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Using DOC to better understand local hydrology in a subarctic watershed

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Abstract

The goal of this study was to gain a better understanding of the hydrology of a permafrost affected watershed using analyses of DOC. DOC from water samples collected in the Caribou–Poker Creeks Research Watershed (CPCRW) was analyzed by several techniques, including pyrolysis-gas chromatography/mass spectrometry (py-GC/MS). Results showed that the ratio of aromatics to nitriles served as a useful indicator of groundwater and runoff contribution to streams. In general, as the conductivity of water samples decreased, the DOC concentration and the ratio of aromatics to nitriles increased. Other analyses showed that as the conductivity increased, labile DOC (LDOC) decreased. The LDOC results were consistent with pyrolysis-GC/MS results. The results showed that organic matter in baseflow can have different aromatic to nitrile ratios, depending on the source and pathway to the stream. In a permafrost watershed were flowpaths are complicated by frozen ground, DOC characteristics proved to be a useful indicator of groundwater entering the watershed from outside the topographic boundary.

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1. Introduction

Permafrost is an effective barrier to groundwater infiltration and has a significant control on watershed hydrology (Woo, 1986) and the resulting stream water chemistry (MacLean et al., 1999; Petrone et al., 2006; Yamazaki et al., 2005). Permafrost is ground that has been below 0 °C for more than two consecutive years. Aside from that definition, however, the spatial extent of permafrost varies considerably. In regions with discontinuous permafrost, such as interior Alaska, permafrost is largely restricted to valley bottoms, north-facing slopes, and areas well shaded by trees or insulated by an organic rich surface soil (Bolton et al., 2004). In watersheds with large spatial extents of permafrost, water is largely restricted to soil environments and, as a consequence, stream discharge tends to increase rapidly during storms (Petrone et al., 2007). In contrast, in watersheds with little permafrost, water can infiltrate into deeper groundwater environments resulting in rainfall being stored within the catchment and stream flows that are far less flashy. A number of studies on subarctic watersheds have focused on infiltration and runoff behavior, particularly during snowmelt (Kane and Stein, 1983; Carey and Woo, 2001a, b; Carey and Quinton, 2005).

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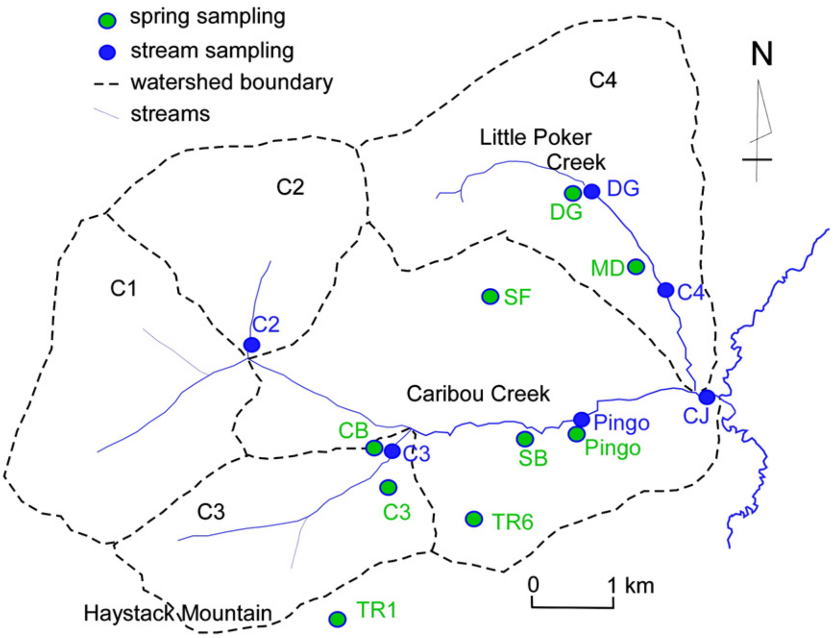

Fig. 1. Map of CPCRW with sampling locations shown.

Streams draining watersheds dominated by permafrost tend to have higher dissolved organic carbon (DOC) concentrations from leaching of soil organic matter but low conductivity due to lower input of weathering derived solutes than watersheds that are mostly permafrost-free (Ray, 1988; MacLean et al., 1999; Carey, 2003). Over the active season, the concentration of DOC decreases in watersheds with lower coverage of permafrost as flow transitions from the organic rich surface layer to deeper mineral layers (Petrone et al., 2006). Petrone et al. (2007) found that in a watershed with high permafrost coverage, the active layer remained a source of DOC throughout the summer. Superimposed on this seasonal pattern, rainfall runoff normally increases the DOC concentration of a stream but dilutes the conductivity. The change in DOC concentration, however, is a function of the active layer thickness and the depth of thaw at the time of the storm (Petrone et al., 2007). Increases in DOC on the rising limb of the hydrograph for a similar watershed have been observed (Carey, 2003). In this research, slopes with permafrost were a greater source of DOC, due to their thicker organic soils, wetter antecedent conditions, and lateral flow in the shallower soil layers than slopes with seasonal frost only. On slopes with seasonal frost, percolation resulted in penetration of DOC into deeper mineral layers (Carey, 2003).

In our research we examined the degree of biological processing of DOC derived from different groundwater sources and streams draining watersheds with varying extents of permafrost. We conducted our research in the Caribou–Poker Creeks Research Watershed (CPCRW), where we sampled a series of streams and springs that flow from both shallow and deep groundwater sources in watersheds with permafrost coverage ranging from 4 to 53%. The goal of this study was to gain a better understanding of the hydrology of permafrost affected watersheds using analyses of DOC.

2. Materials and methods

2.1. Site description

This research was conducted in the CPCRW, located approximately 50 km northeast of Fairbanks, Alaska. The watershed is approximately 10,620 hectares (ha) and consists of year-round emerging springs, forested hills, boggy valley bottoms, and meandering streams with shallow gradients. In CPCRW, temperatures range from −10 to −22 °C in January and +11 to +14 °C in July (Haugen et al., 1982) and annual precipitation is

Table 1
Watershed characteristics (after Petrone, 2005)

Watershed	Area (km^2)	Percent permafrost	Aspect	Winter baseflow as % of annual
C2	5.2	4	S	55
C3	5.7	53	NE	21
C4	10.4	19	SSE	50

about 400 mm. About one-third of all precipitation falls as snow, which covers the ground for an average of 214 days each year. The snow melt period usually begins in mid-April and concludes in late-April to early-May (Bolton et al., 2004).

Approximately 30% of CPCRW is underlain by permafrost, which is found primarily on north-facing slopes and in valley bottoms (Haugen et al., 1982). Vegetation is closely linked with the distribution of permafrost and the slope aspect and altitude. South facing slopes are mainly populated with deciduous forest, including birch (*Betula neoalaskana*) and aspen (*Populus tremuloides*). North-facing slopes are primarily populated with black spruce (*Picea mariana*). Mixed forest occurs on less than 10% of the watershed (Jorgenson et al., 1986).

Our research was focused in three subcatchments of the Caribou Creek Watershed (C2, C3 and C4; Fig. 1). The C2 and C3 subwatersheds have been studied extensively (MacLean et al., 1999; Bolton et al., 2000; Hinzman et al., 2003) since C2 is largely free of permafrost (4% permafrost coverage) and C3 is dominated by permafrost (53% coverage). Little Poker Creek, or C4, offers the opportunity to study a watershed that is a mixture of terrain and medium permafrost coverage (approximately 19%). For this study, a series of springs and streams were sampled. All sampling locations are labeled in Fig. 1. Some details for the watersheds studied are shown in Table 1.

2.2. Sampling

The extent of biological processing of DOC was characterized for spring, stream, and shallow ground water using pyrolysis-GC/MS (Py-GC/MS) and bioassays (Fig. 1). Samples were collected in March, June, and August, 2001 for the py-GC/MS, whereas samples to measure labile DOC (LDOC) were collected across several years. Spring samples were collected using a 60 ml syringe to draw 4 l of water from clear flowing water as near as possible to the surface emergence of the spring. The stream samples were collected as grab samples from below the water surface.

For each sampling event, the Caribou Creek samples (C2, C3 and Pingo Str) were collected on one day and the samples from Little Poker Creek (DG, C4 and CJ) were collected on the next day. This sampling strategy sought to capture the same weather conditions. Both June and August sampling dates occurred during rain events. The winter of 2000 and spring/summer of 2001 were typical years with respect to precipitation and temperature. Nearby in Fairbanks, the period September through December 2000 was slightly drier (5%) and slightly warmer (0.3%) compared to the 72 year record for those months. For the period January through August 2001, Fairbanks was slightly drier (5%) and slightly warmer (6%) than the 72 year record for those months.

For all samples, 4 l of water were collected in 1-liter amber glass bottles. The bottles were then set in a cooler and brought back to the University of Alaska Fairbanks (UAF) laboratories where additional tests were performed. The water samples retrieved from the field were placed in a cooler and refrigerated at 4 °C before being filtered through 0.45 µm glass fiber filters. Filtering occurred within 24 h of sample collection. Conductivity was measured *in-situ* with a hand held conductivity meter, DOC concentration was measured with an Apollo 9000 total organic carbon analyzer and a Shimadzu TOC-5000.

2.3. Pyrolysis-GC/MS

Samples for py-GC/MS were prepared by concentrating the DOC using a rotovap at 40 °C. Concentrated samples were then allowed to air-dry in glass jars. DOC samples were collected from the jars once all water had evaporated. Py-GC/MS was conducted with a CDS Model 2500 pyrolyzer and autosampler in tandem with a gas chromatograph/mass spectrometer (GC/MS). During pyrolysis, the sample was heated from a starting temperature of 25 °C to 700 °C in 0.1 s and held at a constant 700 °C for 9.9 s. The pyrolysis reactor was mounted on an HP 5890 Series II GC, with a Supelco SPB 35 (35% Ph Me silicon) column, 60 m × 0.25 m × 0.25 µm. The GC interface temperature was set at 235 °C. The GC temperature program was 45 °C for 5 min, 2 °C/min to 240 °C and held for 25 min. The GC was plumbed directly to an HP 5971A Series Mass Selective Detector on electron impact mode. The MS scanned mass units 45 to 650. All mass spectra were compared to the NBS54K spectral library. Helium served as a carrier gas at a flow rate of 0.5 cm^3/min. Each sample was injected with a split ratio of 1:50.

Py-GC/MS of DOC produces a complex chromatogram, containing hundreds of peaks that represent individual pyrolysis products. The pyrolysis products may have been organic molecules originally present in the water or they may be thermal breakdown products of large macromolecules. Py-GC/MS has been used to examine litter decomposition and humification of soils (Hempfling and Schulten, 1990; Beyer et al., 2001), to compare organic matter in different soil fractions (White and Beyer, 1999), and to compare various properties of DOC (Bruchet et al., 1990; White et al., 2002; Seelen et al., 2006). For each sample, a total of 12 pyrolysis products were selected from each pyrogram to represent a variety of biopolymers. The twelve pyrolysis products included dimethyl benzene, furfural, methylcyclopentenone, trimethylbenzene, benzaldehyde, benzofuran, benzonitrile, phenylethanone, methylbenzonitrile, naphthalene/azulene, phenol, and 2 methylnaphthalene. The method was used previously in Guo et al. (2004) to describe organic matter in sediments of Russian river deltas. HP Chemstation software was used to quantify the relative abundance of each of the pyrolysis products. The pyrolysis products were compared on a relative abundance basis and were not individually quantified on a per mass of DOC or per water volume basis. For the purposes of this paper, a comparison of the percentage of aromatics to the percentage of nitriles was studied as a ratio. In all cases throughout the paper, the ratio, or relative abundance of the aromatics (i.e., dimethyl and trimethyl benzene) to nitriles (i.e., benzonitrile and methylbenzonitrile), refers to the ratio of the aromatics as a percent of the 12 pyrolysis products to the nitriles as a percent of the 12 pyrolysis products.

2.4. Incubation of water samples to determine labile DOC

Labile dissolved organic carbon (LDOC) was measured as the proportion of DOC that was mineralized over one month long incubations (Servais et al., 1987; Marmonier et al., 1995). Following an initial filtration using 0.45 µm glass fiber filters, water samples were filtered through 0.20 µm membrane filters to remove bacteria, inoculated with a microbial solution prepared by back-flushing filters, incubated for one month in the dark at laboratory temperature, and refiltered (0.2 µm). The filtering and inoculation was done so that a consistent microbial culture was applied to all samples equally. LDOC was quantified as the loss of DOC between initial and final samples.

3. Results and discussion

3.1. Sampling events

The three sampling dates for measurement of py-GC/MS spanned much of the hydrologic variability in CPCRW (Fig. 2). March water samples were presumed to consist only of base flow while the watershed was predominately frozen and under snow cover. June water samples were collected to capture the early summer condition of shallow springs and streams (Fig. 2). The August samples were collected near the end of the summer when soils were near their maximum thaw depth.

3.2. Use of the aromatic to nitrile ratio

Two spring sites were sampled during the June sampling event to test the use of the aromatic to nitrile ratio as a measure of the degree of biological processing. One spring site (TR1) is seasonal, and therefore was assumed to be dominated by interflow with a residence time of less than one year. At the other spring site (TR6), water flows year-round, and therefore was assumed to be fed by a groundwater source with a residence time of more than one year. The conductivity from seasonal spring, TR1, was 47 µS/cm, approximately that of rainwater. The conductivity in TR6, on the other hand, was 130 µS/cm, nearly three times that of the TR1. Since the field evidence, and conductivity values suggest a shorter groundwater residence time for TR1 compared to TR6, the organic matter in these springs was assumed to have undergone different degrees of biological processing. DOC in water from TR1 should have undergone less biologically processing compared to DOC in water from TR6. The aromatic to nitrile ratio was much greater in DOC from TR1 compared to TR6, suggesting that the aromatic to nitrile ratio could serve as a good indicator of biological processing (Fig. 3). A similar method was used in a study by Guo et al. (2004).

3.3. Seasonal change in chemical signature

3.3.1. South facing and valley-bottom sites

The conductivity and DOC values for stream water samples C2, C4, and DG are listed in Table 1. The C2 watershed is south-facing and is the earliest melting subwatershed on Caribou Creek. For C2, the DOC was highest and the conductivity was lowest in June. The DOC values suggest that soils were still thawing in June,

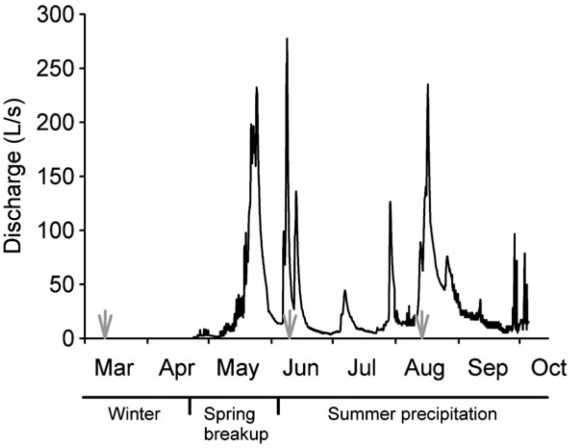

Fig. 2. Sampling periods in accordance to the C3 2001 hydrograph.

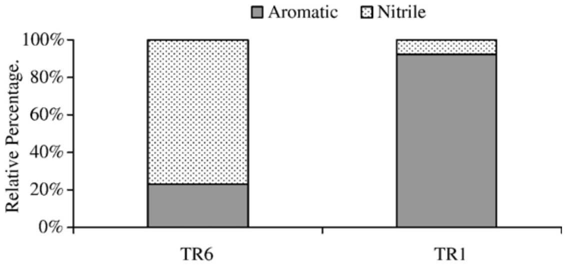

Fig. 3. The relative percentage of aromatics versus nitriles is shown for TR1 and TR6. The high relative abundance of nitriles in TR6 compared to TR1 is an indication that the water emerging from spring TR6 has undergone a greater degree of biological processing.

allowing runoff to leach DOC into the stream after little interaction with the soil. By August, the seasonal frost was gone from the soil, allowing precipitation to percolate to groundwater. As such, the steam conductivity and DOC signatures indicated a mix between the winter baseflow values and the June baseflow/runoff samples. The hydrograph in Fig. 2 shows that both June and August sampling events occurred during high rainfall/ runoff periods in CPCRW.

C4 receives water from north-facing and south-facing subwatersheds and springs. DG and C4 samples were similar in their DOC and conductivity signatures with both showing a progressively increasing DOC concentration over the course of the summer. This result was somewhat different than for C2 where the DOC peak came in June. Since DG and C4 receive water from both north-facing and south-facing water sources, much of the soil was still frozen in June, resulting in lower June DOC concentrations compared to those in August.

In March, baseflow was the only input to stream water in C2, DG, and C4. Sample DOC in March had a much lower aromatic to nitrile ratio than stream water samples taken during the summer (Fig. 4). For all three stream water samples collected during March, the aromatic to nitrile ratio was approximately 0.2. This was the same ratio as was observed for the spring sample TR6. Conductivity values for the March stream samples (C2, DG, and C4) were slightly lower than for TR6, but in the same range.

For sampling site C2, at the outlet of the south-facing watershed, the aromatic to nitrile ratio was highest in June. The very high aromatic to nitrile ratio in the June sample was likely the result of fresh DOC in rainfall runoff that had a low degree of biological processing. The conductivity and DOC data (see Table 2) as well as the occurrence of the sampling event during a period of high runoff (Fig. 2) support this hypothesis.

For samples collected from C4 and DG in June and August, the aromatic to nitrile ratio was greater than 0.6. Since sample sites C4 and DG were both located in the same watershed, seasonal similarity in the aromatic to nitrile ratio was expected. In June, seasonal frost still dominated the watershed areas contributing to C4 and DG. Depending on the antecedent soil moisture condition, runoff was likely exposed to a thin layer of thawed soil before entering the river. The aromatic to nitrile ratio of organic matter in the streams, therefore, was affected by both runoff and baseflow. In August, when the ground was thawed, rain was likely leaching more organic matter into the stream. In general, therefore, it was expected that in DG and C4 samples, the aromatic to nitrile ratio would increase over the course of the sampling period as the DOC became more dominated by surface runoff and interflow. For a subarctic watershed, Quinton et al. (2004) reported very high surface water to groundwater ratios in June (e.g., 0.8) that decreased over the course of the summer to September (0.2). This result suggests that runoff is strongly affected by the presence of surface frost. On the other hand, a number of studies (e.g. Kane and Stein, 1983; Woo, 1986) have shown that in non-

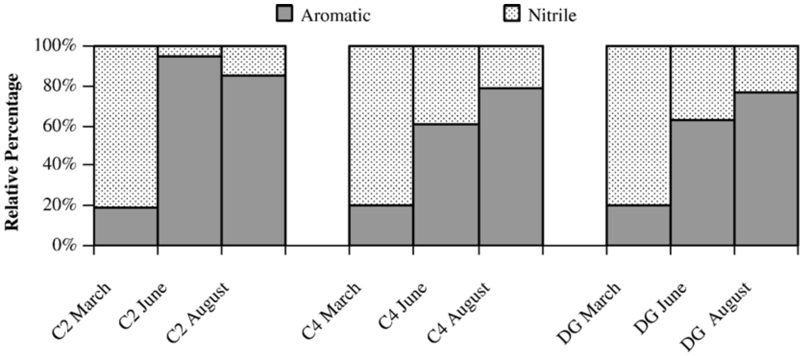

Fig. 4. This figure shows seasonal differences in the relative abundance of nitriles and aromatics in three different streams. The data indicate that in June and August, when stream samples are influenced by surface water, the relative abundance of aromatics is higher than that of nitriles.

Table 2
Conductivity and DOC for Stream water samples

	Conductivity (μS/cm)	DOC mg/L
C2 March (M)	89	1.4
C2 June (J)	55	12
C2 August (A)	73	5.9
C4 M	116	1.8
C4 J	101	4.4
C4 A	92	6.5
DG M	110	4
DG J	118	3.6
DG A	108	6.7
C3 March (M)	117	1.9
C3 June (J)	31	18
C3 August (A)	36	13
Pingo Str M	–	0.9
Pingo Str J	–	3.2
Pingo Str A	–	10.8
CJ M	–	3
CJ J	–	18.3

permafrost areas, surface runoff derived from snow melt is limited (or not observed) due to high infiltration/percolation rates in these soils.

One important difference between the watersheds in Caribou Creek (C2, C3 and Pingo Str) and the Little Poker Creek streams (DG and C4) was seen in the conductivity and DOC data. For C2 and C3, the conductivity decreased dramatically from March to June at the same time that the DOC increased. In DG and C4, the decrease in conductivity and increase in DOC was not nearly so dramatic. We believe this was due to the effect of rainfall during the sampling event. Even though samples were collected on subsequent days, the sampling in C2 and C3 appeared to capture the rainfall runoff, whereas the DG and C4 samples did not. This effect of runoff explains the very high aromatic to nitrile ratio of DOC from C2, compared to that from C4 and DG.

3.3.2. North-facing streams and the Little Poker Creek, Caribou Creek junction

The conductivity and DOC values for stream water samples C3, Pingo Str, and CJ are listed in Table 2. The C3 watershed is north-facing and is formed by a suite of springs. Pingo Str is a sampling site on Caribou Creek downstream from the confluence of the C2 and C3 streams. It is so named because the sample was collected from Caribou Creek just downstream of the discharge from several springs that flow from an open system pingo. The CJ sample was collected just downstream of the confluence of the headwater streams and springs (C2, C3, C4 Pingo Str, DG sampling sites). For C3, the DOC was highest and the conductivity was lowest in June. The June values suggest that soils were starting to thaw in June, allowing runoff to leach DOC into the stream. Conductivity was not measured on the Pingo Str and CJ samples, however, DOC values followed similar patterns as in C3 and the Little Poker Creek samples.

Fig. 5 contains the aromatic to nitrile ratio for samples from C3, Pingo Str, and CJ. While there was an increase in the aromatic to nitrile ratio from March to August, the ratio in the March sampling event for C3 and Pingo Str samples was much greater (~0.7) than for the south facing and valley-bottom stream sites, C4, C2, and DG (<0.2). The Pingo Str sample was collected downstream of the confluence of C2 and C3 subwatersheds and was expected to have a signature that would be a combination of the signatures in C3 and C2. The aromatic to nitrile ratio in the March Pingo Str sample was greater than in both C2 and C3, suggesting that a highly aromatic signature was entering Caribou Creek from another

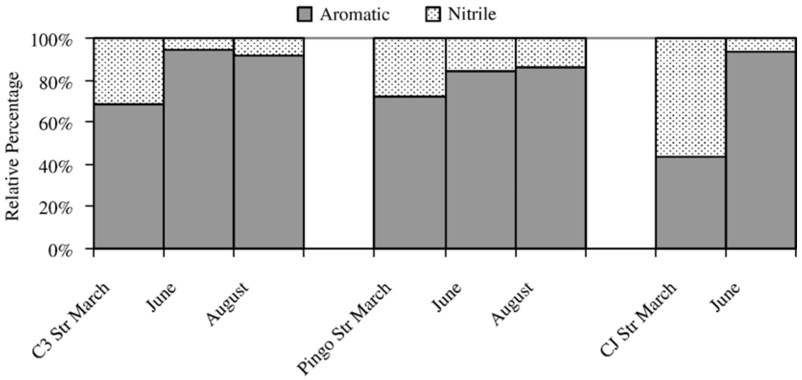

Fig. 5. This figure shows seasonal differences in the relative abundance of nitriles and aromatics in two north-facing streams and the junction of the C3, Ping Str, and streams shown in Fig. 2. The data indicate that in June and August, when stream samples are influenced by surface water, the aromatic to nitrile ratio was higher than during conditions of baseflow.

source. In spite of the high aromatic to nitrile ratio observed in C3, the conductivity of the March stream sample was 117 μS/cm, consistent with other March conductivity values. The results suggest that the water in C3 and the main stem of Caribou Creek at the Pingo Str sampling site was less biologically processed than the water emerging from the C2 watershed or the Little Poker Creek watershed. Much of the C3 watershed is underlain by continuous permafrost. According to previous research, it is believed that water draining from springs in the C3 watershed and entering Caribou Creek, falls as precipitation on the opposite (i.e., south) side of the mountain where exposed bedrock allows for rapid water infiltration (Yoshikawa et al., 2003). By passing through bedrock fractures rather than the loess deposits that underlay the south-facing and valley-bottom aquifers of C2, C4, DG, springwater from the C3 watershed could have undergone little biological processing, yet have spent more than one year in groundwater. This result would be consistent with White et al. (2002) and Yoshikawa et al. (2003). In both studies, py-GC/MS signatures suggested that the water emerging from the C3 watershed had traveled through bedrock cracks, increasing conductivity, but had undergone very little biological processing.

As for the "other source" of water that is entering Caribou Creek, resulting in the high aromatic to nitrile ratio in March, one spring not in the C3 watershed, but entering the Caribou Creek just upstream of the Pingo Str sampling location is the Pingo Spring. This spring had a conductivity of 303 μS/cm and an aromatic to nitrile ratio of 0.9. This spring, and potentially others that were not sampled, could be contributing to what appears to be DOC in the C3 and Pingo Str samples that has undergone very little biological processing. The aromatic to nitrile ratio for June and August from C3 and Pingo Str were similar to the C2 samples. The sample CJ, which was collected at the confluence of all other sampling sites (except TR1 and TR6), had an aromatic to nitrile ratio higher than what appeared to be a realistic mix of the DOC in the nearest Caribou Creek and Little Poker Creek sampling sites, Pingo Str and C4, respectively.

3.4. Relationship between DOC biodegradability and conductivity

LDOC can be an indicator of the degree of biological processing of DOC (Marmonier et al., 1995). Labile DOC has undergone a low degree of biological processing. During baseflow conditions when conductivity was greatest, LDOC concentration was typically <1 mgC/L (see Fig. 6). However, during higher flow conditions when greater flow was derived from runoff, the LDOC concentration increased markedly with concentrations as great as 6.7 mgC/L. The sample at the far right of the graph, at conductivity 303 μS/cm, had a LDOC greater than 1 mgC/L, and greater than many summer samples containing runoff. This result supports the hypothesis that organic material entering Caribou Creek is biologically processed to a lesser degree, suggesting that the water has been transported through cracks in bedrock. The water likely did not pass through a loess layer that would have led to biological decomposition of the organic matter.

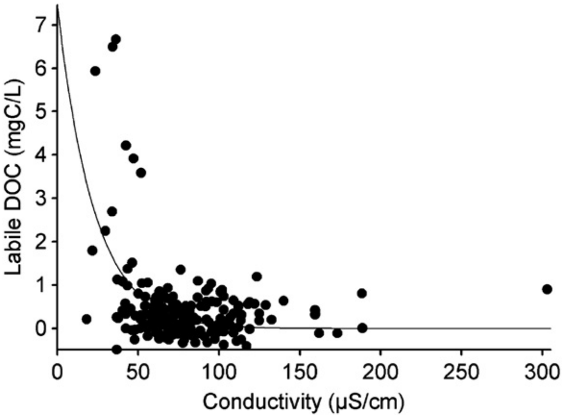

Fig. 6. Labile DOC concentration versus conductivity for samples collected from streams and springs in the CPCRW.

4. Conclusions

This study showed that characteristics of the DOC, indicative of the degree of biological processing, was a useful parameter to contribute to our knowledge of local hydrology in a permafrost watershed. Py-GC/MS proved useful as an analytical tool to draw differences in the level of biological processing of DOC between water sources. The aromatic to nitrile ratio was a useful indicator of the presence of groundwater and runoff from streams and springs. Moreover, the aromatic to nitrile ratio agreed with bioassays of LDOC supporting the assertion that the ratio was a good indicator of the degree of biological processing. The results supported the hypothesis that in a permafrost affected watershed, water in springs and stream baseflow enters the watershed, in part, through infiltration in bedrock cracks outside the topographic watershed boundary.

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