Metal Loads Accounting at a Legacy Mine Site: The Tar Creek Superfund Site, Oklahoma, USA

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Abstract

Legacy mining sites tend to be hydrologically and geochemically complex, with primary and secondary contaminant reservoirs entering the watershed in concentrated and diffuse manners on a range of temporal and spatial scales. Managers of legacy sites must use available funding efficiently, which requires extensive characterization efforts to determine locations where remedial actions will have maximum benefits to ecosystems. This study serves as an exploratory examination of a stream reach in a legacy mine site to determine which parts of the reach may be sources of substantial non-point source metal contamination.

Tar Creek is a second-order stream in the legacy Tri-State Lead-Zinc Mining District of northeastern Oklahoma and southeastern Kansas. Water quality in Tar Creek and its tributaries is influenced by artesian discharges of circum-neutral pH mine water flowing from underground mine workings, runoff and leachate from mine wastes in large piles on the surrounding ground surface, and mine wastes washed into the stream channels. Data evaluated for this study included in-stream trace metal concentrations and flow measurements at multiple locations used to calculate metals loads. These loads were then used to determine potential areas of interest for further study to examine diffuse contaminant transport and determine trends that may be related to remedial activities within the watershed. Data collected in 2023 were also compared to data collected from 2004 to 2010 to evaluate effects of remedial work performed over intervening years.

Although metal loads increase sharply in areas where mine drainage discharges enter Tar Creek, there are also substantial in-stream metal loads not associated with point sources, suggesting increased loads from mine waste. In some sections of Tar Creek, differences between the measured downstream loads and the contributing loads (the sum of loads at the upstream location and the contributing tributaries) exceeded loads from point-source discharges, suggesting that non-point sources are the principal origin of metals in that reach of Tar Creek. Diffuse and tributary loads varied seasonally with fluctuations in mine pool elevation and precipitation.

Accounting for distinct loads from mine discharges and surface-deposited mine wastes helps to identify areas where further studies into surface water-groundwater interactions are needed. Future studies will focus on the hyporheic zone and water stored within mine waste piles and their interactions with wastes and waters in the stream. Additionally, areas where diffuse metal loads were identified may be considered as priority sites for remedial interim measures before more thorough holistic remediation is completed.

Keywords: Mine waste, mine drainage, water quality, Tri-State Mining District

Introduction

In the United States alone, tens of thousands of stream miles are affected by mine drainage (e.g., Naidu et al. 2019). Many of these streams are located within the nearly 1200 National Priorities List (NPL) sites designated by the United States Environmental Protection Agency (EPA), where the party responsible for the contamination is no longer viable (EPA 2023a). Remediation of these sites is complex, and these long-term projects managed by the EPA use funding from the same source as the other NPL sites, so efficient and cost-effective work is essential to the achievement of the goals of protecting human health and the environment and returning the sites to beneficial use.

Long-term sampling is used at contaminated sites of all kinds to monitor changes in site conditions over time and to find areas to target for remediation. At derelict mine sites, spatially dense sampling along a stream reach has been used to determine the effects of the hyporheic zone and surface-deposited mine wastes at different points along the stream (Brown et al. 2007; Jones et al. 2013; Liakopoulos et al. 2010). In these studies, loads are calculated along the stream reach and differences are attributed to hard-to-track sources and sinks such as stormwater runoff, slower seepage from mine waste, hyporheic zone storage, and sorption. Although this method has been adopted for snapshots of long study reaches or seasonal studies of a single area of interest, there are few instances of studies where seasonality is combined with a long study reach to determine whether seasonality and other long-term trends play a role in the diffuse loading of contaminants of concern from various sources at derelict mine sites.

The derelict Tri-State Mining District (TSMD) in northeastern Oklahoma, southeastern Kansas, and southwestern Missouri was mined for lead and zinc from the mid-19th to the mid-20th century (Nairn et al. 2010). The mining-influenced landscape of the TSMD is characterized by large surface deposits of coarse mine waste and fine tailings, many of which have been reworked to extract marketable fractions for asphalt aggregate, as well as artesian discharges of net-alkaline mine drainage that precipitate iron (oxyhydr)-oxide in surface water (Nairn et al. 2010; Datin and Cates 2002). Elevated concentrations of cadmium, lead, zinc, and other trace metals are less visible, but are contaminants of concern throughout the district (Cope et al. 2008). These features have resulted in the TSMD being placed on the NPL as four sites across two EPA jurisdictional regions. Zinc has been noted as the most common of the contaminants of concern to regularly exceed target remedial concentrations (e.g., Quapaw Tribe of Oklahoma 2020). Tar Creek is a second-order stream flowing from north to south in the Kansas and Oklahoma portions of the TSMD. The stream has been sampled as part of long-term research efforts over 20 years, and recent studies have added sampling sites in order to examine the effects of diffuse sources of metals of concern over time. This study synthesizes the available zinc loading data to determine whether seasonal or long-term trends are present and to locate the greatest sources of diffuse loading.

Methods

The University of Oklahoma Center for Restoration of Ecosystems and Watersheds (CREW) began systematic water quality and quantity monitoring of select stream sites in the Tar Creek and adjacent watersheds in 2004. Sites TC-2, TC-4, TC-6, and TC-7 (Fig. 1) were sampled monthly from November 2004 to September 2008, with monitoring of TC-7 continuing on a monthly to quarterly basis as research focus shifted to the southern portion of the watershed. Samples at all points shown in Fig. 1 were collected monthly between March and July of 2023. For each sample, water was collected in 250-mL high density polyethylene bottles after triple-rinsing with water from the stream. Samples were acidified in the field with 2 mL concentrated trace metal grade nitric acid and transported to the CREW laboratory in Norman, Oklahoma. These samples were prepared for analysis using hot acid digestions and analysed using inductively coupled plasma-optical emissions spectroscopy (ICP-OES) following EPA methods 3015 (EPA 2007) and 6010 (EPA 2018). Whenever possible, flow measurements were collected using a SonTek Acoustic Doppler Velocimeter FlowTracker. Flow measurements from TC-7 were supplemented with the United States Geological Survey (USGS) gaging station at that location (station ID: 07185090; USGS 2023a). Physiochemical parameters were measured during sampling events using a Yellow Springs Instruments multiparameter datasonde and handheld controller, and an additional sample bottle was filled to zero head space for the analysis of select anions in the CREW laboratory via Discrete Analyzer.

Zinc loads at each location were calculated by converting the flow measurement from cubic feet per second to litres per minute and multiplying the total recoverable metal concentration in mg/L determined using ICP-OES by the flow. Expected loads at each Tar Creek sampling site were estimated by adding the load at the previous site and loads from any tributaries or seeps that entered Tar Creek between the two sites. If no tributaries were sampled between two sampling sites along Tar Creek, the estimated load was equal to the load measured at the upstream site.

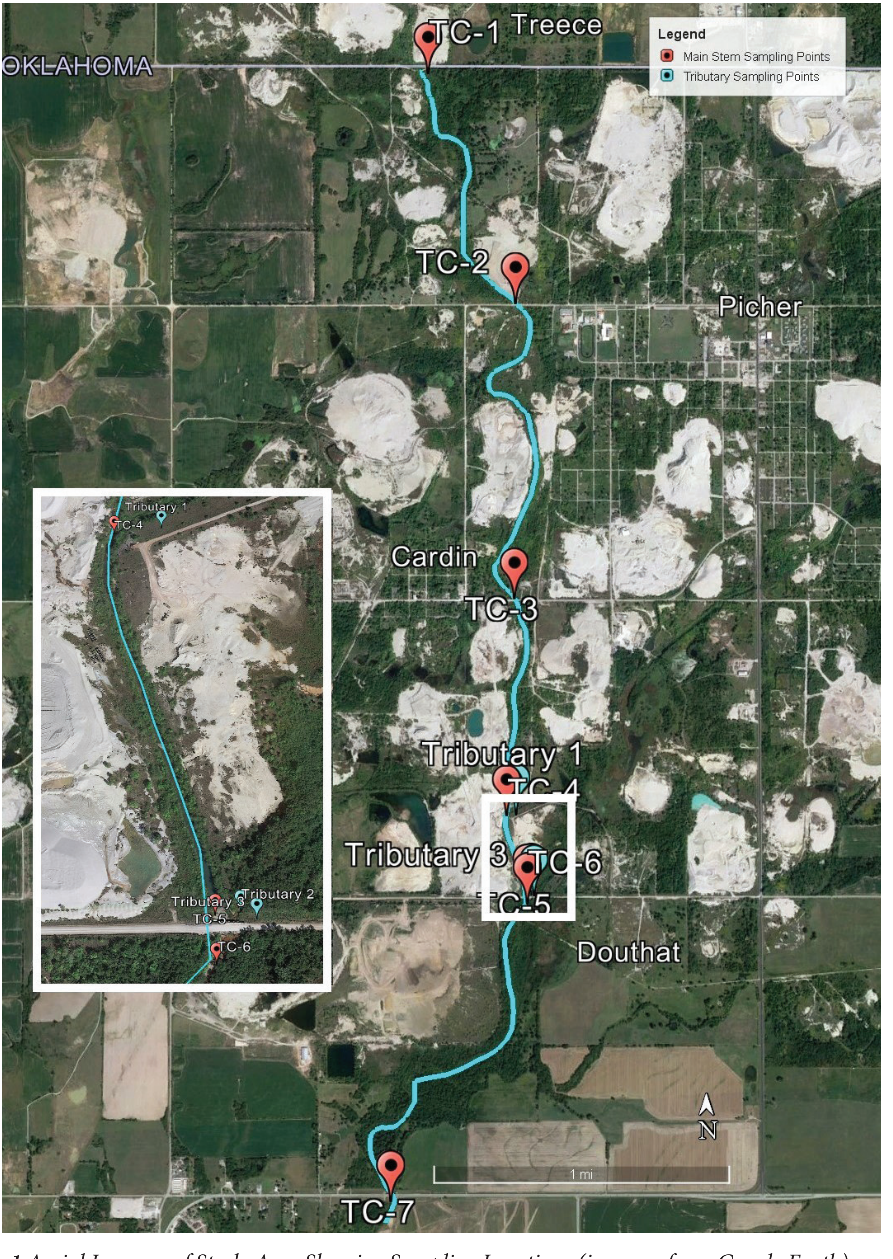

Figure 1 Aerial Imagery of Study Area Showing Sampling Locations (imagery from Google Earth)

Results and Discussion

Zinc concentrations from long-term monitoring sites are displayed in Fig. 2. No long-term trends are apparent, and trends between concentration and time at each site show R^2 values less than 0.2 regardless of the nature of the relationship (e.g., linear, logarithmic, polynomial). Elevated concentrations of zinc seen in 2023 throughout the reach coincided with removal of waste material from the channel and east bank of Tar Creek north of TC-2. As removal efforts have moved away from the creek, concentrations of zinc and other contaminants of concern have decreased, but continued monitoring will be necessary to determine long-term effects, positive or negative, of this removal effort.

Similar, but less dramatic, increases in zinc concentrations were seen in 2006 and 2012. The EPA documented remedial action in the Treece subsection of the Cherokee County Superfund Site to the immediate north of TC-1 in 2012 that may have resulted in the elevated concentrations of zinc at the TC-7 sampling site (EPA 2023b).

A review of aerial imagery confirms that consolidation and capping of mine waste near Tar Creek coincided with the elevated zinc concentrations, along with movement of mine waste north of the confluence of Tar Creek and Tributary 1 (Fig. 1, north of inset area) in 2006. Although these instances of mine waste movement loosely correlate with elevated zinc concentrations, other factors, such as changes to flow patterns within the greater watershed, may contribute to increases in metals loads. Lower-volume flows may also artificially elevate zinc concentrations via evaporative loss; conversely, a few samples at TC-7 in 2022 and 2023 have artificially low concentrations caused by rain events immediately before sampling occurred.

Measured zinc loads for each sampling location on Tar Creek are given in Table 1, as are expected zinc loads, assuming that all contributors to the load were sampled. Sampling events in March through May took place on days when the elevation of water in the underground mine workings, as recorded by a USGS monitoring well (station

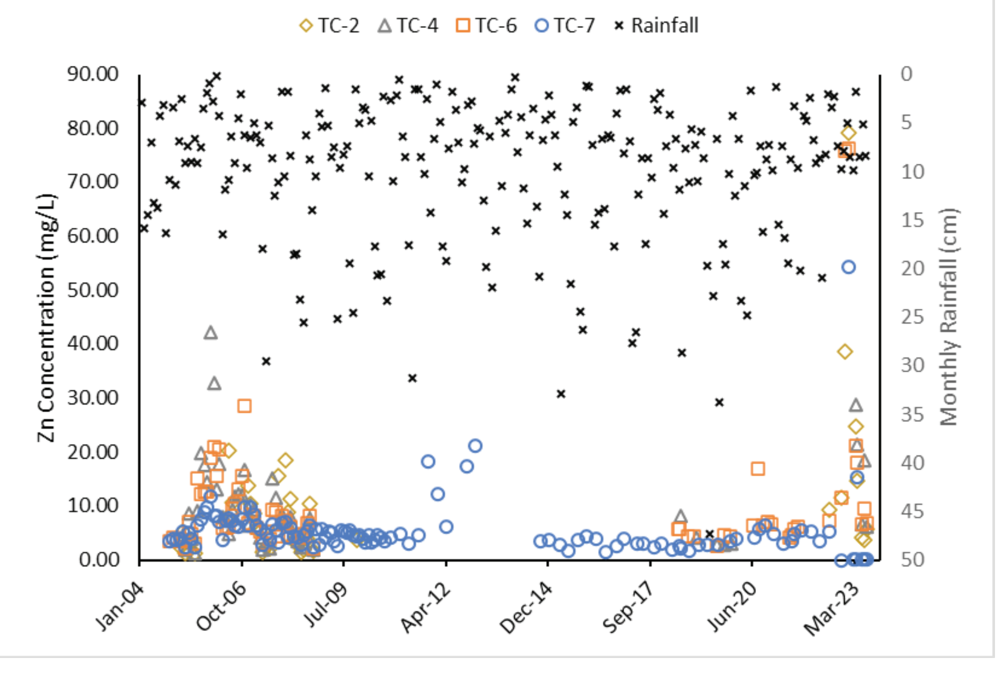

Figure 2 Zinc Concentrations at Select Locations along Tar Creek over 20 Years, with Rainfall Data from the Oklahoma Mesonet (2023)

ID: 365942094504203; USGS 2023b), was close to the long-term average elevation for that day. Water elevation in the underground mine workings was lower than the previous three months in June and July (USGS 2023b), however, precipitation in the watershed the night before the July sampling event caused surface water discharge in Tar Creek well above the average flow (USGS 2023a). Shepherd (2022) linked the quantity of water flowing from seeps and entering Tar Creek in Tributaries 2 and 3 as well as upstream of TC-7 to the elevation of water in the underground mine workings. As this water elevation increases, discharge from the seeps increases, but metals concentrations in the mine drainage are not proportionately diluted (Shepherd 2022). Thus, it can be assumed that more metal mass was contributed by mine drainage at TC-6 and TC-7 in March, April, and May sampling events than the sampling events in June and July.

As can be seen in Table 1, measured zinc loads decrease between TC-2 and TC-3 and between TC-6 and TC-7 for most sampling events. Apparent decreases between TC-2 and TC-3 are attributed to difficulties measuring low water velocities in the volunteer wetland at TC-3. The segment between TC-6 and TC-7, however, does not show a decrease in measured flow downstream, indicating that there is a zinc sink between the two sites. As noted by Cope et al. (2008) and this study (data not displayed), mine drainage discharging from the underground mine workings in the TSMD contains elevated iron concentrations when compared to waters in contact with surface-deposited mine waste. Therefore, because this stream reach receives artesian mine drainage and upstream segments do not, iron (oxyhydr)-oxide forming from the mine drainage water as it is introduced to atmospheric oxygen and precipitated in the stream may act as a sorptive medium for some of the zinc load. The zinc content of these solids would need to be measured to confirm this hypothesis.

Increased measured zinc load when compared to expected zinc load occurs at TC-2, TC-4, and, in some instances, at TC-5 (Table 1). Zinc load increases at these points are hypothesized to be linked to the interaction between mine waste piles on the ground surface, some of which have eroded into the stream in the decades since their placement. These waste piles are the grey-white unvegetated areas that can be seen in the aerial imagery of Fig. 1. Apparent loading due to erosion of the waste piles was especially dramatic at TC-4 in July, when sampling was conducted shortly after a precipitation event, and upstream of TC-2, where a project was in progress during the study period to remove waste from the stream. As this project is completed, it is hypothesized that loads from the waste upstream of the TC-2 site will decrease as stream bed disruption and heavy equipment have moved away from Tar Creek.

Conclusions

Loads of contaminants of concern at legacy mine waste sites like the TSMD are influenced

Table 1 *Comparison of Measured and Expected Zinc Loads at Locations along Tar Creek, with Measured Loads more than 20% Greater than Expected Loads Bolded*

	Measured Zinc Loads (mg/min)					Expected Zinc Loads (mg/min)				
Sites	Mar	Apr	May	Jun	Jul	Mar	Apr	May	Jun	Jul
TC-1	1.9	0.2	3.2	0.03	8.8	-	-	-	-	-
TC-2	**16.4**	**6.6**	**16.0**	0.02	**51.0**	1.9	0.2	3.2	0.03	8.8
TC-3	12.4	11.7	11.6	**0.05**	35.7	16.4	6.6	16.0	0.02	51.0
TC-4	**21.0**	11.5	**38.4**	**0.8**	**121.8**	12.4	11.7	11.6	0.05	35.7
TC-5	**70.9**	**34.8**	54.2	**1.7**	145.2	53.8	19.3	49.6	0.8	123.1
TC-6	86.4	43.8	**70.8**	5.8	155.4	80.7	36.9	58.9	7.5	152.7
TC-7	96.3	36.2	88.5	3.3	70.6	87.6	45.0	87.1	5.9	155.5

by interactions with different types of source material throughout the watershed. As efforts to remediate these sites continue, regular monitoring is necessary both to mark the progress of the clean-up and to point to sites where remediation would most effectively decrease loads of contaminants of concern. This study analysed long-term water quality and quantity data collected along Tar Creek in northeastern Oklahoma to determine whether concentrations of zinc varied seasonally over 20 years and to evaluate the effect of past remediation projects on the concentration of zinc in a selected portion of Tar Creek. Measured and expected loads were also calculated to estimate where diffuse runoff may increase zinc loads in the creek. Seasonal variations and decreases of zinc concentrations over time were not observed, but the zinc load was affected by flow conditions and removal of mine waste adjacent to the creek. Additionally, areas of Tar Creek such as those upstream of sampling points TC-2, TC-4, and TC-5 were identified where interaction with mine waste adjacent to the stream increased zinc loads. These areas will be targets for more in-depth monitoring, including sampling stormwater runoff and measuring metals flux in hyporheic zone porewaters, as monitoring of the watershed continues.

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