

Chapter 6

Evidence for Atmospheric Depositions Using Attic Dust, Spatial Mapping and Multivariate Stats



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Abstract Atmospheric deposition poses significant ecological concerns. It is very important in air pollution researches to provide fast and efficient access to qualitative and quantitative characterization. Case study was introduced in order to implement the multidisciplinary approach in the investigations. When monitoring the distribution of certain substances in the air, it is necessary to choose very carefully the medium that will reflect not only the current but also the long-term atmospheric deposition. Attic dust was examined as historical archive of anthropogenic emissions, with the aim of elucidating the pathways of enrichments associated with exploitation of Cu, Pb and Zn minerals in the Bregalnica river basin region. Attic dust samples were collected from 84 settlements. At each location for attic dust sampling, topsoil samples from the house yards were also collected. Mass spectrometry with inductively coupled plasma (ICP-MS) was applied as an analytical technique for multi-element determination. The universal kriging method with linear variogram interpolation was applied for the construction of spatial distribution maps. Data interpretation was considered in correlation with dominant geological units. Significantly enriched contents for Cd, Cu, Pb and Zn have been correlated with the lithogenic dominance of Rifeous shales. Both Pb-Zn mine environs were identified as the most affected areas with lead and zinc enrichments, due to the

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continually long-time wind dust dispersion from the flotation tailings. Atypical deposition was revealed for In, Te and W, as *silent* tracker for air pollution.

Keywords Air pollution · Attic dust · Kriging modelling · Mass spectrometry

6.1 Introduction

The biosphere is the factor that develops the natural environment. It covers the surface parts of the lithosphere, the lower part of the atmosphere and the hydrosphere. It is a complex system in which numerous biological and physical-chemical processes and reactions take place. The natural balance of these processes is most often disturbed by the action of the anthropogenic factor. Because the relative homeostatic balance in the environment is necessary for survival and survival of the living world, research into the chemical composition of air, water and soil is imposed as an operative. In certain situations where the human activity is the predominant factor, certain degrading processes occur in the soil. During the excavation of geological minerals, the natural balance of most of the chemical elements that in some forms are incorporated into the minerals can be displaced (Sengupta 1993; Salomons 1995). As a result of these activities, there is an absolute imbalance in the environment, thereby shifting the normal habitat conditions of the organisms. As a consequence of this condition, ecological balance in the environment may be endangered. VanLoon and Duffy (2000) term these conditions as *specific environment*. One of the most significant shifts in the natural balance of the environment is the heavy metals that can be deposited in higher areas in certain areas. In this case, toxic conditions are created in certain parts of the environment. The most sensitive to changes in the content of heavy metals is of course the surface layer of the lithosphere. Soils are not the only medium that is threatened and affected by anthropogenic activities. The entire biosphere is affected by changes in the natural distribution of some metals, most notably heavy metals and some toxic semimetals (Athar and Vohora 1995; Siegel 2002; Artiola et al. 2004; Salminen et al. 2005; Duruibe et al. 2007). Excavation of mineral raw materials is most often accompanied by a shift in the natural balance of chemical elements in the soil. This situation is due primarily to the displacement of the basic regolith material, on the basis of which the surface soil is formed. Such destructive changes in the surface of the lithosphere disrupt the natural distribution of the minerals. But on the other hand, these processes also lead to the release of a large amount of dust that is distributed to the environment. The chemical composition of the particles in this dispersed ring is usually high in some heavy metals. Mining and flotation tailings are also subject to the same process, which are deposited in the immediate vicinity of the mines. This mine and flotation waste can be washed by wind as well as rains (Van het Bolcher et al. 2006; Šajin 2006).

6.2 Anthropogenic Effects on Atmospheric Emissions

The emission of toxic substances into the atmosphere is one of the greatest health threats to the light. Lice are directly exposed to the effects of harmful substances through inhalation. Particle gases depend on their size and on the defence capabilities of the respiratory tract. Exposure to toxic substances is usually defined as a function of their concentration and time of exposure, i.e. the phenomenon that occurs with the achievement of direct contact between humans and the environment with the content of pollutants in a given interval of time. The health effects of toxic substances depend on their concentration and the place of their deposition in the respiratory tract. The most at-risk group in the population of harmful effects of airborne particles are children and the elderly, especially those with a weakened cardiovascular and respiratory system. Heavy metal air pollution is a global process that affects every part of the Earth. Rapid increases in the concentrations of pollutants in the atmosphere and the environment are most often associated with the development of technologies for exploitation and processing of mineral raw materials. This change exposes the biosphere to the risk of destabilization of organisms that grow under conditions with low concentrations of these substances and that do not have developed biochemical pathways capable of their detoxification when they are present in high concentrations (Hoenig 2001).

Atmospheric deposition of particles containing potentially toxic metals (“heavy metals”) is the main subject of many studies and usually occurs in industrial areas, in places where natural resources are exploited and processed as well as in areas with large settlements where which heating, traffic and municipal waste are the main sources of pollution (Wong et al. 2006). Heavy metals in the atmosphere originate mainly from the dispersion of dust from metal refining, combustion of fossil fuels and other human activities and remain in the atmosphere until they are removed by various cleaning processes. Substances released into the atmosphere through the combustion process can be transported to places away from wind sources, depending on whether they are in gaseous or solid form. Urban pollution with heavy metals has been the subject of many studies (De Miguel et al. 1999; Ajmone-Marsan et al. 2008; Beelen et al. 2009). Regional soil contamination occurs mainly in industrial regions and in the centres of large settlements, where factories, traffic and municipal waste are the most important sources of environmental pollution. Due to the heterogeneity and the constant change of the urban environment, it is necessary to first determine the natural distribution and the methods for distinguishing artificial anomalies in nature. The natural background itself is variable, which means that higher concentrations of some substances may be normal for one region but abnormal for others. However, there are cases when some industrial processes, especially mining and metallurgical, when located near cities, can lead to an increase in environmental pollution (Ajmone-Marsan et al. 2008).

6.3 General Meaning of the Term “Dust”

The term “dust” does not have a precise meaning, nor is it defined definitively as a premature solid and a dusty particle. When determining hazards, particle size is just as important as the nature of the dust. In general, the most dangerous types of dust are with very small particles that are not visible to the human eye, as is the case with fine powders. These types of particles are small enough to be inhaled, but at the same time they are large enough to stop in the lung tissue and not be able to exhale. However, some substances create a very coarse dust of large particles, which can also be dangerous. Substances can form dusts with particles of different sizes – the fact that you can only see large dust particles does not mean that small particles are not present.

There are several basic types of dust that are released and distributed in the environment:

- **Nanomaterials:** Nanomaterials are used in many modern processes. They are especially dangerous because they can be absorbed directly into the bloodstream by inhalation, through the skin and lung membranes. They should be considered hazardous to health no matter what material they are made of. Conventional protective equipment will not provide adequate protection, so you must consult your laboratory before opening or intentionally sampling such products.
- **Toxic dusts:** Toxic dusts are usually formed when working with substances that are themselves toxic (e.g. lead, mercury, chromium, etc.). Inhalation can damage the lungs, or they can spread throughout the body by entering the bloodstream.
- **Harmful dusts:** Harmful dusts may occur when handling materials such as flour/cereals, resin, tobacco, sugar, paper, dry food, cement, sawdust, coffee beans and tea and black ink (as in toner in a photocopier/printer). These types of dust are usually only irritating, but in concentrated form, they can be dangerous to health. Hard (deciduous) wood dust is carcinogenic.
- **Flames of the flame:** Flames of the flame are prone to flare and flare and the flame can be exposed to fire or explosion. Njihovo zapaljenje može biti izazvano iskrom ili otvorenim plamenom pa čak i slijeganjem na vruću površinu. When it comes to spraying, it is easy to get stuck, it can burn and burns, or it just burns – if you do not open the source of the spark. If there is an explosion in the back of the head, it is possible to increase the risk of leakage, which increases the risk of exposure.

Harmful dust can be found almost everywhere. Some of the most common are paper dust in mail sorting offices and paper mills, cement dust on construction sites and various types of dust in ports, in inland customs warehouses and in the entrepreneur’s business premises and rooms with photocopiers/printers. Toxic or flammable dusts in dangerous concentrations can also be encountered at places of loading, unloading or trans-shipment of bulk cargo (e.g. cereals, metal ores, coal, etc.).

Dusts generally damage the lungs and respiratory system, but some species can also cause cancer. The major diseases associated with inhalation of hazardous dusts are:

- Benign pneumoconiosis. Disease caused by inhalation of harmless dust that accumulates in the lungs to such an extent that they are visible on an X-ray. They do not damage the lung tissue, and therefore the disease does not create difficulties. This condition is most commonly associated with metal dusts such as iron and tin.
- Pneumoconiosis. Common name for a group of chronic lung diseases caused by inhalation of ore dust particles. The term includes several diseases that are named after the dust they are caused by. The most famous are asbestosis (from asbestos dust), silicosis (from dust containing silicates) and talc (from talc dust).
- Pneumonitis. Inflammation of the lung tissue or bronchioles, mainly caused by inhalation of certain metal dusts. The symptoms are reminiscent of pneumonia, but vary in severity, depending on the metal inhaled. It is most often caused by cadmium and beryllium dusts.
- Lung mesothelioma. Lung tumour, mainly caused by asbestos and toxic metals exposure.
- Lung cancer. It can also be caused by exposure to asbestos and heavy metals.

6.4 Dust Emissions and Distribution

The physical properties of dust obey natural laws that are not identical to those that apply to solid and liquid bodies. Thus, for example, the pressure on the walls of a box full of dust does not have to be the same at all points. Dust is harmful for several reasons, because it can cause health problems not only for workers who have daily contact with it but also for the population in the wider environment. Erosions that occur in landfills under the influence of wind are one of the main sources of dust. Landfill work itself also leads to dust emissions. Landfill management is a complex process and often requires constant traffic to and around the landfill where dust emissions also occur.

The intensity of dust release depends on several factors: characteristics of coal, moisture content, particle shape, landfill geometry, position and method of formation and climatic conditions. The determination of the dust generated depends on one key factor and that is the amount of moisture. The moisture that is in the landfills is a consequence of precipitation, the process of washing coal, etc. Climatic conditions affect the amount of dust emission. Regular control of dust emissions at landfills is important because of environmental protection and economy.

The most favourable moment for the selection of systems that serve for protection against dust is in the landfill planning phase. In the end, this turned out to be a much more cost-effective way than taking action afterwards. The basic methods of dust control are wind control, landfill coverings, wetting dust emission control systems

and by fencing the landfill. The dust that collects in the house is a combination of atmospheric dust and dust of human origin, which consists mainly of extinct skin cells and fibres from clothes and blankets. It can be removed with a broom, cloth or vacuum cleaner. Mites, organisms that are often found in carpet fibres and on mattresses, use organic components of house dust for their diet. Landfill dust levels can lead to dust hazard zones. “Monitoring” dust levels can identify dust endangered areas. Certainly, successful airborne dust monitoring requires a good choice of menu locations (Finlayson-Pitts and Pitts 1999).

6.5 Natural Archives of Distributed Dust

Attic dust is defined as dust that accumulates on wooden carpentry of attics, the spaces in which the influence of inhabitants is minimized. Attic dust is derived predominantly from external sources through aerosol deposition and as a result of soil dusting (Davis and Gulson 2005). There is a little influence from household activities (Šajin 2003). Its mineralogy includes phyllosilicates (montmorillonite and illite) and calcite and dolomite in areas of outcropping carbonate rocks (Šajin 2000). The deposition of attic dust seems to be continuous through time in undisturbed attics. Its chemistry, therefore, reflects the average historical levels of the atmospheric pollution. In previous geochemical studies (Šajin 2002, 2003, 2005), the properties of attic dust in Slovenia (regional-scale) were established. Attic dust was also successfully applied in tracing a plutonium halo, a result of atomic bomb experiments, in Nevada (Cizdziel et al. 1998; Coronas et al. 2013). Close to each sampling location, an old house with intact attic carpentry was chosen. Most of the selected houses were at least 100 years old. To avoid collecting particles of tiles, wood and other construction materials, the attic dust samples were brushed from parts of wooden constructions that were not in immediate contact with roof tiles or floors.

The determination of historical emissions is based on the data of heavy metal concentration in the attic dust from different measurement sites of the weight of total monthly air deposit (Lioy et al. 2002; Jemec Auflič and Šajin 2007; Žibret and Šajin 2008; Žibret 2008). The main idea behind determining past emissions is that heavy metal characterization of deposited dust on a small area is multiplied by the concentration of the elements in that area; the mass of the pollutant which has been transported to the place of interest by air can be determinate (Šajin 2006; Žibret 2008; Žibret and Šajin 2008). Undisturbed attic dust is potential archive for atmospherically deposited particles and has been shown to be effective across urban areas and in the vicinity of smelters, mines and other potentially emission sources (Cizdziel et al. 1998; Cizdziel and Hodge 2000; Šajin 2000, 2001, 2002, 2003, 2005, 2006; Alijagić 2008; Alijagić and Šajin 2011; Völgyesi et al. 2014; Angelovska et al. 2016; Balabanova et al. 2019). Atmospheric emissions attributed to the extraction stage of mining come mainly from the action of wind on disturbed land and stockpiles of ore and waste material. As a result of these processes, dust is permanently introduced in the atmosphere (Ilacqua et al. 2003). Usefulness of attic dust as

a suitable long-term monitor for the determination of the status and content in air is proven by numerous studies. Respective analytical work was first presented by Cizdziel et al. (1998), analysing ^{137}Cs and ^{239}Pu near the Nevada nuclear test site. Similar application was conducted across the past 20 years, *hunting* the anthropogenic emissions sources and their impact to the environment (Cizdziel and Hodge 2000; Ilacqua et al. 2003; Gosar et al. 2006; Gosar and Teršič 2012; Tye et al. 2006; Hensley et al. 2007; Balabanova et al. 2011; Bačeva et al. 2012; Coronas et al. 2013; Pavilonis et al. 2015; Balabanova et al. 2019). Despite the metal's enrichment catchment, attic dust should be also considered as a poly-metallic marker for the lithogenic distribution of elements. De Miguel et al. (1999) have proposed a dust model for tracking the natural phenomena of poly-metallic geochemical association in urban areas. However, other investigations emphasize only the anthropogenic enrichments (Fordyce et al. 2005; Goodarzi 2006; Tye et al. 2006; Balabanova et al. 2011, 2019).

6.5.1 *Collecting Attic Dust Protocol*

Attic dust represents the long-term (historical) deposition of distributed dust in the air. This medium, which is created for a long time, is a natural archive of particles that are distributed for a long time in the lower layers of the atmosphere and then under certain conditions are deposited in a certain environment. In this way, the particles that bind various substances (gases, liquids and solids) are collected and thus can give a clear picture of the exposure of organisms to certain pollutants that are distributed in the air. When setting the protocol for collecting this type of sample (i.e. medium) through which the monitoring of the pollution conditions in the environment is performed, one must pay attention to the age of the houses where this dust is collected. There is still a habit among the population not to remove dust from the attic beams for a long time. Before the dust collection process, it is necessary to conduct a survey with the population to determine the age of the house (year of construction) as well as the habits of the people who live there. This is necessary in order to determine for how long the dust has been deposited in a certain place (location) so that the results of the chemical analysis of these samples can be correctly interpreted for a certain period of time.

The process of collecting a single sample needs to be performed very carefully. First, a precisely defined protocol should be set (prepared) for locations from where the samples should be collected. The researcher determines the size of the space around the emission source or the area to be covered by the monitoring. Then the field activities begin, where it is necessary to find houses/dwellings that were built before the emission occurs (in the case of anthropogenic emission or natural disaster, which occurred in a certain period).

The dust sample is collected from the surface of the attic beams. First, the visible dirt that has accumulated on the attic beam is removed, and then the finest dust is carefully collected from the surface with the tip of a polyethylene brush. At least ten



Fig. 6.1 Collecting protocol for attic dust

places are selected from where sub-samples are collected to prepare a representative sample from one location (house). Each sample is collected in plastic bags and delivered to a laboratory for physical-chemical preparation and chemical analysis (Fig. 6.1).

6.6 Data Mapping and Interpretation

The main purpose of such research is to visualize the distribution of certain substances in the air and to determine places of deposit for a longer period of time. The most commonly used model for visualization is the kriging method (Wellmer 1998). This is the methodology that was introduced as a geostatistical model. Classical statistical methods are based on the assumption that individual samples (e.g. sample value at drilled holes or pipes) are statistically independent of each other. This condition is satisfied on the banal example of rolling the dice. If a six is thrown, it means that the chance of her turning again in the next roll is equal to the chance of turning every other number. The chance of turning is $1/6$ because “the chance has no memory”. This type of independence can rarely be applied to mineral deposit (ore) data. Every geologist knows that the chance of digging a hole of a higher class is higher at the site of a previous site of a higher class than at a site of a lower class. There is therefore a certain spatial interdependence. Geostatistics is statistics in which this spatial association is taken into account; there are variables known as regionalized variables (de Smith et al. 2009). We will deal here only with those calculations that can be performed either manually or by diagram. There are two areas where geostatistical calculations can be important, even in the early stages of ore assessment: calculation of errors or uncertainties in reserve estimates and therefore the possibility of classifying assets and reserves and determination of the class for excavated blocks, especially if the application of the class results from individual blocks of ores or untreated finds in ore deposits (de Smith et al. 2009).

6.6.1 *Digital Field Modelling and Possible 3D Views*

Digital terrain modelling aims to form a mathematical model that will faithfully represent the surface of the terrain and enable various analyses and applications (de Smith et al. 2009). In order for these analyses to be performed efficiently, bearing in mind that 3D models usually consist of a large amount of data, special organization and standardization of data is required. In essence, the process of forming a 3D model consists of selecting and implementing a data structure and an appropriate creation method. The surface of the terrain is usually represented by a set of points and lines arranged on the surface of the terrain in an appropriate manner and arranged in the necessary structure for easier handling of this data. Also, an integral part of the 3D model are the methods by which, in addition to the given data structure, the topographic surface is defined in the geometric and geomorphological sense. In general, the surface of the terrain can be presented in three ways, as follows:

- Isohypsies
- Through the functions of two variables
- Volumetric (volume) model

The first way, i.e. the representation of the terrain with isohypsies, is the cross section of the terrain surface and horizontal planes placed at appropriate heights. This section is a curved line that we call isohypsies. This is the most commonly used way when it comes to presenting terrain on the cartographic bases. This way of presenting the terrain surface is characterized by high quality in the geomorphological sense, because all the important relief characteristics of the terrain are included in this way. Also, when the terrain is mathematically represented by isohypsies in digital form, the surface of the terrain is not given explicitly, but it is given implicitly over the cross section of that surface with horizontal planes. That's why this way modelling the terrain surface is not an exact enough method, because the question arises as to what happens to the values of the terrain height between two adjacent isohypsies. This dilemma is especially pronounced in places where characteristic relief forms appear, such as peaks, bottoms, watersheds, watersheds, valleys, etc.

Another way to represent the terrain surface in digital form is to use the function of two variables, where those variables belong to the corresponding domain. Most often, these are functions in which a unique location value is obtained for a given location (usually planimetric coordinates x and y of the local coordinate system, state coordinate system or even geographical coordinates). In this case, it is a 2.5D ($2D + 1D$) model.

Terrain models that enable the representation of surfaces where one height can be obtained for one x, y location, i.e. surfaces for which the surface function $f(x, y)$ has a value in the form of a vector, are called 3D models. In these models, all three coordinates are completely equal. The most well-known and in practice the most common 3D terrain models based on these principles are digital terrain models

(DMT), whose basic data structure is in the form of grid and TIN (triangular irregular network) (Li et al. 2005).

And the third way to represent the surface of the terrain is to use a volumetric model, where the objects of space are represented by volumetric elements. One of the typical examples is the use of voxels (volume elements, most often cubes or prisms) of sufficiently small dimensions. This is analogous to the representation of phenomena in digital raster images (or raster GIS), with the difference that digital images are 2D displays. Namely, in these models, the terrain is presented as a body composed of a set of interconnected voxels. Using this data model, tunnels, caves, buildings and structures, settlements, etc. can be presented very easily. Another type of volumetric models are models based on the representation of bodies in space using the division of space into non-overlapping tetrahedra. This is analogous to using TIN to represent phenomena in 2.5D models with functions of two variables. Finally, it should be said that volumetric models are mainly represented in the presentation of infrastructure facilities and settlements, especially communications and traffic. They are also used in geophysics, but are very rarely used for modelling terrain surfaces (Li et al. 2005).

6.6.1.1 Digital Terrain Modelling in Grid Form

Digital terrain modelling in the form of a grid implies the methodology and technology of displaying the terrain over a set of points with known heights arranged in a regular grid – a grid. In this way, the surface of the terrain is actually represented by a 3D model called the digital elevation model (DEM) (Li et al. 2005). The advantage of digital terrain modelling in the form of grid is reflected in:

- Application of simple algorithms for handling and analysis of height models
- Savings in terms of archiving, i.e. only the heights of points (pixels) are stored, while their planimetric coordinates are implicitly given through the position of the initial network element, network orientation in space, dimensions and position of the observed network element in the height matrix
- Use of algorithms, software tools and formats for archiving and data exchange that are standardly used for raster GIS analysis and digital image processing
- Realization of simple algebraic operations on grid elements, the combination of which can perform very complex analyses, including advanced data compression and record pyramids for representing the terrain in other (different) resolutions

6.6.1.2 Digital Terrain Modelling in the Form of TIN

Digital data modelling in the form of TIN is represented in many practical solutions and software tools for the formation and analysis of 3D terrain models. When modelling terrain in the form of TIN, the vertices (nodes) of triangles are points with known heights (Li et al. 2005). The triangles are interconnected so that they better

approximate the surface of the terrain being modelled. We distinguish between 2D and 3D triangulation. In 2D triangulation, the area covering the input data set in the XoY plane is divided into non-overlapping triangles. In other words, the triangulation of a set of points is a system of triangles whose vertices form a corresponding set, i.e. whose interiors do not intersect with each other and whose union completely covers the surface of the terrain. At the same time, using the values of heights at given points of the grid, spatial triangles are obtained that approximate the surface of the terrain (Li et al. 2005).

Also, in order to better approximate the relief, the terrain model is represented by triangular surface patches. This means, in addition to the height of the vertices of the TIN triangles, additional conditions relate to the values of the normal to the terrain surface at the TIN nodes and the conditions that require minimization of the curvature of the terrain surface. There are a number of criteria and algorithms for forming 2D TIN. The 2D Delaunay triangulation, which has particularly interesting geometric properties, is most commonly formed. Namely, Delaunay's triangulation maximizes the minimum angle of the triangles of the grid, i.e. it eliminates "elongated" triangles of the network. Also, in practice, for modelling the terrain, modifications of Delaunay's triangulation are often used in order to achieve some specific requirements in order to obtain the most accurate representation of the terrain surface. In some cases, it is required to install mandatory lines and polygons (structural characteristics of the terrain) in the model itself, so that these lines must be represented by the sides of the triangle TIN (Li et al. 2005).

When it comes to 3D triangulation, it consists of spatial triangles whose projections in the XoY plane can generally intersect, i.e. overlap. As in the case of 2D triangulation, Delaunay's tetrahedralization or 3D Delaunay's triangulation is most often used here. The data structure that represents the TIN can be based on storing data on the edges of triangles (triangle edges) or on storing data on the triangles themselves. In other words, in addition to the table containing the points (nodes) of the TIN, it is necessary to keep the table with the sides of the triangles for the first approach or the table with the triangles of the TIN for the second approach. In both cases, information that is not stored directly (data on triangles, i.e. on the sides of the network) can be obtained based on the network topology. In order to preserve information related to points, lines and surfaces that may be important for modelling the terrain surface, for TIN elements (nodes, sides and triangles), it is necessary, in addition to their geometry and topology, to keep the appropriate attributes, i.e. heights and mutual relations of the mentioned TIN elements (Li et al. 2005).

6.6.2 Interpolation Methods and Their Basic Features

The term interpolation comes from the Latin word "inter" which means between and the Greek word "polos" which refers to a point or a node. In other words, interpolation is defined as the process of determining a new (unknown) value between

two or more known values of a function. The function in this case may be known, but in a complex form for computation. Also, the function may be unknown, but some other information about it is known, i.e. function values on a given set of points. It is this second case that is common in solving engineering problems and scientific and technical tasks. For example, when measurements yield only a certain number of function values, the so-called discrete set of points, it is necessary to determine the approximate values of a given function at other points. Estimation, i.e. interpolation, can be performed in one, two or three dimensions. The estimation can be performed on the basis of known values of the observed primary variable (autocorrelation) or with the help of the values of one or more other secondary variables in the same area. The condition is that the secondary variables are strongly correlated with the primary variable. Also, there are several methods that include bilinear and bicubic interpolation in two dimensions and trilinear interpolation in three dimensions (Li et al. 2005; de Smith et al. 2009).

Many interpolation procedures and methods are used in various fields of science and research. All these methods, i.e. interpolators, can be divided into several categories:

- Global/local interpolators
- Exact/approximate (approximate) interpolators
- Continuous (gradual, gradual)/intermittent (unconnected, sharp) interpolators
- Stochastic/deterministic interpolators

Global interpolators define a single function that determines values for the entire interpolation area. The change in one of the entered values is reflected in the total display area or interpolation area. Local interpolators use an algorithm that repeats the values of a smaller set of points relative to the whole set of point values. A change in one of the entered values only affects the results within the local area. Exact interpolators treat all points equally with which the interpolation is entered. Namely, the interpolation surface passes through all points whose values are known, i.e. advance date. Approximation interpolators are applied when there are indeterminate or unknown values of a given surface. They are applied in data sets where there are global trends that vary slowly, overshadowed by local fluctuations, and that vary sharply and produce certain errors (deviations) in given values. For these reasons, the smoothing effect reduces the effect of defects on the obtained (interpolated) surface. Gradual interpolators are methods with sufficiently small elements that are interconnected in continuity and that deviate minimally from given points. A typical example of gradual interpolators is the moving surface method (de Smith et al. 2009).

Intermittent approach methods involve sharp transitions and relatively rough barriers in the interpolation process. Interpolators (methods) are based on the concept of random variables. The interpolation surface is projected (imagined) as one of many that have been observed, that is, which can be obtained on the basis of known points with high probability. When it comes to deterministic methods, it should be borne in mind that they do not use probability theory and statistics or models of random processes (de Smith et al. 2009).

Unlike the classical statistical approach, geostatistics takes into account the spatial dependence of variables. Namely, geostatistical methods of interpolation start from the assumption that by knowing the value of a property at known points, it is possible to establish its value at unknown points as well. Assuming that the samples are representative and consistent, the values of the corresponding variable at a new salt location can be obtained using the appropriate interpolation method.

Interpolation methods include a set of procedures for creating assumed values of interest. The methods that can be applied to create a 3D model are:

- Finite element methods
- Interpolation methods using moving surfaces (interpolation with local polynomials, inverse distance method, oblique plane method)
- Methods with variational approach (minimum curvature method, spline method)
- Geostatistical methods (collocation method, linear prediction by least squares method, kriging method)
- Methods of forming TIN models based on input data and interpolation of heights for grid points from TIN data structure
- Methods of data pre-processing using TIN, with the aim of forming an additional set of data (structural terrain lines and points in parts with rare starting data) and their use for interpolation of 3D models using some of the previous procedures

Choosing the appropriate interpolation method is not easy and requires a good knowledge of the characteristics of the terrain being modelled, the characteristics of the input data as well as the characteristics of the available interpolation methods. For interpolation of heights in points of 3D models, all methods can be used which, on the basis of heights given in arbitrarily distributed points, the height for any set point that falls within the area are covered by the input data. Some of these methods have been specially developed for interpolation of heights at grid points.

6.6.2.1 Basic Principles of Variogram Calculation

The introduction showed us how geostatisticians observe the spatial dependence of sampled or analytical values. The variogram is the basic means of evaluation, quantification and spatial dependence. In practice, the variogram represents the root mean square of the difference of two values calculated as a function of the distance of these values. It is the basis of all geostatistical calculations (Wellmer 1998).

The set of all data pairs at the same distance is called the class, and by merging the values for each class, the curve of the experimental variogram is obtained. There are four parameters that can be read from the variogram, and they are (1) deviation (“Nugget”), (2) threshold (“Sill”), (3) range (“Range”) and (4) distance (“Distance”). (1) Deviation (“Nugget”) is a positive value on the y-axis, where the variogram curve intersects that axis. (2) The threshold (“Sill”) is the value corresponding to the variance. Once the curve reaches the threshold, it stops growing properly and generally begins to oscillate around the threshold. (3) Range is the distance along the x-axis from zero to the point where the variogram curve intersects the threshold.

Reach represents the continuity between points of adjacent data. At a greater distance from the intersection of the threshold and the variogram curve, one can no longer speak of continuity between points. (4) “Distance” is the distance on the x-axis at which the data in the variogram direction are compared. Each distance makes one class. This value is often assigned a certain tolerance (offset) in order to increase the number of input data. Thus, we add a certain value of the offset to the class boundary, so the variogram classes are represented by certain intervals (e.g. 0.5–1.5, 1.5–2.5, etc.). Usually the offset is set to 1/2 distance values, which maximizes the number of pairs and at the same time the reliability of the spatial analysis (Wellmer 1998).

6.6.2.2 Kriging

Namely, the kriging method is based on the use of known values of so-called variable control points, the influence of which on the assessment is expressed by appropriate weighting coefficients (Wellmer 1998; de Smith et al. 2009). The most demanding procedure in kriging is to determine the weighting coefficients for each control point individually. During the assessment, it is necessary to meet certain criteria, i.e. to be impartial and defined so that the variance of the difference between the actual and estimated values at the selected points is the smallest (Zeigler et al. 2000). Due to reliable estimates of spatially distributed variables, the kriging method has found great application in many branches of research. It was primarily created for the needs of mobile environments and surfaces in mining and geology, for example, as a means of improving the assessment of ore reserves and natural resources. The basic equation of the kriging method is given by a mathematical expression:

$$z(s_0) = m(s_0) + x(s_0) + e(s_0)$$

where:

$z(s_0)$ – a statistical representation of a surface that with a high degree of probability approximates the actual surface for which data were collected

$m(s_0)$ – surface trend, i.e. quantification of the spatial structure of the surface with (co)

$x(s_0)$ – stochastic part, i.e. evaluation of the value of the function surfaces at given points

$e(s_0)$ – noise, i.e. interference with perception

The most significant property of this interpolation method is to keep the measured quantities as fixed, which means that it includes the original data set that is in the interpolation process will not change. Relationships between existing and estimated values are expressed values of covariance or variogram. Spacious dependence is usually expressed mathematically in form certain functions of spatial coherence such as a semi-variogram or covariance function. Semi-variogram and covariance

function are suitable tools in data analysis and clarification. Even more, the coefficients are weights assigned to interpolation points in kriging. This determined the influence of the known value on the estimated value with respect to their distance (Zeigler et al. 2000).

Also, several techniques or variants of the kriging method have been developed in order to adapt the initial algorithm to the requirements of different data. The most famous are *simple kriging*, *ordinary kriging* and *universal kriging*. Simple kriging is based on the assumption that the covariogram is a decreasing function of distance. This is the result of the assumption about the stationarity of the observed function. The trend is represented by a constant value that is known in advance. The second variant of the kriging method, i.e. ordinary kriging, is especially interesting. Namely, in ordinary kriging, we start from the assumption of quasi-stationarity. It requires that the increments of the function be stationary, but not the function itself. The trend is constant and not known, so it should be assessed on the basis of data. Universal kriging is less restrictive than simple and ordinary kriging, and it assumes only the stationary increment of the regionalized variable and only in the neighbourhood of the observed point (Zeigler et al. 2000; Li et al. 2005).

6.7 Hunting the Anthropogenic Depositions in Mine Environs

Atmospheric deposition poses significant ecological concerns. In this work, attic dust was examined as historical archive of anthropogenic emissions, with the aim of elucidating the pathways of enrichments associated with exploitation of Cu, Pb and Zn minerals in the Bregalnica river basin region. Attic dust samples were collected from 84 settlements. At each location for attic dust sampling, topsoil samples from the house yards were also collected. Mass spectrometry with inductively coupled plasma (ICP-MS) was applied as an analytical technique for the determination of Ag, Bi, Cd, Cu, In, Mn, Pb, Sb, Te, W and Zn. The universal kriging method with linear variogram interpolation was applied for the construction of spatial distribution maps.

6.7.1 Characterization of Investigated Area

The investigated area includes the basin of the river Bregalnica which is found in the area of the east planning region of the Republic of Macedonia (N: 41°27'-42°09' and E: 22°55'-23°01'), covering ~4000 km² (Fig. 6.2). The region of the investigated area is geographically composed of several sub-regions. The area is characterized by two valleys – Maleševska and Kočani valleys. The Maleševska valley represents the upper course of the river Bregalnica where the river source is also

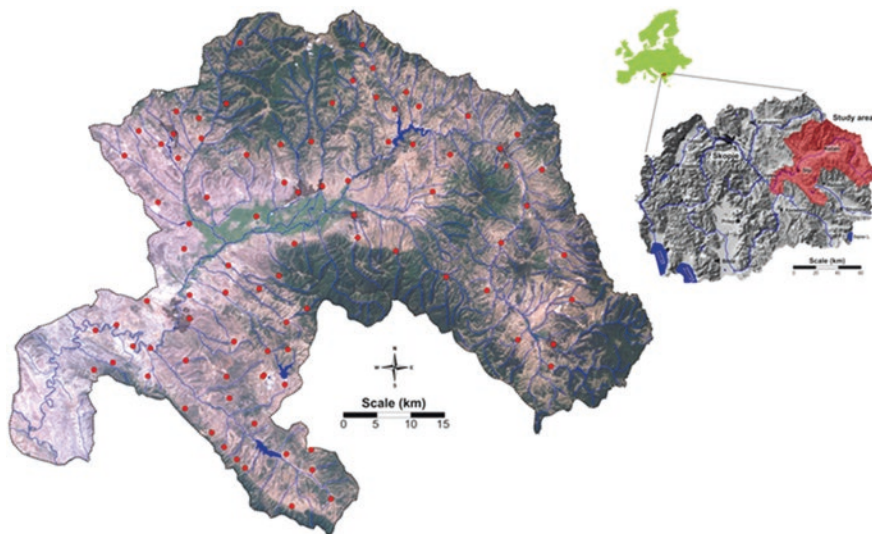


Fig. 6.2 Location of the investigating area and sampling network of attic dust and soil samples

located, with altitude range of 700–1140 m. The valley is enclosed by the Maleševski Mountains on the east, by the Ograzhden Mountain on the south-southeast and by the Plačkovica and Obozna on the west. The average annual precipitation amounts to about 500 mm with significant variations from year to year, as well as in the different sub-regions (Lazarevski 1993). The precipitation is mostly related to and conditioned by the Mediterranean cyclones (Lazarevski 1993). During the summer period, the region is most often found in the centre of the subtropical anticyclone, which causes warm and dry summers. From the central area of the region, as the driest area, the average annual precipitation increases in all directions, because of either the increase in the influence of the Mediterranean climate or the increase in altitude (Lazarevski 1993). In the region are distinguished about ten climatic-vegetation soil areas with considerably heterogeneous climate, soil and vegetation characteristics (Lazarevski 1993). Regarding the demographic structure in the region of the Bregalnica basin, only 4% of the populated areas belong to the category of urban areas, while 96% of the total populated areas are categorized as rural areas. Considering land use, the region is considerably diverse. Along the course of the Bregalnica river dominate agricultural cultivated lands. About 30% belong to the forest regions, localized around the Maleševska valley, represented by the Maleševski Mountains, and then around the Kočani valley, represented on the one side by the Osogovo Mountains and by Plačkovica on the other side. The investigated area that covers the basin of the river Bregalnica lies on the two main tectonic units – the Serbian-Macedonian massive and the Vardar zone (Dumurdzanov et al. 2004). The polyphasal Neogene deformations through the insignificant movements associated with the volcanic activities had direct influence on the gradual formation of the reefs and the formation of deposits in the existing basins. From the middle

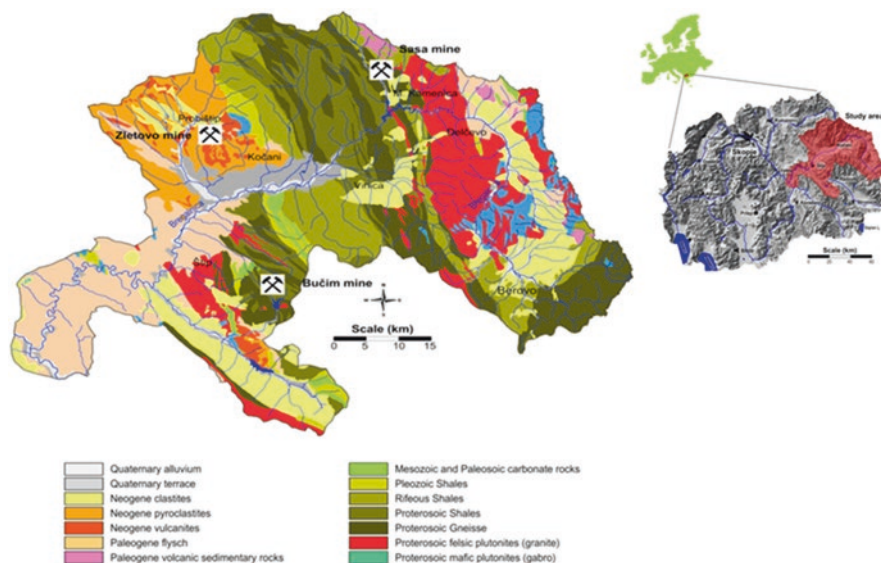


Fig. 6.3 Generalized geology of the investigated area and location of the emission sources – Sasa mine (Pb-Zn hydrothermal exploitation), Kratovo-Zletovo district and Bučim mine area (Cu-Au hydrothermal exploitation)

Miocene to the end of the Pleistocene, there were alternating periods of fast and slow landslides accompanied with variable sedimentation (deposition). The Cenozoic volcanism represents a more recent extension in the Serbian-Macedonian massive and the Vardar zone. The oldest volcanic rocks occur in the areas of Bučim, Damjan, the Borov Dol district and in the zone of Toranica, Sasa, Delčevo and Pehčevo (Dumurdzanov et al. 2004). These older volcanic rocks were formed in the middle Miocene from sedimentary rocks that represent the upper age limit of the rocks. The origin of these oldest volcanic rocks is related to the Oligocene – the early Miocene period. Volcanic rocks are categorized as follows: andesite, latite, quartz latite and dacite. Volcanism appears sequentially and, in several phases, forming sub-volcanic areas. On the other hand, the pyroclastites are most frequently found in the Kratovo-Zletovo volcanic area, where the dacites and andesites are the oldest formations (Fig. 6.3).

6.7.2 Sampling Protocol and Analytics

Attic dust samples were collected from the attics from total of 84 houses built between 1920 and 1970 (Fig. 6.2). The data information for house building period were obtained from the local population at the time of the sampling. The collection of attic dust samples was performed according to the adopted protocol given by Šajin

(2003). The sampling protocol includes (a) removing the dinginess from the attic surface, (b) collecting the corpuscular dust from the attic surface using plastic brush and (c) transferring the collected dust in polyethylene bags. The representative sample from one house was obtained collecting the dust from five to ten attics, depending of the house condition.

The soil samples brought in the laboratory were subjected to cleaning and homogenization, drying at room temperature, or in a drying room at 40 °C, to a constantly dry mass. Then the samples were passed through a 2 mm sieve and finally were homogenized by grinding in a porcelain mortar until reaching a final size of the particles of 125 µm. Following the physical preparation, the samples were chemically prepared by wet digestion, applying a mixture of acids in accordance with the international standards (ISO 14869-1: 2001).

For digestion of attic dust and soil samples, open wet digestion with mixture of acids was applied. Precisely measured mass of dust samples (0.5 g) was placed in Teflon vessels, and 5 mL concentrated nitric acid (HNO₃) was added, until the brown vapours came out from the vessels. Nitric acid is very suitable oxidant for digestion of environmental samples. For total digestion of inorganic components, 5–10 mL hydrofluoric acid was added. When the digest became clear solution, 2 mL of HClO₄ was added. Perchloric acid was used for total digestion of organic matter. After 15 minutes cooling the vessels, 2 mL of HCl and 5 mL of H₂O were added for total dissolve of metal ions. Finally, the vessels were cooled and digests quantitatively transferred to 50 mL calibrated flasks. In this way, the digested soil and sediment samples were prepared for determining the contents of the different elements using atomic emission and mass spectrometry.

PerkinElmer SCIEX ELAN DRC II (Canada) inductively coupled plasma mass spectrometer (ICP-MS, with quadrupole as single detector) was used for measurement of the concentration trace elements, while for the major elements' content determination, atomic emission with inductively coupled plasma (ICP-AES, Varian 715ES) was applied. For this study, reagents with analytical grade, namely, nitric acid, trace pure (Merck, Germany); hydrofluoric acid, p.a. (Merck, Germany); perchloric acid, p.a. (Merck, Germany); hydrochloric acid, p.a. (Merck, Germany); and redistilled water, were used for the preparation of all solutions. Standard solutions of metals were prepared by dilution of 1000 mg/L solutions (11355-ICP multi-element standard). For each element analysed, previous optimization of the instrumental conditions was performed.

6.7.3 Data Processing Methods

After the instrumental analysis, the values obtained contain the contents of the elements, initially co-transformed and normalized. The processing of numerous variables with a heterogeneous distribution structure is often complex and requires careful processing. On the other hand, there is significant deviations from the nor-

mal distribution of data. This state of the obtained variables was improved by applying the transformation of the data set. For the normalization of a heterogeneous set of values, the statistical method of Box-Cox is used (Box and Cox 1964). Normalized values are processed with basic descriptive statistics, using the basic parameters of this method.

Bivariate analysis is used to perform a comparative analysis of the dependencies between variables (set of values for one variable). Two-dimensional scatter-plots are used to display the correlations and identify them visually.

Multivariate analysis is applied to extract dominant associations of variables (Šajn 2006). As a measure of similarity between variables, the product-moment correlation coefficient (r) was applied. There are various rotational strategies that have been proposed (Šajn 2006; Žibret and Šajn 2010). The purpose of the applied statistical data processing models is to obtain the most realistic model of multi-dimensional variable distribution system. For variables, i.e. the data set for the content of a given element, for which the applied factor analysis will deposit low values, they will be excluded from further analysis. Factor analysis used orthogonal varimax rotation. Factor analysis is an interdependence technique because it looks for a group of variables that are similar in that they “move together” and therefore have great interdependence. When one variable has a large value, then the other variables in the group have a large value. For the effective application of factor analysis, as well as other multivariate interdependence techniques, it is necessary to have a minimal amount of redundancy of variables, that is, the variables at least slightly overlap in their meaning. Thanks to this redundancy, it is possible to discover a pattern in the behaviour of variables, that is, the basic idea (factor) by which they are imbued (Žibret and Šajn 2010). Cluster analysis is a statistical technique used to identify how different entities – variables – can be grouped together for the sake of their characteristics. Also known as clustering, it is a preliminary data analysis tool that aims to sort different objects in a group in such a way that those who belong to the same group have the highest degree of association. The most commonly processed dendrograms or clusters are expressed by distance, D_{link}/D_{max} (%).

6.7.4 Evaluation of Data Summary Matrix

Data summary was introduced by Balabanova et al. (2019) generating the following geochemical associations: F1, Ga-Nb-Ta-Y-(La-Gd)-(Eu-Lu); F2, Be-Cr-Li-Mg-Ni; F3, Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn; F4, Ba-Cs-Hf-Pd-Rb-Sr-Tl-Zr; F5, As-Co-Ge-V; and F6, K-Na-Sc-Ti. The total variability for dominant loadings of 81.5% was established (Balabanova et al. 2019).

6.7.4.1 Tracking the Lithogenic Anomalies in the Investigated Area

Multivariate analysis successfully reduced variables by extracting dominant associations of elements. Detailed analysis of these associations, through thorough study and comparative analysis with typical lithology and geologically dominant formations, enabled the generation of the following analytical qualifications. Factor 1 [Ga-Nb-Ta-Y-(La-Gd)-(Eu-Lu)] clearly expresses the typical connection of some basic earth forming process, due to the incorporation of the rare earth. Their sources are mainly natural phenomena such as rock weathering and chemical processes in soil. The second geochemical association (Be-Cr-Li-Mg-Ni) relays also on the effect from the windblown dust from the surface soil layers. These determined elements are considered “natural” because their origin is primarily crustal-soil particles suspended and transported by wind. High factor loadings are related to some old formation such as Paleogene flysch and Quaternary unconsolidated sediments. The occurrence of Factor 4 (Ba-Cs-Sr-Rb-Pd-Tl-Zr-Hf) presents an interesting geochemical association, incorporating the incompatible/hygro-magmatophile elements. Element enrichments occur in areas with predominance of Neogene pyroclastite and sediments. According to generalized geology map (Fig. 6.3), Kratovo-Zletovo region is the unique district in the region located along the continental margin and is closely related to the Tertiary volcanoes and hydrothermal activities in this area. The sixth factor includes K-Na-Sc-Ti. Although it is the least distinguished factor; nevertheless, this geochemical association is related with the lithogenic dominance of the Neogene sediments and Paleogene flysch. Their occurrence in the environment is usually correlated with the major minerals in basaltic and ultramafic rocks which have two kinds of cationic lattice sites: small tetrahedral sites occupied by Si and Al (Balabanova et al. 2019).

6.7.4.2 Selecting Dominant and Silent Anthropogenic Markers

One of the more important goals of this research is to determine the success of this multidisciplinary approach in determining anthropogenic markers (dominant and recessive). Dominant and recessive markers of anthropogenic inputs were identified after multivariate extraction. Factor 3 (Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn) was the most heterogenic geochemical association (Table 6.1). Enriched deposition occurred dominantly on Rifeous shale. These very old rocks occur as transition lithologic units between the Neogene and Paleogene volcanism in the investigated area. Pb-Zn mines *Sasa* and *Zletovo* are located in the areas with dominantly presence of the Oligocene and Neogene volcanism appears sequentially and, in several cases in sub-volcanic areas. On the other hand, the pyroclastites are most frequently found in the Kratovo-Zletovo volcanic area, where the dacites and andesites are the oldest formations. This geochemical association links typical elements which are normally associated with air pollution (Cd-Pb-Zn) and usually are not influenced by lithological background. Spatial patterns show intensive deposition in the area of poly-metallic hydrothermal exploitations, *Sasa*, *Zletovo* and *Bučim*. This geochemi-

Table 6.1 Element distribution according to dominant geological formation in the area of the elements from Factor 3 (median values are given; $N = 84$)

| | Unit | River terraces (Q) | River sediment (Ng) | Pyroclastite (Ng) | Flysch (Pg) | Schists (Pz) | Schists (R) | Schists (Pt) | Gneisses (Pt) | Granite (Pt) |
|----|-------|-----------------------|------------------------|----------------------|----------------|-----------------|----------------|-----------------|------------------|-----------------|
| Ag | mg/kg | 0.53 | 0.48 | 0.59 | 0.45 | 0.60 | 1.3 | 0.44 | 0.43 | 0.58 |
| Bi | mg/kg | 0.28 | 0.28 | 0.31 | 0.29 | 0.26 | 0.61 | 0.45 | 0.35 | 0.22 |
| Cd | mg/kg | 0.42 | 0.45 | 0.44 | 0.52 | 0.33 | 1.5 | 0.28 | 0.25 | 0.31 |
| Cu | mg/kg | 40 | 25 | 27 | 24 | 25 | 43 | 49 | 26 | 29 |
| In | µg/kg | 35 | 28 | 46 | 37 | 42 | 94 | 46 | 34 | 39 |
| Mn | mg/kg | 440 | 450 | 540 | 480 | 560 | 830 | 530 | 370 | 430 |
| Pb | mg/kg | 54 | 83 | 48 | 18 | 30 | 110 | 55 | 22 | 12 |
| Sb | mg/kg | 0.80 | 0.64 | 0.89 | 0.62 | 0.55 | 1.1 | 0.66 | 0.45 | 0.46 |
| Te | µg/kg | 34 | 15 | 30 | 27 | 28 | 63 | 41 | 21 | 19 |
| W | mg/kg | 0.85 | 0.79 | 1.0 | 0.76 | 1.0 | 2.0 | 1.1 | 1.1 | 0.76 |
| Zn | mg/kg | 110 | 130 | 98 | 110 | 90 | 220 | 86 | 72 | 88 |

Q Quaternary, *Ng* Neogene, *Pg* Paleogene, *R* Rifeous, *Pt* Proterozoic, *Pz* Paleozoic

cal occurrence can be used as a poly-metallic marker for anthropogenic emissions. This geochemical association unite some “not very common” elements for air pollution (argentum, indium and tellurium). Generally, most of the trace element distribution is characterized mainly in terms of the different lithological units, as in the case of In (42 $\mu\text{g}/\text{kg}$), Bi (0.30 mg/kg) and Ag (0.54 mg/kg) distribution differs from the rest of the trace elements, due to the dominance of the atmospheric deposition (with median of 31 $\mu\text{g}/\text{kg}$ and max. Value of 1300 $\mu\text{g}/\text{kg}$) vs. soil distribution (median of 17 $\mu\text{g}/\text{kg}$ and max value of 280 $\mu\text{g}/\text{kg}$). Copper contents in air-distributed dust range from 6.7 to 880 mg/kg , while in the topsoil layer, an extended distribution has occurred to 1200 mg/kg . Enriched values for the Cu content in attic dust were obtained from houses located very close to Cu mine *Bučim*. Cadmium contents also have an enrichment trend in air-distributed dust (0.054–25 mg/kg); but cadmium content in the topsoil layer does not indicate any significant enrichment (0.005–9 mg/kg). The distribution of lead and zinc is similar to that of copper and cadmium in the investigated area. Lead content ranges from 0.005 to 3900 mg/kg , while Zn contents show lower enrichments from 26 to 3200 mg/kg . Lithogenic distribution in soil reaches 1200 mg/kg and 590 mg/kg , respectively, for Pb and Zn. According to the dominant lithological units, Rifeous shales are mostly enriched with Pb and Zn, where the median values for Pb and Zn contents are 110–220 mg/kg , respectively. For the spatial distribution of the factor scores, universal kriging with the linear variogram interpolation method was applied for the construction of maps showing the spatial distribution of elemental distribution. The significance is given on those areas where the content of the elements exceeds the 75th percentile of the data distribution for the element content. Attic dust’s element distribution is marked with number 1 at each figure for element distribution. In order to distinguish the lithogenic impact on the element distribution, the topsoil layer was also investigated for the content of the elements (marked with number 2 at each figure for element distribution). Also, this investigation fortifies an extended anthropogenic association (Ag, Bi, In and Mn) that implement some other anthropogenic activities such as agricultural activities (use of urban sludge, manure and phosphate fertilizers) and their occurrence can be a secondary affection from mine poly-metallic pollution (Balabanova et al. 2019). Affiliation of tellurium and wolfram to this group spread up an elemental anomaly in the Berovo region. For all elements that associate in this group, enriched value deposition occurs in this mentioned area. Almost 20 years ago, Arsovski (1997) points to a poly-metallic enrichment in this area, so-called Vladimirovo-Berovo, during the tectonic investigation. The present investigation also interpolates this area as a metallic–/metalloid-enriched zone, with emphasis on the anthropogenic elements. This occurrence was also determined for the geochemical marker (As-Co-Ge-V) established by Balabanova et al. (2019). Spatial mappings for each element are presented in Figs. 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, 6.10, 6.11, 6.12, 6.13, and 6.14.

Geochemical association given as Factor 5 (Balabanova et al. 2019) associates the following elements, As, Co, Ge and V, with predominant occurrence on Rifeous shales (Table 6.2). This kind of geochemical *fingerprinting* occurs along the whole course of the Bregalnica river. Accordingly, the resulting areal distribution map used

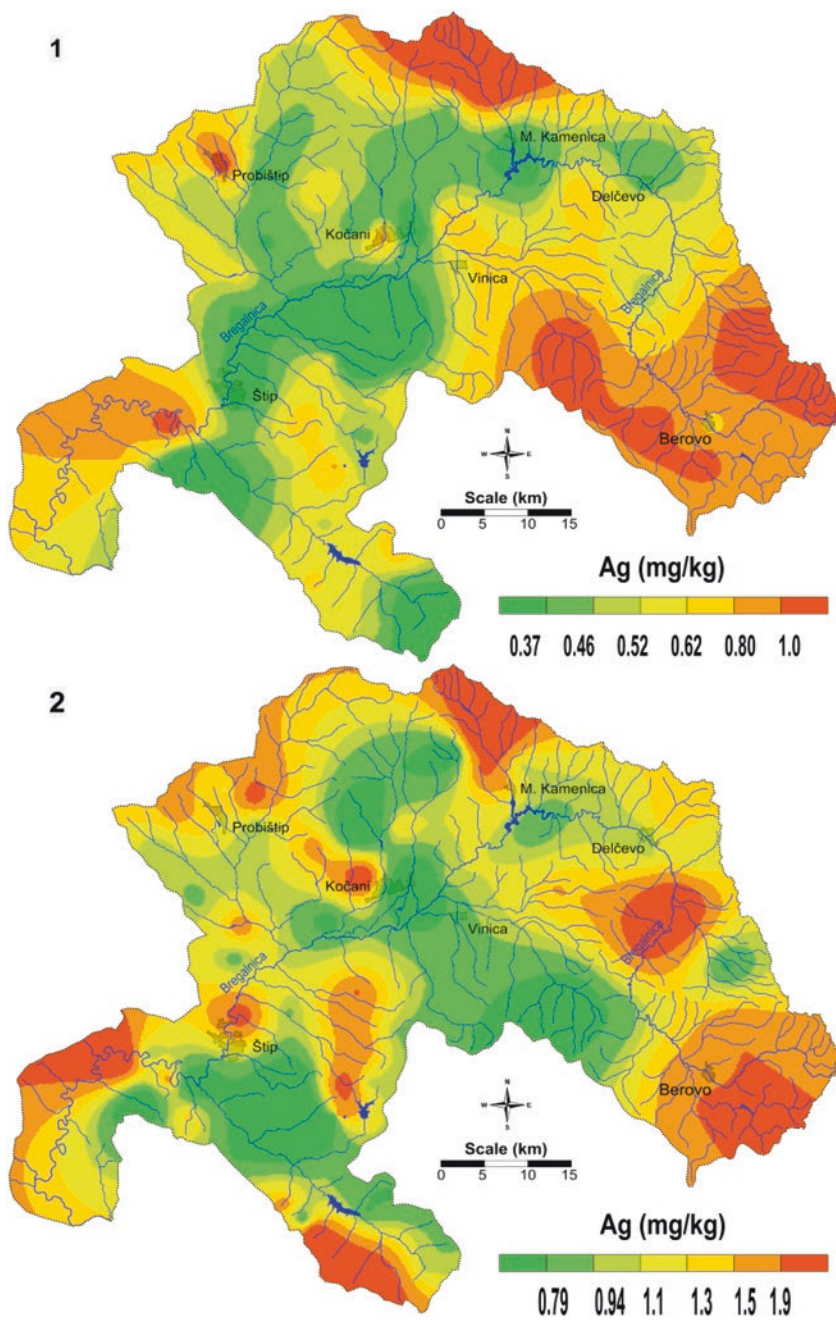


Fig. 6.4 Spatial mapping with *kriging* method, for distribution of silver in attic dust (1) and soil (2)

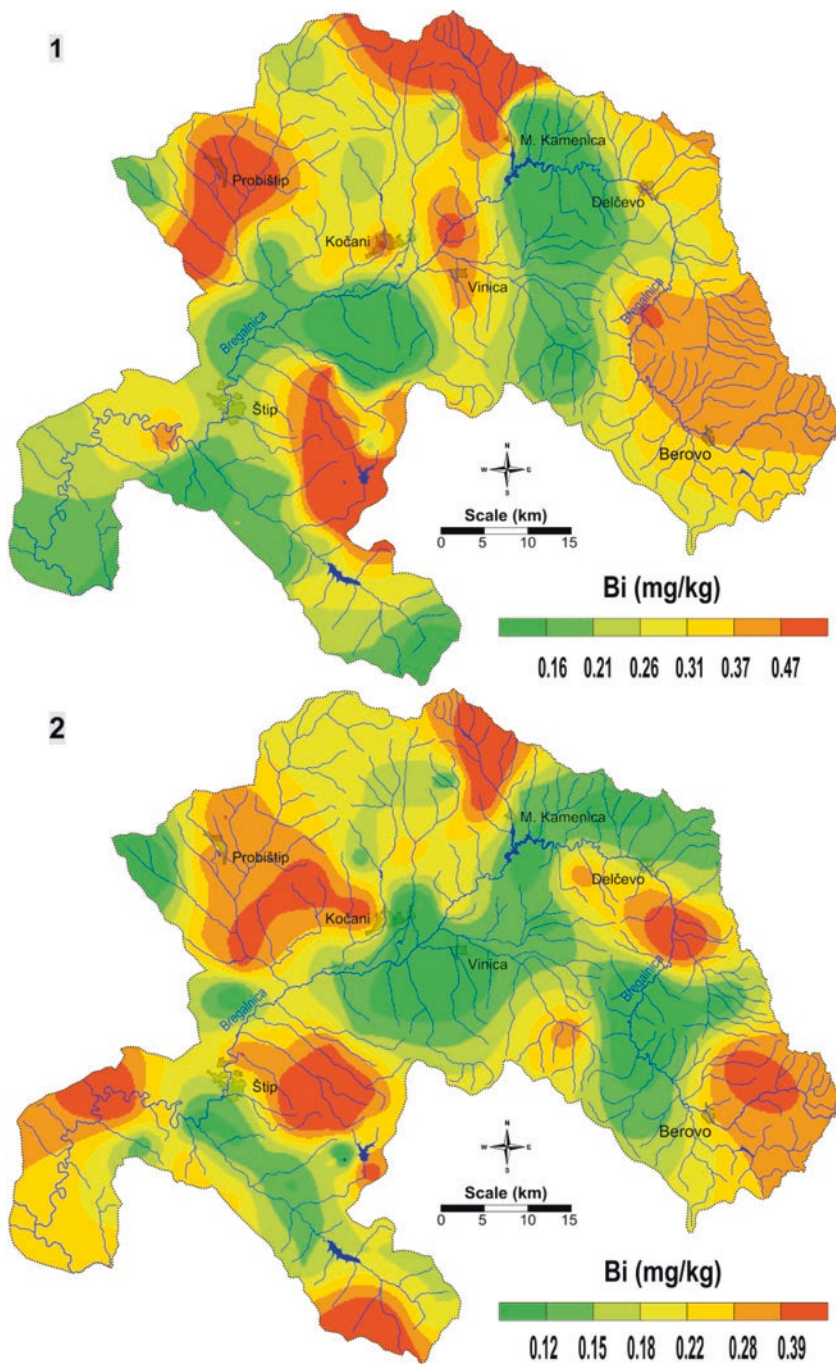


Fig. 6.5 Spatial mapping with *kriging* method, for distribution of bismuth in attic dust (1) and soil (2)

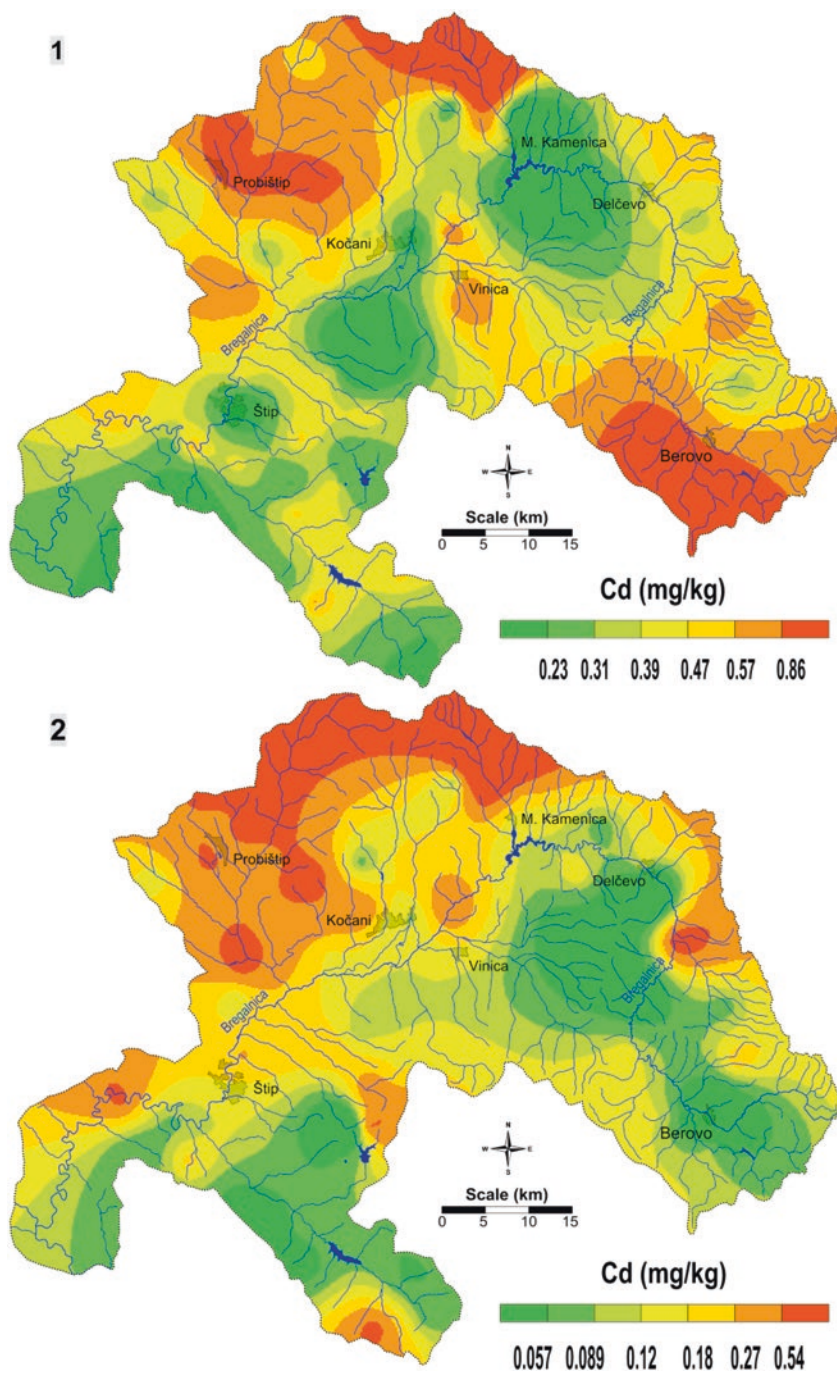


Fig. 6.6 Spatial mapping with *kriging* method, for distribution of cadmium in attic dust (1) and soil (2)

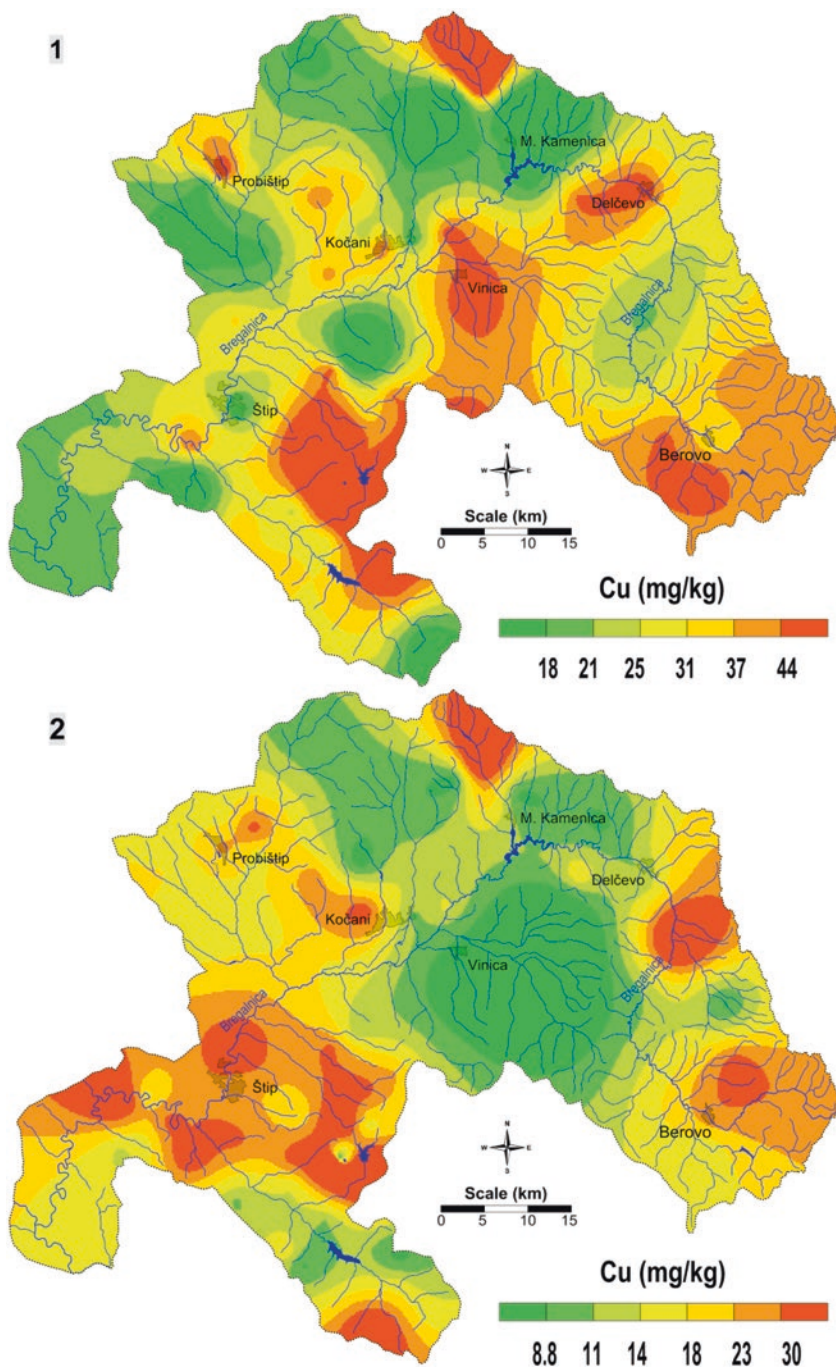


Fig. 6.7 Spatial mapping with *kriging* method, for distribution of copper in attic dust (1) and soil (2)

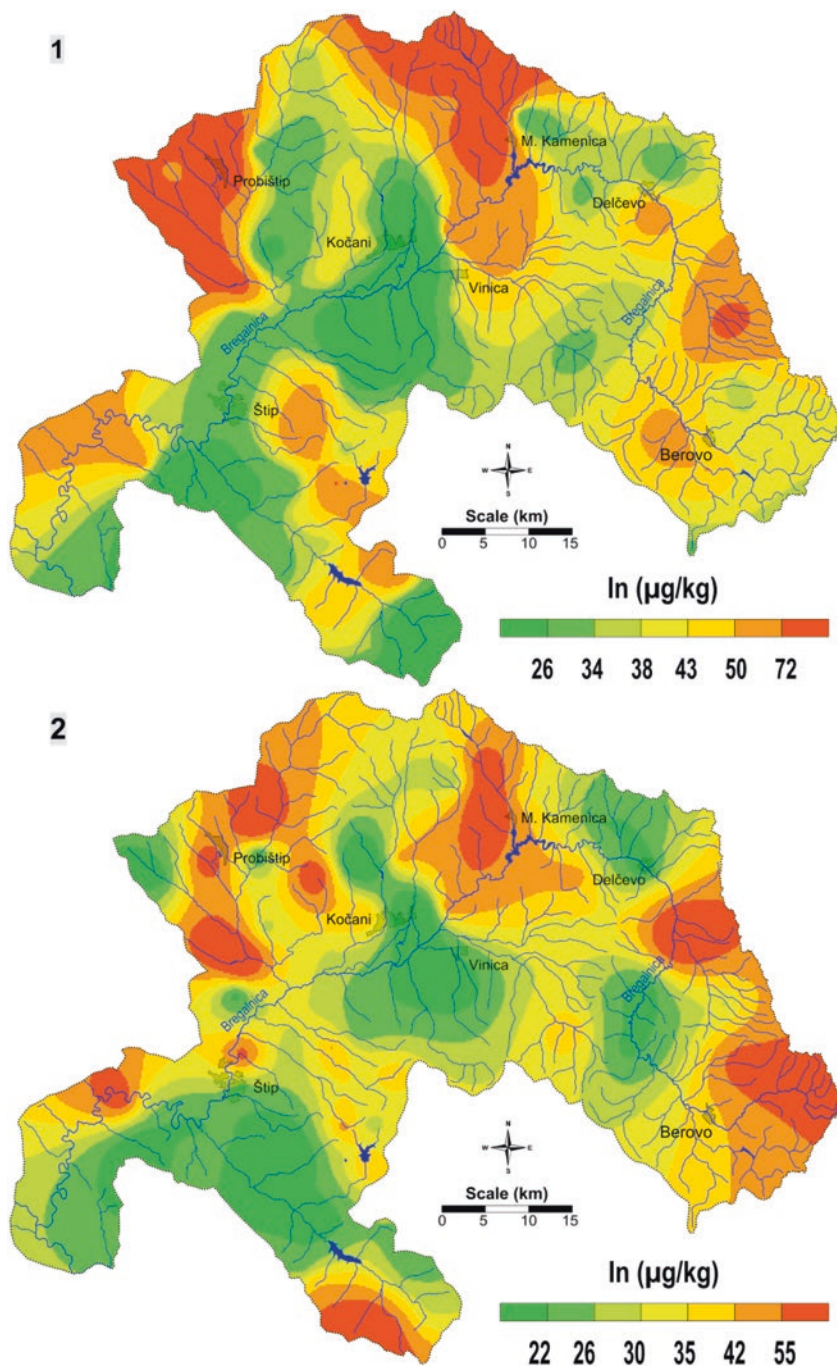


Fig. 6.8 Spatial mapping with *kriging* method, for distribution of indium in attic dust (1) and soil (2)

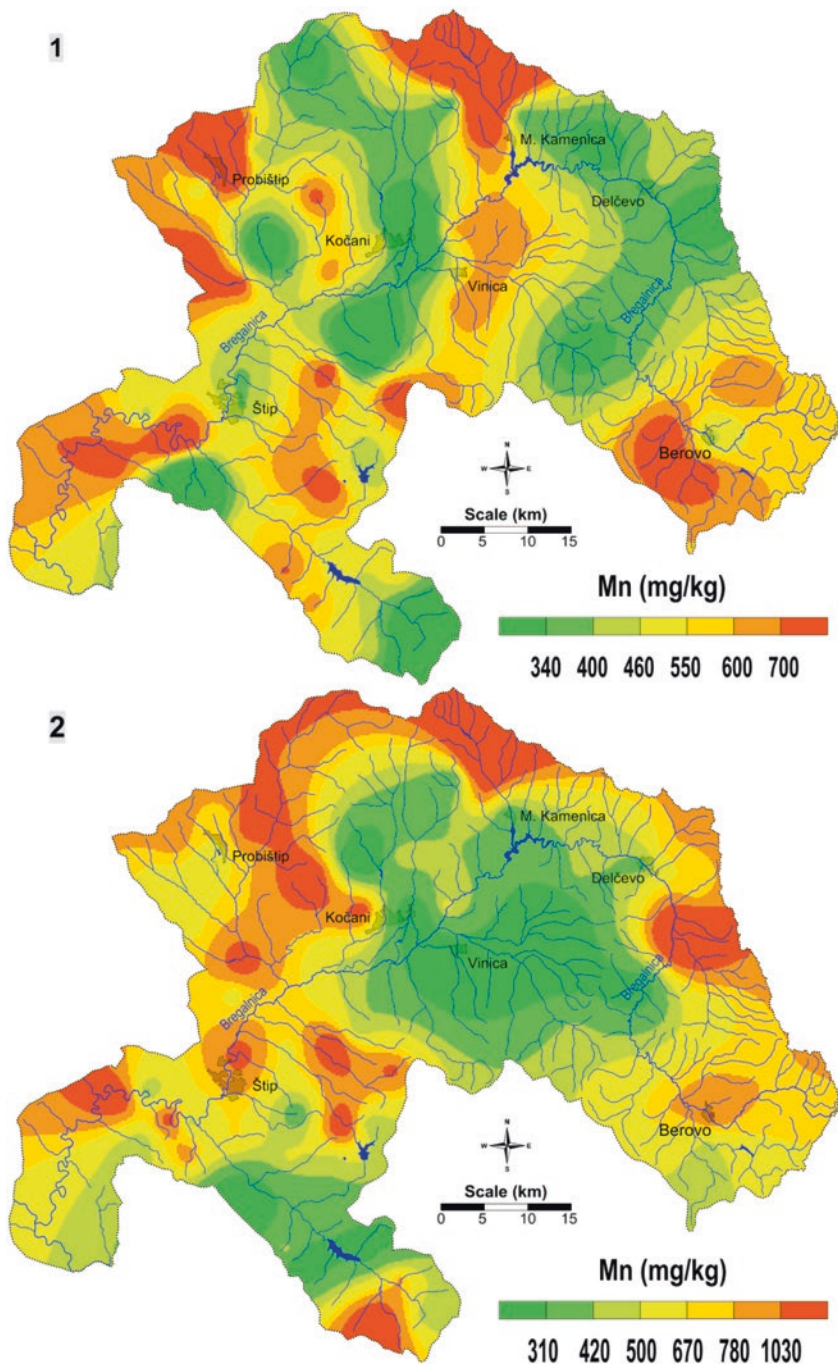


Fig. 6.9 Spatial mapping with *kriging* method, for distribution of manganese in attic dust (1) and soil (2)

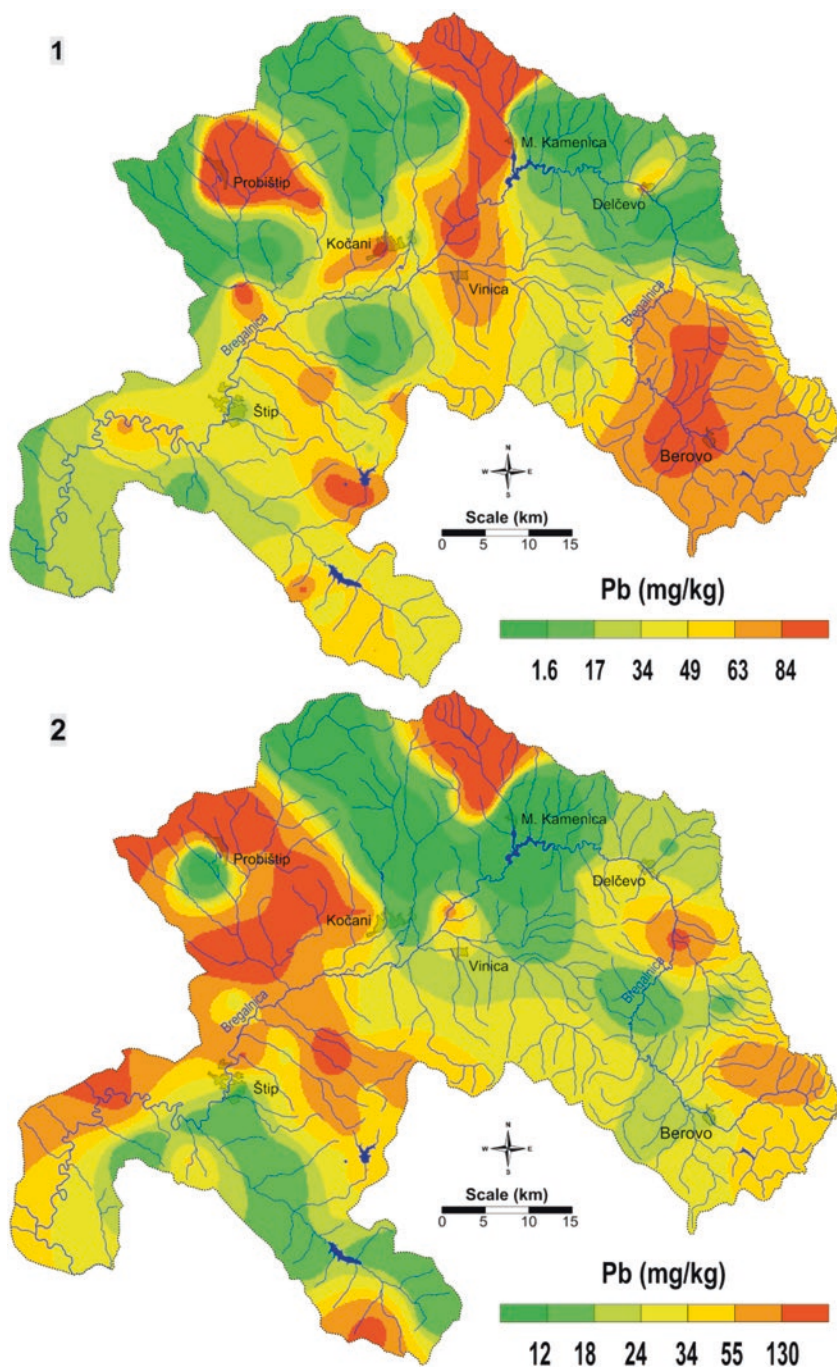


Fig. 6.10 Spatial mapping with *kriging* method, for distribution of lead in attic dust (1) and soil (2)

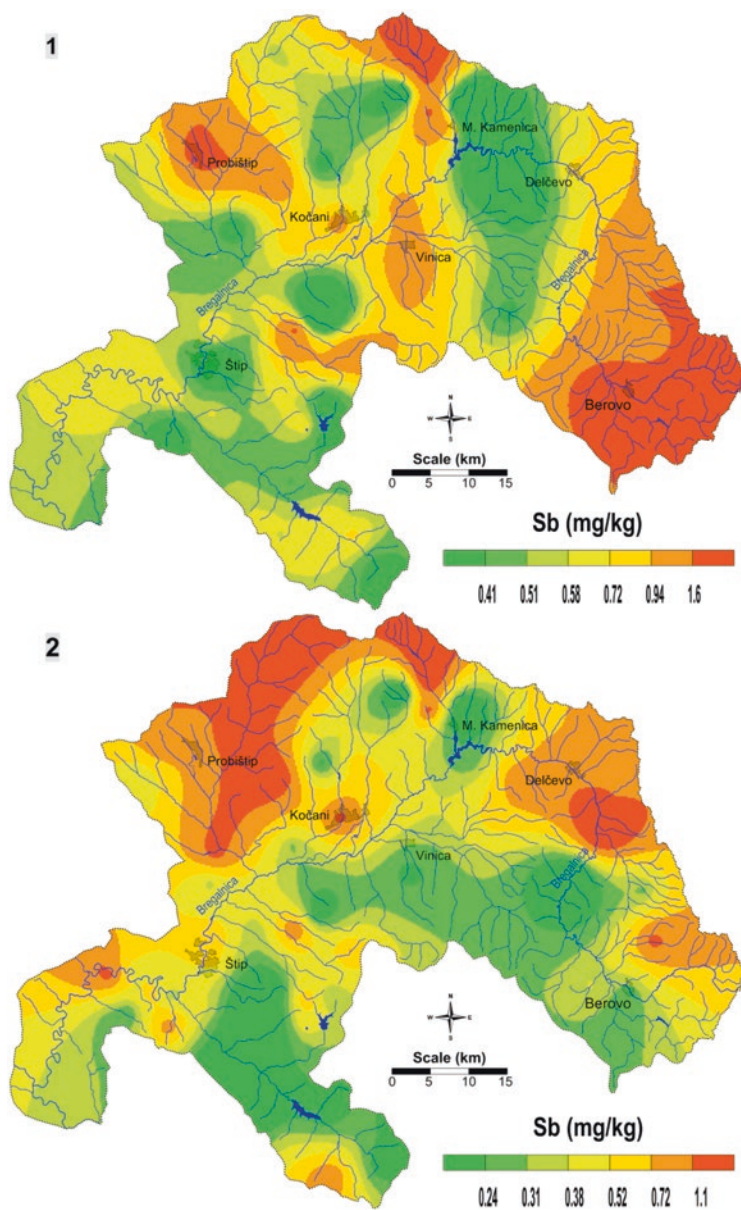


Fig. 6.11 Spatial mapping with *kriging* method, for distribution of antimony in attic dust (1) and soil (2)

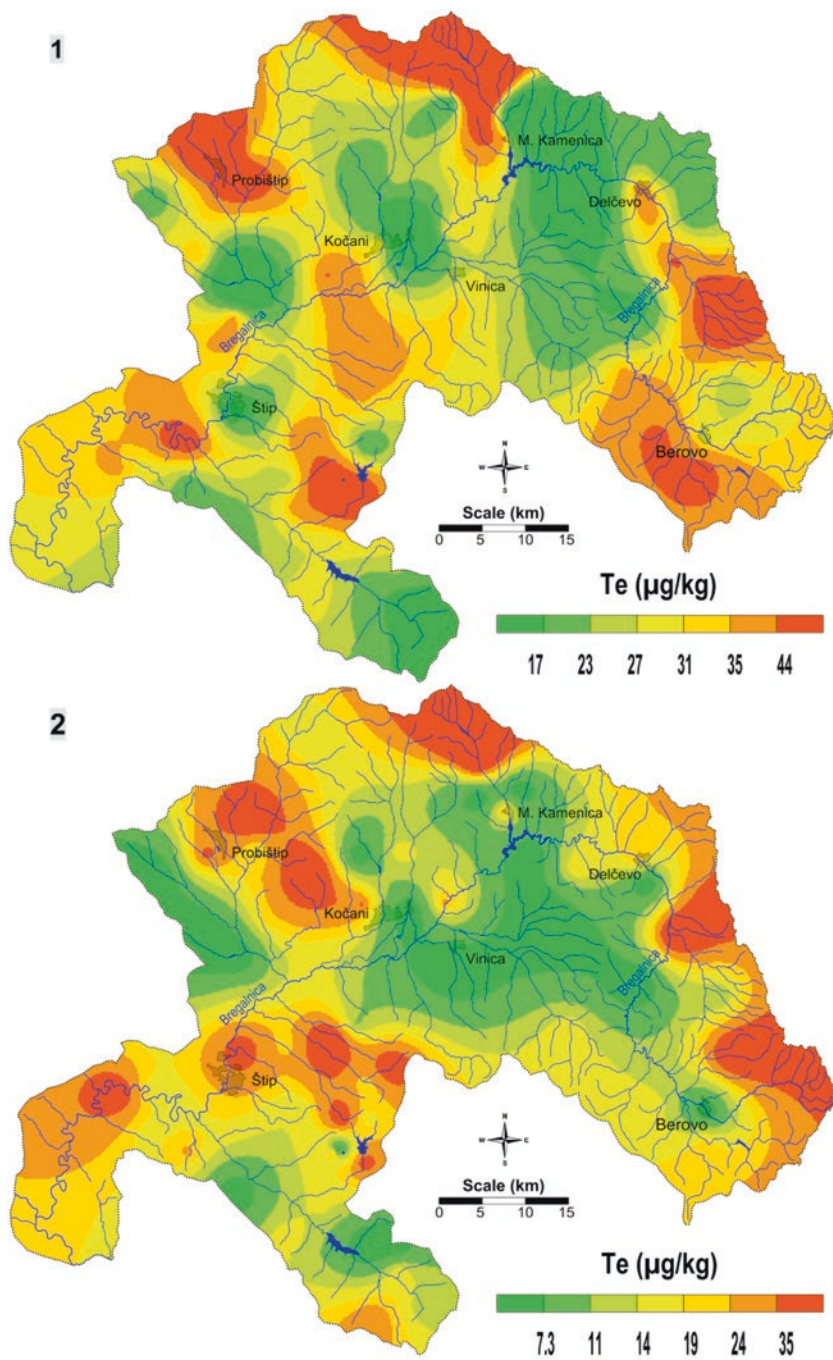


Fig. 6.12 Spatial mapping with *kriging* method, for distribution of tellurium in attic dust (1) and soil (2)

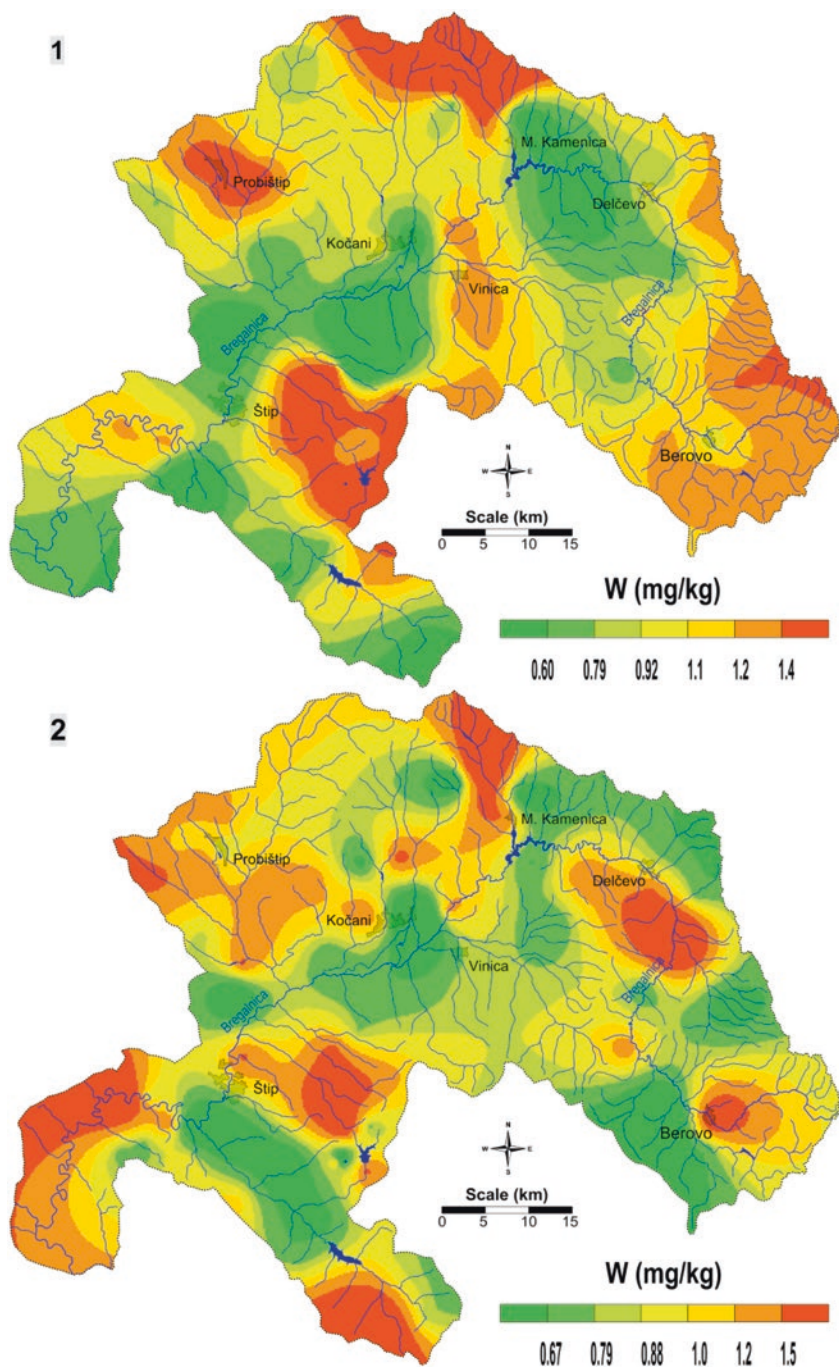


Fig. 6.13 Spatial mapping with *kriging* method, for distribution of wolfram in attic dust (1) and soil (2)

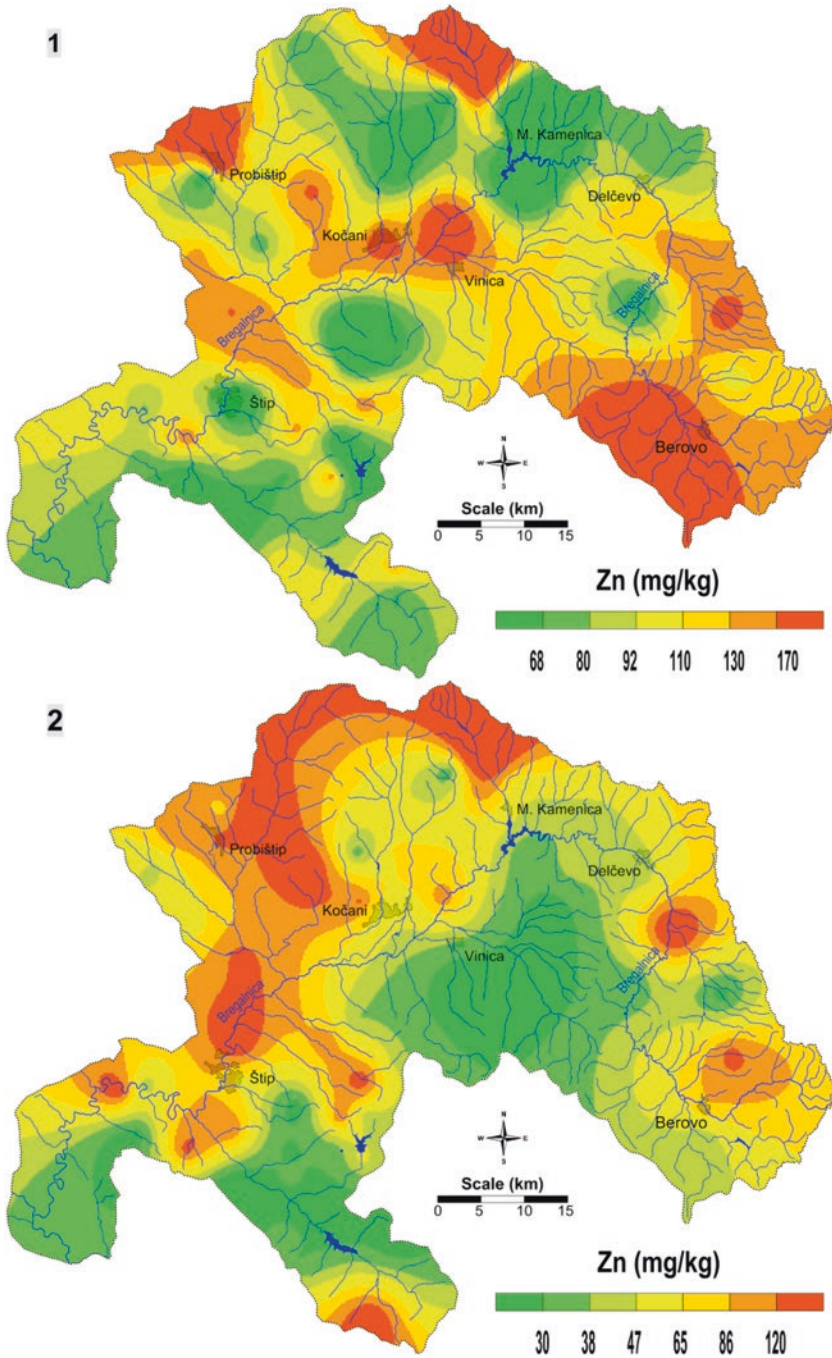


Fig. 6.14 Spatial mapping with *kriging* method, for distribution of zinc in attic dust (1) and soil (2)

Table 6.2 Element distribution according to dominant geological formation in the area of the elements from Factor 5 (median values are given)

| | Unit | River terraces (Q) | River sediment (Ng) | Pyroclastite (Ng) | Flysch (Pg) | Schists (Pz) | Schists (R) | Schists (Pt) | Gneisses (Pt) | Granite (Pt) |
|----|-------|-----------------------|------------------------|----------------------|----------------|-----------------|----------------|-----------------|------------------|-----------------|
| As | mg/kg | 19 | 23 | 16 | 21 | 16 | 26 | 20 | 15 | 14 |
| Co | mg/kg | 6.6 | 5.6 | 7.2 | 6.0 | 7.3 | 9.1 | 6.4 | 6.5 | 7.6 |
| Ge | mg/kg | 0.53 | 0.51 | 0.60 | 0.55 | 0.65 | 0.75 | 0.64 | 0.52 | 0.52 |
| V | mg/kg | 68 | 100 | 79 | 68 | 74 | 75 | 87 | 76 | 71 |

Q Quaternary, Ng Neogene, Pg Paleogene, R Rifeous, Pt Proterozoic, Pz Paleozoic

to support with high certainty the assessment for poly-metallic enrichments as ascribed to urbanization, including vehicular emissions and incinerators and industry. Comparative analysis for the areal patterns singled out a very similar behaviour of the Factor 3 and Factor 5. Clustering method was very useful for the determination of both geochemical associations. Furthermore, there is a strong interconnection between the anthropogenic and lithogenic fingerprinting (Balabanova et al. 2019). Basically, the geochemistry of the element depends on both, atmospheric emissions and lithogenic powdery winds. Therefore, the As-Co-Ge-V distribution can be used as a proposed mechanism for possible tracking of anthropogenic poly-metallic enrichments. Arsenic distribution in the study area is lithological dependent from the old volcanism (surroundings of Probishtip-Kratovo).

Distribution of As ranges from 4 to 150 mg/kg, while in the topsoil layer, it reaches 90 mg/kg. Thus, the arsenic can be identified as an anthropogenic tracer in the investigated area. Mapping data extract the anthropogenic enrichment in the middle course of the river basin, where the agriculture activities dominate in the land use. The investigated area is affected with enriched content in arsenic, especially in the area of Pb-Zn mines. Germanium has a specific and unique distribution in the environment. Its geochemistry is also linked to gallium. The minerals of germanium are extremely rare, and the porous germanium is widespread to a considerable extent. Extraction of germanium from waste dust is complicated, not only because of its low concentrations but also because of its amphoteric properties. Germanium contents in the deposited dust from the investigated area reach 2.1 mg/kg. Similar occurrence has been determined for tin as well. Reimann et al. (2012) explains significant correlations in the geochemistry of both elements. Spatial mappings for arsenic, cobalt, germanium and vanadium are presented in Figs. 6.15, 6.16, 6.17, and 6.18.

6.8 Conclusion

The air is intangible, and most of humanity does not think about its importance while inhaling it; however, it is necessary for the existence and functioning of its living world on the planet Earth. With the development of society and technology, man began to engage in production activities that result in the emission of pollutants into the atmosphere. This has significantly begun to change the chemical composition of the planet's ozone layer. Changes in the atmosphere were not noticed until catastrophic pollution began to occur, which took human lives and destroyed flora and fauna. Although there is evidence of efforts to limit human activity that impairs air quality since the sixteenth century, serious efforts in this field were made only in the 1960s, and since then, humanity has become aware of the need to preserve breathing air. Atmospheric deposition poses significant ecological concerns. Dry deposition is characterized by direct transfer of gas phase and particulates from air to ground, vegetation, water bodies and other Earth surfaces.

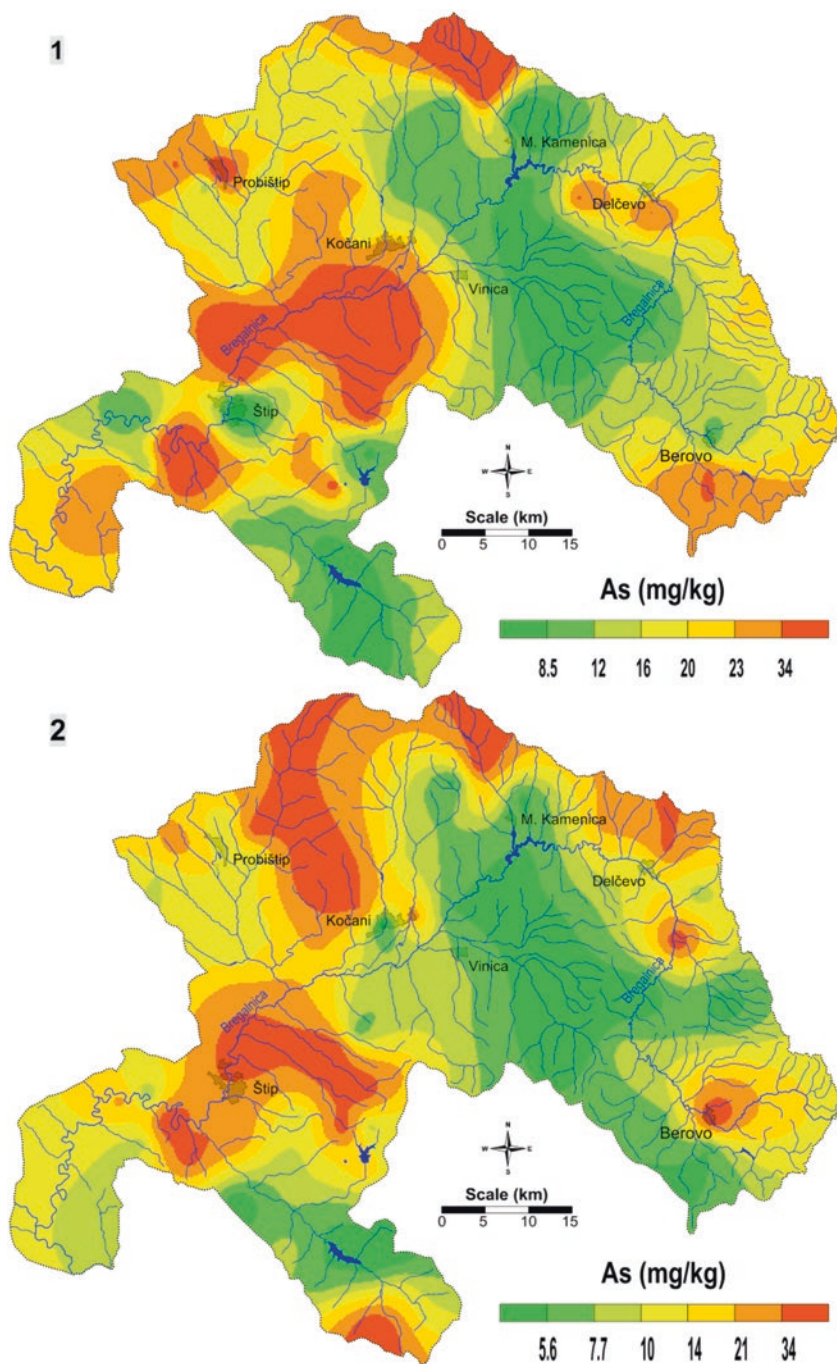


Fig. 6.15 Spatial mapping with *kriging* method for distribution of arsenic in attic dust (1) and soil (2)

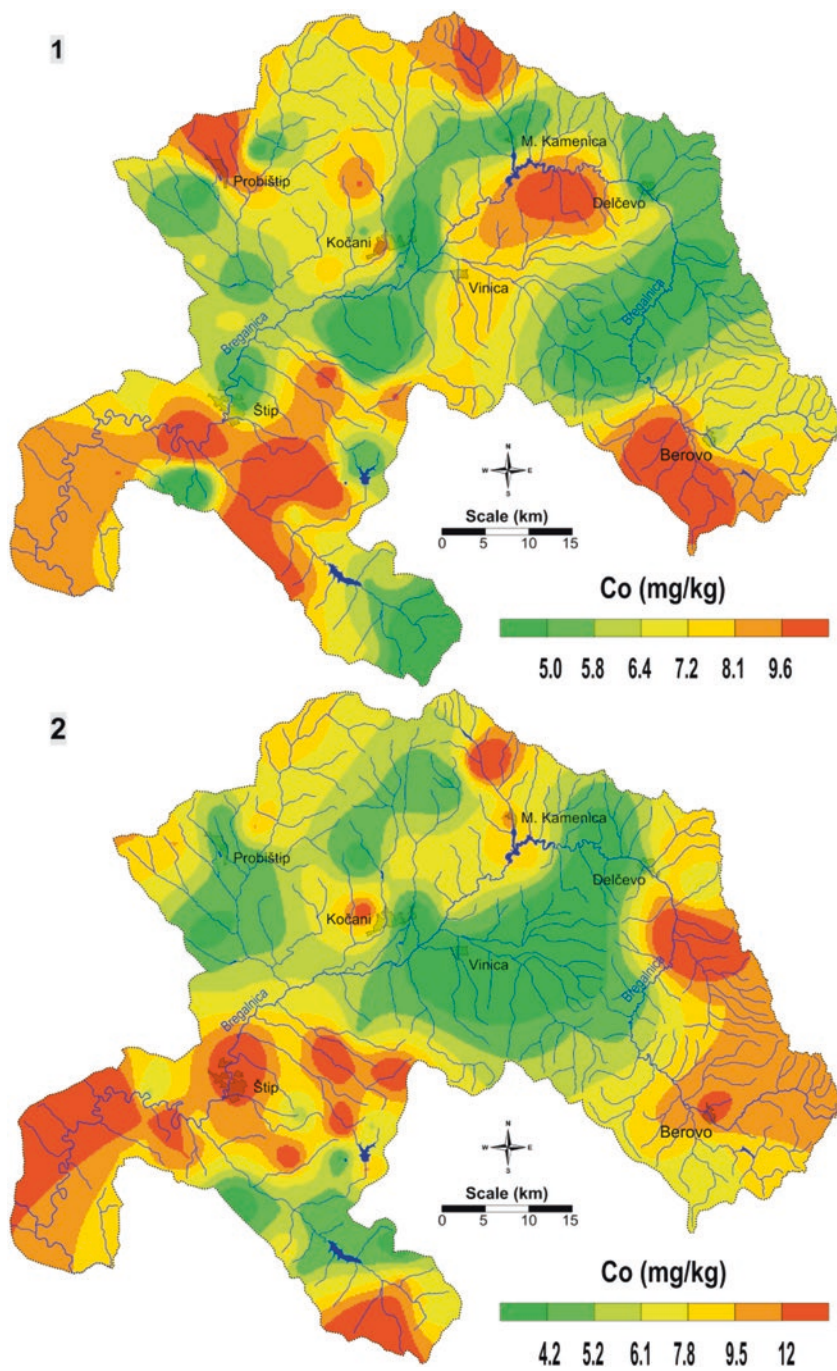


Fig. 6.16 Spatial mapping with *kriging* method, for distribution of cobalt in attic dust (1) and soil (2)

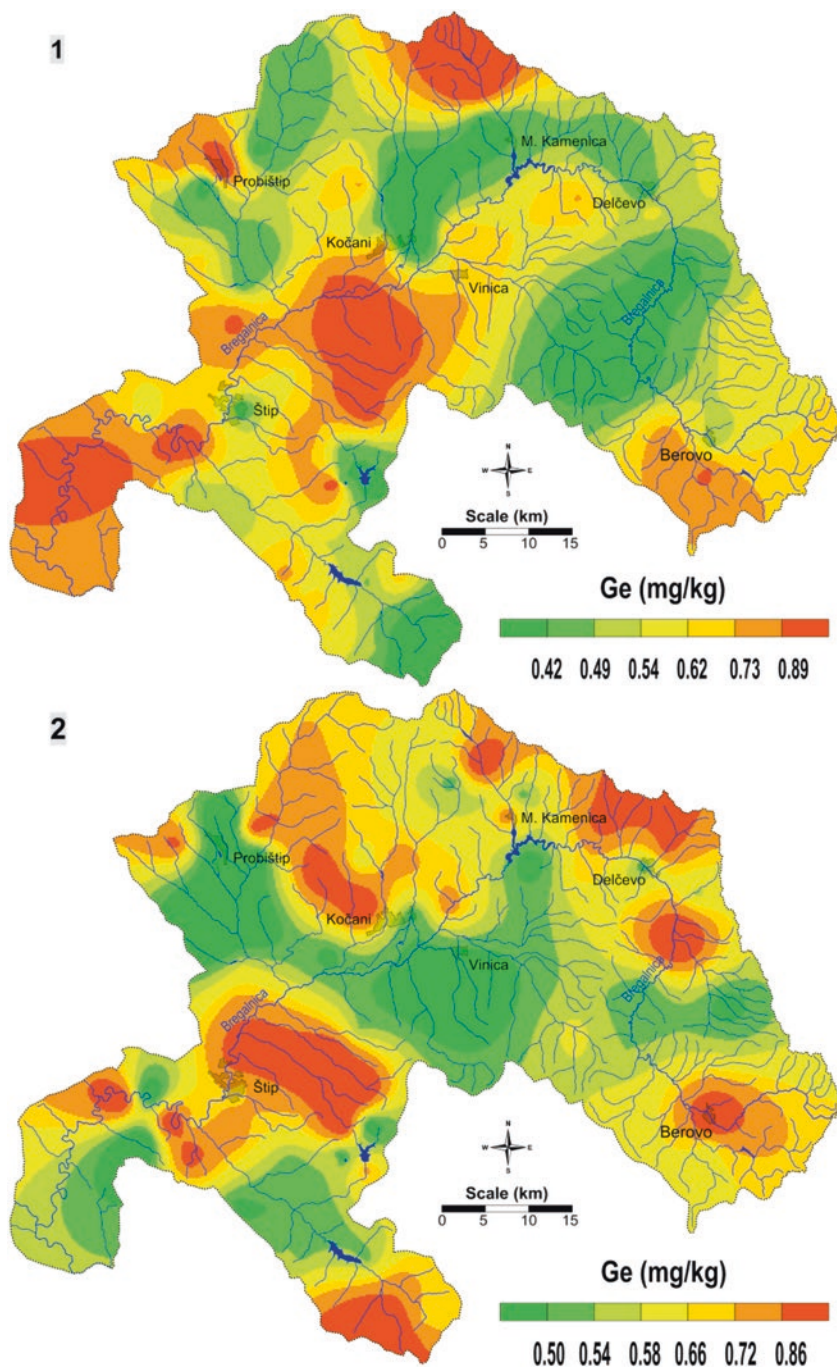


Fig. 6.17 Spatial mapping with *kriging* method, for distribution of germanium in attic dust (1) and soil (2)

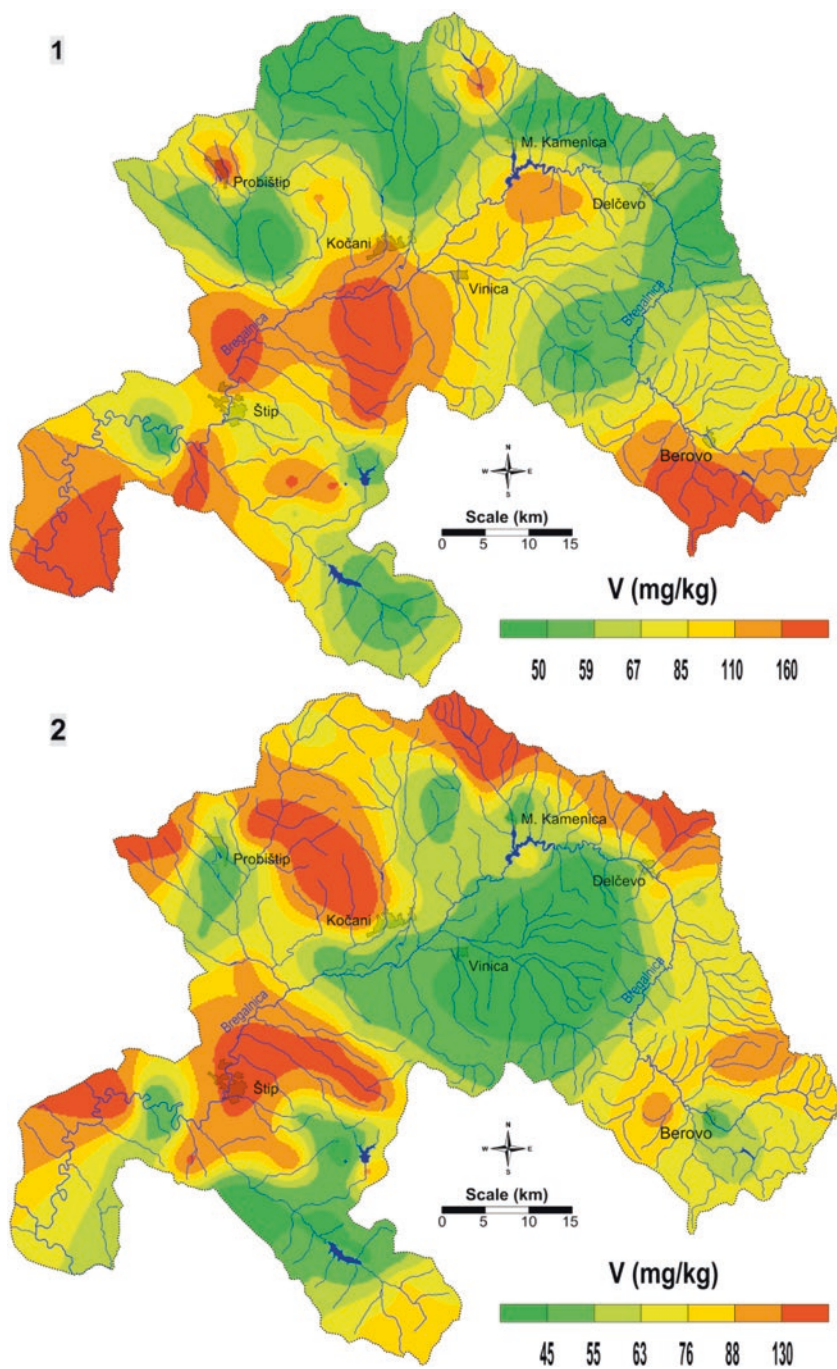


Fig. 6.18 Spatial mapping with *kriging* method, for distribution of vanadium in attic dust (1) and soil (2)

A huge number of toxic substances are continuously emitted into the air, creating unhealthy living arrangements. This “invisible enemy” of the biosphere quietly threatens the life of organisms, including predominantly humans. That is why today a large number of researchers are committed to fast and efficient methodologies for qualitative and quantitative characterization of air and potential emission pollutants. This is especially important for areas where emission sources are not known. The model presented in this research included the characterization of house attic dust in order to determine the long-term deposition of dust emitted from mine and flotation tailings. The applied multivariate analysis in combination with geostatistical models (on spatial visualization of the elemental contents) gave an effective interpretation of the situation with the long-term deposition in the examined area. The applied methodology effectively defined the lithogenic vs. anthropogenic markers in the environment, due to the long-term emissions of potentially toxic metals.

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