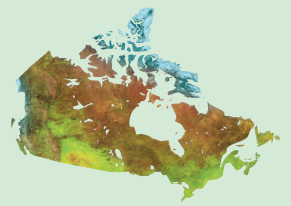




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*A.N. Rencz, R.G. Garrett, I.M. Kettles, E.C. Grunsky,
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Geological Survey of Canada

Current Research 2011-9

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ISSN 1701-4387

Catalogue No. M44-2011/9E-PDF

ISBN 978-1-100-18482-1

doi: 10.4095/288746

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Toll-free (Canada and U.S.A.): 1-888-252-4301

Recommended citation

Rencz, A.N., Garrett, R.G., Kettles, I.M., Grunsky, E.C., and McNeil, R.J., 2011. Using soil geochemical data to estimate the range of background element concentrations for ecological and human-health risk assessments; Geological Survey of Canada, Current Research 2011-9, 22 p. doi:10.4095/288746

Critical review

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Using soil geochemical data to estimate the range of background element concentrations for ecological and human-health risk assessments

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Abstract: A workshop on the role of geochemical data in ecological and human-health risk assessments was sponsored by Health Canada and Environment Canada in 2010. Participants from Geological Survey of Canada developed recommendations for acquiring and analyzing soil geochemical data to support risk assessment and outlined a procedure for estimating geochemical background, released as GSC Open File 6645. The following practices are proposed: 1) the collection of soil samples from pedologic horizons (the C, in particular) rather than depth-based intervals; 2) use of a spatially random sample design; 3) analysis of the less than 2 mm fraction (without ball or ring pulverizing) as a standard. Additionally, analysis of the silt-sized and finer fraction (<0.063 mm) provides more information on the mineral phases and residence sites of elements in soils and the patterns of regional variation; 4) dissolution using the USEPA 3050B aqua regia variant. Additionally, a method for estimating the amount of loosely held 'bioaccessible' amounts of the total-element concentration should be considered (e.g. water leach); 5) archiving of sample splits; and 6) evaluation of chemical data through the insertion, analysis, and monitoring of QA/QC samples.

The procedure for estimating geochemical background is based on plotting maps and graphs using the 'rgr' library and functions in R. R is an open source software environment and is available through CRAN mirror sites linked to <http://www.r-project.org/>. Metadata for 700 geochemical surveys carried out by the GSC and provincial agencies can be accessed through the Geochemical Data Repository at Natural Resources Canada.

Résumé : Un atelier sur le rôle des données géochimiques dans l'évaluation des risques pour l'environnement et la santé humaine, parrainé par Santé Canada et Environnement Canada, a eu lieu en 2010. Les participants de la Commission géologique du Canada ont élaboré des recommandations quant à l'acquisition et l'analyse de données géochimiques sur les sols en vue d'appuyer les évaluations des risques, et ont en outre présenté les grandes lignes d'une procédure pour estimer le fond géochimique, publiée dans le Dossier public 6645 de la CGC. Les pratiques suivantes sont proposées : 1) le prélèvement d'échantillons de sol selon les horizons pédologiques (et dans l'horizon C en particulier) plutôt qu'à des intervalles de profondeur définis; 2) l'utilisation d'un plan d'échantillonnage spatialement aléatoire; 3) l'établissement, comme pratique normale, de l'analyse de la fraction de granulométrie inférieure à 2 mm (fraction obtenue sans pulvérisation par broyeur à disque ou à billes), à laquelle peut s'ajouter l'analyse des particules de la taille des silt et des particules plus fines (< 0,063 mm), qui fournit davantage d'information sur les phases minérales et les sites de résidence des éléments dans le sol, ainsi que sur les tendances des variations régionales; 4) la dissolution selon la variante à l'eau régale de la méthode 3050B de l'EPA (Environmental Protection Agency des États-Unis); il faudrait en outre envisager d'utiliser une méthode d'estimation de la proportion « bioaccessible » faiblement liée de la concentration totale d'un élément (p. ex. lixiviation à l'eau); 5) l'archivage des fractions inutilisées des échantillons; et 6) l'évaluation des données chimiques par l'intégration d'échantillons d'assurance et de contrôle de la qualité parmi les échantillons à analyser, ainsi que la surveillance des résultats de ces analyses.

La procédure pour estimer le fond géochimique est fondée sur le tracé de cartes et de graphiques au moyen de la bibliothèque « rgr » et des fonctions du logiciel R, un logiciel libre disponible par l'entremise de sites miroir CRAN en lien avec le site <http://www.r-project.org/>. On peut consulter les métadonnées de 700 levés géochimiques, effectués par la CGC et par des organismes provinciaux, dans l'Entrepôt de données géochimiques de Ressources naturelles Canada.

INTRODUCTION

Knowledge of geochemistry is an important component of environmental and human-health risk assessments. Although much geochemical information needed to better inform risk assessments already exists, these data are not well represented in many of these assessments. As a step toward improving practice in this area, Health Canada and Environment Canada sponsored a workshop on the role of geochemical data in ecological and human-health risk assessments that was held on March 17–18, 2010, in Halifax, Canada. The Workshop was presented by scientists from the Geological Survey of Canada with recognized expertise in bedrock and surficial sediment geochemistry. Other participants included federal and provincial representatives and members of the environmental consulting community.

At the workshop there were presentations on the following topics relevant to risk assessment: 1) use of geochemical data in risk assessments; 2) causes of variation in geochemical data — natural spatial (horizontal and vertical) and analytical controls; 3) field sampling and analytical protocols; and 4) estimating background geochemical composition. Case studies were used to reinforce concepts and there were discussions on identifying knowledge gaps and on how to improve existing practices. The presentations and notes from discussions were gathered into a final document and released as GSC Open File 6645 (Rencz and Kettles, 2011).

The development of robust soil-quality guidelines requires that methods for collection and analysis of soil geochemical data be consistent and based on sound science. One aim of the workshop was to develop a strategy for improving guidelines by promoting more rigorous use of geochemical information. As a step toward realizing this goal, the GSC participants developed a list of recommended methodologies for acquiring and analyzing soil geochemical data. The original list of recommendations is included in Rencz and Kettles (2011), GSC Open File 6645, a modified version of which is presented here. The methodologies listed support risk assessment and include a procedure for estimating geochemical background. They serve to promote the use of standardized protocols for sampling and analyzing soils. The use of common protocols facilitates the comparison of soil and other data generated by different groups at different times.

The set of procedures proposed here serve as a starting point for data comparisons, but other methodologies should be considered to provide optimal characterization of the sites being assessed. For example, if information on human exposure to metals or bioaccessibility is required, the use of additional methods of sampling and analyzing soils and other media should be considered. These include the sampling of additional soil horizons or intervals and the use of other techniques for sample preparation and analysis such as

the water leach, physiologically-based extraction techniques (PBETs), and element speciation techniques (Garrett et al., 2009b; Dodd, 2011; Parsons, 2011).

Most of the methodologies described were developed or applied as part of the North American Soil Geochemical Landscapes Project (NASGLP) — a tri-national initiative between United States, Canada, and Mexico — as part of which Canada participated between 2004 and 2009. The project was established to meet the need for soil geochemical data by providing a consistent national- and continental-scale framework and database. Protocols for field sampling, chemical analysis, and data application were first tested in 2004 during a Canada–United States pilot study consisting of two sampling transects (east-west and north-south). A set of standard procedures was established as the basis for field sampling and chemical analysis in each of the three countries.

There are four sections in this report covering the spectrum from soil sample collection through data analysis. The first section has the recommendations for site selection, field sampling, and the use of thematic map layers for data plotting. The second covers analytical techniques and provides information on how the different methods of sample preparation and analysis cause variation in the resultant data. The third outlines an approach and provides a procedure for estimating geochemical background. The fourth section has information on how to access existing sets of published geochemical data for Canada.

BACKGROUND INFORMATION

The patterns of variation in the distribution and characteristics of bedrock and the overlying surficial sediments provide a context for understanding the patterns of physical and chemical variations in soils that have developed on them. The distribution of the surficial materials upon which soils have formed in Canada is shown in Figure 1. Figure 2 is a simplified map depicting the diverse types of bedrock that outcrop or underlie them. Descriptions, photographs, and useful references related to the different types of sediments and bedrock are provided in Kettles and Rencz (2011).

It should be noted that the composition of the surficial materials in Canada differs in several important aspects from most other parts of the world where soils have developed from the in situ weathering of bedrock. More than 95% of Canada was covered by glaciers periodically during the last 2 000 000 years and, as a result, the cover of surface sediments consists of materials that were eroded, transported, and deposited by glaciers (DiLabio, 1989; Dyke et al., 1989; Shilts, 1993). This surface cover is composed of unweathered fragments of crushed bedrock derived from diverse sources mixed with reworked older soils and sediments. The clay- to boulder-size materials forming these deposits were mostly eroded from the underlying or nearby bedrock (0 to tens of kilometres), but there is also a component of

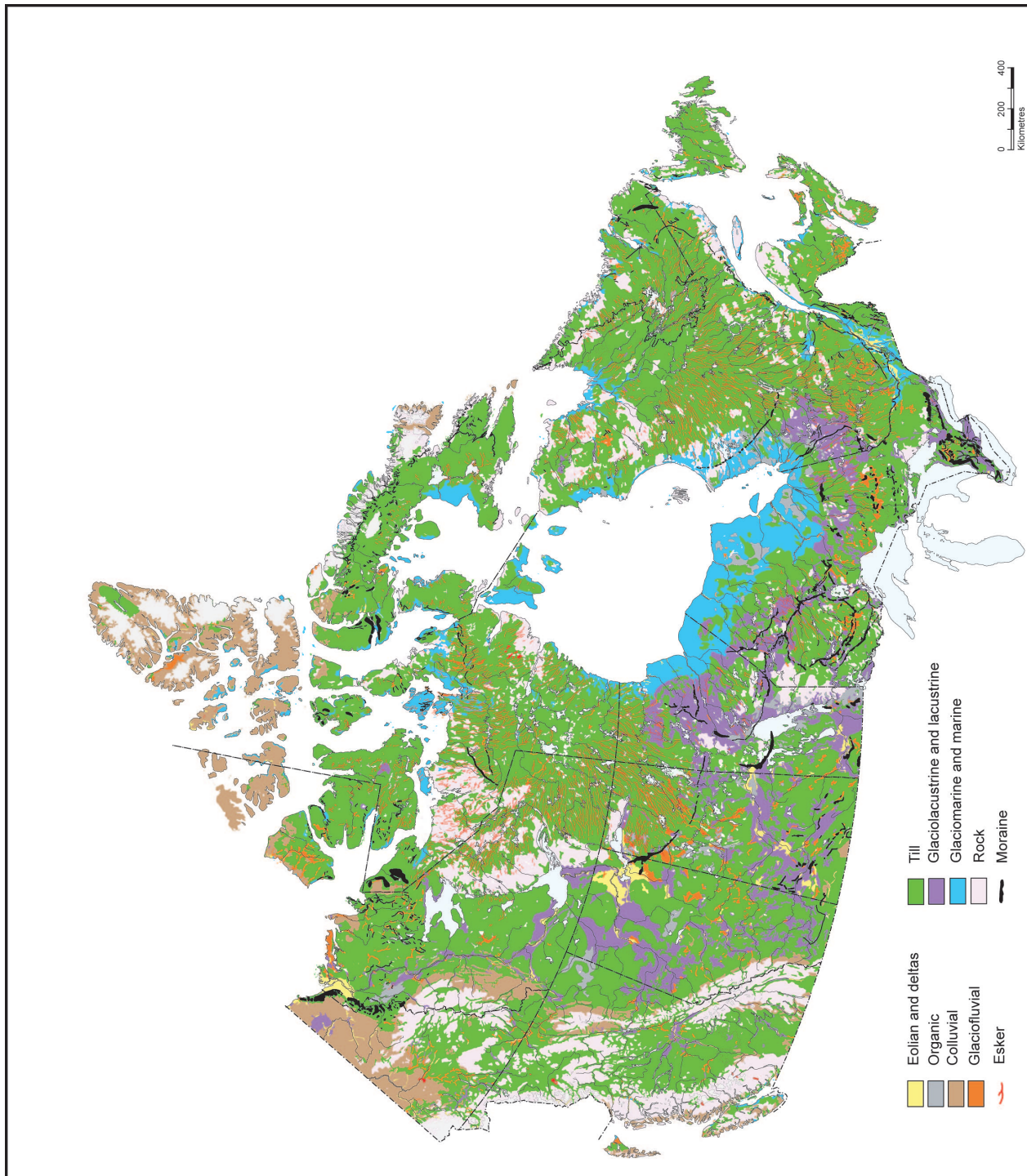


Figure 1. Map shows distribution of surficial materials in Canada (Fulton, 1995).

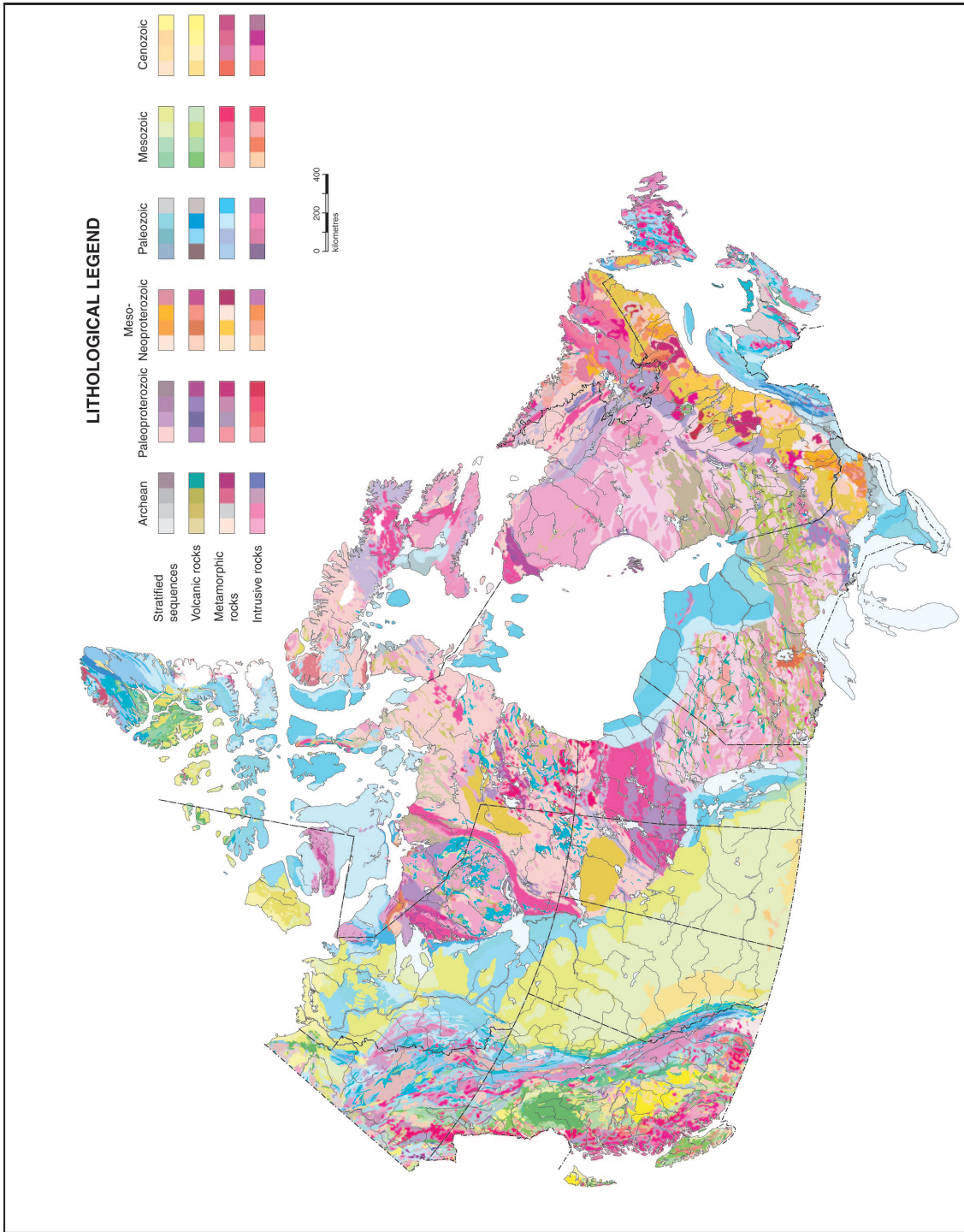


Figure 2. Map showing the bedrock geology of Canada (Wheeler et al., 1997).

exotic material transported hundreds to thousands of kilometres by glacial ice or meltwaters before being deposited. Once deposited, these sediments have only been exposed to surface weathering and soil-forming processes for the 8000 to 10 000 years since the last glaciers melted. Since this is a very short period with respect to geological time, the physical and chemical effects of weathering are generally confined to the uppermost 0–2 m.

An idealized soil profile is shown in Figure 3. Soils types are differentiated on the basis of measured properties of the profile and a hierarchical scheme is used to classify soils from general to specific. They are classified according to Order, Great Group, and Subgroup. Information is available in Chapter 3 of Canadian System of Soil Classification (third edition) (Soil Classification Working Group, 1998) available on line at <http://sis.agr.gc.ca/cansis/taxa/cssc3/chpt3.html>. At its most general level, the Canadian System of Soil Classification recognizes nine different soil orders. Figure 4 is a generalized map for Canada showing the distribution of soils according to type.

SITE SELECTION, FIELD SAMPLING, AND THE USE OF THEMATIC MAP LAYERS FOR DATA PLOTTING

For the development and implementation of a sampling design, several aspects of the geochemical landscape are considered. Two aspects are the patterns of change in soil composition with increasing depth (vertical variation), and the patterns of variability over an expanse of geographic area (horizontal variation). There are also differences in chemical composition between the different types of sample media (e.g. soil vs. vegetation) and between different phases of the same media (e.g. leaves vs. bark in trees), a few of which are noted here.

Vertical spatial variation

Within the uppermost metre of the soil there are variations in the textural, mineralogical, moisture, and organic composition that are expressed as soil horizons (Fig. 3). In most places, the horizons present in the soil profile can be distinguished visually. The chemical makeup of the materials in each horizon reflects the composition of the soil parent materials and the physical, chemical, and biological processes that have affected them over time. Each horizon formed as a result of a characteristic set of soil-forming processes. From one horizon to the next, there is variation in the amounts of sequestering mineral substances such as Fe- and Mn- sesquioxides, clay minerals, and organic matter. The patterns are mostly predictable, as are the effects of the variation on chemical composition. Consequently, based on the assumption that similar soil-forming processes have affected similar horizons, it is easier to explain the causes of geochemical variation in soils if samples are collected from similar pedological horizons. The collection of samples from intervals of fixed depth introduces more variation into the resultant data because the patterns of horizon development and the thicknesses of the individual soil horizons vary significantly from site to site and region to region.

To establish geochemical background and make reliable comparisons of data from different soil surveys, sampling by soil horizon is preferable to sampling by depth interval (McNeil, 2011). Some examples of changes in physical appearance and chemical composition of soil horizons are shown in Figures 3 and 5. Procedures for collecting horizon-based soil samples are documented in Friske et al. (2010).

At a bare minimum, the collection of two types of samples is recommended for risk-assessment purposes. The first is from the C horizon, the data from which are used to establish geochemical background. The C horizon is considered to be the layer least affected by soil-forming processes and the most representative of the soil parent materials. The second

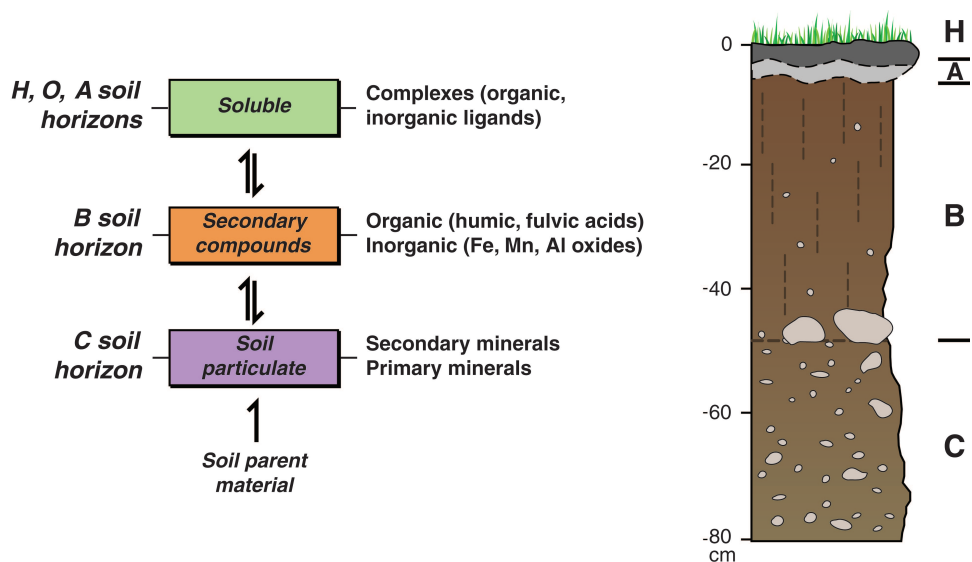


Figure 3. Diagram shows an idealized soil profile (right side) and descriptions of soil materials and mineral phases related to the H, A, B, and C horizons (Klassen, 2011).

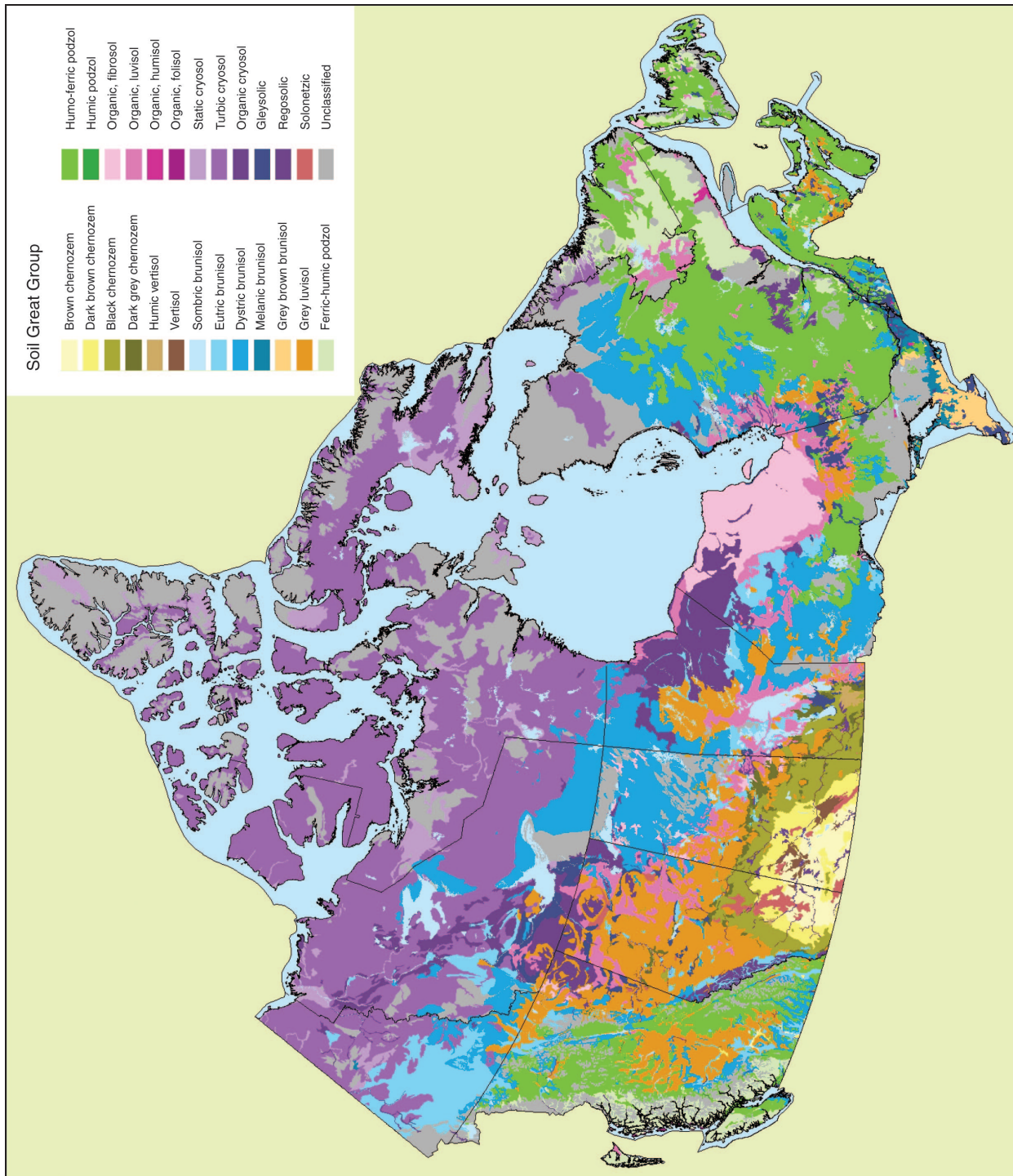


Figure 4. Map shows distribution of soils over Canada (Soil Classification Working Group, 2000).

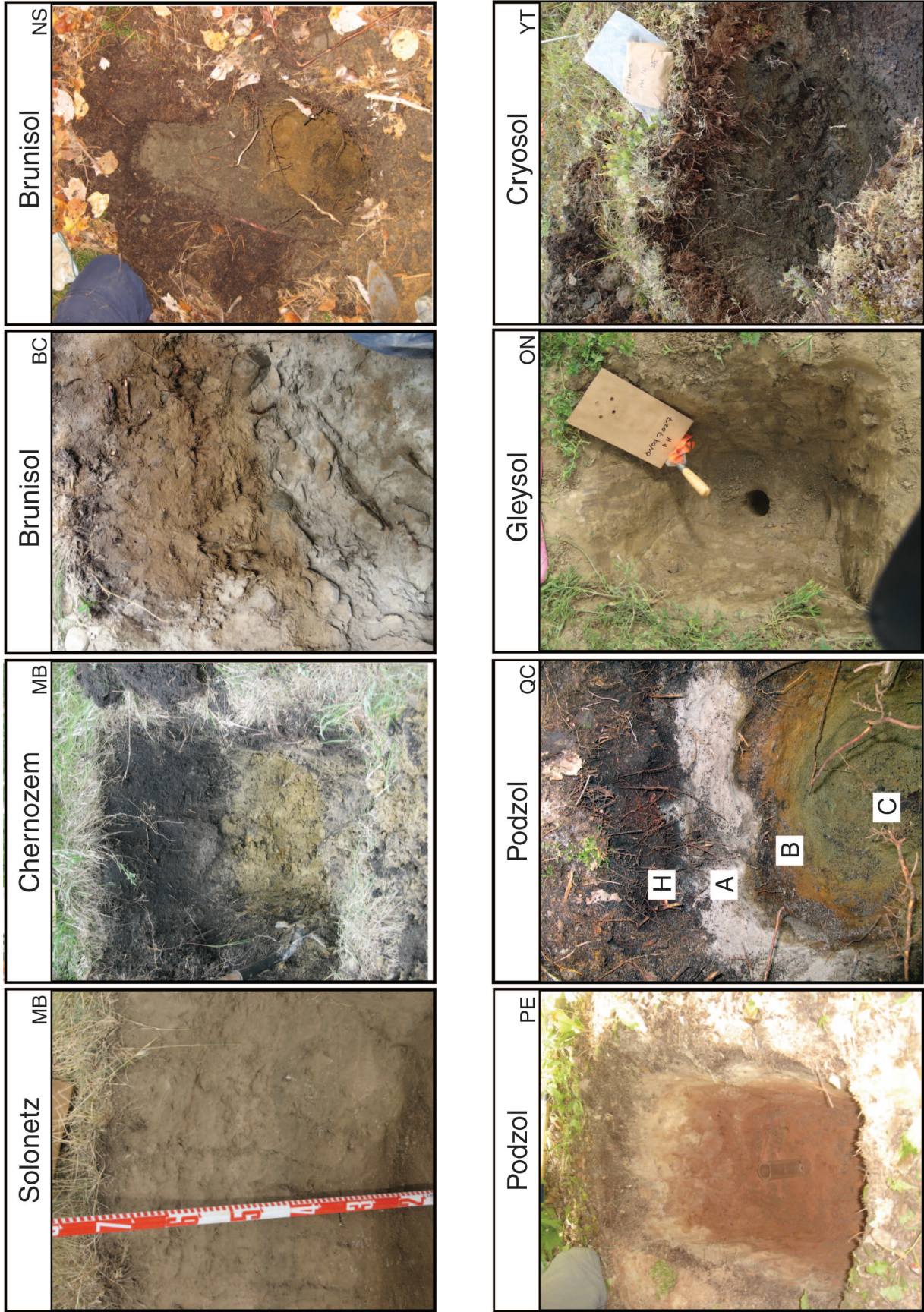


Figure 5. Photographs of common soil profiles sampled as part of the NASGLP in different provinces of Canada (Grunsky and McNeil, 2011). Solonetz, photograph by G. Matile/H. Groom, 2011-084; Chernozem, photograph by G. Matile/H. Groom, 2011-083; Brunisol, photograph by M. McCurdy, 2011-081; Brunisol, photograph by R. McNeil, 2011-078; Podzol, photograph by P. Friske, 2011-080; Podzol, photograph by R. McNeil, 2011-082; Gleysol, photograph by P. Friske, 2011-077; Cryosol, photograph by P. Friske, 2011-079. Some soil horizons are indicated. Abbreviations are as follows: MB = Manitoba, BC = British Columbia, NS = Nova Scotia, PE = Prince Edward Island, QC = Quebec, ON = Ontario, and YT = Yukon.

sample type is the 0–5 cm depth interval and is referred to as the Public Health (PH) layer. Data from this sample type provide information on the risks due to exposure to the soils. Although the PH is a depth interval for sampling as opposed to a pedological horizon, as recommended above, it is the sampling interval currently used by Health Canada. It was chosen because it is the layer of the soil that is in direct contact with living organisms.

If there is to be additional sampling, it is recommended that it follows the principle that horizon-based is preferable to depth interval-based sampling. For example, the United States Geological Survey, as part of the North American Soil Geochemical Landscapes Project, elected to collect and analyze samples from the A horizon (excluding the leached materials from the Ae subhorizon) (Woodruff, 2011). The resulting data provide information on the biologically active zone that is more easily compared at local and regional scales. Also, since the 1960s, samples from the upper B horizon were collected in many areas of Canada for mineral exploration purposes. As part of the NASGLP, one extra procedure for Canada included the collection and analysis of B-horizon samples.

Horizontal spatial variation

A spatially random sample design should be used to ensure statistically defensible estimates of the background range of element concentrations in soils (Garrett, 1983). A stratified random design is preferable because it ensures that all possible sites have an equal opportunity of being sampled. Details on the design used for the North American

Soil Geochemical Landscapes Project are provided in Friske et al. (2010), Garrett and Kettles (2009), and McNeil (2011).

Across Canada soils have developed on different types of surficial materials, including till, glaciofluvial sand and gravel deposits, glacial lake sediments, and glaciomarine sediments. These sediments were derived directly from diverse types of bedrock or indirectly through the recycling of older sediments (Fig. 1, 2). More information on the geological controls on the geochemical composition of soils is provided in Klassen (2010, 2011). When collecting samples to establish geochemical background, it is prudent to assess how representative the targeted site is with respect to overall variability in the area of interest. If the immediate study area is contaminated, a nearby area in the terrane that is pedologically and geologically similar to the contaminated study area should be sampled in order to estimate the most likely properties of background in the contaminated area.

If the objective is to detect contamination arising from natural sources or as the consequence of human activities, prior knowledge of the expected size of the contaminated area is required. This information may be garnered from published geological and geochemical maps, field observations, and historical documents. Samples should be collected on a grid pattern (Garrett and Grunsky, 2011). The area of the individual cells of the grid should be equal to or smaller, preferably by half, than the expected area of the contamination target. Knowledge of the dispersal process from the source of contamination is helpful when setting the orientation of the sampling design. If the ‘targets’ are ‘elliptical’ rather than circular the grid should be rectangular rather than square.

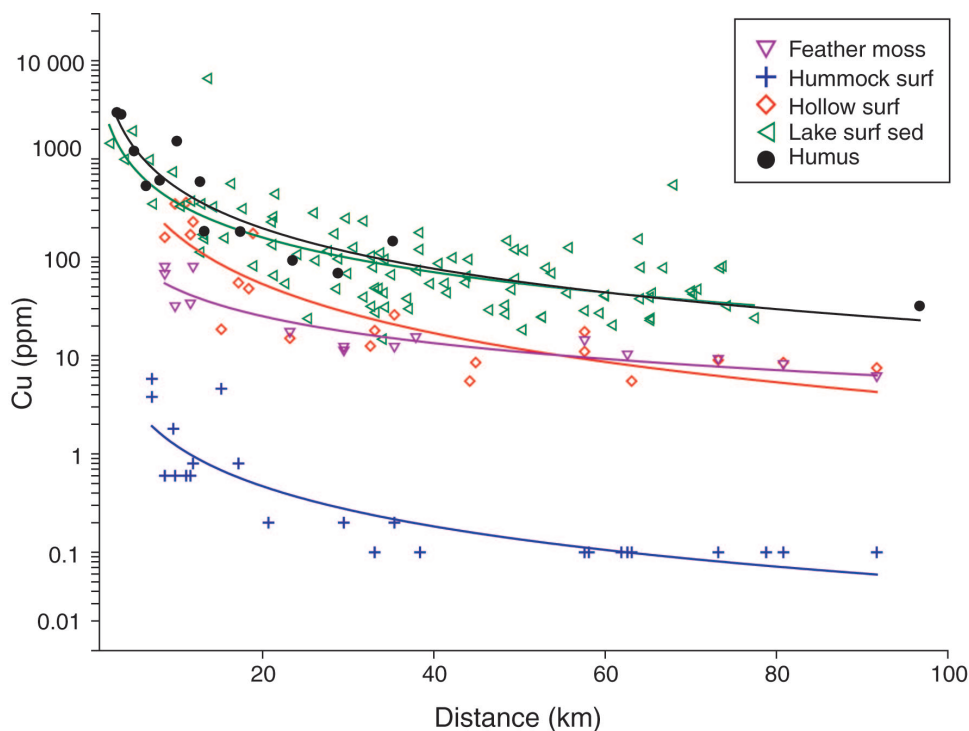


Figure 6. Distribution of copper in samples collected within a 100 km radius of the Horne smelter at Rouyn-Noranda, Quebec, illustrates differences in geochemical characteristics of different types of sampling media (Kettles, 2005). Note the use of a logarithmic scale. Samples were collected from the following types of media: recent growth of feather moss and sphagnum from the flat part of the peatland, sphagnum from the surface and at a depth of 30 cm from peat hummocks in the same peatlands. Elsewhere samples were collected from the humus layer in soils (Henderson et al., 2002) and from surface (surf) and deeper sediments (sed) in lakes (Kliza and Telmer, 2001). Best-fit trendlines are shown for each type of media.

An adequate number of samples are needed (Garrett, 2010; Garrett and Grunsky, 2011). For calculation of geochemical background using univariate statistical methods, 30 samples is the fewest number of samples, with 60 being preferred; however, after 120 samples, it is likely that not much precision is being added to the estimation. When multivariate statistical methods are used, there should be at least eight or nine times as many samples as the number of variables. For example, if there are 10 variables there needs to be at least 80 or 90 samples, with a couple of hundred being better.

Geochemical variation between different sample media

Numerous media (e.g. soils, rocks, water, surficial sediments, plants) have been used to characterize the geochemical nature of the environment. For terrestrial environments, soils are a useful sampling media for risk assessment. They are a direct source of elements for biotic systems and are relatively easy to sample. The following are some other aspects to be considered when choosing sampling media.

An ecosystem is composed of numerous biotic and abiotic components and there is considerable variation in chemical composition between these 'media'. The distribution of Cu in different types of samples collected in Rouyn-Noranda, Quebec, serves as an example (Fig. 6). Even for the same type of biological species, there may be up to a magnitude of difference in the concentration of elements in two types of tissue (e.g. Ni in the roots versus the leaves of sugar maples as described in Ford et al. (1988)). To avoid this variation, it is necessary to select only one type of media and to sample the same materials or tissue types from the selected media.

Biotic and abiotic components are linked in an ecosystem and elements flow from one compartment to the next. Researchers have used biological samples to infer element concentrations in soil; however, there is not necessarily a strong correlation between the two as demonstrated by Ford et al. (1988). Consequently, caution should be exercised in making such comparisons.

Soils are recommended as the preferred media for sampling to establish geochemical background in the terrestrial environment. Their chemical characteristics are less affected by seasonal variations than those of vegetation or living organisms. Samples collected at lower depths, notably the C horizon, are even less likely to be affected by temporal changes including contamination. Soils are present in most places and readily accessible. In addition, there is a large body of knowledge related to the pedological processes that characterize the different soil horizons and their effects on geochemical composition.

Use of thematic map layers for data plotting

In a GIS environment, geochemical data may be contoured or plotted as proportional symbols on thematic map layers (e.g. bedrock geology, surficial geology, soil groups, drainage basin, and land classification). When the distribution patterns of soil data are examined on themed map layers, it provides a visual context for the interpretation of the geochemical variability. Thematic layers also provide a framework for data integration and the generating of data subsets for statistical analysis.

Regional-scale map bases are currently available for all of Canada and all of North America based on eco-classifications. These incorporate all major components of ecosystems: air, water, geology, soil, and biota, including humans. They are based on a hierarchy of ecosystems nested within ecosystems. The State of the Environment Reporting spatial framework developed for Canada is maintained by the Canadian System of Soil Classification (CANSIS) group at Agriculture and Agri-Food Canada. It consists of 15 ecozones, 53 ecoprovinces, 194 ecoregions, and 1021 ecodistricts (Ecological Stratification Working Group, 1996; Marshall and Schut, 1999). The Commission for Environmental Cooperation (CEC; 1997) developed a system for North America, consisting of the following divisions: 15 for Level 1, 52 for Level 2, and 182 for Level 3. The similarities and differences between the two systems were outlined in Kettles (2011).

For studies undertaken at detailed scales or to address specific concerns, comparisons of soil geochemical data based on other spatial criteria may be advantageous. Some examples are soil type, surficial materials unit, underlying bedrock unit, and catchment areas for hydrological drainage basins. There is information on how to acquire existing data sets in Kettles et al. (2011).

ANALYTICAL TECHNIQUES

Sample preparation for chemical analyses

Sample preparation and chemical analyses are discussed in McNeil and Garrett (2011). Many existing practices used for soil sample preparation are documented in Girard et al. (2004) and Sheldrick (1984). The following are aspects to be considered.

For practical purposes, the less than 2 mm fraction is recommended as a standard for geochemical analysis. This fraction has traditionally been used by agronomists and the practice has continued in the field of environmental research and risk assessment. Hence, there is a large body of existing data based on analysis of this fraction; however, there are limitations associated with its use, some of which are considered in Klassen (2011).

There is considerable variation in chemical composition between textural classes. For many trace and minor elements, concentrations increase as particle size decreases. The geochemical substrates that have the capacity to concentrate trace elements have large surface areas, high cation-exchange capacities, and high surface charges (Horowitz, 1991). The most common of such substrates are hydrous manganese oxides, hydrous iron oxides, organic matter, and clay minerals, all of which tend to be concentrated in the finer size fractions. Data from analysis of the silt-sized and finer fractions (<0.063 mm) may provide more information on the mineral phases and residence sites of elements in soils and the patterns of regional variation for many trace elements (Shilts, 1975, 1984).

For Canada, there are existing geochemical data for several hundred regional sampling surveys of till, the most widespread parent material of soils, undertaken by the GSC and the provincial geological surveys for mineral exploration or environmental research purposes. The less than 0.063 mm fraction of the till samples was the one most commonly analyzed, but data for the less than 0.002 mm fraction are available for some parts of the country. The metadata for these surveys are provided in the Geochemical Data Repository at Natural Resources Canada (Spirito et al., 2007).

Ball or ring mill pulverizing should not be considered for risk assessments as the process may bias the final results. Such milling is used only for total analysis (using 4-acid digestions or X-ray or nuclear methods), but not for preparing samples to be treated with aqua regia and its variants, the water leach, or other partial extractions. Although sample materials are dried and screened prior to chemical analysis, if not disaggregated by pulverizing, the mineral fragments resistant to physical and chemical changes remain closer to their natural state.

Splits from all samples should be archived and stored. This provides materials for cross-checking purposes and also for further analyses as new issues arise and/or new analytical methodologies are developed.

Different types of chemical analysis

There are many techniques for chemical analyses, each having their advantages. The following methods are endorsed.

To support consistency, a commonly used aqua regia digestion is recommended. A study undertaken at the Geological Survey of Canada (Garrett et al., 2009a) has shown that there are only small differences between various aqua regia-like digestions involving various combinations of HCl, HNO₃, and water for most trace metals commonly subject to environmental reviews. For this reason it is recommended that the widely used and accepted USEPA 3050B aqua regia variant be used, i.e. a 4:1 HCl-HNO₃ digestion. This is a relatively strong leach. When compared to results

obtained using a total method (INAA), it provides similar total-element recovery for some elements (e.g. Cu, Pb, and Zn), but poorer recovery for others such as Cr and V. Selected results from the aqua regia study are shown in McNeil and Garrett (2011).

In addition to the aqua regia analyses, a method for estimating the amount of loosely held 'bioaccessible' amounts of the total-element concentration should be considered. There are a number of techniques for assessing bioavailability. The water-leach method is one method that it is relatively easy to use (Garrett et al., 2009b).

Speciation is relevant for estimating soil toxicity. For example, there is considerable difference between the toxicity of As⁺³ compared to As⁺⁵. Some information on speciation is provided in Parsons (2011), but additional information and more research are required before methodologies can be recommended. These types of analysis are very costly at present and, hence, any requests for them to be undertaken need to be soundly justified.

Quality assurance and quality control (QA/QC)

The quality of the geochemical survey and the resulting chemical data are evaluated by the insertion, analysis, and monitoring of quality assurance and quality control (QA/QC) samples. Procedures for this undertaking were developed as part of the National Geochemical Reconnaissance Programme at Geological Survey of Canada (Friske and Hornbrook, 1991). Further information is provided in McNeil (2011) and McNeil and Garrett (2011).

The following are the practices recommended for evaluating geochemical data.

A field duplicate should be collected at an appropriate distance from a 'regular' sample site. This distance will be a small proportion of the distance between 'regular' sample sites and reflect the probable uncertainty in reoccupying the site at a later date, usually some distance between 5 m and 10 m.

It is necessary to include analytical duplicates, i.e. a split of one of the field samples in order to determine the analytical precision of the data. When field duplicates have been collected, it is advantageous to generate the analytical duplicate data from a split of one of the field duplicate samples.

It is essential to include aliquots of a control reference material (CRM) in each batch of samples, to ensure that there is no 'analytical drift' during the course of a project, and, if appropriate, between projects. For large projects more than one CRM should be used.

Internationally certified CRMs are available where the analyses have been undertaken with an aqua regia-related digestion. To the greatest possible extent the CRMs should be derived from similar types of surficial materials to those

of the collected samples. If CRM matrices are unrelated to that of the sampled materials, instrument-mineral interference affecting either analytical accuracy or 'drift' may not be recognized.

A frequency of insertion of quality assurance and quality control materials of 15% is a good compromise between adequate QA/QC and minimizing overhead costs. Thus each group of 20 field samples should include three QA/QC samples: a field duplicate, an analytical duplicate, and a CRM.

To ensure that the quality assurance and quality control samples are not treated with additional care by laboratory staff, they should be inconspicuously labelled and placed randomly among the routine survey samples so their locations are not obvious.

A variety of graphical methods are available to monitor and evaluate data quality. Control charts can be plotted for CRMs, using date of analysis or batch number for plotting. Where an established CRM is used, tolerance bounds can be established, and the laboratory can be alerted if samples fall 'out of tolerance'. Field and analytical duplicates can be plotted on Thompson-Howarth diagrams (Thompson and Howarth, 1978). If more than the expected numbers of duplicate analyses fall 'out of tolerance', follow-up should be initiated with the laboratory or a field investigation can be undertaken.

Statistical summaries and analyses should be undertaken. Precision, expressed as the percentage relative standard deviation (RSD) or coefficient of variation (CV), can be estimated from the repeat analyses of the CRM(s) and analytical duplicate pairs. Analysis of variance (ANOVA) can be used to determine if the field or analytical variability are sufficiently small relative to variability across the study area to be able to discuss spatial distribution with confidence. Where the analytical duplicates have been split from the field duplicates, ANOVAs can be undertaken where study area, local field, and analytical variability are evaluated as a whole. It is the responsibility of the investigating scientist to ensure, independently from a service analytical laboratory, the integrity of geochemical survey data.

ESTIMATION OF GEOCHEMICAL BACKGROUND

The discussion of geochemical background that follows is provided in Garrett and Grunsky (2011). The concept of geochemical background was developed in the 1940s and 1950s. It was introduced to differentiate between normal element concentrations and chemical anomalies that might be indicative of ore mineral occurrences. Background was defined by Hawkes and Webb (1962) as: "The normal abundance of an element in barren earth material." They also concluded that "It is more realistic to view background as

a range rather than an absolute value." Today geochemical surveys have equal applicability to environmental issues and concerns.

Geochemically there is no immediate difference between anomalies arising from a natural process, e.g. the formation of a mineral deposit, or as a result of contamination of the natural environment by an anthropogenic process. Both types of processes impose an 'overprint' on the natural regional geochemical background. Although some would argue that natural background no longer exists, anthropogenic processes have distributed contaminants world-wide, a look at regional geochemical maps demonstrate that natural processes still dominate the distribution of trace elements on regional and continental scales (Reimann et al., 2009, 2010).

Two terms related to geochemical background are commonly used: natural background and ambient background. Ambient background is the sum of natural background levels and any anthropogenic additions. Background levels usually differ between sample media, thus levels in air, water, lake, stream and/or river and marine sediments, and soils will be different; however, all will be related to their source materials, i.e. rocks, and these will be modified by the physical, chemical, and transport processes characteristic of the sample media. Difference in rock chemistry (geochemistry) for a single element may vary by orders of magnitude (Garrett, 2005).

Univariate methods

A wide variety of procedures are available for estimating the range of geochemical background variation, (*see* Reimann et al. (2005) and Reimann and Garrett (2005)), and none give similar estimates. On the understanding that geochemical background is a range and not a single value that represents "the normal abundance of an element in barren earth material" (Hawkes and Webb, 1962), where 'barren' indicates devoid of the influence of ore deposits or site specific anthropogenic contamination, a simple approach is to use the percentiles of a set of background geochemical data representing the study area.

To demonstrate the steps needed to estimate geochemical background the authors have used a set of as yet unpublished geochemical data for soil samples collected from selected horizons at sites in the Maritime Provinces of Canada (Friske et al., in press). These data are for the less than 2 mm fraction of samples collected between the ground surface and a depth of 5 cm. The samples were analyzed using ICP-MS after digestion with an aqua regia variant (USA-EPA 3050B). The format of the data set is shown in Figure 7.

Software to construct maps and graphs

The maps and graphs that follow were plotted, except where indicated, using the 'rgr' library (Garrett and Chen, 2007) and functions in R. R is an Open Source software

UniqueID	Lat_NAD83	Long_NAD83	Province	Ecoregion	Soil Type_SLC	SubRx Type
NB071001	45.91	66.70	NB	Maritime Lowlands	Podzolic grey luvisolic	Nonmarine sedimentary rocks
NB071002	45.78	66.53	NB	Maritime Lowlands	Gleysolic	Nonmarine sedimentary rocks
NB071005	46.05	66.87	NB	Maritime Lowlands	Regosolic	Nonmarine sedimentary rocks
NB071009	46.03	66.51	NB	Maritime Lowlands	Podzolic grey luvisolic	Nonmarine sedimentary rocks
NB071011	45.54	66.91	NB	Southern New Brunswick Uplands	Humo-ferric podzolic	Nonmarine sedimentary rocks
NB071012	45.46	67.12	NB	Southern New Brunswick Uplands	Gleysolic	Sedimentary rocks, undivided

UniqueID	As_PH <2 mm_3050B	Pb_PH <2 mm_3050B	C-Organic_PH <2 mm	As_C-hor <2 mm_3050B	Pb_C-hor <2 mm_3050B	C-Organic_C-hor <2 mm
NB071001	0.7	6.7	43.1	12.7	14.2	0.7
NB071002	4.0	22.5	27.1	5.9	8.9	0.1
NB071005	6.1	35.5	16.3	11.6	13.2	0.8
NB071009	3.9	26.4	7.2	6.9	11.9	0.2
NB071011	1.5	75.6	44.6	7.5	11.5	1.2
NB071012	4.2	25.7	19.8	9.1	8.5	0.3

Figure 7. Example from data set used for demonstration purposes to estimate geochemical background (Friske et al., in press). Data were obtained from soils collected as part of the North American Soil Geochemical Landscape Project. The abbreviations represent the following: UniqueID = sample number, Lat_NAD83 = latitude, Long_NAD83 = longitude, Prov = province of Canada, EcoR = Ecoregion of Canada, Soil Type_SLC = soil unit based on the Soil Landscapes of Canada (Soil Landscapes of Canada Working Group, 1996), SubRx Type = underlying bedrock type after Wheeler et al. (1997), As = arsenic, Pb = lead; C-organic = % organic carbon, PH = public health interval (0–5 cm), C-Hor = C horizon of soil; <2 mm = <2 mm fraction of sample, and 3050B = USA-EPA 3050B aqua regia variant.

environment for statistical computing and graphics. It runs on a wide variety of UNIX, Windows, and MacOS platforms. It is managed by the Comprehensive R Archive Network (CRAN) and R and associated packages can be downloaded from a number of CRAN mirror sites linked to <http://www.r-project.org/>. Should it be decided to use R and 'rgr', it is recommended that before downloading any software you set up a working directory on the data drive of your computer (e.g. D:\R\WD) to store the files produced using 'rgr'.

One mirror site is at the University of Toronto, <http://probability.ca/cran/>. Within the site there are versions of R and also 'rgr'. The 'rgr' package is available to be downloaded from the 'Contributed Packages' section. It is downloaded as a zipped file and should be left in that format on your computer. At the same time it is necessary to download and save one other package — akima — from the 'Available Packages' section. It is a dependency needed to run 'rgr'. Use of the 'rgr' package requires that R is up and running on the computer on which the 'rgr' package is to be installed. Figure 8 shows the first window that appears once R is started. The package 'rgr' is brought into R by first clicking on 'Packages' on the drop down menu, as shown in Figure 8, and then clicking on the last option 'Install package(s) from local zip files'. The two dependencies, akima and MASS, need to be installed using the same procedure.

The next step involves installing an 'rgr.first' function (see Appendix 02-01 of Rencz et al. (2011)). Open 'rgr.first' in the software program Notepad and copy the contents of

the file. Return to the R workspace and type: `fix(rgr.first)`. When the editor screen comes up, paste the copied text into the editor. If needed, edit the first line of the copied text so that it exactly the same as the first line in the editor, and then save the editor file. To execute the function type `rgr.first()` after the >prompt. Please, note that from this point on in any new work session, 'rgr' is initiated by typing `rgr.first()` after the >prompt.

In Appendix 02-02 of Rencz et al. (2011) there is an example of a workspace generated using R and saved. It shows the installations described above and also the addition of the Maritime geochemical data used in this example. The session in R is ended by typing: `q()`. Please note that it is important to save the workspace if new data (an object) or any functions have been added during the session so that they can be used again in future. If you have not added any new data (i.e. created a new object) or functions, click the 'no' button.

There were over 100 functions written at GSC to support exploration and applied geochemical survey and research activities. An overview of the 'rgr' functions from Open File 5583 (Garrett and Chen, 2007) is presented in Appendix 02-03 of Rencz et al. (2011). The 'rgr' functions described here fall dominantly under the title of univariate exploratory data analysis tools. Within the R workspace, it is possible to see a list of the functions by typing: `help(rgr)`. Go to the help file to see what can be done in 'rgr'. The 'rgr' package also includes the same test data as that used in Reimann et al. (2008) on applied environmental statistics.

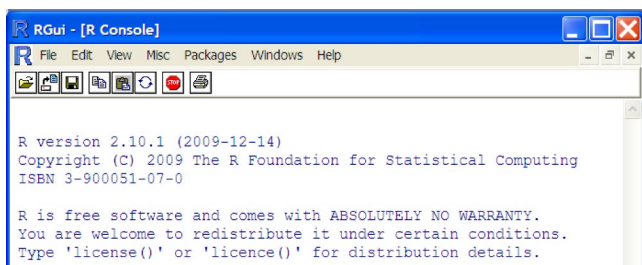


Figure 8. First window that opens in the R software program.

Steps for estimating geochemical background

In the section that follows, three steps for estimating background are outlined in detail. The first step is undertaken to determine if there is only one population in the data, and if there are multiple background populations, to generate data subsets for each. The second step is carried out to identify and remove outliers from the data set or subsets. There are subjective aspects within these first two steps that require the analyst to make observations and choices related to the data set. Some tools are provided to aid this decision making. The third step, the actual calculation of the background range is straightforward; however, there are several ways to make such calculations.

Step 1: ensuring only one population in the geochemical data set

It is necessary to determine if the data are drawn from a single background population. This is accomplished by inspecting the data, element by element, on maps and generating graphical plots of the data and summary statistical tables as described below. Where there are multiple populations, the data set will need to be divided up according to population and background ranges estimated for each.

Inspecting data on maps

The geochemical data for the area of interest should be viewed element by element as maps. If location data for sample sites are available, three ‘eda’ mapping functions in ‘rgr’ are available to display simple spatial plots for data inspections. It should be noted, however, that this function does not replace the use of GIS software packages. Maps, based on geochemical data, plotted using proportional or colour-coded symbols are shown below, were taken from Garrett and Grunsky (2011), and were plotted using Arcview (Fig. 9, 10). The maps show the distribution of As and Pb in the ‘public health’ interval (0–5 cm) of the Maritime soil samples. In some cases, locally coherent patterns unrelated to a contamination source (cf. a mineral occurrence or

deposit) may be clearly visible on the maps. When this is the case, the data should be split into two or more groups and the cause of the spatial differences determined.

Generating summary statistical tables

It is useful to generate summary statistical tables to help estimate the range of background variation. The statistical tables include listings of the minimum, maximum, mean, median, 1st quartile, and 3rd quartiles and the following measures of dispersion – standard deviation, median absolute deviation (MAD), and the coefficient of variation (CV). Shown in Figure 11 are such tables for As and Pb for samples from the PH interval. These were generated using the ‘inset’ function in ‘rgr’. The output appears in a second window entitled [R2 Graphic: Device 2 (ACTIVE)]. The R scripts with ‘rgr’ workspace to generate the plots are shown in Appendix 02-04 of Rencz et al. (2011).

Inspecting data using statistical graphics displays

Data should also be viewed using statistical graphics displays (histograms, box plots, density plots, and Q-Q plots). Histograms, for example, may indicate the presence of more than one population in the data. There are functions in ‘rgr’ to accomplish these tasks (see list at the end of Appendix 02-04 in Rencz et al. (2011)). Histograms and cumulative probability plots are shown in Figure 11. In the case of the Maritime sampling project, the data set was divided, based on the distribution of samples in the three ecoprovinces in the Maritimes — Appalachian and Acadian Highlands, Northumberland Lowlands, and Fundy Uplands (see Kettles, 2011). The data subsets are composed of 43, 56, and 84 samples, respectively. Tukey box plots (Tukey, 1977) and larger scale cumulative probability plots for the Maritime data are shown in Figures 12, 13, and 14. These were generated using the ‘tplot’ and ‘gx.cnplts’ functions from the ‘rgr’ package, discussed above. The scripts used are presented in Appendix 02-05 of Rencz et al. (2011). There are clear differences between the statistical distributions for data from the three ecoprovinces. Note that cumulative probability plots, based on the whole data set, as shown on Figure 11 with the statistical tables, do not clearly indicate the presence of multiple populations. This is not uncommon for mixtures of data with similar means.

Step 2: identification and removal of outliers in the data set

The data set or subsets should be inspected for outliers. Outliers are individual data points that do not appear to ‘belong’ to the data population. There is a need for visual inspection via probability (Q-Q) plots. Outliers may also be identified through calculation. Methods used for calculation are as follows: 1) mean \pm 2 standard deviations

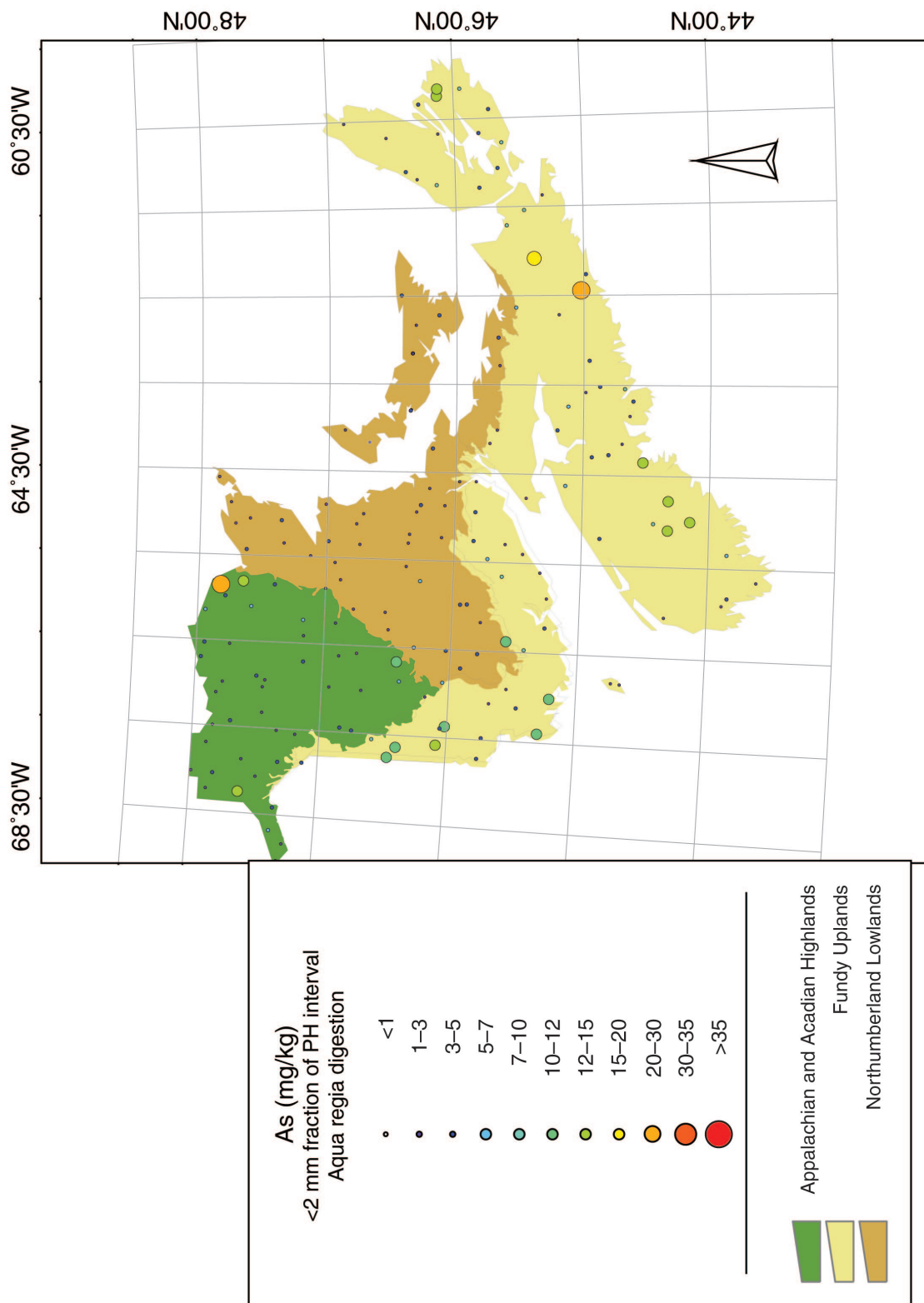


Figure 9. Arsenic in the 'public health' interval (0-5 cm) of soils, based on analysis of the less than 2 mm fraction using an aqua regia variant (USA-EPA 3050B) digestion and the ICP-MS technique.

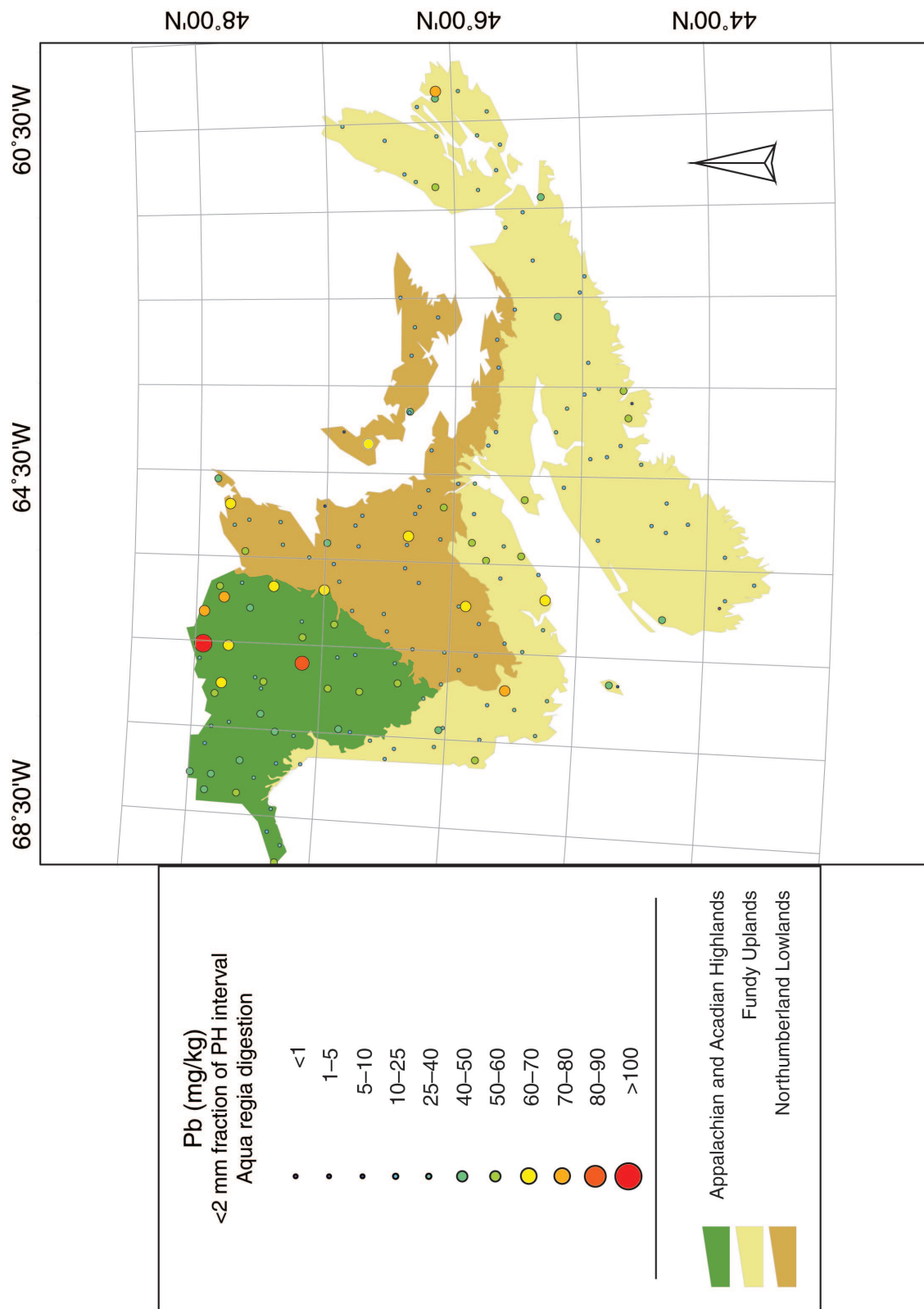


Figure 10. Lead in the 'public health' interval (0-5 cm) of soils, based on analysis of the less than 2 mm fraction using an aqua regia variant (USA-EPA 3050B) digestion and the ICP-MS technique.

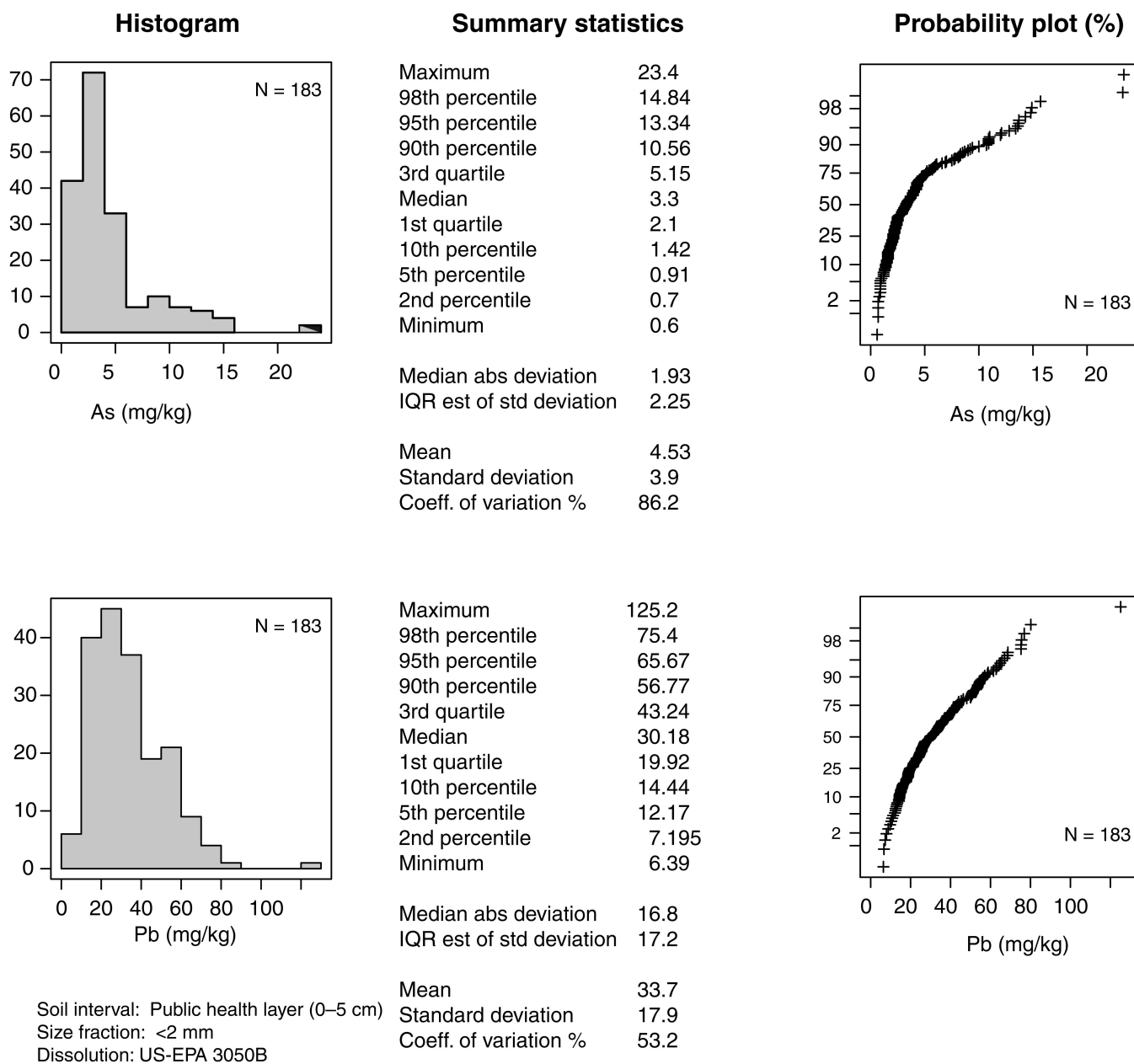


Figure 11. Summary statistics, histograms, and cumulative probability plots for As and Pb in the less than 2 mm fraction of the ‘public health’ interval (PH; 0–5 cm) of soils from the Maritime provinces. Samples were analyzed using an aqua regia variant (USA-EPA 3050B) and the ICP-MS technique. IQR est of std deviation = interquartile range estimate of standard deviation, Coeff. of variation % = coefficient of variation %.

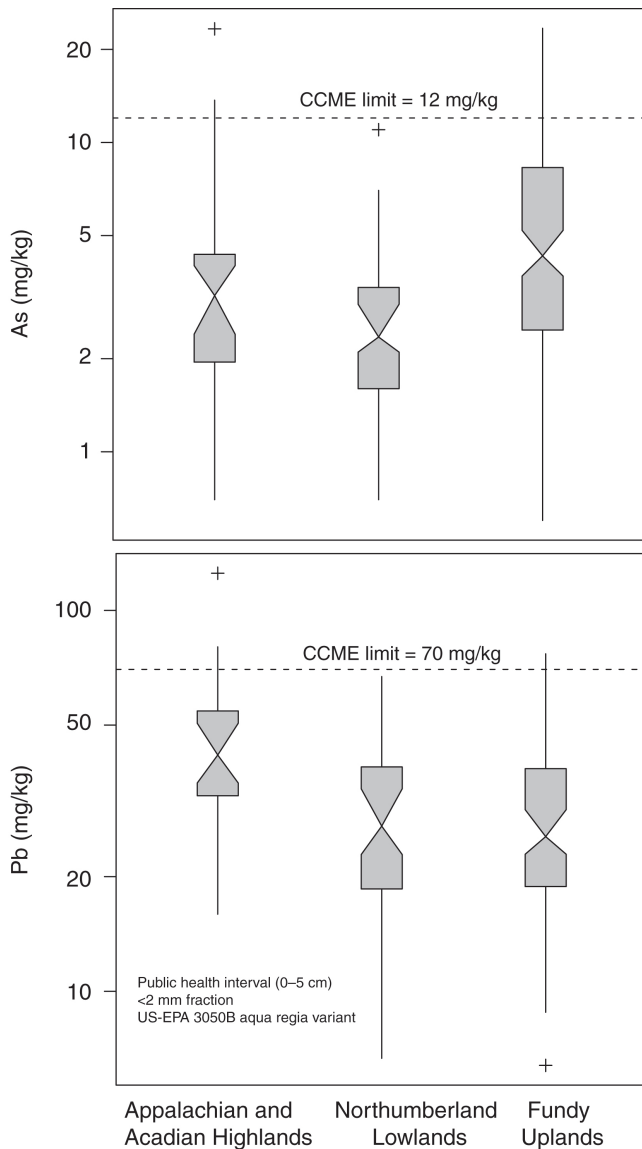


Figure 12. Tukey box plots showing the distribution of As and Pb in the 'public health' interval (0–5 cm) of Maritime soils by ecoprovince. Also shown are the soil quality guideline values for As and Pb set by the CCME (Canadian Council of Ministers of the Environment, 2001).

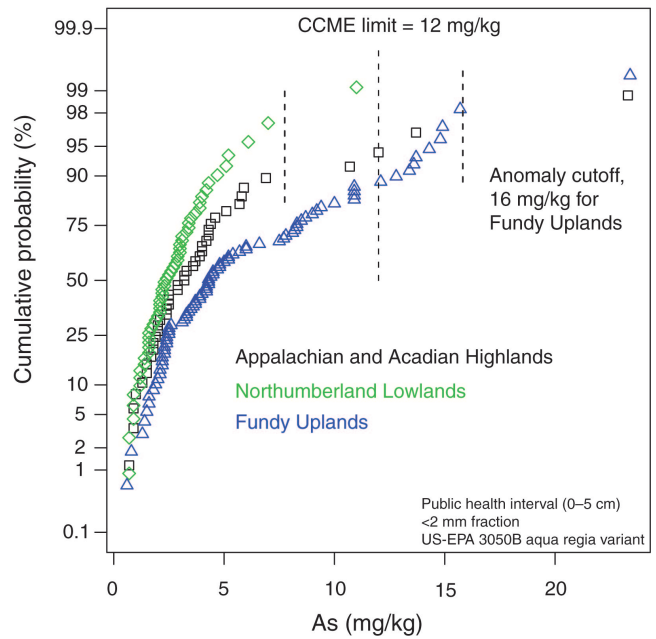


Figure 13. A Q-Q plot of As in samples collected from the 'public health' interval (0–5 cm) of soils in three ecoprovinces of the Maritime provinces. Also shown are the cutoff point for data to be used to estimate geochemical background and the upper limit from the CCME guidelines (Canadian Council of Ministers of the Environment, 2001).

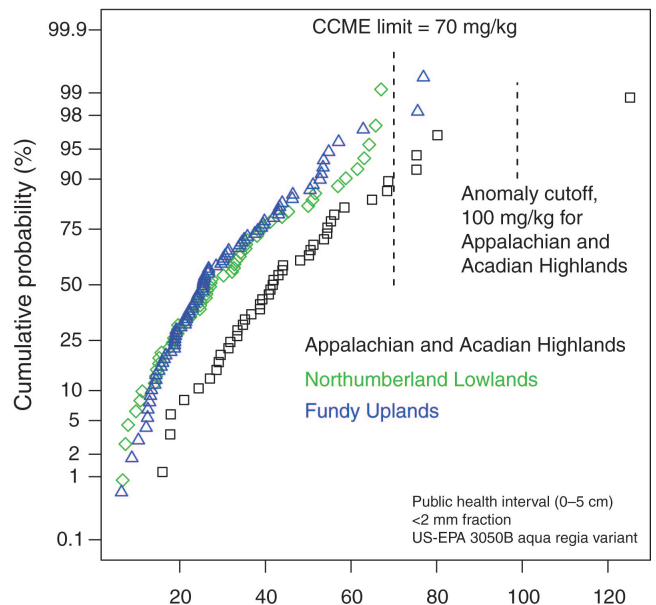


Figure 14. A Q-Q plot of Pb in samples collected from the 'public health' interval (0–5 cm) of soils in three ecoprovinces of the Maritime Provinces. Also shown are the cutoff point for data to be used to estimate geochemical background and the upper limit from the CCME guidelines (Canadian Council of Ministers of the Environment, 2001).

Table 1. Calculated estimates of geochemical background As and Pb for the ‘public health’ interval (0–5 cm) of soil samples collected in the Maritime Provinces of Canada.

<i>As (mg/kg) Appalachian and Acadian Highlands</i>								
As_PH		N = 43		2%ile = 0.868		98%ile = 15.2		
	Mean	SD	Median	MAD	See note	Mean±2SD	Med±2MAD	Tukey fences (actual)
	4.16	4.08	3.2	1.78	+	12.3	6.76	7.95 (6.9)
					-	-4.01	-0.358	-1.65 (0.7)
Log10	0.492	0.321	0.505	0.3	+	13.6	12.7	14.5 (13.7)
					-	0.708	0.803	0.585 (0.7)
<i>As (mg/kg) Northumberland Lowlands</i>								
As_PH		N = 56		2%ile = 0.72		98%ile = 6.91		
	Mean	SD	Median	MAD		Mean±2SD	Med±2MAD	Tukey fences (actual)
	2.79	1.74	2.35	1.11	+	6.27	4.57	6.1 (5.2)
					-	-0.696	0.126	-1.1 (0.7)
Log10	0.377	0.245	0.371	0.243	+	7.38	7.18	10.5 (7)
					-	0.77	0.769	0.517 (0.7)
<i>As (mg/kg) Fundy Uplands</i>								
As_PH		N = 84		2%ile = 1.13		98%ile = 15.2		
	Mean	SD	Median	MAD		Mean±2SD	Med±2MAD	Tukey fences (actual)
	5.87	4.36	4.3	3.11	+	14.6	10.5	17 (15.7)
					-	-2.85	-1.93	-6.26 (0.6)
Log10	0.656	0.323	0.633	0.393	+	20.1	26.3	51 (23.4)
					-	1.02	0.703	0.403 (0.6)
<i>Pb (mg/kg) Appalachian and Acadian Highlands</i>								
Pb_PH		N = 43		2%ile = 17.5		98%ile = 87.4		
	Mean	SD	Median	MAD		Mean±2SD	Med±2MAD	Tukey fences (actual)
	45.4	20.3	41.7	17.7	+	85.9	77.2	87.2 (80.2)
					-	4.88	6.26	-0.152 (15.9)
Log10	1.62	0.186	1.62	0.172	+	97.8	92.1	118 (80.2)
					-	17.6	18.9	15.1 (15.9)
<i>Pb (mg/kg) Northumberland Lowlands</i>								
Pb_PH		N = 56		2%ile = 9.82		98%ile = 67.2		
	Mean	SD	Median	MAD		Mean±2SD	Med±2MAD	Tukey fences (actual)
	30.9	16.4	27.1	15.2	+	63.7	57.5	69.2 (67)
					-	-1.9	-3.22	-11.8 (6.67)
Log10	1.42	0.252	1.43	0.242	+	84.8	82.6	117 (67)
					-	8.31	8.92	6.15 (6.67)
<i>Pb (mg/kg) Fundy Uplands</i>								
Pb_PH		N = 84		2%ile = 9.82		98%ile = 67.2		
	Mean	SD	Median	MAD		Mean±2SD	Med±2MAD	Tukey fences (actual)
	29.5	14.9	25.5	13.2	+	59.3	51.9	67.8 (62.9)
					-	-0.331	-0.9	-10.5 (6.39)
Log10	1.42	0.219	1.41	0.212	+	71.4	67.7	112 (76.9)
					-	9.55	9.59	6.47 (8.81)

Note: The column with the + indicates that on that row the values are for Median+2MAD, Mean+2SD, etc. and the - row is for Median-2MAD, etc. SD = standard deviation, MAD = median absolute deviation.

Table 2. Estimates of background based on statistical analyses of remaining geochemical data obtained using a hybrid procedure.

As (mg/kg)	N	Min	Max	Cutoff	N	Min	98th %ile	Max
Appalachian and Acadian Highlands	43	0.7	23.3	8	39	<i>0.7</i>	<i>6.1</i>	<i>6.9</i>
Northumberland Lowlands	56	0.7	11	8	55			
Acadian Uplands	84	0.6	23.4	16	83		<i>14.8</i>	<i>15.7</i>
Pb (mg/kg)	N	Min	Max	Cutoff	N	Min	98th %ile	Max
Appalachian and Acadian Highlands	43	15.9	125.2	100	42		<i>76.2</i>	<i>80.2</i>
Northumberland Lowlands	56	6.7	67	70	56	<i>6.7</i>	<i>66</i>	<i>67</i>
Acadian Uplands	84	6.4	76.9	70	82	<i>6.4</i>	<i>55.7</i>	<i>62.8</i>
For example, estimates of background range for As in the Acadian Uplands are 0.6–15 mg/kg and for Pb in the Appalachian and Acadian Highlands are 16–76 mg/kg (see numbers in italics).								

(SD); 2) median \pm 2 median absolute deviations (MAD); and 3) Tukey box plot ‘normal’ range (Tukey, 1977). If a calculation is required, Reimann et al. (2005) recommend procedure (2), the use of medians and MADs. These provide upper and lower limits of the expected range of the data based on ‘normal law’. Once the cutoff values are set, outliers, if present, should be removed from the data set or subset.

Figures 12 and 13 show visually, based on Q-Q plots, the identification of outliers and selection of cutoff values for As and Pb concentrations in the 0–5 cm interval of the Maritime soil samples. The R and ‘rgr’ workspace used to generate these plots is shown in Appendix 02-06 of Rencz et al. (2011). Some calculated estimates for As and Pb based on background ranges for the Maritime data set are shown in Table 1. These estimates were obtained using the ‘fences’ function from the ‘rgr’ package and, as noted previously, the different procedures yield different estimates for the range of background. The workspace used is presented in Appendix 02-07 of Rencz et al. (2011). Background range estimates may also be made using a hybrid procedure involving graphical tools to identify and eliminate outliers (see Fig. 12, 13), and then estimating the percentiles of the remaining background data.

Step 3: estimating background

Once it is established that the data represent one population and that there are no outliers, an estimate of geochemical background can be made. Using the remaining data in the set or subset, calculate the percentiles for individual elements. Results for As and Pb using the remaining data following outlier elimination via Figures 13 and 14 are shown in Table 2. Before undertaking these calculations, however, ensure that there are a sufficient number of samples to make a valid statistical comparison. As a rule of thumb, data subsets should have a minimum size of 30, but further information is available from Reimann et al. (2005) and Reimann and Garrett (2005). Select from the percentiles, or even the minimum and maximum (if appropriate), a probable background range

of concentrations for individual elements. For example, the 2nd and 98th percentiles are Ontario’s OTR₉₈ estimates, and, for mineral exploration purposes, the background range is sometimes based on the 5th and 95th percentiles. The choice of percentile range is set depending on the degree of caution required by the risk assessment or remediation activity. It is also possible to estimate a range of background values based on different themes or criteria, for example a specific lithological group, surficial-materials unit, or ecosystem-classification unit.

Multivariate methods

Other types of analyses may be employed for value-added interpretation (Filzmoser et al., 2005; Reimann et al., 2008; Garrett and Grunsky, 2011). An extensive discussion of these methods is beyond the scope of this paper so they are only mentioned here briefly. For example, by analyzing and interpreting the occurrence of groups of elements in soil samples, it may be possible to identify and discriminate between natural and anthropogenic sources.

Where background ranges for several elements are to be determined the univariate procedure can lead to situations where, for different elements, different samples and their data are removed. This is not ideal.

A multivariate equivalent of the probability plot exists, the chi-square plot, where all elements of interest are investigated simultaneously. This procedure requires special transformations of the data as geochemical data are a ‘closed number system’, they sum to a constant, 100%, 1 000 000 mg/kg, etc. Using this approach, a background data set can be prepared and range estimates made for the various elements of interest determined univariately as appropriate. Principal Component Analysis, with a similar caveat regarding data transformation, may be used to identify outliers and gain understanding of interelement relationships (Reimann et al., 2008; Grunsky, 2010).

AVAILABILITY OF GEOCHEMICAL DATA

A catalogue was developed and contains metadata that may be searched and raw data for approximately 700 geochemical surveys carried out by the GSC and provincial geological agencies since the 1950s (Spirito et al., 2007). It can be accessed, along with many other types of data, in the Geochemical Data Repository (GDR) at Natural Resources Canada (http://gdr.nrcan.gc.ca/index_e.php [accessed March 11, 2010]). Information on the geochemical data catalogue in the GDR is available in Kettles et al. (2011).

Digital and user-friendly databases, catalogues, and free downloads are available online from federal and provincial library facilities (e.g. GSC Bookstore; online at http://gsc.nrcan.gc.ca/bookstore/index_e.php [accessed February 9, 2011]).

ACKNOWLEDGMENTS

The authors wish to thank the following: L. White and others at Health Canada and R. Mroz and others at Environment Canada for sponsoring and providing support for the Halifax Workshop; M. McCurdy for reviewing this and also an earlier version of this document; and R. Knight and C. Tarnocai for providing the figures for the surficial and soils maps of Canada, respectively.

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