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Understanding controls on redox processes in floodplain sediments of the Upper Colorado River Basin

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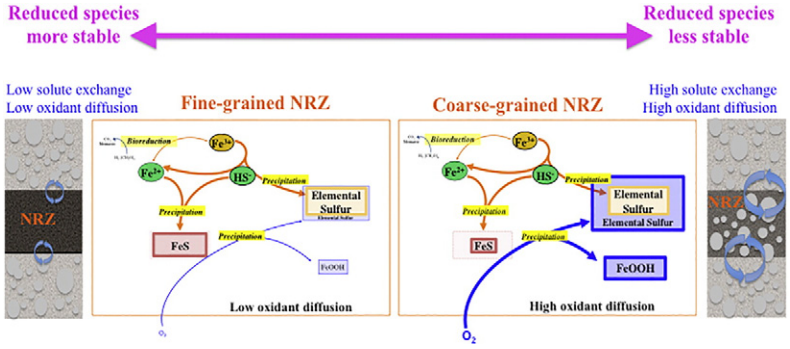
HIGHLIGHTS

- Organic-enriched sediments are common in Upper Colorado River Basin floodplains.
- Reducing conditions are maintained primarily by organic carbon content and moisture
- Particle size governs reactive S(0) and FeS species by mediating oxidant diffusion.
- Organic-enriched sediments mediate groundwater contaminants in floodplains.

GRAPHICAL ABSTRACT



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ABSTRACT

Floodplains, heavily used for water supplies, housing, agriculture, mining, and industry, are important repositories of organic carbon, nutrients, and metal contaminants. The accumulation and release of these species is often mediated by redox processes. Understanding the physicochemical, hydrological, and biogeochemical controls on the distribution and variability of sediment redox conditions is therefore critical to developing conceptual and numerical models of contaminant transport within floodplains. The Upper Colorado River Basin (UCRB) is impacted by former uranium and vanadium ore processing, resulting in contamination by V, Cr, Mn, As, Se, Mo and U. Previous authors have suggested that sediment redox activity occurring within organic carbon-enriched bodies located below the groundwater level may be regionally important to the maintenance and release of contaminant inventories, particularly uranium. To help assess this hypothesis, vertical distributions of Fe and S redox states and sulfide mineralogy were assessed in sediment cores from three floodplain sites spanning a 250 km transect of the central UCRB.

The results of this study support the hypothesis that organic-enriched reduced sediments are important zones of biogeochemical activity within UCRB floodplains. We found that the presence of organic carbon, together with pore saturation, are the key requirements for maintaining reducing conditions, which were dominated by sulfate-reduction products. Sediment texture was found to be of secondary importance and to moderate the

Abbreviations: SSRL, Stanford Synchrotron Radiation Lightsource; XAS, X-ray absorption spectroscopy; XANES, X-ray Absorption Near Edge Structure; EXAFS, X-ray Absorption Fine Structure; LC-LS, linear combination-least squares; RT, room temperature; bgs, below ground surface; OC, organic carbon; UCRB, Upper Colorado River Basin; OEZ, organic-enriched zones; NRZ, naturally reduced zones.

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response of the system to external forcing, such as oxidant diffusion. Consequently, fine-grain sediments are relatively resistant to oxidation in comparison to coarser-grained sediments. Exposure to oxidants consumes precipitated sulfides, with a disproportionate loss of mackinawite (FeS) as compared to the more stable pyrite. The accompanying loss of redox buffering capacity creates the potential for release of sequestered radionuclides and metals. Because of their redox reactivity and stores of metals, C, and N, organic-enriched sediments are likely to be important to nutrient and contaminant mobility within UCRB floodplain aquifers.

1. Introduction

Floodplains are estimated to cover up to 1.5% of the terrestrial surface, and constitute important links between surface and subsurface (Chaopricha and Marín-Spiotta, 2014; Blazejewski et al., 2009). Floodplains act as buffers for flood water and as filters for nutrients and pollutants carried with river water and sediment from upstream source areas. Conversely, river-floodplain sediment systems, heavily used for water supplies, housing, agriculture, mining, and industry, can be long-term sinks for heavy metal contaminants. In this context, sediment-water interactions within floodplains can attenuate or accentuate nutrient and pollutant loads in groundwater (Naiman and Décamps, 1997; Tockner and Stanford, 2002; Pinay et al., 1991; Tabacchi et al., 1998). This behavior is particularly important within the Upper Colorado River Basin (UCRB), where groundwater discharge contributes the majority of total net surface outflow (Miller et al., 2016). In combination with subsurface or hyporheic exchange, groundwater discharge regulates surface water quality (Findlay, 1995). Floodplain sediments exhibit sharp lithologic heterogeneity (Janot et al., 2016). The high heterogeneity of sediment textures and chemical/mineralogical compositions creates chemical gradients that physically juxtapose oxidizing and reducing conditions (Tockner et al., 2010). The stability of contaminants within such sediments is closely linked to redox conditions (Lynch et al., 2014; Schulz-Zunkel et al., 2015). Transport of oxidants and contaminants, including As, Sb, Se, Cr, As, Hg and U, across these heterogeneities drives toxicant accumulation or release (Hua and Deng, 2008; Burton et al., 2011; Hyun et al., 2012; Veeramani et al., 2013). Knowledge of the spatial, hydrological, mineralogical, and biogeochemical controls over redox conditions is therefore critical for understanding the function of floodplain sediments as sinks or supplies of inorganic contaminants. The aim of this work was to contribute to the development of regionally-relevant conceptual models of the biogeochemical function of organic-enriched sediments.

Previous studies suggested that sediment moisture is important for maintenance of reducing conditions in floodplain sediments within the Upper Colorado River Basin (UCRB) (Janot et al., 2016; Campbell et al., 2012). Significantly, within this region, water tables exhibit strong seasonal fluctuation tied to early summer meltwater discharges, which temporarily displace the capillary fringe upwards. The subsequent filling of pore space by water creates the potential for the onset of Fe(III) and sulfate reducing conditions. Thus, seasonal hydrological variations drive cyclic changes of redox conditions (Lair et al., 2009; Weber et al., 2009; Lynch et al., 2014; Schulz-Zunkel et al., 2015). Iron and sulfur mineral transformations (dissolution/precipitation of sulfides and oxides) are driven by these hydrologic changes (Shuman, 1997; Ford et al., 1997; Rickard and Luther, 2007; Qafoku et al., 2009; Canfield et al., 1992; Noël et al., 2014). Consequently, the chemical forms of S and Fe exhibit dramatic variability tied to redox conditions, providing efficient and precise biogeochemical tracers of redox processes.

UCRB floodplain sites are widely impacted by former U ore processing activities. At the Rifle, CO, site, U concentrations >200-fold higher than background concentrations are found within layers of fine-grained, clay-rich sediments having markedly higher organic C content than the sand and cobble alluvium that dominates the floodplain (Janot et al., 2016; Qafoku et al., 2014; Campbell et al., 2012). These sediments may exhibit black coloration from sulfidic mineral precipitation, indicating strongly sulfate reducing conditions, and therefore, have been referred to as 'naturally reduced zones' or NRZs (Campbell et al., 2012). They are suspected to play an important role in maintaining the persistent groundwater U contamination plume at the Rifle site (Janot et al., 2016). Janot et al. noted that other floodplains within the UCRB exhibit similar sediment characteristics, and predicted that sulfidic NRZs are regionally common and responsible for the accumulation of U at other contaminated floodplain sites (Blazejewski et al., 2009; Janot et al., 2016). This hypothesis is supported by similar groundwater compositions in upper CRB aquifers with high sulfate concentrations around 250 mg/L (Report of Department of Energy, 1999, 2003, 2011, 2013). Thus, it was posited that the behavior of the fine-grained, water-saturated NRZs observed at Rifle could be used as a model to understand the functioning of floodplain dynamics and predict contaminant behavior regionally. If correct, this model would provide a valuable tool to understand reduced sediment biogeochemistry and to rationalize and manage the many data-poor U-contaminated floodplain sites within the UCRB.

The objective of this study was to test the validity of the 'Rifle model' of NRZs, starting with a survey across the floodplain at the Rifle site, and extending it to other U-contaminated UCRB floodplain sites managed by the Department of Energy (DOE) Office of Legacy Management. Prior knowledge suggests that reduced sediments are present also at the Grand Junction and Naturita sites (CO) (Davis et al., 2006). The inclusion of these two sites extends the study area to cover a linear distance of 250 km on the Colorado river in the central portion of the UCRB. This study further intended to improve our knowledge of the biogeochemical controls over Fe and S mineralization in order to develop a regionally consistent model of Fe and S redox processes in the UCRB floodplain sediments.

2. Materials and methods

2.1. Field sites, sample collection

The field sites are located on US DOE legacy sites on floodplains in the UCRB (Fig. 1). More information on field sites is available in the Appendix A. Rotosonic drilling (Rifle) or direct push coring (Grand Junction, Naturita) were used to recover intact floodplain sediment cores (in 1.5 m intervals). Recovered cores were cased in N_2-purged plastic tubes. In this study, 4 cores consisted of NRZs were selected from the three field sites; 2 cores (748 and 753) from Rifle, 1 core (GJAST15B) from Grand Junction and 1 core (NAT-M8-1) from Naturita. For each core, the sediment samples were collected every 10 to 40 cm from surface to bedrock (ca. 9.3 m bgs for Rifle, and 5–6 m bgs for Grand Junction and Naturita) (Janot et al., 2016). Pebbles and cobbles larger than about 10 mm were removed, and the remaining sediments were immediately placed into containers. The sediment samples that visibly appeared to be darkened by the presence of sulfides and smelled sulfidic were collected at relatively fine vertical resolution (~5 cm), along with a segment of neighboring over- and underlying sediment, under Ar flow and preserved from oxidation in Ar-purged serum vials (crimp-sealed with rubber stoppers) (Fig. S1). All samples were immediately stored in the dark at 3 °C, and shipped on ice to the laboratory where they were introduced in a glove box in 5%H_2/95%N_2 atmosphere in order to be vacuum-dried. After drying, each sediment sample was