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**REGIONAL GEOCHEMICAL
LAKE SEDIMENT SURVEY,
EAST-CENTRAL SASKATCHEWAN**

E.H.W. Hornbrook
R.G. Garrett

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CONTENTS

	Page
Abstract/Résumé	v
Introduction	1
Acknowledgments	1
Methodology	2
Previous work	2
Geological Survey of Canada	2
Other sources	2
Field	2
Analytical	3
Quality control	4
Compilation and map production	5
Discussion of results	5
Data reliability	5
Threshold values – data separation by catchment basin rock type	6
Selection of threshold values	8
Assessment of raw data	10
Regional trends	11
Statistical correlation studies	12
Inter-element relations	12
Loss-on-ignition relationships	12
Multilinear regression	13
Principal component analysis	13
Conclusions	15
References	16
Appendix A. Index to microfiche in back pocket	19
B. Estimation of 95% confidence bounds about the mean	20
C. Latitude and Longitude of localities in study area	20

Tables

Table 1. Analytical detection limits	4
2. Summary of statistics	6
3. Analysis of variance for data reliability	7
4. Zinc data divided by catchment basin geology	9
5. Uranium data divided by catchment basin geology	9
6. Threshold levels and percentage of samples above threshold	10
7. Correlation matrices for log ₁₀ transformed data	13
8. Multilinear regression	14
9. Principal 5-component analysis	15

Illustrations

Figure 1. Survey area location map	1
2. Centre-lake bottom sediment sampler	3
3. Regional lake sediment geochemistry, east-central Saskatchewan (Cu, Pb, Zn, Ni, Co, Ag)	in pocket
4. Regional lake sediment geochemistry, east-central Saskatchewan (Mo, As, U, Fe, Mn, LOI)	in pocket
Microfiche 74-1 to 74-13 National Geochemical Reconnaissance, East-Central Saskatchewan	in pocket

REGIONAL GEOCHEMICAL LAKE SEDIMENT SURVEY, EAST-CENTRAL SASKATCHEWAN

Abstract

A regional geochemical lake sediment reconnaissance survey was undertaken jointly by the Geological Survey of Canada and the Province of Saskatchewan in 1974 under the terms of the Canada-Saskatchewan Agreement on Mineral Exploration and Development in Northern Saskatchewan. Centre-lake bottom sediments were collected at a density of one sample per five square miles (1 per 13 km²) in a 20 000 square mile (51 800 km²) region of the Canadian Shield and analyzed for their content of Zn, Cu, Pb, Ni, Co, Ag, Mn, U, As, Mo, Fe and Hg. The organic content was estimated by weight loss on ignition.

This paper includes a brief review of the history and development of regional lake sediment sampling including a summary description of the current methodology involved from the collection of samples to publication of the data.

The data on the distribution and concentration of the elements has delineated several element trends or regional zones of increased metal content correlative with features of economic interest. Follow-up studies in 1975 confirmed the anomalous element content of the lake sediments within the trends.

The survey achieved optimum results for U and satisfactory results for most of the remaining elements.

It is significant that Fe, Mn, and organic content do not appear to play dominating roles as scavengers producing artificial anomalies, nor is there a distinct improvement in interpretation of the raw data when extensive statistical treatment is employed.

Résumé

Aux termes de l'Entente Canada-Saskatchewan sur la prospection et l'exploitation des minéraux dans le nord de la Saskatchewan, la Commission géologique du Canada et la province de la Saskatchewan ont entrepris conjointement en 1974, des levés régionaux de reconnaissance sur la géochimie des sédiments lacustres. Des sédiments ont été recueillis dans la partie centrale du fond des lacs, à raison d'un échantillon tous les cinq milles carrés (13 km²), dans une région de 20 000 milles carrés (51 800 km²), du Bouclier canadien; ces sédiments ont ensuite été analysés afin de déterminer leur teneur en chacun des éléments suivants: Zn, Cu, Pb, Ni, Co, Ag, Mn, U, As, Mo, Fe et Hg. Quant à la teneur en matière organique, elle a été estimée par la perte de poids au feu.

Le présent document fait une courte revue de l'histoire et des progrès de l'échantillonnage régional des sédiments lacustres, et il comporte une description sommaire de la méthodologie actuelle employée entre le moment de la cueillette des échantillons et la publication des données.

Les données sur la répartition et la concentration des éléments ont permis de déterminer plusieurs axes préférentiels d'éléments, ou plusieurs zones à teneur métallique accrue, en corrélation avec des caractéristiques présentant un intérêt économique. En 1975, des études complémentaires sur les sédiments lacustres prélevés dans les axes préférentiels ont confirmé la teneur anormale en éléments.

L'étude a donné des résultats optimaux dans le cas de l'uranium et des résultats satisfaisants pour la plupart des autres éléments.

Il est significatif de noter d'une part, que le Fe, le Mn et la teneur en matière organique ne semblent pas jouer de rôles importants en tant que fixateurs produisant des anomalies artificielles, et d'autre part, qu'il n'est pas plus facile d'interpréter des données brutes, par un traitement statistique élaboré.



REGIONAL GEOCHEMICAL LAKE SEDIMENT SURVEY, EAST-CENTRAL SASKATCHEWAN

INTRODUCTION

A regional geochemical lake sediment reconnaissance survey was jointly undertaken by the Geological Survey of Canada and the Province of Saskatchewan in 1974 under the terms of the Canada-Saskatchewan Agreement on Mineral Exploration and Development in Northern Saskatchewan. The Geological Survey of Canada planned and conducted the survey in co-ordination with the Saskatchewan Geological Survey.

E. H. W. Hornbrook was responsible for co-ordinating the Geological Survey of Canada operations and L. S. Beck¹ co-ordinated operations of the Saskatchewan Geological Survey.

The field sampling, carried out under the terms of a contract let to Trigg, Woollett & Associates Limited, Edmonton, Alberta, was planned and supervised by E. H. W. Hornbrook. Samples were dried, sieved, and prepared by project summer staff at La Ronge, Saskatchewan. Chemical analyses were carried out under contract by Barringer Research Limited, Toronto, Ontario, according to contract specifications designed and supervised by J. J. Lynch of the Geological Survey. Data monitoring, compilation, and map production was carried out at the Geological Survey of Canada in the Geochemistry and Cartography Sections under the planning and supervision of R. G. Garrett.

The lake sediment survey was undertaken to obtain information on the distribution and concentration of metals in a 20 000-square-mile (51 800 km²) region of the Canadian Shield (Fig. 1). The objective was to delineate regional zones or belts of increased metal content possibly correlative with features of economic interest worthy of follow-up field investigations. Such regional features have been found and are the subject of follow-up studies by Federal and Provincial governments and the mineral industry.



Figure 1. Survey area location map.

¹L. S. Beck, Director, Saskatchewan Geological Survey.

Centre-lake bottom, organic-rich, samples were collected by means of a specially designed sampling apparatus at an average density of one sample per five square miles (1 per 13 km²) throughout the survey area. Minus 80 mesh (177 μ) processed samples were shipped to the analytical contractor from La Ronge, for the determination of 12 elements - Zn, Cu, Pb, Ni, Co, Ag, Mn, U, Mo, As, Fe, and Hg. The Hg data were not included in the initial publication (Open File 266) because data monitoring revealed that they were not of sufficient analytical quality for statistical or interpretive studies. However, because Hg data are of widespread interest, they will be studied again, including repeat analysis, and may be published in the future. Loss-on-ignition (LOI) determinations to obtain a measure of the organic content were carried out by project staff of the Geological Survey of Canada. Field and analytical data were assessed by various monitoring programs and eventually compiled into a symbol plot map and data listing format for publication.

Because the region was divided into four parts, the survey data, consist of forty-eight geochemical symbol maps, four sample location maps and a listing of field and analytical data. These were released on August 5, 1975 (Hornbrook, *et al.*, 1975b). A complete microfiche set of this material is included in this report and is indexed in Appendix A.

Although the work was carried out under Mineral Exploration Development Agreement the specifications are compatible with the regional geochemical reconnaissance surveys which form part of the Federal Government's Uranium Reconnaissance Program. It is expected that data from this survey, the Uranium Reconnaissance Program, and other Federal or Federal-Provincial programs will eventually be compiled to form a National Geochemical Reconnaissance (NGR) Atlas which will provide nationally consistent geochemical data for compilation and assessment at a broad regional scale.

ACKNOWLEDGMENTS

It is beyond the practical scope of this paper to identify and individually thank all the people in the Federal and Provincial governments and in the contractors' staff for their appreciated co-operation and assistance.

However, the following warrant mention because they played a key role in producing a successful survey: L. S. Beck, Director, Saskatchewan Geological Survey; J. J. Lynch, chief analyst and N. G. Lund, geochemical data systems, Geological Survey of Canada; N. Németh, science contract manager, Department Supply and Services; Trigg, Woollett & Associates Limited, Edmonton, Alberta; Barringer Research Limited, Toronto, Ontario; R. C. Race, Material Management Division, Department Energy, Mines and Resources; A. J. Gracie, Resident

Geologist, La Ronge, Saskatchewan. The symbol maps were made possible through the co-operation and assistance of the Map Production Directorate, Surveys and Mapping Branch. The base map drafting and map production was carried out by the Cartographic Section of the Geological Survey.

METHODOLOGY

The requirements of the Uranium Reconnaissance Program (URP) demand that regional geochemical methods be used to complement, or as an alternative to airborne gamma-ray spectrometry.

Mountainous areas and areas of extensive overburden primarily in the Canadian Shield, have been identified for the application of regional geochemical methods – lake sediment, stream sediment, litho-geochemical and groundwater surveys.

In accordance with Federal Government science policy the work was planned to achieve the objectives by means of contracts with the private sector. Thus, both the analytical service and sample collection requirements were carried out under contracts that were let with the help of the Material Management Division of Energy, Mines and Resources through the services of the Science Procurement Sector, Department of Supply and Services. It is expected that future surveys will be more complex perhaps involving multi-year contracts for all or some of the collection, preparation, analytical, computer programming, and base map compilation activities.

During the past few years there has been considerable research and development in lake sediment geochemistry. The Geological Survey of Canada, universities, and the mineral exploration industry have carried out studies ranging from the investigation of the ion exchange capacity of lake sediments in a few lakes to large-scale orientation studies and application of tested methods at a regional reconnaissance level. A review of the current status of lake sediment geochemistry may be found in Nichol *et al.* (1975). These studies, described below, together with the more recent investigations of Klassen (1975), Timperley and Allan (1974), and Cameron and Ballantyne (1975) are contributing to the growth of knowledge of the complex chemistry of lake sediments, knowledge that is essential for meaningful interpretation of regional element distribution.

Previous Work

Some of the previous work directly relevant to the establishment of the routine application of the centre-lake bottom sediment sampling employed in Saskatchewan would include the following:

Geological Survey of Canada During the winter of 1971-72, approximately 2900 lake bottom sediment samples were collected by Hornbrook and Gleeson within the 13 800 square mile region of Timmins-Val d'Or in Ontario and Quebec. This survey (Hornbrook, 1972; Hornbrook and Gleeson, 1972) demonstrated the potential of the lake bottom sediment sampling method

in a till terrain as well as its limitations in a clay terrain. In the summer of 1972, Hornbrook (1973), using a specially-designed sampling apparatus, collected centre-lake bottom sediments in two orientation study areas on the Island of Newfoundland. The method was found to effectively delineate the known zinc deposits at Daniel's Harbour, western Newfoundland (Hornbrook *et al.*, 1975a). In 1973, using essentially the same method, a 3000-square-mile survey was carried out over Cambro-Ordovician carbonate rocks of western Newfoundland and several anomalous zinc and lead areas were discovered (Davenport *et al.*, 1975). Thus, prior to application in Saskatchewan in 1974, the centre-lake bottom sediment sampling method was researched and developed in orientation studies in 1972 and was successfully applied at a regional level in 1973.

Contemporaneously, other studies were carried out on lake shore sediments by Dyck *et al.* (1971) and Allan *et al.* (1972) which led to a regional geochemical lake shore sediment survey in 1972 by Allan *et al.* (1973) and follow-up studies in 1973 by Cameron and Durham (1974).

Other sources In the early 1970's relevant independent studies of centre-lake bottom sediments were carried out by Coker (1974) at Queen's University, and Closs (1975) at the Ontario Department of Natural Resources. Beginning in 1973, and continuing each summer, the centre-lake bottom sediment method has been used for regional geochemical reconnaissance in northwestern Quebec (C. F. Gleeson, pers. comm.)¹. The reconnaissance surveys for the James Bay Development Corporation, listed by year, number of square miles, and number of sediment samples collected were: 1973, 4314/2215; 1974, 15 200/7806; 1975, 24 080/8017. Also in 1975, 8779 water samples were collected and some experimental collection was done at one sample per 10 square miles.

Field

Two sampling crews, each composed of a sample collector and a navigator-notetaker, and two pilots used a Bell Jet Ranger helicopter on a rotating crew basis for traversing. Both crews normally flew several hours each day. Average sample collection rates achieved were 16 samples per hour based on flying time sampling; and 14 samples per hour based on flying time plus ferry time to and from base camp. Samples were collected at about 3850 sites during the period July 30 to September 4, 1974. A field duplicate sample was collected at one out of every 17 sample sites.

Samples of lake sediment were collected from the deep lake basins, normally the centre of the lake, or in deeper bays of large lakes. Alternatively, only the centre-lake bottom samples were collected from shallow lakes.

¹C. F. Gleeson, C. F. Gleeson and Associates Limited, Ottawa, Ontario.

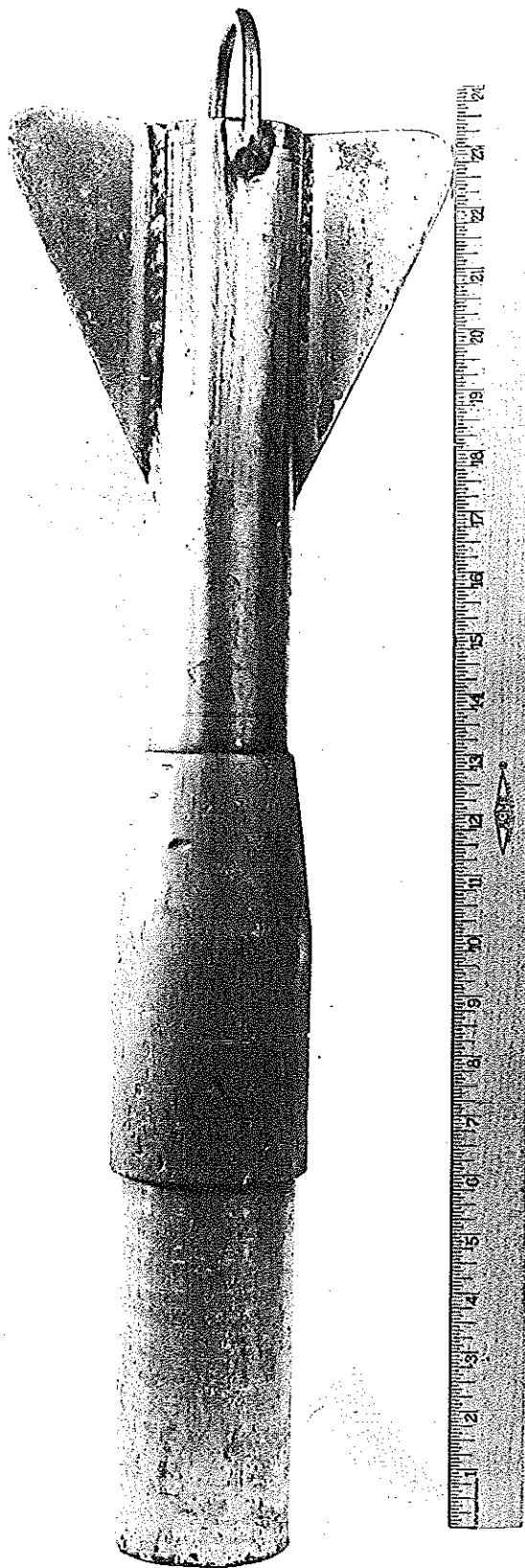


Figure 2. Centre-lake bottom sampler.

Small peat bog ponds and the central parts of very large lakes, for example, Lac La Ronge, were avoided. Lakes with active inflow-outflow drainage activity were preferable to stagnant lakes for sampling. Long linear lakes were sampled more than once, as long as consistent sample density was maintained. Deeper lakes (generally greater than 10 feet deep), were sampled in preference to shallow lakes. Density of sampling was locally adjusted to permit sampling of a lake that appeared to be the focus of a drainage basin rather than sampling a lake exactly in the centre of the 5 square mile grid.

The 1974 sample collection cost was approximately \$27.00 per sample site. However, this survey was not in a remote area because base camps had road access for gas positioning and supplies. Had this survey been in a remote area, the cost per site would probably have increased by approximately 20 per cent to \$32.40 per sample site.

There is a great deal of interest and many inquiries have been received concerning the sampler currently used to collect the centre-lake bottom sediment sample. The original model, developed in 1972 has been described by Hornbrook *et al.*, 1975a and Davenport *et al.*, 1975. The current model (Fig. 2) although apparently similar in appearance has been altered significantly. Essentially, the sampler is a hollow pipe-like device of mild steel with a one-way ball valve in the lower section to prevent the loss of the sample from the core-retaining section during retrieval of the apparatus. The total weight has been increased to 13 pounds to improve penetration into the lake sediment, the ball valve seat now has a machined-bevel to obtain a water-tight seal, the lower section has been increased in size from 6 inches long and 1.875 inches I. D. to 10.5 inches long and 2.5 inches I. D. and the pipe wall thickness is now 0.25 inch thick to increase the lateral compression of lake sediment material after it passes the bevelled cutting edge on the nose. The valve is composed of 0.875 inch ball bearing that seats on a 0.625 inch diameter bevelled hole in 0.25 inch mild steel plate. The upper section, 13 inches long, is made of 0.125 inch thick mild steel tubing 2.25 inches O. D. The upper and lower sections are welded at the valve joint where the weld bead is left during manufacture to provide better adhesion for the smoothly contoured 1.5-pound lead collar. The collar is necessary for weight and to preserve the nose-down attitude of the sampler during free-fall through lake water to the bottom of the lake. The sampler has a capacity of 51.5 cubic inches or approximately 850 ml and will normally provide in excess of one pound of lake sediment material exclusive of excess water. A dried sample will rarely weigh less than 15 grams.

The samplers are manufactured locally in Ottawa at a cost of less than \$100.00 each.

Analytical

Lake sediment samples, which had undergone a preliminary few days of air drying in the field, required at least 2 weeks further drying in the La Ronge, Saskatchewan sample preparation facilities. Dried

samples were broken-up in a household multi-speed blender or hammered and disaggregated prior to sieving to obtain the minus 80 mesh portion. A sample processing rate of 100 per day could be maintained assuming continuous supply of dry samples. Air drying of samples in September is not feasible and supplementary heat is required. At this stage a reference control and blind duplicate sample were added to each block of eighteen field samples to create an analytical block of twenty samples.

For the determination of Zn, Cu, Pb, Ni, Co, Ag, Mn, Fe, and U, a 1 gram sample was reacted with 6 ml of a mixture of 4M HNO₃ and M HCl in a test tube overnight at room temperature. After the overnight digestion, the test-tube was immersed in a hot water bath at room temperature and brought up to 90°C and held at this temperature for 1 hour with periodic shaking. The sample solution was then diluted to 20 ml with metal-free water and mixed. Zn, Cu, Pb, Ni, Co, Ag, Mn, and Fe were determined by atomic absorption spectroscopy using an air-acetylene flame. Background corrections were made for Pb, Ni, Co, and Ag. A 0.1 ml aliquot of the above sample solution was used to determine U by a fluorometric method described by Smith and Lynch (1969). A Turner fluorometer was used for the fluorescence measurements in place of the Jarrel-Ash instrument used by Smith and Lynch (1969).

Arsenic was determined colorimetrically using silver diethyldithiocarbamate. Decomposition was accomplished by heating a 0.5 gram sample with 10 ml of 6M HCl at 90°C for 1 hour. Colorimetric measurements were made at 520 nm.

Molybdenum was determined by atomic absorption spectroscopy using a nitrous oxide-acetylene flame. A 0.5 gram sample was reacted with 1.5 ml concentrated HNO₃ at 90°C for 30 minutes. At this point 0.5 ml concentrated HCl was added and the digestion was continued at 90°C for an additional 90 minutes. After cooling, 8 ml of 1250 ppm Al solution were added and the sample solution was diluted to 10 ml before aspiration.

Jonasson *et al.* (1973) have described the determination of Hg by the cold vapour atomic absorption spectrophotometric method which is based on the procedure of Hatch and Ott (1968). A 0.5 gm sample of sediment was reacted with 20 ml of concentrated HNO₃ and 1 ml of concentrated HCl in a test tube for 10 minutes prior to two hours of digestion, with mixing, in a 90°C water bath. The test tubes were removed from the water bath, cooled, and the solution diluted to 100 ml volume. The Hg present was reduced to its elemental state by the addition of 10 ml of 10% w/v SnSO₄ in M H₂SO₄. The Hg was carried directly to a cell in the light path of the atomic absorption spectrophotometer by a stream of air which was flushed through the solution prior to entering the cell.

Loss-on-ignition was determined using a 200 mg sample; shortage of material dictated this relatively small sample weight. The sample, contained in a 30 ml beaker, was placed in a cold muffle furnace and brought up to 500°C over a period of 2-3 hours. The sample was left at this temperature for 4 hours, then allowed to cool to room temperature for weighing.

Detection limits for the analytical methods are given below in Table 1. The number in brackets is used for reporting values below the detection limit.

Table 1 - Analytical detection limits

Element	Detection Limit	
Zn	2	(1) ppm
Cu	2	(1) "
Pb	2	(1) "
Ni	2	(1) "
Co	2	(1) "
Ag	0.2	(0.1) "
Mn	5	(2) "
U	0.5	(0.2) "
As	1	(0.5) "
Mo	2	(1) "
Fe	0.02	(0.01) %
L. O. I.	-	-

Analytical cost for 12 elements (including Hg) but excluding sample preparation and loss on ignition was \$8.65 per sample for approximately 4000 samples. The rate, or turn-around time, for analytical services varies depending on the time of year, the element, and method of analysis as well as the efficiency of the given analytical laboratory.

Quality Control

Field contract supervision to ensure that the sample collection was carried out in accordance with the general instructions and specifications of the contract was accomplished by periodic field inspection. Further, the contractor was made aware of the possibility that certain areas may be resampled by the contract supervisor to confirm the validity of the sampling.

Quality control of the correct recording of field and analytical data and the assessment of the accuracy and precision of the analytical data was managed by data monitoring programs devised for this purpose. Field data were recorded on a Geochemical Lake Sediment Sample Card (Rev. 74), described by Garrett (1974). Field card data were verified and corrected as required prior to being merged with the analytical data. Analytical data were recorded on an 80-column report sheet that is in standard use at the Geological Survey.

Sample site universal transverse mercator (UTM) grid co-ordinates recorded at the field base camp, using a plastic roamer, were checked by producing a sample location map on a flat-bed plotter using these co-ordinates and comparing site locations to the original sample location map.

Monitoring of the performance of the contracted analytical services was based on a blind duplicate and reference control sample system. Each of these samples were present on a random 5 per cent frequency basis. In each block of 20 samples there were 17 routine field samples, one field duplicate sample, one blind duplicate, and one reference control sample. The field duplicate sample was collected at one of the 17 routine field sites,

the blind duplicate is a split of one of the 18 field samples and the reference control sample was a split from one of several reference bulk samples available.

Rejection or acceptance of data for each block of twenty samples was determined by statistical criteria involving the blind duplicate and reference control sample data and was assisted by means of a computer program. The criterion was appropriately different for each element as required, and of course, varies over the working concentration range. Rejected data were replaced by new data after repeat analyses. The corrected analytical and field data were then merged for preparation of data listings, statistical analysis, and map production.

Compilation and Map Production

The data were subjected to statistical assessment to obtain means, standard deviations, correlation coefficients, separations on rock catchment basin, etc.

A prime consideration in the release of data from this survey and future Uranium Reconnaissance Program surveys was to publish only the raw data in the initial open file release Hornbrook *et al.*, 1975b. Thus, the data were immediately available for use.

As a preliminary interpretation the data were reported in an additional listing in the open file. Samples were grouped according to the geology of lake catchment basins. Threshold values were selected for each element and each catchment basin type. The additional listing contains data for any samples with a value for one or more elements exceeding the threshold values for the appropriate rock type. Threshold values will be discussed below.

Because these survey data will be incorporated into a compiled map in the National Geochemical Reconnaissance Atlas, the map design had to be universal without variation from area to area throughout Canada. Thus, the recurring semilogarithmic cycle of 1, 2, 5, 10 etc. was chosen and 15 symbols were devised to cover a range of 5 decades. The symbols were developed from those used in various African studies from 1963 to 1966 at Imperial College, London, and first described by Webb *et al.* 1964. These were assigned to concentration levels and plotted at the sample site locations as described in the marginal notes of each map. A symbol, a circle with dot, is generally assigned to the histogram mode for a given element. The remaining symbols are assigned to sympathetically give increasing size and blackness with increasing concentration level above the mode and the reverse below the mode. The actual symbol plotting is achieved using a Barr and Stroud PS9 photohead to expose the appropriate symbol onto film on a computer controlled flat bed plotter. Appropriate marginal notes plus cumulative frequency plots and histograms together with symbol plots on a geological-topographical base constitute the standard 1:250 000 scale National Geochemical Reconnaissance map.

Data Reliability

Details of accuracy and precision derived from control reference samples are not given because this geochemical survey is only a single part of the larger on-going Uranium Reconnaissance Program where analytical services are obtained by contract and the control reference samples are still in use to provide year-to-year control. However, the acceptability of the data and the relationship between field sampling and analytical errors can be studied through the field and blind duplicate pairs in each block of 20 analyzed samples.

A summary of data statistics is given in Table 2. The tendency for the data to be positively skewed and be lognormally distributed is indicated by the coefficient of variation (c. v. %). Data for 7 of the elements (Zn, Cu, Pb, Ag, Mn, U and As) are strongly skewed and the remaining elements exhibit varying tendencies to be positively skewed. Taking this into account, and with the knowledge that in an overall sense large sets of geochemical survey data tend to be lognormally distributed, the data were \log_{10} transformed prior to further analysis. Table 2 is based on the analyses of 3808 samples of the 3844 samples collected, this being the number of samples for which data was available for all the chemical variables.

The field sampling and analytical variabilities were studied using analysis of variance techniques based on duplicate pairs of samples (Garrett, 1973). Table 3 presents the variances needed for this study. It is first necessary to decide if the subset of 255 samples, which were field duplicated, are a valid subset of the 3808. The ratio F_1 is computed from the variance of 3808 samples and variance of the first samples of the 255 prints: this should be close to unity. If this ratio is greater than 1.2 the variance exhibited by the subset is significantly low compared with the total data, this is indicated for Zn, Cu, Ni, and Co, and therefore, they are not a completely valid subset. Secondly, from the field duplicates, the variance ratio F_2 is computed in order to determine if the combined sampling and analytical variability is significantly smaller than the overall regional variability as exhibited by the first samples of the 255 pairs. To calculate F_2 the variances of the 255 duplicate field samples are computed for both over the pairs and between the pairs. If this ratio is greater than 1.25 the local sampling and analytical variability is significantly smaller than the overall regional variability. One element, Ag, failed to meet this criterion; this is the result of a variety of factors including a comparatively low regional variability combined with a high analytical variability largely due to the data being at very low levels close to the detection limit. Another element, Mo, has a low F_2 value (1.86), and therefore Mo data should be interpreted with more care. As the F_2 values are satisfactorily

Table 2

Summary of Statistics

	Range	Arith \bar{X}	Std. Dev.	C. V. %	Geom. \bar{X}	\log_{10} S. D.	
Zn	4	7100	97.2	120.4	123.8	88.5	0.178
Cu	1	1600	35.0	32.6	93.1	29.5	0.258
Pb	1	510	3.4	8.8	255.4	2.4	0.344
Ni	1	280	29.4	17.2	58.4	24.5	0.289
Co	1	190	11.9	7.9	66.3	10.1	0.254
Ag	0.1	3.2	0.19	0.17	88.9	0.15	0.255
Mn	30	89000	790.	2673.	338.2	495.	0.318
U	0.2	112.6	3.3	5.3	159.7	2.0	0.458
As	0.5	76	3.3	3.2	97.7	2.3	0.390
Mo	1	69	2.6	1.8	69.4	2.3	0.212
Fe	0.1	30	3.0	2.2	72.1	2.5	0.253
LOI	0.5	91	28.4	17.3	61.1	22.4	0.337

N.B. n=3808, i.e., all those samples for which there are data for all variables. Units of measurement are ppm except for Fe and LOI which are percentages.

$$C. V. \% = \frac{\text{Std. Dev.}}{\text{Arith } \bar{X}} \times 100$$

high for the elements whose F_1 value was unsatisfactorily high, i.e., Zn, Cu, Ni and Co, it is concluded that although strictly speaking these elements fail marginally the F_1 test, in all cases they are still acceptable for regional interpretation. The implications for Ag and Mo are that high values at points may well be valid and should be capable of substantiation on resampling and analysis. However, an absence of Ag or Mo in an area should not be construed as conclusive proof of the absence of these elements.

From the 255 pairs of blind duplicate samples, it is possible to estimate the analytical variance. The sampling and analytical variance, computed from the 255 field duplicates, can be used in conjunction with the analytical variance to estimate the sampling variance, Table 3. The sampling variance is a measure of the homogeneity of the centre-bottom lake sediments and is estimated by difference. However, a negative sampling variance is impossible and in cases where analytical variance exceeds the combined sampling and analytical variance the sampling variance is represented as >0.0001 . The sampling variance can be seen to be considerably smaller than the analytical variance indicating that the centre-bottom lake sediments are a homogeneous sampling medium where samples were collected up to 50 feet apart. If an increase in the quality of data is required attention should be focussed on the analytical aspects of the project. It must be immediately pointed out that this is in contradiction to

most sampling and analytical studies which indicate that sampling is a far more serious problem than analysis. This contradiction underlines the unique homogeneity of centre-bottom lake sediments and their suitability for regional studies of geochemical variability.

Threshold Values - Data Separation by Catchment Basin Rock Type

No single threshold value was used for any chemical element in all rock types; however, a single value of 50% loss-on-ignition was used. The data were divided into groups on the basis of the dominant rock type in each lake catchment basin. Summary statistics and histograms were prepared for each element in each rock type group and threshold values were selected on the basis of these. The rock type selections for each catchment basin were based on the 1:1 267 000 (20 mile to 1 inch) Geological Map of Saskatchewan (1972). This compilation map is satisfactory for a regional study but for detailed investigation and follow-up studies the reader is advised to refer to more detailed geological maps.

The effect of glacial history has always been a concern of geochemists as, under certain circumstances, a complex history of events can render many forms of exploration geochemistry impotent. Generally, the bulk of the till derived from bedrock by glacial action is transported a relatively short distance. According to

Table 3

Analysis of Variance for Data Reliability

Zn	Cu	Pb	Ni	Co	Ag	Mn	U	As	Mo	Fe	LOI	Total Data [†]		Field Duplicate(1) ^{††}		Field Pairs ^{††}		Sampling-Analytical		Analytical Variance ^{†††}		Sampling Variance		F _{2,2}	
												σ _{TD} ²	σ _{TD1} ²	\bar{X}_{D1}	Variance, σ _{D1} ²	Variance, σ _D ²	Variance ² , σ _{SA} ²	Variance ² , σ _{SA} ²	σ _A ²	σ _{TD/σD1} ²	σ _{D/σSA} ²	F _{TD/σD1} ²	F _{D/σSA} ²		
1.947	1.469	0.379	1.398	1.005	-0.817	2.695	0.296	0.357	0.354	0.402	1.350	0.0318	0.0233	0.0256	0.0028	0.0024	0.0004	0.0004	0.0024	0.0024	0.0004	0.0004	1.36*	9.21*	
1.469	0.0666	0.0508	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	0.0511	
0.379	0.1186	0.1162	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	0.1037	
1.398	0.0832	0.0668	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	0.0682	
1.005	0.0644	0.0475	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	0.0474	
-0.817	0.0649	0.0547	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	0.0377	
2.695	0.1013	0.0860	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	0.0854	
0.296	0.2095	0.1972	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	0.1692	
0.357	0.1518	0.1572	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	0.1348	
0.354	0.0450	0.0436	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	0.0334	
0.402	0.0642	0.0624	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	0.0613	
1.350	0.1134	0.1181	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	0.1090	

N.B. All figures are quoted in log₁₀ units.

Number of samples used:

[†] n=3808

^{††} n= 255

^{†††} n= 215

*significant difference at the 95% level

Shilts (1976, p. 209) "Glaciers appear to disperse material in the form of a negative exponential curve, with the concentration of elements, minerals or rocks reaching a peak in till at or close to their source, followed by an exponential decline in the direction of transport. The parameters (slope and dimensions) of the curve appear to be determined by the physical characteristics of the components and the mode of transport. These curves exhibit a rapid decrease in concentration or "head" immediately down-ice of the source, with a more gradual decrease, or "tail", at greater distances." Unless a rock unit is particularly narrow relative to the scale of the sampling and oriented perpendicular to the ice movement direction, the till of the catchment basin of a sampled lake will probably be largely derived from the rock unit underlying the catchment basin.

Tables 4 and 5 respectively present summaries of statistics for Zn and U after the data have been divided by rock type. An immediate point of interest is a comparison between the coefficients of variation of Zn and U. Except for Zn derived from metavolcanic rocks all coefficients of variation for Zn are less than 50%, whereas for U they all exceed 80%. An inspection of the overall regional pattern for Zn and U in Figures 3 and 4 reveals that Zn has a relatively uniform and uninteresting regional geochemistry compared with that of U. The coefficients of variation reflect this, high coefficients are characteristic of positively skewed data due to high metal values indicating areas of high geochemical relief. Thus, in itself, the coefficient of variation is an indication of mineral potential eliminating the need to consult a map at a preliminary level of data investigation. As would be expected, the high coefficient of variation of Zn in metavolcanic rocks indicates the potential for Zn mineralization in those rocks. What is particularly interesting is the apparent higher potential that the U data exhibits for all rock types that appear on the 1:1 267 000 scale geological map; this may be an indication of a lack of "stratigraphic" control on U mineralization in favour of some other control such as structural.

In comparing rock types on the basis of Zn arithmetic data have been used rather than geometric, except for metavolcanics, because on a separated basis, the Zn data are not strongly skewed. The average Zn levels in granites and marbles are observed to be lower than average levels in pelitic schists, metasediments and amphibolites. On the basis of crustal abundance data, for example those of Turekian and Wedepohl (1961), these differences are not surprising and would be expected, i. e. the same differences are found in crustal abundance data. This feature tends to confirm the minor effect glaciation has had on the regional geochemical patterns. The reason metavolcanics and ultramafics are not grouped with the pelitic schists, etc. can be explained by the fact that the metavolcanics include acid to basic varieties and that relatively few samples from catchment basins are underlain by ultramafic rocks. These two facts give rise to the wide 95 per cent confidence bounds on the metavolcanic and

ultramafic rock Zn means through increased standard deviations or decreased numbers of samples (see Appendix B).

In the case of U, the bounds on the geometric means are used when comparing data for different rock types. As might be expected from a study of crustal abundance tables, the U content of samples from metavolcanic and ultramafic underlain areas is significantly lower than all other rock type areas except for meta-arkoses. This evidence again supports the belief that the influence of glaciation has a minor effect on the geochemical patterns on a regional scale.

Selection of Threshold Values

In the selection of thresholds a combination of statistics and visual inspection was used. If the histogram for a particular element and rock type indicated that the distribution was a simple bell-shaped curve, the approximate mean plus 2 standard deviation concentration level was chosen for the threshold. In some instances, e. g., Zn and marbles, no data were found above this level and a threshold was arbitrarily chosen so that a small percentage of the data would be above threshold. In some cases the histograms indicated a bimodal or strongly positive skewed distribution and the calculated threshold was modified by a knowledge of the geological and geochemical reality. A special instance of this was with Ag where as much as 60% of the data is below the detection limit.

The threshold levels and percentiles of these levels are shown for Zn and U respectively in Tables 4 and 5. Table 6 gives the thresholds for all elements and all rock types and also in brackets the actual percentage of samples above the thresholds. It should be noted that 10 rock types are listed in the map legend; however, no samples were ascribed to the conglomerate unit and thus only 9 appear in the table.

The threshold is used by the writers of this report to indicate a level above which it is believed that the chemistry of the sample is probably related to some abnormal process in the geological or surficial environment. In some instances this may be a discrete source of metals, e. g., a mineral occurrence. The thresholds presented here are only a preliminary guide to regional interpretation and they may not necessarily apply in local areas where a more detailed interpretation would be appropriate based on local geology. Thus, in some instances, the levels chosen may be too high, and therefore, samples are not flagged, or may be too low, resulting in samples unrelated to mineral occurrences being flagged.

The data listing of above threshold samples in Appendix A allows the assessment of the data at each sample site in a multiple element manner and above threshold patterns can be plotted and assessed in geological, mineral occurrence or surficial environmental terms. The listing may also be used to modify the single element maps of Open File 266 to upgrade some samples and downgrade others as the maps were plotted without recognition of rock type, except as an

Table 4

Zinc Data Divided by Catchment Basin Geology

No. of Samples	Range	Arith X	Std. Dev.	C. V. %	95% Confidence Bounds on \bar{X}	Geom \bar{X}	log ₁₀ Std.Dev.	95% Confidence Bounds on \bar{X}	ppm	Threshold Percentile			
Granite	1512 16	780	90.3	36.3	40.3	88.5	92.1	84.2	0.168	82.5	85.5	180	99
Metavolcanic	222 20	7100	129.2	475.6	368.3	66.2	192.2	88.3	0.234	82.2	94.8	260	98
Meta-arkose	107 20	196	95.2	31.3	32.9	89.2	101.2	89.7	0.156	83.8	96.1	185	99
Pelitic schist	859 14	450	102.6	39.3	38.3	100.0	105.2	95.2	0.178	92.6	97.8	210	99
Metasediment	157 16	350	112.9	40.2	35.7	106.6	119.3	106.0	0.163	100.0	112.5	225	98
Amphibolite	294 12	245	98.0	31.4	32.0	94.4	101.6	92.1	0.166	88.2	96.2	200	99.5
Marble	32 10	180	79.1	34.9	44.1	66.5	91.7	70.1	0.245	57.7	85.2	170	97
Migmatite	612 4	450	92.1	36.0	39.0	89.2	95.0	85.4	0.181	82.6	88.3	195	99
Ultramafic	50 40	275	96.8	38.2	39.4	86.0	107.7	90.8	0.155	82.3	100.2	185	98

Table 5

Uranium Data Divided by Catchment Basin Geology

No. of samples	Range	Arith \bar{X}	Std. Dev.	C. V. %	95% Confidence Bounds on \bar{X}	Geom \bar{X}	log ₁₀ Std.Dev.	95% Confidence Bounds on \bar{X}	ppm	Threshold Percentile			
Granite	1511 0.2	71.0	3.37	4.55	143.0	3.14	3.60	2.00	0.468	1.90	2.12	16	98
Metavolcanic	222 0.2	15.0	2.00	2.05	102.3	1.73	2.27	1.27	0.449	1.11	1.46	9	97.5
Meta-arkose	106 0.2	52.0	3.05	5.86	191.8	1.92	4.18	1.44	0.543	1.13	1.83	16	97.5
Pelitic schist	859 0.2	82.5	3.05	4.55	149.3	2.75	3.35	1.98	0.418	1.86	2.11	11	97.5
Metasediment	157 0.2	28.8	3.57	3.47	97.1	3.02	4.12	2.31	0.467	1.96	2.74	18	99
Amphibolite	294 0.2	16.5	2.77	2.66	96.1	2.46	3.08	1.84	0.433	1.64	2.06	12	98
Marble	32 0.5	17.8	4.89	3.94	80.4	3.47	6.31	3.75	0.335	2.87	4.90	16	97
Migmatite	612 0.2	112.6	4.46	9.04	202.7	3.74	5.18	2.39	0.458	2.20	2.60	18	97
Ultramafic	50 0.2	8.6	1.90	1.93	101.6	1.35	2.45	1.20	0.452	0.90	1.60	7	94

N.B. Units of measurement are ppm.

overlay. These modifications may reveal new, or emphasize known, areas of interest. Thus areas of mineral potential may be further defined, or refined, for follow-up studies by using the above threshold information in conjunction with the 1:250 000 scale symbol maps.

It is at this detailed level of interpretation that the field parameters are of importance. The writers have not attempted any detailed statistical analysis of the relations of the field parameters listed in Appendix A and explained viz-a-viz coding in Garrett (1974). However, at the detailed interpretation level, where samples and sites are being priority-ranked and local processes are significant, the field data are important. Sediment composition, colour, and loss-on-ignition can be combined for example, to elucidate the material nature of the sample; depth and size of lake with the topographic form of the drainage basin give some idea of area of provenance of the sample; the suspicion of man-induced contamination is obviously important; etc.

Assessment of Raw Data

The primary consideration is to interpret the Saskatchewan survey data at the appropriate level, i. e., regional survey data should be interpreted only on a regional basis and not on a local basis. Thus, evidence of regional features such as the uranium trends associated with the complexes of mixed metasediment and granite and the fact that organic-rich lake sediments are confined to a discontinuous belt on the southern margin of the Canadian Shield are revealed by the contrast and distribution of regional U and loss-on-ignition data. Local features, however, such as a single mineral occurrence or deposit may not necessarily be detected by the distribution pattern or contrast, of an element or elements, but this may happen.

In essence, the effectiveness of a regional geochemical survey is a function of the sample density and geochemical mobility of the elements determined notwithstanding the obvious importance of their mode of occurrence in bedrock and till. The number of sample sites per unit area required for effective interpretation decreases as the mobility of the elements in the geochemical cycle increases. Hence, mobile elements such as U are suitably effective at a sample density of one sample per five square miles (1 sample per 13 km²). Elements which have a lesser degree of mobility are relatively less effective unless the sample density is increased. The Saskatchewan survey was designed to produce optimum data for U and reasonably acceptable data for most of the remaining elements. Since the mobility of an element can vary in response to changes in the environment (Hawkes and Webb, 1962), the effectiveness or quality of the data, may vary among elements and also for a given element in the different environments of the survey area, particularly for the less mobile elements.

The work of Haughton and Lehto (1975) has confirmed the anomalous nature of selected anomalous U, Cu and As sites and they have concluded and U and Cu

Table 6

Threshold Levels and Percentage of Samples above Threshold

	No. of samples	Zn	Cu	Pb	Ni	Co	Ag	Mn	U	As	Mo	Fe	LOI
Granite	1605	180(1.0)	95(1.4)	11(1.6)	85(0.7)	35(1.4)	0.5(4.1)	2100(4.0)	16(1.7)	11(0.8)	6(2.6)	8.1(2.7)	50(14.)
Metavolcanic	237	260(2.1)	145(1.3)	17(3.0)	90(0.4)	34(3.4)	0.4(9.3)	2000(3.8)	9(2.5)	18(1.7)	7(3.8)	7.3(1.3)	50(22.)
Meta-arkose	112	185(0.9)	85(2.7)	15(0.9)	80(0.0)	26(2.7)	0.5(2.7)	1200(4.5)	16(2.7)	11(1.8)	5(1.8)	6.4(1.8)	50(18.)
Pelitic schist	910	210(1.0)	90(1.2)	13(0.5)	80(1.6)	35(2.4)	0.7(2.3)	2000(4.2)	11(2.5)	12(0.2)	6(2.2)	8.4(1.9)	50(11.)
Metasediment	167	225(1.8)	110(1.8)	15(0.6)	95(1.8)	37(2.4)	0.8(5.4)	2000(5.4)	18(0.6)	10(1.8)	6(6.0)	6.9(2.4)	50(4.8)
Amphibolite	307	200(0.3)	95(1.6)	12(1.3)	80(0.3)	30(2.0)	0.7(2.3)	2000(2.0)	12(2.0)	14(1.3)	5(2.6)	6.8(0.3)	50(13.)
Marble	34	170(2.9)	60(2.9)	6(2.9)	60(0.0)	28(2.9)	0.5(5.9)	3300(2.9)	16(2.9)	28(2.9)	6(8.8)	11.6(5.9)	50(8.8)
Migmatite	648	195(0.8)	85(0.5)	13(1.7)	90(0.2)	35(1.9)	0.6(4.5)	2600(3.7)	18(2.8)	9(2.2)	6(2.3)	8.6(2.9)	50(11.)
Ultramafic	52	185(1.9)	135(1.9)	10(3.8)	65(0.0)	36(1.9)	0.4(13.)	2000(7.7)	7(5.8)	12(1.9)	6(1.9)	7.3(1.9)	50(29.)

N.B. Units of measurement are ppm except for Fe and LOI which are percentages.

anomalies appear to define broad geochemical facies and As appears to define localized exploration targets. This work is not yet complete.

The element distributions shown on the symbol plot maps, do not take into account the aspect of different rock catchment basins underlying sample sites. Hence, the different threshold levels associated with different rock types (see Table 6) may be used to modify an element's distribution to include or exclude those sites with above or below threshold values in areas of possible economic interest. Using this combined approach, U, being a highly mobile element, delineates, by anomalous U concentrations, several large regional trends like that associated with the granite migmatite body north of Pelican Narrows¹. Anomalous uranium concentrations also reveal numerous local areas of economic interest as well whereas, most other elements, Cu, Zn and As, for example, show at least one or two regional zones of interest and smaller anomalies of one or two sites. Even lead, usually described as a relatively immobile element, shows regional trends of interest in the McIntosh Lake area north of La Ronge Saskatchewan, and west of Flin Flon, Manitoba. The Flin Flon area is well defined by anomalous concentrations of Cu, Zn, and Pb. At least one of the Flin Flon sites is contaminated. Many of the regional trends of interest are marked by the above threshold presence of more than one element possibly reflecting mineral associations characteristic of the mineralization. Such a zone for Cu, Pb, and Zn occurs in the Robertson Lake area 70 miles northeast of La Ronge. A comparison among the geochemical maps and the Mineral Deposit Map of Northern Saskatchewan (1972), permits a quick assessment of the effectiveness of the regional geochemical survey. The relationship between element trends (arbitrarily defined by grouping mineral occurrences) and the element trends on the geochemical maps is mostly self evident but, for example, would include the following: The Au occurrences north of La Ronge are defined by the distribution of As, a pathfinder element for Au. The Cu occurrences east of Forbes Lake are shown, and the area of interest enlarged upon, by the Cu distribution.

During routine collection of samples, areas of mining or extensive exploration activity were intentionally avoided to prevent the inclusion of possibly contaminated samples. Hence, some deposits that were mined, are not in fact individually detected at a regional scale of operation. However, the region in which such a mine occurs is often delineated, i. e., the Prince Albert Mine, a small gold deposit in the Amisk Lake area, is within a high As, Cu and Pb region and the Flin Flon mine a major Cu-Zn producer is in a high Cu, Zn and Pb region. At Rottenstone Lake the Rottenstone Mine, which contains a single worked nickel-platinum-palladium deposit, is an example of a mine that is not detected. However, this is not unexpected, as Gilboj (1975) points

out "Despite extensive exploration by several companies, in particular Siro Mining Corporation Ltd. in 1960, Sherritt Gordon Mines Ltd. in 1968, and Canadian Occidental Petroleum Ltd. in 1972, only one other similar deposit, the long-known Tremblay-Olson showing, has so far been found".

The regional U trends are not complemented by belts of U occurrences on the Mineral Deposit Map of Northern Saskatchewan. Two occurrences of U near Maribelli and Hickson lakes are actually on the south-east side of a 70-mile-long by 8-mile-wide strong regional U trend. The associations of U-Mo and U-Cu or U-Mo-Cu present outside the survey area are found, for example, near Robertson Lake.

These examples show that numerous single or multi-element trends are revealed by the symbol plot maps and/or the above threshold value data listing. It is considered to be of prime importance that follow-up studies should initially include detailed lake bottom sediment and water sampling to confirm, and further define, anomalous element distributions prior to more follow-up exploration for the possible source of the anomalous metal element content in lake sediments.

Regional Trends

Regional 1: 1 000 000 scale maps (Figs. 3 and 4) are weighted rolling mean maps of raw data where an appropriate degree of smoothing of the data has been carried out to diminish local variations and to clarify the configuration of the regional trends. On the Ag map in Figure 3, the colour grey, normally assigned to data at the mode has been replaced by blue-grey. This was necessitated because most of the Ag data is below the analytical detection limit and a statistical consideration of a Ag mean was not valid. All element maps have some degree of enhancement of anomalous values at the survey area boundary because of extrapolation problems in the plotting program.

The 1: 1 000 000 coloured regional maps are the first example of the compilation format of geochemical data for the National Geochemical Reconnaissance (NGR) Atlas. In the future, such maps may adjoin other survey area maps permitting assessment of gross features of the environment that are reflected by the concentration and distribution of metal elements.

Coombe (1975), in his work on the La Ronge-Wollaston Base Metal Project, pointed out that the data may, with more study, prove to be useful as a metallogenic indicator. He found this to be the case for the high background Cu area near Forbes Lake and the U trend in the migmatite front to the northwest of the La Ronge-Reindeer Belt.

The regional 1: 1 000 000 geochemical maps may be used along or in conjunction with the 1: 250 000 scale symbol plot maps to quickly identify regional characteristics. Thus, thousands of square miles of similar Canadian Shield terrain may be quickly reduced to much smaller areas for concentrated follow-up exploration activities, or evaluated, with other data for resource potential.

¹For latitude and longitude of localities in the study area, see Appendix C.

Statistical Correlation Studies

In the following studies two sets of data were used. Firstly, the set of 3808 samples for which there was recorded chemical data available; and secondly, a set of 1658 samples where Ag was omitted as a result of the analysis of variance in Table 3 and only samples where data for all variables were above detection limits.

Table 7 presents the two correlation matrices, the lower left triangle being for the first set of samples, $n=3808$; and the upper triangle for the second set, $n=1658$. For the correlation coefficients to be significantly different from zero, i. e., a random relationship, they must exceed an absolute value of .03 and .04 respectively at the 95% confidence level. The following discussion will be based on the upper triangle, i. e., coefficients based on those samples where all data is above the detection limits.

Inter-element Relations One of the most common features of geochemical data is the sympathetic correlations of many of the transition elements. This is demonstrated by Fe, Mn, Zn, Cu, Ni, and Co. Another interesting relationship is that corresponding to base metal sulphide deposits, i. e., Zn, Cu, Pb, and Fe. Some dichotomy exists between the transition elements Zn, Cu, and Fe on one hand and the Zn, Pb, and Fe relationship on the other. Scavenging effects are often observed to be partly controlled by Fe and Mn. This feature is often obscured by the natural sympathetic transition element correlation; however, Mo, As and U may be scavenged by Fe and Mn. It is interesting to note that with the exception of Mn-Mo (.19) the correlation coefficients between these elements are less than 0.1. One might deduce from this that scavenging by Fe and Mn is relatively slight in the centre-lake bottom sediment environment of east-central Saskatchewan. The most noticeable feature of U is its relative lack of correlation to other elements compared to cases discussed above. The maximum correlation is observed with Mo, and this could partly be due to the concentration of these elements into granitoid phases, especially pegmatites.

Loss-on-Ignition Relationships Organic content of soil and sediment samples has been long known to exhibit a control on trace element levels. In this project organic content has been estimated by the use of loss-on-ignition (LOI). It should be pointed out that at low levels of LOI the observed loss may not always be related to organic matter alone, the thermal decomposition of clays and carbonates can contribute, but at low ashing temperature of 500°C, decomposition is not significant. The change of ferrous to ferric state is not considered important as this is likely to have occurred during drying and sample preparation prior to analysis. However, it is believed that LOI forms a useful method for studying relative organic content.

Two of the strongest correlations that LOI exhibits are negative with Fe (-0.41) and Mn (-0.30). This could indicate a gross mechanical relationship, i. e., that as the amounts of organic material increase, mineral matter containing Fe and Mn in the form of clays, hydroxides,

and possibly sulphides must decrease. Four other elements also exhibit a negative correlation with LOI, they are Pb, Co, Ni and Zn, which is not really surprising as they are all strongly positively correlated with Fe and Mn through the transition element and base metal deposit relationships. What is of interest is the positive correlation of Cu with LOI as it might be expected to be negatively correlated along with Fe, Mn, Zn, Ni, and Co. Similarly U, Mo and As exhibit positive correlations with LOI as might be expected on the grounds of the scavenging capabilities of organic compounds and their lack of strong correlation with Fe and Mn. In order to further study these relationships multivariate statistical studies were undertaken and are described below.

The apparent lack of correlation of Zn with LOI is a point of interest and was investigated further (Garrett and Hornbrook, 1976). It was apparent that at low levels of LOI (below 12%) there is a sympathetic increase of Zn with LOI at a rate of some 8 ppm Zn per 1% in LOI. Above 12% LOI the Zn data stabilize and in fact decrease slowly at a rate of 0.2 ppm per 1% rise in LOI up to around 50% LOI. Above 50% LOI and Zn values appear to remain constant before decreasing above 70% LOI; however, the data at these high levels of LOI are sparse and only the two sections 0-12% and 12-50% will be discussed further.

This was interpreted as follows, Zn is progressively removed from solution and adsorbed by organic material, there never being enough organic material below 12% LOI to adsorb all the Zn in solution. Above 12% LOI there is an excess adsorbing capacity in the lake sediments and an equilibrium is reached between Zn in solution and adsorbed Zn.

Thus, below 12% LOI the Zn concentrations in lake sediments are partly related to the availability of adsorbent material and Zn patterns may not truly reflect the local geological environment. Above 12% LOI there is an excess adsorbing capacity for background levels of Zn, thus any excess Zn due to non-background processes will be adsorbed and reflected as abnormally high Zn in sediments.

In an area with a high proportion of non-background samples related to mineral occurrences, e. g., an orientation survey, the above relationship may not be apparent due to the small proportion of true background samples. In such a case one might expect the stabilization point at 12% LOI to be far less apparent and the sympathetic increase of Zn with LOI to be the most apparent feature of the data. Thus the feature described here is very much an attribute of background geochemistry. However, this indicates that in fact the most desirable sampling media is one in the range of 12-50% LOI as in this range there is an excess adsorbing capacity for background areas and any high Zn data will be reflecting features related to the geology of the catchment areas.

Similar studies and plots may be prepared for other elements vs. LOI. In contrast to Zn, which has a generally low relief, a study was made of U vs. LOI. A similar plot was obtained; however, the 95% confidence bounds are wider due to the higher relief and about 14% of the data with levels below the detection limit. The main point of similarity, though not as obvious, is the

Table 7

Correlation Matrices for log ₁₀ Transformed Data												
	Zn	Cu	Pb	Ni	Co	Ag	Mn	U	As	Mo	Fe	LOI
Zn		0.49	0.30	0.62	0.59		0.39	0.14	0.07	0.17	0.51	-0.05
Cu	0.61		0.08	0.59	0.40		0.16	0.14	0.19	0.22	0.16	0.26
Pb	0.34	0.24		0.29	0.27		0.21	0.01	-0.07	-0.05	0.32	-0.31
Ni	0.62	0.69	0.43		0.66		0.28	-0.03	0.08	0.07	0.41	-0.12
Co	0.63	0.52	0.31	0.68			0.56	0.02	0.02	0.14	0.58	-0.22
Ag	0.04	0.01	0.05	0.01	0.09							
Mn	0.38	0.19	0.15	0.25	0.56	0.04		0.03	0.01	0.19	0.62	-0.30
U	0.18	0.24	0.08	0.14	0.09	0.01	-0.02		-0.02	0.17	-0.00	0.11
As	0.18	0.27	0.14	0.27	0.20	0.05	0.09	-0.05		0.08	-0.03	0.24
Mo	0.22	0.23	-0.08	0.06	0.17	0.04	0.22	0.16	0.07		0.06	0.18
Fe	0.52	0.26	0.23	0.32	0.59	0.03	0.63	0.10	0.07	0.20		-0.41
LOI	0.16	0.32	-0.25	0.02	-0.08	0.00	-0.20	0.11	0.18	0.25	-0.21	

n=3808 for lower triangle

n=1658 for upper triangle

stabilization of U values at about 12% LOI; however, the plateau of values tends to fall off faster above 50% than for Zn.

Multilinear Regression In the secondary environment Zn and U essentially behave similarly. Therefore a comparative study was made between these two elements using multiple regression analysis in an attempt to relate each of these elements to all the chemical variables. The method of forward selection was used (Efroymsen, 1960) the significance of each step of the regression was determined by an analysis of variance and the regression was continued until an addition to the equation was not significant at the 95% level. A summary of the results is given in Table 8.

The multilinear regression for Zn shows that a total of 54.5% of the variability for Zn may be explained by Ni, Fe, Cu, Co, U, LOI, Pb, and Mo. In fact the first four variables account for 51.6% of the variability and these are the familiar transition elements. The remaining four variables only account for a further 2.93% of the variability. Thus, the dominant control on Zn geochemistry of the lake sediments is an association of elements that indicate a control by bedrock primary geochemical factors.

In contrast the multilinear regression for U shows that a total of only 8.1% of the variability for U may be explained by other variables. This is a reflection of

the "loner" behaviour exhibited in the correlation matrix and discussed earlier (Table 7). Those elements included are Mo, Zn, Ni, Cu and As; however, Ni and As have negative regression coefficients indicating that as Ni and As increase U decreases. It is possible to postulate, as was done earlier, that the Mo-U relationship could be a feature controlled by granitoid pegmatite rocks; whereas the negative Ni-U relationship is a feature of the low backgrounds of U in the Ni-rich ultramafic rocks.

What is clear from these two analyses is that Fe, Mn, and LOI do not appear to play important roles as scavengers causing artificial anomalies and that the dominant controls on Zn and U can be explained in terms of bedrock geochemical processes. On the basis of this conclusion it was decided that no significant improvement in interpretation could be made by preparing regression residual maps.

Principal Component Analysis In a further attempt to elucidate multivariate relationships both factor analyses and principal components were carried out. The following factor analyses were carried out; maximum row R, squared multiple correlation coefficient and centroid (Harman, 1967); however, these did not appear to present any significant improvement over the principal component analysis so they will not be further discussed.

Table 8

Multilinear Regression

<u>Zinc</u>					<u>Uranium</u>				
<u>Variable</u>	<u>Sign</u>	<u>Proportion of Variation</u>			<u>Variable</u>	<u>Sign</u>	<u>Proportion of Variation</u>		
		per cent	cumulative per cent				per cent	cumulative per cent	
1	Ni	+	38.02	38.02	1	Mo	+	2.86	2.86
2	Fe	+	8.21	46.23	2	Zn	+	1.23	4.09
3	Cu	+	3.84	50.07	3	Ni	-	1.92	6.00
4	Co	+	1.48	51.55	4	Cu	+	1.73	7.74
5	U	+	1.25	52.80	5	As	-	0.31	8.05
6	LOI	+	0.65	53.46					
7	Pb	+	0.85	54.31					
8	Mo	+	0.17	54.48					

Table 9 presents the 5-component analysis which accounts for 76.7% of the total variability. Higher component models simply degenerate to single variable components which yield no information on intervariable relationships.

The first component accounts for 23.8% of the total variability. This is divided between Ni, Cu, Zn, Co and Fe (22.6%) and the remaining six elements (1.2%). Thus again it is apparent that the primary control on the data is a group of transition elements behaving in their classical sympathetic manner.

The second component is somewhat more complex and accounts for another 21.6% of the total variability. In this component LOI is balanced against Mn, Fe, Co, Zn, Pb, Mo and Ni, and reflects the negative correlation of LOI with Fe and Mn observed in the correlation matrix (Table 7). As stated before it is believed that this relationship reflects the inverse relationship necessary between the organic and mineral fractions in the centre-lake bottom sediments. Although Pb and Mo are not part of the femic transition series group both these elements can be adsorbed onto Fe and Mn hydroxides which can make up a substantial part of the mineral fraction.

The third component accounts for an additional 11.5% of the total variability and may be a further reflection of the second component as LOI is contrasted against Fe. The pattern is complex with Mo, LOI and Mn being ranged against Fe, Ni and Pb. The dominant elements are Mo and LOI vs. Pb; the sympathetic relationship between Mo and LOI may be explained in terms of adsorption but the inverse relation to Pb is not understood.

The fourth component contains U, Mo and Pb as the major contributing variables accounting for a further 10.1% of the total variability. This component may be

interpreted as being controlled by U in granitoid pegmatite or high potassic rock, the Mo occurring as molybdenite and the Pb being related to potassium through its ability to substitute in the K-feldspar lattice.

The fifth, and last, component considered is a two-variable one consisting of As and LOI and accounts for 9.7% of the total variability. However, 8.8% of components contribution is from As, the other variables, dominated by LOI contributing the remaining 0.9%. Thus this component is virtually a single variable one controlled by As, possibly related to arsenopyrite in rocks, somewhat modified by the adsorption of As onto organics.

One can state that this model accounts for 76.7% of the total variability; however, it is also interesting to view the model from the point of view of each variable, and this may be done through the communalities, the sums of squares of the row entries. If all the variability for a variable is explained by the components presented the communality would be 1.0. Thus, for U, the communality is 0.874 indicating that the 5-component model explains 87.4% of the variability of U, however, this is largely in component 4 which accounts for 86.7%. This is interesting because if the interpretation of component 4 is correct, i.e., a U in granitoid rock component, it would indicate that 86.7% of the U variability in the survey area is related to granitoid rocks. This fact is somewhat in contradiction to conclusions made from Table 5 and in the 6-component model, where U separates as a single variable component which accounts for 96.8% of the U variability. One can only state here that obviously the U-pegmatite association is important but is not conclusively the only relationship present.

Where methods of principal component and factor analysis make their greatest contribution in assisting interpretation is where elements of interest may have

Table 9

Principal 5-Component Analysis

Component	1	2	3	4	5	
Zn	0.702	0.736	- 0.354	- 0.051	- 0.174	- 0.038
Cu	0.774	0.840	0.100	0.168	- 0.110	- 0.138
Pb	0.662	0.221	- 0.300	- 0.674	- 0.261	- 0.026
Ni	0.815	0.859	- 0.213	- 0.147	0.101	0.009
Co	0.744	0.644	- 0.570	- 0.000	0.046	0.041
Mn	0.765	0.177	- 0.842	0.143	- 0.032	- 0.050
U	0.874	0.040	0.044	0.051	- 0.931	0.030
As	0.973	0.067	0.022	0.046	0.032	- 0.982
Mo	0.675	0.116	- 0.244	0.706	- 0.316	- 0.060
Fe	0.742	0.294	- 0.799	- 0.135	- 0.002	0.009
LOI	0.708	0.186	0.605	0.468	- 0.118	- 0.275
Proportion of Variability, Percentage	23.82	21.56	11.52	10.05	9.73	
Cumulative Per cent	23.82	45.38	56.90	66.95	76.67	

their patterns confused by secondary environmental, silicate, or oxide camouflage problems. For instance, in the case of Zn, in an area of Zn-bearing mineral occurrences, the Zn patterns could be related to any of at least five features; Zn adsorbed onto organics, Zn adsorbed onto hydroxides, Zn in sulphides, Zn camouflaged in silicates, e. g., biotites and hornblendes, and lastly Zn in oxides, e. g., magnetite. The principal components do not appear to be interpretable in such terms and offer no greater assistance in interpretation of base metal or Ni-Cu ultramafic associations.

Therefore, even though the results of the analysis are interesting and offer a sharper tool for studying the correlation matrix they do not appear directly to aid interpretation for mineral exploration purposes. For this reason no factor score maps have been prepared as they are not considered to offer any significant improvement over the raw data symbol maps.

CONCLUSIONS

The methodology involved in lake sediment surveys is established to the point where most operations can be routinely carried out on a contract basis with appropriate supervision and specifications. Thousands of square miles of Canadian Shield terrain similar to

the Saskatchewan survey area may be explored to determine areas of regional trends of increased metal element content for follow-up studies. Such studies should be initiated by a higher density sampling survey of the selected regional trends to further define anomalous distribution patterns. Detailed investigations involving geochemical, geological, geophysical, etc. surveys would follow to explain and/or discover the source of the increased element content. Regional element trends will aid, in conjunction with other data such as geological and metallogenic information in evaluating the resource potential of Shield terrain.

Single and multi-element regional trends and local highs in the survey area frequently coincide with known areas of mineralization. Otherwise, they may indicate a potential area of mineralization. In a regional high background Cu trend, tens of square miles of anomalous Cu values occur in an area southeast of Forbes Lake that are related to the Cu in the mafic volcanics. Anomalous As, a pathfinder element for gold, is present from Lynx Lake northeast to Preview and Hebden lakes where there are numerous Au-As occurrences. Cu, Zn and Pb regional trends are formed, and are related to the base metal deposits in the Flin Flon area, Manitoba. U distribution patterns form major trends several hundred square miles in extent, and in some cases,

they may be related to uranium-bearing pegmatites, but further studies regarding their source are desirable. Current information did not satisfactorily suggest the size, configuration, or location of the anomalous areas of potential uranium mineralization.

Correlation and regression studies show that Fe, Mn, and organic content do not appear to play important roles as scavengers causing artificial anomalies. Further statistical studies demonstrate that: the surficial environment is not adversely affecting the raw data for interpretive purposes; and the relationship and interaction of the elements are a reflection primarily of bedrock and geological and chemical processes. Therefore, extensive statistical treatment, beyond separation of the data on a bedrock catchment basin basis, is not required because it does not substantially improve the data for interpretive purposes.

Centre-lake bottom sediment sampling has been shown to be a viable method to determine the concentration and distribution of elements in large regions of the Canadian Shield to support mineral exploration and to aid in resource potential studies.

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APPENDIX A

Index to microfiche

Four map-sheets cover the survey area, these are numbered 1 to 4 in the open file release and consist of all or part of the following NTS sheets: -

<u>Map Sheet</u>	<u>NTS Sheet</u>
1	63K, L, M and N
2	73I, O and P
3	74A
4	64D

Because the National Geochemical Reconnaissance is NTS oriented, index entries are by NTS 1:250 000 sheet number and not by open file sheet number. The microfiche are divided into 4 groups, one group for each open file map-area. The first frame of the first microfiche for each group contains a copy of this index.

The maps (13) for each group are followed by the relevant pages of the open file 266 data listing.

The microfiche are indexed as follows:

74-3-2

1. 74 indicates the year the survey was undertaken
2. 3 indicates that the microfiche is the 3rd of the 74 series
3. 2 is the frame number where the map or document will be found. Frames are numbered from left to right starting in the top left corner

Maps are recoded in 35mm format and computer output in 16mm format. Six 35 mm frames go to form a single microfiche.

In the following index the year number, 74, has been omitted for the sake of simplicity; it should prefix all table entries.

	63K	63L	63M	63N	64D	73I	73O	73P	74A
Index		1-1			4-1	7-1			10-1
Sample Loc.		1-2			4-2	7-2			10-2
Cu		1-3			4-3	7-3			10-3
Zn		1-4			4-4	7-4			10-4
Pb		1-5			4-5	7-5			10-5
Ni		1-6			4-6	7-6			10-6
Co		2-1			5-1	8-1			11-1
Ag		2-2			5-2	8-2			11-2
Mn		2-3			5-3	8-3			11-3*
U		2-4			5-4	8-4			11-4
As		2-5			5-5	8-5			11-5
Mo		2-6			5-6	8-6			11-6*
Fe		3-1			6-1	9-1			12-1
LOI		3-2			6-2	9-2			12-2

Relevant pages of open file 266 computer output data listing are copied in the equivalent frames 4-6 on last microfiche of each group.

	63K	63L	63M	63N	64D	73I	73O	73P	74A
pages from	1	1	9	32	32	50	51	51	69
to		9	32		50	51		69	82
microfiche		3			6		9		12

All the above threshold data are listed on microfiche 74-13.

* ERRATA Please note that on microfiche 74-11 these two maps are transposed.

Mo appears in frame 03

Mn appears in frame 06

APPENDIX B

Estimation of 95% Confidence Bounds about the mean

- X mean
 σ standard deviation
n the number of samples used to compute X and σ
t the tabled value of Student's t for a two-tailed test at the 95% confidence level with n-1 degrees of freedom

$$\text{Bounds} = X \pm \frac{t \cdot \sigma}{n}$$

Where a \log_{10} transform has been used X and σ are in \log_{10} units and the calculation is completed before the upper and lower bounds are converted to ppm or percent values.

APPENDIX C

Latitudes and longitudes of localities in the study area

	<u>Latitude</u>	<u>Longitude</u>
Amisk Lake	54 35	101 53
Flin Flon	54 46	101 53
Forbes Lake	55 51	104 44
Hebden Lake	55 27	104 48
Hickson Lake	56 19	104 22
La Ronge	55 06	105 17
La Ronge Lake	55 00	105 00
Lynx Lake	55 21	104 58
Maribelli Lake	56 13	104 26
McIntosh Lake	55 45	105 08
Pelican Narrows	55 10	102 54
Preview Lake	55 25	104 49
Robertson Lake	55 46	104 05
Rottenstone Lake	56 21	104 51