DISTRIBUTION ANALYSIS OF HEAVY METAL CONTAMINANTS IN SOIL WITH GEOSTATISTIC METHODS; PAPER REVIEW

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ARTICLE INFO	ABSTRACT
	Heavy metal contaminants in the soil will have a direct effect on human life. The spatial distribution of naturally occurring heavy metals is highly heterogeneous and significantly increased concentrations may be present in the soil at certain locations. Heavy metals in areas of high concentration can be distributed to other areas by surface runoff, groundwater flow, weathering and atmospheric cycles (eg wind, sea salt spray, volcanic eruptions, deposition by rivers). More and more people are now using a combination of geographic information science (GIS) with geostatistical statistical analysis techniques to examine the spatial distribution of heavy metals in soils on a regional scale. The most widely used geostatistical methods are the Inverse Distance Weighted, Kriging, and Spatial Autocorrelation methods as well as other methods. This review paper will explain clearly the source of the presence of heavy metals in soil, geostatistical methods that are often used, as well as case studies on the use of geostatistics for the distribution of heavy metals. The use of geostatistical models allows us to accurately assess the relationship between the spatial distribution of heavy metals and other parameters in a map.

INTRODUCTION

Heavy metal contaminants in the soil will be a very serious problem because it takes a long time to repair and restore soil conditions to normal (Handayanto, Nuraini, Muddarisna, Syam, & Fiqri, 2017). Examining these uncertainties is essential for designing and implementing risk mitigation strategies, and only focusing on reducing soil

concentrations when deemed necessary. Statistical analysis has been used across various disciplinary boundaries to address soil contamination problems, including geoscience, soil science, atmospheric studies, environmental engineering, chemometrics (Gholizadeh, Saberioon, Ben-Dor, & Borůvka, 2018).

Heavy metal contamination in soil has become a serious problem globally (Han et al., 2020). A number of hazardous heavy metals can enter the human body from contaminated soil through exposure routes such as direct or indirect consumption, inhalation and skin contact which will potentially result in human health effects (Changfeng Li et al., 2019). Heavy metals can also show ecotoxicity which causes hampered ecological health in addition to bioaccumulation in the food chain (Shahid et al., 2020).

Judging from the dangers posed by heavy metals if they accumulate in soil and sediment, in this case an analysis of the level of heavy metal pollution on soil and sediment quality must be carried out, namely an analysis of soil and sediment quality based on heavy metal content data using several indicators, which can be grouped into a single index (Niu et al., 2020). Single index is an indicator used to calculate contamination of a single metal (only one heavy metal) by calculation (contamination factor) or contamination factor (Werdianti, 2018). The heavy metals that have been studied most intensively in the publications reviewed include Pb, Zn, Cu, Ni, Cr, and Cd, listed in descending order of frequency.

To solve this problem, the fate and transport of heavy metals in soil, as well as remediation of contaminated soil, have been studied intensively. It is also very important to be able to strongly distinguish the spatial distribution of heavy metals in soils on a regional scale, to enable a sound human and ecological risk assessment, and to implement efficient pollution mitigation measures where necessary. Techniques such as geostatistics have an important role in this task. Several specific challenges exist in overcoming heavy metal contamination of soil (Shi et al., 2018): i) heavy metals cannot be degraded and will often naturally accumulate in the soil ii) they cause a wide range of health effects, and health risks are complicated by oxidation states and associated differences in bioavailability (Rahman & Singh, 2019); iii) there are many widespread sources of heavy metal contamination. Understanding heavy metal concentrations on a regional scale is very relevant for policy makers. Regional soil studies help guide action in combating the pollutant link – managing risk rather than molecules. It is important to understand all the uncertainties regarding contaminant concentration, shape, spatial distribution and temporal changes.

In recent years, more and more studies have used integrated geographic formation systems (GIS) and multivariate analysis for regional soil quality assessments. This is partly due to the use of specialized software that can handle the large spatial data sets presented in GIS. However, many statistical techniques fail to recognize the role of spatial correlation. GIS and GIS-based geostatistics have proven to be powerful tools in studying soil contamination and very useful tools for understanding background levels of heavy metals in soils (Hou, O'Connor, Nathanail, Tian, & Ma, 2017). This paper review aims to clearly dissect the source of the presence of heavy metals in soil, geostatistical methods that are often used to determine the distribution of heavy metal contaminants, as well as case studies of the use of geostatistics for the distribution of heavy metals in other countries.

RESEARCH METHODS

The method used in this research is literature study. Activities to collect information relevant to the topic or problem that is the object of research. This information can be obtained from books, journals, proceedings as well as writings related to the research from

the literature review so as to make writings on the Analysis of Distribution of Heavy Metal Contaminants in Soil Using Geostatistical Methods; Paper Review.

RESULTS AND DISCUSSION

1. Source of Heavy Metal Pollution in Soil

Heavy metals naturally exist in the earth's crust and surface soil (Esmaeilzadeh et al., 2019). The spatial distribution of naturally occurring heavy metals is highly heterogeneous and significantly increased concentrations may be present in the soil at certain locations. Heavy metals in areas of high concentration can be distributed to other areas by surface runoff, groundwater flow, weathering and atmospheric cycles (e.g. wind, sea salt spray, volcanic eruptions, deposition by rivers. Typical anthropogenic sources of heavy metal contamination in urban soils include exhaust vehicles, sewage, sewage, industrial emissions.Increased concentrations of heavy metals in rural soils usually come from impurities in agrochemicals such as application of pesticides and fertilizers, irrigation with contaminated water, surface runoff from local industrial facilities, extraction of mineral ores, and subsequent disposal of waste , road dust, sewage sludge, sewage and livestock manure, and atmospheric deposition. Soil heavy metal pollution is usually studied on a regional scale or on a site specific basis. On a regional scale (usually ranging from about 10 km2 to 10,000 km2), investigations are carried out to set geok background level chemistry, source tracking, and public health protection (Chen, Zhou, Gao, & Hu, 2015). Many regional soil quality studies have been carried out, but only in the last two decades have researchers applied a GIS-based approach to geochemical interpretation of soil data. At site-specific scales (typically ranging from 0.01 km2 to 10 km2), investigators typically aim to determine the spatial level, concentration, and fate and transport of contamination to assess risks to human health and ecological systems and to identify remediation alternatives (Wu et al., 2015). Differences between regional and site-specific assessments were also found in the depth, method, and density of sampling.

2. GIS and Geostatistical Methods

GIS was originally developed as a tool for storage, retrieval and display of geographic information, and was later enhanced for spatial analysis (Fotheringham & Rogerson, 2013). It has been widely used in soil-related research fields, such as precision agriculture, engineering geology, soil erosion, and land degradation. Various spatial interpolators were used, including the Inverse Distance Weighted (IDW) Method. Geostatistical methods are used in GIS to estimate unknown soil properties between known sampling locations. Two of the most commonly used methods are kriging and conditional simulation. Both methods calculate the value of land properties based on the weighted values assigned to the sample values at the nearest location. The following subsections provide a brief description of the basics of spatial autocorrelation and the most commonly used spatial interpolators.

- Kriging

The Kriging geostatistical technique was the most widely used interpolation approach among the studies reviewed, with 20 of 29 studies explicitly indicating that they used kriging. Kriging is derived from Regional Variable Theory and was first introduced to the GIS field in the 1990s. Unlike IDW and some other interpolation methods which treat soil properties at unsampled locations as a specific mathematical function of continuous spatial variables, the kriging method is based on a stochastic spatial variation model.

The underlying assumption is that soil properties behave as intrinsically stationary regionalized random variables. Therefore, the kriging method can be used to estimate confidence intervals for derived values at unsampled locations. The general equation for kriging is explained as follows:

$$z(B) = \sum_{i=1}^{n} \lambda_i z(xi)$$ I

where z(B) is the estimate over the ground area and li is the weight, which amounts to one to ensure that there is no bias and, subject to this, is chosen to minimize the variance of the estimate. The accuracy of kriging is affected by the variability and spatial structure of the data, and the choice of variogram modeling parameters including the variogram shape, range, threshold, and nugget value and search radius, and a number of other measurements used in the calculations show that lognormal ordinary kriging can improve estimation precision compared to ordinary kriging. This is particularly relevant for heavy earth metals because the data will often display a log-normal distribution function. The Kriging method invented by the Directorate General of Daniel Gerhardus Krige which was inaugurated in 1960 by an engineer from France, Georges Matheron, is a geostatistical method used to estimate the value of a point or block as a linear combination of sample values located around the point to be estimated. . The kriging weight is obtained from the minimum variance estimation result by expanding the use of the semivariogram. The kriging estimator is an unbiased estimator and the sum of all weights is one. This weight is used to estimate the value of thickness, height, grade or other variables (Bargawa, Nugroho, Hariyanto, Lusantono, & Bramida, 2020). In its development, many kriging methods have been used to solve various cases in geostatistical data, for example, there is a sampled mineral content that does not have a certain trend. The kriging method that is suitable for solving this case is ordinary kriging because this method can be used when the population mean is unknown (Bargawa, 2020).

- IDW Interpolation

The Inverse Distance Weighted (IDW) method has been used in several regional soil quality survey studies that integrate GIS with multivariate statistical analysis (Dongqing Li, Huang, Guo, & Guo, 2015). This method is one of the most frequently used spatial interpolation methods because of its fast implementation, ease of use, and straightforward interpretation. The general equation for IDW is described by the following equation:

$$z_{x,y} = \frac{\sum_{i=1}^{n} z_i d_{x,y,i}^{-\beta}}{\sum_{i=1}^{n} d_{x,y,i}^{-\beta}}$$ II

where zx,y is the point to be estimated, zi represents the control value for the i-th sample point, dx,y,i is the distance between zx,y, and zi, and b is the user-defined exponent. This weighing strategy assigns more weight to spatially close points than distant points based on the reciprocal of the distance to a power, which conforms to logical intuition. The accuracy of the IDW can be increased by wisely choosing the optimal number of surrounding points (n) and exponent value (b) to produce optimal agreement between the measured and estimated data. Its biggest drawback is that it is not based on a specific spatial correlation model for the parameters studied, while, as discussed above, spatial autocorrelation often exists and can be used to provide better interpolations.

- Spatial Autocorrelation

Spatial autocorrelation refers to the lack of independence between pairs of observations at a given distance in space, i.e. the similarity between samples for a particular attribute variable as a function of spatial distance. In the early days of GIS research, spatial

autocorrelation was treated as a problem requiring correction rather than an inherent property of spatial data. However, researchers have found that spatial autocorrelation is ubiquitous, occurring on spatial scales from micrometers to hundreds of kilometers, for reasons ranging from external environmental factors to intrinsic dispersion mechanisms. According to Tobler's First Law of Geography, things that are near are more closely related than things that are far away (Waters, 2017). To obtain values for a given attribute variable in the area between the observed samples, spatial autocorrelation needs to be taken into account.

- Other Methods

Various other geostatistical methods have been used for spatial prediction of soil properties. Keskin & Grunwald found an inverse relationship between the accuracy of the Kriging Regression model and variations in soil properties in the original dataset. A new modified RK method is proposed for further investigation to predict soil properties and classes (Keskin & Grunwald, 2018). Kim et al., used co-kriging with the aim of reducing the economic costs of heavy metal sampling (Kim et al., 2019). They achieved this by measuring the soil cation exchange capacity (CEC) as a covariate, which is easier and cheaper to measure than the Cu, Zn, and Cr determinants of concern. It should be noted that the simple overlay method was used in most of the studies reviewed, although it is not considered a geostatistical method alone.

3. Geostatistical Use Case Study

The following cases are the use of Geostatistical Methods in an area to determine the level of distribution of heavy metals

The Use of Geostatistical Models to Determine the Distribution of Mercury in Soil in Former Mining Areas: Mount Karczówka., Mount Miedzianka., and Rudki (Central-South Poland)

The study, conducted by (Dołęgowska & Michalik, 2019), evaluated metal concentrations in the post-mining soil of Mount Karczówka, Mount Miedzianka, and Rudki for the assessment of pollution levels and to make further decisions on the actions to be taken. The heterogeneous and special character of this area, makes this assessment focus on the anthropogenic and geogenic sources of mercury that have been identified in the three post-mining areas using an integrated map of the spatial distribution of mercury, calculated geochemical factors (BG, LEF), and the results of cluster analysis in the soil due to exposure mining impact. The use of combined geostatistical models confirms a direct relationship between mercury content and ex-mining operations. We document that although mining activity ceased in the mid-twentieth century and even in the case of the Rudkin where reclamation work has been carried out, this correlation is still visible. The highest mean mercury concentration was recorded in soil samples from Miedzianka Mt. (0.501 mg kg−1). Very high enrichment in this metal (20 LEF < 40) was also reported at one location from this area as a result of the occurrence of Hg-rich copper sulphide. Due to the lack of mercury minerals in the soil of Karczówka Mt. and Rudki, the burning of fossil fuels and other emitters (housing and local roads) are classified as the main sources of this element. The correlation between mercury content and history of mining operations can be explained by the presence of clay minerals and Fe/Mn oxides and hydroxides which are scavengers of atmospheric mercury. The results of multivariate analyzes performed for mercury (FA) and non-mercuric (CA) biased data sets emphasize the association between the presence of other trace metals and mercury. The use of a unified geostatistical model which is a combination of multivariate statistics and geostatistical parameters presented by GIS allows us to accurately assess the relationship between the spatial distribution of mercury and other parameters in small-scale maps.

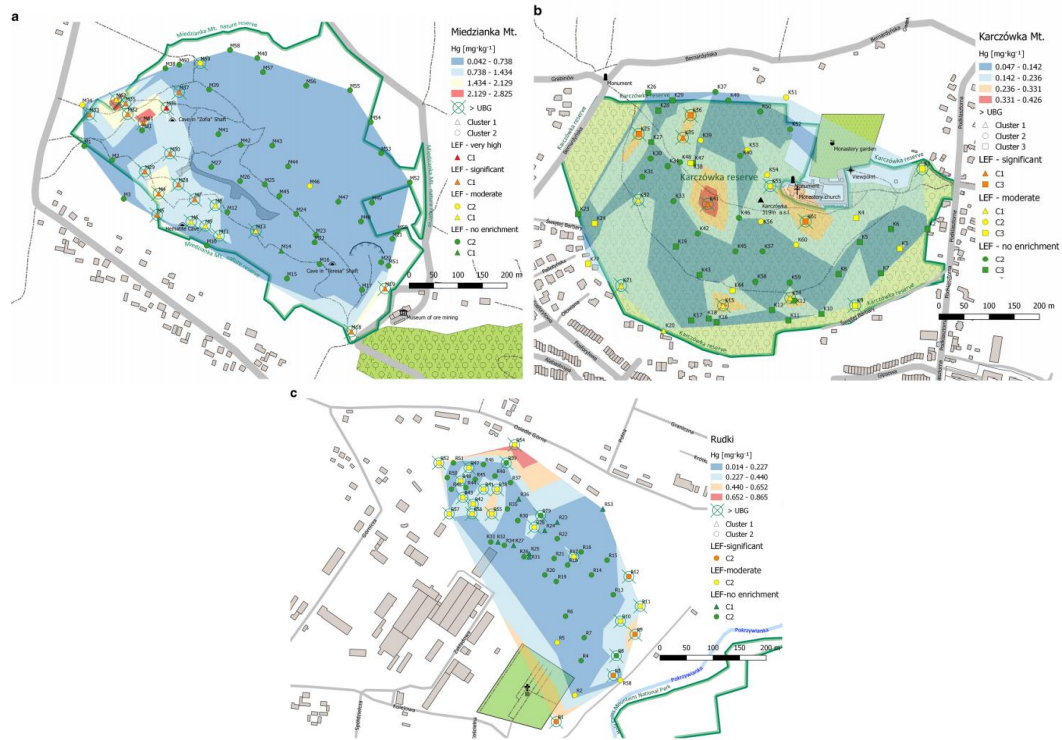**Stefan Daniel Maramis, Rika Ernawati and Waterman Sulistyana Bargawa**

Figure 1. Map of spatial distribution of mercury integrated with geochemical factors a. Mt. Miedzianka, b. Mt. Karczówka, c. Rudki

Geostatistical Modeling and Characteristics of Contaminants and Precious Metals from Cu–Au Tailings Dam Abandoned In Taltal (Chile)

Research conducted by (Tripodi, Rueda, Céspedes, Vega, & Gómez, 2019) in the city of Taltal, located on the northern coast of Chile, with central coordinates S 25° 23 '52" and W 70° 28′ 35 merupakan, is an important area for small-scale mining. Depending on the price of the metal, the population shifts between mining and fishing. From their research, it was found that the main copper minerals detected were chrysocolla, atacamite, tenorite, and chalcopyrite. The gangue mineralogy is dominated by the presence of quartz, feldspar, magnetite, and clay. The particle sizes for S1 and S2 mainly correspond to the clay and silt categories (P80 66.4 m S1 and 46.8 m S2). The degree of release revealed the presence of degrees of occlusion for the different minerals despite the fine particle size. The presence of copper in both tailings composites was mainly associated with oxide and oxidized type minerals (70% for S1 and 41% for S2). Based on the type of mineral, the main Cu content in the S1 composite sample was atacamite (31.46%) and chalcopyrite (29.66%). For S2 the main copper mineral is chalcopyrite (46.65%). Arsenic, mercury and copper are the detected elements with the greatest potential for contamination. More than 90% of the samples exceed Finnish standards. Tailings can have economic added value because they contain significant copper (0.27% S1, 0.48% S2 average) and gold (0.26 ppm S1, 0.53 ppm S2 average).
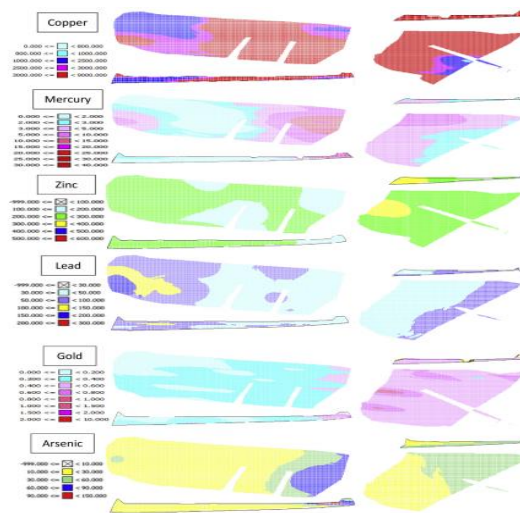
Figure 2. Element distribution according to geostatistical modeling for: A. Copper, B. Mercury, C. Zinc, D. Lead, E. Gold and F. arsenic. The left box shows the concentration range in ppm. The result of S1 is the one from the left side, the right side depicts the graph for tailings dam S2.

In addition, the early presence of different rare earth piles reported in a timely manner should be considered. The line of open interest as a result of this research in terms of contamination and reprocessing, indicates the need for further research aimed at providing additional details in the real contamination problems that can be attributed to the detected metal and/or evaluation of the beneficiation of metallurgical options for value-added metals. The coefficient of variance and the geostatistical model show the differences in the level of dispersion found. In general, moderate or high levels of variability, dispersion and heterogeneity were found for the two tailings. In particular, the variability increased from the low, intermediate values of Zn for As, Cu, Ag, Pb to the high values identified for Hg. The block model allows estimates of total material quantities of 8400 tonnes for S2 and 39794 tonnes for S1. The low concentration and distribution of the contents requires that in order to find out if there are additional benefits, tailings deposits must be considered as a whole.

CONCLUSION

Increased concentrations of heavy metals in soil usually come from impurities in agrochemicals such as application of pesticides and fertilizers, irrigation with contaminated water, surface runoff from local industrial facilities, extraction of mineral ores, and disposal of sewage, road dust, sewage sludge, sewage and sewage livestock, and atmospheric deposition. Soil heavy metal pollution is usually studied in scale areas or based on specific locations. To determine the distribution of heavy metals in an area, geostatistical methods can be used, the most widely used geostatistical methods are the Inverse Distance Weighted, Kriging, and Spatial Autocorrelation methods and other methods. The use of geostatistical models allows us to accurately assess the relationship between the spatial distribution of heavy metals in soil and other parameters in a map. It is hoped that the next literature review will discuss in more detail about each of the renewable geostatistical models.

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