Regional Watershed Survey:

Nut Brook Drainage Basin, St. John's

Stream analysis of a river system in a local industrial zone

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Executive Summary

Nut Brook is a river system on the outskirts of St. John's that drains into the headwaters of the Kelligrews River further downstream. The system that makes up Nut Brook is heavily impacted by industrial activity midway along its path in an industrial zone just off the Foxtrap Access Road. A visual inspection of the area and testing of the water and sediment within the brook have been conducted to reveal the problems connected with the overall contamination and destruction of the river and its associated ecosystems. Through the analysis of the samples collected, the interpretation of the consequent results, and the comparison with a reference site, it was determined that the pollution occurring along the river was linked to the uncontrolled actions of the operations taking place on Incinerator Road. Many recommendations have been suggested regarding the proper management of this problem.

Acknowledgements

Many people and organisations were helpful in the making of this report. First and foremost, Diana Baird and Beni Malone of the NGO group Northeast Avalon ACAP (formerly St. John's Harbour ACAP) are the co-executive directors of the proponent organisation in the study (NAACAP). Without these people at the head of the group, this study would not have occurred. Thanks are also extended to Robert Trenholm at the Fisheries and Marine Institute in St. John's for helping to make it possible to carry out this project. A round of gratitude goes to those in the trace elements lab in the Department of Earth Sciences at Memorial University of Newfoundland, notably Pam King, and also to those who provided equipment and helped out in the labs at the Marine Institute, particularly Judy Perry. Additionally, the GC/MS analysis done by Art Cook at the Environment Canada water quality lab in Moncton was a big help and was much appreciated. An especially big thank-you goes to the Green Team of the Conservation Corps Newfoundland and Labrador (CCNL), who were of invaluable assistance in the field and also in the lab, and in particular Justin Dearing for his unique insight and photographic intuition. More appreciation and thanks go to those at Environment Canada who provided much advice and thought during the sampling and post-sampling periods, notably Glenn Worthman, and to Rondine Herla of Government Works and Services as well. Credit also goes to Environment Canada's support of the ACAP program and to the Science Linkage funding they kindly provided. Of significant mention, the citizen's group KEEP (Kelligrews Ecological Enhancement Program) in Conception Bay South gladly provided endless knowledge of the situation and location of certain problem areas on Nut Brook, and continue to be a much-valued resource of information on the Kelligrews River and its current situation. Credit and recognition go also to the Provincial Department of Environment and Conservation, Water Resources Division for advice and help received, and for the DEM image on page 2. Last, but not least, a gracious thank-you goes to the great lab analysis and usage rates offered by the Marine Institute and MUN Earth Sciences.

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1.0 Introduction

Like any major centre, St. John's and the surrounding townships are bustling with the regular urban and suburban activities associated with a metropolis. Residential, commercial, and industrial developments accommodate the growing populations and economies of the region. However, a close association between urban progress and environmental degradation is also a reality. People, plants, and wildlife rely on rivers, the natural pathways for which water is to travel across the land, but these waterways are very prone to becoming negatively affected by the very people who use them. For being such an active region of the province, anthropogenic forces are disturbing the rivers and streams that bleed through the local watersheds. Of particular note, a small but lengthy and important stream called Nut Brook has been identified on the outskirts of St. John's as a "brown zone" of industrial use, for it has felt the damaging effects caused by the needs of the people and businesses in the area.

The preservation and protection of Nut Brook is vital to all life that is dependent upon it. Trout, birds and ducks, frogs, and multitudes of aquatic insects have been observed in and around the river, as well as native plants of all types. The pollution of this river will have direct and indirect impacts on all of this flora and fauna. Additionally, the brook discharges into the Kelligrews River, which travels through a populated section of Conception Bay South. The Kelligrews River is not a drinking water source, but it is used recreationally for fishing and swimming. Contaminating Nut Brook will in turn have the potential to contaminate the Kelligrews River, which can cause harm to those who use it. Thus, strong measures have to be taken to determine the extent of pollution and its effects on the integrity of Nut Brook, and action must be put forth to prevent any further disgraces to this river system. The inspection of Nut Brook in this report is the most comprehensive and knowledgeable to date.

1.1 Scope

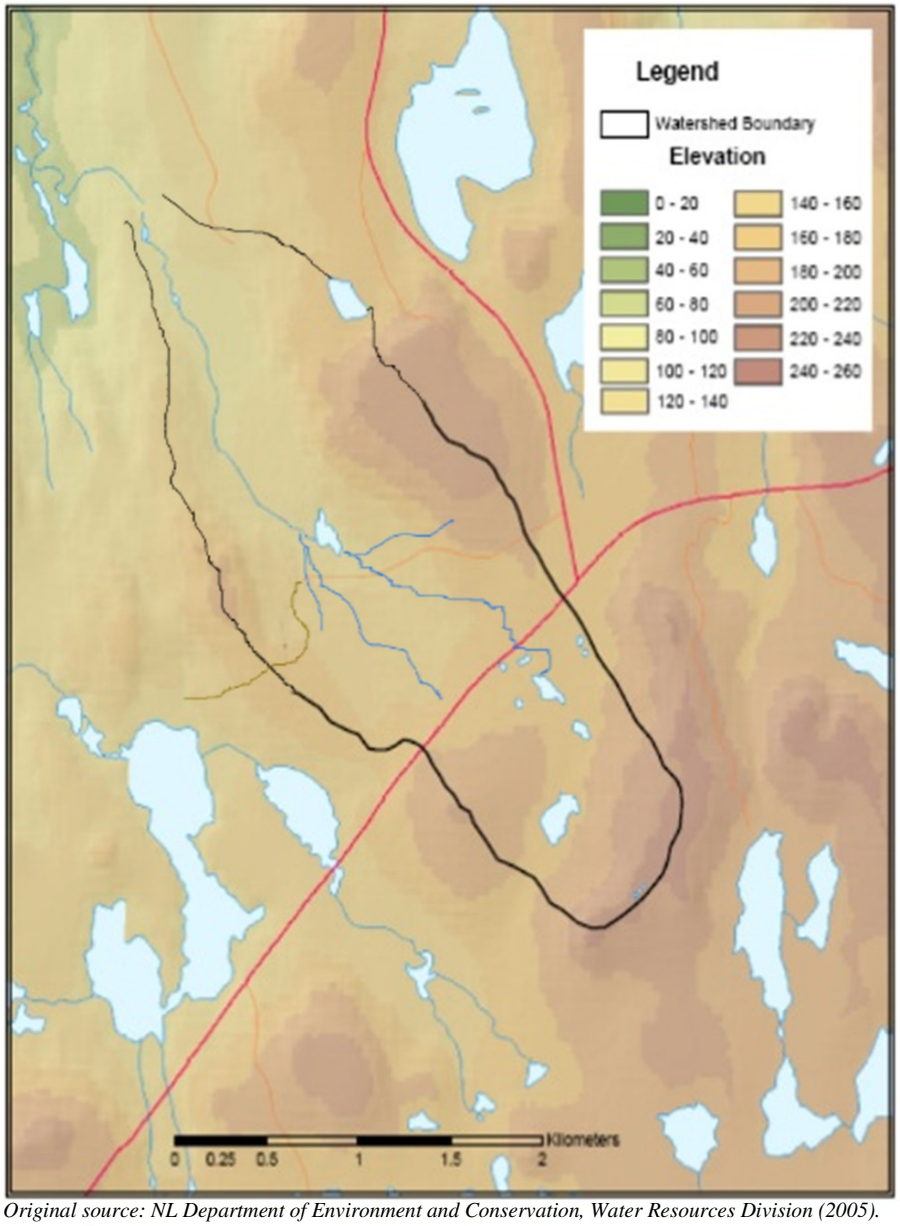
Initiated in 2005, this study focused on investigating the conditions at Nut Brook to essentially provide baseline information so that the problems could be understood and properly addressed. This involved the determination of what is or was contaminating Nut Brook; with what pollutants; by how much; and to what extent they had impacted the environment. In doing so, a detailed work plan was devised.

Preliminary research was first conducted to provide an understanding of the watershed; to find out what could be impacting the watershed; to learn about various contaminants that could affect it; to explore possible methods in field sampling and lab analysis; and to find out what resources were available to accomplish the overall goals of this project.

2.0 Study Area

2.0.1 Description of Watershed

Figure 1: *Digital Elevation Model (DEM) of Nut Brook drainage basin. Note that this diagram was modelled from an out of date topographic map, of which to date no updated versions exist. Due to this fact, not all features were included in the original image, thus the rest of Nut Brook and Incinerator Road, as well as the rest of the watershed outline, were subsequently added, as shown by the darker river and road line colours and lighter watershed boundary outline (Feb 28th, 2006).*



Original source: NL Department of Environment and Conservation, Water Resources Division (2005).

The Nut Brook drainage basin is located mainly within the western outskirts of the City of St. John's just off the Trans Canada Highway (TCH) and the Foxtrap Access Road. It lies within a narrow valley that makes up the watershed boundary and is roughly 0.5 – 1.5km wide at any given point (*Figure 1*). The valley is relatively flat, although its ridges to the east and west can have a slope of more than 20%. The height difference from the head to the mouth is about 100m. The brook flows northwest for about 3.5 – 4km, following the path of the valley and discharges into the headwaters of the Kelligrews River, which flows through a populated section of Conception Bay South and into the bay at Cronin's Head. Although Nut Brook has tributaries of its own, it would also be considered a major tributary of the larger Kelligrews River. This study, however, will only be looking at Nut Brook as its own system.

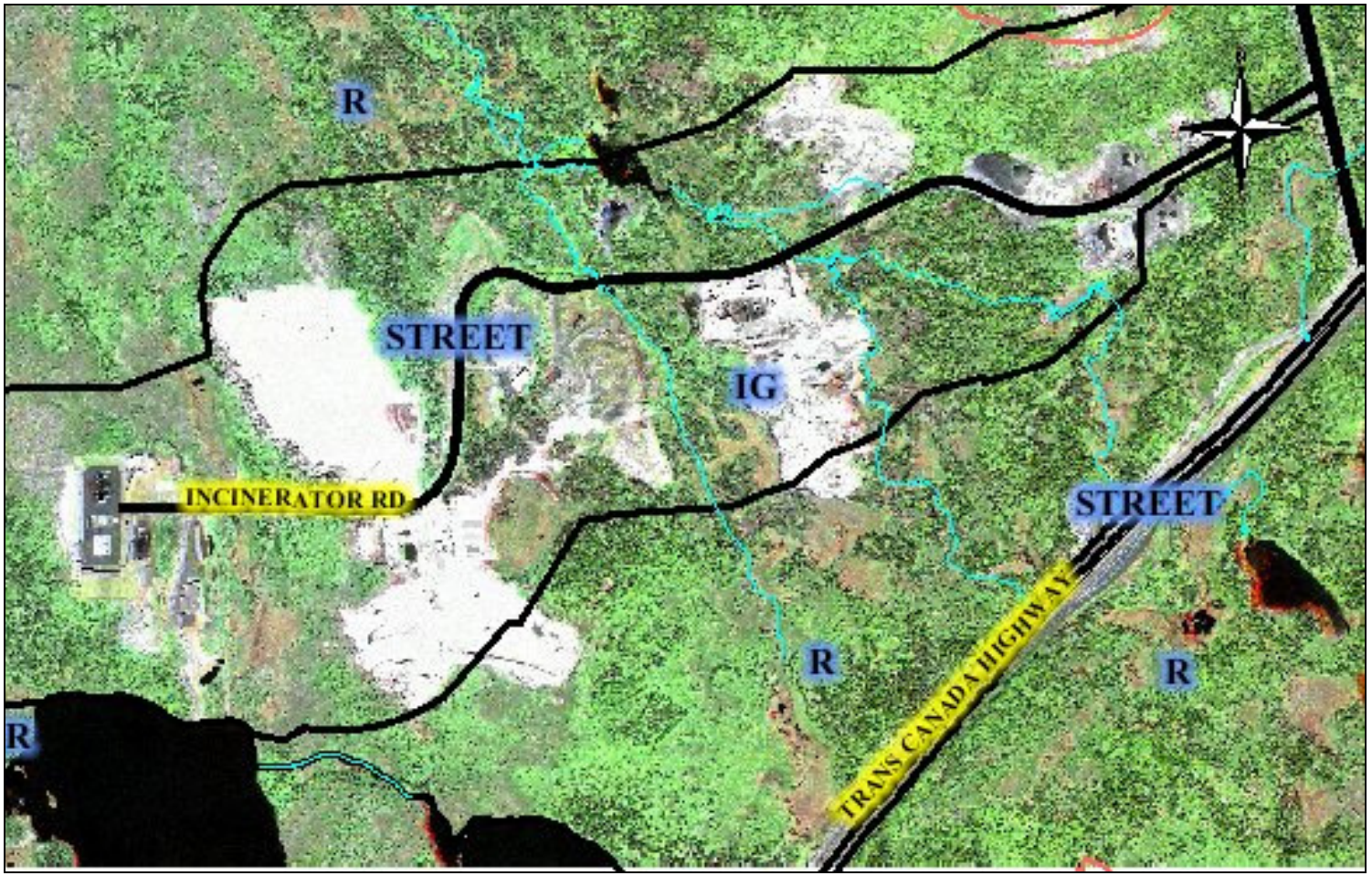
The headlands occur just south of the TCH, and are contained within the southern apex of the valley. The only input of water other than direct rainfall occurs as runoff from the valley ridges on all sides except north. These waters form a small system of shallow ponds, bogs, and fens that are somewhat forested as well. The brook that flows from it is shallow and is anywhere from 0.5 – 2.5m wide. This brook, that is Nut Brook, flows under the TCH just east of the Foxtrap weigh scales and winds through wetland and forested areas until it reaches Incinerator Road to the northwest, at which point it passes underneath and continues to flow through heavily vegetated terrain. Similarly, Nut Brook's own tributaries also follow a similar path and pass under Incinerator Road to the west. Just downstream, Nut Brook meets a small, dammed area after which it flows into an unnamed pond. For identification purposes, the pond was named Nut Brook Pond. The tributaries meet Nut Brook at a point about 75m west and downstream of the pond. From this point, Nut Brook travels northwest for the rest of its journey through wetland and heavy vegetation until it reaches the outflow of Sandy Pond at the headwaters of Kelligrews River.

2.0.2 Observations of Industrial Activity

Nut Brook and its watershed have been affected by current and past industrial activity on Incinerator Road. It has also been altered by the previous construction of the highway over it near the headwaters. The most significant sources of impact do occur as a result of the industrial undertakings on Incinerator Road.

Beginning in the east and heading west, the following activity had been observed on the 2km stretch of Incinerator Road: The Department of Works, Services, and Transportation, across the street from which is a salt depot; an inactive quarry to the west of this on the north side of the road; a septic waste handling facility on the south side of the road; an active quarry behind the waste handling facility; a rendering plant to the west on the north side of the road; the former site of a municipal landfill and tepee incinerator on the south side; another active quarry behind this; a hazardous waste holding facility to the west; the site of an old car wreck depository on the opposite side of the road; a large inactive quarry to the west of this; and a firefighter's training facility at the end of the road to the far west (*Figure 2*).

Figure 2: *Satellite image of Incinerator Road showing Nut Brook, its tributaries, the municipal zoning boundaries (R – rural, IG – industry general), the Trans Canada Highway, and any anthropogenic activity occurring in the region. Approximate scale: 1:17,000*



Source: City of St. John's website. http://www.stjohns.ca/access/maps/index.jsp, 2005.

It is safe to say that Nut Brook stood a serious chance of being affected by the types of activity that would occur with these sorts of operations. It should be noted, however, that the firefighter's training facility was located over a ridge and actually fell within a different watershed, thus its potential for having any sort of impact on Nut Brook was minimal to none, and therefore will not be considered here.

2.0.3 Discussion of Industrial Effects

Upon a visual inspection of the main study area, Nut Brook can be seen as a system that not only has changed due to the industrial development, but also one that is still being affected at a quick pace. For example, from Figure 2 it can be seen that some of the quarries had extended past the Industry General zoning boundaries and into the Rural zoning region. This was just one indicator of how quickly and haphazardly some of the industrial activity in the area is proceeding.

The first things to be viewed on Incinerator Road to the east were the rusting car wrecks inside the Department of Works, Services, and Transportation compound. While this probably does not affect the overall health of Nut Brook, it was an indicator of how the land in this part of the watershed is used.

Across the street, where the salt depot was located, large mounds of salt were piled outside the dome. Two problems arise with this: since salt is very soluble in water, it would be open to dissolution from the rain; and since the depot is actually on a ridge above Nut Brook, salty runoff could potentially contaminate the stream.

The next activities of concern are the quarries. Quarries are large undertakings that mine and process sediment and rock for building materials, such as silt, sand, or gravel. They can have devastating effects on the environment since vast areas of land are cleared and dug up to gain access to the usable materials underneath. In addition to leaving a permanent scar, one of the worst effects of quarrying is surface runoff and the accompanying soil erosion. In addition to the petroleum by-products created by the quarry machinery, various heavy and trace minerals are exposed and can also become a constituent of the runoff. Since the exposed material is generally granular and loosened, and any vegetation to hold it together is removed in the quarrying process, the potential for soil erosion and subsequent transport downstream is also great. If material is eroded in runoff and makes it to the stream, there could be damaging changes made to the stream environment. The water quality could change as more particles get suspended or dissolved in the column, and the river's flow and/or depth could be reduced when the particles are deposited on the riverbed. When the particles are deposited, the sediment/soil composition and texture will change, having a negative effect on the flora and fauna that live within it (Rex & Carmichael, 2002).

At least two of the four quarries on Incinerator Road were in operation at the time of writing. The quarry positioned just southwest of the defunct incinerator was causing the most immediately devastating effects to the integrity of Nut Brook. This quarry, which was elevated above a tributary that runs into Nut Brook about 200m downstream, had experienced the effects of massive erosion, causing vast quantities of sediment to cascade down into the stream at least as far as Nut Brook. So much sediment had entered

the system that it had accumulated 50 – 70cm deep all the way downstream, and had also been deposited up to this depth on the stream's flood region about 5 – 8m on either side. This meant that not only had the stream's depth and flow been greatly reduced, the natural benthic environment had been completely choked, and vegetation, including trees, in the flood region were also being covered and suffocated. Since the natural organic matter of the streambed was replaced by quarry sediment, the chemistry of the water would also be expected to change. Dissolved oxygen, which is essential for aquatic ecosystems, would be the biggest factor expected to change with this regard.

In addition to the quarries, there was also a septic waste handling facility adjacent to Nut Brook where it passed under the road. The facility drained into a ditch towards the east, which discharged directly into Nut Brook just before it passed under Incinerator Road. The aforementioned tributary was also at risk of runoff in a westerly direction since the road was directed downhill to the west. The facility could put the aquatic system at risk because it consisted of a series of aboveground solid waste storage units. Since the units were not buried, they were more susceptible to the deleterious effects of weather. Hence, they may have been subject to leakage, which would cause the microorganism, *Escherichia coli,* to contaminate the stream. *E. coli* is an indicator species of other potential pathogens sometimes found in human waste, and sometimes can be a potential pathogen itself (Patel, 2004). Additionally, there was a smell of sewage around the facility. It should be noted that it was later discovered that a malfunctioning oil-water separator was being used on site as well.

Further west, there was a rendering plant with a visible exhaust vent on the roof that was responsible for the other foul smell present in the air. Rendering plants superheat dead animals, namely pork and poultry at this particular location, in order to separate fat from the bones, meat, organs, and hair. What is left over is fat and proteins, the latter being rendered into meal and bone meal. These products are then used for other purposes.

The rendering plant, which was elevated above Nut Brook Pond and the sediment-loaded tributary that ran into Nut Brook, was of concern because the vent on the roof could possibly contribute volatile organic compounds (VOCs) or other compounds to the river system. Additionally, if the plant was not contained properly, offal from the dead animals could contaminate the stream, namely with potential pathogens and nutrients. Large blue dumpsters with blood leaking from them were observed in the plant driveway at one point, adding to the questionability of the sanitary and containment standards of the rendering plant.

Next were the discontinued landfill, tepee incinerator, and car wreck dumpsite. The landfill had since been filled in, but it was never lined or covered with an impermeable layer, meaning that leachate could still form and flow out of the site. The same could be said of the site containing old vehicles. In a basic sense, leachate can be composed of heavy and trace metals, various chemicals, and/or other organic compounds such as petroleum products. The incinerator was of great concern as well because it had been left as is in an open, rusting state making it susceptible to rain, which would then affect the stream from its runoff. The inside of the incinerator most likely contained a residue of anything that had been incinerated in the past. This residue was likely rich in polynuclear aromatic hydrocarbons (PAHs), which are dangerous by-products of burning. Other similar toxic by-products found in incinerator soot were also probably present as

well. During its past operation, the site may have easily created persistent organic pollutants (POPs), which may still be found in the soil and sediment of the area.

The tributary that runs adjacent to the dumpsite had a deep red colour, a somewhat cloudy appearance, and a bad smell, indicating that leachate had probably entered the system and could still be a contributing factor. The sediment that had been deposited by the quarry next to the river also exhibited red stains and patches of oil, possibly from the leachate as well.

A little further west was the hazardous waste storage facility. This facility was basically a storage unit for hazardous wastes, including compounds such as polychlorinated biphenyls (PCB's). While a pile of old electrical transformers, a source of PCBs, were noted outside the compound, and a small stream was observed to drain from the facility into the nearby tributary, it was believed that the transformers were probably empty and that this particular operation was perhaps of a lower priority, since an ISO registered corporation handled it.

Last but not least, the two roads that cross Nut Brook could also be a contributing factor of contamination. Both of these roads, Incinerator Road and the Trans Canada Highway (TCH), are major thoroughfares for large trucks. These trucks can be quite polluting in themselves and they can add various petrogenic compounds, such as PAHs, to the system as well.

2.1 Site Selection

The drainage basin features were carefully considered during the selection of the sample sites. With the assistance of Rondine Herla and Glenn Worthman, six main sites were selected; one being a reference site to the south, and the other five lying within the Incinerator Road area. An extra sample was also taken at a new location to replace site 6 on the 4th sweep (*Figure 3*).

2.1.1 Site 1

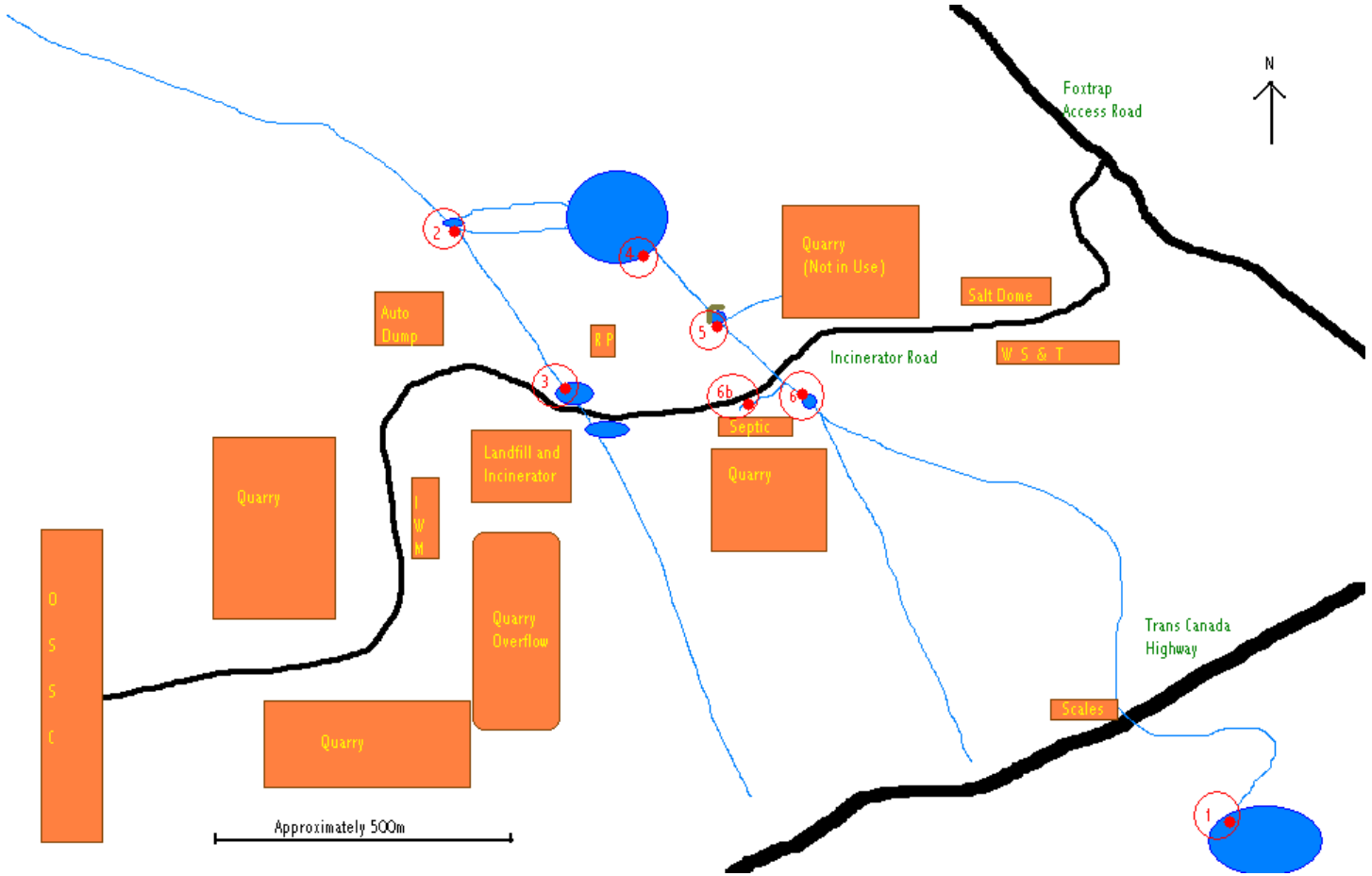
GPS Coordinates:

Longitude N 47' 26.353

Latitude W 052' 58.291

The first site selected was in the seemingly pristine headwaters in the southernmost section of the watershed. This site was selected because it was upstream from all industrial activity, including the TCH, and was, therefore, the least likely spot to be contaminated in the drainage basin. Located in a pond surrounded by trees, it drained into a wetland, forming the beginnings of Nut Brook. Since it represented the natural conditions of the system, it was an ideal location for a reference site. This would be an important tool for determining the extent of anthropogenic impact on the system by comparing and contrasting it with other parts of the brook downstream.

Figure 3: *Nut Brook Study area showing all 6 main sampling sites, plus the extra site 6b. Note, sketch is not exactly to scale (approximately 1:18,000), but otherwise portrays the general positions of the sample sites in relation to the other sites and various points of anthropogenic land use (pink regions). The general direction of flow is approximately northwest.*



Source: Author (2006)

2.1.2 Site 2

GPS Coordinates:

Longitude N 47’ 26.728

Latitude W 052’ 59.310

Site 2 was selected about a 200m hike north of Incinerator Road where the tributary and Nut Brook convened as one. Downstream of all the other sites, this site was chosen to represent an accumulation of contaminants coming from several sources, although it was kept in mind that any input could have been weakened or diluted due to its position on the stream. To get to the site, a hike was required down the sedimented flood region of the tributary. The site itself showed the heavy impact of the quarry material as much of it had been deposited there; there was so much sedimentation that the pool as shown on a topographic map where this site should have been had been largely filled in so that one could actually stand on what should have been water. The water itself was reddish, indicating the leachate from upstream, and it also had an odour. Piles of dead aquatic insects had been observed on the bank and just under the stream surface on one occasion.

2.1.3 Site 3

GPS Coordinates:

Longitude N 47’ 26.628

Latitude W 052’ 59.206

Site 3 was selected in the tributary adjacent to the main branch of Nut Brook, which drained from the pool next to the north side of Incinerator Road across from the incinerator. The site was heavily sedimented and the odour from the visible rendering plant was very strong. The sediment had many red streaks and stains, and oily patches were present as well. The water was also very murky and red and smelled very bad. This site was probably very influenced by leachate from the landfill, as indicated by its colour. It was noted also that at some point hay had been spread over a part of the sediment for reasons unknown. It was speculated that it was a cover for a possible but indefinite spill. Later on during the sampling period (*sweep 3*), sods were planted over the sedimented banks, but a large hole was dug with an excavator and much of the unearthed material was piled in the stream, nearly blocking the flow completely. Much gas was noted saturated in the sediment and if stirred, it would flow into the stream. This site was one of the worst affected locations.

2.1.4 Site 4

GPS Coordinates:

Longitude N 47’ 26.695

Latitude W 052’ 59.103

Site 4 was located at the south end of Nut Brook Pond, and since there were so many lily pads and aquatic plants, it was thought that this site was undergoing eutrophication. If too many nutrients enter the system the plant life can boom, causing the water to become stagnant and the dissolved oxygen levels to be lowered (CCME, 2003). This can cause certain undesirable bacteria species to flourish. The site was an intermediate stage located between the locations where site 5 discharged and where Nut Brook met the abovementioned tributary. It should be noted that the east side of the rendering plant was visible here.

2.1.5 Site 5

GPS Coordinates:

Longitude N 47’ 26.681

Latitude W 052’ 59.039

Site 5 was chosen for the fact that it was a pool created by a man-made dam on Nut Brook. It was just downstream from the septic waste handling facility and a quarry. The water was quite murky and had an oily sheen on the surface. For a comment on dams, they tend to cause substances to accumulate in the reservoir created behind them. Due to the flooding caused by dams, submerged vegetation will also tend to rot under water giving certain bacteria an opportunity to release mercury from the soil. Thus sometimes mercury is expected to show up in dam pools (Barlow and Clarke, 2003).

2.1.6 Site 6

GPS Coordinates:

Longitude N 47’ 26.648

Latitude W 052’ 58.878

The last sampling site picked was located at the mouth of a small pond in a wetland on Nut Brook adjacent to a quarry and the septic waste handling facility. It appeared healthy, showing good flow and relatively clear water. However, due to its proximity to the septic waste handling facility and a quarry this site was under suspicion as well.

2.1.6.1 Site 6b

GPS Coordinates:

Longitude N 47’ 26.637

Latitude W 052’ 58.941

On the last sampling sweep of Nut Brook, it should be noted that site 6 was moved to a different location, due to significant circumstances when a small drainage ditch was noticed just downstream on the immediate south side of Incinerator Road. The ditch was discharging very oily and smelly water that was black grey in colour into Nut Brook. Its origin was a pipe jutting out of a small embankment on the edge of the septic waste handling facility. The flow rate was very high indicating the water was being pumped from the pipe. The sheer volume of oil that was estimated to be in the water would explain the oily sheen on the surface of the water at site 5 a short distance downstream. The rocks in the ditch all had a black coating of oil on them. Visually appalling, it was obvious that site 6 needed to be changed to give this new finding priority. The new site will hereafter be known as site 6b. At the time it was unknown as to why there was oil being pumped into the ditch, but it was seen as major grounds to test this water. It was later found to be the result of a faulty oil-water separator used on site.

3.0 Methodology

In order to characterise the overall quality of the water flowing in Nut Brook, and to establish an idea of what may be polluting the river and by how much, a sampling schedule had to be planned to coincide with the subsequent lab work. Proper field and lab techniques, including methods for determining the flow, had to be researched and formulated for water and sediment samples to lessen the chances of errors and to make the most efficient use of the time available. A catalogue sheet was also developed for efficiently recording data in the field. Additionally, all of the results had to be organised and interpreted in order to make any conclusions and recommendations.

3.1 Sampling

A set of four sampling sweeps were organised for the months of July and August approximately two weeks apart from each other. They occurred on July 14th, July 27th, August 9th, and August 25th respectively. The sampling itself was conducted also with the help of a Green Team, which were hired by the CCNL and contracted by ACAP.

The sampling scheme was developed in hopes of contrasting two rain events with two non-rain events; however logistically that did not work according to plan. Instead, there were three non-rain events and one rain event day. The purpose was to compare a wet day with a dry day to determine whether runoff from the land would create an additional input of contaminants to the river system, and conversely also to see if runoff

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Photo 1: *View of Site 1, the reference site, at the headwaters of the Nut Brook and Kelligrews River watershed. Downstream begins to the left.*

Photo 2: *View of Site 2, where Nut Brook combines with the adjacent tributary. Facing downstream.*

Photo 3: *View of Site 3 in adjacent tributary after sods had been applied to the sediment. Facing downstream*

Photo 4: *View of Site 4, a pond on Nut Brook. Note the abundance of lilies competing at the surface. Facing downstream.*

Photo 5: *View of Site 5 standing on the dam. Note the salt storage dome in background. Facing upstream.*

Photo 6: *View of Site 6 showing a quarry in background. Downstream is towards the right.*

Photo 7: *View of oily discharge flowing from the outfall at Site 6b. Flow is towards the left.*

Photo 8: *Oily discharge flowing from Site 6b towards Nut Brook just beyond culvert (ahead). Facing downstream.*

Photo 9: *Leachate from the landfill in the tributary adjacent to Nut Brook. Facing upstream. Note the deposited sediment on the far bank.*

Photo 10: *Blockage of Site 3 after the channel was disturbed* (sweep 3). *Downstream is towards the left.*

Photo 11: *Example of poor water quality in an affected part of Nut Brook (Site 3). Downstream is to the left.*

Photo 12: *Oil transported from its source downstream to Site 5. Facing upstream.*

Photo 13: *View showing major destruction to the stream from an excavator. Facing downstream.*

Photo 14: *View of sediment fanning over the edge of a hill before depositing into the tributary adjacent to Nut Brook to the left. The source quarry is away to the right.*

Photo 15: *Yardstick buried 24 inches (Approximately 61cm) deep in sediment deposited in the flood zone of the stream bank (Site 3). Downstream is to the left.*

Photo 16: *View of the adjacent tributary and buffer zone (downstream of site 3) choked with sediment and also red with leachate. Facing downstream.*

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would instead dilute the results. Due to the lack of rainfall during the sampling period, this correlation will not be discussed in this report unless otherwise indicated.

In order to take samples, certain bottles, properly labelled, relating to particular testing parameters were collected and prepared. Preparation involved the meticulous washing of the bottles and also of adding small volumes of specific acids to some of them as preserving agents immediately after the samples were taken. Water samples were taken from each of the six sites on every occasion in plastic bottles containing sulphuric acid for solids and nitrogen testing, plastic bottles containing nitric acid for metals, sterilized plastic bottles containing sodium thiosulphate for microbiological analysis, and glass vials for PAH analysis. On two occasions, sediment samples were taken in glass and plastic containers for their appropriate analyses as well.

It should be noted that the water samples were taken every time because water is constantly transporting material and flowing away. Thus the constituents that could be found in water could always be changing. However, the sediment samples were only taken to be tested once each (although it took two occasions to obtain enough sediment). The sediment would be most likely to retain its qualities, considering that sediment tends to be an adsorbent surface and is inclined to remain fairly stationary in one place at the bottom of the river where it was initially deposited (CCME, 2001). Because of this, only enough sediment was needed to be collected to test it once over.

The water samples were taken as grab samples, meaning that the water was only collected in the bottles at the points where they were dipped. With the exception of the previously sterilised microbiological bottles, the other bottles were pre-rinsed with river water that was poured downstream from where the samples were taken to avoid any possible contamination from the bottles.

The sediment samples were also taken as grab samples, which involved scooping the material from the streambed directly into the bottles used. Excess water was decanted and the bottles were then capped.

3.2 Field Analysis

Many tests were performed directly in the field along with the aid of the Green Team. The Marine Institute provided the equipment necessary to perform these tests. A HACH field-testing kit was used to determine four parameters: alkalinity, chloride, ammonia, and nitrite. A Horiba probe was used as well, and it tested for six parameters: pH, conductivity, turbidity, dissolved oxygen, temperature, and salinity. The procedures for each of these tests were performed following the methods stated in the HACH and Horiba manuals.

These tests were very useful, as they eliminated much of the time and costs associated with being in the lab. However, it meant that more time had to be spent in the field. They were also of great assistance because direct results were obtained for each parameter at each site, meaning no other calculations were needed later. It should be noted, however, that the HACH kit occasionally ran out of testing reagents at unexpected times, thus some of the tests could not always be completed.

3.3 Lab Analysis

The rest of the tests were to be conducted in the lab for total solids, total Kjeldahl nitrogen, and *E. coli*, either at the chemistry and microbiological labs at the Marine Institute (MI), and a full metal suite was tested for within the trace elements lab at the Department of Earth Sciences at Memorial University of Newfoundland (MUN). Extractions made from the sediment samples were also sent to the Environment Canada water quality lab in Moncton for PAH analysis.

3.3.1 Total Solids

The total solids, expressed as the mass of the total suspended solids (TSS) plus the mass of the total dissolved solids (TDS), were determined using an oven and a muffle furnace at the chemistry lab at MI. From this the mass of the volatile organic compounds could be determined. The method used was based on a laboratory procedure for the same experiment (Whiteway, 2004). See Appendix D for a description. It involved separating the suspended solids from the dissolved solids with a filter and heating the pre-weighed filters and crucibles containing the separated solids until the water evaporated. From this the crucibles and filters were re-weighed and subtracted from the original weights, giving the TSS and the TDS. Furthermore, the crucibles containing the TDS were superheated in a muffle furnace until the organic content volatilized. Once this occurred, the crucibles could be weighed again and subtracted from the TDS, giving the solids VOC (at 550°C).

3.3.2 Organic Content in Sediment

The organic content of the sediment was measured using the muffle furnace as well. The sediment samples were first weighed and then superheated until the organic matter burned away. The sediment without the organics was then reweighed to determine the amount of volatilized organic matter. This was termed total organic content (TOC). From what was left over, observations of the raw sediment could then be made including approximations of coarseness.

3.3.3 Total Kjeldahl Nitrogen

The total Kjeldahl nitrogen for the water and sediment samples was determined using the Kjeldahl method at the chemistry lab at MI. This method was performed as per a laboratory procedure for the same experiment (Whiteway, 2004). (*See Appendix E for a description*). It involved the addition of concentrated sulphuric acid and a catalyst to tubes containing a pre-weighed amount of sample; superheating it so that the samples were effectively digested by the acid; adding de-ionized water and sodium hydroxide; and distilling the freed ammonia into a flask containing boric acid and an indicator. This solution was then titrated with hydrochloric acid to determine the total amount of ammonia in the sample. Using the quantified ammonia content, a calculation was then performed to determine the overall nitrogen content using the following formula:

%N = ((A x B / C) x 0.014) x 100, - where A is the volume of sample titrant used minus the volume of blank titrant used, B is the normality of the acid used, and C is the weight of the sample

3.3.4 Metals

A wide range of trace elements could be determined using the inductively coupled plasma mass spectrometer (ICP-MS) at the Department of Earth Sciences at MUN. This extremely sensitive piece of equipment works by atomizing, desolvating, and heating the samples at 7,000 – 10,000 degrees Kelvin, creating a plume of argon plasma. The metal analysis is complete when the detection equipment senses the plume. The exact method followed for this procedure was unknown since the samples were analysed by the people working in the trace element lab. The method they used was highly reliable, however, as they were highly trained and experienced individuals.

3.3.4.1 Hardness

Using the results obtained in the metals analysis for the concentrations of calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn), aluminum (Al), strontium (Sr), and barium (Ba), the hardness of the water was calculated using an easily derivable formula, where the sum of the molecular weight of calcium carbonate ($CaCO_3$) divided by the molecular weights of each element was multiplied by the concentration of each element respectively. Using this theory, the following formula was derived:

$CaCO_3$ Hardness (ppm) = [(ppm Ca x 2.497) + (ppm Mg x 4.118) + (ppm Fe x 1.792) + (ppm Mn x 1.822) + (ppm Al x 3.709) + (ppm Sr x 1.142) + (ppm Ba x 0.729)]

3.3.5 *E. coli* and Non-Fecal Coliforms

The determination of fecal coliforms, specifically *Escherichia coli* (*E. coli*), and also non-fecal coliforms, was achieved simultaneously using the membrane filtration technique. This method utilized a selective media called M-coli blue, which only allowed the growth of *E. coli* (blue colonies) and non-fecal (red colonies) coliforms at 37.5 degrees Celsius. The technique involved the filtration of the samples and dilutions made of the samples through a micro-porous membrane via special filtration apparatus with the intention of trapping the bacteria in the pores and letting the water pass through. After the M-coli blue was added, the plates were incubated for a day, giving the colonies sufficient time and the right conditions to grow so they could be counted. The method used in this test followed a laboratory procedure for the same experiment (Patel, 2004). (*See Appendix F for a description*).

3.3.6 Organic Compounds

It was in the original plan to test for various toxic organic substances, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated bi-phenols (PCBs), and other petroleum hydrocarbons because these substances were suspected to be present in the brook. Due to various unforeseen circumstances and limitations, this was not entirely possible or successful. Extractions were attempted on some of the samples, however, at the chemistry lab in the Marine Institute following a procedure outlined in a text explaining an extraction method for the determination of PAHs (Boehnke and Delumyea, 2000). The technique used for the water samples did not work, but with a slight modification and more time it may have been possible to achieve a usable extraction. Unfortunately, this was outside the viable boundaries of this report. Extractions were performed on the sediment samples, however, and at the time were supposedly utilizable. (*See Appendix G for procedure summary*). Though, due to more unforeseen limitations, the extractions were withheld for a further amount of time and were eventually sent to the water quality lab at Environment Canada in Moncton for analysis. There, the extractions were run through their gas chromatograph mass spectrometer (GC/MS) unit, which was well suited for the analysis of PAHs.

3.4 Statistical Analysis

During the interpretation of the results, most of the raw values obtained were put through a statistical analysis to further aid the interpretations, and to add another level of quality control and assurance to the findings of this report. All analyses were performed in a powerful statistical software program called Minitab14® (2005).

Essentially, two types of analyses were carried out. First, the means and standard deviations covering all four sampling sweeps were derived for each variable tested in each sample site (*Appendix C*). Next, analyses of variance (ANOVAs) and Tukey's pairwise comparisons were carried out where it was appropriate. The purpose of the ANOVA was to statistically test whether any of the mean data from any particular site was significantly different from any of the others. The purpose of the Tukey's test was to follow up the ANOVA to tell exactly what sites between 1 and 6 were significantly different. These tests were extremely useful particularly in determining whether there was any significant difference between the reference site and the other sites.

Before an ANOVA and a Tukey's test could be performed, the data had to be classified either as parametric or non-parametric, which was achieved using a Ryan-Joiner test. If the data was non-parametric, which environmental data often tends to be, a Kruskal-Wallis (KW) test could be performed with the hypotheses at a 95% confidence interval (CI) stating:

$$\textit{Where } \alpha = 0.05$$

$$\textit{Either (Null) } H_o\text{: } \mu 1 = \mu 2$$

$$\textit{Or (Alternate) } H_a\text{: } \mu 1 \neq \mu 2$$

The first hypothesis essentially means that if the p-value obtained from the KW is high (greater than 0.05), then the null hypothesis (H_o) fails to be rejected. This signifies that all of the mean values of a particular variable (i.e. pH, hardness, etc.) are not significantly different from each other. The alternate hypothesis (H_a) basically states that if the p-value is low (less than 0.05), then the null hypothesis (H_o) is rejected. This would denote that there is a significant variance in some regard between the sites. If this were the case (i.e. the KW goes in favour of H_a), then an ANOVA would be carried out complimented with a Tukey's test to determine what sites are different from the other sites with respect to the variable tested for.

In the case of parametric data, which can sometimes occur, a Test for Equal Variance (TEV) would have to be performed instead of a KW. The hypotheses would essentially be the same. If rejecting the null hypothesis, then a follow up with an ANOVA on the ranks of the data and a Tukey's test would be performed to determine what sites were significantly different from each other.

Boxplots of the data can be created simultaneously in the ANOVA process. These plots are very useful in that for any test variable they show and compare the entire range of all the values for each sample (*Appendix C*).

It should be mentioned that site 6b could not be included in the statistical analyses because only one sample was taken, thus there was no mean value for any parameter associated with this sample site. However, site 6b was included in the interpretations with this fact in mind.

3.5 Determination of Flow

Another important parameter relating to stream characterization is flow. The flow is measured as cubic meters per second (m^3/s), or the volume of water moving past a certain point, as a line, over a specific time interval. A current meter was borrowed to aid in this, however for the most part it was not needed. The procedure involved taking depths of the stream at spaced intervals (if possible) and creating a theoretical depth profile to obtain an approximate area (m^2) of the stream width. Since calculus was not used, and much interpolation and generalization of the streambed had to be surmised, the area determined through this process was an approximate at best, however it was quite representative.

The next step was to calculate the current. In the three of six sites that were actually flowing and not pooling behind a dam or in a pond, the flow and/or depth was usually not great enough to utilise the current meter. Placing a floating object, such as a leaf, in the stream and timing its path along the three feet of a yardstick crudely overcame this problem. Once converted, this produced a measure of the current in metres per second (m/s). The current multiplied by the area gave the stream flow (m^3/s) at that point on the brook.

4.0 Results and Discussion

This section will summarize the results of the sample analysis on everything that had been tested in Nut Brook. This was essentially achieved by presenting the data means, which were basically the statistical averages of each sample parameter per sample site, in graphical form for ease of interpretation. In some cases mean values could not be derived, such as for sediment data or the single sample taken for site 6b, thus these results were presented in their raw form. All of these results were then evaluated both analytically and statistically to form a very comprehensive interpretation of the water quality and ecological health of Nut Brook. It should be noted that a correlation was not strongly determined regarding the influence of runoff from a rain event in this case, and thus, unless indicated otherwise, will not be discussed in the following sections.

Interpretations were made based on many factors, such as the potential effect of a particular parameter in high concentration on the health of aquatic life with respect to known guidelines or toxicological data on that factor. These interpretations also greatly took into account the contrast of the concentrations of particular parameters in the sites of interest (sites 2 – 6 and 6b) to the concentration of a particular parameter in the reference site (site 1). Additionally, the physical and geographic features of a particular site were taken into account in certain cases when interpreting the data; for example: site 3 experiencing heavy sedimentation, or site 4 existing as standing water.

Statistical analysis of all the data also greatly increased the quality of the interpretations made. For instance, an ANOVA and an accompanying Tukey's test can reveal statistically whether there was a significant difference in the concentrations at one site with another, and these particular tests were very useful in determining whether there was a significant difference between the reference site and the other sites, which could then potentially indicate an anthropogenic input or change of certain parameters within the system away from the reference site. The analytical and statistical interpretations were often made dependently of one another, and raw data presented in the appendices was often taken into account as well to make the most comprehensive analysis and interpretation of the results possible.

4.1 Total Solids

Natural waters are not pure. There will always be various constituents, or solids, either dissolved or suspended in the water column originating from the erosion of the streambed or banks. These solids, which comprise mainly of inorganic material and a smaller amount of organic matter, can also arise from sources further away during a period of runoff, such as when overland flow from precipitation causes solid material to be deposited into the stream.

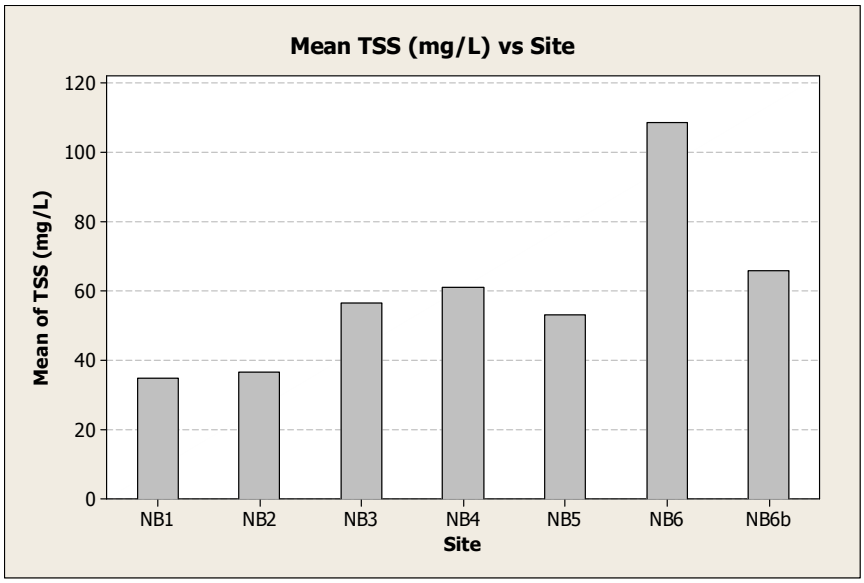
Although it is normal for rivers to accommodate some solids, too much can be harmful to aquatic life. In high concentrations these constituents can lower the amount of dissolved oxygen in the river, due to the reduction in the amount of light entering the stream, resulting in a decrease in photosynthesis. Aerobic microorganisms lower dissolved oxygen even further while decomposing dead plants that are unable to

photosynthesise (Murphy, 2005). While increased suspended solids can provide ideal anchor sites for pathogenic microorganisms, damage the benthic environment as it settles, and cause damage to fish gills while lowering the fish's immunity and growth patterns, a difference in the concentration of dissolved solids can also change the density of the water, dangerously altering the flow of water in and out of an organism's cells (CCME, 2003). Additionally, dissolved solids can combine with toxic compounds and heavy metals, and raise the water temperature, also putting aquatic life at risk (Murphy, 2005). Quarrying, industrial waste, and sewage can lead to increased solids in stream water.

Upon testing the sites at Nut Brook for solids, evidence was generated supporting an industrial input of this parameter. This evidence is shown in the following graphs in the following subsections as the mean concentrations of TSS, TDS, TS and solids VOC for each sampling site. It should be noted that there were no formal guidelines set with regards to solid constituents in water for the protection of aquatic life, however the Province of British Columbia (BC) (1998) has provided some suggestions that are included on some of the figures in this section. The raw data, statistical means, and standard deviations associated with these results can be found in the appendix.

4.1.1 Total Suspended Solids (TSS)

Figure 4: *Mean levels of total suspended solids (TSS) in mg/L per sample site in Nut Brook. (Note: site 6b was only sampled once)*

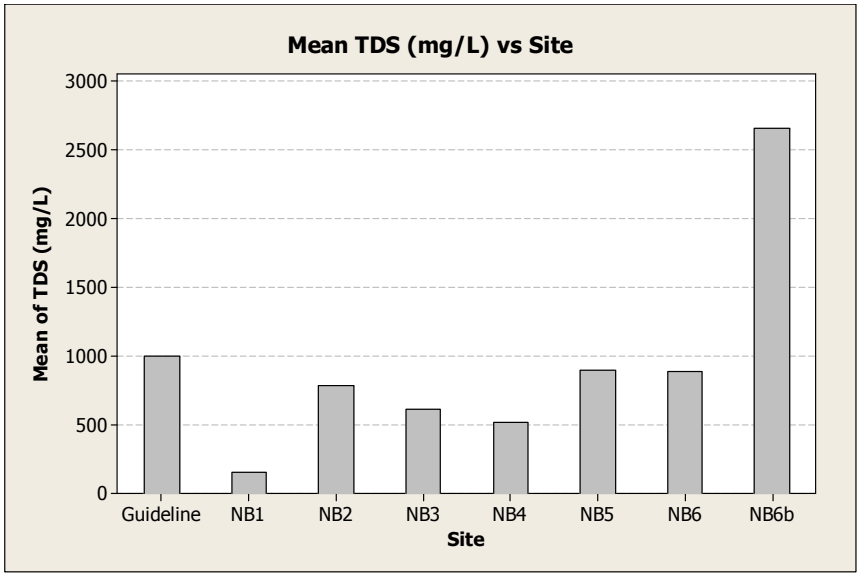


From Figure 4, it would appear that the TSS was a little high in all of the sites, especially in site 6. However, in some cases TSS may have been increased at any given time due to disturbances on the streambed as water samples were being taken, particularly in site 6. Steps were taken to not stir up the sediment as much as possible, but there were times when this was not possible. Thus, the mean TSS concentrations listed here may be slightly higher than they actually normally were in a few of the samples. Overall, the statistical analysis showed the mean concentrations were not significantly

high (*technically: not statistically or significantly different*) when compared with the reference site, so the extra TSS caused by error was not a concern.

4.1.2 Total Dissolved Solids (TDS)

Figure 5: *Mean levels of total dissolved solids (TDS) in mg/L per sample site in Nut Brook versus the recommended maximum of 1000 mg/L as suggested by the Province of BC (1998).*

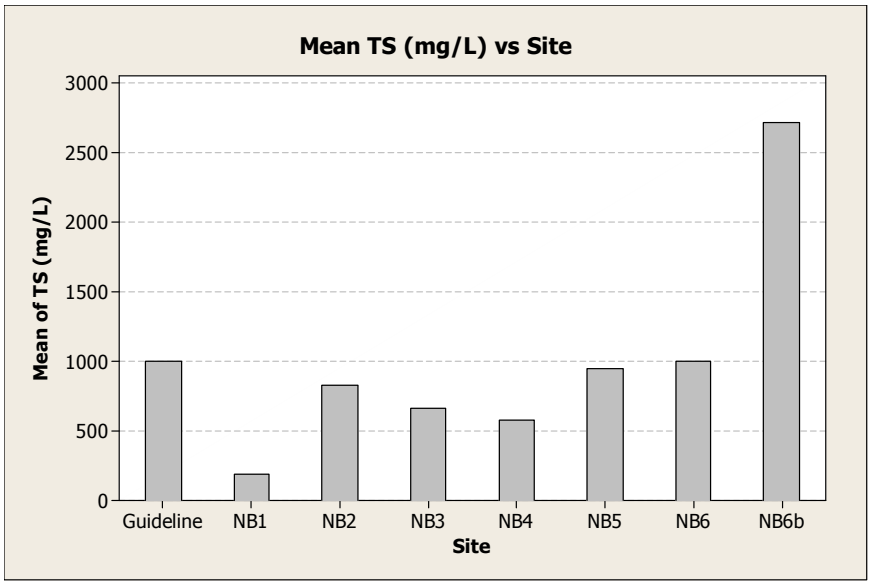


Fresh water is usually limited to 1000mg/L or less of solids, particularly TDS (Province of BC, 1998). Thus for the purposes of this report, mean values of over 1000mg/L have been compared to this guideline as indicators of questionable water quality. Sites 2, 5, and 6 had levels close to this limit on average (*Figure 5*) with mean concentrations of 788.5, 893.5, and 892 mg/L TDS respectively, and at times had exceeded it (*Appendix A*). It should be noted that site 6b showed a dangerously high level of TDS at a value of 2652 mg/L. As it will be shown later this was attributable to the high level of various constituents found in the water at this site.

Although a test for equal variances (TEV) showed that the mean TDS values per sample site were not significantly different from one another (p-value > 0.05), a look at the raw data and boxplot in Appendices A and C showed that there could easily have been a difference between the values from the reference site and those determined in sites 2, 3, 5, and 6. Figure 5 shows that the mean TDS concentrations were all higher than site 1, and the boxplot of TDS also shows that the lowest values of sites 2, 3, 5, and 6 were higher than the highest value recorded in the reference site, indicating a probable input of solids to the system in the vicinity of Incinerator Road.

4.1.3 Total Solids (TS)

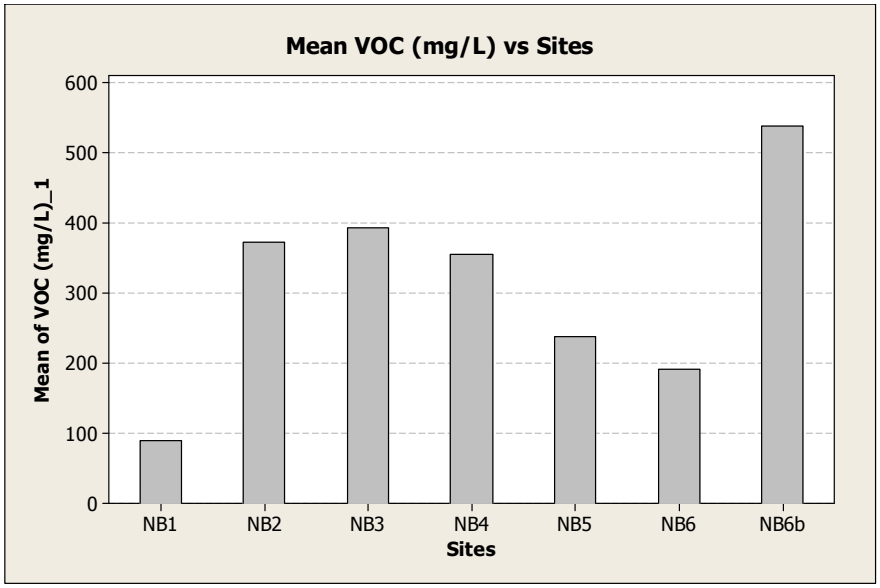
Figure 6: *Mean levels of total solids (TS) in mg/L per sample site in Nut Brook versus the recommended maximum of 1000 mg/L as suggested by the Province of BC (1998).*



In a similar fashion to TDS, the mean concentrations of total solids were high in sites 2 – 6 in comparison to that of site 1 (*Figure 6*). With the addition of TSS, site 6 exceeded the set guideline of 1000mg/L with a value of 1000.7mg/L, and site five came just under the boundary at 946.5 mg/L TS. Although a TEV failed to show any significant statistical difference between the downstream sites and the reference, again for the same reasons as the above discussion on TDS, there was still evidence to show an obvious anthropogenic input of solids to the system.

4.1.4 Volatile Organic Content (solids VOC at 550°C)

Figure 7: *Mean levels of Volatile Organic Content (VOC) at 550°C in mg/L per sample site in Nut Brook.*



According to the Province of BC (1998), total organic content (TOC) in natural waters generally ranges up to 30 mg/L, and although VOC is not necessarily the same as TOC, it would make up at least a part of it. Thus, there appeared to be a considerable amount of volatile organic content in the Nut Brook water samples, since the lowest mean value was 90 mg/L at site 1, and the next lowest was 192 mg/L at site 6 (*Figure 7*). Some of this organic component could have been due to natural organic material in the river, such as decaying plant or animal matter. This could easily have been the case for site 1, since it was standing water and organic matter would tend to collect in this type of situation. However, it was also likely that there may have been petrogenic and even airborne constituents entering the river downstream from the incinerator road area, but only alternate testing for specific VOCs could actually verify this. Any sewage present in the river could have also contributed to the mean levels of VOC present.

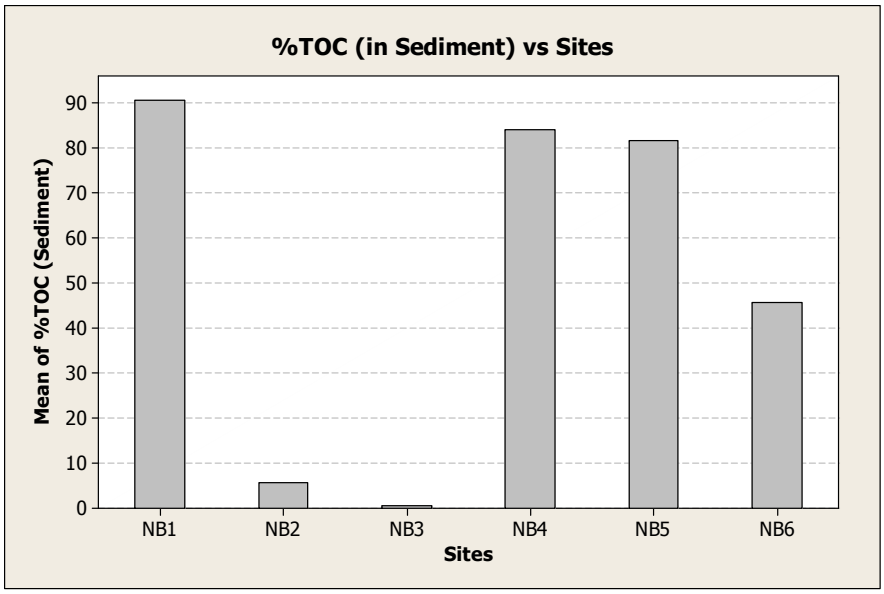
Site 6b had a relatively high level of VOC at 538mg/L. The high amount of VOC can be linked to the amount of oil visible in the water at this station. Sites 2, 3, and 4 also showed high mean values of VOC relative to the reference site (*Figure 7*). When compared to the reference site, all of the other water samples had much higher concentrations of TDS and VOC in almost every case, indicating a probable anthropogenic input of these variables. In the case where some VOC concentrations were lower than the reference (*Appendix A*), it should be noted that solids VOC is determined by the complete volatilization of organic carbon (at 550°C), so it was possible that this was not achieved for the sample in question in this case. It was also possible that some had volatilized in the other samples before testing had began and was lost, resulting in a lower level of VOC. Although a TEV again failed to show any significant statistical

difference between any of the sites, for the reasons given above it would seem more likely that there was an anthropogenic input of VOC to the system.

4.1.5 Total Organic Content in Sediment

The amount of organic matter in the sediment samples could also be determined simultaneously during use of the muffle furnace. Organic matter has a tendency to bind with particular toxins and metals, effectively removing some of them from the water column and making them less bioavailable. Depending on the actual grain size of the inorganic sediment, there could be more or less surface area for the organic matter to occupy, resulting in a variable efficiency of toxin binding. It is also an important component of the benthic environment of a natural stream system. The results of the total organic content (TOC) obtained from the sediment samples on July 14th are as follows:

Figure 8: *Concentration of total organic content (TOC) in Nut Brook sediment recorded in grams of organic material per 1 gram of sample sediment, but shown here in percent (%).*



Sites 2 and 3 show practically no organic matter in the sediment at 5.6 and 0.6% respectively (*Figure 8*). This was most likely due to the fact that the organic matter, which would normally be present in higher concentrations in a naturally flowing stream, was covered and lost in the system when these two sites were affected by the continuous sedimentation from the quarry just upstream. This is an indicator of the heavy damage to an ecosystem that can occur from an uncontained quarry.

Site 6 was much lower than sites 1, 4, and 5, at 45.6mg/L, however the flow at this site was the strongest of all the sites and it would be expected that much organic matter would just naturally flow downstream in these conditions. Site 6 showed a normal bottom environment on visual inspection, and in comparison with sites 2 and 3, it had a much higher TOC (*Figure 8*).

Sites 1, 4, and 5 had very high levels of organic content in their sediment at 90.5, 84, and 81.7% respectively (*Figure 8*). This was due to the fact that they were not under the influence of quarry sediment to much degree (in sites 4 and 5), and also more due to the fact that these were standing water sites, meaning that organic matter was not being transported away by a current and had a much better chance of forming and settling on the bottom. The amount of TOC in the sediment at sites 1, 4, and 5, was characteristic of the standing water conditions.

4.1.6 Raw Sediment

The procedure for determining the TOC of the sediment involved burning all of the organic matter away, leaving the pure sediment behind. This raw product could then be studied to understand the some of the physical properties of the stream and streambed, such as the flow conditions and the status of the benthic environment. The colour of the sediment could be an indicator of its composition as well, however this feature was not considered in detail in this case. The following observations were made about the raw sediment obtained from each site:

Table 1: *Grain size approximations and colour of the raw sediment processed from each site.*

Sample ID	Coarseness/Texture	Colour
1	Clay	Beige
2	Silt	Light brown/pink
3	Fine sand	Red/brown
4	Very fine silt	Light brown
5	Very fine silt	Brown
6	Gravel/sand	Brown/red

In terms of increasing coarseness, the grain size textures were chosen as follows:

Clay, silt, sand, and gravel.

Each texture class had in itself its own array of sizes, ranging simply from fine to coarse. The grain size in each site was an indicator of the flowing conditions of the system at any given point. For the coarser material collected, a certain amount of energy and flow would have been required to carry the finer sediment away. Such was the case in site 6 because there was enough energy to carry the finer sediment away, leaving the coarser grains behind. The very fine material found in the sites with standing water illustrated the lack of flow at these points, such as in sites 1, 4, and 5, since a small amount of energy could have carried this material away if the stream were flowing at those points. The silt and sand found in sites 2 and 3 were not the natural sediment. This was the new sediment added through deposition from the quarry runoff. The original

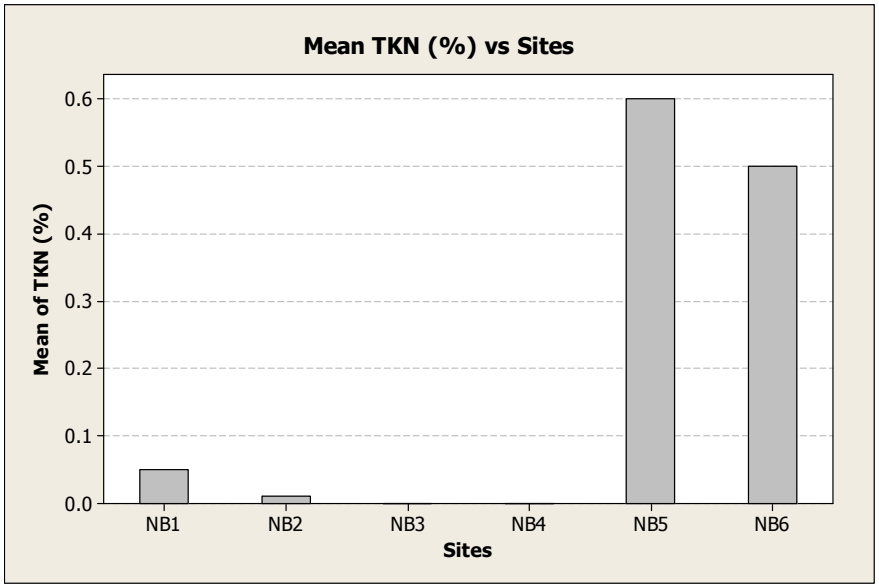
sediment, which would have had much more organic matter in it, would have had to be obtained by digging about 60 cm deep into the silty or sandy deposit.

4.2 Total Kjeldahl Nitrogen

Total Kjeldahl Nitrogen (TKN) is a measure of the sum of the organic nitrogen and ammonia in the sample, and it can indicate an input of organic nutrients into a system. Plants and some aquatic microorganisms need a certain amount of these nutrients to live, and often nitrogen levels in streams are low partly because various organisms are using them. If the levels are too high, the conditions will turn eutrophic, causing some aquatic plants and algae to flourish. Their intense competition within the ecosystem would, however, result in severely diminished levels of dissolved oxygen, harming other forms of life. Certain forms and concentrations of nitrogen can also be harmful to fish and other life forms within the aquatic environment (Murphy, 2005).

The mean results for TKN in the water samples of the first three sweeps, derived by the formula given in section 3.3.3 are listed in the following chart. The TKN values in the sediment samples collected are also portrayed in this section (*Figure 10*). Despite the fact that statistics could not be performed on the water samples, they were analysed in duplicate for quality purposes. The means of each test are listed in Appendix A.

Figure 9: *Mean values of Total Kjeldahl Nitrogen (TKN) in percent (%) per sample site in the Nut Brook water samples.*

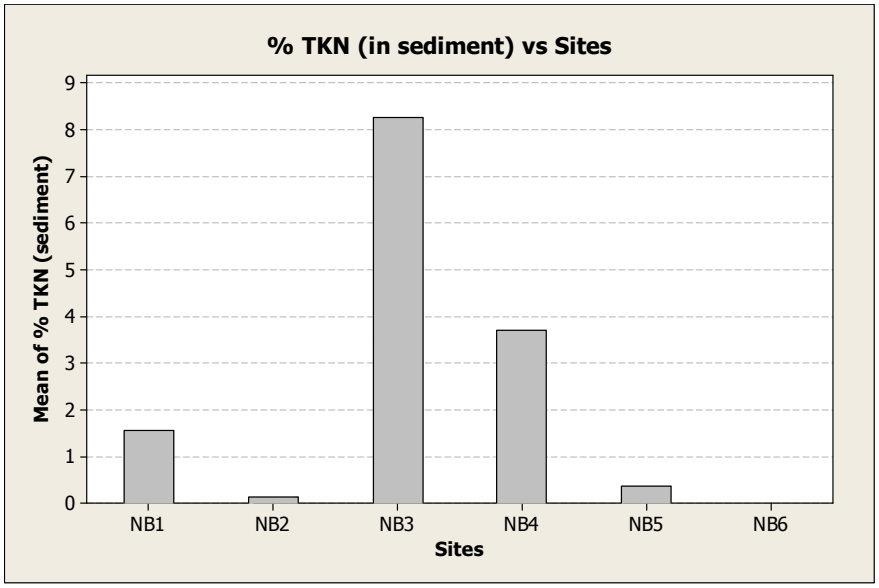


There were no guidelines referring to total Kjeldahl nitrogen, however it can be said that the values listed in this table were not high for the most part, since almost all of them were lower than the amount recovered in the blanks, which were simply nanopure water. Possible errors may have occurred in a few cases because solid data presented later in this report suggest that there may have been sewage in the water and would be

expected to coincide with higher levels of TKN. Additionally, site 4 was highly eutrophied, noted by the large percentage of lily pads and other plant life observed to be covering the surface. Since there were low levels of TKN, it was possible that some other form of nutrient, or perhaps a metal element, contributed to this condition. It was also true that ammonia was difficult to accurately quantify because it is an unstable form of nitrogen. This was another possible reason as to why there were low levels of TKN detected in the samples.

Despite the generally low or non-existent levels of TKN (*Appendix A*), Figure 9 shows that sites 5 and 6 had mean levels of 0.5% (5000 mg/L) and 0.6% (6000 mg/L) respectively. These were unnaturally high values and would most likely indicate an input of sewage to the system.

Figure 10: *Total Kjeldahl Nitrogen (TKN) in percent (%) per sample site in the Nut Brook sediment samples.*



With respect to TKN in sediment samples, the grains in the substrate would normally retain nitrogen more effectively than just water; hence it was easily detected in most of the samples. The sediment at the reference site and at site 4 had fairly high amounts of TKN at 15600 mg/L and 37100 mg/L respectively (*Figure 10*), but this could be attributed to the amount of organic matter that had collected at each site since these sites were standing water. With respect to site 4, however, there may have been other causes as well since a visual inspection of the site showed that it was probably eutrophied. TKN was undetectable in the site 6 sediment, but this site had a healthy flow and a coarser grain size (*Sections 4.1.6 & 4.9*) meaning that finer sediment better suited to the retention of nitrogenous compounds would not be able to settle there.

Two reports, by Hunter (1993) and Makarewicz & Lewis (2004), make a connection between suspended sediments and TKN in that often erosion of sediment in one area also removes nitrogen simultaneously in that area, due to the transport of

nitrogen attached to sediment during runoff. In the same sense, when these particles are detected suspended in the water column downstream, there is often an association with higher values of TKN. Similarly, in the case of the sediment sample in site 3 having a very high value of 82700 mg/L TKN (*Figure 10*), it was probable that when the sediment from the upstream quarry eroded into Nut Brook, nitrogen was most likely transferred as well. Thus, assumedly, when the sediment later settled in site 3, much of the nitrogen settled with it and was therefore retained at the streambed. Additionally, a presence of sewage at that site may also have caused the TKN in the sediment to be elevated.

4.3 Metals

Metals occur naturally in freshwater due to contact with the grains of the substrate on the riverbed or the sediment in standing water. Metallic constituents can also naturally enter a stream or lake via runoff, when soil is washed into the water during a rain event. Anthropogenic sources are quite possible as well, especially when a river traverses through an urban area, or in the case of Nut Brook, flows across a heavy industrial zone. The ground in the watershed can become contaminated with various trace metals when people are using it for industrial, waste, transportation, recreational, or building purposes. This contamination can easily reach a river system when it rains, due to runoff. Metals can also enter a stream as a point source component when contaminants are placed directly into the water, such as what happens when an effluent discharge pipe is positioned on a river.

Metals can occur as particulate matter in the water, such as suspended or settled solids, and they can also be in a dissolved form, which is the more bioavailable form. The toxicity, or bioavailability in this case, of certain trace metals in river water to aquatic life is dependent upon certain factors such as temperature, hardness, and pH, and these characteristics sometimes need to be taken into account when determining the overall toxicity or safety of the water (CCME, 2003). The bioavailability of a trace metal is often linked to its overall solubility and these factors play a big role in determining the extent of the solubility of a metal in the river. For example, a higher temperature is often associated with an increase in solubility, and conversely, a decrease in pH and hardness also often results in a higher solubility (CCME, 2003).

The settling of particulate matter adds additional metallic constituents to the sediment on the riverbed as well. The sediment is essentially a reservoir for metals since these constituents tend to adsorb to the surfaces of the grains in the substrate, which then remain for longer periods of time on the riverbed (CCME, 2003). These trace metals can then either affect the benthic environment directly, or slowly become released into the water column during periods of changes in various water quality parameters.

The section of Nut Brook in study would be expected to have a higher occurrence of some trace metals due to the fact that it would pick up metals naturally from the erosive effects of its traverse along the sediment, soil and bedrock, but also due to the fact that it cross-sects Incinerator Road at various points. Additionally, the bioavailability of some of these metals might also be increased due to warmer summer water temperatures,

however as it will be discussed in section 4.4 due to the relatively high levels of hardness at some of the sites, this effect would be expected to be less in some cases.

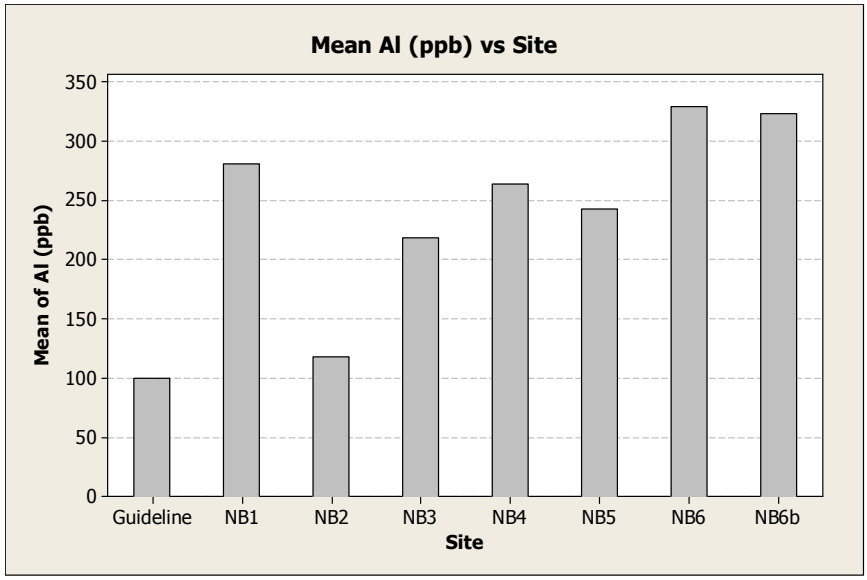
The mean concentrations of some of the metals in the water and the sediment samples are displayed in the following graphs. For organisational purposes, discussions of the trace metal analyses for each graph will occur in the following subsections. All of the raw ICP-MS data resulting from the metal analysis of the water and sediment samples are available in the Appendix. For further reading, detailed descriptions of possible trace metal sources in urban waters for some of the listed metals are available in a report by Powell (1998), which dealt with various constituents entering St. John's Harbour through runoff in the Waterford Basin. An important trend will occur in many of the following subsections and graphs in that the water in site 1 will usually be observed to have the lowest mean values, and that the water in the other sites will often have much higher values. Site 6b will usually show to have by far the highest loadings, and sites 2 and 3 will often be simultaneously noted to have higher mean values, relative to the reference site, for the same parameters. These often reoccurring results will help to aid their associated interpretations.

It should be noted that not all of the results were mentioned here because many of them occurred in very low concentrations or were not detected by the ICP-MS method. However, most of the mentioned figures were based on discussions related to the paper by Powell (1998). If they were available, Canadian Council of Ministers of the Environment (CCME) guidelines for the protection of aquatic life (2003) for some of the metals in freshwater and freshwater sediments are also included for comparison, although in some cases the guidelines were site specific and could not always be included in the graphs. These cases will be noted where applicable.

In the case of the sediment samples, only metals that had CCME related guidelines for sediment in freshwater were discussed in the following subsections. The guidelines related to sediment were broken into two levels of guidance by the CCME (2003). The first was the Interim Sediment Quality Guideline (ISQG), which is a level above which there is scientific evidence leaning towards the possibility that there could be adverse environmental effects. The second was the Probable Effect Level (PEL), above which it has been scientifically shown that there would be a great chance of adverse environmental effects.

4.3.1 Aluminum (Al)

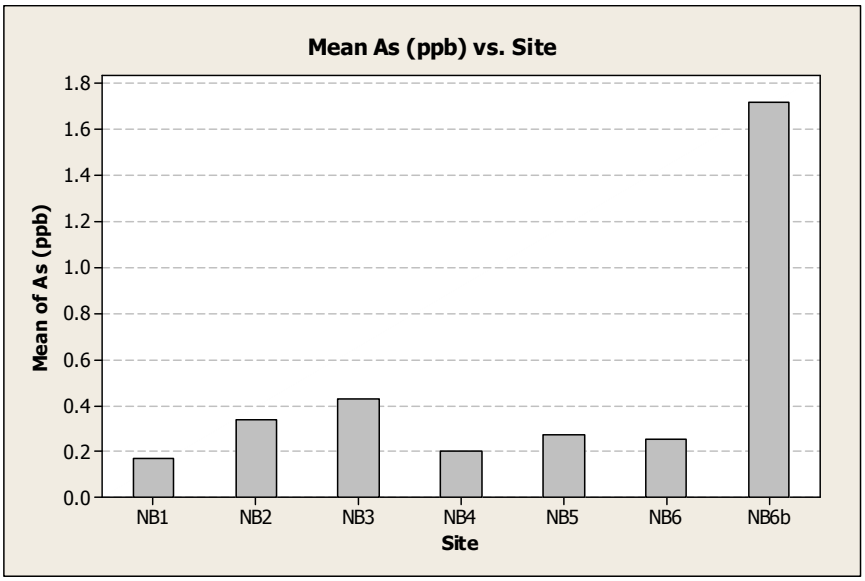
Figure 11: *Mean concentrations of aluminum (Al) in ppb per sample site in the Nut Brook water samples, with a maximum CCME guideline (for the protection of aquatic life, 2003) of 100 ppb derived according to the relative calcium (2^+) ion, pH, and dissolved oxygen content of the samples.*



With respect to the reference site at a mean value of 281.1 ppb, the only value of aluminum in Nut Brook that was statistically different was site 2 (*Appendix C*), and that site had a far lower mean value at 118.3 ppb. In fact, only sites 6 and 6b had slightly higher mean values at 329.2 ppb and 323.3 ppb respectively (*Figure 11*). Thus, despite the fact that a guideline of 100 ppb had been set by the CCME (2003) as a maximum concentration of aluminum allowable for the protection of aquatic life in freshwater (given certain parameters, such as pH, dissolved oxygen, and calcium II ions in the water at each site), it was likely that the aluminum in the water was naturally occurring since the mean value was high at the reference site as well.

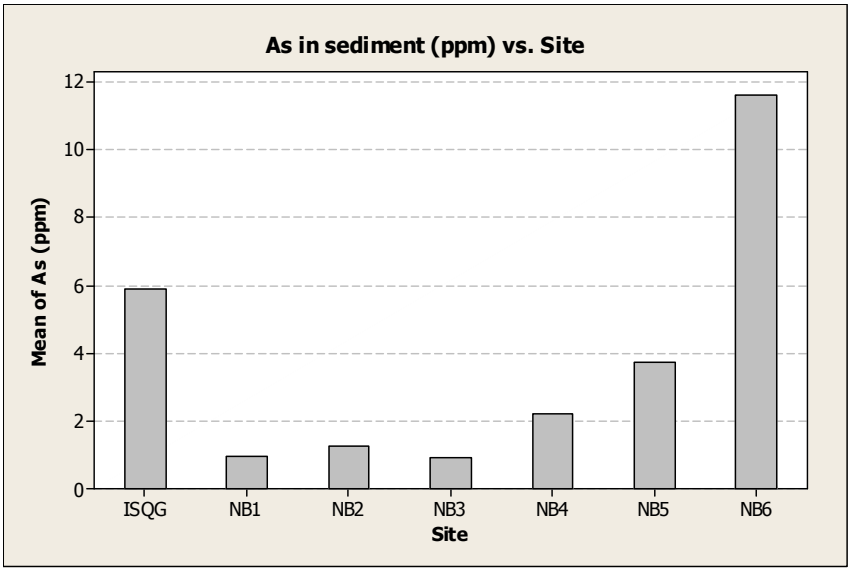
4.3.2 Arsenic (As)

Figure 12: *Mean concentrations of arsenic (As) in ppb per sample site in the Nut Brook water samples.*



The CCME guideline regarding arsenic for the protection of aquatic life in freshwater is set at 5.0 ppb (2003), but none of the samples in Figure 12 had mean values even close to this limit. A slight spike in sites 2 and 3 at mean concentrations of 0.34 ppb and 0.43 ppb respectively was noted in comparison to site 1 at 0.17 ppb, however a TEV test in the statistical analysis gave a high p-value (>0.05) and thus showed there was no significant variance between the values of As at each site. It was likely for that reason that much of the element was naturally occurring. Any accurate interpretation was difficult to obtain because most of the raw values were below the detection limits of the method used to create the results (*Appendix* A). According to statistical advice received, it is occasionally feasible to divide the results in half because it can sometimes give an approximate estimate of what the actual values could be (M. Pippy, personal communication, October 19th, 2005), which was what was done here. It should be noted that site 6b had a notably higher concentration of arsenic than the other sites at 1.72 ppb (*Figure 12*).

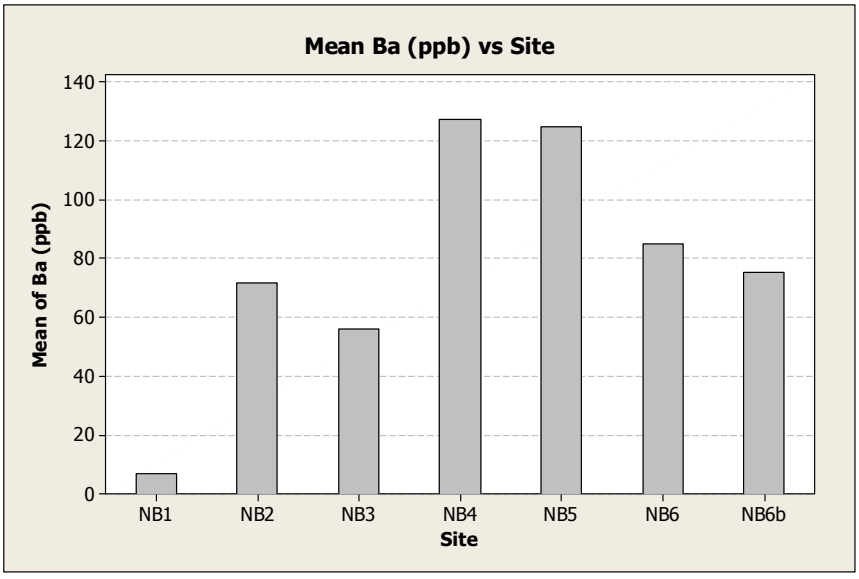
Figure 13: *Concentrations of arsenic (As) in ppm per sample site in the Nut Brook sediment samples, with a CCME Interim Sediment Quality Guideline (ISQG) of 5.9 ppm (for the protection of aquatic life in freshwater sediments, 2003).*



The CCME interim guideline for arsenic in freshwater sediment for the protection of aquatic life (2003) is 5.9 ppm, and the PEL is 17.0 ppm. Although site 6 greatly exceeded the ISQG at 11.59 ppm, none of the sites exceeded the PEL for arsenic (*Figure 13*).

4.3.3 Barium (Ba)

Figure 14: *Mean concentrations of barium (Ba) in ppb per sample site in the Nut Brook water samples.*

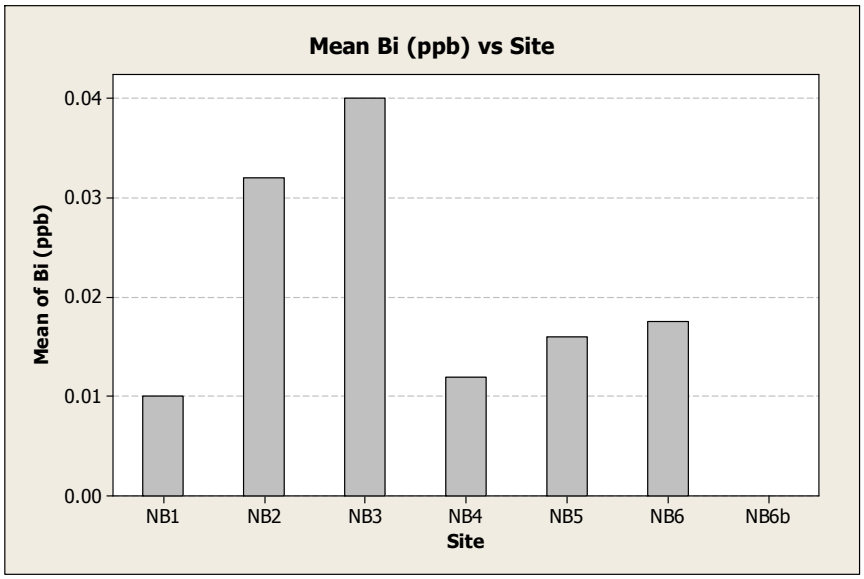


Sites 4 and 5 had the highest mean concentrations of barium in Nut Brook, with respective values of 127 ppb and 125 ppb. Even site 6b at a mean concentration of 75.3 ppb, which in later subsections will show to be extremely polluted, was relatively low in Ba levels compared to sites 4 and 5 (*Figure 14*). Although there was no CCME guideline for Ba for the protection of aquatic life in fresh water, it can be seen in Figure 14 that site 1 at a mean value of 6.81 ppb had a much lower mean value than the other sites.

In a statistical sense, the p-value of the Kruskal Wallis (KW) test was quite low (<0.05), and the results of the ANOVA and Tukey's test show that only site 3 was not significantly different from the reference site. However, the boxplot of barium in Appendix C showed that this fact was debatable as well, since all of the raw data values of sites 2 – 6 were higher (with a minimum magnitude of over 5 times) than the highest value of Ba in site 1 (*Appendix A*). From this overall analysis, it was likely that there was some barium loading into the system.

4.3.4 Bismuth (Bi)

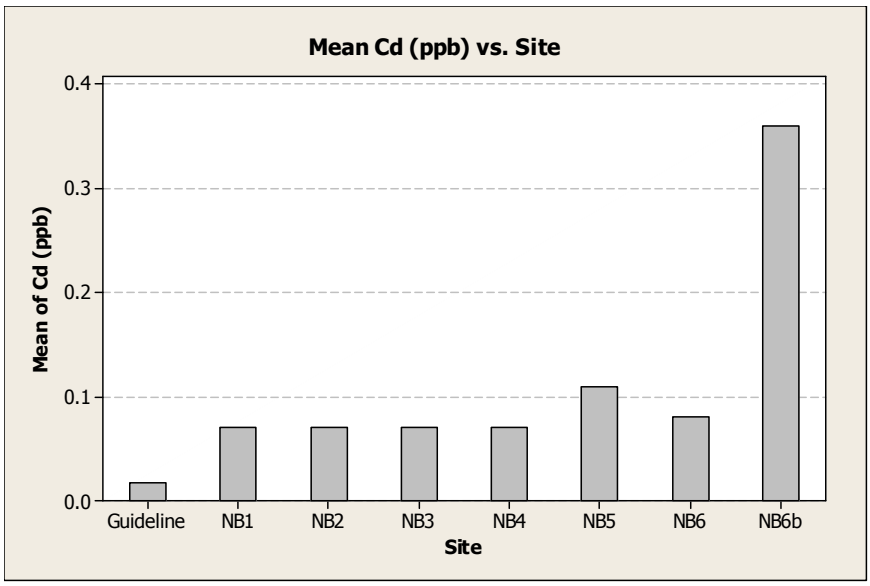
Figure 15: *Mean concentrations of bismuth (Bi) in ppb per sample site in the Nut Brook water samples.*



Bismuth was detected in low quantities in Nut Brook, and many values were below the detection limits. For this reason, any values below the detection limits were divided in half according to statistical advice received on October 19th (M. Pippy, personal communication, 2005) in order to obtain an appropriate estimate of what the mean values could be (between zero and the detection limit). This made the interpretation of Bi difficult, and despite the high p-value of the TEV performed, it was not entirely sure how accurate this result was. However, it can be noted that for the most part, Bi could be detected properly in sites 2 and 3 with mean values of 0.03 ppb and 0.04 ppb respectively (*Figure 15*), meaning that it was possible that they were not naturally occurring, although the mean values were still very small.

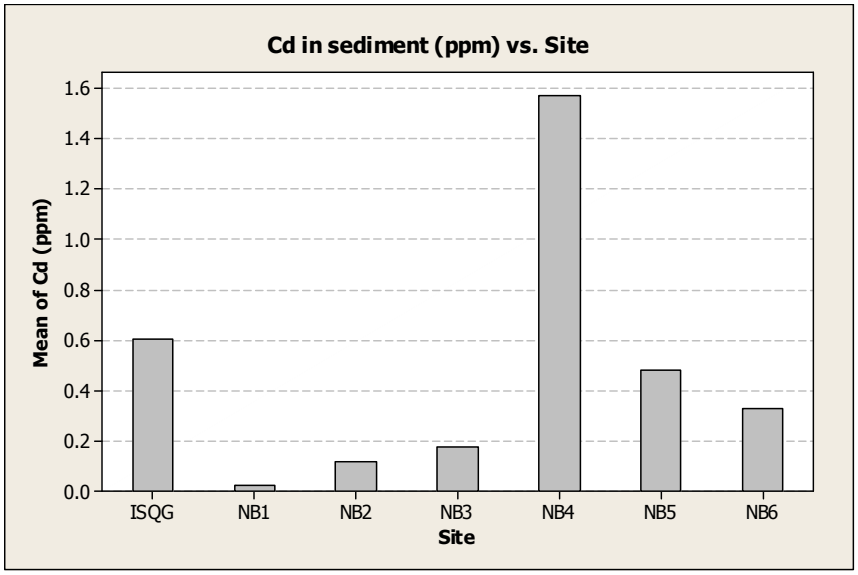
4.3.5 Cadmium (Cd)

Figure 16: *Mean concentrations of cadmium (Cd) in ppb per sample site in the Nut Brook water samples with a CCME guideline (for the protection of aquatic life, 2003) of 0.017 ppb.*



Cadmium was impossible to analyse statistically due to the fact that this element could not be detected for the most part in sites 1 – 4 and 6 (*Appendix A*). In order to make a graph, the detection limits were divided in half, however interpretations could not be made from this alone. On the final sweep, sites 5 and 6b showed a detectable amount of Cd with respective values of 0.18 ppb and 0.36 ppb (*Appendix A*). According to CCME guidelines (for the protection of aquatic life, 2003), a value of 0.017 ppb is dangerous, thus the results obtained in the fourth sweep for sites 5 and 6b were very high. Since the site 6b sample had a very high amount of cadmium in it and site 5 was just downstream, it was probably no coincidence that site 5 also had a high concentration of Cd. Cadmium can be very toxic to aquatic life in high concentrations (CCME, 2003), thus it was a threat to Nut Brook on that particular date of sampling.

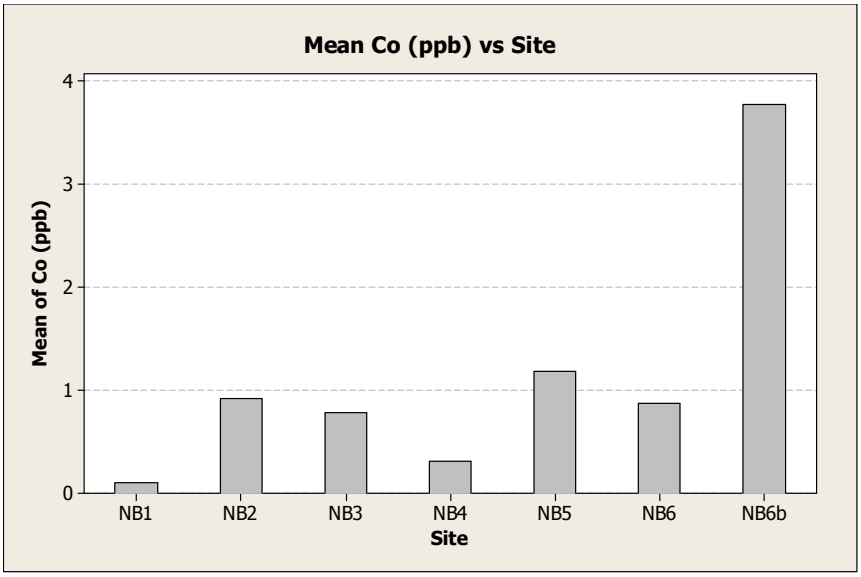
Figure 17: *Concentrations of cadmium (Cd) in ppm per sample site in Nut Brook sediment samples, with a CCME Interim Sediment Quality Guideline (ISQG) of 0.6 ppm.*



The CCME interim guideline for cadmium in freshwater sediment for the protection of aquatic life (2003) is 0.6 ppm, and the PEL is 3.5 ppm. Although site 4 greatly exceeded the ISQG at 1.57 ppm, none of the sites exceeded the PEL for cadmium (*Figure 17*). Site five nearly met the ISQG at 0.48 ppm, and could be related to the fact that cadmium was also detected in the water there at one point. Since site 4 was just downstream of site 5, it was possible that some of the cadmium settled in the sediment as a result of receiving it upstream. Site 4 was quite stagnant; hence cadmium may have been allowed to build up as it entered the Nut Brook pond.

4.3.6 Cobalt (Co)

Figure 18: *Mean concentrations of cobalt (Co) in ppb per sample site in the Nut Brook water samples.*

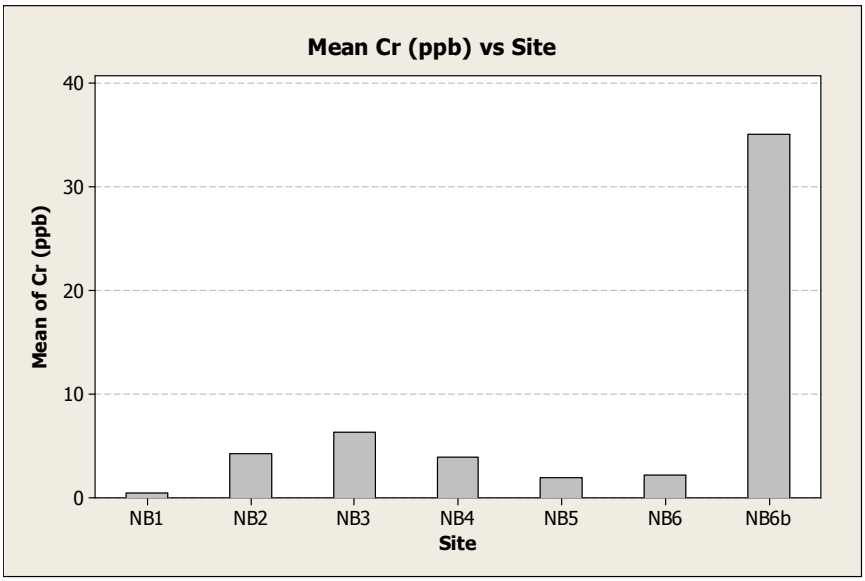


There were no CCME guidelines related to cobalt in freshwater, however it should be noted that all of sites 2 – 6 had a higher mean concentration than site 1 (*Figure 18*), and all of those sites' lowest values (the lowest being 0.2 ppb) were higher than the highest concentration recorded in site 1, which was 0.14 ppb (*Appendix A*). In relation to the other sites, site 6b had a very high concentration at 3.78 ppb.

The statistical analysis showed that the p-value of the Kruskal Wallis (KW) test was <0.05, and the results of the ANOVA and Tukey's test showed that only site 4 was not significantly different from the reference site. However, since the Tukey's test also showed that site 4 was not significantly different from sites 3 and 6 either and that the lowest concentration of Co in site 4 of 0.27 ppb was about twice as high as the highest concentration in site 1 (*Appendix A*), it was quite probable that the reference site differed from site 4 with respect to cobalt as well. The boxplot of cobalt in Appendix C also helps to illustrate this point. From this analysis, there was a likely anthropogenic input of Co to the system.

4.3.7 Chromium (Cr)

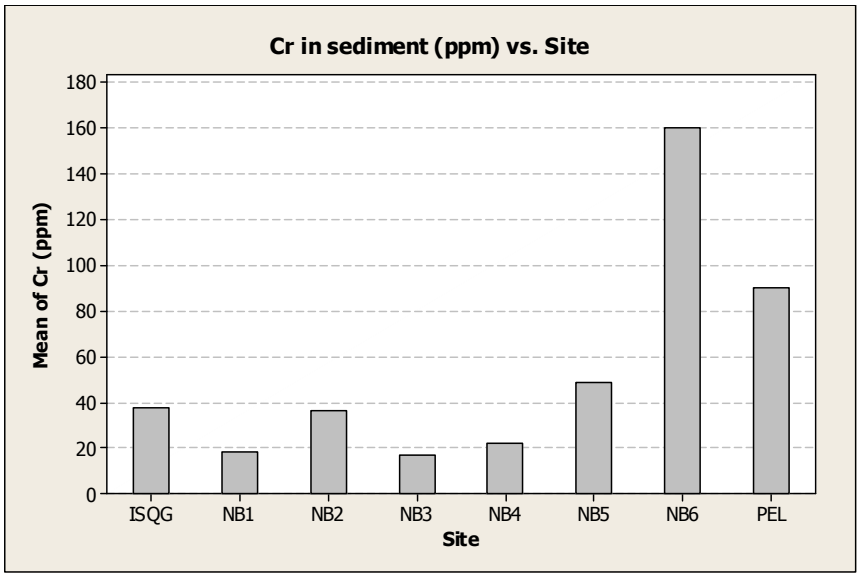
Figure 19: *Mean concentrations of chromium (Cr) in ppb per sample site in the Nut Brook water samples.*



There were guidelines from the CCME (2003) regarding chromium with respect to the protection of aquatic life, however since the valence states of the chromium in the samples were unknown, the guidelines were not directly relevant here. Chromium can be quite toxic, depending upon certain conditions such as the ion's valence state, thus given some of the concentrations recorded in Appendix A, it was possible that Cr was a problem in some of the samples from some of the sites in Nut Brook. The CCME guideline for trivalent chromium (Cr III), for example, was 1.0 ppb; thus since the individual concentrations in every site except for the reference site were higher than 1.0 ppb (*Appendix* A), then if a certain percentage of each sample from 2 – 6 was Cr III, there would be dangerous levels of chromium in Nut Brook. Statistically this would be possible, however it was uncertain if this was the case. From Figure 19, it was observed that the concentration of Cr in site 6b at 35.0 ppb was much higher than all of the other mean values in the other sites, and was thus most likely very toxic.

Of note, the mean concentration in the reference site was again lower than those of all the other sites, indicating a possible anthropogenic input of Cr into Nut Brook. The p-value obtained from the KW test was <0.05, although the results of the ANOVA and Tukey's test showed that sites 5 and 6 were not significantly different from site 1. But since the Tukey's test also showed that site 6 was not significantly different from sites 2 and 4 either and that the lowest known concentration of Cr in site 5 of 1.75 ppb was also higher than the highest known concentration in site 1 of 0.70 ppb (*Appendix A*), it was quite probable that the reference site differed from both sites 5 and 6 with respect to Cr as well. The boxplot of chromium in Appendix C also helps to illustrate this last point. From this data, there was a good chance that there was a certain Cr loading to the system.

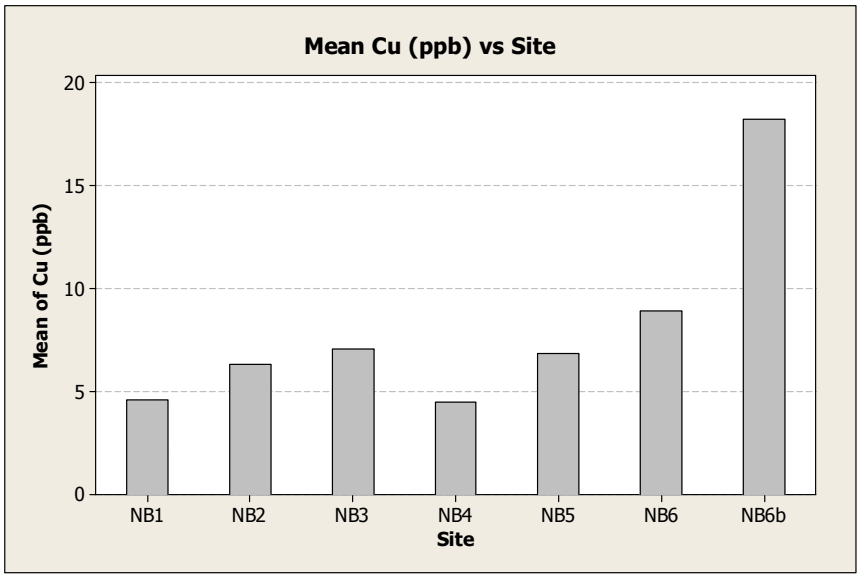
Figure 20: *Concentrations of chromium (Cr) in ppm per sample site in Nut Brook sediment samples, with a CCME Interim Sediment Quality Guideline (ISQG) of 37.3 ppm and a Probable Effect Level (PEL) of 90.0 ppm (for the protection of aquatic life in freshwater sediments, 2003).*



The CCME interim guideline for chromium in freshwater sediment for the protection of aquatic life (2003) is 37.3 ppm, and the PEL is 90.0 ppm. Dangerously high levels of Cr were observed in the sediment sample at site 6 with a concentration of 160.1 ppm, which was nearly twice the PEL. Site 5 exceeded the ISQG at 48.8 ppm, however it did not exceed the PEL for cadmium. None of the other sites had a concentration that surpassed the ISQG, although site 2 came very close with a value of 36.3 ppm (*Figure 20*). It should be noted that some of the chromium may have been naturally occurring due to the fact that site 1 had similar values to those in sites 3 and 4. However, the extremely high Cr level in site 6 indicated an anthropogenic input of this parameter to the sediment at this site.

4.3.8 Copper (Cu)

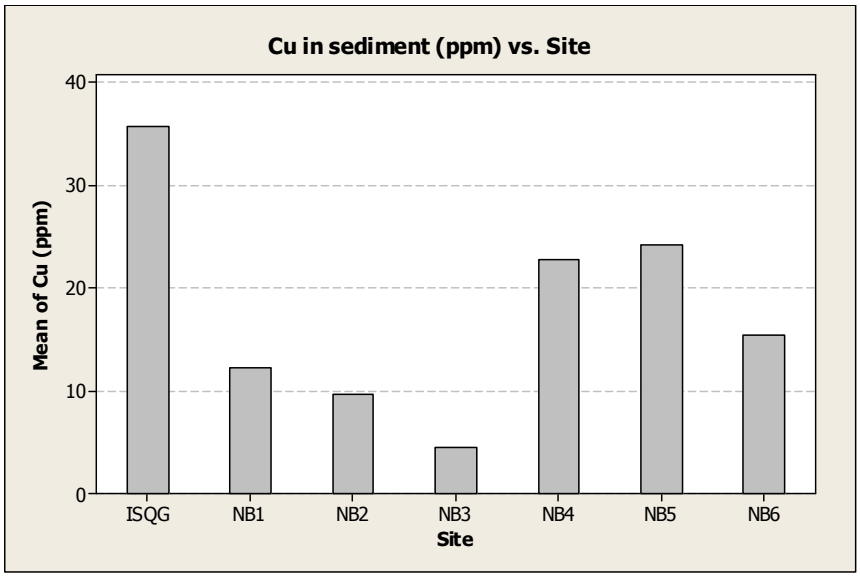
Figure 21: *Mean concentrations of copper (Cu) in ppb per sample site in the Nut Brook water samples.*



There were CCME guidelines related to copper for the protection of aquatic life in fresh water (2003), however they were not included in the graph above because depending upon the $CaCO_3$ concentrations at each site the guideline varied. A description of why the toxicity of a metal such as copper could be affected by the presence of calcium carbonate (*i.e.* $CaCO_3$ hardness) can be found in Section 4.4. The guidelines range from 2.0 ppb to 4.0 ppb, but despite the fact that the sites have varying degrees of hardness associated with them (*Section 4.4*) the mean values of Cu in each station are all above the upper limits (4.0 ppb) of these particular guidelines anyway. Thus, all of the mean values in each site have exceeded the maximum CCME guideline for copper (*Figure 21*). It should be noted, however, that in individual cases not every sample necessarily exceeded the guideline (*Appendix A*), and with a mean value of 4.62 ppb the reference site was almost as high as most of the other sites, and higher than site 4, which had a mean value of 4.48 ppb (*Figure 21*). This could indicate that much of the copper in the system was naturally occurring, and that the ecosystem may have been adapted, thus, accustomed to these dangerous levels, making the concentrations of copper in Nut Brook much less of a threat to the integrity of aquatic life within it. Conversely site 6b did not correlate with this reasoning, as it had a concentration of 18.23 ppb Cu (*Figure 21*). It was more likely in this case that copper was introduced to the system at site 6b.

The statistical analysis showed that the TEV had a high p-value (>0.05), meaning that with the exception of site 6b (not included in stat. analysis) the concentrations of copper in the sites did not significantly vary enough from one another to indicate much anthropogenic input as compared with the naturally occurring amount in site 1.

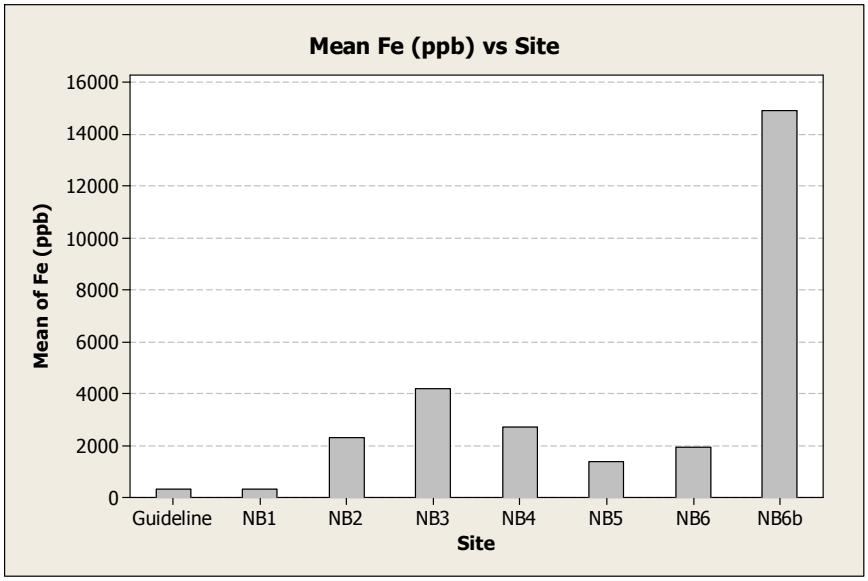
Figure 22: *Concentrations of copper (Cu) in ppm per sample site in the Nut Brook sediment samples, with a CCME Interim Sediment Quality Guideline (ISQG) of 35.7 ppm (for the protection of aquatic life in freshwater sediments, 2003).*



None of the sediment in any of the sites contained enough copper to exceed the ISQG of 35.7, nor did any show levels that nearly exceeded it (*Figure 22*). This would be expected since much of the copper was most likely natural in the system.

4.3.9 Iron (Fe)

Figure 23: *Mean concentrations of iron (Fe) in ppb per sample site in the Nut Brook water samples with a CCME guideline (for the protection of aquatic life, 2003) of 300 ppb.*



With respect to the CCME guideline (2003) of 300 ppb for iron, all of the sites in Nut Brook exceeded it. However, since the reference site barely exceeded it at a concentration of 342.6 ppb and the next lowest concentration was 1393.3 ppb at site 5, it was probable that Fe levels in site 1 were naturally occurring (*Figure 23 above and Figure 24 below*). It should also be noted that site 1 only exceeded the guideline 50% of the time, whereas the other sites were always in exceedance of the guidelines (*Appendix A*). At a concentration of 14,897 ppb, Figure 23 shows the extreme input of iron in site 6b in relation to the unnaturally high amounts found in the other sites 2 – 6. The next highest mean concentration was 4177.5 ppb at site 3. Since this value exceeded the guideline by a factor of about 14, and site 6b had a concentration of just over 3.5 times that of site 3, the amount of Fe in site 6b was enormous at almost 50 times higher than the given guideline. Before doing the statistical analysis, it was clearly evident that iron was very problematic in Nut Brook.

The KW test gave a low p-value (<0.05), and the subsequent ANOVA and Tukey's test showed, with exception to site 5, a significant difference between the concentrations of sites 2 – 6 and the reference site. Since the mean value of site 5 at 1393.3 ppb was nearly 5 times larger than the guideline and over 4 times larger than the concentration at site 1, it was likely that iron originated from an anthropogenic source in site 5 as well. The boxplot of Fe in Appendix C also shows that the lowest value of iron in site 5 was higher than the highest value in site 1. The data presented in Figure 24 further shows that the concentration of iron in sites 2 – 6 was definitely not naturally occurring and very problematic in regard to the ecological health of Nut Brook.

Figure 24: *Mean concentrations of iron (Fe) in ppb per sample site in the Nut Brook water samples with a CCME guideline (for the protection of aquatic life, 2003) of 300 ppb. (Note: for clarity, site 6b was not included here).*

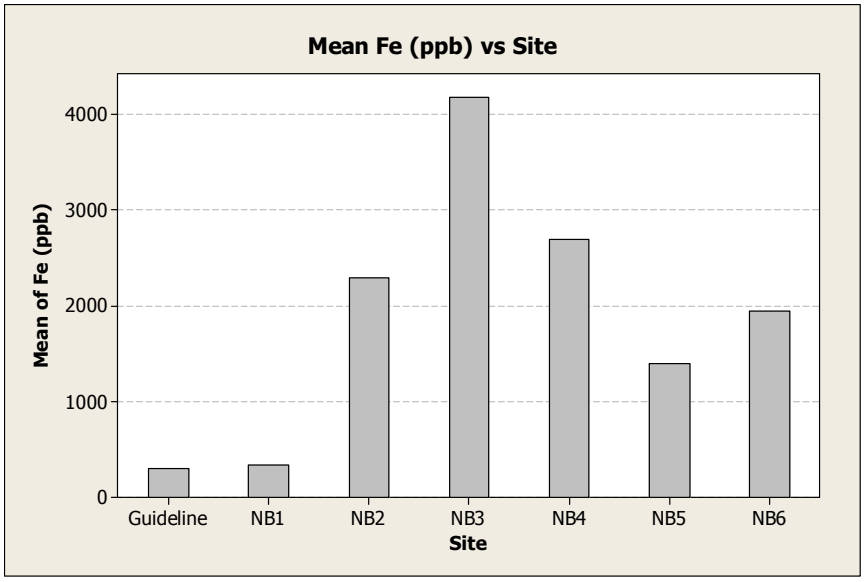
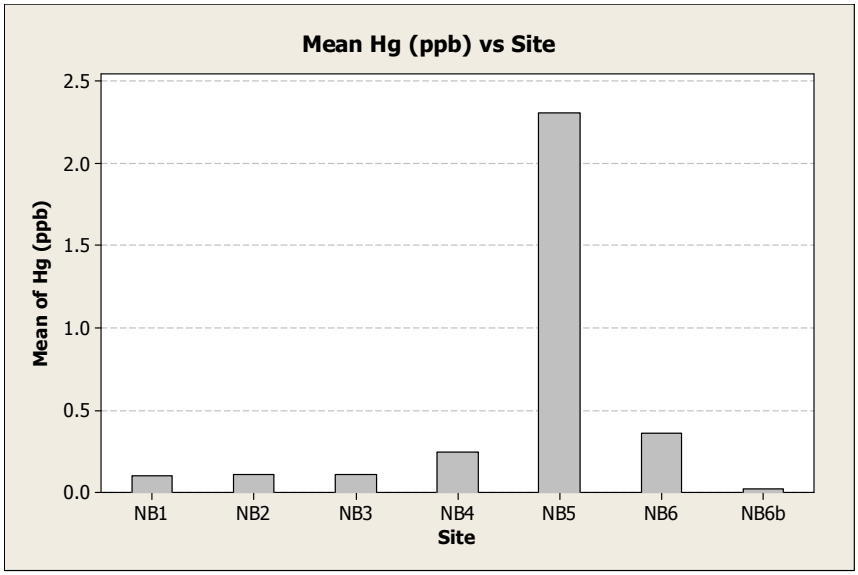


Figure 24 was included to give a more representative illustration of how much more iron was present in sites 2 – 6 in contrast to site 1. This was achieved by removing site 6b from the chart. From this it was quite easy to determine that there was definitely an input of iron from unnatural sources in Nut Brook. The abnormally high mean concentration of 4177.5 ppb in site 3 was also reflective of the leachate suspected to be entering the system from the defunct landfill just upstream, since iron is normally considered to be one of the main constituents in landfill runoff. It was also observed from the red streaks in the sediment that had infiltrated the site that iron was in high enough concentrations to permanently stain the ground. From these observations and interpretations, iron was considered to be a significant threat to this system.

4.3.10 Mercury (Hg)

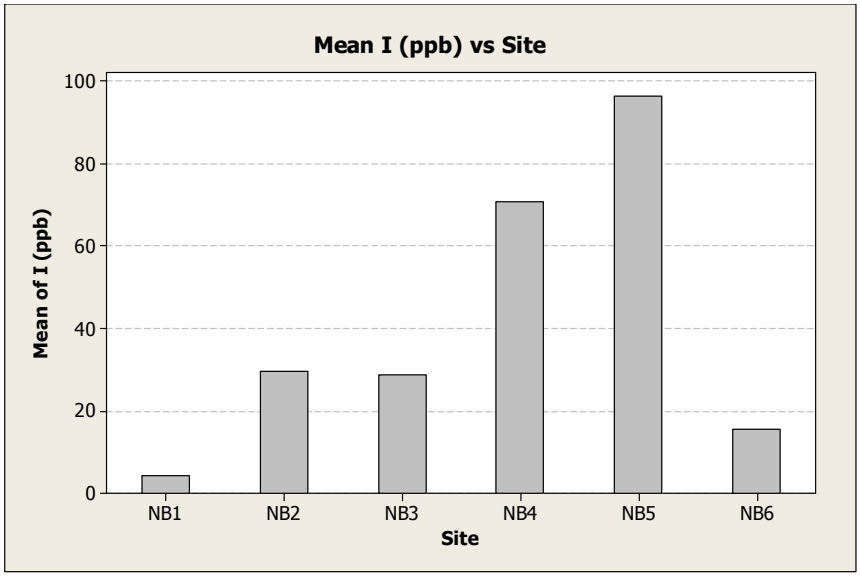
Figure 25: *Mean concentrations of mercury (Hg) in ppb per sample site in the Nut Brook water samples.*



Not much could be interpreted from the mercury results in this case since most of the concentrations obtained from the ICP-MS were below the detection limits. This was generally due to the fact that mercury is one of the few trace elements that will volatilise very easily during the ICP-MS analysis; thus if there was any mercury present in the samples, most of it would have generally been lost as a gas. However, it should be mentioned that despite the fact that ICP-MS was an undesirable method for obtaining Hg concentrations in the water samples, mercury was in fact detected in considerable concentrations in site 5 on more than one occasion and a mean value of 0.24 ppb (*Figure 25*). If the readings were correct, then mercury would be a contributor to adverse conditions at that point in the system. For the reasons discussed in Section 2.1.4, the presence of mercury could be expected to occur due to the proximity of the site to a dam. Hg was also detected once in site 4 and once in site 6 (*Appendix A*), but due to the unreliability of the method used in this case, the results achieved from these samples were also somewhat questionable.

4.3.11 Iodine (I)

Figure 26: *Mean concentrations of iodine (I) in ppb per sample site in the Nut Brook water samples.*



As observed in Figure 26, the reference site had the lowest mean concentration of iodine in Nut Brook with respect to the other sites. Site one also showed very little fluctuation in its individual I concentrations in contrast to the other sites, which had more fluctuations with higher standard deviations (*Appendices A, C*). Additionally the lowest concentration of I in sites 2 – 6 was 8.96 ppb from site 5 and this was nearly twice that of the highest concentration in site 1 at 4.79 ppb (*Appendix A*). Overall, the concentrations in sites 2 – 6 were several to many magnitudes higher than that of site 1, indicating that there may have been some anthropogenic related input of iodine to the system. Runoff from soil disturbance in the area might have been a possible source in this case, since iodine is often found in soil. Of note, on the second sweep, the concentrations detected in sites 4 and 5 at 130.8 ppb and 321.6 ppb respectively were very high in comparison to all other values obtained in all of the sites. Although the result from site 6b was not included in Figure 26, the concentration of iodine at that site was 58.6 ppb, which was quite high with respect to the reference site.

Conversely, although in the statistical analysis a p-value of <0.05 was obtained in the KW test, the results of the ANOVA and subsequent Tukey's test showed that the only site which differed significantly from any of the others was site 4. The lowest concentration of I detected in site 4 was 31.9 ppb (*Appendix A*), and the analysis showed that it was statistically different from sites 1 and 6 with respect to iodine concentrations. Iodine is known to bond easily with organic matter (Goudge, 1986), thus due to the high amount of organic matter in this location and its stagnant nature, Nut Brook Pond is probably an effective sink for iodine. Overall, there may have been some unnatural input of iodine to the system, especially affecting site 4, and probably an isolated incident in site 5 (*see boxplot in Appendix C*). However, it was also possible for some of the sites, such as sites 2, 3, and 6 to have picked up a small amount of iodine naturally and through runoff along the course of the river.

4.3.12 Lithium (Li)

Figure 27: *Mean concentrations of lithium (Li) in ppb per sample site in the Nut Brook water samples.*

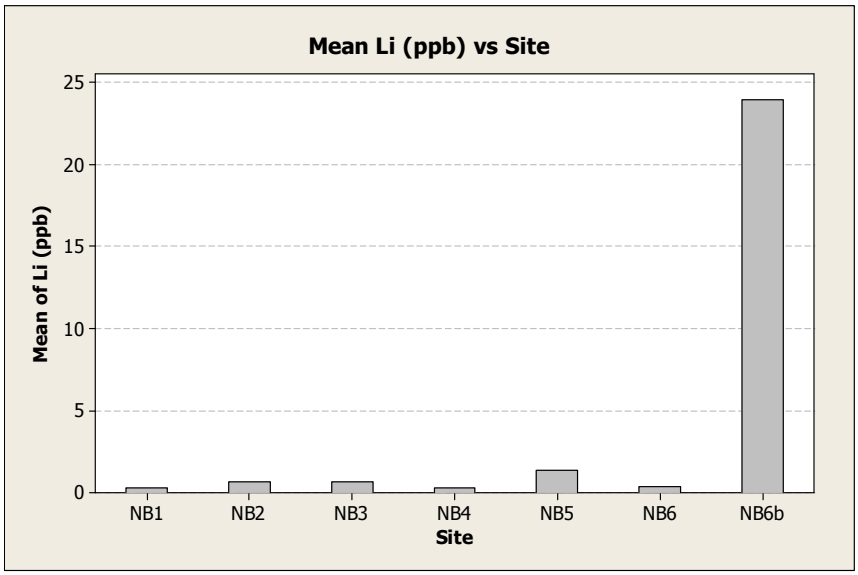
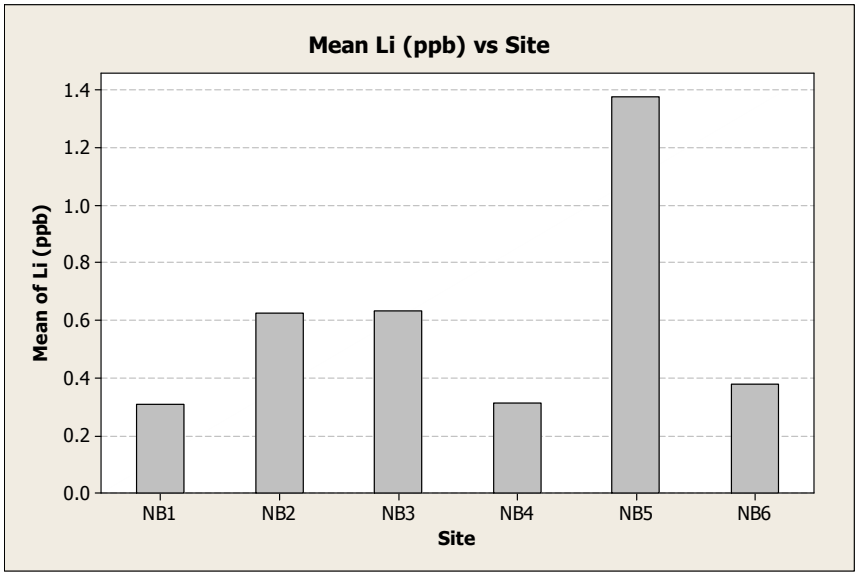


Figure 27 shows the obvious input of lithium into Nut Brook at site 6b. A concentration of 24.0 ppb Li was detected in the sample obtained; the next highest mean concentration was 1.38 ppb at site 5, which, of sites 1 – 6, also had the overall highest individual concentration of 3.98 ppb (*Appendix A*). With respect to site 1 having a mean concentration of 0.31 ppb, it was evident that Li occurred anthropogenically in site 6b. It was unapparent from Figure 27 the amount of Li present in sites 2 – 6 as compared to site 1 due to the high level recorded at site 6b.

Figure 28: *Mean concentrations of lithium (Li) in ppb per sample site in the Nut Brook water samples. (Note: for clarity, site 6b was not included here).*

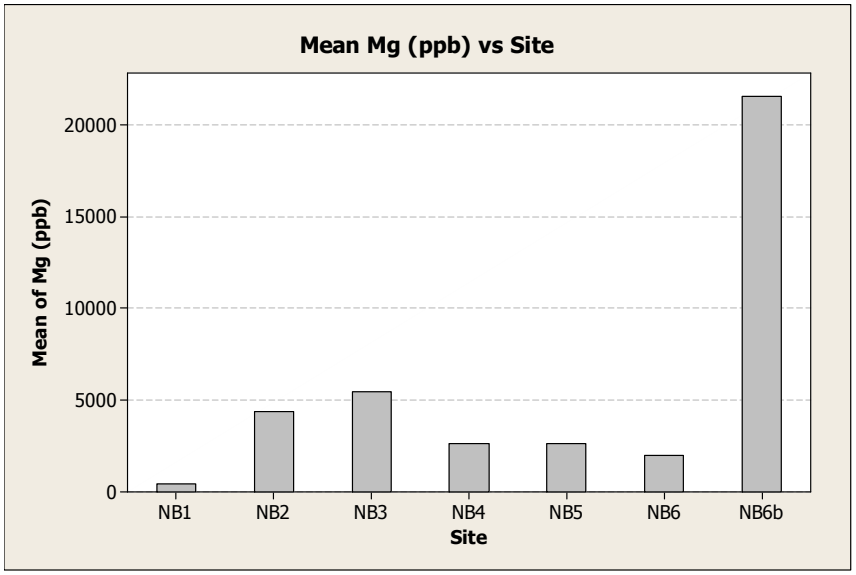


No guidelines exist for levels of lithium in freshwater for the protection of aquatic life and relevant literature is quite limited, so it was uncertain whether any increased Li levels were of real concern in Nut Brook. However Figure 28 was included to give a more representative illustration of how much lithium was present in sites 2 – 6 compared with site 1. This was achieved by removing site 6b from the chart. It was observed that there was a slight spike in mean lithium levels in sites 2 and 3 at 0.62 ppb and 0.63 ppb respectively, and a significant amount (relative to the reference site of 0.31 ppb) in site 5 at a mean concentration of 1.38 ppb. Sites 4 and 6 showed mean Li levels to be similar to that of site 1 (*Figure 28*). Due to the fact that some values in some of the samples were below the detection limits for lithium (*Appendix A*), it should be mentioned that for statistical purposes it was feasible in this case to divide those values in half to obtain a representative figure to derive the mean concentrations shown (*Figure 28*).

The results of the statistical analysis gave a low p-value in the KW test (<0.05) but the ANOVA and Tukey's test showed that only sites 3 and 5 had mean concentrations of lithium that differed significantly from site 1. The boxplot in Appendix C showed that the difference was not extreme for site 3, especially since site 3 had very similar values to that of site 2 (also proven statistically). It was probable that the concentrations of Li in Nut Brook from sites 1 – 4 were mainly naturally occurring. There may have been input, but it would have been slight. Site 5 may have experienced an input of Li from site 6b just upstream, as site 6b was quite contaminated.

4.3.13 Magnesium (Mg)

Figure 29: *Mean concentrations of magnesium (Mg) in ppb per sample site in the Nut Brook water samples.*



There are no CCME guidelines related to magnesium in freshwater for the protection of aquatic life, however it was evident that site 6b was critically contaminated with this element at a concentration of greater than (>) 21,535 ppb (*Figure 29. Note: bar*

for site 6b is lower than actual concentration). The exact concentration is unknown due to the fact that the site was so contaminated the detection limits of the ICP-MS were not high enough to detect the actual amount in the sample. Compared with the mean concentration in the reference site at 453.6 ppb, site 6b had over 47 times the amount of Mg than that of site 1. This greatly shadows the fact that the lowest mean concentration of Mg in sites 2 – 6 was still more than 4 times the mean of site 1, at 2003.4 ppb in site 6.

Figure 30: *Mean concentrations of magnesium (Mg) in ppb per sample site in the Nut Brook water samples. (Note: for clarity, site 6b was not included here).*

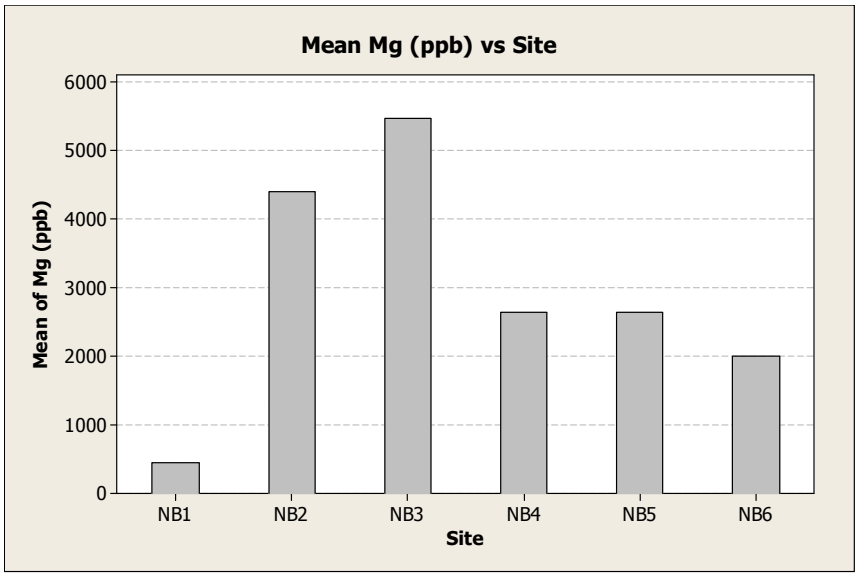
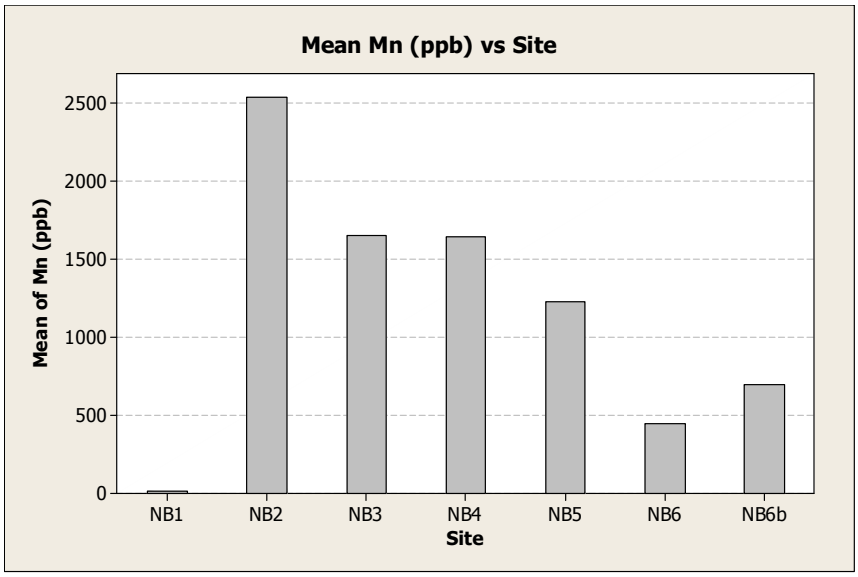


Figure 30 was included to give a more representative illustration of how much more magnesium was present in sites 2 – 6 compared with site 1. This was achieved by removing site 6b from the chart. Of note, all of the sites from 2 – 6 had a higher mean concentration of Mg than in site 1. Site 3, which had a mean concentration of 5478.8 ppb, was greater than 12 times that of the reference and could be reflective of leachate entering that site (*Figure 30*). Site 2, which had a mean concentration of 4397.8 ppb, was most likely influenced from the contamination upstream at site 3.

The KW test in the statistical analysis gave a low p-value (<0.05), and from the results of the ANOVA and Tukey's tests, the concentrations of Mg at site 1 were shown to be statistically different from those of the other sites, except for site 6. Although it was still shown in Figure 30 that the mean concentration of site 6 was four times as large as that of site 1. The boxplot of Mg in Appendix C further illustrates this, and easily shows the overall contamination of all the sites with respect to the reference site. Site 6 was also shown to be statistically similar to sites 4 and 5, which were shown to be statistically different to that of the reference site. The fact that the Tukey's test did not recognise any significant difference from the concentrations of sites 1 and 6 can easily be debated. Of interest, the concentrations at site 3 were shown to be significantly different from those at all the other sites except for site 2. This reflects the additional contamination from the landfill runoff at site 3 as it traveled downstream to site 2.

4.3.14 Manganese (Mn)

Figure 31: *Mean concentrations of manganese (Mn) in ppb per sample site in the Nut Brook water samples.*



In a similar sense to the magnesium loadings in Nut Brook, the mean concentrations of manganese detected were also very high with respect to the reference site. In fact, the lowest mean concentration of sites 2 – 6b was about 446 ppb in site 6, which was about 34 times higher than the mean concentration of site 1 at 13.1 ppb. The highest mean concentration was 2539.7 ppb at site 2, which was more than 193 times that of the reference site (*Figure 31*). There was no CCME guideline with respect to Mn for the protection of aquatic life, so it is unclear in this regard as to whether these concentrations were at dangerous levels. However, Figure 31 clearly shows the difference in the mean Mn concentrations of sites 2 – 6 in contrast to the very low mean value at the reference site, and the fact that the mean values were anywhere from 34 to 193 times that of the natural levels is also a potential indicator of stress.

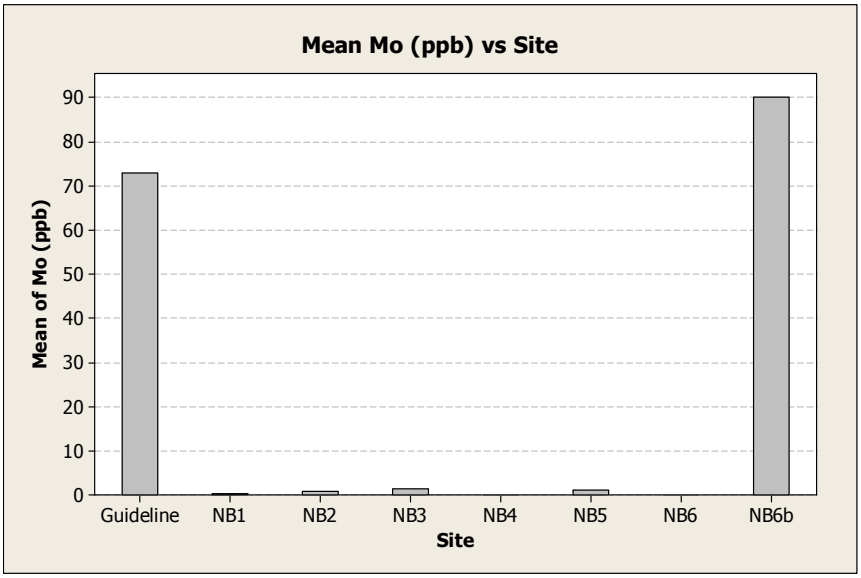
Manganese is generally known to be an essential trace element to aquatic life at low concentrations, but can be potentially toxic at higher levels. The Province of BC has proposed its own criteria for Mn for the protection of aquatic life that is directly dependent on the hardness of the water, thus in this case where the hardness ranged from about 50 ppm to about 125 ppm for sites 2 – 6 to over 300 ppm for site 6b (*Section 4.4*), the guideline ranged from 1100 ppb to over 3800 ppb (Government of BC, 2001). Not including the reference site, all of the mean concentrations except for sites 6 and 6b exceeded this guideline. It is interesting to note that although the concentration in the site 6b sample seemed high, the value detected was relatively low; thus site 6b was not a great contributor of Mn in this case.

The statistical analysis gave a low p-value (<0.05) in the KW test, and the ANOVA and Tukey's tests showed that the concentrations of sites 2 – 5 were significantly different than the reference site. Again, the Mn in site 6 was still in a much

higher concentration than site 1, which indicates a somewhat unnatural occurrence. The boxplot in Appendix C helps to illustrate this as well.

4.3.15 Molybdenum (Mo)

Figure 32: *Mean concentrations of molybdenum (Mo) in ppb per sample site in the Nut Brook water samples.*

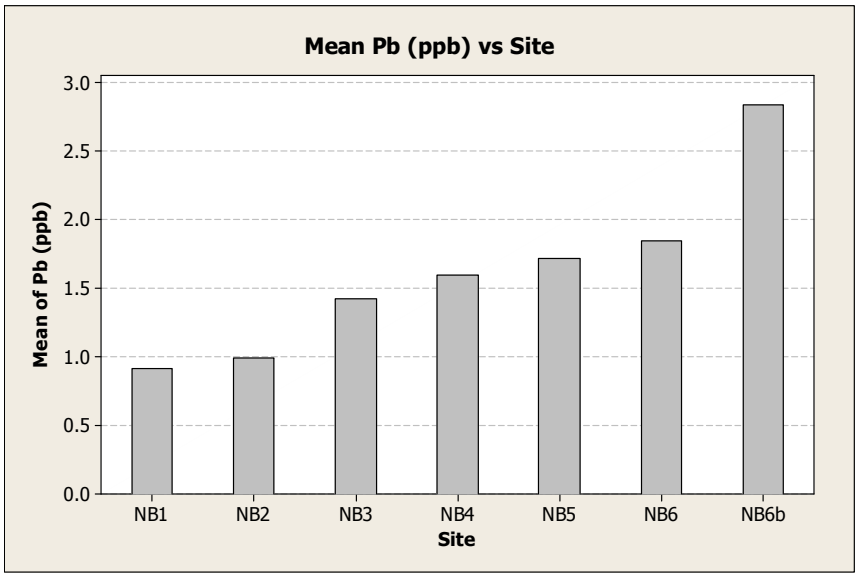


None of the mean concentrations from any of the sites from 1 – 6 came close to exceeding the CCME guideline of 73.0 ppb for molybdenum for the protection of aquatic life (2003), however the concentration of Mo in site 6b did exceed this guideline at 90.1 ppb (*Figure 32*). The dangerously high concentration of Mo at site 6b was over 450 times the mean concentration of the reference site, which was 0.2 ppb. It should be noted that many of the values in the reference site, as well as those in some of the other sites, were divided in half to obtain a workable number to statistically derive the mean since these were values that fell below the detection limits.

Despite the fact that the mean concentrations of all the sites were very low, the ANOVA and Tukey's tests in the statistical analysis still showed, after giving a low p-value (<0.05) in the KW test, that sites 2, 3 and 5 were significantly different in concentration to that of the reference site. This indicates that there may have been a slight anthropogenic source of molybdenum in these parts of Nut Brook as well.

4.3.16 Lead (Pb)

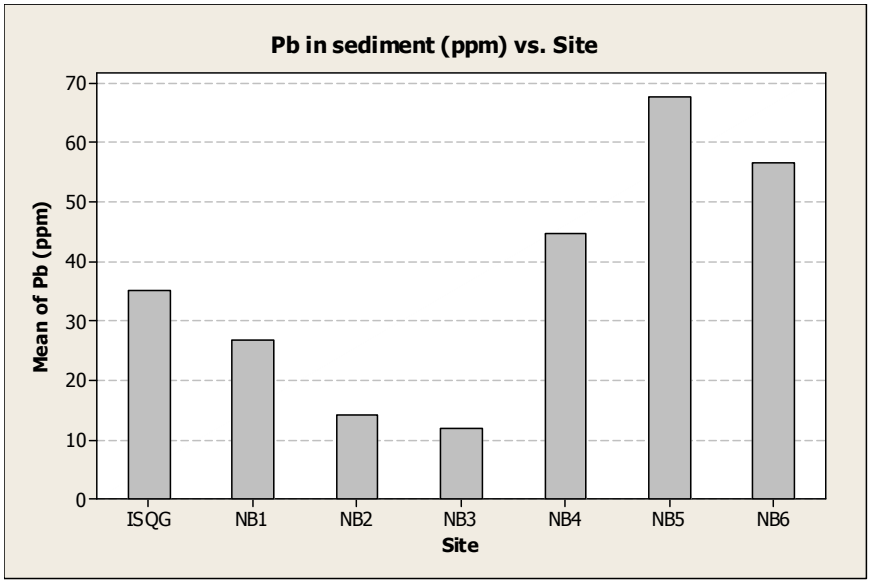
Figure 33: *Mean concentrations of lead (Pb) in ppb per sample site in the Nut Brook water samples.*



The CCME guideline for the protection of aquatic life for lead (2003) varied from 1 – 7 ppb due to its dependency upon the degree of hardness in the water samples and thus was not included in Figure 33 since the hardness differed from sample to sample (*Section 4.4*). Although Pb is one of the few non-essential elements for life and can be quite toxic, only the mean concentrations of sites 4 – 6 exceeded the guideline due to the lower levels of hardness (<60 mg/L) in relation to the amount of Pb detected in the water at those sites. In the case of sites 4 – 6, the guideline would have been 1.0 ppb, and the lowest mean concentration of the three sites was 1.60 ppb in site 4. The highest was 1.85 ppb in site 6 (*Figure 33*). The level of hardness in sites 2, 3, and 6b was high enough to mitigate the effects of the lead, thus raising the guideline higher than the mean levels detected in those sites.

Statistically, the TEV test gave a p-value of greater than 0.05 meaning that none of the sites had mean concentrations that were significantly different from one another, indicating a possible natural occurrence of lead in the system. It should be noted, however, that all of the sites had concentrations of lead that were higher than the reference site, which had a mean concentration of 0.92 ppb (*Figure 33*). This indicates that there may have been a slight input of lead to the system from the activity on Incinerator Road, especially in sites 5 – 6b, where the concentrations were the highest. However much of it may still have been naturally occurring. The boxplot in Appendix C helps to show this.

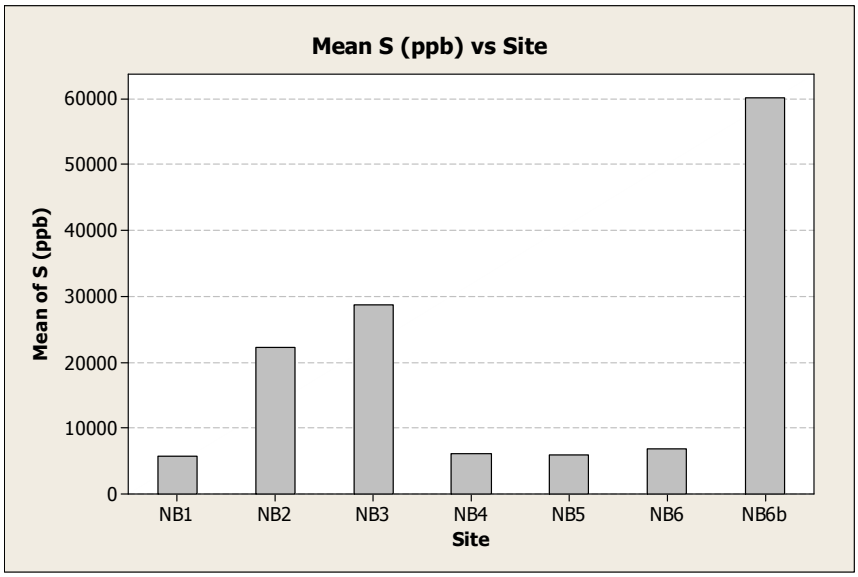
Figure 34: *Concentrations of lead (Pb) in ppm per sample site in the Nut Brook sediment samples, with a CCME Interim Sediment Quality Guideline (ISQG) of 35.0 ppm.*



The CCME interim guideline for lead in sediment for the protection of aquatic life (2003) is 35.0 ppm. Although the PEL is 91.3 ppm, no samples exceeded this extreme. Sites 4 – 6 did exceed the ISQG, with site 5 having the highest concentration of Pb at 67.6 ppm (*Figure 34*). These were the same sites that exceeded the freshwater guidelines for lead, and may support the above indication that there may have been an additional input of lead to the system. It was interesting to note, however, that the lowest concentrations of Pb in the Nut Brook sediment came from sites 2 and 3 at 14.1 ppm and 12.8 ppm respectively, while the reference site had a higher concentration of 26.7 ppm, indicating a natural occurrence in these areas (*Figure 34*).

4.3.17 Sulphur (S)

Figure 35: *Mean concentrations of sulphur (S) in ppb per sample site in the Nut Brook water samples.*

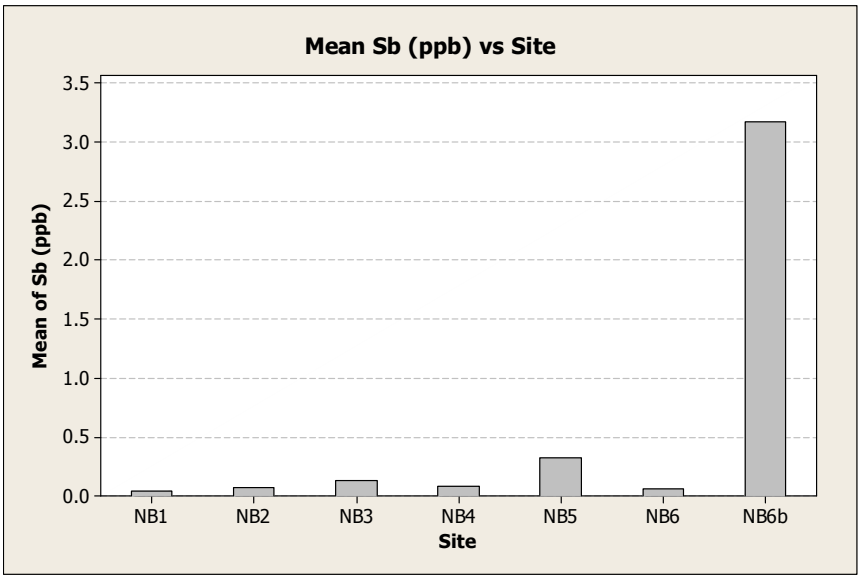


Sulphur was largely undetectable in sites 1, 4, 5 and 6, but was detected in every case in sites 2 and 3, and also in a much higher concentration in site 6b. The mean concentration of S in sites 2 and 3 was 22286.8 ppb and 28693.3 ppb respectively (*Figure 35*) and possibly indicates the presence of leachate in these sites, especially since site 3 was the most concentrated and most adjacent to the dumpsite. There were no CCME guidelines available to gauge whether the mean concentrations of S in sites 2 and 3 were of detriment to Nut Brook at those mean concentrations, but it should be noted that sulphur is often found in various compounds such as sulphate, which could be harmful to aquatic life in certain conditions. Also of note was the very high concentration found in site 6b at 60151 ppb, which reflects the contaminated nature of that site very well (*Figure 35*).

A low p-value (<0.05) was scored in the KW test of the statistical analysis for sulphur. From the accompanying ANOVA and Tukey's tests, it was determined that the values obtained for sites 2 and 3 were significantly different than those obtained for the reference site. This added strength to the evidence of sulphur loading in Nut Brook due to leachate at those points.

4.3.18 Antimony (Sb)

Figure 36: *Mean concentrations of antimony (Sb) in ppb per sample site in the Nut Brook water samples.*



The purpose of Figure 36 was to show the extent of contamination by antimony at site 6b in comparison to all of the other sites. At a concentration of 3.17 ppb, site 6b was almost 10 times more concentrated than the site with the next highest mean concentration, which was site 5 at 0.32 ppb. Site 5 most likely received its Sb load from site 6b just upstream. Although Sb is known to be toxic to aquatic life in certain quantities, there was no CCME guideline related to Sb in fresh water, so it was uncertain as to whether this was having a detrimental effect on Nut Brook.

Figure 37: *Mean concentrations of antimony (Sb) in ppb per sample site in the Nut Brook water samples. (Note: for clarity, site 6b was not included here).*

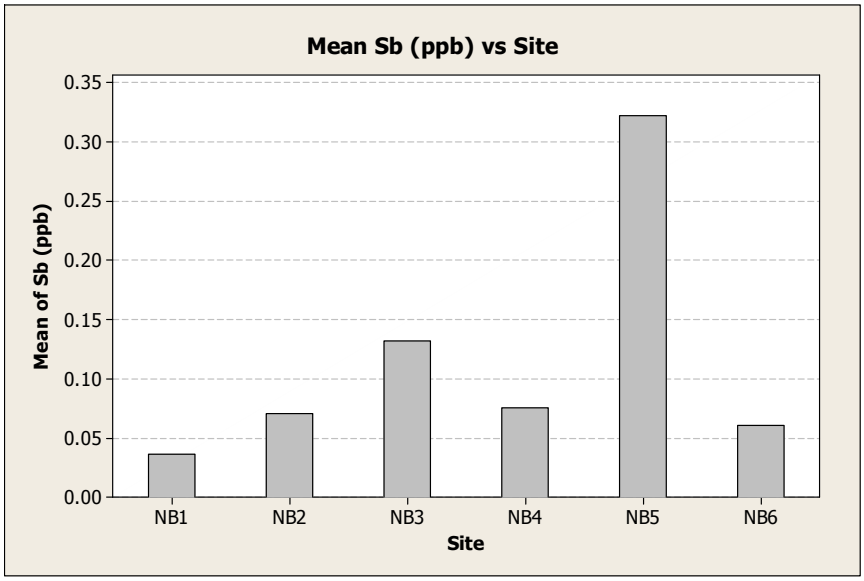


Figure 37 better shows the relation of antimony to the reference site with respect to sites 2 – 6 due to the fact that site 6b was not included in this graph. It can be seen from the figure that the reference site, in which Sb was barely detected, had the lowest mean concentration of all the sites at 0.03 ppb, which was over 10 times less than the mean concentration of site 5 at 0.32 ppb. It should be noted that some of the individual values had to be divided in half for site 1 in order to statistically derive the mean, due to the fact that those values fell below the detection limits (*Appendix A*).

After a low p-value was obtained in the KW test (<0.05), the ANOVA and Tukey's tests in the statistical analysis showed that the mean concentrations of antimony in sites 3 and 5 at 0.13 and 0.32 ppb respectively were significantly different than that of the reference site. This indicated that these sites were possibly anthropogenically contaminated, but due to the low mean concentrations the extent of the contamination was probably not high.

4.3.19 Thallium (Tl)

Figure 38: *Mean concentrations of thallium (Tl) in ppb per sample site in the Nut Brook water samples.*

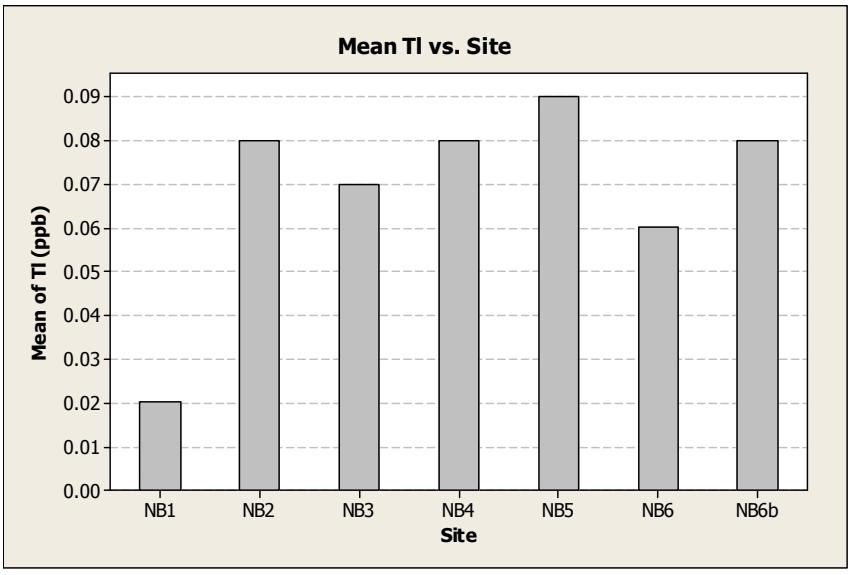


Figure 38 shows increased elevations of thallium in the Incinerator Road area in contrast to the reference site. The lowest mean concentration of sites 2 – 6 was in site 6, which had a mean concentration of 0.063 ppb, whereas site 1 had a mean concentration of 0.02 ppb. The highest mean concentration occurred in site 5 at a value of 0.092 ppb. Of note, in every case on sweeps 2 and 3 all of the sites from 2 – 6 had low concentrations and were sometimes below the detection limits. Where applicable, these values were divided in half to statistically obtain the associated means. However, the values were much higher in every case on sweeps 1 and 4 from sites 2 – 6 (*Appendix A*). There was a CCME guideline related to Tl for the protection of aquatic life (2003) set at 0.8 ppb, but since none of the mean concentrations came close to this, the increased values were of no importance.

The KW test gave a p-value of greater than 0.05, hence statistically there was no significant difference in the mean concentrations between any of the sites. From Figure 38 it would appear that there is some input of Tl to the system downstream from the reference site, however the anthropogenic extent appears to be minimal in this case.

4.3.20 Uranium (U)

Figure 39: *Mean concentrations of uranium (U) in ppb per sample site in the Nut Brook water samples.*

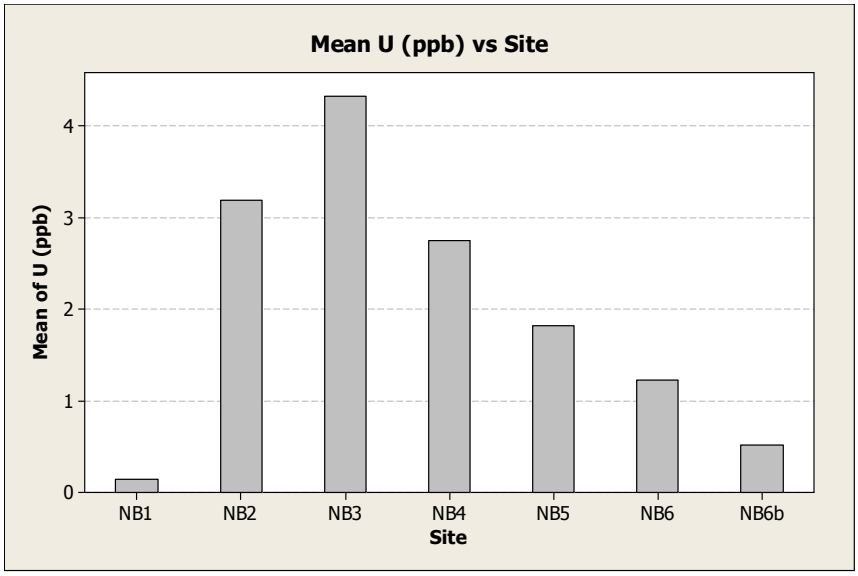


Figure 39 shows that the mean concentrations of uranium in Nut Brook were higher in sites 2 – 6 than in site 1. The reference site showed a mean concentration of 0.14 ppb, whereas the next lowest mean was in site 6 at 1.22 ppb, which was almost 9 times higher. The highest mean concentrations occurred in sites 2 and 3 at 3.19 ppb and 4.33 ppb respectively (*Figure 39*). The mean concentration of site 3 was about 31 times higher than the reference site, and it was possible that this may have occurred due to the sedimentation since U, which is naturally present in the Earth's crust, may have been released and transported during the quarrying process. The relatively high value in site 2 may also reflect this as it received a lot of sediment from upstream. It was interesting to note that site 6b did not appear to be very contaminated with U at a concentration of 0.52 ppb.

After the TEV test in the statistical analysis gave a low p-value (<0.05), the ANOVA and Tukey's tests showed that the mean concentrations of uranium in sites 2 – 4 were significantly different from the reference site. It was possible that some of it was naturally occurring, especially in sites 5 and 6, but the higher values in sites 2 – 4 indicate a more anthropogenic input at those sites. The boxplot in Appendix C helps to illustrate this. Uranium can be radioactive and toxic in certain forms and concentrations, but there was no CCME guideline related to U for the protection of aquatic life, thus it was unclear as to whether any extra U in the system was detrimental.

4.3.21 Zinc (Zn)

Figure 40: *Mean concentrations of zinc (Zn) in ppb per sample site in the Nut Brook water samples with a CCME guideline (for the protection of aquatic life, 2003) of 30 ppb.*

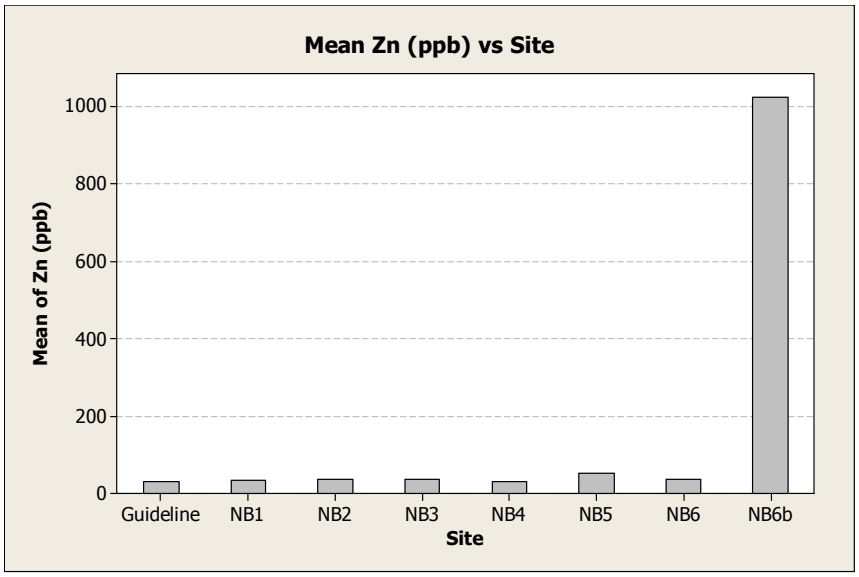
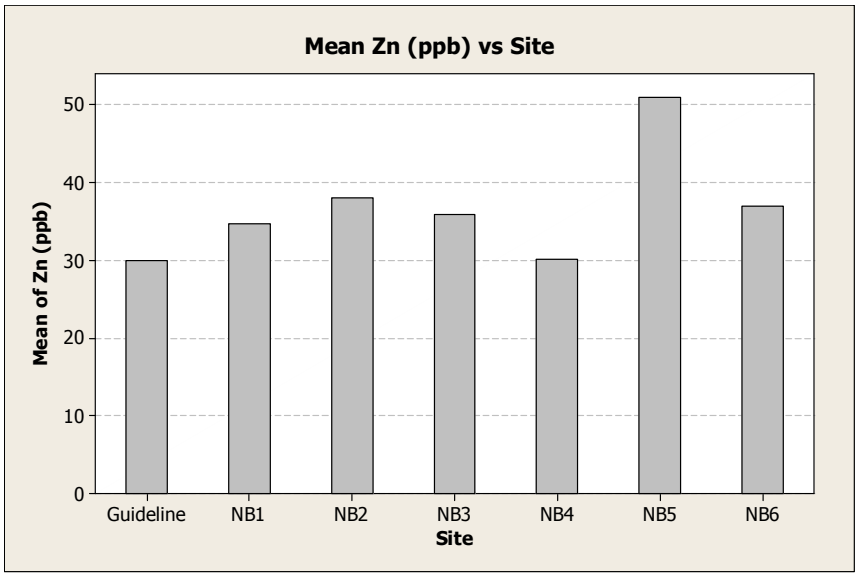


Figure 40 shows the extreme contamination of zinc in the site 6b sample compared with the mean Zn concentrations in all of the other sites. At a concentration of 1023.9 ppb site 6b was over 29 times more contaminated than the reference site, which had a concentration of 34.8 ppb (*Figure 40*). The next highest mean concentration was at site 5 with a value of 50.98 ppb. The slightly higher value of zinc in site 5 was most likely due to the contamination just upstream in site 6b.

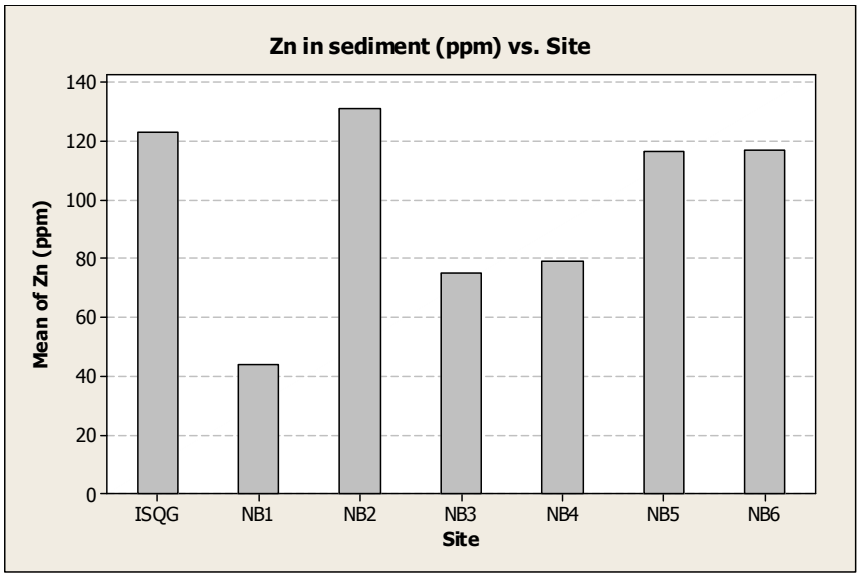
Figure 41: *Mean concentrations of zinc (Zn) in ppb per sample site in the Nut Brook water samples with a CCME guideline (for the protection of aquatic life, 2003) of 30 ppb. (Note: for clarity, site 6b was not included here).*



According to the CCME guidelines for the protection of aquatic life (2003), zinc can be potentially toxic in concentrations greater than 30 ppb. Figure 41 shows that all of the mean concentrations of all the sites had exceeded this guideline, including that of the reference site, and Figure 40 above also shows the high degree in which site 6b exceeded it.

The TEV test in the statistical analysis gave a high p-value (>0.05), thus it was determined that the mean concentrations of zinc in all the sites were not significantly different from one another. Since the mean Zn concentrations in sites 2 – 6 were so similar to site 1, it is safe to say that most of the Zn was naturally occurring. As mentioned above, however, there was a probable slight input to site 5 from site 6b. Other than the extreme concentration in site 6b and the slightly exceeded CCME guideline in all the other sites, zinc was probably not very detrimental to the system in terms of overall concentrations in water due to the fact that it was largely naturally present.

Figure 42: *Concentrations of zinc (Zn) in ppm per sample site in the Nut Brook sediment samples, with a CCME Interim Sediment Quality Guideline (ISQG) of 123.0 ppm (for the protection of aquatic life in freshwater sediments, 2003).*



The CCME interim guideline for zinc in sediment for the protection of aquatic life (2003) is 123.0 ppm. The PEL was 315.0 ppm but no samples came close to this level. Site 2 exceeded the ISQG with a concentration of 131.2 ppm. Sites 5 and 6 nearly exceeded the guideline at concentrations of 116.5 ppm and 116.9 ppm respectively. There may have been a slight anthropogenic input of Zn to the system since the reference site had a relatively low concentration of 44.1 ppm and the other sites had higher concentrations (*Figure 42*). However, considering the above discussion, it was also probable that most if it was naturally occurring.

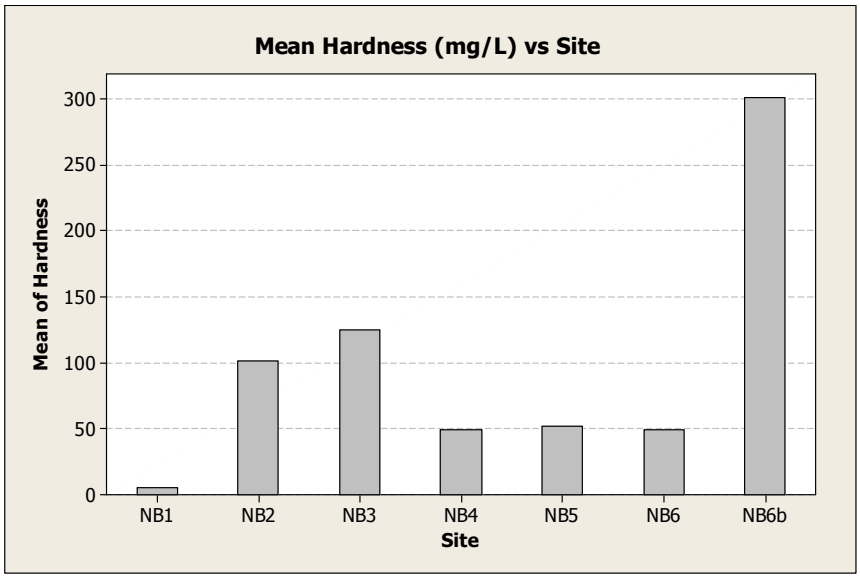
4.4 Hardness

Once the metal analysis for the water samples was complete, the hardness of the water, expressed as the equivalent mg/L $CaCO_{3\ (EQ.)}$, could be summed up using one easily derived formula (*see section 3.3.4.1*). Hardness is mainly regulated by the collective concentrations of calcium and magnesium, but is also slightly affected by the presence of iron, manganese, aluminum, strontium, and barium (CCME, 2003). To get the most representative value for hardness using this method, all of the concentrations resulting from the ICP-MS tests for these elements were taken into account when performing the calculations (*Appendix* A).

Closely related to pH and alkalinity, hardness has the ability to lower toxicity levels in water in some cases. This is particularly due to the fact that metals, for example, tend to form carbonates with calcium and become un-ionized, and thus non – bioavailable. However, this toxicity is directly dependant on the alkalinity and pH of the system as well (CCME, 2003).

The calculated mean values for hardness per sample site are located in the following graph. The raw values for hardness for each site on each sweep are located in Appendix A.

Figure 43: *Mean levels of hardness (expressed as mg/L of equivalent $CaCO_3$) per sample site in Nut Brook.*



The values of hardness in this case were classified as:

Soft: 0 – 20mg/L

Slightly hard: 20 – 60mg/L

Moderately hard: 60 – 120mg/L

Hard: 120 – 180mg/L

Very Hard: >180mg/L

In a region known for particularly soft water, the presence of hardness in this system would indicate the industrial input of the parameters that contribute to hardness. The fact that the samples from the reference site did show very soft water and the rest of the samples were slightly hard to very hard in quality emphasises this. Site 3, the most heavily impacted by the sedimentation, backs this up further because it was shown to be generally hard all the time, except for during sweep 4. The hardness values for sites 2, 3, and 4 plummeted significantly during this time (*Appendix A, sweep 4*). However, those samples were taken during a rain event so they may have been diluted somewhat. Sites 2 and 3, which were shown to be quite mineral heavy had mean values of 101.3 and 124.7 mg/L $CaCO_{3\ (EQ.)}$ respectively, and were reflective of the leachate contamination experienced at those sites. Site 6b showed an obvious spike in hardness, at a value of more than 300 mg/L $CaCO_{3\ (EQ.)}$ and it could easily be said that it was due to the metallic nature of the water at that point as well (*Figure 43*). In fact, there was so much magnesium in the sample that the ICP-MS could only detect it up to a certain

concentration, so only the minimum value for magnesium could be used in the formula. It would be expected that if the actual value for magnesium in 6b could have been derived, its value for hardness would have been even higher than it was. This unnaturally high measure of hardness in site 6b was an indication of the direct impact that industry was having on Nut Brook.

When statistically analysed, the p-value was verified to be less than 0.05 in the KW test, and the resulting ANOVA and Tukey's tests showed that sites 2 – 6 were significantly different than that of the reference site. When compared with site 6, which was the site with the lowest mean hardness of sites 2 – 6, the reference site had a level of hardness of more than nine times lower. The mean values of both were 5.2 mg/L $CaCO_{3\ (EQ.)}$ (site 1), and 49.1 mg/L $CaCO_{3\ (EQ.)}$ (site 6) (*Figure 43*). Interestingly, the values of sites 2 and 3 were statistically shown to be similar to one another, but were also shown to be significantly different from the values of all the other sites from 1 – 6. This was an indicator of the particularly different water quality exhibited by sites 2 and 3 compared with the quality of the others, due to the close proximity of those sites to the landfill and quarry runoff. The associated boxplot in Appendix C also helps to illustrate these points.

It should be noted that the mean levels of hardness in the river were also one major factor that led to the outcome of many of the site-specific CCME guideline derivations, and accounted in part for the reason why some of these guidelines were fairly high and others were a little lower. This meant that the toxicity of certain metals could have been increased or decreased in Nut Brook due to the particular ion-binding capacity of the water within it. In many cases the pH, temperature, alkalinity, and other such factors could also play a role in the overall toxic nature of some of the trace elements.

4.5 *E. coli* and Non-Fecal Coliforms

Many microorganisms known as coliforms exist naturally in soil, sediment, and bodies of water. However a certain enteric group of fecal coliforms, known as *Escherichia coli*, do not exist naturally outside the gastrointestinal systems of warm-blooded animals. Hence, if this particular type of bacteria were found in the environment, it would signal the presence of fecal matter at the sampling location (Patel, 2004). While not all types of *E. coli* are pathogenic, or disease causing, some strains can be especially deadly. Additionally, since fecal matter must be present for *E. coli* to show up in tests, then the presence of this microorganism would indicate the possibility of other pathogenic enteric bacteria and viruses (Patel, 2004). Since Nut Brook flows into the Kelligrews River, where people are known to swim and fish, if high levels of *E. coli* show up in the testing then there could potentially be fecal matter and deadly pathogens travelling to where people may be using the river.

The minimum mean results of the triplicate M-coli blue testing for *E. coli* and non-fecal coliforms for every site are displayed in the following table. It should be noted that dilutions were not performed for any of the tests on the first sweep, as it was unexpected that some of the colony-forming unit (CFU) levels would be as high as they were. Thus, where applicable, averages were derived of results obtained from sweeps 2 – 4 and are considered to be minimum mean CFU counts. Dilutions could range up to

1/100 for some of the tests. The raw data associated with the microbiological testing are located in Appendix A1. Unfortunately, due to the higher than expected CFU at some of the sites, the limited resources to do many tests, and the frequent requirement to conduct larger dilutions, it was not possible to perform a statistical analysis on these results.

Table 2: *Minimum coliform counts (CFU) as averages in Nut Brook.*

Site ID	Non-fecal coliforms – Red colonies (CFU)	*E. coli* – Blue colonies (CFU)
1	>1355	<2
2	>3445	83 – **>10,000**
3	>1915	78 – **>10,000**
4	TNTC	>37
5	>250	**>511**
6	172	53
6b	TNTC	**36,050**

** The results of the M-coli blue testing give a count of non-fecal (red) colonies and E. coli (blue) colonies. In some cases, a minimum estimate was accepted (shown as a range, or indicated by a > or a < symbol) due to the fact that more dilutions were needed (some could have a count of over 10,000 CFU). Note: TNTC refers to "Too Numerous To Count". Note also that a count of >200 CFU for E. coli is cause for concern on a recreational level.*

4.5.1 Non-fecal Coliforms

Non-fecal coliforms were obtained simultaneously with *E. coli* when using the M – coli blue test. These organisms are not necessarily harmful, but represent a count of the bacteria that would be living naturally in the river. In most cases, non-fecal coliforms would be expected to appear in far greater numbers than *E. coli* because water would be one of their natural habitats. Table 1 shows a range of non-fecal coliform populations with respect to each site. The average ranged from as little as 172 CFU in site 6 to clusters so dense that the colonies could not be counted, even at a 1/100 dilution such as in the case of site 6b. Of note, with the exception of site 6 where all of the colonies could be counted, the most representative numbers that could be used in the results were still the smallest numbers or averages possible due to the fact that the non-fecal coliform colonies were practically impossible to count because of their sheer numbers (*Table 2*). Thus, if mean CFU for the red colonies could be determined from all four sweeps in each sample, then the counts would actually be much higher.

4.5.2 *E. coli*

Regardless of the presence of *E. coli* in the water, there should be proportionately more non-fecal coliforms present naturally. In most cases this was true, however, occasionally, there were more *E. coli* present (*Appendix A1*). As stated by the US EPA (1986), the criteria for *E. coli* in freshwater for ambient or recreational use, such as swimming, are no more than 200 counts per 100ml on average. Sites 2 to 5 greatly exceeded this at least once. *E. coli* was present in site 6 as well, but at an average of 53 CFU, it was not present to the same degree as the counts observed in sites 2 – 5 and 6b (*Table 2*). Site 4 had relatively low levels of *E. coli* as well, except on the first sweep when too many colonies were present to count, thus the average count of blue colonies in site 4 was at least 37 CFU. When site 6b was sampled at the drainage pipe of the septic waste handling facility, the mean level of *E. coli* at 36,050 CFU exceeded the limit by a factor of approximately 175, signalling extremely dangerous levels of fecal contamination in the Brook. The high levels just downstream in site 5 at a countable minimum average of 511 CFU reflected this as well (*Table 2*).

Similarly, an extremely high count occurred on the third sweep at site 3, which occurred simultaneously with new development at the site involving freshly laid sods and a newly dug hole (*Section 2.1.3*), and very high counts at the same time just downstream at site 2 also reflect this. The enormously high levels of *E. coli* at this site, in addition to the offensive odour of the water, suggest that perhaps offal from the rendering plant or sewage may have been deposited there. The exact number of blue colonies could not be determined as the resources available to do more and larger dilutions were unavailable in the lab at that time. However, when compared to other high CFU counts from other samples that could be counted, it was estimated that the numbers in sites 2 and 3 during sweep three were at least 10,000 CFU and possibly much higher (*Table 2*).

It should be noted that the reference site rarely showed any signs of *E. coli*, except on the very first trial, and it was likely that the filtration unit used in testing was previously contaminated and not properly sterilized. The presence of fecal matter at all in the first site was low enough to suggest possible contamination by a wild mammal or bird and nothing more, especially since there were no apparent sources of other types of input. With this in mind, Nut Brook was thus very affected by certain activity in parts of the Incinerator Road area and the dangerously high levels of *E. coli* in some of the sites made the water a potential health hazard. The fact that so much *E. coli* was found in the furthest site downstream (site 2) suggested that there could be high levels even further downstream as well.

4.6 Horiba Probe Measurements

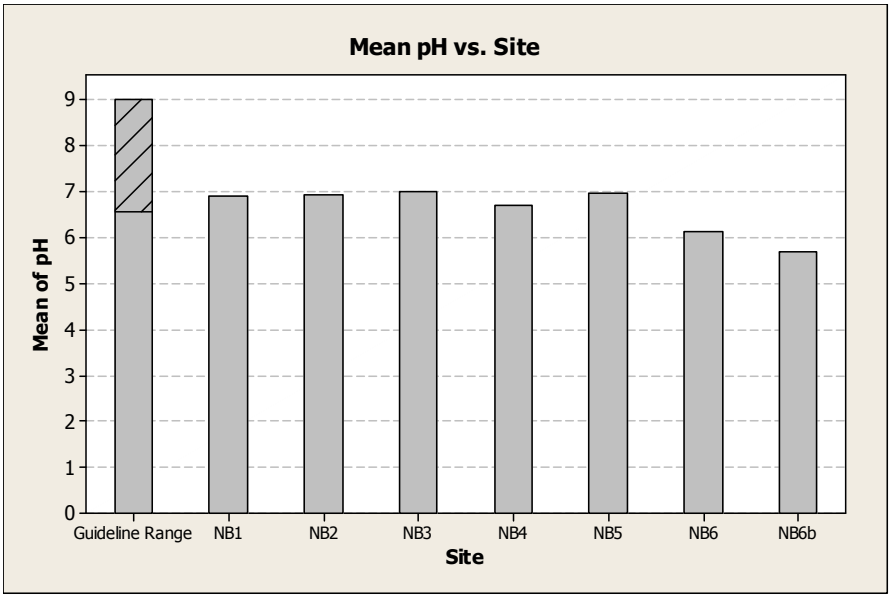
The Horiba probe, which is an *in situ* monitoring device, was very effective in determining many useful water quality parameters at once, including pH, specific conductivity, dissolved oxygen, turbidity, temperature, and salinity. A description of each is listed in the following subsections in addition to the mean results found for each parameter at every site. A discussion of the results will also be included in the

subsections. The raw data obtained from the *in situ* testing is found in Appendix A, and the boxplots and other statistical data can be found in Appendix C.

4.6.1 pH

The pH scale determines, logarithmically, the level of how acidic or basic a water sample is based on the amount of hydrogen ions present in the sample. Since different levels of pH can partially and directly determine the toxicity of certain substances due to a related ionising effect, a certain range of pH is required for a healthy aquatic ecosystem. For example, pH can determine the extent of the solubility of certain metals and ammonia. The higher the solubility of these constituents, the more bioavailable they would be to aquatic life (CCME, 2003). Depending on the toxicity of a substance at a certain pH, this would mean that a higher bioavailability could be more damaging. Industrial inputs of certain constituents could contribute to changes in the pH of a river system.

Figure 44: *Mean values of pH per sample site in Nut Brook, with the CCME guideline (for the protection of aquatic life, 2003) indicating the acceptable range of 6.5 – 9.0 (dashed region).*



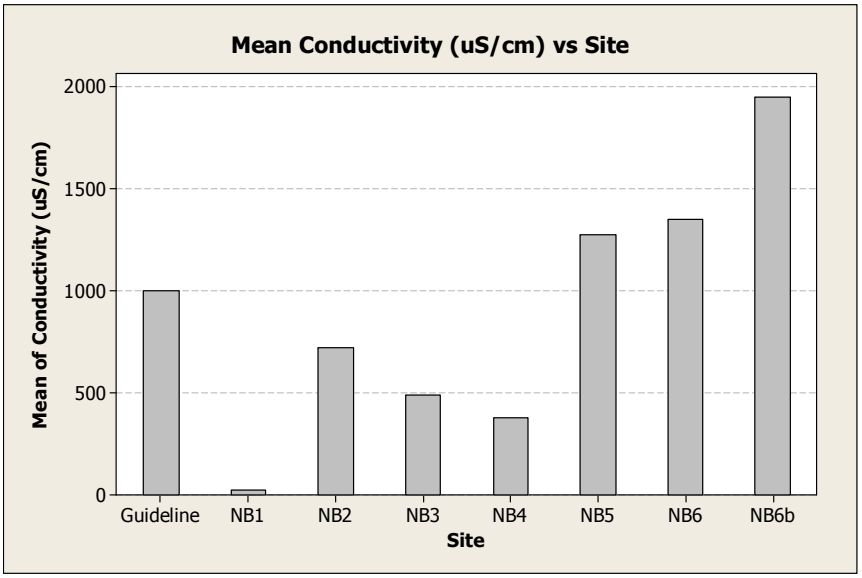
According to the CCME guidelines (for the protection of aquatic life, 2003), the recommended range of pH in rivers in general is between 6.5 and 9.0 (*note: pH has no specific units of measure*). Streams in the Northeast Avalon region can often be naturally below this range due to the natural acids that tend to form in the boggy headwaters, however most of the sites in Nut Brook did actually fit within this range and were generally near the neutral mark. Site 6, at a pH of 6.14 was slightly below this range, but given the nature of pH in streams in the area this was not likely to be detrimental (*Figure 44*).

As mentioned above, often the bioavailability of a substance, such as certain trace elements or heavy metals, are increased by lower or upper ranges of pH in a system. In terms of site 6b at a pH of 5.7, the bioavailability of many of the metals found at that site may have been greatly increased, since the pH was somewhat lower than that of the CCME guideline range (*Figure 44*). Due to the fact that the metal concentrations detected in site 6b were extremely high for many of the elements tested, the water at that site was potentially quite toxic (*Section 4.3*). Conversely, also due to the heavy concentration of some of the metals at that site, section 4.4 showed that site 6b had a hardness of greater than 300 mg/L $CaCO_{3\,(EQ.)}$, meaning that the potential ionising effect the lower pH value may have had on the elements could have been counteracted, in some measure, by the heavy un-ionising effect of the hardness in the sample. Although the sheer volume of elements and substances in site 6b may have been enough on its own to cause toxic conditions, the relatively low pH certainly played a role.

4.6.2 Conductivity

Specific conductance, or conductivity, is a measure of how well water can carry an electric charge, depending on what constituents are in it. Closely related to TDS, the influence of conductivity is based on concentrations of certain substances dissolved in it, including chloride, nitrate, sulphate, phosphate, sodium, magnesium, calcium, and iron (Murphy, 2005). Thus, higher values of conductivity would indirectly infer higher concentrations of these ions, and would also mean that the water would have more saline properties.

Figure 45: *Mean conductivity values in µS/cm per sample site in Nut Brook, with a non-specific guideline of 1000 µS/cm.*



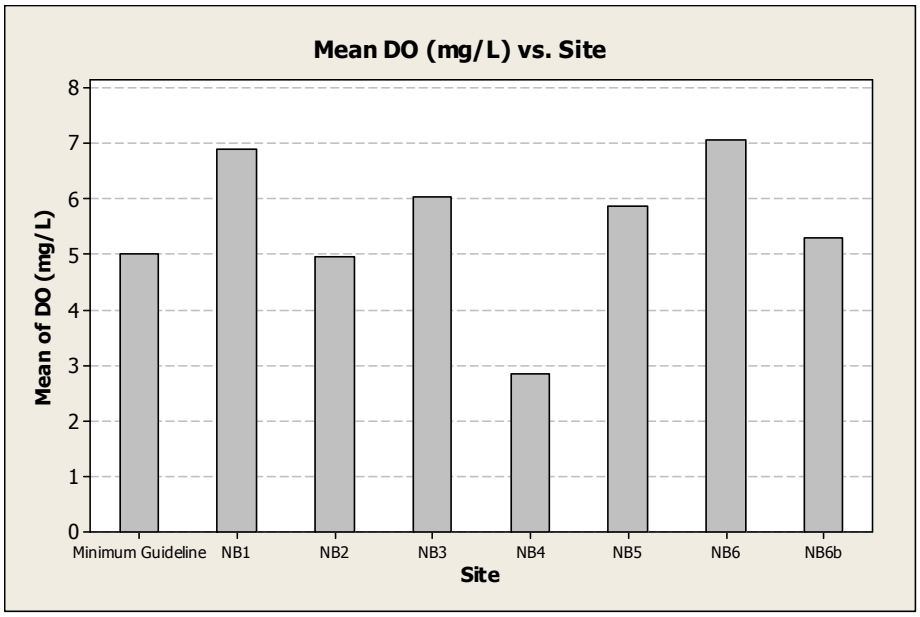
Typically, freshwater is said to have a conductivity of less than 1000 µS/cm, as it would tend to have more saline properties above this value. Although there was no CCME related guideline for conductivity, the value of 1000 µS/cm was chosen as a site-specific guideline for the purposes of this study. Site 6b had a conductivity that was nearly twice this value at 1950 µS/cm (*Figure 45*). The high values of conductivity noted in site 5 just downstream at a mean of 1275 µS/cm were reflective of the contamination in 6b. Site 6 had a high mean value for conductivity as well of 1350 µS/cm. Since salt concentrations are generally associated with conductivity values, the close downhill proximity of sites 5 and 6 to the salt storage unit could also explain in part the higher values of conductivity at these locations. Site 2 had been determined to be problematic in terms of water quality and sedimentation and at a mean value of 721.8 µS/cm, its relation to conductivity was understandable. Despite the fact that in previous sections site 3 was shown to contain high amounts of various anthropogenic constituents, its conductivity at a mean value of 491.8 µS/cm was low relative to most of the other sites. However, in terms of natural bodies of water, this was still quite a high value since the reference site had a mean value of 24.5 µS/cm. Even site 4, which had the lowest mean value of sites 2 – 6b at a measure of 380.0 µS/cm, was still higher than the reference site at a factor of 15.5 times (*Figure 45*).

The KW test in the statistical analysis gave a low p-value (<0.05) and the resulting ANOVA and Tukey's tests showed that there was a significant difference in the values of conductivity at site 1 in relation to all of the other sites except for site 4, indicating a general anthropogenic input of constituents in the Incinerator Road area that would contribute to higher values of conductivity. It can be argued that since site 4 had a mean value of more than 15 times that of the reference site there was most likely some influence from the nearby industrial action at this site also. The boxplot in Appendix C shows this for all of the sites very well, since the lowest value of any of the sites 2 – 6 was much higher than the highest value of conductivity in site 1.

4.6.3 Dissolved Oxygen (DO)

Oxygen dissolved between molecules of water is used by and directly supports aquatic life. The amount of dissolved oxygen (DO) in a sample is dependent on the amount of activity occurring at that site. The more biological respiration occurring by aquatic flora and fauna, the more oxygen will be used up from the water. For example, if the amount of bacteria at a site suddenly increases, the DO will most likely decrease due to the increased use of oxygen. Areas where aquatic biological production is too high to sustain itself will have low levels of DO. Conversely, DO will tend to increase with increasing flow in the system and decrease with stagnation. Other factors that can decrease DO are increased organic matter, increased temperature, and decreased photosynthesis. If there is an increase in the amount of salts at a site in the form of TDS and TSS, turbidity will increase, effectively decreasing the amount of light entering the system, thus affecting the level of photosynthesis (Murphy, 2005). The mean results of dissolved oxygen per site are displayed in the following graph.

Figure 46: *Mean Dissolved Oxygen (DO) levels per sample site in mg/L in Nut Brook, with a CCME guideline (for the protection of aquatic life, 2003) of 5.0 mg/L (minimum) derived according to site-specific criteria (CCME, 2003).*



Dissolved oxygen (DO) is one of the most important factors affecting aquatic life with 4mg/L being the minimum amount for invertebrates and 5mg/L being the minimum for other forms of life such as fish (but not including the highly sensitive embryo stages) [Province of BC, 1998]. For the purposes of this report and based on guidelines derived by the CCME (for the protection of aquatic life, 2003) and the Government of British Columbia (1998), DO values lower than 5mg/L were flagged as being dangerously unacceptable or depending on how much lower, completely unacceptable conditions for supporting aquatic life. Sites 2, 3, and 4 were often below the guideline (*Appendix A*), signalling that something could be very wrong at these sites. It should be noted that 7 – 11 mg/L DO is a more acceptable range, and many more samples fell below 7 mg/L as well.

Sites 2 and 4 were the worst overall, having mean DO concentrations of 4.95 mg/L and 2.86 mg/L respectively (*Figure 46*), and both had an individual concentration of less than 2 mg/L at one time (*Appendix A*). Sites 5 and 6b were diminished towards the 5 mg/L guideline as well at 5.85 and 5.30 mg/L respectively and reflected the troubled conditions in these sites. Site 6 was within the ideal range at a mean concentration of 7.06 mg/L DO (*Figure 46*), and was most likely due to the better flow at that site (*Section 4.9*).

A possible reason why sites 2 and 3 were generally low in DO would be due to the heavy sedimentation that occurred at these stations. The deposits, which had covered the natural bottom layer of the brook, most likely had destroyed any bottom dwelling flora capable of producing oxygen during photosynthesis. Additionally, the landfill leachate and traces of sewage suspected to be present at these sites could have also possibly caused a decrease in dissolved oxygen. Site 4 was very stagnant and appeared heavily eutrophied, which may have been a reason for the extremely low DO levels at this site. The accelerated plant activity in the pond of mainly surface dwelling plants most

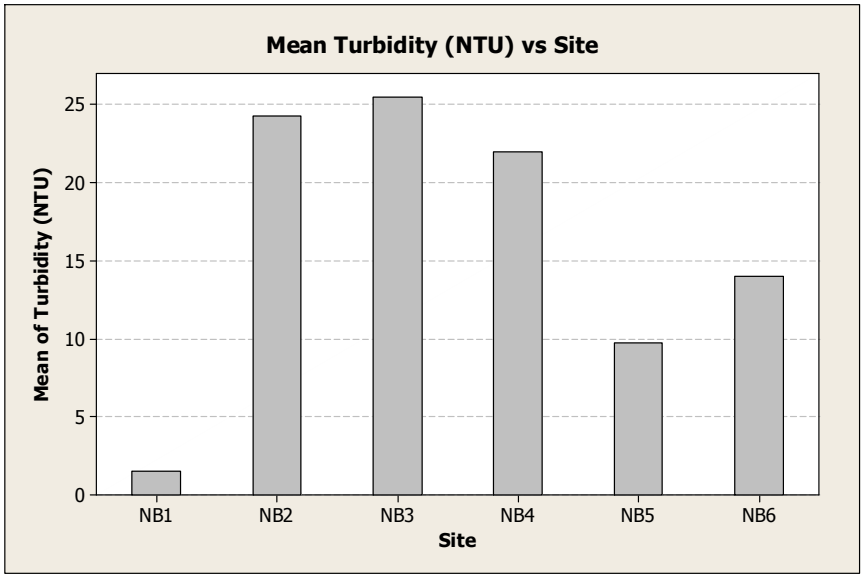
likely competed heavily for space in the water, and probably decreased the amount of light available for aquatic photosynthesis, and hence, resulted in a loss of dissolved oxygen in Nut Brook Pond.

The statistical analysis gave a low p-value (<0.05) in the KW test but only site 4 was determined to be statistically different than the reference site in terms of dissolved oxygen, as the ANOVA and Tukey's tests showed. This was most likely due to the fact that site 1 was standing water and the samples were taken on hot summer days, thus the mean DO concentration was naturally not high for this site. Therefore, with the exception of site 6, since the other sites also generally had low mean concentrations of DO, there would not be a significant difference statistically in the values measured at each site. Hence, due to the fact that site 4 was determined to have a significant difference in terms of DO when compared with the reference site, it was thus very problematic in this respect.

4.6.4 Turbidity

Turbidity is a measure of the amount of light that can pass through water based on the amount of matter present in it. This matter would mainly consist of suspended solids, but could also consist of high numbers of microorganisms. Anything that could cause the water to become cloudy would lead to an increase in turbidity (Murphy, 2005). Since turbidity will impede light within the water sample, plant photosynthesis will subsequently decrease. And as turbidity is mainly suspended solids, particles associated with increased turbidity can house more bacteria and can also choke aquatic life (Province of BC, 1998). The mean results obtained for turbidity per sample site are displayed in the following graph.

Figure 47: *Mean levels of turbidity in NTU per sample site in Nut Brook.*



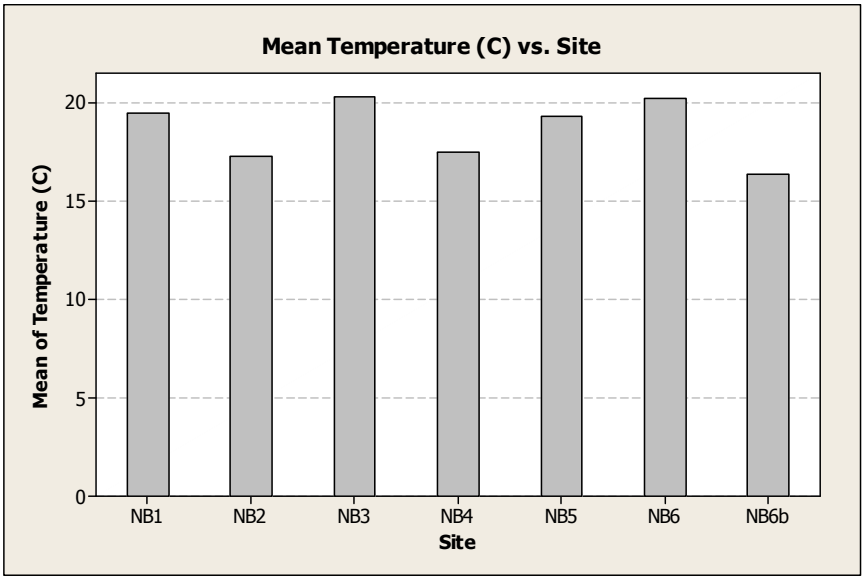
No specific guideline has been specified for turbidity with regard to the preservation of aquatic life, however it is known that turbidity is often caused by factors that adversely affect the aquatic ecosystem. It can be seen from Figure 47 that all of the mean values of turbidity from sites 2 – 6 were higher than that of the reference site, which had a mean value of 1.5 NTU (*note: site 6b was not included in this graph*). The next highest mean value was 9.8 NTU at site 5. While it was evident that some of the turbidity was caused by anthropogenic sources, its overall effect did not seem high. However, it should be noted that on the third sweep, sites 2 and 3 had a significant spike in turbidity at individual values of 63 and 78 NTU respectively (*Appendix A*). This coincided with the fact that the section of river at site 3 had been dug up just previous to that particular sampling time (*Section 2.1.3*), and any new constituents relating to turbidity in site 3 were also reflected in the water at site 2 just downstream. Site 6b was previously shown to be extremely contaminated and the value measured for turbidity at this location helped to back this up, as it had a turbidity of 290 NTU (*Appendix A*), which was more than 193 times that of the reference site.

With the exception to site 6b, and the isolated incident affecting sites 2 and 3, the overall effect of turbidity for the remainder of the samples was quite low. A p-value of more than 0.05 was obtained in the KW test of the statistical analysis, meaning that there were no sites from 1 – 6 showing a significant difference from each other in the values of turbidity measured. Although site 1 did have the lowest overall turbidity values with the least amount of variance, the boxplots in Appendix C help to show that the differences in turbidity in the other sites relative to the reference were not significant.

4.6.5 Temperature

The intensity of stored heat in a body of water is measured as the temperature, and this parameter can influence the solubility of certain substances, making them more or less bioavailable. Depending on the toxicity of the substance, a temperature increase could cause harmful effects in the aquatic ecosystem (CCME, 2003). It also directly affects the solubility of dissolved oxygen, where an increase in temperature results in a decrease of DO (Province of BC, 1998). Temperature can also influence the biological activity of aquatic flora, fauna, and bacteria (Murphy, 2005). The mean results of temperature per sample site are displayed in the following graph.

Figure 48: *Mean values of temperature in ℃ per sample site in Nut Brook.*



While there were no specific CCME guidelines relating to temperature for the protection of aquatic life, the Province of BC (1998) had proposed that freshwater systems should have a maximum temperature of 18 – 19°C with a maximum variability of ± 1 degree. Similarly, the Colorado Department of Public Health and Environment-Water Quality Control Division (CDPHE-WQCD) has stated that waters containing cold-water aquatic life should be no warmer than 20°C (Murphy, 2005). Although these guidelines were derived for aquatic systems in other parts of the continent, it would be expected, at least for a parameter such as temperature, that these conditions would be similar in many regions, since natural water can reach this temperature range locally. With the summer weather conditions, it was expected and concluded (*Figure 48*) that the water was in this upper range.

In a few sites, the temperatures were occasionally slightly above this range (*Appendix A*), and site 6 averaged a temperature of 20.2°C. The reference site had a mean temperature of 19.5°C, and may have been a little warmer on average due to the fact that it was a relatively large body of fairly shallow standing water, unsheltered from the sun. Sites 2 and 4 had lower mean temperatures than the reference of 17.3 and 17.5°C respectively (*Figure 48*). Although still in the upper range of acceptable temperatures, site 2 was fairly sheltered from the sun, owing to its lower mean value. Similarly, the lilies at the surface of site 4 heavily shaded the water from the sun. Site 6b had a one-time measurement of 16.4°C (*Figure 48*), and although this water exhibited heavy bacterial activity, the lower temperature achieved was due to the cooler and rainier weather experienced on that date.

Site 3 had the highest mean temperature of 20.3°C (*Figure 48*), and was due to the one isolated incident on the third sweep when the water became particularly contaminated (*Section 2.1.3)*. The temperature of site 3 on that day was 29.0°C, and was reflective of the hot summer conditions together with the high bacterial activity and any other effluent that may have entered that site at that time (*Appendix A*). This dangerous

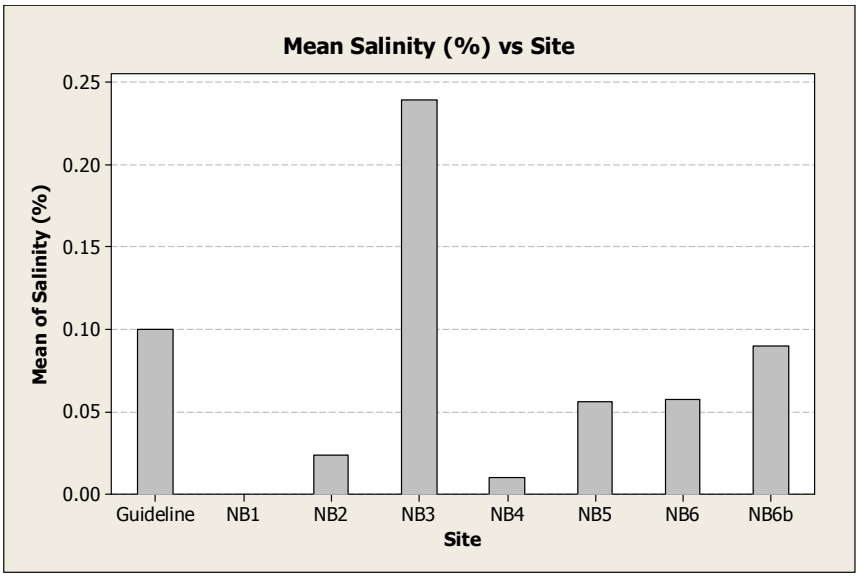
temperature condition was associated with a lowered dissolved oxygen concentration (*Appendix A*), an increased ammonia concentration (*Section 4.7.1*), and a greatly increased *E. coli* count (*Section 4.5.2*). This high temperature could also be associated with an increased solubility rate of many other constituents in the water, such as certain trace elements. This would make these constituents more bioavailable and, thus, toxic to aquatic fauna.

A high p-value (>0.05) was achieved in the KW test; hence, the statistical analysis showed that there was no significant difference in the temperatures measured from one site to the next. This would make sense because there was not much variability between the means at any of the sites, although some were a little warmer than others. The boxplot in Appendix C helps to back this up. This indicates that industrial activity would be contributing very little, if any, to increased temperatures in Nut Brook, and that the range of temperatures detected were mainly due to the natural weather conditions at the time in conjunction with the natural environmental factors, such as vegetative cover, observed at each site. The only notable exception was site 3 on the third sweep when there was an obvious anthropogenic impact to the system, although this one incident alone was not enough to statistically constitute a significant difference in the overall means.

4.6.6 Salinity

The salinity is related to conductivity because it is a measure of the concentration of salts in the water. Freshwater typically has a very low salt concentration relative to seawater. A higher salinity would indicate the input of salts to the system. The mean results of salinity per sample site are displayed in the following graph.

Figure 49: *Mean levels of salinity in % per sample site in Nut brook.*



With regards to salinity, most of the samples fell within the proper range for fresh water, which is less than 1000ppm, or 0.1% salinity (UCAR, 2002). However, in one instance, site 3 gave a very high value of over 9000ppm salinity (0.93%), suggesting highly brackish water, meaning that something had to occur that was atypical of the stream's normal activity (*Appendix A*). The spike was attributed to the previously mentioned incident that occurred on the third sweep (*Section 2.1.3)*. This one-time salt contamination was undoubtedly linked to the same event due to the fact that so many other contaminants and poor water quality indicators were detected simultaneously in the sample at that time. As observed in the raw data, site 3 exhibited an increase in most constituents and, notably, conductivity on the third sample run (*Appendix A*). The increase in salinity simply added to the evidence that a major disturbance had occurred in the stream at that point and time.

In terms of the mean results shown in Figure 49, all of the sites had a higher mean salinity than the reference site. While only site 3 exceeded the guideline, the fact that site 1 had a mean value of 0.00% and all of the other sites had some degree of salinity meant that there was some anthropogenic input of salts to the system, although some of it was probably due to naturally occurring salts picked up during the course of the brook as well. It should be noted that site 6b had a relatively high value of salinity at 0.09%, which was nearly in exceedance of the guideline and reflective of the contaminated conditions at that station. Sites 5 and 6 showed higher mean values as well at 0.07 and 0.06% respectively (*Figure 49*). This was somewhat anticipated, since the salt storage facility was visible on the slope above these two sites and may have potentially contributed to the higher values.

In terms of the statistical analysis, a low p-value (<0.05) was scored in the KW test, and the subsequent ANOVA and Tukey's tests showed that all the sites from 2 – 6, (excluding site 4), had values of salinity that were significantly different than the values obtained for site 1. This would further back up any evidence to show an anthropogenic input of salts to parts of the system. It should be noted, however, that a slight natural increase in salinity downstream was also possible, as site 4 had a mean of 0.01% and zero variability [standard deviation = 0.000], meaning that the salinity increase was very low and remained consistent for that site (*Appendix C*).

4.7 HACH Kit Analysis Results

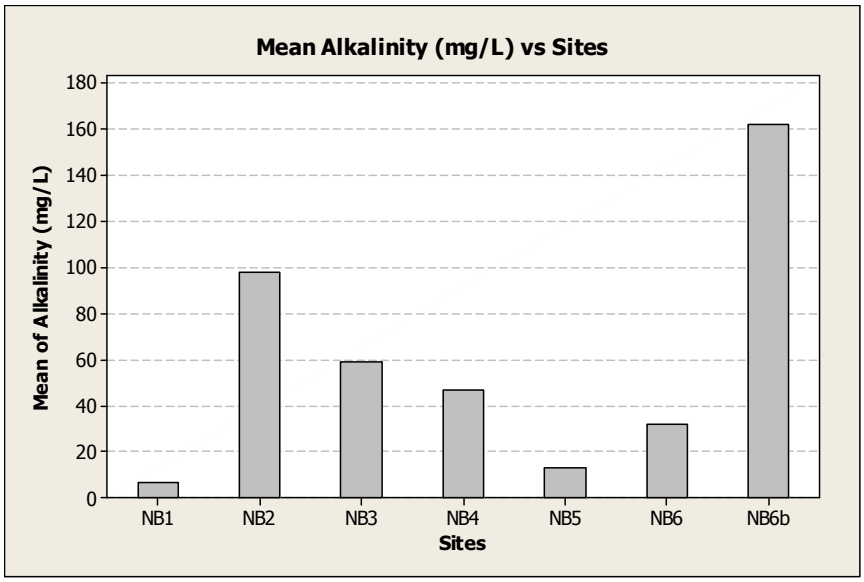
A freshwater HACH field-testing kit was used to test the water samples for alkalinity, ammonia, nitrite, and chloride. Descriptions of each parameter are listed in the following subsections along with the mean results obtained per sample site. Discussions of the results are also included in the subsections. The raw data obtained with the HACH kit are found in Appendix A.

4.7.1 Alkalinity

Depending on the presence of bicarbonate, carbonate or other anions, alkalinity is essentially a measure of the buffering ability of water with regards to changes in pH (Murphy, 2005). It is a very important parameter of water quality because a certain level

of natural alkalinity would have the ability to stabilize the pH in a body of water, such as during acid rainfall, or in industrial runoff. The lower the alkalinity, however, the more susceptible water would be to pH fluctuations. Additionally, when more acid is added to the system, the buffering capacity will weaken and the alkalinity will be lowered (Murphy, 2005). A higher level of alkalinity will tend to be associated with harder water and a higher concentration of sodium salts (Province of BC, 1998). Of note, due to the binding properties of carbonate and bicarbonate, water with a higher alkalinity may be able to cause metals to precipitate out of the water column, lowering the degree of metal toxicity in the water (Murphy, 2005). The mean results for alkalinity per sample site are displayed in the following graph.

Figure 50: *Mean levels of alkalinity in mg/L per sample site in Nut Brook.*



The results given by the HACH kit for alkalinity were quite varied. Alkalinity is measured as an equivalent amount of calcium carbonate (mg/L $CaCO_{3\ EQ.}$), whether $CaCO_3$ is present or not, thus since the bedrock in this region is mainly volcanic and not very carbonaceous (Hayes, 1987) Nut Brook should naturally have low values of alkalinity. This was shown to be the case for the reference site, which had a mean concentration of 6.3 mg/L $CaCO_{3\ EQ.}$, but was not always the case for the other sites, indicating a possible anthropogenic increase in alkalinity. While site 5 with a mean concentration of 12.6 mg/L $CaCO_{3\ EQ.}$ tended to be low relative to site 1, site 2 tended to be quite high with a mean concentration of 97.7 mg/L $CaCO_{3\ EQ}$. Site 6b was also very high with respect to the reference site at a concentration of 162 mg/L $CaCO_{3\ EQ.}$ (*Figure 50*).

While some of the values given in the above tables may have seemed to be high, it should be noted that natural fresh water can generally have an alkalinity of between 20 and 200 mg/L, and that below this range the aquatic system would tend to be fairly sensitive to situations in which the pH would be likely to change (Murphy, 2005). Thus

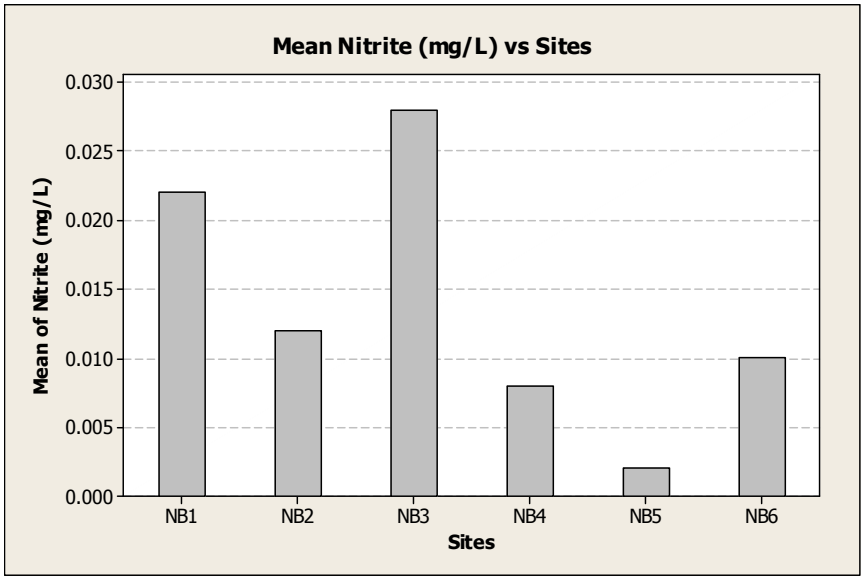
sites 1 and 5, for example, may have been more susceptible to the effects of constituents that could lower the pH, in turn making certain metals present more bioavailable and toxic. Conversely, site 2 gave one individual alkalinity measurement of 232 mg/L equivalent $CaCO_3$ (*Appendix A*), which is quite high in terms of alkalinity, and while it would be able to buffer the effects of a pH change, it may have been due to higher dissolved salts in the water at that time, which would not necessarily be a positive factor in terms of stream health. There was possible evidence that the alkalinity may have increased due to anthropogenic reasons, since in many cases site 2 was known to have a high loading of constituents with regards to dissolved salts and conductivity. Since there was a reference site, alkalinity in this case served as an indicator of natural or anthropogenic inputs of constituents in the Incinerator Road section.

The statistical analysis of alkalinity offered the best means of determining the extent of anthropogenic input of certain contributors to the system. A p-value of less than 0.05 was scored in the KW test, and the results of the ANOVA and Tukey's tests showed that there were significant differences in the values obtained for alkalinity in sites 2 – 4 when compared with site 1. The higher levels of alkalinity in those three sites, especially in site 2, most likely reflected the contamination of Nut Brook at those locations from an anthropogenic source.

4.7.2 Ammonia & Nitrite

Ammonia (NH_3) and nitrite (NO_2^-), two nitrogenous compounds, can be particularly toxic to aquatic life (Province of BC, 1998), but their toxicity is dependant on many factors such as pH, temperature, DO, or the presence of other substances (CCME, 2003). Under normal conditions, these compounds are temporarily present as a function of bacterial metabolism. They are usually present at very low levels and are used by plants and bacteria to their own benefit. Nitrite can be toxic at lower concentrations than ammonia, causing blood disorders in fish, but it tends to be short lived as it is quickly oxidized to nitrate (NO_3^-) by bacteria. Ammonia is even less stable in water, especially with a lower pH, as it is easily converted to the relatively un-toxic ammonium ion (NH_4^+) [Murphy, 2005]. However, certain forms of industrial discharge can add these compounds to the aquatic system. One of the biggest possible anthropogenic sources would be sewage because human waste contains high amounts of nitrite and ammonia (Murphy, 2005). The mean results for nitrite per sample site are displayed in the following graph. Due to the difficulties in obtaining measurements for ammonia in the samples, an associated graph was not included in the following discussion. See Appendix A for the results of ammonia in Nut Brook.

Figure 51: *Mean levels of nitrite in mg/L per sample site in Nut Brook.*



A CCME guideline for the protection of aquatic life relating to nitrite (2003) had been set at 0.06 mg/L, however none of the samples from any of the sites exceeded this. The mean values, shown in Figure 51, were fairly low with the highest being site 3 at less than 0.03 mg/L. It should be noted that the mean values listed in Appendix A had all been rounded, however the actual means, which make up the values in the graph (*Figure 51*) are listed in the statistical section (*Appendix C*). Of interest, site 1 had higher levels of nitrite than most of the other sites and could have been due to the high amount of organic matter present there. This landed in conjunction with the TEV test of the statistical analysis, which scored a high p-value (>0.05), indicating that there were no grounds to test whether there was a significant difference between the values of nitrite at any of the sites. For the purposes of this report, this was interpreted as an indication that anthropogenic input of nitrite may not have been very significant in Nut Brook.

The results for ammonia were low or non-existent for the most part, although as indicated in sections 4.2 and 4.5.2 there may have been sewage in the water at some sites. This added a level of questionability to the reliability of the HACH kit when determining the values in Appendix A. It should be noted, however, that on the third sweep at site 3 where it was suspected that sewage was deposited, the results obtained for ammonia at that site were higher than the detection limits of the HACH test, indicating that there was a lot of ammonia in the water at that time, increasing the trust in the results obtained from the HACH kit. Similarly on the same run, site 2 downstream also showed levels of ammonia to be above the detection limits of the HACH test unit. Ammonia is known to occur in higher concentrations at higher temperatures (CCME, 2003). Since site 3 was shown to have a temperature of 29°C on the third sweep (*Section 4.6.5*), it would be expected that ammonia would be detected in much higher concentrations at that time as well. This, in conjunction with the *E. coli* results from the same sample run helped to back up the fact that sewage had probably entered the system at that time.

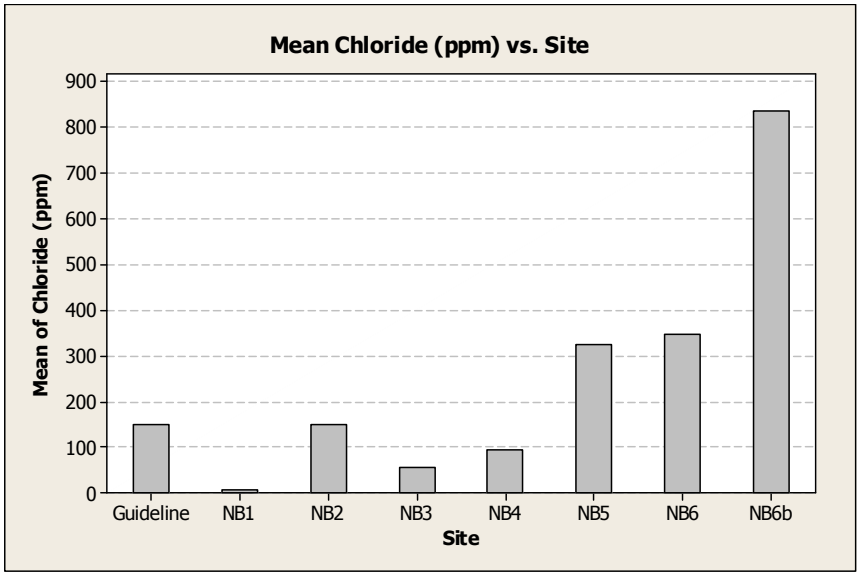
Since high amounts of ammonia and nitrite are found in raw sewage and not the water itself (Murphy, 2005), it was possible that in most cases excluding the reference site, the sewage, if present, would have been quite diluted by the flowing water anyway, and/or decomposed by bacteria within it and the stream, significantly lowering the ammonia and nitrite levels all over. There would probably have to be quite a high concentration of sewage in the water for the detection of these compounds, such as in the incidental case of site 3 during the third sweep. The *E. coli* testing would be a much better indication of sewage in general for most of the samples. Testing for nitrate (NO_3^-) rather than nitrite (NO_2^-) would be a recommendation for future testing, since it is also found in high concentrations in sewage and is quite stable in water (Province of BC, 1998).

4.7.3 Chloride

The chloride ion occurs naturally in freshwater systems, however in much lower concentrations than in saline water. It is sometimes associated with industrial discharge, but in fact higher levels of chloride can react with nitrite and make it less toxic (CCME, 2003). It should be noted that the reagents for chloride in the HACH kit often ran out at inopportune times, thus due to these limitations the field tests could only be carried out on the first four sites, on most occasions. For the purposes of this report, these results will not be analysed in detail, but they are available in Appendix A.

It was noticed, however, that the ICP-MS also tested for chloride during the metal analysis. Hence, since it gave results of chloride for all of the samples every time, and since the ICP-MS results were assumed to be far more accurate, the chloride analysis will be discussed in terms of the ICP-MS results rather than the values obtained from the HACH kit. The mean results for chloride per sample site as received from the ICP-MS analysis are listed in the following graph. Individual results for chloride from this method are available in Appendix A under “Cl”. The results for chloride from the HACH kit are also listed in Appendix A.

Figure 52: *Mean concentrations of chloride in mg/L per sample site in Nut Brook, with a Province of BC ambient water quality guideline for chloride (1998) of 150 ppm. (Note: ICP-MS results shown).*



Chloride can generally exist in high concentrations without being harmful, thus there was no specific guideline set by the CCME in relation to this parameter. However, the Province of BC (1998) recognised that chloride levels in excess of 600 mg/L at any given time could be quite toxic to aquatic life. They also mentioned that mean chloride values in freshwater should not exceed 150 mg/L on a continuous basis, which was the source of the guideline referred to in Figure 52 (*note: mg/L = ppm*).

In relation to the reference site, which had a mean concentration of 5.96 ppm, chloride was generally found to be in a much higher concentration in sites 2 – 6b, indicating that it may have been occurring anthropogenically at those sites (*Figure 52*). Sites 5 and 6 exceeded the guideline by more than twice the value at mean concentrations of about 325 ppm and 346 ppm respectively, and could have been due in part to the sites' close proximity to the salt storage facility. Site 2 practically met the guideline at 149.5 ppm as well (*Figure 52*). Site 3 had the lowest mean concentration of sites 2 – 6b at 54.9 ppm, but it was noted that on the third sweep, there was an individual value detected of about 90.8 ppm (*Appendix A*). This would coincide with the high levels of salinity measured at that site at that time (*Section 4.6.6*), and offered further evidence that a unique contamination event occurred in the vicinity during this sampling period. Site 6b had an extremely high concentration of more than 837 ppm chloride (*minimum*), which not only exceeded the chronic guideline, but also the acute guideline mentioned of 600 ppm. This was related to the excessive overall contamination at that site. It should be noted that the chloride level in site 6b actually was above the detection limits of the ICP-MS, meaning that there was actually more chloride present than shown in Figure 52.

A low p-value (<0.05) was scored in the KW test of the statistical analysis, and the ANOVA and Tukey's tests showed that there was a significant difference in the values of chloride in sites 2, 4, 5, and 6 with that of site 1. This would indicate a mostly anthropogenic input of chloride to the system at those sites. Site 3 did not show any statistical evidence of anthropogenic input; however its mean was more than nine times

greater than that of the reference, and as previously mentioned, the value obtained on the third sweep was certainly due to an isolated non-natural incident. The boxplot in Appendix C greatly helped to illustrate all of these points. The fact that there was a lot of chloride in the samples meant that any adverse environmental effects that nitrite may have had on the system would have been greatly reduced.

4.8 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are known to be generally carcinogenic, and are mainly a sooty by-product of incomplete combustion (Boehnke and Delumyea, 2000). These by-products are found everywhere in soil, water, air and food. The main sources of PAHs in the environment are exhaust and smoke, but can also occur from creosote treated wood and spilled oil (Boehnke and Delumyea, 2000). PAHs can also be introduced to the environment during paving and roofing (Furton and Pentzke, 1998). PAHs are essentially bonded rings of benzene, and the more rings that are bonded or fused; the more potent the carcinogenic effects tend to be (Boehnke and Delumyea, 2000). PAHs are more stable in soil and sediment than in water, as they fuse to soil and road dust particles, or particles of soot in the air. Simple PAHs with fewer rings tend to break down rapidly in water and in sunlight.

Since PAHs were expected to be much more stable in the sediment, the six sediment samples were tested for 16 types of PAHs. These included naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthene, anthracene, fluoranthene, pyrene, benz (*a*) anthracene, chrysene, benzo (*b*) fluoranthene, benzo (*k*) fluoranthene, benzo (*a*) pyrene, indeno (*1, 2, 3 – cd*) pyrene, dibenzo (*a, h*) anthracene, and benzo (*g, h, I*) perylene.

All of the results received from the GC/MS testing were negative for the presence of PAHs, since each PAH in each sample was below the detection limit of the instrument used, which was set at an extremely low concentration of <15 ng/ml (*note: ng/ml reads nanograms per millilitre)*. Thus a formal table or graph was not created in this case. Due to the limitations noted in Section 3.3.6, it was quite possible that the sample extractions were analysed too late and any PAHs present were most likely broken down in storage. Since PAHs are generally so prevalent in the environment (Furton and Pentzke, 1998), they would have been expected to be present in a highly polluted industrial area such as Incinerator Road. Further sampling and testing with a quick and proper analysis of new sediment and possibly new water samples would be highly recommended in the future.

4.9 Flow

Any river with sufficient depth and width will naturally have a higher volume of water flowing through it at a given point per unit of time (streamflow). It is possible for rivers having a smaller width and shallower depth to have a strong current with respect to a larger river, however their channel capacity might be significantly reduced, resulting in a lower streamflow than in a larger river. Likewise, a river of a certain width but also having a deeper channel may have a larger area but a slower current, resulting in a

reduction of overall streamflow. Flow is important to the health of the river ecosystem, but it would be expected to change naturally on a yearly, to monthly, to daily basis. Constant unnatural interruptions to flow could thus damage this natural balance.

The amount of flow measured at sites 2, 3, and 6 (the flowing sites) for the first three sweeps is listed in the following table:

Table 3: *Flow of each site (if applicable) measured in m^3/s during each sweep. A dash (-) means that flow was not measured*

Sample ID	Flow (m^3/s) Sweep 1	Flow (m^3/s) Sweep 2	Flow (m^3/s) Sweep 3
2	-	-	0.04
3	0.03	-	Wind driven
6	0.09	0.08	0.05

Flow was very low for the most part in Nut Brook, although site 6 was healthy in this regard, since anything impeding the flow at that point was a natural occurrence. It should be noted that in site 3 on the third sweep, the flow was almost cut off by the digging that took place. In general, the flow was very low for sites 2 and 3. This was essentially due to the heavy sedimentation, which was choking the brook at those points. The sedimentation was one of the most significant anthropogenic factors affecting Nut Brook.

5.0 Conclusions

Considering the visual state of Nut Brook and the associated unseen conditions uncovered by the field and lab analysis results, Nut Brook was clearly in a state of serious trouble. Since wildlife had been spotted on several occasions in and around the brook, a healthy ecosystem was also being threatened. This coincided with the fact that the suburban Kelligrews River further downstream may also have been inadvertently affected, silently putting at risk the people that use it for recreational purposes.

There were many water quality indicators overall that worked in conjunction to reveal the anthropogenic impact to Nut Brook from the activity on Incinerator Road. Through the findings of this report, it was determined that there were high levels of metals, sewage or fecal contamination, chloride, ammonia, salinity, and TDS at some of the sites. Additionally, the dissolved oxygen levels at some of the sites were dangerously low at times, and where certain sites could flow naturally, the volume of water passing through was inadequate for the most part. This was due to the enormous amount of sediment deposited, which had impeded the flow and completely changed the natural benthic environment of the brook at those points and also the flood region on either side, which was in itself an ecosystem. Of additional note, there were substances suspected to be in the water and sediment that needed to be tested further. Great suspicion had been placed on petroleum hydrocarbons since some stations exhibited an oily sheen, while the colour of site 6b was witnessed to be grey/black with oil.

All of these occurrences have been associated in some way with the industrial action on Incinerator Road, since when compared with the reference site located far upstream from the “brown zone”, the rest of the sample sites were determined to be quite abnormal, adding to the piling evidence of anthropogenic damage to the system. Of note, on the third sweep, when digging was witnessed at site 3, the visual and field inspections revealed a major disruption to the system, and a major source of contamination to the stream. The lab results supported this observation, and the statistical results further supported the lab results. Unless corrective action is taken to control the release of contaminants into Nut Brook and the sedimentation of its tributary, this damage will continue to further compromise the integrity of this ecosystem.

6.0 Recommendations

Since this report consisted mainly of preliminary research, it is highly recommended that a follow-up study be carried out. In particular, since so much *E. coli* was present at some of the sites, it is recommended that further testing be carried out in the future, and that testing for other pathogens, such as *Salmonella* and/or *Giardia lamblia*, be carried out if possible. Additionally, testing for the highly lethal *E. coli* O157:H7 should also be performed because this strain can be transmitted through human waste. Nut Brook should be considered a health hazard due to the high levels of *E. coli* present, and possible contributors should be monitored closely. Other indicators of sewage, such as nitrate, should be tested as well, since this compound is more stable than nitrite and thus easier to detect. It would also be a good idea to retest for PAHs using a more efficient protocol to avoid any future mistakes in processing and storing the samples. Careful consideration of national protocol standards would be key in obtaining the best possible data at any time.

Nut Brook should be monitored regularly to document fluctuations in its water quality over time. Additionally, a full investigation by regulatory agencies should be organised to inspect the activity on Incinerator Road, to confirm whether environmental and sanitary laws are being broken. On this note, it would be a good idea for the provincial and federal government to become involved, and also the City of St. John's since the affected area lies within city limits. A section of the Town of Conception Bay South is also at risk from the effects of contamination; therefore appropriate action should also be taken on their side to properly monitor the Kelligrews River.

Additionally, it is advised that a professional remediation of the affected area be initiated immediately, and that operations involved in creating the polluted conditions be urged to contribute to this effort. Industries that are currently polluting or otherwise negatively impacting the watershed should be required to stop the irresponsible activity and to upgrade their facilities to ensure compliance with existing legislation. Proper enforcement of all ongoing activity will ensure that this damaged ecosystem can be restored, and that aquatic as well as terrestrial life dependent on the river can live safely and normally. Previous undertakings that are no longer in operation but which are still suspected of actively contaminating the system, such as the incinerator and landfill, should be properly taken care of by those municipalities and townships that used them to ensure no more damage is done.

As a final recommendation all people, parties, organizations, businesses, government agencies, and industrial operations who may be involved with and/or affected by the contamination, or who can assist with the cleanup, monitoring, or enforcement of the activity on Incinerator Road should be informed of its present state. Raising awareness would greatly benefit the future health of Nut Brook, especially since it is presently in a state of out-of-site out-of-mind despite being upstream of a residential population in Kelligrews. The more people who are made aware of the problems of Nut Brook, the greater the chance that corrective action will be taken.

7.0 References

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8.0 Appendix A

The individual results and their associated means derived from most water and some sediment quality and characteristic tests performed on the Nut Brook samples for each sample collection sweep are listed in the following tables. Bolded values indicate exceedances to CCME guidelines (for the protection of aquatic life, 2003). See Appendix A1 for mean M-coli Blue test results. See Appendix B for ICP-MS sediment analysis results.

Sample	Date	TSS (mg/L)	TDS (mg/L)	TS (mg/L)	VOC (mg/L)	%TOC (Sediment)
NB1	14-Jul-05	20	112	132	72	
	27-Jul-05	76	312	388	154	
	9-Aug-05	22	150	172	110	
	25-Aug-05	22	52	74	24	
	Mean	35	156.5	191.5	90	90.5
NB2	14-Jul-05	2	414	416	74	
	27-Jul-05	68	**1246**	**1314**	856	
	9-Aug-05	50	850	900	438	
	25-Aug-05	26	644	670	120	
	Mean	36.5	788.5	825	372	5.6
NB3	14-Jul-05	26	450	476	132	
	27-Jul-05	102	968	**1070**	712	
	9-Aug-05	64	628	692	N/A	
	25-Aug-05	34	398	432	334	
	Mean	56.5	611	667.5	392.7	0.6
NB4	14-Jul-05	84	108	192	N/A	
	27-Jul-05	100	**1110**	**1210**	630	
	9-Aug-05	58	660	718	350	
	25-Aug-05	2	188	190	88	
	Mean	61	516.5	577.5	356	84
NB5	14-Jul-05	54	**1102**	**1156**	396	
	27-Jul-05	104	**1138**	**1242**	386	
	9-Aug-05	6	638	644	62	
	25-Aug-05	48	696	744	110	
	Mean	53	893.5	946.5	238.5	81.7
NB6	14-Jul-05	68	944	**1012**	116	
	27-Jul-05	146	**1090**	**1236**	368	
	9-Aug-05	112	642	754	92	
	Mean	108.7	892	**1000.7**	192	45.6
NB6b	25-Aug-05	66	**2652**	**2718**	538	N/A

sample	Date	Total Kjeldahl N (%) Water	Total Kjeldahl N (%) Sediment	Hardness (mg/L)
NB1	14-Jul-05	0		6.2
	27-Jul-05	0		5.3
	9-Aug-05	0.11		4.6
	25-Aug-05	N/A		4.7
	Mean	0.05	1.56	5.2
NB2	14-Jul-05	0		95.3
	27-Jul-05	0.03		89.7
	9-Aug-05	0		161.7
	25-Aug-05	N/A		58.6
	Mean	0.01	0.12	101.3
NB3	14-Jul-05	0		128
	27-Jul-05	0		119.7
	9-Aug-05	0		161.4
	25-Aug-05	N/A		89.6
	Mean	0	8.27	124.7
NB4	14-Jul-05	0		54.1
	27-Jul-05	0		57.5
	9-Aug-05	0		59.6
	25-Aug-05	N/A		25.7
	Mean	0	3.71	49.2
NB5	14-Jul-05	1.79		61.8
	27-Jul-05	0		54.8
	9-Aug-05	0		48.8
	25-Aug-05	N/A		42.7
	Mean	0.6	0.36	52
NB6	14-Jul-05	0		46.8
	27-Jul-05	1.49		52.2
	9-Aug-05	0		48.3
	Mean	0.5	0	49.1
NB6b	25-Aug-05	N/A		>300.9

sample	Date	pH	Conductivity (uS/cm)	DO (mg/L)	Turbidity (NTU)	Temperature ('C)	Salinity (%)
NB1	14-Jul-05	7.43	26	7.25	4	20.1	0
	27-Jul-05	7.72	26	7.27	1	18.9	0
	9-Aug-05	6.66	23	6.27	0	21.9	0
	25-Aug-05	**5.8**	23	5.02	1	17.2	0
	Mean	6.9	24.5	6.45	1.5	19.5	0
NB2	14-Jul-05	7.25	489	7.06	7	18.4	0.02
	27-Jul-05	6.92	400	7.19	12	17.2	0.01
	9-Aug-05	6.97	888	**3.81**	63	17.3	0.03
	25-Aug-05	6.58	**1110**	**1.75**	15	16.1	0.04
	Mean	6.93	721.8	**4.95**	24.3	17.3	0.02
NB3	14-Jul-05	7.31	425	6.9	5	18.3	0.01
	27-Jul-05	7.03	415	7.96	6	19.2	0.01
	9-Aug-05	6.83	757	**4.3**	78	**29**	**0.93**
	25-Aug-05	6.85	370	**4.98**	13	14.5	0.01
	Mean	7.01	491.8	6.04	25.5	20.3	**0.24**
NB4	14-Jul-05	7.51	381	5.65	7	20.3	0.01
	27-Jul-05	6.44	386	**2.44**	2	18.4	0.01
	9-Aug-05	6.45	425	**1.28**	75	17.3	0.01
	25-Aug-05	6.41	328	**2.08**	4	14.1	0.01
	Mean	6.7	380	**2.86**	22	17.5	0.01
NB5	14-Jul-05	7.35	**1260**	5.6	2	19.8	0.05
	27-Jul-05	6.72	**1510**	6.05	24	20.3	0.07
	9-Aug-05	6.89	**1050**	6.7	1	21	0.04
	25-Aug-05	6.83	**1280**	5.05	12	16.1	0.05
	Mean	6.95	**1275**	5.85	9.8	19.3	0.07
NB6	14-Jul-05	**5.96**	**1600**	7.21	0	19	0.07
	27-Jul-05	6.04	**1480**	7.5	30	19.1	0.06
	9-Aug-05	6.43	970	6.48	12	22.5	0.04
	Mean	6.14	**1350**	7.06	14	20.2	0.06
NB6b	25-Aug-05	**5.7**	**1950**	5.3	**290**	16.4	0.09

sample	Date	Alkalinity (mg/L)	Ammonia (ppm)	Nitrite (mg/L)	Chloride (mg/L)	Flow (m^3/s)	Li (ppb)
NB1	14-Jul-05	N/A	0.07	0.02	10.3	N/A	0.4
	27-Jul-05	1	0	0.02	8.5	N/A	<0.23
	9-Aug-05	2	0	0.03	10.3	N/A	0.32
	25-Aug-05	16	0	0.02	9.8	N/A	<0.77
	Mean	6.3	0.02	0.02	9.7	N/A	0.305
NB2	14-Jul-05	N/A	0.26	0	81.2	N/A	0.47
	27-Jul-05	41	0	0.01	**116.6**	N/A	0.38
	9-Aug-05	232	ADL*	0.02	**147.9**	0.04	1.21
	25-Aug-05	20	0	0.02	**278.9**	N/A	<0.89
	Mean	97.7	N/A	0.01	**156.2**	N/A	0.62
NB3	14-Jul-05	34	0.58	0.02	38.9	0.03	0.66
	27-Jul-05	83	0	0.02	41.3	N/A	0.36
	9-Aug-05	97	ADL*	0.03	N/A	Wind Driven	1.05
	25-Aug-05	21	0	0.04	N/A	N/A	<0.91
	Mean	58.8	N/A	0.03	40.1	N/A	0.63
NB4	14-Jul-05	21	0.26	0.02	94.5	N/A	0.35
	27-Jul-05	14	0	0	**109.8**	N/A	<0.23
	9-Aug-05	48	0	0.01	N/A	N/A	0.25
	25-Aug-05	**103**	0	0	N/A	N/A	<1.08
	Mean	46.5	0.07	0.01	**102.2**	N/A	0.31
NB5	14-Jul-05	N/A	0.11	0	N/A	N/A	3.98
	27-Jul-05	12	0	0	N/A	N/A	0.53
	9-Aug-05	23	0	0.01	N/A	N/A	0.52
	25-Aug-05	3	0	0	N/A	N/A	<0.96
	Mean	12.6	0.03	0	N/A	N/A	1.38
NB6	14-Jul-05	8	0.08	0.02	96.8	0.09	0.32
	27-Jul-05	16	0	N/A	N/A	0.08	0.35
	9-Aug-05	72	0	0	N/A	0.05	0.46
	Mean	32	0.03	0.01	N/A	0.07	0.38
NB6b	25-Aug-05	**162**	0	0.01	N/A	N/A	24.00

** Note: "ADL" refers to Above Detection Limits*

sample	Date	Be (ppb)	B (ppb)	Mg (ppb)	Al (ppb)	Si (ppb)	P (ppb)	S (ppb)
NB1	14-Jul-05	<0.29	<8.68	459.7	**494.5**	145	<738	<10856
	27-Jul-05	<0.15	<99.21	464.8	**281.1**	73	<1284	<15473
	9-Aug-05	<0.14	<96.29	434.4	**195.5**	115	<1257	<15151
	25-Aug-05	<0.13	17.8	455.5	**153.3**	181	<2281	<4963
	Mean	0.09	29.97	453.6	**281.1**	128.5	695	5805.4
NB2	14-Jul-05	<0.30	129.57	4437.5	**123.3**	2632	<721	23523
	27-Jul-05	<0.15	<97.59	3999.6	**113.2**	2898	<1263	27783
	9-Aug-05	0.38	210.06	7251.8	**141.3**	4504	1430	27547
	25-Aug-05	0.19	34.51	1896.4	**95.3**	2738	<2380	10294
	Mean	0.2	105.73	4397.8	**118.3**	3193	903	22286.8
NB3	14-Jul-05	<0.30	200.86	6054.0	**148.7**	3610	<725	38532
	27-Jul-05	0.34	184.98	5179.2	**257.6**	3730	<1287	40841
	9-Aug-05	0.41	217.27	7454.4	**191.0**	4815	<1286	20031
	25-Aug-05	0.51	144.58	3227.7	**277.5**	3638	<2437	15369
	Mean	0.35	186.92	5478.8	**218.7**	3948.3	716.9	28693.3
NB4	14-Jul-05	<0.30	10.09	2676.4	**500.8**	1867	<729	<10728
	27-Jul-05	<0.15	<100.41	3103.6	**241.7**	2428	<1299	<15659
	9-Aug-05	<0.15	<97.60	3189.1	**65.6**	2938	<1263	<15220
	25-Aug-05	0.25	24.15	1575.2	**245.8**	2374	<2883	<6935
	Mean	0.14	33.31	2636.1	**263.5**	2401.8	771.8	6067.8
NB5	14-Jul-05	<0.30	33.76	3707.7	**308.6**	1663	<732	<10760
	27-Jul-05	<0.15	<99.58	2949.7	**186.8**	2256	<1288	<15531
	9-Aug-05	<0.15	<99.75	2127.7	**227.0**	2352	<1291	<15557
	25-Aug-05	<0.16	11.43	1796.2	**250.3**	2530	<2554	<6143
	Mean	0.1	36.21	2645.3	**243.2**	2200.3	733.1	5998.9
NB6	14-Jul-05	<0.30	<8.93	1971.9	**243.7**	1694	<735	<10809
	27-Jul-05	<0.15	<98.03	2079.1	**474.2**	2418	<1268	<15288
	9-Aug-05	<0.15	<97.99	1959.1	**269.7**	2551	<1268	<15282
	Mean	0.08	34.16	2003.4	**329.2**	2221	545.2	6896.5
NB6b	25-Aug-05	9.70	1522.36	>21535	**323.3**	4481	3204	60151

sample	Date	Cl (ppb)	Ca (ppb)	Ti (ppb)	V (ppb)	Cr (ppb)	Mn (ppb)	Fe (ppb)	Co (ppb)
NB1	14-Jul-05	6284	601	7.05	<1.38	<1.03	18.36	**553.5**	0.13
	27-Jul-05	5141	608	1.81	<1.49	0.70	11.85	**440**	0.08
	9-Aug-05	4982	709	1.22	<1.45	0.35	7.69	192	0.14
	25-Aug-05	7441	746	0.95	1.2	<0.68	14.61	185	<0.09
	Mean	5962	666	2.76	0.84	0.48	13.13	**342.63**	0.1
NB2	14-Jul-05	77316	26775	4.74	<1.35	2.97	3077.18	**2179**	0.75
	27-Jul-05	114649	27902	6.37	<1.46	1.50	634.46	**1058**	0.20
	9-Aug-05	113973	46873	10.06	<1.45	5.67	4684.82	**3044**	0.95
	25-Aug-05	292250	16786	3.02	0.94	6.72	1762.71	**2884**	1.80
	Mean	149547	29584	6.05	0.77	4.22	2539.7	**2291.3**	0.93
NB3	14-Jul-05	35825	37648	6.87	<1.36	3.30	1536.82	**3020**	0.47
	27-Jul-05	38798	36280	10.49	5.73	3.47	1209.14	**2429**	0.46
	9-Aug-05	90751	45073	14.61	<1.49	8.62	2676.86	**6883**	1.50
	25-Aug-05	54163	26094	7.40	1.10	9.88	1197.21	**4378**	0.68
	Mean	54884.3	36273.8	9.84	2.06	6.32	1655.01	**4177.5**	0.78
NB4	14-Jul-05	91556	13124	5.66	4.53	3.69	961.96	**3603**	0.33
	27-Jul-05	103325	13993	4.02	1.75	3.64	2080.83	**2732**	0.27
	9-Aug-05	111258	14596	1.37	1.47	3.92	2711.20	**2666**	0.29
	25-Aug-05	73515	5418	2.74	4.69	4.58	824.11	**1787**	0.37
	Mean	94913.5	11782.8	3.45	3.11	3.96	1644.53	**2697**	0.32
NB5	14-Jul-05	322986	15325	5.31	1.61	<2.18	2048.15	**1832**	2.01
	27-Jul-05	363925	15152	4.49	<1.49	1.75	993.96	**1176**	0.93
	9-Aug-05	280947	13623	4.50	<1.49	2.16	1356.43	**1494**	1.07
	25-Aug-05	330758	12580	4.29	1.78	2.78	517.69	**1071**	0.74
	Mean	324654	14170	4.65	1.22	1.95	1229.06	**1393.3**	1.19
NB6	14-Jul-05	406993	14129	4.49	<1.38	<2.49	372.07	**954**	0.49
	27-Jul-05	372163	14175	12.42	2.40	3.06	549.88	**2964**	1.39
	9-Aug-05	257401	13959	4.67	<1.47	2.18	415.96	**1930**	0.73
	Mean	345519	14087.7	7.19	1.28	2.16	445.97	**1949.3**	0.87
NB6b	25-Aug-05	>837325	73063	20.72	6.83	35.02	696.43	**14897**	3.78

sample	Date	Ni (ppb)	Cu (ppb)	Zn (ppb)	As (ppb)	Br (ppb)	Se (ppb)	Rb (ppb)
NB1	14-Jul-05	3.63	**10.53**	**50.46**	<0.55	<174.66	<4.50	0.28
	27-Jul-05	<16.24	**3.91**	**37.69**	<0.18	<59.54	<0.70	0.11
	9-Aug-05	<15.90	1.74	**33.58**	<0.17	<57.79	**<1.00**	0.11
	25-Aug-05	<3.09	**2.31**	<34.70	<0.43	<320.99	<0.67	0.24
	Mean	5.31	**4.62**	**34.77**	0.17	76.62	0.86	0.19
NB2	14-Jul-05	1.49	**9.98**	19.46	<0.59	<176.08	<4.40	4.54
	27-Jul-05	<15.97	**3.33**	**40.48**	<0.18	89.37	<0.70	4.80
	9-Aug-05	<15.89	**8.73**	**72.43**	0.61	130.19	<0.70	14.58
	25-Aug-05	6.08	**3.25**	<40.01	<0.74	<334.80	<0.85	2.79
	Mean	5.88	**6.32**	**38.09**	0.34	118.8	0.83	6.68
NB3	14-Jul-05	1.48	**9.68**	28.33	<0.57	<177.16	<4.43	5.70
	27-Jul-05	<16.27	**4.92**	**41.54**	0.39	71.77	<0.71	5.55
	9-Aug-05	<16.26	**9.89**	**53.33**	0.78	117.50	<0.71	11.65
	25-Aug-05	<4.52	**3.72**	<40.98	<0.55	<342.88	<0.81	5.26
	Mean	5	**7.05**	**35.92**	0.43	112.3	0.83	7.04
NB4	14-Jul-05	2.83	**10.98**	**42.85**	<0.60	<178.22	<4.43	1.61
	27-Jul-05	<16.43	**2.38**	27.82	<0.18	127.00	<0.72	2.87
	9-Aug-05	<15.97	**2.66**	25.73	<0.18	134.15	<0.71	2.32
	25-Aug-05	<4.31	1.89	<48.48	<0.65	<405.67	<0.95	1.78
	Mean	10.59	**4.48**	**30.16**	0.2	138.27	0.85	2.15
NB5	14-Jul-05	1.86	**8.63**	**47.76**	<0.72	202.57	<4.40	3.03
	27-Jul-05	<16.30	**8.17**	**71.41**	<0.18	158.96	<0.72	2.83
	9-Aug-05	<16.32	**6.43**	**38.23**	0.23	111.24	<0.72	2.02
	25-Aug-05	<4.44	**4.26**	**46.50**	<0.81	<359.36	<0.92	2.13
	Mean	5.1	**6.87**	**50.98**	0.27	163.11	0.85	2.5
NB6	14-Jul-05	2.20	**15.43**	**33.00**	<0.77	<179.55	<4.44	3.05
	27-Jul-05	<16.04	**4.82**	23.38	0.26	135.80	<0.71	2.75
	9-Aug-05	<16.04	**6.46**	**54.75**	<0.18	120.13	<0.71	1.95
	Mean	6.08	**8.9**	**37.04**	0.25	115.23	0.98	2.58
NB6b	25-Aug-05	13.97	**18.23**	**1023.88**	1.72	3007.35	<2.96	13.84

sample	Date	Sr (ppb)	Mo (ppb)	Ag (ppb)	Cd (ppb)	Sn (ppb)	Sb (ppb)	I (ppb)
NB1	14-Jul-05	6	<0.15	<0.05	<0.24	0.43	<0.07	4.77
	27-Jul-05	5	<0.12	<0.02	<0.11	0.32	<0.03	4.79
	9-Aug-05	5	<0.11	<0.02	<0.11	0.22	<0.03	4.22
	25-Aug-05	5	0.61	<0.05	<0.07	0.18	0.05	3.48
	Mean	5.3	0.2	0.02	0.07	0.29	0.03	4.32
NB2	14-Jul-05	99	0.66	<0.05	<0.24	0.25	0.07	22.56
	27-Jul-05	102	0.39	<0.02	<0.11	1.69	0.04	25.34
	9-Aug-05	178	1.70	<0.02	<0.11	1.13	0.10	55.24
	25-Aug-05	60	0.59	<0.06	<0.08	0.50	0.07	15.47
	Mean	109.8	0.84	0.02	0.07	0.89	0.07	29.65
NB3	14-Jul-05	143	0.56	<0.05	<0.24	0.31	0.08	19.58
	27-Jul-05	138	1.47	<0.02	<0.11	0.32	0.20	23.15
	9-Aug-05	173	1.14	<0.02	<0.11	1.50	0.09	41.15
	25-Aug-05	101	1.73	<0.06	<0.08	0.40	0.16	31.08
	Mean	138.8	1.23	0.02	0.07	0.63	0.13	28.74
NB4	14-Jul-05	44	0.19	<0.05	<0.25	0.38	0.07	46.22
	27-Jul-05	47	<0.12	<0.02	<0.11	0.16	0.04	130.80
	9-Aug-05	48	<0.11	<0.02	<0.11	0.26	0.04	73.73
	25-Aug-05	25	0.13	<0.07	<0.09	0.30	0.15	31.90
	Mean	41	0.11	0.02	0.07	0.28	0.08	70.66
NB5	14-Jul-05	71	2.20	<0.05	<0.25	0.40	1.05	14.78
	27-Jul-05	63	0.57	<0.02	<0.11	0.35	0.12	321.62
	9-Aug-05	48	0.56	<0.02	<0.11	0.31	0.05	39.72
	25-Aug-05	47	0.60	<0.06	**0.18**	0.53	0.07	8.96
	Mean	57.3	0.98	0.02	**0.1**	0.4	0.32	96.27
NB6	14-Jul-05	53	0.20	<0.05	<0.25	0.31	0.09	9.84
	27-Jul-05	53	<0.11	0.03	<0.11	0.18	0.05	22.65
	9-Aug-05	44	<0.11	0.04	<0.11	0.37	0.04	14.36
	Mean	50	0.1	0.03	0.8	0.29	0.06	15.62
NB6b	25-Aug-05	470	**90.14**	<0.06	**0.36**	1.52	3.17	58.63

sample	Date	Cs (ppb)	Ba (ppb)	La (ppb)	Ce (ppb)	Hg (ppb)	Tl (ppb)	Pb (ppb)
NB1	14-Jul-05	<0.01	6.76	1.05	1.89	<0.64	<0.08	**2.09**
	27-Jul-05	0.00	6.96	0.57	0.92	<0.07	<0.01	0.59
	9-Aug-05	0	5.9	0.36	0.67	<0.07	<0.01	0.54
	25-Aug-05	0	7.6	0.27	0.52	<0.03	0.02	0.44
	Mean	0	6.81	0.56	1	0.1	0.02	0.92
NB2	14-Jul-05	0.11	56.52	0.65	1.07	<0.65	0.11	0.95
	27-Jul-05	0.11	40.27	0.41	0.90	<0.07	<0.01	0.81
	9-Aug-05	0.47	94.60	0.72	1.72	<0.07	<0.01	1.45
	25-Aug-05	0.10	95.64	1.12	1.38	<0.04	0.18	0.75
	Mean	0.2	71.76	0.73	1.27	0.1	0.08	0.99
NB3	14-Jul-05	0.10	44.45	0.67	1.56	<0.65	0.10	1.22
	27-Jul-05	0.10	40.34	0.56	1.58	<0.07	0.02	1.53
	9-Aug-05	0.34	88.88	1.07	2.72	<0.07	<0.01	1.75
	25-Aug-05	0.11	49.55	1.12	2.92	<0.04	0.14	1.21
	Mean	0.16	55.81	0.86	2.2	0.1	0.02	1.43
NB4	14-Jul-05	0.12	136.48	4.61	4.14	<0.65	0.13	**3.03**
	27-Jul-05	0.20	135.43	2.71	2.60	**0.58**	<0.01	**1.18**
	9-Aug-05	0.18	146.17	0.98	0.90	<0.07	0.01	0.40
	25-Aug-05	0.07	90.40	3.12	2.71	<0.05	0.19	**1.78**
	Mean	0.14	127.12	2.86	2.59	**0.24**	0.08	**1.6**
NB5	14-Jul-05	0.12	98.63	3.12	3.66	<0.66	0.15	**2.11**
	27-Jul-05	0.11	237.49	1.64	1.87	**8.71**	0.02	**2.44**
	9-Aug-05	0.09	89.51	2.21	2.54	**0.16**	0.02	**1.23**
	25-Aug-05	0.08	74.23	2.14	2.31	<0.04	0.18	**1.11**
	Mean	0.1	124.97	2.28	2.6	**2.31**	0.09	**1.72**
NB6	14-Jul-05	0.14	87.70	3.14	2.79	<0.66	0.15	**1.43**
	27-Jul-05	0.13	80.75	4.29	5.48	**0.71**	0.02	**2.81**
	9-Aug-05	0.08	86.06	2.25	2.99	<0.07	0.02	**1.30**
	Mean	0.12	84.85	3.23	3.75	**0.35**	0.06	**1.85**
NB6b	25-Aug-05	0.22	75.31	0.76	1.90	<0.04	0.08	2.84

sample	Date	Bi (ppb)	U (ppb)
NB1	14-Jul-05	<0.04	0.27
	27-Jul-05	<0.01	0.12
	9-Aug-05	<0.01	0.1
	25-Aug-05	0	0.07
	Mean	0.01	0.14
NB2	14-Jul-05	<0.04	3.37
	27-Jul-05	0.02	2.96
	9-Aug-05	0.08	4.29
	25-Aug-05	0.01	2.15
	Mean	0.03	3.19
NB3	14-Jul-05	<0.04	4.48
	27-Jul-05	0.01	4.79
	9-Aug-05	0.11	4.83
	25-Aug-05	0.02	3.21
	Mean	0.04	4.33
NB4	14-Jul-05	<0.04	3.40
	27-Jul-05	<0.01	5.56
	9-Aug-05	<0.01	1.08
	25-Aug-05	<0.01	0.96
	Mean	0.01	2.75
NB5	14-Jul-05	<0.04	1.77
	27-Jul-05	0.02	1.59
	9-Aug-05	<0.01	2.32
	25-Aug-05	<0.01	1.61
	Mean	0.02	1.82
NB6	14-Jul-05	<0.04	0.47
	27-Jul-05	<0.01	1.53
	9-Aug-05	0.02	1.67
	Mean	0.02	1.22
NB6b	25-Aug-05	<0.01	0.52

8.0.1 Appendix A1

Full mean results of the M-coli Blue testing for *E. coli* and non-fecal coliforms for each sampling sweep are listed in the following tables.

*Average **c**olony counts for the first set of samples showing non-fecal (red) colonies and* E. coli *(blue) colonies. Note that these samples were not diluted, as it was not expected that counts would be so high in some cases ("TNTC" refers to "too numerous to count").*

Sample ID	# Red Colonies	# Blue Colonies
1	TNTC	TNTC (Note, possible cross contamination may have occurred from the apparatus, since there was zero CFU on one of the three plates)
2	TNTC	TNTC
3	TNTC	104
4	TNTC	TNTC
5	TNTC	TNTC
6	85	16

Average colony counts for the second sweep showing non-fecal (red) colonies and E. coli (blue) colonies. Note that these samples were diluted, as it was expected that counts would be high in some cases ("TNTC" refers to "too numerous to count").

Sample ID	Dilution Factor	# Red Colonies (After Dilution Factor)	# Blue Colonies (After Dilution Factor)
1	1:1	TNTC	0
	1:10	1310	0
2	1:1	TNTC	111
	1:10	3140	55
3	1:1	TNTC	75
	1:10	1915	80
4	1:1	TNTC	25
	1:10	TNTC	30
5	1:1	TNTC	TNTC
	1:10	TNTC	1275
6	1:1	15	100
	1:10	245	140

*Average **c**olony counts for the third sweep showing non-fecal (red) colonies and* E. coli *(blue) colonies. Note that these samples were diluted, as it was expected that counts would be high in some cases ("TNTC" refers to "too numerous to count").*

Sample ID	Dilution Factor	# Red Colonies (After Dilution Factor)	# Blue Colonies (After Dilution Factor)
1	1:1	TNTC	0
	1:10	1400	0
2	1:1	TNTC	TNTC
	1:10	TNTC	TNTC
3	1:1	TNTC	TNTC
	1:10	TNTC	TNTC
4	1:1	-	67
	1:10	TNTC	15
5	1:1	30	15
	1:10	470	15
6	1:1	TNTC	26
	1:10	300	20

*Average **c**olony counts for the fourth sweep showing non-fecal (red) colonies and* E. coli *(blue) colonies. Note that these samples were diluted, as it was expected that counts would be high in some cases ("TNTC" refers to "too numerous to count"). Also note that site 6 was taken from the new location.*

Sample ID	**Dilution Factor**	**# Red Colonies** **(After Dilution Factor)**	**# Blue Colonies** **(After Dilution Factor)**
1	1:1	TNTC	35
2	1:10	TNTC	390
	1:100	3,750	1,600
3	1:10	TNTC	540
	1:100	TNTC	TNTC
4	1:1	18	82
	1:10	TNTC	25
5	1:1	117	129
	1:10	720	355
6b	1:1	TNTC	TNTC
	1:10	TNTC	TNTC
	1:100	TNTC	36,050

8.1 Appendix B

The results obtained from the ICP-MS tests performed on the Nut Brook sediment samples are listed in the following tables. Duplicate sample tests are indicated in the first column of each table with a star (*). All values are in ppm.

	calculated on		28-Sep	2005	11:29:24	
Name	Ca	Ti	V	Cr 52	Cr 53	Fe 54
NB_1	3243	838.876	42.487	11.014	18.147	5995
NB_2	12112	1467.979	23.756	13.696	36.274	15760
NB_3	7169	662.682	12.685	2.294	16.926	7252
NB_3*	6452	642.302	10.825	14.638	16.333	6670
NB_4	6378	819.683	77.071	9.521	22.279	6638
NB_5	6395	2783.563	74.637	17.008	48.817	16664
NB_6	10448	2042.330	119.359	11.673	160.083	44574
BLANK-15	7	0.010	0.138	1.740	1.131	577

Name	Mn	Fe 57	Mo	Ag	Cd	Sn
NB_1	60.331	5928	2.042	0.178	0.026	2.023
NB_2	899.223	15265	0.503	0.191	0.116	1.458
NB_3	269.444	7209	0.385	0.118	-0.032	1.556
NB_3*	243.059	6550	0.097	0.120	0.173	1.261
NB_4	228.226	6641	3.720	0.372	1.568	3.574
NB_5	348.791	16495	15.650	0.801	0.481	4.533
NB_6	4122.905	76568	13.965	0.456	0.325	1.443
BLANK-15	3.475	573	0.211	0.027	0.091	4.226

Name	Sb	Te	I	La	Pb	Bi
NB_1	0.188	-0.504	-6.194	17.364	26.679	0.111
NB_2	0.164	-0.397	-7.106	19.702	14.131	0.116
NB_3	0.094	-0.080	-8.985	17.673	12.827	0.098
NB_3*	0.119	-0.322	-7.052	17.463	10.883	0.069
NB_4	0.758	-0.394	-3.323	111.677	44.572	0.173
NB_5	0.839	-0.364	-4.466	96.238	67.627	0.387
NB_6	0.373	-1.331	-11.169	55.377	56.566	0.062
BLANK-15	0.007	-0.332	-5.771	-0.011	0.133	0.013

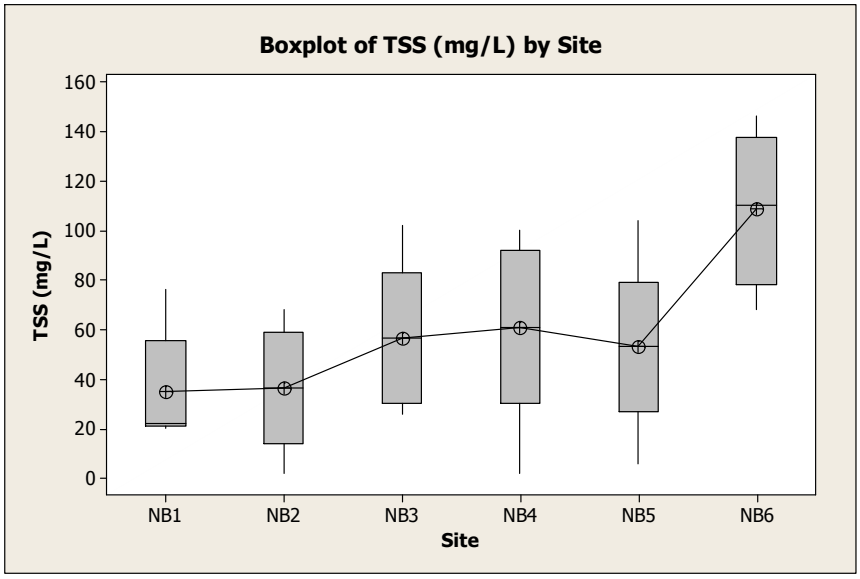
Name	Co	Ni	Cu	Zn	As	Se 77
NB_1	0.875	9.860	12.198	44.081	0.948	3.039
NB_2	2.833	7.074	9.672	131.191	1.262	2.674
NB_3	1.197	4.176	4.998	102.491	0.916	-0.375
NB_3*	1.068	2.216	3.918	47.246	0.922	1.050
NB_4	2.591	32.067	22.755	79.097	2.192	4.571
NB_5	4.325	14.334	24.104	116.523	3.705	5.341
NB_6	36.196	14.211	15.378	116.955	11.590	-2.540
BLANK-15	0.233	0.964	2.689	19.718	0.143	2.820

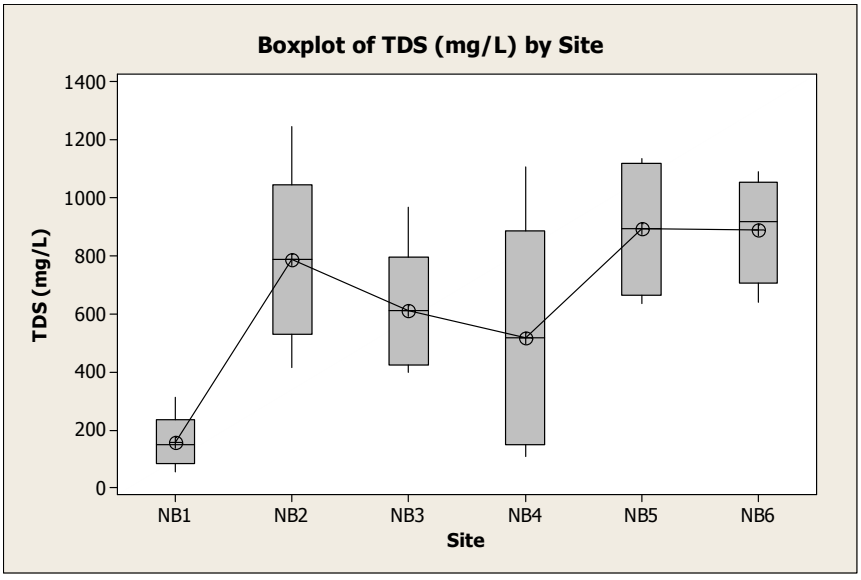
Name	Se 82	Br 79	Ce	Pr	Nd	Er
NB_1	1933.698	860.073	31.963	3.294	12.226	0.753
NB_2	2261.840	1081.249	39.116	3.863	13.165	1.194
NB_3	1715.682	810.081	33.425	3.343	10.903	0.871
NB_3*	1559.620	719.443	33.421	3.314	11.049	0.858
NB_4	747.163	348.605	85.298	15.773	54.027	4.227
NB_5	914.832	431.234	86.865	10.871	36.740	2.503
NB_6	1871.008	846.369	76.594	6.712	22.127	1.648
BLANK-15	1913.270	1034.578	-0.013	0.003	-0.009	0.016

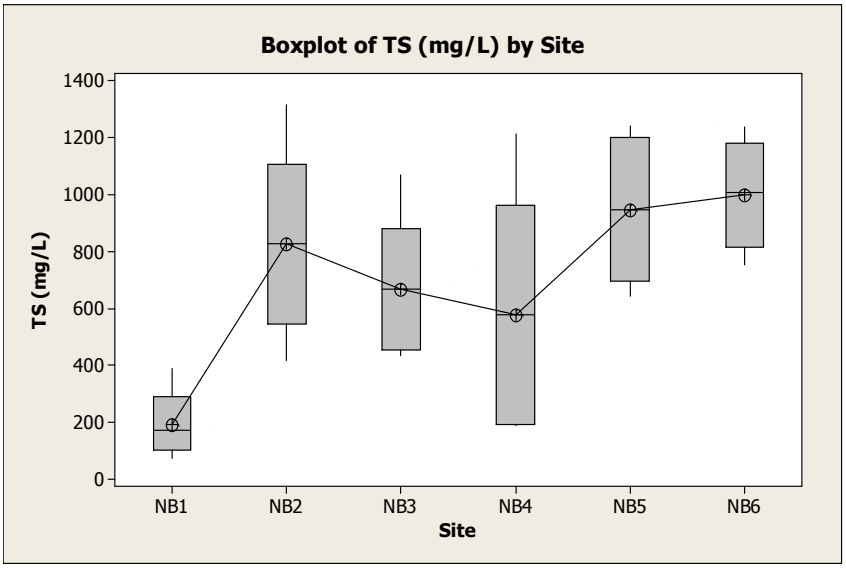
Name	Th	Tm	Lu	W	Hg
NB_1	2.833	0.095	0.092	1.033	-0.117
NB_2	8.526	0.197	0.234	0.914	-0.132
NB_3	4.659	0.134	0.161	0.652	-0.187
NB_3*	5.125	0.135	0.169	0.519	-0.104
NB_4	6.558	0.529	0.501	1.309	-0.045
NB_5	10.213	0.328	0.312	3.954	-0.070
NB_6	6.225	0.225	0.206	1.658	-0.083
BLANK-15	0.084	-0.009	-0.003	0.263	0.026

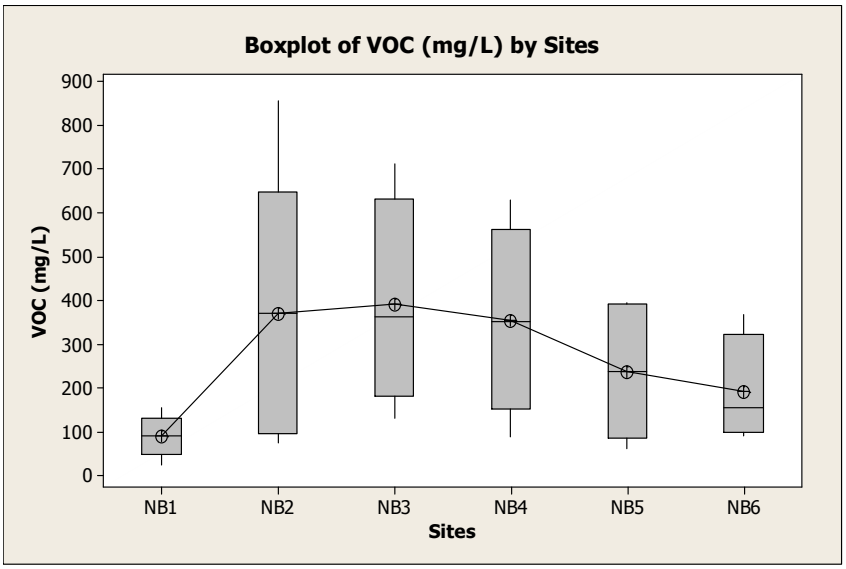
8.2 Appendix C

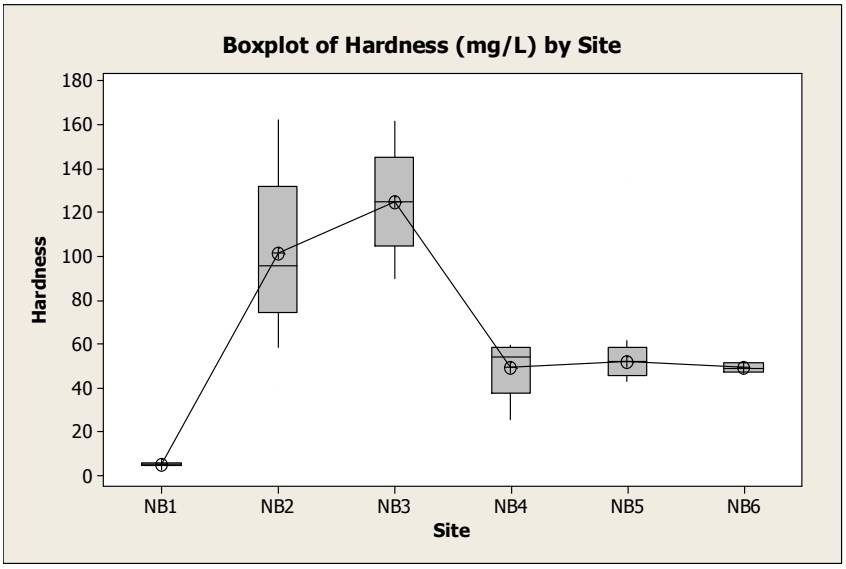
Boxplots derived from the statistical analyses of most parameters are listed in the following graphs. All statistical means and standard deviations for all associated parameters are subsequently listed.

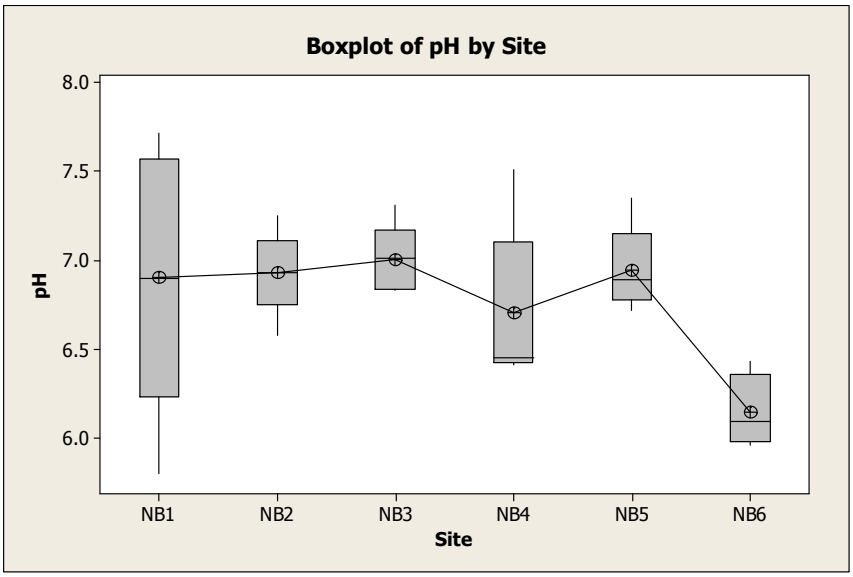


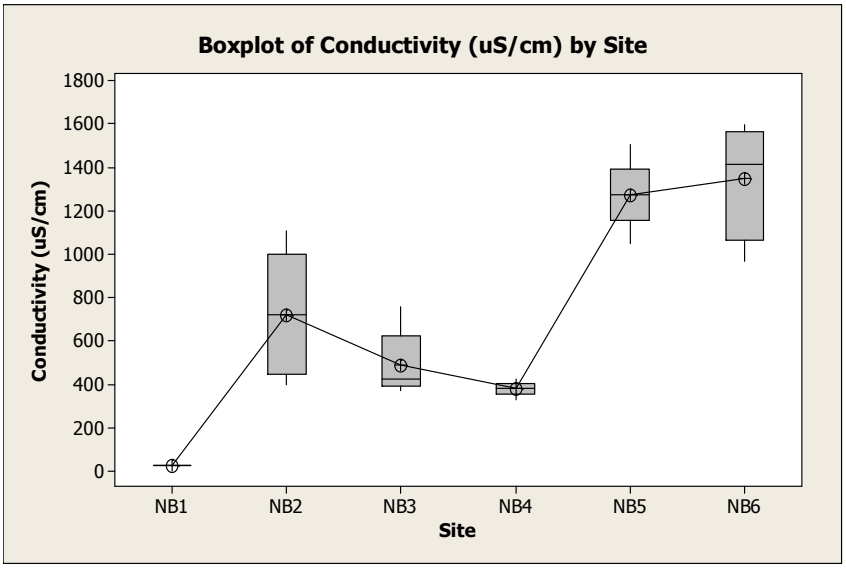


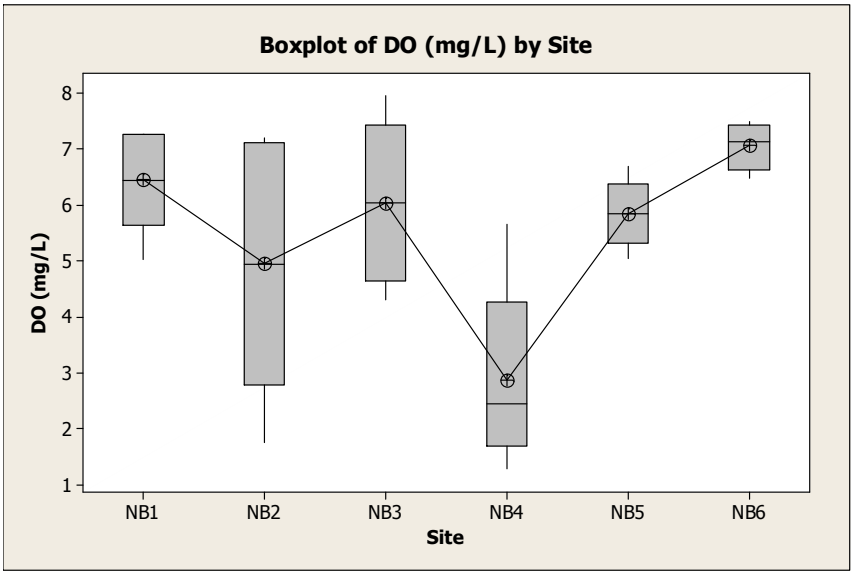

Boxplot of TS (mg/L) by Site
TS (mg/L)
1400
1200
1000
800
600
400
200
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

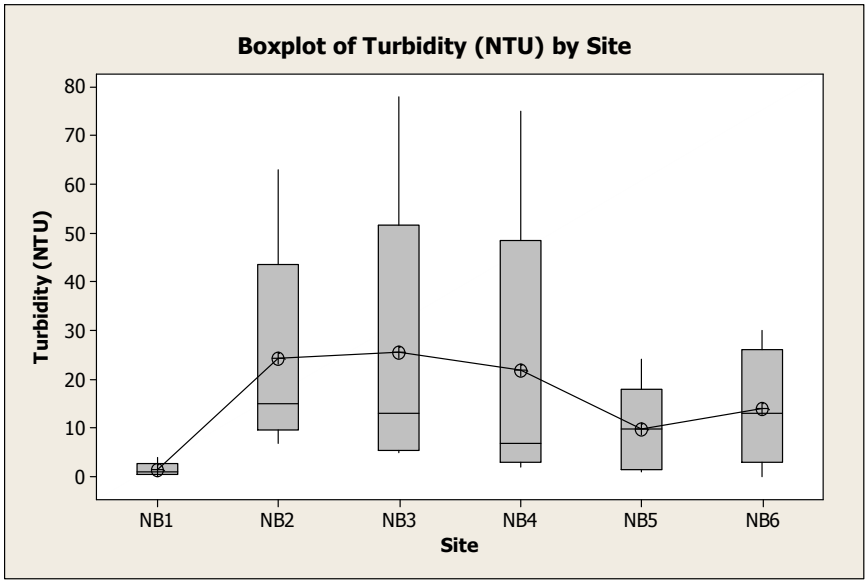

Boxplot of VOC (mg/L) by Sites
VOC (mg/L)
900
800
700
600
500
400
300
200
100
0
NB1
NB2
NB3
NB4
NB5
NB6
Sites

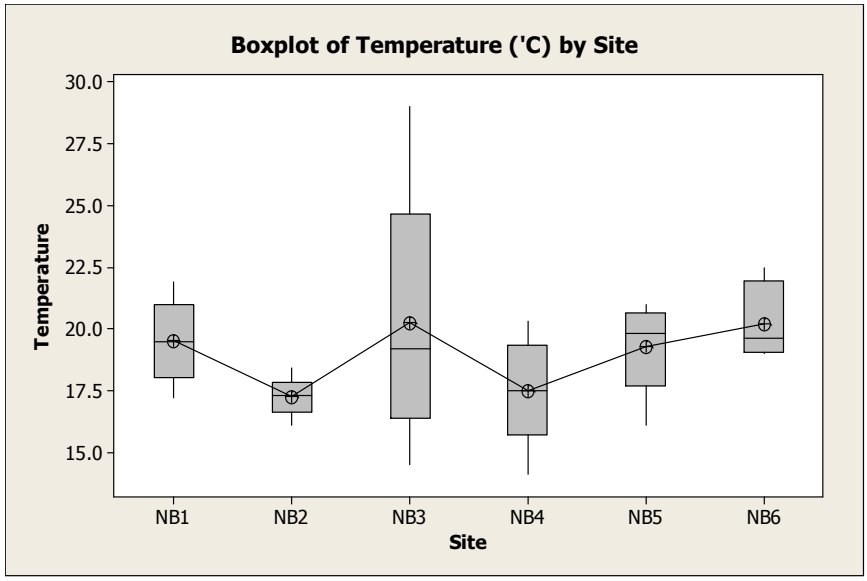

Boxplot of Hardness (mg/L) by Site
Hardness
180
160
140
120
100
80
60
40
20
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

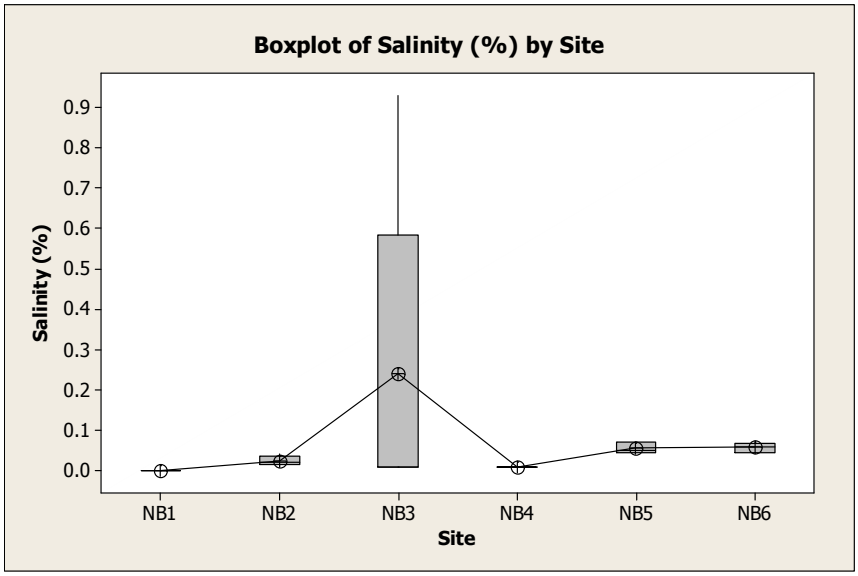

Boxplot of pH by Site
pH
8.0
7.5
7.0
6.5
6.0
NB1
NB2
NB3
NB4
NB5
NB6
Site

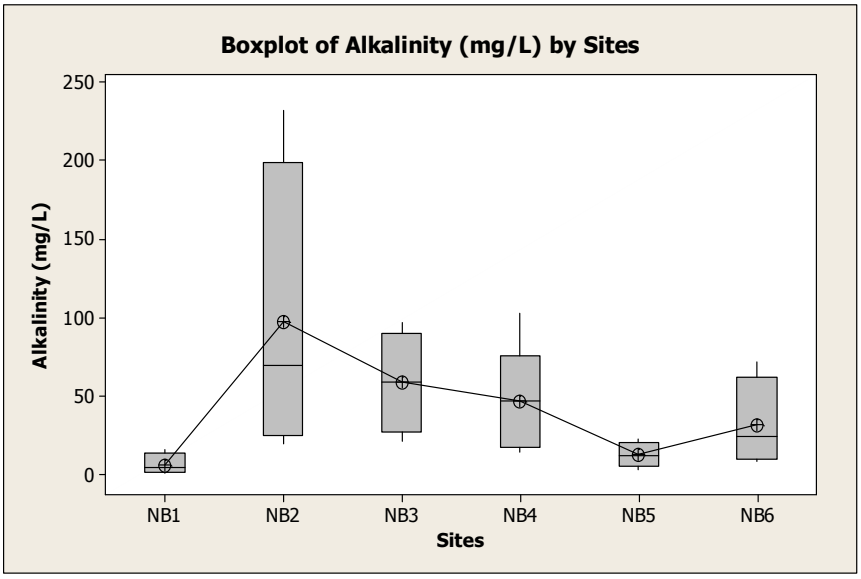

Boxplot of Conductivity (uS/cm) by Site
Conductivity (uS/cm)
1800
1600
1400
1200
1000
800
600
400
200
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

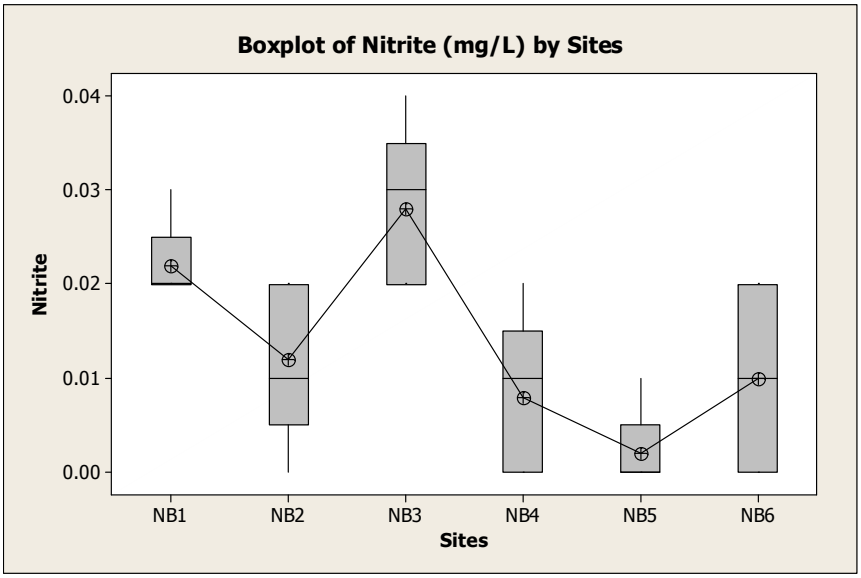

Boxplot of DO (mg/L) by Site
DO (mg/L)
8
7
6
5
4
3
2
1
NB1
NB2
NB3
NB4
NB5
NB6
Site

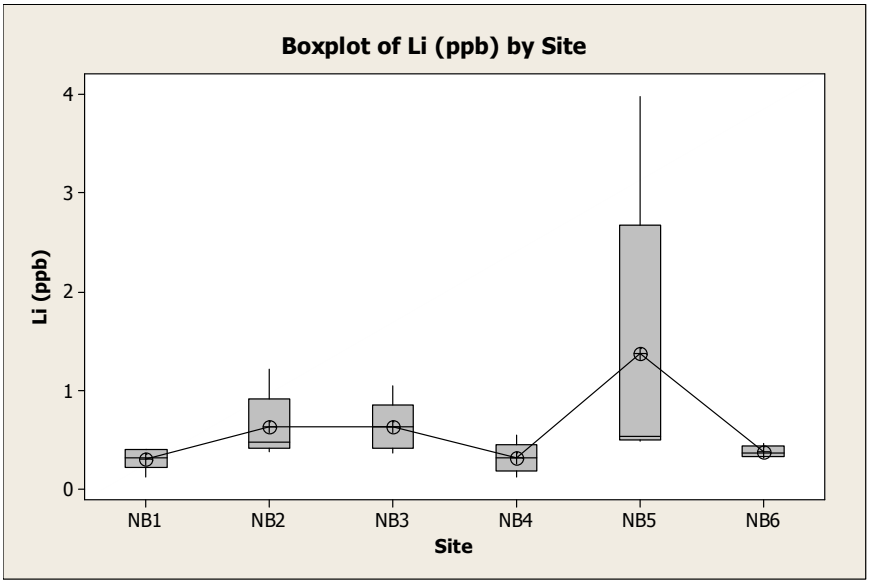

Boxplot of Turbidity (NTU) by Site
Turbidity (NTU)
80
70
60
50
40
30
20
10
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

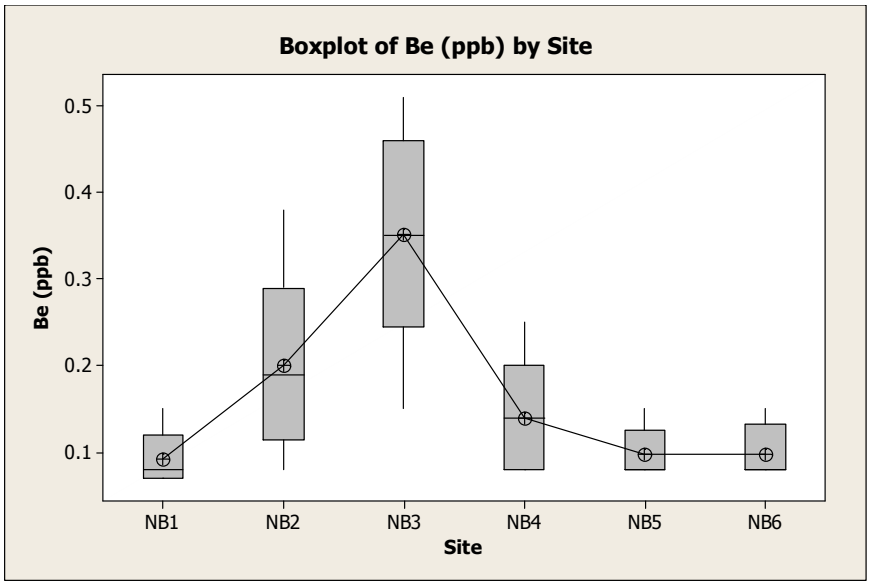

Boxplot of Temperature ('C) by Site
Temperature
30.0
27.5
25.0
22.5
20.0
17.5
15.0
NB1
NB2
NB3
NB4
NB5
NB6
Site

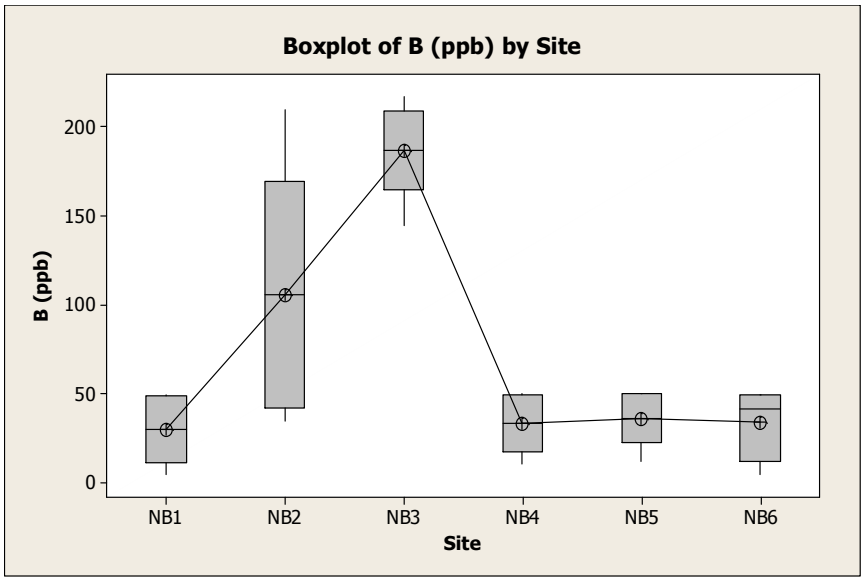

Boxplot of Salinity (%) by Site
Salinity (%)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
NB1
NB2
NB3
NB4
NB5
NB6
Site

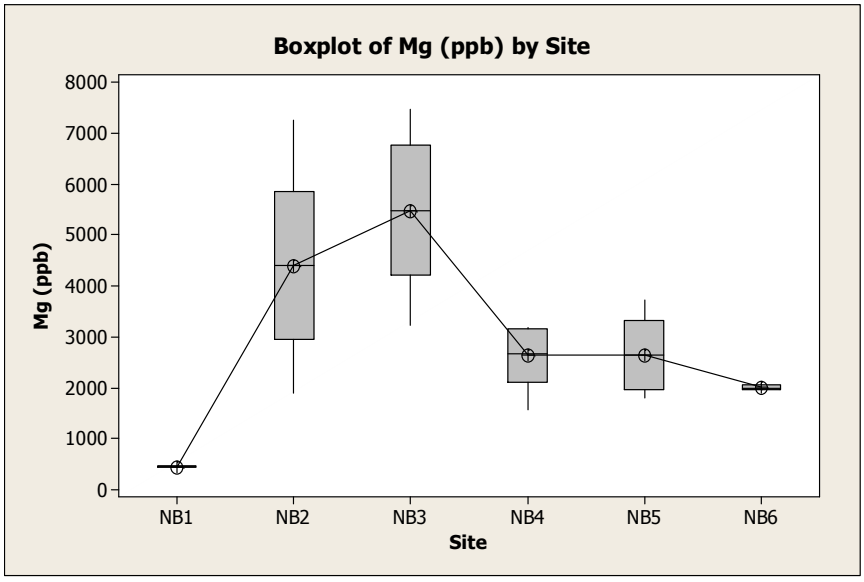

Boxplot of Alkalinity (mg/L) by Sites
Alkalinity (mg/L)
0
50
100
150
200
250
NB1
NB2
NB3
NB4
NB5
NB6
Sites

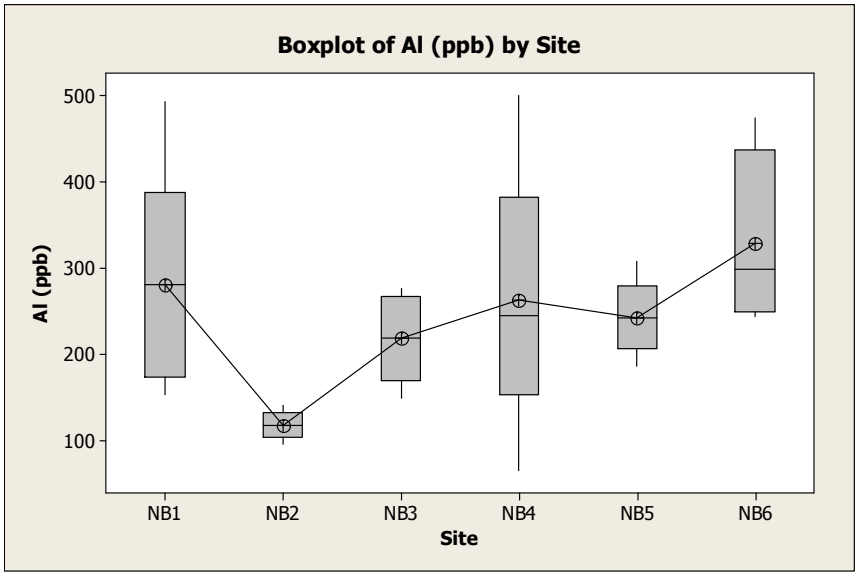

Boxplot of Nitrite (mg/L) by Sites
Nitrite
0.04
0.03
0.02
0.01
0.00
NB1
NB2
NB3
NB4
NB5
NB6
Sites

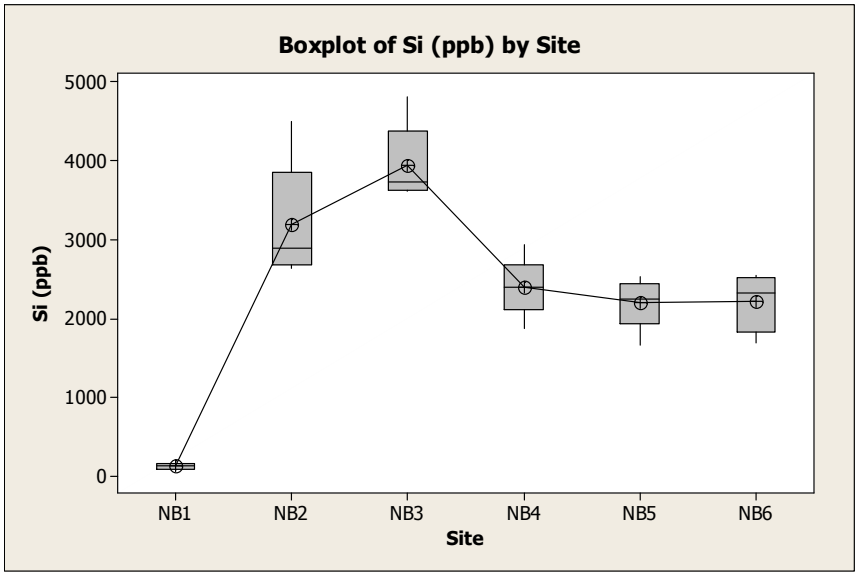

Boxplot of Li (ppb) by Site
Li (ppb)
4
3
2
1
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

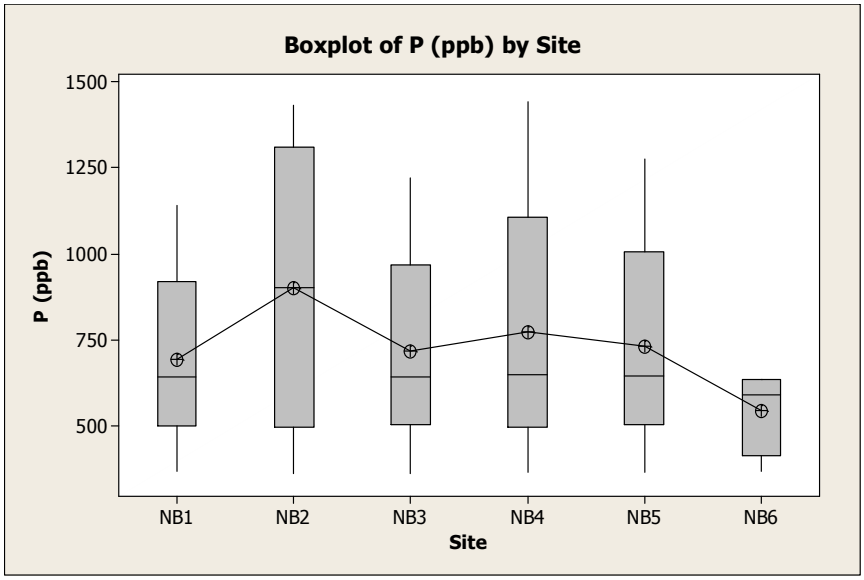

Boxplot of Be (ppb) by Site
Be (ppb)
0.5
0.4
0.3
0.2
0.1
NB1
NB2
NB3
NB4
NB5
NB6
Site

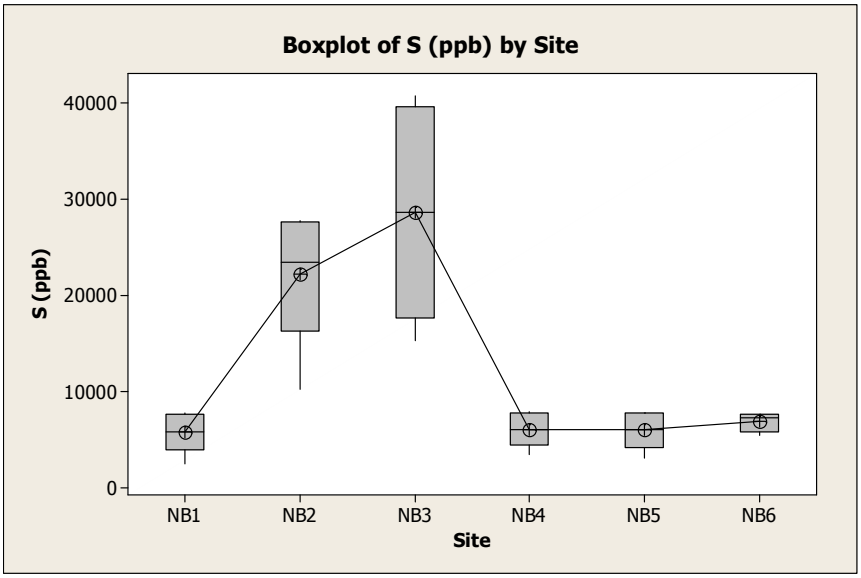

Boxplot of B (ppb) by Site
B (ppb)
200
150
100
50
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

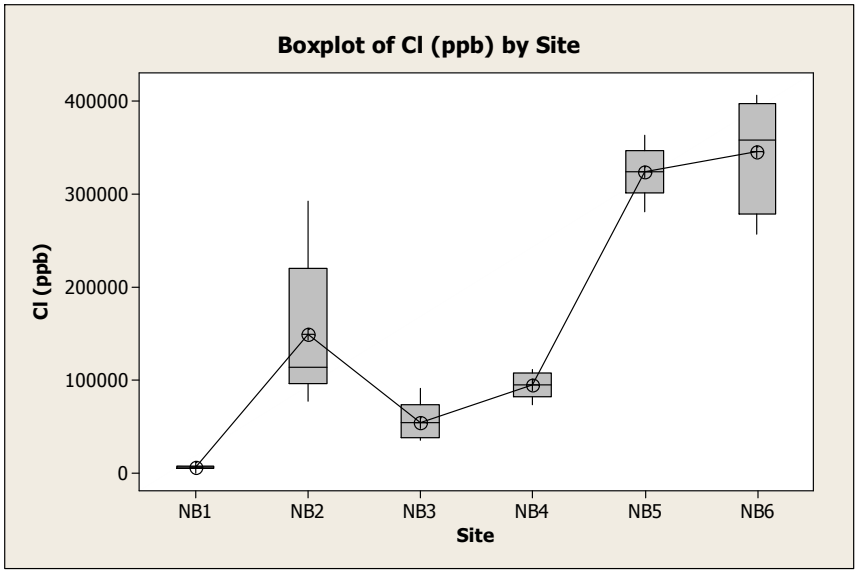

Boxplot of Mg (ppb) by Site
Mg (ppb)
8000
7000
6000
5000
4000
3000
2000
1000
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

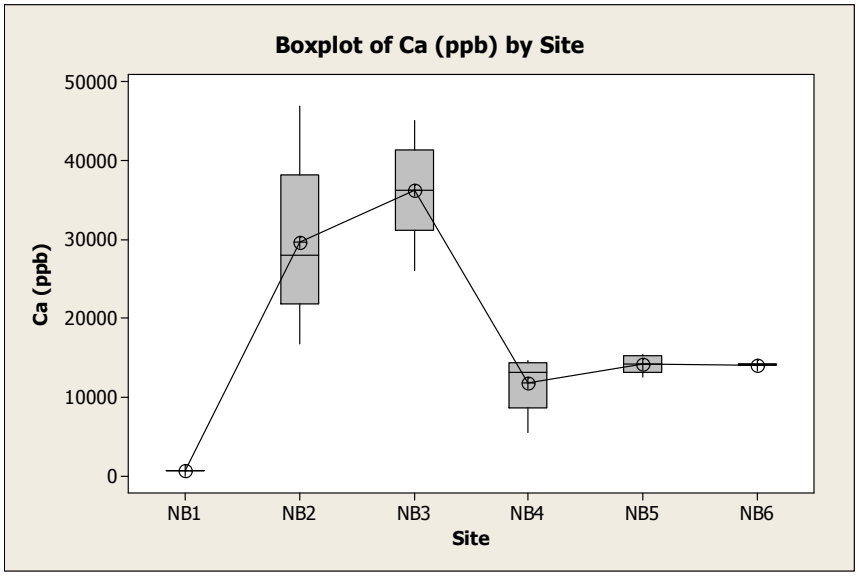

Boxplot of Al (ppb) by Site
Al (ppb)
500
400
300
200
100
NB1
NB2
NB3
NB4
NB5
NB6
Site

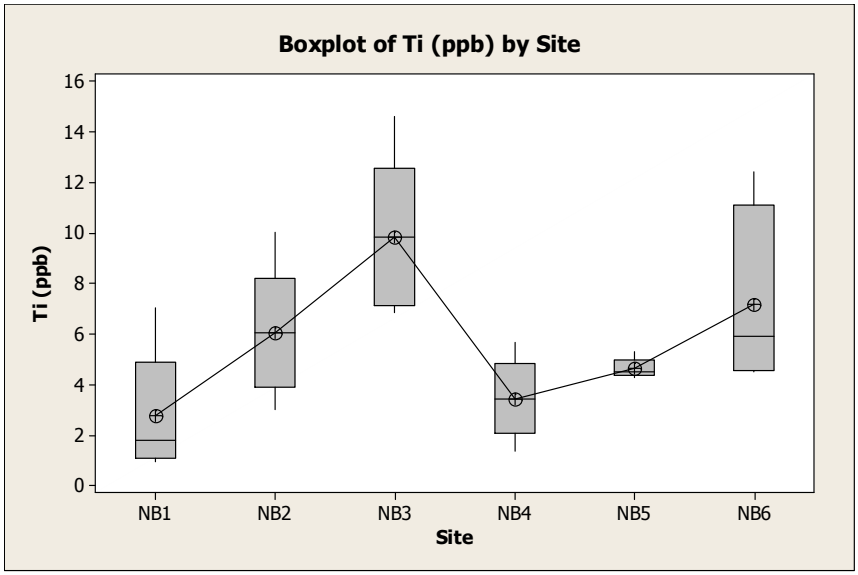

Boxplot of Si (ppb) by Site
Si (ppb)
5000
4000
3000
2000
1000
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

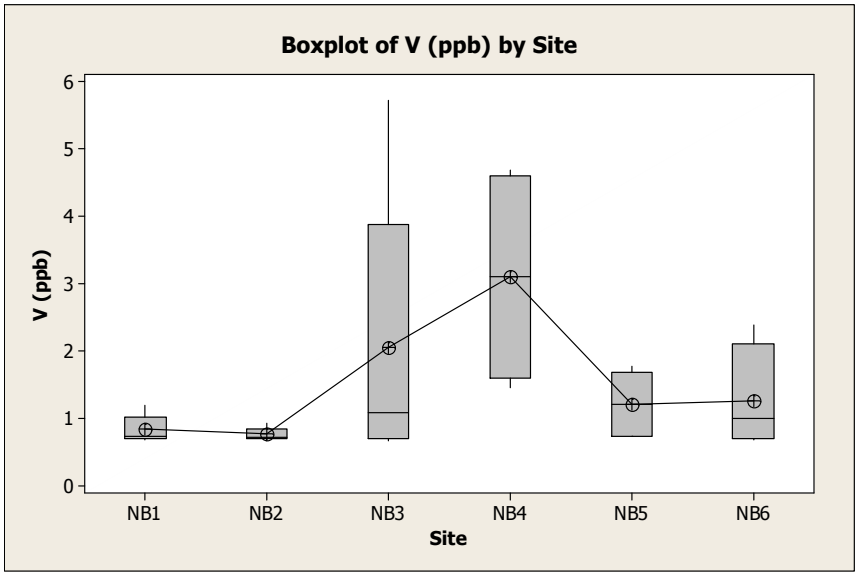

Boxplot of P (ppb) by Site
P (ppb)
1500
1250
1000
750
500
NB1
NB2
NB3
NB4
NB5
NB6
Site

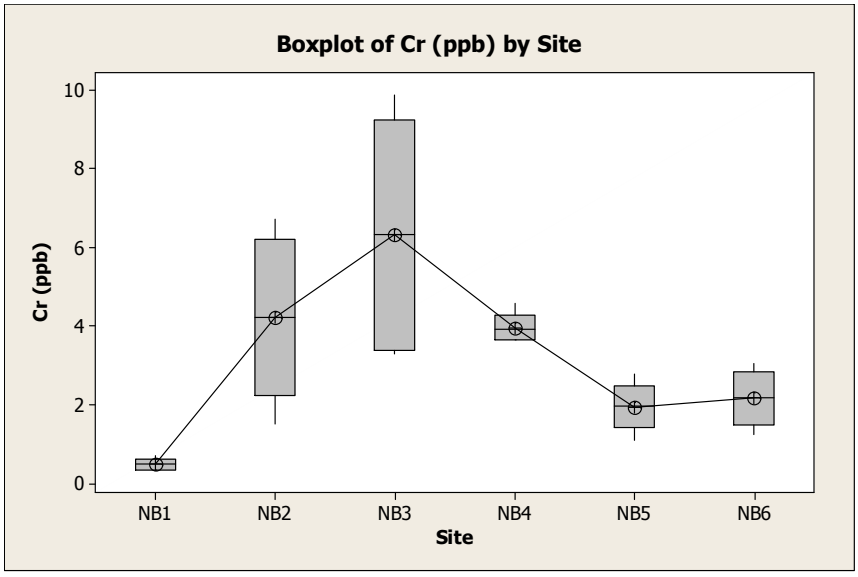

Boxplot of S (ppb) by Site
S (ppb)
40000
30000
20000
10000
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

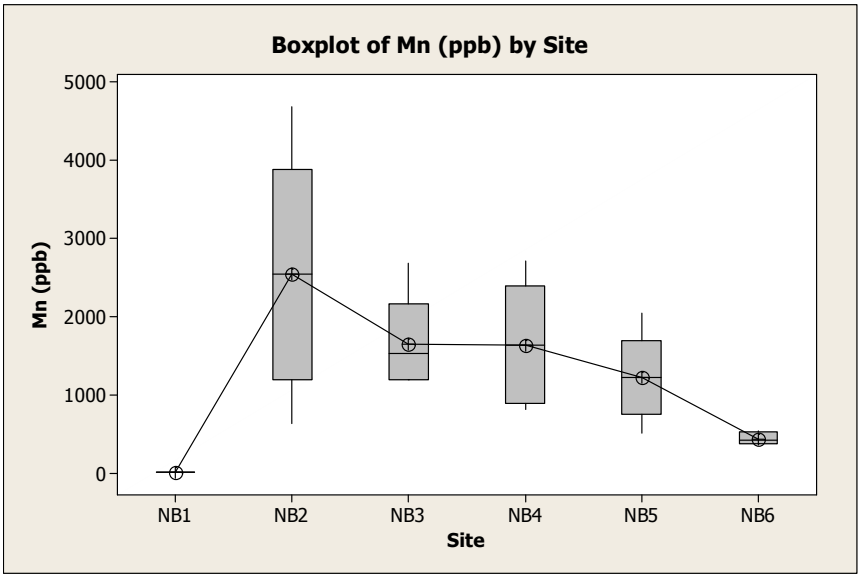

Boxplot of Cl (ppb) by Site
Cl (ppb)
400000
300000
200000
100000
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

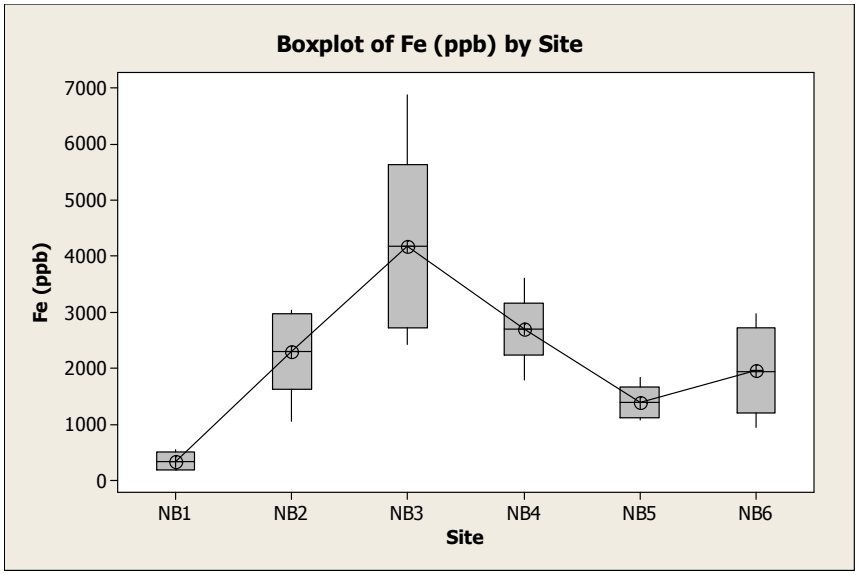

Boxplot of Ca (ppb) by Site
Ca (ppb)
50000
40000
30000
20000
10000
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

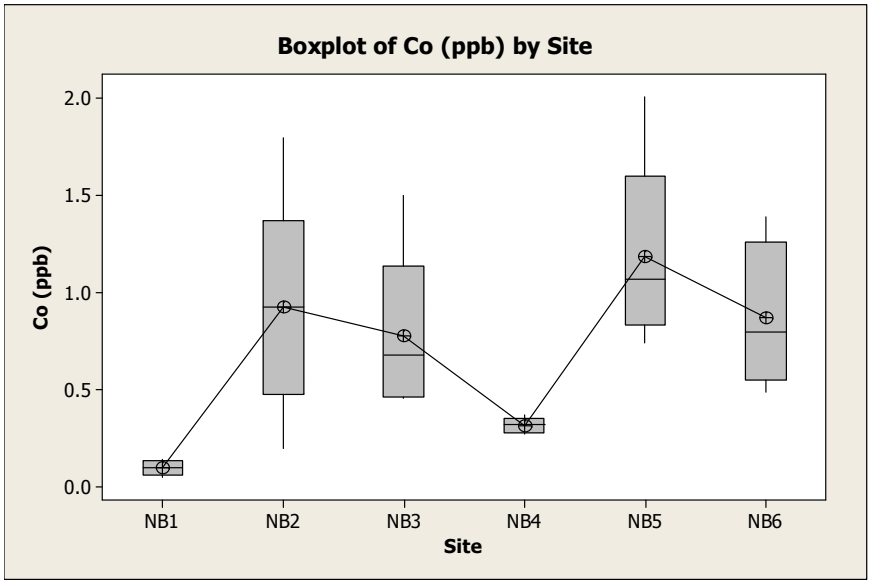

Boxplot of Ti (ppb) by Site
Ti (ppb)
16
14
12
10
8
6
4
2
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

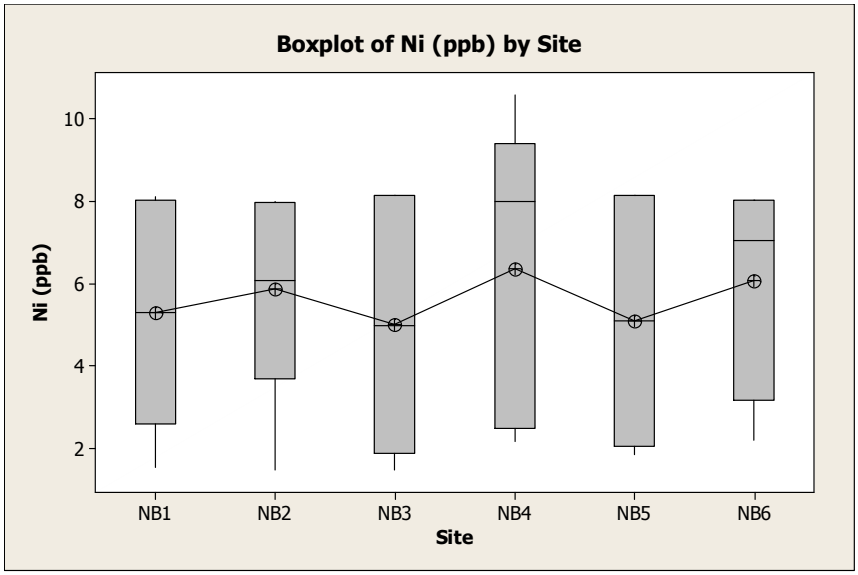

Boxplot of V (ppb) by Site
V (ppb)
0
1
2
3
4
5
6
NB1
NB2
NB3
NB4
NB5
NB6
Site

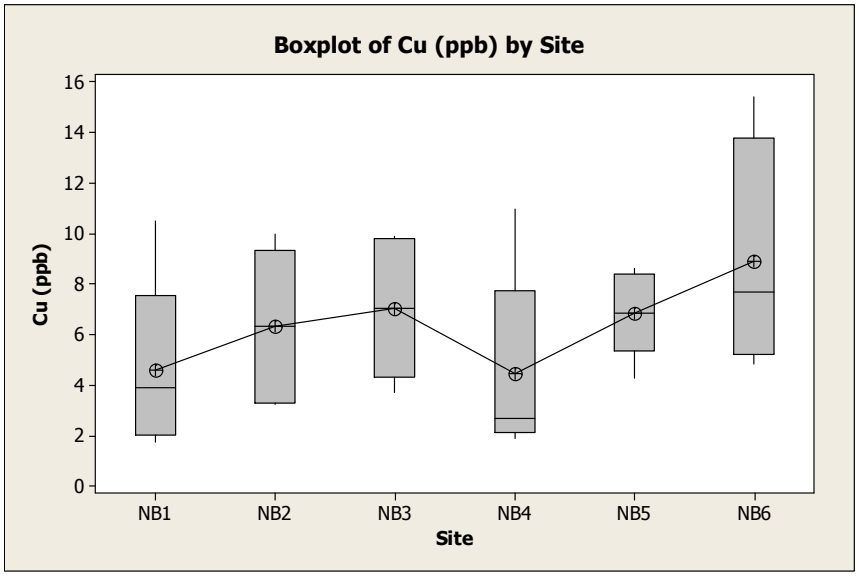

Boxplot of Cr (ppb) by Site
Cr (ppb)
0
2
4
6
8
10
NB1
NB2
NB3
NB4
NB5
NB6
Site

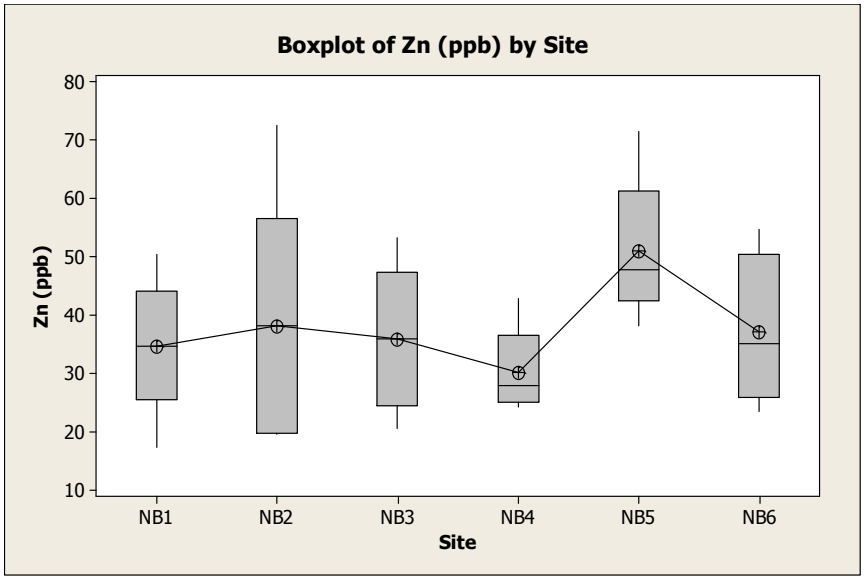

Boxplot of Mn (ppb) by Site
Mn (ppb)
5000
4000
3000
2000
1000
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

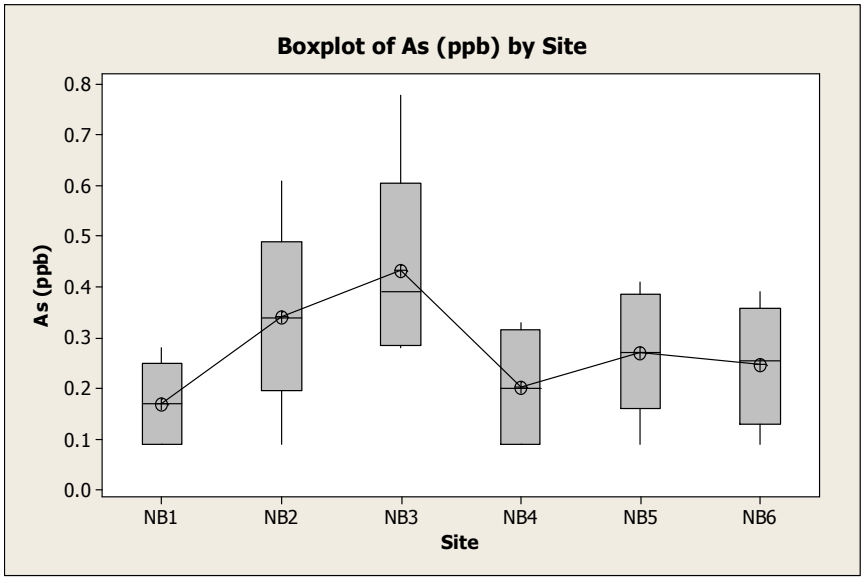

Boxplot of Fe (ppb) by Site
Fe (ppb)
7000
6000
5000
4000
3000
2000
1000
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

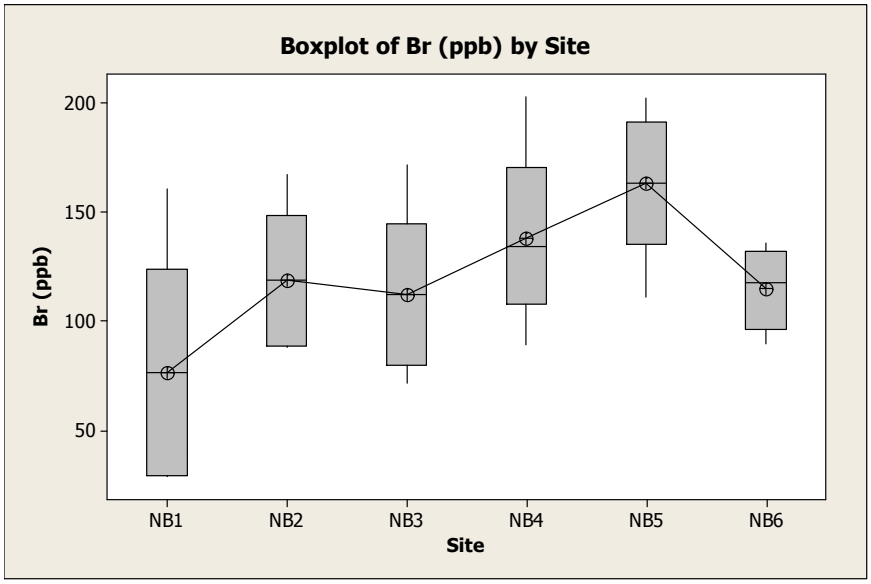

Boxplot of Co (ppb) by Site
Co (ppb)
2.0
1.5
1.0
0.5
0.0
NB1
NB2
NB3
NB4
NB5
NB6
Site

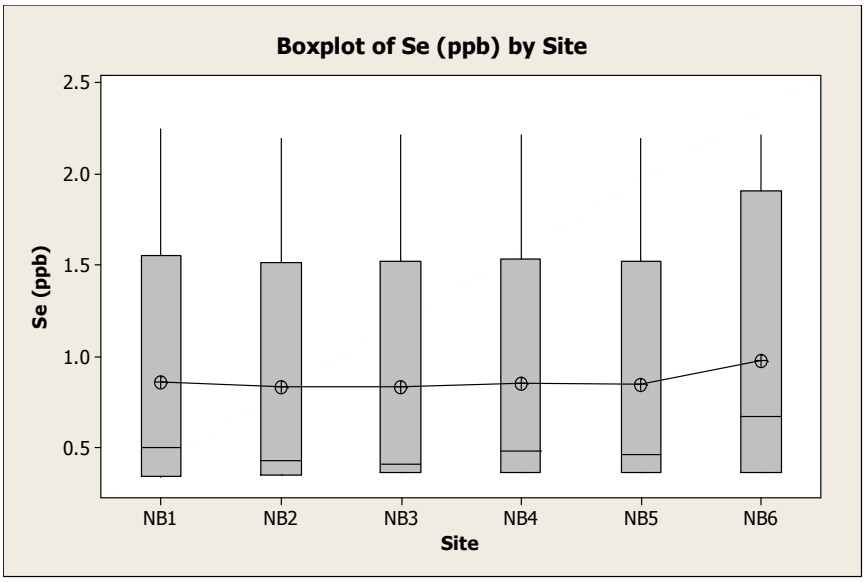

Boxplot of Ni (ppb) by Site
Ni (ppb)
10
8
6
4
2
NB1
NB2
NB3
NB4
NB5
NB6
Site

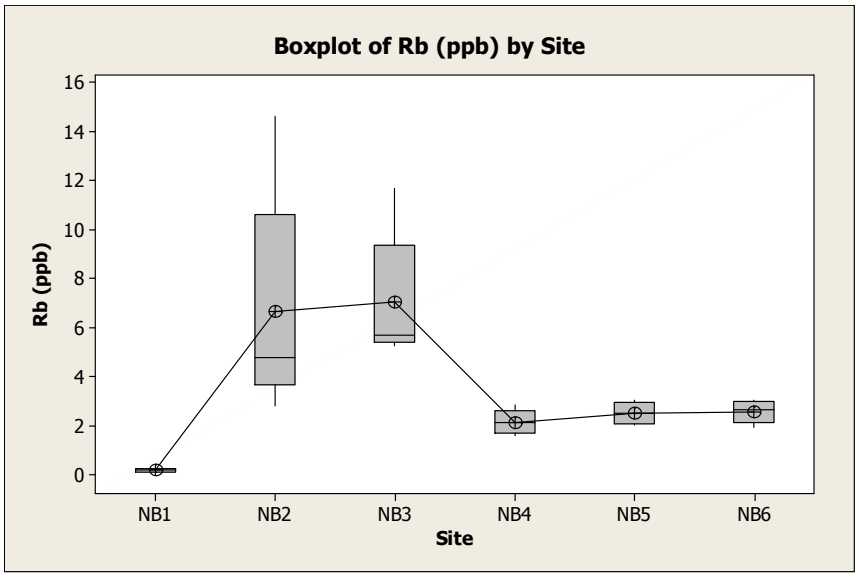

Boxplot of Cu (ppb) by Site
Cu (ppb)
16
14
12
10
8
6
4
2
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

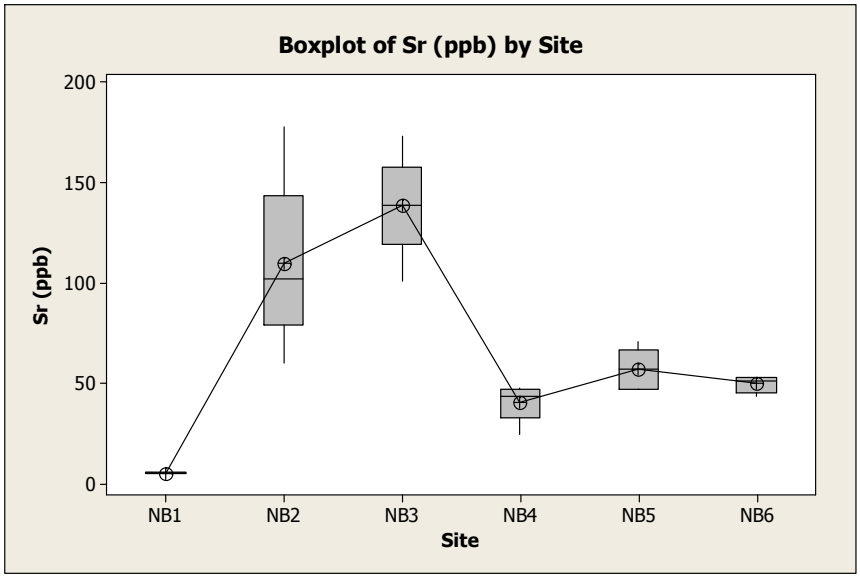

Boxplot of Zn (ppb) by Site
Zn (ppb)
80
70
60
50
40
30
20
10
NB1
NB2
NB3
NB4
NB5
NB6
Site

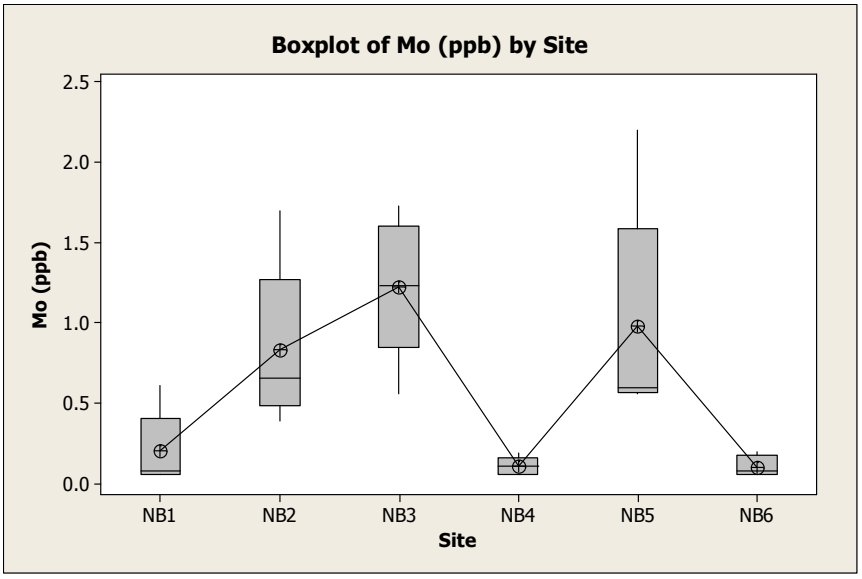

Boxplot of As (ppb) by Site
As (ppb)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
NB1
NB2
NB3
NB4
NB5
NB6
Site

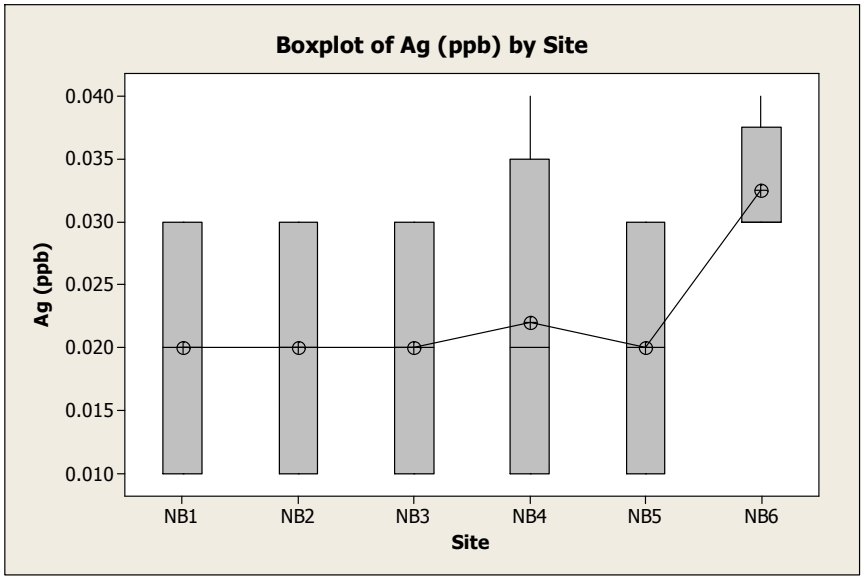

Boxplot of Br (ppb) by Site
Br (ppb)
50
100
150
200
NB1
NB2
NB3
NB4
NB5
NB6
Site

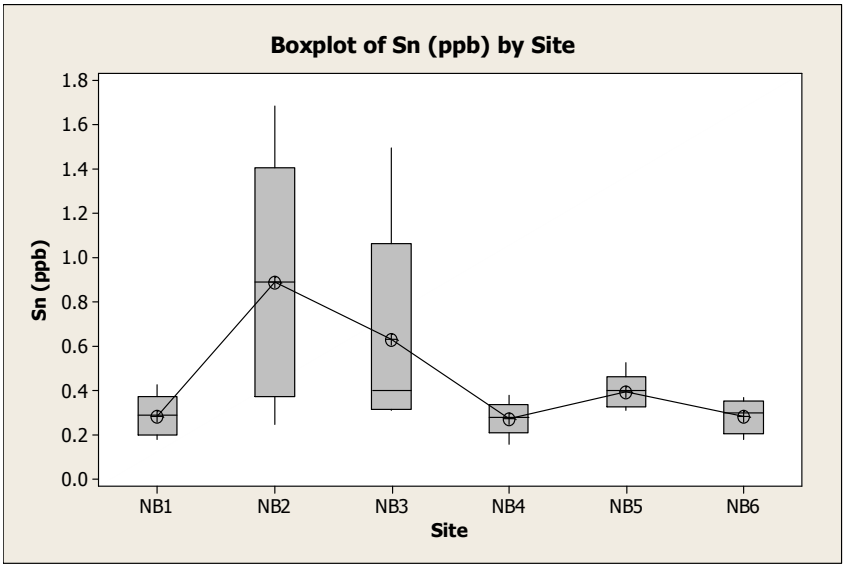

Boxplot of Se (ppb) by Site
Se (ppb)
2.5
2.0
1.5
1.0
0.5
NB1
NB2
NB3
NB4
NB5
NB6
Site

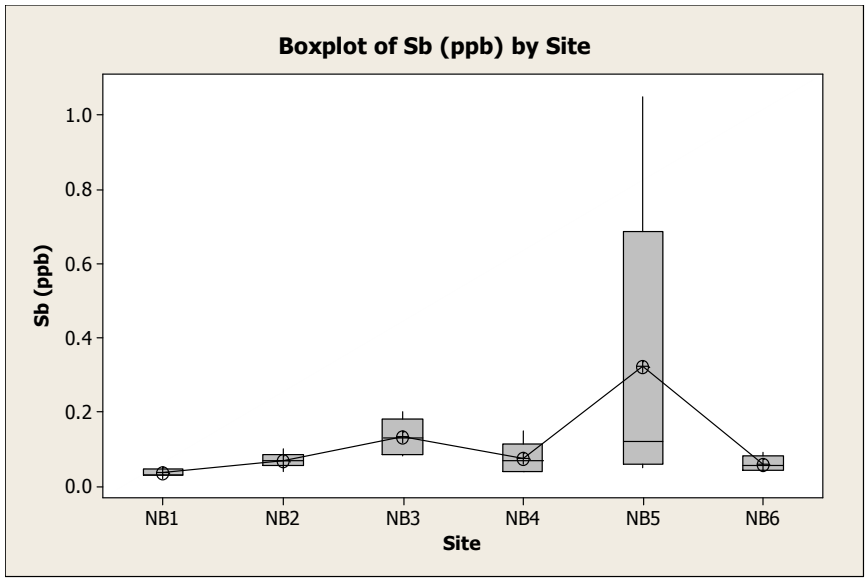

Boxplot of Rb (ppb) by Site
Rb (ppb)
16
14
12
10
8
6
4
2
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

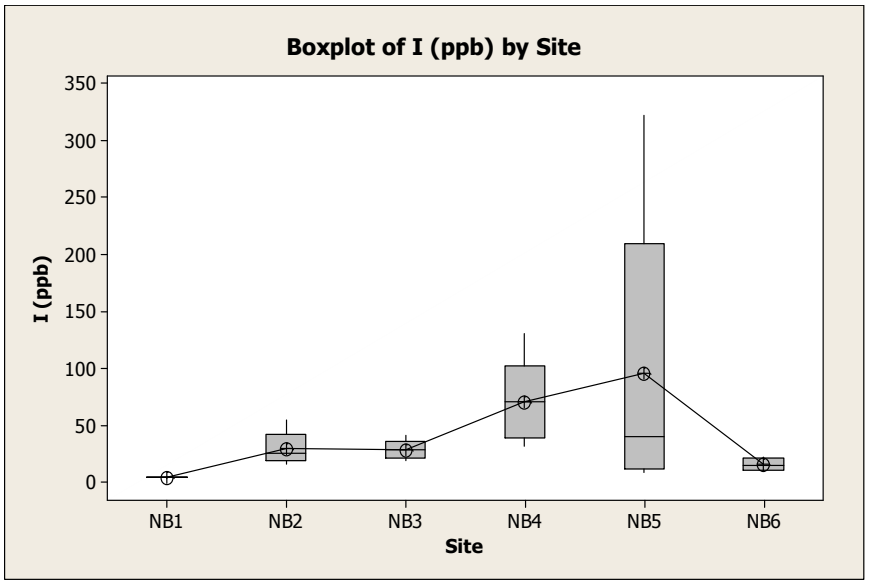

Boxplot of Sr (ppb) by Site
Sr (ppb)
200
150
100
50
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

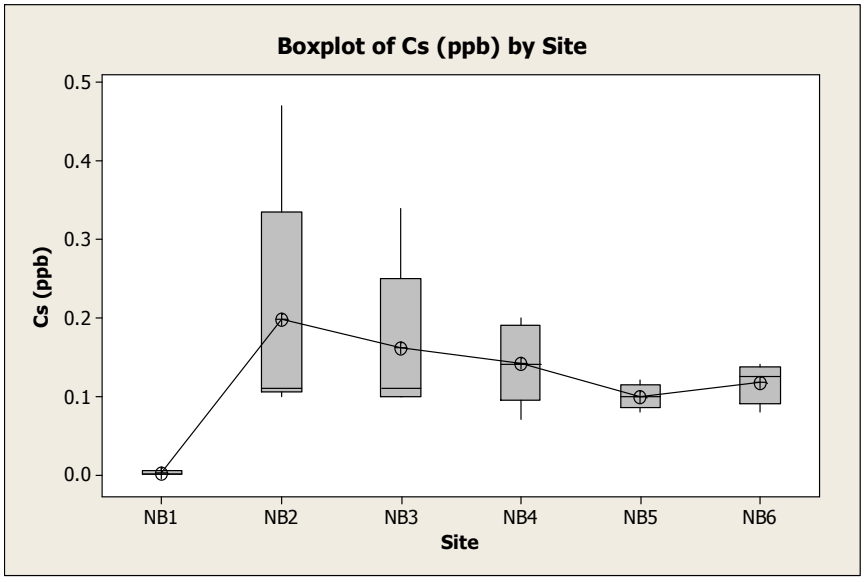

Boxplot of Mo (ppb) by Site
Mo (ppb)
2.5
2.0
1.5
1.0
0.5
0.0
NB1
NB2
NB3
NB4
NB5
NB6
Site

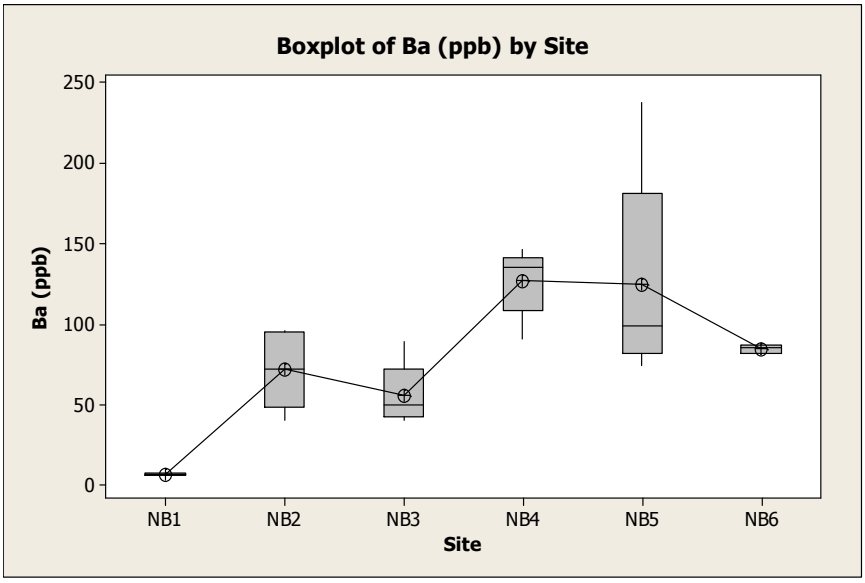

Boxplot of Ag (ppb) by Site
Ag (ppb)
0.040
0.035
0.030
0.025
0.020
0.015
0.010
NB1
NB2
NB3
NB4
NB5
NB6
Site

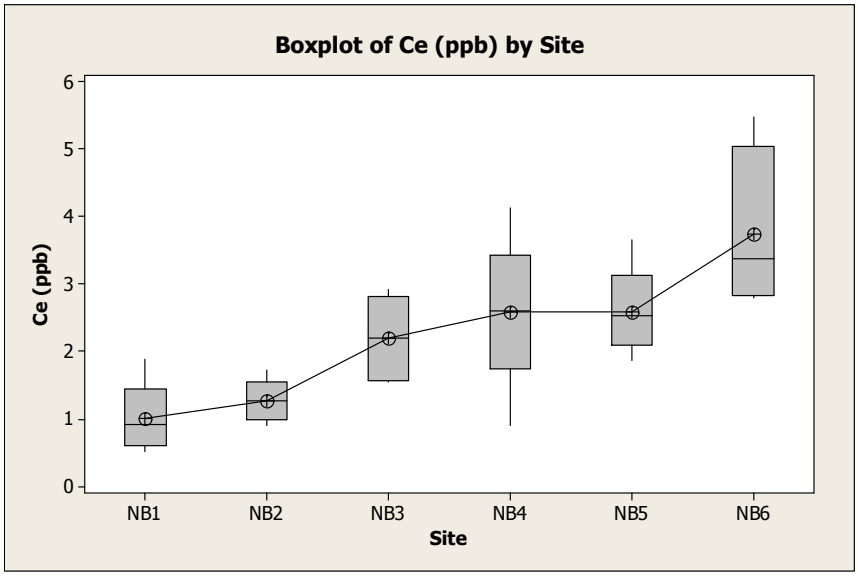

Boxplot of Sn (ppb) by Site
Sn (ppb)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
NB1
NB2
NB3
NB4
NB5
NB6
Site

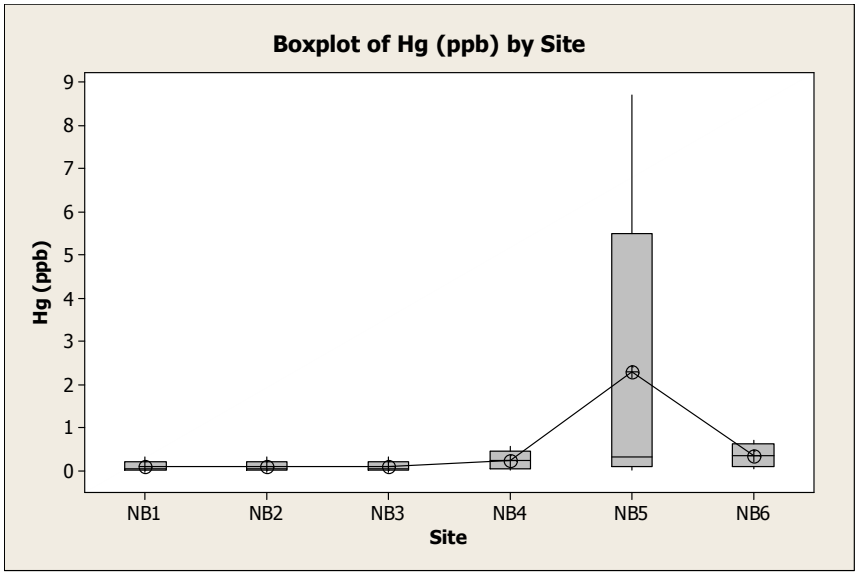

Boxplot of Sb (ppb) by Site
Sb (ppb)
1.0
0.8
0.6
0.4
0.2
0.0
NB1
NB2
NB3
NB4
NB5
NB6
Site

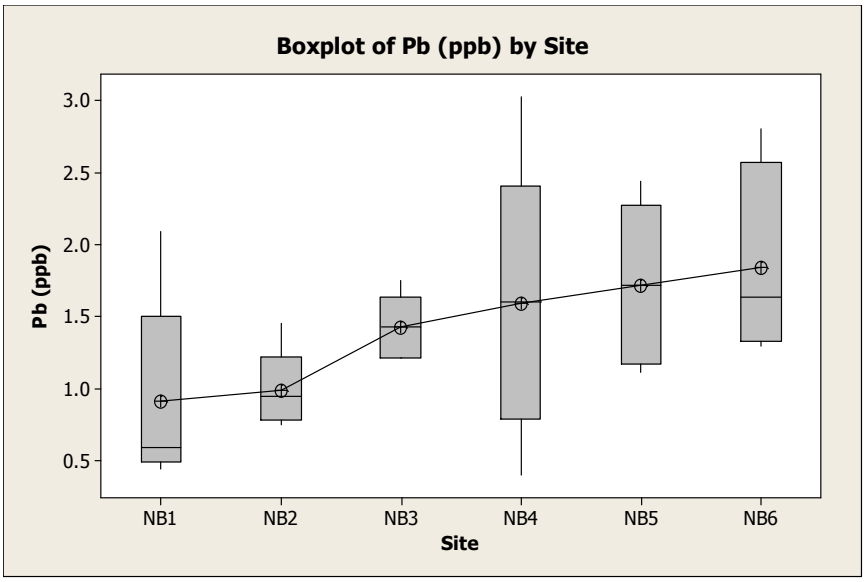

Boxplot of I (ppb) by Site
I (ppb)
350
300
250
200
150
100
50
0
NB1
NB2
NB3
NB4
NB5
NB6
Site

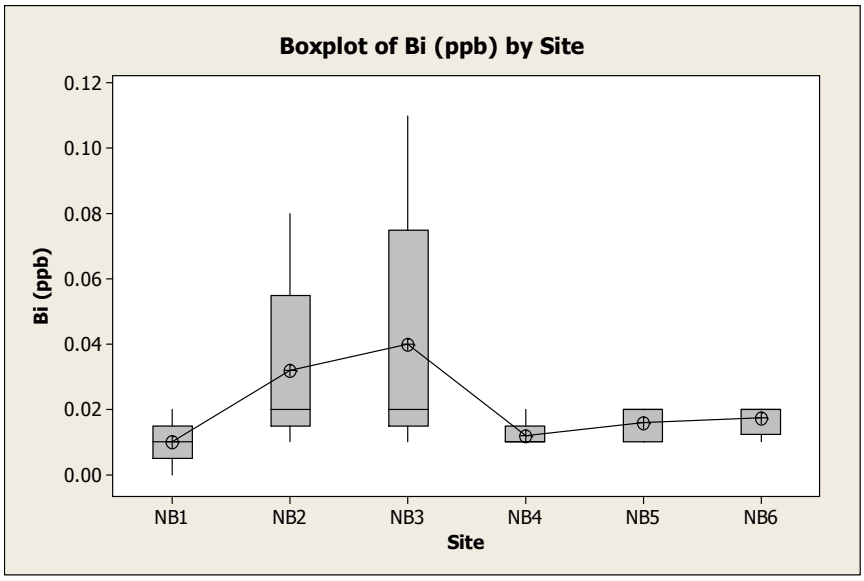

Boxplot of Cs (ppb) by Site
Cs (ppb)
0.5
0.4
0.3
0.2
0.1
0.0
NB1
NB2
NB3
NB4
NB5
NB6
Site

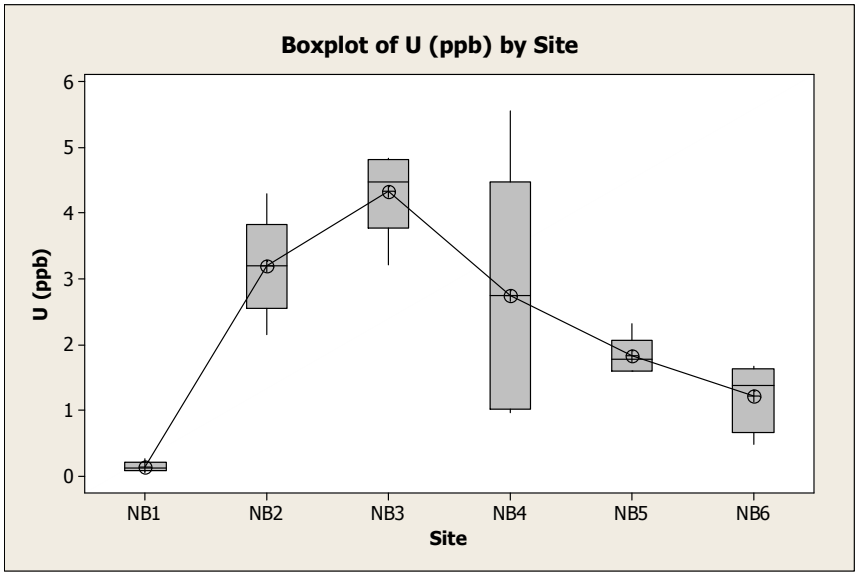

Boxplot of Ba (ppb) by Site
Ba (ppb)
250
200
150
100
50
0
NB1
NB2
NB3
NB4
NB5
NB6
Site


Boxplot of Ce (ppb) by Site
Ce (ppb)
0
1
2
3
4
5
6
NB1
NB2
NB3
NB4
NB5
NB6
Site


Boxplot of Hg (ppb) by Site
Hg (ppb)
0
1
2
3
4
5
6
7
8
9
NB1
NB2
NB3
NB4
NB5
NB6
Site


Boxplot of Pb (ppb) by Site
Pb (ppb)
3.0
2.5
2.0
1.5
1.0
0.5
NB1
NB2
NB3
NB4
NB5
NB6
Site


Boxplot of Bi (ppb) by Site
Bi (ppb)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
NB1
NB2
NB3
NB4
NB5
NB6
Site


Boxplot of U (ppb) by Site
U (ppb)
0
1
2
3
4
5
6
NB1
NB2
NB3
NB4
NB5
NB6
Site

Variable	Site	Mean	StDev
TSS (mg/L)	NB1	35.0	23.7
	NB2	36.5	24.9
	NB3	56.5	29.8
	NB4	61.0	37.2
	NB5	53.0	34.8
	NB6	108.7	31.9
TDS (mg/L)	NB1	156.5	96.3
	NB2	789	306
	NB3	611.0	223.1
	NB4	517	402
	NB5	894	228
	NB6	892.0	186.6
TS (mg/L)	NB1	191.5	118.7
	NB2	825	330
	NB3	668	252
	NB4	578	424
	NB5	947	257
	NB6	1000.7	196.9
VOC (mg/L)	NB1	90.0	47.9
	NB2	372	313
	NB3	393	240
	NB4	356	221
	NB5	238.5	153.5
	NB6	192.0	124.8
Hardness	NB1	5.200	0.636
	NB2	101.3	37.6
	NB3	124.7	25.6
	NB4	49.22	13.72
	NB5	52.02	7.08
	NB6	49.10	2.28
pH	NB1	6.902	0.745
	NB2	6.930	0.238
	NB3	7.0060	0.1926
	NB4	6.702	0.466
	NB5	6.948	0.240
	NB6	6.143	0.205
Cond.	NB1	24.500	1.500
	NB2	722	290
	NB3	491.8	154.5
	NB4	380.0	34.5
	NB5	1275.0	162.9
	NB6	1350	273
DO (mg/L)	NB1	6.452	0.921
	NB2	4.95	2.29
	NB3	6.036	1.464
	NB4	2.862	1.663
	NB5	5.850	0.605
	NB6	7.063	0.429
Turbidity	NB1	1.500	1.500
	NB2	24.3	22.6
	NB3	25.5	30.5
	NB4	22.0	30.7
	NB5	9.76	9.28
	NB6	14.00	12.33
Temperature	NB1	19.520	1.715
	NB2	17.260	0.814
	NB3	20.26	5.35
	NB4	17.52	2.25
	NB5	19.300	1.896
	NB6	20.200	1.627
Salinity	NB1	0.000000	0.000000
	NB2	0.02400	0.01140
	NB3	0.240	0.398
	NB4	0.010000	0.000000
	NB5	0.05600	0.01342
	NB6	0.05750	0.01258
Alkalinity	NB1	6.33	6.85
	NB2	97.7	95.4
	NB3	58.8	32.0
	NB4	46.5	35.0
	NB5	12.65	8.18
	NB6	32.0	28.5
Nitrite	NB1	0.02200	0.00447
	NB2	0.01200	0.00837
	NB3	0.02800	0.00837
	NB4	0.00800	0.00837
	NB5	0.00200	0.00447
	NB6	0.01000	0.01000
Chloride (HACH)	NB1	9.720	0.736
	NB2	156.2	74.7
	NB3	40.100	1.200
	NB4	102.17	7.65
Li (ppb)	NB1	0.3070	0.1126
	NB2	0.626	0.338
	NB3	0.632	0.264
	NB4	0.3140	0.1534
	NB5	1.378	1.503
	NB6	0.3775	0.0602
Be (ppb)	NB1	0.0920	0.0335
	NB2	0.2000	0.1111
	NB3	0.3520	0.1316
	NB4	0.1400	0.0696
	NB5	0.0980	0.0303
	NB6	0.0975	0.0350
B (ppb)	NB1	29.97	19.50
	NB2	105.7	70.3
	NB3	186.9	27.0
	NB4	33.31	16.95
	NB5	36.21	15.74
	NB6	34.2	21.0
Mg (ppb)	NB1	453.60	11.56
	NB2	4397	1908
	NB3	5479	1532
	NB4	2636	643
	NB5	2645	743
	NB6	2003.4	53.8

Al (ppb)	NB1	281.1	131.5	Mn (ppb)	NB1	13.13	3.90
	NB2	118.28	16.65		NB2	2540	1510
	NB3	218.7	51.6		NB3	1655	606
	NB4	263.5	155.1		NB4	1645	785
	NB5	243.2	44.1		NB5	1229	559
	NB6	329.2	103.1		NB6	446.0	75.6
Si (ppb)	NB1	128.5	39.7	Fe (ppb)	NB1	342.6	159.3
	NB2	3193	763		NB2	2291	783
	NB3	3948	502		NB3	4178	1714
	NB4	2402	379		NB4	2697	642
	NB5	2200	325		NB5	1393	297
	NB6	2221	377		NB6	1949	821
P (ppb)	NB1	695	279	Co (ppb)	NB1	0.1000	0.0367
	NB2	903	426		NB2	0.926	0.575
	NB3	717	311		NB3	0.778	0.426
	NB4	772	403		NB4	0.3160	0.0385
	NB5	733	334		NB5	1.188	0.489
	NB6	545.3	125.4		NB6	0.870	0.381
S (ppb)	NB1	5805	2125	Ni (ppb)	NB1	5.31	2.82
	NB2	22287	7128		NB2	5.88	2.65
	NB3	28693	11146		NB3	5.00	3.14
	NB4	6068	1785		NB4	6.36	3.68
	NB5	5999	1952		NB5	5.10	3.06
	NB6	6897	1055		NB6	6.08	2.74
Cl (ppb)	NB1	5962	991	Cu (ppb)	NB1	4.62	3.50
(ICP-MS)	NB2	149547	83763		NB2	6.32	3.06
	NB3	54884	21846		NB3	7.05	2.77
	NB4	94914	14204		NB4	4.48	3.76
	NB5	324654	29549		NB5	6.872	1.717
	NB6	345519	63911		NB6	8.90	4.66
Ca (ppb)	NB1	666.0	62.9	Zn (ppb)	NB1	34.77	11.83
	NB2	29584	10879		NB2	38.09	21.56
	NB3	36274	6763		NB3	35.92	12.55
	NB4	11783	3712		NB4	30.16	7.44
	NB5	14170	1132		NB5	50.98	12.35
	NB6	14088	92.9		NB6	37.04	13.12
Ti (ppb)	NB1	2.76	2.50	As (ppb)	NB1	0.1700	0.0828
	NB2	6.05	2.60		NB2	0.3420	0.1857
	NB3	9.84	3.08		NB3	0.4340	0.2038
	NB4	3.448	1.584		NB4	0.2020	0.1130
	NB5	4.648	0.392		NB5	0.2720	0.1242
	NB6	7.19	3.70		NB6	0.2475	0.1228
V (ppb)	NB1	0.8420	0.2075	Br (ppb)	NB1	76.6	53.9
	NB2	0.7700	0.1002		NB2	118.8	32.8
	NB3	2.064	2.122		NB3	112.3	37.8
	NB4	3.110	1.504		NB4	138.3	41.0
	NB5	1.222	0.476		NB5	163.1	33.7
	NB6	1.278	0.795		NB6	115.24	19.10
Cr (ppb)	NB1	0.4780	0.1470	Se (ppb)	NB1	0.860	0.805
	NB2	4.216	2.080		NB2	0.832	0.790
	NB3	6.32	2.97		NB3	0.836	0.798
	NB4	3.958	0.375		NB4	0.854	0.790
	NB5	1.946	0.615		NB5	0.846	0.783
	NB6	2.163	0.739		NB6	0.980	0.877

Rb (ppb)	NB1	0.1860	0.0764	Cs (ppb)	NB1	0.00200	0.00447
	NB2	6.68	4.63		NB2	0.1980	0.1574
	NB3	7.04	2.67		NB3	0.1620	0.1026
	NB4	2.146	0.494		NB4	0.1420	0.0512
	NB5	2.502	0.435		NB5	0.10000	0.01581
	NB6	2.583	0.464		NB6	0.1175	0.0263
Sr (ppb)	NB1	5.260	0.434	Ba (ppb)	NB1	6.806	0.608
	NB2	109.8	42.7		NB2	71.8	24.1
	NB3	138.8	25.6		NB3	55.81	19.37
	NB4	41.00	9.35		NB4	127.12	21.61
	NB5	57.26	10.16		NB5	125.0	65.5
	NB6	50.00	4.24		NB6	84.84	2.97
Mo (ppb)	NB1	0.202	0.235	La (ppb)	NB1	0.562	0.302
	NB2	0.836	0.509		NB2	0.726	0.255
	NB3	1.226	0.437		NB3	0.856	0.244
	NB4	0.1100	0.0543		NB4	2.856	1.293
	NB5	0.982	0.703		NB5	2.278	0.534
	NB6	0.1050	0.0661		NB6	3.228	0.835
Ag (ppb)	NB1	0.02000	0.01000	Ce (ppb)	NB1	1.000	0.533
	NB2	0.02000	0.01000		NB2	1.268	0.313
	NB3	0.02000	0.01000		NB3	2.196	0.629
	NB4	0.02200	0.01304		NB4	2.588	1.148
	NB5	0.02000	0.01000		NB5	2.596	0.660
	NB6	0.03250	0.00500		NB6	3.753	1.224
Cd (ppb)	NB1	0.0700	0.0300	Hg (ppb)	NB1	0.1040	0.1244
	NB2	0.0700	0.0300		NB2	0.1060	0.1288
	NB3	0.0700	0.0300		NB3	0.1060	0.1288
	NB4	0.0700	0.0300		NB4	0.244	0.228
	NB5	0.1060	0.0508		NB5	2.31	3.70
	NB6	0.0800	0.0300		NB6	0.358	0.274
Sn (ppb)	NB1	0.2880	0.0968	Tl (ppb)	NB1	0.02000	0.01225
	NB2	0.892	0.561		NB2	0.0780	0.0719
	NB3	0.632	0.502		NB3	0.0580	0.0585
	NB4	0.2760	0.0792		NB4	0.0840	0.0780
	NB5	0.3980	0.0829		NB5	0.0920	0.0733
	NB6	0.2875	0.0793		NB6	0.0625	0.0613
Sb (ppb)	NB1	0.03600	0.00894	Pb (ppb)	NB1	0.916	0.681
	NB2	0.07000	0.02121		NB2	0.990	0.275
	NB3	0.1320	0.0497		NB3	1.428	0.226
	NB4	0.0760	0.0451		NB4	1.598	0.961
	NB5	0.322	0.421		NB5	1.722	0.566
	NB6	0.0600	0.0216		NB6	1.848	0.683
I (ppb)	NB1	4.316	0.534	Bi (ppb)	NB1	0.01000	0.00707
	NB2	29.65	15.20		NB2	0.0320	0.0277
	NB3	28.74	8.29		NB3	0.0400	0.0406
	NB4	70.7	37.8		NB4	0.01200	0.00447
	NB5	96.3	130.6		NB5	0.01600	0.00548
	NB6	15.62	5.30		NB6	0.01750	0.00500
				U (ppb)	NB1	0.1400	0.0771
					NB2	3.192	0.771
					NB3	4.328	0.659
					NB4	2.750	1.892
					NB5	1.822	0.296
					NB6	1.223	0.536

8.3 Appendix D

Procedure for Solids Analysis

Part I: Preparation

1. Pre-dry the crucible dishes, filters (Whatman #1) and filter dishes in an oven at ~40 – 50'C for about 30 minutes.
2. Cool dishes and filters for a few minutes and gravimetrically weigh them.
3. Assign a sample number to each crucible and filter.
4. Filter 50ml amounts of the samples using a suction hose apparatus and rinse everything down with deionised water. Let the samples filter for a few minutes.
5. Put the filter back on the silver filter dish and transfer the filtrate to the crucible.
6. Place filters in oven at 70 – 90'C to dry, note their location in the oven so they are not mixed up later.
7. Place crucibles in muffle furnace at low heat (~100 – 110'C) to evaporate all of the water in them. Note their location so they will not be mixed up later.

Part II: TSS

1. When filters have dried fully, let them cool and then gravimetrically weigh them. The increase in mass, calculated as the difference between the initial and final weight, is the concentration of total suspended solids (TSS) per 50ml.
2. Record this weight.

Part III: TDS

1. When all water in the crucibles have evaporated, let them cool and then gravimetrically weigh them. The increase in mass, calculated as the difference between the initial and final weight, is the concentration of total dissolved solids (TDS) per 50ml.
2. Record this weight.

Part III: Solids VOC

1. Place the weighed crucibles back in the muffle furnace and set the temperature to about 550°C. Keep them in for a minimum of one hour (maybe two hours) or until all of the organic content has volatilized from the sample.
2. Remove the crucibles carefully (very hot), and let them cool for 30 – 35 minutes.
3. Re-weigh the crucibles and record the new weight. The decrease in mass, calculated as the difference in the weight of the crucible with the TDS and the final weight of the crucible, is the concentration of the volatile organic content (VOC) per 50ml.
4. Record this weight.

To get concentrations in mg/L just multiply by 20,000

→ (1000mg/g * 2000ml/L [per 50ml])

8.4 Appendix E

Procedure for Kjeldahl Analysis

Do each sample in duplicate.

Remember, meticulous cleaning of all glassware is essential.

Part I: Preparation/Digestion

1. Weigh between 0.2 and 0.3 grams of sample (usually 6 to 7 drops) on a tared weigh boat.
2. Do the same with nanopure water for a blank.
3. Put the weighed sample or blank in a labelled Kjeldahl tube and re-weigh the boat. Subtract the difference and that is the weight of the sample used.
4. Record this value.
5. To each tube with sample, add one Kjeltab catalyst tablet.
6. To each tube with catalyst and sample or blank, add 20ml of concentrated sulphuric acid via Brinkman dispenser.
7. Digest the samples and blank in the digestion unit for about 30 minutes, or until the liquid becomes a pale yellowish colour (maybe 45 minutes).
8. Let the digested samples and blank cool for at least 15 minutes (probably a little more).
9. Prepare 250ml Erlenmeyer flasks for samples and blank by adding 25ml of 4% (w/v) boric acid solution + methyl red/methylene blue indicator to each.

Part II: Distillation

1. When the samples and blank have cooled, add about 75ml of nano or deionised water to each tube.
2. Turn on distillation unit as per instructions on machine.
3. Properly insert tube with digested sample or blank in the left socket, and place the associated flask with boric acid and indicator on the right platform.
4. Make sure the plastic distillation tubes are in the digestion tube and flask below the surface of the solutions.
5. With the steam off, add two pumps of alkali (NaOH) solution to the tube and turn the steam back on.

Careful: make sure the platform is in the "up" position on the left side (best to hold it up) while pumping in the NaOH; otherwise it may spray out of the tube.

6. Distil the sample or blank until 150ml of condensate is collected in the flask. Remove the flask while simultaneously rinsing the exterior of the plastic tube into the flask with deionised water.

Part III: Titration

1. Titrate the condensate in the flask with 0.1N HCl to a purple/red endpoint *(careful, it may not take much).* It might go from light green to brown to red.
2. Record the final volume of titrant used.

8.5 Appendix F

Procedure for M-coli Blue Test

Do in triplicate

1. Sterilise the work area, filtration units, and glass tubes.
2. Place a sterile membrane filter on the filtration apparatus and securely attach the glass tubes with the clamps.
3. Turn on water for suction into the filtration unit.
4. Pour 100 ml of sample into each tube and open suction valves.
5. Rinse the sample bottles with clean water and add the rinse to the tubes. Wash the sides of the tubes with clean water from a squirt bottle.
6. When all water has been filtered, remove the tube, place the filter on a pad in an incubation dish with sterilized tongs, and add the M-coli blue solution.
7. Make sure the dishes have been labelled properly, and place them in an incubator at 37.5°C for 20 – 30 hours.
8. Properly clean and sterilise equipment and workspace.
9. Remove the dishes from the incubator when it is time, and count the colonies under a magnifying light plate. The red colonies are non-fecal coliforms, and the blue colonies are *E. coli*.

To make a 1:10 dilution:

1. Remove 10 ml of sample with a sterile pipette and add it to 90 ml of clean water.

Add this dilution to the tube and filter.

8.6 Appendix G

Solvent Extraction Procedure for PAHs

Part I:

1. Make the internal standard by dissolving 10mg of androstane in hexane.
2. Dilute with hexane up to 100ml in marked 100ml volumetric flask.

Part II:

1. Drain excess water from the sediment samples and weigh approximately 10g of each into marked tared 150ml beakers.
2. Add 50ml of high-grade hexane and methanol (4:1 solution) to each beaker, and then to each add 0.25ml of the internal standard.
3. In the fume hood, place the beakers on a magnetic stir plate. Cover them with watch glasses and stir with magnetic stir bars for about 30 minutes. Depending on the matrix of the sediment, some samples will take longer to extract than others.
4. Gravity filter the samples into marked 150ml beakers with Whatman Number 1 filter paper, and then rinse the previous beakers and funnels with two 5ml portions of hexane into the newly marked beakers with the filtrate.
5. The filtrates combined with the rinsings are then dried with anhydrous sodium sulphate, stirring with a magnetic stir bar.
6. Repeat step 4 with the product obtained from step 5.

7. Evaporate the extracts in the fume hood for 6 – 12 hours. Rinse the sides of the beakers with small amounts of hexane occasionally until the final volume of extract is 1 – 2 ml.
8. The samples are now ready for GC/MS analysis.