DYNAMIC MODEL OF LONG TERM GEOCHEMICAL EVOLUTION OF MINE WATER AFTER MINE CLOSURE AND FLOODING

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ABSTRACT

After closure and flooding of many deep coal and ore mines in the early nineties of last century in Czech Republic the very dynamic and dramatic geochemical evolution of mine water occurred. Despite differences in geological setting, type of ore deposit or hydrogeology, a similar behavior was observed. During the period of several weeks to several months after flooding and discharging mine water to the surface, typical stable concentrations of dissolved species included heavy metals were observed. These concentrations were comparable to those observed during mining and flooding. This initial period was followed by steep increase of dissolved solids concentration by several orders of magnitude. Within one or two years this trend was reversed and exponential decrease lasting several years was observed. Based on detailed long term monitoring data from six ore and coal mines in Czech Republic simple three reservoir dynamic model was defined and kinetic parameters were evaluated. Later verification of this model proved that this description is accurate enough to forecast geochemical evolution of mine water chemistry for periods exceeding ten years. All long term trends are strongly modified by seasonal influences but there is no direct or apparent connection between seasonal and long term trends and hydro-meteorological regime on particular locality. Despite of these common features, spatial and temporal separation of individual components (e.g. iron, manganese, uranium, sulfates etc.) was found. They are caused by different geochemical interaction with host rock and by different mobility of the particular component at the surface conditions. Based on obtained parameters from the dynamic model of mine water geochemical evolution, future trends in concentrations of particular component can be predicted.

1. INTRODUCTION

Closing of many ore and coal mines in Czech Republic at the beginning of 1990 caused many environmental problems at abandoned mine sites. One of the most serious problems was the formation of highly concentrated mine water after mine were completely flooded. There are several features which were characteristic for geochemical evolution of mine water despite the different ore, geological settings and hydrogeological situation. At the beginning after flooding there is lag phase lasting several month. This period is followed by steep increase of all component concentration. After several months, in some cases after up to two years, this trend is replaced by exponential decrease lasting up to ten and more years. This common trend is similar for individual components in mine water and for different ore or coal deposit. Nevertheless there can be distinguished some variation and differences. These involve: (i) time when peak concentration of component is reached, (ii) rate of components concentration decrease, and (iii) background concentration on which the long term trend converges. Long term trends are strongly modified by seasonal trends which are not directly connected to the hydrological or hydrogeological situation and are different for individual components.

In the last ten years the similar evolution of mine water chemistry or some of these phenomena were observed on some ore and coal deposits worldwide, see for example Geller et al. (1998), Ladwig et al. (1984), Marsden et al. (1997), Nuttal and Younger (2004), Younger (1998, 2000a,b, 2001), and Younger et al. (2002). Various individual features of this behavior were described and partial influences linked to local conditions were identified.

Differences between particular components are given by their different geochemical character and by different mobility under surface and subsurface conditions. Similar behavior was observed in six ore and coal deposits in Czech Republic (uranium ore deposits Rožná and Příbram, coal deposits Rosice-Oslavany and Petřvald, polymetallic ore deposits Kaňk and Zlaté Hory). Two examples are presented in this study – uranium ore deposit Rožná and coal deposit Rosice-Oslavany.

2. SITE CHARACTERIZATION

Rosice-Oslavany Coal District

The coal mining started already in 1755 in this district and it has been finished in 1992. The Rosice-Oslavany coal mining district is situated about 17 km to the southwest from the city of Brno. It spreads over the length approximately 10 km between the villages Zastávka and Rosice in the north and Oslavany in the south. All of the mine workings, galleries and pits are hydraulically interconnected, the main drain base of the whole mining work is the Dedicna gallery in Oslavany, about 3 meters above the water level of Oslava river. There are three main geological units in the study area. On the west it is the metamorphic West Moravian crystalline complex, where the main litological types are represented by ortho- and paragneiss, amphibolites, granulites and migmatites. The east part is formed by Brno massif unit, with the main litological types as granodiorites, diorites, ortho- and paragneiss. The middle is formed by Boskovice graben unit of limnic Permo-Carboniferous sedimentary basin. The intrabasinal complex is mostly represented by cyclically arranged fluvial to fluviolacustrine sediments (arkoses, sandstones, siltstones, claystones and micritic carbonates), which are – with the exception of greycoloured units – mostly red in color. Coal was mined on three main seams and on several minor seams. Only two seams were mineable in the whole extent, other seams were exploited only locally (Pešek 2004).

Rozna Uranium Ore District

Rozna ore district has the last active uranium mine in Europe nevertheless some of the shafts were already closed and flooded. Rozna uranium ore district is located in the northeast of Ceskomoravska highland at Tisnov city. Its natural boundaries are Svratka River in the southeast, the Loucka River in the west and the Nedvedicka River in the east. The highest elevation lies is in the North 631 m a.s.l., the lowest part is near the confluence of the Svratka and the Loucka River in the South at 254 m a.s.l. The ore district is formed by two flat crests divided by the Rozsochy syncline. The regional geology consists mainly of metamorphic rocks of the Northwest Strazek part of the Moldanubien. Within the area are predominantly paragneiss, orthogneiss, migmatite, granulite and amphibolite. Much less represented are marble, quartzite, pegmatite and aplite. Nappe structure of Strazek part of the Moldanubien is caused by Variscan orogenesis. Groundwater flow is connected with porous and mainly fractured media. Shallow aquifer is composed of poorly-developed quaternary sediments and the upper part of weathered bed rock. Deeper aquifer is composed of various hard rocks with only fracture porosity. The main uranium ore minerals are uraninite and coffinite (Kříbek et al. 1997).

3. METHODS

Standard procedures were used for sampling and analyses. The pH, Eh, temperature, conductivity, and dissolved oxygen concentration were measured directly on sampling site using WTW Multi 340i multimeter with electrodes SenTix® 41, SenTix® ORP, TetraCon® 325 and Cell¬Ox 325. The samples were sampled and analyzed in certified laboratories of AQUATEST a.s. company and DIAMO, State Enterprise according to EN ISO norms. Samples for heavy metals analyses were stabilized right after sampling by addition 1 mL of concentrated nitric acid, sampling vessels were filled up to the cap, transported in cooling box at 4 °C and analyzed within 24 hours.

4. RESULTS AND DISCUSION

Geochemical Model

As a basis for geochemical model of time evolution of mine water composition simple three reservoir model was used with consecutive simple interactions (Figure 1). Reservoir S is source of components dissolved in mine water.

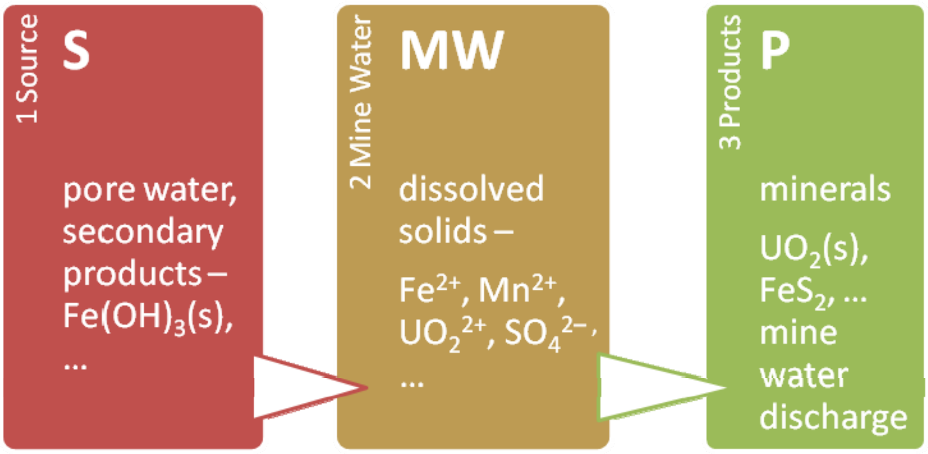

Figure 1. Simple three reservoir model of dynamics of mine water long term chemical evolution. For details see text.

For individual components the source reservoir can be different. In principle this reservoir is constituted by pore water in ore deposit rocks containing concentrated levels of various components. Usually the components are saturated with respect to secondary minerals formed during mining due to oxidation processes. This can be case of dissolved uranium, which is accumulated in pore water in the form of uranyl ion as a result of primary uranium ore oxidation (uraninite UO_2, coffinite UO_2SiO_4).

$$UO_2(\text{uraninite}) + 2\ H^+ + 0{,}5\ O_2(aq) \rightarrow H_2O + UO_2^{2+} \quad (1)$$
$$UO_2SiO_4(\text{coffinite}) + 2\ H^+ + 0{,}5\ O_2(aq) \rightarrow SiO_2(aq) + H_2O + UO_2^{2+} \quad (2)$$

Other components as for example iron are released into pore water by pyrite and other sulfide minerals oxidation in the form of divalent ion

$$FeS_2(\text{pyrite}) + H_2O + 3{,}5\ O_2(aq) \rightarrow 2\ H^+ + 2\ SO_4^{2-} + Fe^{2+} \quad (3)$$

are further oxidized to trivalent ion

$$Fe^{2+} + H^+ + 0{,}25\ O_2(aq) \rightarrow Fe^{3+} + 0{,}5\ H_2O \quad (4)$$

and immobilized and accumulated in the form of oxides and hydroxides mixture of ferric iron in host rocks

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3(am) + 3\ H^+ \rightarrow FeO(OH)(am) + H_2O \quad (5)$$

Gradually there is accumulation of components in pore water and in secondary products during mining within part of ore deposit due to oxidation and this forms a resource of individual components. After flooding ore deposit pore water components are washed out into mine water. Furthermore accumulated oxidation products (minerals) are after flooding again transferred into reducing conditions. Most of them are mobilized reduction processes. As an example may serve oxohydroxides of ferric iron or fourvalent manganese

$$Fe(OH)_3(am) + 3\ H^+ + e^- \rightarrow 3\ H_2O + Fe^{2+} \quad (6)$$
$$MnO_2(\text{pyrolusite}) + 4\ H^+ + 2\ e^- \rightarrow 2\ H_2O + Mn^{2+} \quad (7)$$

By these processes the individual components are released into mine waters and cause their increasing concentration. Some products of oxidation in originally mined and oxidized area of ore deposit undergo reductive immobilization. For example dissolved hexavalent uranium in the form of uranyl ion UO_2^{2+} is reduced to fourvalent uranium and precipitates in the form of uraninite or other fourvalent uranium minerals

$$UO_2^{2+} + 2\ e^- \rightarrow UO_2(\text{uraninite}) \quad (8)$$

Sulfate ions are reduced to hydrogen sulfide

$$SO_4^{2-} + 8\ e^- + 10\ H^+ \rightarrow H_2S + 4\ H_2O \quad (9)$$

which forms with formerly released ferrous iron highly insoluble sulfide – secondary pyrite

$$H_2S(aq) + 0{,}5\ Fe^{2+} \rightarrow 0{,}5\ FeS_2(\text{pyrite}) + e^- + 2\ H^+ \quad (10)$$

By these processes are mine waters depleted and their concentrations are gradually decreasing. Portions of these components are drained away from flooded ore deposit by discharged mine waters.

Numerical Model

Independently of actual processes mechanism and how many reactions take part in processes releasing components into mine waters and independently of processes which bind components from mine water in the first approximation is reasonable to suppose that only one nonreversible process predominates and that this process is governed by the first order kinetics. Based on this presumptions the whole process of component evolution in mine water can be described by simple scheme

$$c_\mathrm{S} \xrightarrow{r_1} c_\mathrm{MW} \xrightarrow{r_2} c_\mathrm{P} \qquad (11)$$

where c_S is concentration of component in source, c_MW is concentration of particular component in mine water, and c_P is concentration of this component in products. Release rate of this component from source is r_1, and "binding" rate of component from mine water is r_2. Rate of processes governed by first order kinetics is directly proportional to concentration of component and rate constant

$$r_1 = k_1 c_\mathrm{S} \qquad (12)$$

$$r_2 = k_2 c_\mathrm{MW} \qquad (13)$$

Rates are expressed in concentrations units – usually in mg L^{-1} – and time unit used in rate constant – day^{-1}. Actual component concentration in mine water is determined by difference of both rates. Concentration change in source is then given by

$$\frac{d[c_\mathrm{S}]}{dt} = -k_1[c_\mathrm{S}] \qquad (14)$$

where $[c_\mathrm{S}]$ is component concentration in ore deposit pore water and which is released into mine water and is not restored, k_1 is rate constant of this process. Just with this rate component in mine water increases, but is consumed by second process. Actual component concentration in mine waters is given by difference of both rates

$$\frac{d[c_\mathrm{MW}]}{dt} = k_1[c_\mathrm{S}] - k_2[c_\mathrm{MW}] \qquad (15)$$

where $[c_\mathrm{MW}]$ is component concentration in mine water and k_2 is rate constant of component immobilization. Immobilized component concentration $[c_\mathrm{P}]$ is directly proportional to the concentration of monitored component in mine water and can described by equation

$$\frac{d[c_\mathrm{P}]}{dt} = k_2[c_\mathrm{MW}] \qquad (16)$$

based on presumption that original component concentration in mine water was negligible $[c_\mathrm{MW}] \approx 0$. This condition is satisfied for some components (concentration of components in mine waters during mining and flooding is several orders lower compare to period after flooding). We can integrate equation (14) and obtain analytical expression for time change of component concentration in pore water or secondary oxidation products, respectively

$$[c_\mathrm{S}] = [c_\mathrm{S0}]e^{-k_1 t} \qquad (17)$$

where$[c_\mathrm{S0}]$ is initial component concentration in pore water, k_1 is rate constant for their release into mine water and t is time. Inserting equation (17) into equation (15) and integrating we obtain expression for component concentration in mine water in the form

$$[c_\mathrm{MW}] = \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)[c_\mathrm{S0}] \qquad (18)$$

where $[c_\mathrm{MW}]$ is component concentration in mine water and k_2 is rate constant of component immobilization by reductive processes and by mine water discharge. During the whole process there has to be fulfilled condition

$$[c_\mathrm{S}] + [c_\mathrm{MW}] + [c_\mathrm{P}] = [c_\mathrm{S0}] \quad (19)$$

which means that component dissolved in mine water, fixed in products by reduction or discharged by mine water has originally its source in pore water and supergene secondary minerals. Inserting for $[c_\mathrm{S}]$ from equation (17) and for from equation (18) and rearranging we obtain for component concentration in third reservoir (products)

$$\left[c_{\mathrm{P}}\right]=\left(1+\frac{k_1e^{-k_2t}-k_2e^{-k_1t}}{k_2-k_1}\right)\left[c_{\mathrm{S0}}\right] \qquad (20)$$

Time after which the maximum component concentration in mine water is reached is given by

$$t_{c_{\mathrm{MW}}\max}=\frac{1}{k_2-k_1}\ln\frac{k_1}{k_2} \quad (21)$$

and for peak component concentration at this particular time we can derive

$$\left[c_{\mathrm{MWmax}}\right]=\left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2-k_1}} \quad (22)$$

Determination of Model Parameters

Usually the only data which can be used and are determined or estimated with enough accuracy and reliability are component concentrations in mine water and their time dependence ($[c_{\mathrm{MW}}]$ as a function of time). Fortunately this one time dependence allow us to determine all parameters of presented model. There are several ways we can use. The simplest way is the use of equation (18) and algorithm implemented in spreadsheet calculator Microsoft Excel® in module "Solver" with least square optimizing criteria. Initial guess was set up for component source concentration $[c_{\mathrm{S0}}]$ and rate constants k_1 and k_2. Based on analyses of mine water during mining the background concentrations of components in mine water were set up zero (concentrations were one or more order lower). This condition was satisfactorily fulfilled for example for uranium and sulfates. It turned out that for example for dissolved iron, manganese a activity of dissolved radium the component concentrations are not converging to zero after infinite or sufficient time but to some "background" values. These concentrations probably represent stationary state which is given by balancing of both rates – rate of component release and rate of immobilization. In this case the original equation (18) was modified by adding another term $[c_{\mathrm{B}}]$, representing stationary concentration of component in mine water

$$\left[c_{\mathrm{MW}}\right]=\frac{k_1}{k_2-k_1}\left(e^{-k_1t}-e^{-k_2t}\right)\left[c_{\mathrm{S0}}\right]+\left[c_{\mathrm{B}}\right] \qquad (23)$$

Model Evaluation and Verification

Presented model of long time geochemical evolution of mine water was used for evaluation of long term changes in mine water chemical composition on six ore and coal deposits in Czech Republic (uranium ore deposits Rožná and Příbram, coal deposits Rosice-Oslavany and Petřvald, polymetallic ore deposits Kaňk and Zlaté Hory). As case studies are presented two examples – uranium ore deposit Rožná and coal deposit Rosice-Oslavany.

Rožná Uranium Ore Deposit

Resulting model parameters for individual components are given in Table 1. Graphic comparison of real and model evolution for particular components are given on Figure 2 and Figure 3.

Table 1. Model parameters of long term evolution of mine water composition on uranium deposit Rožná.

Component	$[c_{\mathrm{S0}}]$ mg L^{-1}	k_1 day^{-1}	k_2 day^{-1}	$t_{\max}$ day	$[c_{\mathrm{MWmax}}]$ mg L^{-1}	$[c_{\mathrm{B}}]$ mg L^{-1}
Fe	36.6	9.271E–3	9.003E–4	278.6	28.5	6.49
Mn	9.1	6.731E–3	5.231E–4	411.5	7.4	0.72
SO_4	1812	1.234E–2	1.357E–4	369.6	1723	–
TDS	3706	1.074E–2	1.494E–4	403.5	3489	–
U	13.07	1.585E–2	1.883E–4	283.0	12.4	–
Ra*	2031	5.686E–3	1.788E–3	296.8	1194	947

$[c_{\mathrm{S0}}]$	initial component concentration in source, from which is released into mine water
k_1	rate constant for process releasing component into mine water
k_2	rate constant of component immobilization (binding from mine water)
$t_{\max}$	time when peak concentration of component is reached
$[c_{\mathrm{MWmax}}]$	peak component concentration in mine water reached in time $t_{\max}$
*	activity in mBq L^{-1}

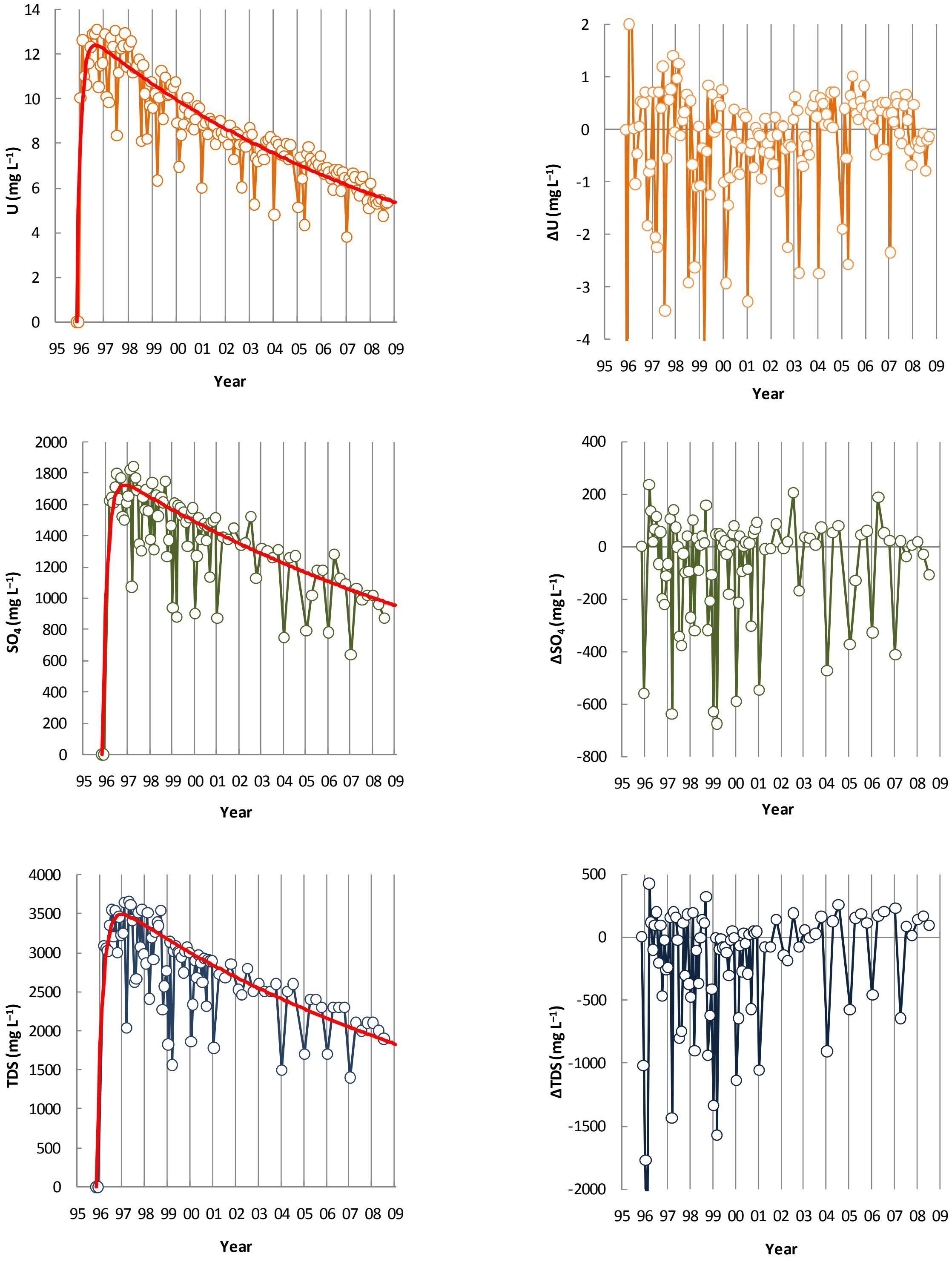

Figure 2. Comparison of real geochemical mine water evolution (color lines and circles) and model long term trend (red line) in mine water on Rožná uranium deposit for dissolved uranium, sulfates, and total dissolved species (left column). In the right column are given seasonal concentration fluctuations obtained by subtraction of real and model trends. Given are components for which trends exponentially converge to zero background value.

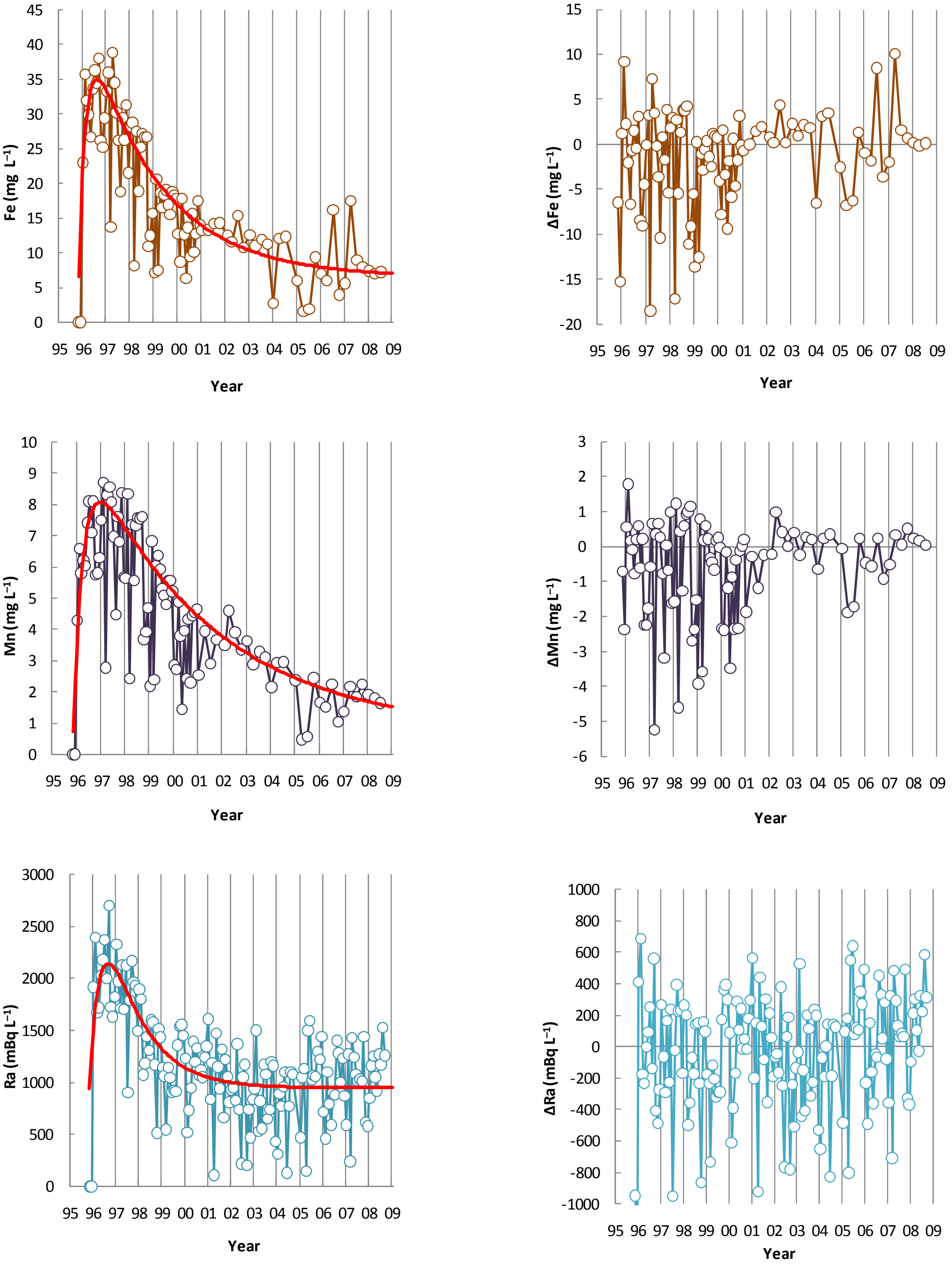

Figure 3. Comparison of real geochemical mine water evolution (color lines and circles) and model long term trend (red line) in mine water on Rožná uranium deposit for dissolved iron, manganese, and activity of radium (left column). In the right column are given seasonal concentration fluctuations obtained by subtraction of real and model trends. Given are components for which trends exponentially converge to specific non-zero background value.

The attached graphs show the good agreement between model and real evolution of component concentrations of monitored components. In this case the model enable us to relatively reliably forecast future evolution of component concentration in horizon of first tens of years and in detail analyze nature and frequency of seasonal fluctuations.

Rosice-Oslavany Coal Deposit

Resulting model parameters for individual components are given in Table 2. Graphic comparison of real and model evolution for particular components are given on Figure 4.

Table 2. Model parameters of long term evolution of mine water composition on Rosice-Oslavany coal deposit.

Component	$[c_{S0}]$ mg L^{-1}	k_1 day^{-1}	k_2 day^{-1}	t_{max} day	$[c_{MWmax}]$ mg L^{-1}	$[c_B]$ mg L^{-1}
Fe	210.2	3.822E-03	3.822E-03	261.6	107	30.3
Mn	9.10	2.404E-02	1.478E-03	123.6	10.7	3.10
SO_4	3054	5.166E-03	1.442E-04	712.7	3633	877

The meaning of symbols is the same as in Table 1.

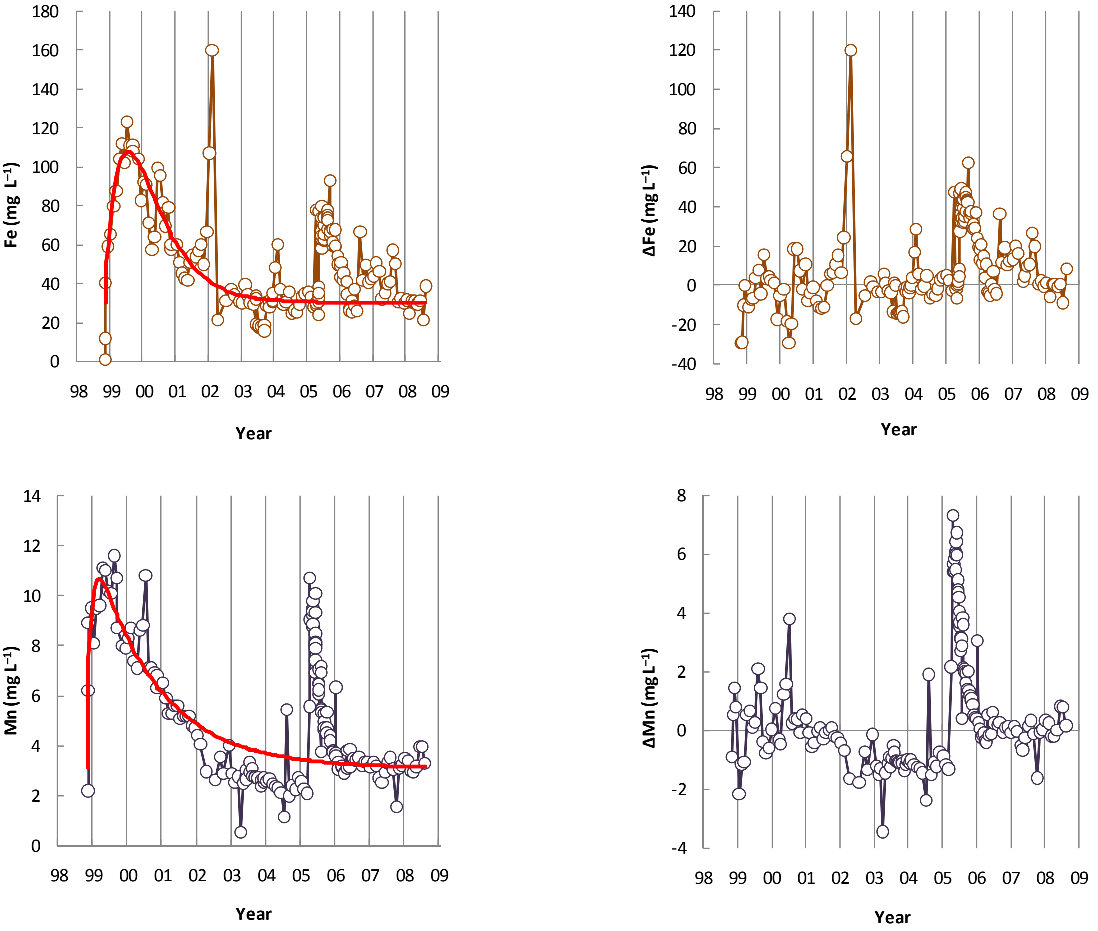

Figure 4. Comparison of real geochemical mine water evolution (color lines and circles) and model long term trend (red line) in mine water on Rosice-Oslavany coal deposit for dissolved iron and manganese (left column). In the right column are given seasonal concentration fluctuations obtained by subtraction of real and model trends. Given are components for which trends exponentially converge to specific non-zero background value.

The steep deviation in component concentrations in 2002 and 2005 years was caused by changes in external conditions (one shaft close to mine water discharging adit was filled up and change in pH values was observed). It is evident that there is very good agreement between model simulation and real mine water geochemical evolution. Obtained parameters can be used for future prediction of mine water behavior.

5. CONCLUSIONS

Mining activity has deep impact on the surface environment. Among the most significant effect belongs the deterioration of ground water quality. As the key factor which determine quality and long term geochemical evolution of mine water was identified change in oxidation-reduction conditions during mining and flooding the ore deposit. Detailed study of long term and seasonal trends of mine waters geochemical evolution of closed and flooded ore deposits showed that it is possible to quantitatively characterize time changes in concentrations of individual components using a relatively simple dynamic model. Quantitative evaluation yields valuable parameters which are otherwise inaccessible. It is for example possible to trace the decrease of “resources” for monitored components, from which soluble species are released into mine water (for example oxohydroxides of ferric iron and fourvalent manganese), and to estimate the time needed for mine water to be cleaned etc. Quantitatively characterized changes and deviations from model long-term trends enable one to effectively deduce mechanisms of processes which determine mine water composition and estimate the influence of individual factors.

6. ACKNOWLEDGEMENTS

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