



## Sources and fates of heavy metals in a mining-impacted stream: Temporal variability and the role of iron oxides



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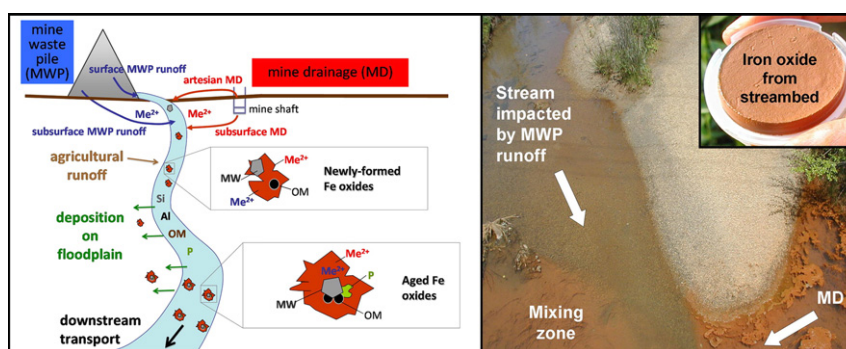
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### HIGHLIGHTS

- We studied fate of Zn, Pb, and Cd and role of Fe oxides in a mining-impacted creek.
- Mine waste pile runoff and mine drainage are both major sources of heavy metals.
- Natural Fe oxide aggregates contain mine waste, organic matter, and other impurities.
- Sequential extractions show multiple phases of Zn, Pb, and Cd in Fe oxide aggregates.
- Pile runoff and mine drainage showed different decadal-scale chemical variations.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 15 January 2014

Received in revised form 25 April 2014

Accepted 29 April 2014

Available online 24 May 2014

Editor: F.M. Tack

#### Keywords:

Heavy metals

Iron oxides

Metal loading

Mine drainage

Mine waste piles

Sequential extractions

### ABSTRACT

Heavy metal contamination of surface waters at mining sites often involves complex interactions of multiple sources and varying biogeochemical conditions. We compared surface and subsurface metal loading from mine waste pile runoff and mine drainage discharge and characterized the influence of iron oxides on metal fate along a 0.9-km stretch of Tar Creek (Oklahoma, USA), which drains an abandoned Zn/Pb mining area. The importance of each source varied by metal; mine waste pile runoff contributed 70% of Cd, while mine drainage contributed 90% of Pb, and both sources contributed similarly to Zn loading. Subsurface inputs accounted for 40% of flow and 40–70% of metal loading along this stretch. Streambed iron oxide aggregate material contained highly elevated Zn (up to 27,000  $\mu\text{g g}^{-1}$ ), Pb (up to 550  $\mu\text{g g}^{-1}$ ) and Cd (up to 200  $\mu\text{g g}^{-1}$ ) and was characterized as a heterogeneous mixture of iron oxides, fine-grain mine waste, and organic material. Sequential extractions confirmed preferential sequestration of Pb by iron oxides, as well as substantial concentrations of Zn and Cd in iron oxide fractions, with additional accumulation of Zn, Pb, and Cd during downstream transport. Comparisons with historical data show that while metal concentrations in mine drainage have decreased by more than an order of magnitude in recent decades, the chemical composition of mine waste pile runoff has remained relatively constant, indicating less attenuation and increased relative importance of pile runoff. These results highlight the importance of monitoring temporal changes at contaminated sites associated with evolving speciation and simultaneously addressing surface and subsurface contamination from both mine waste piles and mine drainage.

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**Abbreviations:** AmOx, non-crystalline iron and aluminum oxide fraction; CO<sub>3</sub>, carbonate fraction; EX, ion-exchangeable fraction; FeOx, iron oxides; MD, mine drainage; MnOX, manganese oxide fraction; MWP, mine waste pile; ORG, organic matter fraction; RES, residual fraction; SOL, water soluble fraction; XtalOx, crystalline iron oxide fraction.

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## 1. Introduction

Abandoned mining sites cause substantial impairment to water quality worldwide (Fields, 2003; Younger et al., 2002). After mining operations cease, oxygen-rich groundwater floods abandoned mine workings and can promote oxidation of pyrite ( $\text{FeS}_2$ ) and other metal sulfide minerals, producing acidity and sulfate and releasing co-occurring trace metals. Over time, seepage from mines can emerge aboveground as metal-rich acid mine drainage. In addition, runoff from large piles of fine-grained tailings and other mining wastes can carry large metal loads as precipitation infiltrates the piles and promotes geochemical weathering of metal-containing primary minerals (Tonkin et al., 2002).

Mitigating impacts from abandoned mines on water quality requires an understanding of the major sources of metal loading and subsequent fate of trace metals. The chemical composition of drainage from underground mines and mine waste piles (MWP) can vary considerably within a watershed, based on host rock composition and flow conditions (Balistrieri et al., 1999; España et al., 2005). At many sites, discrete surface inputs of metals from underground mines and mine waste piles are carried through adits, mine tunnels, and naturally-forming streams. In addition, subsurface inputs also can contribute substantially to metal loading in mining-impacted streams (Kimball et al., 2001; Lachmar et al., 2006). Metals can be removed from the water column by secondary mineral precipitation (e.g., as carbonates or hydroxides), coprecipitation, or sorption onto organic matter (OM) or surface-reactive iron (oxyhydr)oxides, (hereafter referred to as iron oxides), that form following oxidation of ferrous iron (Balistrieri et al., 2003; Dzombak and Morel, 1990; España et al., 2005; Hochella et al., 2005).

Natural iron oxide minerals vary widely in composition, morphology, and physicochemical properties (Perret et al., 2000; Thompson et al., 2011). The ability of iron oxides to sequester heavy metals depends on their mineralogy, size, extent of crystallinity, purity, and aggregation state, as well as competitive interactions between metals and other ions at the mineral surface (Balistrieri et al., 2003; Cismasu et al., 2011; Gilbert et al., 2009; Masue-Slowey et al., 2011; Ostergren et al., 2000). Furthermore, iron phase transformations in natural environmental conditions are common (Hansel et al., 2003; Thompson et al., 2006) and may alter sequestration capacity over time (Henneberry et al., 2012), either by changing the type and availability of sorption sites (Masue-Slowey et al., 2011) or by element-dependent exsolution or more permanent incorporation of metals into the crystal structure (Ford et al., 1997). Therefore, iron oxides formed in situ are heterogeneous and their reactivity towards contaminants is determined by the interplay of system-dependent physical and chemical parameters (e.g., incorporation of impurities such as Al, Si, and OM). Characterizing their composition and behavior is therefore necessary to determine the overall role of iron oxide sequestration in metal transport at a watershed scale.

In this study we employ a novel suite of analytical tools and geochemical speciation modeling to characterize iron oxide aggregate materials that form and evolve in composition as two geochemically distinct sources of heavy metal loading (mine drainage and mine waste pile runoff) mix and move down stream. Our goal is to understand the interplay of these two metal sources both spatially and temporally in order to enable better predictions of metal transport, inventories, and fate. We also present data that point to decadal-scale evolution of metal loading pathways and consider implications for long-term remediation strategies.

### 1.1. Tar Creek Superfund Site

Tar Creek (Oklahoma, USA) drains a portion of the abandoned Tri-State Mining District, a major Zn and Pb producing area from the mid-1800s to the mid-1900s. Ore minerals are primarily associated with the Mississippi Boone formation, with host rocks consisting of fossiliferous limestone and thick beds of nodular chert (Luza, 1986). Metals are concentrated in large piles of mine waste, locally called

chat, a combination of tailings and other mining waste. This mine waste material consists of chert (microcrystalline quartz), calcite, dolomite, marcasite, pyrite, sphalerite ( $\text{ZnS}$ ), galena ( $\text{PbS}$ ), and hemimorphite (Zn silicate) (Carroll et al., 1998; Schaider et al., 2007). Cadmium is present in sphalerite at around 0.5% (O'Day et al., 1998). The site has dozens of major piles, some up to 60 m in height (Luza, 1986), which act as persistent sources of metals into surface water and groundwater. Chat is actively being removed from the site and incorporated into asphalt and other uses as part of remediation at the Tar Creek Superfund Site, which was added to the National Priority List in 1983. Groundwater was actively pumped out of the mines until the cessation of mining activities in 1970, after which the mines filled with metal-rich water that still seeps into Tar Creek. Although mine drainage (MD) is now only slightly acidic due to the acid neutralizing capacity of carbonate-bearing minerals in the host rock, the creek is nonetheless heavily impacted by both artesian seepage discharges from underground mines and runoff from MWPs. While MD is often considered the major source of water contamination at this site, runoff from MWPs adjacent to the creek provides surface and subsurface inputs of water, and discharges of runoff from MWPs and mill ponds provide most of the baseflow to Tar Creek and its main tributary, Lytle Creek (Cope et al., 2008).

Characterizing the chemical composition of MD and MWP runoff at the Tar Creek site is necessary in order to understand the interactions of these two sources and their relative metal loading. Cope et al. (2008) showed substantial loading of Zn, Pb, and Cd along stretches of Tar Creek affected by MWP and MD inputs. However, this study did not characterize these sources individually or distinguish between surface and subsurface inputs. Mine drainage contains highly elevated Fe concentrations, resulting in abundant iron oxide coatings on the Tar Creek streambed and buoyant flocculant material in the water column. Periodic flood events flush streambed iron oxides downstream and into nearby floodplain soils that support residential and agricultural land uses.

Initial work at the Tar Creek site explored metal associations with iron oxide phases in sediments and controls on water column solubility (Carroll et al., 1998; O'Day et al., 1998). X-ray absorption spectroscopy (XAS) analyses of Pb, Cd, and Zn binding environments in streambed sediments (down to 5 cm) showed key differences among these metals (O'Day et al., 1998). Iron oxides appeared important for Zn binding and Pb was associated with both iron oxides and carbonate phases, while Cd was present in primary sphalerite or secondary carbonate phases. A companion paper (Carroll et al., 1998) used equilibrium modeling to explain trends in metal concentrations and to identify controls on metal speciation in the water column. Their results suggested that the parameters controlling metal speciation vary by metal and include degassing of  $\text{CO}_2$ , solubility of carbonate phases, dissolution of galena and sphalerite catalyzed by dissolved iron, and sorption to iron oxides. These results highlight differing metal behavior, although they did not focus specifically on the particles (and particle surfaces) most closely in contact with the water column, including consideration of the role of iron oxides in transport. We build on their work by characterizing metal loading inputs and considering the roles of heavy metal loading from multiple sources and advective flow in determining changes in metal concentrations along the creek.

## 2. Materials and methods

### 2.1. Field sampling

Water samples were collected from Tar Creek, Lytle Creek (a tributary), MWP runoff, and MD discharges during three sampling trips (January and May 2005, June 2006). Based on trace metal analyses of 2005 samples, a 0.9-km stretch of Tar Creek heavily impacted both by MD and MWP runoff was selected for additional sampling in 2006. This stretch had two distinct sections: the upstream portion, Stretch #1 (0.65 km), was primarily impacted by MWP runoff, and Stretch #2

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