Evaluation of Background Concentrations of Contaminants in an Unusual Desert Arroyo Near a Uranium Mill Tailings Disposal Cell - 12260

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ABSTRACT

The U.S. Department of Energy (DOE) Office of Legacy Management (LM) manages 27 sites that have groundwater containing uranium concentrations above background levels. The distal portions of the plumes merge into background groundwater that can have 50 µg/L or more uranium. Distinguishing background from site-related uranium is often problematic, but it is critical to determining if remediation is warranted, establishing appropriate remediation goals, and evaluating disposal cell performance. In particular, groundwater at disposal cells located on the upper Cretaceous Mancos Shale may have relatively high background concentrations of uranium. Elevated concentrations of nitrate, selenium, and sulfate accompany the uranium. LM used geologic analogs and uranium isotopic signatures to distinguish background groundwater from groundwater contaminated by a former uranium processing site.

INTRODUCTION

Restoring contaminated groundwater to background concentrations is often a goal of groundwater remediation efforts. Inaccurate determination of background concentrations can result in unrealistic cleanup goals and regulations. The determination of background can be complicated by release of contaminants from geologic media. An interesting example of the difficulty in determining background concentrations is found at former uranium processing sites located on bedrock of the upper Cretaceous Mancos Shale. The Mancos Shale releases the same suite of contaminants via natural processes as those found in uranium mill tailings.

Field investigations over the last several decades by personnel from the U.S. Geological Survey [1,2,3,4], the University of California Davis [5,6,7], Colorado State University [8,9,10], and others [11] have shown that high concentrations of selenium are typical in surface water resulting from irrigated land in Mancos Shale terrain. The selenium is derived from shale beds in the Mancos. Because selenium concentrations are elevated sufficiently to affect aqueous species in lakes and streams, its occurrence, magnitude, and control measures have been widely researched. Although most of the published material relates to the impact of selenium on surface water, high concentrations of nitrate, selenium, sulfate, and uranium have also been observed in Mancos groundwater. In a recent LM study, groundwater samples were collected from the Mancos Shale at locations covering much of its depositional basin and found to contain high concentrations of these same contaminants [12]. The same suite of contaminants (nitrate, selenium, sulfate, and uranium) is found in groundwater associated with uranium mill tailings disposal cells.

Contaminants (and their concentrations) observed in Mancos Shale groundwater from natural sources are similar to those at a uranium mill tailings site at Shiprock, New Mexico. Two arroyos (Salt Creek Wash and Upper Eagles Nest) located about 8 to 11 km northeast of the disposal cell were studied as representing natural analogs to Many Devils Wash. Isotopic ratios of uranium-234 to uranium-238 are also being investigated as a tool to better define the sources of the uranium in groundwater.

NATURAL CONTAMINATION FROM MANCOS SHALE

The Mancos Shale outcrops over an area of about 3237 km^2 in Arizona, Colorado, New Mexico, and Utah. It has long been known that the Mancos Shale contributes high levels of sulfate and selenium to groundwater and surface water in irrigated terrain. Less well known is that the Mancos also contributes elevated concentrations of nitrate [13] and uranium [12] to groundwater. Uranium and nitrate concentrations found in natural seeps emanating from Mancos groundwater commonly exceed 100 µg/L and 400 mg/L, respectively. Locations with high concentrations of natural contaminants are widely distributed, suggesting that the phenomenon is common. There was no apparent correlation of high concentrations with particular geologic members of the Mancos; however, only seeps emanating from shale and siltstone were contaminated, and those from Mancos sandstone had much lower concentrations.

ANALOGS TO MANY DEVILS WASH AT SHIPROCK

A particularly enigmatic example of the uncertainty in determining background concentrations is found near a former uranium processing site at Shiprock (Figure 1). DOE stabilized tailings and mill residues in a disposal cell, and LM now administers the site. A line of seeps, located about 0.8 km from the disposal cell, contributes about 4 liters per minute (Lpm) to surface water in an arroyo named Many Devils Wash (Figure 2). Because Many Devils Wash is close to the disposal cell, and because it and the disposal cell have similar suites of contaminants, DOE assumed responsibility for Many Devils Wash as part of the mill site remediation. If contaminants in the wash are derived from natural processes rather than from the mill site, then remediation efforts would be futile.

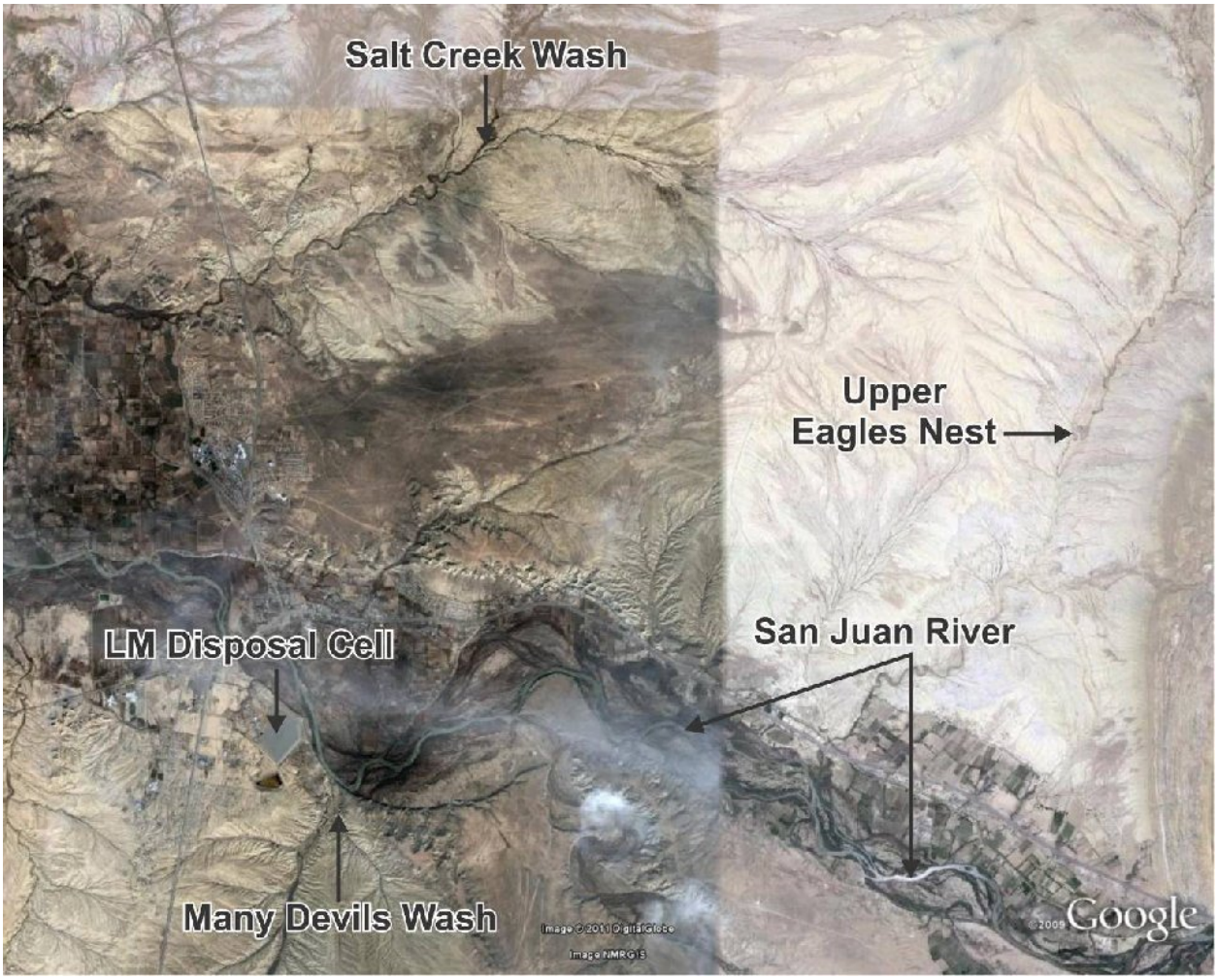

Figure 1. Areas of investigation near the former uranium milling processing site at Shiprock, New Mexico.

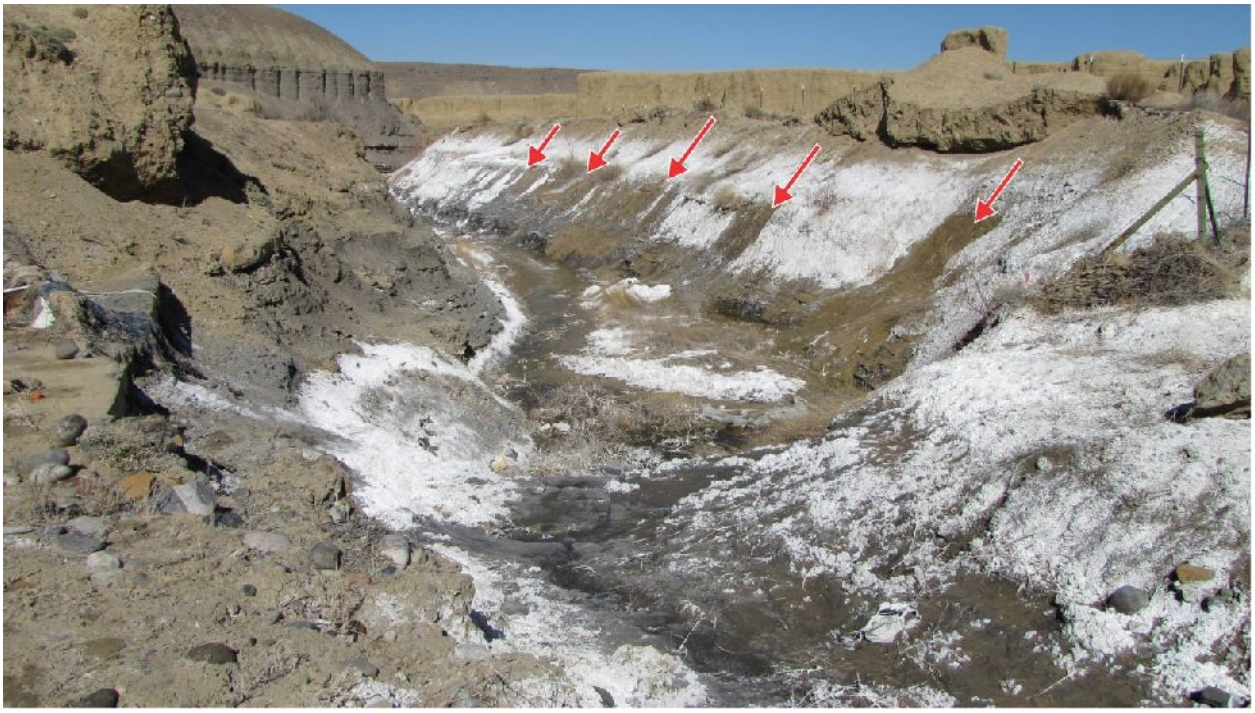

Figure 2. Seeps (marked by arrows) in the Many Devils Wash arroyo.

The seeps in Many Devils Wash are contaminated with nitrate, selenium, sulfate, and uranium, the same contaminants found in the uranium mill tailings and groundwater immediately adjacent to the disposal cell. Concentrations of these contaminants are similar to naturally occurring seeps at two analog sites, the arroyos named Salt Creek Wash and Upper Eagles Nest, located about 8 to 11 km northeast of the disposal cell (Figure 1). Contamination from the former mill site did not influence the analog sites; besides being far removed from the mill site, the analog sites are in different drainages on the opposite side of the San Juan River, and are at higher elevations. Groundwater flowing from the seeps in Many Devils Wash forms yellow to deep-red pools in the arroyo (Figure 3). The color is from dissolved, not particulate, constituents and is not due to iron or manganese, as indicated by the low concentrations of these elements. The same yellow and red coloration is present in seep pools in Salt Creek Wash (Figure 4) and is present at numerous other locations across the Colorado Plateau where groundwater forms natural seeps emanating from Mancos Shale [12]. In Salt Creek Wash, the color of the water, as measured by light absorbance at 465 nanometers normalized to a platinum-cobalt standard method, correlates with dissolved organic carbon (DOC).

Figure 3. Red pool fed by seeps in the Many Devils Wash arroyo.

Figure 4. Red pool fed by seeps emanating from the Mancos Shale in the Salt Creek Wash arroyo.

Figure 5 compares concentrations from several wells located near the uranium disposal cell, and from seeps in Many Devils Wash, Salt Creek Wash, and Upper Eagles Nest. The concentrations of all four constituents are much higher than drinking water standards at all four locations. The tailings groundwater has lower selenium and higher uranium concentrations than

Many Devils Wash or the analog sites. The graphs depict similar chemical signatures for Many Devils Wash, Salt Creek Wash, and Upper Eagles Nest, but a different signature for the tailings.

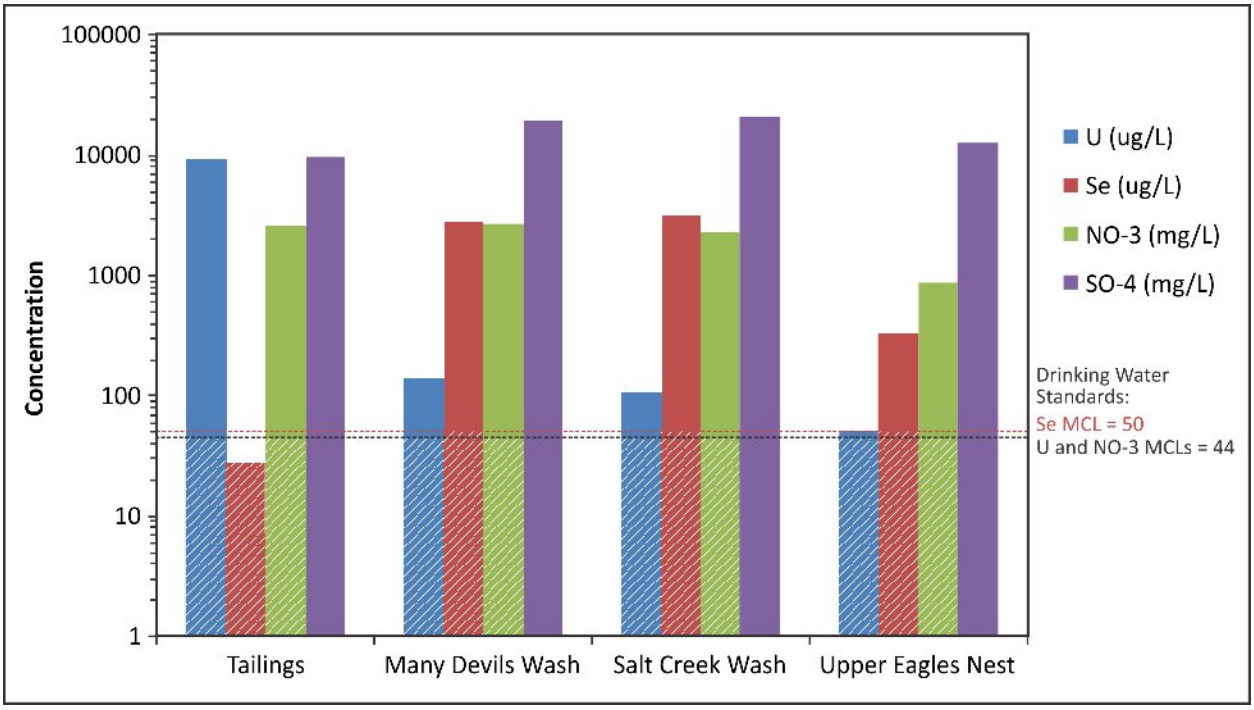

Figure 5. Concentrations of nitrate, selenium, sulfate, and uranium in selected wells near the Shiprock tailings disposal cell, and from seeps in the Many Devils Wash, Salt Creek Wash, and Upper Eagles Nest arroyos. Drinking water standards are indicated (40 CFR 141) [14].

URANIUM ISOTOPIC SIGNATURES

Activity ratio (AR) values of uranium-234 to uranium-238 provide information that can help determine the source of uranium in groundwater. Colorado Plateau uranium ores were deposited for more than 1 million years, a sufficient time to reach secular equilibrium. Thus, AR values in the ores are near 1.0. Aggressive digestion of the ores during milling preserves the AR values near 1.0. Values of AR in groundwater near the Shiprock disposal cell are often close to 1.0, consistent with secular equilibrium; however, some variations exist. Because uranium in most groundwater not associated with uranium processing has higher AR values., Zielinski et al. [15] were able to use AR values to help distinguish natural uranium from that added from a uranium mill near Cañon City, Colorado.

AR values increase in groundwater by alpha recoil [16] whereby the energy released by alpha decay of uranium-238 causes the daughter atom of uranium-234 to be ejected out of the mineral grain and into the pore water. Various other chemical and physical processes (particularly oxidation and mineral damage) that can affect the rate at which uranium-234 concentrates in the groundwater during alpha decay occur [17].

Mancos seeps typically have AR values that are much higher than 1.0 and often exceed 2.0. The seeps in Many Devils Wash and at the analog sites at Salt Creek Wash and Upper Eagles Nest have AR values between 2.0 and 3.0, whereas tailings-derived groundwater has an AR value of about 1.0 (Figure 6). Thus, higher AR values help distinguish uranium in natural Mancos groundwater from uranium contributed by milling processes.

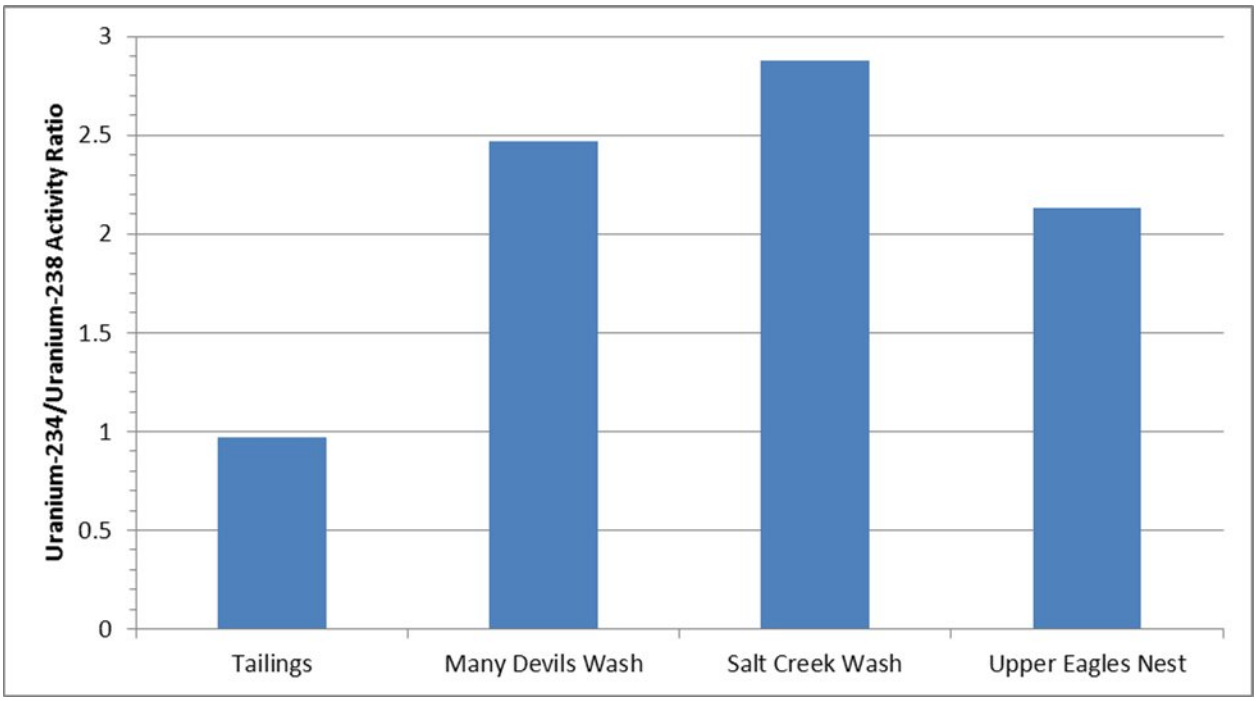

Figure 6. AR values of (1) groundwater wells contaminated by uranium mill tailings and (2) groundwater seeps in Many Devils Wash, Salt Creek Wash, and Upper Eagles Nest arroyos.

SUMMARY AND CONCLUSIONS

The same suite of contaminants is present in groundwater near former uranium processing sites and in groundwater seeps emanating from the Mancos Shale over a broad area. The concentrations of these contaminants in Many Devils Wash, located near LM's Shiprock disposal cell, are similar to those in samples collected from many Mancos seeps, including two analog sites that are 8 to 11 km from the disposal cell. Samples collected from Many Devils Wash and the analog sites have high AR values (about 2.0)—in contrast, groundwater samples collected near the tailings disposal cell have AR values near 1.0. These chemical signatures raise questions about the origin of the contamination seeping into Many Devils Wash.

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