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REVIEW ARTICLE

Anatomy of a Case of Elevated Chloride in the Shallow Black Hand Sandstone Providing Rural Drinking Water Supplies in North-Central Ohio, USA: Hydrogeological and Hydrochemical Characterization by Major and Minor Elements, and δ^2H, δ^{18}O, δ^{13}C and Tritium Isotopes

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Abstract

Elevated chloride concentrations (>250 mg/l) were reported to the Ohio State Environmental Protection Agency in the early 2000s by a rural resident using groundwater for domestic consumption from a private water well. An adjacent commercial oil and gas pipe yard had spread relatively small volumes of oilfield brines from 1998 through 2000 to control dust during summers and to de-ice on the property driveways; county and state agencies used halite and other brines on surrounding rural county and state highways during the winter. There are multiple sources in the immediate area that might have contributed to local groundwater by varying degrees, resulting in elevated chloride concentrations reported in the samples from the on-site monitoring wells and from the neighborhood water wells over the years prior to 2004, the time of our investigations.

An independent investigation was undertaken to characterize the local hydrogeological and geochemical conditions below and surrounding the pipe yard, which has the highest elevation in the area. Data collection to support the investigation consisted of: 1) the installation of nested groundwater monitoring wells (shallow and deep) located at six sites along the periphery and central part of the pipe yard, 2) stratigraphic core drilling, recovery and examination of 220 feet of core, 3) natural gamma and caliper logging of core hole, 4) groundwater sampling for geochemistry and periodic on-site measuring of water levels in each of the monitoring wells, surrounding off-site rural water wells, and up-gradient rural water wells. Formal interviews with residents concerned their use and management of water wells, and any water-softening and/or septic-tank systems' operational histories, and 5) local reconnaissance of spring/seep sites around the area, and sampling a local stream.

Our data were limited to one groundwater sampling period with only two samples filtered in the lab; all other chemical data were reported as total concentrations, which included adsorbed and particle constituents for the purpose of assessing the total hydrochemical load carried in the groundwater. Even with these limitations, we were able to conclude that the elevated chloride concentrations in groundwater from a few wells in the neighborhood, located to the north and adjacent to the subject property, likely resulted from: 1) the poor management of home water-softening systems, 2) the subsurface conditions making groundwater especially vulnerable to rapid recharge from waste releases at the surface, 3) the disposal of domestically generated brines from water-softening regeneration and septic tank effluents flowing into septic-tank leachfields constructed in a thin soil zone overlying a thin zone of glacial till, 4) the use of halite for deicing the county roads and state highways adjacent to the neighborhood water wells, and 5) the unfavorable geological and hydrogeological conditions in the area where shallow, heavily fractured and jointed sandstone receives vertical recharge to the local water table from above, which encourages rapid migration of chloride-impacted recharge sampled by the monitoring wells.

Hydrochemical and stable and radioactive isotope data analyses of δ^{18}O, δ^2H, δ^{13}C (DIC), and ^{3}H in groundwater also confirmed that little mixing has occurred prior to 2004 between the industrial site and neighborhood locations. We concluded that in some instances the groundwater had been altered while migrating through the glacial till during recharge and while moving through the unsaturated zone downward through fractures as well as through the porous media, prior to reaching the water table. The brine spread on the industrial property could not have migrated into the groundwater supplies of neighborhood residents over the five or six years prior to 2004, and thus, these data confirm that the elevated chloride concentrations were attributable to neighborhood activities and to adjacent driveway and roadway activities of de-icing using halite brine during the winter months, with no apparent contribution from the commercial oil and gas pipe yard.

Keywords: Black Hand Sandstone; Cuyahoga shales; siltstones and sandstones; glacial till; rural groundwater supplies; rural water wells; nested monitoring wells; de-icing activities; use of brine; elevated chloride concentrations; major and minor element hydrochemistry; hydrogeological investigations; ^{2}H (deuterium) and ^{18}O isotopes; ^{13}C (DIC); ^{3}H (tritium); Clinton brine; water-softening systems; septic-tank and leachfield/drain field systems

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Introduction

In the year 1998, personnel of an established oil and gas field equipment and associated tubular products company located in central Ohio began to apply brine on their property in a state-permitted activity to control dust. In 2000, the practice was ceased after being advised that a resident adjacent to the property reported to the Ohio Department of Natural Resources (ODNR) that their drinking water had turned salty. De-icing of adjacent county and state roads was commonly practiced during winter to control ice. The county used magnesium chloride, and a corn-based solution mixed with halite and cinders for de-icing on county roads. During the period, the state mixed water with halite from the salt producers in Ohio (Cargill and Morton) and applied the solution by spraying on state highways twice a week during snow and icing conditions [1-4] [150][171].

Chloride and sodium in groundwater have increased in many northern states during the past 50 years. Increases likely are related to road salt and other anthropogenic sources, such as septic systems, wastewater, and contamination from landfills and salt storage areas. But contributions by de-icing activities and septic-tank systems dominate all other sources [5-8], among many other case histories [9] [169].

Personnel of the ODNR conducted a sampling survey of water wells along the rural road adjacent to the reported occurrence and confirmed elevated levels of chloride concentration after repeated sampling; the water well of the original complainant contained chloride as high as 1,200 ppm. Ground water samples taken from wells of nearby residents were elevated but less than that of the original complainant. The EPA recommended maximum contaminant level for chloride as a secondary guideline was 250 mg/l [155].

Apparently, many local residents soon considered the company operations as the probable source of the increased chloride, and in a show of neighborhood responsibility, the company offered to pay for the drilling and construction of new, deeper wells for selected residents exhibiting elevated chlorides from their water wells. Many of the older wells that were replaced were originally drilled in the 1950s, many of which were constructed in basements of the resident houses as was the custom in those days.

The new wells were drilled and constructed by the company during 2001. A new water well was drilled by the company in response to the original complainant (at site Cn) in late 2000 but this well encountered "brackish" groundwater at a depth of 220 feet below grade and the well was abandoned by pressure grouting with a commercial bentonite seal. A replacement well was then drilled nearby and completed at a depth of 130 feet below grade. The water quality was tested as being acceptable (i.e., <250 mg/l chloride).

As before, the resident system was also equipped by the owner with a water-treatment (or softening) system involving the use of salt (halite) to regenerate the cations (in the exchange media) to alter the typical hardness of the raw groundwater for household drinking-water consumption and for improved laundry and other cleaning activities [10]. The system at site Cn originally employed a water softener. ODNR records of the year 2000 indicated that the previous owners reported that the system used 40-80-pounds of rock salt per month, which was an unusually high rate of salt consumption, indicating that the water-softener system was not performing as anticipated and/or was responding to greater hardness related to the increased salinity of the raw water that was well beyond system design capabilities.

In order to evaluate the source(s) of the high chlorides, we sampled the on-site monitoring wells and 12 domestic water wells surrounding the company property (Figure 1).

Sampling and Analyses

We conducted a hydrogeological investigation by first visiting the company site in early 2003 to establish the scope of work for the investigations, and then by reviewing the technical and operational literature on the affected area that included a review of the water well records, records of complaints, and other data supplied by ODNR personnel on their investigations in the area.

In April, 2003, we proposed to core drill to depths below the first shale of significant thickness for the purpose of evaluating the characteristics of the subsurface geology and associated hydrogeological conditions. We also proposed to install a series of monitoring wells on the company property, two at most sites, one shallow and one deep. This would permit assessment of groundwater flow in the subsurface in or near the boundaries of the company property.

Some days after installation and equilibration of the water level in the monitoring wells, the groundwater levels were measured at each well. Afterward, each well was purged and the groundwater sampled, and, for quality control, two field blanks and two duplicate samples were obtained. In addition, 13 neighborhood wells were sampled at locations in and around the periphery of the company property.

For comparison purposes, we also acquired 1) a sample of Clinton brine (produced along with oil and gas from Clinton sandstones within the Abion Sandstone formation of Silurian age generally encountered about 3,000 feet at depth [162, pp.5-6], the same brine used for spreading on the company property and by the state elsewhere), and 2) one water sample from a nearby creek (SW-1).

The Phase I coring, drilling and monitoring well installation program began in December, 2003 and completed in late January, 2004. Phase II water-level measurements and Phase III groundwater sampling were conducted in early June, 2004. The anticipated turn-around-time for completion of the laboratory analyses was 30 to 45 days from time of receipt of the samples at the labs, which were sent by next-day FedEx on ice under full chain of custody to the lab in Pennsylvania. The samples all met holding-time requirements where applicable.

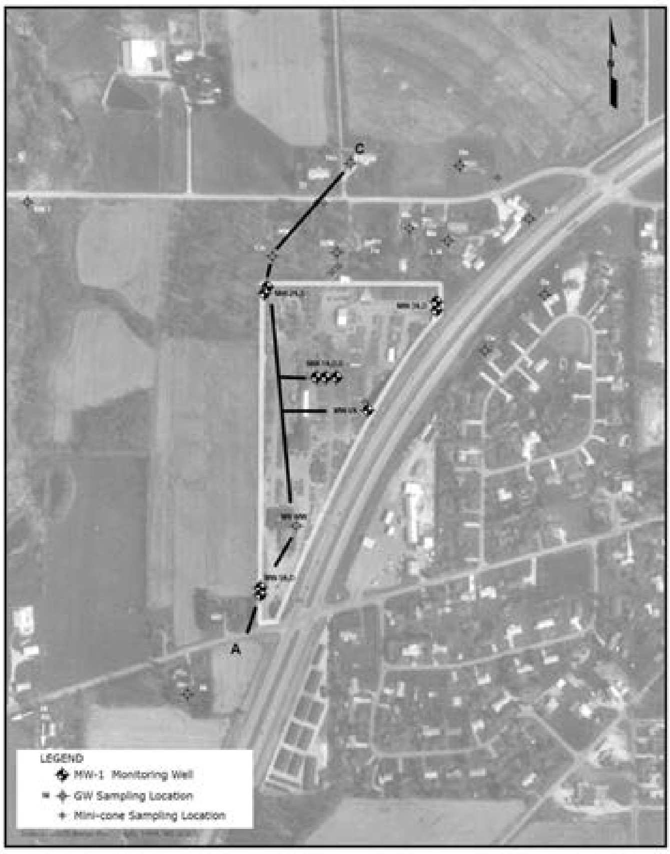


Figure 1: General Location of On-Site Monitoring and Off-Site Neighborhood Wells. (to enlarge figure, click (here))

Early in the field program, we distributed a form to each resident to introduce our purpose in sampling their well and to obtain a release of liability for our activities while measuring the water levels inside their wells. We conducted interviews with residents while we were inspecting their water wells and measuring the groundwater levels in each of the resident wells.

The interviews provided information on the water well, the location of the septic-tank system, its age, and maintenance history, and on whether or not the resident also operated a water softener, the consumption rate of rock salt used for regeneration, and the age and maintenance history of the unit (see Appendix D). After purging the well three well-volumes, or until the field parameters (pH, temperature, and specific conductance) stabilized, eight sample bottles of various sizes and type were filled at each well site. All samples obtained were chilled in ice chests and sent by FedEx overnight under chain-of-custody provisions to a well-known laboratory (Lancaster Laboratories, Inc.) in Pennsylvania (for major and minor chemical analyses) and at the Environmental Isotope Laboratory, University of Waterloo, Canada (for isotope analyses).

Two types of laboratory analyses were conducted: 1) total and dissolved constituent (including bromide) concentrations for hydrochemical characterization of the samples, and 2) concentrations of natural and other isotope ratios such as: ^{13}C/^{12}C (in dissolved inorganic DIC carbon), ^{2}H/^{1}H, ^{18}O/^{16}O, and tritium activity present in the samples to provide information on the residence time and relative age of the groundwater at various sampling sites.

Drilling and Coring

The geological and construction logs for the monitoring wells installed on the company property are presented in Appendix A. The location of the coring and drilling activities, and of the groundwater sampling sites are shown in Figure 1.

Core Hole (MW-1E)

The coring efficiency was good, although typically slow, especially when dealing with winter conditions at the rig. The coring generally recovered 100% of the interval cored, as measured against the kelly bar on the rig. Occasionally, during coring in the lower part of the hole, shale intervals would break into thin, horizontal bagel forms, which indicate minor losses in intervals of soft or vuggy rock. When measured at the kelly bar on the rig, however, the core loss amounted to only a few inches. Mr. M. David Campbell, P.G., Project Hydrogeologist in 2003-4, is shown describing the core samples in Figure 2 and preparing the records for the well logs presented in Appendix A.

A target depth for the coring was established after reviewing a local water well driller's log, which indicated that the first replacement well encountered "brackish water" when drilling to a depth of 220 feet bg. The core-hole location is approximately 600 feet to the south-southeast from the Cn site (see Figure 1). A shallow monitoring well (MW-1S) was drilled nearby to a depth of 78 feet and produced potable water. The hydrochemistry of the groundwater sampled from this well and others nearby will be discussed later.

Coring encountered fine-grained glacial till from just below the soil to a depth of about 5 feet. This is underlain by light brown, heavily jointed sandstone from a depth of about 5 feet to about 120 feet in MW-1D, underlain by a dark to light gray shale and thin siltstones and sandstones. Fractures and joints appear to decrease in abundance with depth.

Figure 2: Core Description.

A near vertical joint in the core at 57 feet bg. was filled with fine-grained, ferruginous material (Figure 3 and the location of the core hole CH-1 (site of MW-1S, MW-1D, and MW-1E), Figure 1). The advanced jointing within the Black Hand sandstone was likely caused by the weight and stress of glaciers that moved across the site during the numerous glacial periods in Ohio or as a result of area rebound after the glaciers retreated [11,12]. For additional details on the core, see Figure 5 and the full geological logs and monitoring well construction details in Appendix A.

The light gray shale underlying the sandstone is approximately 60 feet thick and is in turn underlain by dark gray shale. At approximately 182 feet bg. a fault zone indicated by slickensides near the base of the unit exhibited the characteristic shiny surface and fine groves in the shale (Figure 4). The orientation of the fractures or joints was measured in the core to exhibit two orientations; one set measured approximately 30 degrees and the other 60 degrees from horizontal, which are consistent with glacial loading/unloading or with fault movement in the area.

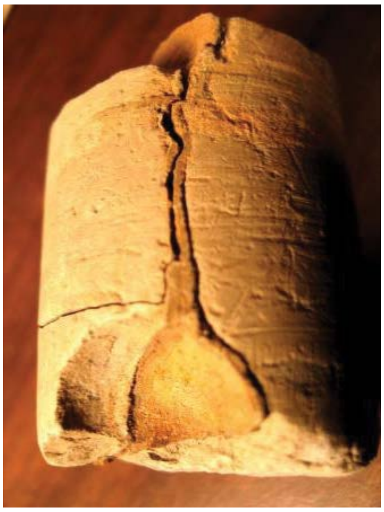


Figure 3: Core Sample from 57 feet bg.

Figure 4: Slickensides in Core at 204 feet bg.

This fault zone is near the contact with very fine-grained gray sandstone. The fault zone cuts the core at an angle of approximately 49 degrees, although the trend or actual orientation of the zone cannot be established with any degree of certainty because of the nature of the rotating coring operations. The zone appears “recent” (no oxidation); such movement might be related to glacial adjustments and/or regional stresses caused by or after bedrock rebound activities. Additional investigations on the core are still in progress (Appendix F and [13]). Also, it should be noted that if the indicated fault extends to depth, the fault zone might be associated with either the Akron Fault/ Magnetic Boundary, located some 30 miles to the NNE or to the well-known Cambridge Fault, major basement fault zone (designated the Cambridge Cross-Strike Structure Discontinuity) in north-central Ohio [14,15]. The ramifications of the presence of this zone will be discussed in greater detail later in this paper.

The coring was terminated at a depth of 218 feet, within the “brackish” zone encountered by the pre-Cn, re-drilled well nearby (Figure 1). We made the decision to convert the core hole (previously designated as CH-1D) to an extra-deep monitoring well (MW-1E) for the purpose of sampling the groundwater at that depth and to obtain water-level (pressure) measurements from this deep zone that would contribute significantly in establishing the hydrogeological flow-net conditions below and around the company property. For additional details on the core (see Appendix A).

Of additional note during examination of the core in the field was that there were thin intervals consisting of pebble-size and coarse-grained sandstone at depths of 49, 53, 69, and 96 feet below ground level described in the log shown in Figure

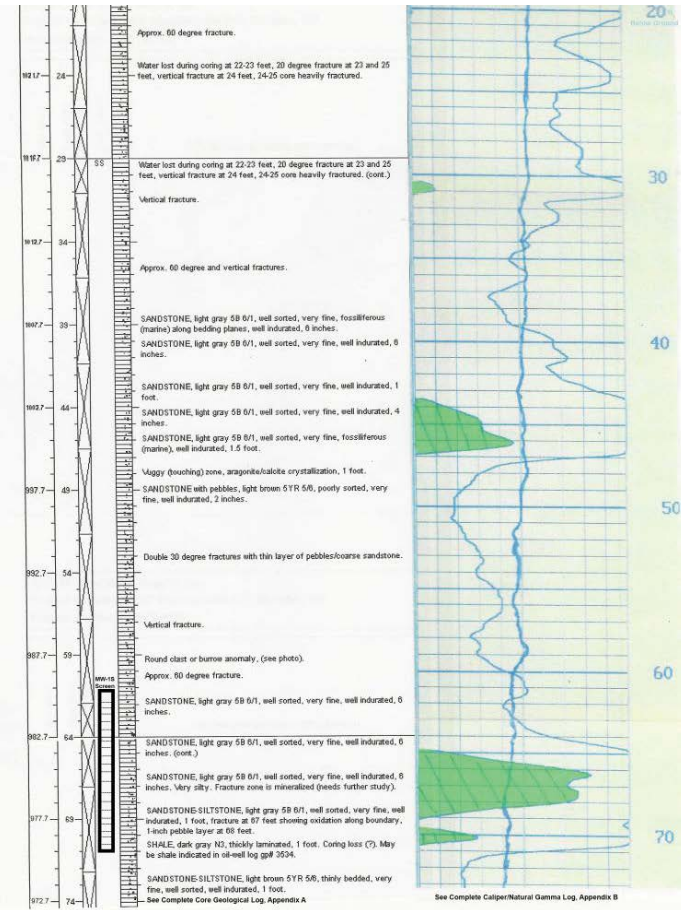


Figure 5: Partial Core Log w/Natural Gamma/ Caliper Log Showing Radioactive Anomalies. (to enlarge, click (here))

5 and core log (Appendix A). For further discussions, see Appendix F.

The vuggy intervals (eroded pebble zones?) and fracture zones appear to represent erosional/depositional periods within the Black Hand Sandstone [13], which would have readily transmitted groundwater to the numerous seeps evident in the field adjacent to the west of the company property and at lower elevations surrounding the hill (Figures 1 and 7). The zones are also discussed further in Appendix F.

Anomalous Radioactive Zones

The entire core hole was logged with caliper and natural gamma geophysical tools for the primary purpose of identifying sand-shale contacts as an aid in setting screens in the monitoring wells (Appendix B). Aside from that, and of particular note, is that there are three anomalous zones of natural gamma indicated in the geophysical log, one over the internal of 30 to 31, 43 to 47 feet, and another from 65 to 71 feet bg. (Figure 5 and geological log in Appendix A). The anomalies occur across intervals of recorded fractures/vugs within the sandstone. The lower anomaly extends across a "mineralized" fracture zone and a sandstone-siltstone contact, as does the monitoring well screen for MW-1S. In the discussions on the hydrochemistry and isotopes that follow, we will be taking a special note of the analytical results from the zone of elevated radioactivity captured by MW-1S (Figure 5).

At present, we can only speculate on the source of the radioactive anomalies indicated in the zones shown in Figure 5, but we are currently examining the indicated zones within the core in some detail, both by thin section and XRF to determine if the anomalies are related to anthropogenic or natural causes (preliminary results are presented Appendix F). Additional test results will be presented when available. We did not run hydrochemical or geochemical analyses for uranium, radium, or other NORM-related radioactive elements at the time of groundwater sampling because our preliminary surface scans of the company property (using a Model 101 Geometrics scintillometer) indicated no abnormal radioactivity on the property and hence there were no NORM-related concerns at the time. However, barium minerals often accommodate radium and associated elements; barium results are available as part of our hydrochemical assessment (Table 2), which will be discussed later in this paper.

The lower anomalous zone is shown in Figure 5A between 65 feet and 70 feet (there was core loss in zone), and shows the **highly oxidized interface or flooding zone** with unoxidized (or reduced) sandstone (see Appendix F). There are two similar intervals above 65 feet at interval 42 feet to 46 feet (also with soft core loss within zone to be discussed later), and another zone above that (Figure 5). These core-loss zones are interpreted as vuggy zones in the core that likely permitted fluid flow from the surface, or from corroded casing of an oil/gas well drilled decades ago.

Figure 5A: Core in Box.

Seeps and Springs

We visited the off-property seep sites mentioned above in June, 2004 and confirmed that the seeps (albeit intermittent springs) were likely to flow during or just after periods of heavy precipitation. The flow could be of sufficient volume to erode small gullies in the field, but which are small enough to be plowed over in the spring before planting each year. We observed no evidence of vegetation stress along the gullies, as might be expected if the effluent contained high concentrations of the chloride ion or other constituents that affect plant growth. Other springs to the north and west can be inferred by the surface topographical features (indicative of fractures in the underlying bedrock) represented as the source of the small streams around the area (see the northern area of Figure 7). It should be noted that a pebble zone was reported during the coring on the company property at about the same elevation of the seeps (see Well Logs in Appendix A and MW-1E).

Other Holes and Monitoring Wells

The other nine holes were drilled with an air-rotary rig and completed as monitoring wells, as shown in Figure 1. Sites MW-4S, 4D, and MW-6D sites were found to be not needed. The selection of screened intervals was based on information provided by the coring and projected to the other drilling sites. In some cases, the drilling dust, mud color, drill cuttings, and apparent zones of water loss guided the selection of well depth and associated screened interval.

After the monitoring wells were installed, we performed well development by pumping each well to remove fine-grained materials that remained in the well as a result of the well-construction activities. Most wells developed rapidly as indicated by monitoring the field parameters (i.e., temperature, pH, and specific conductance and dissolved oxygen); by removing the suspended fines in the water wherein the water turns from muddy to clear, but one well did not. MW-1E did not develop to any extent because of the low permeability of the sandstone interval screened and because of the necessity to employ a small-diameter, low-apacity pump.

Mini-Coring Investigations

A series of small-diameter core-hole samples were taken by a soil-augering tool at various locations during our water-well sampling activities. Mini-coring was conducted to investigate the thickness and characteristics of the soil and underlying glacial till in the county road area (Table 1. Six sites were cored (see Figure 1 for locations.

The soil is unusually thin in the areas we cored above. The soil zone in the area is likely to be thin in some places while thicker in others, especially where the old Oak trees have found anchorage and sufficient thickness of soil for root development and health over the years. The highly weathered and jointed nature of the near-surface sandstone, as indicated from our drilling on the company property nearby (i.e., located 600 to 800 feet to the south, indicates that the top of the sandstone is irregular and is covered by glacial till of at least a few feet in thickness. The septic tanks systems' leachfields and effluent drainage areas in the subject area have limited soil (and till thickness for effective adsorption of effluent and would be expected to readily drain down to the water table via the fractures and joints in the Black Hand Sandstone.

We consider the likelihood is high for septic effluent, charged with periodic disposal of the water softener's brine effluent, to reach the fractured rock underlying the thin soil areas and of being flushed down joints in the bedrock to the water table some 70 to 80 feet below land surface, especially during periods of precipitation (rainfall and snowmelt, or during watering of yards by residents. In addition, any road salt or brine spread during the winter months for ice control on county road or on the resident drive ways would also similarly migrate down through the heavily weathered and jointed sandstone to the groundwater reservoir below thereby elevating the chloride content of the drinking water in the area. This topic will be discussed in greater detail later in this paper.

Field Reconnaissance

We conducted a ground reconnaissance of the cornfield to the west of the company facility to investigate the gullets indicated on a number of aerial photographs (Figures 1 and 2. As indicated previously, these gullets were likely created mostly by surface water run-off from the company facility. However, the aerial photographs also show a trace of what is likely a contact in the rocks below the soil where one of the highly permeable sandstone zones, mentioned above, comes to the surface creating seeps along this trend (see Log of MW-1E at elevation 1,022 ft. MSL. At least five drainage ways are apparent along this trend in the aerial photographs. The plants growing at the time of our visit in and around the gullets exhibited no apparent stress. Some erosional features were noted in the gullets but this was likely related to running water during or after periods of precipitation. Vegetation stress is also not evident in the aerial photographs from previous years. For additional discussions regarding the seeps, see Sampling and Analyses, above.

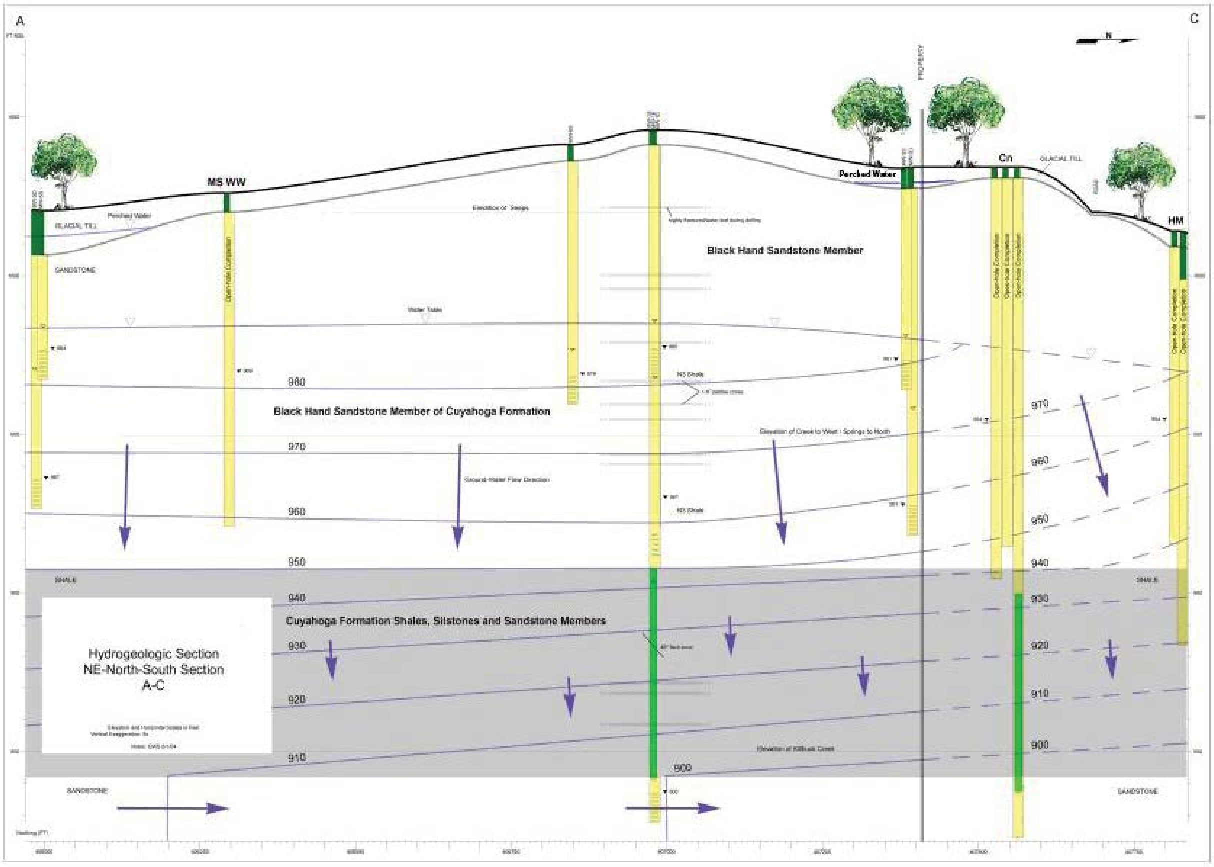


Figure 6: Hydrogeological Section: A – C (VE=5X (to enlarge, click (here))

Figure 7: General Area and Section D-D'. (to expand click (here).

During the reconnaissance, we visited an oil well facility located along the western boundary of the cornfield mentioned above (Figure 2). Present at the site was an electric-driven pump-jack, one crude-oil storage tank and a crude oil/brine-separator tower. The pump jack appeared to be operational although we did not test the voltage on the electric motor that operates the system. Of note here is that a one-inch diameter brine line had been installed from the separator northward along the surface just inside the tree line next to the cornfield.

The brine line runs through and under an old, household refuse dumping site that was observed within the treeline. Based on the trash present, we estimated that it was of 1960s to 1970s vintage. No containers were marked as having contained hazardous material We continued to follow the brine line into the dense bushes for some distance. It either terminated within the high brush and trees or was buried more deeply and terminated elsewhere. A wide drainage way of high bushes trended down into the creek shown in Figure 2. We observed no stressed vegetation in the area. A sample of creek water (SW-1) was taken downstream where the stream passes under county road (Figure 1 and Tables 2 and 3).

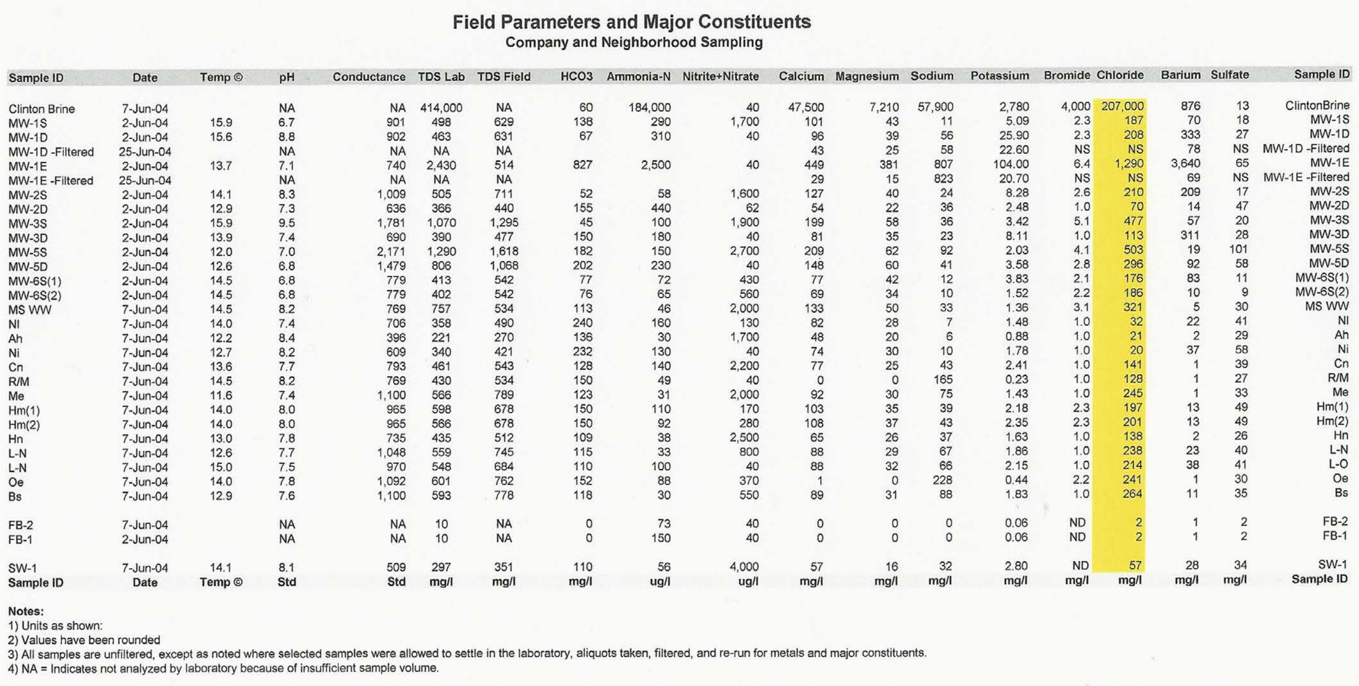
Groundwater-Level Measurements

Water levels were measured for all wells sampled, with the exception of the water well at the Me site, which was an old water well (circa 1957) located in the basement of the residence. The bolts on top of the well casing were rusted. We chose not to risk damaging the wellhead's assembly unit. The other well site locations are shown in Figure 1.

Table 1: Mini-Core Results.

Mini-Core #	Property Located	Depth to Bedrock	Comments
1	R/M	2 feet 5 inches	In back yard
2	“	2 feet 3 inches	140 ft. uphill from # 1
3	NW corner of R/M	2 feet 9.5 inches	Front yard near county road.
4	“	1 foot 8 inches	“ “
5	Next to Hn	> 3 feet	Near county road
6	MW-6S	6 inches	Gravel

Table 2: **(to enlarge, click (here))**

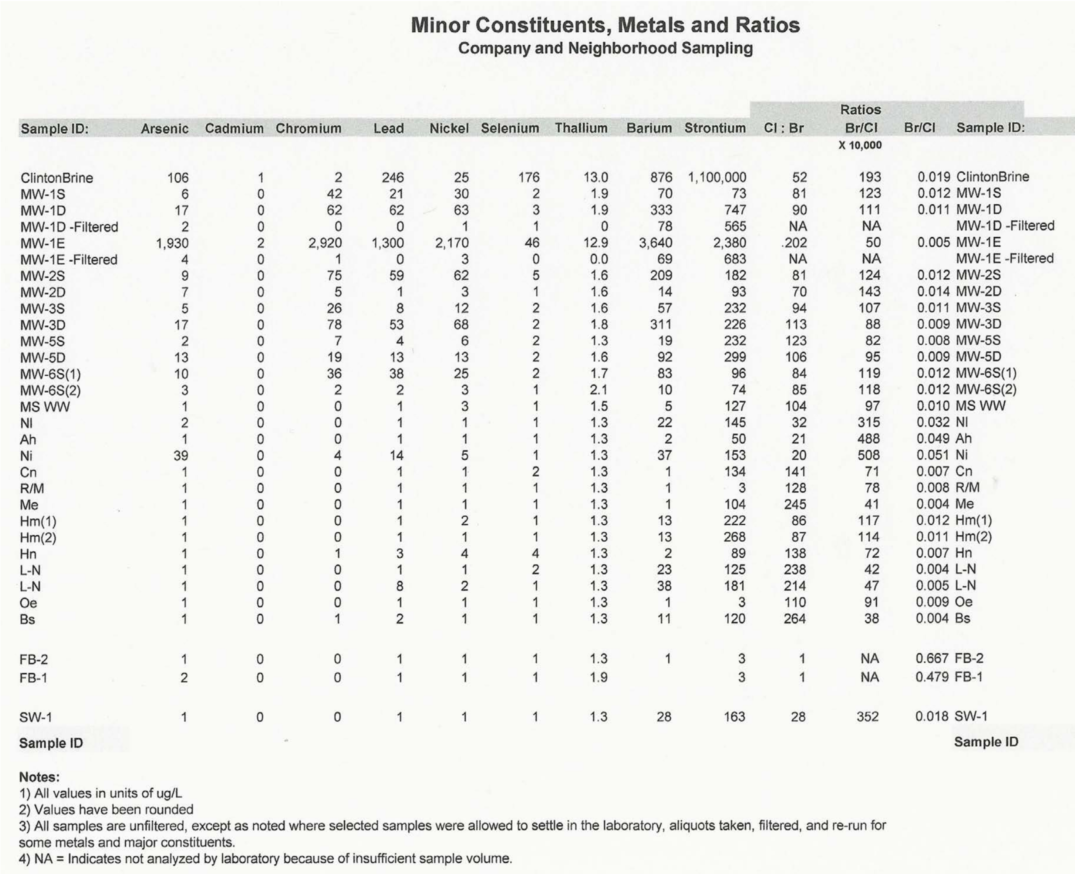


Field Parameters and Major Constituents
Company and Neighborhood Sampling

Sample ID	Date	Temp ©	pH	Conductance	TDS Lab	TDS Field	HCO3	Ammonia-N	Nitrite+Nitrate	Calcium	Magnesium	Sodium	Potassium	Bromide	Chloride	Barium	Sulfate	Sample ID
Clinton Brine	7-Jun-04		NA	NA	414,000	NA	60	184,000	40	47,500	7,210	57,900	2,780	4,000	207,000	876	13	ClintonBrine
MW-1S	2-Jun-04	15.9	6.7	901	498	629	138	290	1,700	101	43	11	5.09	2.3	187	70	18	MW-1S
MW-1D	2-Jun-04	15.6	8.8	902	463	631	67	310	40	96	39	56	25.90	2.3	208	333	27	MW-1D
MW-1D -Filtered	25-Jun-04		NA	NA	NA	NA				43	25	58	22.60	NS	NS	78	NS	MW-1D -Filtered
MW-1E	2-Jun-04	13.7	7.1	740	2,430	514	827	2,500	40	449	381	807	104.00	6.4	1,290	3,640	65	MW-1E
MW-1E -Filtered	25-Jun-04		NA	NA	NA	NA				29	15	823	20.70	NS	NS	69	NS	MW-1E -Filtered
MW-2S	2-Jun-04	14.1	8.3	1,009	505	711	52	58	1,600	127	40	24	8.28	2.6	210	209	17	MW-2S
MW-2D	2-Jun-04	12.9	7.3	636	366	440	155	440	62	54	22	36	2.48	1.0	70	14	47	MW-2D
MW-3S	2-Jun-04	15.9	9.5	1,781	1,070	1,295	45	100	1,900	199	58	36	3.42	5.1	477	57	20	MW-3S
MW-3D	2-Jun-04	13.9	7.4	690	390	477	150	180	40	81	35	23	8.11	1.0	113	311	28	MW-3D
MW-5S	2-Jun-04	12.0	7.0	2,171	1,290	1,618	182	150	2,700	209	62	92	2.03	4.1	503	19	101	MW-5S
MW-5D	2-Jun-04	12.6	6.8	1,479	806	1,068	202	230	40	148	60	41	3.58	2.8	296	92	58	MW-5D
MW-6S(1)	2-Jun-04	14.5	6.8	779	413	542	77	72	430	77	42	12	3.83	2.1	176	83	11	MW-6S(1)
MW-6S(2)	2-Jun-04	14.5	6.8	779	402	542	76	65	560	69	34	10	1.52	2.2	186	10	9	MW-6S(2)
MS WW	7-Jun-04	14.5	8.2	769	757	534	113	46	2,000	133	50	33	1.36	3.1	321	5	30	MS WW
NI	7-Jun-04	14.0	7.4	706	358	490	240	160	130	82	28	7	1.48	1.0	32	22	41	NI
Ah	7-Jun-04	12.2	8.4	396	221	270	136	30	1,700	48	20	6	0.88	1.0	21	2	29	Ah
Ni	7-Jun-04	12.7	8.2	609	340	421	232	130	40	74	30	10	1.78	1.0	20	37	58	Ni
Cn	7-Jun-04	13.6	7.7	793	461	543	128	140	2,200	77	25	43	2.41	1.0	141	1	39	Cn
R/M	7-Jun-04	14.5	8.2	769	430	534	150	49	40	0	0	165	0.23	1.0	128	1	27	R/M
Me	7-Jun-04	11.6	7.4	1,100	566	789	123	31	2,000	92	30	75	1.43	1.0	245	1	33	Me
Hm(1)	7-Jun-04	14.0	8.0	965	598	678	150	110	170	103	35	39	2.18	2.3	197	13	49	Hm(1)
Hm(2)	7-Jun-04	14.0	8.0	965	566	678	150	92	280	108	37	43	2.35	2.3	201	13	49	Hm(2)
Hn	7-Jun-04	13.0	7.8	735	435	512	109	38	2,500	65	26	37	1.63	1.0	138	2	26	Hn
L-N	7-Jun-04	12.6	7.7	1,048	559	745	115	33	800	88	29	67	1.86	1.0	238	23	40	L-N
L-N	7-Jun-04	15.0	7.5	970	548	684	110	100	40	88	32	66	2.15	1.0	214	38	41	L-O
Oe	7-Jun-04	14.0	7.8	1,092	601	762	152	88	370	1	0	228	0.44	2.2	241	1	30	Oe
Bs	7-Jun-04	12.9	7.6	1,100	593	778	118	30	550	89	31	88	1.83	1.0	264	11	35	Bs
FB-2	7-Jun-04		NA	NA	10	NA	0	73	40	0	0	0	0.06	ND	2	1	2	FB-2
FB-1	2-Jun-04		NA	NA	10	NA	0	150	40	0	0	0	0.06	ND	2	1	2	FB-1
SW-1	7-Jun-04	14.1	8.1	509	297	351	110	56	4,000	57	16	32	2.80	ND	57	28	34	SW-1
Sample ID	**Date**	**Temp ©**	**Std**	**Std**	**mg/l**	**mg/l**	**mg/l**	**ug/l**	**ug/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**Sample ID**

Notes:
1) Units as shown:
2) Values have been rounded
3) All samples are unfiltered, except as noted where selected samples were allowed to settle in the laboratory, aliquots taken, filtered, and re-run for metals and major constituents.
4) NA = Indicates not analyzed by laboratory because of insufficient sample volume.

Table 3: (to enlarge, click (here))



Minor Constituents, Metals and Ratios
Company and Neighborhood Sampling

										Ratios			
Sample ID:	**Arsenic**	**Cadmium**	**Chromium**	**Lead**	**Nickel**	**Selenium**	**Thallium**	**Barium**	**Strontium**	**Cl : Br**	**Br/Cl X 10,000**	**Br/Cl**	**Sample ID:**
ClintonBrine	106	1	2	246	25	176	13.0	876	1,100,000	52	193	0.019	ClintonBrine
MW-1S	6	0	42	21	30	2	1.9	70	73	81	123	0.012	MW-1S
MW-1D	17	0	62	62	63	3	1.9	333	747	90	111	0.011	MW-1D
MW-1D -Filtered	2	0	0	0	1	1	0	78	565	NA	NA		MW-1D -Filtered
MW-1E	1,930	2	2,920	1,300	2,170	46	12.9	3,640	2,380	.202	50	0.005	MW-1E
MW-1E -Filtered	4	0	1	0	3	0	0.0	69	683	NA	NA		MW-1E -Filtered
MW-2S	9	0	75	59	62	5	1.6	209	182	81	124	0.012	MW-2S
MW-2D	7	0	5	1	3	1	1.6	14	93	70	143	0.014	MW-2D
MW-3S	5	0	26	8	12	2	1.6	57	232	94	107	0.011	MW-3S
MW-3D	17	0	78	53	68	2	1.8	311	226	113	88	0.009	MW-3D
MW-5S	2	0	7	4	6	2	1.3	19	232	123	82	0.008	MW-5S
MW-5D	13	0	19	13	13	2	1.6	92	299	106	95	0.009	MW-5D
MW-6S(1)	10	0	36	38	25	2	1.7	83	96	84	119	0.012	MW-6S(1)
MW-6S(2)	3	0	2	2	3	1	2.1	10	74	85	118	0.012	MW-6S(2)
MS WW	1	0	0	1	3	1	1.5	5	127	104	97	0.010	MS WW
NI	2	0	0	1	1	1	1.3	22	145	32	315	0.032	NI
Ah	1	0	0	1	1	1	1.3	2	50	21	488	0.049	Ah
Ni	39	0	4	14	5	1	1.3	37	153	20	508	0.051	Ni
Cn	1	0	0	1	1	2	1.3	1	134	141	71	0.007	Cn
R/M	1	0	0	1	1	1	1.3	1	3	128	78	0.008	R/M
Me	1	0	0	1	1	1	1.3	1	104	245	41	0.004	Me
Hm(1)	1	0	0	1	2	1	1.3	13	222	86	117	0.012	Hm(1)
Hm(2)	1	0	0	1	1	1	1.3	13	268	87	114	0.011	Hm(2)
Hn	1	0	1	3	4	4	1.3	2	89	138	72	0.007	Hn
L-N	1	0	0	1	1	2	1.3	23	125	238	42	0.004	L-N
L-N	1	0	0	8	2	1	1.3	38	181	214	47	0.005	L-N
Oe	1	0	0	1	1	1	1.3	1	3	110	91	0.009	Oe
Bs	1	0	1	2	1	1	1.3	11	120	264	38	0.004	Bs
FB-2	1	0	0	1	1	1	1.3	1	3	1	NA	0.667	FB-2
FB-1	2	0	0	1	1	1	1.9		3	1	NA	0.479	FB-1
SW-1	1	0	0	1	1	1	1.3	28	163	28	352	0.018	SW-1
Sample ID													**Sample ID**

Notes:
1) All values in units of ug/L
2) Values have been rounded
3) All samples are unfiltered, except as noted where selected samples were allowed to settle in the laboratory, aliquots taken, filtered, and re-run for some metals and major constituents.
4) NA = Indicates not analyzed by laboratory because of insufficient sample volume.

Of particular note is that the elevation of the water level of early June, 2004 for the MS well indicates that a groundwater mound was present below the company facility when compared to the other measurements of equilibrated water-levels of the neighborhood wells surrounding the facility. However, it should also be noted here that the water levels can be misleading because there is no assurance that the groundwater level of a neighborhood well was under equilibrium conditions at the time of our measurement. Pumping of the subject well or by one of a next-door neighbors well might have just started or just finished and the water level of its cone of depression in either case could have been still rising or falling. Therefore, these measurements are used with appropriate caution [16].

As indicated earlier, because the groundwater occurs in fractured and jointed, consolidated sandstones, the well's typical cone of depression created by pumping is likely to be highly irregular, being heavily influenced by the fracture zones. This can extend for hundreds of feet away from the well along preferred pathways of the fractures and joints in the rock.

Hydrogeological Conditions

We prepared a series of hydrogeological cross sections using the data developed during our investigations. The locations of the section lines are marked in Figures 1 and 7. The sections are illustrated in Figures 6 and 8. Although both fracture flow and porous-media flow are present in the area, both would respond similarly to changes in the hydraulic pressure in the subsurface, as indicated in the flow-net analysis represented in the Figure 6 and 8, where thin, high permeability zones exit (as in pebble zones or in open fracture zones), groundwater flow in the zones would be exacerbated.

Shown in the sections, glacial till is present below the soil and consists of generally very fine-grained sand with a few pebble-sized quartz grains. The till drapes over highly weathered, light brown, fine-grained sandstone that extends some 150 feet below. The till thickens from approximately 6 feet or less on the top of the hill north of the company property to approximately 15 feet in thickness near the southern boundary. Groundwater becomes perched during the spring and was encountered within 10 feet of the surface in MW-5S and 5D at the time of installation. This water probably evaporates or drains down into the fractured sandstone below over the summer months.

The glacial till beyond the northern property boundary (see Figure 6) is about six-feet thick in the area of MW-2S and 2D and seven-feet thick at the site of MW-3S and 3D. This unit would be expected to thin toward the north and in the area of the neighborhood residents where the hill is the highest elevation. This was confirmed by our mini-core activities described above where the soil and till below was less than two-feet, the significance of which will be discussed later in this paper. Geologic and hydrogeologic conditions in and around the company property have allowed the brine applied to the company pipe yard driveways during 1998 to 2000 to migrate into and be absorbed by the shallow, sponge-like glacial till just below the surface on the company property (on-site). Groundwater then becomes perched in the glacial till as it thickens toward the southern part of the On-site facility, and drains off to the east and west and through preferential pathways in the sandstone below via minor surface seeps and springs.

Based on the available information, the groundwater flow in the subject area is dominated by fracture (or joint) flow, either of some specific orientation, as the core shows as either 30 or 60 degrees. In addition, zones exist with nearly horizontal orientation where thin, highly permeable zones represent the principal flow through highly-porous media of the sandstone, with the very fine-grained sandstone unit representing the bulk of the rock being of secondary hydraulic conductivity.

The main groundwater reservoir is located below. Groundwater would flow in the porous media of the Black Hand Sandstone, albeit at a slower rate than in fractures and joints, and ultimately would discharge in the vicinity of Killbuck Creek from surface seeps and springs. Some of these exist along the contact of the sandstone with thick shale in outcrops bordering the Killbuck Creek about a mile to the north and to the east of the subject property. The section flow-net analysis illustrated in Figures 6 and 8 indicates that groundwater flow component is downward. This would be expected for a recharge zone in an area of somewhat elevated topography (Figure 7) [17].

As the flow approaches the gray shale at depth, groundwater flow would refract in shale and would also follow the gradient along the top of the shale toward the east where any lag gravels, pebbles or fractured sandstone of high hydraulic conductivity exist. Travel through the shale would be slow, unless fracture zones of significant permeability were present. It should be noted here that the thin shale units described in the boring log of MW-1E (Appendix A) designated as "N3 Shale" in the cross sections of Figures 6 and 8, also appear to be highly fractured and likely serve as conduits around the seeps and springs around the hill (Figure 7, and indicated seeps, and fracture zones creating springs. We have designated a regional dip shown in Figure 8 of approximately 1 degree to the east for the main shale unit (i.e., known locally as the Wooster Shale member lying below the Black Hand Sandstone and other sandstones, siltstones and thin shales above as part of the Cuyahoga Formation [18] [146].

The indicated movement of a fault zone, as indicated by the presence of the slickensides (Figure 4) did not appear to be highly permeable or mineralized and hence might not have transmitted groundwater to any great extent. This interval might be an example of a fault/joint where glacial rebound or regional pressures have exerted compressional pressure on the joint, and if oriented other than vertical, would force movement of one side or the other (or both) sides of the joint of sufficient duration and movement to create slickensides, and therefore by definition would represent a fault. However, the nature of this fault zone would differ along its strike. Such zones often become major avenues of groundwater migration,

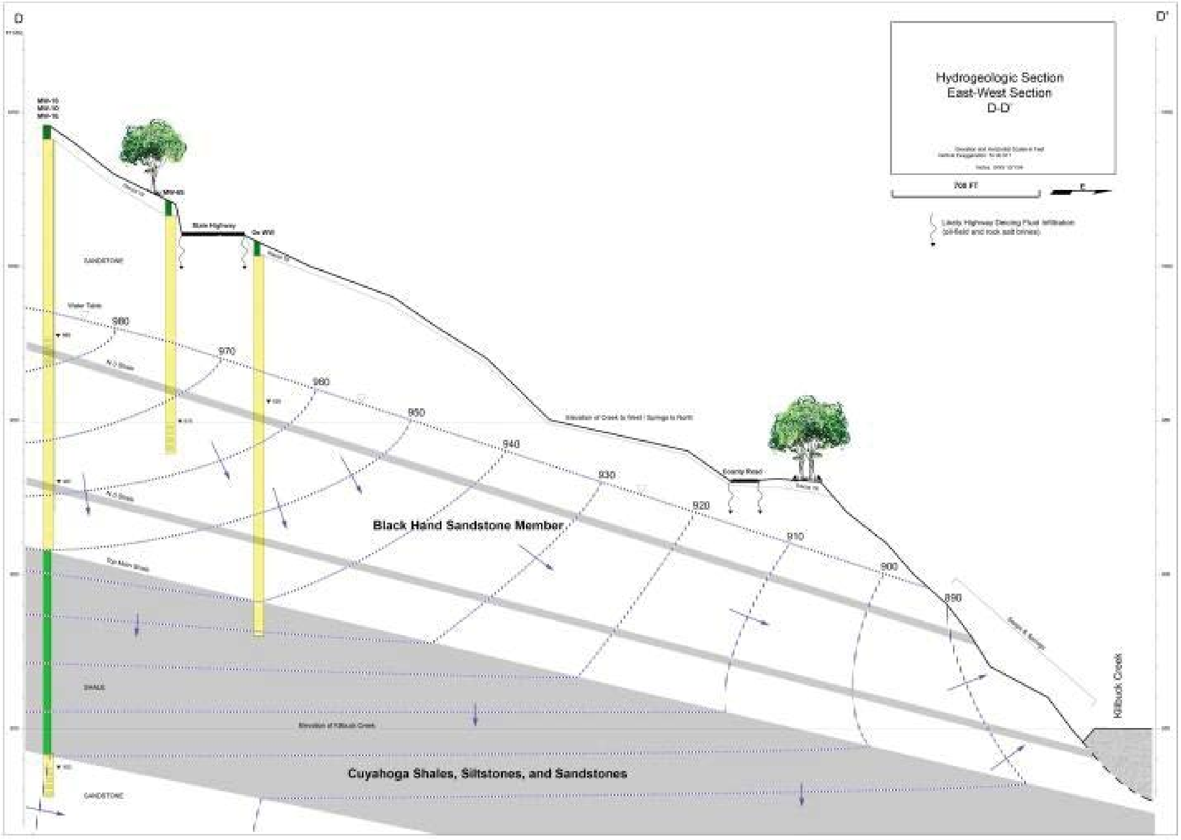


Figure 8: Hydrogeological Section – D – D' (VE-5X). (to enlarge, see (here)).

especially where granulation of bedrock created permeability (see Gotkowitz *et al*. [19], and other researchers [14,20,21]. After the slow, intergranular flow in the porous media of the shale, groundwater would emerge from the bottom of the shale, and the flow would again refract abruptly in a near lateral direction to the north and east, in the direction of discharge below Killbuck Creek (see Figures 6 and 8).

We concluded that based on: 1) an analysis of the groundwater flow, and 2) groundwater levels measured in the neighborhood wells, the shallow groundwater migrates downward, with only a slight lateral direction of the groundwater flow in the direction of neighbor wells toward the north boundary of the company property and principally toward the east (Figure 6 and 7). Flow to the west toward the small creek would also be expected. Additional support is provided by the major and minor elements and isotopes present in the groundwater and streams in the vicinity, which includes an assessment of the hydrochemical analyses from the boundary monitoring wells, especially MW-2S and 2D, and MW-3S and 3D, and which will be discussed later in this paper. We will discuss the three possible sources of elevated chlorides in the groundwater of the subject area, e.g., resulting from spreading the brine (Clinton brine) onsite, the brine (mostly halite) applied to the state and county roads for de-icing, and the brine entering the groundwater from water-softening/septic tank-leachfield systems.

Major and Minor Elements

Of the 11 monitoring wells installed on the company property and of the 13 neighborhood water wells sampled, there are a number of ways to assess how and where elevated chloride existed in the drinking water system within the subject area, the likely source, and the destination. One way to discern the likely history of high chloride in the groundwater of the subject area is to examine the relations of the various constituent concentrations to each other and to their physical environment, (i.e., pH, temperature, and specific conductance). [95].

Hydrochemistry and Water Quality

The hydrochemistry of the various constituents typically found in groundwater can provide a wealth of information on its sources, how long it has been in the ground, and in this case, whether anthropogenic involvement has impacted the groundwater to the extent that it is unfit for human consumption. In some areas of the country the geological conditions have created groundwater reservoirs that are overlain by a protective cover of low-permeability sediments. In other areas, geological conditions have combined to make the groundwater highly vulnerable to contamination from above, introduced either as a result of careless or irresponsible industrial activities, from inadvertent human activities, or from natural conditions in the soil or from underlying sediments or unusual rock types [148].

Most groundwater is strongly reducing. Elevated concentrations of arsenic, iron, manganese, and sulfide (present either as dissolved hydrogen sulfide or as precipitating iron sulfide minerals) are associated with this type of redox environment where pH is lower than 7.0. Some groundwater is oxidizing (or oxic). Nitrate concentrations were detected. In relating groundwater sampling back to the water wells involved, oxidizing conditions are generally found at well locations where either depth to groundwater was shallow (i.e., less than 45 ft. below land surface) or the measured water level was within the open interval (below the cased portion) in the open hole of the well. Wells tapping strongly reducing groundwater are generally found at depths to the water table greater than 60 feet below surface and exhibit measured water levels of 15 feet or more above the open interval of the well within the cased interval of the water well [23]. There are exceptions, sometimes created by a variety of local anthropomorphic activities, such as releases of effluents from improperly sited leachfields (of septic tanks), halite salts used to de-ice roads in winter, inappropriate dumping of household constituents, etc. [162,163, and 164].

One of the reasons for installing monitoring wells on the company property was to permit us to obtain samples of groundwater from various depths in the subsurface. Water wells are already present in the subject neighborhood, although the groundwater enters the wells over many feet of open area of the hole below the casing installed by the water well contractor [24]. This provides for in-hole storage of water ready to be used by the resident at the outset of pumping.

In the open-hole arrangement, the groundwater flows from a range of depths, in the subject cases, from the groundwater within fractures and joints, and more slowly from the porous media, such as glacial tills, sandstones, siltstones, and shales. This provides hydrochemical data that represents a composite groundwater quality coming into the well from a vertical interval, not a specific depth or range of depths. In geologic conditions where flow in fractures and joints dominate over porous-media flow, as indicated previously, the water quality and associated hydrochemistry of major and minor elements, ions, and molecules can be affected rapidly in a matter of less than a few days.

The laboratory results for the groundwater samples obtained from the on-site monitoring wells and from the neighborhood water wells, plus a sample from the nearby creek, one sample of Clinton brine, and the quality-control samples (e.g., field blanks and duplicates) have been presented in Table 2 (Field Parameters and Major Constituents) and in Table 3 (Minor Constituents, Metals and Ratios). The supporting laboratory reports are presented in Appendix D. The isotope analyses data are discussed later in this paper.

Because the Clinton brine has been used in both the application on the company property for dust control and de-icing, and on county roads along the northern and southern boundaries, and along the eastern boundary of a state highway adjacent to the property, this brine serves as the baseline against which subsequent comparisons will be made. Its compositional history and hydrochemical make-up is reviewed to establish the appropriate context. Lowry and Faure [23] evaluated 24 selected brine samples from the "Clinton" sandstones of Silurian age [25]. They found evidence that the brine's chemical compositions can be attributed to mixing of two brines, both of high concentrations of sodium chloride and the second by calcium chloride [26]. They concluded that this is based on the fact that the Clinton brine did not acquire its high concentrations of sodium, chloride, bromide, potassium, magnesium, and calcium by water-rock interactions within the Clinton sandstones.

They also determined that the concentration of Na-rich brine decreases with depth within the Clinton sandstones, whereas the abundance of Ca-rich brine increases [27]. Further, and especially important in our investigations, is that they concluded that the Ca-rich brine component originated from sources at depth, and is mixed with the Na-rich brine formed from the rock salt in the overlying Salina Formation. The available isotope compositions of oxygen and hydrogen from 12 brine samples further supported their conclusions. We also conducted similar studies, which will be discussed later in this paper.

Brines are originally formed as groundwater migrates through the porous media, fractures, and joints, depending on the rock type and compositional makeup, and as it travels through high sodium beds (as in salt intervals or other beds with minerals of evaporitic origin containing sodium, nitrate-nitrite, bromates, etc.) or through limestones or dolomites (dissolving calcium, magnesium, barium, and a range of sulfate and sulfide minerals (depending the pH and Eh of the water) [29][62].

Millions, if not hundreds of millions of years are involved in this migration, unless interrupted by geological processes, such as tectonics, as faulting or uplift, that could introduce new pathways that could more quickly cause mixing with another brine of contrasting chemical and isotopic compositions [30,31,116,150]. Add to this new recharge to the system from above, the new meteoritic water would interact with rock media within pore spaces and fractures that could, because of lowered pH, induce dissolution or precipitation of minerals, ion exchange, oxidation/reduction (if oxygen or reduced carbon are present), and even osmotic effects across shale units, especially where the metal colloids and suspended minerals are present in the water (i.e., extremely small particles of micron size and less). Brines can be formed by long-term travel times in aquifers, increasing their load of chloride and other salts along the way, and not necessarily from ancient seawater as has been incorrectly termed as "connate" water [26][32][80].

Effects more recently introduced to a brine and its chemical and isotopic compositions would also come from the introduction of amended "fresh" water used in hydraulic fracturing for increasing production of oil and gas reservoirs (all of which also contain brine in proportions of some 30:1 or more brine: oil/barrel). In the operations, faulty well casings and cementing (either installed improperly or corroded after decades of service) can leak brine into producing strings or out of casing into fresh-water zones that would be expected to be under some pressure [16][25]. Other methods of contaminating brine are by storing it in an above-ground tank open to mixing with meteoric water (precipitation), and evaporation, and to inappropriate sampling methods and sample treatment prior to analysis.

The Clinton brine sample analyses were used in our evaluations with some reservations, but they were not relied on in any detail except as a general reference in our plots below, with the above history of the Clinton brine discussed in context.

Characterization by Major and Minor Elements

A series of bivariate plots were prepared using the various ions, elements, compounds, and parameters shown in Tables 2 and 3 to characterize different populations of elements and physical parameters to illustrate similarities and associations, when apparent. For an example of the approach, we plotted field chloride vs. sodium of the samples taken during our investigations (Figure 9). Nine subpopulations (or affiliations) were identified at the outset of our assessments and used as the initial baseline for comparison and analysis of the samples' composition in other plots. In other words, how does the grouping hold up when plotted with other ions and elements. Do they (the individual data groupings) have other affiliations or do they remain as is? Which samples plot away from groupings? The question must then be asked whether the sampling was representative of the conditions at the time of sampling.

To address these issues, we obtained duplicate samples from two sites (one set from an on-site monitoring well (MW-6S(1) and MW-6S(2)) and one set from a neighborhood well (Hm(1) and Hm(2)). The results indicate that there were no significant differences in the latter set of duplicates, but that that there were significant differences in the metals content in the former set (MW-6S(1) and (2)), see Table 3, which would have to be considered when assessing groupings.

A related aspect of sampling assessment was to determine the difference between suspended solids and dissolved constituents in groundwater samples from the deep monitoring wells on-site (i.e., MW-1D and MW-1E). These samples were filtered and analyzed in the laboratory. The issue of colloids is treated in some detail later in this paper.

Aliquots were taken of the raw water sample and re-analyzed for selected analyses. The results were reported as "Filtered," as indicated in Tables 2 and 3. As would be expected, the results indicate a significant difference for both samples (i.e., filtered (dissolved) and Total) indicating that most, but not all, metal constituents had been adsorbed on or into solids, which were likely inherited from the sandstones or from the glacial till above during groundwater migration from the surface to the monitoring well sampling zones.

All other samples are therefore considered raw, unfiltered groundwater to assess the impact of natural and anthropogenic recharge to the shallow groundwater. This will be discussed later in various contexts throughout this paper. Also, two field blanks (of deionized water) were inserted as field samples (FB1 and FB2) for laboratory sampling as reported in Tables 2 and 3.

The chemical data review summary reporting on the QA/QC of the sampling and laboratory analyses is available in Appendix C, pp.1-3.

Making the assumption that the samples would show hydrochemical similarities in any immediate area (unless some outside conditions have overprinted the water by addition or subtraction of cations or ions, if the physiochemical conditions forced adsorption, precipitation, or other activities that might be involved in wall-rock-water interactions), the local context is established for the apparent subpopulations of the identified groundwater samples (including a nearby stream sample and a sample of the Clinton brine (used on the subject property to control dust but also on county and state road for deicing in the winter on occasions). The bivariate plot of chloride vs. sodium in Figure 9 shows specific subpopulations (or groupings), but not always in the grouping indicated in Figure 9. However, Whittemore (pers. com., 2017) emphasizes that there are issues with using Cl vs. Na bivariate plots because Na is adsorbed on clays. Even though sandstones often contain only a very small amount of clay, a very small amount is all that is needed to significantly change the Na content of a groundwater with a different (Ca + Mg)/Na ratio than that of the original groundwater because of cation exchange of Na^+ for Ca^{+2} and Mg^{+2} (or reverse depending on the relative ratios of the introduced water and the original water). The sources of elevated chloride in this case are known so the groupings shown in Figure 20 provide a baseline for subsequent comparison with other constituents [132].

Hydrochemical Assessments

As indicated earlier, the purpose of the assessments of the plots is to provide possible explanations for the elevated chloride concentrations at the Cn site and Pre-Cn environment and environs as offered by the physio-chemical characteristics of the groundwater of the neighborhood water wells and those from the monitoring wells. This was to determine if the groundwater below the company property contained elevated chloride concentrations and if so, whether this site served as the source of the chlorides at the Cn site a few hundred feet north of the company boundary (Figure 1 and Figure 7) or whether the company's brine-spreading activities were responsible for the elevated chloride concentrations at the Pre-Cn site.

Subpopulation C represents subsurface conditions away from and up-gradient of the company property (Figure 7). Also note that the Clinton Brine plots at the far extreme of the bivariate plot (as Subpopulation F) and the sample from MW-1E plots along the reference line toward brine as Subpopulation E, as would be expected for the two samples representing relatively deep and very old groundwater. Subpopulation G consists of three samples, MW-6S and MW-6S (Duplicate) and MW-1S.

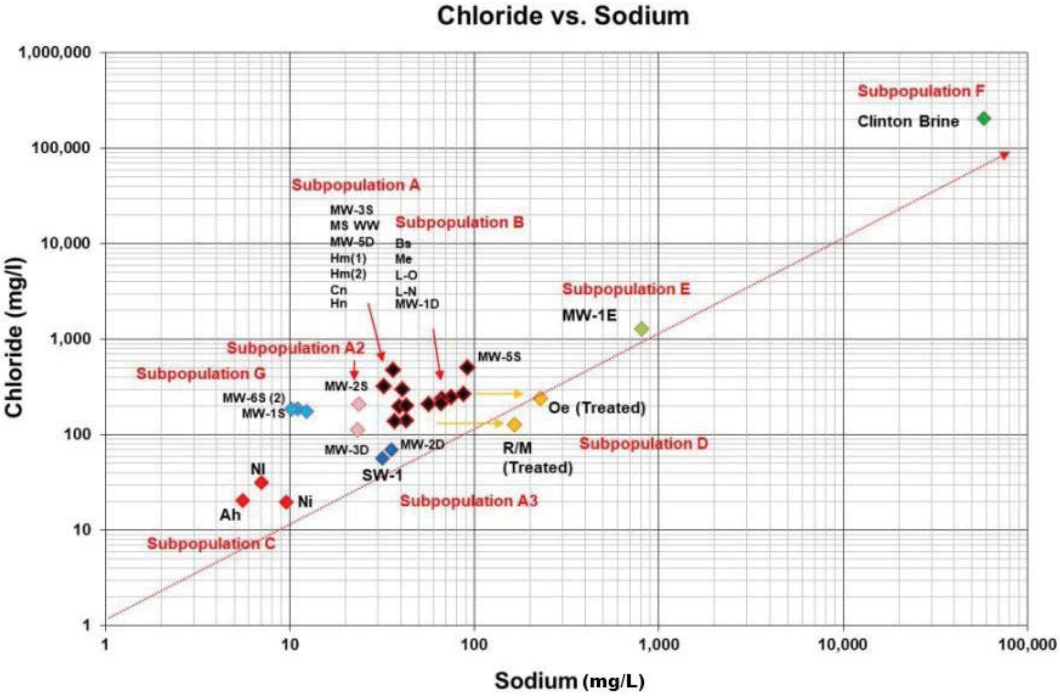


Figure 9: Chloride vs. Sodium.

Subpopulations A and B encompass the rest of the neighborhood well samples and two of the on-site (company) monitoring well samples, i.e., MW-3S, MW-5D, and MW- 1D, plus SW-WW (the on-site water well). Subpopulations A2 and A3 are adjacent but appear to be separate. They consist of MW-2S, MW-3D, MW-2D and the stream sample, SW-1. The last grouping appearing in Figure 9 is Subpopulation D, which are the two sample sites known to have undergone water softening treatment at their sources, i.e., sites R/M and Oe where some metals exchanged as sodium increases and regenerates the halite within the water-softening unit in the resident home while discharging chloride-rich water to the septic tank and leachfield. This will be discussed later in this paper.

To provide additional context to the above sample populations, the bivariate plot of pH against field specific conductance shown in Figure 10, provides data points from the records of the U. S. Geological Survey for groundwater and surface water samples from the Killbuck Creek studies they conducted in the early 2000s a few miles to the north of the subject company property [18,33]. They can be represented as background samples with hydrochemistry useful to compare to samples from higher elevations of the monitoring well samples from the company facility and from the surrounding neighborhood wells. Different symbols represent the four populations, i.e., U.S.G.S. ground water, U.S.G.S. Surface Water, on-site monitoring well data, and neighborhood well data. The distribution shows that a few of the on-site well samples do not cluster with the main cluster.

We prepared a series of plots using the various elements, ions, and radicals shown in Tables 2 and 3 to characterize deferent populations and physical parameters to illustrate similarities, differences, and associations, when apparent. For an example of the approach, we plotted field pH against Total Dissolved Solids shown in Figure 11, which includes data from the records of the U.S. Geological Survey for ground water and surface water samples from the Killbuck Creek studies conducted over the past few years a few miles to the north of the subject property. They represent background samples that would be useful to compare their hydrochemistry with samples from the facility and surrounding neighborhood wells. Different symbols represent the four populations, i.e., U.S.G.S. groundwater, U.S.G.S. Surface Water, company monitoring well data, and neighborhood well data.

The distribution shows that a few of the on-site samples do not cluster with the main cluster. A review of Tables 2 and 3 indicates that the groundwater sample from MW-3S contains abnormal concentrations of nitrite plus nitrate, chloride, and strontium.

The above plots of field parameters involving pH and specific conductance and total dissolved solids provide a lateral context of our sampling results with those of the U.S. Geological Survey sampling program. The vertical context of our sampling is illustrated in Figure 12, which establishes the chloride concentrations reported during our sampling for 23 wells, that is nine monitoring wells and 13 neighborhood water wells, one stream sample, and one sample of the Clinton brine.

The depth profile of Figure 12 indicates the depths at which the groundwater samples were obtained, i.e., from the screened interval of the monitoring wells installed during our

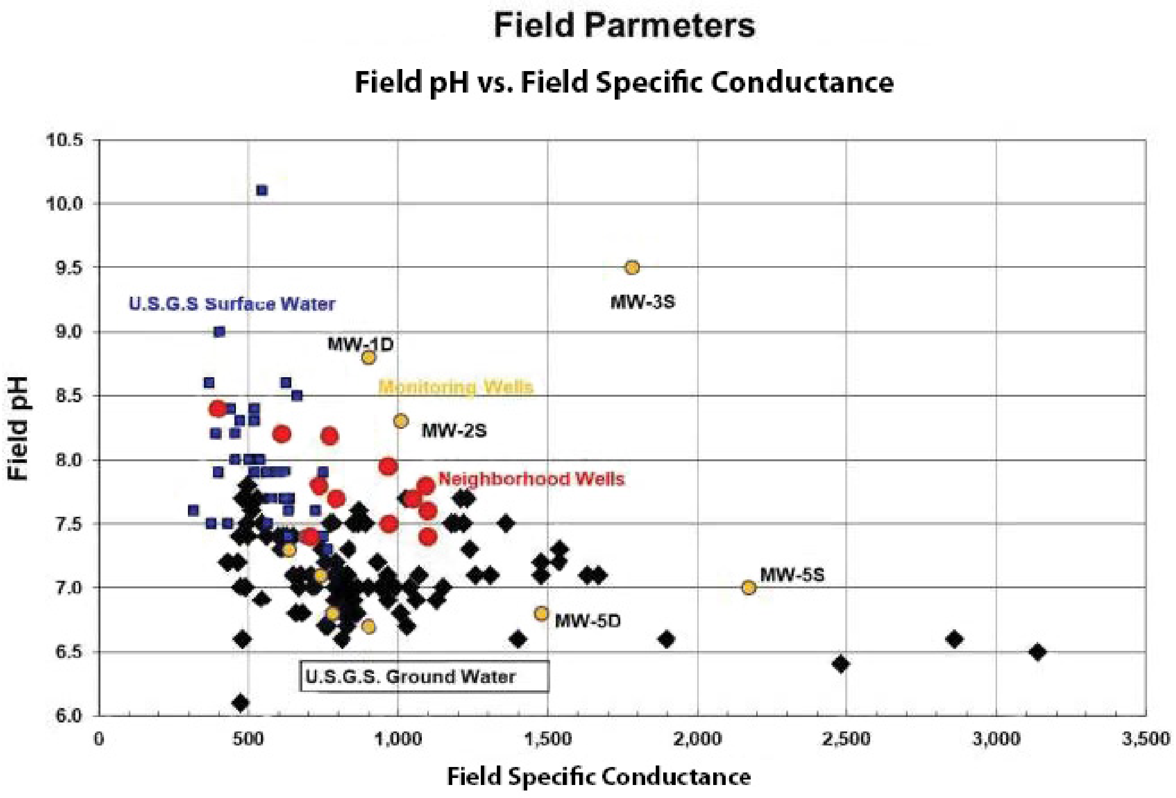


Figure 10: Field Parameters.

investigations (Appendix A for the "as built" designs for each well). And, the neighborhood water wells indicated in black symbols (outlined in gray) were generally drilled and cased to 100 feet with open hole to total depth drilled, which allows for maximum exposure to joints and fractures and other high-permeability zones in the Black Hand Sandstone, discussed earlier.

Note that there are two plotting groups of the samples from the neighborhood wells, one group is up-gradient from all other wells and samples indicate low levels of chloride (samples from three different depths). Other data are also anomalous. Two monitoring wells i.e., MW-3S and MW-5S, plot separately at clearly elevated levels of chloride for samples taken at shallow depths just below the water table. This indicates the presence of local sources of elevated chlorides.

These two samples are in proximity to county and state road de-icing treatments resulting from both oil and gas brine and halite brine sources migrating out of the fine-grained glacial till, because these samples have a strong correlation to oil and gas brine (based on bromide, but also correlate to softener-leachfield effluent (based on the very high nitrate-nitrite content of both samples). The location of MW-3S and MW-5S could also have a bearing on their hydrochemistry. MW-3S exhibited a high pH.

Water-level measurements were taken at multiple times to establish the elevation (=head) of:

1) the water levels within each of the monitoring wells (for the purpose of constructing a series flow-net sections of groundwater flow (Figures 6 and 8))

2) the water table in the area from measuring the water levels within each of the neighborhood wells selected for sampling with open-hole completion (all of their well systems incorporated automatic pumping systems set to supply the household with water as needed, so water levels varied from time to time).

However, because most of the groundwater pumping brings water from the joints, fracture zones and other permeable zones (and from the porous media of the sandstone), water levels within the cones of depression of each well would be expected to recover rapidly after pumping ceased, even around the neighborhood. Finally, as expected both the stream sample (SW-1) and MW-1E plot at the extreme sections, one low in chloride (57 mg/l Cl), and the other high in chloride (MW-1E at 1,290 mg/l Cl). The likely sources of the elevated chloride will be discussed later in this paper.

To provide a depth perspective, we also prepared a depth vs. chloride profile plot for both the on-site monitoring wells and the sampled neighborhood wells. The depth shown is based on the mid-point of the open area of the resident wells, whereas the depth of sampling for the monitoring wells is the mid-point of the filter pack. The plot illustrates the range in depth sampled during the company investigation (Figure 12). The depth coverage of the monitoring wells illustrates that chloride is migrating from above in the neighborhood along the county road, not from subsurface, lateral flow from the company

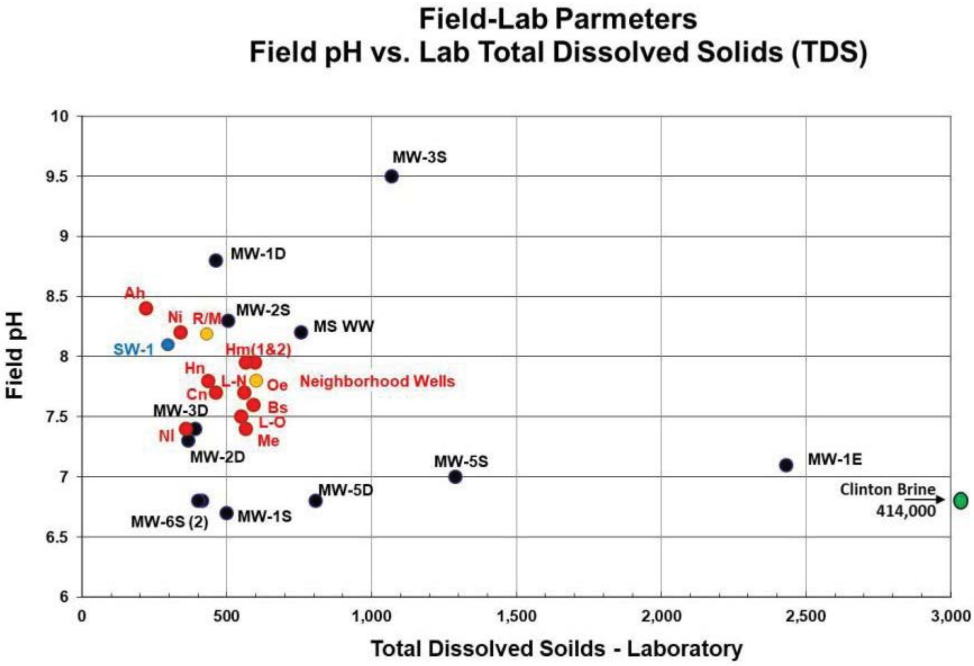


Figure 11: field-lab parameters. Field pH vs. Lab Total Dissolved Solids (TDS).

facility (i.e., MW-2D to the Cn well or MW-3D to the L-N well). There are other lines of support for this view. The hydrochemical context of the sampling is presented in a Piper diagram using the data developed during our investigations (Figure 13).

First, the Clinton Brine occupies the anticipated positions (end points) in the three fields of the Piper diagram in generally linear relation involving the other data plots, especially the Ca-Mg-Na+K and HCO_3-SO_4-Cl sections of the plot, although the upper diamond section trend is less district although present. The other end point is represented by the up-gradient sites that cluster in all three sections of Figure 13, as

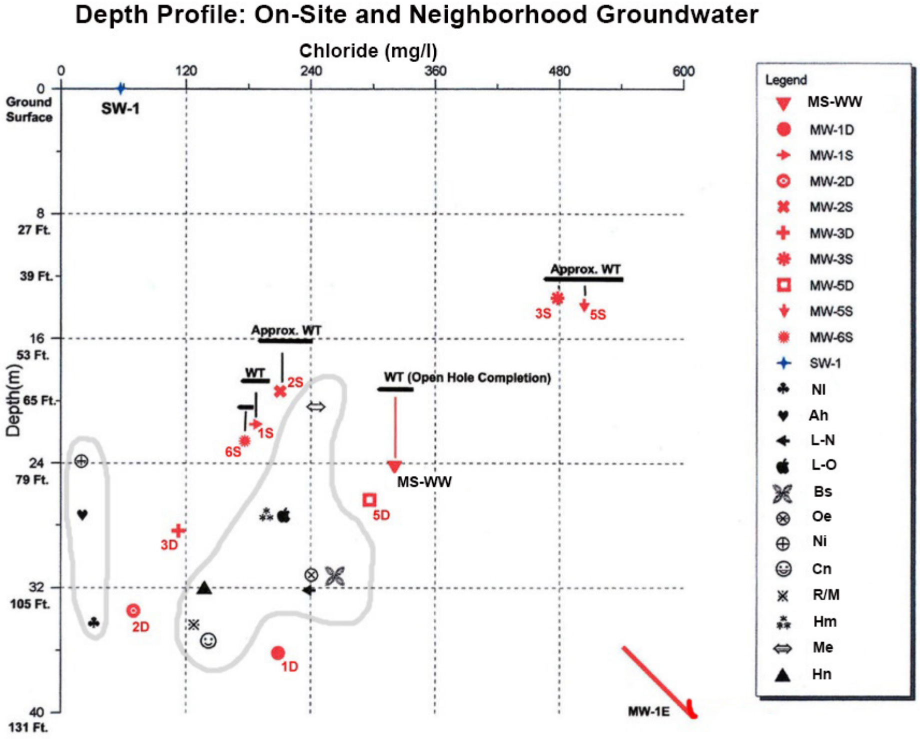


Figure 12: Depth profile: On-site and Neighborhood Groundwater. (to expand, click (here))

they do in most of the other plots discussed in this paper, i.e., sites Ni, Nl, and Ah (Figures 1 and 7 for sampling sites). These end-members are located some distance along the county road south of the company property plot indicating that the groundwater in those areas can be considered as representing hydrochemical background for the constituents involved and therefore qualify as end-members for the sample sets used, although there are some variations that have other explanations [133][135].

It should also be noted that the stream sample (SW-1) is not in an end-member position in any of the three sectors of Figure 13, although it is nearby in two of the plot sections but not in the lower left sector (Ca-Mg-Na+K) where it occupies a medial position along the trend.

Second, two samples from sites R/M and Oe (shown as purple symbols) were reported as softened water clearly plot outside the two of the three trends. However, they are plotted within the chloride trend of the field in the lower right position on the diagram. As will be observed in most other plots, they will also plot apart from the other groupings.

Third, note that a path is shown in red in the lower right triangle of Figure 13. This is one example of groundwater flow with elevated chloride (from a source to be discussed later) that would migrate from the area of MW-2S and Cn toward the stream (and SW-1). The flow direction is based on the flow direction indicated in Figure 7. The Cn sample is similar in low chloride content to MW-2D from approximately 300 feet way.

Fourth, the analysis of the sample from MW-1E plots away from the trend of the Ca-Mg-NA+K field of Figure 13, whereas the sample plots on the periphery of the upper field toward the Clinton brine plot but within the trend of the field at the lower right.

Fifth, the neighborhood wells plot together in two groupings within the trend of the upper diamond field and separated into the up-gradient group at what appears to be the end-member of the trend.

Sixth, and of particular note, is that most of the samples within the company property plot in the field designated as the "permanently hard groundwater" zone of the upper area of the diamond field in Figure 13 [34]. This shows that the hydrochemistry is recharge water containing significant chloride, which has interacted with the aquifer materials [35,36]. But recharge water also interacts with any introduced constituents including sodium, calcium, magnesium, sulfate, etc., that drives the hydrochemistry toward the apex of the field within the Piper diagram [37,38]. See 2018 study from southern Ontario [173, Fig.6].

Further, groundwater samples from the county road north of the subject area plot in a cluster just below the company samples. This indicates that the groundwater in the subject area has experienced a different history than that below the company facility. If on-site groundwater with elevated chloride had migrated as a plume toward the northern county road, the clusters would have merged and would show intermingling within the diamond plot of the Figure 13, not segregated into separate clusters as they appear. The two company samples plotting near the "residents' cluster," are MW-2D and MW-3D, also appear to be unrelated to the hydrochemical characteristics of the samples of the nearby residents, as discussed previously.

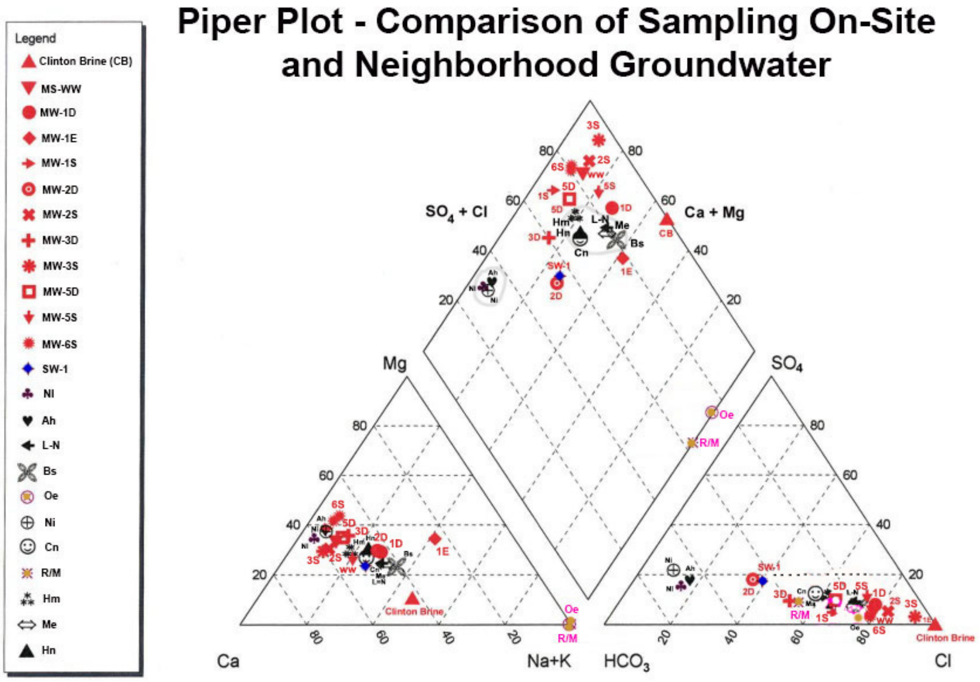


Figure 13: Piper Plot – Comparison of Sampling On-Site and Neighborhood Groundwater. (to enlarge, click (here))

Ambiguities of the Data Sets

Ambiguities are present in the Piper plot when samples are plotted from significantly different elevations and environments, such as the deep saline zone (i.e., MW-1E) plotting next to the shallow Bs sample, for example. This might be explained by the data distribution plotted in the Piper diagram of Figure 13 within in the "permanent hardness" zone (top part of diamond), in which water chemistries are dominated by high calcium + magnesium and high chloride + sulfate. This creates rings on porcelain bowls often stained by the high-iron content of the groundwater. Although useful in describing the general hydrochemical associations between water samples, it is not useful in discriminating between different sources of the contained constituents, especially when the constituent's concentrations have been significantly altered by anthropogenic activities that have added to (or subtracted from) the constituents from the groundwater in the immediate area of the residents' water wells. This plot does appear to show the general affiliations of the groupings, which will be treated further using other plots later in this paper.

Much of our discussion is based on the role that individual sampling sites plays in any clustering of the data within the Piper and other plots employed here. Although sampling is limited in number and time, the groupings (and associated trends) are apparent and remain constrained; we therefore consider the indicated trends to be useful in assessing the likely history of elevated chloride, and additional sampling at the time would have reinforced the presence of the trends in any event.

Sources of Elevated Chlorides

The likely source of salinity of MW-3S and MW-6S, located in proximity to the state highway (Figures 1 and 8) and MW-5S, located south of the company property next to the southern county road (Figures 1, 6 and 7, represent another type of mixing (and dilution) of hydrochemistry of brine and road salt used in deicing the highway in the Winter [2,10,39]. The area of MW-2S and Cn and R/M sites will be used to illustrate the conditions.

In the Spring of 2004, MW-2S sampling showed somewhat elevated chloride (210 mg/L), whereas the deeper sample from MW-2D indicated lower chloride (70 mg/L), providing evidence of recharge from the glacial till above during or after periods of precipitation and subsequent flow to the west and northwest toward the creek (and SW-1). Of critical importance here is to note that the elevated chloride does not appear to migrate into the lower portions of the aquifer at this location only some 40 feet below the sampling interval of MW-2S because the presence of such chloride is not evident in MW-2D, which exhibited very low chloride concentrations in Spring, 2004.

Only a few hundred feet to the north of MW-2D, the Cn well shows chloride values almost double that of MW-2D, both wells drawing groundwater from the aquifer from similar elevations. This indicates that elevated chlorides near the water table have not reached the lower elevations of the aquifer system that would have provided groundwater to the Cn well in this area (Figure 6) and likely drains via preferential fractures into the shallow flow system migrating toward the western creek (Figure 7, and SW-1). This indicates that any elevation of chloride concentrations was locally introduced and did not flow as a plume from the company property northward through the area of the neighborhood water wells. And, there are additional factors confirming this conclusion that came to light during our field investigations.

Local Area Reporting

The report from the neighborhood visits conducted during our investigation revealed four important factors relevant to the reported presence of elevated chlorides in 2004:

1) The history of the Cn well was recorded, when it was drilled and when replaced. The previous owner moved prior to our visit. A new, deeper well was drilled and reported elevated chlorides (see Figure 6), because the groundwater present at that depth interval was subsequently found to be similar to that sampled in MW-1E. A third well was drilled at the time to a depth similar to the original well and found by the new owner to offer acceptable water quality (much lower chloride than reported originally) as indicated in MW-2D located a few hundred feet away of similar depth (Figures 1 and 7). The question arises: where were the indications of high chloride reported earlier by the previous resident (and confirmed by the ONDR)?

2) The field report of activities on the Cn property provided information of interest, which during the inspection of the backyard and garage revealed a stack of 8 to 10 bags of rock salt used in water-softening systems stored in the corner of the garage. The owner at the time of our visit indicated that the previous owner had especially hard water (including high iron) from their well and used a lot of salt for water-softening regeneration, and for de-icing their driveway, which is a common practice in rural and urban roads in the U.S.[40,41] [138].

3) The field report of activities was also of interest regarding the R/M property, next to the Cn property, which indicated that two large Oak trees, located among a row of large Oak trees along the driveway leading to the northern county road were located next to the leachfield of the R/M septic-tank system, and were in the final stages of dying and were being removed during our visit. One of the likely factors contributing to their deaths was excessive salt exposure from the leachfield to the root systems of the two trees. The other trees had also been inspected by professional arborists and were found to be unaffected at that time [136].

4) The field report also indicated whether the home-owners operated or had operated a home water-softening system during the period in question, which in the above matter, Cn installed a new system and reported minimal salt consumption. R/M also operated a water softening system and indicated no unusual salt consumption. There was no way to verify these claims at the time of our visit.

No other resident in the immediate area admitted to operating water-softening systems associated with their drinking water, but all resident had to have septic-tank systems. However, east of the state highway the Oe site did operate a softening system, but the field reports indicate that the Bs site's system was not operating at the time of sampling.

Interpretations of Contrasting Data

With the groundwater around the MW-2D site flowing to the north and northwest toward the Cn and R/M water wells, this flow would be expected to encounter similar hydrochemistry that was likely recharged from above involving effluent from the surface via septic and softening regeneration and the leachfields entering the groundwater at elevations lower than some 50 feet below surface. Furthermore, the similarity and proximity of the plots for MW-2D and that of SW-1 (from the western creek) shown in Figures 7 and 13 confirm that groundwater in this particular area is likely flowing in the direction of the creek, as indicated previously.

Another observation that can be made is the rather tight clustering in Figure 13 of the neighborhood wells along the northern county road, indicating a common or similar source of chloride and other constituents, also likely related to a number of sources of salinity near the surface and believed to have leaked through the thin glacial till downward about 50 feet to the water table. This will be further developed later in this paper.

The data plotting along the chloride trend in the Piper diagram in Figure 13 indicates that the constituents were introduced by oil-field brines used for dust control on the company property. Relatively small volumes of brine were applied to the traffic areas within the subject pipe yard by spreading Clinton brine from 1998 through 2000 to control dust during the summers. However, the plotted trend does not indicate that the chloride is from oil-field brines, just that chloride is a dominant constituent dissolved in the groundwater sampled [2,39]. It became apparent that elevated chloride can also be introduced from brines created by halite used not only in home water-softening systems, but also in road and highway de-icing operations during the winters [31,42,43]. Over the years, there have been a number of studies made to characterize the mixing that occurs under such conditions and this investigation was conducted to address just such matters [6,44,45][139][166][167].

The constituents reported in the hydrochemistry at the MW-1E site differs significantly from that of the Clinton brine (where Figure 14 compares the metals: arsenic, cadmium, chromium, lead, nickel, selenium, thallium, barium, and strontium for both on-site and neighborhood well samples, and for the Clinton brine and stream sample). This figure shows that MW-1E groundwater is enriched relative to the Clinton brine in all of the metals relative to the other samples, except for selenium, thallium, and strontium; for the latter, the Clinton brine exceeds that of MW-1E by almost 500% in the sample, containing 207,000 mg/L chloride, and elevated ammonia-nitrate, sodium, calcium, magnesium, and bromide (Tables 2 and 3). Some metals also occur in road salt although they are not apparent in the neighborhood samples shown in Figure 14 [3].

A Few Anomalies

Of particular significance in Figure 14 is that it shows that the on-site monitoring wells (shown in black) carried a higher load of metals relative to the neighborhood water wells, except for strontium and barium to some extent. Obscured in the figure are the depleted levels of barium and strontium reported for sites R/M and Oe, the two sites having softened water. This has two ramifications. One is that the subject pipe-yard has released metals over the years to be transported down with the normal recharge from rain and snow melt. Combined with this generalized source of metal could be metals from the Clinton brine spread on the property to control dust and for de-icing [46,47]. Tables 2 and 3, and Figure 14 illustrates the presence of such metals, although the brine-spreading operations only persisted a few years until the pre-Cn resident reported the elevated chlorides to the company and to the ODNR, as previously discussed.

There were also positive anomalies shown in Figure 14. Arsenic and lead were found to be above their MCLs in the groundwater sample from site Ni, one of the up-gradient sampling sites south of the company property along the county road (Figure 1). As located, the groundwater flows north and east toward the county road and company property (Figure 7). The wellhead, sited in the middle of the backyard, was rather old and surrounded by machinery of various types. We suspected that the anomalous metals present were eroded from such equipment and found their way through the well casing and down to the groundwater over the past 25 years, at least. The area was once a garden and the property was surrounded by corn fields, either of which could have been the source of arsenic and lead, i.e., used in herbicides, fungicides, etc. [48]. A new well was being planned by the resident during our last contact in any event.

A particularly interesting aspect of the distribution of metals and other elements and ions in the groundwater below the company facility and in the area of the neighborhood wells is illustrated in Figure 14. For all practical purposes, this figure demonstrates that the ground water under the company facility contains significant concentrations of metals, i.e., arsenic, chromium, lead, nickel, selenium, thallium, barium and strontium, whereas just a few feet across the northern company boundary with its neighbors, groundwater samples from the wells in the neighborhood show dramatically lower concentrations of such metals and other constituents [49]. As we have discussed the hydrogeological conditions earlier, this is related to a combination of the downward direction of groundwater flow combined with the density of fluids that have migrated in pulses downward through the shallow glacial till zone, down preferred fracture and jointed zones and then flowing down the regional dip toward the east and north to Killbuck Creek.

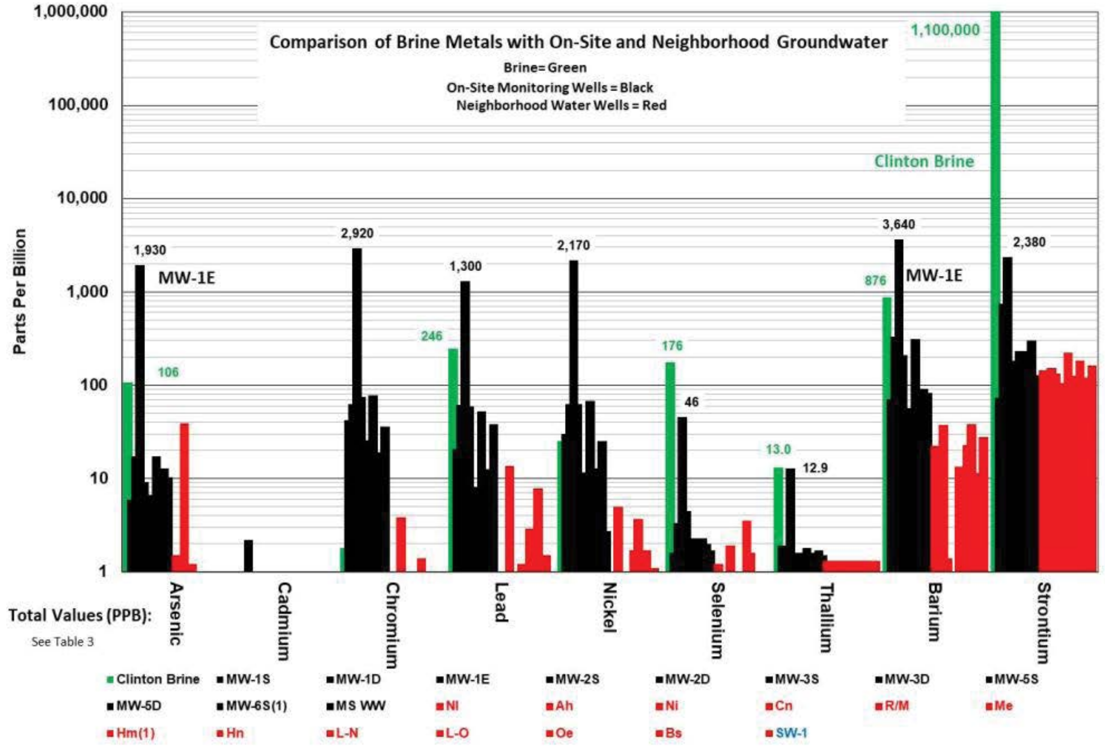


Figure 14: Comparison of Brine Metals with On-site and Neighborhood Groundwater.

Many of the metals and other constituents show a progressive rise in concentrations with depth in monitoring wells: MW-1S and MW-1D above MW-1E. The presence of the fault/joint zone running through the sandstone and the presence of an abandoned oil exploration well within a few feet of the MW-1 series of wells raises the possibility of mineralized groundwater from natural sources (from age of the groundwater, which will be discussed later in context of the isotopes) and from anthropogenic sources involved in a failed plugged oil well (discussed previously) that could have contributed anomalous fluids (now diluted) sometime since abandonment [50].

An increase in metals in the groundwater also occurs at site MW-5S and MW-5D along the southern boundary of the company property, but along the northern boundary, MW-2S and MW-2D, and MW-3S and MW-3D show decreasing metal concentrations with depth (Tables 2 and 3). One possible explanation that would explain both increasing and decreasing concentration with depth would be the presence of pulses of metals (or any other similar constituents) created either by recharge or by rainfall (or snow melt) or by recharge via brine spreading, or both in combination. For example, where relatively higher metal concentrations exist at depth (as in samples obtained in the area of MW-2S-2D and MW-3S-3D located along the northern boundary of the subject property), this shows that the plume containing relatively high metals is migrating downward within the Black Hand Sandstone. Conversely, where relatively higher concentrations are present in the shallow zone as indicated at sites MW-1S and MW-1D, and MW-5S and MW-5D, this also shows that the constituents were introduced at or near the surface (at Cn, R/M, and perhaps Oe sites) and move downward as a pulse of density-driven plume. This vertical movement would be supported by the flow-net analysis of groundwater flow as presented in Figures 6 and 8.

Researchers have attributed abnormal hydrochemistry in groundwater from sandstones in northeast Ohio as originating from great depths as the source for mineralized groundwater. One source involves historical agricultural activities that introduced fertilizers, herbicides, fungicides, etc., containing arsenic and related metals in farming areas that served as groundwater recharge zones [51]. Others suggest that epigenetic sulfides forming in a fine-grained, reducing environment within siltstones and shales were oxidized when exposed to old, oxidized meteoric recharge water to form sulfates, which in turn accumulated arsenic and other metals from bedrock in the process over time [52][140][142][143].

And the most quoted sources over the years of abnormal hydrochemistry are focused on a range of oil and gas operations, from open-pit brine disposal [53], brine-line leaks, or pressure-driven, subsurface releases of fluids from corroded oil/gas well casings in operating or abandoned wells [18,22,54].

A review of Tables 2 and 3 indicates that both groundwater samples from MW-3S, MW-5S, and MW-2S contain abnormal concentrations of nitrite-plus-nitrate and chloride, which indicates that the shallow groundwater in the immediate area could have been influenced by septic-tank drainage. In comparing the metals and other constituents from these wells (Table 3) with the Clinton brine sample constituents, the groundwater samples exhibit somewhat elevated levels, which show that the metals might come from flow through the porous media of the sandstone or from the brine that was applied to the surface above [52]. These factors will be discussed later.

The Na:Cl ratios and the nitrite-nitrate content presented in Figure 15 show six unusual ratios and 10 anomalous nitrite-nitrate analyses that re-enforce the general theme that a small data set can provide some understanding of a complex hydrochemical system using simple tools. The black dots in Figure 15 indicate nitrate/nitrite concentrations present in the groundwater samples obtained in 2004. The red histograms represent the Na:Cl ratio for each of the samples.

The six unusual ratios include samples for the sites: MW-1E (which could be expected based on previous discussions); MW-2D (which reflects possible communication with an "old=deep" high-chloride source and indications of water-softening effluent); Ni (an anomalous ratio and indications of water-softening effluent); the two sites already identified (R/M and Oe) showing indications of water-softening effluents; and SW-1, the stream-water sample, showing very high concentrations of nitrate-nitrite constituents, an indicator at the level of 4.0 mg/L of the presence of septic effluent, which could include agricultural input as would be expected for such streams in a rural setting. Samples above 1.5 mg/L are regarded as possible involvement of such effluent, which includes sites: Cn, R/M? (but N-N removed through softening process), Me, Hn (but proximity to crops and fertilizers) and most of the samples from shallow (S) monitoring wells). Unaffected sites with lower levels of N-N are indicated within and above the red histograms in Figure 15 [169].

In comparing other hydrochemical associations of, for example, the bicarbonate and nitrate + nitrite concentration provides an indication of anthropogenic involvement and to some extent the residence time of the groundwater since migrating from the surface. Although the nitrate + nitrite values are relatively low, an interesting grouping is apparent with bicarbonate (Figure 16A), which indicates that the younger groundwater is present in the subsurface near samples plotting in the upper part of the bivariate plot (i.e., the "S"=shallow monitoring well samples). Whereas, the groundwater is presumably older in samples shown in the lower right of the plot (i.e., the "D"=deep monitoring well samples) having very low nitrate + nitrite values and variable bicarbonate values, the latter likely reflecting the availability of carbonate in the form calcite in the fine-grained rocks and associated vugs and fractures as described in the core (Appendix A: CD-1 (MW-1E).

The former low values of N-N (including those appearing on the non-detect line indicates that the N-N bacterial have been eliminated with depth but continuously replenished in rural stream water (SW-1). Of note is that the Clinton brine sample contained low nitrate-nitrite and low bicarbonate, and the brine sample contained 184,000 ug/l ammonia-nitrogen, perhaps a result of bacterial activity during subsequent storage. Two sites, Oe and R/M shown in orange in Figures 16A and 16B, produced water-softener treated samples showing negligible nitrate-nitrite and bicarbonate concentrations in the 100 to 150 ug/l range.

There are three apparent groups shown in this bivariate plot. One group, of course, consists of those samples having N-N less than 40 ug/L (0.040 mg/L=DL). The two others appear to be of significance.

The on-site sample data plot as "S" (shallow) samples in the upper area of the field and away from the subject neighborhood site of Cn (and R/M, but this hydrochemistry has been altered by the water-softening process), whereas the "D" (deep) samples appear in the lower area of the field (also away from the analyses of the neighborhood well sites, and merge with the "ND" (non-detect) group. Further, the stream sample (SW-1 in blue) serves as the upper end member in a separate group trend consisting of the neighborhood samples, plus MW-5S and MW-1S, with the lower end members characterized by two of the up-gradient sites (Nl and Ni, but not the third (Ah), the latter indicating increased proximity to septic tank or agricultural effluent)).

The same can be cited for the difference between R/M and Oe, the two softened samples that generally plot together with other constituents impacted by the water-softening process and subsurface conditions below the leachfield. Other samples that plot away from any group are the Clinton brine and the sample from MW-1E, both of which plot on the DL line for N-N, and only reflect the difference in bicarbonate concentration. Apparently, bacterial activity as reflected by the N-N has been eliminated but contact oxygen-rich fluids containing calcite within wall-rock and/or permeable zones as recharge to the lower sandstones, siltstones and shales transport carbonate to the groundwater.

The impact of the plot of Figure 16A illustrates that the on-site groundwater is not mixing with the neighborhood ground water to any significant extent, with the two outliers, MW-1S and MW-5S, being located away from the northern boundary representing minor increased effluents via recharge migration from activities in the central and southern onsite areas of the subject property. MW-1S, nevertheless, plots in the middle of the neighborhood grouping.

When plotting another form of nitrogen (Ammonia-Nitrogen) against chloride (Figure 16B), the role of elevated chloride in the environment of elevated nitrogen is less distinct within the main neighborhood group as in Figure 16A plotting N-N against bicarbonate. This plot shows that the field has been split into two groups; the Cn area and the Me area, with the MW-2S being intermediate and other on-site samples plotting on the outside and surrounding the main groups. The significance of MW-6S and MS-WW (located in the center of the on-site property) is uncertain, if any. The anchor of the plot remains with the up-gradient group (Ah, Ni, and Nl) with the stream water sample (SW-1) located between the latter and main grouping.

At the other end, MW-1E and Clinton brine plot as end-members, i.e., the higher the chloride analyses, the higher the ammonia-nitrogen value. Note that the two treated samples (i.e., R/M and Oe) remain within the main group as if the water-softening treatment process had little or no impact on concentrations of these constituents.

Turning to other constituent affiliations, we selected potassium and strontium for the next bivariate plot to consider whether groupings remain as in previous plots of other constituents (Figure 17). Because the strontium concentration was very high in the Clinton brine sample (1,100,000 ug/L (or 1,100 mg/L) and potassium was also high (2,780,000 ug/L (or 2,780 mg/L), this represented an opportunity to evaluate the possible relationships between the two elemental ions within the subject environment. The groups observed in the previous plots are compressed in the potassium vs. strontium bivariate plot. Also note that the neighborhood well data do plot along a linear trend with end-member sites of previous plots only represented by Ah, whereas Ni, and Nl occur within the body of the grouping [161].

The on-site monitoring well data surround the neighbor-hood data with S and D data mixed. Previous plots present groupings of S data at one end of the trend while the D data occupy the positions at the other end. This is not present in this plot. Also, the SW-1 sample plots near the center of the group.

However, MW-1D plot-ted away from the main grouping, and the softened samples plot at the far lower extreme and the Clinton brine sample plotted at the upper extreme of a general trend. Site MS-WW results also plot out the normal group, indicating that MS-WW has another hydrochemical history, which will be discussed later in this paper.

Samples MW-1E and MW-1D were also filtered in the lab by allowing the sediment to settle and taking aliquot to filter through a 0.045 micron filter and run in the lab, to obtain almost totally dissolved constituents, which would have contained little or no particulates. The resulting difference between Total and Filtered (Dissolved) values is substantial in MW-1E indicating that suspended solids and particulates have a range of constituents (and concentrations) adsorbed on and within the solids, or more likely, within colloidal masses in the low-permeability intervals sampled in MW-1E, but less so in MW-1D. This is illustrated in Figure 18. The concentrations of the Filtered (Dissolved) analyses are generally far less than those of the Total analyses, which contain all of the dissolved and constituents of metals adsorbed or attached to very-fined grained particulates in the sample.

In an assessment of the dissolved fraction in the subject samples, we found that the metals were essentially 100% adsorbed on such particulates, whereas the major elements (barium, strontium, calcium, magnesium, sodium, and potassium) were also generally more abundant in total analyses but the non-metal constituents also reported as both total and dissolved constituent values; sodium values reported in equal proportions (Figure 18).

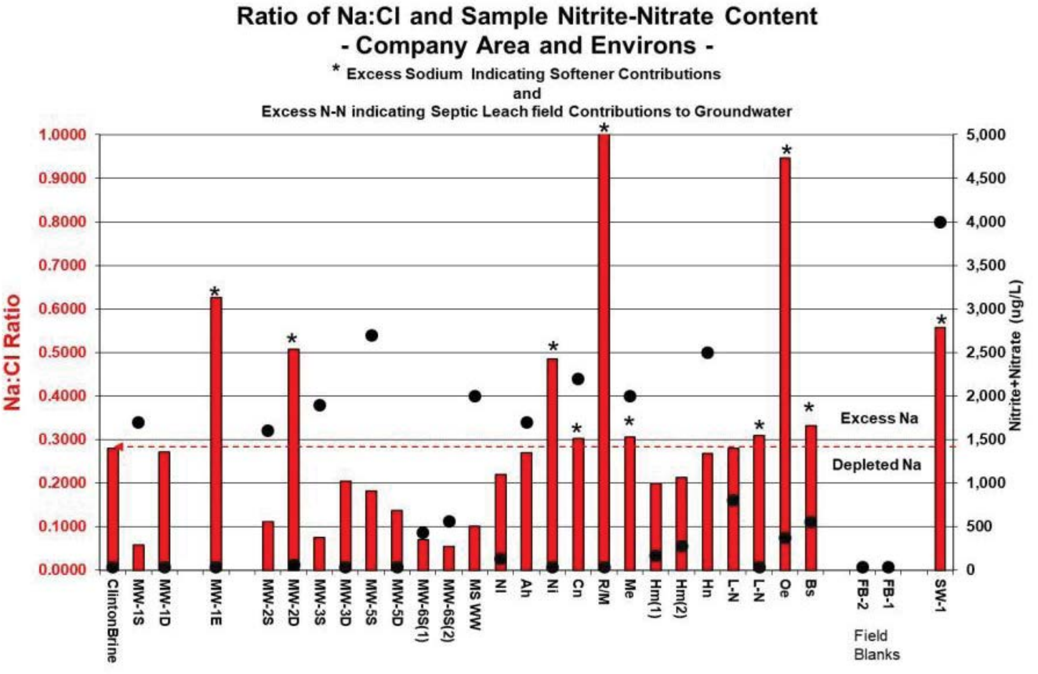


Figure 15: Ratio of Na:Cl and Sample Nitrite-Nitrate Content – Company Area and Environs.

The reason for this is uncertain but heavy, colloidal masses of sodium-rich aggregates and others might have been part of sample, which may not have settled in the flask before the fluid was withdrawn and filtered for analysis of dissolved constituents. Other major elements could have also been attracted, but to a less extent, as shown in Figure 18.

In sample MW-1D, similar adsorption processes have occurred in Filtered sample, but on a lower scale (Figure 18). This can be explained by the lower concentrations of metals and major elements present in the Total sample, but sodium concentrations also reported 100% as Filtered (sodium and potassium).

Because the two Total samples had few particles after they had settled and filtered, the analyses could be considered dissolved, but without actual filtration via typical field methods, the analyses have been designated as Total analyses for the two samples, i.e., MW-1D and MW-1E, which would likely contain extremely fine-grained particles (colloids) in any event.

Barium is the other constituent present in relatively high Total concentrations in MW-1D and especially MW-1E. Figure 19 shows that up-gradient site data are located toward the lower end-member field of the plot, although that group is somewhat dispersed, such as site Ah (Figure 19). Some grouping is evident in S and D segregation, but this is not well developed, although a neighborhood group/on-site group separation is apparent and shows minimal mixing of the two fields in context with chloride. MW-6S (2), but the duplicate sample is likely out of place resulting from laboratory reporting.

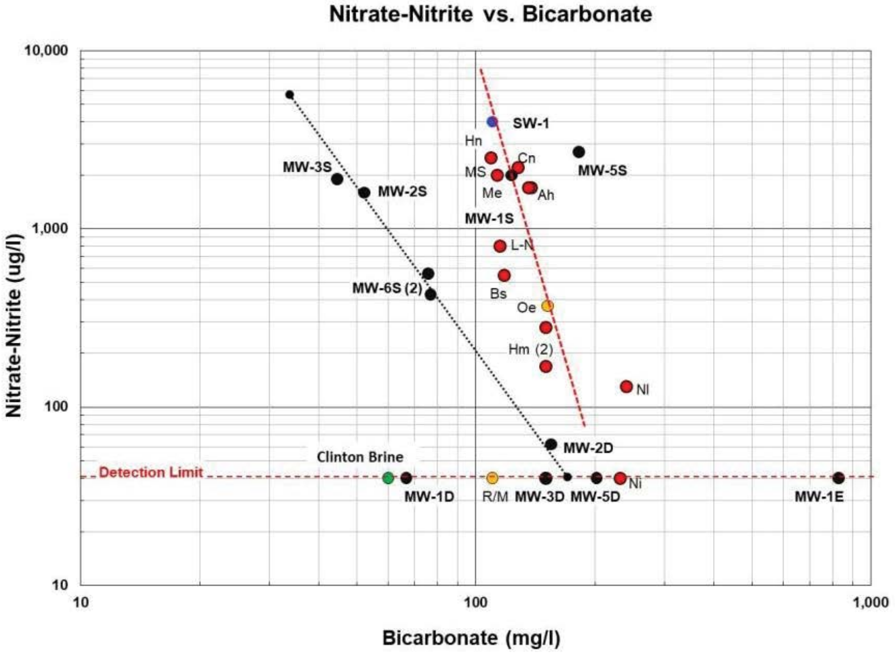


Figure 16 A: Nitrate-Nitrite vs. Bicarbonate.

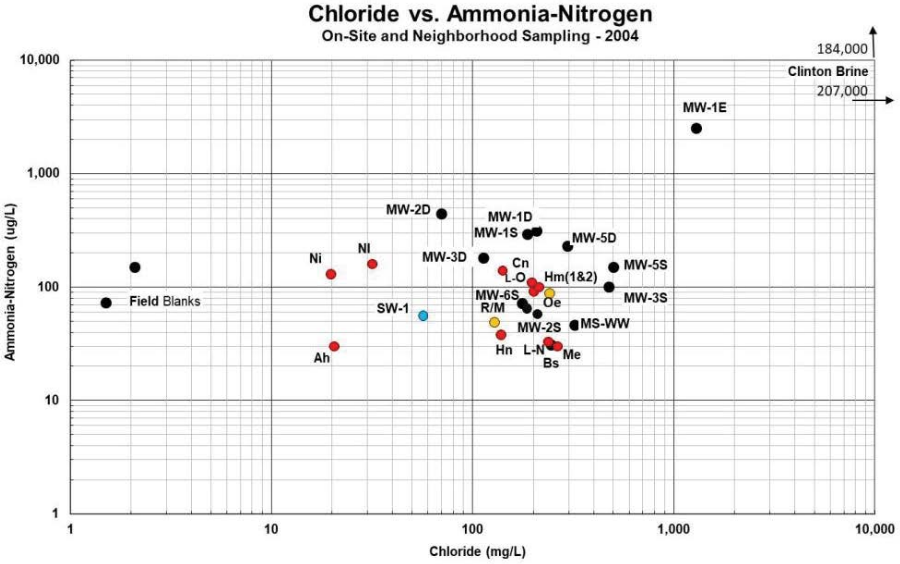


Figure 16 B: Chloride vs. Ammonia-Nitrogen.

Of particular note here is that the zone interval across from the screened zone of MW-1S exhibited unusually high gamma radiation during the geophysical logging of the core hole (Figure 5), the site at which MW-1S, MW-1D, and MW-1E monitoring wells were drilled and installed. The screened zone was installed across intervals of fractures/vugs within the sandstone. The core shows an interval of intense oxidation (Figure 5A), but two other similar zones were also reported in the well log, all three with anomalous gamma radiation (Appendix B and Figure 5). Our preliminary recent assessment of these zones indicates that because the groundwater contains barium and sulfate in low concentrations (relative to the data set of Tables 2 and 3), along with somewhat high bicarbonate, somewhat low chloride, very low in potassium, high in nitrate-nitrite, low in pH, but with a high temperature (relative to MW-1D), these indicate the presence of oxidizing water from the surface or from a nearby abandoned oil and gas exploration well having introduced such fluids over a significant amount of time [50]. Further, both the Clinton brine sample and the sample from MW-1E exhibited very high barium as adsorbed on particulates in the groundwater (i.e., Total vs. (Settled) and Filtered, Tables 2 and 3, and Figure 18).

We did not sample for, or run analyses for radium or associated radioactive constituents, but suspect that they would be present in any event. As there was no evidence of radioactive materials observed at the time of our surveys on the surface, we conclude that radium-laden brine might have escaped in the subsurface from the oil and gas exploration well drilled during the 1960s, which was drilled very near the location of the CH-1 and MW-1S, D, E (Appendix B-1). Additional work on the core via thin-section and laboratory analyses are currently underway.

The Total–Dissolved range for MW-1E and MW-1D is also shown in Figure 19, as in the data point for the duplicate sample for MW-6S. The two migrated toward the other duplicate, both back into the on-site grouping. And of note is that MW-2D data point is associated with the up-gradient group indicating its hydrochemistry (of chloride and barium) has affinities more with the former group than that of the nearby neighborhood groundwater. Also, is the presence of the Cn plotting adjacent to the two known samples of softened water, indicating that some type of softening has affected the Cn hydrochemistry.

Sources of Chlorides: Oil-Field Brine vs. Halite Brine

Based on the selected plots of various hydrochemistry, the on-site and neighborhood samples plot in recurring groupings, notwithstanding statistical considerations. Used in a similar way, bromide: chloride ratio vs. chloride and similar trends have been used over the years to discriminate the source of elevated chlorides in a variety of environments, the hydrochemical data of groundwater samples in the subject area also occurs in reasonably well-constrained specific groupings (Figure 20).

As a check on what Figure 15 shows, we also constructed a similar plot using the bromide: chloride ratio (multiplied by 10,000 to permit the easy plotting). Once again, two populations are evident. One intermediate, but not along the mixing trend for oil and gas-derived brine with the Clinton brine as the end-member. The other trend in the data also favors the salt-solution trend. Data from MW-3S plot near the oil and gas trend but still remain associated with the intermediate trend [43,55-60].

Some of the relevant literature includes that of Richter and Kreitler [24], Davis et al. [61], Knuth et al. [62] and Panno [63]. The former and others cited below have employed the general approach in Figure 20. In applying the plot of Figure 20 then, if the elevated chloride reported by the pre-Cn resident were caused by brine applied on the company property, this plot would confirm it by showing values plotting along the horizontal line leading to the value shown for the Clinton brine. None of the data plot along that trend line. But two others groupings are apparent, one consisting of resident-sample data in an intermediate position between the two trends, indicating a relation to brine released from home-water softeners, and the

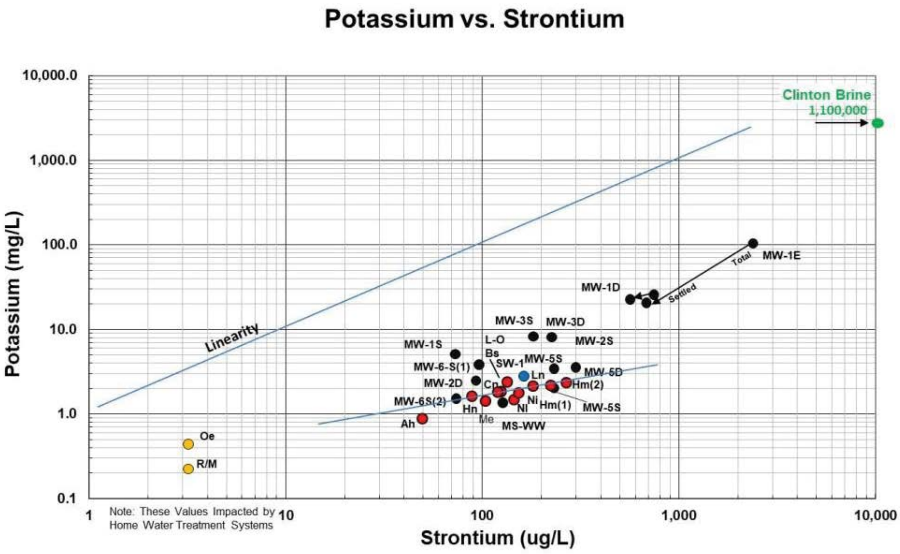


Figure 17: Potassium vs. Strontium.

other grouping trend along the salt-solution zone, indicating an affinity to brine solutions originating from the dissolution of road salt and migration. Both groupings result in diluted brine entering the subsurface and encountering the water table at various depths below the surface.

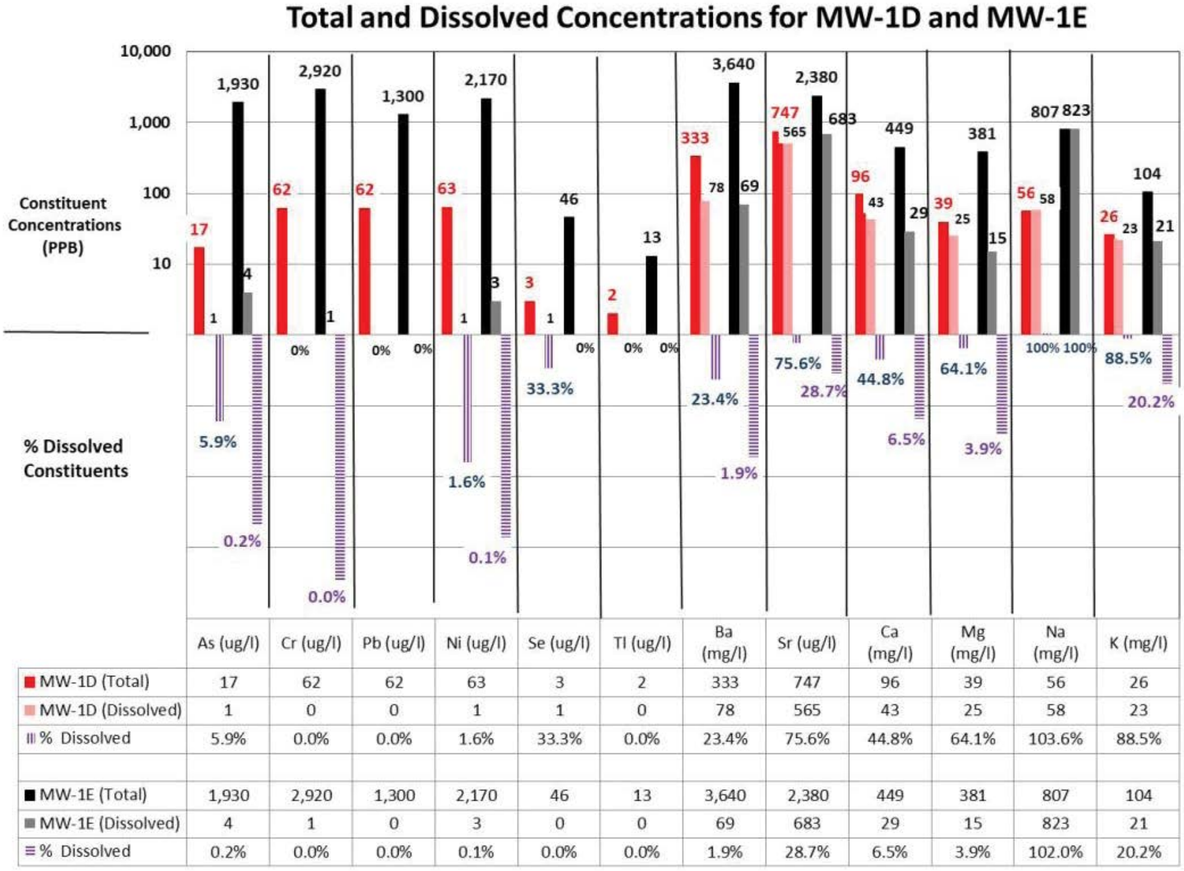
The snapshot in time depicted in Figures 6 and 8 shows the water table at some 50 feet below the surface, the elevation of which would rise rapidly during periods of precipitation (rainfall and snow melt water) but drop slowly during periods of low rainfall and drought as groundwater flows away from the area toward valleys to discharge into creeks below, or withdrawn via water wells for domestic or agricultural uses [31]. If there are introduced mobile constituents stored in the glacial till, they would migrate downward as a pulse of dissolved constituents during and after each significant recharge event. The composition might vary significantly depending on what materials were available on the surface and within the shallow subsurface. Such materials could come from oil and gas-derived brine applied on-site for dust control during three summer periods, halite-derived and oil and gas derived brine for de-icing of adjacent county roads and state highways, and/or brine generated by water-softening systems from local residents' household water use.

All such sources of recharge would migrate into the subsurface of the subject area. Under the hydrogeological conditions described above, pumping of rural water wells with open-hole construction would withdraw groundwater from heavily jointed, fractured sandstones, from hundreds of feet away, where brine below roads and highways would migrate to the residents' water supply [15,64].

Of particular note in Figure 20 is the up-gradient sites that serve as dilute end-members in the plot (see the data points for Ah and Ni samples). Both Nl and the MW-2D samples indicate little association with either the salt-solution brine trend or the oil-and-gas brine trend based on their low chloride and bromide content. However, the impact of the water-softening process on the particular resident's drinking water quality appearing in Figure 20 is not apparent for the Oe and R/M data points as in previous Figures. Both chloride and bromide are not involved in the ion exchange process (of that involved in domestic water softeners) to any great extent, as is the groundwater containing calcium, magnesium, and nitrate-nitrite in the raw groundwater [145][151][153].

Anthropogenic Sources of Chloride

The softening process produces significant increases in sodium and chloride content of the drinking water supply at the tap, removing calcium, magnesium, potassium, barium,



	As (ug/l)	Cr (ug/l)	Pb (ug/l)	Ni (ug/l)	Se (ug/l)	Tl (ug/l)	Ba (mg/l)	Sr (ug/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)
■ MW-1D (Total)	17	62	62	63	3	2	333	747	96	39	56	26
■ MW-1D (Dissolved)	1	0	0	1	1	0	78	565	43	25	58	23
⦀ % Dissolved	5.9%	0.0%	0.0%	1.6%	33.3%	0.0%	23.4%	75.6%	44.8%	64.1%	103.6%	88.5%
■ MW-1E (Total)	1,930	2,920	1,300	2,170	46	13	3,640	2,380	449	381	807	104
■ MW-1E (Dissolved)	4	1	0	3	0	0	69	683	29	15	823	21
≡ % Dissolved	0.2%	0.0%	0.0%	0.1%	0.0%	0.0%	1.9%	28.7%	6.5%	3.9%	102.0%	20.2%

Figure 18: Total and Dissolved Concentrations for MW-1D and MW-1E.

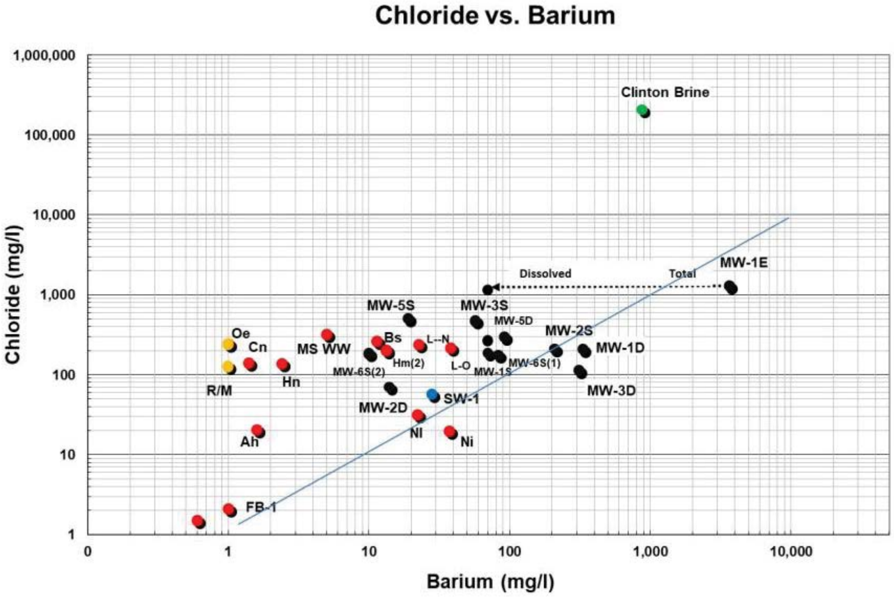


Figure 19: Chloride vs. Barium.

and strontium. The treated and used water is then passed on through the septic-tank system to the leachfield and effluents below, (Table 2 and 3) [65]. At the same time, when regeneration of the softening system is necessary, excess sodium and chloride, as well as the cations of calcium, magnesium, etc. removed during the softening process are purged down the drain as effluent to the septic-tank [4]. This leads to the leachfield, which if constructed in thin soil, permits migration of chlorides and the other constituents to reach the water table below elevating the background chloride concentrations naturally present in the groundwater, unless some of the constituents precipitated from solution within the joints, fractures, and pore space before reaching the water table [66].

Disposal practices of the resulting back-flushed brine (during regeneration of the softening system) and associated chloride contents flushed to the septic-tank and leachfield system raised questions about the likely impact on the shallow groundwater below the subject property and surrounding properties. The combination of subsequent reports of elevated chloride in the original shallow well combined with the report of brackish ground water at depth from one resident would naturally concern the neighborhood residents. In carrying this concern further, one of the residents formed a protest group calling for local regulatory action against the use of brine for spreading on roadways to control dust during the summer as well as to control ice on the roads during the winter. This adverse action was confronted with the fact that at the time that brine use for de-icing and dust control was allowed by the State of Ohio, via a permitting process of allowed use by the state for de-icing on state roads [67].

Problems elsewhere in Ohio and other states related to groundwater contamination by septic tanks (leach-field leakage) and by roadway salting (either by halite products or by brine) are commonplace [1,21,42,43,54, 55, 62,63,68-71].

Because elevated chloride concentrations are at the center of this investigation, chloride ions are considered to be conservative in groundwater flow, meaning that they are not retarded with regard to groundwater flow velocities, they do not biodegrade, do not easily precipitate (react with other ions to form a solid), do not volatilize (turn into a gas), are not involved in (but can damage) biological processes, and do not adsorb (adhere) significantly on mineral surfaces.

Chloride is used as a tracer in water because it is not significantly slowed in its passage through the soil and in groundwater migration studies [72]. Its concentration in surface waters is low, in part because rainfall contains only 0.2-0.4 ppm (this is the average for continental rainfall, as contrasted with coastal rainfall, which has higher levels); North American rivers average 7 ppm except where they come into contact with sea water, evaporites deposits, or brines.

Sources of chloride are sea salt, the release of sodium chloride from the weathering of bedded evaporites and shales, and discharges from human activities. Its presence in water can be detected by a salty taste, sometimes at concentrations as low as 200 mg/L [67]. Health issues have been covered widely [67,73].

Hem [72] also reports that the circulation of chloride through the hydrologic cycle is caused mostly by physical rather than chemical processes. The chloride ion (formed when a chloride salt dissociates and separates in water) passes readily through soil, enters groundwater, and eventually drains into surface waters, although the passage through the groundwater system could require tens of years to millions of years, depending on the complexity of the receiving hydrogeological system. When chloride ions reach a body of water, their removal from water occurs only by seeping through bottom sediments, precipitating as a solid, and/or flushing out of the system via osmotic processes.

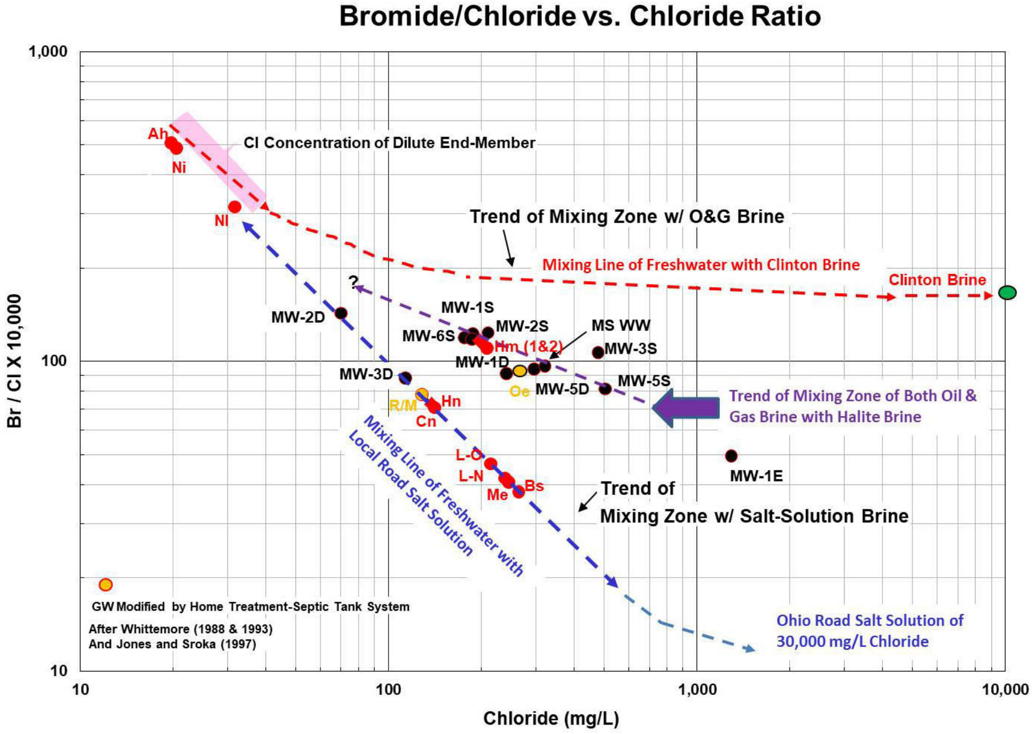


Figure 20: Bromide/Chloride vs. Chloride Ratio. (to enlarge, click (here)).

Amrhein et al. [46] indicate that the chloride ion is negatively charged and typically is not involved in adsorption on soils. As a result, it is transported along water pathways. As soil depth increases, the chloride in soil water disperses and dilutes. Chloride does not seem to have any significant direct impact on soils, although studies indicate that it contributes to the release of heavy metals in soils.

Guntner and Wilke [45] evaluated the effect of chloride on soil microbial activity. They detected a general decrease in microbial activity, but the effects were temporary, and the microbial activity returned to previous levels after the road salt leached from the soil. There is concern about chloride migration of elevated concentrations exceeding water-use standards into shallow aquifers used as drinking water by salt-sensitive populations and about the consequences of channeling high concentration de-icing fluids into small streams, ponds, lakes, and wetlands, threatening ecosystems.

Generally, because of dilution, road-salt contamination is not a problem in flowing bodies of water, and insofar as small water bodies are concerned but concern about road salt concentration levels in groundwater relate directly to rural-water supplies where exposure to de-icing of county and state highways is known to occur in northern states [6,44,45]. If the groundwater reaches public water supplies, road-salt concentrations can be a problem; standards and findings regarding human consumption of sodium and chloride in drinking water are discussed below. As will be observed in the bivariate, trivariate, and other types of plots to be discussed in this paper, these groupings persist even with other cations and ions, elements, compounds, and ratios in many, but not all plots.

Non-grouping behavior nonetheless relays interactional information about a group as well.

Other De-Icers

There are other products used in road de-icing. Calcium magnesium acetate works by interfering with the bond between snow particles and the road surface; in contrast, road salts can chemically breaks down snow and ice as the mix of snowmelt and salts moves downward from the surface [29]. The performance, corrosivity, and environmental impacts have been reviewed more extensively for this product than for any deicing material other than road salt [5-7,44,45,74,75].

Calcium chloride also is used but it is much more expensive than halite. It is hygroscopic (can absorb and retain water) and produces an exothermic reaction when mixed with water. Fritzsche [76] indicated that it is applied in liquid or pellet form and causes widespread surface melting. Calcium chloride deiced twice as fast as road salt and also outperformed potassium chloride. Calcium chloride was able to penetrate ice at all tested temperatures at approximately twice the rate of halite. Another study, however, indicates that after 30 minutes the performance of calcium chloride and road salt equalizes. When used as a wetting agent for road salt (halite), chloride increases the performance of the salt. It also can be mixed with sand to prevent the sand's freezing and clogging of spreaders at low temperatures in the winter (PSC [77] and Tanner and Wood [78]. Frisman [74] reported that with the presence of sand, the mixture bonded to the road surface creating a glaze on the surface making the material difficult to remove for days after a winter storm.

Hydrochemical Assessments

Regarding the temporal and spatial distribution of chloride in the groundwater of the subject neighborhood water wells (Figure 21), localized chloride values were reported as far away as the Hm household well, some 350 feet north of the Pre-Cn well site, the initial site of reported elevated chloride in the drinking water in the area (Figure 1). In addition the nearby study in the Killbuck Creek area, the U.S. Geological Survey also conducted a comprehensive multi-year survey in 1988 through 2002 of potential chloride contamination in the shallow groundwater resulting from highway de-icing in 10 surrounding counties and found evidence of impact in some, but not all counties studied [8].

As indicated in Figure 20, seven sites with the highest concentrations remained elevated over the period from the beginning of the first testing in June, 2000 to the installation of the new wells, i.e., Cn site and next door, the R/M site, and directly across the county road, and Hm sites. Both Cn and R/M households employed water-softening equipment, as did the Tr-N residence prior to the installation of their new well.

It should be noted here two sites, not previously discussed, are introduced, i.e, Tr and Ma (Figure 1). These sites were available for sampling only once (June 7, 2004), and only for chloride (one sample bottle each from the outside spigots). The old Hm well, drilled in 1957 in the basement of the residence, was completed some 30 feet into shale, raising the possibility of encountering groundwater flow from above the shale contact with dense highly-elevated chloride concentrations similar to that previously reported for MW-1E (and in the first re-drilled well at the Pre-Cn residence). Other residents near these sites show significant changes in reported chloride concentrations, e.g., Ma and Me sites.

The chloride concentrations from all sites decreased after new wells were installed and sampled (Figure 21). Pre-CN, R/M and Tr sites show increases in chloride from the initiation of short-term sampling of August 8, 2000 to October 4, 2000, after which a new, deeper hole was drilled, with initial sampling indicating very high chloride concentrations. A second hole was drilled to a depth just above the bottom of the sandstone, with chloride values initially low but the next 5 sampling intervals showing a regular increase, then the last two values decreased (Figure 21). Figure 22 also illustrates the chloride concentrations for all sites mentioned previously, with another site not mentioned (Fn, Figure 1), also offering only chloride concentrations.

The increase, drop, and apparent rebound followed by a decrease in chloride is indicated for all well sites. However, it should also be emphasized that there are significant time breaks between sampling after November, 2000, i.e., two months, two months, 12 months, and 26 months.

This pattern nonetheless shows that chloride concentrations in the area of each new well vary similarly, although offset in time, and decrease in amplitude with distance away from the Cn site. This could also be reflecting the slow movement of chloride migration in porous media (as opposed to flow in joints and fractures).

Also, rainfall might at first be considered the cause of the variations, but there are no synchronous changes and hence the variations are apparently unrelated to recharge event, assuming joint/fracture flow dominates the area. If porous media flow is significant the offset would be consistent with chloride-plume movement.

A significant conclusion is reached from the mixing ratio (Figure 20) and the distribution pattern of the elevated chloride concentrations in groundwater around areas of shallow soil cover where at least one resident employed a water softener with likely operational problems. The leaking systems load local groundwater with chloride, calcium, magnesium, sodium, and other constituents by septic systems (leachfield leakage). This circumstance and the use of road-salt brine and oil-and-gas field brine spreading along the county roads and on neighborhood driveways over past decades in the subject area during winters (pers.com. with state personnel) provided the source of the elevated chloride locally introduced by recycling and re-circulation by pumping of the neighborhood's own wells, with little or no contributions from the activities outside the immediate area of the subject neighborhood wells and their area of influence (cone of depression).

Also, based on available hydrochemical information, elevated chloride was greatest at the pre-Cn site, as indicated by Figures 21 and 22, and other information (poor halite management and disposal at Pre-Cn). Chloride concentrations were the highest reported in the neighborhood at Pre-Cn, and progressively less so at the nearby neighborhood wells (R/M, Tr, Hm, Ma, Me, and L-N) and at company monitoring wells, i.e., MW-2S and MW-2D located on the northern neighborhood boundary, the hydrochemistry of which appeared to be unrelated to that of the neighbor wells data. This is because the latter are up-gradient from the neighborhood water wells and although some hydrochemistry is common to both, MW-2S and MW-2D have little in common to that of the Cn site at the time of sampling.

It should be noted that no one involved in the neighborhood matter realized that the cause of the elevated chlorides was not because of a "bad" well, but because of high-chloride water being pumped from the groundwater within the area of influence of the well's open interval (of 50 feet to 100 feet) while pumping the well. And, because all neighborhood wells were designed as "open completion" below a sanitary seal of cement, the new wells drilled to similar depths as the previous well at the Cn site or somewhat deeper (but not into the shale below the Black Hand sandstone) would have produced similarly elevated chloride. However, they all produced water of markedly lower concentrations of chloride. So again, it would appear that all the wells were the problems, but survey information indicated that most if not all of the old wells were constructed in the basements of the older houses in the neighborhood and the wells were typically drilled to relatively shallow depths before construction of the older houses above.

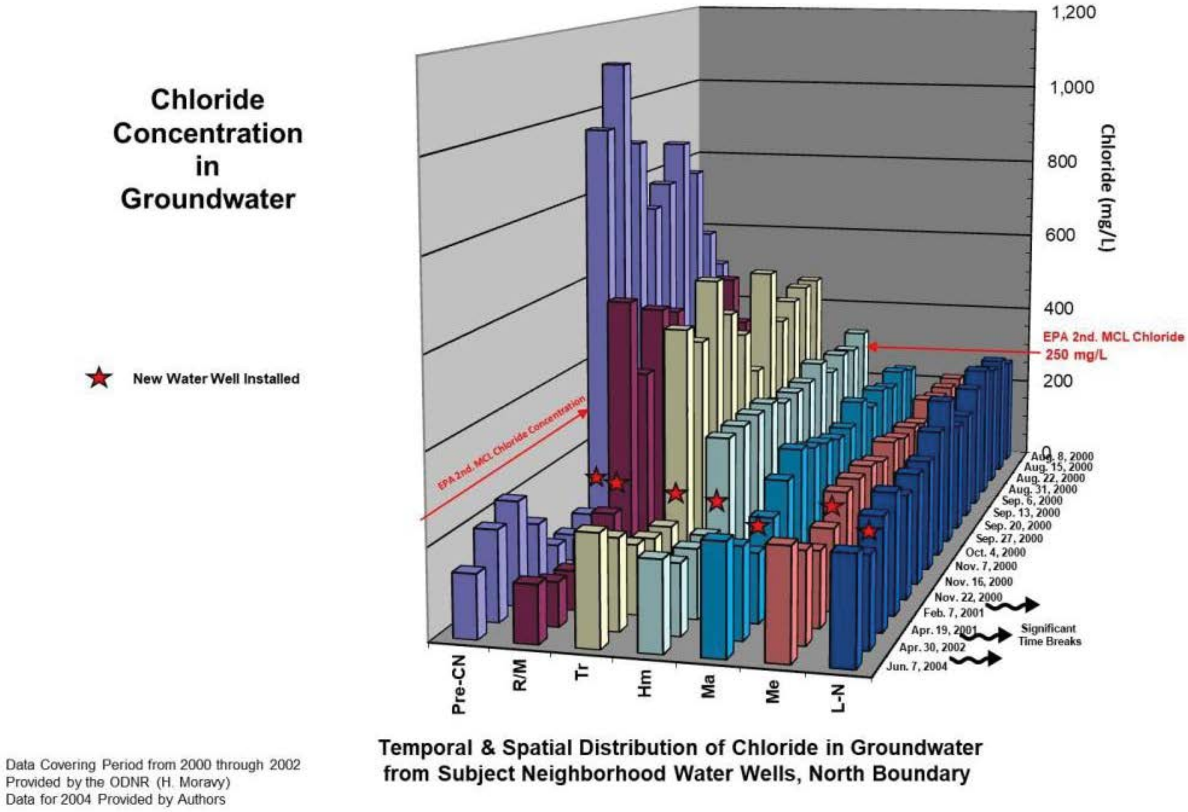


Figure 21: Chloride Concentration in Groundwater.

Combined with the fact that the older septic tanks and leachfield systems continued to discharge effluents to groundwater, and many households used water softener systems periodically and disposed of spent salt, plus used halite for de-icing of driveways during the winter. Thus, they all were likely to have contributed elevated chloride and other constituents to the groundwater below their houses. Added to those chloride sources is the liberal use of salt (halite)-based and oil-and-gas-based brines when applied to the county road in front of the neighborhood homes during winter months [5]. Combining the above issues with the fact that the neighborhood houses are located on top of a hill formed from many periods of glaciation that left behind only a thin layer of the glacial till draped over the top of the hill, all the sites contributed chloride to an aquifer of heavily eroded, jointed, and fractured sandstone underlain by thin shales, siltstones, and sandstones with elevated chloride and other constituents (see especially Figures 6, 7 and 8, and Tables 2 and 3).

Apparent rebound in chloride concentrations after the new wells were installed introduces the issue of timing of the groundwater (and surface water) sampling. Although the sampling data in Figure 21 and 22, show chloride concentrations for groundwater samples from neighborhood wells obtained at weekly intervals from August, 2000 through November, 2000 [period of decreasing rainfall], sampling was conducted eight weeks later, February, 2001 [during winter snow/rain months], again at 10 weeks later, 2001 [during spring rain month], again 12 weeks later in 2002 [during spring rain month], and finally, 24 weeks later in 2004 [during a spring-rain month].

For the period just after the new wells were installed, pumping was conducted at high volume by licensed water-well contractors to remove fine-grained particulates introduced by the drilling and development processes. Once normal withdrawals had been re-established, the principal source ground-water is usually recharged by infiltration from meltwater and rainfall, which in the subject area would have been from any fluids on the surface including halite-derived brine and oil-and-gas-derived brine used for de-icing during the previous winters, passing through the thin glacial till present in the immediate area. Hence, the chloride concentrations would be expected to rise in the spring and decrease during periods of little or no recharge to the groundwater, usually associated with a lag time caused by the saline fluids passing through the till and entering the sandstone and any of the many joints and fractures. Thus, the water table rises in the spring (receiving recharge from above), and falls during periods of no rainfall/meltwater recharge [5].

The data show that the large introduction of additional halite-derived brine likely originating at the Pre-Cn site, has overprinted the natural groundwater hydrochemistry discussed by the introduction of brines with additional sources of dissolved chloride that appears to have impacted adjacent and down-gradient neighborhood wells. However, the sampling events after the installation of the new wells should not be considered a trend because of the significant intervals between sampling events. Neither should rebound (as in Figure 21 and

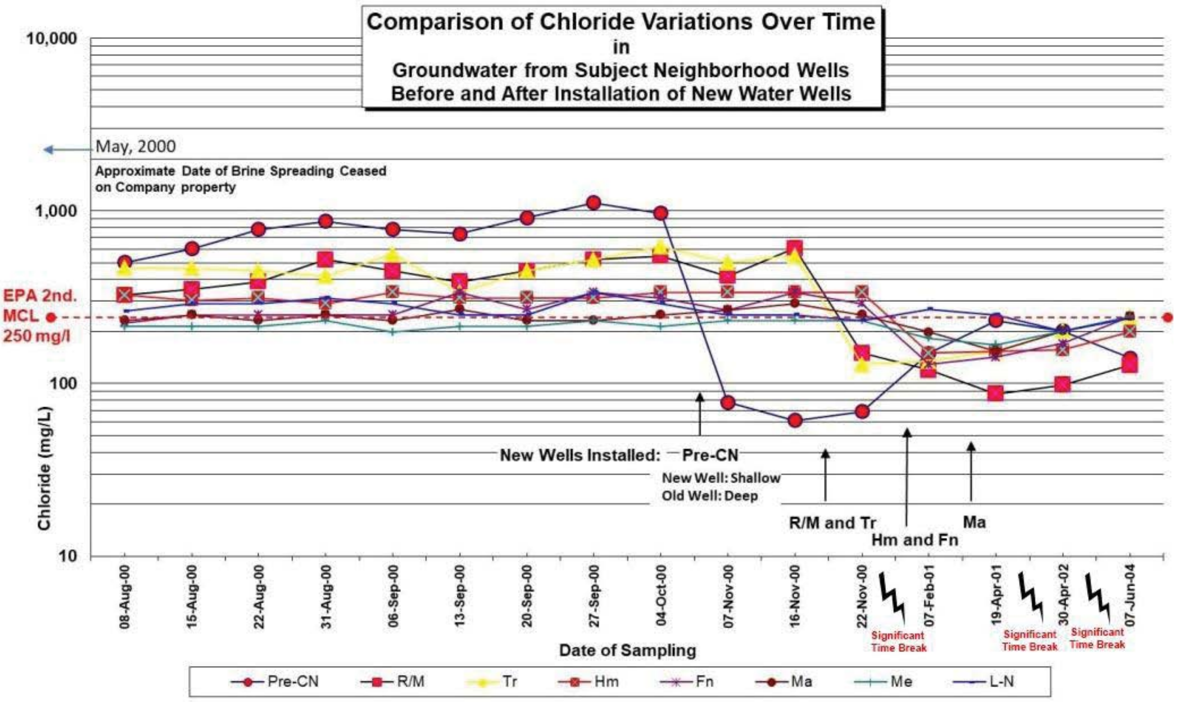


Figure 22: Comparison of Chloride Variations Over Time in Groundwater from Subject Neighborhood Wells, Before and After Installation of New Water Wells.

22) be considered at this time; just data considered for the date acquired. In any event, the impact of a source of halite salt has likely dissipated leaving little or no trace of the soluble salt that was released or transported into the area of Pre-Cn prior to the year 2000.

Three notable aspects are evident in Figures 21 and 22. The first is that although brine spreading on the company property ceased in May of 2000, increases in chloride concentrations continued to occur, even after the new wells had been installed, e.g., the Cn well, the Tr well, the Hm well, Ma well, and the Me well.

If elevated chloride concentrations were somehow migrating from on-site toward the subject neighborhood well against the observed downward hydraulic gradient, the transport through any connecting horizontal or vertical joints and fractures would be rapid and, as the pulse diminished, the chloride concentrations would decline quickly over time. There are no indications that this was the case, and that this scenario is inconsistent with the well-established flow direction known to be occurring on-site. The likely cause of the continued increase in chloride concentrations is the result of the unusually high rainfall that occurred in the summer of 2000 (Figure 23). This would cause increased recharge in the yards of the neighborhood residents through the macropores of the soil zone and down into the thin glacial till in the area causing chloride in soil moisture in the glacial till from septic-tank leach-field effluents and from deicing activities on the driveways and along the county road from previous winters to be flushed, trickling down to the joints and fractures, and entering the water table below.

The second notable aspect is that the old Pre-Cn well exhibited increasing chloride concentrations during August and September of 2000. As indicated above, this period experienced unusually high rainfall for the season and likely promoted significant recharge in the general area (Figures 21and Figure 22 and supporting rainfall records in Figure 23). However, after the new well was installed, the chloride level was unusually low for a well drilled nearby to nearly the same depth as the original well reporting elevated chlorides.

This condition indicates that the chloride was likely introduced at the surface and infiltrated either from near-surface sources of chloride such as a halite dump site leaking septic tank saline fluids, or from brine and/or rock salt spread in years past along the county road and neighborhood driveways within the immediate recharge area and within the area of influence of the Pre-Cn pumping well's cone of depression. The onsite monitoring well, MW-2D, would have reported some remnant of such high concentrations for years later if the elevated chloride came from the direction of the on-site facility, which was not the case.

The third aspect is that a sampling site near the center of the company property (site MS WW), exhibited elevated chloride concentrations in early June of 2004 when we sampled the on-site water well. NOAA reported high levels of precipitation during early June, and local recharge likely sent a pulse of chloride from the glacial till below the company facility to the water table some 60 feet below. Even though the company ceased using Clinton brine for summer dust and odor control in early 2000, this sampling result (from the MS-WW site) represents a possible example of how any first approximation of such sources could be compromised by other candidate sources of elevated chloride. At the outset, Figure 20 shows that the sample has hydrochemical characteristics of a chloride source related to both: 1) the Clinton brine (i.e., relatively high bromide and chloride), and 2) the effluent from a septictank-leachfield system (high nitrite-nitrate, calcium, magnesium, and sodium concentrations relative to the other samples).

If either or both conditions existed at the time, a chloride plume would form at the water table, the size of which would depend on the volume of recharge migrating through the glacial till and downward. If any of the recharge encountered a joint or fracture the flow would be diverted downward or to the horizontal in the direction of the greatest permeability. The chloride plume would experience both dilution and an ability to travel as a cohesive plume mass if the source provided sufficient amounts of chloride from within the glacial till where some fluids could be held until migrating out of the glacial till by recharge from above.

The numerous "vuggy zones" present within the Black Hand Sandstone (Figure 6 and 8) could allow flow if the zones are permeable (many are not because of secondary cementation of pore spaces), and if there is any significant dip of the beds. This would allow for either down dip or lateral flow in high permeability zones, joints, etc., in the direction of regional flow toward the east and northeast, discharging at the springs some distance from the subject facility. Groundwater flow in the deeper high-permeability sands of the valley is expected to discharge to the creek. Some groundwater flow would also be expected toward the west, discharging at the western creek (sampled downstream at site SW-1). The flow rate of both types of discharges would be controlled by the seasonal precipitation and fluctuation of the water table in the general area.

Furthermore, a County Engineer agreed (pers. comm., 2003) that deicing fluids containing magnesium chloride also were used on the subject county roads. Additional support for this view comes from the fact that the deep monitoring well, MW-2D, which is located only a few hundred feet south of the "new" Cn well, shows lower chloride concentrations than those exhibited in 2004 by the Cn well (Table 2). Therefore, on that basis alone it can be demonstrated that the source of elevated chloride did not originate from below the company facility even though there was a nominal horizontal groundwater flow component in the direction of the neighborhood wells, and also to the north and east at depth toward nearby springs, and to the west toward the creek (also shown in Figure 7).

The strong downward flow component was confirmed by the hydrogeological flow-net analyses shown in Figures 6 and 8. However, proximity of the magnesium-sodium bivariate plot indicates some association between the groundwater at Cn and at MW-2S (not MW-2D) shown in Figure 24. This shows that substantial amounts of halite might have been disposed of at the surface over the years (to avoid damage to the septic-tank and leachfield system), and with recharge from rain and snowmelt, the saline solutions generated, found preferred pathways in the glacial till and underlying heavily jointed sandstone in the shallow zones at the time of sampling of Cn, MW-2S (and 2D) in 2004.

The bivariate plot of Figure 24 also shows the expected grouping of results for neighborhood (in red) and on-site monitoring wells (in black) indicating slightly different hydrochemical histories for each group, save for the anomalous sample discussed above (MW-2S). The MW-1D couplet (Total-Dissolved)) represents special conditions related to the age of the groundwater based on tritium dating to be discussed later in this paper. The low sodium concentration sets apart the up-gradient samples as in almost all of the previous plots as do other constituents, i.e., barium (Figure 19), ammonia-nitrogen (Figure 16B), sulfate (Figure 13), chloride (Figure 12).

The anchor analyses of magnesium vs. sodium (Figure 24) and the nearly same grouping pattern in Figure 25 is also evident in the chloride vs. sodium bivariate plot of Figure 25. As is typical, MW-1E also plots away from the main group. Both represent total analyses that include suspended solids (and the adsorbed metals) plus dissolved constituents.

The main groupings also plot within one log cycle, except for MW-2D, and of course the up-gradient sites and the surface-water sample. Other data support the view that on-site activities are not the likely sources of the elevated chloride. The variations in the chloride concentrations reported in the residents' wells were not consistent with chloride flooding (from surface-brine applications) emanating from the on-site facility activities prior to early 2000.

Additional Indices of Hydrochemical Association

The use of hydrochemical indices was explored after reviewing the hydrochemical data for the major and minor anions and cations finding that the bivariate plots are informative and reasonably compelling in identifying the differences between brines from oil-and-gas operations and those derived from halite used for de-icing and in rural water-softening systems. For supporting confirmation, we constructed additional plots that combine the principal hydrochemical constituents to further evaluate associations based on the work of Hounslow [34], in combining two of his indices:

$$Ca/(Ca + SO_4) \text{ vs. } \sqrt{[Na/(Na+Cl) / Ca/(Ca+SO_4)]}$$

One pair, the ratio of the calcium concentration divided by the sum of the concentration of calcium plus sulfate plotted against the index result plotted in Figure 25 produces a distribution of plotted points (Figure 26). To provide a context for the particular plot, we have also included the appropriate data from sampling performed by the U.S. Geological Survey during their investigations in the nearby valley area of the

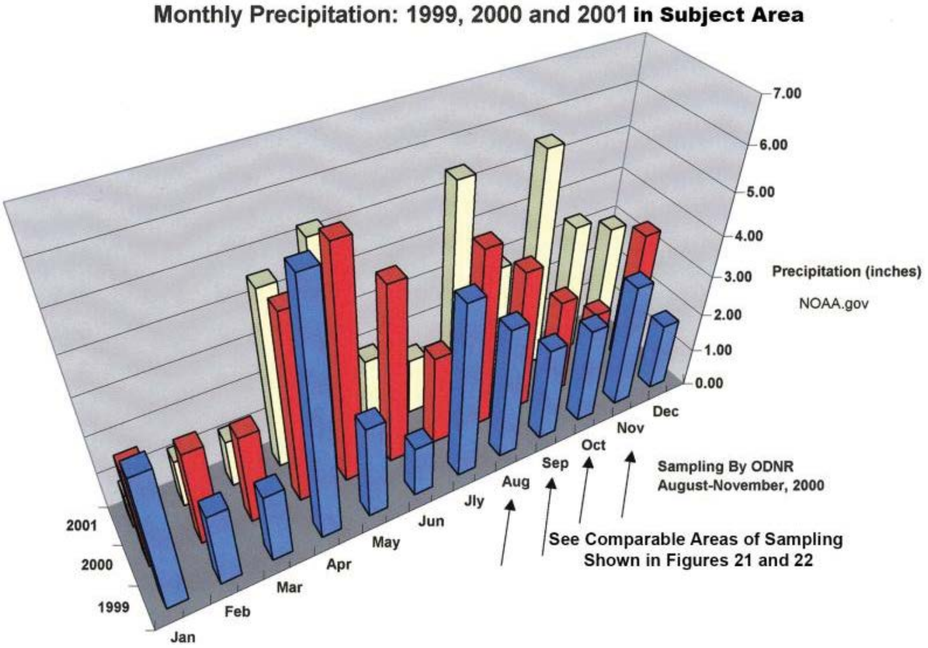


Figure 23: Monthly Precipitation: 1999, 2000 and 2001 in Subject Area.

1980s just a few miles to the north and northeast of the subject site [17]. Both surface-water and groundwater data were included in Figure 26.

This combination of indices enhances and extends the discrimination associated with possible oil-field brines and other sources of brine by illustrating the presence of clustering and trends in the data that are in geographical proximity groupings. This plot also shows the U.S.G.S. sample data in positions in route to the discharge zones in the valley and at the creek. Note that our SW-1 stream sample plots among the U.S.G.S. data. Also, the highly saline samples appear to be offset from the principal trend of the data (see the two trends indicated in the Figure 26). The trend lines have been included to graphically emphasize the trends but were not generated by calculations because of the complexity of the main trend, which would have reflected a similar trend line in any event, if the secondary trend data points were not included.

Of particular note is that data from most of the on-site, shallow monitoring wells (S) cluster near the proximal end of the principal trend. However, the on-site deep monitoring wells (D) cluster is in an intermediate position in the plot between the neighborhood well-sample data and those of the on-site "deep" samples.

The sample data of the neighborhood wells cluster in positions that are in transition to the distal end of the trend and also overlap some of the U.S.G.S. data.

There are two anomalous samples (discounting analytical and local variations): MW-2D, located on the northern boundary of the subject property, and MW-5S, located on the southern. We have discussed the implications of these two data on a number of occasions and in context with various bivariate plots. For example, see Figures 25, 24, 20, 19, 16, 15, 13, 13, 11, 10, and Figure 9, all of which include discussions of data from MW-SD and MW-5S, among only three other samples mentioned as anomalous relative to the groups defined.

In Figure 26, sample ratios of MW-2D, located some 250 feet from the Cn well, plot beyond the up-gradient sample plots of the Ah and Nl sites. These plot associations indicate that the neighborhood well samples have more of an association with the groundwater found in the valley area than with the on-site groundwater, with one exception, MW-5S. This site likely receives surface run-off from the cultivated fields and company facility, which recharges the relatively thick glacial till present below in the area along the southern boundary of the company facility (see Figures 1, 6 and 7, the latter of which shows the location and topographic saddle where MW-5S and D was installed). An increased thickness of glacial till was also reported for the area MW-2S and D (Figure 6).

During the years of brine spreading on the roads within the company facility, most of the fluids would have been absorbed by the soil and by the underlying glacial till. However, it is apparent that some brine-laden fluids have migrated over the surface and into the shallow subsurface during periods of high rainfall because some evidence of residual damage is apparent along the western boundary where a few young trees and vegetation were observed. Intermittent springs and seeps

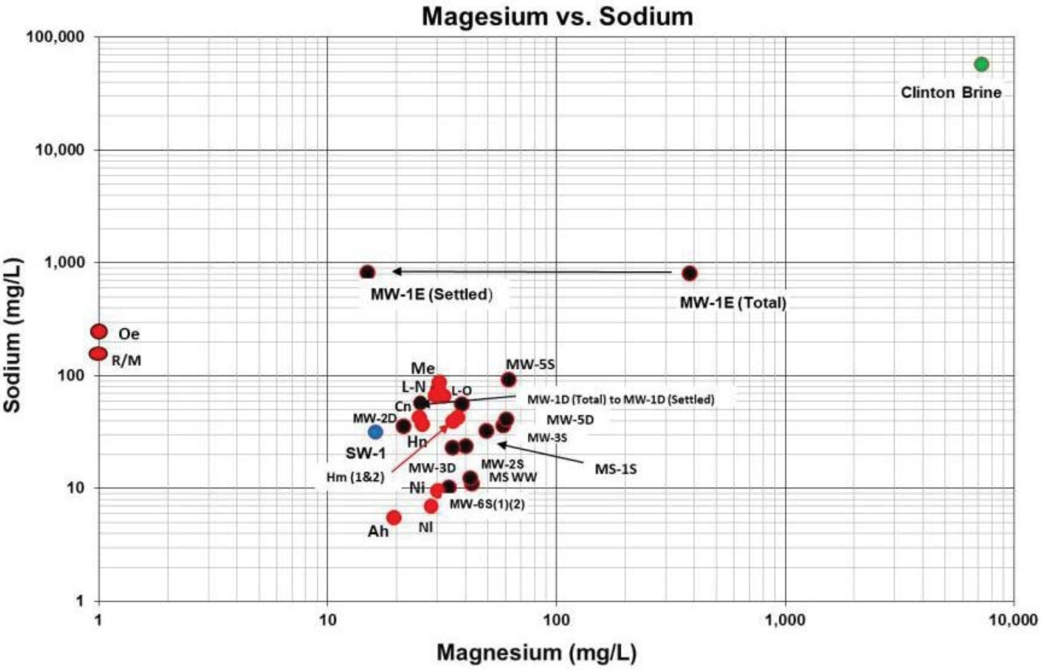


Figure 24: Magnesium vs. Sodium.

are apparent in the field to the west of the company property where they created minor erosional pathways in the field but no apparent stress to the vegetation or crops (Figure 7).

We learned that company personnel installed drainage ditches to manage better storm water run-off along the western and eastern boundaries of the property (Figures 1and 7). We observed no apparent damage surrounding the company property, although company reports indicated that a few of the Pine trees planted along the eastern boundary had been damaged by bark beetles, as reported by Nielsen [79]. Nielsen [79] conducted a study of company pine trees and of potential treatment alternatives indicating that trees under stress are especially susceptible to insect infestation. Perry [44] and Lazarcik and Dibb [80] provide perspectives on the effects of vegetation damage along major highways and roads resulting from salt-and-brine spray and associated surface water runoff and infiltration of saline water during the winter [5,81].

We understand that intermediate levels of chloride in soils can be beneficial to vegetation. Excessive chloride, however, can damage certain types of vegetation, especially old-growth hardwoods.

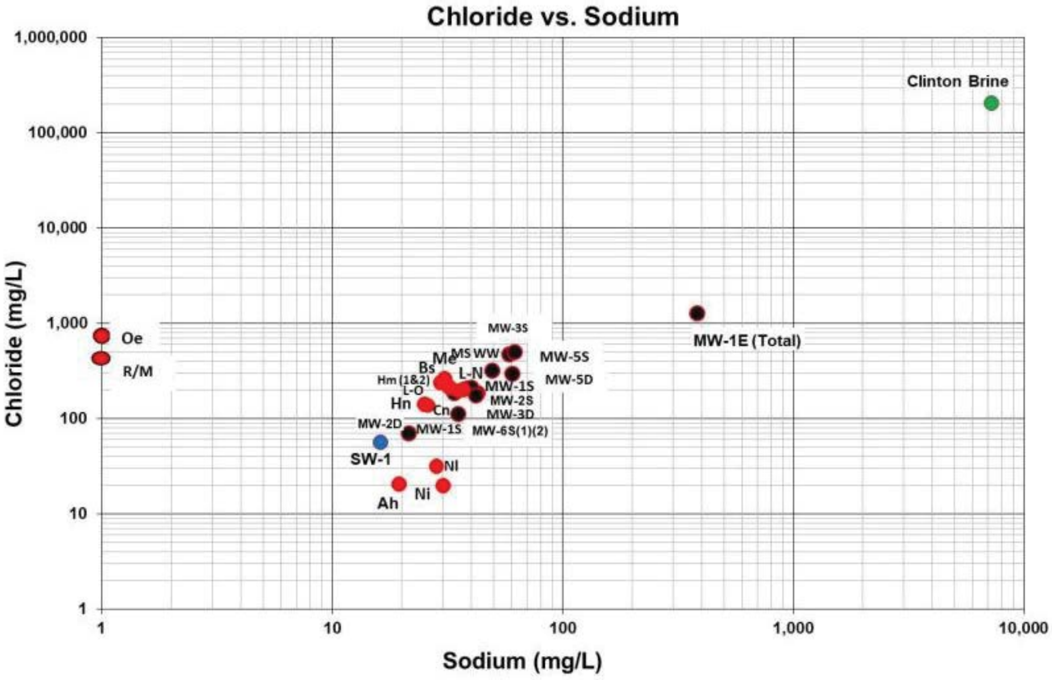


Figure 25: Chloride vs. Sodium.

As discussed previously in Section 2.5, damaged mature Oak trees were reported adjacent to a septic-tank leachfield at the R/M site. In that area, two large trees were being removed while we were in the area for the company sampling program in early June, 2004. An old septic tank system was replaced with a new sanitation system located next to old growth hardwood trees that had just been removed from the front yard of the R/M property.

These incidences support the view that effluent from the old septic tank likely impacted these hardy trees, especially because such large trees transpire water from the water table in significant volumes during the summer months. This implies that the effluent consisted of significant concentration and volume of sodium, chloride, and other constituents from water-softening regeneration that likely has been recharging such effluents to the groundwater in the area for a number of years. This will be discussed further later in this paper.

Alternative Perspectives on Identifying Possible Sources

The above considerations have provided information on subsurface conditions existing in 2004 and before. These are based on independent local surveys of conditions, field measurements via shallow and deep coring and drilling, monitoring well installations, groundwater sampling of on-site and neighborhood wells, groundwater flow-net analyses, and additional assessments and background surveys. The data discussed represent conditions once present in the subject area and should be considered as snapshots in time of the conditions in the subsurface.

The use of cation ratios have been used to identify the source of elevated chlorides, but not without some difficulties. Whittemore et al. [56-60] have widely applied the bromide: chloride and chloride: bromide ratio methods in a number of well documented case histories in the literature without using cation ratios. Although bromide is not typically analyzed for standard hydrochemical investigations because of cost considerations, any investigation of oil-field brines and other brines found in the subsurface from either road deicing or water softening, would be seriously lacking without using bromide. Whittemore, *et al.* [57] provided specific reasons for not using cations ratios other than the bromide: chloride ratio on the following grounds, i.e.:

1) "Ratios involving cations are susceptible to appreciable alteration by adsorption/desorption in clay-containing sediments, and can result in false identifi-cation of a salinity source."

2) "The ion exchange usually causes decreases in the [cation] ratios and increases in the [more compounded] ratios."

We concluded that the above criticisms pertain to the issues discussed in this paper as well. Oil-field brine is only one of the possible sources of elevated chloride in the subject rural area. Because of this brine's historical use, it is to be discounted first, if possible, by demonstrating the basis for how the hydrochemistry of on-site samples was not likely to contain diluted oil and gas-related brine, specifically Clinton brine. Then, assess any contributions from other salinity sources from road salt and/or water-softening/septic-

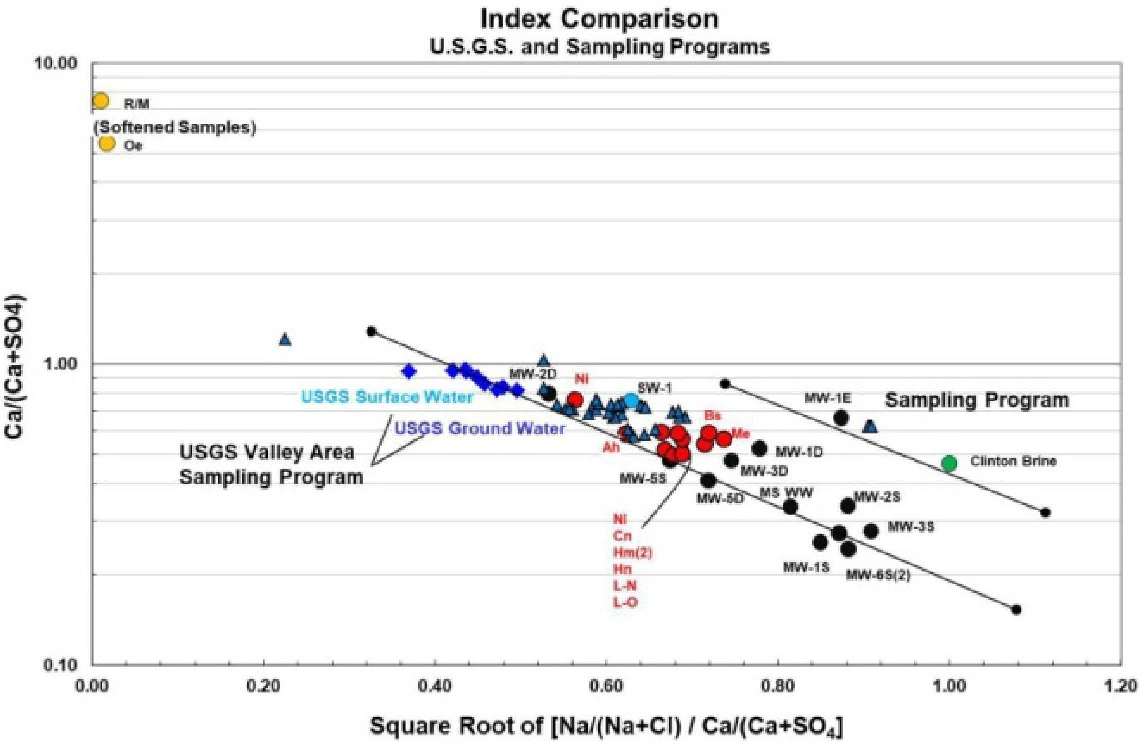


Figure 26: Index Comparison U.S.G.S and Sampling Programs.

tank-leachfield effluent reaching the water table, using bivariate and other plots incorporating a range of ionic ratios, including bromide and chloride known to be conservative constituents in the groundwater, to illustrate any impact of sources in the area.

To evaluate other popular methods developed by Hounslow [34] using complex ionic ratios (Figure 27, we plotted the subject data as follows:

Ca/(Ca+SO4 vs. Na/(Na+Cl

The data are in units of concentration (mg/L, but adjusted from millimols per liter (mmol/L. As in Figure 26, we also provided a background context to the plot by including the U.S. Geological Survey data from the valley investigation nearby, discussed above. It should be noted here that all U.S.G.S. samples were likely filtered before analysis, but this has not been confirmed.

The first plot (Figures 26 and 27 show only the two reference samples (the Clinton brine and MW-1E, plus one aberrant U.S.G.S. sample of groundwater (might be an errant analysis, with all others plotting within the area designated as mixing with oil-field brines (to one extent or another. This illustrates clear groupings like most of the simple bivariate clustering (or groupings in the previous Figures) of: 1) the on-site data of shallow "S" samples (in black with relatively high chloride, 2) the on-site data with relatively low chloride levels from deep ("D" samples (in black, with some exceptions, and merging into a general grouping of neighborhood wells (red, and merging with 3) a cluster of a mix of U.S.G.S. samples with neighborhood well samples, with some notable exceptions.

The samples from sites R/M and Oe plot away from the main groupings as a result of ion exchanges where sodium (and bicarbonate is enhanced in the finished water, and where calcium, magnesium, and nitrate-nitrite are eliminated or suppressed).

All are located near the designated oil-field brine sector of the plot. The Ni site and the SW-1 (the creek sample, and MW-2D, for example, curiously appears to favor the rock-salt brine (evaporites) source of chloride in the plot. The latter supports the position that the Pre-Cn was a potential source of halite, as indicated by previous bivariate plots. Also, MW-1D, Me, and Bs plot just within the oil-field brine field of Figure 27, indicating possible sources of chloride from oil and gas-generated brine (MW-1D and the same brine used on state highways (Bs in Ohio for deicing during 2004. However, the location of the sample plot, Me, is anomalous and problematic (Figure 1.

In using standard units of mg/L, however, the resulting plot is more consistent with the sample data and history indicated by other ratios. In any event, an expected fraction of the samples will plot in the oil-field brine mixing zone, assuming the approach is meaningful for confirming the apparent mix of elevated chloride sources present in the county road area.

As the principal hydrochemical guide in determining the likely source(s of the elevated chloride in the area of the Cn site, we propose that the conservative chloride:bromide ratio used in the approaches by Whittemore, et al. [56-58] and Davis, et al. [61] provide the strongest support in assessing the likely source(s) of the elevated chloride in the county road area. Assessments examined in the various bivariate and ratio plots and other representations provide independent confirmation that the bromide:chloride ratios support this view.

As indicated in Figure 28, by inverting the bromide: chloride ratio shown in Figure 20 to a chloride: bromide ratio, and adjusting scales, the data spread into recognizable trends (after Davis, et al. [61]. There are two primary trends; one showing the data plots of samples demonstrating an affiliation with chloride derived from halite (from road salt and/or from water-softener systems), with the other showing an affiliation with samples having natural recharge mixed with brine from oil and gas operations used to control dust on the traffic way surface of the subject property. Each trend is expressed by sample data from neighborhood sites (in red) and samples from on-site (in black), with some notable exceptions. For example, the Hm duplicate samples are from lower sandstone elevations than the other neighborhood wells and would be expected to exhibit higher chloride concentrations because other nearby deeper wells once reported elevated chloride (new wells at Cn and Hm). The samples also exhibited detectable bromide concentrations (both at 2.3 mg/L), which justifies their presence along the oil-field brine trend. A local release of oil-field brine in the area of the Hm samples was indicated but unconfirmed. The Oe sample, on the other hand, must have been affected by oil-field brine de-icing application from the adjacent state highway (as indicated by detectable bromide (2.2 mg/L), although many of the associated constituents have been affected by the water softening/ leachfield fluids processing by re-cycling of effluents (as indicated by somewhat elevated nitrate-nitrite, and other constituent alterations, see Tables 2 and 3).

The halite trend shows all neighborhood affiliations. Further, the typical up-gradient sites, i.e., Ah, Ni, and Nl, serve as the trend starting points. The surface-water sample (SW-1) plots in the typical position between the up-gradient sites samples and the rest of the sample plots.

We modeled the bromide concentrations and their impact on the halite trend by varying the bromide detection limit set at 2.0 mg/L, and then at 0.5 mg/L, and at 0.4 mg/L. The impact on the trend confirms that the approach allows for separation of groupings into trends, especially for conditions where bromide concentrations are very low (Figure 28).

Septic-Tank (Leachfield Fluids)

Recharge water reaching the water table along the northern and southern county road consists of rain and snow-melt water that mixes with the deicing fluids from rock salt and brine-spreading of years past and migrates into the thin glacial till and then to the groundwater below some 50 feet, as discussed previously. This recharge water is likely held within the glacial till for some time, depending upon the thickness of the till.

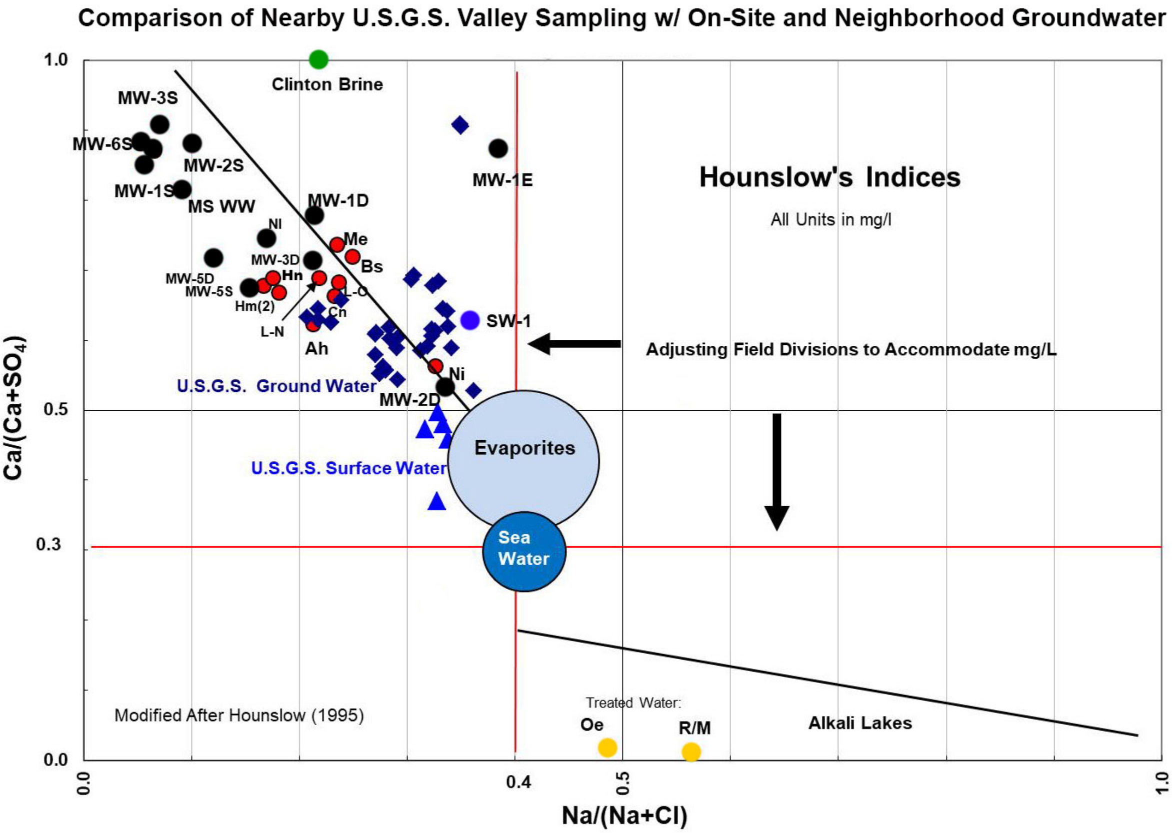


Figure 27: Comparison of Nearby U.S.G.S Valley Sampling w/ On-Site and Neighborhood Groundwater

Once reaching the groundwater, this recharge is mixed with all fluids, including septic-tank regeneration effluent containing chloride, calcium, and magnesium, combined with treated or untreated water applied to irrigate grass in the resident yards during the summer, and any effluents from leachfields constructed in thin soil and underlying thin glacial till. Released fluids travel downward primarily through joints, cracks, crevices, and fractures but also migrate into the porous media of the sandstone and the water table below.

The technical literature supports the view that old or improperly operated and maintained septic-tank systems can be major contributors to groundwater contamination, e.g., Arnade [82] Alhajjar et al. [83], U.S. EPA [84], Fenelon et al. [85], Jagucki et al. [55], Titler [3], Waller [86], Watson et al. [47], Yates [87] Goldstein and Moberg [168], and others.

It should be added here that such issues can develop to no direct fault of the operator (homeowner) or to the system design, but to the underlying geological and hydrogeological conditions below. The subject case is an example of where subsurface conditions are not conductive to the operation of standard septic-tank-leachfield system. The soil interval and underlying glacial till in many places along the county road are too thin for normal operations.

Further, natural groundwater often consists of very hard water that requires heavy usage of softening salts (halite) to produce acceptably soft water for use in a household. This depends on the geological and hydrochemical nature of the aquifer. By using softening materials, the issue of disposing waste salt (halite) becomes problematic and susceptible to expedient dumping and transport into a sensitive subsurface environment that exists along the subject county road. Of course, by including the use of similar salt (halite) and oil-field brine for de-icing of roads during the winter by county and state operations, these activities compound the potential problems in such sensitive rural environments [5,6,67,76].

Reconstruction of Subsurface Hydrochemical Conditions

In the general area of interest in this investigation, the groundwater is composed of cation and anion concentrations (especially calcium, magnesium, iron, etc.) in the ratios illustrated in most of the Figures and tables discussed above (especially where the Oe and R/M plot away from the main groupings, except where chlorine and bromide are involved), and which includes Oe and R/M sample data). In attempting to re-construct the conditions present during early 2004 and before, septic-tank effluent from natural and abnormal operating conditions carrying water-softening regeneration fluids can play a significant role in altering groundwater quality.

The fluids normally flushed by the regeneration process include relatively high concentrations of calcium, magnesium, strontium, sodium, and chloride, which are all likely carried from the

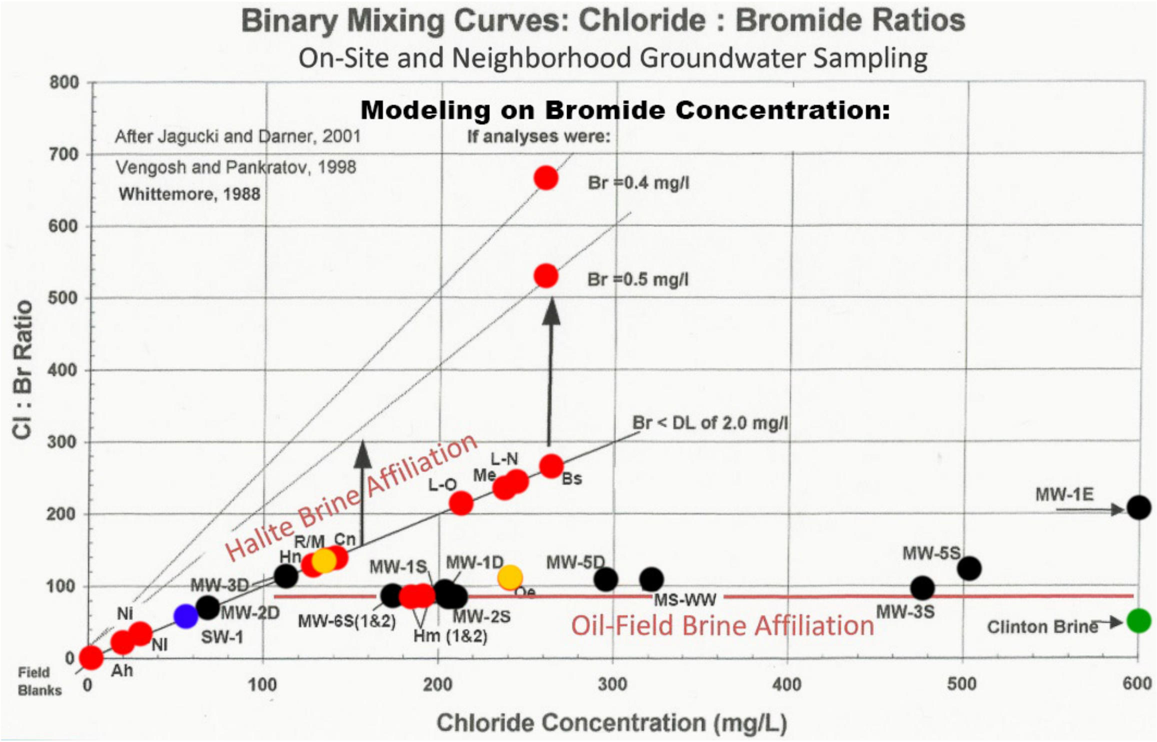


Figure 28: Binary Mixing Curves: Chloride: Bromide Ratios.

leachfields of the Cn and R/M, (before a new well was installed for the latter) and likely mixed with the groundwater already altered by chloride contributions from deicing along county road applied over the past 30 years and more. Pumping the water wells along the county roads would promote further mixing in two ways. One would involve pumping that would periodically drain the joints/fractures, while at the same time draining the groundwater within the porous media of the sandstone at a much slower rate than from the joints and fractures, and from any high-permeability zones within the sandstone (as discussed previously).

Relatively small plumes of such groundwater originating below the Cn and R/M properties would likely have expanded somewhat to the north, northeast, and northwest (toward other properties and the western creek). Because the natural gradient supports such movement (Figures 6-8), as discussed above, the plumes would migrate rather rapidly via the numerous joints/fractures in the sandstone at shallow depths in the subsurface to the water table some 50 feet below.

Because of the relatively high density of rural residences located along the subject section of the northern county road (Figures 1 and 7), a large volume of natural and anthropogenic recharge is generated by this group of residents in this environmentally-sensitive area. Daily pumping of the residents' wells and the expansion and contraction of the wells' cones of depression caused by daily withdrawals of groundwater in fractured rocks of the aquifer, would result in widespread mixing of all sources of recharge and capture of local groundwater flow in the subject area (Figure 29).

In any event, the combination of water qualities (from the various recharge sources) would affect the percentages of the cations and anions in several plots and how they would be interpreted. The interpretation of the Piper plot, the Hounslow plot and variations on the Whittemore plots, as well as most of the bivariate plots developed during this investigation, characterize the numerous sources of chloride and other constituents. Additionally, the variations of recharge hydrochemistry, both natural and anthropogenic, likely impact the distribution of cations and other anions present in the groundwater of the subject area, leading to the conclusion that elevated chloride concentrations are local by nature and any plumes developing from large releases of chlorides, as indicated in the Pre-Cn area before the new wells were installed, had dissipated by rapid flow by 2004 into the joints and fractures in the sandstone below.

Our sampling of the wells along county roads indicate that residents using water-softening equipment increase the sodium in their drinking water by almost 340 per cent, and simultaneously, decrease the potassium by about 850 percent (Tables 2 and 3 for differences in softened water, e.g., samples R/M and Oe) versus raw groundwater (samples from other neighborhood wells)).

During the water-softening process, when regeneration within the salt tank occurs, which is usually set on a timer to operate on a weekly, biweekly, or volume basis, the effluent containing sodium, chloride, calcium, magnesium, potassium, and strontium is drained by piping to the septic pipes below the house, or could be piped to a side yard (which would then infiltrate the soil and glacial till, ultimately reaching the groundwater), but in most cases would then be piped to the septic-tank system and leachfields (Figure 29). The basic designs have been in operation for more than 50 years; only electronic management systems have been improved [15]. Because the northern county road area is just off the top of the hill, the area is underlain by a relatively thin veneer of soil (and below by thin glacial till), any effluent likely migrated rather rapidly through the soil and glacial till (because of the latter's high permeability) down into the porous media, joints and fractures of the Black Hand Sandstone and water table therein some 50 feet below the surface. Individual rural water wells are commonly installed in such conditions for convenience [88], but as demonstrated in this paper they can have problems if not managed properly. High-capacity wells distributing water by PVC pipelines to multiple rural residents minimizes the risk of contaminating groundwater, but requires local management and operational systems to control such systems [22,64,169,170,171].

Areas where the soil and underlying glacial till are relatively thick, adverse impacts would be minimal and protracted in time until the sediments underlying the leachfield become saturated with the effluent which then could migrate into the upper groundwater zones [154].

When this groundwater recharge reaches the water table within the jointed sandstone, the fractures would permit more rapid migration of the groundwater toward pumping wells relatively large cones of depression (or a group of cones as illustrated in Figure 30). All available dissolved and suspended solids, consisting of elevated chloride, sodium, metals, etc., from the leachfields of septic-tank systems would likely then enter domestic water supplies by this pathway.

Even after attempting to improve the water quality, the subject septic-tank systems, softening systems and rural wells are located in a particularly unfavorable subsurface hydrogeological condition capable of inducing groundwater flow containing large chloride concentrations introduced at the surface from multiple sources such as de-icing brines used to clear roads and highways of ice and snow during the winter months [4,5,29,45].

Timing of recharge and subsequent groundwater flow containing elevated chloride and associated constituents, combined with the knowledge of the relative ages of the recharge and groundwater at various locations and depths, could provide additional information on the subsurface conditions indicated by the hydrogeological and/or the hydrochemical data developed for this investigation. To obtain this information, during 2004, we also collected groundwater and surface-water samples for an assessment of some of the common natural and radioactive isotopes in water samples: ^{18}Oxygen, ^{2}Hydrogen (Deuterium), ^{13}Carbon, and ^{3}Hydrogen (Tritium).

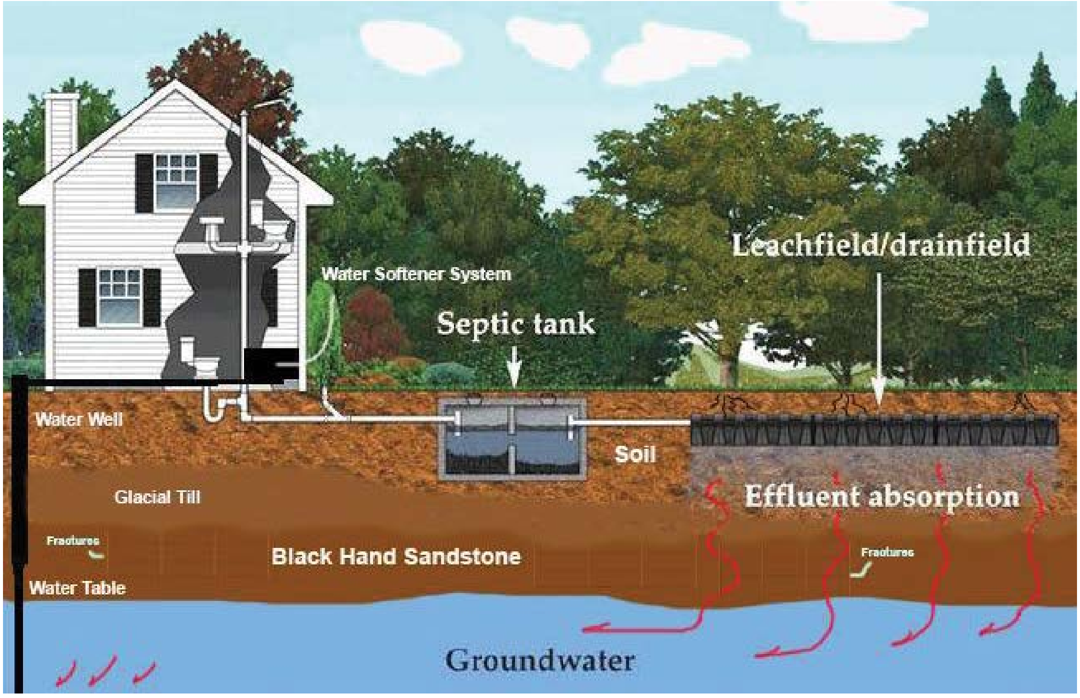


Figure 29: Typical Rural Water Well and Septic-Tank/ Leach Field System and Proposed Migration of Elevated Chlorides Below or Around Rural Residents' Properties. (w/ Typical Softening System)

Isotopes

Stable Isotopes (^{18}O, ^{2}H (Deuterium) and ^{13}C (DIC)

According to Clark and Fritz [89], certain stable and radioactive isotopes in groundwater and surface water can provide some indication of circulation time in the subsurface, and of water quality, geochemical evolution, recharge processes, rock-water interaction, and of the origin of salinity [89]. We submitted samples collected during the on-site sampling program in June, 2004 of groundwater (Tables 2 and 3), of the stream-water sample (SW-1), and of a Clinton brine sample to Dr. Ian D. Clark at the University of Water-loo, Ontario.

The isotopes discussed herein include: ^{18}Oxygen, ^{2}Hydrogen (Deuterium), and ^{13}Carbon, the latter analysis was for dissolved inorganic carbon (DIC), and ^{3}Hydrogen (Tritium). Figure 31 is a map of isotope sampling locations and summary results.

Isotope Analytical Methods

The isotopes will be considered in terms of the widely-used reference to the appropriate ratio and standard, i.e., δ^{18}O 0/00 (VSMOW); δ^2H 0/00 (VSMOW); δ^{13}C 0/00 (VSPDB), and tritium units (TU). Reporting units can be found in [86]. According to Clark et al. [38] (pers.com., 2004), oxygen-18 was analyzed on a triple collector VG SIRA 12 mass spectrometer. Analytical precision (2r) was 0.10%. Results are expressed relative to the Vienna Standard Mean Ocean Water (VSMOW). Corrections for the effect of high salinities were made using the method of Sofer and Gat [90].

2H was analyzed by reduction of water on zinc. Samples were first injected onto a stainless steel filter in an evacuated, heated inlet, which vaporized the sample and removed solutes. Water vapor was frozen onto the zinc in a glass breakseal cooled with liquid nitrogen, then reduced to ^{2}H at 450°C for analysis on a double collector VG 602E mass spectrometer. Results are normalized to VSMOW, with a 2σ precision of 1.5%.

To determine ^{13}C, dissolved inorganic carbon (DIC) was converted to CO_2 by reaction with phosphoric acid, and δ^{13}C was analyzed on a triple collector VG SIRA 12 mass spectrometer. Precision (2σ) of 0.10%. Results are expressed relative to the Vienna Pee Dee Belemnite (VPDB) carbon standard. Carbon-14 was determined by accelerator mass spectrometry at the Isotrace Laboratory, University of Toronto. Tritium was analyzed by the University of Waterloo by liquid scintillation counting following electrolytic enrichment, with a detection limit of 0.8 TU (1 TU=1 ^{3}H per 10^{18} ^{1}H).

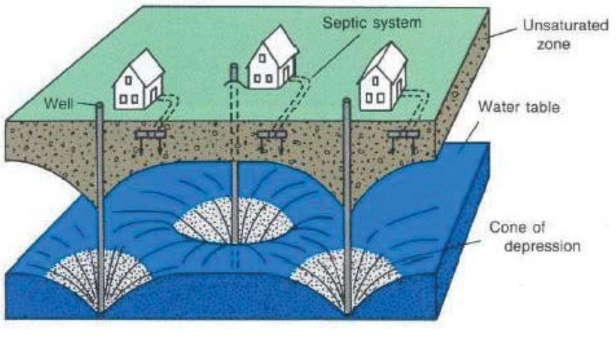


Figure 30: Pumping and Cones of depression (Waller, 1994).

The analytical results of all four isotopes are listed in Table 4 along with the sample-site IDs, for on-site monitoring well, neighbor-hood sites, two sites with duplicate samples, a surface-water sample (SW-1), and a Clin-ton brine sample obtained locally.

After reviewing the laboratory isotope data for appropriateness, we assessed sample-site associations, historical relations, and other possible sources of introduced constituents in context with the bivariate plots of a constituent's value, or selected ratios discussed previously. It should be noted that as with the hydrochemical assessments, the samples represent a snap-shot in time of the conditions present as of 2004.

Stable Isotope Assessments

Craig [91,92] and Dansgaard [93], more than 50 years ago, and others since, worked out the nature of the 18/16oxygen, 2/1hydrogen, (and others 14/13carbon isotopes), and how that they can be used to characterize the history of water as it is condensed as rain, falls to the surface, flows across the land infiltrating the soil, interacts with organics, sediments, and rocks below, and reaching the water table to recharge the groundwater reservoir [24,94-97].

As the new water migrates through the pore spaces of sandstones, siltstones and shale (with increasing residence time), the groundwater of less than neutral pH (when first entering) the subsurface begins to exchange ions and cations and to dissolve and precipitate a variety of constituents within the sediments and rocks along its flow path. This causes changes in pH and concentrations of alkalinity, potassium, sodium, and other constituents, specific conductance, and total dissolved solids in groundwater as it flows toward lower elevations and to eventually discharge to the surface, migrate to larger water bodies such as rivers and the oceans, and evaporate from the oceans beginning the hydrologic cycle once again [97-100]. Isotopes also adjust to these changing environmental and subsurface conditions [101], as our investigations will demonstrate. There are 2018 studies in nearby counties using stable isotopes to track methane in groundwater [174].

It should be noted here that almost all deep saline groundwater once called "connate water" has nothing to do with "trapped original seawater" but rather is the result of very long residence times of groundwater flow in deep permeable rocks. Because chloride concentrations are part of the cycle from ocean, rainfall, and recharge and because chloride generally is considered a conservative tracer in the subsurface which means that chloride does not interact to any significant extent with the solid phases during migration. Thus, the relation between the subject isotopes and chloride and other ions and cations become especially important in reconstructing the history of migration at the surface and recharge through the soil and any underlying glacial till to the sandstone below and to the water table, as have occurred in the subject area under investigation [137].

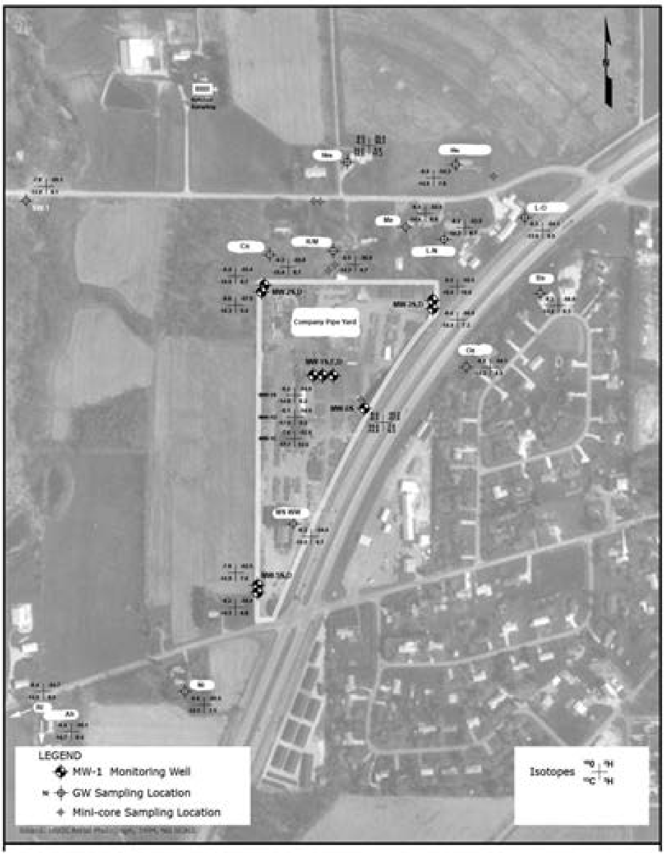


Figure 31: Isotope summary map. (to expand, slick (here))

Water molecules carry unique fingerprints, based in part on differing proportions of the oxygen and hydrogen isotopes that constitute all water having variable numbers of neutrons in their nuclei. Stable-isotope values have been used over the years to assess the temperatures of past climates and environments [102,103]. Stable isotope values (as ratios) are reported using the standard δ-notation:

where:

$\delta^{18}O= [(^{18}O/^{16}O \text{ sample})/^{18}O/^{16}O \text{ standard})-1]*1000$

Where standard is the Vienna Standard Mean Ocean Water (VSMOW)

$\delta^{2}H= [(^{2}H/^{1}H \text{ sample})/^{2}H/^{1}O \text{ standard})-1]*1000$

Where standard is also the Vienna Standard Mean Ocean Water (VSMOW)

and

$\delta^{13}C= [(^{13}C/^{12}C \text{ sample})/(^{13}C/^{12}C \text{ other standard})-1]*1000.$

Where standard is the Pee Dee Belemnite (VPDB)

^{18}O and ^{2}H Isotopes

δ^{18}O isotope markers reflect the isotopic signature of a region, and are influenced by a region's temperatures of climate, elevation, distance from oceans, and the original water source … rainfall (e.g. Dansgaard [93] and Dansgaard [104]. Stable oxygen isotope values are also influenced by seasonal changes, i.e. temperature of the water.

Under strong evaporative conditions (i.e., warmer and/or drier oxygen isotope values increase [93,104]. Additionally, a strict reliance on δ^{18}O values does not allow for the separation of the influences of temperature and precipitation. However, increases in δ^{18}O values during more evaporative conditions do result in a disparity between the oxygen isotope values from evaporation sensitive and evaporation insensitive receptors [52,105, 156].

With the first two stable isotopes, there are two principal factors that control the isotopic character of precipitation at any given location. They are: 1) the temperature of condensation of the precipitation and 2) the degree of rainout of the air mass (the ratio of water vapor that has already condensed into precipitation to the initial amount of water vapor remaining in the air mass). Most water vapor in the atmosphere is derived from evaporation of low-latitude oceans. Precipitation derived from this vapor is always enriched in ^{2}H and ^{18}O relative to the vapor, with the fractionation between the rain and vapor a function of condensation temperature.

As rain-out of moisture-loaded clouds occurs and they move from the tropics through the Gulf states and eastward across the continental U.S., this causes successive rain storms to become increasingly lighter isotopically. For example, non-equilibrium evaporation from the ocean with a δ^{18}O = 0‰ produces vapor of -12‰. Later equilibrium condensation of rain from this vapor results in water with a δ^{18}O = -3‰ and residual vapor with a δ^{18}O = -21‰.

Sample ID	δ^{18}O	δ^{2}H	δ^{13}C	Tritium (TUs)	Sample Depth (bg)
Clinton Brine	-2.56	-35.15	2.174	7.9*	>3000(?)
MW-1S	-8.24	-54.91	-14.787	8.2	70
MW-1D	-8.12	-54.89	-17.602	9.5	119
MW-1E	-7.61	-52.62	-17.681	12.6	211
MW-2S	-8.43	-59.36	-18.945	6.7	64
MW-2D	-8.57	-57.50	-14.322	5.4	110
MW-3S	-8.26	-55.52	-19.361	10.6	44
MW-3D	-8.42	-56.93	-14.424	7.3	93
MW-5S	-7.77	-52.90	-14.896	7.6	46
MW-5D	-8.16	-54.38	-14.344	8.8	87
MW-6S(1)	-8.61	-55.31	-15.778	7.0	74
MW-6S(2)	-8.45	-57.63	-14.791	8.5	74
MS-WW	-8.34	-54.50	-15.894	8.7	80
NI	-8.39	-54.66	-14.889	8.0	113
Ali	-8.35	-58.05	-14.700	8.4	90
Ni	-8.60	-55.52	-14.327	7.1	79
Cn	-8.32	-55.77	-15.378	8.7	117
R/M	-8.49	-56.81	-14.214	6.7	113
Me	-8.35	-54.75	-14.557	8.9	67
Hm(1)	-8.49	-55.35	-14.240	9.9	90
Hm(2)	-8.45	-55.33	-14.529	11.2	90
Hn	-8.46	-54.29	-14.853	7.8	105
L-N	-8.22	-53.88	-14.224	8.7	106
L-0	-8.34	-54.07	-13.874	8.9	90
Oe	-8.45	-54.08	-15.227	8.5	103
Bs	-8.19	-56.03	-14.387	8.3	103
SW-1	-7.83	-50.89	-13.791	8 .1	0
Statistics					
Standard Deviation:	0.0535	0.7075	0.1178	0.4074	
Variance:	00029	0.5005	0.0139	0.2767	

Table 4: Stable and Radioactive Isotopes: On-Site and Neighborhood Sites.

Precipitation is the ultimate source of groundwater in virtually all systems. Hence, knowledge of the factors that control the isotopic compositions of precipitation before and after recharge allows the use of oxygen and hydrogen isotopes as tracers of water sources and processes.

On a regional scale, the distributions of isotopic compositions are controlled by this one factor in the midcontinent regions such as Ohio. Based on the simplifying assumption that the signal can be attributed to temperature change alone, with the effects of salinity and ice volume change ignored, a number of years ago, Epstein *et al.* [95] estimated that a δ^{18}O increase of 0.22‰ is equivalent to a cooling of 1°C (or 1.8°F). More precisely, they provided a quadratic extrapolation for the temperature, as:

$$T=16.5 -4.3\ \delta\ ^{18}O + 0.14\ \delta\ ^{18}O^{2}$$

Where:

T is the temperature in °C (based on a least-squares fit for a range of temperature values between 9°C and 29°C, with a standard deviation of ±0.6 °C, and δ is δ ^{18}O (i.e., for a calcium carbonate sample).

Water contains mostly oxygen-16 (^{16}O). whereas oxygen-18 (^{18}O) occurs in approximately one oxygen atom in every five hundred and is somewhat heavier than oxygen-16, as it has two extra neutrons, which results in a preference for evaporating the lighter ^{16}O containing water and leaving more of the ^{18}O water behind in the liquid state (defined as fractionation). Thus seawater tends to be richer in ^{18}O and rain and snow relatively depleted in ^{18}O.

Stable isotopes can indirectly determine the age of ice or snow, which can help indicate the conditions of the climate in the past. Higher average global temperature would provide more energy and thus an increase in atmospheric ^{18}O water, while lower than normal amounts of ^{18}O in groundwater or an ice layer would imply that the water or ice represents an evaporation origin during cooler climatic eras or even ice ages [82].

Because precipitation in each rain or snowfall event has a specific isotopic signature, and the signatures of subsurface water can also be identified by sampling specific intervals of monitoring wells or water wells, in the subject neighborhood area where open-hole completion is common for most water wells, which indicates that the well is completed in a hole in the rock (exposing an interval of 50 to 75 feet). The composite signature consists of a mix of overland flow that infiltrates the soil and underlying till and into the numerous joints and fractures and the porous media to the water table of the Black Hand Sandstone, and then what happens to the isotope signatures after the water reaches the water table and becomes subsurface flow over hundreds of feet.

Mook [106] and Clark and Fritz [89] developed a general guide to the environmental implications of the hydrogen and oxygen isotopes describing the hydrologic processes affecting oxygen and hydrogen isotopic composition of water (Figure 32). This plot will be used to interpret the isotope data we obtained from our sampling on-site and in the neighborhood during 2004.

The isotope ratios between ^{16}O and ^{18}O and between ^{1}H and ^{2}H decrease inland from distant coasts. The greater the amount of rainfall, the lower the ^{18}O and ^{2}H values of the rainfall; this effect is not evident in snow. At a given location, the seasonal variations in ^{18}O and ^{2}H values of precipitation and the weighted average annual ^{18}O and ^{2}H values of precipitation remain fairly constant from year to year.

This happens because the annual range and sequence of climatic conditions (temperatures, vapor source, direction of air mass movement, etc.) remain fairly constant from year to year. In general, rain in the summer is isotopically heavier than rain in the winter. This change in average isotopic composition is principally caused by seasonal temperature differences but is also affected by seasonal changes in moisture sources and storm tracks [107][134].

Shallow groundwater ^{18}O and ^{2}H values reflect the local average precipitation values but are modified to some extent by selective recharge and fractionation processes that alter the ^{18}O and ^{2}H values of the precipitation before the water reaches the water table (saturated zone) [36,97]. Some of these processes include: evaporation of rain during infiltration, selective recharge, interception of precipitation by the tree canopy, and exchange of infiltrating water with atmospheric vapor. In the case of snow, various post-depositional processes, such as melting and subsequent infiltration and evaporation, alter the isotopic content of the rain and snowpack, often leading to meltwater δ values that become progressively enriched [108].

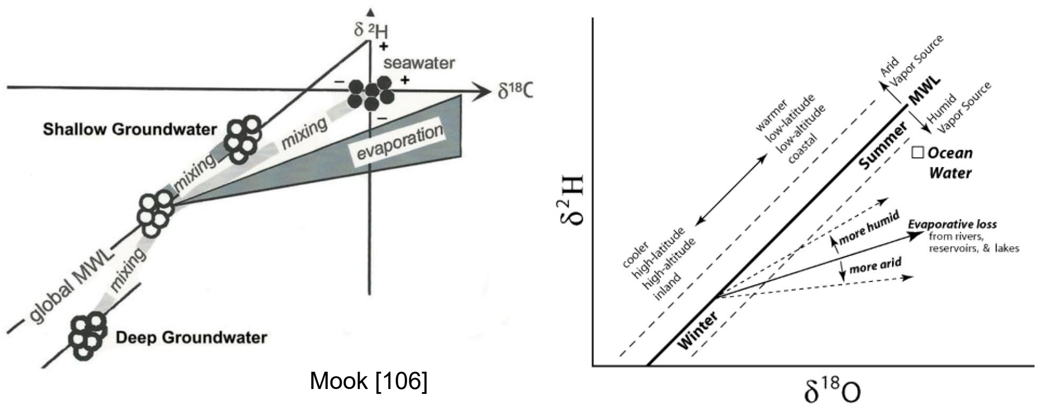
Once the rain or snowmelt passes into the saturated zone below the water table, the isotope values of the subsurface water change only by mixing with waters that have different isotopic contents (at groundwater temperatures below 30 degrees C. The homogenizing effects of recharge and dispersive processes produce groundwater with isotope values that approach uniformity in time and space, and that approximate a damped reflection of the precipitation over a period of years.

Although an individual storm might be large and isotopically very different from the older water in the soil and still in the process of recharging, the amount of precipitation that infiltrates will likely be small compared to the amount of older water in the recharge zone and already in the groundwater. Although there might be significant storm-to-storm and seasonal variations in precipitation ^{18}O and ^{2}H values, groundwater values are expected to remain relatively uniform in humid, temperate areas like the mid-west of the U.S. of our area of interest.

Background of Stable isotope Applications

Temporal and spatial variability in groundwater and base-flow values reflect seasonal variability in precipitation values. However, these variations are less extreme and usually delayed relative to the temporal variations that occur in precipitation [109]. These variations can be utilized for water residence time calculations. Superimposed on the seasonal cycles in precipitation values are storm-to-storm and intra-storm variations in the ^{18}O and ^{2H} values of precipitation. These variations are as large as the seasonal variations. It is this potential difference in values between the relatively uniform older water and variable recent water that allows the determination the relative contributions of older and recent water to a stream during periods of high runoff [110].

Although isotope variability in groundwater is reportedly low in many cases, the 1985 U.S. Geological Survey valley investigations nearby provide data that reflects the monthly variations in δ^{2}H and δ^{18}O values during 1985 [33]. There are two issues that were considered: 1) the standard deviation of the analytical values, and 2) the likely causes behind the encountered variations that are beyond the analytical



Mook [106]

Figure 32: Framework of Stable Isotope Utility. Clark and Fritz [89]

limitations employed in our investigations. Regarding the former, the calculated standard deviations (and variances) for the isotope analyses that were generated during our sampling are presented along the bottom of Table 4 [147].

To assess the monthly isotope variations in the area, we selected a data set from the 1985 study by Breen et al. [33]. Showing a multi-monthly series of six sites plotted on a time line. The February-March data for Well 5 show a three and a half unit increase in δ^2H (Figure 32) and a two and a half unit rise in δ^{18}O (Figure 33). Site 3 shows a two and a half rise in δ^2H. Site 8 shows a rise of two units in δ^2H. Site 7 rose by 0.5 units of δ^2H. However, Site 4 decreased by one and half δ^2H units. The other δ^{18}O values shown in Figure 33 indicate that Site 8 value increased by about 1 unit; Site 3 by 0.5, while the two others remained flat. Then, through the next month, both δ^2H and δ^{18}O for Site 5 decreased by about three units, and afterward both trended lower to early July. With a standard deviation of about 1 δ^2H with 0.1 for δ^{18}O, all of the former show an increasing trend to August followed by three sites showing an abrupt decrease of 2 to 4 units.

Concerning the latter (δ^{18}O), three of the five other sites trend upward, the others are relatively flat to August, afterward the three sites show a marked decrease of one, 0.5 and 0.25 units to later September, which is also shown in the values of δ^2H above.

Based on the above, we conclude that variations occur in both δ^2H and δ^{18}O. However, upon further examination of the environmental conditions present during the U.S. Geological Survey sampling periods, Breen *et al.* [17] reported that a major flood occurred in the immediate area during February, 1985, which contributed to a rise in creek water conductance and promptly fell. They further reported that the dilute meltwater was isotopically anomalous, exhibiting extremely light composition (as explored by Dysart [37]. This rise is evident in Figure 33 and 34.

In the subsurface, any meltwater changes in hydrochemistry during and after the flood went unrecognized in the valley aquifer during sampling at the high-capacity production wells. Isotopic compositions from the valley wells and from the sandstone aquifers sampled in the area also exhibited only minor seasonal variations, with isotopically lighter values tending to occur during summer or fall months. Therefore, if we assume that the isotopic composition of surface water can be considered to be "precipitation," then variations in isotope values can also be expected in response to a range of environmental conditions, e.g., 1) temperatures, 2) seasonal changes in humidity and rainfall, 3) evaporative ponding before infiltration, 4) thickness and hydrochemical conditions and characteristics of the glacial till, 5) thickness of fracture zones within the Black Hand Sandstone from below the glacial till down to the water table and below, 6) nature of fracture zones and vugs and associated mineralization above and below the water table, and 7) differences in flow within the sandstone, i.e., porous media and fractures and joints. Variations caused by one or multiple environmental conditions isotope values of two to three units of δ^2H and one to two units of δ^{18}O can then be expected.

As in our previous assessments of the hydrochemistry of samples, we have prepared the classical stable isotope plots for δ^2H versus δ^{18}O and versus ^{13}C to reveal any groupings, trends, and/or anomalies that might explain the history of the source of the elevated chloride in the subject neighborhood. Because of the complex conditions the isotopes are exposed to, these plots will also serve to characterize the isotopes as they relate the past and current environments of subject area. Then, when compared to the previous hydrochemical plotting

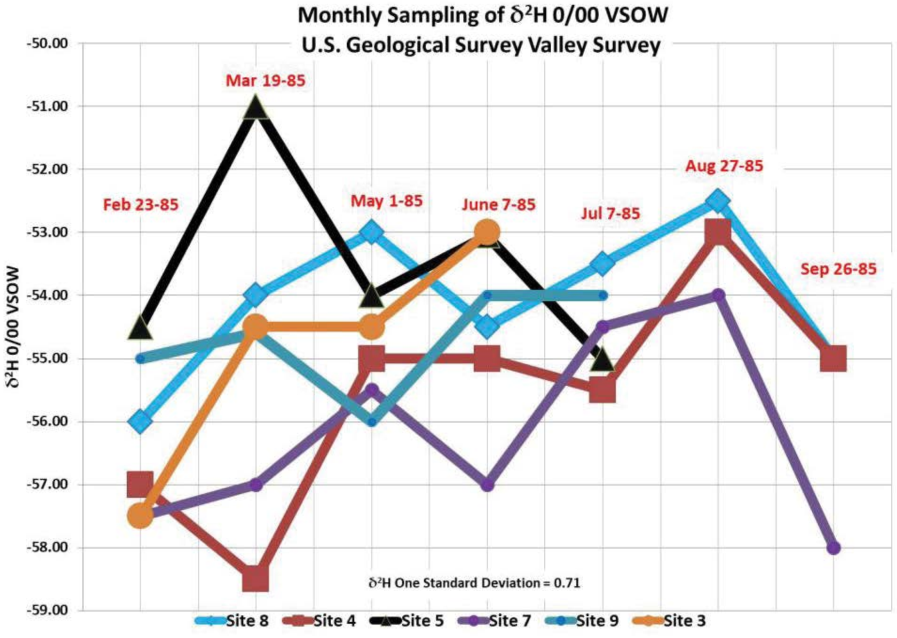


Figure 33: Monthly Sampling of δ^2H 0/00 VSOW. U.S. Geological Survey Valley Survey.

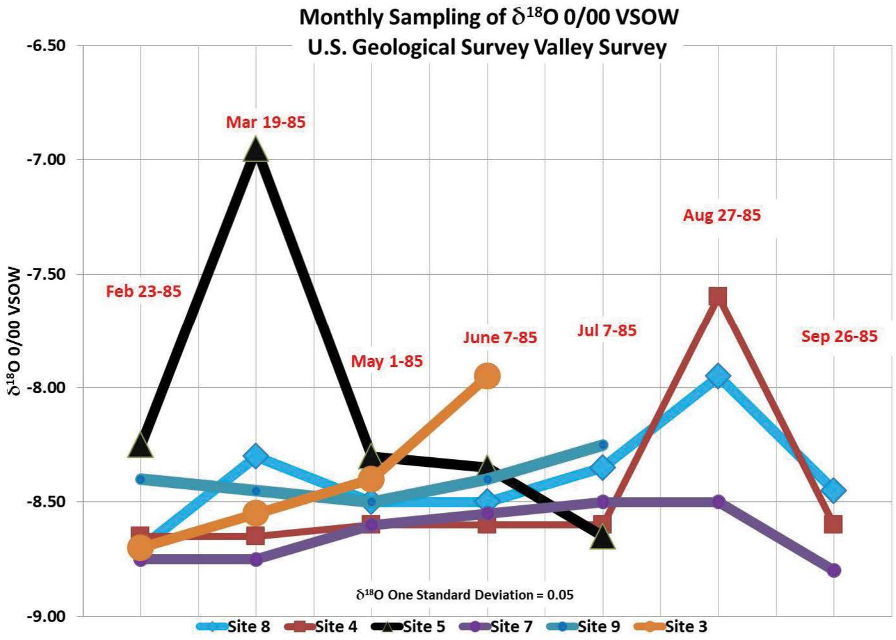


Figure 34: Monthly Sampling of δ¹⁸O 0/00 VSOW. U.S. Geological Survey Valley Survey.

and in applying the age dating information provided by the radioactive isotope ^{3}H-tritium, a few steps toward a more complete framework of the conditions can be presented.

To establish context, Figure 35 illustrates the relation between the Clinton brine and any trends departing from the generalized Local Meteoric Water Line of precipitation [131] [160].

Figure 35 also shows the location of an expanded plot area (Figure 36). Also shown are the two sets of data, one (red and blue dots) consists of the isotope values for samples we obtained from the on-site and neighborhood areas during early 2004, and the other (light blue triangles) are isotope values for samples from the U.S. Geological Survey valley sampling program of 1985. The Clinton brine plot of isotope value shown in Figure 35 agrees well with Breen et al. [33], p. 50), and is located beyond the plot field in Figure 36.

Figure 36 is the classical isotope bivariate plot of δ^{2}H 0/00 VSMOW versus δ^{18}O 0/00 VSMOW. For context, we have plotted the on-site, neighborhood, and U.S. Geological Survey isotope data. The U.S. Geological Survey isotope data, (shown in blue boxes), are plotted with the data from the on-site and neighborhood samples. A Local Meteroric Water Line (blue line) was calculated for these data and we used the line (black) for reference for the on-site and neighborhood isotope samples as well. The latter is capped by the surface-water sample (SW-1).

Note that the Clinton brine value caps the upper Evaporation Line. Sample MW-1E was plotted, but because it comes from well below the Black Hand Sandstone it is not considered part of that environment, and is apparently a representative of a very different environment below a shale in a sandstone-siltstone unit 216 feet bg. However, a fault zone indicated by slickensides was described in the core of CH-1D at 204 feet bg, which occurs within the gravel-pack zone of the screen setting of MW-1E. The unlikely possibility exists that fluids from above might have migrated down the fault zone mixing into the groundwater of the zone screened by MW-1E, but it will not be treated the same as the other samples occurring within the Black Hand Sandstone in our assessments, except for general reference.

For background, we reviewed the literature on regional studies that typically show that isotopic data from groundwater are similar to those of local precipitation, but systematic deviations have been reported where a) groundwater was derived from very old (thousands to millions of years old) precipitation (as explored by Aggarwal, *et al.*[111], Jasechko, *et al.* [112], to b) groundwater recharge being dominated by precipitation from high-elevation sources in mountainous terrains, or c) artificial recharge from "foreign" water constituting a large fraction of the aquifer water (Clark *et al.* [38]; Coplen *et al.* [113].

The latter (Item c) would appear to be applicable in this case, where mixing of water from different sources would be expected, from summer rainfall, from spray-misted oil-field brine, and surface run-off from the property, all recharging the underling glacial till. Spatial isotope ratio variation is known in groundwater, as documented in published investigations of groundwater isotope ratios (Bowen *et al.* [114]; Kennedy *et al.* [115]. In local or regional case studies, analysis of groundwater can show the origin of the water produced in public supply systems, rural water systems and rural water wells, in agriculture, and industry. Isotopic data also have significant potential in forensic applications in conflicts involving a range of contaminants, including elevated chloride concentrations [64,86].

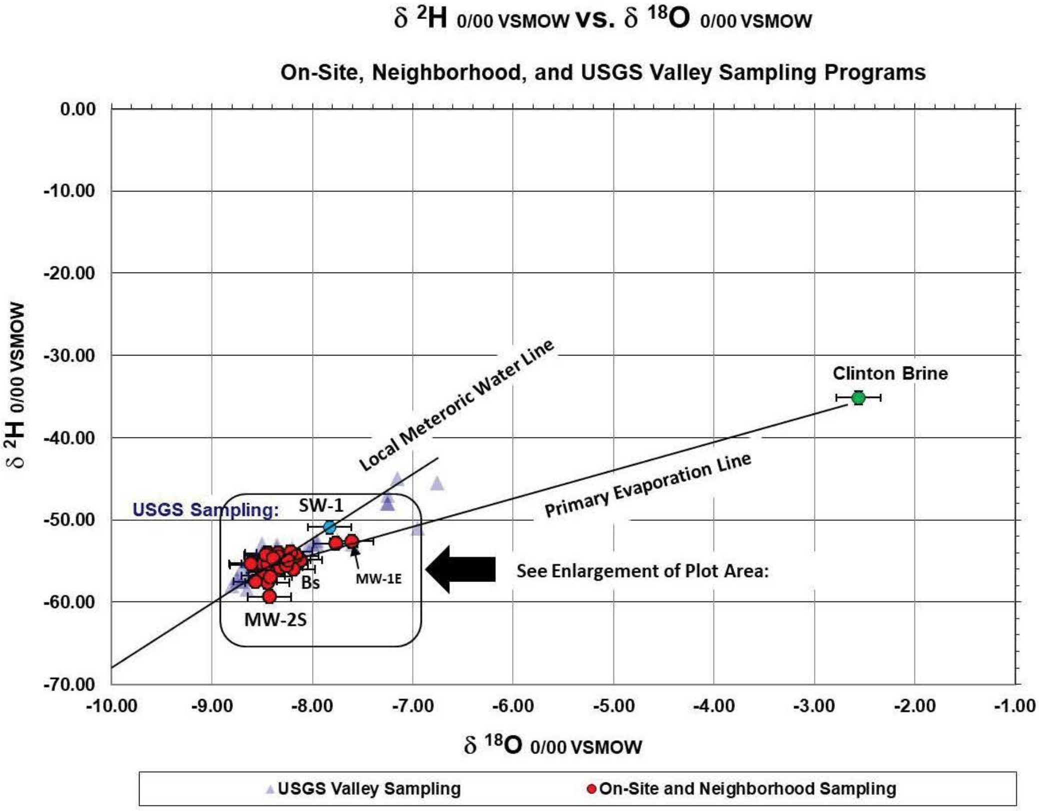


Figure 35: δ ^{2}**H** 0/00 VSMOW vs. δ ^{18}**O** 0/00 VSMOW: On-site, Neighborhood and USGS Valley Sampling Programs.

At first glance, the use of stream samples as indicators of rain or recharge isotopic compositions might appear to be problematic, because streamwater represents a time-varying mixture of groundwater with a plethora of ages, plus recent precipitation. However, there are several reasons that stream water is useful.

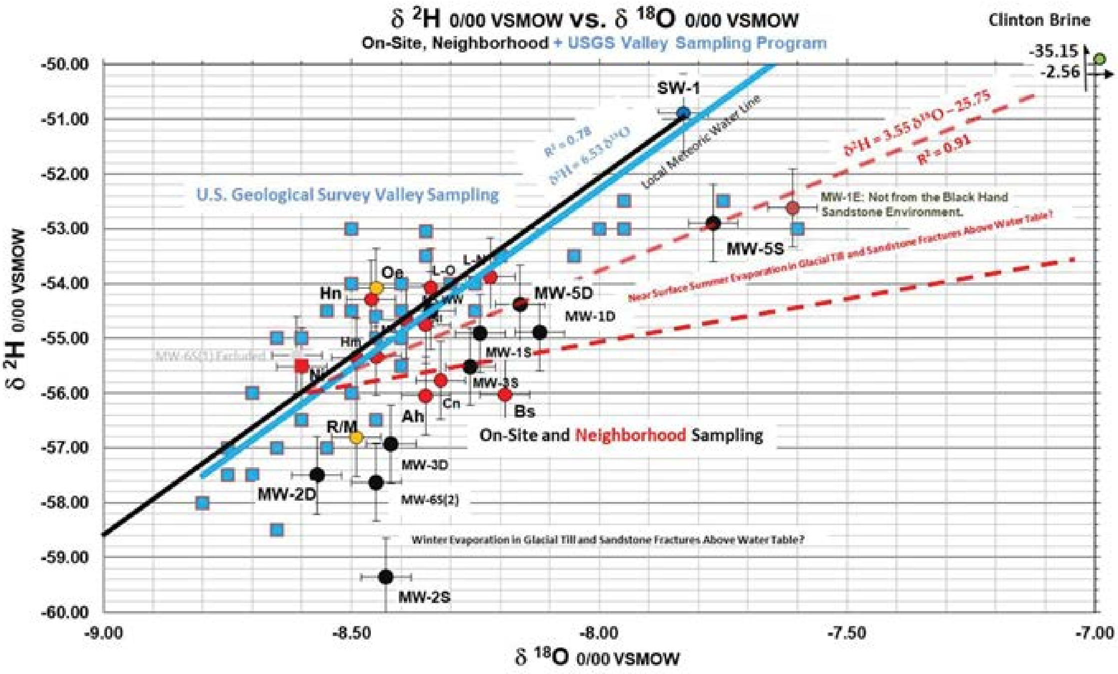


Figure 36: δ ^{2}**H** 0/00 VSMOW vs. δ ^{18}**O** 0/00 VSMOW: On-Site, Neighborhood and USGS Valley Sampling Programs.

The isotopic compositions of shallow groundwater and small streams have been used by many researchers to define what are believed to be repeating isotope patterns in average precipitation (e.g. Friedman *et al.* [96]; Sheppard *et al.* [116]; Fritz *et al.* [117]; Ingraham and Taylor [118]; Yonge *et al.* [119].

The main advantage of using river samples relative to groundwater samples as proxies for precipitation is that they are readily available (i.e. no wells to sample with the associated uncertancies). Also, the U.S. has numerous river- and stream-monitoring networks in place (via the U.S.G.S. and local counties and municipalities), many of which offer on-line, long-term data sets. Also, because a sizable percentage of the river water is very recent rain [120], a small amount of the water has been subject to local processes such as selective recharge and evaporation in the soil (and underlying glacial till) zone, which would tend to alter isotopic and hydrochemical compositions from that of the original precipitation.

River samples are commonly used as substitutes for precipitation samples to determine LMWLs (e.g. Yonge *et al.* [119]), especially in environments where recent rainfall is believed to be a major component of streamflow. Additionally, the compositions during baseflow are commonly used to estimate the isotope values of groundwater and annual mean precipitation (e.g. Friedman *et al.* [96]; Sklash *et al.* [110]) because the isotopic compositions of most groundwater systems are constant and thought to reflect closely the average annual isotopic composition of local precipitation (Yurtsever and Gat [121]). These different usages reflect the dual (composite) nature of streamflow: recent precipitation and older groundwater (baseflow). However, the baseflow component should be viewed as reflecting a spectrum of ages of waters (Michel [122]; Brown *et al.* [123]; McDonnell *et al.* [124].

Because of the difficulty involved in obtaining a reliable average isotope value for precipitation and the problems of spatial variability of rain, shallow groundwater samples are often collected to serve as the average precipitation composition. However, groundwater recharge is often a selective process, excluding rain that runs off to streams or is absorbed within the soil or underlying fine-grained sediments (i.e., glacial till), and thus be more reasonably considered to estimate the 'recharge' composition than the actual composition of the average rain in any local area.

River samples usually contain a complex mixture of recent precipitation and older groundwater, estimation of average precipitation or groundwater compositions at each site requires fitting the data to a hydrologic model. These isotopic compositions can then be compared with available meteoric and groundwater data to improve the estimates of average rain and local recharge compositions [36,104,106,108].

With the Local Meteoric Line established in Figure 36 with the isotopically heaviest sample obtained at stream sample (SW-1), the application of other stable isotope analyses is non-predictive and non-spatial, although they can reveal something of the environmental conditions, especially if a number of them form groupings and/or trends that indicate similar histories and/or environments [27,90]. As presented in the previous hydrochemical discussions, certain samples in Figure 36 (and in the less cluttered Figure 37) exhibit anomalous characteristics (that are also illustrated in most of the bivariate hydrochemical plots, i.e., Figures 9, 10, 11, 13, 15, 16A and B, 19, 20, 26, and 28), as do the isotopic values of many of the same samples. This often involves samples from sites MW-5S and MW-3S from the shallow zone (about 40 feet bg), and samples from MW-2D and MW-3D that were from depths of 90 to 100 feet bg (see Figure 12). We will be discussing these samples and others in discussions on their sample isotope content and their distribution in various classical bivariate isotope plots and how these data are determined by the sources of fluids present in the area of investigation at the time of sampling.

Integration of Anomalous Data

The anomalous sample from site MW-5S, located along the southern boundary of the property (Figure 1), was obtained from a screened zone of about 40 feet bg. As indicated previously, the sample site received run-off from the surface over the many years that the property received brine from both nearby de-icing activities on the county road, and from 1998 through 2000 when Clinton brine was applied on the property for dust control during summers of 1998, 1999, and 2000.

The site is underlain by a relatively thick zone of glacial till, in which perched water was reported during drilling MW-5S and 5D and at MW-2S and 2D (Figure 6). This environment could explain why the sample exhibited anomalous characteristics in hydrochemistry and isotope configuration, i.e., pH and specific conductance (Figure 10), TDS (Figure 11), chloride (Figure 12), nitrite-nitrate (Figure 15), bicarbonate (Figure 16A), affiliation with oil-field brine trend, the trend in sodium-magnesium plot (Figure 24), away from the on-site grouping (Figure 26), confirmatory affiliation with oil-field brine trend (Figure 28), and Figures 36, and 37 below indicating markers of enriched δ^2H and $\delta^{18}O$ values for sample MW-5S. As will be discussed later in this paper, the sample's tritium value indicate that the sample apparently experienced an extensive residence time within the zone of glacial till before migrating down into the water table.

These data also indicate that the sample has experienced an extended period of evaporation (precipitation during hot, humid (summer?). Increased residence time within the perched water zone appears to have caused mixing of water of different ages in some areas, while remaining essentially recharged by recent rainfall as it migrated through the zone on its way to the sandstone below in the unsaturated zone (of aeration) along fractures and in the fine-grained sandstone, eventually reaching the water table at about 35 to 50 feet below the surface.

MW-2S is another anomalous sample site (Figure 37 (without the U.S. Geological Survey data)). This site is located along the northern boundary of the subject property (Figure 1). It also plots well off the LMWL, but not along the Near Surface Evaporation Line as does MW-5S. MW-2S exhibited the lightest δ2H marker of a small grouping, i.e., MW-6S, MW-2D, and MW-3D. This indicates that evaporation of a different type, perhaps via snow melt/ cold water in the spring created these unusually light δ^{2}H markers. However, there are some issues regarding the age of the precipitation, especially for sites MW-2S and MW-2D. These will be discussed further in connection with their tritium values.

There is also a marginal grouping of the isotope markers of neighborhood (red symbols) and on-site samples (black symbols), with the former grouping around the LMWL, whereas the latter are off-set below the LMWL around the evaporation line trending toward MW-5S. This indicates a somewhat different range of temperatures in precipitation or subsequent subsurface history [7].

There are exceptions within the groupings without current explanation (i.e., MS-WW, and Cn, Bs, and Ah). The two samples having been treated (orange symbols) plot on opposite sides of the LMWL.

On the basis that temperatures impact isotopic ratios, we plotted temperature against δ^{2}H markers (Figure 38) and δ^{18}O markers (Figure 39) to explore the resulting distributions within the isotope data sets of the on-site, neighborhood, and the data from the U. S. Geological Survey sampling program (light blue symbols) for context as discussed previously.

Of particular interest is the distribution of the MW-5S and MW-5D markers. The former continues to exhibit unusual characteristics relative to the LMWL line and to the relative relation to the main grouping of markers. The latter segregation is apparent between the on-site and neighborhood isotope markers, with MW-2S exhibiting the lightest δ^{2}H markers, with the exception of the treated samples (R/M) and MS WW that also remain anomalous as in the δ^{2}H vs δ^{18}O plot on Figure 37.

The δ^{18}O plot of Figure 39 reflects a not-so subtle difference, the standard deviations of the analyses notwithstanding. The MW-5S-MW-5D set occupies a similar position as in the δ2H plot, but two trend groupings of isotope markers are apparent in this plot, and one separate grouping. One trend is on or near the LMWL line (Bs (and MW-5D), L-N, Ah, and Me), and the other marker trend is separated from the LMWL line by 0.5 δ^{18}O (i.e., L-O, MS-WW, MW-6S, MW-2S, Nl, MW-3D, HM, MW-2D, and Ni), plus a grouping of MW-3S, MW-1S and 1D. There is no separation between on-site and neighborhood isotope markers, as in the baseline plot of Figure 37 and in Figure 38, but the isolated grouping of MW-3S, MW-1S and 1D occurs in both plots (Figures 38 and 39).

The red trend lines shown in Figures 38 and 39 are to indentify the marker trends discussed only, and not meant to imply statistical significance at this time. However, if the isotope markers reflect temperatures of the time at which precipitation fell in the past, then the trends shown in Figures 38 and 39 reflect seasonal variations over such a period, or a group of periods, sorted into seasonal order from mixing of fluids. But because δ^{2}H and δ^{18}O are sensitive to temperature during precipitation, the sample temperatures were not likely affecting the isotope values resulting from evaporation. Further, a physical cause of fractionation would be required, i.e., evaporation, precipitation, or geothermal exchange with minerals containing oxygen-18 (above 30°C). These conditions were not involved during our sampling.

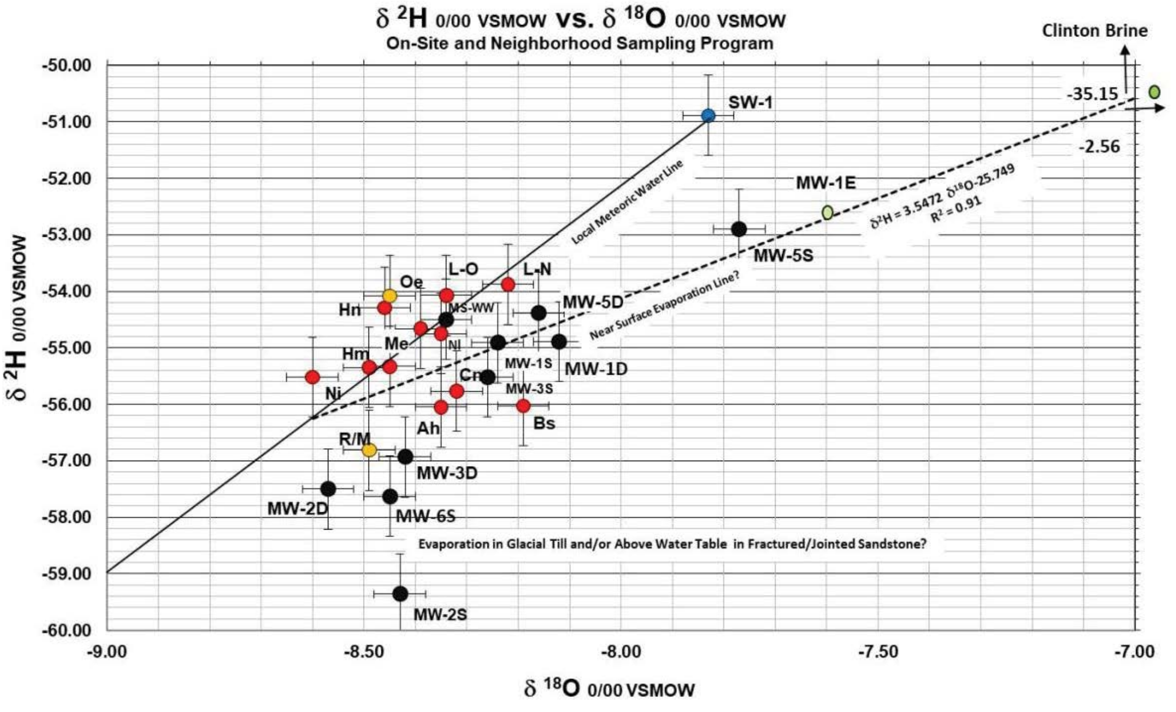


Figure 37: δ ^{2}**H** 0/00 VSMOW vs. δ ^{18}**O** 0/00 VSMOW: On-Site and Neighborhood Sampling Programs.

Further, a depth function with temperature is apparent with the "S" samples, although two of them, 3S and 5S, do exhibit unusual isotopic and sample depth-related characteristics (see Figures 38 and 39 for temperatures, and Figures 41 and 42 for depths of samples). Also of note are the groupings exhibited in Figures 38 and 39, where the former (δ^2H vs. temperature) shows segregation between on-site and neighborhood groupings (with some mixing), whereas in the latter figure ($\delta^{18}O$ vs. temperature) shows that segregation is observed, but with some mixing of groups, plus an anomalous third grouping. In addition MW-5S and 5D plots are similar in both Figures, with 5S below the LMWL. The U.S.G.S. data also have an unusual distribution in Figure 39.

The outliers present within the trends (i.e. where black symbols (on-site) plot within the dominating red symbol grouping (neighborhood) or vice versa) indicate other mixed solutions overprinting the original events, such as that in the area of MW-5S and 5D.

MW-1E, although the sample was from a sandstone more than 100 feet below the Black Hand Sandstone, the temperature at sampling was consistent with the main grouping. The monitoring wells were sampled six months after installation so the water sampled should have been well equilibrated with its subsurface environment. The sample was enriched more in $\delta^{18}O$ (Figure 39) than in δ^2H (Figure 38). As before, the U.S. Geological Survey data provide a context for the sampling temperatures and isotopes. The significance of the on-site and neighborhood data that plot generally above the USGS LMWL is unclear, although with 5S and 1E plots below the line might indicate evaporation or other severe environment, relative to the samples of the main grouping.

MW-5S exhibits significant enrichment in δ^2H almost to the extent of MW-1E (which is from a sandstone well below the Black Hand Sandstone). Also of note is that 5S plots away from the main grouping in the sampling temperature: δ^2H plot of Figure 38 (but neither higher nor lower than that of the main grouping). The MW-6S samples plot away from the main grouping and is somewhat depleted in a δ^2H.

The δ^2H versus chloride bivariate plot of Figure 40 shows the groupings reported previously in this paper, i.e., the up-gradient group (Ah, Ni, and Nl), and three anomalous sites discussed previously, e.g., MW-5S, MW-3S, MW-6S, and MW-2S. Note that the former group shows a low-chloride association to the surface-water sample (SW-1). MW-2S exhibits more depletion in δ^2H than all others in the data set. All shallow samples (i.e., 2S, 6S, 3S, but 5S and 1S) plot below the calculated seasonal water line, indicating that they experienced unique residence environments during recharge within the glacial till and/or as the water migrated downward through fractures, joints and/

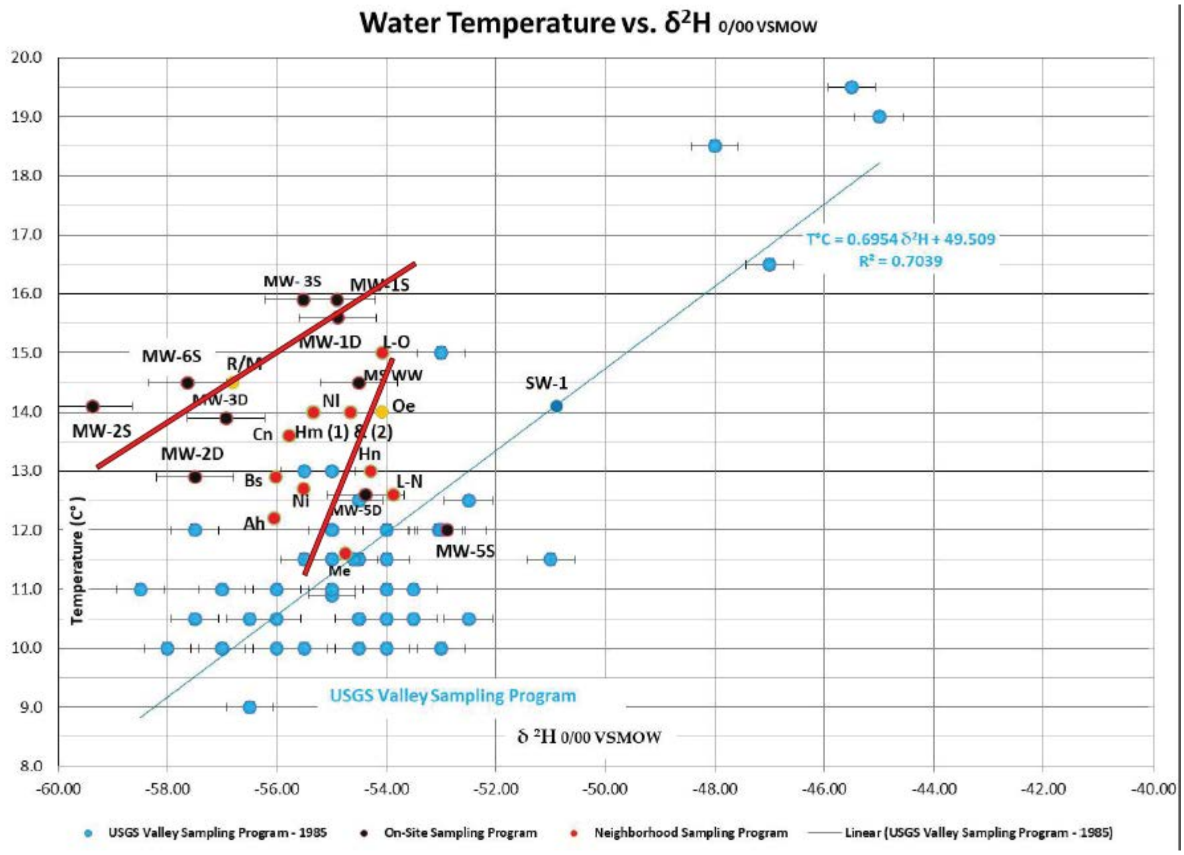


Figure 38: Water Temperature vs. δ **²H** 0/00 VSMOW.

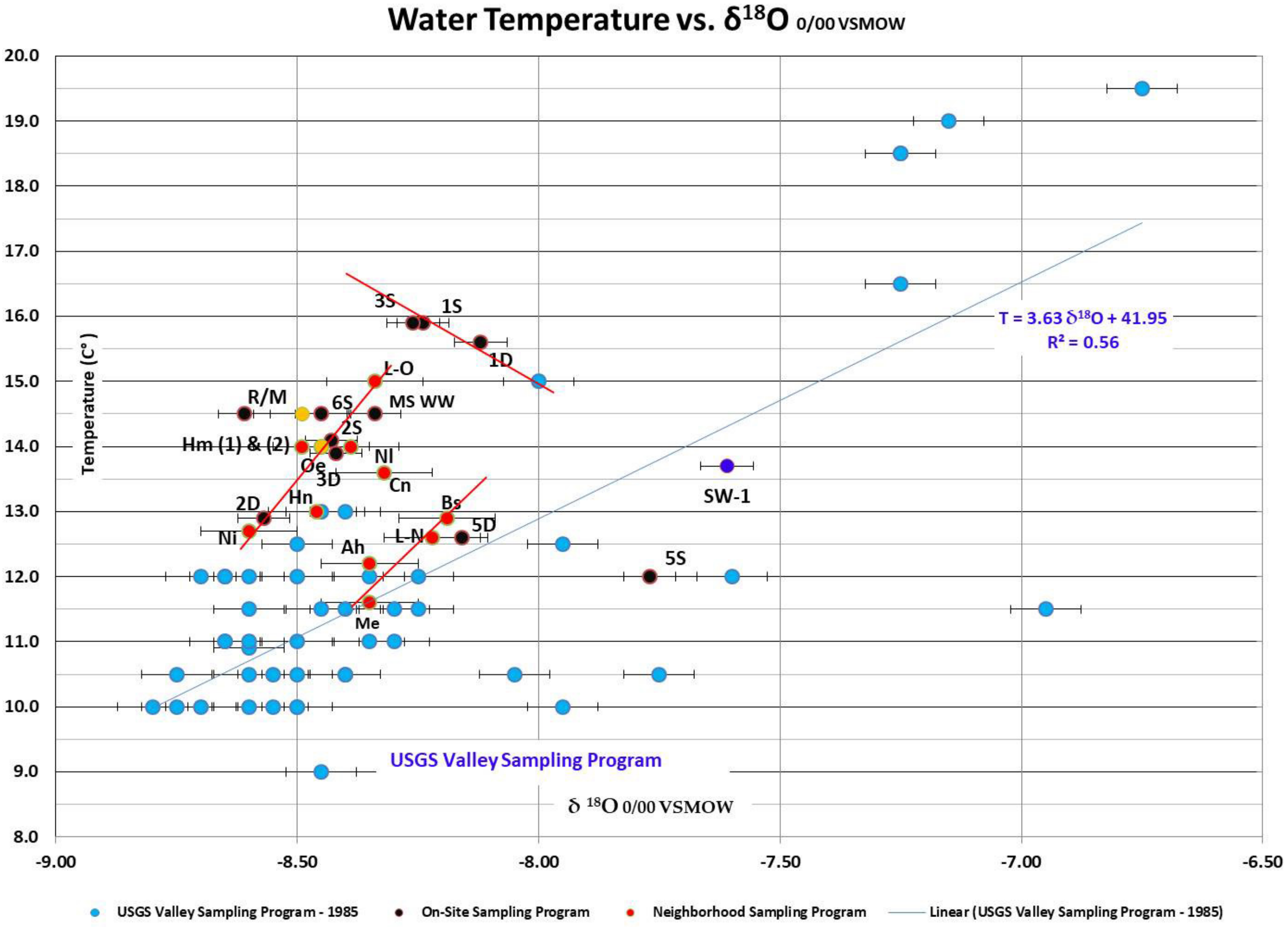


Figure 39: Water Temperature vs. δ ¹⁸**O** 0/00 VSMOW.

or porous media to the water table below. The depths of the sample origins (vs δ^{2}H) are illustrated in Figure 41.

The SW-1 sample shows that it is enriched in both isotopes, although MW-5S sample is of similar enrichment, and MW-1E and Clinton Brine is somewhat less enriched than the surface-water sample (SW-1). This likely has more to do with greater residence time of the two samples than that of the main grouping.

The δ^{18}O versus chloride bivariate plot of Figure 42 shows a similar up-gradient plotting (Ah, Ni, Nl, with extension to SW-1) relative to δ^{2}H plot of Figure 40. The enrichment of MW-5S is illustrated in both δ^{18}O and δ^{2}H, both likely reflecting prolonged residence time and evaporation (relative to other samples) below the glacial till. MW-2S plots within the main grouping in Figure 42, but plots well below the main grouping in Figure 40. The sample for MW-5S was from a shallow zone below the glacial till, but plots in Figure 43 at an enrichment level closer to SW-1. This confirms that special environments existed within and just below the thick glacial till present in the shallow subsurface at the site (Figure 43).

The impact of the δ^{2}H, δ^{18}O, δ^{13}C vs. chloride plots are summarized in Table 5.

In such an environment, δ^{2}H and δ^{18}O isotopes are affected because of the aqueous chemical reactions occurring within the glacial till, altering the chemical and isotopic enrichment or depletion of fluids and as the water trickles down fractures and joints to the water table, ultimately sampled at shallow and deep intervals of on-site monitoring wells and neighborhood wells.

The isotope vs. chloride plots are reasonably straightforward when comparing the sample pairs (MW-1S and MW-1D, MW-2S and MW-2D, etc. in terms of vertical changes in chloride concentration and associated isotope depletion or enrichment with depth (Table 5). The δ^{2}H and δ^{18}O show increases in chloride and minor enrichment with depth between MW-1S and MW-1D, but all other monitoring well sites show decreases in chloride from shallow zones to deeper zones and isotope depletion with depth. For δ^{13}C, the MW-1S-MW-1D series show a net decrease in chloride with depletion at depth, whereas the rest of the well site pairs show decreases in chloride, but enrichment with depth. These data indicate that the subsurface environment contains chloride decreasing with depth at a net change of 21 ppm to 364 ppm from the shallow to deep zones, with depletion prevailing with the δ^{2}H and δ^{18}O isotopes and enrichment in δ^{13}C. With the latter, MW-2S-2D and MW-3S-3D exhibited strong enrichment, i.e., net 4.6 and 4.9 δ^{13}C with depth respectively. MW-3S-3D exhibited strong depletion of δ^{2}H at net 3.41 with a net decrease in chloride by 364 ppm [144][152].

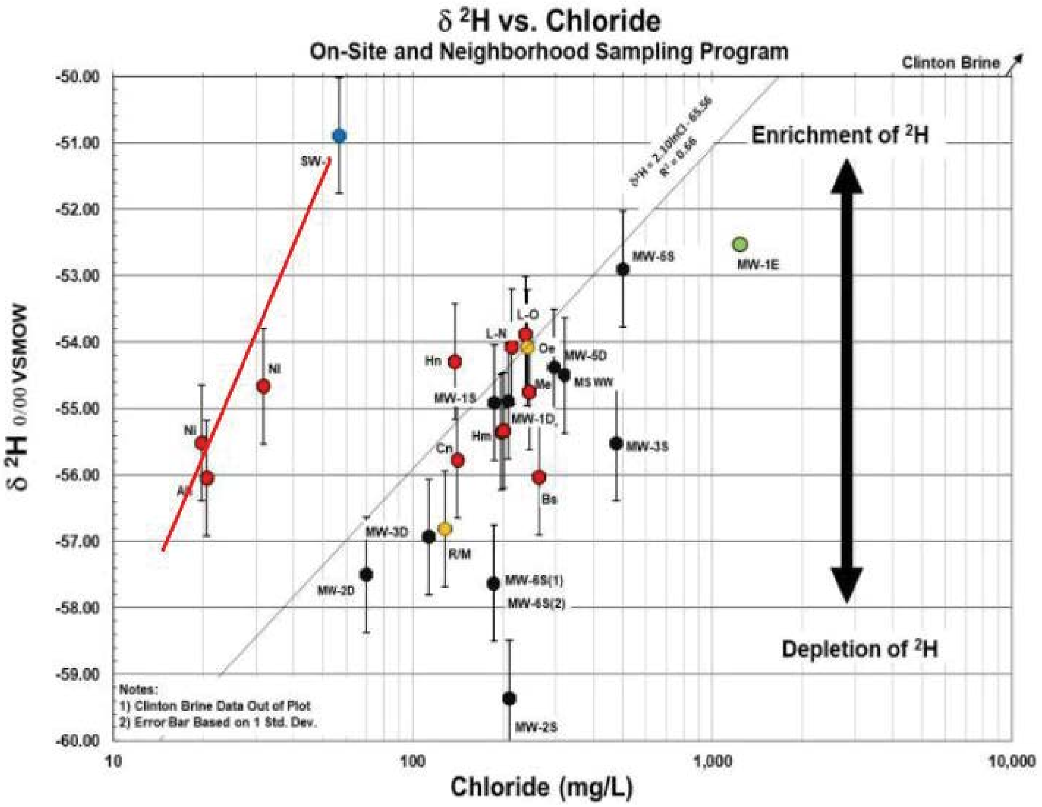


Figure 40: δ ^{2}H vs. Chloride

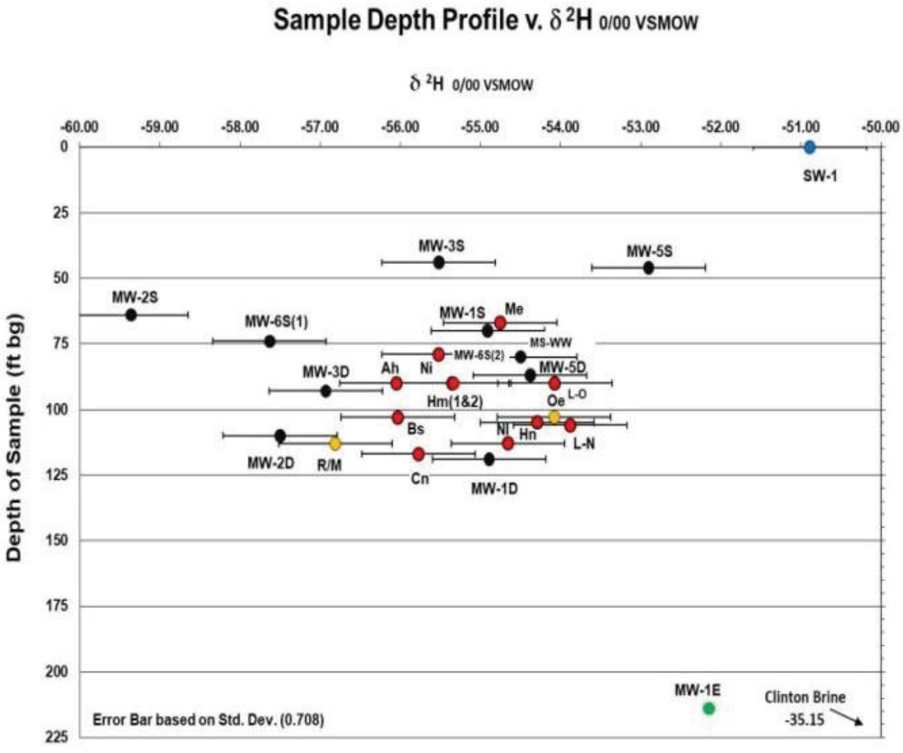


Figure 41: Sample Death Profile v.δ^{2}H 0/00VSMOW

Saturation Index

The δ^{2}H versus Saturation Index (SI) bivariate plot of Figure 44, indicates that about 50% of the samples taken are undersaturated and 50% oversaturated with respect to calcite. Note that calcite was reported in the vugs in the core at a number of intervals (see Appendix A - Geologic Log). The core also exhibited fracture filling and calcite crystals in places. A

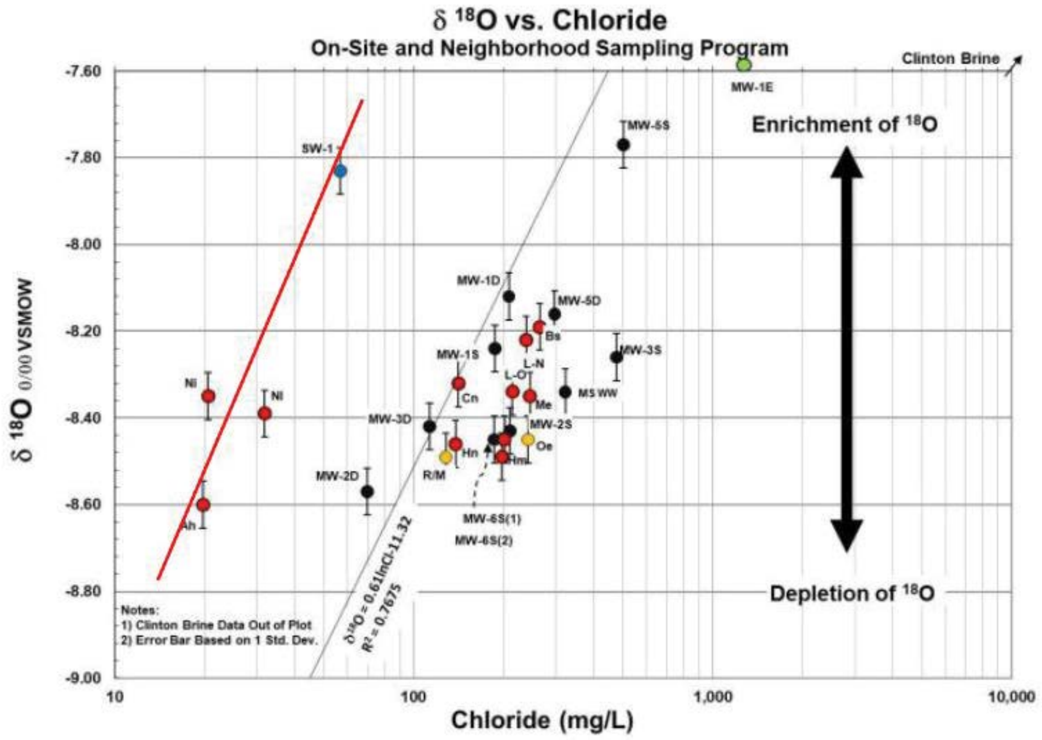


Figure 42: δ ^{18}O vs Chloride

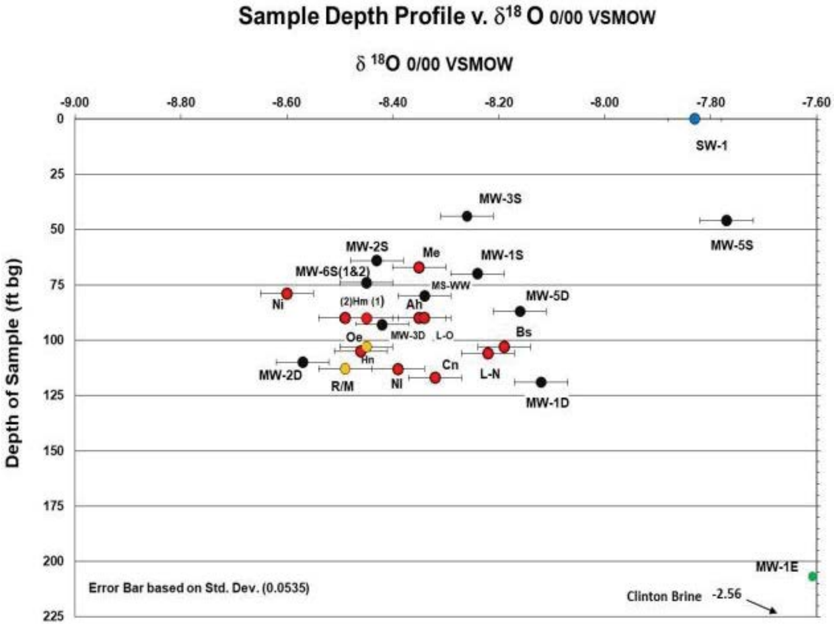


Figure 43: Sample Depth Profile v.δ$^{18\,\mathrm{O}}$ O 0/00 VSMOW

groundwater sample (MW-1S) was undersaturated relative tom calcite in the advanced oxidation zones indicated in the core (see Figure 5A) with a median δ^{2}H value (relative to the central grouping). Anomalous SI include the L-O site (very undersaturated reporting almost -2 SI) and MW-3S reporting approximately +1.5 SI.

Of note is the pattern of the central groupings. The δ^{2}H:SI (Figure 44) and δ^{18}O:SI (Figure 45) plot of neighborhood samples (red symbols) forms the core of the central group, with 5 of the 10 samples (of the red symbols) plotting in vertical sequence on the neutral bar (indicating equilibrium of the water), with the on-site samples (black symbols) occupying positions surrounding the core. Sample MW-5S plots as usual above the main grouping. It exhibited water that was under slightly undersaturated conditions when sampled. The sample from MW-2S is anomalous by plotting below the main grouping and by being more depleted in δ^{2}H. But with respect to δ^{18}O of the sample, it plots within the central region in Figure 45, and was under slightly saturated conditions.

The treated samples, R/M and Oe, plot off the chart to the left as well as the sample from the Bs site, the latter plot value for currently unknown reasons. Also, SW-1 shows a slightly saturated SI, as might be expected in an active stream and plots as very enriched in δ^{2}H, but less enriched in δ^{18}O [125].

^{13}C Isotope

The δ^{13}C isotope is present in streams and rivers, oceans, and groundwater and is useful for identifying the source of the water. This is because atmospheric, carbonate, and plant derived δ^{13}C values all differ with respect to Pee Dee Belemnite (PDB) standard.

Carbon has two stable isotopes, ^{12}C and ^{13}C, and one radioactive isotope, ^{14}C. The stable carbon isotope ratio, δ^{13}C, is fractionated primarily by photosynthesis (Faure and Mensing [126]). The ^{13}C/^{12}C ratio is also an indicator of paleoclimate: a change in the ratio in the remains of plants indicates a change in the amount of photosynthetic activity, and thus in how favorable the environment was for the plants [6,44,107]. Occasional spikes in the global ^{13}C/^{12}C ratio have also been useful as stratigraphic markers, especially during the Paleozoic, especially across the Silurian-Devonian transition, where δ^{13}C peaked at about +5 0/00.

The ^{14}C ratio has been used to track ocean circulation, and groundwater residence times and water-chemistry evolution of groundwater recharge, as an indicator of mixing of groundwater from different sources. To explore what δ^{13}C can bring to characterizing the on-site and neighborhood areas with respect to the timing of the chloride distribution, the bivariate plot in Figure 46 reinforces some of the anomalies identified earlier in this paper. Figure 47 provides the vertical context for the markers. For example, MW-5S once again occurs away from the main grouping. But δ^{13}C markers MW-2S, MW-3S, and also MW-1D, occupy positions away from the main grouping, but well below the MWL indicating significant deletion of δ^{13}C (relevant to the main grouping).

Of note regarding the main grouping is that the core of the group remains of the neighborhood markers (red symbols), with the on-site markers especially surrounding the core. This excludes the three up-gradient markers (i.e., Ah, Ni, and Nl) as in most previous isotope and hydrochemistry bivariate plots developed in this paper. They plot in a grouping well away from and above the MWL.

Also of note are the MW-2D and MW-3D markers, which plot above and away from the MWL. These two markers will be discussed in some detail in the section on tritium (^{3}H) markers. The other common markers consist of the surface-water sample (SW-1, blue symbol), which plots above and away from the MWL, and MW-1E, although not associated with the above groupings, plots in the same generalized area that includes MW-1D, 2S, and 3S in the zone of heavily depleted δ^{13}C.

The δ^{13}C versus Saturation Index (SI) bivariate plot of Figure 48 indicates a pattern with on-site samples (black symbols: MS-WW, MW-1D (with some affiliation with MW-1E), MW-2S and MW-3S) exhibiting increasing oversaturation (with respect to calcite) with increasing depletion of δ^{13}C. Once again, MW-2S and MW-3S occupy unique positions in the plot (relative to previous plots). Once again note re MW-1S and 1D that needle calcite was reported in the vugular spaces in the core at a number of intervals (see Appendix A - Geologic Log). The core also exhibited fracture filling and clear calcite crystals in places.

As in Figures 44 and 45, a groundwater sample (MW-1S) was obtained from the advanced oxidation zones indicated in the core (see Figure 5A) and shows the water from the zone is undersaturated with a median δ^{13}C value (relative to the central grouping). Also, anomalous SI samples include the L-O site (very undersaturated reporting almost -2 SI and slightly enriched in δ^{13}C) and MW-3S reporting approximately +1.5 SI. SW-1 shows a slightly saturated SI.

The stream sample (SW-1) exhibits a positive SI and is slightly enriched in δ^{13}C, the latter of which is consistent with δ^{2}H (Figure 44) whereas SW-1 is somewhat less enriched in δ^{18}O than MW-5S (and MW-1E) indicated in Figure 45.

The treated samples, R/M and Oe, plot off the chart to the left

Monitoring Well Sample Sites	Chloride	Isotope Enrichment/Depletion	Reference Figures
δ^{2}H vs. Chloride	**Increase/Decrease Chloride**	**Enrichment/Depletion δ^{2}H**	**40 and 41**
MW-1S to MW-1D	Increase [21 ppm] in Cl	Enrichment [**0.02 δ^{2}H**] w/ Depth	
MW-2S to MW-2D	Decrease [140 ppm] in Cl	Depletion [**1.86 δ^{2}H**] w/ Depth	
MW-3S to MW-3D	Decrease [364 ppm] in Cl	Depletion [**3.41 δ^{2}H**] w/ Depth	
MW-5S to MW-5D	Decrease [207 ppm] in Cl	Depletion [**1.48 δ^{2}H**] w/ Depth	
δ^{18}O vs. Chloride	**Increase/Decrease Chloride**	**Enrichment/Depletion δ^{18}O**	**42 and 43**
MW-1S to MW-1D	Increase [21 ppm] in Cl	Enrichment [**0.12 δ^{18}O**] w/ Depth	
MW-2S to MW-2D	Decrease [140 ppm] in Cl	Deletion [**0.14 δ^{18}O**] w/ Depth	
MW-3S to MW-3D	Decrease [364 ppm] in Cl	Depletion [**0.16 δ^{18}O**] w/ Depth	
MW-5S to MW-5D	Decrease [207 ppm] in Cl	Depletion [**0.39 δ^{18}O**] w/ Depth	
δ^{13}C vs. Chloride	**Increase/Decrease Chloride**	**Enrichment/Depletion δ^{13}C**	**46 and 47**
MW-1S to MW-1D	Decrease [21 ppm] in Cl	Depletion [**2.82 δ^{13}C**] w/ Depth	
MW-2S to MW-2D	Decrease [140 ppm] in Cl	Enrichment [**4.62 δ^{13}C**] w/ Depth	
MW-3S to MW-3D	Decrease [364 ppm] in Cl	Enrichment [**4.94 δ^{13}C**] w/ Depth	
MW-5S to MW-5D	Decrease [207 ppm] in Cl	Enrichment [**0.55 δ^{13}C**] w/ Depth	

Table 5: Impact of Changes in Chloride and Isotope Enrichment / Depletion with Depth.

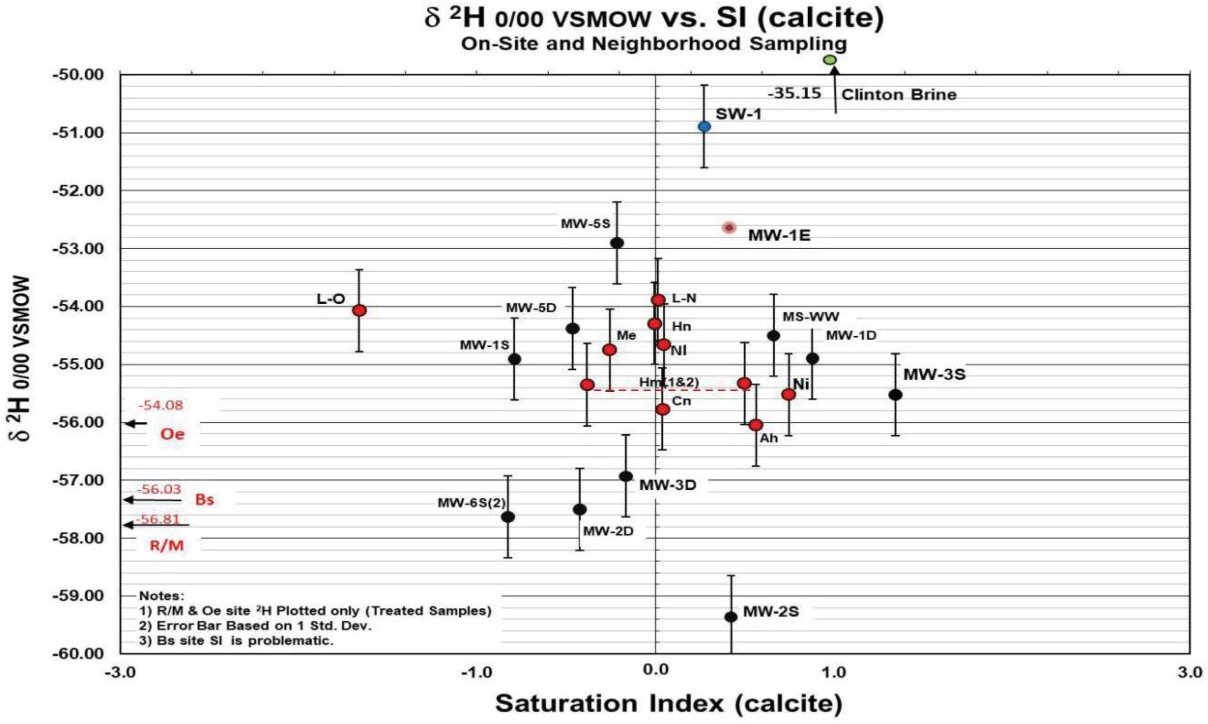


Figure 44: δ ^{2}H 0/00 VSMOV vs. SI (Calcite).

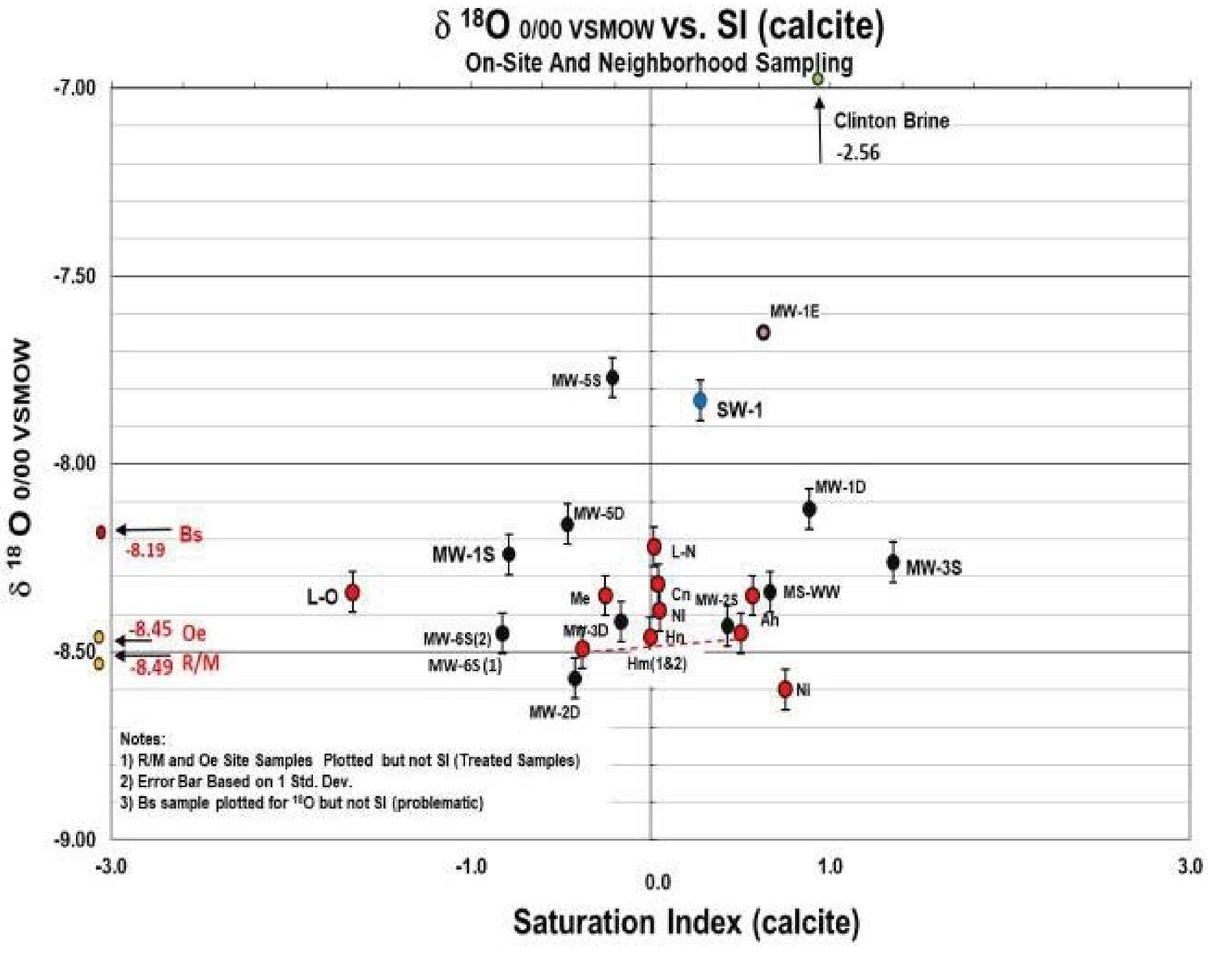


Figure 45: δ ^{18}O 0/00 VSMOW vs. SI (calcite).

as well as the sample from the Bs site, the latter plot value for currently unknown reasons but apparently related to in-home water softening system processes which significantly alters the SI of the samples while the δ^{13}C (Figure 48) and δ^{18}O isotope markers (Figure 45) remain unaffected. The δ^2H markers (Figure 44) indicate some depletion from the main grouping.

Also of note is the pattern of the central groupings where two of the three up-gradient markers (Ah and Ni) and SW-1 were taken from an oversaturated environment and the third (Nl) as well as L-N, Hm and Cn, are from equilibrium conditions. All other on-site markers within the central grouping were from undersaturated conditions, with MW-6S(1) showing some depletion in δ^{13}C although, as a duplicate sample, this might not be significant relative to MW-6S(2).

Integration of Stable Isotope Data

As with hydrochemical data, the tendency for the groundwater samples to form main isotope clusters indicates that there is a common subsurface environment below the neighborhood of the northern county road area and a different environment below the subject facility, as anticipated based on the direction of groundwater flow from the recharge area above.

The hydrochemical and isotope samples provide only a snap-shot in time of the subsurface conditions. Quarterly sampling would have been preferred over two or more years but funding was not available. Although some insight can be gained by the sampling and analytical work obtained in 2004, we concluded at the time that sampling for tritium (^{3}H) could provide information on the age of the samples obtained, or at least when precipitation became recharge in the subject area.

A Radioactive Isotope: ^{3}H (Tritium)

As has been well studied over the years, tritium, although used in the past as part of a trigger for nuclear weapons, is also useful as an atmospheric residue from nuclear-bomb testing of the 1950s and 60s as a marker of atmospheric precipitation. As a complement to stable isotopes, a series of water samples was obtained in 2004 and subsequently analyzed for tritium at Waterloo Laboratories, Ontario, Canada. Because tritium occurs in such low concentrations, the radioactive isotope must be counted in the lab over 90 to 120 days. The resulting tritium analyses are presented in Figure 49. Sample locations are also shown in Figure 31. For associated statistics (standard deviations, variances, and lab and field duplicates), see Appendix D.

The first matter to discuss should be that of the tritium content of the Clinton Brine. The Waterloo laboratory result was reported as 7.9 tritium units (TU), equals 25.2 picoCuries per liter (pCi/l). However, the derived value exhibited a SD of ±8.0, which for our purposes, indicates that the value was actually nil, or otherwise of pre-bomb age, as expected.

Integration of Tritium Data

The δ^2H versus tritium bivariate plot of Figure 50 indicates a pattern showing most of the anomalies reported previously in the hydrochemical and isotope data above.

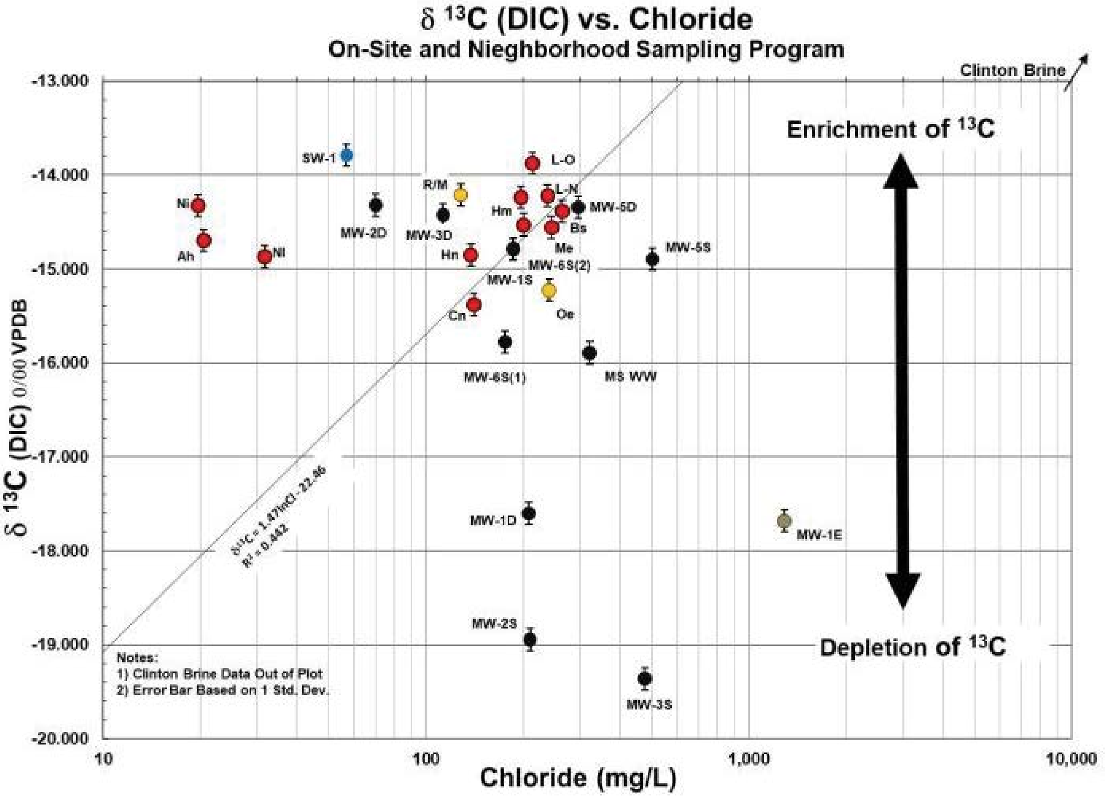


Figure 46: δ ^{13}C (DIC) vs. Chloride.

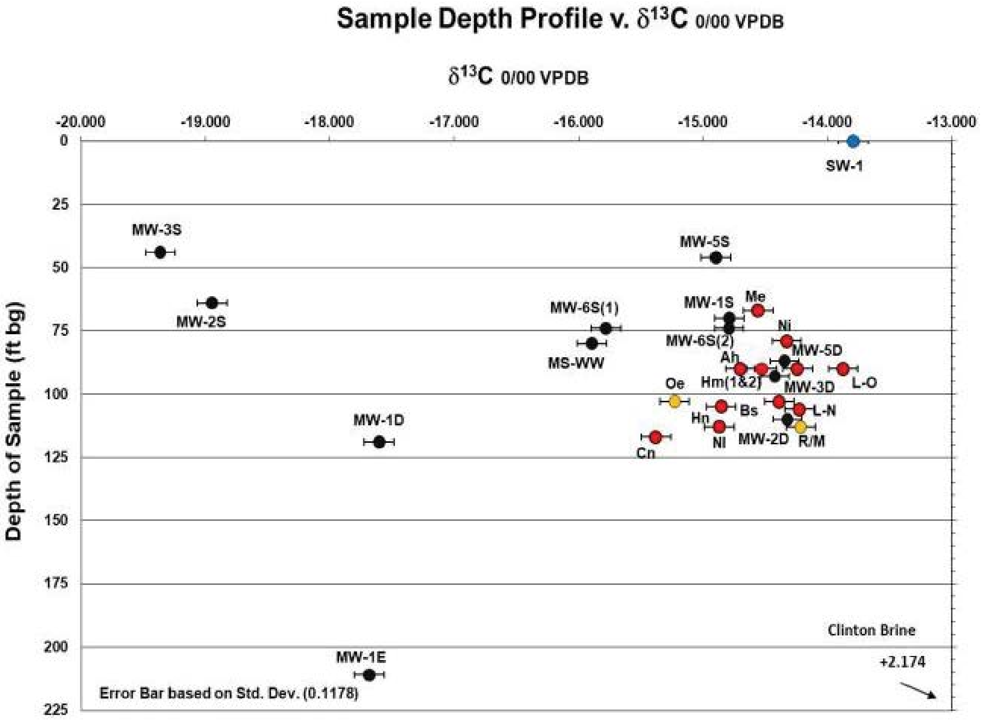


Figure 47: Sample Depth Profile v. δ ^{13}C 0/00 VPDB.

The blue line shows a trend where increasing enrichment of δ^2H, tritium also increases indicating that with increasing age of the samples, came enrichment of δ^2H.

The previous sample anomalies include sites MW-2S and MW-3S, which plot below the trend lines in both Figures 50 and 51. Site Hm produced samples from an original, deep well and a new water well. The former well obtained groundwater from deeper zones than the other neighborhood wells (Figure 54). This indicates that the age of the groundwater is older than that of surrounding, shallow water wells.

This logic also shows that groundwater from MW-3S, by proximity next to the Hm marker plots, is also of an older age, but MW-2S would be younger than MW-3S. However, both MW-2S and MW-3S obtain water from zones well above those of MW-2D and MW-3D. Groundwater from the latter exhibit tritium values that indicate younger ages than those of

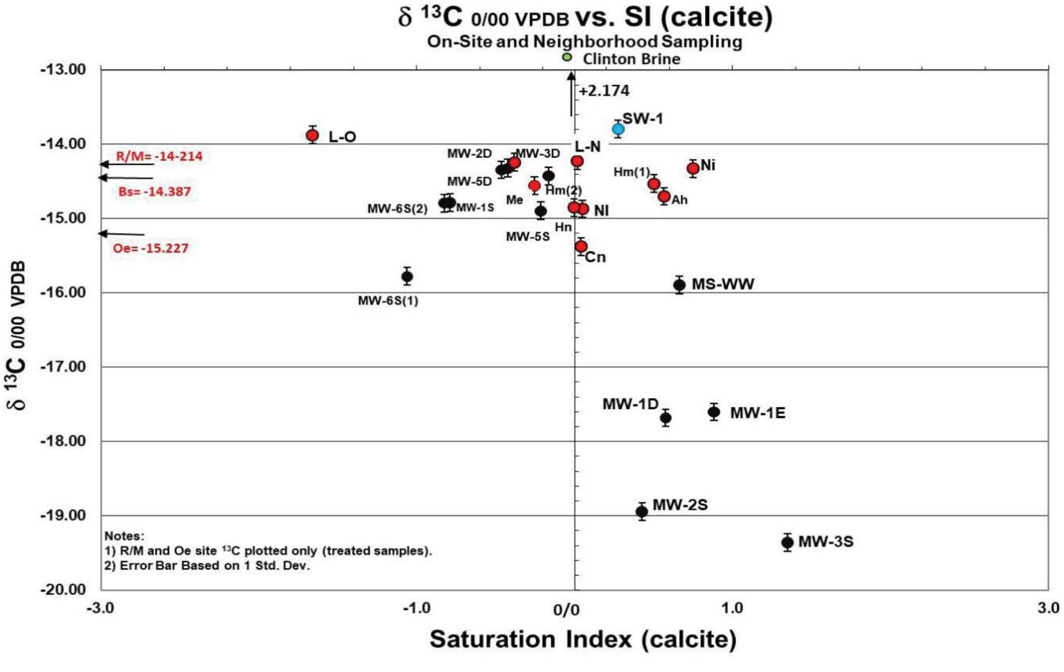


Figure 48: δ ^{13}C 0/00 VPDB vs. SI (calcite).

the upper zones of MW-2S and MW-3S (Figures 52 and 54).

Another anomalous sampling site, MW-5S, also plots well above the trend lines of δ^2H (Figure 50) and $\delta^{18}O$ (Figure 51). Also, the Hm samples plot well away from the main grouping and below the trend lines (for reference). The core of the main grouping is not segregated in both plots of Figure 50 and 51.

The $\delta^{13}C$ versus tritium bivariate plot of Figure 52 also indicates a pattern that includes sampling sites previously considered anomalous, including groundwater samples from sites MW-2S and MW-3S that exhibit substantial depletion of $\delta^{13}C$, with MW-1D less so. Also note that both samples from Hm and MW-5S indicate older relative tritium ages, as well as MW-1E, as expected. The central grouping shows some segregation with neighborhood samples (red symbols) in the core grouping surrounded by $\delta^{13}C$ markers from on-site sample sites, with some exceptions.

Tritium Implications

The tritium present in the groundwater originated in atmospheric precipitation that fell to earth as either rain or snow, and infiltrated into and through the soil zone and, at this site, through the underlying glacial till, ultimately reaching the water table to recharge the local groundwater (Figure 53). As indicated previously, recharge that fell as precipitation in the late 1950s and 1960s was contaminated by tritium created as a result of the thermonuclear testing in the U.S. and elsewhere. Tritium values ranging in the thousands were measured during this period in the area but over time the values have declined as a result of radioactive decay and atmospheric flushing to a current value of approximately 10 to 15 tritium units (TUs) in the northern Ohio area [55].

The values sampled range from a low of near zero for the Clinton brine sample to a high of 12.6 TU in sample MW-1E, the latter from a sandstone well below the Black Hand Sandstone (Figure 54). The history and pathways of the recharge water as it passed from the surface through the glacial till to the water table some 50 to 60 feet below affect all the isotopes to one extent or another, but as is apparent from the isotope groupings (Figures 40, 42, and 46, and the separations within 44 and 45) and with the clear trends in the tritium makers and recurring anomalies (Figures 50 and 51), the environmental conditions within the glacial till and within the fractures of the sandstone impact the hydrochemistry as well as the stable and radioactive isotopes under both undersaturated and saturated conditions.

The tritium distribution is illustrated in the cross-section of Figure 53 (see Figure 1 for the geographical location of the section). Also note that Figure 53 can be enlarged by mouse-over and clicking on the figure.

It shows the chloride and tritium analyses (and indicated recharge years of precipitation) for groundwater samples

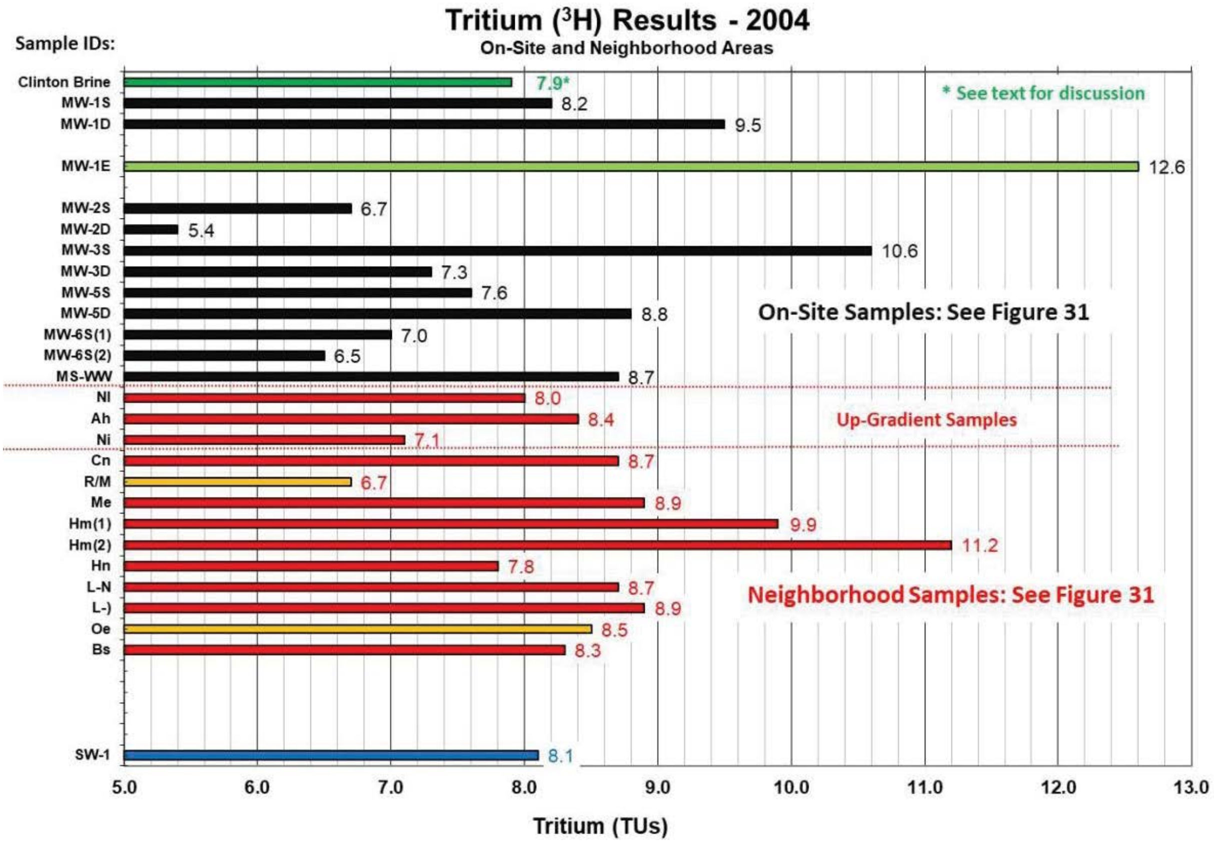


Figure 49: Tritium (^3H) Results – 2004.

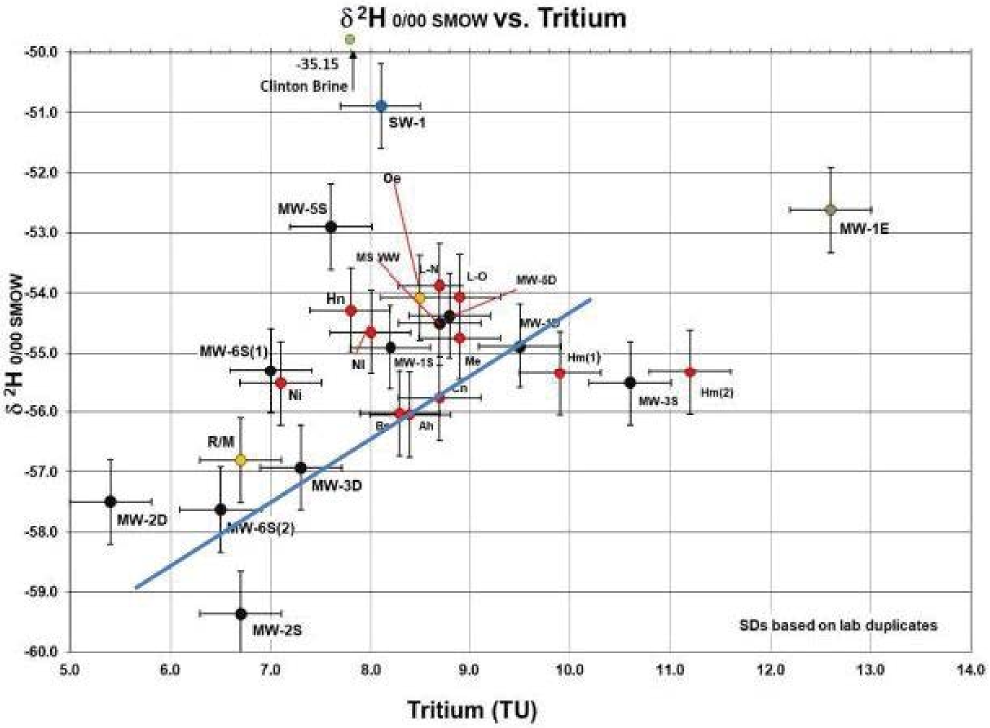


Figure 50: δ ^{2}H 0/00 SMOW vs. Tritium.

obtained from screened zones of the monitoring wells sampled on-site (especially MW-5S (on left of figure) and from two water wells of the neighborhood group sampled and the various wells drilled, i.e., the Cn sites (discussed earlier in this paper) and the Hm sites (including the samples taken from both wells, i.e., Hm(1) and Hm(2), shown on the right.

Mixing of water within the fractures and in the porous media is a significant factor in determining the relative age of the water sampled, especially through pumping neighborhood water wells and on-site monitoring wells. Fractures would typically contain groundwater that was more recently recharged than the groundwater present in the porous media of the sandstone

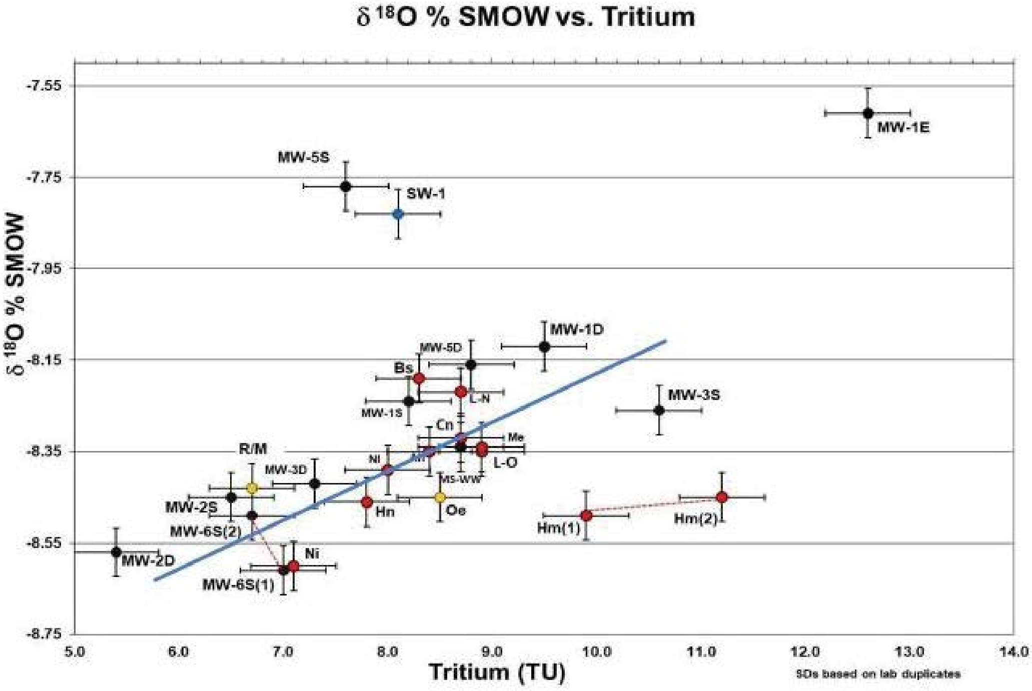


Figure 51: δ ^{18}O % SMOW vs. Tritium.

aquifer. This newer water would carry tritium in concentrations ranging from 7 to 9 TU. The water in the porous media is likely to be very old, perhaps decades preceding atmospheric thermonuclear testing, containing tritium at less than 1 TU.

Single-year tritium contributions from the recharge area were estimated in terms of timing in Figure 54, (see blue curve). A mixing scenario was developed where up to 15 years of recharge are mixed in groundwater (see red curve). This was accomplished by averaging the annual recharge over these 15 years (average of thee values given for the 5 year intervals). Thus, the input function for tritium in precipitation is a smoothed function. Tritium and age of groundwater includes radioactive decay for surficial sources of water, at the surface, but does not include decay calculations during mixing in the subsurface of the recharge environment because of a lack of input functions required for such calculations. However, the results produced for the model shown in Figure 54, are used to determine the time elapsed since recharge at the surface and when the water reached the water table and migrated to the screened intervals of sampling

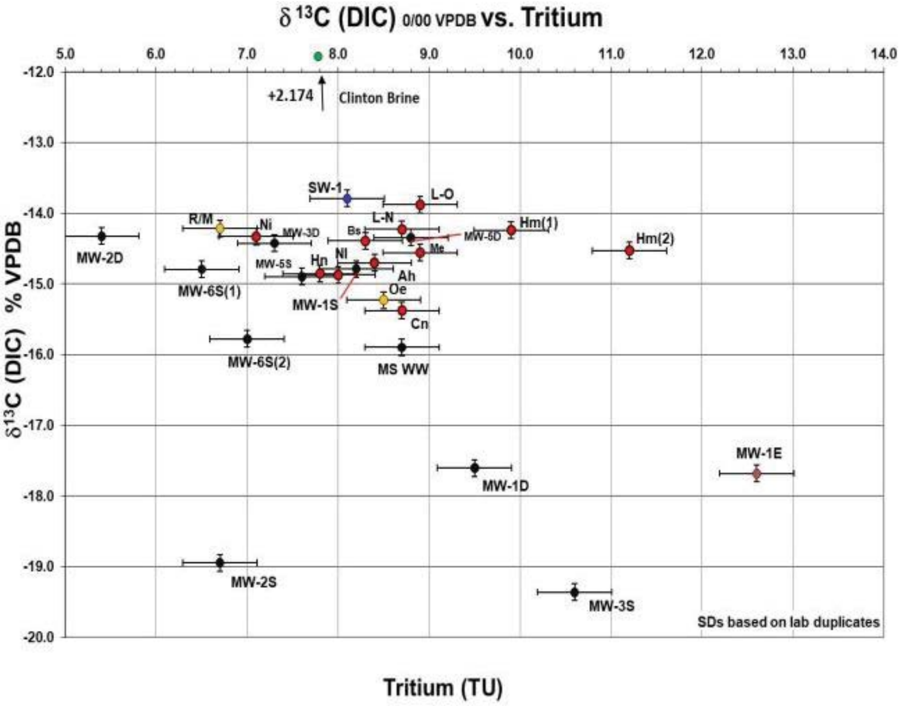


Figure 52: δ ^{13}C (DIC) 0/00 VPDB vs. Tritium.

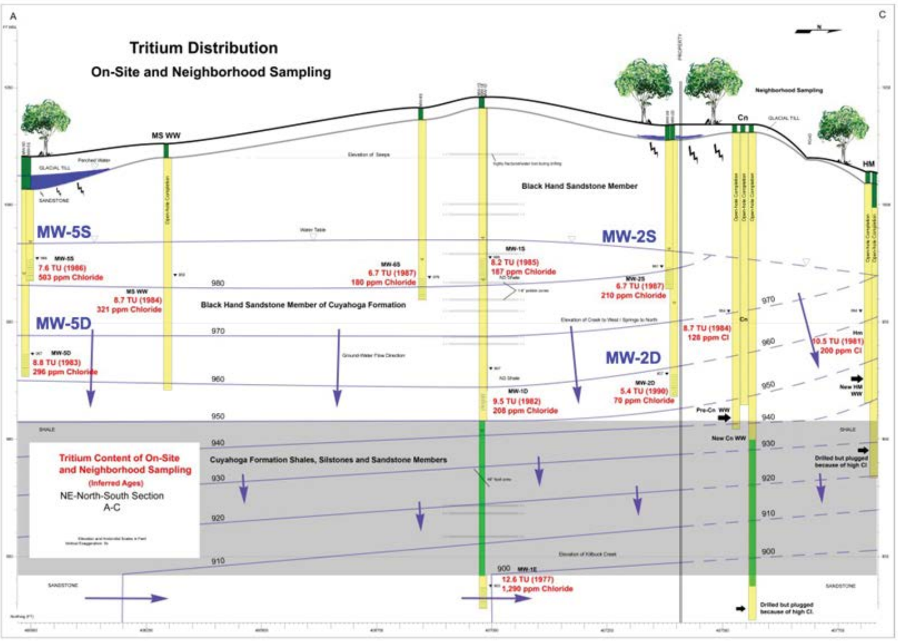


Figure 53: Tritium Distribution Along Cross Section (click to enlarge).

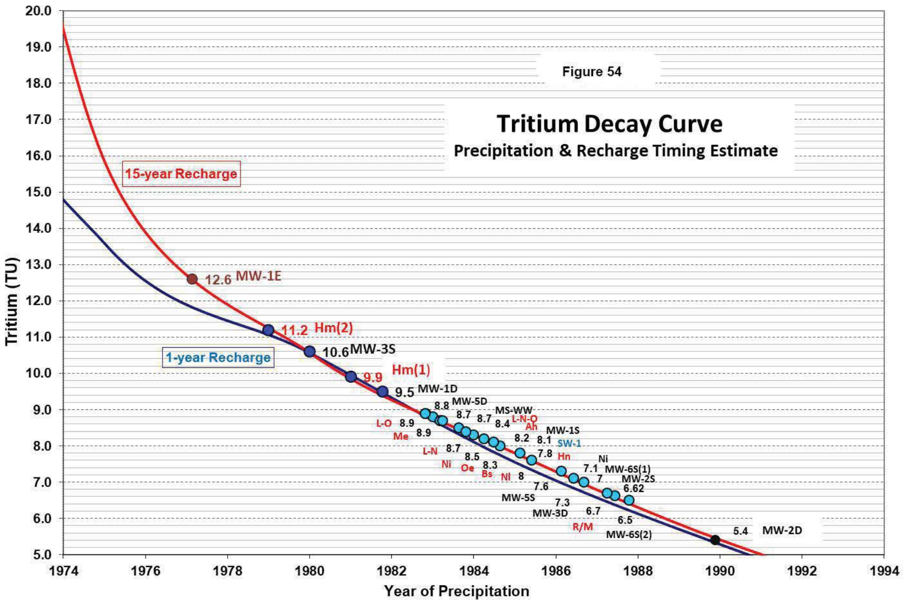


Figure 54: Tritium Decay Curve.

at the on-site monitoring wells and from the open-hole intervals of the neighborhood water wells (some of which are shown in Figure 53). The former represent specific vertical intervals (10 feet of screen, plus gravel pack), whereas the subject water wells produce water from large vertical intervals of holes in sandstone (that consists of water from porous media and from fractures or joints).

Most groundwater samples exhibited tritium values that had decayed to indicate an elapsed time at which water began its recharge and migration of some 15 to 20 years before 2004, which was well before the initiation of spreading brine on-site, but not of brine-spreading on county roads and adjacent state highways as of 2004, but continues today. However, a better modeling of the tritium data will require the full data set of input functions for tritium in precipitation (rather than the 5-year intervals). Seasonal variations in recharge that might affect the overall input curve are assumed herein to be constant (i.e. recharge conditions are assumed to have been similar over that period). The calculations used to construct the curves in Figure 54 are presented in Appendix E [145].

Clark et al. [36] reported that the curves in Figure 54 show that the decline in tritium to less than 5 TU in 2004 is inconsistent with other regional historical records (see Figure 55: Ottawa, Canada; Washington, D.C.; Albuquerque, NM; Cape Hatteras, N.C.), which shows the 2004 tritium concentrations in the 10 to 20 TU range. These plot-inserts

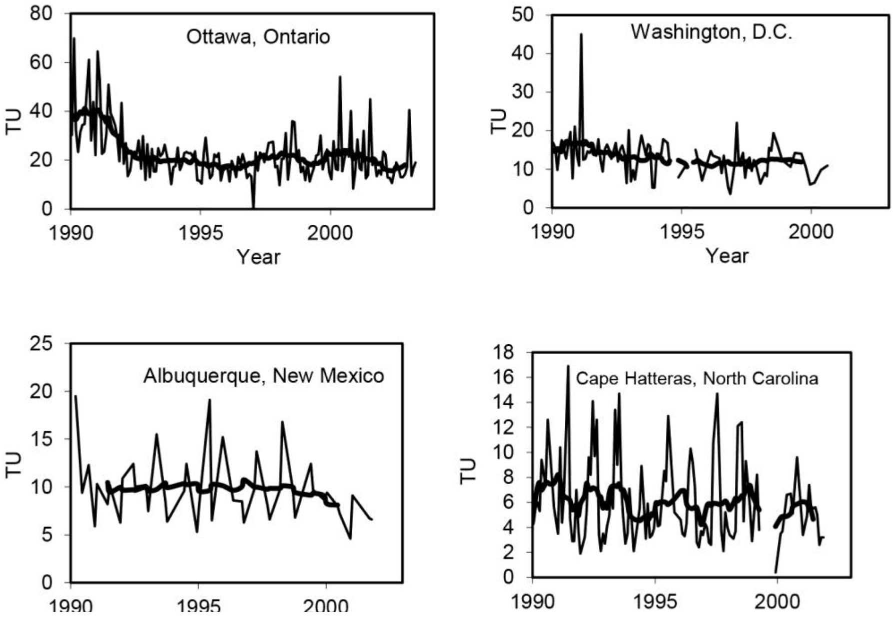


Figure 55: Regional Historical Tritium Records (Precipitation).

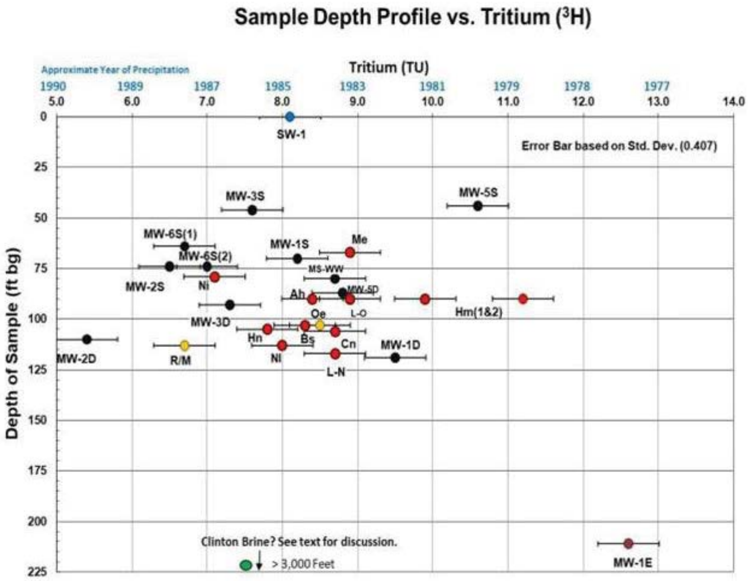


Figure 56: Sample Depth Profile vs. Tritium (^{3}H).

show variations of individual samples and a solid average line. Note that coastal stations like Cape Hatteras have lower tritium than northern and continental stations. Large (high) thunderstorms and gamma rays also produce small amounts of tritium in the atmosphere as well as nuclear testing, although the latter produced far more than the former over the short term now mostly decayed [127]. Should there be additional atmospheric nuclear testing, the decayed tritium curve would again rise and new standard curves would have to be established to reflect the new testing.

Note that the approximate year of initial groundwater recharge has been listed across the top of Figure 56 and the depth of the samples taken during 2004. In any event, the isotopic data support our conclusions that the elevated chloride concentrations evident in the groundwater

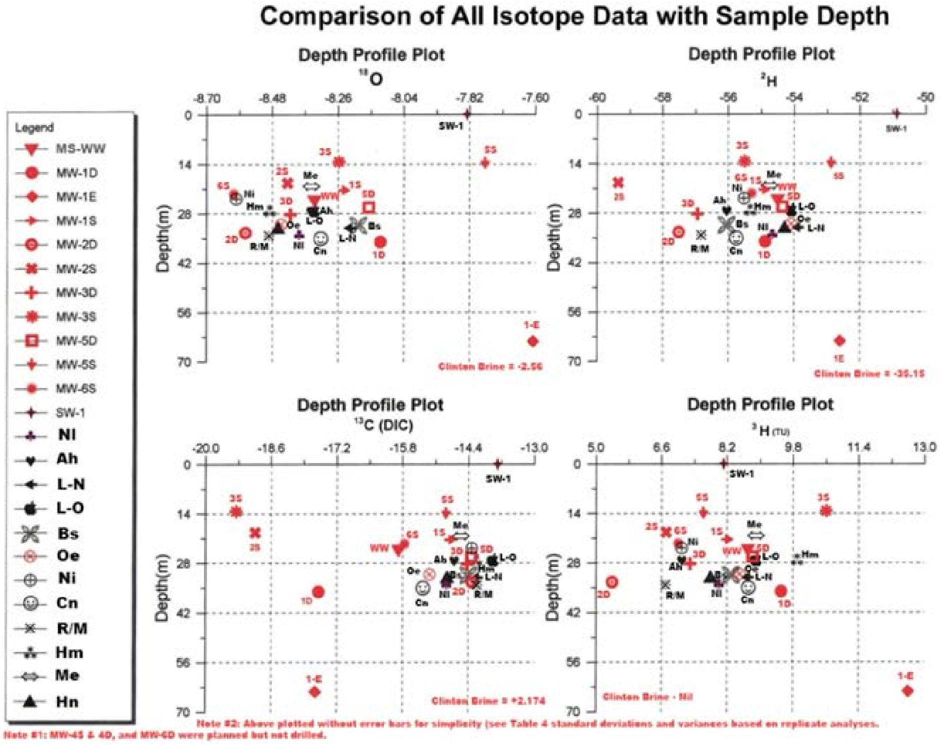


Figure 57: Comparison of All Isotope Data with Sample Depth. (click to enlarge).

from some of the neighborhood water wells were unrelated to the brine-spreading on the subject property. The separation of the on-site and neighborhood well data is not only indicated in the hydrochemistry discussed previously but it is also confirmed by the isotope data. These data are summarized in the Figure 57 below.

The groupings are evident even at the plot scale shown in Figure 57, as are the outliers of anomalous samples that have experienced very different histories in their flow from recharge at the surface to the sampling locations in the subsurface at the various monitoring wells and neighborhood water wells.

Conclusions

Based on the documents and data reviewed, the bivariate plots of hydrochemical and isotopic data assessed, and on the various analyses, scenarios, local circumstances considered at the time of sampling and to date, we have concluded that the elevated chloride concentrations reported in the groundwater samples of a few water wells in the neighborhood located to the north and adjacent to the subject property were likely the result of: 1) the poor management of home water-softening systems, 2) the subsurface conditions that make the groundwater below especially vulnerable to rapid recharge from waste releases at the surface, 3) the disposal of excessive brines from water-softening regeneration and septic tank effluent via septic-tank leachfields constructed in thin soil zone overlying a thin zone of glacial till, 4) the use of halite for deicing the county roads and state highways adjacent to the neighborhood water wells, and 5) the geological and hydrogeological conditions in the area where shallow, heavily fractured and jointed sandstone receives vertical recharge to the local groundwater from above, which encourages rapid migration of chloride-impacted recharge to the water table below [66,82,83,84,87,128].

Hydrochemical and stable and radioactive isotope assessments confirm that on-site and neighborhood groundwater data generally show separate clustering indicating that little mixing has occurred prior to 2004 between the industrial site and neighborhood locations. The brine spread on the industrial property did not appear to have migrated into the groundwater supplies of neighborhood residents over the five or six years prior to 2004, but the local chloride concentrations have been attributed to neighborhood activities and to the adjacent driveway and roadway activities of de-icing using halite brine during the winter months.

Other than separate area clustering, there are also anomalies that became apparent in the hydrochemistry and isotope assessments during our investigations. Sites MW-5S, MW-2S and 2D, and MW-3S exhibited abnormal characteristics both in hydrochemistry and in isotope content relative to the surrounding sites. We concluded that in some instances the groundwater had been altered while migrating through the glacial till during recharge and while moving through the unsaturated zone downward through fractures as well as porous media, prior to reaching the water table.

There were multiple sources in the immediate area that likely contributed by varying degrees in creating the elevated chloride concentrations reported in the samples from the on-site monitoring wells and from the neighborhood water wells over the years prior to 2004. Relatively small volumes of brine were applied to the traffic areas within the subject pipe yard by spreading from 1998 through 2000 to control dust during the summers.

The source of chloride was limited because the new water wells were installed in the neighborhood as of 2004. The previous source of chloride (from both halite introduced by surface disposal and/or soft-water systems) into the subsurface), and from road de-icing using halite and magnesium additives, were flushed through the soil to the groundwater system and intercepted by pumping of water wells through both fractures and porous media within the sandstone aquifer in the immediate area.

The historic hydrochemical records available for the old, replaced, shallow wells were unreliable to evaluate the conditions present in the year 2000 because they lack certain critical analyses that would have provided useful information on hydrochemical associations. The most appropriate approach in determining the source of the elevated chloride concentrations involves testing for nitrogen compounds, chloride, and bromide, among other constituents. For example, bromide is not normally analyzed in water-resource assessments. Using the laboratory results from our 2004 sampling of the groundwater not only in the neighborhood areas but also in the pipe-yard area, we assessed the conditions present at the time of our sampling, i.e., June, 2004 and then made certain projections back to the likely activities and associated conditions present in the year 2000.

Geologic and hydrogeologic conditions in and around the on-site property have allowed the brine applied to the company pipe yard driveways during 1998 to 2000 to migrate into and be retained by the shallow, sponge-like glacial till just below the surface at the company property. Groundwater then becomes perched in the glacial till as it thickens toward the southern part of the company facility, and drains off to the east and west and through preferential pathways in the sandstone below, with some discharge via minor surface seeps and springs. The main groundwater reservoir is located below.

Groundwater flows in the very fine grained porous media of the Black Hand Sandstone, albeit at a slower rate than in fractures and joints, and ultimately discharges in the vicinity of a large creek from surface seeps and springs along the contact of the sandstone with a thick shale observed in outcrops bordering the creek about a mile to the north and to the east of the subject property. Based on an analysis of the groundwater flow, on current groundwater levels measured in on-site monitoring wells, neighborhood wells, and on the basis of the available hydrochemical data, groundwater primarily migrates naturally downward, and not likely in the direction of the neighbor wells.

The initial complainant (Pre-Cn), after reporting high chloride levels in the shallow well to the ODNR, had a replacement well drilled nearby to a depth of 220 feet below surface. Tests indicated "brackish" groundwater was present at this location in the subsurface. A third well was drilled to a depth of 130 feet and samples tested as potable water. Our investigations have encountered relatively high chloride concentrations and other associated constituents in high concentrations in a deep monitoring well to a depth of 218 feet below grade, located near the middle of the company property (i.e., MW-1E). The screened interval is located near the base of a thick shale unit that is underlain by another fine-grained sandstone older than the Black Hand Sandstone.

There is no evidence to indicate that the highly-mineralized groundwater present in the older sandstone below the thick shale has had any impact on the hydrochemistry of the residents' water supply in the surrounding area, with the exception of the Pre-Cn "brackish" deep test well, and the deep Hm well, that encountered a similar zone of unusually mineralized groundwater.

It was apparent that each neighborhood resident's location represents a microcosm of site-specific activities by the particular resident and of site-specific subsurface conditions that likely contributed to the release of dissolved chloride to the subsurface and to the groundwater resources below in sufficient quantities to create the increased chloride levels of the drinking water in the neighborhood. Proximity to county road and state highway also added chloride to the environment via winter ice-control activities conducted by county and state operations, which also likely contributed to the elevation of chloride concentrations in neighborhood wells.

Groundwater hydrochemistry supports the view that flow is not toward the north on the basis that the sample from MW-2D exhibited low chloride, whereas the Cn well, only a few tens of feet away, exhibited higher chloride, and, that MW-3D exhibits low chloride concentrations although the L-N well, only a few more tens of feet away, also exhibits higher chloride concentrations, indicating a local source(s) of chloride.

Groundwater hydrochemistry in the area of the neighborhood wells is characterized by excess sodium and chloride, and anomalous concentrations of calcium, strontium, and other constituents. These are likely related to recharge from a combination of sources, such as septic tank effluent from softening system regeneration, local deicing fluids along county road, and other sources, such as in the area of the Hm site.

Isotope data show that the groundwater from the sampling sites was recharged via fractures and porous media by recent, local precipitation that mixed with older precipitation contained in the groundwater within the porous media of the sandstone. Separate recharge clusters of data from neighborhood wells along the county road and data from on-site monitoring wells, indicated little, if any, lateral flow carrying chloride from the company facility northward toward neighborhood wells.

Isotope data of δ^{18}O, δ^{3}H, and δ^{13}C in groundwater indicate that groundwater sampled in the area experienced a common series of recharge events from precipitation over the years, although for five sites were anomalous in some ways (Table 5, and especially Figures 36, 53, 54, 56, and 57). The value for MW-1E appears to have originated from a separate era, whereas the groundwater samples from MW-1S-D, MW-2S-D, MW-5S-D and SW-1 appear to have experienced significant evaporation in their recharge history. This is consistent with both having been near or at the surface for an appreciable time period, the former being associated with a perched water table only a few feet below the surface and the latter being part of a shallow groundwater flow segment discharging in the western creek.

The ^{13}C content of MW-2S and MW-3S in the groundwater are not likely to have evolved from low values to less depleted values while migrating toward the Cn well or L-N well, respectively. Therefore, both the shallow groundwater sampled in MW-2S and 3S nor the deep groundwater sampled in MW-2D and 3D is likely flowing in the direction of the resident wells along county road. Further, tritium values reinforce the recharge history range and role of fractures and porous media making up of the aquifer and associated groundwater flow. Of particular note is that the groundwater samples from MW-2S and 3S exhibit tritium activities representative of an earlier period than that of the underlying samples from MW-2D and to some extent from 3D (Figure 53). The field records were examined for accuracy and we found no issues regarding sample handling in the field or in the laboratory.

We have concluded that fracture-enhanced permeability in the Black Hand Sandstone caused neighborhood domestic supply wells to intercept this groundwater routing it to the deeper zones 2D and 3D. Groundwater data from the shallow zones sampled (2S and 3S) indicated the groundwater samples were from porous media. This is further confirmed by the chloride and nitrite-nitrate content of the groundwater from each zone, i.e., the shallow zone (2S and 3S) shows elevated chloride, nitrite-nitrate, conductance (and TDS), for example, but younger tritium ages (6.7 and 10.6 TUs). The deep zone (2D and 3D) shows much lower levels of chloride, nitrite-nitrate, conductance (and TDS), yet older tritium ages (5.4 and 7.3 TUs).

This indicates that: 1) the shallow zone produced water from porous media of long residence time, and the water from the deep zone exhibited lower residence time resulting from the groundwater in fractures affected by neighborhood pumping drawing younger water than that migrating in the porous media of the fine-grained sandstone in the shallow zone, and 2) the shallow zone of MW-3S (as indicated in Figure 28) has received elevated chloride (and calcium, magnesium, etc.) from oil-field brine and halite brine from both on-site (from dust-suppression activities) and highway sources (from de-icing activities). MW-2S has received water from surface and near-surface chloride, nitrite-nitrate, etc., sources from leachfield effluents of higher residence time than the groundwater from MW-2D with no indication of input from oil-field brine [129,130].

Isotope data from one of the Hm samples indicate that it is of relatively older precipitation when compared to other samples nearby along county road (Figure 55). The previous Hm well was drilled in the 1950s and was drilled and completed some distance into the shale unit below the subject sandstone, which likely produced groundwater of anomalous hydrochemistry and associated isotope results. Preferential flow at the contact between the sandstone and shale unit could have accumulated ground-water composed of unusual hydrochemistry and mixed isotopic values.

The stable isotope data indicate that elevated chloride concentrations do not originate from other than among the properties along county road. This is supported by considering that δ^2H, δ^{13}C, and δ^{18}O plotted vs. chloride for the MW-2S and 3S sites plot away from the main cluster, although their deeper zones (2D and 3D) are not involved in a significant migration of chloride and other constituents. This shows that the groundwater is flowing via fractures or by porous media in a direction other than to the north, as indicated by the cross-sections (Figures 6 and 8). This also illustrates that groundwater flow is generally toward the east in response to the regional dip of the rocks in the area. The dip of the underlying shale unit ensures that most of the flow is in this direction.

The complexity of the apparent hydrochemistry and isotope relations within the groupings, trends, and anomalies also demonstrate that the data could reveal upon further study additional information about the environmental conditions within the subsurface of the subject site and surrounding areas [165]. Our data were limited in temporal scope and resolution. Additional work on similar sites using a combination of field data, hydrochemistry, and various isotopes could contribute significantly to the understanding of groundwater flow using conservative tracers (such as elevated dissolved chloride, etc.) from glacial tills in the recharge zone and developing methods to characterize the nature of the environment in the unsaturated zone of aeration above the water table and within a sandstone of essentially two flow regimes, porous media and facture zones.

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Appendices

Appendix A – **Core Hole & Monitoring Well Geological Logs and Groundwater Elevation Records**

Appendix B – **Core Hole Geophysical Log**

Appendix B-1 – **Oil & Gas Well Geophysical Log**

Appendix C – **Laboratory Data**

Appendix D – **Statistics**

Appendix E – **Tritium Decay Calculations**

Appendix F – **Petrographic Analyses**