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Risk-based Regional Scale Screening of Groundwater Contamination from Abandoned Mining Sites in Serbia - Initial Results

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Abstract

Mineral mining is recognized as one of the main human activities that influences groundwater and can lead to changes in quantity and quality of groundwater resources. The impact of ongoing and abandoned mining operations on groundwater resources has largely been assessed on a local scale and such assessments have generally been site-specific. However, a number of recent studies of the impact of mining operations on surface water and groundwater resources address the entire catchment area. Apart from the guidelines for the inspection of closed and abandoned mining waste facilities, arising from the "Mining Waste Directive", several methods have been developed to characterize the environmental impact of mining on a regional or national scale

This paper describes methodology focused on screening of groundwater pollution risk induced by abandoned mining sites on a regional scale. The presented methodology is based on a concept developed for groundwater pollution risk mapping, with suitable modifications to highlight and quantify the processes and factors related to the interaction between mining operations/mine wastes and groundwater. Risk screening methodology was undertaken on the basis of an assessment of groundwater pollution potential expressed via groundwater vulnerability, which was followed by characterization of abandoned mining sites as potential hazards. In preliminary groundwater pollution risk screening, the value of the hazard index was multiplied by the groundwater vulnerability index, resulting in the risk index.

Presented methodology was applied on the example of 59 abandoned mining sites across Serbia, related to various types of ore deposits. Initial results show that this methodology can be successfully applied to identify mining sites that pose a high risk of groundwater pollution, as well as to pinpoint catchments and groundwater bodies that are potentially at risk.

Key words: Abandoned mines, risk assessment, mine water, groundwater contamination, Serbia

Introduction

Analysis of interaction between mine facilities and mining wastes with the environment if often based on the risk assessment approach. According to their targets, two types of risk assessment methodologies are recognized (Tiruta-Barna 2007): human health risk assessment and ecological risk assessment. Within the framework of ecological risk assessment, three main phases were separated (EPA 1998): problem formulation, analysis and risk characterization. When assessing pollution related risks, source-pathway-receptor concept is usually applied. Related to groundwater resources, most of the existing approaches for assessing weather contaminated site constitute a risk to groundwater focus on a local scale (Troldborg 2010). Ketelaere et al. (2004) proposed a risk mapping methodology for summarizing the result of risk assessment with regard to the risk spatial distribution that can be applied on catchment or regional scale.

Mining heritage, from small scale mines to large industrial mining complexes, adversely affects natural resources and the environment. Abandoned mining sites, along with associated facilities for the preparation and processing of ores, waste rock disposal sites and tailings, constitute potential hazards

and can have a negative effect on the quality of water resources. In order to decide which sites should be given the highest priority and to rationalize future remedial activities, risk assessment is shown to be very useful. Within the European Union this issue is addressed through so-called "Mining Waste Directive", adopted in 2006 (European Commission 2006), which requires development of an inventory of closed and abandoned waste facilities. In this framework, a preliminary risk assessment and prioritization of abandoned mining sites for future remedial activities need to be undertaken.

With regard to water resources, the impact of ongoing and abandoned mining operations on surface water and groundwater has largely been assessed on a catchment scale (Zobrist et al 2009; Sima et al. 2008; Younger and Wolkersdorfer 2004). Apart from guidelines for the inspection of closed and abandoned mining waste facilities, arising from the Mining Waste Directive, several methods have been developed to characterize the environmental impact of mining on a regional or national scale (Raptanova et al. 2012; Mayes et al. 2009; Hudson-Edwards et al. 2008; Davis et al. 1997; Turner et al. 2011).

This paper describes a GIS-based methodology for preliminary risk assessment of groundwater pollution caused by abandoned mining operations. The presented methodology for preliminary risk assessment is based on a concept developed for groundwater pollution risk mapping (Ketelaere et al. 2004), with suitable modifications to highlight and quantify the processes and factors related to the interaction between mining operations/mine wastes and groundwater. Proposed methodology was tested on a regional scale and this exercise encompassed the territory of Serbia south of the Sava and Danube rivers. The study included 59 abandoned metallic (Cu, Pb-Zn, Au, Fe, Sb, Mo, Bi, Hg), non-metallic mines (coal, Mg, F, B) and closed uranium mines across Serbia.

Methods

Risk screening methodology of groundwater pollution as a result of abandoned mining operations was undertaken on the basis of an assessment of groundwater pollution potential expressed via groundwater vulnerability and level of hazard. As a first step, intrinsic groundwater vulnerability was assessed with the GOD method (Foster 1987), on the basis of readily available data, which was followed by characterization of abandoned mining sites as potential polluters. To assess groundwater vulnerability with the use of GOD method, the following parameters were analyzed: groundwater occurrence, overall aquifer class and depth to groundwater.

The hazard identification process comprised physical characterization of mining sites, related to various types of ore deposits, and hydrochemical assessment of mine water originating from those sites, through development of a simple indexing method for hazard and risk quantification. Abandoned mining sites were classified as hazards on the basis of eight criteria divided into two main groups of factors: Factor S (Source) and Factor T (Transport). Factor S was assessed by means of five criteria: hydrochemistry of mine water, ore type, geological environment, the size of waste rock dump, and the existence of a tailings storage facility. Factor T was assessed trough following criteria: mine water discharge, distance from the nearest watercourse and stream order of the receiving water body.

In preliminary groundwater pollution risk screening, the value of the hazard index was multiplied by the groundwater vulnerability index obtained by the GOD method, resulting in the risk index. Workflow with necessary steps for the implementation of the methodology is shown in Figure 1.

Filed work comprised of collecting data on the extent of mining, the presence of tailings and flotation agents, the mining method (underground or open-cast), presence of mine water discharge and sampling of mine water. Along with the filed work, assessment of each potential hazard was based on the use of topographic and satellite maps, and published and fond documentation from archives and relevant agencies.

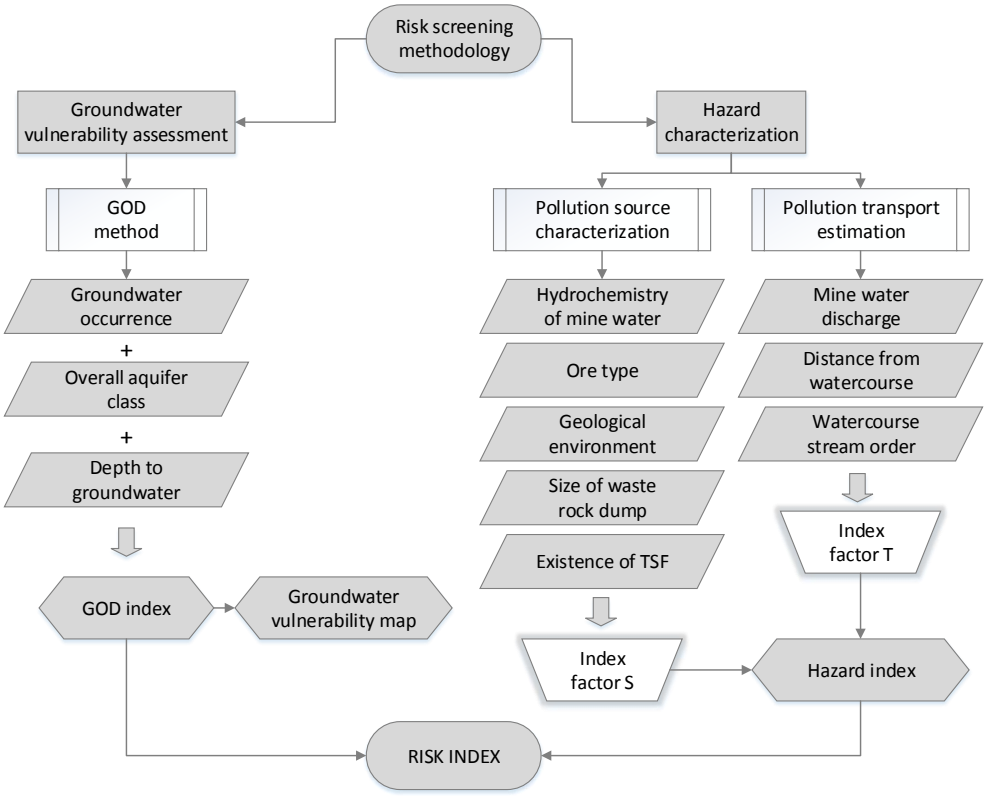

Figure 1 *Workflow of groundwater pollution risk screening induced by mining activities.*

Sampling and chemical analyses

The study included 80 mine water samples from 59 abandoned mining sites. Measurements of pH, electrical conductivity (EC) and temperature were performed in the field with an Mi805 instrument fitted with an MA851D/1 multiparameter probe. To prevent precipitation of metals, a portion of each sample was acidified with an HNO_3 solution at pH<2. Dry residue (after drying at 180ºC), total hardness and $KMnO_4$ demand were tested in the laboratory. Gravimetry was used to determine TDS and volumetry to test for hardness and $KMnO_4$ demand. With regard to macrocomponents, Na^+, Ca^{2+}, Mg^{2+}, K^+ were determined by AAS (Atomic Adsorption Spectrometry), CO_3^{2-}, HCO_3^-, Cl^- by the volumetric method, and SO_4^{2-} by the turbidimetric method. The concentrations of NH_4^+, NO_3^-, NO_2^- and P were established by means of UV-VIS spectrophotometry, and silica concentrations by ICP-OES spectrometry. The concentrations of metals and metalloids (Fe total, Mn total, Cr total Al, Zn total, Cu total, Pb total, Cd total, Ni total, As total) were determined by AAS, as were the specific elements depending on the types of ore deposits (Mo total, F, Sb total, U total).

Hierarchical Cluster Analysis

In view of the fact that the research encompassed abandoned mines of several types of mineral resources, originating from diverse deposits in very different geological and hydrogeological settings, the hydrochemical characteristics of the tested mine water samples varied to a considerable extent. Given the specific chemical compositions, a multivariate statistical method, or more precisely the Hierarchical Cluster Analysis (HCA), was used to group and classify mine waters. To produce data that could be used in an environmental study, HCA was applied to parameters indicative of pollution, such as pH, TDS, SO_4^{2-}, Fe and As (Atanacković et al. 2013). IBM SPSS Statistics 19.0 software was used for statistical analysis. Based on the selected parameters, the mine water samples were grouped into three primary clusters and six sub-clusters.

Groundwater vulnerability assessment

Groundwater vulnerability was assessed on a regional scale, including the eastern, western, central and southern parts of Serbia. Given the size of this area, the GOD method (Foster 1987) was applied. The main criteria for the selection of this method were their relative simplicity, applicability to different

types of aquifers and availability of input data. The vulnerability index was based on three parameters: groundwater occurrence, overall aquifer class and depth-to-groundwater. A modified scheme (Živanović 2011) was used to quantify these parameters. The reference document was the geological map of Serbia (S = 1:300,000).

Risk screening methodology

The preliminary characterization of the groundwater pollution risk from abandoned mining sites was based on a comparison of the intrinsic groundwater vulnerability and the potential pollution sources (hazards), which were abandoned mines in the present case. This risk characterization approach is based on a concept developed and used for groundwater pollution risk mapping (Ketelaere et al. 2004). First the intrinsic groundwater vulnerability was assessed with the use of GOD method, which was followed by characterization of the potential hazards. A calculation model was developed for these purposes, based on the parameters/characteristics of abandoned mines, which might have an effect on groundwater quality.

Abandoned mining sites were classified as hazards on the basis of eight criteria divided into two main groups of factors: Factor S (Source) and Factor T (Transport). Factor S relates to the characterization of the abandoned mining sites themselves, as direct sources of pollution, assessed by means of five criteria: physicochemical properties of mine waters identified by the relevant HCA cluster, ore type, geological environment, size of waste rock dump, and existence of a tailings storage facility. The criteria were selected so as to be relatively simple and readily available but, on the other hand, to also be hydrogeologically relevant to the assessment of the groundwater pollution potential.

Within the Factor S, a weight was assigned to each criterion. The criteria were compared and the weights determined by means of Pair-wise Comparison Matrices (Saaty 1994; Turner et al. 2011). The value of Factor S for each of the studied mines was obtained by adding up the product of the values of each criterion and the associated weight, according to the formula:

$$Factor\ S = \sum_{i=1}^{n} Si * wi$$

With regard to Factor T, parameters that affect the pollutant transport potential were assessed, including: the amount of mine water discharged by the abandoned mine, distance to the nearest surface stream and stream order of the recipient. The value of Factor T was determined based on the assumption that the pollutant transport potential increases as the distance to the nearest surface stream decreases and as the amount of water discharged by the abandoned mine increases, and that it is inversely proportional to the flow rate of the receiving watercourse. Given that flow data on a large number of affected streams were not available, the amount of water was expressed in relative terms, via the stream order (the higher the stream order, the higher the flow rate, and, consequently, the higher the pollution attenuation potential). Factor T was the quotient of the sum of nearest-stream distance indexes (T1), water quantity indexes (T2), and stream order indexes (T3), according to the following formula:

$$Factor\ T = \frac{T1+T2}{T3}$$

The hazard assessment parameter (Hi) was quantified by simply adding up the values of Factors S and T. In preliminary groundwater pollution risk screening, the value of the hazard index was multiplied by the groundwater vulnerability index obtained by the GOD method, resulting in the risk index Ri:

$$Ri = Hi * GOD$$

The values of Factors T and S were calculated and the hazards and risks classified using the calculation model shown in Figure 2.

In view of the fact that preliminary risk screening was performed on a regional scale, the abandoned mining sites were depicted as point futures. The highest value of the GOD index over a 1 km radius from the point feature was the representative vulnerability index to be included in the estimation of the risk index. The presented methodology for regional scale screening of the groundwater pollution risk was developed for implementation in a GIS environment. Neutral local thresholds based on the

classification of natural breaks were used to arrive at cut-off values that served as a basis for determining classes with different indexes for the applied hazard quantification criteria.

Factor S

Cluster (S1)	
Subcluster	Value
A1	200
A2	100
B3	300
B4	300
C5	300
C6	300

Ore type (S4)	
Type of ore	Value
Industrial minerals	100
Coal	200
Metallic ores	300

Waste rock dump (S3)	
Dump scale	Value
< 10 000 m²	100
> 10 000 m²	200

Geological environment (S5)	
Host rock	Value
Carbonate	100
Carbonate -silicate	150
Silicate	200

Tailings storage facility (S2)	
TSF	Value
No	0
Yes	200

Factor T

Distance to water body (T1)	
Distance (m)	Value
< 300	30
300 – 1000	20
> 1000	10

Mine water discharge (T2)	
Discharge (L/s)	Value
< 1	10
1 – 10	20
> 10	30

Receiving watercourse (T3)	
Stream order	Value
1	1
2 - 3	2
> 3	3

$$Factor\ T = \frac{T1 + T2}{T3}$$

$$Factor\ S = \sum_{i=1}^{n} Si * wi$$

Weight (w)

Weight	
Parameter	Value
Cluster (w1)	0.28
TSF (w2)	0.26
Waste rock dump (w3)	0.20
Ore type (w4)	0.16
Geological environment (w5)	0.10

$$Hi = Factor\ S + Factor\ T \qquad Ri = Hi * GOD$$

Hazard index	
Hazard category	Value
very low	< 120
low	120 – 145
moderate	145 – 170
high	170 – 195
very high	> 195

Risk index	
Risk category	Value
very low	< 20
low	20 – 45
moderate	45 – 80
high	80 – 120
very high	> 120

Figure 2 *Calculation model applied for screening of regional-scale groundwater pollution risk*

Results and discussion

Groundwater vulnerability

Regional groundwater vulnerability was assessed applying the GOD method. The study region was comprised of hilly and hilly-and-mountainous areas south of the Sava and Danube rivers, while the area that falls within the Pannonian Plain (the Province of Vojvodina) was not considered because its geology is such that there are no substantial deposits of metallic minerals or coal. In terms of land area, more than 50% of the terrain belongs to the class of negligible-to-low vulnerability, 25% to moderate vulnerability, and 20% to high-to-extreme vulnerability (comprised of karst terrains and alluviums of large rivers) (fig. 3).

In Serbia, 153 groundwater bodies have been identified (Official Gazette RS, 2010), 129 of which are located in the study region. Abandoned mining sites potentially affect 26 of them. The spatial distribution of groundwater vulnerability was assessed relative to the groundwater bodies and the presence of abandoned mines. The assessment showed that the vulnerability index of most water bodies associated with abandoned mines was from 0.2 to 0.32, while in the case of groundwater bodies in areas where there were no abandoned mining sites the range was slightly wider (0.2 - 0.45). With regard to potentially affected groundwater bodies, the low groundwater vulnerability class was found to be dominant. High-to-extreme vulnerability exists to a much lesser extent and is generally associated with carbonate formations.

Hazard identification

Slightly less than 30% of the study cases exhibited a hazard index of less than 145 (i.e. they belonged to the hazard class with a low pollution source potential). The largest number of abandoned mining sites (40%) belonged to the moderate hazard category, while the remaining 30% had a hazard index greater than 170 and constituted significant pollution sources (fig. 4 - left).

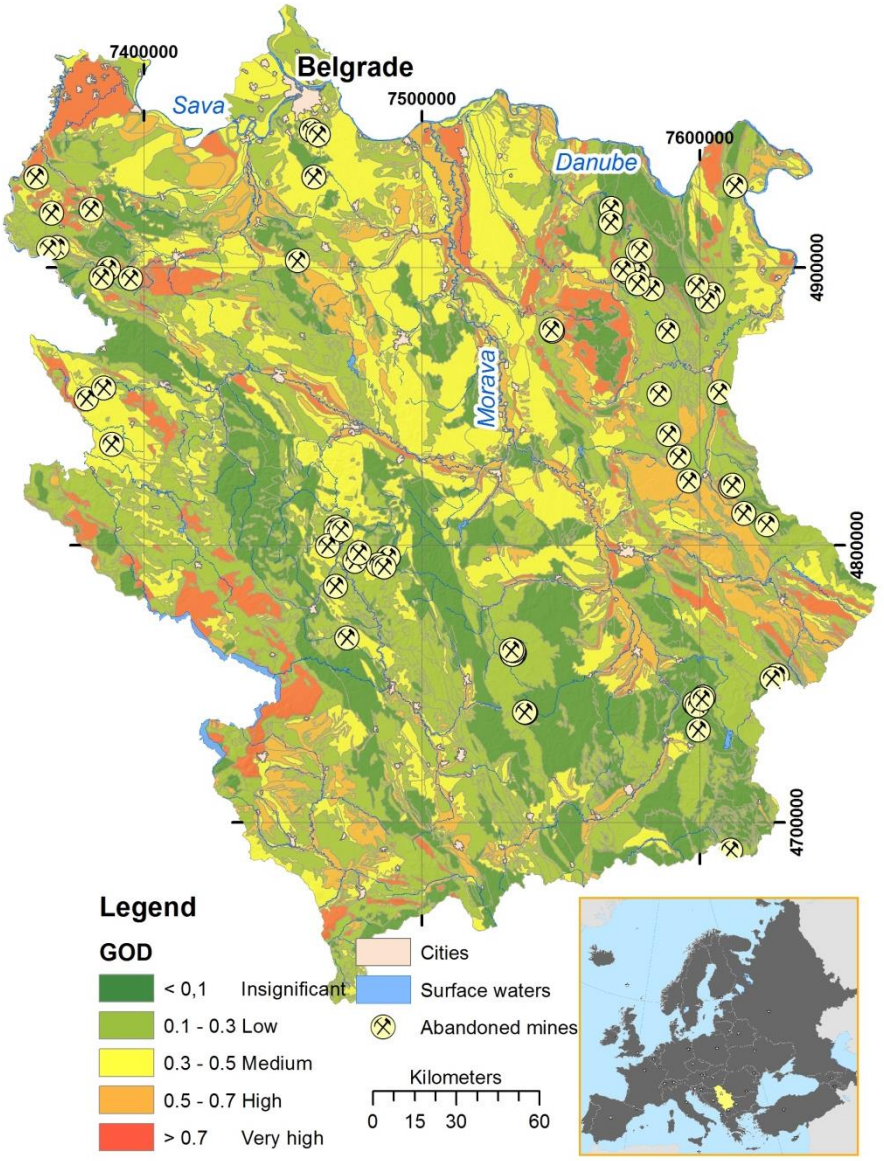

Figure 3 *Groundwater vulnerability map (GOD method)*

With regard to the types of minerals, abandoned copper, lead, zinc, mercury and antimony mines were classified into the highest hazard category. Abandoned mining sites affect the natural water environment, mostly through uncontrolled discharge of mine water into surface water bodies. In such circumstances, the mine water impact needs to be assessed and quantified not only at the point of discharge, but also in terms of the downstream transport and attenuation of water pollutants along the different water pathways and environments (Younger and Wolkersdorfer 2004). In this regard, apart from the characterization of hazards, a preliminary impact assessment for catchment areas was undertaken. Depending on the number and classes of hazards, the level to which associated catchments are potentially impacted was described using three categories (low, moderate and high). Catchments characterized as moderate or high require a detailed assessment of the impact of abandoned mining sites on a catchment scale.

Risk screening

The risk screening methodology applied in this research resulted in the identification of abandoned mining sites according to their potential for causing an adverse impact on groundwater resources. Most of the studied cases (two-thirds) belonged to the group that exhibited no risk or a very low risk of groundwater pollution. Some 17% of the abandoned mining sites were characterized as posing a

moderate risk, while 15% of the studied mines were found to pose a high or very high risk (fig. 4 - right).

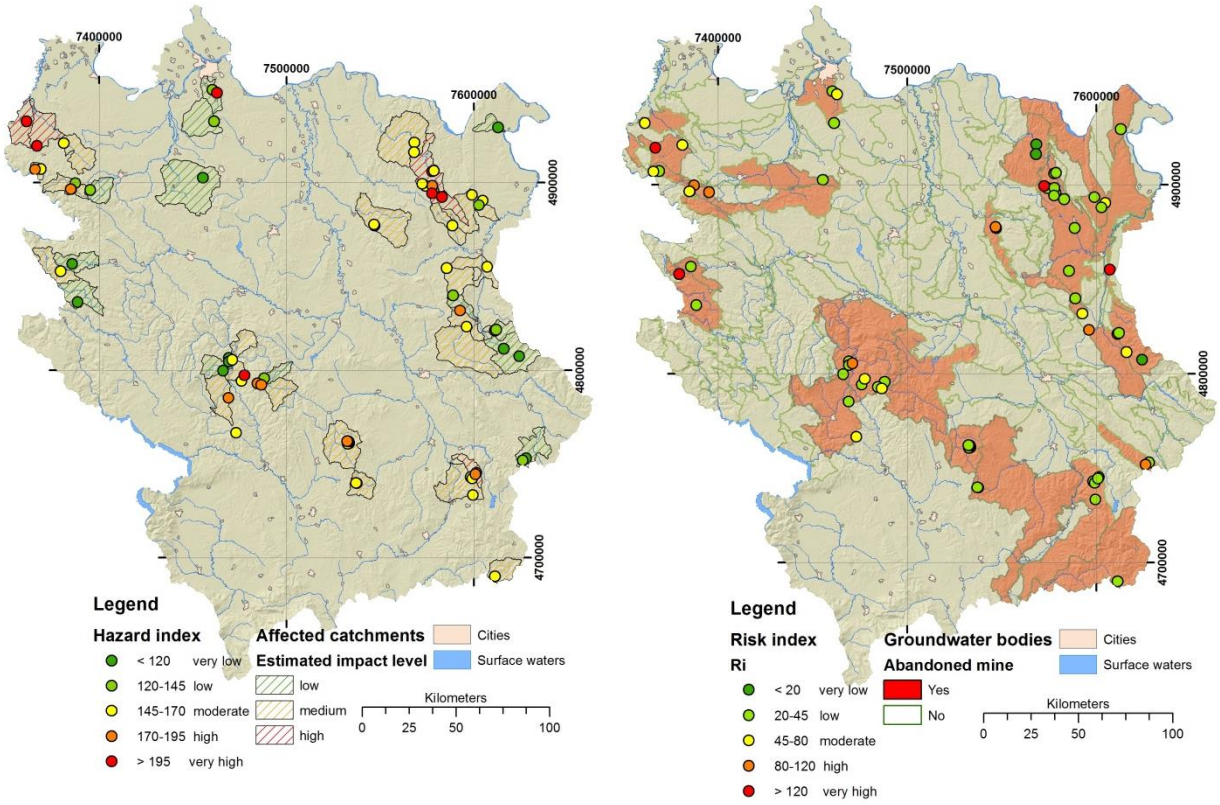

Figure 4 *Map of studied region showing abandoned mining sites.*
Left - hazards and estimated impact level within associated catchments.
Right - categorized according to risk index, and potentially affected groundwater bodies

The spatial distribution of the abandoned mines is such that they are associated with 26 groundwater bodies. The level of impact of these mines on groundwater quality needs to be studied in detail, primarily within the zones of abandoned mines classified as posing a high or very high risk. The screening showed that the highest risk to groundwater quality exists in western Serbia. Although the largest number of abandoned mining sites, which constitute significant hazards, are located in eastern Serbia, they were found to pose a low risk of groundwater pollution. The primary reason for this is that most of these mines are situated within the Timok igneous rock complex, which is a significant metallogenic zone but exhibits a low hydrogeological potential for groundwater circulation and storage.

Conclusion

Risk screening of groundwater pollution as a result of abandoned mining operations was undertaken on the basis of an assessment of groundwater pollution potential expressed via groundwater vulnerability and level of hazard. Groundwater vulnerability was assessed applying the GOD method, while the hazards were characterized and quantified by a specially-developed calculation model based on the physical characteristics of the abandoned mining sites and the hydrochemistry of the mine waters. Approach described above was successfully applied to identify mining sites that pose a high risk of groundwater pollution, as well as to pinpoint catchments and groundwater bodies potentially at risk, where monitoring needs to be established. It was the first step toward the development of this method. Further efforts will focus on the inclusion of additional parameters, more detailed analysis of pollutant transport and uncertainty analysis and prioritization between contaminated sites. Given that groundwater monitoring and protection constitute mandatory but also very challenging tasks, which require substantial resources, the above-described methodology can be used in the initial stages of the development of national groundwater monitoring programs, as well as to improve resource management in groundwater protection and remediation.

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