



TECHNICAL MEMORANDUM

DATE: October 27, 2014
TO: Heidi Kaiser, Hydrometrics, Inc.
FROM: Scott Mason, Hydrometrics, Inc.
SUBJECT: Prediction of Spoil Water Quality

Background

The effects of spoils on groundwater quality in southeastern Montana have been studied extensively by the Montana Bureau of Mines and Geology (MBMG) (Van Voast and others, 1978 and 1988) for the past forty years. These studies have documented that groundwater in spoils is typically somewhat higher in dissolved solids (e.g., Total Dissolved Solids (TDS)) and soluble salts than in pre-mining groundwater in coal beds. The predominant cause of the high TDS content of spoils groundwater is the occurrence of highly soluble salts in coal overburden. These salts are produced by weathering and oxidation of the overburden and accumulate in overburden because of the arid – semi-arid climate of the area and the lack of water in the form of precipitation infiltration to leach and flush salts to the underlying groundwater system. As described by Van Voast et al (1988) and observed in Otter Creek Mine overburden also (see discussion of saturated paste leach results below), the lack of deep percolation and leaching of salts often leads to a depth profile where the leachable-salt content of overburden is highest near the surface and decreases with depth.

Upon exposure of spoils to groundwater, overburden salts are readily dissolved and mobilized in the groundwater system during an “initial flush” period. Because the rate of dissolution of the salts by water is much faster than the generation of additional salt from weathering/oxidation of overburden, once salts are leached during the initial flush period, salt concentrations in spoils groundwater decline with further flushing and approach pre-mining

levels. Van Voast and others (1978 and 1988) document that the primary factors controlling spoils groundwater quality, both in field conditions and in laboratory testing, are the initial salt content of the overburden and the amount of water with which the overburden is leached (i.e., liquid to solid ratio). The importance of liquid to solid ratio (L/S) in controlling solute concentrations in water is also recognized in USEPA (2010) guidance for characterizing coal combustion residues and other materials through leach testing. Van Voast et al (1978) conducted a series of column and batch leaching experiments to characterize overburden salt leaching and to develop methods to predict groundwater quality in spoils. Results of column leaching experiments (Figure 1) demonstrated that high salt concentrations (e.g., high TDS) and specific conductance (SC) in the initial flush were short-lived and that spoils water approach ambient groundwater after flushing with 1 to 3 pore volumes of water. Similar initial rises, followed by declines, in SC and salt levels in spoils groundwater are observed at operating mines in southeast Montana as described in Van Voast and Reiten (1988); although the authors caution that a long time period may be required to achieve geochemical equilibrium between groundwater and mine spoils.

Since column leach tests can be excessively time-consuming, particularly for low permeability materials, Van Voast et al (1978) evaluated the use of batch leach testing using the USDA saturated paste methodology as a surrogate for column testing. Results of saturated paste leach testing were similar to column leach tests in that there was a strong correlation between the amount of water used in the paste tests and salt concentrations in spoils leach water quality. Van Voast et al (1978) concluded that: 1) saturated paste concentrations are similar to average concentrations in the first pore volumes of column leach tests; and 2) there was a sufficiently good correlation between saturated paste salt concentrations and spoil water quality to develop nomographs and regression equations for the purpose of predicting spoils water major cation (Ca, Mg, Na) concentrations from saturated paste test results. In Van Voast and Reiten's later (1988) review of hydrologic responses to long-term mining in southeastern Montana, they state that saturated paste extracts provide only approximations of average concentrations that might be expected, since salt concentrations are expected to be higher during the initial saturation and flushing of spoils and lower with further flushing. Based on a mathematical model of flushing assuming

a first order dissolution rate equation, Van Voast and Reiten (1988) conclude that one pore volume is a reasonable estimate of the flushing required to approach a pre-mining salt balance in spoils water quality.

Figure 1 – Results of Column Leach Testing (from Van Voast 1978)

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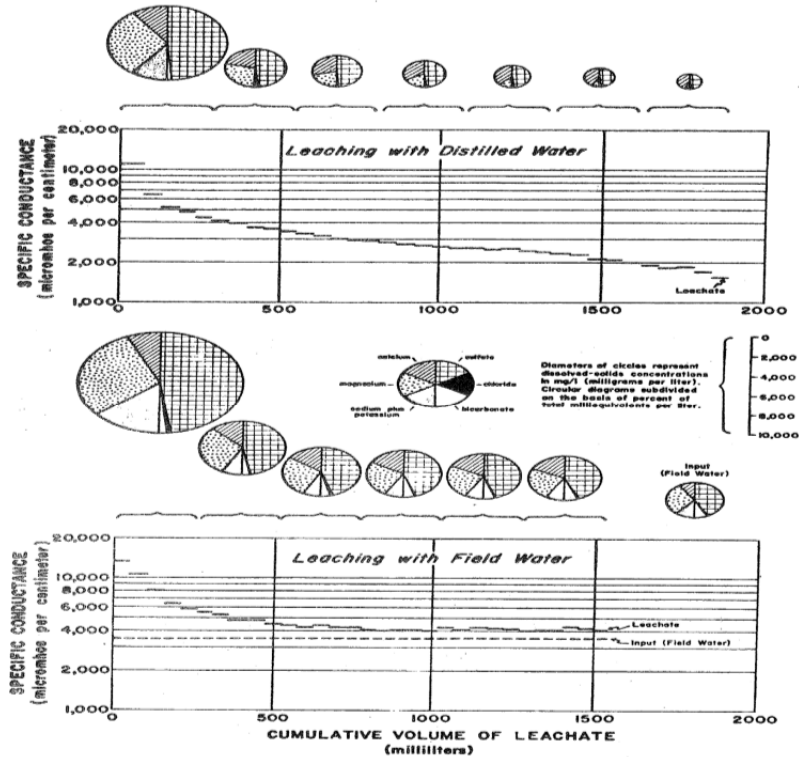


Figure 19.-Examples of spoil leaching experiments using distilled water (specific conductance, 10 micromhos per centimeter) and ground water collected in the field (specific conductance, 3530 micromhos per centimeter).

Method of Prediction of Otter Creek Mine Spoils Water Quality

Predictions of spoils water quality for the Otter Creek Mine are based on column and batch (saturated paste) leach testing of overburden following the methods described by Van Voast et al (1978) and USEPA (2010). The appropriateness of these techniques for Otter Creek overburden is evaluated and confirmed by comparison with field and laboratory results of Van Voast (1978 and 1988). A summary of spoils water quality predicted by the various methods (column leach, saturated paste leach, and comparison to pre-mining water quality) is provided in Table 1. Description of the derivation of the predictions is provided in the

following sections. Overall, all spoils water quality prediction methods estimate that levels of soluble salts (TDS, SC, sulfate, nitrate + nitrite, selenium) will be higher than ambient groundwater in the Knobloch Coal during initial saturation of the overburden material. After refilling, salt concentrations will decline and will become similar to pre-mining groundwater with continue rinsing and flushing of overburden material by groundwater. With the exception of selenium during the initial saturation, all metal concentrations are predicted to remain low and better than Montana groundwater standards.

Table 1. Spoils Water Quality Estimated by Various Methods

	Units	Pre-Mining Ambient Groundwater in Knobloch Coal	Estimate Based on Pre-Mining Water Quality	Estimate Based on Saturated Paste Leach Tests – Overburden Material ³	Short-Term Estimate Based on Column Leach Tests (Composite of Pre-strip and Overburden) ¹	Long-Term Estimate Based on Column Leach Tests (Composite of Pre-strip and Overburden) ²
TDS	mg/L	1,750	2,625 to 5,250		4,000 to 15,000	1,800 to 2,100
Specific Conductance	µmhos/cm	900 to 6,900	1,350 to 13,800	3,150 to 3,260	4,500 to 14,000	1,800 to 3,000
Sodium Adsorption Ratio (SAR)				19.99 to 20.15	23 to 49	16 to 30
pH				8.04 to 8.09	7.9 to 8.6	8.3 to 9.2
Sulfate	mg/L			NA	2,000 to 10,000	70 to 700
Calcium	mg/L				36 to 171	10 to 46
Sodium	mg/L				1,033 to 3,230	451 to 672
Magnesium	mg/L				47 to 439	10 to 21
Nitrate + Nitrite	mg/L			3.4 to 9.5	2 to 50	<1
Boron	mg/L				< 1	< 1
Fluoride	mg/L				1 to 7	1 to 3
Arsenic	mg/L				0.002 to 0.005	0.002 to 0.005
Selenium	mg/L	.001			0.2 to 0.33	0.001 to 0.002

NA = parameter not analyzed

1) Short-term estimate based on average concentrations of first pore volume of column leachate representing initial saturation or flooding of overburden by groundwater. Column tests included pre-strip material that will not be placed in mine pits. Thus, column tests may overestimate leach concentrations.

2) Long-term estimate based on concentrations of second through fourth pore volume of column leachate representing continued flushing of overburden by groundwater. Column tests included pre-strip material that will not be placed in mine pits. Thus, column tests may overestimate leach concentrations

3) Saturated paste range of values is median and weighted average values of all tests.

Comparison with Pre-Mining Water Quality

Van Voast et al. (1988) noted that average TDS concentrations in mine spoil of southeastern Montana mines are 50 to 200 percent higher than average concentrations in undisturbed aquifers. Given an average TDS of approximately 1,750 mg/L for the Knobloch Coal, TDS in spoils groundwater could range from 2,625 to 5,250 mg/L. Groundwater from overburden monitoring wells in the study area ranged from 1,310 to 7020 mg/L TDS.

Saturated Paste Leach Testing

Pre-Strip and overburden samples were collected from 55 boreholes during the 2011 Ark Land exploration drilling program and samples were submitted for chemical analysis of saturated paste extract. Weighted averages and weighted 75th percentiles of results of saturated paste analyses are provided in Table 2. Concentrations of major ions in saturated paste extracts have been found to compare favorably to those occurring in the first pore volume of column leachate (Van Voast et al., 1978). For comparison purposes, average values of the same parameters for baseline water quality samples from the Knobloch Coal were; pH = 8.1, SC = 2,489 μ mhos/cm, and SAR = 36.4 (Baseline Report 304E - Water Resources Data Report).

Table 2 – Saturated Paste Results for Overburden and Pre-Strip Material

	Pre-Strip Material		Overburden Material Excluding Pre-Strip	
	Weighted Average	75 th Percentile	Weighted Average	75 th Percentile
pH (std. units)	7.80	8.09	8.08	8.18
Specific Conductance (SC) (μ mhos/cm)	5,570	6,660	3,230	4,050
Sodium Adsorption Ratio (SAR)	18.53	22.02	19.97	23.94
Nitrate + Nitrite (mg/L)	7.96	12.73	3.38	9.53

Column Leach Testing

Column leach testing was conducted on representative samples of overburden (including pre-strip) from four boreholes (1109, 1113, 1140, and 1135). Boreholes were selected by dividing the mine area into quadrants, from north to south, and randomly choosing one borehole from each quadrant. Refer to Map 15 – Drill Hole Locations, for borehole

locations. During overburden borehole advance, samples were collected and composited from approximately 5 foot intervals. Each 5-foot depth interval was tested by saturated paste leaching as described above. Representative samples for column testing were made by compositing equal sub-samples of each 5-foot interval sample to make 1 bulk sample (approximately 1.6 kg) for each borehole. The composite samples were mixed to simulate mixing that would occur during backfilling of overburden. These composite samples represent conservative or worst-case conditions since they include subsamples of pre-strip material which is known to contain higher salt contents than deeper overburden material; and under the proposed mining plan, pre-strip material would be removed prior to dragline stripping and would not be placed in mine pits.

Column leach testing of overburden samples was conducted as follows:

1. Representative composite samples were processed by crushing to pass a 10 mesh (2 mm maximum particle diameter) sieve.
2. Samples were homogenized by mixing and then split to yield duplicate samples for leach testing.
3. Samples were placed into identical 48-inch long, 2-inch diameter clear plexiglass columns (see photograph in Figure 2).
4. Influent leaching solutions were applied to the top of the columns. One column for each sample was leached with deionized water (DI) while the duplicate sample was leached with groundwater from the Knobloch Coal (composite sample from wells K-1, K-5, and B-6). In all cases one pore volume was 340 ml.
5. Nitrogen pressure (5 psi) was applied to the columns.
6. Effluent leachate from the columns was collected in pre-cleaned sample bottles for analysis.
7. Leaching continued until 1 or more pore volumes of effluent leachate were collected (borehole samples 1113, 1135 and 1140) or the columns became plugged and ceased to yield effluent (borehole 1109 and borehole 1113 DI leach).
8. Borehole 1109 columns never became fully saturated and did not yield effluent leachate water under column conditions. Sample material was removed from the columns and the sample was subjected to sequential paste extractions at liquid to

solid ratios of 0.333, 1, 2, 3, 4, and 5 pore volumes. Results from the sequential paste extractions are believed to be equivalent to column results for soluble salts, SC and TDS but are not believed to be representative for dissolved metal constituents. Due to the difficulty in sample filtration and the likely presence of particulate (non-dissolved) metals in leachate samples, metal concentrations are believed to be biased high in sequential extraction leachate samples.

9. Borehole 1113 columns were very slow to drain but eventually yielded one pore volume when leached by DI water but only 0.333 pore volume was obtained from the well water leached column.

Leach testing protocols were similar to methods used by Van Voast et al (1978) and to guidelines outlined in EPA Method 1314 (Liquid-Solid partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials Using an Up-Flow Percolation Column Procedure) as described in USEPA (2010). However, modifications from Method 1314 were necessary because of the low permeability of overburden materials and the slow rate of leachate flow through the columns. These modifications included use of a down-flow column, application of nitrogen gas pressure (5 psi) to the columns to increase percolation rate, and much longer hydraulic residence times (1,000 hours per pore volume versus 24 hours as described in Method 1314). Van Voast et al (1978) noted the difficulty of conducting column leach test with low permeability materials and also used pressurized, down-flow columns in their studies.

Results of column leach testing are shown in Figures 3 through 6. Overall, column leach test results for Otter Creek overburden exhibit similar characteristics as observed and described by Van Voast et al (1978). Salt concentrations are initially high (TDS of 3,000 to 15,000 mg/L; SC of 4,000 to 14,000 $\mu\text{mhos/cm}$) during the time that overburden is partially saturated (less than one pore volume) and decrease rapidly after full saturation is achieved. Salt concentrations continued to decline with additional leaching and by four pore volumes were very similar to well water.

Figure 2. Otter Creek Column Leach Set Up (photo courtesy Energy Labs, Helena)



Results for other soluble salt parameters were similar. Nitrate + nitrite concentrations initially ranged up to 47 mg/L in the first column drainage but declined to 1 mg/L or less in the second pore volume in all columns and remained below the Montana groundwater standard of 10 mg/L for all subsequent pore volumes.

Figure 3. Column and Sequential Paste Leach Test Results - TDS

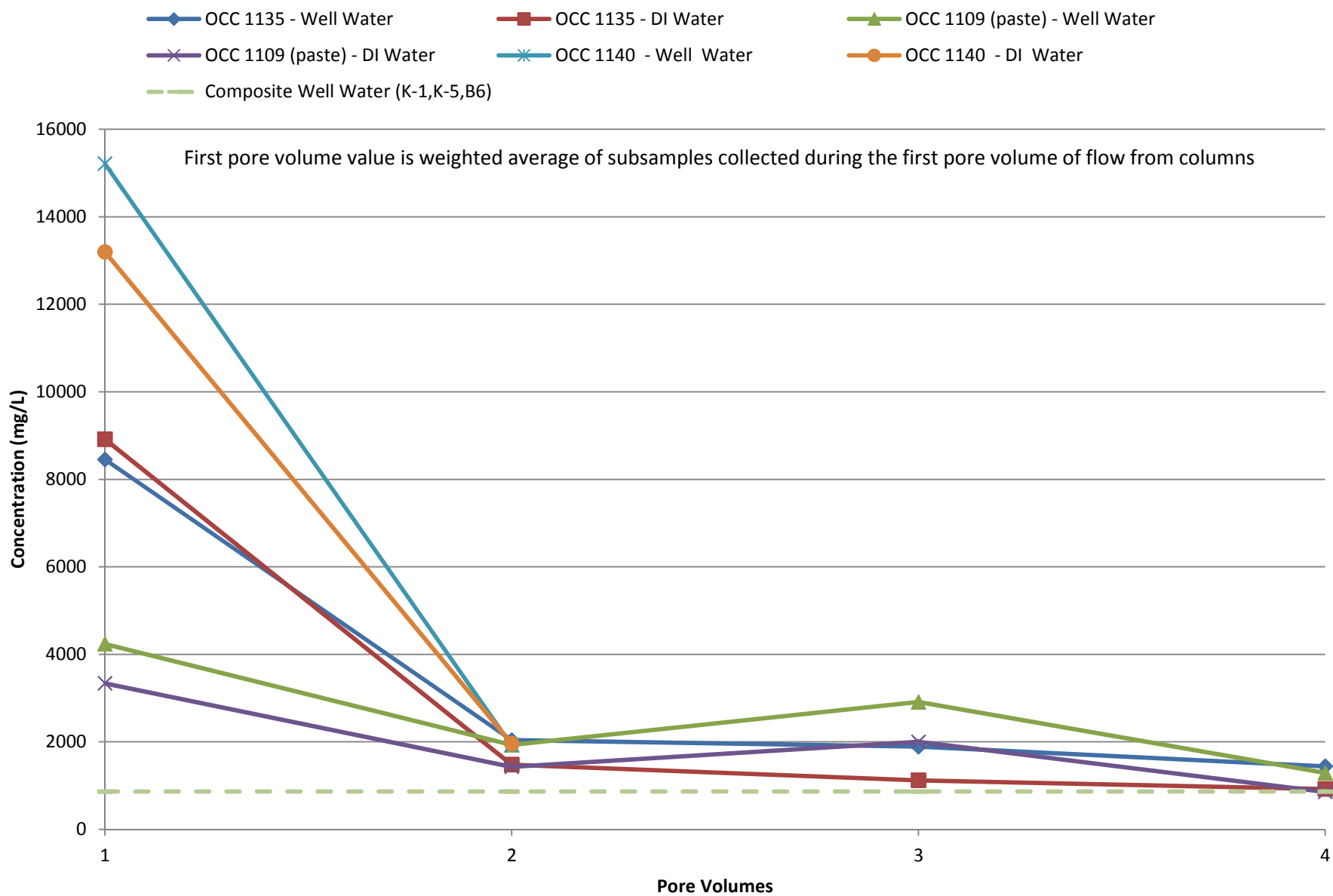


Figure 4. Column and Sequential Paste Leach Test Results - SC

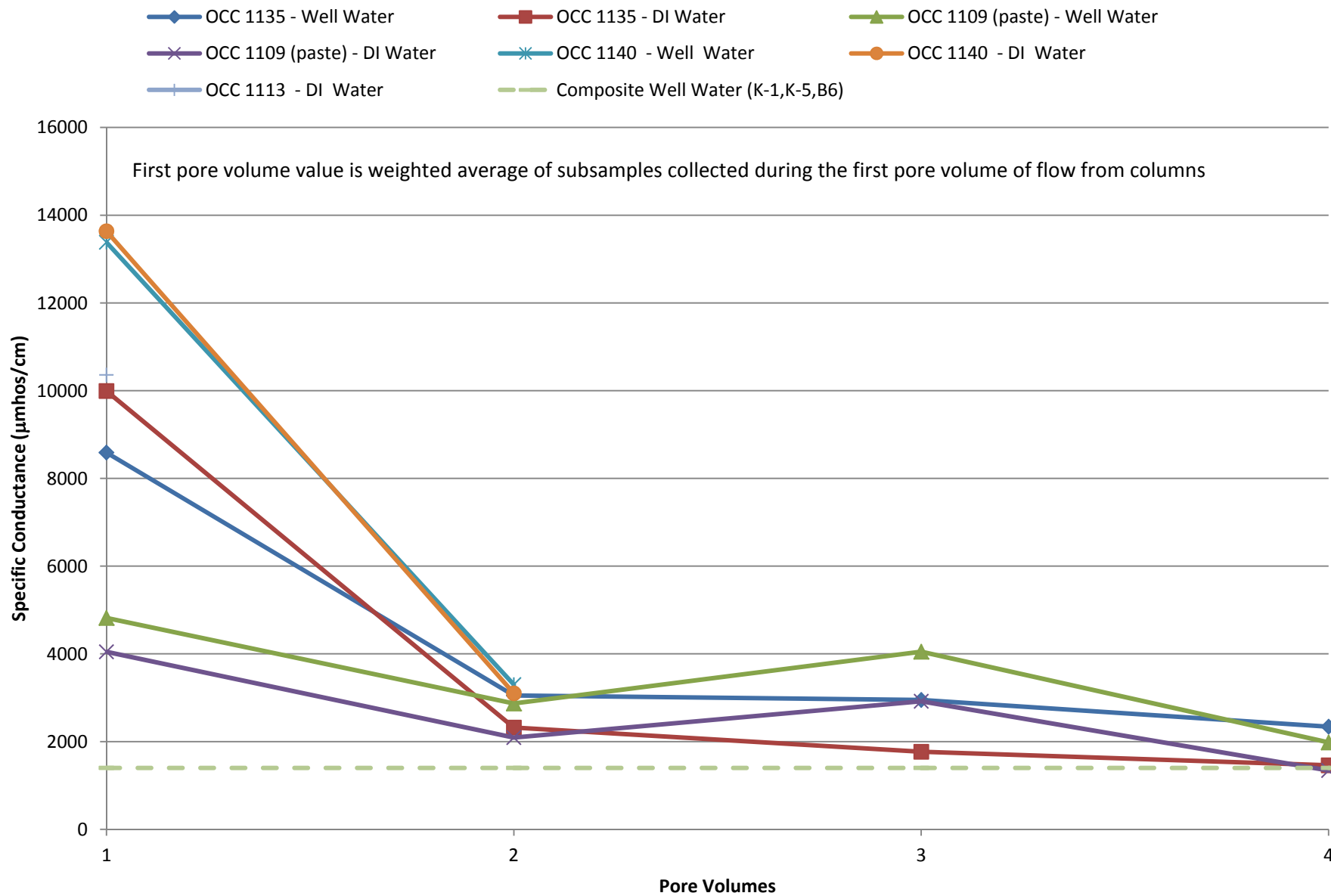


Figure 5. Column and Sequential Paste Leach Test Results - Selenium

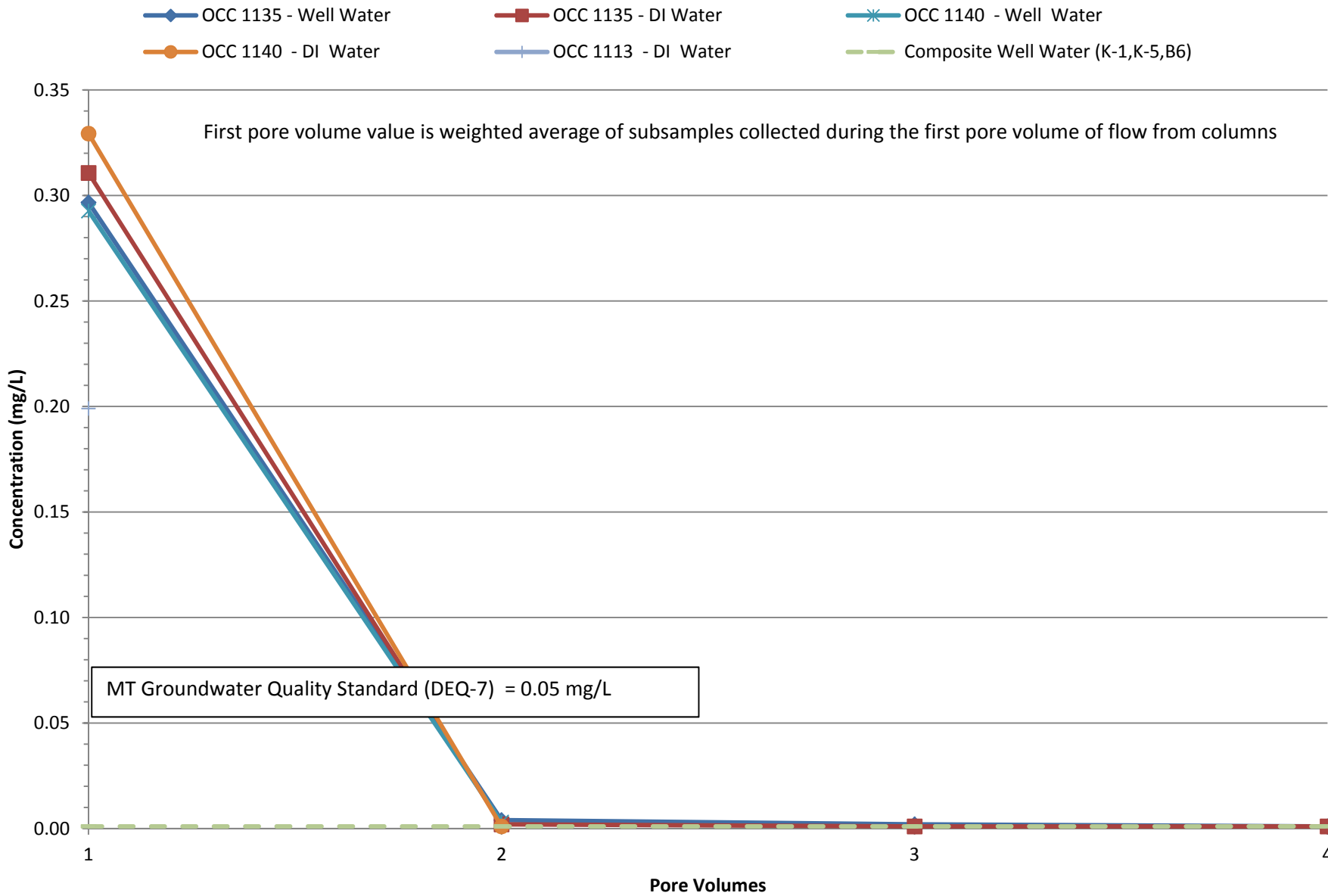
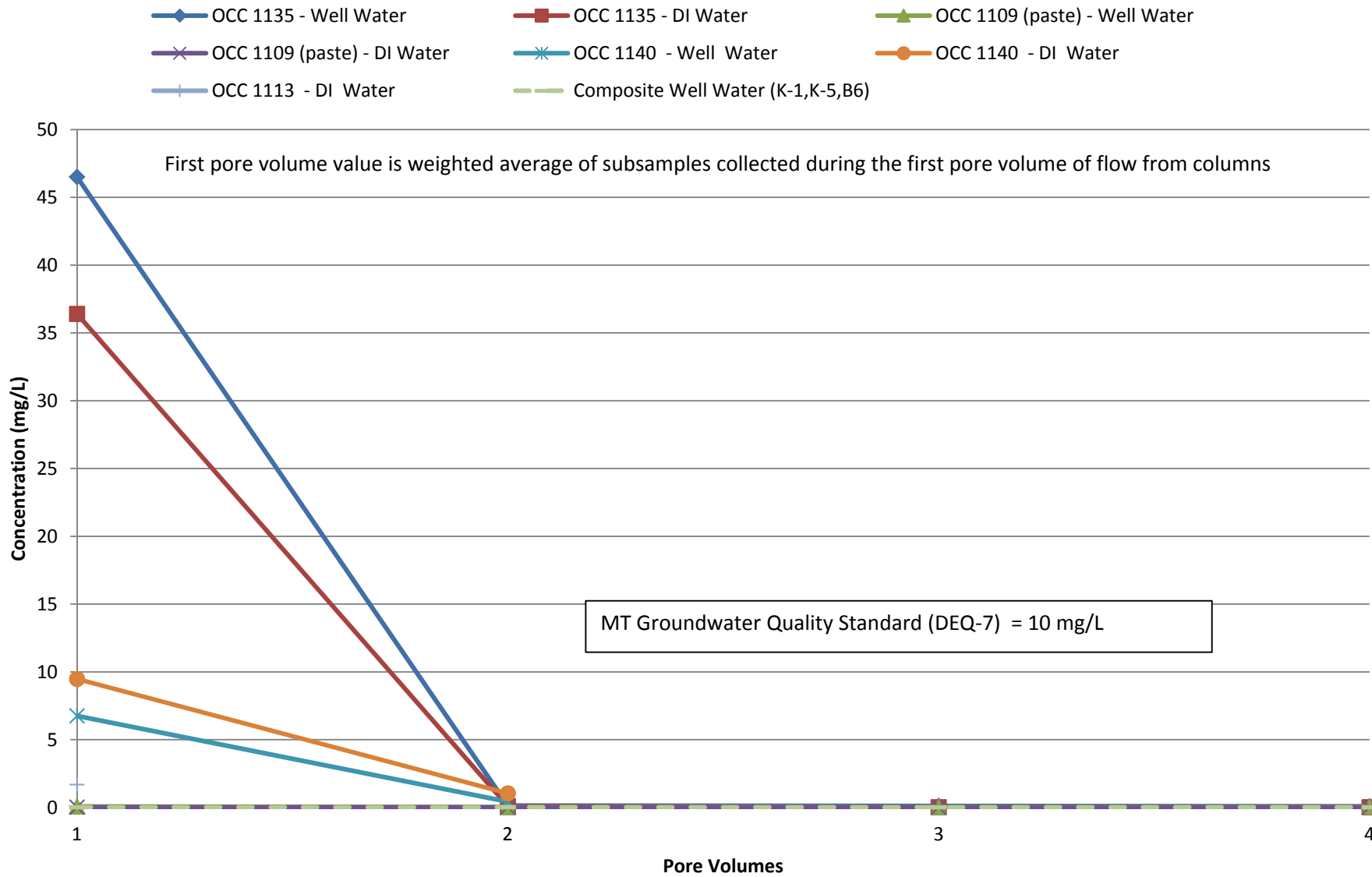


Figure 6. Column and Sequential Paste Leach Test Results - Nitrate + Nitrite



Discussion

As noted above, Van Voast and others (1978 and 1988) identified the primary factors controlling spoils groundwater quality, both in field conditions and in laboratory testing, as the initial salt content of the overburden and the amount of water with which the overburden is leached (i.e., liquid to solid ratio). The importance of liquid to solid ratio (L/S) in controlling solute concentrations in water is also recognized in USEPA (2010) guidance. Consequently, groundwater quality in re-saturated backfilled spoil will be a function of the amount of soluble salt available, or load, and the amount of solvent, or dilution factor.

Column leach testing provides a measure of the quantity of soluble material, or load, in the test sample. In the column leach tests, the typical L/S ratio was 340 ml/1600g, or 0.21. For overburden saturated paste samples, the weighted average saturation percentage was 71.25 percent, or a L/S ratio of 0.71. Differences in maximum SC between saturation paste analysis and column leach testing in Table 1 above are largely accounted for by the difference in L/S ratios. That is, both methods measure similar amounts of soluble material, but yield different concentrations.

For both column leach and saturation paste extractions, samples are ground to a maximum size of 2 mm, or 10 mesh. This procedure maximizes the available solute material by maximizing the surface area of the rock particles. Particle size distribution data for backfilled spoils at Montana mines is not available, but studies of spoils at ten surface coal mines in West Virginia (Plass and Vogel 1973) showed an average of just 37 percent below 2 mm in size. It seems likely, therefore, that grinding samples to a maximum size of 2mm represents a worst case, and that solute load availability in backfilled spoils would be less by an unknown amount, since experimental data are not available.

Given the variables and uncertainties associated with laboratory testing, estimation of groundwater quality in backfilled spoils using laboratory extraction data is inexact. It does seem likely, however, that the column leach and saturation paste methods bracket the extremes of the range in SC, with the former likely over-estimating and the latter under-

estimating field conditions. A value mid-way between would place a reasonable SC estimate in the range of 6500 to 7500 $\mu\text{mho}/\text{cm}$ for spoils at Otter Creek Mine.

Metal Parameters

In addition to soluble salts, column leach extract analysis also included a number of metals.

Results for metal parameters are summarized as follows:

- Arsenic – Arsenic concentrations ranged from 0.003 to 0.005 mg/L and were lower than the MT groundwater standard of 0.010 mg/L in all pore volumes from all column leach tests.
- Barium - Barium concentrations ranged from 0.009 to 0.09 mg/L and were lower than the Montana groundwater standard of 0.004 mg/L in all pore volumes from all column leach tests.
- Beryllium – was not detected (<0.001 mg/L) in any pore volumes from any column leach tests. Overburden leachable beryllium concentrations are less than the Montana groundwater standard of 0.004 mg/L
- Cadmium – Cadmium concentrations were less than 0.001 mg/L and were lower than the Montana groundwater standard of 0.005 mg/L in all pore volumes from all column leach tests.
- Chromium – Chromium concentrations were less than 0.025 mg/L and were lower than the Montana groundwater standard of 0.1 mg/L in all pore volumes from all column leach tests.
- Copper – Copper concentrations were less than 0.04 mg/L and were lower than the Montana groundwater standard of 1.3 mg/L in all pore volumes from all column leach tests.
- Iron concentrations were low in all columns and was less than the detection limit (<0.05 mg/L) in all but one sample.
- Lead - Lead concentrations were less than 0.04 mg/L and were lower than the Montana groundwater standard of 0.015 mg/L in all pore volumes from all column leach tests.

- Mercury - was only detected in one sample (0.00006 mg/L) and all concentrations were lower than the Montana groundwater standard of 0.002 mg/L in all pore volumes from all column leach tests.
- Nickel - nickel concentrations were equal or less than the Montana groundwater standard of 0.1 mg/L in all pore volumes from all column leach tests.
- Selenium – concentrations were initially elevated in all columns (0.2 to 1.0 mg/L) but decreased rapidly and were below the Montana groundwater standard of 0.05 mg/L in the second third of the first pore volumes from all column leach tests and declined further in subsequent pore volumes.
- Zinc - was only detected in two samples (0.02 mg/L) and all concentrations were lower than the Montana groundwater standard of 2.0 mg/L in all pore volumes from all column leach tests.

References

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