Sources and transport of surface sediment and metals in B.C. fjord, Tahsis Inlet

June 2015

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Acknowledgments

I would like to thank Dr. Julian Sachs, primarily, but also Ashley Maloney and Dr. Arthur Nowell for their help in conducting this study and writing this paper. Also, to Dr. Andrea Ogston for her help with designing the original study and for her assistance with grain size analysis. Thank you to Kathy Newell for all of her patience in helping me with the grain size analysis. A general thank you to Julia Marks and Trevor Harrison for their assistance in the background research. Dr. John Crusius and Dr. Rick Keil both forced me to look at the data in a completely new way, and none of this would have been possible without them. Dr. Julie Keister and Rick Berg were instrumental in helping me learn the statistical analyses for this project. I am thankful to Jemima Rama and Alex Mitchell-Morton for being my pipette analysis assistants for a while. Finally, infinite thanks to the School of Oceanography for allowing me the resources to do this project and the crew of the R/V Thomas G. Thompson for helping with sample collection.

Abstract

Metals introduced to rivers bind to fine sediment and are transported to the seafloor where a variety of complex sediment transport processes occur. Some of these metals can be hazardous to the marine biosphere, and it is therefore crucial to quantify the magnitude of these processes to understand where sediment containing toxic metals is accumulating. For this study, 20 surface sediment samples were collected from Tahsis Inlet, Nootka Sound, BC. An understudied region in Canada, Tahsis Inlet is a steep, narrow fjord with high tidal energy and is characterized by a sidewall river delta, a mid-inlet passage to another fjord, and two rivers at its head. Sediment samples were analyzed for grain size, loss on ignition, and concentrations of 22 metals. Grain size distributions in Tahsis Inlet varied widely from very coarse (rocks, gravel, sand) around the sidewall delta to very fine (silt and clay) at both ends of the inlet. There were distinct patterns between different types of metals, where certain metals tended to co-vary along the sampling transect. Additionally, the toxic metal, arsenic, was detected at several of the Tahsis Inlet stations. The connections among metal concentrations and local mining activities, physical transport via currents and landslide deposition, and biological processes is described.

Introduction

Studies on the sources and transport mechanisms of metals in sediment are numerous because several metals are highly toxic to the marine biosphere (Bryan, 1992; Mustafa, 2009). Growing anthropogenic input of these metals creates additional concern, due to the potential for overwhelming natural processes (Caetano, 2002; Soto-Jimenez, 2003; Huang, 2003). Understanding current processes controlling metals concentrations in sediment can be used to study how environmental conditions in the sedimentary environment have changed over time.

The study of sources and transport of metals and organic carbon in surface sediment is widely pursued (Balistrieri, 1986; Tam, 2000; Buggy, 2008; Hoff, 2014). Oxygen content has a marked effect on redox sensitive metals in sediment (Calvert, 1993; Crusius, 1996; Morford, 1999). Organic composition and grain size can have a variety of complex effects on the concentration of metals in sediment. However, since these two factors are also correlated, it is often difficult to differentiate primary causes of grain size or organic content to metal concentration patterns (Emerson, 1988; Zonta, 1994; Hedges, 1995; Wang, 2000; Lin, 2002).

Therefore, it is crucial to expand on the current knowledge of metals transport, especially in surface sediment since that is where benthic biological uptake and re-suspension into the water column occurs. This study seeks to contribute to the information base on this subject, as well as inform on fjord systems more specifically. Tahsis Inlet, on the western coast of Vancouver Island is a highly understudied fjord system, especially in the winter season. In particular, the processes surrounding the transport of metals and organic carbon in surface sediment in Tahsis Inlet are not known. However, there have been studies in similar fjord systems in Canada (Pocklington, 1979; Skei, 1979; Pelletier, 1988; Saulnier, 2000; Walsh, 2008).

By studying fjords in particular, there is an opportunity to study anthropogenic and terrigenous inputs, due to their proximity to the coast and therefore to civilization. Tahsis Inlet is particularly interesting because the majority of the region is under-populated, except in localized areas. It provides an opportunity to spatially discern anthropogenic and terrigenous processes.

By measuring the grain size and loss on ignition, as well as concentrations of a suite of 22 metals in Tahsis Inlet, this study attempts to find correlations between sources of various metals and to understand how they are transported after entering the system. Groups of metals will tend to co-vary by their primary source (marine, terrigenous, anthropogenic), and then will accumulate in sediment based on spatial and temporal variations in the character and redox state of bottom and pore waters.

Methods

Fieldwork

Study Area

Sampling took place in Tahsis Inlet, B.C., around 49^{o} N and 126^{o} W, from December 16-17, 2014. Tahsis Inlet is a fjord on the western coast of Vancouver Island, British Columbia. It is characterized as steep-walled and narrow (1.2 km mean width), with a sidewall river delta from the output of the Tsowwin River, and two rivers (Tahsis and Leiner) at its head (Tully, 1937; Dodimead, 1984; Kasper, 1992). The sidewall river delta coincides with a mid-inlet sill, in addition to the sill at the opening to Nootka Sound (Pickard, 1963). There is also an entrance called Hecate Channel on the western side of the fjord which leads to Zeballos Inlet to the northwest. The inlet varies from approximately 50 to 210 m depth and is about 39 km long (Dodimead, 1984).

At the Tsowwin and Leiner rivers, samples were taken at the mouth of each river. All other samples were taken mid-inlet, and the stations to the north and south of the Tsowwin Narrows were spaced approximately 1.5 km apart, while the stations over the Tsowwin Narrows sill were spaced about .25 km apart (Figure 1).

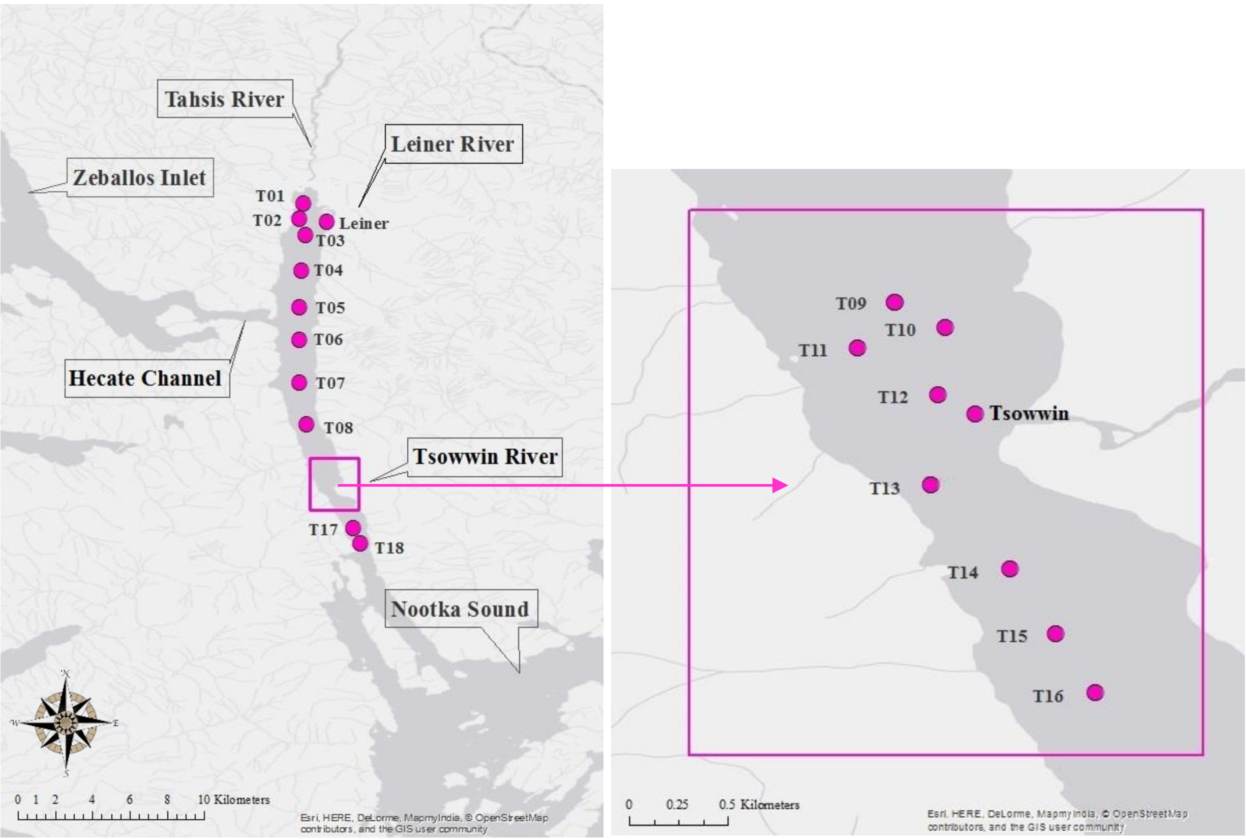

Figure 1. A map of all of the sampling sites in Tahsis Inlet. The first map is a wide view of the inlet and surrounding bodies of water, the second is a close-up of the stations in the Tsowwin Narrows. The southern end connects to Nootka Sound. The Tsowwin Narrows stations were spaced closer than the northern and southern stations.

Sampling Methods

Twenty surface sediment samples were collected using Van Veen and Shipek grabs. Samples T01-T08 and T17, T18 were too fine for the Van Veen grab to get accurate surface samples. The Van Veen over-penetrated, and most of the surface was lost with the ascent through the water column. Therefore, the Shipek grab was used for these samples, and the Van Veen was used for the coarser Tsowwin Narrows samples. “Leiner” and “Tsowwin” were samples from the mouth of the Leiner and Tsowwin rivers, and these were collected from a small boat with a Van Veen grab. For all samples, once the grabs came to the surface, the top ~5 cm were scooped with a gardening hand shovel into Whirlpak bags and stored at 4^{o} C.

Sample Analyses

Grain Size Analysis

Each sediment sample was homogenized and 20-30 g was sub-sampled for grain size analysis. These sediments were stripped of organic matter with 15 mL of 30% hydrogen peroxide. Then, the samples were wet sieved through a 63 micron filter to separate silts and clays from coarser particles. The portions of each sample that were greater than 63 microns were then dried and shaken through a nest of sieves, starting at -4^{ϕ} (pebbles), and proceeding by 0.5^{ϕ} increments until $+4^{\phi}$ (63 microns, sand/silt boundary). Each size fraction was weighed and characteristics of the sample, such as shell and wood content, were noted with an approximation of the percentage by volume of these characteristics. At stations T01-T08, T23, and T24, where the sediment consisted primarily of mud, grains smaller than 63 microns were analyzed using a pipette-based settling technique (Poppe et. al., 2000). For the coarse (sand/gravel) Tsowwin Narrows stations, the fine (silt/clay) portion ($> +4^{\phi}$) was dried and weighed without further size distribution analysis. All of the procedures followed the guidelines of the U.S. Geological Survey publication on sediment grain size analysis procedures (Poppe et. al., 2000).

The mass data for each of the particle sizes for each sample was processed using the program GRADISTAT (Blott and Pye, 2001). The program calculated the D50 (median) grain size.

Metals and Loss on Ignition

A ~30 g aliquot of each surface sediment sample was oven-dried at 60 - 70° C and crushed with a mortar and pestle before analysis of ^{7}Be activity by gamma ray-spectroscopy. While this should not have had any effect on the other analyses, it is worth mentioning that the samples underwent another procedure for a different study of the same region before the following. Approximately 1-2 g of these same sediments were digested by the EPA 3050B method (1996). Then they were run by ICP-MS (Inductively Coupled Argon Plasma Mass Spectrometry) to test for metals concentrations using the Thermo Scientific 61E model.

Organic carbon content was evaluated by loss on ignition (LOI). Approximately 1 g of dried and crushed sediment was baked for 12 hours in an oven at 400° C. These samples were then weighed again (Schumacher, 2002). The LOI was calculated as the percentage mass lost from the total sub-sample.

The metals, organic carbon, and grain size data were all analyzed using Principal Components Analysis (PCA). PCA is a statistical analysis that finds linear covariance across many dimensions (Culman, 2008). The metals data across stations were highly variable; Al was on a scale of 10^3 ppm while Cd was on a scale of 0-10 ppm, for example. PCA does not analyze data on highly variable scales well, so the data was standardized by standard deviation of each metal, across the sample stations. This retained the patterns of each variable, while allowing PCA to compare them on the same scale. The PCA was performed using the PC-ORD statistical program with the Variance/Covariance (centered) option in variables space (McCune and Mefford, 2006).

Results

Loss on ignition is widely accepted as a proxy for concentrations of organic carbon. From here forth, the loss on ignition results are referred to as organic carbon content, or OC (%). The PCA of D50, metals, and OC (%) data revealed a covariance between D50, OC%, Ca, B, Si, S, Na, and K. These have been referred to as Type I variables. The Type II metals contained: Cu, Cr, Ni, Pb, Mo, Mg, Cd, Se, Al, and Fe (Figure 2). Outliers that did not plot within the Type I or Type II clusters were: Ba, Zn, As, P, and Mn. These were all negative on Axis 2. Most of the other variables were positive or slightly less than zero on Axis 2.

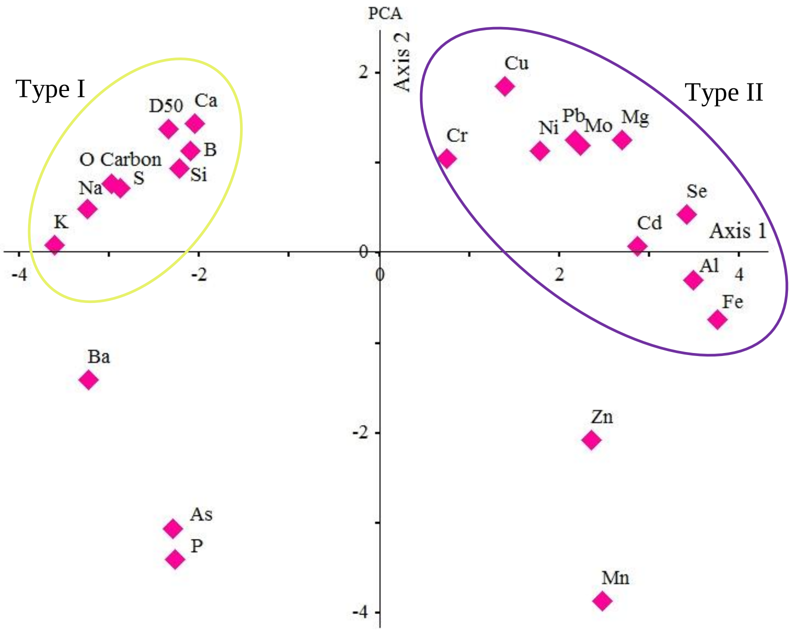

Figure 2: The graphical results of the PCA, plotted on Axis 1 and 2. The data tended to group itself into two variables, named Type I and Type II. The outliers, Ba, Zn, As, P, and Mn all were largely negative on Axis 2. Most of the other variables were greater than 0 on Axis 2.

Axis 1 explained 55% of the variance, and Axis 2 explained 22% of the variance within the entire dataset. Axis 3 explained 6% of the variance, and due to the rapid drop in percentage, Axes 3 and higher were considered to be random or minor variability and therefore non-significant to analysis of results.

Axis 1 shows a split between variables at Axis 1 = 0. The split between variables on Axis 2 is less stark, as expected from the variance which it explains, but in statistical terms is still meaningful to analyze.

The D50, and OC (%) were highly correlated (Figure 3a, b). The notable differences in the two trends are the Leiner and Tsowwin stations. While, the D50 at these two stations remains close to the D50 at other stations, the OC (%), in contrast, plummets from fairly high values of organic carbon to approach zero at these two stations. Both D50 and OC (%) display an anomalous point in the Tsowwin Narrows at station T11. OC (%) in general is much greater in comparison to the organic carbon contents generally seen in fjord surface sediments (Seiter, 2004; Smith, 2015). When stripping the samples of organic matter during the grain size analysis procedures, the addition of 30% hydrogen peroxide yielded a highly explosive reaction in all of the same samples with >10% organic carbon content. The reaction was so unexpectedly explosive that, on the first run, samples T16 and T17 were lost and had to be repeated.

For grain size analysis, there are three sources of error: small scale variability in the seabed, sampling bias (as mentioned, the Van Veen Grab and Shipek were used under different conditions, which may have introduced a bias), and errors in laboratory analyses (weighing error and sample loss during transfer). In particular, it should be noted that pipette analysis commonly gives negative values owing to the fact that very small masses must be handled and weighed. Static electricity can cause the scale to misreport the weight, and while weighing samples, I neglected to tie up my hair which could have easily caused error in the measurements, due to generation and transfer of static electricity. The negative values from the pipette analysis of this study never exceeded -.5 g, and therefore, these values were considered 0 in the calculations of the D50. Since most of the weights of each size fraction at least exceeded 1 g, this was considered to be a minor error.

For ease of visualization, one metal was selected from each of the Type I and Type II metals to serve as a proxy for that Type. For the Type I metals, potassium was used, and for the Type II metals, the proxy was molybdenum (Figure 3c, d). The results of the PCA are confirmed by the stark contrast between Type I and Type II metals. There is a greater variability within Type I, where the general trend is: low at the northern end of Tahsis Inlet, a drastic increase until T08, then a general low concentration at the Tsowwin Narrows (the exception being the anomalous T11), and finally a parabolic arc for the southern stations. The Type II metals are less variable and follow the general trend of high concentrations at the northern end of Tahsis Inlet, and a steady decrease and stability until the southern stations, where the trend follows a parabolic curve, resembling that of the Type I metals. The Type II metals do not follow the T11 anomaly of the Type I metals.

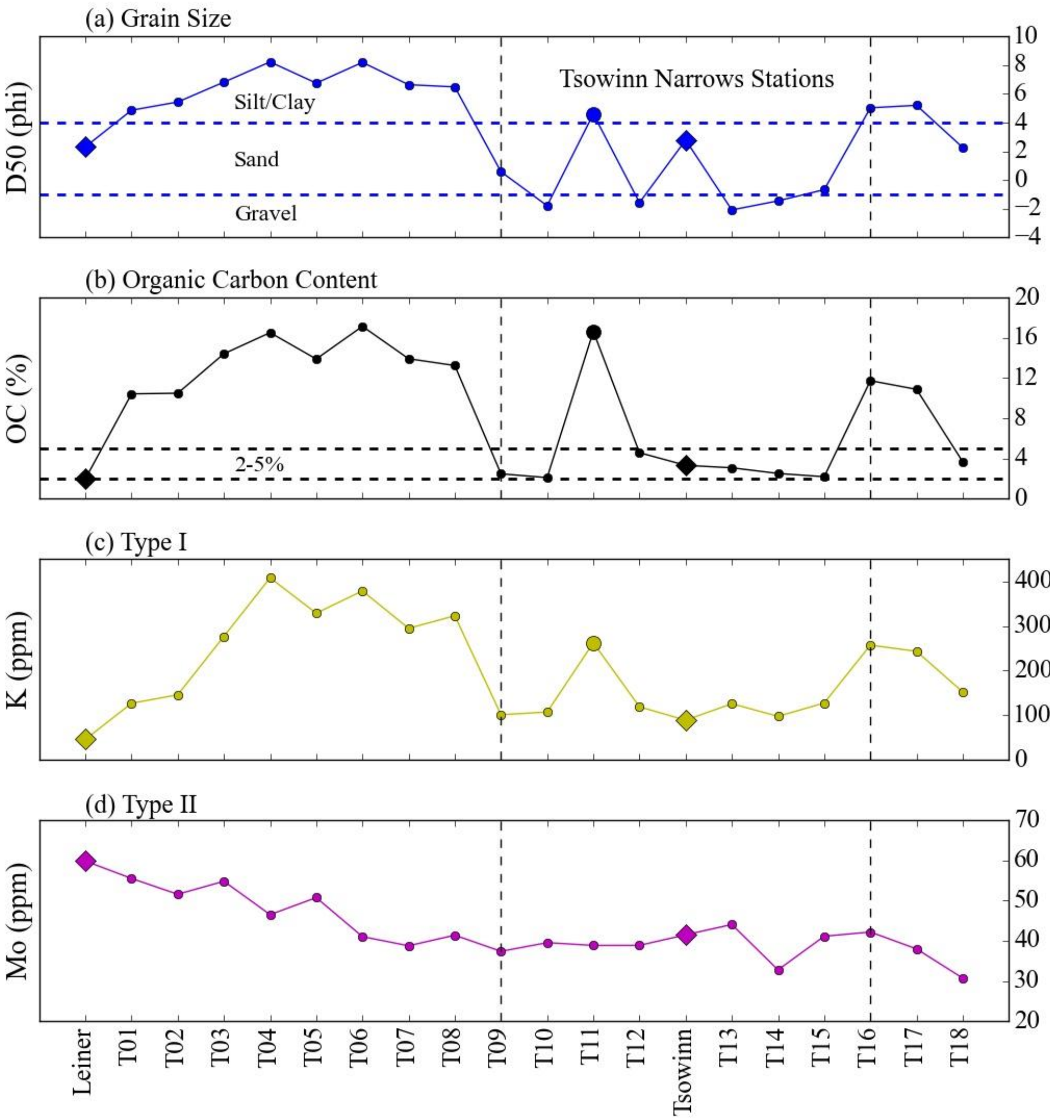

Figure 3: The D50 (a) and OC (%) (b) plotted along a transect of the stations from North to South. The average range of OC (%) in fjords has been plotted on (b) (Smith, 2015). The transects of the two major types of metals, using K as a proxy for Type I (c) and Mo for Type II (d). Stations of note: Leiner, T11, and Tsowwin. Leiner and Tsowwin are marked as diamonds in each plot. T11 is a large dot on graphs (a), (b), and (c). The Tsowwin Narrows stations are on an expanded distance metric, to be clearer where they lie on this transect.

Comparing the ratios of metals to aluminum for different samples is a widely accepted way to determine how much of the metal is lithogenic in origin (Horowitz, 1985; Schropp, 1988). Aluminum is abundant in the earth’s crust and has negligible input from other sources. This was performed for four metals in the Type II group that tend to be redox sensitive (Cd, Fe, Mg, Mo). Comparison of these four metals to aluminum was done at the two stations each for the highest and lowest bottom water O_2 concentrations (Table 1). Though dissolved oxygen was not measured in the sediment pore fluids the bottom oxygen content is presumed to be a good indicator of the redox state of near-surface sediments. Additionally, the two stations selected for their low oxygen concentrations were chosen to be fairly far away from each other, so as to avoid comparing sites with similar input functions. The highest variances of ratios to Al between stations were for Fe and Mg, but they were still not much greater than zero, and Cd and Mo were essentially zero.

Station	**Depth of Measurement (m)**	**Actual Depth (m)**	**O_2 (mL L^{-1})**	**Cd/Al**	**Fe/Al**	**Mg/Al**	**Mo/Al**
T01	~60	64.8	~2.2	3.5E-4	1.77	0.923	2.7E-3
T17	~100	107	~1.4	3.7E-4	1.67	0.890	2.6E-3
*T04**	190	199	0.48	5.E-4	2.33	1.41	4.E-3
T08	~125	128	~0.6	4.5E-4	1.99	0.944	3.1E-3
Variance				5.2E-09	0.09	0.06	3.9E-07

Table 1. The depth of CTD measurements, as well as the true depth of the station, the O_2 content at the near-bottom depth, the four ratios to Al, and the variance of these ratios. ***** Only T04 is an actual bottle measurement from a water sample at that depth. The others are measurements from the CTD sensor.

Samples were troublesome to analyze for arsenic concentrations. When first analyzing samples for metal concentrations, only six samples were sent to be analyzed. This was to determine if the analysis would be worth pursuing for all 20 samples. Among these samples were the Leiner, T01, T09, Tsowwin, T15, and T18 samples. The Tsowwin River sample came back with high As concentrations (~13 µg g^{-1}). Due to this, all of the other un-tested samples were sent, and the Tsowwin River sample was sent again, as a test to check the accuracy of the result. This time, the Tsowwin River sample came back with only trace amounts of As. It was hypothesized that this was due to the random sub-sampling procedure creating too coarse of a sample to be analyzed appropriately the second time. The Tsowwin River sample was sieved, and a very fine fraction ($>+4^{\phi}$) and a sandy fraction ($+1^{\phi}$) were sent to be analyzed separately.

The very fine fraction came back with the same arsenic concentration as the first test, and the sandy fraction came back with trace arsenic. Only nine of 20 stations came back with detectable arsenic (≥ .056 µg g^{-1}) (Figure 5). This value is so close to 0, that it is negligible in comparison to the concentrations of stations with As detected. Furthermore, though certain samples were given the designation "trace As," this definition was ambiguous, and therefore, for this study, trace and not detected designations were treated as essentially the same.

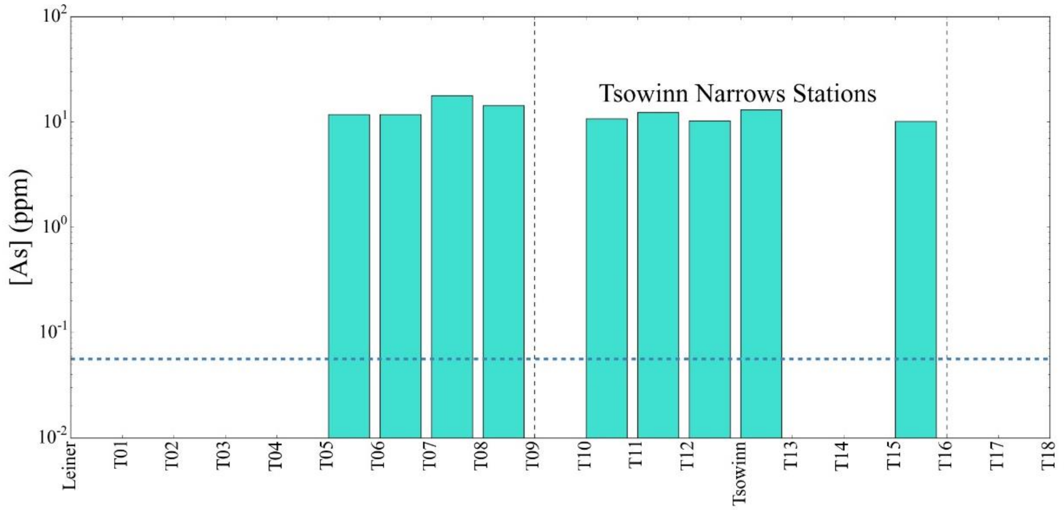

Figure 5. Arsenic concentrations along the transect of stations. The dashed line represents the detection limit for arsenic, since the values samples that returned with no detection of arsenic could be anything < .056 µg g^{-1}. The y-axis is plotted on a log-scale to make the detection limit clearer. The Tsowwin Narrows stations are on an expanded metric.

Discussion

Metals, grain size, and organic carbon trends in a fjord like Tahsis Inlet offer a unique perspective into (i) sediment and metal sources and (ii) subsequent transport of these properties. First, the potential marine source of the Type I metals will be discussed. The next section describes the anthropogenic or terrigenous influences of the Type II metals and the potential to use these metals as transport tracers of recently deposited sediment, since they do not display significant redox trends. Finally, the last section will address specific issues with arsenic data interpretation and its possible correlation with mining activity.

4.1 Type I Metals

Because the Type I metals have such a large variability, they offer a good opportunity to understand sediment sources in Tahsis Inlet. It is likely that the cause of this variability is salty pore water. □^{13}C analysis revealed that there is a large marine organic sediment peak around the Hecate Channel entrance into Zeballos Inlet (Figure 6). There is also a peak of the Type I metals in this area and generally low values around the Tahsis and Leiner Rivers to the north and the Tsowwin River at the Tsowwin Narrows. In addition, there is a peak of Type I metals close to the entrance to Nootka Sound, where the salinity is high from being in direct contact to the open ocean. The metals included in the Type I set are all among the most abundant in seawater, and the samples were not washed of their salt ions before undergoing ICP-MS analysis.

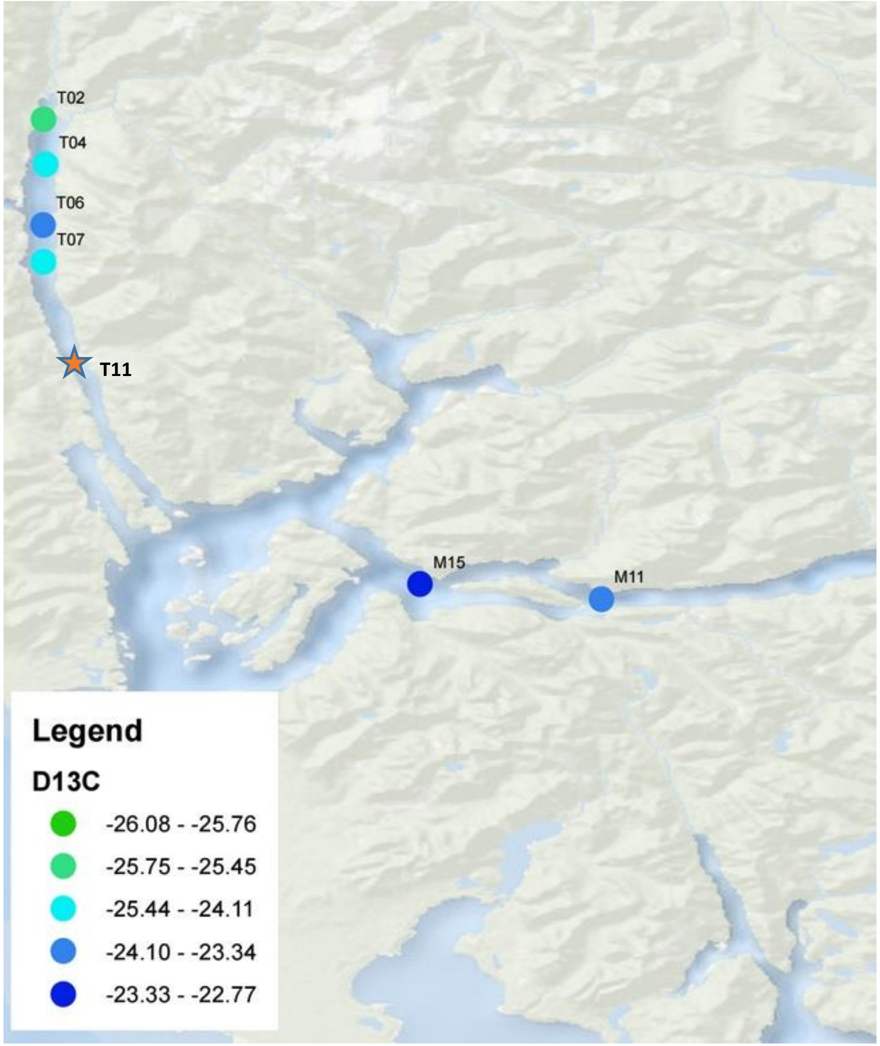

Figure 6. □ ^{13}C values in Tahsis and Muchalat Inlets. This figure was obtained and not adapted from Trevor Harrison of the University of Washington. Lower values indicate higher marine organic source, and higher values indicate higher terrestrial organic source. In Tahsis Inlet, the values vary spatially from highly terrestrial at the far North of the fjord, near the Tahsis and Leiner rivers. The interesting anomaly is the peak right around the Hecate Channel entrance. The value there is comparable to the M15 and M11 values that are close to Nootka Sound. While there is no T11 measurement, it has been indicated where it lies on this map. It would be beneficial to have □ ^{13}C data for this station, because it is likely all recently deposited landslide material.

The greatest issue with this theory is the T11 anomaly. However, in that area, it was noted that the Van Veen was picking up landslide debris. Logging activities are particularly heavy in that area of Tahsis Inlet, and logging has been shown to have a dramatic effect on increasing size and frequency of landslide events (Guthrie, 2002). The T11 sample was estimated to be composed of ~80% lignin and woody matter in the sandy grain sizes. That station contained high organic carbon content, which was probably almost entirely made up of lignin and woody matter. Unfortunately, that assertion cannot be confirmed without further analysis $\delta^{13}C$ analysis of this and surrounding samples. The area is made up of mostly carbonate rocks (Alt and Hyndman, 1995). Several of the Type I metals are also abundant in the surrounding crust: Ca, Si, and K are the strongest cases.

However, while these are reasonable explanations for the sources of the metals and the sediment containing the metals, there is another explanation for the spatial pattern of the Type I metals. The D50 follows the same pattern as the Type I metals, down to the T11 anomaly. It is possible that these metals are merely only preserved by attachment to very small grains. The correlation between the preservation of certain metals in sediment and grain size is well known (Tam, 2000; Lin, 2002).

To that, the counter would be the apparent difference between D50, the Type I metals, and organic carbon content at the river stations. If grain size was the major controlling factor of Type I metals concentration, rather than saltwater or landslide input, the Type I metals and organic carbon content would be expected to increase at the river stations, as the D50 decreases, but this is not the case. This is most likely because of the freshwater input lacking the seawater ions or a large mass of landslide material. Certainly, grain size has a clear correlation with these metals concentrations, but it is possible that grain size is merely also an effect (like the metal concentrations and organic carbon content) of the primary marine and landslide processes of introducing sediment into Tahsis Inlet.

4.2 Type II Metals

The Type II metals consist of some elements that are usually redox sensitive, and therefore, vary under different oxygen content conditions. However, throughout Tahsis Inlet, these metals have similar ratios to aluminum, regardless of bottom dissolved oxygen concentration (Table 1). Therefore, these metals are most likely entirely reflecting transport of sediment in Tahsis Inlet. These metals are discharged from rivers, then advected with bottom currents of Tahsis Inlet.

If Tahsis Inlet follows the classic estuarine circulation of most fjords, then the net transport of its bottom water, which controls the transport of sediment, will be to the north (Pickrill, 1987). These metals also appear to be largely concentrated at the north of the inlet with a general decrease until the Tsowwin Narrows. The far southern stations near the entrance to Nootka Sound could reflect this same trend as well. Even if net bottom transport is to the north in Tahsis Inlet, if these metals derive from the Tsowwin River, there are still periodic southward tidal currents that could sweep the metals toward the southern end of the sill, and as the particles settle, they are caught in the bottom currents that trend northward. They are then trapped behind the sill when they finally settle, reflecting the peak of concentration just south of the sill and the Tsowwin river.

4.3 Arsenic and Mining

It is likely that the bulk of the arsenic results from this, many of which are reported as zero or undetectable, resulted from the non-zero detection limit of .056 µg/g with the ICP-MS technique. Because of the issues with the Tsowwin river sample due to grain size considerations, it is possible if not likely, that the stations without detectable arsenic detected actually contained a non-zero amount of As. Future studies of metals, arsenic in particular, should consider sieving sediments before analysis of metals.

This makes it difficult to analyze the arsenic data, though it is one of the more compelling datasets. Arsenic is extremely toxic, and it is present in consistently high levels in the surface sediments of Tahsis Inlet. Discovering the source is clearly important, for there could be an environmental hazard in the area.

Through some research into the government of B.C.'s information on mining and mineral potential in the Nootka Sound area, it was discovered that the area at the head of Zeballos Inlet has been heavily mined for gold and copper in the past, among other metals (Yorath and Nasmith, 1995; Yorath, 2005). Several reports of the mineral potential have been conducted in that area, as well as notices of mining work, mostly in the past (Figure 7). These reports show that there are arsenic veins within the same structures that contain the gold and copper being mined (iMapBC). It is entirely likely that the arsenic originates from these old mines.

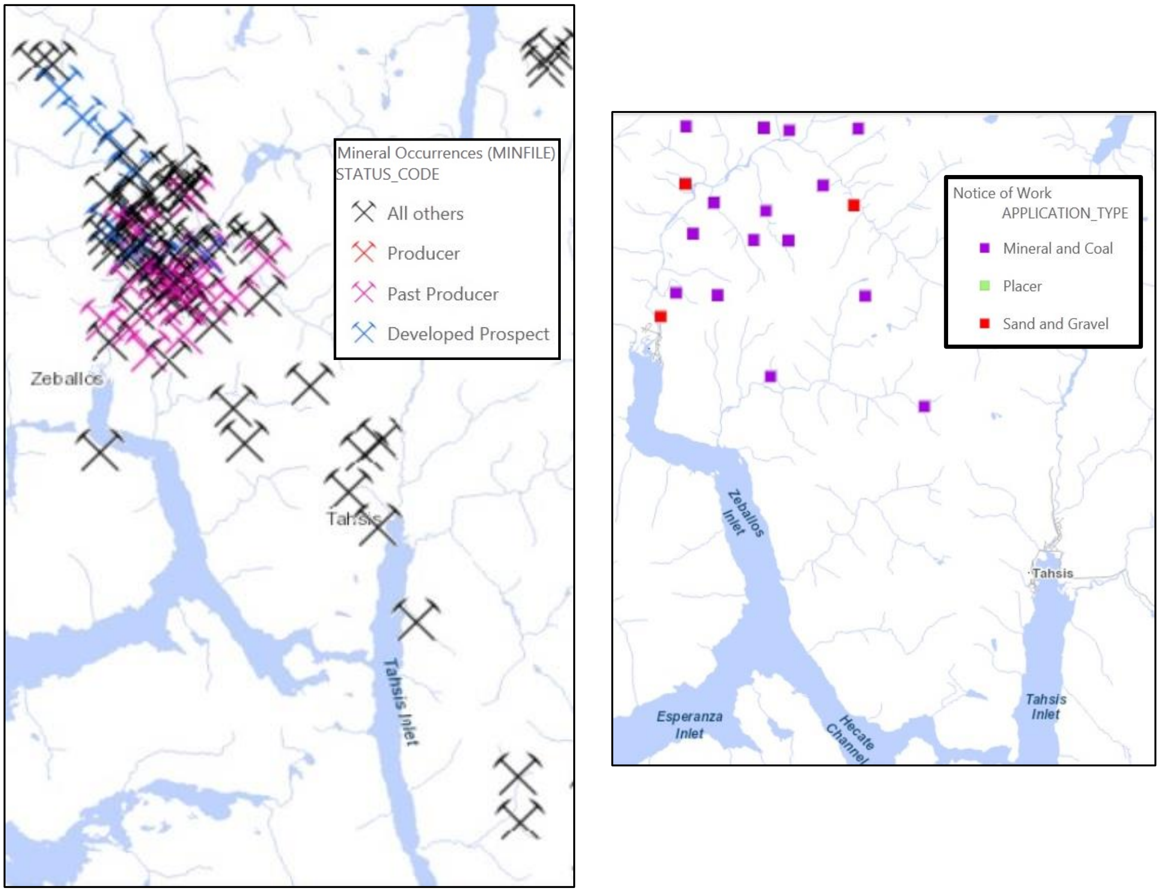

Figure 7. (a) A display of the Mineral Occurrences reports for currently producing mines, old mines, developed mines, and regions for which a study was done without mining involvement. (b) A map of the currently active mines and their type. Obtained from iMapBC, created by the Province of British Columbia.

This could be an alternate explanation for the elevated signal to the north of Tahsis Inlet for the Type II metals. Most of these are shown to be contained in the same structures that were being mined. If the mining released these metals into ground or surface waters, then this would reach Zeballos Inlet at its head. Circulation of water east in Zeballos and through Hecate Channel would bring this salty, dense water into the bottom of northern Tahsis Inlet. Of all the Type II metals, copper makes the strongest case for this interpretation (Figure 8). The copper mining in the area peaked approximately 80 years ago and has declined dramatically since then (Yorath and Nasmith, 1995; Yorath, 2005). That could reasonably be the time required for copper to be leached from mine tailings and transported via surface or ground waters to Zeballos and then to Tahsis.

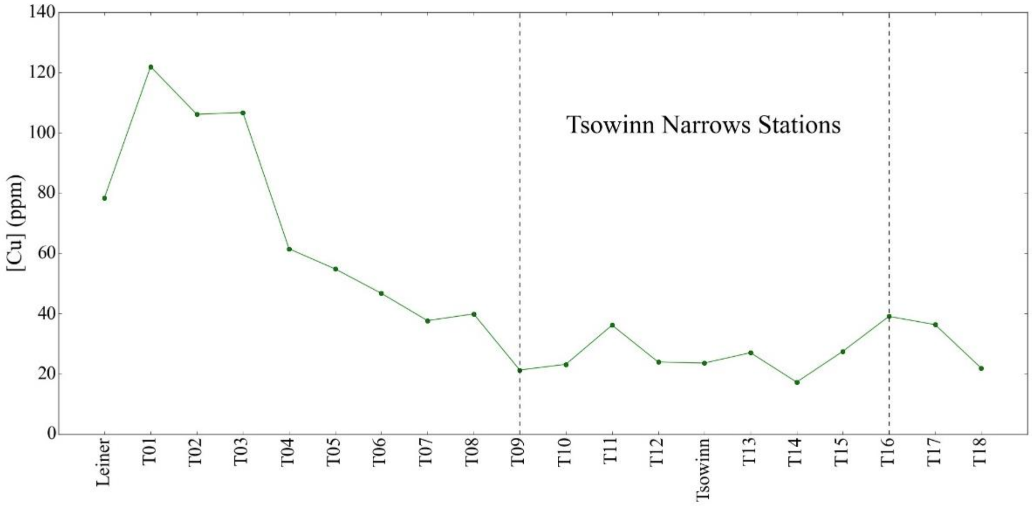

Figure 8. The transect of [Cu] down Tahsis Inlet. Values are highly elevated at the northern end of Tahsis, which could be an indicator of large input from Zeballos Inlet through Hecate Channel.

4.4 Future Research

Tahsis Inlet surface sediment is potentially becoming an environmental hazard because of mining in Zeballos. A repeat analysis of metals in Tahsis Inlet surface sediments should be performed to confirm these findings. If confirmed, then regular monitoring may be warranted. It is possible that some of these metals that are just recently being introduced into Tahsis Inlet from

Zeballos Inlet can be used as tracers for sediment transport in Tahsis Inlet, but that requires further study.

The same type of measurements should be done in Zeballos Inlet and Hecate Channel to confirm whether the mining in that area is the source of the various metal contaminants. Also, a study into the circulation dynamics between Zeballos and Tahsis is too large in scope for this study, but this study has shown that there are clear patterns requiring more detailed and dedicated research.

Finally, there should be an analysis of washed samples from Tahsis Inlet to understand the mechanics of this study’s Type I metals without the seawater factor. Because the Type II metals behave in such interesting patterns, there is the potential for interesting patterns in the Type I metals if the influence of seawater can be removed. In addition to that, a study should be done studying metals concentrations within various grain sizes in Tahsis Inlet. Since the correlation between grain size and Type I variables was so strong, there must be a relationship there, but a causal mechanism linking the two will require a more systematic analysis of metal concentrations in different size fractions of sediment.

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Appendices

Metal	First Run			Second Run		
	QC	QC True	Error (%)	QC	QC True	Error (%)
Al	4.94	5.00	1.1	3.65	5.00	27
As	4.90	5.00	2.0	5.25	5.00	5.1
B	5.03	5.00	0.5	4.99	5.00	0.2
Ba	5.03	5.00	0.5	5.01	5.00	0.2
Ca	25.4	25.0	1.8	24.8	25.0	0.8
Cd	5.05	5.00	1.0	4.98	5.00	0.3
Cr	4.78	5.00	4.5	4.95	5.00	0.9
Cu	5.02	5.00	0.5	5.01	5.00	0.3
Fe	4.98	5.00	0.5	4.78	5.00	4.4
K	49.4	50.0	1.2	49.9	50.0	0.3
Mg	4.96	5.00	0.8	4.86	5.00	2.9
Mn	5.01	5.00	0.1	4.98	5.00	0.3
Mo	5.05	5.00	0.9	5.01	5.00	0.2
Na	4.78	5.00	4.3	4.85	5.00	2.9
Ni	4.87	5.00	2.7	4.96	5.00	0.8
P	10.2	10.0	2.1	10.3	10.0	2.7
Pb	5.05	5.00	1.0	4.93	5.00	1.4
S	5.00	5.00	0.0	4.98	5.00	0.3
Se	5.00	5.00	0.0	5.00	5.00	0.0
Zn	5.04	5.00	0.8	4.99	5.00	0.3
Si	4.85	5.00	3.0	4.73	5.00	5.3
Ag	4.98	5.00	0.4	4.91	5.00	1.9
Hg				247	250	1.2

Table 2. The error calculated error for each metal. It is unclear whether the second run error for Al is accurate or a typographical error. Hg was only run one time for all samples. First run was for stations: Leiner, T01, T09, Tsowwin, T15, and T18. The second run was for Tsowwin and all others not in the first run.

Stations	**Al (µg/g)**	**B (µg/g)**	**Ba (µg/g)**	**Ca (µg/g)**	**Cd (µg/g)**	**Cr (µg/g)**	**Cu (µg/g)**	**Fe (µg/g)**	**K (µg/g)**
Leiner	21762.27	82.17658	4.199099	14082.23	8.06036	81.28108	78.42432	42220.56	460.3874
T01	20385.22	116.667	9.184502	13776.79	7.062731	38.30812	121.9179	36109.4	1268.981
T02	14510.37	125.3033	12.71124	14673.38	6.518411	67.57461	106.0891	35289.87	1458.447
T03	14875.98	148.0982	13.99804	16662.03	7.516699	65.27112	106.6886	36745.73	2766.707
T04	11644.95	144.193	19.26236	22495.61	5.86597	50.79658	61.48669	27108.27	4076.6
T05	11229.45	128.6794	15.74216	19002.05	6.080392	52.52157	54.80882	28542.41	3285.335
T06	10385.02	131.5285	19.22146	16770	5.405512	70.09744	46.72244	25371.26	3784.847
T07	10008.01	118.4272	30.1699	12134.54	5.182524	54.3699	37.6699	26295.57	2947.092
T08	13571.48	125.3614	18.02711	19537.01	6.141566	49.23795	39.90161	27024.64	3227.581
T09	12611.91	60.90543	7.64794	6139.604	5.192884	41.25468	21.28184	29119.29	1012.814

T10	13208.13	75.9566	9.695283	9848.17	6.032075	30.14057	23.19717	32928.81	1072.244
T11	13353.86	136.7992	14.42843	12217.95	5.346918	33.29125	36.17594	23682.58	2622.278
T12	13399.43	87.58241	6.787037	11512.9	5.692593	27.53704	23.95	30074.74	1189.622
Tsowwin	13817.84	68.50205	11.82859	9536.943	6.39011	35.9713	23.61154	32361.95	890.2264
T13	14954.59	83.5783	13.72264	7926.259	6.495283	41.61604	27.03208	34904.47	1259.655
T14	11289.85	62.23443	8.688581	11512.66	4.661765	25.91522	17.28028	24743.59	975.8555
T15	14605.12	77.96409	10.11602	12873.04	5.717311	45.26888	27.47422	31262.04	1274.798
T16	14659.77	130.2528	13.9839	15543.77	5.530303	36.73864	39.07955	25815.96	2570.652
T17	14486.6	105.967	15.07479	19113.95	5.416264	40.61019	36.34127	24140.67	2432.167
T18	11877.5	65.3671	11.44703	14516.71	4.305762	20.13476	21.91543	22168.43	1520.23
	Mg (µg/g)	**Mn (µg/g)**	**Mo (µg/g)**	**Na (µg/g)**	**Ni (µg/g)**	**P (µg/g)**	**Pb (µg/g)**	**S (µg/g)**	**Se (µg/g)**
Leiner	21428.83	563.7369	59.83694	2538.211	90.71712	529.6964	47.72613	334.7126	455.3135
T01	18824.3	410.7048	55.50277	14584.88	54.06365	768.2537	43.46033	4849.078	398.9188
T02	17913.53	387.437	51.5688	14398.16	72.74419	679.1143	43.36725	5623.886	374.9041
T03	19621.93	395.1179	54.80747	31646.07	70.33497	959.3202	46.13851	11619.26	393.1817
T04	16459.43	270.9667	46.50856	46654.6	53.19582	898.6426	36.89259	13765.23	304.346
T05	14314.62	311.5824	50.73333	35856.05	53.90392	864.9892	35.07843	17201.18	300.6245
T06	12993.47	257.4183	41.03543	40592.86	64.74705	1035.032	33.84055	10000.7	275.8031
T07	11432.47	243.6641	38.75146	26540.59	53.14369	961.1922	28.62816	10181.44	267.2553
T08	12812.65	296.2058	41.39357	30386.34	48.24598	1380.945	35.78514	9703.293	279.2861
T09	12657.06	452.9925	37.37547	5152.947	46.63483	912.0627	27.75468	1134.268	285.382
T10	13173.97	690.4679	39.53113	6822.143	39.15566	1066.842	32.75283	1061.141	306.8142
T11	14315.7	295.5239	38.84791	35173.76	37.9175	1037.534	30.95427	5523.775	267.2137
T12	14111.8	485.4907	38.85556	12913.66	36.33889	848.4889	32.2537	1838.24	295.2333
Tsowwin	13720.55	456.0878	41.4859	3947.194	42.74592	845.6604	30.54238	816.8498	315.7713
T13	14170.01	1343.896	44.04528	6717.418	49.23208	1063.689	36.23774	999.1019	334.1104
T14	11615.54	361.3304	32.76298	6919.576	31.70415	759.378	23.91436	2222.979	250.5156
T15	14414.32	440.2256	41.12615	6781.692	48.10589	884.1556	32.28821	1947.23	306.3048
T16	13190.59	287.4091	42.17898	22122.32	40.31913	836.2945	34.8447	9016.58	275.2083
T17	12894.17	290.3482	37.97807	18153.61	43.85593	865.1255	33.02613	6254.833	266.894
T18	10028.96	309.9136	30.71004	7251.292	26.5381	701.8039	26.62082	2358.748	241.1208
	Si (µg/g)	**As (µg/g)**	**Zn (µg/g)**	**Hg (µg/kg)**					
Leiner	484.4477	ND	78.16847	ND					
T01	1052.484	ND	82.13284	ND					
T02	1273.622	ND	75.68314	ND					
T03	1960.159	TR	81.34086	ND					
T04	1833.539	TR	65.81464	ND					
T05	1458.162	11.77059	73.72157	ND					
T06	1766.454	11.6811	65.97146	0.31					
T07	1126.112	17.81942	77.6233	ND					

T08	1351.445	14.21687	69.7249	ND
T09	514.3633	ND	67.69663	ND
T10	695.6415	10.73679	70.23679	ND
T11	1121.442	12.28032	63.22366	0.43
T12	674.7778	10.28056	65.38889	ND
Tsowwin	687.9614	13.08872	93.15251	ND
T13	761.5575	TR	81.92075	ND
T14	474.6453	ND	75.25433	ND
T15	611.0783	ND	74.29558	ND
T16	1003.753	10.12027	70.58239	ND
T17	899.0353	TR	70.74377	ND
T18	583.816	ND	62.45632	ND

Table 3. All of the raw data for each of the metals at each of the stations. TR = Trace. ND = Not Detected. Ag was also measured, and it was undetected at every station. The detection limit for Hg was 1.4E-4 µg/kg and for As, it was .056 µg/g.