

Effects of mining on fine sediment quality; a comparison with regional metal background concentrations

Thesis MSc. Hydrology

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Abstract

The impact of an abandoned hydraulic gold mine and an open cast copper-gold mine on the quality of fine-grained sediment ($<63\text{ }\mu\text{m}$) was investigated at several creeks in the Quesnel river catchment catchment in British Columbia, Canada. Bed sediment samples, suspended sediment samples, vertical profiles and/or corings were collected at five field sites. Bed sediment samples were collected at weekly intervals and the suspended sediment samples were collected at 3 weeks intervals using time-integrated isokinetic samplers. Vertical profiles were taken at four sites and corings were taken at two sites.

Three field sites drain an open cast copper-gold mine, one site drains an abandoned hydraulic gold mine, and one site drains a natural area and was used as control site.

Enrichment ratios were calculated for all the samples with aluminium or iron as reference metal. Background values for these calculations are taken from a data of a geochemical atlas of British Columbia (*Jackaman and Balfour, 2008*). Examining these background values shows that the three geological units in which the sample sites are located have significantly different background values:

- Kamloops group has lower selenium (Se) values than the other two geological units.
- Snowshoe group has higher manganese (Mn) values than the Kamloops group, has lower mercury (Hg) values than the other two geological units, has higher lead (Pb) and zinc (Zn) values than the other two geological units .
- Nicolai group has higher arsenic (As), manganese (Mn), and copper (Cu) values than the other two geological units.

All the field sites show enrichment of one or several metals. Selenium enrichment is occurring at sites that are draining the open cast copper-gold mine and the control site. Manganese enrichment is occurring at sites that drain the open cast copper-gold mine. Copper enrichment occurs at location two sites that are draining this mine. Arsenic enrichment is occurring at locations in one specific geological unit. And Lead enrichment is occurring only at the abandoned hydraulic gold mine.

Selenium and copper enrichment is probably originating from the tailings from the mine. Arsenic enrichment could be originating from exposure of quartz-calcite veins, these veins are exposed due to logging (which increases erosion) and/or road construction, and lead enrichment at the abandoned hydraulic gold mine could be due to exposure of a vein of lead. Weathering and erosion of this vein may have caused the enrichment of lead at the sample site.

At locations draining the open cast copper-gold mine, samples that hold younger sediment show more enrichment in selenium and manganese than samples with older sediment, whereas the control site does not show differences between younger and older sediment. At the location near the abandoned hydraulic gold mine only the vertical profile samples are enriched with lead, the bed and suspended sediment samples are not enriched.

Results from this study were compared with results from *Smith and Owens (2010)* who conducted research on the impact of various land uses on the quality of fine-grained sediment ($<63\text{ }\mu\text{m}$). One of the same sites that has been used in this study (site H1) was used by *Smith and Owens (2010)* as well. Cadmium seems to be less (factor 0.4) in this study and manganese and selenium seems to be higher in this study with a factor of 2.1 and 2.3 respectively. Also copper seems to be lower in this study, although not much. The decreased metal production at the mine could explain the lower copper values. The increased tailings may be an explanation the higher selenium values.

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1 Introduction

1.1 Background and Problem definition

Metals are very common elements on earth. About 50% of the mass of the earth consists of metals and about 25% of the mass of the crust of the earth consists of metals. They can occur in rocks as native elements or as ions mixed with non metallic elements in a great variety of minerals. Nature can attack those rocks with two forms of weathering, mechanical en chemical weathering (Marshack, 2005).

Mechanical weathering breaks intact rocks into unconnected grains or chunks. This can for instance be done by frost wedging. Freezing water can break rocks because water expands when it freezes. If water is trapped in a crack in the rocks and it freezes it forces the crack to open and may cause the crack to grow. Other forms of mechanical weathering are root wedging, salt wedging and thermal expansion (Marshack, 2005).

Chemical weathering of crustal rocks is one of the principal processes controlling the geochemical cycle of elements at the Earth surface (Aiuppa et al., 2000). Chemical weathering alters or destroys minerals due to chemical reactions that take place when rocks come in contact with water solutions or air. Because many of these chemical reactions proceed more quickly in warm and wet conditions, chemical weathering takes place much faster in the tropics than in deserts (Marshack, 2005).

Acid rain is an example of chemical weathering. Rainfall can become acid if atmospheric carbon dioxide dissolves in the rainwater, producing carbonic acid. If rain contains carbonic acid in such quantities that its pH is reduced to e.g. 4 it can dissolve rocks that contain calcium carbonate. The effects are visible in karst landscapes (Marshack, 2005).

Chemical erosion consumes atmospheric and/or endogenous carbon dioxide and extracts metals from the rocks, these metals are being released to rivers and shallow groundwater and finally discharged into the ocean (Aiuppa et al., 2000). These are the natural processes of weathering. Sometimes these processes are influenced by humans.

In today's society humans use resources like metals, wood, oil and sand extensively. Metals are used for a variety of purposes ranging from buildings and cars to cooking pans. Usually they are extracted from mines and this extraction can cause some environmental problems. Mine tailings are one of those problems. Tailings are the materials left over after the process of separating the ore from the waste rocks (Brookfield et al., 2006). The composition of tailings is directly dependent on the composition of the bedrock and the process of mineral extraction used on the ore. Certain mineral process methods require pulverizing the rocks. The leftovers from this extraction process are put on large heaps (tailings) (Brookfield et al., 2006). The pulverization (artificial mechanical weathering) speeds up the chemical weathering process because the pulverized rocks have a larger surface area exposed to the atmosphere. Weathered minerals from these pulverized rocks can leach into the groundwater or runoff to river systems. This can cause a larger than usual input of certain elements in the environment, depending on the type of bedrock and related processes. This can potentially be harmful for the environment.

Several mines are located in the Quesnel catchment. Some of these mines are active and some of them are abandoned but they might both have an influence on the geochemistry of the fine sediments in the downstream gravel-bed rivers. In the summer of 2007 *Smith and Owens* conducted research on the impact of various land use activities (forestry, mining, and agriculture) on the quality of fine-grained sediment (<63 µm) in the Quesnel River Basin. Several suspended sediment traps were placed at various locations throughout the catchment. This sediment was collected with monthly intervals and the < 0.063 mm fraction was taken for metal content analysis (*Smith and Owens*, 2010). Their study concluded that arsenic, copper and selenium concentrations were elevated at location draining a mining area. It is therefore expected that there is some influence from activities at the mine sites on the geochemistry of the fine sediment. Water that has leached through the tailings that are present at the mine site may have entered the local hydrological system. Also atmospheric deposition of enriched dust may be a source of metals in the sediments (*Van der Perk*, 2006).

Because one of the mines is an active copper-gold mine it is expected that copper concentrations and associated metals such as arsenic (Oyarzun et al., 2004; Colbourne et al., 1975) are elevated compared to the background concentrations of these metals (i.e. the metal concentrations that occur under natural circumstances, without human influence). It is also expected that the local geology influences the geochemistry of the sediment. Fordyce et al. (2010) have successfully predicted differences in selenium concentration in soils in Scotland by using geological parent material only. Weathering of in-situ rocks releases metals into the environment (Aiuppa et al., 2000), and therefore the geologic setting of the region governs the background concentration of metals (Gałuszka, 2006).

1.2 Objectives

The principle aim of this study is to assess the influence of antropogenic activities on the geochemistry of fine grained sediment ($<63\text{ }\mu\text{m}$). The main focus in this study will be on the influence of mining on the geochemistry of fine grained sediment ($<63\text{ }\mu\text{m}$). In order to perform this study, bed sediment and suspended samples were collected near and in creeks draining mining area. Furthermore a control site was sampled. These field data were completed with a dataset from a study on the impact of various land use activities (forestry, mining, and agriculture) on the quality of fine-grained sediment ($<63\text{ }\mu\text{m}$) in the Quesnel River Basin (*Smith and Owens, 2010*) and the data of a geochemical atlas of British Columbia (*Jackaman and Balfour, 2008*).

The first research question that will be answered in this thesis is whether the geochemical composition of the sediment differs between the geological units in the study. The second research question is whether the enrichment of metals occurs in the study area and if so, why this enrichment occurs (Question 3). For this purpose, the data from *Jackaman and Balfour (2008)* were used to calculate enrichment ratios.

Additional research questions that are asked are:

- Are there differences in the enrichment between suspended sediment samples and bed sediment samples? (Question 4)
- How do our data compare with the data of *Smith and Owens (2010)*? (Question 5)

2 Study Area

The study area is located in the province of British Columbia in Canada. It is located approximately 600 kilometers north of the city of Vancouver and 300 kilometers south of Prince George, close to the town of Likely (52°37'00.73"N, 121°34'03.89"W). The study area is located in the Quesnel and Cariboo river catchment. The Quesnel River and Quesnel Lake are located in the Quesnel River catchment and the Cariboo River and Cariboo Lake are located in the Cariboo River catchment.

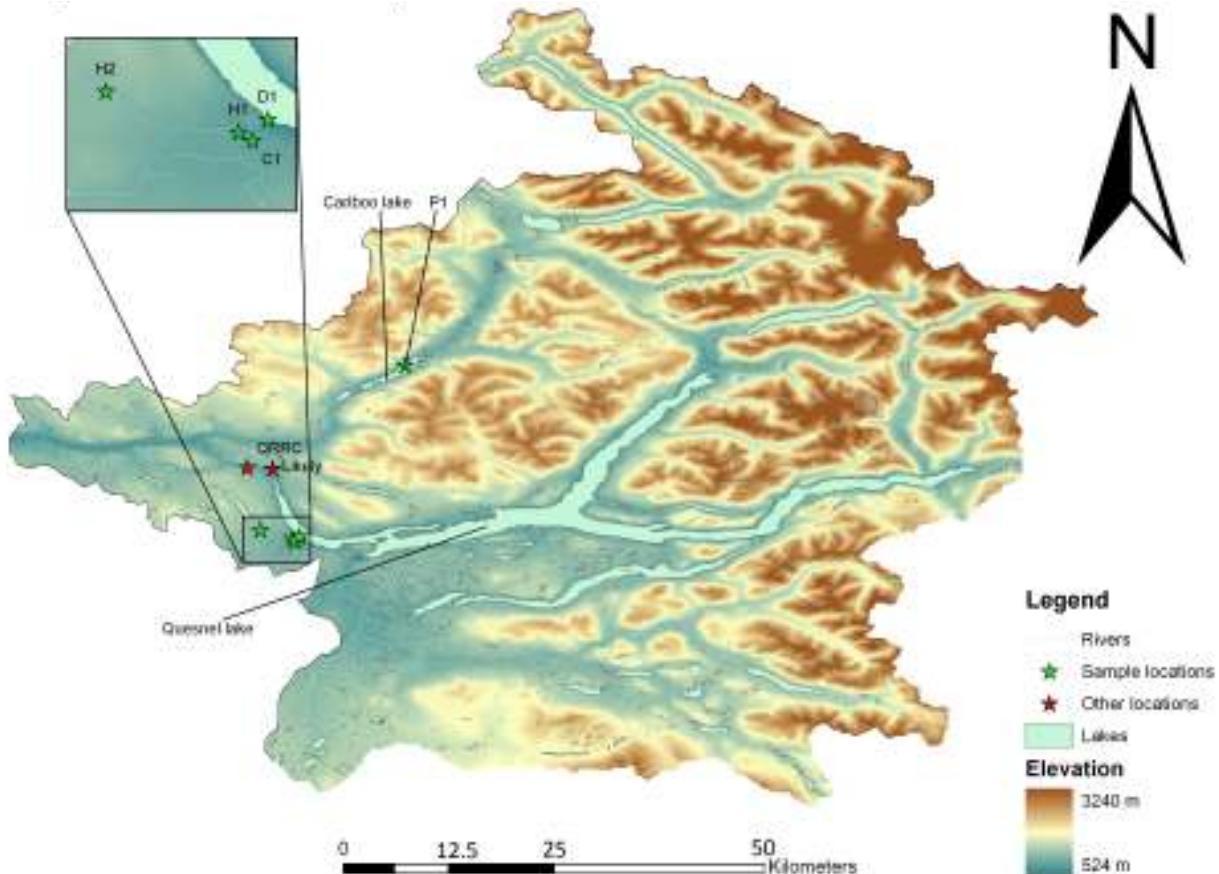


Figure 1: Research area with sampling locations (source: <http://www.geobase.com>, 2011).

These catchments are sub-catchments of the larger Fraser river catchment and are important for several reasons; they provide drinking water for many people and they are home to the great salmon run every year. The salmon run is an import part of the nutrient cycle in these catchments. The salmons that die provide the system with nutrients from their decomposing bodies.

The highest point is the study area (~3,200 meters above sea level) is located in the Cariboo Mountains, which are located in the east of the study area (see Figure 1) and the lowest point is about 500 meters above sea level.

In this study area several sampling sites where selected. These sampling sites where located in small creeks (see Figure 2).

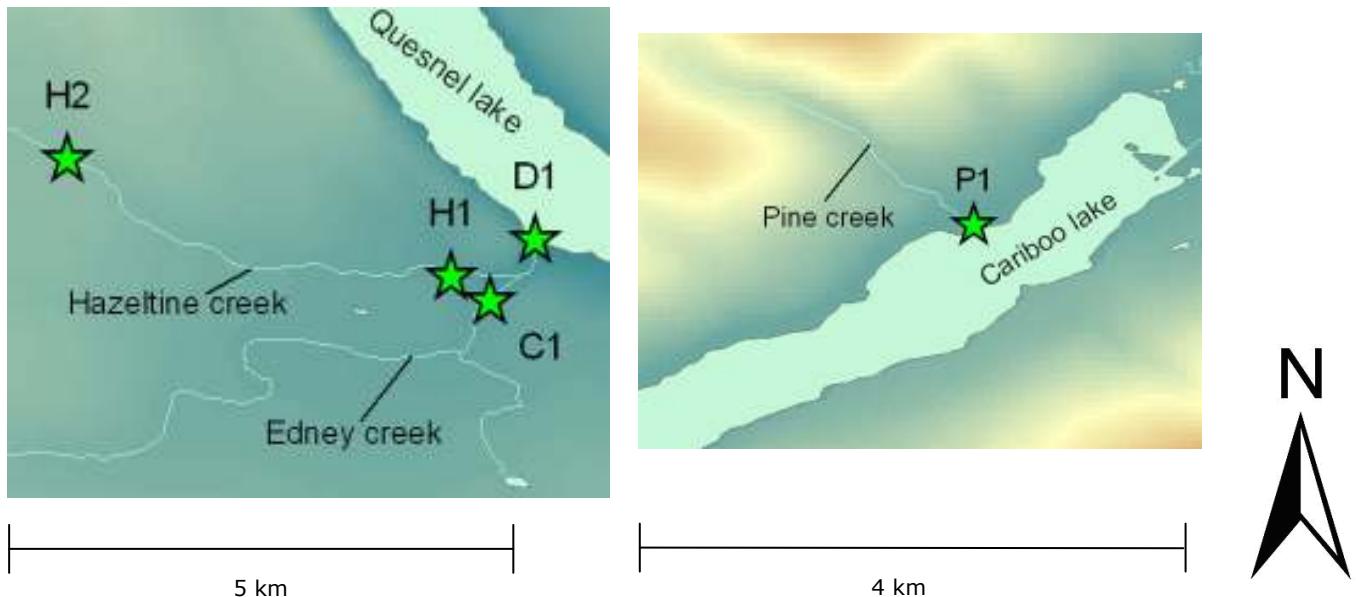


Figure 2: Location of the sampling sites.

According to the Köppen climate system the study area is located in the *Dfb* classification (Warm Summer Continental or Hemiboreal climates). The area does not have a dry winter and summer and the warmest month is below 22 °C (see Figure 3 and Table 1).

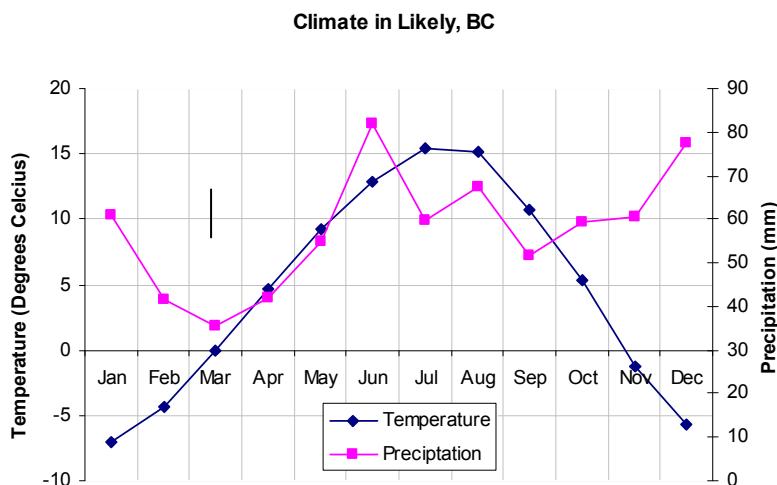


Figure 3: Climate in Likely, BC (source: Environment Canada, 2011, <http://www.ec.gc.ca/>)

Table 1: Climate data for Likely (source: Environment Canada, 2011, <http://www.ec.gc.ca/>)

| | |
|---------------|----------|
| Average high | 11.2 °C |
| Average low | -1.2 °C |
| Precipitation | 692.4 mm |

2.1 Geology

The geological history of British Columbia can be viewed as four distinct plate-tectonic phases. The rifting/open margin phase lasted from initial breakup at about 700 Ma (late Proterozoic) until 400 Ma (Middle Devonian), when widespread subduction began along the margin. The Oceans and Islands phase commenced as subduction built arcs and the continent retreated away from them, creating a scenario like the modern south-eastern Pacific ocean. This phase lasted until about 180 Ma (Early Jurassic), when opening of the Atlantic ocean reversed the motion of North America such that it drove strongly westward relative to the long-standing subduction zones off its west coast, creating a broad zone of compression in the offshore arcs and ocean basins as well as its own miogeocline (collisional/orogenic phase). The final, post-collisional phase

commenced during the Early Tertiary when parts of the East Pacific Rise subducted under the continent and turned the plate margin from pure subduction to a regime with both transcurrent faulting and continued subduction of short, remnant segments. Industrial mineral deposits formed during each of these tectonic phases. Combined effects of two or more phases were required to form some of these deposits (*Nelson and Colpron, 2007* and *Pike et al., 2010*).

A geological mapping program in the Cariboo region of central British Columbia, the Quesnel Mineral Belt Project, was conducted over four succeeding field seasons between 1985 and 1988. The main objective was to remap and re-interpret the central Quesnel volcanic belt, also known as the Quesnel Trough, in the vicinity of Quesnel and Horsefly lakes and to the north and south of Quesnel and Horsefly rivers. The outcomes of this mapping program were published by *Panteleyev et al. (1996)*. Information about mineral occurrence and the geological history presented in *Panteleyev et al. (1996)* will be used in this thesis as explanation for the occurrence of several metals in the fine sediment fraction (<63 µm).

The field sites of this study are located in three different geological units, Kamloops (EKaca), Snowshoe (uPrPzSn) and Nicola group (uTrNvb) (Figure 4). The Kamloops group is a small geological unit located at the southside of the Quesnel lake. The Snowshoe group is located at the north and south side of the Quesnel lake and the Nicola group is a widespread geological unit located around Cariboo lake.

In the study area several mines are located. Two of these mines are located close to the sample sites. An active open cast copper-gold mine is located north-west of sampling site H2 (see Figure 7). This mine was active from 1997-2001 and from 2005-present. The other mine is located just upstream of location P1. This mine is an abandoned hydraulic gold mine and was active in the mid 1900s. During the period of 1930-1960 manual mining occurred downstream of the old mine, in the delta area. In the next sections the characteristics of these geological units will be further elucidated.

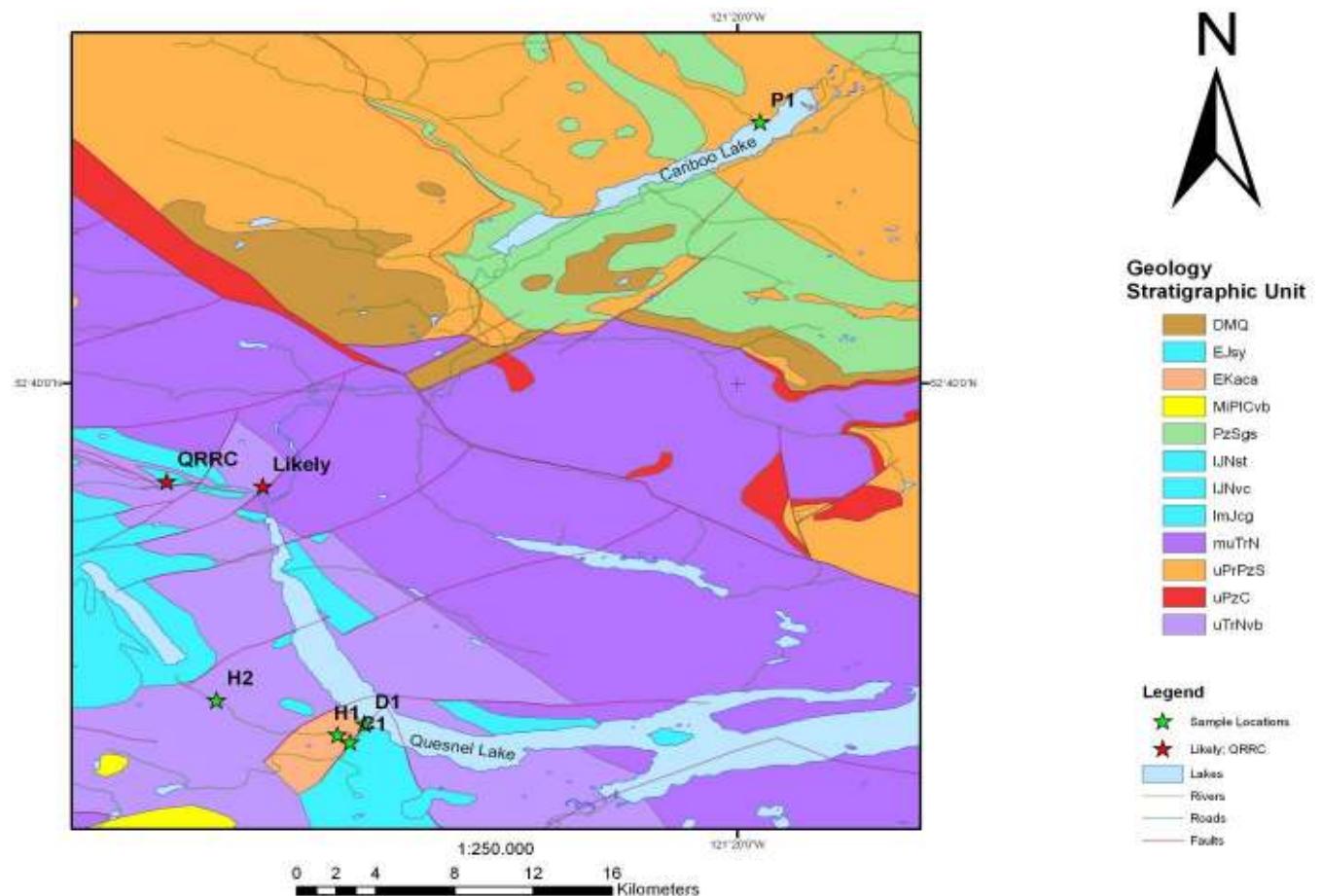


Figure 4: Geological map with the sample locations (source: *Massey et al., 2005*).

2.1.1 Kamloops group

This geological unit was formed in the Eocene and consists of calcareous alkaline volcanic rocks. The abbreviation EKaca stands for, (E)ocene, (Ka)mloops group, (c)alc-(a)lkaline volcanic rocks. Field sites H1, C1 and D1 are located in this geological unit. According to *Panteleyev et al.* (1996) this geologic unit contains quartz-calcite veins. These veins contain elements such as arsenic, mercury, barium and silver.

2.1.2 Snowshoe group

This geological unit was formed in the upper Proterozoic to Palaeozoic. The abbreviation uPrPzS stands for, (u)pper (Pr)oterozoic to (P)aleo(z)oic, (S)nowshoe group. The type of rock is undivided metamorphic rock. Field site P1 is located in this geological unit. Upstream of the measurement location there is an abandoned hydraulic gold mine. According to the mineral occurrence database on the website of the government of British Columbia (<http://webmaps.gov.bc.ca/imfx/imf.jsp?site=imapbc>, 2011) a vein of lead has formed near the surface of the earth close to site P1. It also says that there is mineral occurrence of gold, lead, silver, zinc and copper in the upstream area of site P1.

2.1.3 Nicola group

This geological unit was formed in the upper Triassic and consists of basaltic volcanic rocks. The abbreviation uTrNvb stands for, (u)pper (Tr)iassic, (N)icola group, (v)olcanic (b)asaltic rocks. Field site H2 is located in this geological unit. Research has shown that this area has widespread copper mineralization (*Panteleyev et al.*, 1996 and *Preto*, 1979). The open cast copper-gold mine is also located in this geological unit. The mine is a recent operation and has operated in two periods, from 2000 to 2001 and from 2005 to now.

2.2 Soil, vegetation and land-use

While tectonics has established the architecture of the province (see chapter 2.1), the detail has been brought by Pleistocene glaciation. Glaciers formed in southern Alaska more than 9 million years ago, early in the late Tertiary mountain-building episode (*Pike et al.*, 2010). Remnants of past glaciers can still be seen as the depositions on top of the bedrock.

In *Pike et al.* (2010), it can be seen that part of our study area has humo-ferric podzols (location P1) and another part has gray luvisols (location C1, H1, H2 and D1). Podzolic soils are formed in cool, humid to perhumid climates beneath coniferous forests. Hence, they are widespread along the coast of British Columbia and, except at the lowest elevations, throughout the mountain regions. Formed as a result of intense leaching, these soils are characterized by relatively high acidity and strong profile development. Podzols also tend to develop on volcanic ash that is distributed over parts of southern British Columbia. Humo-Ferric podzols occur in slightly less moist mountainous areas along the lee side of the Coast and Insular Mountains and in the Interior mountains. They display a red horizon (Bf) where iron and aluminium have accumulated, and less organic accumulation (*Pike et al.*, 2010).

Luvisols are associated with forest vegetation (including mixed forest and boreal forest), parent materials that are base-saturated and fine-grained, and regions of moderate precipitation. These soils are characterized by leaching, which results in the accumulation of clay to form a Bt horizon. Gray luvisols are distinguished by the presence of an Ae (white, eluviated) horizon and are typically more acidic than other Luvisols (*Pike et al.*, 2010).

The forests in the study area is partially community forest. This means that some logging is taking place, but this is only on a small scale. In the past however, the logging in the study area occurred more frequently. This can be seen if aerial photographs from 1967 are compared with photographs from 2005 (see Figure 5 and Figure 6). In the photo from 1967 more area seems to be logged than in 2005.

The sampling sites are located in two different hydrological systems. Location H1, H2, C1 and D1 are all located in the Quesnel river catchment and location P1 is located in the Cariboo river catchment. Location H1, H2 and D1 are located in Hazeltine creek.

Location C1 is located in Edney creek, which confluences with Hazeltine creek between location H1 and D1 (see Figure 2). P1 is located in Pine creek.

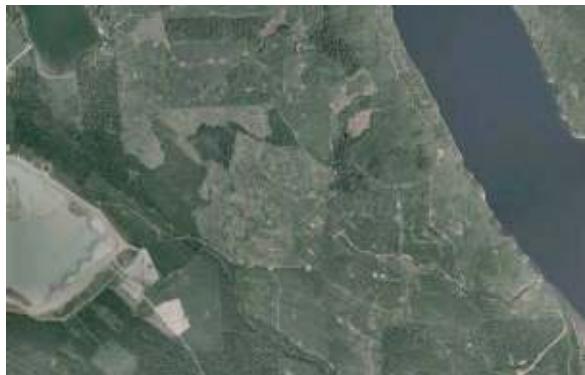


Figure 5: Study area around Hazeltine creek and Edney creek in 2005.

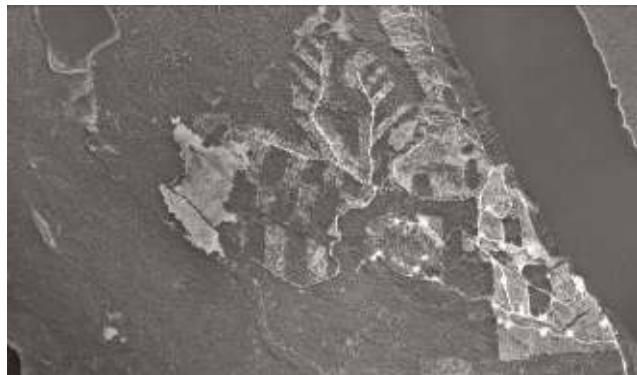


Figure 6: Study area around Hazeltine creek and Edney creek in 1967.

3 Field Methods

3.1 Sampling locations

3.1.1 Hazeltine creek (location H1, H2 and D1)

Location H1 is located in Hazeltine creek, which is a creek that drains a substantial area of an open cast copper-gold mine (see Figure 7). A dirt road -'Ditch road' (named after the ditch next to the road, which supplied water to the nearby Bullion Pit hydraulic gold mine) crosses the creek by bridge at this location.

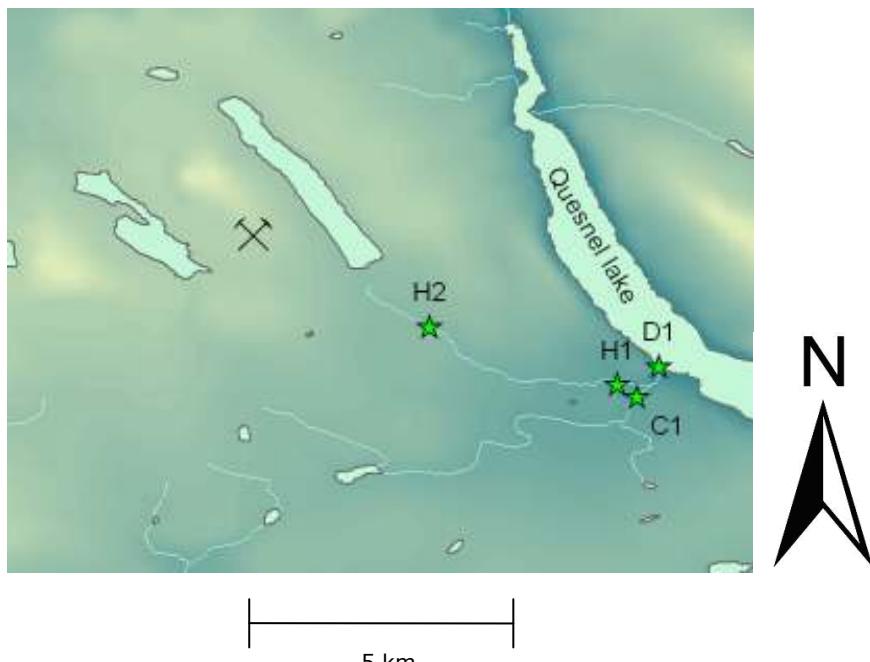


Figure 7: Open cast copper-gold mine and Hazeltine creek.

Location H2 is also situated in the 'Hazeltine creek'. This location is located upstream of location H1 and closer to the open cast copper-gold mine. At this location there is a weir (see Figure 8) which created a small pond upstream of it.



Figure 8: Hazeltine creek location H2 with the weir and the pond upstream of it.

Site D1 is located where Hazeltine creek enters Quesnel lake. The creek created a small delta on this location. Upstream of this location Edney creek confluences with Hazeltine creek. This location is only accessible by boat. That is why only 2 rounds of bed sediment sampling took place at this location. The creek bed at the three locations in

Hazeltine creek consists of mostly pebbles and some cobbles, with small amounts of stored fine grained sediment.

3.1.2 Edney creek (location C1)

Site C1 is located in Edney creek, where the Ditch road crosses the creek. This creek is draining part of the tailings pond of the open cast copper-gold mine and much of the region has been previously deforested, but due to a lack of evidence of recent disturbance within this part of the catchment, the sediment can be considered to be derived from inputs from natural coniferous forest. This is why this creek was chosen as a control site. The creek bed at the sample site in Edney creek is the same as the creek bed at the locations in Hazeltine creek. The only difference is that there is more organic material present in the matrix between the cobbles and pebbles.

3.1.3 Pine creek (location P1)

This site is located in Pine creek. This is a creek that drains an old abandoned hydraulic gold mine. The mine was closed around 1960 Since then the area has been left fairly undisturbed. The creek flows into Cariboo lake (see Figure 2) with a very steep gradient. At this location there is very little vegetation (see Figure 10). Aerial photographs show that the course of the creek varies greatly over time, showing an eastward moving trend in the past ~60 years. If we look at Figure 9a to 9d, we can see that in the period from 1957 until 2006 the creek has moved eastward.

The creek bed at the sample site in Pine creek consists of cobbles with very little stored fine grained sediment.



Figure 9a: Pine creek in 1957.

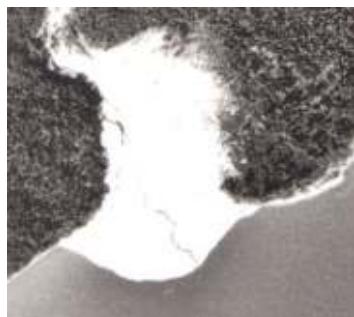


Figure 9b: Pine creek in 1967.



Figure 9c: Pine creek in 1994.



Figure 9d: Pine creek in 2006.



Figure 10: Pine creek with very little vegetation.

3.2 Site selection and sampling methods

During the fieldwork that took place (in the summer of 2010) before the writing of this thesis, sediment samples were taken from several creeks in the Quesnel and Cariboo catchment. The type of samples that were taken are: suspended sediment samples, bed sediment samples, corings and vertical profiles. These samples were processed at the Quesnel river research center (QRRC) and sent to a laboratory in Vancouver (ALS Minerals) where they were analyzed for metals and semi-metals. The elements that will be discussed in this thesis are aluminium(Al), arsenic (As), cadmium(Cd), copper(Cu), iron (Fe), mercury (Hg), manganese (Mn), lead (Pb), selenium (Se), strontium (Sr), and zinc (Zn), although more elements were analyzed in the lab. However, these are the metals that are relevant for this study and that were analyzed by both this study and the other two studies mentioned in chapter 1.2.

3.2.1 Site selection and sampling period

To collect the data, accessible sampling site were needed that would drain a mining area. The largest and active mine in the area of the QRRC is a gold and copper mine. The mine is drained by the Hazeltine creek. Hazeltine creek can be accessed by logging roads. Close to Hazeltine creek a second creek can be found, Edney creek. This creek drains mostly forested area and is therefore used as the control site.

During the fieldwork period of 7,5 weeks, these sites are visited once a week to collect bed sediment samples. samples were collected two times after a period of three weeks. In addition, a core was taken from a wetland that has formed near the upstream part of the Hazeltine creek (location H2).

Downstream, Edney creek confluences with Hazeltine creek and enters Quesnel lake (see Figure 2). Here a delta has been formed. In the area of this delta where fine grained material has been deposited, a core has been taken. The core is approximately 50 cm deep. At this location, bed sediment samples have been collected as well, but only twice during the fieldwork period because the site is only accessible by boat.

In comparison with this active mine, a non-active mine was sampled as well. This is an abandoned hydraulic gold mine near Cariboo lake. This abandoned mine is drained by Pine creek which forms a delta in Cariboo lake. Suspended sediment samplers were also placed in Pine creek (location P1). Two suspended sediment samplers were placed and left for a period of three weeks. Bed samples were taken every week during this period of three weeks.

At every location, vertical profiles were taken to obtain a historical record for heavy metal content.

3.2.2 Bed-sediment sampling

The bed sampling took place on a weekly basis at all locations except D1. For the collection of the gravel-stored fine sediment, a re-suspension cylinder was used (a stainless-steel bottomless trashcan) (Figure 11).



Figure 11: Re-suspension cylinder

The gravel bed inside the sampler was stirred with a stainless steel fork up to a depth of approximately 5 cm. Then a 10L bucket was filled with as much water containing resuspended sediment as possible to determine the bulk-metal concentration at a field location. This whole procedure was repeated at three locations at every sample site. At the end of the procedure the 10L bucket is filled with water from each of the three locations from one sample site.

3.2.3 Suspended sediment sampling

The suspended sediment has been sampled over 2 periods of 3 weeks. The suspended sediment sampler was constructed after the model of the Philips sampler (*Phillips et al., 2000*). It is made of a PVC tube of about 1 meter in length and a diameter of about 10 cm. When the water flows into the sampler the velocity drops with a factor 600 due to an increase of the cross-section of the sampler (see Figure 12).

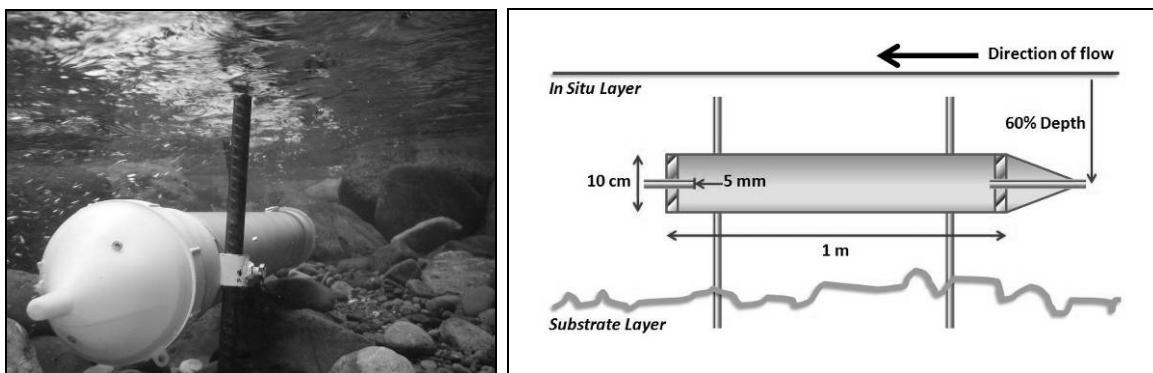


Figure 12: Isokinetic sediment sampler deployed in the field (left) and in cross-section (right) (*Smith and Owens, 2010*).

The sampler stays fixed at one location by inserting two iron bars into the river bed and attaching the sampler to it (Figure 12). After placement, the sampler can be left for a period of time. The sample was collected by taking the sampler out of the water, taking the bottom off, and pouring the water with the sediment in a 10L bucket.

3.2.4 Vertical profile sampling

At each study site, a spot was chosen next to the creek with relatively small grain sizes to examine the variation of metals with depth. Layers of fine sediment were collected in separate bags.

Sampling of the vertical profile is a very difficult procedure. Therefore, the method and the size of the samples changes per location. The basis for this way of sampling is to keep the ground level constant, and sample layer by layer, without mixing the sediment over the separate layers.

3.2.5 Coring

Several corings have been taken during the fieldwork. PVC tubes (diameter of 10 cm) have been used to take the corings. These tubes have been 'drilled' into the ground to the desired depth. They were dug out if possible and otherwise the core was just lifted up. After the core was retrieved from the ground it was tried to keep it upright as much as possible in order to prevent mixing of the sediments. The only time that it was lain down was when it was cut open and when samples were taken from it.

3.3 Laboratory Analysis

3.3.1 Processing cores

The core was cut open with a small circular saw. It was tried to disturb the sediment in the core as less as possible with the saw. The core was cut lengthwise at two places opposing each other. After that the sediment in the core was cut open with a small string sliding through the sediment. When this did not work the core was carefully cut open with a knife (stainless steel). Then the sediment in the core was described for each desired increment of length (ranging from 1 to 10 cm).

In order to get the least disturbed core samples only the sediment that did not touch the PVC pipe was used as sample. Sediment touching the PCV pipe tends to stick to the pipe causing horizontal disturbance of the sediment. Another reason to only take sediment that was not touching the pipe was to minimize pollution and disturbance from the saw that might have occurred during the cutting process. During the description of the cores several properties have been noted, namely:

- Colour
- Material
- Presence of organic material
- Remarks

The categories for materials were:

- Heavy clay
- Light clay
- Course sand
- Very course sand
- Peat

The presence of organic material has been noted with a code system:

Table 2: Codes for organic content and their description

| Code | Description |
|-------------|---------------------------|
| 0 | No organic material |
| 1 | A little organic material |
| 2 | Some organic material |
| 3 | Much organic material |

Now the sediment was collected in small sample bags. Those samples have been dried in a low temperature oven (60 °C). Next, the samples were sieved through a a 63 µm stainless steel mesh. This was the last step before the samples were sent to the laboratory for further analysis. In the laboratory the sediment has been analyzed for metal content by ICP-MS after aqua regia digestion.

3.3.2 Processing bed and suspended sediment samples

After the stirred up water from the bed sediment sampling and the water from the sediment traps has been put in the 10L buckets the buckets had to rest for 1 or 2 days in order to let all the sediment settle in the buckets. When all the sediment had settled, the

water has been siphoned from the buckets. After this, the sediment has been collected in smaller bottles. Those bottles go into the centrifuge for about an hour, where the high density substances (sediment) are separated from the low density substances (water).



Figure 13: centrifuge bottle (left) and the centrifuge (right).

After the bottles have been centrifuged, the supernatant (water) was separated from the sediments. Now the sediment was collected in small sample bags. Those samples are dried in a low temperature oven (60°C). After this process most of the water has evaporated, now the samples were dry enough to sieve. This has been done with a $63\text{ }\mu\text{m}$ sieve. The sediment size fraction $< 63\text{ }\mu\text{m}$ is a frequently used fraction to measure contamination (Salomons & Förstner, 1984). Grain size influences the surface area and settling velocity and the deposition rate of suspended sediment in water (Tsai et al., 1987). It also influences the degree of chemical partitioning onto the sediment (Horowitz & Elrick, 1987). A significant increase of several metals is shown with decreasing grain size by several studies that where examining fluvial sediments impacted by land use activities (Tessier et al., 1982; Förstner & Wittmann, 1983; Brook & Moore, 1988; Martincic et al., 1990; Vaithianathan et al., 1993; Stone & Droppo, 1996).

After the samples had been sieved the samples were sent to the laboratory for further analysis. There the sediment has been analyzed for metal content by ICP-MS after an aqua regia digestion.

3.4 Statistical analysis

To determine the contamination of metals due to the influence anthropogenic activities, measurements done in these environments have to be compared with measurements where these anthropogenic influences are minimal and there is only natural occurrence. These natural background concentrations can be obtained from pristine regional soil data of a catchment (Murray, 1996), by analyzing core sediment data (Peterson et al., 1990; Valette-Silver, 1993; Loring and Rantala, 1992; Birch et al., 1998), or by using mean metal concentrations of sediment that are texturally-equivalent reported in literature (Turekian and Wedepol, 1961). In this study pristine regional soil data of the catchment will be used as representative background concentration. In 2008 Jackaman and Balfour published a geochemical atlas of British Columbia. As part of this project, a selection of archived stream sediment samples has been reanalyzed (the samples where originally taken in the period from 1976 to 1985) by inductively coupled plasma mass spectrometry (ICP-MS) (see appendix for detection limits, Table 9). This technique provides a wide range of new analytical information at improved detection levels plus greater data compatibility with analytical methods currently being employed. This data will be used for background concentrations in this study. The data was chosen because the samples were taken from 1976 to 1985 when the population in the area was smaller. The anthropogenic influence was probably also smaller.

Natural occurrence of metals and geographical mineralogical variation can hamper the accurate assessment of anthropogenic input of metals. The effects of geographical variations and sediment grain size are minimized by normalizing the concentrations of each metal in samples and background measurements using reference elements (Hwang et al., 2009). A reference element is "conservative" (i.e., the element of which the content in samples originates almost exclusively from the earth's crust. The most

common reference elements in the literature are aluminum (Al), zirconium (Zr), iron (Fe), scandium (Sc), and titanium (Ti) (*Loska and Wiechuya, 2005*).

A common approach to estimate the anthropogenic impact on sediments is to calculate the enrichment ratio. Similar methods were used by *Salomons and Förstner (1984)*, *Dickinson et al. (1996)* and *Hornung et al. (1989)*. Anthropogenic input of metals can be suspected when the normalized concentrations of metals in samples are higher than the background value levels. The enrichment ratio is usually defined as:

$$\text{Enrichment ratio (ER)} = C_{\text{Sample}}/C_{\text{Prediction}} \quad (4)$$

$C_{\text{Prediction}}$ is the regression prediction of the local background concentrations of a certain metal and C_{Sample} is the concentration of the metal in a sample measured in the laboratory.

$C_{\text{Prediction}}$ is estimated by means of linear regression of the metal concentrations on the aluminium (or iron) content of the data from the geochemical atlas of British Columbia (*Jackaman and Balfour, 2008*) (see Figure 19, Figure 20, Figure 21 and Table 10). For each sample the concentration of a certain metal was plotted against the concentration of the reference element. The data from one geological unit was plotted in a graph and a linear regression line was fitted through. This equation was used to predict the concentration of a certain metal in a sample, based on the reference element content in the sample. Outliers were manually removed from the BC data samples and on the samples from this study. If a data point was far outside the cloud of data points and/or if one data point was influencing the regression line significantly that data-point was removed.

To determine the enrichment factor in the study area aluminium was used as reference element, because it is the most commonly used normalizing element in the geochemical literature (*Sutherland, 2000*). For arsenic and manganese, iron was used as a reference metal. Linear regression showed very low correlation coefficients for aluminium and these two metals. Iron is also used as reference metal (*Hwang et al., 2009*). Reference element data was taken from the geochemical atlas of British Columbia (*Jackaman and Balfour, 2008*) (From now on this dataset will be referred to as BC data).

Example:

For aluminium and copper in the Kamloops group the following regressing equation was found: $y = 19.235x + 0.674$ (x = percentage aluminium and y is ppm copper). If there was 2 percent of aluminium in a sample this equation predicts the corresponding amount of copper as 39.144 ppm (this is $C_{\text{Prediction}}$). If the actual copper concentration in the sample (C_{Sample}) was 50 ppm the enrichment ratio would be $50/39.144 = 1.28$.

But when is a sample enriched? In principle a sample is enriched when it has an enrichment ratio above 1. However, if this principle was followed, almost all the samples would have to be discussed. Therefore the line is drawn at an enrichment ratio of 3.5. All samples with an enrichment ratio above 3.5 will be discussed. Samples with ER's below 3.5 will be regarded as natural variation.

4 Results and discussion

4.1 Differences between geological units

In chapter 2.1 it was explained that the field sites are located in three different geological units. In this chapter the differences between those units will be discussed.

If the BC data from the geological units are compared, it can be seen that there are differences between them (see appendix, Figure 17 and Figure 18 , also see the mean values in Table 3, 4, and 5 (mean values of metals per geological unit are calculated from the BC data)). Performing t-tests show that these differences are significant (see appendix, page 34 to 37). The most important and obvious differences are:

- Kamloops group has lower Se values than the other two geological units.
- Snowshoe group has higher Mn values than the Kamloops group, has lower Hg values than the other two geological units, has higher Pb and Zn values than the other two geological units .
- Nicolai group has higher As, Mn and Cu values than the other two geological units.

Therefore, the three geological units in the study area are treated separate.

Panteleyev *et al.* (1996) state that the Kamloops group contains quartz-calcite veins and that these veins contain certain metals, including arsenic. The mean value of arsenic in the BC data in the Kamloops group however is lower than in the other two units (see table 2). This is can be attributed to the possible reason that the samples taken in the Kamloops group are not representative for the geological unit or that the veins may not have been exposed to weathering during the time of sampling.

Panteleyev *et al.* (1996) also state that Nicola group has large copper deposits. This is a very probable explanation for the higher copper values in the BC data from this geological unit. Copper values in the Nicolai group are higher than in the other two units. Because the BC data has been taken before the open cast copper-gold mine in the area was present this means that the copper values in this area are higher because of natural occurrence and not because of anthropogenic influence.

According to the mineral occurrence database of the government of British Colombia (<http://webmaps.gov.bc.ca/imfx/imf.jsp?site=imapbc>, 2011) the Snowshoe group has lead and zinc occurrence. Lead and zinc values in this geological unit are higher relative to the other two geological units (which do not have mineral occurrence of lead and zinc according to the mineral occurrence database of the government of British Columbia).

Arsenic is often associated with hydrothermal activity (Colbourn *et al.*, 1975). Panteleyev *et al.* (1996) mention past hydrothermal activity in the area of the open cast copper-gold mine. This might explain the higher arsenic values in Nicolai group.

Mercury can be associated with faults (Panteleyev *et al.*, 1996; Engle *et al.*, 2001). If we look at the geological map (Figure 4) it can be seen that geological units Kamloops and Nicolai group contain relatively more faults than the Snowshoe group. This may be the cause for the higher mercury values in the Kamloops and Nicolai group.

Manganese is not mentioned in literature on the study area. Emsley (2003) reported that the natural variability of manganese ranges from 7 to 9000 ppm. The values from the BC data fall well within this range. It is therefore likely that the differences in manganese values are part of natural variation.

Table 3: Mean metal content for Kamloops group (n=9) (Jackaman and Balfour, 2008)

| Element | Al | As | Cd | Cu | Fe | Hg | Mn | Pb | Se | Sr | Zn |
|--------------------|------|------|------|-------|------|-------|--------|-------|------|-------|-------|
| Mean | 1.01 | 2.12 | 0.19 | 18.77 | 1.82 | 55.00 | 320.00 | 5.39 | 0.28 | 58.94 | 40.71 |
| Standard deviation | 0.31 | 1.22 | 0.14 | 8.92 | 0.63 | 37.47 | 133.83 | 1.93 | 0.16 | 32.35 | 10.02 |
| Skewness | 0.75 | 1.51 | 1.32 | 1.45 | 0.82 | 0.81 | 1.68 | -0.11 | 0.47 | 0.21 | 0.45 |
| Unit | % | ppm | ppm | ppm | % | ppb | ppm | ppm | ppm | ppm | ppm |

Table 4: Mean metal content for geological unit uTrNvb (n=56) (Jackaman and Balfour, 2008)

| Element | Al | As | Cd | Cu | Fe | Hg | Mn | Pb | Se | Sr | Zn |
|---------|----|----|----|----|----|----|----|----|----|----|----|
|---------|----|----|----|----|----|----|----|----|----|----|----|

| | | | | | | | | | | | |
|---------------------------|------|------|------|-------|------|-------|---------|------|------|-------|-------|
| Mean | 1.39 | 7.74 | 0.30 | 38.20 | 2.74 | 62.82 | 1062.82 | 5.70 | 0.59 | 61.44 | 54.52 |
| Standard deviation | 0.58 | 7.29 | 0.21 | 24.35 | 0.82 | 30.22 | 1452.85 | 1.86 | 0.47 | 30.05 | 20.05 |
| Skewness | 1.06 | 2.70 | 1.61 | 2.98 | 0.16 | 1.09 | 4.79 | 1.07 | 1.82 | 1.34 | 1.50 |
| Unit | % | ppm | ppm | ppm | % | ppb | ppm | ppm | ppm | ppm | ppm |

Table 5: Mean metal content for geological unit uPrPzSn (n=192) (Jackaman and Balfour, 2008)

| Element | Al | As | Cd | Cu | Fe | Hg | Mn | Pb | Se | Sr | Zn |
|---------------------------|------|------|------|-------|------|-------|--------|------|------|-------|-------|
| Mean | 1.20 | 3.18 | 0.26 | 20.91 | 2.26 | 34.68 | 500.91 | 9.52 | 0.50 | 30.58 | 62.32 |
| Standard deviation | 0.46 | 7.74 | 0.44 | 13.58 | 0.94 | 23.34 | 634.76 | 6.01 | 0.52 | 34.68 | 36.18 |
| Skewness | 0.94 | 8.59 | 5.56 | 2.93 | 1.48 | 2.04 | 7.15 | 2.42 | 2.96 | 4.17 | 2.86 |
| Unit | % | ppm | ppm | ppm | % | ppb | ppm | ppm | ppm | ppm | ppm |

4.2 Enrichment in the study area

Table 6 shows the mean ER for all the data from this study falling into the corresponding geological unit. Several elements have a relatively high ER.

Table 6: Calculated average enrichment ratios for each geologic unit (data from this study)

| Geological unit | As ER* | Cd ER | Cu ER | Fe ER | Hg ER | Mn ER* | Pb ER | Se ER | Sr ER | Zn ER |
|--------------------------|--------|-------|-------|-------|-------|--------|-------|-------|-------|-------|
| Kamloops group (n=41) | 3.77 | 1.56 | 1.85 | 1.61 | 0.86 | 2.47 | 1.24 | 7.30 | 1.04 | 1.81 |
| Nicolai group (n=22) | 1.22 | 1.07 | 1.73 | 0.82 | 1.81 | 2.49 | 1.16 | 4.69 | 1.59 | 1.48 |
| Snowshoe group (n=15) | 2.92 | 1.87 | 2.87 | 1.82 | 0.55 | 1.34 | 5.41 | 1.73 | 2.05 | 1.91 |

Arsenic in the Kamloops group has a relatively high ER (3.77). Panteleyev et al. (1996) mentiones that the Kamloops group contains quartz-calcite veins and that these veins contain metals including arsenic. According to Garelick et al. (2008) these veins are common sources of naturally occurring arsenic. The data from this study suggests that there is arsenic enrichment in the Kamloops group. This could be due to exposure, weathering and erosion of the quartz-calcite veins caused by logging (which increases erosion (Wilson, 1999)) and/or road construction (Sidle et al., 2004; Rice, 1999).

Selenium seems to be elevated in the Kamloops (ER = 7.30) and Nicolai group (ER = 4.69). In the environment, selenium is generally associated with sulfur and it is found in metal-sulfur deposits (Conde and Sanz Alaejos, 1997) such as silver, copper, lead, mercury and nickel (Fishbein, 1983). This is a probable source of the enrichment in selenium in the Kamloops and Nicolai group since there is an open cast copper-gold mine located in the Nicolai group. The Kamploops group is located downstream of the Nicolai group. Hazeltine creek may have transported the selenium enriched sediment from the Nicolai group downstream to geological unit of the Kamloops group.

Lead has a high ER (5.41) in the Snowshoe group. According to the mineral occurrence database on the website of the government of British Columbia (<http://webmaps.gov.bc.ca/imfx/imf.jsp?site=imapbc>, 2011) a vein of lead is located near the surface close to site P1 in the area of the abandoned mine. The abandoned hydraulic gold mine may have exposed the vein of lead. Weathering and erosion of this vein may have caused the enrichment of lead at the sample site. Table 7 shows that actually only the vertical profile samples are enriched and not the bed and suspended sediment (see Figure 14 for the distribution of lead in the vertical profile).

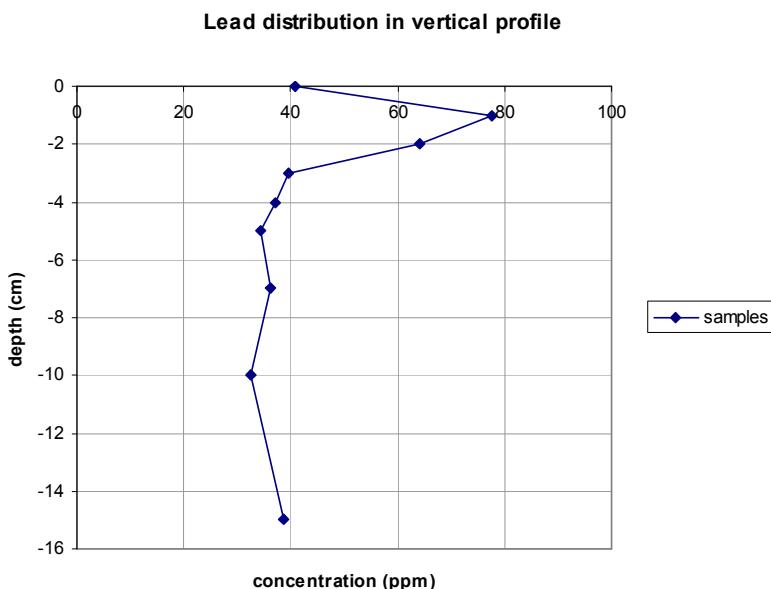


Figure 14: Lead distribution in the vertical profile sample at location P1.

Because the bed sediment and the suspended sediment are younger than the sediment from the vertical profile this implies that the enrichment took place primarily in the past and that enrichment is not actively taking place.

Table 7: Calculated enrichment factors per location and type of sample (BS = bed sediment, SS = suspended sediment, VP = vertical profile, CR = coring) (* = calculated with iron as reference metal).

| Description | As ER* | Cd ER | Cu ER | Fe ER | Hg ER | Mn ER* | Pb ER | Se ER | Sr ER | Zn ER |
|-----------------------|--------|-------|-------|-------|-------|--------|-------|-------|-------|-------|
| <i>Kamloops group</i> | | | | | | | | | | |
| C1 BS (n=6) | 4.34 | 2.05 | 1.42 | 1.70 | 0.72 | 2.60 | 1.17 | 4.36 | 1.06 | 2.17 |
| C1 VP (n=4) | 5.45 | 1.65 | 1.89 | 1.91 | 1.00 | 2.02 | 1.97 | 4.94 | 1.20 | 1.71 |
| H1 BS (n=6) | 3.61 | 2.17 | 3.00 | 1.54 | 1.13 | 5.23 | 1.03 | 18.29 | 1.43 | 2.87 |
| H1 SS (n=2) | 4.30 | 2.34 | 3.78 | 1.27 | 1.63 | 9.13 | 0.99 | 30.47 | 1.74 | 2.05 |
| H1 VP (n=1) | 3.97 | 2.66 | 2.40 | 1.86 | 1.18 | 3.22 | 1.77 | 7.77 | 1.38 | 2.06 |
| D1 BS (n=2) | 3.42 | 1.64 | 1.83 | 1.50 | 0.97 | 3.69 | 1.05 | 6.75 | 1.04 | 1.80 |
| D1 CR (n=20) | 3.27 | 1.07 | 1.41 | 1.58 | 0.68 | 0.87 | 1.20 | 3.07 | 0.81 | 1.38 |
| <i>Nicola group</i> | | | | | | | | | | |
| H2 BS (n=6) | 1.44 | 1.23 | 2.05 | 0.84 | 1.89 | 5.57 | 1.13 | 7.63 | 1.91 | 1.84 |
| H2 SS (n=1) | 1.60 | 1.51 | 2.45 | 0.81 | 2.26 | 7.20 | 1.37 | 10.14 | 1.99 | 2.38 |
| H2 VP (n=1) | 1.44 | 1.13 | 3.70 | 1.02 | 2.43 | 0.61 | 3.02 | 3.04 | 1.89 | 1.58 |
| H2 CR (n=14) | 1.13 | 1.00 | 1.57 | 0.82 | 1.75 | 1.24 | 1.16 | 3.40 | 1.47 | 1.34 |
| <i>Snowshoe group</i> | | | | | | | | | | |
| P1 BS (n=4) | 3.10 | 2.01 | 2.08 | 1.75 | 0.63 | 1.37 | 3.04 | 2.09 | 1.21 | 2.15 |
| P1 SS (n=2) | 2.78 | 1.76 | 1.91 | 1.70 | 0.41 | 1.29 | 2.78 | 1.67 | 1.67 | 1.65 |
| P1 VP (n=9) | 2.87 | 1.83 | 3.44 | 1.89 | 0.54 | 1.33 | 7.04 | 1.59 | 2.52 | 1.87 |

Table 7 lists the calculated enrichment factors from this study per location and sample type.

Although location C1 is chosen as control site, arsenic and selenium ER values are elevated (ER = 4.34 and 5.45 for arsenic and ER = 4.36 and 4.94 for selenium). The elevated selenium concentrations suggest that the influence of the mining activity exceeds Hazeltine creek. This could be due to local groundwater flow from the mine, the mine tailings or Hazeltine creek into Edney creek (location C1 is in Edney creek). A similar process was observed in *Brookfield et al. (2006)*.

The arsenic enrichment might be due to exposure, weathering and erosion of the quartz-calcite (which contain arsenic) located in geological unit Kamloops group (this is also the case at location H1).

Location H1 is enriched with copper (ER = 3.78), arsenic (ER = 3.61 and 4.30) and selenium (ER = 18,29 and 30.47). It has been reported that copper can be enriched at sites near a copper mine (*Pestana et al., 1997 and Karbassi et al., 2008*) and that selenium is associated with the copper deposits (*Conde and Sanz Alaejos, 1997; Fishbein, 1983*). This might also be the case at this location. Hazeltine creek is draining large parts of the mining area (open cast copper-gold mine). Due to Hazeltine creek draining the mining area, selenium and copper enriched sediment from the mine enters the creek. However, selenium occurrence in the copper deposits in the study area is not mentioned in literature.

Location D1 shows enrichment in selenium (ER = 6.75). Location D1 is located downstream of the confluence of Hazeltine and Edney creek. . If we look at the ER for D1 BS we see that the ER for selenium is lower than in H1 BS but higher than in C1 BS. Any enrichment that may have been in Hazeltine creek upstream of the confluence will have been diluted by the addition of the cleaner sediment from Edney creek. The dilution of enrichment due to confluencing rivers was also observed in a study by *Hudson-Edwards et al. (2001)*. Furthermore at location H2 copper seems to be enriched in the VP sample. This is possibly due to the copper-gold mine but it is not known why this sample is enriched with copper and the other samples at this location are not.

At H2 selenium is enriched in the bed and suspended sediment samples, just as at location H1. Because both sample site H1 and H2 are located in Hazeltine creek it is believed that the elevated selenium values have the same origin, namely, the open cast copper-gold mine.

Manganese values seem to be enriched on the field sites in Hazeltine creek (H1, H2 and D1). Manganese is the 12th most abundant element in the world and the range in which manganese occurs naturally is wide (7 to 9000 ppm) (*Emsley, 2003*). The concentration of manganese in the samples from this study fall within those boundaries and therefore it is concluded that despite the elevated enrichment ratios the manganese concentrations are part of the natural variation.

4.3 Differences between sample types

The different types of samples that have been taken during this fieldwork represent different ages. The time from deposition increases with increasing sample depth. Conclusions drawn from the differences in ER values between different sample types may support earlier findings from chapter 4.2.

At location C1 differences in ER values for BS and VP (the only two sample types that were taken) are small and probably fall within the error margin.

Selenium enrichment at location H1 is the highest in the SS then the BS and then the VP. The fact that the older sediments show less enrichment supports the conclusion that selenium enrichment is a recent event and might therefore be coming from the mine.

At location H2 and D1 the ER values for selenium in the corings (older sediment) are lower than in the bed sediment (younger). This is also supporting the conclusion that selenium enrichment is a recent event and might therefore be coming from the mine. Other metals at locations H1, H2 and D1 do not have large differences in ER values.

At location P1 the ER values of the bed sediment samples and the suspended sediment samples are very similar. In Table 7 it can be seen that actually only the vertical profile sample is enriched with lead and not the bed and suspended sediment. The bed sediment and the suspended sediment were deposited more recently than the sediment from the vertical profile. This means that the enrichment took place primarily in the past and that enrichment is not actively taking place. The exposure of the lead vein probably took place when the mine in this area was still active. This is why the older sediment (VP) shows lead enrichment. The younger sediment (BS and SS) does not show enrichment because the vein may have been eroded or may have been covered again.

4.4 Comparison with previous work

Table 8 shows the metal values for location H1 with the data from *Smith and Owens (2010)* and from this study. *Smith and Owens (2010)* conducted research on the suspended sediment at this location. The time of year in which the suspended sediment samplers from this study and the study of *Smith and Owens (2010)* were placed in the

creek is approximately the same (from August till September in 2010 and 2007 respectively).

Table 8: Metal content for location H1.

| | Al | As | Cd | Cu | Fe | Hg | Mn | Pb | Se | Sr | Zn |
|-------------------|------|------|------|--------|------|------|------|-----|-----|--------|-------|
| This study (H1SS) | 1.44 | 11.4 | 0.49 | 101.65 | 2.42 | 0.16 | 3595 | 7 | 9.1 | 140.25 | 100 |
| Smith and Owens | 1.24 | 6.8 | 1.3 | 134.9 | 1.42 | 0.1 | 1702 | 8.2 | 4 | 117.1 | 129.1 |
| Unit | % | ppm | ppm | ppm | % | ppb | ppm | ppm | ppm | ppm | ppm |
| Ratio | 1.2 | 1.7 | 0.4 | 0.8 | 1.7 | 1.6 | 2.1 | 0.9 | 2.3 | 1.2 | 0.8 |

If we look at the ratios, we see that the differences are small. Cadmium, which is sometimes associated with copper mine tailings (*Arentoli et al., 2008; Vermeer and Castilla, 1991*) seems to be less (factor 0.4) in this study. Manganese and selenium seems to be higher in this study with a factor of 2.1 and 2.3 respectively.

If we look at the production of the open-cast copper gold mine (Figure 15) it can be seen that the total production of metals has decreased since 2007. This could mean that there is also less copper available to enter the environment. If we look at Table 8 it can be seen that the amount of copper in the sediment has indeed decreased, although it is not much.

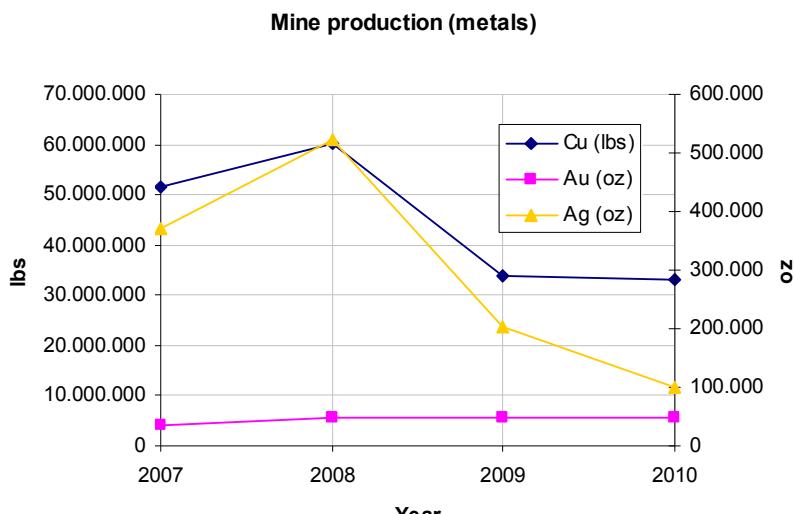


Figure 15: Mine production, metals mined (source: <http://www.imperialmetals.com>, 2011)

The amount of ore that was milled has increased since 2007 (see Figure 15). Together with the decreased metal production this implies that it is more difficult to reach ore bodies and that the amount of tailings that are present at the mine site may have increased.

The higher selenium values could be explained by the increased tailings. There are more tailings that water can leech through and transport selenium to the groundwater and Hazeltine creek.

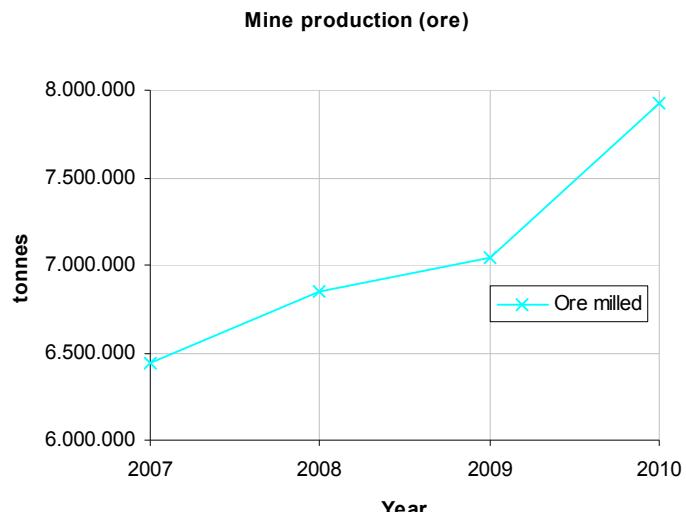


Figure 16: Mine production, ore milled (the amount of ore that was milled in 2010 is estimated from the three quarter year production) (source: <http://www.imperialmetals.com>, 2011)

5 Conclusions

This chapter summarizes the answers to the research questions raised in *chapter 1.2*.

Question 1: Do the geological units in the study area differ from each other in terms of geochemistry?

Answer 1: If t-tests are performed on the metals in the different geological units it was found that there are several significant differences between the geological units:

- The Kamloops group has lower Se values than the other two geological units.
- The Snowshoe group has higher Mn values than the Kamloops group, has lower Hg values than the other two geological units, has higher Pb and Zn values than the other two geological units.
- The Nicolai group has higher As, Mn and Cu values than the other two geological units.

The literature also suggests that mineral occurrences differ per geological unit. Therefore the three geological units in the study area are treated separately.

Question 2: Does enrichment occur in the samples from this study? Which metals and at which location?

Answer 2: If we look at the calculated enrichment values (Table 7) it shows that there are several samples that show enrichment according to the criteria proposed in chapter 4.3. Selenium shows the most enrichment. After that manganese, copper arsenic and lead also show enrichment. Selenium enrichment occurs at Hazeltine creek (see fig. 2 for the sampling locations) that drains the active copper-gold mine (locations H1 and H2), the delta (D1) and the control site Edney creek (C1). Manganese enrichment occurs mostly at location H1, H2 and D1. Copper enrichment occurs mostly at location H1, H2. Arsenic enrichment occurs at location C1 and H1 and lead enrichment occurs only at location P1.

Question 3: Why does this enrichment occur?

Answer 3: Selenium enrichment is occurring at location C1, H1 and H2. In the environment, selenium is generally associated with sulfur and it is found in metal-sulfur deposits such as silver, copper, lead, mercury and nickel. Since there is a large open cast copper-gold mining operation present upstream of location H2 (in Hazeltine creek), this has exposed the rocks to weathering. This is most likely the source of the enrichment in selenium in the area. Hazeltine creek has transported the selenium enriched sediment from H2 downstream to location H1. Although location C1 is chosen as control site, selenium values are elevated. The elevated selenium values imply that the influence of the mining activity extends Hazeltine creek. This could be due to local groundwater flow from the mine, the mine tailings or Hazeltine creek into Edney creek.

Manganese values seem to be enriched only on the field sites in Hazeltine creek (H1, H2 and D1). Manganese is the 12th most abundant element in the world and the range in which manganese occurs naturally is wide (7 to 9000 ppm). The concentration of manganese in the samples from this study fall within those boundaries and therefore it is concluded that despite the elevated enrichment ratios the manganese concentrations are part of the natural variation.

Copper enrichment is occurring mostly at location H1, H2. It has been reported that copper can be enriched at sites near a copper mine. It is believed that it is also the case at this location. The reason for this is that Hazeltine creek is draining large parts of the mining area. By doing so, copper enriched sediment from the mine enters Hazeltine creek.

Arsenic is not enriched at H2 (which is upstream of H1) and arsenic enrichment at C1 and H1 is roughly the same. The enrichment is probably originating from exposure weathering and erosion of quartz-calcite veins (which contain arsenic), these veins are exposed due to logging (which increases erosion) and/or road construction.

Upstream of location P1 an abandoned hydraulic gold mine has exposed a vein of lead. Weathering and erosion of this vein caused the enrichment of lead at the sample site.

Question 4: Are there differences in enrichment in the different types of samples?

Answer 4: At location C1 differences in ER values for BS and VP (the only two sample types that were taken) are small and probably fall within the error margin.

Selenium enrichment at location H1 is the highest in the SS then the BS and then the VP (this is the same as for manganese, but the differences are smaller). The fact that the older sediments show less enrichment supports the conclusion that selenium enrichment is a recent event and might therefore be coming from the mine.

At location H2 and D1 the ER values for selenium in the corings (older sediment) are lower than in the bed sediment (younger). This is also supporting the conclusion that selenium enrichment is a recent event and might therefore be coming from the mine. Other metals at locations H1, H2 and D1 do not have large differences in ER values.

At location P1 only the vertical profile samples are enriched with lead and not the bed and suspended sediment. The bed sediment and the suspended sediment are younger than the sediment from the vertical profile. This means that the enrichment took place primarily in the past and that enrichment is not actively taking place. The exposure of the lead vein took place when the mine in this area was still active. This is why the older sediment (VP) shows lead enrichment. The younger sediment (BS and SS) does not show enrichment because the vein has been eroded or is covered again.

Question 5: How does our data compare with the data of *Smith and Owens (2010)* and what are reasons for the differences?

Answer 5: If we look at the ratios, we see that the differences are small. Cadmium seems to be less (factor 0.4) in this study and manganese and selenium seems to be higher in this study with a factor of 2.1 and 2.3 respectively. Also copper seems to be lower in this study, although not much.

The decreased metal production may explain the lower copper values and the higher selenium values may be due to the increased tailings.

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Website 4: <http://www.geosciencebc.com/s/Quest.asp>

Website 5: <http://www.imperialmetals.com>

Website 6: <http://www.ec.gc.ca/>

8 Appendix

| Element | | Detection limit | Units |
|----------------|----|------------------------|--------------|
| Aluminum | Al | 0.01 | % |
| Antimony | Sb | 0.02 | ppm |
| Arsenic | As | 0.1 | ppm |
| Barium | Ba | 0.5 | ppm |
| Bismuth | Bi | 0.02 | ppm |
| Cadmium | Cd | 0.01 | ppm |
| Calcium | Ca | 0.01 | % |
| Chromium | Cr | 0.5 | ppm |
| Cobalt | Co | 0.1 | ppm |
| Copper | Cu | 0.01 | ppm |
| Gallium | Ga | 0.2 | ppm |
| Iron | Fe | 0.01 | % |
| Lanthanum | La | 0.5 | ppm |
| Lead | Pb | 0.01 | ppm |
| Magnesium | Mg | 0.01 | % |
| Manganese | Mn | 1 | ppm |
| Mercury | Hg | 5 | ppb |
| Molybdenum | Mo | 0.01 | ppm |
| Nickel | Ni | 0.1 | ppm |
| Phosphorous | P | 0.001 | % |
| Potassium | K | 0.01 | % |
| Scandium | Sc | 0.1 | ppm |
| Selenium | Se | 0.1 | ppm |
| Silver | Ag | 2 | ppb |
| Sodium | Na | 0.001 | % |
| Strontium | Sr | 0.5 | ppm |
| Sulphur | S | 0.02 | % |
| Tellurium | Te | 0.02 | ppm |
| Thallium | Tl | 0.02 | ppm |
| Thorium | Th | 0.1 | ppm |
| Titanium | Ti | 0.001 | % |
| Tungsten | W | 0.1 | ppm |
| Uranium | U | 0.1 | ppm |
| Vanadium | V | 2 | ppm |
| Zinc | Zn | 0.1 | ppm |

Table 9: Detection limits for sediments samples analyzed by ICP-MS.

Welch Two Sample t-tests

```
data: uTrNvb Al and uPrPzS Al
t = 2.2633, df = 75.819, p-value = 0.02648
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
0.0229003      0.3588854
sample estimates:
mean of uTrNvb Al      mean of uPrPzS Al
1.388393            1.197500

data: uTrNvb Al and EKaca Al
t = 2.8977, df = 18.457, p-value = 0.009418
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
0.1042289      0.6503346
sample estimates:
mean of uTrNvb Al      mean of EKaca Al
1.388393            1.011111

data: EKaca Al and uPrPzS Al
t = -1.7012, df = 9.661, p-value = 0.1208
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-0.4316707      0.0588929
sample estimates:
mean of EKaca Al      mean of uPrPzS Al
1.011111            1.197500

data: uTrNvb As and uPrPzS As
t = 4.0586, df = 94.249, p-value = 0.0001019
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
2.327722      6.786266
sample estimates:
mean of uTrNvb As      mean of uPrPzS As
7.739286            3.182292

data: uTrNvb As and EKaca As
t = 5.3236, df = 62.746, p-value = 1.455e-06
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
3.508393      7.725734
sample estimates:
mean of uTrNvb As      mean of EKaca As
7.739286            2.122222

data: EKaca As and uPrPzS As
t = -1.5345, df = 58.237, p-value = 0.1303
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-2.4428256      0.3226867
sample estimates:
mean of EKaca As      mean of uPrPzS As
2.122222            3.182292

data: uTrNvb Cd and uPrPzS Cd
t = 1.0171, df = 191.488, p-value = 0.3104
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-0.04078421      0.12762945
sample estimates:
mean of uTrNvb Cd      mean of uPrPzS Cd
0.3007143           0.2572917

data: uTrNvb Cd and EKaca Cd
t = 2.0398, df = 14.94, p-value = 0.05946
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-0.00501447      0.22644304
sample estimates:
mean of uTrNvb Cd      mean of EKaca Cd
0.3007143           0.1900000
```

```

data: EKaca Cd and uPrPzS Cd
t = -1.2002, df = 17.206, p-value = 0.2463
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-0.18547060    0.05088727
sample estimates:
mean of EKaca Cd      mean of uPrPzS Cd
0.19000000            0.2572917

data: uTrNvb Cu and uPrPzS Cu
t = 5.0881, df = 65.279, p-value = 3.284e-06
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
10.50507     24.07856
sample estimates:
mean of uTrNvb Cu      mean of uPrPzS Cu
38.19911        20.90729

data: uTrNvb Cu and EKaca Cu
t = 4.4059, df = 31.949, p-value = 0.0001109
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
10.44368     28.40564
sample estimates:
mean of uTrNvb Cu      mean of EKaca Cu
38.19911        18.77444

data: EKaca Cu and uPrPzS Cu
t = -0.681, df = 9.827, p-value = 0.5116
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-9.128025    4.862331
sample estimates:
mean of EKaca Cu      mean of uPrPzS Cu
18.77444        20.90729

data: uTrNvb Fe and uPrPzS Fe
t = 3.7254, df = 100.501, p-value = 0.0003222
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
0.2243567     0.7354945
sample estimates:
mean of uTrNvb Fe      mean of uPrPzS Fe
2.742321       2.262396

data: uTrNvb Fe and EKaca Fe
t = 3.8784, df = 12.835, p-value = 0.001946
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
0.4059228     1.4298311
sample estimates:
mean of uTrNvb Fe      mean of EKaca Fe
2.742321       1.824444

data: EKaca Fe and uPrPzS Fe
t = -1.9877, df = 9.743, p-value = 0.07566
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-0.93064596   0.05474318
sample estimates:
mean of EKaca Fe      mean of uPrPzS Fe
1.824444        2.262396

data: uTrNvb Hg and uPrPzS Hg
t = 6.4326, df = 75.151, p-value = 1.046e-08
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
19.42859     36.86010
sample estimates:
mean of uTrNvb Hg      mean of uPrPzS Hg
62.82143       34.67708

data: uTrNvb Hg and EKaca Hg
t = 0.5958, df = 9.744, p-value = 0.5649
alternative hypothesis: true difference in means is not equal to 0

```

95 percent confidence interval:
 -21.53317 37.17603
 sample estimates:
 mean of uTrNvb Hg mean of EKaca Hg
 62.82143 55.00000

data: EKaca Hg and uPrPzS Hg
 $t = 1.6124$, df = 8.293, p-value = 0.1442
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 -8.564288 49.210121
 sample estimates:
 mean of EKaca Hg mean of uPrPzS Hg
 55.00000 34.67708

data: uTrNvb Mn and uPrPzS Mn
 $t = 2.8169$, df = 61.24, p-value = 0.006517
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 163.0632 960.7567
 sample estimates:
 mean of uTrNvb Mn mean of uPrPzS Mn
 1062.8214 500.9115

data: uTrNvb Mn and EKaca Mn
 $t = 3.7289$, df = 59.815, p-value = 0.0004293
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 344.3276 1141.3153
 sample estimates:
 mean of uTrNvb Mn mean of EKaca Mn
 1062.821 320.000

data: EKaca Mn and uPrPzS Mn
 $t = -2.8293$, df = 32.266, p-value = 0.007958
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 -311.11476 -50.70816
 sample estimates:
 mean of EKaca Mn mean of uPrPzS Mn
 320.0000 500.9115

data: uTrNvb Pb and uPrPzS Pb
 $t = -7.6396$, df = 245.189, p-value = 4.889e-13
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 -4.801658 -2.833193
 sample estimates:
 mean of uTrNvb Pb mean of uPrPzS Pb
 5.698929 9.516354

data: uTrNvb Pb and EKaca Pb
 $t = 0.4456$, df = 10.546, p-value = 0.6649
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 -1.216221 1.829633
 sample estimates:
 mean of uTrNvb Pb mean of EKaca Pb
 5.698929 5.392222

data: EKaca Pb and uPrPzS Pb
 $t = -5.325$, df = 16.815, p-value = 5.791e-05
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 -5.759525 -2.488739
 sample estimates:
 mean of EKaca Pb mean of uPrPzS Pb
 5.392222 9.516354

data: uTrNvb Se and uPrPzS Se
 $t = 1.1752$, df = 97.765, p-value = 0.2428
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 -0.05902614 0.23045471
 sample estimates:

mean of uTrNvb Se mean of uPrPzS Se
 0.5857143 0.5000000

data: uTrNvb Se and EKaca Se
 $t = 3.7806$, df = 36.641, p-value = 0.0005586
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 0.1428446 0.4730284

sample estimates:
 mean of uTrNvb Se mean of EKaca Se
 0.5857143 0.2777778

data: EKaca Se and uPrPzS Se
 $t = -3.4633$, df = 18.18, p-value = 0.002741
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 -0.3569319 -0.0875125

sample estimates:
 mean of EKaca Se mean of uPrPzS Se
 0.2777778 0.5000000

data: uTrNvb Sr and uPrPzS Sr
 $t = 6.5211$, df = 101.618, p-value = 2.749e-09
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 21.47212 40.24544

sample estimates:
 mean of uTrNvb Sr mean of uPrPzS Sr
 61.44107 30.58229

data: uTrNvb Sr and EKaca Sr
 $t = 0.217$, df = 10.344, p-value = 0.8324
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 -23.02606 28.01931

sample estimates:
 mean of uTrNvb Sr mean of EKaca Sr
 61.44107 58.94444

data: EKaca Sr and uPrPzS Sr
 $t = 2.5622$, df = 8.884, p-value = 0.03088
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 3.271284 53.453022

sample estimates:
 mean of EKaca Sr mean of uPrPzS Sr
 58.94444 30.58229

data: uTrNvb Zn and uPrPzS Zn
 $t = -2.0855$, df = 165.97, p-value = 0.03855
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 -15.1881278 -0.4158901

sample estimates:
 mean of uTrNvb Zn mean of uPrPzS Zn
 54.52143 62.32344

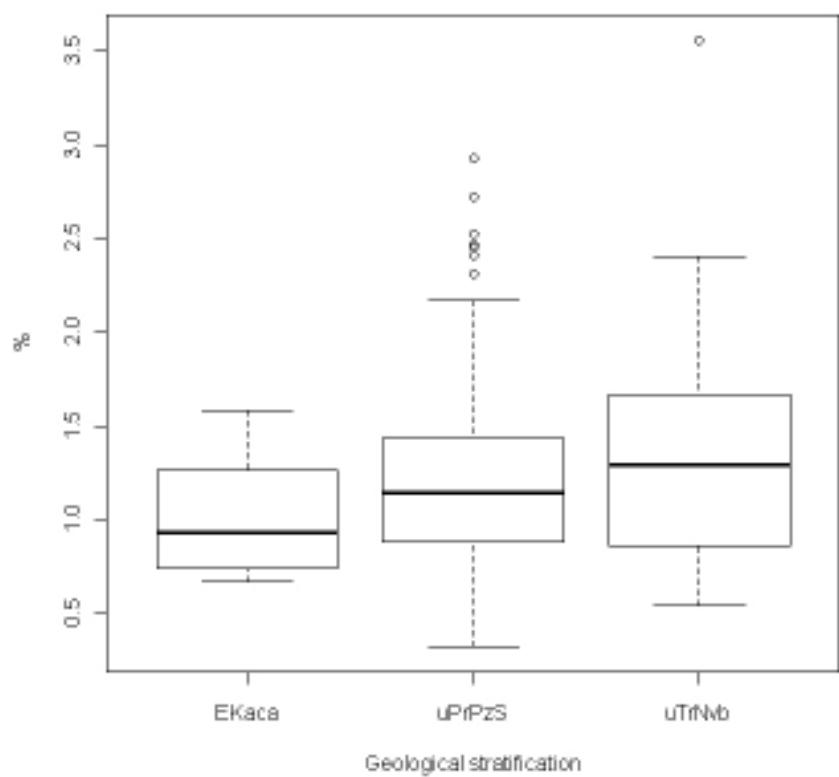
data: uTrNvb Zn and EKaca Zn
 $t = 3.2244$, df = 20.367, p-value = 0.004181
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 4.886396 22.734239

sample estimates:
 mean of uTrNvb Zn mean of EKaca Zn
 54.52143 40.71111

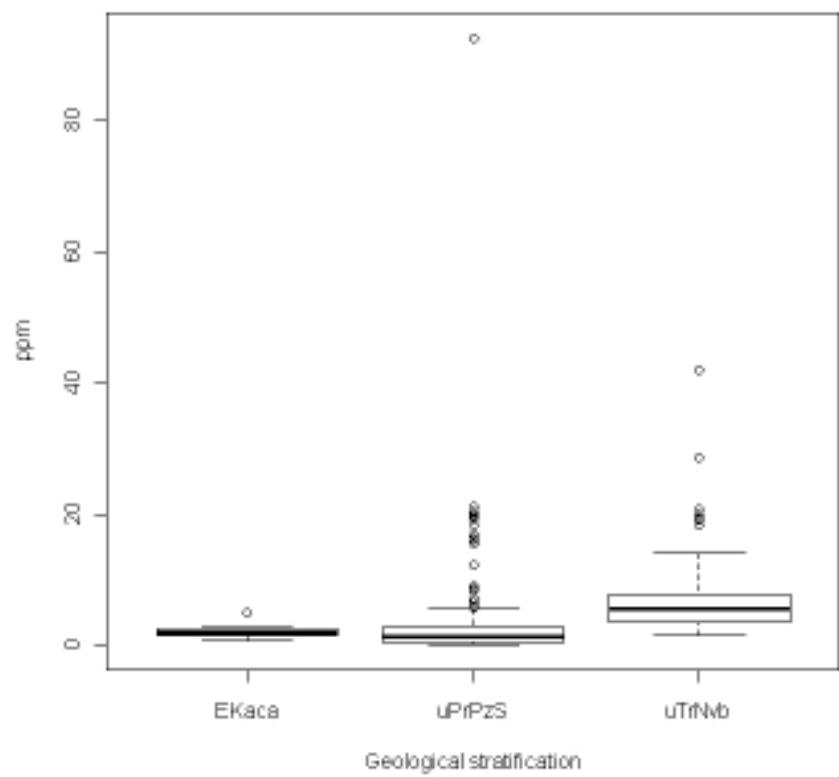
data: EKaca Zn and uPrPzS Zn
 $t = -5.0964$, df = 20.431, p-value = 5.174e-05
 alternative hypothesis: true difference in means is not equal to 0
 95 percent confidence interval:
 -30.44628 -12.77837

sample estimates:
 mean of EKaca Zn mean of uPrPzS Zn
 40.71111 62.32344

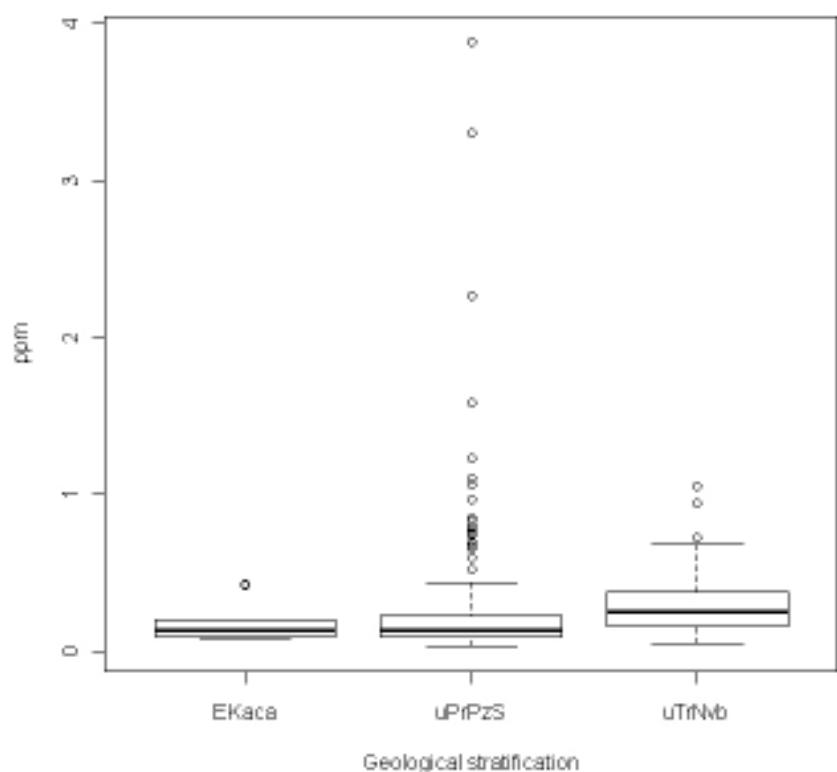
Aluminium



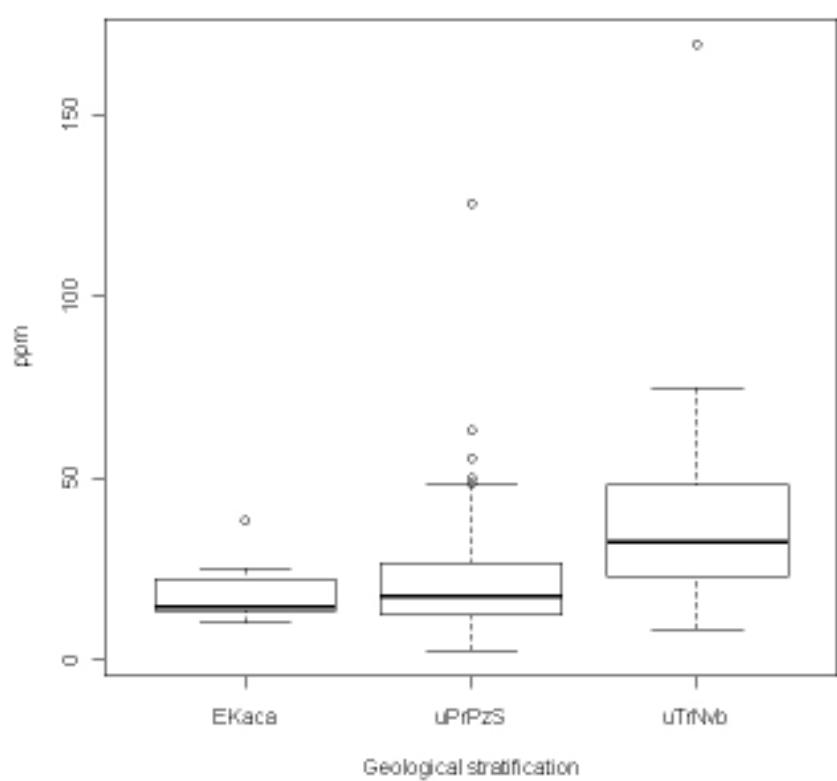
Arsenic



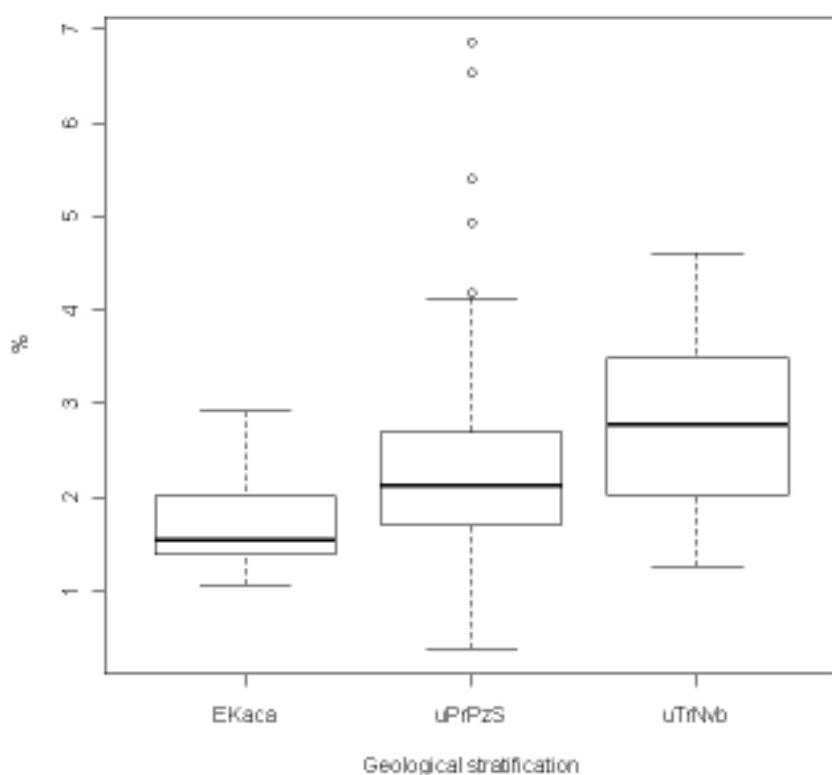
Cadmium



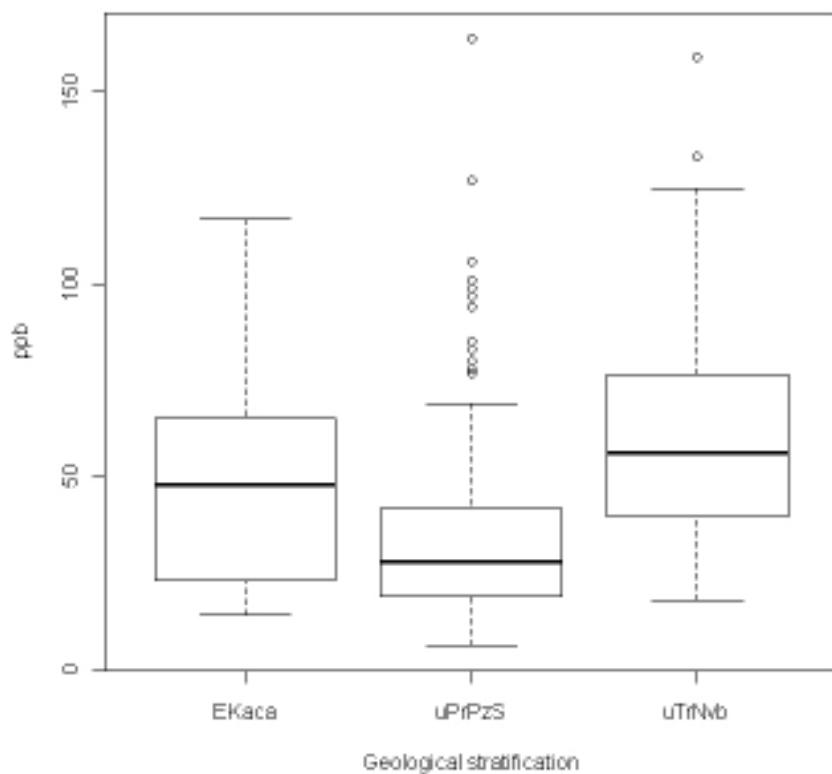
Copper



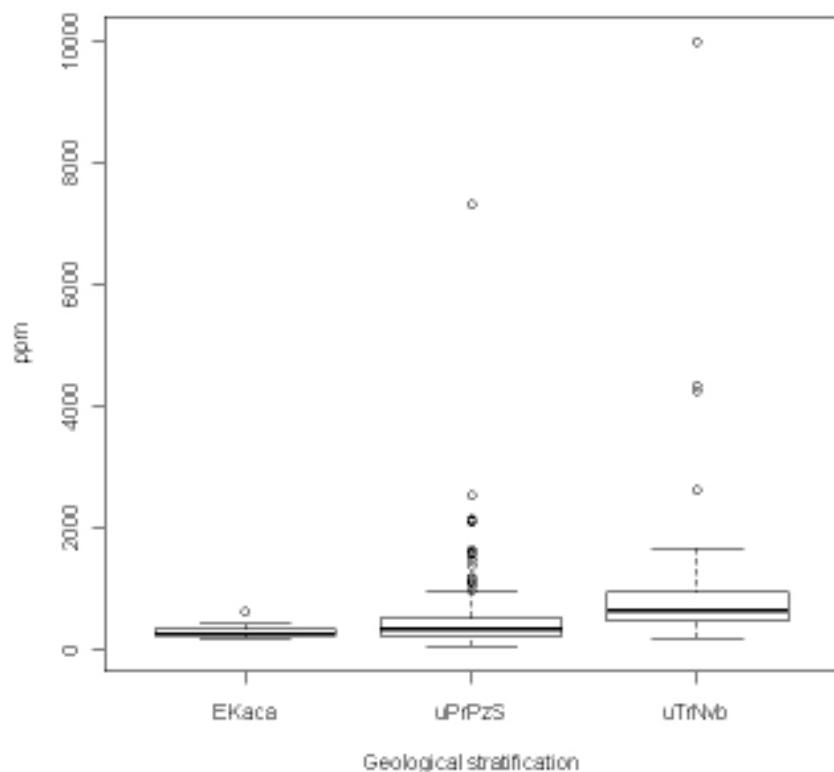
Iron



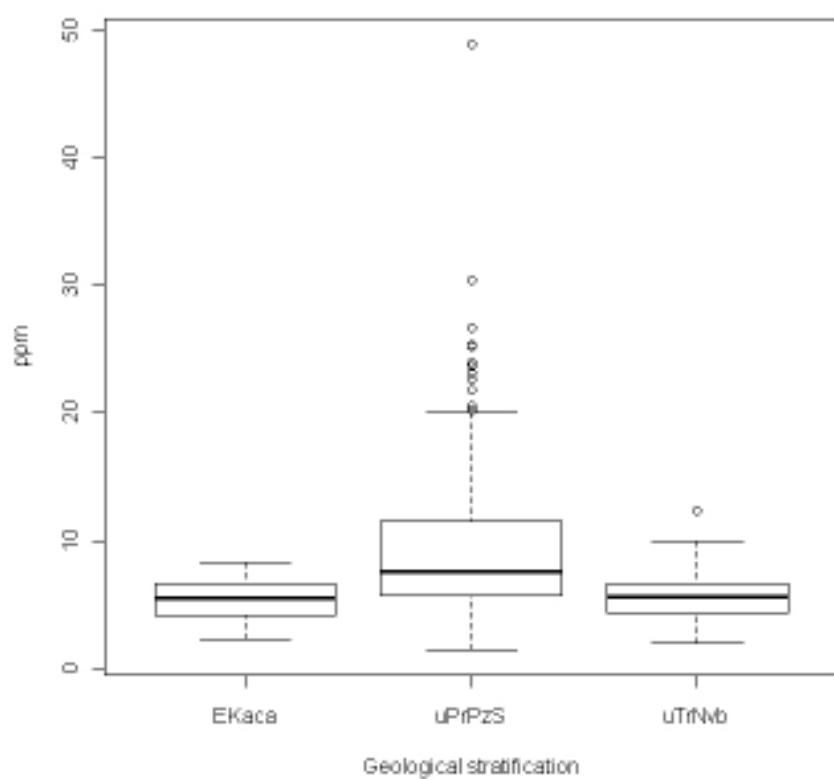
Mercury



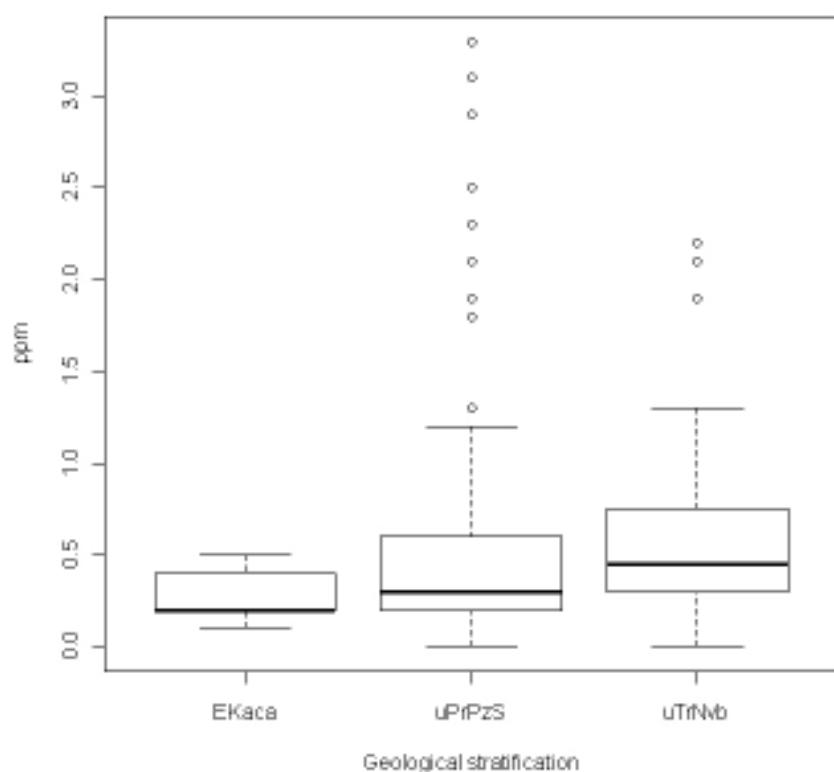
Manganese



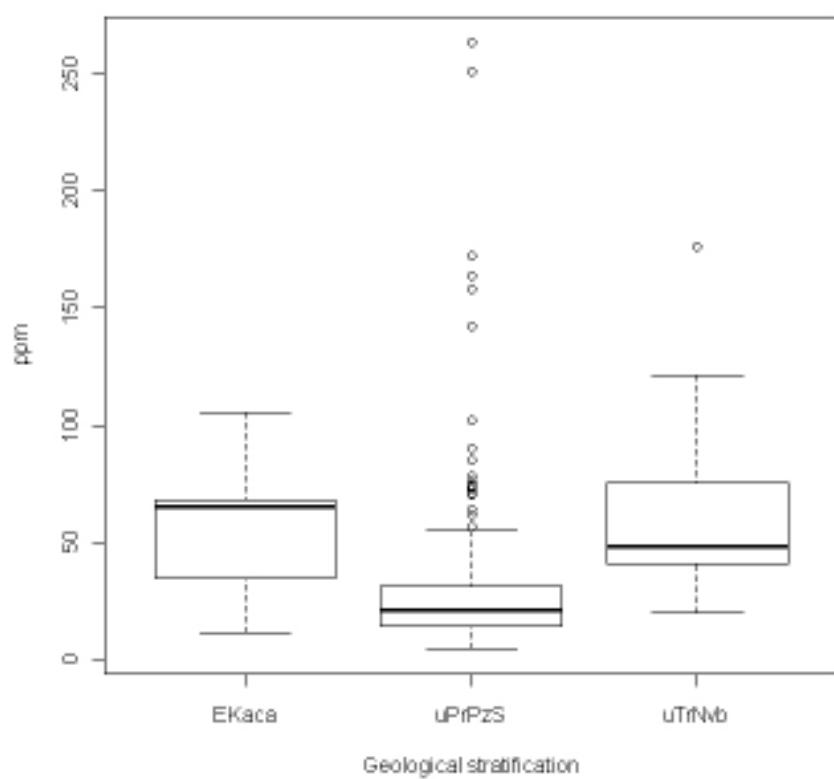
Lead



Selenium



Strontium



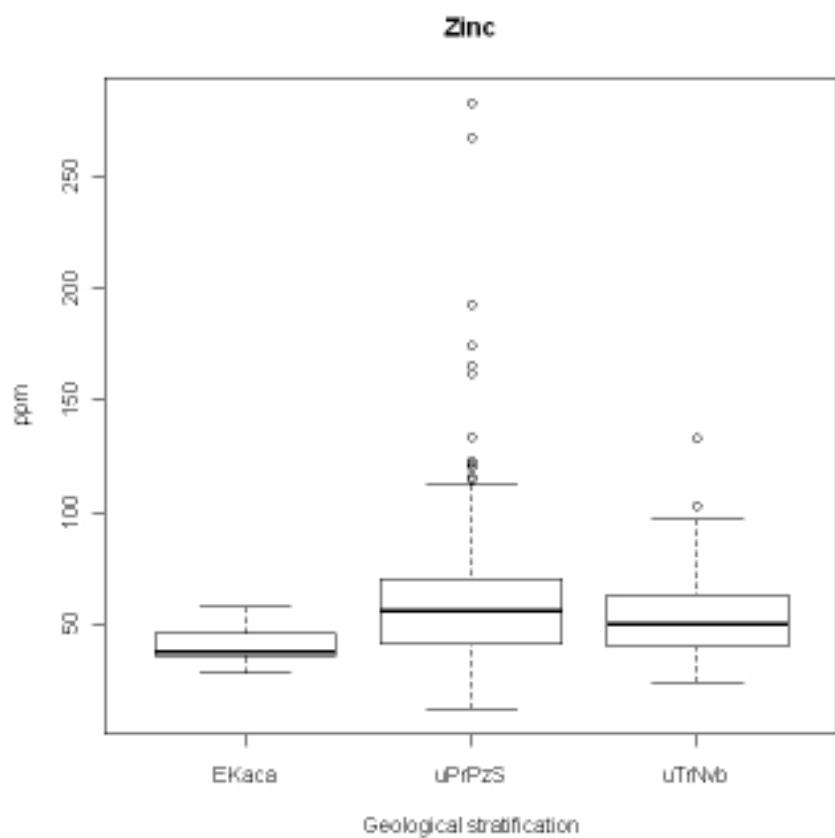
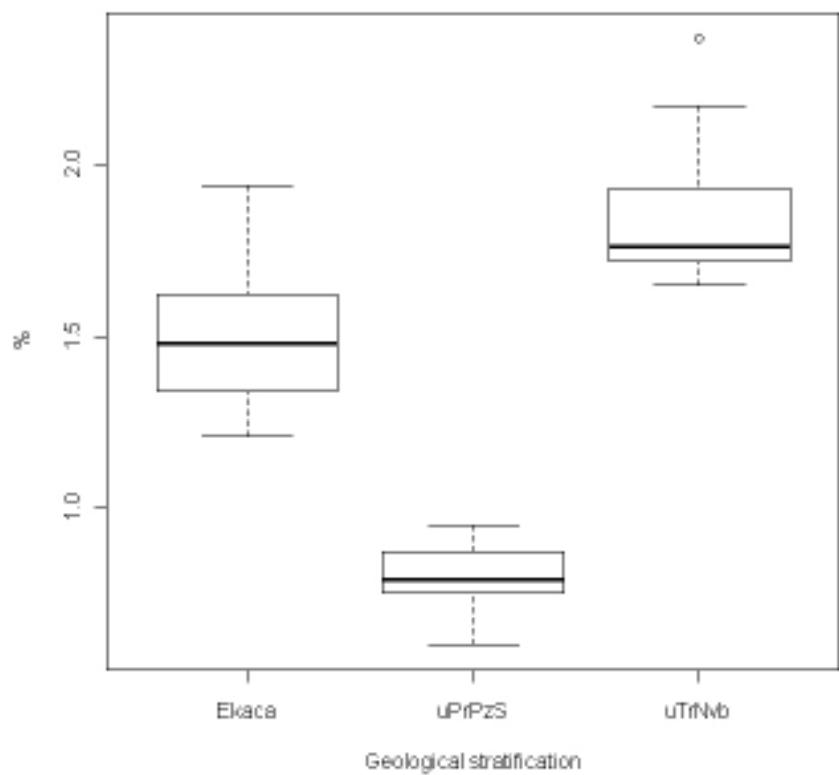
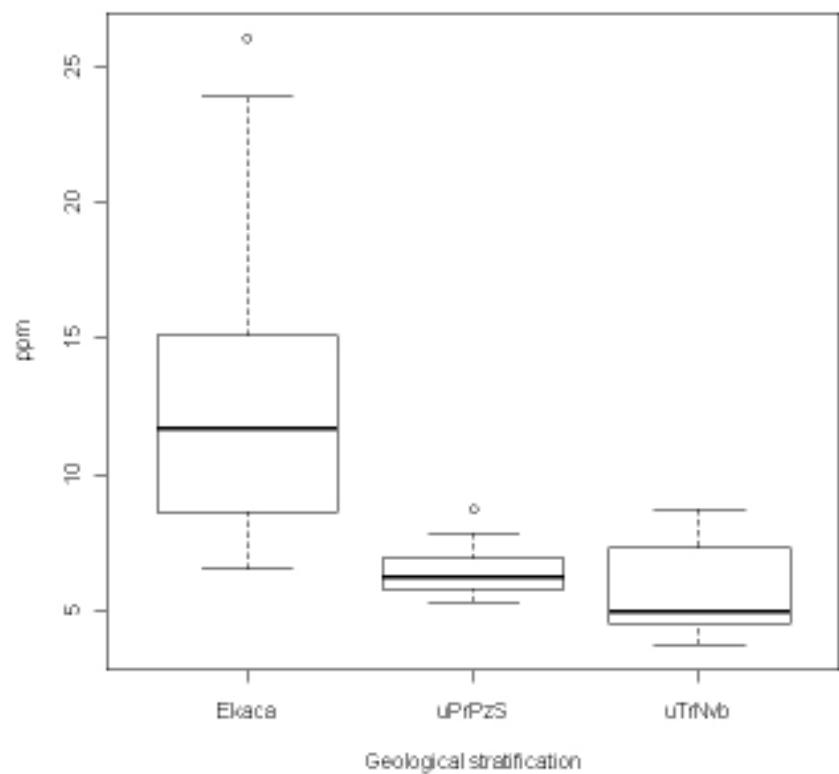


Figure 17: Boxplots for Al, As, Cd, Cu, Fe, Hg, Mn, Pb, Se, Sr and Zn from the BC data.

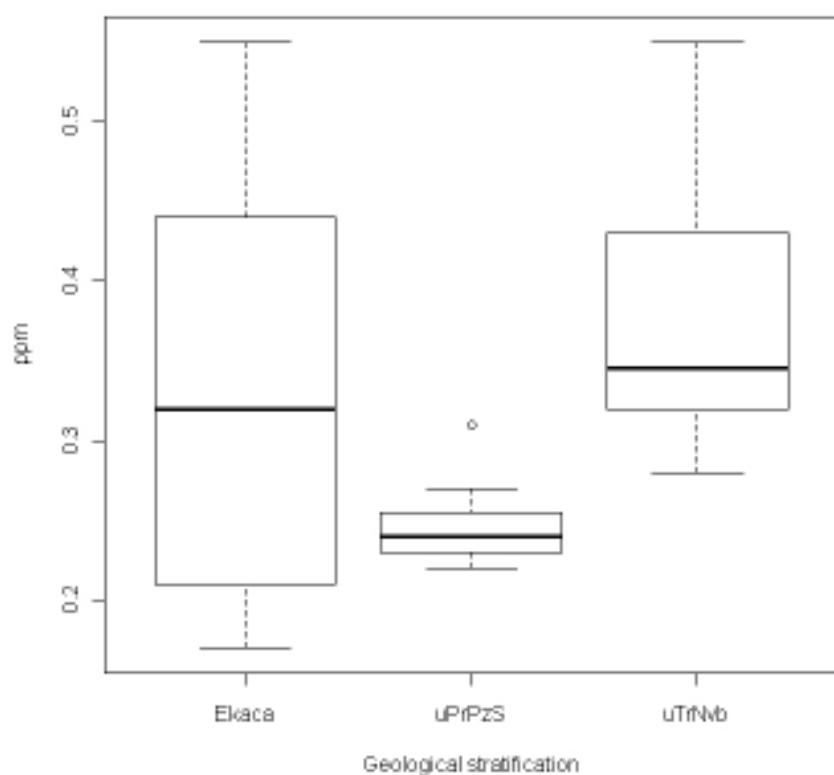
Aluminium



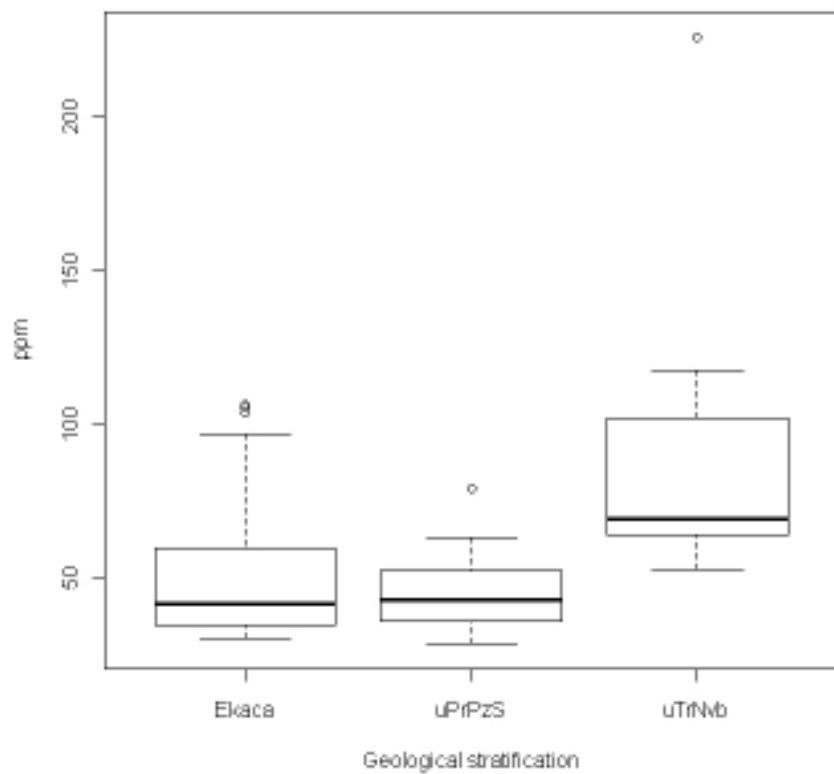
Arsenic



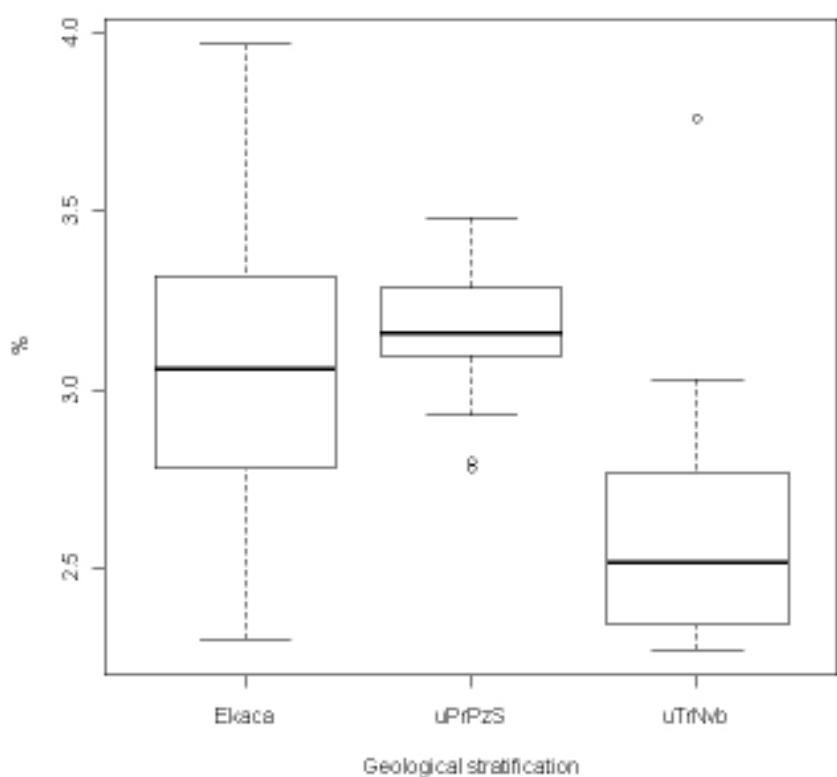
Cadmium



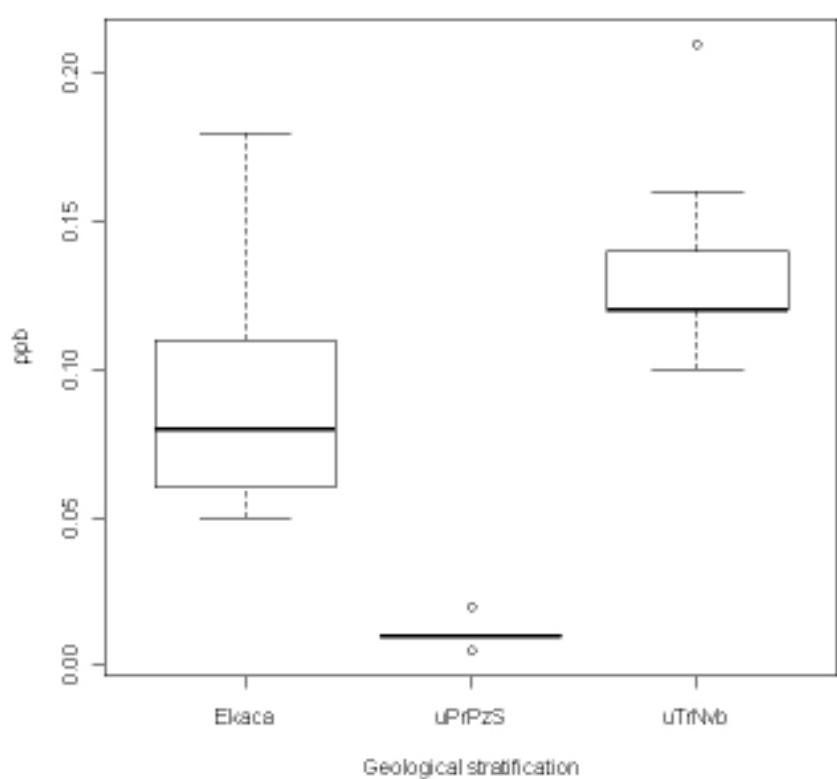
Copper



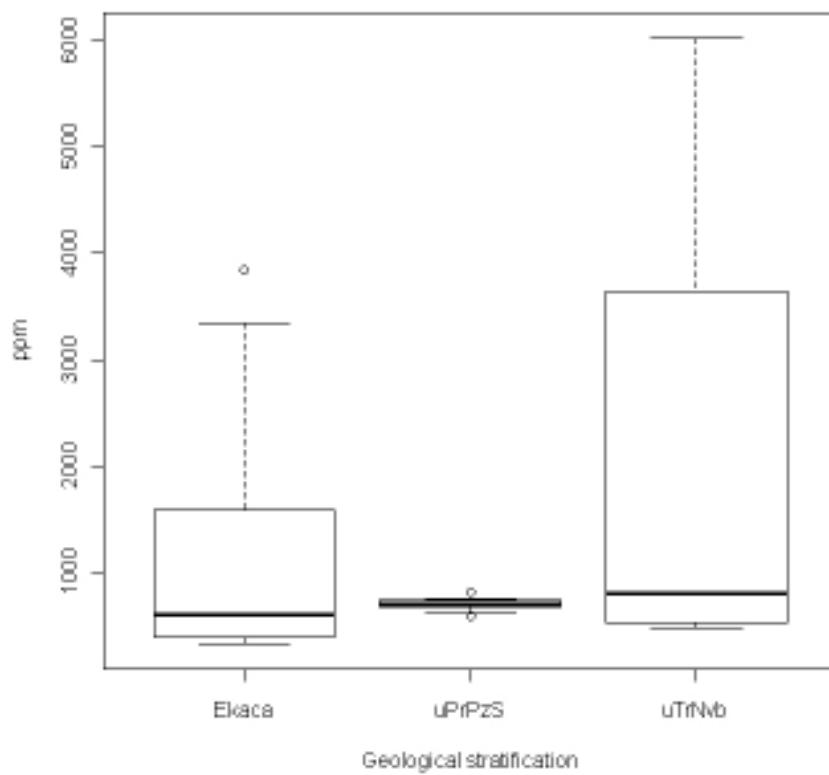
Iron



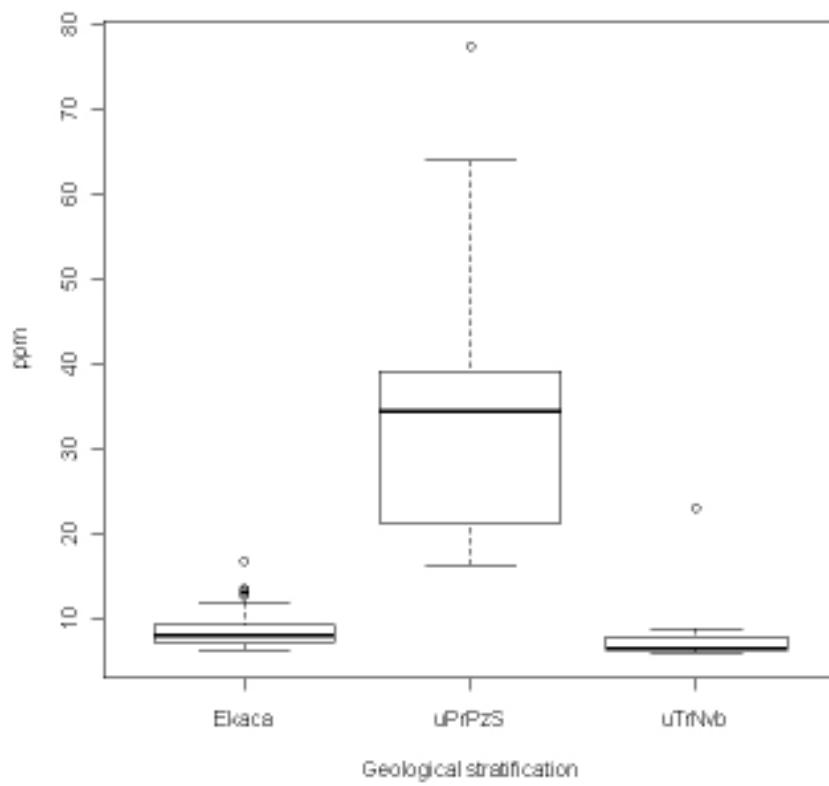
Mercury



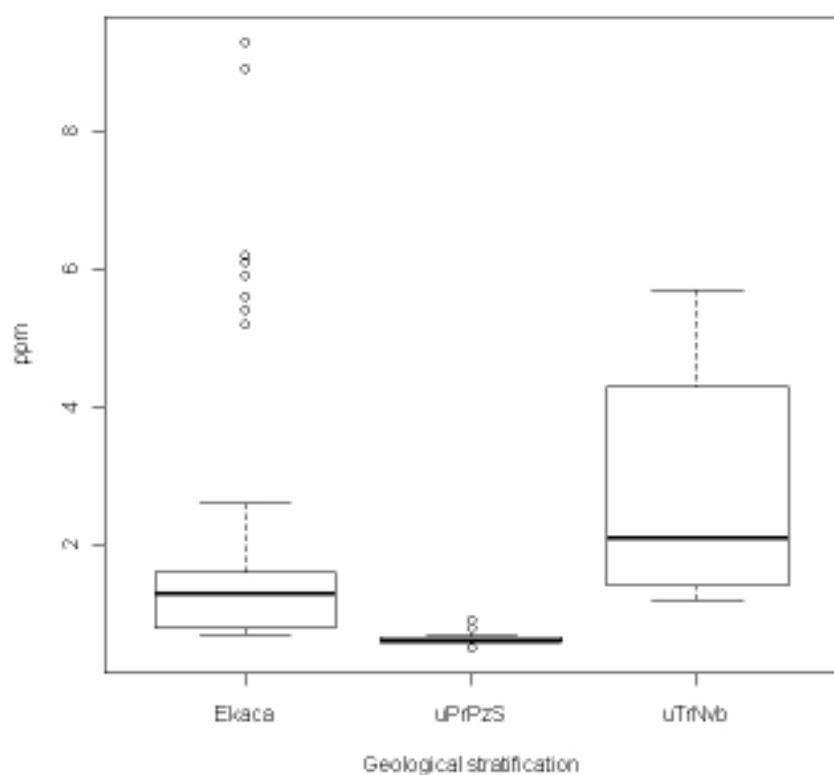
Manganese



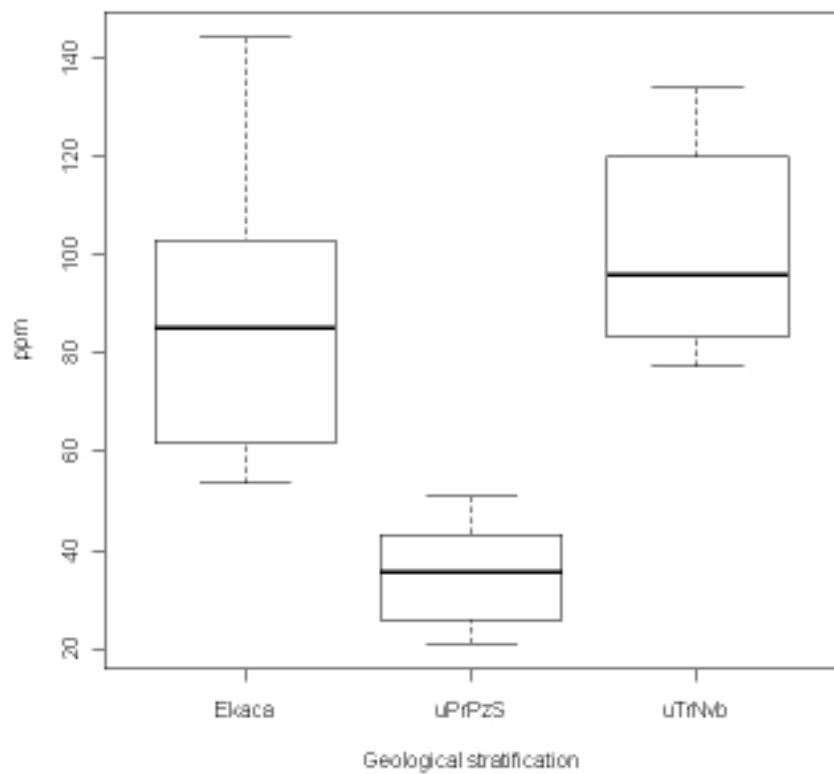
Lead



Selenium



Strontium



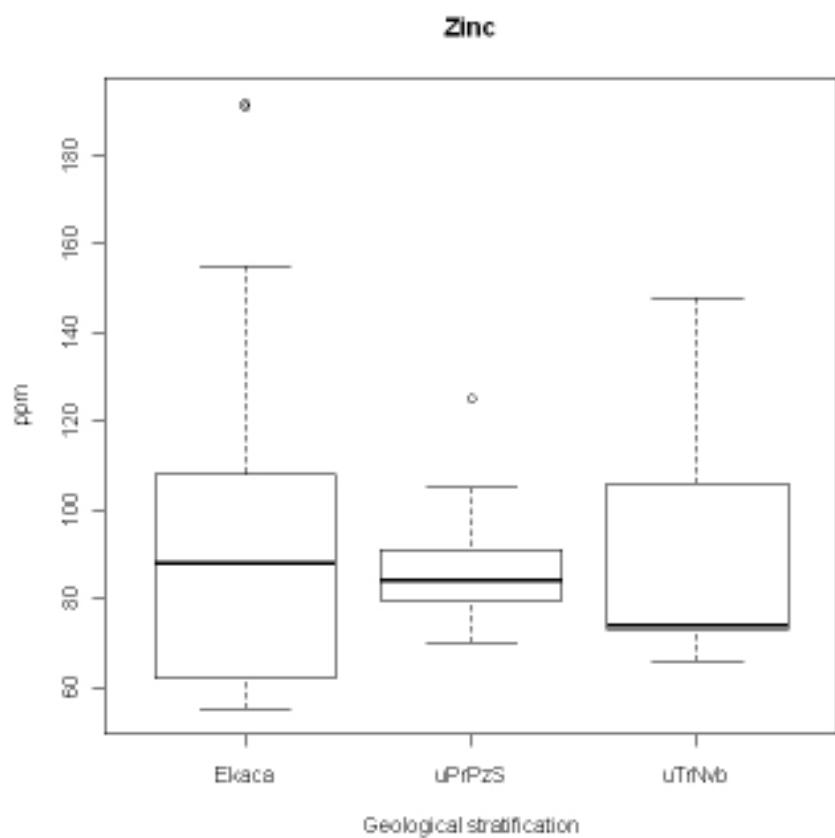
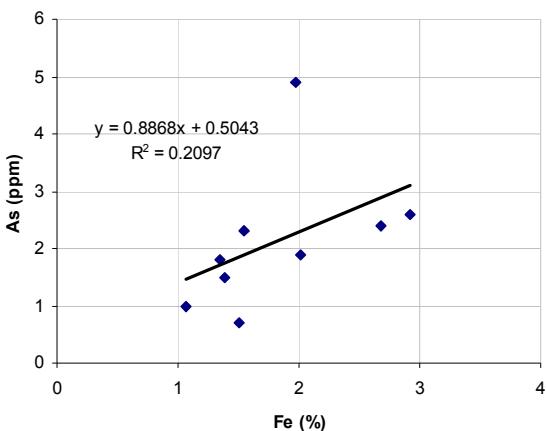
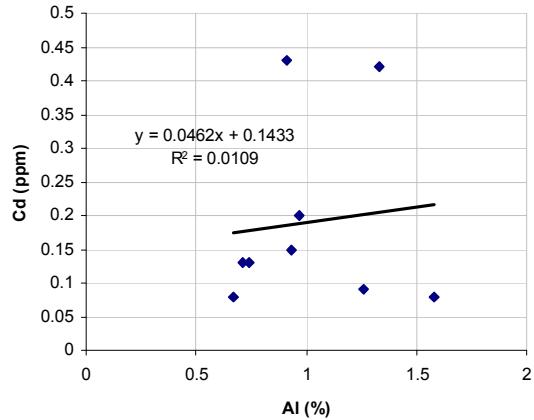
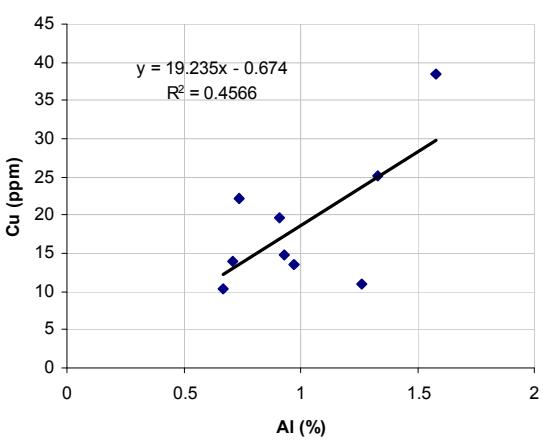
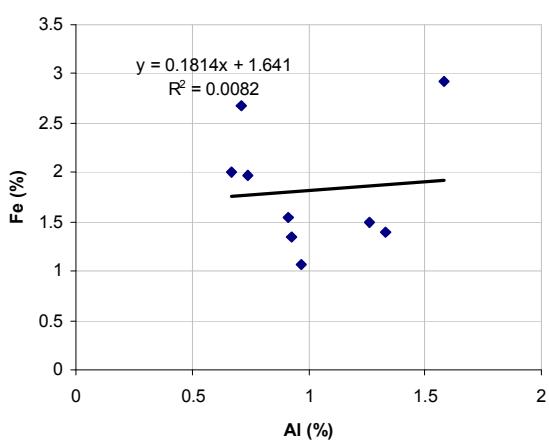
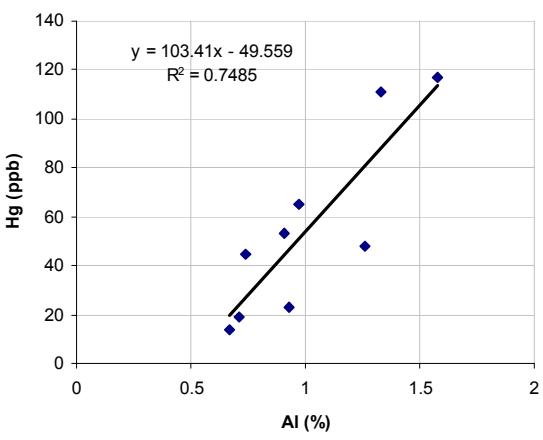
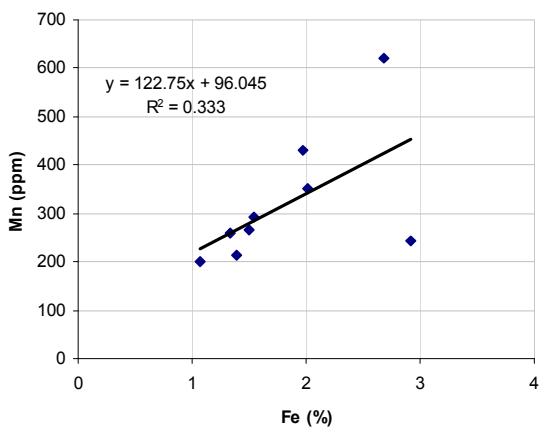


Figure 18: Boxplots for Al, As, Cd, Cu, Fe, Hg, Mn, Pb, Se, Sr and Zn from data from this study.

Fe-As regression**Al-Cd regression****Al-Cu regression****Al-Fe regression****Al-Hg regression****Fe-Mn regression**

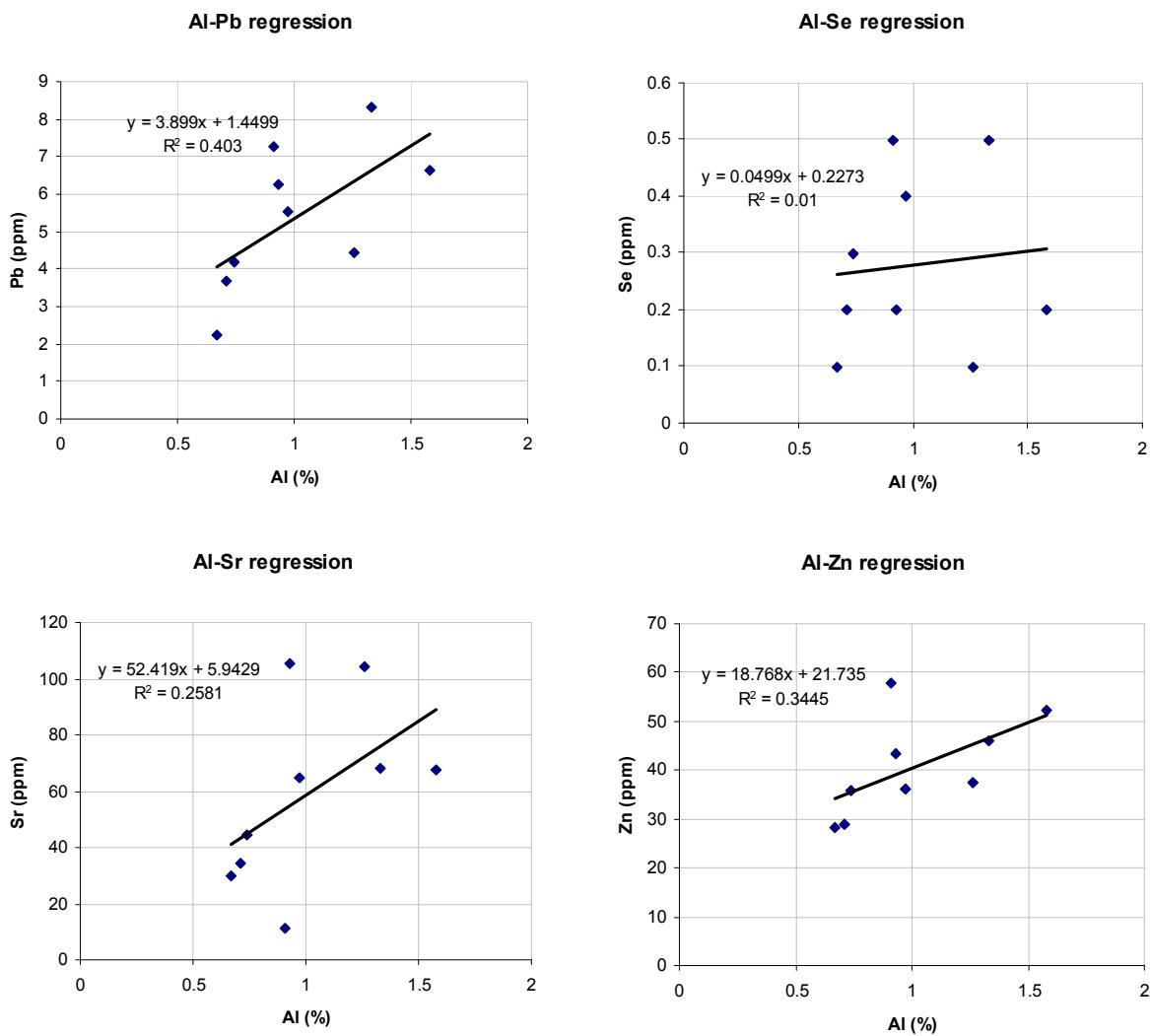
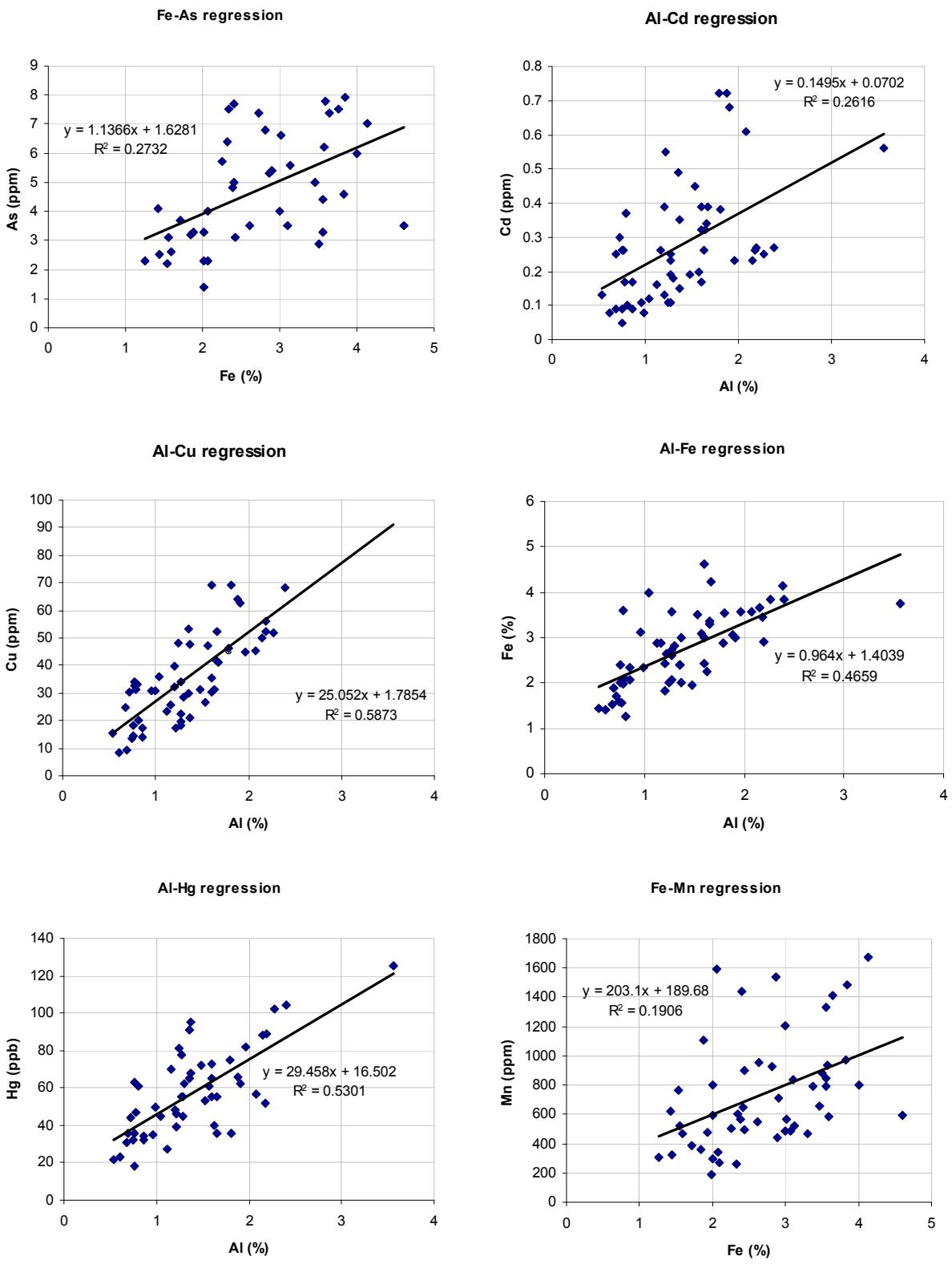


Figure 19: Regression predictions for geological unit Kamloops group



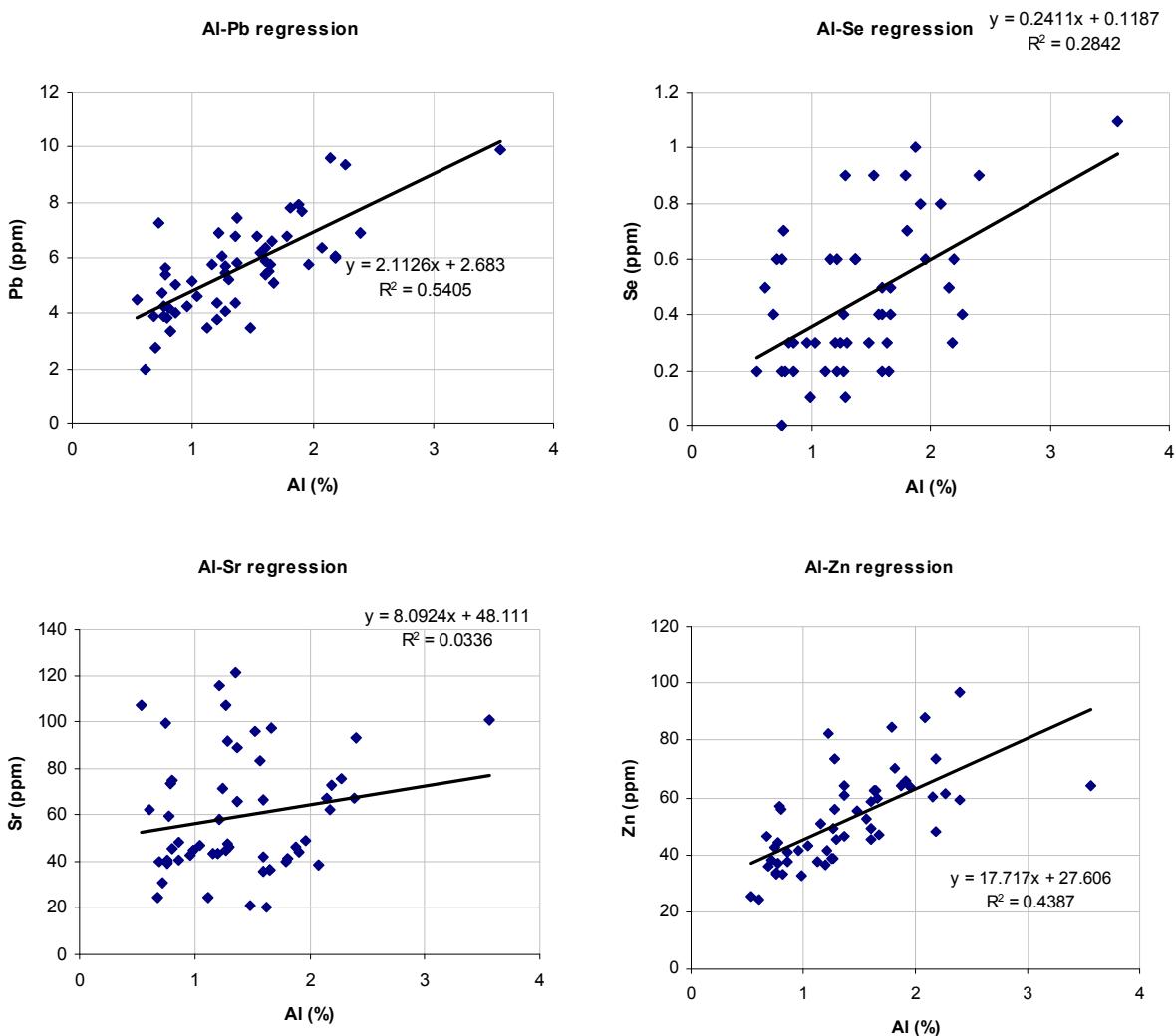
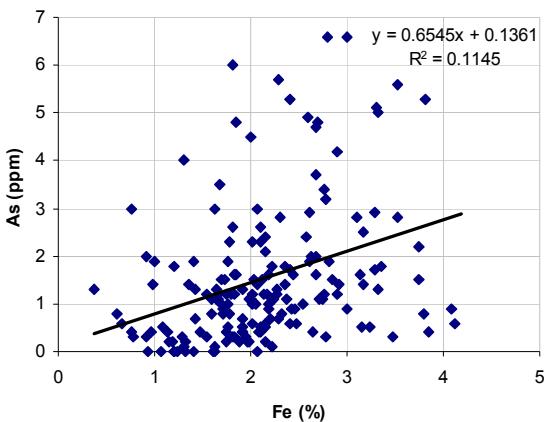
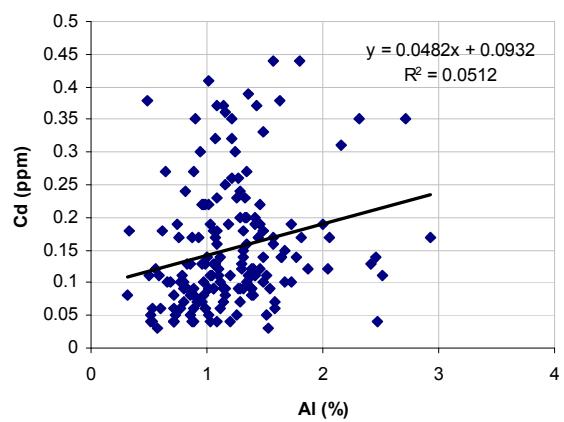
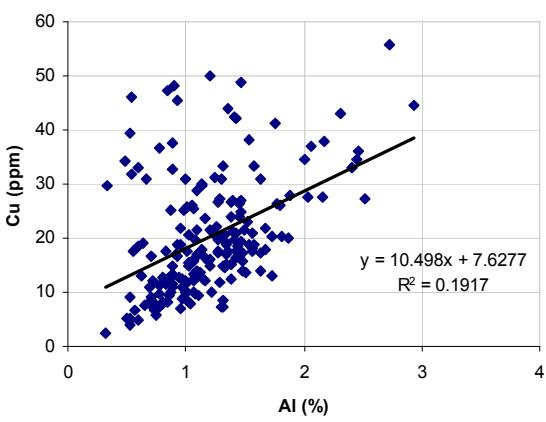
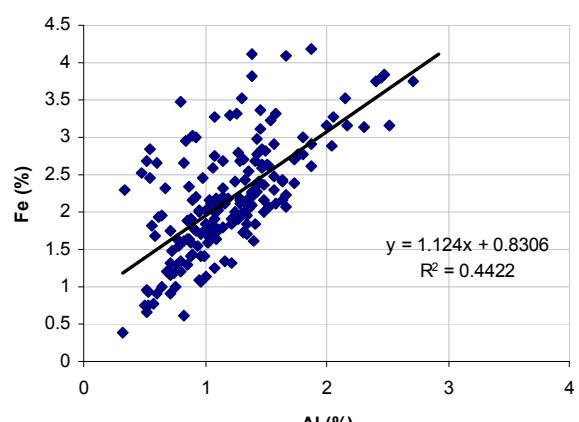
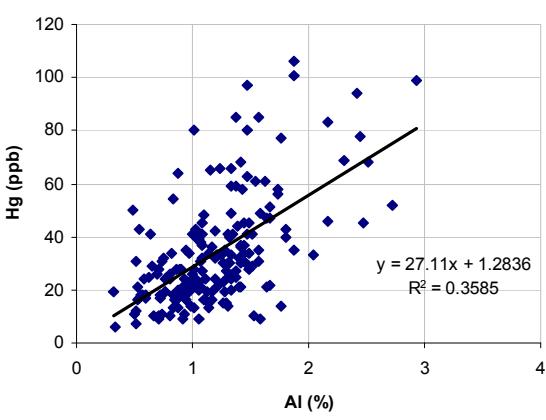
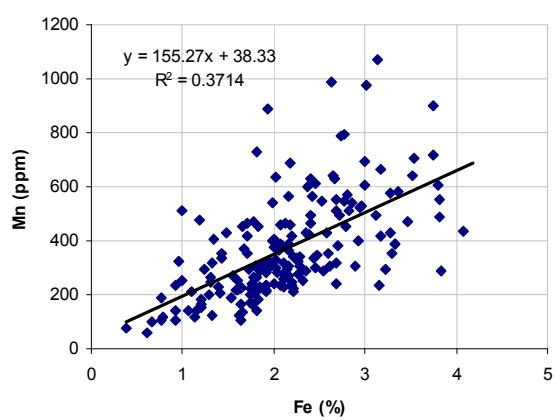


Figure 20: Regression predictions for geological unit Nicolai group

Fe-As regression**Al-Cd regression****Al-Cu regression****Al-Fe regression****Al-Hg regression****Fe-Mn regression**

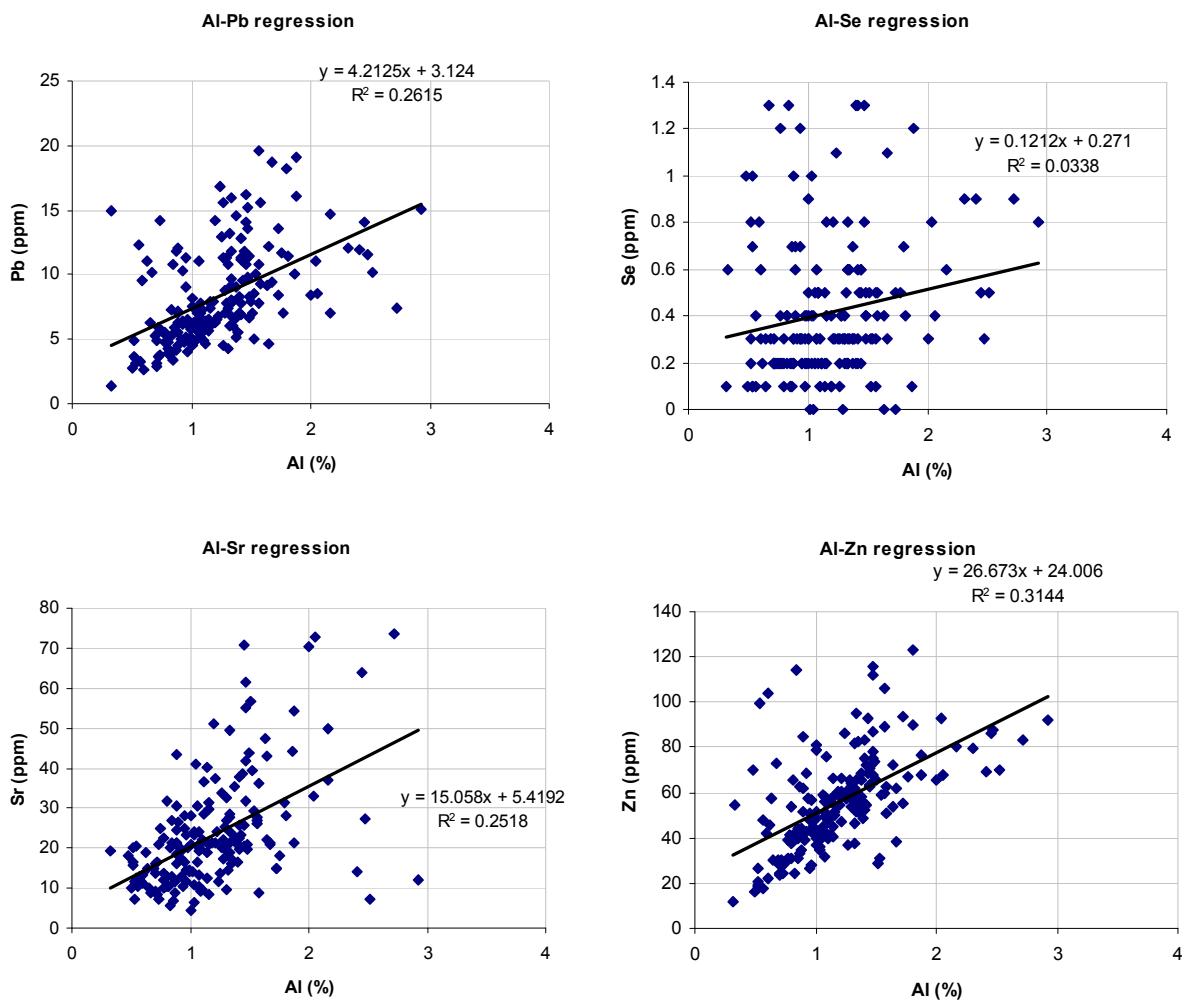


Figure 21: Regression predictions for geological unit Snowshoe group

Table 10: Regression equations from figure 18, 19 an 20 in a table.

| Geological unit | Element | Reference element | Formula | R ² |
|-----------------|---------|-------------------|----------------------|----------------|
| Kamloops | As | Fe | y = 0.8868x + 0.5043 | 0.2097 |
| Kamloops | Cd | Al | y = 0.0462x + 0.0109 | 0.0109 |
| Kamloops | Cu | Al | y = 19.235x + 0.674 | 0.4566 |
| Kamloops | Fe | Al | y = 0.1814x + 1.641 | 0.0082 |
| Kamloops | Hg | Al | y = 103.41x + 49.559 | 0.7485 |
| Kamloops | Mn | Fe | y = 122.75x + 96.045 | 0.333 |
| Kamloops | Pb | Al | y = 3.899x + 1.4499 | 0.403 |
| Kamloops | Se | Al | y = 0.0499x + 0.2273 | 0.01 |
| Kamloops | Sr | Al | y = 52.419x + 5.9429 | 0.2581 |
| Kamloops | Zn | Al | y = 18.768x + 21.735 | 0.3445 |
| Nicolai | As | Fe | y = 1.1366x + 1.6281 | 0.2732 |
| Nicolai | Cd | Al | y = 0.1495x + 0.0702 | 0.2616 |
| Nicolai | Cu | Al | y = 25.052x + 1.7854 | 0.5873 |
| Nicolai | Fe | Al | y = 0.964x + 1.4039 | 0.4659 |
| Nicolai | Hg | Al | y = 29.458x + 16.502 | 0.5301 |
| Nicolai | Mn | Fe | y = 203.1x + 189.68 | 0.1906 |
| Nicolai | Pb | Al | y = 2.1126x + 2.683 | 0.5405 |
| Nicolai | Se | Al | y = 0.2411x + 0.1187 | 0.2842 |
| Nicolai | Sr | Al | y = 8.0924x + 48.111 | 0.0336 |
| Nicolai | Zn | Al | y = 17.717x + 27.606 | 0.4387 |
| Snowshoe | As | Fe | y = 0.6545x + 0.1361 | 0.1145 |
| Snowshoe | Cd | Al | y = 0.0482x + 0.0932 | 0.0512 |
| Snowshoe | Cu | Al | y = 10.498x + 7.6277 | 0.1917 |
| Snowshoe | Fe | Al | y = 1.124x + 0.8306 | 0.4422 |
| Snowshoe | Hg | Al | y = 27.11x + 1.2836 | 0.3585 |
| Snowshoe | Mn | Fe | y = 155.27x + 38.33 | 0.3714 |
| Snowshoe | Pb | Al | y = 4.2125x + 3.124 | 0.2615 |
| Snowshoe | Se | Al | y = 0.1212x + 0.271 | 0.0338 |
| Snowshoe | Sr | Al | y = 15.058x + 5.4192 | 0.2518 |
| Snowshoe | Zn | Al | y = 26.673x + 24.006 | 0.3144 |