

**SECOND FIVE-YEAR REVIEW REPORT FOR
FOOTE MINERAL CO. SUPERFUND SITE
EAST WHITELAND TOWNSHIP
CHESTER COUNTY, PENNSYLVANIA**



Prepared by

**U.S. Environmental Protection Agency
Region 3
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A handwritten signature in blue ink, appearing to read "Paul Leonard", is written over a horizontal dashed line.

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September 20, 2019

Date

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LIST OF ABBREVIATIONS & ACRONYMS

ARAR	Applicable or Relevant and Appropriate Requirement
BTAG	Biological and Technical Assistance Group
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
CFR	Code of Federal Regulations
COC	Contaminant of Concern
EPA	United States Environmental Protection Agency
ESD	Explanation of Significant Differences
FYR	Five-Year Review
GPRA	Government Performance and Results Act
IC	Institutional Control
MCL	Maximum Contaminant Level
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NPL	National Priorities List
OU	Operable Unit
O&M	Operation and Maintenance
PADEP	Pennsylvania Department of Environmental Protection
PADER	Pennsylvania Department of Environmental Resources
PPA	Prospective Purchaser Agreement
RAO	Remedial Action Objective
RD	Remedial Design
ROD	Record of Decision
RPM	Remedial Project Manager
SDWA	Safe Drinking Water Act
SVOC	Semi-Volatile Organic Compound
SWRAU	Site Wide Ready for Anticipated Use
UU/UE	Unlimited Use and Unrestricted Exposure
VOC	Volatile Organic Compound

I. INTRODUCTION

The purpose of a Five-Year Review (FYR) is to evaluate the implementation and performance of a remedy in order to determine if the remedy is and will continue to be protective of human health and the environment. The methods, findings, and conclusions of reviews are documented in five-year review reports such as this one. In addition, FYR reports identify issues found during the review, if any, and document recommendations to address them.

The U.S. Environmental Protection Agency (EPA) is preparing this FYR pursuant to the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) Section 121, consistent with the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) (40 CFR Section 300.430(f)(4)(ii)) and considering EPA policy.

This is the second FYR for the Foote Mineral Co. (Foote) Superfund Site (the Site). The triggering action for this statutory review is the previous FYR dated September 30, 2014. This FYR has been conducted because hazardous substances, pollutants, or contaminants remain at the Site above levels that allow for unlimited use and unrestricted exposure.

The Site is considered a single Operable Unit (OU) which encompasses all components of the remedy and which will be addressed in this FYR. The Site is comprised of the waste materials and contaminated soils, groundwater, surface water and sediment located on and extending from a former lithium processing facility.

The FYR was conducted by an EPA team including James Feeney, Remedial Project Manager; Ryan Bower, Hydrogeologist; Jennifer Hubbard, Toxicologist; Bruce Pluta, Biologist and Gina Soscia, Community Involvement Coordinator. Support from the Pennsylvania Department of Environmental Protection (PADEP) included Joshua Crooks, Project Manager. The current Site owner, Whiteland Holdings, L.P. was notified of the initiation of the FYR. The review began on April 11, 2019, with a meeting of the project team, and the review of relevant documents.

Site Background

The Site includes a former lithium processing facility previously owned and operated by the Foote Mineral Company (Foote Mineral) and the plume of contaminated groundwater extending to the east-northeast. The former processing facility was on property located at 15 South Bacton Hill Road in East Whiteland Township, Chester County, Pennsylvania (the Property as shown in Figure 1). The Property was used primarily for the production of lithium metal and lithium chemicals. The company also resized imported ores, and processed a variety of other specialty chemicals. Waste streams from lithium processing were directed to two preexisting on-Site limestone quarries (North Quarry and South Quarry) which caused contamination of the underlying groundwater. The boundaries of the Site include the former facility and the downgradient plume of contaminated groundwater.

The facility operated from the 1940's until it was closed in 1991 and contained over 50 process buildings and storage areas. At various times throughout active operations, production wastes were disposed in the on-Site quarries which became the primary source for underlying groundwater contamination.

After the facility ceased operations in 1991, the Site owner at the time, Cyprus Foote Mineral Co., arranged for the removal of equipment and demolition of the remaining buildings down to foundations. In 1998, Frazer Exton Development, LP (FED) purchased the Site property, accepting responsibility for cleaning up the Site. The remedy detailed in the March 31, 2006 Record of Decision (ROD) for the Site entailed excavating and consolidating the foundations and areas of contaminated soils into the quarry area. The quarries were combined into a single disposal area, graded and capped as a landfill. Lithium is the primary contaminant and the existing groundwater contamination plume extends from the quarry area approximately 10,000 to the east-northeast.

The areas overlying the plume and surrounding the Site are a mix of commercial and residential developed properties that are supplied by public water. Impacted wells were abandoned when public water was furnished in 2004. In December 2016, Whiteland Holdings, LP (WH), the holder of the first mortgage on the property, foreclosed and acquired the Site property from FED. WH has long-term plans to redevelop the non-landfilled areas of the Property as commercial or residential. Currently, however, the Property remains vacant and fenced.

Additional Site background, history and dates are provided in Attachment 1.

Five-Year Review Summary Form

Site Name: Foote Mineral Co.		
EPA ID: PAD077087989		
Region: 3	State: PA	City/County: East Whiteland/Chester
NPL Status: Final		
Multiple OUs? No	Has the site achieved construction completion? Yes: October 28, 2010	
Lead agency: United States Environmental Protection Agency		
Author name (Federal Remedial Project Manager): James J. Feeney		
Author affiliation: United States Environmental Protection Agency, Region 3		
Review period: April to September 2019		
Date of site inspection: June 18, 2019		
Type of review: Statutory Review		
Review number: 2		
Triggering action date: September 30, 2014		
Due date: September 30, 2019		

II. RESPONSE ACTION SUMMARY

Basis for Taking Action

Starting in 1941, various owners and operators of the Foote facility used the Property for the production of lithium chemicals and the processing of a variety of ores. At various times throughout active operations at the Site, production wastes were disposed in the quarries. The South Quarry was used primarily for the disposal of spent mineral waste slurries and process waters with high levels of residual lithium and other elements. These wastes leached into the underlying groundwater causing a contaminated groundwater plume. Downgradient public and private groundwater wells were contaminated with unacceptable levels of boron, lithium, chromium and bromate.

Low levels of Site-related contaminants were also found in the downgradient surface water of East Valley Creek, believed to be a result of groundwater discharges to the creek. An Ecological Risk Study was developed to evaluate impacts to potential ecological receptors in East and West Valley Creeks. Results showed elevated levels of lithium and boron in East Valley Creek and subtle alterations of fish tissue and differences in fish communities which appeared to be correlated with contaminant levels.

Additionally, during investigations conducted at the Site, several discrete areas of soil were discovered to be contaminated with low-level radiation believed to be the residual dust from certain mineral ores.

Response Actions

Initial Response

In 1969, the Pennsylvania Department of Environmental Resources (now the Pennsylvania Department of Environmental Protection, or (PADEP)) became aware of the facility's waste water discharge into the South Quarry and requested that Foote Mineral conduct monitoring of the groundwater from beneath the property and from nearby residential wells. In 1975, PADEP ordered Foote Mineral to discontinue burning wastes in the burn pit, stop discharging waste water to the South Quarry and initiate quarterly sampling of nearby residential wells for lithium. In 1987, PADEP allowed Foote Mineral to reduce the frequency of the well monitoring to semi-annual sampling.

EPA added the Site to the National Priorities List (NPL) in October 1992.

Remedy Selection

Following a Remedial Investigation and Feasibility Study (RI/FS), EPA's initial selected remedy for the Site was documented in the ROD issued March 31, 2006. The Remedial Action Objectives (RAOs) from the ROD are listed below:

- Reduce or eliminate risk posed by direct human contact with the waste materials in the Quarries and contaminated soils present at the Site;

- Reduce or eliminate the potential for direct human or ecological exposure to radiologically contaminated soils;
- Minimize the potential human and ecological exposure to unacceptably contaminated groundwater;
- Reduce the contamination leaching into the groundwater to allow the groundwater in the Downgradient Contaminant Plume to be returned to beneficial use; and
- Comply with applicable or relevant and appropriate regulations.

The remedy selected in the 2006 ROD (the Remedy) required the following major components:

- To prevent direct contact with radiologically contaminated soils, the soils will be excavated and shipped off-site for disposal at an appropriately permitted facility.
- The South Quarry waste will be stabilized using an in-situ soil stabilization (ISS) technology to reduce contaminant migration to groundwater.
- To prevent direct contact with contaminated soils on the Property and reduce contaminant migration to groundwater, contaminated soils will be excavated and consolidated in either the North or South Quarry. In addition, other waste materials, debris, or demolition waste may also be consolidated and placed into the Quarries prior to final capping
- The Quarries will be capped to reduce contaminant migration from the waste in the Quarries to the groundwater.
- Monitoring of groundwater will be conducted to determine if the above source control measures are effective in reducing contaminant concentrations in groundwater to drinking water standards.
- LNAPL in Well MW-2 will be removed to prevent its migration into the groundwater
- Institutional controls shall be implemented to prevent residential use of impacted groundwater, prevent residential use of the capped Quarry areas and preserve the integrity of the Remedy.

During field activities conducted after the ROD, it was determined that the volume of debris, waste materials and soil would exceed the available capacity in the two quarries. As a result, EPA issued an Explanation of Significant Differences (ESD) April 7, 2008, to modify the ROD, authorizing the following three changes:

- Expansion of the horizontal extent of capping outside the current limits of the quarries, and increasing the elevation above surrounding grade for the final capped area.
- Use of less stringent numerical soil cleanup standards for antimony, arsenic, lithium and thallium (*Numerical standards were based on actual leach testing from site soils to replace standards generated by modelling assumptions*).
- Use of low permeability barriers, consisting of a single layer geomembrane, to be installed horizontally at depths of fifteen feet or greater below the final ground surface in some of the areas of soil contamination. These barriers would minimize downward migration of any residual contamination at depth. (*Ultimately this option was not used at the site as the depths of contaminated soils were less than fifteen feet in most areas.*)

Status of Implementation

FED implemented the Remedy in accordance with a July 24, 2008 Consent Decree for Remedial Design and Remedial Action and continues to be responsible for the long-term operation and maintenance of the Site.

All soils with above-background radiation levels were excavated, transported and disposed off-site at an appropriately permitted disposal facility in accordance with the Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM) decommissioning methodology.

The demolished building foundations and contaminated soils were excavated and consolidated into the North Quarry. Soils were excavated to the cleanup criteria specified in the ROD as modified by the ESD. During the Remedial Action, building foundations and other structures left from prior demolition activities were removed, crushed or broken and consolidated into the Quarries. Ultimately, 36 individual and combined areas were excavated and consolidated into the quarries.

In the South Quarry, the previously disposed slurry waste materials were stabilized with a cement slag reagent to reduce permeability and prevent leaching to the groundwater. The average permeability of the waste mass after treatment was calculated at 1.5×10^{-7} centimeters per second; almost seven times lower than the requirement in the ROD, and two orders of magnitude lower than the untreated waste. The March 9, 2010, final Remedial Action Report detailing the implementation of the ISS process and certifying the area treated and the final permeability was approved by EPA in a letter dated May 10, 2010.

Following stabilization and consolidation, the quarry area was graded and covered with an engineered impermeable cap and a vegetated topsoil layer. Capping prevents direct contact with waste materials and minimizes or eliminates infiltration of water into and through the waste. The design of the cap system included drainage and discharge features to address increased runoff and to avoid erosion issues and adverse impacts to adjacent properties. Construction of the cap was completed the week of October 17, 2010.

The Remedy includes long-term monitoring of the inorganic contaminants in the downgradient groundwater plume, in accordance with the approved July 2008 Groundwater Monitoring Plan (GMP), to determine if the source control measures are effective in reducing contaminant concentrations to drinking water standards. The GMP also includes the monitoring of volatile organic contaminants (VOCs) in the one well (MW-22) that contained VOCs during the RI. Results from that well will be utilized to determine the potential for vapor intrusion impacts to any buildings that may be planned for construction above the contaminated groundwater plume.

Six existing on-site monitoring wells were selected for continued monitoring of inorganic contaminants, with one well, MW-22, also monitored for organics. In 2010, in accordance with the GMP, ten additional groundwater monitoring wells were installed at varying depths in four locations, designated GMZ-1 through GMZ-4, to the east-northeast (downgradient) of the source areas. These downgradient wells are monitored for inorganics. The well locations were approved by EPA and the United States Geological Survey and are shown on Figure 2.

Four surface water locations upgradient and downgradient of likely groundwater discharge points on East Valley Creek are also sampled to determine downgradient surface water quality. The approved Groundwater Monitoring Plan (GMP) required that these wells and surface water locations be sampled quarterly for the first two years of operation followed by semi-annual sampling in subsequent years.

The ROD also required that the light non-aqueous phase liquid (LNAPL) found in on-site monitoring well MW-2 be removed with a passive recovery device or oil-absorbent boom placed within the well. During the Remedial Action and sampling events in the long-term monitoring activities, however, no LNAPL was observed in well MW-2. The GMP requires continued periodic sampling of the well, but it is believed that the source of the LNAPL was removed during the extensive excavations in the area surrounding the well.

Institutional Controls

The ROD required that institutional controls be implemented to prohibit future residential development on the capped areas of the North and South Quarry. An Environmental Covenant for Institutional Controls was negotiated with the current property owner, WH, and the prior owner, FED. The Environmental Covenant was signed and recorded with the Recorder of Deeds Office, Chester County, on September 28, 2017, functionally implementing the restrictions.

The ROD also required an institutional control to prevent the use of contaminated groundwater for drinking water purposes. Based on the groundwater monitoring results, the boundaries of a Groundwater Management Zone were formally established and shared with the Chester County Health Department (CCHD). Subject to Chapter 500, Section 501 of the *Chester County Health Department Rules and Regulations, Water Well Construction, Monitoring Wells, and Individual Semi-Public and Public Water Supplies and Geothermal Boreholes*, CCHD has identified this area for required groundwater testing and restriction on the installation of new wells in areas found to be contaminated. This action formally implements the groundwater restriction and satisfies the requirement for the Institutional Control.

IC Summary Table

Summary of Planned and/or Implemented ICs

Media, engineered controls, and areas that do not support UU/UE based on current conditions	ICs Needed	ICs Called for in the Decision Documents	Impacted Parcel(s)	IC Objective	Title of IC Instrument Implemented and Date (or planned)
Landfill	Yes	Yes	Capped Landfill and Ancillary Structures	Prohibit residential use of the Capped Landfill and protect the components of the Cap System	Environmental Covenant for Institutional Controls, signed, and recorded with the Recorder of Deeds Office, Chester County, on September 28, 2017
Groundwater	Yes	Yes	Downgradient Groundwater Plume	Prohibit use of contaminated groundwater as a source of drinking water	Chapter 500, Section 501, Chester County Rules and Regulations

Systems Operations/Operation & Maintenance

Maintenance of the physical components of the cap and storm water control features is required by the Operations and Maintenance Plan which was submitted to EPA and approved as Section 7 of the 2011 Remedial Action Report for the Soils, Waste Materials and Debris Consolidation and Capping of the North and South Quarry. Site inspection and maintenance activities are required to ensure that the landfill cap remains intact and effective in preventing direct contact with the consolidated wastes. Keeping the vegetated top layer of soil cover in good condition serves to protect the underlying soils and synthetic membrane materials of the cap. The stormwater control features are inspected and maintained to ensure there is no erosion of the cover materials and that storm water is captured and channeled off-site. Cap inspections were required quarterly for the first year post-construction, followed by annual inspections thereafter. In practice however, the cap and stormwater features have been inspected by FED monthly since the cap was completed, with most maintenance activities, such as repair of soil erosion areas and reseeding, occurring within the first few months following completion of the cap. The most recent inspection checklist, dated June 26, 2019, is included as Attachment 2.

In accordance with the approved GMP, downgradient groundwater and surface water monitoring is conducted to measure and evaluate the levels of contamination in the downgradient groundwater. Samples are analyzed for fluoride, bromide, bromate, antimony, arsenic, chromium, thallium, boron and lithium. Because lithium is the predominant and most persistent contaminant with the highest concentrations throughout the contaminant plume, the downgradient extent of lithium defines the extent of contamination from the Site. A summary of

lithium results in the wells and surface water samples since monitoring began in December 2010 is included in Attachment 3 and discussed in the Data Review section below.

Due to financial difficulties, FED had discontinued the monitoring program and missed five quarters of sampling in 2012 and 2013. FED restarted the program in September 2013 and has conducted the monitoring under EPA supervision consistently since that time.

III. PROGRESS SINCE THE LAST REVIEW

The protectiveness statement from the first FYR Report for the Site, signed September 30, 2014, is reproduced below:

A protectiveness determination of the Remedy cannot be made at this time until further information is obtained. There is insufficient data to determine the protectiveness of the Remedy with respect to the environment because of the limited surface water and groundwater monitoring data. Currently, Site-related contaminants are still present in the surface water of East Valley Creek near the groundwater discharge area, but a declining trend, as seen in the two upgradient monitoring wells, is not yet evident in the East Valley Creek. For the Remedy to be protective of the environment, the long-term groundwater and surface water monitoring must demonstrate that the remedial measures implemented at the Site are effective in minimizing the downgradient migration and discharge of contaminants to the Creek. Evaluation of the monitoring data will be conducted annually to determine the protectiveness of the remedy with respect to the environment.

The Remedy implemented at the Site is protective of human health in the short term because exposure pathways that could result in unacceptable human health risks are being controlled. The Site is currently unoccupied and surrounded by security fencing. Direct contact with contaminated soils has been minimized by containment of the soils in the capped quarry area. There are no current drinking water wells using contaminated groundwater and institutional controls prohibit the installation of new wells in the contamination plume. To be protective of human health in the long term, legally enforceable institutional controls must be implemented to protect the components of the Remedy and prevent residential use of the capped quarry area. Additionally, because the soil areas were excavated to ROD-specified cleanup levels, and toxicity factors have become more conservative for some of the contaminants, an updated risk assessment on the remaining soils outside the capped quarry area must be conducted to determine that the remedial action related to the soil areas remains protective.

The groundwater and surface water monitoring program was restarted as of September 23, 2013 and the groundwater and surface water sampling will be continued, as required in the ROD and Groundwater Monitoring Plan. The data from the monitoring program will be used to support and possibly modify the institutional controls that prevent the installation of drinking water wells in the area of contaminated groundwater. The data will also be used to evaluate the effectiveness of the source control components of the remedy on mitigating contamination in the downgradient groundwater. As set forth in the ROD, if groundwater cleanup is unlikely to occur in a reasonable time frame, a focused Feasibility Study may be required to determine if alternative remedial action is necessary.

The Issues and Recommendations from the last FYR are summarized below with the current implementation status for the recommendations.

Table 1: Status of Recommendations from the 2014 FYR

#	Issue	Recommendations	Current Status	Current Implementation Status Description	Completion Date (if applicable)
1.	Groundwater and surface water monitoring was discontinuous.	EPA will closely oversee the schedule and implementation of the monitoring	Completed	Monitoring was restarted in September 2013 and is ongoing.	9/30/2013
2.	Data collected was insufficient to determine the need for a Focused Feasibility Study as required in the ROD.	EPA will evaluate data annually and ensure appropriate data is collected	Completed	Additional data has demonstrated downward trends in groundwater and surface water. A Focused Feasibility Study is unnecessary at this time.	8/3/2017
3.	Institutional Controls to protect the components of the Remedy and prohibit residential reuse of the capped quarry area of the Site are not in place.	EPA will work with the Site owner to develop the appropriate Institutional Controls	Completed	Environmental Covenant for Institutional Controls, signed, and recorded with the Recorder of Deeds Office, Chester County, on September 28, 2017.	9/28/2017
4.	Vinyl chloride is a known breakdown product of TCE and PCE, but is not a required sampling parameter for MW-22	Include vinyl chloride in the sampling program	Completed	Split sampling showed non-detect levels of vinyl chloride in MW-22. No further sampling is planned at this time.	8/3/2017
5	Toxicity values for lithium and other contaminants have become more conservative.	Update the risk assessment to evaluate soil using current toxicity values	Considered But Not Implemented	Toxicity values are frequently revised; so updated risk assessment is recommended when development is planned.	N/A
6	Contaminants are still present in East Valley Creek.	Evaluate groundwater and surface water data annually	Completed	Monitoring and evaluating data has been performed annually.	8/1/2017

Further Explanation of Implementation Status

Additional explanation of the current status of the 2014 Issues and Recommendations is presented below:

1. Groundwater and surface water monitoring was discontinuous.

The Site owner in 2012, FED, had discontinued the monitoring program due to financial difficulties. However, after five missed quarters, FED restarted the program in September 2013 and has conducted the monitoring under EPA supervision consistently since that time. As discussed in detail in the Data Review section below, the groundwater and surface water results

have indicated that the contaminant levels in the downgradient groundwater and surface water have decreased with time as was anticipated in the ROD.

2. Insufficient data to determine the need for a Focused Feasibility Study.

The ROD specified that at the first FYR, “if it is determined that groundwater restoration throughout the plume is unlikely to occur in a reasonable timeframe, a Focused Feasibility Study may be required to determine if alternative remedial action is necessary.” Due to the break in the groundwater and surface water monitoring, there was non-continuous and insufficient data to make this determination in the FYR. Now, with the additional available data, downward trends in downgradient groundwater and surface water have been identified (see Attachment 3) indicating that restoration of the downgradient plume is likely, and a Focused Feasibility Study is unnecessary at this time. Higher levels of contaminants in the on-Site wells will continue to be evaluated and alternate remedial strategies may be considered in the future.

3. Institutional controls needed to protect the remedy and prohibit residential use.

An Environmental Covenant for Institutional Controls to prohibit future residential development on the capped areas of the North and South Quarry was negotiated with the current property owner, WH, and the prior owner, FED. The Environmental Covenant was signed, and recorded with the Recorder of Deeds Office, Chester County, on September 28, 2017, functionally implementing the restrictions.

4. Vinyl chloride should be sampled in MW-22.

Split sampling conducted by EPA’s contractor Weston during the owner’s scheduled sampling event showed non-detect levels of vinyl chloride in MW22. No further sampling is planned at this time. However, since vinyl chloride is a breakdown product of the VOCs that are expected to decline over time, continued monitoring of VOCs and periodic evaluation of the need for further monitoring of vinyl chloride is recommended.

5. Toxicity values for lithium and other contaminants have become more conservative.

Site soils were excavated to achieve the most conservative standard, acceptable risk for a child resident, using the standards current during the 2010 Remedial Action. The FYR recognized that some toxicity values had changed which could affect the risk assessment, such that the risk assessment should be updated. The Site is currently fenced and vacant with no specific plans for redevelopment and toxicity values are frequently updated. Therefore, an update to the risk assessment should be conducted when actual plans for Site use are developed, in consideration of the planned use and Site conditions existing at that time.

6. Contaminants are still present in East Valley Creek.

Approximately one mile downgradient of the Foote Site, East Valley Creek flows across a geologic fracture zone where contaminated groundwater discharges into the stream. Elevated levels of lithium are present in the creek starting in the discharge area and decreasing with distance downstream. EPA has continued to evaluate stream samples and contaminant levels and has noted decreasing contaminant trends as further discussed in the Data Section below.

Five-Year Review Addendum

In August 2017 EPA issued a FYR Addendum for the Site to acknowledge that the 2014 Issues and Recommendations had been addressed, allowing the protectiveness statement to be revised to “Protective of human health and the environment in the short term.” The Addendum further stated that “To be protective of human health in the long term, legally enforceable institutional controls must be implemented to protect the components of the remedy and prevent residential use of the capped quarry area.”

Since the 2017 Addendum, EPA completed negotiations for the Environmental Covenant for Institutional Controls, which protects the components of the constructed remedy and prohibits residential use of the landfilled area. The Environmental Covenant was ultimately signed, and recorded with the Recorder of Deeds Office, Chester County, on September 28, 2017.

IV. FIVE-YEAR REVIEW PROCESS

Community Notification, Involvement & Site Interviews

The level of public interest in the Site has been low since construction was completed in the Fall of 2010. In the past five years EPA has received only a few comments, questions or correspondence from the general public, and those few were concerned more with work on the nearby Sunoco Mariner 2 gas pipeline in West Whiteland than the Site itself. The property adjacent to the Site on the western border was used in 2017 and 2018 to park and store construction vehicles for the pipeline. Although that property was permitted and inspected by Chester County Conservation District, one resident called with concerns that construction activity and dust was being seen on the property. That property was not part of the Site and the lease for the property and the activities have concluded.

EPA placed an advertisement in the Daily Local News on June 3, 2019 (Attachment 5). The ad informed the community of the purpose of the FYR, the location and the protectiveness of the Site, and the upcoming availability of the report. EPA has received no questions, comments or response from this advertisement. This FYR report will be made available online at <https://www.epa.gov/superfund/footemineral>

Interviews

For this FYR, EPA contacted the East Whiteland Township Manager’s Office which reported that no recent questions or concerns have been raised by the community other than the contractor activity and dust issue described above. .

On June 18, 2019, during the Site inspection, the RPM interviewed a representative of the Site owner who reported that no community questions, issues or concerns with the Site have been received by the owner. The RPM also discussed community involvement with representatives of PADEP who reported that the only questions or concerns they had received were associated with the work on the Sunoco Mariner 2 gas pipeline and the contractor’s yard. No community issues were identified related to the Site itself.

Data Review

The groundwater sample results presented in the periodic monitoring reports for the five years from September 2013 through October 2018 were reviewed and summarized in tables and plotted on graphs (Attachment 3) for qualitative analysis. For longer term comparison, the tables and graphs also include the prior data beginning December 2010, the start of the sampling program. Lithium is the Site-related contaminant that appears at the highest levels and is the most persistent in the groundwater; therefore, the sample results for lithium offer the best indication as to the extent of Site-related contamination in the groundwater plume.

The ROD presented a risk-based screening level of 260 µg/l as the groundwater cleanup target for lithium. This number was based on EPA's provisional toxicity factor at the time. With newer studies available, EPA has since revised the provisional toxicity factor and now recommends a level of 40 µg/l as the appropriate cleanup target for lithium.

The last five years of groundwater sample results show apparent downward trends in contaminant concentration in the two downgradient well clusters closest to the Site, GMZ-3 and GMZ-4. In GMZ-3, the nearest downgradient well cluster, approximately 2,200 feet from the quarry area, the levels of lithium appear to be dropping in all three monitored zones. Lithium levels have decreased from 6,100 µg/l to 3,520 µg/l in the deep zone, a 42% decrease; from 6,300 µg/l to 3,340 µg/l in the intermediate zone, a 47% decrease; and from 4,700 µg/l to 1,330 µg/l in the shallow zone, a 72% decrease. Graphing the results of the lithium concentrations indicate a clear declining trend over time in all three zones at this location. Graphs are included in Attachment 3.

In GMZ-4, the next downgradient well cluster, approximately 4,400 feet from the quarry area, the levels of lithium also appear to be dropping in all three monitored zones. Lithium levels in the deep zone have decreased from a high of 2,700 µg/l to 1,540 µg/l, a 43% decrease; in the intermediate zone from 2,700 µg/l to 1,360 µg/l, a 50% decrease; and from 1,800 µg/l to 949 µg/l in the shallow zone, a 47% decrease.

Lithium results from the furthest monitoring well, GMZ-1, which is a single deep well located approximately 8,400 feet from the quarry area, have been variable within the range from 610 µg/l to 940 µg/l. The results suggest an apparent increasing contaminant trend which at this location could be an expression of the lag time associated with groundwater movement. As this monitoring point is over 8,000 feet distant from the quarry area, it is believed that the well is still showing the temporary increase in contamination due to the disturbance of the waste caused by the remedial activities conducted between 2007 and 2010; the expected reduction in groundwater contamination as a result of stabilizing and capping the waste would not have had time to travel the distance to this well.

Inspection of the results from wells GMZ-3 and GMZ-4, the monitoring wells closest to the source areas, indicate declining concentrations trends for lithium, the primary Site contaminant in the downgradient plume. However, inclusion of the results from well GMZ-1 shows that a comprehensive decrease in lithium concentrations throughout the entirety of the 10,000-foot downgradient contaminant plume has not yet been established. Results for bromate also suggest mostly downward trends but the results are more variable, and the suggested trends are not as strongly indicated.

As discussed above, concentrations in the downgradient plume indicate that the expected decline in downgradient contamination is progressing. However, concentrations of lithium in on-Site monitoring well MW-22 have remained high - and relatively stable - in the range of 13,000 to 25,000 µg/l as shown in the graph in Attachment 3. Continuing sampling data will be evaluated and potentially considered for alternative remedial strategies. It is important to remember that MW-22 and other on-Site wells are within the former facility area of the Site which is subject to the drinking water institutional controls implemented by Chester County and the non-disturbance requirements of the Environmental Covenant.

Surface water from four locations on East Valley Creek are also sampled during each groundwater monitoring event. The sampling results are summarized in Attachment 3. Originally the four sampling locations were SW-1, SW-2, SW-3 and SW-4 (depicted on Figure 2). Of the original four locations SW-1 is furthest from the quarry area at approximately 8,400 feet to the east; however, it is immediately downstream of an identified groundwater discharge and has historically showed the highest levels of site-related contaminants. Location SW-2, closer to the Site at approximately 7,800 feet from the quarry area, has displayed significantly lower concentrations of site-related contaminants. The two locations closest to the quarry area, SW-3 and SW-4, typically displayed very low or non-detect levels of site related contaminants and were, therefore discontinued in 2015. The further downstream locations SW-5 and SW-6 were selected as replacement locations.

EPA does not have ecotoxicological benchmarks for lithium and there is limited information in the literature for the toxicity of lithium to ecological receptors in surface water (Attachment 4). One of the few available studies indicated that concentrations of Li as low as 500 µg/l can produce observed ecological effects, specifically, reduced fathead minnow growth and reduced Ceriodaphnia reproduction. A more recent study, using water with different hardness parameters suggests that observed effects could be exhibited at lower concentrations.

Results of the surface water sampling (summarized in Attachment 3) show a high degree of variability caused by seasonal or precipitation effects on the creek. Stream flow volume, and therefore dilution, responds stronger and faster to precipitation events; the response in underlying groundwater is more moderate. The highest concentrations of lithium in the creek, ranging from 294 to 1100 µg/l, have been reported at location SW-01. It is believed that this location is at the end of the groundwater discharge area; water samples taken further downstream report lower concentrations as a result of dilution.

The surface water sample results for the last five years are beginning to suggest downward trending of the contaminant concentrations. And because of the downward trends already identified in monitoring wells GMZ-4 and GMZ-3, it is expected that the contaminant levels in the groundwater discharging to the creek will also continue to decrease with time, resulting in lower contamination levels in the stream. If, however, decreasing trends do not continue, EPA may consider a further evaluation of the creek and possible alternative remedial strategy.

Site Inspection

The Site inspection for this FYR was conducted on June 18, 2019. In attendance from EPA were the Remedial Project Manager and Hydrogeologist. Representing PADEP were the Project

Manager and his Supervisor. Also in attendance was a representative of FED and the current owner. The purpose of the inspection was to assess the physical conditions of the Site property and the integrity of the cap. The conditions of the monitoring wells are inspected twice yearly during the sampling events, are in good condition and secured with locking well caps, and therefore were not inspected at this time.

The overall condition of the capped landfill area, including the drainage and erosion control features, was very good and appears to be functioning as designed. The vegetative cover is intact and there are no apparent erosion issues. The storm water drainage features appeared fully functional and the retention basin was dry. The rest of the property is mostly level and vegetated with areas of unfinished construction where redevelopment activities had been started.

V. TECHNICAL ASSESSMENT

QUESTION A: Is the remedy functioning as intended by the decision documents?

Yes. All of the areas of soil contamination identified during the Remedial Investigation and the Remedial Action have been addressed. The areas identified with radiation-contaminated soils were excavated to background and removed from the Site for proper disposal. The non-radiation soil contamination areas were excavated to the ESD-specified criteria, consolidated in the former quarry area, and covered with an engineered cap system. The landfill cap was installed in accordance with the ROD and the Remedial Design, and is in good condition, thereby minimizing direct exposure risks from the consolidated wastes. In combination with the ISS treatment of the South Quarry wastes, the cap also minimizes the potential for migration of contaminants from the landfill to the groundwater.

The site property is currently fenced and not being used, and additional institutional controls to further protect the physical components of the Remedy and prevent residential use of the landfilled area have been negotiated with the current owner leading to the Environmental Covenant for Institutional Controls, signed, and recorded with the Recorder of Deeds Office, Chester County, on September 28, 2017.

All of the impacted, and potentially impacted, downgradient residential wells were abandoned when public water was furnished. EPA has been informed by Aqua America that the former municipal supply well in the plume area has been shut down permanently. The groundwater management zone, instituted under Chester County Health Department's well permitting regulations, prohibits any new wells from being installed and used for drinking water in the identified groundwater contamination plume.

Although groundwater monitoring had been temporarily discontinued at the time of the last FYR due to the bankruptcy of the site owner, monitoring has since resumed and has been consistent.

The ROD stated: "At the First Five Year Review, EPA will evaluate the monitoring data to determine the effectiveness of the source control components of the remedy and whether the cleanup of groundwater throughout the entire plume is likely to occur in a reasonable timeframe. If restoration of the aquifer is unlikely to occur, a Focused Feasibility Study may be required to determine if alternative remedial action is necessary for the areas of the plume where cleanup

levels will not be achieved in a reasonable timeframe.” The data available at the first FYR were not sufficient for such an evaluation. The 2017 FYR Addendum plotted the groundwater data and concluded, “Now, with the additional available data, downward trends in groundwater and surface water have been identified indicating that restoration for the downgradient plume is likely and a Focused Feasibility Study is unnecessary at this time.” Data collected since 2017 further supports this conclusion.

QUESTION B: Are the exposure assumptions, toxicity data, cleanup levels, and remedial action objectives (RAOs) used at the time of the remedy selection still valid?

No. However, the Remedy is effective in preventing exposure to contaminated soil and groundwater. The following specific questions address the protectiveness of the remedy in light of changes to risk assessment inputs and methodology.

Changes in Standards and TBCs

Have standards identified as ARARs, newly promulgated standards, and/or changes in TBCs been revised, and would such revisions call into question the protectiveness of the remedy?

The MCLs listed in Table III of the ROD are still current. Table III also contained two risk-based standards (RBRs) for boron and lithium, which had (and have) neither MCLs nor MCLGs. The provisional toxicity factor for lithium has become 10X more conservative, and the ROD’s RBR for lithium of 260 µg/L would no longer be protective. The current tap water Regional Screening Level (RSL) for lithium is 40 µg/L. Boron’s toxicity factors were updated in 2004 and the current RSL of 4,000 µg/L is greater than the ROD’s RBR of 1,340 µg/L. However, the ROD also set an overall groundwater cleanup goal that “the total cancer risk for Site-related contaminants in groundwater shall not exceed EPA’s acceptable cancer risk range (1E-4 to 1E-6), and the target organ Hazard Indexes for Site-related groundwater chemicals shall not exceed 1” although “cleanup will not be required below background levels.” That total risk standard is still protective, and thus the groundwater ROD goals, taken as a whole, are still protective.

The groundwater goals have not been met yet. Monitoring data since the last Five-Year Review show MCL exceedances in recent rounds for bromate, boron, lithium, benzene, TCE, and PCE. (Exceedances for arsenic and chromium occurred early in the monitoring period, but not in the past few years.) The groundwater is not currently used and groundwater monitoring will continue to be performed.

The soil cleanup goals were set in the ROD and changed in the ESD to the “Final Cleanup Standards” shown in ESD Table 2. (Although “Alternate Cleanup Standards” were also identified in ESD Table 2, for soils beneath a geomembrane at depths greater than 15 feet, reportedly these Alternate goals were never used. The Final Cleanup Standards were achievable at depths less than 15 feet or at bedrock.)

The soils disposed offsite, and the soils beneath the cap, have been effectively removed from contact with potential receptors. However, the remaining soils that met the Final Cleanup Standards are available for potential future uses, including possible residential use, as described

in the ROD and ESD. Therefore, the risk assessment in Attachment 6 was performed to determine whether the Final Cleanup Standards would still be protective.

The HIs for child residents exposed to these goals would exceed 1 for fluoride, manganese, and thallium; for adult residents, the HI would exceed 1 for manganese. Therefore, the ESD soil goals would not still be protective. The hexavalent chromium cancer risk for future residents would be approximately $1\text{E-}4$.

However, the actual concentrations left in the soil are not likely to mirror the cleanup standards exactly, and may be much lower. Also, background concentrations have to be considered. Finally, in addition to these chemical-specific goals, the ESD also identified a total risk standard [“contaminant levels in the soils that remain following excavation shall not present an unacceptable direct contact risk (target goals of calculated cancer risk level greater than $1\text{E-}04$ or hazard index greater than 1) for the future resident child scenario.”] Therefore, an updated risk assessment using the actual soil concentrations would be recommended to make the final determination on protectiveness. The 2017 FYR Addendum concluded, “The site is currently fenced and vacant with no specific plans for redevelopment and toxicity values are frequently updated. Therefore, an update to the risk assessment should be conducted when actual plans for site use are developed, in consideration of the planned use and site conditions existing at that time.”

Soil-to-groundwater migration was also considered when the soil goals were set. However, the site conditions have now been altered by excavation, backfilling, ISS, and capping, with the intention of reducing migration to groundwater. Rather than relying on models and assumptions, the groundwater can now be monitored directly to determine if migration is occurring. Groundwater monitoring will continue to be performed.

Changes in Toxicity and Risk Assessment Methods

Have toxicity factors or other contaminant characteristics changed in a way that could affect the protectiveness of the remedy? Have EPA’s standardized risk methodologies or guidance changed in a way that could affect the protectiveness of the remedy?

Toxicity factors for many chemicals, including chromium, lithium and TCE, have changed. Methodology for mutagenic risk estimates, especially for TCE, has changed. However, the overall groundwater goals were based on cumulative risk and are still protective. The soil risks were evaluated in Attachment 6 and are discussed above, along with the soil-to-groundwater pathway.

Changes in Exposure Pathways

Have current or reasonably anticipated future land uses on or near the site changed? Might they change in the near future (including redevelopment or changed resource use)? If so, would this affect the protectiveness of the remedy?

No. The Site is currently fenced and vacant, and the senior community that was contemplated earlier has not been built. However, the prospective use of the Site, which is restricted over the

capped quarries, but available elsewhere for uses including residential use, has not changed. As noted above and in the 2017 FYR Addendum, an update to the soil risk assessment should be conducted when actual plans for Site use are developed.

Have routes of exposure or receptors been newly identified or changed in a way that could affect the protectiveness of the remedy? Have physical conditions or the understanding of these conditions changed in a way that could affect the protectiveness of the remedy?

Given the presence of VOCs in the subsurface environment at MW-22 (PCE up to 240 ug/L in October 2018), vapor intrusion may be a concern if redevelopment occurs at the Site. Vapor intrusion should be evaluated for any new buildings, unless vapor mitigation is incorporated into the construction. No construction is imminent at this time.

Surface water was not identified in the ROD or ESD as a medium of concern, and therefore no cleanup goals were established. However, site-related metals are still present in surface water. Therefore, surface water was evaluated to ensure that it would still not be a medium of concern. Surface water data from June and October 2018 were available.

As discussed above, East Valley Creek flows across a geologic fracture zone approximately one mile downgradient of the Site where contaminated groundwater discharges into the creek. Because of this zone the highest concentrations of metals were found in SW-1 and SW-5, relatively far from the Site. The presence of lithium and bromate indicates that the metals are site-related. The 2018 monitoring data were screened against ten times the tap water RSLs (to account for the expectation that surface water recreational exposure would be at least 10X less than tap water exposure). Arsenic, chromium, lithium, thallium, and bromate exceeded these screening levels. A simple risk assessment was performed for potential 15-kg child recreational exposure, using the maximum 2018 surface water concentrations for those five metals and assuming an ingestion rate of 50 mL/hr, 2.6 hrs/day exposure (both from Risk Assessment Guidance for Superfund, or RAGS, Volume I Part A), an exposure frequency of 100 days/year (as a conservative estimate), for six years (from EPA's 1991 and 2015 Standard Default Exposure Factors), and assuming an exposed skin surface area about half of the body, or 3200 cm². The partition coefficient (Kp) was the metal default Kp of 1E-3 cm/hr from RAGS Volume I Part E (except for chromium, where the chemical-specific 2E-3 cm/hr was used), and the toxicity factors were the same as those listed in the fall 2018 RSL Table. Even under these conservative conditions, the Hazard Index would not exceed 1, and the cancer risk would be approximately 5E-5, within the acceptable risk range.

Therefore, it can be concluded that while site-related metals are present in surface water, the concentrations are currently within the acceptable range for human recreational exposure.

EPA does not have ecotoxicological benchmarks for lithium and there is limited information in the literature for the toxicity of lithium to ecological receptors (Attachment 4). One of the few available studies indicated that concentrations of Li as low as 500 µg/l can produce observed ecological effects, specifically, reduced fathead minnow growth and reduced Ceriodaphnia reproduction. A more recent study, using water with different hardness parameters suggests that observed effects could be exhibited at lower concentrations.

Are there any newly identified contaminants or contaminant sources leading to a potential/actual pathway not previously addressed by the remedy? Are there unanticipated toxic byproducts or daughter products of the remedy not previously addressed by the decision documents?

Vinyl chloride is a carcinogenic breakdown product of more highly chlorinated ethenes, and therefore MW-22 should be monitored for vinyl chloride. This was recommended in the first FYR, and the 2017 FYR Addendum reported that EPA had obtained at least one sample that was non-detect for vinyl chloride. However, since vinyl chloride is a breakdown product of the VOCs that are expected to decline over time, periodic monitoring of VOCs and evaluation of the need for further monitoring of vinyl chloride is recommended.

For sites where volatile solvents have been found, EPA has become aware that the solvent stabilizer 1,4-dioxane may be present also. However, 1,1,1-trichloroethane, the chemical most closely associated with 1,4-dioxane, was not detected at substantial concentrations in the RI. (It was detected occasionally at trace to low levels.) Therefore, sampling for 1,4-dioxane was not conducted.

Expected Progress Toward Meeting RAOs

Is the remedy progressing as expected toward meeting RAOs? Have new site conditions (e.g., discovery of new contaminants) impacted RAOs and remedy protectiveness?

The remedy does appear to be progressing, although there have been data gaps, which lead to the following conclusions:

The groundwater goals have not been met yet. Groundwater monitoring should continue.

The ESD soil cleanup goals no longer meet the protectiveness standard for a future resident, but the actual soil concentrations may be protective. An updated risk assessment using the actual soil concentrations is recommended when a new use of the Site is proposed to make the determination on protectiveness.

If buildings are constructed at the Site before the VOCs in well MW-22 dissipate, then vapor intrusion should be evaluated for new buildings, unless vapor mitigation is incorporated into the construction.

Vinyl chloride is a carcinogenic breakdown product of more highly chlorinated ethenes, and therefore MW-22 should be monitored periodically for vinyl chloride to detect any change in concentration.

QUESTION C: Has any other information come to light that could call into question the protectiveness of the remedy?

No. There is no new information that would question the protectiveness of the remedy.

VI. ISSUES/RECOMMENDATIONS

OU(s) without Issues/Recommendations Identified in the Five-Year Review:	
OU1 - Sitewide	

No issues that would affect current or future protectiveness at this Site were identified.

OTHER FINDINGS

Toxicity values for lithium and other contaminants have become more conservative. Therefore, an update to the risk assessment should be conducted when actual plans for Site use are developed, in consideration of the planned use and Site conditions existing at that time.

Vinyl chloride is a carcinogenic breakdown product of more highly chlorinated ethenes, and therefore there is the potential for it to be generated in MW-22. The 2017 FYR Addendum reported that a split sample from MW-22 showed only low levels of organics and was non-detect for vinyl chloride. However, periodic monitoring of vinyl chloride should be considered as part of the FYR process. If redevelopment of the Site is planned at the Site before the VOCs in well MW-22 dissipate, the potential for vapor intrusion should be evaluated for new buildings, unless vapor mitigation is incorporated into the planned construction.

EPA will continue to monitor lithium concentrations in groundwater and the creek and, if the declining trends do not continue, may evaluate the need for alternative remedial strategies. Because EPA does not have ecotoxicological benchmarks for lithium, and there is limited information in the literature for the toxicity of lithium to ecological receptors, EPA will continue to monitor the literature for applicable studies.

VII. PROTECTIVENESS STATEMENT

<i>Operable Unit:</i> 1 - Sitewide	<i>Protectiveness Determination:</i> Protective
Protectiveness Statement: The Remedy at the Site is protective of human health and the environment because exposure pathways that could result in unacceptable risks are being controlled. The Site is currently unoccupied and surrounded by security fencing. Direct contact with contaminated soil has been minimized by containment of the soils in the capped quarry area. There are no current drinking water wells using contaminated groundwater and institutional controls prohibit the installation of new wells in the contaminated plume. The groundwater and surface water data demonstrate that the remedial measures implemented at the Site are effective in minimizing the downgradient migration and discharge of contaminants to the surface water. Downgradient groundwater data is showing declining contaminant concentrations over time and, in response, surface water samples are also showing declining trends in the groundwater discharge area. Monitoring data will continue to be evaluated as concentrations continue to decline.	

VIII. GOVERNMENT PERFORMANCE AND RESULTS ACT MEASURES

As part of this five-year review, the Government Performance and Results Act (GPRA) Measures have been reviewed. The GPRA Measures and their status are as follows:

Environmental Indicators

Human Health: Current Human Exposures Controlled and Protective Remedy in Place (HEUC-HEPR)

Groundwater Migration: Contaminated Groundwater Migration Under Control (GMUC)

Sitewide Ready for Anticipated Use (SWRAU)

The Site has achieved SWRAU (1/5/2018)

IX. NEXT REVIEW

The next FYR for the Site is required five years from the date of this review.

Figure 1

Site Location Map

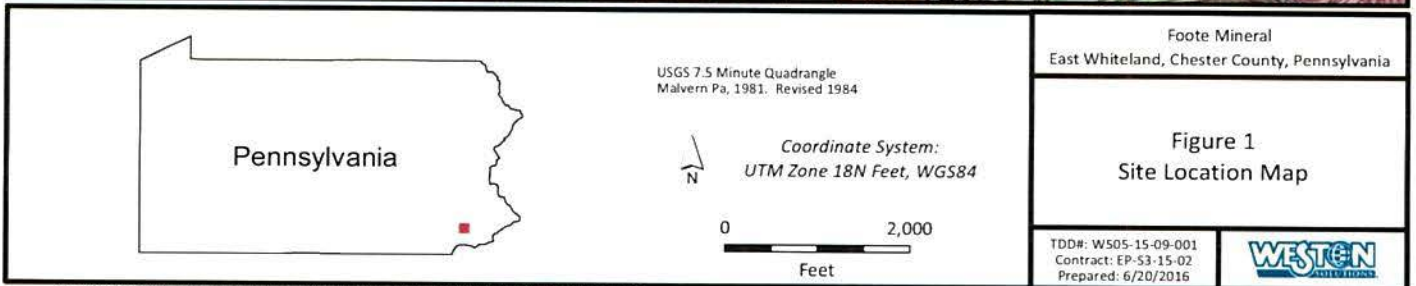
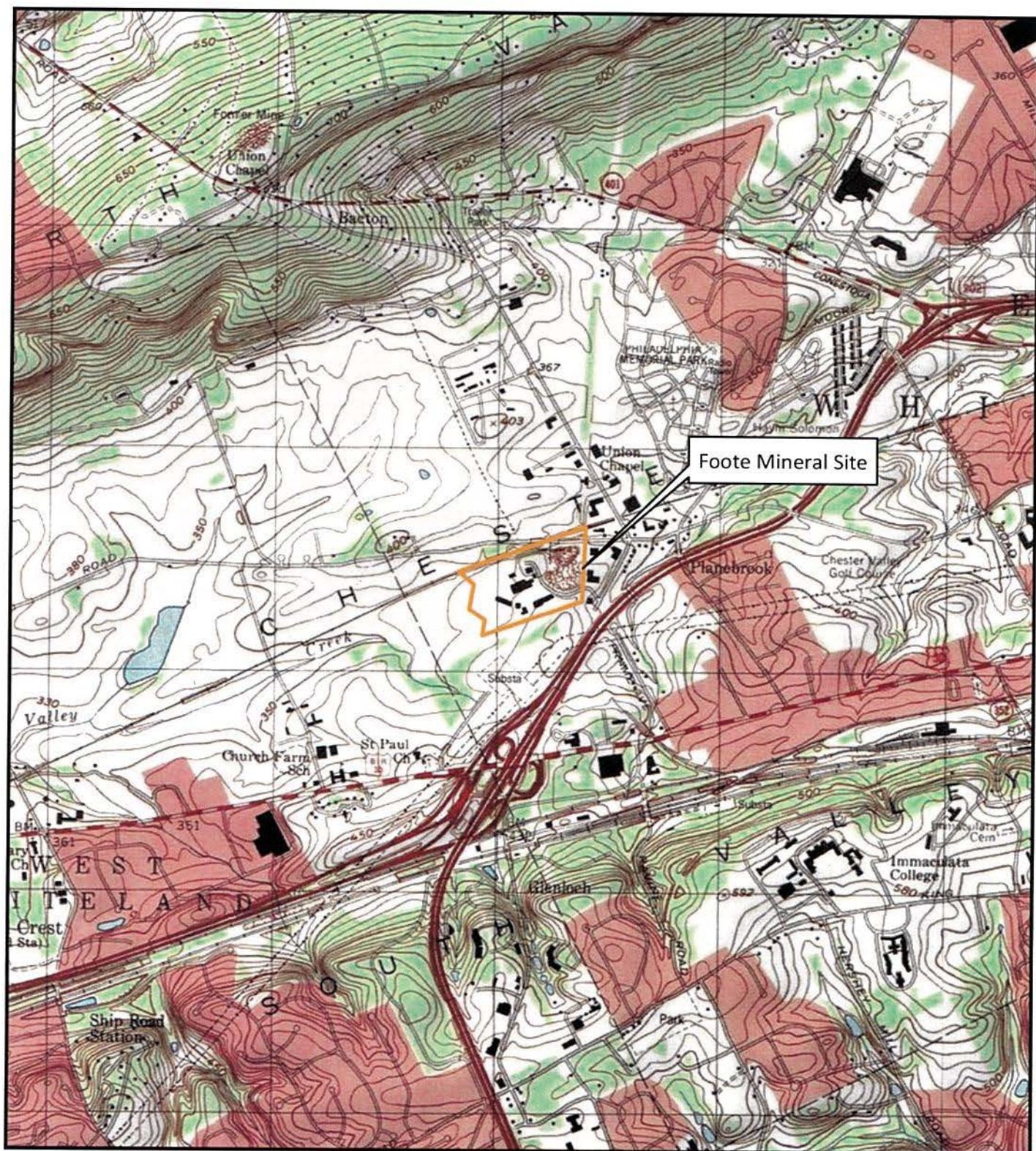
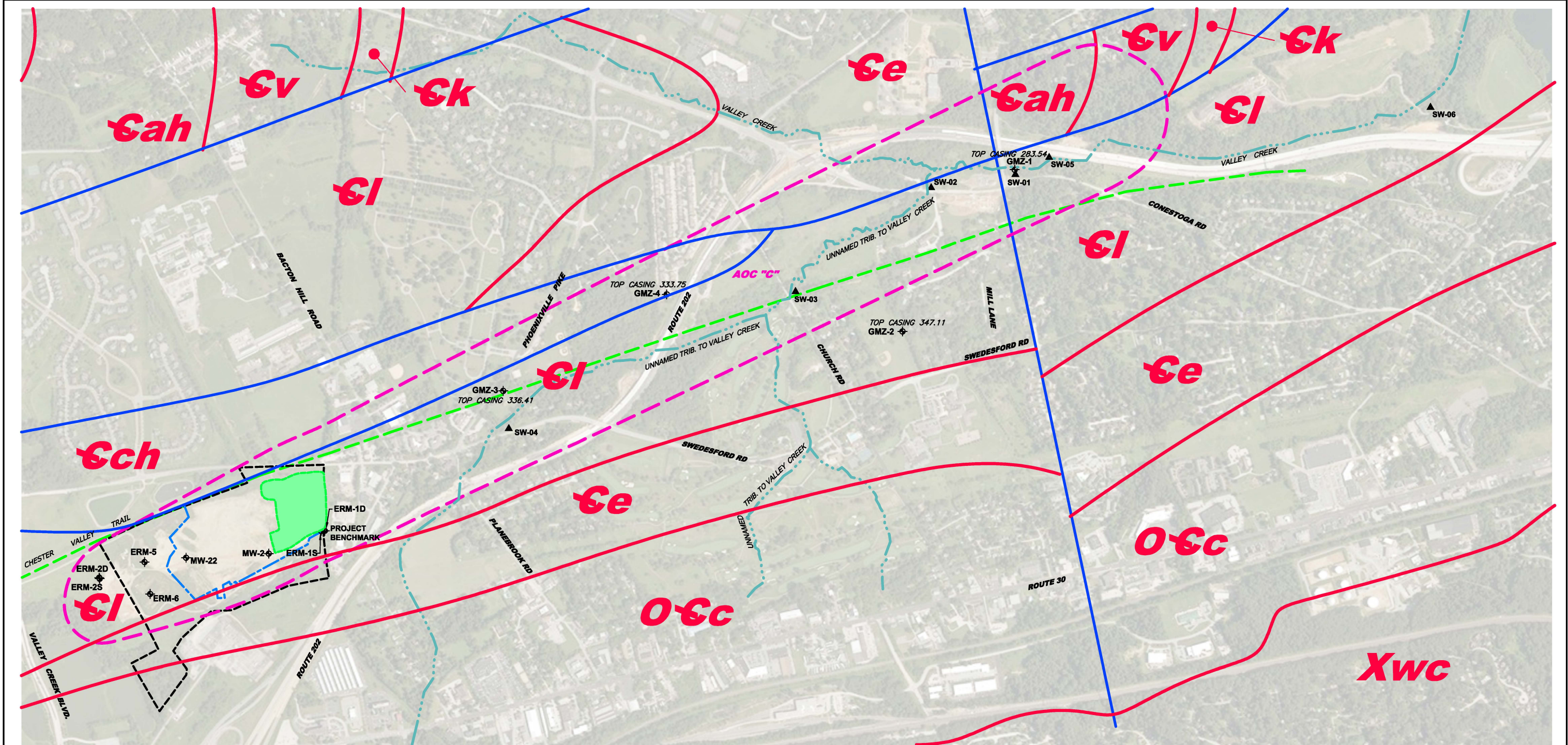


Figure 2

Site Layout: Property and Surface Water
and Monitoring Well Locations



LEGEND

- PROPERTY BOUNDARY
- SUPERFUND SITE BOUNDARY
- PROPOSED GROUNDWATER AREA OF CONCERN (AOC) AS DEFINED IN ROD
- GEOLOGIC FORMATION CONTACT LINE
- FAULT LINE
- EAST VALLEY CREEK AND UNNAMED TRIBUTARIES
- TRAIL (FORMER RAILROAD)
- SURFACE WATER SAMPLING LOCATION
- BENCHMARK/MONITORING WELL LOCATIONS
- QUARRY CAP

NOTES

1. ALL LOCATIONS ARE APPROXIMATE.

Sch CHICKIES FORMATION

Se ELBROOK FORMATION

Sl LEDGER FORMATION

Sah ANTIETAM-HARPERS FORMATION

OSc CONESTOGA FORMATION

Sv VINTAGE FORMATION

Sk KINZERS FORMATION

Xwc OCTORARO FORMATION

REFERENCE

1. BASE MAP INFORMATION FROM "AS-BUILT GROUNDWATER MANAGEMENT ZONE PLAN" FROM EDWARD B. WALSH AND ASSOCIATES, INC., MAY 6, 2015.

BENCHMARK AND WELL LOCATIONS

BENCHMARK DESCRIPTION:
1.7 MILES SOUTHWEST OF FRAZER ALONG PENNSYLVANIA RAILROAD BRIDGE AT THE GLENLOCH STATION, AT NORTHERLY-MOST RAILROAD BRIDGE OVER PHOENIXVILLE PIKE AT THE SOUTHWEST WING WALL. STANDARD DISK STAMPED K 106 1935, ELEVATION=431.93, DATUM: NGVD 1929

POINT ID	NORTHING	EASTING	ELEVATION
IP FND	264,889.817	2575468.331	386.96

WELL COORDINATES:

POINT ID	NORTHING	EASTING	ELEVATION
GMZ-1	269034.1737	2583091.8555	283.54
GMZ-2	267219.3652	2581883.5308	347.11
GMZ-3	266474.3748	2577472.4092	336.41
GMZ-4	267579.1973	2579263.1050	333.75

0 550 1100 2200

SCALE IN FEET

REV. NO.	DATE	DESCRIPTION OF REVISION	REV. BY	ENG	CHKD BY	APPVD BY
PROJECT MANAGER:	W. TORRES	DRAWN BY:	D. TAYLOR	DATE: 05.08.15		

TerranearPMC

FIGURE 1

FOOTE MINERAL GMP GROUNDWATER AOC, SITE BOUNDARY, GMZ WELL COORDINATES, AND GEOLOGIC FORMATIONS

EAST WHITELAND TOWNSHIP, CHESTER COUNTY, PA

PROJECT NO.	TASK NO.	CHKD:	DRAWING NUMBER	REV. NO.
10104	100	ENG.	100A201-1A	0
		APPVD:	SCALE: 1" = 1100'	

Foote Mineral Figure 2 - Monitoring Well and Surface Water Locations

Attachment 1

Additional Site Background and Dates

Attachment 1: Additional Background and Dates

Chronology of Site Events

Event	Date
Initial discovery of problem or contamination	1969
National Priorities List listing	10/14/1992
Remedial Investigation/Feasibility Study started	9/30/1996
Removal Action for waterline installation Physical construction completed	8/20/2004
Record Of Decision (“ROD”)	3/31/2006
Remedial Design start	1/22/2007
Remedial Design complete	7/06/2007
Start of On-Site Physical Construction (physical construction began on one part of the Remedy before the design of all components was approved)	5/25/2006
Remedial Action start	7/06/2007
Explanation of Significant Differences (“ESD”)	4/07/2008
Remedial Action Completion (In-Situ Stabilization)	5/10/2010
Preliminary Close Out Report (“PCOR”) (Denotes Completion of On-Site Physical Construction)	10/28/2010
Remedial Action Completion (Excavation, Waste Consolidation and Capping)	9/28/2011
First Five-Year Review	9/29/2014
Five-Year Review Addendum	8/03/2017
Environmental Covenant for Institutional Controls	9/28/2017

Site Background

Physical Characteristics

Site Features

The Foote Mineral Co. Superfund Site (the “Site” depicted in Figure 1) is comprised of the waste materials and contaminated soils, groundwater, surface water and sediment located on and extending from an approximately 79 acre property (the “Property”). The street address at the front of the Property is 15 South Bacton Hill Road in East Whiteland Township, Chester County, Pennsylvania. The eastern portion of the Property was previously operated as a lithium processing plant called the Frazer Facility of the Foote Mineral Company (“Foote Mineral”) and includes two former quarries (“North Quarry” and “South Quarry”) that were used for waste disposal and a large chemical processing area formerly occupied by over fifty buildings and settling ponds. The western portion of the Property was historically used for farming and was determined to be uncontaminated. The township boundary crosses through the Property such that the western, uncontaminated, portion is located in West Whiteland Township. Only the contaminated areas of the Property - the eastern portion - are included as part of the Site. But the Site also includes the area of groundwater contamination that has migrated eastward, away from the Property. Site-related contamination has been found in groundwater approximately 10,000 feet east-northeast of the quarries.

Land and Resource Use

The contaminated areas located on the Property have been remediated; all old process buildings and foundations were removed, all contaminated soils were excavated and consolidated in the quarries, and the quarry area filled, graded and capped, so that the Property appears as a capped, vegetated landfill surrounded by open, partially excavated fields. The contaminated groundwater plume extends underground to the east of the Property. Residential wells were abandoned when public water was furnished in 2004. Aqua America shut down the former municipal supply well in the plume area in 2002. The areas above the plume and surrounding the Site are a mix of commercial and residential developed properties that are supplied by public water. The current owner of the Property has long-term plans to redevelop the Property as residential; however, currently the Property remains vacant and fenced.

Regional Geology

The Site is located in the Chester Valley, a topographic basin shown in the United States Geological Survey’s Malvern quadrangle. Bedrock of the valley floor is made up of largely carbonate limestone and dolomitic rocks. Harder, metamorphic quartzite and schists are found along the valley walls. Chester Valley bedrock is broken by many geologic faults. These faults mostly parallel the east-west axis of the valley. Dolomite of the Ledger formation directly underlies the Property. Directly north of the Property the ground surface is underlain by a wedge of the Chickies Formation quartzite. The boundary between these two rock types is a highly fractured, thrust fault zone. This fault zone forms a linear feature that is oriented roughly east-

northeast. In the area of the Property the fault almost coincides with the Property's northern boundary.

Groundwater in the Chester Valley flows primarily through the fractures in the bedrock. These fractures may be oriented in many directions so that flow direction in specific locations is variable. But overall, the predominant orientation of the fractures is east-northeast, which corresponds to the general orientation of regional groundwater flow.

The specific groundwater and contaminant flow characteristics in the area of the Site were described by the United States Geological Survey (USGS) in an August 2005 report entitled Evaluation of Hydrogeology and Ground-water flow and Transport at the Foote Mineral company Superfund Site, East and West Whiteland Townships, Chester County, Pennsylvania. The USGS report was commissioned by EPA in December 2004.

The USGS report describes the local groundwater flowing in a direction that is primarily west to east through the Ledger dolomite. Contaminants leaching from sources on the Property enter the groundwater and are carried along the same path. The resulting contaminant plume has been found to be very long and narrow. The plume of contaminants was estimated to extend approximately 10,000 feet east-northeast from the quarries, but the width of the contaminant plume is relatively narrow as a result of clean water flowing into the fault zone from both the south and north sides of the valley. This tends to restrict the contaminants to the immediate area of the fracture zone. However, if new wells were installed near the plume they could potentially pull water from the plume and cause the contamination to spread.

Surface Water Hydrology

West Valley Creek is located near the western border of the Property. West Valley Creek flows east to west and receives surface drainage from the Property. East Valley Creek is located to the north and east of the Property. Some of the groundwater, and contamination, that flows beneath the Property eventually discharges to a section of East Valley Creek, near Mill Lane, about a mile and a half from the Property.

History of Contamination

In 1932, and for some years prior, the northeastern portion of the Property was quarried for limestone. During quarrying operations, a limestone processing plant operated on the Property. Starting in 1941 various owners and operators of the Foote facility used the Property for the production of lithium chemicals and the processing of a variety of ores. During World War II, a portion of the Property was nationalized and operated under the Defense Corporation of America for the production of lithium salts. In 1991, Foote shut down all remaining operations at the facility and moved offsite. At various times throughout active operations at the Property, production wastes were disposed of in the quarries. Construction and demolition debris, waste water, and some municipal wastes were disposed of in the North Quarry. The South Quarry was used primarily for the disposal of spent mineral waste slurries and process waters.

Other areas of the Property were also used for disposal including three settling ponds which were used to remove magnetic iron from lepidolite ore, which resulted in residual lithium contamination. Pyrophoric (extremely flammable) wastes were burned in a pit on the southwest portion of the Site. Burned wastes contained diethyl ether, n-hexane, n-pentene, benzene, tetrahydrofuran and methanol. An unlined pond on the northwest portion of the facility was utilized to wash production equipment. These areas were subsequently backfilled. Process water was also discharged, after treatment, through a permitted discharge to West Valley Creek.

Over the years these operations generated large amounts of waste materials, some of which were disposed of on the Property resulting in:

- Large volumes of waste in the two on-site quarries
- A groundwater plume contaminated with lithium, chromium, boron, and bromate, and a small area beneath the Property where groundwater was contaminated with organic chemicals, including benzene and tetrachloroethylene;
- Public and private groundwater wells to the east of the Property contaminated with unacceptable levels of boron, lithium, chromium and bromate;
- Areas of the Property where soil was contaminated with petroleum hydrocarbons and wastes from processing ores and minerals;
- Runoff, caused by precipitation, carrying sediment into nearby surface water; and
- Discrete areas of soil contaminated with low-level radiation believed to be the residual dust from certain mineral ores.

Attachment 2

April 4, 2019, Site Inspection Checklist

SITE INSPECTION CHECK LIST
CAP COVER
FOOTE MINERALS SUPERFUND SITE
EAST WHITELAND TOWNSHIP, PA

Date of Inspection: 4-3-19

Initials of Inspector: AS

ITEM	Requires Attention	Adequate	Not Observed	COMMENTS
A. General Conditions of Cover Material				
1.) Saturated Areas				
a.) Areas that are constantly wet			✓	
b.) Areas that are soft and muddy			✓	
c.) Areas rutted during mowing events			✓	
d.) Areas rutted by other vehicle traffic			✓	
2.) Ponded Surface Water				
a.) Standing water observed			✓	
b.) New ponding areas observed			✓	
c.) Is the ponded water discolored			✓	
d.) Does the ponded water drain or does the water remain stagnant			✓	
e.) Areas where surface drainage is is blocked or backed-up			✓	
B. Settlement Control				
1.) Depressions				
a.) Bowl shaped areas observed			✓	
b.) Observed "potholes" within the landfill cap limits			✓	
c.) Are the depressed areas holding water (See A.3 above)			✓	
d.) Soil placement needed for repair			✓	
C. Erosion Control				
1.) Erosion Rills				
a.) Soil cover washed away			✓	
b.) Observed cracks in the soil cover			✓	
c.) Soil needed to repair damage			✓	
d.) Is eroded sediment leaving the site			✓	
e.) Silt fence installation necessary			✓	
f.) Bare spots observed			✓	

**SITE INSPECTION CHECK LIST
SURFACE WATER MANAGEMENT
FOOTE MINERALS SUPERFUND SITE
EAST WHITELAND TOWNSHIP, PA**

Date of Inspection: 4-3-19
Surface Water Management

Initials of Inspector [Signature]

ITEM	<u>Needs Attention</u>	<u>Adequate</u>	<u>Not Observed</u>	<u>COMMENTS</u>
A. Condition of Channels				
1.) Channel Integrity		✓		
2.) Riprap Integrity		✓		
3.) Flow outside of the channel limits			✓	
4.) Channel discharges to the basin		✓		
5.) Perimeter Soil Berm		✓		
B. Settlement Control				
1.) Water directed into the basin		✓		
2.) Drainage paths holding water			✓	
3.) Depressions collecting runoff			✓	
C. Erosion Control				
1.) Runoff causing erosion rills			✓	
2.) Runoff is delaying mowing			✓	
3.) Rutting from mowing is cause of erosion			✓	
D. Silt/Sediment Accumulation				
1.) Sediment leaving the site			✓	
E. Spillways				
1.) Condition of emergency spillway		✓		
2.) Principal spillway blocked			✓	
F. Integrity of Outfall				
1.) Outfall pipe blocked			✓	
2.) Outfall pipe in working condition		✓		
3.) Outfall pipe damaged by settlement			✓	
4.) Animal nests in outfall pipe			✓	
5.) Erosion in plunge pool			✓	
6.) Scouring in Rails to Trails channel			✓	
G. General Basin Conditions				
1.) Faircloth Skimmer damaged			✓	
2.) Erosion in rip rap lined side slopes			✓	
3.) Woody vegetation growing in basin			✓	

NOTES:

- 1.) Areas identified for repair should be amended prior to the next site inspection.
- 2.) Areas identified as in need of repair should also be approximately located on the attached site figure.
- 3.) A site inspection should be performed following a rain event exceeding 3 inches over a 24-hour time period and then followed up 2 days later.

Additional Observations:

Attachment 3

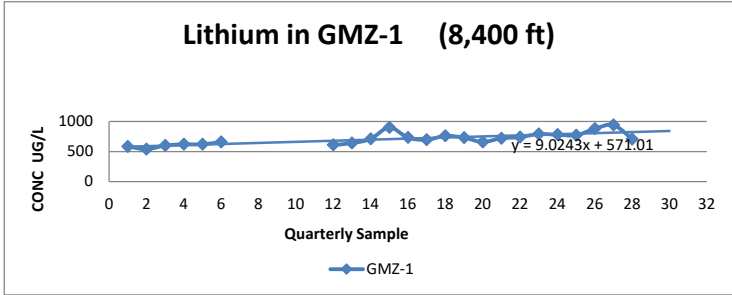
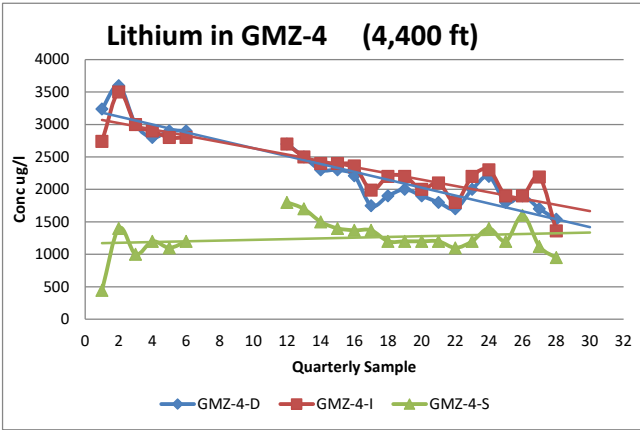
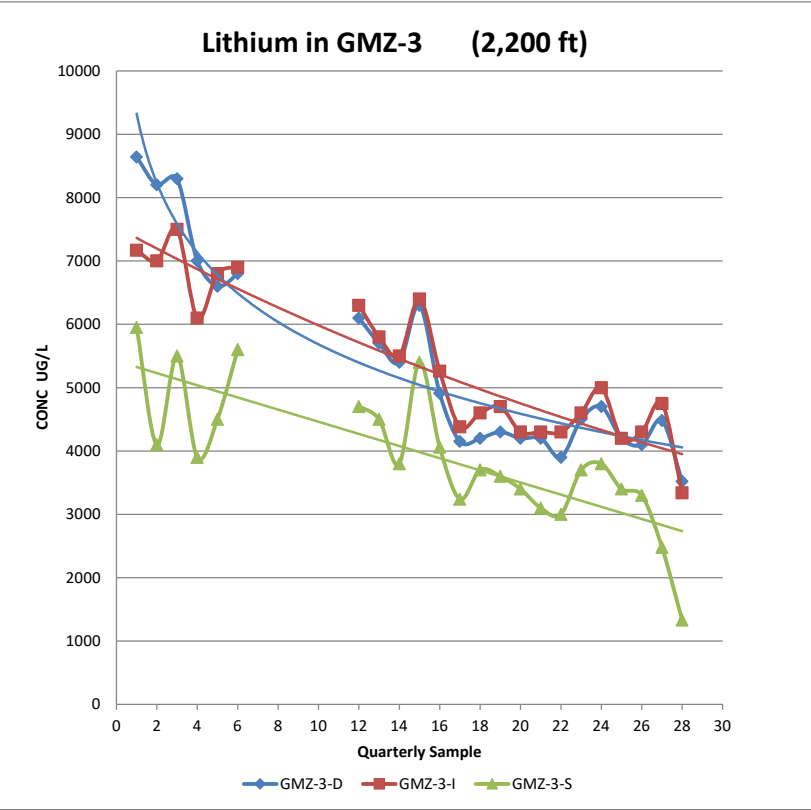
Summary of Sampling Results Tables and Graphs

FOOTE MINERAL SUPERFUND SITE
GROUNDWATER MONITORING RESULTS

LITHIUM (STD-260)

	1	2	3	4	5	6		12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
(on-site)	2010 DEC	2011 MAR	2011 JUN	2011 SEP	2011 DEC	2012 MAR		2013SEP	2013DEC	2014MAR	2014JUN	2014OCT	2015MAR	2015JUN	2015SEP	2015NOV	2016MAR	2016MAY	2016SEP	2016DEC	2017JUN	2018JAN	2018JUN	2018OCT
ERM 1D	8475.8	7600	7200	6800	6700	7200		6400	5900	5600	6800	5680	4770	5300	NS	4500	4500	4000	5100	4800	2800	4300	2170	1500
ERM 1S	492.6	200	240	330	250	330		270	600	330	370	NS	170	220	NS	NS	NS	NS	NS	NS	NS	NS	ns	
ERM 2D	91.8	92	99	87	81	90		91	89	84	87	75	81.3	75	ND	83	83	73	89	85	84	81	74.5	8.1
ERM 2S	357.5	370	330	320	320	360		330	350	380	360	341	330	330	2.1J	310	350	350	350	400	340	350	372	306
ERM 5	26.5	28	27	30	16	25		24	27	24	30	30.8	285	24	24	27	21	23	24	32	29	31	23.5	24.6
MW 22	24198	20000	26000	13000	14000	12800		20000	21000	16000	15000	23100	13200	18000	19000	17000	17000	22000	17000	23000	22000	19000	27300	24800
(plume)	2010 DEC	2011 MAR	2011 JUN	2011 SEP	2011 DEC	2012 MAR		2013SEP	2013DEC	2014MAR	2014JUN	2014OCT	2015MAR	2015JUN	2015SEP	2015NOV	2016MAR	2016MAY	2016SEP	2016DEC	2017JUN	2018JAN	2018JUN	2018OCT
GMZ-1	585	540	600	620	620	660		610	640	710	900	732	696	760	730	660	720	740	790	780	770	880	940	708
GMZ-2-D	3.1	4.5	3.8	0.44	3.8	11		10 U	10 U	ND	ND	0.59 j	1.7J	1.6j	81	8.4j	1.1J	1.8J	1.9j	1.6	2.2	2.5j	6	4.2j
GMZ-2-I	2.7	2.2	2.6	10 U	4.2	10 U		10 U	10 U	ND	ND	2.8 j	2.5J	4.1j	5j	6.7j	4J	3.2J	3.5j	3.5	4	4.1j	4.1j	3.3j
GMZ-2-S	4.2	1	0.98	10 U	0.42	10 U		10 U	10 U	ND	ND	1.2 j	0.56J	2.0j	340j	5.9j	1.6J	1.7J	1.5j	1.2	1.3	1.1j	2.6j	2.6j
GMZ-3-D	8640	8200	8300	7000	6600	6800		6100	5700	5400	6300	4910	4150	4200	4300	4200	4200	3900	4500	4700	4200	4100	4480	3520
GMZ-3-I	7170	7000	7500	6100	6800	6900		6300	5800	5500	6400	5260	4380	4600	4700	4300	4300	4300	4600	5000	4200	4300	4750	3340
GMZ-3-S	5950	4100	5500	3900	4500	5600		4700	4500	3800	5400	4060	3240	3700	3600	3400	3100	3000	3700	3800	3400	3300	2480	1330
GMZ-4-D	3240	3600	3000	2800	2900	2900		2700	2500	2300	2300	2210	1750	1900	2000	1900	1800	1700	2000	2200	1800	1900	1700	1540
GMZ-4-I	2740	3500	3000	2900	2800	2800		2700	2500	2400	2400	2360	1990	2200	2200	2000	2100	1800	2200	2300	1900	1900	2190	1360
GMZ-4-S	444	1400	1000	1200	1100	1200		1800	1700	1500	1400	1370	1370	1200	1200	1200	1200	1100	1200	1400	1200	1600	1120	949
(Surf Wtr)	2010 DEC	2011 MAR	2011 JUN	2011 SEP	2011 DEC	2012 MAR		2013SEP	2013DEC	2014MAR	2014JUN	2014OCT	2015MAR	2015JUN	2015SEP	2015NOV	2016MAR	2016MAY	2016SEP	2016DEC	2017JUN	2018JAN	2018JUN	2018OCT
SW-01	880	530	500	470	460	690		760	900	560	730	1060	730	700	1000	790	660	610	75	750	830	1100	829	470
SW-02	484	150	76	58	320	270		352	500	380	490	408	350	230	300	200	220	38	21	35	71	99	17.4	418
SW-03	3.2	15	3.3	40	42	10 U		5 U	10 U	18	17	4.1												
SW-04	2.4	1.7	2.4	ND	1.4	10 U		5 U	10 U	ND	NS	NS												
SW-05													740	670	1000	800	670	590	53	770	870	1100	900	453
SW-06													560	450	880	720	520	38	35	760	680	900	579	441
#NAME?																								

Foote Mineral Downgradient Wells (distance from source)



FOOTE MINERAL SUPERFUND SITE
GROUNDWATER MONITORING RESULTS

LITHIUM

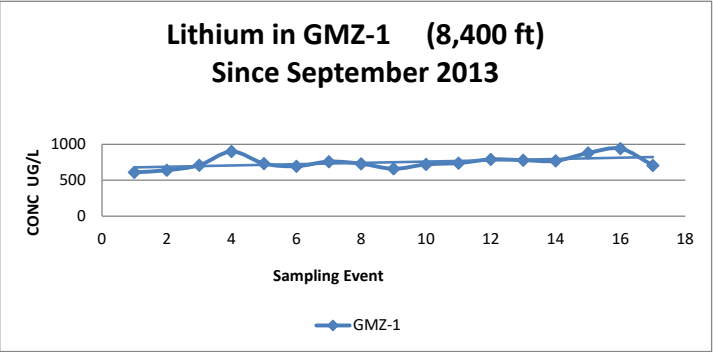
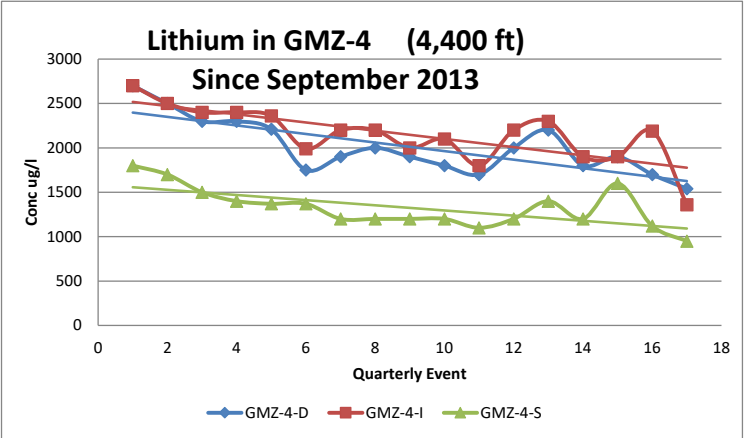
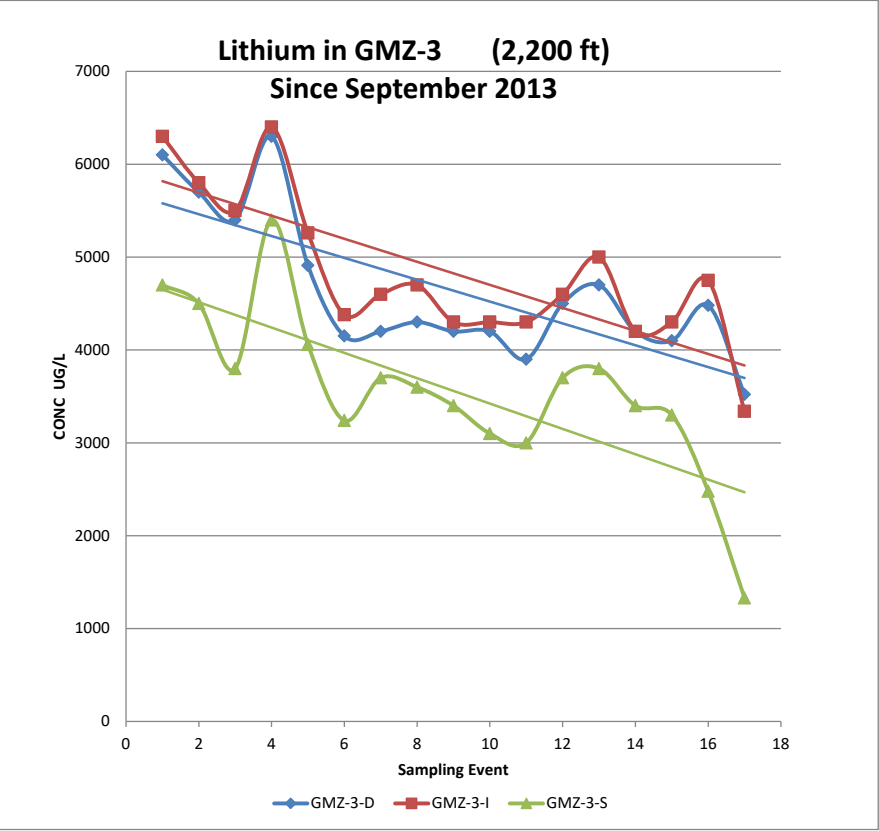
	1	2	3	4	5	6	7	7	9	10	11	12	13	14	15	16	17
(on-site)	2013SEP	2013DEC	2014MAR	2014JUN	2014OCT	2015MAR	2015JUN	2015SEP	2015NOV	2016MAR	2016MAY	2016SEP	2016DEC	2017JUN	2018JAN	2018JUN	2018OCT
ERM 1D	6400	5900	5600	6800	5680	4770	5300	NS	4500	4500	4000	5100	4800	2800	4300	2170	1500
ERM 1S	270	600	330	370	NS	170	220	NS	NS	NS	NS	NS	NS	NS	NS	ns	NS
ERM 2D	91	89	84	87	75	81.3	75	ND	83	83	73	89	85	84	81	74.5	8.1
ERM 2S	330	350	380	360	341	330	330	2.1j	310	350	350	350	400	340	350	372	306
ERM 5	24	27	24	30	30.8	285	24	24	27	21	23	24	32	29	31	23.5	24.6
MW 22	20000	21000	16000	15000	23100	13200	18000	19000	17000	17000	22000	17000	23000	22000	19000	27300	24800

(plume)	2013SEP	2013DEC	2014MAR	2014JUN	2014OCT	2015MAR	2015JUN	2015SEP	2015NOV	2016MAR	2016MAY	2016SEP	2016DEC	2017JUN	2018JAN	2018JUN	2018OCT
GMZ-1	610	640	710	900	732	696	760	730	660	720	740	790	780	770	880	940	708
GMZ-2-D	10 U	10 U	ND	ND	0.59 j	1.7j	1.6j	81	8.4j	1.1j	1.8j	1.9j	1.6	2.2	2.5j	6	4.2j
GMZ-2-I	10 U	10 U	ND	ND	2.8 j	2.5j	4.1j	5j	6.7j	4j	3.2j	3.5j	3.5	4	4.1j	4.1j	3.3j
GMZ-2-S	10 U	10 U	ND	ND	1.2 j	0.56j	2.0j	340j	5.9j	1.6j	1.7j	1.5j	1.2	1.3	1.1j	2.6j	2.6j
GMZ-3-D	6100	5700	5400	6300	4910	4150	4200	4300	4200	4200	3900	4500	4700	4200	4100	4480	3520
GMZ-3-I	6300	5800	5500	6400	5260	4380	4600	4700	4300	4300	4300	4600	5000	4200	4300	4750	3340
GMZ-3-S	4700	4500	3800	5400	4060	3240	3700	3600	3400	3100	3000	3700	3800	3400	3300	2480	1330
GMZ-4-D	2700	2500	2300	2300	2210	1750	1900	2000	1900	1800	1700	2000	2200	1800	1900	1700	1540
GMZ-4-I	2700	2500	2400	2400	2360	1990	2200	2200	2000	2100	1800	2200	2300	1900	1900	2190	1360
GMZ-4-S	1800	1700	1500	1400	1370	1370	1200	1200	1200	1200	1100	1200	1400	1200	1600	1120	949

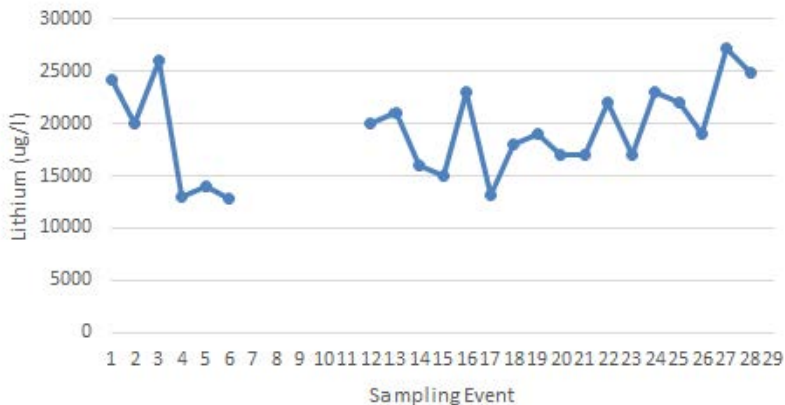
(Surf Wtr)	2013SEP	2013DEC	2014MAR	2014JUN	2014OCT	2015MAR	2015JUN	2015SEP	2015NOV	2016MAR	2016MAY	2016SEP	2016DEC	2017JUN	2018JAN	2018JUN	2018OCT
SW-01	760	900	560	730	1060	730	700	1000	790	660	610	75	750	830	1100	829	470
SW-02	352	500	380	490	408	350	230	300	200	220	38	21	35	71	99	17.4	418
SW-03	5 U	10 U	18	17	4.1												
SW-04	5 U	10 U	ND	NS	NS												
SW-05						740	670	1000	800	670	590	53	770	870	1100	900	453
SW-06						560	450	880	720	520	38	35	760	680	900	579	441
#NAME?																	

Foote Mineral Downgradient wells (Distance from source)

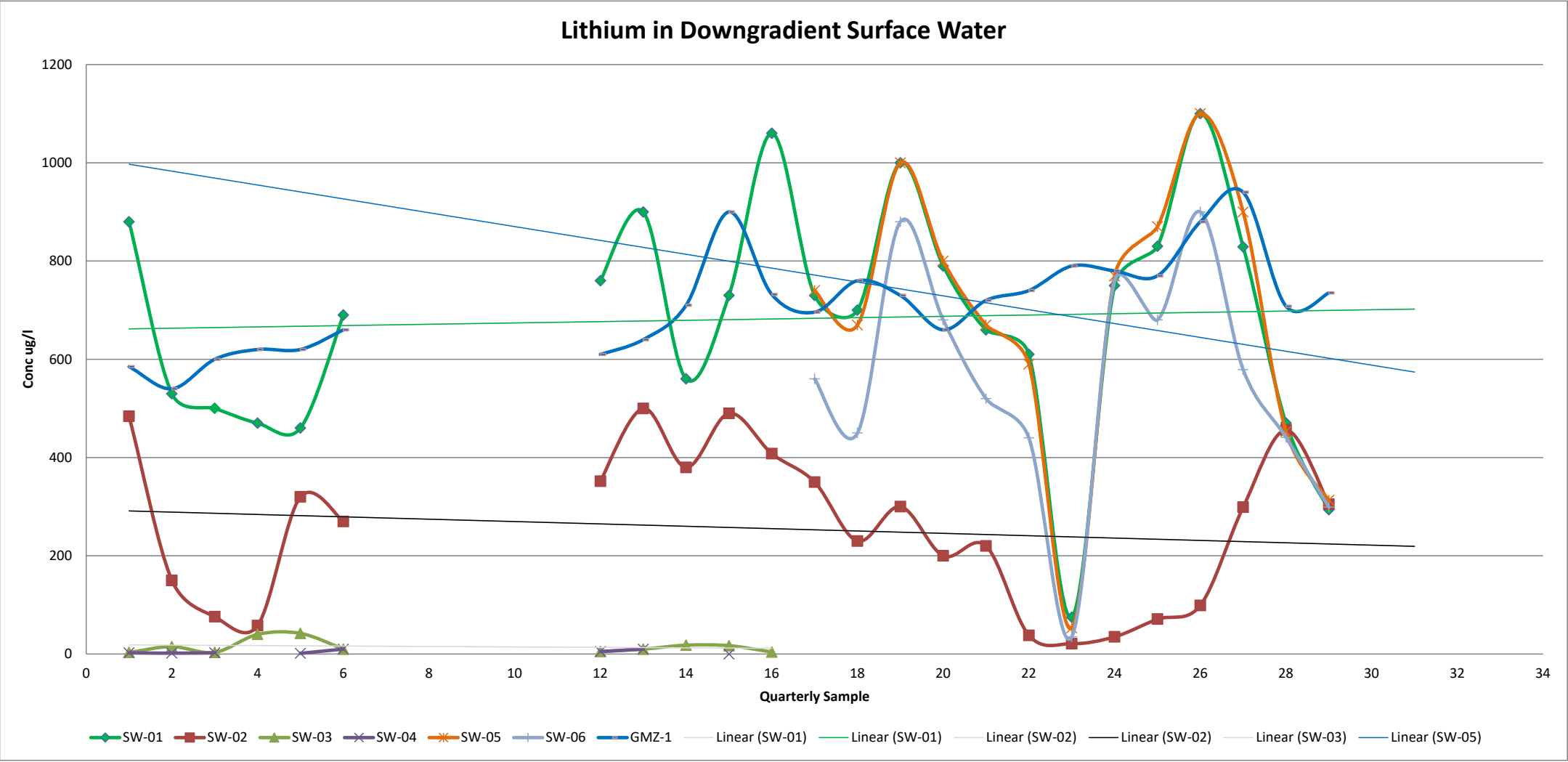
September 2013 to October 2018



Lithium in On-Site MW 22 - Dec 2010 to Oct 2018

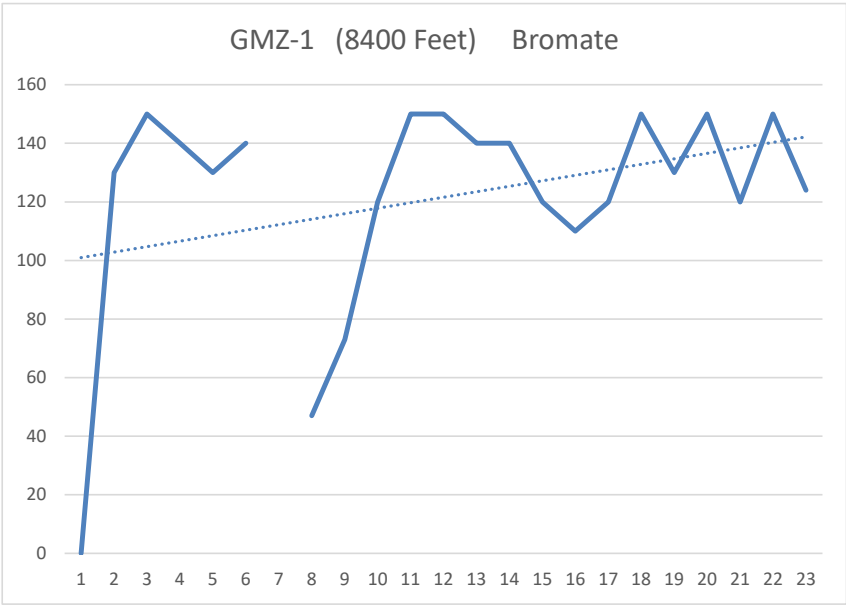
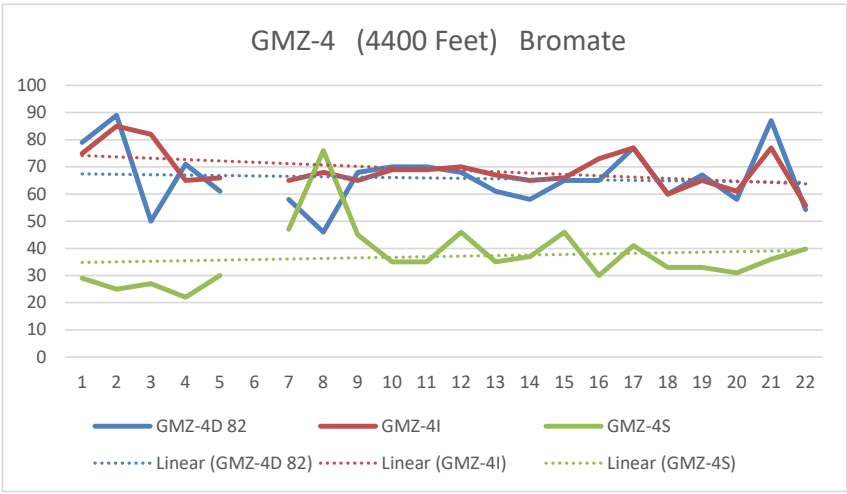
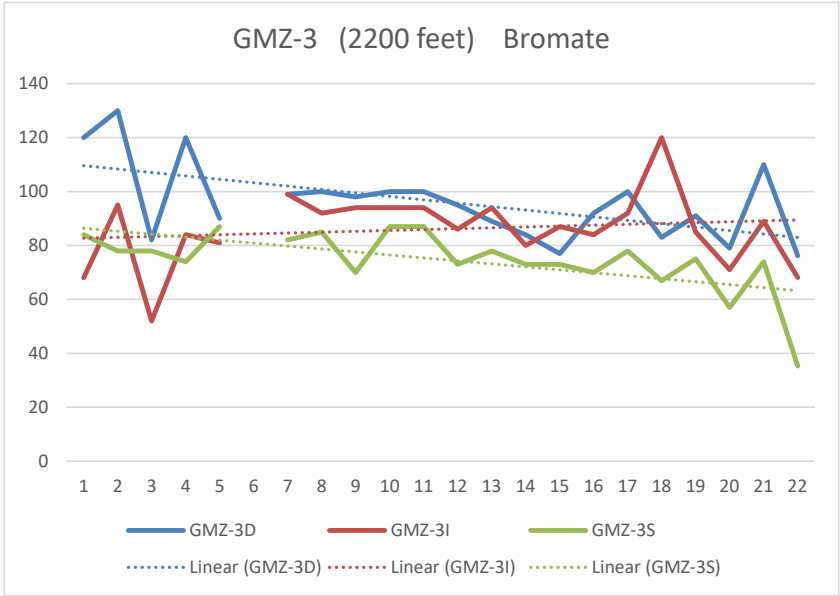


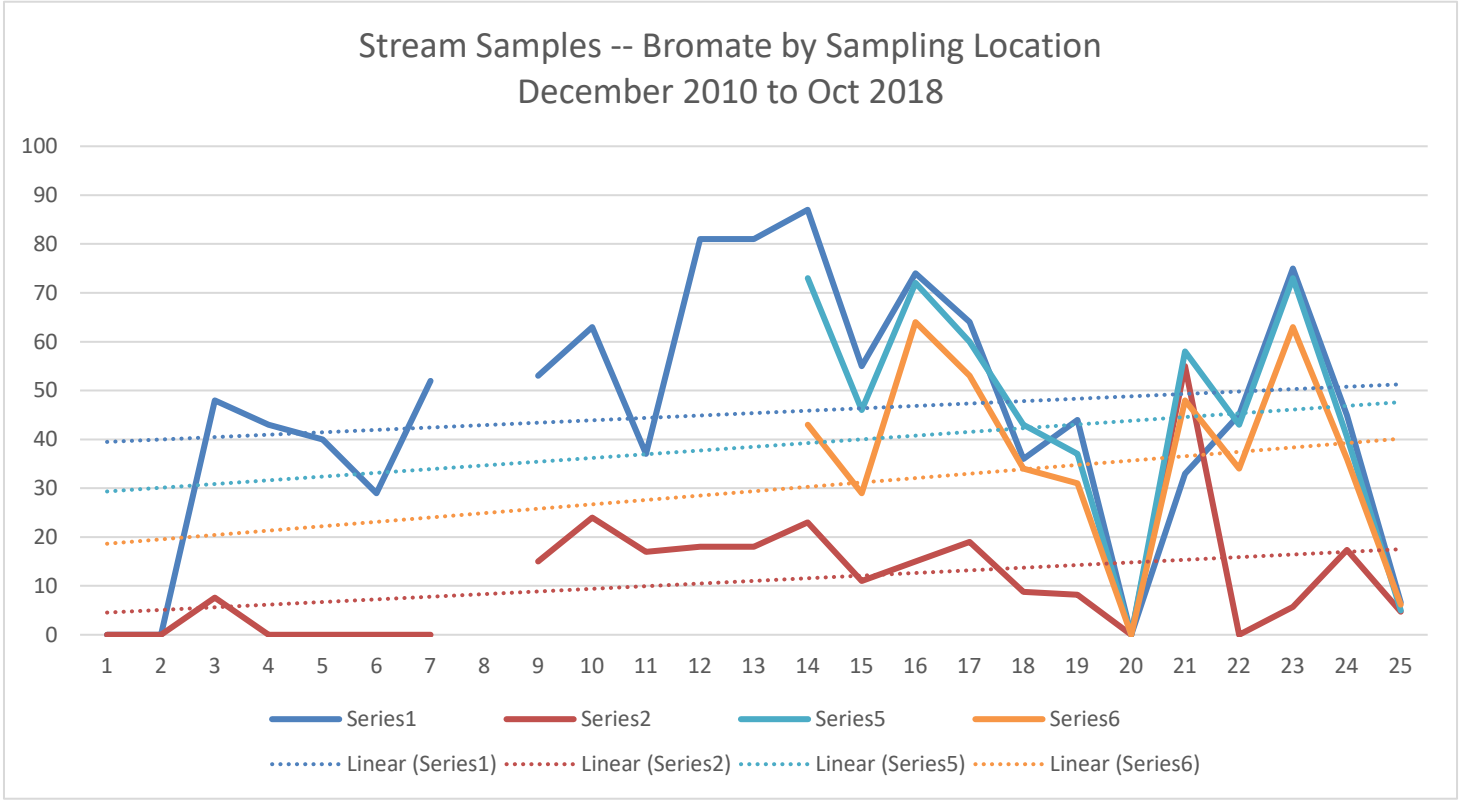
LITHIUM (STD-260)		1	2	3	4	5	6	7	8	9	10	#	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
(Surf Wtr)		2010 DEC	2011 MAR	2011 JUN	2011 SEP	2011 DEC	2012 MAR						2013 SEP	2013 DEC	2014 MAR	2014 JUN	2014 OCT	2015 MAR	2015 JUN	2015 SEP	2015 NOV	2016 MAR	2106MAY	2016 SEP	2016 DEC	2017 JUN	2017 DEC	2018 JUN	2018 OCT	2019 MAR
SW-01		880	530	500	470	460	690						760	900	560	730	1060	730	700	1000	790	660	610	75	750	830	1100	829	470	294
SW-02		484	150	76	58	320	270						352	500	380	490	408	350	230	300	200	220	38	21	35	71	99	299	456	305
SW-03		3.2	15	3.3	40	42	10						5	10	18	17	4.1													
SW-04		2.4	1.7	2.4		1.4	10						5	10	ND	NS														
SW-05																		740	670	1000	800	670	590	53	770	870	1100	900	453	313
SW-06																		560	450	880	680	520	440	35	760	680	900	579	441	299
GMZ-1		585	540	600	620	620	660						610	640	710	900	732	696	760	730	660	720	740	790	780	770	880	940	708	735



FOOTE MINERAL SUPERFUND SITE
GROUNDWATER MONITORING RESULTS (unfiltered, except where noted)

BROMATE	(STD-10)																							
	1	2	3	4	5	6	12	13	14	15	16	17	18	19	20	10	22	23	24	25	26	27	28	
(on-site)	2010 DEC	2011 MAR	2011 JUN	2011 SEP	2011 DEC	2012 MAR	2013 SEP	2013 DEC	2014 MAR	2014JUN	2014OCT	2015MAR	2015JUN	2015SEP	2015NOV	2016MAR	2016MAY	2016SEP	2016DEC	2017JUN	2018JAN	2018JUN	2018OCT	
ERM 1D	140	240	200	210	280	250	220	240	220	210	210	200	190	NS	180	200	230	190	200	190	230	189	37	
ERM 1S	0	<5	<5	5U	5U	5U	5U	ND	ND	NS	ND	ND	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	
ERM 2D	0	<5	<5	5U	5U	5U	5U	ND	ND	ND	ND	ND	ND	ND	12	ND	ND	ND	ND	ND	ND	ND	ND	
ERM 2S	0	<5	<5	5U	5U	5U	5U	ND	ND	ND	ND	ND	ND	ND	ND	18	ND	ND	ND	ND	ND	ND	ND	
ERM 5	0	<5	<5	5U	5U	5U	5U	ND	ND	ND	ND	ND	ND	ND	ND	ND	47	ND	ND	ND	ND	ND	ND	
MW 22	ND	<5	<5	5U	5U	69	5U	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	6.5	ND	ND	ND	ND	ND	
(plume)	2010 DEC	2011 MAR	2011 JUN	2011 SEP	2011 DEC	2012 MAR	2013 SEP	2013 DEC	2014 MAR	2014JUN	2014OCT	2015MAR	2015JUN	2015SEP	2015NOV	2016MAR	2016MAY	2016SEP	2016DEC	2017JUN	2018JAN	2018JUN	2018OCT	
GMZ-1	0	130	150	140	130	140	47	73	120	150	150	140	140	120	110	120	150	130	150	120	150	124	35.9	
GMZ-2D	0	5.4	<5	5U	5U	5U	5U	ND	ND	ND	ND	ND	ND	ND	16	ND	ND	ND	ND	ND	ND	ND	ND	
GMZ-2I	0	<5	<5	5U	5U	5U	5U	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
GMZ-2S	0	<5	<5	5U	5U	5U	5U	ND	ND	9.2	9.2	ND	ND	ND	ND	9.5	30	<25	ND	ND	ND	ND	ND	
GMZ-3D	110	120	130	82	120	90	99	100	98	100	100	95	89	84	77	92	100	83	91	79	110	76.2	7.97	
GMZ-3I	0	68	95	52	84	81	99	92	94	94	94	86	94	80	87	84	92	120	85	71	89	68.1	7.39	
GMZ-3S	110	84	78	78	74	87	82	85	70	87	87	73	78	73	73	70	78	67	75	57	74	35.3	ND	
GMZ-4D	82	79	89	50	71	61	58	46	68	70	70	68	61	58	65	65	77	60	67	58	87	54.3	7.83	
GMZ-4I	55 F	75	85	82	65	66	65	68	65	69	69	70	67	65	66	73	77	60	65	61	77	55.8	9.35	
GMZ-4S	78 F	29	25	27	22	30	47	76	45	35	35	46	35	37	46	30	41	33	33	31	36	39.8	ND	
(Surf Wtr)	2010 DEC	2011 MAR	2011 JUN	2011 SEP	2011 DEC	2012 MAR	2013 SEP	2013 DEC	2014 MAR	2014JUN	2014OCT	2015MAR	2015JUN	2015SEP	2015NOV	2016MAR	2016MAY	2016SEP	2016DEC	2017JUN	2018JAN	2018JUN	2018OCT	
SW-01	0	48	43	40	29	52	53	63	37	81	81	87	55	74	64	36	44	ND	33	45	75	44.9	6.59	
SW-02	0	7.6	<5	5U	5U	8.5U	15	24	17	18	18	23	11	15	19	8.8	8.2	ND	55	ND	5.7	17.4	4.7	
SW-03	0	<5	<5	5U	5U	5U	5U	ND	ND	ND	ND													
SW-04	0	<5	<5	5U	5U	5U	5U	ND	ND		NS													
SW-05												73	46	72	60	43	37	ND	58	43	73	40.5	4.99	
SW-06												43	29	64	53	34	31	ND	48	34	63	36	6.15	



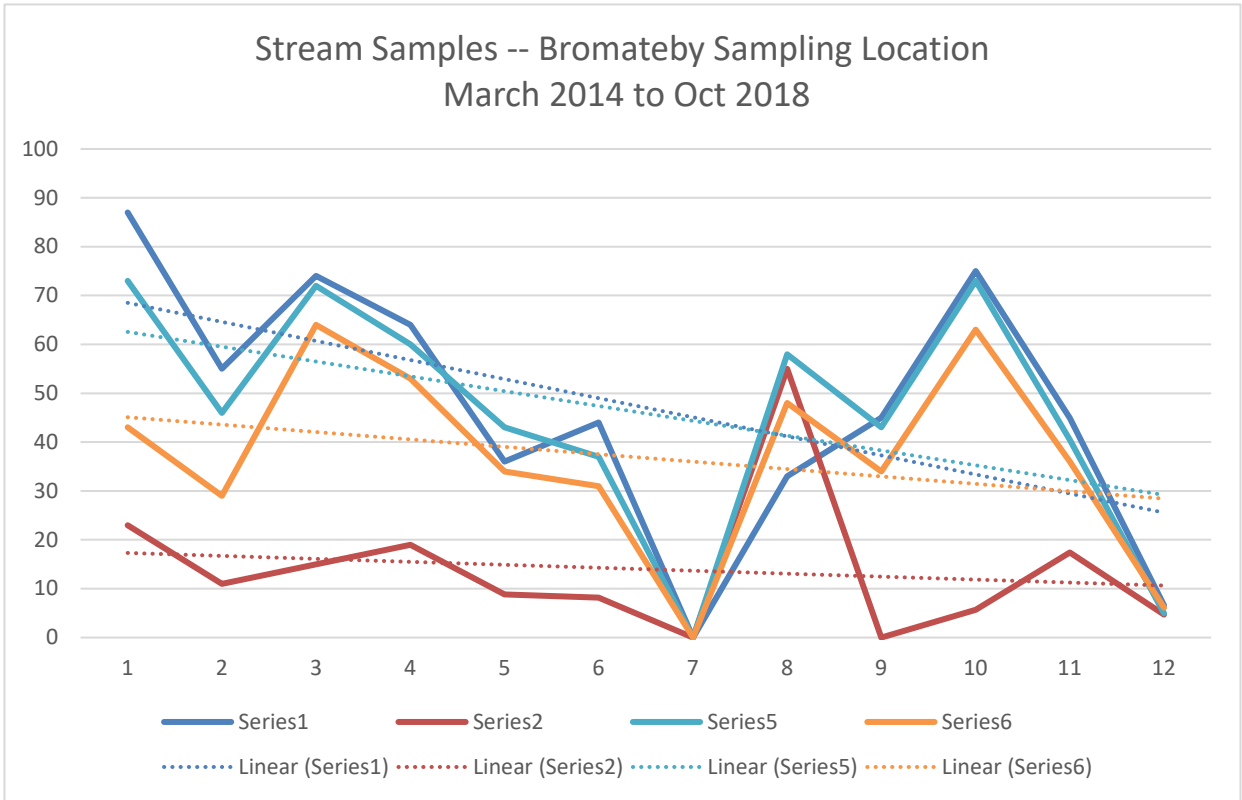


SW-1 = Series 1

SW-2 = Series 2

SW-5 = Series 5

SW-6 = Series 6



Attachment 4

Toxicity of Lithium to Ecological Receptors



Review of Lithium in the Aquatic Environment: Distribution in the United States, Toxicity and Case Example of Groundwater Contamination

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Accepted January 8, 2002

Abstract. Lithium is found at low concentrations in the major rivers of the United States (about 0.002 mg l^{-1}) and as a mineral or salt in pegmatites and brines. The United States produces many lithium materials and consumes the greatest amount of Li in the world for use in ceramics, glass, aluminum, pharmaceuticals, batteries, etc. From 1950 to 1970, Li was central to many nuclear-related US Department of Energy (DOE) activities. The historical and current use of Li has not prompted many studies of the toxicity of this element to aquatic organisms. Here, we review the distribution and use of Li in the US with emphasis on usage by DOE. We also summarize information on the toxicity of lithium to aquatic biota. A case-example is provided which demonstrates the potential for contamination of groundwater with Li, evaluates the toxicity of the Li-contaminated groundwater, and identifies a treatment alternative.

Keywords: lithium; distribution; toxicity; groundwater

Introduction

Much information exists on the uses of lithium (Li), and on the location and concentration of Li in soils, minerals, and clays in the USA; much less information exists on the concentrations of Li in ambient waters or on the effects of Li on aquatic organisms. Lithium is clearly important to modern man—domestic consumption has been level since 1997 at about 2,800 metric tons per year (Ober, 2001). The US is the leading producer of Li materials, and the leading consumer of Li. Lithium materials are important in the ceramics and glass industry, aluminum production, pharmaceuticals, batteries, and in nuclear reactor

coolant. Historically, military applications were also important and, as we demonstrate in this paper, the military use of lithium in weapons production may now manifest in the US (and perhaps in other countries) as a waste disposal issue. With a few exceptions (Emery et al., 1981; Hamilton, 1995; Long et al., 1998), the increased use of Li has not prompted many studies of the toxicity of this element to aquatic organisms. As with many naturally-occurring and man-made chemicals, until the right circumstances evolve, scant attention is given. Recent examples include not only the Li example that we describe here, but minute amounts of pharmaceuticals that are now believed to alter the reproductive biology of aquatic species, and polybrominated biphenyl compounds which behave environmentally like polychlorinated biphenyl (PCB) compounds (Gouin et al., 2001; Manchester-Neesvig et al., 2001).

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We became interested in Li in relation to aquatic biota initially as the result of an effluent toxicity investigation at a Department of Energy (DOE) facility, the details of which are described later in this paper. In the course of this investigation, a literature search for information on Li toxicity revealed that information on this subject was sparse and narrowly focused. Information on the toxicity of Li consisted largely of laboratory dose-response tests with one or two species, with little attention given to broader-scale issues of Li distribution or use. And although we found literature on Li as a mineral resource and much information on the industrial uses of Li, these reports provided little or no information about the metal from a toxicological perspective. This inclusion of toxicological information would be very valuable to persons charged with responsibilities for storing or disposing of Li-rich wastes, and to those dealing with Li that have responsibilities for protecting surface water resources. Here, we briefly review the use of lithium, its occurrence in the aquatic environment, the toxicity of Li to aquatic biota, and provide a case example of treating groundwater contaminated with lithium.

Overview

Lithium is the lightest metal, in its elemental form, and is highly reactive as a pure element. Because of its reactivity, Li does not occur naturally as a pure element—it occurs instead in stable minerals and salts (Bleiwas and Coffman, 1986). Identified resources of Li in the USA are on the order of 7.6×10^8 kg; these reserves occur primarily as pegmatites (in the Carolina lithium belt), or in the form of brines (predominately in Nevada, Utah and California) (Cannon et al., 1975; Evans, 1978). Information about the occurrence of Li-bearing minerals and Li-rich brines in the USA and elsewhere is given by Probst and Pratt (1973), Shacklette et al. (1973), Vine (1976), Penner (1978), Vine and Dooley (1980), Shacklette and Boerngen (1984), and Hem (1992). Li concentrations of $<20 \text{ mg kg}^{-1}$ are common for most limestones and sandstones, and Li concentrations in shaley rocks commonly are $20\text{--}100 \text{ mg kg}^{-1}$ (Vine and Dooley, 1980). Closed desert basins or playa deposits in volcanic terrain are favorable settings for finding lithium-rich brines. Until 1998, the US was a net exporter of Li. Chile is currently the largest lithium chemical

producer in the world and the US is the leading consumer of Li minerals and compounds (Ober, 2001).

Commercial production of Li in the US began in 1925, but significant usage of Li did not occur until World War II. Then, Li was used for CO_2 absorption in submarines (as $\text{LiOH} \cdot \text{H}_2\text{O}$), to inflate emergency signal balloons (as lithium hydride), and in high-temperature resistant greases (Comer, 1978; Bleiwas and Coffman, 1986; FMC, 1992). In 1953, the Atomic Energy Commission required large amounts of LiOH, from which the lithium-6 isotope (^6Li) was separated and reserved for use in the production of thermonuclear weapons (DOE, 1995; National Research Council, 1989). Bombarding ^6Li with neutrons produces tritium as an endproduct, plus large amounts of ^3He and ^4He . For about five years, the US government was the largest consumer of Li. In the late 1950s and early 1960s, uses for Li were developed in the air conditioning industry (as LiBr) and in the synthetic rubber industry (butyllithium). By 1960, uses for Li were well established in the marketplace. By 1994, ceramics and glass production and primary aluminum production were the largest consumers of Li (as LiCO_3) (Ober, 2001). Other uses of Li include synthetic rubber, pharmaceuticals, chemical manufacturing, lubricants, batteries, coolant in nuclear reactors, and air treatment. Aluminum-lithium and Al-Cu-Li alloys (2–3% Li by weight) are used for airframe structural materials by the aerospace industry, due largely to their lighter weight ($\sim 10\%$ less than non-alloyed aluminum). Lithium recovered from spent Li batteries may be used to improve the longer-term stability of concrete in some applications. Because of the numerous uses for Li, both past and present, there are many potential opportunities for contaminating groundwater and surface water with Li.

Lithium in the aquatic environment

Measurement of Li concentrations in surface waters is often overlooked because naturally occurring concentrations are typically low (usually less than 0.04 mg l^{-1} ; Emery et al., 1981; Tanner, 1995; Mathis and Cummings, 1973; Hill and Gilliom, 1993). Information on the general distribution and biological activity of Li in surface waters is very sparse or totally lacking in many widely used water-related textbooks (cf. Hutchinson, 1975; Wetzel 1983; Cole, 1994). Bradford (1963) found that about 25% of 400 water

samples representative of water resources of California contained Li at concentrations greater than or equal to 0.05 mg l^{-1} . The USGS reported Li of $<10 \mu\text{l}^{-1}$ in Missouri Creek, Missouri (Feder, 1972). A search of the US Geological Survey website revealed that streams in North Dakota may contain up to 0.17 mg l^{-1} and typically contain $0.05 \text{ mg Li l}^{-1}$. Lithium at concentrations greater than 1 mg l^{-1} also has been reported for wetland areas near Stillwater Wildlife Management Area in Nevada (Hallock and Hallock, 1993).

We did not find much published information on the concentrations of Li in drinking water. Surveys have shown that Li in drinking water can range from 1 to $10 \mu\text{l}^{-1}$ (Durfor and Becker, 1964; Sievers and Cannon, 1975; Anderson et al., 1988). In seven US bottled mineral waters, Li ranged from 2 to $1,450 \mu\text{g l}^{-1}$ (Allen et al. 1989).

Lithium compounds that are highly soluble (e.g., LiCl) and relatively inert chemically when dissolved have been used as conservative tracers in hydrological studies of streams (cf. Bencala et al., 1990; Tate et al., 1995; Stewart and Kszos, 1996) and for evaluating water-source in geothermal reservoirs (cf. Fouillac and Michard, 1981).

Hot-spring spas advertising benefits of their Li-rich waters at world-wide web sites are listed for New Zealand, Korea, Canada, Mexico, Italy, Chile, Czechoslovakia, Germany, France and the USA. Within the USA, Li-rich hot-spring spas are present in South Dakota, New Mexico, Wyoming, California, Colorado, Utah and Texas. In cases where the Li concentrations are reported for such spas, values typically are on the order of about $1\text{--}10 \text{ mg l}^{-1}$.

Toxicity of lithium to aquatic organisms

A summary of the literature on the toxicity of Li to aquatic species is given in Table 1. In 96 h tests, the sensitivity of fish measured as the LC50 (the concentration that kills 50% of the fish) ranged from 13 mg l^{-1} for *Pimephales promelas* (fathead minnow) to $>100 \text{ mg l}^{-1}$ for several other fish (Dwyer et al., 1992; Hamilton, 1995; Long et al., 1998). In longer exposures, juvenile rainbow trout (*Oncorhynchus mykiss*) was more sensitive with a lowest observed effect concentration for survival of 0.6 mg Li l^{-1} (Emery et al., 1981) and fathead minnows had a 26 d LC50 of 1.4 mg Li l^{-1} (Long et al., 1998). Anderson (1946) reported that Li concentrations of about 1.2 mg l^{-1} were sufficient to immobilize *Daphnia magna* in 64 h. Stockard's (1906) study showed that the "minimal poisonous dose" of LiCl to *Fundulus* eggs was 1.7 mg Li l^{-1} , for tests conducted in "a fresh water series" (i.e., dilutions). The term "minimal poisonous dose" in this case refers to the lowest concentration preventing the formation of an embryo.

Most of the Li-toxicity information related to amphibians is in the form of studies on embryonic development (e.g., Backstrom, 1953; Bustuobad et al., 1977; Biwa and Gimlich, 1989). Hall (1942) found that effects of Li salt solutions on *Rana pipiens* development varied with (1) addition of CaCl_2 and K_3PO_4 , and (2) replacing LiCl with Li_2SO_4 . Through various experiments, Hall (1942) was able to produce microcephaly in salamanders (*Ambystoma punctatum* and *A. tigrinum*) and several frogs, including *Rana clamitans*, *R. sylvatica*, *R. catesbeiana*, and *R. pipiens*.

Table 1. Toxicity of lithium to aquatic species

Species	Endpoint	Lithium (mg l^{-1})	Reference
<i>Daphnia magna</i>	64 h immobilization	<1.2	Anderson, 1948
Insect larvae (<i>Chironomus</i> sp.)	15 d LOEC (habitation)	0.4	Emery et al., 1981
Periphyton	15 d LOEC (algal biomass)	3.5	Op. cit.
<i>Oncorhynchus mykiss</i> (rainbow trout)	10 d LOEC (juvenile survival)	0.6	Op. cit.
<i>Procheilus lucius</i> (Colorado squawfish; 1.7 g)	96 h LC50	41	Hamilton, 1995
<i>Xytrichus texanus</i> (razorback sucker; 2.0 g)	96 h LC50	156	Op. cit.
<i>Gila elegans</i> (bonytail; 2.6 g)	96 h LC50	65	Op. cit.
<i>Pimephales promelas</i> (fathead minnow; embryo-larval)	96 h LC50	42	Long et al., 1998
	96 h NOEC	13	Op. cit.
	26 d LC50	1.4	Op. cit.
	26 d EC50	1.0	Op. cit.
<i>Morone saxatilis</i> (striped bass; 1.8 g)	96 h LC50	>105.0	Dwyer et al., 1992
<i>Fundulus heteroclitus</i> (mummichog)	Embryo formation	1.7	Stockard, 1906

A study by Lazou and Beis (1993) demonstrated that Li affected the plasma membrane protein pattern of early amphibian embryos.

In a very intriguing study, Subba Rao et al. (1998) demonstrated that enriching cultures of the marine diatom *Pseudo-Nitzschia multiseries* with Li caused the alga to produce substantially higher levels of the neurotoxin, domoic acid. These authors speculate that a domoic acid episode in Cardigan Bay (Prince Edward Island, Canada) might have been linked to a massive freshwater run-off event involving a dump adjacent to the bay, which introduced extra Li into the bay. If supported by additional research, Subba Rao et al.'s (1998) suggestion that greater production of domoic acid can result from an influx of Li poses a fascinating possibility: namely, that Li might secondarily contribute to ambient toxicity by encouraging the activity of naturally occurring toxic organisms.

Potential sources of lithium to groundwater and surface water

Anthropogenic sources of lithium to groundwater and surface water could include DOE waste-disposal areas, chemical manufacturing, or spills from manufacturing or recycling facilities. In this paper, our focus is on historical waste-disposal activities at the DOE's Y-12 Plant which resulted in the release of Li. For example, water from two small streams at the Y-12 Plant in Oak Ridge, Tennessee that receive seepage from a materials-burial area near the Y-12 Plant contains Li at concentrations as great as 0.15 mg l^{-1} (ESERP, 1997), a value some 75 times greater than the median concentration of Li in major rivers of North America (0.002 mg l^{-1} ; Durfor and Becker, 1964).

From 1950 to 1970, lithium was central to many nuclear-related DOE activities. In various forms, tens of millions of kg of Li were purchased, handled, and used in isotope enrichment operations and research and development activities (e.g., lithium batteries, fusion energy) at various DOE facilities. During the 1950s and 1960s, production of Li hydride and Li-deuteride materials for the nuclear weapons program resulted in Li-contaminated waste that was land-disposed in units such as the Bear Creek Burial Ground. After 1964, unused LiOH material was stored at the Oak Ridge K-25 Site in Tennessee. As

of October 1995, 30.8 million kg of LiOH were in storage at the K-25 Site and Portsmouth (DOE, 1995). Much of the isotopically depleted Li at the Oak Ridge Y-12 Plant was repackaged and sent to Portsmouth. In 1974, DOE declared stockpiles of LiOH to be excess and available for sale; nearly 36.4 million kg of Li was put up for sale in 1989. In August 1997, approximately 70% was sold to TOXCO, a California-based company; the final removal and sale was completed in 2001 (DOE, 2001). The hazard screening analysis reported by DOE (1995) for LiOH stored at the K-25 Site noted the following:

The screening found that the worst case potential consequence of such an event [natural event or fire] would be that a flow of water (with dissolved lithium components) could quickly make its way to Poplar Creek (a tributary of Clinch River and major watershed for the valley), allowing the solid LiOH to escape. This scenario assumes that 10% of the drums were ruptured. Should a LiOH spill reach a water body, mortality of aquatic organisms could occur (DOE, 1993). The lethal concentration of dissolved lithium for human ingestion is 5 g l^{-1} which would be easily realized in Poplar Creek.

The information above focuses on the historical use of Li at DOE facilities. However, information on the toxicity of Li to aquatic biota that is developed later in this report could affect how DOE manages its current surplus and planned use and disposal of Li. Other governments, private industry and the international community also may benefit from the information we provide here. In 2000, for example, the US exported 2.2 million kg of lithium carbonate to Canada, Germany and Japan and 1.3 million kg of LiOH to Japan (Ober, 2001). These examples suggest that international shipping, use, and storage of large quantities of Li could impose environmental risks to aquatic resources in other parts of the world. We assume, too, that substantial quantities of Li were used in the manufacture of nuclear weapons in Russia and other countries with nuclear weapons production capabilities. If so, historical contamination from the production of enriched Li, much like the contamination that occurred at the Oak Ridge Y-12 Plant, could be important in those countries as well.

testing, the minnow larvae were acclimated to $25 \pm 1^\circ\text{C}$. *Ceriodaphnia* were cultured individually in the Toxicology Laboratory of the Environmental Sciences Division at Oak Ridge National Laboratory. Culture water for *Ceriodaphnia* was diluted mineral water (DMW), consisting of one part "Perrin" water to three parts deionized distilled water. The DMW was aerated overnight prior to use, to allow equilibration of dissolved gases. The cultures were maintained at $25 \pm 1^\circ\text{C}$ and a photoperiod of 16:8 (light:dark) in environmental chambers. *Ceriodaphnia* were fed a mixture of yeast, Cerophyl[®] and trout chow (YCT) augmented with the green alga *Scenedesmus capricornutum*.

Test methods. Short-term chronic toxicity tests with fathead minnows and *C. dubia* were conducted using methods very similar to EPA method 1000.0. Fathead minnow, *P. promelas*, larval survival and growth test and method 1002. *C. dubia*, survival and reproduction test (EPA, 1994). Detailed procedures are available in Kszos et al. (1996). For simplicity, these tests are referred to hereafter as the fathead minnow test and the *C. dubia* test. Each fathead minnow test was initiated by putting 10 larvae in each of four replicate 600 ml beakers containing 250 ml of test solution. Each *C. dubia* test was initiated by putting 1 neonate that was <24 h old in each of 10 replicate 30 ml beakers containing 15–18 ml of test solution (i.e., one organism per beaker). Negative controls (DMW and minnow larvae were fed newly hatched brine shrimp (*Artemia salina*) twice daily. *Ceriodaphnia* in each test chamber were fed 100 μl of YCT and 100 μl of *S. capricornutum* daily. The water temperature and photoperiod were the same as the culture conditions. Mortality was recorded every 24 h, at the time of water renewal; growth (dry weight) of minnow larvae was determined at 7 d and reproduction of *Ceriodaphnia* was recorded every 24 h for 6 or 7 d (until >60% of the animals in DMW had produced three broods). *Ceriodaphnia* reproduction was calculated as offspring per female. During testing, the control water had an average pH of 7.9, a conductivity of 208 $\mu\text{S cm}^{-1}$, an alkalinity of 83.5 mg l^{-1} (as CaCO_3) and a hardness of 97.4 mg l^{-1} (as CaCO_3). The NOEC was calculated per EPA methods (EPA, 1994) and is the lowest concentration tested that had no effect on minnow survival or growth or *Ceriodaphnia* survival or reproduction.

Case example: Groundwater contamination, toxicity, and treatment alternative

The Groundwater Treatment Facility (GWF) at the Oak Ridge Y-12 Plant treats groundwater from a burial ground contaminated with chlorinated hydrocarbons and trace amounts of oil contaminated with PCBs and Li; the Li was present at concentrations of 10–19 mg l^{-1} . Treatment of the groundwater removes oil, volatile organic compounds, and PCBs. Treated effluent is discharged through a National Pollutant Discharge Elimination System (NPDES) monitoring station to East Fork Poplar Creek. Lithium is not removed from the water by this treatment system.

Tests with fathead minnows (*P. promelas*) and *Ceriodaphnia dubia* have been used to characterize GWF effluent toxicity since December 1991. The GWF effluent's no-observed-effect concentration (NOEC) that concentration causing no reduction in survival, growth, or reproduction compared to the control) was routinely 25% for *Ceriodaphnia*, and 100% for fathead minnow larvae, until water from additional seeps was routed to the groundwater collection system for treatment at the GWF. The NOECs for *Ceriodaphnia* and fathead minnow larvae declined when water from these seeps was added; typical NOEC values then ranged from <1% to 12%. An evaluation of suspected contaminants revealed that the increase in toxicity (i.e., lower NOEC values) coincided with an increase in the effluent's concentration of Li, from ~0.2 to 15 mg l^{-1} . The source of the Li was most likely the result of land disposal of Li-contaminated waste from production of Li-hydride and Li-deuteride materials in the 1950–1960s. Due to the increase in toxicity, we conducted tests to (1) verify a process for selective removal of the Li from the groundwater, and (2) show that removal of Li reduced the toxicity of GWF effluent.

Materials and methods

Test organisms. Fathead minnow larvae (*P. promelas*) for the tests were obtained from Aquatic Biosystems, Inc. (Fort Collins, Colorado). Each batch of larvae was shipped overnight; the fish were ~48 h old at the time of test initiation. When the larvae arrived, their water was kept aerated and they were fed ~1 μl of newly hatched brine shrimp (*Artemia salina*) per larvae. Before being used for

Lithium removal from ground water treatment facility effluent. No commercially available ion exchange resin was found that would provide highly selective removal of Li, thus a special material, SuperLig 7 resin from IBC Advanced Technologies, Inc. (IBC) was purchased. Preliminary tests by IBC indicated that the material would remove Li from water simulating GWTF effluent. The resin was prepared using 35- to 60-mesh silica as the support. Approximately 210 g of the material was packed into each of two glass columns; the columns were used in series. Each column was 5 cm in diameter and 25 cm in height. The resin was held in the columns by glass wool pads, at the top and bottom of each column. Water to be treated was pumped through the columns in an up-flow direction with a peristaltic pump. After being used for treating the water, the resin in the columns was rinsed and eluted, also in an up-flow direction.

Three tests were performed to evaluate Li removal by the resin. The first two tests used a simulated groundwater effluent, prepared using reagent-grade salts or acids and deionized water. In these tests, the columns were eluted with 0.5 or 1 M HCl. The elution step was preceded and followed by rinsing the resin-bed with deionized water. The pH of the feed solution was <10.5 to avoid degrading the silica support. The Li-selective ligand was deprotonated with 0.05 M K_2CO_3 , adjusted with 1 M HCl to a pH <10.5. For the second test, the silica was preloaded with Ca, using 0.1 M $CaCl_2$. The third test used actual GWTF effluent. The resin was prepared as for the second test with the simulated effluent. Twenty liters of 25% diluted mineral water (pH 8.6) was fed through the resin columns. Following the 20 l rinse with DMW, about 21 l of GWTF effluent (adjusted to pH 8.8 with NaOH) were processed through the two columns. The columns were then rinsed with deionized water to displace the remaining groundwater, and eluted with 1.1 l of 1 M HCl provided at a rate of 40 ml min⁻¹. *Ceriodaphnia* tests were conducted with the initial eluant to determine if toxic compounds eluted from the "clean" resin and with the treated GWTF effluent to determine if Li removal reduced the toxicity. In this experiment, inductively coupled plasma emission spectroscopy (ICP-ES) was used to analyze for elements in the liquid samples (e.g., treated and non-treated GWTF effluent, acid eluant, etc.).

Table 2. Chemical composition of actual and simulated groundwater effluent samples (GWTF: Groundwater Treatment Facility)

Element	Average GWTF effluent (mg l ⁻¹)	GWTF effluent adjusted to pH 8.8 and used with test columns (mg l ⁻¹)	Simulated effluent used with test columns at IBC facilities (mg l ⁻¹)
Li	15	12	18
Ca	100	49	98
Na	22	86	43
Mg	20	17	—
K	10	9	12
B	60	41	—

Results

Lithium removal from GWTF effluent. The compositions of the three samples used to evaluate the resin are shown in Table 2. The GWTF effluent used with the test columns had lower-than-average concentrations of Ca and higher-than-average concentrations of Na, but contained levels of Li typical of those measured on average in GWTF effluent (i.e., about 15 mg l⁻¹).

In the first Li-removal test using simulated effluent, water passing through the columns became elevated with respect to K^+ , at the expense of Ca^{2+} . This result implied that significant quantities of Ca bound to the silica support, displacing K^+ ions. To prevent this situation, the second test involved pumping 0.1 M $CaCl_2$ and water through the columns after the resins had been acclimated with K_2CO_3 . The $CaCl_2$ conditioning step removed labile K^+ and preloaded Ca^{2+} onto the blank silica, reducing exchange of these elements in the water being processed for Li removal.

Lithium removal data for the first two tests with simulated effluent were nearly identical: Li was successfully removed in the columns at an effluent feed rate of 120 ml min⁻¹. The loading capacity was calculated to be about 0.15 mmol Li per gram of resin.

For the test with groundwater, we assumed that the loading capacity of the resin for Li would be the same as it had been for the simulated effluent. Based on this loading rate, the test was stopped just before predicted Li breakthrough. However, sample analyses later showed that Li breakthrough had already occurred in the trailing column (data not shown). Thus, the loading capacity was not as high during the test with actual groundwater effluent as it had been for simulated effluent. During this test, the feed rate of groundwater through the columns was 133 ml min⁻¹.

Water exiting each column was analyzed for Li, Na, Ca and K. The final concentration of lithium was reduced from about 15.0 to 1.62 mg l⁻¹. The concentrations of Na and K remained relatively constant during the Li-removal test at ~90 and 10 mg l⁻¹, respectively, but the concentrations of Ca decreased in the trail column from ~60 to 20 mg l⁻¹, indicating continued removal of Ca from the water by the resin. Lithium and Ca also were the primary cations eluting from the columns.

Toxicity tests. Results of the toxicity tests of GWTF effluent processed through the columns are shown in Tables 3 and 4. The removal of Li from the GWTF effluent clearly reduced the effluent's toxicity. The NOEC for *Ceriodaphnia* in the non-treated effluent was 3%, compared to a NOEC of 50% in the treated effluent. Although minnow survival in the controls associated with the treated effluent was less than acceptable per EPA methods (EPA, 1994), the differences in survival and growth in the treated versus non-treated effluent clearly show the benefits of treatment (i.e.,

removal of Li). The NOECs for fathead minnows in the non-treated and treated effluent were 6% and 12%, respectively. The reduced survival, growth and reproduction in the higher concentrations of effluent (treated and non-treated) were related to the Li concentration. Lithium in the 25% concentration of the non-treated GWTF effluent was 3.1 mg l⁻¹ and Li in the full-strength resin treated GWTF effluent was 1.62 mg l⁻¹.

Discussion

In the present study, we document one example of a historical waste-disposal practice that resulted in the contamination of groundwater with Li, at concentrations great enough to be toxic to *Ceriodaphnia* and fathead minnows in laboratory tests. Lithium concentrations in the treated groundwater during our evaluation averaged 15 mg l⁻¹. In tests with LiCl and Li₂B₄O₇, we found that Li at concentrations as low as 0.5 mg l⁻¹ reduced fathead minnow growth and *Ceriodaphnia* reproduction (Kszos and Stewart, 2003). A Li concentration of 0.15 mg l⁻¹ inhibited

Table 3. *Ceriodaphnia* survival and reproduction in non-treated and resin-treated GWTF effluent (lithium in 25% non-treated effluent = 3.1 mg l⁻¹, lithium in 100% treated effluent = 1.62 mg l⁻¹, NT = not tested. Asterisks (*) indicate those concentrations significantly lower than control.)

Effluent concentration (%)	<i>Ceriodaphnia</i> survival (%)		<i>Ceriodaphnia</i> reproduction (offspring/female; mean ± SD)	
	Non-treated	Treated	Non-treated	Treated
Control	100	100	26.2 ± 2.9	28.7 ± 3.0
100	NT	0*	NT	NT
50	NT	100	NT	24.4 ± 3.3
25	0*	100	0*	27.9 ± 2.3
12	10*	80	3.7 ± 5.4*	21.7 ± 10.9
6	100	80	19.3 ± 4.4*	22.8 ± 6.7
3	100	NT	26.0 ± 3.0	NT

Table 4. Fathead minnow survival and growth in non-treated and resin-treated GWTF effluent. (lithium in 25% non-treated effluent = 3.1 mg l⁻¹, lithium in 100% treated effluent = 1.62 mg l⁻¹, NT = not tested. Asterisks (*) indicate those concentrations significantly lower than control.)

Effluent concentration (%)	Fathead minnow mean survival (%)		Fathead minnow growth (mg/larvae; mean ± SD)	
	Non-treated	Treated	Non-treated	Treated
Control	92.5	62.5	0.51 ± 0.04	0.59 ± 0.08
100	NT	57.5	NT	0.21 ± 0.03*
50	NT	27.5	NT	0.51 ± 0.06*
25	0*	42.5	—	0.52 ± 0.04*
12	32.5*	77.5	0.09 ± 0.03*	0.61 ± 0.08
6	95.0	65.0	0.47 ± 0.03	0.57 ± 0.03
3	77.5	NT	0.58 ± 0.04	NT

the feeding of *Elimia* (a locally abundant freshwater snail) in laboratory tests (Kszos and Stewart, 2003). Removal of Li from the groundwater with a highly selective resin decreased the water's toxicity to *Ceriodaphnia* and minnows. We know of no other documented occurrences of Li contamination in groundwater or industrial effluents, but it seems very likely that Li contamination could be important areas where Li is processed (such as in Nevada, North Carolina, and Tennessee; see Ober, 2001) or used in quantity for fabrication or production of ceramics, glass, cosmetics, or other materials. Acknowledgement that Li has the potential to be discharged in industrial effluents is evident in Long et al. (1998). However, these authors did not elaborate on the specific process accounting for the Li-tainted effluent that they tested. It is also reasonable to presume that other countries which processed Li to obtain ^6Li for nuclear devices could potentially have groundwater or surface water contaminated with Li, at sites where quantities of Li were processed, stored, or disposed. Awareness of the potential for Li to impact aquatic ecological communities as demonstrated in this paper and in Kszos and Stewart (2003) is important for effective pollution prevention and waste management at processing or production facilities as well as for evaluating ecological risk.

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TOXICITY OF SIXTY-THREE METALS AND METALLOIDS TO *HYALELLA AZTECA* AT TWO LEVELS OF WATER HARDNESS

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Abstract—The toxicity of all atomically stable metals in the periodic table, excluding Na, Mg, K, and Ca, was measured in one-week exposures using the freshwater amphipod *Hyalella azteca* in both Lake Ontario, Canada, and soft water (10% Lake Ontario). Metals were added as atomic absorption standards (63 metals), and also as anion salts for 10 metals. Lethal concentrations resulting in 50% mortality (LC50s) were obtained for 48 of the metals tested; the rest were not toxic at 1,000 µg/L. The most toxic metals on a molar basis were Cd, Ag, Pb, Hg, Cr (anion), and Tl, with nominal LC50s ranging from 5 to 58 nmol/L (1 to 58 nmol/L measured). These metals were followed by U, Co, Os, Se (anion), Pt, Lu, Cu, Ce, Zn, Pr, Ni, and Yb with nominal LC50s ranging from 225 to 1,500 nmol/L (88–1,300 nmol/L measured). Most metals were similarly or slightly more toxic in soft water, but Al, Cr, Ge, Pb, and U were >17-fold more toxic in soft water; Pd was less toxic in soft water. Atomic absorption (AA) standards of As and Se in acid had similar toxicity as anions, Sb was more toxic as the AA standard, and Cr and Mn were more toxic as anions. One-week LC50s for *H. azteca* correlate strongly with three-week LC50s and three-week effect concentrations resulting in 50% reduction in reproduction (EC50s) in *Daphnia magna*.

Keywords—Metals Toxicity *Hyalella azteca* Periodic table

INTRODUCTION

Under the Canadian Environmental Protection Act, 1999 [1], 23,000 substances on Canada's Domestic Substances List (DSL) must be categorized by 2006. Categorization (as defined in the Canadian Environmental Protection Act) involves evaluation of the substances on the basis of their persistence, bioaccumulation, and inherent toxicity. Substances that meet specified criteria for inherent toxicity, as well as either persistence or bioaccumulation, will undergo screening assessments. For the 1,500 mostly metal-containing inorganic substances and organic metal salts on the DSL, toxicity is a key determinant of the outcome of categorization. A common ion approach will be used to increase the efficiency of the process. For example, for all copper-containing substances that are water-soluble and fully dissociate, toxicity will be estimated on the basis of lethal concentrations resulting in 50% mortality (LC50s) for dissolved forms of the Cu ion [2]. Although categorization of substances on the DSL for inherent toxicity ideally should use both aquatic (including benthic) and terrestrial species, an overwhelming majority of experimental ecotoxicological data has been obtained in tests with aquatic species. In addition, virtually all of the quantitative structure-activity relationship estimates (as well as experimental toxicity data) have been generated employing external effect concentrations in the aquatic environment. Therefore, the aquatic compartment, applying external median lethal (LC50) or effective (EC50) concentrations, has been used systematically to categorize the substances on the DSL [2].

The inherent toxicity criterion is extremely important in this exercise. The term inherent toxicity, as applied to the

assessment of substances in a regulatory-legal milieu, can be defined as "the degree of being poisonous" [3]. In the present context, acute toxicity testing to aquatic organisms is the approach selected to assess inherent toxicity due to the paucity of published data for toxicity of inorganic substances and organic metal salts on the DSL. Application of the same test to the majority of substances being categorized (i.e., in well-controlled and well-documented experimental conditions) allows the determination of the relative toxicity or potency of these chemicals. The categorization of inherent toxicity is based on a criterion of 1 mg/L for acute LC50 values (dissolved forms of the metal ion in the present case). This numerical cut-off is in agreement with some well-recognized international initiatives, such as the Organization for Economic Cooperation and Development's Screening Information Data Set [2]. To assist in the categorization process, two federal government laboratories (one using *Hyalella* and another using *Daphnia*) have conducted tests for acute lethality using standard methodologies approved by the Canadian stakeholders interested in the process [2]. In this paper, we present the results of a suite of aquatic toxicity tests performed by the National Water Research Institute (Burlington, ON, Canada). The toxicity of all atomically stable metals in the periodic table (in this paper we use the term metals loosely to include metalloids such as As and Se) was determined in one-week toxicity tests conducted using the freshwater amphipod *Hyalella azteca* (Crustacea) in both Burlington City tap (Lake Ontario, Canada) and soft (10% tap) water. The only metals excluded from this study were those that do not possess stable isotopes (Tc, Pm, and elements with atomic numbers above 83, other than U and Th) and the major ions Ca, Mg, Na, and K. The latter four ions are present in excess of 1 mg/L in tap water and are considered of little toxicological interest.

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A one-week toxicity test with young *Hyalalella*, including feeding, was used because 48-h acute tests without food are difficult to conduct with young *Hyalalella*, which swim and stick to the surface if not fed. The one-week test corresponds to the first week of a four-week or 10-week chronic test, therefore, allowing data from the first week of chronic tests to be compiled together with and compared to data from one-week tests using the same or other substances. The time interval between one-week and four to 10-week chronic toxicity tests is shorter than between 48- or 96-h acute tests and four to 10-week chronic tests, and one-week toxicity is presumed more likely to be proportional to (and hence predictive of) chronic toxicity; the one-week test fits well within a 7-d work week (tests can be set up any day of the week, maximizing the number of tests that can be run). Reproduction in *Hyalalella* usually begins after about five to six weeks in chronic toxicity tests initiated with less than one-week-old animals, and 10-week tests are sufficient to obtain reliable estimates of the effects of toxic substances on reproduction [4–6]. Metals were tested at concentrations of up to 1,000 (soft water) or 3,150 (tap water) $\mu\text{g/L}$. A one-week test represents roughly one-tenth the time required for measuring reproduction, although individual amphipods can live for many months in the laboratory. Compared to typical tests conducted with *Daphnia magna* (acute test = 2 d, reproduction test = 21 d [7]), this 7-d test still should be considered an acute test.

The data presented here provide a single set of toxicity values for all metals at two levels of water hardness for a single test species collected under identical conditions. Although these data were collected specifically for categorization of substances on Canada's DSL, they also provide a useful overview of metal toxicity to *Hyalalella*, including rarely studied metals, and indicate which metals are highly toxic and perhaps deserve further scrutiny.

METHODS

Hyalalella used for toxicity tests originated from Valens Conservation Area (ON, Canada), in 1985 and were cultured as described in Borgmann et al. [8]. Culture water was dechlorinated Burlington City tap (Lake Ontario, Canada) water (hardness 124 mg/L, carbonate alkalinity 84 mg/L, Ca 35 mg/L, Mg 8.7 mg/L, Na 13 mg/L, K 1.6 mg/L, SO_4 32 mg/L, Cl 25 mg/L, and dissolved organic carbon [DOC] 1.1 mg/L from January 2001 to October 2003, $n = 69$, coefficient of variation = 3–12%, except DOC, which was 74%). Culturing and toxicity tests were conducted in an incubator at 24 to 25°C under a 16:8-h light:dark photoperiod. Culture water was renewed and young separated from adults weekly on Mondays. Toxicity tests were set up Tuesday to Friday, making the initial age of the test animals 1 to 11 d at the start of the test.

Most experiments were conducted using atomic absorption standards containing 1 g metal/L. This was less expensive than purchasing metals salts, and the stock solutions can be expected to contain fully dissolved metals. A list of all standards used in the toxicity tests is provided in Table 1. For selected metals commonly present as oxy-anions (As, Cr, Mn, Mo, Sb, Se, Sn, Te, V, and W), tests were repeated using Na salts (i.e., sodium arsenate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$; chromate, Na_2CrO_4 ; permanganate, NaMnO_4 solution in water; molybdate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$; antimonate, NaSbO_3 ; selenate, Na_2SeO_4 ; stannate, $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$; tellurite, Na_2TeO_3 ; orthovanadate, Na_3VO_4 ; tungstate, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$). Anion salt stocks were made up to 0.1 g/L expressed as mass of metal.

Table 1. List of metal standards and preservative used in toxicity tests

Preservative	Preservative concn. (%)	Metal standards used
None (water)	—	B, Nb ^a
HCl	1	Cs, Hf, ^a Li, Rb
HCl	2	Al, Au, Ba, Be, Bi, Ce, Dy, Er, Eu, Fe, Ga, Gd, Ho, In, La, Lu, Mo, Nd, Pr, Re, Sc, Se, Sm, Sr, Tb, Th, Tm, V, Y, Yb
HCl	5	Pd, Pt, Zr ^a
HCl	8	Sn ^a
HCl	10	Ir, Os, Rh, Ru
HCl	20	Sb, Te, ^b Ti
HNO ₃	1	Ge, Tl ^a
HNO ₃	2	Ag, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, U, Zn
HNO ₃	3.2	Hg ^a
HNO ₃ /HF	1/0.1	Ta ^a
KOH	2	Te ^b , W ^a

^a Obtained from Sigma-Aldrich (Oakville, ON, Canada); all others from Delta Scientific (Mississauga, ON, Canada).

^b Both Te standards preserved in HCl and KOH were tested.

To test a large number of metals with a minimum of test treatments (i.e., the fewest number of redundant tests at 0% and 100% mortality), the basic experimental design was modified from the classical toxicity test. Instead of testing one or a few metals at many concentrations at once, a large number of substances were tested simultaneously at one concentration only (either the maximum concentration of interest, or a concentration close to the predicted toxic threshold) in the first experiment. The concentration of each substance was then either increased or decreased in the next experiment, depending on whether mortality was observed. This procedure was repeated until the toxic range was covered for each substance, or until the substance was demonstrated to cause less than 50% mortality at the highest concentration of interest. Repeat tests were then conducted on either side of the LC50. If estimates of survival from replicate test containers for each concentration near the LC50 differed by more than 25%, tests were repeated giving a total of up to 2 to 5 replicates per test concentration. The number of concentrations tested was reduced from the usual 10, 18, 32, 56, 100 logarithmic series to 10, 32, 100. This provided a less precise estimate of the LC50, but allowed determination of LC50s for a much larger number of metals within a shorter time frame. Chronic toxicity test data already were available for a number of metals in tap water (Co, Cu, Hg, Mn, Ni, Pb, Tl, Zn). Data from the first week of these chronic tests were extracted and used to compute one-week LC50s. For these metals in tap water, the more usual concentration series (10, 18, 32, 56, 100) was used.

Tests were static, nonrenewal, one-week exposures conducted in 400 ml of test water in 500-ml polyethylene cups (snap-top specimen containers). Relatively large test volumes were used in order to reduce the surface area:volume ratio and decrease potential adsorption, and also to reduce pipetting variability from handling small volumes of stock solutions. Two sets of experiments were run, one in tap (Lake Ontario) water (see above for chemistry), and another in soft water consisting of 10% tap water and 90% Milli-Q[®] (Millipore, Bedford, MA, USA) deionized water (soft water measured hardness 18 mg/L, carbonate alkalinity 14 mg/L, Ca 5.6 mg/L, Mg 0.90

Table 2. Number of readings, pH, and conductivity ($\mu\text{S}/\text{cm}^2$) at the end of one-week exposures for test solutions made with metal standards or anion salts. Values are listed separately for controls and standards with different acid concentrations

Sample	n	pH	Range	Conductivity	Range
Soft (10% tap) water					
Controls	142	7.37	(6.79–7.84)	46	(34–70)
0–5% Standards ^a	448	7.39	(6.44–8.52)	66	(35–235)
8–10% HCl standards	20	7.71	(7.26–8.16)	235	(50–360)
20% HCl standards	18	8.27	(7.67–8.68)	447	(222–614)
Tap water (Lake Ontario, Canada)					
Controls	109	8.39	(8.09–8.84)	311	(288–345)
0–5% Standards ^a	384	8.21	(7.23–8.83)	345	(288–958)
8–10% HCl standards	47	8.30	(7.82–8.93)	515	(296–1,290)
20% HCl standards	23	8.46	(7.93–8.98)	730	(303–1,670)

^a Includes HCl, HNO₃, and KOH standards as well as anion salts without acid.

mg/L, Na 1.4 mg/L, K 0.15 mg/L, SO₄ 3.4 mg/L, Cl 2.5 mg/L, and DOC 0.28 mg/L, $n = 17$, coefficient of variation = 5–11%, except for Ca 45%, alkalinity 51% and DOC 69%). Calcium and alkalinity in the soft water were more variable than the other ions and ranged from 10 to 20% of expected concentrations because an airstone was inadvertently used to aerate the test water. Soft water tests were designed to simulate a reasonable worst-case condition for Canada (e.g., dilute waters of the Canadian Shield with a low DOC content), while still falling within the range tolerated by *Hyalella*. A solution of 19 parts 1 M NaHCO₃ plus 1 part 1 M KOH (similar to the Na:K ratio of the test water) was used to neutralize excess acid in the metal standards and control pH. Sufficient buffer to control pH, if required, was added first, followed by addition of the metal standard. This resulted in better survival of acid-controls than adding the metal solution first. Buffer was not added for tests with anion salts. Neutralization was required primarily for tests conducted in soft water. Acid-controls consisted of acid and neutralizing solution additions equal to the amount added in the tests with acidified metal standards. Survival in acid-controls was 82% of survival in soft water controls at the highest metal concentration (1,000 $\mu\text{g}/\text{L}$) for metal stocks supplied in 10% HCl, however, this dropped to 32% at 1,000 $\mu\text{g}/\text{L}$ for metal stocks supplied in 20% HCl. Hence, toxicity measured at 1,000 $\mu\text{g}/\text{L}$ for Sb, Te (in HCl), and Ti in soft water partly may be caused by the acid and not the metal. Following addition of neutralizing buffer and metal, the water was aerated gently overnight to allow equilibration of pH and CO₂, and any rapid changes in metal speciation that might occur. Initial pH and conductivity were then measured. A piece of 2.5 × 2.5-cm cotton gauze and 2.5-mg Tetra-Min® (Ulrich Baensch, Melle, Germany) fish food flakes were then added to each container, followed by addition of 15 young *Hyalella*. Test containers were not aerated during the test. An additional 2.5 mg of food was provided midweek. After 7 d, the pH, conductivity, and ammonia and oxygen concentrations were measured, and the number of survivors was counted.

Each experiment consisted of three controls, three acid controls, if needed, and one replicate of each metal to be tested in that experiment. As many metals as possible were tested in each experiment. Depending on the test results, the concentration of each metal was either increased (if nontoxic) or decreased (if toxic) by a factor of 10 in the next experiment. Once the toxic range was bracketed, intermediate concentrations (i.e., 3.15-fold higher or lower) were tested. This procedure was repeated until each metal was tested at least twice at a concentration resulting in <25% survival, at a concen-

tration resulting in >75% survival, and at all intermediate concentrations, relative to controls. Only data from experiments with ≥80% control survival were used. Using this procedure made it possible to cover the toxic range of a much larger number of metals than would have been possible if each metal had been tested sequentially in a concentration series.

Routine major ion analyses were performed on tap water and on each batch of soft (10% tap) water used (see above for chemistry). In addition, DOC was measured in randomly selected samples of the test containers at the end of the 7-d exposure and averaged 1.4 mg/L ($n = 83$, coefficient of variation 31%, range 0.7–3.6). Major ion and DOC analyses were conducted by the National Laboratory for Environmental Testing.

Water samples for metal analyses were not collected for tests conducted in tap water using atomic absorption (AA) standards, which were completed first, but were collected from all test solutions at the end of the 7-d exposure in tests conducted in soft water, and all tests with anion salts. Measured metal concentrations in tap water also were available for previously conducted toxicity tests with some metals. Filtered (0.45 micron) samples were collected using disposable filter cartridges (Acrodisk®, Pall Canada Limited, Mississauga, ON) attached to polypropylene syringes, acidified with high purity nitric or hydrochloric acid (or preserved with KOH), and stored in 14-ml capacity Falcon® (Becton Dickinson, Franklin Lakes, NJ, USA) polypropylene disposable round bottom tubes with snap caps. Water samples were preserved in the same acid (or KOH) and concentration that was supplied with the metal standards. Metal analyses were performed by inductively coupled plasma mass spectrometry by the National Laboratory for Environmental Testing. Quality assurance/quality control methodology included calibration checks at the initiation and completion of each run, and verification and drift standards. Certified reference standards also were included when available (about half the metals). Also included were machine blanks, sample blanks (collected at the same time as the samples), control samples (from control exposures without added metals), and acid controls (from exposures without added metal but with acid and base additions equivalent to those added along with the metals).

The concentration resulting in 50% mortality (LC50) and 95% confidence limits were computed using the Trimmed Spearman-Kärber method [9]. In cases where the confidence limits could not be computed reliably (e.g., if there were no partial effect concentrations), the concentrations tested on either side of the LC50 are listed. Most curve fitting methods

Table 3. *Hyalella* one-week lethal concentrations resulting in 50% mortality ([LC50] $\mu\text{g/L}$) and confidence limits (CL) for metals in tap and soft water added as atomic absorption standards in acid (unmarked) or in base (KOH) or as anion salts

Atomic no.	Metal	Soft water (nominal)		Soft water (measured)		Tap water (nominal)		Tap water (measured)	
		LC50	(95% CL)	LC50	(95% CL)	LC50	(95% CL)	LC50	(95% CL)
3	Li	650	(447–945)	650	(456–928)	3,130	(1,743–5,622)	—	—
4	Be	120	(89–163)	67	(53–85)	240	(181–316)	—	—
5	B	2,773	(1,548–4,968)	2,935	(1,638–5,258)	>3,150	—	—	—
13	Al	186	(165–210)	89	(79–100)	>3,150	—	—	—
21	Sc	100	(76–131)	29	(25–33)	175	(100–315)	—	—
22	Ti	979	(707–1,355)	<272	—	>3,150	—	—	—
23	V	989	(616–1,588)	1,251	(790–1,980)	1,032	(675–1,577)	—	—
23	V (anion salt)	334	(247–452)	368	(271–500)	>1,000	—	—	—
24	Cr	>1,000	—	—	—	>3,150	—	—	—
24	Cr (anion salt)	2.9	(2.2–3.9)	3.1	(2.4–4.0)	159	(123–205)	137	(106–176)
25	Mn	>1,000	—	—	—	5,049 ^a	(3,967–6,426)	2,729	(2,140–3,479)
25	Mn (anion salt)	181	(100–315)	92	(55–147)	774	(315–1,000)	169	(100–197)
26	Fe	>1,000	—	—	—	>3,150	—	—	—
27	Co	16	(11–23)	16	(11–23)	89 ^a	(75–106)	61	(52–72)
28	Ni	77	(58–101)	75	(55–101)	147 ^b	(133–162)	133	(119–147)
29	Cu	56	(32–100)	36	(21–61)	121 ^c	(109–135)	90	(82–99)
30	Zn	70	(59–83)	56	(46–68)	404 ^c	(366–446)	222	(201–245)
31	Ga	>1,000	—	—	—	>3,150	—	—	—
32	Ge	190	(152–236)	209	(167–261)	>3,150	—	—	—
33	As	465	(298–724)	494	(319–765)	426	(293–618)	—	—
33	As (anion salt)	596	(449–790)	581	(437–772)	484	(395–594)	483	(393–594)
34	Se	60	(32–100)	41	(24–63)	118	(88–158)	—	—
34	Se (anion salt)	49	(41–59)	43	(36–52)	432	(319–584)	371	(283–487)
37	Rb	>1,000	—	—	—	>3,150	—	—	—
38	Sr	>1,000	—	—	—	>3,150	—	—	—
39	Y	183	(136–245)	66	(44–101)	549	(394–764)	—	—
40	Zr	>1,000	—	—	—	>3,150	—	—	—
41	Nb	250	(177–354)	26	(16–43)	1,938	(1,692–2,219)	—	—
42	Mo	>1,000	—	—	—	>3,150	—	—	—
42	Mo (anion salt)	>1,000	—	—	—	>1,000	—	—	—
44	Ru	>1,000	—	—	—	>3,150	—	—	—
45	Rh	980	(648–1,482)	804	(517–1,251)	>3,150	—	—	—
46	Pd	>1,000	—	—	—	570	(443–732)	—	—
47	Ag	1.72	(1.00–3.15)	0.25	(0.07–1.00)	1.05	(0.88–1.26)	—	—
48	Cd	0.57	(0.43–0.76)	0.15	(0.12–0.19)	4.41	(3.47–5.60)	1.60	(1.21–2.11)
49	In	>1,000	—	—	—	>3,150	—	—	—
50	Sn	>1,000	—	—	—	>3,150	—	—	—
50	Sn (anion salt)	>1,000	—	—	—	>1,000	—	—	—
51	Sb	576	(460–720)	687	(553–855)	>3,150	—	—	—
51	Sb (anion salt)	>1,000	—	—	—	>1,000	—	—	—
52	Te	>1,000	—	—	—	1,519	(1,093–2,111)	—	—
52	Te (KOH)	>1,000	—	—	—	2,336	(1,747–3,124)	—	—
52	Te (anion salt)	>1,000	—	—	—	>1,000	—	—	—
55	Cs	>1,000	—	—	—	>3,150	—	—	—
56	Ba	>1,000	—	—	—	>3,150	—	—	—
57	La	229	(162–322)	18	(18–19)	1,665	(1,000–3,150)	—	—
58	Ce	131	(88–197)	32	(14–70)	651	(521–813)	—	—
59	Pr	183	(161–209)	35	(30–41)	441	(332–585)	—	—
60	Nd	337	(260–436)	55	(45–67)	511	(315–1,000)	—	—

Table 3. Continued

Atomic no.	Metal	Soft water (nominal)		Soft water (measured)		Tap water (nominal)		Tap water (measured)	
		LC50	(95% CL)	LC50	(95% CL)	LC50	(95% CL)	LC50	(95% CL)
62	Sm	296	(231–378)	74	(57–95)	846	(603–1,188)	—	—
63	Eu	405	(239–688)	112	(69–181)	717	(535–962)	—	—
64	Gd	450	(319–636)	150	(107–209)	599	(424–845)	—	—
65	Tb	365	(252–528)	84	(58–122)	693	(455–1,054)	—	—
66	Dy	485	(140–1,676)	162	(34–769)	897	(671–1,198)	—	—
67	Ho	494	(397–614)	143	(109–188)	755	(528–1,079)	—	—
68	Er	559	(335–933)	191	(101–362)	929	(696–1,239)	—	—
69	Tm	721	(458–1,133)	0.01	(0.01–0.02)	739	(492–1,110)	—	—
70	Yb	248	(189–326)	69	(48–99)	278	(216–357)	—	—
71	Lu	120	(90–160)	29	(21–39)	1,054	(756–1,471)	—	—
72	Hf	>1,000	—	—	—	>3,150	—	—	—
73	Ta	353	(285–436)	2	(1.8–2.1)	1,977	(1,750–2,234)	—	—
74	W (KOH)	>1,000	—	—	—	>3,150	—	—	—
74	W (anion salt)	>1,000	—	—	—	>1,000	—	—	—
75	Re	>1,000	—	—	—	>3,150	—	—	—
76	Os	93	(69–125)	81	(61–108)	57	(49–67)	—	—
77	Ir	>1,000	—	—	—	>3,150	—	—	—
78	Pt	131	(102–168)	110	(86–140)	221	(165–296)	—	—
79	Au	841	(590–1,199)	446	(151–1,319)	>3,150	—	—	—
80	Hg	8.4	(6.9–10.2)	NA ^d	—	10.0 ^c	(8.7–11.6)	2.1	(1.9–2.5)
81	Tl	12	(9–16)	12	(9–16)	49 ^c	(45–53)	46	(42–49)
82	Pb	4.8	(3.3–7.1)	1.0	(0.7–1.5)	113 ^c	(101–126)	11	(10–12)
83	Bi	722	(315–1,000)	25	(10–36)	2,543	(1,720–3,758)	—	—
90	Th	473	(303–737)	5.2	(4.4–6.2)	>3,150	—	—	—
92	U	54	(44–65)	21	(17–26)	1,651	(1,451–1,878)	—	—

^a W. P. Norwood (National Water Research Institute, Burlington, ON, Canada, unpublished data).^b Data from Borgmann et al. [4].^c Data from Borgmann et al. [5].^d Not available. Hg appears to have been lost from samples upon storage.^e Data from Borgmann et al. [6].

Table 4. Percent survival and measured metal concentrations at 315 and 1,000 $\mu\text{g/L}$ for metal solutions where lethal concentrations resulting in 50% mortality (LC50) could not be calculated (i.e., $>1,000$ or $>3,150$ $\mu\text{g/L}$ values in Table 3). Survival values have not been corrected for control survival

Atomic no.	Metal	% Survival at 315 $\mu\text{g/L}$ in soft water	% Survival at 1,000 $\mu\text{g/L}$ in soft water	Measured metal at 315 $\mu\text{g/L}$ in soft water	Measured metal at 1,000 $\mu\text{g/L}$ in soft water	Survival at 1,000 $\mu\text{g/L}$ in tap water
5	B	—	80 ^a	—	1,058	94
13	Al	16	30 ^a	150	198	95
22	Ti	80	44 ^a	<272	<272	77
23	V (anion salt)	50	0 ^a	336	1,187	67
24	Cr	89	71	—	63	93
25	Mn	77	67	344	595	65 ^a
26	Fe	—	73	—	15	95
31	Ga	82	48	326	750	88
32	Ge	20	0 ^a	351	—	87
37	Rb	83	64	—	970	92
38	Sr	82	87	—	1,029	93
40	Zr	60	60	20	4.2	70
42	Mo	—	97	—	1,090	87
42	Mo (anion salt)	—	97	—	937	100
44	Ru	77	63	229	688	68
45	Rh	70	43 ^a	239	822	71
46	Pd	87	87	—	355	20 ^a
49	In	89	87	—	10	90
50	Sn	87	60	<638	<638	87
50	Sn (anion salt)	—	97	—	<638	100
51	Sb (anion salt)	—	90	—	197	93
52	Te (anion salt)	—	90	—	265	93
52	Te (HCl)	87	47	417	1,064	73 ^a
52	Te (KOH)	—	75	—	142	82 ^a
55	Cs	—	89	—	1,048	77
56	Ba	84	93	—	1,102	89
72	Hf	87	90	—	2.9	93
74	W (anion salt)	—	90	—	1,058	90
74	W (KOH)	—	68	—	1,080	94
75	Re	90	80	—	1,123	86
77	Ir	—	78	—	1,107	83
79	Au	80	37 ^a	22	758	77
90	Th	60	20 ^a	3.3	9.1	90

^a See Table 3 for LC50 estimate.

could not be used because mortality curves for *Hyaella* tend to be fairly steep and a concentration series with each concentration increasing by a factor of 3.15 over the previous concentration usually will result only in one partial effect concentration. The LC50s for Cu and Cd were compared to previously published values by performing linear regressions of $\log(\text{LC50})$ against pH, $\log(\text{hardness})$ and $\log(\text{test duration})$ for available published data, and comparing observed LC50s in this study to predicted LC50s from the regressions based on published data.

Table 5. Ratio of the lethal concentration resulting in 50% mortality (LC50) in soft (10% tap) water divided by the LC50 in tap water for different metals

LC50 ratio	Metals
<0.6	Pd
0.6–1	Ag, As, As (anion), Os
1–2.5	Be, Cu, Dy, Er, Eu, Gd, Hg, Ho, Nd, Ni, Pr, Pt, Se, Se, Tb, Tm, V, Yb
>1	B
2.5–10	Bi, Cd, Ce, Co, La, Li, Lu, Mn (anion), Nb, Se (anion), Sm, Ta, Ti, Y, Zn
>2.5	Au, Rh, Sb, Th, Ti, V (anion)
>10	Al (>17), Cr (anion, 54), Ge (>17), Pb (23), U (31)

RESULTS AND DISCUSSION

Addition of AA standards and neutralizing buffer contributed to conductivity somewhat, and this was most noticeable for AA standards made up in $>5\%$ HCl. The effect was proportionately greater in soft water (Table 2). Final oxygen values ranged from 7 to 10 mg/L ($n = 1,161$) and temperature from 24 to 25°C (mean 24.7, $n = 46$). Of 1,252 ammonia readings, all were <0.1 mM, except for 10 that ranged from 0.1 to 0.24 mM. In eight of these cases, survival ranged from 80 to 100%, and in the other two it was 60 to 67% (both for solutions of Ge at 3,150 $\mu\text{g/L}$ in tap water with ammonia at 0.21 mM). The four-week LC50 for ammonia in tap water is about 0.95 mM [10]. Ammonia, therefore, does not appear to have contributed noticeably to toxicity.

We obtained LC50s and corresponding confidence limits for 48 of the 63 metals tested, either as AA standards or anions in either soft or tap water (Table 3). The LC50s for the other metals were $>1,000$ $\mu\text{g/L}$ in soft water or $>3,150$ $\mu\text{g/L}$ in tap water (Table 4). The LC50s in tap water usually were either similar to (0.6–2.5-fold) those in soft water, or slightly higher (2.5–10-fold, Table 5). Some metals, including the AA standards of Al, Ge, Pb, and U, and the anion form of Cr, were much more toxic (>17 –54-fold) in soft water. Palladium was more toxic in tap (LC50 = 570 $\mu\text{g/L}$) than in soft water ($>1,000$ $\mu\text{g/L}$). When this unusual observation was first made

Table 6. Comparison of atomic absorption (AA) standards in acid and anion (KOH standards or anion salts*) lethal concentrations resulting in 50% mortality (LC50, μg metal/L) based on nominal and measured (in parentheses) concentrations

Metal	Soft water		Tap water	
	Acid AA standard LC50	Anion LC50	Acid AA standard LC50	Anion LC50
Similar toxicity				
Se	60 (41)	49 (43)	118	432 (371)
As	465 (494)	596 (581)	426	484 (483)
More toxic as AA standard				
Sb	576 (687)	>1,000	>3,150	>1,000
More toxic as anion				
Cr	>1,000	2.9 (3.1)	>3,150	159 (137)
Mn	>1,000	181 (92)	5,049 (2,729)	774 (169)
More toxic as anion in soft water only				
V	989 (1,251)	334 (368)	1,032	>1,000
Low toxicity for both				
Mo	>1,000	>1,000	>3,150	>1,000
Se	>1,000	>1,000	>3,150	>1,000
Te	>1,000	>1,000	1,519	>1,000
Te (KOH)	—	>1,000	—	2,336
W	—	>1,000	—	>1,000
W (KOH)	—	>1,000	—	>3,150

* Na_xMO_y , Y = 3 (Sb, Sn, Te) and 4 (all other salts); valence = 4 (Sn, Te), 5 (Sb, V), 6 (Se, As, Cr, Mo, W), or 7 (Mn).

for Pd, another experiment was set up with two replicates of Pd at 1,000 $\mu\text{g}/\text{L}$ in both tap and soft water, measured simultaneously using the same batch of test animals. This verified that survival was greater in soft water (9 and 13 survivors out of 15) than in tap water (one and three survivors).

The LC50 confidence limits provided in Table 3 should be viewed as an approximate guide to data reliability only. When

confidence limits are computed using a standard test procedure (i.e., a concentration range with all concentrations tested simultaneously), the limits provide a measure of reliability for that specific test, and not for the chemical in question. True confidence limits should be computed by repeating the test multiple times, estimating the LC50 for each test separately, and computing the mean and standard deviation of those

Table 7. Comparison of metal toxicity (lower of the lethal concentration resulting in 50% mortality [LC50] in soft and tap water) on a mass and molar basis grouped according to metal solubility (measured metal in solution recovered at the end of the one-week exposure)

Rank	LC50	<10% Recovery	10–75% Recovery	>75% Recovery
Mass basis				
1	<3.2 $\mu\text{g}/\text{L}$	—	Ag, Cd	Cr (anion salt)
2	3.2–10 $\mu\text{g}/\text{L}$	—	Hg, Pb	—
3	10–32 $\mu\text{g}/\text{L}$	—	—	Co, Ti
4	32–100 $\mu\text{g}/\text{L}$	—	Cu, Se, U	Ni, Os, Se (anion salt), Zn
5	100–320 $\mu\text{g}/\text{L}$	La	Al, Be, Ce, Lu, Mn (anion salt), Nb, Pr, Sc, Sm, Y, Yb	Ge, Pt
6	320–1,000 $\mu\text{g}/\text{L}$	Bi, Ta, Th, Ti, Tm	Au, Dy, Er, Eu, Gd, Ho, Nd, Pd, Tb	As, As (anion salt), Li, Rh, Sb, V, V (anion salt)
7	>1,000 $\mu\text{g}/\text{L}$	Cr, Fe, Hf, In, Sn, Sn (anion salt), Zr	Mn, Ru, Sb (anion salt), Te (anion salt), Te (KOH)	B, Ba, Cs, Ga, Ir, Mo, Mo (anion salt), Rb, Re, Sr, Te (HCl), W (anion salt), W (KOH)
Molar basis				
1	<16 nmol/L	—	Ag, Cd	—
2	16–50 nmol/L	—	Hg, Pb	—
3	50–160 nmol/L	—	—	Cr (anion salt), Ti
4	160–500 nmol/L	—	U	Co, Os
5	500–1,600 nmol/L	—	Ce, Cu, Lu, Pr, Se, Yb	Ni, Pt, Se (anion salt), Zn
6	1,600–5,000 nmol/L	Bi, La, Ta, Th, Tm	Au, Dy, Er, Eu, Gd, Ho, Mn (anion salt), Nb, Nd, Sc, Sm, Tb, Y	Ge, Sb
7	>5,000 nmol/L	Cr, Fe, Hf, In, Sn, Sn (anion salt), Ti, Zr	Al, Be, Mn, Pd, Ru, Sb (anion salt), Te (anion salt), Te (KOH)	As, As (anion salt), B, Ba, Cs, Ga, Ir, Li, Mo, Mo (anion salt), Rb, Re, Rh, Sr, Te (HCl), V, V (anion salt), W (anion salt), W (KOH)

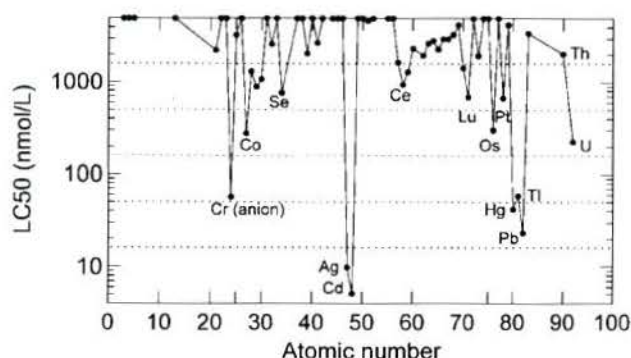


Fig. 1. One-week lethal concentrations resulting in 50% mortality ([LC50] lower value of tap and soft water) for metal toxicity to *Hyalomma azteca* plotted against atomic number. All metals with LC50s above 5,000 $\mu\text{mol/L}$ are shown along the top of the figure. In cases where tests were conducted using both the anion salt and the atomic absorption standard, the more toxic form is shown. The equivalent LC50s for all 63 metals expressed as $\mu\text{g/L}$ are listed in Table 3.

LC50s. In the present study, multiple tests were conducted, but only one or a few concentrations of each metal were included in each test. The data were then pooled and analyzed as if they had all been obtained from a single test. This provides an approximate guide to data reliability, but the statistical procedures were not really designed to evaluate results from the novel test procedure used in this study, as necessitated by the large number of metals tested.

Toxicity of anion salts compared to AA standards

A number of metals commonly are present in the environment as anions under oxic conditions at pH 7 to 8 (e.g., HAsO_4^{2-} , CrO_4^{2-} , SeO_3^{2-}) [11]. These metals are not always the same forms as expected at low pH values in acidified AA standards. Although the anion may be favored thermodynamically, the conversion to the thermodynamically stable form could be a slow process and may not be completed within the first few days of the experiment. Therefore, it is possible that use of AA standards could under- or overestimate toxicity observed under natural conditions for these metals. To investigate this possibility, the toxicity of several anion salts also was tested and compared to the toxicity of the AA standards. The toxicity of metal anions, if measurable, usually was similar to or greater than that of the AA standards in acid (Table 6). The metalloids As and Se demonstrated similar toxicity as AA standards and anions. Chromium and Mn were much more toxic as anions than as AA standards. Vanadium was more toxic in anionic form, but only in soft water. A number of metals (Mo, Sn, Te, W) were relatively nontoxic regardless of their ionic form. Antimony (Sb) was the only metal clearly more toxic as the AA standard. However, the AA standard of Sb was preserved in 20% HCl, the highest acid concentration (Table 1), and required considerable neutralization. Some of this toxicity may have been associated with the acid preservative, rather than the metal itself. Similarly, the slightly higher toxicity of the acid AA standard of Te compared to the KOH standard (Table 6), although not statistically significant (Table 3), might have been associated with the much higher (20%) amount of acid compared to the amount of base (2%) required in the preservative (Table 1). The toxic AA standards of Se, As, Cr, Mn, and V (Table 6) were all preserved in low acid (2%), and the acid likely did not affect toxicity. The similar toxicity between anions and AA standards in acid observed

for a number of these metals implies that either their toxicity is equivalent or that the conversion from one ionic form to the other occurs sufficiently rapidly that differential toxicity is not observed in the one-week tests. Overall, anion toxicity, if measurable, usually was greater in soft than in tap water (except for As), analogous to the situation for most AA standards (Table 6).

Relative toxicity ranking

The ranking of metal toxicity can be done on either a mass or molar basis. Most published data report metal toxicity on a mass basis (i.e., $\mu\text{g/L}$). Furthermore, metal AA standards are produced and sold on a mass basis. Toxicity tests in this study, therefore, were set up and the results compared to other published data, using mass units. Ranking on a mass basis also is more relevant from an environmental hazard classification perspective, because chemicals are shipped and regulated on a mass basis. However, ranking by molar units is more relevant on a chemical stoichiometric basis. Either way, Ag and Cd are the most toxic metals, followed by Hg, Pb, and then Tl (Table 7). The anion of Cr, on the other hand, is extremely toxic on a mass basis, but slightly less so on a molar basis. This occurs because it is a much lighter (52 g/mol) element than Ag, Cd, Hg, Pb, or Tl (108–204 g/mol). Similarly, Al and Be, two very light elements (27 and 9 g/mol), are much more toxic (rank 5) on a mass than on a molar (rank 7) basis (Table 7). Cobalt, Cu, Ni, Se, Zn (59–79 g/mol), and several other less toxic metals also are slightly less toxic on a molar basis, relative to the heavier elements. On the scientifically more relevant molar basis, Ag and Cd are the metals most toxic to *Hyalomma*, followed by Pb, Hg, Tl, and Cr (anion). The LC50s range from 5 to 58 nmol/L nominal, or 1 to 58 nmol/L based on final measured concentrations. Next most toxic are Co, Os, and U with LC50s between 225 and 490 nmol/L nominal, or 88 and 430 nmol/L measured. These metals are followed by Se, Ce, Lu, and Pt and then Ni, Cu, Zn, Pr, and Yb, with LC50s ranging from 670 to 1,500 nmol/L nominal or 160 to 1,300 nmol/L measured (Fig. 1, Table 7). This list includes most of the commonly studied metals, but it also includes a number of less well-studied metals (e.g., Os, U, Ce, Lu, Pt, Pr, and Yb).

Metal toxicity expressed as metal added (nominal) is affected by solubility. The more toxic metals were all either soluble (>75% recovery at the end of the one-week exposure) or partly soluble (10–75% recovery). None of the sparingly soluble metals (<10% recovery) were extremely toxic (Table 7).

Comparison to other published LC50s for *Hyalomma*

Four- to 14-d LC50s for metal toxicity to *Hyalomma* measured in other studies compare favorably with those reported here, especially for Cd and Cu that have been studied most extensively (Table 8). Nickel and Se appeared to be slightly more toxic in the present study than in others, but in both cases there was only one other study with an LC50 for >4 d. Both test duration and water chemistry can affect toxicity. The hardness effect is well-studied for metals but is not necessarily due to Ca or Mg ions; it could be due to any associated cations (e.g., K^+ in the case of Tl toxicity [6]), or even anions (e.g., SO_4^{2-} in the case of selenate [12]), which increase in concentration roughly in proportion with hardness. It also partly can be the result of increased carbonate or hydroxide complexation and, hence, reduced metal bioavailability at the higher alkalinity associated with increased hardness [13]. A de-

Table 8. Comparison of published data on 4- to 14-d lethal concentrations resulting in 50% mortality (LC50, $\mu\text{g/L}$) for toxicity of metal cations and the selenate anion to *Hyalella azteca* at different hardnesses and pH (uncertain values followed by ?)

Test duration (days)	Hardness (mg/L)	Alkalinity (mg/L)	pH	Ag	Al	Cd	Cu	Hg	Mn	Ni	Pb	Se (anion)	U	Zn	Reference
4	6–10	9–21	6.9–8.0	—	—	—	66	—	—	—	—	—	—	—	[15]
4	6–28	8–18	5.5–7.7	—	—	2.8	—	—	—	—	—	—	—	—	[16]
4	9	—	6.4	—	—	—	—	4	—	—	—	—	—	—	[17]
4	10	8	7.0	—	—	3.8	—	—	—	—	—	—	—	—	[18]
4	10–15	10–22	6.9–7.5	6.8	—	—	—	—	—	—	—	—	—	—	[19]
4	15.3	5.2	5.0	—	>1,000	12	—	—	—	—	10	—	—	—	[20]
4	15.3	5.2	5.5	—	>400	16	—	—	—	—	21	—	—	—	[20]
4	15.3	5.2	6.0	—	>400	33	—	—	—	—	18	—	—	—	[20]
4	26	40	8	—	—	—	—	—	3,000	—	—	—	—	—	[21]
4	34	31	7.1	—	—	8	—	—	—	—	—	—	—	—	[22]
4	35.2	32.3	7.7	1.9	—	—	—	—	—	—	—	—	—	—	[23]
4	52?	—	6.7	—	—	—	—	—	—	—	—	741	—	—	[24]
4	80	80	8.3	—	—	—	—	—	8,600	—	—	—	—	—	[21]
4	80–124	8	7.0	—	—	6–12	—	—	—	—	—	—	—	—	[18]
4	90	—	7.4–8.1	—	—	6.5–14	34–53	—	—	—	—	—	—	200–350	[25]
4	98	64	7.7–8.0	—	—	—	—	—	—	3,045	—	—	—	—	[26]
4	100	60	—	—	—	—	—	—	—	—	—	—	—	436	[27]
4	120–140	75–100	7.5–8.5	—	—	13	210	—	—	3,620	—	—	—	—	[28]
4	133	302	8.6	—	—	—	—	—	—	—	—	1,868	—	—	[29]
4	143	—	7.4–8.2	—	—	—	—	—	—	—	—	1,350–3,580	—	—	[12]
4	164	164	8.4	—	—	—	—	—	13,700	—	—	—	—	—	[21]
4	185–379	8	7.0	—	—	12–55	—	—	—	—	—	—	—	—	[18]
4	280–300	225–245	6–6.5	—	—	230	17	—	—	2,000	<90	—	—	1,200	[30]
4	280–300	225–245	7–7.5	—	—	<25	24	—	—	1,900	>5,400	—	—	1,500	[30]
4	280–300	225–245	8–8.5	—	—	5	87	—	—	890	>5,400	—	—	290	[30]
7	6–10	9–21	6.9–8.0	—	—	—	53	—	—	—	—	—	—	—	[15]
7	6–28	8–18	5.5–7.7	—	—	1.7	—	—	—	—	—	—	—	—	[16]
7	18	14	7.4	1.72 (0.25)*	186 (89)	0.57 (0.15)	56 (36)	8.4	>1,000	77 (75)	4.8 (1.0)	49 (43)	54 (21)	70 (56)	This study
7	124	84	8.3	1.05	>3,150	4.41 (1.60)	121 (90)	10 (2.1)	5,049 (2,729)	147 (133)	113 (11)	432 (371)	1,651	404 (222)	This study
10	6–10	9–21	6.9–8.0	—	—	—	67	—	—	—	—	—	—	—	[15]
10	6–28	8–18	5.5–7.7	—	—	1.2	—	—	—	—	—	—	—	—	[16]
10	<10	<10	6.9–7.0	—	—	—	42	—	—	—	—	—	—	—	[31]
10	10–15	10–22	6.9–7.5	5.8	—	—	—	—	—	—	—	—	—	—	[19]
10	34?	31?	6.8?	—	—	—	59	—	—	—	—	—	—	—	[32]
10	34	31	7.1	—	—	<2.8	—	—	—	—	—	—	—	—	[22]
10	22–64	22–63	7.4–8.2	—	—	—	92–143	—	—	—	—	—	—	—	[31]
10	44	45	7.3	—	—	—	31	—	—	—	—	—	—	—	[33]
10	44–47	45–46	6.7–7.4	—	—	—	—	—	—	780	—	—	—	—	[34]
10	44–47	45–46	6.7–7.4	—	—	—	—	—	—	—	<16	—	—	73	[35]
10	133	302	8.6	—	—	—	—	—	—	—	—	1,135	—	—	[29]
14	6–10	9–21	6.9–8.0	—	—	—	44	—	—	—	—	—	—	—	[15]
14	6–28	8–18	5.5–7.7	—	—	0.65	—	—	—	—	—	—	—	—	[16]
14	98	64	7.7–8.0	—	—	—	—	—	—	>120	—	—	—	—	[26]
14	157	137	7.91	—	—	—	—	—	—	—	—	—	1,520	—	[36]

* Nominal (measured values in parentheses).

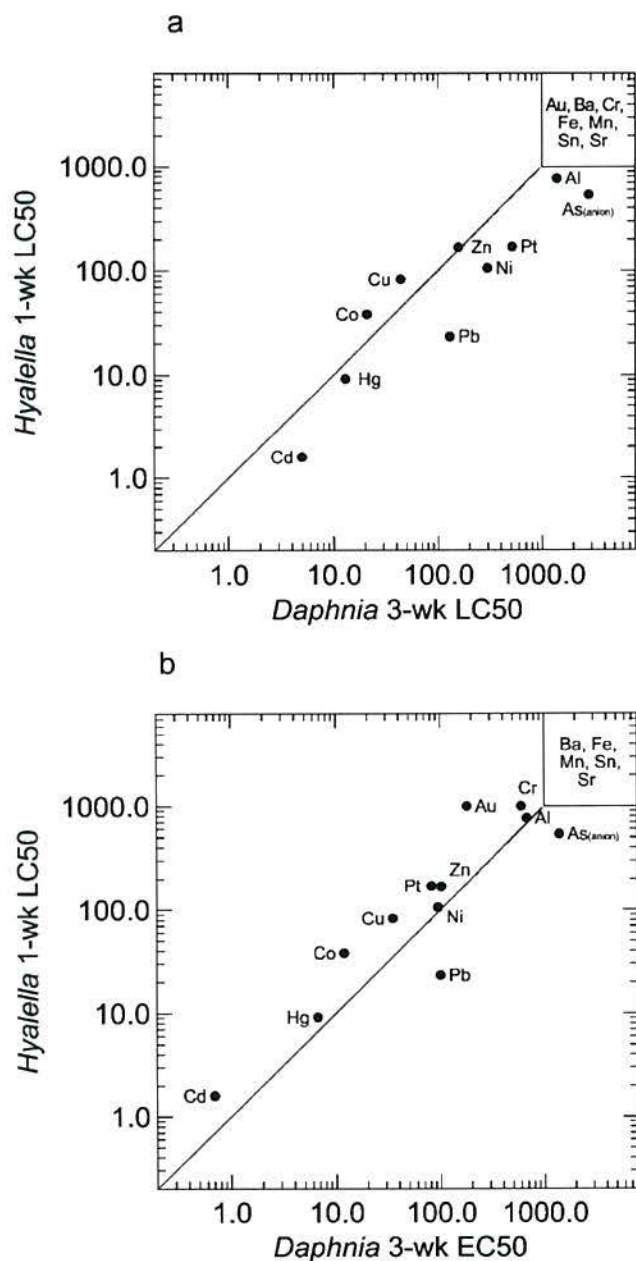


Fig. 2. Comparison of one-week lethal concentrations resulting in 50% mortality ([LC50] µg/L, geometric mean of soft and tap water values) for *Hyalella azteca* with (a) three-week LC50s and (b) three-week EC50s for reproduction in *Daphnia magna* in Lake Superior (Canada) water [7]. The geometric means of LC50s for *Hyalella* in soft and tap water were used for this comparison because Lake Superior water chemistry is approximately equal to the geometric mean of the soft and tap water used in this study. Metals for which LC50s or EC50s for both species exceed 1,000 µg/L are listed in the upper right-hand corner.

tailed quantitative comparison of results obtained in this study with published values is difficult for most metals due to the low number of published values and the range of water chemistry and exposure times. However, for Cu and Cd, the most extensively studied metals, regressions of log(LC50) against pH, log(hardness) and log(test duration) were performed using only previously published data (i.e., excluding the present data, omitting values reported only as less than, and using the average hardness or LC50 where a range is given). This produced

$$\log(\text{LC50}_{\text{Cd}}) = 3.790 + 0.8233 \log(\text{hardness}) - 0.4417 \text{ pH}$$

$$- 1.835 \log(\text{days duration}) \quad \text{and}$$

$$\log(\text{LC50}_{\text{Cu}}) = -1.228 + 0.3998 \text{ pH}$$

with r^2 values of 0.8216 for Cd and 0.5342 for Cu. The above coefficients for hardness, pH, and exposure time all were significant at $p < 0.01$ (hardness and exposure time were not significant for Cu, $p > 0.4$). Using these relationships, the ratios of the observed (data from this study) to predicted (from regression of literature values) LC50, based on measured concentrations at the end of the exposure in the present study, were 0.15 and 0.81 for Cd and 0.67 and 0.73 for Cu for soft and tap water, respectively. Based on nominal LC50s, the ratios were 0.56 and 2.23 for Cd and 1.04 and 0.98 for Cu for soft and tap water, respectively. Hence, the LC50s measured in this study (especially the nominal values) are close to previously reported values for Cd and Cu for *Hyalella*.

Comparison of metal toxicity to *Hyalella* and *Daphnia*

Relatively few databases report the toxicity of many metals for the same species in the same test medium, but one of the most extensive is the study of metal toxicity to *Daphnia magna* in Lake Superior (MN, USA) water [7]. The Lake Superior water chemistry (hardness 45.3, alkalinity 42.3, Ca 13.7 mg/L, Mg 3.2 mg/L, pH 7.74) was similar to the geometric mean of the tap and soft waters used in this study (hardness 46.8, alkalinity 34.2, Ca 14.0 mg/L, Mg 2.8 mg/L, pH 7.87). Consequently, the geometric mean of the metal toxicity to *Hyalella* in soft and tap water was computed for comparison with toxicity to *Daphnia*. Biesinger and Christenson [7] reported toxicity at three weeks for more metals than at 48 h. Using their three-week data, the trend in metal toxicity was very similar between the two species, with *Hyalella* one-week LC50s usually falling slightly under the *Daphnia* three-week LC50s (except for Co, Cu, and Zn, Fig. 2a) and slightly above the *Daphnia* three-week EC50 for reproductive impairment (except for As and Pb, Fig. 2). The rank order of toxicity was the same for Cd < Hg < Co < Cu < Zn in both species. Nickel and Pt toxicity were close to that of Zn, although the exact ranking varied between *Daphnia* and *Hyalella*, and between the LC50 and EC50. Lead, however, appears to be more toxic to *Hyalella* (ranked between Hg and Co) than to *Daphnia* (toxicity similar to Zn).

The correlation between *Hyalella* and *Daphnia* is not as close if the 48-h *Daphnia* LC50s are used in the comparison instead of the three-week LC50s. For example, the relative toxicity ranking of Cd and Hg is now reversed (Fig. 3). The 48-h LC50 for Cu without food (9.8 µg/L) is particularly low for *Daphnia*, compared to the 48-h LC50 with food (60 µg/L, Fig. 3), the three-week LC50 (44 µg/L), or even the three-week threshold for reproductive impairment (a 16% drop in reproduction at 22 µg/L [7]). Similarly, the one-week LC50s for *Hyalella* in tap water did not correlate extremely well with the 48-h LC50s for *Daphnia* in hard (240 mg CaCO₃/L) water as reported by Khangarot and Ray [14], especially for Cd (Fig. 3). The acute-chronic ratios in the LC50s are quite variable in *Daphnia*, especially for acute tests without food [7], suggesting that 48-h tests with *Daphnia* should be interpreted with caution when used to estimate potential chronic effects.

The overall similarity in metal toxicity to *Hyalella* (one-week LC50s) and *Daphnia* (three-week LC50s or EC50s), both among the most sensitive of aquatic organisms to toxic chem-

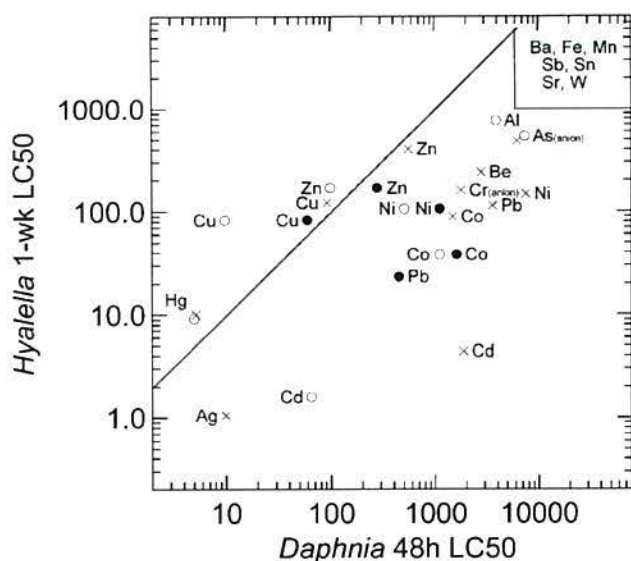


Fig. 3. Comparison of one-week lethal concentrations resulting in 50% mortality ([LC50] $\mu\text{g/L}$, geometric mean of soft and tap water values) for *Hyalella azteca* with 48-h LC50s for *Daphnia magna* in Lake Superior (Canada) water with (●) or without (○) food [7], and one-week LC50s (tap water) for *Hyalella* with 48-h LC50s for *Daphnia* in hard well water (crosses) [14]. Metals for which LC50s exceed 1,000 (*Hyalella*) or 6,000 (*Daphnia*) $\mu\text{g/L}$ are listed in the upper right-hand corner.

icals, suggests that the data presented here should be a useful guide to the relative toxicity of metals to sensitive crustaceans in general.

CONCLUSION

The toxicity of 63 metals to *Hyalella* was determined in one-week tests in both Lake Ontario (tap) and soft (10% tap) water. The most toxic metals on a molar basis were Cd, Ag, Pb, Hg, Cr (anion), and Tl, followed by U, Co, Os, Se (anion), Pt, Lu, Cu, Ce, Zn, Pr, Ni, and Yb. Most metals were similarly or more toxic in soft water, but Pd was more toxic in tap water. The LC50s for *Hyalella* correlate strongly with three-week LC50s and three-week EC50s for reproduction in *D. magna*.

All 63 of the metals tested are constituents of one or more of the 1,500 inorganic substances and organic metal salts on Canada's Domestic Substances List. For metal-containing substances that are water-soluble and fully dissociate, toxicity will be estimated based on the LC50 for the metal that, most of the time, will be the chemical entity of concern in these substances. An LC50 of <1 mg/L for *Hyalella*, or any other aquatic species, is one of the triggers that will determine if that substance must undergo a screening assessment under the Canadian Environmental Protection Act. The LC50s for 49 of the metals tested were below 1 mg/L in either tap or soft water, for metals tested either as AA standards or as anion salts. Substances containing these metals, therefore, have the potential for being classified as inherently toxic.

Although these data were collected primarily for the purpose of categorizing substances on the DSL, they also provide a useful overview of the relative toxicity of metals to *Hyalella* that can be used for comparison to other species, for identification of metals potentially contributing to toxicity in environmental samples, or for modeling studies relating physicochemical properties of metals to toxicity.

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Attachment 5

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Published June 3, 2019

Daily Local News
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EPA PUBLIC NOTICE

EPA REVIEWS CLEANUP

FOOTE MINERAL CO. SUPERFUND SITE

The U.S. Environmental Protection Agency (EPA) is reviewing the cleanup that was conducted at the Foote Mineral Co. Superfund Site located in East Whiteland Township, Pennsylvania. EPA inspects sites regularly to ensure that cleanups conducted protect public health and the environment. EPA's 2014 review of the site concluded that the cleanup was working as designed and is protective with continued groundwater monitoring. Findings from the current review will be available in September 2019.

To access detailed site information, including the review report once finalized, visit: <https://www.epa.gov/superfund/footemineral>

For questions or to provide site-related information for the review, contact:

Gina Soscia, EPA Community Involvement Coordinator
215-814-5538 or soscia.gina@epa.gov

Attachment 6

Documentation for Soil Risk Assessment

ATTACHMENT 6

Supporting Documentation for Soil Risk Assessment

The current protectiveness of the final soil cleanup goals from the ESD Table 2 was evaluated in a risk assessment for potential future residents. Ingestion and dermal exposure were evaluated, using the exposure equations from RAGS A and RAGS E, respectively.

The following standard default exposure assumptions were used. Most factors were from the EPA 1991 and 2015 Standard Default Exposure Factors; the soil-to-skin adherence factor was from RAGS E.

Factor	Child Assumption	Adult Assumption
Soil ingestion rate (mg/day)	200	100
Exposure frequency (days/yr)	350	350
Exposure duration (yrs)	6	24
Body weight (kg)	15	80
Averaging time, cancer (days)	365 * 70	365 * 70
Averaging time, non-cancer (days)	365 * ED	365 * ED
Skin surface area (cm ²)	2373	6032
Soil-to-skin adherence factor (mg/cm ²)	0.2	0.07

The following chemical-specific inputs were used, in accordance with the EPA Region III Dermal Exposure Assessment Guidance:

Chemical	Dermal absorption factor
Benzene	0.0005
Bromoform	0.03
Carbon tetrachloride	0.0005
Chloroform	0.0005
Ethylbenzene	0.03
PCE	0.03
TCE	0.03
12DCA	0.03
12DCE	0.0005
Arsenic	0.03
All other metals	0.01

In addition, an oral absorption factor of 0.6 was used for arsenic in soil; this factor is discussed in more detail in Section 5.10 of the RSL Table User's Guide.

The following toxicity factors were used:

Chemical	RfDo	CSFo	RfDd	CSFd
Benzene	4E-3	5.5E-2	4E-3	5.5E-2
Bromoform	2E-2	7.9E-3	2E-2	7.9E-3
Carbon tetrachloride	4E-3	7E-2	4E-3	7E-2
Chloroform	1E-2	3.1E-2	1E-2	3.1E-2
Ethylbenzene	0.1	1.1E-2	0.1	1.1E-2
PCE	6E-3	2.1E-3	6E-3	2.1E-3
TCE**	5E-4	9.3E-3 (muta) 3.7E-2 (non-muta)	5E-4	9.3E-3 (muta) 3.7E-2 (non-muta)
12DCA	6E-3	9.1E-2	6E-3	9.1E-2
12DCE	2E-3	--	2E-3	--
Antimony	4E-4	--	6E-5	--
Arsenic	3E-4	1.5	3E-4	1.5
Chromium (hex)*	3E-3	0.5	7.5E-5	20
Fluoride	4E-2	--	4E-2	--
Iron	0.7	--	0.7	--
Manganese	2.4E-2	--	9.6E-4	--
Thallium	1E-5	--	1E-5	--
Boron	0.2	--	0.2	--
Lithium	2E-3	--	2E-3	--

These toxicity factors and their original sources are shown on the EPA RSL Table.

12DCE was treated as the more conservative cis isomer in this assessment.

*Chromium was treated as carcinogenic via a mutagenic mode of action, and default ADAFs were applied accordingly (see the EPA RSL Table documentation for more discussion of this).

***TCE was also treated as carcinogenic via a mutagenic mode of action, and its CSFs were split into mutagenic and nonmutagenic portions, as indicated in the material provided on IRIS for TCE.

Combining exposure and toxicity, the following risks were generated:

Chemical	Child HI	Adult HI	Cancer risk (CR)
Benzene	7E-5	6E-6	2E-9
Bromoform	5E-4	5E-5	9E-9
Carbon tetrachloride	1.5E-4	1E-5	5E-9
Chloroform	5E-4	5E-5	2E-8
Ethylbenzene	1E-3	1E-4	2E-7
PCE	6E-3	6E-5	9E-10
TCE	1E-3	1E-4	5E-9
12DCA	1E-4	1E-5	6E-9
12DCE	2E-3	2E-4	--
Antimony	0.6	6E-2	--
Arsenic	0.3	3E-2	2E-5
Chromium (hex)	0.2	2E-2	1E-4
Fluoride	2	0.2	--
Iron	1	0.1	--
Manganese	26	3	--
Thallium	8	0.8	--
Boron	1E-2	9E-4	--
Lithium	0.8	8E-2	--
TOTAL	40	4	1.5E-4

EPA's goal is for cancer risks not to exceed the 1E-6 to 1E-4 range, and for Hazard Indices to be 1 or less. The HIs for child residents exposed to these goals would exceed 1 for fluoride, manganese, and thallium; for adult residents, the HI would exceed 1 for manganese. The hexavalent chromium cancer risk for future residents would be approximately 1E-4. Therefore, the ESD soil goals fall outside the acceptable risk range.

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