and GIS techniques. The total concentration of Fe and Mn were determined for 188 samples collected from the contaminated area. The mean concentration of Fe (7629 mg kg^{1}) was high. The highest and the lowest standard deviation were observed in the Fe (1749) and pH (0.81), respectively. Analysis of the isotropic variogram indicated that the Fe semivariogram was well described with the Gaussian model, with the distance of spatial dependence being 1354 m, while Mn was well described with the spherical model, with the distance of spatial dependence being 833 m. The ordinary kriging estimates of Fe and Mn maps showed that high concentrations of these metals occured in the low-lying areas like bils (lakes). For both the investigated heavy metals the prediction of goodness (G) value was greater than zero. This indicates that spatial prediction is better than assuming mean of observed value as the property value for any unsampled location. Thus the geostatistical method was spatial variability of Fe and Mn.

Keywords: *Heavy metals, geostatistics, spatial variability, accuracy assessment*

Introduction

Apart from transport and municipal services, industrial plants constitute the main source of heavy metals released to environment (Hjortenkrans *et al.* 2006). Heavy metals in wastewater coming from industries and municipal sewage are one of the main causes of water and soil pollution (Gupta *et al.* 2010; Chopra and Pathak 2012; Ghosh *et al.* 2012). Soils are the ultimate and most important sink for trace elements in the terrestrial environment and have a great capacity for receiving, purifying and decomposing wastes and pollutants of different kinds (Boon and Soltanpour 1992). The effect of industrial effluents on soil and the use of municipal and industrial wastewater for irrigation of crops are well documented (Kaur and Rani 2006; Reza *et al.* 2015a).

With growing public concern throughout the world over health hazards caused by polluted agricultural products, many studies have been conducted on metal and metalloid contamination in soils, water and sediments due to use of industrial wastewater (Ghosh *et al.* 2012). It is known that serious systemic health problems can develop as a result of excessive accumulation of dietary heavy metals in the human body (Petrisor *et al.* 2004). Heavy metals are of great concern in soil pollutants because they can threaten the health of human beings and animals through the food chain (Ladwani *et al.* 2012).

Geostatistics is a technology for estimating the soil property values in non sampled areas or areas with sparse samplings (Yao *et al.* 2004). These non-sampled areas can vary in space (in one, two or three dimensions) from the sampled data (Zhu *et al.* 2005). Geostatistical techniques incorporating spatial information into predictions can improve estimation and enhance map quality (Mueller and Pierce 2003). Geostatistics is extensively used to assess the level of soil contamination and estimation of risk in contaminated sites by preserving the spatial distribution and uncertainty of the estimates. In addition, geostatistics and GIS provide useful tools for the study of spatial uncertainty and hazard assessment (McGrath *et al.* 2004; Komnitsas and Modis 2006; Reza *et al.* 2013, 2014, 2015b).

*Corresponding Author Email: reza_ssac@yahoo.co.in

In the northeastern India, the wastewater produced and released by the Morigaon paper mill factory in Morigaon district of Assam, India drains directly into the agricultural fields, where the water is used for the irrigation of paddy crops. Our study investigates the extent of soil contamination by Fe and Mn using statistics, geostatistics and GIS techniques in order to reveal the spatial distribution patterns and provide a basis for hazard assessment.

Materials and Methods

Study area

The study site in Jagiroad, Morigoan paper mill, Assam, extends between 26°05'47[11] to 26°11'35[11] N latitude and 92°08'33[11] to 92°16'11[11] E longitude with 4605 ha (Fig. 1) area. The climate is humid subtropical. The maximum temperature is 33 °C during July and August; a minimum temperature falls as low as 7 °C in the month of January. Annual rainfall is 2169 mm and about 80% of rainfall is from the south-west monsoon.

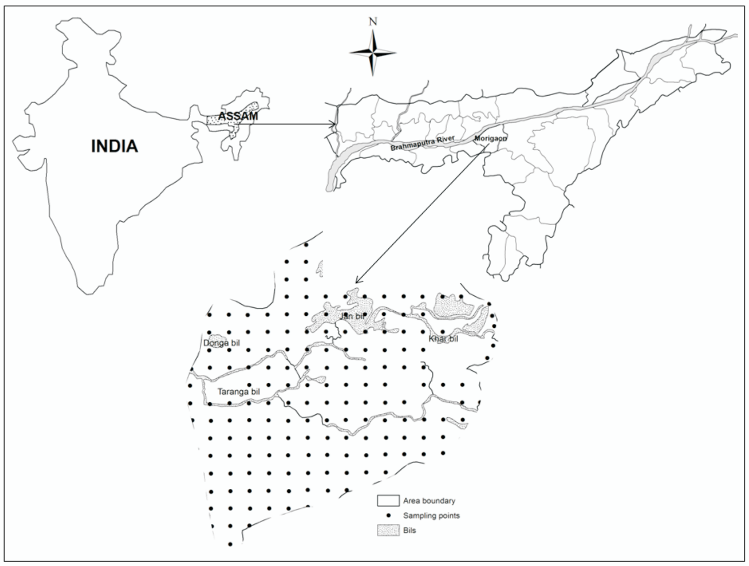

Fig. 1. Location and grid map of the study area

Soil sampling and analysis

A total of 188 surface soil samples were collected from 0-25 cm depth (plough layer) using a square (500 x 500m.) grid (Fig. 1) covering not only the waste disposal site, but also the surrounding cultivated areas with the help of a hand-held global positioning system (GPS). Soil samples were air-dried and ground to pass through a 2 mm sieve. Digestion of 0.50 g samples was performed with concentrated HNO_3, HF and $HClO_4$ in a microwave digester (model Start D, Milestone). Subsequently, the total concentration of Fe and Mn was determined by a Shimadzu AA6300 atomic absorption spectrophotometer.

Statistical analysis

The main statistical parameters, including mean, median, standard deviation, coefficient of variance, and maximum and minimum values, which are generally accepted as indicators of the central tendency and of the data spread, were analyzed. These statistical parameters were calculated with EXCEL® 2007 and SPSS 15.0.

Geostatistical analysis based on GIS

Spatial interpolation and GIS mapping techniques were employed to produce spatial distribution maps for the heavy metals. In ArcGIS, kriging can express the spatial variation and allow a variety of map outputs and at the same time minimize the errors of predicted values. Moreover, it is very flexible and allows users to investigate graphs of spatial autocorrelation. Kriging, as applied within moving data neighbourhoods, is a non-stationary algorithm which corresponds to a non-stationary random function model with varying mean but stationary covariance (Deutsch and Journal 1992). In kriging, a semivariogram model was used to define the weights of the function (Webster and Oliver 2001), and the semivariance is an autocorrelation statistic defined as follows (Mabit and Bernard 2007):

$$y(h) = \frac{1}{2N(h)} \sum_{i-1}^{N(h)} [z(x_i) - z(x_1 + h)]^2$$

Where $z(x_i)$ is the value of the variable z at location of x_i, h the lag and N (h) the number of pairs of sample points separated by h

During pair calculation for computing the semivariogram, maximum lag distance was taken as half of the minimum extent of sampling area. In this study, omni directional semivariogram was computed for the heavy metals because no significant directional trend was observed. Best-fit model with minimum root mean square error (RMSE) was selected for each heavy metal.

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^{N} [z(x_i) - z(x_1)]^2}$$

Using the model semivariogram, basic spatial parameters such as nugget (C_o), sill ($C + C_o$) and range (A) were calculated from the fitting curves which provide information about the structure as well as the input parameters for the kriging interpolation. Nugget is the variance at zero distance, sill is the lag distance between measurements at which one value for a variable does not influence neighboring values and range is the distance at which values of one variable become spatially independent of another (Lopez-Granados *et al.* 2002).

Accuracy assessment

Accuracy of the spatial distribution maps was evaluated through cross-validation approach (Davis 1987; Reza *et al.* 2010). Among three evaluation indices used in this study, mean absolute error (MAE), and mean squared error (MSE) measure the accuracy of prediction, whereas goodness of prediction (*G*) measures the effectiveness of prediction. MAE is a measure of the sum of the residuals (*e.g.* predicted minus observed) (Voltz and Webster 1990).

$$MAE = \frac{1}{N} \sum_{i=1}^{N} [z(x_i) - z(x_1)]^2$$

Where $\hat{z}(x_i)$ is the predicted value at location *i* Small MAE values indicate less error. The MAE measure, however, does not reveal the magnitude of error that might occur at any point and hence MSE was calculated,

$$MSE = 1/N \sum\nolimits_{\downarrow} (i=1)^{\uparrow} N = [z(x_{\downarrow} i) - \hat{z}(x_{\downarrow} i)]^{\uparrow} 2$$

Squaring the difference at any point gives an indication of the magnitude, *e.g.* small MSE values indicate more accurate estimation, point-by-point. The *G* measure gives an indication of how effective a prediction might be relative to that which could have been derived from using the sample mean alone (Schloeder *et al.* 2001).

$$G = \left[1 - \frac{\sum_{i=1}^{N} [z(x_i) - \hat{z}(x_i)]^2}{\sum_{i=1}^{N} [z(x_i) - \hat{z}]^2} \right] x100$$

Where *z* is the sample mean. If *G* = 100, it indicates perfect prediction, while negative values indicate that the predictions are less reliable than using sample mean as the predictors. The comparison of performance between interpolations was done using mean absolute error (MAE).

Results and Discussion

Descriptive statistics of Fe, Mn and other soil properties

The statistical characteristics like minimum, maximum, mean, standard deviation (SD), coefficient of variation (CV), skewness and kurtosis of pH, organic carbon, Fe and Mn are listed in Table 1. The mean concentration of Fe was high (7629.3 mg kg^{1}). The highest and the lowest standard deviation were observed in the Fe (1749) and pH (0.81), respectively. The higher standard deviation indicates higher variations in heavy metal distribution from the point source of discharge to the adjacent areas. Organic carbon and Mn exhibit a high variation (>50%) according to guidelines provided by (Warrick 1998).

Table 1. Summary statistics of Fe and Mn concentrations and selected soil properties

	pH	Organic carbon (%)	Fe	Mn
			mg kg$^{\circ 1}$	
Mean	5.3	1.63	7629.3	952.9
SD	0.81	0.90	1749.0	788.9
CV (%)	15.3	55.2	22.9	82.8
Minimum	3.6	0.15	4107.5	61.0
Maximum	7.8	5.40	13339.6	4041.7
Skewness	0.68	1.10	0.55	0.88
Kurtosis	°0.18	1.57	0.62	0.39
Distribution pattern			Normal	Normal

Semivariogram analysis of Fe and Mn

Semivariogram parameters (nugget, sill and range) for Fe and Mn with best-fitted modal were identified based on minimum root mean square error (RMSE). Analysis of the isotropic variogram indicated that the Fe semivariogram was well described with the Gaussian model, ~~with~~ the distance of spatial dependence being 1354 m, while the Mn semivariogram was well described the spherical model, with the distance of spatial dependence being 833 m (Table 2).

Table 2. Semivariogram model and parameters of Fe and Mn

Heavy metals	Fitted model	Nugget ($C_\circ$)	Sill ($C^\circ C_\circ$)	Range (A) (m)	Nugget/Sill
Fe	Gaussian	0.268	0.392	1354	0.684
Mn	Spherical	0.503	0.779	833	0.645

The nugget values were positive for both the metals. This spatial random variance is caused by the artificial nature of heavy metal pollution in soil; meaning that anthropogenic input like paper mill effluents is a significant source of heavy metals in the study area. The ratio of nugget and sill is commonly used to express the spatial auto-correlation of regional variables, which also indicates the predominant factors among all natural and anthropogenic factors (Robertson *et al.* 1997). The ratios of nugget and sill between 0.25 and 0.75 represented moderate spatial dependence; those below 0.25 represented strong spatial dependence; and all others represented weak dependence.

Spatial distribution and accuracy assessment

With the use of the available measurements for Fe and Mn concentration as well as the aforementioned structural models, we produced spatial maps of these pollutants using the ordinary kriging procedure. The spatial distribution maps of Fe and Mn (Fig. 2(a) and 2(b), respectively) showed that there was a high concentration of heavy metals located in the low-lying areas like bils (lakes and swamps), namely Donga, Jan, Khar and Taranga. The higher concentration of heavy metals in the soils of low-lying areas may be due to the paper mill effluents draining directly into the agricultural fields situated to the north-east, where the water is used for the irrigation of paddy crops. The evaluation indices for soil heavy metals in terms of mean absolute error (MAE), mean square error (MSE) and goodness of prediction (G) obtained from cross-validation procedures are shown in table 3.

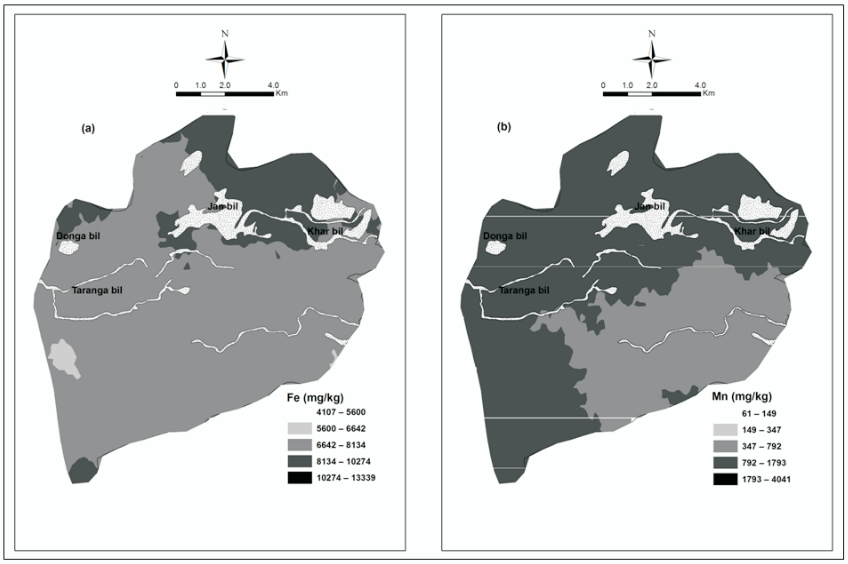

Fig. 2. Spatial distribution maps of (a) Fe and (b) Mn

For both the metals the G value was greater than zero. This indicates that spatial prediction is better than assuming mean of observed value as the property value for any unsampled location. This also shows that semivariogram parameters, obtained from fitting of experimental semivariogram values, reasonably describe the spatial variation (Reza *et al.* 2012).

Table 3. Evaluation performance of ordinary kriged map of heavy metals through cross-validation

Heavy metals	Mean absolute error (MAE)	Mean square error (MSE)	Goodness of prediction (G)
Fe	°24.98	110477	96
Mn	12.15	70040	86

Conclusions

Geostatistics and statistics have been employed for assessment and mapping of soil Fe and Mn pollution in the agricultural soils around the Jangiroad paper mill area in the Morigaon district of Assam, India. The summary statistics for soil properties showed that there was difference in the CV of the soil properties. A good variogram structure of heavy metals was observed, showing that there are clear spatial patterns of heavy metals on the distribution map and also that the current sampling density is sufficient enough to indicate such spatial patterns. The ordinary kriging interpolated map showed that there was a high concentration of heavy metals located in the low-lying areas like bils (lakes and swamps), namely Donga, Jan, Khar and Taranga. In general the geostatistical method on a large scale could be accurately used to evaluate spatial variability of soil heavy metals in northeastern India.

References

Boon, D.Y. and Soltanpour, P.N. (1992). Lead, cadmium and zinc contamination of aspen garden soils and vegetation. *Journal of Environmental Quality* **21**, 82-86.

Chopra, A.K. and Pathak, C. (2012). Bioaccumulation and translocation efficiency of heavy metals in vegetables grown on long-term wastewater irrigated soil near Bindal River, Dehradun. *Agricultural Research* **1**: 157-164.

Davis, B.M. (1987). Uses and abuses of cross-validation in geostatistics. *Mathematical Geology* **19**: 241-248.

Deutsch, C.V. and Journal, A.G. (1992). *Geostatistical software library and user's guide*. Oxford University Press, New York.

Ghosh, A.K., Bhatt, M.A. and Agrawal, H.P. (2012). Effect of long-term application of treated sewage water on heavy metal accumulation in vegetables grown in Northern India. *Environmental Monitoring and Assessment* **184**, 1025-1036.

Gupta, S., Satpati, S., Nayek, S. and Garai, D. (2010). Effect of wastewater irrigation on vegetables in relation to bioaccumulation of heavy metals and biochemical changes. *Environmental Monitoring and Assessment* **165**, 169-177.

Hjortenkrans, D., Bergback, B. and Haggerud, A. (2006). New metal emission patterns in road traffic environments. *Environmental Monitoring and Assessment* **117**, 85-98.

Kaur, R. and Rani, R. (2006). Spatial characterization and prioritization of heavy metal contaminated soil-water resources in peri-urban areas of National Capital Territory (NCT), Delhi. *Environmental Monitoring and Assessment* **123**, 233-247.

Komnitsas, K. and Modis, K. (2006). Soil risk assessment of As and Zn contamination in a coal mining region using geostatisretics. *Science of the Total Environment* **371**, 190-196.

Ladwani Kiran, D., Ladwani Krishna, D., Manik, V.S. and Ramteke, D.S. (2012). Assessment of heavy metal contaminated soil near coal mining area in Gujarat by toxicity characteristics leaching procedure. *International Journal of Life Sciences Biotechnology and Pharma Research* **4**, 73-80.

Lopez-Granados, F., Jurado-Exposito, M., Atenciano, S., Gracia-Ferrer, A., De La Orden, M.S. and Gracia-Toreres, L. (2002). Spatial variability of agricultural soil parameters in Southern Spain. *Plant and Soil* **246**, 97-105.

McGrath, D., Zhang, C. and Carton, O.T. (2004). Geostatistical analyses and hazard assessment on soil lead in Silvermines area, Ireland. *Environmental Pollution* **127**, 239-248.

Mueller, T.G. and Pierce, F.J. (2003). Soil carbon maps: Enhancing spatial estimates with simple terrain attributes at multiple scales. *Soil Science Society of America Journal* **67**, 258-267.

Petrisor, I., Dobrota, S., Komnitsas, K., Lazar, I., Kuperberg, C.M. and Serban, M. (2004). Artificial inoculation perspectives in tailings phytostabilization. *International Journal of Phytoremediation* **6**, 1-15.

Reza, S.K., Baruah, U. and Sarkar, D. (2012). Spatial variability of soil properties in Brahmaputra plains of North-eastern India: a geostatistical approach. *Journal of the Indian Society of Soil Science* **60**, 108-115.

Reza, S.K., Baruah, U. and Sarkar, D. (2013). Hazard assessment of heavy metal contamination by the paper industry, north-eastern India. *International Journal Environmental Studies* **70**, 23-32.

Reza, S.K., Baruah, U. and Singh, S.K. (2014). Soil risk assessment of heavy metal contamination near Oil Refinery area, Northeastern India. *International Journal of Environment and Biotechnology* **7,** 787-795.

Reza, S.K., Baruah, U. and Singh, S.K. (2015a). Accumulation and translocation of heavy metals in soil and crop irrigated with paper mill effluents. *Journal of the Indian Society of Soil Science* **63**, 242-244.

Reza, S.K., Baruah, U., Singh, S.K. and Das, T.H. (2015b). Geostatistical and multivariate analysis of soil heavy metal contamination near coal mining area, Northeastern India. *Environmental Earth Sciences* **73,** 5425-5433.

Reza, S.K., Sarkar, D., Baruah, U. and Das, T.H. (2010). Evaluation and comparison of ordinary kriging and inverse distance weighting methods for prediction of spatial variability of some chemical parameters of Dhalai district, Tripura. *Agropedology* **20**: 38-48.

Robertson, G.P., Klingensmith, K.M., Klug, M.J., Paul, E.A., Crum, J.C. and Ellis, B.G. (1997) Soil resource, microbial activity, and primary production across an agricultural ecosystem. *Ecological Applications* **7**, 158-170.

Schloeder, C.A., Zimmermen, N.E. and Jacobs, M.J. (2001). Comparison of methods for interpolating soil properties using limited data. *Soil Science Society of America Journal* **65**, 470-479.

Voltz, M. and Webster, R. (1990). A comparison of kriging, cubic splines and classification for redicting soil properties from sample information. *Journal of Soil Science* **41**, 473-490.

Warrick, A.W. (1998). *Spatial Variability in Environmental Soil Physics*. In: Hillel, D. (Eds.). Academic Press, USA. pp.655-675.

Yao, L.X., Zhou, X.C., Cai, Y.F. and Chen, W.Z. (2004). Spatial variability of soil properties at different sampling intensities and accuracy of their estimation. *Soils* **36**, 538-542.

Received : December, 2015 *Accepted : April, 2016*