

Influence of site and soil properties on the DRIFT spectra of northern cold-region soils



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ABSTRACT

We investigated the influence of site characteristics and soil properties on the chemical composition of organic matter in soils collected from a latitudinal transect across northern cold-region through analysis of diffuse reflectance Fourier transform mid infrared (DRIFT) spectra of bulk soils. The study included 119 soil samples collected from 28 sites including tundra, boreal forest, grassland, and coastal rainforest ecosystems. Organic, mineral, and cryoturbated soil horizons, both seasonally and perennially frozen, representing a variety of depths and edaphic conditions were examined. The amount and chemical composition of organic matter, as well as site and soil properties, exerted a strong influence on the DRIFT spectra. The spectra were highly sensitive to the extent of organic matter decomposition, enabling the ordination of organic (Oi, Oe and Oa) horizons. Differences in absorbance intensity for several spectral bands indicated that Oi horizons contained greater abundance of relatively fresh residues, phenolic-OH compounds, aliphatic compounds, and carbohydrates. In contrast, Oa horizons had a greater presence of amide groups, aromatics, C=C bonds, carboxylates and carboxylic acids. Another significant factor differentiating these horizons was the incorporation of clays and silicates into the Oa horizons. Calculated ratios of characteristic spectral bands showed a clear trend of increasing decomposition from Oi to Oe to Oa. The DRIFT spectra were related to many site/soil attributes including land cover type, parent material, and associated factors, such as permafrost presence/absence, drainage class, horizon depth, bulk density, cation exchange capacity, and pH. A single DRIFT spectral band was identified that might be used in future studies to quickly estimate the organic carbon, total nitrogen, and carbon:nitrogen ratios of northern soils. Our results demonstrate that the information contained in DRIFT spectra of soil integrates the quantity and chemical composition of soil organic matter with soil properties and highlights the potential for using this information to assess the degradation state of organic matter stored in northern cold-region soils.

1. Introduction

Soils in arctic and subarctic regions contain large amounts of organic matter that accumulated over millennia, largely due to environmental factors limiting microbial activity (Hugelius et al., 2014; Tarnocai et al., 2009). Now, climatic change is causing region-wide warming, permafrost degradation, hydrologic changes, and other related disturbances with potential implications for the persistence of the organic matter stored in the region's soils (Brown et al., 2015; Jorgenson et al., 2010; Romanovsky et al., 2010; Rowland et al., 2010; Schuur et al., 2015). Thus, improved understanding of the relationships between environmental factors and regional soil organic matter (SOM)

stocks and their potential decomposability is of great importance for predicting SOM responses to changing climatic conditions (Mishra et al., 2013).

The combined effects of soil forming factors (climate, parent material, organisms, topography and time) determine soil development and the characteristics that impact SOM stocks and their vulnerability to environmental changes. Climate, especially low temperatures, is one of the most influential factors affecting the formation of northern soils (Johnson et al., 2011; Ping et al., 2015). In the case of Gelisols (soils underlain by permafrost), soil formation is greatly shaped by unique cryopedogenic processes driven by the combination of low temperatures, water movement, and freeze-thaw cycles (Ping et al., 2015). For

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example, fresh organic materials can be buried and mixed with mineral soil at depth through the process of cryoturbation produced by frost heave, cracking, and churning (Bockheim, 2007; Kaiser et al., 2007; Michaelson et al., 2008; Ping et al., 2008a,b; Tarnocai and Smith, 1992). Low temperatures, sometimes coupled with saturated and reducing conditions and/or acidic microenvironments, can also lead to greater storage of relatively fresh SOM than is found in more temperate regions because the SOM is preserved by slowed decomposition rates (Diochon et al., 2013; Mueller et al., 2015; Pedersen et al., 2011; Xu et al., 2009a). Parent material and weathering processes determine soil mineralogy and other properties affecting the composition and stability of SOM (Mitchell and Soga, 2005). Soils in the northern cold-region mostly formed on sediments deposited by water (alluvium), wind (loess) and glaciers (outwash, moraine or drift), residuum (in-situ weathering of bedrock) and volcanic deposits (tephra). As a result, soils with distinct chemical characteristics related to differing parent materials have developed over time (Ping et al., 1998, 2017). Arctic and subarctic soils support a wide variety of vegetative communities including coniferous and deciduous forest, dwarf and low shrubs, and a variety of tundra types and wetlands (Chapin et al., 2006; Walker et al., 2005). Vegetation type affects the chemical composition of litter inputs and SOM. For example, marked differences in species composition exist between acidic and non-acidic tundra (Walker et al., 2005), which are related to differences in the quantity and chemical composition – functional groups and molecules – of SOM under those vegetation types (Xu et al., 2009a,b). Topography, slope position, and aspect play a significant role in northern soil formation via localized influences on soil hydrology, temperature, and related controls on vegetative community composition (Chapin et al., 2006; Ping et al., 2015).

A number of studies have investigated the relationships of edaphic and environmental factors to the storage and distribution of organic carbon in northern cold-region soils (e.g., Hugelius and Kuhry, 2009; Johnson et al., 2011; Mishra and Riley, 2012; Ping et al., 2008b). Yet, detailed information is lacking on how such factors influence the chemical composition of SOM, which is needed to improve predictions of cold-region SOM responses to environmental perturbations (Hugelius et al., 2012; Kuhry et al., 2013; Purton et al., 2015; White et al., 2004). For example, upon finding only small differences in the chemical composition of SOM across a latitudinal climosequence spanning the boreal forest-prairie ecotone in west-central Saskatchewan, Canada, Purton et al. (2015) concluded that within profile processes appeared to have greater effects on SOM composition than processes operating at landscape and regional scales. However, this climosequence was relatively limited (46 km) in extent. In many instances local-scale patterns can have regional-scale impacts. For example, similarities in chemical composition between SOM in the upper permafrost and active-layer organic horizons confirm that relatively fresh organic materials can be incorporated and preserved in the upper permafrost via cryoturbation. This within-profile process has potential implications for the heterogeneity of SOM composition across the permafrost region (Ernakovich et al., 2015; Ping et al., 2015; Xu et al., 2009a). Further, Baldock et al. (1992, 1997) found that both large scale (soil order – the highest classification category of soil taxonomy) and fine scale (soil particle size) factors were strongly related to the chemical composition, degree of decomposition, and bioavailability of SOM.

Indeed, the chemical composition of SOM has been used to assess and compare its relative degradation state and potential decomposability in both organic and mineral soils. Generally, the proportions of carbohydrates decrease and aliphatics increase as peat decays, while the trends observed in other moieties, such as aromatics, can vary depending on vegetative composition and other factors (Hodgkins et al., 2014; Preston et al., 1987; Sjögersten et al., 2016). Similar increases in the proportion of aliphatic carbon on mineral particle surfaces have been associated with greater SOM degradation in mineral soils (Baldock et al., 1992; Feng et al., 2016). The chemical composition of SOM in northern soils shows evidence that microbial processing is occurring,

even under anaerobic and cold conditions. Microbial products such as organic acids and carboxylates (Pérez et al., 2002) have been found in both active layer and permafrost horizons (e.g. Ernakovich et al., 2015). Thus, characterization of SOM composition, including the relative depletion or accumulation of certain organic compounds, may help to discern key factors affecting the size and degradation state of SOM stocks at landscape and regional scales and their susceptibility to climatic change and related disturbances (Feng and Simpson, 2011).

Previous studies of soils across Alaska and Canada have provided a wealth of information from different bioclimatic zones that vary in permafrost presence (continuous or discontinuous), land cover type, SOM content, and many other soil physical and chemical characteristics (e.g., Michaelson et al., 2013; Ping et al., 1997, 2008a). The archived samples associated with these studies provided the opportunity to investigate which site and soil characteristics are most strongly related to variations in the chemical composition of SOM for a wide range of northern cold-region soils. In this study, we obtained DRIFT spectra for a large number of soil samples – collected from pedons along a latitudinal transect across Alaska and Canada – that are well characterized in terms of site attributes and soil physical and chemical properties. Our objectives were to assess the suitability of DRIFT spectroscopy to distinguish properties specific to northern cold-region soils, and identify whether characteristic spectral bands can be used to resolve the extent of SOM decomposition in these soils.

2. Materials and methods

2.1. Site locations and site/soil characteristics

Study soils were collected from 27 sites across Alaska, U.S.A. and one site on Ellef Ringness Island, Nunavut, Canada. The sites are distributed along a latitudinal gradient from 55.3525°N to 78.7858°N with longitudes that varied from 103.5519°W to 151.7339°W and extending across 2800 km (Table 1). The sites were sampled from 1981 through 2008 for various projects, and all soil samples were processed and archived at the University of Alaska Fairbanks. The soil profiles were described and samples were taken by horizon from the exposed profiles of soil pits according to Soil Survey Division Staff (1975) and Soil Survey Staff (1999). The nomenclature of soil horizons were updated according to Schoeneberger et al. (2012) and Ping et al. (2013). A subset of 119 samples were selected from this archive to provide a wide range of site and soil characteristics for this study.

Seven categorical factors describing site/soil physical attributes (land cover, parent material, soil drainage class, horizon, horizon depth, permafrost presence/absence, and cryoturbation presence/absence) were determined in the field for each sample (Table 1). Across the sites, forests (53%) and tundra (36%) were the dominant land cover types, while grasslands and shrublands were less abundant. The sites differed greatly in parent material, which included alluvium, colluvium, glacial drift, glaciomarine sediments, glacial outwash, lacustrine deposits, loess, glacial moraine and tephra. Colluvium, glacial moraine, and tephra were exclusively found at forest sites, while glacial drift was only present at tundra sites. The other parent materials were associated with various land cover types. Poorly drained soils occurred at 44% of the forest sites, but the majority of tundra sites, 90%, were poorly drained. Of the sampled soils included in the dataset, 27% were designated as organic horizons and 73% as mineral horizons. About 17% of the soils were collected from permafrost and 13% were cryoturbated, the majority of which were from tundra sites (Table 1).

Samples were also analyzed for 16 quantitative factors characterizing soil chemical/physical properties (Table 2). Bulk density (BD) measurements were obtained by methods appropriate to specific horizon types including the clod method (Soil Survey Staff, 2014) and measured dimensional block and core volume methods (Ping et al., 2013), adjusting for coarse fragments. Prior to other analyses, samples were air-dried at room temperature and passed through a 2-mm sieve to

Table 1

Location, land cover, parent material, soil drainage classification, and analyzed soil horizons for each site of the latitudinal transect.

Site	Lat. °N long. °W	Land cover ^a	Parent material	Soil drainage	Soil horizons ^b
Ketchikan	55.3525 131.6673	EVF	Colluvium	Poor	Oe, Bw, C1
Sukoi	57.0000 135.0000	EVF	Tephra	Poor	Oi, Bh, Bsm
Kachemak	59.7167 151.5167	GRASS	Tephra	Well	Oe, C, 2C1, 2C2
Mutnala	59.7921 151.7339	EVF	Tephra	Well	Bhsb1, Bhsb2, Eb, Bsb
Kashwitna	61.4167 150.0833	EVF	Loess	Well	Oe, E/A, Bs1, BC
Knik	61.6172 149.3681	DF	Loess/Moraine	Well	AE, Bw, 2BC, 2C2
Copper River/Kenny Lake	61.7000 144.7333	MF	Loess	Well	Oi, Bw1, AB, Bw2, C
Bartlett Hills	62.2500 150.0333	MF	Tephra	Well	A, Bhs, Bs3
Northway Junction	63.0604 141.8302	EVF	Tephra	Well	A, Bw1, Bw2
Cantwell	63.3668 149.0035	ST	Loess	Poor	E, Bhs, BC
Quartz Lake Rd.	64.1919 145.8686	EVF	Loess	Poor	A2, Afjj, Cf
Shoefly-Bonanza Creek	64.7698 148.2648	EVF	Loess	Well	A, Bw1, Bw2
Gilmore	65.0943 147.8511	MF	Loess	Well	Oi, A, Bw1
Goldstream	65.1517 147.4872	EVF	Alluvium	Very poor	Oe, Oa, Bgjff, Cf
Coldfoot Forest	67.2003 150.2703	EVF	Moraine	Poor	Oi/Oe, Oa, Ajj, Bg/Wfm, Cf
Coldfoot	67.2122 150.2589	SHRUB	Lacustrine	Well	O, A, Bw, Oajj, C2
Marion Creek	67.3232 150.1480	MF	Alluvium	Well	Oi, Oa, Bw, BC
Nolan	67.4317 150.1281	DF	Glacial outwash	Well	Oi, A, Bwb, 2BC, 2C1
Galbraith Lake	68.4817 149.4669	MNT	Lacustrine	Poor	Oe/Oa, AC, Bg2, Cf4
Toolik Lake 1	68.6342 149.6450	MNT	Glacial drift	Poor	Oi/Oe, A2, Cf/Wf
Toolik Lake 2	68.6461 149.5903	MAT	Glacial drift	Poor	Oajj, Bw2, Bg1, Bgf/Oaf, Oab, Oa/Cjjf
Happy Valley	69.1468 148.8485	MAT	Loess	Poor	Oi, Oe, Bg1, Bg3, Oeij, Oe/Cjjf, Cf
Sagwon 1	69.4168 148.6835	MAT	Loess	Poor	Oi/Oe, Oaf1, Cf1, Cf2
Sagwon 2	69.4336 148.6698	MNT	Loess	Poor	Ajj1, Ajj4, Bw5, Cf1/Oajj, Cf2
Franklin Bluffs	69.6746 148.7213	MNT	Alluvium	Poor	Abjj, Bg2jj, Bg3jj, Oabjj, Cf1
Howe Island	70.3164 147.9941	DNT	Alluvium	Mod. well	Oajj, Bwf, Cf
West Dock	70.3764 148.5525	WNT	Alluvium	Very poor	Oa, Bg/Oajj, Oe, Oef, Oe/2Cf1jj, 2Cf1/Oeij, Cf2
Isachsen	78.7858 103.5519	ML	Glaciomarine	Poor	Bw1, A1, A2, A3, Cf

^a EVF, evergreen forest; GRASS, grassland; DF, deciduous forest; MF, mixed forest; ST, sedge tundra; SHRUB, shrubland; MNT, moist non-acidic tundra; MAT, moist acidic tundra; DNT, dry non-acidic tundra; WNT, wet non-acidic tundra; ML, moss/lichen.

remove roots and coarse fragments. Aliquots of each sieved soil sample were homogenized and ground to a fine powder in a stainless-steel high energy shaker ball mill (Spex SamplePrep 8000D Mixer/Mill) for 2 min., oven dried overnight at 65 °C, and analyzed for total carbon (TC) and nitrogen (TN) concentrations by dry combustion at 900 °C with an elemental analyzer (vario MAX cube; Elementar Americas, Inc., Mt. Laurel, New Jersey). Total organic carbon (TOC) concentration was determined with the same analyzer at 650 °C (Provin, 2014). Inorganic carbon (IC) concentration was determined by difference (TC – TOC). Subsamples of air-dried and sieved soil were dried at 105 °C, and all other chemical/physical analyses were expressed on an oven-dry basis

(Soil Survey Staff, 2014). Soil pH was determined by hydrogen ion electrode in a 1:1 soil-to-deionized water suspension. Cation exchange capacity (CEC) and exchangeable cations (Ca, Mg, K, and Na) were determined by extraction with 1 M ammonium acetate at pH 7.0 followed by steam distillation-titration of ammonium (CEC) and atomic absorption or inductively coupled plasma spectrometry (cations). Percent base saturation (BS) was calculated as the sum of exchangeable cations divided by the CEC multiplied by 100, with the value set to 100 when carbonates were present in the soil. Particle-size distribution (percent sand-, silt-, and clay-sized particles) was determined by the hydrometer method.

Table 2

Number (n) of available data points, mean, standard deviation and range for all quantitative factors used in the PCA correlation analysis, and in the CCA.

Variable	n	Mean	Std. Dev.	Range
TOC %	119	10.60	13.57	0.19–49.79
TC %	119	10.97	13.43	0.24–49.88
TN %	119	0.47	0.55	0.02–2.22
TOC:TN ratio	119	20.13	10.71	5.4–73.38
IC %	119	0.43	0.84	0–3.70
Bulk density g/cm ³	96	0.86	0.49	0.04–1.92
pH	109	6.02	1.39	3.22–8.10
CEC cmol/Kg	108	35.29	31.64	0.81–144.39
Ca cmol/Kg	103	18.68	26.52	0.03–158.50
Mg cmol/Kg	103	8.16	16.06	0.03–93.19
K cmol/Kg	103	1.15	2.91	0–22.45
Na cmol/Kg	102	0.28	0.57	0–3.70
Base saturation %	108	64	35.36	2–100
Sand %	74	34.18	19.90	6.0–96.9
Silt %	74	50.46	19.85	2.4–86.8
Clay %	74	15.42	14.67	0.7–57.2

2.2. Mid-infrared spectroscopy

DRIFT spectra were generated with a Spectrum 100 Series Fourier transform spectrometer (PerkinElmer, Waltham, Massachusetts) equipped with a potassium bromide (KBr) beam splitter, a deuterated triglycine sulphate detector, and an AutoDiff automated diffuse-reflectance accessory (PIKE Technologies, Madison, Wisconsin). Soil subsamples previously ground to a fine powder for elemental analysis using the stainless-steel high energy shaker ball mill were dried overnight at 65 °C and further homogenized and mixed by hand with an agate mortar and pestle before analysis. Twenty replicate aliquots of each soil were carefully loaded into AutoDiff sample cups and leveled with a spatula. Spectra were acquired for each aliquot at 4 cm⁻¹ resolution from 4000 to 625 cm⁻¹ with 16 co-added scans per spectrum. Potassium bromide was used to correct for background signal intensity. Spectra were obtained in reflectance units and converted to pseudo-absorbance (log [1/Reflectance]) by using PerkinElmer Spectrum 10 software. An average spectrum for each soil was calculated from the 20 replicates by removing any outliers and averaging the remaining spectra. Spectra that deviated by 1 SD or more from the mean value at two selected wavenumbers (wn) were considered to be outliers. The selected wn for outlier analysis were those that exhibited the greatest variation in absorbance for each soil (commonly around 3380 and 1380 cm⁻¹). To evaluate the intensity of decomposition among organic horizons, we calculated the ratios of aromatic to aliphatic bands as proxies for the decomposition state of organic matter (R1 = 1648:2934, R2 = 1648:2853, R3 = 1648:1431). We also calculated band ratios comparing aromatic or aliphatic moieties to O-containing groups (R4 = 1648:1724 and R5 = 2934:1724), which have been used as measures of resistance to decomposition. We optimized the specific bands used to calculate these ratios for our soils by selecting the loadings peaks identified through Principal Component Analysis (PCA) of samples from organic horizons that were closest to putative band assignments in the existing literature as shown in Table 3 (see Section 2.3 Statistical analyses, for further description of the PCA). The absorbance intensity at selected bands was used for all band ratio calculations.

Spectral signals from water were observed at 3600–3000 cm⁻¹ in all soils because samples were dried at 65 °C to minimize thermal degradation of labile organic constituents and related impacts on TOC concentrations (Duboc et al., 2016; Stumpe et al., 2011). Heating the soil above 100 °C has been shown to increase the solubility of SOM, as well as favor nitrogen mineralization (Enwezor, 1967). To assess the effects of water, we compared the spectra of soils with varying composition after drying at 65 °C and 105 °C. On average, we observed a

17% increase in area under this wn range for soils dried at 65 °C compared to those dried at 105 °C. In addition, mineral soils showed a 25% reduction in the area under the 1220–625 cm⁻¹ range (data not shown). Although we acknowledge the influence of water in the spectra, we present results based on the spectra of soils dried at 65 °C because (1) all samples were treated the same and (2) spectral bands in these ranges did not affect the interpretation of results.

2.3. Statistical analyses

To determine which site/soil factors best explained variations in the spectral dataset, we performed a PCA of all spectra (n = 119) using GRAMS IQ 9.2 software (Thermo Fisher Scientific, Inc., Waltham, Massachusetts). The averaged spectra for each soil were baseline corrected and mean centered prior to executing the PCA, which included entire spectra. Pearson correlations of all site and soil factors with the first three principal components (PC1, PC2, PC3) were then determined by using PC-ORD 6.2 (MjM Software Design, Gleneden Beach, Oregon).

Because clear differences between soils from organic and mineral horizons were seen in the PCA of the entire dataset, we then performed separate PCA and correlation analyses for soils from organic (Oi, Oe and Oa) horizons (n = 32) and mineral (A, B, E and C) horizons (n = 87). Cryoturbated horizons were assigned to organic or mineral groups according to the dominant horizon type (i.e., the horizon designation that appears first – for example, Bgf/Oaf was placed in the mineral horizon group). Pearson correlations were calculated as above.

We used the PCA loadings on each of the first three principal components to determine those spectral bands that best explained the distribution of component scores in each of the datasets (all soils, organic horizons, and mineral horizons). In all cases, the first three components explained > 90% of the variation in the dataset. Component loadings were plotted across the scanned wn to identify the bands associated with loading peaks. We selected only those peaks that were greater than ± 0.3, as these loadings were considered to have an acceptably high correlation with the principal components. Putative characterizations of soil organic and mineral constituents were assigned to the wn of selected peaks on the basis of existing literature (Table 3). For the organic samples, we conducted one-way Analysis of Variance (ANOVA) to determine differences in characteristic band absorbance and band ratios among different organic horizons.

Canonical Correlation Analysis (CCA) was carried out with CANOCO version 5.01 software (Plant Research International, The Netherlands) to evaluate relationships among quantitative soil factors (Table 2) and selected spectral bands. Only uncorrelated soil chemical/physical properties were included in the CCA. Pearson's correlations among the soil chemical/physical data (Supplemental Table S1) were calculated with the SAS 9.0 software package (SAS Institute, Inc., Cary, North Carolina). When the correlation between soil properties was strongly significant (p < 0.001) only one of the measurements was used as a variable in the CCA. The soil properties selected for CCA were percent clay, exchangeable K, TOC concentration, exchangeable Ca, and IC concentration; all other measured properties were excluded. For example, TN concentration, CEC, BD, TOC:TN ratio and pH were all highly correlated with TOC concentration and, therefore, were omitted from the CCA.

3. Results

In the initial PCA analysis of DRIFT spectra, which included all 119 soils, PC1 explained 77.1% of the variance; PC2 and PC3 explained about 9% and 5% of the variance, respectively. Because many of the site/soil factors were categorical and wide variations in quantitative soil factors occurred among the different horizon types, we did not use a PCA biplot to illustrate relationships between site/soil properties and component scores. Rather, we present significant relationships by plotting the mean and standard error of the principal component scores

Table 3

DRIFT absorption bands identified from principal component peak loadings greater than ± 0.3 in PCAs of organic, mineral, and all soil horizons, putative band characterizations, and assignment references.

Organic horizons	Mineral horizons	All horizons	Characterization	(wn), citation
<i>wn (cm⁻¹)</i>				
1092	1046	1046, 1095	Polysaccharides, Phenol Ester, C-O-C, C-OH stretch	(1030–1090), Grube et al., 2006
1170	1135, 1174	1112, 1128, 1169–70	Aliphatics, O–H, C-OH stretch	(1150–1190), Veum et al., 2014
1222	1224	1223	C-O stretch, OH deformation and clay minerals	(1230), Calderón et al., 2011
	1339		COO– and aliphatic CH	(1320–1350), Veum et al., 2014
1378	1362	1382	Phenolic (lignin) and aliphatic structures. C–O stretch, OH deformation	(1371), Parker, 1971
1431	1417	1424	Humic acids (carboxylate/carboxylic structures)	(1426), Parker, 1971
1461	1455, 1468	1455	Phenolic (lignin) and aliphatic C–H bend	(1450), Parker, 1971
1513		1519	Lignin/phenol, aromatic C=C stretch	(1513–1515), Cocozza et al., 2003
1551	1559	1554, 1559	Amide II, proteinaceous origin	(1550), Ibarra et al., 1996; Zaccheo et al., 2002; Parikh et al., 2014
1564	1574		Silicate inversions	(1570), Parikh et al., 2014
1648	1645		Amides C=O, aromatic C=C, or carboxylates	(1640), Calderón et al., 2011
1665–7	1651–9	1660	Amide I, proteinaceous origin	(1653), Ibarra et al., 1996; Zaccheo et al., 2002
	1696, 1705		Carbonyl content of amide	(1700–1740), Veum et al., 2014
	1716	1724	Carboxylic acids C=O stretch, aromatic esters	(1720), Niemeyer et al., 1992
1736			Carbonyl C=O stretch	(1700–1740), Veum et al., 2014
	1807, 1924	1830, 1869, 1927	Silicates	(1790–2000), Calderón et al., 2011
	2515		Carbonates	(2520), Parikh et al., 2014
2853, 2934	2855, 2932	2852, 2922	Aliphatics C–H	(2850, 2923), Niemeyer et al., 1992
	3081		Aromatic C–H	Parikh et al., 2014
3467	3466	3451	O–H, N–H stretch	(3435, 3460), Veum et al., 2014; Calderón et al., 2011
3623	3682	3655, 3673, 3697	Smectite, kaolinite clays	(3620), Nguyen et al., 1991

for defined groups (Fig. 1). For the categorical factors, these groups were defined by the categories (e.g., the 5 soil horizon types or presence/absence of permafrost). Quantitative factors were grouped by

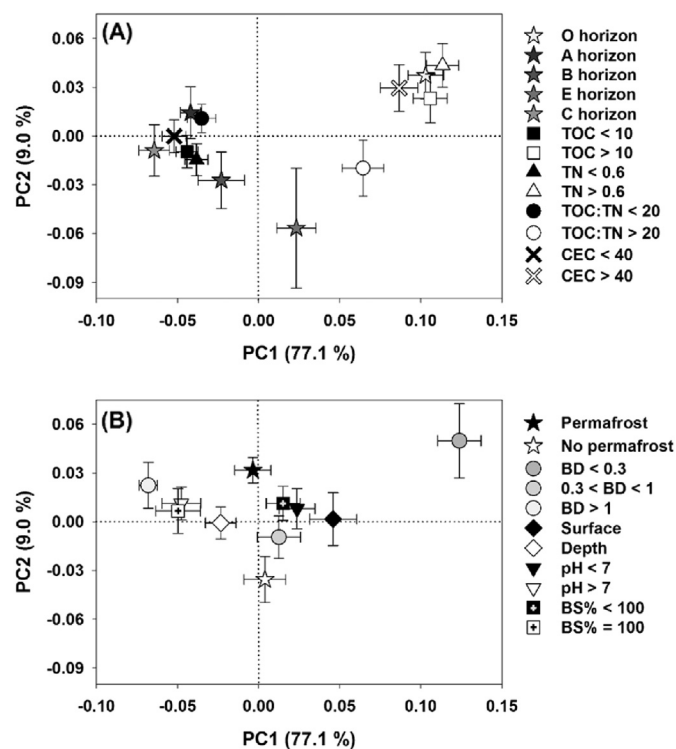


Fig. 1. PCA of DRIFT spectra including all soil samples. Significant relationships between site/soil properties and component scores, shown as the mean (points) and standard error (error bars) of DRIFT spectra PC1 and PC2 scores, include: soil horizon, TOC and TN concentrations (TC overlaps with TOC and is not shown), TOC:TN ratios, and cation exchange capacity (CEC) (A) and permafrost (PF) presence/absence, bulk density (BD), soil surface versus depth, pH and percent base saturation (BS) (B). The percentage of spectral variation accounted for by each PC is shown in parenthesis.

determining a threshold value that best separated positive component scores from negative scores for each significantly correlated soil property. For example, the variation in PC1 component scores strongly separated soils into high and low TOC groups at a threshold value of 10% (Fig. 1A). Bulk density was the only soil property that naturally separated into three groups instead of two (Fig. 1B). This was due to clear separation of samples with high SOM content ($BD < 0.3$; $n = 15$), which had only positive scores, from samples with high mineral content ($BD > 1$; $n = 39$), which had only negative scores, and a third group of samples with positive and negative scores as a result of variable organic matter content within the mineral matrix ($0.3 < BD < 1$; $n = 42$).

PC1 was strongly correlated ($P < 0.0001$) with SOM content – distinctly separating soils with high from those with low TOC ($r = 0.80$), TC ($r = 0.79$), and TN ($r = 0.78$), concentrations, TOC:TN ratios ($r = 0.53$), and CEC ($r = 0.70$) (Fig. 1A). Together, TOC, TC and TN concentrations explained about 60% of the variation in PC1. Soil horizon was also highly correlated ($r = 0.58$) with PC1, separating organic from mineral horizons and explaining about 33% of the variation in PC1 (Fig. 1A). Bulk density ($r = -0.51$), pH ($r = -0.44$), horizon depth ($r = -0.36$) and percent BS ($r = -0.34$) were negatively correlated ($P < 0.001$) with PC1 (Fig. 1B). PC2 was only correlated ($P < 0.001$) with permafrost presence/absence ($r = 0.37$) (Fig. 1B).

Given the strong influences of SOM and horizon type on the PCA results, we confirmed that organic horizons had significantly greater TOC, TC and TN concentrations than the mineral horizons (Table 4). Although, C horizon soils generally had the lowest TOC and TC concentrations and TOC:TN ratios, mean values for these parameters did not differ significantly from those of the other mineral horizons (Table 4). Thus, we performed separate PCA analyses for organic and mineral horizon soils. These analyses reduced the variance in DRIFT spectra explained by PC1 to 66.8% for organic horizon soils and 69% for mineral soils. But, the variance explained by the combination of PC2 and PC3 increased to 27% and 22.8%, respectively.

For the organic horizons, PC1 was again strongly correlated ($P < 0.0001$) with TOC ($r = 0.74$), TC ($r = 0.74$), and TN ($r = 0.74$), separating soils with high from those with lower concentrations and

Table 4

Sample size (n), mean, standard deviation (in parenthesis), of TOC, TC, IC, TN concentrations (%) and TOC:TN ratios for organic and mineral horizons.

Horizon	n	TOC	TC	IC	TN	TOC:TN
O	32	27.4 (14.5)	27.5 (14.3)	0.1 (0.7)	1.1 (0.6)	26.3 (13.4)a
		a	a	a	a	
Oi	10	38.4 (9.4)	38.5 (9.2)	0.1 (0.4)	1.1 (0.5)	37.9 (14.6)
Oe	12	28.8 (13.9)	28.8 (13.9)	0.0 (0.3)	1.3 (0.6)	23.2 (11.6)
Oa	10	23.0 (10.6)	23.2 (10.4)	0.2 (0.7)	1.3 (0.5)	18.7 (4.4)
A	19	8.2 (9.5)b	8.5 (9.5)b	0.3 (0.6)	0.4 (0.5)	19.8 (6.4)ab
		a	b	a	b	
E	3	4.2 (2.0)b	4.2 (2.0)b	0.0 (0.1)	0.2 (0.1)	20.5 (4.7)ab
		a	b	a	b	
B	40	3.7 (4.3)b	4.2 (4.7)b	0.5 (1.0)	0.2 (0.2)	18.6 (10.8)ab
		a	b	a	b	
C	25	2.7 (2.6)b	3.3 (2.6)b	0.6 (1.0)	0.2 (0.2)	14.9 (5.0)b
		a	b	a	b	

Values with different letters are significantly different at $P \leq 0.05$ on the basis of Duncan's Multiple Range Test (Oi, Oe, and Oa horizons not included in this analysis).

high/low CEC values ($r = 0.45$, $P < 0.01$) (Fig. 2A). PC2 explained a greater percentage of the variance in DRIFT data than PC3, but it could not be clearly associated with any of the evaluated factors other than TOC ($r = -0.51$) and TC ($r = -0.50$) concentrations and TOC:TN ratios ($r = -0.59$), which were negatively correlated with PC2 ($P < 0.01$). In contrast, PC3 was strongly correlated ($P < 0.0001$) with land cover ($r = -0.69$) – clearly separating tundra from forest and shrubland soils. PC3 also was strongly correlated ($p < 0.0001$) with permafrost presence/absence ($r = -0.73$) (Fig. 2B) and with percent BS ($r = 0.69$), pH ($r = 0.65$), and exchangeable Ca ($r = 0.63$, $P < 0.001$) (Fig. 2C). In addition, PC3 was correlated ($P < 0.01$) with TOC:TN ratio ($r = -0.52$), horizon type ($r = -0.48$), and horizon depth ($r = 0.46$) – with the highly decomposed Oa horizons clearly separating from the lightly decomposed Oi horizons along PC3 (Fig. 2C). Indeed, comparison of the averaged spectra for the three organic horizon types revealed differences in characteristic band absorbance and significant differences in three of the band ratios calculated as proxies for the extent decomposition (Fig. 3A, B, C).

For the mineral horizons, even though SOM contents were much lower than in organic horizons, PC1 clearly separated soils with high from those with low TOC ($r = 0.71$), TC ($r = 0.65$), and TN ($r = 0.51$) concentrations, and TOC:TN ratios ($r = 0.60$) ($P < 0.0001$), (Fig. 4A). PC1 was negatively correlated ($P < 0.0001$) with pH ($r = -0.60$) and percent BS ($r = -0.58$) (Fig. 4B). PC1 was also positively correlated ($P < 0.001$) with CEC ($r = 0.43$), parent material ($r = 0.40$), and bulk density ($r = 0.38$) (Fig. 4A, C and D respectively). Interestingly, PC1 showed tephra to be quite different from the other parent materials. Similar to the PCA results for organic horizons, PC2 was not clearly associated with any of the evaluated factors (data not shown). PC3 was correlated ($P < 0.0001$) with permafrost presence/absence ($r = -0.69$), drainage class ($r = 0.57$), and land cover ($r = 0.53$), clearly separating permafrost tundra sites with poorly drained soils from soils underlying other vegetation types (Fig. 4B, D). PC3 was also positively correlated with exchangeable Ca ($r = 0.53$) and IC concentration ($r = 0.40$) (Fig. 4B, D).

In the PCA including all soils, high PC1 loadings indicated that organic horizon soils had greater absorbances than mineral horizon soils in the broad region around 3451 cm^{-1} and at 2922 , 2852 , 1724 , 1660 , 1554 – 9 , 1519 , 1455 , 1424 , 1382 , 1223 , and 1095 cm^{-1} whereas mineral horizon soils exhibited stronger absorbance at 1869 cm^{-1} (Fig. 5A, Table 3). Loadings for PC2 indicated that organic horizon soils had greater absorbance than mineral horizon soils in the region around 1169 – 1046 cm^{-1} (Figs. 1A, 5A, Table 3), but mineral horizon soils absorbed more at 1927 and 1830 cm^{-1} . Loadings for PC3 (data not shown) showed greater absorbance by mineral horizon soils in the areas

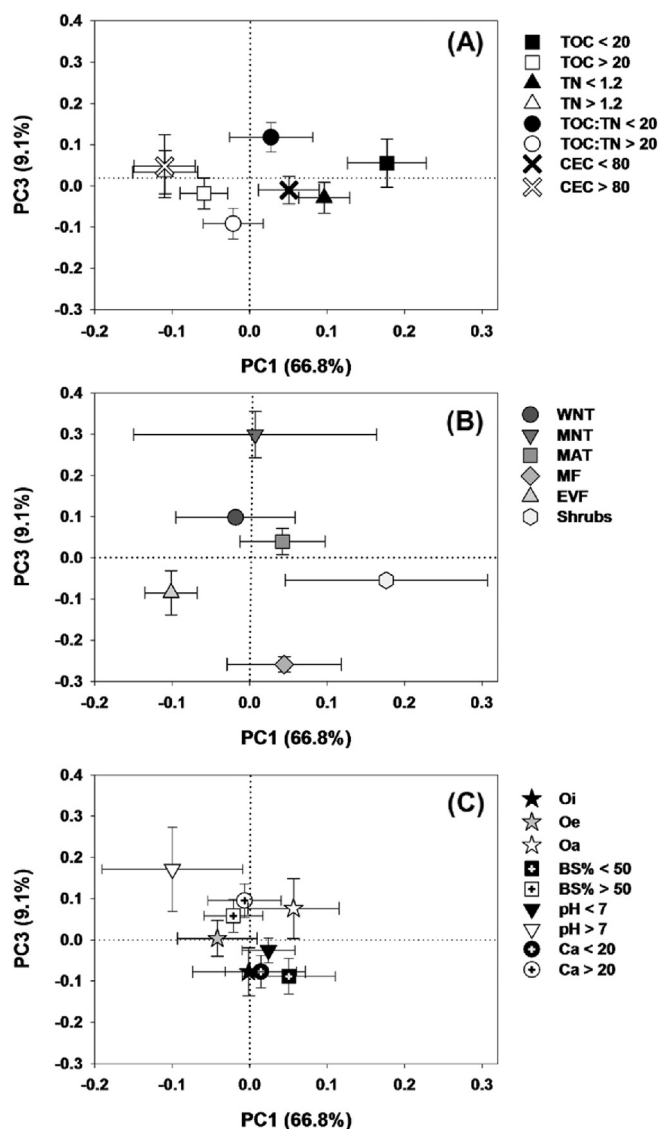


Fig. 2. PCA of DRIFT spectra including only samples from organic horizons. Significant relationships between site/soil properties and component scores, shown as the mean (points) and standard error (error bars) of DRIFT spectra PC1 and PC3 scores, include: TOC:TN ratios, TOC and TN concentrations (TC overlaps with TOC and is not shown) and cation exchange capacity (CEC) (A), land cover type and permafrost (PF) presence/absence (B), and percent base saturation (BS), pH, exchangeable Ca, and organic horizon type (C). The percentage of spectral variation accounted for by each PC is shown in parenthesis.

3697 , 3655 cm^{-1} (Table 3).

When the PCA was limited to organic horizons, highly organic soils with TOC concentrations $> 20\%$ and TN concentration over 1.2% were distinguished by absorbance at 3467 , 2934 , 2853 , 1736 , 1665 , 1648 , 1551 , 1513 , 1461 , 1431 , 1378 , 1222 , 1170 , and 1092 cm^{-1} , which had reverse loadings on PC1 (Figs. 2A, 5B, Table 3). PC3 loadings suggest that organic horizons from high pH soils such as non-acidic tundra were associated with high absorbance at 3623 , 1667 , and 1564 cm^{-1} (Figs. 2B, 5B, Table 3). When PCA included only mineral horizon soils, PC1 loadings suggest that the soil samples with TOC concentrations $> 4\%$ and tephra-derived soil parent material have higher absorbance at around 3682 , 3466 , 3081 , 2932 , 2855 , 2515 , 1924 – 1807 , 1716 , 1705 – 1696 , 1651 , 1645 , 1574 , 1559 , 1468 – 1455 , 1417 , 1362 , 1339 , 1224 , 1174 – 1135 , 1046 cm^{-1} compared to the rest of the parent materials (Figs. 4A and C, 5C, Table 3). PC3 loadings showed that tundra areas clustered with permafrost presence/absence and very poor

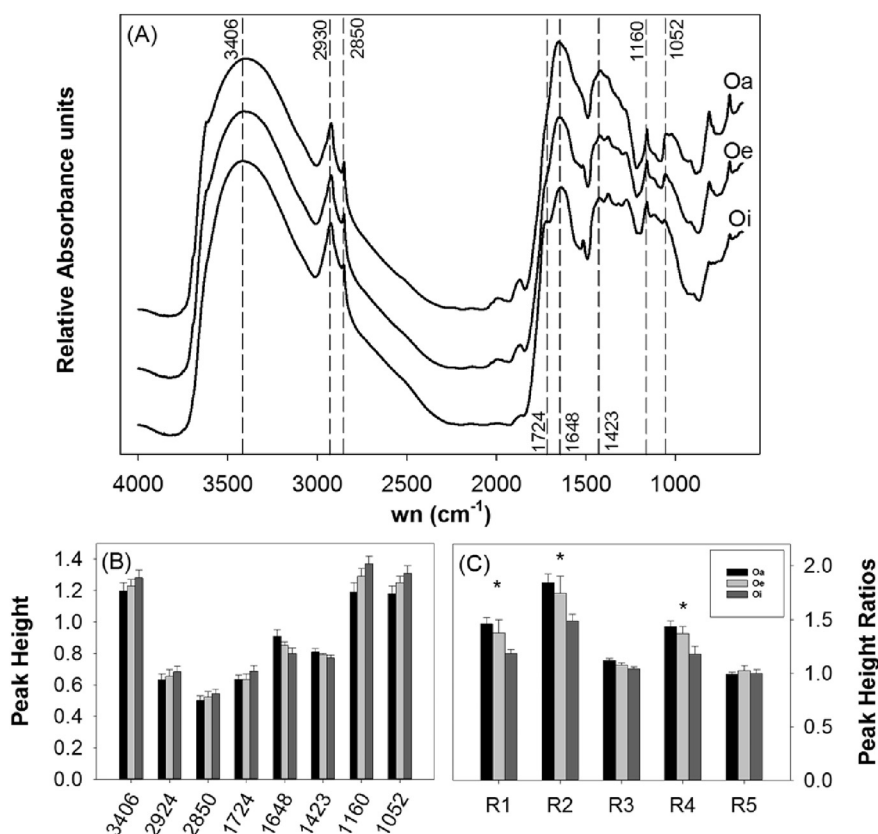


Fig. 3. Averaged DRIFT spectra (A), characteristic band absorbance (B); and band ratios (R1 = 1648:2934; R2 = 1648:2853; R3 = 1648:1431; R4 = 1648:1736 and R5 = 2934:1736) (C) for the three organic horizons (Oi, Oe, Oa). * denotes ANOVA statistically significant differences between Oi and Oa at $P < 0.05$.

drainage soils with higher absorbance at around 1659, 1645, and 1468 cm^{-1} (Figs. 4B and D, 5C, Table 3).

A strong positive correlation between TOC concentration and absorbance at 2922 and 2852 cm^{-1} and a negative correlation with absorbance at 1869 cm^{-1} was shown by the CCA vectors (Fig. 6). IC concentration was uncorrelated with TOC concentration, but correlated positively with exchangeable Ca. IC concentration was negatively correlated with both exchangeable K and clay content. Percent clay increased with absorbance at 3673 and 3697 cm^{-1} . Given the results of the CCA, the relationship between absorbance at 2922 cm^{-1} and TOC concentration was examined by non-linear regression (Fig. 7). A single-point regression using the absorbance at 2922 cm^{-1} had an R^2 of 0.85.

4. Discussion

Overall, our results demonstrate that the information contained in DRIFT spectra of northern cold-region soils integrates the chemical composition of SOM with site environmental characteristics and soil physical/chemical properties. The DRIFT spectra were related to many site/soil attributes including land cover type, parent material, and related factors, such as permafrost presence/absence, drainage class, soil depth, BD, CEC, BS, and pH, in addition to C and N concentrations. Importantly, DRIFT spectra were highly sensitive to the extent of SOM decomposition, particularly for organic horizons, suggesting that absorbance at specific spectral bands or band ratios might be useful for enabling rapid assessments of SOM degradation state. Surprisingly, we found that absorbance intensity at a single spectral band, such as 2922 cm^{-1} , could be used to rapidly estimate soil TOC, TC, and TN concentrations and the TOC:TN ratio of northern cold-region soils.

The spectral properties of cold-region soils were dominated by the absorbance of organic matter, and PCA illustrates the large contribution of TOC concentration in explaining the variation in absorbance patterns among the 119 soils included in the study. Spectral variations indicative of TOC concentration and related soil properties separated horizons

dominated by organic matter from those more strongly characterized by their mineral content. Soils with TOC concentrations > 10% were mostly organic horizons and clustered together in the positive quadrant framed by PC1 and PC2, as did soils with low BD, high TN concentration, and high CEC (Fig. 1A, B). Most mineral soils (A, B and C horizons) clustered together on the negative side of PC1 with soils characterized by low TOC and TN concentrations, low CEC, and high BD (Fig. 1A, B). In contrast, E horizon soils did not cluster with other mineral soils. The E horizon soils ordered between soils from other mineral horizons and soils from organic horizons along PC1, even though the mean TOC concentration of E horizon soils (4.2%) was less than that of A horizon soils (8.2%) and not much greater than B horizon soils (3.7%). The unique features of the highly leached E horizons – including loss of silicate clays, iron, aluminum and/or humus leaving a high concentration of sand and silt particles (Weil and Brady, 2017) – are likely responsible for this separation from all other horizons, especially along PC2. However, specific analyses of soil properties (e.g., iron and aluminum status) that might account for the unique spectral differences associated with E horizon soils were beyond the scope of this study.

Many studies have shown that mid-infrared (MIR) reflectance spectroscopy is a useful method for predicting/estimating physical, chemical, and biological soil properties (e.g., soil water content, texture, C and N concentrations, CEC, exchangeable Ca and Mg, pH, the concentrations of metals/metalloids, microbial biomass and activity) in many different soils (see reviews by Kuang et al., 2012; Soriano-Disla et al., 2014). Predictive multivariate models of soil properties have been constructed from MIR spectra across multiple scales – from single sites to regions – with varying accuracies (e.g., Janik et al., 1998; McBratney et al., 2006; Stenberg and Viscarra-Rossel, 2010; Viscarra Rossel et al., 2006). To estimate soil properties of an unknown sample, predictive models must be calibrated with a sample range that represents the unknown sample's attributes (Ludwig et al., 2016; Soriano-Disla et al., 2014). One strategy for constructing robust predictive models is to implement sample classification criteria that split

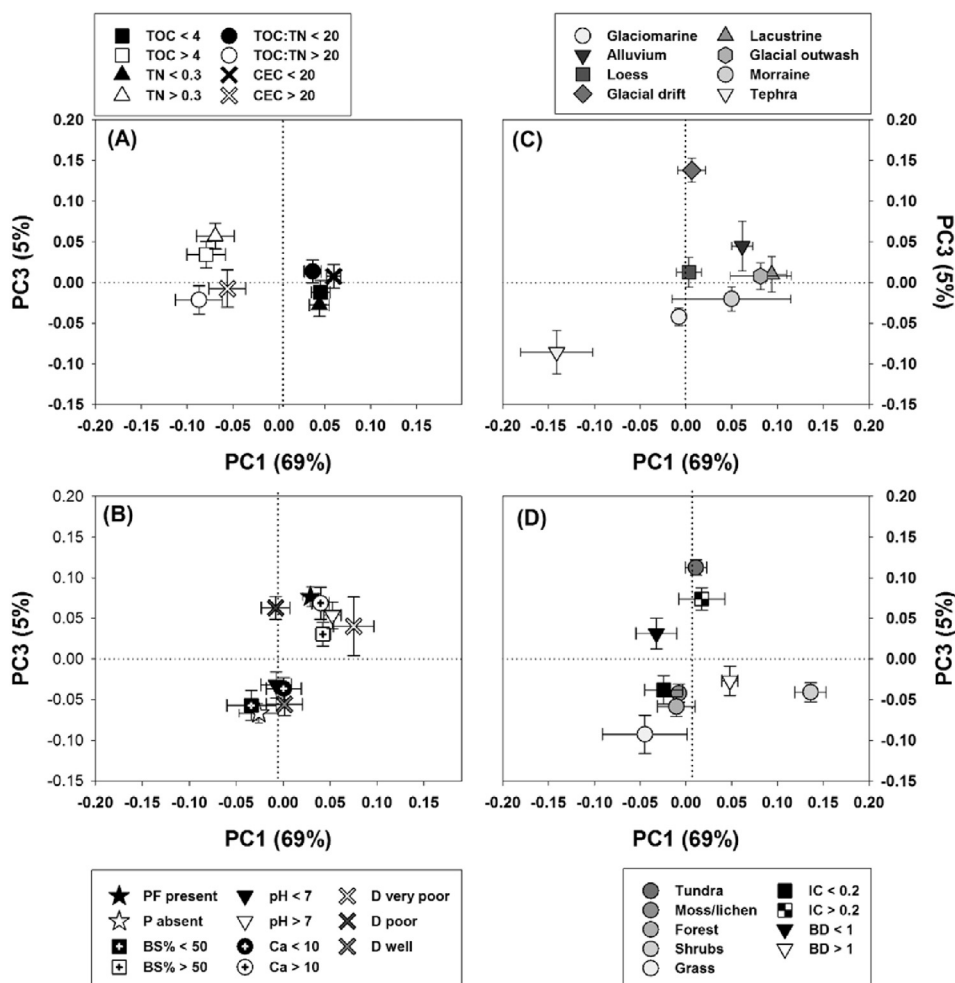


Fig. 4. PCA of DRIFT spectra including only samples from mineral horizons. Significant relationships between site/soil properties and component scores, shown as the mean (points) and standard error (error bars) of DRIFT spectra PC1 and PC3 scores, include: TOC and TN concentrations (TC overlaps with TOC and is not shown), TOC:TN ratios, and cation exchange capacity (CEC) (A), permafrost (PF) presence/absences, percent base saturation (BS), pH, exchangeable Ca, and soil drainage class (B), parent material (C), and land cover type, IC concentration, and bulk density (BD) (D). The percentage of spectral variation accounted for by each PC is shown in parenthesis.

calibration samples into specific categories or groups that are most suitable for estimating the attributes of unknown samples (Soriano-Disla et al., 2014). Our PCA analysis, coupled with the remarkable predictive capability of a single absorbance band (Fig. 7), suggests that development of predictive models encompassing a wide range of northern cold-region soils might be possible for soil properties directly linked to SOM content, such as TOC and TN concentration, TOC:TN ratio, and CEC. However, separate predictive models for organic and mineral horizons are likely to result in more accurate estimates of other soil properties more strongly linked to soil minerals or other site attributes. But, given the unique spectral features observed for E horizon soils, any generalized predictive models developed for the northern cold-region will require detailed exploration to determine their potential applicability to E horizon soils.

Previous work has shown that the light fraction of temperate soils, which is enriched in carbon with a low mean residence time, absorbs markedly at 3400, 2950–2870, and several other spectral bands in the organic fingerprint region between 1750 and 1350 cm^{-1} (Calderón et al., 2011). Similarly, our study soils were dominated by organic matter absorbance at 3451, 2922, 2852, 1724, 1660, 1559–4, 1519, 1455, 1424, 1382, 1223, 1170–1112, and 1095–1046 cm^{-1} (Figs. 2A, 5A, Table 3). Our findings support other research suggesting that cold-region soils often contain significant amounts of relatively fresh, lightly decomposed material compared to more temperate soils, even in some mineral horizons (Diochon et al., 2013; Gentsch et al., 2015; Höfle et al., 2013; Mueller et al., 2015; Paré and Bedard-Haughn, 2013; Pedersen et al., 2011; Xu et al., 2009a).

Absorbance at the observed organic matter dominated bands was also related to differences in soil depth, CEC, percent BS, and pH

(Fig. 1A and B). Because cold-region forest and tundra soils often have thick surface organic horizons with high TOC concentrations (Michaelson et al., 1996; Ping et al., 2002, 2010), the clean separation of surface soils from deeper soil along PC1 is not surprising. In permafrost soils, however, cryoturbated and buried organic horizons can occur well below the surface in varying degradation states compared to surface organic horizons (Gentsch et al., 2015; Ping et al., 2010; Xu et al., 2009a). Thus, Ernakovich et al. (2015) found that absorbance at 3400, 2930, 1740, 1660, 1220–1090 cm^{-1} helped to resolve the organic active layer and cryoturbated upper permafrost from the mineral active layer and deeper permafrost layers with lower organic matter contents at an arctic tundra site. In tundra and boreal forest soils, CEC is controlled more by SOM than mineral surfaces, and SOM stocks and TOC concentrations tend to be greater when soil pH and base saturation are low (Ping et al., 1998, 2005, 2010). Hence, high CEC soils clustered tightly with O horizon soils and those with high TOC concentrations > 10%, while pH and BS ordered cleanly along PC1 with an inverse relationship to TOC concentration (Fig. 1A, B). Indeed, the close association between TOC concentration and CEC was evident even within mineral soils, (Fig. 4A).

Overall, DRIFT spectra were sensitive to soil characteristics related to climate, vegetation, and parent material. The presence of permafrost affected soil spectral properties, and this was reflected by the distinct separation of permafrost soils from those that thaw annually along PC2 (Fig. 1B). Mineral soils from permafrost layers were likely to cluster with soils characterized by high pH, BS, exchangeable Ca, and IC concentrations at sites with very poor or poor drainage, whereas the opposite was true for annually thawed mineral soils (Fig. 4B, D). Because these soil characteristics were related somewhat to vegetation

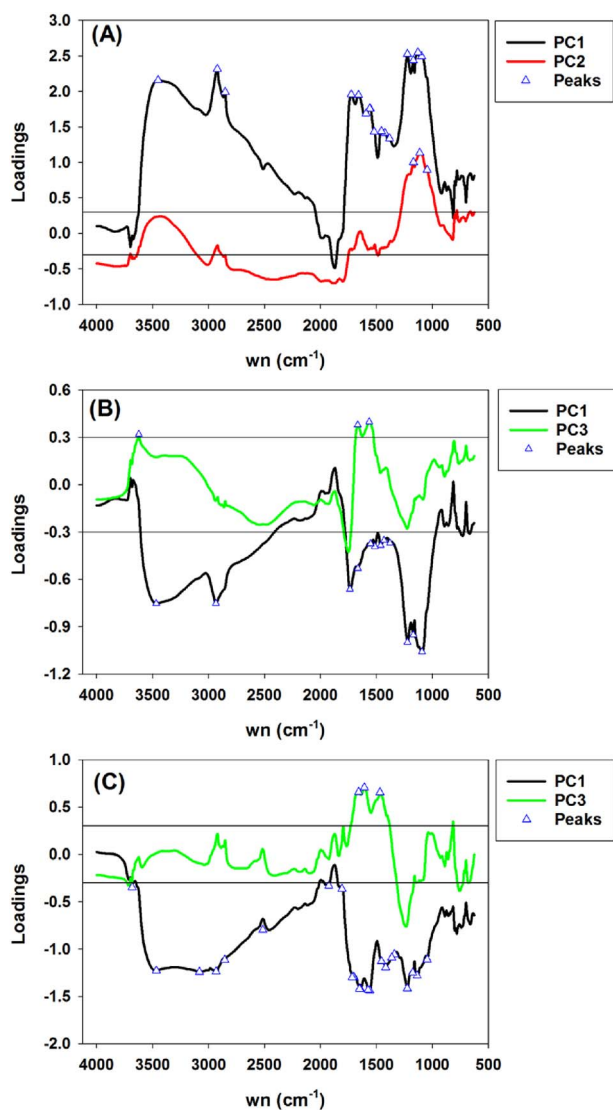


Fig. 5. PC loadings (lines) for each wavenumber (wn) and loading peaks (triangles) from the PCA of all samples (A), organic horizons only (B) and mineral horizons only (C). Horizontal lines denote loading intensities ± 0.3.

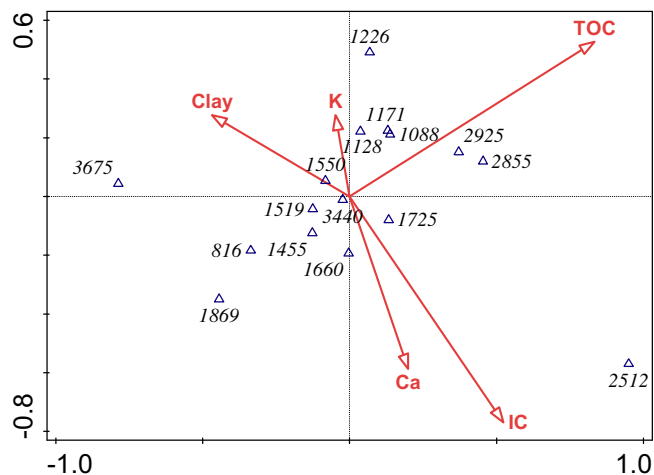


Fig. 6. CCA of selected DRIFT spectral bands for all soil samples versus un-correlated soil physical/chemical factors (see text). Explained fitted variation of axis 1 is 21.1% and 8.9% for axis 2.

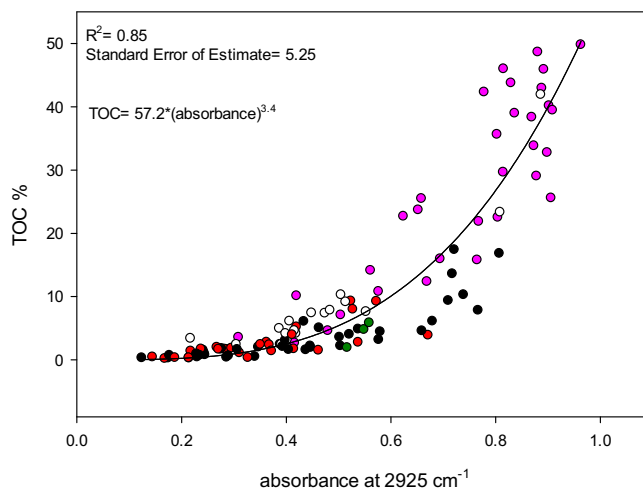


Fig. 7. Relationship of TOC concentration in all soil samples with baseline-corrected absorbance at 2922 cm⁻¹. The best fit line for a power regression is shown. Horizons: O = pink, A = white, B = black, E = green, C = red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

types, mineral soils from most tundra sites clustered with soils from permafrost layers in the positive quadrant framed by PC1 and PC3, and soils from forest sites (some of which were located south of the permafrost zone) scored in the negative quadrant with better drained, more acidic, and annually thawed soils (Fig. 4D). Mineral soils from the shrub-dominated site, however, were distinctly separated from other vegetation types by their spectral properties along PC1, which could be related to its lacustrine parent material (Fig. 4C, D). Although CEC in mineral soils was tightly related to SOM along PC1 (Fig. 4A) as discussed previously, exchangeable Ca and IC concentration were correlated with PC3 (Fig. 4B, D). Ping et al. (2005) noted that carbonate-rich glacial drift, loess, and alluvium, coupled with poor drainage conditions, leads to carbonate accumulation and buffering against the acidification caused by SOM decay in areas of northern Alaska.

Similarly, the separate PCA of soils from organic horizons revealed the capability of DRIFT to distinguish organic soils formed under different vegetation types (Fig. 2B). In addition to separating tundra organic horizons from those of forest and shrubland sites, differences in spectral properties were discernable among acidic and non-acidic tundra types and between evergreen and mixed forest. The large variation within vegetation types and considerable overlap between types along PC1 reflects the range in TOC concentrations for most land covers in the cold region. But, the greater separation of vegetation types by PC3 suggests DRIFT is also sensitive to variations in the chemical composition of SOM related to the effects of site environment and parent material (Fig. 2C) (Baldock et al., 2013; D'Acqui et al., 2010) and to differences in litter quality (Koger-Knabner, 2002) and/or extent of SOM decomposition (Fig. 2A, C) (Haberhauer and Gerzabek, 1999; Calderón et al., 2011).

Indeed, O horizon types (Oi, Oe, and Oa) were ordered along PC3 according to their degradation state, in parallel with the ratio of TOC:TN (Fig. 2A, C). Because the Oi and Oa horizons were cleanly separated by PC3, direct comparison of the DRIFT spectral properties of these horizons might provide useful information on changes in chemical composition resulting from the decomposition process for northern cold-region soils. The Oi horizons are characterized in the field by the presence of slightly decomposed but recognizable plant materials, specifically a rubbed fiber content of ≥ 40% by volume; whereas, the organic materials in Oa horizons are more highly decomposed and characterized by a rubbed fiber content of ≤ 17% (Schoeneberger et al., 2012). A comparison of the averaged spectra for the Oi, Oe, and Oa horizons (Fig. 3A, B) found a non-significant trend of

greater absorbance peaks for Oi compared to Oa horizons at 3467, 2934, 2853, 1736, 1170, and 1092 cm^{-1} . These differences suggest that Oi horizons contain somewhat more relatively undecomposed materials associated with greater absorbance as shown by other studies of O-H/N-H bonds at 3467 cm^{-1} (Calderón et al., 2011), aliphatic bonds at 2934, 2853, and 1170 cm^{-1} (Artz et al., 2008; Niemeyer et al., 1992; Senesi and Loffredo, 2005; Veum et al., 2014), and carbohydrates (C–O) usually associated with peaks in the range of 1092 for organic samples (Grube et al., 2006). In contrast, soils from Oa horizons had higher absorbance for peaks associated with aromatics, C=C bonds, COO– and H bonded C=O at 1652–48 cm^{-1} (Calderón et al., 2011; Ibarra et al., 1996; Zaccheo et al., 2002) and carboxylate and carboxylic structures at 1431 cm^{-1} (Parker, 1971).

Nevertheless, the loading peaks (Fig. 5B) indicate that a much reduced number of spectral bands were key drivers of PC3 variance, showing only significant loadings at 3623, 1667, and 1564 cm^{-1} . Absorbance at 3623 cm^{-1} could be due to the incorporation of silicate clays (Madejová, 2003; Nguyen et al., 1991) into the decomposing organic matter of Oa layers. Also, it has been shown that more decomposed SOM has a tendency to absorb at 1670–1600 cm^{-1} , suggesting the presence of amide groups, possibly from microbial cells, and/or aromatic C=C (Parikh et al., 2014). Ratios of DRIFT spectral bands (R1, R2, and R3) indicating the proportion of aromatic versus aliphatic absorption intensity have been used as a measure of the decomposition state of organic matter for several substrates and for agricultural soils (Chefetz et al., 1998; Inbar et al., 1989; Veum et al., 2014). Ratios R4 and R5 may represent a measure of resistance to decomposition (Chefetz et al., 1998; Ding et al., 2002; Wander and Traina, 1996; Veum et al., 2014). Soils with higher ratios indicate a greater level of decomposition and overall soil maturity. In our study, R1, R2, and R4 were significantly higher, and R3 was higher but only marginally significant ($P = 0.07$), for Oa compared to Oi horizons. These ratios confirm field designations of increasing decomposition for Oi to Oe to Oa horizons. These results provide evidence that the DRIFT spectral signature reflects humification processes (increasing aromaticity and amide presence) across the wide range of land cover types and site attributes encompassed by the latitudinal transect, and indicate the potential utility of DRIFT spectra and band ratios for determining the SOM decomposition state of northern cold-region organic soils.

Not surprisingly, the influence of parent material on DRIFT spectral properties was only apparent for mineral horizons (Fig. 4C). Other studies have shown that soil mineralogy must be taken into account when producing calibration models to predict TOC concentrations across large scales (Baldock et al., 2013) and/or regional scales (D'Acqui et al., 2010). Much of Alaska was affected by glaciation periods during the last 3 million years, although the Late Wisconsin glaciation (about 20,000 years ago) occupied only 48% of the state and large areas of the interior as well as the coastal plains were not glaciated at that time (Ping et al., 2017). Glacial processes produced a variety of parent materials for both modern soils and paleosols across Alaska, including glacial till (fragments of rocks in a matrix of finer material), loess (fine wind-blown deposits), glacial outwash (water transported sands and gravels), lacustrine deposits (glacial lake sediments) and others. In addition, regional events have created other parent materials, such as tephra (volcanic ash deposits) found mostly in the southern areas, or glaciomarine sediments found in some coastal areas. Mineral horizons varied in spectral properties due to the type of parent material, and tephra appeared to be distinctly different from the other parent materials. Component loadings were consistent with soils derived from tephra having higher organic matter compared to other parent materials. Except for glacial drift, the other parent materials appeared to be clustered near zero along both PC1 and PC3. It is likely that the mixing of different parent materials, variations in the extent of weathering, or modification due to surface erosion/sedimentation have occurred over time (Ping et al., 2017). For example, deposition of loess over the primary parent material could result in masking of differences

among them. Because of these processes, parent material classifications may not reflect the mineralogy detected by DRIFT spectra. Thus, we do not recommend field classification of parent material as a separation basis for development of calibration models for northern cold-region soils. The development of calibration models to predict soil C or N concentrations, or other soil properties, and their scale of valid application (local field to regional or even global) is an open research topic (Bellon-Maurel and McBratney, 2011; Reeves, 2010). Whether or not robust prediction models can be calibrated and applied over large spatial areas or more localized models are needed depends on the basis by which soils are selected or included in the models – which might include variations due to factors such as analyte levels, soil type, climate, texture, soil mineralogy or other attributes that might vary across regions (Reeves, 2010). On the other hand, the presence of carbonates (IC concentrations) in some soils throughout the region suggests an important basis by which northern cold-region soils might require segregation for predictive model development (Reeves, 2010).

The canonical correlation analysis (Fig. 6) indicates that the DRIFT data contain specific spectral bands that can be used to gauge the amounts of particular soil properties. The aliphatic CH spectral bands at 2922 and 2852 cm^{-1} correlated positively with TOC, while the silicate band at 1869 cm^{-1} correlates negatively, as expected. The relationship of TOC concentration with 2922 cm^{-1} ($R^2 = 0.85$) is remarkable, although the prediction error becomes larger as TOC concentrations increase. In all likelihood, the strength of this relationship is due to the relatively large proportions of lightly decomposed particulate organic matter that is rich in plant constituents and preserved, even in many mineral horizons, by the cold climate (Diochon et al., 2013; Mueller et al., 2015; Xu et al., 2009a,b). The existence of such a strong relationship is significant because the ability to use a single wavenumber to predict TOC could simplify analyses, and multivariate analyses for calibration development could be circumvented when only one approximate value of TOC concentration is needed. However, partial least squares (PLS) calibrations which utilize the entire spectrum (e.g., Baldock et al., 2013) are bound to improve the R^2 when precise quantification across a wide range of TOC concentration is required. It has to be noted, nonetheless, that spectral bands that correlate with TOC concentration will also correlate with TN concentration, TOC:TN ratio, BD, CEC, and pH by proxy. In addition, the correlation of clay content with the band at 3673 cm^{-1} has been shown for many other soils and is generally associated with hydroxyl stretching of clay minerals (Dixon and Weed, 1989; Nguyen et al., 1991; Janik et al., 1998; and many others). This relationship might become useful in future studies evaluating the role of clay protection on the storage or potential decomposability of organic matter in northern cold-region soils.

5. Conclusions

Results from this latitudinal transect study demonstrate that the information contained in DRIFT spectra of northern cold-region soils integrates the chemical composition of SOM with site environmental conditions and soil properties. DRIFT spectra were directly related to TOC, TC, and TN concentrations, and other factors, including TOC:TN ratios, BD, CEC, pH, exchangeable Ca, and soil drainage class. Differences in vegetation cover, parent material and permafrost presence also influenced soil DRIFT spectra, although to a lesser extent than carbon concentration. The DRIFT spectral properties of tundra soils were distinct from those of soils from forest and shrubland sites. Further, differences in the spectral properties of organic soil horizons were clear among acidic and non-acidic tundra types and between evergreen and mixed forest. For organic soils, evidence of SOM decomposition was found in all horizon types. Ratios of characteristic spectral bands showed increases in aromaticity and the presence of other C functional groups that generally indicate greater decomposition and SOM maturity – suggesting these band ratios might serve as useful proxies for assessing the extent of SOM decomposition in northern cold-

region soils. A significant relationship between the aliphatic band at 2922 cm^{-1} and measured TOC, TC and TN concentrations suggests that this band can be used to rapidly determine these constituents across northern cold-region soils and holds great promise for building a robust region-wide multivariate predictive model for these soils.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.geoderma.2017.05.014>.

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