

ANALYSIS OF GROUNDWATER QUALITY SAMPLING METHODS

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ABSTRACT

In the complex hydrogeology of the Piceance Basin Colorado and in the oil shale region in general, the location and construction of monitoring wells play a significant role in determining the nature of the water quality data collected. In addition, the methods used to collect samples have an appreciable influence on monitoring data.

Data collected by pumping of alluvial wells on Tract C-b and USGS deep aquifer wells in the Piceance Basin indicate that appreciable changes in water quality can occur during the pumping period. When wells are bailed to collect samples, care must be taken to collect samples consistently from the same aquifer interval. Vertical profiles of water quality measured on Tract C-a show significant changes with depth in deep aquifer wells.

Field studies such as these provide the basis for recommendation of groundwater quality monitoring procedures for oil shale development. Sampling methods must provide consistent and representative water quality samples in order to both characterize the hydrogeologic systems and to serve as monitoring tools.

INTRODUCTION

Tempo's Water Resources Program has been conducting an in-depth evaluation of groundwater quality monitoring for oil shale development. One of the initial observations of this analysis was the wide range of concentration reported for various water quality constituents for the major bedrock aquifers in the Piceance Basin. A small sampling of these ranges is shown in Table 1.

Some of this divarication can be explained natural variability in the hydrogeochemical system. However, the observed data variability is also appreciably influenced by such factors as well construction and sampling methods. A series of sampling activities was initiated to test this hypothesis and to arrive at some indication of the extent of the well construction/sampling influences. Some of the

results of this testing program are summarized in this paper.

Table 1. Range of water quality observations - Tract C-b, 1974-76.

<u>CONSTITUENT</u>	<u>UPPER AQUIFER</u>	<u>LOWER AQUIFER</u>
CONDUCTIVITY	800 - 4,200	630 - 45,000
pH	8.1 - 9.1	8.1 - 9.3
TOC	1 - 9	1 - 40
DOC	NO DATA	2 - 175
NH ₃	0.1 - 7.9	0.1 - 200
HCO ₃	340 - 2,100	100 - 25,000
Ca	3 - 120	2 - 220
Cl	2 - 510	1 - 9,300
As	<0.001 - 0.06	0.001 - 0.02
Ba	0.009 - 0.6	0.02 - 8
B	0.01 - 18	0.05 - 400
F	0.1 - 190	4 - 48
Hg	<0.0003 - 0.0031	<0.00003 - 0.0027

WELL SAMPLING BY PUMPING

Of the various approaches commonly utilized to sample wells, pumping is the generally preferred method from a strictly technical standpoint. Combined consideration of cost and effectiveness is a more complex issue and this general preference may not be strictly true.

The major sampling question related to pumping is the variation in water quality with pumping time. Several rules-of-thumb exist, such as pumping two well volumes (the volume of water standing in the well bore) before sample collection. However, the question of variation in water quality with time (or cumulative pumped volume) is not that straight forward, as shown by field data from the Piceance Basin.

During the Spring of 1980, the variation of water quality with pumping time was evaluated by sampling alluvial wells on Federal Lease Tract C-b. Pumping is the method used on Tract C-b to sample alluvial wells as part of the developer's environmental monitoring program. During this survey, two types of data were collected. At frequent intervals, pH, temperature and specific conductance (conductivity) of the well discharge were measured in the field. In addition, at selected intervals samples were collected for more extensive chemical analysis.

Figure 1 shows the changes in conductivity with well discharge of Well A-2. A decline from nearly 1400 $\mu\text{hos/cm}$ to a stable level of about 1300 $\mu\text{hos/cm}$ occurred during the discharge of the first two well volumes. During the pumping of Tract C-b Well A-6, a quick increase of about 400 $\mu\text{hos/cm}$ (40 percent) was observed very soon after the initiation of pumping (Figure 2). The implication of these observations is that the selection of sampling method (e.g. bailing water standing in the well bore vs. pumping) and the volume removed prior to sampling are key influences on the results of water quality monitoring. It should be noted that approximately monthly, samples are bailed from these wells for analysis of pH, conductivity and temperature. These bailed-sample data may contribute to observed water quality variability when combined with the quarterly pumped-sample data.

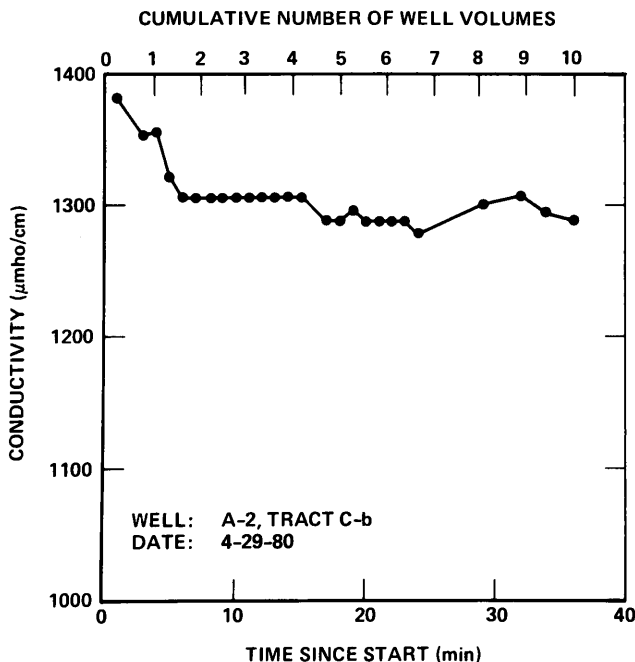


Figure 1. Variation in specific conductance with continued pumping, alluvial Well A-2, Tract C-b, 1980.

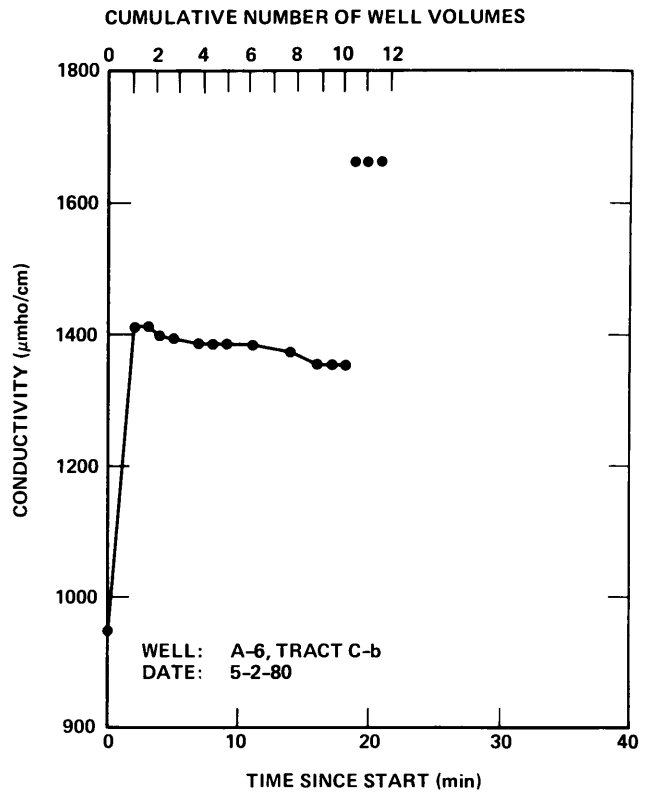


Figure 2. Variation in specific conductance with continued pumping, alluvial Well A-6, Tract C-b, 1980.

The decline in conductivity with pumping observed at Tract C-b alluvial Well A-2 is also reflected in TDS and calcium concentration data (Table 2). The concentrations of other major inorganic ions was relatively stable through the pumping period, and slight increases are noted (after initiation of pumping) for several constituents. Most of the trace constituents (arsenic, boron, and selenium) and DOC were stable through the test period. Potassium, fluoride and ammonia were variable with continued pumping. Water quality data for Well A-6 are somewhat inconsistent with the observed conductivity increases during pumping.

The U.S. Geological Survey (USGS) has installed 24 deep aquifer wells in the Piceance Basin. Typical well construction is shown in Figure 3. The open interval in these wells is several hundred feet (depending on the depth of the Mahogany Zone) in the upper aquifer zone and 300 feet in the lower aquifer zone.

Table 2. Water chemistry of samples collected after discharge of varying well volumes, Alluvial Wells A-6 and A-2, Tract C-b, 1980.

CONSTITUENT	WELL							
	A-6				A-2			
	WELL VOLUMES DISCHARGED							
	0	3	6	10	0	2.5	3	10
TDS	950	1000	990	1000	1200	900	890	880
CALCIUM	120	120	120	130	120	120	97	—
MAGNESIUM	58	66	68	71	72	71	72	70
SODIUM	150	150	160	170	120	130	130	130
POTASSIUM	3.9	2.7	2.8	2.9	2.9	2.7	3.5	1.8
BICARBONATE	530	480	500	500	440	470	460	460
CARBONATE	—	—	—	—	<1	<1	<1	<1
SULFATE	270	320	260	300	260	300	290	270
CHLORIDE	60	53	57	56	49	58	60	54
FLUORIDE	0.5	0.5	0.5	0.5	0.6	1.3	0.9	1.0
AMMONIA	0.8	1.0	0.3	0.6	<0.4	0.2	0.1	0.4
ARSENIC	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
BORON	0.2	0.1	0.2	0.2	0.1	0.1	0.1	0.1
MERCURY	<0.0002	<0.0002	<0.0002	<0.0002	0.0002	0.0002	<0.0002	0.0002
SELENIUM	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DOC	2	2	<1	3	6	8	5	7

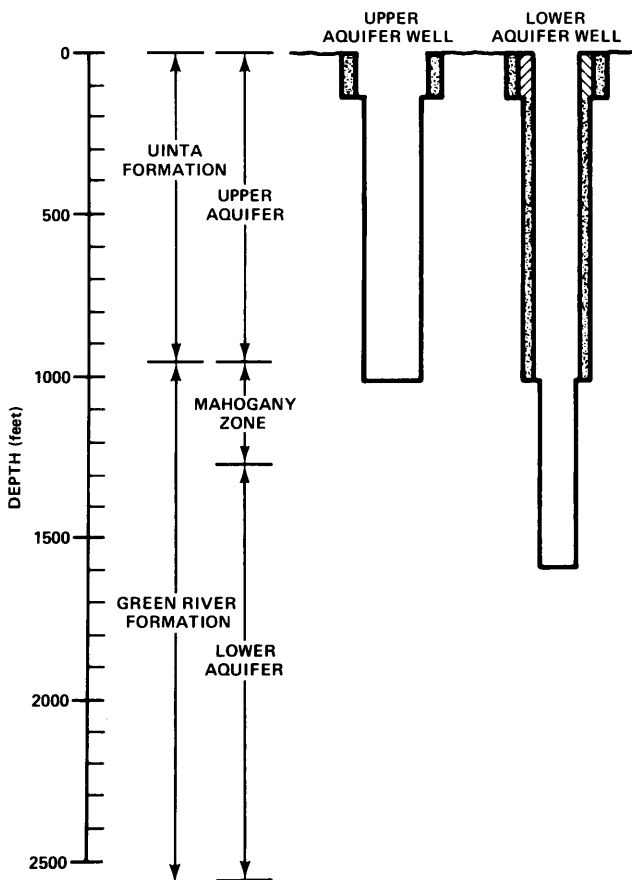


Figure 3. USGS upper and lower aquifer monitoring well design.

As shown in Figures 4 thru 6, several types of variation in specific conductance (conductivity) were observed. In some cases an initial rapid and large change was measured (Figure 4). Figure 4 shows a drop of about 750 $\mu\text{mhos/cm}$ (about 40 percent) from the initial well discharge conductivity in a period of a few minutes. Gradually a fairly stable level is reached. Clearly water bailed from this well (assuming it samples the initial well discharge) would be very different from water collected after several minutes of pumping.

In Core Hole #3, conductivity steadily declined throughout the 100-minute aquifer test (Figure 5). Over this time period, the conductivity declined to about 20 percent of the initial observation.

Increasing conductivity with time was observed in Well TH 75-1B (Figure 6). During the test of Well TH 75-1B the conductivity was fairly stable at around 30,000 $\mu\text{mhos/cm}$ until 80 to 90 minutes into the test. The conductivity at this point increased to about 58,000 $\mu\text{mhos/cm}$ in a very short period and appeared to stabilize at this higher conductivity.

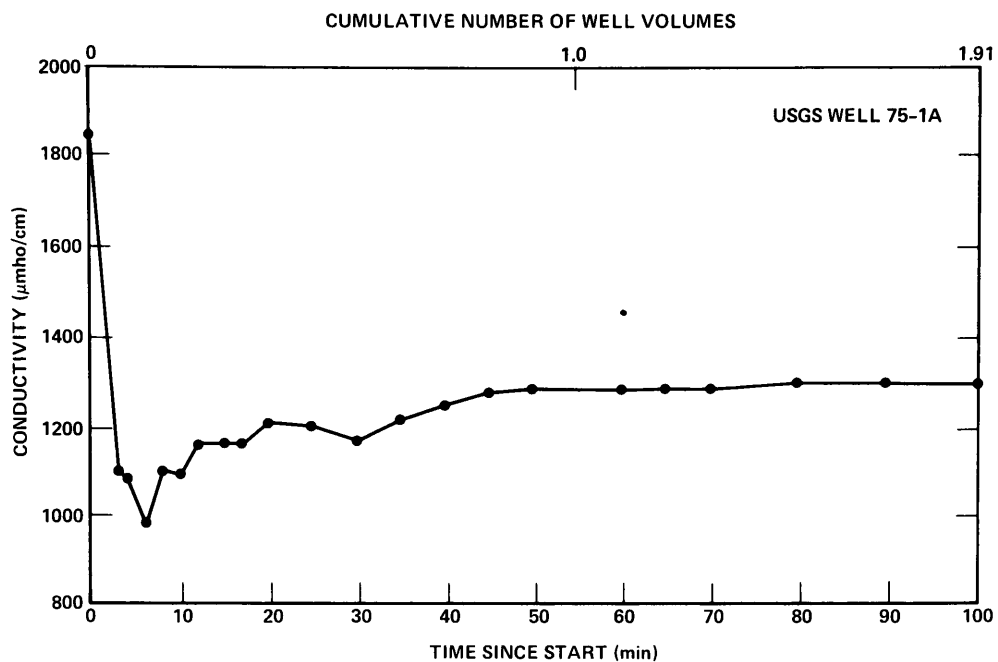


Figure 4. Variation in specific conductance with continued pumping, USGS Well 75-1A, 1980.

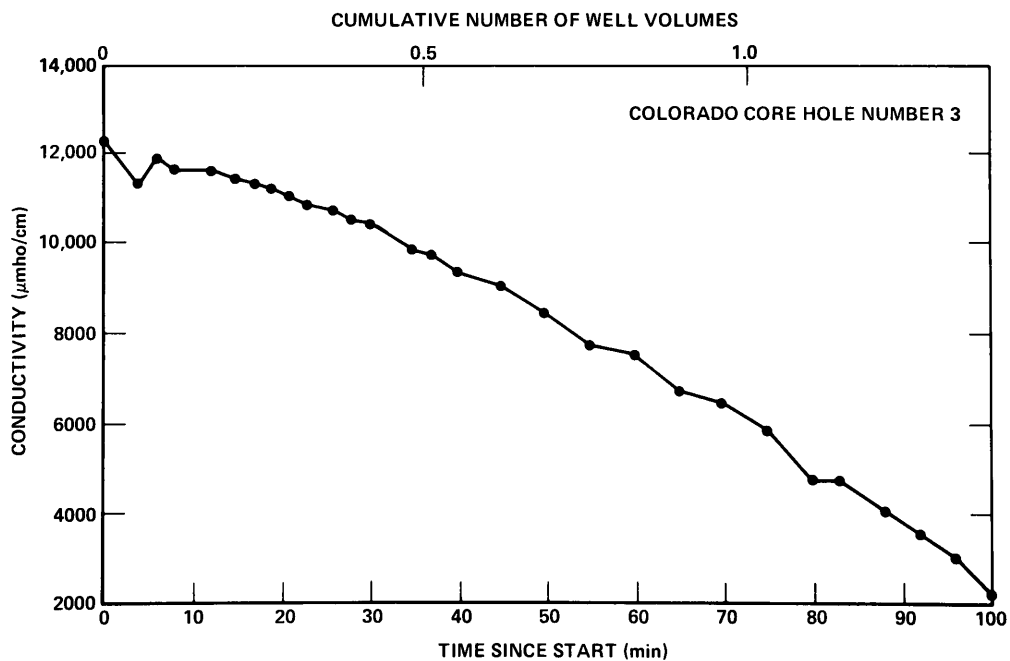


Figure 5. Variation in specific conductance with continued pumping, USGS Core Hole Number 3, 1980.

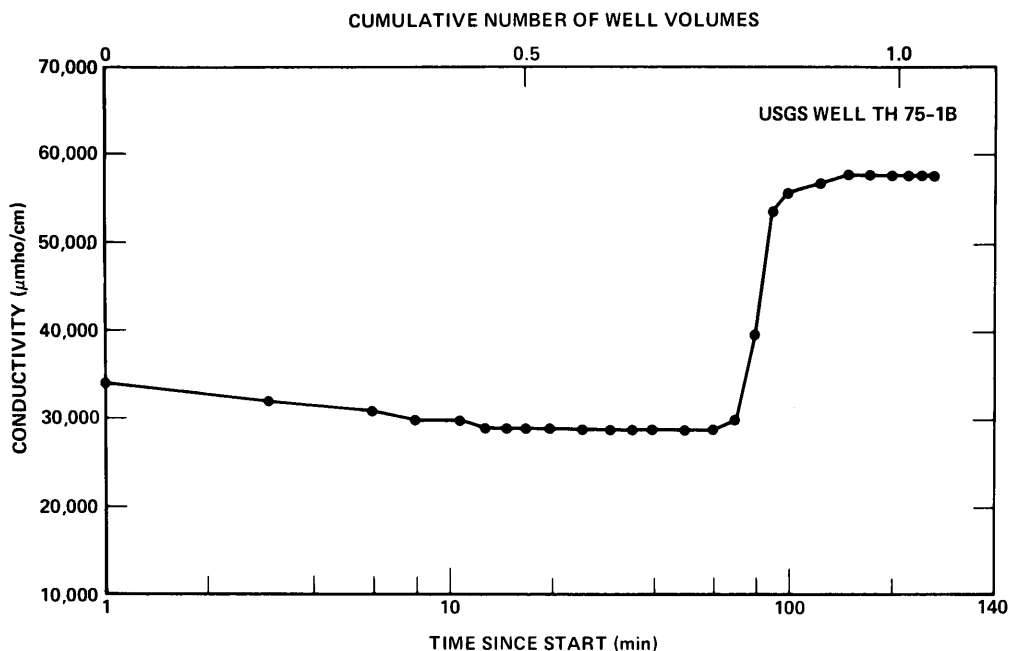


Figure 6. Variation in specific conductance with continued pumping, USGS Well 75-1B, 1980.

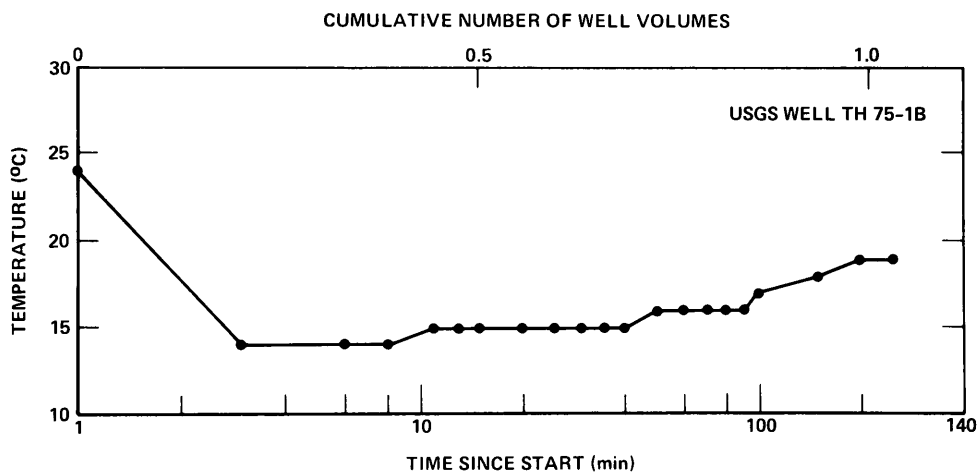


Figure 7. Variation of temperature of pumped discharge, USGS Well 75-1B, 1980.

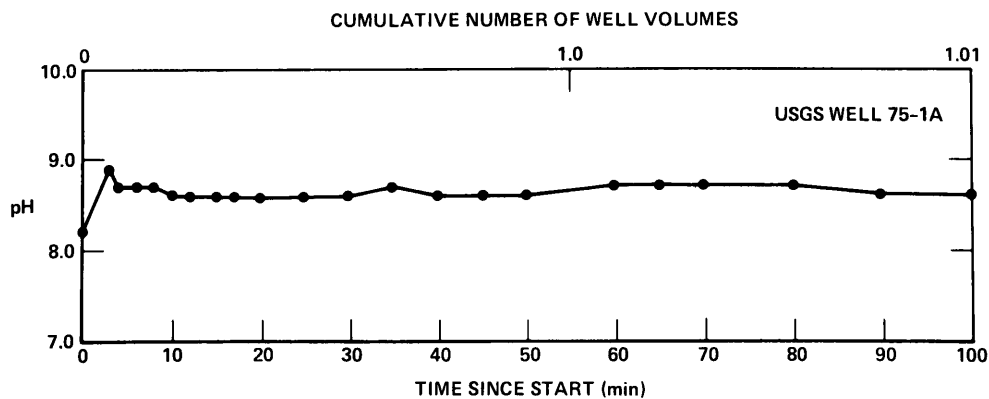


Figure 8. Variation in pH with continued pumping, USGS Well 75-1A, 1980.

Other constituents monitored in the field also changed during the pumping period. For example, at Well TH 75-1B, the temperature of the well discharge declined considerably at first and then appeared to be increasing (Figure 7). The pH of Well 75-1A showed an initial increase of nearly one pH unit and then stabilized after about 10 minutes of pumping (Figure 8).

These patterns of change in water quality are also reflected in the more detailed water chemistry analysis (Table 3). The large change in conductivity observed during pumping of USGS Well TH 75-1A is repeated for several major inorganic ions (potassium, sodium, bicarbonate, chloride and sulfate), alkalinity, TDS, and fluoride concentrations. Most of the trace constituents (arsenic, boron, mercury and selenium) were largely unchanged through the pumping test. It is interesting that calcium, magnesium, and DOC concentrations increase during the pumping period.

Piceance Basin are composed of several fractured permeable intervals. The water quality and hydraulic characteristics of these zones is quite variable and clearly can influence the results of water quality monitoring. Vertical variations within a given well and changes over time are factors to be considered in collecting and utilizing these monitoring data.

Changes in water quality with continued pumping result from the interaction of several factors, including:

- (1) Local hydrogeochemical changes in the aquifer due to well construction. For example, local depressurizing and degassing of confined aquifers or exposure of leachable minerals to water in and near the well bore.
- (2) Horizontal variability within aquifers from natural influences.
- (3) Vertical variability in water quality among the aquifer zones to which a well is open.
- (4) Vertical variability in hydraulic characteristics among the aquifer zones.

Table 3. Water Chemistry of samples collected after discharge of varying well volumes, USGS wells, Piceance Basin, 1980.

CONSTITUENT	WELL								
	TH75-1A			CORE HOLE NO. 3		TH75-1B			
	WELL VOLUMES DISCHARGED								
	0	1	2	0	1	0	0.2	1	
TDS	1176	816	836	7148	3276	22880	22400	45220	
CALCIUM	4.3	13.8	11.7	1.8	3.2	3.6	2.0	1.5	
MAGNESIUM	32	54.9	52.5	24.6	29.3	4.4	2.2	2.8	
SODIUM	429	235	225	2910	1320	10200	9900	19650	
POTASSIUM	1.2	0.4	0.4	21.3	13.6	22.5	22.1	32.5	
BICARBONATE	944	695	708	3496	1719	23300	23640	48560	
CARBONATE	<1	5	<1	39.5	14.1	32.5	<1	<1	
SULFATE	184	149	144	229	228	131	87.2	61.7	
CHLORIDE	85.7	10.7	12.3	2236	852	1540	1670	3730	
FLUORIDE	0.6	0.2	0.2	0.4	0.2	17.3	17.2	18.4	
AMMONIA	0.4	0.3	0.2	5.6	2.3	8.0	8.3	8.2	
ARSENIC	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.02	0.01	
BORON	0.3	0.3	0.4	0.5	0.4	0.8	0.8	0.9	
MERCURY	<1	<1	<1	<1	<1	<1	<1	<1	
SELENIUM	<0.01	<0.01	<0.01	0.01	0.01	<0.01	<0.01	<0.01	
DOC	10.1	13.1	34.5	26.3	24.0	23.4	26.9	24.4	

The observed changes in water quality of well discharges are a reflection of the character of the aquifers in the Piceance Basin. The deep or bedrock aquifers (or more precisely aquifer zones) in the

This latter factor is important in several ways. The aquifer zones with the highest hydraulic head will eventually dominate water in the well bore and perhaps more generally due to flow from these

higher head zones to lower head intervals within the aquifer. Pumping lowers the head in these dominant zones and eventually, with continued pumping, the influence of other zones (perhaps of differing water chemistry) may be observed in the well discharge. These processes imply some period of equilibration after a well is constructed. Thus the characteristics of a well with regard to sampling may change after a period of months or years.

WELL SAMPLING BY BAILING

Well sampling by bailing was evaluated by surveys conducted on Tract C-a. Deep aquifer wells on Tract C-a are completed in a manner similar to the USGS wells with relatively large open intervals (Figure 9). The surveys were conducted by bailing samples from several depths within the well. In this manner variations with depth could be examined.

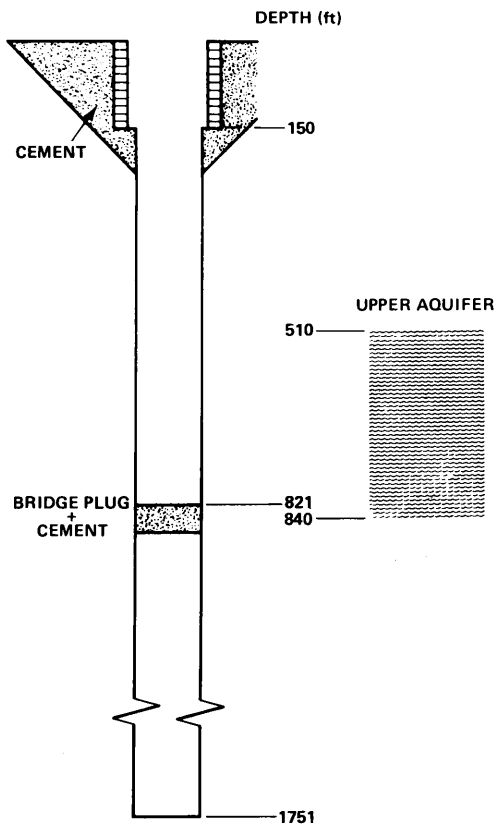


Figure 9. Well Diagram of Upper Aquifer Well GS-13, Tract C-a.

Figure 10 shows the conductivity and temperature profile of Well GS-13 (diagrammed in Figure 9). Over the approximately 375 feet of water standing in the well bore, conductivity levels declined from about 2300 $\mu\text{mhos/cm}$ at the water surface to about

1600 $\mu\text{mhos/cm}$ near the bottom of the open interval. Temperature measurements were much more uniform with depth.

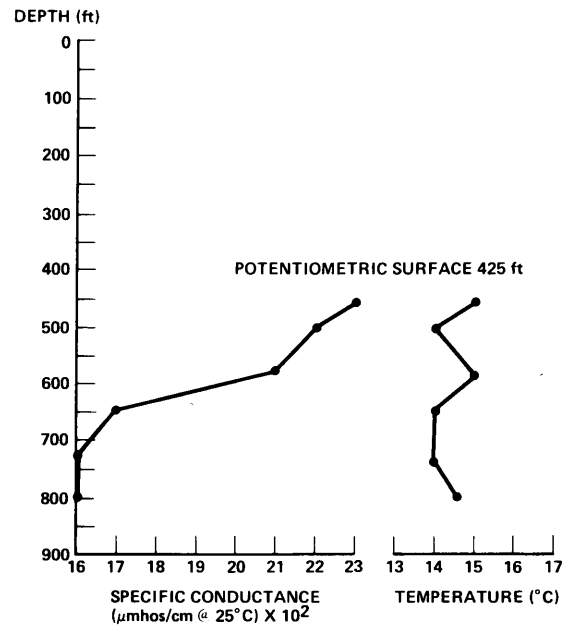


Figure 10. Variation in specific conductance and temperature with depth, Upper Aquifer Well GS-13, Tract C-a, 1980.

Other wells on Tract C-a showed appreciable increases in conductivity with depth, e.g. Well D-17 (Figure 11). In Well D-18, conductivity measurements increased approximately on order of magnitude in a very small interval near the bottom of the well (Figure 12), while readings were very stable above that level.

The decline in conductivity with depth noted in Tract C-a Well GS-13 is also seen in the water chemistry data (Table 4). Appreciable changes in the major inorganic ions with depth were also observed. Trace constituents and DOC were more stable with depth. The general ionic composition is fairly consistent at all three depths sampled in Well GS-13 although sulfate concentrations decreased with depth to a greater extent than most other ions and the chloride concentration increased in the deepest sample.

The increases in conductivity with depth observed in Wells D-17 and D-18 are also shown in the more detailed water chemistry analysis (Table 4). Most of the increase in Well D-17 is in the form of sodium bicarbonate. Magnesium, carbonate and sulfate levels

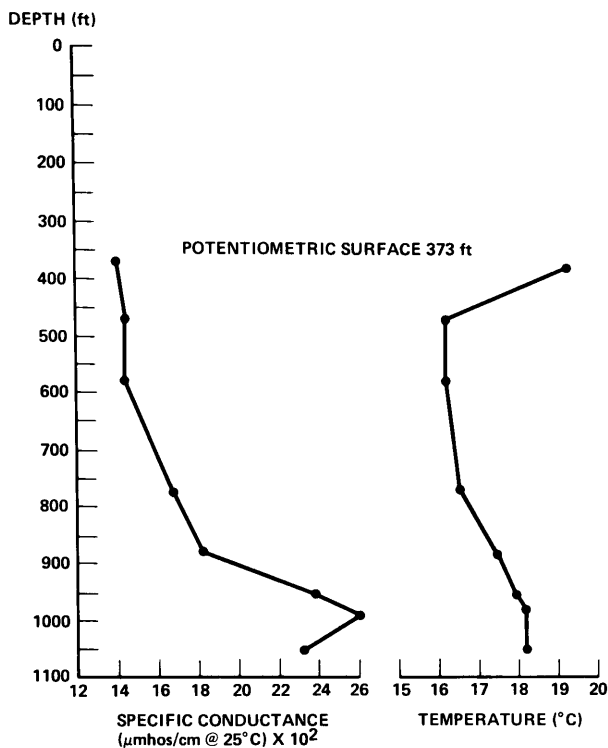


Figure 11. Variation in specific conductance and temperature with depth, Lower Aquifer Well D-17, Tract C-a, 1980.

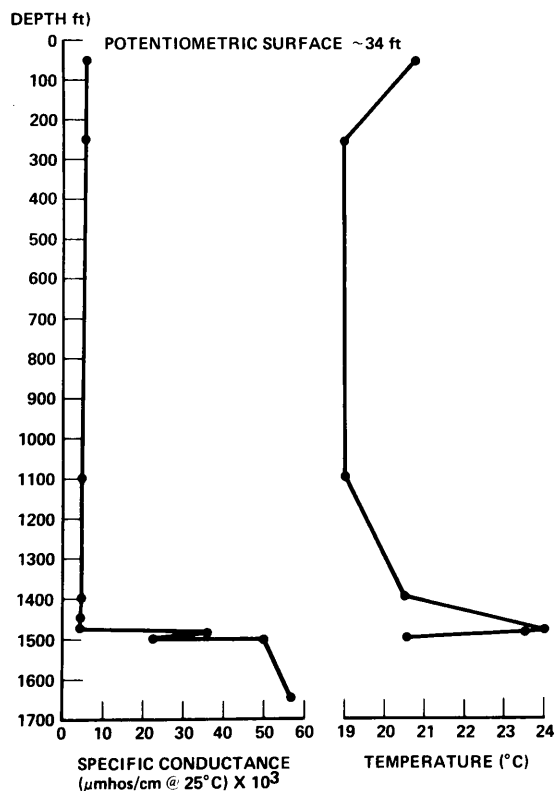


Figure 12. Variation in specific conductance and temperature with depth, Lower Aquifer Well D-18, Tract C-a, 1980.

decline with depth. Thus the salinity of the water in the well increased and the ionic composition of the well water changed.

Similarly, the large increases in conductivity noted near the bottom of Well D-18 are reflected mostly in sodium and bicarbonate concentrations, although several constituents increase appreciably (Table 4). A likely explanation of these observations is that Well D-18 was drilled deeper than the actual aquifer zone and into nahcolite (sodium bicarbonate) deposits. The nahcolite was thus subject to leaching by water in the well bore. Thus these waters at the bottom of D-18 do not reflect aquifer water.

CONCLUSIONS AND RECOMMENDATIONS

The procedures employed to collect water quality samples from wells play a significant role in determining the results of such sampling efforts. Both the general character of the samples (e.g. salinity, pH) and the ionic composition can be greatly affected by the joint effect of sampling protocol and well construction. These factors must be considered in the collection of data and in the interpretation of the data collected.

The two most commonly used groundwater quality sampling methods are pumping and bailing of wells. When wells are pumped, care must be taken to assure that the well has been thoroughly flushed out and that the pump discharge has equilibrated, prior to collection of samples for water chemistry analysis. The time associated with obtaining a stable or equilibrated well discharge will vary depending on the well location and construction.

When wells are bailed to collect samples, care must be taken to collect samples consistently from the same aquifer interval. Variations within the well bore can be very significant.

Whether pumping or bailing is the selected sampling method, wells need to be individually tested and evaluated in order to adequately define and justify sampling protocols for each well. The sampling protocol may vary from well to well due to local hydrogeologic factors and well construction. For wells with large open intervals, periodic recharacterization may be useful in the analysis of monitoring data.

The process of defining sampling protocols begins with the initial drilling and testing of wells. Data collected during drilling, geophysical logs, etc. are useful in defining the vertical hydrogeologic variability at a given location. Evaluation of

Table 4. Variation in water quality with depth in selected deep aquifer wells, Tract C-a, July 1980.

CONSTITUENT	WELL								
	GS-13			D-17			D-18		
	DEPTH (feet)								
	450	575	725	475	875	990	1400	1500	
pH	7.3	7.5	7.5	9.1	9.0	8.6	8.2	8.1	
SPECIFIC CONDUCTANCE	1940	1559	1344	1344	1790	2210	3856	64794	
TDS	1409	1140	1160	1093	1174	1524	2954	37839	
CALCIUM	67	46	42	3.4	3.9	5.0	2.2	2.8	
MAGNESIUM	118	89	82	32	30	24	6.6	6.8	
SODIUM	281	213	194	372	417	557	1224	16816	
POTASSIUM	0.8	0.5	0.4	1.9	2.6	2.3	2.3	14.2	
BICARBONATE	775	551	637	686	898	1355	3089	45682	
CARBONATE	<1	<1	<1	8.8	13.1	4.8	<1	<1	
SULFATE	610	466	262	304	170	118	97	220	
CHLORIDE	13.4	11.4	35.7	28.2	53.6	59.0	47.2	480	
FLUORIDE	0.48	<0.1	<0.1	1.6	2.6	5.6	9.3	10.1	
AMMONIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	3.9	
ARSENIC	0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	
BORON	0.29	0.31	0.31	0.31	0.53	0.73	0.79	0.87	
MERCURY	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	
SELENIUM	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
DOC	28.6	30.6	27.2	24.1	35.0	25.7	12.4	21.0	

this variability is an essential factor in monitor well design. Hydraulic variability (e.g. vertical variations in head, interconnection of fracture zones (vertically and horizontally), etc.) is as important as variations in water quality. An initial focus on the analysis hydraulic properties of various aquifer zone will enhance collection of representative water quality samples.

Once sampling protocols are defined, wells should be sampled consistently. Trends in water quality data can be created by changing sampling procedures.

Consideration of sampling factors and their influence on water quality data is an important part of the collection and use of monitoring data. Without this due consideration, the interpretation and use of monitoring data for engineering, regulatory or scientific purposes can be severely constrained.

ACKNOWLEDGEMENTS

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