Spatial distribution based on optimal interpolation techniques and assessment of contamination risk for toxic metals in the surface soil

Citation for published version:
Saha, A, Sen Gupta, B, Patidar, S & Martínez-Villegas, N 2022, 'Spatial distribution based on optimal interpolation techniques and assessment of contamination risk for toxic metals in the surface soil', *Journal of South American Earth Sciences*, vol. 115, 103763. https://doi.org/10.1016/j.jsames.2022.103763

Digital Object Identifier (DOI):
10.1016/j.jsames.2022.103763

Published In:
Journal of South American Earth Sciences

Spatial Distribution based on Optimal Interpolation Techniques and Assessment of Contamination Risk for Toxic Metals in the Surface Soil

Arnab Saha[1], Bhaskar Sen Gupta[1,*], Sandhya Patidar[1], Nadia Martínez-Villegas[2]

[1] Institute of Infrastructure and Environment, School of Energy, Geoscience, Infrastructure and Society, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom; as2059@hw.ac.uk (A.S.); s.patidar@hw.ac.uk (S.P.)

[2] Applied Geosciences Department, IPICyT, San Luis Potosi, 78216, Mexico; nadia.martinez@ipicyt.edu.mx

[*] Corresponding author: Bhaskar Sen Gupta; b.sengupta@hw.ac.uk

Abstract

The condition of the soil environment is critical for human health and agricultural sustainability. As a result, the environmental and ecological issues impacting the soils throughout the world are receiving more attention. This research focuses on local site-specific studies in Cerrito Blanco, Matehuala municipality, San Luis Potosi, Mexico, and describes different types of GIS interpolation techniques, multivariate statistical analysis, and various contamination indices to investigate the relationship between predictive accuracy, levels of contamination risk, and soil toxic metal elements variation . Inductively coupled plasma optical emission spectroscopy (ICP-EOS) used to test 39 digested surface soil samples for significant toxic metals (Ag, Cd, Co, Cr, Li, and Ni) after suitable dilution with deionised water. According to the results, we found that only the mean value of cadmium (Cd) exceeded the permissible standard value. After evaluating the four types of interpolation techniques, the Inverse Distance Weighting (IDW) was determined to be the optimal interpolation model for assessing the spatial distribution patterns of toxic metal concentration in the research area. The calculated contamination risk indices showed no significant high contamination risk due to soil-borne toxic metals. These results provide a comprehensive analysis of the impact of past mining activities on toxic metal concentrations in non-cultivated surface soil.

Keywords: Toxic metals; Soil contamination; Contamination indices; Spatial distribution; GIS

1. Introduction

Earth's soil is a valuable environmental resource that could be easily damaged by excessive agricultural, industrial, and other economic or adverse environmental activities. Heavy toxic elements in the environment from anthropogenic sources can be found naturally in the crust of the earth and surface soil. The environment is inextricably linked to human interaction, and pollution has long been a source of worry (Du et al., 2021). Toxic metals and inorganic compounds are inherent components of the overall ecosystems, and they circulate between the atmosphere, hydrosphere, lithosphere, and biosphere (Bargagli, 2000; Raulinaitis et al., 2012). Heavy toxic elements in highly contaminated regions can be distributed to other regions by surface water runoff, sediment deposition, groundwater movement, erosion, volcanic activity, and other environmental activities (Boening, 1999; Nouri et al., 2008; Hasan et al., 2016; Khound and Bhattacharyya, 2017; Ahmadi et al., 2018; Vargas-Solano et al., 2019). Toxic heavy metals in the soil have an impact on ecological, environmental, and sustainable agriculture, and become a health risk to humans (Liu et al., 2016; Phoungthong et al., 2016; Hou et al., 2017). Some heavy metals are necessary for human nutrition if concentrations do not exceed the acceptable limits, otherwise, they cause a variety of health issues.

Heavy metal contaminants vary substantially across the surface of the ground, making it impossible to get a precise spatial variability of toxic substances. Toxic metals in polluted soil can affect humans by explicit or implicit consumption, inhalation, and contact with the skin, posing a threat to human health. Human activities such as mining, industrialization, transportation, trash burning and dumping, fertilization, pesticide, and chemical use in agricultural farming can all contribute to heavy metal pollution in the soil (Soffianian et al., 2014). In addition to biotoxicity in the nutrition cycle, toxic elements can show habitat loss, resulting in impaired ecological environmental health. To confront this problem, researchers have been studying the distribution and transportation of toxic metals in soil, including the restoration of polluted soils (Li et al., 2012; Guan et al., 2015; Mondal and Pal, 2015; Hou et al., 2016; Li et al., 2020).

To precisely analyze the heavy metal concentration of soils, several techniques are used, including multivariate statistics, geostatistics, remote sensing, geographic information systems (GIS), and soil science (Davis et al., 2009; Chen et al., 2018; Kwiatkowska-Malina and Borkowski, 2020). Intensive and repetitive sampling is often challenging due to the high expense. Therefore, geographical interpolation techniques are needed to visualize the geospatial distribution of different soil contamination. It is feasible to assure the precision of the studies while minimising the use of people and physical expenses by combining statistical approaches with deterministic and geostatistical spatial interpolation techniques. Nevertheless, there are several challenges throughout the real analysis. For non-GIS specialists, major challenges include the determination of a suitable framework and the interpolation inside the study region (Du et al., 2021). Interpolation methods by multivariate generalized models and geostatistics include inverse distance weighting (IDW), kriging, radial basis functions (RBF), local polynomial (LP), and spline, which have become common in soil pollution studies and contamination mapping (Lee et al., 2006; Xie et al., 2011; Nickel et al., 2014; Soffianian et al., 2014).

Geostatistical spatiotemporal algorithms can provide a statistical probability approach for data assessment and assumptions based on the combination of geographic location and time dependency of observations (Kyriakidis and Journel, 1999). Various geostatistical tools have been combined with GIS functionalities for implementations that characterise semi-variogram analysis. Such approaches spatially interpolate dispersed estimations to develop spatially extensive large data sets and analyse the precision and accuracy of the resulting layers of information (Goovaerts et al., 2005; Burrough et al., 2015). The data must generally meet several criteria, including observational reliability, precise or relative homogeneity, and extensive and repetitive sampling in the standard statistical approach. However, the concentration of toxic heavy metals in soil samples is typically skewed and geographically autocorrelated in soil contamination studies (Ke-Lin et al., 2006; Kishné et al., 2003). Thus, data on metal concentrations might be shown as a topographical study based on spatial interpolation in a selected region. The initial process entails interpolation, proceeded by the interpolated data within defined geological regions (Kwiatkowska-Malina and Borkowski, 2020). Based on the characteristics of a particular component, aggregation assigns an average or median of the concentration of a component (material) to a specific geological region (Saito and Goovaerts, 2000; Namysłowska-Wilczyńska, 2019).

In the study of Bhunia et al., 2018, five different interpolation methods in a GIS environment are evaluated and compared for estimating the spatial distribution of soil organic carbon (SOC). The findings indicate that ordinary kriging (OK) was the most reliable method among the five different techniques due to the cross-validation approach of the least root mean square error (RMSE) as well as the highest R^2 value for interpolation. The study of Soffianian et al., 2014, identified eleven different types of heavy metal pollution in the hotspots using geostatistical interpolation methods based on the mean absolute error (MAE) and mean bias error (MBE) indices. Ha et al., 2014, studied the heavy metal pollution in soils by determining the concentrations of eleven heavy metals based on the large datasets of soil samples collected from industrial and residential sites using the geostatistical kriging interpolation technique to generate distribution maps of nonpoint sources of heavy metal contamination. The study of Goovaerts, 2010, presents a general formulation of a geostatistical kriging interpolation approach that allows the combination of both point and areal data in the applications to soil science and medical geography. Many more different types of studies have been done where different types of deterministic and geostatistical interpolation techniques have been used to extract soil heavy metal concentrations (Gotway et al., 1996; Imperato et al., 2003; Li et al., 2013; Chen et al., 2016; Liao et al., 2018).

This study presents a comprehensive contamination risk assessment of 39 soil samples containing heavy metals like Silver (Ag), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Nickel (Ni), and light toxic metal like Lithium (Li) in Matehuala, San Luis Potosi, Mexico. The analyses used a mix of GIS interpolation methods, multivariate statistical analysis, and different types of contamination indices to present the spatial distribution that helped in the estimation of the contamination risk level of toxic heavy metal contaminants in the surface soil. This research focuses on local site-specific studies and describes different types of GIS interpolation techniques, multivariate statistical analysis, and various contamination indices to investigate the relationship between predictive accuracy, levels of contamination risk and soil toxic metal elements variation on a local level. The results might provide valuable information to regulatory authorities as well as professionals working in the areas of environmental soil monitoring, conservation, and risk assessment.

2. Study Area

The study area lies in Cerrito Blanco, Matehuala municipality, San Luis Potosi, Mexico. It is located between 23°40'30"N latitude and 100°35'27" W longitude, having a total geographical area of approx. 4.84 ha. (Figure 1). The study area is Joya Verde soccer sports club, which is around fourteen years old and has three soccer fields. It was constructed on property that had user rights for farming purposes between 1974 and 2003. It is encircled by semi-desert vegetation and undeveloped agricultural cropland (Martínez-Villegas et al., 2018). The location is close to a mining region where concentrations of gold, silver, copper, lead, and zinc from El Fraile hill have been exploited for over 240 years. (Castillo-Nieto and Carranza-Alvarado, 1996; Castro-Larragoitia et al., 1997; Razo et al., 2004; Martínez-Villegas et al., 2013). Slags and developing construction waste materials from an abandoned metal ore furnace that functioned within Matehuala city until the 1960s have contaminated the environment (Manz and Castro, 1997; Martínez-Villegas et al., 2013; Saha et al., 2022). The earlier research has shown that mining and metallurgical waste polluted soils, water, agricultural farmlands and adversely affected the population in an area of over 100 km^2 surrounding the mining region (Castro-Larragoitia et al., 1997; Yáñez et al., 2003; Chapa-Vargas et al., 2010; Martínez-Villegas et al., 2013; Martínez-Villegas et al., 2018; Mendoza-Chávez et al., 2021). The average yearly temperature at this location is 14 degrees Celsius. The rainy season lasts from June to September with an estimated mean rainfall of 300 mm. According to the National Meteorological Service, Matehuala station, the average annual rainfall is 470 mm from 1925 to 1999 (Razo et al., 2004).

Figure 1: Map of study area showing soil sampling locations

3. Materials and Methods

3.1 Sampling and chemical analyses

A total of 39 soil samples at the depth of 0-5 cm were collected using an auger from the study area including soccer fields, grass-off zones between fields, bare soil, and scrublands (Martínez-Villegas et al., 2018). Soil samples were equally locatedover the study region, with an average distance between sampling locations of around 40-50 meters. A Garmin Etrex Personal navigator GPS device was used to georeference the sample locations. A fraction less than 2 mm was obtained by drying all soil samples at room temperature and sieving them. After that, the soil samples were digested following the ISO 11466:1995 procedure. This procedure describes a method for extracting trace elements from soils and other materials having less than around 20% (m/m) organic carbon using aqua regia. Additional nitric acid treatment will be required for materials having more than around 20% (m/m) organic carbon (ISO 11466:1995, 2015). Aliquots of digested samples were analysed for Ag, Cd, Co, Cr, Li, and Ni after suitable dilution with deionised water by inductively coupled plasma optical emission spectroscopy (ICP-EOS) (USEPA, 1994).

3.2 Interpolation approaches for toxic metals

The prediction of values of an attribute at unsampled areas using accessible data from other sampling areas is known as interpolation. Interpolation techniques consider the geographical location of sample points except for traditional modelling approaches (Schloeder et al., 2001). The approaches presented in this work were deterministic, such as IDW (Inverse Distance Weighted), LP (Local Polynomial), and RBF (Radial Basis Functions), and geostatistical interpolation like OK (Ordinary Kriging). All of the widely used interpolation techniques (Xie et al., 2011; Arslan and Turan, 2015; Bhunia et al., 2018) to estimate the spatial distribution of heavy toxic metals.

3.2.1 Inverse Distance Weighting (IDW)

This deterministic interpolation technique assumes those variables which are adjacent to one another are more similar than those that are farther apart. This technique analyses the values obtained surrounding the prediction point to estimate a value for any unobserved point. The measured values that are closer to the predicted location have a greater impact on the projected value than those that are further away. The weights are significantly dependent on the distance of the measured and predicted points raised to the power value. The impact of distant points is reduced as the power increases. The following formula is used in this interpretation (Arslan and Turan, 2015; Bhunia et al., 2018).

$$\mathrm{Z} = \sum_{i=1}^{n} (Z_i/d_i^p) \Big/ \sum_{i=1}^{n} (1/d_i^p)$$

Where Z is the estimated value at an interpolated point, Z_i is the measured value at point i, n is the total number of measured values which are used in interpolation, d_i is the distance between interpolated value Z and measured value Z_i, p denote the weighting power that defines how the weight decreases as the distance increases. Figure 2 shows a methodology flowchart that describes how the soil samples are collected and sub-sequent techniques for the identification of toxic content in the surface soil.

Figure 2: Methodology flowchart of interpolation techniques

3.2.2 Local Polynomial (LP)

Polynomial interpolation is the process of determining which polynomial may pass through a compilation of given locations (Liao et al., 2018). The global polynomial model and the standard moving average approach are combined in the local polynomial interpolation model, although local polynomial interpolation fits a required polynomial order (zero, first order, second order, third order, etc.) using points inside a specific region. The fitted polynomial at the centre of the region's points is utilized for each prediction, and the value used for each prediction is the value of the fitted polynomial at the centre of the region (Esri, 2021).

3.2.3 Radial Basis Functions (RBF)

Radial Basis Functions (RBF) are accurate and reasonably fast deterministic interpolation techniques. This interpolation technique has much more functionality, possibility, and parameters decision than others. Radial basis functions are a broad variety of precise interpolators that employ a fundamental equation based on the distance between the predicted and measured locations (Xie et al., 2011). This fundamental equation requires addressing the fact that the interpolation function minimizes a suitable function that indicates some aspect of the function's smoothness (Aguilar et al., 2005). In the report of Johnston et al., 2001, RBF minimizes the overall curvature of a surface by fitting it through observed data points. The following equation is the sum of two components that can be used to describe the prediction point value (Mitášová and Mitáš, 1993; Aguilar et al., 2005; Xie et al., 2011).

$$\mathrm{Z}(x) = \sum_{i=1}^{m} a_i f_i(x) + \sum_{j=1}^{n} b_j \psi(d_j)$$

Where, $\psi(d_j)$ denotes the radial basis functions and d_j shows the distance between each measured sample point to prediction point x. The trend function $f_i(x)$ is considered as a member of a basis for the space of polynomials of degree $< m$. The coefficients a_i and b_j must be determined using the mean of the following system of $n + m$ linear equations and their resolution; n is the total number of measured sampling points which are used in the interpolation as below:

$$\mathrm{Z}(x_k) = \sum_{i=1}^{m} a_i f_i(x_k) + \sum_{j=1}^{n} b_j \psi(d_{jk}) \qquad \text{for } k = 1,2,3\ldots\ldots n$$

$$\sum_{j=1}^{n} b_j f_k(x_j) = 0 \qquad \text{for } k = 1,2,3\ldots\ldots m$$

In this study, we have evaluated the different radial basis functions; completely regularized spline (CRS), spline with tension (ST), multi-quadratic function (MQ), inverse multi-quadratic function (IMQ), and thin-plate splines (TPS). The following functional equations are used for each radial basis functions cases (Aguilar et al., 2005; Xie et al., 2011).

CRS: $\psi(d) = \ln\left(\frac{cd}{2}\right)^2 + E_1(cd)^2 + \gamma$

ST: $\psi(d) = \ln\left(\frac{cd}{2}\right) + I_0(cd) + \gamma$

MQ: $\psi(d) = \sqrt{d^2 + c^2}$

IMQ: $\psi(d) = 1/\sqrt{d^2 + c^2}$

TPS: $\psi(d) = c^2 d^2 \ln(cd)$

Where, d shows the distance between measured and predicted points, c denotes the smoothing factor, I_0 indicates the modified Bessel function and γ is the Euler's constant.

3.2.4 Ordinary Kriging (OK)

Kriging assumes that the interpolated value can be considered as a regionalized variable. Various methods of kriging are used based on the stochastic characteristics of random fields. There are several types of kriging in the interpolation including ordinary kriging, simple kriging, indicator kriging, universal kriging, probability kriging, disjunctive kriging, and empirical Bayesian kriging. But the most prevalent interpolation technique used in geostatistical analyses is ordinary kriging (OK) (Güler et al., 2014; Arslan and Turan, 2015). It is a linear estimate approach that is both optimum and unbiased (Lin et al., 2001). Ordinary kriging provides approximate value by combining a linear combination of measured values whose weights are selected depending on the spatial correlation using the following equation (Arslan and Turan, 2015; Liao et al., 2018; Metahni et al., 2019):

$$\mathrm{Z}(x) = \sum_{i=1}^{n} \lambda_i Z(x_i)$$

Where $\mathrm{Z}(x)$ is the interpolated value at location x, $Z(x_i)$ is the measured value at position x_i, λ_i is the corresponding weight given to the residual of $Z(x_i)$, and n is the number of the sample data used at identified locations within the neighbourhood.

In the equations of kriging, the weights of ordinary kriging are determined by the semi-variogram function. The intensity of the statistical correlation depicts by semi-variogram as a function of distance. Semi-variogram was applied as the primary tool for studying spatial distribution patterns of the soil characteristics (Bhunia et al., 2018). An empirical semi-variogram function can be used to evaluate the semivariance parameter as well as the nugget effect (Webster and Oliver, 2007; Xie et al., 2011). The following equation is the function of semi-variogram, which is half of the mean squared difference between the paired data values based on intrinsic assumptions and the regionalized variable model (Robinson and Metternicht, 2006; Xie et al., 2011; Kabir et al., 2017; Bhunia et al., 2018).

$$\gamma(h) = \frac{1}{2n(h)} \sum_{i=1}^{n(h)} [Z(x_i) - Z(x_i + h)]^2$$

Where, $\gamma(h)$ is the semivariance value at the lag distance h, Z is the parameter of the soil property, $n(h)$ is the number of pairs of samples within the lag distance h, $Z(x_i)$ and $Z(x_i + h)$ are two sample values at two different locations of x_i and $x_i + h$ by the lag distance h.

3.3 Cross-validation and assessment of different interpolation results

A variety of techniques can be implemented to assess the correlations between the measured and predicted data values. The most popular approaches for comparing interpolation techniques are cross-validation using independent sample data. In this study, cross-validation has been used because the measured sample dataset was limited. For comparing the relation between predicted and measured values, cross-validation requires removing randomly measured data points and interpolating a value from the remaining dataset (Mueller et al., 2004). The mean relative error (MRE) and the root mean square error (RMSE) were calculated from the measured and predicted values to evaluate the accuracy of different interpolation techniques. The MRE and RMSE with the lowest values indicate the most accurate predictions. MRE and RMSE were derived using the following formulas:

$$MRE = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{Z^*(x_i) - Z(x_i)}{Z(x_i)} \right|$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} [Z^*(x_i) - Z(x_i)]^2}{n}}$$

Where, n is the number of measured sample data points, $Z(x_i)$ is the measured value at the i^{th} location, and $Z^*(x_i)$ is the predicted value at the i^{th} location.

According to previous research, the efficiency of interpolations was validated by randomly selecting 20% of all measured sample points from the contaminated soil dataset (Kazemi and Hosseini, 2011; Ghosh et al, 2012; Hu et al., 2016). In this study, we compared the spatial differences of polluted regions calculated by different interpolation approaches using the raster analysis feature of ESRI's ArcGIS software. The prediction accuracy of the interpolation method was assessed for the correlation between measured and predicted values, as well as for estimating the optimal application conditions for interpolation techniques as compared with other techniques.

3.4 Contamination risk assessment of toxic metals using indices

3.4.1 Geo-accumulation index (I_{geo})

According to Muller's (1969) formulation, the geo-accumulation index (I_{geo}) was used to estimate the hazardous heavy metal concentration in the soil by considering the total heavy metal contents detected to its background value or reference level concentrations. I_{geo} is computed using the following equation to determine the heavy metal contamination in the soil:

$$I_{geo} = \log_2 \frac{C_n}{1.5\ B_n}$$

Where, C_n is the measured metal concentration examined in the soil (mg/kg), B_n represents the reference value of n metal in the soil (mg/kg), and for the probable inconsistencies induced by anthropogenic influences, a factor of 1.5 was applied to fix the reference values of particular metal (Maurya and Kumari, 2021). Based on levels of contamination I_{geo} is classified into seven different classes, as listed in Table 1.

3.4.2 Contamination factor (C_f)

The contamination factor is considered a valuable approach for measuring and identifying toxic metal concentrations over a period. The contamination factor (C_f) is also known as the single pollution index (Hakanson, 1980). The following equation is used to calculate the contamination factor (C_f):

$$C_f = \frac{C_m}{C_b}$$

Where, C_m is the measured metal concentration of the soil sample and C_b is the background concentration of the metal. The contamination factor (C_f) is classified into seven categories, as shown in Table 1.

Table 1: Classification based on contamination indices for soil

3.4.3 Degree of contamination (C_d)

The total contamination in soil is determined using the degree of contamination (C_d). The degree of contamination (C_d) is calculated by adding the contamination factors of all measured metals. C_d is calculated by the following equation:

$$C_d = \sum_{i=1}^{n} C_f$$

Where, C_d is the degree of contamination, C_f is the contamination factor, and n is the total number of metals in the soil. The degree of contamination (C_d) is classified into four categories, as shown in Table 1.

3.4.4 Modified degree of contamination (mC_d)

The modified degree of contamination is calculated by dividing the degree of contamination by the total number of detected toxic metals in the soil to obtain the relative degree of contamination in a given sample. This mC_d index was first presented by Abrahim (2005). The degree of contamination (mC_d) is assessed using the following formula:

$$mC_d = \frac{C_d}{n}$$

Where, C_d refers to the degree of contamination and n is the total number of metals in the soil. The modified degree of contamination (mC_d) is classified into seven categories, as shown in Table 1.

3.4.5 Pollution load index (PLI)

The Pollution load index (*PLI*) presents a comprehensive assessment of the toxicological extent of pollutant metals in a specified soil sample by defining how much time the concentration of metals in the soil exceeded the normal background value. The nth number root of multiplications of the contamination factor of each hazardous metal in the soil sample determines the *PLI* (Maurya and Kumari, 2021). The *PLI* is also used to measure the overall level of contamination in the soil. This *PLI* index makes it simple to demonstrate the degradation of soil properties as a reaction of heavy metal concentration (Varol, 2011). The pollution load index (*PLI*) is determined using the following formula:

$$PLI = \sqrt[n]{C_f 1 \times C_f 2 \times C_f 3 \times \ldots .. \times C_f n}$$

Where, C_f is the contamination factor and n is the total number of analyzed toxic metals. *PLI* is classified into four different classes, as listed in Table 1.

3.4.6 Nemerow pollution index (PI_N)

The Nemerow Pollution Index (PI_N) is a method for determining the overall pollution status of the soil surfaces by contamination factor and incorporates the analysis of all toxic metal contents (Cheng et al., 2007; Qingjie et al., 2008). PI_N is calculated using the following formula:

$$PI_N = \sqrt{\frac{(Cf_{max})^2 + \left(Cf_{average}\right)^2}{2}}$$

Where, Cf_{max} is the maximum value of contamination factor for the individual toxic metals and $Cf_{average}$ is the mean value of contamination factor of all soil samples for the individual toxic metals. Based on PI_N values, toxic metal contamination of soil is classified into five different classes, as listed in Table 1.

4. Results and Discussion

4.1 Descriptive statistics of metals

Table 2 summarises the results of the descriptive statistical analysis done on 39 soil samples for five different heavy metals and one toxic light metal. The result of the distribution of toxic heavy metals in soil samples are represented by the mean (measured), standard error, median, standard deviation, sample variance, kurtosis, skewness, range, minimum, maximum, sum, coefficient of variation (CV), confidence level (95.0 %), and permissible limits (mg/kg). For higher kurtosis, chromium (Cr) has a higher peak (a larger positive deviation) in comparison with other metals. In this study, chromium (Cr) has a higher skewness value, and cadmium (Cd) has a lower skewness value. According to the study of Webster and Oliver, 2007, if the skewness of a variable is more than one, then the logarithmic transformation is used, but there are many different opinions of researchers. In our study, there has been a wide range of variations in lithium (Li), while cobalt (Co) has a more normal distribution.

The coefficient of variation is a valuable measure of the overall variation, though it is the ratio of standard deviation and means. The most essential component in determining the variation of toxic metal characteristics was the coefficient of variation (CV). The CV was used to classify the data according to the amount of variability as "low variability" (≤15 %), "moderate variability" (15–35 %), or "high variability" (>35 %) (Wilding, 1985; Arslan and Turan, 2015). This study reveals that all metals in the region had a high variation except lithium (Li) which was found to have a moderate variability. The highest variability was found in Silver (Ag) (86.39 %), while the lowest variability was found in Lithium (Li) (33.48 %). The different studies have suggested that data homogeneity and the CV might have an impact on the effectiveness of spatial interpolation techniques (Gong et al., 2014; Xie et al., 2020).

Table 2: Descriptive statistics for metal toxicants of soil samples

The toxic metal concentrations in soil were compared with permissible limits guidelines, according to previous studies (Ogundele et al., 2015; Kolesnikov et al., 2020). Soil contaminations by cobalt (Co), chromium (Cr), lithium (Li), and nickel (Ni) in the study area were far below the permissible limits, and silver (Ag) and cadmium (Cd) contaminants in some soil samples were also lower than the permissible limits. The amounts of silver (Ag) in the soil samples varied from 0.60 – 11.31 mg/kg (mean: 3.25 mg/kg), which are generally below the permissible guideline values defined by Kolesnikov et al., 2020. However, several samples exceeded these limits. Cadmium (Cd) concentration in the soil varied from 0 – 2.18 mg/kg (mean: 0.95 mg/kg), with several locations being above the permissible limit standards defined by Ogundele et al., 2015. Cobalt (Co) contaminants in soil samples ranged between 0 – 2.19 mg/kg (mean: 0.76 mg/kg), all samples were below the permissible guideline values according to Kosiorek and Wyszkowski, 2020. The concentrations of chromium (Cr) varied from 0.28 – 11.10 mg/kg (mean: 2.96 mg/kg), which did not exceed the permissible limit of 100 mg/kg (Ogundele et al., 2015). Lithium (Li) concentration also did not exceed the permissible limit of 25 mg/kg (Yalamanchali, 2012). Similarly, nickel (Ni) concentration values, which were between 0.24 – 8.37 mg/kg, were also below the permissible limits of 35 mg/kg (Ogundele et al., 2015). The essential data for the toxic metals measured in this study are summarised in the box and whisker plots presented in Figure 3. As a comparison with the background reference values of these toxic metals in the soil, all the samples had mean concentrations less than the reference values, confirming that the surface soils had not been contaminated by any anthropogenic causes but according to the study of Martínez-Villegas et al., 2018, arsenic contamination was found to be high in this study area due to metallurgical activity.

Figure 3: Box and whisker plots of the toxic metal concentrations

4.2 Assessment of interpolation techniques

Methods such as IDW (powers of 1, 2, 3, and 4), local polynomial (order of polynomial 1, 2, and 3), ordinary kriging (OK), radial basis functions (functions- CRS, ST, MQ, IMQ, and TPS) were used to analyse the spatial variation of toxic metals. The root means square error (RMSE) and mean relative error (MRE) values of cross-validation are summarized in Table 3. The most suitable technique is likely to be the one that gives the minimum RMSE and MRE values. However, if MRE wasn't the lowest value while RMSE is the lowest, the technique with the lowest RMSE value is more accurate (Arslan and Turan, 2015). When the RMSE values are equivalent, MRE values are also considered to identify the most effective technique.

The results show that IDW and its increased weighting power interpolations had the minimum RMSE and MRE values compared with other interpolation techniques. In addition to LP-3, RBF-IMQ, and RBF-TPS had large RMSE values. And for lithium and nickel, IDW-1 had higher RMSE values than the other methods. IDW-2 had the lowest RMSE values for silver (Ag) and cobalt (Co); however, for cadmium (Cd), chromium (Cr), lithium (Li), and nickel (Ni) were best-estimated using IDW-4. The interpolation accuracy is influenced significantly by the weight parameter. It is found that the higher the weighting power of IDW, the lower were RMSE and MRE of interpolation. But the higher the order of polynomial of LP, the higher were RMSE and MRE of cross-validation. The results of mean relative errors (MRE) of interpolation were similar to the RMSE. With lower MRE, IDW-4 was more accurate than other techniques. Among all heavy metals, lithium (Li) had the lowest MRE value of interpolation, and chromium (Cr) had the highest MRE value of interpolation. In Table 3, LP-3, RBF-IMQ, and RBF-TPS showed the higher RMSE and MRE values and should not be used to interpolate for metal contamination in soil.

Table 3: Accuracy of interpolation techniques used for identification of toxic metal content in the soil

Figure 4: Best fitted techniques of interpolation for mapping of toxic metals (a) Ag using IDW-2 (b) Cd using IDW-4 (c) Co using IDW-2 (d) Cr using IDW-4 (e) Li using IDW-4 (f) Ni using IDW-4

4.3 Validation of interpolation techniques

Spatial maps were created through different interpolation approaches using the GIS software and were validated by excluding 20% of the sample dataset and estimating for that sampling point, based on the remaining soil samples. Table 3 shows the results of the validation of spatial distribution maps for targeted metals. Spatial maps of heavy toxic metals prepared through different interpolation techniques were presented in Figures 4a, 4b, 4c, 4d, 4e, and 4f. The spatial variability of cobalt, cadmium, chromium, and nickel was similar, indicating that toxic metals soil sampling points were within permissible limits from northeast to southwest, although lithium showed comparable spatial variability.

4.4 Spatial distribution of heavy metals based on optimal interpolation approach

To interpolate the spatial distribution of heavy toxic metals, best-fitted interpolation techniques were applied (Figure 4). GIS software was used to map polluted regions for Ag, Cd, Co, Cr, Li, and Ni. Silver (Ag) was mapped into four categories for soil using IDW-2 (Figure 4a). A category has been divided according to the permissible limit of Ag in soil. Ag contaminations in the study area were above the permissible limit of 4.40 mg/kg throughout 20% of the study area. Cd contaminations ranged from 0 to 0.80 mg/kg in approximately 46.5 % of the study area, representing permissible limits of non-polluted soil, whereas it ranged from 1.61 to 2.18 mg/kg in about 17 % of the study area representing a severe hazard (Figure 4b).

Using IDW-2, cobalt (Co) was mapped into four categories (Figure 4c). The permissible limit for Co in the soil is usually less than 40 mg/kg, accordingly, 100 % of the study area was found as non-polluted soil. If the permissible limit of chromium (Cr) is considered, the whole area could be categorised as non-polluted (Figure 4d). But even then, it has been divided into fourcategories. Cr contaminations ranged from 0.28 to 2.30 mg/kg in close to 36 %, ranged from 2.31 to 5 mg/kg in close to 55 %, ranging from 5.01 to 8.40 mg/kg in close to 1 %, and ranged from 8.41 to 11.10 mg/kg in close to 8 %. Using IDW-4, lithium (Li) was mapped into four categories (Figure 4e). The permissible limit for Li in the soil is less than 25 mg/kg; accordingly, 100 % of the study area was found to be non-polluted. Using IDW-4, nickel (Ni) was also mapped into four categories (Figure 4f). As the map shows, the whole study area could be classified as non-polluted considering the permissible limit of Ni is 35 mg/kg. Silver (Ag) and cadmium (Cd) levels have been found in higher permissible limits in this area due to their legacy mining exploration of silver, cadmium, and other heavy toxic metals like copper, lead, zinc etc.

4.5 Principal component analysis for toxic metals

Principal component analysis (PCA) with VARIMAX normalized rotation was used to determine the distribution of toxic metals in the soils since it has been proven to be an efficient approach for determining the source of toxic contaminants (Hu et al., 2013; Wang et al., 2018). Two major components are identified by the Kaiser criteria (Kaiser, 1960) where eigenvalues greater than 1 were retrieved from the variables for additional investigation. Table 4 shows the results of the PCA for the toxic metal concentrations. The communalities indicated by the elements, including the two key components, ranged from 59.6 per cent for Ag to 96.3 per cent for Ni, demonstrating that these two primary components effectively identified all toxic metals. Component values more than 0.71 are usually considered good in the evaluation of PCA patterns, whereas those less than 0.32 are considered unsatisfactory (Nowak, 1998; Hu et al., 2013). Cd, Cr, Li, and Ni were included in the first principal component category (PC1), which described 61.35 per cent of the variation and contained Ag and Co in the second principal component category (PC2) representing 18.86 per cent of the overall variation. PC1 could be interpreted as a combination of anthropogenic and lithogenic sources, because of past mining activities. In PC2, high Ag and Co contents of soils from various effluent runoff. However, the past mining activities are believed to have caused toxic metals accumulation in the soil of this study area.

Table 4: Principal component analysis of toxic metals (components greater than 0.32 are shown in bold)

4.6 Cluster analysis for toxic metals

This study also used the hierarchical cluster analysis approach to find the overall homogenous groupings of toxic metals. Figure 5 shows that the dendrogram of the toxic metals obtained by the between-groups linkage clustering method using a measuring interval of squared euclidean distance. Cd-Co and Cr-Ni were found to be strongly correlated with each other and created a cluster. The cluster analysis revealed that Ag comprised the third individual group and suggesting that different distribution patterns. Li was separated from the other toxic metals in the soil, indicating a lack of interaction with other metals.

Figure 5: Dendrogram showing clustering of the toxic metals

4.7 Correlation matrix of toxic metals

A correlation matrix for toxic metals was constructed in an attempt to identify connections between metals and detect their common source in the soil. The correlation matrix of toxic metals in the surface soil is shown in Table 5. A strong positive correlation is observed among the metals examined, according to Pearson's correlation coefficient values. Cr and Ni have a correlation value of 0.936, indicating the strongest correlation at the 0.01 significance level and a common source for both metals. Li-Ni and Cd-Ni generated another strongly correlated bond with a correlation value of 0.882 and 0.867, indicating that they probably came from the same source. Ag had a negative significant correlation with Cd, Cr, Li or Ni and no significant correlation with Co, suggesting that the sources could be different from those of the other metals. Also, Co had no significant correlation with Cr and Li.

Table 5: Pearson's correlation matrix of selected toxic metals in the soil surface

4.8 Assessment of contamination using indices

The assessment of toxic metal contamination and environmental risk of the soils were evaluated using C_f, I_{geo}, PLI, C_d, mC_d, and PI_N in Table 1.

I_{geo} was used to evaluate the level deposition and concentration of toxic metal in the soils. Overall, the order of average value of I_{geo} was Cd (-0.42) > Ag (-1.43) > Li (-1.83) > Ni (-4.32) > Co (-5.28) > Cr (-6.01). According to the I_{geo} values, the toxic metals were less than zero in the soil, indicating that there is 'no contaminated' area. The I_{geo} values of Ag and Cd indicate a 'slight to moderate contamination' category for a few soil samples, as shown in Figure 6.

Figure 6: I_{geo} values of toxic metals for soil samples

The results and scattered plot of contamination factors (C_f) are shown in Table 6 and Figure 7. According to the C_f assessment result, the ranges for the respective toxic elements are as follows: Ag, 0.14 – 2.57; Cd, 0.00 – 2.73; Co, 0.00 – 0.05; Cr, 0.00 – 0.11; Li, 0.16 - 0.79; and Ni, 0.01 – 0.24. Hence the order of average value of C_f was Cd (1.19) > Ag (0.74) > Li (0.45) > Ni (0.09) > Cr (0.03) > Co (0.02). The C_f values for Cd in the soils of this study area showed a 'low to moderate contamination' category, while the C_f values for Ag, Li, Ni, Cr, and Co indicated a 'low contamination'. *PLI*, C_d, and mC_d values for all the metals studied for each soil sample are shown in Figure 8. The degree of contaminations (C_d) and modified degree of contaminations (mC_d) are reflected in the variations of pollution load index (*PLI*) of toxic metals. According to the range of *PLI* from 0.00 - 0.00009494, and the mean *PLI* value of 0.00000803, the study area was not polluted by these six metals. The degree of contaminations (C_d) for toxic metals at each soil sampling location indicated a low degree of contamination (Figure 8). Also, the measured modified degree of contaminations (mC_d) values for each soil sampling displayed a 'very low degree of contamination.

Figure 7: Scattered plot showing contamination factor of toxic metals

According to the Nemerow pollution indices (PI_N), Figure 9 indicates the spatial distribution characteristics of toxic metal contamination in the soils. The toxic metals at slightly contaminated levels were found in most parts of this region. Based on the spatial distribution of PI_N result, the contamination levels are as follows: slightly contaminated (2.31 ha area) ($1 \leq PI_N < 2$) > safe region (1.50 ha area) ($PI_N < 0.7$) > precaution region (1.02 ha area) ($0.7 \leq PI_N < 1$). However, arsenic contamination and risk has already been reported previously for this study area (Martínez-Villegas et al., 2018). The slightly contaminated and precautionary levels were found in the area surrounding soccer pitches, due to past metalliferous mining.According to the results, regions with a background of mining and industrial activities but low population density have a low risk of metal pollution, although high risk has been seen also. .

Figure 8: Scattered plot showing (a) pollution load index, (b) degree of contamination, and (c) modified degree of contamination in the study area

Table 6: The toxic metal pollution and risk assessment by Geo-accumulation index (I_{geo}), Contamination factor (C_f), Pollution load index (PLI), Degree of contamination (C_d), Modified degree of Contamination (mC_d) and Nemerow pollution index (PI_N)

Figure 9: The spatial distribution of the toxic metal contamination level using Nemerow pollution index (PI_N)

5. Conclusion

This study explored the application of different interpolation techniques and statistical analysis for detecting toxic metal contamination of soil as well as the risk associated with it. The interpolation techniques in this study are evaluated by statistical error estimation approaches. The error estimations are represented by the root mean square error (RMSE) and mean relative error (MRE). The study shows that the deterministic IDW interpolation technique gives more efficient than the geostatistical approach. It was observed that IDW-2 offers the best match for silver (Ag) and cobalt (Co), while IDW-4 offers the best match for cadmium (Cd), chromium (Cr), lithium (Li), and nickel (Ni). A local polynomial with higher-order, RBF-IMQ, and RBF-TPS techniques was not effectual, deriving higher RMSE and MRE than other interpolation methods. The best interpolation approach for each toxic metal was used to create maps indicating hazardous regions.

All of the toxic metals analysed have lower mean concentrations than their normal background reference values in the study soil. Based on the I_{geo} assessment guidelines, the mean level of contamination of all the toxic metals was below the threshold limit values. Cd was classified as having low to moderate contamination levels by the C_f classification standard, whereas the remaining metals were classified as having low levels of contamination. The correlation matrix and cluster analyses revealed that Co, Cr, Li, and Ni were primarily derived from lithogenic factors, whereas Ag and Cd were influenced by anthropogenic sources in the surface soils. From the overall comprehensive assessment of contamination risk, the results indicate that the surface soil collected from inside the Joya Verde soccer sport club, Cerrito Blanco, Matehuala municipality showed different levels of metal contamination, especially for the irrigated area of the soccer pitches showing low level of metal contamination. Among the six metals studied in this work, Ag and Cd indicated prominent contamination risk factors, which should be recognized as toxic metals present in surface soils. Anthropogenic activities and mining exploration areas surrounding them have led to relatively high levels of silver and cadmium in soil. The spatial interpolation techniques might be given more effective results with more near sampling and enough topographical information. Finally, the results contribute to the spatial distribution of reliable toxic metal contamination maps, which could also assist in the appropriate application of soil contamination studies and findings are valuable for preventing and reducing toxic metal contamination in soils.

Acknowledgements

Thanks to the Institute of Infrastructure and Environment, EGIS, Heriot-Watt University, Edinburgh. The authors are thankful to The School of Energy, Geoscience, Infrastructure and

Society (EGIS), Heriot-Watt University, Edinburgh for providing student bursary to the first author for doctoral research through the James Watt Scholarship. The author would also thanks to IPICyT, San Luis Potosi, Mexico for providing feedback and support.

Funding

This work was partly funded by the British Council UK-Mexico Institutional Grant No. 629008622. The grant supported the part-time research assistantship of Mr Arnab Saha.

References

Abrahim, G. M. S. (2005). Holocene sediments of Tamaki Estuary: Characterisation and impact of recent human activity on an urban estuary in Auckland, New Zealand. Ph.D. thesis, University of Auckland, Auckland, New Zealand, 361p.

Aguilar, F. J., Agüera, F., Aguilar, M. A., & Carvajal, F. (2005). Effects of terrain morphology, sampling density, and interpolation methods on grid DEM accuracy. Photogrammetric Engineering & Remote Sensing, 71(7), 805-816. Doi: 10.14358/PERS.71.7.805

Ahmadi, S., Jahanshahi, R., Moeini, V., & Mali, S. (2018). Assessment of hydrochemistry and heavy metals pollution in the groundwater of Ardestan mineral exploration area, Iran. Environmental earth sciences, 77(5), 1-13. Doi: 10.1007/s12665-018-7393-7

Arslan, H., & Turan, N. A. (2015). Estimation of spatial distribution of heavy metals in groundwater using interpolation methods and multivariate statistical techniques; its suitability for drinking and irrigation purposes in the Middle Black Sea Region of Turkey. Environmental monitoring and assessment, 187(8), 1-13. Doi: 10.1007/s10661-015-4725-x

Bargagli, R. (2000). Trace metals in Antarctica related to climate change and increasing human impact. Reviews of Environmental Contamination and Toxicology, 166, 129-174.

Bhunia, G. S., Shit, P. K., & Maiti, R. (2018). Comparison of GIS-based interpolation methods for spatial distribution of soil organic carbon (SOC). Journal of the Saudi Society of Agricultural Sciences, 17(2), 114-126. Doi: 10.1016/j.jssas.2016.02.001

Boening, D. W. (1999). An evaluation of bivalves as biomonitors of heavy metals pollution in marine waters. Environmental monitoring and assessment, 55(3), 459-470. Doi: 10.1023/A:1005995217901

Burrough, P. A., McDonnell, R. A., & Lloyd, C. D. (2015). Principles of geographical information systems. Oxford university press.

Caeiro, S., Costa, M. H., Ramos, T. B., Fernandes, F., Silveira, N., Coimbra, A., ... & Painho, M. (2005). Assessing heavy metal contamination in Sado Estuary sediment: an index analysis approach. Ecological indicators, 5(2), 151-169. Doi: 10.1016/j.ecolind.2005.02.001

Castillo-Nieto, F., Carranza-Alvarado, M. (1996). Geological Mining Monograph of the State of San Luis Potosí. Consejo de Recursos Minerales, Pachuca, Mexico.

Castro-Larragoitia, J., Kramar, U., & Puchelt, H. (1997). 200 years of mining activities at La Paz/San Luis Potosí/Mexico—Consequences for environment and geochemical exploration. Journal of Geochemical Exploration, 58(1), 81-91. Doi: 10.1016/S0375-6742(96)00054-4

Chapa-Vargas, L., Mejia-Saavedra, J. J., Monzalvo-Santos, K., & Puebla-Olivares, F. (2010). Blood lead concentrations in wild birds from a polluted mining region at Villa de La Paz, San Luis Potosi, Mexico. Journal of Environmental Science and Health, Part A, 45(1), 90-98. Doi: 10.1080/10934520903389242

Chen, T., Chang, Q., Liu, J., Clevers, J. G. P. W., & Kooistra, L. (2016). Identification of soil heavy metal sources and improvement in spatial mapping based on soil spectral information: A case study in northwest China. Science of the total environment, 565, 155-164. Doi: 10.1016/j.scitotenv.2016.04.163

Chen, Y., Jiang, X., Wang, Y., & Zhuang, D. (2018). Spatial characteristics of heavy metal pollution and the potential ecological risk of a typical mining area: A case study in China. Process Safety and Environmental Protection, 113, 204-219. Doi: 10.1016/j.psep.2017.10.008

Cheng, J. L., Zhou, S. H. I., & Zhu, Y. W. (2007). Assessment and mapping of environmental quality in agricultural soils of Zhejiang Province, China. Journal of Environmental Sciences, 19(1), 50-54. Doi: 10.1016/S1001-0742(07)60008-4

Davis, H. T., Aelion, C. M., McDermott, S., & Lawson, A. B. (2009). Identifying natural and anthropogenic sources of metals in urban and rural soils using GIS-based data, PCA, and spatial interpolation. Environmental Pollution, 157(8-9), 2378-2385. Doi: 10.1016/j.envpol.2009.03.021

Du, Q., Li, G., Zhou, Y., Wu, G., Chai, M., & Li, F. (2021, April). Distribution Characterization Study of the Heavy Metals for a Mining Area of East Tianshan Mountain in Xinjiang Based on the Kriging

Interpolation Method. In IOP Conference Series: Earth and Environmental Science (Vol. 719, No. 4, p. 042063). IOP Publishing. Doi: 10.1088/1755-1315/719/4/042063

Esri. (2021). How local polynomial interpolation works—ArcGIS Pro | Documentation. Retrieved August 19, 2021, from Arcgis.com website: https://pro.arcgis.com/en/proapp/2.7/help/analysis/geostatistical-analyst/how-local-polynomial-interpolation-works.htm

Ghosh, S., Gelfand, A. E., & Mølhave, T. (2012). Attaching uncertainty to deterministic spatial interpolations. Statistical Methodology, 9(1-2), 251-264. Doi: 10.1016/j.stamet.2011.06.001

Gong, G., Mattevada, S., & O'Bryant, S. E. (2014). Comparison of the accuracy of kriging and IDW interpolations in estimating groundwater arsenic concentrations in Texas. Environmental research, 130, 59-69. Doi: 10.1016/j.envres.2013.12.005

Goovaerts, P., AvRuskin, G., Meliker, J., Slotnick, M., Jacquez, G., & Nriagu, J. (2005). Geostatistical modeling of the spatial variability of arsenic in groundwater of southeast Michigan. Water Resources Research, 41(7). Doi: 10.1029/2004WR003705

Goovaerts, P. (2010). Combining areal and point data in geostatistical interpolation: Applications to soil science and medical geography. Mathematical geosciences, 42(5), 535-554. Doi: 10.1007/s11004-010-9286-5

Gotway, C. A., Ferguson, R. B., Hergert, G. W., & Peterson, T. A. (1996). Comparison of kriging and inverse-distance methods for mapping soil parameters. Soil Science Society of America Journal, 60(4), 1237-1247. Doi: 10.2136/sssaj1996.03615995006000040040x

Guan, Y., Shao, C., Gu, Q., Ju, M., & Zhang, Q. (2015). Method for assessing the integrated risk of soil pollution in industrial and mining gathering areas. International journal of environmental research and public health, 12(11), 14589-14609. Doi: 10.3390/ijerph121114589

Güler, M., Arslan, H., Cemek, B., & Erşahin, S. (2014). Long-term changes in spatial variation of soil electrical conductivity and exchangeable sodium percentage in irrigated mesic ustifluvents. Agricultural Water Management, 135, 1-8. Doi: 10.1016/j.agwat.2013.12.011

Ha, H., Olson, J. R., Bian, L., & Rogerson, P. A. (2014). Analysis of heavy metal sources in soil using kriging interpolation on principal components. Environmental science & technology, 48(9), 4999-5007. Doi: 10.1021/es405083f

Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. Water research, 14(8), 975-1001. Doi: 10.1016/0043-1354(80)90143-8

Hasan, M. R., Khan, M. Z. H., Khan, M., Aktar, S., Rahman, M., Hossain, F., & Hasan, A. S. M. M. (2016). Heavy metals distribution and contamination in surface water of the Bay of Bengal coast. Cogent Environmental Science, 2(1), 1140001. Doi: 10.1080/23311843.2016.1140001

Hou, D., Gu, Q., Ma, F., & O'Connell, S. (2016). Life cycle assessment comparison of thermal desorption and stabilization/solidification of mercury contaminated soil on agricultural land. Journal of cleaner production, 139, 949-956. Doi: 10.1016/j.jclepro.2016.08.108

Hou, D., O'Connor, D., Nathanail, P., Tian, L., & Ma, Y. (2017). Integrated GIS and multivariate statistical analysis for regional scale assessment of heavy metal soil contamination: A critical review. Environmental Pollution, 231, 1188-1200. Doi: 10.1016/j.envpol.2017.07.021

Hu, Y., Liu, X., Bai, J., Shih, K., Zeng, E. Y., & Cheng, H. (2013). Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization. Environmental Science and Pollution Research, 20(9), 6150-6159. Doi: 10.1007/s11356-013-1668-z

Hu, Y., Jia, Z., Cheng, J., Zhao, Z., & Chen, F. (2016). Spatial variability of soil arsenic and its association with soil nitrogen in intensive farming systems. Journal of soils and sediments, 16(1), 169-176. Doi: 10.1007/s11368-015-1182-7

Imperato, M., Adamo, P., Naimo, D., Arienzo, M., Stanzione, D., & Violante, P. (2003). Spatial distribution of heavy metals in urban soils of Naples city (Italy). Environmental pollution, 124(2), 247-256. Doi: 10.1016/S0269-7491(02)00478-5

ISO 11466:1995. (2015). ISO 11466:1995 Soil quality — Extraction of trace elements soluble in aqua regia, Retrieved March 1, 2022, from ISO website: https://www.iso.org/standard/19418.html

Johnston, K., Ver Hoef, J. M., Krivoruchko, K., & Lucas, N. (2001). Using ArcGIS geostatistical analyst (Vol. 380). Redlands: Esri.

Kabir, M. S., Salam, M. A., Paul, D. N. R., Hossain, M. I., Rahman, N. M. F., & Latif, M. A. (2017). Geo-statistical models for determining spatial variation and spatial dependency of soil arsenic in Bangladesh. Journal of the National Science Foundation of Sri Lanka, 45(2). Doi: 10.4038/jnsfsr.v45i2.8035

Kaiser, H. F. (1960). The application of electronic computers to factor analysis. Educational and psychological measurement, 20(1), 141-151. Doi: 10.1177/001316446002000116

Kazemi, S. M., & Hosseini, S. M. (2011). Comparison of spatial interpolation methods for estimating heavy metals in sediments of Caspian Sea. Expert systems with Applications, 38(3), 1632-1649. Doi: 10.1016/j.eswa.2010.07.085

Ke-Lin, H. U., Zhang, F. R., Hong, L., Huang, F., & Bao-Guo, L. I. (2006). Spatial patterns of soil heavy metals in urban-rural transition zone of Beijing. Pedosphere, 16(6), 690-698. Doi: 10.1016/S1002-0160(06)60104-5

Khound, N. J., & Bhattacharyya, K. G. (2017). Multivariate statistical evaluation of heavy metals in the surface water sources of Jia Bharali river basin, North Brahmaputra plain, India. Applied Water Science, 7(5), 2577-2586. Doi: 10.1007/s13201-016-0453-9

Kishné, A. S., Bringmark, E., Bringmark, L., & Alriksson, A. (2003). Comparison of ordinary and lognormal kriging on skewed data of total cadmium in forest soils of Sweden. Environmental monitoring and assessment, 84(3), 243-263. Doi: 10.1023/A:1023326314184

Kolesnikov, S. I., Tsepina, N. I., Sudina, L. V., Minnikova, T. V., Kazeev, K. S., & Akimenko, Y. V. (2020). Silver Ecotoxicity Estimation by the Soil State Biological Indicators. Applied and Environmental Soil Science, 2020. doi: 10.1155/2020/1207210

Kwiatkowska-Malina, J., & Borkowski, A. S. (2020). Geostatistical modelling of soil contamination with arsenic, cadmium, lead, and nickel: the Silesian voivodeship, Poland case study. AIMS Geosciences, 6(2), 135-148. Doi: 10.3934/geosci.2020009

Kyriakidis, P. C., & Journel, A. G. (1999). Geostatistical space–time models: a review. Mathematical geology, 31(6), 651-684. Doi: 10.1023/A:1007528426688

Lee, C. S. L., Li, X., Shi, W., Cheung, S. C. N., & Thornton, I. (2006). Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. Science of the Total Environment, 356(1-3), 45-61. Doi: 10.1016/j.scitotenv.2005.03.024

Li, X., Liu, L., Wang, Y., Luo, G., Chen, X., Yang, X., ... & He, X. (2012). Integrated assessment of heavy metal contamination in sediments from a coastal industrial basin, NE China. PloS one, 7(6), e39690. Doi: 10.1371/journal.pone.0039690

Li, F., Huang, J., Zeng, G., Yuan, X., Li, X., Liang, J., ... & Bai, B. (2013). Spatial risk assessment and sources identification of heavy metals in surface sediments from the Dongting Lake, Middle China. Journal of Geochemical Exploration, 132, 75-83. Doi: 10.1016/j.gexplo.2013.05.007

Li, Z., Lu, W., & Huang, J. (2020). Monitoring, Diffusion and Source Speculation Model of Urban Soil Pollution. Processes, 8(11), 1339. Doi: 10.3390/pr8111339

Liao, Y., Li, D., & Zhang, N. (2018). Comparison of interpolation models for estimating heavy metals in soils under various spatial characteristics and sampling methods. Transactions in GIS, 22(2), 409-434. Doi: 10.1111/tgis.12319

Lin, Y. P., Chang, T. K., & Teng, T. P. (2001). Characterization of soil lead by comparing sequential Gaussian simulation, simulated annealing simulation and kriging methods. Environmental Geology, 41(1-2), 189-199. Doi: 10.1007/s002540100382

Liu, J., Yang, T., Chen, Q., Liu, F., & Wang, B. (2016). Distribution and potential ecological risk of heavy metals in the typical eco-units of Haihe River Basin. Frontiers of Environmental Science & Engineering, 10(1), 103-113. Doi: 10.1007/s11783-014-0686-5

Manz, M., & Castro, L. J. (1997). The environmental hazard caused by smelter slags from the Sta. Maria de la Paz mining district in Mexico. Environmental Pollution, 98(1), 7-13. Doi: 10.1016/S0269-7491(97)00107-3

Martínez-Villegas, N., Briones-Gallardo, R., Ramos-Leal, J. A., Avalos-Borja, M., Castañón-Sandoval, A. D., Razo-Flores, E., & Villalobos, M. (2013). Arsenic mobility controlled by solid calcium arsenates: A case study in Mexico showcasing a potentially widespread environmental problem. Environmental Pollution, 176, 114-122. Doi: 10.1016/j.envpol.2012.12.025

Martínez-Villegas, N., Hernández, A., Meza-Figueroa, D., & Sen Gupta, B. (2018). Distribution of arsenic and risk assessment of activities on soccer pitches irrigated with arsenic-contaminated water. International journal of environmental research and public health, 15(6), 1060. Doi: 10.3390/ijerph15061060

Maurya, P., & Kumari, R. (2021). Toxic metals distribution, seasonal variations and environmental risk assessment in surficial sediment and mangrove plants (A. marina), Gulf of Kachchh (India). Journal of Hazardous Materials, 413, 125345. Doi: 10.1016/j.jhazmat.2021.125345

Mendoza-Chávez, Y. J., Uc-Castillo, J. L., Cervantes-Martínez, A., Gutiérrez-Aguirre, M. A., Castillo-Michel, H., Loredo-Portales, R., ... & Martínez-Villegas, N. (2021). Paracyclops chiltoni inhabiting water highly contaminated with arsenic: Water chemistry, population structure, and arsenic distribution within the organism. Environmental Pollution, 284, 117155. Doi: 10.1016/j.envpol.2021.117155

Metahni, S., Coudert, L., Gloaguen, E., Guemiza, K., Mercier, G., & Blais, J. F. (2019). Comparison of different interpolation methods and sequential Gaussian simulation to estimate volumes of soil contaminated by As, Cr, Cu, PCP and dioxins/furans. Environmental pollution, 252, 409-419. Doi: 10.1016/j.envpol.2019.05.122

Mitášová, H., & Mitáš, L. (1993). Interpolation by regularized spline with tension: I. Theory and implementation. Mathematical geology, 25(6), 641-655. Doi: 10.1007/BF00893171

Mondal, D., & Pal, S. (2015). A multi-parametric spatial modeling of vulnerability due to arsenic pollution in Murshidabad district of West Bengal, India. Arabian Journal of Geosciences, 8(10), 8047-8054. Doi: 10.1007/s12517-015-1809-4

Mueller, T. G., Pusuluri, N. B., Mathias, K. K., Cornelius, P. L., Barnhisel, R. I., & Shearer, S. A. (2004). Map quality for ordinary kriging and inverse distance weighted interpolation. Soil Science Society of America Journal, 68(6), 2042-2047. Doi: 10.2136/sssaj2004.2042

Muller, G. (1969). Index of geoaccumulation in sediments of the Rhine River. Geojournal, 2, 108-118.

Namysłowska-Wilczyńska, B. (2019). Application of Geostatistical Techniques for the Determining of an Anomalous Zone of Copper Ore Deposit in the Area of Polkowice Mine (Region of Lubin-Sieroszowice, SW Part of Poland). Geoinfor Geostat: An Overview, 7(1), 1-22. doi: 10.4172/2327-4581.1000202

Nickel, S., Hertel, A., Pesch, R., Schröder, W., Steinnes, E., & Uggerud, H. T. (2014). Modelling and mapping spatio-temporal trends of heavy metal accumulation in moss and natural surface soil monitored 1990–2010 throughout Norway by multivariate generalized linear models and geostatistics. Atmospheric Environment, 99, 85-93. Doi: 10.1016/j.atmosenv.2014.09.059

Nouri, J., Mahvi, A. H., Jahed, G. R., & Babaei, A. A. (2008). Regional distribution pattern of groundwater heavy metals resulting from agricultural activities. Environmental Geology, 55(6), 1337-1343. Doi: 10.1007/s00254-007-1081-3

Nowak, B. (1998). Contents and relationship of elements in human hair for a non-industrialised population in Poland. Science of the Total Environment, 209(1), 59-68. Doi: 10.1016/S0048-9697(97)00298-2

Qi, Z., Gao, X., Qi, Y., & Li, J. (2020). Spatial distribution of heavy metal contamination in mollisol dairy farm. Environmental Pollution, 263, 114621. Doi: 10.1016/j.envpol.2020.114621

Qingjie, G., Jun, D., Yunchuan, X., Qingfei, W., & Liqiang, Y. (2008). Calculating pollution indices by heavy metals in ecological geochemistry assessment and a case study in parks of Beijing. Journal of China university of geosciences, 19(3), 230-241. Doi: 10.1016/S1002-0705(08)60042-4

Ogundele, D. T., Adio, A. A., & Oludele, O. E. (2015). Heavy metal concentrations in plants and soil along heavy traffic roads in North Central Nigeria. Journal of Environmental & Analytical Toxicology, 5(6), 1. doi: 10.4172/2161-0525.1000334

Phoungthong, K., Xia, Y., Zhang, H., Shao, L., & He, P. (2016). Leaching toxicity characteristics of municipal solid waste incineration bottom ash. Frontiers of Environmental Science & Engineering, 10(2), 399-411. Doi: 10.1007/s11783-015-0819-5

Raulinaitis, M., Ignatavičius, G., Sinkevičius, S., & Oškinis, V. (2012). Assessment of heavy metal contamination and spatial distribution in surface and subsurface sediment layers in the northern part of Lake Babrukas. Ekologija, 58(1), 33-43. Doi: 10.6001/EKOLOGIJA.V58I1.2348

Razo, I., Carrizales, L., Castro, J., Díaz-Barriga, F., & Monroy, M. (2004). Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. Water, Air, and Soil Pollution, 152(1), 129-152. Doi: 10.1023/B:WATE.0000015350.14520.c1

Robinson, T. P., & Metternicht, G. (2006). Testing the performance of spatial interpolation techniques for mapping soil properties. Computers and electronics in agriculture, 50(2), 97-108. Doi: 10.1016/j.compag.2005.07.003

Rutkowski, P., Diatta, J., Konatowska, M., Andrzejewska, A., Tyburski, Ł., & Przybylski, P. (2020). Geochemical referencing of natural forest contamination in Poland. Forests, 11(2), 157. Doi: 10.3390/f11020157

Saha, A., Gupta, B. S., Patidar, S., & Sen Gupta, B. (2022). Evaluation of potential ecological risk index of toxic metals contamination in the soils. Proceedings of the 1st International Online Conference on Agriculture - Advances in Agricultural Science and Technology, MDPI: Basel, Switzerland, doi:10.3390/IOCAG2022-12214. https://sciforum.net/paper/view/12214

Saito, H., & Goovaerts, P. (2000). Geostatistical interpolation of positively skewed and censored data in a dioxin-contaminated site. Environmental Science & Technology, 34(19), 4228-4235. Doi: 10.1021/es991450y

Schloeder, C. A., Zimmerman, N. E., & Jacobs, M. J. (2001). Comparison of methods for interpolating soil properties using limited data. Soil science society of America journal, 65(2), 470-479. Doi: 10.2136/sssaj2001.652470x

Soffianian, A., Madani, E. S., & Arabi, M. (2014). Risk assessment of heavy metal soil pollution through principal components analysis and false color composition in Hamadan Province, Iran. Environmental Systems Research, 3(1), 1-14. Doi: 10.1186/2193-2697-3-3

Tomlinson, D. L., Wilson, J. G., Harris, C. R., & Jeffrey, D. W. (1980). Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgoländer meeresuntersuchungen, 33(1-4), 566-575. Doi: 10.1007/BF02414780

United States Environmental Protection Agency (USEPA). (1994). Method 200.7: Revision 4.4, Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry; United States Environmental Protection Agency: Cincinnati, OH, USA.

Vargas-Solano, S. V., Rodríguez-González, F., Arenas-Ocampo, M. L., Martínez-Velarde, R., Sujitha, S. B., & Jonathan, M. P. (2019). Heavy metals in the volcanic and peri-urban terrain watershed of the River Yautepec, Mexico. Environmental monitoring and assessment, 191(3), 1-15. Doi: 10.1007/s10661-019-7300-z

Varol, M. (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. Journal of hazardous materials, 195, 355-364. Doi: 10.1016/j.jhazmat.2011.08.051

Wang, X., Deng, C., Yin, J., & Tang, X. (2018). Toxic heavy metal contamination assessment and speciation in sugarcane soil. In IOP Conference Series: Earth and Environmental Science (Vol. 108, No. 4, p. 042059). IOP Publishing. Doi: 10.1088/1755-1315/108/4/042059

Webster, R., & Oliver, M. A. (2007). Geostatistics for environmental scientists. John Wiley & Sons.

Wilding, L. P. (1985). Spatial variability: its documentation, accomodation and implication to soil surveys. In Soil spatial variability, Las Vegas NV, 30 November-1 December 1984 (pp. 166-194).

Xie, Y., Chen, T. B., Lei, M., Yang, J., Guo, Q. J., Song, B., & Zhou, X. Y. (2011). Spatial distribution of soil heavy metal pollution estimated by different interpolation methods: Accuracy and uncertainty analysis. Chemosphere, 82(3), 468-476. Doi: 10.1016/j.chemosphere.2010.09.053

Xie, B., Jia, X., Qin, Z., Zhao, C., & Shao, M. A. (2020). Comparison of interpolation methods for soil moisture prediction on China's Loess Plateau. Vadose Zone Journal, 19(1), e20025. Doi: 10.1002/vzj2.20025

Yáñez, L., García-Nieto, E., Rojas, E., Carrizales, L., Mejía, J., Calderón, J., ... & Díaz-Barriga, F. (2003). DNA damage in blood cells from children exposed to arsenic and lead in a mining area. Environmental Research, 93(3), 231-240. Doi: 10.1016/j.envres.2003.07.005