COMMUNITY-DRIVEN RESEARCH: EFFLUENT CHARACTERIZATION OF LEGACY CONTAMINATION CONTAINING TRACE METALS IN AN ALKALINE OUTFALL ENTERING THE ALLEGHENY RIVER NEAR CADOGAN, PENNSYLVANIA

By

Andrew Ryan Michanowicz

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This essay is submitted

by

Andrew Ryan Michanowicz

on

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and approved by

Essay Advisor: _____
Conrad D. Volz, DrPH, MPH
Assistant Professor
Department of Environmental and Occupational Health, Graduate School of Public Health,
Scientific Director, Center for Healthy Environments and Communities,
Director, Environmental Health Risk Assessment Certificate Program, University of Pittsburgh

Committee Member: _____
James P. Peterson, PhD
Associate Professor
Department of Environmental and Occupational Health, Graduate School of Public Health
University of Pittsburgh

Committee Member: _____
Ravi K. Sharma, PhD
Assistant Professor
Department of Behavior & Community Health Science, Graduate School of Public Health
University of Pittsburgh

Committee Member: _____
Emily A. Collins, JD
Clinical Assistant Professor and Supervising Attorney, Environmental Law Clinic, School of Law
University of Pittsburgh

Conrad Volz, DrPH, MPH

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Andrew Ryan Michanowicz, MPH

University of Pittsburgh, 2009

Abstract

This essay presents surface water, groundwater, soil and river sediment measurements of total metal concentrations collected from an effluent source existing as the historical disposal site of Pittsburgh Plate Glass Industries, near Cadogan, Pennsylvania, along the Allegheny River. We sought to compare total metals concentrations and water quality measures to evaluate active site dynamics and make inferences of elemental physiochemical reactions within a hydraulic mixing zone.

Community concerns for site conditions were demonstrated through the 2008 Allegheny River Stewardship Project (ARSP). Environmental site assessment documents were obtained from the Pennsylvania Department of Environmental Protection (PA DEP) to determine the scope of contamination, and provide initial information to researchers of constituents of concern. Media sampling was conducted proximal to effluent seeps and along seven (7) river transects to evaluate concerned constituents dynamics. Samples were quantified using ICP-MS methods for trace metals analysis.

Conclusions: Site identification would not have occurred had the community-based model design not been implemented. Elevated metal levels, specifically arsenic and lead concentrations, are present in site effluent that is extremely basic; maximum pH = 10.94.pH. pH is of significant concern, both in terms of elevated hydroxide content, and subsequent physiochemical reactions with oxyanion metal solubility. Significance of mean difference of pH ($p<.000$) was displayed when comparing riverbank transects to both upstream and downstream pH, verifying a localized effect on the Allegheny River. The presence of hydroxide-producing materials is fostering the retention of the majority of metal species, though mobilizing arsenic and lead. During the course of this research, the PADEP issued an administrative order to the liable entity, requiring collection and treatment of contaminated discharge, as well as appropriate warning signage.

Public Health Implications: The elevated hydroxide concentration of the effluent is an imminent danger of health for recreationalists who would come in contact with effluent. The risks associated with direct contact of surface soil, surface water, and sediments containing elevated metals pose a concern to ecological and human receptors. The public should be warned of potential risks from local seeps, as the use of the area is recreational.

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PREFACE

1.0   INTRODUCTION

This research supplements the 2008 Allegheny River Stewardship Project (ARSP), which was based on a hybrid community-based participatory research (CBPR) method melded with an ecological model of environmental exposure assessment. ARSP was an effort through the University of Pittsburgh Graduate School of Public Health, working with concerned citizens of the Alle-Kiski Valley river communities to examine the levels of trace metals and xenoestrogenic chemicals in fish as proxies for Allegheny River quality.

The increase in anthropogenic nonessential human metals release is very much linked to the development of industrial societies. Liberation of metals such as: lead, mercury, arsenic, zinc, cadmium, chromium, selenium, copper, cobalt have increased threefold compared to background pre-industrial loads. Metal consumption has increased by 300% in the last fifty years, and has resulted in the increased concentrations in various environmental media (Grenthe & Puigdomench, 1997). Therefore, an ongoing need exists to further understand and predict the fate and consequences of metal fluxes in highly complex environmental waste systems.

The site of concern, currently owned by the Borough of Ford City, exists as the historical disposal site of waste materials associated with flat glass and off-spec glass materials from the Ford City Pittsburgh Plate Glass Industries Works Number 5 facility,

and waste materials from Eljer Plumbing Inc (Baker Environmental Inc., 1993). Formerly the largest plate glass factory in the world, Pittsburgh Plate Glass Inc. (PPG) operated for over 100 years in Ford City, Pennsylvania, approximately 38 miles northeast of Pittsburgh on the east bank of the Allegheny River. The site of concern is located along the west bank of the Allegheny River, just south of Ford City. No remediation has occurred to date.

We sought to compare total metals concentrations and water quality measures to evaluate active site dynamics and make inferences of elemental physiochemical reactions in a hydraulic mixing zone. Environmental site assessment documents were obtained from the Pennsylvania Department of Environmental Protection (PA DEP) to determine the scope of contamination, and provide initial information to researchers of constituents of concern. Comparisons of measured trace metal concentrations to known regulatory standards are provided.

Arsenic, lead, chromium, and iron concentrations have been found to be of significant concern through private consultants, EPA, and PADEP human and ecological risk assessments. Movement of contaminants to surface water is evident as leachate is present on the steep slopes leading to the river and collecting in a drainage ditch that parallels the river. Total metal concentrations in environmental compartments, along with soil and aqueous state characteristics, e.g., pH, can give an indication of elemental physiochemical reactions present from previous scientific observations.

The environmental impact of metals is directly related to its bioavailability. pH is a fundamental determinant for molecular metal species diversity in aquatic systems. Arsenic, selenite and hexavalent chromium *predominately* exists as an oxyanion species

in soils and freshwater. Sorption mechanisms are highly dependent on pH and decreases greatly with increasing pH, as hydroxide competition is significant. A maximum pH of 10.94 was recorded in seep effluent.

Site identification would not have occurred had the community-based model design not been implemented. This research project has provided a means for concerned citizens to become stakeholders in environmental investigations of intimate concern. These environmental-participatory methods may be further examined and perfected to provide a model that will intrinsically posses influence due to public citizen support. This influence can be observed by the outcomes of this research.

On March 9, 2009, The Pennsylvania Department of Environmental Protection (PADEP) issued an administrative order to PPG Industries, requiring the collection and treatment of effluent discharging from the disposal site, and to restrict access to the site and to the section of the Allegheny River impacted by the discharge. The order requires PPG Industries to begin monitoring within 30 days, and supply the PADEP, for review and approval, a plan to permanently collect, treat and dispose of the waste water, as well as a schedule for plan implementation.

2.0   METALS IN THE ENVIRONMENT

The environmental impact of metals is directly related to their bioavailability. The consequence of a metal on a biotic system will depend on its speciation, which will describe its sorption ability, redox state, and its electrochemical behavior. Once the most important constituents of a system have been identified, the chemical reactivity of these elements is important in understanding how they transform into new compounds. Chemical systems are governed by thermodynamics and kinetics, which characterize why and how chemical reactions occur (Grenthe & Puigdomench, 1997).

The metals selected for testing and discussion in this document are lead (Pb), chromium, (Cr), arsenic (As), mercury (Hg), cadmium (Cd), zinc (Zn), copper (Cu), selenium (Se), cobalt (Co), and manganese (Mn). Arsenic and selenium are technically metalloids, but the term 'metal' is used throughout to describe these elements; keeping with many other authors. Metals, unlike organic compounds, cannot be degraded, but some can transform their chemical state, affecting characteristics such as toxicity and sorption (Grenthe & Puigdomench, 1997).

2.2   METAL TRANSPORT IN THE ENVIRONMENT

The physical properties of a metal often determine its environmental partitioning. Persistence in a certain compartment can either inhibit or induce toxicity. Total metal

concentrations provide limited information to bioavailability and mobility mechanisms, yet many data exist in this form. Total metal concentrations in environmental compartments, along with soil and aqueous state characteristics, e.g., pH, can give an indication of metal species present from previous scientific observations. In order to predict chemical fate and environmental effect, it is necessary to analyze physiochemical species and relevant interactions between them (Samiullah, 1990).

Metals associated with the aqueous phase; soluble state and as colloidal substituents, are subject to movement with ground and surface water. Immobilization of metals by sorption and precipitation to a solid are important processes governing metal retention in soils and are also mechanisms that must be addressed in remediation efforts. Sorption can be divided into adsorption and absorption processes. The former refers to metal accumulation at the surface of a solid while the latter is a process whereby the metal penetrates or integrates into a solid. Factors influencing sorption are: water solubility, ionic character, octanol/water partitioning coefficient, acid/base chemistry, and redox chemistry (Piwoni & Keeley, 1990). Metals exist in soil and sediment as either free, uncomplexed metal ions, complexed inorganic and organic ligands, or with mobile inorganic and organic colloidal material (E. J. McLean & E. Bert Bledsoe, 1992).

2.3   PH EFFECT ON METAL MOBILITY

pH is a fundamental determinant for molecular metal species diversity in aquatic systems. Small changes in pH can have considerable effects in altering physiochemical reactions of pollutants as a pH change from 8 to 10 will increase hydroxide content 100 fold. Adverse effects or toxicity, therefore, can depend greatly upon pH and can either directly or indirectly affect several mechanisms of metal retention in soil or solution. The general trend of naturally existing cationic metals, e.g., Pb, Cu, Zn and Ni in the environment is an increase in adsorption occurrences as pH increases. (E Joan Mclean & E. Bert Bledsoe, 1992). Oxyanionic metals, e.g., arsenite, selenite and hexavalent chromium tend to decrease sorption with increasing pH, therefore potentially decreasing retention. As the pH decreases, the amount of negative sites for cationic adsorption decreases while the number of sites for metal anion adsorption increases. The pH dependence of adsorption mechanisms of cationic metals is partly due to the preferential adsorption of the hydrolyzed metal species over the free metal ion species (Davis & Leckie, 1978; McBride, 1977; McLaren & Crawford, 1973; E. J. McLean & E. Bert Bledsoe, 1992).

2.1 BEHAVIOR AND CONSEQUENTIAL TOXICITY OF SPECIFIC METALS

2.1.1 Arsenic

Arsenic *predominately* exists as an oxyanion in soils and freshwater. Dissolving $(As_2O_5)_n$ in water yields arsenic acid (H_3AsO_4) and salts containing arsenate ions $[AsO_4]^{3-}$, $[HAsO_4]^{2-}$ and $[H_2AsO_4]^{4-}$ governed by pH conditions. Arsenate, $(As[V]$, $[AsO_4^{3-}])$ is the thermodynamically favorable form under normal dissolved oxygen levels and predominates in freshwater and groundwater. Arsenite, $(As[III]$, $[AsO_2^{-}])$ is generally present together with arsenate and is up to 4-10 times more soluble than arsenate in the soil environment, and will predominate as the pH increases or redox potential decreases. (Frankenberger, 2002; E Joan Mclean & E. Bert Bledsoe, 1992).

Sorption of arsenate/arsenite is highly dependent on pH and redox and decreases greatly with increasing pH, as hydroxide competition becomes significant. Aluminum and iron oxides have displayed maximum adsorptions with arsenate at pH 3-4, followed by a gradual decrease in adsorption with increasing pH (Anderson, Ferguson, & Gavis, 1976; Hingstong, Posner, & Quick, 1971; E. J. McLean & E. Bert Bledsoe, 1992). High silica (SiO_2) levels has shown to interfere with arsenic sorption onto iron oxides and hydroxides (Cullen & Reimer, 1989; Ferguson & Gavis, 1972).

Toxicity of arsenic varies greatly by differing valence states, oxidation states, and organic and inorganic substituents. The majority of human toxicity cases have been associated with inorganic arsenic species exposure. Inorganic trivalent arsenic (arsenite, As[III]) is more cytotoxic than As(V) due to cellular membrane permeability. As(III) at

low concentrations has been shown to enhance blood vessel growth or angiogenisis and tumorigenesis in animal models (Soucy et al., 2003). Acute toxicity can cause nausea, vomiting, abdominal pain, encephalopathy, and peripheral neuropathy. (ATSDR, 2005; Bartolome, Nieto, & al., 1999; Lee & Kelly, 1995; Ratnaike, 2003).

2.1.2   Lead

In natural environment, lead exists in a stable divalent form (Pb^{2+}), and tends to be ionic and of very low solubility. Lead is not readily affected by redox conditions in marine systems due to its existence in a monooxidaiton state, Pb(II) (Sadiq, 1992). Lead has a tendency to react with clays, phosphates, hydroxides, carbonate, sulfate, and organic matter which greatly reduces the solubility characteristic of Pb. These particles or colloids consist of lead carbonate, lead oxide, lead hydroxide or substituents of like particles. At pH values above 6, Pb is either adsorbed or forms lead carbonate and lead phosphate in the presence of limestone and phosphates and high soil pH (E. J. McLean & E. Bert Bledsoe, 1992). A considerable portion of Pb transported by water is expected to be in an undissolved state (Xintaras, 1992). The strong affinity for organic ligands and the formation of complexes may greatly increase the mobility of Pb in soil (E. J. McLean & E. Bert Bledsoe, 1992; Prasad, 2001; Puls, Powell, Clark, & Paul, 1991).

In general lead is a moderate toxicant and the cationic form, Pb^{2+} is more toxic than all other inorganic complexes. Chloride and carbonate ions will form complexes with Pb, therefore increased salinity and hardness should result in the decrease of Pb^{2+}, hence, the decrease of overall toxicity (Huling, 1989). Other sorbent acting particles such

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as Fe and Mn oxyhydroxides tend to adsord Pb^{2+} and thus are capable of decreasing the toxic form. Toxic anion Pb compounds exist in the form of ortho-arsenate ($Pb(AsO_2)_2$) and lead (II) chromate of which are considerable insoluble and profoundly toxic. The organic fraction, or methylated Pb compounds, e.g., tetraethyl lead, has shown to be 10-100 times more toxic than inorganic Pb complexes. Tetraethyl lead is highly volatile and rapidly evaporates in air (Kvesitadz, Khatisashvili, Sadunishvili, & Ramsden, 2006). Lead is taken up into the body through inhalation or ingestion routes. Lead replaces Ca^{2+} in bone and is a bioaccumulating toxin that can lead to anemia, kidney failure, neurological damage, and ultimately, death (Prasad, 2001).

2.1.3   Chromium

Chromium exists in two oxidation states in natural soils; trivalent chromium, Cr(III) and a hexavalent chromium, Cr(VI). Hexavalent chromium will exist as an oxyanionic chromate ion, $HCrO_4^-$ at pH<6.5, and CrO_4^{2-} at pH>6.5. The dichromate ion, $Cr_2O_7^{2-}$ predominates at higher concentrations between pH 2-6, and poses a greater toxicity than chromate ions, yet both Cr(VI) forms are more toxic than Cr(III) ions. Like As(III), the anionic nature of Cr(VI) will limit adsorption to positively charged exchange sites which decrease with increasing pH, though Cr(VI) is commonly described as mobile when compared to Cr(III). Song, et al. observed the implications of Cr(VI) speciation from leachate of the wood preservative; chromate copper arsenate. Results showed that Cr(VI) only leached from discarded treated wood in the presence with an alkaline leachate (pH>9) (Song, Dubey, Jang, Townsend, & Solo-Gabriel, 2005). Cr(VI) Iron and

aluminum oxides have shown to adsorb CrO_4^{2-} at acidic and neutral pH (Davis & Leckie, 1978; Zachara, Girvin, Schmidt, & Resch, 1987).

Cr(VI) in aquatic systems is highly toxic, while Cr(III) has a low toxicity to aquatic life. Cr(VI) is a strong oxidant with a high redox potential that can account for rapid generation of reactive oxygen species and resultant toxicity. Cr has shown to effect plant growth and development through alterations of the germination process, photosynthesis, water relations, and mineral nutrition (Shanker, Cervantes, Loza-Tavera, & Avudainayagam, 2004).

3.0   RESEARCH GAPS

The majority of studies of metals behavior have been carried out under equilibrium conditions. Data from these studies determines which reactions are favorable under prescribed conditions, but do not indicate kinetics or a time interval, which is essential for geochemical modeling. Data on oxidation/reduction, precipitation/dissolution, and absorption/adsorption reactions involving metals suffer from a lack of time factor considerations, which can greatly affect overall exposure assessment of toxicant metal behavior in a microenvironment.

pH effect on metal adsorption is not generally modeled at pH levels above 9.0 or 10.0. It can only be inferred that the effect shall continue on similar trends such as the decrease of arsenate adsorption with increasing pH as increase in hydroxide content may be up to 100x greater. The majority of environmental media assessments sample by total

metal concentrations only, which limit the ability to fully understand the scope of contamination, toxicity and exposure.

The presence Alkailiphilic organisms, diatoms, and bacteria existing at a pH of 11 are extremely rare in this area of the United States. The discussion of these extremophiles is beyond the scope of this article, yet the observation of these life forms in regards to the high pH, toxic metal concentrations, and high silica content warrants further research.

4.0   HISTORICAL BACKGROUND

Formerly the largest plate glass factory in the world, Pittsburgh Plate Glass Inc. (PPG) operated for over 100 years in Ford City, Pennsylvania approximately 38 miles northeast of Pittsburgh, PA on the Allegheny River. The facility produced commercial construction glass and fabricated architectural colored glass. Industrial glass chemical processing consists of fusing pure silica (SiO_2) with common oxides, e.g., calcium oxide (CaO) (obtained from limestone), and sodium carbonate (Na_2CO_3) (soda-lime-glass). Fe, Mn, Co, Zn, Cd, Se, Sb, Mg, Su, Cu, Pb, As, and Hg are elements that were used in glass production processes to produce special properties such as; color, transparency, and hardness.

Cadogan, PA, is located approximately 38 miles northeast of Pittsburgh along the west bank of the Allegheny River. The site of concern, currently owned by the Borough of Ford City, exists as the historical disposal site of waste materials associated with flat

glass and off-spec glass materials from the Ford City Pittsburgh Plate Glass Industries, and waste materials from Eljer Plumbing Inc. The disposal site currently subsists on the opposing descending bank right, or west bank near the town of Cadogan, North Buffalo Township, Armstrong County (Figure 1). The site property of approximately 150 acres was acquired by PPG in numerous transactions beginning in 1899 (PPG, 1991). The property was sold by PPG to the Borough of Ford City in 1972 (Baker Environmental Inc., 1993).
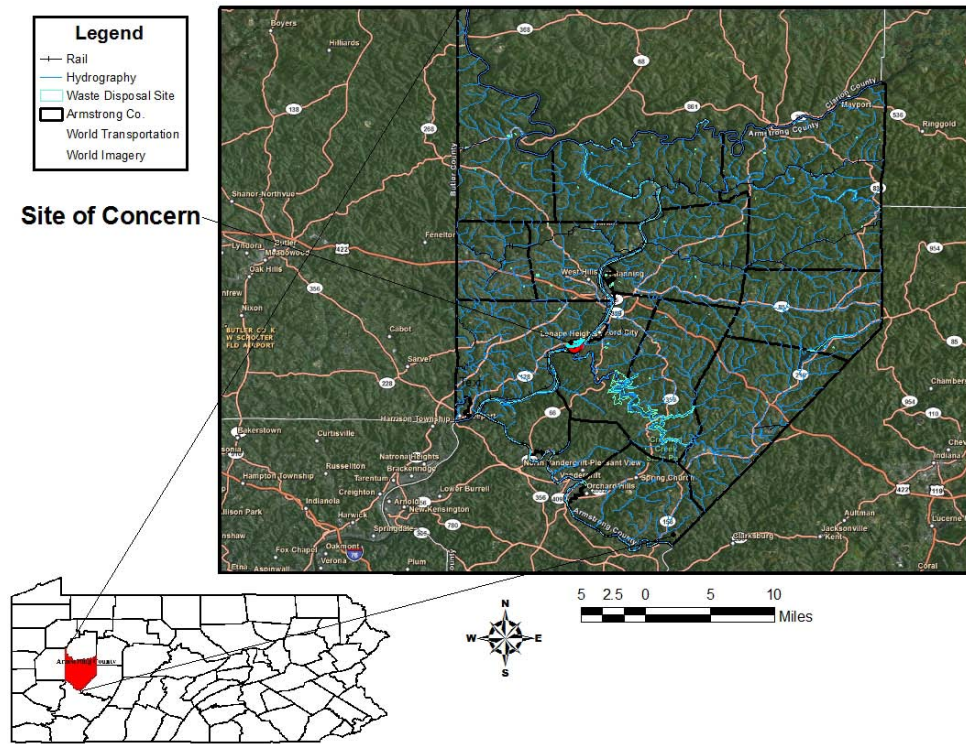
Figure 1. Site of concern along Allegheny River, Armstrong County, PA (ESRI, 2009).

The site was historically used for agriculture prior to PPG's acquisition. From 1900 to 1927, a sandstone quarry and sand plant operated to supply sand to the Ford City plant for glass manufacturing. From the 1920s to 1967 the southeastern portion of the site, currently the solid waste disposal area, was used for the disposal of PPG plant materials. The Commonwealth of Pennsylvania issued an Industrial Waste Permit to

PPG in 1950 allowing the dumping of grinding and polishing wastes to fill the sandstone quarry pit, which continued until 1970. This area, now called the slurry lagoon area (SLA), appears to be the main source of the effluent (Baker Environmental Inc., 1993).

PPG Industries, Inc. existed along the descending bank left of the Allegheny River in Ford City, PA from 1889 to 1993. PPG manufactured commercial construction glass and fabricated architectural colored glass until the late 1960s, yet glass fabrication continued until 1993. Numerous remedial investigations and environmental assessments have been performed on site, dating back to the D'Appolonia Report in 1971. No remediation efforts have occurred to date.

4.1 SITE DESCRIPTION

The site is contained on the north by PA State Route 128, to the west by Glade Run stream, to the east by residential property, and to the south by the Pittsburgh and Shawmut Railroad Company line which traverses the Allegheny River. The adjacent Allegheny River flows towards the southwest. The former PPG SWDA and SLA is situated on a relatively level terrace along the west bank of the Allegheny River, in North Buffalo Township, Armstrong County, Pennsylvania. The site elevation is approximately 890 to 920 feet above mean sea level, and extends up to 130 feet above river level (Baker Environmental Inc., 2001). A steep slope or cliff bank exists along the entire southern length of the site paralleling a narrow right descending river bank, where numerous point source pipes, and effluent seeps have been identified.

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The SWDA was designated to receive glass materials and solid wastes of glass production. The lagoon area served as a disposal site for slurry material that resulted from the polishing process. The Eljer Landfill, consisted of plumbing fixture wastes disposal, and is located 200 feet northeast of the solid waste disposal area. Eljer Plumbing closed their Ford City Plant in 2008. Multiple remedial investigation reports and exposure assessments have characterized the site as containing potential hazardous chemicals in various media (Table 1).
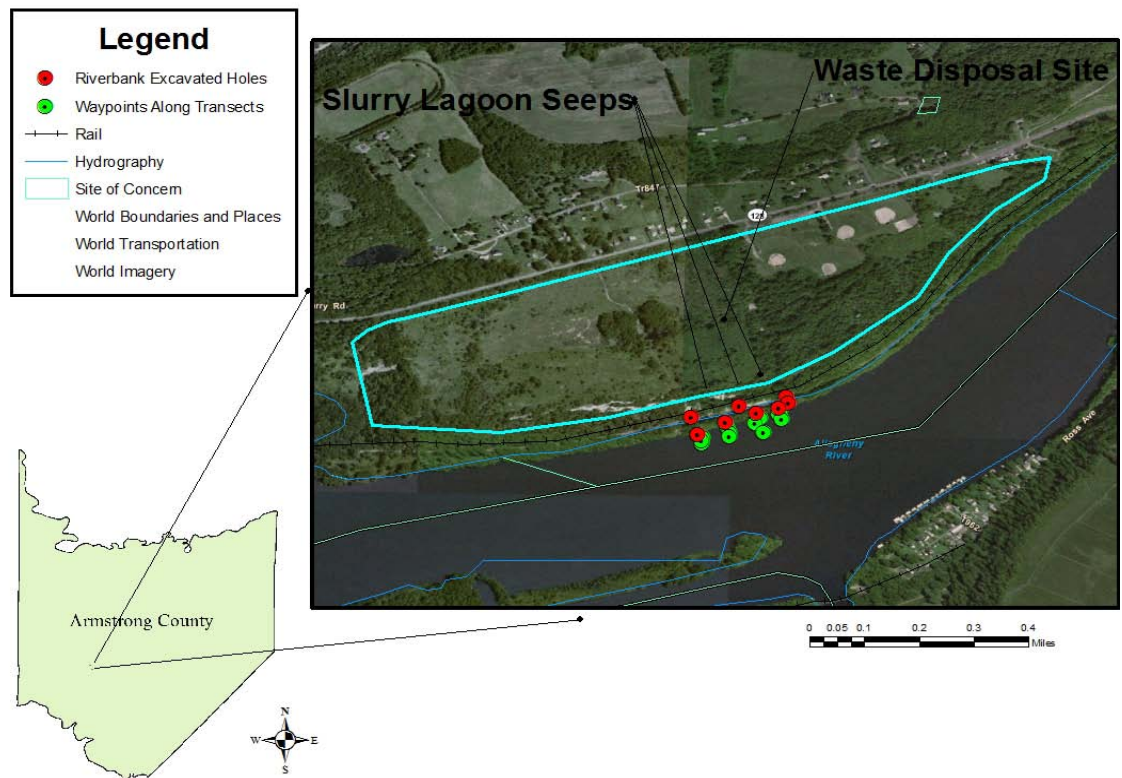
Figure 2. Waste disposal area, slurry lagoon seeps, excavated river bank holes and river transects 003, 004, 005, 006. Recreational use is evident by baseball fields in northeastern portion of site of concern (ESRI, 2009).

5.0 PREVIOUS SITE ASSESSMENTS

Human and ecological risk assessments and addendums were performed by multiple environmental non-governmental entities. These assessments provided researchers summation of legacy contamination from the disposal site for comparison purposes and research objectives for this study. Baker Environmental, Inc. and Key Environmental, Inc. performed the most recent investigations of the site, and have both produced addendums to previous work performed. Table 1 lists the contaminants of concern (COCs), in various sampling media summarized from previous assessments.

Table 1. Constituents of Concern, addendum to the Remedial Investigation report by Baker Environmental, Inc.

Medium	Area of Concern	Constituents of Concern (COCs)
Groundwater	Entire Site	Arsenic Chromium Lead
Surface Water	Slurry Lagoon Area	Antimony Arsenic Iron Lead
	Scripp's Pond	No COCs
Sediment	Slurry Lagoon Area	Arsenic Chromium Lead
Surface Soil	Slurry Lagoon Area	Lead

5.1   SURFACE AND GROUNDWATER

Addendum media sampling (2001) revealed higher metals concentrations in; arsenic, calcium, manganese, potassium, and selenium than was previously recorded in original sampling performed in 1992 by Baker Environmental. Antimony, arsenic, iron, and lead were determined as COCs in surface waters (Table 1).

The original ecological risk assessment indicated potential effects on aquatic organisms associated with lead exposure to surface water seeps (Baker Environmental Inc., 1993). The revised ecological risk assessment *"did not indicate levels that would represent significant potential for adverse effects to ecological receptors in significant habitats (Baker Environmental Inc., 2001)."* Yet, "*lead continues to pose a potential risk to some terrestrial and aquatic or benthic organisms (Baker Environmental Inc., 2001)"*.

5.2   ALLEGHENY RIVER

Potential impact of elemental migration into the Allegheny River was evaluated using river water samples collected by Dames & Moore (1992). With respect to human risk assessment, no constituents were identified in samples, so no risk calculations were formulated (Baker Environmental Inc., 2001).

5.3   ARSENIC

The elevated groundwater arsenic levels originate from surface seepage, which infiltrates into the alluvium before entering the river column (Baker Environmental Inc., 2001). It was stated that arsenic exists as arsenite, the trivalent As(III) species as site pH and redox conditions influence. Adsorption of arsenic to hydrous iron oxides, along with coprecipitation, and combination with sulfides should also retain arsenic in soils. *"The potential impact of the arsenic migration is limited by the hydrogeology of the slurry lagoon area to a very shallow and localized area between the seeps or drainage ditch and the Allegheny River (Baker Environmental Inc., 2001)."*

6.0   METHODS

6.1   COMMUNITY-BASED PARTICIPATORY RESEARCH

Community concerns for site conditions were demonstrated through the 2008 Allegheny River Stewardship Project's (ARSP) environmental qualitative prioritization process. The "disposal site near Ford City" was nominated consistently by concerned citizens when asked to prioritize their environmental concerns. Through these community meetings, prioritization processes and community focus groups, the Allegheny River area near Cadogan, PA was chosen as one of the four river areas to be sampled along the

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Allegheny River for ARSP. ARSP encompassed a community-based participatory environmental research project in which a goal was to biomonitor the Allegheny River for metals and xenoestrogen using common fish species.

Once sampling and analysis of data were collected, data and results were presented to both PA DEP and PPG Industries to fulfill the moral obligation of the 'basis to know' and also 'lack of information' aspects of ethical public health practice. This action is justified as public health implications of this study concluded imminent significant harm to human health if exposed to seep effluent. Community-based participatory research also shares an intrinsic quality by which the community must be presented with results and implications to research concerns that they helped to make known. This information is presented to communities so that it may help in implementing policies or programs that protect and promote health. Follow-up community meetings concerning ARSP results are scheduled for the summer months of 2009. The community meeting concerning the Cadogan waste site is scheduled for April 23, 2009 at the Ford City High School Gymnasium at 7pm.

6.2   COLLECTION OF BACKGROUND INFORMATION

Environmental site assessment documents were obtained from the PA DEP to determine the scope of contamination, and provide initial information to researchers of constituents of concern. Information obtained from these site assessments was also used as historical documentation for previous site conditions that were compared to current

conditions for site dynamics. File reviews were conducted from March 5-7th and August 13th, 2008 to obtain and review the following documents:

- D'Appolonia Report (1971)

- FIT Site Inspection Report by Ecology and Environmental, Inc. (1991)

- Remedial Investigation and Feasibility Study by Dames & Moore (1992)

- Remedial Investigation and Work Plan presented to the Pennsylvania Department of Environmental Resources (PADER) by Baker Environmental (1993)

- Cummings Riter Works #5 Facility Remedial Investigation (2001)

- Baker Environmental addendums (2001): Revised human health and ecological risk assessment, additional sampling events by PADER and Baker (1994), Benthic Macroinvertebrates study by PADER (1994)

- Key Environmental Addendums (2001)

6.3   SAMPLING METHODS

ARSP community fishing day took place near Ford City on May 10th 2008. Water and sediment sampling of the site of concern took place on May 4th, 17th, 18th, June 30th, and July 1st 2008. It is of note that media sampling was not conducted within the waste site, only along the riverbank and within the river. Surface water and sediment samples in Allegheny River were collected using a 1.7L Niskin by General Oceanics and a Ponar style sediment grab by WildCo., respectively. Seven (7) Allegheny River sampling transects were formulated through Garmin Mapsource Topo 2008, and Garmin

GPSMAP 60CSx waterproof handheld global positioning system (GPS) units. Surface, middle, and bottom water samples, as well as sediment samples were taken from each waypoint spread equidistantly along upstream and downstream transects. Total metal concentrations were analyzed in water and sediments by inductively coupled plasma mass spectrometry (ICP-MS) for As, Pb, Co, Cu, Cd, Cr, Hg, Mn, and Zn, and were performed by The Trace Elements Core Facility, Center for Environmental Health Sciences at Dartmouth College. This technique allowed superior detection limits of metals concentrations. Real-time water indicator variables, such as pH, total dissolved solids, turbidity, and dissolved oxygen, were measured using a Hanna Instrument 9128 multiparameter water quality meter. Only pH and metals concentrations values are presented in this study. One-half detection limit values were inserted for metals concentrations found to be below detection limits (BDL) for averaging and comparison purposes.

Sampling transects 003, 004, 005, and 006 extend perpendicularly from the riverbank excavated holes (1-4) and RDB (right descending bank) holes 1-3 to obtain levels of elemental contaminants in groundwater 6 inches above the riverbank and at 1, 2, and 3 meter depths in the river to examine impact by depth rather than by distance (Figure 3). River bank holes were excavated approximately 6 inches above river head gradient to compare both elemental movement by distance from site and metal sorption coefficients between groundwater and soil. All water samples for metals testing were collected in clear glass vials with polypropylene lids by Fischer Scientific. All sediment and soils samples were collected in amber glass jars by Fischer Scientific, and were stored at 35 degrees Fahrenheit to preserve contents.
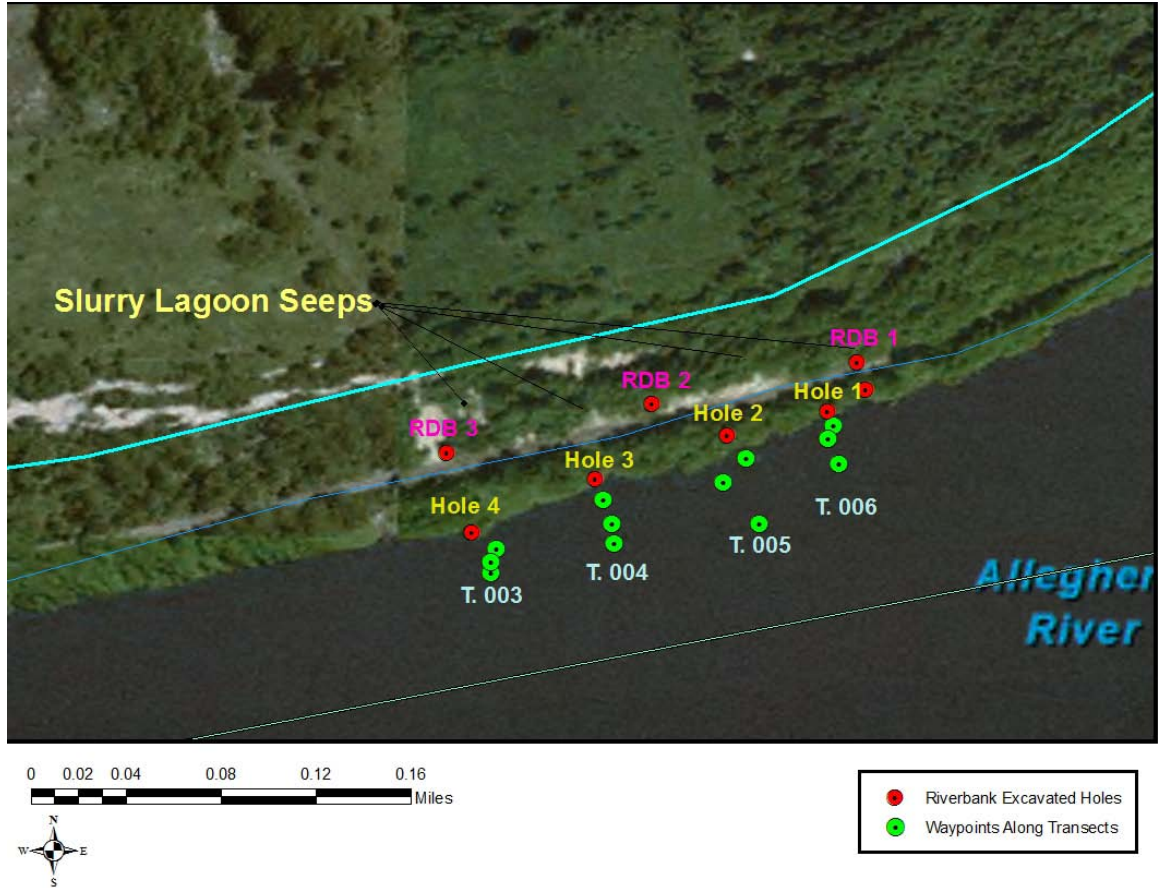
Figure 3. Bottom river sampling transects T.003-006 (green) and riverbank excavated holes (red), approximately 6 inches above river head gradient. Purple excavated holes (RDB) are located directly below effluent seeps. (ESRI, 2009).

Sediment samples, as well as water quality measures, using the multiparameter meter were taken at each waypoint. Upstream (007) and downstream (002) transects were formulated to obtain a control volume (Table 2). Metals concentrations were compared statistically using SPSS 16.0, and SAS 9.2 to evaluate difference of sample distributions and to validate control volume estimations and determine impact of site on river quality.

Samples were also taken at effluent seep locations along the southern bank of the site.

Four (4) holes, located directly adjacent to the cliff face effluent seeps were excavated to

sample both soils and groundwater. All excavated holes were allotted a 24 hour time period to clear sediment and dissolved solids before water samples were collected.

7.0   RESULTS

Arsenic, lead, chromium, and iron concentrations have been found to be of significant concern through private consultants, EPA, and PADEP human and ecological risk assessments. Movement of metals to surface water is evident as leachate is present on the steep slopes leading to the river and collecting in the drainage ditch that parallels the river.

Normality tests displayed non-normal distributions of all metals concentrations (p-values <0.0001, using SAS 9.2 Shapiro-Wilk). Table 2 shows Mann-Whitney-Wilcoxon tests for metals concentrations distribution differences conducted on the Allegheny River upstream (007) and downstream (002) transects to validate control volume.   Upstream transect is approximately ¾ mile from site, while downstream transect is just below the mouth of glade run approximately 0.5 mile from effluent seep 1. No significance of difference was displayed in upstream compared to downstream metals concentrations. Therefore, the designated control volume can be assumed to be a steady state, and further mass balance calculations could be performed under this assumption. Metal concentrations in upstream sampling waypoints displayed higher mean concentrations than downstream concentrations for all metals tested.

River metals concentrations did not differ significantly when transects 003-006 were compared to upstream transect 007 using both Krusal-Wallis and Mann-Whitney-U

tests for distribution difference. Mann-Whitney-U displayed a difference for lead concentration (p=0.066) and significance for arsenic (p=0.193) for river transect 003 compared to upstream T. 007.

Table 2. Average concentrations of total metals in Allegheny River upstream (T.007) and downstream (T.002) samples and Mann-Whitney-Wilcoxon tests for difference between distributions using SPSS 16.0.

Element	Mean T. 007 (μg/l)	Mean T. 002 (μg/l)	Z Value	Significance (two-tailed)
Arsenic	0.206	0.074	-1.617	0.106
Selenium	0.075	0.049	-0.866	0.386
Mercury	0.023	0.004	-1.093	0.274
Cadmium	0.011	0.0002	-1.812	0.070
Cobalt	0.346	0.273	-1.299	0.194
Copper	2.208	1.670	-1.097	0.273
Zinc	20.49	13.974	-0.784	0.433
Chromium	0.685	0.552	-1.761	0.078
Lead	0.095	0.090	-1.097	0.507
Manganese	73.999	59.819	0.273	0.273

Table 3 presents aqueous pH values sampled in concurrent effluent, riverbank holes and river transects. Seep effluent pH had a maximum value of 10.94 and average value of 10.80 which represent the area of highest hydroxide concentrations. A pH of 10.94 is equal to a hydroxide concentration of 8.71×10^{-4}M. Groundwater pH values sampled from riverbank holes also indicate basic conditions. The tributary stream in Table 3 is described as surface water runoff from effluents 1 and 2 entering river. River sampling waypoints along transects 002, 003, 004, 005 do vary by depth, extending out to

1, 2, and 3 meter depths, respectively. Higher pH values in river column were recorded in samples closer to riverbank. Transect 003 displayed a maximum pH value of 9.36, which was located in the river, streamlined from the tributary stream, originating from effluent surface runoff.   Transects 002-upstream and 007-downstream indicate approximate Allegheny River pH background levels.   The upstream river transect displayed both higher maximum and average pH values.

Two sample t-tests of difference of means were performed to examine localized effect of pH. Transects 003, 004, 005 and 006 pH values were combined and compared to both upstream and downstream transect mean pH values (Table 3).   Comparisons revealed significant difference of mean pH values when riverbank transects were compared to both upstream and downstream transects, p=.024 and p=<.000, respectively.

Table 3. pH values of aqueous samples from effluent, riverbank holes, and Allegheny River sampling transects using Hanna Instruments real time multiparameter water quality sampling meter. Two-sample t-tests comparing difference of pH means between riverbank transects v. upstream and downstream transects.

Transect	Max. pH	Mean pH	# Samples	T-Statistic	Significance (2-tailed)
Effluent 1,2	10.94	10.80	3		
Riverbank Holes	9.81	9.18	4		
Riverbank Hole 1	8.05	8.05	1		
Riverbank Hole 2	9.66	9.66	1		
Riverbank Hole 3	9.81	9.81	1		
Riverbank Hole 4	9.21	9.21	1		
Tributary Stream	9.81	9.25	3		
Glade Run	7.73	7.66	6		
T. 002-downstream	7.84	7.58	23		
T. 003	9.36	8.37	4		
T. 004	8.15	8.06	3		
T. 005	8.41	8.23	3		
T. 006	8.07	8.03	3		
T. 007-upstream	8.18	7.93	15		
T.003-006 v. T.007		8.19/7.92	13/13	-2.407	.024
T.003-006 v. T. 002		8.19/7.58	13/23	-6.213	<.000

Table 4 displays total metal concentrations surface water and groundwater in parts per billion (ppb). A total maximum arsenic concentration in aqueous effluent was 173ppb, which exceeds the As US EPA Drinking Water Standard by factor of 17. As concentrations in all waterfall effluents, tributary streams and 3 of the 4 groundwater samples also exceed the Drinking Water Standard of 10ppb. Previous investigations have recorded arsenic levels as high as 0.396 mg/l (~396ppb) in surface water from seeps (Baker Environmental Inc., 2001). Mercury in all effluent samples exceeds the US EPA Drinking Water Standard (2ppb) by a range of 1.4 – 4.9 times. Pb in effluent exceeds the US EPA Drinking Water Standard in all samples (range 2.0 to 8.8x).

Table 4. Detection limits and concentrations of elements sampled from seep effluent and groundwater from excavated holes in parts per billion (ppb)

Sample	As (ppb)	Pb (ppb)	Hg (ppb)	Se (ppb)	Cr (ppb)	Mn (ppb)
Detection Limit (Effluent)	0.002	0.0005	0.001	0.002	0.002	0.0005
US EPA Drinking Water Standard[a]	10.0	15.0	15.0	50.0	100.0[b]	NA
Waterfall Effluent 1, EF1	173.75	145.45	2.81	0.95	1.97	44.30
Waterfall Effluent 2, EF2	72.34	41.45	9.75	1.37	2.67	67.52
Waterfall Effluent 2, EF2[b]	70.69	33.95	6.70	1.03	2.25	65.48
Hole 1, 6" above river level	14.21	12.35	BDL[d]	0.54	2.55	250.82
Hole 2, 6" above river level	90.73	10.91	0.25	1.38	5.25	411.18
Hole 3, 6" above river level	14.76	3.07	0.24	0.49	1.67	236.00
Hole 4, 6"above river level	1.00	2.31	BDL[d]	0.13	0.82	263.46

[a] US EPA Drinking Water Standards (US EPA, 2009)
[b] Total chromium
[c] Duplicate sample
[d] BDL, Below Detection Limit

Table 5 represents total metal concentrations in soils from excavated holes along riverbank in milligrams per kilogram (mg/kg). Background levels for As and Pb were

taken near the site by Baker Environmental on March 3, 1993 and were 11.0 mg/kg and

63.0 mg/kg for As and Pb, respectively. pH concentrations taken from excavated hole

groundwater are listed for evaluation of pH effect on metal mobility in Tables 4 and 5.

Comparison with groundwater metal concentrations from identical holes is presented to

help determine environmental partitioning of metal transport and consequential physical

properties. Note that As concentration in soil; 17.04 mg/kg equals approximately 17,040

ppb.

Table 5. Groundwater pH and total metal concentrations of As, Pb, Cd, Cu, and Mn in soils from excavated holes approximately 3 feet deep along descending right bank of Allegheny River in milligrams/kilogram.

Sample	pH (groundwater)	As (mg/kg)	Pb (mg/kg)	Hg (mg/kg)	Se (mg/kg)	Cr (mg/kg)	Mn (mg/kg)
Hole 1	8.05	17.04	43.18	1.2	1.11	21.84	2562.25
Hole 2	9.66	13.12	32.74	0.97	1.81	14.55	3240.27
Hole 3	9.81	9.65	40.46	0.91	1.25	12.87	2467.74
Hole 4	9.21	13.08	50.85	1.67	2.05	24.67	2287.58

8.0   DISCUSSION

Site identification would not have occurred had the community-based model

design not been implemented. This research project has provided a means for concerned

citizens to become stakeholders in environmental investigations of intimate concern.

These environmental-participatory methods may be further examined and perfected to

provide a model that intrinsically posses influence due to public citizen support. This participatory influence can be observed by an outcomes of this research; an administrative order calling for mitigation.

Soil and groundwater samples results represent levels of contamination hydraulically down gradient from the waste disposal site. Effluent samples represent pH values and metals concentrations emanating directly from waste site groundwater and surface waters. Total metal concentrations in site media are elevated within localized effluent seeps, and the legacy of effluent contamination is worth considering as elemental mass loading has been occurring for decades. Total metal concentrations environmentally partitioned, along with pH levels, serve as a proxy measure of site constituents and serve as a mode for examining facilitative physicochemical reactions. Hydraulic mixing zones are of special concern when concentrations of metal compounds, organic compounds, pH of aqueous solvent, and ionic strength can influence reverse sorption or decomplexation of metal complexes from mobile particles. Reverse sorption mechanisms may occur once colloids of sorbed metal constituents come in contact with river column due to the decrease of pH.

By the assumption; increasing pH increases oxyanionic metal solubility (aqueous state), As and Cr total soil concentrations in Holes 1 - 4 follow this trend as concentrations in soil (retained) reflect pH changes between holes. Arsenic and chromium groundwater concentrations do not correlate exactly with pH theoretical sorption trend. Selenium as selenite (SeO_3^{2-}) or selenate (SeO_4^{2-}) (both oxyanions) may also be following this trend to some degree when comparing sorption coefficients between holes 1 and 2. The reverse process trend of pH retention was observed with Mn

concentrations in soils comparison of holes 1 to 2 and 3 to 4, but was not observed from holes 2 to 3.

pH is significant concern, both in terms of elevated hydroxide content, and subsequent physiochemical reactions with oxyanion metal solubility. Significant difference of means of pH values for riverbank transects (003-006) verifies the localized effect of the waste site. Elevated pH concentrations in river transects 003-006 near river bank may indicate a breakout of effluent via hydrogeologic gradient as all samples in these transect were taken at river bottom. All metals analyzed displayed higher concentrations upstream, which may indicate a buffering capacity from alkaline effluent within river column, though downstream pH would be expected to be higher, which was not observed. Analytical and statistical results suggest negligible impact on Allegheny River quality due to the large mixing volume. Though the significance ($p=0.066$) of lead in T. 003 compared to upstream concentration is worth addressing as T.003 only has 3 samples.

Lead has been identified in elevated concentrations in surface water by this research team and in previous site sampling. Soil samples from excavated riverbank holes of Pb are slightly elevated compared to the background levels within the area. Elevated total Pb concentrations within alkaline leachate may indicate Fe and Mn oxyhydroxide complexes as well as carbonate complexes with Pb^{2+}. Lead in surface water and effluent are likely being mobilized as undissolved colloids or as ligands in complexation compounds, which relates to Pb in a less toxic state. Lead displayed the least significant difference in concentration compared to upstream ($p=0.507$).

Decomplexation of lead colloids is plausible within the river water due to an average downstream pH of 7.5.

Metal in an aqueous state implies mobility, which relates to potential increased geographic exposure in a hydraulic mixing zone. Baker Environmental states that arsenic migration is limited to seeps and drainage ditch which further verifies localized hazard. The fraction arsenic, selenium, lead and chromium released should be considered, taking into account the solubility of the metal species, the ionic character, specific gravity of the solid and the porosity of the substrate, as well as actual total concentration between holes.

High silica (SiO_2) levels has shown to interfere with arsenic sorption onto iron oxides and hydroxides (Cullen & Reimer, 1989; Ferguson & Gavis, 1972), and has been a concern of utilities striving to improve arsenic removal. Aforementioned glass production processes consist mainly of fusing silica with calcium oxides. Glass composition in the slurry lagoon by weight was estimated at 16.35%, the second largest percentage behind only sand (76.89%) (Baker Environmental Inc., 1993). Iron was estimated at 0.90% composition (Baker Environmental Inc., 1993). It is suggested by Korte, Fernando and Moore that higher concentrations of silica in solution, coupled with higher pH, could cause mobilization of arsenic from sediments and soil (Korte & Fernando, 1991; Moore, 1991).

9.0   CONCLUSIONS

Site identification would not have occurred had the community-based model design not been implemented. On March 9, 2009, The Pennsylvania Department of Environmental Protection issued an administrative order to PPG Industries, requiring the collection and treatment of effluent discharging from the disposal site, and to restrict access to the site and to the section of the Allegheny River impacted by the discharge (Appendix A).

No significance of difference was displayed in upstream versus to downstream metals concentrations. Metal concentrations in upstream sampling waypoints displayed higher mean concentrations than downstream concentrations for all metals tested. Significance of mean difference of pH was displayed when comparing riverbank transects to both upstream and downstream pH, verifying a localized effect on the Allegheny River.

The presence of hydroxide-producing materials is fostering the retention of the majority of metal species. Arsenic and chromium in oxyanionic states will increase in solubility with increasing pH as hydroxides compete for sorption binding sites.

To thoroughly examine the complex dynamics and full implications of elemental fate at this site, the speciation of metal species, specifically; arsenicals, lead and chromium should be performed. Total metal concentrations testing is the standard for metal contamination, yet it is the suggestion to perform metal speciation testing as the next step in fully understanding the dynamics of contamination within this unique,

complex environment. To confirm partitioning assumptions and hypothesis a speciated partitioning model should be modeled to obtain soil sorption coefficients.

10.0   PUBLIC HEALTH IMPLICATIONS

Community-based participatory research was instrumental in raising the researcher's awareness of the site of concern. Without the qualitative environmental prioritization process, the characterization of the site by the researchers would not have occurred.

Researchers experienced irritation of the mucous membranes as well as minor skin irritation. Current research investigations immediately concluded the potential health risks of effluent are imminent.

Former human and ecological risk assessments performed by aforementioned entities have deemed lead and arsenic exposure from groundwater and surface soils. This assessment has determined that the basicity of leachate or hydroxide concentration is hazardous to health through ingestion and inhalation routes of exposure. Potential exposure routes for direct human contact consist of contaminants in surface soil/sediment, four ball fields located near the solid wastes disposal area, ground water movement, and exposed leachate and wastes (Baker, 1997).

Bioaccumulation of toxic metals and elements can occur in fish, and the presence of the Roston Eddy Marina directly across from the waste site has been observed to be a heavily fished area. Recreational river activities have also been observed, as well as

hikers in the proximity of the 150 acre site of concern. Aquatic species are sensitive to pH fluctuations, and it has been demonstrated in previous research that most aquatic organisms cannot survive in a pH above 10.10.

The presence of alkaliphilic microorganisms at a pH 11.00 is extremely rare and warrants further research that could benefit heavy metal remediation technologies. Further research of these implications and other metal redox reactions should be further investigated.

APPENDIX

Administrative order from the Pennsylvania Department of Environmental

Protection to PPG Industries, March 9, 2009

PITTSBURGH (March 9) -- The Department of Environmental Protection issued an administrative order to PPG Industries, requiring it to collect and treat contaminated water discharging unabated from the site containing decades-old waste from its former Ford City plant, and to restrict access to the site and to the section of the Allegheny River impacted by the discharge.

The site, located in Cadogan and North Buffalo townships, Armstrong County, was used from 1949 through 1970 as a disposal area for glass polishing waste slurry produced by its former Ford City facility. PPG created a 77-acre slurry lagoon area, 90 percent of which has a vegetated cover.

In the 1920s, PPG established a solid waste disposal area on the site in which was disposed off-spec glass and other solid wastes until 1967.

DEP staff was contacted by Allegheny River Stewards to discuss the results of field testing it had conducted on the river, which indicated that the discharge from the site was raising the pH of the Allegheny River to unacceptably high levels.

Rain and snow melt filter through the soil and, after mixing with or running through the waste, become contaminated by pollutants including antimony, arsenic and lead and become highly alkaline. The polluted water then seeps out of the slurry lagoons, and possibly the landfill, at several locations. It then flows to or is conveyed untreated to the Allegheny River and Glade Run

The order requires PPG within 30 days to begin monitoring the quality and quantity of the seepage and the receiving streams and to submit to DEP an interim abatement plan for review and approval.

Within 90 days, PPG is required to submit to DEP for review and approval a plan to permanently collect, treat and dispose of the waste water, as well as a schedule for plan

implementation. PPG also is required to provide to DEP written monthly reports documenting the measures taken in the previous month and those planned for the following month to address the site conditions.

Finally, the order requires PPG to submit a plan to DEP detailing how it will limit access to the site and to the effected areas of the Allegheny River and Glade Run. A pH level of 12 standard units has been detected. To provide perspective, bleach has a pH level of 12.5.

In 1972, PPG sold the site to Ford City for $1. A parcel of the site which is located north of the solid waste disposal area currently serves as a recreation area.

BIBLIOGRAPHY

Anderson, M. C., Ferguson, F. J., & Gavis, J. (1976). Arsenate adsorption on amorphus aluminum hydroxide. *J. Colloid INterface Sci., 54*, 391-399.

ATSDR. (2005). *Toxicological Profile for Arsenic*: Agency for Toxic Substances and Disease Registry.

Baker Environmental Inc. (1993). *Remedial Investigation for the PPG Ford City Site*.

Baker Environmental Inc. (2001). Addendum to Remedial Investigation for the PPG FOrd City Site.

Bartolome, B. C. S., Nieto, S., & al., e. (1999). Acute arsenic poisoning: Clinical and histopathological features. *Br J Dermatol, 141*, 1106-1109.

Cullen, W., & Reimer, K. (1989). Arsenic speciation in the environment. *Chem Rev, 89*, 713-764.

Davis, J. A., & Leckie, J. O. (1978). Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. *Enviro. Sci. Technol., 12*, 1309-1315.

ESRI. (2009, 2009). ArcGIS Online Standard Map Services. Retrieved March 3, 2009, 2009, from http://www.esri.com/software/arcgis/arcgisonline/std_map_services.html

Ferguson, F. J., & Gavis, J. (1972). A review of the arsenic cycle in natural waters. *Water Res, 6*, 1259-1272.

Frankenberger, T. W. J. (Ed.). (2002). *Environmental Chemistry of Arsenic* (1st ed.). New York, NY: Marcel Dekker, Inc.

Grenthe, I., & Puigdomench, I. (Eds.). (1997). *Modeling in Aquatic Chemistry*. Stockholm, Sweeden: OECD/NEA Data Bank.

Hingstong, F. J., Posner, M. A., & Quick, P. J. (1971). Competitive adsorption of negatively charged ligands on oxide surfaces. *Faraday Soc., 52*, 334-342.

Huling, G. S. (1989). *Facilitated Transport*. Ada, OK: Environmental Protection Agency,.

Korte, N., & Fernando, Q. (1991). A review of arsenic (III) in groundwater. *Crit Rev Environ Control, 21*, 1-39.

Kvesitadz, I., Khatisashvili, G., Sadunishvili, T., & Ramsden, J. (2006). Biochemical Mechanisms of Detoxification in Higher Plants: Basis of Phytoremediation (pp. 262): Birkhauser.

Lee, D. C., & Kelly, R. J. (1995). Whole-bowel irrigation as an adjunct in the treatment of radiopaque arsenic [Letter]. *Am J Emerg Med, 13*(2), 244-245.

McBride, M. B. (1977). Copper (II) interaction with kaolinite facotrs controlling adsorption. *Clays Clay Miner, 26*, 101-106.

McLaren, R. G., & Crawford, D. V. (1973). Studies on soil copper: II. The specific adsorption of copper by soils. *Soil Sci., 24*, 443-452.

McLean, E. J., & Bledsoe, E. B. (1992). Behavior of Metal in Soils. In Environmental Protection Agency (Ed.). Ada, OK: EPA.

Mclean, E. J., & Bledsoe, E. B. (1992). *Behavior of Metals in Soil* (No. EPA/540/S-90/018). Washington, D.C.

Moore, J. (1991). *Inorganic Contaminants of Surface Water*. New York: Springer-Verlag.

Piwoni, D. M., & Keeley, W. J. (1990). Basic Concepts of Contaminant Sorption at Hazardous Waste Sites, *Ground Water Issue* (pp. 7). Ada, OK.

PPG. (1991). Letter to Ecology and Environment, Inc. from PPG Industries, Inc.

Prasad, M. N. V. (Ed.). (2001). *Metals in the Environment*. New York, NY: Marcel Dekker, Inc.

Puls, W. R., Powell, R., Clark, D., & Paul, C. (1991). Facilitated transport of inorganic contaminants in ground water: Part II. colloidal transport. In United States Environmental Protection Agency (Ed.). Ada, OK: US EPA Robert S. Kerr Environ. Res. Lab.

Ratnaike, R. N. (2003). Acute and chronic arsenic toxicity. *Postgraduate Medical Journal, 79*, 391-396.

Sadiq, M. (1992). *Toxic metal chemistry in marine environments* (illustrated ed.): CRC Press.

Samiullah, Y. (1990). *Prediction of the Environmental Fate of Chemicals*. London, UK: The British Petroleum Company p.I.c.

Shanker, K. A., Cervantes, C., Loza-Tavera, H., & Avudainayagam, S. (2004). Chromium toxicity in plants. *Environmental International, 31*, 739-753.

Song, J., Dubey, B., Jang, Y., Townsend, T., & Solo-Gabriel, H. (2005). Implication of chromium speciation on disposal of discarded CCA-treated wood. *J. of Hazardous Materials B128*, 280-288.

Soucy, N., Ihnat, M., Kamat, C., Hess, L., Post, M., Klei, L., et al. (2003). Arsenic stimulates angiogenesis and tumorigenesis in vivo. *Toxicol Sci., 76*(2), 271-279.

US EPA. (2009, March 18, 2009). Drinking Water Contaminants. Retrieved April 20, 2009, 2009, from http://www.epa.gov/safewater/contaminants/index.html

Xintaras, C. (1992). *Impact of Lead-Contaminated Soil on Public Health*. Retrieved April 21, 2009. from http://wonder.cdc.gov/wonder/prevguid/p0000015/P0000015.asp#head007000000 000000.

Zachara, J. M., Girvin, D. C., Schmidt, R. L., & Resch, C. T. (1987). Chromate adsorption on amorphous ion oxyhydroxide in presence of major ground water ions. *Enviro. Sci. Technol., 21*, 589-594.