

## TRACE METAL DISTRIBUTION AND MOBILITY IN DRILL CUTTINGS FROM MARCELLUS SHALE GAS EXTRACTION

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**Keywords:** Drilling Waste Management; Long-term Metal Release; TCLP; Sequential Extraction; Marcellus Shale

### Introduction

Unconventional shale gas production using hydraulic fracturing has become an increasingly common energy extraction technique worldwide. The Marcellus Shale in the Appalachian Basin is a major unconventional gas reservoir in northeastern USA. Drilling operations from the Marcellus can generate estimated 375 tons of Marcellus shale drill cuttings from a typical horizontal portion of the drilling alone, and in Pennsylvania (PA) more than 1.2 million tons of drilling wastes from the Marcellus formation were generated in 2013 (Phan et al., 2015). The resulting drill cuttings may contain significant amounts of water-, oil- or synthetic-based drilling fluids along with the black shale rock cuttings, which can contain elevated organic matter and trace metal (e.g., As, Ba, Ni, Zn, Cu and U) content. Currently in the USA, drill cuttings are permitted to be deposited in on-site burial pits, municipal solid waste (MSW) landfills, or reused as road fills (Stuckman et al., 2015). However, there is limited information on the environmental impact of drill cuttings at these disposal sites. This study characterizes metal distribution and mobility in drill cuttings under different disposal scenarios (e.g., rainfall and landfill conditions), the results of which could assist in decision making for optimum waste management and disposal strategies.

### Methods

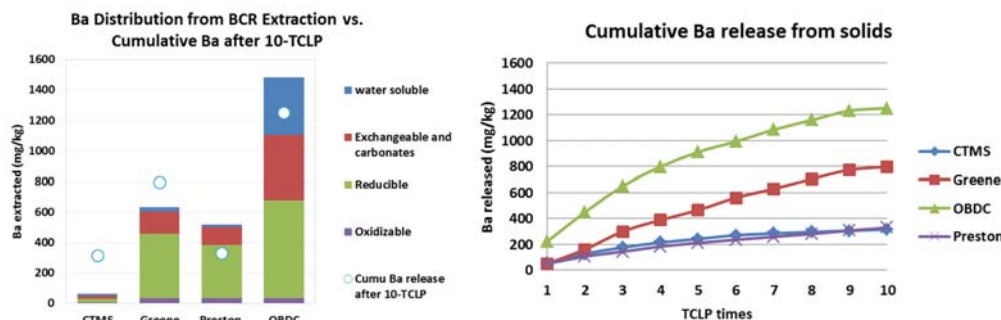
This study used one Marcellus outcrop from NY (CTMS), two water-based (Greene and Preston) and one oil-based sample (OBDC) of Marcellus shale drill cuttings from PA and West Virginia (WV), USA for solid characterization and leaching experiments (See Figure 1). The elemental compositions of all samples were determined by LiBO<sub>2</sub> fusion followed by inductively coupled plasma optical emission spectrometry and mass spectrometry (ICP-OES and -MS) analysis. X-ray diffraction (XRD) was utilized to determine mineral phases in all samples. A Community Bureau of Reference (BCR) sequential extraction (Rauret et al., 1999) was conducted to evaluate metal distribution in different solid fractions. All samples underwent short-term leaching experiments (18-24 hr) to simulate different disposal scenarios, including, 1) USEPA Method 3051 Toxicity Characteristic Leaching Procedure (TCLP), which simulates MSW landfill conditions, 2) USEPA Method 3052 Synthetic Precipitation Leaching Procedure (SPLP), which simulates acid rain leaching at an open pit or a cutting-filled road site, and 3) extraction tests using real rain water collected in Pittsburgh, PA. Single TCLP has been reported to underestimate mobility of selected contaminants with slow kinetics in selected wastes, due to limited pH neutrality of TCLP leachate and short contact time (Karamalidis et al., 2008). Therefore, we performed additional TCLP tests on the solids using a sequential 10-time extraction on all solids; where the TCLP leachate is renewed 10 times in 10 sequential leaching steps to evaluate potential long-term metal release under landfill conditions.

### Results

XRD results indicate that the Marcellus outcrop and drill cuttings consist primarily of quartz and various clays (illite, chlorite), with minor amounts of carbonate (calcite/dolomite), feldspar and pyrite. Halite (NaCl)

and barite (BaSO<sub>4</sub>) were also detected in selected drill cuttings, likely a result of barite having been used as the weighting agent and halite from drilling fluids in addition to the connate water in Marcellus shale (Phan et al., 2015). All solids have passed regulatory short-term leaching tests (TCLP and SPLP), and thus could be eligible to be disposed of in MSW landfills and open-pits or used as road-fills. However, leachates from these short-term tests contained significant amounts of ions released from drill cuttings (e.g., Na, Ca and Cl at 1-5.5 g/L each).

Results from the BCR extraction and sequential TCLP tests showed that BCR extractable trace metals could be mobilized completely by multiple-time TCLP. For example, Ba in drill cutting samples can be significantly extracted by BCR steps targeting exchangeable/carbonates phases and reducible phases (See Figure 1). Ba also exhibited long-term mobility from 10-time TCLP with cumulative Ba release up to 1250mg/kg, equivalent to 84% of total BCR-extractable Ba from oil-based drill cuttings (OBDC, see Figure 1). Similarly, multiple divalent metals (e.g., Cu, Ni, Zn, Cd and Co), mainly associated with oxidizable phases, showed long-term release potential and their cumulative TCLP release resembled total BCR extractable concentrations ( $\pm 35\%$  difference). Results also show that oxyanion-forming elements (e.g., As, Se, Sb, V and Mo) largely partitioned into the water soluble phase in OBDC, resulting in more rapid and extensive (up to 10 times larger) release from OBDC than those from water-based drill cuttings.



**Figure 1.** Ba distribution from BCR extraction (left panel) and cumulative Ba released from solids in sequential TCLP (right panel) of tested Marcellus shale samples. All units are in mg/kg.

## Conclusion

This study demonstrates that total dissolved solids pose major short-term release concern while divalent trace metals (e.g., Ba, Ni, Co, Cu and Zn) may be of risk for long-term mobility from drill cuttings. In addition, drill cutting types (oil-based vs. water-based) may affect oxyanion release behavior. This research improves the understanding of metal and oxyanion mobility from different Marcellus shale drill cuttings under different disposal scenarios and can inform future drilling waste management options.

## References

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