Real-time Monitoring of Surface Water Quality Water Downstream of a Mine

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Abstract

Nowadays environmental monitoring of mines and mine water treatment systems relies on infrequent sampling and laboratory analysis. Real-time monitoring can allow fast response to changes. Optical test bench was developed and tested in monitoring of mine impacted river water quality. The water quality of the studied river is poor when compared to surrounding water bodies. The real-time analyses revealed that water quality fluctuates much more than seen with few grab samples. Thus real-time monitoring is recommended to detect water quality changes. Of the chosen methods, pH, conductivity, oxygen and UV-Vis measurements are the most recommended.

Key words: real-time monitoring, surface water, mine effluent, optical spectroscopy, ultraviolet-visible, near infrared, fluorescence, camera, multivariate analysis

Introduction

The importance of mining to the economy of Northern and Eastern Finland has increased dramatically over the last few years. According to current estimates, 7-9 metal mines will start in this area during the next 3-4 years. More than forty Finnish and international companies are either conducting mining or mine exploration in Finland (GTK 2007). In Finland, the emphasis is on open pit mining. However, the impacts of mining on environment and water quality and the ways to minimise such changes need to be studied more closely in order to prevent environmental changes.

The release of organic and inorganic matter must be considered in open pit mining. Mining results in local changes in groundwater levels and surface water flows. The total water flow from mines to the environment is case-specific and not well known as it depends on rock fractures and their connectivity to the surrounding environment and surface water systems. Pollution risks are associated with mine drainage water, the treatment of ore and formation of mine tailings and their storage. As a result of mining, geological deposits are exposed to oxygen and minerals in reduced state are oxidised. The oxidation of sulphide minerals leads to the formation of acidic metal- and sulphate-containing water, so called acid mine drainage with raised concentration in e.g. arsenic and nickel (depending on pH). Also explosives and process treatment chemicals may pose a risk to the environment and nutrients may be released to the environment causing eutrophication. Acid mine drainage has been shown to have a negative impact on aquatic foodweb (Levings et al. 2004). Furthermore, acid mine drainage affects public health and economy of many countries (Alvarez-Aliaga 2005). The risks associated can be minimised by mine water treatment and further reduced by monitoring the impacts of mining on surface water quality. In mines with existing mine water treatment, more risks may be associated with mine closure than mine operation itself.

Current practices in environmental monitoring of mines and mine water treatment systems rely on infrequent sampling and laboratory analysis. Samples are taken from water leaving the mines typically at day to month intervals. However, these sampling frequencies may be too low to observe changes and disturbances in the ongoing processes. Real-time monitoring and integrated process control, especially, can be used as an early warning system to allow fast response to changes. New methods to monitor and control the fate of mine pollutants are needed.

Optical measurement methods may be useful in monitoring mine environments, since they do not require reagents and can be used in real-time measurements. Optical techniques are based on the interaction of light with the sample. Ultraviolet-Visible spectroscopy (UV-Vis) is capable of measuring many quality parameters of water samples efficiently. The UV-Vis spectrum of any water sample composes of the spectra of its constituents such as dissolved organic matter, suspended solids and salts. Near infra-red (NIR) spectra of water can be obtained using either transmittance or reflectance methods. Properties of water such as chemical oxygen demand (COD) can be resolved from water spectrum using multivariate analysis. Optical methods have advantages, such as low

running costs, elimination of sampling errors and simultaneous determination of many parameters. Furthermore, their running costs are low and they are simple to use (Bourgeois et al. 2001). Thus, they are useful in early warning systems and monitoring of closed mines.

Finnish surface waters are shallow and thus sensitive to pollution (Finnish Environment Institute 2007). In the current study, an optical test bench was developed and applied in monitoring of surface water quality downstream of a mine in Kainuu region.

Methods

Water quality was monitored for 20 days in a river, in which treated mine water is released. The water was pumped from river to test bench and optical measurements were conducted in flow-cells using fiber-optical probes. The test-bench consisted of an FT-NIR spectrometer and a UV-Vis spectrometer. A wavelength range from 185 to 2500 nm (UV-Vis-NIR) was used.

A gray scale CCD camera (GUPPY F-080B/C, Allied vision, Germany) was used to capture images of white disc submerged into river water at about 30 cm depth. Images were captured every 15 min. Conductivity, dissolved oxygen and pH probes (Global Water Instrumentation Inc., USA) were placed directly into the river for real-time measurements.

Water samples were taken 5 days a week and analysed for COD, suspended solids, turbidity, nickel and conductivity in laboratory. COD was analysed with $KMnO_4$ method according to SFS standard 3036 (SFS 1981). Suspended solids were analysed according to SFS standard 3037 (SFS, 1974). pH and conductivity were measured using MPC227 meter (Mettler Toledo). Turbidity was measured using a Hach 2100N Turbidimeter. Ni concentrations were measured with Spectroquant cuvette test (Merck, Germany). Four reference analyses were made at an external laboratory to determine Ni concentrations using SFS standard 5502 (SFS 1990) and As concentrations using standard 5704 (SFS 1990).

The measurement results were analysed using multivariate analysis, such as principal component analysis (PCA) and partial least squares (PLS) analysis, with Unscrambler software (CAMO, Norway).

Results and discussion

In real-time measurements the conductivity of water ranged from 15 to 50 mS/m and was 38 mS/m on average (Figure 1A). The measured laboratory values were in the same scale, although slightly higher, 54 mS/m on average. The observed variation in laboratory and real-time measurements may be due to sampling error and measurement errors of field-scale measurements, such as probe drifting, mismatching calibrations etc. (Rosen et. al. 2007). Both the real-time and laboratory conductivity values are higher than those of average Finnish surface waters and those of same river system. The increased conductivity results from mine-deriving increased dissolved salts. The river receives effluent from mine water treatment as well as diffuse loads of acidic and metalliferous drainage deriving from weathering of black shale (Anon, 2008). The changes in conductivity may be due to seasonal changes, such as precipitation, as well as variation in the flow rate of mine effluent.

The pH of river water varied between 5,8 to 7,5 (Figure 1B). The variation is slightly higher than that of average Finnish surface water pH, 6-7, due to the impact of mine water effluent. Dissolved oxygen was monitored only for one week due to probe malfunctions. Dissolved oxygen as saturation percentage was rather constant, but saturation is a temperature-dependant parameter and thus changes would be more visible if the values were converted into mg O_2/l.

The turbidity of river water was between 2,2 and 5,5 FTU in laboratory measurements. Real-time measurements of turbidity will be incorporated into future measurements. In real-time measurements, temperature in the studied river water varied between 6,3 and 12,0ºC and was 9,3ºC on average (Figure 1B). This range is the normal autumnal variation. Suspended solids were measured in laboratory and they were 4,9 mg/l on average. Their concentration varied between 0,4 to 8,1 mg/l.

Chemical oxygen demand (COD) was 21 mg/l on average and varied between 17 and 26 mg/l. The water is abundant in humic matter, which is common to surface waters in Kainuu and Finland in general. COD in the mine effluent itself is fairly low (results not shown) and thus it does not increase COD of river water. The correlation coefficient R^2 in cross-validated PLS of COD and UV-Vis spectra was 0,66. The correlation of COD and UV-Vis spectral data has been noticed previously. However, the published correlation coefficients are higher than in the current study.

Figure 1 A. Dissolved oxygen (saturation-percentage, upper curve) and conductivity (mS/m, lower curve). B. Temperature (°C, upper curve) and pH (lower curve) changes over studied period.

A
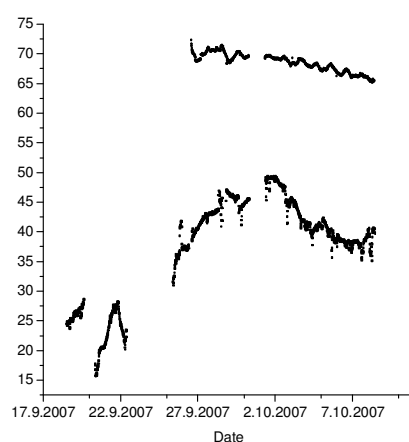
B
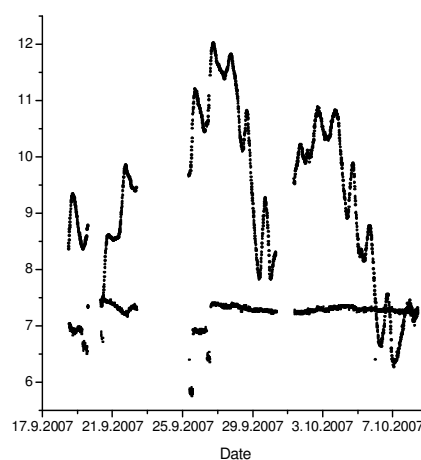
The results of the cuvette test in analyzing nickel concentrations were 10 times higher than those analysed by an accredited laboratory. Thus the test proved unreliable. Nickel concentrations of reference analyses showed that Ni concentration in river water varied between 52 and 63 µg/l. In future, real-time analysis of metal concentrations will be attempted with ion-selective electrodes, both using unspecific and metal-specific electrodes. The number of Ni analyses was too low to evaluate any correlations with optical measurements.

Multivariate analysis (PLS) of NIR and water quality parameters showed that the NIR spectrum did not describe single water quality parameters. However, comparing PCA results (residual x variance) to other sensory data such as conductivity reveals that the NIR-spectra is sensitive to water quality changes. On the other hand, NIR is more sensitive to disturbing factors, such as bubbling and contamination, than more widely used UV-Vis techniques.

Analysis of CCD camera images showed that the white disc could be seen throughout the measurement period. However, the depth of the disc varied since the level of water surface was not constant. The images also showed that the disc suffered from fouling, but cleaning every two days kept it fairly clean. The images cannot be compared more thoroughly since no reference measurements were made to study light intensity during the measurement period. Furthermore, measurements with common CCD camera can only be used qualitatively (Klaveness, 2005).

The water quality of the studied river is poor when compared both to surrounding water bodies (Anon, 2008) and to Finnish water quality criteria. However, the mine tries to minimize effluent flows to the river by aiming at closed water circulation and by using best available techniques (BAT) for mine water treatment. The real-time analyses revealed that water quality varies much more than seen with few grab samples. Thus, use of real-time measurements is recommended to reveal water quality changes. However, real-time analyses cannot replace laboratory analyses and may even increase their use as data from real-time measurements is interpreted.

All the used methods, grab samples and laboratory analyses, real-time measurements with probes and real-time spectroscopic measurement, have uncertainties. The relative share of sampling error is high in laboratory measurements, but errors in laboratory analyses themselves must also be considered. Measurement error is higher in probe and spectroscopic measurements than in laboratory analyses. Errors observed in spectroscopic measurements are due to e.g. absorbance repeatability, spectrophotometer drift, nonlinearity of absorbance scale, detector nonlinearity and finite bandwith of radiation (Sooväli et al. 2006). These facts need to be taken into consideration in combining several types of data in multivariate analysis.

Conclusions

The real-time analyses revealed that water quality fluctuates much more than seen with few grab samples. Thus real-time monitoring is recommended to detect water quality changes. Of the chosen methods; pH, conductivity, oxygen and UV-Vis measurements are the most recommended.

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