

Regional-scale screening of groundwater pollution risk induced by historical mining activities in Serbia

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Abstract Europe has a long mining history, with some mining sites dating back to prehistoric times. Mining activities have boosted industrial development in many European countries; however, on the other hand, they left behind large degraded areas and polluted sites. This mining heritage, from small-scale mines to large industrial mining complexes, adversely affects natural resources and the environment. Exploration and mining of mineral ores have been quite extensive in Serbia. Most exploited were as follows: coal, copper, Pb–Zn ores, accompanying gold and silver and antimony. Groundwater resources are frequently impacted by mining operations, both during mining activities and after mine closure. For proper protection and management of groundwater resources, it is necessary to identify and characterize pollution sources within groundwater bodies. 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 groundwater quality. This paper describes a methodology developed for regional-scale screening of the groundwater pollution risk from abandoned mining sites. As a first step, intrinsic groundwater vulnerability was assessed on the basis of readily available data. As potential polluters, 59 abandoned mining sites were included in the analysis. The hazard identification process comprised physical characterization of mining sites and hydrochemical assessment of mine water originating from those sites. A simple indexing method was developed for hazard and risk quantification. To assess the spatial distribution of the groundwater pollution risk, all data were incorporated and analyzed in a GIS environment. As a result of initial screening, several abandoned, mostly metallic mines were found to have higher-risk ratings for groundwater contamination. The methodology based on examples from Serbia can also be used in other regions for developing management strategies and directing of remediation activities.

Keywords Mine water · Abandoned mine · Risk assessment · Groundwater contamination · Serbia

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Introduction

Given Europe’s long mining history, there are abandoned mining sites in nearly all European countries. This mining heritage, from small-scale mines to large industrial mining complexes, has an adverse effect on the environment. The European Union recognized the problem and adopted the so-called Mining Waste Directive in 2006 (European Commission 2006), which requires that an inventory of closed and abandoned waste facilities be created. In this framework, a preliminary risk assessment and prioritization of abandoned mining sites for future remedial activities need to be undertaken. 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 (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 (Rapantova et al. 2013; Mayes et al. 2009; Hudson-Edwards et al. 2008; Davis et al. 1997; Dragišić 1995).

Mineral ore mining is recognized as one of the main human activities that essentially influence groundwater resources (UNESCO 2004). To support preventative action and protect these resources, the methods generally applied include groundwater vulnerability assessment and groundwater risk mapping. Additionally, environmental impact assessment of mining operations increasingly involves pollution risk screening, commonly based on the source–pathway–receptor concept (Goldscheider 2002).

The present paper describes a GIS-based methodology for preliminary risk assessment of groundwater pollution caused by abandoned mining operations. The study was conducted on a regional scale and encompassed the territory of Serbia south of the Sava and Danube rivers. The 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.

Materials and methods

The study encompassed abandoned metallic mines (Cu, Pb–Zn, Au, Fe, Sb, Mo, Bi, Hg), nonmetallic mines (coal, Mg, F, B) and closed uranium mines in central, eastern, western and southern Serbia (Fig. 2). The micro-locations of abandoned mining sites were determined by field work, and data were collected on the extent of mining, the presence of tailings and flotation agents, the mining method (underground or opencast) and mine water discharge.

Sampling and chemical analyses

The study included 80 mine water samples from 59 abandoned mining sites. Water samples for chemical analyses were collected at the points of discharge of mine waters from adits and pools formed at the lowest stages of open-pit mines. At each sampling point, measurements of environmental parameters: pH, electrical conductivity (EC) and temperature, were taken in the field. All the variables were

recorded with a Mi805 instrument fitted with MA851D/1 multiparameter probe. Two water samples at each sample station were collected in polyethylene bottles. To preserve metal concentrations, a portion of each sample was acidified with an HNO₃ solution at pH < 2. Dry residue (after drying at 180 °C), total hardness and KMnO₄ demand were tested in the laboratory. Gravimetry was used to determine TDS and volumetry to test for hardness and KMnO₄ demand. Main anions CO₃²⁻, HCO₃⁻, Cl⁻ were determined by the volumetric method and SO₄²⁻ by the turbidimetric method. The concentrations of NH₄⁺, NO₃⁻, NO₂⁻ 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) and major base cations (Na⁺, Ca²⁺, Mg²⁺, K⁺) were determined by AAS (atomic adsorption spectrometry), as were the specific elements (Mo total, F, Sb total, U total) depending on the types of ore deposits (Atanacković et al. 2013).

Hierarchical Cluster Analysis

The research encompassed abandoned mines related to different mineral resources and deposit types. Mine waters originating from those sites are formed in very different geological and hydrogeological settings. The complexity and differences in conditions in which mine waters are formed resulted in considerable variations in the hydrochemical characteristics of the tested mine water samples. 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, SO₄²⁻, Fe and As (Atanacković et al. 2013). For statistical analysis, IBM SPSS Statistics 19.0 software was used. On the basis of the selected parameters, the mine water samples were classified and grouped into three primary clusters and six sub-clusters (Table 1).

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 (Vrba and

Table 1 Summary table of geometric mean values of analyzed mine water quality parameters by clusters (Atanacković et al. 2013)

| Cluster | Num. of samples | Sub-cluster | Num. of samples | Water type | pH | TDS (mg/L) | SO ₄ ²⁻ (mg/L) | Fe tot. (mg/L) | As tot. (mg/L) |
|---------|-----------------|-------------|-----------------|-----------------------|-----|------------|--------------------------------------|----------------|----------------|
| A | 64 | A1 | 22 | Ca-SO ₄ | 5.9 | 1090 | 444 | 2.41 | 0.003 |
| | | A2 | 42 | Ca-HCO ₃ | 7.3 | 511 | 46.8 | 0.14 | 0.005 |
| B | 7 | B3 | 6 | Ca-SO ₄ | 2.9 | 2542 | 1830 | 38.6 | 0.003 |
| | | B4 | 1 | Mg-SO ₄ | 3.3 | 3500 | 13,600 | 15.80 | 0.0002 |
| C | 4 | C5 | 2 | Ca-SO ₄ | 2.7 | 6504 | 4450 | 930 | 3.50 |
| | | C6 | 2 | Ca-Mg-SO ₄ | 3.8 | 11,200 | 6775 | 1825 | 0.69 |

Zoporozec 1994; Foster et al. 2002; Živanović 2011) was used to quantify these parameters. The reference document was the geological map of Serbia (scale 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 (Hötzl 2004). First, the intrinsic groundwater vulnerability was assessed by the GOD method, and then, the hazards were characterized. A calculation model was used 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. Also, a weight was assigned to each criterion within Factor *S*. The criteria were compared and the weights determined by means of pairwise comparison matrices (Saaty 1994; Turner et al. 2011), as given in Table 2.

The weight (*w*) was calculated by dividing the sum of the row (*M_i*) by the denominator of the matrix, according to the following equation (Turner et al. 2011; Wang et al. 2010):

$$w = M_i / \sum_{i=1}^n M_i$$

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:

$$\text{Factor } S = \sum_{i=1}^n S_i \times w_i$$

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 discharge of the receiving watercourse. Given that discharge 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 discharge 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:

$$\text{Factor } T = \frac{T_1 + T_2}{T_3}$$

The hazard assessment parameter (*H_i*) 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 *R_i*:

$$R_i = H_i \times \text{GOD}$$

Table 2 Pairwise comparison matrix for calculating the weight index for each of the applied criteria

| Criterion | HCA cluster | Ore type | Geological environment | Waste rock dump | Tailings storage facility | Sum of rows (Mi) |
|---------------------------|-------------|-------------|------------------------|-----------------|---------------------------|------------------|
| HCA cluster | 1 | 2 | 2 | 2 | 2 | 8 |
| Ore type | 0.5 | 1 | 2 | 0.5 | 0.5 | 4.5 |
| Geological environment | 0.5 | 0.5 | 1 | 0.5 | 0.5 | 3 |
| Waste rock dump | 0.5 | 2 | 2 | 1 | 0.5 | 6 |
| Tailings storage facility | 0.5 | 2 | 2 | 2 | 1 | 7.5 |
| Sum of columns | 2 | 7.5 | 9 | 6 | 4.5 | 29 |
| Weight (w) | 0.28 | 0.16 | 0.10 | 0.20 | 0.26 | 1.00 |

Bold value indicates calculated weight index

The values of Factors *T* and *S* were calculated and the hazards and risks classified using the calculation model shown in Fig. 1.

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

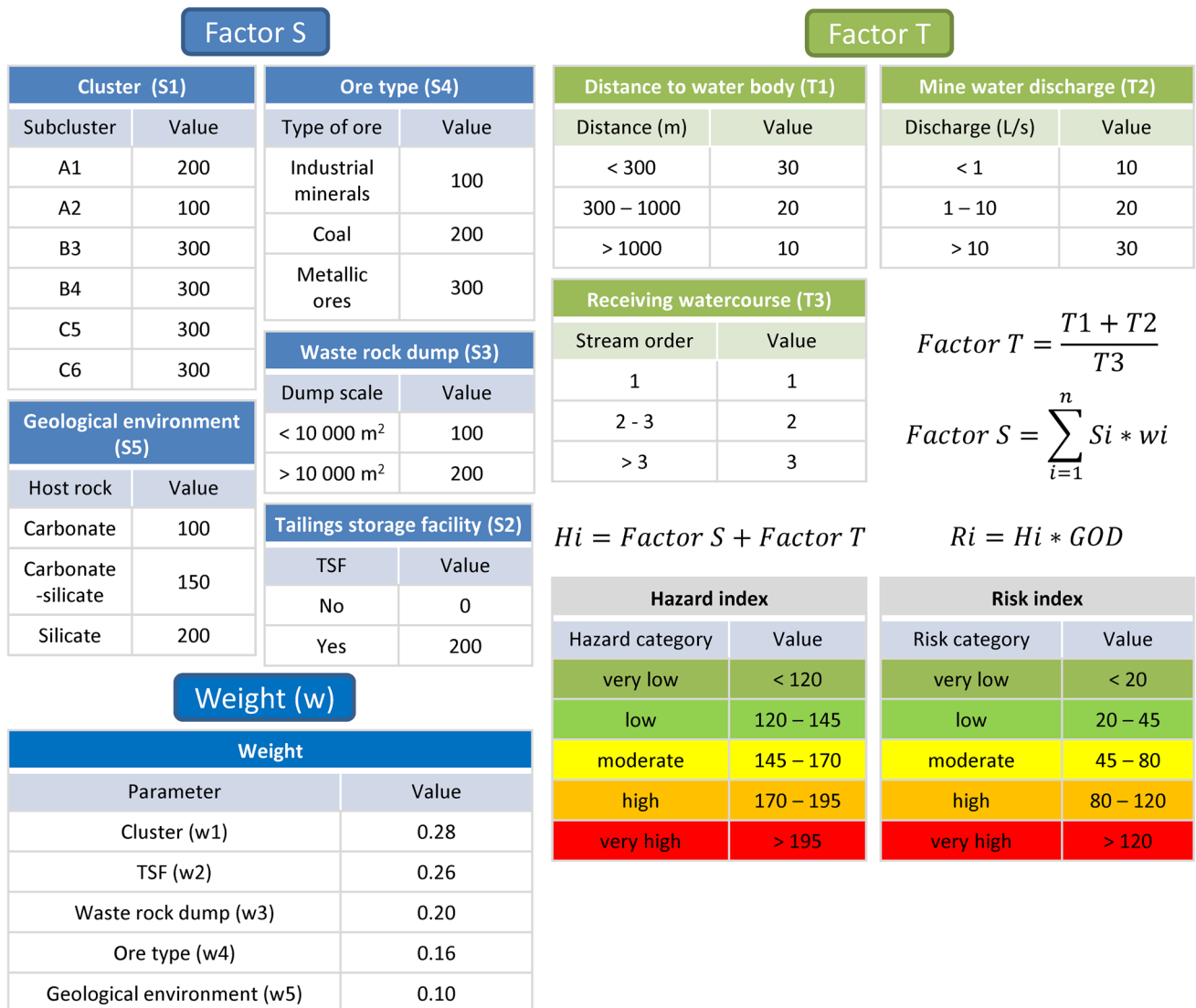


Fig. 1 Calculation model applied for screening of regional-scale groundwater pollution risk

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.

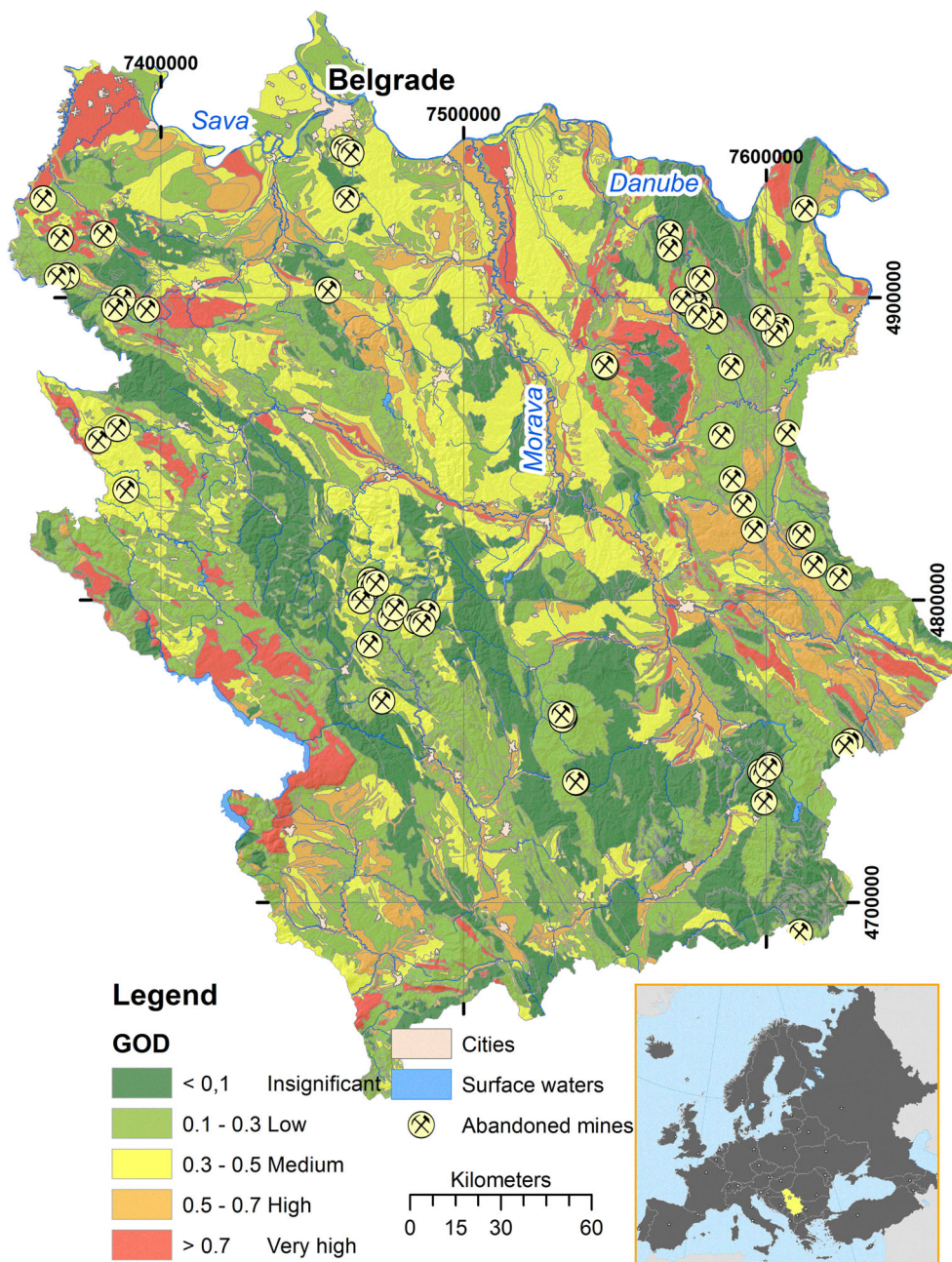
Neutral local thresholds based on the classification of natural breaks were used to arrive at cutoff values that served as a basis for determining classes with different indexes for the applied hazard quantification criteria.

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

Fig. 2 Groundwater vulnerability map (GOD method)



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. 2).

In Serbia, 153 groundwater bodies have been identified (Official Gazette 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. 3-left).

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

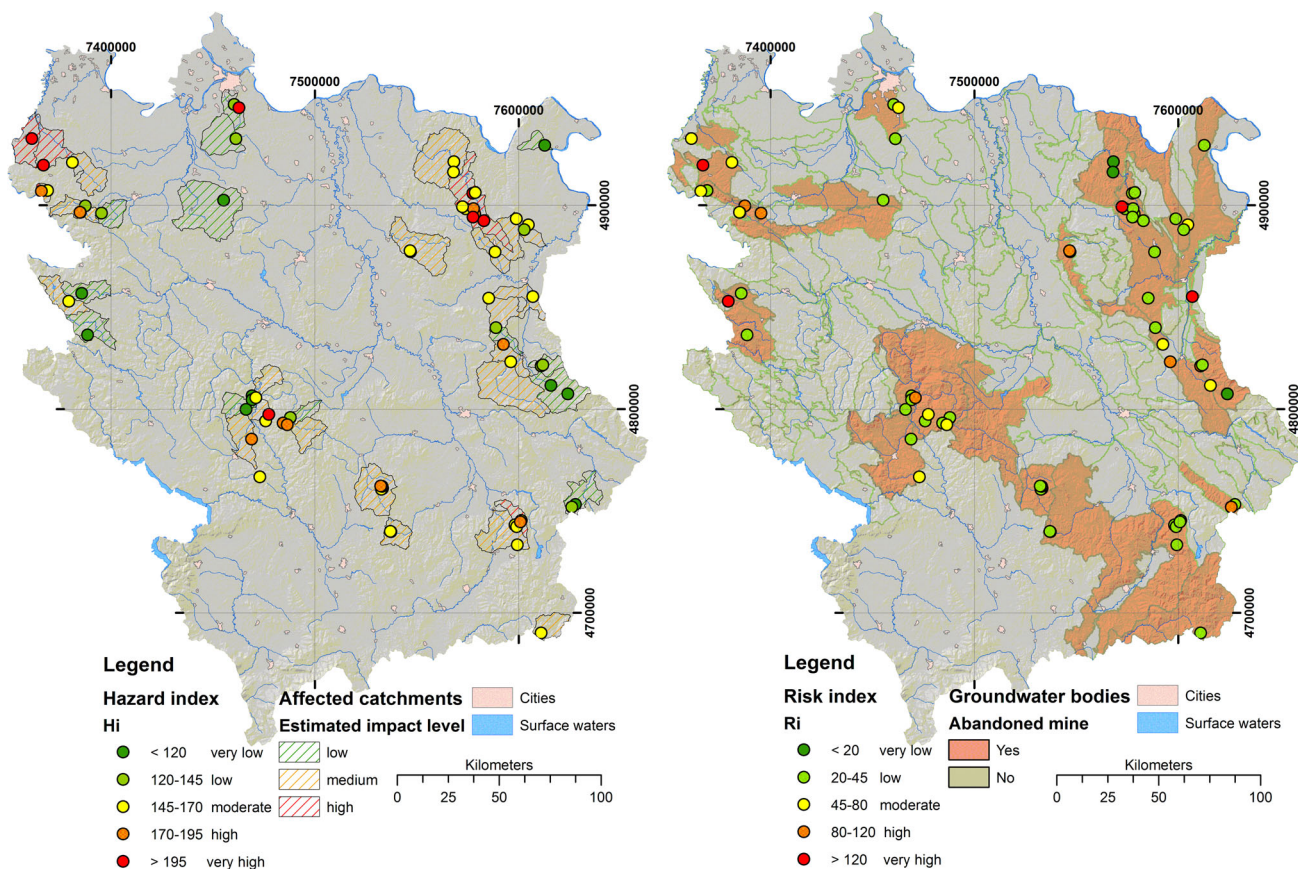


Fig. 3 Map of studied region showing abandoned mining sites. *Left* hazards and estimated impact level within associated catchments. *Right* categorized according to risk index and potentially affected groundwater bodies

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. 3-right).

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 numbers 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 metallogenetic 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. The 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 vulnerability assessment parameters and a more detailed analysis of pollutant transport and hydraulic

links between surface water and groundwater bodies. 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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References

- Atanacković N, Dragišić V, Stojković J, Papić P, Živanović V (2013) Hydrochemical characteristics of mine waters from abandoned mining sites in Serbia and their impact on surface water quality. *Environ Sci Pollut Res* 20(11):7615–7626. doi:[10.1007/s11356-013-1959-4](https://doi.org/10.1007/s11356-013-1959-4)
- Davis G, Butler D, Mills M, Williams D (1997) A survey of ferruginous mine water impact in the Welsh coalfields. *J Chart Inst Water Environ Manag* 11(2):140–146
- Dragišić V (1995) An example of groundwater contamination due to a polluted mine waters impact. *Proceeding of Symposium “Zaštita voda”*, Tara, pp 130–134 (in Serbian)
- European Commission (2006) Directive 2006/21/EC. The management of waste from extractive industries
- Foster S (1987) Fundamental concepts in aquifer vulnerability, pollution risk and protection strategy. In: Van Duijvenboden W, Van Waegeningh HG (eds) *Vulnerability of soil and groundwater to pollutants*, vol 38. TNO Committee on Hydrogeological Research, Proceedings and Information, The Hague, pp 69–86
- Foster S, Hirata R, Gomes D, D’Elia M, Paris M (2002) *Groundwater quality protection, a guide for water utilities, municipal authorities, and environment agencies*. The International Bank for Reconstruction and Development/The World Bank, Washington
- Goldscheider N (2002) *Hydrogeology and vulnerability of karst systems—examples from the Northern Alps and Swabian Alb*, PhD Thesis (Dissertation), Fakultät für Bio-und Geowissenschaften, University of Karlsruhe, 236s, Karlsruhe
- Hötzl H (2004) Risk assessment concept. In: Zwahlen F (ed) *Vulnerability and risk mapping for the protection of carbonate (karst) aquifers*, COST Action 620. European Commission, Directorate-General for Research, EUR 20912, Luxemburg, pp 108–112
- Hudson-Edwards KA, Macklin MG, Brewer PA, Dennis IA (2008) *Assessment of metal mining-contaminated river sediments in England and Wales*. Science Report: SC030136/SR4, Environment Agency, Bristol
- Mayes WM, Johnston D, Potter HAB, Jarvis AP (2009) A national strategy for identification, prioritization and management of pollution from abandoned non-coal mine sites in England and Wales. I. Methodology development and initial results. *Sci Total Environ* 407:5435–5447. doi:[10.1016/j.scitotenv.2009.06.019](https://doi.org/10.1016/j.scitotenv.2009.06.019)
- Official Gazette RS (2010) Official gazette of the republic of Serbia No. 110-00-299/2010-07
- Rapantova N, Licbinska M, Babka O, Grmela A, Pospisil P (2013) Impact of uranium mines closure and abandonment on groundwater quality. *Environ Sci Pollut Res* 20(11):7590–7602. doi:[10.1007/s11356-012-1340-z](https://doi.org/10.1007/s11356-012-1340-z)

- Saaty TL (1994) Highlights and critical points in the theory and application of the Analytic Hierarchy Process. *Eur J Oper Res* 74(3):426–447. doi:[10.1016/0377-2217\(94\)90222-4](https://doi.org/10.1016/0377-2217(94)90222-4)
- Sima M, Zobrist J, Senila M, Levei EA, Abraham B, Dold B, Balteanu D (2008) Environmental pollution by mining activities—a case study in the Cris Alb catchment, Western Carpathians, Romania. *Proceedings Swiss-Romanian research programme on environmental science & technology (ESTROM). Geo-Eco-Marina* 14:9–21, ISSN: 2248–2776
- Turner AJM, Braungardt C, Potter H (2011) Risk-based prioritisation of closed mine waste facilities using GIS. In: Rude RT, Freund A, Wolkersdorfer Ch (eds) *Mine water—managing the challenges*, Aachen, Germany, p 667–671
- UNESCO (2004) *Groundwater resources of the world and their use*. United Nations Educational, Scientific and Cultural Organization, Paris. ISBN 92-9220-007-0
- Vrba J, Zoporozec A (eds) (1994) *Guidebook on mapping groundwater vulnerability*, vol 16. Hannover, International Contributions to Hydrogeology (IAH), p 131
- Wang J, Chen J, Ju W, Li M (2010) IA-SDSS: a GIS-based land use decision support system with consideration of carbon sequestration. *Environ Model Softw* 25(4):539–553. doi:[10.1016/j.envsoft.2009.09.010](https://doi.org/10.1016/j.envsoft.2009.09.010)
- Younger P, Wolkersdorfer C (2004) Mining impact on the fresh water environment: technical and managerial guidelines for catchment scale management. *Mine Water Environ* 23:s2–s80. doi:[10.1007/s10230-004-0028-0](https://doi.org/10.1007/s10230-004-0028-0)
- Živanović V (2011) *Pollution vulnerability assessment of groundwater—examples of karst in Serbia*, Msc Thesis. University of Belgrade. Faculty of mining and geology, Belgrade, p 1–215
- Zobrist J, Sima M, Dogaru D, Senila M, Yang H, Popescu C, Roman C, Bela A, Frei BD, Balteanu D (2009) Environmental and socioeconomic assessment of impacts by mining activities—a case study in the Certej River catchment, Western Carpathians, Romania. *Environ Sci Pollut Res* 16(Suppl 1):S14–S26. doi:[10.1007/s11356-008-0068-2](https://doi.org/10.1007/s11356-008-0068-2)