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# AN ENVIRONMENTAL CHARACTERIZATION OF UNBOUND MINING RESIDUALS FROM THE TRI-STATE MINING DISTRICT

By

SCOTT GREENWOOD
B.S., University of New Hampshire, 2005

THESIS

Submitted to the University of New Hampshire
In Partial Fulfillment of
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in

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## ABSTRACT


AN ENVIRONMENTAL CHARACTERIZATION OF UNBOUND MINING RESIDUALS FROM THE TRI-STATE MINING DISTRICT

by,

Scott L. Greenwood

University of New Hampshire, May, 2008

The mining and processing of mineral ores presents significant waste management issues due to the large quantities of waste generated and the environmental characteristics of that waste. Conventional waste management options are considered unsustainable and impractical, therefore consideration of alternative options, such as recycling, require investigation. This research analyzed the environmental characteristics of three mining residual samples from the Tri State Mining District to determine if they could be potentially recycled into an unbound highway application.

Testing found that all three samples could be a potentially acceptable aggregate substitute if implemented correctly. Leaching tests showed that the materials did not leach cadmium, lead or zinc above the EPA national drinking water MCL at neutral pH values. Slightly acidic concentrations can yield

cadmium and lead concentrations above the MCL, however no acid generation potential was witnessed in any of the samples tested.

# CHAPTER 1

# INTRODUCTION

## 1.1 Background

In 2005, mineral mining operations in the United States produced $16.3 billion of metal ores (NMA, 2007). Demands for these ores and the commodities they are use in are increasing ad infinitum, due to the industrialization of developing countries and the continuous growth of our world population. In turn, this demand is not only creating an increasing need for additional raw ore, but for other additional resources, which are required for their procurement. Large land reserves are necessary for not only the extraction of ore but for the disposal of residual waste as well. It is estimated that 1.8 billion tons of mineral residuals are produced in the United States annually from these beneficiation processes (Collins, 1994). This large quantity of material has traditionally been considered a waste; however, due to rising demand for aggregate, mineral residuals could potentially serve a secondary use application that provides a more sustainable solution to mining practices.

Mineral residuals are defined by the Resource Conservation and Recovery Act (RCRA) as waste generated by the extraction and beneficiation of ore and minerals. These mineral residuals are typically divided in two categories, waste rock and mine tailings. Mine tailings are the residual materials generated from the excavation and processing of high mineral content ore which were

originally mined from the earth. Tailings are generally the byproduct of processing through a series of proprietary procedures, including but not limited too; milling, gravity separation and flotation ponds. As a result, mine tailings are generally uniform, fine sized particles of angular siliceous material. Despite the extensive processing that mined materials undergo, tailings often retain high mineral concentrations. Figure 1.1 illustrates a general mining process from which waste rock and tailings are produced.

Waste rock is the excavated material (e.g., overburden) which has little to no mineral value and is generally not processed beyond its removal from the mine shaft or pit. Generally waste rock is separated from high mineral content ore at an early stage of processing. In comparison to tailings, waste rock has a wide range of particle sizes, ranging from large boulders to fines silts and sands.

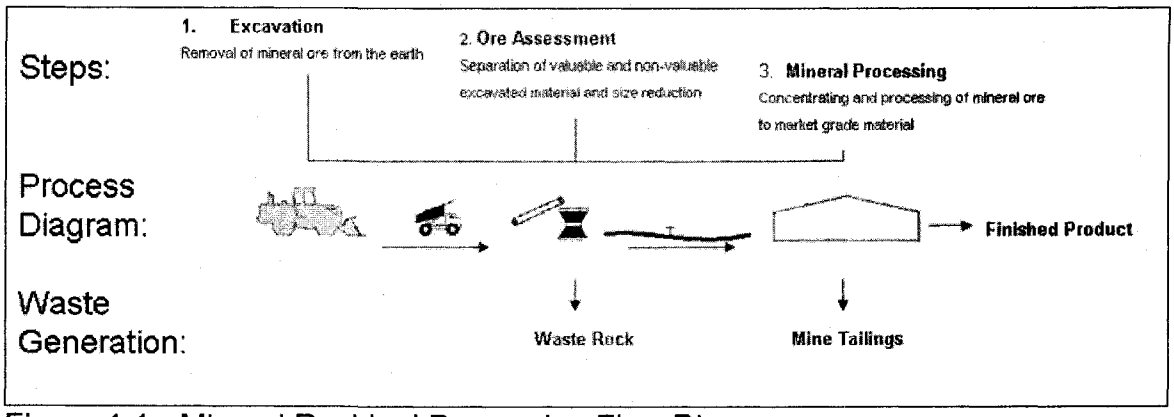

Figure 1.1 - Mineral Residual Processing Flow Diagram

It is a common practice for most mining operations to reuse a portion of their residuals on site for various applications. One example of this reuse is the reprocessing of old residuals to recover a greater amount of marketable mineral product. In some instances residuals are reprocessed using new technology; in

other instances low grade oxides present in waste rock are leached to produce a greater quantity of market grade product. Residuals can also be recycled on site in various construction projects. Mining is a dynamic process in which the landscape is continuously changing. This requires the construction of new roads, berms and impoundments on a regular basis. Residuals can often provide ample aggregate of acceptable quality for these requirements. On-site construction projects only account for a small percentage of the mine waste generated each year (Collins, 1976), therefore off site utilization is a critical component to the sustainable management of mineral residuals produced by mining operations.

Utilization of mineral residuals outside of mining operations is currently practiced in several states. The most common beneficial use is the substitution of mining residuals for natural aggregate in the production of asphalt and concrete. At least 34 states have reportedly implemented at least one application of mineral processing waste into their highway construction program (RMRC, 2007). Recycling generally occurs in locations where it is geographically and economically viable. However, expanding the responsible reuse of mineral residuals will be increasingly important as natural aggregate sources diminish and the demand for natural aggregate continues to increase.

To account for the diminishing virgin aggregate supplies, the use of mineral residuals should be expanded to facets beyond conventional bound applications. Options within the transportation industry include the reuse of residuals in unbound applications such as alternatives to natural aggregate in road base and sub base layers. In regards to volume, these applications are

more desirable because they require a larger percentage of total material for each highway mile. This again, will alleviate pressure on virgin sources and establish a greater demand for recycled mineral residuals, creating a more sustainable management option for both mining and construction industries.

Barriers inhibiting the safe and appropriate use of mineral residuals in secondary use applications will still need to be overcome. A first obstacle is to ensure the physical properties of a mineral residual will meet or exceed the engineering specifications and performance criteria of that application. Tailings generally have less than optimum particle size distribution, containing a large percentage of fines, which could either prohibit their use in an application or would require the material to be blended with another aggregate in order to meet certain engineering specifications. Secondly, mineral residuals may have environmental properties which could produce adverse effects to human health and the local ecosystem if not properly implemented. Tailings may have high trace metal concentrations or acid generating potential, which would need to be investigated and addressed prior to reuse. A final barrier is the economic viability of utilizing mineral residuals compared to alternative materials. A large percentage of mines are located in remote regions, requiring the transportation of residuals over extended distances to construction locations. This, in combination with any blending or treatment could increase the expense to utilize the material in a secondary application. A material that is not cost effective will be difficult or impossible to implement.

Although real barriers do currently exist for utilizing mineral residuals in large scale recycled applications, an effort to responsibly employ these materials has been a policy focus. The Safe, Accountable, Flexible, and Efficient Transportation Equity Act of 2005 and the "Chat Rule" by the Federal Highway Administration (FHA) and Environmental Protection Agency (EPA) are moving the responsible use of mineral residuals forward (EPA 2007). Additionally, state universities, departments of transportation, departments of environmental quality, and mining corporations have all conducted extensive research on the beneficial use of mineral residuals (Wasiuddin, 2005; Zanko, 2003). These like-minded efforts will be required in order to develop sustainable solutions to the ever increasing demand for natural resources on our planet.

## 1.2 Objective and Scope

The physical and environmental characteristics of mineral residuals may vary greatly, depending upon the mineralogy of the raw material and processing operations. Consequently these differences will affect the performance and behavior of any secondary use application in which the material is utilized. It would be difficult to account for all residual characteristics without a large comprehensive statistical review, which is beyond the scope of this report. As a result, this research focused on a specific mineral residual that has well-documented history and is important to the future beneficial use of mineral residuals; chat. Chat is a mined residual waste which originated from several

mining operations in the 20th Century. The residual is currently stockpiled throughout the Tri State Mining District; a region covering portions of Missouri, Oklahoma and Kansas.

In this report, chat was investigated primarily as a granular aggregate. This focus on granular applications is primarily due to the large volumes of residuals unbound applications would require, as discussed in the introduction. Specifically the report will investigate leachate and total concentrations of cadmium, lead and zinc. These elements are the primary constituents of concern to human health and the environment in the Tri-State Mining District (EPA, 2000) and were therefore the trace metals of primary focus in this study; however, other inorganic constituents were included as well.

The overall objective of this research is to characterize three mineral mining residual samples in order to better understand the risks they could pose to human health and the environment when placed in an unbound engineering application. To better define the objective and scope of this project, three narrower focused goals were developed:

1) Examine the history of mineral residual management in the Tri-State Mining District to identify positive and negative impacts of regulation regarding chat as well as the responsible or unsuitable management techniques that were practiced.

2) Identify the physical and chemical composition of three mineral residual samples to evaluate the potential direct hazards associated with the material as well as compare it to larger characterized cross sections of material in the Tri-State Area.

3) Characterize the leaching potential of the material and conduct geochemical speciation modeling to better understand the risk posed to ground and surface waters under various conditions.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

This chapter includes previous research and discussion relevant to the use of mineral mine residuals in unbound highway applications. It provides an overview of the Tri State Mining District, specifically the two superfund sites from which material was analyzed; a history of the material's past applications and subsequent regulations created from their mismanagement; and an overview of leaching procedures with a focus on the importance of accurate environmental characterization.

## 2.2 Mineral Residuals

There are two primary mineral residual stockpiled in the Tri State Mining District, chat and fine tailings. Chat, is the coarser and more common of the two materials. It was formed from the jigging and tabling milling processes of mineral ore during the active mining period in the district. Chat is much coarser than the tailings produced by the mining industry today. Its particle size distribution consists of ¼ in. crushed aggregate with 10% to 50% fines. The material is

composed primarily of the cryptocrystalline sedimentary rock chert with traces amounts of metal, dolimite and calcite. Fines are less common than chat in the Tri State District but are still present in large volumes. They were commonly produced from one of three benefication processes: the screening of feed material for gravity separation processes; from froth flotation; or the screening (washing) of chat to produce commercial aggregate (Dames and Moore, 1995). Fines are more consistent today in terms of their physical distribution than mine tailings produced. They generally consist of sand to silt sized particles with 30% to 60% of the material passing a #200 sieve.

## 2.3 The Tri State Mining District

The Tri-State Mining District is a 2500 square mile area located at the intersection of the Missouri, Oklahoma and Kansas state borders (Figure 2.1). The district covers a large geographical range spanning from the eastern fringes of the great plains to the northwest edge of Ozark uplift covering portions of northeast Oklahoma, southeast Kansas and south west Missouri. Locations within the district have been subjected to heavy mining in the past because of large deposits of lead and zinc ore in the area. Mining operations began in the mid 1800's and continued on until the last smelting operation closed in the 1970s. Although no mining activities are currently active in this area, the cessation of mining operations has left four national priority list (NPL) superfund sites. Superfund status is mainly due to the elevated concentrations of cadmium,

lead and/or zinc (hazardous substances as identified under CIRCLA §101) in soil, groundwater and surface waters on or near the sites. The NPL sites are: Jasper County, Missouri; Newton County, Missouri; Cherokee County, Kansas and the nation's largest superfund site Tar Creek, Oklahoma.

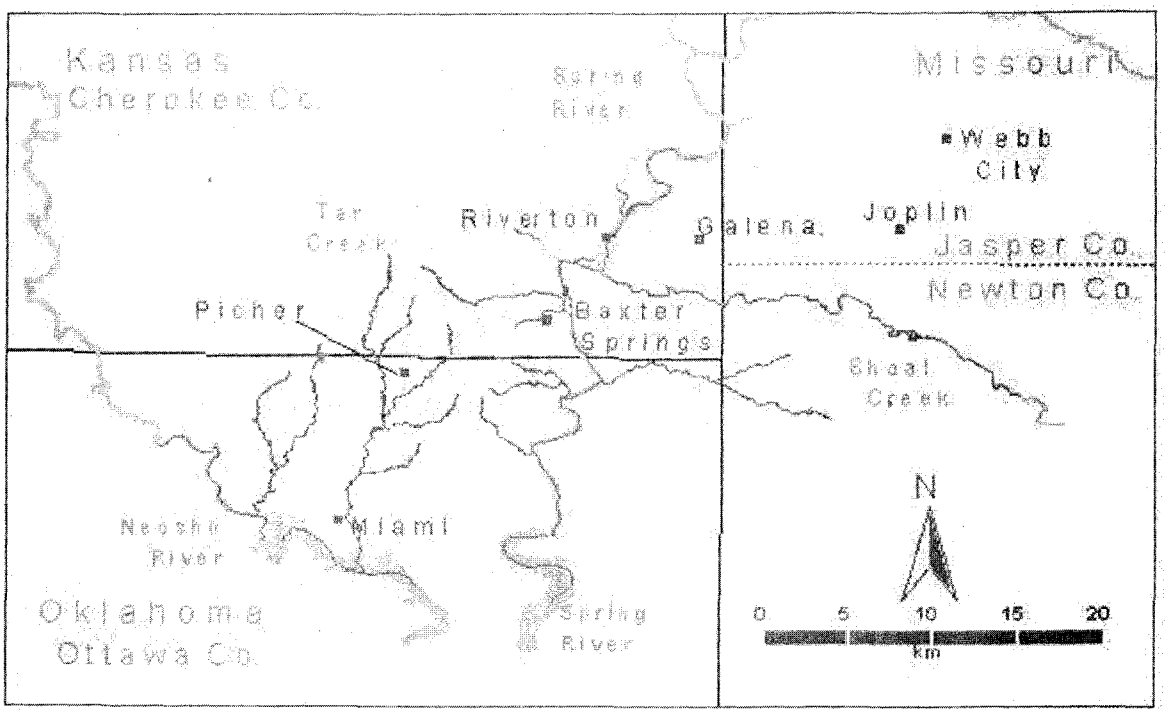


Figure 2.1 – The Tri-State Mining District
Source: Beyer W.N. et al., 2005

For this study, samples were obtained from two of the four superfund sites, Jasper County and Tar Creek. Therefore, a more detailed background of these two locations is provided in this section. The history and condition of these superfund sites are an important part of this research as it documents the environmental and human health impacts that the improper closure of mining operations can have on an area. Secondly, the background illustrates the need

to develop responsible and sustainable management practices for these materials. It can also be used as an educational tool to understand the successes and failures of the practice and policies surrounding this material so that recycling and reuse may be better implemented in the future.

### 2.3.1 Jasper County

Jasper County Superfund Site, otherwise known as the Oronogo-Duenweg Mining Belt Superfund Site, is 20 square miles and located just north of Joplin, Missouri. Mining operations over the past two centuries have included hundreds of mines and 17 smelting operations (EPA, 2000). These activities have left an estimated 10 million tons of stockpiled mine waste as well as exposed shafts, pits and a maze of underground workings in the area (EPA, 1988). Figure 2.2 shows the designated areas (DA's) that were investigated in the 1993 remedial investigation of the area. The focus of this investigation was the characterization of mined materials and soils, surface water, ground water, terrestrial and aquatic biota land use and demography, air quality and human food sources (Dames and Moore 1995).

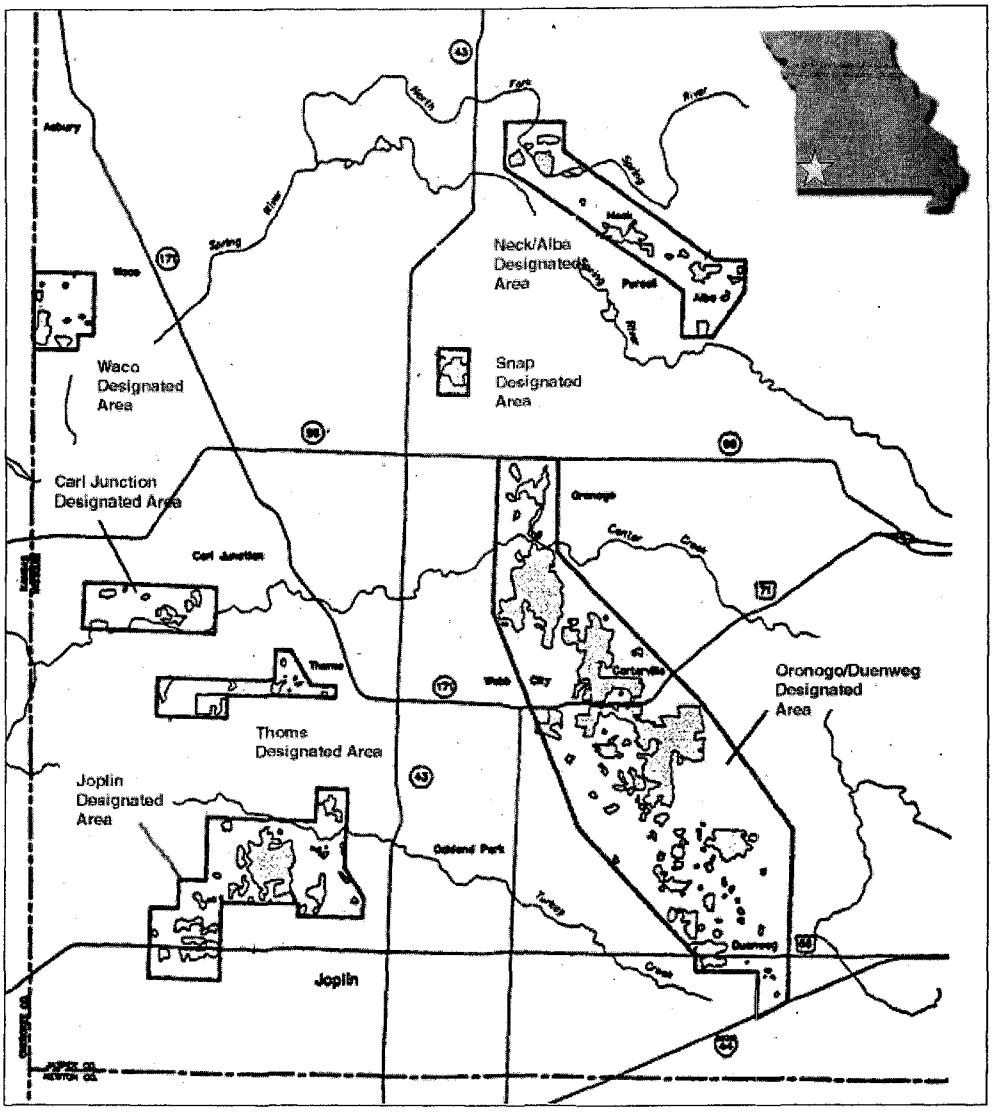


Figure 2.2 – Jasper County Superfund Site Map
Source: Dames and Moore, 1995

The extent of the contamination from mining activities has been assessed by several local and federal agencies. Metal concentrations in the top soil were sampled and analyzed by Dames and Moore in a 1995 final remediation study. Soils located within the DA regions shown above, were found to have slightly elevated metals concentrations compared to the US average. Soils tested in closer proximity to areas that were once actively mined yielded higher

concentrations. Transition material within 200 ft. of mine, milled or smelter related waste had concentrations of cadmium, lead and zinc that were a magnitude greater than that of the DA soils (Dames & Moore, 1995). Average concentrations and ranges of DA soils, transition soils from Jasper County and the US averages soil concentrations are shown in Table 2.1.

Table 2.1 – Jasper County Soil Concentrations

| Element | DA Soils | | Transition Zone Soils | | US Soil Average |
|---|---|---|---|---|---|
| | Average (mg/kg) | Range (mg/kg) | Average (mg/kg) | Range (mg/kg) | Average (mg/kg) |
| **Cd** | 4 | 0.25-21 | 27 | 1-288 | 0.35 |
| **Pb** | 90 | 17-321 | 472 | 20-3,900 | 19 |
| **Zn** | 422 | 50-2,900 | 3,986 | 57-45,400 | 60 |

Note: One-half the detection limit was used for non-detects when calculating average concentrations
Source: Dames and Moore 1995

Groundwater was also affected by mining activity. There are two aquifers in Jasper County which are separated by about 400 ft of composed limestone, shale and dolomite. The shallow aquifer provides drinking water to limited portions of the Jasper County Site. The deeper aquifer is located below 600 to 750 feet below the grounds surface and is a primary drinking water source for western Jasper County. Metals dissolved from exposed minerals in the underground working area spread into the shallow aquifer due to the generation of week sulfuric acid from the oxidation of calcium sulfate. As a result, cadmium concentrations above the drinking water maximum contamination limits (MCLs) were detected in well water from the shallow aquifer (Dames & Moore, 1995). Although the effects were generally limited to ½ mile from the mined zones, the

Missouri Department of Natural Resources has estimated that 400,000 to 740,000 acre-feet of groundwater have been impacted (MoDNR, 2003). Average concentrations for the shallow aquifer and ambient groundwater are shown in Table 2.2. The shallow aquifer and six wells upgradient of affected mining areas were sampled at two separate periods in 1993 by Dames and Moore. Concentrations for the three trace metals were, on average, an order of magnitude greater for wells sampled in the district than those upstream. Minimum detection limits for cadmium, lead and zinc are 0.1 mg/L, 1 mg/L and 5 mg/L. No contamination was observed in the deep aquifer and a conceptual groundwater flow modeling program predicted that contamination in the deep aquifer is unlikely to occur; instead the model predicts that the flux of metals would be upward, into nearby streams (Dames and Moore, 1995).

Table 2.2 – Jasper County Groundwater Concentrations

| Element | Upgradient Control | | Shallow Aquifer | |
|---|---|---|---|---|
| | Average *(ug/L)* | Range *(ug/L)* | Average *(ug/L)* | Range *(ug/L)* |
| **Cd** | 0.2 | ND - 0.6 | 10 | ND – 220 |
| **Pb** | 2 | ND - 5 | 16 | ND – 290 |
| **Zn** | 160 | 14 - 748 | 1,600 | 8 - 21,800 |

ND = Non detect
Note: one-half the detection limit was used for non-detects when calculating average concentrations
Source: Dames and Moore 1995

Surface waters have also been found to have elevated levels of metals. Zinc is the most common contaminant exceeding ambient water quality criteria (AWQC) criteria maximum concentration (CMC); however, elevated levels of lead

and cadmium have also been found in the area. The Spring River Basin is the primary drainage system for Jasper County, which is composed several waterways including Spring River, Turkey Creek, Center Creek and Short Creek. These tributaries are generally neutral in pH, if not slightly basic, and have a hardness of around 100 to 200 mg/L $CaCO_3$ (Dames & Moore, 1995). Testing and monitoring revealed that portions of the Center Creek, Short Creek and Turkey Creek have all exceeded the EPA AWQC for zinc at one time in history but concentrations appear to be declining over time (MoDNR, 2003). Zinc loading in the Spring River at low flow is primarily attributed to groundwater recharge to Center Creek, which flows into Spring River. During periods of high flow zinc loading increased due to increased run off from exposed mineral areas (Dames & Moore, 1995).

Mining operations have caused environmental effects to the local ecosystem. These effects have been documented through the inspection of vegetation, small mammals, birds and reptiles in the area (Dames & Moore, 1995; MoDNR, 2003; Beyer, 2005). Vegetation has been most notably been altered at locations where mining operations were once conducted. Groundcover population and production of local species are significantly different in these areas relative to areas that have been undisturbed by mining activities. No apparent difference in diversity was observed between the two areas however (Dames & Moore, 1995). Inspection of local wildlife yielded various results. Visual inspection of captured mice did not reveal any abnormal or unhealthy specimens (Dames & Moore, 1995). However, fish and invertebrate tissue

collected from local streams in Jasper County were found to contain elevated concentrations of zinc, lead and cadmium metals (MoDNR, 2003)

Bird populations at locations close to areas that were disturbed by mining operations had smaller populations than those at comparable sites further away. This effect is attributed mostly to the reduced vegetation cover in mined areas. It has been found that birds such as the American Robin, Northern Cardinal and various waterfowl have elevated concentrations of lead in their tissue compared to reference birds (Beyer, 2004). Elevated cadmium and zinc concentrations were also found to occur in the kidneys and liver in other bird species in the study.

The federal government has worked extensively with different state and private organizations to establish Jasper County as a superfund site and began remedial efforts in the area in 1990. As of 2002, the EPA had to identified and eliminated the greatest potential sources of risk to human health. This included the removal of contaminated soil from residential yards with lead soil levels greater than 500 mg/kg and the construction of a public water supply system to provide clean drinking water to people with contaminated wells. These remedies are reportedly functioning as designed (EPA, 2002). Even with the extensive effort that has been made in Jasper County since the site was established as a NPL, many ecological problems in the region have not yet been addressed and 10 million tons of stockpiled chat still remain.

### 2.3.2 Tar Creek

Tar Creek Superfund Site is located in the north central part of Ottawa County near Pitcher, Oklahoma (Figure 2.3). Mining operations began in Oklahoma in 1891 but the industry was not established in the area until 1914, when high mineral content ore was discovered just north of Pitcher (Brown & Root, 1995). Operations from that point forward focused on the Boone Formation, a shallow aquifer located 100 to 400 feet below the surface. Operations continued until 1970 at which point a total of 1.3 million tons of lead and 5.2 million tons of zinc had been produced. The active mining of the formation generated over 500 million tons of mine waste, 100 million tons of which remain on the 40 square mile superfund site today (EPA, 1995). A large portion of this area is reservation land inhabited by the Quapaw Tribe which integrates the Bureau of Indian Affairs into the Superfund process.

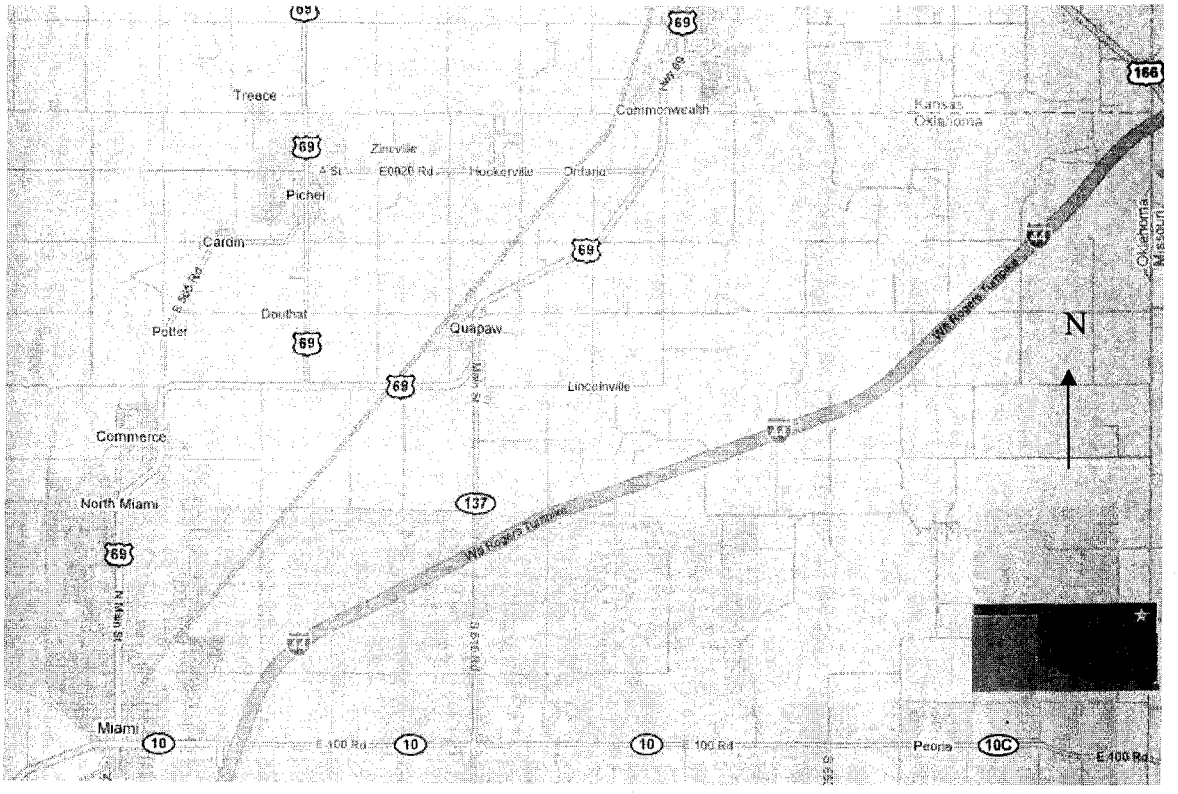


Figure 2.3 – Tar Creek Superfund Site Map
Source: Google Maps, 2007

Mining operations have had an impact on local ground and surface waters. The active mining of the Boone formation required the use of dewatering operations to access the mineral ore. After closure, pumping operations ceased which allowed the ground water level to rise and flood the abandoned mine shafts. This resulted in the contamination of over 123 million cubic yards of groundwater in the Boone Aquifer (Wasiuddin, 2003). Due to alterations in the surface profile, contaminated groundwater seeped to the surface and spilled into Tar Creek. The acidity of the mine drainage mixing with the alkaline waters of the creek precipitated ferric hydroxide staining the banks of the river. This

reaction was a highly visible repercussion of the condition up river and gained large amounts of public attention to Tar Creek.

In response to the environmental impacts found after the closure of mining operations, a task force was appointed in 1980 by the Governor of Oklahoma to determine the extent of damage. The task force reported that, other than aesthetic damages, no long term environmental impact extended to surface waters beyond Tar Creek (Wasiuddin, 2005). Downstream water bodies were left undamaged due to the high majority of the metals that precipitated into the Tar Creek sediment. The task force also determined that the Roubidoux Aquifer, the primary drinking water source in the area, was at risk of contamination. The Roubidoux Aquifer is located directly under the Boone Aquifer and is connected in some locations by leaky boreholes and wells through which contaminated groundwater had the potential to travel (Wasiuddin, 2005).

## 2.4 Chat

### 2.4.1 Historical Applications of Chat

Chat has historically been used in several recycled applications throughout the Tri State Mining District. Recycling the residual initially started because it was inexpensive and highly availability. Chat gained appeal as it continued to be utilized in new applications and proved itself as a comparable substitute to virgin aggregate. In fact, the implementation of chat into all of these

applications and products created a considerable market and significant source of income to the Tar Creek area at one point in time (EPA, 2005).

Historical uses of chat ranged widely in application without regard to the elevated concentrations of trace metals within the material and the health effects they might incur on end users. The material was used in bound and unbound applications by a wide array of manufacturers and producers. Reference in this document to bound applications includes products where the aggregate is physically altered from a granular material to a monolithic substrate, generally, although not always, through the use of a cement (Portland or petroleum based). Chat specifically, was used in bound applications such as aggregate for asphalt and concrete and applied in a variety of civil engineering projects including roadways, driveways, alleyways and parking lots. It was also used as a raw material in manufacturing. Several glass and ceramic manufactured products have been produced including ceramic floor tile, roof tile, bricks, pavers, and fence posts.

Unbound applications of chat were equally prevalent historically. Unbound applications are situations where the material is placed as an aggregate, in a granular state, lacking any cohesive additives binding or coating the material. Some applications may have been appropriately utilized and have not been associated with any negative effects in the literature. Other applications of chat however, were unsuitable for civil engineering projects, and resulted in unacceptable level of exposure to humans and the environment. It was these projects that caused some of the most dramatic health and environmental issues

in the area. Applications included the use of chat as fill for commercial and residential construction, such as top soil in the construction of new lawns where the material could come into direct contact with people. Chat was used as the top layer on unpaved roads where it could easily be suspended into the air and inhaled (Figure 2.4). Chat was even used as impact absorbing material in recreational facilities such as playgrounds and sport fields where the material came into direct contact with children.

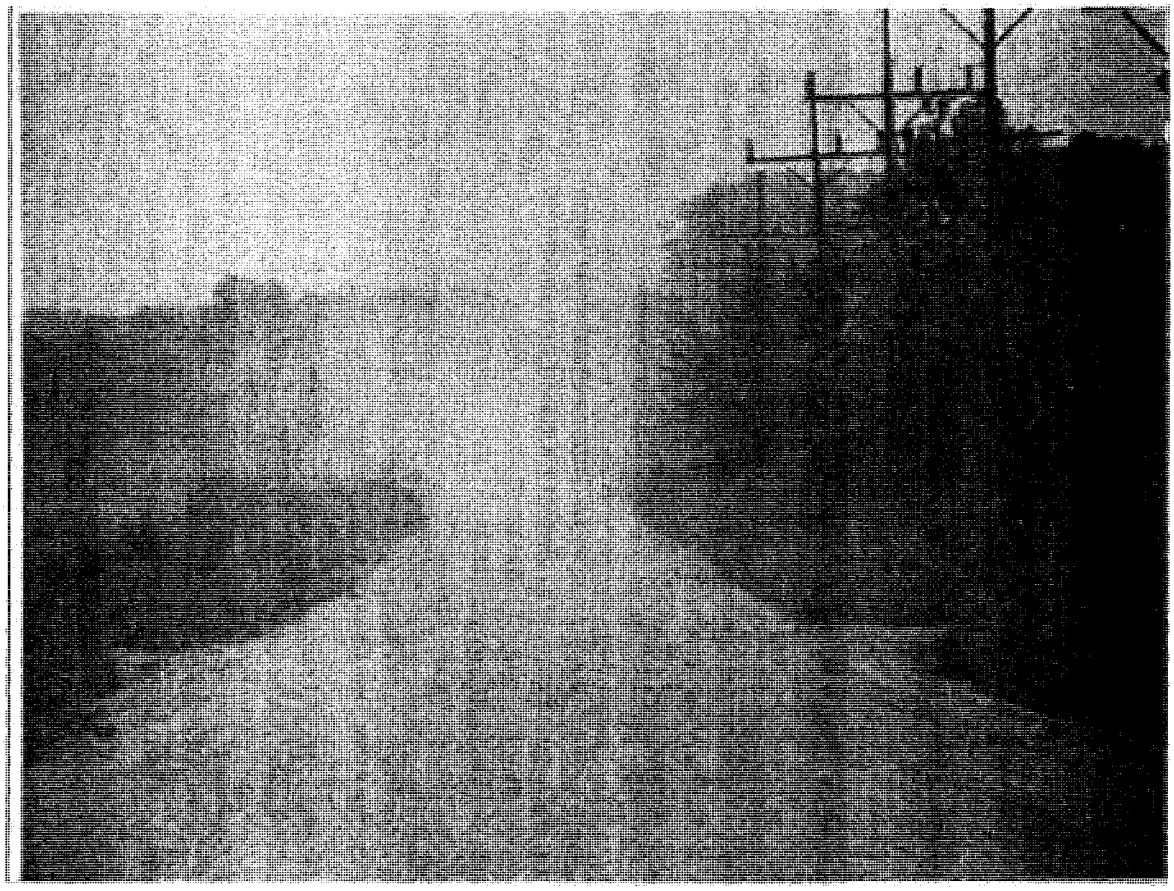

Figure 2.4 – Air Blown Chat from an Unpaved Chat Road
Source: Wasiuddin et al., 2005

### 2.4.2 Concerns with Historical Chat Applications

By the late 1950s significant concerns about the health and safety of reutilizing chat were being raised (Wasiuddin, 2005). It was not until 1994, however, that the Indian Health Service notified the EPA that 34% of children tested had an elevated lead blood levels (EPA, 2005). A large quantity of the remaining mining waste in Ottawa County is located on Native American land. This has put Native Americans and their children at a greater exposure to the negative impacts of the material. Similar elevated blood levels in children were also being discovered in Jasper County and Cherokee County. A study conducted by the Missouri Department of Health and Senior Services found that exposure to lead contaminated soils was the primary cause of elevated lead blood levels to the children living on the superfund sites. These reports contributed to EPA's conclusion that chat represented an unacceptable risk to human health and the environment (EPA, 1994).

As a result, the EPA launched a massive clean up effort throughout the Tri State Mining district removing contaminated soil from residential properties and areas of high accessibility. The efforts included the removal of over 84,400 cubic yards of material. (EPA, 2005). In addition, the Bureau of Indian Affairs placed a moratorium on the sale and use of chat in 1997 removing 80% of the stockpiled chat at Tar Creek from the market (Wasiuddin, 2005).

A complete ban of the sale and use of chat was quickly realized to be an impractical stance on the management of chat due to the existing stockpiles which remained a large environmental hazard throughout the area. Over 100

million tons of stockpiled chat remained in Tar Creek alone. The Bureau of Indian Affairs lifted its moratorium five years later in August of 2001 and US EPA Region's 6 and 7, as well as the state environmental departments, provided public guidance on chat use in MO, KS and OK. Currently, the Safe, Accountable, Flexible, and Efficient Transportation Equity Act of 2005 requires the EPA to create criteria to establish acceptable risk applications for chat use in transportation construction applications. Proposals for non transportation, non residential applications are also being considered (EPA 2007).

EPA Region 7 has compiled a list of unacceptable uses for chat including, material for sport fields and play grounds, material for sandblasting and agricultural purposes (EPA, 2007). The use of chat would likely fall under the beneficial use guidelines, sometimes called beneficial use determinations (BUD) by the states. Some states have formal BUD permit processes and some do not. Some uses of chat have been approved. Currently, the most common use is in the production of hot mix asphalt (HMA). Washed chat is widely used as an aggregate in HMA in Missouri, Kansas and Oklahoma, mostly in wear coats because of the improved frictional factor the material provides and the lack of natural aggregate in the areas.

## 2.5 Properties of Chat

This section will discuss the mineralogy of chat, its physical properties that are relevant to the materials environmental characterization; and the

environmental properties that have been investigated to date. Much of this information has already been summarized by the School of Civil Engineering and Environmental Science at The University of Oklahoma in their final report to the Oklahoma Department of Environmental Quality: A Laboratory Study to Optimize the Use of Raw Chat in Hot Mix Asphalt for Pavement Application (2005).

Chat's primary reutilization application has been as an aggregate in asphalt and concrete. For this reason much of the research preformed on these materials has been focused on the physical properties of these materials and its performance in these applications. Environmental testing has also been conducted by the EPA, primarily to characterize total metal concentrations as a result of the Superfund status of the area.

### 2.5.1 Mineralogy of Chat

The majority of the chat stockpiled in the Tri State Mining District consists of ¼ inch crushed angular fragments ranging from 10% to 50% fines. Chat is the residual waste created from the jigging operations of a chert/calcite/dolomite matrix for lead and zinc ore during the active mining period of the area. Chert, a main component of the matrix, is a silicious mineral described by the American Geology Institute as a hard, extremely dense, compact, dull to semi-vitreous, cryptocrystalline sedimentary rock consisting of primarily of cryptocrystalline silica (chiefly fibrous chalcedony) (Wasiudden, 2005).

Chat, the residual waste, is primarily composed of only chert after its processing with some lead and zinc residual remaining (Wasiudden, 2005). X-ray diffraction performed by Drake (1999) on stockpiled chat did not find any

galena or spalerite present (PbS or ZnS). These minerals were the principle ores present when the material was mined. Testing found that main components of the matrix had been removed by processing with only traces of the dolomite and calcite present in the stockpiled chat (Wasiuddin, 2005).

### 2.5.2 Physical Properties of Chat

An important physical characteristic to both the environmental and physical properties of a material is its particle size distribution or gradation. Physically, gradations strongly govern the engineering properties of a material. Environmentally, gradation analysis is important in defining the amount of fine particles associated with a material. It has been widely observed in the literature that finer particles generally have higher trace metal concentrations associated with them and this phenomenon has been specifically observed with chat regarding the total concentrations of cadmium, lead and zinc (Dames & Moore, 1995). Studies by Drake in 1999 found increased concentrations of these trace metals coupled with decreasing particle size of chat. Fine particles may also exhibit higher risks to human health and the ecosystem because fine particles are more likely to be suspended in the air with wind, which can spread the particles and create adverse air quality in the region (USGS, 2004).

Chat ranges in particle size from a fine gravel to a silt, passing the number 200 sieve. Figure 2.5 shows a gradation curve for a combined bulk sample from Jasper County conducted by Dames and Moore (1995). The bulk sample is comprised of 80 lb samples from five different stockpiles which exhibited the most common grain sizes in the area.

Gradations have also been preformed on Jasper County fines and chat from Tar Creek. The Jasper County fines were primarily composed of material passing the #65 sieve (212 um) with 30% to 65% passing the #200 sieve (75 um) (Dames & Moore, 1995). Tar Creek Chat has a comparable grain size distribution to the Jasper County Chat.

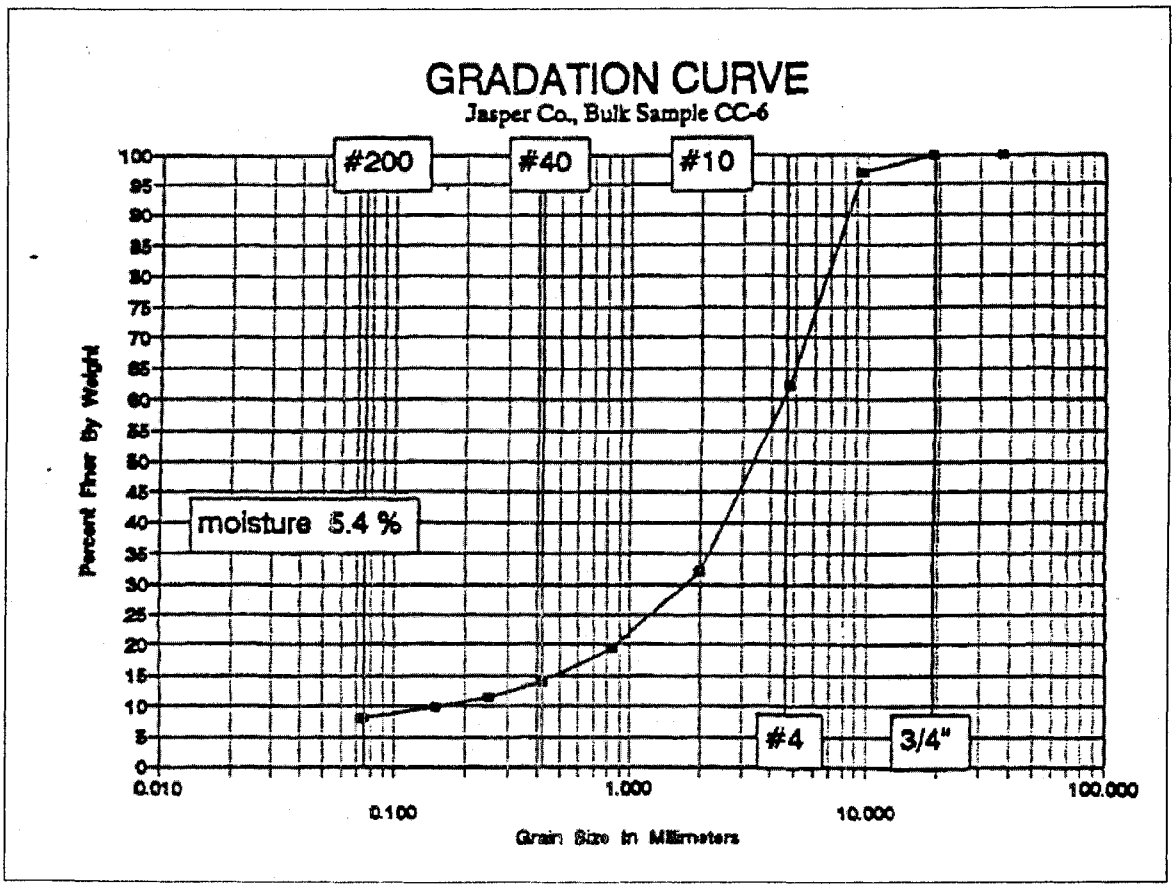


Figure 2.5 – Gradation of Jasper County Bulk Chat Sample
Source: Dames and Moore, 1995

## 2.5.3 Environmental Properties of Chat

Previous environmental studies of mineral mine tailing from the Tri State Mining District focused on total concentrations of trace metals within mineral

residuals as well as the amount of leachable metals in the materials. Total metal concentrations in the district are an important property of a chat for characterization purposes as well as for regulatory reasons. The EPA has deemed any residential soil lead concentrations above 500 mg/kg warrants remedial action because of the adverse health effects of direct exposure to lead (EPA, 1997).

Analysis of concentration of total metal in Tar Creek chat was conducted by Datin and Cates in 2002. The research surveyed four piles in the Tar Creek Superfund Site: Kenoyer North, Kenoyer South, Atlas and Ottawa. Jasper County chat total metal concentrations were conducted by Dames and Moore (1995). Chat from Jasper County was sampled from seven different designated areas (DAs) on the superfund site (Figure 2.2). Reported total concentrations are displayed in Table 2.3. The average concentrations of cadmium appear to be relatively consistent between Jasper County Chat, Jasper County Fines and Tar Creek Chat. Lead and zinc values vary significantly between the three different materials. Jasper County fines have the largest range in concentration with also the highest peaks for cadmium, lead and zinc.

Table 2.3 – Total Metal Concentrations in Tri-State County Residuals

| Element | Tar Creek Chat | | Jasper County Chat | | Jasper County Fines | |
|---|---|---|---|---|---|---|
| | Average (mg/kg) | Range (mg/kg) | Average (mg/kg) | Range (mg/kg) | Average (mg/kg) | Range (mg/kg) |
| **Cd** | 40 | 16 - 96 | 51 | 3.7 - 152 | 36 | 0.8 - 664 |
| **Pb** | 1071 | 258 - 2,207 | 608 | 22 - 6,000 | 1478 | 24 - 24,100 |
| **Zn** | 16611 | 8,876 - 34,407 | 8546 | 466 - 37,200 | 4872 | 80 - 71,500 |

Source: Dames and Moore, 1995 and Datin & Cates 2002

Datin and Cates (2002) also made important statistical observations regarding total trace metal concentrations of the bulk of chat stockpiled over the entire Tar Creek site. A much larger variability in concentration was observed between different piles than within a single pile. This observation is important in defining representative samples of a pile or designated area for secondary beneficial use or other treatment options. The Kenoyer North pile was found to have the highest average lead concentrations in Tar Creek (1314 mg/kg) while Kenoyer South has the highest average cadmium and zinc concentrations (63 mg/kg and 17115 mg/kg).

Concentrations of leachable metals are commonly established by leaching tests. The Toxic Characteristic Leaching Procedure (TCLP) is one of the most established leaching tests in the United States and has been the primary protocol used to understand the leaching potential of chat. Leaching tests provide information about the release of trace metals from a material into an aqueous phase which is much more mobile. The TCLP protocol also serves as regulatory test under the Resource Conservation Recovery Act. More discussion will be included in following sections (Section 2.6).

TCLP testing on chat from the Ottawa, Atlas and Kenoyer North piles in Tar Creek was performed by The Oklahoma Department of Environmental Quality and The University of Oklahoma. Table 2.4 shows the reported concentrations of three areas of Tar Creek.

Table 2.4 – Tar Creek Chat TCLP Concentrations

| Samples | # of Samples | Cd (mg/L) | Pb (mg/L) | Zn (mg/L) |
|---|---|---|---|---|
| **Ottawa Raw Chat** | 1 | 0.792 | 18.02 | - |
| **Atlas Raw Chat** | 2 | 0.586 | 4.494 | - |
| **Kenoyer North Raw Chat** | 20 | 0.402 | 8.378 | 155.7 |

"-" = No analysis was preformed
Source: Wasiuddin, 2005 and ODEQ, 2000

## 2.6 Leaching

Leaching tests are batch laboratory test methods that are designed to simulate the mobility of organic and/or inorganic analytes present in liquid, solid or multiphase liquids. Typically the test is preformed by mixing a defined mass of solid material with a defined volume of liquid (generally reagent grade water) for a given period of time. The liquid is then prepared and analyzed for the presence of trace metals or other constituents. Leaching tests are important environmental characterization and are most often used to describe the release of hazardous contaminates from waste material. They provide important analytical data which can be used to describe the chemical interactions of a specific system; produce geochemical speciation models and serve as a regulatory assessment for the appropriate disposal of the waste.

There are several factors that control the rate and total quantity of constituents that is leached from a material. Chemical factors include the pH of the leachant, the liquid to solid (LS) ratio of the material to the leachant, buffering

capacity of the material and the acid generation capability of the material. Physical factors are also important, such as surface area and particle size. Various leaching protocols account for these factors differently in an attempt to accurately describe how a material will leach in a particular situation.

As discussed previously, one of the most recognized leaching tests in the United States is the Toxicity Characterization Leaching Procedure (TCLP). Reliance on the leaching protocol may be due its regulatory position under the Resource Conservation Recovery Act (RCRA). TCLP was initially established to replace the Multiple Extraction Procedure and serve as a new single test which would determine if a waste was appropriate for disposal in a municipal landfill. Problems occur when the protocol is extended to define leaching scenarios beyond its original design. Monofills and other non standard disposal methods typically do not have the same leaching conditions as these municipal waste landfills and therefore are inadequately characterized by the TCLP protocol. The limitations are also recognized regarding the reutilization of waste products (residuals) in secondary use applications. The Scientific Advisory Board has specifically criticized the umbrella policy usage of TCLP on the basis of technical considerations including its limited range to accurately represent the controlling parameters for different applications (SAB, 1999).

The applicability of the TCLP protocol for citing appropriate secondary use applications of mineral mine wastes is equally inadequate although it has been the dominate procedure used in evaluating the leaching characteristics of mineral residual waste. A primary incongruity is that mineral mine waste is not classified

by RCRA as a solid waste. This is because the Bevill Amendment in 1980 determined that all mineral mine waste is exempt from RCRA regulations (3001(b)(3)(A)(ii)). This exemption denotes that mine tailings can not be classified as a hazardous waste, as it is solely a RCRA establishment. Therefore, in terms of regulation, it makes little sense to use TCLP as a test to cite appropriate secondary use applications for mineral mine residuals. Additionally, as the Scientific Advisory Board reports, TCLP is a limited in the range of leaching conditions is can accurately simulate. Secondary use application can often be extremely diverse in pH, exposure and various other controlling parameters. Therefore TCLP, which only evaluates a constant pH, is a technically limited protocol as well. More in depth leaching tests are clearly required to properly access materials in reuse applications.

As an alternative, Kossen et. al. (2002) has developed a series of testing protocols to better evaluate the leaching potential of a material under various conditions. This framework includes the varying liquid to solid ratio leaching test (LS Dependent) and the pH dependent leaching test. Both are comprehensive tests that describe the leachability of a material over a wide range of conditions. Broader, more encompassing leaching tests are in general better equipped to properly cite residual materials in secondary use applications. This is because secondary use applications may differ widely in their natural pH, exposure to runoff and infiltration, and other controlling parameters. In addition, more panoptic testing needs to be implemented to protect adjacent natural resources. The lack of physical barriers between a secondary use applications and the

environment increases the susceptibility of groundwater and/or other natural water bodies to potential contamination. For these reasons it is critical to understand how residuals will perform in the application in which they are utilized.

# CHAPTER 3

# METHODS AND MATERIALS

## 3.1 Overview

Extensive laboratory testing and modeling was performed to accurately characterize three mine tailing samples. Testing included Grain Size Distribution Analysis, Acid Base Accounting, Total Metal Analysis, Acid Neutralization Capacity, pH Dependent Leaching and Varying Liquid to Solid Ratio Dependent Leaching.

## 3.2 Materials

Three materials from the Tri State Mining District were evaluated in this study. Two materials, Jasper County Fines (Jasper Fines) and Jasper County Chat (Jasper Chat), are from the Jasper County Superfund Site in Jasper County, Missouri. The Jasper Fines are a traditional tailing, ranging in size between a silt/clay sized particle and a sand. Fines in the Jasper County DAs have been reportedly products of gravity separation processes, froth floatation or sieved fractions of commercial aggregate. The specific source of this material is unknown.

Jasper Chat is the more prevalent of the two residuals at Jasper County and is composed of 1/4 in. crushed chert with 10% to 50% fines. The two Jasper County samples were provided and sampled by the US EPA, Region 7. Approximately 80lbs of each residual was sampled from stockpiles and shipped in its raw form. No washing or pre-treatment was performed on the material prior to the shipment to the University of New Hampshire. The materials were sampled and delivered in the fall of 2006.

The third material, Tar Creek Chat (Tar Chat), was sampled from the Tar Creek Superfund Site in Ottawa County, Oklahoma. Two mine wastes currently exist on the Tar Creek compound; a coarse chat accounting for 70% of mill feed discards and the remaining finer chat. Tar chat is a courser material which is composed of processed chert from the Boone Formation. The material was sampled from the Wilson Pile, south of Cardin, by the US EPA, Region 6 and shipped in the same accordance as Jasper County samples.

## 3.3 Methods

### 3.3.1 Grain Size Distribution Analysis

Particle size is an important physical characteristic that can have a large effect on the physical and environmental properties of a material. Environmentally, smaller particle sizes have been reported to have larger total

metal concentrations. Particle size also has a large effect on the leachability of a material according to a 1999 Scientific Advisory Board review (SAB, 1999). The grain size distribution of an aggregate is an important physical property of the aggregate in regards to its performance in bound and unbound engineering applications as well. Highway aggregates are generally characterized by gradations, as it affects critical factors such as their maximum density and permeability. In bound applications, such as hot mix asphalt, the gradation of an aggregate can affect properties such as stiffness, stability, durability, permeability and fatigue resistance.

A standard dry sieve analysis was performed at UNH according to ASTM D6919–04 for each of the three materials. Between 500g and 700g of dried material was shaken for 10 minutes passing through sieves ¼ inch (6.3mm) mesh to #200 (75um) mesh.

### 3.3.2 Acid Base Accounting

Acid rock drainage is a particularly important parameter for mined materials which may contain iron sulfide. Pyrite, pyrrhoite or polymetalic sulfide deposits will oxidize in the presence of water, oxygen and acidophilic bacteria. This oxidation produces sulfuric acid which can drastically lower the pH of the water and have large impacts on the leaching characteristics of the area. A large acid generation capacity may not only effect the direct material but could also change the leaching characteristics other nearby aggregates, creating groundwater that is either caustic and/or toxic due to elevated concentrations of metals.

Acid Base Accounting (ABA) of the samples was determined by the Modified ABA Method. Testing was performed by Sierra Environmental Monitoring, Inc. This method, otherwise known as the Modified Sobek Method, consists of two independent analysis; the determination of the Acid Generation Potential (AGP) and the Neutralization Potential (NP) of the material in question. For each analysis the mineral residuals tested were size reduced to < 75um.

The Acid Generation Potential (AGP) is based upon the amount of sulfuric acid that can be generated by a material due to its metal sulfide concentration. AGP is determined by identifying the total pyritic sulfur concentration in material (i.e., metal sulfide concentration) and generally reported in tons of calcium carbonate per 1000 tons of mine waste. The concentration of pyretic sulfur is analytically determined through the use of a combustion-infrared spectrophotometer (e.g., LECO[2] furnace).

The Neutralization Potential is based upon the amount of acid neutralizing carbonate mineral present in the material. NP is determined by a 24 hour acid digestion at ambient temperature. At the end of the digestion the material is required to have a pH between 1.5 and 2.0. To calculate the amount of acid consumed, a titration is conducted with sodium hydroxide (NaOH) from the final pH of the digestion to an endpoint of 8.3. NP is generally reported in tons of calcium carbonate per 1000 tons of material.

Based upon the AGP and the NP, the net-neutralizing potential (NNP) or the NP/AGP ratio can be determined. These values classify materials into different categories to help determine the potential for acid rock drainage. The

NNP is calculated by subtracting the AGP from the NP. This determines if there is a greater acid generation capability in the material then neutralizing capability. If so, there is a strong potential for the material to produce sulfuric acid under certain conditions and possibly create an acid rock drainage complications. The same is true of the NP/AGP ratio, if the ratio is greater than one, there is a greater potential acid producing dynamic than neutralization ability in the material.

There are several interpretations that have been established to determine if the material has a "high", "uncertain" or "low" acid producing potential. ABA classification follow Brodie and others (1999) criteria, which required a material to have a NP/AGP ratio of 3 to 1 to be considered non-acid producing (White III, 1999).

### 3.3.3 Inductively Coupled Plasma – Atomic Emission Spectroscopy

Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) is the inorganic (trace metals) detection method for the Total Metals Analysis, pH Dependent Leaching Analysis and LS Dependent Leaching Analysis. Testing was conducted at UNH using a Varian Vista AX machine and performed in accordance with method EPA 6010C. Concentrations were detected for each sample between the minimum detection limit of the element and 50 mg/L of the trace metal. Digested samples were at a minimal pH, and required no preservation. The only preparation required was dilution in some cases with deionized water to establish a concentration within the detection limit range. The leached samples (LS and pH dependent leaching tests) required preservation

with 100 µl of High Purity 70% Nitric Acid prior to analysis, to ensure constituents remained soluble. In specific circumstances dilution was also required. Each sample was evaluated for presence and concentration of the cations: aluminum, arsenic, antimony, barium, beryllium, cadmium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, nickel, lead, selenium, silver, strontium, thallium, vanadium and zinc.

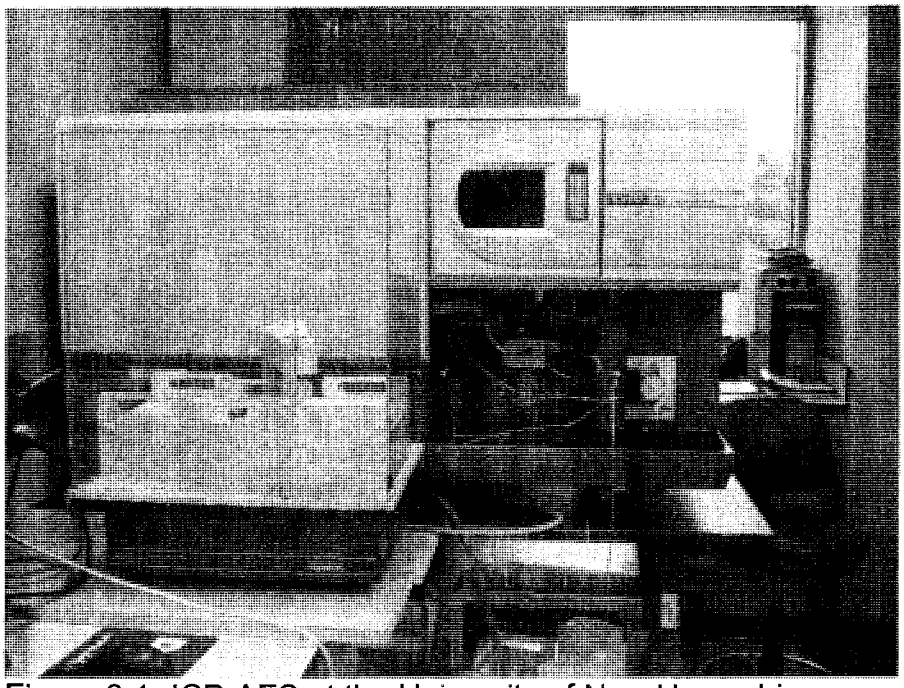

Figure 3.1- ICP-AES at the University of New Hampshire

Quality was ensured through the use of NIST standards, calibration blanks and calibrations verifications in each analysis. A matrix spike was also performed to ensure elemental interferences were not affecting the detection capabilities of the analysis. NIST as well as the calibration verifications were included at least every 20 samples for every analysis. This insured that three critical analysis components were of acceptable quality. First, they ensure the calibration standards were prepared correctly. Secondly, they ensured that the

sample concentrations remained consistent over the time of analysis. And lastly the use of calibration verification solutions ensure various labs conducting trace metals analysis are detecting similar concentrations of a prepared solution. Detection consistently reported concentrations within a range of 80% to 120% of the calibration verification solution. Solution matrix spikes were only conducted once but were held to the same standards as the calibration verification solutions.

### 3.3.4 Total Metals Analysis

A total metal analysis for this study was achieved through microwave assisted acid digestion of the mined residuals (EPA Method 3052). 500 ug of samples were digested in a sealed Teflon coated HDPE reaction vessel with 9 ml of High Purity 70% Nitric Acid; 4 ml of High Purity` 30% Hydrochloric Acid; and 2 ml of High Purity 70% Hydrofluoric Acid. A Microwave Acceleration Reaction System 5 (MARS5) was utilized to facilitate the digestion. Sample temperatures were increased from ambient conditions to 180 degrees Celsius in a period of 10 minutes. The samples were then held for an additional 10 minutes at 180°C. Following the digestion, samples were diluted to appropriate concentrations for ICP-AES analysis.

### 3.3.5 Acid Neutralization Capacity

The acid neutralization capacity is a pretest to the pH dependent leaching test as well as an important characterizing parameter of a material. This test will define the buffering capacity of the material; a crucial element to counteracting

any acid generating potential it may have or may be exposed to in the environment due to acid rain or the acid generation of materials adjacent to the area. Buffering capacity is generally linked to the presence of carbonates but it can also be attributed to organic carbon as well.

The acid neutralization capacity was conducted during the pH dependent leaching for this study. Various doses of 4 N nitric acid or 4 N sodium hydroxide were included into a 10 liquid to solid ratio of deionized water and sample. The samples were closed, sealed from the atmosphere, and mixed end over end for a 48 hour period. At the conclusion of mixing a pH reading was taken using Schott Blueline dirty solution probe. Probes were calibrated before every use.

### 3.3.6 pH Dependent Leaching

Variations in pH can have a large effect on the leaching properties of a material; therefore evaluating a material over a wide pH range is critical to the proper characterization of the material and the safe implementation into a secondary use application. This is due impart to two factors, the range of pH conditions that a material may be exposed to in an uncontrolled setting and the proximity of the application to sensitive natural resources. The pH of a system maybe controlled by a number of variables including the pH of the rain, local groundwater, nearby soils or the chemistry of the material itself. These parameters can vary drastically between different environments, so an understanding of the leaching characteristics over a wide range of conditions is a necessary segment to adequately protect local ground and surface waters.

PH dependent leaching was performed according to Kosson et al, 2002 A.2. SR002.1 at UNH laboratories. Each material was leached in triplicate at all nominal pH values between 2 and 12. Forty gram samples were mixed in 400 ml of deionized water/nitric acid/sodium hydroxide solution to create the appropriate pH leaching conditions as defined by the acid neutralization capacity test. Samples were mixed in a 500 ml sealed HDPE container isolated from the atmosphere in an end over end mixer (standard TCLP mixer) at a rate of 28 rpm for a period of 48 hours. At the conclusion of the mixing period samples were filtered through a 0.45 um filter and preserved with 100 ul of high purity 70% $HNO_3$ to ensure ions remain is solution.

### 3.3.7 LS Dependent Leaching

The varying leachability of a material due to the liquid to solid ratio of the material and leachate provides insight into how a material may leach over time. The increasing ratio of the liquid to solid components simulate an increasing amount of groundwater or rain (leachant) that a material is exposed too. If the flow characteristics of rain infiltration or groundwater exposure are understood and quantifiable, then the leachant exposure can be converted to a time variable. This allows the concentration of analytes leached over a period of time to be estimated. SR003.1, a LS dependent leaching test developed by Kosson, subscribes to this theory and in doing so simplifies a sometimes complex percolation column study into a batch test.

Varying liquid to solid ratio (LS) dependent leaching was performed in accordance with Kosson et al, 2002 A.3. SR003.1 at UNH laboratories. Liquid to

solid ratios included 0.5, 1.0, 2.0, 5.0 and 10 L/g of material (dry weight) in deionized water. Samples were leached for 48 hours at their natural pH (between 8.0 and 9.5) in an end over end standard TCLP mixer at a rate of 28 rpm. Samples were contained in a sealed HDPE container isolated from the atmosphere. Container size ranged between 200ml and 500ml and was sighted for the appropriate LS ratio. At the conclusion of the mixing period samples were filtered through a 0.45 um filter and preserved with 100 ul of high purity 70% $HNO_3$ to ensure ions remain is solution.

### 3.3.8 Geochemical Speciation Modeling

Geochemical speciation modeling was used to identify possible solid phase mineral complexes which control the leaching behavior of the Jasper County Chat sample. LeachXS (Leaching eXpert System) is a package developed by the Netherland Energy Research Foundation (ECN) and was used in these modeling exercises. The program utilizes ORCHESTRA (Objects Representing CHEmical Speciation and TRAnsport models) to integrate multiple mineral complexation solubility behaviors, chemical reactions and transport modeling to determine the leaching characteristics of a material. ORCHESTRA consists of two parts, a generic calculation kernel and a file with model definitions in object format which allows the program to provide geochemical leaching characteristics similar to other commonly known geochemical speciation models, such as MINTEQ (Meeussen, 2007). The program allows the user to input leaching concentrations of multiple elements from various leaching protocols to

cross reference against calculated solubility diagrams from a database of various mineral speciation manipulated by the concentrations within the sample.

For the modeling conducted in this research, dissolved ionic leachate concentrations from the pH dependent leaching test of Jasper County Chat were entered into LeachXS. As with the leaching tests, cadmium, lead and zinc are the three primary elements of focus due to the historical environmental implications of this material. To determine possible solid phase minerals that control the leaching behavior of these elements, redox conditions of the material first needed to be established. Iron(III), Manganeses(II) and Chromate were selected as design elements and were modeled at various pE+pH values ranging from 10 to 20. The strongest pE + pH correlation was then implemented in the analysis of cadmium, lead and zinc.

In addition to redox conditions, surface complexation due to the presence of iron and aluminum oxide was also evaluated to account for the concentration of free ions particularly at low pH values. Amorphous and crystalline hydrous ferric oxide concentrations were determined through extraction procedures from Meima & Comans (1997) as described by Fallman, Taylor and Salaneck in AFR-Report 252 to the Swedish Environmental Protection Agency (Fallman A, 1999). The sorption effects of aluminum oxide concentrations in the materials were also considered in the geochemical modeling of cadmium, lead and zinc (Meima & Comans 1997).

Possible mineral complexes of these elements were then evaluated based upon their "Figure of Merit" (FOM). FOM is an internal calculation within the

program which numerically compares the Saturation Indices (SI) of a known mineral to the SI values of the sample under investigation. The sample and potential mineral correlation is rated by how many matches exist within a defined SI range ($FOM_{Hit}$) and the closest fit between the comparable SI values to the evaluated material ($FOM_{Fit}$). These values are combined to identify the mineral species which best match the solubility characteristics of the material question. Following the objective first selection of several adequate speciation possibilities, according to their figure of merit, the mineral species are then subjected to a visual inspection to determine which one most closely follows the solubility characteristics of the material being analyzed. Graphical assessments can then be made as to how well the potential mineral complex solubility reflects the leaching behavior of the sample in question.

### 3.3.9 Fate and Transport Modeling

A solute transport model, MYGRT 3.1 (MYGRAtion Transport model), was used to model the fate and transport of a contaminate of concern (e.g., cadmium) leached from a highway fill section into local groundwater. MYGRT is a software package developed by the Electric Power Research Institute that was designed to mange the disposal of coal combustion products. The program simulates a single contaminant, generated from a surface source, migrating downward through the unsaturated soil layer, mixing with the underlying groundwater, and then migrating horizontally downgradient through the aquifer through the incorporation of advection, dispersion and retardation.

The MYGRT program consists of 22 analytical models based on analytical solutions to mass transport equations using the integral transform technique. The integral transform method starts with a partial differential equation, boundary conditions, and initial conditions of a transport problem and proceeds to an exact solution of it. The partial differential equation is commonly known as the advection dispersion equation and accounts for solute concentration relative to sorption, advective flux and dispersive flux. Steady water flow in saturated or uniformly saturated conditions in homogenous media is represented by

$$\frac{\partial C_w}{\partial t} + \frac{\rho}{\theta_w}\frac{\partial S}{\partial t} = D\frac{\partial^2 C_w}{\partial x^2} - v\frac{\partial C_w}{\partial x}$$

Where,

$C_w$ = solute concentration in the water (mass/volume)

$\rho$ = dry bulk density of permeable material (soil) (mass/volume)

S = sorbed phase

$\theta_w$ = volumetric water content

v = average pore water velocity (distance/time)

D = dispersion coefficient

The terms on the left hand side of the equation represent the rate of change in solute mass in the solution phase in summation with the rate of change if the solute mass in the sorbed phase. The right hand side terms represent the hydrodynamic dispersion flux component and the advective flux component. The program can also account for substrate decay; however this is

not relevant to the analysis of inorganic analytes. Given the appropriate parameter selection this equation yields solute concentration over time and space.

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Overview

The results of the physical and environmental tests outlined in the methodology section are presented and discussed in this section. Here, as elsewhere in the report, Jasper County Fines are referred to as Jasper Fines, the Jasper County Chat as Jasper Chat and the Tar Creek Chat as Tar Chat. It is reemphasized that the materials tested in this report are small sub-samples and are not meant to be representative of the accumulation of the total material located at either of the two locations from which the residuals originated.

## 4.2 Moisture Content

The results of the moisture content analysis for the three mineral residuals are shown in Table 4.1. The Jasper County Fines tested at UNH were lower than moisture content range for Cherokee Creek fines given in the literature. Jasper Fines were compared to fines from the Cherokee Creek Superfund Site in Kansas due to limited data in Jasper County. Cherokee Creek was investigated by the same company that performed to remediation investigation for Jasper

County and both fines were reported to be similar in nature (Dames and Moore, 1995). Jasper County fines were measured to contain 10.9% moisture.

Moisture content for chat in Jasper County was cited between ranges 3.5% and 5.8% in the literature while samples tested at UNH found a much lower moisture content at 0.67%. The literature also reported that chat sampled during drier months can decrease in moisture content to ranges between 1% and 3% (Dames & Moore, 1995). While both Jasper County samples tested low, the Tar Creek Chat sample tested (6.3% MC) was slightly above the Jasper County Chat moisture content range.

Table 4.1 – Moisture Content of Tri-State Residuals

| **Material** | **Moisture Content** *(%)* |
|---|---|
| Jasper Fines | 10.9 |
| Jasper Chat | 0.67 |
| Tar Chat | 6.3 |

There are several explanations for why the tested moisture contents vary from those cited in the literature. Specific sampling methods and sampling locations from the pile are unknown for the materials tested. Material sampled may have also been more exposed to the atmosphere and local weather which may have increased or decreased the moisture content of the material sampled. It is also submitted that both Jasper County materials, which had low MC values, were sampled by the same party, while the Tar Creek chat was sampled by a second party, which may suggest sampling methodology had a role.

Evaporation may have also occurred while the materials were in transport or in storage, although this is unlikely because all three samples were shipped and stored in the same manner. Materials were shipped in 5 gallon sealed containers and then stored around 20°C in the container in which it was shipped or a 500 ml HDPE container prior to analysis.

## 4.3 Sieve Analysis

Gradations were conducted in triplicates for the three materials sampled. A sieve analysis consistent with ASTM D 6919 – 04 requirements was performed to determine the particle size distribution and ensure that the materials tested were consistent with reported gradations of the greater population of the respective materials. The results, shown in Figure 4.1, display the gradation curves for Jasper Fines, Jasper Chat and Tar Chat. The particle size of the material is given on the x-axis, proceeding from larger to smaller particle size and the percentage of the material passing that diameter is given on the y-axis. From this figure, it can be observed that Jasper Fines is poorly graded material with the majority of the material between 833um and 2000um. Alternatively, Jasper Chat and Tar Chat are displayed to be relatively well graded between 10mm and 0.3mm.

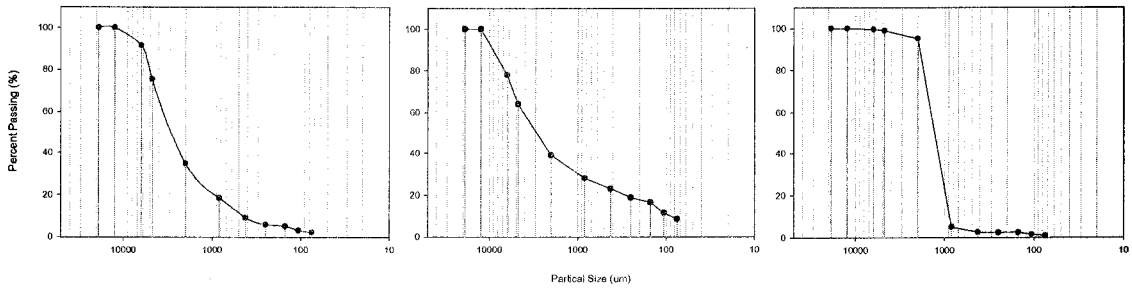


Figure 4.1 – Sieve Analysis of Tri-State Residuals
(a) – Tar Chat
(b) – Jasper Chat
(c) – Jasper Fines

The two chat samples analyzed by UNH are fairly consistent with the general description of chat in the literature. Chat is generally described as ¼ in material with 30% to 60% fines (passing the #4 sieve). The two UNH chat samples have 65% and 75% fines, a slightly larger percentage than generally described.

Chat samples were also graphically compared to a bulk chat sample representative of the larger population of chat on the Jasper County Superfund Site. The bulk sample is composed of five 5-gallon samples which were recovered from different accumulations representing the most common grain size distribution of 24 stockpiles in six designated areas (Dames & Moore, 1995). A visual inspection reveals that chat from Tar Creek and Jasper County is fairly consistent in gradation to the bulk analysis performed on a representative sample of Jasper County Chat.

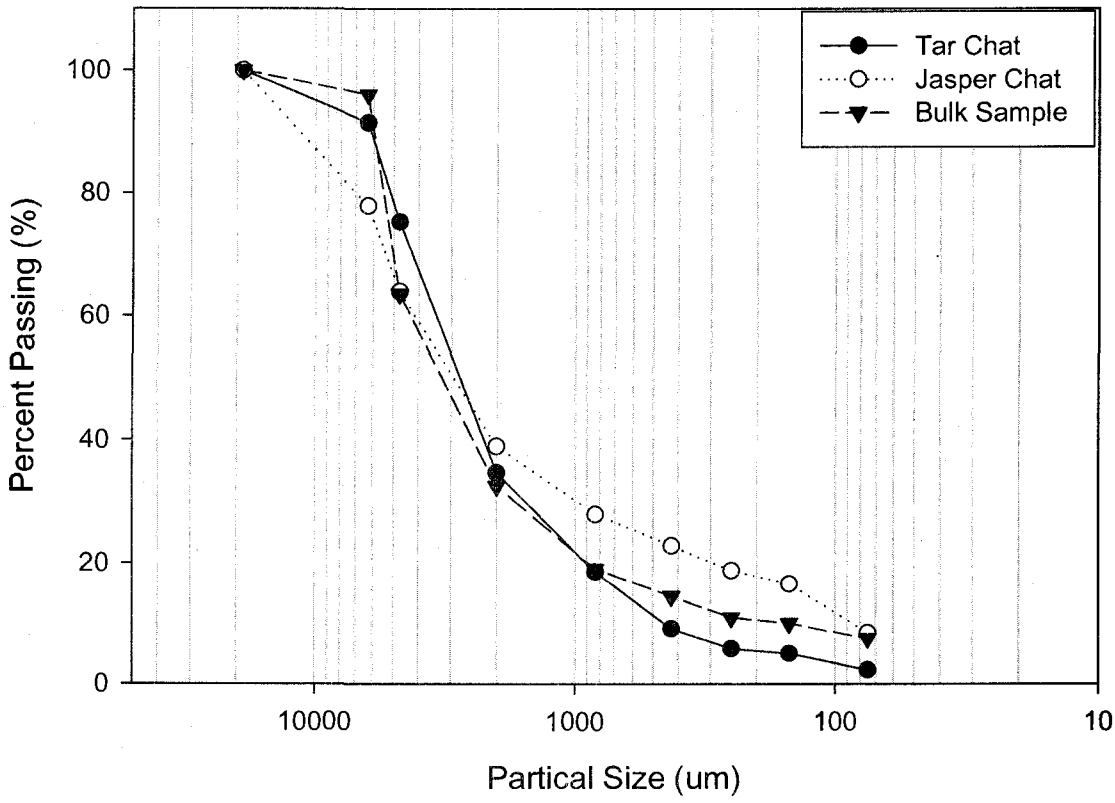


Figure 4.2 – Reported Chat Gradation vs. Measured Chat Gradations
Bulk Chat Source: Dames & Moore, 1995

Gradation curves display the particle size distribution over a material exceptionally well; however other visual representations are sometimes helpful to compare the variation between materials. To observe the dominate particle size fractions between the three samples, Figure 4.3 shows the percentage of total composition associated with a particle size range.

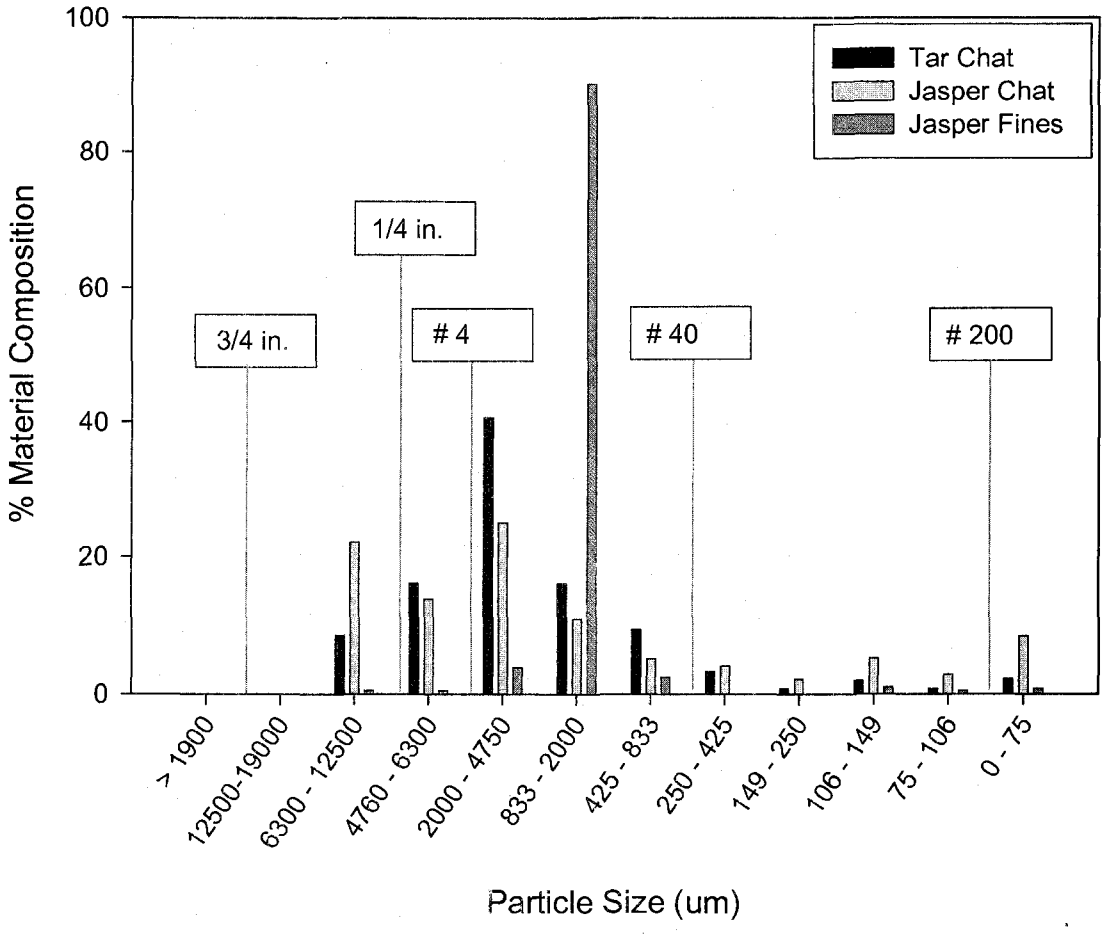


Figure 4.3 – Grain Size Distribution of Tri-State Materials

Over 90% of particles are between 833um and 2000um for the Jasper County Fines sample. This is not consistent with the literature which reports fines to consist of 30% to 65% passing the #200 sieve (< 75um) with the remainder consisting of medium sand sized particles passing the #65 sieve (< 208um). The majority of the sample tested did not pass the # 65 sieve, which is well above the #200. The Jasper Fines sample was observed to exhibit a slightly smaller bulk diameter than the chat samples; however the particle size range

was more centralized than the chat samples. Jasper Chat is fairly evenly distributed between >6300um and 833um while Tar Chat is less evenly distributed over the same range with almost half of the sample ranging between 2000um and 4760um.

## 4.4 Acid Base Accounting

A Modified Sobek Analysis was performed by Sierra Environmental Monitoring, Inc. at the request of UNH. Testing showed that all three materials have low acid producing potential according to ABA classifications. Table 4.2 shows the Acid Generation Potential (AGP), the Neutralization Potential (NP) and the NP/AGP ratio.

Table 4.2 – Modified ABA Results of Tri-State Chat and Tailings

| Material | AGP | NP | NP/AGP |
|---|---|---|---|
| **Jasper Fines** | 9.5 | 250 | 26.3 |
| **Jasper Chat** | 4.6 | 270 | 58.7 |
| **Tar Chat** | 1.4 | 17 | 12.1 |

Note: AGP & NP values are in tons/ 1000 tons of material
AGP based upon sulfide content

The NP/AGP must be greater than 3 to be considered a low acid producing potential material according to the Brodie and others classification (White, WW, 1999). As shown in Table 4.2, all three materials have a NP/AGP well above this standard and are therefore have an extremely low acid producing potential.

These results are inconsistent with the effects of acid rock drainage observed in the Tri State Mining District. Although no acid base accounting of materials from Jasper County or Tar Creek was included in the literature review; remediation investigations of Jasper County have reported that nearby tributaries, ponds and streams as well shallow groundwater within ¼ to ½ mile of mined/mineralized zones to be calcium sulfate dominated, with low alkalinity ( <100mg/L) (Dames & Moore, 1995). Calcium sulfate water chemistry is controlled by acid rock drainage processes and was found in Jasper County to have elevated zinc concentrations ( >1.0 mg/L). The results of UNH testing can not account for the calcium sulfate dominated water chemistry, as there was minimal acid generation potential present in any of the three samples tested. Differing results do not necessarily contradict previous reports and may be a result of the limited quantity of material analyzed.

## 4.5 Total Digestion

A total digestion of the samples was performed under EPA Method 3052, microwave assisted acid digestion, and analyzed by ICP-AES to quantify inorganic constituents within the solid matrix. The concentrations of Jasper County Chat, Tar Creek Chat and Jasper County Fines are shown in Figure 4.4. Each material was digested in triplicate for this analysis which revealed that total metal concentrations between the three samples are similar. Aluminum, calcium, iron, potassium and zinc are the primary elements present in all three

samples. Visual inspection indicates that the concentrations are generally consistent between the three residuals tested, suggesting the three materials have similar elemental compositions. Antimony, selenium and thallium were also tested but not reported in Figure 4.4 because their concentrations were below the detection limit of the instrument (9.2, 36.1 and 16.5 ug/l). Lower detection limits are possible with the use of an ICP-MS (inductively coupled plasma – mass spectroscopy) but this level of analytical analysis was beyond the scope of this study.

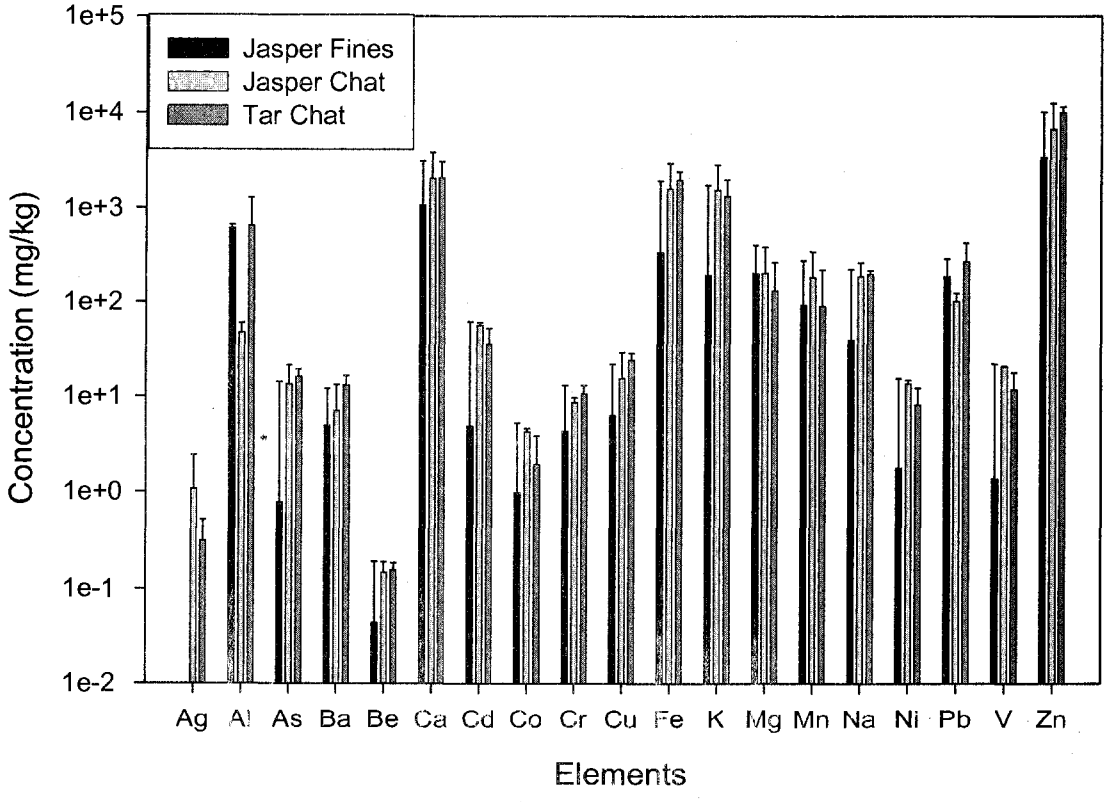


Figure 4.4 – Total Metal Concentrations of Tri-State Residuals
Note: Sb, Se & Tl are BDL and therefore not reported.

Figure 4.5 compares the total elemental concentrations (mg/kg) of the three chat samples to EPA's Suggested Soil Screening Levels (SSLs). SSLs are risk based concentration goals developed by the EPA to provide guidance for the reclamation of superfund sites. Although the samples were provided from a superfund site, SSLs have been included in this analysis solely as a point of comparison to evaluate the relative concentration of the samples, not to serve any regulatory purpose. SSLs vary depending upon the dominate route of exposure. Total metal concentrations in the figure below are based upon acceptable health risks through direct ingestion, inhalation of the material and leaching impacts to groundwater (with a 20 dilution attenuation factor (DAF) incorporated).

Several elements have concentrations above one or multiple soil screening levels. Arsenic and beryllium concentrations, in all three materials analyzed, are above the Ingestion SSL. Other elements reported concentrations only slightly below the ingestion level, such as cadmium, lead and zinc. No metal concentrations were reported above the Inhalation SSL. Cadmium and zinc concentrations for all three materials were reported above the 20 DAF groundwater level.

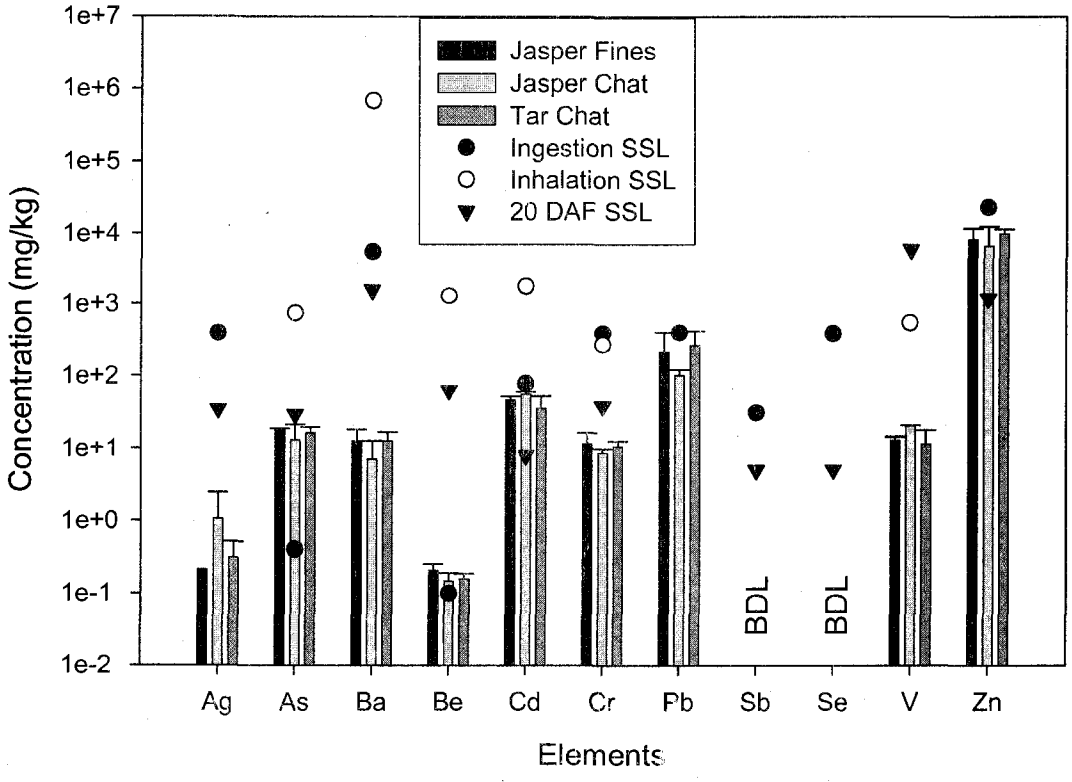


Figure 4.5 – Total Metal Concentrations in Compared with SSLs
Note: BDL – Below Detection Limit
SSL – Soil Screening Level

While some concentrations do breach the comparative SSLs, it is important to remember which applications these materials are being utilized in. Ingestion is not a likely route of exposure in a bound application over the dominate period of that applications life. This is due to the physical changes an aggregate is subjected to in the transformation of an aggregate to a bound application. Transformation acts to limit ingestion exposure routes in two ways. First the binding of an aggregate into a monolithic structure limits the suspension of fines into the air, where they are more likely to be ingested. Additionally the binding of aggregate also acts to dilute the total concentration of trace metals in

the material. Total metal digestions and leaching tests performed on chat hot mix asphalt millings have confirmed lower total concentrations exist in bound applications than in the raw aggregate (Wasiuddin, 2005).

In proposed unbound applications of chat and fine tailings, such as stabilized base and subbase aggregates, the same logic can be applied as with bound applications. Cover material would limit direct exposure of the material to humans through ingestion, making it a likely exposure route only during construction and deconstruction. A more likely long term route of exposure for these applications would be release of constituents to groundwater. Infiltration from precipitation, distance to the water table and vadose zone soil properties will dictate leaching mechanisms of unbound applications and their effect on groundwater quality. In these situations however, digestions are not the ideal testing method to demonstrate the leaching potential of the materials. Digestions provide the total concentration of metals within the entire material matrix which do not necessarily translate to leaching availability (Vandersloot, H.A., 1997). Further testing such as pH and LS dependent leaching must be employed to evaluate leachability of trace metals to the water column.

A final comparison was included in this analysis to contrast reported UNH sample concentrations to bulk sample total concentrations, representative of the larger material population. Figure 4.6a compares the two chat samples to ninety-seven Jasper County chat samples reported in the literature. Figure 4.6b compares the UNH Jasper County Fines sample to 156 tailing samples in Jasper County.

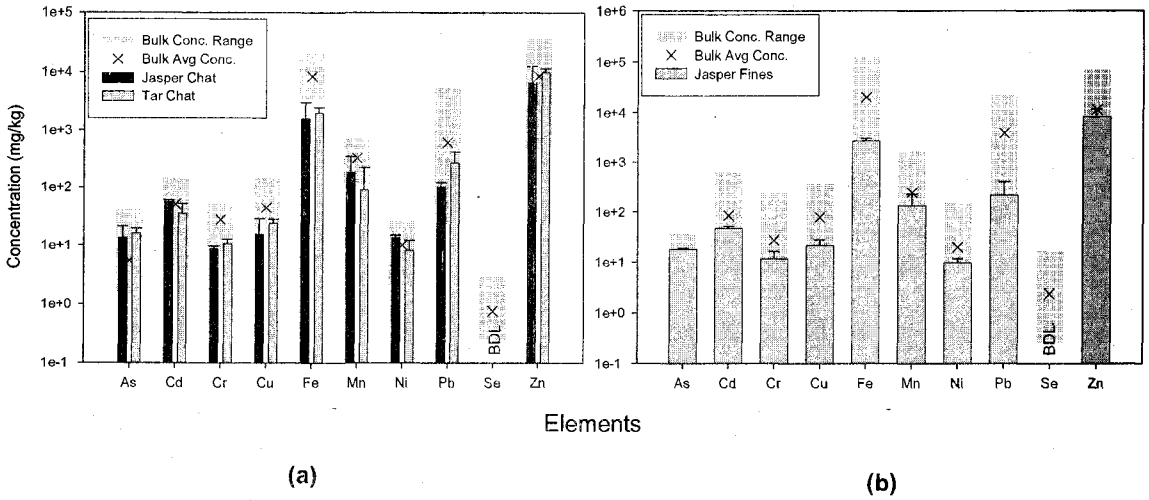


Figure 4.6 - Measured Total Metal Concentrations v. Reported Values
(a) – Chat Samples
(b) – Fine Tailing Sample
Source: Bulk concentration average and range (Dames & Moore, 1995)

Total concentrations are in general below the average reported literature values but within the given range. Samples were not washed or treated before analysis by UNH, although mineral residuals may have been exposed to weathering while stockpiled.

## 4.6 pH Dependent Leaching Results

pH dependent leaching tests quantified the release of metals into solution at various pH values, ranging from 2 to 12. Kosson et al. (2002), Method A.2.SR002.1, was the protocol used to perform this pH dependent leaching study. The tables and figures in this section present the leached concentrations of the primary analytes of concern in the Tri-State Area and analytes of concern

according to the total digestions discussed earlier for the materials tested. The elements of interest according to previous studies in the Tri-State Area are cadmium, lead and zinc. Total arsenic concentrations were also reported just below the 20 DAF SSL. pH leaching diagrams for arsenic are not included in the results section but are present in the appendix.

Tables report the maximum and minimum concentrations recovered from each material with their associated pH range at that concentration. The method detection limits (MDL) and the primary or secondary EPA drinking water maximum contamination limits (MCL) are also presented for each element if relevant. Primary MCLs are denoted by a superscript 1 and secondary are denoted by the number 2. Relative MCLs are included in the analysis to serve as a conservative point of comparison for the concentrations of analyte leached. They do not represent any direct regulatory limit of acceptable leachate concentrations (groundwater or surface water limits could also serve to provide a similar framework of comparison, but are not included here.)

Although there is no direct limitation, leachate samples below the MCL will not impact the ambient water to concentrations above the MCL and therefore negatively impacting groundwater column from a human health perspective. Conversely, leachate concentrations that do exceed the MCL should include more specific analysis such as fate and transport modeling. These procedures can provide a more conclusive evaluation of the impact elevated leachate values will have on the local groundwater. The pH dependent leaching results for Tar Creek Chat are displayed in Table 4.3.

The leaching of this material was conducted over the entire pH range from 2 to 12. It should be noted that detection limits for arsenic, antimony and thallium are above the maximum contaminate levels for these elements. This detection limitation makes it impossible to determine if concentrations below the detection limit are above the MCL with this method of detection. As discussed earlier other methods of detection could be used however were beyond the scope this research. Results for these elements were reported at BDL, to define the relative concentrations which they are below.

Finite concentrations above the primary MCL were observed for cadmium and lead in the Tar Creek Chat sample. Aluminum, iron, manganese and zinc exceeded the secondary drinking water limits. Because cadmium, lead and zinc are the primary elements of interest in this analysis, the pH dependent leaching characteristics of these trace metals for Tar Creek Chat were the primary focus of the following figures. The dynamic leaching concentrations of cadmium, lead and zinc under various pH conditions for the three materials tested are illustrated in Figure 4.7. The concentration of the leachate is presented in ug/L on the y axis and pH is presented on the x-axis. The figures show a slightly amphoteric curve for lead and zinc, with the highest concentrations occurring at the most acidic conditions.

Table 4.3 – Tar Creek Chat pH Dependent Leaching Concentrations

| Element | Maximum Concentration (ug/L) | Corresponding pH | Minimum Concentration (ug/L) | Corresponding pH | MDL (ug/L) | MCL (ug/L) |
|---|---|---|---|---|---|---|
| **Ag** | BDL | - | BDL | - | 0.4 | 100[2] |
| **Al** | 2,650 | 2 | 4.2 | 7 | 2.3 | 200[2] |
| **As** | BDL | - | BDL | - | 13.8 | 10[1] |
| **Ba** | 66.9 | 3 | 2.6 | 10 | 0.05 | 2000[1] |
| **Be** | 1.4 | 2 | BDL | 9 – 10 | 0.03 | 4[1] |
| **Cd** | 714 | 5 | 0.7 | 10 | 0.3 | 5[1] |
| **Co** | 16.3 | 3 | 0.6 | 11 | 1.4 | n/a |
| **Cr** | 20.5 | 2 | BDL | 6 – 8 | 0.6 | 100[1] |
| **Cu** | 859 | 2 | 1.4 | 7 | 0.7 | 1300[1] |
| **Fe** | 7,060 | 2 | BDL | 8 | 1.2 | 300[2] |
| **Mg** | > 50,000 | 2 - 4 | 16.3 | 12 | 4.2 | n/a |
| **Mn** | 631 | 3 | 0.5 | 10 | 0.08 | 50[2] |
| **Ni** | 103 | 2 | BDL | 9 – 12 | 1.5 | n/a |
| **Pb** | 20,400 | 2 | 14.1 | 8 | 7 | 15[1] |
| **Sb** | BDL | - | BDL | - | 9.2 | 6[1] |
| **Se** | BDL | - | BDL | - | 36.1 | 50[1] |
| **Tl** | BDL | - | BDL | - | 16.5 | 2[1] |
| **V** | 20.7 | 2 | BDL | 5 – 9 | 1 | n/a |
| **Zn** | 299,000 | 2 | 116 | 9 | 0.3 | 5000[2] |

Note: pH range from 2 to 12 excluding pH value 3 and 4
BDL = Below Detection Limit; MDL = Method Detection Limit; "-" = entire pH range tested
MCL = US EPA Primary and Secondary Maximum Contamination Levels for Drinking Water
[1]Primary MCL
[2]Secondary MCL

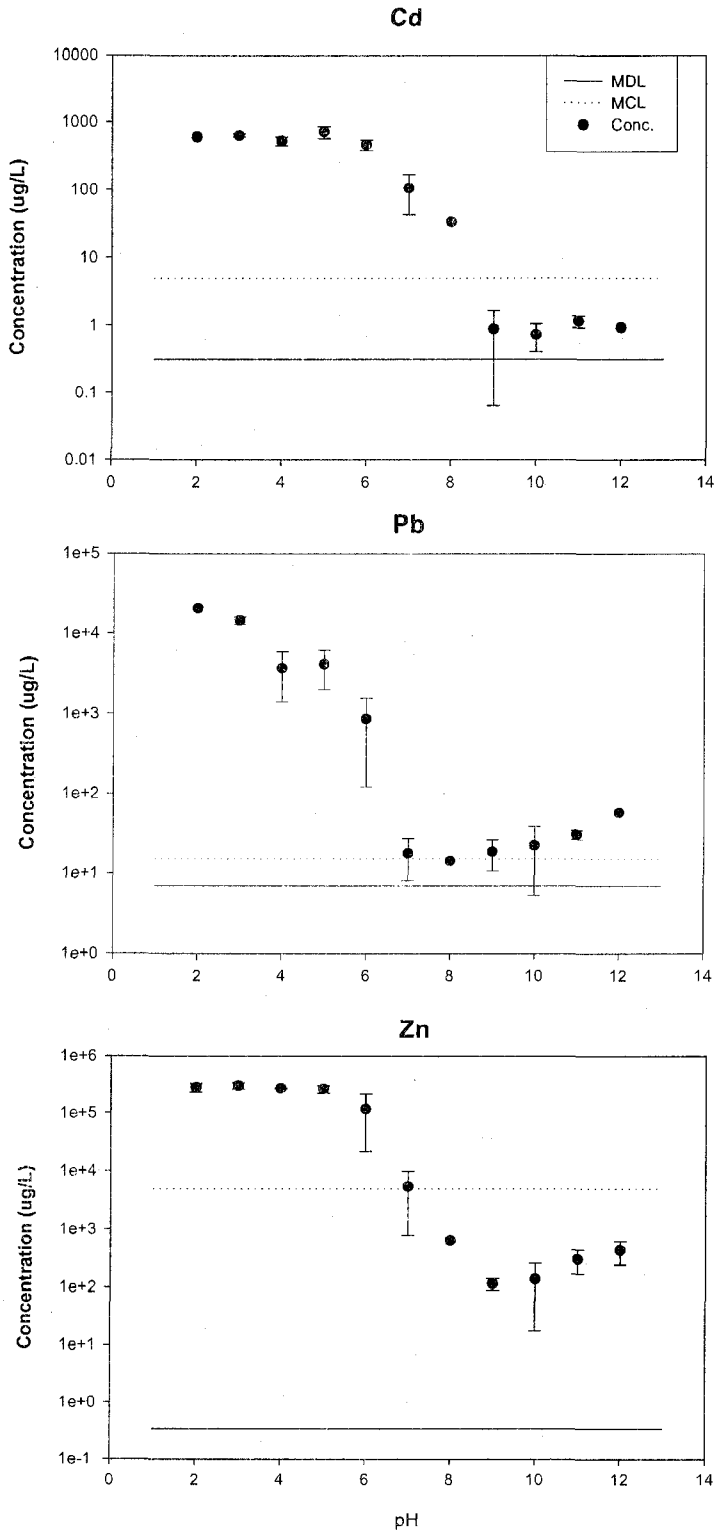


Figure 4.7 – pH Dependent Leaching Curves for Tar Creek Chat

Tar Chat leaches lead at concentrations above the primary drinking water MCL for the entirety of the pH range. Zinc is above the secondary standard at pH's below 7. All three samples leach the greatest concentrations under low pH conditions; however concentrations do not appear to rise again for cadmium at the upper pH boundaries as significantly as they do for lead and zinc.

The acid neutralization capacity of the mine tailing samples was also determined. Figure 4.8 shows the buffering capacity curves for the three materials that were tested. Tar Chat's entire pH range from 2 to 12 was able to be analyzed is due to the relatively low buffering capacity of the material. Acid Base Accounting affirms that the buffering capacity is the lowest of the three materials sampled by quantifying the materials acid neutralization capability. Tar Chat Neutralization Capacity (NC) is 17 tons of $CaCO_3$ per 1000 tons of material (Section 4.4) as opposed to Jasper County Chat which had 270 tons/ 1000 tons. These trends can also be demonstrated and compared through acid neutralization curves. In this figure acid/base addition is shown on the x-axis demonstrating the milli-equivalents/gram that are required to vary the pH (shown on they y-axis). Positive meq/g represents the addition of acid, negative meq/g represents the addition of base.

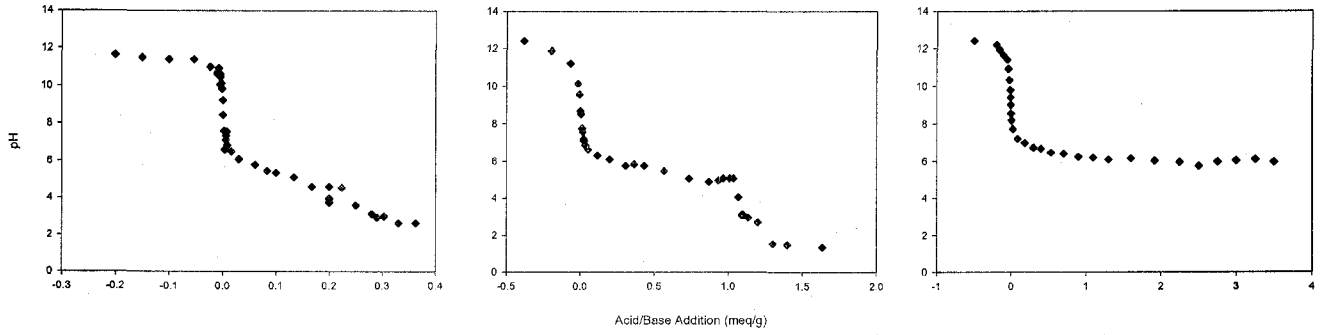


Figure 4.8 – Tri-State County Chat and Fines Buffering Capacity
Note: Values have been altered to statistically smooth the data
(a)– Tar Chat
(b)– Jasper Chat
(c)– Jasper Fines

All three materials exhibit low buffering capacity near their natural pH (meq/g = 0) with increasing capacity as the pH is driven to the upper and lower bounds. Jasper County Fines (Figure 4.8c) was only analyzed between pH 6 and pH 12. This is due to the enormous buffering capacity of the material, which prohibited the pH adjustment below a pH of 6. As a result a large acid generation potential would be required to bring Jasper Fines below a pH of 6, therefore pH dependent leaching test were only preformed at neutral and basic ranges.

Table 4.4 and 4.5 present the results of the pH dependent leaching tests for Jasper County Chat and Jasper County Fines. In addition to cadmium and lead leaching above the primary drinking water standards at selective pH ranges, Jasper County Chat and Fines both leach arsenic over the MCL at a single pH value. It is important to note that the MDL for arsenic is above the MCL for this

method of ICP-AES analysis and that concentration below the detection limit are not necessarily below the primary drinking water limit. Aluminum, iron,

Table 4.4 – Jasper Chat pH Dependent Leaching Concentrations

| Element | Maximum Concentration (ug/L) | Corresponding pH | Minimum Concentration (ug/L) | Corresponding pH | MDL (ug/L) | MCL (ug/L) |
|---|---|---|---|---|---|---|
| **Ag** | 0.9 | 2 | BDL | 5 – 12 | 0.4 | 100[2] |
| **Al** | 11800 | 2 | 24.2 | 7 | 2.3 | 200[2] |
| **As** | 199 | 2 | BDL | 5 – 11 | 13.8 | 10[1] |
| **Ba** | 488 | 2 | 3.2 | 11 | 0.05 | 2000[1] |
| **Be** | 2.8 | 2 | BDL | 7 – 12 | 0.03 | 4[1] |
| **Cd** | 874 | 2 | BDL | 9 – 12 | 0.3 | 5[1] |
| **Co** | 91.1 | 2 | BDL | 8 – 12 | 1.4 | n/a |
| **Cr** | 72.5 | 2 | BDL | 5 – 11 | 0.6 | 100[1] |
| **Cu** | 1070 | 2 | 3.1 | 7 | 0.7 | 1300[1] |
| **Fe** | 531000 | 2 | 1.7 | 10 | 1.2 | 300[2] |
| **Mg** | > 20,000 | 2 – 6 | 9.5 | 12 | 4.2 | n/a |
| **Mn** | 24000 | 2 | BDL | 12 | 0.08 | 50[2] |
| **Ni** | 281 | 2 | BDL | 12 | 1.5 | n/a |
| **Pb** | 1650 | 2 | BDL | 6 – 11 | 7 | 15[1] |
| **Sb** | 11.6 | 2 | BDL | 5 – 12 | 9.2 | 6[1] |
| **Se** | BDL | - | BDL | - | 36.1 | 50[1] |
| **Tl** | BDL | - | BDL | - | 16.5 | 2[1] |
| **V** | 20.4 | 2 | BDL | 5 – 9 | 1 | n/a |
| **Zn** | 307000 | 5 | 57.8 | 12 | 0.3 | 5000[2] |

Note: pH range from 2 to 12 excluding pH value 3 and 4
BDL = Below Detection Limit; MDL = Method Detection Limit; "-" = entire pH range tested
MCL = US EPA Primary and Secondary Maximum Contamination Levels for Drinking Water
[1]Primary MCL
[2]Secondary MCL

manganese and zinc all leach above their respective secondary MCL for given pH ranges. The range of analysis for the two Jasper County samples should be considered as well. Jasper County Chat was analyzed over the full pH range from 2 to 12 however nominal pH values 3 and 4 are not included in this analysis due to technical limitations that can be witnessed in Figure 4.8b. The vertical

trend in this figure denotes low buffering capacity present within the Jasper County Chat between pH values 3 and 4. For this reason it was difficult to isolate these pH integers and they were omitted in this analysis.

Acid additions were unable to acidify Jasper County Fine leaching samples below a pH of 6, as discussed previously, due to the materials buffering capacity in this range. These limitations of analysis are more readily witnessed in the pH dependent leaching curves shown in Figure 4.9.

Table 4.5 --Jasper Fines pH Dependent Leaching Concentration

| Element | Maximum Concentration (ug/L) | Corresponding pH | Minimum Concentration (ug/L) | Corresponding pH | MDL (ug/L) | MCL (ug/L) |
|---|---|---|---|---|---|---|
| **Ag** | 0.9 | 11 | BDL | 6 - 9, 12 | 0.4 | 100[2] |
| **Al** | 627 | 12 | BDL | 8 - 9 | 2.3 | 200[2] |
| **As** | 33.8 | 12 | BDL | 6 - 11 | 13.8 | 10[1] |
| **Ba** | 203 | 6 | 1.1 | 12 | 0.05 | 2000[1] |
| **Be** | 1.1 | 6 | BDL | 7 - 12 | 0.03 | 4[1] |
| **Cd** | 1,830 | 6 | BDL | 11 - 12 | 0.3 | 5[1] |
| **Co** | 148 | 6 | BDL | 9 - 12 | 1.4 | n/a |
| **Cr** | 1.8 | 12 | BDL | 6 - 7 | 0.6 | 100[1] |
| **Cu** | 58.7 | 12 | 5.5 | 7 | 0.7 | 1300[1] |
| **Fe** | 7,490 | 6 | 5.8 | 7 | 1.2 | 300[2] |
| **Mg** | 33,900 | 6 | 6 | 12 | 4.2 | n/a |
| **Mn** | 5060 | 6 | 0.3 | 10 | 0.08 | 50[2] |
| **Ni** | 213 | 6 | BDL | 9 - 12 | 1.5 | n/a |
| **Pb** | 45.5 | 6 | BDL | 7 - 11 | 7 | 15[1] |
| **Sb** | BDL | - | BDL | - | 9.2 | 6[1] |
| **Se** | BDL | - | BDL | - | 36.1 | 50[1] |
| **Tl** | BDL | - | BDL | - | 16.5 | 2[1] |
| **V** | 6.3 | 2 | BDL | 6 - 9 | 1 | n/a |
| **Zn** | 494,000 | 6 | 13.2 | 10 | 0.3 | 5000[2] |

Note: pH range from 2 to 12 excluding pH value 3 and 4
BDL = Below Detection Limit; MDL = Method Detection Limit; "-" = entire pH range tested
MCL = US EPA Primary and Secondary Maximum Contamination Levels for Drinking Water
[1]Primary MCL
[2]Secondary MCL

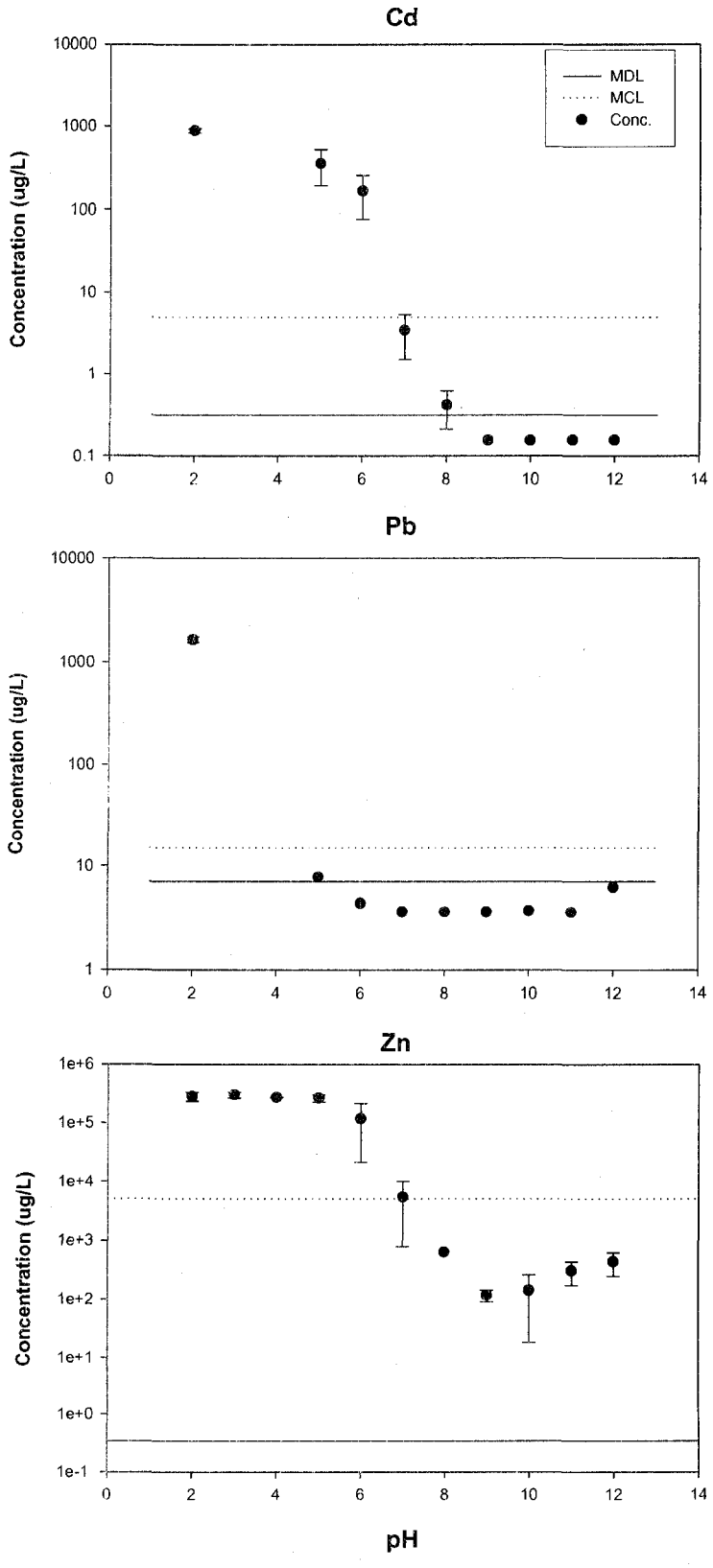


Figure 4.9 – Jasper Chat pH Dependent Leaching Curve

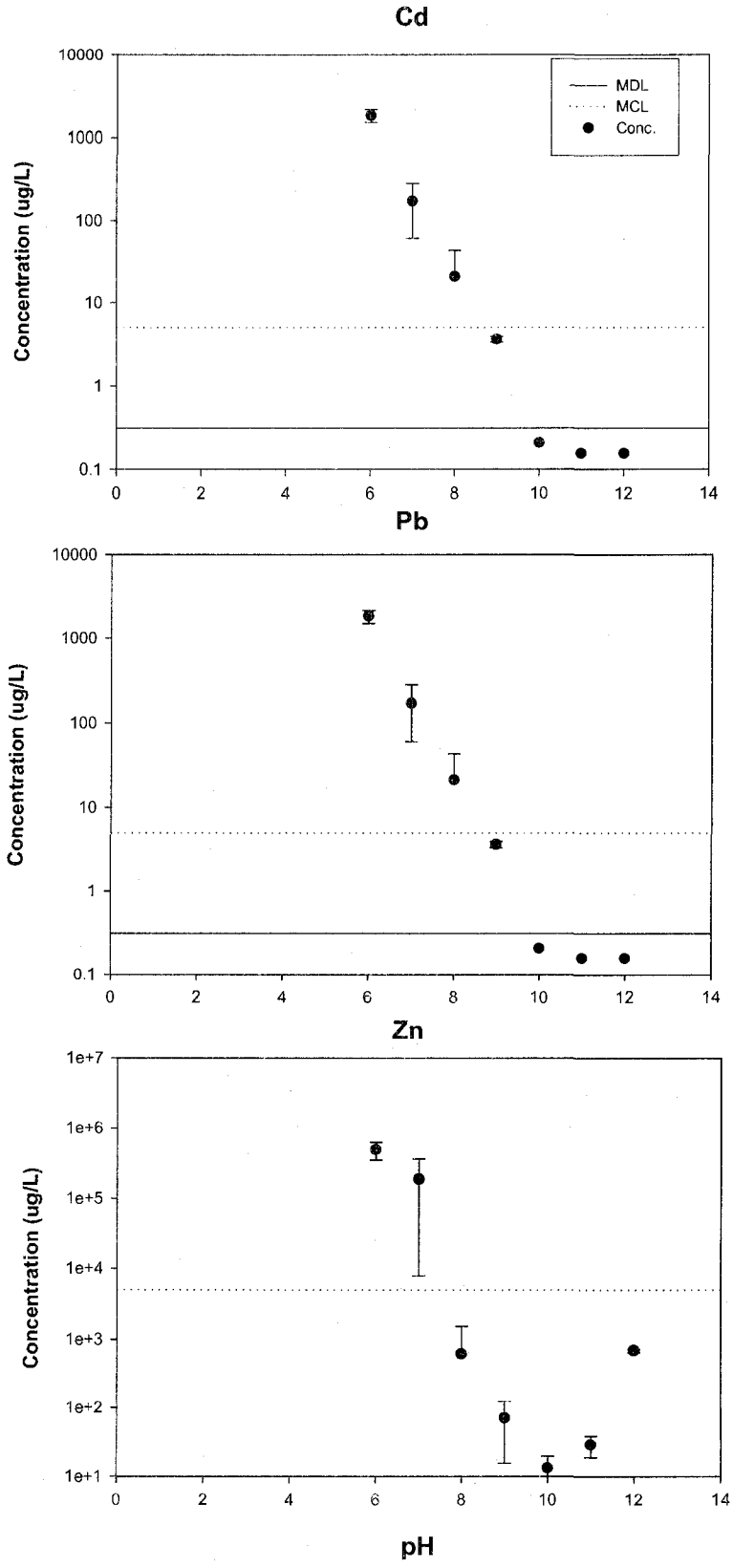


Figure 4.10 – Jasper Fines pH Dependent Leaching Curve

Zinc displays the same amphoteric behavior for Jasper Chat and Jasper Fines as with Tar Creek Chat. Maximum leached concentrations of lead are similar between the three materials however the remainder of the concentrations and their leaching behavior differs. Cadmium follows the same leaching trends but concentrations at specific pH values do differ between the three materials.

## 4.7 LS Dependent Leaching Results

Liquid to solid dependent leaching quantifies the dynamic leachability of a material when subjected to leachant at various liquid to solid ratios. This method is particularly useful in describing the long term leaching potential of a material based upon exposure to transient ground water or surface water infiltration. Protocol followed Kosson et al, 2002 (A.3. SR003.1) leaching the three materials at there natural pH.

Tables 4.6 through 4.8 show the maximum and minimum leached concentrations for each element as well as the corresponding liquid to solid ratios at which the concentrations occurred. The MDL and MCL are also included in the tables.

Table 4.6 – Tar Chat Maximum and Minimum LS Dependent Leached Values

| Element | Maximum Concentration (ug/L) | Corresponding LS Ratio (g/L) | Minimum Concentration (ug/L) | Corresponding LS Ratio (g/L) | MDL (ug/L) | MCL (ug/L) |
|---|---|---|---|---|---|---|
| Ag | BDL | - | BDL | - | 0.4 | 100[2] |
| Al | 38.3 | 10 | 21.7 | 2 | 2.3 | 200[2] |
| As | BDL | - | BDL | - | 13.8 | 10[1] |
| Ba | 26.6 | 0.5 | 11.2 | 10 | 0.05 | 2000[1] |
| Be | BDL | - | BDL | - | 0.03 | 4[1] |
| Cd | 18.3 | 1 | 0.9 | 10 | 0.3 | 5[1] |
| Co | BDL | - | BDL | - | 1.4 | n/a |
| Cr | 1.2 | 1 | BDL | 10 | 0.6 | 100[1] |
| Cu | 54.3 | 0.5 | 10.2 | 10 | 0.7 | 1300[1] |
| Fe | 39.9 | 10 | 22.5 | 0.5 | 1.2 | 300[2] |
| Mg | 10,500 | 0.5 | 847 | 10 | 4.2 | n/a |
| Mn | 26.8 | 0.5 | 0.2 | 10 | 0.08 | 50[2] |
| Ni | 4.6 | 0.5 | 0.7 | 10 | 1.5 | n/a |
| Pb | 17.7 | 5 | BDL | 2 | 7 | 15[1] |
| Sb | BDL | - | BDL | - | 9.2 | 6[1] |
| Se | BDL | - | BDL | - | 36.1 | 50[1] |
| Tl | BDL | - | BDL | - | 16.5 | 2[1] |
| V | BDL | - | BDL | - | 1 | n/a |
| Zn | 186 | 0.5 | 41.6 | 2 | 0.3 | 5000[2] |

BDL = Below Detection Limit; MDL = Method Detection Limit; "-" = entire LS range tested BDL
MCL = US EPA Primary and Secondary Maximum Contamination Levels for Drinking Water
[1]Primary MCL
[2]Secondary MCL

Table 4.7 – Jasper Chat Maximum and Minimum LS Dependent Leached Values

| Element | Maximum Concentration (ug/L) | Corresponding LS Ratio (g/L) | Minimum Concentration (ug/L) | Corresponding LS Ratio (g/L) | MDL (ug/L) | MCL (ug/L) |
|---|---|---|---|---|---|---|
| **Ag** | 2.4 | 10 | BDL | 1 - 5 | 0.4 | 100[2] |
| **Al** | 71.2 | 0.5 | 21.8 | 1 | 2.3 | 200[2] |
| **As** | BDL | - | BDL | - | 13.8 | 10[1] |
| **Ba** | 49.7 | 0.5 | 10.5 | 10 | 0.05 | 2000[1] |
| **Be** | BDL | n/a | BDL | n/a | 0.03 | 4[1] |
| **Cd** | 3 | 1 | BDL | 10 | 0.3 | 5[1] |
| **Co** | 2.2 | 1 | BDL | 0.5, 2 - 10 | 1.4 | n/a |
| **Cr** | 1.1 | 1 | BDL | 10 | 0.6 | 100[1] |
| **Cu** | 7.5 | 0.5 | 3.3 | 10 | 0.7 | 1300[1] |
| **Fe** | 56.7 | 0.5 | 4.1 | 1 | 1.2 | 300[2] |
| **Mg** | >20,000 | .5* | 4660 | 10 | 4.2 | n/a |
| **Mn** | 34.5 | 0.5 | 0.4 | 10 | 0.08 | 50[2] |
| **Ni** | 11.8 | 0.5 | 0.8 | 10 | 1.5 | n/a |
| **Pb** | BDL | n/a | BDL | n/a | 7 | 15[1] |
| **Sb** | BDL | n/a | BDL | n/a | 9.2 | 6[1] |
| **Se** | 22.9 | 0.5 | BDL | 1 - 10 | 36.1 | 50[1] |
| **Tl** | BDL | n/a | BDL | n/a | 16.5 | 2[1] |
| **V** | BDL | n/a | BDL | 1 - 2 | 1 | n/a |
| **Zn** | 111.1 | 0.5 | 6.3 | 10 | 0.3 | 5000[2] |

BDL = Below Detection Limit; MDL = Method Detection Limit; "-" = entire LS range tested BDL
MCL = US EPA Primary and Secondary Maximum Contamination Levels for Drinking Water
[1]Primary MCL
[2]Secondary MCL

Table 4.8 – Jasper Fines Maximum and Minimum LS Dependent Leached Values

| Element | Maximum Concentration (ug/L) | Corresponding LS Ratio (g/L) | Minimum Concentration (ug/L) | Corresponding LS Ratio (g/L) | MDL (ug/L) | MCL (ug/L) |
|---|---|---|---|---|---|---|
| **Ag** | BDL | - | BDL | - | 0.4 | 100[2] |
| **Al** | 12.1 | 2 | 4.5 | 1 | 2.3 | 200[2] |
| **As** | BDL | - | BDL | - | 13.8 | 10[1] |
| **Ba** | 30.8 | 0.5 | 11.9 | 10 | 0.05 | 2000[1] |
| **Be** | BDL | - | BDL | - | 0.03 | 4[1] |
| **Cd** | 43.9 | 0.5 | 1.3 | 10 | 0.3 | 5[1] |
| **Co** | BDL | - | BDL | - | 1.4 | n/a |
| **Cr** | 1 | 1 | BDL | 10 | 0.6 | 100[1] |
| **Cu** | 69.1 | 0.5 | 10.1 | 10 | 0.7 | 1300[1] |
| **Fe** | 3.6 | 2 | BDL | 0.5 - 1 | 1.2 | 300[2] |
| **Mg** | > 55,000 | 0.5 | 4310 | 10 | 4.2 | n/a |
| **Mn** | 82 | 0.5 | 0.4 | 10 | 0.08 | 50[2] |
| **Ni** | 6.1 | 0.5 | BDL | 5 - 10 | 1.5 | n/a |
| **Pb** | BDL | - | BDL | - | 7 | 15[1] |
| **Sb** | BDL | - | BDL | - | 9.2 | 6[1] |
| **Se** | BDL | - | BDL | - | 36.1 | 50[1] |
| **Tl** | BDL | - | BDL | - | 16.5 | 2[1] |
| **V** | BDL | - | BDL | - | 1 | n/a |
| **Zn** | 419 | 0.5 | 2 | 10 | 0.3 | 5000[2] |

BDL = Below Detection Limit; MDL = Method Detection Limit; "-" = entire LS range tested BDL
MCL = US EPA Primary and Secondary Maximum Contamination Levels for Drinking Water
[1]Primary MCL
[2]Secondary MCL

These tables reveal that the only constituent which leaches above the federal EPA primary drinking water standards is cadmium and lead in the Tar Creek Chat and cadmium in the Jasper County Fines. Manganese leaches above the secondary drinking water limits in the Jasper County Fines at a LS ratio of 0.5 L/kg, but quickly drops below the limit at 1 L/kg. Most of the other primary drinking water contaminates are not detected across the LS range.

Figures 4.12 through 4.14 show the change in leachate concentration as the liquid to solid ratio increases. The presentation of the results in these figures varies slightly from the pH dependent figures. In these figures the y axis reports the cumulative metal leached from the material (ug/kg), not the concentration of the leachate. This format more acutely demonstrates the total quantity of trace metal that will be leached from a matrix. If the LS dependent leaching behavior of a material is understood and the local hydrological conditions are known, a direct translation can be established to predict the contaminant release from the material over time.

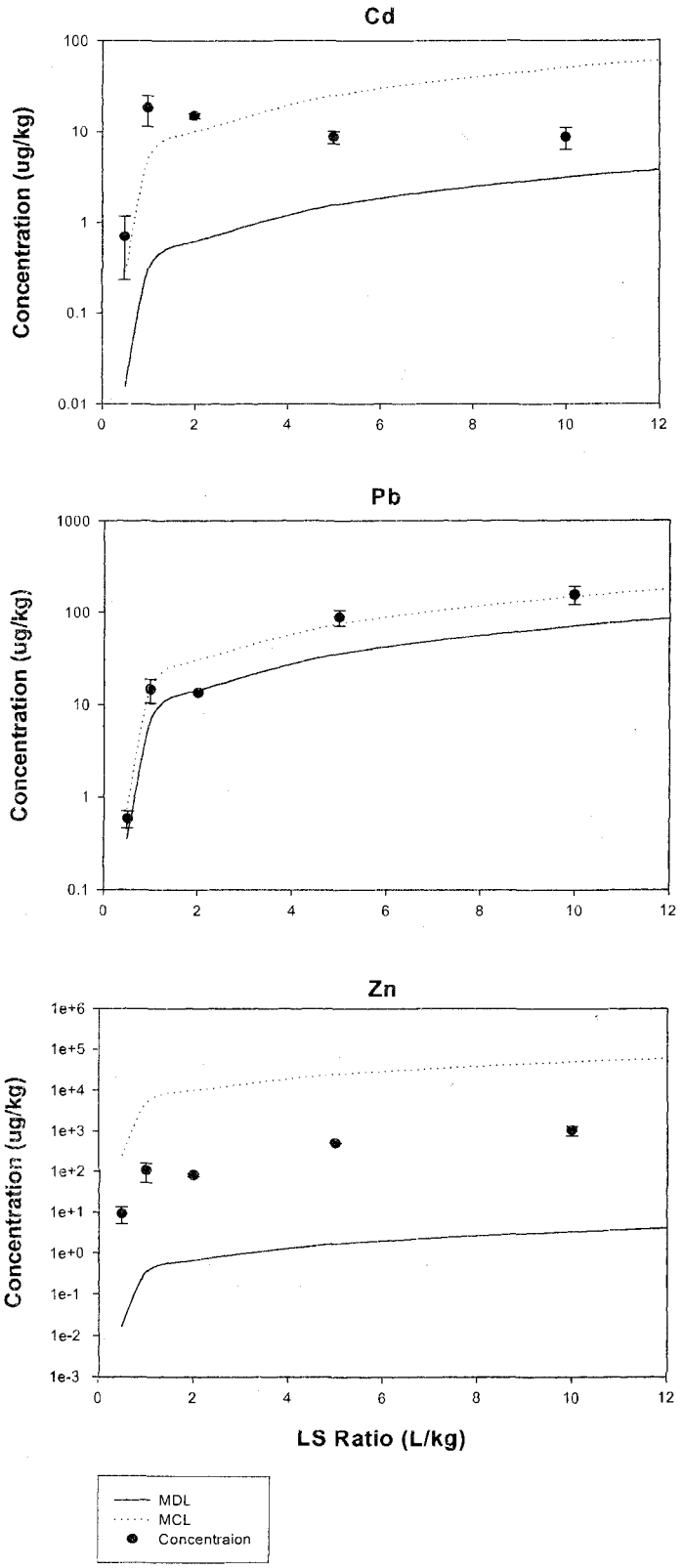


Figure 4.11 – Tar Chat LS Dependent Leaching Curves

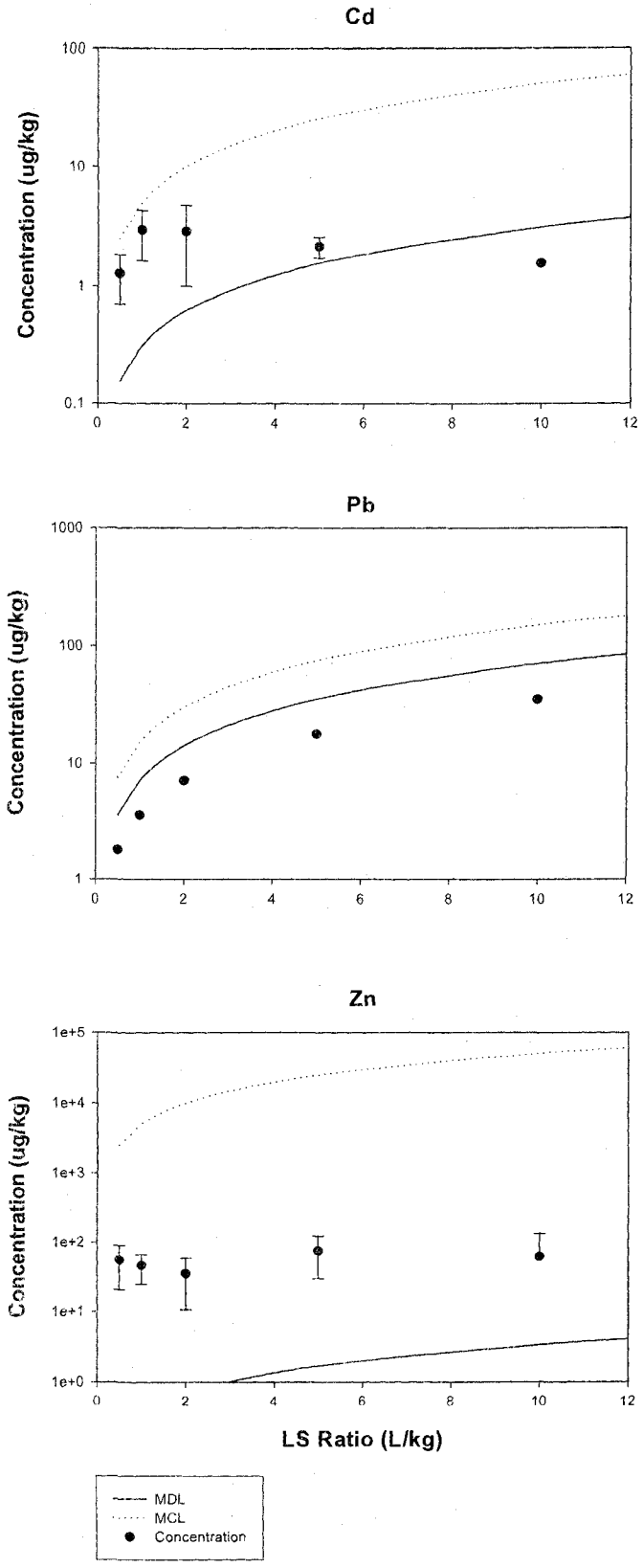


Figure 4.12 – Jasper Chat LS Dependent Leaching Curves

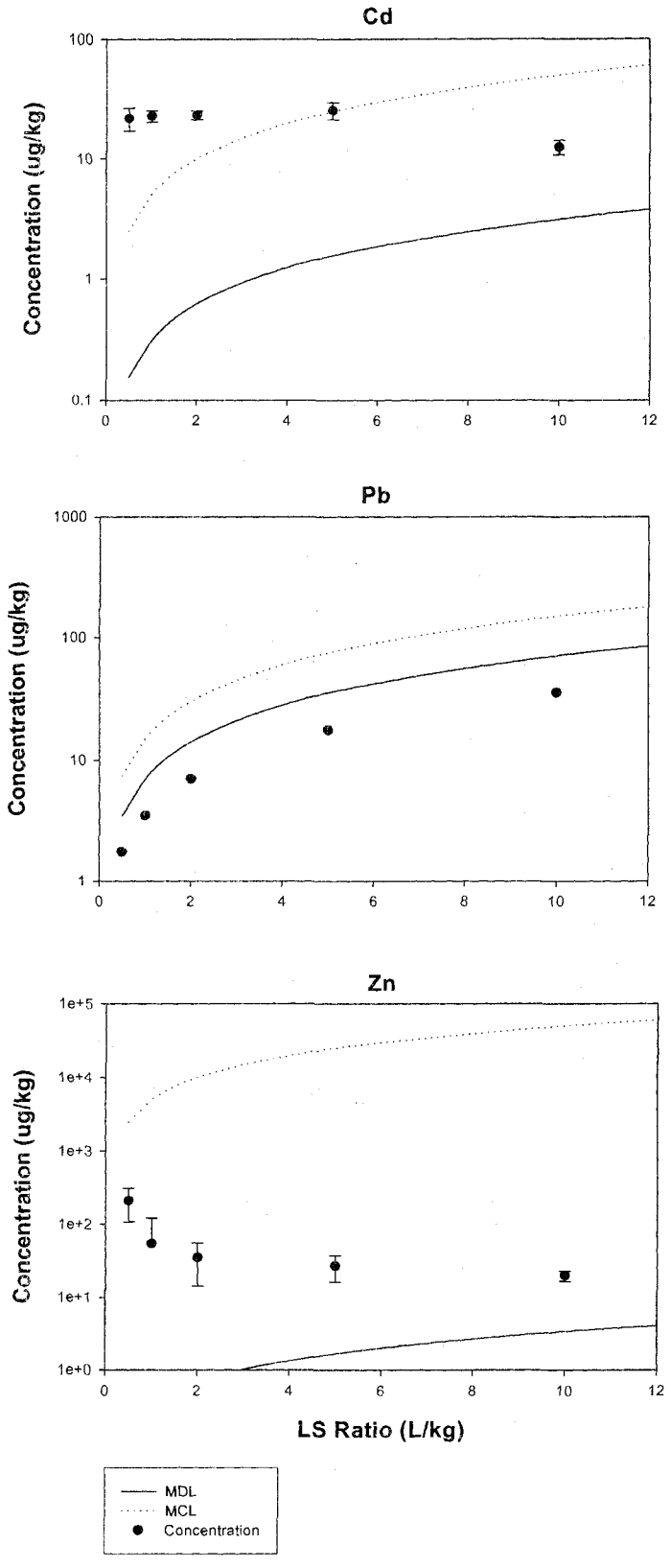


Figure 4.13 – Jasper Fines LS Dependent Leaching Curves

## 4.8 Geochemical Speciation Modeling Results

This section reports and provides discussion about geochemical speciation modeling of Jasper County Chat to identify possible solid phase mineralogy controlling the leaching behavior of cadmium, lead and zinc. Modeling is dependent upon numerous conditions; among those considered for this study include the reduction/oxidation (redox) state of the material, the concentration of hydrous ferric oxides present within the material and the solid phase speciation of the elements present.

Modeling of Jasper County Chat was conducted using LeachXS. An extensive data set was included in the analysis consisting of several analytical methodologies. All average cation concentrations from the pH dependent leaching test were included as well as dissolved nitrate, phosphate and sulfate anion concentrations over a pH range of 2 to 12. Hydrous ferric oxide concentrations and aluminum oxide concentrations were also directly measured and included in the analysis to effectively define the material.

### 4.8.1 Reduction/Oxidation State

Reduction/Oxidation reactions (redox) of soils can have a large effect on the leaching behavior of a material. No ORP values (Oxidation Reduction Potential) were recorded during the performance of pH or LS dependent leaching tests so the redox state of the material within the leaching vessel is not directly

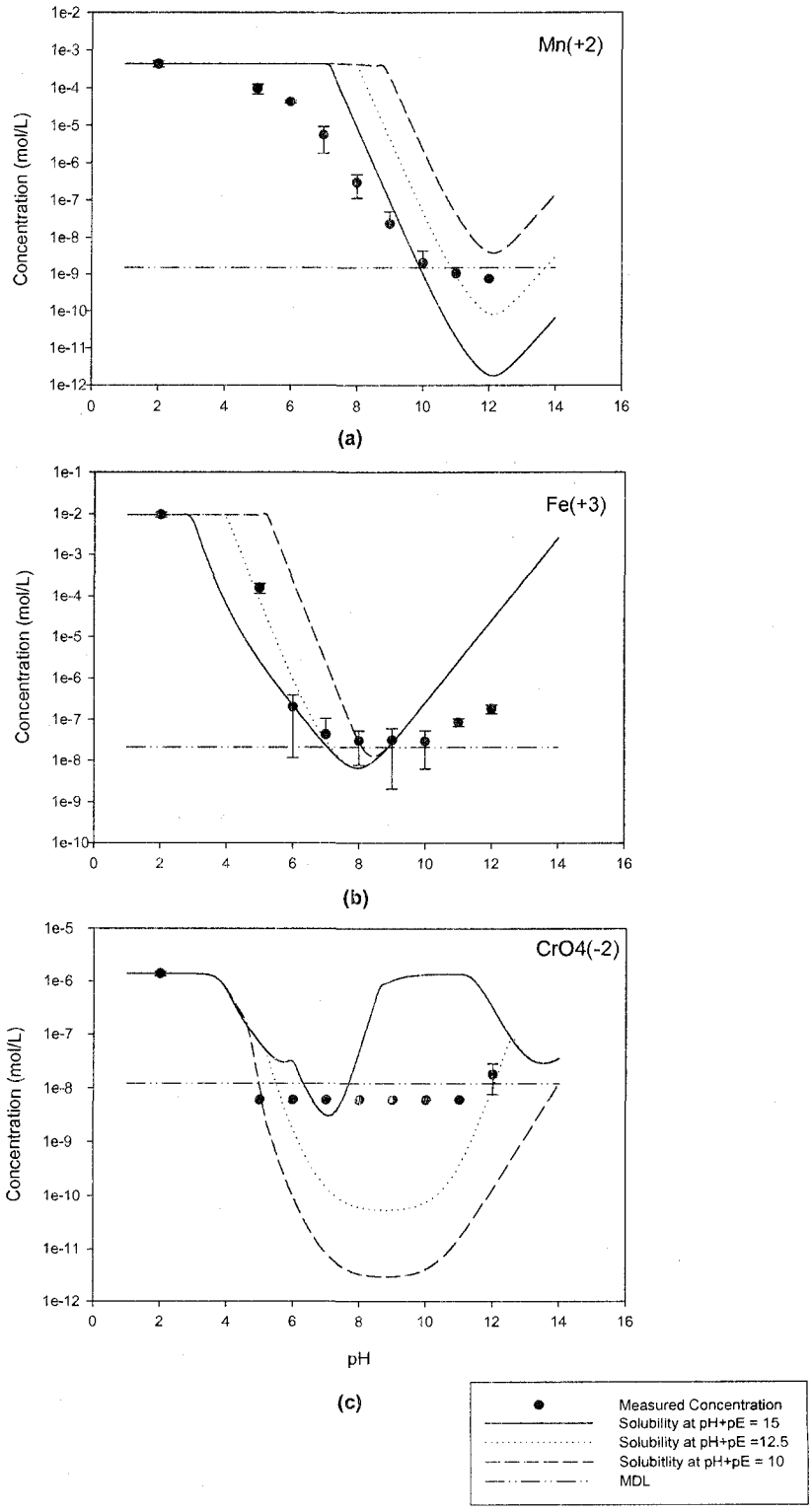


Figure 4.14 – Solubility of Metals at Various pE+pH Values
(a)- Manganese
(b)- Iron
(c)- Chromium

known. To determine these conditions chromium, iron and manganese solubility characteristics were modeled at constant pE + pH values over a pH range from 2 to 12. ORP was then evaluated due to the correspondence between measured ion concentrations and the modeled solubility diagrams at a specific pE+pH value. Chromium, iron and manganese were chosen due to their sensitivity to oxidation states and their relative limited sensitivity to hydrous ferric oxide concentrations.

Figure 4.14 shows the results of this modeling exercise. Chromium, iron and manganese solubility concentrations over a pH range of 2 to 12 are modeled for pE + pH values of 10, 12.5 and 15. While no curve corresponds exactly to the measured leaching test, a pE + pH value of 12.5 was assumed because it is the best fit between the three analyses. The solubility diagram at pE + pH =12.5 is not the outlying trend for any of the elements investigated and has the greatest correspondence with observed iron leaching behavior.

Figure 4.15 provides the modeled solid/liquid phase solubility diagram of possible complexes at the assumed pE + pH value 12. Measured ionic concentrations of chromium, iron and manganese from the pH dependent leaching tests imposed on the surface of the solubility area plot. As with the pH dependent leaching tests any values reported below the MDL are beyond the limits of this analysis and are reported as half the method detection limit.

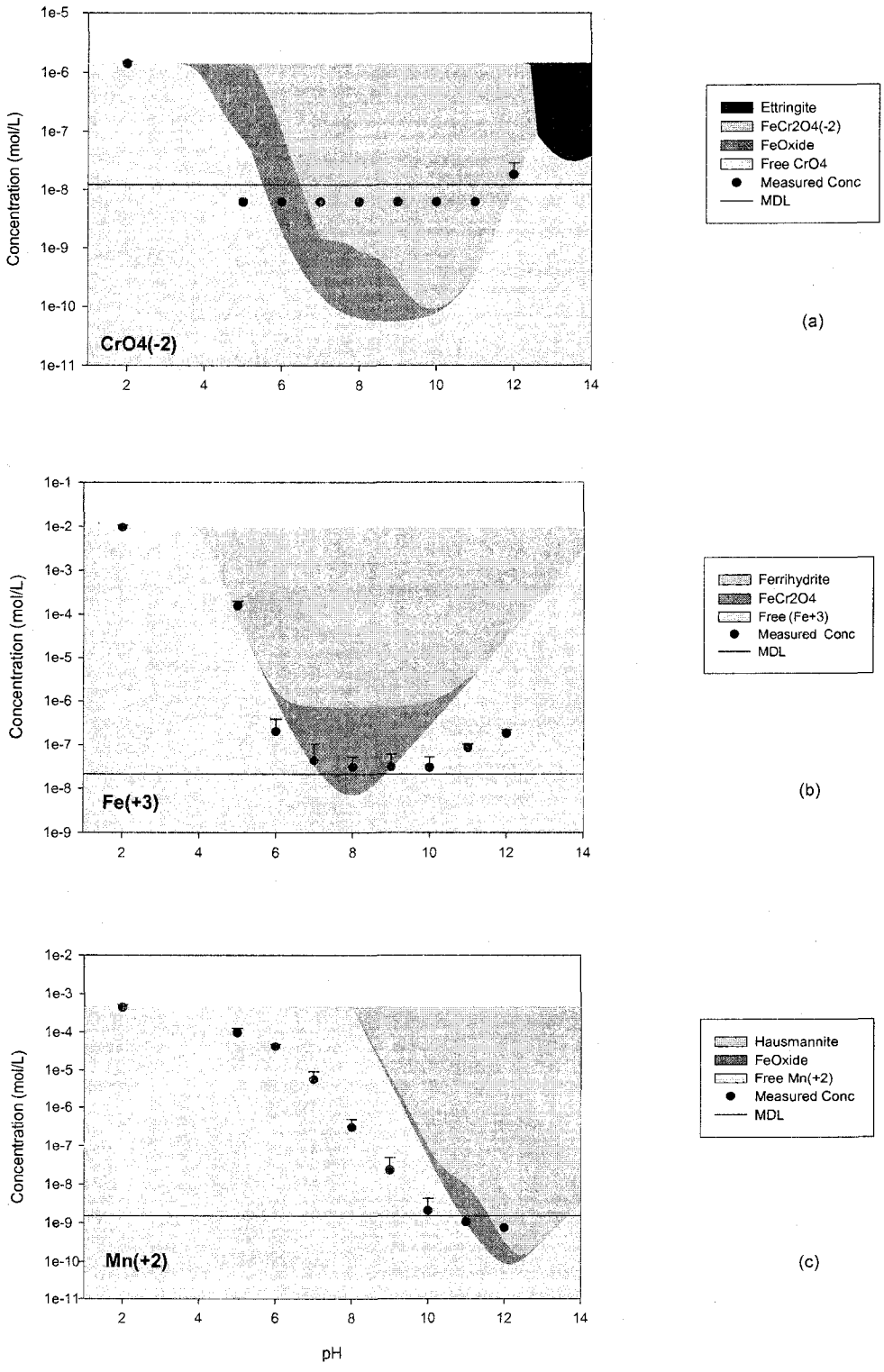


Figure 4.15 – Solid/Liquid Phase Mineralogy with Observed Leached Values
(a)- Chromium
(b)- Iron
(c)- Manganese

### 4.8.2 Surface Complexation

The presence of hydrous oxide concentrations within a material may also have a large effect on that material's leaching behavior. Figure 4.16 shows the solubility curves of lead hydroxide at three hydrous ferric oxide concentrations ranging from 0% to 1%. Surface complexation is clearly shown to have an effect on the leaching behavior of lead. Solubility of lead hydroxide dramatically decreases with increasing hydrous ferric oxide concentrations within the material matrix. Furthermore, surface complexation is shown to have greater effect on the leaching behavior at low pH values. As pH increases beyond 10, little to no variations in solubility occur between the variable ferric oxide concentrations. Similar leaching behavior can also be witnessed for cadmium and zinc at various iron oxide concentrations.

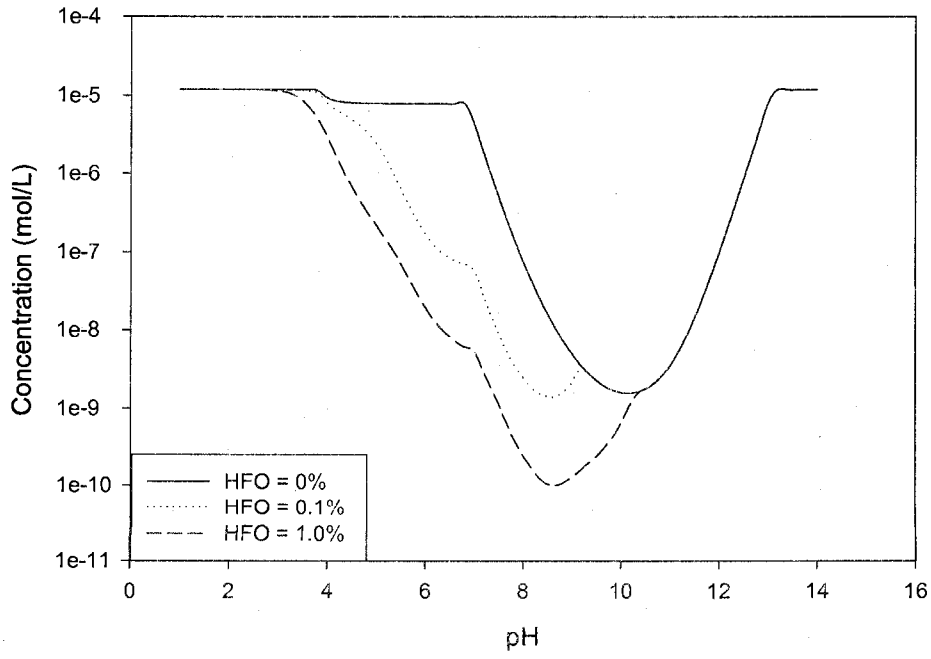


Figure 4.16 – Effects of HFO Concentrations on Lead Hydroxide

### 4.8.3 Solid Phase Mineralogy

Solid phase mineral complexes of cadmium, lead and zinc were modeled to determine their potential role in controlling the leaching behavior of Jasper County Chat. Leaching parameters were established from previous testing or modeling and are displayed in table 4.9. Jasper County Chat pH dependent leaching tests were performed at a liquid to solid ratio of 10 L/kg. PE+pH values were determined from previous modeling and HFO concentrations were directly measured as described in the methods and materials section (Section 3.3.8). Clay and dissolved organic carbon concentrations were not measured and assumed to be 0 kg/kg.

Table 4.9 – Geochemical Speciation Modeling Parameters

| Parameter | Value |
|---|---|
| Liquid to Solid Ratio | 10.0 *L/kg* |
| pE + pH Value | 12.5 |
| HFO Concentration | 1.10E-3 *kg/kg* |
| Clay Concentration | 0.00 *kg/kg* |
| DOC Concentration | 0.00 *kg/L* |

Figure 4.17 shows the modeling scenario results of cadmium, lead and zinc in Jasper County Chat. For all three elements, the observed leached concentrations are less than the modeled solubility of the considered solid phase minerals. In some instances values between the modeled and measured concentrations range over several orders of magnitude. There are several explanations that could account for this discrepancy including limitations of the model and limitations in the data.

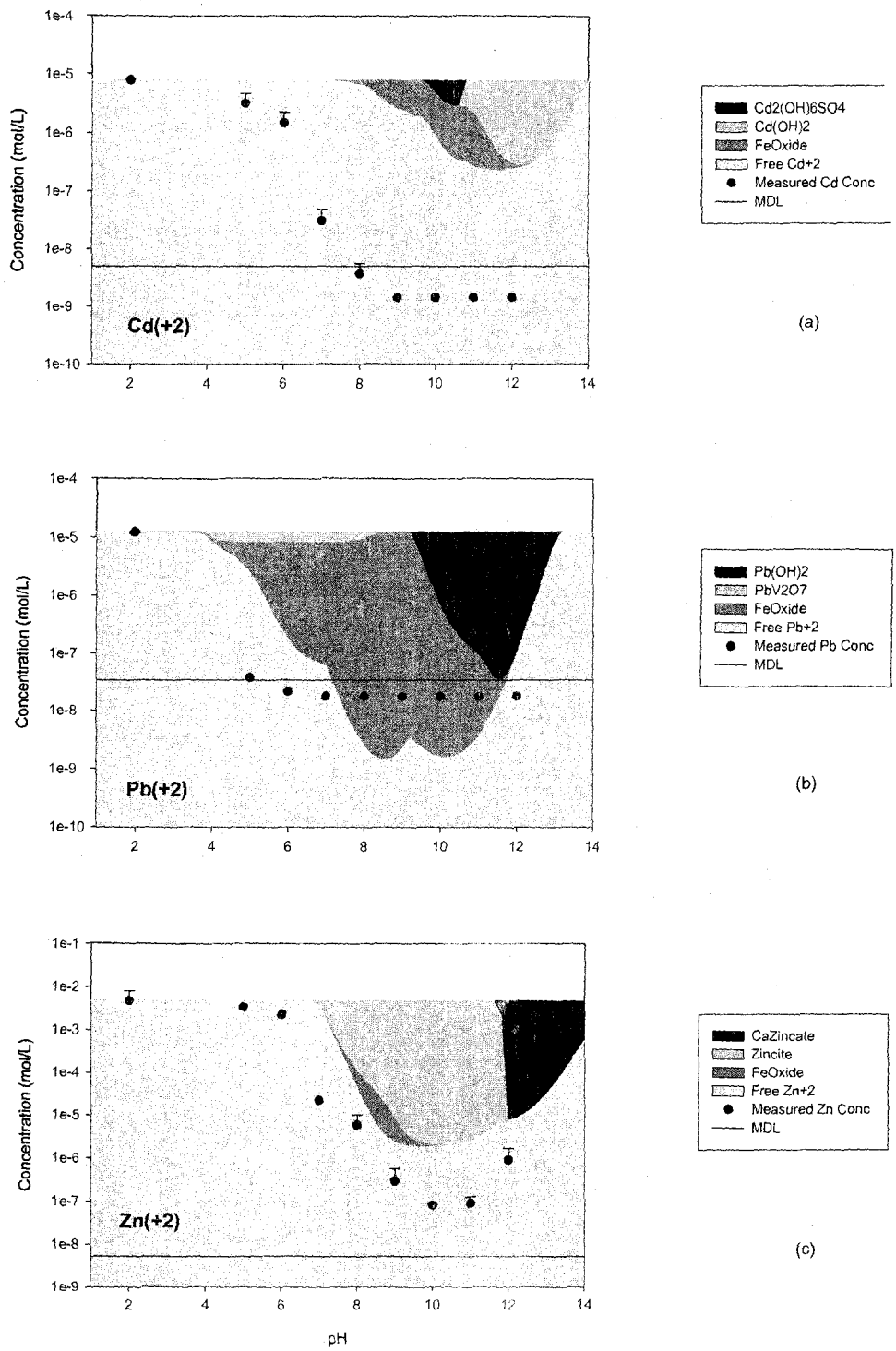


Figure 4.17 – Modeled Solid/Liquid Phase Complexes vs. observed Concentrations

(a) Cadmium
(b) Lead
(c) Zinc

. Regarding cadmium specifically, the literature has reported that cadmium occurs within the crystal lattice of sphalerite (ZnS) and galena (PbS). These minerals are only present at trace amounts within Jasper County Chat and the ratio of zinc to cadmium or lead to cadmium present within these minerals is only 168:1 and 220:1(Dames & Moore, 1995). Geochemical speciation modeling reinforces this theory, showing that observed leaching behavior is largely inconsistent with the solubility of cadmium hydroxide.

The two solid phase solubility trends, one directly measured in the lab and the other modeled on LeachXS based on data from the lab, deviate from each other at certain pH values. The magnitude of the deviation varies depending upon the pH range and the element of consideration. For example, variation between observed and modeled solubility for cadmium is not as great as those observed for lead and zinc. Differences do still exist however. A first possible explanation for the observed variation is a limitation of data. Although an extended analysis of the material was considered, several potential data fields were still incomplete. Incomplete or missing data sets may negatively impact the model by predicting a limited solution that does not adequately represent of the observed laboratory solubility of these complexes.

A second possibility is the sorption of lead and zinc is occurring at a greater margin of sites than predicted by the model. This may be due to greater concentrations of ferric oxide than determined by the Meima and Comans dithinite test. It could also reflect potential sorption from another component within the material matrix. To display the effects greater sorption would have on

the solubility of lead, Figure 4.18 shows the leaching behavior of lead and zinc with a 0.1% and 10% HFO concentration. This figure demonstrates the significant influence of HFO on the leaching behavior of Jasper County Chat.

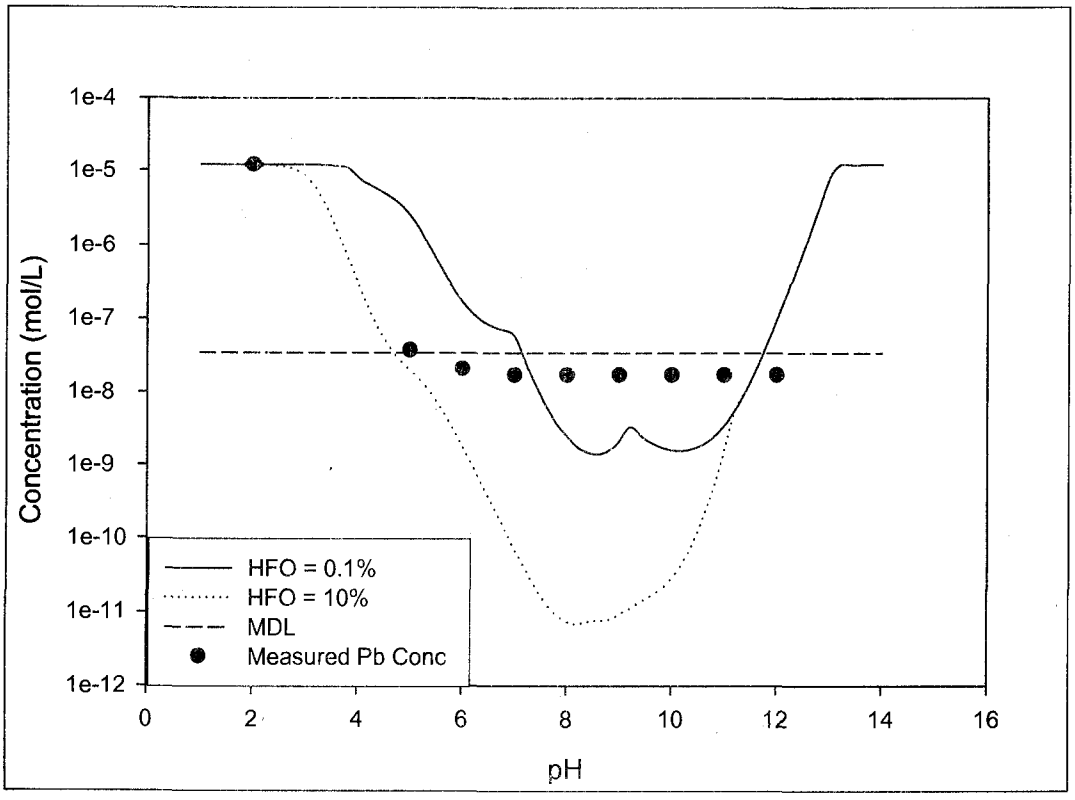


Figure 4.18 – Effects of HFO on Jasper County Chat Lead Solubility

Lastly, this material has been processed, potentially numerous times through various methods to extract the largest amount of lead that is economically feasible. These procedures may have some effect on the behavior of this material which the model can not account for.

## 4.9 Fate and Transport Modeling

Trace cadmium concentrations leached from Jasper County Fines were modeled in a fate and transport exercise using MYGRT, migration transport model, developed by the Electric Power Research Institute. The fines were selected amongst the three materials due to the residual's leaching characteristics. As shown in Section 4.7, Jasper County Fines will leach trace concentrations of cadmium above the EPA primary drinking water limit at low liquid to solid ratios (0.5 L/kg & 1.0 l/kg). As the LS ratios were increased, the concentrations of cadmium leached declined (measured in mg/L). At an LS ratio of 2 ml/g, concentrations were reported below the MCL and remained below the MCL for every LS batch test >2 ml/g. As discussed in previous sections, LS dependent leaching tests can be used to determine the leaching behavior of a material subjected to a leachant over time. This concept is used in conjunction with MYGRT modeling to compare the fate and transport of trace cadmium concentrations in groundwater from a material source that shifts leaching characteristics over time and space intervals. A schematic of the leaching scenario is shown in figure 4.20.

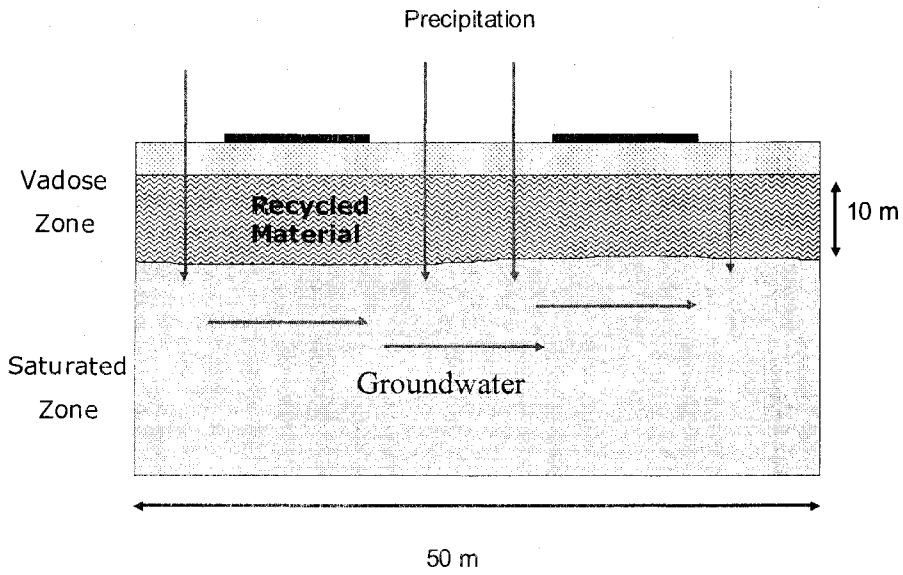


Figure 4.19 – Hypothetical Highway Fill Section Schematic

Several constraints were required to properly define a leaching scenario for the model to examine. Factors were selected to mimic a highway type application in Missouri, the source of the material. Several factors are taken directly from literature describing the area; however, generic values were also selected from a broader database or at the discretion of the designer. The application chosen for the utilization of Jasper County Fines was a fill section for a road bed embankment (figure 4.20). The material was modeled as a pure blend (100% Jasper County Fines), placed adjacently above the groundwater table so that transient groundwater flow would not come into contact with the material. The hypothetical fill section spans 1000 meters in length, and covers a 50 meter by 10 meter cross section. Annual precipitation figures for Jasper

County were reported to be 39.5 in/year with only 25% of the average rainfall infiltrating into the ground water or entering streams as surface run off (Dames and Moore, 1995). Jasper County Fines were also physically analyzed by UNH and found to have a maximum density of 122.4 pcf. These parameters in addition to the LS dependent leaching tests conducted at UNH determined the leaching schedule of the source, shown in table 4.10.

Table 4.10 – Hypothetical Source Leaching Schedule

| **Time** *(years)* | **Leached Concentration** *(mg/l)* |
|---|---|
| 0 | 0.000 |
| 39 | 0.044 |
| 78 | 0.023 |
| 156 | 0.012 |
| 391 | 0.005 |
| 781 | 0.001 |

Saturated zone parameters were also required in the model. The literature reported that most of the surface soils in the area were developed from one of three parent materials: Mississippian cherty limestone, Pennsylvanian shale and sandstone or loess (Dames and Moore, 1995). Rain water infiltration may either travel as groundwater to brecciated regions, recharging the shallow aquifer located at a depth of about 150 feet or follow a subterraneous path to recharge surficial water bodies. This exercise will assume ground water is consistently located at the bottom of the fill zone and will travel in a direction perpendicular to the length of the embankment. Volumetric porosity of the

saturated region will be assumed to be 30%, coinciding with the accepted range of limestone formations (Schwartz, 2003). The hydraulic conductivity and hydraulic gradient are assumed to be 1000 m/yr and 0.002 m/m. Mixing depth and dispersion coefficients were calculated by the modeling program to be 12.3 m and 66.7 $m^2$/yr.

Lastly plume solute descriptions were defined. Groundwater in the region can range in pH but generally averages at a pH of 7. Bulk density of the downgradient zone was assumed to be 1.6 g/ml. The partition coefficient for cadmium suggested within the modeling software was 110 ml/g, however a more conservative figure from the EPA Office of Solid Waste was used, 2.9 ml/g (EPA, 1999). Additional parameters are required for multidimensional analysis, however the aforementioned values were sufficient for the scope of this exercise. All parameters discussed in this section are provided in table 4.10 for convenience.

Table 4.11 – Fate and Transport Modeling Parameters

| Parameters | Value |
|---|---|
| ***Berm Dimensions*** | |
| Length (perpendicular to GW flow) | 1000 m |
| Width | 50 m |
| Height | 10 m |
| ***Unsaturated Zone Properties*** | |
| Vertical Infiltration Rate | 0.251 m/yr |
| Volumetric Moisture Content | 0.21 $cm^3/cm^3$ |
| Depth to Water Table Below Source | 0 m |
| Vertical Dispersion Coefficient | 0 $m^2/yr$ |
| Retardation Factor | 1 |
| ***Saturated Zone Properties*** | |
| Hydraulic Gradient | 0.002 m/m |
| Hydraulic Conductivity | 1000 m/yr |
| Volumetric Porosity | 0.3 $cm^3/cm^3$ |
| Horizontal Seepage Velocity | 4.88 m/yr |
| Scale Distance Dispersion Coefficient | 100 m |
| Horizontal Dispersion Coefficient | 48.8 $m^2/yr$ |
| ***Plume Description*** | |
| Bulk Density | 1.6 g/ml |
| pH value | 7 |
| Background Cd Concentration | 0 mg/L |
| Partition Coefficient | 2.9 ml/g |
| Retardation Factor | 8.8 |

The first analysis analyzed cadmium concentrations downgradient of the fill section along the horizontal (x-y plane) at distances of 1m, 25m, 100m and 250m. The results of this modeling exercise are shown in Figure 4.20. Concentrations at 1m most closely represent leached concentrations from the plume source. The figure displays that concentrations at this location are stepped over time. This is a result of employing LS dependent leaching tests to define to leached concentrations from the source. Source concentrations do not

actually behave in this fashion; however the simplification adequately reflects diminishing source concentrations over time for this exercise. Figure 4.21 also reveals that cadmium concentrations above the EPA primary drinking water limits are not mobile beyond 250 m from the source.

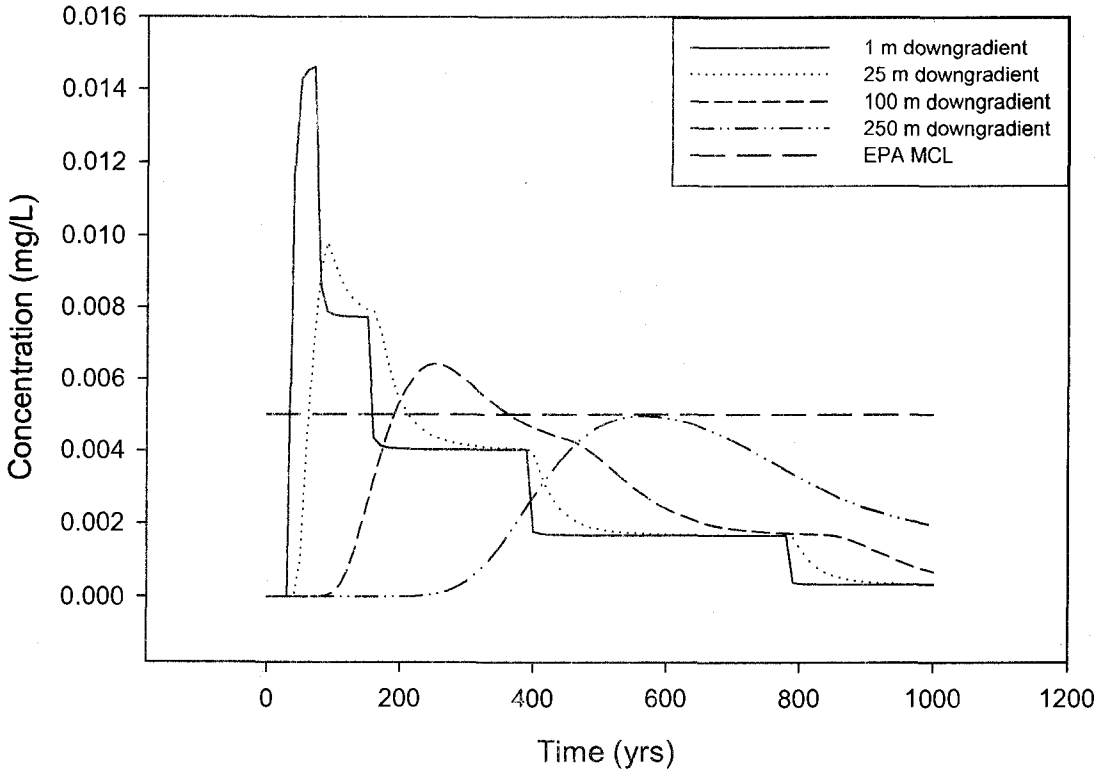


Figure 4.20 – Cadmium Fate and Transport Concentrations over Time
EPA MCL – EPA Primary Drinking Water limits for Cadmium

Although most civil engineering projects are generally only designed for a 100 year life span, a fill section below a highway project could remain indefinitely. Given this reasoning the time span of the x-axis is appropriate for a highway fill section application. It is likely that even if the road was to be reconstructed or if it was abandoned, the fill would remain in place. Concerns regarding boundary

issues such as sensitive rivers or streams running adjacent to the project of drinking water wells located in the vicinity may be appropriately represented by fate and transport modeling. In such circumstances, figure 4.20 could provide useful information to provide a responsible placement of the highway. Of coarse, catering parameters to accurately represent conditions of the region is a paramount inclusion if sensitive natural resources are at risk.

A 2-dimensional plot was also formulated using the same parameters discussed above with the inclusion of a cross gradient horizontal seepage velocity (0.488 m/yr) which was calculated by the modeling software. These plots do not provide a great deal of additional information about the fate and transport of cadmium traveling through the groundwater; however, they do represent the data from more of a plan view perspective of the plume over time. This prospective allows the effects of advection and dispersion over time to have an enhanced visual representation.

Figure 4.21 is a contour plot of the groundwater cadmium concentration over the x-y plane at four time intervals (100 yrs, 250yrs, 500yrs and 1000yrs). The distances perpendicular and parallel to groundwater flow are displayed on the x and y axis, the center of the fill section is located at coordinates (0,0). Cadmium concentrations are depicted by the contour lines and labeled accordingly. The groundwater direction noted in plot 4.22a and applies for all four plots.

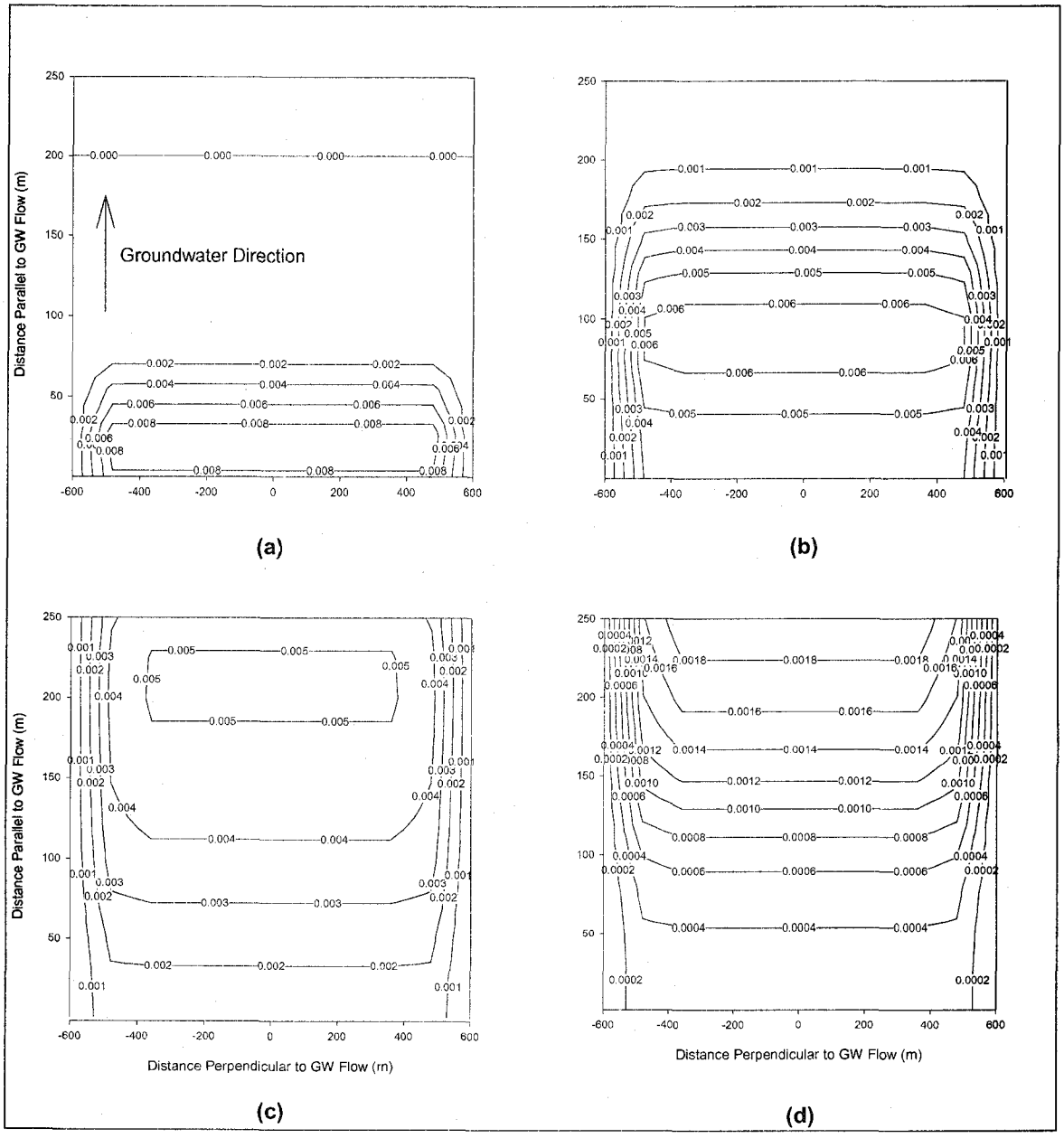


Figure 4.21 – Contour Plots of Plume Concentrations Over Time and Distance
(a) – Time = 100 years
(b) – Time = 250 years
(c) – Time = 500 years
(d) – Time = 1000 years
Note – Units in mg/L

Several observations concerning the plume are discernable from the figure. Primarily, the relative movement of bulk concentration in the direction

of the groundwater in comparison to other directions, such as perpendicular and against the direction of groundwater flow, is much greater. Bulk concentrations traveling in the direction of flow travel over 300 m in 500 years where as locations 100 feet perpendicular to the direction of flow see little additional cadmium concentrations to their background concentrations. Additionally, the decrease in bulk solution concentration can also be witnessed over time and distance. These observations suggest that distance as well as the relative location of a potential plume source is important in the placement of a material.

A second modeling exercise was conducted to determine the sensitivity of the model to alterations in the fill section's dimensions. The migration of cadmium from the same beneficial use scenario as described previously in table 4.11 was remodeled, with the berm depth adjusted from 10 meters to 1 meter fill. This variance in dimension is not directly input into the modeling program however; fill section depth manifests itself through the leaching schedule of the material, so the schedule must be altered accordingly. As a result, less total mass is subjected to the same rate of rainfall infiltration and therefore less cadmium is released along a different time line. Figure 4.21 shows a comparison of cadmium migration due to the ten and one meter deep berm leaching scenarios. Figure 4.21a, the 10 m scenario, shows a much greater peak concentration at locations downgradient of the fill section than the 1 m scenario, shown in Figure 4.21b.

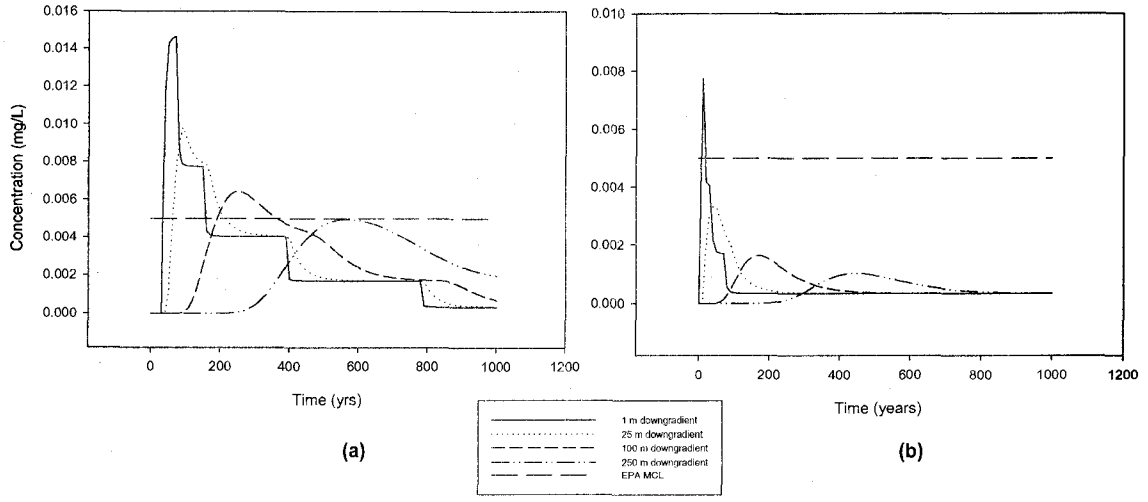


Figure 4.22 – Cadmium Concentrations Over Time at 10 m and 1 m Fill Depths
(a) – 10 meter deep fill section
(b) – 1 meter deep fill section

Similar modeling could be performed for any inorganic element analyzed by LS dependent leaching tests for all three of the materials examined in this study. The fate and transport of cadmium leached from Jasper County Fines was selected for this modeling exercise due to the proximity of the concentration of leachate to regulatory limits set by the EPA. LS dependent leaching determined that lead from Tar Creek Chat also leached in close proximity to primary drinking water levels. Cadmium and lead in the materials not mentioned as well as zinc in all three materials tested did not leach concentrations that would warrant fate and transport modeling according to the metrics applied in this scenario. This is not to say that they will not have any negative implications if more sensitive limitations than the EPA primary and secondary drinking water limits should be applied to the area or the leaching tests do not accurately reflect the conditions in the area. Source concentrations were determined by leaching

materials at natural pH values under anoxic conditions. As with the other parameters defined in this modeling exercise, leaching tests not representative of the conditions at which the material is utilized will result in inaccurate modeling that may either jeopardize sensitive resources in the region or exclude potentially acceptable material from being utilized.

# CHAPTER 5

## RESIDUAL MANAGEMENT

Management of the mined residual waste residing in the Tri-State Mining District has gained national attention in acknowledgement of the four superfund sites within the districts boundaries. Landfilling and other conventional disposal techniques for the 100 million tons of material has been deemed impractical, however the presence of unstabilized waste throughout the district continues to present an unacceptable risk to the environment. In response, the recycling of residuals into highway applications has re-emerged as a potentially sustainable management solution. Some applications have been responsibly established in the area notwithstanding elevated concentrations of trace metals within the material. As discussed previously, the risk cadmium, lead and zinc pose to human health is not solely a function of total concentration but dependent upon exposure and availability. To limit metal release, beneficial utilization of chat is generally reserved for bound applications such as asphalt in highway construction. These applications limit the exposure of the raw chat, and as a result, have been demonstrated to limit the release of metals to the environment. In addition chat has also been shown to provide an acceptable aggregate performance in asphalt products (Wasiuddin, 2005).

Because recycling chat into asphalt products is the dominant secondary management utilization, management of the residual stockpiles are dependent

upon the demand for asphalt products. A rough estimation of residual usage on the Tar Creek site is put at 50,000 tons a year (EPA, 2007). At the rate of current usage, it will require 2000 years to deplete the stockpiled material. If beneficial reuse is going to be a contributing management option for mineral mine waste in the Tri-State Mining District, broader applications need to be established and implemented.

A possible beneficial use expansion within the transportation industry would be the implementation of mineral residuals in stabilized unbound applications. This would include products such as road base, subbase and embankment aggregates. The inclusion of these products would greatly increase the quantity of raw material that could be managed under a beneficial utilization program. It is undeniable that an expansion of beneficial uses may raise the risk profile to environmental conditions where these utilizations occur. However, as demonstrated in this study, improvements in characterization techniques and modeling technology can abate some of this risk, to allow the responsible expansion of beneficial secondary use to commence.

This research has focused on the environmental properties of chat and fine tailings as an initial step to qualify mineral residuals as acceptable materials for unbound applications. Only a small portion of the bulk of material was tested in this analysis; however this testing establishes preliminary results regarding the materials behavior. Dominant routes of exposure vary over the stages of unbound materials application in a highways life cycle. These stages are

simplified into two sections for the purposes of this discussion; the construction phase and application phase. The construction phase is defined as any period that the material is not in its final application including transport, construction and deconstruction. The application is defined as the time period where a material is implemented and performing its intended application.

Dominant routes of exposure will vary depending upon the unbound application's phase and therefore any risk associated with the material will change accordingly. Direct exposure, such as ingestion and inhalation, are the dominant routes of exposure during the construction phase of a materials life cycle. This is because the material has a much greater physical exposure to the environment and therefore humans and the immediate environment are more susceptible to these routes of exposure. After the material is stabilized in the final application phase the direct routes of exposure will be limited. The dominant route of exposure at this point will shift from direct exposure to indirect exposure through the leaching of trace metals from the material to groundwater. As discussed previously, only a small sample of mining residuals were analyzed in this study, and therefore results of this study are not representative of the total material present on the site. Discussion will continue however, regarding the results reported, and their relevance to qualifying mineral residuals as acceptable aggregate materials in beneficial use scenarios.

Total metal analysis found that the three materials analyzed had arsenic and beryllium concentrations elevated beyond the Ingestion SSL. Similarly

cadmium, lead and zinc concentrations were very close to the ingestion SSL and beyond the inhalation levels for cadmium and zinc. Soil screening levels are not regulatory limits which can reject potential materials from secondary beneficial use applications; however, SSLs are important risk based levels and the handling of any materials that exceed their concentrations should incorporate appropriate precautionary measures to limit exposure to any humans and the environment. Detailed risk assessment assays should be conducted to further evaluate the material in this phase prior to any personal exposure to the material.

The total concentration of a material is most critical to direct routes of exposure, which in a highway application is limited to the construction phase. This phase occurs for only a small percentage of the applications total life cycle. The more enduring phase is the application period. During this stage of the product's life, the leaching of constituents to groundwater is the dominate route of exposure. SSLs are established to determine the potential risk of leaching to groundwater however pH dependent and LS dependent leaching tests are a much more inclusive analysis to determine a materials potential leaching ability.

Analysis found that the mining residuals tested will potentially leach concentrations of cadmium, lead and zinc (the primary constituents of concern) above the EPA primary and secondary drinking water MCLs. Metal release was found to be highly dependent upon leachant pH, leaching greater concentrations in acidic conditions. Acid base accounting showed that there was little possibility of acid generating potential from the materials however these results were

inconsistent with other broader studies of the Tri-State Mining District. Because of these exceendances, it is important to include fate and transport modeling specific to the design application and region which the material will be utilized so that the appropriate level of risk can be quantified.

In summary, this research illustrates the mismanagement of mineral residuals into recycled application can and has had considerable negative health and environmental effects. In recognition of this history, the continual depletion of natural aggregate in conjunction with the growing stockpiles of mineral residuals requires that mined residuals be considered in potential stabilized unbound applications. This utilization should only be considered if a thorough knowledge of the residual and application is understood and maintained; and any risk presented from that application is limited to acceptable levels throughout the entire life cycle of the application.

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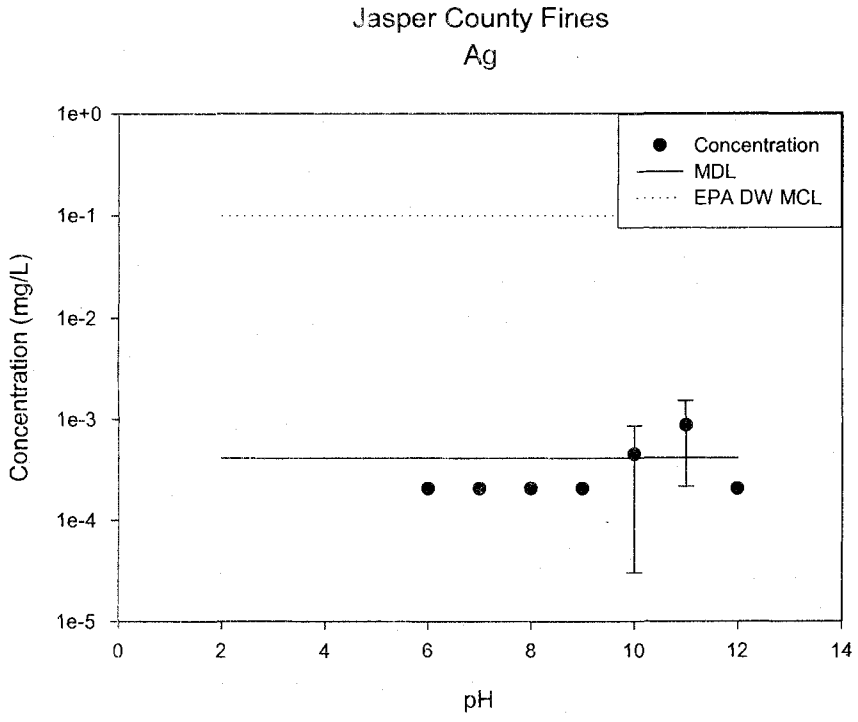
# APPENDIX

## pH AND LS DEPENDENT LEACHING RESULTS

## pH Dependent Leaching

**Note:**

**MDL – Minimum Detection Limit**
**DW MCL – EPA Primary and Secondary Drinking Water Limits**
**1) All concentrations below the MDL are reported and averaged as half the MDL**



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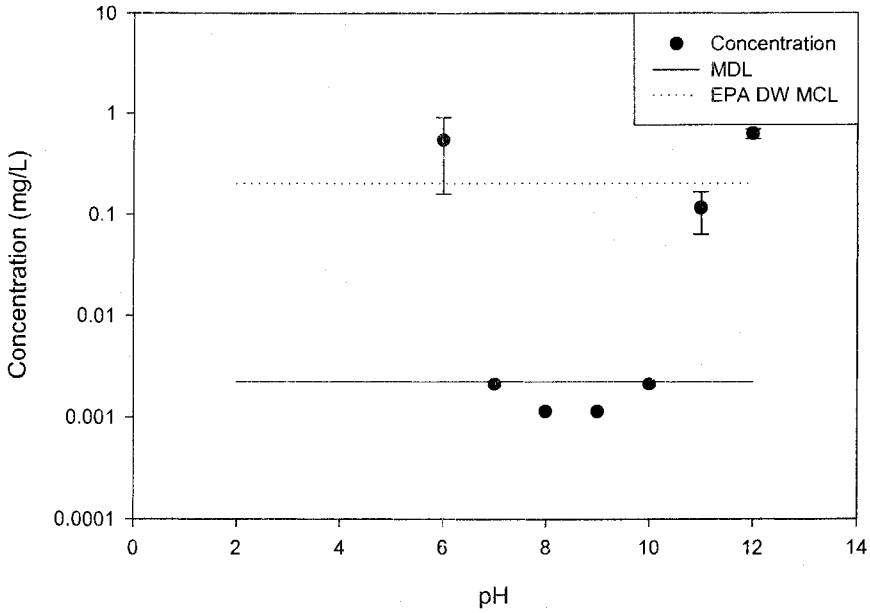


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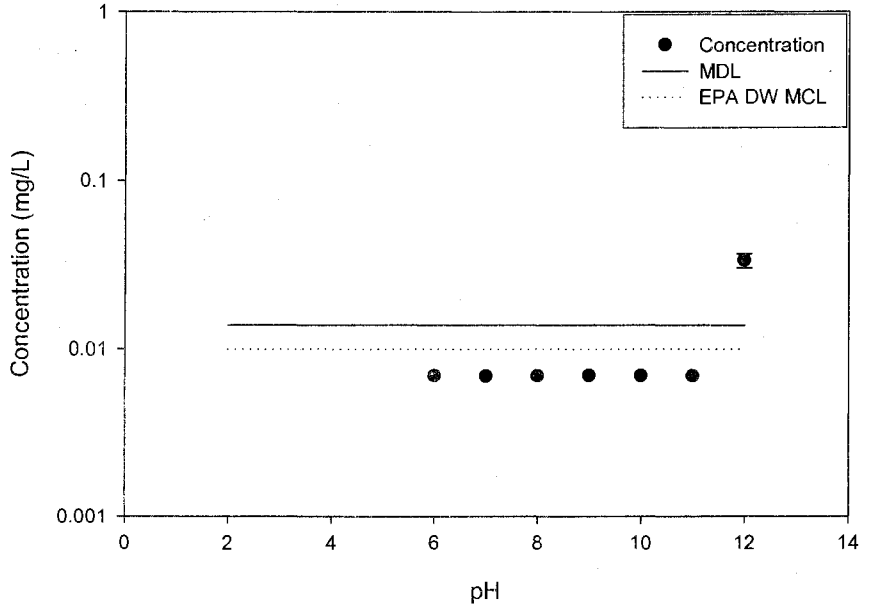
As



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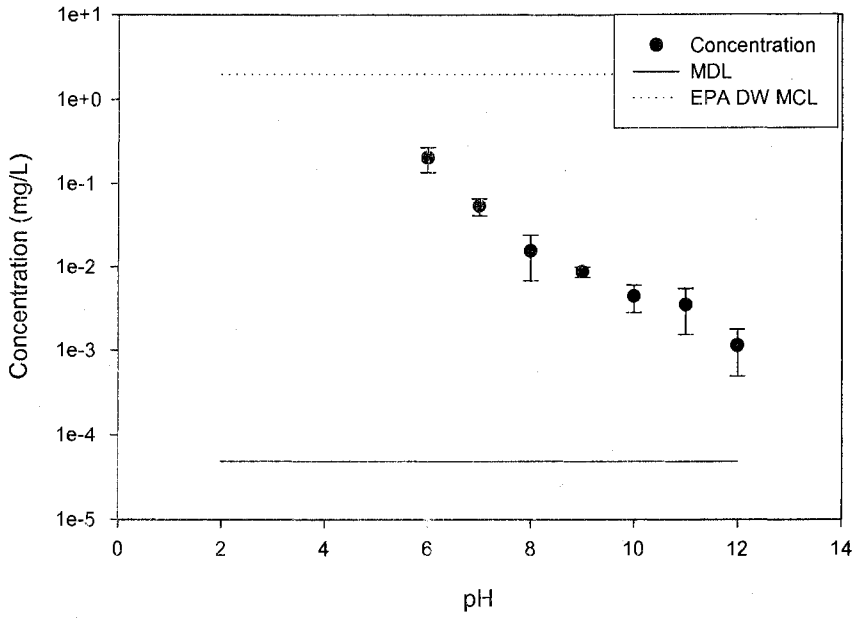
Ba

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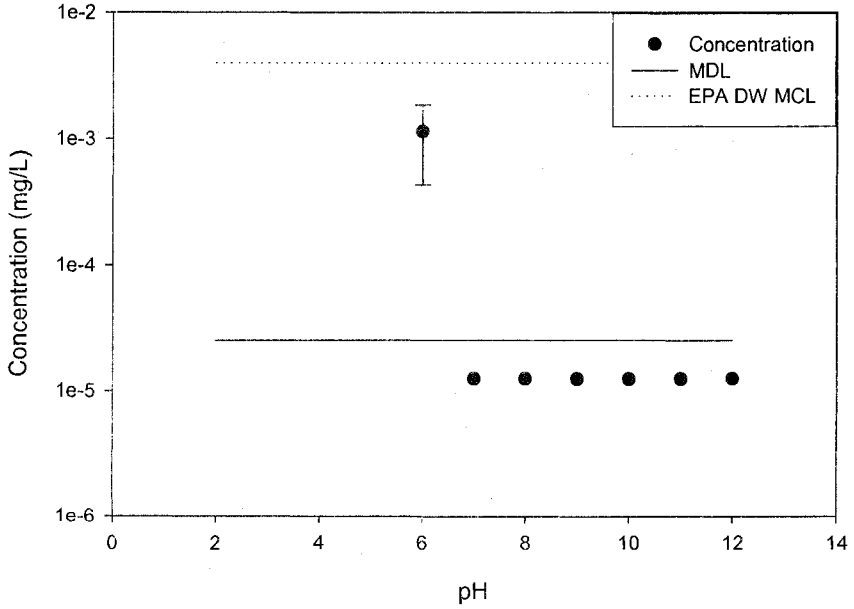
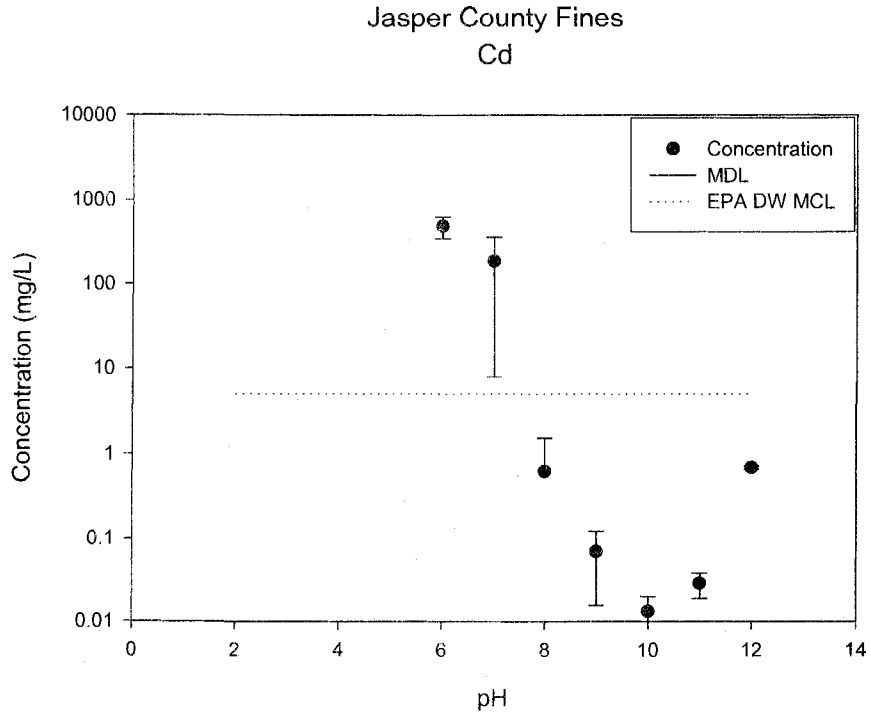
Be




Jasper County Fines
Cd
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
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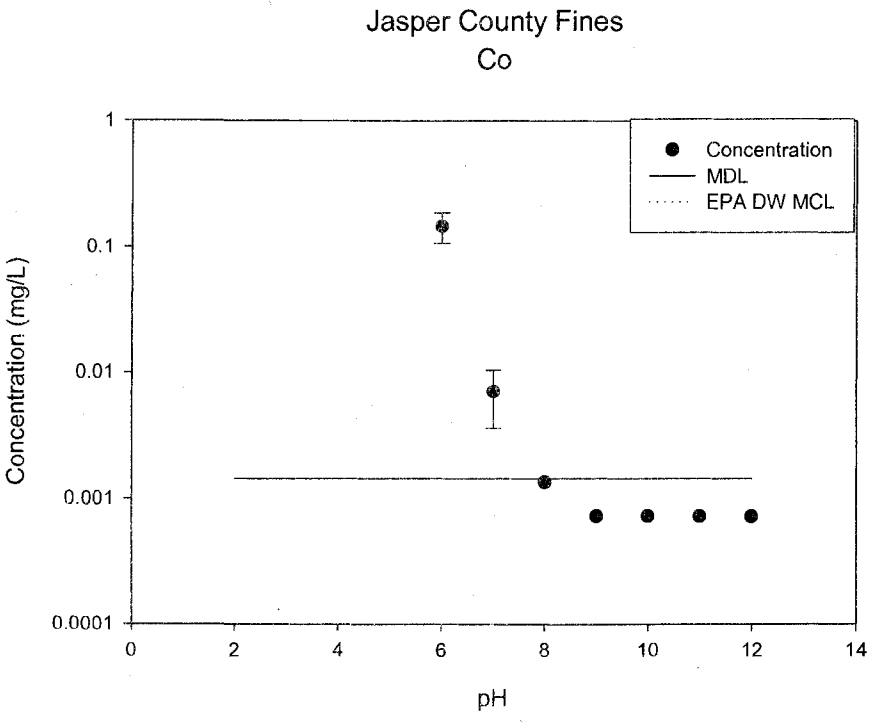
1000
100
10
1
0.1
0.01
0
2
4
6
8
10
12
14
pH


Jasper County Fines
Co
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
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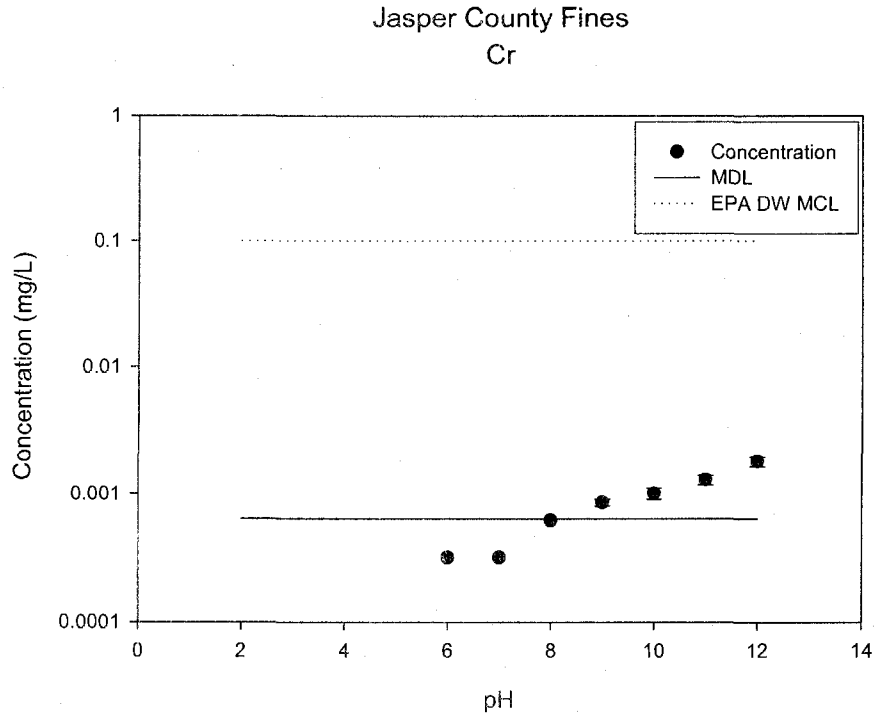
0.1
0.01
0.001
0.0001
0
2
4
6
8
10
12
14
pH


Jasper County Fines
Cr
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
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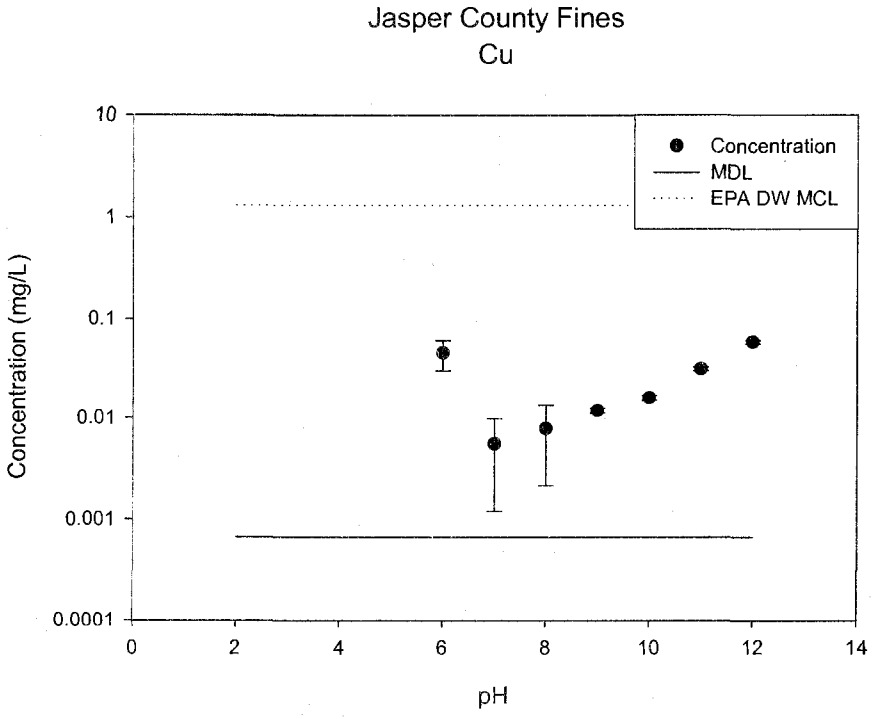
0.1
0.01
0.001
0.0001
0
2
4
6
8
10
12
14
pH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Cu
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
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2
4
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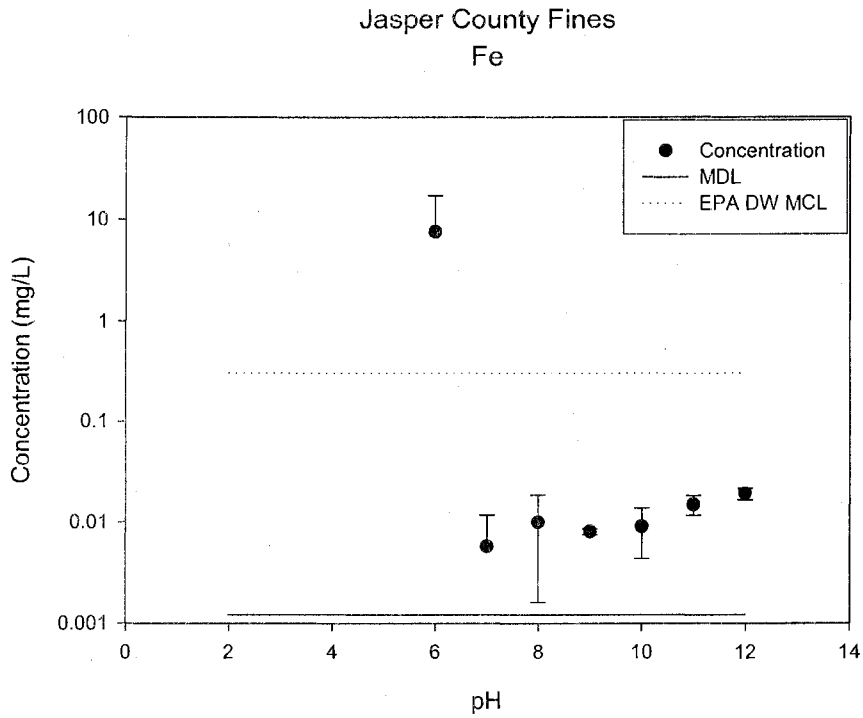
10
12
14
pH


Jasper County Fines
Fe
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
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10
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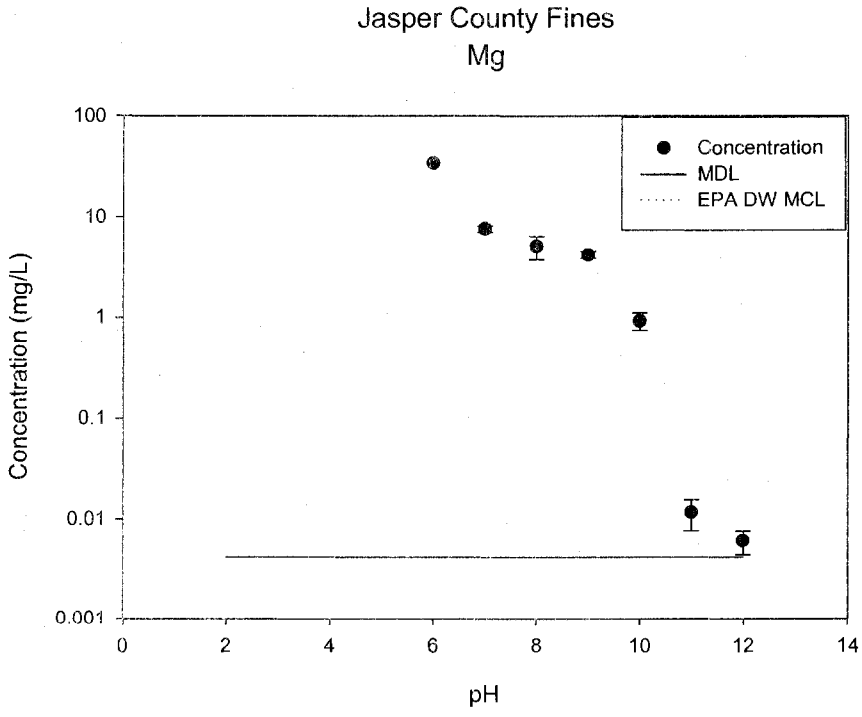
0.01
0.001
0
2
4
6
8
10
12
14
pH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Mg
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
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2
4
6
8
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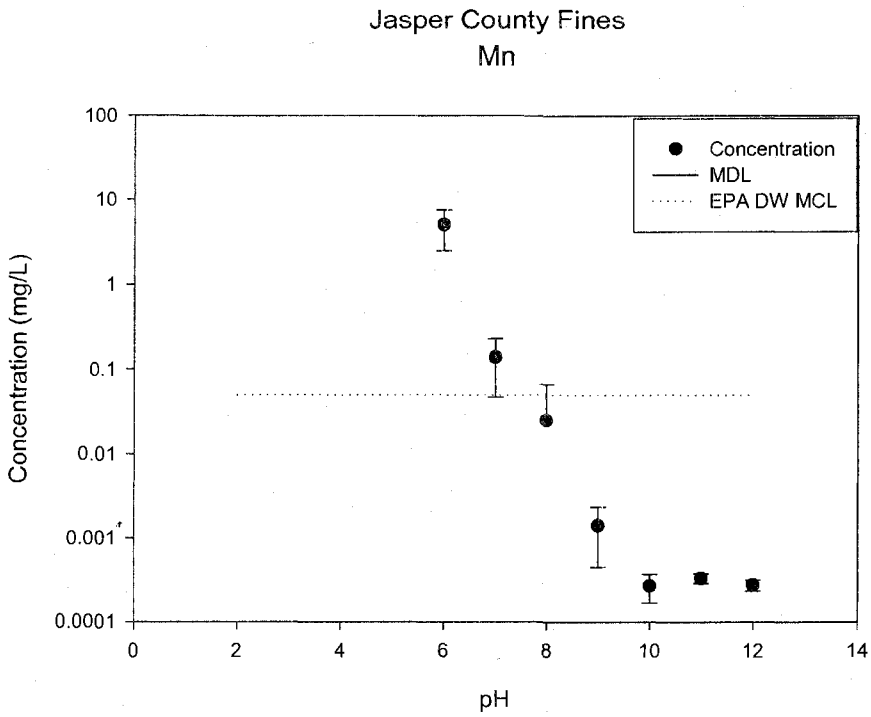
12
14
pH


Jasper County Fines
Mn
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
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2
4
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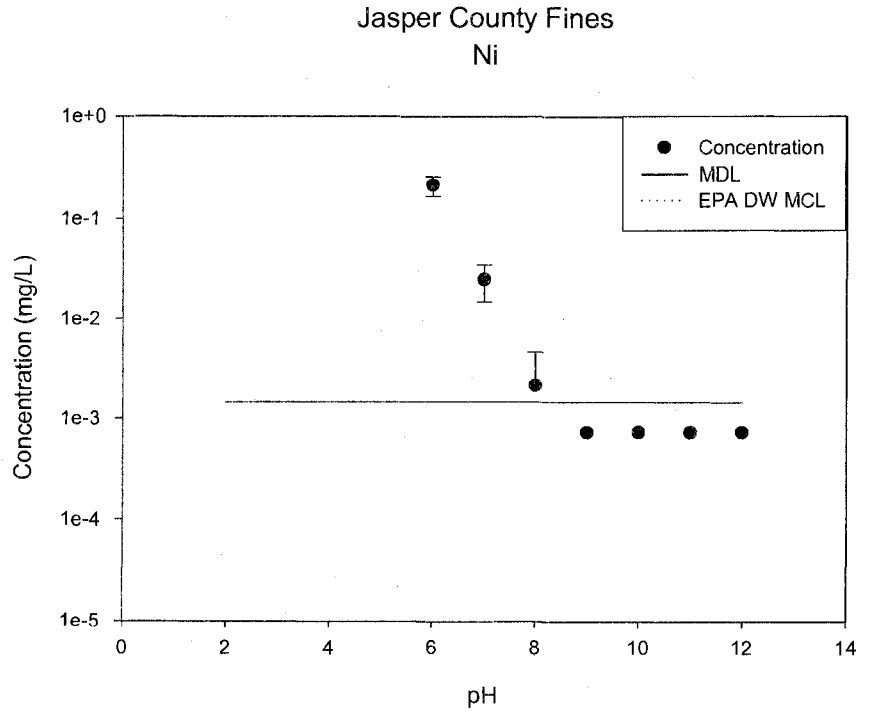
10
12
14
pH


Jasper County Fines
Ni
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
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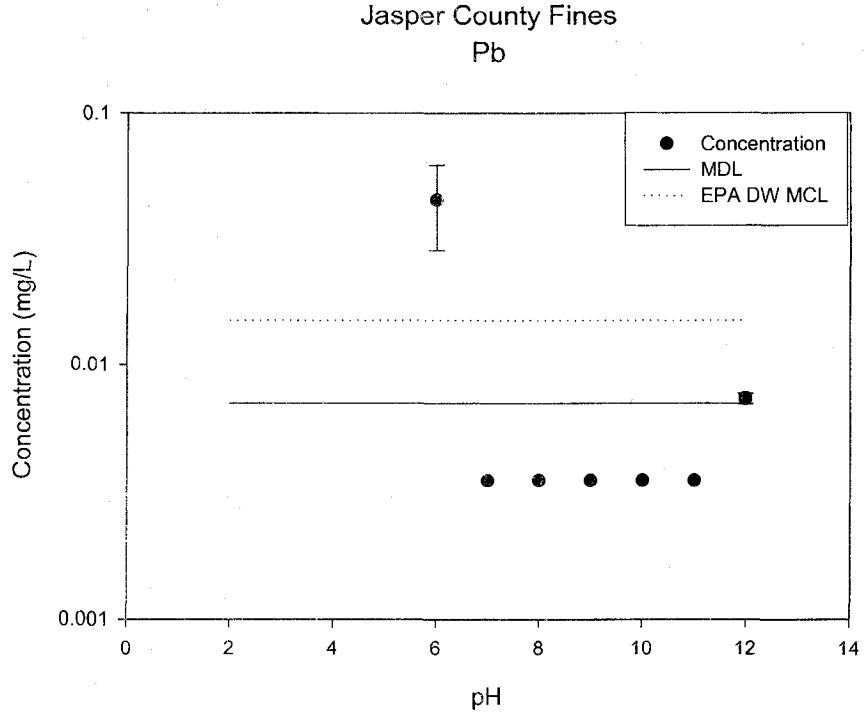
10
12
14
pH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MDL
EPA DW MCL
Concentration (mg/L)
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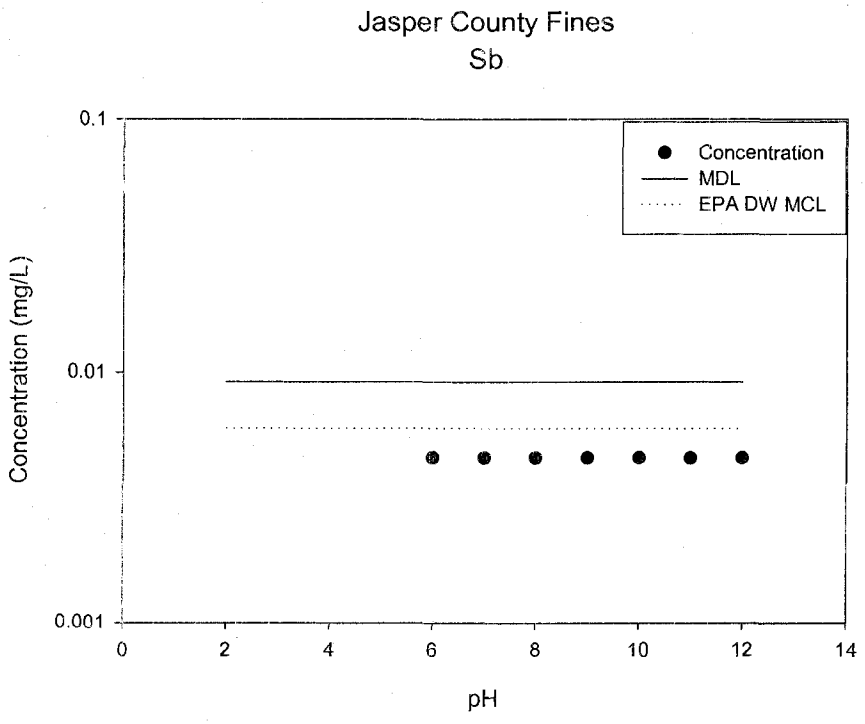
14
pH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Sb
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MDL
EPA DW MCL
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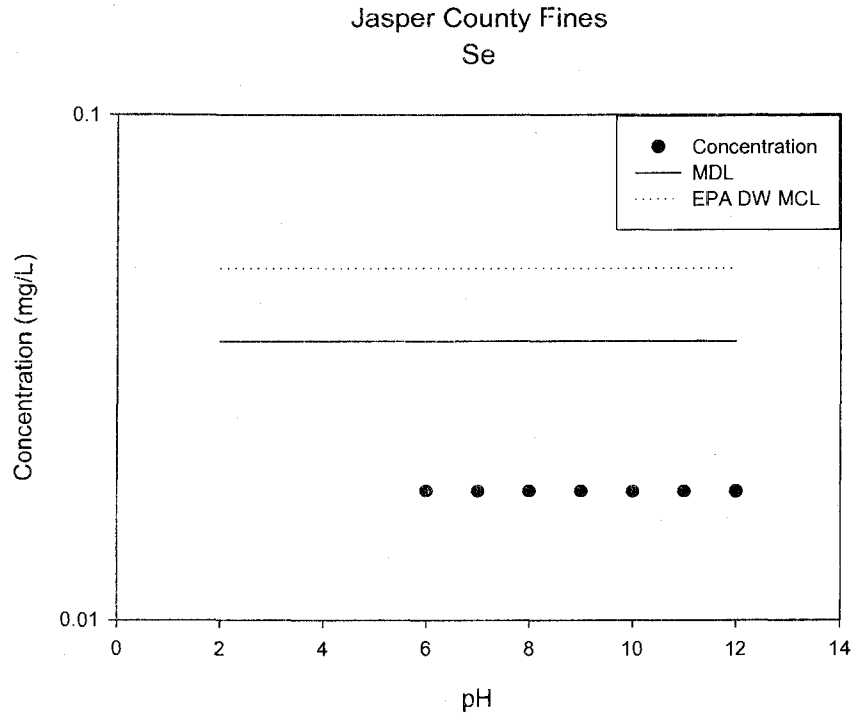
10
12
14
pH


Jasper County Fines
Se
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
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2
4
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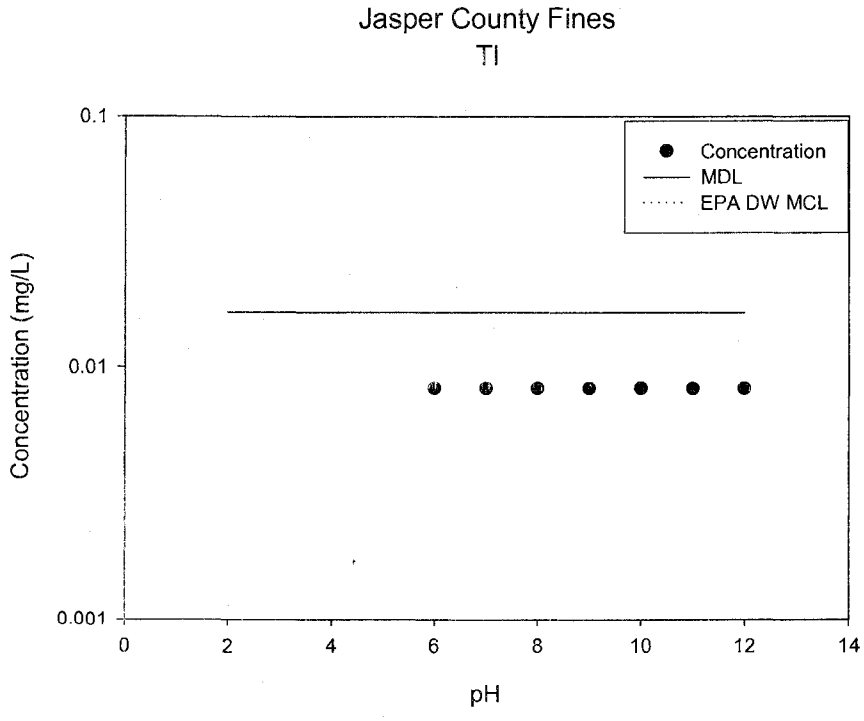
10
12
14
pH


Jasper County Fines
Tl
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
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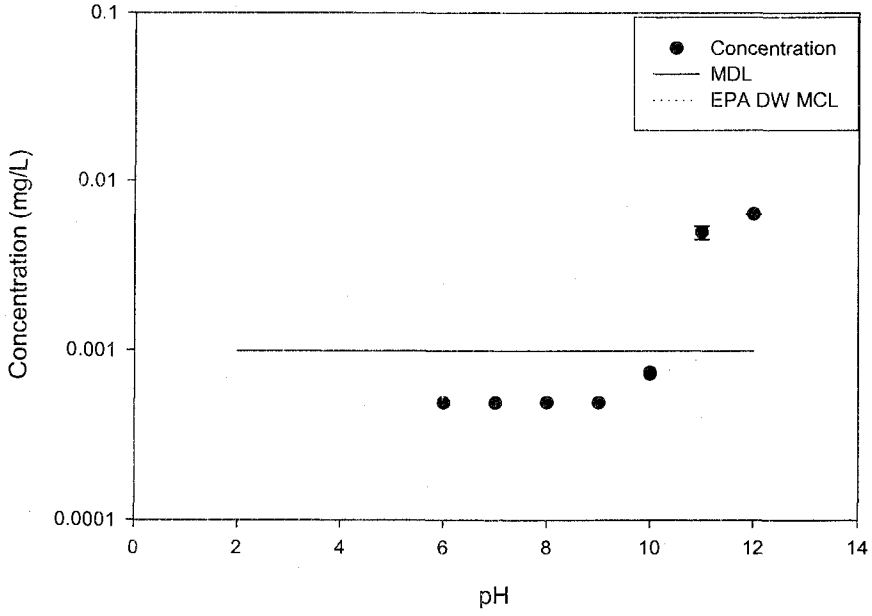
0.01
0.001
0
2
4
6
8
10
12
14
pH

Jasper County Fines
V

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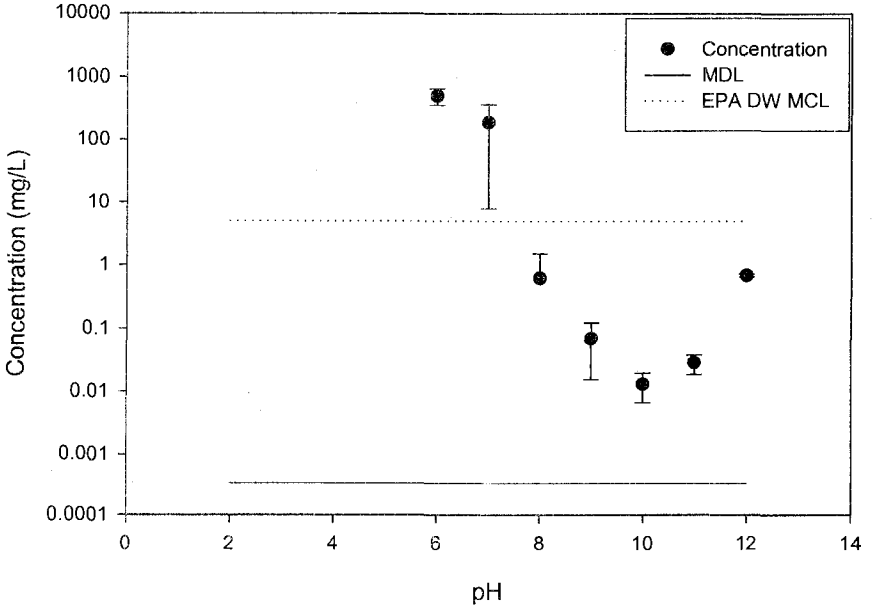

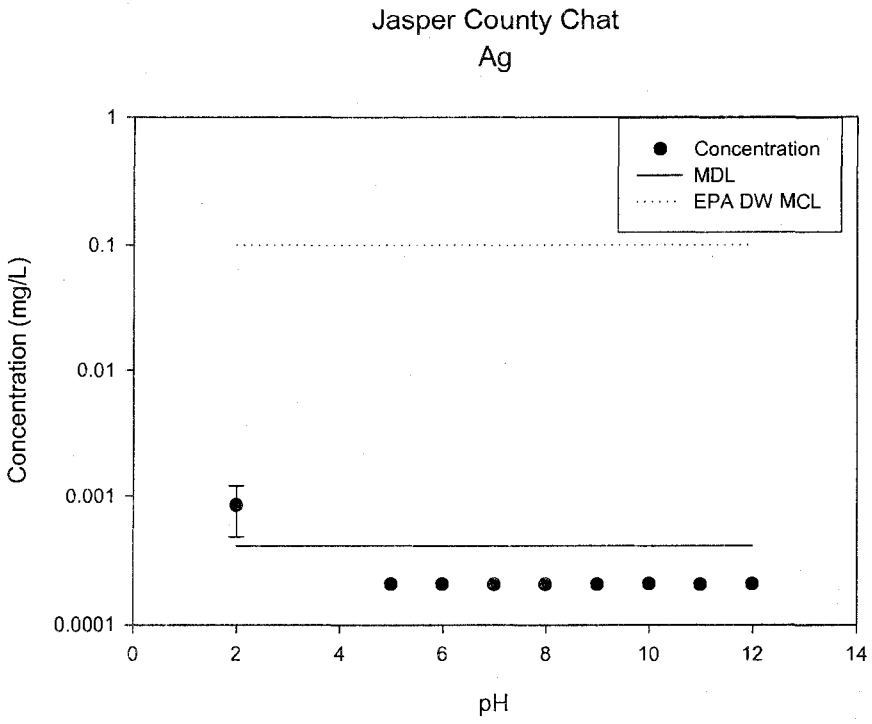
Jasper County Chat
Ag
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
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2
4
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8
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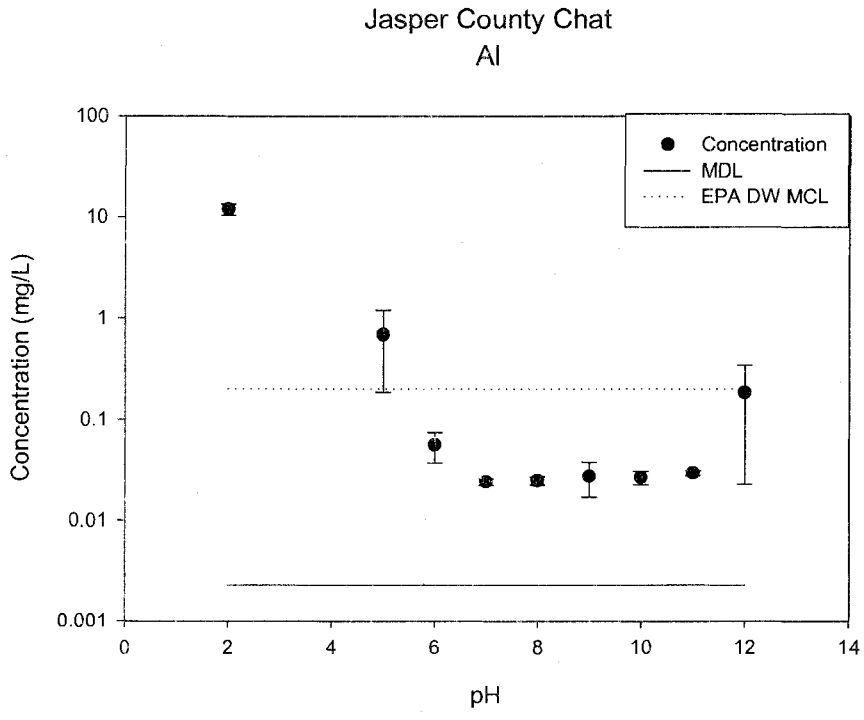
pH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Al
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
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10
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14
pH

Jasper County Chat
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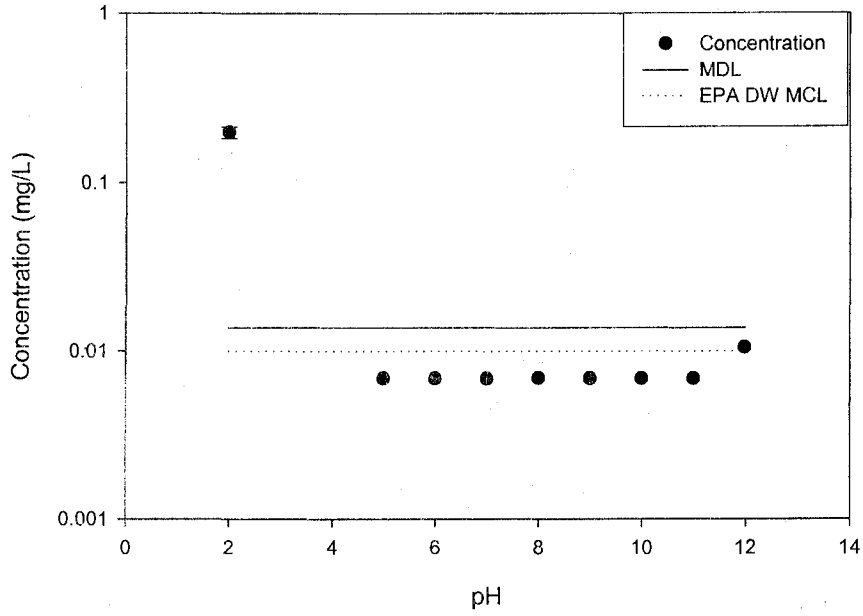


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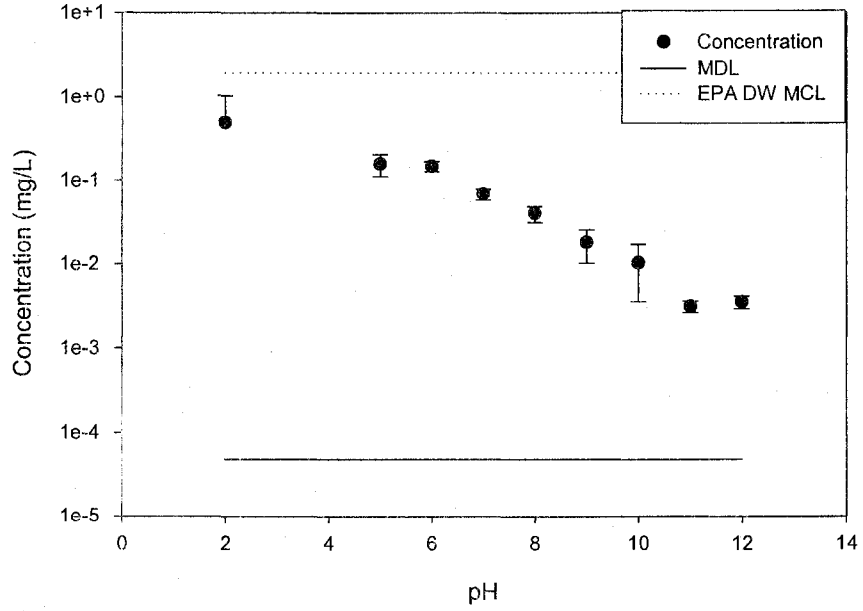

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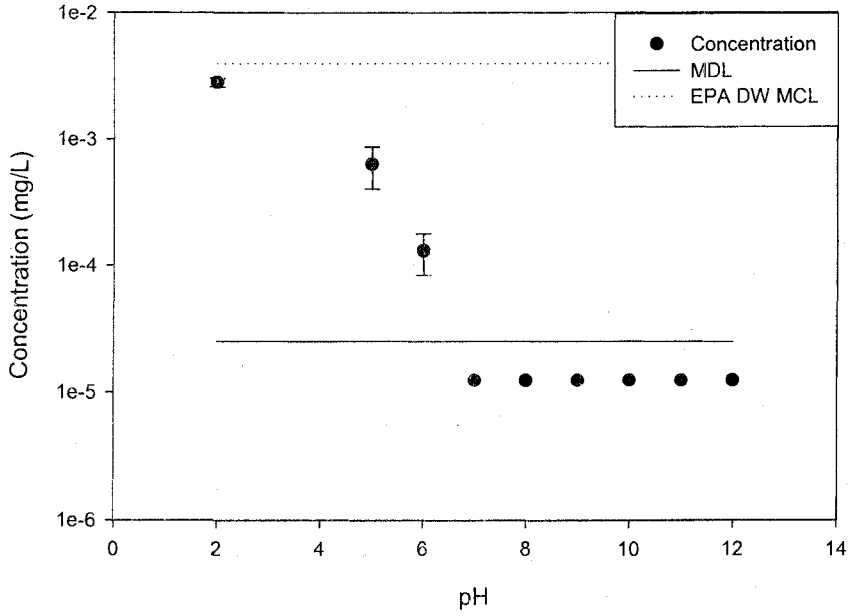
Be

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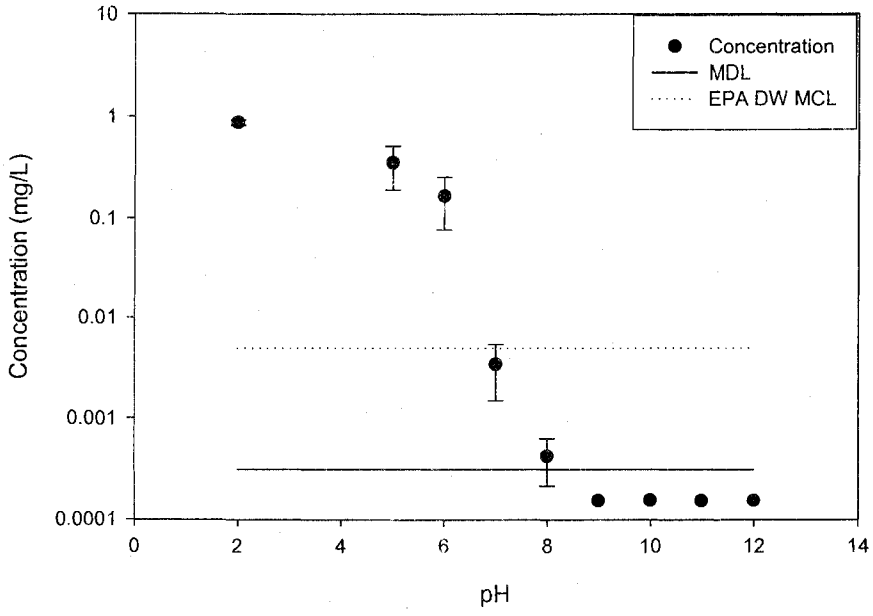

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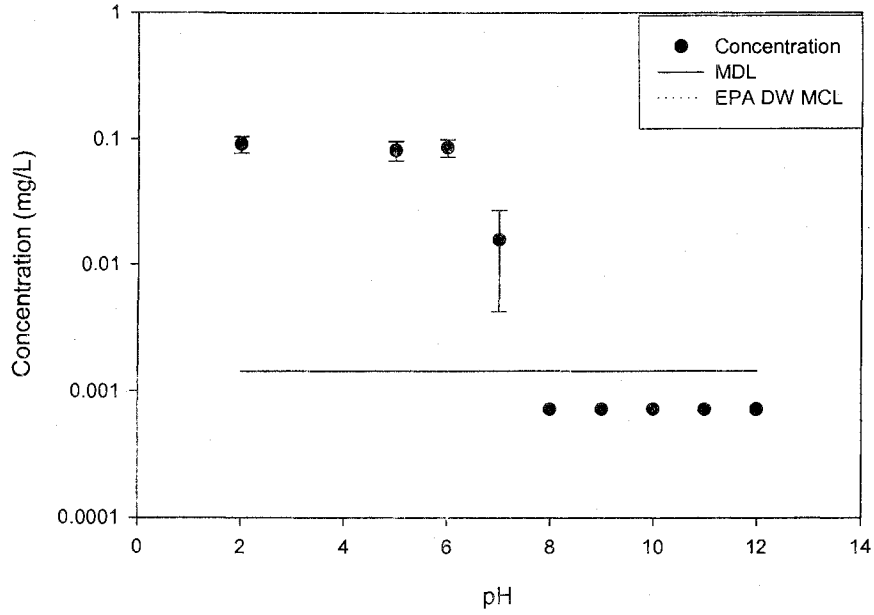
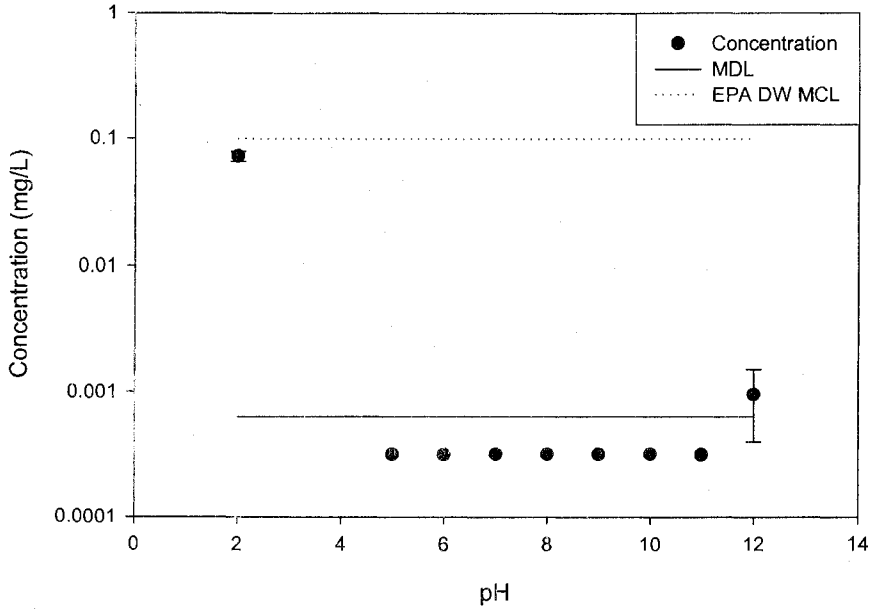
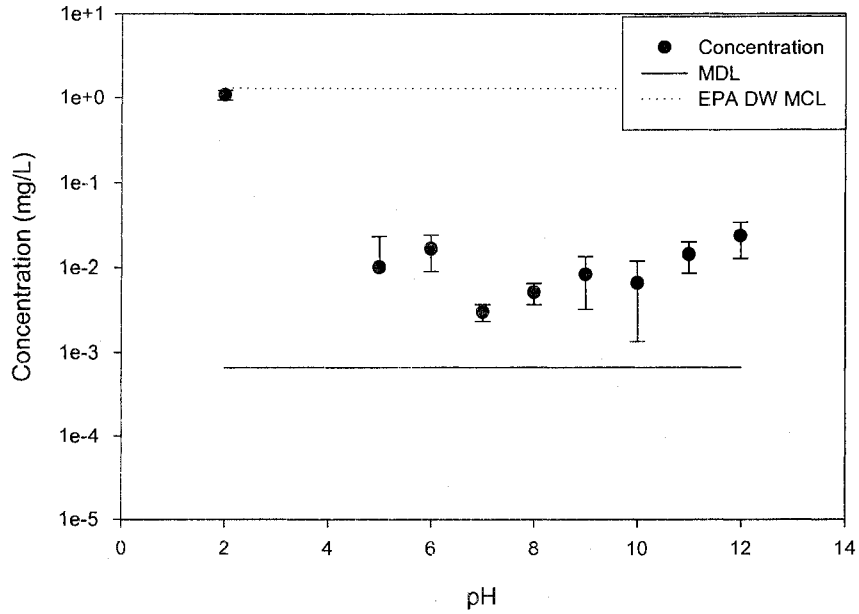


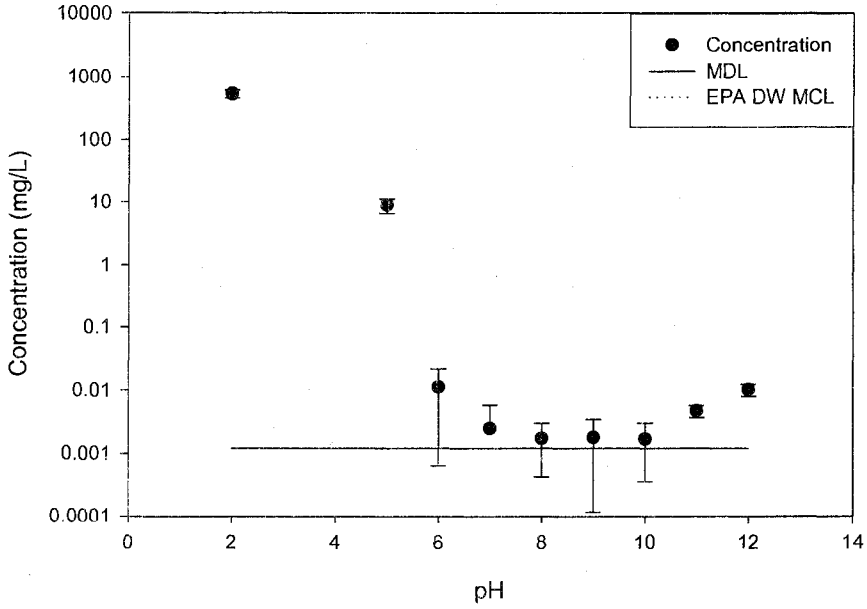

Jasper County Chat
Cr



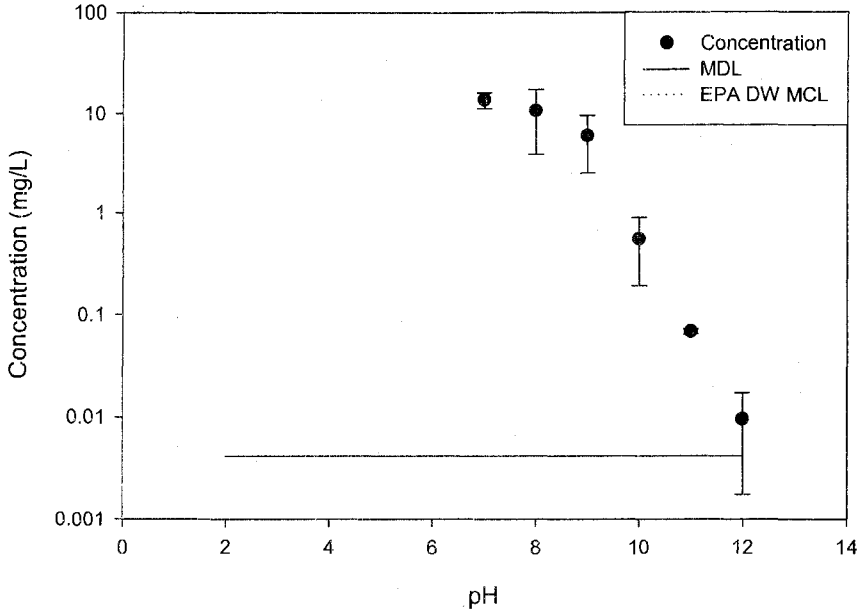
Jasper County Chat
Cu



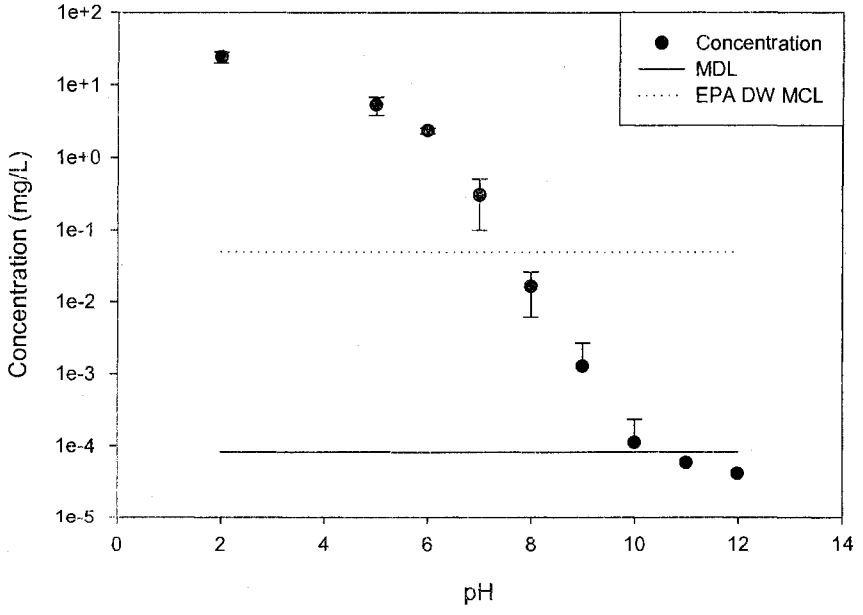

Jasper County Chat
Fe



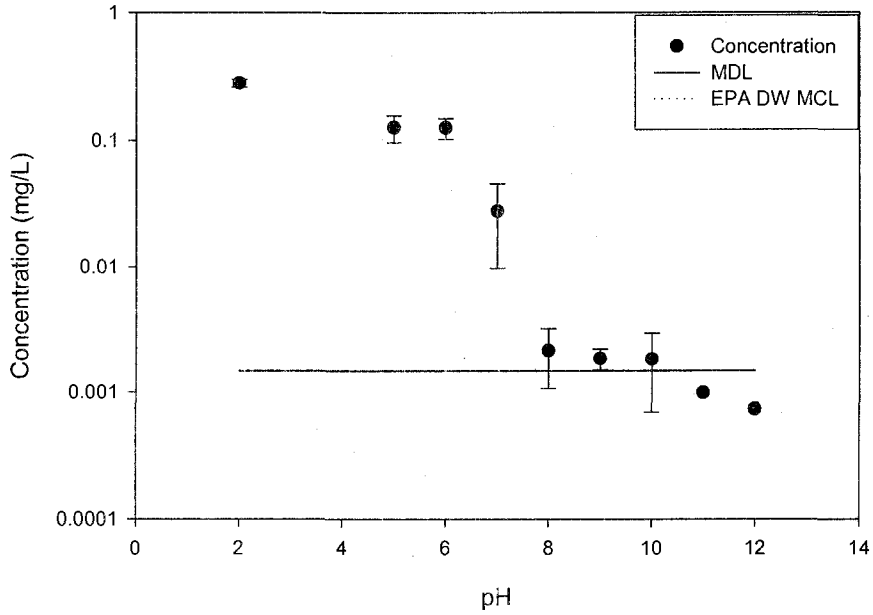
Jasper County Chat
Mg



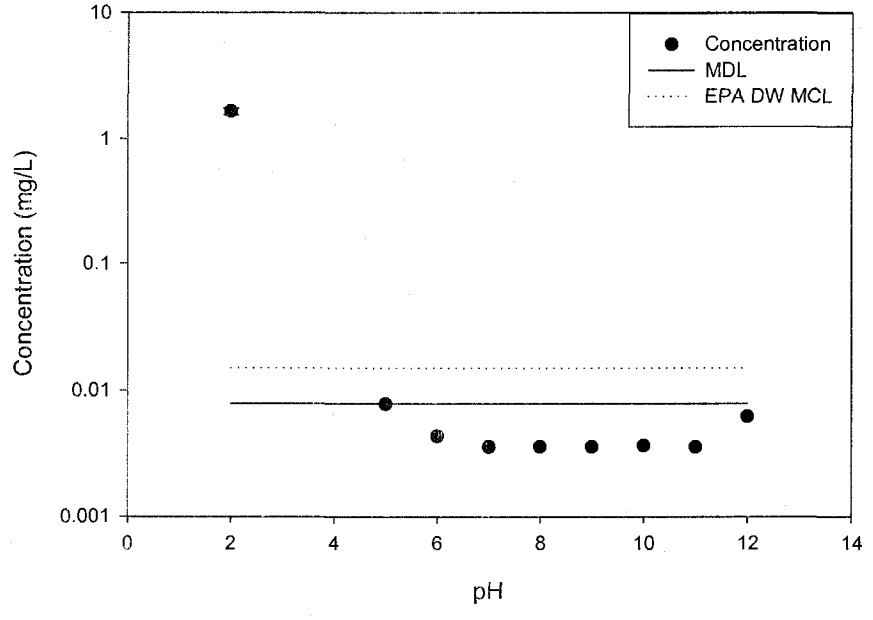

Jasper County Chat
Mn

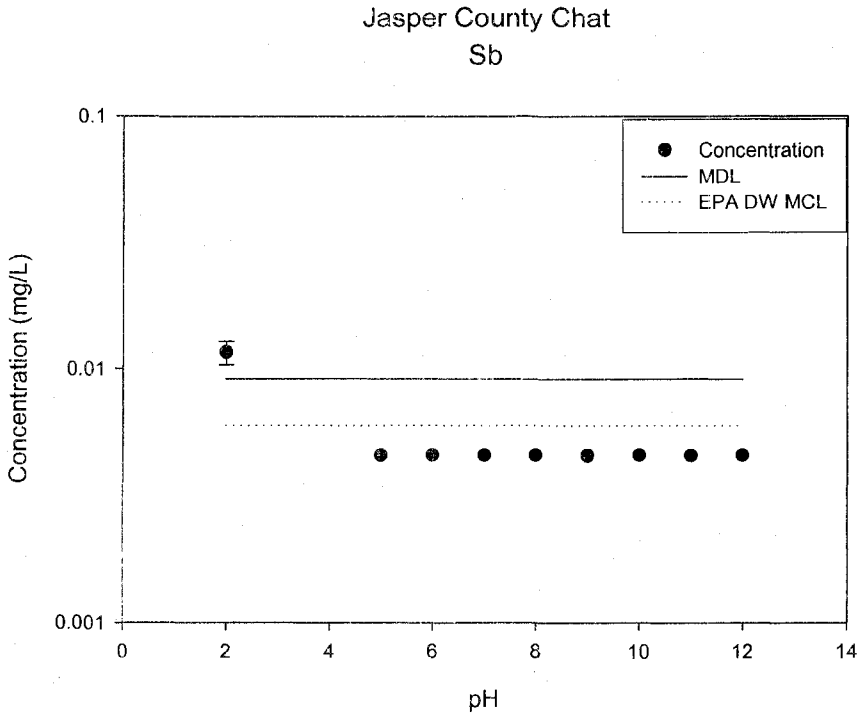


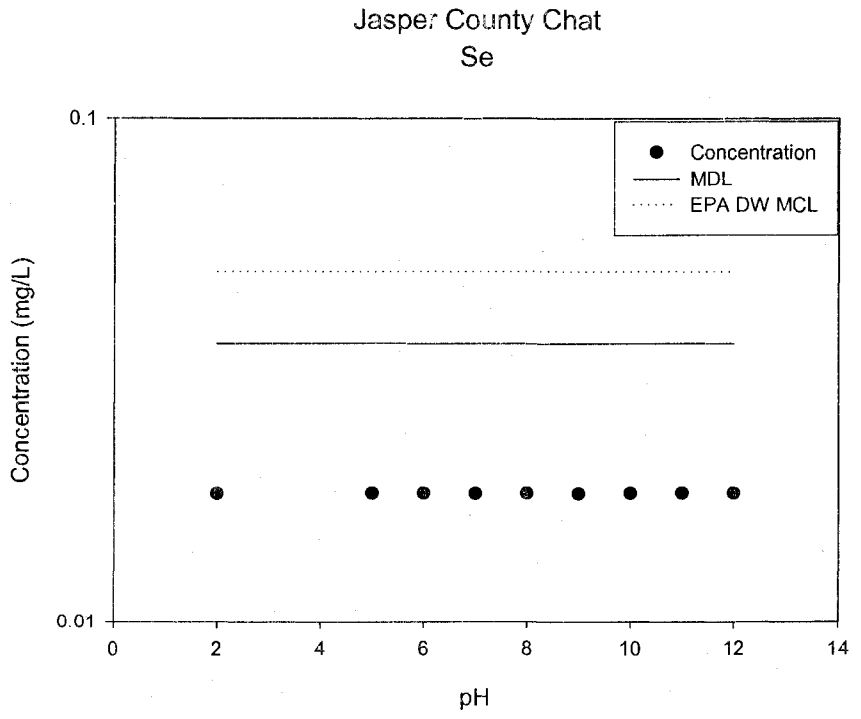
Jasper County Chat
Ni

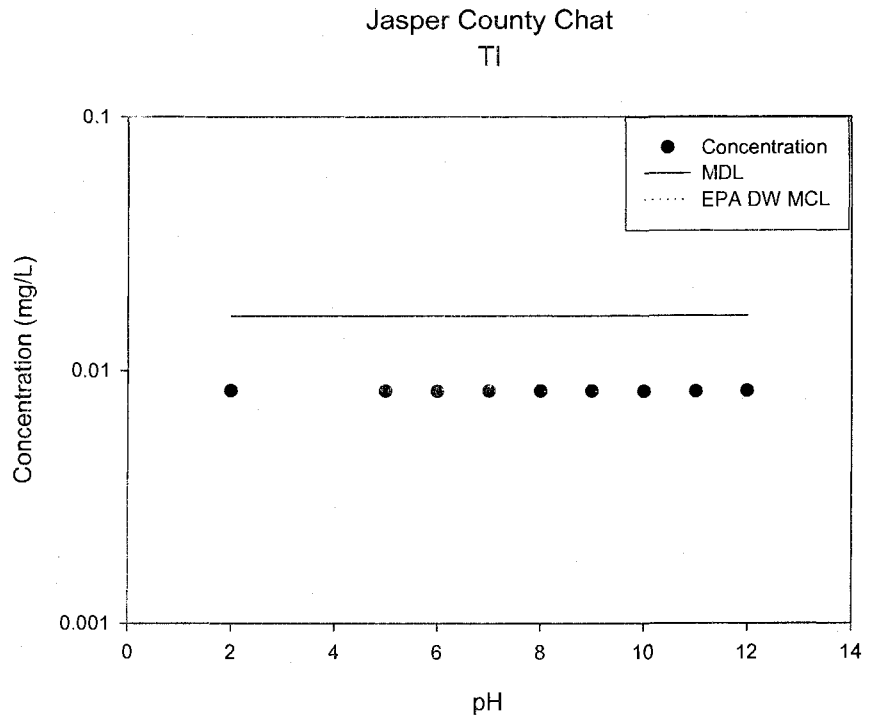


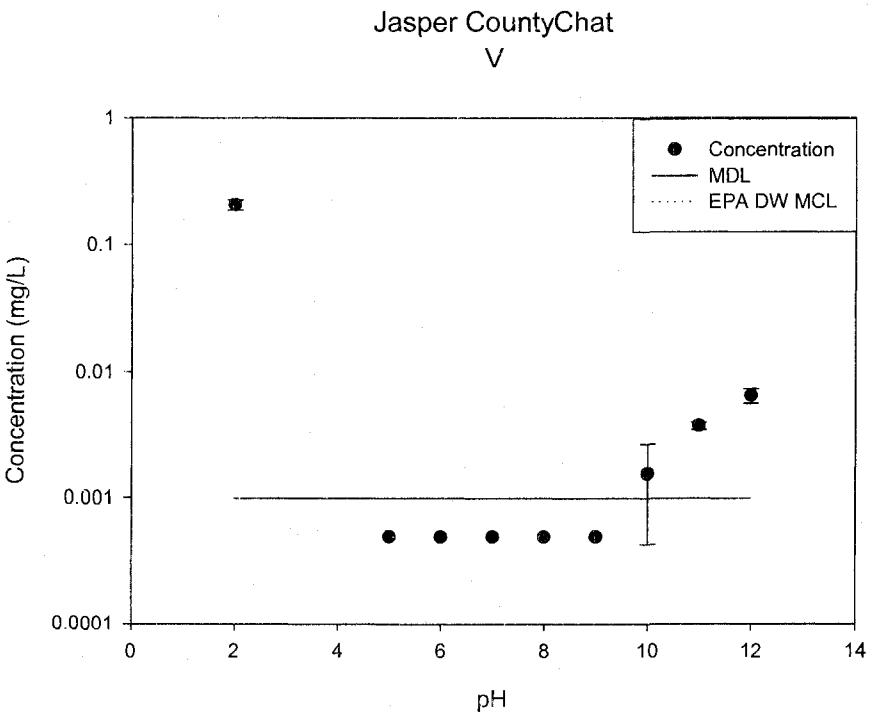

Jasper County Chat
Pb

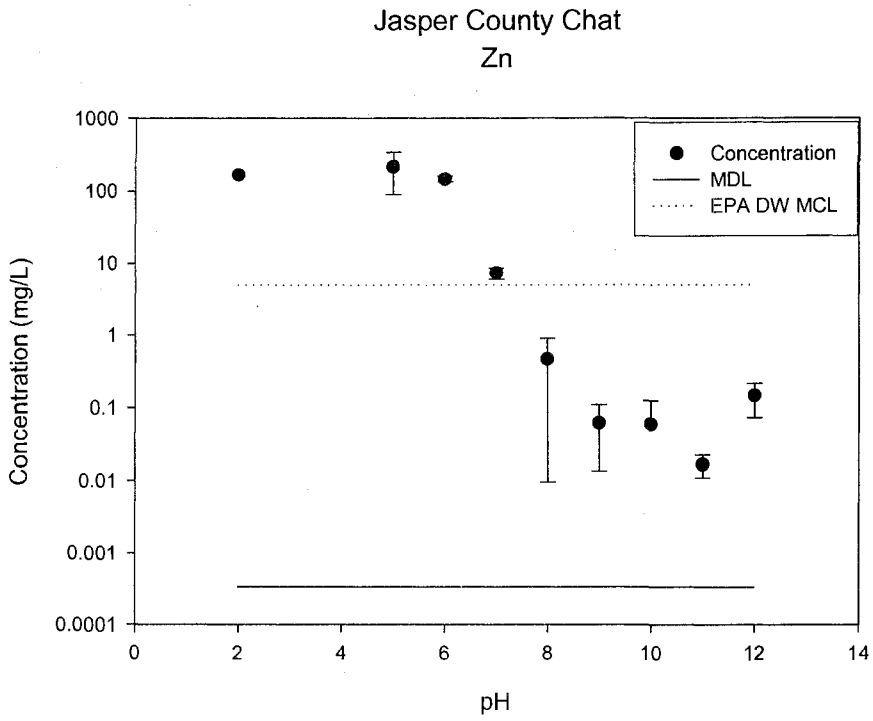



Jasper County Chat
Sb
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
0.1
0.01
0.001
0
2
4
6
8
10
12
14
pH

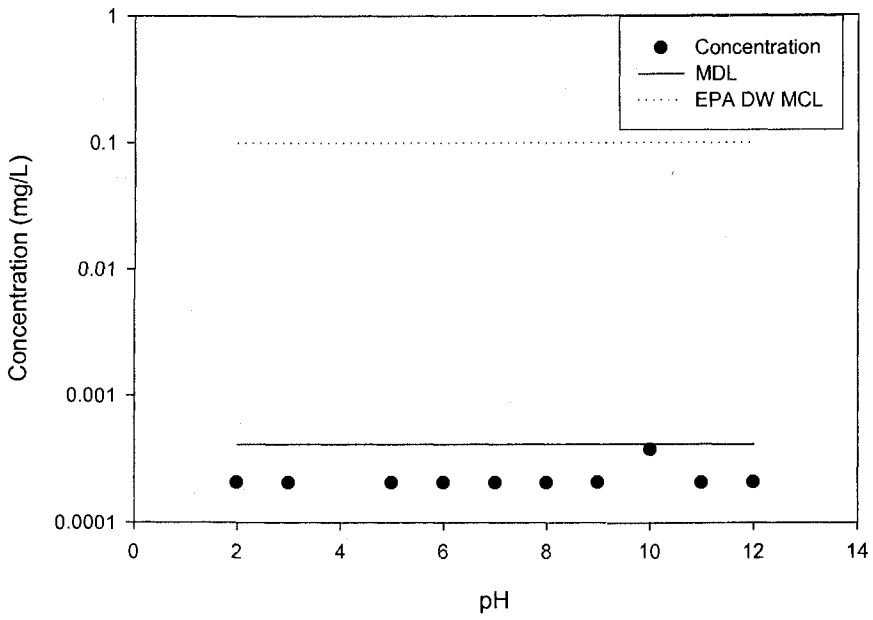

Jasper County Chat
Se
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
0.1
0.01
0
2
4
6
8
10
12
14
pH


Jasper County Chat
Tl
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
0.1
0.01
0.001
0
2
4
6
8
10
12
14
pH

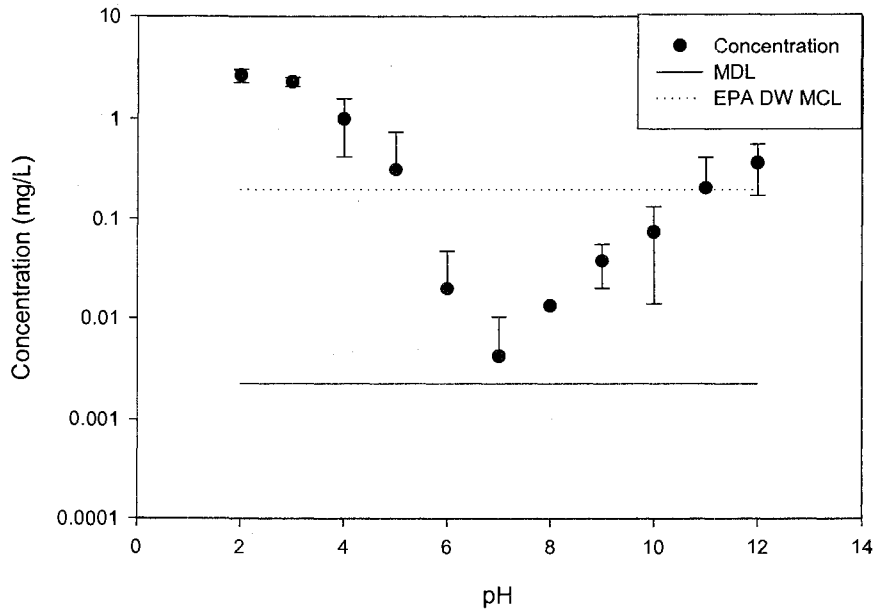

Jasper CountyChat
V
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
1
0.1
0.01
0.001
0.0001
0
2
4
6
8
10
12
14
pH


Jasper County Chat
Zn
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
1000
100
10
1
0.1
0.01
0.001
0.0001
0
2
4
6
8
10
12
14
pH

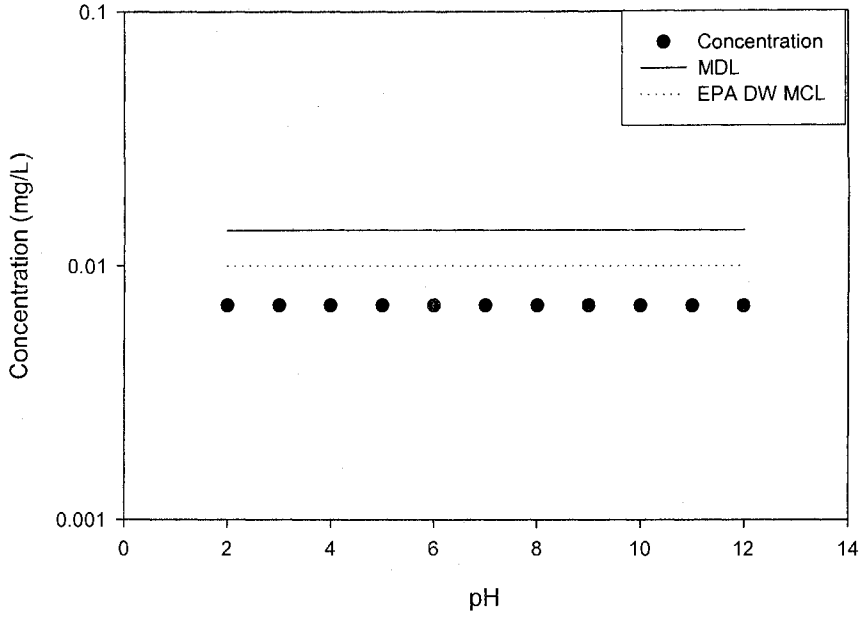
Tar Creek Chat
Ag



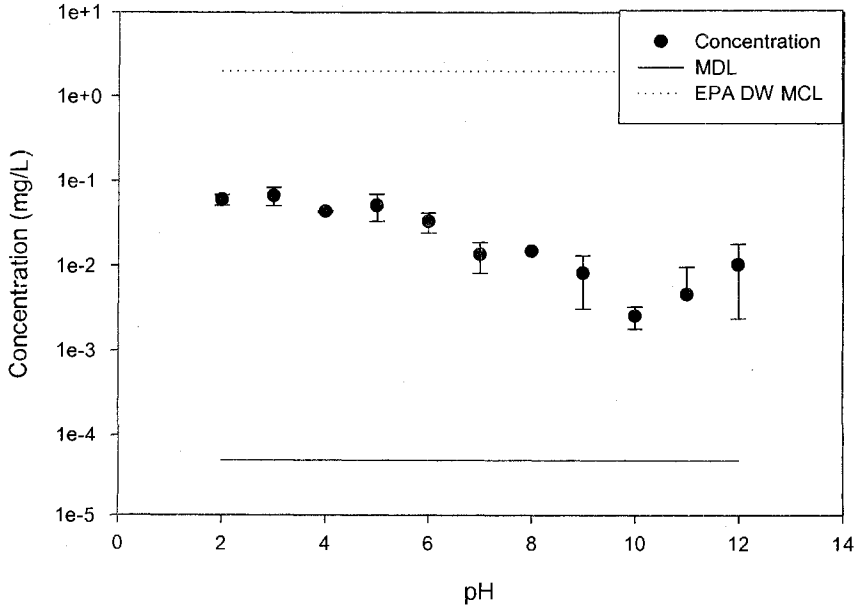

Tar Creek Chat
Al



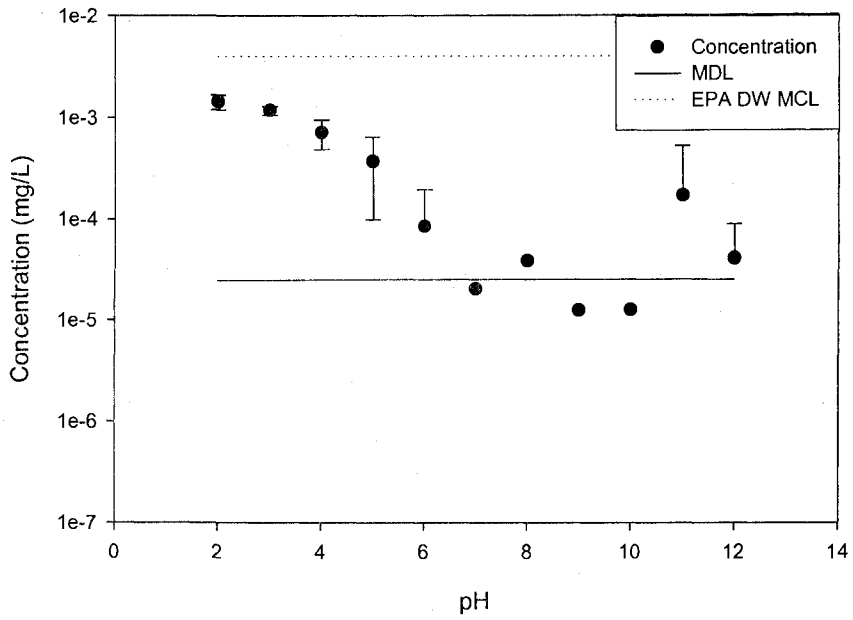
Tar Creek Chat
As



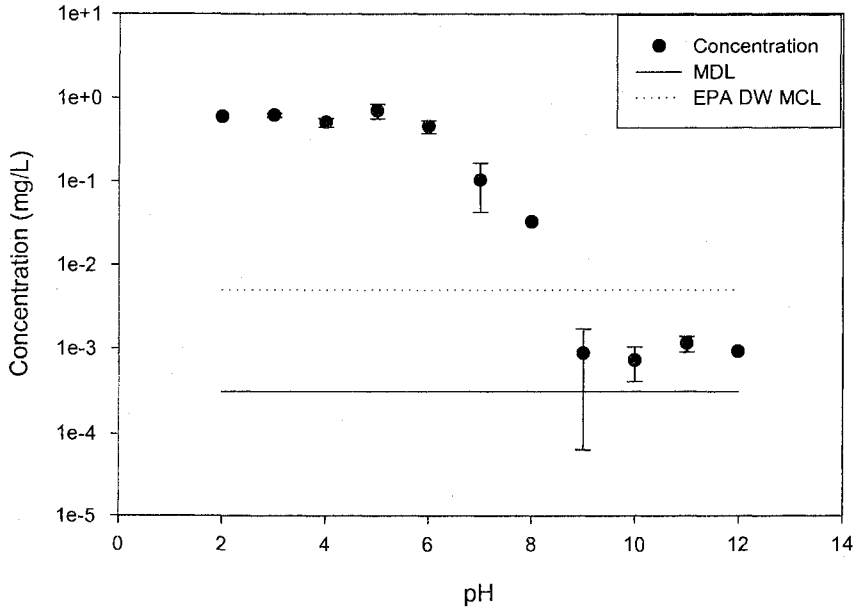

Tar Creek Chat
Ba



Tar Creek Chat
Be




Tar Creek Chat
Cd



Tar Creek Chat
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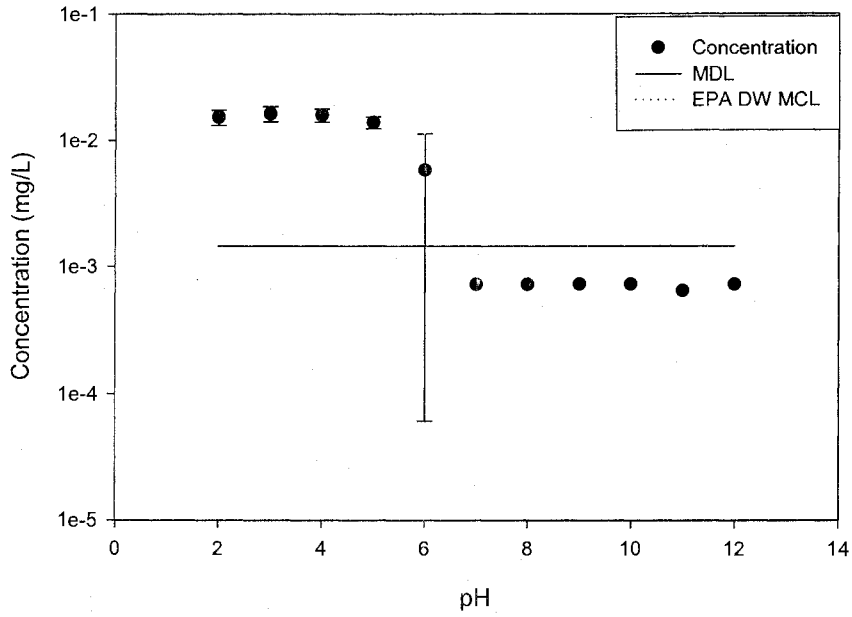
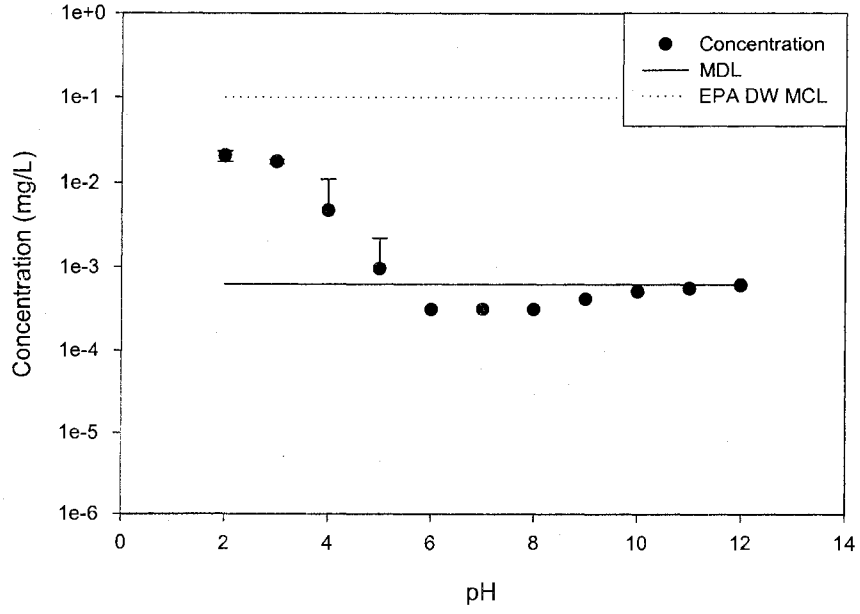
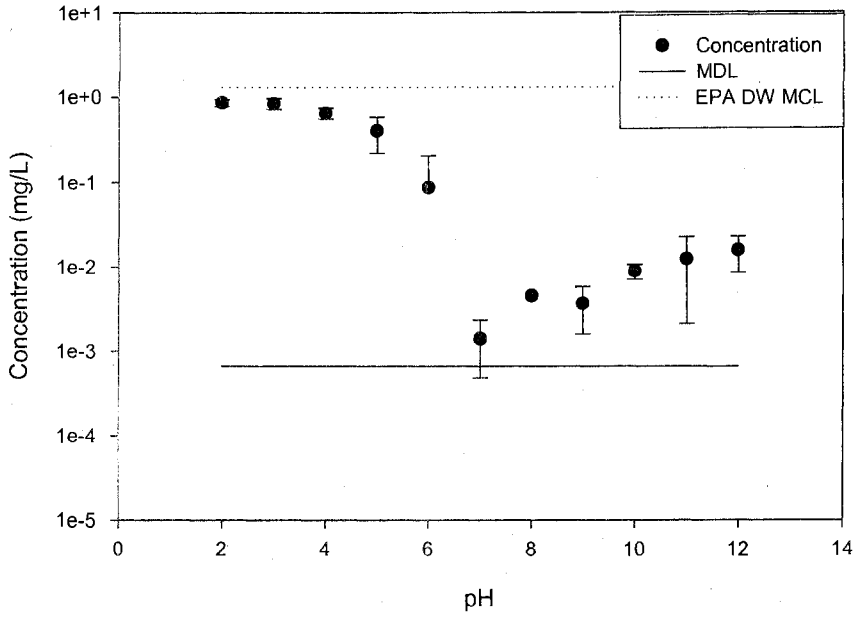


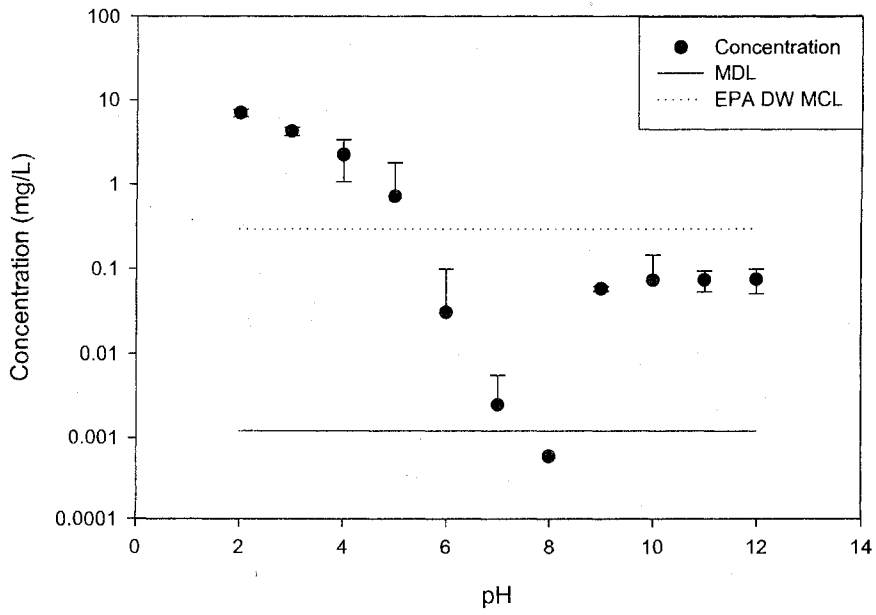

Tar Creek Chat
Cr



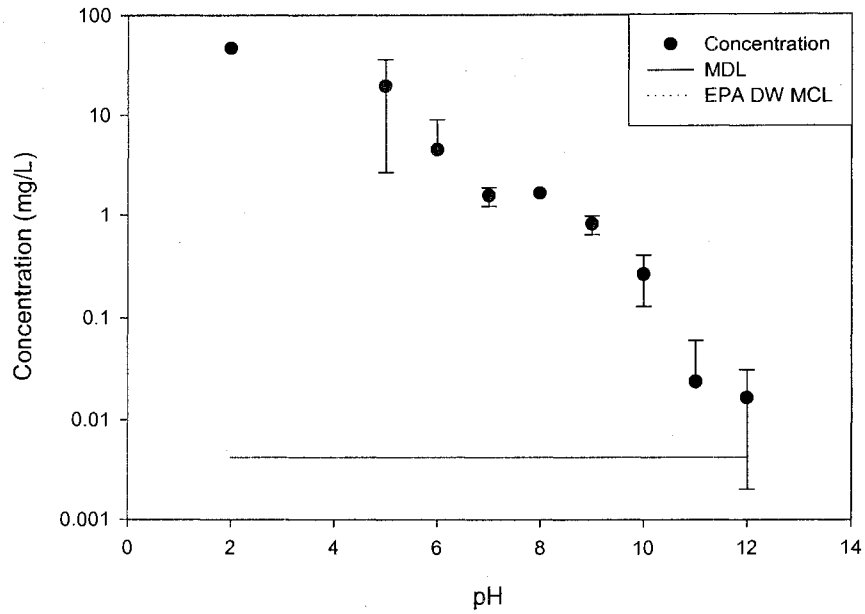
Tar Creek Chat
Cu




Tar Creek Chat
Fe



Tar Creek Chat
Mg




Tar Creek Chat
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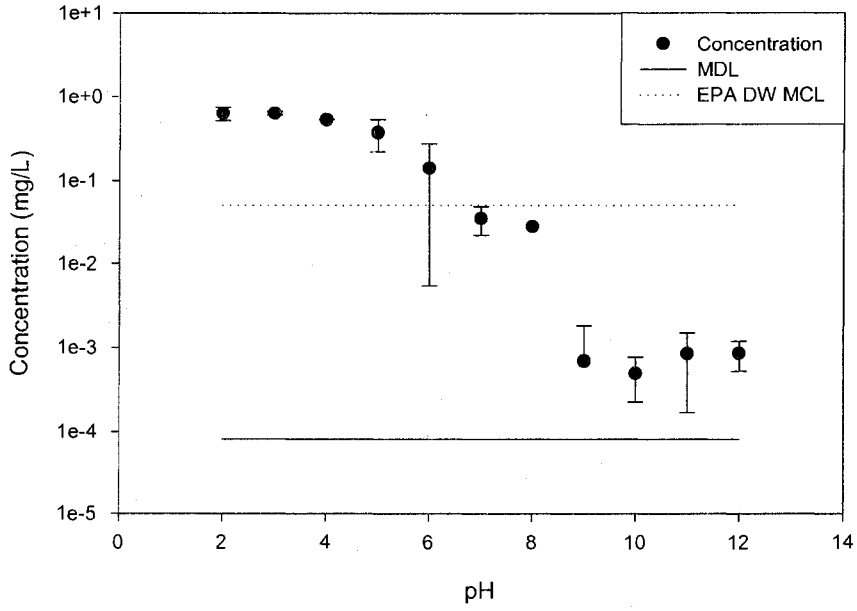
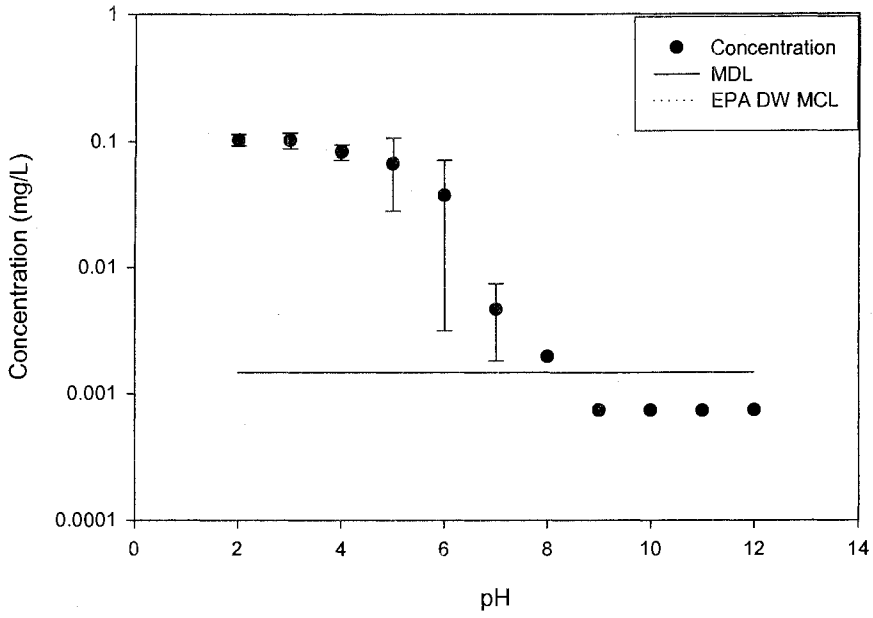
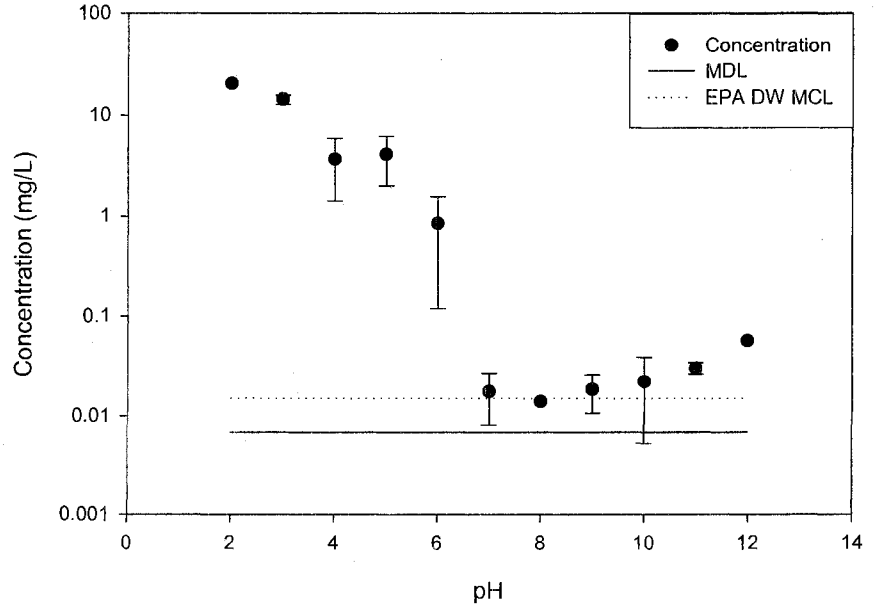


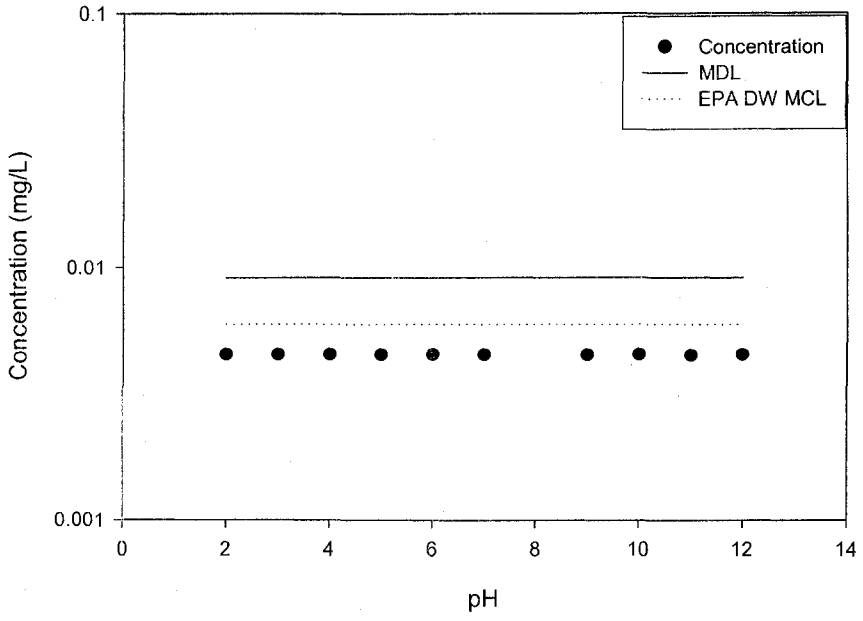
Tar Creek Chat
Ni



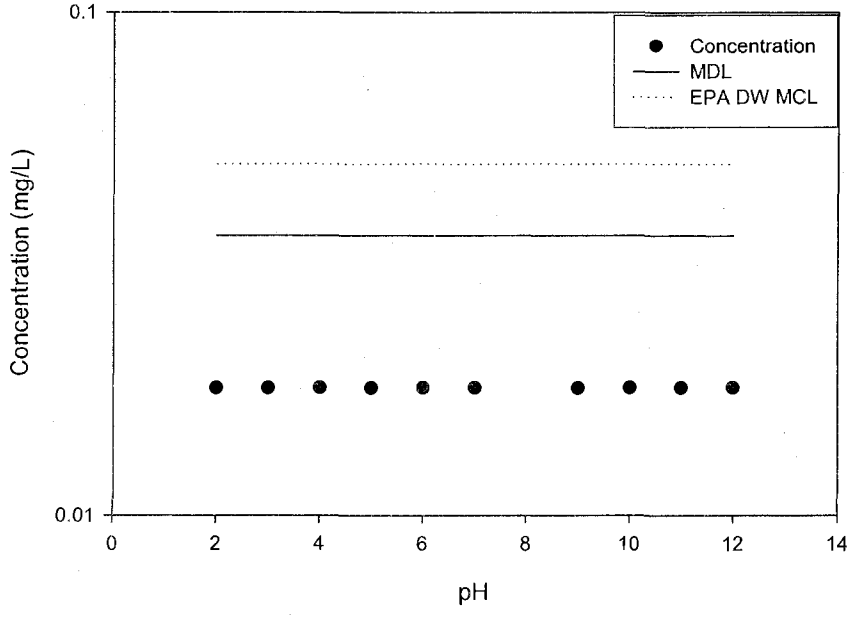

Tar Creek Chat
Pb



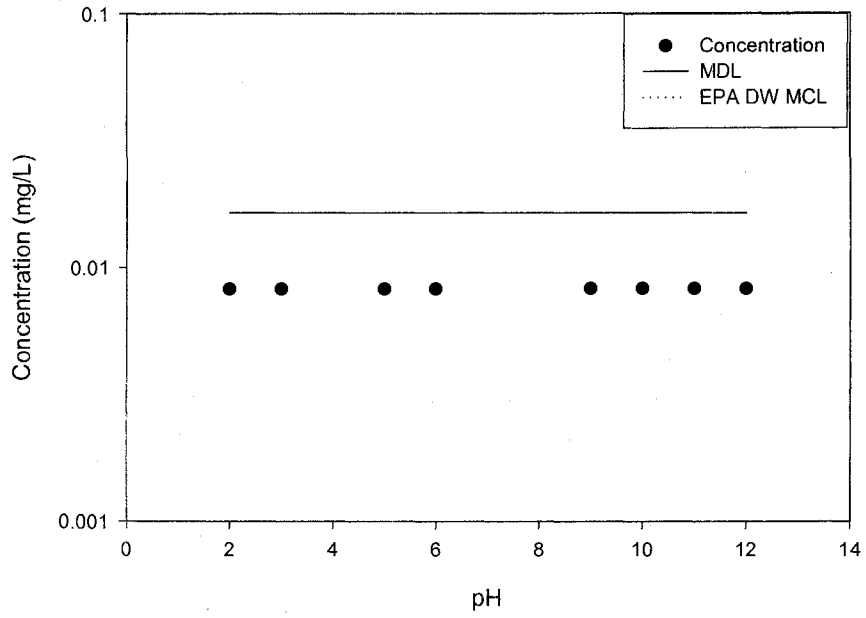
Tar Creek Chat
Sb



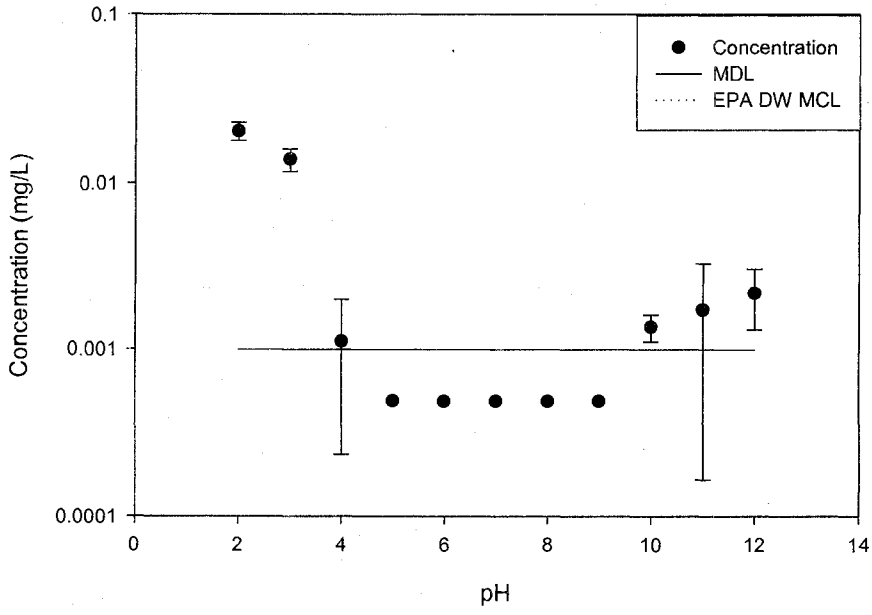

Tar Creek Chat
Se

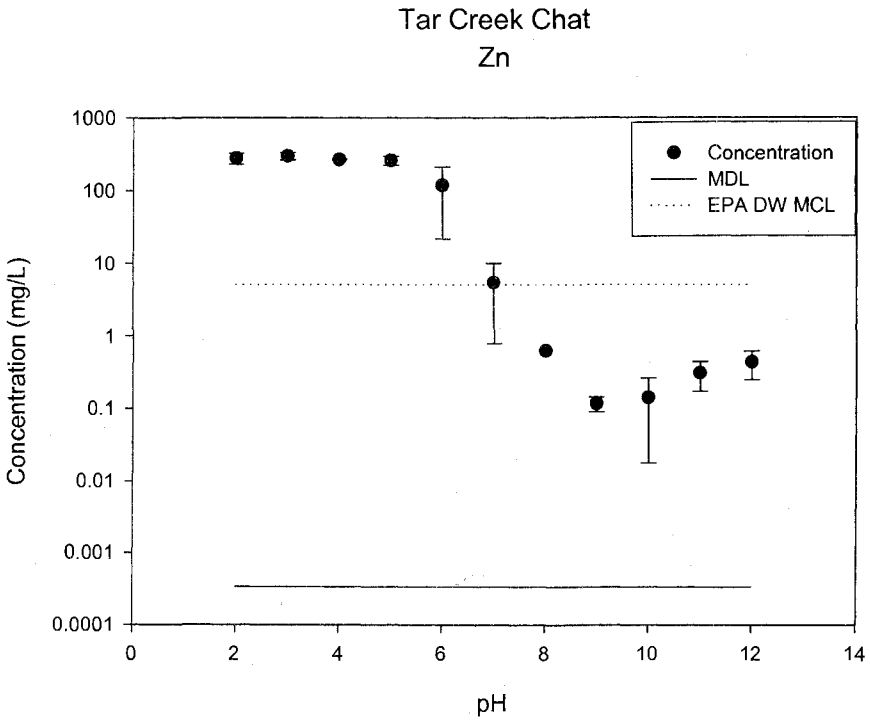


Tar Creek Chat
Tl




Tar Creek Chat
V

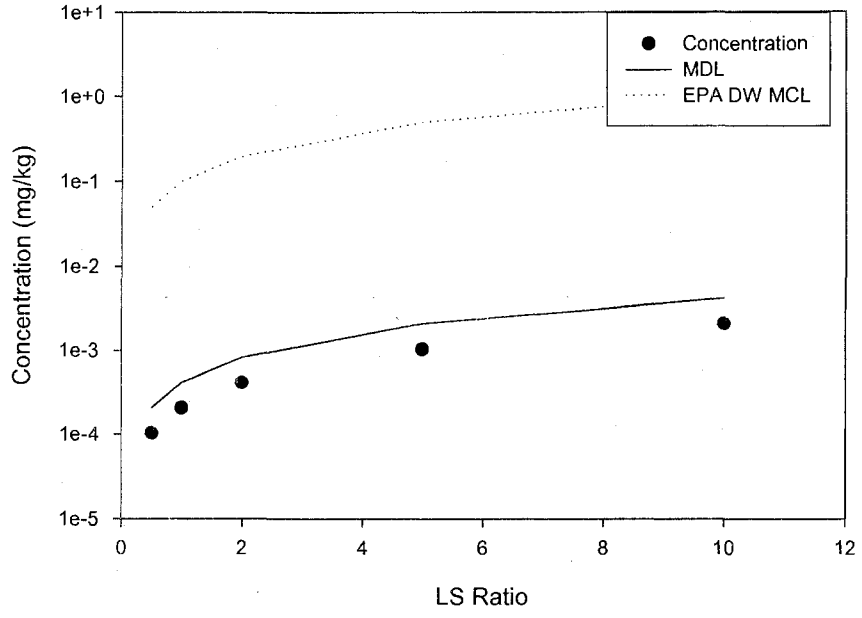



Tar Creek Chat
Zn
Concentration
MDL
EPA DW MCL
Concentration (mg/L)
1000
100
10
1
0.1
0.01
0.001
0.0001
0
2
4
6
8
10
12
14
pH

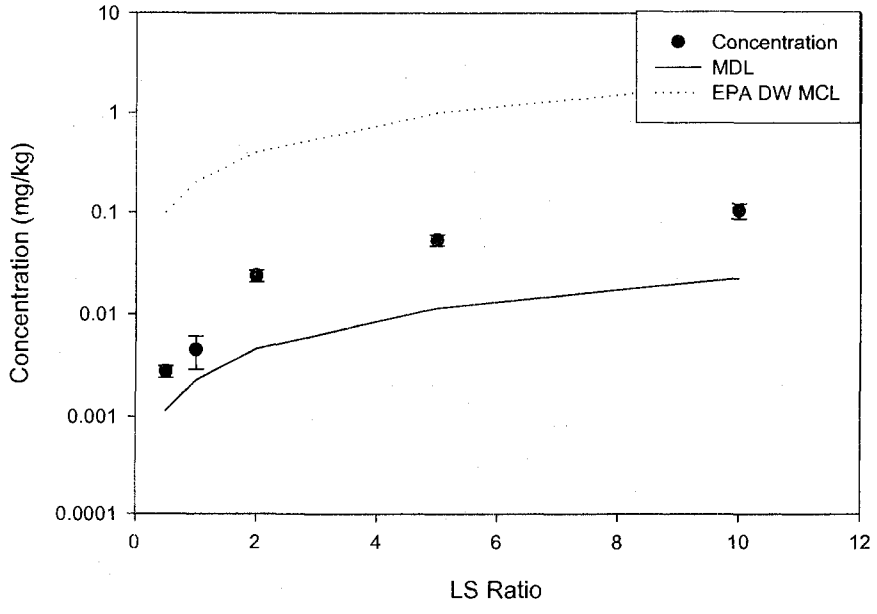
## LS Dependent Leaching Results

**Note: 1) All tests were preformed at the materials natural pH**

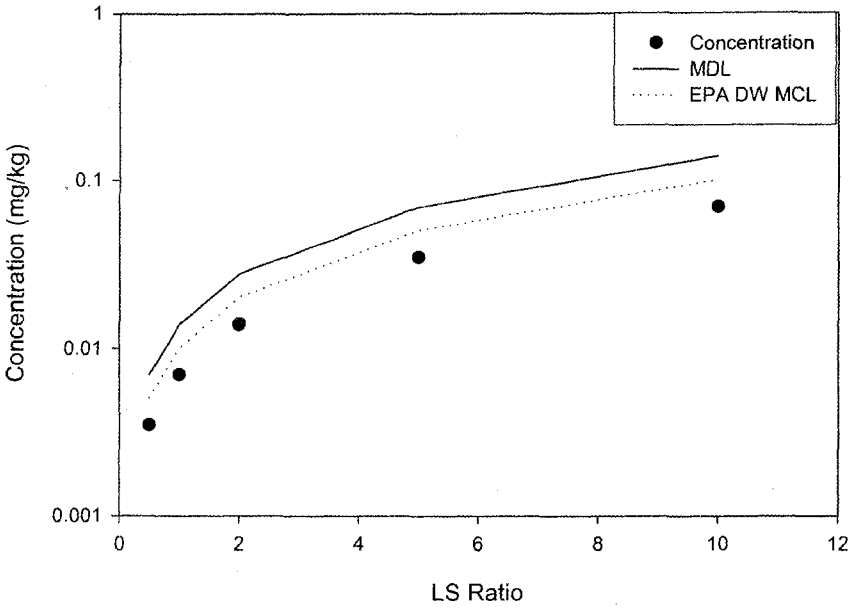
Jasper County Fines
Ag



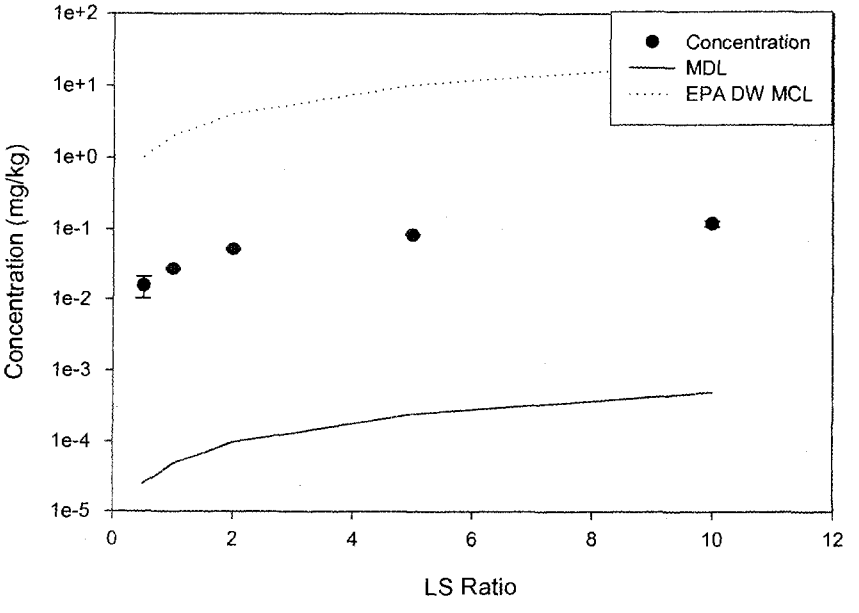

Jasper County Fines
Al



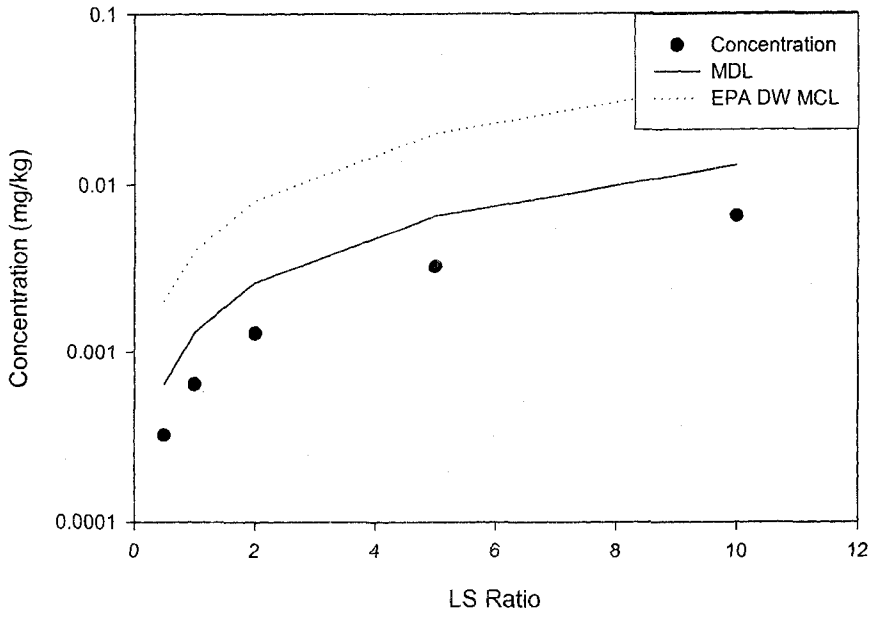
Jasper County Fines
As



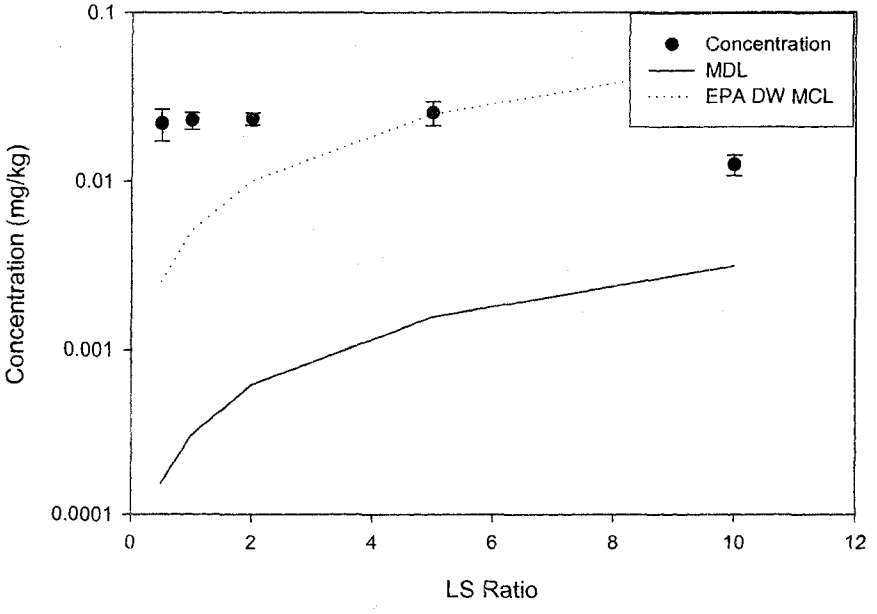

Jasper County Fines
Ba



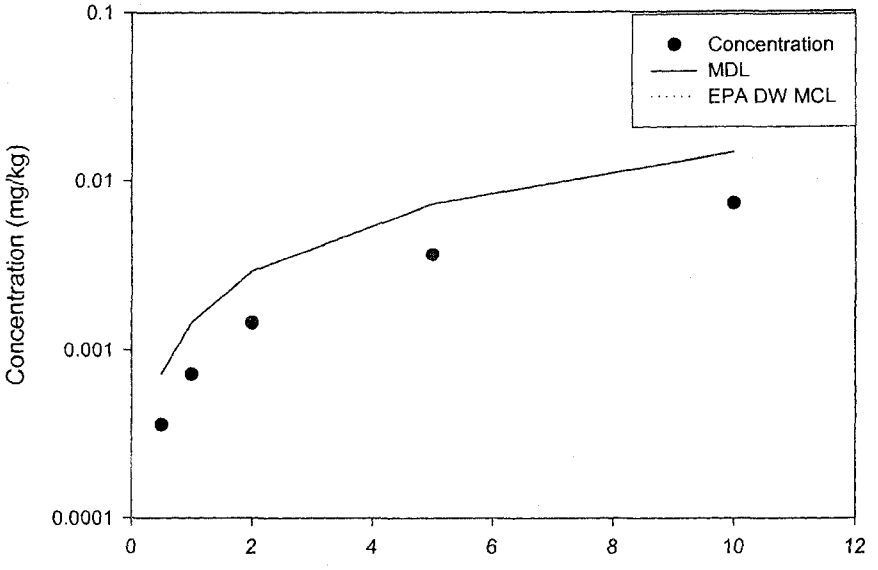
Jasper County Fines
Be



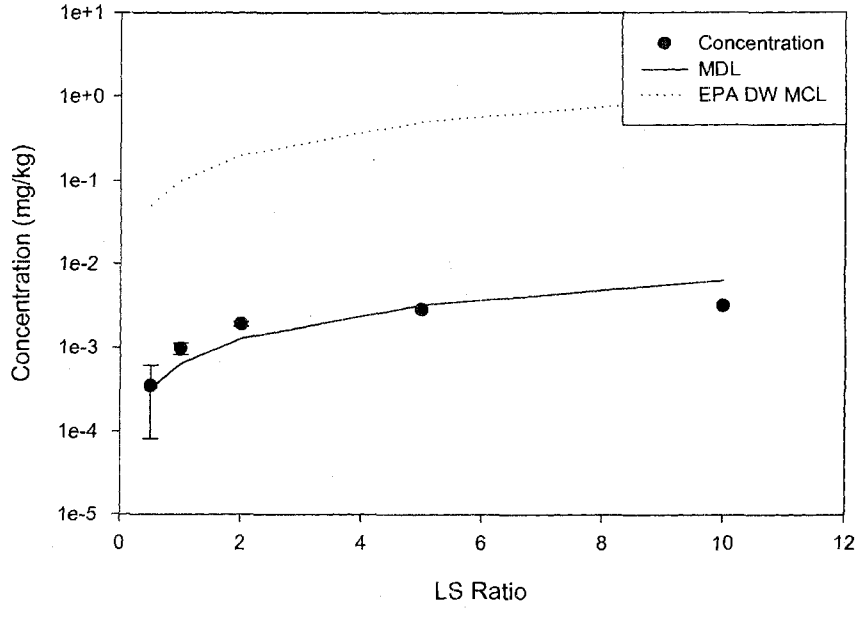

Jasper County Fines
Cd

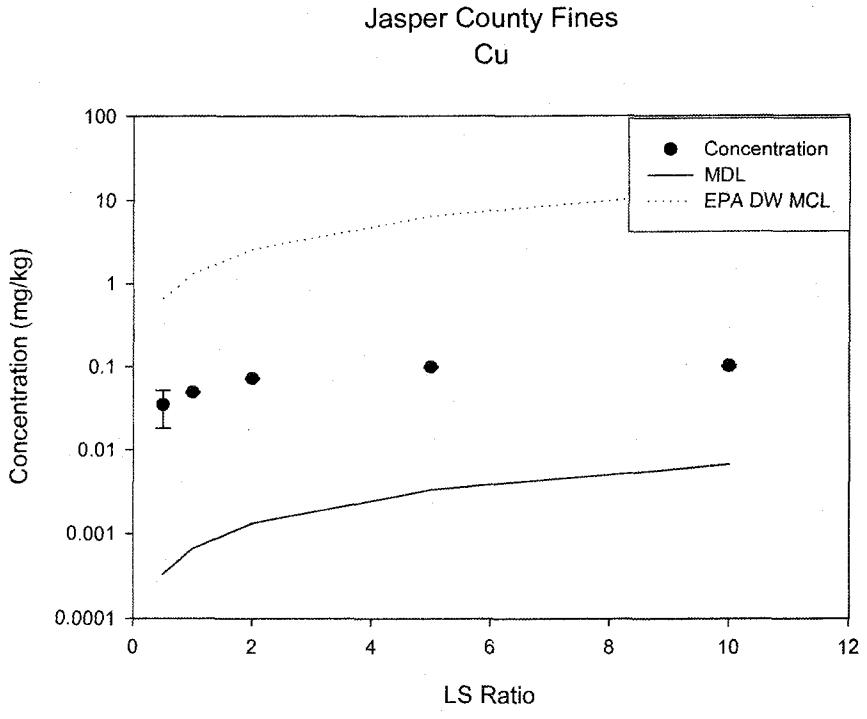


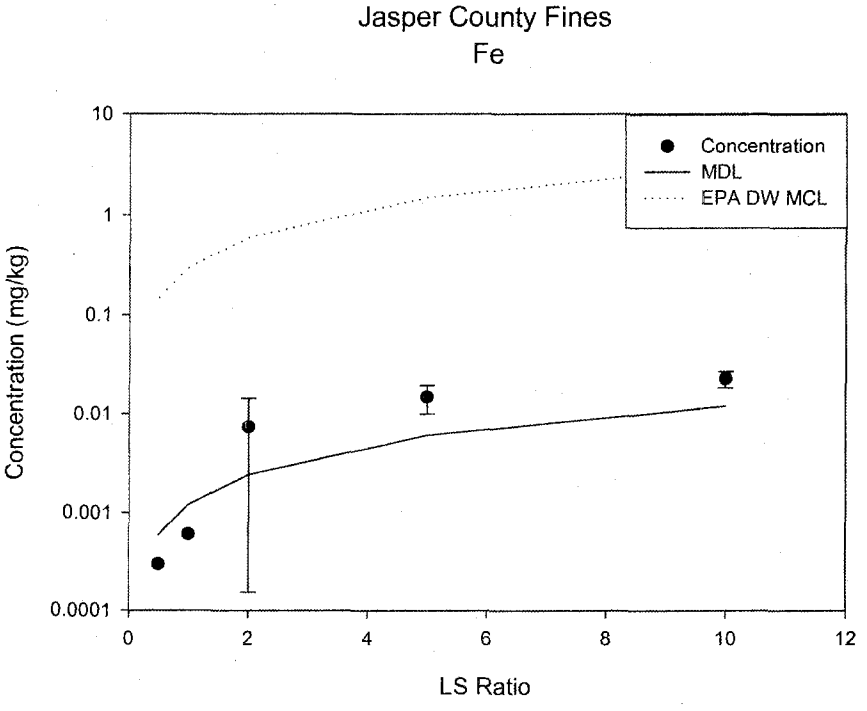
Jasper County Fines
Co



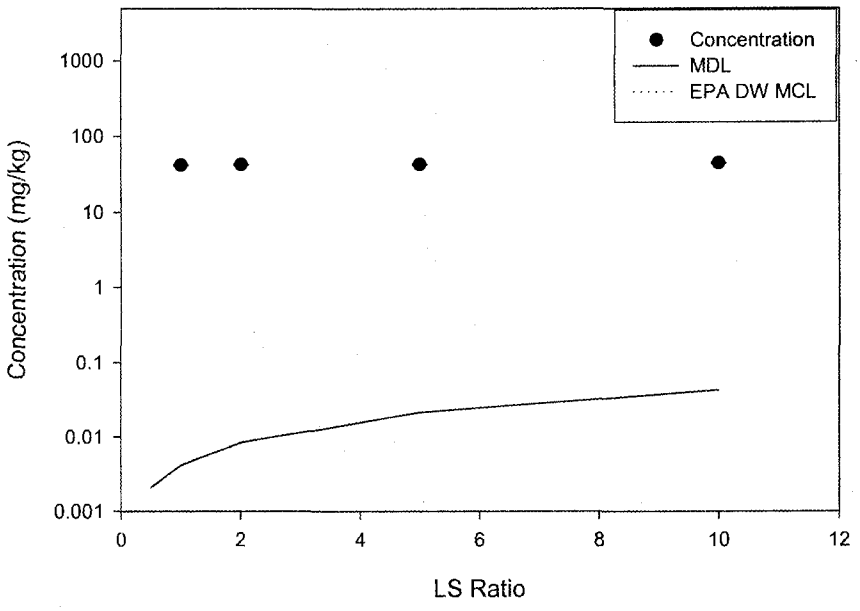

Tar Creek Fines
Cr



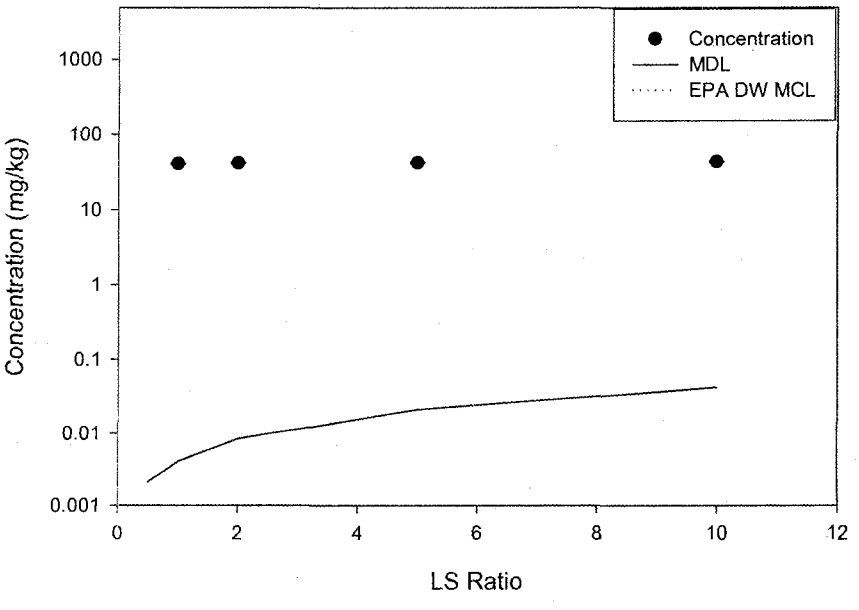

Jasper County Fines
Cu
Concentration
MDL
EPA DW MCL
Concentration (mg/kg)
100
10
1
0.1
0.01
0.001
0.0001
0
2
4
6
8
10
12
LS Ratio

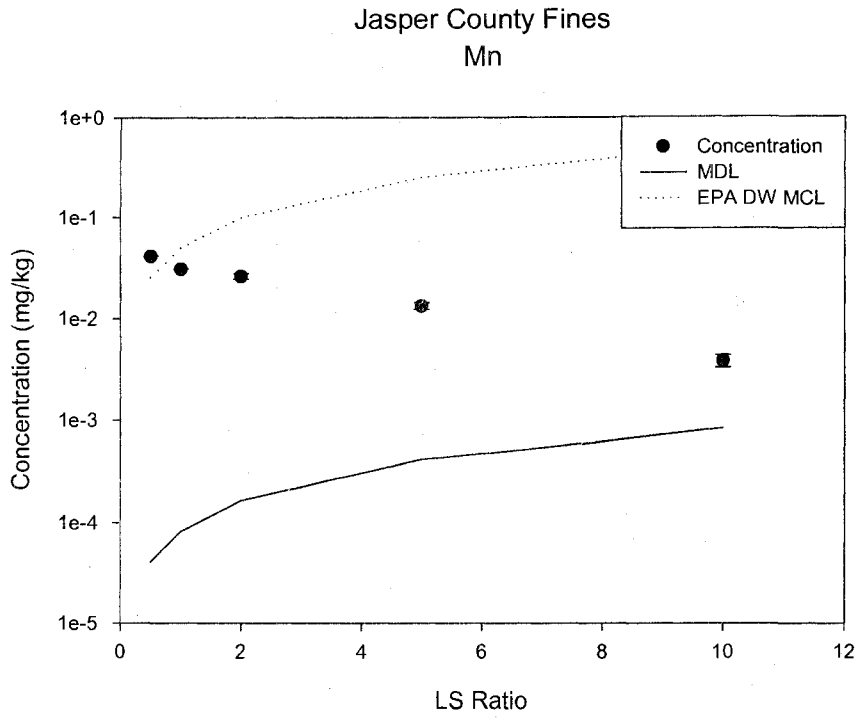

Jasper County Fines
Fe
Concentration
MDL
EPA DW MCL
Concentration (mg/kg)
10
1
0.1
0.01
0.001
0.0001
0
2
4
6
8
10
12
LS Ratio

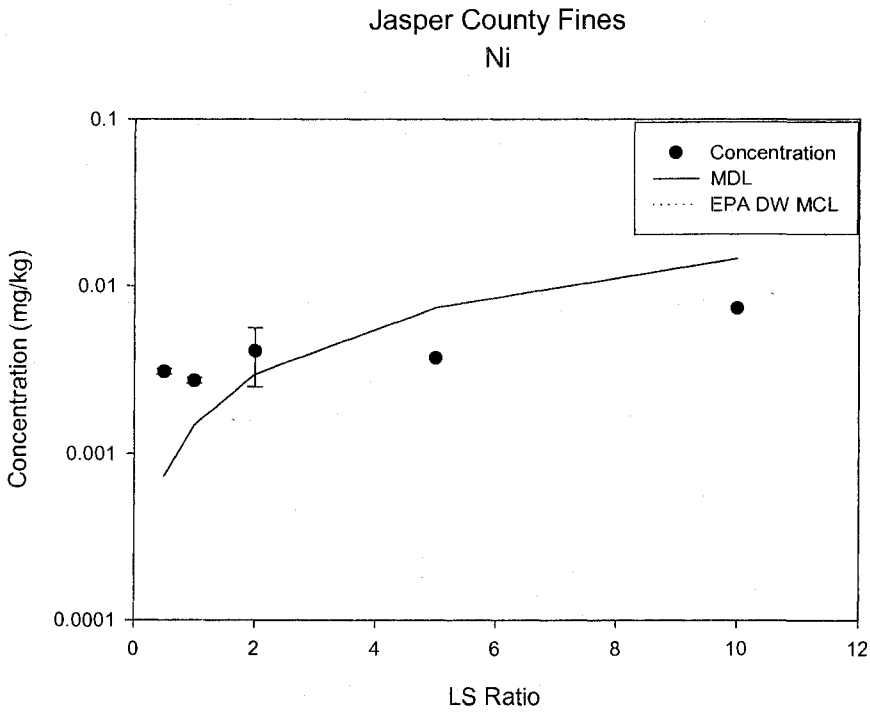
Jasper County Fines
Mg



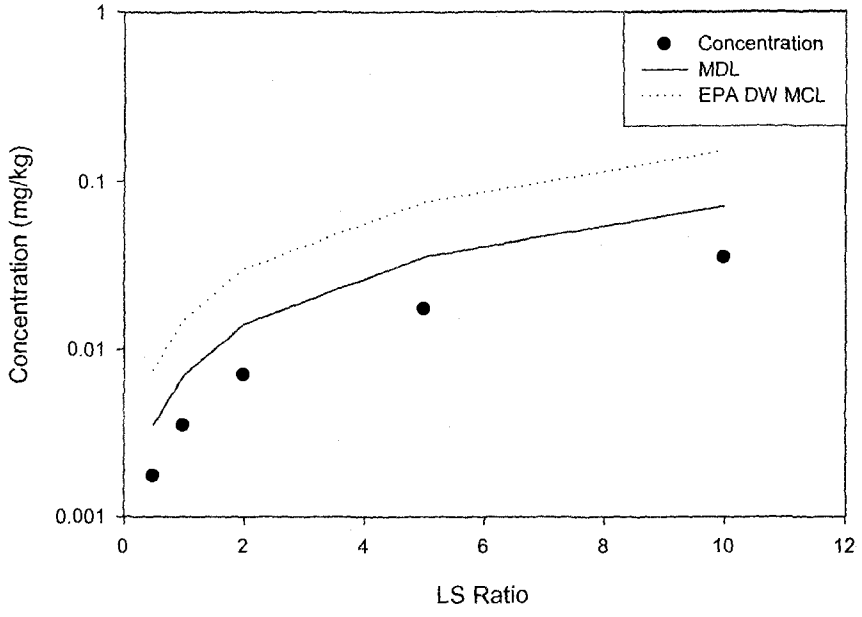

Jasper County Fines
Mg



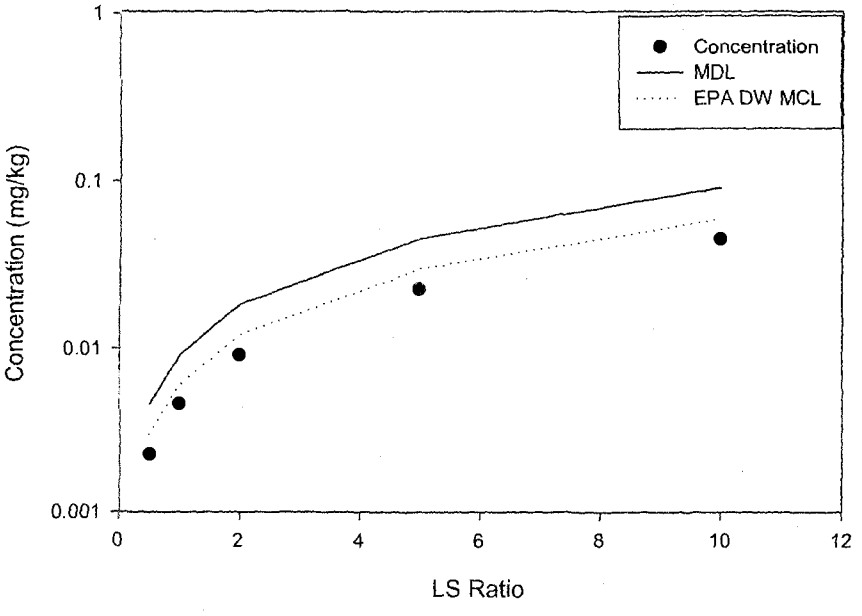

Jasper County Fines
Mn
Concentration
MDL
EPA DW MCL
Concentration (mg/kg)
1e+0
1e-1
1e-2
1e-3
1e-4
1e-5
0
2
4
6
8
10
12
LS Ratio


Jasper County Fines
Ni
Concentration
MDL
EPA DW MCL
Concentration (mg/kg)
0.1
0.01
0.001
0.0001
0
2
4
6
8
10
12
LS Ratio

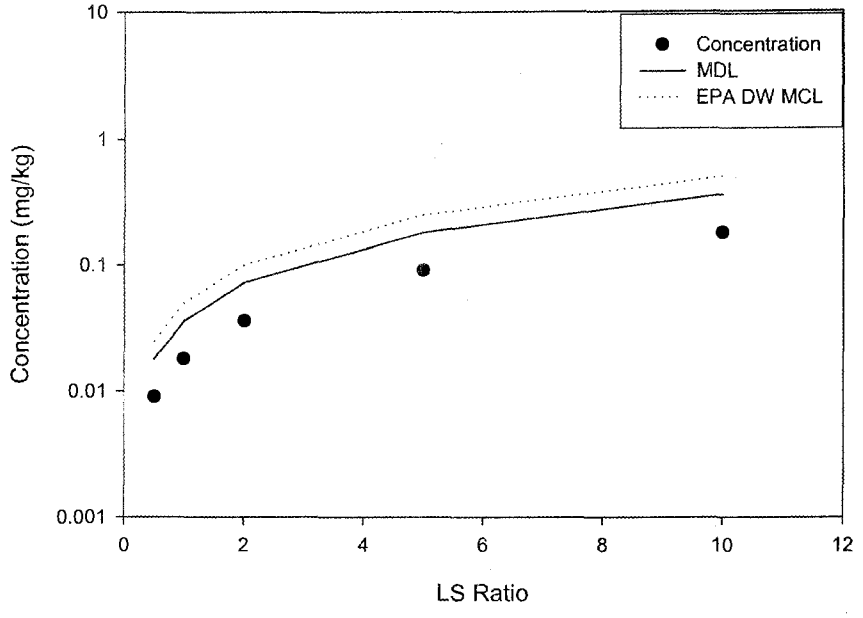
Jasper County Fines
Pb



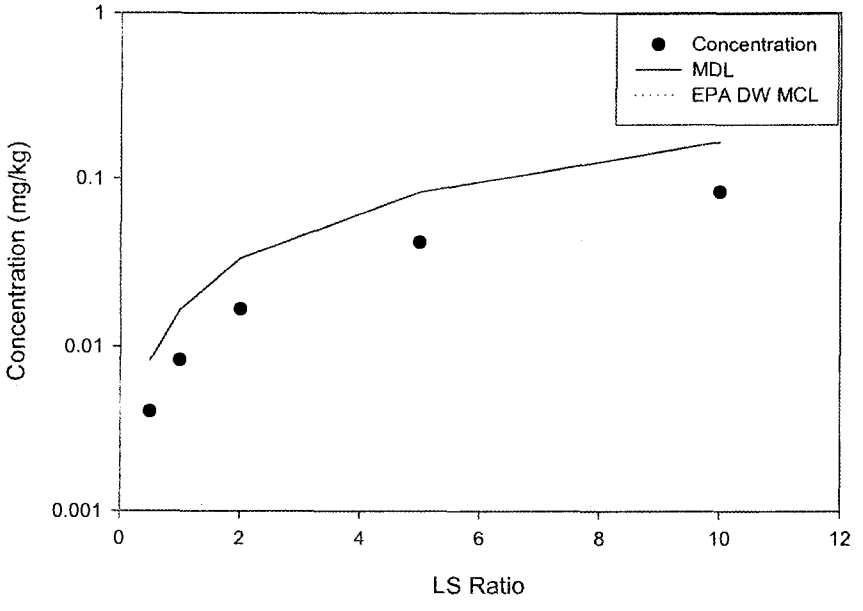

Jasper County Fines
Sb



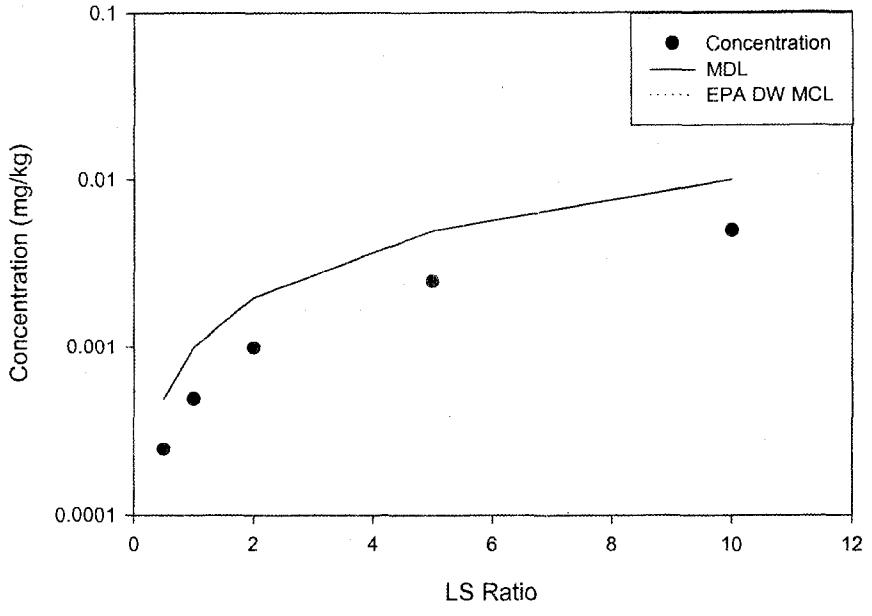
Jasper County Fines
Se



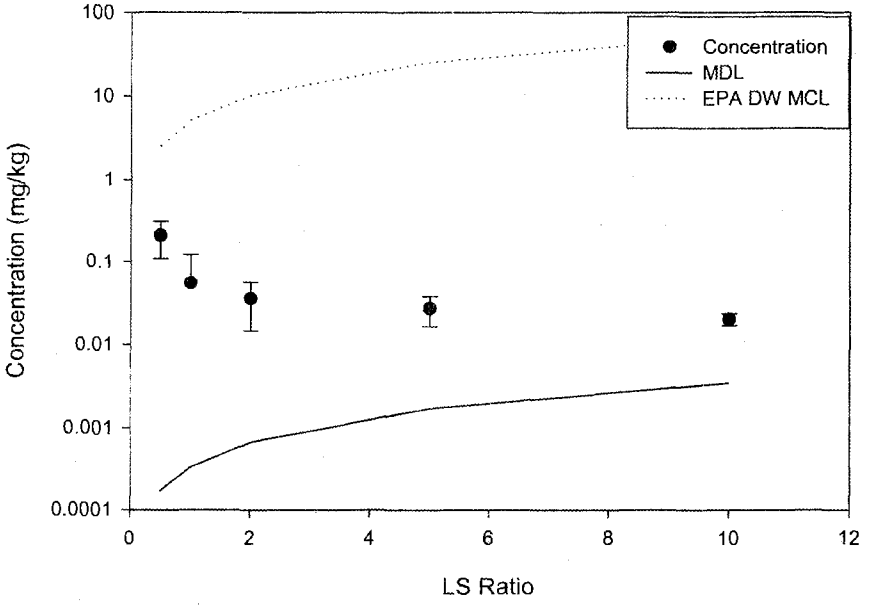

Jasper County Fines
Tl



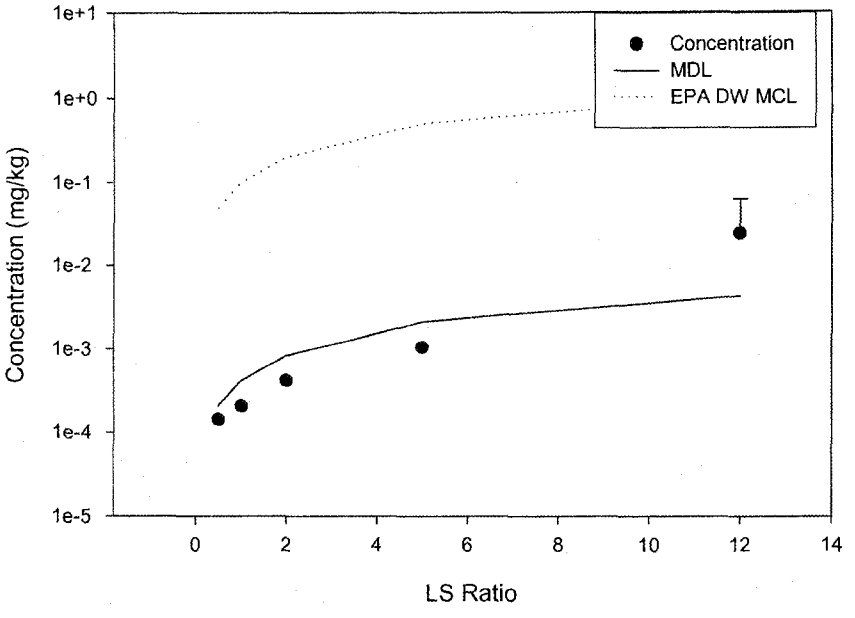
Jasper County Fines
V



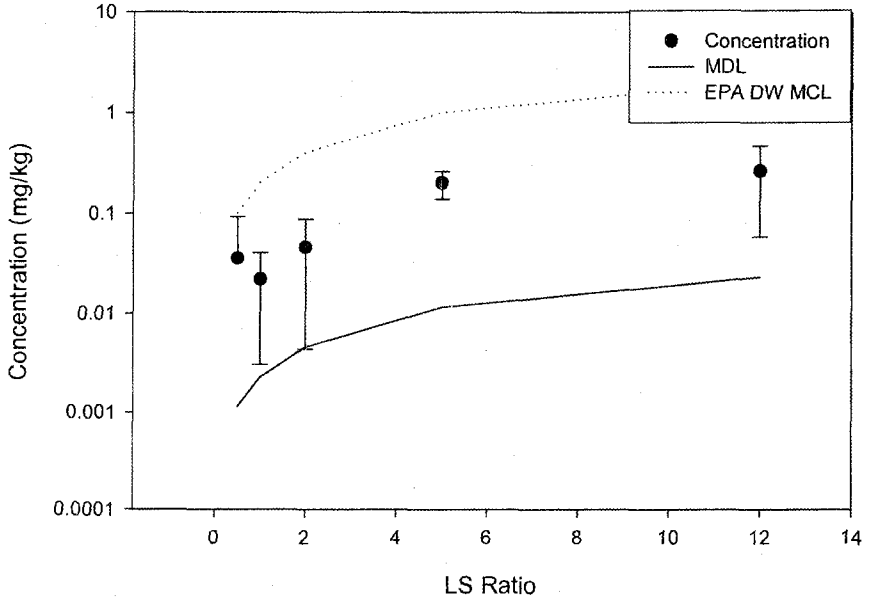

Jasper County Fines
Zn



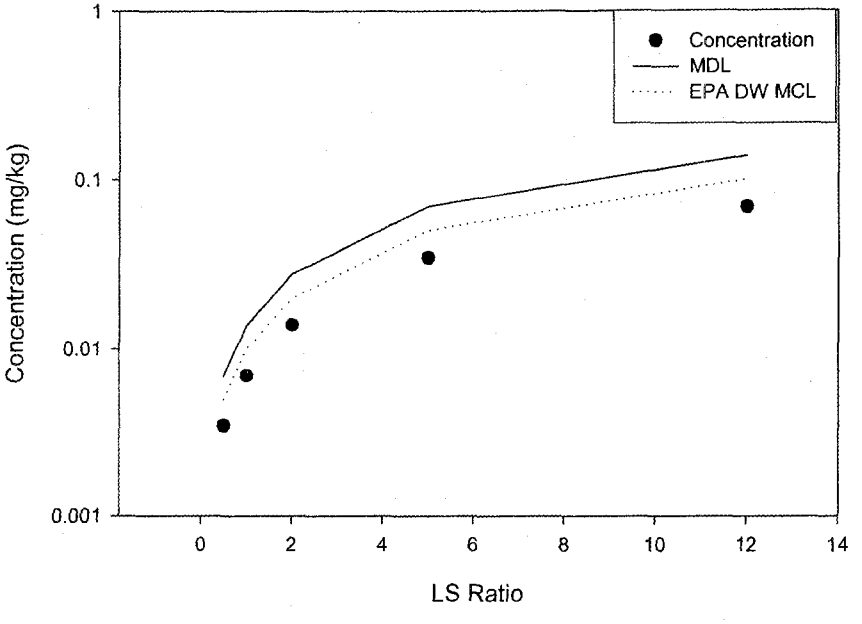
Jasper County Chat
Ag




Jasper County Chat
Al



Jasper County Chat
As




Jasper County Chat
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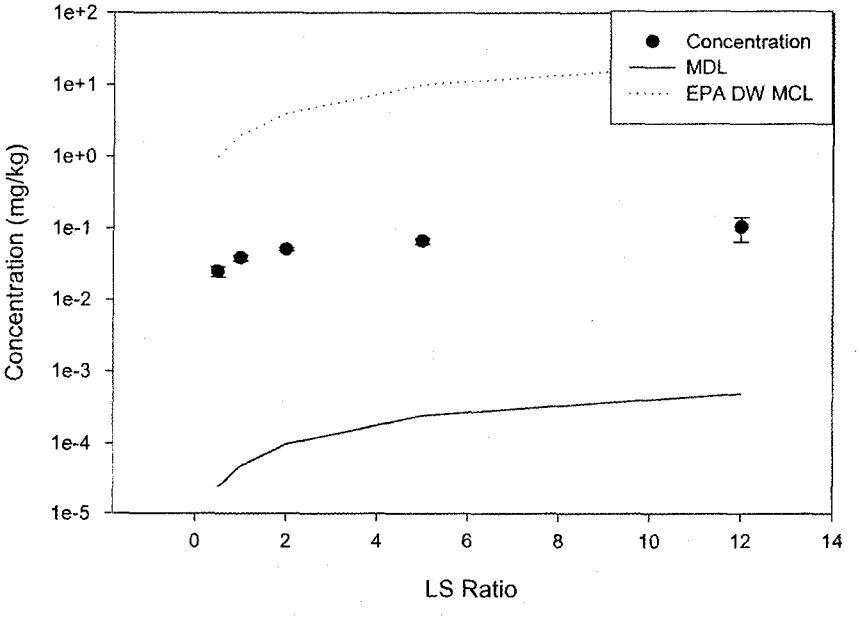
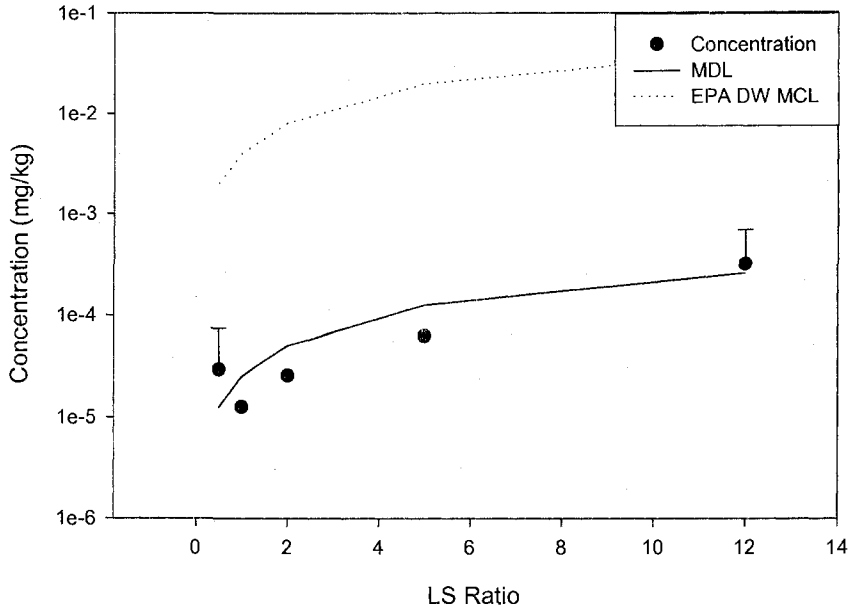


Jasper County Chat
Be




Jasper County Chat
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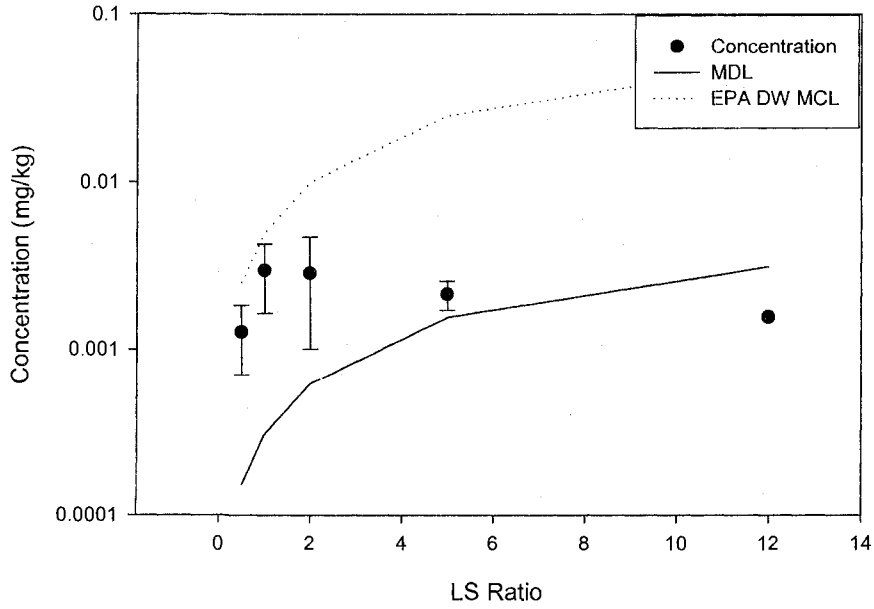

Jasper County Chat
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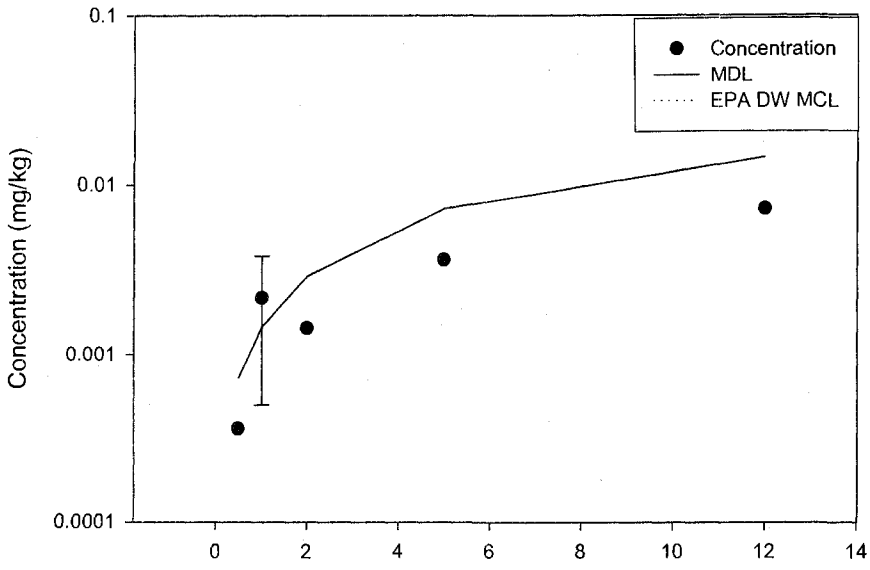
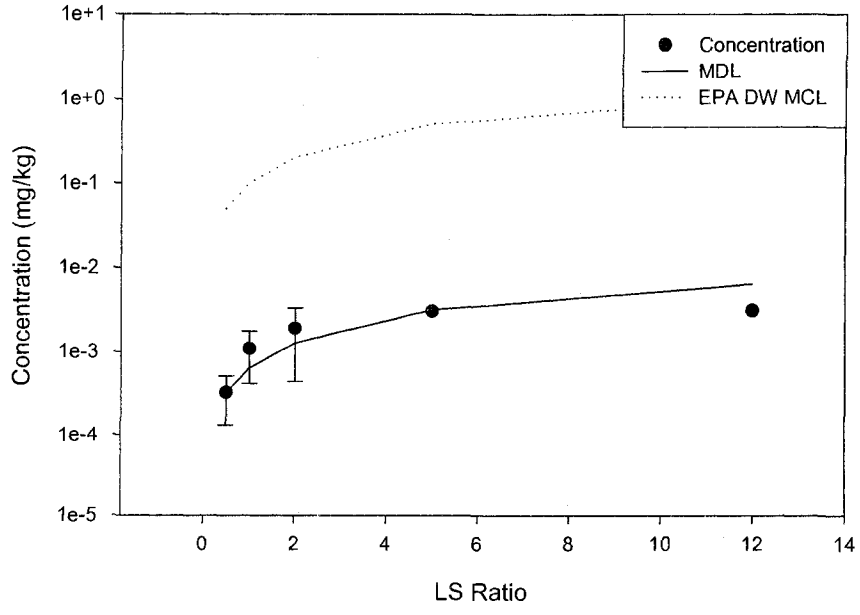
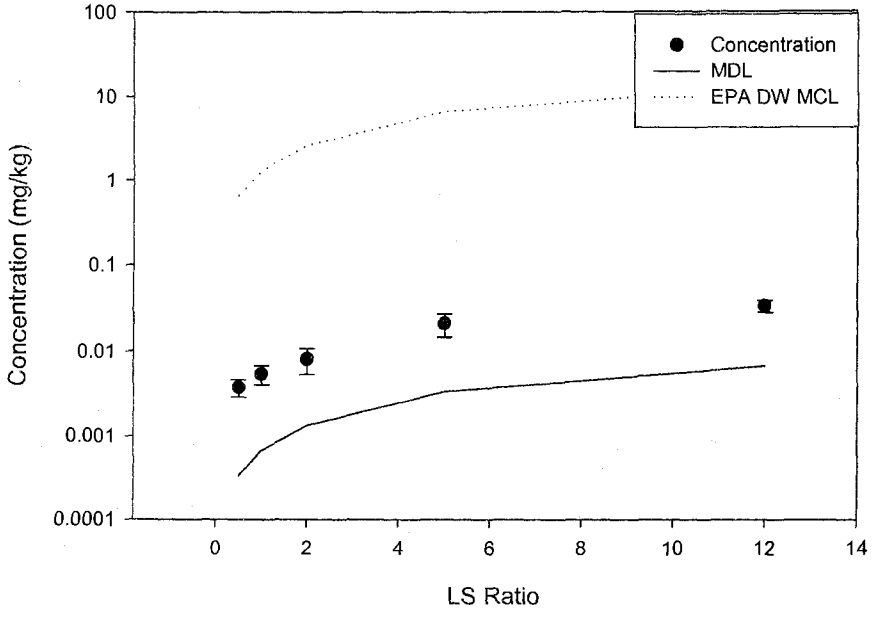



Tar Creek Chat
Cr



Jasper County Chat
Cu




Jasper County Chat
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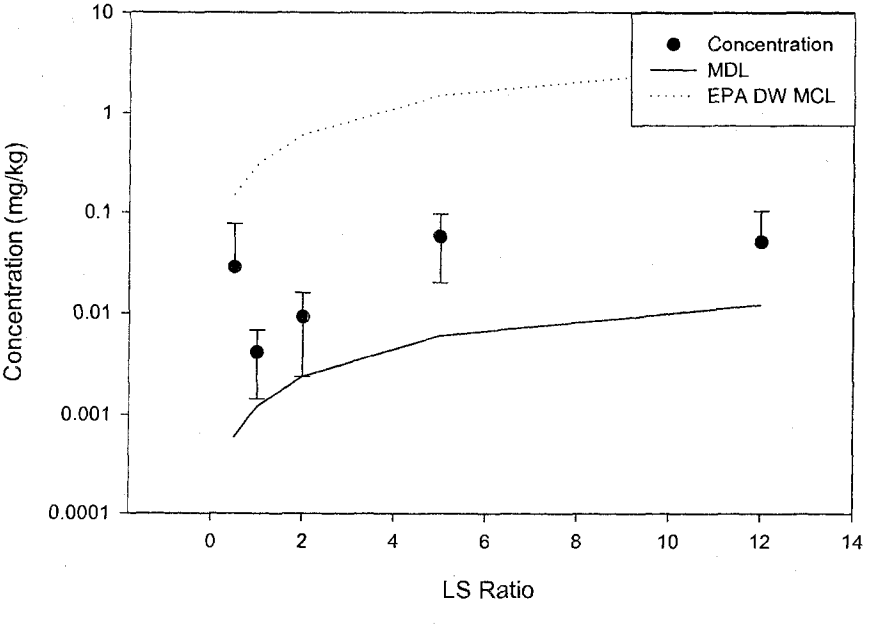

Jasper County Chat
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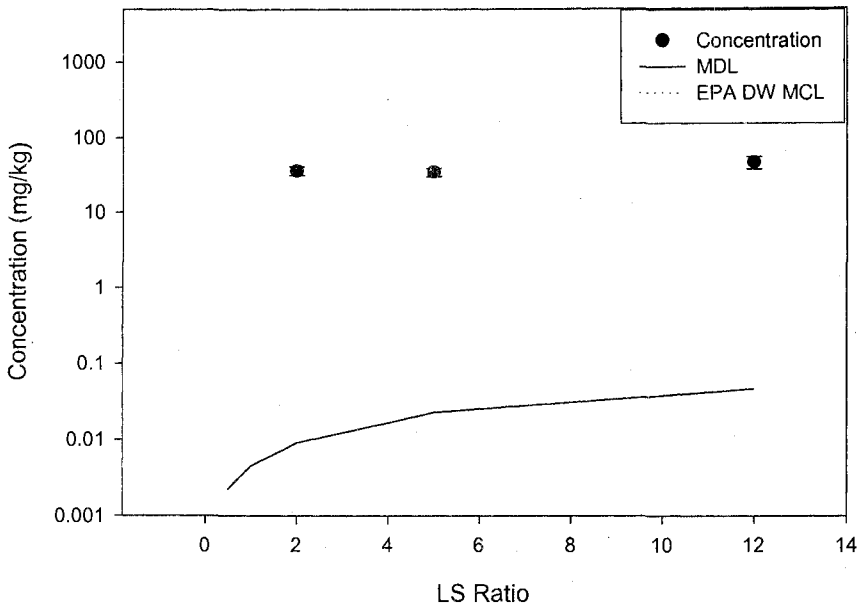


Jasper County Chat
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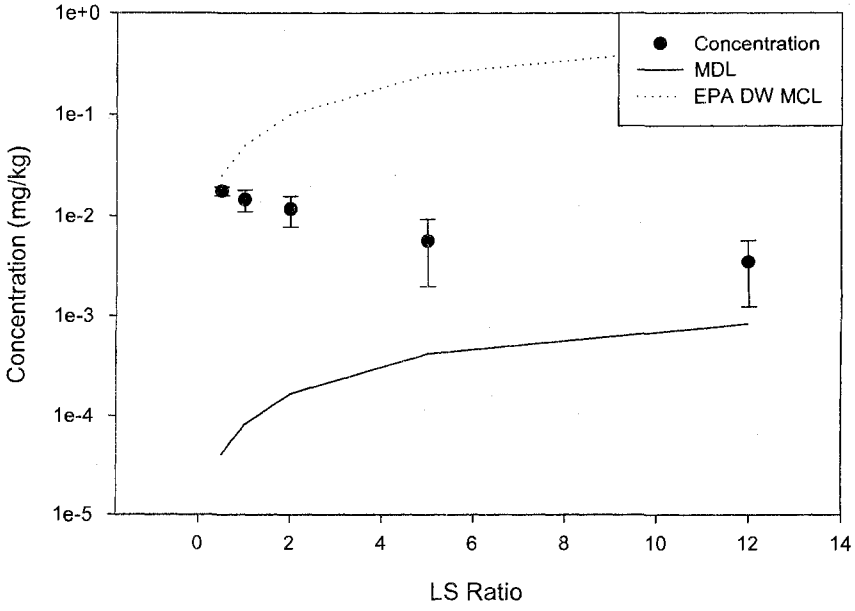

Jasper County Chat
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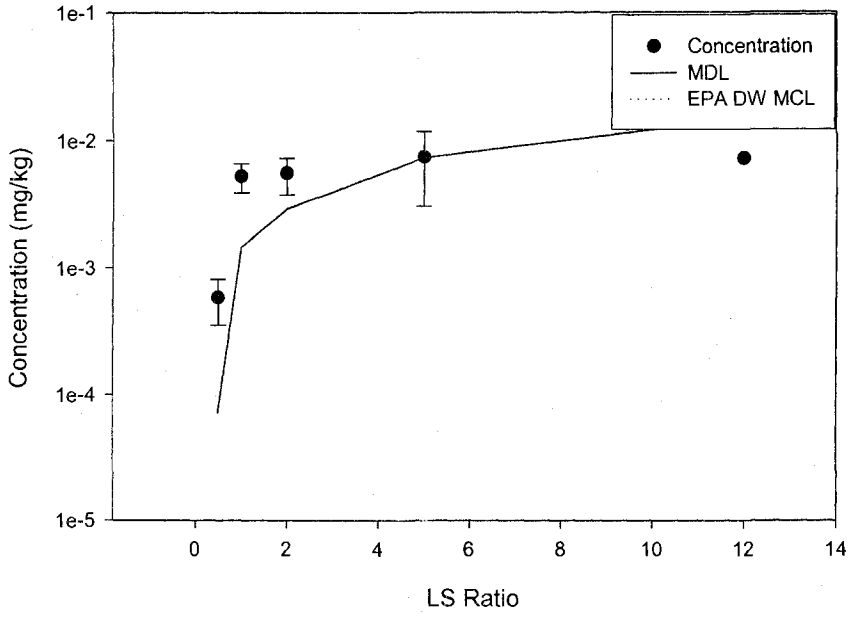


Jasper County Chat
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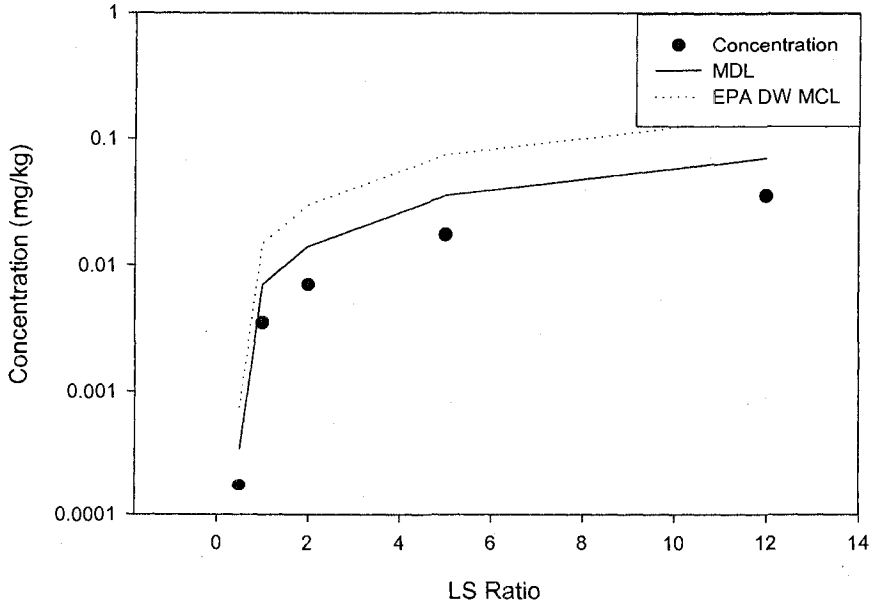

Jasper County Chat
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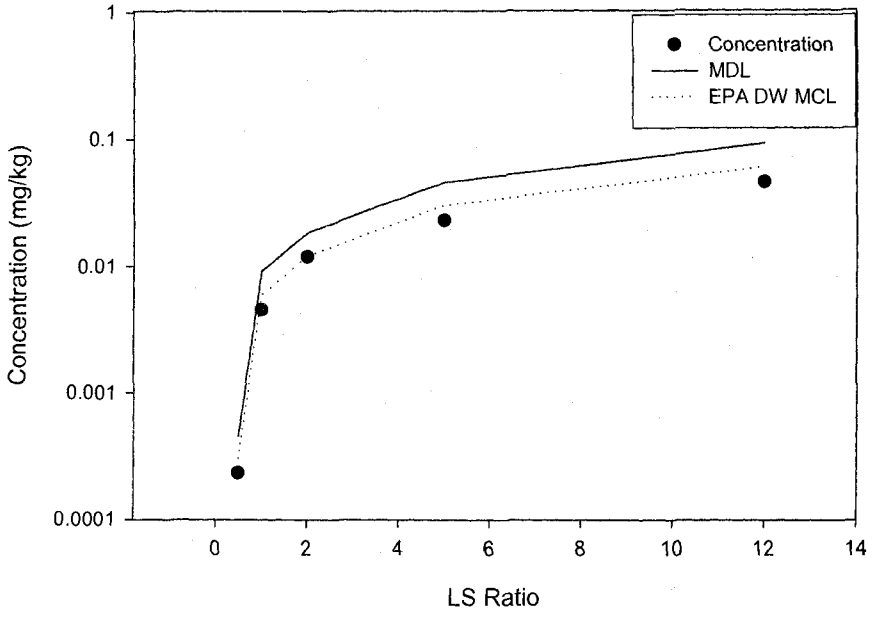


Jasper County Chat
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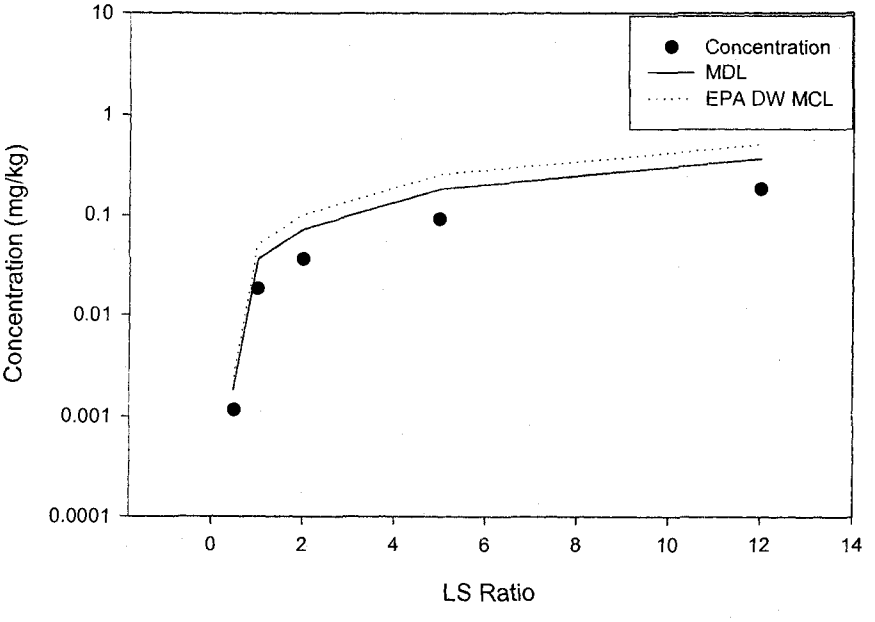
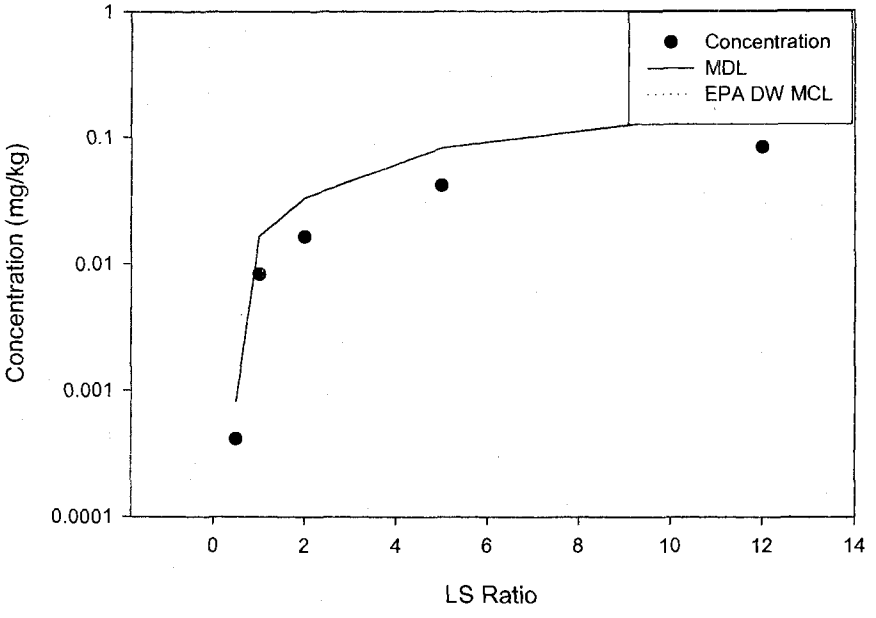


Jasper County Chat
Tl




Jasper County Chat
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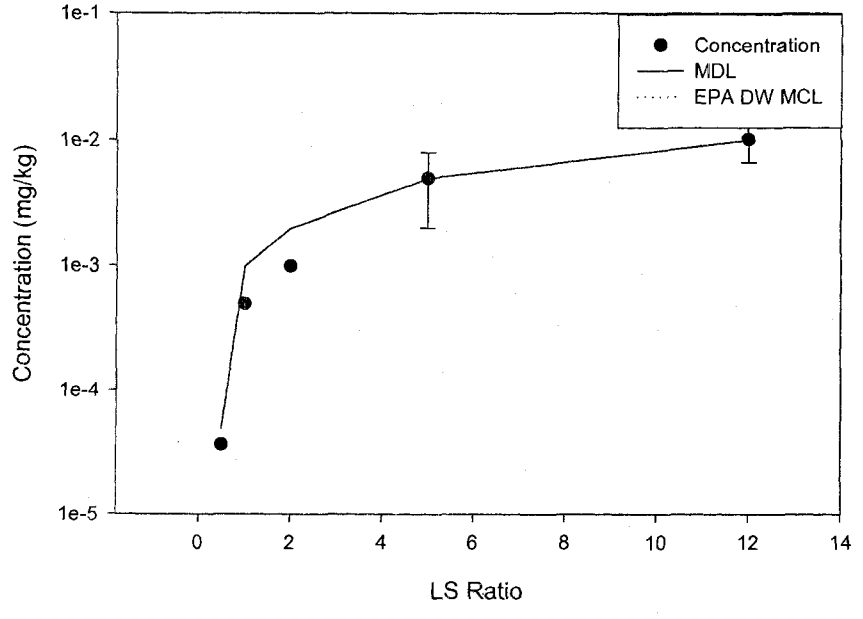
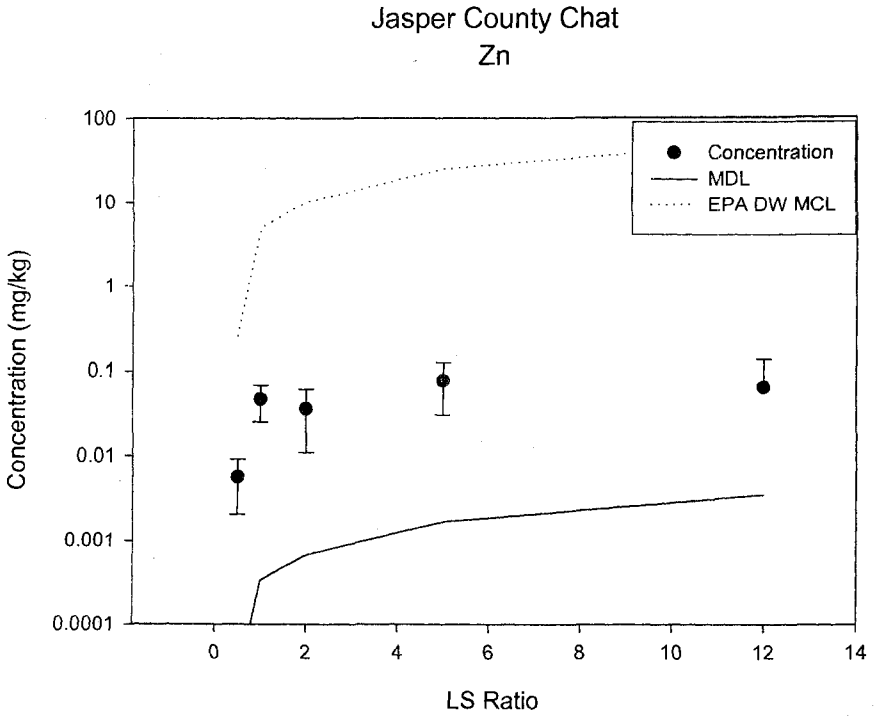
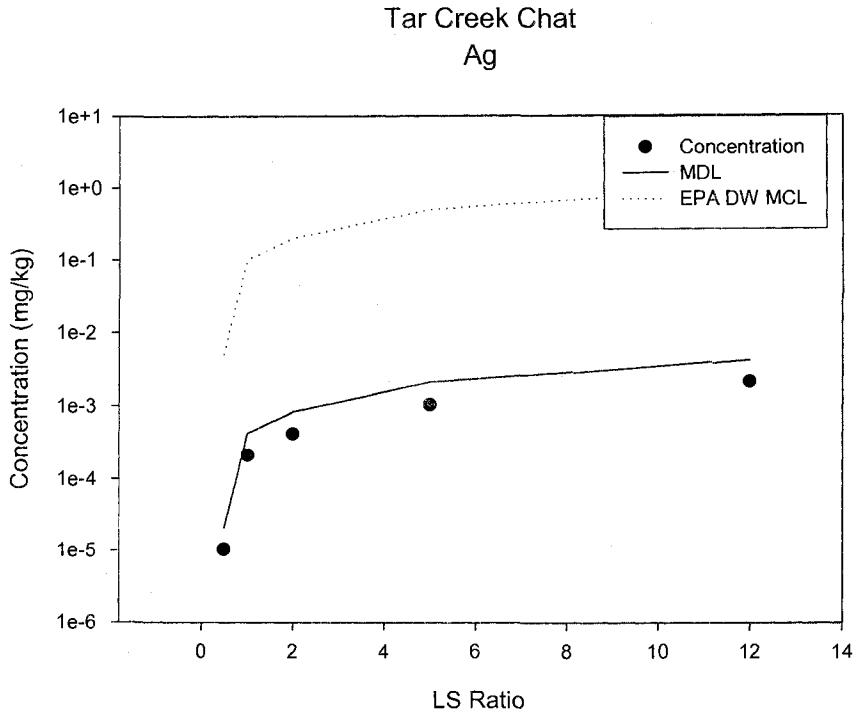
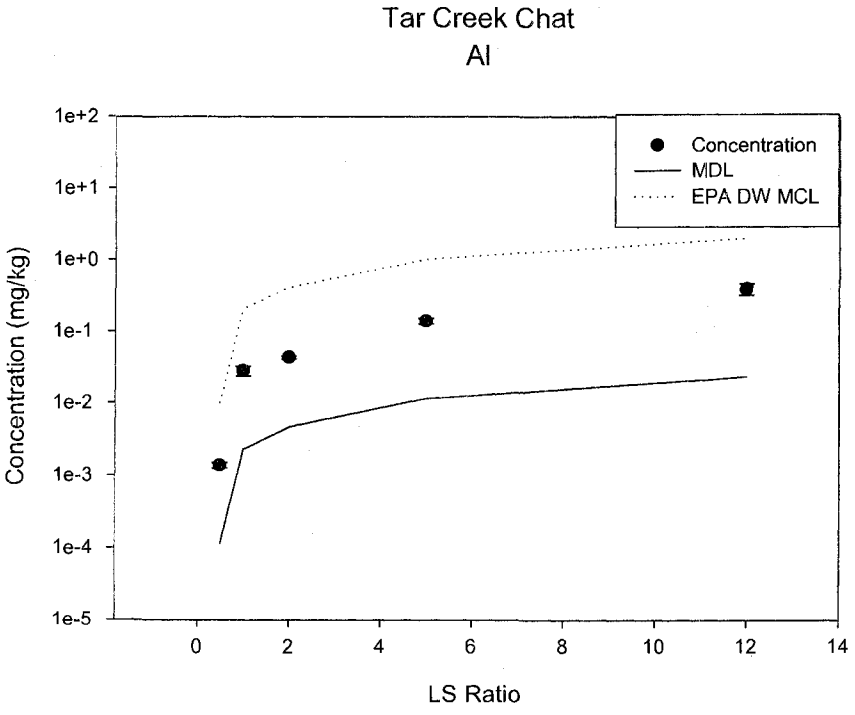
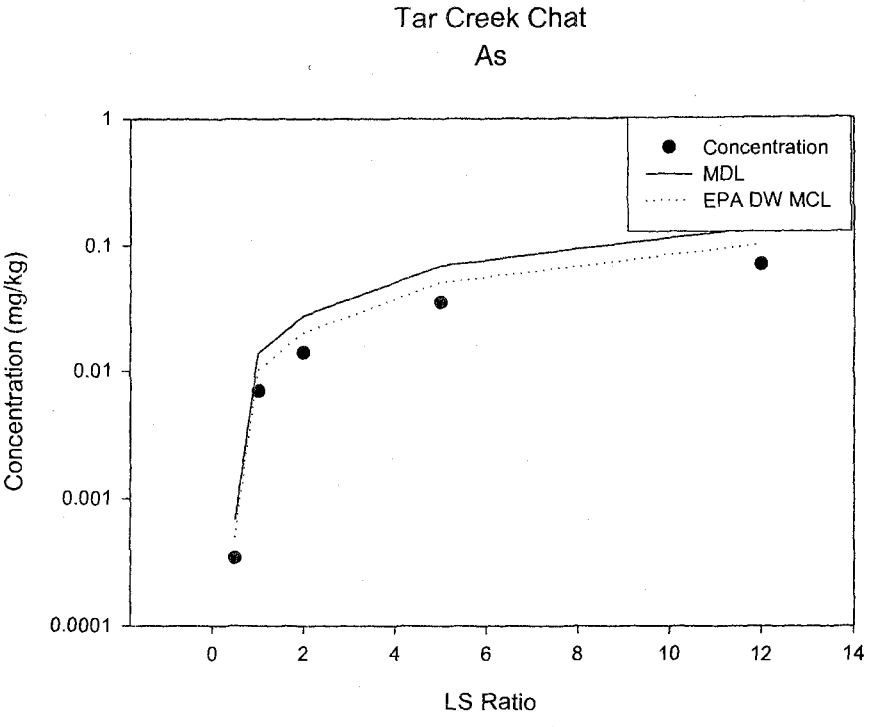
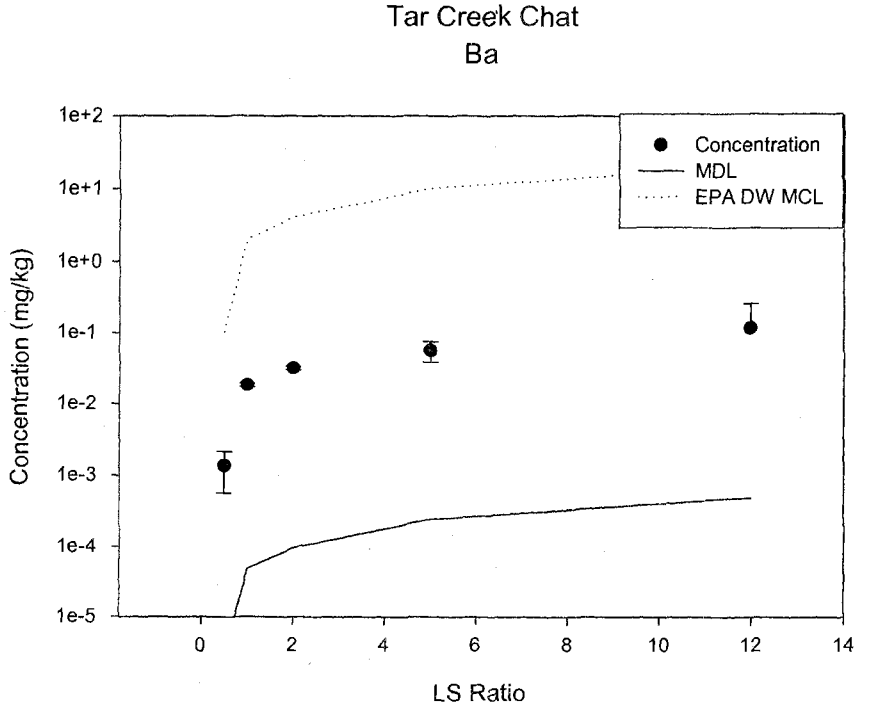


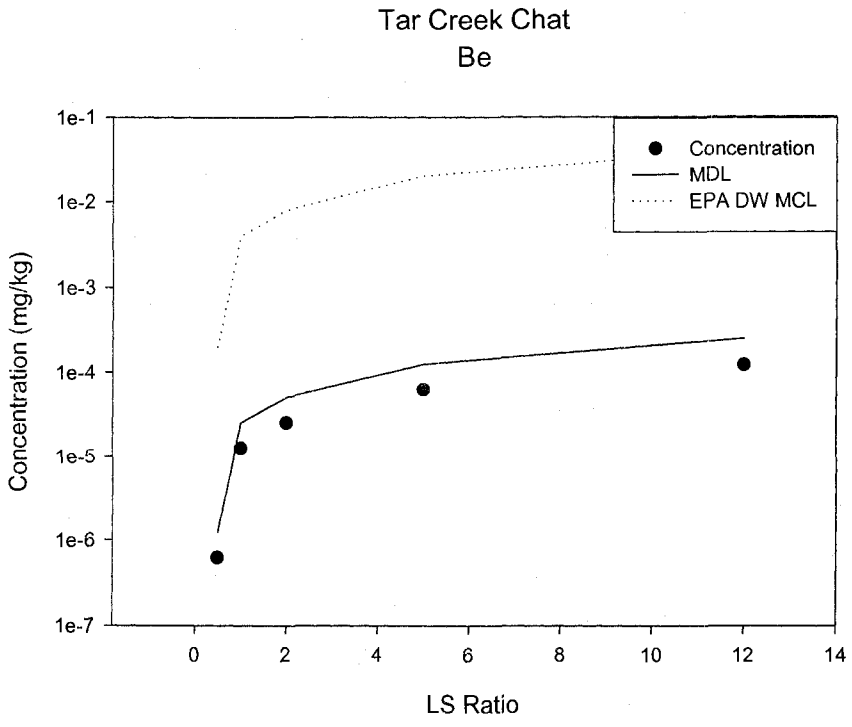

Jasper County Chat
Zn
Concentration
MDL
EPA DW MCL
Concentration (mg/kg)
100
10
1
0.1
0.01
0.001
0.0001
0
2
4
6
8
10
12
14
LS Ratio

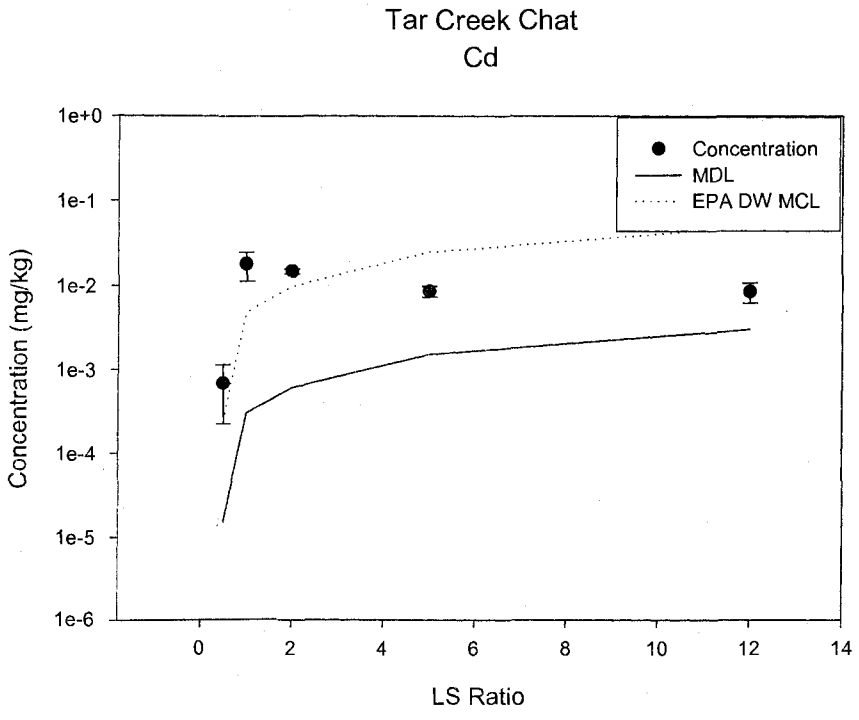

Tar Creek Chat
Ag
Concentration
MDL
EPA DW MCL
Concentration (mg/kg)
1e+1
1e+0
1e-1
1e-2
1e-3
1e-4
1e-5
1e-6
0
2
4
6
8
10
12
14
LS Ratio


Tar Creek Chat
Al
Concentration
MDL
EPA DW MCL
Concentration (mg/kg)
1e+2
1e+1
1e+0
1e-1
1e-2
1e-3
1e-4
1e-5
0
2
4
6
8
10
12
14
LS Ratio

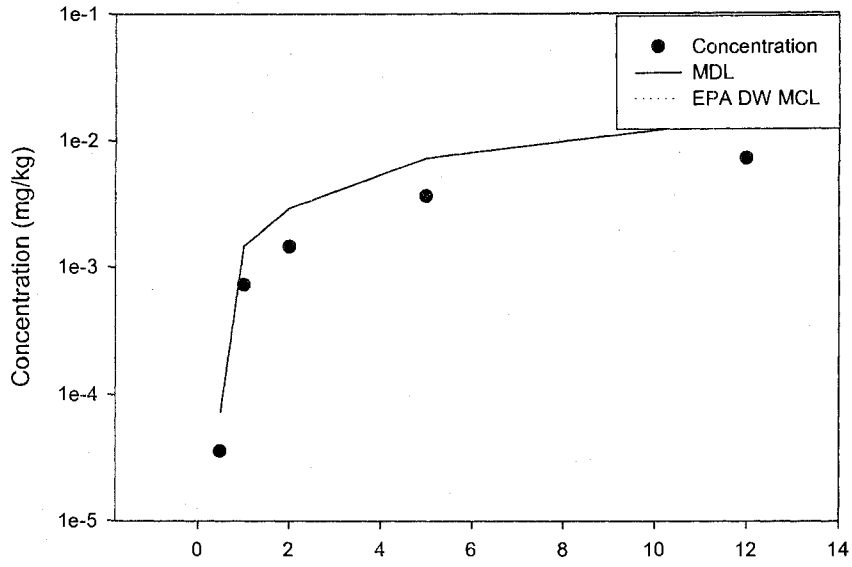

Tar Creek Chat
As
Concentration
MDL
EPA DW MCL
Concentration (mg/kg)
1
0.1
0.01
0.001
0.0001
0
2
4
6
8
10
12
14
LS Ratio


Tar Creek Chat
Ba
Concentration
MDL
EPA DW MCL
Concentration (mg/kg)
1e+2
1e+1
1e+0
1e-1
1e-2
1e-3
1e-4
1e-5
0
2
4
6
8
10
12
14
LS Ratio


Tar Creek Chat
Be
Concentration
MDL
EPA DW MCL
Concentration (mg/kg)
1e-1
1e-2
1e-3
1e-4
1e-5
1e-6
1e-7
0
2
4
6
8
10
12
14
LS Ratio


Tar Creek Chat
Cd
Concentration
MDL
EPA DW MCL
Concentration (mg/kg)
1e+0
1e-1
1e-2
1e-3
1e-4
1e-5
1e-6
0
2
4
6
8
10
12
14
LS Ratio

Tar Creek Chat
Co




Tar Creek Chat
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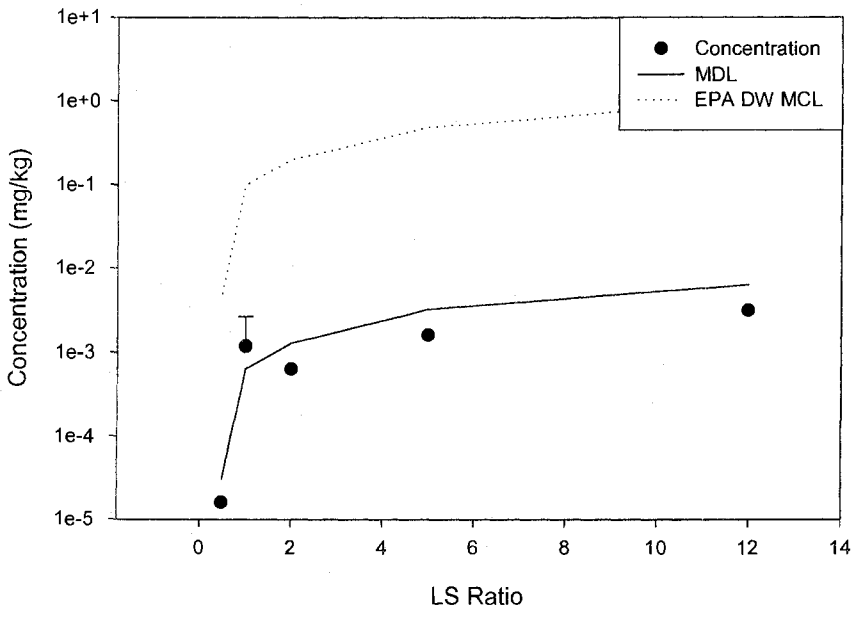
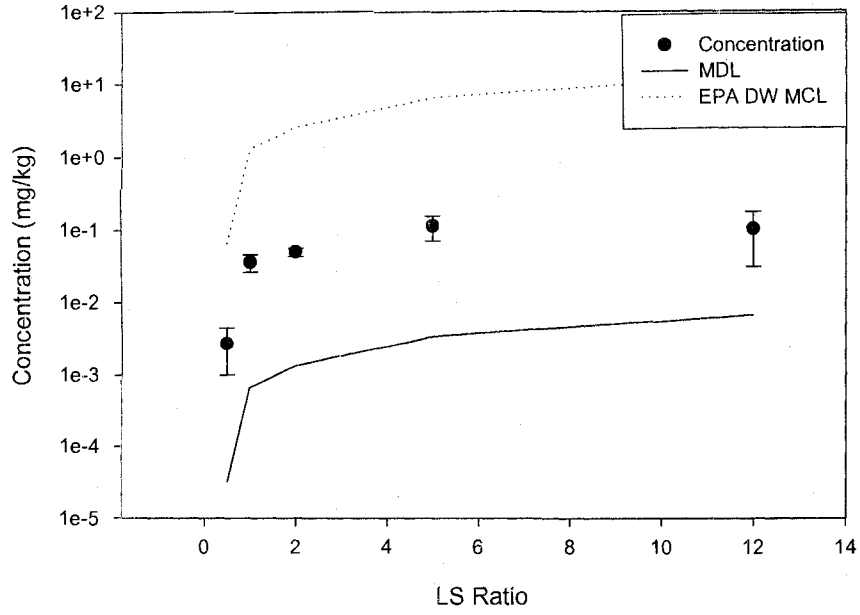
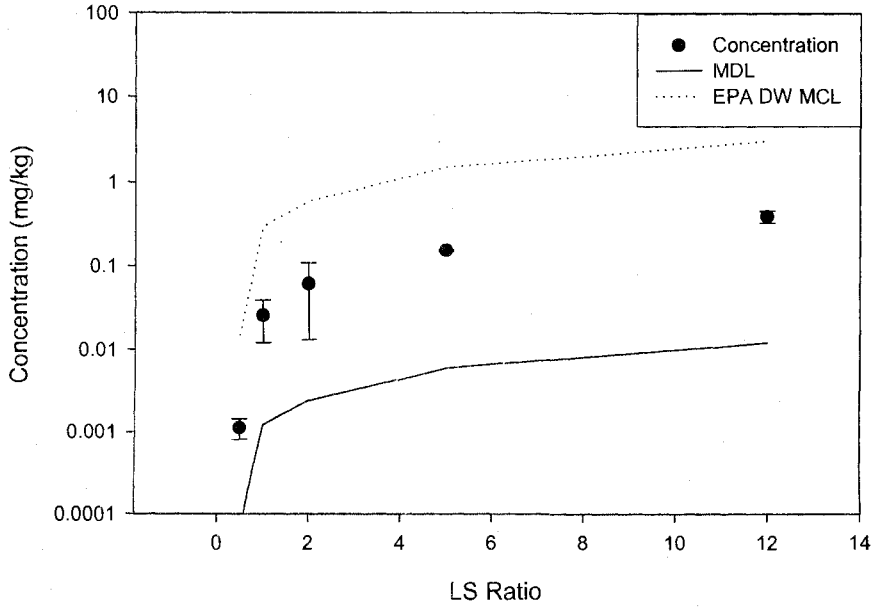


Tar Creek Chat
Cu




Tar Creek Chat
Fe



Tar Creek Chat
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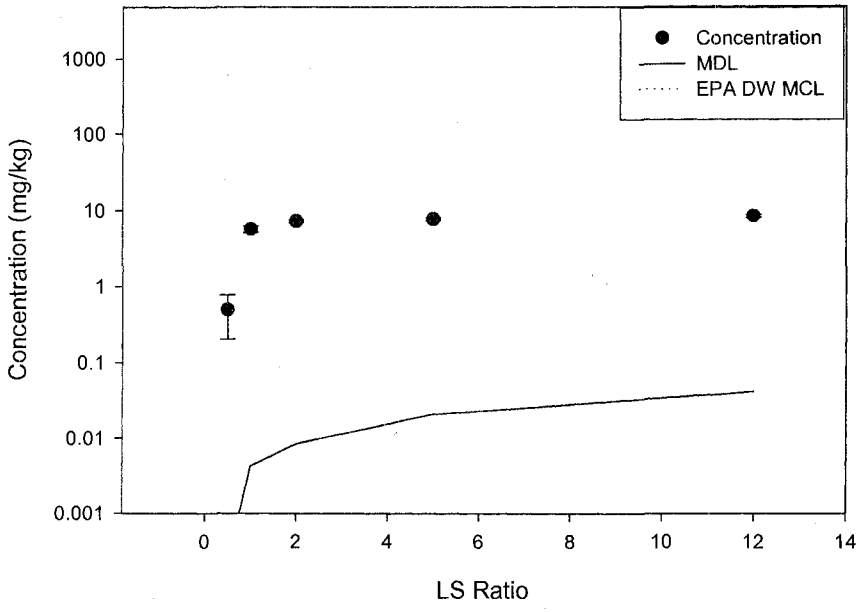


Tar Creek Chat
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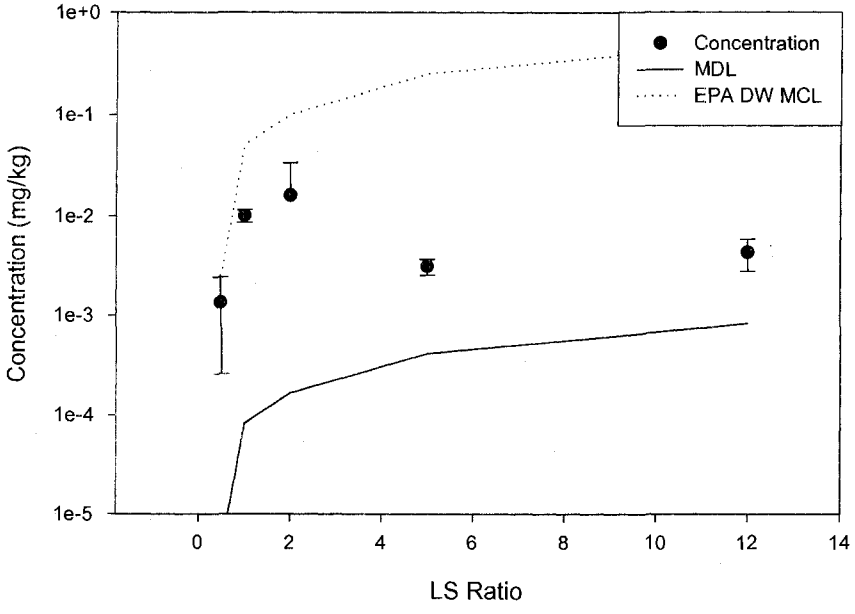

Tar Creek Chat
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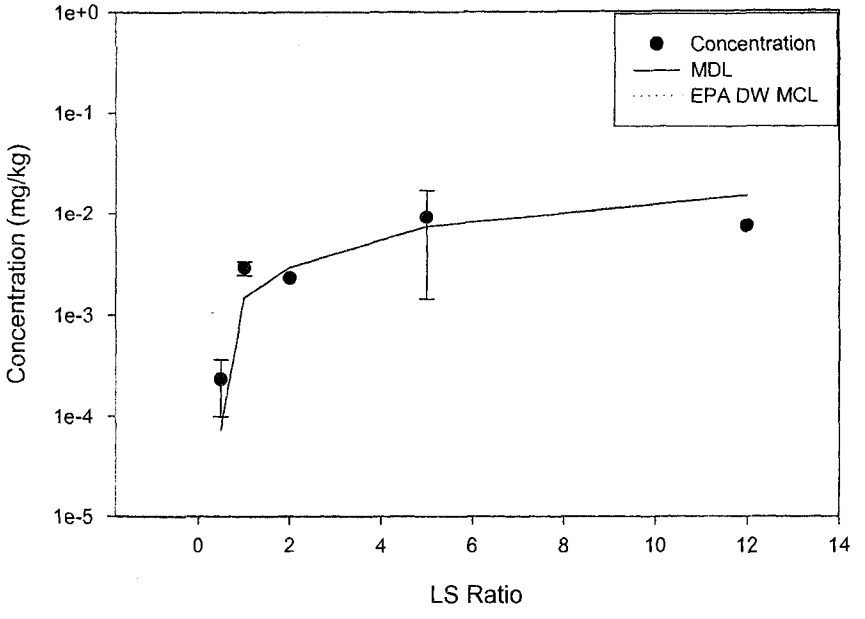


Tar Creek Chat
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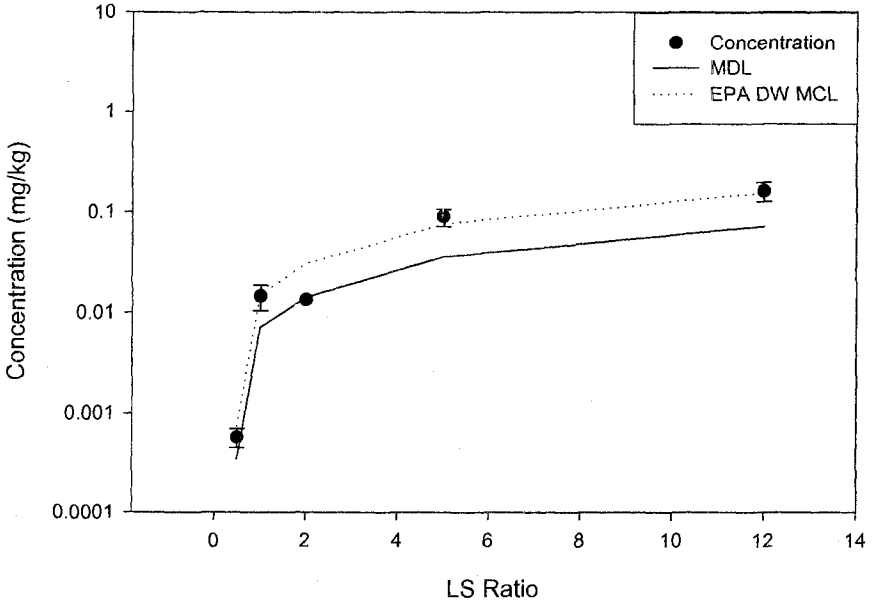
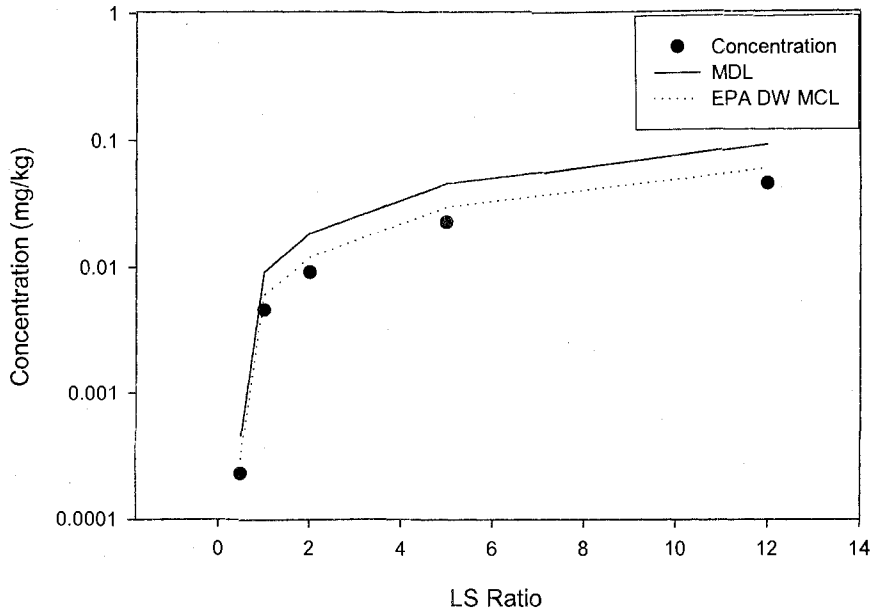


Tar Creek Chat
Sb




Tar Creek Chat
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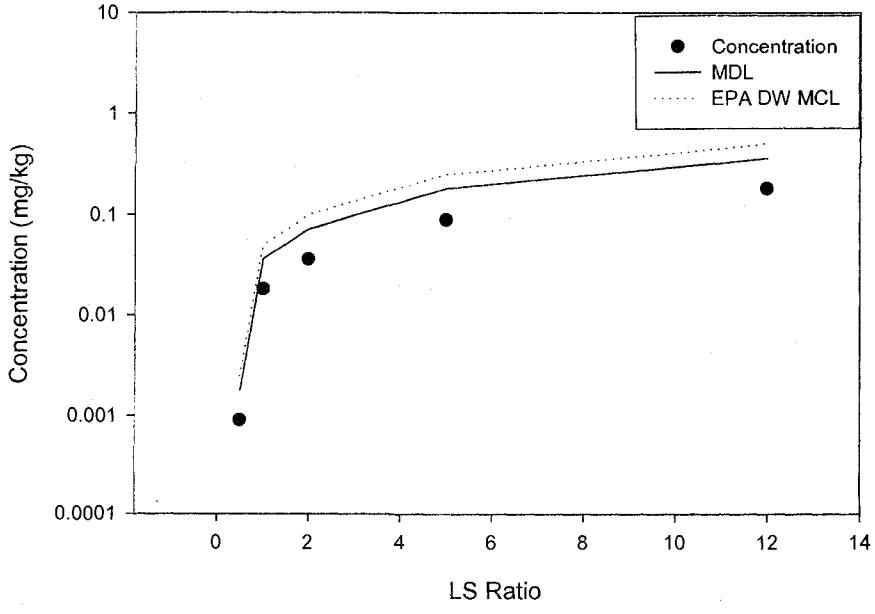
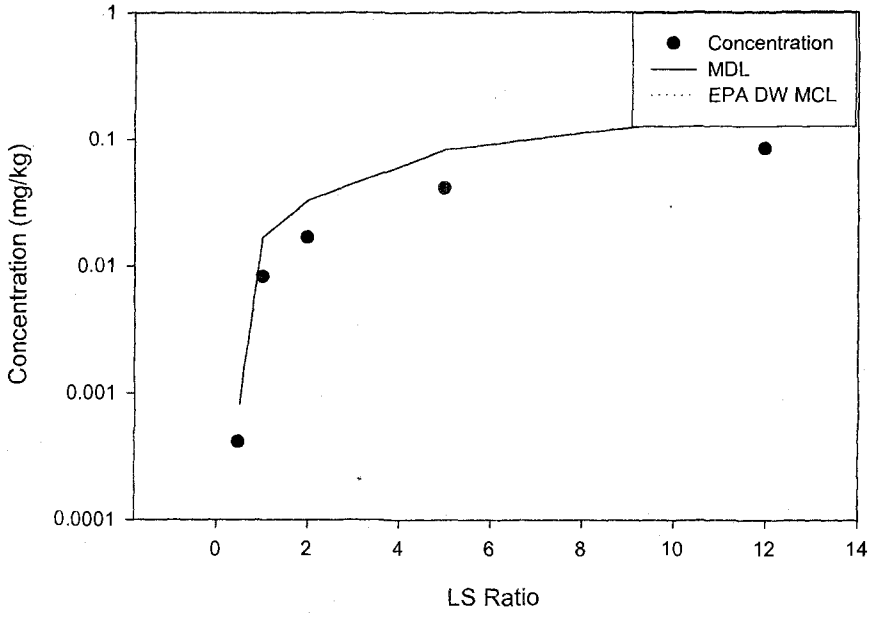


Tar Creek Chat
Tl




Tar Creek Chat
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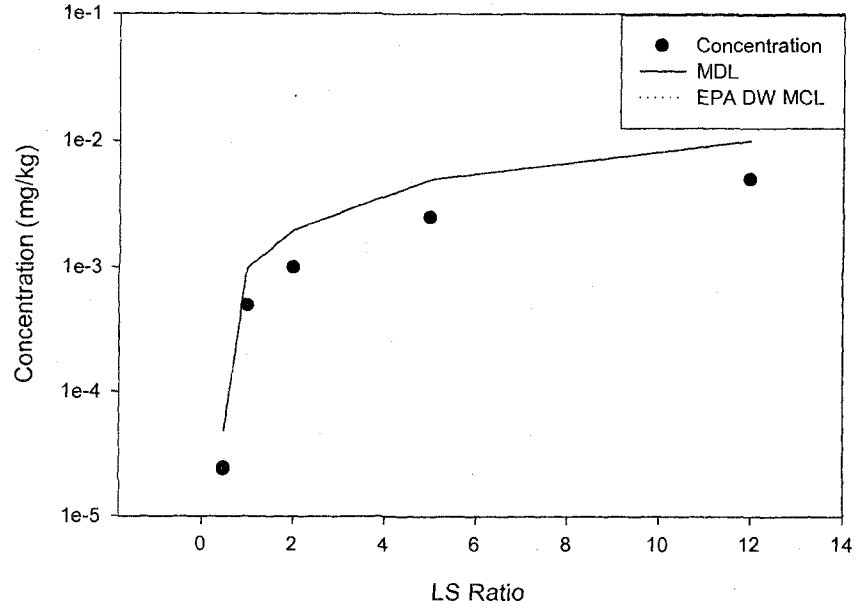

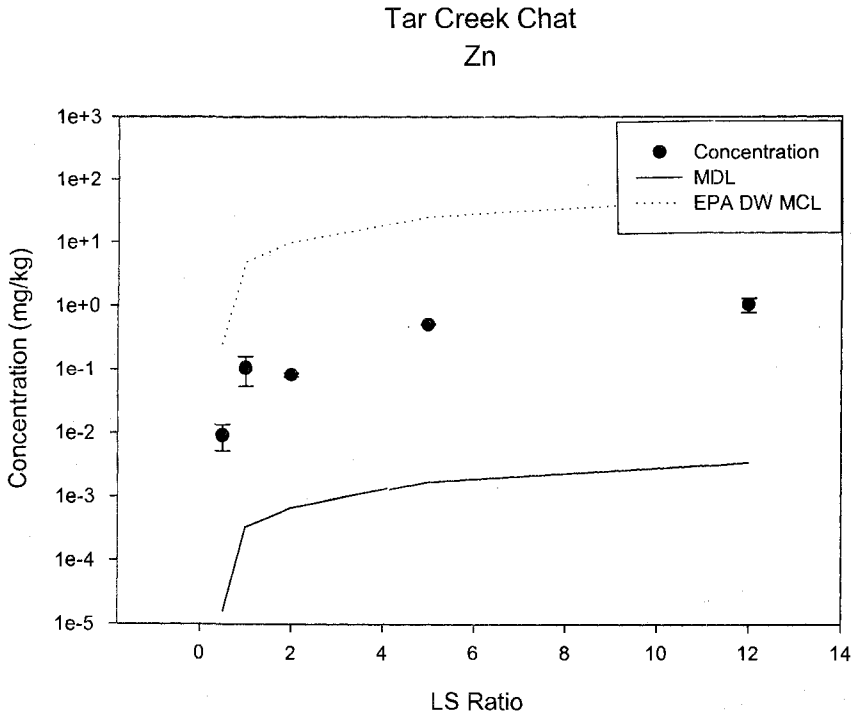
Tar Creek Chat
Zn
Concentration
MDL
EPA DW MCL
Concentration (mg/kg)
1e+3
1e+2
1e+1
1e+0
1e-1
1e-2
1e-3
1e-4
1e-5
0
2
4
6
8
10
12
14
LS Ratio