

# CCP Groundwater Monitoring – Importance of Groundwater Redox Conditions

**Michael J. Alowitz<sup>1</sup>, Kevin G. Armstrong<sup>1</sup>**

<sup>1</sup>MWH Americas, Inc., 11153 Aurora Ave., Des Moines, IA 50325

KEYWORDS: CCP, CCR, groundwater, monitoring metals, redox, arsenic, selenium, iron, leachate, ORP

Coal Combustion Products Monofills and Groundwater Monitoring

## ABSTRACT

Assessment of the impact of a coal combustion products (CCP) monofill on groundwater is usually accomplished through traditional groundwater monitoring methods. The compounds of primary concern are typically metals, which may be found in CCP and leachate generated in a CCP monofill. When assessing groundwater conditions, the effect of reduction-oxidization (redox) conditions on metal speciation must be considered. Under different redox conditions (e.g., an oxidizing environment or a reducing environment) the speciation, mobility, and toxicity of metals varies. Redox conditions can change naturally, resulting in metals concentrations unrelated to the release of leachate. As a result, redox conditions should be measured along with metals and other traditional monitoring parameters in order to interpret metals results and provide another line of evidence for evaluating the potential release of leachate to groundwater.

At a former greenfield site developed as a CCP monofill, MWH observed a range in metals concentrations, including non-detect values of some metals found in abundance at other monitored locations on site. Further monitoring indicated a range of redox conditions corresponding to the presence of metals in certain groundwater monitoring wells. Changes in redox condition may lead to observation of metals in groundwater samples that were previously present in a less mobile form rather than a release of leachate from the monofill.

## INTRODUCTION

Regulations for CCP monofills are expected to become more rigorous with standards established at the Federal level. Groundwater monitoring at CCP monofills is a required component of monofill operation in many states, but the extent of these programs is variable. Future regulations at the Federal level will likely make this monitoring mandatory and establish minimum requirements for frequency and possibly analytes. These same regulations will also likely require a composite liner system at CCP monofills. The changing regulations will likely lead to a more robust monitoring program that includes additional analytes at existing and new disposal facilities.

Analysis of dissolved metals will be part of the monitoring program, to help assess potential leachate releases from CCP monofills. Unlined disposal areas may gradually expand or be long-standing operations; whereas new, composite lined monofills will represent a new phase of large-scale construction at many facilities. With this new land development, the groundwater conditions are likely to be affected and vary from current conditions.

This paper presents data from a CCP monofill where metals concentrations in groundwater varied significantly between wells. The differences appear to be related to reduction-oxidation (redox) conditions (i.e., metals concentrations varied based on oxidizing or reducing groundwater conditions). The implication of this data is the appropriateness of collecting oxidation-reduction potential (ORP) readings during background investigations and groundwater monitoring events to help assess the potential for metals already in the subsurface to be mobilized versus released from the monofill.

## BACKGROUND

The analytical data presented herein is from a former greenfield site developed as a CCP monofill. The site was formerly used for agriculture and was developed into a multi-cell composite-lined CCP monofill for disposal of fly ash, bottom ash, and flue gas desulfurization waste ash. Site geology includes layers of sands, silts, and clays consistent with alluvial flood plain deposits. The general site lithology is composed of approximately 2 feet of silty clay, sandy silt, or silt over a layer of medium-to fine-grained sand with varying quantities of silt that extends to approximately 25 feet below ground surface (bgs). Several borings completed during the background investigation encountered clay layers up to 50 feet thick. In borings that were extended more than 26 feet, the sand unit generally coarsened and was less sorted. The deepest boring advanced on site was drilled to over 100 feet bgs and bedrock was not encountered.

Prior to site development groundwater monitoring was conducted across the site and one of the background investigation wells remained as an upgradient background sampling location for the monofill development and monitoring program.

Although groundwater flow is generally toward a nearby river, reversals of groundwater flow direction have been observed when the river levels increased. In recent years, river levels have remained elevated for extended periods of time relative to the previous decade.

Groundwater at this site is typically sampled on a quarterly basis from monitoring wells within 30 feet of all sides of the waste placement boundary plus the background monitoring location.

## MONITORING DATA

Groundwater monitoring results after cell construction showed varying levels of arsenic, iron, and selenium even in wells less than 500 feet apart. Figures 1, 2, and 3 show concentrations of dissolved arsenic, iron, and selenium in groundwater samples from four selected wells with the longest monitoring record at the site. MW-1 serves as a background monitoring well located away from the fill area. Monitoring wells MW-10 and MW-11 are on the upgradient side of the fill areas, and MW-12 is located cross-gradient. Monitoring wells MW-10 through MW-12 were installed after the initial phase of cell construction was completed. The monofill has been expanded since the initial phase but these wells have remained in the same position relative to the site (i.e., upgradient has remained upgradient).

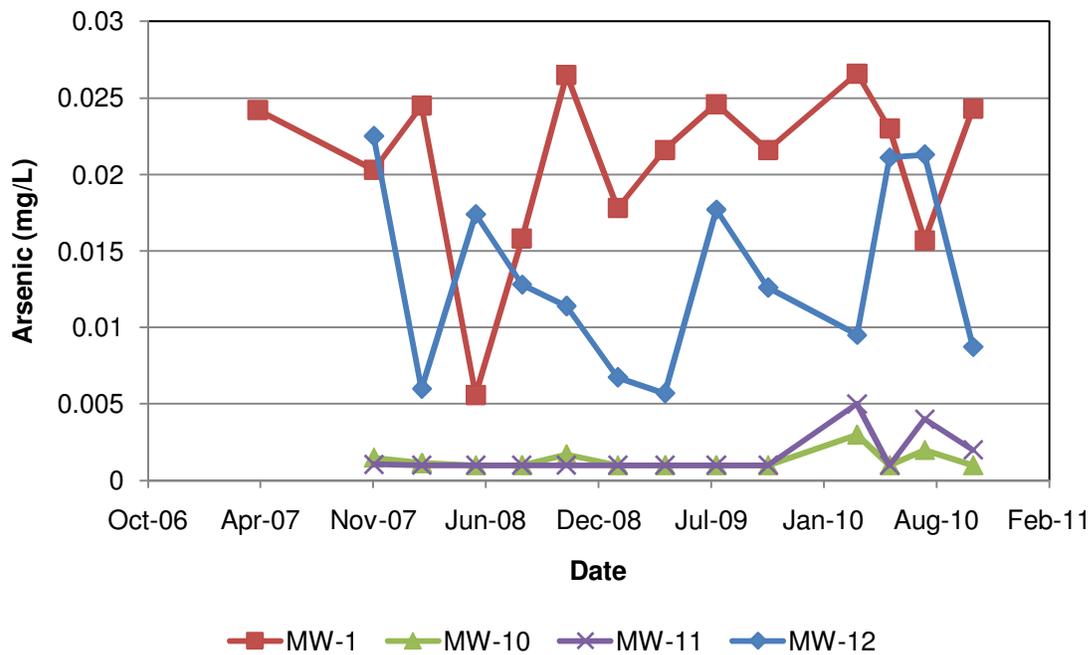


Figure 1. Dissolved arsenic in groundwater.

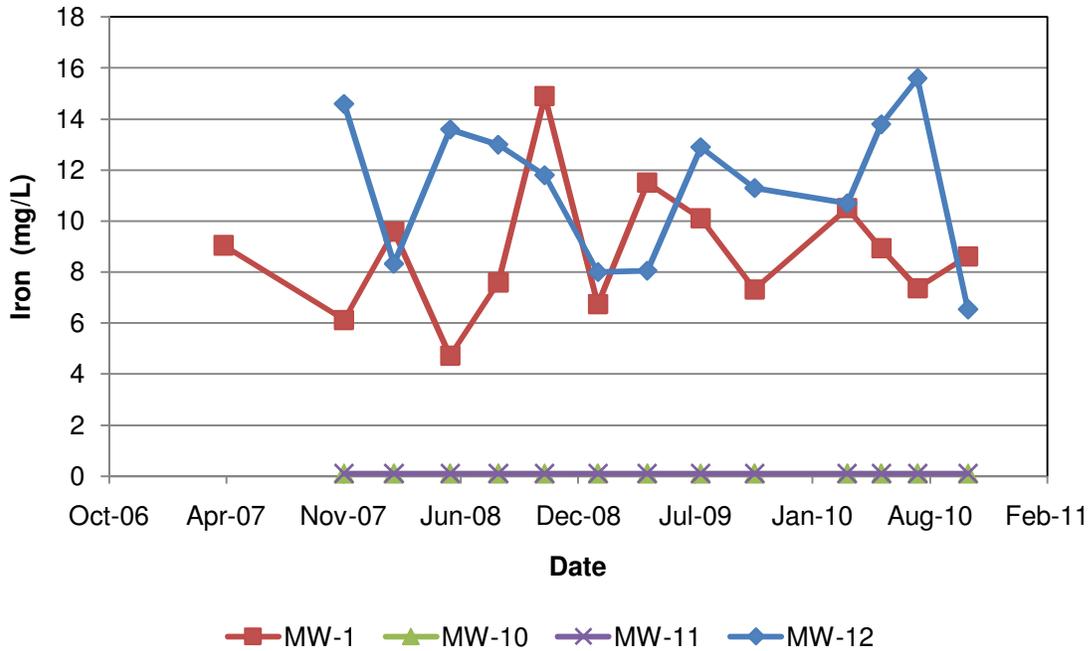


Figure 2: Dissolved iron in groundwater.

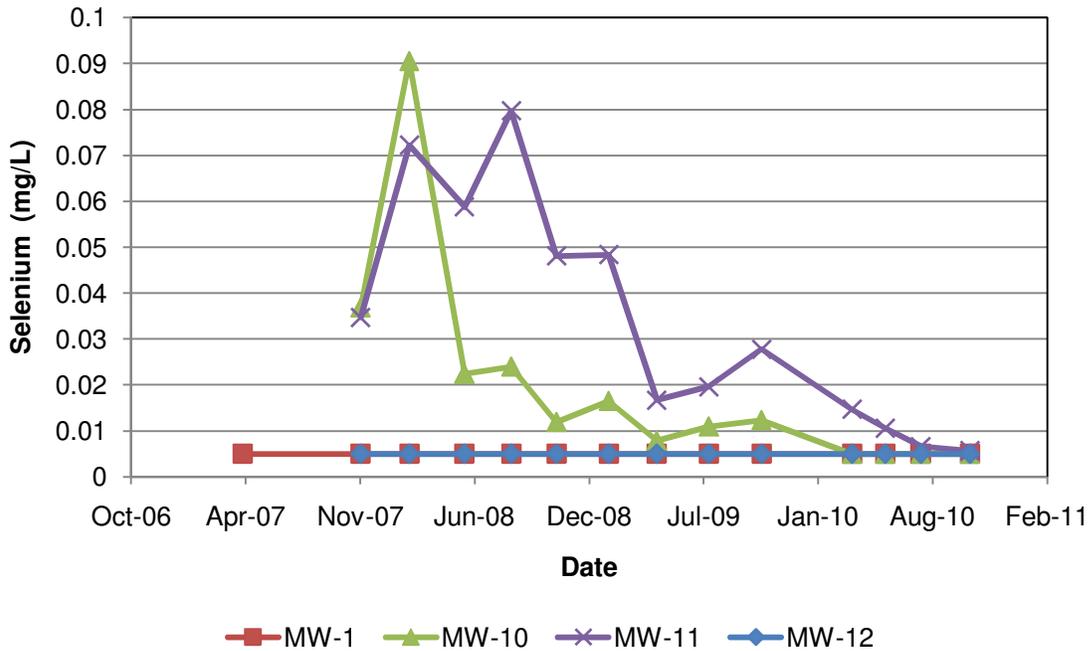


Figure 3. Dissolved selenium in groundwater.

Despite the close proximity of MW-10, MW-11, and MW-12, significantly different patterns of metals detected in groundwater were observed. Monitoring wells MW-1 and MW-12 typically exhibit arsenic and dissolved iron, while MW-10 and MW-12 results are typically non-detect for these analytes. Selenium has typically been reported in MW-10

and MW-11, but not detected in MW-1 and MW-12. The strong pattern of iron concentrations led to the hypothesis that redox conditions may be partially responsible for the different patterns in metal concentrations.

In addition to pH, temperature, and conductivity data which were routinely collected from the monofill wells in 2009 and 2010; ORP readings were also collected. Figure 4 shows the ORP data on the same timescale as Figure 1, 2, and 3.

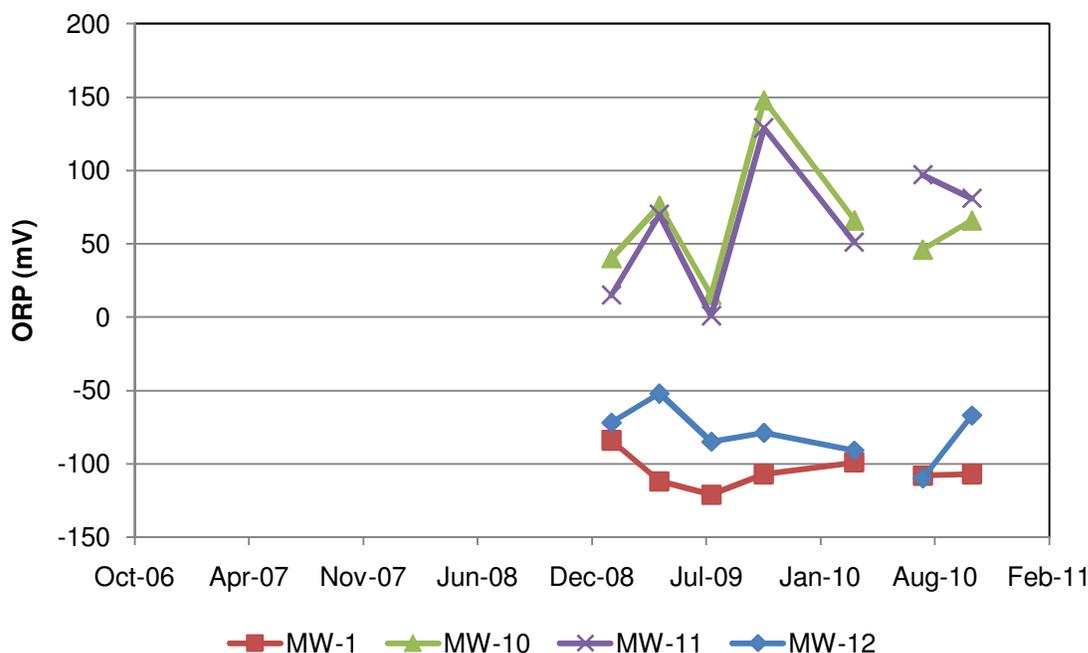


Figure 4. ORP readings for select monitoring wells.

The data in Figure 4 show two distinct geochemical regimes are present in the monitoring wells. Oxidizing conditions are consistently reported in monitoring wells MW-10 and MW-11, while reducing conditions are reported in MW-1 and MW-12. These data suggest detection of arsenic, selenium, and iron at this site parallels trends in redox conditions. The more recent decrease in selenium concentrations, however, is not mirrored in the ORP values (i.e., the selenium decreases at MW-1 and MW-12 are not paired with a corresponding increase in ORP). Because the samples were field-filtered, the potential for turbidity impacts on metals concentrations is considered minimal for these samples.

Groundwater pH can also affect which metals may be present, as many metals can form carbonate complexes or oxides and precipitate from solution. The pH data for the site showed little spatial or temporal variability as shown in Figure 5.

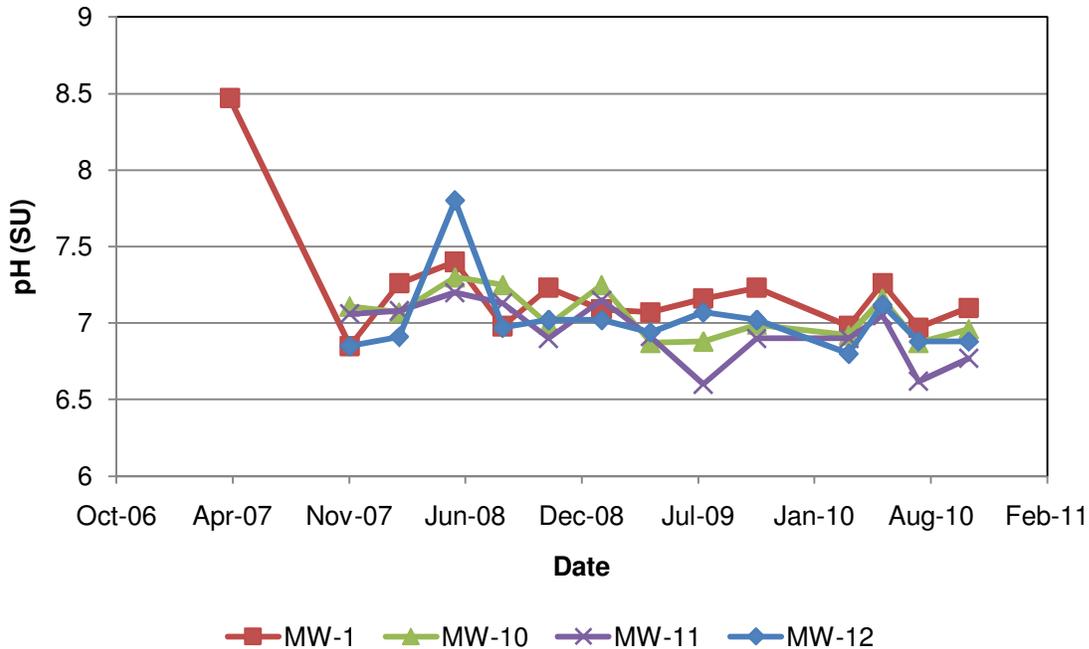


Figure 5. Groundwater pH at selected monitoring locations.

## DISCUSSION

Given the new construction of a composite-lined monofill cell at a former greenfield site, observation of groundwater impacts was not expected after CCP disposal was initiated. However, selenium in particular, which was not detected during background groundwater sampling, was reported in multiple groundwater samples following the initiation of monofill operations. Given the timeframe and sheer volume of leachate that would be required to cause such an impact, it was apparent the cause of selenium detections was not a release from the monofill. Additional data collection indicated differing geochemical conditions were influencing the metals present.

The cause of the variable geochemical conditions at the site, however, is not clear. The monitoring locations around the monofill are all close to locations of wells used for background sampling and were consistent with MW-1 results. In the course of constructing the monofill subgrade, dewatering was completed so adequate compaction could be achieved. This work in 2008 may have increased the oxidative effect of the shallow aquifer by exposing previously saturated areas to soil vapor. However, there has been no significant decrease in ORP observed at MW-10 and MW-11 despite more than two years of operation without nearby dewatering activities. A dewatering well was also in operation near MW-12 during construction but aquifer characteristics remained reducing. Groundwater elevation measurements indicate the depressed groundwater levels from dewatering rebounded when groundwater monitoring was first completed following the completion of monofill construction.

The presence of the monofill itself could have an impact on groundwater geochemistry as percolation is decreased relative to an agricultural field, resulting in less dissolved oxygen being transported to the underlying soils. However, the change observed was the appearance of oxidizing conditions. Iron was detected in all background (pre-construction) monitoring points but selenium was not detected at any background location. Since construction, in addition to the wells shown here, several other monitoring locations have exhibited non-detect concentrations of iron, including downgradient monitoring wells installed after other cells were constructed in 2009.

Oxidation state of metals can significantly affect mobility and toxicity. Some metals such as mercury and lead tend to be relatively immobile under most common groundwater conditions. In general, reduced forms of arsenic, cadmium, copper, and iron are more mobile in a reduced form and oxidized forms of chromium and selenium tend to be more mobile than their reduced state. Some of the more redox sensitive metals and their common valence state are shown in Table 1. The species of metals present can depend on concentrations of other ions (e.g., carbonate ions), pH, soil types, and ORP. At the CCP monofill site discussed, soil conditions and pH were similar at all sampled locations.

**Table 1. Valence state, relative toxicity and mobility of common metals species.**

Metal	Reduced Forms	Oxidized Forms	Source
Arsenic	As <sup>3+</sup> More Mobile More Toxic	As <sup>5+</sup> Less Mobile Less Toxic	[1], [2]
Chromium	Cr <sup>3+</sup> Less Mobile Less Toxic	Cr <sup>6+</sup> More Mobile More Toxic	[1]
Iron	Fe <sup>2+</sup> More Mobile	Fe <sup>3+</sup> Less Mobile	
Selenium	Se <sup>4+</sup> Less Mobile More Toxic	Se <sup>6+</sup> More mobile Less Toxic	[1]

## IMPLICATIONS AND RECOMMENDATIONS

The evaluation of groundwater data at this site indicates metals found in groundwater are likely naturally occurring and are present in a dissolved phase based on the groundwater geochemical environment. For example, although arsenic was not routinely detected in MW-10 and MW-11, it is likely present in an immobile form under the oxidizing conditions and would exhibit higher concentrations if reducing conditions were present. These changes in groundwater geochemistry can lead to difficulty in assessing the possible impact of leachate releases at sites without significant monitoring history or sufficient site data.

To help accurately assess the role of geochemical changes in metals concentrations at CCP monofills, a thorough background assessment should be completed. Ideally this assessment would allow for at least a year of monitoring, as seasonal fluctuations in groundwater elevations could cause changing conditions. Groundwater monitoring should also include a robust array of field parameters such as pH, conductivity or total suspended solids, ORP, and potentially dissolved oxygen. If total metals will be monitored in addition to dissolved metals it will be imperative to measure turbidity and attempt to minimize turbidity in sample collection procedures.

Based on observations at this site, it appears the disruption to the subsurface soils and groundwater caused by monofill construction may have a lasting impact on groundwater conditions. Therefore, frequent groundwater sampling following construction of a composite liner should be completed; even before CCP is placed in a new monofill, if possible. This will help provide documentation of the impacts of the construction on the subsurface and provide another baseline for comparison of future results after the potential for leachate releases exists. In long-term monitoring the collection of field parameters such as pH and ORP, in addition to routine laboratory data, will help characterize site conditions and better assess the potential impact of possible leachate releases.

## REFERENCES

[1] Mclean, Joan E., and Bert E. Bledsoe. Ground Water Issue Behavior of Metals in Soils. United States Environmental Protection Agency EPA540/S-92/018, October 1992.

[2] Watts, Richard J. Hazardous Wastes: Sources Pathways Receptors. John Wiley & Sons. 1998.