Water Chemistry of Fens in the Beartooth Mountains, Park County, Wyoming

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ABSTRACT

Water samples were collected from 13 fen sites in the Beartooth Mountains that spanned the known range of elevation, setting and vegetation structure. Collections were made from peat cores and from associated open water features. The pH was measured in the field, and laboratory analyses were made of pH, conductivity and 32 ions and trace minerals. Results were used to categorize fen types based on pH and calcium, which suggest that fen types range from extremely rich to poor fens. Needs were identified for further evaluation of relationships between fen type and water chemistry values along the elevation gradient, evaluation of distinctions between poor fens and transitional fens, and further corroboration of the heterogeneity within sites. This investigation is presented as a framework for preliminary characterization of fen sites in the Beartooth Mountains, and springboard for expanded research.

INTRODUCTION

In 2009, water chemistry samples were collected in the Beartooth Mountains at representative fen sites to characterize the fen types present. The relationship between fen types and water chemistry has been a central topic in fen characterization (Moore and Bellamy 1974, Mitsch and Gosselink 2000, Rydin and Jeglum 2006). The framework rests primarily on pH values and concentrations of major cations, particularly calcium (Ca^{2+}), as well as magnesium (Mg^{2+}) and sodium (Na^{+}). This framework has been routinely applied to cordilleran fens in the western United States (Bursik 1990, Chadde et al. 1998, Cooper and Andrus 1994, Lesica 1986, Weddell 2005), often with limited water chemistry analysis, following conventions developed in distant regions (reviewed in Cooper and Andrus 1994).

STUDY AREA

Peatlands of the Wyoming-portion of the Beartooth Mountains have been extensively mapped and field-verified, spanning over 200 mi² (520 km² or 52,000 ha), and extending from about 6000-11,000 ft (1828-3353 m) from montane to alpine zones (Heidel and Rodemaker 2008, USDI Geological Survey 2009). They are found across a wide range of elevations and settings that are either basin (topogenous) or sloping (soligenous). They support vegetation having a range of vegetation structures (Table 1).

Soils characteristics and peat depth characteristics of fen sites in the Beartooth Mountains are presented in Heidel and Rodemaker (2008), as part of Walford et al. (2001), and as part of wetland documentation by ERO (2000). The soils of study area sites are characterized as fibrists and the peat depths equal or exceed 40 cm, except in parts of the two alpine fen study sites.

Table 1. Fen vegetation structure by elevation and setting in the Beartooth Mountains, WY (from Heidel and Rodemaker 2008)

Elevation	**Basin Settings**	**Sloped Settings**
Montane (below 8500 ft; 2590 m)	Floating Mat, Graminoid Fen, Patterned Fen, Shrub Fen	Patterned Fen, Shrub Fen, Tree Fen
Subalpine (8500-10,000 ft; 2590-3048 m)	Graminoid Fen	Patterned Fen
Alpine (10,000+ ft; 2048+ m)	-	Patterned Fen

The geology of fen sites in the Beartooth Mountains is mapped as including Early Archean bedrock with extensive faults and fractures that outcrops across much of alpine, subalpine and montane habitat; glacial till and outwash that drapes over gentle topography and valleys at montane and subalpine elevations; and alluvium/colluvium in the Clarks Fork valley at the lower montane elevations of the area (Love and Christiansen). The 1:500,000 scale of this map does not lend itself to assigning surface geology units to individual fen sites with certainty, but provides an overview.

METHODS

Water samples were collected from peat core holes at 13 representative fen sites spanning elevation, setting, and vegetation conditions among fens of the Beartooth Mountains. Sampling was conducted between 21-23 July 2009. At each site, a McAuley auger was used to core into peat at least 5 cm below the water table (usually 10-20 cm), in centrally-located areas of relatively homogeneous vegetation structure (Table 1). Depth to water table (cm) was measured from the base of the bryophyte or vascular plant cover to standing water. Field pH was measured using an Oakton pH meter (Acorn), calibrated daily to pH 4, 7, and 10 values. Water samples were collected in glass beakers and poured into 250 ml polyethylene containers, labeled, and stored on ice. Water samples were also collected from open water features at fen sites. The depth of the standing water was recorded as one of five categories (1-5 cm, 5-10 cm, 10-20 cm, and 20-100 cm, and 100+ cm; the latter included deepwater settings). Geographic Positioning System points were recorded at each collecting point.

Previous fen inventory work provided a pool of potential sites (Heidel and Rodemaker 2008). The boundaries of each fen site had previously been digitized, sensitive plant surveys had been conducted at many sites, and vegetation structural zones identified at many sites (tree-, shrub-, or graminoid-dominated; plus floating mat and patterned fen). The three factors (elevation, setting, and vegetation structural zones) were primary considerations in selecting representative water sampling sites. The size and condition of the fen site, access, and general logistics were also considered.

Water samples were consistently taken in central peat-forming vegetation zones. If more than one peat-forming vegetation structural zone was present, then peat samples were taken in other prevalent zones. In patterned fen sites, pairs of water samples were collected within the directly-adjoining peat mound and the peat swale. Not all fen sites had open water features. Sample numbers ranged from one-six samples per site, for a total of 23 water samples from shallow peat cores and 16 water samples from open water features.

Water sample sets were shipped on ice via United Parcel Service late in the day on 22 July and 23 July from Cody, WY to the Wyoming Department of Agriculture – Analytical Services Laboratory in Laramie, WY. Sample shipments arrived the next morning. and were promptly filtered through 0.45µ hydrophilic PTFE syringe filters to remove suspended material, acidified to 1% v/v with both trace metal grade nitric and hydrochloric acid, and directly analyzed using collision-reaction cell inductively-coupled plasma mass spectrometry (cICP-MS; Agilent 7500ce) for 32 prevalent cations and trace minerals using a method based on EPA methodology (2008). Aliquots of unfiltered, whole water samples were used to determine pH using *Standard Methods* 4500-H^+-B and electrical conductivity using *Standard Methods* 2510B. Both analyses were carried out using a Radiometer TIM870 Titration Manager with a pH2001-8 Red Rod combination pH electrode calibrated at pH4 and pH10 and checked at pH7 and with a CDC566T 4-pole conductivity cell calibrated with 0.01M KCL (1406 µS/cm) corrected to 25^{o}C.

Fen sites were provisionally assigned to fen types based on pH and Ca^2 concentration values combined. There are not universally-recognized thresholds but different ranges of values assigned different fen types in different studies, as reviewed by Cooper and Andrus (1994), with updates in Mitsch and Gosselink (2000), and Rydin and Jeglum (2006).

RESULTS

Five of the 13 study area fen sites had water pH values from peat that were circumneutral to strongly alkaline, characteristic of extremely rich or rich fen types (Figure 1, Table 2 - Fen Type column). Threshold values vary in the published research, and were not selected in advance. Instead, breaks in pH vs. Ca^{2+} were used to delimit extremely rich from rich fen at pH >/= 7.0 and Ca^{2+} >/= 50 mg.L. The delimitation between rich fen and transitional fen seemed to sort mainly by Ca^{2+} > 20 mg/L for some (but not all) sites having pH values > 6.0.

Calcium was present at the highest concentrations of all ions in peat, and over the widest absolute and relative range of values (Table 2, Appendix A). The other major cation and conductivity results from peat (Figures 2-4) were generally consistent with calcium results. The site with the highest pH, conductivity, and major cation values was Swamp Lake (Appendix A).

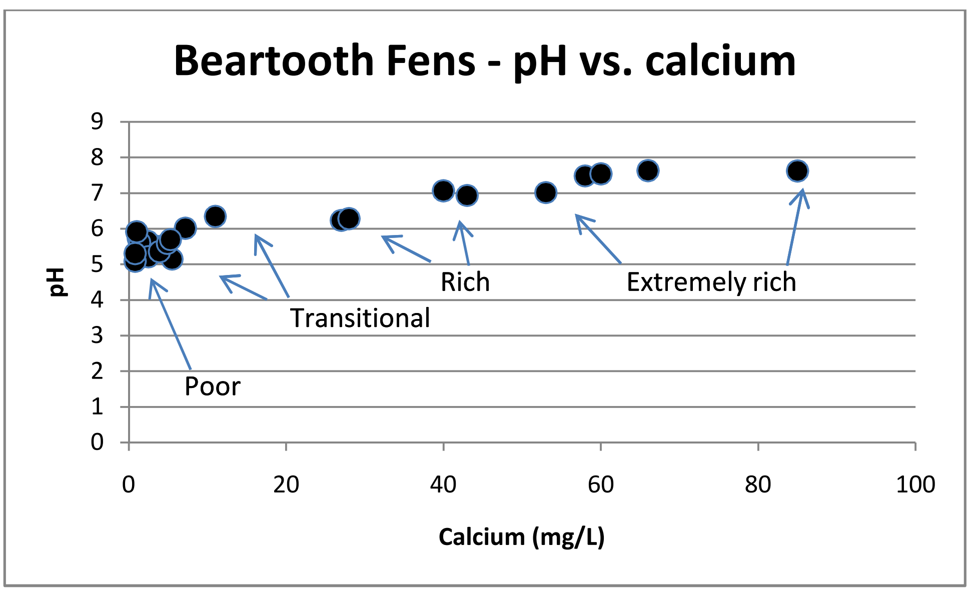
Two of the three rich fen sites had samples that fit into more than one fen type. Clay Butte Fen had one set of water chemistry values placed in extremely rich fen, collected from the shrub zone most influenced by groundwater or runoff from an adjoining calcareous landform (Clay Butte), whereas the rest of results placed the site in a rich fen category. Lily Lake Fen had one set of water chemistry values that placed it in a transitional fen, collected from a peat zone that is much smaller and less representative of the site than the sample in rich fen conditions.

The majority of study area fen sites (eight) were slightly to moderately acidic, in transitional or poor fen categories. The water chemistry values of the eight were highly clustered (Figure 1). To investigate potential causal relations, pH results were presented against elevation (Figure 5). In general, pH appeared to be inversely related to elevation. The six subalpine and alpine sites are all patterned fens and are provisionally categorized as transitional (Table 2).

For any given site, water samples collected from peat consistently had lower pH values than the samples collected from open water features at the same site (Table 2). For any given site, water samples collected from peat consistently had higher cation values than the samples collected from open water features at the same site (Table 2).

Of the twenty-nine other ions and trace minerals that were analyzed in peat samples and open water, four were present in all samples (aluminum, barium, silicon, and strontium) and 14 more were present in at least one sample (Appendix A). Mean values were calculated if more than half of the samples had detectable amounts, and undetectable values were treated in the calculation of means as if they were zero (Appendix A). Comparison between the mean values of water from peat compared with the mean values of water from open water features at the same site showed higher mean values in peat samples than open water samples except for strontium.

Figure 1. [1]



[1] These data points represent the 23 water samples collected from peat at 13 fen sites, after Glaser (1987), presented by Mitsch and Goseelink (2000).

Table 2. Water chemistry results in peat samples from fens in the Beartooth Mountains and associated open water features (see Table 1 for elevation and setting categories)

Site	Elev.	Setting	Fen Type	pH (peat)	Depth to water (cm)	Vegzone	# of samples in peat	Ca^{2+} (mg/L) (peat)	Mg^{2+} (mg/L) (peat)	Na^{+} (mg/L) (peat)	EC (μS/cm) (peat)	pH (water)	Depth of water (cm)	Waterzone	# of samples in open water	Comparison comments
Camp Creek Swamp	M	F	Extremely rich fen	7.5	1	peat tree	1	60	17	6.8	450	none	none	none	0	None
Clay Butte Fen	S	B	Rich Fen	6.2-7.1	0	peat shrub, peat floating mat	3	27.0-53.0	3.6-6.3	0.9-1.1	180-320	6.9-7.6	5-10, 10-20, 100+	chara pool, oxbow pool, lily pool	3	Highest barium levels among water samples
Fantan North Fen	S	F	Subalpine - Transitional?	5.6	4	peat mound	1	2.4	0.3	1.6	34	6.1	20+	patterned pool	1	None
Ghost Creek Fen	M	B	Poor Fen?	5.6-5.7	2-11	peat floating, peat gram	2	4.9-5.3	2.0-2.3	3.3-4.0	67-78	6.6	100+	small central pool	1	None
Lily Lake East Fen	M	B	Poor Fen?	5.3-6.0	0-1	peat floating, peat gram	2	3.9-7.2	1.5-2.6	2.1-2.9	54-60	6.4	100+	eastern pool	1	Highest zinc levels among peat samples
Lily Lake Fen	M	F	Rich Fen	6.3	0-5	peat shrub, peat mound	2	11.0-28.0	2.6-5.2	3.0-3.6	91-180	7.2-7.4	10-20, 20-100	Upper, lower patterned pools	2	Highest chromium levels among peat samples in peat mound, highest iron levels among water samples in upper pool
Little Bear Lake Fen	S	F	Subalpine - Transitional?	5.5-5.7	0-10	peat mound, peat swale	2	1.2-3.6	0.3-1.0	1.0-5.0	14-73	6.1	10-20	small central pool	1	Highest titanium levels among peat samples in peat mound; highest zinc levels among open water samples
Littlerock Creek Fen	A	F	Alpine - Transitional?	5.9	1	peat mound	1	1	0.3	1.4	19	6.6	5-10	stream	1	None
Lower Sheepherder Fen	S	F	Subalpine - Transitional?	5.1-5.3	0-11	peat mound, peat swale	2	0.8	0.2	0.1-0.3	7.8-11	none	none	none	0	One of two sites with detectable mercury in peat
Meadow Lake Fen	S	F	Subalpine - Transitional?	5.1-5.6	0-15	peat mound, peat swale	2	1.4-5.5	0.2-0.7	0.8-3.8	13-71	6.7	100+	lake	1	Highest iron levels among peat samples in peat mound; highest of few peat samples with measurable arsenic
Mud Lake Fen	M	B	Rich Fen	6.9	0	peat gram	1	43	8.7	3.6	270	7.9	100+	lake	1	Highest silicon levels among both peat samples and water samples
Swamp Lake Fen	M	F, B	Extremely rich fen	7.5-7.6	0-10	peat gram, peat mound, peat tree	3	58.0-85.0	30.0-49.0	6.0-11.0	530-770	7.3-8.4	10-20, 100+	outlet, peat swale, lake	3	Highest pH levels, highest levels of major cations, Ca^{2+}, Mg^{2+}, and Na^{+} among both peat and water samples, highest beryllium, lithium, and strontium levels among both peat and water samples, highest molybdenum and potassium levels among peat samples, highest copper levels among water samples
Wyoming Creek	A	F	Alpine - Transitional?	5.2	0	peat mound	1	2.5	0.6	2	43	5.7	1-5	peat swale	1	Highest manganese levels among both peat and water samples, highest cobalt and nickel levels among peat samples, one of two sites with detectable mercury, highest aluminum levels among water samples

Table 3. Comparison of fen water chemistry in the Beartooth Mountains with previously published literature on peatlands (table updated from Cooper and Andrus 1994)

	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)
Beartooth Mountains - peat samples				
Range	5.1-7.6	0.8-85.0	0.2-49.0	0.1-11.0
Mean	6.2 (n=23)	22.2 (n=23)	7.6 (n=23)	3.1 (n=23)
SD	0.9	26.3	13.1	2.6
Beartooth Mountains - open water samples				
Range	5.71-8.37	0.7-60	0.2-27	0.9-9.8
Mean	6.99 (n=16)	20.9 (n=16)	6.9 (n=16)	2.7 (n=16)
SD	0.7	21.9	9.3	2.8
Wind River Range - open water samples				
Range	5.9-6.8	1.4-5.3	0.2-1.0	0.9-2.3
Mean	6.2 (n = 25)	2.9 (n = 15)	0.5 (n = 18)	1.3 (n = 17)
SD	0.5	1.2	0.2	0.4
Bogs				
Glaser et al. 1981	3.8-4.1	0.5-2.1		
Glaser 1983	3.9-4.1	0.6-1.6		
Glaser et al. 1990	3.9-4.0	0.8-1.1		
Poor fens				
Sjors 1963	4.1-5.4	2.0	0.5	
Karlin and Bliss 1994	3.5-6.1	2.0-12.0	1.0-3.0	
Glaser et al. 1981	4.0-4.6	2.6-4.8		
Glaser 1983	3.7-5.2	0.6-5.5		
Glaser et al. 1990	4.6-5.3	3		
Vitt et al. 1975	5.2	2.3	0.4	3.0
Transitional fens				
Chee and Vitt 1989	5.3-7.1	19.5-22.1	4.3-5.3	
Comeau and Bellamy 1986	5.5	15.0	6.0	7.0
Zoltai and Johnson 1985	6.0	28.0	11.0	
Rich fens				
Glaser et al. 1981	5.2-6.9	4.3-18.4		
Glaser 1983	5.0-6.2	3.6-30.4		
Schwintzer 1978	5.7-7.0	11.0-75.0	2.8-19.8	
Glaser et al. 1990	6.6-7.5	16.0-30.0		
Extremely rich fens				
Slack et al. 1980	6.8-7.9			
Karlin and Bliss 1984	7.2-8.2	31.0-120.0	10.0-53.0	
Cooper 1991	7.7-8.6	43.0-94.0	21.0-44.0	7.0-32.0

Figure 2.[2]

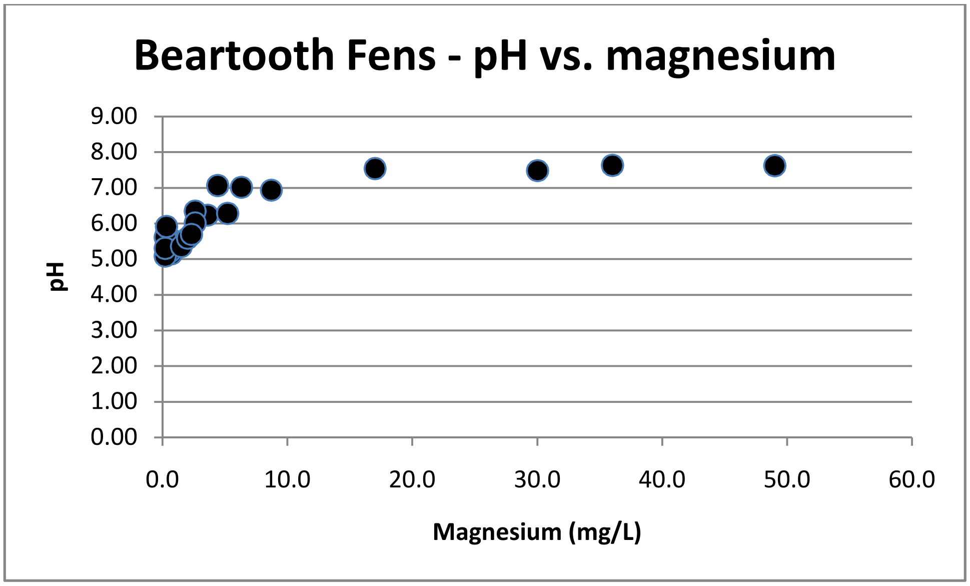
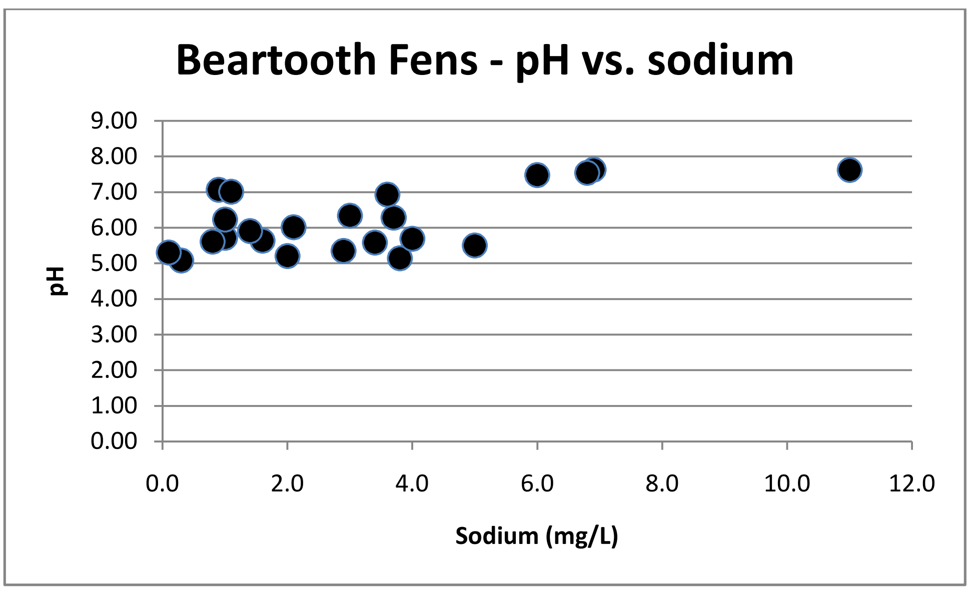


Figure 3.[3]



[2] These data points represent the 23 water samples collected from peat at 13 fen sites.
[3] These data points represent the 23 water samples collected from peat at 13 fen sites.

Figure 4.[4]

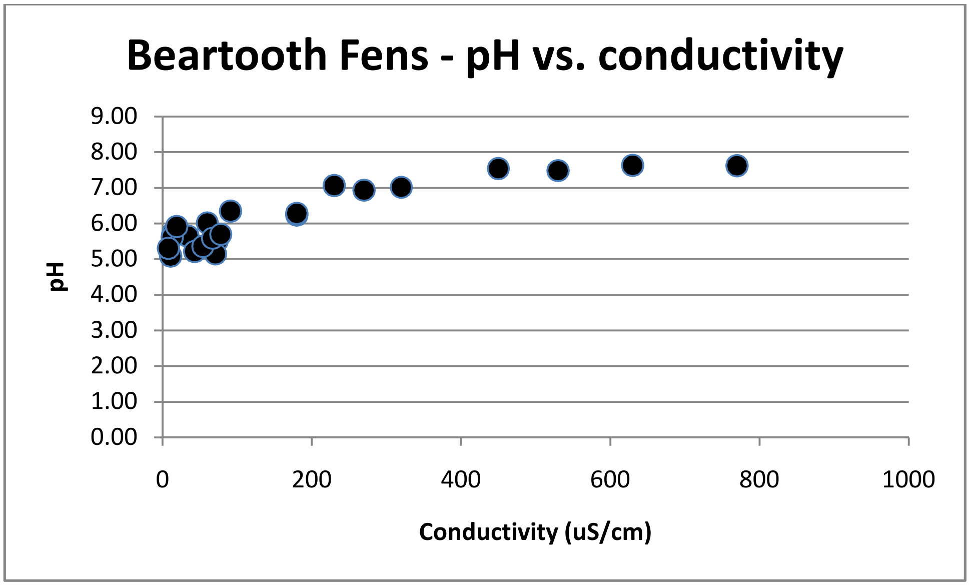
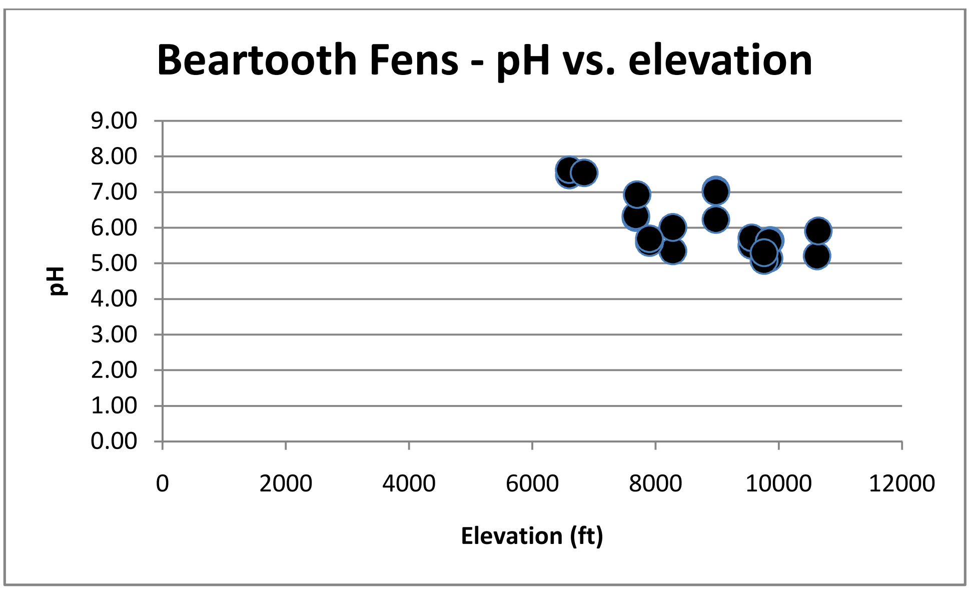


Figure 5.[5]



[4] These data points represent the 23 water samples collected from peat at 13 fen sites.
[5] These data points represent the 23 water samples collected from peat at 13 fen sites.

DISCUSSION

The results from this study suggest that there is a wide range of fen types present in the Beartooth Mountains of Wyoming, from poor fen to exceptionally rich fen. Results from this study will be incorporated into description of the environmental conditions of fens in the Beartooth Mountain collectively, and in characterizing individual sites. Site classifications at alpine and subalpine elevations, and at moderately to strongly acidic pH are provisional.

The only published fen characterizations in Wyoming were a Wind River Range study by Cooper and Andrus (1994), and a palynology study that restricted its scope of research to poor fens or bogs over very large areas of the Great Lakes and Rocky Mountains (Booth and Zygmunt 2005). Cooper and Andrus (1994) concluded that circumneutral pH values characterized their study sites as rich fens, while low values of Ca^{2+} and other major cations characterized their study area sites as transitional fens. The authors linked fen characterization to lithology, and all of their study sites were on granite bedrock. The palynological researchers included two Beartooth Mountains sites in the broad geographic scope of research, based on reports from botanists of well-developed floating mat zones. Their pH measurements indicated that poor fen habitat was present in these zones.

The difference in outcomes between this study and the Wind River study of Cooper and Andrus (1994) could reflect the differences in peat sampling methodologies. They sampled only in standing water, and this study shows that water collected from open water had consistently higher pH but consistently lower cation concentration than water collected from open water features in the same site (Table 2). The differences between the two studies may also reflect study area differences in the nature or breadth of surface geology, elevation, and study area scale.

The rich or extremely rich fen sites were most readily distinguished and may be influenced by adjoining calcareous bedrock and glacial till or alluvium deposits rich in carbonates, even though they are not directly underlain by calcareous bedrock. The difficulty in discerning between transitional and poor fen appears to be confounded by the elevation gradient. Literature reviews did not turn up any systematic evaluations of fen water chemistry as they vary with elevation. The six highest-elevation Beartooth Mountains sites were among the most acidic, but did not have the unique vascular plant species or vegetation ascribed to poor fens of the montane zone in the Rocky Mountains (Chadde et al. 1998).

It may be noteworthy that the water chemistry found in open water features at high-elevation fens was dilute compared to water chemistry found in open water features at other fens, but still magnitudes more concentrated than precipitation by at least an order of magnitude (Table 4). This interpretation was based on comparison between results to the water chemistry of precipitation at the nearest National Deposition Monitoring Program (NADP) permanent monitoring station, Tower Junction in Yellowstone National Park (NADP 2009). The mean water chemistry of Tower Junction precipitation for the month of July (1980-2009) is reported below.

Table 4. Mean water chemistry in July precipitation at Tower Junction, Yellowstone National Park (1980-2009)

	pH	**Ca^{2+} (mg/L)**	**Mg^{2+} (mg/L)**	**Na^{+} (mg/L)**	**EC (µS/cm)**
Tower Junction	5.3	0.2	0.03	0.07	8.7

Despite the outcome similarities based on water chemistry in the Beartooth Mountains and those used to characterize fens elsewhere, there may be one major difference. Peatlands at high latitudes have bi-modal pH frequency distribution (Wheeler and Proctor 2000, Tahvanainen and Tuomaala 2003), i.e., a preponderance of sites with high and low values. By contrast, cordilleran peatlands appear to have a pH frequency distribution that more closely approaches a bell curve, with circumneutral values in the majority. This appears among unpublished Beartooth fen field pH data, though not in this study with its intent to represent sites across the spectrum. The clustering of circumneutral values warrants further evaluation, suggests that there may be more of a continuous gradient, confounding cation-based fen characterization at low concentrations.

A review of the recent fen classification literature shed light on the pH standards used for characterization. The variability of on-site pH measurement over space at a single site and over time in a single growing season is reviewed and the variability is further compounded by different methodologies (Tahvanainen and Tuomaala 2003). There were pH value ranges that differed by as much as 1.5 at two Beartooth Mountains sites (Clay Butte and Meadow Lake). In general, peat pH values found in floating mat zones were consistently lower than in adjoining graminoid zones (Clay Butte Fen, Lily Lake East Fen, Ghost Creek Fen). Likewide, peat pH values found in peat mounds were consistently lower than in adjoining peat swales of patterned fens (Little Bear Lake, Lower Sheepherder Fen, Meadow Lake Fen). The authors recommended that mid-season water chemistry measurement be preceded by installation of monitoring cores long before samples are taken but do not discuss placement of monitoring stations. The wide range of variability for water chemistry measurements documented within a single site calls to question the merit of classifying a site based on a limited number of rapidly-collected samples, and points to the fact that there can be fundamentally different water chemistry characteristics within a single fen site.

Field pH measurements have been taken at some of the 13 sites in the past, and generally mirror results reported in this study. However, earlier measurements contrast for Lily Lake East Fen, the most acidic fen site reported in the Beartooth Mountains. In 2002, two different research teams took pH measurements in the same week of June. Palynologists took pH values in the water extracted (squeezed) from *Sphagnum*, as part of research to evaluate testate amoebae as water chemistry indicators in the peat profile (Booth and Zygmunt 2005). They found values ranging from 3.7-5.6. Field biologists took pH values in the surface waters of a floating mat and graminoid zone in the same week (Heidel and Laursen 2003). They found values ranging from 4.3-5.0. These differences are consistent with methodological differences. By contrast, pH values taken in 2009 from the same site and zones as the 2002 field biology samples ranged from 5.3-6.0 in peat cores (Table 2). The 2002 sampling did not core into peat, a possible factor. It is not known whether the 2002 drought conditions could have produced major pH differences in pH as compared to readings taken under the near-average 2009 moisture conditions. This is particularly important because the range of pH values from Lily Lake East Fen transcend the thresholds used to distinguish poor fen from transitional fen.

Even more far-reaching, the review of recent peatland characterization literature determined that there are proposals to redefine the most fundamental peatland categories, bog and fen, by pH rather than by water source (Wheeler and Proctor 2000). The authors also propose redefining fen trophic status by major plant nutrients (N, P, and K), rather than by major cations, consistent with limnological classification. This information came to light after the field season, so these factors were not addressed in water chemistry analyses.

The literature review identifies a need to re-evaluate the framework, and the literature is scant in documenting fen types across a wide range of montane conditions. In any case, there is a need for closer evaluation of water chemistry values along the elevation gradient. This study also raises questions about the stability/dynamics of fen states over space (within site) and time (between years, and between climatic events). There may be few cordilleran landscapes better-suited for such evaluation than in the Beartooth Mountains, with their accompanying range of environmental conditions.

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