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

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Abstract

Metal contaminants in marine sediments can pose a threat to marine biota and can bio-accumulate in the higher trophic levels of fjord communities (Bryan 1992, Buggy 2008). Mining activity on land can be a source of metal-contaminated dissolved and suspended sediments to estuaries and fjords where they can accumulate on the seafloor. Nootka Sound, western Vancouver Island, British Columbia, Canada, is an area of known metal mining activity adjacent to marine estuarine systems. In this two-year study in December 2014 and 2015, 40 surface marine sediment samples were collected in the coastal fjord region of Nootka Sound, including Tahsis and Zeballos Inlets. Each sample was analyzed for grain size, loss on ignition (LOI), and concentrations of 22 different metals. Principal Components Analysis (PCA) revealed distinct patterns of co-variation between metals. Two major groupings of variables were created by the first two principal component axes, and they were deemed Type I (D50, OC%, Ca, B, Si, S, Na, and K) and Type II (Cu, Cr, Ni, Pb, Mo, Mg, Cd, Se, Al, and Fe) variables. The Type I variables were concluded to be marine derived elements, while Type II showed an anthropogenic and terrigenous influence. Higher heavy metal concentrations were observed in marine sediments close to river mouths in Zeballos and Tahsis Inlets. These enrichments are attributed to local mining activities, physical transport via currents and landslide deposition

Introduction

Metal contaminants, especially in marine sediments, pose a great threat to marine biota and can ultimately bio-accumulate in the higher trophic levels of a fjord community (Bryan 1992, Buggy 2008). These metals are an important topic of research as some metals, including arsenic and mercury, have been proven to be toxic to organisms in the marine environment (Bryan 2009). Mining activity on land within the watershed of a given region can result in runoff and sediments containing metal entering the estuary. As metals enter the estuarine system, they bind to suspended sediment and eventually settle on the seafloor.

Nootka Sound, British Columbia, Canada, is an area of known metal mining activity adjacent to marine estuarine systems. This study will evaluate metal 'hotspot' regions while tracing metal concentrations in the surface sediments of Tahsis, Zeballos, and Esperanza Inlets in the coastal fjord region in the vicinity of Nootka Sound.

Tahsis Inlet (39 km in length), Zeballos Inlet (25 km), and Esperanza Inlet (11 km) are a series of fjords on the western coast of Vancouver Island, British Columbia. Tahsis Inlet is characterized as steep-walled and narrow (1.2 km mean width), with an average depth of 135 m, a sidewall river delta at the mouth of the Tsowwin River, and two rivers (Tahsis and Leiner) at its head (Fig. 1) (Tully, 1937; Dodimead, 1984; Kasper, 1992). The sidewall river delta coincides with a mid-inlet sill with a depth of 57 m, and the mouth of the inlet has a sill depth of 50 m where it joins Nootka Sound. Nootka Sound in turn has a sill with a depth of ~40 m at its terminus with the northeast Pacific Ocean (Pickard, 1963). The narrow (~0.3 – 0.4 km wide) Hecate Channel (Google Earth

measurement) on the northwest side of the fjord leads to Zeballos Inlet and Esperanza Inlet beyond.

Zeballos Inlet is also considered narrow (mean width of 1.5 km) with an average depth of 195 m (Pickard, 1963). It has two rivers (Zeballos and Little Zeballos) that discharge into the northern section of the inlet (Fig 2). Zeballos Inlet drains into Tahsis Inlet via Hecate Channel to the east, and Esperanza Inlet to the west. Esperanza Inlet is ultimately discharged into the Pacific Ocean on the western side of Vancouver Island, British Columbia.

The nearby source and fluvial transport of metals results in a near ideal framework for this type of study. By studying fjords in particular, there is an opportunity to study anthropogenic and terrigenous inputs, due to their large coastal area and proximity to mining, logging, and industrial activities. The source of metals into Zeballos Inlet is the well-documented mining activity in the Zeballos River watershed, where there are over 15 historical gold and copper mines (Stevenson, 1950). The metals are transported to the fjords from mine discharges or leaching from tailing piles associated with the mines. The metals, once mobilized into the environment, are transported through fluvial processes to the inlets and deposited on the floor of the fjords (Wilson 2008).

Historically, the correlation between organic carbon and metals in surface sediment has been well studied (Balistrieri and Murray, 1986; Tam and Wong, 2000; Buggy and Tobin, 2008; Hoff et. al., 2014). Organic composition grain size, and surface area of sediments can have a variety of complex effects on the concentration of metals in sediment. However, since these factors are also correlated, it is often difficult to

differentiate primary causes of grain size or organic content to metal concentration patterns (Emerson and Hedges, 1988; Zonta et. al., 1994; Hedges and Keil, 1995; Wang, 2000; Lin et. al., 2002). In addition, it is imperative to monitor deep-water oxygen levels, as oxygen concentrations are important for the reduction of metals (Calvert and Pedersen, 1993; Crusius et. al., 1996; Morford and Emerson, 1999).

The goal of this study is to expand on the knowledge of this region and, in particular, increase the understanding of metal transport and accumulation in marine sediments. The study allows for relating metal occurrences in marine sediments to mining activity on land. The amount of metals in the marine sediment may allow us to predict their impact on the ecological community, which may influence future regulations of mining activity in the region, and elsewhere. This study tracks the spatial distribution of grain size, organic carbon, and concentrations of 22 different metals along the length of Zeballos and Tahsis Inlets, in addition to parts of Esperanza Inlet and areas more distal to mining activity.

Methods

Study Area

Sampling took place in Zeballos, Esperanza, and Tahsis Inlets, B.C., around 49^{o} N and 126^{o} W, on December 16-17, 2014, and again on December 12-18, 2015. In the inlets, aside from samples collected at the mouths of the four rivers (Tsowwin, Leiner, Zeballos, and Little Zeballos), surface sediments were collected near the centerline of the channel. The stations to the north and south of Tsowwin Narrows were spaced approximately 1.5 km apart, and those within Tsowwin Narrows were spaced about 0.25

km apart (Fig. 1). In Zeballos Inlet, eight samples were taken: one from the mouth of the Zeballos and Little Zeballos rivers, and six from a transect down the inlet towards Hecate Channel. Only one sample was taken Esperanza Inlet due to timing and sampling constraints on the 2015 cruise. Three end-member stations were selected in 2015 to compare their metal concentrations to those closer to the mining source. In total, 40 samples were taken over the two years of this study.

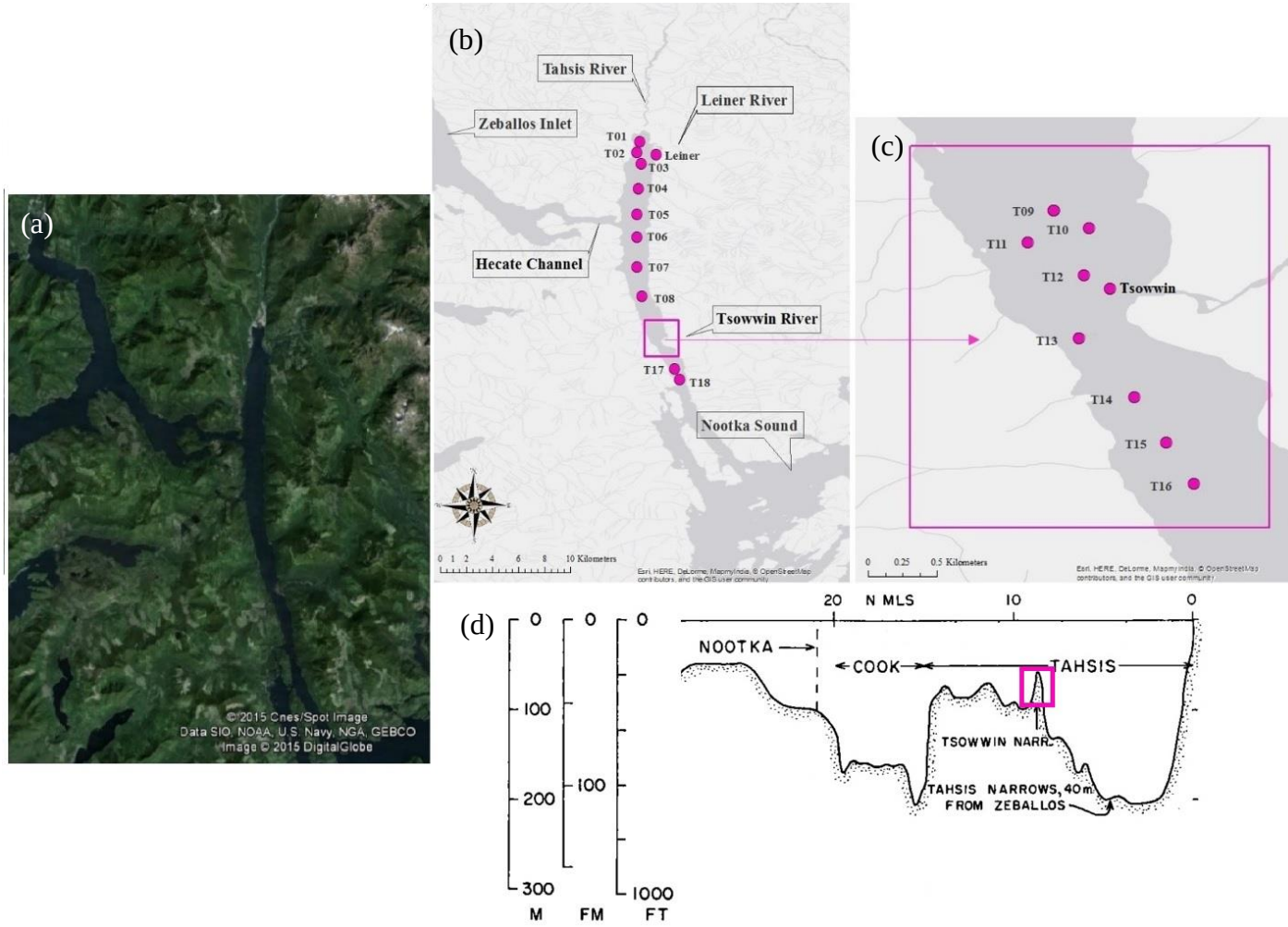


Figure 1. A map of all of the 2014 sampling sites in Tahsis Inlet. (a) is a Google Earth image of the area for a better visual of the relief, (b) is a wide view of the inlet and surrounding bodies of water, (c) is a close-up of the stations in the Tsowwin Narrows, and (d) is a modified figure from Pickard (1963) to show the bathymetry of Tahsis Inlet. The pink box corresponds to the pink box over the Tsowwin Narrows in (b). It should be noted in (d) that Tahsis Narrows is part of Hecate Channel, and Cook Channel is the side channel to the direct entrance to Nootka Sound from Tahsis. The southern end of Tahsis

Inlet connects to Nootka Sound. The Tsowwin Narrows stations were spaced closer than the northern and southern stations.

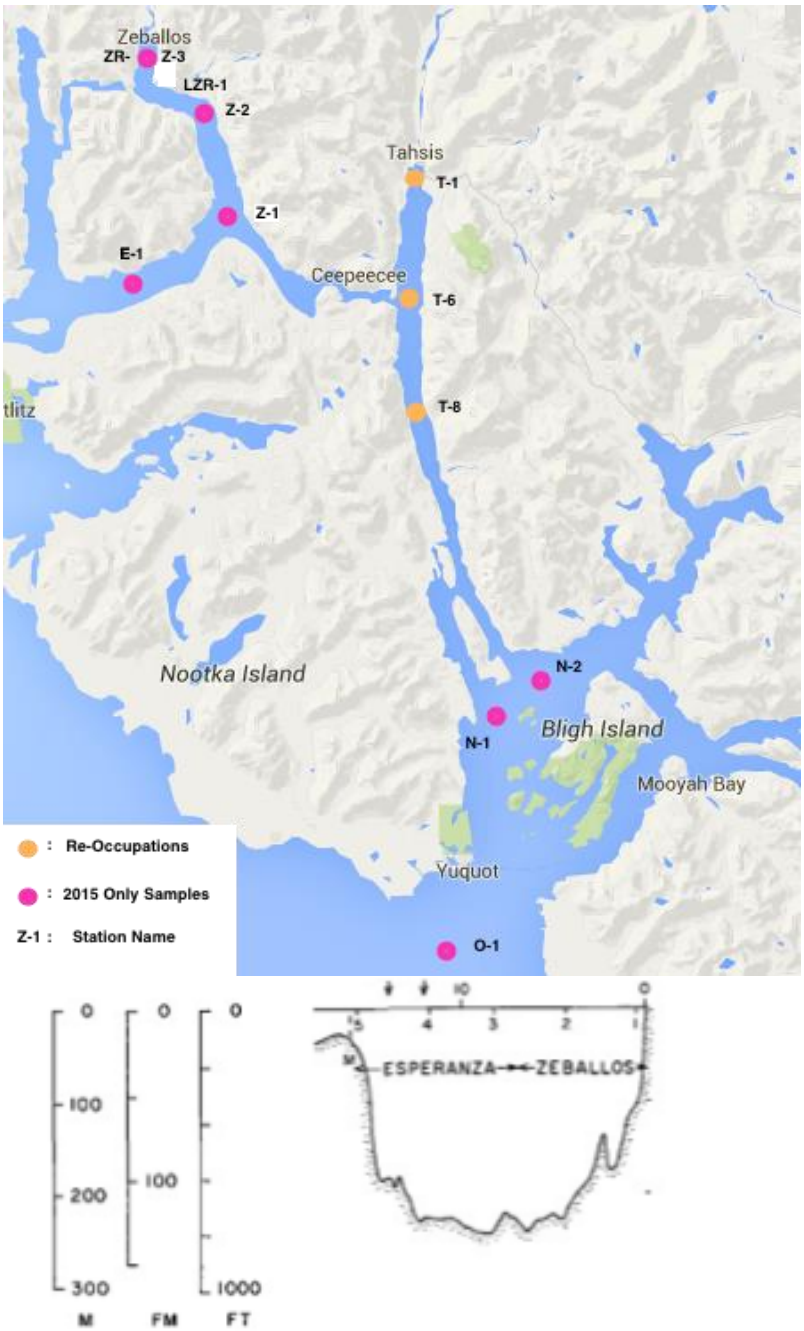


Figure 2. A map of all of the 2015 sampling sites in Tahsis, Zeballos, and Esperanza Inlets. The three stations in Tahsis Inlet were re-occupations of the 2014 samples taken. Two samples were taken outside the drainage of Tahsis Inlet into Nootka Sound, along with one outside Nootka Sound. (Top) is a Google Maps image of the area for a better visual of the relief, (bottom) is a modified figure from Pickard (1963) to show the bathymetry of Zeballos and Esperanza Inlets.

Sampling Methods

Over the course of this two-year study, 40 surface sediment samples were collected using Van Veen and Shipek grabs. In 2015, all of samples were taken using the Shipek grab. However, in 2014, the Van Veen grab was used on stations T09-T16 due to the coarseness of sediment. Stations T01-T08 and T17, T18 were characterized by fine-grained muds that resulted in over-penetration of the Van Veen grab and sample wash-out during recovery, necessitating the use of the Shipek grab. "Leiner", "Tsowwin", ZR-1, and LZR-1 were samples from the mouth of rivers, and these were collected from a small boat with a hand-held Van Veen grab. Once on board, the top ~5 cm of sediment was scooped off the top of the sampler with a trowel or measuring cup and placed into Whirlpak bags, with subsequent storage at 4^{o} C.

Analysis of Metals

A ~150 g aliquot of each surface sediment sample was oven-dried at 60 - 70^{o} 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. Following ^{7}Be analysis, 1-2 g of sediment was digested in acids to liberate metals according to the EPA 3050B (1996) method. Sediment digests were analyzed for a suite of 22 metals (Ag, Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, Zn) using Inductively Coupled Argon Plasma Mass Spectrometry (Thermo Scientific Model 61E ICP-MS).

Grain Size Analysis

Grain size analysis was based on the U.S. Geological Survey publication on sediment grain size analysis procedures (Poppe et. al., 2000). Briefly, each sediment sample was homogenized and 20-30 g subsamples were removed for grain size analysis. Sediments were stripped of organic matter with 15 mL of 30% hydrogen peroxide then wet-sieved through a 63 µm filter to separate silts and clays from coarser particles. The >63-µm fraction was then oven dried at 60^{o} C and shaken through a nest of sieves, starting at -4$^{\phi}$ (pebbles), and proceeding by 0.5$^{\phi}$ increments until +4$^{\phi}$ (63 µm, sand/silt boundary). Each size fraction was weighed and characteristics of the sample, such as shell and wood content, were approximated as a volume percentage. At stations N-1, N-2, Z-1, Z-3, T-1-T-8, T-23, and T-24, where the sediment consisted primarily of mud, the <63 µm fraction was further size-fractionated with a pipette-based settling technique (2014 samples) (Poppe et. al., 2000) or fractioned using a SediGraph (2015 samples). At the Tsowwin Narrows stations, Z-2, ZR-1, LZR-1, and O-1, where sediment was composed of sand and gravel, the fine (silt/clay) portion (> +4$^{\phi}$) was dried and weighed without further size distribution analysis. GRADISTAT software and MATLAB scripts were used to calculate the D50 (median) grain size and the sorting of each sample (Blott and Pye, 2001)

Loss on Ignition Analysis

Organic carbon content was evaluated by loss on ignition (LOI). Widely accepted as a proxy for organic carbon concentration (Dean, 1974), LOI results are reported as weight-% organic carbon (OC%). Approximately 1 g of dried and crushed sediment was

placed into a 16 mL glass sample bottle, and all of the bottles were wrapped together as one package in aluminum foil and baked for 12 hours in a VWR lab oven at 400^{o} C. These samples were then weighed again (Schumacher, 2002). The LOI was calculated as the percentage of mass lost from the total sub-sample.

Exposure time, temperature, and placement of each sample within the oven can influence LOI (Heiri et. al., 2001). To minimize error in the LOI measurements, this study followed a procedure of lower exposure temperature (some studies use 500 – 550^{o} C for a fraction of the time) for a longer time. This procedure could cause an underestimation of OC% because the temperature may not have been hot enough to oxidize all of the organic carbon, but because we increased the exposure time following the procedures of Schumacher (2002), the error is likely the same as a high temperature, fast bake procedure. Also, the oven used in this procedure was very small, and the beakers were contained within a small area on the same level. Therefore, the LOI error is minimal and negligible as long as small differences in OC% between samples is disregarded (Heiri et. al., 2001).

Principal Component Analysis

The metals, organic carbon, and grain size data were analyzed using Principal Components Analysis (PCA) in order to identify linear covariance across multiple dimensions (Culman et. al., 2008). Owing to the large range of concentrations, the data were standardized by standard deviation of each metal across sample stations before applying PCA using PC-ORD software (2014) and MATLAB scripts (2015) with the Variance/Covariance (centered) option in variables space (McCune and Mefford, 2006).

Separate analyses were run with different programs to eliminate a bias in the PCA method.

Results

The PCA of D50, metals, and OC (%) data revealed a covariance between D50, OC%, Ca, B, Si, S, Na, and K, here referred to as Type I variables. The Type II variables were comprised of Cu, Cr, Ni, Pb, Mo, Mg, Cd, Se, Al, and Fe (Fig. 3). Parameters that did not plot within the Type I or Type II clusters were: Ba, Zn, As, P, and Mn (%OC in the case of the 2015 PCA). In the 2014 PCA, the outlying parameters were all negative on Axis 2 whereas in the 2015 PCA these anomalies were explained by variance in Axis 1. In 2014, most of the other variables were positive or slightly less than zero on Axis 2. In 2015, Type I variables were negative on Axis 2 and Type II variables were positive on Axis 2, but showed the same trends and groupings of the Type I and Type II metals seen in 2014 (Fig. 3).

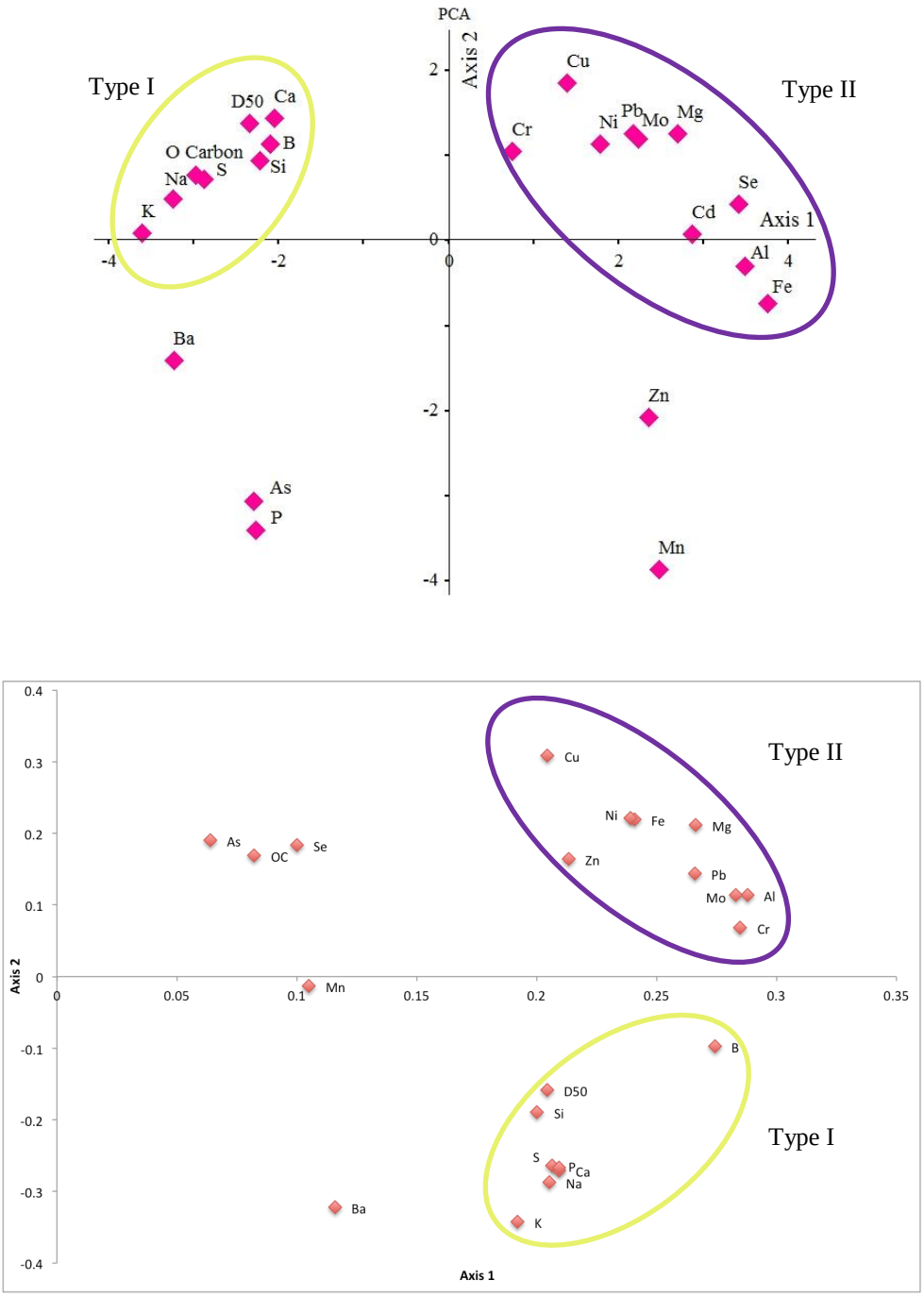


Figure 3: The graphical results of the PCA's, (2014 on top, 2015 on bottom) plotted on Axis 1 and 2. The data tended to group itself into two variables, named Type I and Type II. The outliers, Ba, Zn, As, P, and Mn.

In 2014, Axis 1 explained 55% of the variance, and Axis 2 explained 22% of the variance within the entire dataset. In 2015, Axis 1 explained 46% of the variance, and Axis 2 explained 21% of the data set's variance. With just 6% and 8% of the variance

explained by Axis 3 in 2014 and 2015, respectively, its significance was not further explored.

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 40 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 $\mu g\ g^{-1}$). 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 may have resulted from sub-sampling the coarse fraction of an inhomogeneous sediment sample. In the third attempt at measuring As in the Tsowwin River sample the sediment was sieved through 63 and 500 µm screens, and separate fine (>+4ϕ) and coarse fractions (+1ϕ) were 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, confirming our hypothesis.

In total, 11 of 29 stations came back with detectable arsenic ($\geq .056\ \mu g\ g^{-1}$) (Fig. 4). This value is sufficiently close to 0 that it was deemed negligible in comparison to the As concentrations at stations where As was 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. Ten stations in Tahsis Inlet had elevated arsenic concentrations of ~10-18 ppm. However, the highest concentration of arsenic was found at the northernmost station in Zeballos Inlet (85.7 ppm), closest to the mining source.

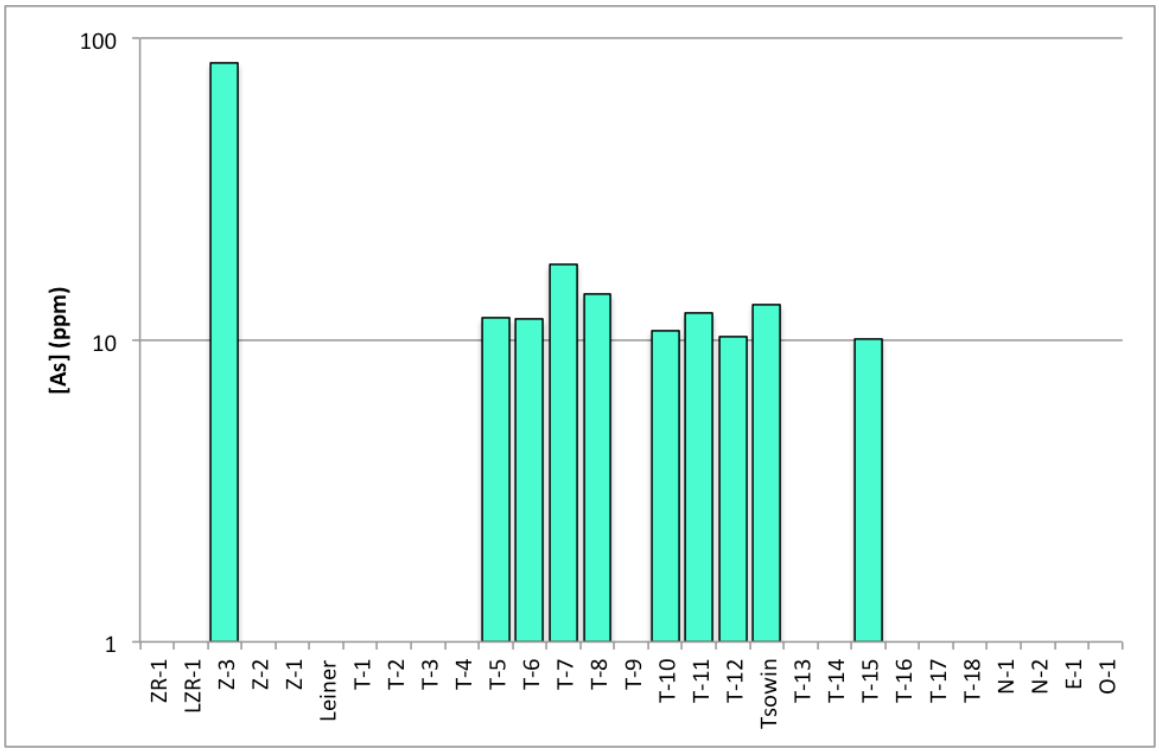


Figure 4 - Arsenic concentrations along the transect of stations. Arsenic is plotted in parts per million (ppm). The y-axis is plotted on a log-scale to make the detection limit clearer, and to not skew the graph with the high concentration seen in Z-3.

D50 and OC (%) were highly correlated (Fig. 5a, b). The notable differences in the two trends are the Leiner, Tsowwin, N-1, and N-2 stations. At stations N-1 and N-2 the OC (%) is similar to nearby stations (Fig. 5B), but D50 values of 11ϕ indicate the finest sediments of all 29 stations in the Nootka-Esperanza fjords (Fig. 5A). In the case of the Leiner and Tsowwin stations, while the D50 at these stations remains close to that at other stations, the OC (%) plummets from high values of organic carbon (~10-15%) to near zero at these two stations. Both D50 and OC (%) display an unusual point in the Tsowwin Narrows at station T11. The high OC (%) and fine D50 were dissimilar to nearby stations. Yet, they are similar to other stations within Tahsis Inlet, specifically stations T-3 through T-8.

Overall, OC (%) in general is much greater in comparison to the organic carbon contents generally observed in fjord surface sediments (Seiter et. al., 2004; Smith et. al.,

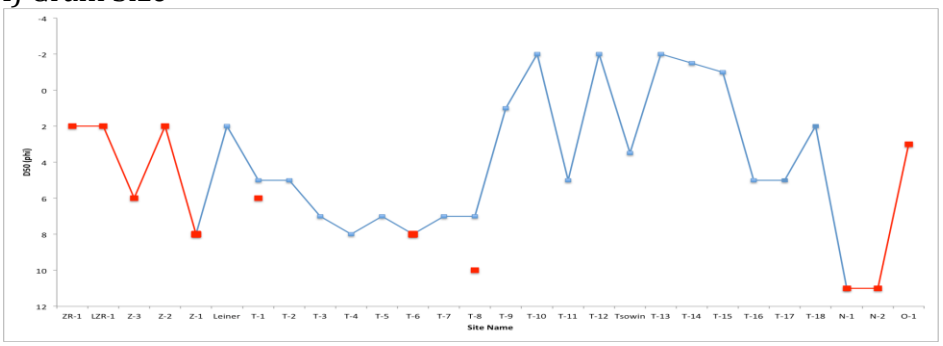
2015). However, It is unlikely that these values are a measurement error due to the additional observation that when stripping the samples of organic matter during the grain size analysis procedures, the addition of 30% hydrogen peroxide yielded an explosive reaction in samples with >10% organic carbon content. This caused loss of material from samples T16 and T17 that were subsequently repeated.

Three sources of uncertainty are considered to be important in the grain size analyses: 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, hair and clothing may have generated static electricity. The negative values from the pipette analysis of this study never exceeded -0.5 g, and therefore, these values were considered 0 in the calculations of the D50. Since most of the weights of each size fraction exceeded 1 g, this was considered to be a minor source of error.

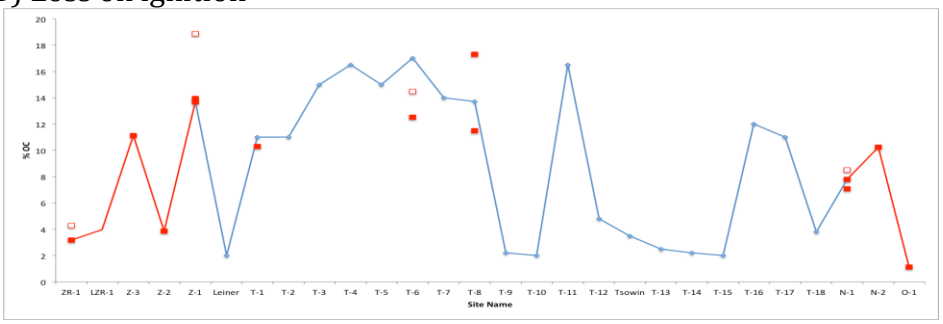
For ease of visualization, one metal was selected from each of the Type I and Type II metals to serve as a proxy for that Type. For the Type I metals, potassium was used, and for the Type II metals, the proxy was molybdenum (Fig. 5c, d). There is a greater variability within Type I, where the general trend is: low at the northern end of Zeballos and the head of the two rivers, with an increase as you move toward Hecate Channel. Continuing the trend, low concentrations (~1220-1270 ppm K) were observed at the northern end of Tahsis Inlet, a drastic increase until T08, then a general low

concentration at the Tsowwin Narrows (the exception being T11), and finally a parabolic arc for the southern stations in Tahsis. The Nootka Sound stations showed very high concentrations (~3400-4000 ppm K) and decreased dramatically once you enter the open ocean to the station outside Nootka Sound. The Type II metals are less variable and follow the general trend of mid- to high-ranged concentrations at the northernmost station in Zeballos inlet, followed by a slow, but steady decrease heading south in Zeballos Inlet. High Mo (Type II) concentrations near 60 ppm at the northern end of Tahsis Inlet gradually declined to about 40 ppm at stations T-9 through T-12, and declining to about 30 ppm in the southern basin of Tahsis Inlet,

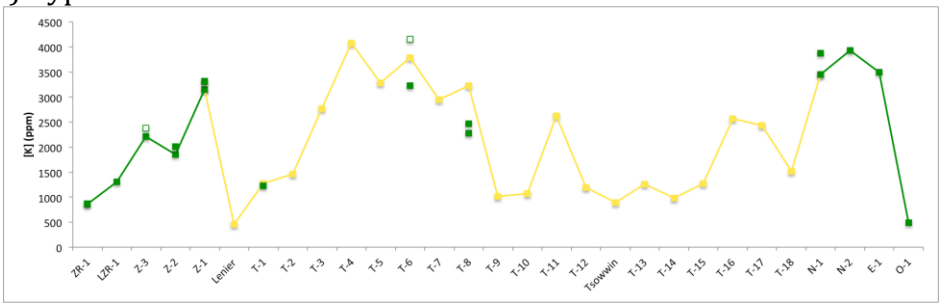
A) Grain Size



B) Loss on ignition



C) Type I



D) Type II

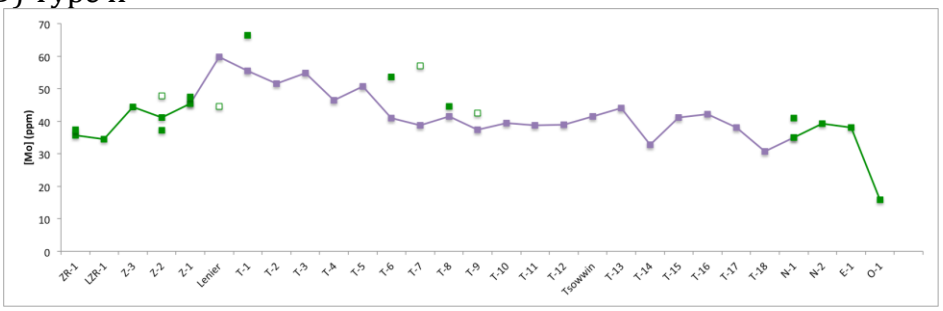


Figure 5: The D50 (a) and OC (%) (b) plotted along a transect of the stations from North to South. The average range of OC (%) in fjords has been plotted on (b) (Smith et. al., 2015). The transects of the two major types of metals, using K as a proxy for Type I (c) and Mo for Type II (d). Things to note: in plots A and B, blue lines indicated samples taken in 2014 whereas red lines show 2015 samples. For the metals plots, yellow (K) and purple (Mo) indicate 2014 samples, while green lines show data from 2015.

The calculation of an enrichment factor can be useful for studying the elevation of a metal's concentration in comparison to a reference value (Huang and Lin, 2003; Delgado et. al., 2010). Often the average concentration in shale is used as the reference in continental rocks and sediments (Pastorinho et. al., 2012). For this study, each metal concentration was normalized to aluminum. The reference concentrations for shale were taken from Turekian and Wedepohl (1961). The enrichment factor was calculated using the following equation:

$$EF = ([Metal]/Al)_{sample}/([Metal]/Al)_{shale} \quad (1)$$

Results for each metal at each station are tabulated in the Appendix. Average EFs for Tahsis and Zeballos Inlets were calculated to assess metal enrichments or depletions in those fjords (Fig. 6). While Delgado et al (2010) considered an enrichment ≥ 2 to be a highly enriched element, that study had more accurate background values for the region and thus did not use the Turekian and Wedepohl's (1961) reference concentrations. For this study, the following classifications were used by way of adapting Delgado et al (2010) to these results. Shown are the average enrichment factors for our study:

(1) Enrichment factor ≤ 1: poorly enriched **(K, Ba, Si)**

(2) Enrichment factor 1 ≤ EF ≤ 5: slightly enriched **(Ca, Cr, Fe, Mn, Ni, Zn, As)**

(3) Enrichment factor ≥ 5: strongly enriched element **(B, Cd, Cu, Mg, Mo, Na, P, Pb, S, Se)**

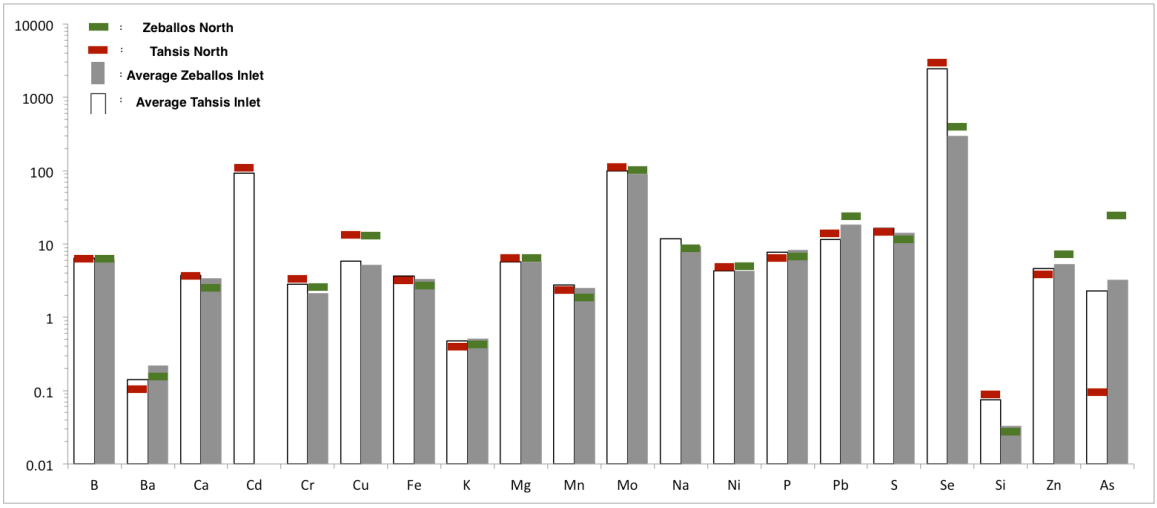


Figure 6: The average enrichment factors of each metal in Tahsis and Zeballos Inlets, using the average values in shale (Turekian and Wedepohl, 1961). The y-axis is on a log scale. The data includes 2014 and 2015 combined dataset of enrichment factors. The red colored bars indicate the northernmost stations in Tahsis Inlet (T-1-T4) in the, while the green bars show the northernmost stations in Zeballos Inlet (Z-3). The clear bars show the average concentration throughout Tahsis Inlet, while the grey bars show average concentration throughout Zeballos Inlet.

Discussion

Metals, grain size, and organic carbon trends along the axis of fjords like Tahsis and Zeballos Inlets offer a unique perspective into the source, fate and transport of lithogenic and anthropogenic material in the coastal zone. Below we propose that the Type I metals have a marine origin and the Type II metals have an anthropogenic and terrigenous origin and use these results to trace the transport of leachates from mining activities in the Nootka and Esperanza Sound region.

Type I Metals

Because the Type I metals have such a large variability, they offer a good opportunity to understand sediment sources in Tahsis and Zeballos Inlets. It is likely that the cause of this variability is organic matter derived. $\delta^{13}C$ analyses of organic carbon in surface sediment along the fjord indicate that the sedimentary organic material near the mouth of the Hecate Channel (at the entrance to Zeballos Inlet) had a higher proportion

of marine organic matter than elsewhere in Tahsis Inlet, as evidenced by values near -23‰ compared to -25‰ to the north and south (Fig. 7) (Walsh et al, 2008). 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 to the south. In addition, there is a peak of Type I metals close to and inside Nootka Sound, where the salinity is high from being in direct contact with the open ocean, and made clear by the high $\delta^{13}C$ values of surface sediment organic carbon near Nootka Sound (e.g., in Muchalat Inlet; Fig. 7). The metals included in the Type I follow the trend of organic matter (Fig 5a). The Type I metals are highest where LOI is the greatest, suggesting that these metals are largely associated with organic matter in these sediments Likely, Zeballos Inlet is a source of sediment and salty bottom water containing high organic matter to Tahsis Inlet by way of Hecate Channel.

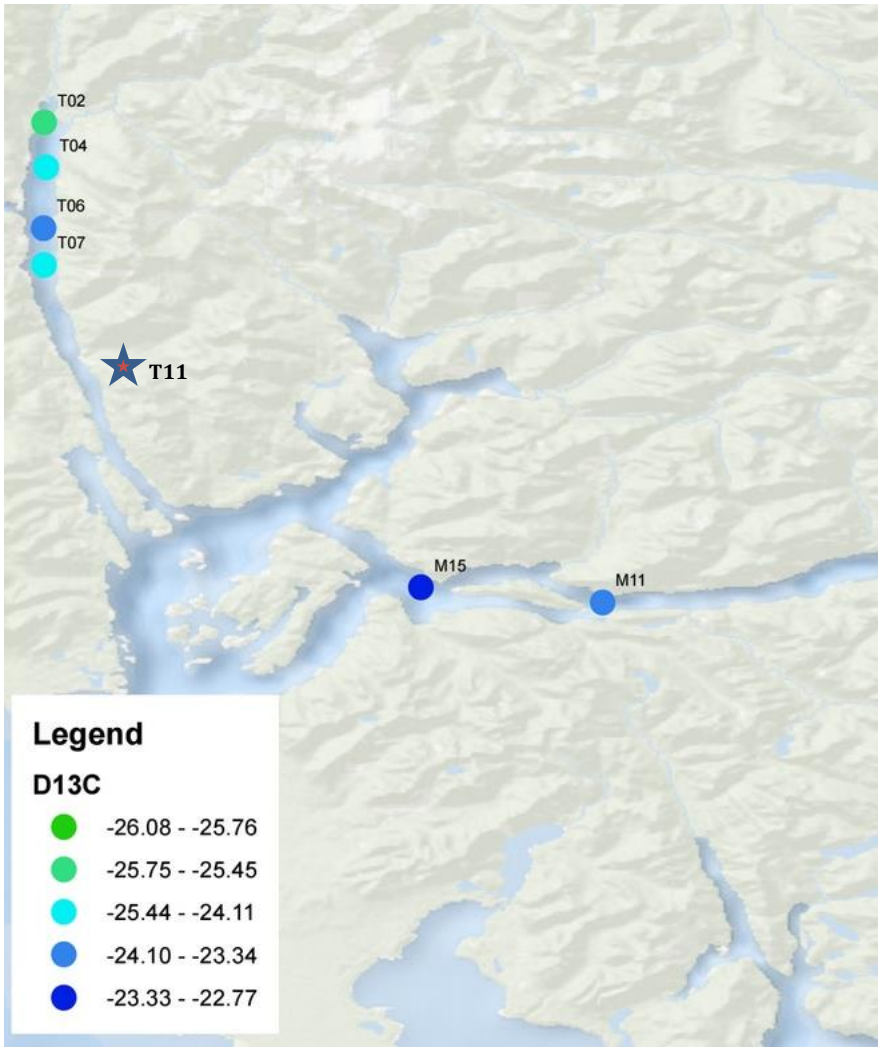


Figure 7. $\delta^{13}C$ values in Tahsis and Muchalat Inlets. This figure was obtained and not adapted from Trevor Harrison of the University of Washington (unpublished research). Lower values indicate higher marine organic source, and higher values indicate higher terrestrial organic source. In Tahsis 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 $\delta^{13}C$ 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 sediment sampler was recovering landslide debris. Logging activities are particularly prevalent in that area of Tahsis Inlet, and logging has been shown to promote a higher frequency of landslide events (Guthrie, 2002).

In addition, the T11 sample was estimated to be composed of ~80% woody material in the sandy grain sizes. Lastly, the surrounding hill slopes are predominantly carbonate rock (Alt and Hyndman, 1995), which would explain the prevalence of Type I metals such as Ca, Si, and K in the sample.

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 sorbed onto small sediment grains since the association of certain metals with fine grain size particles is well known (Tam and Wong, 2000; Lin et. al., 2002).

Countering that possibility is the apparent difference between D50, Type I metals and organic carbon content at the river stations. If grain size was the major controlling factor of Type I metals in Tahsis and Zeballos Inlets surface sediment rather than marine pore fluids or landslide input, the Type I metals and organic carbon content would be expected to peak near rivers where D50 declines. This was not observed in the river stations. This is most likely the result of riverine water lacking sea salt ions and significant landslide material. Certainly, grain size has a clear correlation with these metals, but that association may simply be an effect of the primary marine and landslide processes of introducing sediment into Tahsis Inlet.

Type II Metals

The Type II metals consist of some elements that are usually redox sensitive, and therefore, vary under different oxygen conditions. However, throughout Tahsis and Zeballos Inlets, these metals have similar ratios to aluminum, regardless of bottom

dissolved oxygen concentration. Jacobs et al (1985) studied the oxic to anoxic interface in an anoxic fjord in Norway and found that nickel was unaffected by the redox processes of cadmium, copper, and iron, but, in this study, the PCA analyses revealed a covariance between nickel and these elements. This is further evidence for the lack of redox effects on the Type II metals. Therefore, it is proposed that Type II metals such as Mo are derived from continental runoff and the transport of terrigenous sediments in Tahsis and Zeballos Inlets by surface and bottom current.

If Tahsis and Zeballos Inlets follow the classic estuarine circulation of most fjords, then the net transport of its bottom water, which controls the transport of sediment, will be toward the heads of the inlets; in the case of Tahsis and Zeballos, to the north (Pickrill, 1987). Type II metals are largely concentrated at the north of each inlet and generally decline in concentration toward the open ocean. Even if net bottom transport is to the north in Tahsis Inlet, metal-containing particles emanating from the Tsowwin River would still be influenced by periodic southward tidal currents that sweep them over the southern edge of the sill, where the prevailing northward bottom currents would trap them against the sill, explaining their peak concentrations just south of the sill and the Tsowwin river. With no sill in Zeballos inlet, an uninterrupted trend of southward decreasing metal concentrations was observed. The lowest concentrations of all Type II metals occur at the station furthest from the river mouths, and closest to the open ocean.

Arsenic and Mining

Arsenic concentrations in the stream sediments of Zeballos and Tahsis Inlets have been found to be anomalous in past studies (Bancroft, 1940; White and Chabot, 1981; Matsyek and Day, 1987; Houle, 2008; Shearer, 2013). Often, these are assessments of the gold and

mineral potential in these areas, and therefore, the arsenic anomalies are noted without further investigation. The arsenic levels reported here from the sediments within Tahsis and Zeballos Inlets are similarly anomalous (Fig. 4).

It seems likely that the bulk of the arsenic anomaly stems from the same mechanism driving the Type II metal distribution in the inlets, although it is not plotted in the same grouping in the PCA analyses. Arsenic concentrations are high in stations nearest the Zeballos mining source in addition to stations in Tahsis Inlet located near Hecate Channel and the Lenier River. However, arsenic was either present in high levels, or not present at all, which could affect its covariance with other Type II metals. Arsenic is extremely toxic, and it is present in consistently high levels in the surface sediments of Tahsis and Zeballos Inlets. The results of subsampling 5-10% of a sediment sample with a spatula for subsequent metals analysis compared to subsampling sieved and homogenized sediments revealed that analysis of random samples with a large portion of coarse grains made the ICP-MS procedure inaccurate for those samples. It is possible if not likely, that the stations without detectable arsenic (< 0.056 µg/g) actually contained non-negligible concentrations of arsenic. Future studies of metals, arsenic in particular, should consider sieving sediments before analysis of metals.

Arsenic has been an issue in Barkley Sound, where campgrounds in Toquaht were shut down after findings of high levels of arsenic, selenium, and cobalt in the soil and marina (B.C. News, 2013; Canadian Press, 2013). Barkley Sound is close to Tahsis Inlet, being just south of Nootka Sound on the western coast of Vancouver Island. The government of B.C. linked the heavy metal contamination at the Toquaht campgrounds to tailings from the Brynnor Mine which was active in the 1960s (B.C. News, 2013).

Because of concerns such as these, discovering the sources of arsenic in Tahsis and Zeballos Inlets sediment is clearly important.

Because the region north of Zeballos Inlet has been heavily mined for gold and copper in the past, among other metals (Yorath and Nasmith, 1995; Yorath, 2005) it is likely that a portion of the arsenic in Zeballos and Tahsis Inlets originate from these old mine tailings. Several reports of the mineral potential in that area show that there are arsenic veins within the same structures that contain the gold and copper (iMapBC) (Fig. 8)

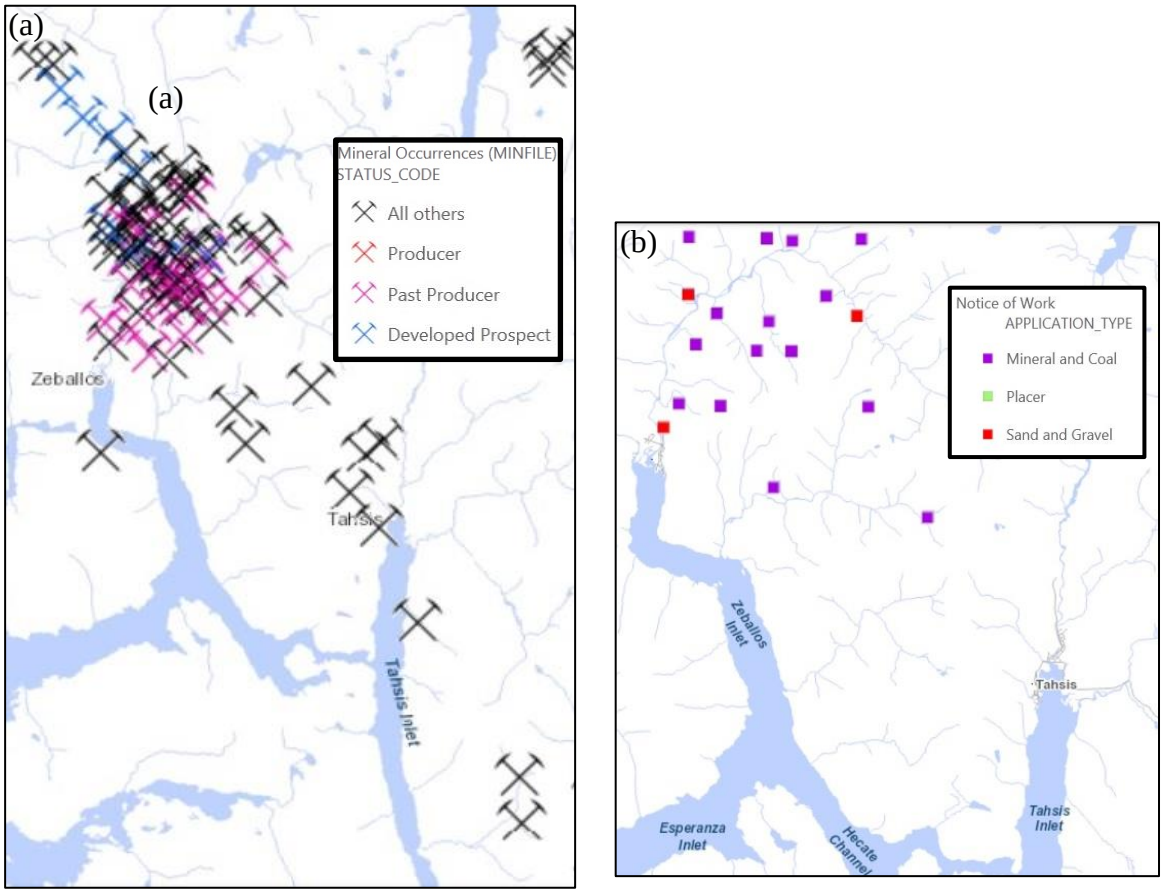


Figure 8. (a) A display of the Mineral Occurrences reports for currently producing mines, old mines, developed mines, and regions for which a study was done without mining involvement. (b) A map of the currently active mines and their type. Obtained from iMapBC, created by the Province of British Columbia.

Mining activity could be an alternative explanation for the elevated Type II metal concentration in the northern parts of Tahsis and Zeballos Inlets. Most of the Type II metals are found in association with the minerals being mined in the region. If the mining activity released these metals into ground or surface waters, they would reach Zeballos Inlet and be transported into northern Tahsis Inlet through Hecate Channel. Of all the Type II metals, copper makes the strongest case for this interpretation (Fig. 9). The copper mining in the area peaked approximately 80 years ago and has declined since then (Yorath and Nasmith, 1995; Yorath, 2005). Since sediment transport is a continuous process that happens over time, 80 years 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. It is important to note that copper concentrations were highest at the northernmost stations in both Tahsis and Zeballos inlet, shown by the two peaks in the transect (Fig 9). The three-reoccupation sites used from 2014 show that data collected in 2015 strongly correlates. In stations T-1, T-6, and T-8, copper concentrations are shown with both years of data. Site T-1, near the Leiner River, showed copper concentrations within two parts per million from 2014 to 2015 samples; T-6 and T-8 were within ten parts per million. Because the studies were done a year apart, this adds consistency to the idea that the Type II metals associated with mining are transported from Zeballos Inlet to Tahsis Inlet through Hecate Channel bottom water.

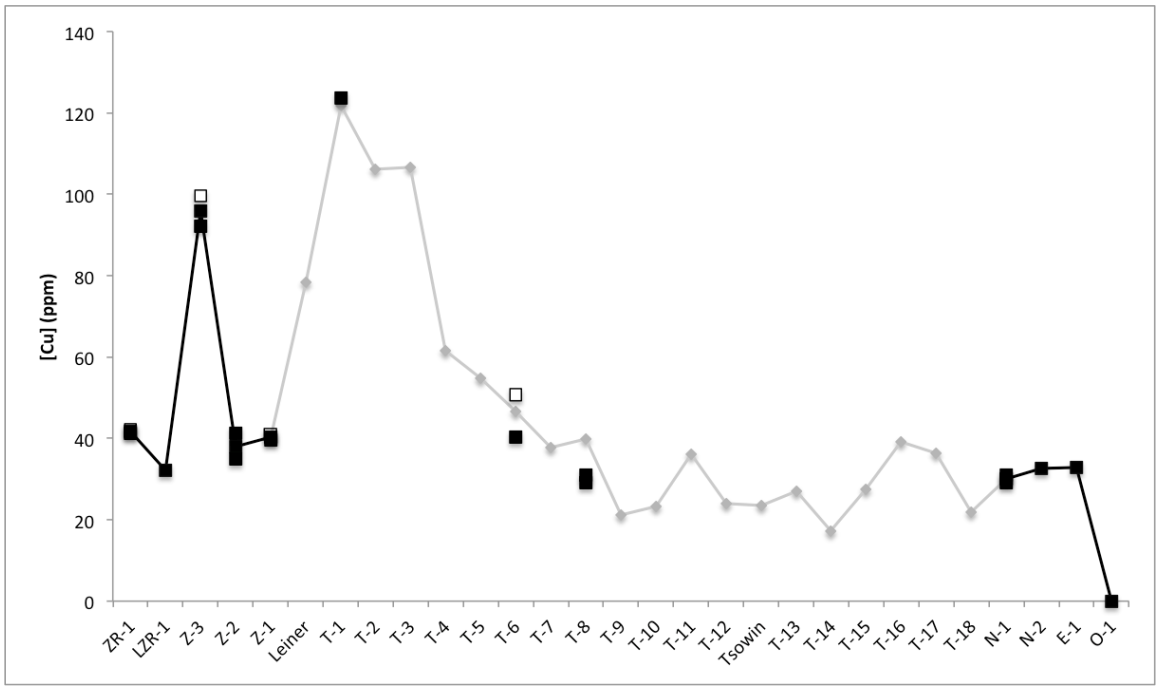


Figure 9. The transect of [Cu] down Tahsis and Zeballos Inlets. 2014 (grey) and 2015 (black) are shown. Black squares with no fill, like the ones in T-6 and Z-3, indicate washed samples. Values are highly elevated at the northern Tahsis, which could be an indicator of large input from Zeballos Inlet through Hecate Channel.

As seen with copper and other Type II metals (Fig. 5, Fig. 9), concentrations are low at the end-member sites including the two inside the Nootka Sound basin (N-1 and N-2) and the station outside of Nootka Sound (O-1). This rules out the notion that Type II metals could be entering from sources outside Tahsis Inlet and Nootka Sound. Instead, we suggest that various Type II metals are associated with mining activity in the Zeballos Inlet watershed region.

Two of the same metals that caused the campground to shut down in Barkley Sound, selenium and arsenic, are also enriched in Tahsis and Zeballos Inlets. Selenium, in particular, was enriched by a factor of more than 3000 in 2014. Cadmium, a highly toxic element that has been an issue for Canadian ecology, particularly in British Columbia, was enriched over 100-fold in Tahsis Inlet (Outridge et. al., 1994). Indeed, the

marine and estuarine sediments of Zeballos Inlet have been identified as an area of hazardous cadmium contamination, although cadmium was not present in samples in 2015 (Outridge et. al., 1994). Random sub-sampling and changes in the ICPM-S detection limits could be a possible reason why cadmium was not found in Zeballos inlet during this study. It is noteworthy that the cadmium anomaly in Tahsis Inlet is not associated with dissolved oxygen, as it often is elsewhere (Westerlund et. al., 1986). This leads to the probable conclusion that the high concentration of cadmium in Tahsis Inlet sediments are related to mining activity.

It should be noted that little is known about the concentrations of these metals in the surrounding rock. Until more accurate baseline concentrations of metals in the surrounding bedrock are found it is difficult to say for certain that the values we observe are indeed anomalous (Delgado et. al., 2010). But the elevated concentrations relative to average shale are reason enough to motivate further study of a potential environmental hazard.

In addition to monitoring metal concentrations in these fjords, supplementary assessments on the rivers in the Zeballos and Tahsis watersheds are warranted. Studies have shown that higher metal concentrations in streams can dramatically change the environment and alter the terrestrial-aquatic interactions of these systems (Kraus et al., 2016). High concentrations of heavy metals including copper, cadmium, and arsenic can lead to a shift in fish diet. As the concentration of heavy metals in streams increases, the amount of aquatic insects decreases (Kraus et al. 2016). This can lead to terrestrial insects ultimately subsidizing the fish's diet, which can lead to fewer insects for land animals like birds and bats. It is important to know if these shifts are occurring in the Zeballos and

Tahsis watershed's rivers, as it can have an impact on ecosystems downstream as well as inside the fjords.

Conclusions

Forty surface sediment samples were analyzed for organic carbon, grain size, and the concentration of 21 metals in Tahsis and Esperanza Inlet fjords, northwest Vancouver Island, Canada. Principal Components Analysis of these variables revealed two clusters named Type I and Type II variables. The Type I variables, D50, OC%, Ca, B, Si, S, Na, and K were the most abundant ions in seawater and therefore likely reflected organic matter transported through Zeballos Inlet.

The Type II metals consisted of Cu, Cr, Ni, Pb, Mo, Mg, Cd, Se, Al, and Fe. These redox-sensitive metals might have been expected to co-vary with bottom water oxygen concentrations in the intermittently suboxic or anoxic fjords. But no association between bottom water O_2 and Type II metals was observed in Tahsis Inlet. Instead we interpret the Type II metals as being largely derived from mine tailings in the Zeballos region.

Most notably, samples from the three reoccupations sites in Tahsis Inlet were nearly identical to those taken a year earlier. In the case of copper, one of the main metals previously mined, concentrations were within two parts per million. Because of this and the evidence for the importance of sediment and deep-water transport to northern Tahsis Inlet from Zeballos Inlet via Hecate Channel, tracking these metals are important as they may have hazardous effects to ecosystems in Tahsis and Zeballos Inlets. Arsenic, cadmium, and selenium were the clearest issues due to their high enrichment factors compared to average shale.

References

Alt, David; Hyndman, D. 1995. Northwest Exposures: A Geologic Story of the Northwest, Mountain Press Publishing Company.

Balistrieri, L. S., and J. W. Murray. 1986. The surface chemistry of sediments from the Panama Basin: The influence of Mn oxides on metal adsorption. Geochim. Cosmochim. Acta **50**: 2235–2243.

Bancroft, M. F. 1940. Zeballos mining district and vicinity, British Columbia.

Blott, S. J., and K. Pye. 2001. Gradistat: A grain size distribution and statistics package for the analysis of unconsolidated sediments. Earth Surf. Process. Landforms **26**: 1237–1248.

Bryan, G. W., and W. J. Langston. 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Environ. Pollut. **76**: 89–131.

Buggy, C. J., and J. M. Tobin. 2008. Seasonal and spatial distribution of metals in surface sediment of an urban estuary. Environ. Pollut. **155**: 308–319.

Caetano, M., and C. Vale. 2002. Retention of arsenic and phosphorus in iron-rich concretions of Tagus salt marshes. Mar. Chem. **79**: 261–271.

Calvert, S., and T. Pedersen. 1993. Geochemistry of Recent oxic and anoxic marine sediments: Implications for the geological record. Mar. Geol. **113**: 67–88.

Crusius, J., S. Calvert, T. Pedersen, and D. Sage. 1996. Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. Earth Planet. Sci. Lett. **145**: 65–78.

Culman, S. W., H. G. Gauch, C. B. Blackwood, and J. E. Thies. 2008. Analysis of T-RFLP data using analysis of variance and ordination methods: A comparative study. J. Microbiol. Methods **75**: 55–63.

Dodimead, A. J. 1984. A review of some aspects of the physical oceanography of the continental shelf and slope waters off the west coast of Vancouver Island. Can. Manuscr. Rep. Fish. Aquat. Sci. **1773**: 309 p.

Emerson, S., and J. I. Hedges. 1988. Processes controlling the organic carbon content of open ocean sediments. Paleoceanography **3**: 621.

EPA. 1996. Method 3050B: Acid Digestion of Sediments, Sludges, and Soils.

Guthrie, R. 2002. The effects of logging on frequency and distribution of landslides in three watersheds on Vancouver Island, British Columbia. Geomorphology **43**: 273–292.

Hedges, J. I., and R. G. Keil. 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis. Mar. Chem. **49**: 137–139.

Hoff, N. T., R. C. L. Figueira, and D. M. S. Abessa. 2014. Levels of metals, arsenic and phosphorus in sediments from two sectors of a Brazilian Marine Protected Area (Tupinambás Ecological Station). Mar. Pollut. Bull. **91**: 403–409.

Horowitz, A. 1985. A Primer on Trace Metal- Sediment Chemistry.

Houle, J. 2008. Summary Report on the Zeballos Property.

Huang, K. M., and S. Lin. 2003. Consequences and implication of heavy metal spatial variations in sediments of the Keelung River drainage basin, Taiwan. Chemosphere **53**: 1113–1121.

Jacobs, L., and S. Emerson. 1982. Trace metal solubility in an fjord. Earth Planet. Sci. Lett. **60**: 237–252.

Jacobs, L., S. Emerson, and J. Skei. 1985. Partitioning and transport of metals across the interface in a permanently anoxic basin: Framvaren Fjord, Norway. Geochim. Cosmochim. Acta **49**: 1433–1444.

Kasper, B. 1992. Geological and Geochemical Report on the VIG 6 Property.

Kraus, Johanna M., et al. "Aquatic pollution increases use of terrestrial prey subsidies by stream fish." *Journal of Applied Ecology* 53.1 (2016): 44-53.

Lin, S., I.-J. Hsieh, K.-M. Huang, and C.-H. Wang. 2002. Influence of the Yangtze River and grain size on the spatial variations of heavy metals and organic carbon in the East China Sea continental shelf sediments. Chem. Geol. **182**: 377–394.

Matysek, B. P. E., and S. J. Day. 1988. Geochemical Orientation Surveys: Northern Vancouver Island, Fieldwork and Preliminary Results.

McLaren, P. 1981. An interpretation of trends in grain size measures. J. Sediment. Petrol. **51**: 611–624.

McLaren, P., and D. Bowles. 1985. The effects of sediment transport on grain size distributions. J. Sediment. Petrol. **55**: 457–470.

Ministry of Citizen's Services and Open Government. 2013. iMapBC. Prov. Br. Columbia

Morford, J. L., and S. Emerson. 1999. The geochemistry of redox sensitive trace metals in sediments. Geochim. Cosmochim. Acta **63**: 1735–1750.

Ozturk, M. 1995. Trends of Trace-Metal (Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb) Distributions at the Oxic-Anoxic Interface and in Sulfidic Water of the Drammensfjord. Mar. Chem. **48**: 329–342.

Pelletier, E., and G. Canuel. 1988. Trace metals in surface sediment of the Saguenay Fjord, Canada. Mar. Pollut. Bull. **19**: 336–338.

Pickard, G. L. 1963. Oceanographic Characteristics of Inlets of Vancouver Island, British Columbia. J. Fish. Res. Board Canada **20**: 1109–1144.

Pickrill, R. 1987. Circulation and sedimentation of suspended particulate matter in New Zealand fjords. Mar. Geol. **74**: 21–39.

Pocklington, R., and J. D. Leonard. 1979. Terrigenous Organic Matter in Sediments of the St. Lawrence Estuary and the Saguenay Fjord. J. Fish. Res. Board Canada **36**: 1250–1255.

Poppe, L. J., A. H. Eliason, J. J. Fredericks, R. R. Rendigs, D. Blackwood, and C. F. Polloni. 2000. chapter1 @ pubs.usgs.gov. U.S. Geological Survey.

Pastorinho, M. R., T. C. Telfer, A. J. A. Nogueira, A. M. V. M. Soares, and J. F. Ranville. 2012. An evaluation of trace metal distribution, enrichment factors and risk in sediments of a coastal lagoon (Ria de Aveiro, Portugal). Environ. Earth Sci. **67**: 2043–2052.

Saulnier, I., and A. Mucci. 2000. Trace metal remobilization following the resuspension of estuarine sediments: Saguenay Fjord, Canada. Appl. Geochemistry **15**: 191–210.

Schropp, S. J., and H. L. Windom. 1988. A Guide To the Interpretation of Metal Concentrations in Estuarine Sediments.

Schumacher, B. A. 2002. Methods for the Determination of Total Organic Carbon in Soils and Sediments. Carbon N. Y. **32**: 25.

Seiter, K., C. Hensen, J. Schröter, and M. Zabel. 2004. Organic carbon content in surface sediments - Defining regional provinces. Deep. Res. Part I Oceanogr. Res. Pap. **51**: 2001–2026.

Shearer, J. T. 2013. Airphoto Interpretation Assessment Report on the Nootka Island Property.

Skei, J., and P. E. Paus. 1979. Surface metal enrichment and partitioning of metals in a dated sediment core from a Norwegian fjord. Geochim. Cosmochim. Acta **43**: 239–246.

Smith, R. W., T. S. Bianchi, M. Allison, C. Savage, and V. Galy. 2015. High rates of organic carbon burial in fjord sediments globally. Nat. Geosci. 1–5.

Soto-Jiménez, M., F. Páez-Osuna, and a. C. Ruiz-Fernández. 2003. Geochemical evidences of the anthropogenic alteration of trace metal composition of the sediments of Chiricahueto marsh (SE Gulf of California). Environ. Pollut. **125**: 423–432.

Stevenson, J. S. "Geology and Mineral Deposits of the Zeballos Mining Camp, 6. C. Ministry of." *Energy, Res., Miscellaneous Report. Mines& Pet. Res., Bull* 27 (1950).

Tam, N. F., and Y. S. Wong. 2000. Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. Environ. Pollut. **110**: 195–205.

Tully, J. P. 1937. Oceanography of Nootka Sound. J. Biol. Board Canada **3**: 43–69.

Turekian, K. K., and K. H. Wedepohl. 1961. Distribution of the elements in some major units of the Earth's crust. Geol. Soc. Am. Bull. **72**: 175–192.

Walsh, E., A. Ingalls, and R. Keil. 2008. Sources and transport of terrestrial organic matter in Vancouver Island fjords and the Vancouver-Washington Margin: A multiproxy approach using d 13Corg, Limnol. Oceanogr. **53**: 1054–1063.

Wang, F. 2000. Relation of sediment characteristics to trace metal concentrations: a statistical study. Water Res. **34**: 694–698.

Wilson, J., H. Schreier, and S. Brown 2008. "Arsenic in groundwater in the Surrey-Langley area." Fraser Health Authority.

White, G. D., and G. E. Chabot. 1981. Report on a Reconnaissance Geochemical Survey Conducted on the TAH 1 to 19 Claims.

Yorath, C. 2005. The Geology of Southern Vancouver Island, Harbour Publishing.

Yorath, C.J.; Nasmith, H. W. 1995. The Geology of Southern Vancouver Island: A Field Guide, ORCA Book Publishers.

Zonta, R., L. Zaggia, and E. Argese. 1994. Heavy metal and grain-size distributions in estuarine shallow water sediments of the Cona Marsh (Venice Lagoon, Italy). Sci. Total Environ. **151**: 19–28.

2013a. Toquaht Bay Marina Campground and Boat Launch Closed. B.C. News

2013b. Arsenic Shuts Campground and Marina Near Ucluelet, B.C. Can. Press