Spatial and Temporal Variations of Groundwater Chemistry Before and During Coal Mine Reclamation Using Flue Gas Desulfurization (FGD) Materials

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Abstract

Water quality in the uppermost aquifer system underlying a surface coal mine is analyzed to determine the impact of reclamation using flue gas desulfurization (FGD) gypsum. Water samples collected monthly from nine monitoring wells surrounding the reclamation area and two nearby surface water bodies are analyzed for over 27 water quality constituents. Based on results from 18 months of “pre-reclamation” monitoring, the background water quality was determined to assess both temporal and spatial variations. The background data is then analyzed to explore the similarity of hydrochemical properties among the monitoring wells and surface waters using hierarchical cluster analysis (HCA). The Ward’s method used in HCA groups water samples into three major groups, which have distinctive predominant cations and anions. The observed similarity is likely correlated to the geological layers where the groundwater samples are collected from, as well as the direction of groundwater flow. Four important components, which explain over 80% of the variability observed in the water quality data, are extracted from the monitored water quality constituents using principal components analysis (PCA). Principal Component 1 (PC1) corresponds to major ions (e.g., SO_4^{-2}, Cl^-, K^+, Ca^{2+}, and Na^+) and the resulting comprehensive parameters (i.e., electrical conductivity and TDS). PC2, PC3, and PC4 are correlated with Si, alkalinity, and B, respectively. Currently, over 170,000 tons of FGD gypsum and sulfite-rich material have been used for the on-going reclamation activity. The impact on water quality is assessed using data collected from over 12 months of “during-reclamation” monitoring with a statistical trend analysis method.

1. Introduction

The presence of abandoned mine lands (AMLs) posts serious threats to human and environments, including disrupting nearby surface water streams, discharging acid mine drainages (AMDs), creating dangerous highwalls, and establishing unsafe habitats to wild animals. It is estimated that, in Ohio, the unreclaimed strip mine lands contribute as much as 250 tons per acre per year of sediments into streams and lakes[1]. About 1,300 miles of streams in the state have been impacted by acid mine drainage[2]. In addition, many miles of potentially dangerous highwalls (height ranging from 20 feet to 100 feet) are created. The reclamation of AMLs is imperative to improve the quality of the environment of impacted regions, particularly in east and southeast of Ohio. However, funds earmarked to these reclamations are limited.

Utilizing FGD by-products (including fixated sulfite rich FGD and sulfate rich FGD gypsum) for mine reclamation applications can be an effective and economical approach[3]. Comparing to reclamation using natural materials, the FGD reclamation approach can reap cost savings. A number of studies utilizing FGD by-products (mainly fixated FGD material) to reclaim AMLs have been reported. However, using FGD synthetic gypsum has yet been demonstrated. Due to operational reasons, forced oxidation process has become the preferred FGD technology[4]. As a result, more FGD synthetic gypsum is produced over the years. Because of different engineering and chemical properties between fixated FGD material and FGD gypsum, the environmental and engineering responds of these two materials to the reclamation are expected to be different.

To assess the feasibility of using FGD synthetic gypsum in large volume for reclamation at surface coal mine, a full-scale demonstration project is carried out at an abandon highwall pit near Conesville, OH. The original highwall pit is about 1200 feet long and up to 100 feet in height with an estimated FGD gypsum backfill capacity of about one million tons. The reclamation started from July, 2011, and currently, more than 170,000 tons of FGD gypsum has been backfilled. To evaluate the impact of the reclamation operation on the water quality of the uppermost aquifer system underlying the reclamation site, the variations of 27 water quality constituents in the nine monitoring wells surrounding the reclamation area and two nearby surface waters are closely monitored.

In this paper, based on 18 months of “pre-reclamation” monitoring results, the temporal and spatial variations of the background water quality are discussed. In addition, the impact of reclamation operation on the water quality is assessed using data collected from over 12 months of “during-reclamation” monitoring.

2. Water Quality Monitoring

The Conesville reclamation site sits on the Middle Kittanning No.6 Coal bed seam. The bottom of No.6 coal seam is about elevation 817 ft at the site and is underlain by approximately 15 to 20 feet of shale units (under clay). The No.6 coal seam was extensively surface mined at the site prior to 1977 (i.e., before enactment of the surface mine Control and Reclamation Act), resulting in exposed abandoned highwalls, open pits, and adjacent mine spoil deposits.   The exposed highwalls above the No.6 coal seam are predominately sandstone.

The groundwater samples are collected monthly from the nine monitoring wells surrounding the site. The relative locations of these wells can be seen in Figure 1. In brief, monitoring well MW-0901 is located on the hill top above the fractured highwall, which is a hydraulically upgradient well. The well is screened in the Middle Kittanning No.6 Coal seam. MW-0902 is located on the top of the minespoil bank and also screened in Middle Kittanning No.6 Coal seam. MW-0903 and MW-0904 are located on top of the adjacent minespoil banks and are screened at the base of the mine spoils. Four feet away from MW-0903 is MW-1001, whose bottom of the screen is within the Middle Kittanning No.6 Coal horizon. MW-0905 and MW-0906 collect water from the Clarion sandstone and the unconsolidated sediments associated with the glacial sediments, respectively. MW-1101s and MW-1101d are clustered to monitor the water quality of the colluvial/mine spoils and Clarion sandstone, respectively. These two clustered wells are located at the estimated 5-year travel time down-gradient from the reclamation site. Surface water samples are collected from a nearby pond (i.e., Oxford Pond) and water in the highwall pit (i.e., East Pond).

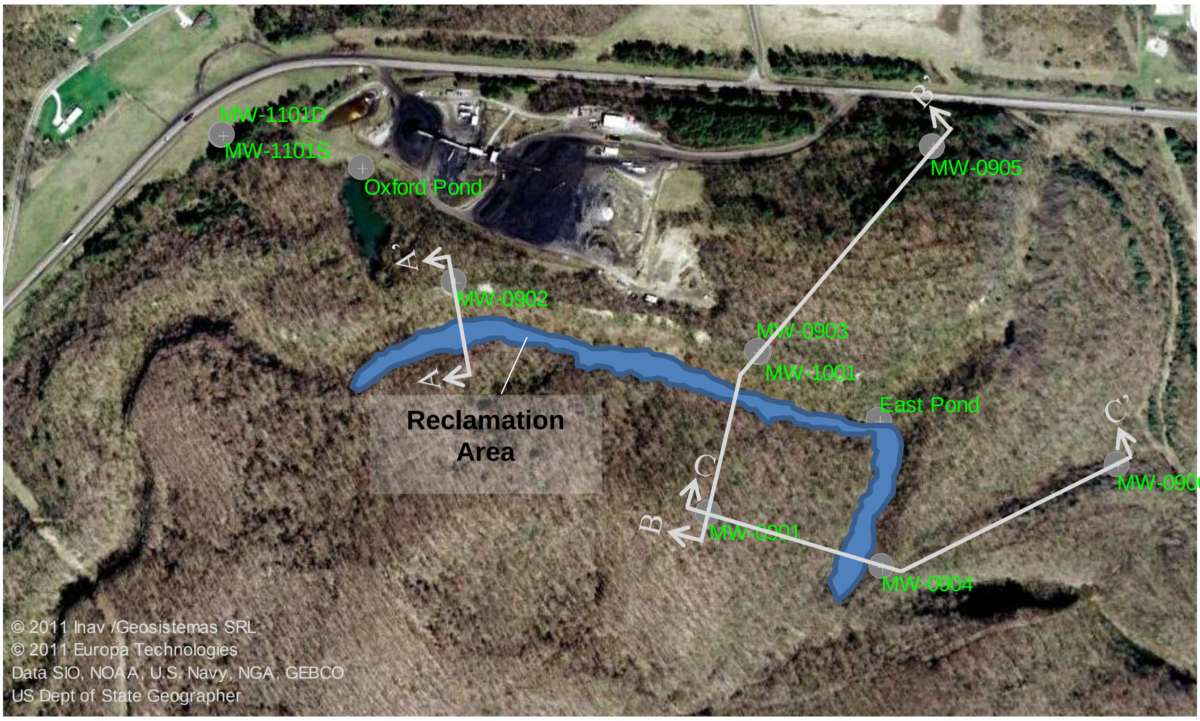

Figure 1. Conesville Five Point Site. Gray circles represent the approximate locations of groundwater monitoring wells and surface water sampling points, respectively. The reclamation area is marked as light blue for identification.

Groundwater sample is collected from each well using a low-flow purging and sampling procedure, except for MW-0903, where the bailing method is used. Before representative sample is collected, water is purged at a proper flow rate until both pH and conductivity of the water stabilize. After purging, water sample is filtered and collected into two 250-mL HDPE sample bottles. A new disposable filter cartridge with 0.45μm pore size is used for each well. One of the two collected samples is preserved with 2% nitric acid for elemental analysis, which includes aluminum (Al), arsenic (As), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), copper (Cu), chromium (Cr), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), mercury (Hg), nickel (Ni), and selenium (Se), sodium (Na), silver (Ag), thallium (Tl), and zinc (Zn). Another sample is analyzed for acidity, alkalinity, chloride (Cl), fluoride (F), sulfate (SO_4^{-2}), and total dissolved solids (TDS). The pH and conductivity of collected samples are measured on site. During every sampling event, field duplicate and trip blank are included as part of the QA/QC procedure.

3. Statistical Analysis

The statistical analysis carried out in this study was performed by either JMP Pro. 9.0 or ProUCL Version 4.1[5].

4. Results and Discussion

4.1 Upper Prediction Limits

Based on the groundwater data collected during a period from November, 2009 to July, 2011 before reclamation started, the upper prediction limit (UPL) of each monitored constituent was estimated to establish a “not-to-exceed” threshold value for every well and nearby surface water. Establishing the prediction limits allows the monitoring program to provide convenient and statistically valid values to evaluate if significant changes occur after reclamation starts.

Depending on the distribution of the monitoring data, UPL was determined by normal, lognormal, Gamma, or non-parametric Kaplan-Meier models. The non-detects were replaced by half their detection limits if the percentage of non-detects is less than 15%. A parametric robust regression on order statistics (ROS) procedure was employed to estimate the non-detects when there are 50% or fewer non-detects. A non-parametric Kaplan-Meiler method was used for data set that has more than 50% of non-detects. If no detectable value was observed in the data set, the Double Quantification Rule (DQR) will be applied to determine if exceedance occurs.

4.2 Spatial Variation

As described, the groundwater samples at the reclamation site are collected from different geological layers. As expected, the hydrochemial properties of water from different sampling locations vary. Figure 2 demonstrates the spatial variations of four selected parameters, i.e., pH, TDS, sulfate, and magnesium, based on the background monitoring data.

To examine the similarity in the hydrochemical properties of the monitored groundwater and surface water, hierarchical cluster analysis (HCA) with Ward's method was used to group water samples into classes on the basis of 16 parameters, i.e., pH, conductivity, alkalinity, TDS, Cl, SO_4^{-2}, K, Ca, Mg, B, Fe, Mn, Na, Ba, Si, and Sr. The Ward's method uses an analysis of variance approach to minimize the sum of squares of any two hypothetical clusters. The dendogram from HCA is shown in Figure 2. The linkage distances between the clusters in the dendogram illustrate relative similarities in the water chemistry of the samples.

As demonstrated in the figure, the water samples can be classified into three major groups. The number of clusters was selected by considering the minimum number of clusters that explain most of the variation in the hydrochemical properties of water samples. The first cluster contains monitoring wells, i.e., MW-0901, MW-0905, and MW-1001, screened in the clay shale or sandstone layers. The surface water in East Pond has similar properties. In general, the water samples in this cluster have low concentration levels of major ions and total dissolved solids. From the linkage distance, this cluster can be further divided into two sub-groups. The characteristics of groundwater collected from MW-0901 and MW-1001 are very comparable. The Piper's tri-linear diagram shown in Figure 3 illustrates the similarity. The figure is consisted of two triangular fields showing the percentage milliequivalent (meq) values of major cations (i.e., Ca, Mg, Na, and K) and anions (HCO_3^-, CO_3^{-2}, Cl^-, and SO_4^{-2}), as well as a central diamond-shaped field representing the overall characteristics of water. According to the Piper's diagram, water samples collected from MW-0901 and MW-1001 have mixed dominating cations (i.e., Ca, Mg. K/Na) and anions (HCO_3^{-2}, SO_4^{-2}, and Cl^-) compositions. On the other hand, Ca and SO_4^{-2} are the dominating ions in MW-0905 and East Pond, respectively.

The HCA dendogram in Figure 3 also shows the water samples collected from MW-0902 and MW-0903 have similar hydrochemical properties and are statistically different from samples collected from other locations. The waters in these two wells have the highest total dissolved solids, which is due to high levels of Ca, Mg, and SO_4^{-2}. MW-0903 is screened in the minespoil layer. Although the screen of MW-0902 is located in the No.6 coal seam, the vertical fractures of the geological condition suggests the chemical properties of the water from this well might be affected by the overlaying mine spoil layer. The Piper's diagram shows the waters of these two wells are either Mg or Ca-sulfate types. The hydrochemical properties of water samples in the third cluster are very similar to the ones in the second cluster but with lower concentration levels of major ions and total dissolved solids. The linkage distance further demonstrates that the water properties of MW-0904 and MW-0906 are very similar. Both wells are located on the east side of the reclamation site. Groundwater recharged from the East Pond flows from MW-0904 toward to MW-0906. The increases of TDS and the concentrations of major elements as groundwater travels downstream suggest dissolution process along the groundwater path.

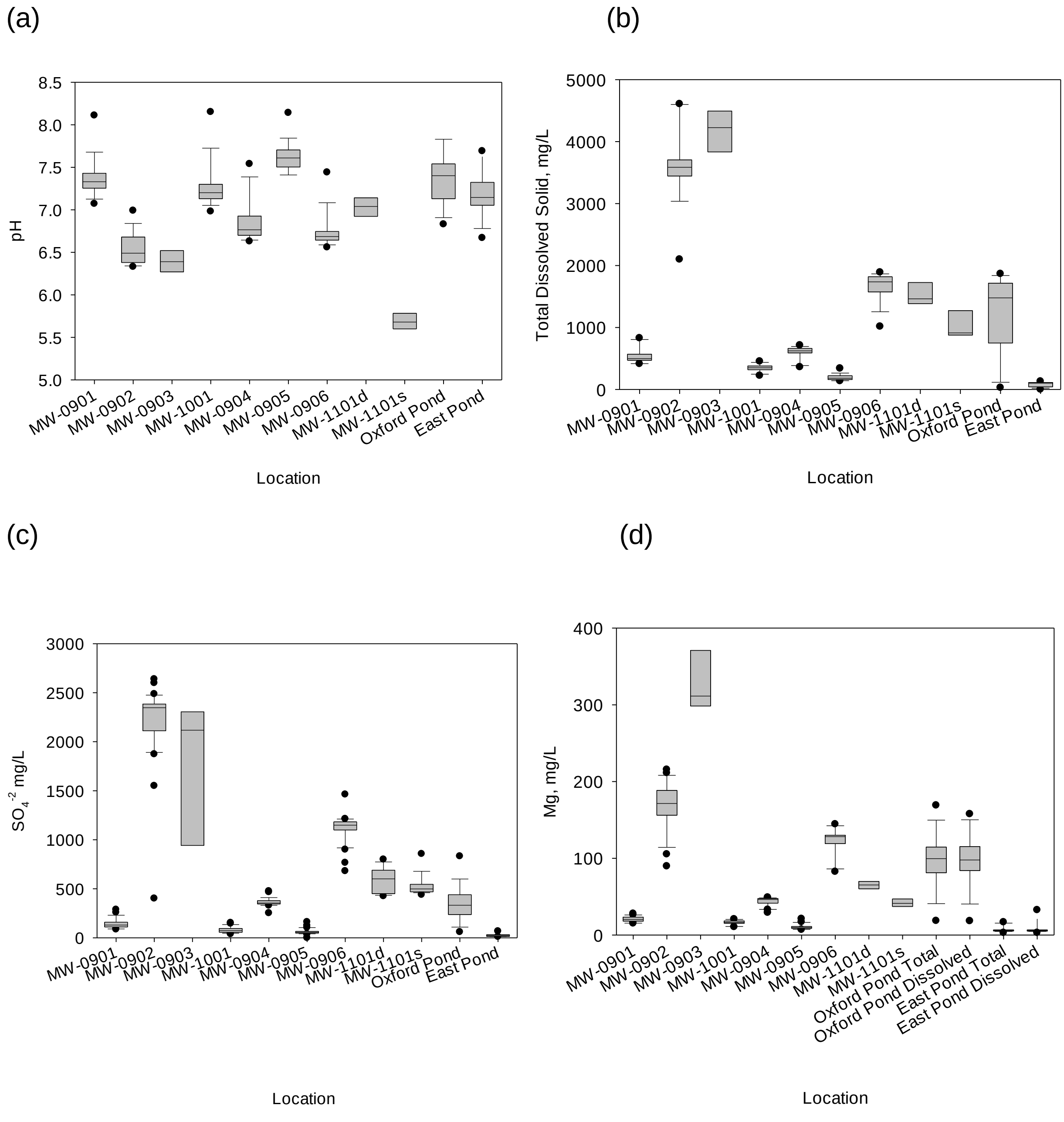

Figure 2. Summary of (a) pH, (b) total dissolved solids, (c) sulfate, and (d) iron in groundwater wells and surface waters during pre-reclamation period.

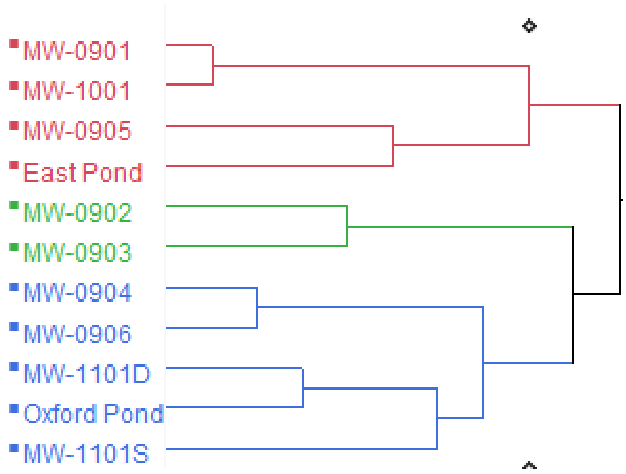

Figure 3. HCA dendogram based on background water quality

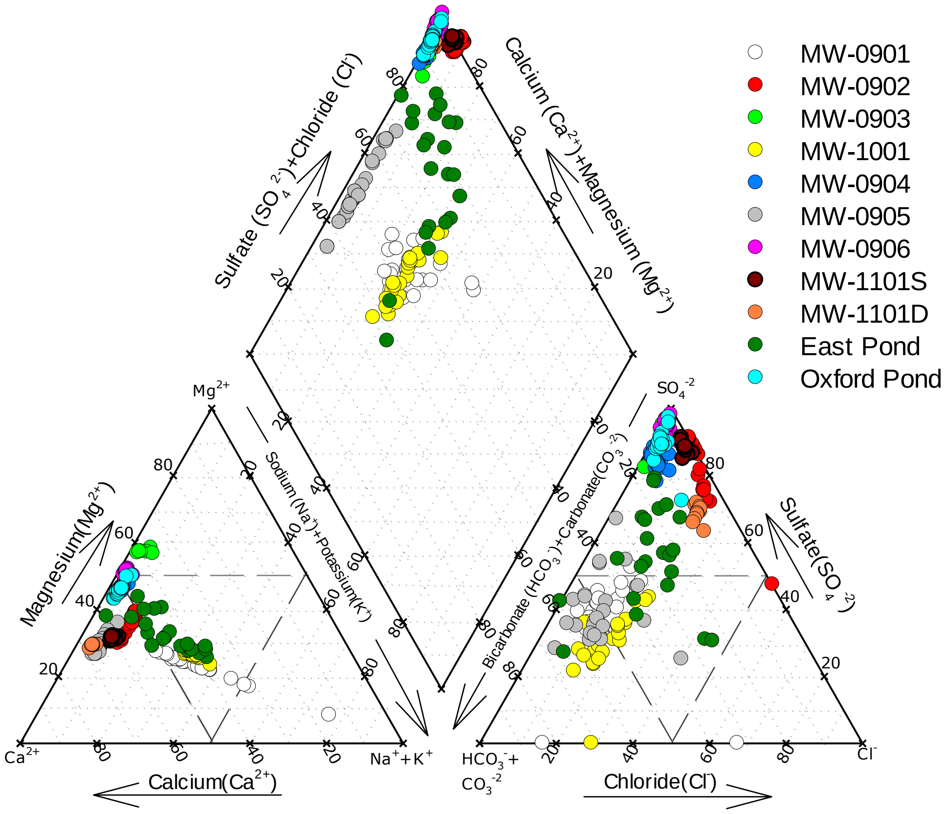

Figure 4. Piper's diagram

The important components that explain most of the variances among water samples were evaluated by principal components analysis (PCA). Four components with eigenvalues greater than 1 were extracted from PCA, which explain most of the variability observed in the water data. The cumulative variance explained by the four components is 81.36%. The variable loadings in each component were considered to be strong when the correlation coefficient is greater than 0.75. The first component (PC1), accounting 40.82% of the total variance, is correlated with a number of major ions, such as SO_4^{-2}, Cl^-, K, Ca, Mg, Na, and Sr, as well as the comprehensive parameters, such as electrical conductivity and TDS. PC1 is likely related to the natural characteristics of the geological layers or locations where water samples are collected from. The second component, explaining 15.84% of variance, is correlated with Si. It might be due to the weathering of silicates. The most significant PC2 contributors are MW-0901 and MW-1001 where the groundwater samples are collected from the clay shale and/or sandstone layers. The third component, explaining 15.66% of variance, is correlated with alkalinity, indicating the dissolution of carbonates also plays significant role in controlling the groundwater and surface water properties at the site. The fourth component is correlated with B and Ba, which explains 9.05% of variance.

4.3 Effect of Reclamation Activity

The temporal trends of selected water quality parameters, i.e., pH, total dissolved solids, SO_4^{-2}, and Mg, are shown in Figure 5. Only results from Oxford pond and groundwater monitoring wells adjacent to the reclamation site are included. MW-0903 is excluded from the figure because the well was mostly dry during the monitoring period. East Pond was pumped dry as the reclamation at the highwall pit progresses. In the figure, the upper prediction limits (UPLs) of the four selected parameters in each sampling location are shown as dashed lines. As demonstrated, the values of the selected parameters are within the range of background variation. It is also true for all other monitored parameters (data not shown).

The results indicate that currently the reclamation operation has no statistically significant impact on the water quality of the underlying aquifer system. In addition, based on a non-parametric Mann-Kendall test with a confidence level of α=0.005 (Table1), no significant positive or negative trend in pH, total dissolved solid, sulfate, and magnesium is observed over the period of monitoring.

Table 1. Well, number of observations (obs.), and Mann-Kendall trend Statistics (MK state) for pH, total dissolved solids (TDS), sulfate (SO_4^{-2}), and magnesium (Mg) in water samples collected from monitoring wells and surface water around the reclamation highwall pit. Trend is statistically significant when $p<0.005$.

Location	Obs.	pH		TDS		SO_4^{-2}		Mg	
		MK stat	*p*-Value	MK stat	*p*-Value	MK stat	*p*-Value	MK stat	*p*-Value
MW-0901	13	1.467	0.071	0.671	0.251	0.915	0.184	1.769	0.038
MW-0902	13	0.061	0.476	-0.305	0.38	0.000	0.524	2.013	0.022
MW-1001	13	-0.368	0.383	-1.403	0.080	-0.915	0.184	1.647	0.05
MW-0904	13	-1.168	0.121	-0.061	0.476	0.671	0.255	1.891	0.029
MW-0905	13	-0.733	0.232	2.379	0.009	0.793	0.214	1.403	0.080
MW-0906	13	-0.368	0.383	-0.793	0.218	-2.013	0.021	1.281	0.100
Oxford pond	13	-0.183	0.427	1.281	0.102	1.647	0.050	2.013	0.022

5. **Conclusions**

The water quality of the uppermost aquifer system underlying a highwall pit was continuously monitored for 18 months before the reclamation using FGD gypsum at the abandoned surface mine started. Using the established background data, we estimated the upper prediction limit (UPL) for each of the 27 monitored water quality constituents. The “not-to-exceed” threshold value is determined to evaluate if significant changes occur during (including site preparation and FGD gypsum backfill) and after reclamation. By comparing the results collected from 12 months of “during reclamation” monitoring with UPLs, the reclamation operation showed no statistically significant impact over the reported monitoring period. In addition, no distinctive increasing or decreasing trend in the values of selected water quality parameters, i.e., pH, total dissolved solid, sulfate, and magnesium, is observed.

The similarity in the hydrochemical properties of samples collected from different groundwater wells and surface waters was examined using a hierarchical cluster analysis (HCA) method. The water samples can be classified into three major groups. The first group contains water samples from the monitoring wells adjacent to the reclamation site that are screened in the clay shale or sandstone layers. The water quality of the East Pond also belongs in this group. The second group comprises water samples owning the highest total dissolved solids, which is likely associated with the presence of minespoil bank around the sampling location. In the third group, water samples collected from the groundwater monitoring wells or surface water in close vicinity show similar characteristics, which might be correlated to the directions of groundwater flow.

At present, the reclamation of the highwall pit is still ongoing. The water monitoring at the site will continue throughout the reclamation stage, as well as after the reclamation is completed. With the data collected from the long-term water quality monitoring program implemented in this demonstration project, it allows the environmental response to the approach of using FGD gypsum in the reclamation of abandoned mine land to be accurately characterized.

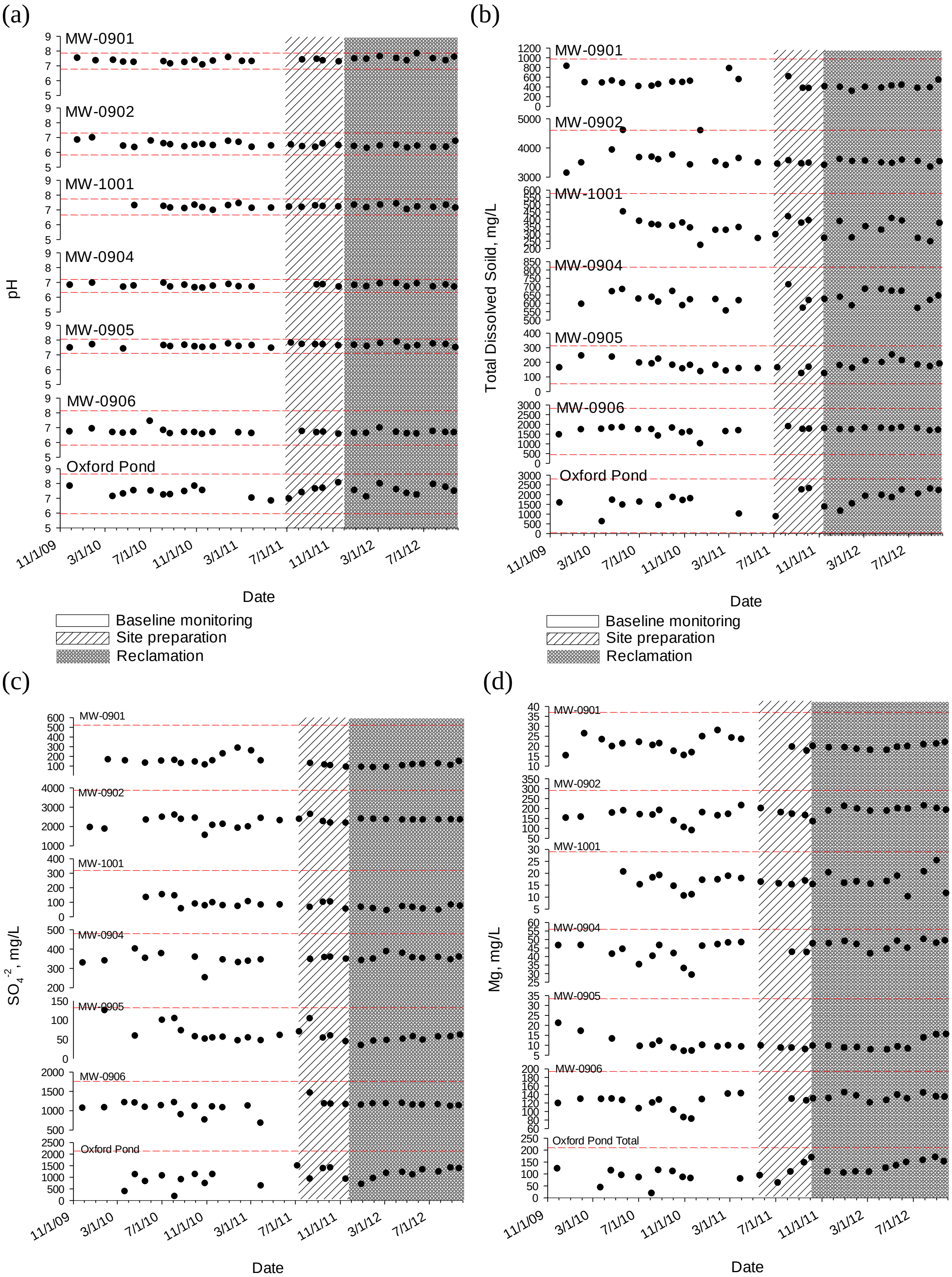

Figure 4. Temporal trends of (a) pH, (b) total dissolved solid, (c) sulfate, and (d) magnesium in the water samples collected from groundwater wells and surface water adjacent to the reclamation site. The dashed lines represent the upper prediction limits.

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