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Geochemical Background in Soil and Till

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Introduction: Geochemical data at the GSC

by A.N. Rencz, Geological Survey of Canada, ESS

The Geological Survey of Canada (GSC) has a long history in environmental geochemistry providing both data and knowledge on geochemical processes across Canada. The first geochemical surveys at the GSC date to the mid fifties when R.W. Boyle initiated the development of a geochemistry laboratory to support his work on stream and spring waters and sediments at Keno Hill, Yukon. In 1956 Boyle undertook the "first" GSC regional geochemical survey in southwestern Nova Scotia. In the years that followed near-surface geochemical sampling expanded to other media notably: till, lake sediments, lake waters, peat, and other biological materials. Today the GSC has considerable geochemical data holdings. The most comprehensive data set exists within the National Geochemical Reconnaissance (NGR) programme (Friske and Coker, 1994). Some 2.3 million km^2 of Canada have been covered by the NGR, ~110,000 lake sediment and ~90,000 stream sediment samples. There are also considerable holdings of till geochemical data. GSC Open File 4703 (Spirito et al., 2004) compiled metadata for 186 surveys of till across Canada. Of these, 75 were GSC data while the remaining surveys were undertaken by provincial or territorial agencies. A follow-up study has added an additional 118 surveys (Spirito et al., in press).

The data have been applied to a variety of applications in mineral exploration and in environmental geochemistry (Bonham-Carter and Garrett, in preparation). The concept of background is important in the field of geochemical exploration for mineral deposits. By understanding background, it becomes possible to identify anomalies that may be due to the dispersal of pathfinder elements from a mineral deposit, as distinct from unmineralized rocks. Similarly, in environmental impact studies, the presence of an anomaly that is outside the range of natural background can be used to identify the source and extent of chemical contamination (Reimann and Garrett, 2005).

An understanding of the behaviour and abundance of chemical substances in the environment is critical for assessing the impacts of environmental change. In order to evaluate the effects of change, knowledge of the natural variability of a substance and the factors that affect its abundance in the setting under consideration are essential. The concept of a natural background, and those factors that affect it, is useful for summarizing the characteristics and distribution of a particular element in the environment.

Many government organizations either have in place, or are currently developing, ecological guidelines for a variety of environmental media that establish the abundance levels at which chemical substances may be toxic. The usual approach is to evaluate the harmful effects of a substance in the medium under study using laboratory toxicology studies. This involves the use of dose-response data that show the effects of different toxicant abundances on particular life forms. In some situations, the No Observed Effects Level (NOEL) estimated by this method is within the normal background concentration range of the substance under natural conditions. Sometimes this occurs in the translation of the toxicology results, usually obtained with soluble salts or miscible liquids, to the natural environment where a variety of inorganic and organic complexes and species that are not bioaccessible, but are measured by the analytical procedure, contribute to the abundance in the media of concern. In other instances the NOEL may be truly within the normal background range. Setting guidance values without considering background is clearly undesirable and may lead to values within the natural background range and subsequently to unwarranted expense in attempting to reduce substance abundance levels to below the range of natural abundance. This could inadvertently damage the environment that is to be protected. It is therefore essential to consider natural background as part of any protocol for setting action or guideline levels for environmental media. Likewise, for guideline values established to protect human health it is generally inappropriate to establish limits that are considerably less than natural background concentrations.

This report and subsequent follow-up reports will focus on background geochemical values in soil and till across Canada. Almost all of Canada has undergone glacial erosion during the Quaternary (i.e. the last 1.8 million years). Sediments derived directly from glacial erosion are referred to collectively as till, and they blanket large regions of the country to depths varying from a few centimetres to hundreds of metres. Their chemistry is primarily controlled by the bedrock from which they were derived. Soils form on the immediate surface of the earth and serve as a natural medium for the growth of plants. Whilst soil chemistry is largely controlled by the nature of the underlying parent material (which is frequently till in Canada), it may be highly modified as a result of surface biogeochemical and anthropogenic processes.

The report is divided into four parts. Part 1 provides an explanation of “background” as it applies to geochemical data. Parts 2 and 3 deal specifically with the development of background ranges for till across Canada. Part 2 presents the development of the database used to estimate the background ranges and Part 3 provides actual values for background ranges for nine elements (As, Co, Cr, Cu, Ni, Pb, Th, U and Zn) in till across Canada. Part 4 concludes the report with a preliminary comparison between the background levels derived in Part 3 with background levels cited in other studies. Future reports will add elements and will reflect on-going efforts to improve the database and the procedures for estimating background values.

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Part 1: Defining natural background in geochemical surveys

by G.F. Bonham-Carter and R.G. Garrett, Geological Survey of Canada, ESS

Modified from part of a report prepared for Open File publication: Establishing Natural Background in Geochemical Surveys by G.F. Bonham-Carter and R.G. Garrett.

Introduction

The usual abundance of a chemical element in unmineralized earth materials (e.g., rocks, soils, sediments, water, vegetation, air) is often referred to as ***background***. Background is an abundance range, not a single value. Element abundances that occur outside background are said to be ***anomalous*** (Reimann and Garrett, 2005). Using a fixed ***threshold*** to separate anomalous from the outer limit of background is not ideal (although often done for practical reasons), because many factors that change spatially and temporally affect geochemical abundance.

The concept of background is important in the field of geochemical exploration for mineral deposits. By understanding background, it becomes possible to identify anomalies that may be due to the dissolution and dispersal of pathfinder elements from a mineral deposit, as distinct from unmineralized rocks. Similarly, in environmental impact studies, the presence of an anomaly that is outside the range of natural background can be used to identify the source and extent of chemical contamination.

The Earth is a complex biogeochemical system. The complexity of this system is often simplified using biogeochemical cycles as models that depict the abundance of an element in various compartments, and the rates at which an element is transferred from one compartment to another. Whereas cycles provide a valuable global space- and time-averaged view of the distribution of an element, the variability of elements with respect to time and space is studied by using time-series and maps, respectively. Many factors may affect element abundances temporally and spatially. In some instances it may be possible to identify and account for particular sources of variation. Some well known examples are: temporal variation in element levels in stream water as a function of the season, or spatial variation in elemental abundances in soil caused by differences in mineralogy and chemistry of the underlying parent material (e.g. bedrock or till). In such situations, element background may be modelled to allow for the prediction of changes in space or time. In other situations, it may be too difficult or expensive to identify and characterize the factors affecting variation, so background encompasses a broad range of abundance levels that occur for a variety of unspecified reasons.

Another source of variation affecting geochemical data values is the result of poor sampling and measurement protocols. A review of sampling and analytical protocols is beyond the scope of this report. However, well-defined protocols for sample collection, storage and preparation, as well as the method of chemical dissolution, if one is used, and instrumental analysis, are absolutely vital for generating data that will yield reliable estimates of background. Systematic differences in element abundance values can be the result of either poorly defined protocols, or lack of adherence to established protocols. Quality control measures, including the analysis of standard reference materials, and systematic sample and analytical duplicates are the best way to monitor and ensure data quality.

Several methods have been applied in geochemical exploration to model background and thereby identify anomalies. The methods are based on various statistical approaches, and always consider frequency information, as may be summarized, for example, in a histogram or probability plot. They should also consider spatial or temporal variability, depending on the survey, with appropriate maps, profiles or displays. Some methods use a multi-element approach, but most involve a single element, univariate approach.

This report provides a definition of background, discusses various sources of natural variation to be expected in earth materials, and outlines various methods of determining background, illustrating them with examples.

General geochemical definition of background and anomaly

Rose et al. (1979, p. 31-32) state that "the normal abundance of an element in unmineralized earth materials is commonly referred to as *background*. For any particular element, the normal abundance is likely to differ considerably from one type of earth material to another. Furthermore, the distribution of an element in any particular earth material is rarely uniform. Thus it is usually more realistic to *view background as a range* rather than as an absolute value, even in a relatively uniform environment."

Stating this another way, it can be said that the geochemical background in a particular earth material is the 'natural' range of concentration values over which the element occurs in the absence of anthropogenic contamination.

An **anomaly** is, by definition, a deviation from the norm. "A geochemical anomaly, more specifically, is a departure from the geochemical patterns that are normal for a given area of geochemical environment" (Rose et al., 1979, p.34). There are several different ways of approaching the idea of background and anomaly. The most popular approach is to define a level that distinguishes two groups of samples on the basis of a threshold. Individual observations are either anomalous or background. Another approach discussed later is to estimate the degree to which each sample is anomalous as well as the degree to which it is background—and this can be done in various ways.

Threshold

Garrett (1991) discussed the concept of threshold in relation to mineral exploration, and these remarks apply also to threshold for anomalies caused by environmental contamination. "The concept of threshold is as old as geochemical prospecting and much has been written about it, both as a concept, and on its estimation. Intimately related to threshold are the concepts of background and anomaly. Threshold is the 'line' dividing the two, and a simple working definition is: ***Threshold is the outer limit of background variation.*** Note the use of the word 'outer' rather than the more traditional 'upper'. As geochemists have gained access to data for more elements, many significant negative patterns are being recognized, and a negative anomaly in a pathfinder element is sometimes as useful as a positive one. This definition implies that the background data can be thought of as a cloud of points. These are clustered around some 'average background', and the concept of a cloud implies that the data also have a spread; they may occur in a tight mass, or more diffusely. These two data attributes are expressions of the geochemical concepts of background level and relief.

It must be stressed that in many instances there is no single threshold in a survey area unless it is restricted to a single geochemical landscape. Geochemical landscape means a unique bedrock-surficial environment combination. Each geochemical landscape will have an appropriate threshold that is a function of the geochemical background of the bedrock and the surficial processes that have influenced the element in its pathway from the bedrock to the sample medium. The situation in fresh bedrock surveys is simpler, as the surficial environment is not a factor."

Geological factors affecting background

There are many compilations of background values for geochemical elements in the Earth's crust, e.g., Reimann and de Caritat (1998).

Figure 1: Average and range of the content of the principal minor elements in normal rocks (from Rose et al., 1979, fig. 2.5, p. 31), expressed in ppm (mg kg^{-1}).

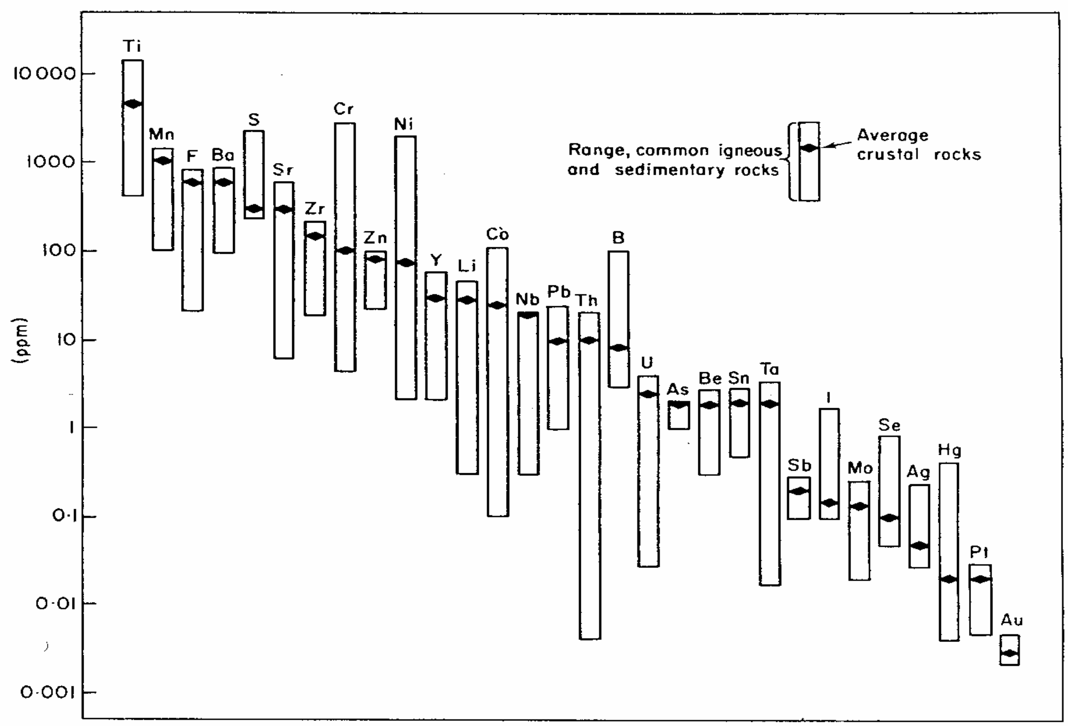

Figure 1 (from Rose et al., 1979) shows both the average value and range for most of the common minor elements on a global scale. Several metals, such as Cr and Ni, have broad abundance ranges up to 4 orders of magnitude. Others, such as As and Au, have much narrower ranges, of about one half of one order of magnitude. The main message from this diagram relevant to the determination of geochemical background is that the range of abundances differs greatly between elements. Some elements have a very large range, and therefore background values for these elements are likely to differ widely depending on local conditions. Rocks are the principal source of elements in all environmental sample media, so variation of abundance levels by rock type plays a vital role in affecting differences locally in geochemical background. Average abundance levels for selected elements by principal rock type are summarized in Table 1 (from Garrett, 2005).

Table 1: Compilation of average geochemical background data for the Earth's crust and selected rock types (after Garrett, 2005)

	Hg µg kg^{-1}	**Pb** mg kg^{-1}	**Cd** mg kg^{-1}	**Cr** mg kg^{-1}	**Ni** mg kg^{-1}	**As** mg kg^{-1}	**Cu** mg kg^{-1}	**Zn** mg kg^{-1}	ref
Earth's crust									
	80	13	0.2	100	75	2	55	70	1
	90	12	0.2	110	89	2	63	94	2
Upper continental crust									
		20	0.1	35	20	1.5	25	71	3
	80	13	0.2	77	61	1.7	50	81	2
Igneous rocks									
Ultramafic	4	1	0.1	1600	2000	1	10	50	4
Mafic	13	6	0.2	170	130	2	87	105	4
Intermediate	21	15	0.1	22	15	2	30	60	4
		10		55	30		60		3
Felsic (4)	39	19	0.1	4	5	1	10	39	4
Sedimentary rocks									
Sandstone	57	14	0.02	120	3	1	15	16	5
Limestone	46	16	0.05	7	13	2	4	16	5
Shale	270	80	0.2	423	29	9	45	130	5
Black shale		15	4.0	18	68	22	50	189	6
		100		700	300		200	1500	7

1 Taylor, S.R., 1964.
2 Lee Tan and Yao Chi-Lung, 1970.
3 McLennan, S.M., 1992.
4 Turekian, K.K. & Wedepohl, K.H., 1961.
5 Faust, S.D. and Aly. O.M., 1981.
6 Dunn, C.E., 1990.
7 Vine, J.D. and Tourtelot, E.B., 1970.

In general, geochemical data indicate that Co, Cr and Ni are greatly enriched in ultramafic rocks as compared to the average for the crust, whereas granites are enriched in Mo, Pb and U, shales in As, Bi, Cd, Hg, Mo, Sb, Se, U and Zn, and coal in As, Hg, Sb and Se. As a general rule, it may be expected that the natural background of these elements in media such as soil, water and vegetation in regions underlain by rock types with enriched values (as compared to average crust) will also be enhanced. There are of course other modifying factors, because of the complexity of chemical and biogeochemical processes that operate on the material weathered and transported from parent rocks to other environmental compartments. Where mineral deposits are present, characteristic suites of elements may have elevated concentrations (Boyle, 1974; Garrett, 2005). As a general rule, geological bedrock composition should always be considered in establishing local background values.

Methods of defining background and anomalies

Hawkes and Webb (1962) stated: “A fully dependable value for threshold can come only from an orientation survey in an area of known geology and mineralization, conducted and interpreted by a geologist experienced in geochemical interpretations. There is as yet no real substitute for a competent visual estimate based on a comparison of the geochemical patterns given by a series of tentative threshold values, correlated with the known distribution of metal in the bedrock”.

Although various statistical methods have been proposed and used to determine thresholds, the use of an orientation survey where known anomalies (either from mineral deposits or from environmental contamination) can be identified remains the ideal approach. In practice, however, exploration geologists (or their environmental counterparts) seldom have the luxury of such a survey. Even if such a survey is available, there are likely to be unidentified sources of geochemical elements that have not been recognized that complicate the interpretation.

Many statistical methods have been proposed to define and separate background samples from anomalous samples in geochemical surveys. Most methods are restricted to considering one element at a time, although some multivariate approaches have also been proposed. In most methods, a constant threshold is assumed, because there are insufficient data about spatial or temporal variability of causative factors on which to base subsets. Usually, only frequency information is used to characterize background and anomalies. Often, samples come from mixed populations with overlapping ranges, and it may be desirable to estimate the probability that a given sample is either in a background group, or in an anomalous group. These methods usually ignore spatial or temporal location in the statistical analysis, although making plots of the sample values in space and time is highly desirable and a ‘common-sense’ check. Simple methods that are “robust” (i.e. little influenced by extreme high or low values that may be present) are preferred. The Tukey boxplot procedure is such a method and has much to recommend it (Reimann et al. 2005).

Alternative approaches are now sometimes used, particularly with data in a Geographic Information System (GIS), that take advantage of both spatial and frequency information in defining background. Usually these methods assume that the sampling is sufficiently dense that interpolation on to a regular grid is reasonable. The grid can then be visualized as a geochemical surface or image. The concentration-area method (Cheng et al., 1994, 1996) assumes a constant threshold, but considers both spatial and frequency information. Fourier analysis (and other methods) can also be applied to geochemical grids, decomposing them into components based on spatial frequency. In effect, this allows the decomposition of a geochemical surface into a variable background surface (low spatial frequencies) and an anomaly surface (high spatial frequencies).

Several multivariate methods have been proposed for identifying anomalous samples. Some of them use the multi-element geochemical data only, whereas others use independent information, such as the geological composition of drainage basins associated with sample sites. The objective of such methods is either to determine if some samples have anomalous characteristics based on a multi-element association (using principal components analysis for example), or to model background based on measurements that characterize the geology (major element compositions, or areas of rock types in drainage basins).

In reality, geochemical data are usually complex, and are the end product of multiple biogeochemical processes acting in time and space. The notion that all samples can be put into just two clearly identified groups, or populations, is a simplification that is useful from a practical standpoint, but is usually subjective and arbitrary.

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Part 2: Till geochemistry data compilation: methodology

by S.W. Adcock, Geological Survey of Canada, ESS

Introduction

The goal of this sub-activity was to assemble a large dataset of geochemical data from across Canada in a standardised format. This facilitated statistical analysis of the data, to determine the range of natural variability of metal concentrations in till, as described in Part 3.

As part of an earlier study, almost 200 till surveys carried out by the GSC and its Provincial counterparts over the past 50 years were identified and summarised in GSC Open File 4703 (Spirito et al., 2004). These surveys varied greatly in many key characteristics:

1. Areal extent
2. Number of samples collected
3. Sampling density
4. Sampling protocol
5. Sample preparation prior to analysis
6. Analytical methods
7. Data presentation

The task of compiling all of the surveys into a single dataset was too large for the available resources (time and people) and probably not required to provide representative samples across Canada. Therefore, the data compilation was limited to surveys published by the GSC, for which digital data were available.

Because the motivation for the compilation was to facilitate statistical analysis of the data, it was important to restrict the dataset to standardised sample media and sample preparation procedures. Till was chosen as the sample medium, because it comprises the vast majority of the available samples. The till samples are commonly prepared to <63 µm and/or <2 µm size fractions. The two size fractions have significantly different geochemical signatures. The GSC has large amounts of data for both size fractions, identified on a survey-by-survey basis in Open File 4703. However we did not feel it necessary to present both data sets and decided to compile only the <63 µm data for the following reasons (Garrett, 2004):

> "The <2 µm fraction is costly and time consuming to separate/prepare in/from settling columns - and that contact with water could mobilize and remove into solution the loosely held metals that are the most bioavailable. The <2 µm fraction tends to have greater amounts of many elements 'attached' due to the larger surface area of particles in this size fraction relative to their volume than the <63 µm fraction. Furthermore, the GSC

> and several provincial geological surveys, are the only Canadian agencies, we are aware of, that have extensive data holdings for this size fraction. It is the fine fraction (dominantly <10 µm) of the soil/till that when entrained as dust is inhaled by humans/mammals/etc. From a risk assessment point this size fraction is easily ingested and the very fine materials can wind up deep in the lungs. The loosely held trace elements on the surface of these fine particles are in a form that tends to make them bioavailable. However, if the tills from which the <2 µm fraction is recovered are not exposed and dust entrained there is no receptor exposure and therefore no risk.
>
> From a mineral exploration and geochemical mapping point of view the <63 µm fraction is more often than not a better choice. Although levels for many trace elements, e.g., Cu, Zn, Ni, Co, etc., are not as high as in the <2 µm fraction the geochemical contrast is higher. Also, and importantly, the <63 µm fraction can be recovered by sieving, and therefore is widely used, and could be used by contractors. The <2 µm fraction requires the samples to be centrifuged."

Thus, the potential datasets for compilation were limited to those meeting the following criteria:

1. GSC authorship
2. digital data available
3. till samples
4. <63 µm size fraction

Applying these criteria to the datasets catalogued in GSC Open File 4703, approximately 50 surveys were identified. The locations of these surveys are identified by green boxes on the maps that accompany this report (see below).

Analytical constraints

In order to compare analytical values between different surveys, the analytical techniques must be very similar. In particular, it is important to consider whether the technique gives a "partial" or a "total" analysis (see Open File 4703 for more details). For example, instrumental neutron activation analysis (INAA) involves analysing the solid material directly, without the need for dissolving the sample, and therefore gives a total analysis. Similarly, dissolution by a strong acid solution (usually based on hydrofluoric acid) leads to virtually the entire solid being dissolved and hence a "near-total" analysis. On the other hand, dissolution by a weaker acid solution (typically a mixture of hydrochloric and nitric acids, referred to as aqua regia) generally dissolves only part of the sample, and results in a "partial" analysis.

The instrumentation used to measure the concentrations of elements in the solution is less important than the dissolution technique. For example, it is reasonable to compare atomic absorption spectroscopic (AAS) data with inductively coupled plasma – atomic emission spectroscopic (ICP-AES) data, if the same dissolution technique was used.

The most common techniques used in the surveys were INAA and ICP-AES following an aqua regia digestion. Therefore, for this compilation, we looked at two categories of analytical techniques:

1. INAA
2. aqua regia, followed by ICP-AES or AAS

The elements analysed by these techniques are summarised in Table 2 below. Note that for any given survey, only a subset of these elements was analysed.

Table 2: List of elements and analytical techniques used in the surveys.

Element	Technique	
	INAA	Aqua regia
Ag	✓	✓
Al		✓
As	✓	✓
Au	✓	
Ba	✓	✓
Be		✓
Bi		✓
Br	✓	
Ca	✓	✓
Cd	✓	✓
Ce	✓	✓
Co	✓	✓
Cr	✓	✓
Cs	✓	
Cu		✓
Eu	✓	
Fe	✓	✓
Ga		✓
Hf	✓	
Hg	✓	✓
Ho	✓	
Ir	✓	
K		✓
La	✓	✓
Li		✓
Lu	✓	
Mg		✓
Mn		✓
Mo	✓	✓
Na	✓	✓
Nb		✓

Nd	✓	
Ni	✓	✓
P		✓
Pb		✓
Rb	✓	✓
Sb	✓	✓
Sc	✓	✓
Se	✓	
Sm	✓	
Sn	✓	✓
Sr	✓	✓
Ta	✓	✓
Tb	✓	
Te	✓	✓
Th	✓	
Ti		✓
Tl		✓
U	✓	✓
V		✓
W	✓	✓
Y		✓
Yb	✓	
Zn	✓	✓
Zr	✓	✓

Results

Twenty surveys were successfully compiled into a standardised format. The final output was a single table stored in an MS Access database. The raw data were obtained from the published GSC Open Files. The compiled surveys are summarised in Table 3.

Table 3: List of geochemical surveys compiled to create the data base for deriving national statistics.

Survey Key	Record count	Metadata hyperlink	Raw data hyperlink
3001	194	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=210001	Diskette to accompany GSC Open File 3091
3003	842	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=210003	Diskette to accompany GSC Open File 2823
3005	1827	http://gdr.nrcan.gc.ca/geochem/metadata_prj_e.php?key=210005	Open File 2270 CD-ROM
3008	136	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=210008	Diskette to accompany GSC Open File 2909
3013	227	http://gdr.nrcan.gc.ca/geochem/me	Diskette to accompany GSC

		tadata_svy_e.php?key=210013	Open File 3317
3018	2156	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=210018	Diskette to accompany GSC Open File 2118
3026	134	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=210026	Open File 4019 CD-ROM
3027	1931	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=210027	Diskette to accompany GSC Open File 3243
3032	923	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=210032	Diskette to accompany GSC Open File 2745
3041	133	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=210041	Diskette to accompany GSC Open File 3387
3042	112	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=210042	Diskette to accompany GSC Open File 3654
3044	86	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=210044	Diskette to accompany GSC Open File 3412
3052	2410	http://gdr.nrcan.gc.ca/geochem/metadata_prj_e.php?key=210040	Diskette to accompany GSC Open File 3213
3059	160	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=210059	Diskette to accompany GSC Open File 3360
3076	764	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=210299	Open File 4543 CD-ROM
5002	38	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=050002	Diskette to accompany GSC Open File 3269
5004	307	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=050004	Diskette to accompany GSC Open File 2246
5005	330	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=050005	Diskette to accompany GSC Open File 2560
11001	330	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=110001	Diskette to accompany GSC Open File 3348
11002	165	http://gdr.nrcan.gc.ca/geochem/metadata_svy_e.php?key=110002	Open File 3815 CD-ROM
	13205	Total Number of Samples.	

The final table contains 13205 records, corresponding to 13205 distinct samples. A few of the samples correspond to laboratory control references, and several hundred correspond to duplicates collected at the same site. There are 11565 distinct sites in the table.

Most of the source data required extensive manual manipulation to fit into a standardised format. Some problems were particularly common:

1. The map datum was very rarely specified. For data collected before the mid 1980s, it is safe to assume that the map datum is NAD27. For more recent surveys, the map datum could be either NAD27 or NAD83. Unspecified datums were assumed to be NAD27. In the compiled dataset, all of the geographic

coordinates are based on the NAD83 datum. NAD27 coordinates were converted to NAD83 using the NTv2 algorithm. If the NAD27 assumption is incorrect, then sample locations will be in error by up to 1 km.

2. Data below the determination limit were handled inconsistently in the original surveys. Sometimes, the determination limits were not specified. Sometimes, within the raw data listing, values below determination were adjusted to half of the determination limit. Analytical data become less accurate as they approach the determination limit, so it is important to know what that limit is. Detection limits for many analytical techniques varied from one survey to another.
3. Quality Assurance (QA) data (control references and duplicate analyses) were treated very differently from one survey to the next. Within the time constraints, it was not possible to assemble all of the QA data into a consistent format.
4. The raw data were often highly formatted within Excel spreadsheets. This was done to facilitate the production of printed reports. But it made it impossible to easily extract the raw data.

Geospatial data integration

Having compiled the 13205 records, comprising 11565 distinct sites, the final stage was to add geospatial attributes for each site. The goal of the study was to statistically analyse the variability in element concentrations in till samples from across the country, to get a sense of what "natural background" levels might be.

To facilitate this analysis, it is desirable to characterize each sample location, according to criteria which could reasonably be expected to influence the chemistry of the sample. Bedrock lithology is one obvious criterion to choose. Another potential criterion is ecological classification.

For bedrock lithology, there is no detailed lithological compilation available for the whole country. Wheeler et al.'s (1996) geological map compilation provides only a very crude lithological classification (see map 1). The Canadian landmass can be subdivided into 16 regions, each of which has a distinctive geological history (Whitmore et al., 1968). These regions can be used to classify each sample location. Wheeler et al. (1996) provided a digital map layer which can be used as a reduced classification of geological regions (just 7 distinct regions, corresponding to the areas of responsibility of the individuals who compiled the map). Although still very crude, this provides a slightly more refined classification than one based on lithology (see map 2). The relationship of Wheeler et al.'s 7 regions to the 16 regions of the usual classification is given in Table 4.

For ecological classification, we chose the ecozone / ecoprovince / ecoregion / ecodistrict system, described by Marshall and Schut (1999), and summarised in Table 5 (see map 3). The ecological classification is significantly influenced by the underlying geology.

Table 4: Geological Region classification

Whitmore et al. (1968)	Wheeler et al. (1996)	Category
Bear	Churchill	Canadian Shield
Slave	Churchill	Canadian Shield
Churchill	Churchill	Canadian Shield
Nain	Churchill	Canadian Shield
Superior	Superior	Canadian Shield
Southern	Superior	Canadian Shield
Grenville	Grenville	Canadian Shield
Cordilleran	Cordilleran	Phanerozoic orogen
Innuitian	Arctic	Phanerozoic orogen
Appalachian	Appalachian	Phanerozoic orogen
Arctic	Arctic	Phanerozoic platform
Interior	Cordilleran	Phanerozoic platform
Hudson	Hudson	Phanerozoic platform
St. Lawrence	Appalachian	Phanerozoic platform
Arctic	Arctic	Coastal plain
Pacific	Cordilleran	Coastal plain

Table 5: Ecological classification (after Marshall and Schut, 1999)

Classification unit	Number of units	Description
Ecozone	15	At the top of the hierarchy, it defines the ecological mosaic of Canada on a sub-continental scale. They represent an area of the earth's surface representative of large and very generalized ecological units characterized by interactive and adjusting abiotic and biotic factors. Canada is divided into 15 terrestrial ecozones.
Ecoprovince	53	A subdivision of an ecozone characterized by major assemblages of structural or surface forms, faunal realms, and vegetation, hydrology, soil, and macroclimate. For example, the Newfoundland ecoprovince (no. 6.4) is one of six ecoprovinces within the Boreal Shield Ecozone.
Ecoregion	194	A subdivision of an ecoprovince characterized by distinctive regional ecological factors, including climate, physiography, vegetation, soil, water, and fauna. For example, the Maritime Barrens ecoregion (no. 114) is one of nine ecoregions within the Newfoundland ecoprovince.
Ecodistrict	1021	A subdivision of an ecoregion characterized by a distinctive assemblage of relief, landforms, geology, soil, vegetation, water bodies and fauna. For example, the Jeddore Lake ecodistrict (no. 473) is one of five within the Maritime Barrens ecoregion.

The ecological and geological map layers were imported into MapInfo GIS software, along with the 11565 sites. It was then straightforward to assign ecological and geological attributes to each site. The sites were saved to a new Microsoft Access database, containing columns with the added attributes. This updated database was used for the subsequent statistical analysis reported in Part 3.

Table 6 lists the number of samples which lie within each of the geological regions, broken down by survey. Most surveys sampled either entirely or overwhelmingly from just a single region, the only exception being survey 3052 (southern Labrador).

Table 7 is similar to Table 6. In this case, the samples are classified by ecozone and ecoregion.

Table 6: Classification of sample sites by geological region

Survey Key	Region	Sample Count
3001	Churchill	194
3003	Appalachian	842
3005	Cordillera	1827
3008	Cordillera	136
3013	Churchill	199
3018	Churchill	2155
3026	Churchill	133
3027	Churchill	1929
3032	Cordillera	808
3032	Superior	8
3041	Churchill	133
3042	Churchill	112
3044	Churchill	84
3052	Churchill	1728
3052	Grenville	301
3052	Superior	209
3059	Arctic	2
3059	Churchill	158
3076	Churchill	732
3076	Hudson	3
5002	Superior	38
5004	Appalachian	307
5005	Appalachian	330
11001	Churchill	320
11001	Cordillera	7
11002	Cordillera	165

Table 7: Classification of sample sites by ecozone and ecoregion

Survey Key	EcoZone		EcoRegion		Sample Count
	ID	Name	ID	Name	
3001	3	Southern Arctic	41	Takijua Lake Upland	184
3001	5	Taiga Shield	68	Coppermine River Upland	10
3003	6	Boreal Shield	108	Long Range Mountains	42
3003	6	Boreal Shield	112	Central Newfoundland	799
3003	6	Boreal Shield	114	Maritime Barrens	1
3005	14	Montane Cordillera	199	Omineca Mountains	551
3005	14	Montane Cordillera	202	Fraser Plateau	596
3005	14	Montane Cordillera	203	Fraser Basin	680
3008	14	Montane Cordillera	202	Fraser Plateau	120
3008	14	Montane Cordillera	204	Chilcotin Ranges	16
3013	3	Southern Arctic	41	Takijua Lake Upland	147
3013	5	Taiga Shield	68	Coppermine River Upland	52
3018	5	Taiga Shield	71	Selwyn Lake Upland	92
3018	6	Boreal Shield	88	Churchill River Upland	2062
3018	6	Boreal Shield	89	Hayes River Upland	1
3026	5	Taiga Shield	68	Coppermine River Upland	43
3026	5	Taiga Shield	69	Tazin Lake Upland	90
3027	3	Southern Arctic	44	Dubwant Lake Plain/Upland	5
3027	3	Southern Arctic	45	Maguse River Upland	1924
3032	6	Boreal Shield	91	Lake of the Woods	9
3032	9	Boreal Plains	139	Mid-Boreal Uplands	72
3032	9	Boreal Plains	145	Western Alberta Upland	4
3032	9	Boreal Plains	148	Mid-Boreal Lowland	34
3032	9	Boreal Plains	149	Boreal Transition	110
3032	9	Boreal Plains	155	Interlake Plain	42
3032	10	Prairies	156	Aspen Parkland	212
3032	10	Prairies	157	Moist Mixed Grassland	113
3032	10	Prairies	158	Fescue Grassland	22
3032	10	Prairies	159	Mixed Grassland	161
3032	10	Prairies	160	Cypress Upland	8
3032	10	Prairies	162	Lake Manitoba Plain	24
3032	10	Prairies	163	Southwest Manotoba Uplands	5
3041	3	Southern Arctic	41	Takijua Lake Upland	133
3042	3	Southern Arctic	41	Takijua Lake Upland	112
3044	3	Southern Arctic	36	Coronation Hills	37
3044	3	Southern Arctic	38	Bathurst Hills	2
3044	3	Southern Arctic	41	Takijua Lake Upland	45
3052	5	Taiga Shield	74	New Quebec Central Plateau	209
3052	5	Taiga Shield	75	Ungava Bay Basin	176
3052	5	Taiga Shield	76	George Plateau	7
3052	5	Taiga Shield	77	Kingarutuk-Fraser River	462
3052	5	Taiga Shield	78	Smallwood Reservoir-Michikamau	921
3052	5	Taiga Shield	79	Coastal Barrens	108

3052	5	Taiga Shield	80	Mecatina River	213
3052	5	Taiga Shield	84	Harp Lake	21
3052	5	Taiga Shield	85	Nipishish Lake	14
3052	6	Boreal Shield	101	Central Laurentians	46
3052	6	Boreal Shield	105	Lake Melville	61
3059	3	Southern Arctic	36	Coronation Hills	22
3059	3	Southern Arctic	38	Bathurst Hills	7
3059	3	Southern Arctic	41	Takijua Lake Upland	131
3076	1	Arctic Cordillera	5	Baffin Mountains	14
3076	1	Arctic Cordillera	6	Baffin Islands Coastal Lowlands	1
3076	2	Northern Arctic	23	Melville Peninsula Plateau	196
3076	2	Northern Arctic	24	Baffin Island Uplands	522
3076	2	Northern Arctic	25	Foxe Basin Plain	3
5002	5	Taiga Shield	72	La Grande Hills	35
5002	5	Taiga Shield	73	Southern Ungava Peninsula	3
5004	7	Atlantic Maritime	118	Northern New Brunswick Highlands	78
5004	7	Atlantic Maritime	119	New Brunswick Highlands	229
5005	7	Atlantic Maritime	118	Northern New Brunswick Highlands	124
5005	7	Atlantic Maritime	119	New Brunswick Highlands	206
11001	5	Taiga Shield	69	Tazin Lake Upland	317
11001	6	Boreal Shield	87	Athabasca Plain	1
11001	9	Boreal Plains	136	Slave River Lowland	9
11002	4	Taiga Plains	64	Hay River Lowland	1
11002	4	Taiga Plains	66	Muskwa Plateau	81
11002	9	Boreal Plains	137	Clear Hills Upland	3
11002	12	Boreal Cordillera	183	Northern Canadian Rocky Mountains	80

List of maps

1. 1:7 500 000 map of Canada, showing sample locations, underlain by bedrock lithology.

2. 1:7 500 000 map of Canada, showing sample locations, underlain by geological regions.

3. 1:7 500 000 map of Canada, showing sample locations, underlain by ecozones.

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Paul Stacey performed the bulk of the data compilation. Nelson O'Driscoll assisted in the gathering of details concerning analytical methodologies. Paul Stacey also managed all aspects of the GIS integration.

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Part 3: Background calculations for nine elements in soil and till across Canada

by R.G. Garrett, Geological Survey of Canada, ESS

Introduction

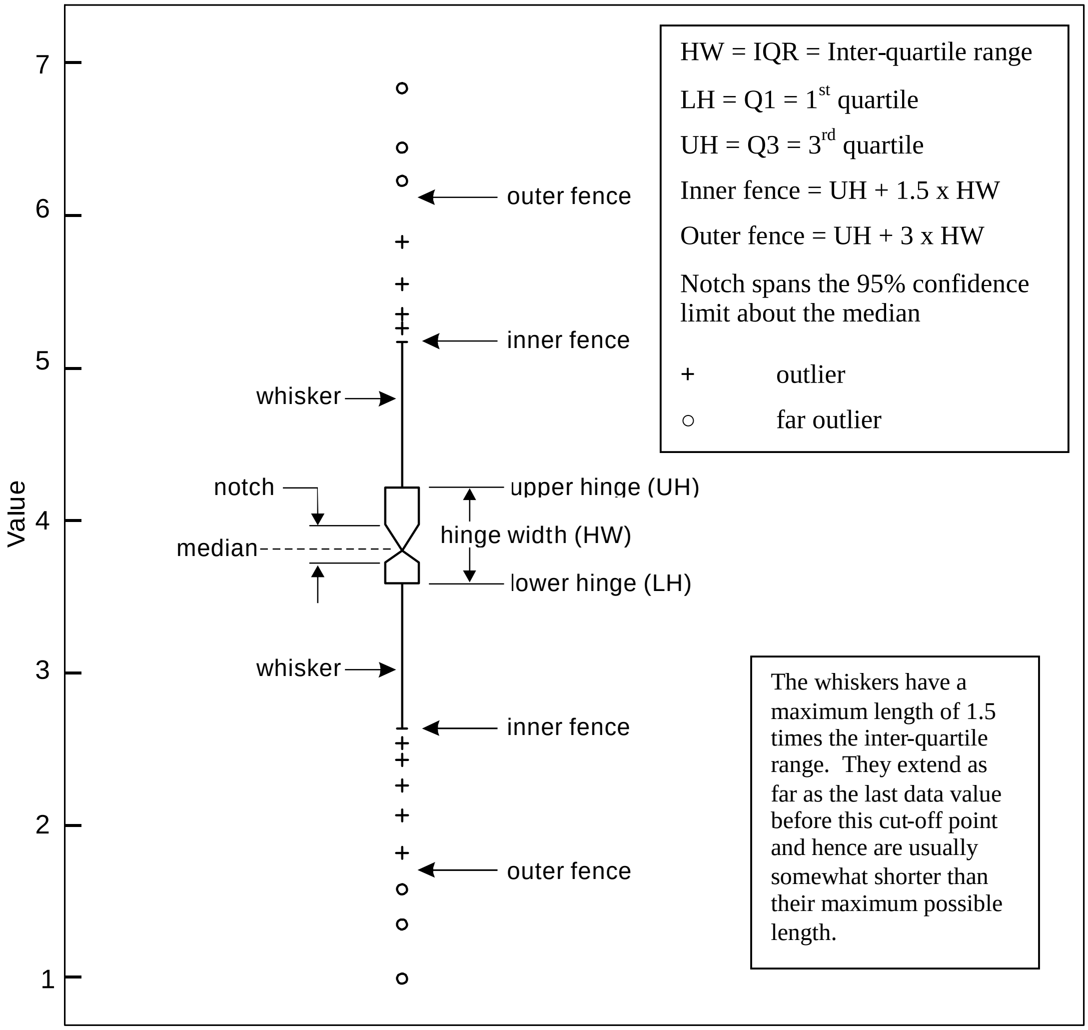
A data set of geochemical data for soils, as described in Part 2, was used as the starting point for statistical analyses. This data set comprised 13205 records. The fields for INA_As and SPEC_Co (AAS & ICP-ES) data were further checked to determine data availability for the two types of analyses. A total of 301 records contained no information for either of these fields, and a total of 12904 records contained data for either or both of these fields. A working subset of 12904 records for As, Cr, Th, U, Co, Cu, Ni, Pb and Zn was exported from Microsoft Access and imported into S-Plus (Insightful, 2001, 2002). INA analyses were used for As, Cr, Th and U. Spectroscopic analyses were used for Co, Cu, Ni, Pb and Zn. To keep variable names to a consistent length SPEC was changed to ICP.

Data preparation

Summary statistics were prepared for the 9 selected elements. These took two forms: 1) a histogram, cumulative probability plot and summary statistics display; and 2) a set of four plots: a histogram, Tukey boxplot, an empirical cumulative distribution plot, and a cumulative probability plot. The Tukey boxplot uses a criterion based on ‘normal’ theory to identify outliers. The outliers are divided into two groups, near outliers and far outliers (separated by the outer fence); the former are plotted as crosses, and the latter as circles (O for outlier). The inner and outer fences used to identify outliers are based on the middle 50% of the data, and their calculation is thus a robust procedure insensitive to the presence of extreme outliers. The fences are set to 1.5 and 3 times the interquartile range (a.k.a. hinge width) above the 3rd quartile (upper hinge) or below the 1st quartile (lower hinge). The notches in the box indicate the 95% confidence limits on the median. Velleman and Hoaglin (1981) explain the statistical construction of boxplots.

The plots are presented on a logarithmic scale as the data span in excess of 2 orders of magnitude for all elements, and 3 orders for As, Cr, Co, Cu, Ni and Zn. The calculations for the location of the Tukey fences were undertaken in logarithmic units in order to obtain symmetry for the middle 50% of the data.

Figure 2 Cartoon diagram of a Tukey boxplot



Element by element analysis - entire data set

Arsenic

(see p31 for plots): Some 7% of the data are less than the detection limit (0.5 mg/kg). The data are negatively skewed with evidence of at least two main data populations (≈ 9 mg/kg [95%] & ≈ 80 mg/kg [5%]) and some strongly anomalous data, >150 mg/kg. All tills were collected from areas with no industrial development except for one survey at Yellowknife, N.W.T. Except in the Yellowknife survey, one would not expect the tills to be contaminated by anthropogenic processes. The Tukey upper inner fence, one estimate of the upper limit of background variation with limited influence from mineral occurrences, is 85 mg/kg, corresponding to the 99th percentile.

Chromium

(p32): There are three different detection limits in the data (1, 5 & 20 mg/kg). The data are strongly bimodal (≈ 60 mg/kg [99%] & ≈ 800 mg/kg [1%]). It is probable that the upper mode represents glacial tills derived from ultramafic rocks. A few highly anomalous samples have >1000 mg/kg. The Tukey upper inner fence is 310 mg/kg, however, this estimate does not take the presence of ultramafic source rocks into account as they represent less than 1% of the total data set. Thus for an area without ultramafic rocks 310 mg/kg is a reasonable estimate. The large number of near outliers in the Tukey boxplot reflects the presence of ultramafic rocks in the survey areas. If ultramafic rocks are present a locally derived upper limit of background would be required, that would probably be ≈ 1000 mg/kg.

Cobalt

(p33): The cobalt data have a detection limit of 0.5 mg/kg, with <0.1% of the data reported at levels less than the detection limit. Up to 10 mg/kg the data are reported to the closest mg/kg, resulting in distinctive clustered patterns in the histogram and probability plots. There is evidence of bimodality (≈ 5 mg/kg [75%] & ≈ 40 mg/kg [25%]) and the presence of a limited number of anomalous outliers > 90 mg/kg. The Tukey upper inner fence estimate of the upper limit of background is 95 mg/kg; no data exceeds this value.

Copper

(p34): The copper data have a detection limit of 1 mg/kg, and some 0.8% of the data are below that limit. Up to 10 mg/kg the data are reported to the nearest mg/kg. The data are likely bimodal (5 mg/kg [50%] & 50 mg/kg [50%]), and there are outliers present, >400 mg/kg. The Tukey upper inner fence estimate of the upper limit of background is 368 mg/kg. An inspection of the cumulative probability plot suggests that the upper limit of background, including Cu-rich source rocks and Cu-bearing mineral occurrences is 500 mg/kg.

Lead

(p35): Some 4% of the data are less than the detection limit of 2 mg/kg, and the data are reported to the nearest mg/kg up to 20 mg/kg. The data are probably bimodal (≈ 7 mg/kg [99%] & 60 mg/kg [1%]) and outliers are present >80 mg/kg. The Tukey upper inner fence estimate of the upper limit of natural background is 33 mg/kg. However, an upper limit of 80 mg/kg would include Pb-enriched igneous rocks, and likely result in only samples influenced by Pb-bearing mineral occurrences being above the upper limit.

Nickel

(p36): The detection limit is 1 mg/kg with some 0.15% of the data falling below that limit. Up to 10 mg/kg the data are reported to the nearest mg/kg. The data appear to be weakly bimodal, with anomalous sites where Ni > 400 mg/kg. The Tukey upper inner fence estimate of the upper limit of background is 214 mg/kg. This estimate is probably low and does not reflect the presence of Ni-enriched rocks or Ni-bearing mineral occurrences. A figure of some 400 mg/kg is probably more realistic.

Thorium

(p37): There are 4 samples with Th levels below the detection limit of 0.2 mg/kg. There is some evidence for polymodality (≈ 8 mg/kg [60%] & ≈ 20 mg/kg [40%]), best seen in the histogram. The Tukey upper inner fence estimate of the upper limit of background variation is 63 mg/kg, corresponding to the 99th percentile.

Uranium

(p38): Some 3% of the data are less than the detection limit of 0.5 mg/kg, there are measured values in the

0.3 to 0.5 mg/kg range. There is evidence of bimodality (≈ 3 mg/kg [98%] & ≈ 15 mg/kg [2%]) and positive skewness in the data, and the presence of outliers >45 mg/kg. In the absence of any anthropogenic sources the anomalous U data are most probably due to the presence of U-bearing mineral occurrences. The Tukey upper inner fence estimate of the upper limit of geochemical background is 9.3 mg/kg. However, this estimate is low due to the skewness and bimodality of the data. A more realistic estimate would be 42 mg/kg that would accommodate the presence of U-rich granitic rocks of many geological ages and uraniferous Precambrian sediments.

Zinc

(p39): A small fraction of the data, <0.1%, are below the detection limit of 2 mg/kg. Up to 10 mg/kg the data are reported to the nearest mg/kg. The data are bimodal (25 mg/kg [60%] & 90 mg/kg [40%]), with the upper population being positively skewed. This skewness becomes evident above 200 mg/kg, and a group of clear outliers exists above 400 mg/kg. The bimodal distribution probably reflects: 1) a lower background resulting from carbonate and coarse clastic sediments and their metamorphic derivatives and felsic igneous rocks; and 2) the upper background related to mafic igneous rocks and shales and their metamorphic equivalents. The skewness in the upper distribution reflects the presence of Zn-bearing mineral occurrences and their host rocks. The Tukey upper inner fence estimate of the upper limit of background is 408 mg/kg, in general agreement with a visual inspection of the cumulative probability plot.

These interpretations of the data and provisional ranges of natural background are summarised in Table 8. The final column in Table 8 gives an upper limit that would be more reasonable in areas of mineralisation.

Table 8 Provisional background ranges of selected elements in till

Element	Provisional Range mg/kg	Local Upper Limit mg/kg
As	<0.5 – 85	
Cr	5 – 310	1000 (ultramafic bedrock)
Co	1 – 95	
Cu	<1 – 370	500 (mineralised bedrock)
Ni	1 – 210	400 (ultramafic bedrock)
Pb	<2 – 80	
Th	1 – 63	
U	1 – 9	42 (uraniferous granites or sandstones)
Zn	2 – 410	

Element by element analysis - subdivided by structural province, ecozone, ecoregion and survey

The data may be subdivided through their classification into geological and ecological frameworks. The geological framework is very general and based on Canada's structural provinces; the data fall into 7 provinces, and a number of unclassified sample sites. The classification into the ecological framework results in the sites being classified into 11 EcoZones, 56 EcoRegions and 279 EcoDistricts. Tukey boxplots were prepared for the data subdivided by structural province, EcoZone and EcoRegion. Summary statistics have not been computed for the data divided by the above subdivisions.

The data break down as follows:

Geologic Province	'Null'	Appal.	Arctic	Church.	W Cord	Grenv.	Hudson	Super.
N	340	1479	2	7582	2943	301	3	254

where: Appal. = the Appalachians; Arctic = Arctic Platform; Church. = Churchill; W Cord = Western Cordillera; Grenv. = Grenville; Hudson = Hudson Platform; and Super. = Superior.

EcoZone	1	2	3	4	5	6	7	9	10	12	14
N	15	721	2709	82	769	2770	637	274	545	80	1963

where: 1 = Arctic Cordillera; 2 = Northern Arctic; 3 = Southern Arctic; 4 = Taiga Plains; 5 = Taiga Shield; 6 = Boreal Shield; 7 = Atlantic Maritime; 9 = Boreal Plains; 10 = Prairies; 12 = Boreal Cordillera; and 14 = Montane Cordillera.

The 340 'Null' samples in the breakdown by geologic province correspond to samples for which there are no geographic coordinates (i.e. laboratory quality control samples).
The number of samples falling into the 56 EcoRegions included in the surveys range from 1 to 1810 (18 have sample sizes ≤ 15), and from 1 to 1429 for the 279 EcoDistricts. Due to the small statistical sample sizes statistics or boxplots have not been prepared for the division by EcoDistricts; 215 EcoDistricts have sample sizes ≤ 15. Descriptions of each of the ecoregions can be found on Environment Canada's web site (http://www.ec.gc.ca/soer-ree/English/Framework/Nardesc/TOC.cfm).

Tukey boxplots for the data subdivided by: Geological Province, EcoZone, EcoRegion and Survey are presented on pages 36 to 53 for each of the nine elements.

A number of notable patterns are observable in the data subdivided by Structural Province:

- The mid 50% of the data for Cr are remarkably consistent across the sampled Structural Provinces, though many of the medians are significantly different from one another. The similarity of background variations provides evidence that the Cr, and likely all of the other INA analyses are consistent in a QA/QC sense across the separate surveys;
- The pattern for U is similar to that of Cr, except that the Appalachian data shows greater variability than any other Structural Province;
- The mid 50% of data for As and Cu in samples from the Appalachians and Western Cordillera are at levels higher than the same fraction of the data from the Churchill, Grenville and Superior Provinces. The pattern for Zn is generally similar, but the Appalachian data shows greater variability than any other Structural Province. The data for Co are again generally similar, except that Co in Superior Province samples is elevated relative to the Churchill and Grenville Provinces;
- Conversely, Th data shows the opposite pattern for the Western Cordillera, the Appalachian data shows greater variability than any other Structural Province;

- The mid 50% of data for Ni are elevated in samples from the Western Cordillera and Superior Provinces relative to the others; and
- The mid 50% of the data for Pb is higher in the Appalachian Province than in the other Structural Provinces.

The data were compiled from 20 separate surveys as per Table 3 in Part 2. There was not a consistent set of control reference materials available, so QA/QC studies were not possible to ensure that the apparent differences following geological and ecostratification division are real and not partly due to analytical or sampling inconsistency. Therefore a set of plots was prepared that present the data subdivided by the separate surveys, to illustrate the survey-by-survey variability.

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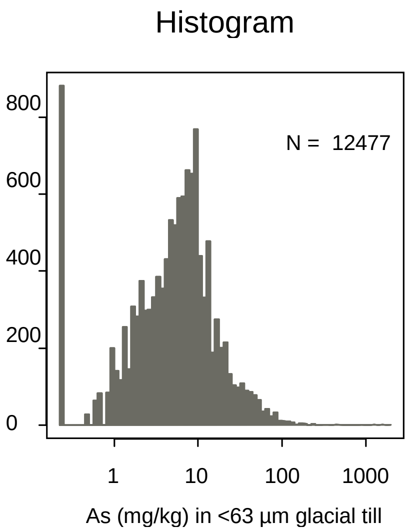
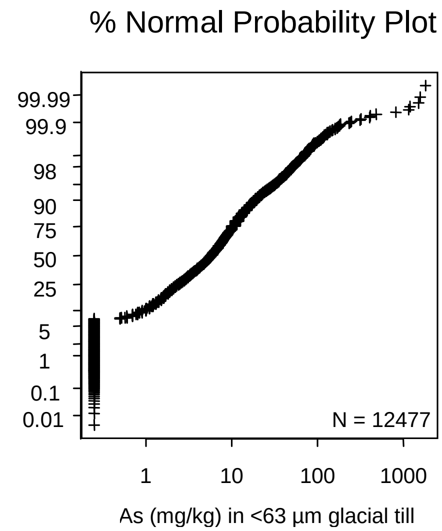
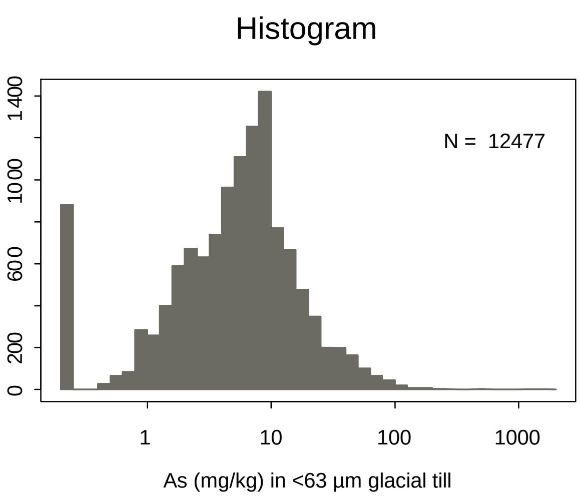
Figure 3 Arsenic summary statistics

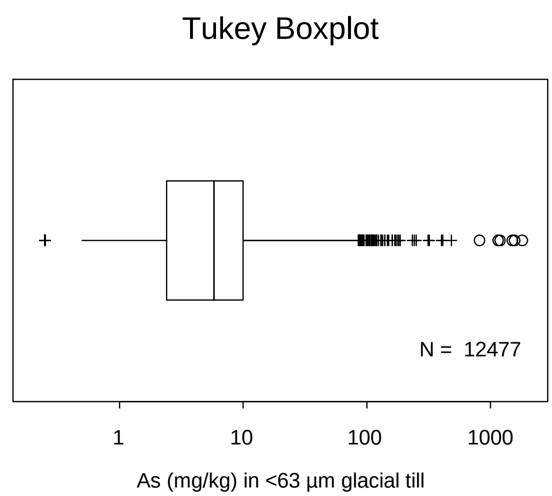


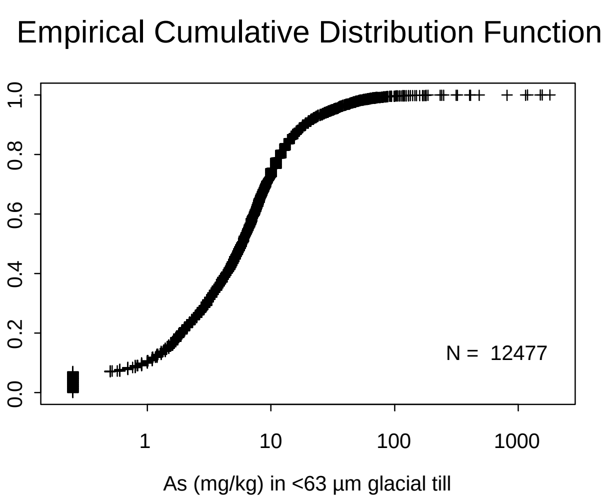
Summary Statistics

Number of Observations	12477
Maximum	1800
98th Percentile	51
95th Percentile	31.58
90th Percentile	19
3rd Quartile	10
2nd Quartile - Median	5.8
1st Quartile	2.4
10th Percentile	1
5th Percentile	0.25
2nd Percentile	0.25
Minimum	0.25
Median Abs. Deviation	5.63
IQR Estimate of Std. Dev.	5.6
Mean	9.97
Standard Deviation	33.7
Coeff. of Variation, %	338









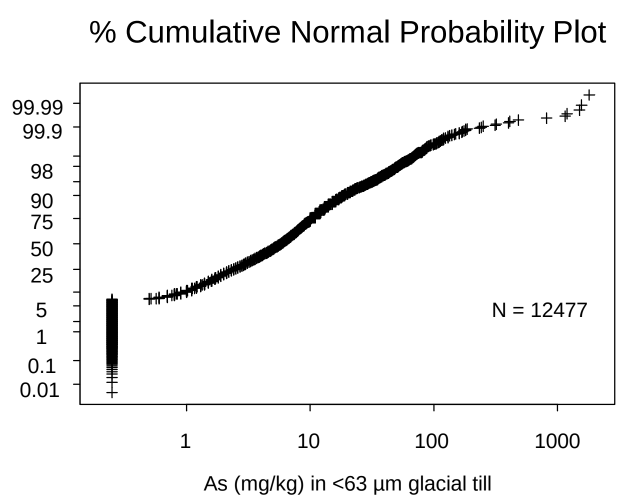
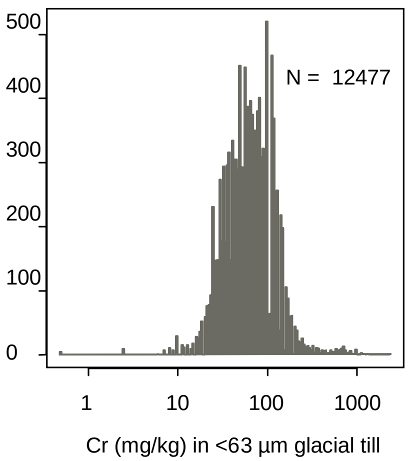


Figure 4 Chromium summary statistics

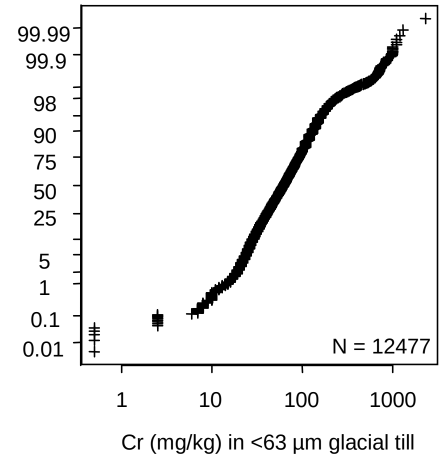
Histogram



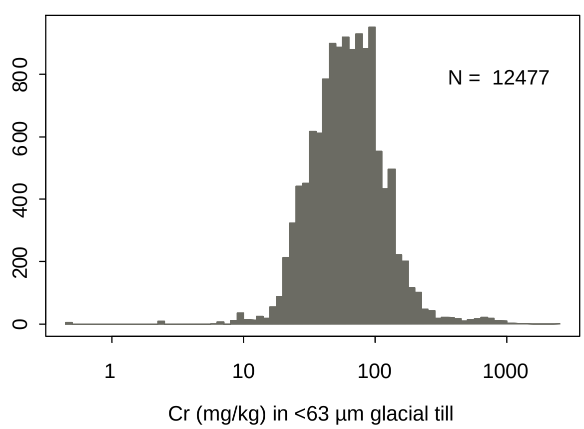
Summary Statistics

Number of Observations	12477
Maximum	2300
98th Percentile	240
95th Percentile	160
90th Percentile	130
3rd Quartile	93
2nd Quartile - Median	62
1st Quartile	41
10th Percentile	28
5th Percentile	24
2nd Percentile	15
Minimum	0.5
Median Abs. Deviation	37.1
IQR Estimate of Std. Dev.	38.3
Mean	78
Standard Deviation	79
Coeff. of Variation, %	101

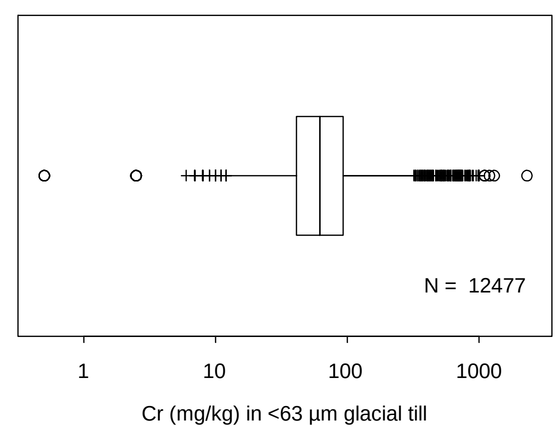
% Normal Probability Plot



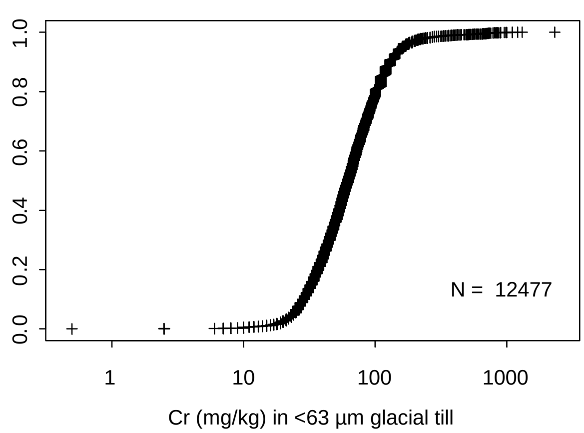
Histogram



Tukey Boxplot



Empirical Cumulative Distribution Function



% Cumulative Normal Probability Plot

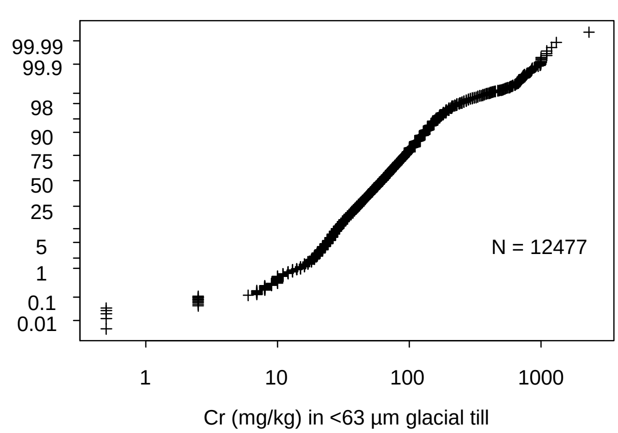
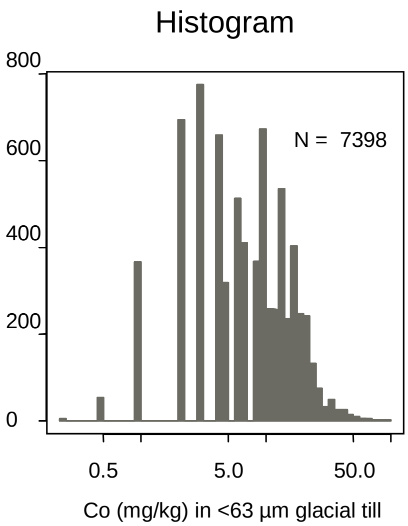
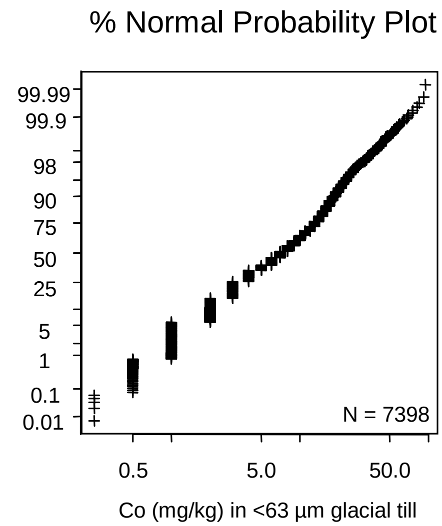


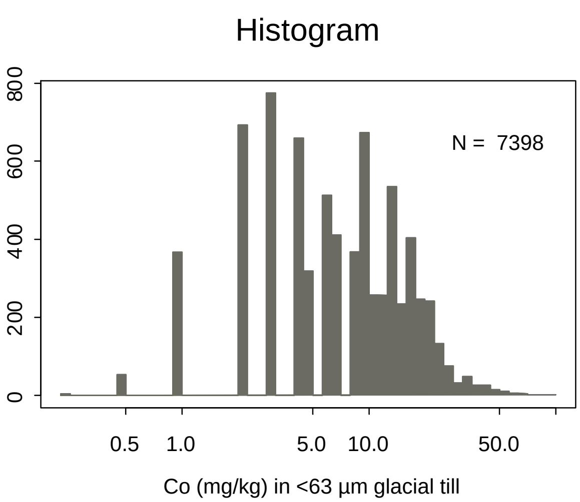
Figure 5 Cobalt summary statistics

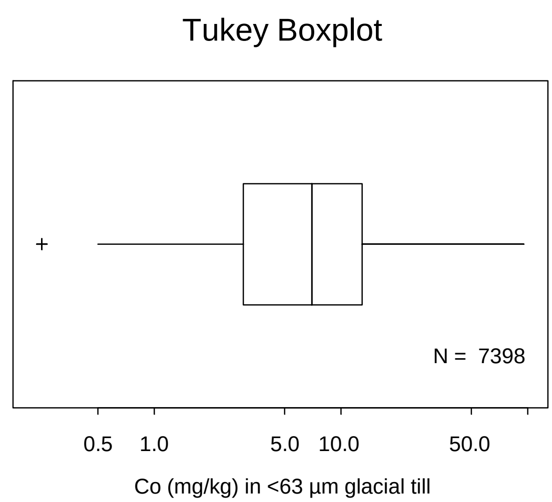


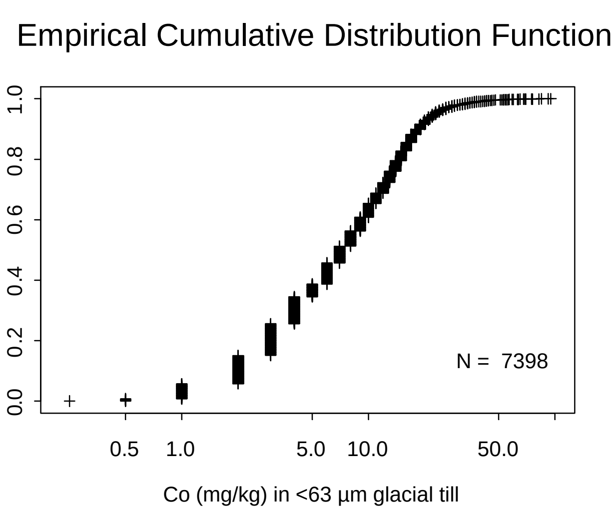
Summary Statistics

Number of Observations	7398
Maximum	95
98th Percentile	31
95th Percentile	23
90th Percentile	19
3rd Quartile	13
2nd Quartile - Median	7
1st Quartile	3
10th Percentile	2
5th Percentile	1
2nd Percentile	1
Minimum	0.25
Median Abs. Deviation	5.93
IQR Estimate of Std. Dev.	7.36
Mean	9.3
Standard Deviation	8
Coeff. of Variation, %	86









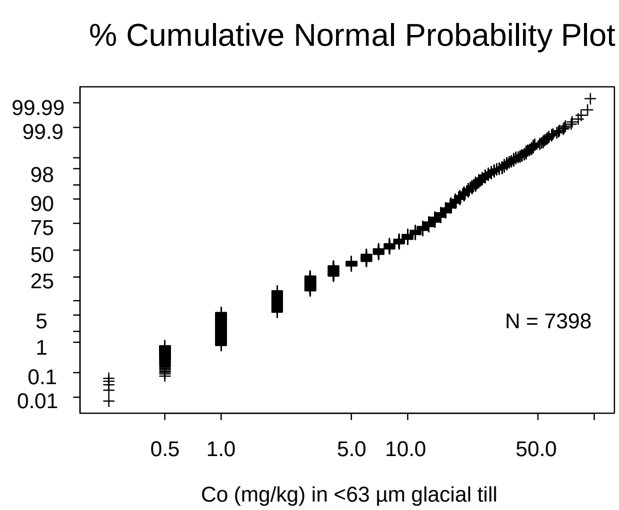
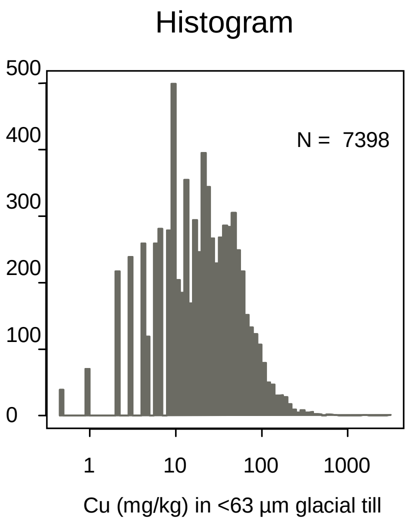
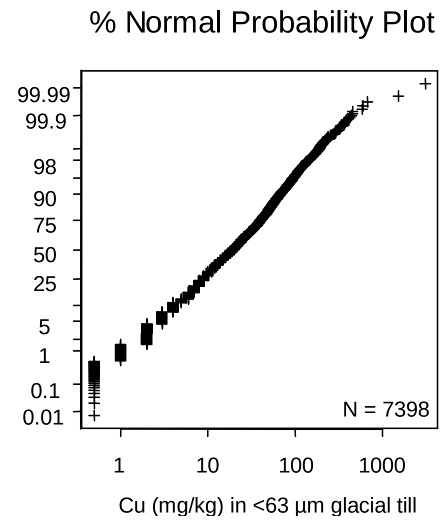


Figure 6 Copper summary statistics



Summary Statistics

Number of Observations	7398
Maximum	3113
98th Percentile	142.1
95th Percentile	95
90th Percentile	68
3rd Quartile	40
2nd Quartile - Median	19
1st Quartile	9
10th Percentile	4
5th Percentile	3
2nd Percentile	1
Minimum	0.5
Median Abs. Deviation	17.8
IQR Estimate of Std. Dev.	22.8
Mean	31.9
Standard Deviation	55.9
Coeff. of Variation, %	176



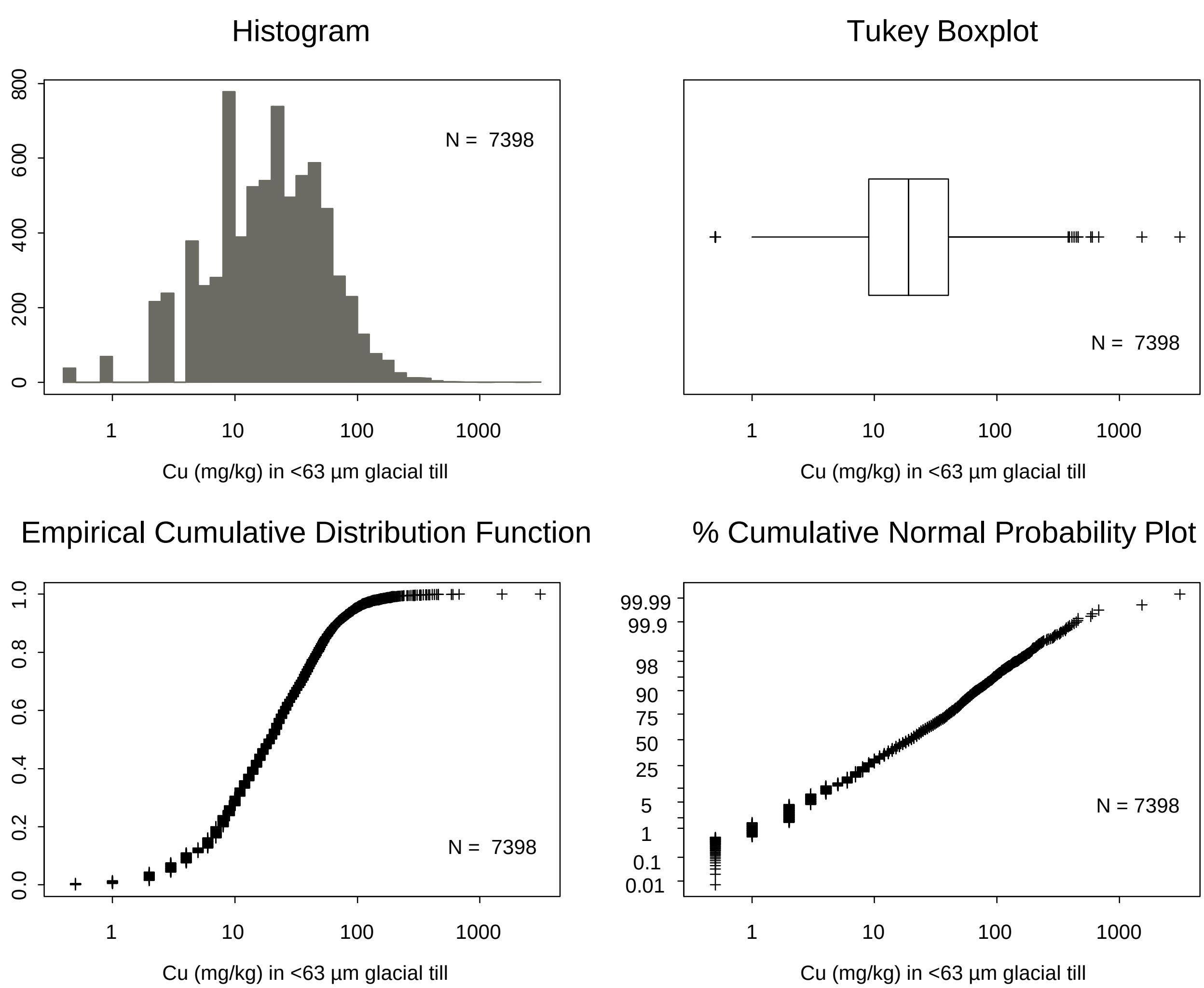


Figure 7 Lead summary statistics

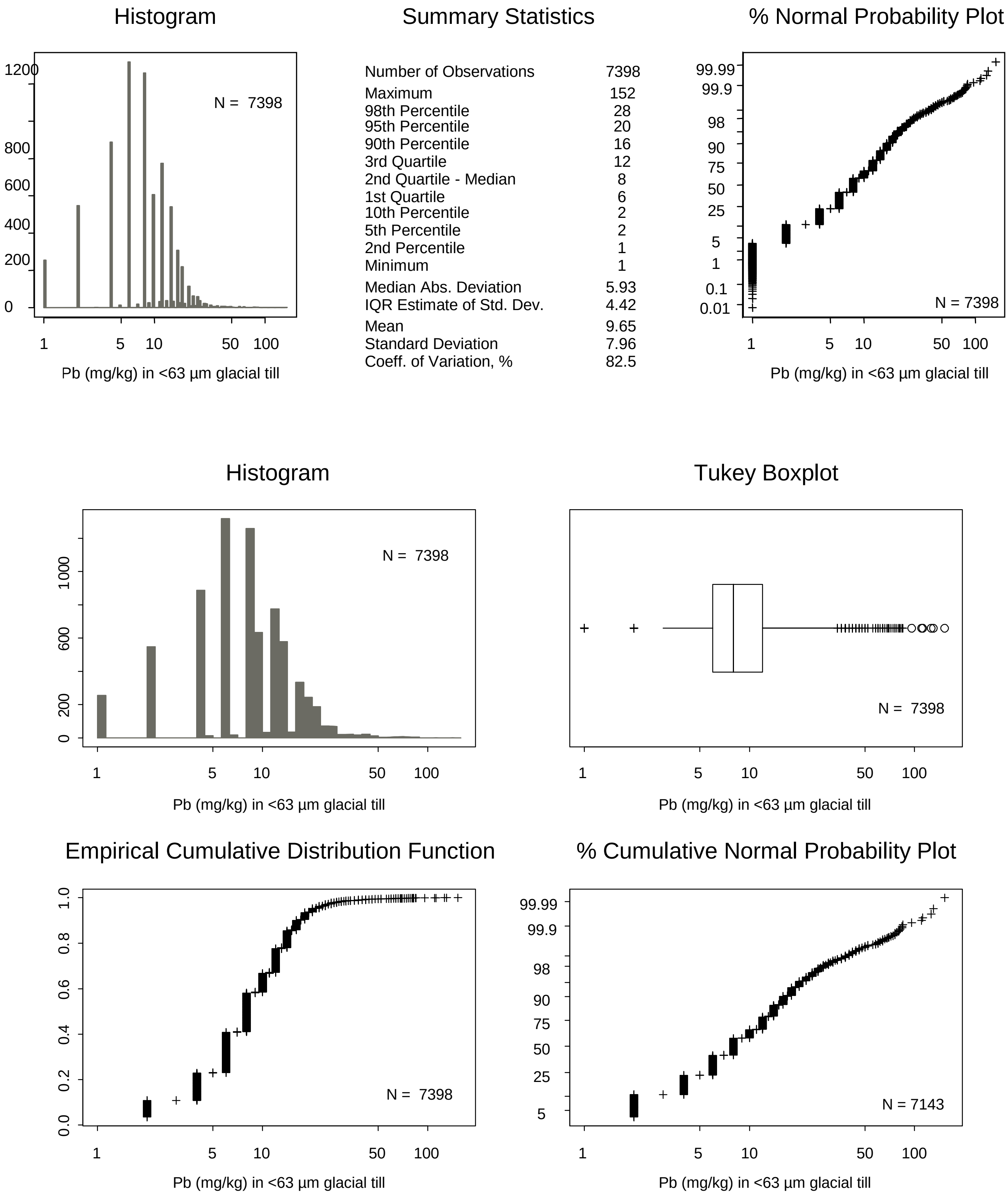
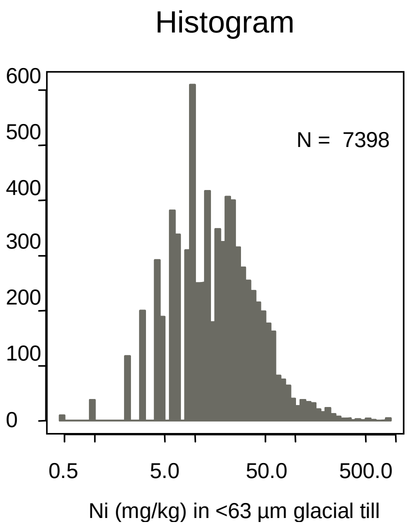
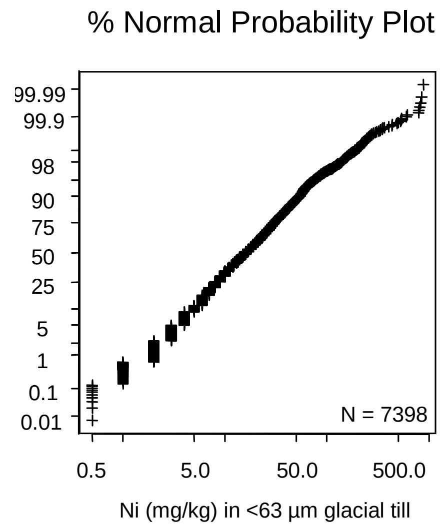


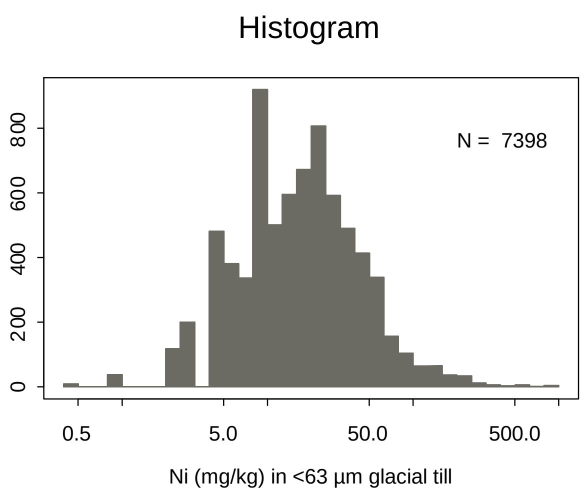
Figure 8 Nickel summary statistics

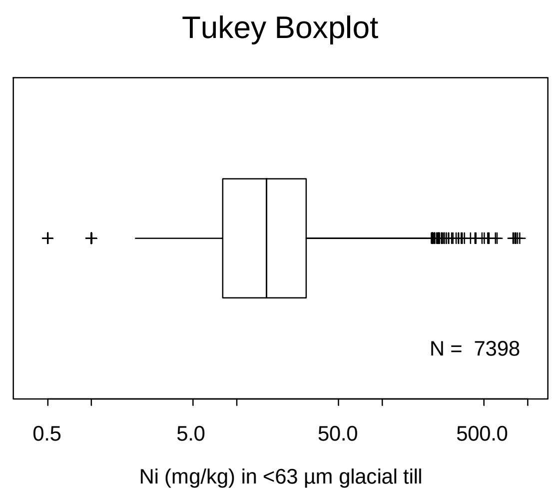


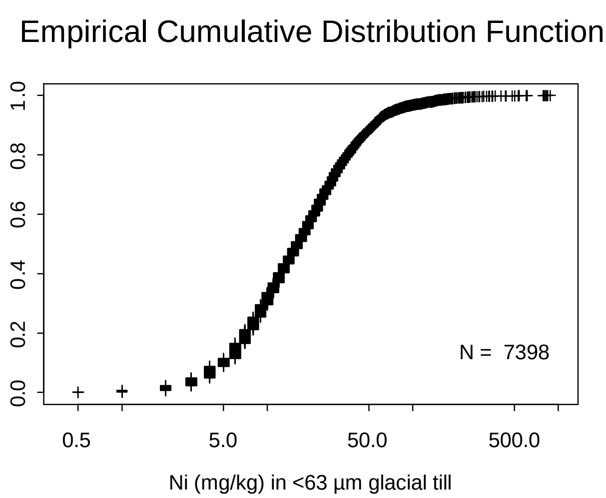
Summary Statistics

Number of Observations	7398
Maximum	881
98th Percentile	139
95th Percentile	75
90th Percentile	54
3rd Quartile	30
2nd Quartile - Median	16
1st Quartile	8
10th Percentile	5
5th Percentile	4
2nd Percentile	2
Minimum	0.5
Median Abs. Deviation	13.3
IQR Estimate of Std. Dev.	16.2
Mean	26.8
Standard Deviation	42.8
Coeff. of Variation, %	160









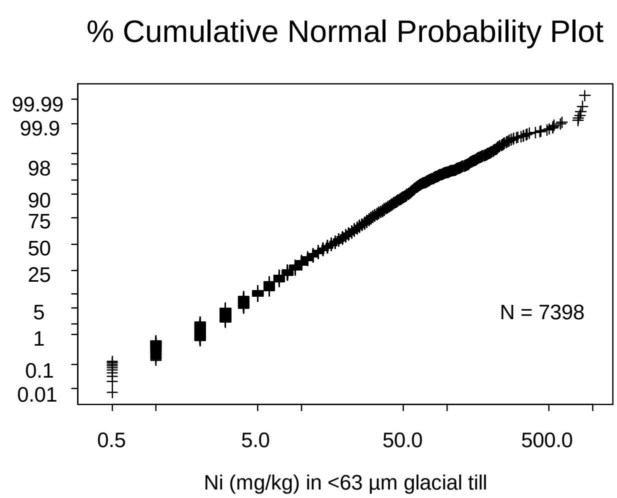
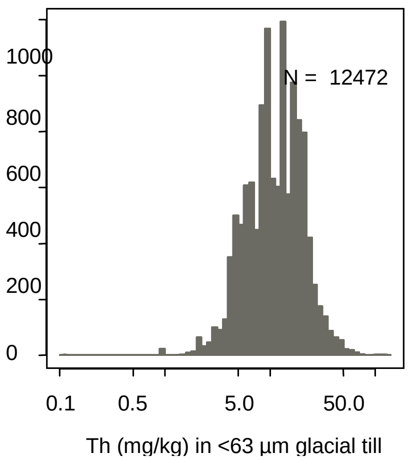


Figure 9 Thorium summary statistics

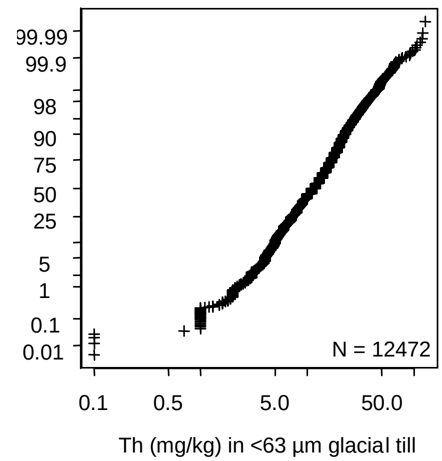
Histogram



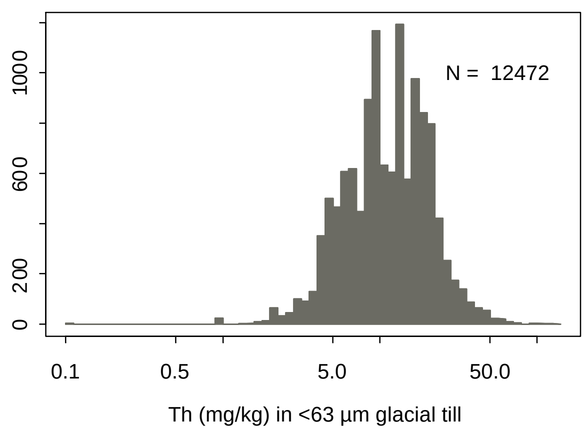
Summary Statistics

Number of Observations	12472
Maximum	128
98th Percentile	36.6
95th Percentile	28
90th Percentile	22.79
3rd Quartile	17
2nd Quartile - Median	11.9
1st Quartile	7.1
10th Percentile	5
5th Percentile	4
2nd Percentile	2.2
Minimum	0.1
Median Abs. Deviation	7.27
IQR Estimate of Std. Dev.	7.29
Mean	13.2
Standard Deviation	8.71
Coeff. of Variation, %	65.8

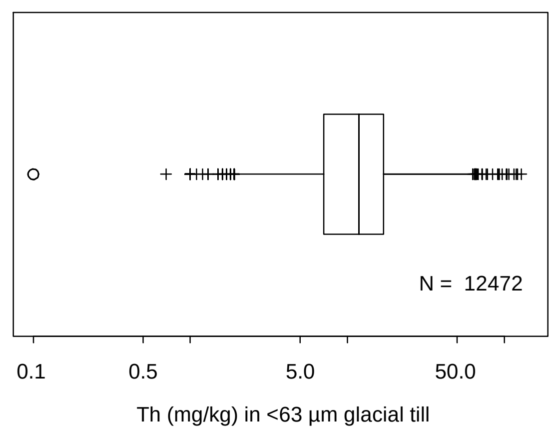
% Normal Probability Plot



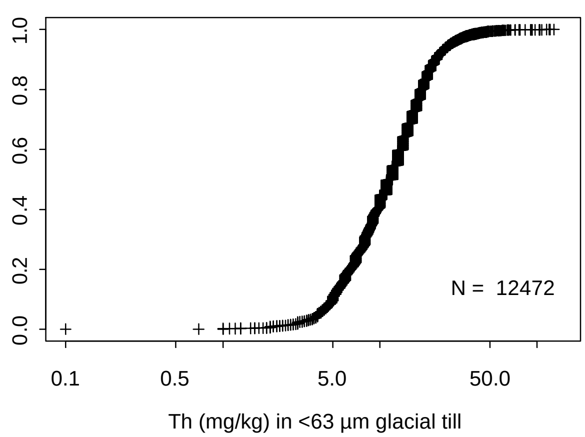
Histogram



Tukey Boxplot



Empirical Cumulative Distribution Function



% Cumulative Normal Probability Plot

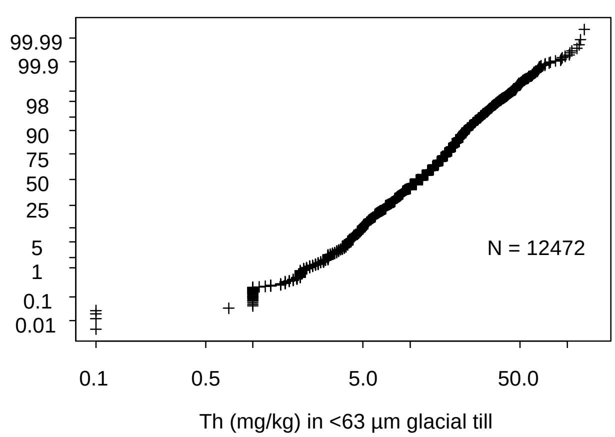
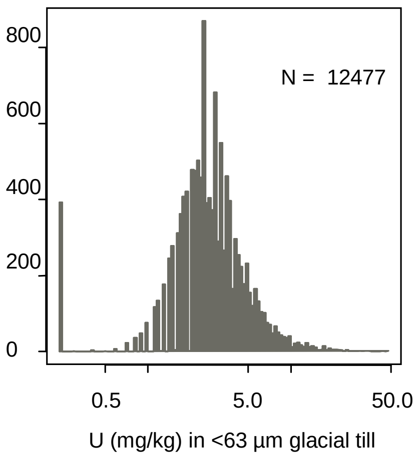


Figure 10 Uranium summary statistics

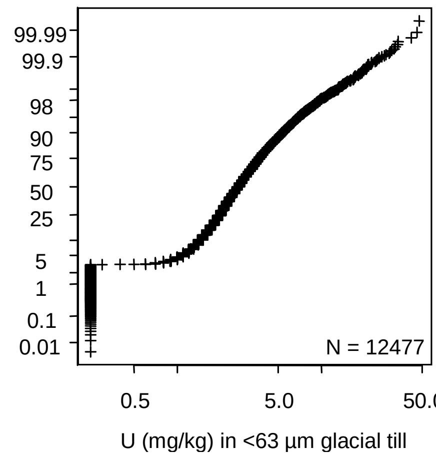
Histogram



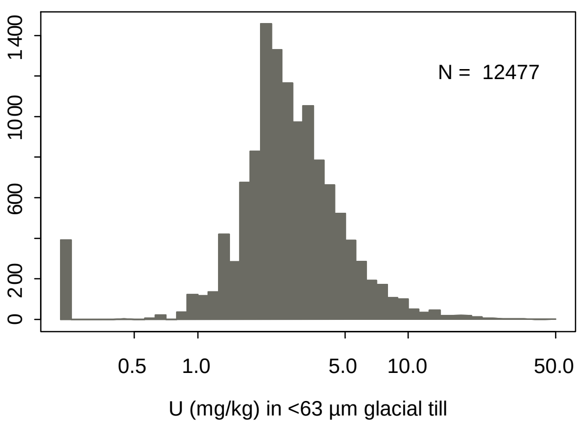
Summary Statistics

Number of Observations	12477
Maximum	47.6
98th Percentile	9.8
95th Percentile	6.9
90th Percentile	5.4
3rd Quartile	3.7
2nd Quartile - Median	2.7
1st Quartile	2
10th Percentile	1.4
5th Percentile	1.1
2nd Percentile	0.25
Minimum	0.25
Median Abs. Deviation	1.19
IQR Estimate of Std. Dev.	1.25
Mean	3.2
Standard Deviation	2.43
Coeff. of Variation, %	76

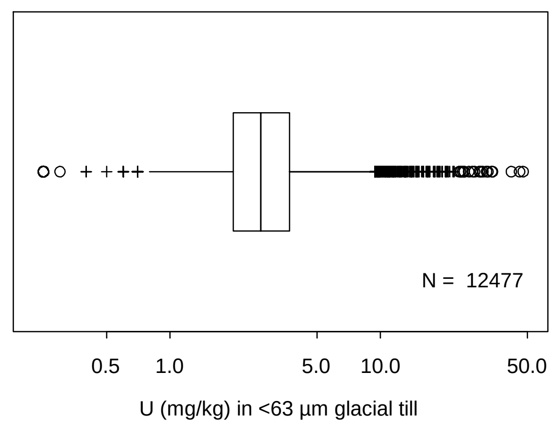
% Normal Probability Plot



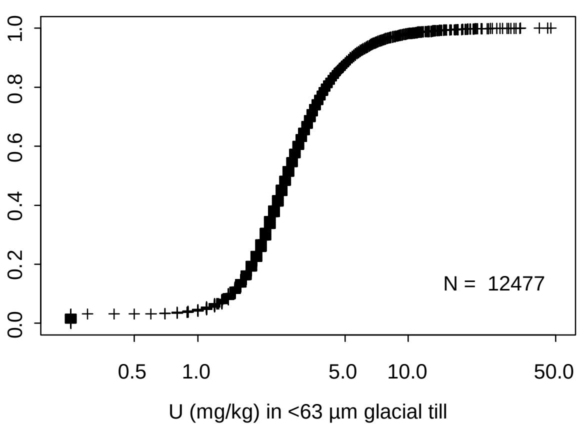
Histogram



Tukey Boxplot



Empirical Cumulative Distribution Function



% Cumulative Normal Probability Plot

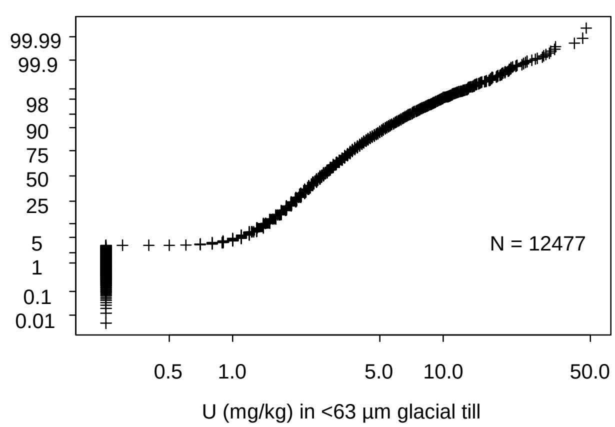
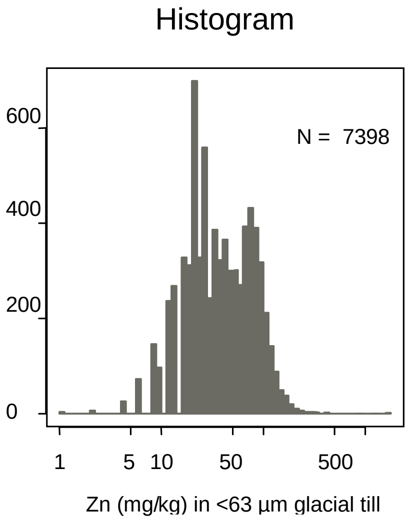
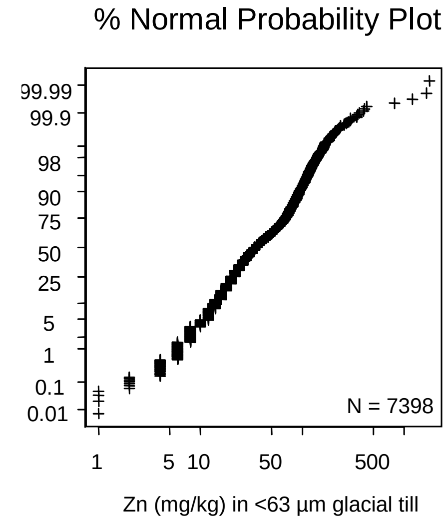


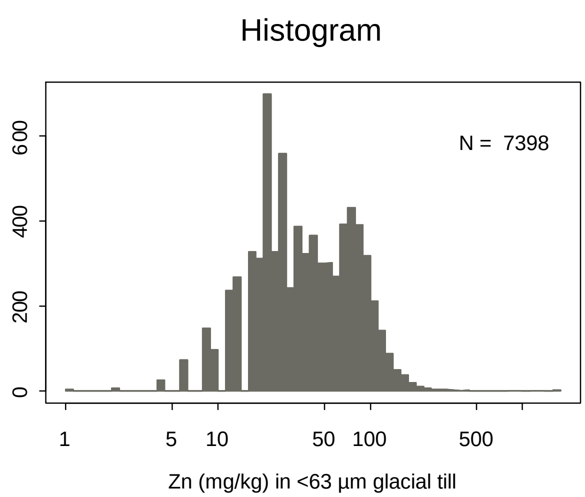
Figure 11 Zinc summary statistics

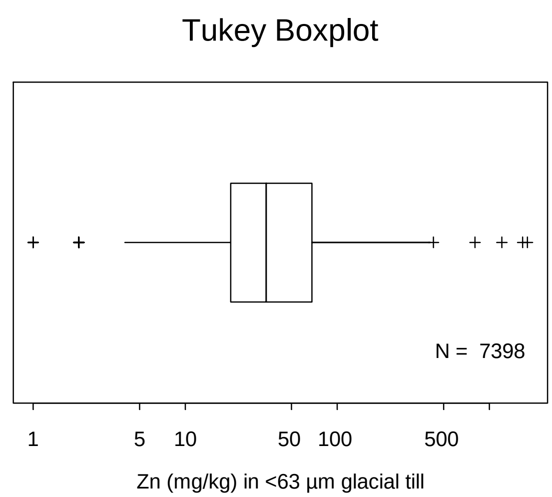


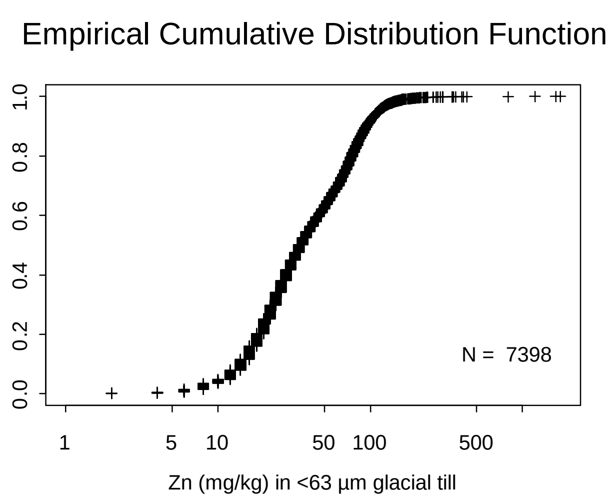
Summary Statistics

Number of Observations	7398
Maximum	1770
98th Percentile	140
95th Percentile	114
90th Percentile	94
3rd Quartile	68
2nd Quartile - Median	34
1st Quartile	20
10th Percentile	14
5th Percentile	12
2nd Percentile	6
Minimum	1
Median Abs. Deviation	26.7
IQR Estimate of Std. Dev.	35.4
Mean	48.1
Standard Deviation	48.4
Coeff. of Variation, %	101









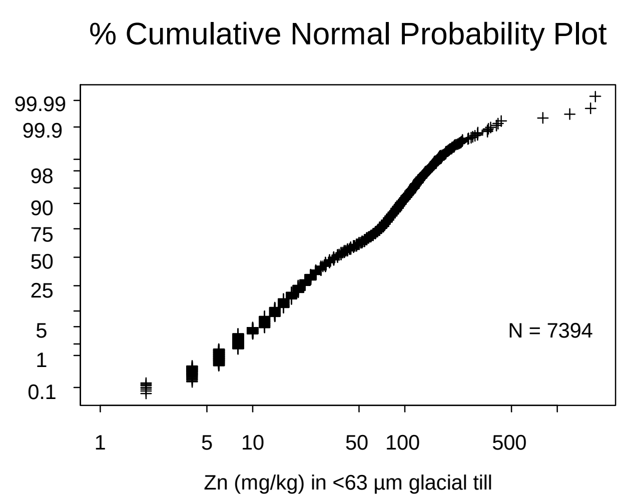
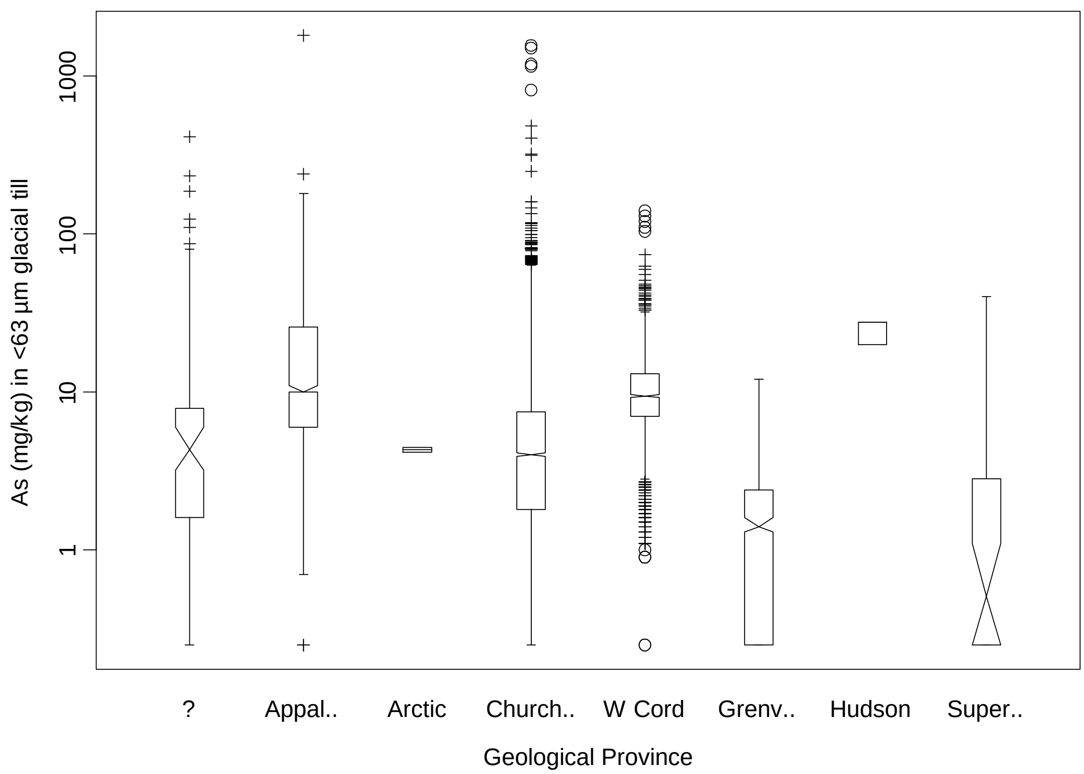
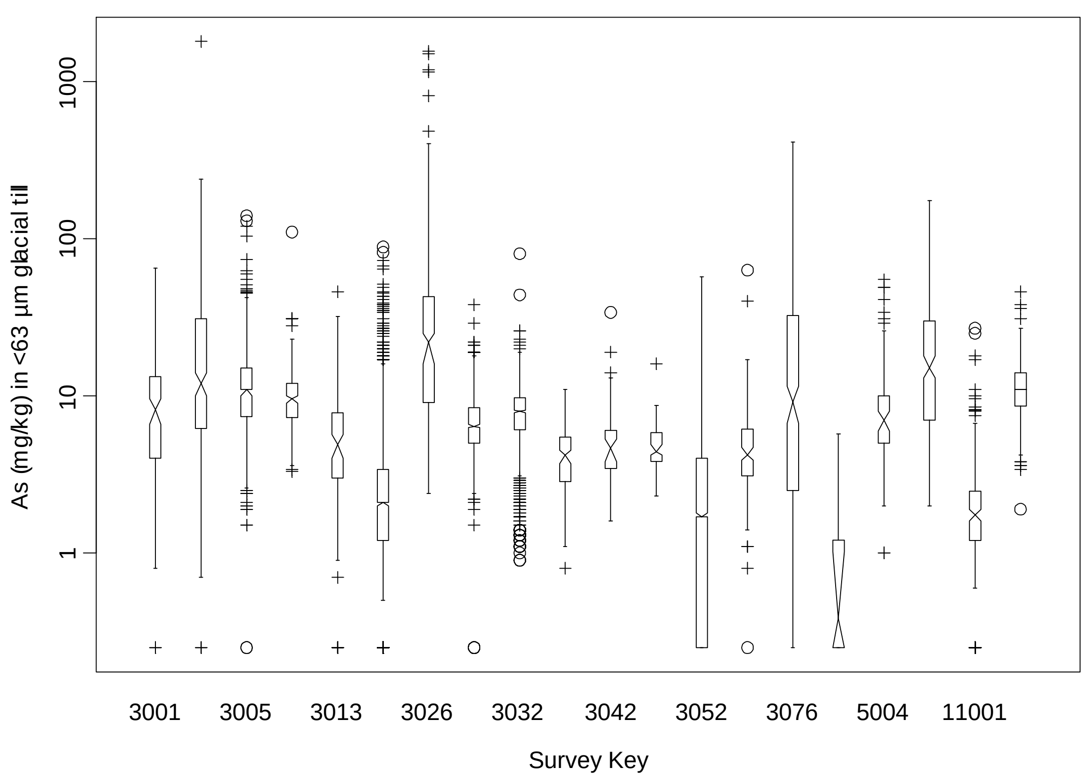
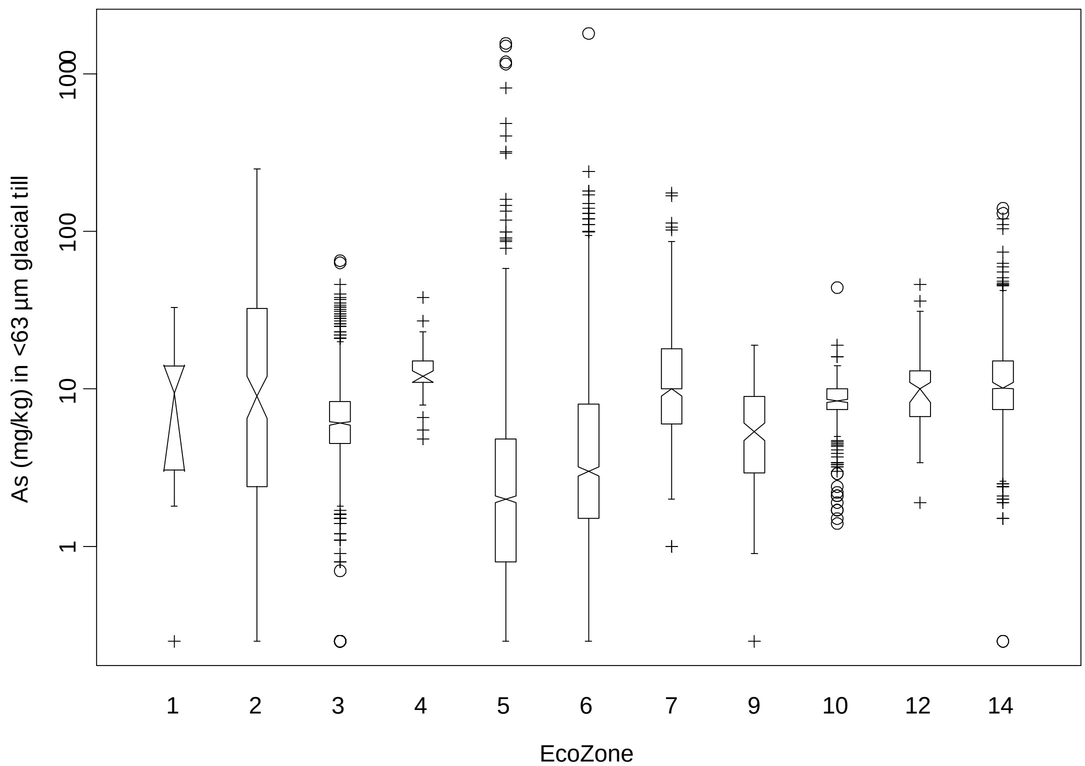


Figure 12 Arsenic Tukey boxplots






As (mg/kg) in <63 µm glacial till
1
10
100
1000
1
2
3
4
5
6
7
9
10
12
14
EcoZone

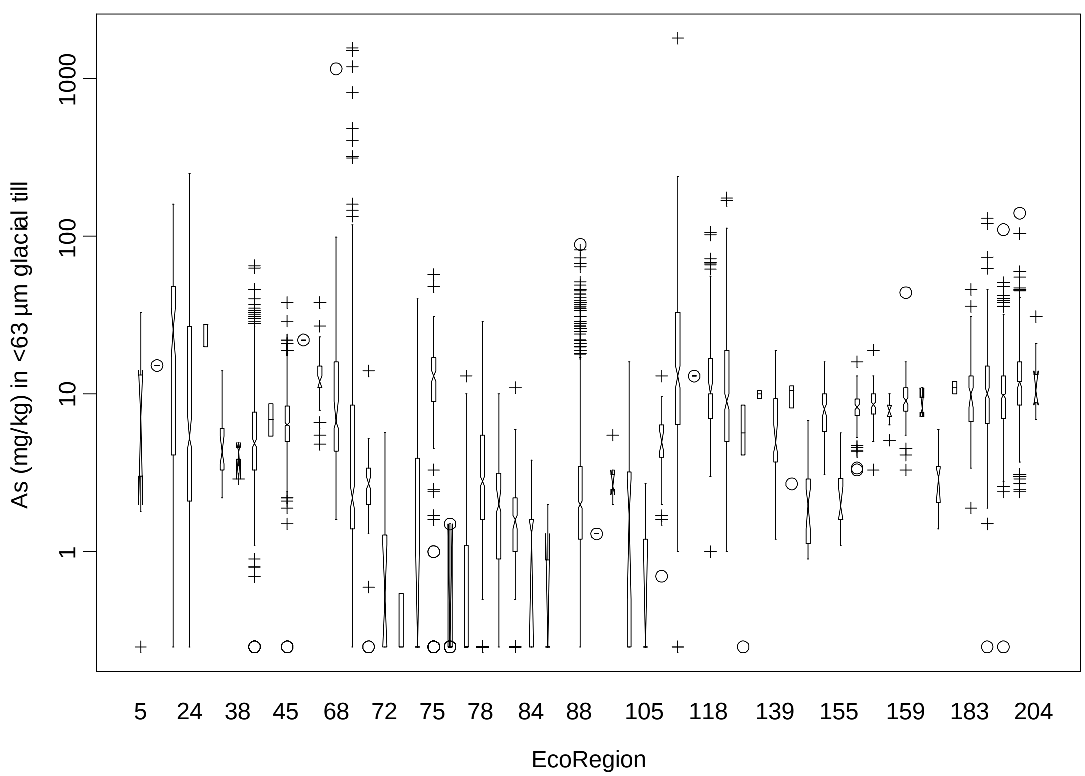
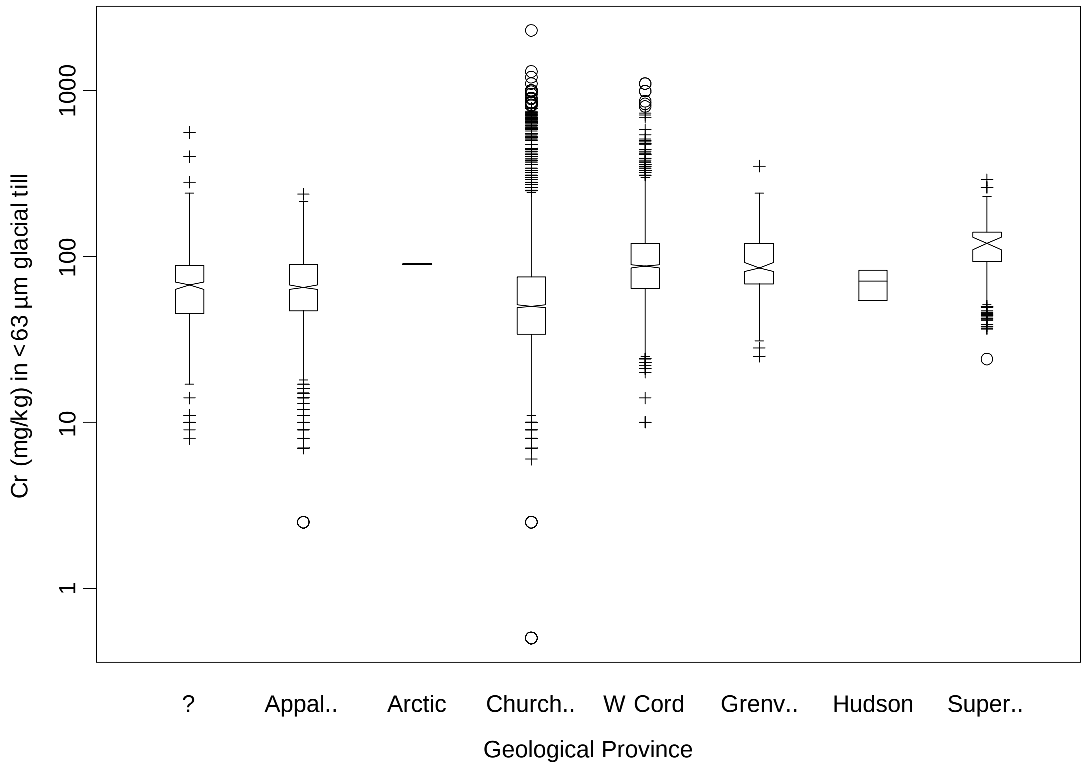
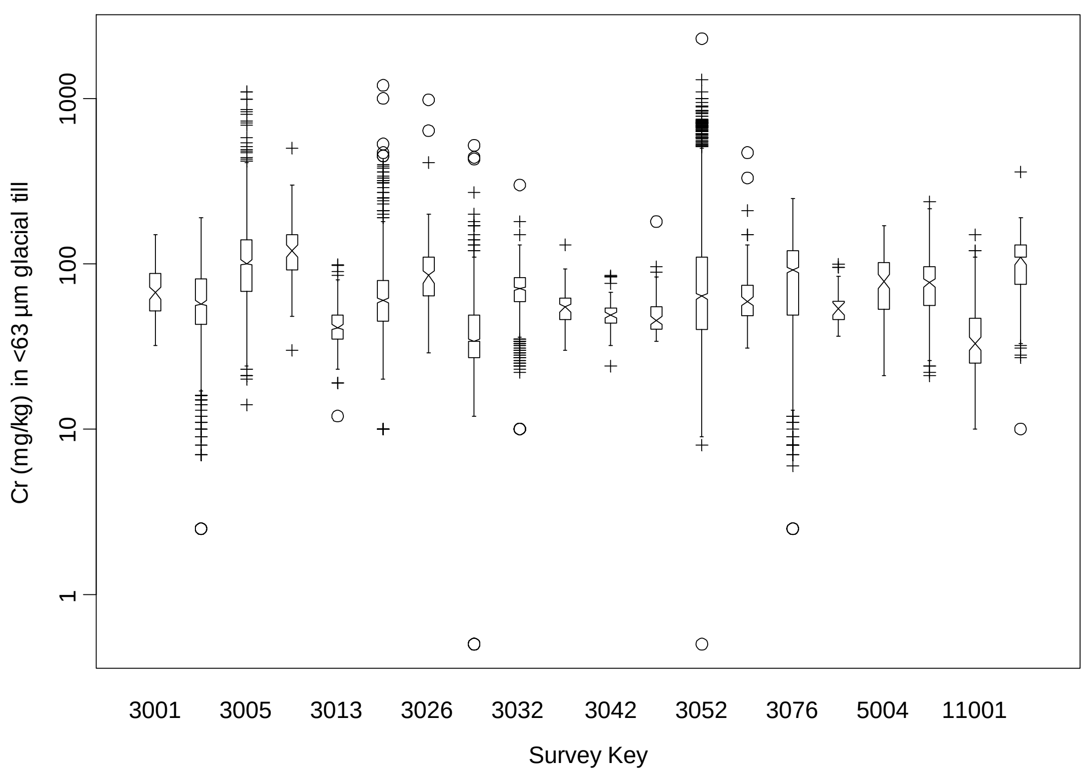
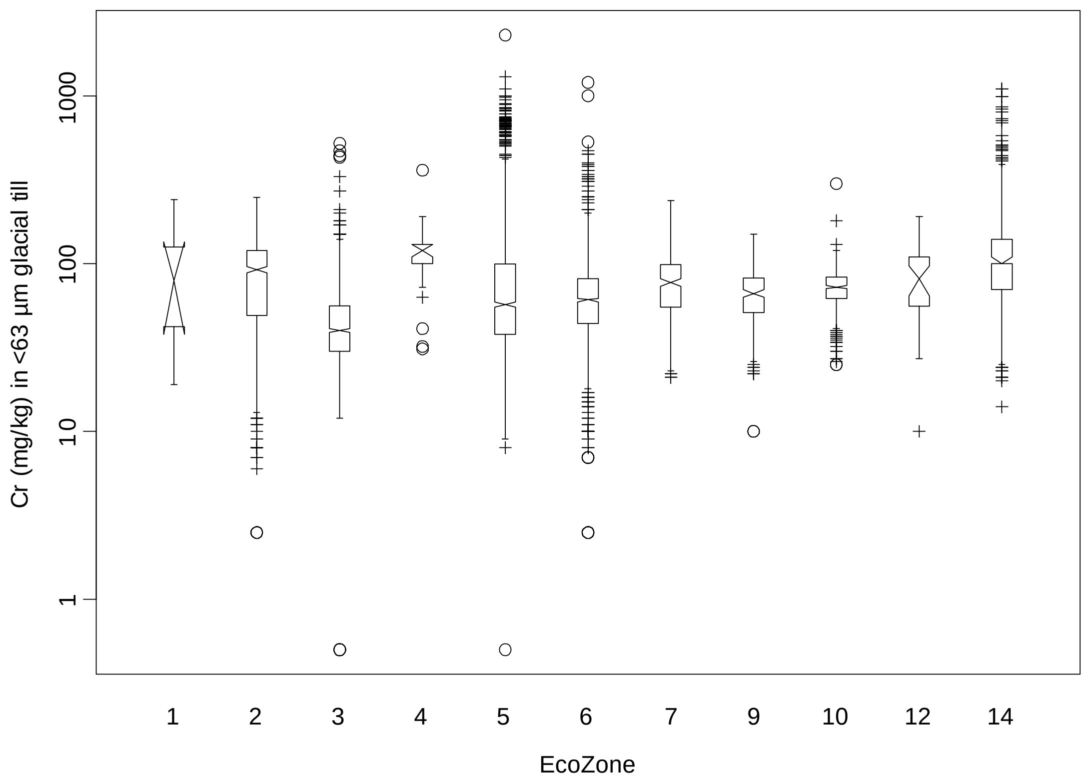

As (mg/kg) in <63 µm glacial till
1
10
100
1000
5
24
38
45
68
72
75
78
84
88
105
118
139
155
159
183
204
EcoRegion

Figure 13 Chromium Tukey boxplots






Cr (mg/kg) in <63 µm glacial till
1
10
100
1000
1
2
3
4
5
6
7
9
10
12
14
EcoZone

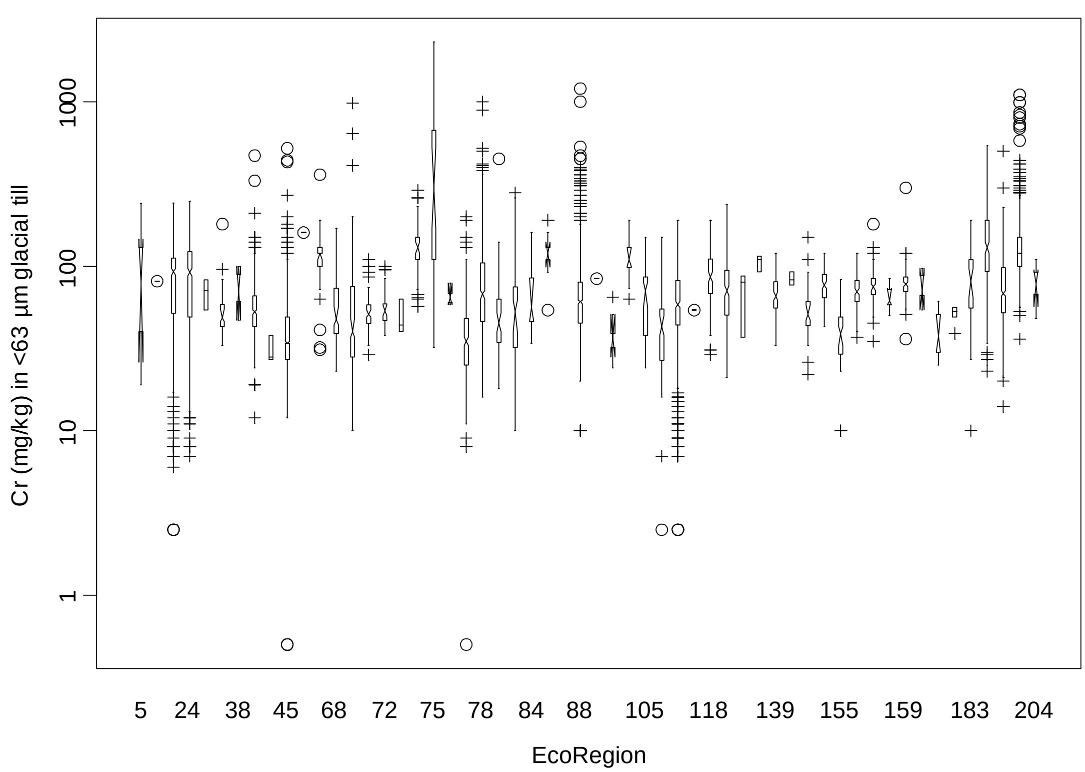
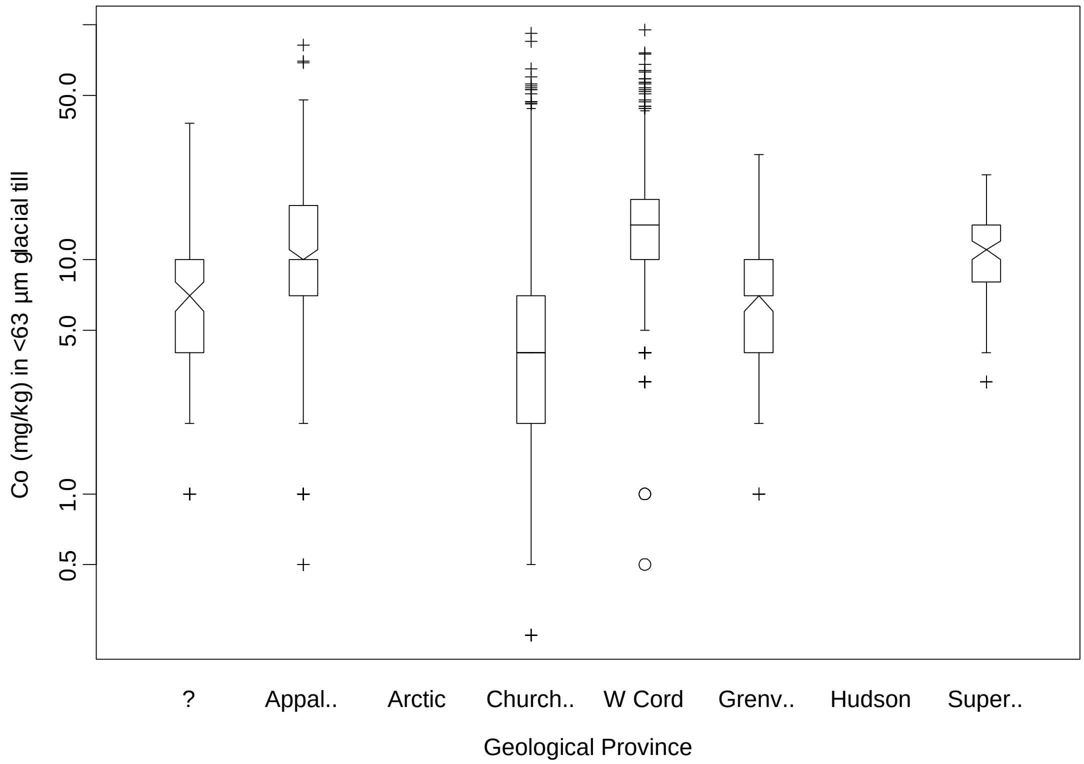
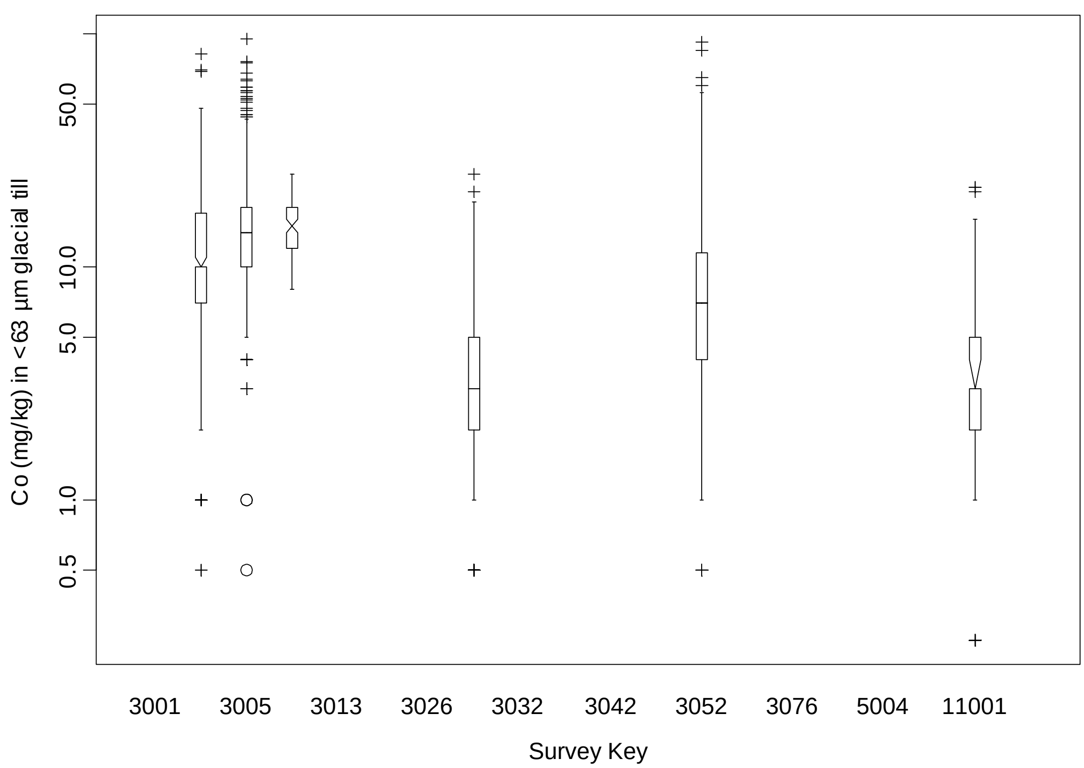
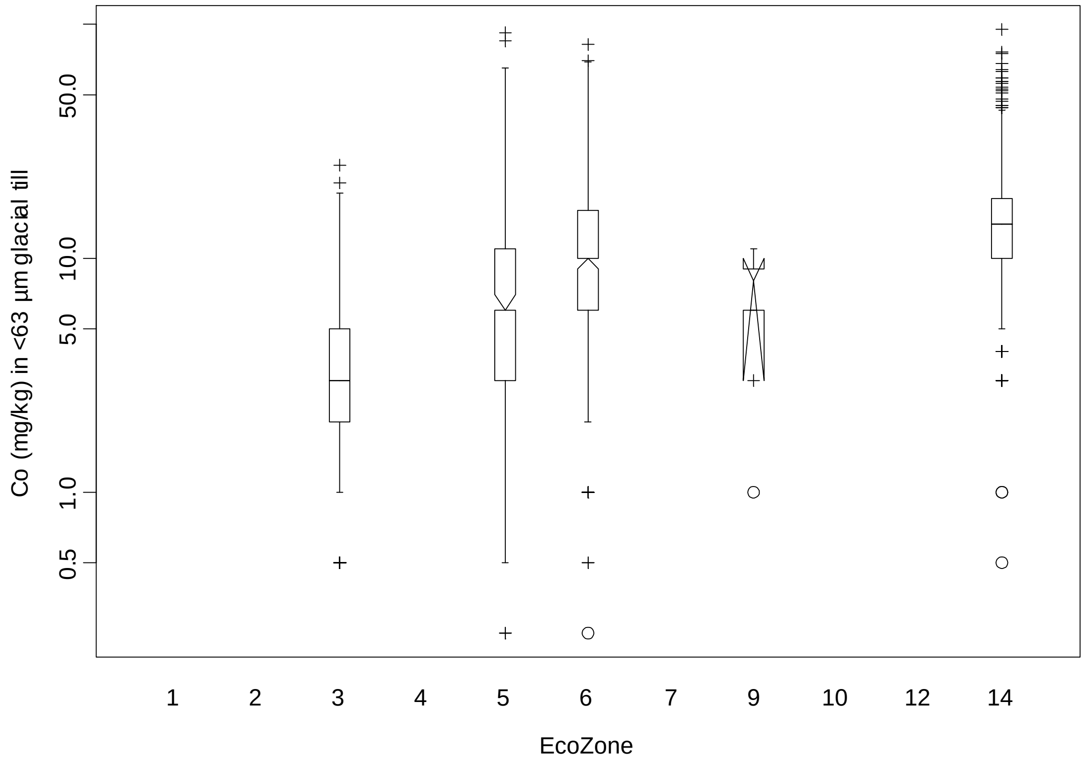

Cr (mg/kg) in <63 µm glacial till
1
10
100
1000
5
24
38
45
68
72
75
78
84
88
105
118
139
155
159
183
204
EcoRegion

Figure 14   Cobalt Tukey boxplots






Co (mg/kg) in <63 µm glacial till
0.5
1.0
5.0
10.0
50.0
1
2
3
4
5
6
7
9
10
12
14
EcoZone

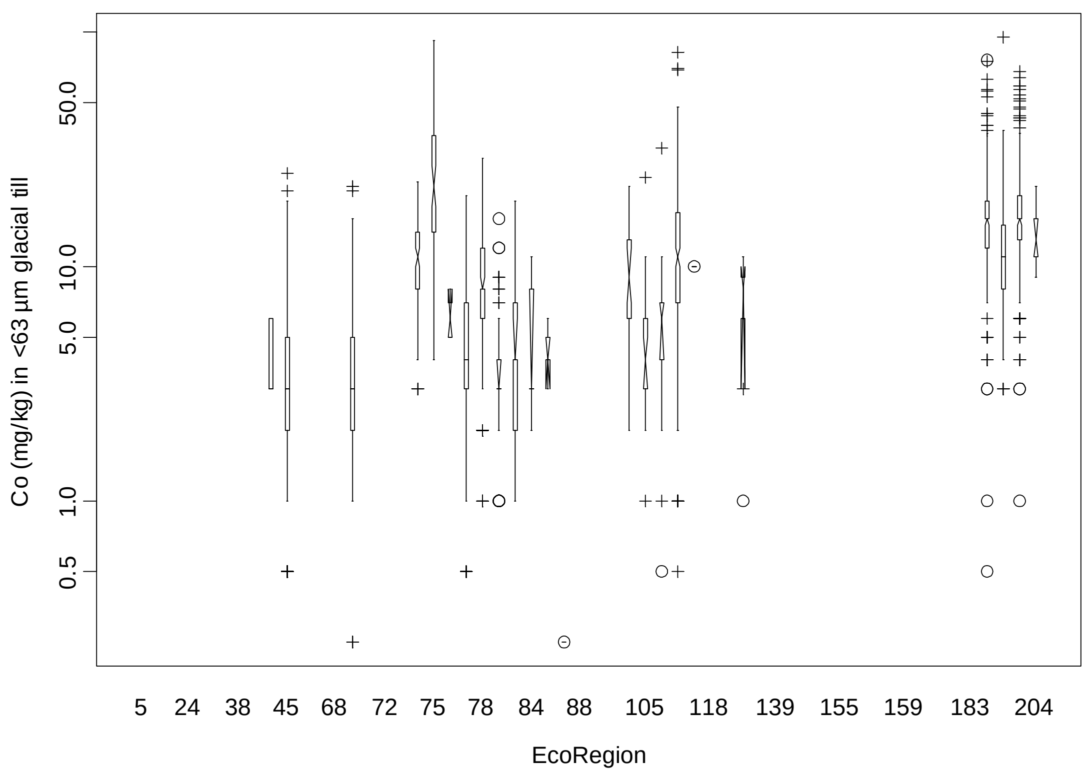
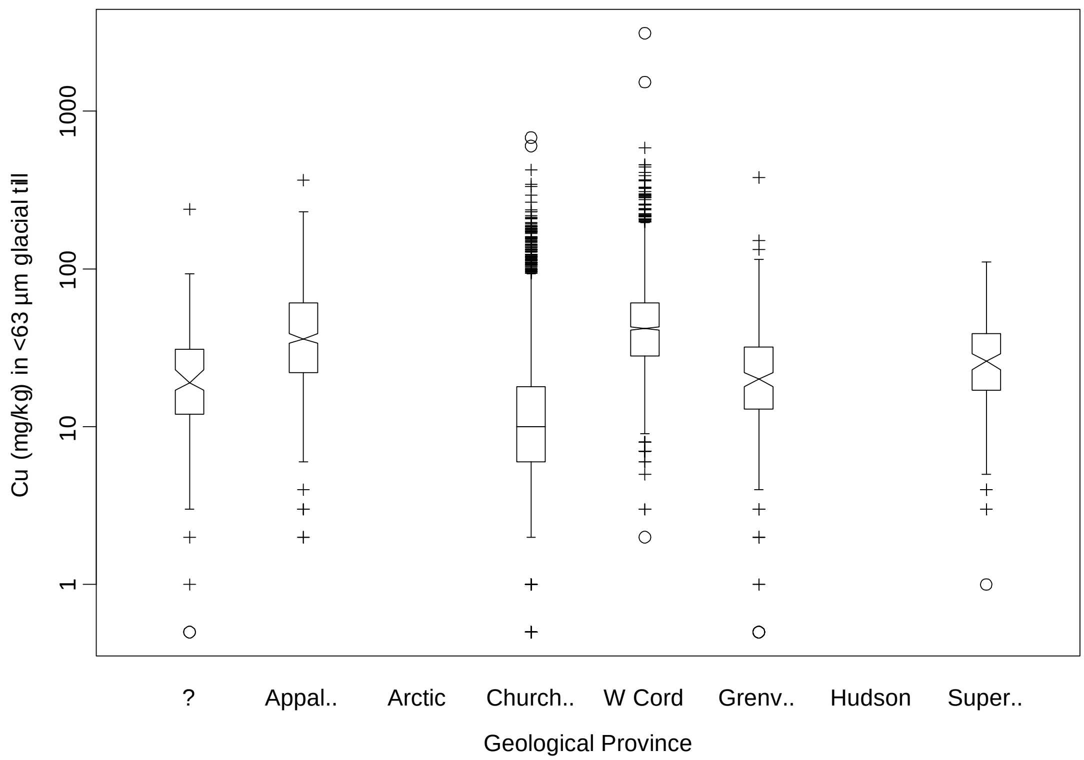
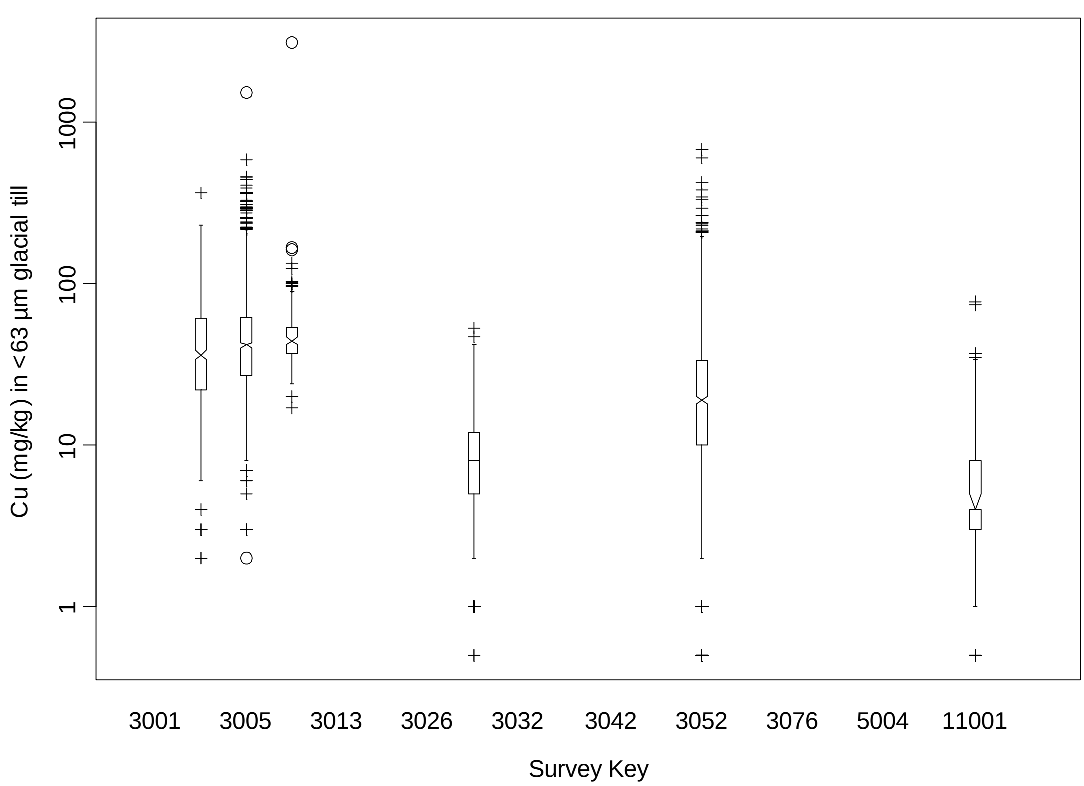
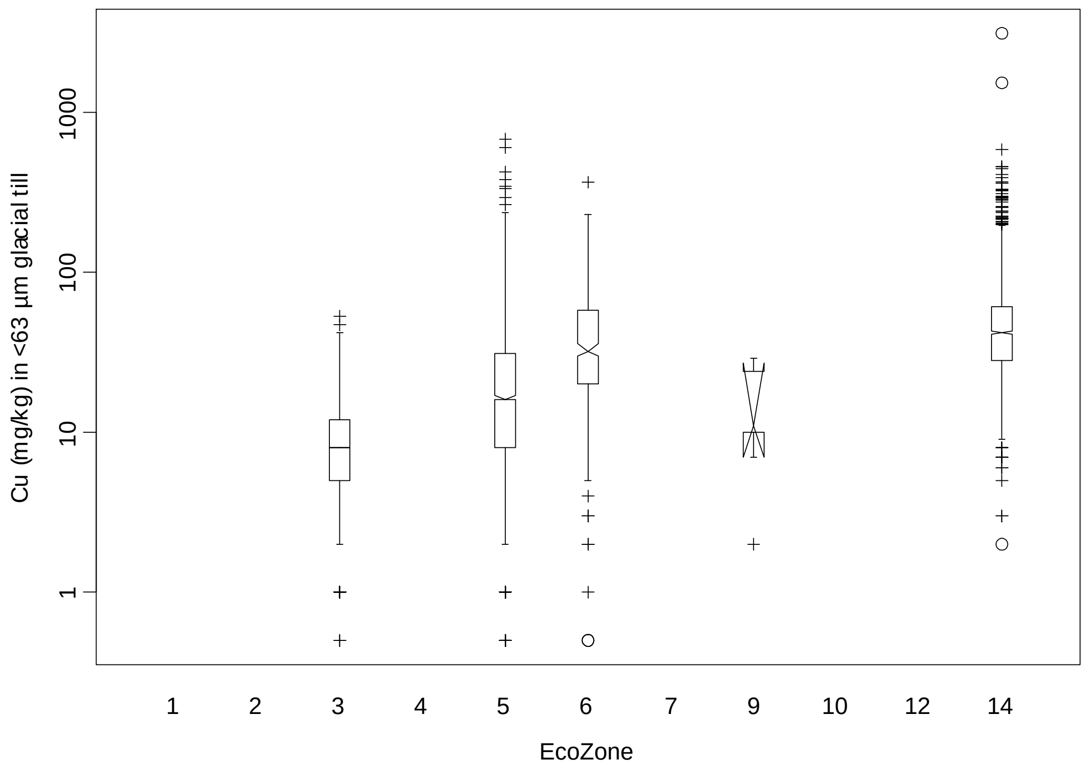

Co (mg/kg) in <63 µm glacial till
0.5
1.0
5.0
10.0
50.0
5
24
38
45
68
72
75
78
84
88
105
118
139
155
159
183
204
EcoRegion

Figure 15 Copper Tukey boxplots






Cu (mg/kg) in <63 µm glacial till
1
10
100
1000
1
2
3
4
5
6
7
9
10
12
14
EcoZone

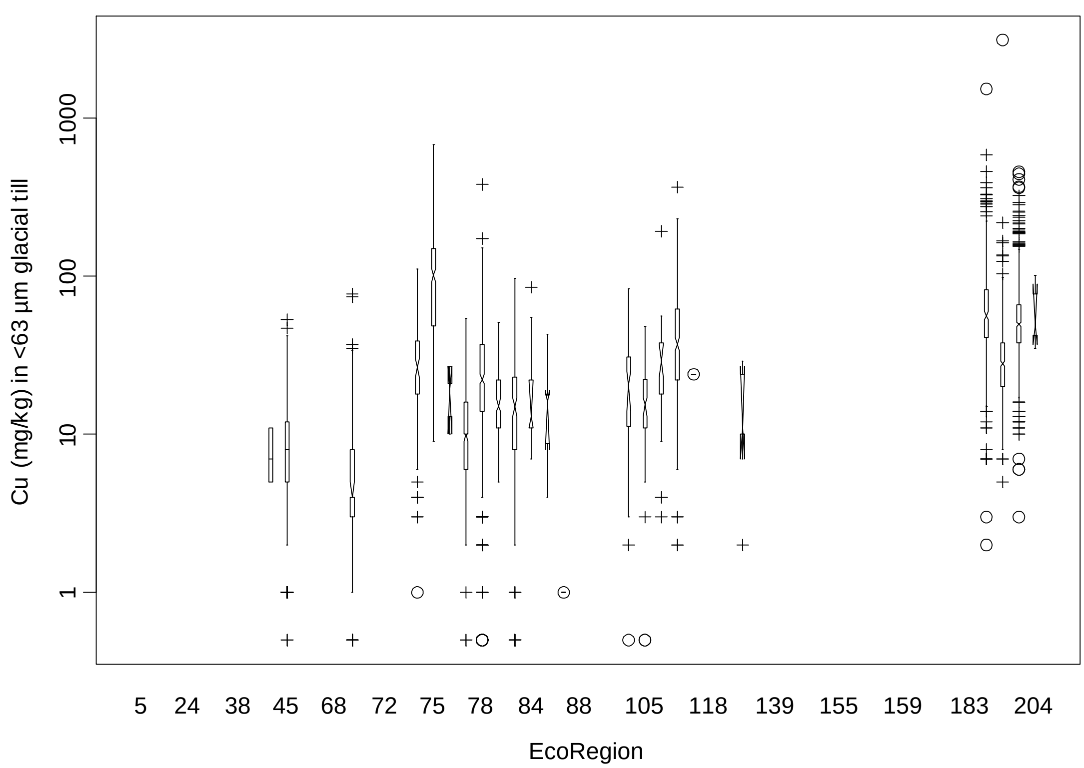
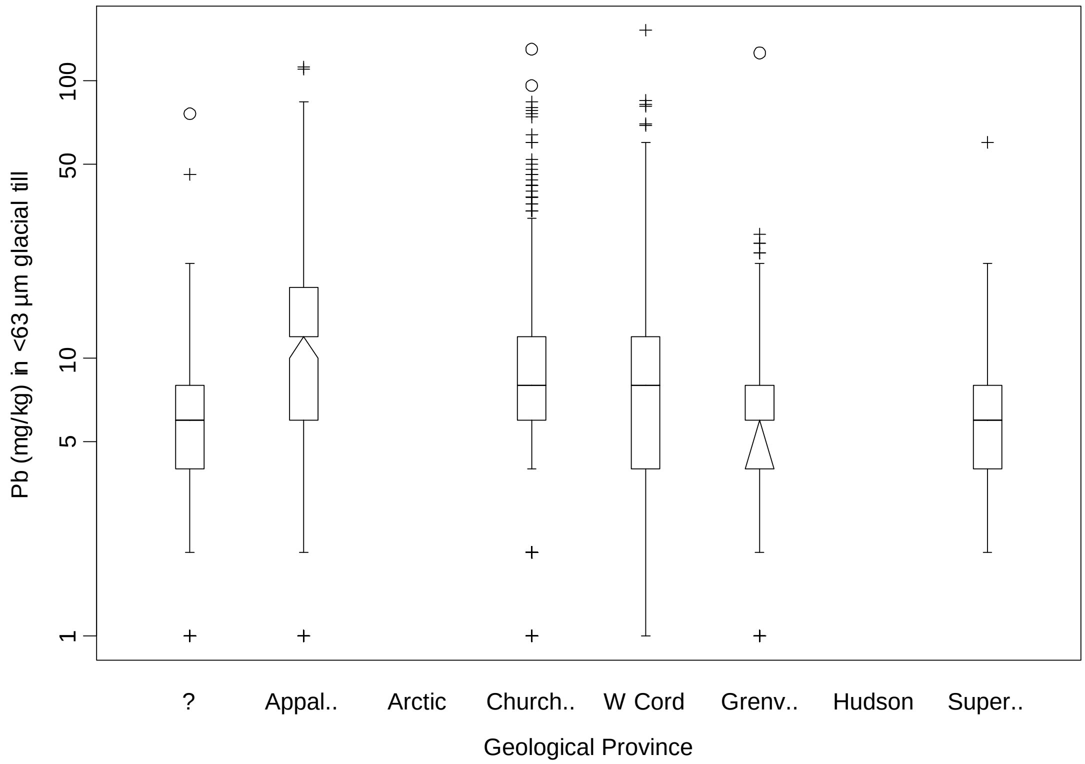
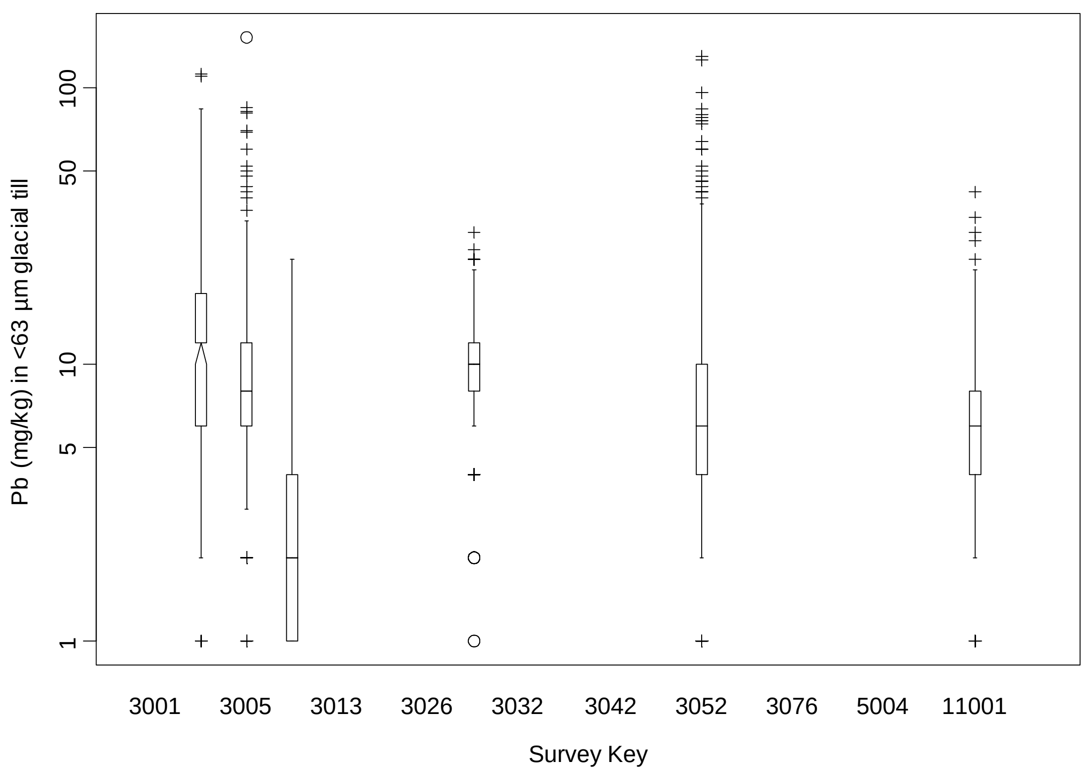
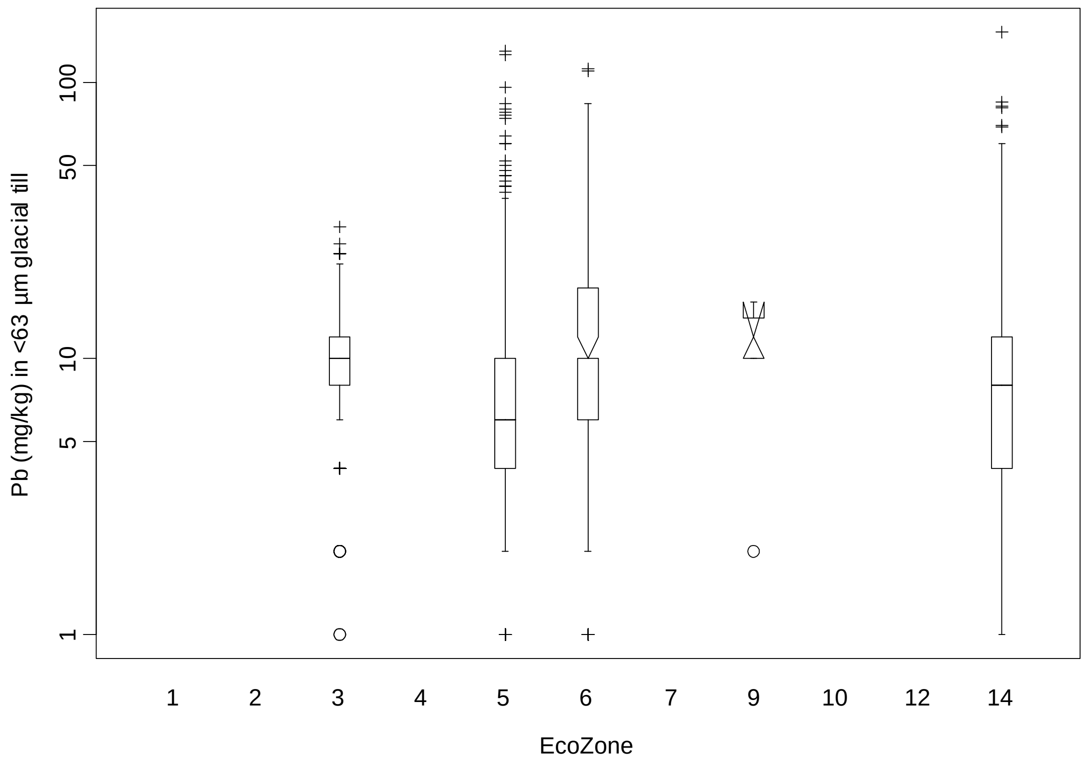

Cu (mg/kg) in <63 µm glacial till
1
10
100
1000
5
24
38
45
68
72
75
78
84
88
105
118
139
155
159
183
204
EcoRegion

Figure 16   Lead Tukey boxplots






Pb (mg/kg) in <63 µm glacial till
1
5
10
50
100
1 2 3 4 5 6 7 9 10 12 14
EcoZone

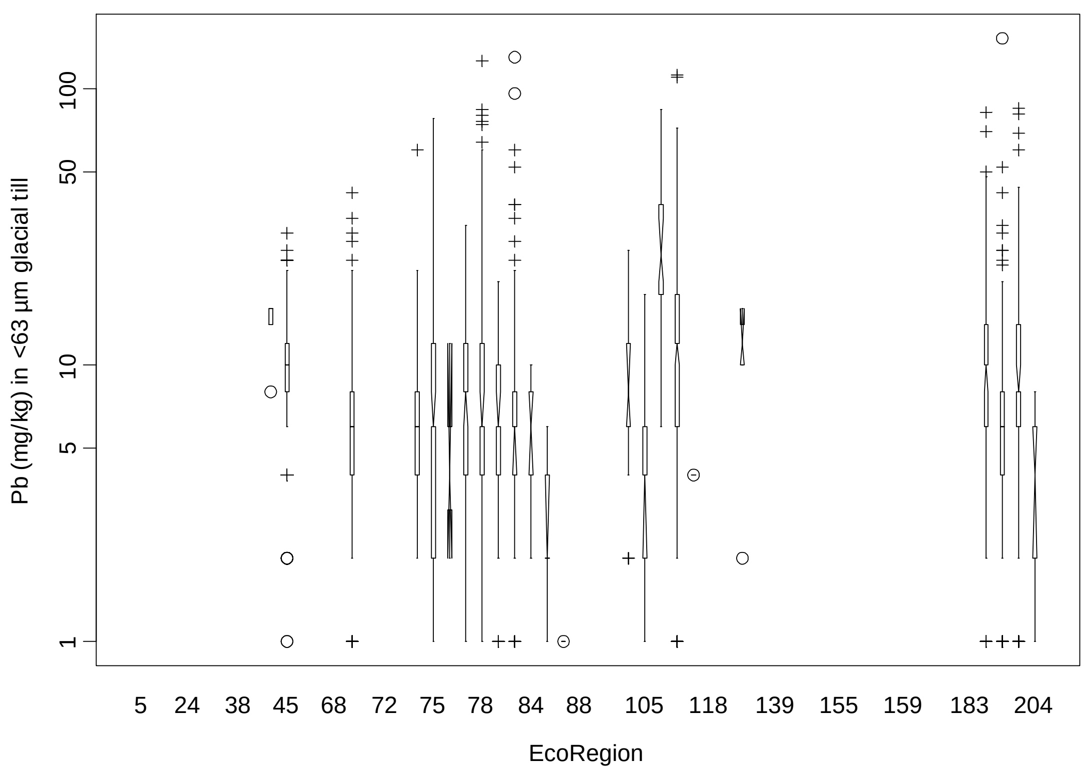
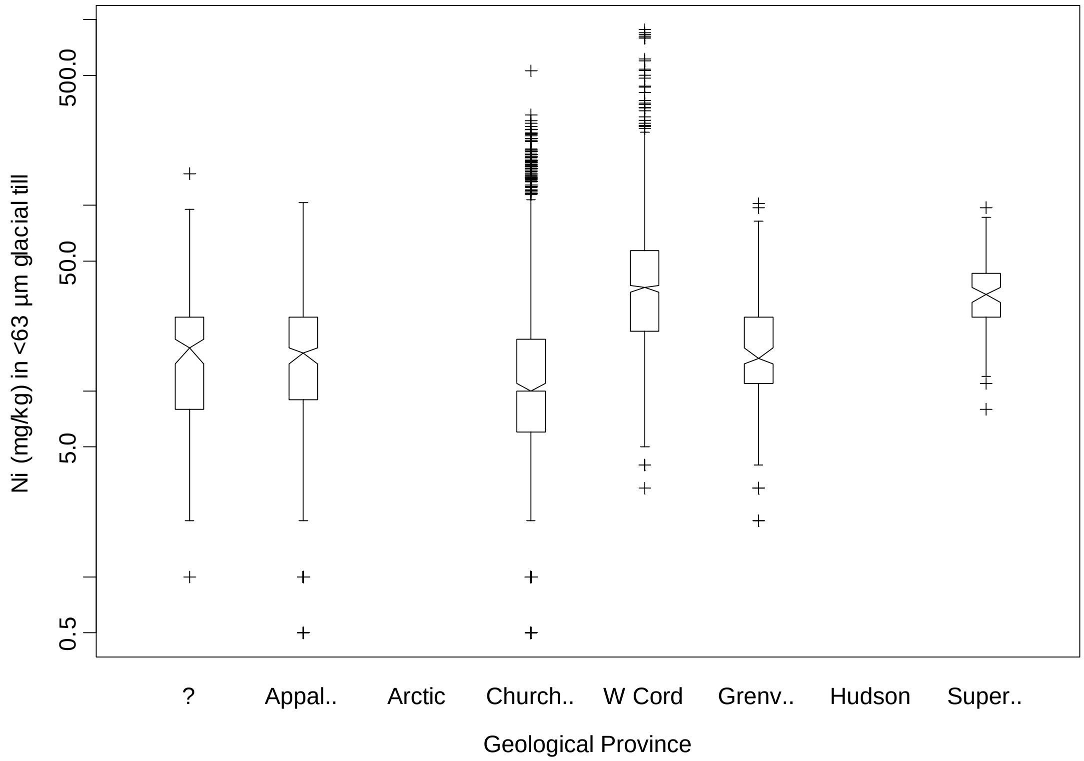
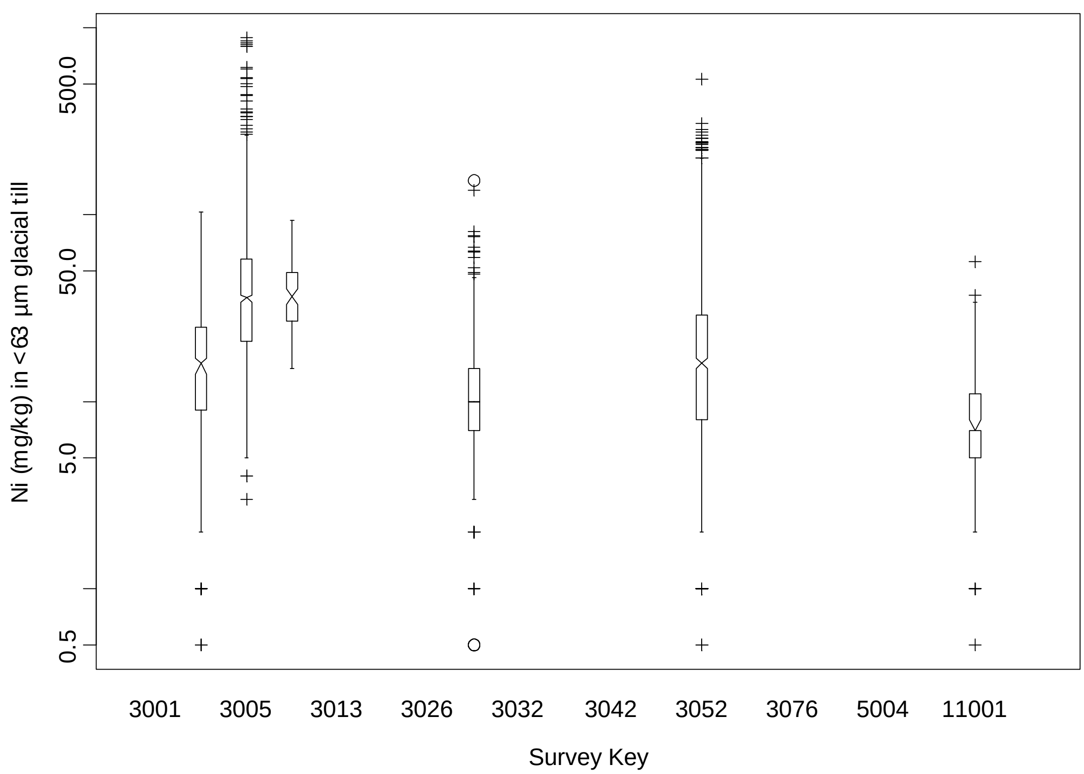
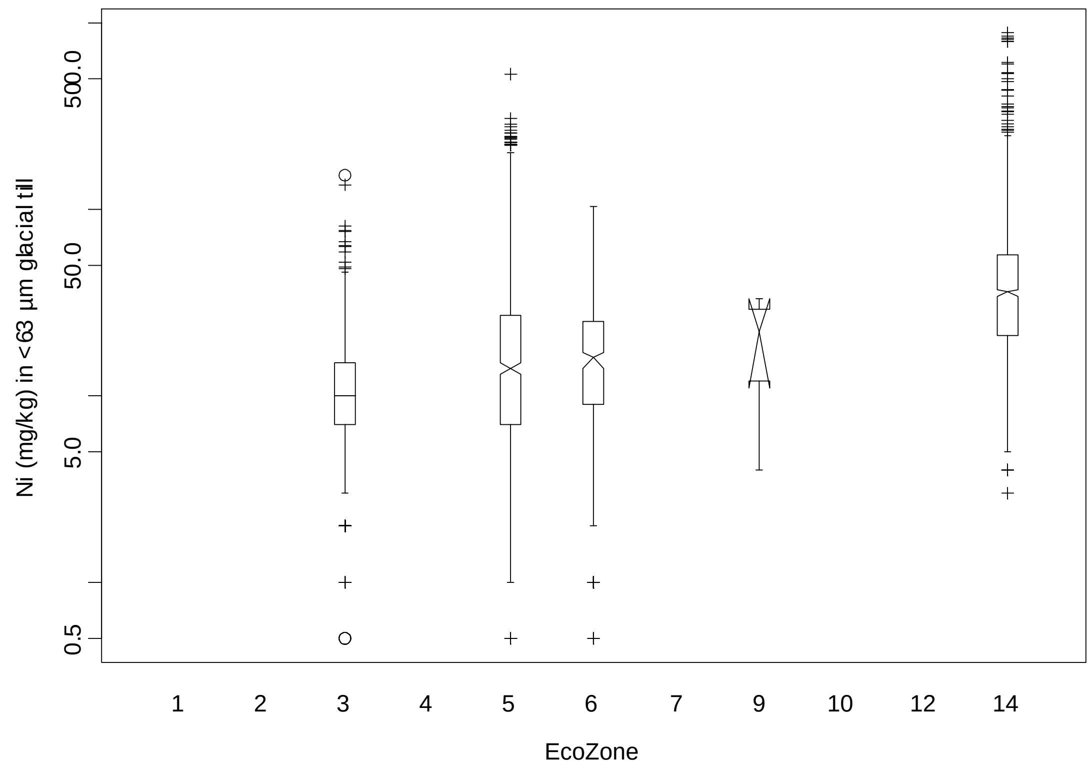

Pb (mg/kg) in <63 µm glacial till
1
5
10
50
100
5 24 38 45 68 72 75 78 84 88 105 118 139 155 159 183 204
EcoRegion

Figure 17 Nickel Tukey boxplots






Ni (mg/kg) in <63 µm glacial till
500.0
50.0
5.0
0.5
1
2
3
4
5
6
7
9
10
12
14
EcoZone

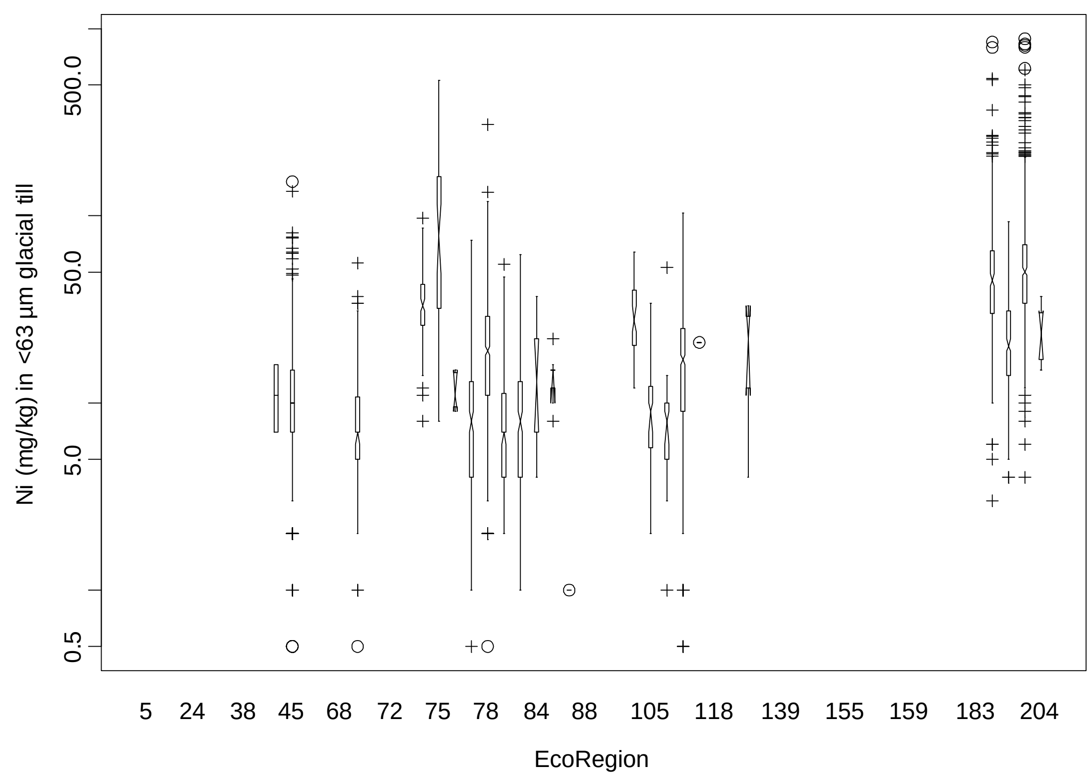
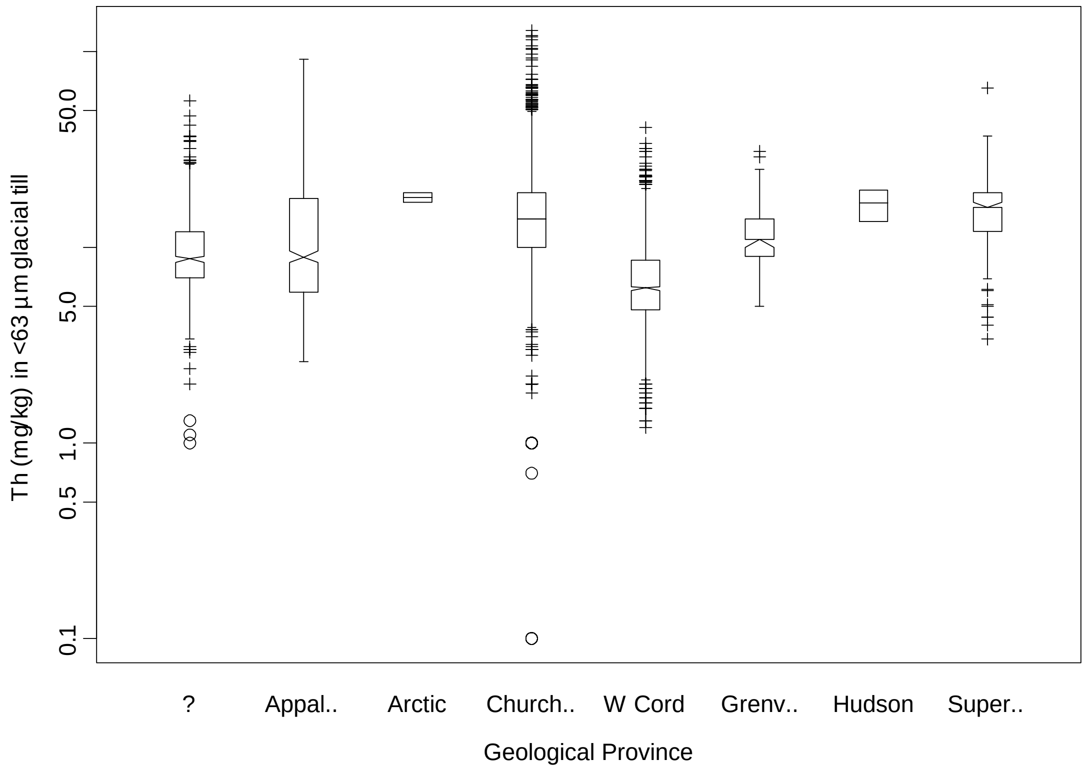
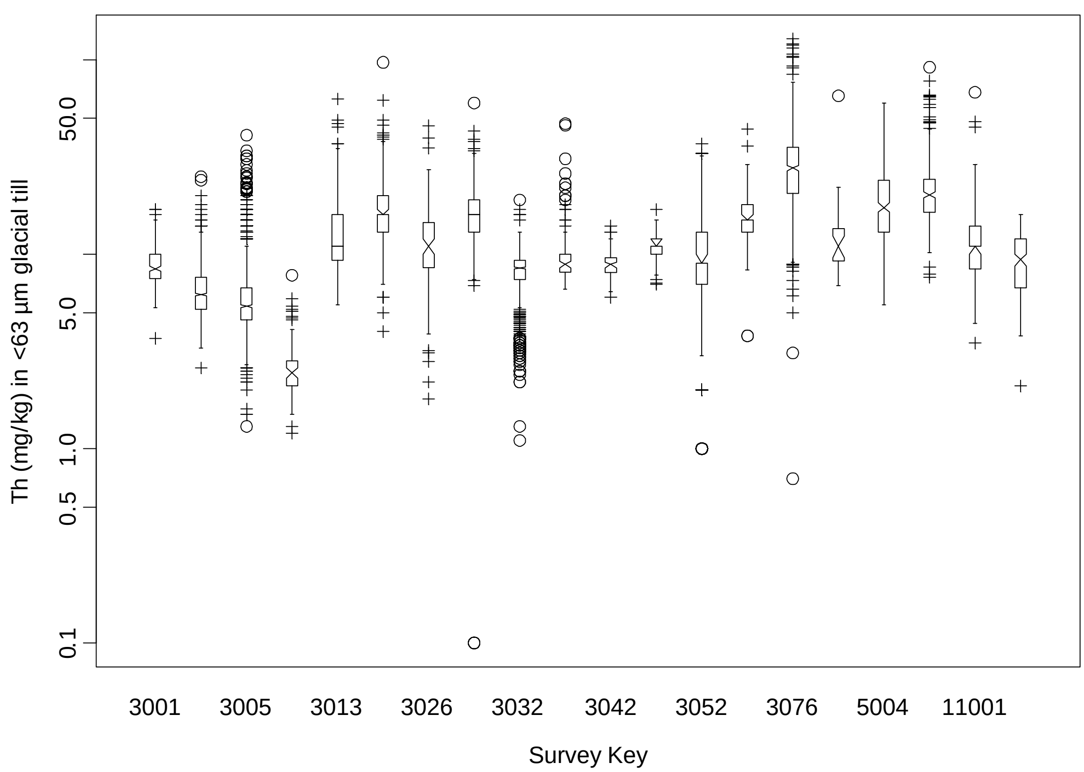
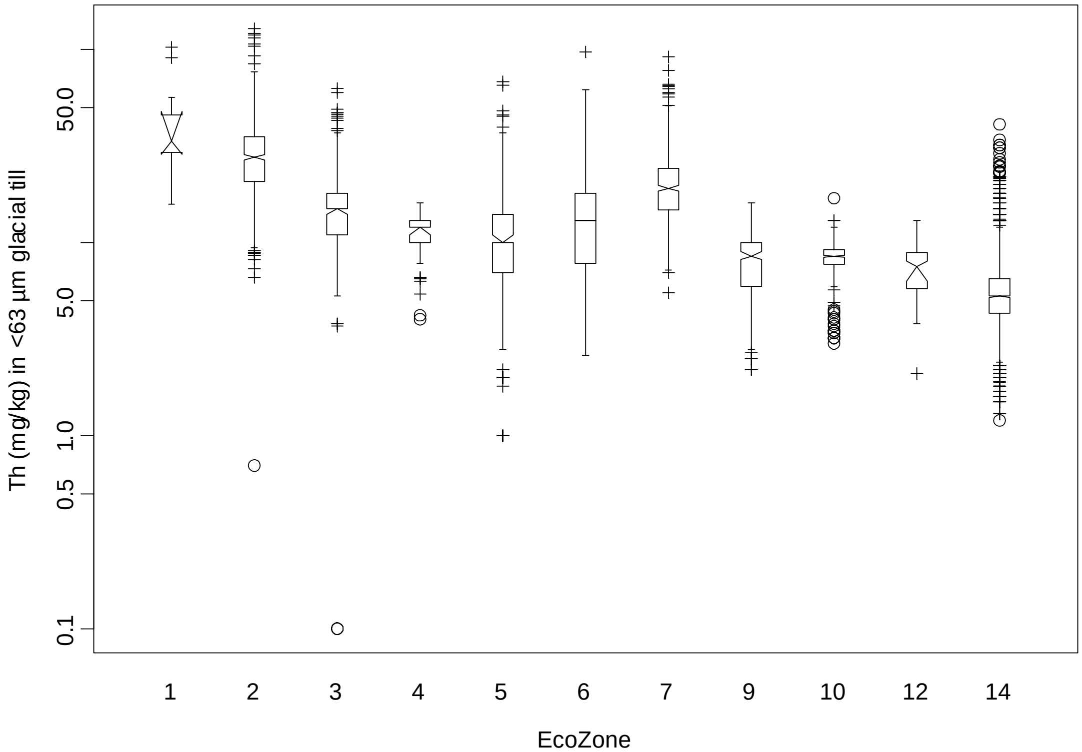

Ni (mg/kg) in <63 µm glacial till
500.0
50.0
5.0
0.5
5
24
38
45
68
72
75
78
84
88
105
118
139
155
159
183
204
EcoRegion

Figure 18   Thorium Tukey boxplots






Th (mg/kg) in <63 µm glacial till
50.0
5.0
1.0
0.5
0.1
1
2
3
4
5
6
7
9
10
12
14
EcoZone

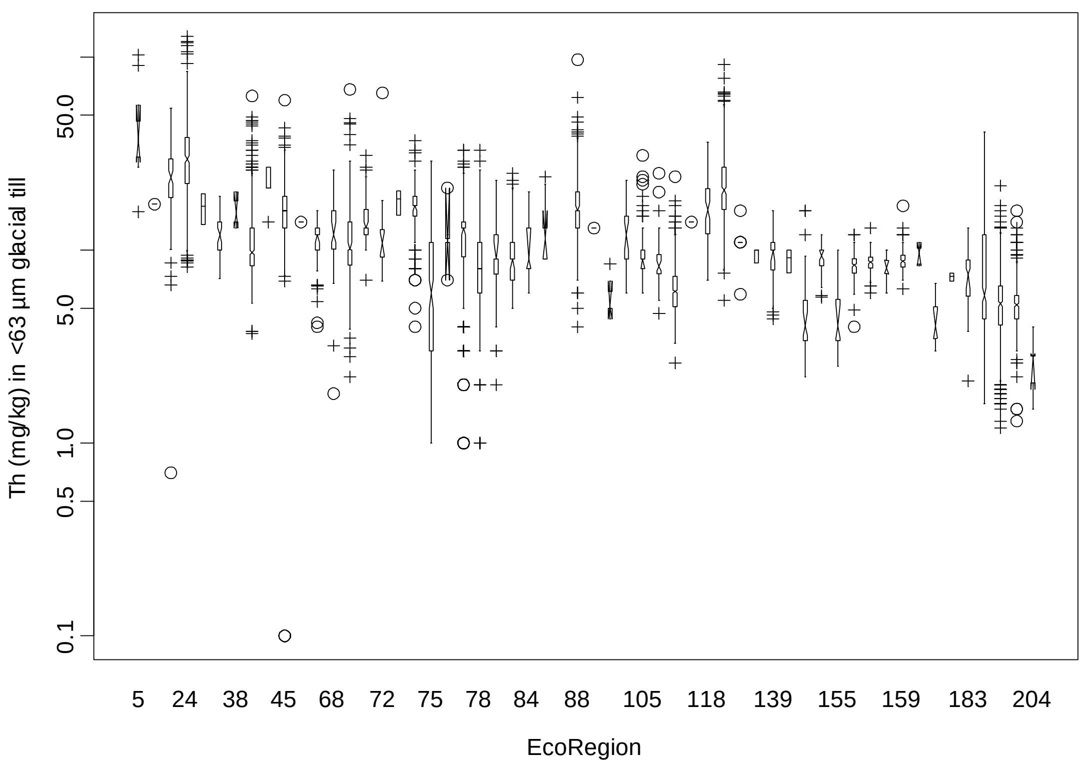
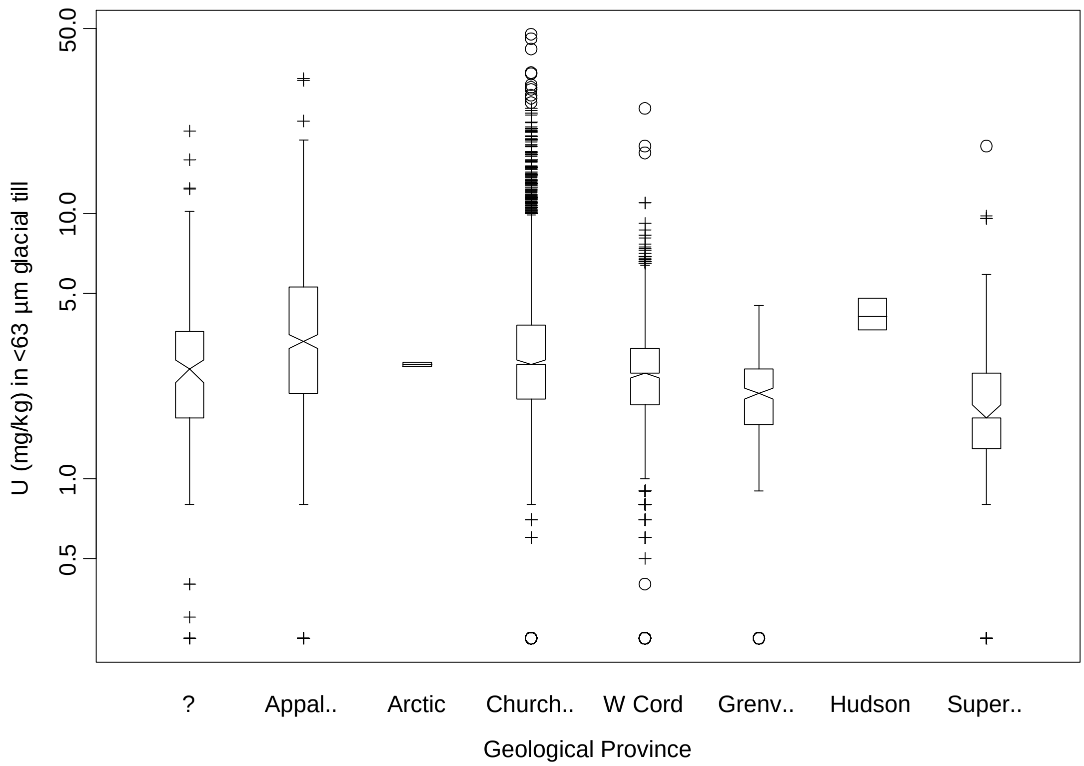
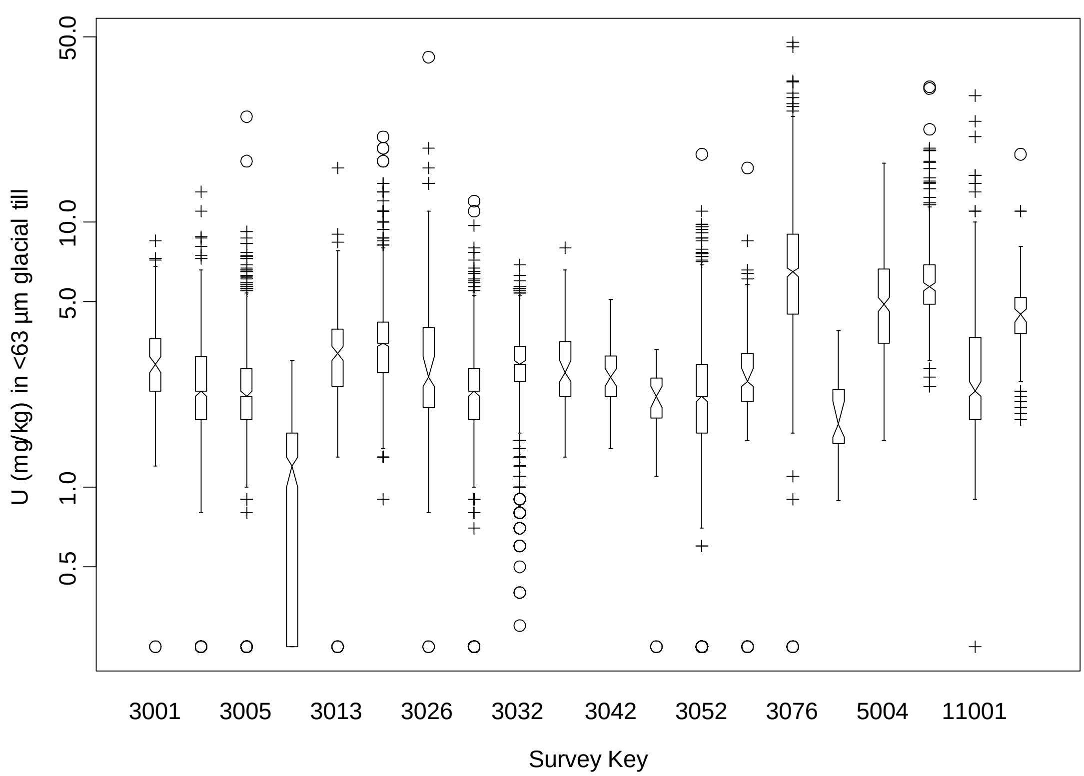
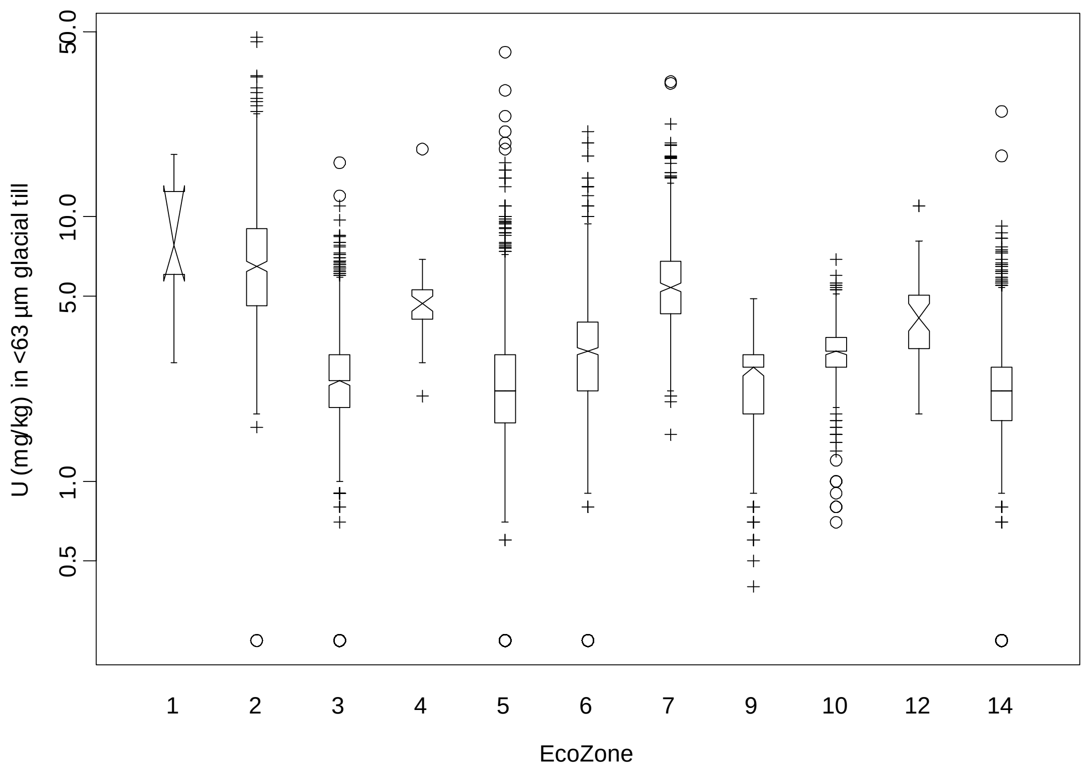

Th (mg/kg) in <63 µm glacial till
50.0
5.0
1.0
0.5
0.1
5
24
38
45
68
72
75
78
84
88
105
118
139
155
159
183
204
EcoRegion

Figure 19 Uranium Tukey boxplots






50.0
10.0
5.0
1.0
0.5
U (mg/kg) in <63 µm glacial till
1
2
3
4
5
6
7
9
10
12
14
EcoZone

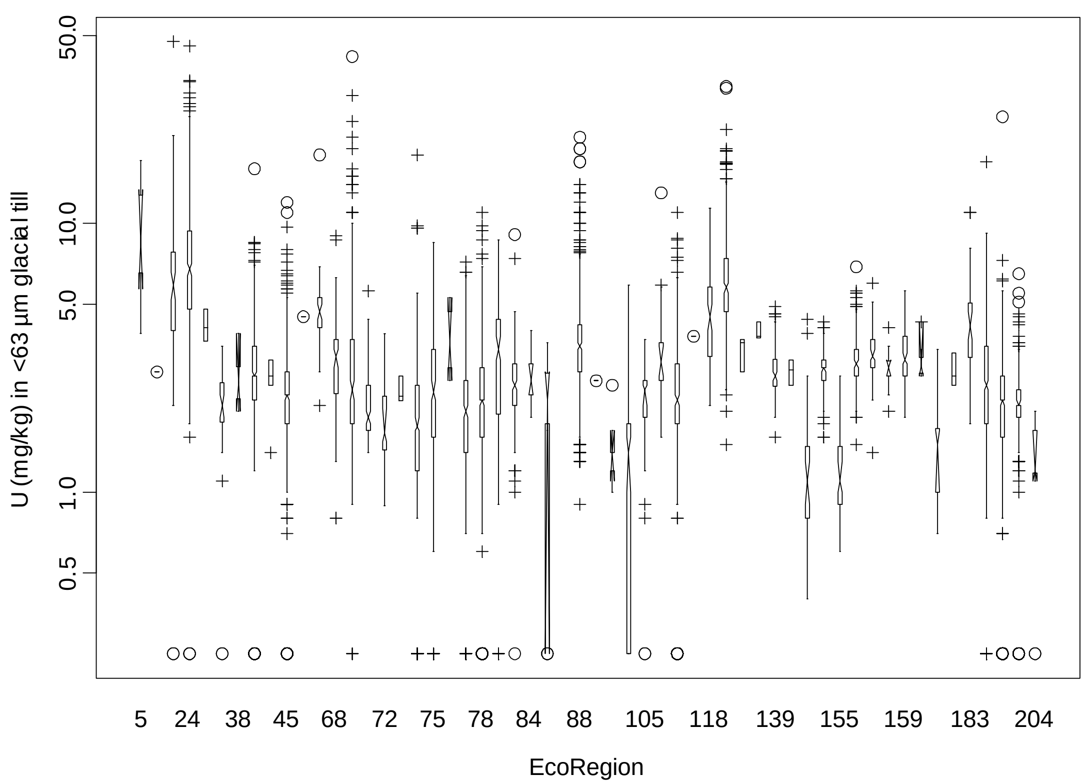
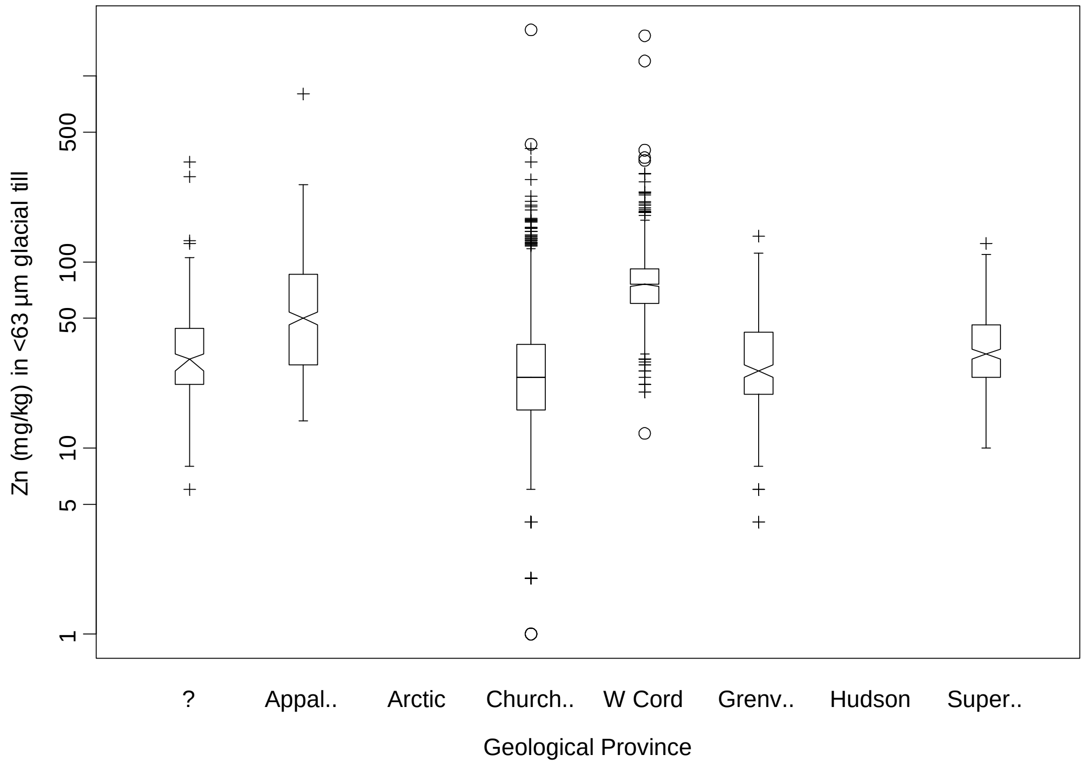
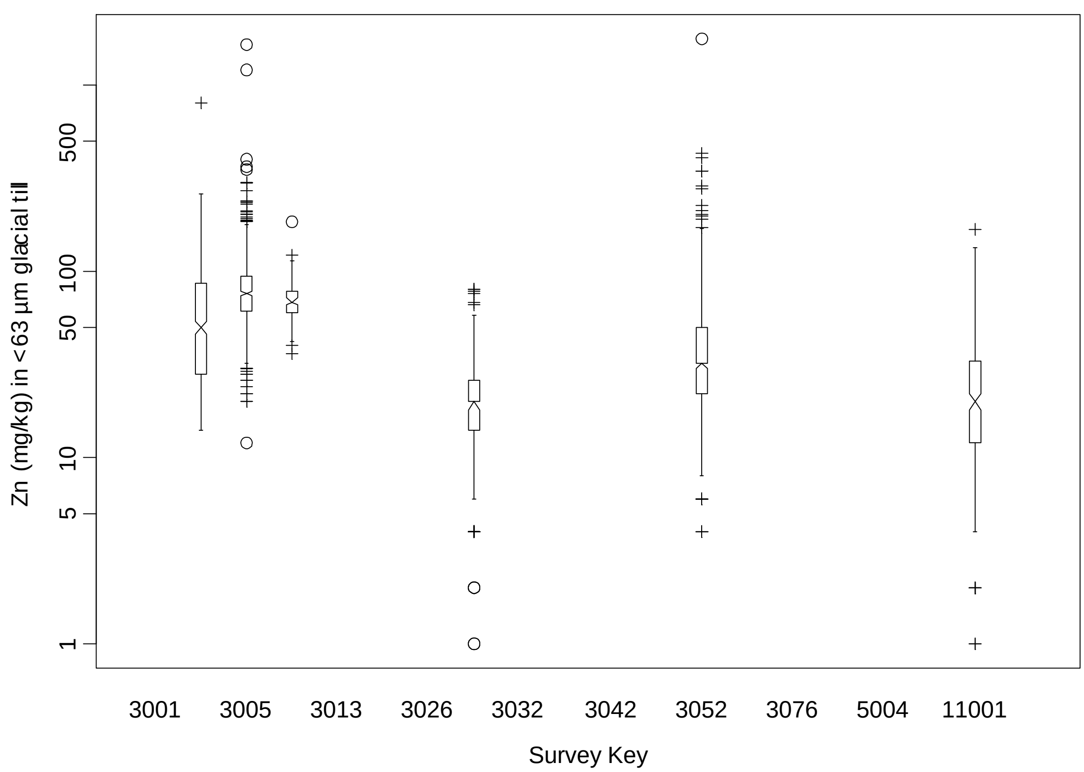
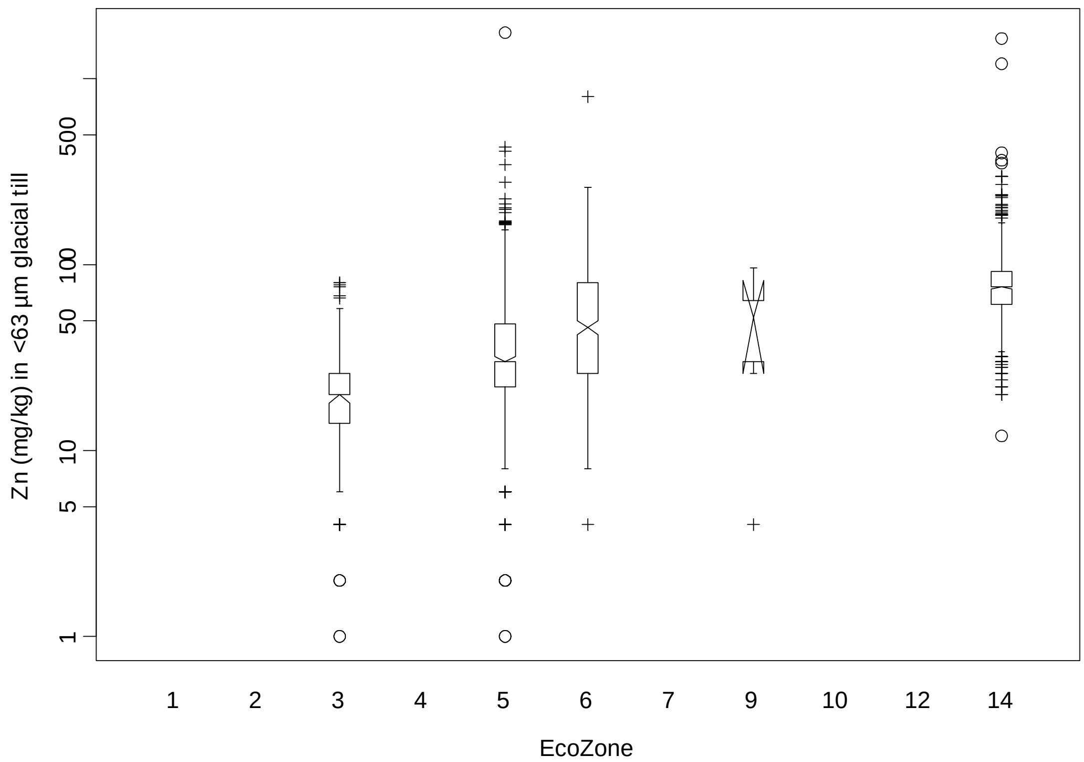
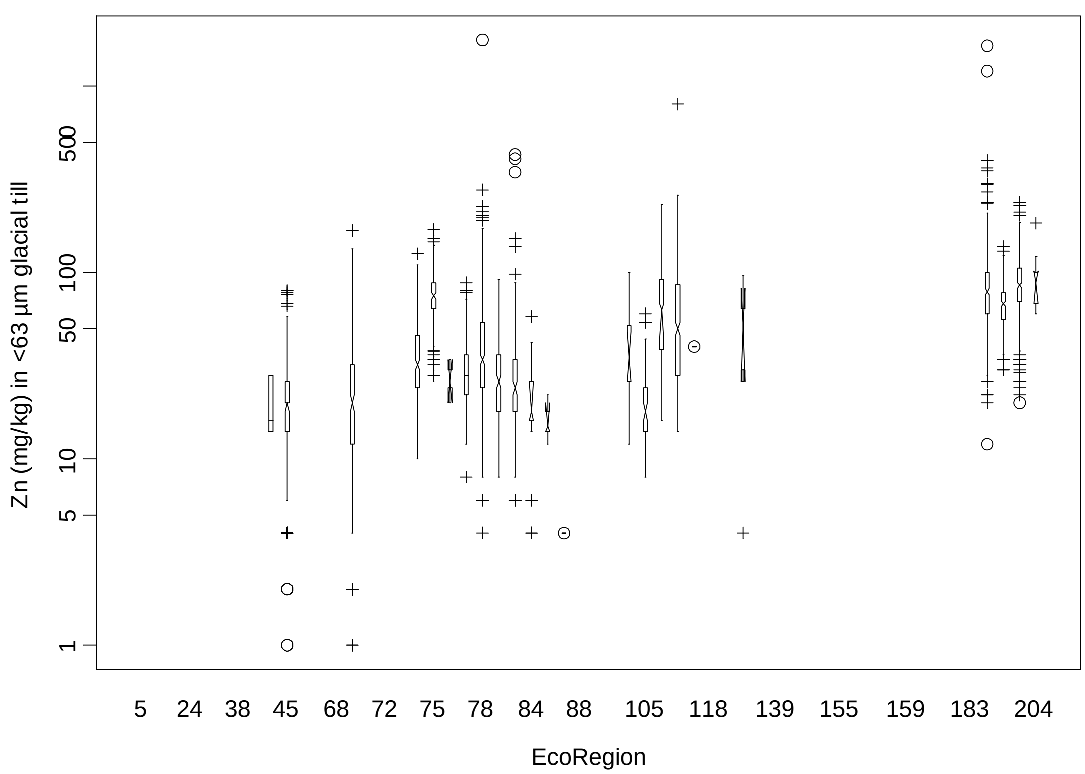

50.0
10.0
5.0
1.0
0.5
U (mg/kg) in <63 µm glacial till
5
24
38
45
68
72
75
78
84
88
105
118
139
155
159
183
204
EcoRegion

Figure 20 Zinc Tukey boxplots






Zn (mg/kg) in <63 µm glacial till
1
5
10
50
100
500
1
2
3
4
5
6
7
9
10
12
14
EcoZone


Zn (mg/kg) in <63 µm glacial till
1
5
10
50
100
500
5
24
38
45
68
72
75
78
84
88
105
118
139
155
159
183
204
EcoRegion

Part 4: Relating till geochemical data to soil quality guidelines

by S.W. Adcock, Geological Survey of Canada, ESS

A primary objective of this study was to assess the relevance of till geochemical data to scientists and engineers tasked with remediation of contaminated sites across Canada. As of November, 2005, there were 4326 potentially contaminated sites identified in the Federal Government's inventory (WWW link listed below). Assessing the extent of contamination at a particular site is often very difficult, because the pre-contamination state of the site is unknown. A database of chemical analyses from uncontaminated sites in similar environments could be very useful in such situations.

Table 9 Trace elements of particular interest in environmental health studies

Element	RGAB	Adriano	CEPA	US EPA	CCME	OTR	HC
Ag		✓		✓		✓	✓
As	✓	✓	✓	✓	✓	✓	✓
B		✓					
Ba		✓			✓	✓	✓
Be		✓		✓		✓	✓
Cd		✓	✓	✓	✓	✓	✓
Co	✓	✓					✓
Cr	✓	✓	✓	✓	✓	✓	✓
Cu	✓	✓		✓	✓	✓	✓
F		✓	✓			✓	✓
Hg		✓	✓	✓	✓	✓	✓
Mn		✓				✓	✓
Mo		✓					✓
Ni	✓	✓		✓	✓	✓	✓
Pb	✓	✓	✓	✓	✓	✓	✓
Sb		✓		✓		✓	✓
Se		✓		✓	✓	✓	✓
Sn		✓					
Th	✓						
Tl		✓		✓	✓	✓	✓
U	✓					✓	✓
V		✓			✓	✓	✓
Zn	✓	✓		✓	✓	✓	✓

Table 2 in Part 2 gives an indication of the large number of elements that are present in measurable quantities in till (and also in other surficial materials such as soil, lake sediments and vegetation). Of these elements, a relatively small number have been identified as being of particular interest from the perspective of environmental contamination Table 9 lists elements that have been the focus of particular studies and/or government legislation. The seven categories in the table are:

- RGAB: Rencz, Garrett, Adcock and Bonham-Carter (this Open File), Part 3;
- Adriano: elements discussed in detail in Adriano's (2001) book, which gives an overview of the scientific basis for risk assessment and management of metal-contaminated sites;
- CEPA: The Canadian Environmental Protection Act, 1999 (CEPA 1999) established a "Toxic Substances List", which includes several trace elements (WWW links listed below);
- US EPA: The United States Environmental Protection Agency (EPA) includes thirteen metals on its Priority Pollutants List (Adriano, 2001, table 1.3);
- CCME: The Canadian Council of Ministers of the Environment (CCME) maintains a set of environmental guidelines for various media, including soil (CCME, 2004);
- OTR: The Ontario Provincial Government published a document entitled "Ontario Typical Range of Chemical Parameters in Soil, Vegetation, Moss Bags and Snow" (OTR), which lists values for many trace elements. These values are used as the basis for guidelines established by the Provincial Government's Environmental Protection Act (WWW links listed below);
- HC: The current report was commissioned by Health Canada, to assist in their task of managing federally owned contaminated sites across Canada. Health Canada supplied an initial list of sixteen elements of particular interest (Mark Richardson, pers. comm., 2004).

The statistical analysis presented in Part 3 of this report clearly demonstrates that natural concentrations of trace metals in till (and hence soils) vary enormously. A median value obtained from a large dataset may be highly inappropriate for a specific contaminated site. The variability is summarized in Table 10, along with CCME (2004) soil quality values for agricultural land use.

Table 10 Summary statistics for trace element concentrations in till (mg kg^{-1})

Element	Median	Range	Inter-Quartile Range	Threshold	CCME	
					SQG	ISQC
As	5.8	<0.5 - 1800	2.4 – 10	85	12	20
Co	7	< 0.5 - 95	3 – 13	310 (1000)		
Cr	62	<1 - 2300	41 – 93	95	0.4	8
Cu	19	< 1 – 3113	9 – 40	370 (500)	1100	150
Ni	16	< 1 - 881	8 – 30	210 (400)		
Pb	8	< 2 - 152	6 – 12	80	70	375
Th	11.9	< 0.2 - 128	7.1 – 17	63		
U	2.7	< 0.5 – 47.6	2 – 3.7	9 (42)		
Zn	34	< 2 - 1770	20 – 68	410	200	600

Threshold	Upper limit of background (from Table 8)
SQG	Soil Quality Guideline
ISQC	Interim soil quality criterion

The values in Table 10 can be compared to summary tables presented elsewhere:

- Cannon (1978): summarises trace element concentrations in different rock types; data are similar to those presented above, in Figure 1 and Table 1 (the data are reproduced in Adriano (2001; p801));
- Kubota (1978): summarises trace element concentrations in soils;
- Adriano (2001): table A.24 (p818) is a compilation of summary statistics for trace elements in soil from several sources;
- OTR: Ontario Typical Range values (see WWW link below).

A common weakness in all of these compilations is the inaccessibility of the raw data from which the statistics were calculated. The geographic distribution of the samples is not shown. Sampling protocols and analytical methodologies are not described. This makes it extremely difficult to assess the validity of the data. Nevertheless, the different compilations are in general agreement with one another.

This report examined only a small fraction of the till geochemical samples collected by the Federal and Provincial Governments across Canada. The derived database should be considered as an initial, provisional compilation. Further work is underway to enhance and expand the database. Statistical analysis of the expanded database should lead to background values related to the characteristics of the local natural environment.

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WWW links

Environment Canada

CEPA 1999 Toxic Substances List
http://www.ec.gc.ca/CEPARegistry/subs_list/Toxicupdate.cfm

Management of Toxic Substances http://www.ec.gc.ca/toxics/en/index.cfm

CCME http://www.ec.gc.ca/ceqg-rcqe/English/ccme/default.cfm

Health Canada

Contaminated Sites http://www.hc-sc.gc.ca/ewh-semt/contamsite/index_e.html;

Treasury Board

The Federal Contaminated Sites and Solid Waste Landfills Inventory
http://publiservice.tbs-sct.gc.ca/dfrp-rbif/cs-sc/home-accueil.asp?Language=EN

Government of Ontario

Standards for use with the Ontario Environmental Protection Act
http://www.ene.gov.on.ca/envision/gp/4697e.htm

"Ontario Typical Range" parameters
http://www.ene.gov.on.ca/envision/sudbury/ontario_typical_range/

Guidelines for the use of biosolids on agricultural land
http://www.ene.gov.on.ca/envision/gp/3425e.pdf

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