

A PRELIMINARY LABORATORY STUDY OF SUBAQUEOUS DISPOSAL OF CONTAMINATED MINE WASTE¹

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Abstract: Understanding the fate and transport of contaminants produced from mine waste leaching in both surface and ground water environments is essential in effective remediation designs. At the Tar Creek Superfund Site in Oklahoma, subaqueous disposal of chat waste rock (processed dolomitic chert contaminated with elevated lead, zinc and cadmium) is being considered as a remedial option via injection of dry or slurried material directly into flooded underground mines or collapse features. Laboratory studies were conducted to simulate subaqueous disposal of these lead-zinc mine wastes into both contaminated mine pool waters (anoxic, elevated dissolved solids) and into surface waters (oxic, low dissolved solids). Mean contaminant concentrations of chat used in the study were: 1,314 mg/kg Pb, 16,895 mg/kg Zn and 33 mg/kg Cd. Concentrations varied with particle size; greatest concentrations were found in the <0.425 mm size fraction. A total of 360 bench-top microcosms were employed and sampled periodically for one year. Resulting water-column contaminant concentrations varied temporally but demonstrated an initial flush followed by a longer-term attenuation. Results of this study will help develop better understanding of the impacts of disposing of chat in aqueous environments, a currently suggested method of land remediation.

Additional Key Words: tailings, hard rock mine, mine drainage, waste rock disposal, lead, zinc, cadmium

¹ Paper was presented at the 2007 National Meeting of the American Society of Mining and Reclamation, Gillette, WY, 30 Years of SMCRA and Beyond June 2-7, 2007. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

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Proceedings America Society of Mining and Reclamation, 2007 pp 395-402
DOI: 10.21000/JASMR07010395

Introduction

The Tar Creek Superfund site in northern Ottawa County, Oklahoma is part of the former Tri-State Mining District, where underground mining for Pb and Zn took place from the mid-1800s until the early 1970s (EPA, 2004). When mining ceased, millions of tons of waste rock (chat) and flotation fines were left behind. Today, approximately 75 million tons of chat remains on the surface in the Tar Creek area (EPA, 2004). Chat is composed primarily of angular chert fragments with a nominal size of less than $\frac{1}{4}$ inch. In general, this material contains elevated concentrations of metals (Pb, Zn, and Cd) in the form of sulfide minerals, particularly in the $<0.425\text{mm}$ fraction (Datin and Cates, 2002). The uncontrolled nature of these piles and ponds poses a substantial human and ecological health risk. Also, the leaching of metals from the chat piles during rainfall events may contribute to elevated metals concentrations in adjacent waterways. In addition to these issues, the existence of the piles limits viable options for profitable land usage.

Chat has been used extensively as aggregate in asphalt, as gravel for roads and driveways, and as fill material (Datin and Cates, 2002; Nairn, et al., 2005). A remedial option that is currently being considered to speed the removal of chat is subaqueous disposal, either in the mine pool or in collapse features. The underground mine voids in the Superfund site are connected to the surface in many places by mine shafts and boreholes. Numerous collapse features also exist in the mining area, with a potential for additional subsidence in the future (Nairn et al., 2001). With subaqueous disposal, dry or slurried chat is injected directly into shafts, boreholes, and collapse features, effectively plugging the holes and eliminating physical hazards.

The subaqueous disposal option presents many questions that must be answered before it is employed on a wide scale. One of the most pertinent questions is what effect addition of contaminant-laden material will have on the quality of water in both underground mine voids and collapse features filled with surface water. The water in the mines is characterized by low dissolved O₂ concentrations and high dissolved solids concentrations. Conversely, water in collapse features is oxic with low dissolved solids concentrations.

In order to address this question, a one-year laboratory microcosm study was conducted to determine the effects of the addition of chat on water quality in these environments and to examine whether those effects differ in mine water and surface water.

Methods

Sampling Methods

Chat samples were collected at the Kenoyer North pile in the Tar Creek Superfund site (Fig. 1) following clean techniques, using a stainless steel shovel. Nine new ten-gallon buckets were filled with composite materials taken from 21 equidistant points along the south face of the pile. The shovel was dry decontaminated (cleaning with a brush) between each sampling point. Buckets were capped, taped tightly to prevent cross contamination and returned to the Center for Restoration of Ecosystems and Watersheds laboratories at the University of Oklahoma for use in the microcosm study.

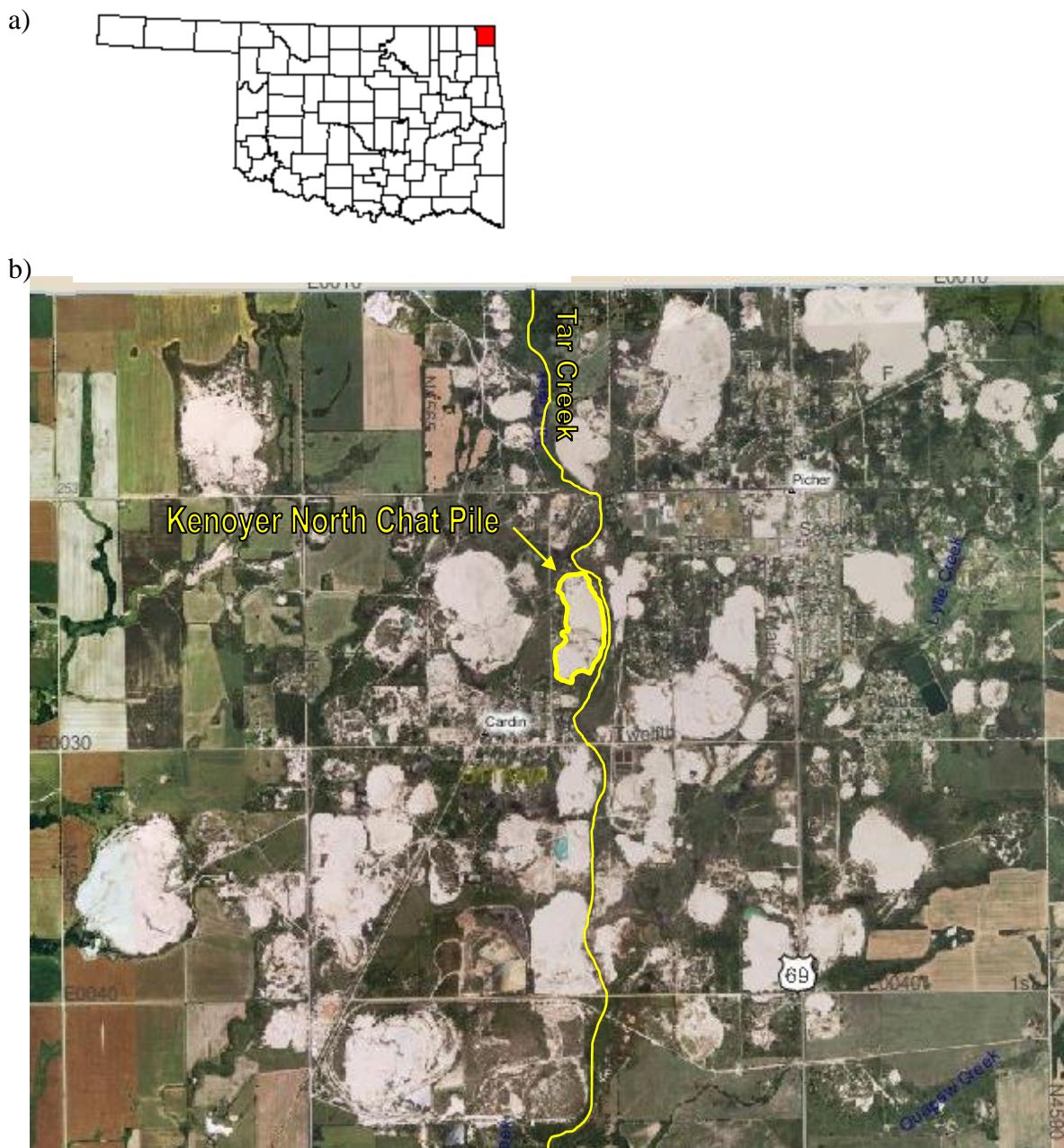


Figure 1. Site map showing a) location of Ottawa County (red) within the State of Oklahoma and b) aerial photograph of the central portion of the Tar Creek Superfund Site showing major drainage (Tar Creek) and sampled chat pile (Kenoyer North) among other chat piles, tailings ponds and communities.

Laboratory Methods

A total of 360 microcosms were constructed in 500 mL-HDPE bottles containing 50g of pile run (raw) chat (not size separated) in each bottle. Half of the bottles were then filled with mine water (anoxic, 0.016 mg/L Cd, 184 mg/L Fe, 0.055 mg/L Pb and 10.7 mg/L Zn) and half were

filled with simulated surface water (oxic, 0.003 mg/L Cd, 0.211 mg/L Fe, 0.013 mg/L Pb and 0.124 mg/L Zn). Mine water microcosms were filled on-site from a flowing mine water discharge of typical quality near Commerce, Oklahoma. Surface water microcosms were filled with simulated surface water mixed in the laboratory based on collapse feature water quality data obtained from Cates and Sharp (2004). Samples of the mine water and simulated surface water were collected prior to addition to the microcosms. At least three replicate microcosms from each set were sacrificed at 1, 2, 4, 8, 24, and 48 hours, approximately weekly for six weeks, and monthly for one year.

For every sample collected, three aliquots were taken. The first aliquot was acid-preserved and stored for metals analysis. The second was refrigerated and analyzed for anions within 48 hours. The third aliquot was immediately analyzed for temperature, dissolved O₂, pH, conductivity, alkalinity, and turbidity.

Temperature, dissolved O₂, pH, and conductivity were measured using a properly calibrated Accumet AR60 multiparameter meter. Alkalinity was measured via titration with H₂SO₄ (1.6M for mine water and 0.16M for surface water) using a Hach digital titrator.

Turbidity was measured with a Hach 2100P portable turbidity meter. Preserved samples for metals analysis were first digested with nitric acid in a CEM MARSXpress Digestion System following EPA Method 3015. The digested samples were then analyzed for Fe, Pb, Zn, and Cd concentrations with a Varian Vista-PRO simultaneous axial Inductively Coupled Plasma-Optical Emission Spectrometer following EPA Method 6010. The samples retained for anion analysis were filtered through 0.2µm nitrocellulose filters and analyzed for sulfate concentrations with a Dionex 300 ion chromatograph following EPA Method 300.0.

Results and Discussion

Substantial changes were noted in several of the water quality parameters throughout the study. The most notable of these changes were in pH and conductivity. Surface water microcosms showed a decrease in pH and an increase in conductivity, and the mine water microcosms showed increases in both pH and conductivity. These changes are shown below in Fig. 2 and 3.

It was noted early in the study (at approximately two weeks) that the microcosms were not completely closed to the atmosphere, denoted by precipitated Fe oxides in the mine water vessels. This observation was also supported by changes in pH, most likely due to CO₂ in the microcosms coming to equilibrium with the atmosphere. The open atmosphere led to substantial increases in dissolved oxygen concentrations, particularly in the mine water microcosms. There was also a notable decrease in alkalinity in the mine water microcosms, most likely due to the proton acidity produced via hydrolysis of iron; alkalinity is therefore not included in the analysis.

Conductivity in the mine water dropped substantially, from 3.02 mS/cm to 1.24 mS/cm, in the first three months of the study. It was expected that conductivity would increase due to dissolution of metals in the chat. Conductivity did begin to increase, however, before the end of the study. From the four-month sampling episode until the end of the study, conductivity in the mine water microcosms increased steadily from 1.19 mS/cm to 1.45 mS/cm. Conductivity in the surface water microcosms did increase in the first two hours after addition of the chat, from 0.214 mS/cm to 0.262 mS/cm. Conductivity in the surface water peaked at 0.602 mS/cm at three

weeks. Overall, the surface water microcosms showed an increase in conductivity with a final measurement of 0.371 mS/cm.

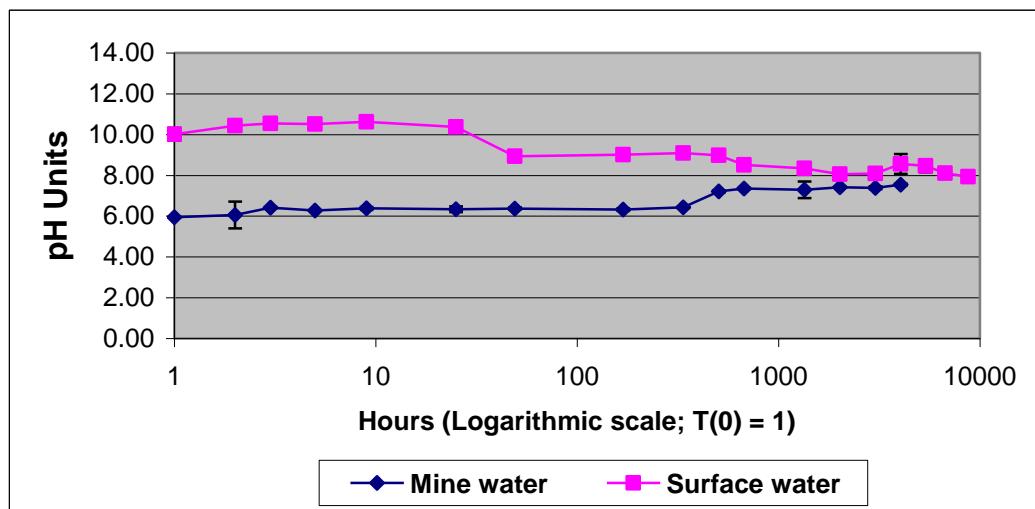


Figure 2. pH in mine and surface water microcosms.

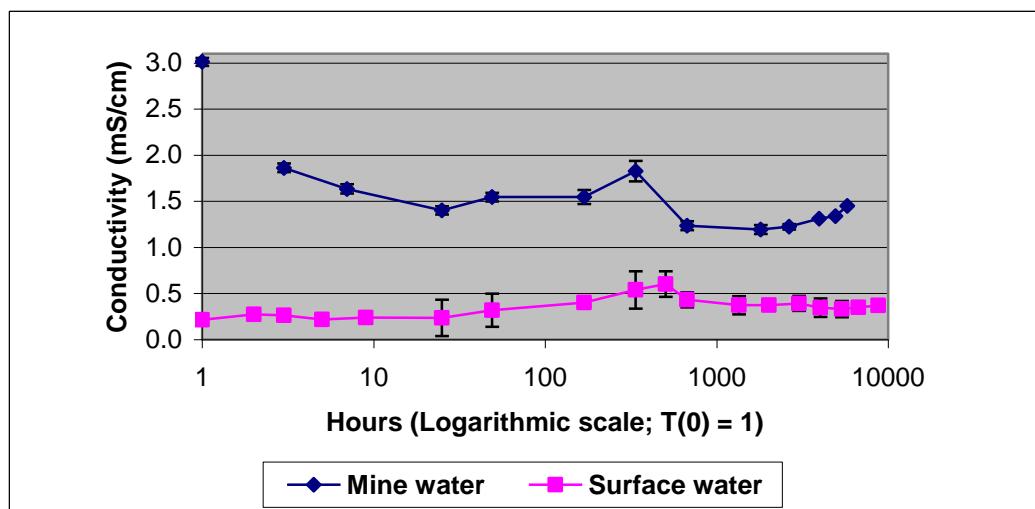


Figure 3. Conductivity in mine and surface water microcosms.

All of the metals included in this analysis (Cd, Pb, Zn, and Fe) showed a dramatic increase in concentration at the beginning of the study, likely due to the fact that samples were collected without filtering and may have contained a significant amount of solids. Once the solids settled, concentrations decreased in most cases. A notable exception was Cd, shown in Fig. 4.

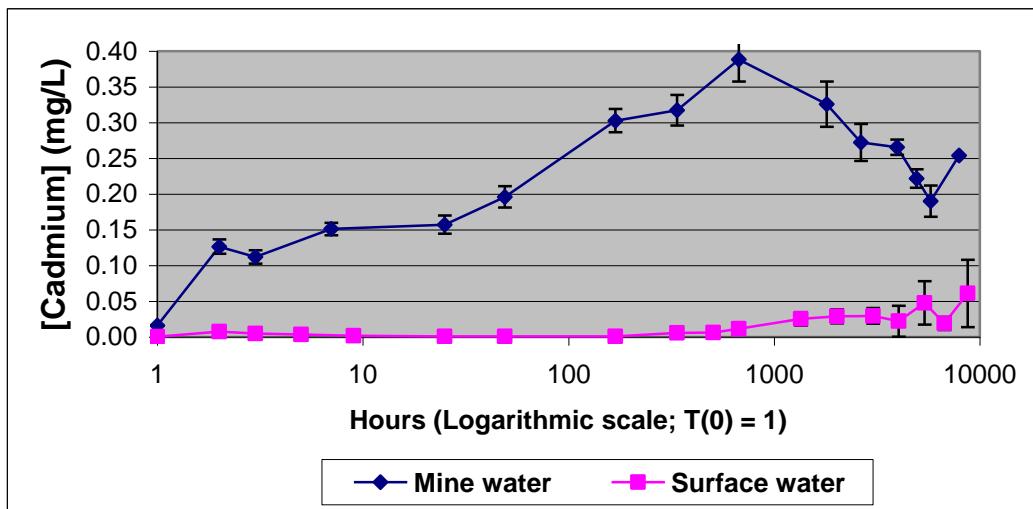


Figure 4. Cadmium in mine and surface water microcosms.

In the surface water microcosms, Cd concentrations continued to increase throughout the study, with a final average concentration of 0.061 mg/L. In the mine water microcosms, the Cd concentration decreased after approximately two weeks. In the last sampling period, however, it appeared to increase again. The final Cd concentration in the mine water microcosms was 0.254 mg/L. Although Pb is the primary risk driver at the field site, Cd concentrations should also be taken into account.

Lead concentrations in both sets of microcosms showed an initial increase, but concentrations decreased once solids had settled. However, the concentration did continue to increase past this point, as shown in Fig. 5. The final concentration of lead in the mine water microcosms was 0.158 mg/L and the final concentration in the surface water microcosms was 0.063 mg/L.

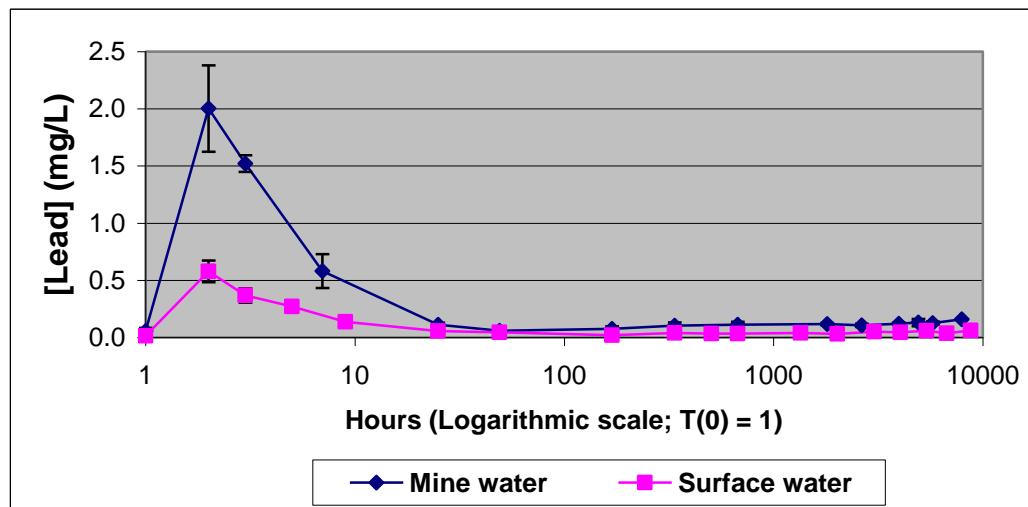


Figure 5. Lead in mine and surface water microcosms.

Zinc concentrations in both sets of microcosms also showed a substantial increase after the initial addition of water. In the surface water microcosms, Zn concentrations did not appear to recover, with a final concentration (0.120 mg/L) nearly identical to the initial concentration (0.124 mg/L). Zinc concentrations in the mine water microcosms appeared to be following the same trend until the last sampling period. In the last month of incubation, Zn concentration climbed to more than triple the previous concentration. The final zinc concentration in the mine water microcosms was 46.98 mg/L, compared to an initial concentration of 10.67 mg/L. The Zn results for both sets of microcosms are shown in Fig. 6.

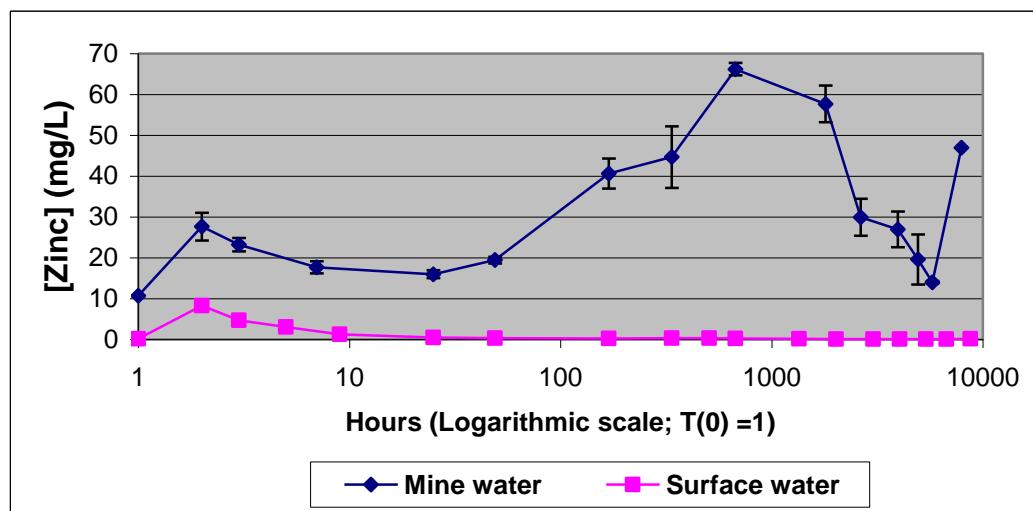


Figure 6. Zinc in mine and surface water microcosms.

As with both lead and Zn concentrations, Fe concentrations in the surface water peaked directly after the addition of water. However, this concentration dropped significantly within the first 48 hours, as shown in Fig. 6, as solids settled. Over the period in which the study was conducted, Fe concentrations decreased to a level below the initial concentration (from 0.21 mg/L to 0.06 mg/L). Iron concentrations in the mine water microcosms did not peak after the addition of water. In fact, by the time the study had reached 3 weeks, most Fe had precipitated. This drastic decrease in Fe can also be seen in Fig. 7.

Conclusions

Despite the fact that the study was not run in a closed atmosphere, i.e., dissolved O₂ and CO₂ were not held constant, it was demonstrated that the introduction of chat into mine pool and surface waters may cause consequential changes in water chemistry. The introduction of contaminant-laden materials into aqueous environments may pose human and ecological health risks. Cadmium and Pb concentrations in both the mine water and surface water microcosms are elevated enough to warrant further investigation of the merit of subaqueous disposal of chat; of particular concern were changes in Cd concentrations.

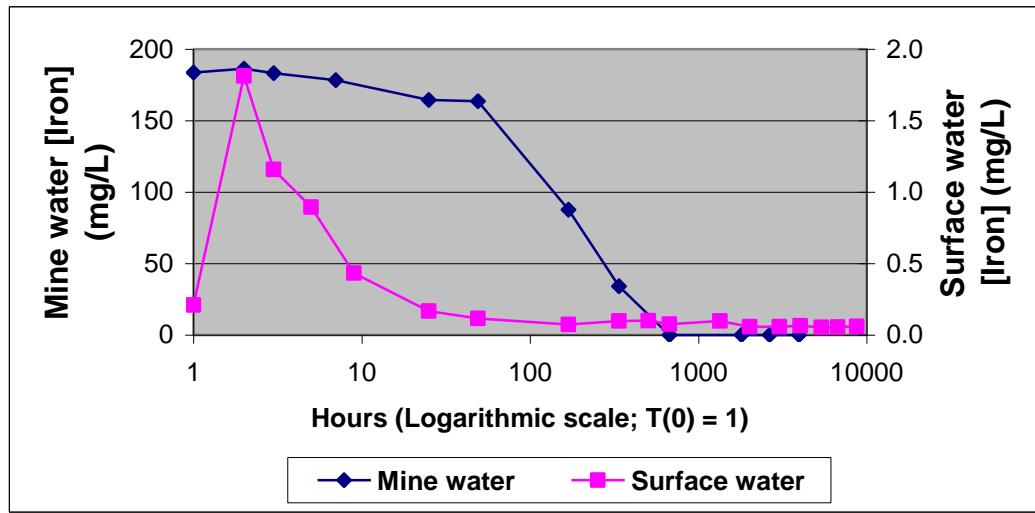


Figure 7. Iron in mine and surface water microcosms.

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