ANALYSIS OF CORRELATION BETWEEN WATER FLOW AND pH IN THE SMOLNIK CREEK AFFECTED BY ACID MINE DRAINAGE

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EXTENDED ABSTRACT

Water quality monitoring has one of the highest priorities in environmental protection policy. The main objective is to control and minimise the incidence of pollutant-oriented problems and to provide water of appropriate quality. The Smolnik deposit is one of the historically best-known and richest Cu-Fe ore deposits in the Slovak Republic. The discharging mine waters of pH 3.7-4.1 containing high concentrations of sulphates, Fe, Mn, Cu, Zn and Al have a negative effect mainly on the Smolnik creek. The results of metal concentrations depend on pH and water flow rates. Heavy rainfall causes an increase in the flow of watercourse, which is connected with increasing of pH and precipitation of metals (Fe, Al, Cu, Zn).

The paper deals with the study of pH variation in dependence on water flow rates in the Smolnik creek that vary between 0.3 and 2.0 m³/s (monitored in 2000 – 2012) after their mixing with acid mine drainage from abandoned sulphide mine Smolník with a flow rate of 5-20 litre per second. The statistical analysis confirms the significance of the exponential relation between the values of pH of surface water and the flow rate of the Smolnik creek.

Keywords: pH, water flow rate, acid mine drainage, heavy metals

1. INTRODUCTION

Acid mine drainage (AMD) is considered as one of the worst environmental problems associated with mining activity. In Slovak Republic there are some localities with existing AMD generation conditions (Andras et al., 2012). The most critical values were observed in the abandoned deposit Smolník (Petriláková and Bálintová, 2011). Overflowed mine Smolník produces AMD with high metal concentrations and low value of the pH (about 3-4) as a result of chemical oxidation of sulphides and other chemical processes. This AMD acidifies and contaminates the Smolník creek water, which transports the pollution into the Hnilčec river catchment (Luptakova et al., 2008; Singovszka and Balintova, 2009). Increasing of the pH of water is connected with the metal precipitation in the form of hydroxides. Metals deposited in contaminated bottom sediments can be released to the water column with changes in different hydrobiological and physico-chemical conditions such as pH, redox potential, salinity (Hakansson et al, 1989). Because the flow rate of the Smolník creek varies depending on rainfall conditions and tributary of AMD is in the range 5-10 L/s, this study was focused to the analysis of the correlation between pH and flow rate of the Smolník creek.
2. MATERIALS AND METHODS

2.1. Study area

The stratiform deposit Smolná belongs to the historically best-known and richest Cu – Fe ore deposits in Slovakia. In 1990 the mining activity at the locality was stopped. The mine was flooded till 1994. In 1994 an ecological collapse occurred, which caused the fish-kill and the global negative influence on the environment. The mine-system represents partly opened geochemical system into which rain and surface water drain. (Spaldon et al., 2006; Luptáková et al., 2007). More than 6 million tons of pyrite ores of various qualities have been abandoned in this mine. The analysis of water in the deserted mine and in the broader area surrounding this mine was made after the ecological accident in the Smolná creek in 1995. Waters from the earth surface penetrated the mine and they were enriched with metals and their pH values decreased (Sotník et al., 2002). Acidity is caused mainly by the oxidation of sulphide minerals. The shaft Pech receives the majority of waters draining from the flooded Smolná mine area and discharge them in form of acid mine drainage (pH = 3-4, Fe 500-400 mg/l; Cu 3-1 mg/l; Zn 13-8 mg/l and Al 110-70 mg/l). This water acidified and contaminated the Smolná creek water which transported pollution into the Hnilec River catchment (Luptáková et al., 2008).

The continuation of AMD generation at the locality of Smolná is not possible to stop and there is no chance for situation self-improvement. It is necessary to respect this situation, monitor the quality of these waters, and develop methods for their treatment. That was the reason to start a systematic monitoring of geochemical development in acid mine drainage to prepare a prognosis in terms of environmental risk.

2.2. Monitoring of surface water quality

In order to study the influence of AMD on pH of surface water two localities were monitored (Fig. 1). The sampling locality no. 1 was an outflow of AMD from shaft Pech and locality no. 2 was situated before the inflow of the Smolná creek into the Hnilec river. In the two sampling sites flow rate and pH were monitored. For the better interpretation of results a part of the data (flows of the Smolná creek) was provided by the Slovak Hydrometeorological Institute (SHMI).

Figure 1. Sampling localities
Flow and pH were measured twice a year for shaft Pech (sampling locality no. 1) and once a month for the Smolnik creek (sampling locality no. 2) during years 2000-2012. Distance between sampling localities is approximately 9 kilometres. The chosen physical and chemical parameters were determined by multifunctional equipment METTLER TOLEDO in situ.

3. STUDY OF THE EFFECT OF WATER FLOW ON THE pH OF SURFACE WATER IN THE SMOLNIK CREEK

Surface water in the Smolnik creek is polluted by acid mine drainage from shaft Pech. The average flow rates $Q$ and pH values of acid mine drainage from the shaft Pech are presented in Table 1. It can be observed that both flow rate and pH are in a very narrow interval of values. Due to this fact the data from this locality have not been considered for further analysis.

Table 1. The average annual values of pH and water flow rates of acid mine drainage from the shaft Pech in 2002-2012

<table>
<thead>
<tr>
<th>Year</th>
<th>2002</th>
<th>2003</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q$  (L/s)</td>
<td>5.65</td>
<td>6.57</td>
<td>7.3</td>
<td>8.89</td>
<td>7.01</td>
<td>5.25</td>
<td>5.89</td>
<td>6.29</td>
<td>8.24</td>
<td>6.13</td>
<td>4.19</td>
<td>6.49</td>
</tr>
<tr>
<td>pH</td>
<td>3.92</td>
<td>3.94</td>
<td>4.01</td>
<td>3.86</td>
<td>3.88</td>
<td>4.11</td>
<td>3.99</td>
<td>3.94</td>
<td>3.81</td>
<td>3.97</td>
<td>3.99</td>
<td>3.95</td>
</tr>
</tbody>
</table>

Figure 2 shows the average monthly flow of water in the Smolnik creek for the period 2000 - 2011. From the picture it is evident that in winter the majority of the water flow rates are in the range 0.3 - 0.6 m$^3$/s. The increase of the flow rate occurs in spring due to melting of snow and ice. In 2010, the flow rates reached higher values due to the floods in Slovakia.

3.1. Regression analysis of the flow rate and pH of surface water in the Smolnik creek

Regression analysis (Bhattacharyya, G.K., Johnson, R.A., 1977) was made in order to find dependence of pH, denoted as $\omega$, on the flow $Q$ of water in the Smolnik creek. For
the better interpretation of correlation, the extreme flow rates more than 2 m³/s were excluded.

According to the nature of the data, exponential relation between the values of ω (pH) and the flow rate Q, expressed in cubic meters per second, was considered. The chosen model

$$\omega = b - ae^{-cQ}$$

requires in numerical analysis nonlinear least squares method to determine the estimates \(\hat{a}, \hat{b}, \hat{c}\) of the unknown parameters \(a, b, c\). The computer program gnuplot (www.gnuplot.info) was used, in particular the command fit which fits a user-defined function to a set of data points. The obtained results are shown in Figure 3.

By assumption, the estimate \(\hat{b}\) is approximately equal to 7, because increasing flow rate neutralizes acidic nature of the surface water, thus pH = 7. The other two parameters reflect the chosen exponential dependency.

In view of the result evaluation and the relevance of the model, the calculation was supplemented by a statistical analysis. First, the calculation assumed normality of the distribution of values \(\omega\) with a constant standard deviation \(\sigma\). The estimate of the standard deviation \(S\), calculated also by the fit command is the weighted sum of squared residuals (WSSR) which means minimization of \((\omega_i - \hat{\omega}_i)^2\), where \(\hat{\omega}_i = \hat{b} - \hat{a}e^{-\hat{c}Q_i}\).

Assuming normality of the distribution, 95% of the measured data are ranged in the interval \((\hat{\omega}_i - 2\sigma, \hat{\omega}_i + 2\sigma)\). This interval is also shown in Fig. 1, where the standard deviation \(\sigma\) is estimated by \(S\). The fit command also provided asymptotic standard error as a criterion for qualitative assessment of the fit parameters estimates \(\hat{a}, \hat{b}, \hat{c}\). Using this asymptotic error, the parameter estimates can be written as \(\hat{a} = 4.256 \pm 0.379\), \(\hat{b} = 6.985 \pm 0.178\), \(\hat{c} = -2.673 \pm 0.484\).

![Figure 3](image)

**Figure 3.** Dependence of pH on the water flow, regression analysis

Although the measured data are rather scattered, affected by factors not included into the experiment such as precipitation of metals, which lowers the pH (Balintova and
Petrilakova 2011, Calmano et. al, 1993), the obtained results can be used to predict the values of pH (ω), depending on the flow rate Q.

4. CONCLUSIONS

Acid mine drainage discharged from abandoned mine Smolnik (shaft Pech) contaminates the downstream from the Smolnik mine works to confluence of the stream with the Hnilec river, because of decreasing pH and heavy metal production. The values of pH in the Smolnik creek are influenced by flow rate, too. The statistical analysis confirms the significance of the exponential relation between the values of pH and the flow rate Q. The obtained numerical results also provide expected values of parameters in the proposed model. The confidence is limited by the scattered character of the experimental data caused by phenomena not considered in the test.

Because the variability of pH can influence the sediment-water partitioning of heavy metals, this model can be used for prediction of the influence of water flow rate on pH of surface water influenced by acid mine drainage.

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