Geochemical Expression in Soil and Water of Carbon Dioxide Seepages Near the Nazko Cone, Central British Columbia (NTS 093B/13)

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Introduction

Travertine deposits, soil gas seepages, organic soil mixed with calcium carbonate mud and pools of stagnant or slow-flowing water are among surface features observed in two wetlands, informally called the North and South bogs, near the Nazko cone (unofficial place name), British Columbia (Figure 1). During preliminary geothermal exploration conducted at these wetlands in 2012, Alterra Power Corp. detected carbon dioxide with traces of methane and helium in the seepage gas (C. Hickson, pers. comm., 2013; N. Vigouroux, pers. comm., 2013). The isotopic composition (d13C between –6.2 and –6.9 per mil Pee Dee Belemnite [PDB]) of the gases suggests that they are magmatic in origin (G. Williams-Jones, pers. comm., 2013).

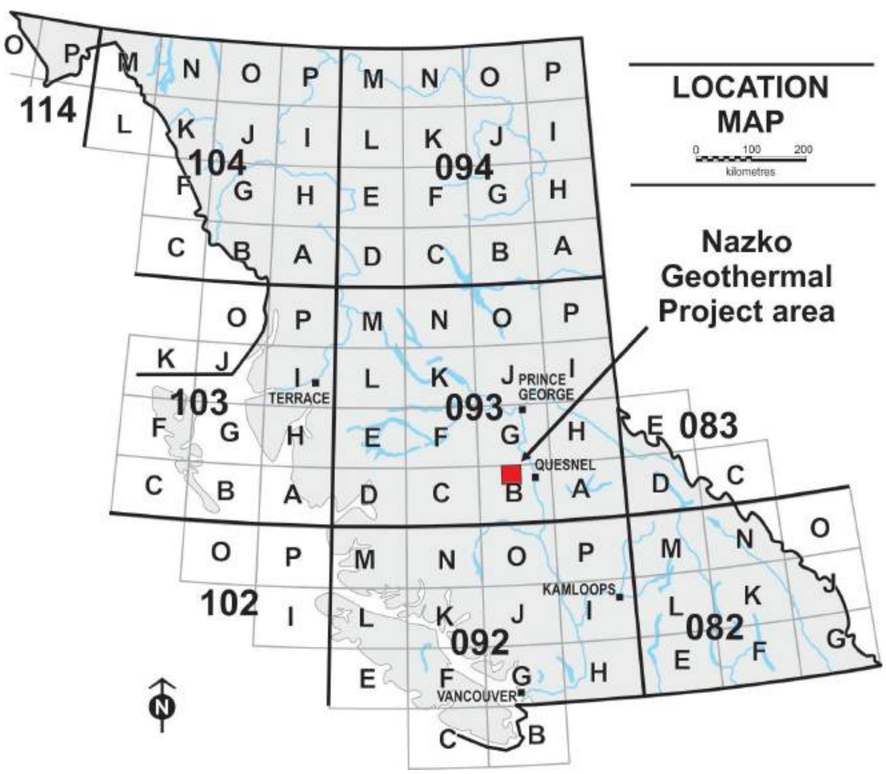

Figure 1. Location of the Nazko Geothermal Project area, near the Nazko cone, central British Columbia.

Analysis of the carbonate mud in the bogs reveals a dominance of aragonite (66%), with equal parts remaining of calcite and dolomite, precipitated from the carbon-enriched surface water. Although the surface water temperature is typically below 12°C, the carbon dioxide seepages, travertine deposits and the nearby Nazko cone together suggest a magmatic, possibly geothermal, source for the gas, similar to the setting described by Fouke et al. (2000) at Mammoth hot springs, Wyoming (Yellowstone) and at the Mt. Etna volcano, Italy (D'Alessandro et al., 2007). Magmatic carbon dioxide discharging into the near-surface environment forms 'thermogenic' travertine that is predominantly calcite and aragonite enriched in ^{13}C and ^{18}O (Pentecost, 1995; Ford and Pedley, 1996).

Even though the cool surface waters do not suggest an active near-surface geothermal source beneath the Nazko wetlands, springwater temperatures in other areas of Canada where there are travertine deposits can be as low as 20°C, such as at the Rabbitkettle spring, Northwest Territories (Fouke et al., 2000). The springwater chemistry in these areas typically shows elevated Ca, dissolved CO_2, Li and B. At the Starlite mineral occurrence (MINFILE 082KSW074; BC Geological Survey, 2013) near the village of Hills, BC, travertine deposits on Arthur Creek are associated with warm springs.

This paper includes a description of groundwater, surface water and soil sampling in the Nazko bogs and the sur-

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rounding area to study the geochemical signature associated with carbon dioxide gas seepages. This study is being supported by Geoscience BC as part of the 2013 TREK Project and was designed to complement earlier investigations on the potential for geothermal occurrences in the region (G. Williams-Jones, pers. comm., 2013) and support local community interest in geothermal resources.

Geology and Surface Environment

The North and South bogs lie within the Anahim volcanic belt, an east-trending belt of Pleistocene–Holocene volcanoes that include the Nazko cone (Cassidy et al., 2011; Riddell, 2011). Eocene Ootsa Lake Group, Miocene Endako Group and Pleistocene–Holocene volcanic and sedimentary rocks underlie the area. Souther at al. (1987) tentatively estimated that the Nazko volcanism began during the Fraser glaciation, forming a pyroclastic mound beneath the Cordilleran Ice Sheet. A subaerial, flow-layered, nonvesicular basalt buried by more recent tephra and till is the earliest eruptive rock. This unit is partially covered by a later, blocky, highly vesicular basalt and tuff breccia forming the western part of the cone. Postglacial deposition of red pyroclastic ash, lapilli and volcanic bombs ejected from vents in the cone created the present-day edifice. During this eruption event, two olivine basalt lava streams flowed for several hundred metres from the volcano to the south and west. In 2007, an earthquake swarm occurred a few kilometres to the west of the Nazko cone (Hickson et al., 2009).

Glacial deposits in the area include till and glaciofluvial sediments (as eskers) that extend from the base of the cone into the wetlands. Souther et al. (1987) described sampling a 6 m vertical profile in the 'volcano bog' (probably the North bog) northwest from the Nazko cone. Sediments sampled here were a mix of gravel and mud overlain by gyttja and more than 5 m of peat interbedded with a tephra layer. This ash layer was interpreted by Souther et al. (1987) to have been deposited by an eruption from the cone at an estimated 7200 years BP.

Parts of the North and South bogs are covered by sedge and scattered wetland shrubs; calcium carbonate–rich mud; stagnant pools or slow-moving streams; small, isolated outcrops of travertine; forest-dominated bogs and meandering streams flowing through the wetlands. In the carbonate-mud–dominated parts of the bog, carbon dioxide can be observed as bubbles seeping through the bottom sediment of stagnant ponds and a calcium-carbonate (possibly aragonite) precipitate often occurs on the water surface (Figure 2). Two streams draining uplands to the east and south flow west though the bogs into Fishpot Lake (Figure 3). Luvisolic and brunisolic soils exist on the better drained hillslopes above the wetlands, whereas gleysolic soils have formed along the bog margin where the water table is close to the land surface. Peat mixed with calcium-carbonate mud is the most common organic bog soil.

Travertine is typically a rusty to white coloured rubble forming small, isolated and elevated areas in the bogs. Near the northern edge of the North bog, there is a small, 35 cm high inverted cone-shaped travertine deposit concealed by undergrowth. This cone encloses a partially submerged vent from which there is a steady flow of carbon dioxide. There is a less active carbon dioxide seep from another vent on a rusty travertine mound close to the east edge of the South bog. Figure 4 shows the wetland surface features including the location of the two carbon dioxide discharging vents.

Fieldwork

In July and August 2013, fieldwork in the North and South bogs and surrounding area completed the following:

- Bog surface features, such as gas discharge vents and travertine deposits, were mapped.
- Groundwater was sampled from shallow dug pits, springs and gas vents. Water pH, temperature, salinity and conductivity were measured on-site with an Oakton PCSTestr 35 multimeter. Details of the site such as water flow rates, water table depth and presence of discharging carbon dioxide were recorded.
- Surface water was sampled in bog pools, streams flowing into and out of the wetland and from Fishpot Lake. Water pH, temperature, salinity and conductivity were measured and site details such as water flow rates, channel width and depth were recorded. Channel sediment was also collected at several stream sites.
- Bog and well-drained soil and travertine deposits were sampled.

Sample Preparation and Analysis

Three water samples were collected in high-density polyethylene (HDPE) bottles at each site. The samples underwent the following analyses:

- Within 12 hours of collection, one sample was analyzed for Na with a HANNA model pHep® pocket meter and total alkalinity and dissolved carbon dioxide were measured with Hach® field test kits.
- A second sample was filtered through a Phenex™ polyethersulfone (PES) 0.45 μm membrane, and stored at 4°C for later analysis by ALS Global (Vancouver) for hardness, total alkalinity, bicarbonate alkalinity and hydroxyl alkalinity by titration and for Br^-, Cl^-, F^-, NO_3^-, NO_2^- and SO_2^{-4} by ion chromatography.
- A third sample was filtered through a Phenex™ polyethersulfone (PES) 0.45 μm membrane, acidified with ultrapure nitric acid to pH 1 and later analyzed by ALS

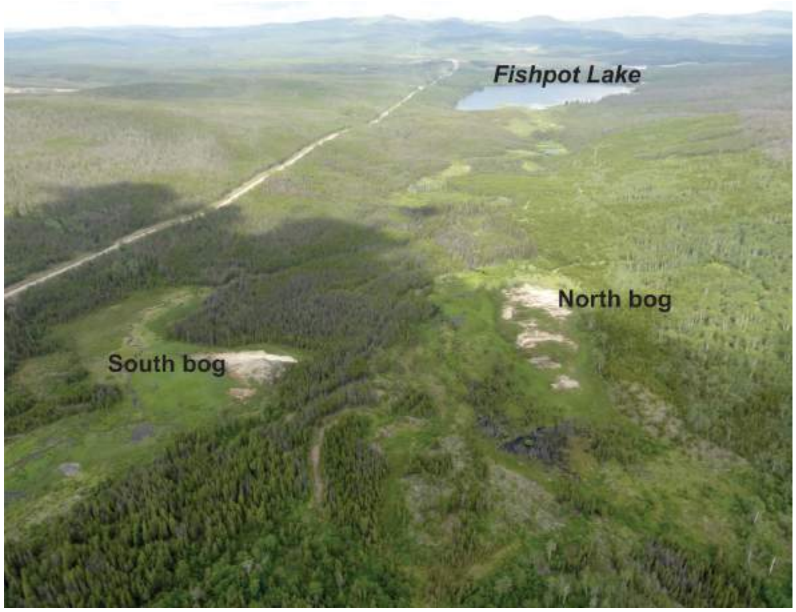

Figure 2. Photograph of the North and South bogs and Fishpot Lake to the west.

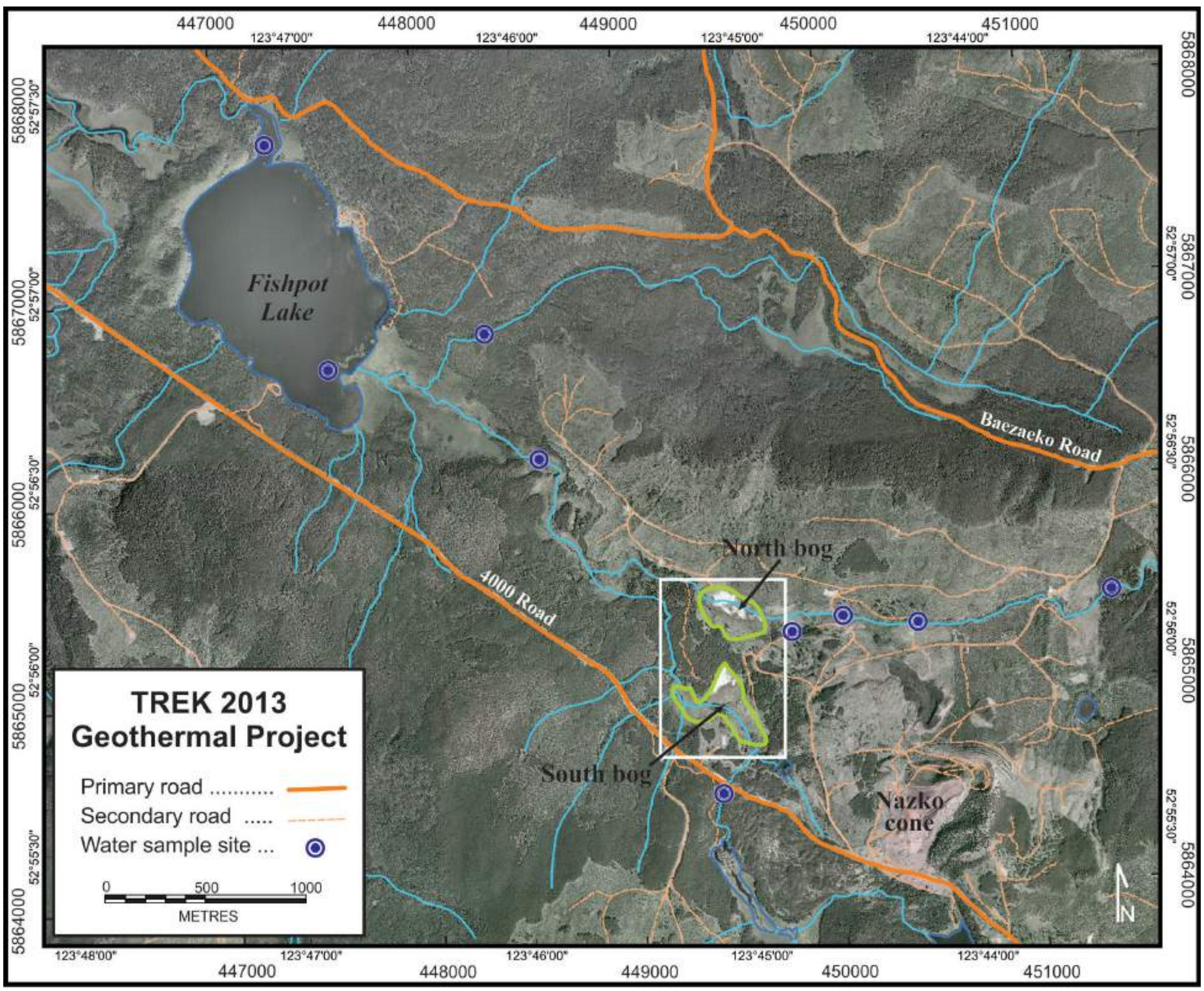

Figure 3. Streams draining from the Nazko cone area through the North and South bogs into Fishpot Lake.

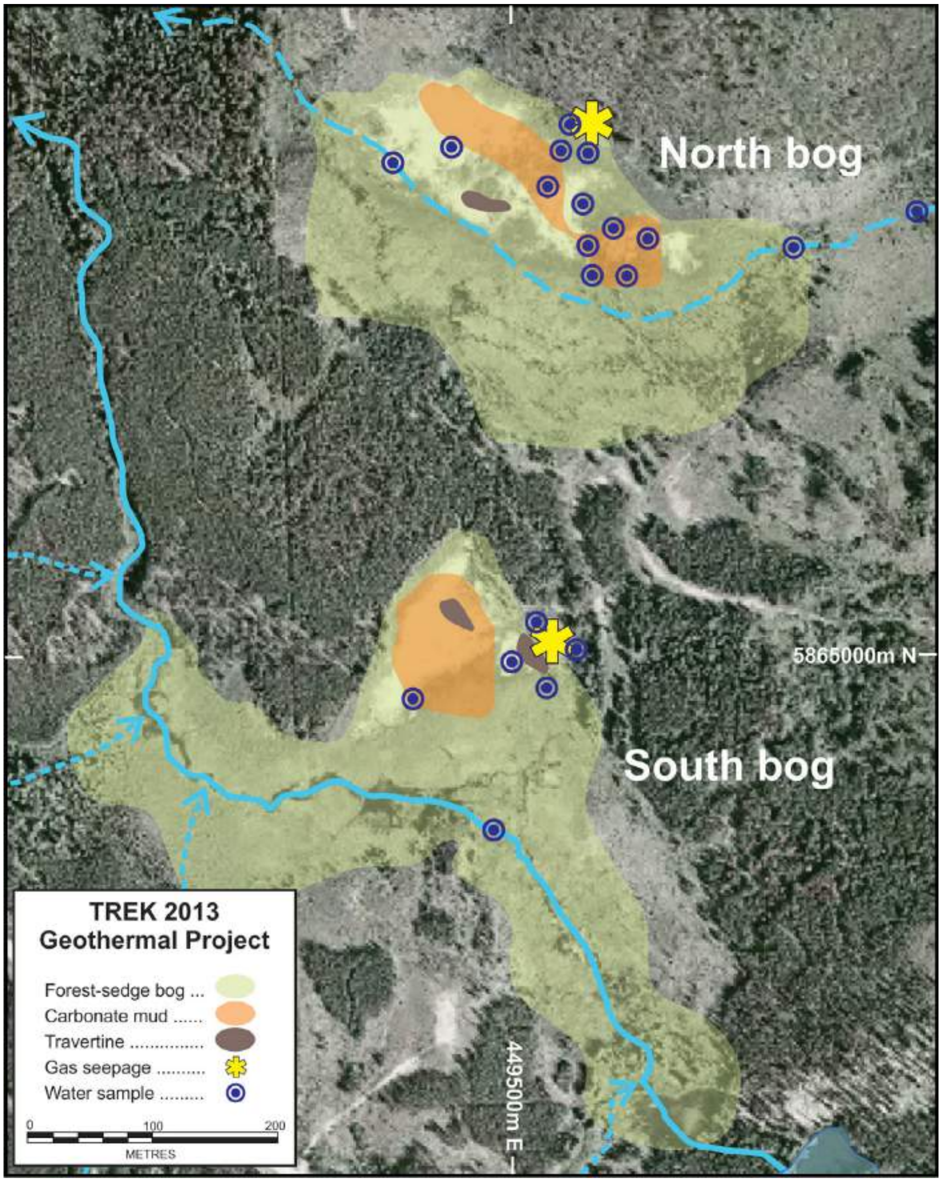

Figure 4. North and South bog surface features and distribution of water samples.

Global for Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mn, Mo, Na, Ni, P, Pb, Rb, Re, Sb, Se, Si, Sn, Sr, Te, Th, Ti, Tl, U, V, Y, Zn and Zr by high-resolution mass spectrometry. Three distilled, deionized water sample blanks and two samples of the National Research Council Canada (NRCC) river water standard, SLRS 3, were analyzed with the field samples to monitor data accuracy and precision.

Sediment samples were dried at below 60°C, sieved to –80 mesh (<0.177 mm) and the –80 fraction was analyzed at Acme Laboratories Ltd. (Vancouver) for trace and minor elements including Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Hg, K, Li, Mn, Mo, Na, Ni, P, Pb, Rb, Re, Sb, Se, Si, Sn, Sr, Te, Th, Ti, Tl, U, V, Y, Zn and Zr by aqua regia digestion and inductively coupled plasma–mass spectrometry (ICP-MS); major oxides by lithium borate fusion–ICP-MS; C and S by Leco analysis; loss on ignition (LOI) by sintering at 1000°C; and B by sodium peroxide sinter–ICP-MS.

Water Geochemistry: Preliminary Results

Table 1 lists element detection limits, the mean measured value for water standard SLRS 3, the percent relative standard deviation (%RSD) calculated from two SLRS 3 analyses and an element value for the SLRS 3 standard where reported by NRCC. Analyses of filtered water blanks reveals that only Li, Sr and Ca are detected in concentrations that are less than twice the detection limit. Only Be and Li in the water standard SLRS 3 have %RSD values that are more that 10%. Where the NRCC reports a value for an element in SLRS 3, the detected concentration is within 10% of the recommended value.

Table 1. Analytical detection limits and results of National Research Council Canada river water standard SLRS 3 duplicate analysis. Abbreviations: NRCC, National Research Council Canada; RSD, relative standard deviation; SLRS 3, river water standard.

Analyte	Detection limit	Mean SLRS 3	%RSD	NRCC SLRS 3
Br (ppm)	0.05			
Cl (ppm)	0.5			
F (ppm)	0.02			
NO_3 (ppm)	0.005	392	0.4	
NO_2 (ppm)	0.001	–0.05	0	
SO_4 (ppm)	0.5	–25	0	
Al (ppb)	1	33	0.6	31
Sb (ppb)	0.01	0.17	0.8	0.12
As (ppb)	0.05	0.84	1.9	0.72
Ba (ppb)	0.1	14.1	1.5	13.4
Be (ppb)	0.005	0.0096	28.0	0.005
Bi (ppb)	0.05	–0.05	0.00	
B (ppb)	5.00	9.70	10.2	
Cd (ppb)	0.005	0.0148	6.2	0.013
Ca (ppm)	0.076	5.505	4.2	6
Cs (ppb)	0.005	0.0064	0.0	
Cr (ppb)	0.5	–0.5	0.0	0.3
Co (ppm)	0.05	–0.05	0.0	0.027
Cu (ppb)	0.2	1.52	2.3	1.35
Ga (ppb)	0.05	–0.05	0.0	
Fe (ppb)	30.0	100.0	7.1	100
Pb (ppb)	0.05	0.072	1.0	0.068
Li (ppb)	0.2	0.5	25.1	
Mg (ppm)	0.1	1.6	7.6	1.6
Mn (ppb)	0.2	4.10	0.9	3.9
Mo (ppb)	0.05	0.224	0.3	0.19
Ni (ppb)	0.2	0.84	1.7	0.83
P (ppm)	0.3	–0.3	0.0	
K (ppm)	2	–2	0	0.7
Re (ppb)	0.005	–0.005	0.0	
Rb (ppb)	0.02	1.70	3.0	
Se (ppb)	0.2	–0.2	0.0	
Si (ppm)	0.05	1.66	3.0	
Ag (ppb)	0.005	–0.005	0.0	
Na (ppm)	2	2.5	5.7	2.3
Sr (ppm)	0.001	0.0319	2.9	0.028
Te (ppb)	0.010	–0.01	0.0	
Tl (ppb)	0.002	0.007	1.0	
Th (ppb)	0.005	0.014	1.5	
Sn (ppb)	0.2	-0.20	0.0	
Ti (ppb)	0.2	0.70	8.1	
W (ppb)	0.01	–0.01	0.00	
U (ppb)	0.002	0.041	0.69	0.045
V (ppb)	0.05	0.320	2.0	0.3
Y (ppb)	0.005	0.128	3.3	
Zn (ppb)	1.00	1.60	0.00	1.04
Zr (ppb)	0.05	0.08	8.7	

Comparison of surface- and groundwater geochemistry statistics listed in Table 2 reveals the following:

- Surface water has a higher pH than groundwater. Streams flowing into the wetlands have a pH above 8. Vesicular basalt outcrops along the bank of one stream has abundant calcite in the vesicles and dissolution of this calcite may explain the alkaline streamwater. The highest pH value detected (9.26) is from a water sample from Fishpot Lake.
- Groundwater has a higher mean dissolved carbon dioxide value than surface water, reflecting the active flow of carbon dioxide from seeps into the groundwater and precipitation of calcium carbonate mud.
- Mean groundwater temperature is slightly lower than surface water. The lowest water temperature (5.6°C) was measured in water from the active gas flow from the travertine cone vent in the North bog.
- Mean element concentrations are higher in groundwater compared to surface water. Water that has accumulated in the travertine cone vent in the North bog has the highest detected levels of dissolved As, Cd, Fe and Ni.

Future Work

Completion of this project will involve

- preparation and geochemical analysis of the soil and rock samples for major oxides, loss on ignition, minor and trace elements;
- statistical analysis and interpretation of water, soil and sediment data; and
- final reporting, which is scheduled to be published in spring 2014.

Summary

Geology, surface features, carbon dioxide seepages and anecdotal evidence of a thermal anomaly beneath the Nazko bogs and surrounding area (such as snow-free wetland areas in winter), combined with the preliminary results from this and other recent studies, support the existence of a geothermal source. Clear evidence for geothermal activity, such as the presence of thermal springs, may be absent, however, because of masking by the wetland geochemistry and sediments and possibly because of the amount of recharge/groundwater flow in the area. It is also possible that any thermal anomaly, such as hot water, is lost to deeper aquifers, which would explain the presence of cold, noncondensable gases only at the surface. Additional field studies intended to better detect evidence for concealed geothermal activity could include resampling groundwater in the bogs where high levels of carbon dioxide have been recently detected in soil gas, $^{16}O/^{18}O$ isotope analysis of the groundwater near seeps and $^{13}C/^{12}C$ isotope analysis of the seepage gas. Further soil sampling and soil gas flux moni-

Table 2. Mean, median, 3rd quartile (quart.) and maximum statistics calculated from data for 11 groundwater and 20 surface water samples; Ag, Bi, Cl^-, Ga, P, Re, Sn, Tl, and were not included because most values are below the detection limit. Hardness and alkalinity are reported in parts per million $CaCO_3$. Abbreviations: bicarb, bicarbonate; Cond, conductivity; GW, groundwater; SW, springwater; TDS, total dissolved solids; Temp, temperature.

Analyte	Mean GW	Median GW	3rd quart. GW	Max. GW	Mean SW	Median SW	3rd quart. SW	Max. SW
pH (Field)	6.61	6.59	6.745	7.03	7.6	7.73	8.15	9.26
Temp (field)	12.2	13.5	14.4	14.8	13.7	14	15.6	23
Cond (µS; field)	2907	3390	3635	4380	1000	333	1670	4450
Na (ppm; field)	208	160	235	450	127	70	138	900
Salinity (ppm; field)	1606	1740	1900	2460	488	155	735	2250
TDS (ppm; field)	2355	2520	2740	3380	552	206	499	3080
Alkalinity (ppm; field)	2364	2400	2800	3000	763	160	1850	3000
CO_2 (ppm; field)	414	400	525	750	149	38	194	850
Hardness (ppm)	1617	1570	1745	2570	548	148	874	2500
Alkalinity, Bicarb (ppm)	2218	2410	2490	3260	708	165	1275	3230
Total Alkalinity (ppm)	2218	2410	2490	3260	708	165	1275	3230
F (ppm)	0.47	0.47	0.505	0.54	0.241	0.1715	0.4	0.59
NO_3 (ppm)	0.1	0.1	0.1	0.11	0.1	0.02	0.1	0.44
NO_2 (ppm)	0.02	0.02	0.02	0.02	0.01	0.001	0.02	0.089
SO_4 (ppm)	15	16	18	29	6.6	2.8	10.125	32
Al (ppb)	1.79	2	2.05	3.8	10.59	3.05	16.15	49.3
Sb (ppb)	0.029	0.02	0.0365	0.066	0.093	0.043	0.0508	0.618
As (ppb)	0.6	0.1	0.66	2.56	0.5	0.53	0.7	0.85
Ba (ppb)	175	182	202	234	62	53	67.3	204
Be (ppb)	0.016	0.005	0.025	0.059	0.0133	0.005	0.016	0.045
B (ppb)	376	380	446	637	89	11.4	207	430
Cd (ppb)	0.0245	0.0171	0.0238	0.0916	0.026	0.005	0.0061	0.203
Ca (ppm)	221	220	235	383	74	29	68	358
Cs (ppb)	2.047	2.08	2.625	3.18	0.535	0.0139	0.745	3.93
Cr (ppb)	0.64	0.5	0.75	1	0.5	0.5	0.5	0.5
Co (ppm)	1.1	0.114	1.221	6.73	0.132	0.077	0.206	0.44
Cu (ppb)	0.31	0.21	0.4	0.64	0.71	0.405	0.7	3.05
Fe (ppb)	566.4	147	430.5	3920	282.9	68.5	352	1290
Pb (ppb)	0.07	0.05	0.1	0.137	0.05	0.05	0.05	0.057
Li (ppb)	335	341	379.5	475	105.4	5.06	231.5	547
Mg (ppm)	259	247	307	393	88	18	170	390
Mn (ppb)	225	193	203.5	657	83	35.6	125	278
Mo (ppb)	0.221	0.13	0.341	0.574	0.725	0.655	1.1975	1.64
Ni (ppb)	12.96	2.42	22.57	44	2.28	1.015	2.035	13.4
K (ppm)	30.6	31.5	35.5	41.4	10.64	3.95	17.1	41.1
Rb (ppb)	39.1	40.1	45.55	52.4	12.86	3.415	24.1	56.1
Se (ppb)	0.3	0.2	0.3	0.4	0.7	0.2	0.4575	3.26
Si (ppm)	12.2	12.3	15.3	16.8	13.7	13.65	15.13	18.7
Na (ppm)	267	281	302.5	412	69	9.25	157.5	311
Sr (ppm)	8.6	7.68	8.725	15	2.479	0.249	2.58	15.9
Tl (ppb)	0.106	0.004	0.1895	0.429	0.045	0.002	0.006	0.487
Th (ppb)	0.006	0.005	0.0075	0.01	0.0072	0.005	0.008	0.018
Ti (ppb)	0.36	0.35	0.4	0.64	1.06	0.36	1.34	4.28
W (ppb)	0.013	0.01	0.015	0.02	0.014	0.01	0.01	0.042
U (ppb)	0.14	0.061	0.1165	0.687	0.081	0.079	0.108	0.242
V (ppb)	0.513	0.157	0.66	2.36	1.387	1.22	1.68	5.73
Y (ppb)	0.1404	0.0464	0.1717	0.64	0.238	0.081	0.458	0.927
Zn (ppb)	5.5	3.6	9.85	12.6	2.4	1	1.575	10.3
Zr (ppb)	1.303	0.55	2.08	4.67	0.727	0.51	0.96	4.79

toring could map the carbon dioxide seeps. Over a wider area around the Nazko cone, additional work could find evidence for thermal water in other springs and seepages. For example, a self-potential geophysical survey may be useful for detecting structures capable of transporting thermal water into the bogs.

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