

# Chemical Characterization of Underground Water at Sites Near the Sanford Underground Research Facility

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## Introduction

The Sanford Underground Research Facility (SURF) is located deep underground in the former Homestake gold mine in Lead, SD. In the labyrinth of tunnels surrounding SURF, there are numerous water microenvironments that are hypothesized to contain unique microbial communities of potential interest to microbiologists. Borehole water samples have been taken near the Davis Campus on the 4850-foot level (Stetler 2015); these and three additional sites have been characterized by Osburn et al. (2014). However, water from the 4100-foot level and the 17 Ledge on the 4850-foot level has not been extensively

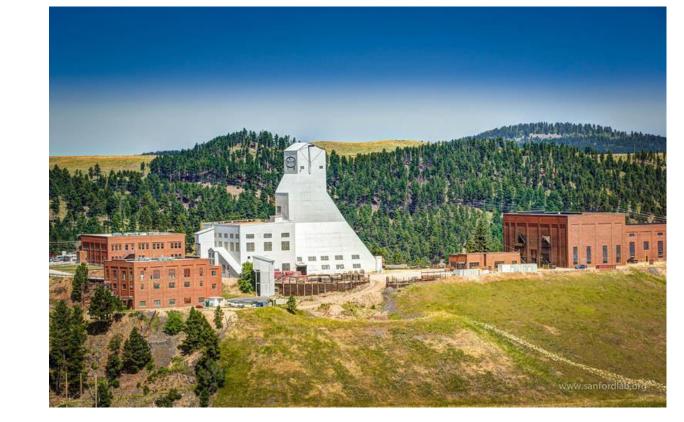


Table 2. Sampling Methods

Air Temperature In situ Vernier Temperature Probe

Method

Vernier Temperature Probe

Vernier pH Probe

Vernier Conductivity Probe

Vernier Pressure Probe

Vernier Dissolved Oxygen

Vernier Ammonium ISE

AAS

AAS

HACH® Fe Test (filtered)

HACH® Fe Test (unfiltered)

**ICP-MS** 

**ICP-MS** 

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HACH® SO<sub>4</sub><sup>2-</sup> Test

pH Titration

pH Titration

**Potentiometric Titration** 

HACH® NO<sub>3</sub> Test

pH Titration

**EDTA Titration** 

Location

In situ

BHSU

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The objective of this study was to characterize water chemistry at distinct and previously unsampled locations in the tunnels surrounding SURF, with particular emphasis on those areas undergoing microbial study

#### Methods

Test sites were located at the 4100-foot level (3 locations) and 4850-foot level (6 locations) of SURF (Table 1). In situ testing using Vernier probes was performed at each site. Filtered and unfiltered samples were taken aboveground and analyzed for other chemical parameters using HACH® kits, titrations, atomic absorption spectroscopy (AAS – Perkin Elmer AAnalyst 300), and inductively coupled plasma mass spectrometry (ICP-MS – Agilent 7900) at Black Hills State University (Table 2). Data between the levels was analyzed using t-tests, with significance predetermined at p < 0.05.

Parameter

Temperature

Conductivity

Air Pressure

**Dissolved Oxygen** 

 $NH_4^+$ 

Na⁺

Ca<sup>2+</sup>

Fe<sup>2+</sup>

Fe (total)

Cu

Cd

Se

SO<sub>4</sub><sup>2-</sup>

CO<sub>3</sub><sup>2</sup>-

HCO<sub>3</sub>

**Total Alkalinity** 

**Total Hardness** 

Table 1. Sampling Locations

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Level	Site	Designation	Location
4100	1	4100-1	Northwest corner
			of crosscut
	2	4100-2	Drift south of
			crosscut
	3	4100-3	Drift north of Yates
			air door
	1	4850-1	17 Ledge wooden
			pallet cavern
	2	4850-2	Thiothrix Falls
			outflow
	3	3 4850-3	17 Ledge Cave
4850	3		Silver cavern
4630	4 4850-4	Outflow from 4700	
		4030 4	level
	5	4850-5	South end of drift
			to 17 Ledge
	6	4850-6	North end of drift
	U	4030-0	to 17 Ledge



Cave Silver near Sample 4850-3

Photo Credit: Madeline Valentin

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### Results

Table 3. Water Quality Characteristics from each Site

Darameter	Units	Location								
Parameter	Units	4100-1	4100-2	4100-3	4850-1	4850-2	4850-3	4850-4	4850-5	4850-6
Air Temp	°C	23.9	23.6	23.4	32.2	23.2	29.5	26.2	23.2	23.2
Water Temp	°C	23.2	23.3	22.4	30.9	29.9	30.5	25.2	21.5	20.9
рН		6.78	7.71	7.90	8.40	8.33	8.39	8.54	8.62	8.29
Conductivity	mg/L TDS	8960	4397	8493	579	970	983	1241	1898	1002
Air Pressure	mmHg	721.5	720.9	723.4	737.5	738.4	744.0	742.6	745.0	746.9
Dissolved Oxygen	mg/L	1.6	3.3	4.1	6.4	4.0	6.9	7.4	7.0	6.5
NH <sub>4</sub> <sup>+</sup>	mg/L	14.5	11.0	18.1	0.4	0.7	1.6	1.4	3.3	2.4
Na⁺	mg/L	367.4	365.4	338.0	214.8	341.7	335.9	306.4	569.0	316.2
K <sup>+</sup>	mg/L	184.8	112.0	201.8	9.6	16.9	17.0	19.1	32.3	20.3
Mg <sup>2+</sup>	mg/L	2586.0	801.0	2654.0	1.1	8.0	2.7	80.1	15.5	20.6
Ca <sup>2+</sup>	mg/L	449.9	302.7	453.1	1.5	3.2	2.1	7.0	2.9	9.1
Fe <sup>2+</sup>	mg/L	2.31	0.07	0.03	0.04	0.06	0.13	0.03	0.07	0.11
Fe (total)	mg/L	10	9	1.26	-	-	-	0.13	-	-
Ва	μg/L	22.4	29.9	20.0	-	-	50.3	4.8	9.8	17.3
As	μg/L	4.9	5.8	15.9	-	-	18.8	16.8	83.1	43.5
Mn	μg/L	6640.4	40.8	79.9	-	-	4.3	< 1.0	8.5	14.2
Sb	μg/L	< 0.1	< 0.1	< 0.1	-	-	0.4	0.2	0.7	0.8
Zn	μg/L	< 50.0	< 50.0	< 50.0	-	-	6.5	< 5.0	< 100.0	6.1
Cu	μg/L	< 10.0	< 10.0	< 10.0	-	-	2.6	< 1.0	2.6	4.8
Cr	μg/L	< 1.0	< 1.0	1.1	-	-	< 0.1	< 0.1	0.5	0.2
Pb	μg/L	< 5.0	< 5.0	11.9	-	-	< 0.5	< 0.5	< 10.0	< 0.5
V	μg/L	< 1.0	< 1.0	< 1.0	-	-	< 0.1	< 0.1	1.2	0.5
Cd	μg/L	< 1.0	< 1.0	< 1.0	-	-	< 0.1	< 0.1	0.1	0.1
SO <sub>4</sub> <sup>2-</sup>	mg/L	10000	3100	8000	16	130	150	600	510	150
CO <sub>3</sub> <sup>2-</sup>	mg/L	0	0	0	-	-	58.9	187	209	0
HCO <sub>3</sub> -	mg/L	362	181	189	-	-	557	267	538	688
Cl <sup>-</sup>	mg/L	38.7	33.9	83.9	-	-	46.6	28.7	55.7	59.3
NO <sub>3</sub> -	mg/L	0.6	1.0	0.9	0.8	1.2	1.2	0.7	1.2	0.3
Total Charge (Cations)	meq/L	256.8	100.4	261.9	9.8	16.2	15.5	20.8	27.2	16.6
Total Charge	meq/L	215.2	68.5	172.0	0.3	2.7	15.5	23.9	28.0	16.1
(Anions)	- /I	0	0	0			E0.0	107	200	0
CO <sub>3</sub> <sup>2-</sup>	mg/L	0	191	180	-	_	58.9	187	209	0
HCO <sub>3</sub> -	mg/L	362	181	189	-	-	557	267	538	688
Total Alkalinity	mg/L CaCO <sub>3</sub>	297	148	155	-	-	555	531	790	565
Mg <sup>2+</sup>	mg/L	2586.0	801.0	2654.0	1.1	8.0	2.7	80.1	15.5	20.6
Ca <sup>2+</sup>	mg/L	449.9	302.7	453.1	1.5	3.2	2.1	7.0	2.9	9.1
Total Hardness	mg/L CaCO <sub>3</sub>	10862	3731	13267	13	44.9	22	396.5	77.0	118

Water chemistry at each sampling site was relatively unique (Table 3). Water from location 4100-1 had a higher concentration of dissolved iron than any other site. This sample also had a manganese level two orders of magnitude higher than water samples from the other two sites on the 4100-foot level. Site 4100-2 water had a much lower concentration of magnesium and lower total water hardness than water from sampling locations 4100-1 and 4100-3. Sampling site 4100-3 was the only location with water containing detectable levels of lead. Water from site 4850-1 had the lowest conductivity of any location. At the 4850-foot level, water from location 4850-4 was much harder than water from any of the other sites at this elevation: the 17 ledge samples (sites 4850-1 and 4850-3) had soft water, while water from the 4850-5 and 4850-6 sites was moderately hard. Water from the drift between the Ross Campus and the 17 Ledge (Samples 4850-5 and 4850-6) had arsenic levels much higher than water collected from the other sites.

Several significant differences in water chemistry were observed between the 4100-foot and 4850-foot levels (Table 4). The 4100-foot level had significantly higher conductivity readings, concentrations of cations (with the exceptions of sodium and iron), and total hardness readings than the 4850-foot level. However, the 4850-foot level had significantly higher mean pH, dissolved oxygen, and total alkalinity values than the 4100-foot level.

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Table 4. Mean (SD) Water Quality Characteristics from each Level

Parameter	Units	De <sub>l</sub>	P-Value	
raiailletei		4100	4850	r-value
N		3	6	
Air Temp	°C	23.6 (0.3)	26.3 (3.8)	0.293
Water Temp	°C	23.0 (0.5)	26.5 (4.6)	0.241
рН		7.5 (0.6)	8.4 (0.1)	0.005
Conductivity	mg/L TDS	7283.2 (2510.6)	1111.9 (439.9)	0.000
Air Pressure	mmHg	721.9 (1.3)	742.4 (3.7)	0.000
Dissolved Oxygen	mg/L	3.0 (1.3)	6.4 (1.2)	0.006
NH <sub>4</sub> <sup>+</sup>	mg/L	14.5 (3.6)	1.6 (1.1)	0.000
Na <sup>+</sup>	mg/L	356.9 (16.4)	347.3 (117.9)	0.896
K <sup>+</sup>	mg/L	166.2 (47.7)	19.2 (7.4)	0.000
Mg <sup>2+</sup>	mg/L	2013.7 (1050.7)	21.3 (29.7)	0.002
Ca <sup>2+</sup>	mg/L	401.9 (85.9)	4.3 (3.0)	0.000
Fe <sup>2+</sup>	mg/L	0.8 (1.3)	0.07 (0.04)	0.183
Fe (total)	mg/L	6.8 (4.8)	0.1	0.353
Ва	μg/L	24.1 (5.2)	20.5 (20.5)	0.784
As	μg/L	8.8 (6.1)	40.5 (30.9)	0.148
Mn	μg/L	2253.7 (3799.1)	6.8 (6.0)	0.275
Sb	μg/L	0.0 (0.0)	0.5 (0.3)	0.026
Zn	μg/L	0.0 (0.0)	3.1 (3.6)	0.203
Cu	μg/L	0.0 (0.0)	2.5 (1.9)	0.085
Cr	μg/L	0.4 (0.7)	0.2 (0.2)	0.565
Pb	μg/L	4.0 (6.9)	0.0 (0.0)	0.286
V	μg/L	0.0 (0.0)	0.4 (0.6)	0.266
Cd	μg/L	0.0 (0.0)	0.06 (0.06)	0.206
SO <sub>4</sub> <sup>2-</sup>	mg/L	7033.3 (3550.1)	259.3 (236.1)	0.002
CO <sub>3</sub> <sup>2-</sup>	mg/L	0.0 (0.0)	113.7 (100.6)	0.114
HCO <sub>3</sub> -	mg/L	244.0 (102.2)	512.5 (176.7)	0.068
Cl <sup>-</sup>	mg/L	52.2 (27.6)	47.6 (13.7)	0.780
NO <sub>3</sub> -	mg/L	0.8 (0.2)	0.9 (0.4)	0.784
<b>Total Charge (Cations)</b>	meq/L	206.4 (91.8)	17.7 (5.9)	0.001
Total Charge (Anions)	meq/L	151.9 (75.4)	14.4 (11.1)	0.002
CO <sub>3</sub> <sup>2-</sup>	mg/L	0.0 (0.0)	113.7 (100.6)	0.114
HCO <sub>3</sub> -	mg/L	244.0 (102.2)	512.5 (176.7)	0.068
Total Alkalinity	mg/L CaCO₃	200.0 (84.1)	610.3 (120.7)	0.004
Mg <sup>2+</sup>	mg/L	2013.7 (1050.7)	21.3 (29.7)	0.002
Ca <sup>2+</sup>	mg/L	401.9 (85.9)	4.3 (3.0)	0.000
Total Hardness	mg/L CaCO₃	9286.7 (4959.3)	111.9 (144.7)	0.002

# Discussion

The differences in water chemistry among the sites could be due to differences in rock mineral composition and microflora associated with each sampling location. The unique water chemistry at each site suggests that there is either little water movement among the sampling locations, or water chemistry changes as a result of water moving from site to site underground. For example, the relatively large differences in hardness between site 4100-2 compared to the other 4100-foot locations would appear to indicate a different water source. Although there is little published information regarding the underground water chemistry at SURF, the results of this study support those previously reported for two sites (17 Ledge and 4700 ramp) by Osburn et al. (2014).

This study is the first to report significant differences in water chemistry between levels at SURF. These differences include 100-fold differences in Ca<sup>2+</sup> and Mg<sup>2+</sup>, 9-fold differences in total hardness, and 10-fold differences in hydrogen ion concentration. Although very complex and not well characterized, some of these differences may be explained by the types of rock the water has moved through before coming to rest at our sampling sites. Another important difference is that the 4850-foot level was underwater from January 2008 until May 2009. This last explanation could be tested by further water surveys both above and below the 4530-foot level; the highest level to which the water rose (Heise & DUSEL Collaboration 2010). Additionally, the higher sulfate levels in water from the 4100-foot level could be caused by sulfide-oxidizing bacteria (Voordouw et al. 1996). Rock chemistry likely explains the relatively similar sodium levels at both levels (Davis et al. 2003). These significant differences in water chemistry also suggests that significant differences in the microorganism populations should be found between these levels.

Manganese levels were very high in water from site 4100-1. This is most likely due to the high dissolved iron concentration of the water, since manganese is often found in iron-rich minerals (Nova Scotia Department of the Environment, 2008). Very high arsenic levels, exceeding normal arsenic levels in Black Hills water (0.4-4.2 μg/L) (Williamson and Carter 2001) as well as the US EPA drinking water standard of 10 μg/L (United States Environmental Protection Agency 2001) were detected in the drift going to the 17 Ledge. This could be due to the samples actually touching the rock rather than sitting on a mud/sludge layer, because the rock surrounding SURF is naturally high in arsenopyrites (Davis et al. 2003).

The differences in magnesium and hardness from water collected at site 4850-4 in comparison to the other sites at the 4850-foot level could be because the water in this sample actually originated at the 4700-foot level. This sampling location was at a point where water from the 4700-foot level flowed down a ramp to the 4850-foot level. We do not know if samples taken from the 4700-foot level would produce similar results because we could not gain access to this level.

The results of this preliminary study describing the chemistry of water from different locations within SURF provide the basis for microbial research and further investigation into the sources and flow of water throughout the facility. Additional research is needed to determine the influence of rock mineral composition and microbiota on water chemistry at SURF, the possible movement of water among the sites, and the effect of flooding on the water chemistry of the 4850foot level.