Environmental Geochemistry of Metals Associated with Abandoned Gold Mines on Unga Island, Alaska: Developing an Understanding of Water Quality on Unga Tribal Lands

Undergraduate Research in the Community Award
Final Report

by Amanda Chriest, BS Geological Sciences Major

Faculty Mentor: Dr. LeeAnn Munk, Department of Geological Sciences

Community Partners: Mike Brubaker, Aleutian Pribilof Island Association, Inc.
John Foster, Unga Tribal President

Abstract

An investigation of the environmental geochemistry of water and sediment at the abandoned Apollo and Sitka gold mine sites on Unga Island, Alaska was undertaken in order to understand the impact of the mine workings and tailings on the environment. Both of the abandoned mines are located in the same watershed which contains two anadromous streams that empty into Delarof Harbor.

Water, streambed sediment and precipitates were collected from seven streams within the drainages and analyzed for major and trace elements by ICP-MS. The water samples were also analyzed for anions by IC and H and O isotopes by stable isotope mass spectrometry. In situ measurements of pH, SC and T were made at each site. Alkalinity was measured on site by titration.

At the Apollo mine site pH increases from 6.26 at the main adit to 6.53 downstream before it enters the main stream channel. Alkalinity is low (27-29 mg/L) and sulfate ranges from 146.1 to 146.9 mg/L. Dissolved elemental concentrations of Al, Cu, Zn and Pb decrease with distance away from the mine with the exception of a small increase in Al and Zn 300 feet downstream of the main adit. Precipitate concentrations of Al, Fe and Zn decrease with distance from the adit and an increase in pH. The precipitates also have an increase in Cu, Mg, Cd and Mn downstream.

At the Sitka mine site pH ranges from 6.25 upstream of the mine site to 5.21 just below the main waste rock pile. Alkalinity is 30 mg/L up stream from the waste rock to <10 mg/L at the waste rock site. Sulfate ranges from 2.8 to 36.0 mg/L. Dissolved Fe was below detection limits at these sites and total Fe decreases from 276.61 ppb to 107.12 ppb as a function of decreasing pH; however dissolved Al, Cu, Zn, Mg and Pb concentrations increase with decreasing pH. Streambed sediments from upstream of the rock waste pile have decreases concentrations of Al, Fe, Pb, and As than those below the rock waste pile. Cu and Zn concentrations are less than half at the rock waste pile in comparison to the streambed sediment upstream.

The Sitka and Apollo mine sites are contributing elevated concentrations of Al, Mn, Cu, Zn, and Pb to the local aquatic environment. At the Apollo site elements are partitioned between the dissolved phase and Al-rich precipitates on the streambed as a function of distance downstream and an increase in pH. The Al oxyhydroxides act as a sorbent for trace metals. At both mine sites dissolved metal concentrations decrease to at or below detection however, some metal concentrations in the streambed sediments remain elevated.

I. Introduction

I. a. Research Problem

Like other Native Alaskans, the Aleuts of Unga Island have lived a subsistence way of life for centuries and depend upon the quality of natural resources of the land and sea for nearly every need. Modern day Aleuts rely on fish, shellfish, ducks, birds, seals, otters, herbs, vegetables, roots and berries among other natural products on and near their island. These resources provide physical, economic, cultural, and spiritual well-being for the Native Alaskans of Unga Island. Therefore, the health and quality of all these resources, notably water resources, is fundamental to their existence.

The chemical composition of surface water is dependent on its sources, pathways and lifecycle. Some of the natural factors that affect the composition of surface water are lithology and mineralogy of bedrock, solubility of minerals, ion exchange, mixing and dilution of the water bodies, and in some arid regions evaporation causing the precipitation of minerals. In addition, to these natural sources of chemical elements, there are many anthropogenic sources of elements or contaminants to surface water. Some examples include landfill leachate, waste from various industries, and acid mine drainage that originates in areas associated with sulfide, gold, or coal mining. In many cases, the concentration of metals including iron, aluminum, lead, mercury, copper, zinc, and nickel (among others) will increase due to the natural occurrence and/or disturbance of mineralized (metal-rich) zones. In addition, environmental parameters including pH (acidity) and temperature may increase the dissolution of metals and other elements from the bedrock into the water. Once the metals enter the streamwater they may remain dissolved or form solid precipitates rich in metal content. If the concentrations of chemical elements or compounds exceed certain concentrations and are consumed they can pose health hazards to aquatic wildlife and humans.

One prominent anthropogenic source of metals to the environment on a global scale is abandoned sulfide and gold mines. In the case of mines it is often important to distinguish between the amount of metals naturally released into the environment and those that are increasingly input due to the breakup, crushing and subsequent increased exposure to weathering from the mining activities. Areas that have been mined for metal sulfides and gold often have anomalies of metals associated with them.

The two main mines on Unga Island, Alaska (Apollo and Sitka mines) (Figure 1) have not been in operation since the early 1900's, but may be leaching metals into the surface water creating a potential hazard to humans, animals, and biota in and near the drainages from the old mining adits. Members of the Unga Tribe and the Aleutian Island Pribilof Association, Inc. (APIA) have made observations of these old mine sites and have a serious concern about the water quality near the abandoned mines because of visible changes in the color of the water and precipitates forming on the streambed. Both of the abandoned mines are located in the same watershed that contains two anadromous (salmon spawning) streams that empty into Delarof Harbor (Figure 1). Members of the Unga Tribe are additionally concerned that the drainage from the abandoned mines may be affecting their subsistence food sources including salmon.

The US Geological Survey has identified geochemical anomalies of many metals including gold, silver, zinc, copper, tin, and lead in the bedrock in areas of mineralization as well as in streambed sediments (Rheile, 1999). This is the first study to date of the water quality in the streams draining from the old mines and further studies are required to further determine the true hazards that may be associated with these sites.

The goal of this research was to determine the source(s), transport and fate of metals associated with the mineralized sites on Unga Island with a focus on the Apollo and Sitka gold mine sites and to disseminate this information in an understandable and useable format to the members of the Unga Tribe.

The main research questions are:

1. **Are potentially toxic metals weathered from the abandoned mine sites and entering the aquatic ecosystem and becoming bioavailable in the environment?**

2. **What are the geochemical mechanisms operating in this environment to transport and deposit the metals?**

3. **Can we assess the potential hazard of metals to the natural resources and members of the Unga Tribe?**

Preliminary results from this study are the first step in answering these questions and will be given to the Unga tribe for them to use as they see fit.

A.

B.

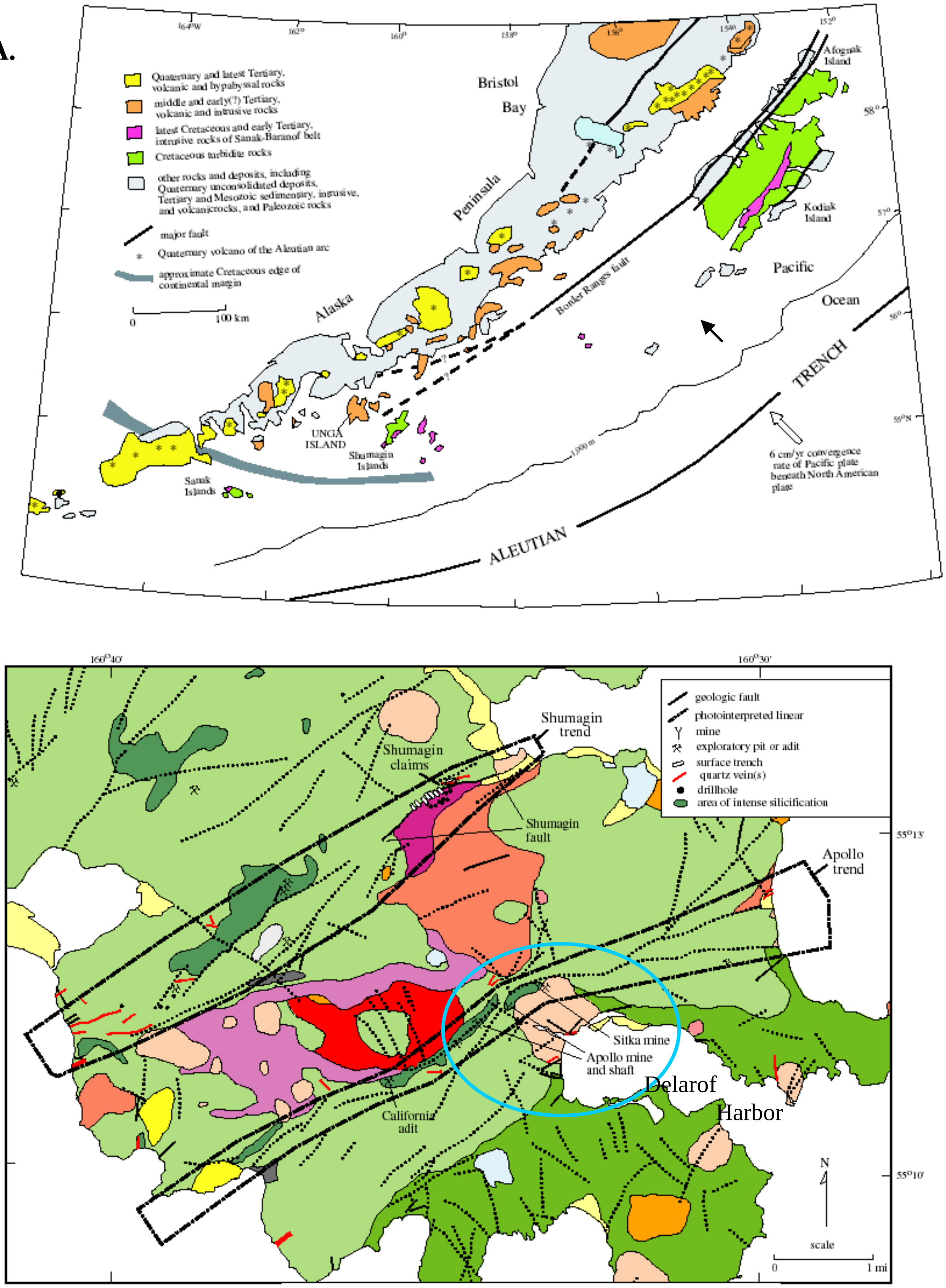


Figure 1. Location and simplified geologic map of Unga Island in the Aleutian Islands, Alaska (A.) and more detailed geologic map showing locations of the Apollo and Sitka mines on Unga Island (B.), primary study area outlined in blue. (Taken from Riehle et al. (1999) for a complete description of geologic units indicated by color see Riehle et al. (1999)).

II. Support of the Community Partner

This project is a joint effort between the Unga Tribe, APIA, and the University of Alaska Anchorage, Geological Sciences. The planning of this project began three years ago when Dr. LeeAnn Munk (UAA) began working with Chris Riggio at APIA to help design a sampling plan to investigate the abandoned mined sites on Unga Island at the request of the Unga Tribe. Dr. Munk has been actively working with APIA to assist in determining a sampling strategy and plan for helping the Native Alaskan population on Unga Island to better understand their water quality, particularly in areas associated with abandoned gold mines where tribal members have major concerns about the water quality. I was then involved as a student working in conjunction with Dr. Munk, the Unga tribe and APIA. This project not only benefited me as a student conducting independent research but I was also able to provide much needed data and results to the Unga Tribe and APIA so that there is a better understanding of water quality on Unga Island.

Additionally, the funding provided from the Environmental Protection Agency (EPA) Indian General Assistance Program (IGAP) to the Unga Tribe helped support our travel, lodging, and per diem, and we did share some of the analytical data as well. This project was also significant to me because it is an opportunity to get involved with the Alaskan community in multiple ways. I was able to help provide information and skills to members of the Unga Tribe so they may have a better understanding of water quality on their land, learn how to take environmental samples, and conduct future monitoring of their water quality. Also, as a young scientist I had the opportunity to conduct an original research project.

III. Present Understanding and Knowledge

III a. Geology

Unga Island is a part of the Shumagin Islands in the Aleutians Island chain and is situated on the continental shelf southwest of Kodiak Island. The island was formed through volcanic activity and concurrent sedimentation as a result of the Pacific plate subducting beneath the North American plate (Figure 1A.).

Unga Island has 18 identified volcanic and sediment rock units. The dominant rock types are fine-grained marine conglomerate sandstones and siltstones that grade upward into volcaniclastic rocks which contain ash flow tuffs and submarine lava flows. These rocks are overlain by younger undifferentiated volcanic rocks composed of lava flows and flow breccias of andesitic composition. The Apollo lineament is one of the dominant structures on the island along which mineralization occurred to form gold ore deposits. Both the Apollo and Sitka mines lie along the trend of the Apollo lineament (Figure 1B.). The major rock types in the area of the mines are large basaltic and andesitic domes, which contain local veinlets and vugs of the minerals: zoelites and chert. The host rocks at the mine sites are predominantly volcanic flows with a basaltic and andesitic dome (Reihle, 1999).

The gold deposits originated from hot circulating water (hydrothermal activity) while the intrusive and volcanic rocks cooled. The thermal waters traveled along fractures or small channels in the host rock and when cooled deposited gold and other metals. Other evidence of hydrothermal activity is changes in the primary mineral phases in the volcanic host rocks which have produced alteration zones that can be traced along the Apollo lineament.

III b. Hydrology

Two of the main streams feeding into Delarof Harbor come in contact with drainage from the Apollo and Sitka mines. At the Apollo mine site there is a small stream starting at the adit, it flows to a small pond, and then drains to Apollo Creek, which also receives drainage from Apollo Lake. Apollo Creek then drains into a small lagoon prior to entering Delarof Harbor. This watercourse is the main area where both members of the Unga Tribe and APIA suspect there is acid mine drainage being produced and entering the environment. The Sitka mine is located near a main river that runs through a meadow then down into Delarof Harbor. Previous site visits have noted the presence of salmon and possibly trout in these rivers (QAPP, 2006).

III. c. Description of the Abandoned Gold Mines

Apollo Mine

The Apollo mine is 3-5 miles west of the native village of Unga. There are two tunnels both of which have mine shafts. Tunnel 1 is 1200 feet long and tunnel 2 is 315 feet below tunnel 1 and 3200 feet long. Multiple items have been abandoned at the site including old vehicles, a bulldozer, office and living trailers, gas cylinders, fuel drums and other items that clearly do not date back to the time of operation. None of the equipment is operable and there is no evidence of continued operation after the exploratory work done in the 1980's. Some equipment was pushed off the side of the main mineshaft. On the east side of the river there is a pile of tailings along with other debris and to the south of the tailing pile there is a graded bed of tailings where the abandoned trailers are located. Northeast where the adit is there is an old shed with rock cores, trolleys with batteries and in the woods there is batteries and drums (QAPP, 2006).

Sitka Mine

The Sitka mine is west of the Apollo mine and is near a river. The mine was opened by a vertical three-compartment shaft at 350 feet in depth. At the site there is a mine shaft, a rock and gravel pad of tailings that drops off into some alders and a meadow. There is some drums and debris but not to the extent of Apollo mine. At this site there is a smelter on the edge of the tailings. Runoff from the tailings is observed to flow into the meadow where the river flows through (QAPP, 2006).

III. d. Geochemistry of Rocks, Streambed sediment, and Heavy-Mineral concentrate

Data reported in the USGS Open File Report 99-136 (1999) was collected during the 1982-1988 mineral resource assessment of the Port Moller and adjacent quadrangles. The sampling was done in conjunction with geologic mapping. The samples taken where single grab rock samples, composite rock samples, and streambed samples from both first and second order streams. The rock samples where screened and panned until most of the lower density and clay size materials where removed. The streambed samples where sieved and only fine grained materials where analyzed. Heavy-mineral concentrate samples where collected, sieved, and then separated into three magnetic fractions.

The samples where analyzed for 31 elements as well as trace elements. The data obtained helped to determine the thresholds for anomalous concentrations. The thresholds where determined based on a comparison of data from over 5,000 samples collected throughout the Alaskan Peninsula. Anomaly thresholds for the rock samples were chosen approximating the 90^{th} percentile for the moderately anomalous samples and the 98^{th} percentile for the highly anomalous samples.

The gold and silver anomaly maps indicate that neither the Apollo mine nor the Apollo-trend contributed to the development of stream sediment or heavy-mineral concentrate anomalies in the basin that drain this area. However, the rock samples showed a wider distribution of anomalies that were evenly distributed throughout the older volcanic and volcaniclastic rocks of the Meshik Volcanics of the bedrock. Copper, lead, and zinc stream sediment and heavy mineral concentrate samples tend to match the distribution of silver and gold (Rheile, 1999).

IV. Summary of Current Understanding of Geochemistry of Water Associated with Mined Areas

All metals occur in the natural environment to some extent. It is important to be able to identify natural vs. anthropogenic sources of the metal in the study area. When oxidation of sulfides such as pyrite (FeS_2) occurs at or near the surface of the earth surface water becomes acidic and enriched in sulfate, iron, aluminum and other trace elements including lead, copper, zinc, nickel, and cadmium (Munk et al., 2002). Because surface water provides oxidizing conditions and has the ability to dissolve minerals and rock this if the predominant weathering environment on the planet. When the metal sulfides oxidize and release H^+ ions into solution the water becomes acidic. As a function of distance from the source of metals (ie. bedrock that is weathering) and/or pH and other environmental variables, the metals will either remain in solution and/or begin to precipitate out of solution. Mined areas have various sources of metals in addition to the mineralized bedrock including tailings or waste rock piles, underground adits and some times other chemicals used in processing the metals such as mercury and cyanide in the case of gold mines.

Acid Rock Drainage vs. Acid Mine Drainage

Acid rock drainage (ARD) is a natural process in which sulfuric acid is produced from the weathering of sulfide bearing rocks-for example pyrite (FeS_2) - that is exposed to water and oxygen. This occurs along exposed outcrop or other exposed areas or rock. ARD is produced naturally in un-mined areas. Acid mine drainage (AMD) is a greatly magnified process of ARD. Rocks that contain valuable metals generally contain sulfides (metals combined with sulfur). The relation is due to hydrothermal processes that are responsible for the deposition and formation of metallic ores such as copper and gold. Due to the lack of sulfides at the sites in question there may not be an AMD problem; however there are elevated concentrations of metals and other trace elements in the surface water at the sites. There is also a presence of tan-white precipitates, which is an indication of metal accumulation in the streams (QAPP, 2006). The precipitate is produced by sorption. This is the ability for ions in solution to precipitate out as a function of pH. In a low pH environment the particles have a positively charged surface attracting water molecules and as pH increases or the water is dilutes the surface becomes negatively charges there for being attracted to the surface particles and precipitating out. The pH that this process occurs is dependent on the metal ions. Not all metals have the same charge density; they're for not all metals precipitate out at the same pH levels.

V. Objectives and Goals of the Research

1) Investigate the occurrence and distribution of metals in stream water and mineral precipitates as a function of distance away from mined areas (tailings or adits)
2) Model the geochemical affinity of metals to remain in the stream water or to form solids
3) Link the water geochemistry to sources of metals in the bedrock and mineralized zones
4) Teach members of the Unga Tribe about the chemistry and other processes operating in their environment and teach them how to take their own samples for future monitoring
5) Disseminate the findings of the research to APIA and the Unga Tribe in a written report as well as through oral presentations

VI. Methods

In order to achieve the above goals the following sampling plan, field measurements and lab analyses were preformed.

VI. a. Field Sampling

Field sampling of water, precipitates and streambed sediment were collected from May 25th through May 27th, 2007. At each site, measurements of pH, temperature, conductivity, and alkalinity of the stream water were taken. Sample site selection has already been planned following the recommendations from the Unga Tribe and APIA. Additional sites were selected on site based an examination of other areas that may be impacted by the abandoned mines. Three water samples were collected at each sampling site. All samples were collected in pre-cleaned plastic bottles following procedures outlined in Dr. Munk's Standard Operating Procedures. One water sample was collected directly from the stream and preserved with high purity trace-metal grade nitric acid. This sample is representative of the total load of elements in the stream. Another sample was filtered through a 0.45 µm filter to remove suspended particles and most microorganisms that may be living in the water, the sample was then preserved with nitric acid as described above. This sample is representative of the elements dissolved in the stream. The third sample was also filtered through the 0.45 µm filter and was collected in a sample bottle with no preservative added. This sample was analyzed for anions (no preservative required) and was kept cool until returned to the Applied Science and Engineering Laboratory at UAA for analysis.

In addition to water samples, streambed sediments and precipitate samples were also collected. These samples were collected at the same sites as the water samples following the Standard Operating Procedures of the UAA Environmental Geochemistry Lab. Sediment samples were collected with a plastic scoop and stored in plastic bags. Precipitate samples were vacuumed from the stream bed using a syringe and plastic tubing and then stored in plastic sample bottles. These samples were kept cool until processed in the lab at UAA.

Dr. Munk and I also assisted others from APIA to collect a suite of samples for hydrocarbon analyses that will be performed in a separate lab.

VI. b. Sample Preparation

Precipitates and stream bed sediments were taken back to the lab at UAA where they were dried at low temperature in a drying oven for 24 hours. The samples were then homogenized using a mortar and pestle or sediment mixer. A known weight of each sample was leached in a solution of 2M nitric acid in plastic beakers for 48 hours. Each sample was then be decanted and filtered to remove any remaining particles, brought to volume in 250 ml plastic volumetric flasks with a solution of 5% nitric acid.

VI. c. Sample Analysis

All water and solutions were analyzed for major and trace elements (40 total) including the metals of interest by Inductively Coupled Plasma Mass Spectrometery (ICP-MS) and the anion samples were analyzed by Ion Chromatography (IC) in the ASET lab at UAA. All analyses were done by the analytical research chemist (Dr. Birgit Hagedorn) and following the Standard Operating Procedures of the lab.

VII. Geochemical Results

VII.a Apollo Mine Site

At the Apollo mine site pH increases from 6.26 at the main adit to 6.53 downstream before it enters the main stream channel. Alkalinity is low (27-29 mg/L) and sulfate ranges from 146.1 to 146.9 mg/L. Water samples collected near the Apollo adit had elevated levels of Al, Mn, Cu, Pb and Zn Figure 2a) with proximity to the site. As a function of distance down stream the concentrations of dissolved metals begin to decline. After the confluence of the small adit stream and the Apollo stream, concentrations of dissolved metals are at or below detection limits indicating a dilution effect.

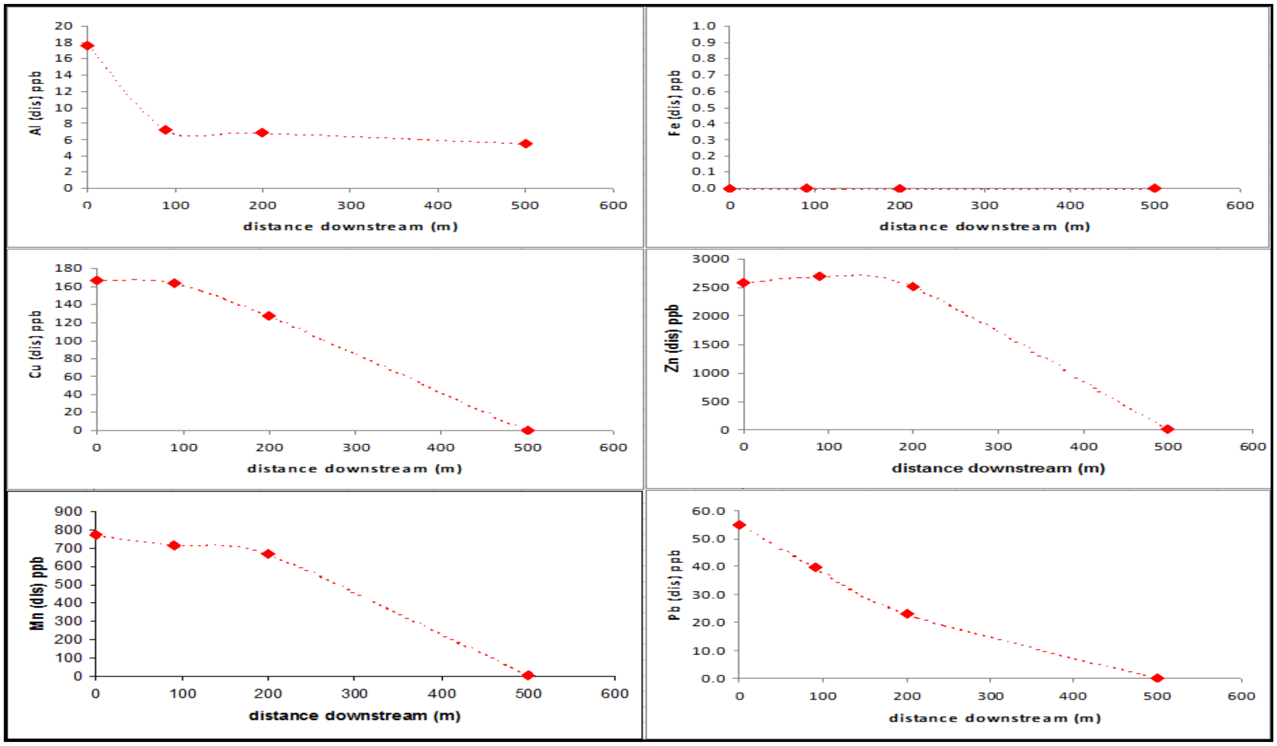
Streambed precipitates collected from the Apollo mine adit stream increase in Al and Fe concentrations as a function of distance from the mine sites and an increase in pH. Concentrations of Mn, Cu, Pb and Zn increase with distance from the mine site (figure 2b). At this site elements are partitioned between the dissolved phase and Al-rich precipitates on the streambed as a function of distance downstream and an increase in pH. The aluminum oxyhydroxides acts as a sorbent for the trace metals. The high concentrations are a result of the metals hitting a maximum sorption point at which time they can no longer sorb to the precipitate and must remain in solution. The pH is also a controlling factor of the ability for a metal to remain in solution or precipitate out. At the Apollo site the lowest pH is 6.13, which is a neutral pH, so there is not a large effect on the elements.

VII.b Sitka Mine Site

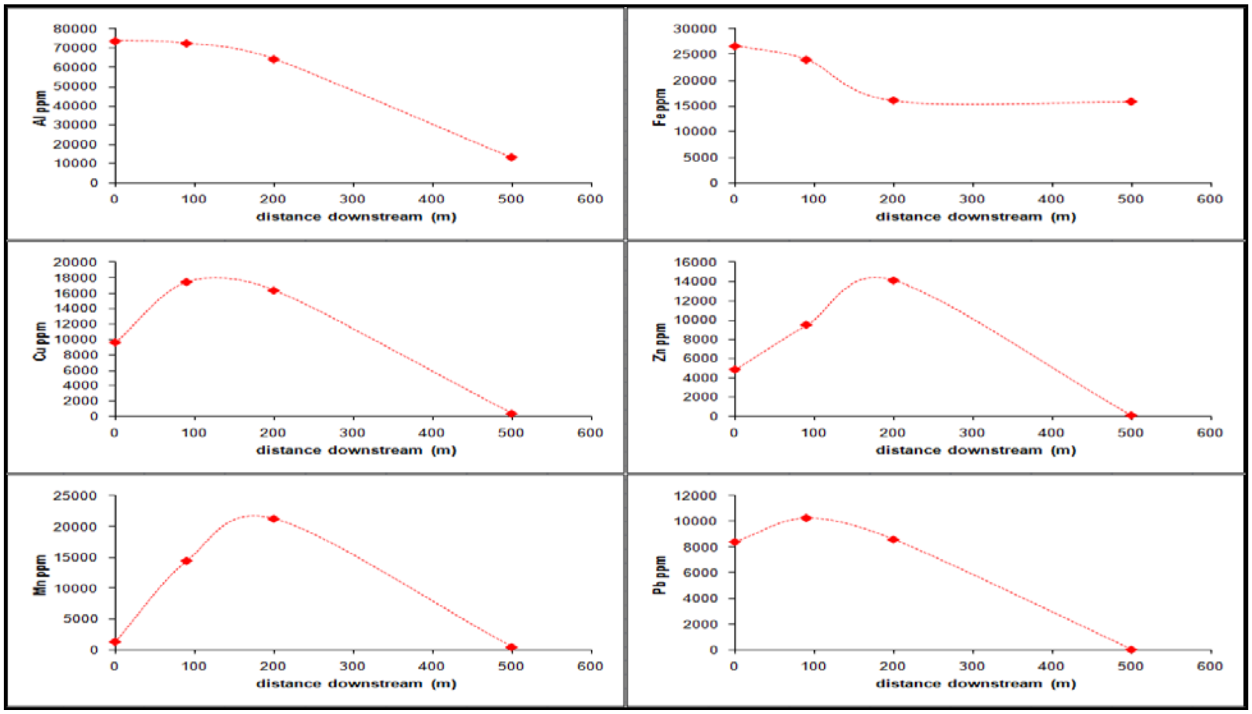
At the Sitka mine site pH ranges from 6.25 upstream of the mine site to 5.21 just below the main waste rock pile. Alkalinity is 30 mg/L upstream from the waste rock to <10 mg/L at the waste rock site. Sulfate ranges from 2.8 to 36.0 mg/L. Dissolved Fe was below detection limits at these sites and total Fe decreases from 276.61 ppb to 107.12 ppb as a function of decreasing pH; however dissolved Al, Cu, Zn, Mg and Pb concentrations increase with decreasing pH. The elevated concentrations occur approximately 30 meters below the waste rock pile (figure 3A). The stream that was sampled merges with the Sitka Stream and concentrations were at or below detection limit were sampled downstream of the confluence which is interpreted to be a dilution effect.

Streambed sediments were collected both upstream and downstream of the waste rock pile at the Sitka mine site. Concentrations of metals in the sediment spiked at the sample location 30 meters below the waste rock pile (figure 3B). Levels of Fe, Cu and Pb decrease downstream of the confluence and Al has a slight decrease in concentration but less of a decline than the others. Mn and Zn have higher concentrations in the main stream below the confluence than in the tributary that comes into contact with the waste rock pile and this is most likely due to other contributions from another source.

A

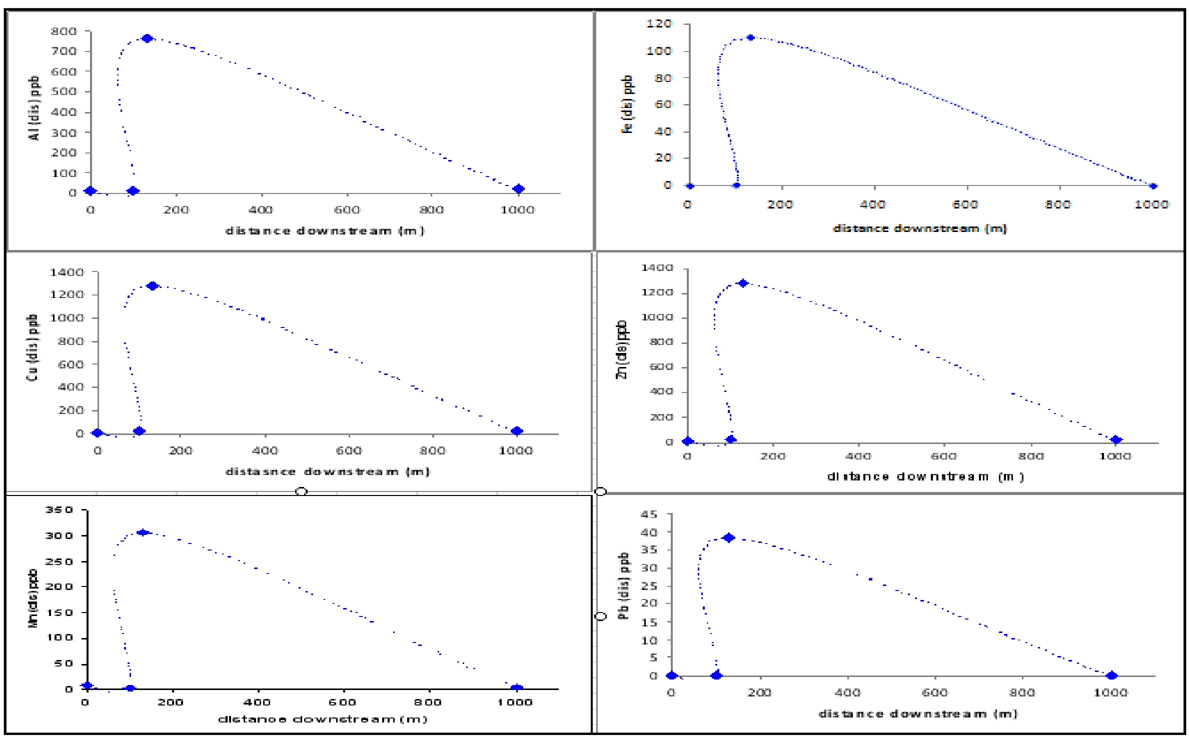


B

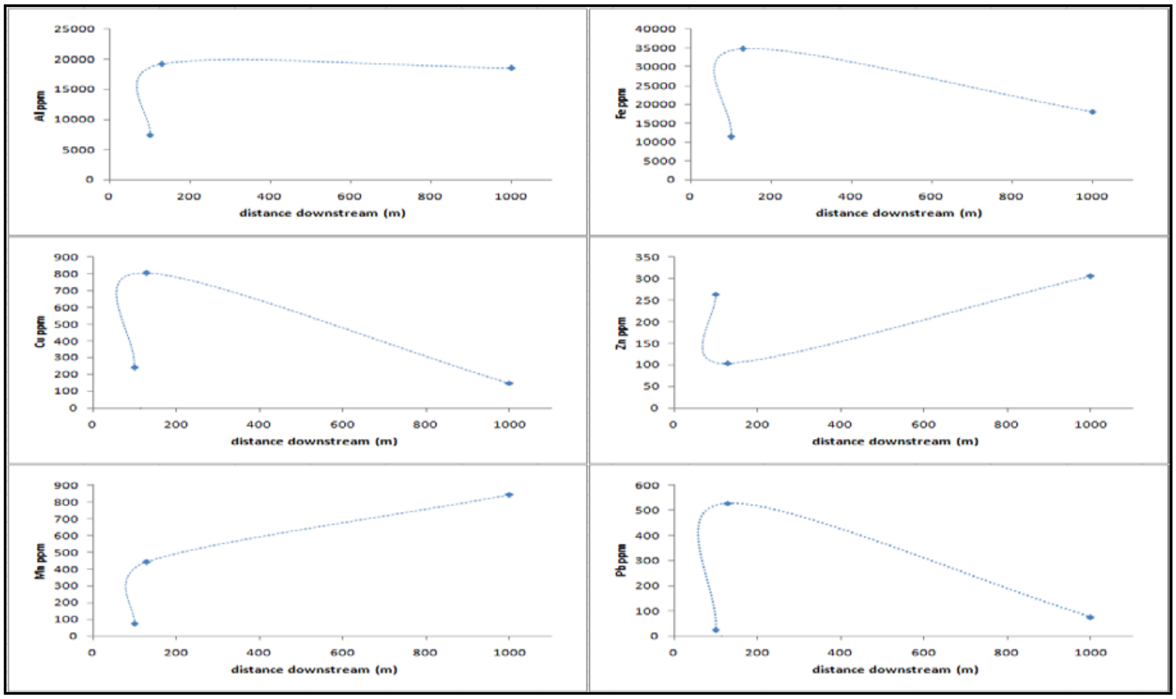


(Figure 2: A- Apollo mine site water chemistry with concentration in ppb on the Y axis and distance downstream in meters on the X axis. B- Apollo mine site precipitate data with concentration in ppm on the Y axis and distance downstream on the X axis. For both A and B the first sample point was located at the entrance to the adit.)

A



B



(Figure 3: A- Sitka mine site water chemistry metal concentration in ppb on the Y axis and distance downstream in meters on the X axis. B- Sitka mine site stream sediment chemistry with concentration in ppm on the Y axis and distance downstream on the X axis.)

VIII. Conclusion

Overall concentrations of metals in the small tributary streams that are in contact with the old mine sites are higher than those of the larger streams in the area. We see that at both the Apollo and Sitka mine there is a contribution of metals from the mine that is accumulating in the sediments at Sitka and sorbing to the Al oxyhydroxide precipitate at the Apollo site as well as metals remaining in solution in the dissolved phase at both locations. At Apollo the metals are partitioning between the dissolved phase and the solid phase. At both sites we observed and modeled the concentrations as a distance downstream and see the trend of increased concentrations with proximity to the mine site as well as an overall dilution effect as the small tributaries merge with a larger mass of water giving almost undetectable limits of the metals with the exception of Mn and Zn in the sediments of the Sitka Stream.

VIII. References

Riehle, J.R. Bailey, E.A., Cady, J.W., Church, S.E., Shew, N., Singer, D.A., Smith, B.D., White, W.H., and Wilson, F.H., 1999. Geological and geophysical setting of the gold-silver vein systems of Unga Island, Southwestern Alaska. U.S. Geological Survey Open-File Report 99-136. U.S. Geological Survey Anchorage, AK.

Eby, G.N., 2004. Principles of environmental geochemistry, Thomson Brooks/Cole: California, p.352.

Munk, L.A., Faure, G., Pride, D.E., and Bigham, J.M., 2002. Sorption of trace metals to an aluminum precipitate in a stream receiving acid rock-drainage; Snake River, Summit County, Colorado. Applied Geochemistry. 17, 421-430.

Riggio, C.M., Foster, J., Grepo-Grove, G., Santina, G., Araki, R., 2006. Quality Assurance Project Plan (QAPP) Apollo and Sitka Mine Sites, Unga Island, Alaska, 108p.