YGS Open File 2017-4

Assessment of Yukon regional stream sediment catchment basin and geochemical data quality

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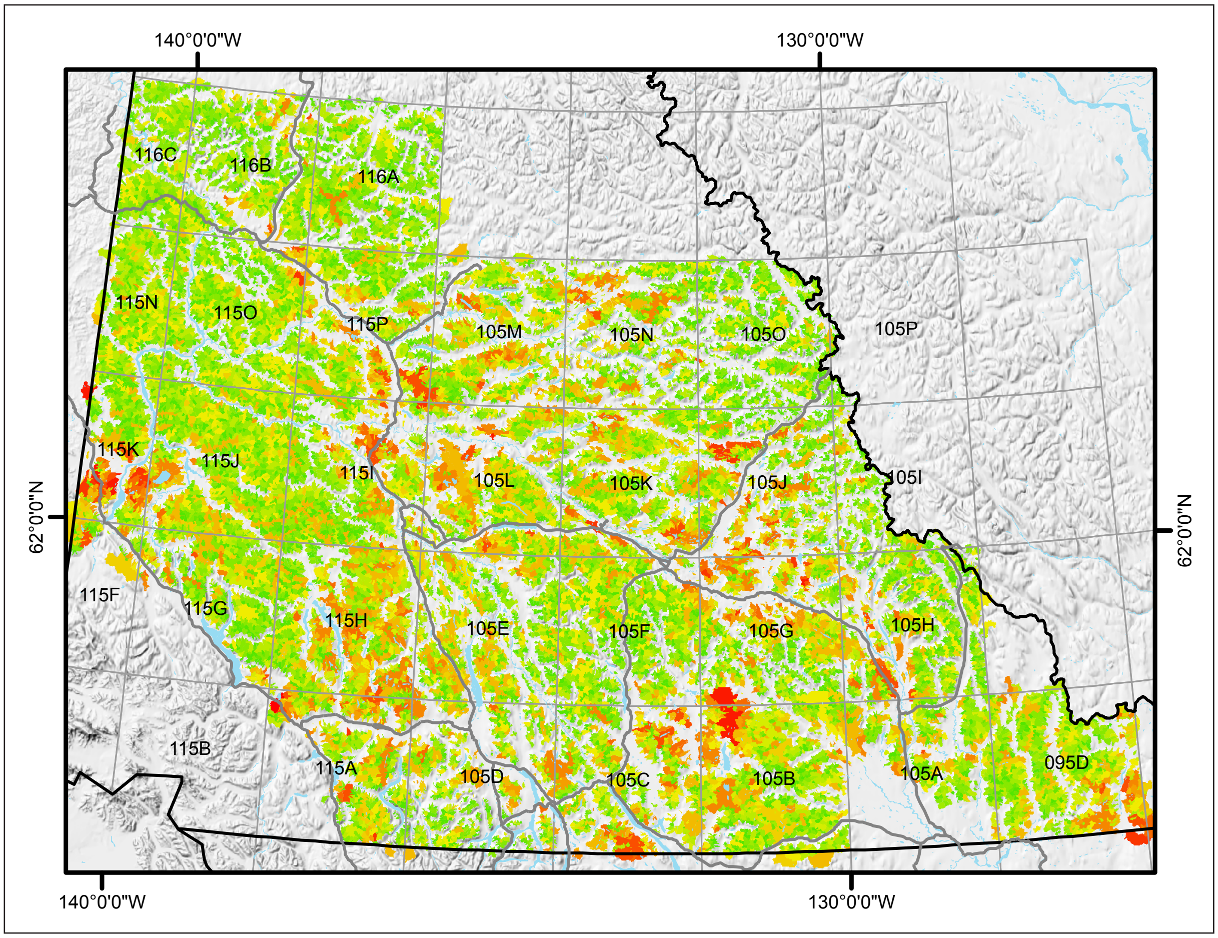

Catchment basins, associated with locations of recent stream sediment geochemical reanalysis, ranked by catchment quality.

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PREFACE

This report presents a comprehensive evaluation of regional stream sediment (RGS) data covering most of Yukon south of 65° N. The report accompanies a digital spatial geodatabase containing catchment boundaries and quality indices for the study area. The report and associated spatial data were commissioned by the Yukon Geological Survey and benefitted from funding provided by the Canadian Northern Economic Development Agency. The data evaluated are from recent (2011 to 2016) re-analyses of archived stream sediment samples. Stream sediment samples are evaluated here based on catchment quality and analytical reproducibility. The direct evaluation of catchment quality provides a solid foundation for locating future stream sediment sampling campaigns, while the evaluation of analytical results aids in the interpretation of existing data. Yukon Geological Survey is making this report available as part of ongoing efforts to support the mineral exploration industry.

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ABSTRACT

Stream catchment areas digitized from existing regional stream sediment sample locations are assessed for quality and confidence of sample site location, catchment surface area (used as a proxy for downstream dilution), surface material type, slope angle and slope aspect. Rankings for each of these attributes are combined into quality indices to give an overall impression of reliability for each catchment that can be incorporated into mineral exploration targeting criteria and design of further sampling programs. Data from quality control samples included with each sample batch during a recent re-analysis program are also assessed for some key elements. Standard reference materials included in two separate re-analysis campaigns show slight shifts in bias even though the same analytical method was used in both instances. Some elements, particularly Au, show an unacceptable amount of scatter in repeat analyses of the standard reference materials indicative of a non-homogenous distribution of Au in the materials for the small sample mass (0.5 grams) used for analysis. Data precision is assessed using field and blind duplicate analyses for selected elements. The Au analyses show the poorest precisions, with data from Cu giving the best precision and data for As yielding intermediate precisions.

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INTRODUCTION

The use of catchment basin analysis to highlight areas prospective for a mineral deposit(s) is a well-established methodology (*e.g.*, Carranza, 2009). Various data treatments can be employed to reduce the influence of lithologic variation and scavenging of metal ions by secondary oxides and hydroxides (Bohnam-Carter and Goodfellow, 1986). A correction can be applied to individual elements or index values to take into account the effect of dilution with increasing catchment area (Hawkes, 1976). While these techniques are integral to proper interpretation of stream sediment geochemistry, potential underlying issues remain concerning overall confidence and quality of recorded sample locations, site selection, survey design and analytical reproducibility, as well as geomorphological controls on the dilution of geochemical anomalies associated with mineralization (Shahrestani and Mokhtari, 2017).

Following the completion of an extensive re-analysis program completed by the Yukon Geological Survey (YGS) that resulted in new ICP-MS data for 24 279 regional stream sediment samples, a series of catchment map products were generated by CSA Canada Global Geosciences Ltd. to target different mineral deposit types (Table 1). Catchment basins were generated from a digital elevation model (DEM) by the YGS using the hydrology module in ESRI ArcMap™. Enhanced analysis of the new geochemical data investigated two approaches to correcting for the influence of variable bedrock lithology and metal scavenging on commodity and pathfinder elements of interest to mineral explorers.

One approach used by Mackie *et al.* (2015a) was to level individual elements by the dominant bedrock lithology within the catchment basins. This approach requires that the sample location be accurately located on the stream that was sampled, assumes that sediment supply from an individual lithological unit is proportional to its mapped surface area, and requires that the geology of the catchment basins is well constrained. The influence of geochemically distinct but geographically minor lithological units is under-estimated using this approach.

The second approach used by Mackie *et al.* (2015a) involved principal component analysis of the geochemical data to identify geochemical associations related to lithology, scavenging of metals by organic material, clays or secondary Fe and/or Mn hydroxides, or to mineral deposits. Individual commodity and pathfinder elements were regressed against one or more principal components to normalize for the effects of variable lithological background geochemistry and the effects of scavenging. This approach relies on the main principal components clearly reflecting lithological or scavenging element associations.

Processing of the geochemical data was carried out over 29 complete and partial NTS 1:250 000 map sheet areas covering southern and central Yukon (Fig. 1; Table 1). Digital copies of deposit-specific geochemical prospectivity maps and data packages are available for all maps sheets from the YGS website (http://data.geology.gov.yk.ca/; see Mackie *et al.*, 2015b for an example). The results of both approaches are presented in the form of weighted sums models (*i.e.*, Garrett and Grunsky, 2001) for specific mineral deposit types and were visually tested against known mineral deposits and occurrences in each map area. The results of the previous work raised questions about the overall quality of the catchment basins. The work presented in this report is designed to address catchment and data quality.

Table 1. Summary of Enhanced Interpretation of Stream Sediment Geochemistry Open File releases with corresponding NTS sheet name and number.

NTS	NTS Name	Reanalysis of archival stream sediment data	YGS Open File	Catchment-based enhanced interpretations	YGS Open File
105K	Tay River	Jackaman, W., 2011b	2011-28	Mackie *et al.*, 2015b	2015-25
105G	Finlayson Lake	Friske *et al.*, 2008a	2008-3	Mackie *et al.*, 2015c	2015-26
105H	Frances Lake	McCurdy *et al.*, 2009a	2009-1	Mackie *et al.*, 2015d	2015-27
105F	Quiet Lake	Jackaman, W., 2015c	2015-8	Mackie *et al.*, 2015e	2015-28
105N	Lansing Range	Day *et al.*, 2009	2009-27	Mackie *et al.*, 2015f	2015-29
95D and 105A	Coal River and Watson Lake	Jackaman, W., 2012d	2012-10	Mackie *et al.*, 2015g	2015-30
105I and 105J	Little Nahanni River and Sheldon Lake	McCurdy *et al.*, 2009b; Friske *et al.*, 2008b	2009-26; 2008-4	Mackie *et al.*, 2015h	2015-31
105B	Wolf Lake	Jackaman, W., 2015a	2015-6	Mackie *et al.*, 2016a	2016-8
105E	Lake Laberge	Jackaman, W., 2015b	2015-7	Mackie *et al.*, 2016b	2016-9
105L	Glenlyon	Jackaman, W., 2015d	2015-9	Mackie *et al.*, 2016c	2016-10
115H	Aishihik Lake	Jackaman, W., 2015g	2015-13	Mackie *et al.*, 2016d	2016-11
105C	Teslin	Jackaman, W., 2015e	2015-11	Mackie *et al.*, 2016e	2016-12
115F and 115G	Part of 115G and Kluane Lake	Jackaman, W., 2015i	2015-15	Mackie *et al.*, 2016f	2016-13
115I	Carmacks	Jackaman, W., 2015h	2015-14	Mackie *et al.*, 2016g	2016-14
115J and 115K	Stevenson Ridge and Part of 115J	Jackaman, W., 2011a	2011-28	Mackie *et al.*, 2016h	2016-15
105D	Whitehorse	Jackaman, W., 2015f	2015-12	Mackie *et al.*, 2016i	2016-26
105M	Mayo	Jackaman, W., 2012b	2012-8	Mackie *et al.*, 2016j	2016-27
105O and 105P	Niddery Lake	Jackaman, W., 2011c	2011-30	Mackie *et al.*, 2016k	2016-28
115A	Dezadeash Range	Jackaman, W., 2016b	2016-5	Mackie *et al.*, 2016l	2016-29
115N and 115O	Stewart River and Part of 115O	Jackaman, W., 2016a	2016-4	Mackie *et al.*, 2016m	2016-30
115P	Mcquesten	Jackaman, W., 2012c	2012-9	Mackie *et al.*, 2016n	2016-31
116B and 116C	Dawson and Part of 116B	Jackaman, W., 2012a	2012-6	Mackie *et al.*, 2016o	2016-32

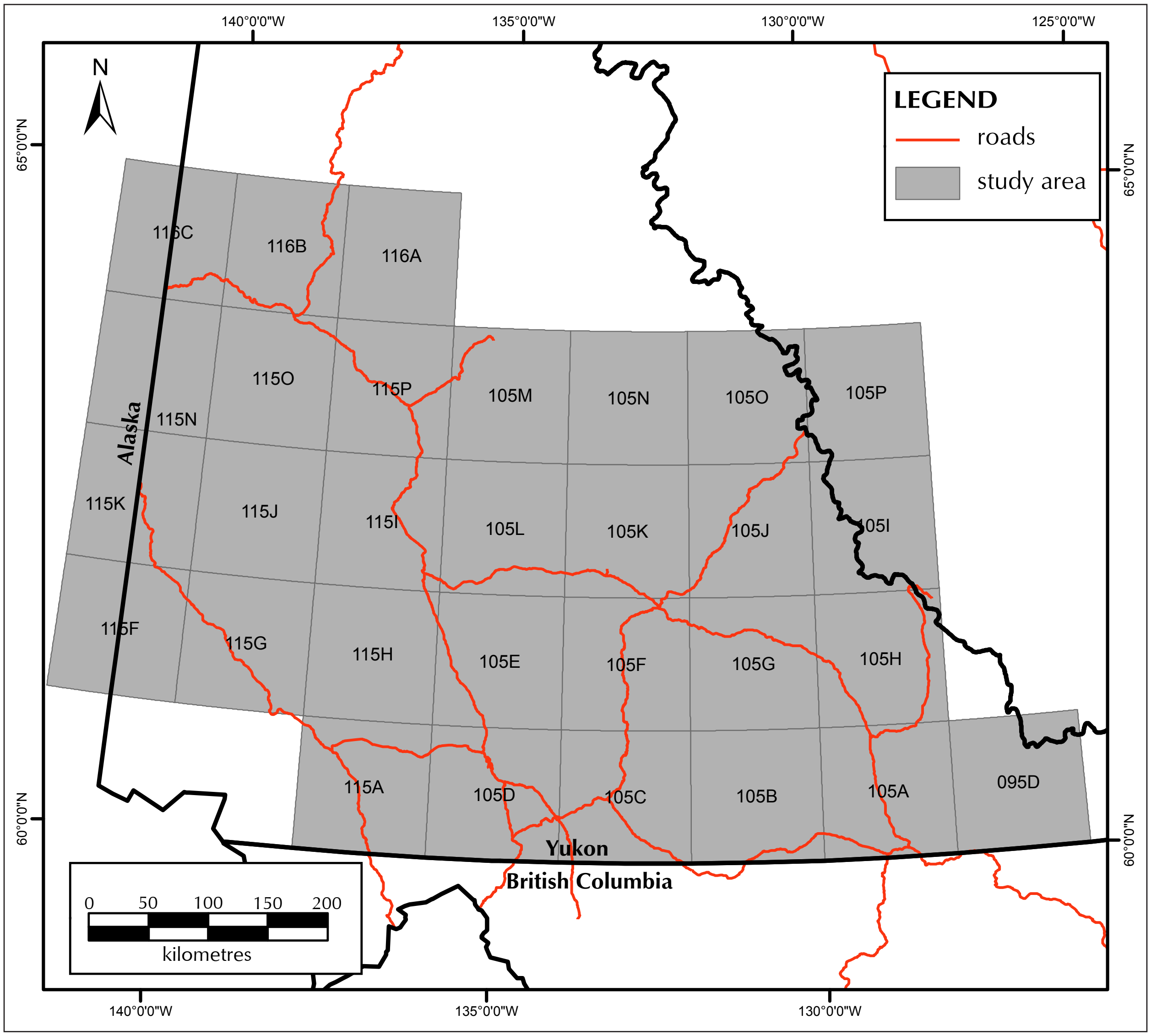

Figure 1. *Plan map of central and southern Yukon indicating NTS map areas included in this study.*

CATCHMENT QUALITY

As described below, previously digitized catchment basins are ranked based on the confidence and quality of sample site location, catchment area, surface material type, slope and slope aspect. The ranking by each of these attributes is combined to generate an overall measure of quality for each catchment. This information can be used by explorers as part of targeting criteria and confirmatory sampling programs.

LOCATION

Many of the original stream sediment sampling programs were conducted prior to the advent of hand-held GPS units and thus there is uncertainty in the precise location of the samples. Historical sample locations were recorded on hard copy maps, transcribed by hand and then subsequently converted to new datums. When location uncertainty is combined with improved resolution of topographic data it means that historical sample locations often do not intersect drainage lines from modern hydrology models. Because the intersection of sample points and drainage lines is a requirement for proper digitization of catchment basins, sample points are snapped by an automated process to the nearest drainage. In cases where a sample site is far from any drainage no catchment was generated. Without access to the original sampling maps it is not possible to confirm that each sample has been placed on the correct drainage. However, by partnering spatial topographic data and sample site descriptions with knowledge of stream sediment sampling strategy and an understanding of catchment basin analysis principles, an assessment of the digitized catchment basins can be made retroactively.

There is therefore uncertainty in the locations of some historical sample sites and the original sample locations do not necessarily always intersect with drainage features. To remedy this for catchment digitization, sample points were moved to the nearest drainage using a snap-to function in ArcMap™. It is possible that the wrong drainage was used as the process is automated and does not distinguish between drainages that were likely or unlikely to have been sampled. By visually comparing the position of the new sample point and resultant catchment polygon with the location of the original sample point and surrounding drainage features, each catchment can be assigned a level of confidence. Three levels of confidence were used: Low, Moderate and High (Table 2). A low confidence ranking means that one or more other drainage features were equally likely to be the correct drainage and thus the position of the digitized catchment is suspect (Fig. 2). A moderate confidence ranking indicates that while other drainages could be correct the selected drainage is the most likely choice. This decision is based on the overall understanding that first and second-order streams were the target of the original sampling program. Another consideration in assigning a moderate rank is the consequence of selecting the wrong drainage. A sample location update that leads to the selection of one of two small basins has a small negative consequence as both streams are likely to drain the same ridge. Alternatively, a sample location update that could move a sample to a much larger drainage or a drainage on the opposite side of the valley should be assigned a low confidence ranking. A high confidence ranking indicates that the selected drainage is the only reasonable choice and no other drainages are proximal the updated sample location.

Table 2. *Summary of location quality ranking.*

Rank	Confidence	Number of Catchments	Percentage
3	High	15 882	75
2	Moderate	3 987	19
1	Low	1 361	6

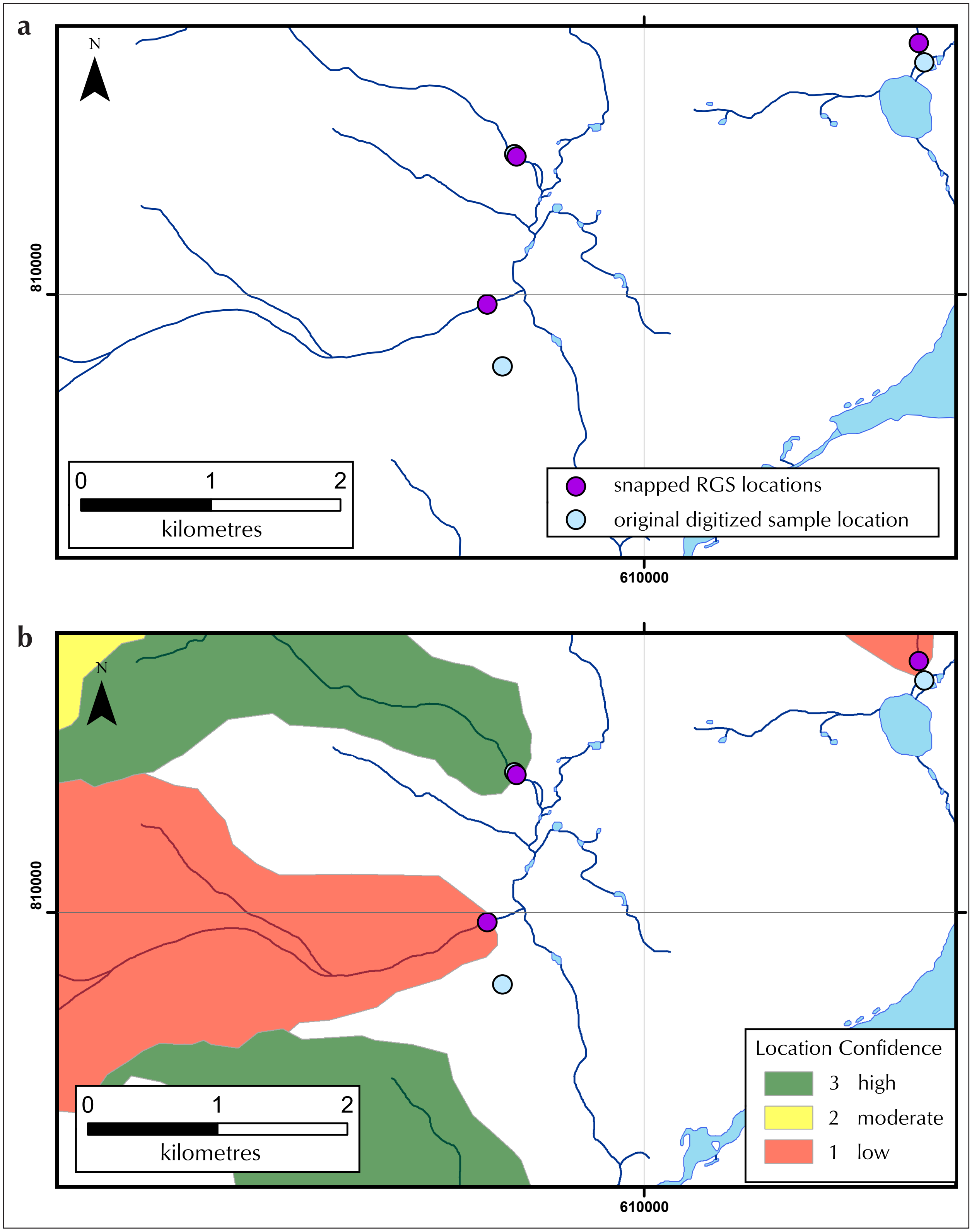

Figure 2. *Plan map comparing, in relation to hydrology,* ***(a)*** *original and updated sample locations and* ***(b)*** *derived catchment polygons coloured by location confidence rank. This example illustrates that there are several scenarios where use of the snapping tool could produce an incorrect interpretation of the actual sample location. Therefore, the confidence level of the snapped sample location (purple dot in centre of map) is low resulting in a catchment quality of 1.*

CATCHMENT AREA

Catchment area is used as a proxy for dilution of geochemically anomalous responses derived from mineralized rocks by sediment from barren rocks. The larger the catchment relative to the area of exposed mineralization, the greater the dilution effect should be (Hawkes, 1976), assuming equal erosion of material throughout the catchment. In general, large catchments define regional geochemical background, which is why they are often used for country or continent-wide geochemical characterization studies. An outcome of this observation is that maximum effective catchment areas can be determined, either theoretically using the approach of Hawkes (1976) or empirically where existing data occur. Previous empirical studies have shown that a maximum effective catchment area for regional stream sediment surveys in the Canadian Cordillera is on the order of 10 km^2 (Mackie *et al.*, 2015b; Arne and Brown, 2015; Arne and Bluemel, 2011).

While element values and indices can be corrected for dilution, it is argued that this is only applicable when a catchment is of reasonable size and the elements of interest are above regional background concentration. Extremely large catchments (*i.e.*, >30 km^2) are suspect in the sense that they are likely a consequence of incorrect sample locations given that sampling of substantial drainages or rivers was not the mandate of the original sampling program. Even if the sample location is correct leading to a very large catchment, it is more likely that any geochemical anomalism observed is related to secondary hydrological processes, such as scavenging or accumulation, rather than an indication of anomalism related to a nearby erosion of bedrock. Based on these factors each catchment has been given a score related to its 2-dimensional area as shown in Table 3.

The majority (68%) of catchments are within the less than ten square kilometre threshold that is ideal for capturing a mineral deposit signature (rank 3). Catchments with a rank of 1 and 2 are derived from samples collected at lower elevations often corresponding to higher-order drainages (Fig. 3). Areas covered by large catchments are under-sampled presenting an opportunity for infill sampling and further exploration despite moderate to low concentrations of elements of interest.

Table 3. *Distribution of catchments by rank based on catchment area.*

Catchment Area	Rank	Quality	Number of Catchments	Percentage
<10 km^2	3	High	14 343	68
>10 and <30 km^2	2	Moderate	4 872	23
>30 km^2	1	Low	2 015	9

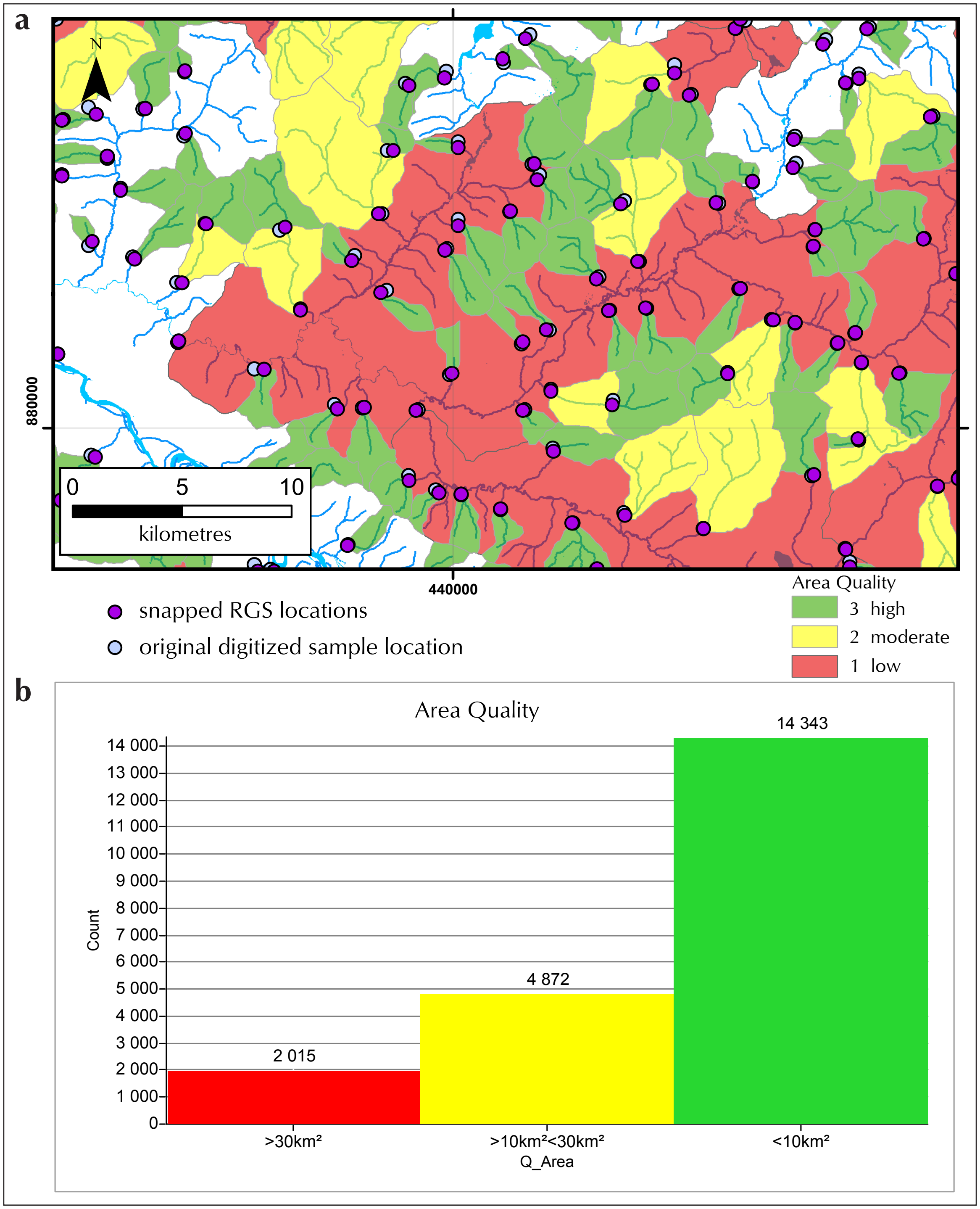

***Figure 3. (a)** Plan map and **(b)** histogram of catchment areas coloured by assigned area rank. Much of the area shown is covered by one very large, low-rank catchment that relates to a sample taken in the western part of the area.*

MATERIAL

The composition of stream sediment is, in large part, dictated by what material is present and eroding into the corresponding stream. In the recent study by Mackie *et al.* (2015a) it was shown that compositional variation of stream sediment is strongly controlled by bedrock geology, in agreement with previous studies in the Selwyn basin (*e.g.*, Bonham-Carter and Goodfellow, 1986). However, unconsolidated sediments are likely to provide an important contribution when they constitute a significant portion of catchment area, particularly as they are easily eroded. Regardless of whether these sediments have an increasing or decreasing effect on a given element, they potentially obscure signals from proximal bedrock sources. The origin of the sediment is also an important consideration. Weathering of bedrock to produce colluvium or soil has some effect on composition; however, it is likely that an anomaly derived from this media would still be traceable to the original source given a limited transport distance. Conversely, a geochemical anomaly in stream sediment derived from thick deposits of till (till blanket) would be considerably more difficult to source as the ultimate provenance of the anomaly may lie outside the catchment sampled. Incorporation of re-worked alluvial and glacio-fluvial sediments further complicates effective follow-up. Using these considerations each catchment is ranked based on the dominant material type as shown in Table 4 and Figure 4. The dominant material type was determined using an overlay query in ESRI ArcMap™ to intersect catchment polygons with a custom map product generated from published YGS bedrock and surficial maps (http://www.geology.gov.yk.ca/databases_gis.html [accessed March, 2017]).

Table 4. *Distribution of catchments by rank based on dominant surface material type.*

Material Type	**Rank**	**Quality**	**Number of Catchments**	**Percentage**
Bedrock, colluvium, till veneer	3	High	17 705	83
Till blanket	2	Moderate	2 656	13
Alluvial, fluvial, eolian, lacustrine (& glacial equivalents)	1	Low	869	4

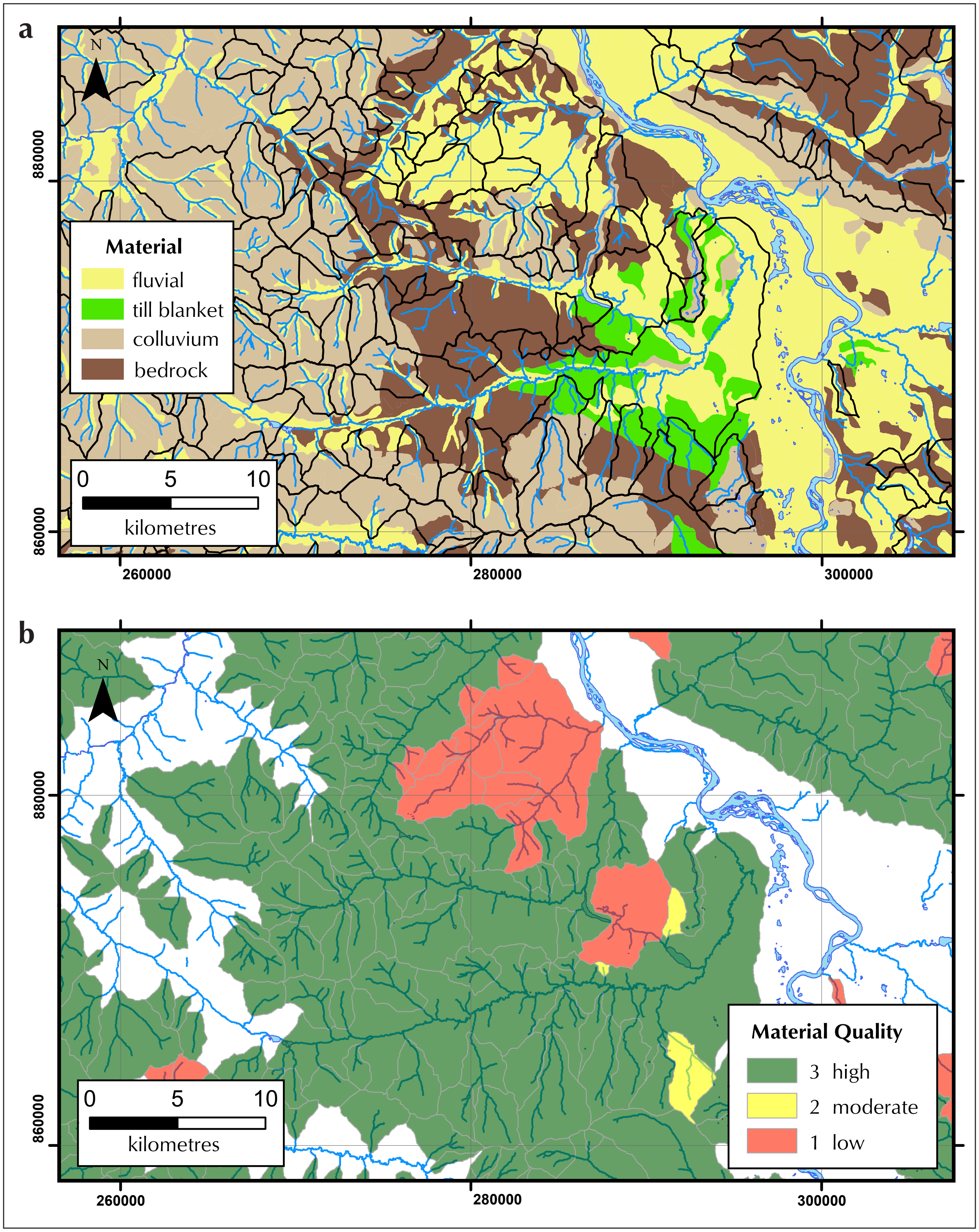

Figure 4. ***(a)*** *Plan maps comparing, in relation to hydrology, surface material type and* ***(b)*** *catchment polygons coloured by assigned material rank. Low-rank catchments correspond to regions dominated by fluvial outwash and till blanket. Geochemical anomalies in associated samples could be related to these transported sediments with the ultimate bedrock source being outside the digitized catchment.*

SLOPE ANGLE

Another method to determine if a stream is likely to be eroding bedrock and thus also likely to contain sediment with a substantial component of local bedrock detritus is to investigate slope steepness characteristics (*e.g.*, Shahrestani and Mokhtari, 2017). While slope information was recorded for each sample site at the time of sampling it is reported in a qualitative way (shallow, moderate, steep) and determined by what each sampler perceived the slope to be near the sample site. Rather than rely on the perception of the sampler, each catchment is attributed a slope angle from a slope raster derived from digital elevation models (DEM). DEM files were obtained from Natural Resources Canada (http://ftp.geogratis.gc.ca/pub/nrcan_rncan/vector/canvec/shp/Elevation/ [accessed March, 2017]) at a scale of 1:50 000. The slope raster was generated in ArcMap™ using the Spatial Analyst toolbox. To better represent a region proximal to the sample site, each catchment was truncated at the next upstream sample site. The majority slope value (mode) for each truncated catchment was determined using the Zonal Statistics tool. By examining the catchments coloured by majority slope in conjunction with topographic features threshold values were selected. As described in Table 5 and shown in Figure 5, catchments occurring in topographically subdued areas were given the lowest rank on the basis that they are likely to represent non-ideal sample sites. Our experience indicates that such low-relief catchments are often affected by metal scavenging effects on organic material or secondary Fe and/or Mn hydroxides.

Table 5. *Distribution of catchments by rank based on majority degree slope within catchment area.*

Majority Slope	Rank	Quality	Number of catchments	Percentage
>8 degrees	3	High	13 179	62
>3 and <8 degrees	2	Moderate	4 520	21
<3 degrees	1	Low	3 531	17

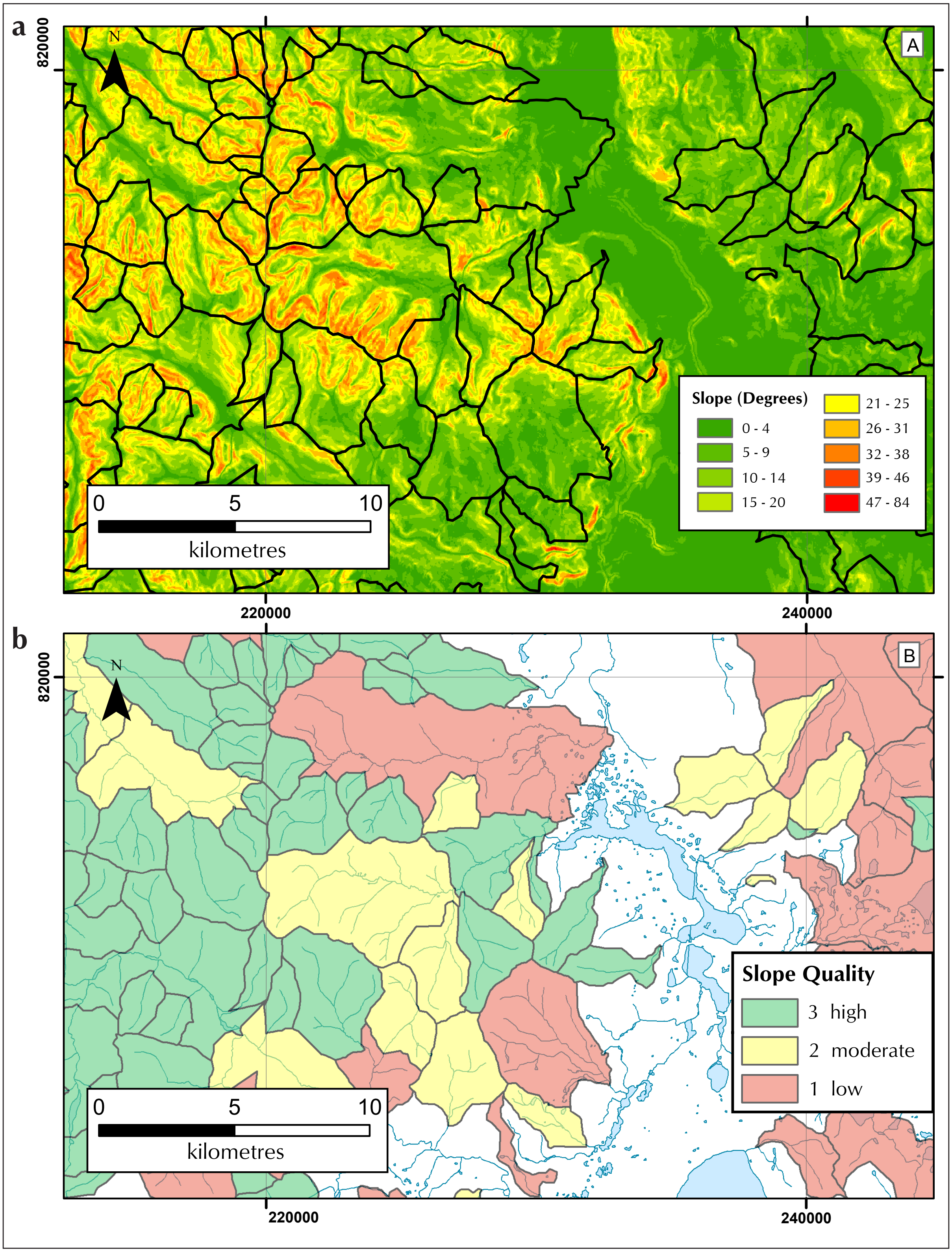

Figure 5. (a) *Plan maps comparing, in relation to hydrology, a derived slope raster and **(b)** catchment polygons coloured by assigned slope rank. Catchments that cover low lying areas (green-dark green), are given a lower quality ranking than those that cover an area of significant relief where it is more likely that stream sediments were derived from local bedrock.*

SLOPE ASPECT

The project area straddles sporadic to extensive-discontinuous permafrost zones (Heginbottom *et al.*, 1995). Permafrost develops preferentially on north-facing slopes at high latitudes due in large part to lower summer solar radiation (Cote, 2002; McKillop *et al.,* 2013). Low lying areas are also prone to permafrost development but given these are not the sites of stream sediment samples this is of less importance to the present work. As suggested by Frey *et al.* (2007), permafrost likely acts as a barrier limiting the interaction between surface waters and bedrock leading to low solute concentrations in stream waters. South-facing slopes, by contrast, receive more solar radiation which contributes to rock fatigue through expansion and contraction likely resulting in higher sediment load. While it is accepted that predicting permafrost distribution is a complex problem involving the interplay of many factors (*e.g.*, climate, snow cover, vegetation, organic layer thickness, soil moisture, elevation temperature inversions, slope and solar radiation) we use slope aspect as a first order predictor of where permafrost is likely to occur.

Additionally, as documented by Jackson *et al*. (2009), lower sections of north-facing slopes in the Dawson Range are often sites of loess accumulation due to prevailing southerly winds and the lack of glaciation in this region. These accumulations, when mixed with soil by cryoturbation, can dilute geochemical anomalies related to mineral deposits (Bond and Sanborn, 2006). Soil geochemical investigation of the Denali zone on the Coffee gold property by McKillop *et al.* (2013) shows evidence that mineralization signals are significantly subdued on north-facing slopes. Extrapolating this to stream sediments suggests that catchments with a high proportion of north-facing slopes are likely to have lower metal concentrations compared to those with dominant south-facing slopes given similar bedrock or colluvial geochemical characteristics.

Slope aspect was determined using 1:50 000 scale DEM in ESRI ArcMap™. Following the criteria of Smith *et al.* (2009), slope azimuths between 300 and 60° were classed as 'north-facing'. The percentage of north-facing slope for each catchment was determined using an overlay query. Threshold percentages of north-facing slopes were chosen arbitrarily through comparison of determined aspect, catchment distribution, and topography. The three categories of slope aspect are shown in Table 6. Example maps of the north-facing aspect and resultant catchment quality are shown in Figure 6.

Table 6. *Distribution of catchments by rank based on percentage of catchment area that contains north-facing slopes.*

% north-facing	Rank	Quality	Number of Catchments	Percentage
< 50	3	High	13 122	62
> 50 and < 75	2	Moderate	5 740	27
> 75	1	Low	2 368	11

OVERALL CATCHMENT QUALITY

An overall catchment quality index can be made by combining the rankings determined for location confidence, surficial material, catchment area, slope and slope aspect. Two indices have been generated: an equal-weight sum; and a weighted-sum produced by downgrading the influence of slope and slope aspect by 50%. The rankings for each attribute and index are appended to the catchment shapefile in a digital release accompanying this report allowing for other quality indices to be generated by the user.

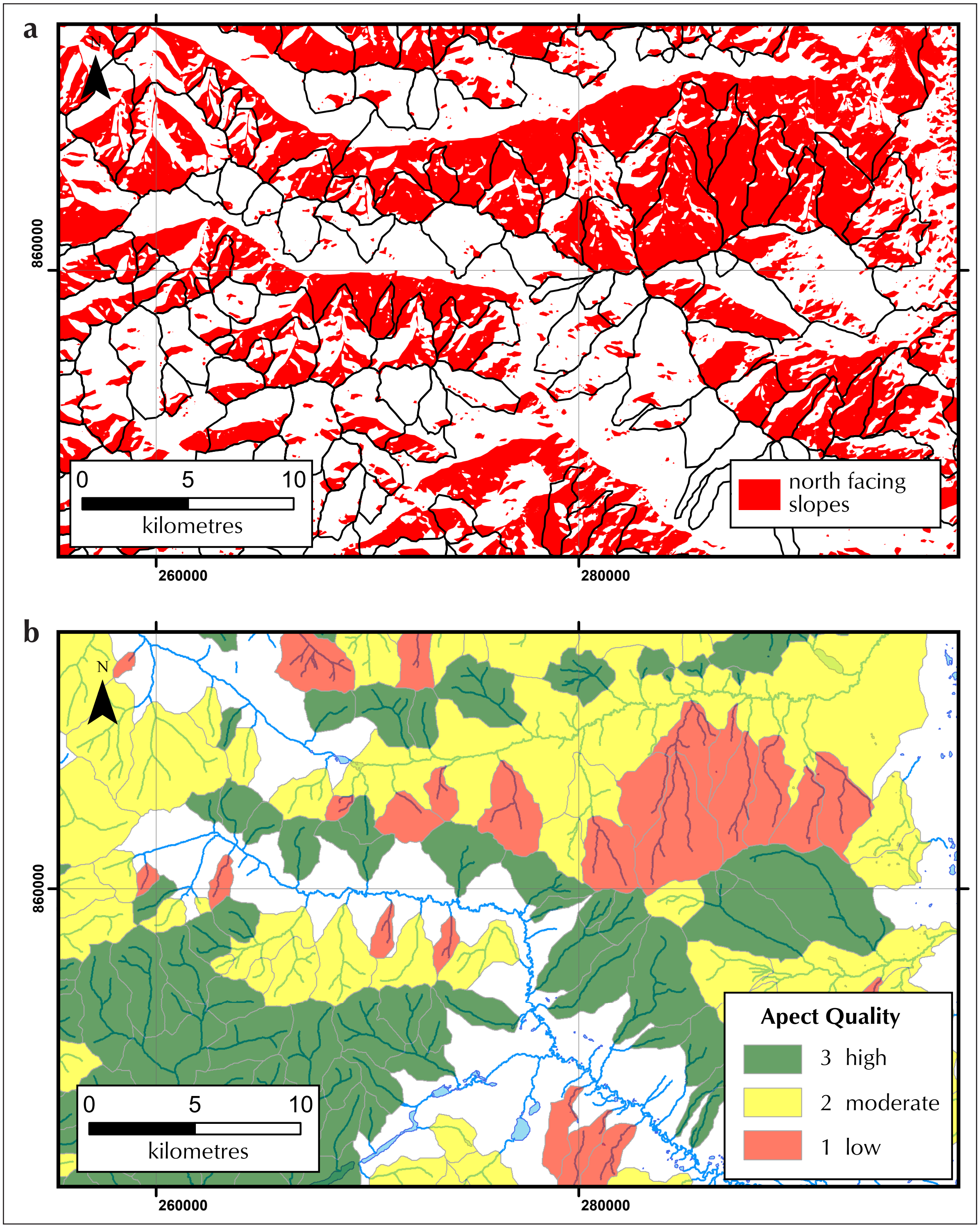

Figure 6. (a) *Plan maps comparing a north-facing aspect raster and* ***(b)*** *catchment polygons coloured by assigned aspect rank. Catchments that contain >75% of predominantly north-facing slopes are assigned a lower ranking given likely permafrost development and loess accumulation. Catchments with >50% but <75% north-facing slopes are assigned a moderate ranking. Catchments with a high quality ranking contain <50% north-facing slopes.*

GEOCHEMICAL DATA QUALITY

The re-analysis of archived stream sediment samples from Yukon between 2011 and 2016 (Table 1) was accompanied by a quality control program that included the insertion of standard reference materials and blind duplicate samples into the sample sequence at the rate of 1 every 20 samples. In addition, field duplicate samples collected with the original stream sediment samples were also re-analyzed at the same rate. The blind duplicates were generally taken from the field duplicate where there was sufficient material (W. Jackaman, personal communication, March 21, 2017). These data allow an assessment to be made of both accuracy and precision of the data from the re-analyzed samples.

Re-analysis of stream sediment samples occurred in two campaigns separated by approximately two years. For the first campaign re-analyses were done by AcmeLabs using digestion of a 0.5 g aliquot by a modified aqua regia acid consisting of a hot 1:1:1 mixture of H_2O:HNO_3:HCl followed by an ICP-AES or ICP-MS instrumental finish (method 1F04). These analyses were undertaken in 2011 and 2012 at AcmeLabs' laboratory on Cordova Street in Vancouver. A second campaign of re-analyses occurred in 2015 and 2016 using a similar methodology by Bureau Veritas (which acquired AcmeLabs in 2014) at a laboratory located on Shaughnessy Street in Vancouver (method code AQ250-EXT). The methodology used for the analyses is believed to have been the same as that used by AcmeLabs in 2011 and 2012.

Only two of the reference materials used, Canmet STSD-1 and Red Dog, were submitted in both re-analysis campaigns. Of the remaining reference materials, Canmet STSD-4 and Bonanza were submitted only to AcmeLabs during the first campaign and Canmet Till-1, Canmet Till-3, BC Till-A and BC Till-B were only submitted to Bureau Veritas during the second campaign. In the following discussion emphasis has been placed on those elements for which certified reference materials (CRM) were used (*i.e.*, the Canmet CRM), and those elements that had the most relevance for catchments analysis and weighted sums modelling carried out using the re-analyzed data by Mackie *et al*. (2015).

DATA PRECISION

A statistical summary of relative standard deviations (RSD; also known as the coefficient of variation, or CoV) is presented in Table 7. For reference, CRM should have RSD <5% for those elements considered to be well homogenized. Many elements shown in Table 5 have RSD >5% and therefore display more variation than would normally be acceptable in a CRM, even for levels that are well above the lower limit of detection (LLD). Whether this is a function of variability at the laboratory or reflects inhomogeneity in the CRM is not clear from the data, as only the four Canmet CRM are certified and homogeneity testing data are not available with the certificates.

There are differences in RSD values for Canmet STSD-1 and Red Dog across the two re-analysis campaigns, but these are not consistent. The Bureau Veritas RSD for both reference materials are lower than the AcmeLabs RSD for most elements, although there are a number of instances where the Bureau Veritas RSD are higher. The Au RSD are always high, >66% and commonly >100%, even where the certified or long-term average values are more than an order of magnitude above the LLD and so theoretically should be relatively precise. However, the Au data suffer from a nugget effect using a 0.5 g aliquot, and this is also evident in the duplicate sample data.

Table 7. *Summary of results for reference materials submitted with the archived stream sediment samples for re-analysis.*

Canmet STSD-1 n= 185	Ag (ppb)	As (ppm)	Au (ppb)	Cd (ppm)	Cr (ppm)	Co (ppm)	Cu (ppm)	Fe (pct)	Hg (ppb)	Pb (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	Sb (ppm)	V (ppm)	Zn (ppm)
Certified Value	300	17	8	0.8	28	14	36	3.5	110	34	3740	2	18	2	47	165
Average Value	335	19.6	11.6	1	26.8	14	36	3.2	112	35.8	3597	1	20.1	2	43	162.6
Average ACME Value	331	18.8	16.4	0.9	26.2	13.5	33.8	3.1	108	33.6	3464	1	19.3	1.8	41	154.1
Average Bureau Veritas Value	338	20.1	8.1	1	27.3	14.3	37.5	3.2	115	37.3	3694	1	20.6	2.1	44	168.7
Total Average RSD (%)	9.6	6.3	315	9.2	6.1	6.9	8	4.2	9.4	8.8	4.6	8.6	6.5	11.7	6.2	7.4
Average ACME RSD (%)	12.4	6.3	327	8.2	6.5	6.8	6.8	4.1	11.1	8	3.5	10.3	6.3	10.2	6	4.5
Average Bureau Veritas RSD (%)	6.9	4.6	173	8.2	5.3	5.8	5.8	3.2	7.4	6.6	3.3	6.7	5.2	8.3	5.1	6.5
Average Relative Bias (%)	12	15	44.7	18.6	-4.1	-0.2	-0.1	-9.4	1.8	5.2	-3.8	-51	11.4	0.6	-8.2	-1.5
Average ACME Bias (%)	10	11	105	13	-6.5	-3.8	-6	-12	-1.6	-1.1	-7.4	-53	7.3	-8.2	-11	-6.6
Average Bureau Veritas Bias (%)	13	18	1	23	-2.4	2.4	4.2	-7.7	4.2	9.8	-1.2	-50	14.4	6.9	-5.8	2.3
Red Dog n=270	Ag (ppb)	As (ppm)	Au (ppb)	Cd (ppm)	Cr (ppm)	Co (ppm)	Cu (ppm)	Fe (pct)	Hg (ppb)	Pb (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	Sb (ppm)	V (ppm)	Zn (ppm)
Recommended Value	85	5.6	25.7	0.23	20.1	11.6	167	4.22	21	7.1	409	13.2	13	0.14	91	51.4
Average Value	85	5.7	42.7	0.23	20.1	11.4	164.4	4.19	21	7	406	12.9	12.5	0.14	90	50.8
Average ACME Value	85	5.8	48	0.22	20.1	11.3	161.5	4.17	21	6.7	404	12.7	12.4	0.13	91	49.5
Average Bureau Veritas Value	85	5.7	36.2	0.23	20	11.6	167.9	4.23	22	7.2	408	13.2	12.6	0.15	90	52.4
Total Average RSD (%)	12.5	10.5	235	15.4	6.2	5.7	5.6	3.5	36.2	8.2	4.8	6.9	5.1	23.5	5.7	7.5
Average ACME RSD (%)	12.8	11.5	252	13.8	6.3	5.7	5.6	3.5	45.4	7.9	4.6	6.6	5.3	19.1	5.6	6
Average Bureau Veritas RSD (%)	12.2	8.8	185	17	6	5.5	5	3.4	22	6.7	4.9	6.5	4.7	23.8	5.8	7.9

***Table 7** continued.*

Average Relative Bias (%)	0	1.8	66.1	0	0	-1.7	-1.6	-0.7	0	-1.4	-0.7	-2.3	-3.8	0	-1.1	-1.2
Average ACME Bias (%)	0	3.6	86.8	-4.3	0	-2.6	-3.3	-1.2	0	-5.6	-1.2	-3.8	-4.6	-7.1	0	-3.7
Average Bureau Veritas Bias (%)	0	1.8	40.9	0	-0.5	0	0.5	0.2	4.8	1.4	-0.2	0	-3.1	7.1	-1.1	1.9
Canmet STSD-4 n=80	Ag (ppb)	As (ppm)	Au (ppb)	Cd (ppm)	Cr (ppm)	Co (ppm)	Cu (ppm)	Fe (pct)	Hg (ppb)	Pb (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	Sb (ppm)	V (ppm)	Zn (ppm)
Certified Value	300	11	4	0.6	30	11	66	2.6	930	13	1200	2	23	3.6	51	82
Average ACME Value	346	11.4	3.9	0.4	29.3	10	64.5	2.5	906	12.5	1148	1.2	24.1	4.2	44.8	78
Average ACME RSD (%)	6.4	6.9	176	9.4	6.2	6.4	8	3.8	13.1	8	4	8	6.5	3.6	5.3	5.2
Average ACME Bias (%)	15	4	-3.1	-38	-2.4	-2.2	-2.2	-4.7	-2.6	-3.8	-4.4	-41	4.7	16	-12	-4.9
Canmet Till-1 n=76	Ag (ppb)	As (ppm)	Au (ppb)	Cd (ppm)	Cr (ppm)	Co (ppm)	Cu (ppm)	Fe (pct)	Hg (ppb)	Pb (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	Sb (ppm)	V (ppm)	Zn (ppm)
Certified Value	200	13	13		30	12	49	3.4	92	14	1020	1	17		48	71
Average Bureau Veritas Value	230	16.3	10.2	0.23	26	12.7	47.4	3.1	94	15.3	1100	0.7	17.3	4.7	51	65.8
Average Bureau Veritas RSD (%)	6.2	4.6	107	19.3	6	6.1	5.3	3.4	7.9	30.8	3.4	6.8	5.1	12.8	4.7	6
Average Bureau Veritas Bias (%)	15	25	-21	n/a	-13	5.6	-3.3	-8.8	2.4	9.5	7.8	-35	1.9	n/a	6.3	-7.3
Canmet Till-3 n=79	Ag (ppb)	As (ppm)	Au (ppb)	Cd (ppm)	Cr (ppm)	Co (ppm)	Cu (ppm)	Fe (pct)	Hg (ppb)	Pb (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	Sb (ppm)	V (ppm)	Zn (ppm)
Certified Value	1400	84	6		73	10	23	2.2	107	17	310	1	32		33	43
Average Bureau Veritas Value	1625	87.3	3.9	0.09	63.3	10.9	21.9	2	109	18.4	313	0.6	32.4	0.54	31.2	40.1
Average Bureau Veritas RSD (%)	7.4	4.7	127.9	39.7	5.3	6	5.6	3.4	10.1	7.6	4.8	8.4	5.4	12.2	4.5	6.9
Average Bureau Veritas Bias (%)	16	4	-35	n/a	-13	9	-4.8	-11.4	1.7	8.5	0.9	-39	1.1	n/a	-5.4	-6.8

***Table 7** continued.*

Bonanza n=143	Ag (ppb)	As (ppm)	Au (ppb)	Cd (ppm)	Cr (ppm)	Co (ppm)	Cu (ppm)	Fe (pct)	Hg (ppb)	Pb (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	Sb (ppm)	V (ppm)	Zn (ppm)
Recommended Value	93	8.3	1.4	0.23	17.2	6.8	11.9	1.55	20	11.6	248	0.55	13.6	0.29	26	54.8
Average ACME Value	95.8	8.4	2.6	0.23	17.5	6.7	12	1.6	22	11.8	247	0.56	13.6	0.29	25.9	55.1
Average ACME RSD (%)	21.8	7.6	226	11	7.5	6.9	8	3.7	94	7.8	4.8	8.9	6.9	12.2	6.2	5.5
Average ACME Bias (%)	3	1.2	85.7	0	1.7	-1.5	0.8	3.2	10	1.7	-0.4	1.8	0	0	-0.4	0.5
BC Till-A n=78	Ag (ppb)	As (ppm)	Au (ppb)	Cd (ppm)	Cr (ppm)	Co (ppm)	Cu (ppm)	Fe (pct)	Hg (ppb)	Pb (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	Sb (ppm)	V (ppm)	Zn (ppm)
Recommended Value	91	7.3	6.5	0.1	46.2	15	72	3.7	53	10.9	333	0.77	37.9	0.28	51	77.1
Average Bureau Veritas Value	92	7.3	8.2	0.1	46.3	15	72	3.7	54	10.8	338	0.77	38.1	0.29	50	76.8
Average Bureau Veritas RSD (%)	8.6	5	66	15	4.8	6	5.1	3.2	14	6	5	5.8	4.9	14	3.5	5.4
Average Bureau Veritas Bias (%)	1.1	0	26.2	0	0.2	0	0	0	1.9	-0.9	1.5	0	0.5	3.6	-2	-0.4
BC Till-B n=79	Ag (ppb)	As (ppm)	Au (ppb)	Cd (ppm)	Cr (ppm)	Co (ppm)	Cu (ppm)	Fe (pct)	Hg (ppb)	Pb (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	Sb (ppm)	V (ppm)	Zn (ppm)
Recommended Value	95	7.2	6.8	0.1	46.6	14.8	71.4	3.73	54	10.6	340	0.78	38.2	0.27	51	75.9
Average Bureau Veritas Value	94	7.2	9.5	0.1	46.3	14.8	71.6	3.7	59	10.7	340	0.76	38	0.28	50	76.7
Average Bureau Veritas RSD (%)	8.6	6	98	17	6.3	6.8	6.9	3.6	54	7.2	4.9	7.4	5.8	16	4.4	7.1
Average Bureau Veritas Bias (%)	-1.1	0	39.7	0	-0.6	0	0.3	-0.8	9.3	0.9	0	-2.6	-0.5	3.7	-2	1.1

Data precision has also been calculated for blind sample duplicates for a limited suite of elements (Fig. 7; As, Cu, Au) through the calculation of average RSD using the root mean squared (RMS) approach described by Stanley and Lawie (2007) and favoured by Abzalov (2008). Only data at, or greater than, an order of magnitude above the LLD have been used for assessment, but this was most of the data in all three cases. For example, Cu, which is taken to be representative of the base metals, has a RSD of 5.4%, comparable to values obtained for the reference materials. On the other hand, As shows a large total RSD of 15.8%, but this is largely due to high variability of the As data from Bureau Veritas (20%) compared to that obtained from AcmeLabs (7.8%). As expected, Au displays a large average RSD of 63.7%, comparable to the lower end of that observed in the reference materials.

The blind duplicate data can be compared to that obtained for field duplicates (Fig. 8). An average RSD for Cu of 10.8% was obtained for the field duplicates, consistent with sampling variance being a major source of error in the Cu data. By contrast, the As field duplicates yield an average RSD of 13.7%, with the Bureau Veritas data having a slightly higher average RSD. This is equivalent to the value calculated from the blind duplicates. The average RSD for Au is 60.5%, also similar to that obtained for the blind duplicates. The data for As and Au suggest large uncertainties associated with preparation and analysis of the sieved material rather than natural variability at the sampling sites.

Gold data from the original analyses were obtained from an average 10-gram fire assay or larger samples for instrumental neutron activation. These results were used by Mackie *et al*. (2015a) in weighted sums models. Some of these samples were analyzed a second time, so it is possible to obtain average Au values from two fire assays. The average RMS RSD for 119 field duplicate pairs having average Au values of at least 10 ppb is 86%. This is similar to the average RMS RSD obtained for 899 pulp duplicate pairs of 94%. Although slightly higher than the average RMS RSD obtained from the blind duplicates samples analyzed by ICP-MS, the Au precisions for both data sets are poor although the original Au data can be improved by averaging the pulp duplicate data.

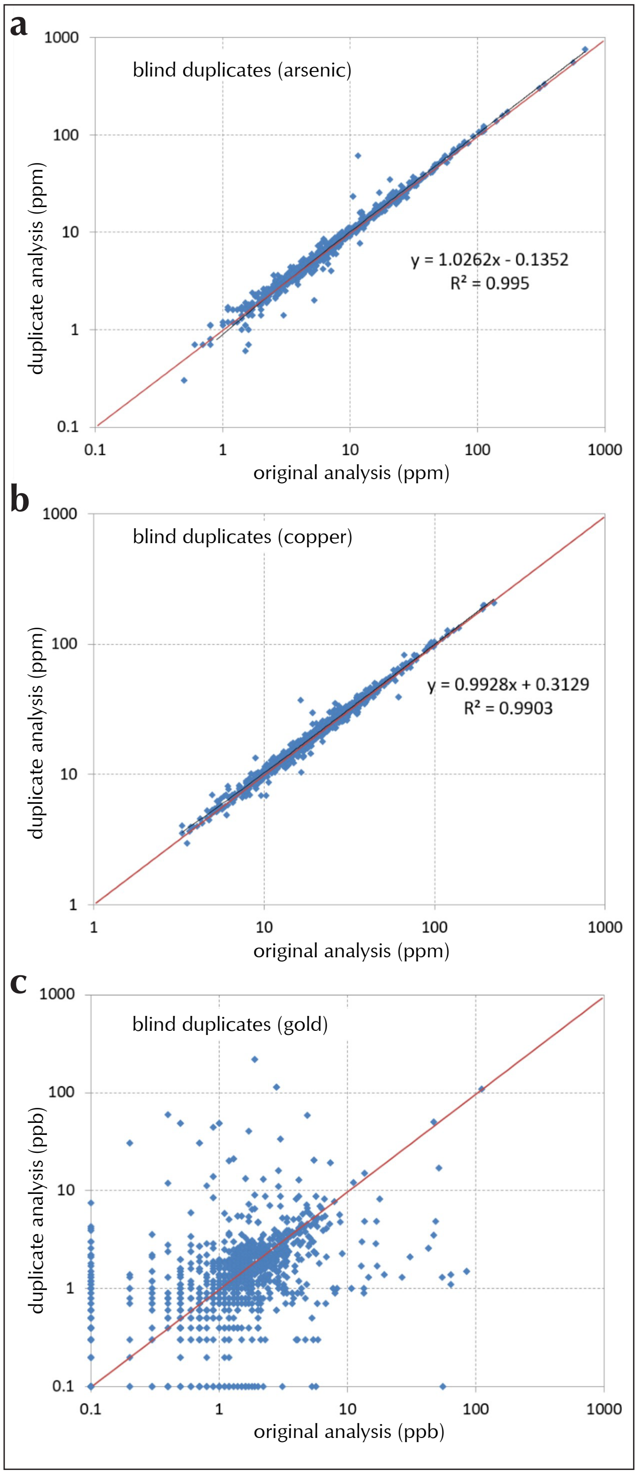

Figure 7. *Summary of blind (pulp) duplicates for **(a)** As, **(b)** Cu and **(c)** Au data analyzed by ICP-MS.*

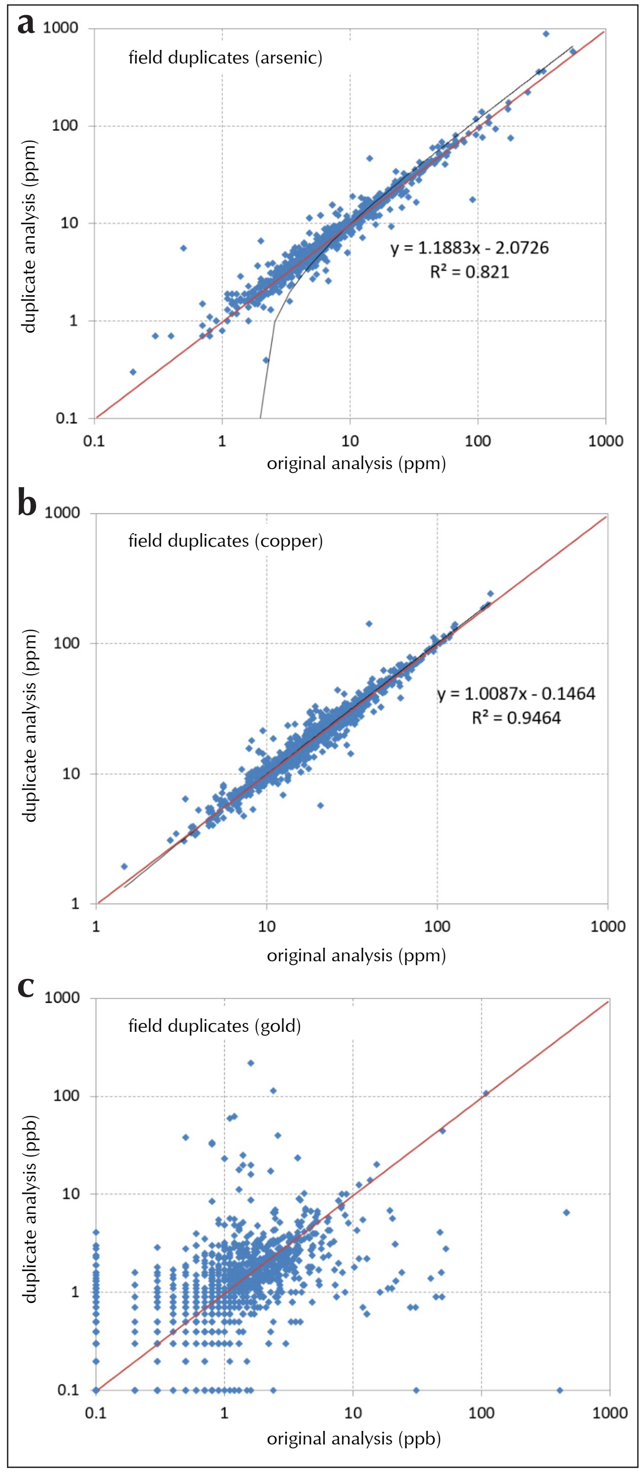

Figure 8. *Summary of field duplicates for **(a)** As, **(b)** Cu and **(c)** Au data analyzed by ICP-MS.*

DATA ACCURACY

Data accuracy has been assessed from repeat analyses of reference materials, only four of which are CRM (Canmet series STSD-1, STSD-4, Till-1 and Till-3). Average biases for these CRM are summarized in Table 7 for those elements for which certification is available. Long-term averages after removal of statistical outliers are available from multiple analyses of the non-certified reference materials for projects in British Columbia using the same methods at AcmeLabs and Bureau Veritas used for the Yukon re-analyses campaigns (R. Lett, personal communication, March 21, 2017). The average biases for the CRM are variable, being either positive or negative depending on the element, and often large (*i.e.*,>5%). By contrast, the biases for the reference materials analyzed using the same digestion as that used for the re-analysis campaigns (*i.e.*, dilute aqua regia) are typically less than 5%. This observation suggests that the dilute aqua regia digestions used for certification of the Canmet CRM are different than those used by AcmeLabs and Bureau Veritas. Caution must also be used when assessing average biases as they may disguise individual analyses that are wildly inaccurate. For this reason, they should be viewed in conjunction with precision estimates calculated for the reference materials (*see* previous section). Vertical error bars in Figures 9 and 10 represent two RSD uncertainties derived from repeat analyses for each reference material.

Only one CRM spans both re-analysis campaigns (STSD-1) and different biases are evident for analyses by AcmeLabs and Bureau Veritas (Fig. 9). Based on these elements, it is evident that data for most elements generated by Bureau Veritas for Canmet STSD-1 are slightly higher than that obtained by AcmeLabs. Biases have therefore been calculated separately for both laboratories in Table 7 for Canmet STSD-1. There are also several control sample failures at three standard deviations (3SD) for Fe and As due to long-term negative and positive bias in the data, respectively, although these may not be significant given the error bars overlap with the 3SD control line.

Data for the Red Dog reference material are presented in Figure 10. As Red Dog is not a CRM, the data are plotted against long-term means calculated for the data set, with the control lines based on multiples of the standard deviations of the means after removal of obvious statistical outliers. There is no clear shift in the Red Dog As data between the two laboratories, in contrast to the data from Canmet STSD-1, but there is a suggestion of a slight positive shift in the Fe and Cu data. Many of the elements analyzed at Bureau Veritas show a positive bias compared to the AcmeLabs data (Table 7). There are several failures at 3SD for As, although the error bars overlap the control line.

The Au data show considerable variability due to the nuggetty distribution of Au particles within the reference materials. However, most values for Canmet STSD-1 fall approximately one standard deviation (1SD) below the certified value and there is no obvious shift in data between the two re-analysis campaigns. A few Au analyses for both Canmet STSD-1 and Red Dog exceed the 3SD limits (Figs. 9 and 10) though only some of these failures are statistically significant given the large uncertainties associated with the Au analyses.

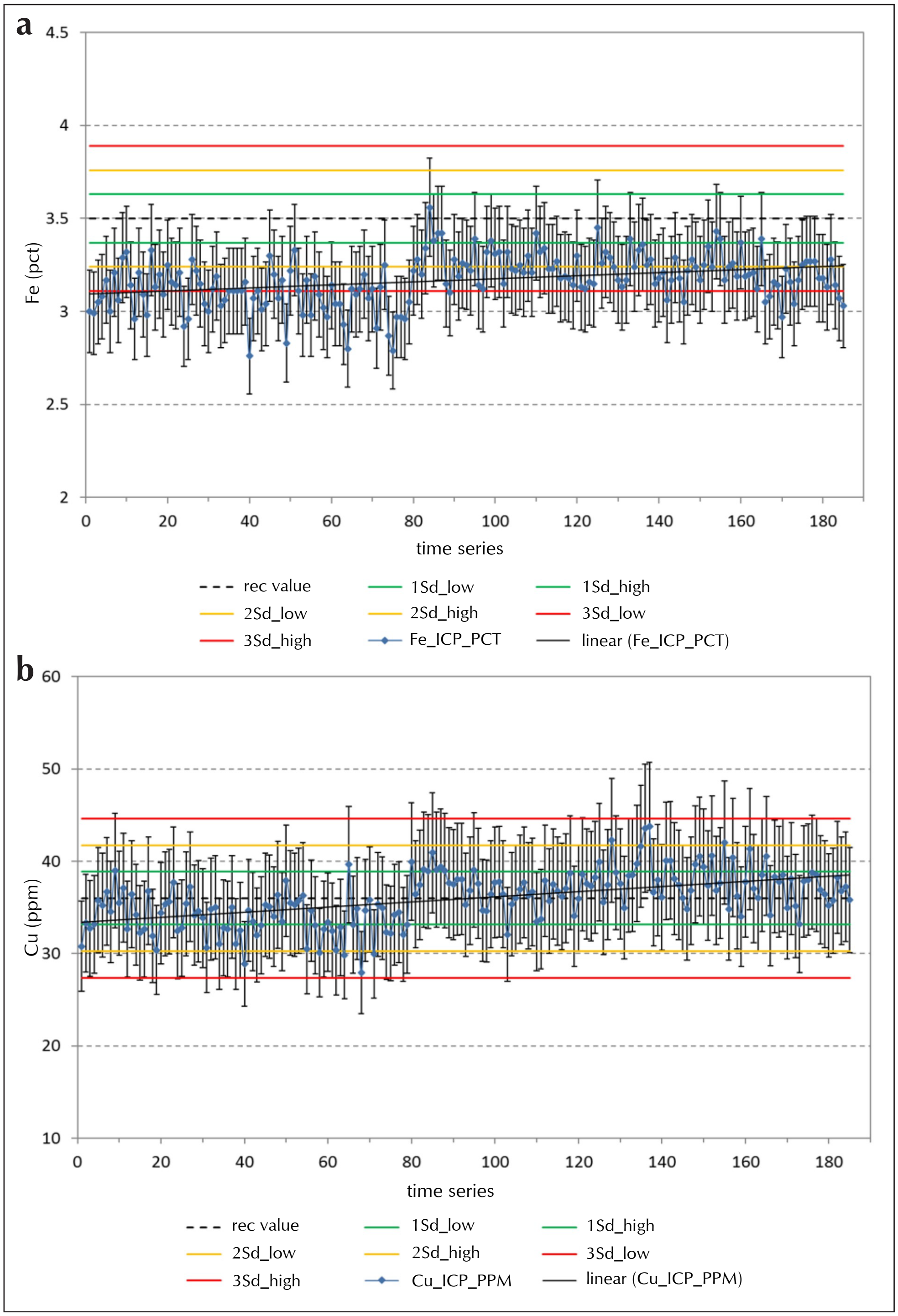

Figure 9. *Run charts for CRM Canmet STSD-1 plotted in chronological order for* ***(a)*** *Fe,* ***(b)*** *Cu,* ***(c)*** *As and* ***(d)*** *Au. The two-year gap between the two re-assay campaigns occurs at analysis number 80. See next page for (c) and (d).*

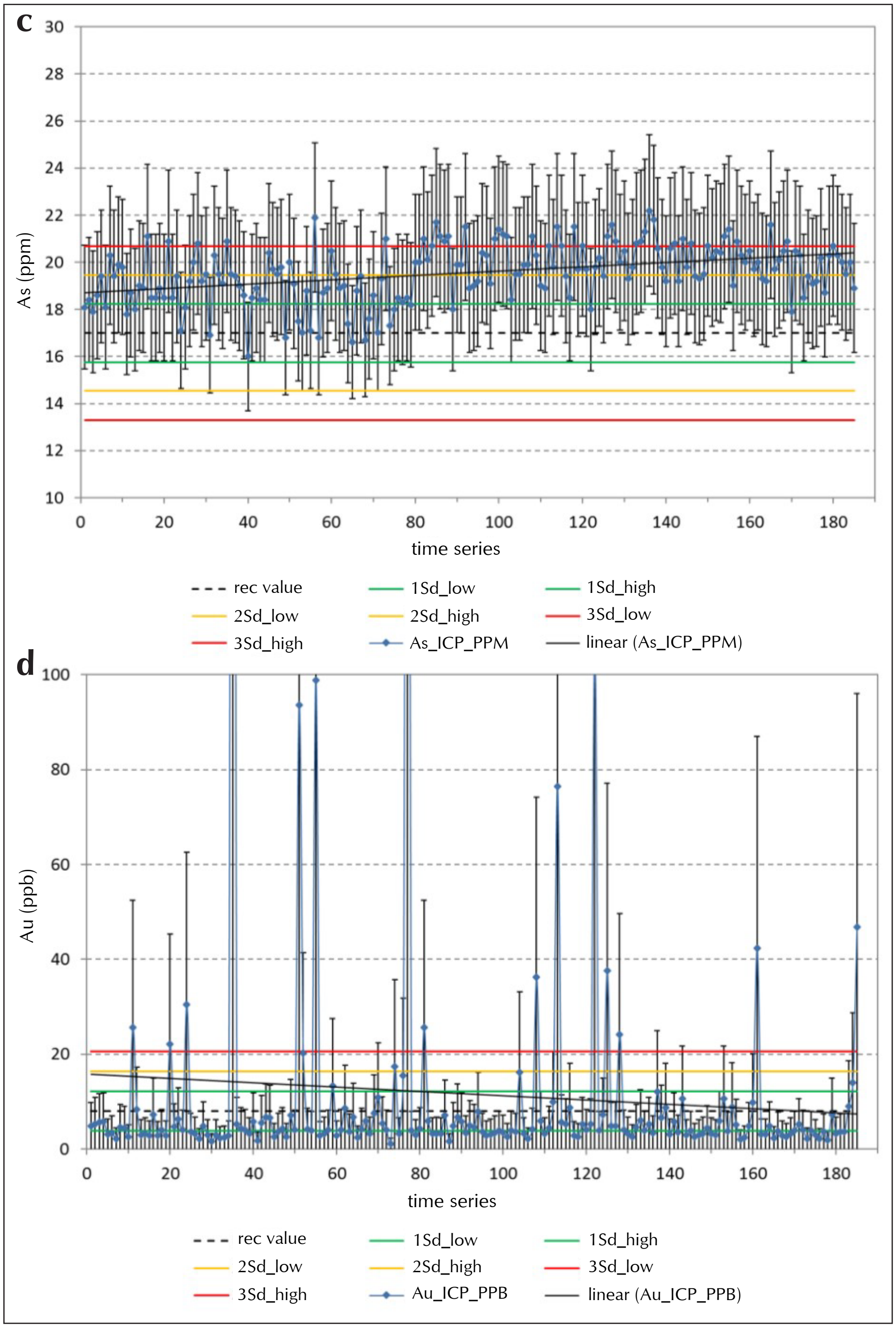

Figure 9 continued. *Run charts for CRM Canmet STSD-1 plotted in chronological order for **(a)** Fe, **(b)** Cu, **(c)** As and **(d)** Au. The two-year gap between the two re-assay campaigns occurs at analysis number 80. See previous page for (a) and (b).*

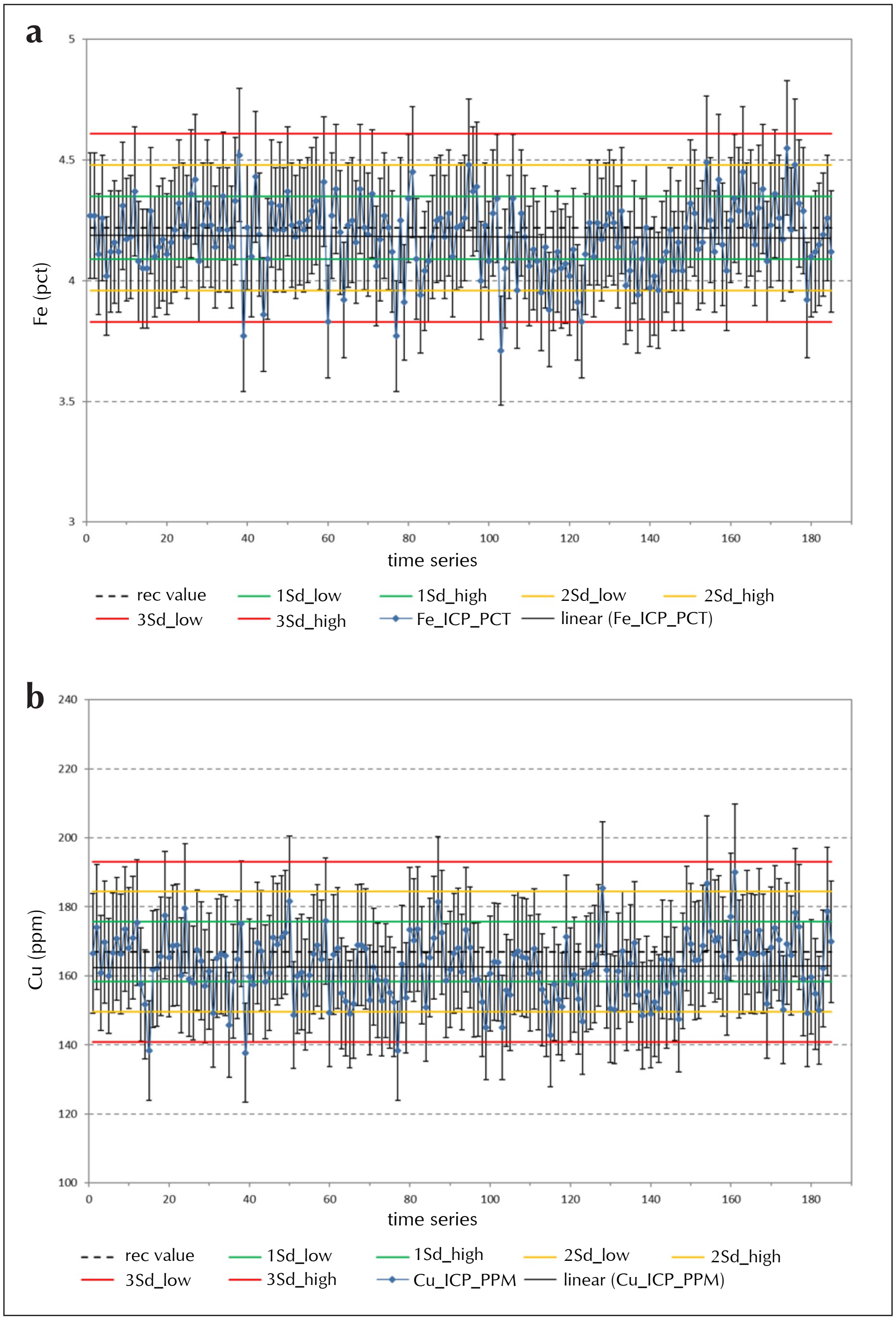

Figure 10. *Run charts for the Red Dog reference material plotted in chronological order for* ***(a)*** *Fe,* ***(b)*** *Cu,* ***(c)*** *As and* ***(d)*** *Au. The two-year gap between the two re-assay campaigns occurs at analysis number 149. See next page for (c) and (d).*

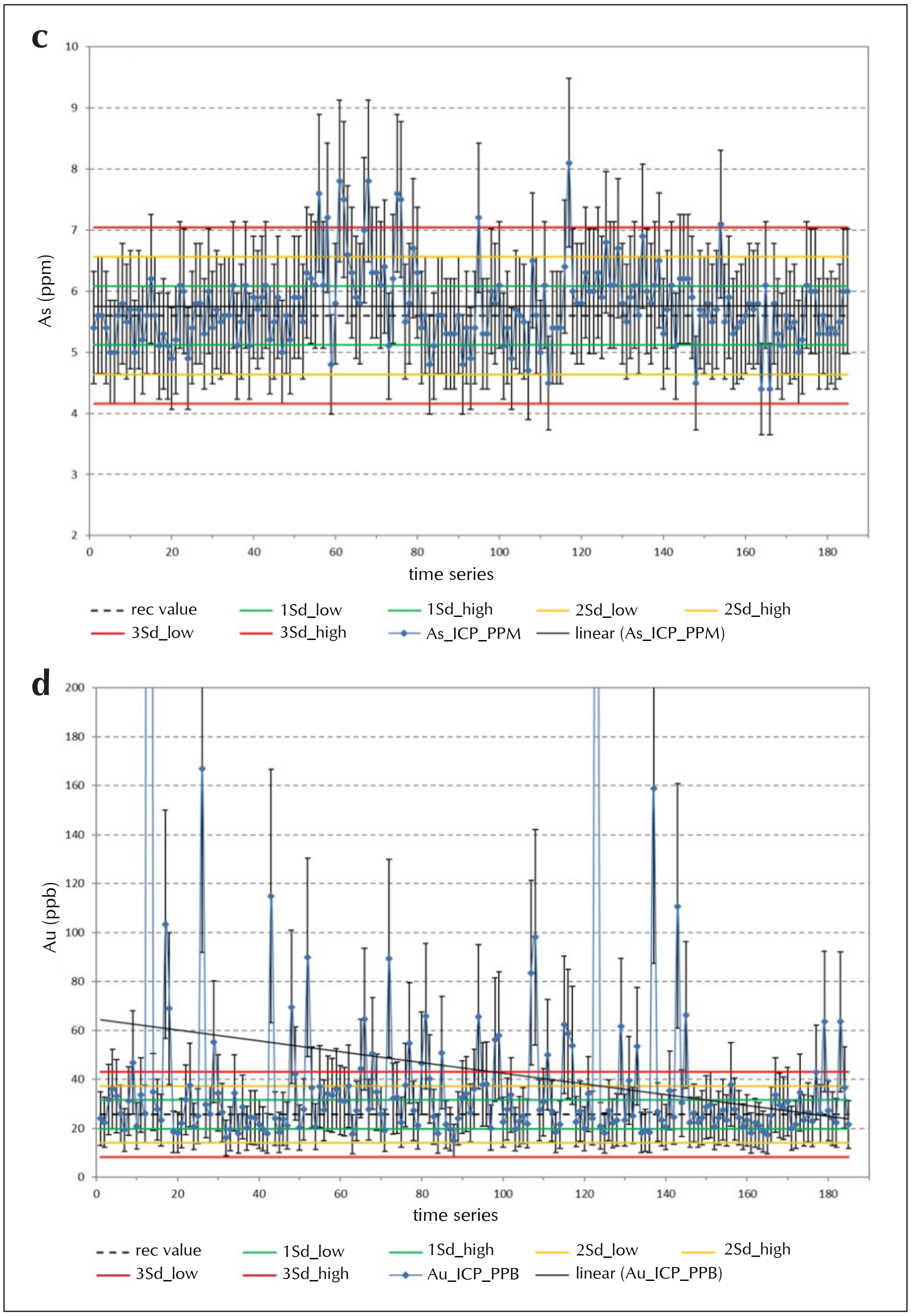

Figure 10. *Run charts for the Red Dog reference material plotted in chronological order for **(a)** Fe, **(b)** Cu, **(c)** As and **(d)** Au. The two-year gap between the two re-assay campaigns occurs at analysis number 149. See previous page for (a) and (b).*

CONCLUSIONS

By ranking catchment quality across five different qualitative and quantitative attributes, we identified catchments where problems with location, area, surface material, slope or aspect may impact or mask a bedrock geochemical signal in the stream sediment sample. By weighting each attribute with a value representative of the overall impact in disrupting or distorting underlying bedrock geochemistry, an overall quality ranking for each catchment was obtained and can be utilized in evaluating the reliability of the published enhanced interpretation of the stream sediment geochemistry.

Re-analysis of archived stream sediment pulp samples was accompanied by a rigorous quality control program that involved the analysis of field duplicates, pulp (blind) duplicates and reference materials, each submitted at the rate of 1 in 20 samples. The reference materials show a range of variability assessed using relative standard deviations that is generally greater than expected for reference materials for many elements (*i.e.*, generally greater than 5%), as well as variable biases for the CRM that are sometimes greater than 5%, possibly due to differences in the digestions used for certification compared to those used by AcmeLabs and Bureau Veritas. The variability in the repeat analyses of Au in the reference materials is similar to or greater than that displayed by either the field duplicate and pulp duplicate analyses. In addition, data for Canmet STSD-1 indicate a slight increase in values for many certified elements in this CRM analyzed at the Bureau Veritas laboratory in 2015 and 2016 compared to analyses by the same method at AcmeLabs in 2011 and 2012. Evidence for this shift in the Red Dog reference material is less obvious but still present. Overall, with the exception of Au, the re-analysis data are adequate for the purpose of regional exploration. Significant variations in data for key commodity and pathfinder elements from map sheet to map sheet may be present that would necessitate levelling of the data prior to merging.

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