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MATHEMATICAL MODELS OF CONTAMINATION WITH HEAVY METALS FROM THE ABANDONED MINES IN THE MADJAROVO ORE FIELD, EASTERN RHODOPES

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ABSTRACT. Mathematical 3D models of the flow field and of the mass transport are developed for the groundwater contamination caused by the abandoned mines waters and for the possible drainage of the polluted groundwater flow into the Arda River. Behaviour of heavy metals Zn, Pb, Cd, and Ni in the water-saturated medium is studied and assessments of their possible distribution in the aquifers are made. The scheme of convection-diffusion transport is used in the mass transport models, taking into consideration the complementary processes of reversible elimination (sorption-desorption), mechanical dispersion, and mixing. On the basis of model solutions, the water budget elements are assessed and the current limits and degree of groundwater and surface water pollution are determined for the area of the abandoned mines in the Madjarovo ore field. A prognosis for the expansion of the negative processes in the period up to 2030 is also made. The 3D mathematical models are developed using the computer programmes Modflow and MT3D-MS.

Keywords: groundwater contamination, flow model, mass transport model, contamination with heavy metal, Madjarovo ore field

МАТЕМАТИЧЕСКИ МОДЕЛИ НА ЗАМЪРСЯВАНЕТО С ТЕЖКИ МЕТАЛИ ОТ ЗАКРИТИТЕ МИНИ В МАДЖАРОВСКОТО РУДНО ПОЛЕ, ИЗТОЧНИ РОДОПИ

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РЕЗЮМЕ. Разработени са математически филтрационни и миграционни 3D модели на замърсяване на подземните води с изтичащи от старите мини руднични води и възможното дрениране на замърсения подземен поток в р. Арда. Изследвано е поведението на тежките метали Zn, Pb, Cd и Ni във водонаситена среда и са направени оценки за тяхното възможно разпространение във водоносните хоризонти. В миграционните модели е използвана схемата на конвективно-дифузионен пренос на вещество с отчитане на съпътстващите процеси обратимо елиминиране (сорбция-десорбция), механична дисперсия и смесване. Въз основа на моделните решения за района на старите мини в Маджаровското рудно поле е направена оценка на елементите на водния баланс , определени са съвременните граници и степен на замърсяване на подземните и повърхностните води и е изготвена прогноза за развитието на негативните процеси в периода до 2030 г. Математическите 3D модели са съставени с компютърните програми Modflow и MT3D-MS.

Ключови думи: замърсяване на подземните води, филтрационен модел, миграционен модел, замърсяване с тежки метали, Маджаровското рудно поле

Introduction

The development of Madjarovo ore field started in 1958 and ended in 1997. The exploited ore bodies were grouped in several mining areas – Arda, Harman Kaya, Momina Skala, and Brousevtsi (Fig. 1). The parts of the rock massif that are affected by mining activities are characterised by a very high water permeability and play the role of complex drainage systems. Data from the system monitoring conducted by East Aegean River Basin Directorate (EARBD) along Arda River, as well as hydrochemical studies carried out in 2015 by our team, revealed increased contents of Fe, Mn, Zn, Pb, Cd, As, Ni, and other heavy metals in the mine and surface waters in the region of Arda mining area.

The abandoned mines are the main source of contamination. The established connections between the galleries create conditions for gravitational drainage of all mine waters to the cross gallery at horizon -30 m and their storage in the deep impermeable parts of the rock massif. The large hydraulic head of the waters coming from the higher horizons, combined with the reduced relief forms, the tectonic faults and the presence of near-surface hydraulically connected mine workings, is responsible for the formation of ascending flows and the resulting underground drainage of mine waters into the terrace of Arda River at the big meander after the town of Madjarovo (Fig. 1). Here, during rainy seasons, these waters outflow at the ground surface along the left slope of the gorge in the area nearby the Spomagatelna shaft. According to the determined concentrations of heavy metals in mine waters, the soluble forms of Zn, Pb, Cd, and Ni are identified as key contaminants.

Applying the Modflow and MT3D-MS computer programmes, several 3D numerical models are composed, regarding the conditions for the key pollutants distribution in the main hydrogeological structures of Arda mining area – the Paleogene poor water-bearing complex and the Quaternary aquifer. The main objective of the model studies is to make a quantitative assessment and a medium-term forecast of the groundwater pollution caused by the abandoned mine workings and of the possible drainage of the contaminated underground flow into the Arda River.

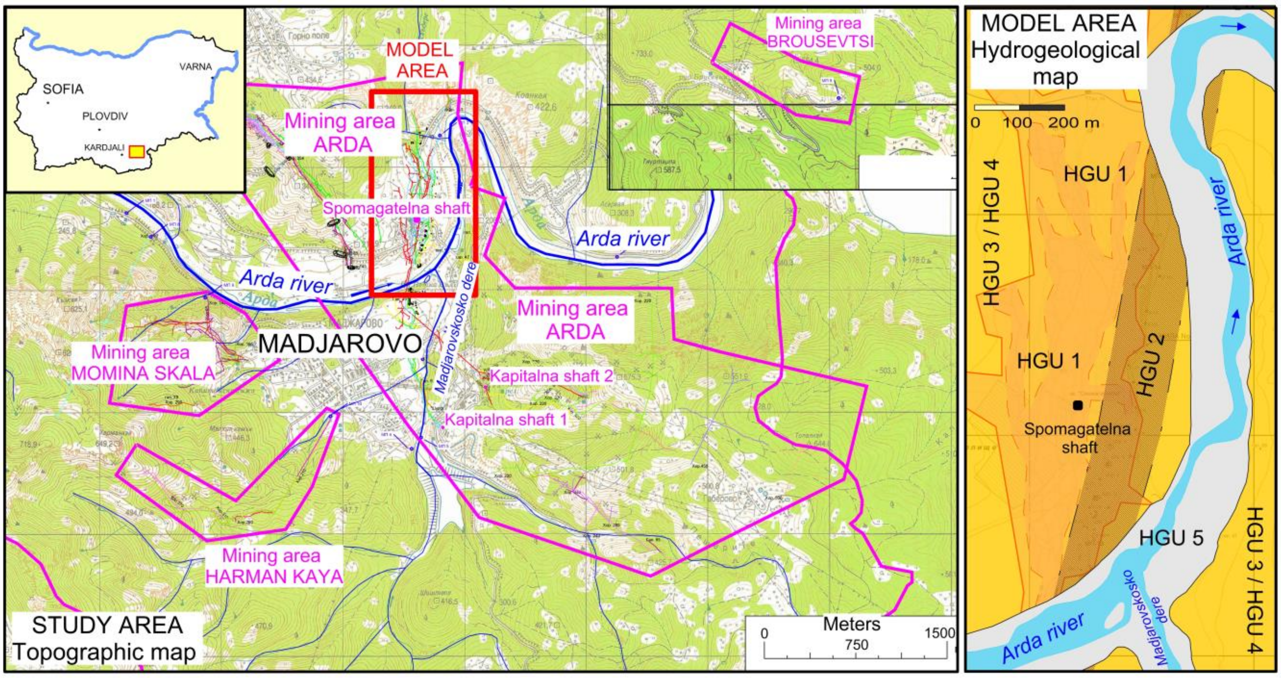


Fig. 1. Location of the study area and hydrogeological background

Conceptual model of the hydrogeological and mining technology conditions

The following general concept for the hydrogeological and mining technology conditions is accepted at the stage of development of the 3D numerical models:

- Two major hydrogeological units (HGU) – the Paleogene poor water-bearing complex (Pg-cmx) and the Quaternary aquifer (Q-cmx) are determined in the section down to horizon -30 m.
- The Paleogene poor water-bearing complex is composed of volcanic rocks (latites and pyroclastites), crossed by dikes, small intrusive bodies and faulted ore-bearing structures. Taking into account the specific geologic-tectonic conditions and the large-scale mining activities carried out in the past, four hydrogeological units of lower rank (HGU1, HGU2, HGU3, and HGU4) are differentiated into the Paleogene poor water-bearing complex.
- The Quaternary aquifer (HGU5) is formed in the alluvial deposits that fill the Arda river terrace. It is represented by cobblestones, gravels, and sands with a total thickness of about 5–6 m.
- The characteristics of the so-determined hydrogeological units of different rank and the model zones delimited in their boundaries are presented in Table 1 and Table 2.
- The hydrogeological complexes are unconfined to weakly confined. The hydraulic head is very high only in the deeper parts of HGU1 and HGU2. In the elevated part of the studied territory, the water table is at a depth of 40–50 m, and around the Arda River – at 1–5 m below the ground.
- The groundwater flow structure is generally controlled by the Arda River. Local distortions are observed in the region where mine workings are present and in the tectonic zone. The main direction of groundwater in the Paleogene complex is targeted towards the river terrace and the Arda River, and the hydraulic gradient ranges from 0.008 to 0.03. The groundwater flow in the Quaternary aquifer is orientated along the river course and the average gradient is 0.0014.
- The recharge of groundwater is accomplished by a variety of sources – precipitation, small rivers with unstable runoff, slope waters, groundwater flow along the ore field boundaries, and in high water periods, also by Arda River (Table 3). According to the water permeability of the near-surface layer, two zones characterised by different degree of recharge are separated (MZW-1.1 and MZW-1.2). Their range coincides with the outcrops of the Paleogene poor water-bearing complex and the Quaternary aquifer. The recharge rates for the two zones are determined as a function of the average annual precipitation (577 mm), the average annual air temperature (13°C), and the average hydraulic coefficient in the respective zone. The achieved values of 6E-5 m/d for MZW-1.1 and 3E-4 m/d for MZW-1.2 are refined during the calibration of the flow model.
- The main part of the naturally clean and technogenically contaminated waters in the Paleogene complex is drained underground in the Arda river terrace, while a small part streams on the surface and discharges into the river network. Part of the groundwater flow in the Quaternary aquifer (clean and polluted), especially in low water periods, is drained into the Arda River. The remaining part drains underground beyond the boundaries of the study area.
- Main sources of contamination are mine waters from the galleries above horizon 25 m, mine waters from the galleries in the southern part of the Arda area, and an ascending mine waters flow from horizon -30 m. The concentrations of key pollutants in the galleries above horizon 25 m are assumed according to data from chemical analyses of mine waters from surface run-offs. Therefore, in the simulated by the models conservative scenario, the following values are implemented as initial concentrations in this source: Cd – 0.04 mg/l; Pb – 0.38 mg/l; Ni – 0.065 mg/l; Zn – 62.0 mg/l. The concentrations in the ascending flow from horizon -30 m and in the mine waters coming from south are unknown values that are determined during the calibration of the mass-transport models, and the above-mentioned values are used as input data in the calibration procedure.

Table 1. *Hydrological units and model zones. Hydraulic coefficient k*

Hydrological unit (HGU)		General description (scope)	HGU №	Model zone №	Hydraulic coefficient k, m/d
I-st rank	II-nd rank				
Paleogene poor water-bearing complex	First high permeability zone	Parts of the rock complex affected by the mining activities – galleries, shafts, shattered zones, pillars	HGU1	MZK-1.1; MZK-2.1; MZK-3.1	3.0
	Second high permeability zone	Tectonic zones	HGU2	MZK-1.2; MZK-2.2; MZK-3.2	4.5
	Low permeability zone	Regionally fractured and secondary altered parts of the rock complex down to elevation 110 m	HGU3	MZK-1.3	0.35
	Very low permeability zone	Weakly affected by secondary changes parts of the rock complex (between elevations -30 and 110 m)	HGU4	MZK-2.5; MZK-3.5	0.02
Quaternary aquifer	-	River terrace - cobblestones, gravels, and sands	HGU5	MZK-1.4	100

Remark: The hydraulic coefficient values are assumed according to reference data for similar medium types. The values, presented in the table, are refined during the basic flow model calibration.

Table 2. *Physical and mass transport characteristics of the hydrogeological units*

HGU №	Volumetric mass density ρ_n, kg/m^3	Longitudinal dispersivity α_L, m	Coefficient of molecular diffusion D_M, m^2/d	Coefficients of distribution K_D, cm^3/g			
				Cd	Pb	Ni	Zn
HGU1	1850	3.0	5E-4	9.5	15.0	22.0	7.3
HGU2		4.5					
HGU3	2150	10.0	7E-4	10.5	16.0	24.5	10.0
HGU4							
HGU5	2100	5.5	3E-4	8.5	14.0	20.5	4.5

Remark: Main sources of the implemented averaged values of ρ_n, α_L, D_M, and K_D for Cd, Pb, Ni, and Zn: (1) Spitz, K., J. Moreno. 1996. A practical guide to groundwater and solute modelling. JW&S, Inc., NY, p. 460; (2) Enviro Base – software product of Waterloo Hydrogeologic Inc., Ontario Canada.

Table 3. *Boundary conditions*

Definition of the boundary condition	Type	Model layers	Index
Western – groundwater flow from the uncontaminated part of the Paleogene complex that is drained in the mine workings and the river terrace	GHB	ML-1, ML-2, ML-3	GHB-W ML 1-2-3
Eastern – groundwater flow from the uncontaminated part of the Paleogene complex that is drained in the river terrace	GHB	ML-1, ML-2, ML-3	GHB-E ML 1-2-3
Southern (near-surface part of the section) – groundwater flow from the uncontaminated part of the Quaternary aquifer	GHB	ML-1	GHB-S ML 1
Southern (in depth) – lateral flow (mine waters) from the galleries in the southern part of the Arda mining area that gravitationally that is drained in the cross gallery at horizon -30 m	GHB	ML-2, ML-3	GHB-S ML 2-3
Cross gallery and mine galleries at horizon -30 m – ascending flow (mine waters)	Specified Head	ML-3	SH – B ML 3
Rivers – Arda River and Madjarovsko dere	River	ML-1	Riv ML-1
Recharge from precipitation	Recharge	ML-1	MZW 1, MZW-2

- The baseline concentrations of Cd, Pb, Ni, and Zn in uncontaminated groundwater (Table 4) have been employed as starting conditions in the mass transport models.

Table 4. *Baseline concentration of Cd, Pb, Ni, and Zn*

Hydrogeological unit (HGU)	Baseline concentration C_{0i}, mg/l			
	Cd	Pb	Ni	Zn
HGU2, HGU3, HGU4	8.00E-5	9.50E-3	3.50E-4	1.24E-2
HGU5	3.00E-3	9.75E-3	2.25E-3	1.50E-2

- The hydrogeological conditions and the characteristics of the key pollutants suggest that the mass transport is performed through convection, accompanied by molecular diffusion processes, mechanical dispersion, reversible elimination (sorption-desorption), and mixing.

Methodology

A mathematical simulation of the conditions for pollutant mass transport is performed by means of five 3D numerical models, taking into account the past mining in the Arda area. The models are composed using computer programmes Modflow and MT3D-MS (McDonald, Harbaugh, 1988; Zheng, Wang, 1999; etc.). The applied approach is successfully tested for modelling the mass transport of pollutants in different hydrogeological conditions and for diverse in type and intensity technogenic sources of contamination on the territory of the Republic of Bulgaria – Kozloduy NPP; Panagyurishte mining and ore processing region; uranium ore deposit Momino; etc. (Stoyanov, 2012, 2019; etc.). One basic flow model and four mass transport models are developed.

The basic flow model is a 3D simulation of the groundwater flow structure in the model area. The model includes 3 layers (ML) and 10 zones characterised by a different degree of water permeability (MZK) and 2 infiltration zones (MZW) simulating the spatial limits of the hydrogeological units and the high heterogeneity of the medium (Fig. 2). The different boundary conditions – lateral and ascending flows, rivers and recharge (Table 3 and Fig. 2A), are defined with the help of the respective packages. The model is calibrated, taking into account the groundwater and surface water levels at four monitoring points, applying variation in the hydrodynamic coefficient and in the infiltration and runoff rates.

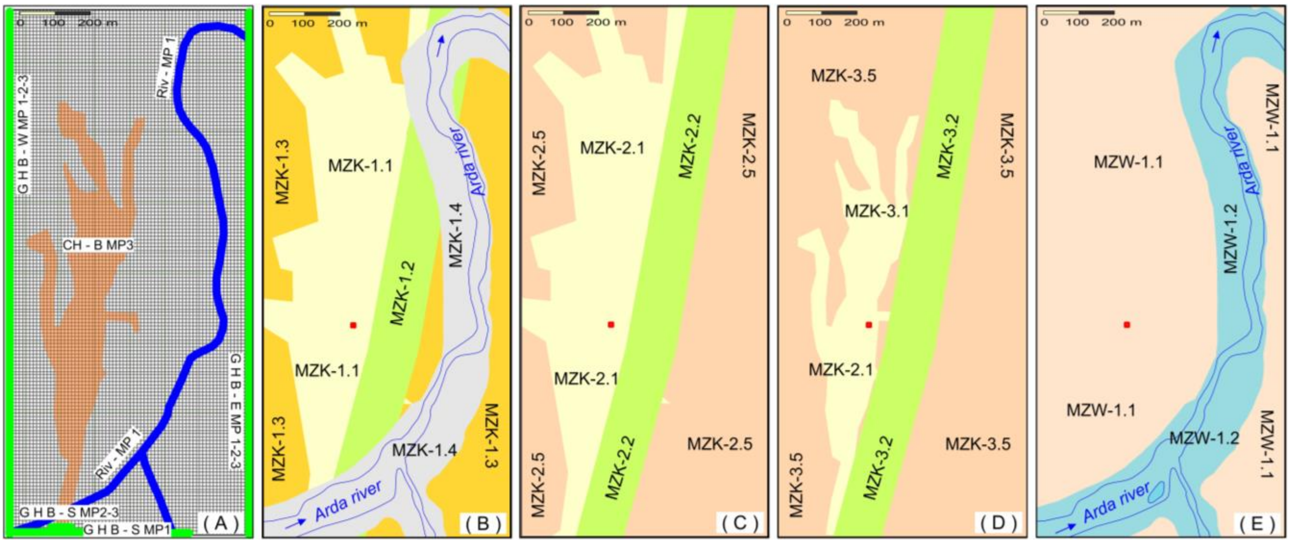


Fig. 2. Spatial gridding of the model area, boundary conditions, and model zones: *A*, modelling grid and boundary conditions; *B–D*, zoning according to the hydraulic coefficient in model layers ML-1, ML-2 и ML-3; *E*, zoning according to the recharge rate in model layer ML-1

The 3D mass transport models simulate the movement of the key pollutants Cd, Pb, Ni, and Zn. They are based on the developed flow model. The calculation scheme takes into account the processes of convection, reversible elimination, dispersion, diffusion, and mixing. The implemented averaged values for the parameters volumetric mass density ρ, longitudinal dispersivity α_L, coefficient of molecular diffusion D_M and coefficients of distribution K_D are presented in Table 2. The transverse horizontal and vertical dispersivities (a_{TH} and a_{TV}) are determined applying the ratio $a_L = 10\ a_{TH} = 100\ a_{TV}$. In the uncontaminated part of the model area, the specified baseline concentrations of Cd, Pb, Ni, and Zn (Table 4) are set. The same initial values are set in the rivers and in the groundwater flows from the unpolluted parts of the Paleogene and the Quaternary complexes located along the external borders of the model. In the zones with presence of galleries (MZK-1.1, MZK-2.1, MZK-3.1) the concentrations characteristic for mine waters and specified in the conceptual model are set. When the mass transport models are calibrated, these values are assumed to be initial in the ascending flow and in the mine waters along the southern border. The model simulation covers the period 1995–2030.

Results and discussion

The basic flow 3D model determines the spatial distribution of hydraulic heads, gradients and velocities. The model solution revealing the structure of the flow field is illustrated in Figure 3. The obtained good correspondence between real and model piezometric data guarantees the reliability of the hydrodynamic base for the mass transport models. The water budget for the Quaternary aquifer is presented in Table 5.

The Cd, Pb, Ni, and Zn concentration ranges defined by the 3D mass transport models are illustrated with maps of the contamination spread that represent the scale, magnitude and dynamics of the negative processes in the studied subsurface area (Figs 4–7). The selected zoning scale takes into account the natural background, the threshold values and the quality standards for drinking water. Only on the Pb maps, the external boundary is outlined by the acceptable standard value because the values recorded for this ingredient exceed the background and threshold values. The presented solutions provide a quantitative esteem for the contamination of groundwater with heavy metals by 2015 and a forecast for its development in the period up to 2030. Based on the model solutions, a summary map of the chemical impact on groundwater caused by the abandoned mines in the Madjarovo ore field (Fig. 8) is composed.

Table 5. *Water budget in the Quaternary aquifer*

Income elements, Q_I^{IN} , l/s		
Recharge along the western boundary of the model (from the outer parts of the Quaternary aquifer)		11.24
Recharge from Arda River		0.21
Recharge from the Paleogene poor water-bearing complex	Inflow along the fault zone	33.21
	Inflow from the zone of the galleries	4.58
	Inflow from the undisturbed rock massif	8.84
Recharge from precipitation		1.19
	Total	59.27
Outcome elements, Q_I^{OUT} , l/s		
Drainage across the eastern boundary of the model (towards the outer parts of the Quaternary aquifer)		6.12
Drainage in Arda River		53.14
Drainage towards the Paleogene poor water-bearing complex in the scope of the fault zone		0.02
	Total	59.28
Budget error 0.02% (difference)		

The presented results of the performed model studies give reason to make the following summaries and conclusions:

- The groundwater flow is directed from the old galleries to the river terrace. The difference in the hydraulic head between the levels of the river terrace and mine waters in the near-surface galleries is 2–3 m, and if compared to the mine water in the cross gallery at horizon -30 m it is 1–2 m higher. This creates conditions for ascending flows that uplift mine waters to the surface. The large gradients of the groundwater flow along the left slope of the gorge suggest intense drainage of mine waters into the river terrace.

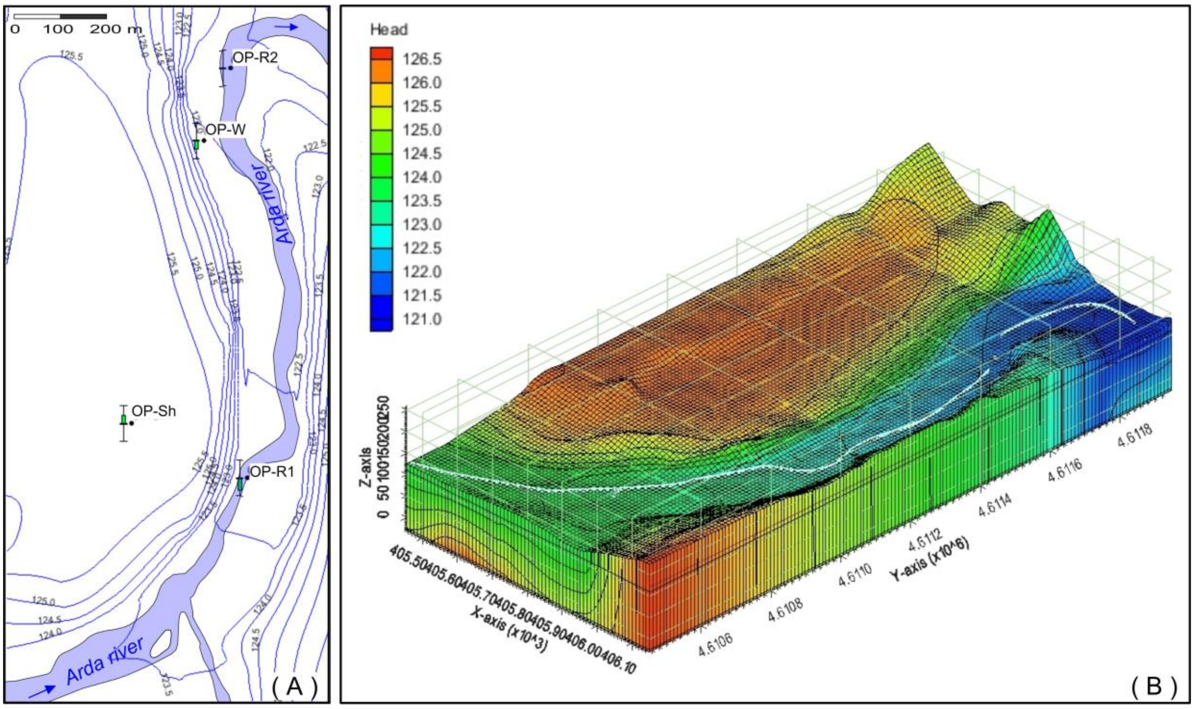
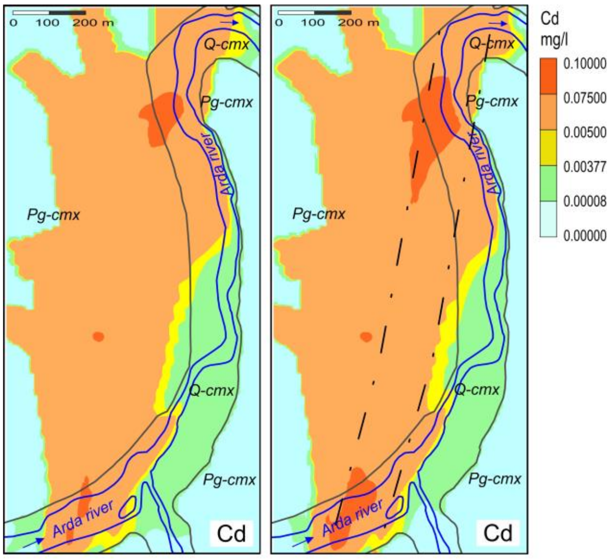
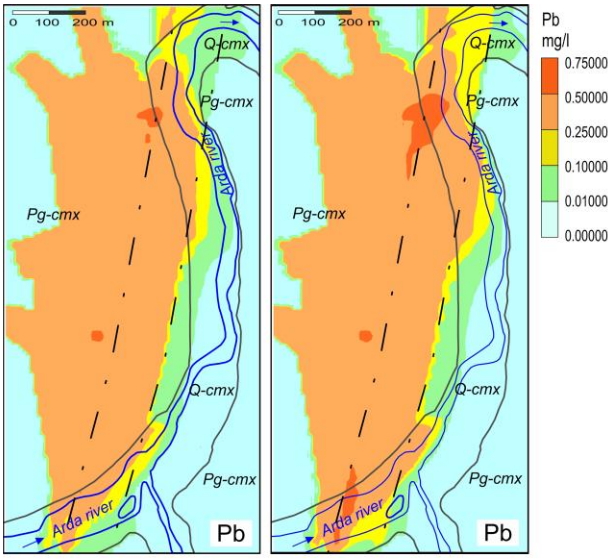


Fig. 3. Basic 3D flow model; hydraulic head distribution in the model area



(A) Estimated for the year 2015 (B) Estimated for the year 2030

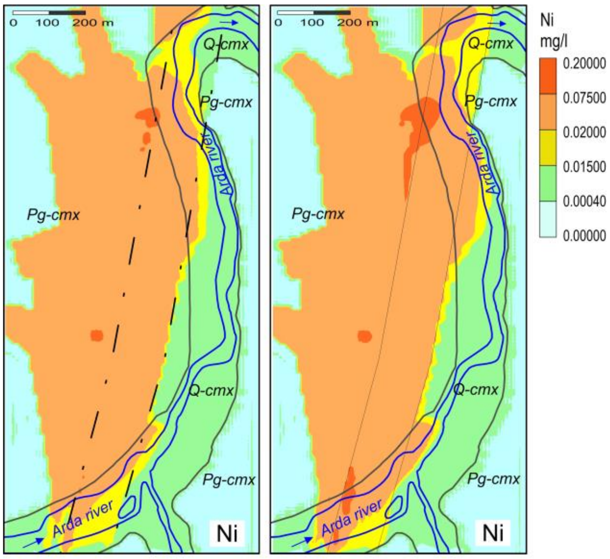
Fig. 4. Mass transport 3D model; maps of Cd contamination



(A) Estimated for the year 2015 (B) Estimated for the year 2030

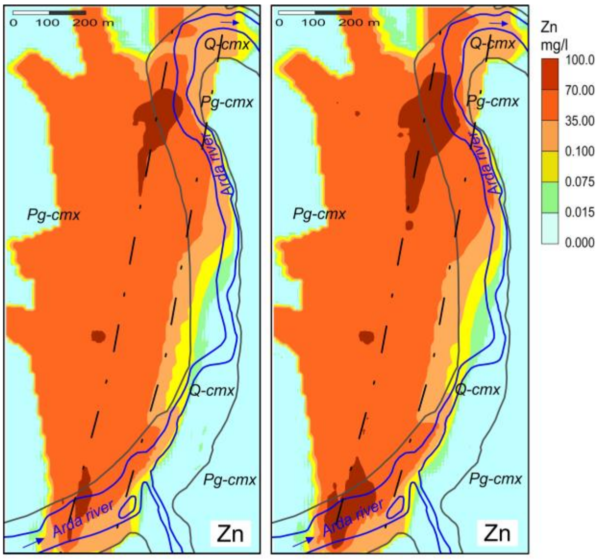
Fig. 5. Mass transport 3D model; maps of Pb contamination

- The total flow from the Paleogene complex towards the Quaternary aquifer is 46.63 l/s, and these are predominantly (over 80%) mine waters and contaminated groundwater. The mine waters are drained into the river terrace along the fault zone as ascending flows with a total outflow of about 30 l/s.
- Within the boundaries of the studied area, the mine and highly contaminated waters (about 38 l/s) form about 65% of the Quaternary aquifer resources. This implies an abrupt change in the chemical composition of groundwater in the river terrace, accompanied by a noticeable deterioration in their properties.
- Around 90% of the groundwater flow formed in the terrace is drained in the narrowing at the big meander of Arda River, which is the cause of heavy metals pollution, accompanied by a significant deterioration of the quality of river waters.
- Groundwater pollution is concentrated in the range of mine workings along the left slope of the gorge and in the river terrace in the area before the big meander of Arda River.
- The total area of these parts of the Paleogene poor water-bearing complex and of the Quaternary aquifer, where groundwater is contaminated by mining activities is about 0.85 km^2.
- The established boundaries and extent of the negative impact caused by the abandoned mine galleries on the groundwater and surface waters in the region remain relatively constant over time until 2030. The prognosis calculations show that a slight displacement of the impact zone can be expected in the direction of Arda River.



(A) Estimated for the year 2015 (B) Estimated for the year 2030

Fig. 6. Mass transport 3D model; maps of Ni contamination



(A) Estimated for the year 2015 (B) Estimated for the year 2030

Fig. 7. Mass transport 3D model; maps of Zn contamination

Conclusions

The results of the performed model studies show that the abandoned mines in the Madjarovo ore field have a noticeable negative impact on the composition and qualities of groundwater and surface waters in the region between the town of Madjarovo and the big meander of Arda River. The underground inflow of mine waters contaminated with heavy metals is significant (about 40 l/s) and covers a section of the river terrace over 1 km in length. Partially affected by heavy metals pollution are the Paleogene poor water-bearing complex, in which the ore mining activities have developed, and the Arda River waters.

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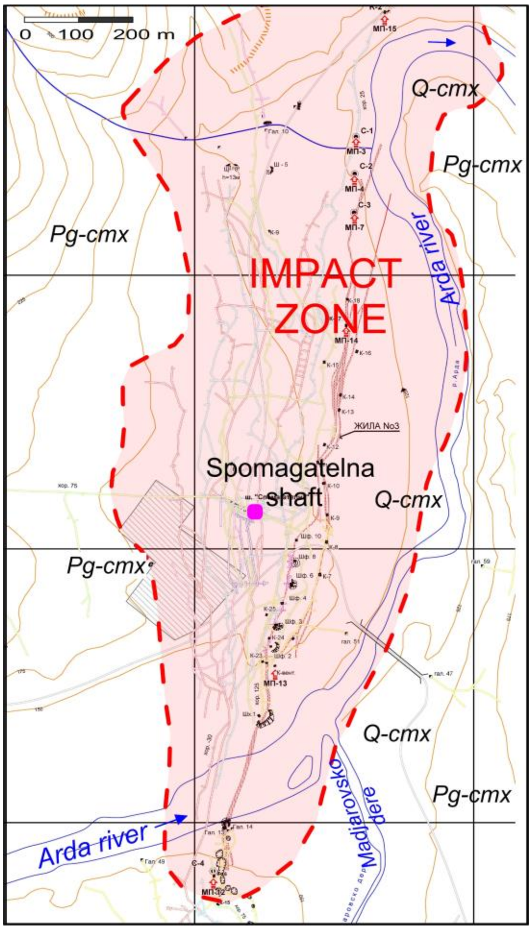

Fig. 8. Boundaries of the zone where impact on groundwater is observed, caused by the abandoned mines in the Madjarovo ore field

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