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To: K. Rosenberger
M. Layton

From: M. Millings
J. Noonkester
L. Bagwell

Reviewed by:
M. Denham

cc: H. H. Burns M. Denham
S. Marra D. Kaplan
T. Oliver R. Aylward

Summary Dissolved Oxygen in Water Table Wells at SRS

The fate and transport modeling in the FTF and HTF Performance Assessments utilizes an independent waste release conceptual model (Denham, 2007). This waste release model assumes that water infiltrating the waste tanks is in equilibrium with atmospheric oxygen. SRNL staff performed a review of soil gas and groundwater data to evaluate this assumption. In particular, SRNL staff reviewed available geochemical data from the SRS Environmental Restoration Data Management System (ERDMS) in addition to various P Well studies and reports to determine summary statistics for dissolved oxygen (DO) for water table wells at the Savannah River Site. No soil gas data were found during this review. However, modeling of P Well water table data near the F Area Tank Farm provides insight into the fugacity (or approximate vapor pressure) of oxygen in the vadose zone at the water table.

Results from this exercise show that the modeling assumption of water being in equilibrium with the atmosphere is reasonable, if not slightly conservative. The F-Area tanks are located in the vadose zone, so it can be assumed that the actual partial pressure of oxygen to which the tanks will be exposed is between atmospheric oxygen and the partial pressure in equilibrium with groundwater DO measurements. Portions of many H-Area tanks are below the water table and, for these portions, it can be assumed that DO values measured in groundwater represent the partial pressure of oxygen to which they will be exposed. In modeling of the degradation of tank grout reducing capacity, the rate of degradation is roughly proportional to the partial pressure of oxygen in equilibrium with infiltrating water. Hence, the assumption that infiltrating water is in equilibrium with atmospheric oxygen is the worst case.

DO measurements in typical P Wells screened in the water table range from 5.6 to 8.9 mg/L with an average of 7.7 mg/L and a median of 7.6 mg/L. In addition to P Well data, data from the ERDMS database was also reviewed to gain a rough estimate of DO measurements in other SRS water table wells. DO measurements averaged 5.3 mg/L with a median of 5.5 mg/L, however these data likely reflect sites impacted by operations and/or remediation systems.

Background

Solubility and Measurement of Oxygen in Groundwater

Oxygen solubility in Coastal Plain groundwater is primarily a function of temperature, barometric pressure, and salinity. With the low salinities and moderate temperatures (~18 to 23 C) typical of the water table aquifers at SRS, oxygen solubility is expected to range from approximately 8 to 10 mg/L. As reference, Table 1 presents oxygen solubility in fresh surface water as a function of temperature assuming normal air composition, moist air, a barometric pressure at 760 mm Hg (or 1 atm) and 0 salinity. The highlighted box represents typical oxygen solubilities expected in water table aquifers at SRS. Note that elevated salinities and lower barometric pressures (from low pressure weather fronts) will slightly decrease oxygen solubility.

DO values are typically measured in the field using membrane electrochemical sensors. Traditional field oxygen sensors operate by measuring a changing electrical current produced by a reaction of the analyte (e.g. oxygen) with a sensing material that catalyzes the reaction. The amount of current is proportional to the rate of oxygen reduction and the amount of oxygen available for the reaction. Because the sensing material is generally not specific to oxygen, these sensors often use a membrane or barrier to limit sensor exposure to other reactive substances. These sensors are useful for making multiple or continuous dissolved oxygen measurements in the field. They typically involve easy one-point calibrations by measuring the oxygen level in water-saturated air and correcting for barometric pressure, temperature and salinity. Many of these sensors have detection levels of approximately 2 umol/L (0.06 mg/L) (White et al, 1990), with an accuracy of approximately ±3 umol/L (±0.1 mg/L) and a precision of ±1.5 umol/L (±0.05 mg/L) (APHA, 1998).

Many problems associated with the electrochemical sensors involve the membrane. Since electrochemical sensors rely on oxygen diffusing through the membrane, they can be limited by the amount of diffusion, which can be problematic for small sample volumes. The delicate nature of the membranes can lead to erroneous measurements if the membrane is damaged; an air bubble is trapped beneath the membrane when the membrane is installed; or by "poisoning" effects (fouling) produced by hydrogen sulfide and organic compounds. Long-term effects on the performance of these electrochemical membrane sensors include consumption of the reactant (e.g., oxidation of the lead anode), and aging or degradation of the barrier (membrane) or electrolyte. These effects can lead to changing response and the need for frequent calibration. Despite these possible issues, the electrochemical sensors are often the preferred method of choice for measuring DO in the field. With careful calibration and use, the electrochemical sensors yield good quality DO data in the field, providing care in sampling is taken to eliminate contamination by atmospheric oxygen.

For this review, DO data from P Wells and other SRS water table wells were compiled. DO values beyond typical oxygen solubilities (i.e., greater than 100% saturation) were considered suspect and likely the result of problems with the probe membrane or other parts of the sensor.

P Wells

During the 1980's, SRNL (then known as the Savannah River Laboratory) installed a series of observation well clusters in remote and background areas (upgradient of operating facilities) at the Savannah River Site. These well clusters are referred to as the P Wells and are part of SRNL's current regional water level monitoring program. Since their installation, SRNL has periodically monitored these wells using the data to determine overall changes and impacts to the regional groundwater systems, to establish horizontal and vertical gradients, to determine geochemistry of the units, and to provide lithologic information for coastal plain sediments down to bedrock.

In recent years, P Well data have been utilized in local and regional groundwater flow models performed at SRS in support of various Performance Assessments, the Composite Analysis, the Underflow Study conducted by the USGS, remedial action evaluations, and facility siting(s). In addition, data from the P Wells have provided the ability to track long-term water levels and to document the "head reversal" underneath SRS that protects drinking water aquifer.

For our analysis, the P Wells are considered the primary data source because 1) the screen zones are well documented and we are confident that the monitoring well data reflect water table wells (as opposed to deeper aquifers) and 2) the data reflect background conditions un-impacted by existing plumes, which might affect DO. Figure 1 provides the location of the P Wells used in this review. Note that the FC-2 cluster is located closest to the F Tank Farm.

ERDMS

The Area Completion Projects (ACP) ERDMS database serves as a comprehensive environmental database management system for the automated collected, review, storage and dissemination of environmental data related to SRS waste sites and watersheds. Data from ERMDS reflect monitoring well data from "D" wells, which are typically considered water table wells at SRS. The data includes all data available regardless of whether the data were collected during special tests or at on-going remediation sites.

Soil Gas

A significant volume of soil gas data exists, mostly for SRS's RCRA/CERCLA waste sites, including several sites in the General Separations Area where the F-Area tanks are located. However, because these data were collected as part of waste site characterization, the target soil gases were mostly contaminants. We reviewed the soil gas data for the Burial Ground Areas (Pirkle and Masdea, 1992) and found no oxygen data or other data that would be useable for this effort

Analysis and Interpretations

Figure 2 provides a summary of the DO data for the available P Well water table measurements. One of the water table wells, P27D, typically exhibits low DO. This monitoring well has also shown elevated total organic carbon, which may account for the low DO (e.g., the oxygen may be consumed as organic matter decays). DO levels in the remaining water table wells range from 5.6 to 8.9 mg/L with an average of 7.7 mg/L and a median of 7.6 mg/L. This average is slightly less than the values expected for fully saturated fresh surface water (8 to 10 mg/L).

Figure 3 provides a 2005 depth profile for the FC cluster, the P Well cluster nearest the F Area Tank Farm. DO for the water table wells (the Upper Aquifer Zone of the Upper Three Runs Aquifer) ranged from 6.7 to 7.9 mg/L. DO gradually decreases with depth as expected since underlying aquifers would have less input of fresh surface water or rainwater with higher DO concentrations.

DO measurements from other water table wells across SRS range from little DO (0.1 mg/L) to saturated with oxygen. DO in the ~1471 measurements averaged 5.3 mg/L with a median of 5.5 mg/L. However, it should be noted that these statistics reflect all available "D" well data from ERDMS regardless of location or timing (e.g., whether the data were collected at seeplines, within contaminant plumes, at ongoing remediation sites, or during special tests). Contaminant plumes can lower DO levels due to the presence of organics and higher salinity. DO values greater than 9.5 mg/L were not considered in the analysis since they likely reflect non-typical conditions or instrument problems.

As part of this review, sampling data collected in 2005 from FC-2F, a water table P Well near F Area, was speciated using Geochemist's Workbench to calculate oxygen fugacity. Results yielded an oxygen fugacity of 0.152, which is only slightly less than an open system (0.2 fugacity).

The waste release model by Denham (2007) assumes that water infiltrating the waste tanks is in equilibrium with atmospheric oxygen and uses a dissolved oxygen value of 8.0 mg/L. Results from this review, which includes DO measurements from water table wells and modeling of P Well water table data, indicate that the modeling assumption of water being in equilibrium with the atmosphere is reasonable, if not slightly conservative.

References

ALPHA. 1998. Standard Methods for the Examination of Water and Wasterwater. 20th Edition. American Public Health Association, Washington, D. C.

Colt, J. 1984. Computation of Dissolved Gas Concentrations in Water as Functions of Temperature, Salinity, and Pressure. America Fisheries Society Special Publication 14, Bethesda, Maryland. 154p.

Denham, M. E. 2007. Conceptual Model of Waste Release from the Contaminated Zone of Closed Radioactive Waste Tanks. WSRC-STI02007-00544. Washington Savannah River Company, Aiken, SC, November 2007.

Pirkle, R. J. and D. J. Masdea. 1992. Final Report Soil Gas Investigations at the Burial Ground Complex, Savannah River Site Augusta, 1991-May, 1992. Microseeps, University of Pittsburgh Applied Research Center, Pittsburgh, PA.

White, A. F., M. L. Peterson, and R. D. Solbau. 1990. Measurement and Interpretation of Low Levels of Dissolved Oxygen in Ground Water. Ground Water, v.28, n.4, p.584-590.

Table 1: Solubility of Oxygen (mg/L) as a Function of Temperature (from Colt, 1984)

Temp (C)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	14.602	14.561	14.520	14.479	14.438	14.398	14.358	14.318	14.278	14.238
1	14.198	14.159	14.120	14.081	14.042	14.004	13.965	13.927	13.889	13.851
2	13.813	13.776	13.738	13.701	13.664	13.627	13.591	13.554	13.518	13.482
3	13.445	13.410	13.374	13.338	13.303	13.268	13.233	13.198	13.163	13.128
4	13.094	13.060	13.025	12.991	12.957	12.924	12.890	12.857	12.824	12.790
5	12.757	12.725	12.692	12.659	12.627	12.595	12.563	12.531	12.499	12.467
6	12.436	12.404	12.373	12.342	12.311	12.280	12.249	12.218	12.188	12.158
7	12.127	12.097	12.067	12.037	12.008	11.978	11.949	11.919	11.890	11.861
8	11.832	11.803	11.774	11.746	11.717	11.689	11.661	11.632	11.604	11.577
9	11.549	11.521	11.493	11.466	11.439	11.412	11.384	11.357	11.331	11.304
10	11.277	11.251	11.224	11.198	11.172	11.145	11.119	11.093	11.068	11.042
11	11.016	10.991	10.965	10.940	10.915	10.890	10.865	10.840	10.815	10.791
12	10.766	10.741	10.717	10.693	10.669	10.645	10.620	10.597	10.573	10.549
13	10.525	10.502	10.478	10.455	10.432	10.409	10.386	10.363	10.340	10.317
14	10.294	10.271	10.249	10.226	10.204	10.182	10.160	10.137	10.115	10.094
15	10.072	10.050	10.028	10.007	9.985	9.964	9.942	9.921	9.900	9.879
16	9.858	9.837	9.816	9.795	9.774	9.753	9.733	9.712	9.692	9.672
17	9.651	9.631	9.611	9.591	9.571	9.551	9.531	9.512	9.492	9.472
18	9.453	9.433	9.414	9.395	9.375	9.356	9.337	9.318	9.299	9.280
19	9.261	9.242	9.224	9.205	9.187	9.168	9.150	9.131	9.113	9.095
20	9.077	9.058	9.040	9.022	9.004	8.987	8.969	8.951	8.933	8.916
21	8.898	8.881	8.863	8.846	8.829	8.812	8.794	8.777	8.760	8.743
22	8.726	8.709	8.693	8.676	8.659	8.642	8.626	8.609	8.593	8.576
23	8.560	8.544	8.528	8.511	8.495	8.479	8.463	8.447	8.431	8.415
24	8.400	8.384	8.368	8.352	8.337	8.321	8.306	8.290	8.275	8.260
25	8.244	8.229	8.214	8.199	8.184	8.168	8.153	8.139	8.124	8.109
26	8.094	8.079	8.065	8.050	8.035	8.021	8.006	7.992	7.977	7.963
27	7.949	7.934	7.920	7.906	7.892	7.878	7.864	7.850	7.836	7.822
28	7.808	7.794	7.780	7.766	7.753	7.739	7.725	7.712	7.698	7.685
29	7.671	7.658	7.645	7.631	7.618	7.605	7.592	7.578	7.565	7.552
30	7.539	7.526	7.513	7.500	7.487	7.475	7.462	7.449	7.436	7.424
31	7.411	7.398	7.386	7.373	7.361	7.348	7.336	7.324	7.311	7.299
32	7.287	7.274	7.262	7.250	7.238	7.226	7.214	7.202	7.190	7.178
33	7.166	7.154	7.142	7.130	7.119	7.107	7.095	7.083	7.072	7.060
34	7.049	7.037	7.026	7.014	7.003	6.991	6.980	6.969	6.957	6.946
35	6.935	6.924	6.912	6.901	6.890	6.879	6.868	6.857	6.846	6.835
36	6.824	6.813	6.802	6.791	6.781	6.770	6.759	6.748	6.738	6.727
37	6.716	6.706	6.695	6.685	6.674	6.664	6.653	6.643	6.632	6.622
38	6.612	6.601	6.591	6.581	6.570	6.560	6.550	6.540	6.530	6.520
39	6.509	6.499	6.489	6.479	6.469	6.460	6.450	6.440	6.430	6.420
40	6.410	6.400	6.391	6.381	6.371	6.361	6.352	6.342	6.333	6.323

Note: assumes normal air composition, moist air, a barometric pressure at 760 mm Hg (or 1 atm) and 0 salinity; shaded box shows typical oxygen solubilities expected in water table aquifers at SRS

Figure 1. Location of P Wells

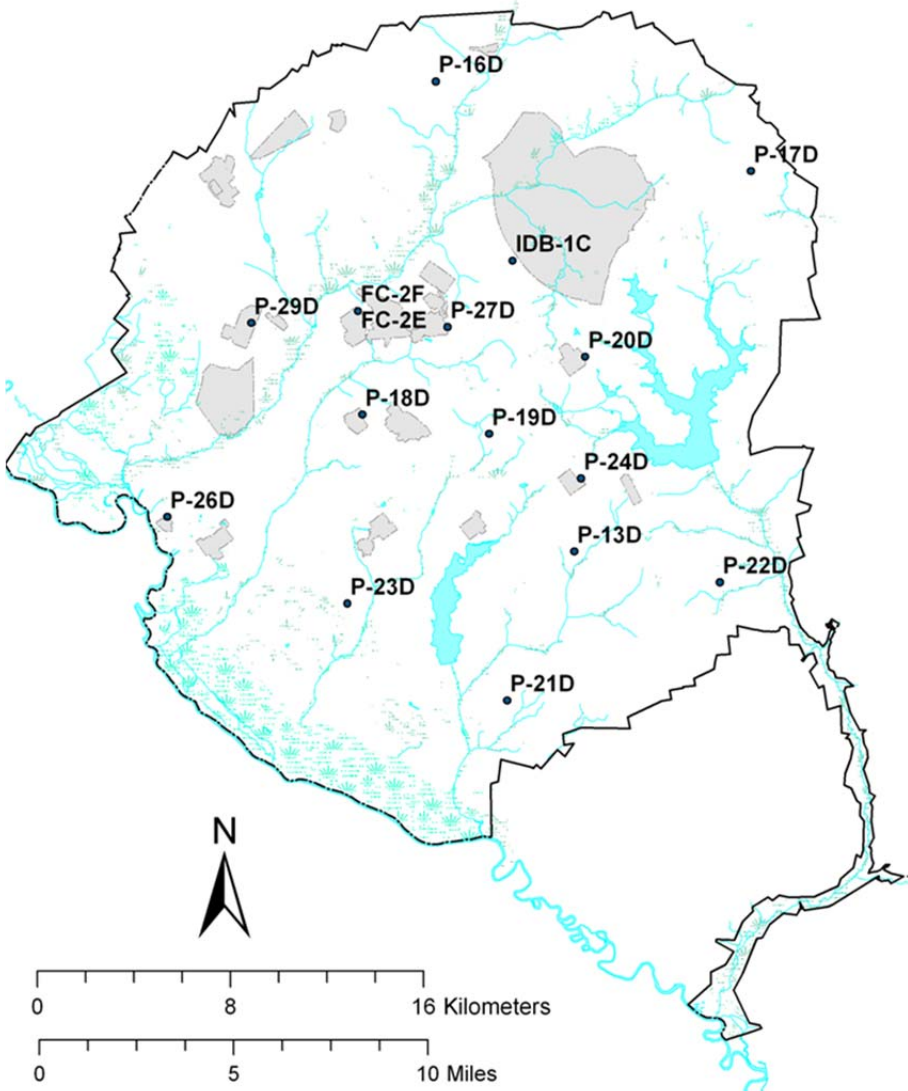


Figure 2. Summary DO data from P Well Water Table Wells

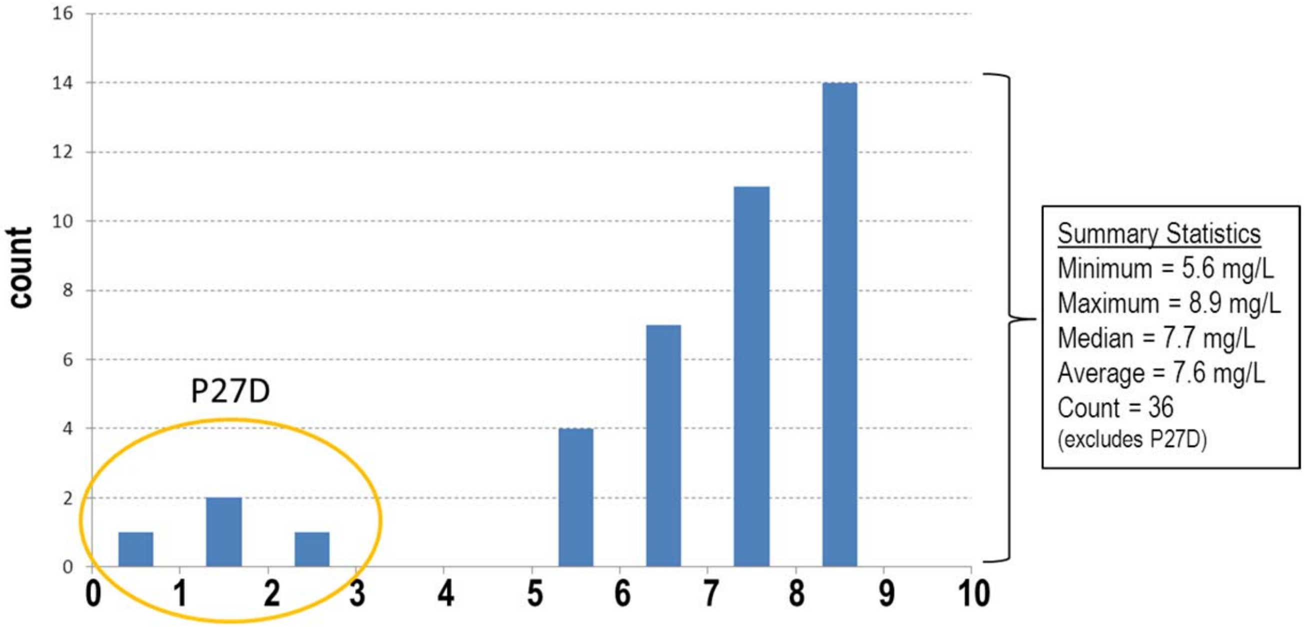
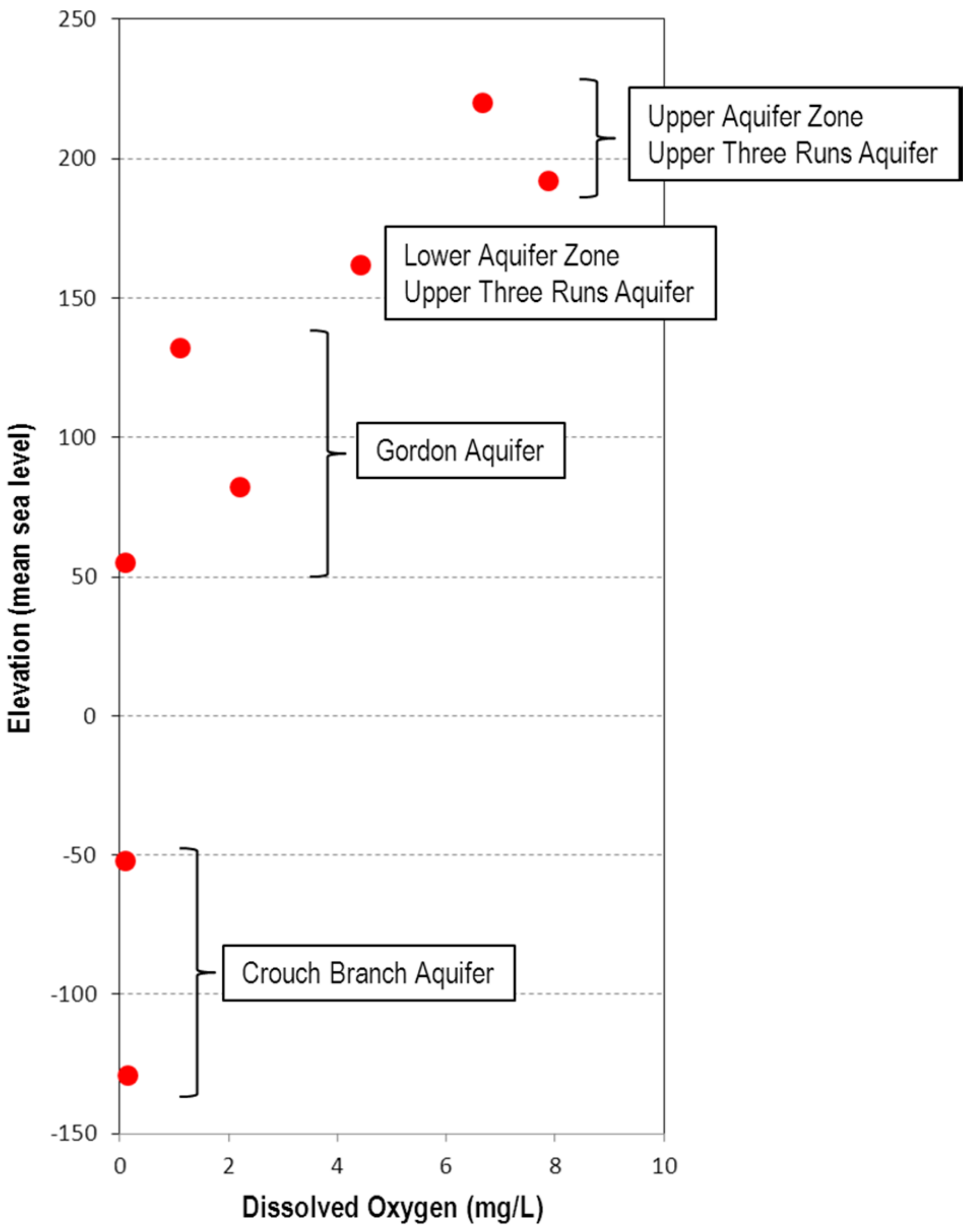


Figure 3. DO Depth Profile in FC Cluster



Attachment 1: P Well Data

General Location	Well ID	Sample Date	Temperature (Celsius)	DO (mg/l)	ORP (mV)	Source	UTME	UTMN
adjacent to C reactor	P-18D	7/5/1994	24.08	8.68	114	WSRC-NB-94-21	437355.75	3679339.58
adjacent to C reactor	P-18D	4/1/2002	18.85	8.5	135	WSRC-NB-98-00128	437355.75	3679339.58
adjacent to C reactor	P-18D	4/2/2002	26.81	7.27	91	WSRC-NB-98-00128	437355.75	3679339.58
adjacent to F Area; part of P28 cluster	FC-2E	2/5/1989	20.40	5.62	239	P Well database	437164.46	3683618.75
adjacent to F Area; part of P28 cluster	FC-2E	6/16/1994	21.99	7.88	181	WSRC-NB-94-21	437164.46	3683618.75
adjacent to F Area; part of P28 cluster	FC-2E	4/1/2002	21.09	6.78	218	WSRC-NB-98-00128	437164.46	3683618.75
adjacent to F Area; part of P28 cluster	FC-2E	4/2/2002	21.50	6.92	182	WSRC-NB-98-00128	437164.46	3683618.75
adjacent to F Area; part of P28 cluster	FC-2E	7/31/2002	21.22	8.14	181	WSRC-NB-98-00128	437164.46	3683618.75
adjacent to F Area; part of P28 cluster	FC-2E	11/4/2005	20.96	7.87	328	P Well database	437164.46	3683618.75
adjacent to F Area; part of P28 cluster	FC-2F	6/16/1994	22.88	8.49	167	WSRC-NB-94-21	437162.96	3683620.30
adjacent to F Area; part of P28 cluster	FC-2F	11/3/2005	23.08	6.66	261	P Well database	437162.96	3683620.30
adjacent to H Area	P-27D	2/19/1985	19.00	1.23	17	P Well database	440875.24	3682966.02
adjacent to H Area	P-27D	4/1/2002	19.93	0.92	224	WSRC-NB-98-00128	440875.24	3682966.02
adjacent to H Area	P-27D	4/4/2002	20.03	1.31	152	WSRC-NB-98-00128	440875.24	3682966.02
adjacent to H Area	P-27D	8/1/2002	21.61	2.18	157	WSRC-NB-98-00128	440875.24	3682966.02
adjacent to P reactor	P-24D	2/7/1985	19.90	7.69	92	P Well database	446400.39	3676707.19
adjacent to P reactor	P-24D	7/12/1994	21.21	8.94	130	WSRC-NB-94-21	446400.39	3676707.19
adjacent to P reactor	P-24D	4/1/2002	19.96	8.74	189	WSRC-NB-98-00128	446400.39	3676707.19
adjacent to P reactor	P-24D	4/4/2002	20.18	8.95	151	WSRC-NB-98-00128	446400.39	3676707.19
adjacent to R reactor	P-20D	8/19/1994	21.12	7.46	163	WSRC-NB-94-21	446587.36	3681733.86
adjacent to R reactor	P-20D	5/22/1995	21.4	6.45	158	WSRC-NB-94-343	446587.36	3681733.86
adjacent to R reactor	P-20D	4/1/2002	20.80	7.72	188	WSRC-NB-98-00128	446587.36	3681733.86
adjacent to R reactor	P-20D	4/4/2002	21.32	5.56	177	WSRC-NB-98-00128	446587.36	3681733.86
adjacent to R reactor	P-20D	7/30/2002	20.96	6.52	164	WSRC-NB-98-00128	446587.36	3681733.86
B area	P-29D	2/18/1985	20.80	7.33	237	P Well database	432756.72	3683130.98
B area	P-29D	5/25/1994	20.50	8.42	307	WSRC-NB-94-21	432756.72	3683130.98
center of site; no facilities nearby	P-19D	12/6/1984	20.20	6.27	183	P Well database	442603.10	3678542.15
center of site; no facilities nearby	P-19D	5/5/1994	18.50	8.5	255	WSRC-NB-94-21	442603.10	3678542.15

General Location	Well ID	Sample Date	Temperature (Celsius)	DO (mg/l)	ORP (mV)	Source	UTME	UTMN
N boundary of site; no facilities nearby	P-16D	6/29/1995	21.20	8.9	240	WSRC-NB-94-343	440388.32	3693111.31
NE boundary of site; no facilities nearby	P-17D	5/5/1994	19.40	6.2	150	WSRC-NB-94-21	453444.12	3689404.85
NE boundary of site; no facilities nearby	P-17D	9/16/1994	20.10	5.84	-34	WSRC-NB-94-21	453444.12	3689404.85
NE boundary of site; no facilities nearby	P-17D	5/9/1995	20.20	8.69	-33	WSRC-NB-94-343	453444.12	3689404.85
SE site; no facilities nearby	P-13D	5/5/1994	18.60	8.3	246	WSRC-NB-94-21	446124.24	3673679.83
SE site; no facilities nearby	P-21D	12/6/1985	18.30	7.54	132	P Well database	443340.26	3667530.22
SE site; no facilities nearby	P-21D	8/23/1994	18.60	7.11	145	WSRC-NB-94-21	443340.26	3667530.22
SE site; no facilities nearby	P-22D	2/21/1985	19.70	8.43	117	P Well database	452153.11	3672418.20
SE site; no facilities nearby	P-22D	5/5/1994	18.40	7.4	194	WSRC-NB-94-21	452153.11	3672418.20
SE site; no facilities nearby	P-22D	9/15/1994	18.80	8.69	262	WSRC-NB-94-21	452153.11	3672418.20
SW site; no facilities nearby	P-23D	4/1/2002	27.02	7.94	249	WSRC-NB-98-00128	436728.99	3671541.76
T Area	P-26D	8/29/1994	19.00	6	255	WSRC-NB-94-21	429265.66	3675114.85