

**GEOCHEMISTRY AND MINERALOGICAL ASSOCIATION OF
HEAVY METAL CONTAMINANTS IN FINE GRAINED SEDIMENT,
WELLAND RIVER, SOUTHERN ONTARIO.**

by

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Abstract

This investigation of geochemistry and mineralogy of heavy metals in fine grained (<63 μ m) sediment of the Welland River was undertaken to: 1) describe metal dispersion patterns relative to a source, identify minerals forming and existing at the outfall region and relate sediment particle size to chemistry; 2) to delineate sample handling, preparation and evaluate, modify and develop analytical methods for heavy metal analysis of complex environmental samples.

A joint project between Brock University and Geoscience Laboratories was initiated to test a contaminated site of the Welland River at the base of Atlas Speciality Steels Co. Methods were developed and utilized for particle size separation and two acid extraction techniques: 1) Partial extraction; 2) Total extraction.

The mineralogical assessment identified calcite, dolomite, quartz and clays. These minerals are typical of the carbonate-shale rock basement of the Niagara Peninsula. Minerals such as, mullite and ferrocolumbite were found at the outfall region. These are not typical of the local geology and are generally associated with industrial pollutants.

Partial and total extraction techniques were used to characterize the sediments based on chemical distribution, elemental behaviour and analytical differences. The majority of elements were lower in concentration in the partial extraction technique; suggesting these elements are bound in an acid extractable phase (exchangeable, organic and carbonate phases). The total extraction technique yielded higher elemental concentrations taking difficult oxides and silicates into solution.

Geochemical analyses of grain size separates revealed that heavy metal (Co, Ni, V, Mn, Fe, Ba) concentrations did not increase with decreasing grain size. This is a function of the anthropogenic mill scale input into the river. The background elements (Sc, Y, Sr, Mg, Al and Ti) showed an increase in concentration to the finest grain size suggesting that it is directly related to the local mineralogy and geology.

Dispersion patterns of metals fall into two distinct categories: 1) the heavy metals (Co, Cu, Ni, Zn, V and Cr), and 2) the background elements (Be, Sc, Y, Sr, Al and Ti). The heavy metals show a marked increase in the outfall region, while the background elements show a significant decrease at the outfall. This pattern is attributed to a "dilution effect" of the natural sediments by the anthropogenic mill scale sediments. Multivariant statistical analysis and correlation coefficient matrix results clearly support these results and conclusions.

These results indicate the outfall region of the Welland River is highly contaminated with heavy metals from the industrialized area of Welland. A short distance downstream, the metal concentrations return to baseline geochemical levels. It appears, contaminants rapidly come out of suspension and are deposited in close proximity to the source. Therefore, it is likely that dredging the sediment from the river may cause resuspension of contaminated sediments, but may not distribute the sediment as far as initially anticipated.

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Table of Contents	Page
Chapter 1: Introduction	1
1.1: Background	1
1.2: General Geology and Study Area	3
1.3: Mineralogical Method Description	8
1.4: Geochemical Method Descriptions	8
Chapter 2: Sample Collection, Treatment and Analytical Methods	11
2.1: Sample Collection	11
2.2: Sample Pretreatment	11
2.3: Grain-size Separation Methods	15
2.4: Mineralogical Analysis	16
2.4.1: Sample Preparation	16
2.4.2: Instrumentation	17
2.5: Digestion Techniques	17
2.5.1: Total Extraction Technique	17
2.5.2: Partial Extraction Technique	19
2.6: Instrumental Analysis of Partial and Total Extraction Samples	20
2.6.1: Instrumentation	20
2.6.2: Geochemical Analysis by ICP-OES	20
2.7: Precision and Accuracy: Quality Control	22
2.7.1: Data Quality Objectives	22
2.7.2: Analytical Considerations	23

2.7.3: Evaluation Criteria - Fitness for Purpose	25
2.7.4: Data Assessment	25
2.7.5: Data Presentation and Acceptability	29
Chapter 3: Results and Discussion	32
3.1: Mineralogical Analysis	32
3.2: Geochemical Analyses	32
3.2.1: Total Extraction Analyses	35
3.2.2: Partial and Total Extraction Analyses - Comparisons	42
a) Group A: Co, Cu, Ni, Zn, Cr, Mn	42
b) Group B: Be, Sc, Y, Sr, Ti, Al	43
c) Group C: V, Mg	48
d) Group D: Fe	50
e) Group E: Ba	50
3.2.3: Geochemical Analyses of Grain Size - Concentration Comparisons	53
a) Group 1: Co, Ni, Mn, Fe, V	54
b) Group 1b: Ba	57
c) Group 2: Mg, Sr, Ti, Al, Y, Sc	57
d) Group 3: Cu	58
3.3: Dispersion Patterns	62
3.4: Discussion of Data Comparisons	67
3.5: Statistical Analysis - Multivariant Analysis (Factor Analysis) - Correlation Coefficient Matrix	70 70
Chapter 4: Summary and Conclusions	74
References	79
Appendices	83

	Page
List of Tables	
Table 1: Analytical preparation and instrument techniques.	10
Table 2: Cyclosizer operating conditions and limiting particle separation size.	16
Table 3. Concentrations of reagent blanks and concentration difference and precision calculations of duplicate samples.	26
Table 4. Variation in concentration of analyses of Standard Reference Materials.	27
Table 5. Trueness of several analyses of Standard Reference Materials.	28
Table 6. Lowest limit (2xHACL) for which data are acceptable.	29
Table 7. Elemental assessment of data by ICP-OES.	31
Table 8. Sample labelling scheme according to technique for grain size separation techniques.	34
Table 9. Data used to evaluate geochemical analyses for Welland River sediments.	35
Table 10. Summary of data, quality levels and impact according to the Provincial sediment quality guidelines (Persaud et al., 1993).	40
Table 11. Elemental groups for partial and total extraction results.	42
Table 12. Groups defined by their geochemical pattern of grain size to chemistry correlations and controlling environmental factors.	53
Table 13. Correlation coefficient matrix among chemical analyses from Welland River sediments.	72
Table 14. Varimax rotated factor analysis of Welland River sediments.	73

List of Figures		Page
Figure 1.	Locality map of the Welland River, Niagara Peninsula, southern Ontario.	4
Figure 2.	Field map of sample locations on Welland River.	6
Figure 3.	Field photograph of Atlas Speciality Steels Co. in the industrialized region of the Welland River.	7
Figure 4.	Flowchart delineating the analytical procedures required for sample pretreatment, preparation and chemical analysis.	9
Figure 5.	Field photograph of the outflow region (Atlas-Mansfield storm sewer) of the Welland River.	12
Figure 6.	Field photograph of the Welland River upstream from the Atlas-Mansfield discharge point source.	13
Figure 7.	Field photograph of the Welland River downstream from the Atlas-Mansfield discharge point source.	14
Figure 8.	Schematic diagram of a conventional simultaneous ICP-OES system (Thompson and Walsh, 1989).	21
Figure 9.	Precision of data as concentration approaches the Limit of detection of the method.	24
Figure 10.	X-ray diffraction patterns for unusual mineral phases found at the Atlas-Mansfield discharge source.	33
Figure 11.	Geochemical data normalized to average continental crust (Taylor and McLellan, 1985).	36
Figure 12.	Geochemical data normalized to the average control samples from the Welland River.	39
Figure 13.	Geochemical data compared to Provincial sediment quality guidelines (Persaud, 1993).	41
Figure 14a.	Partial and total extraction comparisons for group A.	44
Figure 14b.	Partial and total extraction comparisons for group A.	45

	Page
Figure 15a. Partial and total extraction comparisons for group B.	46
Figure 15b. Partial and total extraction comparisons for group B.	47
Figure 16. Partial and total extraction comparisons for group C.	49
Figure 17. Partial and total extraction comparisons for group D.	51
Figure 18. Partial and total extraction comparisons for group E.	52
Figure 19a. Grain size to chemistry correlation comparisons for group 1 and 1b.	55
Figure 19b. Grain size to chemistry correlation comparisons for group 1 and 1b.	56
Figure 20a. Grain size to chemistry correlation comparisons for group 2.	59
Figure 20b. Grain size to chemistry correlation comparisons for group 2.	60
Figure 21. Grain size to chemistry correlation comparisons for group 3.	61
Figure 22. Dispersion patterns for Cu, Zn, Ni, Cr, V and Co. Heavy metals are highly concentrated at the outflow area.	64
Figure 23. Dispersion patterns for Be, Sc, Y, Sr, Ti and Al. Analytes show a significant decrease at the outflow area.	65
Figure 24. Dispersion patterns for Ba, Mg, Fe and Mn. Each distribution is unique because a different source is attributed to the pattern.	66
Figure 25. Scatter diagrams of geochemistry of the Welland River data produced from this study, Welland River data produced by MOEE, 1995, MOEE PSQG, 1993 and Niagara River data (Mudroch and Duncan, 1986).	68

	Page
Figure 26. Scatter diagrams of geochemistry of the Welland River sediments. Data produced from this study and the Welland River dredging demonstration environmental workshop (report by Acres, 1991).	69

	Page
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List of Appendices

Appendix 1: Geochemical Data.	83
Appendix 2: Microwave Digestion Technique.	92
Appendix 3: pH Data of the Water of the Welland River.	100
Appendix 4: Sample Key.	102
Appendix 5: Field Sample Description Data.	104

Chapter 1: Introduction

1.1: Background

Sediments are important in the hydrocycle due to their ability to carry metals. As such, they reflect the current and historical geochemistry of a region (Salomons and Forstner, 1984). Many studies emphasize the correlation between the geochemistry of the finer grained materials and the trace metal contamination in lake and river sediments (Moore et al., 1989; Salomons and Forstner, 1984; Forstner, 1982; Thorne and Nickless, 1981; Ackemann, 1980; Jenne et al., 1980; Filipek and Owen, 1977; Wilber and Hunter, 1979; Gibbs, 1977; Helmke et al., 1977; Whitney, 1975; and Oliver, 1973). Others investigate the distribution of sediment-associated contaminants in waterways (Mudroch, 1984, 1985, Young et al., 1987, Mudroch and Stone, 1989, Gatz et al., 1989, Crecelius et al., 1991, and Bodur and Ergin, 1994). Higher metal concentrations occur in fine grain size fraction sediments ($<63 \mu\text{m}$) due to their large surface area/volume ratio. Often, this metal occurrence is attributed to adsorption, coating, coprecipitation or complexing.

Grain size separation is beneficial in local environmental studies because only a few samples are essential. Samples consisting of fractions greater than $173 \mu\text{m}$ material contain a high percentage of large grains and are generally not high in metals (Salomons and Forstner, 1984). Typically, the $<63 \mu\text{m}$ fraction is recommended for contamination studies because trace metals are mainly associated with silt and clay size particles. This fraction is nearly equivalent to the size of material carried in suspension, which is known to transport a high percentage of contamination (Forstner and Salomons, 1980). Metal concentration is not altered by sieving and numerous metal studies are performed on the $<63 \mu\text{m}$ fraction,

The first step in the process of developing a curriculum is to identify the needs of the students. This involves a thorough analysis of the current curriculum and the needs of the students. The next step is to develop a list of learning objectives. These objectives should be specific, measurable, and achievable. The third step is to select the content and materials that will be used to teach the objectives. This involves choosing textbooks, articles, and other resources that are relevant to the objectives. The fourth step is to develop the lessons and activities that will be used to teach the content. This involves creating a sequence of lessons and activities that will lead the students to achieve the learning objectives. The fifth step is to evaluate the curriculum. This involves assessing the effectiveness of the curriculum in meeting the needs of the students and making any necessary revisions.

The process of developing a curriculum is a continuous one. It requires ongoing communication and collaboration between all those involved in the process. It also requires a commitment to ongoing evaluation and improvement. Only through a careful and thoughtful process can a curriculum be developed that meets the needs of the students and prepares them for the future.

allowing better comparison of results (Forstner and Salomons, 1980) The ability to analytically process samples of a highly complex nature is important now and will become critical in the future, as a better understanding of chemical species in environmental studies become known, the need for lower detection limits will be essential.

To obtain a comparative basis for environmental studies, the background concentrations of trace metals should be established in similar sample media (Forstner and Wittmann, 1979). There are four concepts that can be employed to achieve this: 1) average shale composition as a global standard value; 2) fossil aquatic sediments from defined environments as a standard, (taking into account natural allochthonous and autochthonous factors and mechanisms and regional influences); 3) recent deposits in relatively unpolluted areas; and 4) short, dated sediment cores, which provide a historical record of events occurring in the watershed of a particular river. The background concentration of major and trace elements in the suspended load is obviously affected by the composition of soils and bedrock geology of the drainage basin and varies over the local area (Mudroch and Duncan, 1986).

Often, environmental studies will involve chemical extractions of specific grain sizes of sediment. Metals in sediments are concentrated by physical (grain size, surface area) or chemical (cation exchange capacity, mineralogy, concentration of geochemical substrates) factors (Horowitz et al., 1989). By employing both of these concepts, the geochemistry of sediments can provide insights into processes that affected the sediment-trace element distributions. Changes in ambient conditions of the environment could cause mobilization of metals. Subsequently, the metals may be available to the organisms in the environment.

Often trace metals are present in the sediment as surface "coatings". Metals in such coatings are the easily extracted, and therefore, readily available for solution testing (Simon et al., 1992).

The objectives of this thesis are to evaluate, modify and develop analytical methods for heavy metal analysis of complex environmental samples, relate sediment particle size to chemistry, and to describe metal dispersion patterns relative to a source region in the Welland River. Finally, from this information, minerals forming and existing in the Welland River will be assessed and metal presence and dispersion patterns explained.

1.2: General Geology and Study Area

The Welland River is located in the Niagara Peninsula. Starting along a sandy moraine near Ancaster, it meanders across the Haldiman Clay Plain where it used to drain into the Niagara River at Chippawa, south of Niagara Falls, Ontario (Fig. 1). The Welland River actually does not flow into the Niagara River any longer. The last four miles of the river serves as an intake for the Chippawa-Queenston power canal. In addition, further downstream, the river is forced through two siphons under the Welland Canal in the City of Welland (Chapman and Putnam, 1984). The river has a high suspended sediment load (Brindle, personal communication). The water has a relatively high pH (average 7.8, Appendix 3), which is a reflection of the carbonate rock environment which consists of dolostones of the Lockport Formation, capping the local bedrock.

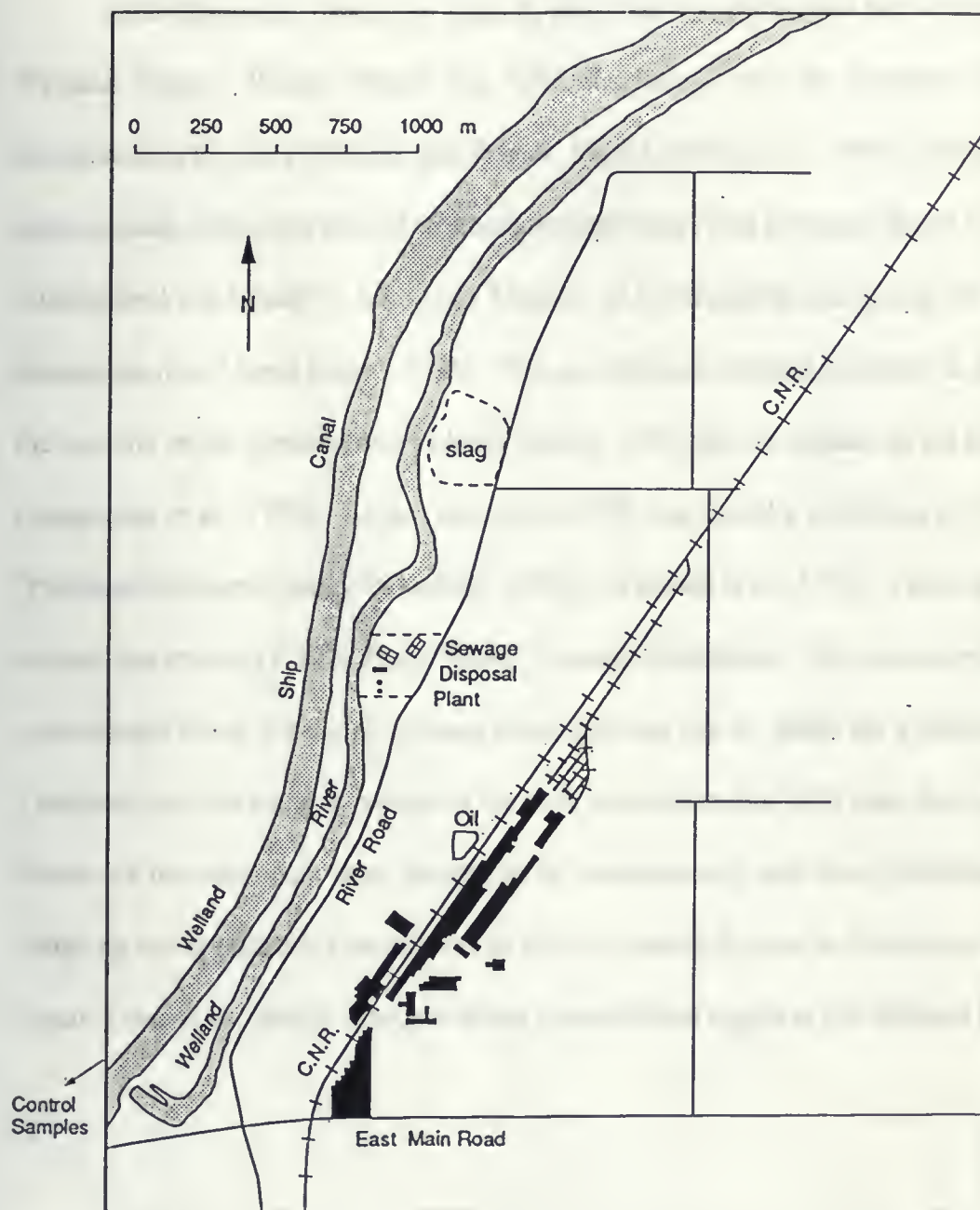


Fig.1 Sample area of the Welland River located in Welland, Niagara Peninsula.

The overburden on the Paleozoic rocks ranges from 50-150 feet thick, increasing in a southerly direction (Chapman and Putnam, 1984).

Atlas Speciality Steels Co. (Fig. 3) and other industrial sites are located on the Welland River. Waste effluent has been discharged into the Welland River for approximately 60 years (Thomas and Palmer, 1989; Dickman et al. 1990). Recognition of contamination of the river has led to a commitment from Atlas speciality Steels Co., Acres International (on behalf of Atlas) and Ministry of Environment and Energy (MOEE) to cleanup the river (Acres Report, 1991). This commitment resulted in studies to determine the severity of the contamination (Acres Report, 1991) and the impact on the local biota (Jaagumagi et al., 1995). At this time, the MOEE had issued a preliminary draft of the "Provincial Sediment Quality Guidelines" (PSQG) (Persaud et al., 1993). These new limits replace the ministry's 1976 Open Water Disposal Guidelines. This document contains contaminant levels for which cleanup considerations can be based for a particular site. Therefore, for this study, a portion of the river was selected in 1991 near Atlas Specialty Steels, as the sediments were thought to be contaminated with heavy metals and oils. Sampling was completed in the summer of 1991 (Appendix 5), prior to the dredging project. Figure 2 shows the sample locations in the industrialized region of the Welland River.

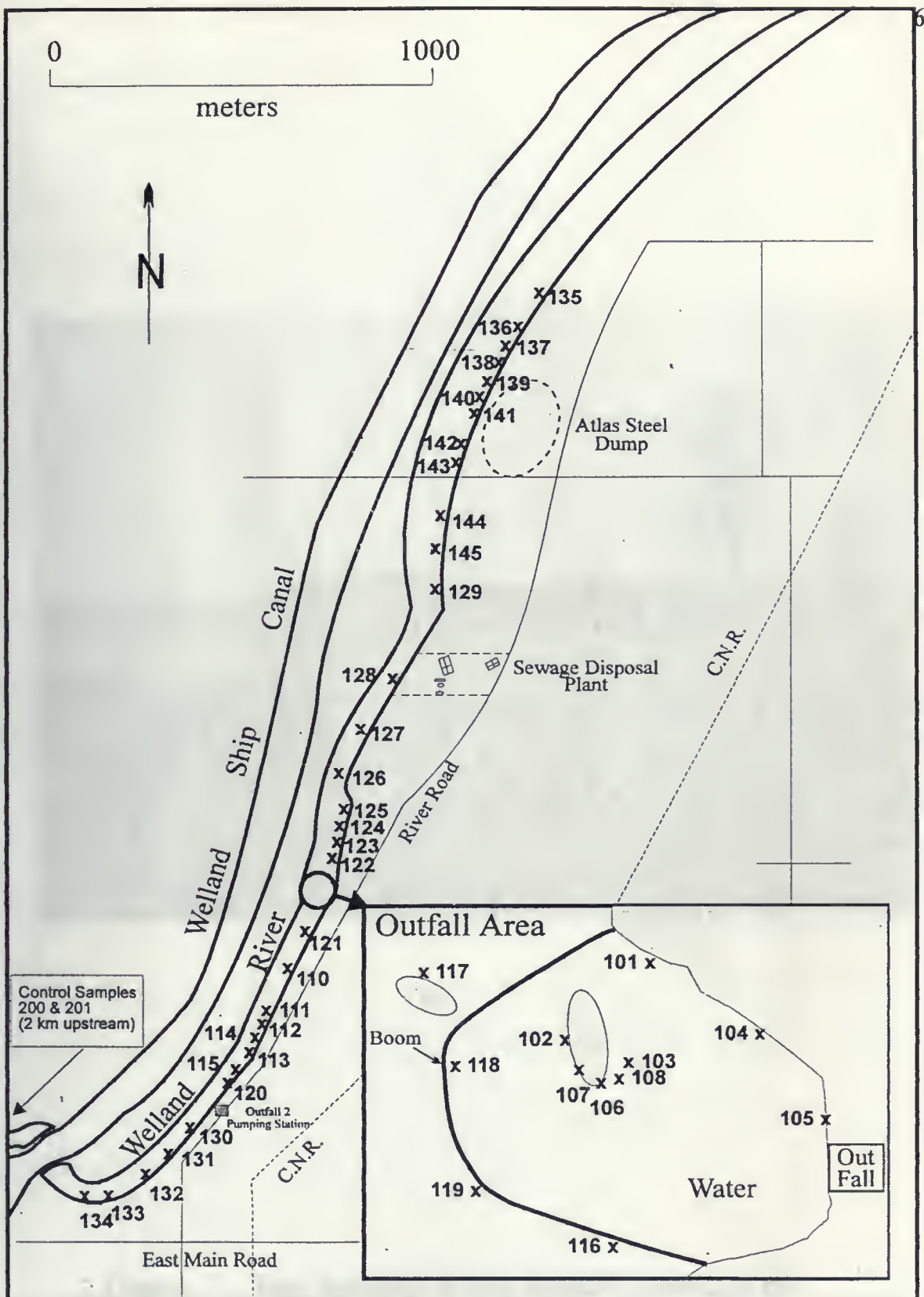


Figure 2: Field map of sample localities on the Welland River.



Figure 3. Field photograph of Atlas Speciality Steels Co. in the industrialized region of the Welland River.

1.3: Mineralogical Method Description

Mineralogical analyses were performed on the samples to identify unique mineral existing or forming in the Welland River. Traditional X-ray diffraction (XRD) analyses were carried out at Geoscience Laboratories on the samples. Details of the technique and instrumentation are available in Chapter 2.6 - Mineralogical Analysis and are available at Geoscience Laboratories (Lab Manual ref. MP 149).

1.4: Geochemical Method Descriptions

In the analysis of trace metals for environmental geochemical studies, a partial extraction or HCl-HNO₃ leach may be used to identify metals available to the surrounding environments such as plants, animals, and in surface or ground waters. In contrast, a total digestion technique may be used to determine all metals in the sample; those available from the natural/geological environment and those introduced as contamination.

Investigation into methodology, equipment availability and applicability have resulted in the delineation of a scheme for sampling and for analytical procedures (Fig. 4). These procedures were extensively tested and proved optimal for the study. More detail on the procedures and techniques is available in Chapter 2.4 - 2.5. In this study, a number of analytical preparation and instrumentation techniques were used at several institutes. These are tabulated in Table 1.

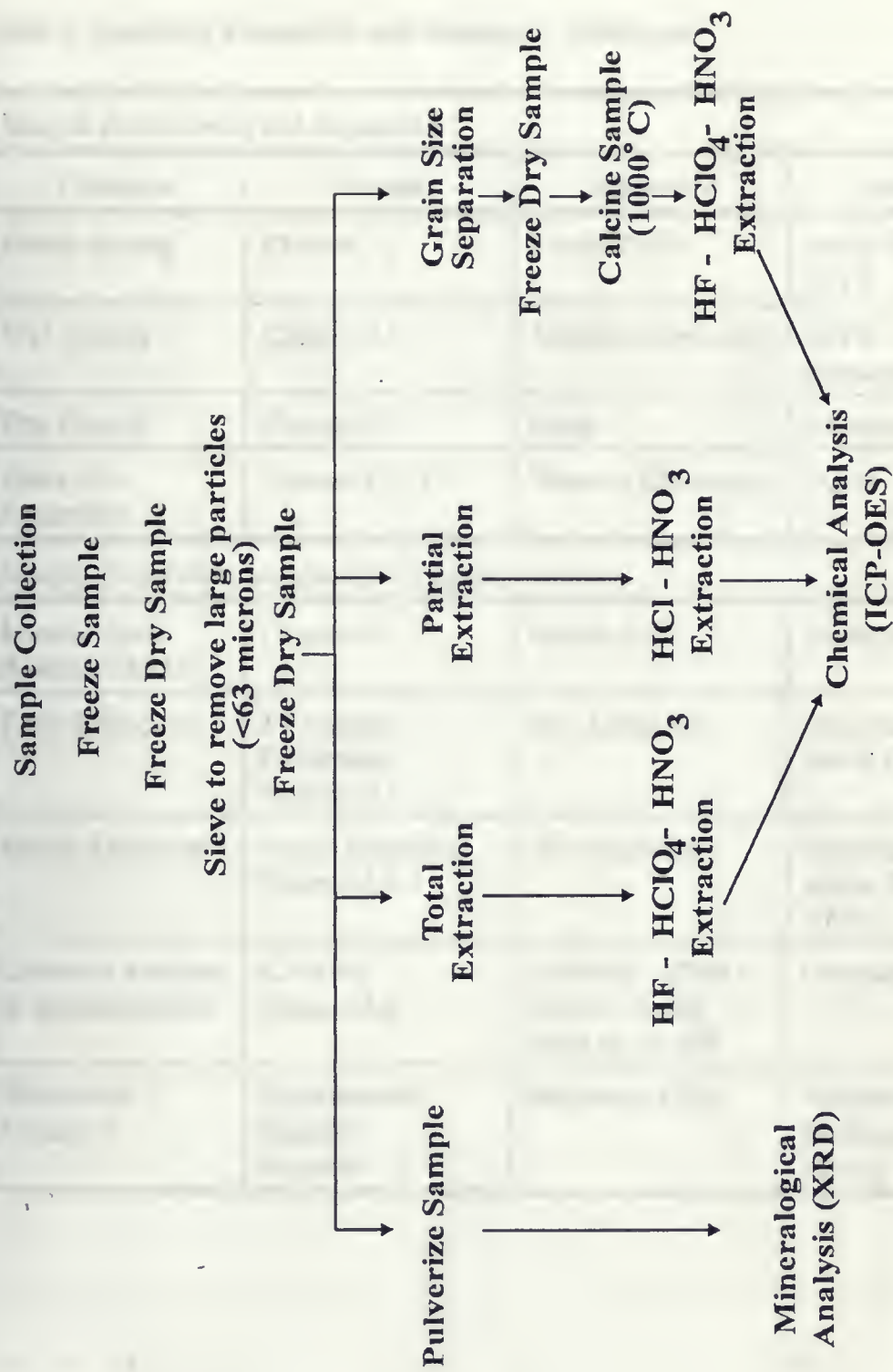


Figure 4. Flowchart delineating the analytical procedures required for sample pretreatment, preparation and chemical analysis.

Table 1: Analytical Preparation and Instrument Techniques

Sample Pretreatment and Separation			
Technique	Chapter	Instrument	Institution
Freeze Drying	Chapter 2.2	Freeze Dryer	Brock University CCIW
Wet Sieving	Chapter 2.2	Stainless steel sieve	CCIW Geoscience Labs
Dry Sieving	Chapter 2.2	Rotap	Geoscience Labs
Grain Size Separation	Chapter 2.2, 2.3	Warman Cyclosizer	CCIW
Sample Preparation and Analytical Instrumentation			
Mineralogical Analysis (XRD)	Chapter 2.4	Philips XRD	Geoscience Labs
Total Extraction	T2 Sample Preparation Chapter 2.5.1	Not Applicable	Geoscience Labs Brock University
Partial Extraction	Partial Extraction Chapter 2.5.2	Not Applicable	Geoscience Labs advise from XRAL
Chemical Analysis & Instrumentation	ICP-OES Chapter 2.6	ICP-OES - JY48+, Thermo Jarrell Ashe ICAP 61E	Geoscience Labs
Microwave Digestion	Experimental Digestion Appendix 2	Milestone 1200	Ministry of Environment & Energy

Chapter 2: Sample Pretreatment and Analytical Methods

2.1: Sample Collection

A total of 50 bottom sediment samples, including two control samples, were collected from the Welland River (Fig. 1). Grab samples were obtained from the outfall area (Fig. 5), upstream (Fig. 6), and downstream (Fig. 7) from the Atlas-Mansfield discharge point source (Fig. 2). Each sample was located on an airphoto and given a sample label. The samples were collected with the use of a plastic implement to ensure that metal contaminants were not added in the sampling procedure. Wet samples were placed in plastic bags without draining off the excess water. This procedure maintained sample integrity as fine grained material in suspension was not lost. The samples were brought to the laboratory and stored in a freezer until initial pretreatment.

2.2: Sample Pretreatment

The samples were taken from the deep freezer, freeze-dried, and stored. A selected set of samples were wet-sieved through a 63 μ m stainless-steel sieve to separate the coarse material from the finer material of interest. The coarse fraction (>63 μ m) was stored and the fine-grained material was freeze-dried with the exception of the samples that would be further separated into six grain sizes (<11 μ m, 11-15 μ m, 15-23 μ m, 23-33 μ m, 33-44 μ m, 44-63 μ m) following the procedure used by the Canada Centre for Inland Waters (CCIW), then freeze-dried and stored in vials. Another set of samples were dry sieved using a stainless steel sieve and Rotap to separate samples mechanically to less than 63 μ m grain size. This set was completed in this manner because of the speed of the method.



Figure 5. Field photograph of the outfall region (Atlas-Mansfield storm sewer) of the Welland River.



Figure 7. Field photograph of the Welland River downstream from the Atlas-Mansfield discharge point source.



Figure 6. Field photograph of the Welland River upstream from the Atlas-Mansfield discharge point source.

2.3: Grain size Separation Methods

Several experiments were performed to assess the method most feasible for grain size separation below $63\mu\text{m}$. The method used by Geoscience Laboratories was more appropriate for larger grain size than the finer grain sized (below $63\mu\text{m}$) material of interest in this study. The use of sodium hexametaphosphate could interfere with trace metal analysis. Dry sieving the samples failed because the mesh was too fine and the sediment did not pass through the sieve easily. Finally, a Warman Cyclosizer was used to separate particles by centrifuging in the sub-sieve range. A suite of 18 samples were randomly chosen to encompass a distribution along the river. Each sample was wet sieved, the $<63\mu\text{m}$ fraction was introduced to the Cyclosizer. The Cyclosizer separated the sample into five grain size ranges, the sixth sample range ($<11\mu\text{m}$) was obtained by allowing the waste water and sediment from the instrument to settle in a large container for 48 hours. The limiting particle separation size at standard conditions and the conditions at which the Cyclosizer operates are summarized in Table 2.

Once the sample was separated in each cyclone it was decanted into a clean beaker and allowed to settle. After settling, the grain size split was transferred to a plastic vial for freeze-drying.

Table 2.: Cyclosizer operating conditions and limiting particle separation size.

Cyclone No.	Particle Limit	Error (μm)
1	44 microns	± 2
2	33 microns	± 1
3	23 microns	± 1
4	15 microns	± 1
5	11 microns	± 1
Conditions		
Water Flowrate	11.6 L/min	
Water Temperature	20°C	
Particle Density	2.65 g/cm ³	
Time of elutriation	infinite	

2.4: Mineralogical Analysis

2.4.1: Sample Preparation

Sediments were pulverized using an agate mortar and pestle until a fine powder was obtained. The sample was poured into a special aluminum well mount. A glass slide was held in front of the ring and tapped until the powder was packed down. This method avoided preferred orientation of minerals. This preparation is a non-destructive method, so all samples were retained after XRD analysis.

2.4.2: Instrumentation

Mineralogical analysis was performed by Phillips X-ray Diffraction (XRD) system. The powder mount was placed into the diffractometer and held by a spring clip for even illumination by the X-ray beam. The diffractometer analyzes ranges from 5° to $65^\circ 2\theta$. Once the analysis was complete, the diffraction pattern was printed and compared to the JCPDS search database to match their peaks to a mineral. Details of the techniques and procedures are outlined in OGS 1990.

2.5: Digestion Techniques

2.5.1: Total Extraction Technique

An initial attempt at a total extraction procedure EA18 (T2) (OGS, 1990) method resulted in an incomplete digestion with a large amount of residue. Several modifications of this procedure were tested to digest the samples as completely as possible and yield the most accurate and precise data attainable. The acids were introduced to the samples at varying times, but this yielded no significant difference in the completeness of the digestion. Since oil was observed in samples during sample collection, it was possible that the residue was an organic material. Accordingly, H_2O_2 (hydrogen peroxide) was added to the digestion. However, residues were still present. Finally, the sample was calcined at $1000^\circ C$ prior to acid digestion to combust oils and volatiles (CO_2 , S, H_2O , As, Hg, Se). This resulted in a much cleaner and complete digestion. This modification was tested using Standard Reference Materials to assess the effect on the analytes to be determined.

A total of 52 river samples were analyzed using a total extraction technique. A weight of 0.5g of sample was placed in a PTFE beaker. Normally a mixed acid attack of HNO_3 - HClO_4 - HF (1:2:8) yielded a total decomposition of samples to produce an analytical solution. An amount of 15 mL of acid was added to the beaker and the contents gently swirled to ensure wetting of the entire sample. The beakers were placed on a hot plate at 150°C . Digestion took approximately 20 hours and eventually the sample was evaporated to dryness. Once dry, the beakers were gently tapped to break the residue and cause any droplets of acid around the top portion of the beaker to fall to the bottom. The beakers were returned to the hot plate until fuming ceased. This step was repeated until the sample was completely dry. Subsequently, 2 mL of HNO_3 was added to the dry residue and heated for 1 minute on the hot plate. The sample was removed, 0.5 mL of HCl added and the beaker returned to the hot plate once the reaction had subsided for approximately 1 minute. The residue should appear to be dissolved in the acid solution. At this point, 15 mL of deionized water was added to the beaker and heated for 15 minutes. Record of any incompletely dissolved residue was indicated on the worksheet. Once the solutions cooled, they were transferred to 50 mL graduated cylinders and brought up to volume with deionized water. The cylinder was covered with parafilm and mixed. The solution was transferred to a bottle or test tube to await ICP-OES analysis. The dilution factor for ICP-OES analysis was 100. Occasionally, if a sample yielded a large amount of residue, an XRD scan was performed to identify the mineral phases not completely digested in the acid attack.

Microwave digestion was also tried hoping to yield a total digestion. HNO_3 and HCl were used in the attack. However, HF could not be introduced to the bombs because of MOEE safety requirements. The digestion that resulted was not a total extraction and was very time consuming (12 samples per day), so the procedure was abandoned. See Appendix 2.

2.5.2: Partial Extraction Technique

Several experiments were performed to assess the most precise and accurate partial extraction technique to be used. Initially, HNO_3 was added and HCl later. This resulted in erratic analytical results. Varying temperature and digestion times yielded limited differences. However, adding HCl first and then HNO_3 later and increasing the temperature to 90°C resulted in consistently precise and accurate (within $\pm 20\%$) data (Obdebeck, XRAL, personal communication; Scriver et al., 1995).

A total of 52 river sediments were analyzed using a partial extraction technique. A weight of 0.25g of river sediment of less than $63\mu\text{m}$ was placed into a glass test tube with 2 mL of HCl and placed in a water bath at $80\text{--}90^\circ\text{C}$ for 30 minutes. Subsequently, 1 mL of HNO_3 was added and the sample returned to the water bath for 2.5 hours. Each tube was shaken using a Vortex shaker every 20 minutes. The test tubes were cooled and solutions transferred to 25 mL volumetric flasks and brought up to volume with deionized water.

2.6: Instrumental Analysis of Samples by Partial and Total Extraction

2.6.1: Instrumentation

ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) analysis is an effective way of determining most elements on the Periodic Table. Most analytes exhibit a linear response over five orders of magnitude, with limits of detection in the low ppm range (Thompson and Walsh, 1989). Figure 8 shows a schematic diagram of a conventional simultaneous ICP-OES system. A sample is introduced to the plasma as an aqueous aerosol via a nebulizer, passes through a spray chamber to remove large droplets, then injected into the plasma (Greenfield and Montaser, 1992). The atoms or ions are energized, and when reverting to a lower energy state emit a photon of energy. This photon is then converted to an electrical signal by the photomultiplier in the spectrometer. The intensity of the electrical signal is compared to that of previously measured known solutions and consequently, a concentration can be calculated (Thompson and Walsh, 1989).

2.6.2: Geochemical analysis by ICP-OES

Analysis was done by ICP-OES because of its analytical range (low ppm to mid percent levels). This analytical range was found to be the range required for these samples and for the analytes in question. ICP-OES also has the capability of analyzing several elements at a time. This was important due to the small sample size obtained from the grain size splits. Often there was only enough sample for one preparation. Therefore, it was crucial to be able to analyze for all analytes simultaneously.

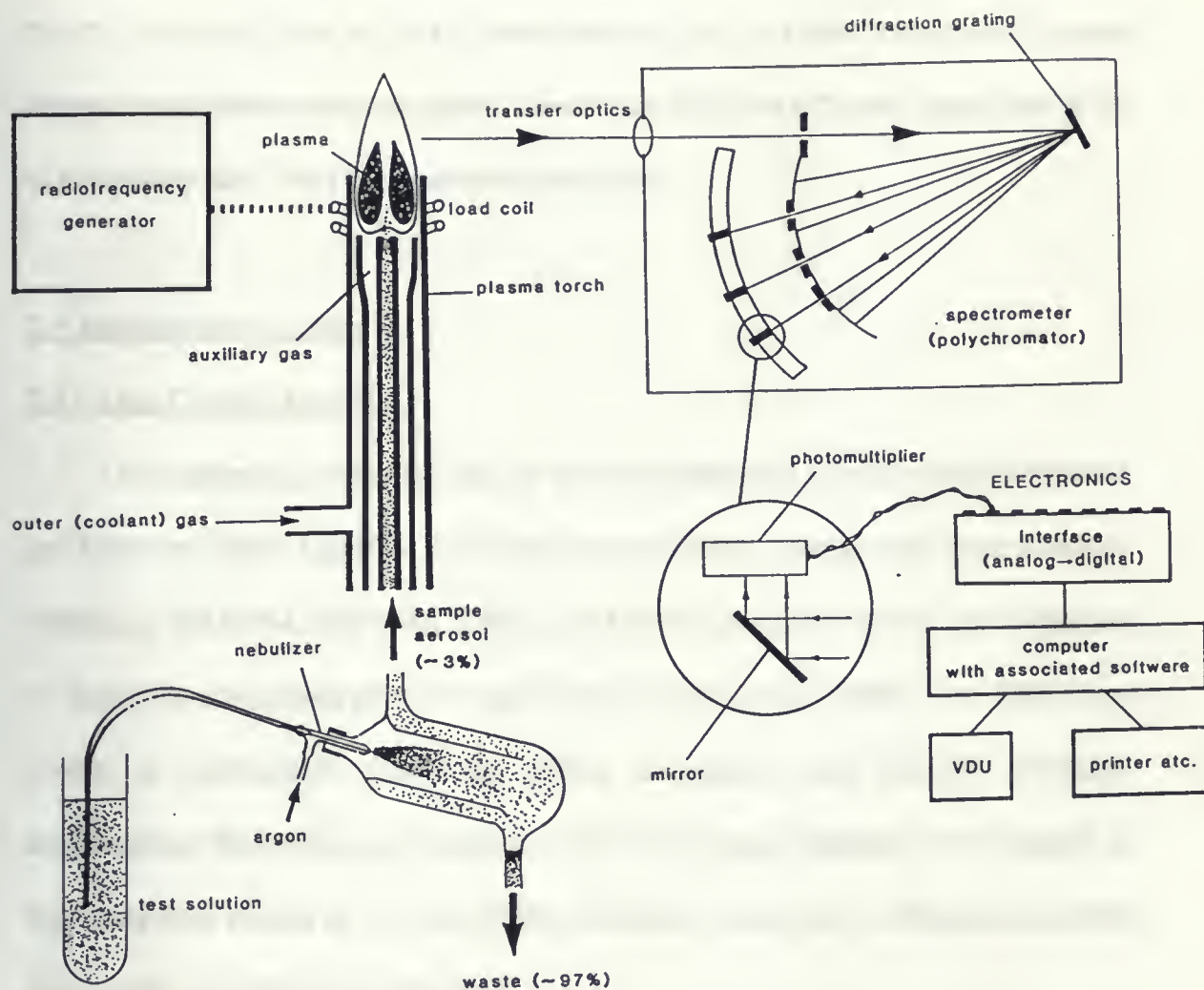


Figure 8. Schematic diagram of a conventional simultaneous ICP-OES system (Thompson and Walsh, 1989)

Preliminary results and experimental data for Be, Co, Cu, Mo, Ni, Sc, V, Y, Sr, W, Zn, Ti, Al, Fe, Mg, Mn, Ba and Cr were obtained using a JY48+ Inductively Coupled Plasma-Optical Emission Spectrometer (Toronto, pre 1992) and a Thermo Jarrell Ashe ICAP 61E (Sudbury post 1992) at Geoscience Laboratories.

2.7: Precision and Accuracy

2.7.1: Data Quality Objectives

Evaluation of geochemical data are well established and are outlined in Richardson and Morrison (1995), Lightfoot (1993) and Johnson (1993). Standard reference materials (SRM) (i.e. NIST2704, NIST1646, STSD-2 and LKSD-3) were used in each set of analyses to determine appropriate precision and accuracy (Govindaraju, 1989). The SRM were chosen to approximate closely the matrix, composition and expected elemental concentrations (Richardson and Morrison, 1995) of the stream sediments. The elements in this study were chosen on the basis of their elemental background representation, health implications and environmental impact.

Samples, standards and blanks were used to assess the precision, accuracy and laboratory technique contamination levels of all the data. A recoverability of 80% of the certified value was achieved in the partial extraction data and total extraction data. An assessment of the quality control samples was to determine technique contamination, precision and accuracy in all batches.

2.7.2: Analytical Considerations

Concentrations of some elements in the SRM used were less than Method Detection Limit (MDL) of the method (ICP-OES). e.g. Mo - MDL < 6ppm, W - MDL < 35ppm, where the only alternative to this problem was to use a more sensitive method. Before acceptably good accuracy is possible, one must have acceptable precision. If data are between Method detection limit and Limit of Quantification (LOQ), [where the LOQ = 3.3 x MDL], the precision will be poor (ie. Tungsten has a method detection limit of 35ppm, therefore, the precision is worse than $\pm 100\%$ because it cannot be measured well). The only alternative to improve this is to use a more sensitive method or increase the sample size. (See Fig. 9).

Some of the duplicates do not agree well, probably due to sample inhomogeneity (Table 3). Each sample was sieved to $<63\mu\text{m}$, then, in turn, divided into grain size splits A through F. These splits are of the bulk samples ($<63\mu\text{m}$, primary focus of the study) and are not representative of the sampling environment. Thus, they do not yield the same volume subsample uniformly, hence the potential for these splits to be inhomogeneous is high. Small sample size is known to contribute to this effect.

The potential of spattering of extremely high concentration samples into low concentration samples resulted in some ambiguity in elements with low sample concentrations. Overall, the anthropogenically contaminated sediments have elemental concentrations 1 to 4 orders of magnitude higher than those of the background samples and the SRM.

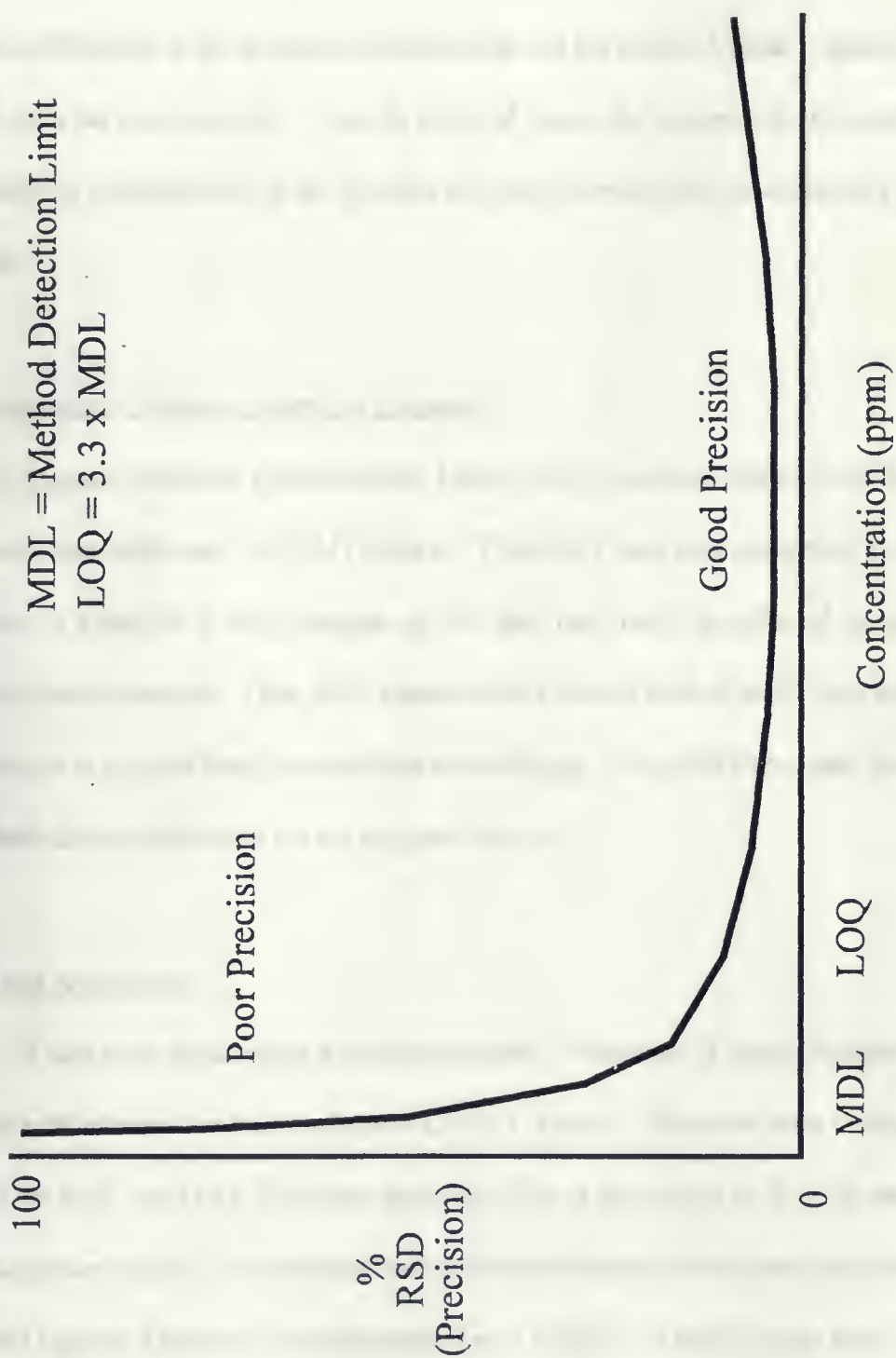


Figure 9. Precision of data as concentration approaches the method detection limit.

However, differences in the measured concentration and the certified value is generally less than 20 ppm for most analytes. Thus, in terms of fitness for purpose, the elevated levels differences in concentration in the samples are negligible and can be interpreted without difficulty.

2.7.3: Evaluation Criteria - Fitness for Purpose

A Highest Analytical Contamination Level (HACL) was established from the blank values and "ppm difference" of SRM (Table 4). This HACL was then multiplied by 2. This was done to establish a safety margin on the data that might be affected by potential laboratory contamination. Thus, each element had a cut-off limit at which low level data was accepted or rejected based on analytical methodology. All results higher than the HACL were deemed acceptable data for the purpose the study.

2.7.4: Data Assessment

All data were separated on a per-element basis. Evaluation of blanks, duplicates and SRM for each element are summarized in Tables 3, 4 and 5. The data were considered in terms of the MDL and LOQ. Only data above the MDL of the method (ICP-OES) were used. Only background levels (ie. concentrations in samples obtained from upstream) above the MDL and Highest Analytical Contamination Level (HACL) (Table 7) were used.

Table 3: Concentration of reagent blanks and concentration difference and precision calculation of duplicate analyses.

Sample #	Be	Sc	Y	Sr	Co	Cu	Ni	Cr	V	Zn	Al	Ba	Fe	Mg	Mn	Ti
Blank-1	0	0	0	0	0	11	3	17	1	4	38	4	79	6	1	4
Blank-2	0	0	0	0	0	1	1	2	1	6	41	1	10	0	0	3
Blank-3	0	0	0	0	0	1	1	5	1	1	39	1	25	0	0	4
Blank-4	0	0	0	0	0	0	0	2	1	1	37	1	23	0	0	4
Blank-5	0	0	0	0	0	1	1	1	1	1	9	0	9	0	0	3
Average	0	0	0	0	0	6	2	9	1	2	23	2	44	3	1	3
Sample #	Be	Sc	Y	Sr	Co	Cu	Ni	Cr	V	Zn	Al	Ba	Fe	Mg	Mn	Ti
108-A	0.06	1.31	2.58	13.62	153.5	776.8	6254	12630	112.6	138.9	3577	91.63	21060	2288	6241	256.4
108-A-DUP	0.06	1.18	2.44	14.05	156.6	854.3	6339	13650	119.1	137.5	3629	89.09	20780	2475	6298	249.0
108A ppm diff	0.00	-0.13	-0.14	0.43	3.10	77.5	85.0	1020	6.50	-1.40	52.0	-2.54	-280	187	57.0	-7.40
108A-percent diff	-2.45	10.14	5.35	-3.16	-2.02	-9.98	-1.36	-8.08	-5.77	1.01	-1.45	2.77	1.33	-8.17	-0.91	2.89
124-A	0.41	1.64	3.20	24.27	120.4	673.7	4780	15090	153.3	138.2	6927	297.4	223400	2656	5097	443.1
124-A-DUP	0.45	1.72	3.38	25.74	125.3	710.4	4874	15640	160.9	139.4	6984	303.6	225600	2675	5037	474.7
124A ppm diff	0.04	0.08	0.18	1.47	4.90	36.7	94.0	550	7.60	1.20	57.0	6.20	2200	19.0	-60.0	31.6
124A-percent diff	-8.56	-5.00	-5.46	-6.06	-4.07	-5.45	-1.97	-3.64	-4.96	-0.87	-0.82	-2.08	-0.98	-0.72	1.18	-7.13
104-C	1.00	6.74	18.62	210.5	10.78	282.2	69.46	130.9	55.62	172.3	53710	427.2	23760	14480	686.8	3803
104-C-DUP	0.92	6.57	18.26	205.1	9.97	277.7	75.24	138.5	50.39	92.07	52110	434.2	23240	14170	669.7	3841
104C ppm diff	0.08	0.17	0.36	5.40	0.81	4.50	-5.78	-7.60	5.23	80.23	1600	-7.00	520	310	17.10	-38.0
104C-percent diff	8.40	2.55	1.93	2.57	7.50	1.59	-8.32	-5.81	9.40	46.56	2.98	-1.64	2.19	2.14	2.49	-1.00
115-C	2.12	12.91	18.72	176.3	21.51	510.3	176.4	476.9	125.4	268.2	89830	599.3	50880	18680	556.0	5235
115-C-DUP	2.31	13.81	19.77	178.4	22.7	537.5	179.0	442.6	130.0	273.6	89330	588.1	51450	18350	554.7	5263
115C ppm diff	0.19	0.90	1.05	2.10	1.19	27.20	2.60	-34.30	4.60	5.40	-500	-11.2	570	-330	-1.30	28.0
115C-percent diff	-9.05	-6.97	-5.61	-1.19	-5.53	-5.33	-1.47	7.19	-3.67	-2.01	0.56	1.87	-1.12	1.77	0.23	-0.53
125-C	1.65	5.20	8.75	127.8	155.6	1180	7556	25540	275.2	587.8	32320	2499	213900	11650	4157	1645
125-C-DUP	1.60	5.27	8.97	129.7	154.1	1213	7371	25210	279.2	585.1	32620	2565	243000	11520	4331	1696
125C ppm diff	-0.06	0.07	0.22	1.90	-1.50	33.0	-185	-330	4.00	-2.7	300	66.0	29100	-130	174	51.0
125C-percent diff	3.39	-1.42	-2.51	-1.49	0.96	-2.80	2.45	1.29	-1.45	0.46	-0.93	-2.64	-13.60	1.12	-4.19	-3.10
127-C	2.01	11.41	16.12	158.6	27.31	543.8	464.4	1757	129.6	387.1	76070	520.2	70880	17670	886.9	4282
127-C-DUP	2.10	11.68	16.39	163.4	27.74	515.9	472.6	1979	132.5	394.4	78410	569.8	72910	18200	922.6	4271
127C ppm diff	0.09	0.27	0.27	4.80	0.43	-27.90	8.20	222.0	2.90	7.30	2340	49.6	2030	530	35.7	-11.0
127C percent diff	-4.44	-2.37	-1.67	-3.03	-1.57	5.13	-1.77	-12.64	-2.24	-1.89	-3.08	-9.53	-2.86	-3.00	-4.03	0.26
200-C	1.83	11.03	20.53	172.7	15.25	379.6	36.83	60.63	89.34	124.3	77060	528.5	32500	10530	279.6	5027
200-C-DUP	1.91	10.94	19.67	169.8	15.78	382.5	39.35	65.11	90.98	125.6	74640	529.2	32260	10260	276.9	4618
200C ppm diff	0.09	-0.09	-0.86	-2.90	0.53	2.90	2.52	4.48	1.64	1.30	-2420	0.70	-240	-270	-2.70	-409
200C percent diff	-4.66	0.82	4.19	1.68	-3.48	-0.76	-6.84	-7.39	-1.84	-1.05	3.14	-0.13	0.74	2.56	0.97	8.14
101-D	1.92	7.50	17.53	239.9	242.0	2933	10140	22300	361.7	2029	52320	1354	35570	28870	9062	2581
101-D-DUP	1.42	5.58	12.99	171.9	178.8	2027	7537	16310	268.5	1490	37780	1000	27900	21620	6558	1955
101D ppm diff	-0.50	-1.92	-4.54	-68.0	-63.2	-906	-2603	-5990	-93.2	-539	-14540	-354	-7670	-7250	-2504	-626
101D-percent diff	26.26	25.60	25.90	28.35	26.12	30.89	25.67	26.86	25.77	26.56	27.79	26.14	21.56	25.11	27.63	24.25
113-D	2.46	14.02	20.10	176.1	36.83	962.2	558.0	1936	171.2	430.8	94820	617.8	74470	21430	677.2	5622
113-D-DUP	2.24	12.50	18.01	150.3	30.97	792.0	473.0	1572	147.1	361.0	77650	507.3	62610	17630	563.6	4556
113D ppm diff	-0.23	-1.52	-2.09	-25.8	-5.86	-170	-85.0	-364	-24.1	-69.8	-17170	-111	-11860	-3800	-114	-1066
113D-percent diff	9.18	10.84	10.40	14.65	15.91	17.69	15.23	18.80	14.08	16.20	18.11	17.89	15.93	17.73	16.77	18.96
123-D	1.82	5.99	10.97	165.5	175.1	1301	9330	28390	288.9	634.5	35810	1740	207200	15940	4145	1850
123-D-DUP	1.92	6.18	11.24	170.5	178.0	1356	9496	28920	295.4	644.3	37140	1240	206700	16420	4206	1912
123D ppm diff	0.10	0.20	0.27	5.00	2.90	55.0	166	530	6.50	9.80	1330	-500	-500	480	61.0	62.0
123D-percent diff	-5.22	-3.29	-2.46	-3.02	-1.66	-4.23	-1.78	-1.87	-2.25	-1.54	-3.71	28.74	0.24	-3.01	-1.47	-3.35
130-D	2.24	12.92	18.16	157.3	22.59	1048	181.5	385.7	122.6	380.8	84340	564.6	45100	15350	351.8	5190
130-D-DUP	2.25	13.03	18.25	159.6	23.06	1034	182.0	408.3	123.2	379.4	84280	568.8	45430	15410	356.0	5080
130D ppm diff	0.01	0.11	0.09	2.30	0.47	-14.0	0.50	22.6	0.60	-1.4	-60.0	4.2	330	60.0	4.20	-110
130D percent diff	-0.31	-0.85	-0.50	-1.46	-2.08	1.34	-0.28	-5.86	-0.49	0.37	0.07	-0.74	-0.73	-0.39	-1.19	2.12
201-D	2.18	13.73	18.99	157.4	16.20	786.9	48.99	64.38	118.5	173.3	88830	557.0	41080	12950	307.9	6008
201-D-DUP	2.27	14.13	19.75	160.1	16.57	802.5	54.71	96.36	123.2	175.5	87950	558.8	41450	12660	311.2	5884
201D ppm diff	0.08	0.40	0.76	2.70	0.37	15.60	5.72	31.98	4.70	2.20	-880	1.80	370	-290	3.30	-124
201D-percent diff	-3.80	-2.91	-4.00	-1.72	-2.28	-1.98	-11.68	-49.67	-3.97	-1.27	0.99	-0.32	-0.90	2.24	-1.07	2.06

All values in ppm.

Table 4: Variation in concentration of analyses of Standard Reference Materials.

Sample #	Be	Sc	Y	Sr	Co	Cu	Ni	Cr	V	Zn	Al	Ba	Fe	Mg	Mn	Ti
91-1646 ppm diff	0.4	1.2	3.4	2.6	1.8	4.0	9.0	7.1	19.6	12.7	10263	73.9	8419	1752	38.4	192
92-1646 ppm diff	0.4	1.4	2.9	6.0	2.9	4.8	10.0	3.6	21.5	20.1	9993	77.9	8489	1472	41.7	325
93-1646 ppm diff	0.3	0.1	2.0	13.0	1.1	0.9	3.7	2.7	10.3	2.5	4923	24	4139	832	1.6	425
94-1646 ppm diff	0.3	0.2	2.6	20.4	0.6	0.2	3.7	1.7	7.5	2	1993	38	3319	372	4.6	675
95-1646 ppm diff	0.3	0.30	2.6	20.8	0.1	1.2	4.2	4.7	5.2	0.5	2733	21.7	3809	902	2.9	664
AVERAGE	0.3	0.6	2.7	12.6	1.3	2.2	6	4	12.8	7.6	5981	47.1	5635	1066	18	456
91-2704 ppm diff	NA	0.7	NA	26.1	3.0	20.8	12.5	12.2	24.1	76.3	11752	82.3	9205	2076	95.2	246
92-2704 ppm diff	NA	0.5	NA	9.5	1.0	9.1	4.9	20.2	9.0	23.2	3232	21.3	3505	226	15.3	254
93-2704 ppm diff	NA	0.4	NA	10.7	0.7	6.9	5.8	0.7	11.9	42.3	5442	28	4225	806	36.5	463
94-2704 ppm diff	NA	0.9	NA	3.8	0.7	1.8	5.5	0.1	8.6	19.4	2892	42.3	2845	456	21.9	987
95-2704 ppm diff	NA	0.7	NA	5.3	0.5	5.7	4.0	2.6	8.8	28.6	5272	33.8	4145	796	34.7	828
AVERAGE	NA	0.6	NA	11.1	1.2	8.9	6.5	7.2	12.5	38.0	5718	41.5	4785	872	40.7	556
93-lksd-3 ppm diff	0.2	0.7	4.4	31.4	3.8	2.8	13.8	0.6	10.6	8.8	5232	32.6	4984	896	29.0	340
95-lksd-3 ppm diff	0.2	0.9	5.0	21.2	3.9	1.5	13.3	5.1	9.4	8.3	2462	34.8	4584	516	14.0	420
AVERAGE	0.2	0.8	4.7	26.3	3.8	2.1	13.6	2.8	10.0	8.6	3847	33.7	4784	706	21.5	380
93-slsd-2 ppm diff	0.7	1.6	6.7	51.5	2.7	7.2	16.1	1.8	15.1	50.1	6770	8.3	1470	1710	4.0	110
94-slsd-2 ppm diff	0.7	1.6	7.2	36.7	3.2	10.0	14.3	14.1	13.0	30.3	6930	24.0	760	1690	13.0	174
95-slsd-2 ppm diff	0.7	1.7	6.9	42.2	3.2	4.5	13.8	15.1	13.0	20.4	4220	10.8	2100	1220	10.0	295
AVERAGE	0.7	1.6	6.9	43.5	3.0	7.2	14.7	10.3	13.7	33.6	5973	14.4	1443	1540	9.0	193

All values in ppm.

Certified values from primary certificates.

1646 = NIST 1646 - Estuarine Sediment

2704 = NIST 2704 - Buffalo River Sediment

lksd = CANMET Lake Sediment

slsd = CANMET Stream Sediment

NA = Data not available

Table 5: Trueness of several analyses of Standard Reference Materials.

% Accuracy Calculations		Be	Sc	Y	Sr	Co	Cu	Ni	Cr	V	Zn	Al	Ba	Fe	Mg	Mn	Ti
Sample #																	
91-1646 percent diff		28.1	11.0	16.3	1.5	16.9	22.2	28.2	9.3	20.9	9.2	16.4	17.9	25.1	16.0	10.3	3.8
92-1646 percent diff		28.2	12.6	13.9	3.5	27.8	26.7	31.3	4.7	22.9	14.6	16.0	18.9	25.3	13.5	11.2	6.4
93-1646 percent diff		0.2	1.1	9.6	7.6	10.7	5.1	11.6	3.6	11.0	1.8	7.9	5.8	12.4	7.6	0.4	8.3
94-1646 percent diff		0.2	1.9	12.2	12.0	5.8	1.0	11.6	2.2	8.0	1.6	3.2	9.2	9.9	3.4	1.2	13.2
95-1646 percent diff		0.2	2.8	12.3	12.2	1.2	6.5	13.2	6.1	5.5	0.4	4.4	5.3	11.4	8.3	0.8	13.0
AVERAGE		11.4	5.9	12.9	7.4	12.5	12.3	19	5	13.6	5.5	9.6	11.4	16.8	9.8	4.8	9.0
91-2704 percent diff		NA	6.0	NA	20.1	21.6	21.1	28.3	9.0	25.4	17.4	19.2	19.9	22.4	17.3	17.1	5.4
92-2704 percent diff		NA	4.1	NA	7.3	7.2	9.2	11.2	15.0	9.5	0.0	5.3	5.1	8.5	1.9	2.7	5.6
93-2704 percent diff		NA	3.2	NA	8.2	5.1	7.0	13.0	0.5	12.5	9.7	8.9	6.8	10.3	6.7	6.5	10.2
94-2704 percent diff		NA	7.2	NA	2.9	4.7	1.8	12.5	0.1	9.1	4.4	4.7	10.2	6.9	3.8	3.9	21.7
95-2704 percent diff		NA	5.6	NA	4.1	3.4	5.8	9.1	1.9	9.3	6.5	8.6	8.2	10.1	6.6	6.2	18.2
AVERAGE		NA	5.2	NA	8.5	8.4	9.0	14.8	5.3	13.1	7.6	9.4	10.0	11.6	7.3	7.3	12.2
93-1ksd-3 percent diff		0.1	5.0	14.7	13.1	12.6	7.9	29.4	0.7	12.9	5.8	7.9	4.8	12.5	7.4	2.0	10.2
95-1ksd-3 percent diff		0.1	7.0	16.8	8.8	13.0	4.3	28.3	5.8	11.4	5.5	3.7	5.1	11.5	4.3	1.0	12.6
AVERAGE		0.1	6.0	15.8	11.0	12.8	6.1	28.8	3.3	12.2	5.6	5.8	5.0	12.0	5.9	1.5	11.4
93-std-2 percent diff		0.1	9.8	18.1	12.9	13.9	15.3	30.5	1.6	15.0	20.4	7.9	1.5	2.5	9.2	0.0	2.3
94-std-2 percent diff		0.1	10.1	19.4	9.2	16.8	21.4	27.0	12.2	12.9	12.3	8.1	4.4	1.3	9.1	1.2	3.6
95-std-2 percent diff		0.1	10.4	18.6	10.6	17.1	9.5	26.0	13.0	12.9	8.3	4.9	2.0	3.6	6.5	0.9	6.1
AVERAGE		0.1	10.1	18.7	10.9	15.9	15.4	27.8	8.9	13.6	13.7	7.0	2.7	2.5	8.3	0.7	4.0
1646 certified		1.5	10.8	21	170	10.5	18	32	76	94	138	62487	413	33501	10918	372	5096
2704 certified		NA	12	NA	130	14	98.6	44.1	135	95	438	61058	414	41125	12004	558	4556
std-2 certified		5.2	16	37	400	19	47	53	116	101	246	85230	540	58280	18660	1060	4870
1ksd-3 certified		1.9	13	30	240	30	35	47	87	82	152	66138	680	39866	12064	1440	3330

All values are percent.

Certified values from primary certificates.

NA = Data not available.

2.7.5: Data Presentation and Acceptability

All SRM analyses were evaluated in two ways. First, the difference of the concentration in ppm was calculated (Table 4);

$$(\text{certified value} - \text{measured value})$$

and then by trueness was calculated (Table 5);

$$\frac{(\text{certified value} - \text{measured value})}{\text{certified value}} \times 100\%$$

Possible analytical contamination was evaluated on the basis of these concentrations and average of concentration of the blanks. The acceptable data limits are tabulated in Table 6.

Table 6. Lowest limit (2 x HACL) for which data are acceptable.

Sc > 3 ppm	Y > 14 ppm
Sr > 100 ppm	Co > 8 ppm
Cu > 42 ppm	Ni > 32 ppm
Zn > 153 ppm	Ti > 1970 ppm
Cr > 41 ppm	V > 48 ppm
Ba > 160 ppm	Fe > 18400 ppm
Mn > 190 ppm	Mg > 4150 ppm
Al > 23500 ppm	

In conclusion, for the objectives of the thesis, all data above the LOQ and/or the HACL was accepted as fit for purpose as outlined in Table 7. The effect of these limitations on the data is summarized as follows: 1) Sc, Sr, Co, Cu, Ni, Cr, V, Ba, Mg and Mn data can be used to document both background levels and anthropogenic input, as the data exceed

HACL for all elements. 2) Y data can be used to determine background levels, since they decrease in concentration in the contaminated river samples. However, anthropogenic input data cannot be assessed because the Y concentration decreases below the HACL. This surprising conclusion will be discussed in more detail in the Chapter 3. 3) Zn, Fe, Ti and Al data can be used to determine anthropogenic input but not background levels, as the data fall below HACL.

Table 7: Elemental assessment of data by ICP-OES.

Element	MDL (ppm)	LOQ (ppm)	Range Required (ppm)	HACL (ppm)	Acceptable Data (2xHACL) (ppm)	Environments for which Data is suitable.
Sc	1	3	1-27	2	>3	Background & Anthropogenic
Y	2	6	3-42	7	>14	Background only
Sr	1	3	13-340	52	>100	Background & Anthropogenic
Co	5	15	9-340	4	>8	Background & Anthropogenic
Cu	5	15	33-3900	21	>42	Background & Anthropogenic
Mo	6	18	4-1400	7	>14	Anthropogenic only
Ni	2	6	27-12000	16	>32	Background & Anthropogenic
Cr	NA	NA	48-34000	21	>41	Background & Anthropogenic
V	5	15	48-400	24	>48	Background & Anthropogenic
W	35	105	0-600	8	>15	Anthropogenic only
Zn	2	6	68-3100	76	>150	Anthropogenic only
Al	NA	NA	3577-87430	11752	>23500	Anthropogenic only
Ba	NA	NA	89-5300	82	>160	Background & Anthropogenic
Fe	NA	NA	11000-260000	9200	>18400	Anthropogenic only
Mg	NA	NA	2288-44300	2076	>4150	Background & Anthropogenic
Mn	NA	NA	255-7800	95	>190	Background & Anthropogenic
Ti	NA	NA	192-11000	987	>1970	Anthropogenic only

Chapter 3: Results and Discussion

3.1: Mineralogical Analyses

The expected background mineralogy of carbonates (calcite and dolomite), and silicates (feldspars, quartz, chlorite and clays) were identified in all samples collected from the river, which are a reflection of local rock mineralogy. Unusual mineral phases present were ferrocolumbite, mullite, wuestite, with hematite and magnetite in large quantities (Fig. 10), which are unaccountable by local geology, but are minerals generally found in a number of industrial processes (Scriver et al, 1995).

3.2: Geochemical Analyses

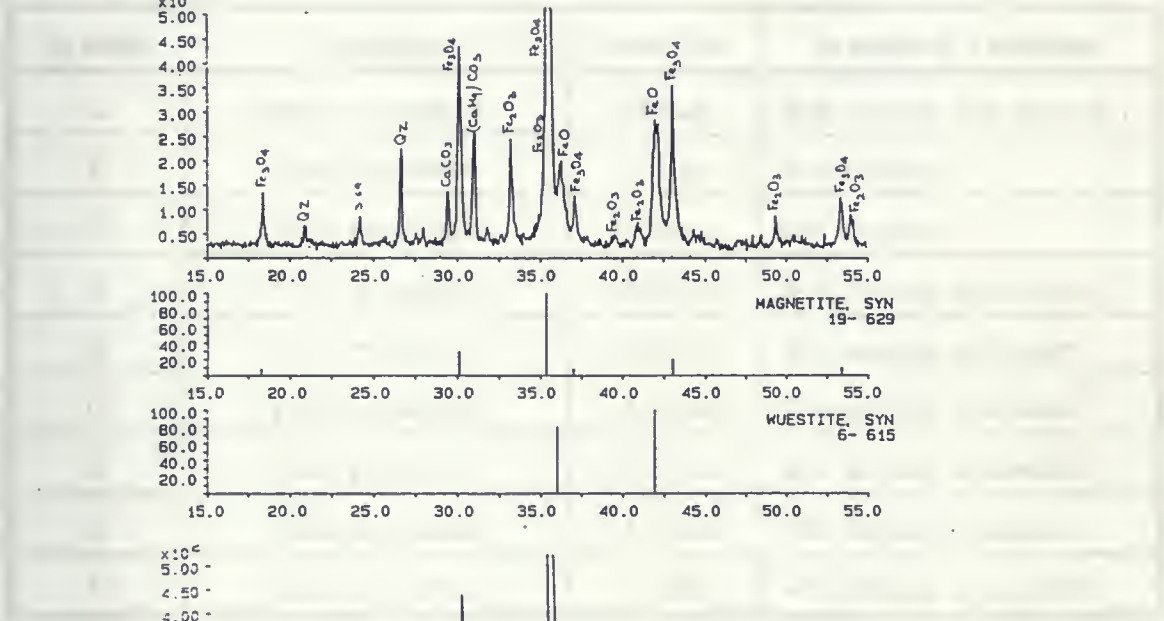
Samples were extracted by two different techniques, (1) partial extraction (denoted "L") and (2) total extraction (denoted "P" and "Q"). Further total extractions were performed on samples that were separated by grain size (denoted "A" through "F" Table 8.)

1.1. Introduction

The purpose of this book is to provide a comprehensive overview of the current state of research in the field of [topic]. The book is organized into several chapters, each focusing on a different aspect of the field. Chapter 1 provides an overview of the field and its history. Chapter 2 discusses the current state of research and the challenges that remain. Chapter 3 presents a new approach to the problem of [topic]. Chapter 4 discusses the implications of this approach for the field as a whole. Chapter 5 presents a new approach to the problem of [topic]. Chapter 6 discusses the implications of this approach for the field as a whole. Chapter 7 presents a new approach to the problem of [topic]. Chapter 8 discusses the implications of this approach for the field as a whole. Chapter 9 presents a new approach to the problem of [topic]. Chapter 10 discusses the implications of this approach for the field as a whole.

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3

Table 8: Sample labelling scheme according to technique for grain size separation techniques.

Symbol	Technique	Grain Size	Separation Technique
L	Partial extraction	1-63 μ m	Wet sieving, Dry sieving
P	Total extraction	1-63 μ m	Wet sieving
Q	Total extraction	1-63 μ m	Dry sieving
A	Total extraction	44-63 μ m	Wet sieving, cyclosizer
B	Total extraction	33-44 μ m	Wet sieving, cyclosizer
C	Total extraction	23-33 μ m	Wet sieving, cyclosizer
D	Total extraction	15-23 μ m	Wet sieving, cyclosizer
E	Total extraction	11-15 μ m	Wet sieving, cyclosizer
F	Total extraction	<11 μ m	Wet sieving, cyclosizer

3.2.1: Total Extraction Analyses

All total extraction analyses were evaluated to 3 sets of data (Table 9): Average continental crust (ACC) from Taylor and McLellan, 1985 (Fig. 11); the average of the control samples from the Welland River (WRC) (Fig. 12) and the lowest effect level (LEL) data of the Provincial Sediment Quality Guidelines for metals and nutrients (PSQG) (Fig. 13) from MOEE, 1993 in aquatic sediments.

Table 9.: Data used to evaluate geochemical analyses for the Welland River sediments. ACC = Average Continental Crust, WRC = Welland River Control samples, PSQG = Provincial Sediment Quality Guidelines, LEL = Lowest Effect Level, SEL = Severe Effect Level (Persaud et al., 1993).

Element	ACC(ppm)	WRC (ppm)	PSQG-LEL(ppm)	PSQG-SEL(ppm)
Be	1.5	2.07	-	-
Co	29	17.15	-	-
Sc	30	13.48	-	-
Cu	75	35.08	16	110
Ni	105	42.15	16	75
V	230	110.3	-	-
Y	20	21.41	-	-
Zn	80	146.3	120	820
Sr	260	184.9	-	-
Al	84100	82736	-	-
Ba	250	529.1	-	-
Fe	70700	42600	20000	40000
Mg	32000	12051	-	-
Mn	1400	380.9	460	1100
Ti	5400	5110	-	-
Cr	185	73.2	26	110

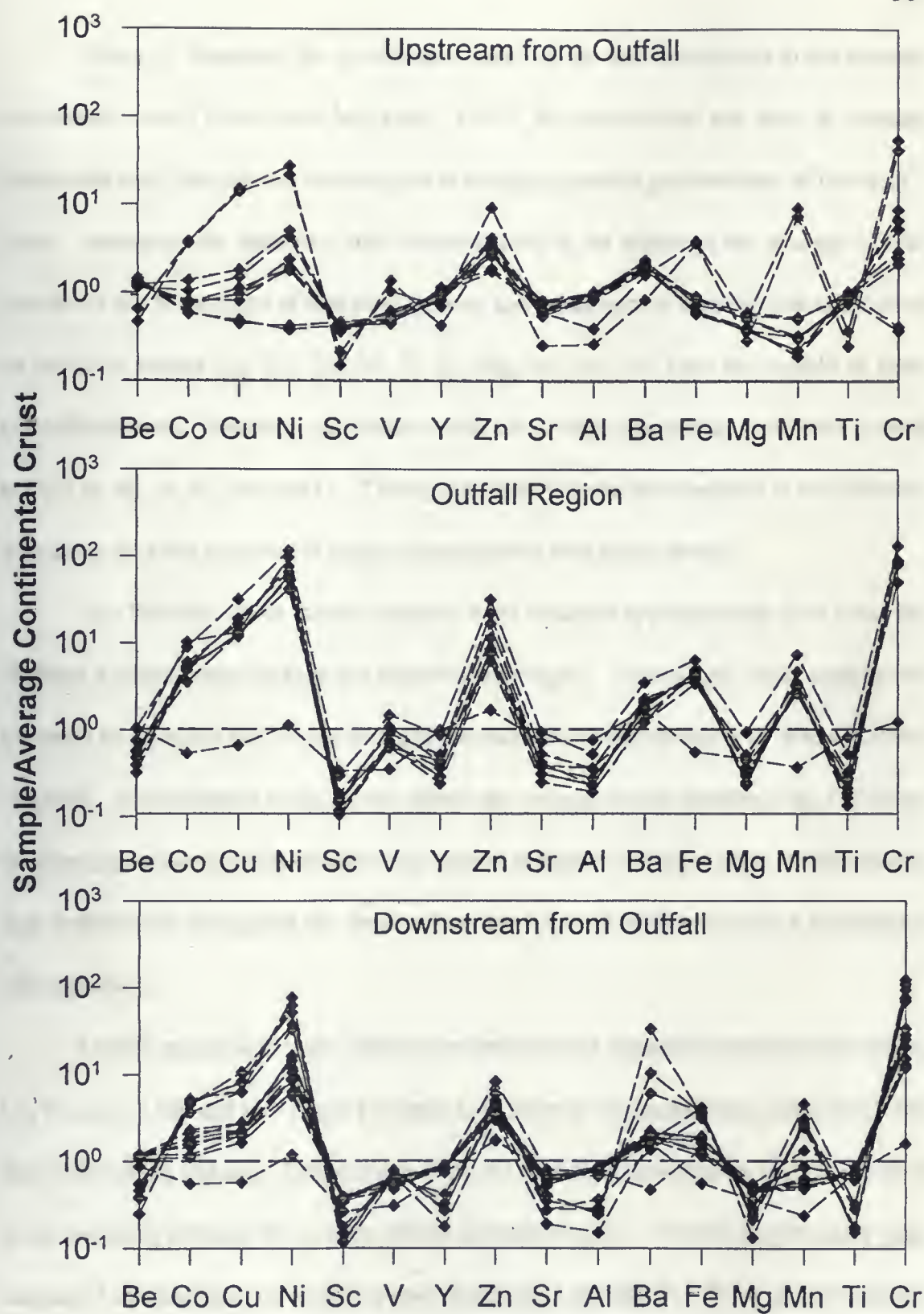


Figure 11. Geochemical data normalized to average continental crust (Taylor and McLellan, 1985).



Hourly Average Concentration (ppm)

Figure 11 illustrates the enrichments found in the data normalized to the average continental crust (Taylor and McLellan, 1985). By normalizing the data to average continental crust, the data can be compared to average expected geochemistry of the earth's crust. Generally, the transition row elements tend to be higher in the average crustal abundance due to inclusion of data from igneous and metamorphic material that could have an influx of metals (eg. Co, Cu, Ni, V, Fe, Mg, Mn and Cr) from the mantle or from mineralized zones. Elemental enrichments over the average continental crust were present in Co, Cu, Ni, Zn, Fe, Mn and Cr. These particular elements are observed in the sediment indicating the river sediment is highly contaminated with heavy metals.

The Welland River control samples were obtained approximately 2km (near the Welland Airfield) upstream from the industrialized region. Accordingly, these samples are assumed to represent the natural background elemental concentrations of Welland River sediment. Normalization of the sample data to the average control samples (Fig. 12) shows the elemental concentrations relative to the control samples. The appearance of enrichments and deficiencies throughout the data set become apparent with respect to a background concentrations.

Outfall region sediments exhibit clear evidence of increased concentrations of Co, Cu, Ni, Zn, Fe, Mn and Cr. These elements are known to be contaminants associated with the steel-making industry. Downstream from the outfall, these elements are still enriched in the sediment, although the concentrations declined slightly. Three samples had a large amount of oil clinging to the sediment upon sampling (Appendix 5). These samples located approximately 50 to 100m downstream from the outfall show an anomalous increase in

barium concentrations.

Normally, it would be expected that the samples upstream from the outfall should be relatively uncontaminated. However, there is evidence of minor contamination of heavy metals. This suggests that either there could be other source(s) of contamination via other storm sewers located upstream or the river dynamics are such that contaminants move upstream from the Atlas-Mansfield outfall towards the Welland Canal siphons.

Finally, the data was compared to the Provincial Sediment Quality Guidelines (PSQG) set by the Ministry of the Environment and Energy (MOEE) in 1993. The purpose of these guidelines is to protect and manage sediment quality in Ontario waters. It is of concern that many toxic substances exist for long periods of time and can accumulate in the benthic communities (Biomagnification). Subsequently, these contaminants can transfer up the food chain (Persaud et al., 1993). The guidelines are defined to three categories: 1) No Effect Level (NEL); 2) Lowest Effect Level (LEL) and 3) Severe Effect Level (SEL) (Table 10). The criteria for these levels are summarized in the following table as outlined by the PSQG set by the MOEE.

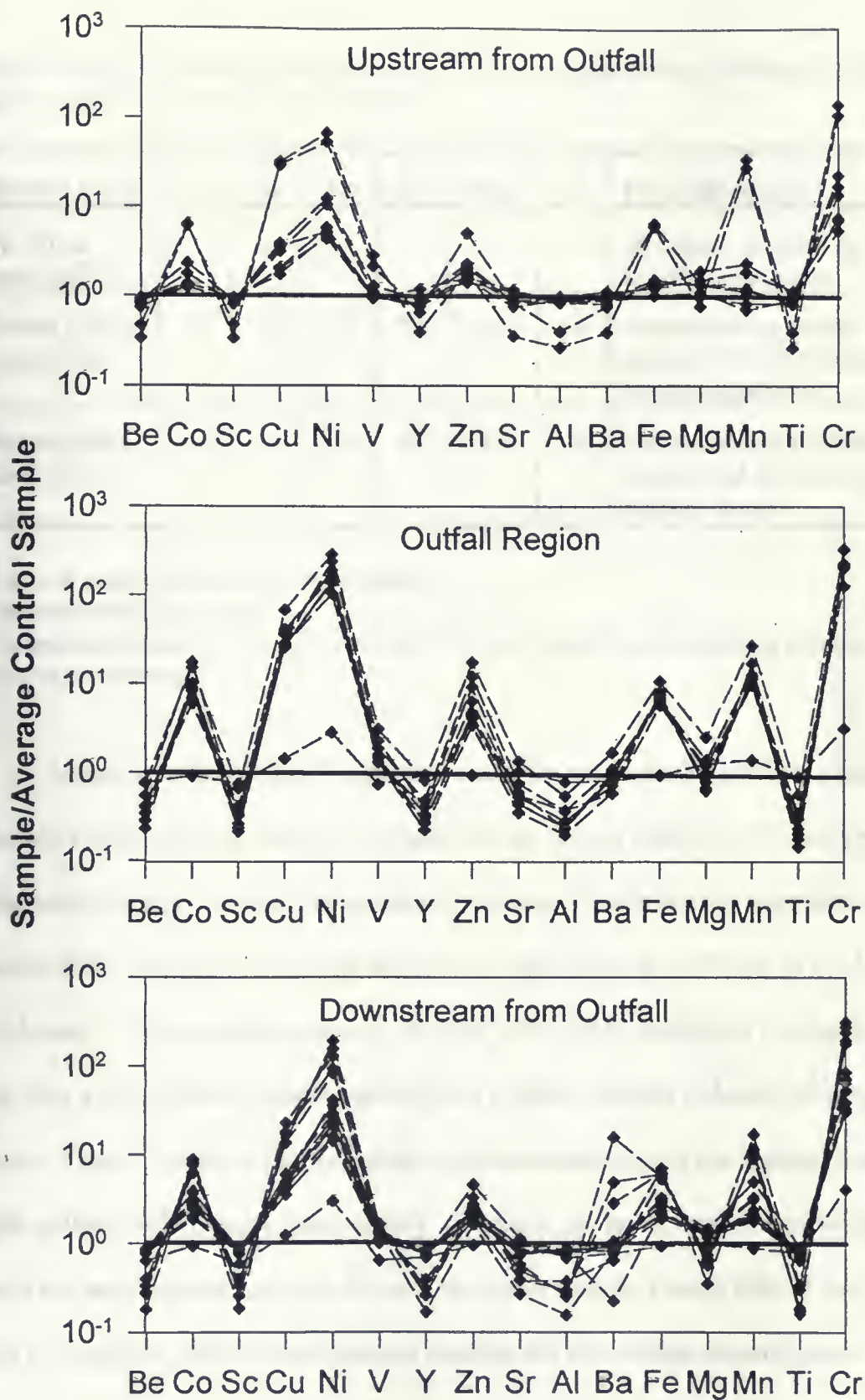


Figure 12. Geochemical data normalized to the average control samples of the Welland River.



Annual landscape epiphyllous

Figure 1. Landscape epiphyllous (1990-2005)

Table 10: Summary of data, quality levels and impact according to the Provincial Sediment Quality Guidelines (Persaud et al., 1993).

Quality Level	Cu	Ni	Zn	Fe	Mn	Cr	Potential Impact*
No Effect Level (NEL)	-	-	-	-	-	-	no impact on water or benthic community
Lowest Effect Level (LEL)	16	16	120	2%	460	26	contamination can be tolerated by majority of benthic organisms
Severe Effect Level (SEL)	110	75	820	4%	1100	110	concentrations are likely detrimental to majority of benthic species

All data in ppm, unless otherwise indicated.

"-" denotes insufficient data.

*The potential impact is based on ecotoxic effects of chronic and long-term effects on the benthic community.

According to the PSQG, if background values for metals are derived from areas not affected by industrial point sources are greater than the "Lowest Effect Level", then the local background chemistry will form the practical lower limit. Results from the upstream control samples of the Welland River exceed the Lowest Effect Level of the PSQG for Cu, Ni, Zn, Fe, Mn and Cr. Nevertheless, comparing the data to the PSQG establishes a comparison of data with a government regulating guideline to support evidence of highly contaminated regions. Figure 13 indicates that the outfall and downstream areas of the Welland River are highly polluted with respect to heavy metals. Generally, the levels upstream are lower than that of the outfall region, although they still are higher than the Lowest Effect Level of the PSQG. In addition, there are two upstream samples that have similar contamination to that of the outfall area.

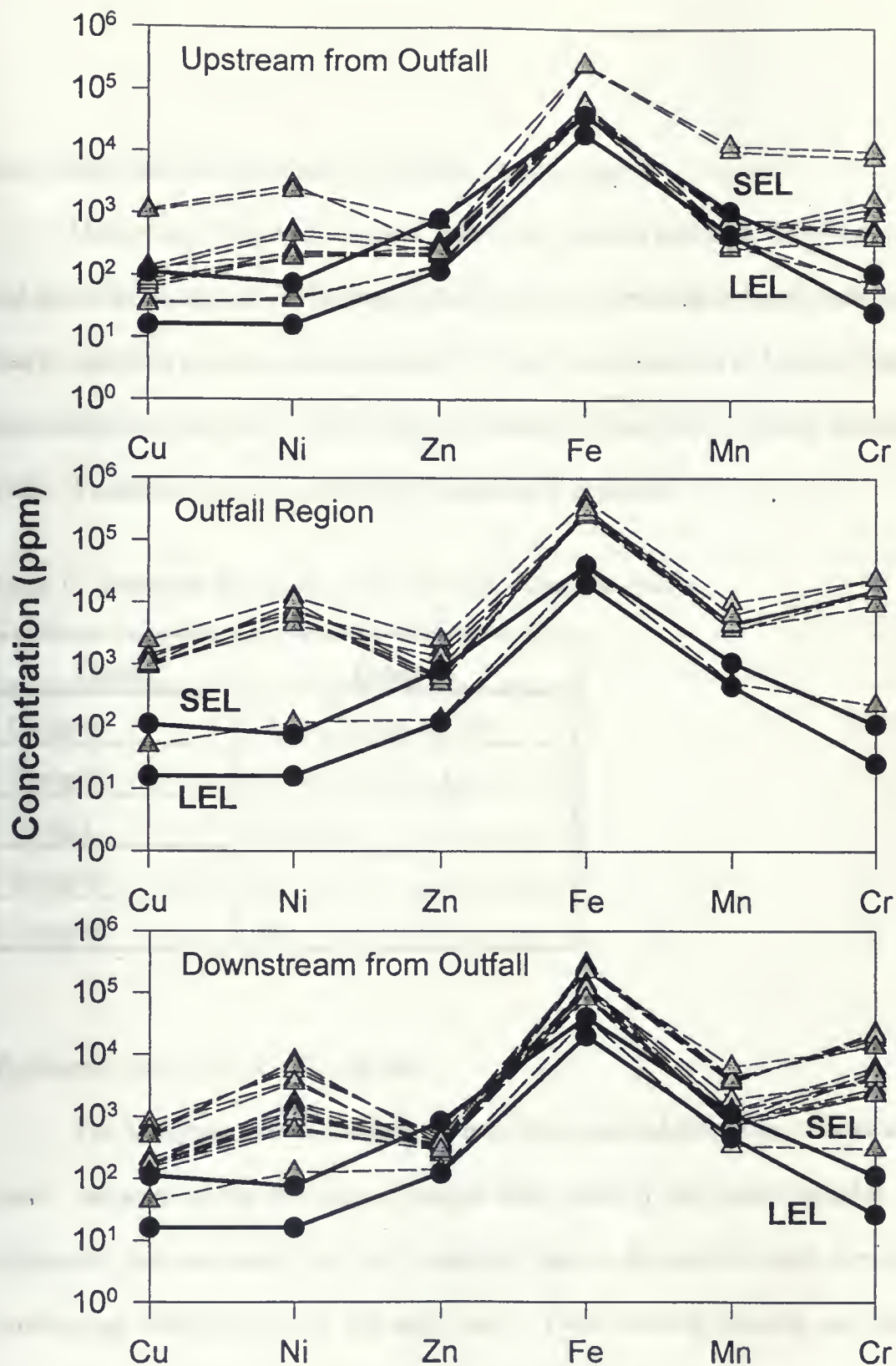


Figure 13. Geochemical data compared to Provincial Sediment Quality Guidelines (MOEE, 1993).
Lowest Effect Level = LEL, Severe Effect Level = SEL.



3.2.2: Partial and Total Extraction Analyses - Comparisons

Metal concentrations show clear separations between upstream, the outfall region and downstream samples. Outfall region samples contain considerably higher mean values than the upstream and downstream samples. Elements were separated in 5 groups based on their pattern from upstream to downstream, elemental behaviour, and analytical differences. Table 11 outlines the groups into which each element is divided.

Table 11: Elemental groups for partial and total extraction results.

Group	Elements
Group A	Co, Cu, Ni, Zn, Cr, Mn
Group B	Be, Sc, Y, Sr, Ti, Al.
Group C	V, Mg
Group D	Fe
Group E	Ba

a) Group A: Co, Cu, Ni, Zn, Cr and Mn.

The background concentrations are low, with a marked difference, a factor of 2 or more, between partial and total extraction data shown in the outfall samples. The differences between partial and total extraction data in the upstream and downstream samples are slight and exhibit the same trend. These divalent elements are first-row transition elements and are metals typically used in the steel industry.

Total Co values approach 300 ppm, Cu and Zn concentrations are an order of magnitude higher (3000 ppm) and Ni and Mn values exceed 10000 ppm in the outfall region. The total Cr levels approach 25000 ppm and show a distinct elevation over the partial extraction data in the outfall region (Fig. 14a,b). The apparent difference in concentration of Cr between the partial and total extraction data in the outfall area suggests that the chromium resides in the total extraction phase and therefore is not immediately available to the environment. The presence of enrichments occurring in the partial extraction data, in the outfall region samples, indicate that these elements are available to the environment if the ambient environmental conditions persist for extraction (i.e. decrease in pH, increasing the acidity of the water).

b) Group B: Be, Sc, Y, Sr, Ti and Al.

Generally, the partial extraction concentrations are low, with a relatively flat trend throughout the river samples (except Y). The total extraction values are elevated at the outfall region and have a variable trend. Be, Sc, and Y show a slight enhancement in the total extraction concentration over the partial extraction data (a few ppm). Sr shows an enrichment of 20 to 150 ppm over the partial extraction data. Al and Ti show marked differences between the extraction results (10000 - 65000 ppm and 600 - 5000 ppm, respectively) (Fig. 15a,b).

Examine the various dimensions of the life cycle and the different stages of life. Consider the various factors that influence the life cycle, such as genetics, environment, and lifestyle. Discuss the various stages of life, from birth to death, and the various experiences that shape the individual. Consider the various factors that influence the life cycle, such as genetics, environment, and lifestyle. Discuss the various stages of life, from birth to death, and the various experiences that shape the individual. Consider the various factors that influence the life cycle, such as genetics, environment, and lifestyle. Discuss the various stages of life, from birth to death, and the various experiences that shape the individual.

Chapter 10: The Life Cycle

The life cycle is a series of events that occur from birth to death. It is a process that is influenced by many factors, including genetics, environment, and lifestyle. The life cycle is a process that is influenced by many factors, including genetics, environment, and lifestyle. The life cycle is a process that is influenced by many factors, including genetics, environment, and lifestyle. The life cycle is a process that is influenced by many factors, including genetics, environment, and lifestyle.

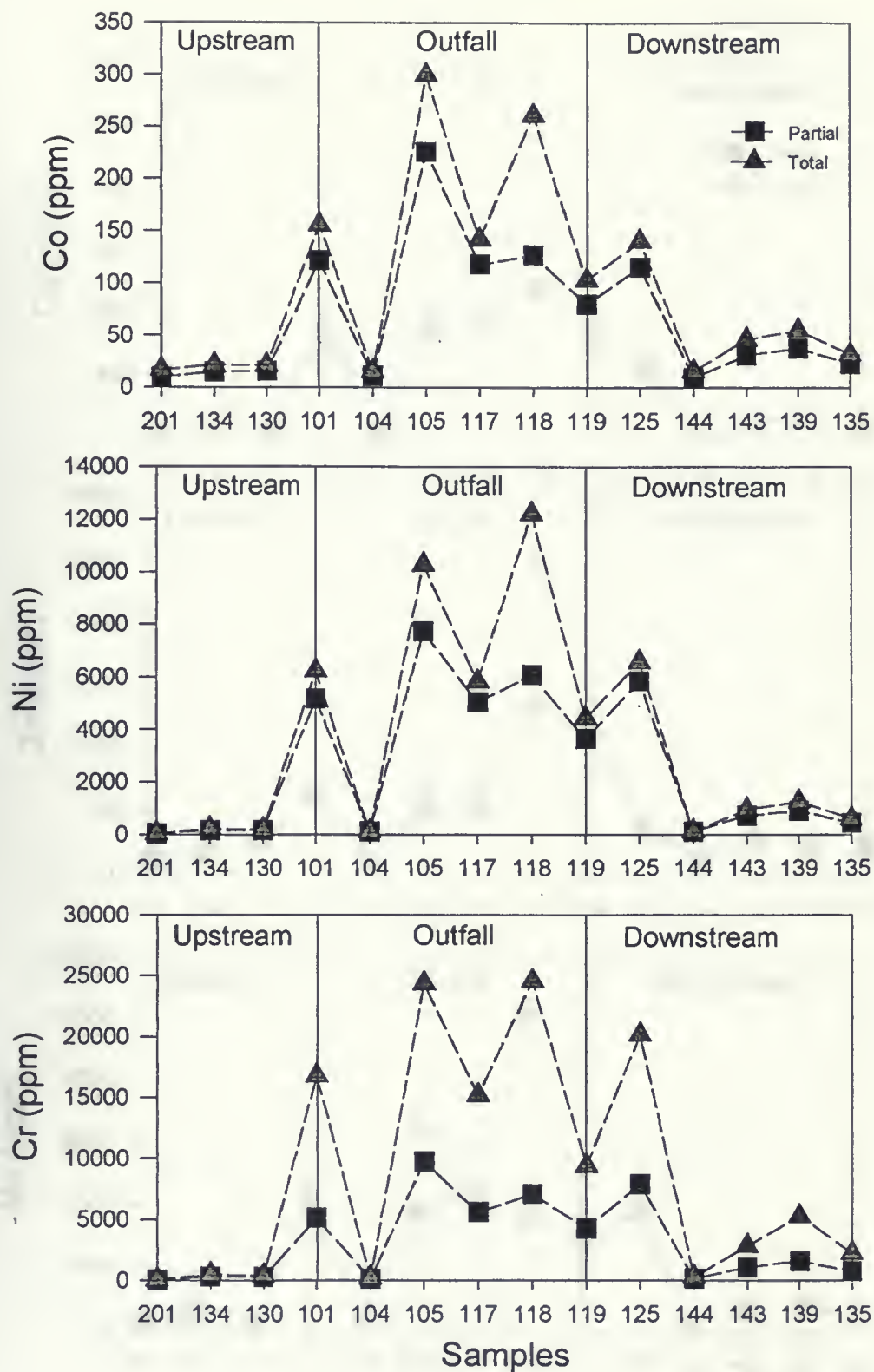


Figure 14a. Partial and Total extraction comparisons for Group A.



Figure 1. Concentration of Cu, Pb and Zn in the soil of a grassland area over time.

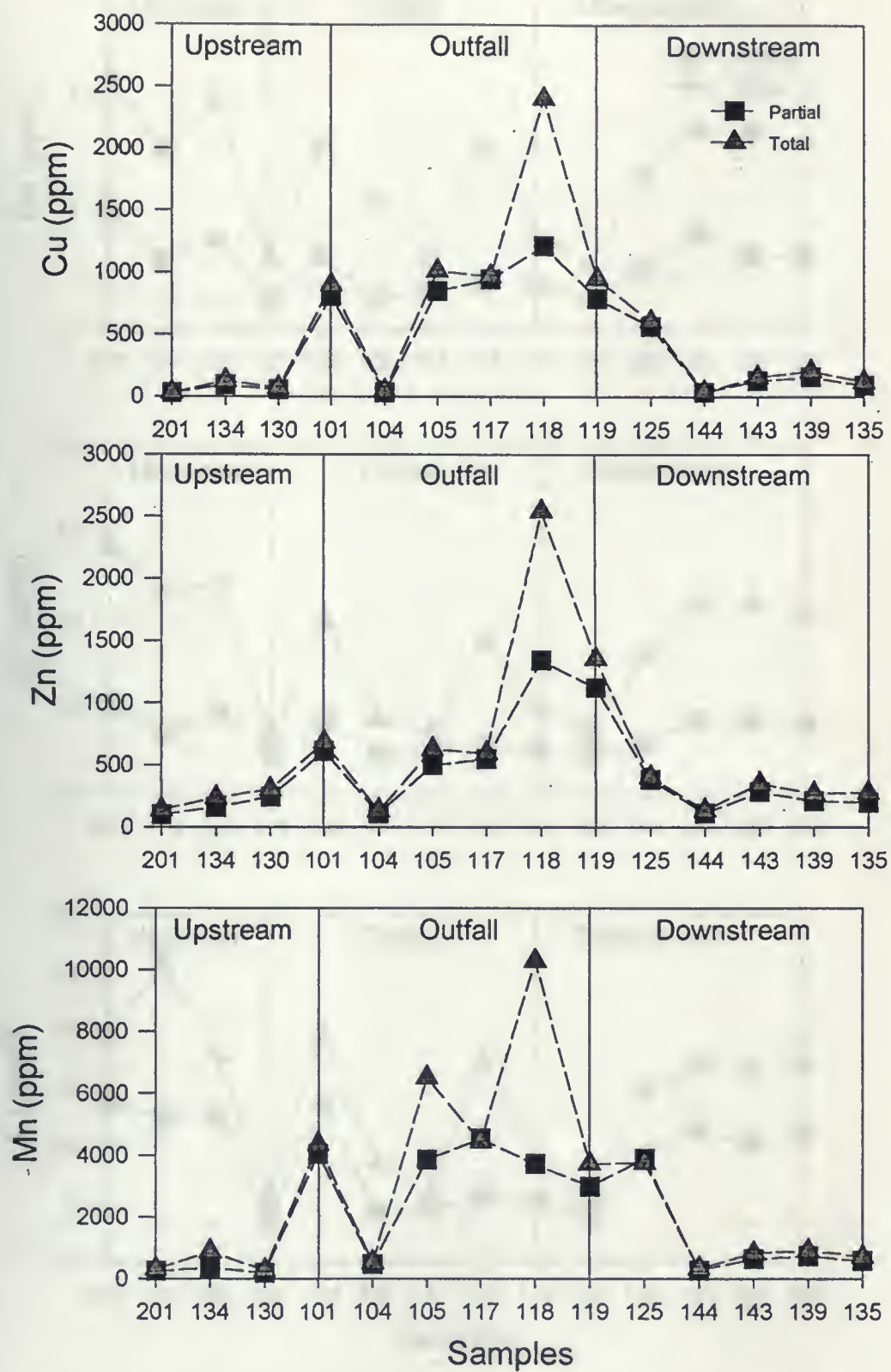


Figure 14b. Partial and total extraction comparisons for Group A.



Figure 1: Concentration of substance over time for three different conditions.

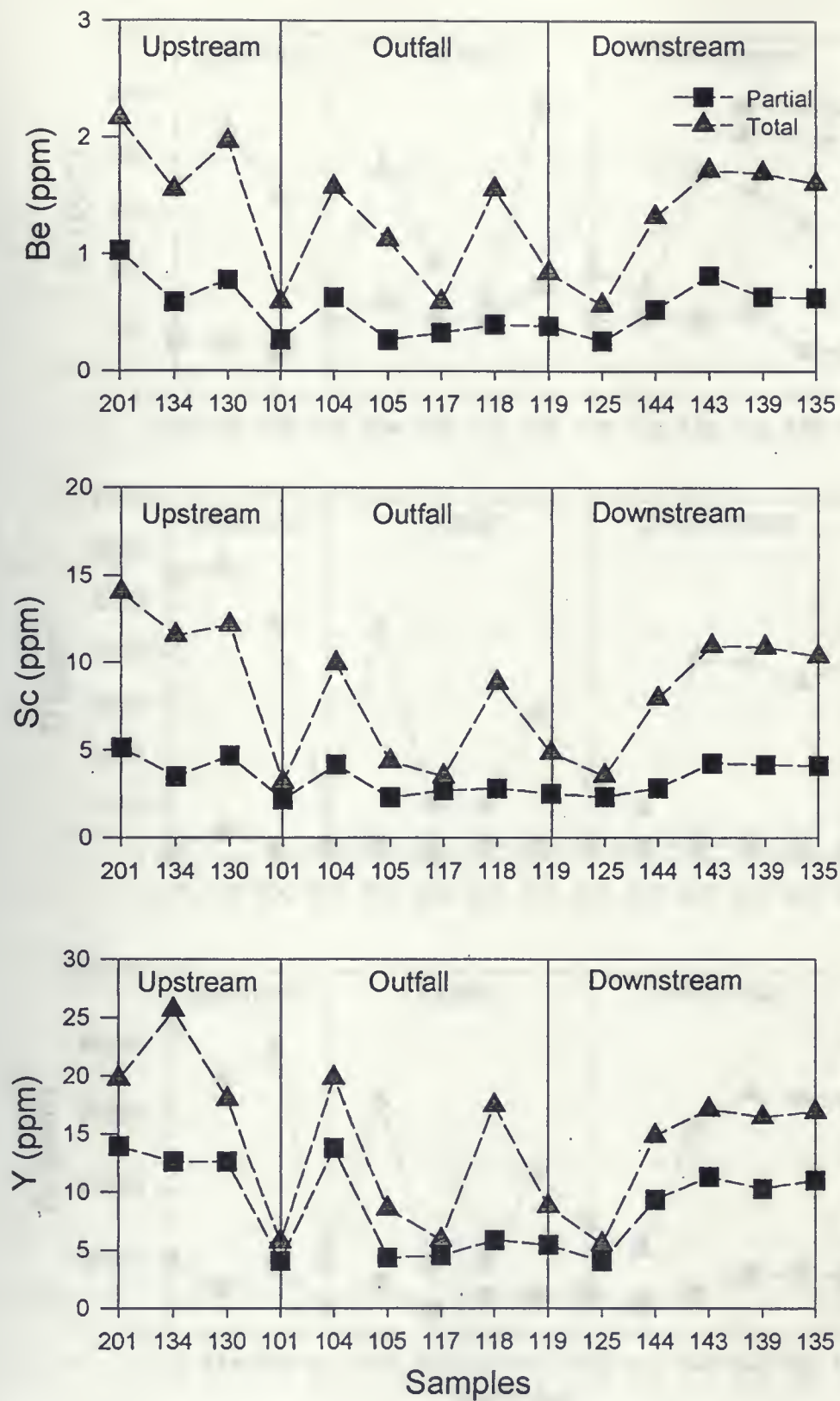


Figure 15a. Partial and total extraction comparisons for Group B.



Figure 1. Effect of temperature on the growth of *L. monocytogenes* and *L. casei* in Tryptone, Casein and Tryptone + Casein media.

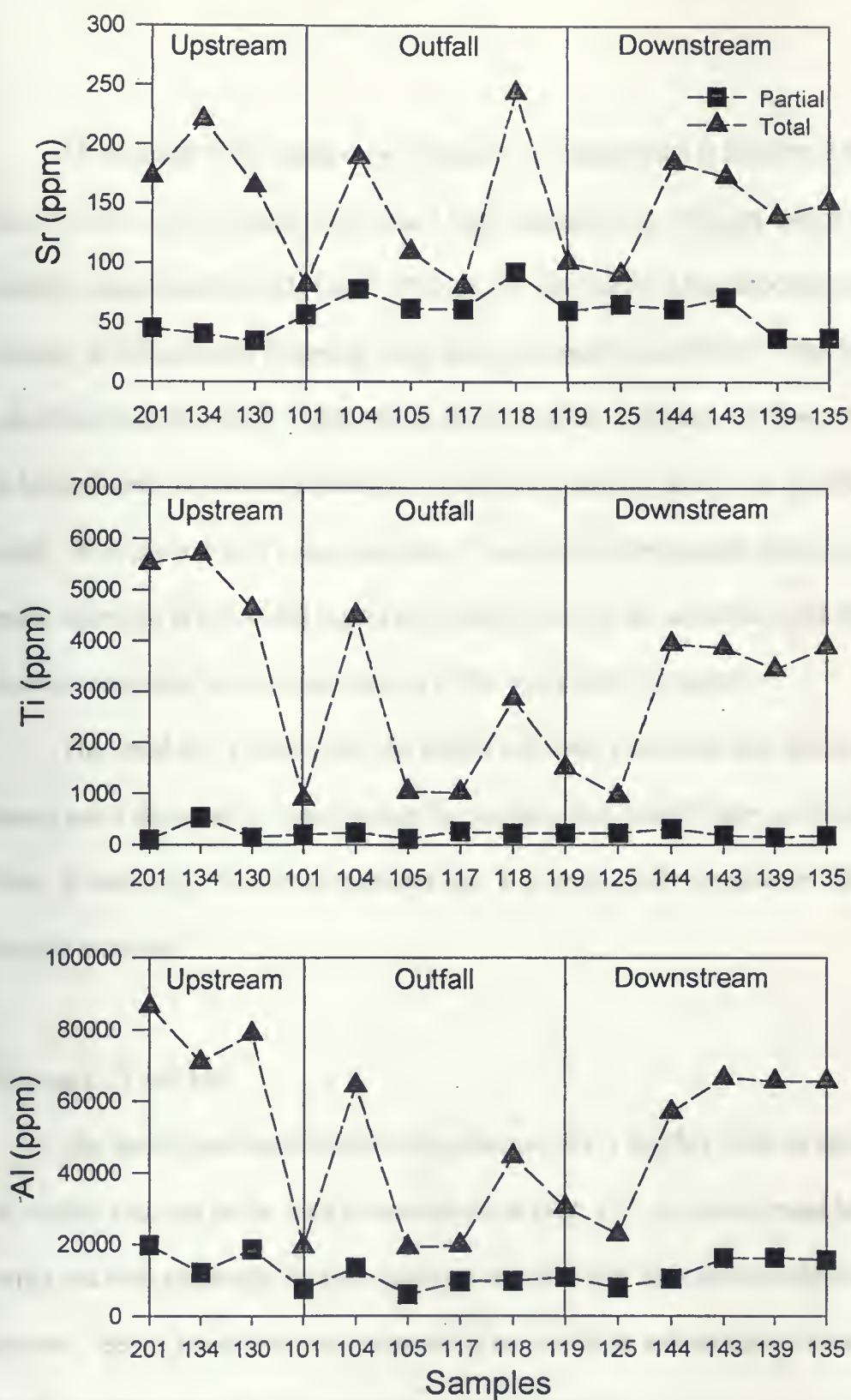


Figure 15b. Partial and total extraction comparisons for Group B.



Figure 1. pH (pH) and pH (pH) over time (days) for the three experiments.

All elements of this group show a decrease in concentration in samples at the outfall. These samples in the outfall area have a high concentration of heavy metals (Group A elements) suggesting that the Group B elements are derived from the carbonate and silicate structure of the minerals occurring there (compositionally controlled). This decrease in concentration in the outfall region and an increase in the upstream and downstream areas can be attributed to a dilution effect of mill scale anthropogenic sediments introduced at the outfall. With the influx of a large amount of water and anthropogenic particles, often the natural sediments in the outfall region are washed away by the turbulence and diluted with the newly deposited particles settling out of the water from the outfall.

The trend for Y show both the partial and total extraction data follow a similar pattern and a decrease in concentration for samples that usually show an enrichment of Group A elements. This trend indicates that Y is more easily extractable than the other Group B elements.

c) Group C: V and Mg.

The partial and total extraction concentrations for V and Mg show an enrichment in the outfall area and in the total extraction phase (Fig. 16). A similar trend between the partial and total extraction for both elements indicates that they are extractable with each digestion. Hence, these elements are probably derived from anthropogenic mineral phases and/or natural minerals (e.g. iron oxides and carbonates).

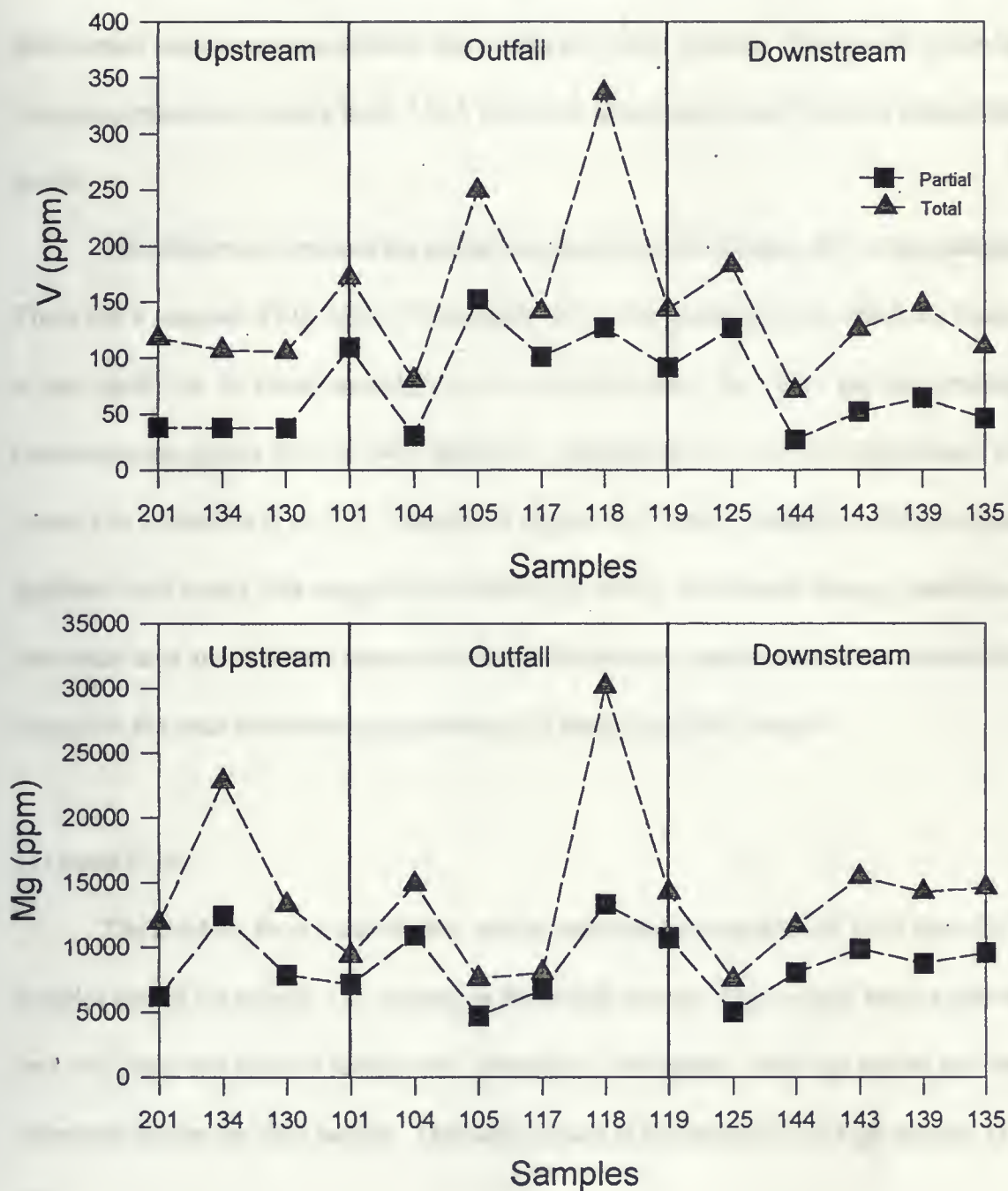


Figure 16. Partial and total extraction comparisons for Group C.



Figure 1: Effect of the concentration of the substance on the concentration of the substance over time.

d) Group D: Fe.

The background concentrations are relatively low and the iron levels in the downstream samples are considerably lower than the outfall samples. The outfall region has iron concentrations ranging from 3 to 5 orders of magnitude higher than the background levels.

The differences between the partial and total extraction results for Fe are complex. There are 4 samples, (101, 105, 117 (outfall), 125 (downstream)) all of which are located at the outfall or in close proximity to the outfall region, that have partial extraction concentrations greater than the total extraction concentrations. Fe is the only element that shows this behaviour (Fig. 17). Incomplete digestion of heavy minerals or anthropogenic particles (mill scale), like magnetite and hematite, which were found in large quantities at the outfall area are likely the reason the partial extraction concentrations are elevated with respect to the total extraction concentrations in these particular samples.

e) Group E: Ba.

The trend for Ba is relatively flat, with a concentration variation of 1000 ppm for all samples except for sample 125, located in the outfall region. This sample has a value two and half times the relative background chemistry (2500 ppm). Both the partial and total extraction follow the same pattern. This trend occurs in the anomalously high sample (Fig. 18).

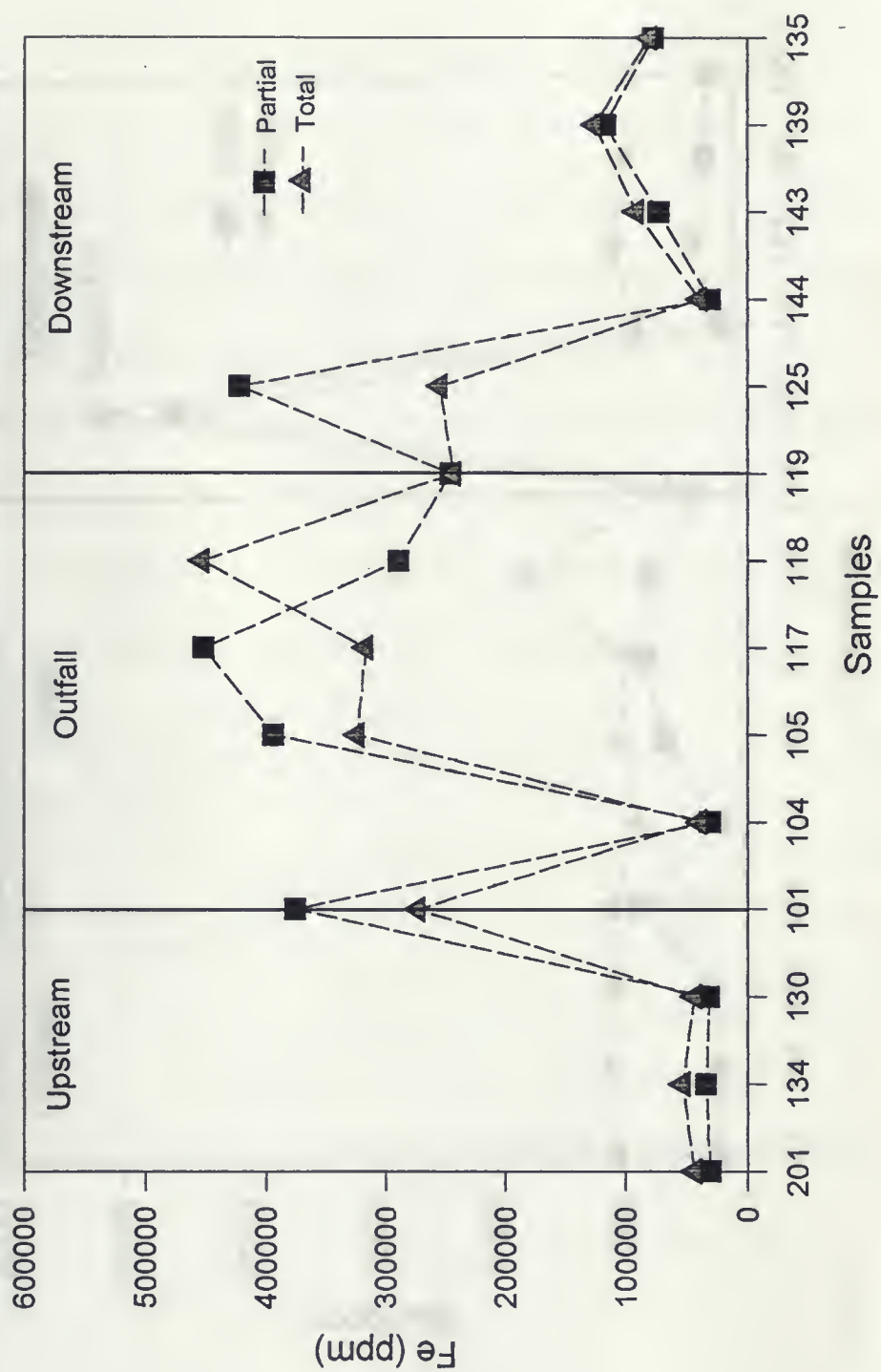


Figure 17. Partial and total extraction comparisons for Group D.

Figure 1. The effect of the concentration of the reagent on the reaction rate.



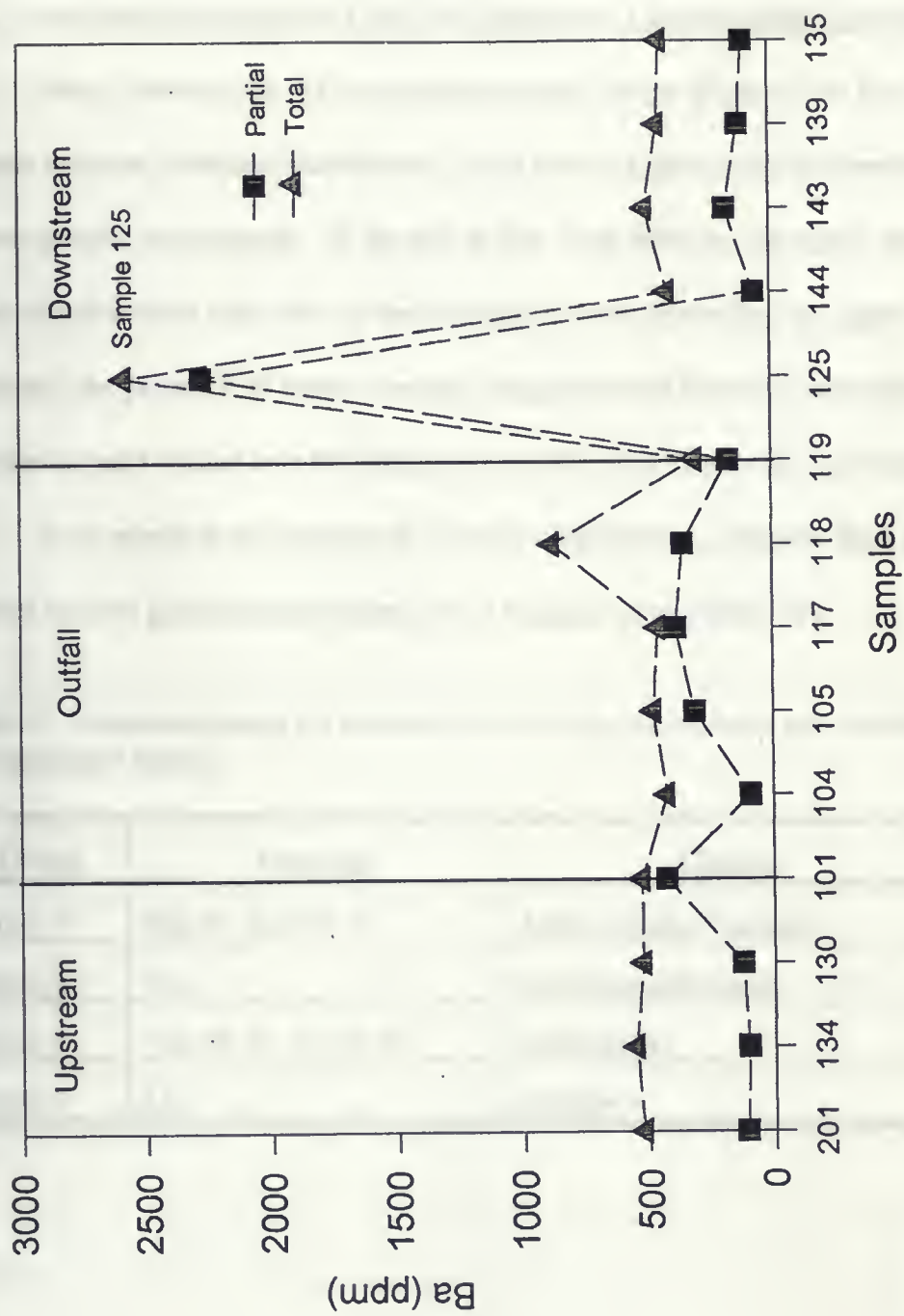


Figure 18. Partial and total extraction comparisons for Group E.

Figure 1. Effect of temperature on the rate of polymerization of styrene in the presence of Cu^{2+} and Cu^{+} ions.



3.2.3: Geochemical Analyses of Grain Size Separates - Concentration Comparison

Metal contents are not homogeneous over a range of grain size fractions. Finer grained fractions, containing mainly clays, often show a higher metal concentration than its coarse grained counterparts. In the silt to fine sand fraction, the metal concentrations generally decreased with size as the fraction is more dominated by quartz. In coarse fractions, the presence of heavy minerals (magnetite and hematite) may cause a further increase in metal content over the background geochemistry (Salomons and Forstner, 1984).

In the results of the grain size to chemistry correlations, generally there are 3 groups defined by their geochemical patterns across the grain sizes (Table 12).

Table 12: Elemental groups for grain size to chemistry correlations and controlling environmental factors.

Group	Elements	Control
Group 1	Co, Ni, Mn, Fe, V	Anthropogenic (metals)
Group 1b	Ba	Anthropogenic (oils)
Group 2	Mg, Sr, Ti, Al, Y, Sc	Lithological
Group 3	Cu	Unknown

Group 1: Co, Ni, Mn, Fe, V.

Group 1 is a suite of elements that exhibit no significant correlation with grain size (Fig. 19a,b). In typical sediments, the enrichment in concentration tends to be in the finest fraction. This occurs due to several physical, chemical and mechanical properties such as; large surface area on clay size sediments, cation exchange capacity, magnetic properties, surface charge and composition. This lack of the expected increasing concentration toward the fine grained sediment pattern is the function of the input of anthropogenic mill scale particles into the environment. With increased levels of heavy minerals (hematite and magnetite), often the grain size pattern appears flat, with the occasional peak or anomaly. For example, the peak that is consistent at grain size fraction D, occurs for Co, Ni, Mn and V. These anomalies represent field sample 101, which is located directly at the outfall. The Fe and Mn patterns show an increase in concentration at both A and F. That increase should normally be present at F due to physical and chemical partitioning. The presence of these heavy minerals suggests that source of Fe and Mn contamination or at least in part is derived from the particulate load. The majority of the Fe concentrations range from 1% to 15%, with the exception of three samples (125, 124 and 101). Sample 101 is located at the outfall, the remaining anomalies are located less than 100m downstream from the outfall. The concentrations of Fe in these samples ranges from 15% to 25%, therefore strengthens the argument that the iron is in the form of anthropogenic mill scale grains and is derived from the steel-making industry.

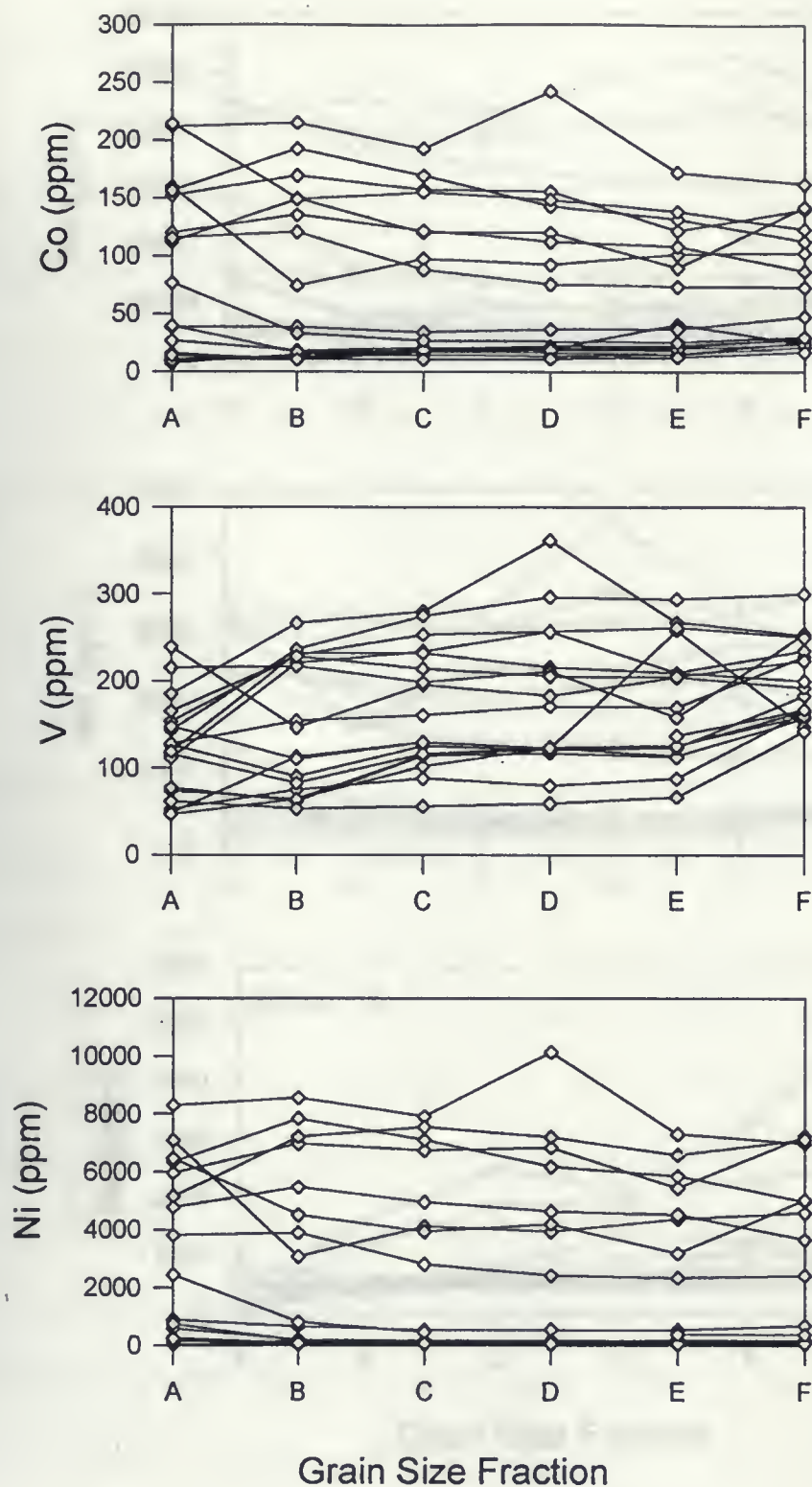


Figure 19a: Grain size to chemistry correlation comparisons for Group 1 and 1B.
 A=63-44, B=44-33, C=33-23, D=23-15, E=15-11, F=<11.

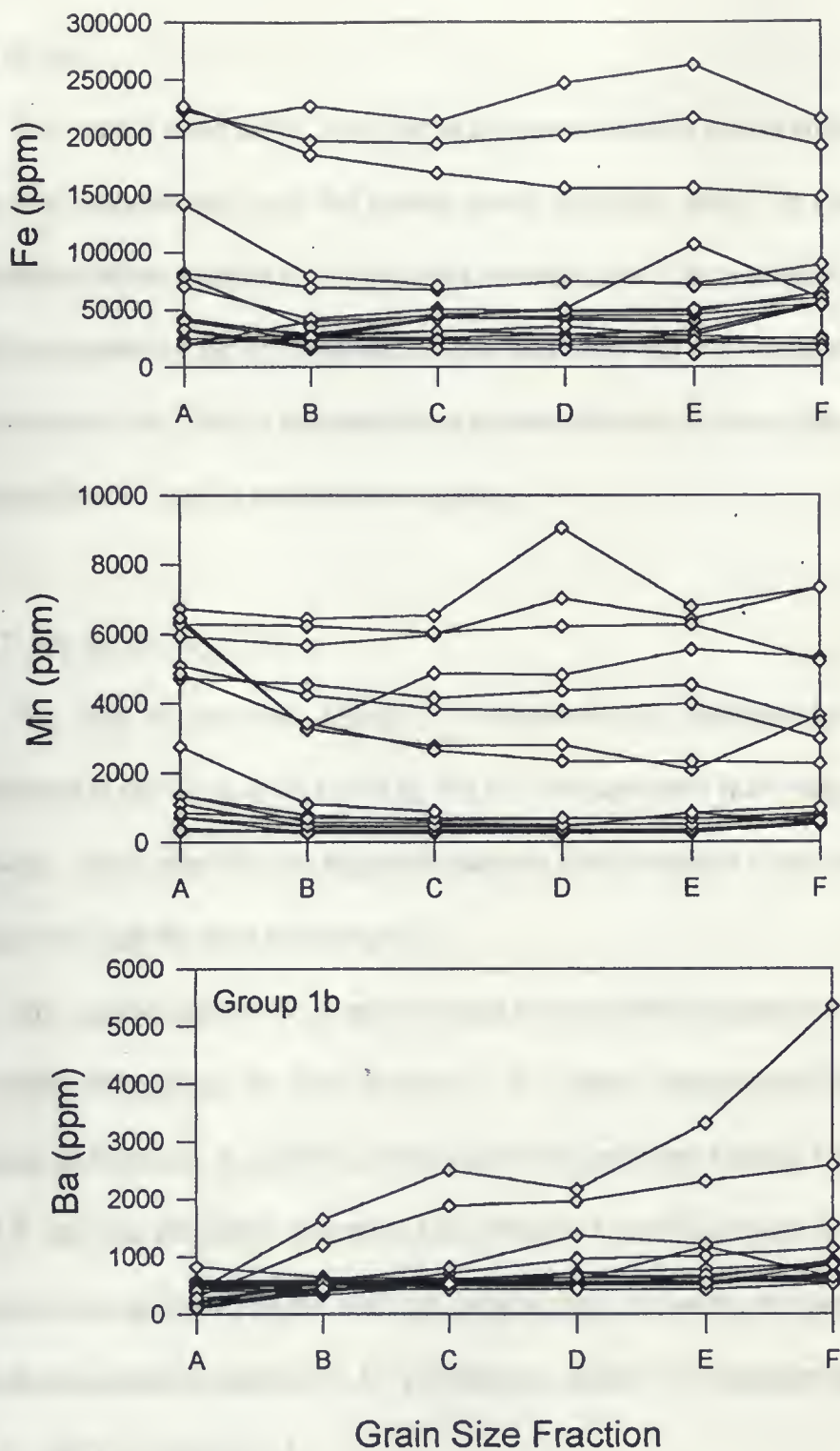


Figure 19b: Grain size to chemistry correlation comparisons for Group 1 and 1B.
 A=63-44, B=44-33, C=33-23, D=23-15, E=15-11, F=<11.

Group 1b: Ba.

The overall trend of Ba is similar to the other elements in this group, in that they have a low concentration and flat pattern across the grain sizes. In contrast, the Ba concentrations of two samples (125, 124) are extremely high. These particular samples are located approximately 100 m downstream from the outfall and were observed to contain a large quantity of oil. The Ba concentrations are only elevated in these individual samples implies that the Ba may be attributed to the oils.

Group 2: Mg, Sr, Ti, Al, Y, Sc.

The suite of elements (Group 2) demonstrates the relationship of increasing concentration to the finest grain size (Fig. 20a,b). The parameter that controls this pattern is lithology. These elements are major components in the minerals of the carbonate-shale basement rock and the soils in the region.

The concentrations of Sr, Y and Ti appear to be variable in grain size fraction A and less variable throughout the finer fractions. Al content demonstrates this variability throughout all fractions. A positive anomaly occurs in grain size fraction E for Mg, Sc, Ti, Sr and Y and was identified as sample 132, which is located upstream from the outfall, although in close proximity to the Welland Canal siphon. However, this particular sample also produces a negative anomaly in Al. Furthermore, sample 115 demonstrates high values for Ti, Sr and Y in grain size A.

The patterns produced by Al and Ti suggest that the concentrations of these elements may be attributed to clay minerals such as illite. Since Sr levels are greatest in the coarse

fraction it is likely derived from the carbonate minerals. Furthermore, Mg values are consistent across the grain size range also supports the X-ray patterns identification of detrital dolomite in the samples. Sc and Y produce a trend expected of background elements (not influenced by metal contamination). The concentrations of these elements are directly related to the silicate and/or carbonate bond structure. Finally, Sc and Y concentration variability between samples is not significant in terms of analytical uncertainty due to the low concentrations approaching the method detection limit. However, they were included in this group because they produce a consistent pattern similar to the other elements in this group.

Group 3: Cu.

Cu was placed into a group by itself due to the strong correlation between grain size and chemistry (Fig. 21). The pattern shows a steady increase in copper content up to grain size E and then a slight decrease at grain size F. This trend is perhaps explained that industrial Cu is of grain size range E (11-15 μ m). The trend is similar to group 2, with the exception of the decrease in Cu concentration at grain size fraction F. In contrast to the partial and total extraction data, Cu behaved similarly to Co, Ni, Zn, Cr and Mn. Group 3 demonstrates the same anomalies, sample 101 at grain size D, sample 132 at grain size E, in Groups 1 and 2 respectively. In addition, sample 119 has a high Cu value (4000 ppm), a factor of 4 above background levels, at grain size E.

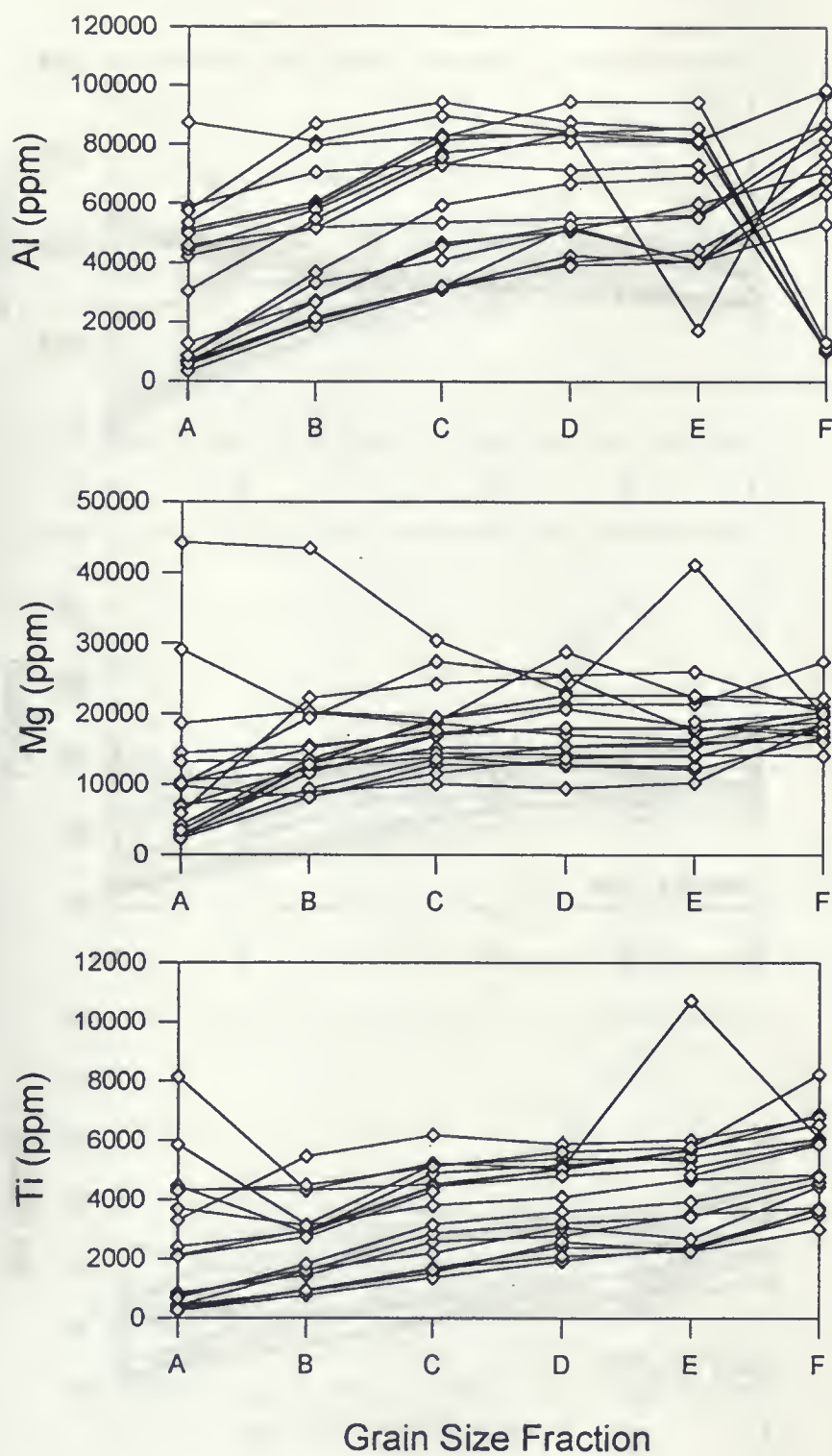


Figure 20a. Grain size to chemistry correlation comparisons for Group 2.
Grain sizes as in Figure 19.

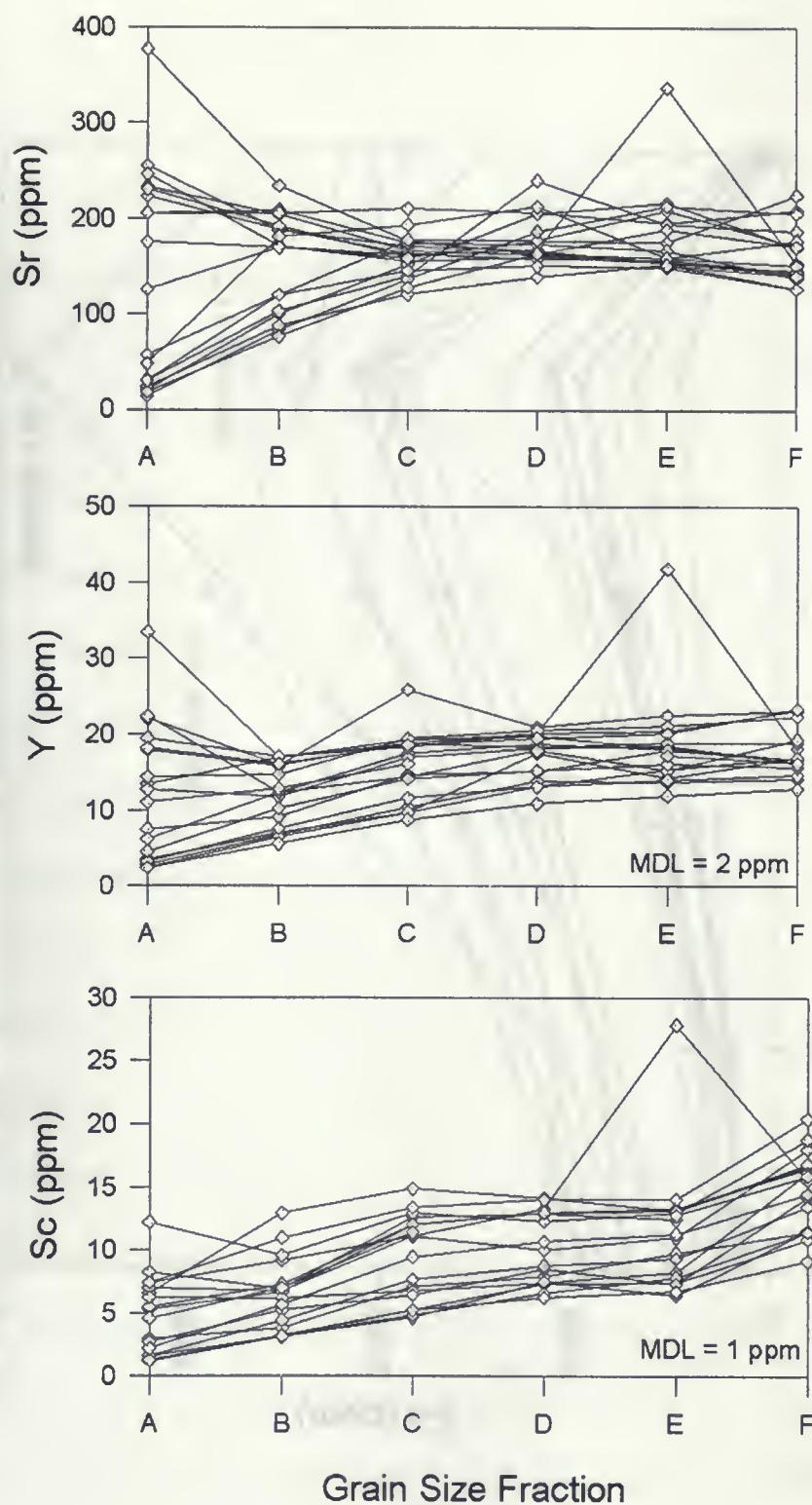


Figure 20b. Grain size to chemistry correlation comparisons for Group 2. Grain sizes as in Figure 19.

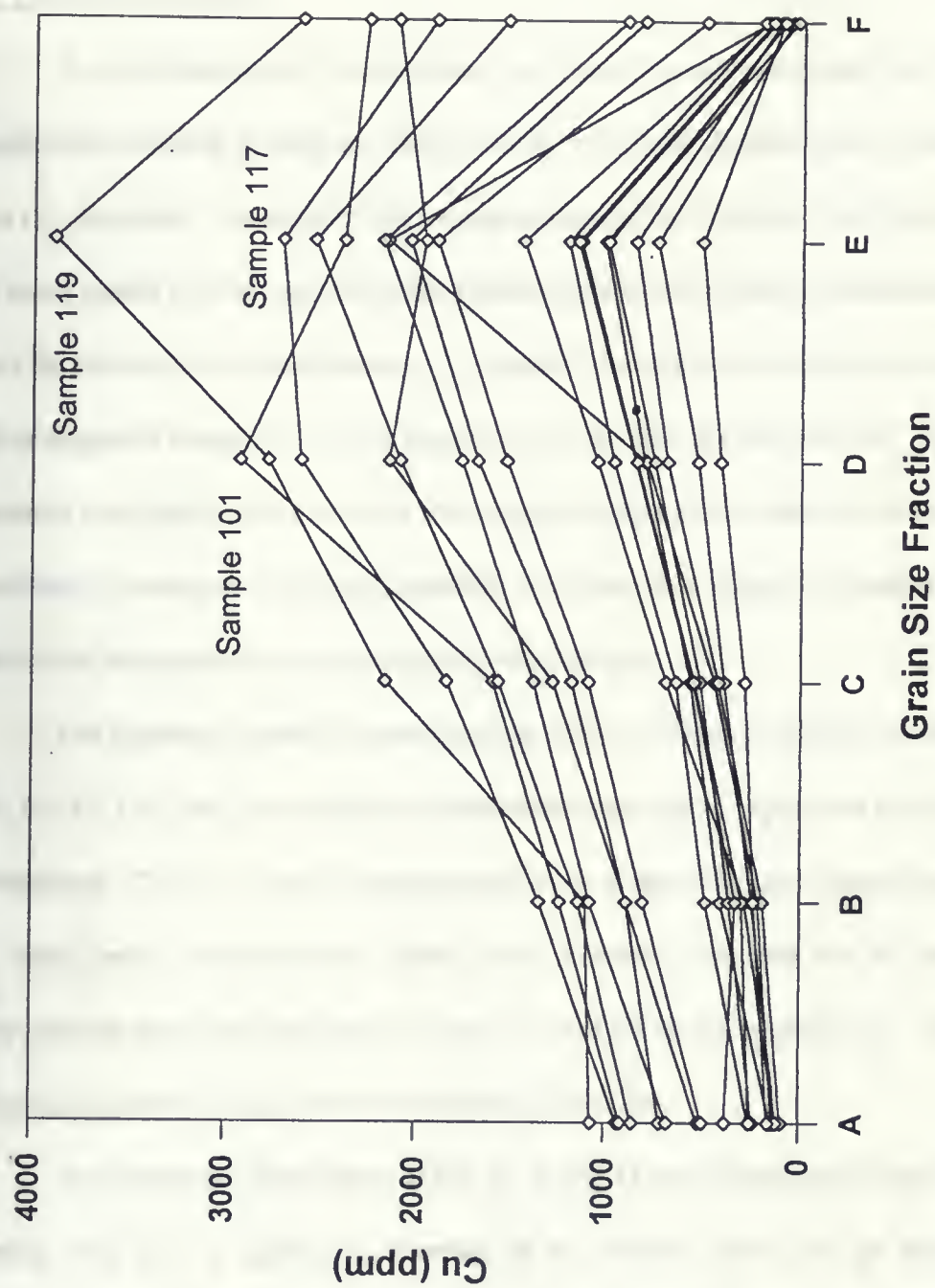


Figure 21. Grain size to chemistry correlation comparisons for Group 3. Grain sizes as in Figure 19.

3.3: Dispersion Patterns

River sediments are deposited and resuspended by erosion depending on the river morphology (scouring of banks and deposition on point bars), flooding and influences from man (ie. dredging). As particles are transported along the river bed, they bring with them the heavy metals that are comprise in the sediment in the form of heavy minerals or that they carry by chemically bound processes. Eventually, the sediment will settle out of solution and be deposited elsewhere. This is especially true for fine-grained material. The location at which it is finally deposited may have a greater impact than where it originated from. Therefore, assessment of the contamination levels and their dispersion pattern are crucial in terms of resuspension and consequently redeposition.

The dispersion patterns demonstrated in Figure 22 clearly indicate the heavy metals (Cu, Co, Ni, Cr, V and Zn) are highly concentrated in the outfall region and decrease further downstream. Cu, Co, V and Zn contamination levels at the outfall are approximately greater by three orders of magnitude. Metal contamination is greatest for Ni and Cr with concentration levels ranging from 0.5% to 1.5% and 1% to 3% respectively. The relative dispersion pattern between these two elements is similar.

The elemental contribution of Be, Sc, Y, Sr, Ti and Al exhibits a relatively similar pattern (Fig. 23); a significant decrease at the outfall region for all analytes. The concentration differences between upstream, outfall and downstream and are greatest for Ti and Al. The upstream distribution represents background concentrations of typical river sediment of this mineralogical composition (Chapman and Putnam, 1984). The downstream

patterns for Be, Sc and Al return to the usual pattern. The downstream distribution for Y, Sr and Ti appears erratic. This overall distribution is inverse with respect to the pattern observed by the heavy metals in Figure 22. The decrease in concentration at the outfall in Figure 23 is attributed to a dilution of the naturally occurring sediments.

The dispersion pattern in Figure 24 are individually unique. Ba concentrations remain relatively flat and consistent throughout the river, with the exception of 3 samples that have high values. It is probable that the Ba is related to the oils observed in the river. The Mg pattern is similar to that of Figure 23, with the exception of some of the downstream samples show some depletion of Mg; suggesting a possible mixed anthropogenic (steel) and background (carbonates) source for Mg. Finally, the dispersion patterns for Fe and Mn are similar, however vary dramatically in concentration. The apparently high Fe levels observed at the outfall coincide directly with the metal filings found in the sediment and subsequently identified with XRD as magnetite, hematite and wuestite. Both the Fe and Mn can be attributed to an anthropogenic source.

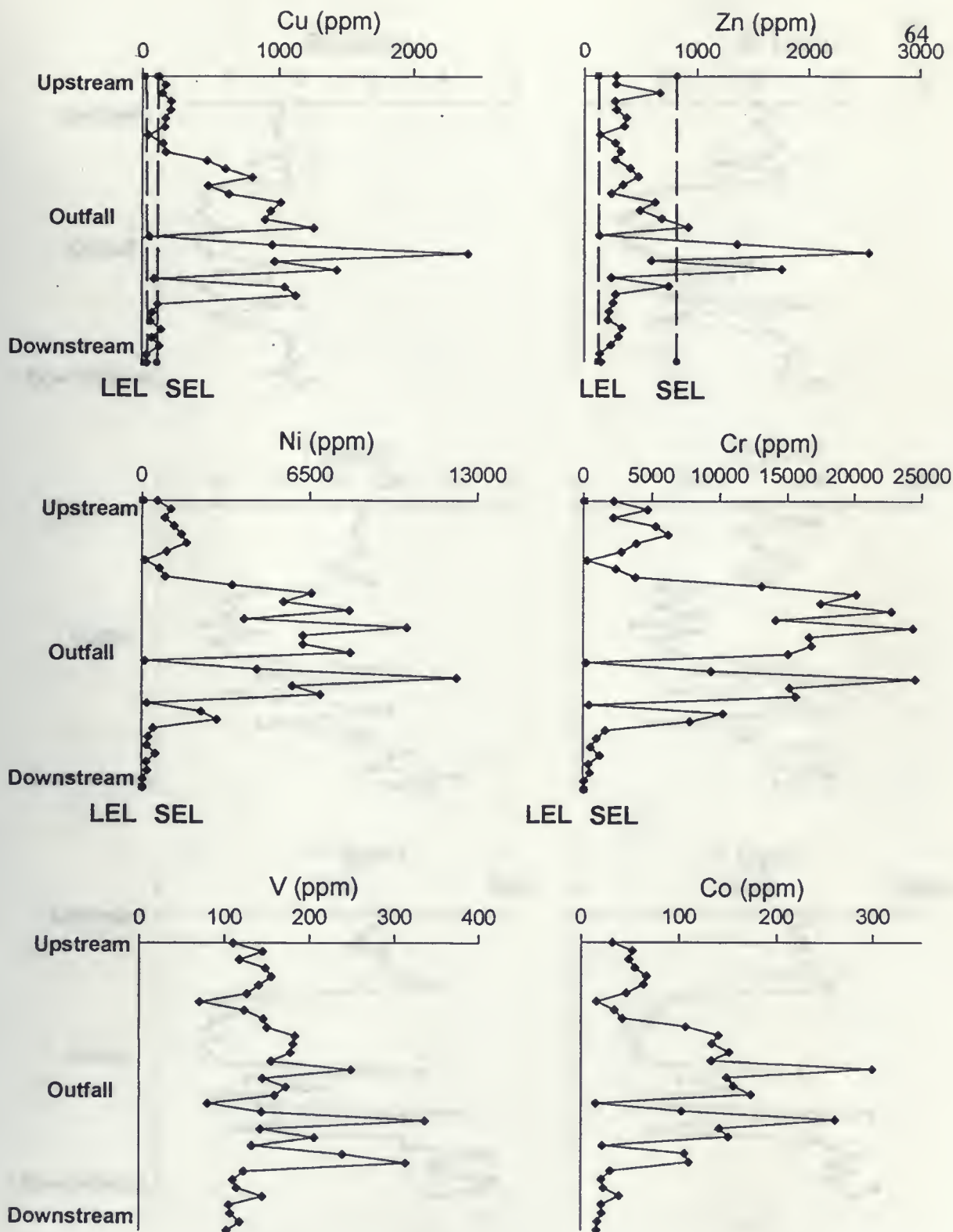


Figure 22. Dispersion patterns for total metal concentrations of Cu, Zn, Ni, Cr, V, and Co. Heavy metals are highly concentrated at the outfall region. LEL = Lowest Effect Level, SEL = Severe Effect Level (MOEE, 1995).

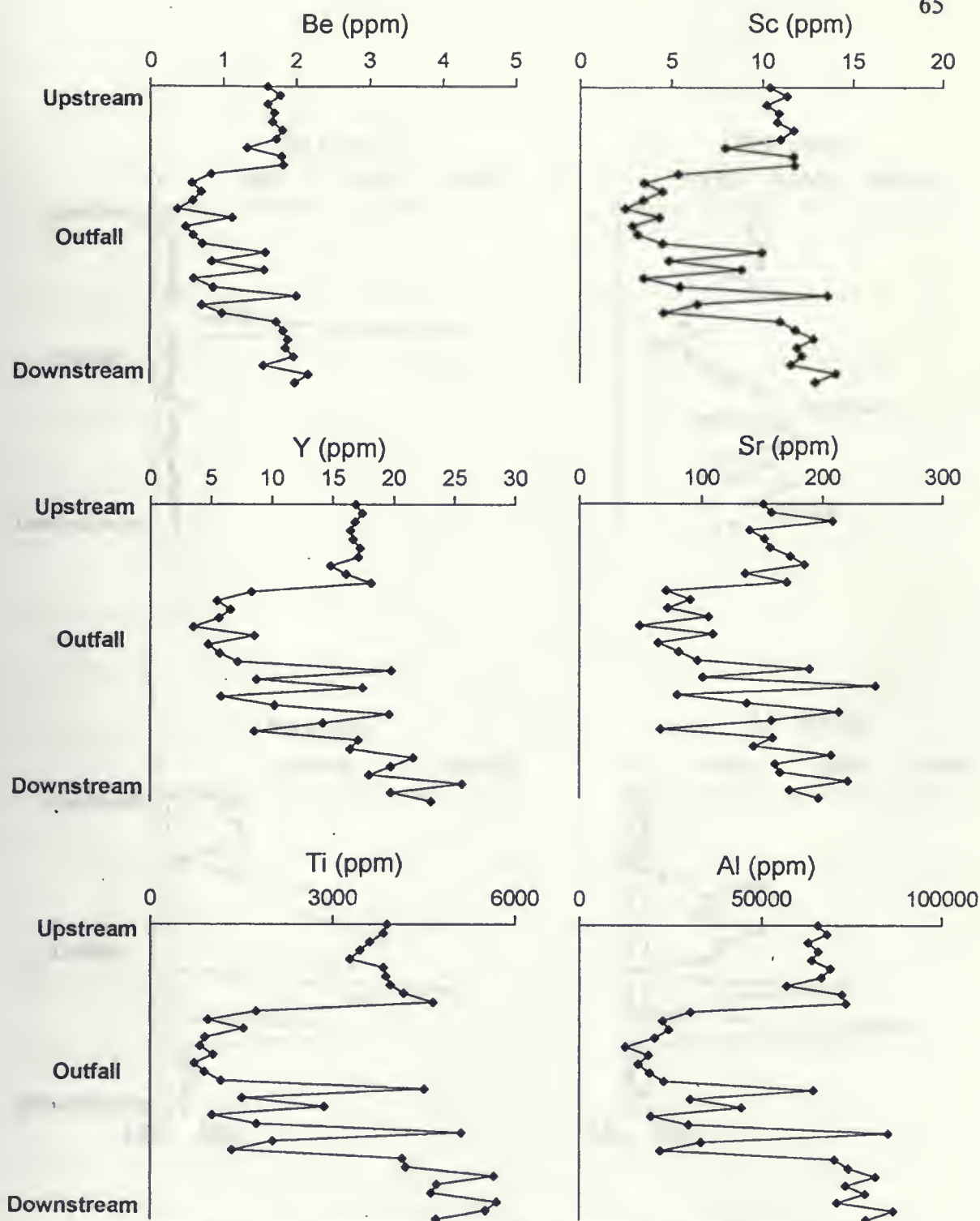


Figure 23. Dispersion patterns for Be, Sc, Y, Sr, Ti, and Al. Metal concentrations show a significant decrease at the outfall area. This decrease clearly shows the dilution effect by mill scale and other anthropogenic materials on river sediment composition.

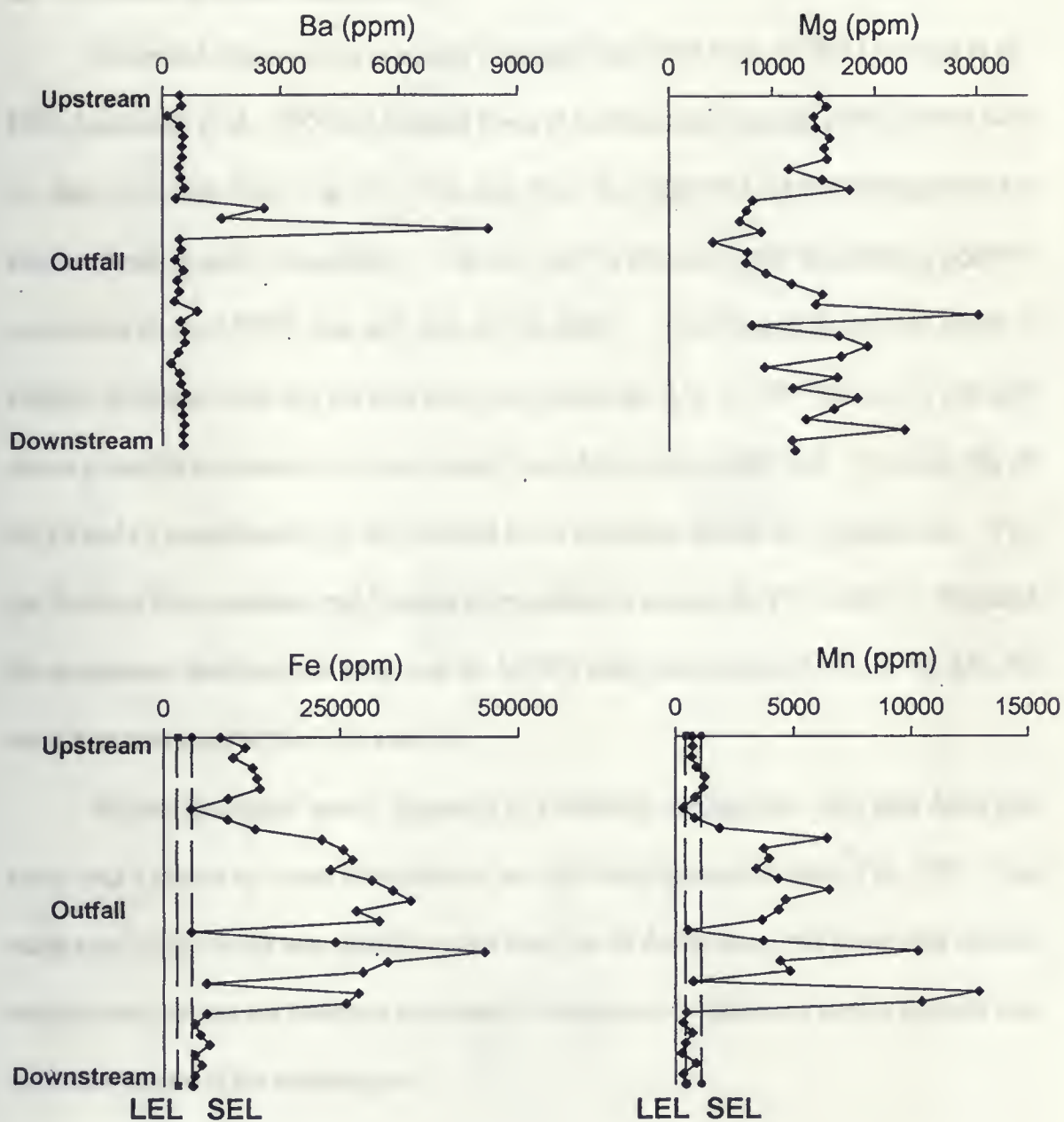


Figure 24. Dispersion patterns for Ba, Mg, Fe, and Mn. Each distribution is unique in that a different source attributes to the pattern.

LEL = Lowest Effect Level, SEL = Severe Effect Level (MOEE, 1995).

3.4: Discussion of Data Comparisons

Elemental comparisons in scatter diagrams have data from MOEE (Persaud et al., 1993, Jaagumagi et al., 1995) and Niagara River (Mudroch and Duncan, 1986) plotted with the data from this study (Fig. 25). The data from this study and the MOEE study have a similar trend in each comparison. The Cu and Ni chemical plot illustrates a positive correlation in the MOEE data and data of this study. The Niagara River data shows a slightly different trend and the data does not exceed the SEL for Ni. The Fe vs. Mn plot shows a positive correlation with increasing Fe and Mn in the outfall area. The majority of the Zn and Cr concentrations of the Welland River are higher than that of the Niagara River. Yet, the Welland River sediment and Niagara River sediment exceed the PSQG for Cr. Welland River sediment data from this study and the MOEE study have levels of Ni, Cu, Fe, Mn, Zn and Cr exceed the PSQG's LEL and SEL.

Figure 26 depicts scatter diagrams of elemental comparisons with data from this study and a report by Acres International Inc. for Atlas Speciality Steels Co., 1991. The study area for this thesis was slightly smaller than that of Acres study, but the results of both studies conclude that the sediment was heavily contaminated with heavy metals and oils and was recommended for remediation.

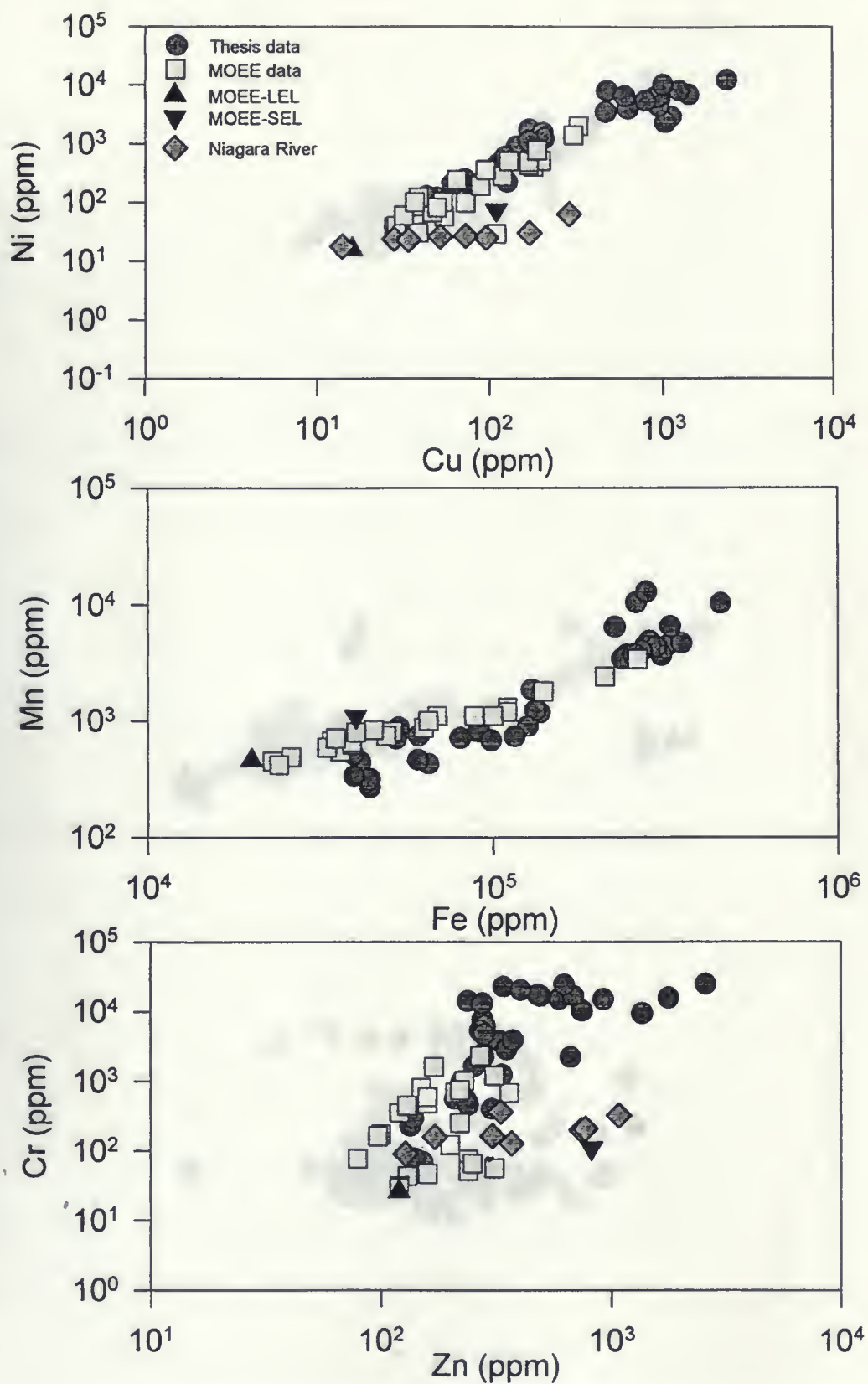


Figure 25. Scatter diagrams of geochemistry of the Welland River data produced from this study, Welland River data produced by MOEE, 1995, MOEE PSQG, 1993 and Niagara River data (Mudroch and Duncan, 1986).



Figure 1. Scatter plots showing the relationship between Time (min) and Distance (km) for three different groups: 10 min, 20 min, and 30 min. The plots show a clear negative correlation between Time and Distance for all three groups.

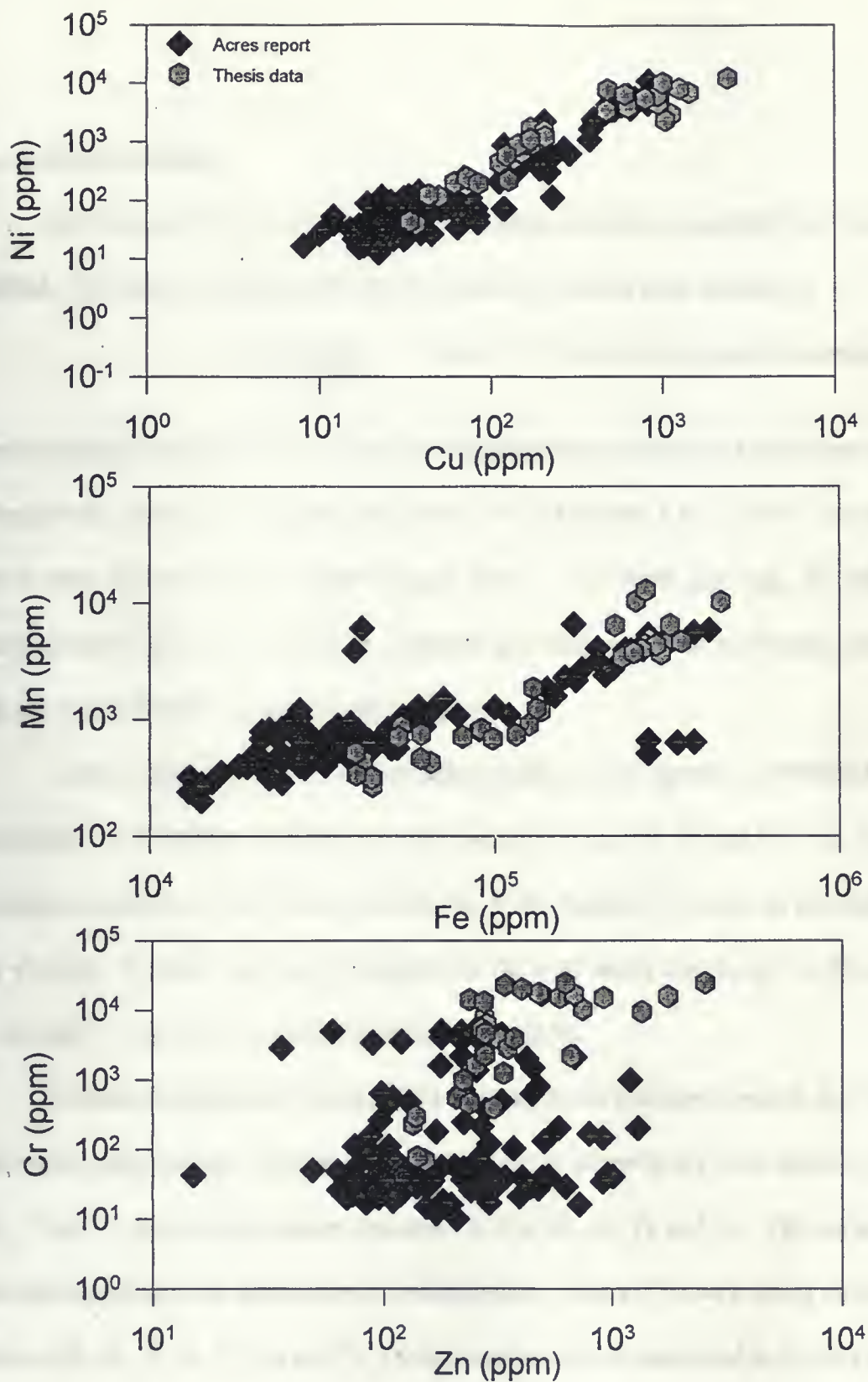


Figure 26. Scatter diagrams of geochemistry of the Welland River sediments. Data produced from this study and Welland River dredging demonstration environmental workshop (report by Acres, 1991).

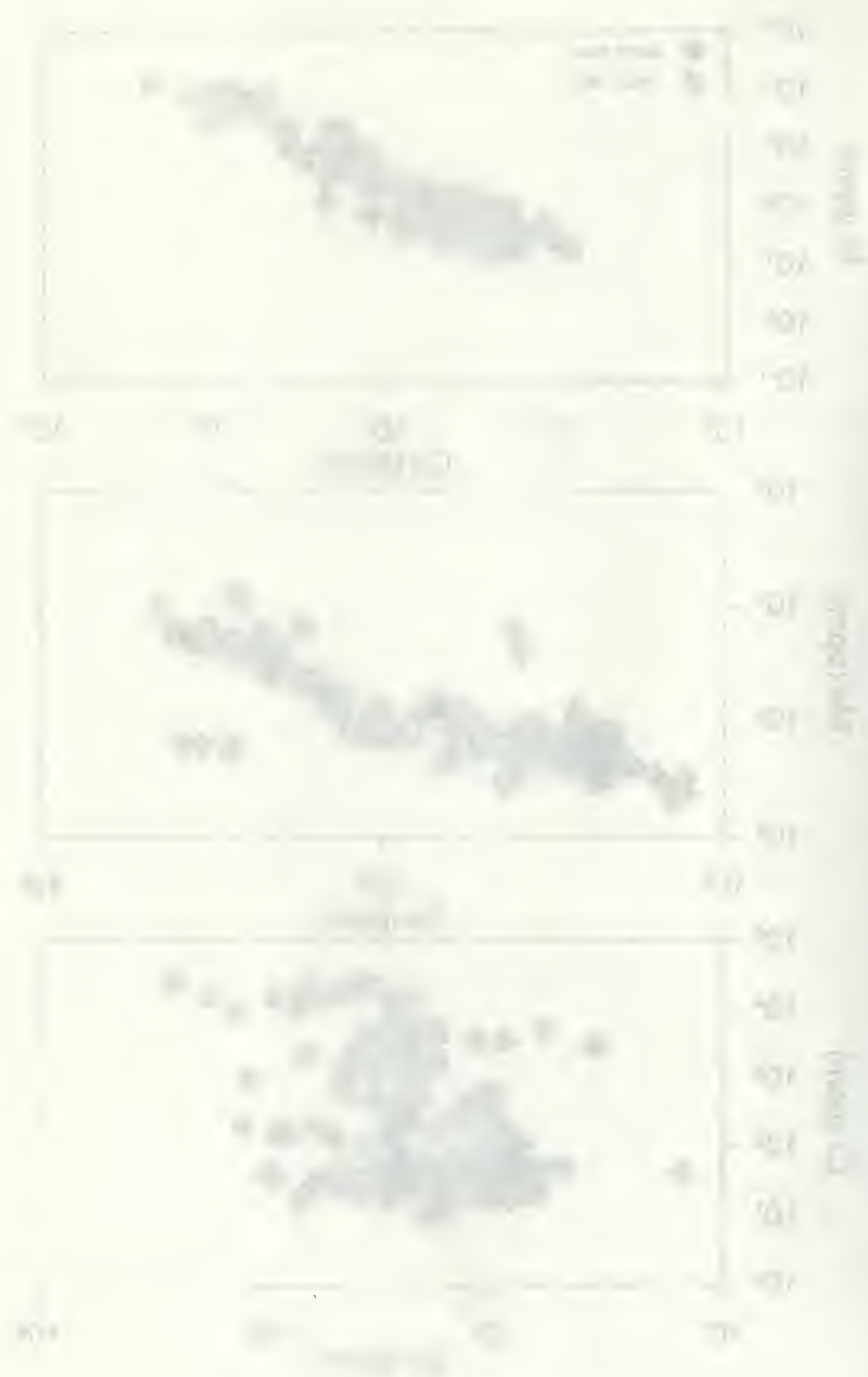


Figure 1. Relationship between age and blood pressure, heart rate, and cholesterol levels. (a) Blood pressure (mmHg) vs. age (years). (b) Heart rate (b/min) vs. age (years). (c) Cholesterol (mg/dL) vs. age (years). The legend indicates two groups: Normal (open circles) and Hypertensive (filled circles).

3.5: Statistical Analysis

Statistical analysis was performed on elements derived through the total digestion method. The data was standardized by the following formula prior to analysis.

$$Z = \frac{(X_i - \bar{X})}{STD}, \quad \text{where } X_i \text{ is the actual measured concentration}$$

Standardizing the data, makes each observation independent of units and significance orders of magnitude (unitless) of the same unit (Davis, 1973, Marriott, F.H.C., 1974). In order to assess data that have concentration ranges from 1 to 100000 ppm (eg., Sc and Fe), standardization allows the data to be compared as similar units and to compare variables that are very different (e.g. apples and oranges).

Table 13 reports a matrix of correlation coefficient for variables of Welland River sediments. An excellent correlation exists among Co, Cu, Ni, Fe and Cr. An inverse excellent correlation is present between Be, Sc, Y, Sr, Al and Ti. Ba has no correlation to any element. A weak correlation is apparent in Zn to all heavy metals, but not Be, Sc, Y, Sr, Al and Ti. Mg shows a good correlation to Y and Sr.

Varimax rotated factor analysis of the Welland River sediments records four factors that explain geochemical variation between loadings of elements for these samples (Table 14). Factor 1 shows a correlation between Co, Cu, Ni, Zn, Fe and Cr. This reflects the elements associated with anthropogenic contamination. Factor 2 shows a strong correlation between Be, Sc, Y, Sr, Al, Mg and Ti. These elements are with associated to the background geochemistry of the sediment. The close, high loadings among the elements accounts for

a distribution of elements typical of sediment composition. The third factor shows a strong correlation between V and Mn and accounts for 15% of the variation. These elemental levels are contributed from both background and contaminate chemistries. Subsequently, these 3 factors also support the correlation found in the Pearson correlation matrix and account for 85% of the total variation.

The correlation matrix and factor analysis further support the observations and results presented earlier in this chapter. The heavy metals (Co, Cu, Ni, Fe, Mn and Cr) exhibit strong correlations among each other and an inverse correlation to the background elements (Be, Sc, Y, Sr, Al, Mg and Ti).

Table 13: Correlation Coefficient Matrix among Chemical Analyses for Welland River Sediments

	Be	Co	Cu	Ni	Sc	V	Y	Zn	Sr	Al	Ba	Fe	Mg	Mn	Ti	Cr
Be	1															
Co	-0.67	1														
Cu	-0.603	0.859	1													
Ni	-0.674	0.969	0.87	1												
Sc	0.979	-0.752	-0.649	-0.745	1											
V	-0.391	0.76	0.827	0.7	-0.461	1										
Y	0.911	-0.693	-0.549	-0.69	0.944	-0.39	1									
Zn	-0.276	0.635	0.851	0.694	-0.312	0.618	-0.218	1								
Sr	0.782	-0.469	-0.311	-0.431	0.805	-0.236	0.898	0.072	1							
Al	0.966	-0.809	-0.714	-0.491	0.992	-0.549	0.93	-0.372	0.789	1						
Ba	-0.288	0.215	0.034	0.336	-0.278	0.12	-0.29	-0.03	-0.155	-0.258	1					
Fe	-0.785	0.928	0.919	0.915	-0.822	0.764	-0.766	0.664	-0.562	-0.875	0.152	1				
Mg	0.575	-0.21	0.069	-0.16	0.605	0.099	0.718	0.417	0.829	0.558	-0.185	-0.217	1			
Mn	-0.618	0.713	0.82	0.639	-0.632	0.866	-0.513	0.538	-0.368	-0.697	0.042	0.81	-0.06	1		
Ti	0.928	-0.799	-0.683	-0.781	0.964	-0.541	0.957	-0.362	0.825	0.974	-0.272	-0.864	0.597	-0.656	1	
Cr	-0.778	0.95	0.8	0.963	-0.827	0.685	-0.787	0.559	-0.564	-0.865	0.413	0.925	-0.311	0.675	-0.862	1

NUMBER OF OBSERVATIONS: 35

Table 14 : Varimax Rotated Factor Matrix of Welland River Sediments

Element	Factor 1	Factor 2	Factor 3	Communality
Be	-	0.815	-	1.000
Co	0.793	-	-	1.000
Cu	0.823	-	-	1.000
Ni	0.856	-	-	1.000
Sc	-	0.830	-	1.000
V	-	-	0.803	0.975
Y	-	0.906	-	0.992
Zn	0.879	-	-	0.953
Sr	-	0.948	-	0.95
Al	-	0.791	-	1.000
Ba	-	-	-	0.879
Fe	0.731	-	-	0.995
Mg	-	0.892	-	0.941
Mn	-	-	0.809	0.954
Ti	-	0.818	-	0.991
Cr	0.718	-	-	0.995

Factor	% Variance	Eigenvalue	Diagnosis
1	32.57	10.567	Elements associated with contamination
2	38.31	2.915	Elements associated to background chemistry
3	14.55	0.534	Elemental levels contributed from both background and contaminate chemistries.

Chapter 4: Summary and Conclusions

The investigation of a site of the Welland River was initiated to describe chemical dispersion patterns in close proximity to the outfall region as compared to samples obtained upstream from the industrialized zone.

The results of this study can be used as a template in terms of analytical method development and modification. Numerous analytical techniques, typically used on soils, sediments, and rocks were applied. Some were found to work well, while other techniques did not. Generally, the typical sample pretreatment and separation techniques for sediments worked well. Good laboratory practices were used to ensure integrity of the samples prior to chemical analysis. In contrast, the usual extraction and digestion techniques did not work well. Due to the complex nature of the samples, much research, development, and modification had to be employed in order to ensure the most accurate and precise data possible. The amount of iron oxide minerals found in the samples, those in particular, found at the outfall, were responsible for difficulty in dissolving the sediment.

The mineralogy of the Welland River sediments contains expected background minerals (calcite, dolomite, quartz and clays). These mineral phases are directly related to the background carbonate-shale basement and the glacial clay plains found in the Niagara Peninsula. Others minerals that cannot be attributed to the local geology (eg. mullite and ferrocolumbite), are likely associated with the industrial companies in Welland.

Normalization of total digestion data exhibits clear evidence of heavy metal contamination in comparison to the average control samples obtained upstream from the effected area. Comparison of the results to average continental crust (Taylor and McLellan,

1985) also suggests heavy metals are elevated in the study area. Chemical analyses of the sediments were compared to the Provincial Sediment Quality Guidelines (PSQG) devised by the Ontario Ministry of Environment and Energy (MOEE), since the MOEE has been involved with Atlas Specialty Steels to eliminate or minimize the impact in Welland. These results concluded that metal concentrations (Cu, Ni, Zn, Fe, Mn and Cr) are in excess of the PSQG severe effect level (SEL) at the outfall region. In addition, samples upstream and downstream from the outfall region contain metal concentrations exceeding the PSQG lowest effect level (LEL).

Partial and total extraction results were divided into 5 groups based on their chemical distribution, elemental behaviour and true analytical differences. The patterns observed in the partial extraction data tends to dependant upon the extractability of the element or phase that binds the analyte. This in turn, determines the ease of availability of metals into the surrounding environment and, therefore, its impact on the organisms that depend on that environment. The majority of analytes were lower in concentration in the partial extraction relative to the total digestion results, with the exception of iron. This suggests that most of the elements have an acid extractable phase. Therefore, these trace elements are bound in exchangeable, carbonate, oxide, or organic phases. The total extraction values are generally higher than the partial extraction concentrations, suggesting that the acid attack use in takes most analytes bound to exchangeable, organic, carbonate, oxide and silicate phases. However, it was observed that the partial extraction concentrations were greater than the total extraction concentrations for iron for four samples located at the outfall region. It is suggested that incomplete digestion of heavy minerals or anthropogenic particles (magnetite

and hematite) resulted in this abnormal behaviour between partial and total extraction for iron.

Geochemical analyses of six grain size separates were divided into 3 categories based on their geochemical patterns of grain size separates from fine sand ($63\mu\text{m}$) to clay ($4\mu\text{m}$). The correlation observed for group 1 elements were identified as a function of an anthropogenic input in to the system. Group 2 elements demonstrate an increasing concentration to the finest grain size suggesting this trend is directly related to the silicate and/or carbonate mineralogy. Finally, Cu was designated to its own group due to the strong correlation between grain size and chemistry. According to several researchers observations (Salomons and Forstner, 1984, and Forstner, 1982), the fine grained material should possess the highest concentrations of metals. In contrast, the pattern observed in copper is slightly different than expected. The concentrations increase toward the finer grained material, before decreasing significantly at the finest grain size. It is unknown what controls this result.

The dispersion patterns are demonstrated largely by two distinct categories 1) the heavy metals (Co, Cu, Ni, Zn, V and Cr) and 2) the background elements (Be, Sc, Y, Sr, Al and Ti). The heavy metals show a significant increase at the outfall region and decrease further downstream. Ni and Cr levels are extremely high at the outfall. Elemental concentrations of background elements exhibit a marked decrease at the outfall, then returning to higher levels downstream. This negative anomaly observed in these elements at the outfall is attributed to a dilution effect of the natural sediment and subsequent concentration of mill scale sediment. Generally it would be expected that consistent

environmental conditions would exist locally. However, it was recognized that "hotspots" or "non-hotspots" occur in the river. Sample 104 is located at the outfall region, adjacent to samples that were highly contaminated with heavy metals, yet the chemistry of this particular samples resembles that of the controls samples.

Multivariant statistical analysis and correlation coefficient matrix results concluded that the heavy metals (Co, Cu, Ni, Zn, Fe, Mn and Cr) correlate strongly. Accordingly, the background elements (Be, Sc, Y, Sr, Al and Ti) show an inversely strong correlation. Occasionally, an element would behave slightly different between various kinds of statistical correlations (e.g. Zn weakly correlated with the heavy metals).

Based on visual and mineralogical observations of the sediment, it is apparent that the majority of the heavy metal contamination is in a detrital form. This is further supported by the lack of precipitation type mineral (e.g. goethite).

In conclusion, this study has shown that the outfall region and areas further downstream are highly contaminated with respect to heavy metals from the industrialized zone. Typically, fine-grained sediments are of great concern, because of their capacity to uptake and disperse contaminants, consequently moving them to areas of undesired impact. However, in this particular case it appears, the majority of the heavy metals are localized at the outfall region and slightly downstream. At some distance downstream, the heavy metals return to lower background levels. Accordingly, this suggests that the contamination is settling out of suspension and is redepositing in close proximity to the source. With this information, in terms of dredging the river, it is likely that resuspension of heavy metals will occur, however, may not prove to be as mobile as initially anticipated. It was observed that

a large amount oil existed in the river sediment, this study did not attempt explanation of organic influences on the sediment nor the surrounding environment.

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Appendix 1

Geochemical Data of Welland River Sediments

Appendix 1: Geochemical data of partial extraction/lon analysis for dry sieved samples (All data in ppm).

Sam	locality	Be	Co	Cu	Ni	Sc	V	Y	Zn	Sr	Al	Ba	Fe	Mg	Mn	Ti	Cr
200QL	1	0.92	10.32	31.88	30.17	4.98	33.60	15.92	115.4	58.62	17680	141.2	38722	6824	350.5	194.8	28.8
201QL	2	1.03	10.09	30.28	33.53	5.15	38.24	13.93	103.9	45.15	19766	111.2	30867	6229	245.7	101.1	30.4
134QL	3	0.59	15.14	94.73	168.0	3.49	37.58	12.61	161.1	40.37	12017	102.7	34331	12435	359.5	539.7	325.0
130QL	4	0.78	15.79	55.68	161.7	4.67	37.36	12.59	244.2	34.54	18556	125.1	31969	7896	191.4	147.4	271.6
120QL	5	0.70	28.47	104.0	383.3	4.37	61.72	11.78	258.8	37.92	16034	128.8	47094	9830	292.4	213.7	679.3
114QL	6	0.82	16.58	64.58	211.8	4.68	43.77	11.90	194.8	40.63	18966	143.4	34776	7500	255.3	113.0	722.2
113QL	7	0.69	24.29	97.48	421.9	4.24	55.64	11.91	213.0	40.13	16374	129.5	50913	11043	366.6	239.4	1140
116QL	8	0.35	118.4	1198	5642	2.59	130.4	5.92	1435	83.62	8832	381.6	271916	12577	3726	217.2	6943
117QL	9	0.33	117.8	948.6	5039	2.70	100.9	4.54	549.5	61.25	9529	385.0	452071	6729	4529	264.1	5589
118QL	10	0.40	126.8	1216	6076	2.81	127.3	5.83	1342	92.53	9705	353.9	289228	13313	3709	222.2	7079
119QL	11	0.39	79.90	794.5	3646	2.51	91.68	5.43	1122	60.59	10747	171.4	245572	10722	2976	229.0	4251
104QL	12	0.63	11.30	36.1	109	4.17	30.72	13.76	110.1	78.07	13311	89.44	31191	10922	466.2	235.2	98.0
102QL	14	0.33	136.8	1175	6654	2.66	103.7	4.96	858.5	67.60	8834	278.7	373519	9915	3566	147.9	5607
101QL	15	0.27	121.5	810.2	5159	2.18	109.4	4.07	613.5	56.54	7439	426.2	376034	7160	4028	202.4	5136
105QL	16	0.27	225.4	851.3	7721	2.29	151.9	4.34	497.9	61.81	5887	311.2	393908	4693	3852	117.6	9730
123QL	17	0.26	130.9	477.5	7389	2.29	122.7	4.37	345.3	76.93	7190	6777	394453	6711	3662	204.5	8010
124QL	18	0.30	95.47	705.4	4120	2.62	114.8	4.52	412.6	40.07	8557	1219	400992	4734	3788	320.3	6447
125QL	19	0.26	115.5	569.1	5825	2.34	126.8	4.03	384.8	65.69	7814	2267	421849	4976	3887	227.5	7893
126QL	20	0.34	86.16	443.9	2827	3.00	101.0	5.93	255.8	29.74	9858	202.3	395458	5779	3502	153.9	4976
127QL	21	0.64	27.91	132.4	653.8	4.21	52.11	10.21	232.5	35.26	16504	133.1	102043	9710	932.8	170.9	1109
128QL	22	0.77	26.41	127.4	555.6	4.95	53.23	11.66	229.9	38.40	19640	146.9	94116	9770	700.8	163.2	1064
144QL	23	0.53	9.59	37.77	113.0	2.83	27.35	9.32	113.4	61.76	10373	64.4	31072	8039	266.0	313.2	158.3
143QL	24	0.82	31.43	132.1	725.5	4.26	51.90	11.27	284.0	71.45	16014	174.9	73159	9875	639.9	185.8	1076
142QL	25	0.81	40.88	140.6	1329	4.24	57.11	10.61	290.6	54.89	16540	169.6	108105	9194	944.5	183.1	1408
140QL	26	0.82	42.97	171.1	1199	4.18	68.06	11.03	234.1	54.89	15492	207.4	124843	10397	1041	165.9	1988
139QL	27	0.64	37.97	162.1	907.3	4.17	64.34	10.28	211.6	36.82	16189	120.7	116851	8745	729.9	152.9	1590
138QL	28	0.62	35.98	110.8	670.1	3.94	48.08	10.28	549.1	96.98	14853	127.4	79547	8863	518.8	193.3	779.0
136QL	29	0.72	37.49	140.4	855.7	4.63	63.66	11.92	233.4	54.68	17962	154.1	94254	10244	579.1	176.2	1507
135QL	30	0.63	23.26	94.43	443.4	4.11	45.93	11.01	200.8	37.34	15611	103.3	77325	9558	580.2	184.2	763.1

Appendix 1: Geochemical data of partial extraction analysis for wet sieved samples (All data in ppm).

Sam	locality	Be	Co	Cu	Ni	Sc	V	Y	Zn	Sr	Al	Ba	Fe	Mg	Mn	Ti	Cr
201PL	1	1.12	13.11	38.81	39.18	6.19	41.92	16.37	121.3	46.96	24314	153.8	33638	7350	233.8	126.4	37.8
130PL	3	0.92	14.87	70.02	158.4	4.83	36.67	12.82	270.4	35.53	19268	134.4	33380	8231	195.5	125.9	259.0
134PL	4	0.82	16.72	78.54	147.9	4.32	42.51	15.22	209.5	47.43	15274	125.4	38155	13246	362.1	338.7	267.1
112PL	6	1.23	68.19	1234	2349	3.73	253.9	8.54	344.5	41.10	13486	113.5	174744	9596	3263	75.1	2380
121PL	7	0.89	11.90	88.18	114.3	4.81	37.50	11.77	209.5	50.32	18937	122.9	39207	9899	308.6	113.0	137.8
117PL	8	0.60	92.70	987.7	4846	2.56	91.27	4.64	680.0	64.70	10427	411.6	386371	6883	4086	257.5	4916
118PL	9	0.46	65.29	877.7	3542	1.78	71.64	3.75	972.2	58.22	7039	215.4	156234	8531	2179	163.6	3791
119PL	10	0.65	64.73	948.2	3361	2.59	85.12	5.80	1352	67.79	12193	192.8	206357	11121	2855	199.0	3399
104PL	11	0.80	9.81	35.63	72.21	4.73	32.54	15.04	119.0	87.17	15506	105.1	33392	10780	479.7	218.1	54.6
102PL	12	0.65	108.5	1453	6124	2.87	79.21	6.00	1218	77.18	12071	327.0	254820	11850	2720	144.0	2983
101PL	13	0.61	110.1	1002	5458	2.21	110.5	4.61	915.6	69.28	8645	541.4	355600	8485	4057	202.5	4904
108PL	14	0.54	91.47	978.6	4783	2.23	87.14	4.51	694.6	64.75	8392	318.0	354541	7583	3901	148.0	4443
105PL	15	0.72	131.1	1654	5362	2.59	116.2	6.38	1502	69.39	9222	477.8	276143	6959	2867	126.1	3817
122PL	16	0.66	103.0	829.9	4421	2.19	144.7	3.96	477.5	66.89	8453	662.3	389843	5127	3848	435.8	6049
125PL	17	0.61	87.00	565.6	5149	2.16	124.1	4.32	490.3	75.55	8176	2311	332741	5488	3084	248.0	7424
129PL	19	0.98	30.80	162.4	593.1	4.97	55.01	11.59	1041	59.60	19007	170.5	67184	10147	426.0	103.4	491.7
145PL	21	0.97	36.03	212.4	889.2	5.49	64.76	14.30	386.7	61.22	21545	397.6	84588	12032	632.5	186.2	1855
144PL	24	0.60	11.32	41.85	8646	3.30	30.41	10.62	106.4	52.88	13003	84.7	31337	8013	259.7	339.4	115.8
143PL	26	0.95	37.16	176.5	689.9	5.32	57.35	14.26	410.3	68.51	20539	257.1	73075	11399	607.7	163.7	1133
139PL	27	0.64	41.10	176.6	1009	3.94	68.88	11.19	195.5	37.60	14302	134.5	150495	9381	1040	188.0	1844
135PL	28	0.79	22.33	127.6	360.9	4.61	47.14	12.77	260.2	43.56	17820	135.2	65048	10188	459.9	190.5	596.2

The data in the following pages does not exclude the data below the HACL, the detection limit of the instrument and the limit of quantification of the method. These limits are summarized in the table below. Utilize accordingly.

Elemental assessment of data by ICP-OES.						
Element	MDL (ppm)	LOQ (ppm)	Range Required (ppm)	HACL (ppm)	Acceptable Data (2xHACL) (ppm)	Environments for which Data is suitable.
Sc	1	3	1-27	2	>3	Background & Anthropogenic
Y	2	6	3-42	7	>14	Background only
Sr	1	3	13-340	52	>100	Background & Anthropogenic
Co	5	15	9-340	4	>8	Background & Anthropogenic
Cu	5	15	33-3900	21	>42	Background & Anthropogenic
Mo	6	18	4-1400	7	>14	Anthropogenic only
Ni	2	6	27-12000	16	>32	Background & Anthropogenic
Cr	NA	NA	48-34000	21	>41	Background & Anthropogenic
V	5	15	48-400	24	>48	Background & Anthropogenic
W	35	105	0-600	8	>15	Anthropogenic only
Zn	2	6	68-3100	76	>150	Anthropogenic only
Al	NA	NA	3577-87430	11752	>23500	Anthropogenic only
Ba	NA	NA	89-5300	82	>160	Background & Anthropogenic
Fe	NA	NA	11000-260000	9200	>18400	Anthropogenic only
Mg	NA	NA	2288-44300	2076	>4150	Background & Anthropogenic
Mn	NA	NA	255-7800	95	>190	Background & Anthropogenic
Ti	NA	NA	192-11000	987	>1970	Anthropogenic only

Appendix 1: Geochemical data of total extraction analysis for dry sieved samples (All data in ppm).

Sample	Loc	Be	Co	Cu	Ni	Sc	V	Y	Zn	Sr	Al	Ba	Fe	Mg	Mn	Ti	Cr
200Q	1	1.98	16.83	36.5	40.0	12.92	102.90	23.08	151.7	196.80	78962	535.8	41247	12204	445.8	4701.8	69.2
201Q	2	2.16	17.46	33.6	44.3	14.04	117.70	19.74	140.8	172.90	86510	522.4	43953	11899	316.0	5518.2	77.1
134Q	3	1.55	21.76	127.4	221.6	11.57	106.89	25.63	237.2	221.01	70857	552.9	53395	22829	878.6	5702.0	513.4
130Q	4	1.96	21.46	71.8	187.8	12.16	105.60	17.98	303.5	165.00	78757	522.2	43987	13291	268.3	4618.5	397.7
120Q	5	1.86	39.75	136.9	530.3	11.92	144.30	19.75	335.7	161.00	73296	501.0	65100	16016	427.8	4713.3	1240.7
115Q	6	1.89	23.68	61.2	204.3	12.81	114.56	21.57	209.8	206.91	81610	596.2	52400	18282	710.0	5655.9	549.7
114Q	7	1.82	21.30	72.6	248.7	11.81	109.90	16.42	223.6	143.30	73982	467.7	43739	12026	314.9	4193.4	992.2
113Q	8	1.73	30.48	112.4	452.6	10.98	122.40	17.08	254.7	158.60	70161	438.5	60820	16324	461.9	4137.0	1641.5
112Q	9	0.98	110.21	1127.6	2898.0	4.58	313.23	8.59	277.5	66.62	22263	209.5	258114	9273	10438.6	1351.5	7825.5
111Q	10	0.71	105.79	1043.8	2300.3	6.44	239.47	14.19	746.4	157.62	33348	405.2	275464	16728	12897.8	2022.4	10240.7
121Q	11	2.00	22.15	84.6	197.5	13.58	131.47	19.60	239.6	213.39	85080	570.6	60980	19289	748.5	5111.1	458.5
116Q	12	0.86	150.60	1433.0	6907.0	5.48	205.70	10.24	1755.0	137.40	29960	567.8	281664	16503	4843.9	1750.7	15599.4
117Q	13	0.59	141.60	971.5	5820.0	3.51	141.60	5.84	594.8	80.13	19681	455.0	316757	8051	4436.5	1024.0	15162.0
118Q	14	1.56	260.91	2403.0	12204.0	8.87	336.40	17.43	2542.9	243.93	44473	877.5	453438	30153	10284.7	2863.7	24539.4
119Q	15	0.85	103.20	952.1	4434.0	4.86	143.30	8.74	1354.0	101.00	30387	304.4	243198	14225	3716.7	1519.7	9369.6
104Q	16	1.57	15.57	49.7	117.9	9.97	80.34	19.80	134.3	189.10	64340	422.2	39304	14879	520.6	4498.9	228.4
102Q	17	0.72	173.60	1260.0	8074.0	4.51	158.70	7.19	922.1	96.84	23241	373.8	304564	11881	3664.5	1172.2	15049.4
101Q	18	0.59	155.80	900.4	6228.0	3.17	172.00	5.71	684.6	81.54	19343	524.5	272933	9396	4360.5	896.5	16765.8
108Q	19	0.49	149.00	941.4	6229.0	2.89	144.10	4.78	494.1	64.94	16230	307.8	348772	7482	4651.6	730.5	16607.0
105Q	20	1.12	299.49	1013.2	10266.5	4.34	249.10	8.56	626.0	109.38	18985	475.3	323804	7581	6503.1	1037.2	24357.8
122Q	21	0.38	133.30	634.7	3929.0	2.50	154.70	3.58	238.9	49.42	12775	429.5	294531	4253	4345.9	822.7	14123.8
123Q	22	0.59	151.70	484.2	8022.0	3.46	177.40	5.63	340.7	106.00	20732	8254.9	235940	8928	3419.5	902.0	22765.1
124Q	23	0.70	133.60	801.9	5456.0	4.52	180.70	6.59	479.2	72.25	24502	1501.5	267489	6836	3968.3	1539.6	17459.1
125Q	24	0.57	140.20	609.7	5562.0	3.53	182.70	5.50	404.7	90.72	22816	2577.1	254294	7507	3744.4	956.7	20129.0
126Q	25	0.83	106.90	476.0	3473.0	5.38	149.50	8.32	275.9	71.36	30494	338.9	224306	8100	6418.1	1747.7	13118.9
127Q	26	1.82	42.81	172.1	912.5	11.77	145.07	18.12	325.2	170.13	73232	555.4	129267	17552	1868.8	4646.7	3823.9
128Q	27	1.80	34.44	150.8	668.0	11.72	122.90	16.07	275.4	136.20	72193	465.6	90188	14911	809.7	4159.9	2418.4
144Q	28	1.33	16.12	43.3	125.7	7.98	70.79	14.80	138.8	184.80	56926	406.1	39483	11645	335.4	3941.8	296.8
143Q	29	1.72	46.49	162.0	952.6	10.97	125.90	17.08	351.3	173.00	66427	492.8	91294	15382	826.6	3874.9	2823.8
142Q	30	1.81	63.96	170.9	1729.0	11.70	139.60	17.23	373.5	156.50	68997	500.7	136557	15073	1187.9	3826.6	3885.6
140Q	31	1.67	67.09	206.8	1530.0	10.81	154.40	16.64	283.6	152.00	63860	527.6	132393	15648	1238.8	3280.5	6211.8
139Q	32	1.70	55.12	209.3	1243.0	10.91	147.80	16.42	269.9	139.50	65559	442.4	125857	14241	902.5	3446.7	5280.5
138Q	33	1.61	49.19	144.4	895.6	10.22	117.10	16.77	664.9	208.00	62786	118.0	98603	14084	681.0	3605.6	2214.5
136Q	34	1.78	52.68	171.2	1110.0	11.32	144.00	17.39	280.3	157.70	68043	479.9	115355	15339	737.7	3828.7	4696.1
135Q	35	1.61	32.35	124.0	598.0	10.39	110.00	16.88	279.9	151.00	65454	430.9	80535	14589	711.1	3886.6	2250.3
117QD		0.61	142.70	999.5	5802.0	3.63	140.30	6.09	611.7	81.79	20265	465.6	302480	8274	4914.7	1026.7	14689.7
120QD		1.81	38.60	130.5	500.7	11.42	139.60	19.10	322.7	154.70	69304	483.3	62546	15480	413.4	4531.0	1311.6
123QD		0.59	157.60	509.1	8561.0	3.56	179.40	5.78	346.1	105.80	20884	8713.2	235728	9011	3452.1	931.6	24030.3
124QD		0.68	129.90	785.0	5264.0	4.41	174.90	6.47	471.4	71.50	24070	1486.7	253093	6748	3823.2	1506.4	16517.9
138QD		1.58	48.49	141.0	872.1	10.07	115.00	16.80	650.1	205.50	61647	182.6	98080	13771	669.9	3563.6	2124.2
139QD		1.71	55.45	216.8	1220.0	11.08	149.50	16.45	278.7	140.30	66012	445.7	128521	14408	917.0	3325.0	5353.2
142QD		1.75	61.21	165.3	1595.0	11.38	134.00	16.58	361.0	152.10	67068	489.4	127149	14718	1125.4	3689.3	2779.6
201QD		2.19	17.64	34.0	44.2	14.00	118.40	20.14	141.8	172.60	86458	521.9	43813	11854	317.1	5289.2	77.0

Appendix 1: Geochemical data of total extraction analysis for wet sieved samples (All data in ppm).

Sample	Loc	Be	Co	Cu	Ni	Sc	V	Y	Zn	Sr	Al	Ba	Fe	Mg	Mn	Ti	Cr
201P	1	2.32	19.47	41.8	56.6	17.01	141.87	22.93	167.9	184.31	101479	624.2	48937	15127	495.5	6928.1	95.3
130P	3	1.99	21.63	81.9	174.7	12.64	107.10	19.02	299.2	155.50	79853	510.4	43245	13724	262.0	4863.3	325.5
134P	4	1.74	21.03	121.3	176.3	12.42	112.43	24.56	263.3	196.47	74702	533.8	52065	21028	765.7	5582.0	361.6
112P	6	3.02	126.58	1727.3	3757.9	11.95	537.88	17.52	502.9	130.68	63760	431.2	222739	18502	6658.5	3792.2	8225.1
121P	7	2.07	21.65	112.2	169.0	14.69	133.38	20.27	269.8	185.52	89137	567.3	58400	18478	666.7	5590.0	394.5
117P	8	0.83	155.46	1320.6	6584.5	5.94	195.60	10.51	990.3	122.87	31214	689.9	349136	12563	7332.9	1884.2	15818.1
118P	9	1.26	170.48	2012.5	7998.5	7.78	235.01	14.02	2137.0	177.44	39405	625.8	307850	22705	7033.8	2501.6	14924.5
119P	10	1.03	110.11	1215.9	4827.8	6.52	175.56	12.07	1686.9	127.13	38099	395.2	249898	17751	5423.0	2202.3	9446.1
104P	11	1.75	15.69	40.9	80.9	11.38	90.21	21.27	138.8	191.30	70690	441.7	41064	15008	510.0	4781.6	139.0
101P	13	0.68	177.20	1101.0	7044.0	3.89	189.40	6.97	936.1	95.20	24311	657.2	302532	11337	5456.8	1183.5	18225.9
108P	14	0.65	160.36	1243.3	6851.9	4.75	185.83	8.92	808.1	99.22	24834	460.2	342123	11499	7386.3	1369.8	16430.3
105P	15	1.44	230.92	2193.8	8285.2	7.05	266.54	13.40	1931.7	128.69	35108	776.5	316321	12525	6190.8	2083.7	19454.7
122P	16	0.58	160.10	827.5	5108.0	3.20	199.40	5.87	398.3	73.78	19121	645.5	313897	5998	4456.1	1127.4	15145.1
125P	17	1.06	144.44	671.9	6922.6	5.30	234.57	8.95	572.6	114.64	28022	2816.3	328546	9358	5756.5	1599.6	21347.0
129P	19	2.34	45.52	200.6	773.1	15.31	166.65	20.09	1306.3	175.06	87876	601.5	91653	18641	852.9	5417.3	949.6
145P	21	2.44	48.71	261.9	1205.0	15.71	179.32	21.25	493.0	178.32	91831	823.2	113001	21608	1294.5	5675.7	4338.8
144P	24	1.24	14.99	39.7	93.9	9.43	81.30	16.49	126.7	193.59	65429	484.4	40134	12547	511.6	5454.0	181.8
143P	26	2.28	49.68	241.6	930.9	15.00	163.84	21.46	508.4	191.32	88935	669.3	98319	20002	1212.1	5653.7	2635.7
139P	27	1.68	56.52	210.3	1339.2	10.63	160.52	17.62	251.9	155.43	64695	472.0	163548	15628	1937.6	4182.8	5845.0
135P	28	1.95	30.32	142.0	475.1	13.18	135.60	19.87	316.5	188.60	83517	556.8	84402	18200	951.1	5400.0	1922.2
108PD		0.85	161.46	1389.6	6985.0	5.83	193.18	10.81	1030.4	126.74	31621	562.0	336712	14325	7363.6	1742.1	16565.4
145PD		2.53	50.67	256.2	1227.5	16.07	183.47	21.90	516.3	184.50	94117	863.2	116321	22442	1337.6	5851.4	3874.5

Appendix 1: Geochemical data of grain size separated samples (All data in ppm).

Sample	Sc	Y	Sr	Co	Cu	Ni	V	Al	Ba	Fe	Mg	Mn	Ti
200A	7.42	17.97	254.6	11.30	113.8	54.34	52.61	59060	559.3	24880	7099	413.7	4357
200B	9.19	15.85	187.7	13.11	244.2	30.77	74.55	70840	531.2	28100	8982	261.1	4312
200C	11.09	25.87	171.1	15.00	387.6	36.20	88.18	73510	509.1	31500	10080	268.1	4533
200D	10.03	20.99	166.4	13.91	526.0	32.95	79.77	71570	493.3	28760	9451	255.9	5018
200E	11.00	22.53	153.1	15.64	740.9	37.52	87.86	73410	494.9	31320	10250	270.3	5669
200F	18.03	23.09	145.4	25.66	60.73	62.47	165.4	11080	664.4	56220	18640	495.6	6881
201A	6.54	13.53	245.9	7.39	143.0	27.18	48.6	57650	576.8	20070	6916	322.7	3315
201B	12.92	16.90	171.4	15.70	403.3	45.75	112.8	87330	582.8	39810	12420	312.9	5467
201C	14.85	19.24	155.0	17.70	558.9	50.84	129.8	94500	577.3	44770	13880	326.5	6188
201D	14.13	19.75	160.1	16.57	802.5	54.71	123.2	87950	558.8	41450	12660	311.2	5884
201E	13.15	18.19	154.4	15.33	1013	45.13	114.2	85410	546.5	39410	12140	298.2	6016
201F	16.68	16.69	142.3	21.41	33.27	58.17	157.2	10560	611.9	53470	16820	514.6	6779
132A	7.01	22.03	175.1	11.36	133.3	156.6	73.33	42310	389.1	40250	44270	732.2	4477
132B	6.73	15.98	169.9	10.65	211.9	66.72	63.67	51920	415.4	28780	43460	449.7	2883
132C	11.10	18.80	161.8	17.29	437.7	82.38	102.0	73230	509.3	43630	30450	445.0	4421
132D	13.32	20.15	168.1	20.04	790.6	91.65	123.2	84800	569.4	51160	23210	433.0	5065
132E	27.84	41.76	336.7	41.00	2161	204.7	258.3	17410	1161	106900	41150	851.5	10720
132F	15.59	18.18	152.8	24.21	175.7	117.6	148.5	97390	622.9	59410	19820	515.2	6079
131A	8.24	22.34	233.4	16.28	90.82	260.3	77.21	51380	514.1	43250	9774	731.5	5855
131B	6.89	12.38	204.3	11.17	189.1	97.22	61.32	60870	537.0	26470	8163	276.4	3159
131C	12.64	17.43	166.4	19.60	417.8	137.3	114.0	83430	569.3	42850	12810	343.1	5186
131D	12.90	18.71	162.5	19.38	682.6	140.7	117.1	83700	562.0	43260	12890	337.4	5391
131E	12.42	18.01	155.4	18.57	853.6	131.3	112.6	80750	534.3	40980	12640	322.3	5335
130A	5.30	12.70	223.3	9.77	118.6	145.0	46.61	49880	499.3	20680	10410	365.0	2433
130B	6.68	11.69	188.5	12.54	279.3	124.0	63.61	59390	497.5	24780	11870	280.8	2913
130C	12.06	16.94	163.2	20.57	686.3	176.6	114.7	81590	528.7	42600	15210	346.6	4897
130D	12.92	18.16	157.3	22.59	1048	181.5	122.6	84340	564.6	45100	15350	351.8	5190
130E	13.25	18.45	157.0	23.22	1443	179.4	125.3	85920	560.2	45650	15630	357.5	5458
130F	16.50	16.26	143.9	27.71	184.6	205.3	166.0	10230	687.4	55380	17590	560.9	6062
115A	12.22	33.46	377.0	27.01	234.8	580.5	126.3	87430	819.1	70570	29120	1362	8144
115B	9.56	16.90	234.1	18.70	360.1	213.6	90.13	81260	635.4	42110	20150	588.0	4324
115C	12.91	18.72	176.3	21.51	510.3	176.4	125.4	89830	599.3	50880	18680	556.0	5235
115D	12.31	18.29	163.0	20.55	749.1	159.0	120.4	84870	553.6	49070	17040	518.1	5051
115E	12.94	18.85	158.7	21.37	998.8	149.4	123.4	82180	536.0	48560	16310	491.0	5710
115F	18.77	18.93	151.1	28.74	93.00	201.2	183.7	11530	694.7	64910	19670	772.1	6539

Appendix 1: Geochemical data of grain size separated samples (All data in ppm).

Sample	Sc	Y	Sr	Co	Cu	Ni	V	Al	Ba	Fe	Mg	Mn	Ti
108A	1.18	2.44	14.1	156.60	854.3	6339	119.1	3629	89.09	20780	2475	6298	249.0
108B	3.09	6.44	83.5	192.70	1140	7850	232.3	19110	384.5	26330	12820	6242	779.1
108C	4.82	9.74	136.5	169.70	1568	7101	232.6	31080	557.7	24470	19490	6047	1361
108D	6.53	13.14	186.8	143.20	2090	6177	216.1	40390	693.9	23430	22640	6230	1926
108E	7.85	15.44	213.0	132.10	2541	5853	209.5	44630	769.8	23040	22620	6270	2416
108F	11.45	16.96	205.2	112.60	1534	4974	200.6	68190	872.2	18820	22310	5210	3672
105A	2.71	6.19	48.0	214.60	712.0	6464	215.4	8812	187.5	33030	5937	6480	768.9
105B	5.20	12.33	181.2	150.00	891.5	4515	217.1	33490	532.8	18950	22300	3262	1650
105C	6.40	14.47	193.6	120.50	1279	3941	198.7	41160	593.6	16110	24270	2771	2194
105D	8.51	17.87	212.4	120.10	2148	4205	211.3	51370	705.8	15760	25270	2810	3072
105E	7.32	15.20	159.2	89.99	1963	3185	158.2	40860	525.2	11520	17480	2083	2684
105F	14.19	19.36	177.0	142.30	2114	5038	254.6	76780	832.1	14750	20410	3648	4452
124A	1.64	3.20	24.3	120.40	673.7	4780	153.3	6927	297.4	223400	2656	5097	443.1
124B	4.43	7.58	87.6	135.60	1080	5479	229.8	27020	1194	197300	9412	4249	1602
124C	7.66	11.57	120.9	122.00	1380	4959	253.6	45740	1874	194400	13630	3843	2858
124D	8.78	13.15	139.0	112.60	1766	4638	257.0	52840	1948	202300	15460	3786	3215
124E	9.34	14.05	152.1	108.60	2184	4518	261.9	55750	2300	216900	16110	3985	3433
124F	13.44	14.67	126.9	87.10	906.5	3669	250.1	81770	2578	192000	16060	2977	4607
125A	1.25	2.39	18.4	112.70	514.1	5158	143.6	6176	401.7	210500	2297	4721	283.5
125B	3.16	5.59	76.5	149.30	889.6	7220	236.4	21740	1637	227400	8176	4562	932.6
125C	5.20	8.75	127.8	155.60	1180	7556	275.2	32320	2499	213900	11650	4157	1645
125D	6.24	10.86	163.7	148.90	1680	7197	296.7	39250	2158	247600	13730	4369	2094
125E	6.71	11.94	188.8	138.70	2043	6586	294.3	40720	3306	263100	14240	4529	2262
125F	9.16	12.84	170.6	123.30	815.1	7120	300.4	53070	5342	215600	14100	3465	3007
126A	2.18	4.53	30.2	115.70	491.7	3813	165.6	8808	118.0	227100	3445	4874	686.4
126B	5.65	10.23	119.9	120.80	802.5	3903	228.4	37030	426.9	185300	12840	3439	1815
126C	9.45	14.12	145.5	88.38	1091	2807	214.7	59700	594.9	168600	17020	2650	3160
126D	10.68	15.26	150.8	75.80	1526	2419	205.8	67060	640.2	156000	18110	2344	3608
126E	11.31	16.10	149.2	73.79	1901	2345	205.3	69320	666.1	155900	18160	2331	3937
126F	14.47	15.69	126.8	73.18	497.9	2432	223.9	87350	843.5	147700	17630	2263	4787
127A	4.59	11.00	125.6	76.86	376.0	2449	147.4	30610	283.4	141900	10120	2770	2094
127B	7.00	12.85	169.4	33.41	326.6	813.4	110.6	55100	444.0	79440	15180	1104	2735
127C	11.41	16.12	158.6	27.31	543.8	464.4	129.6	76070	520.2	70880	17670	886.9	4282
127E	12.75	17.22	151.3	25.63	1155	383.3	137.4	81560	530.6	70550	18960	845.7	4828
127F	15.87	16.21	139.8	30.23	158.6	382.5	167.7	98800	629.1	76910	20160	1007	5868

Appendix 1: Geochemical data of grain size separated samples (All data in ppm).

Sample	Sc	Y	Sr	Co	Cu	Ni	V	Al	Ba	Fe	Mg	Mn	Ti
113A	7.42	19.50	230.2	38.76	254.0	892.2	128.1	53550	523.4	81980	18700	1353	4307
113B	10.97	17.04	191.8	38.90	479.1	668.6	154.2	79880	587.4	69520	20380	790.1	4500
113C	13.37	18.30	160.0	34.39	634.4	534.0	160.8	82670	544.0	67670	19340	622.9	5119
113D	14.02	20.10	176.1	36.83	962.2	558.0	171.2	94820	617.8	74470	21430	677.2	5622
113E	14.02	20.42	175.4	36.99	1206	539.3	169.8	94710	610.3	72600	21490	674.1	5783
113F	20.40	23.17	224.4	48.03	201.9	700.5	228.8	13510	929.4	89070	27470	832.2	8231
121A	5.48	14.39	205.4	40.02	250.2	747.6	116.1	44430	456.4	78830	14490	1098	2141
121B	7.27	14.79	208.9	17.50	295.1	175.5	82.43	58180	497.5	35240	15440	473.8	2971
121C	12.01	19.47	174.4	18.81	537.7	119.5	116.6	77450	516.4	46360	17460	478.0	4450
121D	12.97	20.51	172.8	19.03	844.2	116.4	123.6	81480	529.1	49560	17950	496.9	4816
121E	13.13	21.10	167.1	19.92	1139	120.7	125.7	81960	523.3	50640	17920	500.7	5080
121F	16.85	22.42	137.6	23.94	144.4	137.1	160.5	98740	601.9	60360	18830	674.0	5945
117A	1.26	2.88	20.2	152.80	933.9	5971.0	111.7	5625	124.6	19710	2917	5956	377.9
117B	3.20	6.80	100.6	169.40	1346	6970	220.9	20870	472.5	26260	11630	5686	951.3
117C	5.19	10.31	152.0	157.70	1844	6741	234.3	31850	699.6	25830	16880	5980	1684
117D	7.33	13.83	205.7	155.80	2609	6844	257.0	42590	949.3	28780	20710	7036	2400
117E	7.38	13.74	215.9	122.00	2711	5446	209.9	40640	991.4	23610	18250	6431	2386
117F	10.87	14.21	169.6	140.30	1913	7249	235.3	63320	1132	25370	16940	7333	3498
119A	2.96	7.47	57.1	160.10	1069	7090	239.2	12990	214.9	31900	9974	6352	864.1
119B	3.79	9.09	119.9	74.49	1103	3076	146.5	27360	330.4	16470	19500	3284	1443
119C	7.03	14.69	177.9	97.76	2165	4129	195.6	46990	482.7	21340	27450	4877	2579
119D	7.92	15.19	177.8	92.80	2783	3944	183.1	50980	482.2	19650	25460	4816	2787
119E	9.79	17.96	208.5	101.70	3898	4371	204.5	60280	544.0	21580	26020	5551	3512
119F	11.45	16.72	171.0	102.80	2615	4589	192.7	71120	555.1	20000	20290	5329	3732
104A	6.24	18.17	205.5	14.51	157.4	238.5	61.27	45970	438.1	40480	13260	854.3	3701
104B	6.17	16.08	205.7	10.78	234.3	81.37	52.92	52000	441.1	23090	13490	688.5	3127
104C	6.74	18.62	210.5	10.78	282.2	69.46	55.62	53710	427.2	23760	14480	686.8	3803
104D	7.44	19.51	206.1	11.66	410.5	58.56	59.20	55240	424.3	24810	14230	699.2	4095
104E	8.23	20.16	195.2	12.87	509.9	58.67	66.55	56510	421.9	27680	13940	688.6	4690
104F	16.12	23.33	208.0	17.10	100.4	80.77	142.6	86840	513.6	54440	18640	603.0	4838
101A	1.64	3.55	30.9	212.20	915.6	8303	185.4	6794	216.8	21110	4241	6741	442.4
101B	3.10	7.02	102.9	215.00	1238	8567	266.6	21820	582.8	26320	13580	6452	911.9
101C	4.62	9.73	139.8	193.50	1597	7913	280.6	31860	802.0	31520	18870	6546	1536
101D	7.50	17.53	239.9	242.00	2933	10140	361.7	52320	1354	35570	28870	9062	2581
101E	6.41	14.31	194.2	172.70	2387	7303	267.6	40500	1204	27610	22290	6796	2280
101F	11.52	16.91	186.8	162.20	2269	6986	252.6	67610	1542	24000	21230	7345	3733

Appendix 2

1. Introduction & Scope of the Method

The purpose of this method is to provide a reliable and reproducible procedure for the determination of the concentration of various elements in a sample. The method is based on the use of microwave digestion followed by atomic absorption spectrometry (AAS).

2. Materials

The following materials are required for the method: microwave digestion vessel, microwave oven, AAS, standard solutions, sample, and reagents. The microwave oven should be capable of operating at 2450 MHz and 700 W. The AAS should be capable of measuring the elements of interest. The standard solutions should be prepared from high-purity reagents. The sample should be representative of the material to be analyzed. The reagents should be of analytical grade.

$$C = \frac{A - A_0}{S - S_0} \times C_s$$

Appendix 2

Microwave Digestion Technique

Step	Time (min)	Power (W)	Notes
1. Weighing	5	0	Accurately weigh the sample into the digestion vessel.
2. Addition of reagents	5	0	Add the required amount of reagents to the sample.
3. Digestion	15	700	Place the vessel in the microwave oven and digest for 15 minutes.
4. Cooling	5	0	Remove the vessel from the microwave oven and allow it to cool.

The following steps should be followed for the microwave digestion technique:

1. Weighing: Accurately weigh the sample into the digestion vessel.
2. Addition of reagents: Add the required amount of reagents to the sample.
3. Digestion: Place the vessel in the microwave oven and digest for 15 minutes.
4. Cooling: Remove the vessel from the microwave oven and allow it to cool.

Appendix 2:

Microwave Digestion Technique

Experiments with microwave digestion techniques were performed at Ministry of the Environment under supervision of Dr. B. Campbell. Several parameters were experimented with different reagents, times and pressures of the system.

Calibration:

To calibrate the working power of the microwave system, a volume of water (1L) was heated in the microwave system for 1 minute. The measurement was repeated 3 times. An initial and final temperature was obtained. Following equation 1, the working power of the microwave system was calculated.

$$(1) \text{ Working Power (W)} = 70 \times (T_f - T_i), \text{ where}$$

T_f - final temperature,
 T_i - initial temperature.

Table 1.

	Ti(°C)	Tf(°C)	W(watts)
trial 1	19	37	1270
trial 2	19	36	1190
trial 3	19	36	1190
expected power			1200

The digestion was performed at half the power of this reading (600 W).

Sample Digestion Procedure: (Table 2,3a,4a).

- sample weighed in Teflon bomb (0.2-0.3g)
- HNO₃ or aqua regia added (varying amounts)
- inserted into microwave for digestion
- once completed the bombs were removed and cooled in water
- pressure released and bombs uncapped
- solution transferred and deionized water added to bring up to 50 ml
- residue was filtered and retained
- colour of solution and residue recorded

Further testing of the residues and solutions included:

1. XRD of the residue to identify mineral present
2. chemical analyses of the solutions to identify % recovery of standard reference materials

Results of these tests:

1. XRD identified only minerals with a silicate structure. There were no oxides or carbonates present
2. chemical analyses indicated there was a recovery of approximately 70% (Table 3a,3b,4a,4b).

Pros:

-all minerals except silicate minerals went into solution

Cons:

-Ministry of the Environment would not authorize the use of HF in bombs. The certified values for standard reference materials that were used were results for total extraction, not partial extraction. Without the use of HF in the digestion, the analyses could not be validated for accuracy.

-The final solutions contained an acid concentration of approximately 30%. This was not optimal as a final working solution for ICP analysis. Dilution of the solutions made some elements undetectable.

-Time allocation needed for method development, validation and generation of chemical results was limited.

Table 2.

Experiments with Microwave Digestion, Run 1 through 3: Using program 4 for steps 1 through 4, program 5 for step 5.

Step	Reagent	Power	Time
1	HNO ₃	120	2
2	"	200	2
3	"	400	2
4	"	600	5
5	"	600	4

vessel	sample	sample weight	reagent volume	colour solution	colour residue
run1					
1	101a	.3088	8ml	green	black grains
2	101b	.2998	"	green	"
3	101c	.3019	"	green	brown pwd
4	101d	.3007	"	green	"
5	101e	.3024	"	yellow-green	"
6	108a	.3086	"	yellow-green	black grains
Run2					
1	127c	.3022	8ml	lg yellow	lg brown
2	"	.3018	"	"	"
3	"	.3034	"	"	"
4	"	.3011	"	clear	"
5	"	.2990	"	"	"
6	"	.3018	"	lg yellow	"
run3					
1	127c	.2042	8ml	clear	lg brown
2	"	.1993	"	"	"
3	"	.2026	"	"	"
4	"	.1998	"	"	"
5	"	.1992	"	"	"
6	"	.2015	"	"	"

note: no chemical analyses for these samples.

Table 3a.

Run 1 and 2: Using program 4 for steps 1 through 4, program 5 for step 5.

Step	Reagent	Power	Time
1	HNO ₃	120	2
2	"	200	2
3	"	400	2
4	"	600	5
5	"	600	4

vessel	sample	sample weight	volume	solution colour	residue colour
run1					
1	blka	0	8ml	clear	lg brown
2	blkb	0	"	"	"
3	2704	.1984	"	"	"
4	2704d	.1966	"	"	"
5	1646	.2009	"	"	"
6	1646d	.2004	"	"	"
run2					
1	blk1	0	8ml	clear	lg brown
2	blk2	0	"	"	"
3	blk3	0	"	"	"
4	blk4	0	"	"	"
5	blk5	0	"	"	"
6	blk6	0	"	"	"

remarks: 0.200g in 50ml = 250 Dilution Factor.

Table 3b.

Results of initial microwave digestion of blanks, NIST-2704 and NIST-1646. Digestion reagent was HNO₃ (achieved approx. 80-90% digestion).

Smps	Be	Co	Cu	Ni	V	Y	Zn	Mo	Sc
blka	0	2.0	2.37	9.84	0.87	0.49	16.3	3.6	1.18
blkb	0	2.29	2.10	9.13	0.99	0.57	17.3	3.43	1.35
2704	0.92	12.78	95.16	48.32	37.23	16.23	449.5	0.88	5.8
2704D	0.86	13.05	85.14	47.84	35.19	15.76	463.3	1.73	6.1
1646	0.91	10.06	17.85	34.87	52.89	15.35	121.7	0.04	7.5
1646D	0.88	10.03	18.15	34.56	49.65	14.94	117.9	0.12	7.1
blk1	0	2.8	2.5	10.48	1.61	0.77	1.78	4.14	1.55
blk2	0	1.83	0.423	9.36	0.13	0.28	1.26	3.5	1.1
blk3	0	1.97	1.1	10.18	0.44	0.48	1.83	3.37	1.13
blk4	0	1.95	0.91	10.15	0.32	0.36	1.39	2.96	1.03
blk5	0	1.88	1.17	10.07	0.30	0.26	1.94	3.44	1.18
blk6	0	2.21	0.72	10.04	0.28	0.31	1.67	4.26	1.12
Certified value 2704	NA	14.0	98.6	44.1	95.0	NA	438.0	NA	NA
accuracy 2704 (%)	NA	8.7 6.8	3.5 13.6	9.6 8.5	60.8 62.9	NA	2.6 5.8	NA	NA
Certified value 1646	1.5	10.5	18.0	32.0	94.0	NA	138.0	NA	10.8
accuracy 1646 (%)	39.3 41.3	4.2 4.5	0.8 0.8	9.0 8.0	43.7 47.2	NA	11.8 14.6	NA	30.5 34.3

$$\text{Accuracy (\%)} = \frac{(\text{known value} - \text{measured value})}{(\text{known value})} \times 100$$

Table 4a. Experiments with Microwave Digestion. Run 1 through 3: Using program 4 for steps 1 through 4.

vesse l	smp	smp wt	reagent	Vol	soln	residue	step	Pwr	time
1	blk1	0	HNO ₃	8ml	clear	lgbrown	1	120	2
2	blk2	0	"	8ml	"	"	2	200	2
3	2704	0.1504	"	8ml	"	"	3	400	2
4	2704D	0.1520	"	8ml	"	"	4	600	9
5	1646	0.1502	"	8ml	"	"			
6	1646D	0.1477	"	8ml	"	"			
1	blk1	0	HNO ₃	8ml	"	"	1	120	2
2	blk2	0	"	"	"	"	2	200	2
3	2704	0.1503	"	"	"	"	3	400	2
4	2704D	0.1499	"	"	"	"	4	600	9
5	1646	0.1499	H ₂ O ₂	1ml	"	"	5	160	3
6	1646D	0.1509			"	"			
1	blk1	0	HNO ₃ +HCl(3:1)	8ml			1	120	2
2	blk2	0	"	"			2	200	2
3	2704	0.1509	"	"			3	400	2
4	2407D	0.1489	"	"			4	600	9
5	1646	0.1525							
6	1646D	0.1514							

remarks: .150g in 25ml = 166.67 Dilution Factor.

Table 4b. Results of initial microwave digestion of blanks, NIST-2704 and NIST-1646. Digestion reagent for set 1 was HNO_3 , set 2 was $\text{HNO}_3 + \text{H}_2\text{O}_2$, and set 3 was $\text{HNO}_3 + \text{HCl}$ (aqua regia).

Smps/Set 1	Be	Co	Cu	Ni	V	Y	Zn	Mo	Sc
blka	0	0	0	2.2	0	0	2.1	1.2	0
blkb	0	0	0	2.0	0	0	2.1	4.0	0.2
2704	0.9	10.3	82.6	39.4	43.6	16.5	403.8	0	5.4
2704D	0.95	10.0	80.8	37.9	45.4	16.0	383.6	0	5.8
1646	0.8	6.9	12.75	24.6	53.7	13.9	107.3	0	6.0
1646D	0.88	6.8	12.6	25.5	56.4	14.5	109.0	0	6.4
accuracy 2704 (%)	NA	26.4 28.6	16.2 18.1	10.7 14.1	54.1 52.2	NA	7.8 12.4	NA	NA
accuracy 1646 (%)	46.7 41.3	34.3 35.2	29.2 30.0	23.1 20.3	42.9 40.0	NA	22.2 21.0	NA	44.4 40.7
Set 2	Be	Co	Cu	Ni	V	Y	Zn	Mo	Sc
blka	0	0	0	3.5	0	0	0	1.5	0
blkb	0	0	0	2.6	0	0	3.6	1.4	0
2704	0.95	10.4	83.5	39.3	44.6	16.6	394.5	0	5.8
2704D	0.97	10.8	83.5	40.6	43.6	16.5	399.5	0	5.9
1646	0.93	7.4	13.3	28.8	58.7	15.5	115.8	0	7.1
1646D	0.88	7.3	12.8	28.0	56.6	14.9	150.4	0	6.7
accuracy 2704	NA	25.7	15.3	10.9	53.1	NA	9.9	NA	NA
accuracy 1646	38.0	29.5	26.1	10.0	37.6	NA	16.1	NA	34.3
Set 3	Be	Co	Cu	Ni	V	Y	Zn	Mo	Sc
blka	0	0.5	1.5	2.7	0	0	3.1	1.4	0.4
blkb	0	0.4	1.5	3.4	0	0	2.9	1.3	0.4
2704	1.43	11.9	91.4	44.9	70.2	18.7	432.8	0	9.6
2704D	1.5	12.1	88.6	44.3	72.5	19.5	425.0	0	10.
1646	1.1	8.8	17.1	31.7	66.0	15.7	123.8	0	8.4
1646D	1.05	8.9	17.0	32.5	65.3	15.7	122.2	0	8.5
accuracy 2704	NA	15.0	7.3	1.8	26.1	NA	1.2	NA	NA
accuracy 1646	26.7	16.2	50.	0.9	29.8	NA	10.3	NA	22.2

Note: See Table 3b. for certified values. All chemical data are in ppm.

Appendix 3

pH Data of the Water of the Welland River

Appendix 3: pH of water of the Welland River.

Sample Site	pH Reading
101	7.34
102	7.85
103	8.10
104	7.80
105	7.58
108	8.13
Average	7.80

*Temperature of water at time of measurement 20°C.

Appendix 4**Sample Key**

Appendix 4: Sample Key

Particles sizes (μm)

A - 63-45

B - 44-32

C - 31-23

D - 22-13

E - 12-11

F - <11

P - bulk of grain sizes <63 μm -wet sieving

Q - bulk of grain sizes <63 μm -dry sieving

Appendix 5

Field Sample Description Data

Appendix 5: Field Sample Description Data of Welland River Samples

<u>Sample ID</u>	<u>Location</u>	<u>Description</u>	<u>pH</u>
101	at outfall	lots of oil, large pebbles	7.34
102	at outfall	lots of oil, varying grain size	7.85
103	at outfall	lots of oil, foul smell, very black	8.10
104	at outfall	medium brown colour, fine-grained sediment	7.80
105	at outfall	lots of oil,	7.58
106	at outfall	rock sample	
107	at outfall	rock sample	
108	at outfall	lots of oil, metal, black sample	8.13
110	50m upstream	fine brown sediment, oil present	
111	100m upstream	fine brown sediment, oil present	
112	125m upstream	fine brown sediment, oil present	
113	175m upstream	fine brown sediment, oil present	
114	150m upstream	fine brown sediment, oil present	
115	200m upstream	fine brown sediment, oil present	
116	outside boom at outfall	lots of oil in water and sample	
117	at second reef	metal and oil in sample	
118	slightly inside boom at outfall	lots of oil in water and sample	
119	outside boom at outfall	lots of oil in water and sample	
120	225m upstream	strong organic smell	
121	10m upstream	very organic sample, alot of algae	
122	30m downstream	black mud with very strong smell	
123	50m downstream	strong organic smell, lots of oil in sample	
124	70m downstream	strong organic smell, lots of oil in sample	
125	100m downstream	strong organic smell, lots of oil in sample	
126	200m downstream	strong smell	
127	400m downstream	strong smell	
128	at sewage disposal plant	strong smell	
129	100m downstream sewage	strong smell	
130	20m upstream from outfall 2	fine brown sediment	
131	50m upstream from outfall 2	fine brown sediment	
132	70m upstream from outfall 2	fine brown sediment, metal, zebra mussels in sample	
133	150m upstream from outfall 2	fine brown sediment, metal chunks, glass in sample	
134	200m upstream from outfall 2	fine brown sediment	
135	400m down from Dump	mud sample	
136	300m down from Dump	mud sample, oil and metal present	
137	275m down from Dump	mud sample, oil and metal present	
138	225m down from Dump	mud sample, oil and metal present	
139	170m down from Dump	mud sample, oil and metal present	
140	50m down from Dump	mud sample, metal and alot of oil present	
141	under Atlas Steel Dump	mud sample, metal and alot of oil present	
142	120m up from Dump	mud sample, brown in colour	
143	200m up from Dump	mud sample, brown in colour	
144	400m up from Dump	mud sample, brown in colour	
145	500m up from Dump	mud sample, brown in colour	

