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Effect of different soil layers on porewater to remediate acidic surface environment at a close mine site

Environmental Monitoring and Assessment

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Abstract

This paper describes the chemistry of porewater when constructing different soil layers on acidic weathered rock of a closed mine to remediate the surface environment. Three cases were set on a flat surface of the site, all under different layer systems. Case 1 was only composed of weathered rocks. A top neutralization layer was constructed on the weathered rocks in case 2, whereas both an upper low permeable and middle neutralization layers were constructed on the weathered rocks in case 3. The low permeable layer of 30 cm thick consists of clay, and the neutralization layer of 30 cm thick consists of the mixture of the weathered rock and calcium carbonate as a neutralizer. Porewater sampling systems and soil sensors to measure temperature, water content, and electrical conductivity were set at different depths. In case 1, steadily high concentrations of heavy metals were observed regardless of the depth, and the pH ranged from 2 to 4. In cases 2 and 3, a dramatic decrease in concentrations of heavy metals was observed, even below the neutralization layer. For both cases pH values were circumneutral. There were no significant seasonable changes in heavy metals concentrations and pH of porewater by considering the temperature and precipitation. In addition, the water content of the layers in case 3 fluctuated more mildly than that in cases 1 and 2, indicating that the low permeable layer reduced the rate of infiltration. Therefore, a significant reduction in the load of heavy metals released from the site can be achieved by both implementing neutralization and low permeable layers.

Keywords: porewater; in situ monitoring; soil layers; heavy metals; closed mine

Introduction

Environmental pollution originating from abandoned or closed mines has become a very important source of contamination both in soil and water due to the formation of acid mine drainage (AMD) and the acidification of the surrounding soils (Fernández-Caliani et al. 2009; Passariello et al. 2002; Salomons 1995). In the light of the legislation aimed at safeguarding the environment and the heightened public awareness of environmental issues, remedial action in most of the cases can no longer be postponed (Bone et al. 2010) by considering that a gradual increase in the number of abandoned mines and a lack of maintenance or failure of them have severely enhanced the risk of pollution spreading to areas related with mining activities (Liao et al. 2008) and their surroundings (Ciccu et al. 2003). Environmental Protection Agency (EPA) rated problems related to mining wastes as second only to global warming and stratospheric ozone depletion in terms of ecological risk (EEB 2000). The report concluded with high certainty that the release of mining wastes to the environment could result in profound, generally irreversible destruction of ecosystems. Some polluted sites will persist as long as hundred of years or until the pyrite supply is exhausted (Younger 1997; Younger et al. 2002), while the other polluted sites may never be fully restored since the pollution is so persistent that there is no available remedy (EEB 2000).

Remediation actions can involve a long range of activities designated to enhance the quality of the affected good (air, water and/or soil) that may include the excavation and removal of contaminated soil and/or rocks (Mulligan et al. 2001; Simón et al. 2008). Even though this method seems like a logical answer to overcome this problem, it is not realistic in many cases due to the vast size of the contaminated

area and the high cost of money and energy involved (Boisson et al. 1999). It is worth considering a more cost-effective alternative for soil remediation by in situ treatment of heavy metals to reduce the risk of the contaminants through groundwater, surface water, or atmospheric exposure pathways (Basta & McGowen 2004), such as the addition of soil amendments (Gray et al. 2006; Lee et al. 2010), minerals (García-Sánchez et al. 1999), microorganisms (Groudev et al. 2001), or others (Dermont et al. 2008).

In this context, the characterization of mining wastes is important to assess the risk of potential environmental mobility of toxic trace metals contained in the wastes (Marguí et al. 2004). Part of this characterization is the monitoring of the porewater chemistry in the soils at closed mine sites that eventually leads to the formation of AMD. Some researchers have conducted in situ monitoring to understand more this phenomenon (Birkefeld et al. 2006; Fakhri et al. 2008; Hulshof et al. 2006), but few have considered the addition of a soil layer system as remediation technology at the site.

In this paper we evaluated the efficiency of in situ soil layer systems, consisting of a neutralization layer and a low permeable layer, as a remediation method to improve the quality of the acidic soils and porewater, by monitoring porewater chemistry, volumetric water content, electrical conductivity (EC), and temperature for more than one year. The data collected in this study will help assess the effectiveness of this approach as remediation technology.

Materials and methods

Outline of the closed mine site

The site where the in situ experiments were carried out is a former gold (Au) and silver (Ag)

mine, located in Kazuno city, northeast of Akita Prefecture, Japan (Fig. 1). The geology of the area consists of the Tertiary green tuff / tuff breccia and rhyolite. The Kuroko ore body and iron sulfide dissemination zone in the strata were excavated to produce Au, Ag, copper (Cu), lead (Pb), and zinc (Zn). However, the mine was closed in 1978. After that, a water treatment plant has been operated for neutralizing the AMD from drifts and shafts of the mine, and the seepage from dams and waste rocks. The total flow rate to be treated is approximately $0.6 \text{ m}^3/\text{min}$, and the raw water has a pH of 2.8 with high contents of heavy metals.

Construction and characterization of soil layer systems

Three different surfaces were prepared on a flat surface at the top part of the closed mine to carry out the in situ monitoring and porewater sampling. The area occupied is 16 m^2 ($4\text{m} \times 4\text{m}$) for each case. Case 1 is solely composed of the surface weathered rocks. Calcium carbonate (CaCO_3), as a neutralizer, was mixed with the weathered rocks on the upper 30 cm at a ratio of 30 kg CaCO_3 per 1 m^3 weathered rock in case 2, while extra upper 30 cm of a clay layer in addition to the neutralization layer was set up in case 3 to construct a double-layer system consisting of a low-permeable layer and a neutralization layer, as shown in Fig. 2. The surface weathered rocks were mixed with powdered CaCO_3 using a backhoe. The mixing ratio was based on the results of batch neutralization experiments. These experiments were carried out by varying the mixing ratio of rocks and neutralizer to obtain the optimal amount of CaCO_3 needed to raise the pH of the acidic rocks to around pH 7 (Salinas et al. 2009). The clay used for the upper layer in case 3 was taken near the site.

After the construction of the layers system, soil samples from the three cases were taken to obtain the physical and chemical properties. The hydraulic conductivity was determined based on the falling head method. The pH, oxidation-reduction potential (ORP), and EC of the three layers (weathered rock, neutralization, and low-permeable layers) were determined by batch leaching experiments. The solutions were made by adding 20 g of the layer sample and 200 ml of deionized water in a 250 ml Erlenmeyer flask, and mixed at 120 rpm for 24 hours at room temperature.

Setup of porewater sampling and monitoring systems

Five soil sensors (5TE, Decagon Devices, Germany) with the respective data logger (Em50, Decagon Devices) were set at different depths (GL -15, -45, -70, -80, and -95 cm) in each case to measure volumetric water content, temperature, and EC, shown in Fig. 2. The data were stored every 2 hours for over a year (from October 2009 to December 2010) in the logger. Simultaneously, a water sampling system using porous cups was set at different depths (GL -15, -45, -70 and -95 cm), as shown in Fig. 2. Sampling was done by using a vacuum pump. Six sampling campaigns were carried out over the monitoring period mentioned above.

Chemical and mineralogical analysis

Three weathered rocks (K_1 , K_2 , and K_3) and one fresh rock (K_4) samples were obtained at the ground surface of the mine. As pretreatments, the rock samples were dried and crushed. The chemical composition of the samples was quantified using an energy dispersive X-ray fluorescence spectrometer,

Xepos (Rigaku Corporation, Japan) while their mineralogical composition was identified using an X-ray diffractometer, Multiflex (Rigaku Corporation, Japan).

Chemical analysis of the porewater samples was also carried out. Dissolved heavy metals concentrations greater than 0.1 mg/L were analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPE-9000, Shimadzu Corporation, Japan) whereas concentrations of several dissolved metals less than 0.1 mg/L were measured using an ICP-AES coupled with an ultrasonic aerosol generator, which had a detection limit of 0.01 to 0.001 mg/L. The results of the analyses using ICP-AES had a margin of error of ca. 2 - 3% while the ultrasonic aerosol generation process had an uncertainty of ca. 5%. The concentrations of the major cations were measured by using a cation chromatograph (Dionex, ICS-90, USA), and the concentrations of the major anions were measured by using an anion chromatograph (Dionex ICS-1000, USA). Both chromatographs had a margin of error of ca. 2 – 3%. Concentrations of HCO_3^- were obtained by titration using 0.02 N sulfuric acid. The other parameters such as pH, ORP and EC, were also measured.

Results and discussion

Properties of surface rocks and layers

The rock samples used to characterize the site were surface weathered rocks and fresh rock collected near the experimental site for the in situ monitoring. The chemical and mineral compositions of the rocks are listed in Tables 1 and 2, respectively. Table 1 shows that the surface rocks contain both significant amounts of heavy metals (Cu, Pb, Zn) ranging from 10 to 98 mg/kg and sulfur ranging from

0.48 to 1.0% whether the rock is weathered or fresh. Table 2 shows that the presence of pyrite (FeS) was detected in the fresh rock only, but not in the weathered rocks. However, an electron microscopy of the weathered rocks showed the presence of pyrite even in the weathered samples. This indicates that the content of pyrite decreases with the progress of weathering.

Physical and chemical properties of the weathered rock, neutralization and low-permeable layers are shown in Table 3. The low-permeable layer has a hydraulic conductivity of 1.52×10^{-6} cm/s that is about 10,000 times lower than the other two layers. The permeability of the layers is important because this property determines the amount and retention time of water percolating into the system monitored. The retention time also influences the interaction between the infiltrating water and the layers that in turn affects the mobility of the toxic heavy metals such as Cu, Pb, and Zn.

The pH was highly increased from pH 3.8 of the weathered rock layer to pH 8.1 and 6.2 for the neutralization and low-permeable layers, respectively.

Effects of layers system on pH and ORP

The pH profiles of porewater samples are shown in Fig. 3. Acidic pH for all depths and sampling campaigns ($\mu=3.32$, $\sigma=0.35$) in case 1 were observed. Here, μ is the arithmetic mean and σ is the standard deviation. The source of the acidity is attributed to the weathering of the residual sulfide minerals contained in the surface weathered rocks. In case 2, the pH was increased to the circumneutral region ($\mu=7.84$, $\sigma=0.51$) irrespective of the depth and sampling campaign. The increase in pH is attributed to the presence of CaCO_3 in the neutralization layer that reduces the acidity of the system. The pH in the

weathered rocks under the neutralization layer (deeper than GL -30 cm) also increased to circumneutral, indicating that the dissolution of CaCO_3 progressed down to the deeper layer. In case 3, the pH in the system ($\mu=7.58$, $\sigma=0.81$) was similar to case 2, although the mean was smaller and standard deviation was higher based on the results obtained for the shallowest porous cup ($\mu=6.70$, $\sigma=0.31$), which was located in the low-permeable layer (GL-15 cm). Nonetheless, the weathered rocks under the neutralization layer (deeper than GL -60 cm) remained, as in case 2, in the circumneutral region for all sampling campaigns.

The results of ORP were positives for all cases and depths, as shown in Fig. 4. The following results in case 1 ($\mu=437.5$ mV, $\sigma=58.9$ mV), in case 2 ($\mu=172.5$ mV, $\sigma=40.3$ mV), and in case 3 ($\mu=174.5$ mV, $\sigma=44.8$ mV) were obtained. These results indicate favorable conditions for the oxidation of sulfide minerals in case 1, but the values were reduced in cases 2 and 3 although the conditions were still oxic. However, a significant reduction of ORP for the sampling campaign in August 2010 was observed, which is attributed to a much higher environmental temperature of over 30 °C at the site (at least 15°C higher than the other sampling campaigns). This may reduce the dissolved oxygen concentration of the porewater.

Effects of layers system on heavy metals and major ions concentrations

The vertical profiles of heavy metals concentrations (Cu, Pb and Zn) in case 1 are shown in Fig. 5. Copper concentrations ($\mu'=1.47$ mg/L, $\sigma'=2.34$ mg/L) do not show a clear trend with depth by considering the results of different sampling campaigns. Here, μ' is the expected value and σ' is the standard deviation assuming that the concentration is lognormally distributed. Similar results are observed

for Pb ($\mu' = 3.99$ mg/L, $\sigma' = 2.78$ mg/L) and Zn ($\mu' = 0.67$ mg/L, $\sigma' = 0.55$ mg/L). According to discriminant analysis based on a t-test between the cold season (Nov-09, Dec-09, and Nov-10) and the warm season (Jun-10, Aug-10, and Oct-10), there was no significant difference in heavy metals concentrations. This means that heavy metals leaching occurred throughout the first meter of the rock layer even though remarkable fluctuations in concentration were observed.

Heavy metals concentrations in cases 2 and 3 for all depths and campaigns were below the detection limits. This indicates that the CaCO_3 layer is effective in reducing the mobility of the heavy metals irrespective of the rate of water infiltration in the layer. By considering the pH values (Fig. 3), it is thought that a significant reduction of heavy metals concentration, including iron (Fe), is caused by the co-precipitation with Fe(III)-(oxy)hydroxide and/or adsorption to the Fe(III)-(oxy)hydroxide surface because no Fe was detected in the porewater for any of the last two cases compared to the Fe concentration ($\mu' = 2.68$ mg/L, $\sigma' = 10.49$ mg/L) in case 1.

The concentrations profiles of Ca and SO_4^{2-} as major coexisting ions are presented in Fig. 6. Higher concentrations of Ca and SO_4^{2-} were observed in cases 2 ($\mu'_{\text{Ca}} = 93.6$ mg/L, $\sigma'_{\text{Ca}} = 77.2$ mg/L, $\mu'_{\text{SO}_4} = 275$ mg/L, $\sigma'_{\text{SO}_4} = 588$ mg/L) and 3 ($\mu'_{\text{Ca}} = 91.7$ mg/L, $\sigma'_{\text{Ca}} = 234$ mg/L, $\mu'_{\text{SO}_4} = 375$ mg/L, $\sigma'_{\text{SO}_4} = 1317$ mg/L) than in case 1 ($\mu'_{\text{Ca}} = 3.04$ mg/L, $\sigma'_{\text{Ca}} = 2.83$ mg/L, $\mu'_{\text{SO}_4} = 87.8$ mg/L, $\sigma'_{\text{SO}_4} = 98.1$ mg/L). An increase in Ca concentration is attributed to the dissolution of the neutralizer in the layer in cases 2 and 3, whereas an increase in SO_4^{2-} is attributed to enhancement of the oxidation of pyrite contained in a trace amount in the rocks due to pH increase for the same cases. According to Evangelou (1995) and Tabelin and Igarashi (2009), the oxidation rate of pyrite or pyrite-bearing rocks increased with pH. This phenomenon can be

observed in Fig. 6.

A correlation analysis between pH and concentrations of heavy metals and major ions for all cases was applied. For the three heavy metals, Cu, Pb and Zn, a negative correlation was obtained. The correlation coefficients of Pb, Zn and Cu were -0.732, -0.757 and -0.590, respectively, which indicates that as the pH of the porewater is increased, a reduction of the concentrations of heavy metals occurs. This means that a significant availability of heavy metals occurs in the acidic region (pH 2.9 to 4.1) but not in the circumneutral region (Jurjovec et al. 2002; Salinas et al. 2009). On the other hand, the analysis for Ca indicates a positive correlation coefficient of 0.513 whereas the analysis for SO₄ indicates a weak positive correlation coefficient of 0.275.

Seasonal change in temperature and water content in the layers system

The temperature changes as a function of time in case 1 are shown in Fig. 7. Almost the same pattern of changes was observed in cases 2 and 3. Surfaces for all cases were covered with thick snow during the winter season (December to March), when the temperature was stable ranging between 0 and 5 °C, depending on the depth. That is, the shallowest depth was the coldest and the deepest was the warmest. The infiltration of water into the soil during this season is restricted for all three cases. Then, the temperature started to increase gradually from April until August, and it reached its peak at around 30 °C at the shallowest depth in July to August. After that the temperature decreased again steadily. The great fluctuation in the temperature depending on the season did not affect the ion concentrations of the porewater.

The monitored data of volumetric water content as a function of depth and the daily rainfall data are presented in Fig. 8 for cases 1 and 3. The figure of case 2 is not shown since the trends are very similar to that of case 1. The water content during the winter season in case 1 did not fluctuate dramatically due to the snow cover on the field, which prevented water from infiltrating. Nonetheless, from May to November a great fluctuation was observed, especially when it rained. Although the water content tends to change more mildly with depth, the fluctuations are still noticed regardless of the depth, which is expected from the high hydraulic conductivity value found in Table 3 for the weathered rocks. Similar values are also found for the neutralization layer, which explains the similarity of trends between cases 1 and 2.

For case 3, the volumetric water content did not fluctuate (from May to November) as severely as it did for the previous cases, due to the presence of the low-permeable layer on the top 30 centimeters. This indicates that the low-permeable layer setup at the top prevented sharp fluctuations in volumetric water content and reduced high water infiltration into the weathered rock and neutralization layers. However, the sensor located at GL -45cm showed a large fluctuation from the end of the snow cover season (April) compared to the other sensors. This is attributed to an incomplete backfilling of the cable to the sensor, which could allow water to pass through the cable from the ground surface to the sensor. Some points are missing in Fig. 8 (August 2010 to September 2010) for case 3 due to electrical power failure.

Table 4 shows the variances of the volumetric water content at each depth for cases 1 and 3 with snow cover (December to April) and without snow cover (May to November). The results demonstrate that greater variances were found when there was no snow cover compared with those without the snow cover

for both cases, due to the lower infiltration of water during the snow cover season. Moreover, generally greater variances were found for case 1 compared with case 3 due to the low-permeable layer at the top in case 3, although some depths did not agreed with the assumption, due to the reason stated above.

Conclusion

This study was conducted to evaluate the effectiveness of a soil layers system in the porewater chemistry to remediate surface acidic soil environments in closed mine sites. Three cases were set to elucidate the seasonal change in porewater chemistry, volumetric water content and temperature at the site. When only a weathered rock layer was present (case 1), heavy metals concentrations (Cu, Pb and Zn) were high and the pH was low. Concentrations of heavy metals were similar irrespective of depth (GL -15, -45, -70, -80 and -95 cm) and season. When a neutralization layer was applied on top of the rock layer (case 2), the concentration of heavy metals decreased so drastically that they were below the detection limit of the analytical equipment used. The pH was also raised to the circumneutral zone. Finally, when a low-permeable layer was added on top of the layers (case 3), less fluctuation of volumetric water content for the layer was observed. This indicates that the addition of a neutralization layer reduces the heavy metals leaching while the addition of a low-permeable layer reduces rapid infiltration of water through the rock layers. Therefore, both a low-permeable layer and neutralization layer are required to reduce the formation of AMD and improve the surface environmental conditions. However, the durability of the performance of the layers should be further researched.

Acknowledgments

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Figure captions

Fig. 1 Study area

Fig. 2 Schematic of layer systems and location of soil sensors and porous cups; a plan view (lower right)

and three vertical views of cases 1 to 3

Fig. 3 Vertical pH profiles: case 1, case 2, and case 3

Fig. 4 Vertical ORP profiles: case 1, case 2, and case 3

Fig. 5 Vertical profiles of heavy metals concentrations in case 1: Cu, Pb, and Zn

Fig. 6 Vertical profiles of Ca and SO_4^{2-} concentrations: case 1, case 2, and case 3

Fig. 7 Changes in temperature at different depths in case 1

Fig. 8 Changes in volumetric water content at different depths: case 1, and case 3.



Fig.1

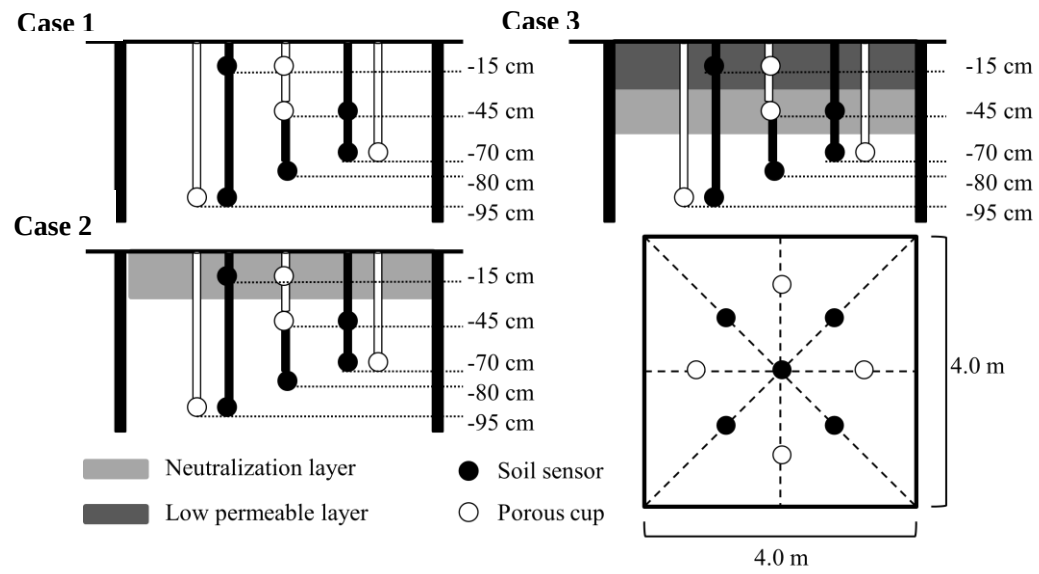


Fig.2

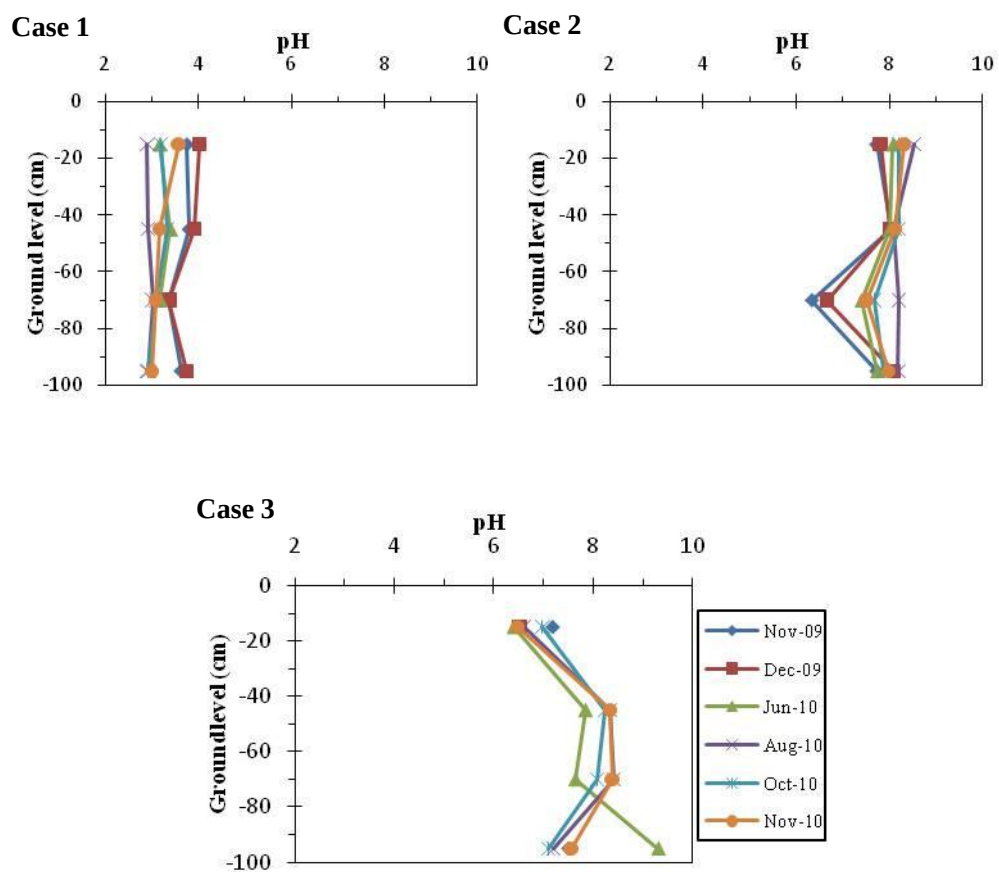


Fig.3

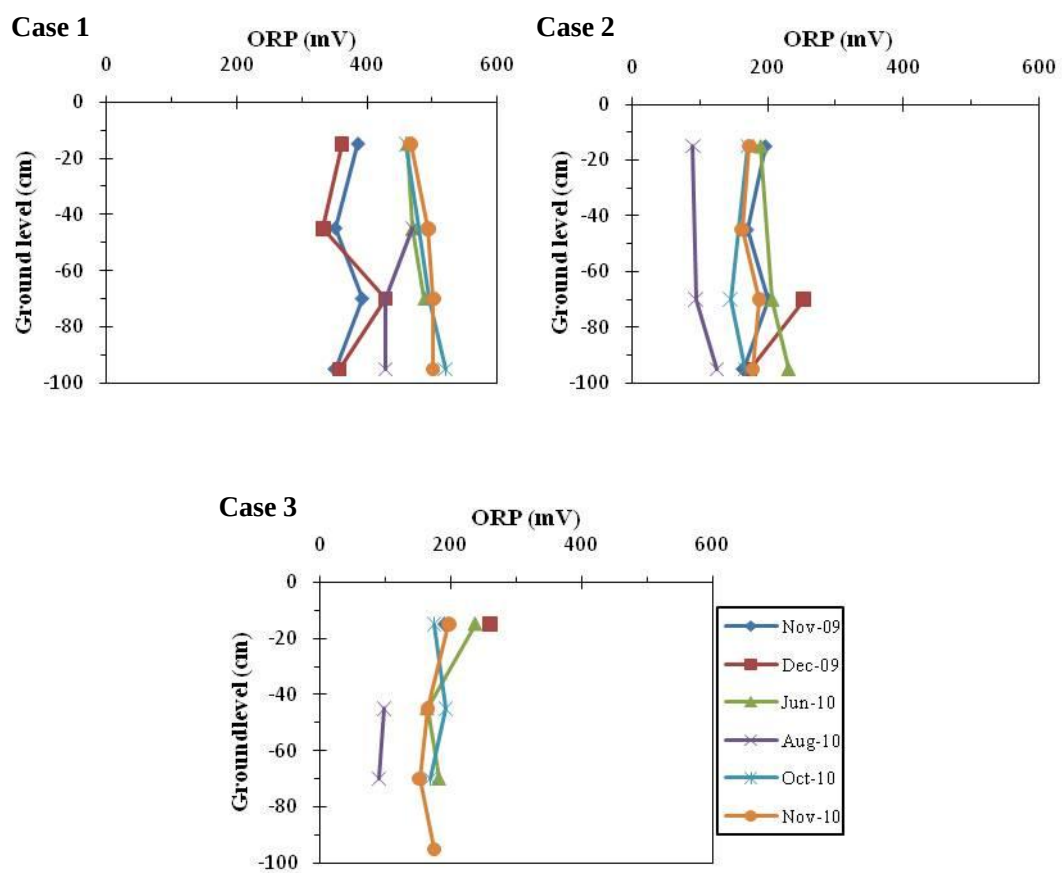


Fig. 4

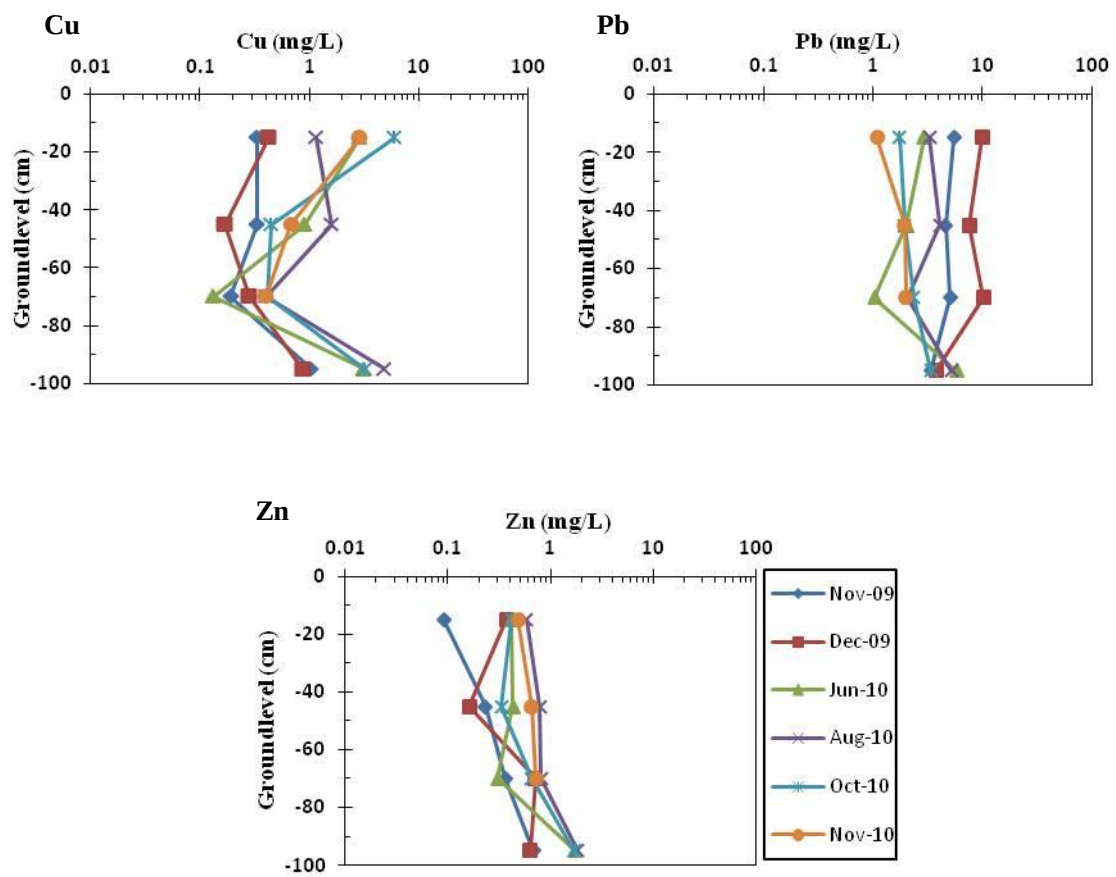
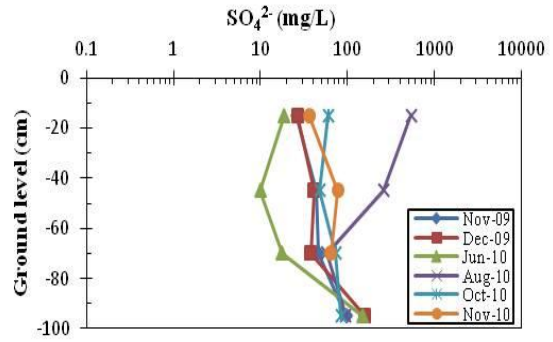
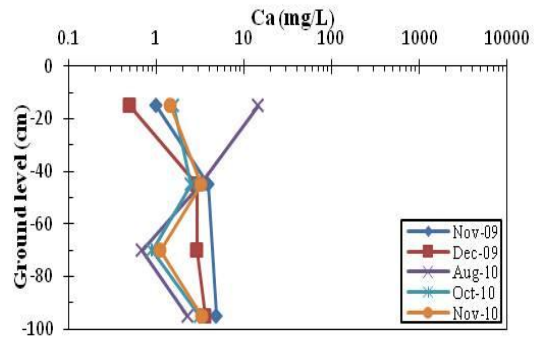
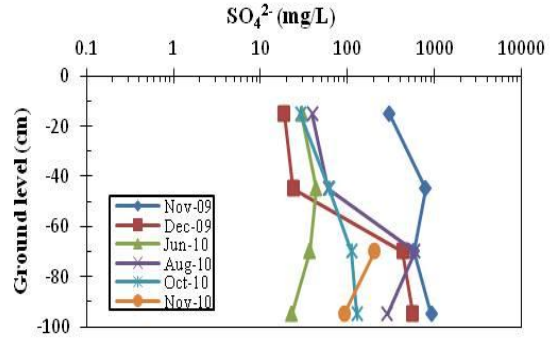
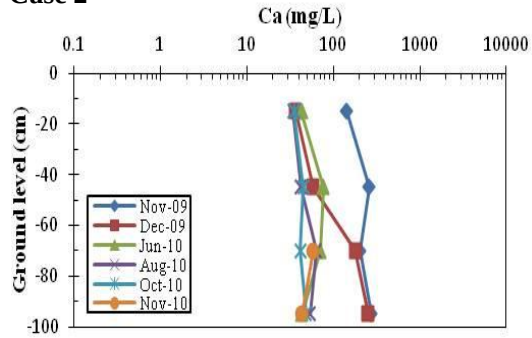


Fig. 5

Case 1



Case 2



Case 3

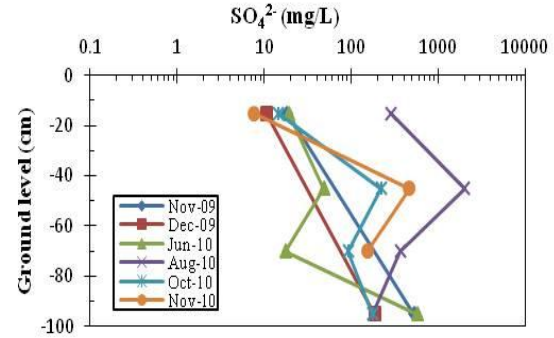
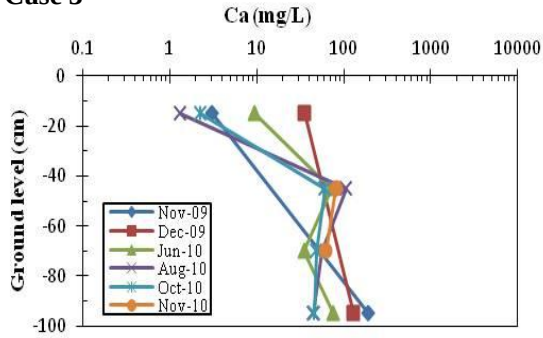


Fig. 6

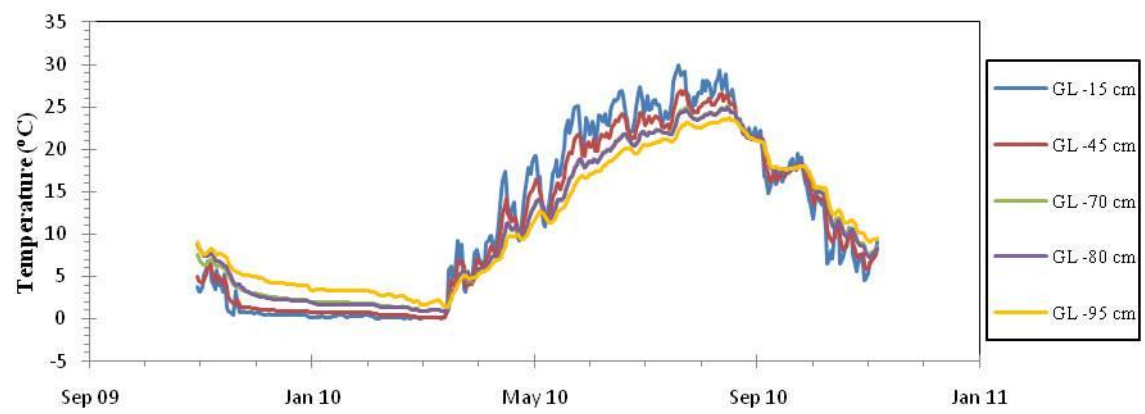
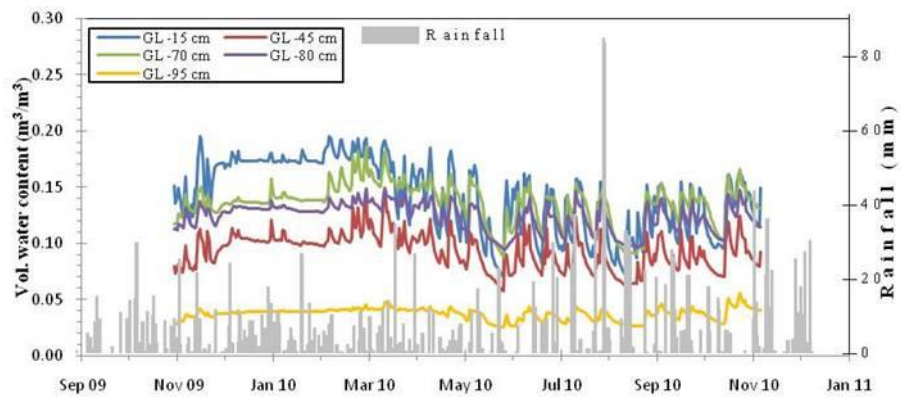


Fig.7

Case 1



Case 3

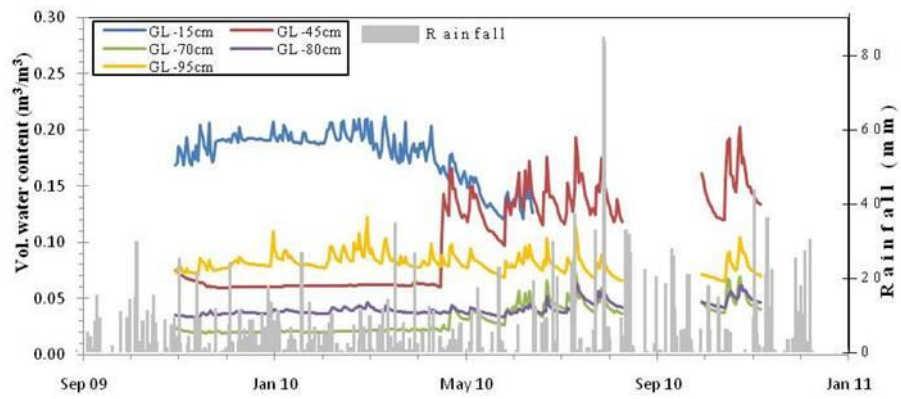


Fig.8

Table 1 Chemical composition of the surface rocks

Sample/ Element	K ₁	K ₂	K ₃	K ₄
SiO ₂ (wt.%)	63.2	69.0	70.3	72.7
TiO ₂ (wt.%)	0.72	0.69	0.65	0.13
Al ₂ O ₃ (wt.%)	11.8	9.29	8.94	12.5
Fe ₂ O ₃ (wt.%)	6.52	5.82	5.13	2.54
MnO (wt.%)	0.03	0.03	0.05	0.01
MgO (wt.%)	3.93	2.78	2.62	1.31
CaO (wt.%)	2.58	2.91	2.55	0.01
Na ₂ O (wt.%)	0.24	1.0	0.7	0.19
K ₂ O (wt.%)	2.39	1.86	2.33	3.96
P ₂ O ₅ (wt.%)	0.09	0.08	0.02	0.03
S (wt.%)	0.77	0.48	0.61	1.0
LOI (wt.%)	3.72	7.46	3.71	5.8
Cu (mg/kg)	34.0	39.8	37.2	98.2
Zn (mg/kg)	94.7	81.8	90.4	31.0
Pb (mg/kg)	15.5	10.3	13.7	22.8

Table 2 Mineral composition of the surface rocks

Sample name	Identified mineral
K ₁	quartz
K ₂	quartz, feldspars, barite
K ₃	quartz
K ₄	quartz, pyrite

Table 3 Physical and chemical properties of layers

Layer	Wet density (g/cm ³)	Dry density (g/cm ³)	Hydraulic conductivity (cm/s)	pH*	ORP* (mV)	EC* (μS/cm)
Weathered rock	1.95	1.58	1.05×10^{-2}	3.80	420	55.5
Neutralization	1.94	1.58	1.46×10^{-2}	8.14	187	164
Low permeable	1.81	1.23	1.52×10^{-6}	6.15	267	27.2

* The pH, ORP and EC are the data of suspension of layer material.

Table 4 Variances in the volumetric water content for cases 1 and 3 with or without snow cover

Case	Depth	Snow cover season	No snow cover season
1	-15	2.5E-04	6.5E-04
	-45	1.3E-04	2.0E-04
	-70	1.4E-04	3.5E-04
	-80	3.7E-05	1.7E-04
	-95	5.2E-06	3.6E-05
3	-15	8.6E-05	8.8E-02
	-45	1.6E-06	7.9E-04
	-70	8.6E-07	1.2E-04
	-80	5.5E-06	4.5E-05
	-95	5.8E-05	7.0E-05