Report for 2002AK4B: Molecular characterization of organic matter in soil leachates from the Caribou Poker Creeks Watershed

- Conference Proceedings:
  - Autier, V. D. White, and D. S. Garland, (2002), Seasonal variation of organic matter chemistry in a boreal watershed, 53rd Arctic Science Conference, American Association for the Advancement of Science, Fairbanks, Alaska.
- Articles in Refereed Scientific Journals:
  - White, D. K. Yoshikawa, and D. Garland, (2002), Fingerprinting dissolved organic matter to support hydrologic investigations, Cold Regions Science and Technology, Vol. 35, pp. 27-33.
- Dissertations:
  - Vincent Autier (2002), Predicting Contaminant Transport Pathways in the Caribou-Poker Creeks Watersheds. MS. Civil Engineering, Thesis, University of Alaska Fairbanks.

Report Follows:

Problem and Research Objectives:

The Caribou and Poker Creek Research Watershed (CPCRW) is an important component of the Bonanza Creek Long Term Ecological Research (LTER) Program. A broad range of research is conducted at the CPCRW, including studies on the interactions between hydrology, ecology, meteorology, and permafrost. Previous studies at the CPCRW attempted to characterize the nature and origin of organic matter in water below or above permafrost, in interpermafrost springs, and in streams (Autier, 2002).

Contaminants are ubiquitous in the Arctic. It is therefore imperative to understand their mobility. Organic matter is believed to serve as a primary carrier of contaminants in Alaskan surface and ground waters. Understanding the origin of organic matter is important for studies of drinking water treatment and use, and its affinity for contaminants.

The primary objective of this project was to obtain and characterize soil leachates from the CPCRW in an attempt to understand contaminant transport in a permafrost-dominated watershed. The hypothesis of this work is that soil leachates from different source vegetation will exhibit different characteristics that can be quantified using pyrolysis-gas chromatography/mass spectrometry (py-GC/MS). If follows that leachates from different areas of the watershed would thereby have different potentials to mobilize contaminants.

Natural organic matter (NOM) in soil leachates from soil cores was collected and subjected to a number of analytical processes, including pyrolysis-GC/MS. This "molecular fingerprinting" analysis was used to help determine similarities and differences in organic matter leached from areas with different cover vegetation. Understanding the characteristics of the organic matter from different soils could help us determine what vegetation types deposit organic matter likely to mobilize contaminants.

Methodology

Site Selection

Soil cores were collected during summer 2002 from 11 sites in the CPCRW with different primary vegetation. Duplicate soil cores were removed from each site. Table 1, below, lists soil core identification and descriptions.

Table 1

Soil Core Identification	Vegetation Description
Haystack Ridge	Sphagnum moss, Dwarf birch, Low bush cranberry, Blueberry, Black spruce
Haystack Ridge 2	Feather moss, Sphagnum moss, Dwarf birch, Low bush cranberry, Blueberry, Black spruce
South Haystack 1	Birch, Feather moss, Cranberries,

(S. Hay 1)	Graminoids**,** White spruce
South Haystack 2 (S. Hay 2)	White spruce, Birch, Grass litter, Little feather moss
Hard wood Lower Boundary (HWLB)	Aspen and birch trees, Sporadic white spruce**,** Feather moss, Labrador tea, Low bush cranberries,
Upper Black Spruce (UBS)	Black spruce, Feather moss, Salix, Low bush cranberry, Very little blueberry, Labrador tea, Dwarf birch, Willow
Lichen Ground	Black spruce, Lichen, Low bush blueberry, Low bush cranberry, Salix, Dwarf birch
Active Pingo	Black spruce, Willow, Wild Rose, Feather moss, Aspen leaf litter, Spruce cones
Pingo 2	Open black spruce, Dwarf birch, Sphagnum moss
Pingo 3	Black spruce, Lichen, boundary between Sphagnum and Feather moss,
Creek Side of Collapsed Pingo (CSCP)	Feather moss, Dwarf birch, Salix, Blueberries, Graminoids

Py-GC/MS of CPCRW water samples

Py-GC/MS was conducted with a CDS Model 2500 pyrolyzer and state of the art autosampler in tandem with a gas chromatograph/mass spectrometer (GC/MS). During pyrolysis the sample was heated from a starting temperature of 25 ^oC to 700 ^oC in 0.1 seconds and held at a constant 700 ^oC for 9.9 seconds. The pyrolysis reactor was mounted on an HP 5890 Series II GC, with a Supelco SPB 35 (35% Ph Me silicon) column, 60 m x 0.25 m x 0.25 µm. The GC interface temperature was set at 235 ^oC. The GC temperature program was 45 ^oC for 5 minutes, 2 ^oC /min to 240 ^oC and held for 25 min. The GC was plumbed directly to an HP 5971A Series Mass Selective Detector on electron impact (EI) 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/minute. Each sample was injected with a split ratio of 1:50.

Sample preparation and py-GC/MS of soil leachates

To obtain the soil leachate, each core was mixed with 7.5L of water treated by reverse osmosis. The soil was sieved to break down aggregates and homogenize the solution. The soil-water solution was stirred and left soaking overnight. All leachable organics were removed from the solution and were dried under vacuum at 40 ^{o}F to prevent loss of organic matter to volatilization. The solids remaining from the drying procedure were collected and subjected to fingerprinting analysis using a py-GC/MS. Samples were subjected to the same py-GC/MS procedure as CPCRW waters except the temperature program was 40 ^{o}C held for 30 minutes, 1 ^{o}C/min for 80 min, 20 ^{o}C/min for 50 minutes and 10 ^{o}C/min for 10 minutes and held for 10 minutes.

Principal findings and significance

The fingerprinting technique provided us with generalizations and specifics about the chemical make-up of leachable organics. As in White and Beyer (1999), we expected that different soil leachates would be correlated if the cover vegetations were different. We also expected that soil leachates would be uncorrelated if the cover vegetation was different.

Strongest Positive Correlations

The strongest correlation was defined as those correlations with an “r” greater than 0.95; 9 such correlations existed (see Table 2). Results suggested that those soil cores with common vegetation appeared to be most strongly correlated. Among the strongest correlated were the samples collected from areas containing spruce trees. Both black spruce and white spruce are common in CPCRW. Additionally, common vegetation, among some or all of the 9 strongest correlated samples, was sphagnum moss or feather moss (see Figure 1). The distinction between moss covers was not shown in the correlations.

Weakest Positive Correlations

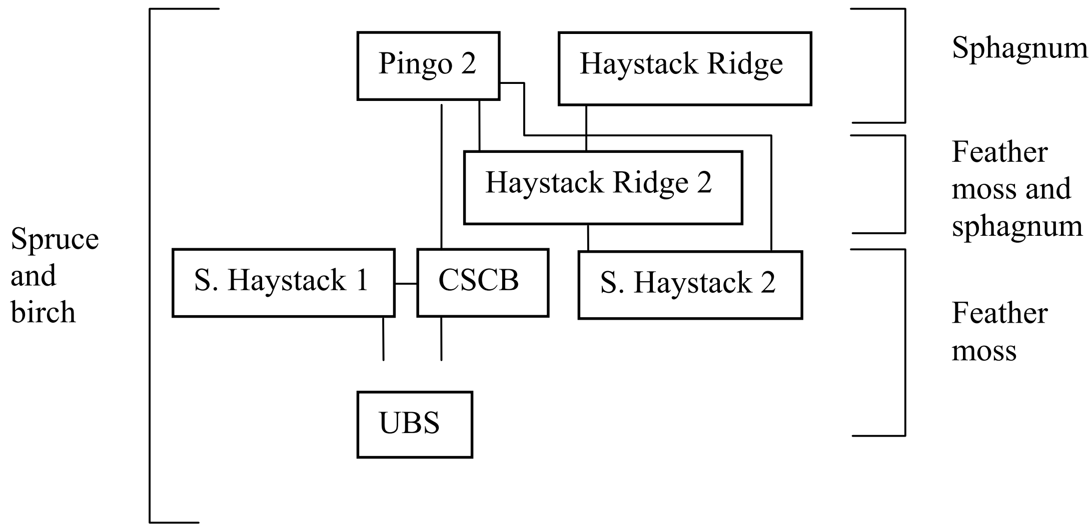
As expected, preliminary results indicated that those cores with dissimilarities in vegetation appeared to be uncorrelated. Those soil cores with r < 0.50 were considered uncorrelated. Five combinations resulted in a correlation less than 0.50 (see Table 2). The primary explanation for this appeared to be the presence or absence of aspen trees in the contributing to soil litter. The hardwood lower boundary sample, for instance, contained aspen, birch, and spruce trees. This core was correlated below 0.50 with five of the ten cores even though sporadic spruce were present at the HWLB.

Table 2. Correlations among Soil Cores

	Active Pingo	Haystack 2	Haystack Ridge	HWLB	Lichen Ground	Pingo 2	Pingo 3	CSCP	S Hay 1	S Hay 2
Haystack Ridge 2	**									
Haystack Ridge	*	0.97								
HWLB	0.28	*	*							
Lichen Ground	*	**	**	0.49						
Pingo 2	*	0.98	***	*	**					
Pingo 3	*	**	**	0.42	***	**				
CSCP	*	**	**	0.48	***	0.97	**			
S Hay 1	*	**	**	*	**	**	**	0.96		
S Hay 2	**	0.98	**	*	**	0.96	**	**	**	
UBS	*	**	**	0.42	**	**	**	0.97	0.96	**

*r = 51-75, ** r = 76-95

(a)



(b)

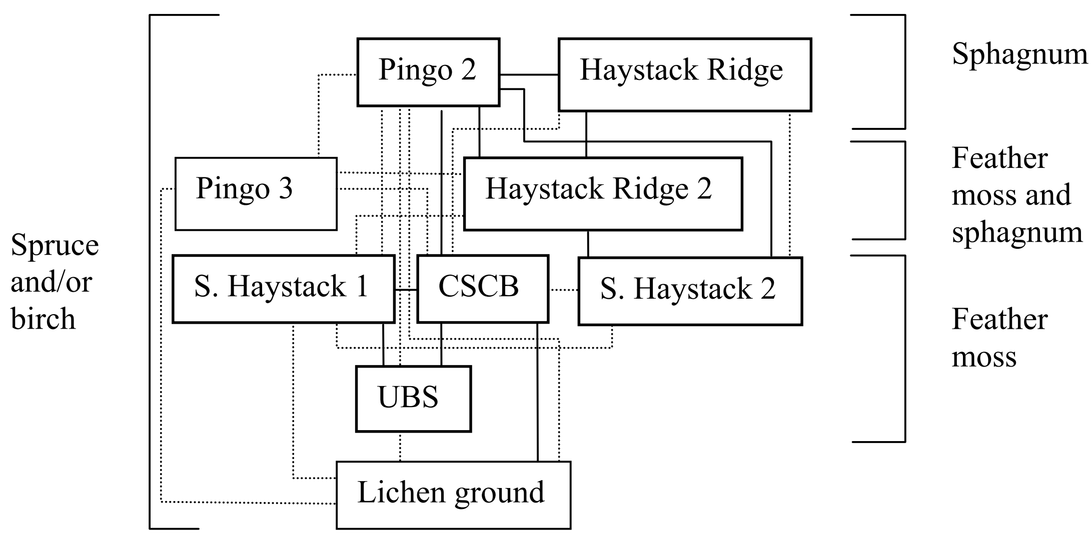


Figure 2. Correlation between leachates from different samples. The solid lines represent correlations r>0.95 (a), dotted lines represent correlations with r>0.89 (b).

Conclusions of work to date

Preliminary results suggest that the chemical make-up of organic matter in leachate from soil under different dominant vegetation types was statistically different. In particular, samples containing birch and spruce were well correlated, even if the groundcover was different. On the other hand, the presence of aspen trees at a site caused the leachate to be statistically different even if spruce trees were present. Other factors, such as the moisture content of the soil, incident sunlight, and soil depth will be considered as factors affecting soil leachate chemistry.

Additional effort will focus on studying the chemical differences between these sites. Knowing the basic chemical make-up of different soil leachates improves our ability to protect infiltration areas most susceptible to contaminants.

References

White, D.M. and Beyer, L., (1999) “Pyrolysis-GC/MS and GC/FID of three Antarctic soils”, *Journal of Analytical and Applied Pyrolysis*, Vol. 50, pp. 63-76.

Vincent Autier (2002), “Predicting Contaminant Transport Pathways in the Caribou-Poker Creeks Watersheds.” MS. Civil Engineering, Thesis, University of Alaska Fairbanks.