Origins of Black Sediments in Wells

As with other aspects of the subsurface gas invasion in Bainbridge Township, DMRM and E&A reached dissimilar opinions concerning (1) causes for the occurrence of black sediments (a.k.a. black goo) in some water wells (Figure 3-111) in the investigation area, and (2) degradation of groundwater quality due to the presence of methane gas in the surface aquifers (pages 1-13 and 1-14). Before describing the additional field data and analyses used to address these disputed issues, we address some the field sampling protocols and laboratory techniques that were used to formulate these opinions.

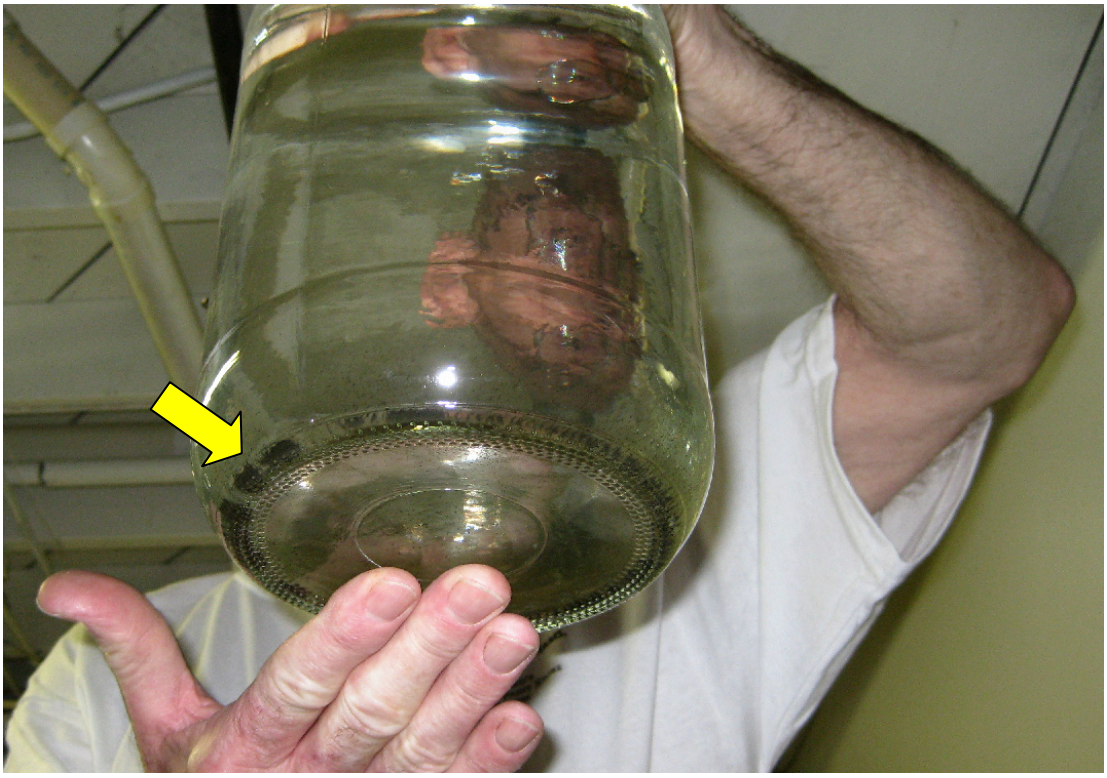


Figure 3-111. Black sediment particles from Szabo well (17904 English Dr).

Sampling and Analysis Concerns

Although not included as a slide in the May 2009 PowerPoint presentation, E&A made statements to the effect that the "black goo" reported in several residential release subsequent to the overpressurization of the English #1 well was the direct result of: (1) small particles of the Ohio Shale (asperities) that became entrained in the fugitive gas and transported upward into the overlying drinking water aquifers, and/or (2) the sustained intrusion of methane-enhanced reducing conditions altered the geochemistry of the aquifer, which led to the (a) mobilization of toxic metals, and (b) stimulation of microbial biofilms that primarily composed the black goo. E&A also stated that the solid particles recovered from samples of well waters in the impacted area contained dangerously high levels of toxic metals.

These findings, however, are to be based on a poorly designed sampling plan and an analytical methodology not suitable for quantitative assessment of the metals in the black particles. Of the three sediment samples collected by E&A and stated as having toxic levels of heavy metals caused by the presence of methane gas, one was obtained from the Rutana well (7982

Scotland Dr), which never had a wellhead LEL reading greater than 2 percent (Appendix F). Another sediment sample collected by E&A and stated as having toxic levels of heavy metals caused by the presence of methane gas was obtained from the Stover well (17860 English Dr), which never had a wellhead LEL reading above zero (Appendix F). It is illogical to use sediment samples from residential wells that never had substantial, let alone very low, wellhead LEL readings as evidence that the sustained intrusion of methane gas enhanced reducing conditions in the aquifers, which (a) altered the aquifer geochemistry causing mobilization of toxic metals from the aquifer materials, and (b) created the black goo from stimulation of biofilms by the intrusion of gas, as stated by E&A in the meeting on May 13, 2009. The negligible wellhead LEL readings in the Rutana well and the complete lack of detection of methane gas in the Stover well calls into question the conclusions E&A drew from the sediment samples collected in these wells. (The September 2, 2009, borehole videotape of the Stover well shows a hole in the surface casing at a depth of 15 feet into which soil, sediment, and organic matter can enter the well. See Appendix C).

Figure 3-112. Black sediment in water filters at Stover well (17860 English Dr).

In addition to this concern, simply collecting solids that accumulate in a container without also measuring the total mass of particulates per unit volume of liquid cannot provide an accurate assessment of the concentrations of toxic metals; nor does it address the rate and magnitude of exposure of residents based on their volumetric consumption of their own well water. Phillip von Hohenheim, a 16th century Swiss physician, is commonly cited for coining the adage "the dose makes the poison." For example, highly toxic uranium is present in ocean water at a concentration of approximately 3 micrograms per liter (µg/L) (Murphy and Shock, 1999). Even though uranium is present in ocean water, the concentration is sufficiently low that it is not a threat to ocean life or to the consumption of saltwater fish, shellfish, and plants. Another example of von Hohenheim's adage is the chemical Warfarin, a rat poison, was patented in 1948 by the Wisconsin Alumni Research Foundation. A strong anticoagulant, it caused rats and

other small animals to bleed to death. Several years later, in much lower dosages, Warfarin was found to be an effective blood thinner for humans. Under the pharmaceutical name Coumadin, Warfarin has helped recovering heart attack patients for the past five decades. von Hohenheim's adage is widely known among physicians, toxicologists, and writers of the three *CSI* series on television. Regrettably, it was not used to qualify the sensational statements made about the potential toxicity of the black particulates in some well waters. Without sufficient information on the concentration of metals in the well waters and the volume of well water consumed in their normal diet, it is not possible to even guess at the potential health risk to residents in the investigation area from the black sediments

A third concern is the use of an Environmental Scanning Electron Microscope – Energy Dispersive x-ray Spectroscopy (ESEM-EDS or EDS), the technique used by E&A to characterize the black sediments. ESEM-EDS detects elements, not compounds. For example, using ESEM-EDS it is not possible to determine if the copper, lead, mercury, etc. are bound in solid particles with oxygen, silica, or other anions in solid forms that could pass completely through the human digestive system without dissolving and presenting a health risk. ESEM-EDS also cannot be used to quantitatively assess the metal content in the sediments. It can only make a rough assessment of the presence or absence of a given element. The EDS unit contracted by E&A at the Environmental Scanning Electron Microscopy facility at the University of Akron generally can detect the presence of elements in solid phases at concentrations as low as 2 mg/g of solid. EDS is also more sensitive to the detection of elements with relatively high atomic masses (i.e., heavy metals). As such, EDS would likely detect lead (Pb, atomic mass 207) more readily than silicon (Si, atomic mass 28), if these elements were present in equal concentrations in a solid phase. As a result, EDS can provide an inaccurate indication of the concentration of heavy metals present in a solid phase because it is very sensitive in detecting elements with relatively high atomic masses, whereas its sensitivity is much lower when detecting elements with relatively low atomic masses.

The E&A field report does not state where the water samples and samples of black powder were taken. As a result, it is not possible to determine if the samples were collected directly from the wellhead or if the samples were taken after the well water passed through water pipes, water softeners, and/or water heaters. A simpler more likely explanation for the source of some of the heavy metals indicated by the EDS analysis would be that they come from the well materials or plumbing systems in the homes where the samples were collected. For example, copper water pipes are common in older homes like those in the investigation area, silver is sometimes used in solder, older well casing materials contain a lot of iron, and zirconium is used in the pumps. All of these heavy metals were detected by the EDS analysis. Because of the inadequate sampling plan, identification of the source of these heavy metals remains unresolved. At best, the EDS data used by E&A should only be considered an indication of the presence of heavy metals with the true source of the heavy metals not known.

Additional Data Requests and Analyses

The expert panel recognized that the disputed conclusions reached by E&A and DMRM were based on too few field data and that a better sampling plan was needed. The expert panel requested that DMRM collect additional sediment samples from water wells using a sampling plan developed by DMRM and reviewed by the expert panel (DMRM Expert Panel Sampling Plan, 2009). The goal of the additional sediment and water samples was to characterize the mineralogy of the sediment particles, determine the aqueous chemistry of the well waters, and

characterize microorganisms associated with the well waters. DMRM personnel, under the direction of Dr. Senko, carried out the approved field sampling plan. Instead of EDS analysis, x-ray diffraction (XRD) analysis was used on the sediment particles under the direction of Dr. Senko, who also oversaw the bacterial analyses. These analyses were performed in the laboratories in the Department of Geology and Environmental Science (DGES) at the University of Akron.

Are Black Sediments Asperities from the Ohio Shale?

In Chapter 8 – Faults, of John Suppe's 1985 textbook on structural geology, he presents the classic work by F.P. Bowden (Bowden and Tabor, 1950) on friction between sliding metal surfaces. According to Bowden's theory, surface roughness causes even the best-prepared surfaces to contact one another only at protuberances, or asperities (Figure 3-116). As the two solids slide past one another the material composing the asperities yields, which increases the microscopic area of contact along the interface. The asperities continue to be ground down until the microscopic contact area multiplied by the normal yield stress equals the applied normal force. Although Bowden's experiments were performed with blocks of metal, Suppe (1985) states that "Bowden's concept of flattening of asperities and increasing microscopic contact area with increasing normal stress appears to be correct for rocks, although at low temperatures [similar to those at the depths above the Clinton sandstone in Bainbridge], the asperities undergo both fracture and plastic flow," (i.e., the asperities are not ground down, they chip off and smear).

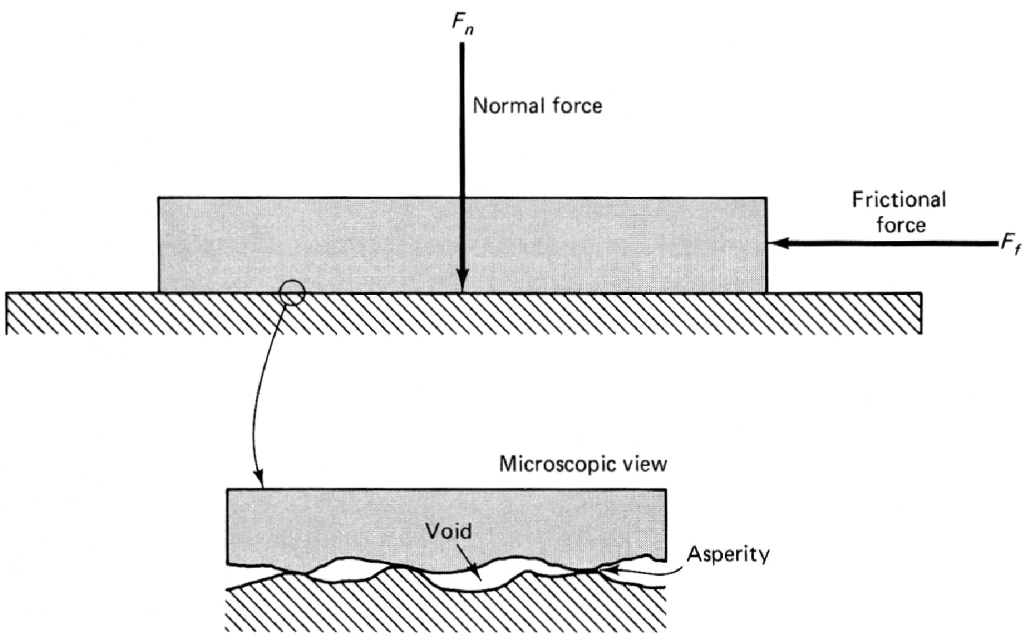


Figure 3-113. Schematic diagram of friction experiment (Suppe, 1985).

The application of these concepts by E&A to the creation of the black particles found in water wells in the investigation area following the English #1 well incident requires there to be differential movement (faulting) along the fracture interfaces in the Ohio Shale purportedly created during overpressurization of the surface-production casing annulus. In other words, it would be the sliding of shale against shale during fault movement that would create the black sediments from ground down asperities (ignoring the limitations posed by low temperatures).

Faulting is not uncommon in northeast Ohio. Dozens of small earthquakes have occurred along deep basement faults in the area of Ashtabula, Ohio (Hansen and others, 2001). A check of earthquakes in Ohio recorded by the OhioSeis network of seismographs with a Richter scale magnitude of 2.0 or greater shows that no earthquakes occurred during November or December 2007 (Appendix I), when the production casing annulus in the English #1 well was overpressured. During this period, residents in the impacted area did not report dishes rattling, liquids sloshing in containers, upper floors of houses and buildings shaking, or furniture sliding, which are telltale observations of an earthquake. The Modified Mercalli scale of earthquake intensity is based on these common observations. Without evidence of an earthquake causing differential movement, it is difficult to fathom creation of asperities in the Ohio Shale, particularly at the low temperatures within 5,000 feet of the land surface.

The postulated trip taken by asperities derived from the Ohio Shale would require them to be transported by free gas (think bubbles) more than two thousand feet upward in the Ohio and Bedford shales along vertical joints and their intersections with bedding planes, through pinpoint-size intergranular pores in the Berea Sandstone, along more vertical joints and bedding planes in the Cuyahoga Shale, and finally into uncased wellbores in residential wells in the investigation area. Figure 3-117 is a force vector diagram similar to Figure 3-79. It shows that asperities with densities of 3.5 to 8.0 gm/cm^3 cannot be entrained in natural gas with a density of approximately 0.65 gm/cm^3 unless the gas is migrating at abnormally high velocities (think sand blasting).

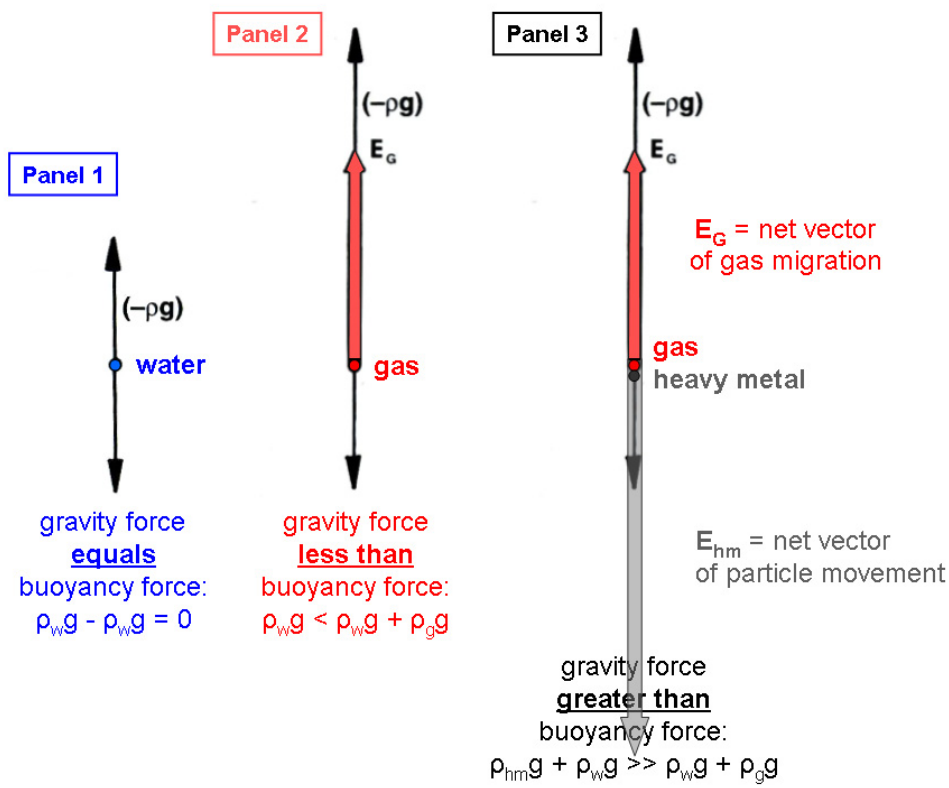


Figure 3-114. Force vectors showing gravity forces acting on a particle of heavy metal greatly exceed buoyancy forces acting on gas.

The 2500-foot, tortuous trip becomes even less probable, when it is recognized that gas, unlike water, has no surface tension. The small amount of tension on a water surface enables it to

support small, light particles like water bugs and grains of pepper. In contrast, salt grains sink below the water surface because they are too dense and exceed the ability of the surface tension to support them. The disparity between the density of heavy metal particles and the surface tension of a gas bubble is infinitely greater because gas has no surface tension. As a result, free gas moving at typical groundwater velocities in thick sequences of fractured shale and through intergranular pores in sandstone is not likely to entrain particles of heavy metal asperities, even if there was undetected faulting in the Ohio Shale to produce them during overpressurization of the English #1 well.

Are Dissolved Methane Concentrations Similar to Other Methane Invasion Studies?

The pressure and concentration of methane gas are central to understanding the migration pathways of fugitive gas from the English #1 well to water wells in the area of investigation. Methane (CH_4) can migrate as free gas (think bubbles) within intergranular pores and along bedding planes and joints in rock. Methane also can occur as dissolved gas in water, just like carbon dioxide (CO_2) is dissolved in a bottle of soda. When the bottle is opened the pressure is decreased and the CO_2 exsolves from solution and becomes free gas. Methane does not dissolve easily into water at the temperatures and pressures at Earth's surface, where its solubility is between 28 to 30 milligrams of methane in a liter of water (mg/L) (U.S. Geological Survey, 2006). The solubility of methane in water increases with increasing pressure (e.g., with increasing depth below the water table). The methane gas emanating from the English #1 well is predominantly free gas, although minor concentrations of dissolved methane are likely to be present in groundwater in the investigation area.

As a gas, methane is colorless, tasteless, and odorless. Other components of natural gas can cause color, taste, and odor (think sulfur, but don't evoke its smell). In confined spaces, methane can cause oxygen-deficient atmospheres and flammable and explosive environments, as evidenced by the house explosion at 17975 English Drive. In addition to being a potential problem at oil/gas wells, methane gas can also be a problem in coal mines. Several studies at oil/gas wells and in coal mining areas were examined to compare values of dissolved methane at these locales to those at the Bainbridge investigation area. In February and March 2008, DMRM collected water samples at 73 residences in the investigation area. Many of these samples were taken at outside and basement wells. Other samples had to be taken at places that were less ideal for keeping methane gas in solution such as at pressure tanks, water heaters, faucets, sinks, and bathtubs. The samples were analyzed at the Ohio EPA-certified DMRM lab in Cambridge, Ohio. Of the 73 samples analyzed, samples from 30 wells contained dissolved methane in concentrations below the detection limit of 0.01 mg/L. The maximum concentration was 1.04 mg/L. Well depths were known from drillers' logs and borehole videotapes for 42 of the 73 water samples. Table 3-10 lists the dissolved methane concentration in these 42 samples, the depth of the sampled water well, and the uncased geologic units in well.

The median dissolved methane concentration of the 42 well-water samples listed in Table 3-10 is 0.25 mg/L. These data were used to create Figure 3-117, which shows the median dissolved methane concentrations for five categories of uncased geologic units in the wells. The horizontal bars are arranged from the shallowest geologic unit (Sharon Sandstone) to the deeper geologic units in which the water wells are completed. Figure 3-117 shows a definitive decreasing trend in dissolved methane concentrations in the shallower geologic units.

Table 3-7. Dissolved Methane Concentrations in 42 Water Wells

Owner	Address	Date	Dissolved Methane (mg/L)	Well Depth (ft)	Uncased Geologic Units
Cloninger	7780 Bainbridge	03/05/08	**0.57**	> 127	C, B
Police station	8353 Bainbridge	02/22/08	**0.69**	280	C, B
Adams	17820 English	02/19/08	**0.25**	300	C, B, Bd
Stover	17860 English	02/21/08	**< 0.01**	95	S, C
Burns	17888 English	03/03/08	**0.73**	> 141	C
McGuire	17925 English	02/21/08	**0.18**	85	C
Donaldson	17938 English	02/27/08	**0.21**	43	S
Gaub	17939 English	02/27/08	**0.34**	43	S
Cooper	17954 English	02/19/08	**0.09**	36	S, C
Weber	17955 English	02/19/08	**0.82**	41	S
Payne	17975 English	02/27/08	**0.24**	40	S, C
Jordan	17990 English	02/27/08	**0.25**	160	C, B
Czernicki	17995 English	02/19/08	**0.47**	> 75	C
Brinkman	17898 Kenston	02/20/08	**< 0.01**	61	C
Zarlingo	18032 Kenston	03/05/08	**< 0.01**	140	C
Fisher	18050 Kenston	03/05/08	**< 0.01**	120	C
Kenen	18055 Kenston	03/05/08	**< 0.01**	90	S
Halfacre	17885 Kingswood	03/05/08	**< 0.01**	85	C
Johnson	17926 Kingswood	02/20/08	**0.59**	183	C, B
Prochazka	17927 Kinsgwood	02/20/08	**0.51**	210	S, C, B, Bd
Vincenti	17936 Kingswood	02/21/08	**0.01**	210	C, B
Petherbridge	17937 Kingswood	02/27/08	**0.03**	102	C, B
Brady	17949 Kingswood	03/05/08	**< 0.01**	72	C
Bryant	17956 Kingswood	02/20/08	**0.01**	96	C
Savel	17961 Kingswood	02/20/08	**< 0.01**	90	S
Calo	17969 Kingswood	02/21/08	**0.18**	175	S, C, B
Wozniak	17970 Kingswood	02/20/08	**0.02**	121	C
DeGaetano	17971 Kingswood	02/20/08	**0.47**	245	C, B, Bd
Ohara	7846 Scotland	02/19/08	**0.60**	134	C, B
Mesmer	7868 Scotland	02/19/08	**0.49**	66	C
Hupp	7881 Scotland	02/20/08	**< 0.01**	41	S
Vowell	7882 Scotland	02/19/08	**0.05**	44	C
Buddenhagen	7897 Scotland	02/27/08	**0.78**	180	C, B
Mechler	7898 Scotland	02/19/08	**< 0.01**	33	C
Mowery	7915 Scotland	02/19/08	**0.69**	75	C
Hupp	7916 Scotland	02/20/08	**< 0.01**	46	C
Selby	7927 Scotland	02/21/08	**0.73**	72	C
Mason	7941 Scotland	02/21/08	**1.04**	138	C, B
Komocki	7950 Scotland	03/03/08	**0.72**	194	B
Sanborn	7955 Scotland	02/19/08	**0.92**	123	C
Kukoleck	7969 Scotland	02/19/08	**0.98**	140	C
Bastifell	7981 Scotland	02/27/08	**0.94**	150	C, B

Detection limit for dissolved methane = 0.01 mg/L

B = Berea Ss Bd = Bedford Sh C = Cuyahoga Sh S = Sharon Ss

Samples from east of the saddle in the top of Berea Sandstone surface

Samples with concentrations < 0.01 mg/L

This observation combined with the data from the wellhead LEL measurements, which are a relative measure of free gas methane concentrations, demonstrate that both dissolved gas and free gas concentrations dissipate upward as methane slowly disperses to the atmosphere (see the Cooper, Donaldson, Gaub, Hupp, Rutana, Weber, and Wozniak LEL graphs in Appendix F).

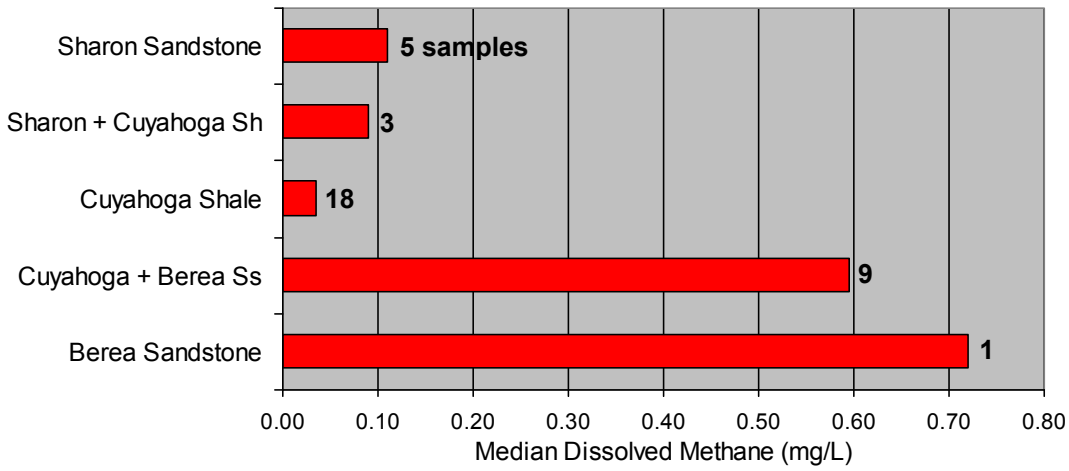


Figure 3-115. Median dissolved methane values of water well samples.

The data in Table 3-7 are the basis for Figure 3-116, which shows the pattern of dissolved methane concentrations relative to the depths of the water wells from which the samples were taken. Statistically, there are no trends present in the overall set of data. However, insight is gained when the data are labeled with the uncased geologic units in the well.

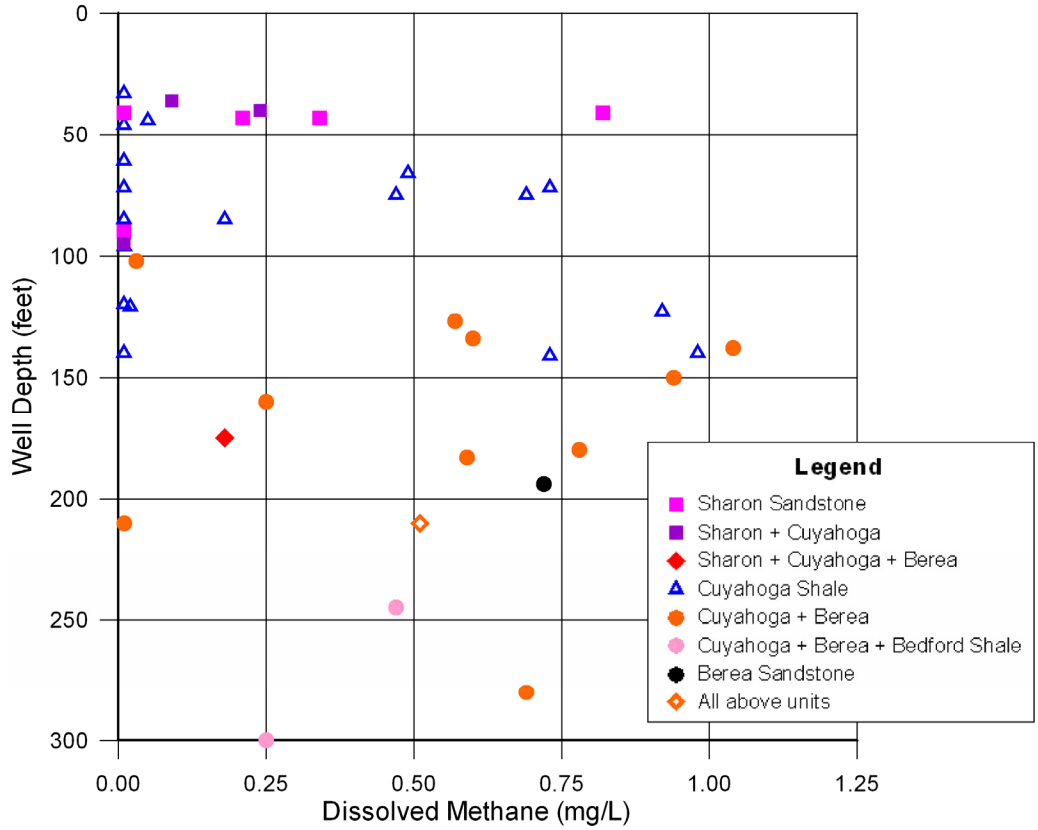


Figure 3-116. Dissolved methane concentrations versus depth of wells.

For example, several samples from wells open solely to the Cuyahoga Shale (open blue triangles) have dissolved methane concentrations at or below the detection limit of 0.01 mg/L. Table 3-7 shows that these six samples (yellow background) are from wells east of the saddle in the top of the Berea Sandstone surface (Figure 3-80), where little free methane gas reached (Figures 3-85 and 3-86). Figure 3-116 and Table 3-7 also show that dissolved methane concentrations less than 0.01 mg/L also occur in five wells (light green background) completed in the Sharon Sandstone or in the upper part of the Cuyahoga Shale at low elevations at the bottom of the hill descending from Bainbridge Road, where the wells are shallow and groundwater mixes with infiltrating rainwater and snowmelt.

Table 3-8 compares dissolved methane concentrations from four other studies of methane impacts in residential water wells to values measured in the Bainbridge Township investigation area. While examining the table, keep in mind that all of the gas invasion studies except the one in Bainbridge Township, Ohio, involved long-term, continuous sources of methane gas, whereas the overpressurization of the English #1 gas well in Bainbridge Township was a one-time, pulse source of methane gas.

Table 3-8. Studies of Dissolved Methane in Residential Water Wells

Situation (reference)	**Location**	**Wells Sampled**	**Min. Methane Conc.** (mg/L)	**Max. Methane Conc.** (mg/L)
Overpressurized gas well (this report)	Bainbridge Township, Geauga Cty, Ohio	73	**non-detect**	**1.04**
Oil & gas production along fault zone (ATSDR, 2009)	North Royalton, Cuyahoga Cty, Ohio	9	**1**	**11**
Underground natural gas storage (Breen and others, 2007)	Tioga Junction, Tioga Cty, Pennsylvania	91	**non-detect**	**92**
Coal beds, coal mining (USGS, 2006)	43 counties, West Virginia	170	**non-detect**	**68.5**
Oil & gas production (Van Stempvoort and others, 2005)	Lloydminster, Alberta, Canada	14	**1**	**78**

Table 3-8 shows that the dissolved methane concentrations at the two sites in Ohio are well below methane saturation of 28 to 30 mg/L at atmospheric pressure and land temperatures. The highest dissolved methane concentrations at the other three sites are 2 to 3 times greater than the range of saturation concentrations and contain 60 to 90 times more dissolved methane than the highest dissolved methane concentration measured in the Bainbridge Township investigation area. This means that in the three studies outside Ohio, methane gas readily exsolved from solution and became free gas because of the very high concentrations of dissolved methane in solution and the long-term source of methane. This is not the case at the Bainbridge Township site.

In the large-scale study in West Virginia based on samples from 170 residential wells in 47 counties (USGS, 2006), dissolved methane was detected in 131 wells. Methane was present in concentrations greater than 28 mg/L (saturation) in 13 wells. Another 13 wells had concentrations ranging from 11.9 to 24.3 mg/L and 32 wells had concentrations ranging from

1.00 to 10.0 mg/L. Thus, 58 out of 170 residential wells tested in the West Virginia study had dissolved methane concentrations greater than the highest dissolved methane concentration measured in the Bainbridge Township investigation area (Table 3-8). The advice given by the U.S. Geological Survey (2006) to residential well owners in West Virginia is based on the U.S. Department of the Interior, Office of Surface Mining guidance (Eltschlager and others, 2001) and is nearly identical to that given by DMRM in its 2008 report.

Kelley and others (1985) also studied the effects of methane gas from a gas well blow out in North Madison, Ohio, on local groundwater chemistry but did not report concentrations of dissolved methane in the seven residential wells that were sampled.

Are Black Sediments the Result of Microbial Sulfate Reduction?

At the May 13, 2009, meeting, E&A attributed the black goo to microbial sulfate reduction coupled with the oxidation of methane and the resultant formation of sulfide-containing mineral phases. A literature review revealed that this reaction has been reported at other methane gas intrusion sites (Van Stempvoort and others, 2005; Kelley and others, 1985). To address this concept, multiple lines of evidence were explored including:

1. *sediment samples from five wells were analyzed by x-ray diffraction (XRD),*
2. *the presence of sulfate-reducing bacteria in selected wells was evaluated,*
3. *geochemical conditions in the aquifer units were assessed as to whether or not they favored sulfate reduction,*
4. *constituent concentrations in water samples from wells inside the investigation area were compared to concentrations in samples from wells outside the investigation area that were unaffected by the subsurface release of methane gas at the English #1 well.*

Analysis of each of these lines of evidence is presented below.

1. Does XRD analysis identify the presence of sulfide minerals?

X-ray diffraction (XRD) analysis was conducted on the sediments recovered from five water samples collected during a field sampling event in September 2009. The sediment particles were separated from the well water by centrifugation and mounted for XRD analysis in the x-ray facility at DGES. The XRD spectra of well-water sediment samples were compared to the spectra from samples of the Berea Sandstone and the Cuyahoga Shale, the two geologic formations that produce most of the well water in the investigation area. XRD can be used to identify different crystalline mineral phases present in a sample, but it does not necessarily provide quantitative analysis of the elemental composition of the materials.

Results of the XRD analyses are shown in Figure 3-117. As expected, the samples of these two rock types, Berea Sandstone and Cuyahoga Shale, are dominated by quartz (roughly SiO_2) and aluminosilicate clays (Figure 3-117). Sediment particles recovered from the Davidson (17826 Kingswood Dr), Johnson (17926 Kingswood Dr), and (new) Payne (17975 English Dr) wells exhibited XRD spectra closely matching that of the Cuyahoga Shale, with major contributions of quartz and aluminosilicates to the XRD spectra (Figure 3-117). Wells at these properties draw water from the Cuyahoga Shale (Attachments 5 and 6, Appendices C and D), indicating that the sediments found in the well-water samples from these wells are very likely derived from the

rock material exposed in the uncased portion of the wells. The XRD spectrum of sediment particles from the water sample collected at the (new) Payne well indicate the presence of goethite, an iron hydroxide that resembles rust. This material is likely derived from the 35-year old well casing, based on the borehole video that showed orange-brown iron hydroxide coatings on the 29-foot long steel casing in the well (Appendix C).

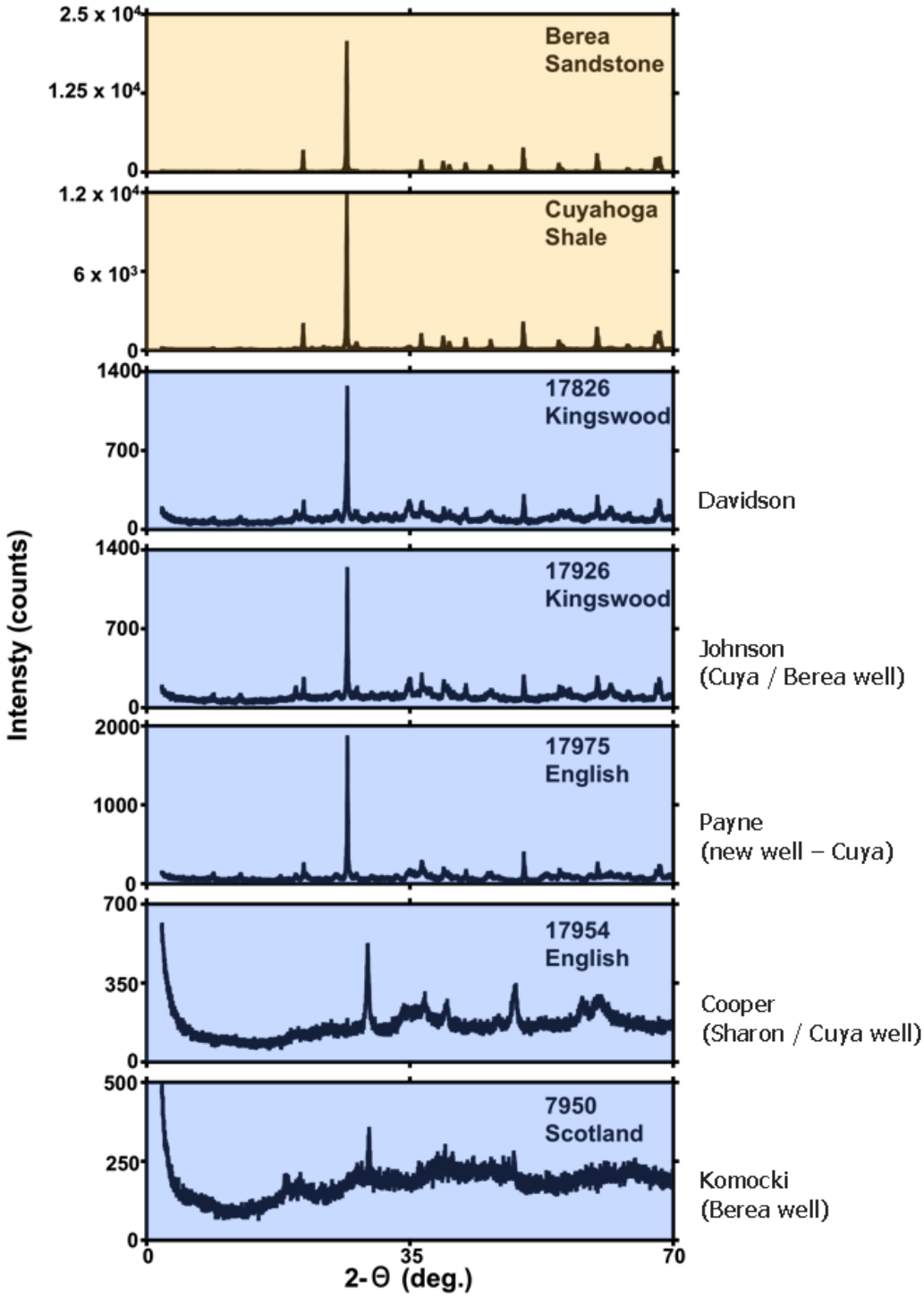


Figure 3-117. X-ray diffraction spectra of Berea Sandstone, Cuyahoga Shale, and particles collected from water wells and plumbing systems near the English #1 well.

The XRD spectrum of sediment particles from the Cooper well (17954 English Dr) were relatively amorphous (think glass with no regular arrangement of atoms like salt crystals), as indicated by the relatively low peak intensities, making identification of the crystalline mineral phases difficult (Figure 3-117). The XRD spectra suggest the presence of iron-sulfide and iron-hydroxide minerals (e.g., pyrite or lepidocrosite). These minerals are black. This well draws water from the Sharon Sandstone, which commonly has prominent rust-colored iron staining from iron-oxide cement (Figure 3-1). The XRD spectrum of sediment particles from the Komocki well (7950 Scotland Dr) were similarly amorphous, but indicated the presence of calcium and/or magnesium carbonate minerals, such as calcite and aragonite (Figure 3-117). These precipitates are white. This sample was collected down flow of the water heater. Calcium and magnesium carbonates are not unexpected in the Berea Sandstone, nor were they seen in the XRD spectra from the Berea Sandstone sample, which is the aquifer from which this well draws water (Attachment 5 and Appendices C and D). According to Jagucki and Darner (2001), groundwater in the Berea Sandstone is dominated by carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) in solution and has a pH ranging from 7.2 to 8.7. In the Komocki well, it is likely that heating the well water, which is rich in dissolved carbonate / bicarbonate, led to the degassing of carbon dioxide (CO_2) from the water, which further increased pH and precipitated calcium and/or magnesium carbonate ($CaCO_3$ or $Ca,MgCO_3$) (Hem, 1985).

To summarize, the sediments from well-water samples analyzed by XRD can be divided into two broad groups: (i) particles derived from the aquifer material itself (17826 and 17926 Kingswood Dr and 17975 English Dr), and (ii) particles produced by geochemical reactions leading to precipitation minerals after the water was removed from the well and affected by plumbing and water heaters (17954 English Dr and 7950 Scotland Dr). Wells drawing water from the Cuyahoga Shale contained sediments that closely matched that of the Cuyahoga Shale sample. Wells drawing water from sandstone aquifers, either the Berea Sandstone (7950 Scotland Dr) or the Sharon Sandstone (17954 English Dr), contained mineral precipitates that likely are derived from geochemical reactions occurring after the water is heated following its removal from the aquifer or occurring within the pore spaces of the aquifer material. Based on these findings, only one sediment sample (Cooper well at 17954 English Dr) contained iron-sulfide minerals, which could be formed by sulfate reduction, although it is worth noting that the Cooper well never had an LEL value greater than 1.2 percent, which only occurred once.

2. Are sulfate-reducing bacteria present?

Microorganisms are ubiquitous in the environment. As examples, one gram of topsoil may contain 100 million to 3 billion bacteria and microorganisms may grow at depths reaching several kilometers below the land surface (Madigan and others, 1997). Most microbial species in the environment are benign (i.e., very few cause disease). Many bacteria mediate desirable processes including breakdown of environmental contaminants, production of nutrients for higher organisms (i.e., plants and animals), and processing of foods for human consumption (think beer, wine, cheese, yogurt, vinegar, etc.).

To grow, microorganisms exploit energy from a variety of chemical reactions. For instance *aerobic* organisms (including humans) use energy for growth from the reaction of organic carbon (depicted generically as CH_2O) with oxygen:

Aerobic respiration: $CH_2O + O_2 \rightarrow CO_2 + H_2O$

Similarly, some microorganisms can use the reaction of organic carbon with other chemical species for growth when there is no oxygen available (e.g., below ground and in some groundwaters). These are considered *anaerobic* respiration and can be thought of as "breathing" manganese (III/IV), iron (III), or sulfate:

Manganese respiration: $CH_2O + 2\ MnO_2 + 4\ H^+ \rightarrow CO_2 + 2\ Mn^{2+} + 3\ H_2O$
Iron respiration: $CH_2O + 4\ Fe(OH)_3 + 8\ H^+ \rightarrow CO_2 + 4\ Fe^{2+} + 11\ H_2O$
Sulfate respiration: $CH_2O + 0.5\ SO_4^{2-} + 0.5\ H^+ \rightarrow CO_2 + 0.5\ HS^- + H_2O$

Other microorganisms can gain energy from the conversion of some types of organic carbon to methane and carbon dioxide, a process referred to as methanogenesis, which can be broadly depicted as:

Methanogenesis: $CH_2O \rightarrow 0.5\ CH_4 + 0.5\ CO_2$

Whether these reactions occur is partially dependent on how much energy an organism can obtain from these reactions. Aerobic respiration yields the most energy, followed by manganese respiration, iron respiration, and finally sulfate respiration. Evidence of these microbially mediated reactions can be observed through their products. For example, abundant dissolved Mn^{2+} is evidence of manganese respiration. Abundant dissolved Fe^{2+} is evidence of iron respiration, and abundant sulfide (HS^-) is evidence of sulfate respiration. If a substrate (i.e., oxygen, nitrate, manganese, iron, sulfate) is available that yields more energy, then that substrate generally will be utilized by a community of microorganisms before a substrate that yields less energy is utilized. For instance, if abundant oxygen and sulfate are available in an aquifer, microbial communities will tend to use oxygen for respiration despite the presence of abundant sulfate. Only after all the oxygen is depleted, will sulfate reduction occur.

In September 2009, groundwater samples were collected for enumeration of sulfate-reducing bacteria from wells at 7859 Scotland Drive (McGee), 8353 Bainbridge Road (Police station), and 17860 English Drive (Stover). The well-water samples were collected in sterile bottles that were subsequently sealed with butyl rubber stoppers so the samples contained no headspace (no air). Sulfate-reducing bacteria in the samples were enumerated by the most-probable number (MPN) technique (Colwell, 1979), using medium described by Tanner (1989). Sample tubes were scored based on the appearance of a black iron-sulfide precipitate after three weeks of incubation.

Sulfate-reducing bacteria were detected in groundwaters from the wells at 7859 Scotland Drive (McGee) and 8353 Bainbridge Road (Police station), but were not detected in groundwater from the well at 17860 English Drive (Stover) (Table 3-9). The wells at 7859 Scotland Drive and 8353 Bainbridge Road draw water from the Cuyahoga Shale and Berea Sandstone, whereas the well at 17860 English Drive draws water only from the Cuyahoga Shale. Neither sulfide nor sulfate reducing-bacteria were detected in groundwater from the well at 17860 English Drive indicating that little or no sulfate-reducing bacterial activity is present in the aquifer surrounding this well. Sulfate reducing bacterial communities that can use shale-derived organic carbon can be found in sandstones above or below the shale, but not necessarily in the shale itself (Krumholz and others, 1997). This may explain the lack of evidence for sulfate-reducing bacterial activities in the well at 17860 English Drive, which draws water from the Cuyahoga Shale but not the Berea Sandstone.

Table 3-9. Enumeration of Sulfate-Reducing Bacteria in Wells and and Plumbing Systems

Address (Owner)	Sulfate Reducing Bacteria MPN (cells/ml)
7859 Scotland Drive (McGee)	220
8353 Bainbridge Road (Police station)	15
17860 English Drive (Stover)	<0.06 (no SRB detected)

MPN = most probable number

The lack of sulfate-reducing bacteria in water from 17860 English Drive confirm the conclusion from the XRD analysis for this well, which was that the sediments in the well are not a product of sulfate reduction. Instead, these sediments likely originated in the soil zone (the Stover well has a hole in the casing) or as sediments that now compose the aquifer. The presence of sulfate-reducing bacteria in the other two wells indicates that microbial-mediated sulfate reduction could be occurring in the McGee well and in the Police station well.

3. Do geochemical conditions favor sulfate reduction to sulfide?

If sulfate reduction is occurring in the groundwaters in the investigation area, reaction products should be manifest in well-water samples and detected as total sulfide including dissolved (hydrogen sulfide gas) and particulate forms (iron sulfide precipitates), as shown below. After the English #1 well incident, additional organic carbon to support anaerobic respiration may have invaded the aquifers in the form of methane (CH_4). Methane may support sulfate respiration as shown below:

$$CH_4 + SO_4^{2-} + H^+ \rightarrow CO_2 + HS^- + 2H_2O$$

The reaction shown above yields insufficient energy to support microbial life. The overall process is catalyzed by two types of microorganisms that work in partnership whereby one type of organism catalyzes the oxidation of methane to CO_2 and H_2 (shown below), and a sulfate-reducing bacterial partner consumes H_2 (shown below), making the overall process energetically favorable for both organisms involved in the partnership (Knittel and Boetius, 2009).

$$CH_4 + 2\ H_2O \rightarrow CO_2 + 4\ H_2$$
$$4\ H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4\ H_2O$$

In the literature, microbiological evidence of methane oxidation with sulfate reduction is largely described in marine systems (Knittel and Boetius, 2009). Isotopic evidence indicates this process may occur in terrestrial aquifer systems (Grossman and others, 2002; Van Stempvoort and others, 2005), but the microbiology of the process in aquifer systems is poorly understood.

The total sulfide concentrations measured in well-water samples collected in the investigation area are shown in Table 3-10. Total sulfide was measured in the water well samples recovered during the September 2009 sampling event from wells at 17990 English Drive (Jordan), 17860 English Drive (Stover, both inside and outside taps), 17888 English Drive (Burns), 17971 Kingswood Drive (de Gaetano), 17926 Kingswood Drive (Johnson), and 7950 Scotland Drive (Komocki). Unfiltered samples for sulfide analysis were preserved in the field with 10 percent zinc acetate and subsequently analyzed using methylene blue assay (Cline, 1969).

Table 3-10. Sulfide Concentrations in Residential Well Waters in the Investigation Area

Address (Owner)	Total Sulfide (mg/L)
17990 English Drive (Jordan)	0.90
17860 English Drive, inside tap (Stover)	≤ 0.01
17860 English Drive, outside tap (Stover)	≤ 0.01
17954 English Drive (Cooper)	0.18
17888 English Drive (Burns)	0.27
17971 Kingswood Drive (de Gaetano)	1.44
17926 Kingswood Drive (Johnson)	0.45
7950 Scotland Drive (Komocki)	0.45

Sulfide was detected in all the samples except at 17860 English Drive (Stover), where the sulfide concentration was below the detection limit of the instrument (0.10 mg/l). The wells sampled draw water from the Cuyahoga Shale and Berea Sandstone. The Cuyahoga Shale contains microscopic pyrite (FeS_2), which contains reduced sulfur (Figure 3-4). A previous survey of groundwater samples taken from wells completed in the Cuyahoga Shale and Berea Sandstone reported the detection of sulfide at concentrations as high as 0.4 mg/l (Jagucki and Darner, 2001). Although the presence of sulfide in groundwater from these aquifers is not unusual, higher sulfide concentrations (as high as 1.44 mg/L) were detected in some well waters in the investigation area. The production of sulfide in subsurface aquifers is attributable to the activities of sulfate-reducing bacteria.

Sulfate-reduction in the investigation area was evaluated using additional chemical data. A classification system developed by the U.S. Geological Survey (McMahon and Chapelle, 2008) was used to evaluate the type of microbial respiration or "redox" reactions occurring in water samples from the investigation area using information presented on pages 3-134 and 3-135. The classification system requires sample concentrations be known for dissolved oxygen, nitrate, manganese, iron, sulfate, and sulfide. The classification system categorizes waters using the chemical criteria shown in Table 3-11 and described in detail by Jurgens and others (2009).

An attempt was made to use this classification system to evaluate redox conditions in waters produced by nine wells in the investigation area that tap both the Cuyahoga Shale and the Berea Sandstone. All nine wells produced methane at some point in the investigation (personal communication, Scott Kell, DMRM). Unfortunately, the available data were not ideal for use with this classification scheme. For a given well, constituent concentrations from samples collected on different dates and analyzed by different labs had to be combined to get the required input data. Some analytical results were available only as totals, which include both dissolved and suspended components, instead of as dissolved constituent concentration that the scheme is designed to use. Finally, no dissolved oxygen concentrations were measured at the nine wells. The resulting redox classifications are shown in Table 3-12. Three of the nine wells lacked nitrate data and could not be classified. However, sulfate reduction was identified as a redox process occurring (i.e., sulfate was the substrate used for microbial respiration) in three of the nine wells (Prochazka at 17927 Kingswood, de Gaetano at 17971 Kingswood, and Police station at 8353 Bainbridge Rd).

Table 3-11. Criteria and Threshold Concentrations for Identifying Redox Processes in Groundwater

Redox Process	Criteria for inferring process from water-quality data					
	Dissolved oxygen (mg/L)	**Nitrate, as Nitrogen** (mg/L)	**Manganese** (mg/L)	**Iron** (mg/L)	**Sulfate** (mg/L)	**Iron / sulfide** (mass ratio)
O_2	≥ 0.5	- - -	< 0.05	< 0.1	- - -	
Suboxic	< 0.5	< 0.5	< 0.05	< 0.1	- - -	
NO_3	< 0.5	≥ 0.5	< 0.05	< 0.1	- - -	
Mn(IV)	< 0.5	< 0.5	≥ 0.05	< 0.1	- - -	
Fe(III)/SO_4	< 0.5	< 0.5	- - -	≥ 0.1	≥ 0.5	no data
Fe(III)	< 0.5	< 0.5	- - -	≥ 0.1	≥ 0.5	> 10
Fe(III)-SO_4	< 0.5	< 0.5	- - -	≥ 0.1	≥ 0.5	≥ 0.3, ≤ 10
SO_4	< 0.5	< 0.5	- - -	≥ 0.1	≥ 0.5	< 0.3
CH_4gen	< 0.5	< 0.5	- - -	≥ 0.1	< 0.5	

Modified from McMahon and Chapelle (2008). Redox process: O_2 = oxygen reduction; NO_3 = nitrate reduction; Mn(IV) = manganese reduction; Fe(III) = iron reduction; SO_4 = sulfate reduction; CH_4gen = methanogenesis.

To evaluate if the sulfate-reducing conditions observed in the three wells identified as sulfate reducing or as possibly sulfate reducing (page 3-139) were triggered by the introduction of methane into the aquifers, water-quality data for domestic wells across Geauga County were retrieved from the U.S. Geological Survey's National Water Information System Database and classified using the same methods described above. Results from the chemical classification, shown in Table 3-12, indicate that sulfate reduction is occurring in groundwater in several geologic units tapped by wells across Geauga County (GE-109, 151, 202, 147, 77, 103, 126), even in wells where methane is not present (GE-109, 151, 202, 77, 103).

Despite the fact that sulfate-reducing conditions are common in Geauga County, it is possible that the introduction of methane (a carbon source) could stimulate the sulfate-reducing reaction, resulting in more reaction products (i.e., bicarbonate, sulfide).

Table 3-12. Redox Processes Identified for Wells Sampled by USGS Across Geauga County

Well ID	Sample Date	Geologic Unit	Redox Process
GE-109	4/22/1986	Sharon Sandstone	SO_4
GE-109	6/15/1999	Sharon Sandstone	Fe(III)
GE-109	6/11/2009	Sharon Sandstone	O_2-Fe(III)
GE-151	4/29/1986	Sharon Sandstone	SO_4
GE-151	6/8/1999	Sharon Sandstone	Fe(III)
GE-151	6/15/2009	Sharon Sandstone	O_2-Fe(III)
GE-202	4/16/1986	Sharon Sandstone	SO_4
GE-202	6/22/1999	Sharon Sandstone	Fe(III)
GE-202	6/9/2009	Sharon Sandstone	Fe(III)
GE-332	6/14/1999	Sharon Sandstone	O_2
GE-332	6/18/2009	Sharon Sandstone	O_2
GE-85A	6/15/1999	Sharon Sandstone	O_2
GE-85A	6/19/2009	Sharon Sandstone	O_2
GE-147	4/30/1986	Cuyahoga Shale	SO_4
GE-147	6/16/1999	Cuyahoga Shale	Fe(III)
GE-147	6/16/2009	Cuyahoga Shale	O_2-Fe(III)-SO_4
GE-185A	6/28/1999	Cuyahoga Shale	Fe(III)
GE-185A	6/10/2009	Cuyahoga Shale	Fe(III)
GE-234	6/21/1999	Cuyahoga Shale	Fe(III)
GE-234	6/17/2009	Cuyahoga Shale	O_2-Fe(III)
GE-341	6/23/1999	Cuyahoga Shale	O_2-Mn(IV)
GE-341	6/12/2009	Cuyahoga Shale	O_2-Mn(IV)
GE-77	4/22/1986	Cuyahoga Shale	SO_4
GE-77	6/8/1999	Cuyahoga Shale	Fe(III)
GE-77	6/16/2009	Cuyahoga Shale	O_2-Fe(III)-SO_4
GE-120	4/18/1986	Cuyahoga + Berea	Suboxic
GE-120	6/29/1999	Cuyahoga + Berea	Suboxic
GE-120	6/10/2009	Cuyahoga + Berea	O_2
GE-103	8/21/1980	Berea Sandstone	SO_4
GE-103	5/1/1986	Berea Sandstone	SO_4
GE-103	6/24/1999	Berea Sandstone	Fe(III)
GE-103	6/9/2009	Berea Sandstone	Fe(III)
GE-126	4/30/1986	Berea Sandstone	SO_4
GE-126	6/17/1999	Berea Sandstone	Fe(III)-SO_4
GE-126	6/17/2009	Berea Sandstone	O_2-SO_4

Dissolved methane detected in well

Sulfate-reducing conditions

Van Stempvoort and others (2005) were the first researchers to design and execute a field experiment documenting the attenuation of fugitive methane from an oil well by dissimilatory bacterial sulfate reduction at low temperature (~ 5° C) under anaerobic conditions. Based on a survey of private well owners in the Lloydminster area in Alberta, Canada (Maathuis and Jaworski, 1997) observed a strong inverse relationship between the concentration of sulfate and methane in groundwater. This relationship suggested that elevated dissolved methane

concentrations may persist only at low concentrations of sulfate and would be analogous to the inverse relationship between sulfate and dissolved methane concentrations observed in marine sediment profiles, which has been shown to be related to coupling of dissimilatory bacterial sulfate reduction and methane oxidation (Van Stempvoort and others, 2005).

The field experiment was performed over a 7-year period (1995 to 2002) and involved the sampling of 13 multi-level monitoring wells for calcium, sodium, magnesium, potassium, sulfate, chloride, bicarbonate, nitrate + nitrite, and dissolved total iron and total manganese, plus isotopes of sulfur and carbon. The monitoring wells were divided into two groups. The "remote" wells were more than 50 m from the oil well, whereas the "proximal" wells were within 10 m of the oil well. Their work showed that dissolved methane concentrations were generally lower in 2002 than in six previous years of the study. This was particularly true for the proximal monitoring wells where the 2002 methane concentrations were approximately an order of magnitude lower than those measured in 1995 and 1996. This suggested that the equation below may be an important overall reaction in the proximal zone.

$$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O \qquad (2)$$

According to equation (2), hydrogen sulfide, bicarbonate and water are created by the reaction of dissolved methane and sulfate. If this reaction is occurring there should be a decrease in methane and sulfate concentrations and an accompanied increase in hydrogen sulfide and bicarbonate in groundwater samples. Figure 3-118 shows the relationship between dissolved sulfate and bicarbonate seen by Van Stempvoort and others (2005) proximal to an oil well where methane gas escaped into the subsurface environment. This is the graphic relationship that describes the forward reaction in described by equation (2) above.

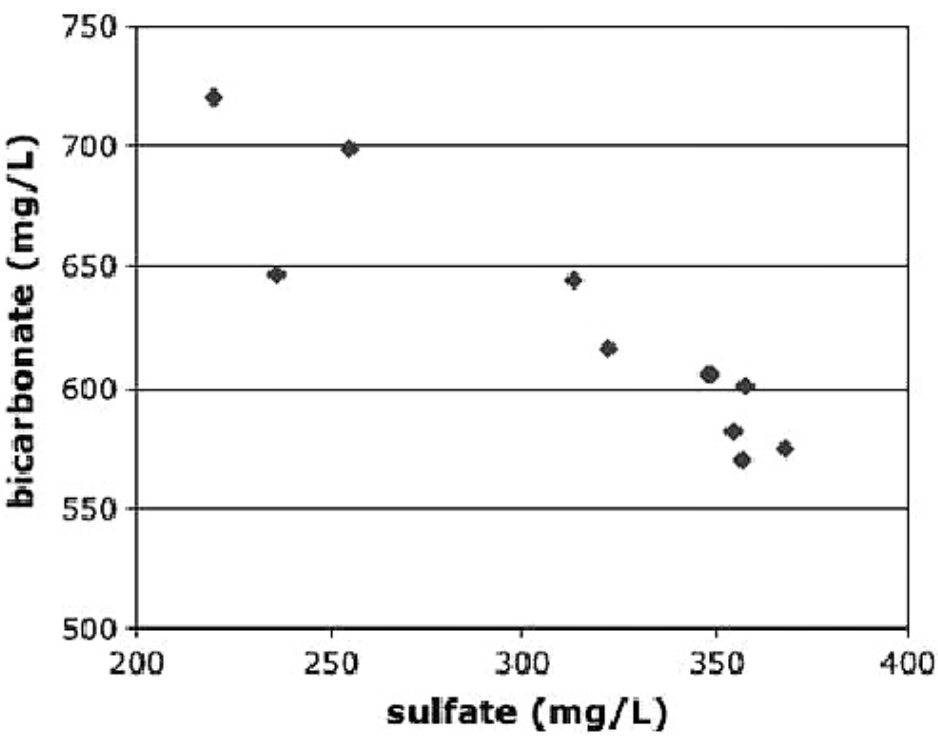


Figure 3-118. Inverse relationship between sulfate and bicarbonate documented by Van Stempvoort and others (2005) near an oil well that released methane gas to the subsurface.

At the Bainbridge investigation area, bicarbonate was not among the parameters measured during analysis of the 2008 residential well samples; however, alkalinity was measured. In most groundwaters, alkalinity is derived almost entirely by bicarbonate (Hem, 1992), especially for groundwaters within the pH range measured in the samples from the residential wells in the investigation area (Figure 3-120).

Figure 3-119 shows the relationship between sulfate and alkalinity from eight residential wells in the investigation area and two background wells. The inverse relationship between bicarbonate (alkalinity) and sulfate concentrations documented by Van Stempvoort and others (2005) is not seen in the samples from residential wells in the investigation area. If the reaction in equation (2) is occurring in the Bainbridge investigation area, the sulfate and alkalinity data from the police station well, which has been exposed to methane for a longer time than any water well in the area, would likely plot further to the left, near the tip of the red arrow. The data on Figure 3-119 suggest there is no relationship between sulfate and alkalinity in the Bainbridge area, as seen by the large range of alkalinity values occurring over a small range of sulfate values indicating that the concentration of alkalinity is independent of the concentration of sulfate.

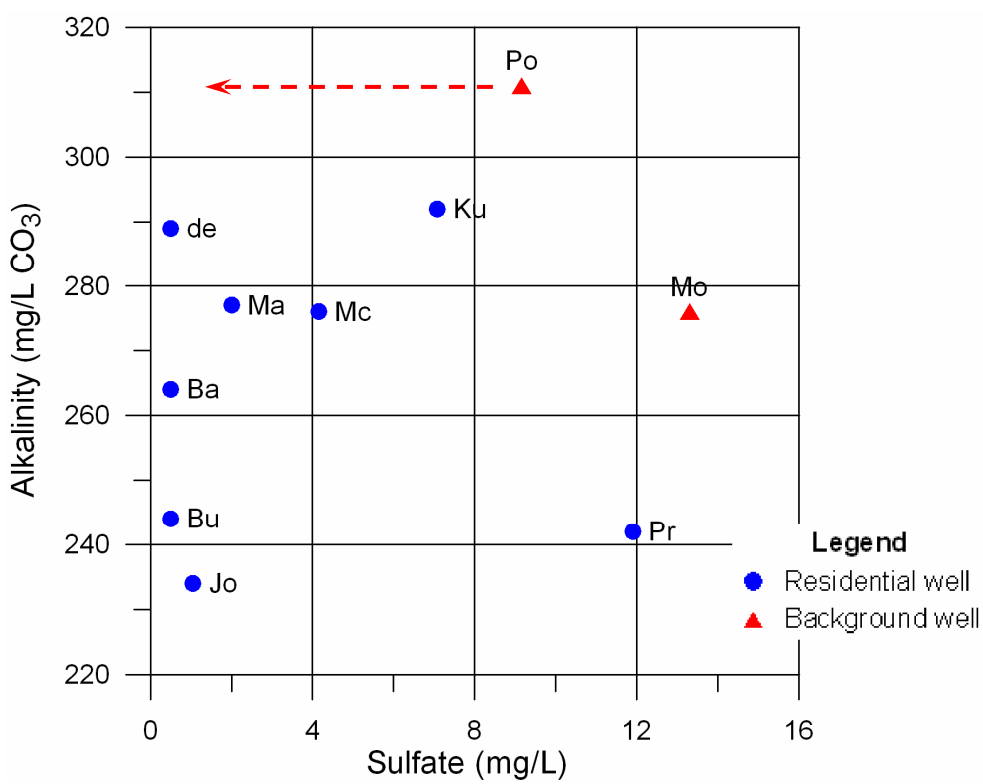


Figure 3-119. Plot of sulfate versus alkalinity from 10 wells in the Bainbridge area including eight residential wells in the investigation area.

One reason why the products of the reaction (HS^- and HCO_3^-) from equation (2) are not found in the Bainbridge investigation area could be related to the low concentrations of the reactants (CH_4 and SO_4^{2-}). Table 3-11 shows that the maximum concentration of dissolved methane at the Alberta, Canada, field site studied by Van Stempvoort and others (2005) was 78 mg/L, whereas the maximum concentration of dissolved methane in the investigation area was 1.04 mg/L. At the Alberta field site, the sulfate concentrations range between 200 to 450 mg/L (Figure 3-121), whereas sulfate concentrations in the Bainbridge investigation area range from

1.55 to 42.0 mg/L (Table 3-13). As a result of the low concentrations of reactants, the inverse relationship between sulfate and bicarbonate (alkalinity) has not developed in the area of investigation.

4. Do water-quality data show sulfate reduction is triggered by methane gas?

Because DMRM did not serendipitously have residential well-water samples "before" and "after" the gas invasion at residential wells in the investigation area (with the exception of the police station well), it compared the range of constituent concentrations observed in the investigation area after the subsurface gas release to that observed elsewhere in the county (DMRM, 2008). The expert panel felt that this was a reasonable approach and the only option available to DMRM. To make the comparison more rigorous, however, the expert panel suggested that (1) statistical comparisons be made rather than simple range comparisons, and that (2) these comparisons be done on data grouped by aquifer because Jagucki and Darner (2001) found that concentrations of certain water-quality constituents vary by aquifer in Geauga County. To that end, wells completed in both the Cuyahoga Shale and the Berea Sandstone were chosen for statistical analysis because these wells had all produced gas at some time during the investigation (personal communication, Scott Kell, DMRM) and contained the highest dissolved methane concentrations (Table 3-7).

To determine if detrimental changes in groundwater quality occurred as a result of natural gas invading the shallow aquifers tapped by residential water wells, a suite of dissolved chemical species was measured in water samples taken in eight wells inside the area of investigation (labeled as "inside" wells). These data were then statistically compared to water-quality data from wells completed in the same geologic units outside the area of investigation but in Bainbridge Township (labeled as "outside wells"). The data are from Ohio EPA analyses of samples taken in public water-supply wells outside the investigation area between 1976 and 2004 (Table 3-13). The "outside" group includes six wells at Lake Lucerne Station (a private housing community), the well at the Montesorri School on Chillicothe Road, and the police station well on Bainbridge Road, which has a known history of producing methane gas (Appendix I) and high concentrations of dissolved arsenic. All the "outside" wells are uncased in portions of the Cuyahoga Shale and Berea Sandstone.

Table 3-13. Locations of Water Wells Sampled by DMRM and by Ohio EPA

Address (Owner) of Water Wells Sampled by DMRM ("inside" sample locations, taken two months after gas invasion incident)	**Background Public Water-Supply Wells Sampled by OEPA** ("outside" sample locations, taken before gas invasion incident)
17990 English Dr (Jordan)	Lake Lucerne Station 3, #6
17927 Kingswood Dr (Prochazka)	Lake Lucerne Station 3, #11
17971 Kingswood Dr (de Gaetano)	Lake Lucerne Station 3, #12
7859 Scotland Dr (McGee)	Lake Lucerne Station 3, #13
7969 Scotland Dr (Kukoleck)	Lake Lucerne Station 5, #14
7981 Scotland Dr (Bastifell)	Lake Lucerne Station 4, #16
7897 Scotland Dr (Buddenhagen)	8353 Bainbridge Rd, Police station
7941 Scotland Dr (Mason)	17892 Chillicothe Rd, Montesorri School

The "inside" water-quality data are from DMRM samples taken in February 2008, prior to formation of the expert panel, in residential wells that are also uncased in portions of the Cuyahoga Shale and Berea Sandstone (Table 3-13). The "inside" samples taken by DMRM were split and then analyzed by DMRM at its Ohio EPA certified lab in Cambridge, Ohio, and by Biosolutions LLC, Chagrin Falls, Ohio.

As often is the case when attempting to compare water-quality data from studies having different purposes, samples are not always taken at a consistent location such as the wellhead, or prior to plumbing fixtures such as water heaters and water softeners, or at spigots, sinks or bathtubs. Differences in where a water sample is taken can introduce variability into statistical comparisons. For example, investigators interested in health exposure calculations take water samples at the spigot because it is the best place to obtain a sample that represents the water quality consumed by users. In contrast, investigators interested in discerning geochemical reactions occurring within the wellbore or within the aquifer take water samples at the wellhead because it is the best place to obtain a sample that represents in-situ water quality. Another source of variability is introduced when some investigations include both dissolved and suspended solids in a sample, whereas other investigations require only dissolved solids. Yet another source of variability is introduced when water sampled taken on different dates or in different years are grouped together in one dataset. This assumes that there is no seasonal or annual variability of water-quality parameters, which generally is an unrealistic assumption in shallow groundwater flow systems like in the area of investigation. Perhaps the most common source of difficulty occurs when one investigation uses different analytical techniques or does not analyze samples for the same set of anions, cations, and physical parameters as the other investigations being used in the statistical comparison.

All of the sources of unwanted variability described above are present in the two datasets used in the statistical comparison of water-quality parameters inside the investigation area and outside the investigation area. As a consequence, the comparison of "outside" water-quality data from Ohio EPA to the "inside" water-quality data from DMRM is not straight forward and not above criticism. The statistical comparison is also limited by the small number of water-quality parameters common to both datasets. As a result, less statistically robust non-parametric tests were used to compare the data. In 20-20 hindsight, these sources of variability could have been minimized or eliminated if a statistically-based comparison of water quality had been designed and implemented at the beginning of the investigation.

The following parameters are common to both the "inside" and the "outside" datasets: pH, alkalinity, and dissolved concentrations of sulfate, barium, iron, manganese, chloride, calcium, magnesium, and sodium. An Excel worksheet containing these data can be downloaded from the DMRM website at www.ohiodnr.com/mineral. These data were used to compare the two sets of data statistically using the Wilcoxan Rank Sum (WRS) test and visually using boxplots. The WRS test determines whether there is a statistically significant difference between the median value of each dataset based on a 95 percent confidence limit. The p-value computed using the WRS test expresses the probability, with 95 percent confidence, that the median values of the two groups of data are statistically different and, therefore, the two groups are dissimilar. Boxplots enable visual comparison of median concentrations, interquartile ranges (the distribution of data that lie between the 75th and 25th percentiles), and the total range of data values (Figure 3-120).

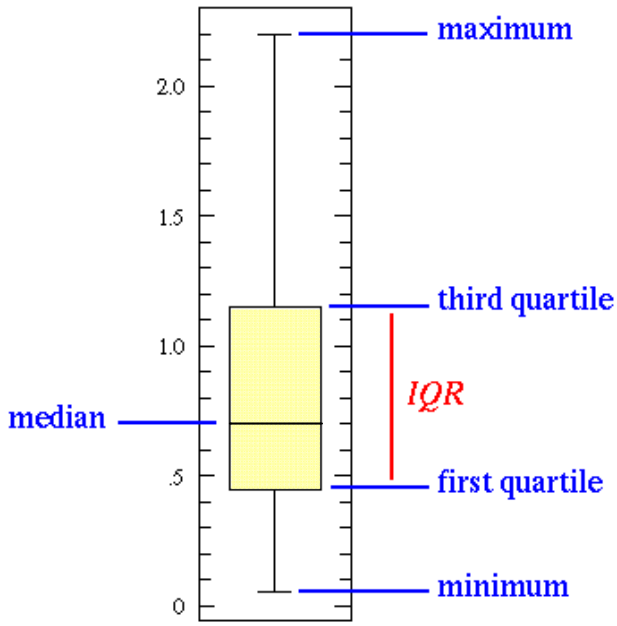


Figure 3-120. Boxplot structure showing interquartile range (IQR) and other statistical measures.

Before performing these tests, we chose to exclude the Biosolutions data, which represented a duplicate set of values for the "inside" well-water samples that had no complement in the data from the "outside" well-water samples. In other words, combining the DMRM water-quality values with the Biosolutions water-quality values introduced a source of variability not present in the other dataset. We chose the exclude the Biosolutions data because the detection limits of its equipment often was higher than for the equipment used by DMRM and because of mass balance errors between of the sum of cations and anions in some samples.

The WRS p-values given in Table 3-14 indicate that at a 95 percent confidence level there is little difference in water chemistry between the "outside" well-water samples taken at public water-supply wells and the "inside" well-water samples taken at residential wells in the investigation area (Table 3-14, Figure 3-121) that may have been exposed to methane. The only parameter with a statistically significant difference is barium (WRS p-value = 0.047), which has lower values in the "inside" well-water samples than in the "outside" well-water samples. All of the other water-quality parameters, pH, alkalinity, sulfate, nitrate, chloride, arsenic, calcium, total iron, total manganese, and sodium, demonstrate that there is no statistical difference at a 95 percent confidence level between the "inside" and the "outside" water well samples.

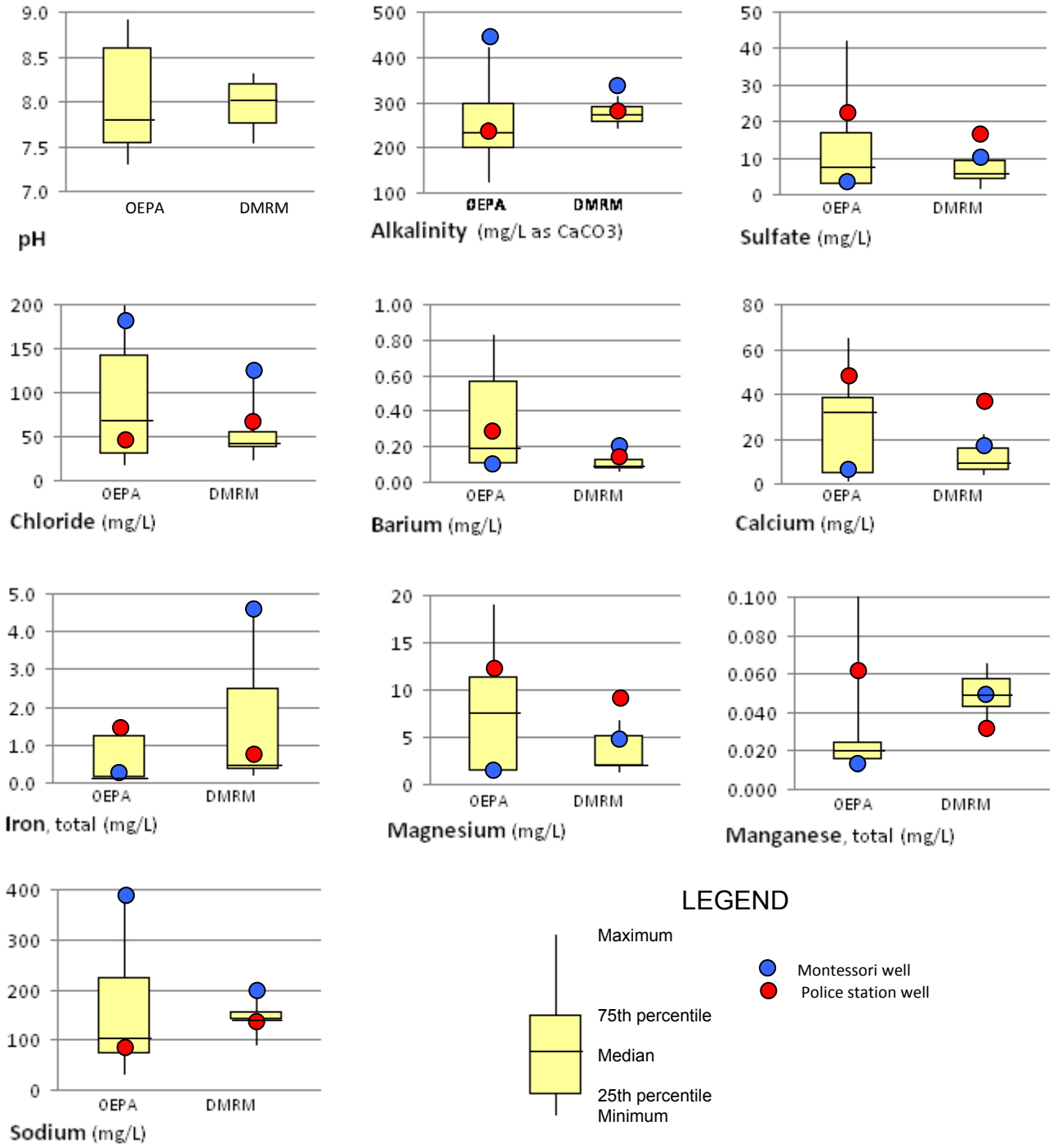
Table 3-14. Statistical Comparison of Well Waters "outside" the Area of Investigation (OEPA) with Well Waters "inside" the Area of Investigation (DMRM)

	OEPA **pH** Lab (S.U.)	DMRM **pH** Lab (S.U.)	OEPA **Alkalinity** (mg/L CO_3)	DMRM **Alkalinity** (mg/L CO_3)	OEPA **Sulfate** (mg/L)	DMRM **Sulfate** (mg/L)	OEPA **Nitrate** (mg/L)	DMRM **Nitrate** (mg/L)
25th percentile	7.5	7.7	196	254	2.50	4.18	< 0.1	< 0.1
Maximum	8.9	8.3	422	311	42.00	11.90	< 0.1	< 0.1
Minimum	7.3	7.5	120	242	2.00	1.55	< 0.1	< 0.1
75th percentile	8.6	8.2	299	290	17.00	9.16	< 0.1	< 0.1
Median	7.8	8.0	224	270	8.00	7.08	< 0.1	< 0.1
Samples	6	4	7	8	7	5	6	7
WRS p-value	0.914		0.161		0.082		- - - - -	
Montessori			230	276	20.00	13.30	0.36	< 0.5
Police station			422	311	< 2	9.16	< 0.10	- - - - -

	OEPA **Chloride** (mg/L)	DMRM **Chloride** (mg/L)	OEPA **Arsenic** (mg/L)	DMRM **Arsenic** (mg/L)	OEPA **Barium** (mg/L)	DMRM **Barium** (mg/L)	OEPA **Calcium** (mg/L)	DMRM **Calcium** (mg/L)
25th percentile	29.50	37.73	0.0028	< 0.002	0.10	0.07	4.42	6.07
Maximum	198.00	118.00	0.0240	< 0.002	0.83	0.16	65.00	21.90
Minimum	17.00	21.40	0.0020	< 0.002	0.10	0.05	0.56	3.72
75th percentile	143.00	56.45	0.0083	< 0.002	0.57	0.13	38.50	16.05
Median	70.00	46.05	0.0030	< 0.002	0.20	0.10	26.00	6.38
Samples	7	8	6	6	7	7	7	8
WRS p-value	0.645		- - - - -		***0.047***		0.372	
Montessori	46.00	62.50	< 0.01	<0.002	0.21	0.11	44.00	36.20
Police station	175	118.00	0.0240	- - - - -	< 0.1	0.16	3.54	16.00

	OEPA **Iron** total (mg/L)	DMRM **Iron** total (mg/L)	OEPA **Magnesium** (mg/L)	DMRM **Magnesium** (mg/L)	OEPA **Manganese** total (mg/L)	DMRM **Manganese** total (mg/L)	OEPA **Sodium** (mg/L)	DMRM **Sodium** (mg/L)
25th percentile	0.145	0.357	1.37	1.84	0.015	0.042	71.00	139.75
Maximum	1.610	4.430	19.00	6.70	0.210	0.065	380.00	191.00
Minimum	0.110	0.186	0.81	1.22	0.010	0.034	30.00	87.50
75th percentile	1.250	2.479	11.35	5.17	0.025	0.058	224.50	155.25
Median	0.170	0.528	7.70	2.16	0.020	0.050	103.00	147.50
Samples	7	3	7	8	7	3	7	8
WRS p-value	0.099		0.328		0.137		0.235	
Montessori	1.440	0.590	12.00	9.07	0.060	0.030	82.00	119.00
Police station	0.110	4.430	0.94	4.92	0.010	0.050	380	191.00

- WRS p-values less than 0.05 (bold italics) indicate that the medians are statistically different with greater than 95% confidence.
- Comparison of constituents with less than 5 samples (e.g. pH, iron, and manganese) is not statistically defensible.



Data from the Montesorri and police station wells are plotted with the DMRM "inside" dataset solely to illustrate natural temporal variations.

Figure 3-121. Boxplots of water-quality parameters common to the "outside" (OEPA) and the "inside" (DMRM) well-water samples.

The wells at the Bainbridge Police Station and the Montessori School are the only ones in the OEPA database or in the DMRM database where water samples were taken and analyzed before

and after the English #1 well incident. Water-quality data from these two wells can be compared to water-quality data from the wells "inside" the area of investigation to make highly qualified assessments about temporal changes in water quality. Any water-quality assessment based on data from one or two wells is certainly not robust and any insights and/or findings need to be highly qualified. With these caveats firmly in mind, the water-quality data from the police station and Montessori School wells show some general, albeit statistically-thin, relationships when compared with the water-quality data from residential wells "inside" (DMRM) the area of investigation.

The police station well is on the east side of the saddle in the top of Berea Sandstone surface (Figure 3-80) and is nearly 4,000 feet away from the English #1 well. As noted by Ohio EPA, it has produced substantial quantities of natural gas for many years (Appendix I). As such, the rocks proximal to this well have been exposed to natural gas longer than any residential wells in the area of investigation, which makes the police station unique among all the wells within the combined Ohio EPA / DMRM datasets. Based on the pathways of fugitive gas migration described in Figures 3-81 to 3-96, the police station well was not impacted by fugitive gas emanating from the English #1 well, although water in the wellbore likely felt the pressure pulses moving through the Berea Sandstone during the 31-day shut-in period prior to the home explosion on December 15, 2007 (pages 3-55 to 3-62).

Overall Conclusions Regarding Black Sediments and Redox Reactions

The XRD analyses indicated that the precipitation of black sediment is not widespread. The geochemical reactions creating black, iron sulfide particulates were identified in only one of five wells analyzed from the investigation area. Because this study was actuated by the accidental release of methane gas to the subsurface environment, any water well sampling strategy had to be compromised because of a paucity of water-quality data both inside and outside the investigation area prior to the gas invasion incident. Analysis of the available water-quality data suggest that the low dissolved methane concentrations in wells in the investigation area may limit sulfate-reduction reaction products in the geologic units tapped by residential wells, which with the available data cannot be distinguished from sulfate-reduction reactions known to be occurring naturally in Geauga County in the same geologic units.

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