MODELS FOR ASSESSING AND PREDICTING THE SUBSURFACE TRANSPORT OF CONTAMINANTS FROM THE WASTEWATER IN THE EFFLUENT CHANNEL OF KCM AD - PLOVDIV, SOUTHERN BULGARIA

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ABSTRACT. Until the end of the 20th century, the uncontrolled discharge of highly polluted emissions from the non-ferrous metals companies in Bulgaria was the cause of heavy contamination in vast areas around these industrial sites. In the last two decades, after the introduction of good environmental practices and the closure of polluting industries, a deceleration of the negative processes and a gradual cleaning of the already polluted waters and soils are observed. In order to evaluate and predict these processes, numerical 2D models of the conditions for the subsurface transport of contaminants from the wastewater in the effluent channel of KCM AD-Plovdiv are developed using the VS2DI computer programme. The scheme of convection-diffusion mass-transport is applied, taking into account the concomitant processes of reversible elimination, mechanical dispersion and mixing. Employing the developed models, the fate and transport of pollutants typical for this type of industrial sites – sulphate ions and cadmium (SO_4 and Cd) are studied, taking into account their concentration in the wastewater before and after the application of modern technologies and equipment for remediation of contaminated water. The computer simulation encompasses the period from the construction of the effluent channel till 2035.

Keywords: environment protection, mass transport models, groundwater and soil contamination, heavy metal pollution.

Introduction

A large number of publications show that the production of non-ferrous metals in many regions in the past is the cause of heavy contamination in vast areas around these industrial sites (Izydorczyk et al., 2021; Zhao et al., 2023). In this aspect, the accomplishment of proper solutions applied in order to reduce the harmful impact and respectively, the assessment of their efficiency, is an important and particularly relevant topic.

In the second half of the 20th century, the non-ferrous metal smelter KCM-Plovdiv was a major polluter of the environment in the area between the cities of Plovdiv and Asenovgrad (Figure 1). In the period from its construction in 1963 to the beginning of the 21st century, the extensive development of various productions and the lack of a proper environmental policy caused large and intensive contamination. A detailed assessment of the ecological conditions in the area of the non-ferrous metal smelter was performed in the period 2001/2004 (Petkov et al., 2003; Benderev et al., 2004, 2012). It was established that gas emissions had been the cause not only for the severe air pollution, but also for the presence of acid rain. They had led to surface contamination of soils with heavy metals and metalloids (cadmium Cd, arsenic As, zinc Zn, lead Pb, etc.) and sulphate ions (SO_4). Local pollution of groundwater has also been recorded in some places. Another large source of pollution was the wastewater from various production processes, which was poured untreated into a specially constructed effluent channel and from there into Chepelarska River (Figure 1). Part of these waters, penetrating underneath the bottom of the effluent channel, were the cause for an intense pollution of the unsaturated zone with heavy metals and of the groundwater with sulphate ions.

A turning point in the attitude to environmental problems was the beginning of 2000, when the construction of modern facilities and installations started for the purification of gas and liquid emissions released by the non-ferrous metal smelter. New environmentally friendly productions were successively put into operation, and in 2005, a treatment plant for KCM's wastewater began to operate. As a result, in the last 10-15 years a deceleration of the negative processes and a gradual cleaning of the already polluted waters and soils are observed (Benderev et al., 2009).

Fig. 1. Location of the studied area

Currently, the potential source of groundwater contamination caused by the non-ferrous metal smelter production activity is the wastewater effluent channel. The main reasons for this assumption are: (i) part of the wastewater continues to infiltrate through the lining of the effluent channel, and its quantity will increase due to the erosion of the concrete elements composing it; (ii) wastewater is treated to the standard values for discharge into rivers and open water bodies, which exceed not only the background, but also the threshold values for groundwater; (iii) untreated wastewater previously infiltrated underneath the effluent channel bottom represents a significant secondary source of pollution.

The objective of the performed model study is to obtain a quantitative assessment of the already accomplished pollution of the subsurface space caused by untreated wastewater from the effluent channel, to evaluate the effect of the wastewater treatment, and to study the contaminant fate and transport. Two numerical 2D models are developed revealing the conditions for the migration of SO_4 and Cd through the concrete lining of the effluent channel and their subsurface transport into soil and groundwater – the M2D-SO_4 model and the M2D-Cd model. In the models, a continuous inflow of wastewater from the channel is simulated, taking into account the reduced concentrations of pollutants at the source after the construction of the treatment plant for KCM's wastewater.

Methodological approach and modelling tools

The applied methodological approach has been successfully approbated in our previous studies in modelling the fate and transport of pollutants from various surface sources into groundwater and soils (Stoyanov, 2018; Stoyanov and Dimovski, 2020, 2021). Briefly, the development of the M2D-SO_4 and the M2D-Cd numerical models is based on the following assumptions and general schemes:

(i) Two conservative scenarios for the contamination underneath the effluent channel bottom are considered for the example of the pre-selected site - specific key pollutants SO_4 and Cd. The main criteria for selecting these pollutants are their concentration at the source; their mobility in groundwater and soils; their ability to affect geochemical barriers; their harmful effects on human health and environment. The M2D-SO_4 model outlines the maximum spread of possible pollution in the subsurface area, and the M2D-Cd model defines the most intense heavy metal contamination around the source.

(ii) The three major components of the mass transport field are included within the models' boundaries: engineering barrier – the concrete lining at the bottom of the effluent channel; unsaturated zone - from the engineering barrier to the groundwater level; saturated zone – the potentially endangered aquifer. Formally, the engineering barrier is part of the unsaturated zone.

(iii) The subsurface space is determined by the main parameters of the low-rank hydrogeological units established in the near-surface section: geometric parameters – top and bottom layers $z = f(x)$, average thickness m; physical properties – density ρ, porosity n; hydrodynamic properties – saturated hydraulic conductivity k, saturated water content θ_s, residual water content θ_r, unsaturated hydraulic conductivity function (relative hydraulic conductivity) k_r; hydraulic characteristic functions – relations between pressure head h, moisture content θ and relative hydraulic conductivity k_r; mass transport parameters – distribution coefficient of the key pollutant K_D^{SO4}, dispersivity α, molecular diffusion D_M, coefficient of irreversible elimination γ.

(iv) The groundwater recharge by infiltration and percolation is set in accordance with the specific climatic, soil and technogenic conditions.

(v) The mechanism of the mass transport of pollutants is in its full form: convective transport, accompanied by reversible elimination (adsorption and ion exchange), irreversible elimination (precipitation or decay), mechanical dispersion (longitudinal and transverse), molecular diffusion and mixing.

(vi) The simulated in the mathematical models potential surface contaminator is set as a line source of pollution. The concentrations of the key pollutants in the wastewater are set as variable values taking into account the specific technogenic conditions.

(vii) The computer simulation covers the period from the construction of the effluent channel to 2035. The results of the study are presented by vertical maps of the concentration field at a specific moment t_i.

The two models of the conditions for the mass transport of pollutants in a variably saturated porous media are compiled with the software package VS2DTI v.1.3 (Hsieh et al., 2000).

Conceptual model

The numerical models M2D-SO4 and M2D-Cd are developed in accordance with the following prerequisites:

(i) Model area. Comprises the hydrogeological section that passes along the axis of the effluent channel and reaches Chepelarska River (Figure 2).

(ii) Hydrogeological units (HGU). Three low-rank hydrogeological units are established in the near-surface section: HGU1 – low-permeability layer (fine-grained sands, clayey sands and sandy clays); HGU2 – permeable layer (sands and gravels) and HGU3 – high-permeability layer (boulders, gravels and sands). The engineering barrier (the concrete lining of the effluent channel) is regarded as low-rank hydrogeological unit HGU4.

(iii) Groundwater level. In the area of the non-ferrous metal smelter, the groundwater level is at a depth of 10 - 12 m, and it is at about a meter below ground surface near Chepelarska River.

(iv) Hydrogeological parameters. The hydraulic conductivity k and the physical characteristics density ρ and porosity n are defined according to unpublished data from in-situ observations and laboratory tests conducted for the study area (slug tests, tracer tests, granulometric analysis, petrophysical analysis, etc.). The mass transport field characteristics (distribution coefficient K_D reflecting the fate of SO_4 and Cd, longitudinal dispersion α_L, molecular diffusion coefficient D_M) are determined according to literature data for similar soil types (Pentchev et al., 1990; Adams and Gelhar, 1992; Spitz and Moreno, 1996; Stoyanov, 2003; Gerginov et al., 2003; Enviro Base, 2003; Benderev et al., 2012). The values of the physical, hydrodynamic and mass transport characteristics, applied in the developed models, are presented in Table 1.

(v) Rainfall recharge.

Infiltration rate W_b. With an average annual value of precipitation of 561 mm and an average annual air temperature of 12,3°C, the infiltration rate, calculated according to Bredencamp (1990) is W_b = 2,1E-5 m/d.

Concentration of SO_4 and Cd in rainfall. With some conditionality, it is accepted that the presence of SO_4 and Cd in precipitation is negligible, i.e., $C_b^{SO4} = C_b^{Cd} = 0$ mg/L.

(vi) Wastewater infiltration underneath the effluent channel bottom.

Wastewater infiltration rate W_p. It is determined after varying its values in a large number of variants of the computer models preserving all other conditions equal and keeping a constant water level in the effluent channel. Model solutions are found to be stable at W_p no higher than 5,0E-04 m/d. With a large margin of confidence, this value is accepted when composing the models.

Concentration of SO_4 and Cd in wastewater. According to averaged data on the composition of wastewater discharged into the effluent channel before the construction of the treatment plant, the concentrations of SO_4 and Cd are C_P^{SO4} = 1500 mg/L and C_P^{Cd} = 0,5 mg/L, respectively. Subsequently, according to the permissible norms for liquid emissions, the concentrations of SO_4 and Cd in the treated wastewater do not exceed the defined limit values, i.e., C_P^{SO4} < 400 mg/L and C_P^{Cd} < 0,1 mg/L, respectively.

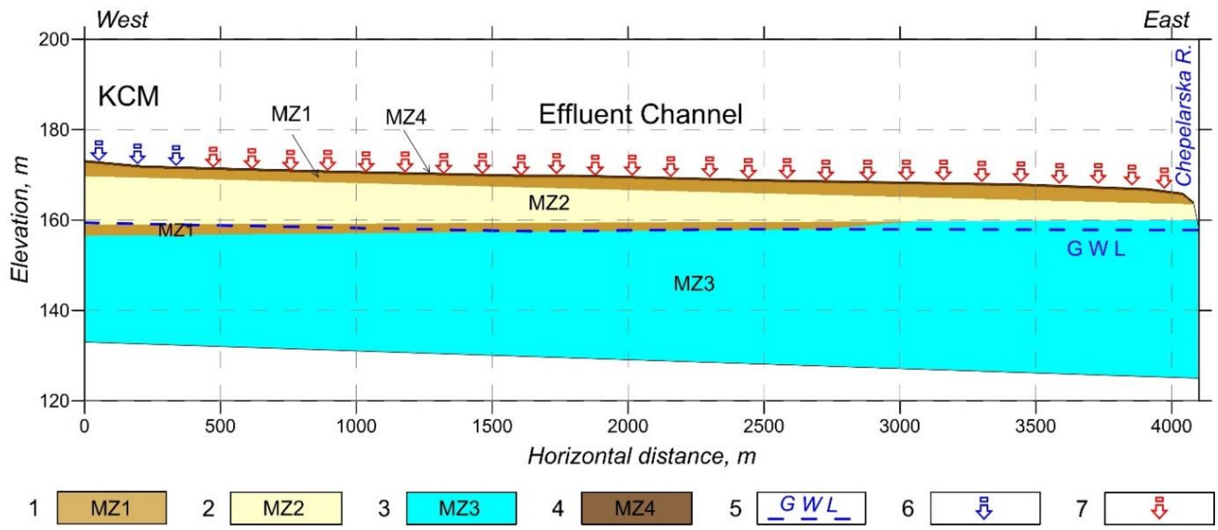

Fig. 2. Conceptual framework of the two-dimensional models: 1 – Low-permeability layer (Model zone MZ1), 2 – Permeable layer (Model zone MZ2), 3 – High-permeability layer (model zone MZ3), 4 – Engineering barrier (Model zone MZ4), 5 – Groundwater level; 6 – Rainfall infiltration; 7 – Wastewater infiltration underneath the effluent channel bottom

Table 1.*Physical, hydrodynamic and mass transport field characteristics of the hydrogeological units*

Hydrological unit (HGU)	Model zone №	Volumetric mass density	Porosity	Hydraulic coefficient	Longitudinal dispersivity	Coefficient of molecular diffusion	Coefficients of distribution	
		ρ_n, g/cm³	n, -	k, m/d	α_L, m	D_M, m²/d	K_D^{SO4}, cm³/g	K_D^{Cd}, cm³/g
HGU1	MZ1	1,95E00	5,0E-02	1,0E00	4,8E00	7,5E-04	7,1E-01	1,28E+01
HGU2	MZ2	2,00E00	2,0E-01	4,0E+01	7,5E00	6,0E-04	2,6E-01	1,52E+01
HGU3	MZ3	2,10E00	2,0E-01	8,0E+01	5,5E00	4,0E-04	2,4E-01	1,52E+01
HGU4	MZ4	2,40E00	1,0E-02	1,0E-03	1,5E00	3,5E-04	7,5E-01	1,45E+01

Remark: Main sources of the implemented averaged values of ρ_n, n, k, α_L, D_M, K_D^{SO4}, and K_D^{Cd}: (1) Stoyanov, 2003; (2) Spitz and Moreno, 1996; (3) Pentchev et al., 1990; (4) Adams and Gelhar, 1996; (5) Enviro Base, 2003 – software product of Waterloo Hydrogeologic Inc., Ontario Canada; (6) Gerginov et al., 2003; (7) Benderev et al., 2012.

Composition of the numerical models

The VS2DTI program and the main prerequisites presented in the conceptual model are used for composing the numerical models M2D-SO4 and M2D-Cd.

The mathematical models are two-dimensional. They reproduce the fate and transport of the key pollutants SO_4 and Cd in the section along the profile illustrated in Figure 2. The determined low-rank hydrogeological units are simulated with four model zones MZ1, MZ2, MZ3, and MZ4. Each zone is set with its geometry and hydrodynamic and mass transport field characteristics corresponding to the real ones (Table 1).

An orthogonal grid with cell dimensions of 2,0 x 0,5 m is applied for the spatial discretisation of the model area. The time of the computer simulation is divided into 65 stress periods, each lasting 1 year. The relationship between pressure head, moisture content and relative hydraulic conductivity is modelled using the functions proposed by van Genuchten (1980). In this case, parameters α and β incorporated in the computer programme values for similar types of soil are used for the variable residual moisture content RMC and for the isotherm. The Henry linear isotherm is applied in order to model the solid-liquid reactions. The initial hydraulic condition is specified as an equilibrium profile, which is set as the initial pressure head equals the negative elevation head above a water table.

Along the lateral boundaries of the model in the saturated part of the section, a boundary condition *Specified total head* is set, and in the unsaturated part of the section, a boundary condition *Possible seepage face* is accepted. A boundary condition *Specified flux into domain* is set along the upper boundary of the model area with the following input data:

(i) The infiltration rate W_p is constant for the whole period of the model simulation. Underneath the effluent channel bottom its value is 5,0E-04 m/d, and outside the limits of the effluent channel – 2,1E-05 m/d.

(ii) During the entire period of the model simulation, the presence of the key pollutants SO_4 and Cd in precipitation is negligible, i.e., $C_b^{SO4} = C_b^{Cd}$ = 0 mg/L.

(iii) In the conservative scenarios considered in both models, the key pollutants concentration in the wastewater infiltrating underneath the effluent channel bottom is set as variable. In the M2D-SO4 model, in the initial period of the computer simulation 1970/2005, the SO_4 concentration is C_b^{SO4} = 1500 mg/L, and in the following period 2005/2035, after the construction of the treatment plant – C_b^{SO4} = 400 mg/L. In the M2D-Cd model, in the initial period of the computer simulation 1970/2005, the concentration of Cd is C_b^{Cd} = 0,5 mg/L, and in the following period 2005/2035, after the construction of the treatment plant – C_b^{Cd} = 0,1 mg/L.

Results and discussion

With the developed models M2D-SO4 and M2D-Cd, at the end of each stress period, a quantitative prognosis is made for the extent and degree of possible subsurface contamination caused by the wastewater in the effluent channel of KCM AD-Plovdiv. The results of the computer simulations of the fate and transport of the selected key pollutants are illustrated with the obtained model solutions, presented in Figure 3 and Figure 4. They display the extent and degree of subsurface and groundwater contamination in different periods of the effluent channel operation (2005 and 2020) and demonstrate the acquired forecast for the development of these negative processes by 2035. The complex analysis of the obtained model solutions gives reason the following conclusions to be drawn.

(i) The amount of wastewater infiltrating underneath the effluent channel bottom is generally a function of the near-surface layer permeability. According to a preliminary assessment, the wastewater infiltration rate is low due to the very low permeability of the concrete lining and the clayey-sandy sediments in the upper part of the section.

(ii) Pollutants entering the soil and groundwater travel not only in depth underneath the effluent channel bottom, but also in a horizontal direction. Due to the differences in the concentration between contaminated and uncontaminated groundwater, pollutants gradually migrate downwards. The direction of the horizontal components of the mass transport velocity vectors is controlled predominantly by the flow field gradients. Therefore, the contamination front will follow the groundwater flow direction.

(iii) The studies of the fate and transport of the most mobile and practically non-absorbable SO_4, conducted with the M2D-SO4 model, show a large-scale and very dynamic development of mass transport processes (Figure 3).

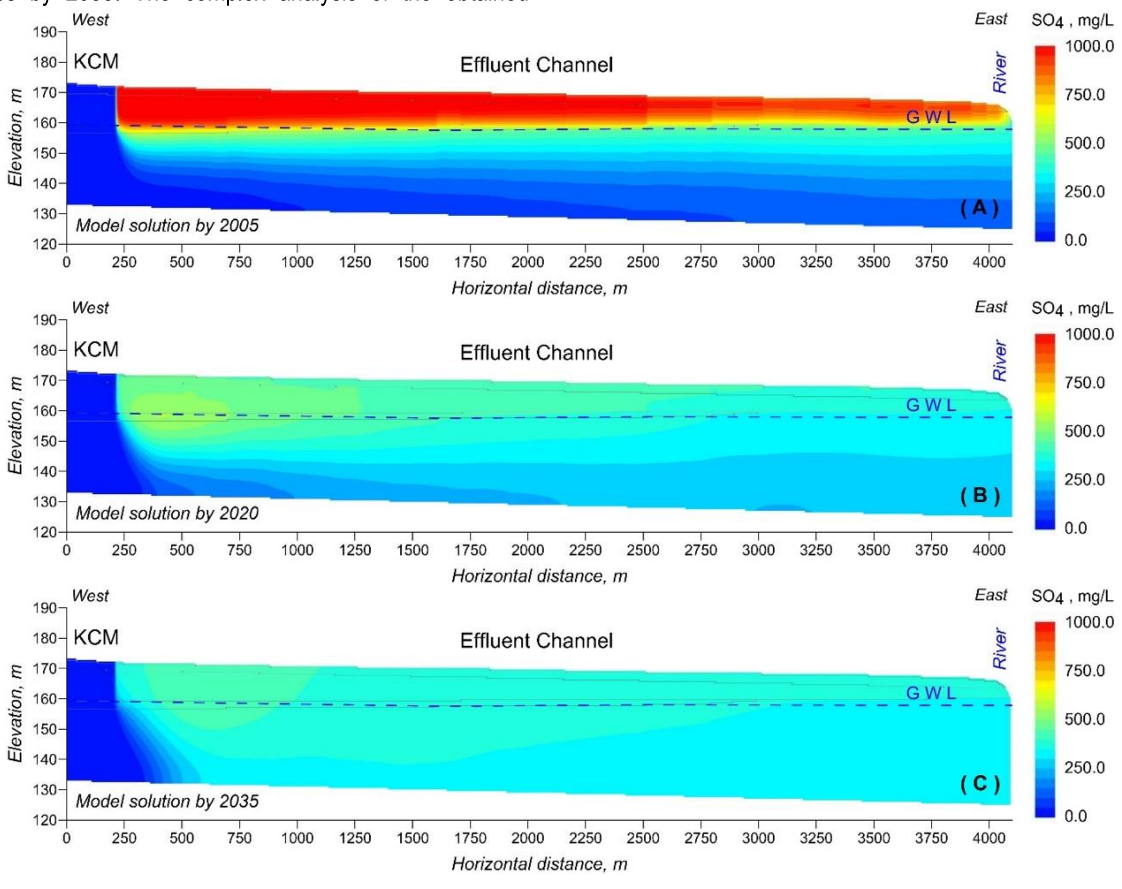

Fig.3. Model M2D-SO4. Results of the computer simulations of the subsurface SO_4 contamination at 2005, 2020, and 2035:
(A) and (B) – model solutions for different periods of the effluent channel operation, respectively at 2005 and 2020, (C) – model solution, prognosis for 2035

Sulphate ions contained in wastewater pass through the engineering barrier and the unsaturated zone for about 2 years. The average concentration of SO_4 in the wastewater infiltrating into groundwater during the first 10 years is about 300 mg/L, and, in 2003/2005, this value increases to 700 - 750 mg/L. Subsequently, due to a sharp drop in the concentration of SO_4 in wastewater and as a result of hydro-dispersion and mixing, there is a gradual decrease in the concentration of SO_4 in the contaminated waters entering the aquifer. In the period from 2010 to 2035, the average SO_4 concentration decreases from 600 to 250 mg/L.

(iv) The simulations, performed with the M2D-Cd model (Figure 4), show some very important trends in the development of the mass transport processes. The presence of an engineering barrier and a low-permeability layer in the upper part of the section prevent the infiltration of large quantities of wastewater with a high concentration of Cd. The high sorbability and very low mobility of Cd further slow its spread downwards. In 2005, the zone with heavy metals contamination was established at a depth of 1,5 - 2,0 m. The concentration of Cd in this zone is between 0.005 and 0.05 mg/L, with high values being characteristic for the uppermost part of the section to a depth of 0,2 - 0,5 m. The toxic pollution zone covers mainly the concrete lining of the effluent channel and the low-permeability clay layer. Subsequently, after the treatment plant for KCM's wastewater began to operate, the concentration of Cd in wastewater decreased sharply. The contaminated area in 2020 is down to a depth of about 2,7 m underneath the effluent channel, and in 2035, it will advance down to 3,2 m. At the same time, the concentration of Cd in this zone will gradually decrease to values within the range of 0,005-0,03 mg/L.

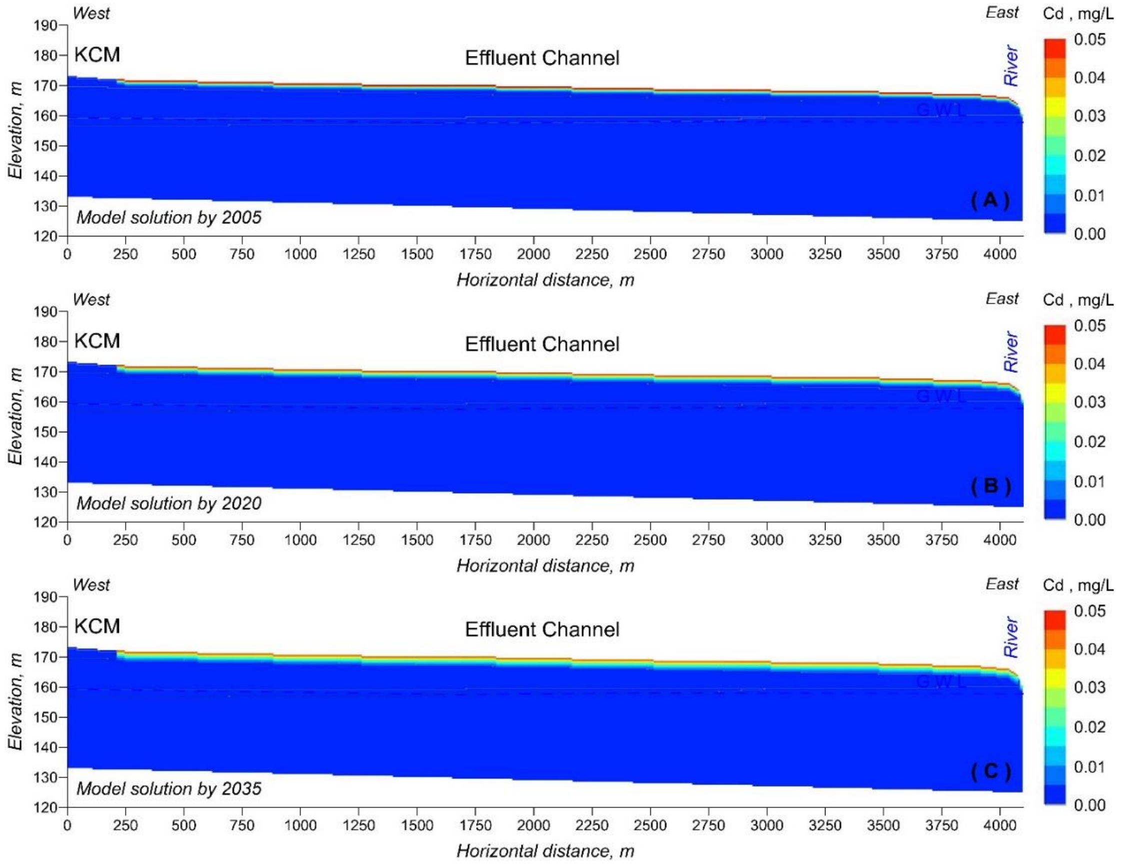

Fig. 4. Model M2D-Cd. Results of the computer simulations of the subsurface Cd contamination at 2005, 2020, and 2035: ***(A) and (B) – model solutions for different periods of the effluent channel operation, respectively at 2005 and 2020, (C) – model solution, prognosis for 2035.***

Conclusion

The results from the performed model studies give reasons to draw the following two very important conclusions, regarding the fate and transport of contaminants from the wastewater in the effluent channel of KCM AD-Plovdiv, the soil and groundwater pollution and the tendencies in its future development.

(1) Sulphate ions are highly mobile and migrate with the velocity of the fluid flow. In a very short time, they pass through the engineering barrier and the unsaturated zone and then begin to enter the saturated zone. The concentration of SO_4 in wastewater varies from 300 to 750 mg/L. After the treatment plant for KCM's wastewater is put in operation, in the period 2020/2035, these values will drop to 250 mg/L. The medium-term forecast is for a gradual self-cleaning of the unsaturated zone and for a strong reduction in the risk of groundwater pollution.

(2) The transport of heavy metals in depth, as illustrated on the example of Cd, is a very slow process with a tendency for gradual attenuation. This tendency is very well pronounced after the treatment plant for KCM's wastewater is put in operation. In the period 2020/2035, the Cd-contaminated soils underneath the bottom of the effluent channel will be of negligible size. The front of the Cd-contaminated zone will advance at an average rate of about 3-4 cm/an, with a decreasing trend until complete attenuation. If these conditions are maintained, there will be no real danger for pollution of groundwater with Cd or other heavy metals.

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