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Origin of High Levels of Ammonium in Groundwater, Ottawa County, Michigan

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ORIGIN OF HIGH LEVELS OF AMMONIUM IN GROUNDWATER, OTTAWA COUNTY, MICHIGAN

by

Derrick Lingle

A thesis submitted to the Graduate College in partial fulfillment of the requirements for the degree of Master of Science Department of Geosciences Western Michigan University December 2013

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Groundwater from wells located in and around Hemlock Crossing Park in Ottawa County, Michigan has elevated levels of ammonium. High ammonium concentrations in potable water wells are a common indicator of anthropogenic impact, such as landfill leachate or agricultural activity. Ammonium can also occur in groundwater through the decay of natural organic material. Along with the retrieval of a complete glacial sediment core via rotasonic drilling, numerous chemical and isotopic parameters were used to determine the source of ammonium in the impacted aquifer.

Buried organic material, deposited during the Athens subepisode interglacial period, is in contact with groundwater containing elevated concentrations of ammonium and iron. High methane concentrations (20 to 41 mg/L) signify methanogenic conditions in the aquifer system and indicate very reducing conditions. A multi-isotopic approach, involving $^3$H and $^{18}$O/$^2$H, provides evidence that the aquifer system is not receiving recent recharge influenced by agricultural activity. Nitrogen isotopes support that the ammonium most likely originated from in situ organic material and not from anthropogenic sources. Potable wells in the confined aquifer system are at risk from the potential impact of methane migration and nitrification of ammonium, along with the aesthetic impact of high chloride concentrations.
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Derrick Lingle
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INTRODUCTION

Groundwater from wells in and around Hemlock Crossing Park in Ottawa County, Michigan contains elevated levels of ammonium. At current concentrations, ammonium is detrimental to aquatic organisms and could have negative health effects on humans. Due to an unknown source of high levels of ammonium in park wells, officials posted advisory notices in 2010 about the use of this water for drinking.

Common potable water quality parameters include nitrate (NO$_3^-$), chloride (Cl$^-$), and iron (Fe$^{2+}$) (Barcelona et al., 1985). Ammonium (NH$_4^+$) is typically not included in this suite of parameters due to low levels generally seen in natural groundwater. Naturally occurring NH$_4^+$, caused by the decay of buried organic matter, commonly occurs in groundwater at concentrations of 0.2 mg/L or less (WHO, 1996). Elevated NH$_4^+$ concentrations in groundwater are often associated with anthropogenic sources such as sewage effluent, leaking manure lagoons, and landfill leachate (Warner, 2000; Christensen et al., 2001). For example, leachate from the KL Landfill in Kalamazoo, Michigan contained NH$_4^+$ concentrations as high as 61 mg/L (Kehew and Passero, 1990).

Study Area

Hemlock Crossing Park is located in Ottawa County, Michigan (Figure 1). Prior to 1997, a blueberry farm was located on the land that surrounds the park’s nature center. The Pigeon River flows through the 239-acre park and empties into Lake Michigan, approximately 5.5 km downstream to the west. The Pigeon River watershed is comprised
of 49% agricultural land, whereas another 36% is forested (MacDonald et al., 2001).

Figure 1. Location of Hemlock Crossing Park and nearby potential anthropogenic sources of ammonium.

In early 2010, fish in a new aquarium at the park’s nature center died as employees attempted to set the aquarium up. An ensuing investigation by the Ottawa County Health Department (OCHD) discovered unusually high concentrations of NH$_4^+$-N
(7.87 to 18.47 mg/L) in the park’s two wells. Due to a leaking inactive landfill approximately 0.8 km west of the park, groundwater samples were analyzed for a wide range of parameters including metals and volatile organic compounds. Except for NH₄⁺, no other parameters were reported at concentrations above expected natural background levels (OCHD, unpublished data). The landfill was ruled out as a possible source of NH₄⁺ because the park is hydraulically upgradient of the landfill and, in addition, constituents commonly seen in leachate are not present. Further investigation by the health department was unable to determine a probable source of NH₄⁺ (Spencer Ballard, OCHD, personal communication, 2012).

Nearby agricultural activity is also a potential source of NH₄⁺ in the study area. Blueberry fields, row crops, and poultry farms are the prevalent forms of agriculture in Port Sheldon and Olive Township (Figure 1). There are no wet manure lagoons in Ottawa County; however manure is commonly applied to row crops as an inexpensive alternative to synthetic fertilizer (Charles Gould, Ottawa County Michigan State University Extension, personal communication, 2013).

Bedrock Geology

Paleozoic bedrock units below the surface of Michigan form an intracratonic basin known as the Michigan basin. Cambrian outcrops, which form the rim of the basin, occur in the Upper Peninsula of Michigan, Wisconsin, Illinois, Indiana, as well as in Ontario, Canada. Pennsylvanian bedrock subcrops beneath the glacial drift at the center of the basin in the Lower Peninsula of Michigan. Jurassic redbeds are also present under
glacial drift in the central region of the Lower Peninsula.

Bedrock below the study site is the Mississippian Coldwater Shale, with a depth to bedrock between 36.6 and 45.7 m below the surface. The contact between the Coldwater Shale and the Marshall Sandstone is located approximately 0.8 km to the east of Hemlock Crossing Park. Coldwater Shale is grayish in color and appears to have undergone a significant amount of weathering at the bedrock surface. The depositional environment of the Coldwater Shale is a prograding deltaic complex (Cohee, 1979), which thins distally from a source in southwestern Ontario. Trending east to west, the thickness of the formation in Michigan varies from 396 m to 152 m (Potter and Pryor, 1961; Cohee, 1979). In the western half of the basin, the Coldwater Shale is interbedded with one or more carbonate beds (Monnett, 1948).

Glacial Geology

The Laurentide Ice Sheet covered the Great Lakes region during at least six glaciations since 780 ka (Fullerton, 1986). The most recent glaciation, the Wisconsinan, occurred from 80,000 to 11,500 cal. yr B.P. and reached southern Indiana at the maximum extent (Patrick Colgan, personal communication, 2013). Glacial deposits from Illinoian (190 to 128 ka) and pre-Illinoian (>190 ka) glaciations occur in Ohio, Indiana, and Illinois, although correlations of pre-Illinoian sediment have been controversial (Hallberg, 1986; Larson and Schaetzl, 2001; Thompson and Goldstein, 2006; Patrick Colgan, personal communication, 2013). The Sangamonian interglaciation, which separates the Wisconsinan and Illinoian glaciations, is recognized by a thick B-horizon
paleosol ranging from Iowa and Kansas eastward to Ohio and is thought to have
developed during warmer and dryer conditions than that of the current climatic regime,
due to extensive leaching (Follmer, 1978; Schaetzl, 1986; Curry and Pavich, 1996;
Larson and Schaetzl, 2001). Although poorly studied, the oldest recognized glacial
deposits in Michigan are probably from the Ontario subepisode or pre-Wisconsinan in age (Eschman and Mickelson, 1986; Monaghan et al., 1986; Monaghan, 1990; Patrick Colgan, personal communication, 2013).

Glacial advances during the Michigan subepisode (35,000 to 11,500 cal. yr B.P.)
had an enormous impact on the current topography in the Lower Peninsula of Michigan
(Leverett and Taylor, 1915; Monaghan et al., 1986; Kehew et al., 1999; 2005; Beukema, 2003). The average thickness of glacial sediment in the Lower Peninsula is 85 m, however the total thickness of glacial drift varies from zero to >365 m (Rieck and Winters, 1993; Alan Kehew, personal communication, 2013). Approximately 21,000 $^{14}$C yr B.P., the Laurentide Ice Sheet began retreating from its last maximum extent and a group of lobes formed along the southern margin (Kehew et al., 1999). During the overall retreat of the Laurentide Ice Sheet, three lobes, the Lake Michigan, Saginaw, and Huron-Erie Lobe, made multiple readvances over southern Michigan (Figure 2) (Farrand and Eschman, 1974; Kehew et al., 1999).
The Lake Michigan Lobe flowed out of the Lake Michigan basin into southwestern Michigan on multiple occasions (Rieck, 1988; Hansel and Johnson, 1992; Kehew et al., 1999). During interglacial periods, proglacial lakes formed in the Lake Michigan basin, beginning with Glacial Lake Milwaukee (Schneider and Need, 1985; Larson and Schaetzl, 2001). Readvances of the Lake Michigan Lobe occurred approximately 15,000, 13,000, 11,800, and 10,000 $^{14}$C yr B.P., altering the size and in some cases, the existence of proglacial lakes in the Lake Michigan basin (Mickelson et al., 1982; Larson and Schaetzl, 2001). Around 15,500 to 15,000 $^{14}$C yr B.P., the Lake Michigan Lobe readvanced into Lake Milwaukee on the eastern side of the basin (Kehew et al., 2012).
et al., 1999; Kehew et al., 2005; Larson and Schaetzl, 2001). Following the retreat of the Lake Michigan Lobe, Glacial Lake Chicago formed in the Lake Michigan basin and drained south into the Illinois Valley through an outlet near Chicago (Leverett and Taylor, 1915). Glacial readvance around 13,000 $^{14}$C yr B.P. caused the catastrophic drainage of Lake Saginaw through the Grand Valley and into Glacial Lake Chicago (Leverett and Taylor, 1915; Eschman and Karrow, 1985; Kehew, 1993). Following the readvance around 11,800 $^{14}$C yr B.P. when Glacial Lake Chicago was reestablished, the lake drained for the last time and Lake Algonquin formed (Hansel et al., 1985; Colman et al., 1994; Lewis et al., 1994; Larson and Schaetzl, 2001).

The glacial stratigraphy along the southwestern coastline of Michigan is composed mostly of sediment from the Wisconsinan (Monaghan et al., 1986). The generalized stratigraphy along the Lake Michigan bluffs near Glenn Shores, Michigan, approximately 56 km south of Hemlock Crossing Park, is highly discontinuous (Figure 3). The lowest unit of the section, which is not currently exposed, is composed of a silt- and sand-rich till known as the Glenn Shores till. Overlying the Glenn Shores till are thin layers of gravel, followed by approximately 1.8 m of silt and sand. Both layers contain organic matter that has been dated as Athens subepisode. Above the organic matter is the sandy Ganges till, overlain by a thick sandy lacustrine layer and the Saugatuck till. Capping the Glenn Shores section is a deposit of Lake Chicago sediment. Sharp contacts exist between all layers above the Ganges (Monaghan et al., 1986).
Figure 3. Stratigraphy of the Glenn Shores section (Monaghan et al., 1986).

Buried Organic Material in Michigan

Buried organic matter in the subsurface of Michigan was first reported by Leverett (1899, 1904, 1917) and Leverett and Taylor (1915). Buried organic matter in the glacial drift of Michigan is concentrated in several regions throughout the state (Figure 4) (Rieck and Winters, 1982; Winters et al., 1986). The majority of buried organic matter in Michigan occurs in low spots in the bedrock topography (Figure 5). An estimated 70% of buried organic material reported by Rieck and Winters (1982) lies above or near bedrock lowlands. Bedrock lowlands make up only 20% of the bedrock surface in the Lower Peninsula (Rieck and Winters, 1976, 1980). It is possible that
organic matter not in proximity to bedrock lowlands was eroded by glacial activity (Alan Kehew, personal communication, 2013). Most buried organic material occurs near its place of origin and was not transported by glacial ice and deposited in a new location (Rieck and Winters, 1988).

Figure 4. Clustered locations of buried organic matter in Michigan. Values in each polygon indicate the number of sites in a cluster, while individual sites are represented by a dot (Modified from Rieck and Winters, 1988).

Wood fragments (<2 cm) recovered in the silt, sand and gravel layers above the Glenn Shores till were estimated to be between 37,150 and >48,000 $^{14}$C yr B.P. (Monaghan et al., 1986). At John Ball Park in Grand Rapids, wood fragments provided $^{14}$C ages of >36,000 to >40,000 yr B.P. Pollen from spruce, pine, and birch were also recovered (Zumberge and Benninghoff, 1969). The presence of these tree species suggests that parts of Michigan were ice-free during the Athens subepisode. Buried
organic material along the western side of what is now Michigan, was likely deposited in a floodplain or evolving shoreline where a predecessor to Lake Michigan flooded boreal forests in lowlands such as bedrock valleys (Winters et al., 1986).

Figure 5. Simplified cross-section depicting the relationship between bedrock lows and buried organic material (Rieck and Winters, 1980).

Decay of Buried Organics and Ammonium in Groundwater

Recent work has correlated high levels of $\text{NH}_4^+$ in groundwater to the decay of naturally buried organic matter under anaerobic conditions (Denne et al., 1984; Schilling, 2002; Roy et al., 2003; Hinkle et al., 2007; Glessner and Roy 2009; Jiao et al., 2010; Lindenbaum, 2012; Mastrocicco et al., 2012). During an investigation of wells screened in glacial valleys in eastern Kansas, Denne et al. (1984) concluded that several of the wells penetrated an organic rich layer in the glacial drift. Ammonium levels in these wells vary from <0.1 to 4.2 mg/L and correlate with depleted $\text{NO}_3^-$ concentrations and elevated concentrations of $\text{Fe}^{2+}/\text{Mn}^{2+}$, which indicate reducing conditions.

Roy et al. (2003) first proposed that the organic rich Robein silt, deposited around 27,000 yr B.P., was the source for elevated levels of $\text{NH}_4^+$ (>2 mg/L) in wells located in
east-central Illinois. Glessner and Roy (2009) were later able to show that the Robein silt acts as both a source and sink for NH$_4^+$ through sorption, ion exchange, and weathering. A genus of bacteria, *Cellulomonas*, which is known to break down organic material in cellulose and cause nitrate reduction, was present in the Robein silt (Glessner and Roy, 2009). Other former glaciated regions, including Iowa, show a correlation between groundwater with elevated levels of NH$_4^+$ and buried organic material in the glacial drift (Schilling, 2002).

**Redox Environment**

The transfer of electrons between two chemical species can be expressed by a redox reaction. Oxidation takes place when an electron is lost by a species while reduction occurs when an electron is gained. During a redox reaction, an oxidized atom will donate an electron to a reduced atom. A redox reaction will occur until the supply of electron donors and acceptors is exhausted, followed by the transformation to a different redox environment.
Microorganisms often use organic carbon as an electron donor to drive redox reactions. Compared to other common electron acceptors, oxygen reduction is the most thermodynamically favorable redox reaction. Once the concentration of oxygen has been depleted to a point where oxygen reduction is not thermodynamically favorable, a series of common redox reactions involving NO$_3^-$, MnO$_2$, Fe(OH)$_3$, SO$_4^{2-}$, and CO$_2$ will take place (Figure 6). The final redox stage, methanogenesis, occurs when methane (CH$_4$) acts as the electron acceptor and an abundance of organic carbon is present (Kehew, 2000).
Ammonium and the Nitrogen Cycle

In anoxic waters, \( \text{NH}_4^+ \) is the dominant species of ammonia (\( \text{NH}_3^+ \)) at a pH of 9 or less (Figure 7) (Pruel and Schroepfer, 1968). Ammonia is toxic to organisms at concentrations exceeding 0.02 mg/L (U.S. EPA, 1977). Thurston et al. (1981) proposed that when total nitrogen concentrations are below 20 to 50 mg/L and the pH is around 8, the toxic effect of \( \text{NH}_4^+ \) is less important because \( \text{NH}_3 \) is 300 to 400 times more toxic than \( \text{NH}_4^+ \). Thurston et al. (1984) concluded that at a pH as low as 7.5, there might be enough \( \text{NH}_3 \) present to be a toxic threat to rainbow trout, if total nitrogen levels are high enough. While there are no current U.S. EPA drinking water standards for \( \text{NH}_4^+ \), the limit in the United Kingdom is 0.5 mg/L (Erskine, 2000). Elevated levels of \( \text{NH}_4^+ \) in municipal water can react with chlorine, used as a disinfectant, and lead to an increase in total coliform populations (U.S. EPA, 1999). Ammonium can also oxidize to \( \text{NO}_3^- \), which can lead to decreased levels of dissolved oxygen and the eutrophication of coastal ecosystems. Nitrates in drinking water may cause methemoglobinemia, an oxygen deficiency, which can be deadly to infants (WHO, 2008). The minimum contaminant level for \( \text{NO}_3^- \) in drinking water in the United States has been set at 10 mg \( \text{NO}_3^- \)-N/L.
Due in part to a wide range of possible oxidation states ranging from +5 to -3, nitrogen (N) can form various chemical species, including nitrogen gas (N$_2$), nitrous oxide (N$_2$O), ammonium (NH$_4^+$), ammonia (NH$_3$), nitrate (NO$_3^-$), nitrite (NO$_2^-$), and organic nitrogen (N$_{\text{organic}}$). These forms of nitrogen are transformed during the numerous processes shown below in the nitrogen cycle (Figure 8).
Figure 8. Common processes of the nitrogen cycle (Modified from Harms-Ringdahl, 2007).

Nitrogen Fixation

During nitrogen fixation, \( N_2 \) is converted to a usable form of N, such as \( \text{NH}_4^+ \) or \( \text{NO}_3^- \), which is then taken up by plants and converted to amino acids during assimilation. Nitrogen fixation often occurs due to cyanobacteria, which live in root nodules. When other forms of nitrogen are depleted, \( N_2 \) can be used as a nitrogen source for nitrogen fixation in methanogens (Lobo and Zinder, 1992).

Ammonification

Under anoxic conditions, heterotrophic microbes break down soil organic matter and produce \( \text{NH}_4^+ \), seen in the generalized form of Equation 1 (Kresic, 2007). The
concentration of NH$_4^+$ produced by ammonification is typically low, due to the limited amount of organic matter present in the subsurface. In certain environments, large quantities of buried organic matter can decay and cause elevated levels of NH$_4^+$ in the groundwater. Cases like this have been discovered in coastal environments, such as in Italy and Vietnam, and glacial depositional environments, like in Kansas, Iowa, and Illinois (Denne et al., 1984; Schilling, 2002; Roy, 2003; Glessner and Roy 2009; Lindenbaum, 2012; Mastrocicco et al., 2012).

\[
\text{N}_{\text{organic}} \rightarrow \text{NH}_4^+ \quad \text{Eq. 1}
\]

**Nitrification**

Nitrification occurs under oxic conditions where NH$_4^+$ is oxidized to form NO$_3^-$. This process takes place when bacteria such as *Nitrosomonas* (Nitrobacteraceae) convert NH$_4^+$ to NO$_2^-$ and then *Nitrobacter* bacteria oxidize NO$_2^-$ to NO$_3^-$, as seen in the overall reaction (Equation 2) (Kendall, 1998; Freeze and Cherry, 1979).

\[
\text{NH}_4^+ + 2\text{O}_2 \rightarrow 2\text{H}^+ + \text{NO}_3^- + \text{H}_2\text{O} \quad \text{Eq. 2}
\]

**Denitrification**

Denitrification involves the reduction of NO$_3^-$ to N$_2$ by facultative aerobes that use NO$_3^-$ as an electron acceptor. The intermediate steps that occur during NO$_3^-$ reduction are expressed in Equation 3 (Korom, 1992).

\[
\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \quad \text{Eq. 3}
\]
Dissimilatory reduction of nitrate to ammonium (DRNA)

Similar to denitrification, DRNA also involves the reduction of \( \text{NO}_3^- \) under anaerobic conditions, but \( \text{NH}_4^+ \) is produced instead of \( \text{N}_2 \). When an excess of \( \text{NO}_3^- \) is present, denitrification will be the dominant process of \( \text{NO}_3^- \) reduction. In environments with little available \( \text{NO}_3^- \), but where carbon is still accessible, DRNA will be the dominant process of organic matter oxidation. While studying an anoxic plume that originated from a waste treatment pond, Bulger et al. (1989) were able to show that in the presence of excessive dissolved organic carbon (DOC), bacteria reduced \( \text{NO}_3^- \) to \( \text{NH}_4^+ \) (Equation 4).

\[
\text{DOC} + \text{NO}_3^- \rightarrow \text{HCO}_3^- + \text{NH}_4^+ \\
\text{Eq. 4}
\]

Anaerobic ammonium oxidation (Anammox)

Under anaerobic conditions, \( \text{NH}_4^+ \) can be oxidized by \( \text{NO}_3^- \) to form \( \text{N}_2 \). Besides denitrification, anammox is one of the few natural processes that can remove nitrogen from the subsurface (Carson, 2011).

Environmental Isotopes

Isotopes of an element contain the same number of protons but a different number of neutrons, which causes the atomic mass of each isotope to differ. The atomic mass of a radioisotope will decay at a constant probability. Radioactive isotopes have been extensively used in radiometric dating. The atomic mass of a stable isotope will not
decay or change with time. Elements can have multiple stable isotopes; therefore isotopic values are determined by comparing the ratio for the isotope of interest to the most prevalent isotope of an element. For example, the stable isotopes of hydrogen are $^1$H (protium) and $^2$H (deuterium). Although they do not decay, stable isotopes undergo fractionation during physical and chemical processes. This property enables us to use hydrogen, carbon, nitrogen, oxygen, and sulfur isotopes as valuable tracers in understanding several environmental events such as aquifer recharge, biogeochemical processes, and geochemical reactions (Aravena and Wassenaar, 1993; Kendall, 1998; Böhlke et al., 2006). When using stable isotopes as tracers, the approach is to measure the ratios of an isotope in the reactant and product. For instance, the ratio of $^2$H/$^1$H and $^{18}$O/$^{16}$O in vapor and liquid water, or the ratio of $^{18}$O/$^{16}$O in skeletal carbonates, are all influenced by environmental factors. In practice, rather than measuring the absolute ratio, the ratios are compared with an internationally accepted standard and expressed as $\delta$ (Equation 5). The unit of measurement for a $\delta$ value is permil ($‰$) or parts per thousand.

$$\delta_{\text{sample}} = \left[ \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right] \times 1000 \quad \text{Eq. 5}$$

A positive $‰$ value indicates that a sample is enriched in the heavy isotope in relation to the standard, while a negative $‰$ value indicates that a sample is depleted of the heavy isotope. The two common stable isotopes for oxygen ($^{16}$O and $^{18}$O) and hydrogen are reported relative to the reference standard Vienna Standard Mean Ocean Water (VSMOW). The standard for the two stable nitrogen isotopes ($^{15}$N and $^{14}$N) is atmospheric N$_2$ (AIR).
Oxygen/Deuterium

Dansgaard (1964) elegantly worked out the details of fractionation for hydrogen and oxygen in the major processes of the hydrological cycle, namely evaporation and rainout. The $\delta^{18}$O–$\delta^{2}$H variations, independently or in combination, can be used to characterize factors influencing aquifer recharge including source of precipitation, evaporation, and climate/seasonality variation (Machavaram and Krishnamurthy, 1995; Grasby et al., 2000; Chen et al., 2011). Due to the correlation between enriched $\delta$ values and higher temperatures, seasonal differences in $\delta^{18}$O and $\delta^{2}$H values may be observed in surface water and the shallow unsaturated zone; however aquifer mixing ensures that most groundwater samples are representative of average annual precipitation (Clark and Fritz, 1997).

A very useful tool for studying surface water-groundwater interactions is the Global Meteoric Water Line (GMWL), defined by Craig (1961) as the predictable relationship between $\delta^{18}$O and $\delta^{2}$H in meteoric water worldwide (Equation 6). This line defines the locus of isotope ratios in global precipitation. A better approach to studying regional hydrological problems is to use the Local Meteoric Water Line (LMWL) and investigate how it compares with the GMWL (Kendall and Coplen, 2001; Murad and Krishnamurthy, 2008). For example, in the study area of this research, the LMWL (Equation 7) defined by Machavaram and Krishnamurthy (1994), is more pertinent than the GMWL. It must be noted that in most temperate climates, the two lines do not deviate much.
The deuterium excess (d), defined by the rearrangement of the GMWL equation (Equation 8), shows potential in quantifying the influence of regional water bodies on precipitation (Dansgaard, 1964; Gat et al., 1994; Machavaram and Krishnamurthy, 1995). The d-excess is controlled by physical conditions such as humidity, air temperature, and water body temperature (Merlivat and Jouzel, 1979). Evaporation from the ocean, when humidity is less than 100%, is reflected in the d-excess of water vapor and subsequent precipitation. Most evaporation in the ocean occurs when the humidity is greater than 85%, which is why the d-excess for the GMWL is 10‰ (Clark and Fritz, 1997). Water vapor that undergoes a secondary process, such as evaporation from a lake, becomes more depleted and the resulting d-excess value in precipitation increases (Ziegler et al., 1989; Machavaram and Krishnamurthy, 1995).

\[
d = \delta^2H - (8 \times \delta^{18}O)
\]

Nitrogen Isotopes

Nitrogen in the subsurface can follow multiple pathways (Figure 8), including nitrogen fixation, nitrification, and denitrification. Common anthropogenic sources of nitrogen in an aquifer include landfill leachate, septic and manure effluent, and leaching from fertilizers. Nitrogen isotopes can provide valuable information when tracing the source of NO$_3^-$ or NH$_4^+$ in an aquifer (Aravena et al., 1993; Böhlke et al., 2006; Hinkle et al., 2007). Tracing nitrogen sources with stable isotopes requires a sound understanding
of potential fractionation processes and should be paired with other lines of evidence.

Values of $\delta^{15}$N-$\text{NH}_4^+$ from animal manure are enriched (+10‰ to +25‰) due to the preferential removal of the lighter $^{14}$N through ammonia volatilization (Figure 9) (Karr et al., 2002). Ammonium generated by DRNA will be isotopically depleted due to the preferential use of $^{14}$N (Lehmann et al., 2003). Ammonium generated by nitrogen fixation will have $\delta^{15}$N values ranging from -3 to +1‰ (Kendall et al., 2007). A small amount of fractionation occurs when $N_{\text{organic}}$ undergoes ammonification and produces $\text{NH}_4^+$. Böhlke et al. (2002) reported $\delta^{15}$N values of +2‰ to +7‰ for $\text{NH}_4^+$ produced from organic matter overlying a karst aquifer.

Figure 9. Expected range of $\delta^{15}$N-$\text{NH}_4^+$ values for different sources of $\text{NH}_4^+$ (Modified from Lindenbaum, 2012). Data collected from Heaton (1986), Böhlke et al. (2002), Robertson et al. (2012), Karr et al. (2002), and Kendall et al. (2007).

Values of $\delta^{18}$O-$\text{NO}_3^-$ are a useful tool when studying the source of $\text{NO}_3^-$, especially when biologically and synthetically produced fertilizers are a potential source. Oxygen in synthetic fertilizer primarily originates from atmospheric $O_2$ while most of the oxygen in mineralized fertilizer comes from water (Figure 10). The combination of $\delta^{15}$N and $\delta^{18}$O is also beneficial when tracing denitrification in groundwater (Aravena and
Robertson, 1998).

Figure 10. Relationship between δ\textsuperscript{15}N and δ\textsuperscript{18}O from NO\textsubscript{3}\textsuperscript{-} (Modified from Clark and Fritz, 1997). Data from this study (sampling locations W-9 through W-11) are included.

Tritium

The unstable hydrogen isotope, tritium (\textsuperscript{3}H), has a half-life of 12.32 years and decays to \textsuperscript{3}He (Lucas and Unterweger, 2000). Tritium levels are recorded in tritium units (TU), which is equal to 1 tritium atom for every 10\textsuperscript{18} atoms of hydrogen (Harteck, 1954). Natural levels of tritium are generally low (<10 TU), but between 1952 and 1963, a large amount of tritium was released into the hydrologic cycle due to aboveground nuclear weapon testing (Fetter, 1988). Tritium levels in precipitation peaked around 1963.
Values between 1,000 and 6,000 TU were recorded in Ottawa, Canada (Clark and Fritz, 1997). Tritium is commonly used to assess the age of groundwater because of the widespread anthropogenic input of the radioisotope over a limited time. According to Clark and Fritz (1997), the following TU values can be applied to continental regions, however current values have decreased by 1.5 times the half-life from 1997 to 2013:

- <0.8 TU: Submodern recharge before 1952
- 0.8 to ~4 TU: Mixture between submodern and recent recharge
- 5 to 15 TU: Modern (<5 to 10 years)
- 15 to 30 TU: Some “bomb” $^3$H present
- >30 TU: Considerable component of recharge from 1960s or 1970s
- >50 TU: Dominated by 1960s recharge

Assuming an initial activity ($A_o$) of 7.87 TU used by Clark and Fritz (1997) for 1952, submodern recharge before 1952 would have a final activity ($A$) of less than 0.23 TU (Equation 9). $T$ is the half-life of $^3$H while $t$ is the number of years elapsed since nuclear weapons testing began (1952 to 2013). The detection limit for $^3$H using gas proportional counting is around 0.05 TU (Povinec, 2010).

$$A = A_o 2^{-t/T} \quad \text{Eq. 9}$$

$^{14}$C Dating CH$_4$

The production of in situ CH$_4$ can occur along two biotic pathways, CO$_2$ reduction (Equation 10) and acetate fermentation (Equation 11). In Illinois, CH$_4$ produced from buried organics has had an economic value (Meents, 1960). Work by Parkin and Simpkins (1995) and Simpkins and Parkin (1993) showed that CH$_4$ production in glacial drift correlates to the distribution of buried organic carbon. A
limitation with radiocarbon dating CH\textsubscript{4} is that it generally does not originate near the recharge area of an aquifer and under most conditions cannot be used as a conservative tracer for calculating residence time. Therefore, \(^{14}\text{C}-\text{CH}_4\) only provides information about the age of the carbon from which the CH\textsubscript{4} originated (Aravena and Wassenaar, 1993). The mean life of \(^{14}\text{C}\) is 8,266.6 years, which limits the application to <50,000 years. In a study by Aravena and Wassenaar (1993) on the Alliston aquifer in southern Ontario, Canada, \(^{14}\text{C}-\text{CH}_4\) ages range from 15,000 to 44,000 yr B.P., proving that the CH\textsubscript{4} is not of bedrock thermocatalytic origin; otherwise the CH\textsubscript{4} would have no detectable carbon. Methane dates from the Alliston aquifer can be divided into two age groups, one group that correlates with peat from the Plum Point Interstade, while the second group correlates to peat from the Port Talbot Interstade (Karrow, 1984; White, 1975).

\begin{align*}
\text{CO}_2 + 4\text{H}_2 &\rightarrow \text{CH}_4 + 2\text{H}_2\text{O} & \text{Eq. 10} \\
\text{CH}_3\text{COOH} &\rightarrow \text{CH}_4 + \text{CO}_2 & \text{Eq. 11}
\end{align*}

**RESEARCH OBJECTIVES**

The first goal of this research is to characterize the glacial drift stratigraphy of the study site, locate buried organic material, and identify the characteristics of the impacted aquifer system (i.e. confined or unconfined). The second goal is to determine the source of NH\textsubscript{4}\textsuperscript{+} by using multiple geochemical and isotopic parameters to better understand the subsurface redox environment and temporal aquifer recharge process.
METHODS

Investigation into the source of NH$_4^+$ in the groundwater at Hemlock Crossing Park and the nearby surrounding area was achieved through three methods: 1) characterization of glacial sediment, 2) geochemical analyses of the groundwater, 3) a multi-isotopic investigation into aquifer recharge and potential NH$_4^+$ sources.

Glacial Sediment Characterization

Buried organics are commonly reported in water well logs in Ottawa County, however the precise depth of buried organic matter varies with each log. Rotasonic drilling allows for nearly complete recovery of the strata and has been used recently by others in Michigan and elsewhere to study glacial stratigraphy (Barnes, 2007; Woolever, 2008; Kehew et al., 2012).

A complete glacial sediment core (OT-12-01) was collected from Hemlock Crossing Park in July 2012 using the rotasonic method (Figure 11). With the help of Mr. John Esch of the Michigan DEQ, a gamma ray log of the boring was recorded using a Mt. Sopris MGXII with a 2PGA Gamma Sonde. Gamma rays originate from the radioactive decay of uranium, thorium, potassium, and many other radioisotopes. Minerals in clay, particularly feldspar, emit gamma rays during the primary decay of $^{40}$K. Sand and gravel units do not generally emit a strong gamma ray signature because they are dominated by quartz. This allows a gamma ray log to differentiate between clay-rich and sand layers.
Due to borehole collapse and swelling clays, a gamma ray log is useful for correcting the depth of layer boundaries in a rotasonic core.

![Figure 11. Recovery of a glacial sediment core via rotasonic drilling. Drilling method vibrates the casing into the ground at a high frequency without the use of an auger.](image)

After core OT-12-01 was collected, a monitoring well (W-1) was installed in the borehole. A 5.1 cm polyvinyl chloride (PVC) well was set between 18.29 and 21.34 m depth and a sand pack was put in place to filter out fine-grained sediment. The well screen depth was selected so that groundwater below the buried organic material could be sampled. The borehole above and below the sand pack was grouted with bentonite clay. Upon completion, the well was developed with a downhole pump until water ran relatively clear.
With the assistance of Patrick M. Colgan, two sediment samples from 17.37 and 17.83 m depth were collected from an organic rich silt unit and submitted for radiocarbon dating. A wet sample of ~350 to 700 g of sediment was dried at 105°C over a 24-hour period to ensure all moisture in the sediment was removed. Samples were sent to Beta Analytic Radiocarbon Laboratory in Miami, Florida for \(^{14}\)C dating and \(\delta^{13}\)C analysis. Radiocarbon ages were acquired using the accelerator mass spectrometry (AMS) method while \(\delta^{13}\)C analysis was performed with an isotope ratio mass spectrometer and reported relative to Vienna Pee Dee Belemnite (VPBD) (Colgan, 2013a). The sample from 17.83 m did not contain enough organic material for radiocarbon dating (Patrick Colgan, personal communication, 2012). The same procedure was followed for samples that were later collected from the organic rich silt unit.

Description of Grain-Size Analysis

Grain-size analysis was used to characterize the glacial sediments. The following technique was implemented as described by the American Society for Testing and Materials (1970), and was also performed by Barnes (2007), Woolever (2008) and Kehew et al. (2012). Samples from the core were collected every 1.5 m or at a visually obvious change in sediment type. A sample consisting of ~450 g was dried at 105°C over a 24-hour period. If the sample was composed mostly of fines (silt and clay), the sample underwent wet sieving (described below). Samples composed mostly of coarse material (sand and gravel) were processed using dry sieving techniques. The following
steps were taken to complete dry sieving:

1. After drying for 24 hours, the sample was disaggregated carefully with a mortar and pestle, and a new weight (dry weight) was recorded.

2. The sample was then placed in a stack of sieves, in the order of #10, #18, #35, #60, #120, #230, with a pan at the bottom (Figure 12). After pouring the sample into the coarsest sieve (#10), a lid was placed on top to ensure that no fine particles escaped during shaking.

3. The stack of sieves was put in a sieve shaker device, where it was shaken for 10 minutes.

4. The weight of sediment collected in each pan was recorded. Fine material collected in the bottom pan was used for silt/clay separation, which is described in detail below.

<table>
<thead>
<tr>
<th>Particle Length</th>
<th>Sieve Size ASTM No. (U.S. Standard)</th>
<th>Grade</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>mm</td>
<td>5</td>
<td>granules</td>
<td>Pebbles</td>
</tr>
<tr>
<td>4.0</td>
<td>10</td>
<td>very coarse</td>
<td>Sand</td>
</tr>
<tr>
<td>2.0</td>
<td>18</td>
<td>coarse</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>35</td>
<td>medium</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>60</td>
<td>fine</td>
<td></td>
</tr>
<tr>
<td>0.250</td>
<td>120</td>
<td>very fine</td>
<td></td>
</tr>
<tr>
<td>0.125</td>
<td>230</td>
<td>coarse</td>
<td></td>
</tr>
<tr>
<td>0.063</td>
<td>Pan</td>
<td>medium</td>
<td>Silt</td>
</tr>
<tr>
<td>0.031</td>
<td></td>
<td>fine</td>
<td></td>
</tr>
<tr>
<td>0.015</td>
<td></td>
<td>very fine</td>
<td></td>
</tr>
<tr>
<td>0.008</td>
<td></td>
<td>Coarse</td>
<td></td>
</tr>
<tr>
<td>0.004</td>
<td></td>
<td>Fine</td>
<td></td>
</tr>
<tr>
<td>0.002</td>
<td></td>
<td>Very fine</td>
<td>Clay</td>
</tr>
</tbody>
</table>

Figure 12. Scale for sediment grain-size. Distribution given in phi (Ø) units, sieve sizes, and Wentworth classes (Modified from USGS, 2006).

The following steps were taken to complete wet sieving for samples that were
dominated by fine material (clay and silt sized):

1. After drying for 24 hours, a new weight (dry weight) was recorded, and the disaggregated sample was wetted in a beaker with tap water.

2. The slurry sample was washed through a #230 sieve with a pan underneath. This was done to separate fines from coarser material.

3. The slurry that pooled in the bottom pan was comprised of the silt and clay portion of the sample. Material that collected in the sieve made up the coarse fraction of the sample.

4. Contents from the sieve and bottom pan were washed into two separate pans and then dried at 105°C for 24 hours. Dried coarse material underwent dry sieving, as explained in the previous section.

5. Dried fine material, which collected in the bottom pan, was mixed with the fine material collected during dry sieving. This material was used for clay/silt separation.

Separation of silt and clay was performed using the gravitational sedimentation method. According to Stoke’s law, after a 2-hour period at 20°C, clay-sized grains remain suspended while silt-sized grains settle from a height of 10 cm (Hillel, 1998; Boggs, 1995). A 10 g sample of fine material was put in a 1 L beaker, which was then filled to 700 mL with a 0.5% alkaline solution so that the sediment slurry reached a height of 10 cm. The solution contained 20 g of sodium hexametaphosphate, which assisted in deflocculating clay particles (Hillel, 1998). The sample was agitated by ultrasonic vibrations for 20 minutes and then allowed to settle for 2 hours (Beukema, 2003). After the 2-hour settling period, the solution containing the clay was extracted
and placed in a pre-weighed tray while the silt was washed out of the beaker into another pre-weighed tray. Both trays were dried over a 24-hour period and changes in weight for each tray were recorded. The additional weight in each tray represents the percent of clay and silt in a sample.

Groundwater Chemistry and Isotope Analysis

Groundwater samples were collected from wells W-1 through W-14 for analysis of an array of parameters (Figure 13). Well W-1 was a monitoring well installed after the recovery of core OT-12-01. Wells W-2 and W-3 supply water to the Hemlock Crossing Nature Center and parking lot restroom, respectively. Wells W-4 through W-11 are residential wells located throughout the study area. Wells W-12 through W-14 were shallow hand augured wells located near well W-1. Wells were analyzed for a combination of CH$_4$, DOC, alkalinity, and a suite of common ions, including Fe$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, NH$_4^+$, Na$^+$, K$^+$, SO$_4^{2-}$, NO$_3^-$, and Cl$^-$. Select wells were also analyzed for $\delta^{18}$O/$\delta^2$H, $^3$H, $\delta^{15}$N-NH$_4$, $\delta^{15}$N/$\delta^{18}$O-NO$_3$, and $^{14}$C-CH$_4$. 


Figure 13. Sampling locations.

Well Sampling

Wells W-1 through W-6 and W-8 were selected to define conditions for the confined aquifer system in contact with buried organic material. Well logs show a 3.66 to 19.2 m thick confining clay unit above the aquifer system. Well W-7 was sampled to determine conditions in an unconfined aquifer right above the glacial till. Wells W-9 through W-11 are screened in a shallow unconfined aquifer downgradient of agricultural
fields and were sampled to create a baseline for agriculturally influenced $\delta^{15}$N values. Wells W-12 through W-14 are screened near the surface of a shallow unconfined aquifer and were sampled for $\delta^{18}$O/$\delta^2$H analyses of recent groundwater recharge. A summary of sampled wells and well logs can be found in Table 1 and Appendix A, respectively.

Before sample collection, well W-1 was pumped for 30 minutes with a submersible pump to ensure that samples were representative of in situ groundwater conditions. Outdoor faucets from wells W-2 through W-11 were run for 20 minutes. Pumping was reduced to the lowest setting possible during sample collection. Prior to residential well sampling, owners were asked if outdoor faucets bypassed any water treatment systems (i.e. water softener). Wells W-12 through W-14 were purged by bailing 3 well volumes of water with a plastic bailer.

Table 1
Summary of sampled wells

<table>
<thead>
<tr>
<th>Well #</th>
<th>Type</th>
<th>Screened Interval (m depth)</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-1</td>
<td>Monitoring</td>
<td>18.29 – 21.34</td>
<td>Common Ions, DOC, CH$_4$, $\delta^{18}$O/$\delta^2$H, $^3$H, $\delta^{15}$N-NH$_4$, $^{16}$C-CH$_4$</td>
</tr>
<tr>
<td>W-2</td>
<td>Public II</td>
<td>14.63 – 16.15</td>
<td>Common Ions, DOC, CH$_4$, $\delta^{18}$O/$\delta^2$H, $^3$H, $\delta^{15}$N-NH$_4$</td>
</tr>
<tr>
<td>W-3</td>
<td>Public II</td>
<td>17.37 – 20.42</td>
<td>Common Ions, DOC, CH$_4$, $\delta^{18}$O/$\delta^2$H, $^3$H, $\delta^{15}$N-NH$_4$</td>
</tr>
<tr>
<td>W-4</td>
<td>Residential</td>
<td>26.82 – 29.87</td>
<td>Common Ions, DOC, CH$_4$, $\delta^{18}$O/$\delta^2$H, $^3$H, $\delta^{15}$N-NH$_4$</td>
</tr>
<tr>
<td>W-5</td>
<td>Residential</td>
<td>24.99 – 28.04</td>
<td>Common Ions, DOC, $\delta^{18}$O/$\delta^2$H</td>
</tr>
<tr>
<td>W-6</td>
<td>Residential</td>
<td>18.9 – 23.77</td>
<td>Common Ions, DOC, $\delta^{18}$O/$\delta^2$H</td>
</tr>
<tr>
<td>W-7</td>
<td>Residential</td>
<td>9.75 – 12.8</td>
<td>Common Ions, DOC, $\delta^{18}$O/$\delta^2$H</td>
</tr>
</tbody>
</table>
Common Ions, DOC, $\delta^{18}$O/$\delta^2$H

<table>
<thead>
<tr>
<th>Location</th>
<th>Type</th>
<th>Range</th>
<th>Inclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-8</td>
<td>Residential</td>
<td>27.13 – 30.18</td>
<td>Common Ions, DOC, $\delta^{18}$O/$\delta^2$H</td>
</tr>
<tr>
<td>W-9</td>
<td>Residential</td>
<td>8.53 – 12.19</td>
<td>Common Ions, $\delta^{18}$O/$\delta^2$H, $\delta^{15}$N/$\delta^{18}$O-NO$_3$</td>
</tr>
<tr>
<td>W-10</td>
<td>Residential</td>
<td>7.62 – 8.99</td>
<td>Common Ions, $\delta^{18}$O/$\delta^2$H, $\delta^{15}$N/$\delta^{18}$O-NO$_3$</td>
</tr>
<tr>
<td>W-11</td>
<td>Residential</td>
<td>7.62 – 8.53</td>
<td>Common Ions, $\delta^{18}$O/$\delta^2$H, $\delta^{15}$N/$\delta^{18}$O-NO$_3$</td>
</tr>
<tr>
<td>W-12</td>
<td>Temporary</td>
<td>1.37 – 2.9</td>
<td>Common Ions, $\delta^{18}$O/$\delta^2$H</td>
</tr>
<tr>
<td>W-13</td>
<td>Temporary</td>
<td>1.52 – 2.44</td>
<td>Common Ions, $\delta^{18}$O/$\delta^2$H</td>
</tr>
<tr>
<td>W-14</td>
<td>Temporary</td>
<td>1.37 – 2.9</td>
<td>Common Ions, $\delta^{18}$O/$\delta^2$H</td>
</tr>
</tbody>
</table>

Field Parameters

Conductivity and pH were recorded using a Myron Company Ultrapen and HUNNA pHep hand held meter, respectively. Static water level readings were also recorded at W-1 before and after pumping events, using a water level tape. To decrease the likelihood of cross contamination, all sampling instruments were rinsed with ultrapure water ($\geq$18 megaOhM) between sampling locations.

Common Ions

Samples were collected in 50 mL plastic centrifuge vials. Two ion samples were collected at each well, one of which was preserved with four drops of concentrated HNO$_3$. With the exception of CH$_4$, H$_2$S, $^3$H, $\delta^{18}$O/$\delta^2$H, and $^{14}$C-CH$_4$, all samples were field filtered with a 0.45 $\mu$m syringe filter and refrigerated until analyses were performed. Analyses for common ions were carried out at the Western Michigan University Geochemistry Lab. UV-Vis spectrophotometry was used to quantify alkalinity (1.33 mg/L), H$_2$S (0.56 mg/L), NH$_4^+$ (1 mg/L), and Fe$^{2+}$ (0.2 mg/L) concentrations; detection
limits in brackets. Non-acidified samples were analyzed for total alkalinity concentrations on the day of sampling using the bromophenol blue method (Sarazin et al., 1998). For H₂S analysis, 5 mL plastic vials were pre-treated with a trap solution to prevent H₂S from oxidizing. Sulfide concentrations were obtained using the methylene blue method (Grasshoff et al., 1983). Non-acidified samples were analyzed for NH₄⁺ by following the indophenol blue method described by Grasshoff et al. (1983). Acidified samples were analyzed for Fe²⁺ using the FerroZine method (Stookey, 1970). All UV-Vis analyses were performed within 48 hours of sample collection. After prepping acidified samples with 1000 µg/L yttrium international standard, Ca, Mg, Na, K concentrations were determined using a Perkin Elmer ICP-OES. The reporting limit for parameters run on the ICP is 0.5 mg/L. Acidified samples were run for SO₄²⁻ (0.48 mg/L), NO₃⁻ (0.46 mg/L) and Cl⁻ (0.42 mg/L) on a Dionex ion chromatograph (IC); detection limits in brackets. Samples run on the ICP-OES and IC were frozen until analysis was performed.

Methane

Samples analyzed for CH₄ were collected in 40 mL glass VOA vials with zero headspace. Vials were preserved with concentrated HCl to a pH of <2. ALS Environmental Labs in Holland, Michigan performed the CH₄ analysis. Concentrations were determined using United States EPA approved method RSK 175 with a detection limit of 0.38 µg/L.
DOC

Samples analyzed for DOC were collected in 250 mL amber glass jars and acidified with concentrated H\textsubscript{2}SO\textsubscript{4} to a pH of <2. DOC analysis was performed at KAR Labs in Kalamazoo, Michigan. Concentrations were acquired using United States EPA approved method SM 5310 C with a detection limit of 1 mg/L.

δ\textsuperscript{18}O and δ\textsuperscript{2}H

Samples analyzed for δ\textsuperscript{18}O and δ\textsuperscript{2}H were collected in an 8 mL glass vial and sent to Isotech Laboratories in Champaign, Illinois. Analysis was performed by CRDS (cavity ring-down spectroscopy), with an error of ± 0.3‰ δ\textsuperscript{18}O and ± 1.0‰ for δ\textsuperscript{2}H. Samples were re-analyzed at the Western Michigan University Stable Isotope Laboratory, using similar methods.

Tritium

Tritium samples were collected in 1 L HDPE plastic bottles and analyzed by the University of Miami Tritium Laboratory using methods described by Östlund (1987) for gas proportional counting. The accuracy of this method is ± 0.09 TU.

Nitrogen Isotopes

For δ\textsuperscript{15}N-NH\textsubscript{4} analysis, 100 mL of sample was collected in a HDPE plastic bottle and acidified to a pH of 4-5 with concentrated H\textsubscript{2}SO\textsubscript{4}. Samples were frozen and analyzed
using methods provided by Brooks et al. (1989). For $\delta^{15}\text{N} / \delta^{18}\text{O}$-NO$_3$ analysis, 750 mL of sample was collected in a 1 L plastic bottle and acidified to a pH of 3-5 with concentrated HCl. Samples were frozen and analyzed using methods provided by Silva et al. (2000). All nitrogen isotope analyses were performed at the University of Waterloo Environmental Isotope Laboratory.

$^{14}\text{C}$-CH$_4$

A single groundwater sample was collected from well W-1 for $^{14}\text{C}$ analysis. After purging the well for 30 minutes, a 5-gallon bucket was filled with groundwater. Pumping was then turned to the lowest setting and a 1 L plastic bottle was filled with water. Keeping the hose inserted into the bottle, the container was inverted and submerged in the 5-gallon bucket until 2 volumes of water was displaced from the sample bottle. While underwater, the tube was removed and a cap with a bactericide capsule was screwed onto the bottle. After taping around the cap, the bottle was shipped upside down to Isotech Laboratories where the dissolved CH$_4$ was combusted to CO$_2$. Before combustion, the dissolved gas composition was analyzed using a gas chromatograph. The CO$_2$ sample was then sent to DirectAMS in Bothell, Washington for $^{14}\text{C}$ analysis using AMS dating methods.

RESULTS AND DISCUSSION

Glacial Geology
Core OT-12-01 was collected from Hemlock Crossing Park with the intent of acquiring a complete record of glacial sediment from the subsurface. Drilling of the core tagged the Coldwater Shale bedrock at 39.32 m depth. In Figure 14, the core is described by lithology, gamma log, grain size distribution, and the setting of well W-1. Results of individual sieve tests can be found in Table 2 and Appendix B.

**OT-12-01 Core Description**

The surface unit (Unit 1) consists of yellowish brown (Munsell soil color 10YR 5/4) lacustrine sand and extends to a depth of 3.35 m depth. The sand is saturated below 1.5 m depth. The average grain-size distribution is 2.2% gravel (4 to 2 mm), 96% sand (<2 mm), 1.5% silt, and 0.4% clay (Table 2). A dark gray (Munsell soil color 5Y 4/1) clayey silt unit (Unit 2) extends from 3.35 m to 5.79 m depth and had a high plasticity when removed from the ground. Unit 2 has a grain-size distribution of 11.8% sand (<2 mm), 71.6% silt, and 16.6% clay (Table 2). Sandy silt pockets a few centimeters in diameter are present throughout the layer.

A bluish gray (Munsell soil color 5BG 5/1) diamicton layer is present from 5.79 to 13.41 m depth. The diamicton layer is significantly more brittle than Unit 2, and shale clasts (5 to 30 mm) are present throughout. The diamicton layer has been tentatively divided into two units (3 and 4) at 10.36 m depth based on changes in sediment color, size and frequency of clasts; however there is no clear contact boundary. The grain-size distribution for Unit 3 is 1.4% gravel (4 to 2 mm), 14.9% sand (<2 mm), 42% silt, and 41.8% clay, while the distribution for Unit 4 is 1.7% gravel (4 to 2 mm), 27% sand (<2
mm), 35.1% silt, and 36.3% clay (Table 2). Pink clasts, 5 to 10 cm long, are intermittent through Unit 3. There are occasional pinkish-red fine-grained inclusions (3 to 4 mm) in Unit 3.

An organic-rich silt layer (Unit 6) is present from 15.85 to 18.9 m depth. A 0.6 m sand lens, possibly from borehole collapse during drilling, is present in the bottom half of the organic-rich silt layer. The grain-size distribution for Unit 6 is 39.9% sand (<2 mm), 42.3% silt, and 17.8% clay (Table 2). The top of the unit is very dark grayish brown (Munsell soil color 2.5Y 3/2) and compacted; then transitions to black (Munsell soil color 5Y 2/2) organic-rich sandy silt that easily breaks apart. Highly abraded wood slivers (≤10 mm) occur from 16.46 to 17.37 m depth and ostracod shells (≤3 mm) are present from 16.76 to 17.37 m depth. The organic-rich silt layer is bound above by 2.44 m of sand (Unit 5) and below by 1.83 m of sand (Unit 7). The grain-size distribution for the fining upward Unit 5 is 0.1% gravel (4 to 2 mm), 90.1% sand (<2 mm), 7.9% silt, and 1.9% clay, while the distribution for Unit 7 is 0.5% gravel (4 to 2 mm), 96.9% sand (<2 mm), 2.3% silt, and 0.3% clay (Table 2). Both dark yellowish brown (Munsell soil color 10YR 4/4) lacustrine sand layers are well sorted and were saturated when removed from the ground.

A compact diamicton (Unit 8) is present from 20.73 to 26.82 m depth. The unit gradually transitions from gray (Munsell soil color 5Y 5/1) to reddish brown (Munsell soil color 5YR 5/3) with depth. Gray rock clasts up to 50 mm are present in the upper 1.4 m of the section while small gray rock clasts (<5 mm) are dominant throughout the remainder of the diamicton. The grain-size distribution for Unit 8 is 4.7% gravel (4 to 2
mm), 31.3% sand (<2 mm), 36.9% silt, and 27% clay (Table 2).

From 26.82 to 28.96 m depth, a uniform, brown (Munsell soil color 10YR 5/3) silty sand section (Unit 9) is present. The grain-size distribution for Unit 9 is 50.4% sand (<2 mm), 42.2% silt, and 7.3% clay. The final layer is a dark reddish brown (Munsell soil color 5YR 3/2) diamicton (Unit 10) from 28.96 to 39.32 m depth. A 0.26 m lens of sand is present near the middle of the diamicton. Rock clasts <30 mm are present in the upper 7.3 m while larger rock clasts (50 to 90 mm) are prevalent in the lower 2.7 m of the diamicton. The grain-size distribution for Unit 10 is 8.7% gravel (4 to 2 mm), 44% sand (<2 mm), 30.7% silt, and 16.6% clay (Table 2). There are no obvious weathering or carbonate-leached zones below Unit 7. Coldwater Shale is present beneath Unit 10. The upper 0.7 m of bedrock is highly eroded and saturated.

Table 2

Textural results for OT-12-01

<table>
<thead>
<tr>
<th>Unit</th>
<th>Description</th>
<th># of Samples</th>
<th>Depth (m)</th>
<th>Thickness</th>
<th>Gravel</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sand</td>
<td>3</td>
<td>0 - 3.35</td>
<td>3.35</td>
<td>2.2</td>
<td>96.0</td>
<td>1.5</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>Silt</td>
<td>2</td>
<td>3.35 - 5.79</td>
<td>2.44</td>
<td>0</td>
<td>11.8</td>
<td>71.6</td>
<td>16.6</td>
</tr>
<tr>
<td>3</td>
<td>Diamicton</td>
<td>3</td>
<td>5.79 - 10.36</td>
<td>4.57</td>
<td>1.4</td>
<td>14.9</td>
<td>42.0</td>
<td>41.8</td>
</tr>
<tr>
<td>4</td>
<td>Diamicton</td>
<td>2</td>
<td>10.36 - 13.41</td>
<td>3.05</td>
<td>1.7</td>
<td>27.0</td>
<td>35.1</td>
<td>36.3</td>
</tr>
<tr>
<td>5</td>
<td>Sand</td>
<td>3</td>
<td>13.41 - 15.85</td>
<td>2.44</td>
<td>0.1</td>
<td>90.1</td>
<td>7.9</td>
<td>1.9</td>
</tr>
<tr>
<td>6</td>
<td>Organic rich</td>
<td>4</td>
<td>15.85 - 18.9</td>
<td>3.05</td>
<td>0</td>
<td>51.1</td>
<td>34.4</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>silt</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Sand</td>
<td>1</td>
<td>18.9 - 20.73</td>
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<td>0.5</td>
<td>96.9</td>
<td>2.3</td>
<td>0.3</td>
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<tr>
<td>8</td>
<td>Diamicton</td>
<td>4</td>
<td>20.73 - 26.82</td>
<td>6.09</td>
<td>4.7</td>
<td>31.3</td>
<td>36.9</td>
<td>27.0</td>
</tr>
<tr>
<td>9</td>
<td>Silty Sand</td>
<td>1</td>
<td>26.82 - 28.96</td>
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<td>0</td>
<td>50.4</td>
<td>42.2</td>
<td>7.3</td>
</tr>
<tr>
<td>10</td>
<td>Diamicton</td>
<td>7</td>
<td>28.96 - 39.32</td>
<td>10.36</td>
<td>10.8</td>
<td>47.5</td>
<td>27.2</td>
<td>14.6</td>
</tr>
</tbody>
</table>
Figure 14. Boring log of OT-12-01.
OT-12-01 Interpretation

Below the surficial lacustrine sand layer (Unit 1), glaciolacustrine clayey silt (Unit 2) is interpreted to be an offshore deposit of Glacial Lake Chicago. The surface elevation of Glacial Lake Chicago varied from 202 m during the Glenwood I level (15,500 to 15,000 $^{14}$C yr B.P.) to 184 m during the Toleston level (approximately 11,000 $^{14}$C yr B.P.) (Patrick Colgan, personal communication, 2013). The surface elevation of Unit 2 is 179 m, making it difficult to determine during which stage the sediment was deposited. Due to the absence of a sharp contact, Unit 2 was likely deposited during a single stage of Lake Chicago.

The diamicton unit between 5.79 and 13.41 m depth is tentatively correlated to the Saugatuck (Unit 3) and Ganges (Unit 4) tills, due to their position above organic material (Unit 6) similar to that of the Glenn Shores section (Monaghan et al., 1986); however the contact location between the two tills remains a question. Former work by Monaghan et al. (1986) on the Glenn Shores section, Wong (2002) in Allegan County, and Beukema (2003) in Van Buren County, were unable to distinguish between the Saugatuck and Ganges till based solely on grain-size analysis (Figures 15 and 16).

Using X-ray diffraction analysis, differences between the Saugatuck and Ganges tills were established by 7/10Å ratios in clay (Monaghan et al., 1986; Wong, 2002; and Beukema, 2003). Based upon their work, the expected range in 7/10Å ratios for the Saugatuck and Ganges tills are 0.32 to 0.67 and 0.64 to 0.91, respectively. Preliminary work (Colgan, unpublished data, 2013) shows that most of the diamicton above the
organic rich silt probably correlates to the Ganges till with 7/10Å ratios of 0.75 to 1.0, n = 7. A thin layer (<1.5 m) just below Unit 2 may relate to the Saugatuck till (7/10Å ratios of <0.70, n = 2); however, more work is needed to conclude whether the thin layer is glacial till or lacustrine clay (Patrick Colgan, unpublished data, 2013). It is entirely possible that the Saugatuck till is missing since there is no lacustrine sand layer in between the two units as seen in the Glenn Shores section.

Figure 15. Comparison of grain-size distribution for the Saugatuck till. Data compiled from Monaghan et al. (1986), Wong (2002), Beukema (2003), and this study. Values from this study do not include the gravel fraction (≥2mm).
Below the upper till(s), an organic-rich silt layer (Unit 6) is bounded by well-sorted lacustrine sand (Unit 5 and 7). The surface elevation for Unit 6 is 166.4 m, which is similar to the elevation of buried organic material (167 to 168 m) in nearby Holland (Rieck and Winters, 1980). Dr. Brandon Curry of the Illinois State Geological Survey identified material from aquatic plants and ostracod shells, but was unable to determine any species (Figure 17) (Patrick Colgan, personal communication, 2013). Two samples of organic fragments, taken from a depth of 15.87 m and 17.37 m, were dated at 43,630-45,940 and 41,920-42,950 cal. yr B.P. (two sigma error), respectively (Colgan, 2013a; Colgan, unpublished data). A third sample, from 18.37 m depth, yielded a non-finite age of >43,500 cal. yr B.P. (Colgan, unpublished data). The two lacustrine sand layers, with an interbedded organic rich silt layer, could be indicative of changes in the elevation of a local lake. Buried organic matter (>36,000 and >40,000 ¹⁴C yr B.P.) from the John Ball Park section (approximately 37 km to the west of Hemlock Crossing Park) was
interpreted as being deposited in a small lake basin (Zumberge and Benninghoff, 1969). Samples that were submitted for $^{14}$C analysis had $\delta^{13}$C values of -26.7‰ (15.87 m depth), -23.0‰ (17.37 m depth), and -29.7‰ (18.37 m depth) (Colgan, unpublished data, 2012; 2013). According to Troughton et al. (1975), typical $\delta^{13}$C values for C$_3$ and C$_4$ plants are -28.1 ± 2.5‰ and -13.5 ± 1.5‰, respectively. Cool and temperate climates with high CO$_2$ concentrations favor C$_3$ over C$_4$ plant growth (Ehleringer and Björkman, 1977).

Figure 17. Organic material from OT-12-01. Individual wood fragments (left) and organic-rich silt (right).

Below the lacustrine sand and organic-rich silt, a compact diamicton (Unit 8) is tentatively correlated to the Glenn Shores till, due to its stratigraphic position below Unit 6. Monaghan et al. (1986) reported a Glenn Shores till grain-size distribution of 46% sand (<2 mm), 34% silt, and 20% clay, which is similar to the textural analysis from this study (Figure 18). Preliminary clay 7/10Å ratios (Colgan, unpublished data, 2013) for Unit 8 vary from 1.0 to 1.4 (n = 6) and correlate to the mean clay 7/10Å ratio of 1.22 for
the Glenn Shores till (Monaghan et al., 1986). Due to positioning of the Glenn Shores till below organic material from an ice-free Athens subepisode, the till has to have been deposited during the Ontario subepisode or Illinoian Episode (Monaghan, 1990). Unit 8 could correlate to the upper Winnebago Formation in Illinois (Figure 19). Separating the Glenn Shores till and the lowest till layer (Unit 10) is a cemented silty sand layer (Unit 9). The layer has occasional shale clasts (2 to 3 mm), reacts with acid, and does not have any white secondary precipitation; ruling out a loess or paleosol deposit. While Unit 9 does not have any visible laminations, it is a possible lacustrine or fluvial deposit.

The basal diamicton (Unit 10) has been interpreted as a separate till from the Glenn Shores till based upon the presence of Unit 9, differences in physical properties (color, clast frequency, and clast size) between the two tills, and a much higher 7/10Å ratio (1.4 to 2.0, n = 9) (Colgan, unpublished data, 2013). The unnamed till could correlate to either the lower Winnebago or Glasford Formations in Illinois.

Based upon similar 7/10Å ratios, Monaghan et al. (1986) correlated the Saugatuck (Unit 3) and Ganges (Unit 4) tills to the Wadsworth and upper Yorkville members of the Wedron Group in Illinois. The Robein Silt separates the Wedron Group (25,000 to 12,000 $^{14}$C yr B.P.) and underlying Winnebago and Glasford Formations (180 to 125 ka) (Soller et al., 1999).
Figure 18. Comparison of grain-size distribution for the Glenn Shores and unnamed tills.
Data compiled from Monaghan et al. (1986) and this study.

<table>
<thead>
<tr>
<th>~Age (cal. yr B.P.)</th>
<th>Diachronic Units</th>
<th>Lithostratigraphic Units (Northern Illinois)</th>
<th>Lithostratigraphic Units (Eastern Wisconsin)</th>
<th>Informal Lithostratigraphic Units (Western Michigan)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11,500</td>
<td>Hudson Episode</td>
<td>Two Rivers member</td>
<td>Orchard Beach till</td>
<td>Montague till</td>
</tr>
<tr>
<td></td>
<td>Michigan Subepisode</td>
<td>Manitowoc member</td>
<td>Valders member</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sherrwood member</td>
<td>Ozaukee member</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wadsworth member</td>
<td>Oak Creek Formation</td>
<td></td>
</tr>
<tr>
<td>35,000</td>
<td>Wisconsin Episode</td>
<td>Haeger member</td>
<td>Waubeka member</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yorkville member</td>
<td>New Berlin member</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Malken member</td>
<td>Tiskilwa member</td>
<td></td>
</tr>
<tr>
<td>60,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>128,000</td>
<td>Sangamonian Episode</td>
<td>Sangamon Geosol</td>
<td>Glenn Shores till? (Unit 8)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Capron member</td>
<td>Capron member</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>unamed loess</td>
<td>unamed lacustrine? (Unit 9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Clinton member</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Allens Grove member</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Foxhole member</td>
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</tr>
<tr>
<td>190,000</td>
<td>Illinoian Episode</td>
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<td>Unnamed tills? (Unit 10)</td>
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</tr>
<tr>
<td></td>
<td>Pre-Illinoian Episode</td>
<td>Banner Formation</td>
<td></td>
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</tr>
</tbody>
</table>

Figure 19. Correlation of western Michigan and northern Illinois glacial deposits
(Compiled from Patrick Colgan, personal communication, 2013; Johnson and Hansel, 1990; Lineback et al., 1974; Stiff and Hansel, 2004).
Buried Organic Material

In Port Sheldon and Olive Township, at least 66 water well logs have reported buried organics (Appendix C). The presence of buried organic material in these townships is expected since these locations are within the Grand Haven/Holland cluster of buried organic material (Figure 4). Depth to organics varies between 5.8 and 32 m. Most organic material is interbedded in sand and located below a diamicton layer(s) (Figure 20). Shallow organics above any till layers, are generally reported closer to the Lake Michigan shoreline. Drillers used terms such as peat, wood fragments, muck, and swamp. The reported spatial distribution of buried organics in the region is highly variable because of inconsistencies in interpreting lithology units from water well logs. In Ottawa County, at least 137 well logs report the presence of buried organic material, which may correlate to organic material reported in this study, based upon positioning below till layers from the Michigan subepisode (Colgan, 2013b).
Figure 20. Generalized cross section of area surrounding Hemlock Crossing Park. Confined aquifer system with buried organic material, overlying confining till, and surficial sand are outlined. Elevation in meters above sea level.
Aquifer Characteristics

Due to a lack of monitoring wells available in the study site, the flow direction for groundwater in contact with the organic rich silt layer (Unit 6) was calculated using three nearby water levels from wells screened in the same confined setting. Static water levels were recorded from a cluster of three residential well logs, 2.5 km southwest of Hemlock Crossing Park. All three wells were installed in September 2005. Direction of groundwater flow is to the west-northwest direction. The hydraulic gradient is 0.035 (Appendix D). The gradient value has large error bars, given that the readings were recorded to the nearest foot and that the well casings were not surveyed for proper elevation. Groundwater flow in the study area is upgradient of the Pigeon River and Lake Michigan. Static water level readings for well W-1 varied between 2.68 and 2.73 m depth before purging the well. The average static water level reading for wells W-12 through W-14 was 1.68 m depth, indicating that well W-1 is set in a different aquifer than wells W-12 through W-14.

The hydraulic conductivity (K) was calculated using data from a single well pump test performed in July 2009 at Hemlock Crossing Park by Koops Well Drilling in Holland, Michigan (OCHD, unpublished data). Using the Cooper-Jacob method (Equation 12), a transmissivity (T) of 18.11 m²/day was calculated using a pumping rate (Q) of 0.00378 m³/s (Figure 21). The pump test occurred in a 3.05 m thick sand layer (Unit 7) and a K of 5.94 m/day was estimated from the test. Typical hydraulic conductivity values for unconsolidated Quaternary sand are on the order of 1 to 100
m/day (Younger, 2006).

\[ T = \frac{(2.3Q)}{(4\pi\Delta S)} \]  
Eq. 12

Figure 21. Single well pump test at Hemlock Crossing Park (OCHD, unpublished data).

Geochemistry

In an effort to characterize the horizontal extent and redox environment of the ammonium-rich groundwater, samples were analyzed for an array of parameters. A summary of groundwater chemistry results is provided in Appendix E.
Redox Conditions

For wells screened in the confined aquifer system (W-1 through W-6 and W-8), \( \text{NH}_4^+ \)-N concentrations range from 4.5 to 13.49 mg/L whereas \( \text{Fe}^{2+} \) concentrations vary from 3.27 to 9.65 mg/L (Figure 22). Well W-6 is an outlier for this group of wells because \( \text{NH}_4^+ \) and \( \text{Fe}^{2+} \) are below detection limits (BDL). Higher \( \text{NH}_4^+ \) and \( \text{Fe}^{2+} \) concentrations were expected in well W-6 based upon results of other wells screened in the same confined aquifer system. It is possible that the well owner was unaware that the outdoor faucet may have been hooked up to a water softener. Samples collected in the unconfined aquifer were BDL for \( \text{NH}_4^+ \) and \( \text{Fe}^{2+} \).
Figure 22. Distribution of select ions in wells W-1 through W-8.

Samples were not analyzed for dissolved oxygen and pe due to the presence of CH$_4$. 

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indicating very reducing conditions. The dissolved gas composition from well W-1 is CH$_4$: 77.04 (mol. %), N$_2$: 17.12, CO$_2$: 4.46, O$_2$: 1.04, Ar: 0.339, and ethane: 0.001. Any O$_2$ could be due to sampling error. Simpkins and Parkin (1993) identified low pe values under methanogenic conditions in glacial drift aquifers. Methane concentrations in wells W-1 through W-4 vary between 20 and 46 mg/L. The Michigan DEQ Flammability and Explosivity Screening Level for CH$_4$ in groundwater is 0.52 mg/L (Michigan DEQ, 2012). A 10-m thick aquitard (Unit 2-4) likely prohibits the migration of any CH$_4$ towards the subsurface; however, fractures in the till and poor well construction could provide a pathway for CH$_4$, thus creating an explosion hazard in poorly vented basements. Methane from well W-1 has an age of 38,807 cal. yr B.P., similar to the age of organic material in Unit 6 of OT-12-01. The $\delta^{13}$C value for CH$_4$ from well W-1 is -77.4‰, which is within the expected range for biogenically produced CH$_4$ (Grossman et al., 1989; Schoell, 1980).

Although a rotten egg odor is present at wells screened in the confined aquifer system, H$_2$S is BDL in wells W-1 and W-3 through W-6. The lack of H$_2$S is likely due to the formation of iron sulfides. Sulfate concentrations vary from 5.17 to 59.19 mg/L for wells where H$_2$S is BDL. Elevated SO$_4^{2-}$ concentrations are unexpected since sulfate reduction is a thermodynamically favored over methanogenesis. Sulfate is typically reduced before methanogenic conditions occur (Grossman et al., 1989; 2002; Zhang et al., 1998). However, a glacial drift aquifer in Iowa had similar reported methanogenic conditions with SO$_4^{2-}$ (2.2 to 81.5 mg/L) and CH$_4$ (4.4 to 41.6 mg/L) concentrations both elevated in the same wells. The presence of SO$_4^{2-}$ was attributed to the oxidation of FeS
during well construction (Simpkins and Parkin, 1993). Sulfate could also be migrating from the nearby Marshall Sandstone subcrop (see discussion below).

Groundwater Chemistry

The dominant species for the confined aquifer system is sodium bicarbonate (Figure 23). The cation results for well W-6 shows that the sample is dominated by \( \text{Na}^+ + \text{K}^+ \) (approximately 99.5%) with almost no \( \text{Ca}^{2+} \), a classic example of ion exchange from a water softener. The alkalinity UV-Vis procedure used for this study measured total alkalinity. Due to the pH of the groundwater samples, it is assumed that \( \text{HCO}_3^- \) is the dominant inorganic carbon species and would nearly equal total alkalinity concentrations (Drever, 1997). It is possible that bicarbonate concentrations are actually lower than total alkalinity concentrations because of the amount of organic acids present in the confined aquifer system (Alan Kehew, personal communication, 2013).
Figure 23. Groundwater species for the study site.

The concentration of Cl\(^-\) in well W-7 (unconfined aquifer) is 4.46 mg/L, which is within the range typically seen in glacial drift aquifers. The Michigan residential aesthetic drinking water standard for Cl\(^-\) is 250 mg/L (Michigan DEQ, 2012). Chloride concentrations vary from 80.06 to 337.57 mg/L in the confined aquifer system, which is relatively high for groundwater in glacial sediment along the west side of Michigan. In a study of 532 potable wells screened in glacial sediment across 19 states, Mullaney et al.
(2009) concluded that 1.7% of these wells had Cl\(^-\) concentrations greater than 250 mg/L. Unpublished data provided by the Ottawa County Health Department shows that Cl\(^-\) and Na\(^+\) concentrations in a residential well on the same property as well W-5 was >550 mg/L and 523 mg/L, respectively. The well, which was screened (37.8 m depth) in a confined aquifer below the aquifer system (Units 5 and 7) that contains buried organic material, was plugged because the drinking water had an aesthetically displeasing salty taste. In the summer of 2012, farmers in Ottawa County unknowingly pumped Cl\(^-\)-rich groundwater from the Marshall Sandstone for irrigation purposes. Because the contact between the Marshall Sandstone and Coldwater Shale is <1.6 km east of the study site, it is possible that elevated Cl\(^-\) and SO\(_4^{2-}\) concentrations in the confined aquifer system could be caused by brines advecting from the sandstone (David Long, personal communication, 2013). Groundwater in the western portion of the Marshall Sandstone flows towards the Michigan Lowlands, located primarily in Ottawa and Muskegon County (Mandle and Westjohn, 1989). For wells completed in the Marshall Sandstone in Ottawa County, Cl\(^-\) and SO\(_4^{2-}\) concentrations are on the order of 100 to 1,000 mg/L and \(\leq100\) mg/L, respectively (Ging et al., 1996). In central Michigan (Bay County), high Cl\(^-\) concentrations in glacial drift and Marshall Sandstone aquifers have been attributed to the upward migration of formation brines found deep in the Michigan basin (Kolak et al., 1999; Long et al., 1988).

Isotope Investigation
Aquifer Recharge

Comparison of data between Isotech and WMU laboratories (Figure 24) shows a general agreement in results for δ²H values but not for δ¹⁸O values. Isotech δ¹⁸O values for wells W-12 through W-14 were more enriched than expected and therefore replaced by values from WMU, which were reproduced multiple times (Table 3). All other Isotech values were used for interpretation of aquifer recharge.

Figure 24. Comparison of δ¹⁸O and δ²H values from Isotech and WMU laboratories.

<table>
<thead>
<tr>
<th>Well</th>
<th>WMU δ²H</th>
<th>WMU δ¹⁸O</th>
<th>Isotech δ²H</th>
<th>Isotech δ¹⁸O</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-12</td>
<td>-58.7</td>
<td>-8.56</td>
<td>-55.9</td>
<td>-6.89</td>
</tr>
<tr>
<td>W-13</td>
<td>-66.7</td>
<td>-10.08</td>
<td>-64.5</td>
<td>-8.07</td>
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</tbody>
</table>
Results of $\delta^{18}$O/$\delta^{2}$H analyses are divided into three groups: wells in confined aquifers (W-1 through W-6 and W-8), wells in unconfined aquifers (W-7 and W-9 through W-11), and shallow wells with screens that intersect the water table (W-12 through W-14) (Figure 25). Values from all three well settings fall along the same general trend as the local meteoric water line (LMWL) (Equation 7). Changes in climatic conditions can cause data to deviate from the LMWL, which was only collected over a three-year period (Machavaram and Krishnamurthy, 1994).

![Graph of $\delta^{18}$O vs. $\delta^{2}$H for groundwater at the study site. Values follow an expected trend along the LMWL. The LMWL was calculated by Machavaram and Krishnamurthy, 1994.](image)

LMWL: $y = 7.66x + 14.76$
Due to cooler climatic conditions during glaciations, the presence of highly depleted δ¹⁸O and δ²H values in confined glacial aquifers can be used to determine if recharge occurred prior to the Holocene (Kehew, 2000). Work on the Alliston Aquifer in southern Ontario, Canada revealed modern recharge values of -12.4 to -10.8‰ for δ¹⁸O and -88 to -78‰ for δ²H. More depleted values in certain regions of the aquifer (-14.7 to -13.5‰ for δ¹⁸O and -101 to -95‰ for δ²H) implies that some recharge occurred during a cooler climate than present day conditions (Aravena et al., 1995). In southern Ontario, δ¹⁸O values range from -15 to -20‰ for aquifer recharge from the Early Holocene or Late Pleistocene (Desaulniers et al., 1981). Post-glacial (modern) aquifer recharge in Michigan will likely have a δ¹⁸O value between -12 and -8.5‰, while recharge from the Pleistocene will be much more depleted (Sheppard et al., 1969; Ging et al., 1996). In this study, data for wells in the confined aquifer system (-11.07 to -9.3‰ for δ¹⁸O and -82.8 to -65.5‰ for δ²H) shows that primary recharge has occurred during the Holocene.

Based upon d-excess values in confined wells that are almost all below expected values (Figure 26), it is possible that recharge in the confined aquifer system occurred during a different climatic regime when Michigan did not receive precipitation from Lake Michigan. While the average worldwide d-excess value is 10‰, typical values for precipitation in Michigan vary from 15.6 to 23.7‰, depending on the season (Machavaram and Krishnamurthy, 1994). D-excess values are higher in Michigan because precipitation originates from both the ocean and Lake Michigan. Other locations that do not receive precipitation from the Great Lakes, such as St. Louis, Missouri and
Waco, Texas, have an average d-excess of ~7‰ (Machavaram and Krishnamurthy, 1994).

Figure 26. d-excess vs. δ¹⁸O for study site. Most d-excess values from confined wells are lower than expected values from Michigan precipitation.

Using solute transport modeling of ¹⁸O, Darcy’s Law calculations, and ¹⁴C-DIC dating, Simpkins and Bradbury (1992) determined that the age of groundwater in Wisconsin’s Oak Creek Formation (Figure 19) of the Lake Border moraine system varies between 213 and 6,000 years. The Lake Border moraine is also present in Ottawa County where the surficial tills correlate to the Saugatuck (possibly Unit 3) and Ganges (Unit 4) tills (Monaghan et al., 1986). Groundwater travel time through a diamicton, such as the Saugatuck and Ganges tills, is dependent on the occurrence of fractures and
heterogeneity of the unit, both of which can serve as a preferential pathway for water flow in glacial sediments (Simpkins and Bradbury, 1992).

Results from samples analyzed for $^3$H can be found in Appendix E. Tritium analysis for well W-3 was provided by the Ottawa County Health Department (unpublished data, 2010). Very low levels of tritium ($\leq 0.17$ TU), in all three wells that were sampled, indicates no significant groundwater recharge has occurred in the confined aquifer system since 1952.

Nitrogen Isotopes

Results from $\delta^{15}$N-NH$_4$, $\delta^{15}$N-NO$_3$ and $\delta^{18}$O-NO$_3$ are presented in Table 4. Ammonium in the confined aquifer system has undergone an insignificant amount of fractionation, ruling out manure or septic effluent as a possible source of the NH$_4^+$. Ammonium that originated from these anthropogenic sources would be expected to have much higher $\delta^{15}$N-NH$_4$ values ($\geq 10\%$) than NH$_4$ produced from the decay of in situ organic material (Figure 9). If NO$_3^-$ from manure or septic effluent was totally reduced to NH$_4^+$, the expected $\delta^{15}$N-NH$_4$ values would be higher than observed in this study (Hinkle et al., 2007). For example, in an investigation of an alluvial and lacustrine sand aquifer in Oregon, Hinkle et al. (2007) concluded that the source of N in the surficial part of the aquifer was from septic effluent ($\delta^{15}$N-NO$_3$ values enriched up to +12.8$\%$), while N in deeper portions of the aquifer originated from the mineralization of in situ organic N ($\delta^{15}$N-NH$_4$ values varied from +2.5$\%$ to +3.9$\%$).
Table 4

Results of nitrogen isotopes

<table>
<thead>
<tr>
<th>Well</th>
<th>$\delta^{15}$N-NH$_4$</th>
<th>$\delta^{15}$N-NO$_3$</th>
<th>$\delta^{18}$O-NO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-1</td>
<td>1.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>W-2</td>
<td>0.96</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>W-3</td>
<td>0.81</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>W-4</td>
<td>1.38</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>W-9</td>
<td>-</td>
<td>7.81</td>
<td>2.44</td>
</tr>
<tr>
<td>W-10</td>
<td>-</td>
<td>33.54</td>
<td>14.61</td>
</tr>
<tr>
<td>W-11</td>
<td>-</td>
<td>24.06</td>
<td>12.6</td>
</tr>
</tbody>
</table>

The enrichment of both $\delta^{15}$N-NO$_3$ and $\delta^{18}$O-NO$_3$ is likely due to denitrification of NO$_3^-$ that originated from manure or septic effluent (Figure 10). As denitrification proceeds from NO$_3^-$ to N$_2$, isotope values follow a predictable enrichment trend (Clark and Fritz, 1997). In groundwater below feedlots, Komor and Anderson (1993) suggest that $\delta^{15}$N-NO$_3$ values from manure vary from +22 to +43‰ due to denitrification. The isotopic value from well W-9 is significantly more depleted than values from wells W-10 and W-11 (Figure 10). Due to the proximity of agricultural fields, the source of NO$_3^-$ in well W-9 is likely from manure effluent that has not undergone denitrification. Effluent from a nearby septic field is also a possible source of NO$_3^-$.  

CONCLUSIONS

Although a prior investigation by the Ottawa County Health Department ruled out an inactive landfill as the cause for elevated ammonium levels in Hemlock Crossing Park and nearby residential wells, a source was never determined. In this study, a buried
organic-rich silt layer was discovered to be in contact with the ammonium-rich aquifer system. A local lake likely deposited the organic material during the Athens subepisode interglacial period. Numerous reports of buried organic material have been made throughout Ottawa County. Nearly 10 m of diamicton and fine lacustrine material provide an excellent confining unit above the impacted aquifer system.

Conditions in the confined aquifer system were determined to be methanogenic with elevated iron concentrations. High ammonium concentrations occur in all confined wells that were properly sampled. Tritium and $\delta^{18}$O/$\delta^2$H analyses revealed that the primary recharge in the aquifer system occurred during the Holocene but before nuclear weapons testing in the 1950’s and 60’s. Recharge in the confined aquifer system does not appear to be impacted by current agricultural practices. The presence of a significant source of decaying organic material along with the age of aquifer recharge, suggest that the ammonium is produced naturally and not by human activity. Nitrogen isotopes confirm that the ammonium does not originate from manure or septic effluent but is probably from the decay of in situ organic material.

While not likely harmful to humans at concentrations in this study, ammonium in drinking water can diminish disinfection processes, oxidize to form nitrates, and degrade the overall aesthetic quality of water being used for consumption. Nitrates are of particular concern because high levels of dissolved nitrate, while non-toxic for adults, are deadly to infants. Because the extent of the confining unit is unknown, ammonium may threaten the health of fish in surface water bodies, due to groundwater flow into lakes and rivers. Unless properly vented, high methane concentrations also pose an explosion
hazard to homes with poorly constructed wells. Glacial drift wells located near Hemlock Crossing Park are screened in either a confined aquifer system with high ammonium concentrations or in an unconfined aquifer that is at risk for nitrate contamination from agricultural activity. There are likely similar hydrogeologic conditions throughout Michigan and other formerly glaciated regions where buried organic material is present.
REFERENCES


Carson, L. 2011. Evidence for participation of anammox in nitrogen attenuation observed in groundwater impacted by a manure lagoon (Master’s thesis). University of Waterloo, Waterloo, ON, Canada.


Michigan DEQ (Department of Environmental Quality), 2012. MDEQ-RRD Operational Memorandum #1, September 28, 2012.


APPENDIX A

Well Logs of Sampled Wells
## Water Well And Pump Record

**Import ID:**

**Completion is required under authority of Part 127 Act 668 PA-1978.**

**Failure to comply is a misdemeanor.**

### Drilling Method:
- **Rotary**

### Well Depth:
- **53.00 ft.**

### Well Type:
- **Nin**
- **Date Completed:** 11/15/2002

### Casing Type:
- **PVC plastic**
- **Height:** 2.00 ft. above grade

### Casing Joint:
- **Solvent welded/gluead**

### Casing Fitting:
- **Centralizer**

### Diameter:
- **5.09 in. to 48.00 ft. depth**

### Borehole:
- **8.75 in. to 58.00 ft. depth**

### Pump Installed:
- **Yes**
- **Pump Installation Only:** No

### Pump Installation Date:
- **HP:** 1.50

### Manufacturer:
- **Amtral**

### Pump Type:
- **Submersible**

### Model Number:
- **Pump Capacity:** 40 GPM

### Drop Pipe Length:
- **110.00 ft.**

### Pump Voltage:
- **1.25 in.**

### Drilling Record ID:

### Draw Down Seal Used:
- No

### Pressure Tank Installed:
- Yes

### Pressure Tank Type:
- Diaphragm/bladder

### Manufacturer:
- Amtral

### Model Number:
- WX 350

### Tank Capacity:
- 119.0 Gallons

### Pressure Relief Valve Installed:
- No

### Static Water Level:
- 12.75 ft. Below Grade

### Well Yield Test:
- Pumping level 45.00 ft. after 3.00 hrs. at 30 GPM

### Yield Test Method:
- Air

### Screen Installed:
- Yes

### Filter Packed:
- Yes

### Screen Diameter:
- Blank: 0.00 ft.

### Screen Material Type:
- Stainless steel-wire wrapped

### Slot:
- **15.00 ft.**

### Length:
- **5.00 ft.**

### Set Between:
- 48.00 ft. and 53.00 ft.

### Fittings:
- None

### Well Grouted:
- Yes

### Grouting Method:
- Grout pipe outside casing

### Grouting Material:
- Bentonite slurry

### Bags:
- 6.00

### Additives:
- None

### Depth:
- 6.00 ft. to 43.00 ft.

### Wellhead Completion:
- Piston adapter, 12 inches above grade

### Formation Description:

<table>
<thead>
<tr>
<th>Formation Description</th>
<th>Thickness</th>
<th>Depth to Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Topsoil</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Band</td>
<td>15.00</td>
<td>15.00</td>
</tr>
<tr>
<td>Gravel</td>
<td>3.00</td>
<td>18.00</td>
</tr>
<tr>
<td>Gray Clay</td>
<td>19.00</td>
<td>37.00</td>
</tr>
<tr>
<td>Gray Clay &amp; Gravel</td>
<td>3.00</td>
<td>40.00</td>
</tr>
<tr>
<td>Gravel</td>
<td>3.00</td>
<td>53.00</td>
</tr>
<tr>
<td>Sand Course</td>
<td>10.00</td>
<td>53.00</td>
</tr>
<tr>
<td>Gray Clay</td>
<td>3.00</td>
<td>56.00</td>
</tr>
</tbody>
</table>

### Geology Remarks:

### Nearest Source of Possible Contamination:
- Septic Tank

### Distance:
- 250.00 ft.

### Direction:
- Northwest

### Drilling Machine Operator Name:
- J.L. Neubecker

### Employment:
- Employee

### Contractor Type:
- Water Well Drilling Contractor

### Reg No:
- 70-2354

### Business Name:
- Raymer Company, Inc.

### Business Address:
- 1357 Coats St, MArne, MI

---

**Water Well Contractor's Certification**

This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

**Signature of Registered Contractor**

**Date**

---

**General Remarks:**
- PUMP CAPACITY - 30 GPM
- 30 PSI TANK CAPACITY - 119 GALLONS
- 44 GALLONS DRAW

**Other Remarks:**

---

## Water Well And Pump Record

Completion is required under authority of Part 127 Act 368 PA 1973. Failure to comply is a misdemeanor.

### Drilling Method: rotary
### Well Depth: 67.00 ft.
### Well Use: Type II public

### Casing Type: PVC plastic
### Height: 1.00 ft. above grade
### Casing Joint: Solvent welded/glued
### Casing Fitting: None
### Diameter: 5.00 in. to 7.00 in. depth SDRI: 21.00
### Borehole: 8.50 in. to 87.00 ft. depth

### Static Water Level: 15.69 ft. Below Grade

#### Well Yield Test:
- Pumping level 60.95 ft. after 6.00 hrs. of 60 GPM

#### Screen Installed: Yes
#### Screen Diameter: 5.00 in.
#### Screen Material Type: Stainless steel wire wrapped
#### Slot Length: 0.22 ft.
#### Slot Between: 10.00 ft.
#### Fittings: None

### Well Grouted: Yes
### Grouting Material: Bentonite slurry
### Grouting Material Bags: 4.00
### Additives: None
### Depth: 6.00 ft. to 55.00 ft.

### Wellhead Completion:
- Pile less adapter, Other, 12 inches above grade

### Geology Remarks:
- clay deeper than 67'

### Nearest Source of Possible Contamination:
- Septic tank
  - Type: Distance: 160 ft.
  - Direction: North

### Drilling Machine Operator Name: Russ Berkley
### Employment: Employee

### Contractor Type: Water Well Drilling Contractor
### Business Name: Koops Well Drilling
### Business Address: 3811 58th Street, Holland, MI 49423

### Water Well Contractor's Certification
This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

### Signature of Registered Contractor: Date

### Other Remarks:
- Coordinate Source Google Well address geocoding

### ECQ-2017 (4/2010) Page 1 of 1
- Pump Asked: 10/14/2010 4:04 PM
- Contractor: 7/21/2009 4:55 PM
Water Well And Pump Record

Completion is required under authority of Part 127 Act 368 PA 1978.
Failure to comply is a misdemeanor.

<table>
<thead>
<tr>
<th>Drilling Method:</th>
<th>Rotary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well Depth:</td>
<td>56.00 ft</td>
</tr>
<tr>
<td>Well Type:</td>
<td>New</td>
</tr>
<tr>
<td>Well Use:</td>
<td>Household</td>
</tr>
<tr>
<td>Date Completed:</td>
<td>6/21/2012</td>
</tr>
<tr>
<td>Casing Type:</td>
<td>PVC plastic</td>
</tr>
<tr>
<td>Height:</td>
<td>1.00 ft, above grade</td>
</tr>
<tr>
<td>Casing Joint:</td>
<td>Solvent welded/glued</td>
</tr>
<tr>
<td>Casing Fitting:</td>
<td>None</td>
</tr>
<tr>
<td>Diameter:</td>
<td>5.50 in. to 88.90 ft. depth SDR 21.00</td>
</tr>
<tr>
<td>Borehole:</td>
<td>8.50 in. to 88.90 ft. depth</td>
</tr>
<tr>
<td>Pump Installed:</td>
<td>Yes</td>
</tr>
<tr>
<td>Pump Installation Date:</td>
<td>12/18/2012</td>
</tr>
<tr>
<td>Pump Installation Only:</td>
<td>Yes</td>
</tr>
<tr>
<td>Manufacturer:</td>
<td>Franklin Electric</td>
</tr>
<tr>
<td>Pump Type:</td>
<td>Submersible</td>
</tr>
<tr>
<td>Model Number:</td>
<td>16FV654-2V220</td>
</tr>
<tr>
<td>Pump Capacity:</td>
<td>10 GPM</td>
</tr>
<tr>
<td>Drop Pipe Length:</td>
<td>60.00 ft</td>
</tr>
<tr>
<td>Pump Voltage:</td>
<td>230</td>
</tr>
<tr>
<td>Drop Pipe Diameter:</td>
<td>1.25 in</td>
</tr>
<tr>
<td>Driveway Seal Used:</td>
<td>No</td>
</tr>
<tr>
<td>Drilling Record ID:</td>
<td>70000009550</td>
</tr>
<tr>
<td>Pressure Tank Installed:</td>
<td>Yes</td>
</tr>
<tr>
<td>Pressure Tank Type:</td>
<td>Diaphragm/bladder</td>
</tr>
<tr>
<td>Manufacturer:</td>
<td>Amrol</td>
</tr>
<tr>
<td>Model Number:</td>
<td>WX220</td>
</tr>
<tr>
<td>Tank Capacity:</td>
<td>13.0 Gallons</td>
</tr>
<tr>
<td>Pressure Relief Valve Installed:</td>
<td>Yes</td>
</tr>
</tbody>
</table>

| Static Water Level: | 42.09 ft. Below Grade |
| Well Yield Test:    | Yield Test Method: Test pump |
| Pumping level: 56.00 ft. after 1.00 hrs. at 30 GPM |

| Screen Installed: | Yes |
| Filter Packed:    | Yes |
| Screen Diameter:  | 5.00 in. |
| Blank:            | PVC-slotted |
| Slot Length       | Set Between |
| 0.02              | 10.00 ft. |
| 0.08             | 88.90 ft. and 90.00 ft. |

| Fittings: | None |
| Well Grouted: | Yes |
| Grouting Material: | Grout pipe outside casing |
| Bags: | None |
| Additives: | None |
| Depth: | 0.00 ft. to 80.00 ft. |

| Wellhead Completion: | Plugless adapter, 12 inches above grade |
| Drilling Machine Operator Name: | Russ Backley |
| Employment: | Employee |
| Contractor Type: | Water Well Drilling Contractor |
| Reg No: | 03-2342 |
| Business Name: | Koops Well Drilling Inc |
| Business Address: | 3811 58th Street, Holland, MI 49423 |

**Water Well Contractor's Certification**
This well/pump was constructed under my supervision and I hereby certify that the work complies with Part 127 Act 368 PA 1978 and the well code.

Signature of Registered Contractor: [Signature]
Date: [Date]

General Remarks: 600X Gravel Park

Other Remarks:

ECQ-2017 (4/2012) Page 1 of 1 Pump Added 12/19/2012 2:23 PM Contractor 6/22/2012 3:02 PM
### Water Well and Pump Record

#### Michigan Department of Public Health

**Permit Number:**

<table>
<thead>
<tr>
<th>Formation Description</th>
<th>Inclined Screen</th>
<th>Depth to Bottom of Screen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>10 10</td>
<td></td>
</tr>
<tr>
<td>Brown Clay</td>
<td>15 25</td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>1 26</td>
<td>10</td>
</tr>
<tr>
<td>Brown Clay</td>
<td>23 49</td>
<td>15</td>
</tr>
<tr>
<td>Sand &amp; Gravel</td>
<td>1 50</td>
<td></td>
</tr>
<tr>
<td>Red Clay</td>
<td>10 60</td>
<td></td>
</tr>
<tr>
<td>Sand &amp; Gravel</td>
<td>1 61</td>
<td></td>
</tr>
<tr>
<td>Red Clay</td>
<td>16 77</td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>1 78</td>
<td></td>
</tr>
<tr>
<td>Red Clay</td>
<td>1 82</td>
<td></td>
</tr>
<tr>
<td>Med. To Fine Sand (sand)</td>
<td>10 92</td>
<td></td>
</tr>
</tbody>
</table>

- **Static Water Level:** 35 ft. below ground surface, Free
- **Pumping Level:** 6.2 ft. after 2,500 gpm
- **Well Shunted:** No
- **Well Shunted Completion:** No
- **Well Shunted Reasons:** No
- **Well Shunted Date:** No
- **Well Shunted Duration:** No
- **Well Shunted Cost:** No

### Water Well Contractor's Certification

**Koops Well Drilling Inc.**

**Address:** 3911 59th St, Holland, MI 49423

**Signed:** April 19, 1984

**Authority:** MDH

**Completion:** Required

**Penalty:** Not specified

**Date:** 4/4/91

**Notes:**

- **Groundwater Source:** Med. To Fine Sand (sand)
- **Groundwater Type:** Sand, Brown Clay, Sand, Brown Clay, Sand & Gravel, Red Clay, Sand & Gravel, Red Clay, Med. To Fine Sand (sand)
- **Static Water Level:** 35 ft. below ground surface, Free
- **Pumping Level:** 6.2 ft. after 2,500 gpm
- **Well Shunted:** No
- **Well Shunted Completion:** No
- **Well Shunted Reasons:** No
- **Well Shunted Date:** No
- **Well Shunted Duration:** No
- **Well Shunted Cost:** No

**Groundwater Source:** Med. To Fine Sand (sand)

**Groundwater Type:** Sand, Brown Clay, Sand, Brown Clay, Sand & Gravel, Red Clay, Sand & Gravel, Red Clay, Med. To Fine Sand (sand)

**Static Water Level:** 35 ft. below ground surface, Free

**Pumping Level:** 6.2 ft. after 2,500 gpm

**Well Shunted:** No

**Well Shunted Completion:** No

**Well Shunted Reasons:** No

**Well Shunted Date:** No

**Well Shunted Duration:** No

**Well Shunted Cost:** No
## Water Well And Pump Record

Completion is required under authority of Part 127 Act 368 PA 1978. Failure to comply is a misdemeanor.

### Drilling Method:
- **Rotary**

### Well Depth:
- **78.00 ft.**

### Well Use:
- **Household**

### Well Type:
- **New**
  - **Date Completed:** 7/15/2001

### Casing Type:
- **PVC plastic**

### Casing Joint:
- **Welded**

### Casing Fitting:
- **None**

### Diameter:
- **5.00 in. to 82.00 ft. depth**

### Borehole:

### Static Water Level:
- **37.00 ft. Below Grade**

### Well Yield Test:
- **Yield Test Method:** Air
- **Pumping level 37.00 ft. after 1.00 hrs. at 40 GPM**

### Screen Installed:
- **Yes**

### Filter Packed:
- **Yes**

### Screen Diameter:
- **5.00 in.**
  - **Blank:** *a*

### Screen Material Type:
- **Stainless steel wire wrapped**

### Slot Length:
- **5.00 ft.**
- **Set Between:** 62.00 ft. and 78.00 ft.

### Fittings:
- **Unknown**

### Well Grouted:
- **Yes**

### Grouting Material Type:
- **Bentonite slurry**

### Bags:
- **4.00**

### Additives Depth:
- **None**
  - **0.00 ft. to 60.00 ft.**

### Wellhead Completion:
- **Pitless adapter**

---

### Geology Remarks:

---

### Nearest Source of Possible Contamination:
- **Type:** Septic tank
- **Distance:** 50 ft.
- **Direction:** West

---

### Drilling Machine Operator Name:
- **LYLE**

### Employment:
- **Unknown**

### Contractor Type:
- **Water Well Drilling Contractor**
  - **Reg No:** 63-0458

### Business Name:
- **BRDEKHUIS BROS**

### Business Address:
- **Water Well Contractor's Certification**
  - This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

### Signature of Registered Contractor:

---

### General Remarks:

### Other Remarks:

---

**Water Well And Pump Record**

Completion is required under authority of Part 127 Act 388 PA 1078.
Failure to comply is a misdemeanor.

- **Import ID:**
- **Drilling Method:** Rotary
- **Well Depth:** 42.00 ft.
- **Well Use:** Household
- **Well Type:** New
- **Date Completed:** 12/13/2010

- **Casing Type:** PVC plastic
- **Casing Joint:** Solvent welded/ glued
- **Casing Fitting:** None
- **Diameter:** 5.59 in. to 32.00 ft. depth
- **Borehole:** 8.59 in. to 42.00 ft. depth

- **Pump Installed:** Yes
- **Pump Installation Only:** No
- **Pump Type:** Submersible
- **Manufacturer:** Sta-Rite
- **Model Number:** 20SP4E02H
- **Drop Pipe Length:** 20.00 ft.
- **Drop Pipe Diameter:** Drilling Record ID:
- **Draw Down Seal Used:** No
- **Pressure Tank Installed:** Yes
- **Pressure Tank Type:** Unknown
- **Manufacturer:** Well-X-Trol
- **Model Number:** 3X2
- **Tank Capacity:**
- **Pressure Relief Valve Installed:** No

**Static Water Level:** 6.00 ft. Below Grade

**Well Yield Test:**

<table>
<thead>
<tr>
<th>Yield Test Method</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pumping level 11.00 ft. after 1.00 hrs. at 33 GPM</td>
<td></td>
</tr>
</tbody>
</table>

**Screen Installed:** Yes
**Filter Packed:** Yes
**Screen Diameter:** 5.00 in.
**Blank:**
**Screen Material Type:** PVC-slooted

<table>
<thead>
<tr>
<th>Slot</th>
<th>Length</th>
<th>Set Between</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.00</td>
<td>19.00 ft.</td>
<td>32.00 ft. and 42.00 ft.</td>
</tr>
</tbody>
</table>

| Fittings | Unknown |

**Well Grouted:** Yes
**Grouting Method:** Unknown
**Grouting Material:** Bentonite slurry
**Bags:** 3.00
**Additives:** None
**Depth:** 0.60 ft. to 30.00 ft.

**Wellhead Completion:** Pile cap, 12 inches above grade

**Formation Description**

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness</th>
<th>Depth to Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>18.00</td>
<td>18.00</td>
</tr>
<tr>
<td>Sand/W/Cty</td>
<td>6.00</td>
<td>24.00</td>
</tr>
<tr>
<td>Gravel/Dry</td>
<td>18.00</td>
<td>42.00</td>
</tr>
</tbody>
</table>

**Geology Remarks:**

**Nearest Source of Possible Contamination:**

<table>
<thead>
<tr>
<th>Type</th>
<th>Distance</th>
<th>Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Septic tank</td>
<td>60 ft.</td>
<td>South</td>
</tr>
</tbody>
</table>

**Drilling Machine Operator Name:** LANCE KOOPS
**Employment:** Employee

**Contractor Type:** Water Well Drilling Contractor
**Reg No:** 03-6764
**Business Name:** KOOPS WELL DRIG

**Water Well Contractor's Certification**

This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

**Signature of Registered Contractor**

**Other Remarks:** Yearly Test Method: Air & test pumping

**General Remarks:** 500 LBS GRAVEL PACK

## Water Well And Pump Record

**Completion is required under authority of Part 127 Act 369 PA 1973.**

**Failure to comply is a misdemeanor.**

<table>
<thead>
<tr>
<th>Drilling Method</th>
<th>Rotary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well Depth</td>
<td>90.00 ft</td>
</tr>
<tr>
<td>Well Type</td>
<td>New</td>
</tr>
<tr>
<td>Well Use</td>
<td>Household</td>
</tr>
<tr>
<td>Date Completed</td>
<td>8/10/2000</td>
</tr>
<tr>
<td>Casing Type</td>
<td>PVC plastic</td>
</tr>
<tr>
<td>Casing Joint</td>
<td>Welded</td>
</tr>
<tr>
<td>Casing Fitting</td>
<td>None</td>
</tr>
<tr>
<td>Diameter</td>
<td>5.00 in. to 89.00 ft. depth</td>
</tr>
<tr>
<td>Borehole</td>
<td>8.50 in. to 99.00 ft. depth</td>
</tr>
</tbody>
</table>

**Pump Installed:** Yes  
**Pump Installation Only:** No  
**Manufacturer:** Sta-Rite  
**Pump Type:** Submersible  
**Model Number:** 16SP4D02H  
**Pump Capacity:** 10 GPM  
**Drop Pipe Length:** 60.00 ft.  
**Drop Pipe Diameter:** Drilling Record ID:  
**Draw Down Seal Used:** No  
**Pressure Tank Installed:** Yes  
**Pressure Tank Type:** Unknown  
**Manufacturer:** Amrol  
**Model Number:** WX-250  
**Tank Capacity:** 14.0 Gallons  
**Pressure Relief Valve Installed:** No

| Static Water Level       | 40.00 ft. Below Grade       |
| Well Yield Test          | 51.00 ft. after 1.00 hrs. at 25 GPM |
| Pumps                   | 51.00 ft. after 1.00 hrs. at 25 GPM |
| Test Method              | Air                         |
| Screen Installed         | Yes                         |
| Filter Packed            | Yes                         |
| Screen Diameter          | 5.00 in.                    |
| Screen Material Type     | PVC-dotted                 |
| Slot                     | 0.02                        |
| Length                   | 10.00 ft.                   |
| Set Between              | 99.00 ft. and 99.60 ft.     |
| Fittings                 | Unknown                     |
| Well Grouted             | Yes                         |
| Grouting Method          | Unknown                     |
| Grouting Material        | Bentonite slurry 6.00       |
| Bags                     | None                        |
| Additives                | None                        |
| Depth                    | 0.00 ft. to 85.00 ft.       |
| Geology Remarks          |                             |
| Wellhead Completion      | Pipeless adapter, 12 inches above grade |

**Nearest Source of Possible Contamination:**

<table>
<thead>
<tr>
<th>Type</th>
<th>Distance</th>
<th>Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Septic tank</td>
<td>75 ft</td>
<td>South</td>
</tr>
</tbody>
</table>

**Drilling Machine Operator Name:** CORBY CALLAWAY  
**Employment:** Employee

**Contractor Type:** Water Well Drilling Contractor  
**Reg No:** 63-2341  
**Business Name:** KOOPS WELL DRILLING  
**Business Address:**

**Water Well Contractor's Certification:**

This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

**Signature of Registered Contractor**

**General Remarks:** 500 LBS GRAVEL PACK  
**Other Remarks:**

EC#2017-452010  Page 1 of 1  State of Michigan  10/3/2003 3:10 PM
### Water Well And Pump Record

Completion is required under authority of Part 127 Act 368 PA 1978.
Failure to comply is a misdemeanor.

<table>
<thead>
<tr>
<th>Drilling Method:</th>
<th>Rotary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well Depth:</td>
<td>40.00 ft.</td>
</tr>
<tr>
<td>Well Type:</td>
<td>Replacement</td>
</tr>
<tr>
<td>Date Completed:</td>
<td>7/27/2007</td>
</tr>
<tr>
<td>Casing Type:</td>
<td>PVC plastic</td>
</tr>
<tr>
<td>Casing Joint:</td>
<td>Solvent welded/glued</td>
</tr>
<tr>
<td>Casing Fitting:</td>
<td>None</td>
</tr>
<tr>
<td>Diameter:</td>
<td>5.50 in. to 8.00 ft. depth</td>
</tr>
<tr>
<td>Borehole:</td>
<td>7.87 in. to 40.00 ft. depth</td>
</tr>
<tr>
<td>Static Water Level:</td>
<td>12.00 ft. Below Grade</td>
</tr>
<tr>
<td>Well Yield Test:</td>
<td>1.00 hrs. at 20 GPM</td>
</tr>
<tr>
<td>Yield Test Method:</td>
<td>Air</td>
</tr>
<tr>
<td>Screen Installed:</td>
<td>Yes</td>
</tr>
<tr>
<td>Screen Diameter:</td>
<td>4.00 in.</td>
</tr>
<tr>
<td>Screen Material Type:</td>
<td>PVC-wire wrapped</td>
</tr>
<tr>
<td>Slot:</td>
<td>None</td>
</tr>
<tr>
<td>Well Grouted:</td>
<td>Yes</td>
</tr>
<tr>
<td>Grouting Material:</td>
<td>Bentonite slurry</td>
</tr>
<tr>
<td>Grouting Method:</td>
<td>Grout pipe outside casing</td>
</tr>
<tr>
<td>Wellhead Completion:</td>
<td>Fitrace adapter, 12 inches above grade</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formation Description</th>
<th>Thickness</th>
<th>Depth to Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>40.00</td>
<td>40.00</td>
</tr>
</tbody>
</table>

| ScreenPacked: | Yes |
| Screen Dia: | 4.00 in. |
| Blank Dia: | 3.00 in. Above |
| Screen Mat: | PVC-wire wrapped |
| Slot: | None |
| Length: | 7.00 |
| Set Between: | 12.00 ft. |
| Well Grouted: | Yes |
| Grouting Material: | Bentonite slurry |
| Grouting Method: | Grout pipe outside casing |
| Grouting Additives: | None |
| Grouting Depth: | 0.60 ft. to 20.00 ft. |

| Nearest Source of Possible Contamination: | Septic tank 85 ft. North |
| Drilling Machine Operator Name: | David Mckma |
| Contractor Type: | Water Well Drilling Contractor |
| Business Name: | Dawid Well Drilling, Inc. |
| Business Address: | 9999 Henry Ct. Zeeland, MI |
| Well Well Contractor's Certification: | Water Well Drilling Contractor's Certification |

| Abandoned Well Plugged: | No |
| Reason Not Plugged: | Well still in use for non-drinking water purposes |

| General Remarks: | |
| Other Remarks: | Tank manufactured by: Fipitrace adapter |

85
## Water Well And Pump Record

### Completion is required under authority of Part 127 Act 368 PA 1978. Failure to comply is a misdemeanor.

<table>
<thead>
<tr>
<th>Drilling Method:</th>
<th>Auger/Bored</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well Depth:</td>
<td>29.00 ft</td>
</tr>
<tr>
<td>Well Use:</td>
<td>Household</td>
</tr>
<tr>
<td>Well Type:</td>
<td>Replacement</td>
</tr>
<tr>
<td>Date Completed:</td>
<td>5/22/2010</td>
</tr>
<tr>
<td>Casing Type:</td>
<td>PVC plastic</td>
</tr>
<tr>
<td>Height:</td>
<td>1.00 ft. above grade</td>
</tr>
<tr>
<td>Casing Joint:</td>
<td>Solvent welded/igued</td>
</tr>
<tr>
<td>Casing Fitting:</td>
<td>None</td>
</tr>
<tr>
<td>Diameter:</td>
<td>5.00 in. to 25.00 ft. depth</td>
</tr>
<tr>
<td>Borehole:</td>
<td>10.00 in. to 30.50 ft. depth</td>
</tr>
<tr>
<td>Static Water Level:</td>
<td>7.00 ft. Below Grade</td>
</tr>
<tr>
<td>Pump Installed:</td>
<td>Yes</td>
</tr>
<tr>
<td>Pump Installation Date:</td>
<td>5/22/2010</td>
</tr>
<tr>
<td>Manufacturer:</td>
<td>Berkeley</td>
</tr>
<tr>
<td>Model Number:</td>
<td>10SP4002J</td>
</tr>
<tr>
<td>Pump Type:</td>
<td>Submersible</td>
</tr>
<tr>
<td>Drop Pipe Length:</td>
<td>20.00 ft.</td>
</tr>
<tr>
<td>Drop Pipe Diameter:</td>
<td>1.25 in.</td>
</tr>
<tr>
<td>Draw Down Seal Used:</td>
<td>No</td>
</tr>
<tr>
<td>Pressure Tank Installed:</td>
<td>Yes</td>
</tr>
<tr>
<td>Pressure Tank Type:</td>
<td>Diaphragm/bladder</td>
</tr>
<tr>
<td>Manufacturer:</td>
<td>Sta-Rite Signature</td>
</tr>
<tr>
<td>Model Number:</td>
<td>SR35-10</td>
</tr>
<tr>
<td>Tank Capacity:</td>
<td>35.0 Gallons</td>
</tr>
<tr>
<td>Pressure Relief Valve Installed:</td>
<td>No</td>
</tr>
</tbody>
</table>

### Well Yield Test:
- **Yield Test Method**: Test pump
- **Pumping level**: 20.00 ft. after 1.00 hrs. at 15 GPM

### Geology Remarks:

### Nearest Source of Possible Contamination:
- **Type**: Septic tank
- **Distance**: 75 ft.
- **Direction**: East

### Abandoned Well Plugged:
- **Yes**

### Drilling Machine Operator Name:
- **Jeff DeWind**

### Contractor Type:
- **Water Well Drilling Contractor**
- **Reg No**: 70-1922

### General Remarks:
- **DATE CODES**: Pump-I0203P Tank-I030H, Pulls & pumped 2

### Water Well Contractor's Certification:
This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

### Signature of Registered Contractor

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|-------------------------|---------|-------------|-------------------|

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# Water Well And Pump Record

**Import ID:**

**Water Well And Pump Record**

Compliance is required under authority of Part 127 Act 368 PA 1978. Failure to comply is a misdemeanor.

<table>
<thead>
<tr>
<th>Drilling Method:</th>
<th>Auger/Bored</th>
<th>Well:</th>
<th>Household</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well Use:</td>
<td>Household</td>
<td>Well Use:</td>
<td>Household</td>
</tr>
<tr>
<td>Well Type:</td>
<td>Replacement</td>
<td>Date Completed:</td>
<td>5/30/2002</td>
</tr>
<tr>
<td>Casing Type:</td>
<td>PVC plastic</td>
<td>Height:</td>
<td></td>
</tr>
<tr>
<td>Casing Joint:</td>
<td>Welded</td>
<td>Diameter:</td>
<td>5.00 in. to 25.00 ft. depth</td>
</tr>
<tr>
<td>Casing Fitting:</td>
<td>None</td>
<td>Borehole:</td>
<td>10.00 in. to 28.00 ft. depth</td>
</tr>
<tr>
<td>Static Water Level:</td>
<td>6.00 ft. Below Grade</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Well Yield Test:</td>
<td>Test pump at 8 GPM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Screen Installed:</td>
<td>Yes</td>
<td>Filter Packed:</td>
<td>Yes</td>
</tr>
<tr>
<td>Screen Diameter:</td>
<td>5.00 in.</td>
<td>Screen Material Type:</td>
<td>PVC-slit</td>
</tr>
<tr>
<td>Screen Material Type:</td>
<td>PVC-slit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slot:</td>
<td>Length:</td>
<td>Set Between:</td>
<td></td>
</tr>
<tr>
<td>7:00</td>
<td>3:00 ft.</td>
<td>25.00 ft. and 28.00 ft.</td>
<td></td>
</tr>
<tr>
<td>Fittings:</td>
<td>Unknown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Well Grouted:</td>
<td>Yes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grouting Material</td>
<td>Bags</td>
<td>Additives</td>
<td>Depth</td>
</tr>
<tr>
<td>Bentonite slurry</td>
<td>2.00</td>
<td>None</td>
<td>0.60 ft. to 25.00 ft.</td>
</tr>
<tr>
<td>Wellhead Completion:</td>
<td>Pitless adapter, 12 inches above grade</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nearest Source of Possible Contamination:</td>
<td>None</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drilling Machine Operator Name:</td>
<td>JIM BOLLES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Employment:</td>
<td>Employee</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contractor Type:</td>
<td>Water Well Drilling Contractor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reg No:</td>
<td>20-1922</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Business Name:</td>
<td>DEWIN WELL DRILL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Business Address:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Well Contractor's Certification:</td>
<td>This well was drilled under my supervision and this report is true to the best of my knowledge and belief.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Signature of Registered Contractor:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Date:</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Formation Description**

<table>
<thead>
<tr>
<th>Sand</th>
<th>Fine</th>
<th>Silty</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.00</td>
<td>28.00</td>
<td></td>
</tr>
</tbody>
</table>

**Other Remarks:**
APPENDIX B

Sieve Results for OT-12-01
<p>| Sample ID | Depth (m) | Unit | 5 (φ = -2) | 10 (φ = -1) | 18 (φ = 0) | 35 (φ = 1) | 60 (φ = 2) | 120 (φ = 3) | 230 (φ = 4) | Silt (φ ≥ 5) | Clay (φ ≥ 5) | Total Weight (g) |
|-----------|-----------|------|-------------|--------------|-------------|-------------|-------------|-------------|-------------|-------------|--------------|----------------|-----------------|
| 1         | 0.14      | 1    | 0           | 0.6          | 0.25        | 2.28        | 33.23       | 29.69       | 2.99        | 2.37        | 0.67         | 72.08          |
| 2         | 0.90      | 1    | 0.67        | 2.82         | 10.71       | 67.58       | 268.36      | 79.31       | 3.53        | 2.43        | 0.41         | 435.82         |
| 3         | 2.45      | 1    | 15.06       | 3.58         | 2.94        | 18.17       | 205.31      | 127.6       | 6.48        | 2.47        | 0.28         | 381.89         |
| 4         | 3.82      | 2    | 0           | 0.04         | 0.05        | 0.24        | 1.45        | 8.1         | 73.19       | 250.50      | 52.82        | 386.39         |
| 5         | 5.03      | 2    | 0           | 0.06         | 0.04        | 0.15        | 1.04        | 2.44        | 4.26        | 284.20      | 70.79        | 362.98         |
| 6         | 6.55      | 3    | 2.55        | 1.74         | 1.5         | 3.41        | 13.61       | 16.44       | 11.67       | 168.58      | 147.28       | 366.78         |
| 7         | 8.08      | 3    | 4.21        | 1.6          | 1.4         | 2.74        | 13.63       | 21.03       | 14          | 150.99      | 161.16       | 370.76         |
| 8         | 9.60      | 3    | 3.86        | 1.34         | 1.56        | 2.88        | 17.53       | 27.48       | 16.13       | 145.77      | 155.68       | 372.23         |
| 9         | 11.13     | 4    | 5.95        | 1.72         | 2.67        | 5.52        | 28.03       | 42.37       | 23.02       | 136.96      | 140.84       | 387.08         |
| 10        | 12.65     | 4    | 3.27        | 2.2          | 2.87        | 5.35        | 28.81       | 44.57       | 25.35       | 133.83      | 139.23       | 385.48         |
| 11        | 13.84     | 5    | 0           | 0.28         | 0.31        | 0.93        | 4.38        | 114.75      | 190         | 57.29       | 11.57        | 379.51         |
| 12        | 14.60     | 5    | 0           | 0.72         | 19.73       | 169.81      | 143.7       | 24.71       |             | 27.92       | 9.95         | 396.54         |
| 13        | 15.41     | 5    | 0.26        | 0.8          | 2.67        | 23.92       | 191.64      | 171.19      | 11.09       | 6.76        | 0.65         | 408.98         |
| 14        | 16.29     | 6    | 0           | 0            | 0.01        | 0.75        | 9.5         | 12.44       | 1.57        | 132.16      | 85.51        | 241.94         |
| 15        | 17.03     | 6    | 0           | 0.08         | 1.28        | 5.97        | 9.05        | 10.25       | 24.03       | 93.02       | 24.39        | 168.07         |</p>
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Depth (m)</th>
<th>Unit</th>
<th>5 (φ = -2)</th>
<th>10 (φ = -1)</th>
<th>18 (φ = 0)</th>
<th>35 (φ = 1)</th>
<th>60 (φ = 2)</th>
<th>120 (φ = 3)</th>
<th>230 (φ = 4)</th>
<th>Silt (φ ≥ 5)</th>
<th>Clay (φ ≥ 5)</th>
<th>Total Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>17.68</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0.33</td>
<td>7.37</td>
<td>188.84</td>
<td>116.22</td>
<td>13.88</td>
<td>41.50</td>
<td>17.35</td>
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<td>17</td>
<td>18.43</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>0.59</td>
<td>10.08</td>
<td>84.7</td>
<td>177.44</td>
<td>57.66</td>
<td>12.30</td>
<td>342.79</td>
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<tr>
<td>18</td>
<td>19.76</td>
<td>7</td>
<td>0.62</td>
<td>1.35</td>
<td>1.59</td>
<td>31.2</td>
<td>225.86</td>
<td>128.16</td>
<td>23.38</td>
<td>9.84</td>
<td>1.13</td>
<td>423.13</td>
</tr>
<tr>
<td>19</td>
<td>21.35</td>
<td>8</td>
<td>7.43</td>
<td>5.94</td>
<td>7.36</td>
<td>10.15</td>
<td>30.39</td>
<td>41.75</td>
<td>28.16</td>
<td>160.38</td>
<td>123.60</td>
<td>415.16</td>
</tr>
<tr>
<td>20</td>
<td>23.23</td>
<td>8</td>
<td>9.69</td>
<td>5.56</td>
<td>5.98</td>
<td>8.83</td>
<td>26.8</td>
<td>36.98</td>
<td>24.51</td>
<td>164.54</td>
<td>120.00</td>
<td>402.89</td>
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<tr>
<td>21</td>
<td>25.01</td>
<td>8</td>
<td>9.96</td>
<td>7.7</td>
<td>8.57</td>
<td>12.5</td>
<td>45.91</td>
<td>67.04</td>
<td>40.49</td>
<td>143.25</td>
<td>80.99</td>
<td>416.41</td>
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<tr>
<td>22</td>
<td>26.25</td>
<td>8</td>
<td>23.56</td>
<td>6.9</td>
<td>6.6</td>
<td>9.52</td>
<td>32.35</td>
<td>43.77</td>
<td>26.71</td>
<td>136.49</td>
<td>117.47</td>
<td>403.37</td>
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<td>23</td>
<td>27.95</td>
<td>9</td>
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<td>0</td>
<td>0.03</td>
<td>0.19</td>
<td>1.6</td>
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APPENDIX C

Wells Reporting Buried Organics in Port Sheldon and Olive Township
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<th>Drillers Description of Organics</th>
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<td>15379 Baldwin St.</td>
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<td>Muck &amp; wood</td>
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<td>21.95-24.99</td>
<td>Muck</td>
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<td>144th &amp; Port Sheldon</td>
<td>25.91-28.96</td>
<td>Sand &amp; wood</td>
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<td>Sand &amp; lots of wood</td>
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<td>24.08-25.6</td>
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<td>26.21-30.48</td>
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<td>21.95-28.35</td>
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<td>7.62-7.92</td>
<td>Sand &amp; wood</td>
</tr>
<tr>
<td>6655 Timber Cove</td>
<td>6.4-6.71</td>
<td>Muck</td>
</tr>
<tr>
<td>6407 Wildwood Dr.</td>
<td>7.92-8.84</td>
<td>Muck</td>
</tr>
<tr>
<td>Lakeshore &amp; Wildwood</td>
<td>10.97-11.28</td>
<td>Sand &amp; wood</td>
</tr>
<tr>
<td>9410 136th Ave.</td>
<td>16.46-19.2</td>
<td>Clay, sand, and wood</td>
</tr>
<tr>
<td>13444 Young Forest</td>
<td>11.58-17.07</td>
<td>Sand and gravel with wood</td>
</tr>
<tr>
<td>13565 Port Sheldon Rd.</td>
<td>22.56-26.52</td>
<td>Muck &amp; wood</td>
</tr>
</tbody>
</table>
APPENDIX D

Groundwater Flow Direction and Gradient of Confined Aquifer System
<table>
<thead>
<tr>
<th>Well Address</th>
<th>Well ID</th>
<th>Date of Installation</th>
<th>Elevation (ft)</th>
<th>Static Level (ft depth)</th>
<th>Potentiometric Surface (ft)</th>
<th>Distance Between Wells (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15433 River Trace</td>
<td>A</td>
<td>Sep. 01, 2005</td>
<td>598</td>
<td>25</td>
<td>573</td>
<td>A – B = 256.87</td>
</tr>
<tr>
<td>River Trace entrance</td>
<td>B</td>
<td>Sep. 10, 2005</td>
<td>603</td>
<td>21</td>
<td>582</td>
<td>B – C = 805.11</td>
</tr>
<tr>
<td>15522 River Woods</td>
<td>C</td>
<td>Sep. 26, 2005</td>
<td>603</td>
<td>32</td>
<td>571</td>
<td>C – A = 1057.16</td>
</tr>
</tbody>
</table>

Distance between 573’ & 579’:

\[(1.27”/256.87”) = (0.85”/X)\]

\[X = 171.92’\]

Gradient (from 573’ to 579’):

\[6’/171.92’ = 0.035\]
## Water Well And Pump Record

**Completion is required under authority of Part 127 Act 588 PA 1978. Failure to comply is a misdemeanor.**

### Import ID:

<table>
<thead>
<tr>
<th>Tax No:</th>
<th>Permit No:</th>
<th>County:</th>
<th>Township:</th>
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<tr>
<td>70-11-14-430-221</td>
<td></td>
<td>Citrus</td>
<td>Port Sheldon</td>
</tr>
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</table>

### Well ID: 700000006689

- **Elevation:** Not specified
- **Latitude:** 42.900377
- **Longitude:** -86.168129
- **Method of Collection:** Address Matching/Street Centerline

#### Drilling Method:
- **Rotary**

#### Well Information:
- **Type:** New
- **Depth:** 84.00 ft.
- **Well Use:** Household

#### Casing Information:
- **Type:** PVC plastic
- **Height:** 1.00 ft. above grade
- **Fitting:** None
- **Diameter:** 5.00 in. to 7.00 ft. depth
- **Borehole:** 8.50 in. to 8.00 ft. depth

#### Pump Information:
- **Type:** Not specified
- **Installation Date:** 9/1/2005
- **Manufacturer:** Not specified
- **Model Number:** Not specified
- **Capacity:** Not specified
- **Pressure Tank:** Yes
- **Relief Valve Installed:** Yes

#### Static Water Level:
- **Level:** 26.00 ft. Below Grade

#### Well Yield Test:
- **Yield Test Method:** Test pump
- **Fuming level:** 39.00 ft. after 1.00 hrs. at 25 GPM

#### Screen Information:
- **Installed:** Yes
- **Material:** PVC slotted
- **Length:** Not specified
- **Height:** 5.00 ft.
- **Set Between:** Above
- **Filter Packed:** Yes

#### Fittings:
- **Not specified**

#### Well Grouted:
- **Yes**

#### Geology Remarks:
- **Clay Below**

#### Nearest Source of Possible Contamination:
- **Type:** Septic tank
- **Distance:** 59 ft.
- **Direction:** South

#### Drilling Machine Operator Name:
- **Russ Beckley**

#### Contractor Type:
- **Water Well Drilling Contractor**

#### Business Address:
- **Koops Well Drilling**
- **2611 98th Street, Hilland, MI 49423**

#### Contractor Information:
- **Reg No:** 03-2342
- **Business Name:** Koops Well Drilling

---

**Water Well Contractor’s Certification:**

This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

---

**Signature of Registered Contractor:**

**Date:** 9/19/2010 10:56 AM

---

**General Remarks:** 500# Gravel Pack

**Other Remarks:** Coordinate Source/Google well address geocoding
**Water Well And Pump Record**

**Completion is required under authority of Part 127 Act 368 PA 1976.**

**Failure to comply is a misdemeanor.**

### Table: Well Information

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<td></td>
</tr>
<tr>
<td>Latitude:</td>
<td>42.90088</td>
</tr>
<tr>
<td>Longitude:</td>
<td>-86.168104</td>
</tr>
<tr>
<td>Method of Collection:</td>
<td>CCG - Centroid</td>
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<tr>
<td>Drilling Method:</td>
<td>Rotary</td>
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<tr>
<td>Well Depth:</td>
<td>74.00 ft.</td>
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<td>Well Use:</td>
<td>Irrigation</td>
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<td>New</td>
</tr>
<tr>
<td>Date Completed:</td>
<td>9/10/2005</td>
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<tr>
<td>Casing Type:</td>
<td>PVC plastic</td>
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<tr>
<td>Height:</td>
<td>1.00 ft. above grade</td>
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<tr>
<td>Casing Joint:</td>
<td>Solvent welded/glued</td>
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<tr>
<td>Casing Fitting:</td>
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<td>Diameter:</td>
<td>5.00 in. to 64.00 ft. depth</td>
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<tr>
<td>Borehole:</td>
<td>8.50 in. to 74.00 ft. depth</td>
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<td>Static Water Level:</td>
<td>21.00 ft. Below Grade</td>
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<td>Well Yield Test:</td>
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<td>Yield Test Method:</td>
<td>Test pump</td>
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<td>Pumping level:</td>
<td>34.00 ft. after 1.00 hrs. at 30 GPM</td>
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<td>Screen installed:</td>
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<td>Filter Packed:</td>
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<tr>
<td>Blank:</td>
<td>Above</td>
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<tr>
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<tr>
<td>Slot Length:</td>
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<td>Set Between</td>
<td>64.00 ft. and 74.00 ft.</td>
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<td>Fittings:</td>
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<td>Well Grouted:</td>
<td>Yes</td>
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<tr>
<td>Grouting Method:</td>
<td>Good pipe outside casing</td>
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<td>Grouting Material:</td>
<td>Bentonite slurry</td>
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<td>Bag:</td>
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<td>Additives:</td>
<td>None</td>
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<td>Depth:</td>
<td>0.00 ft. to 60.00 ft.</td>
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<td>Wellhead Completion:</td>
<td>Filtered adapter, 12 inches above grade</td>
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<td>Nearest Source of Possible Contamination:</td>
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</tr>
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<td>Type:</td>
<td></td>
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<td>Distance:</td>
<td></td>
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<tr>
<td>Direction:</td>
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<td>Drilling Machine Operator Name:</td>
<td>Corby Callaway</td>
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<td>Employment:</td>
<td>Employee</td>
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<td>Pump Installer:</td>
<td>Chad &amp; Phil</td>
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<td>Contractor Type:</td>
<td>Water Well Drilling Contractor</td>
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<tr>
<td>Reg No:</td>
<td>03-2341</td>
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<tr>
<td>Business Name:</td>
<td>Koops Well Drilling</td>
</tr>
<tr>
<td>Business Address:</td>
<td>1811 56th Street, Holland, MI 49423</td>
</tr>
<tr>
<td>Water Well Contractor's Certification:</td>
<td>This well was drilled under my supervision and this report is true to the best of my knowledge and belief.</td>
</tr>
<tr>
<td>Signature of Registered Contractor:</td>
<td></td>
</tr>
<tr>
<td>Date:</td>
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**General Remarks:** 550# Gravel Pack

---

98
**Water Well And Pump Record**

**Completion is required under authority of Part 127 Act 368 PA 1976.**

**Failure to comply is a misdemeanor.**

<table>
<thead>
<tr>
<th>Tax No.</th>
<th>Permit No.</th>
<th>County</th>
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</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td>Port Sheldon</td>
</tr>
</tbody>
</table>

**Well ID: 700000006744**

**Elevation:**
Latitude: 42.90158
Longitude: -86.16915
Method of Collection: Address Matching-Street Centerline

**Drilling Method:** Rotary
**Well Depth:** 66.00 ft.
**Well Use:** Household
**Well Type:** New
**Date Completed:** 9/26/2005

**Casing Type:** PVC plastic
**Height:** 1.06 ft. above grade
**Casing Joint:** Solvent welded/glued
**Casing Fitting:** None
**Diameter:** 5.50 in. to 8.10 in. ft. depth
**Borehole:** 8.50 in. to 8.60 in. ft. depth

**Pump Installed:** Yes
**Pump Installation Only:** No
**Pump Installation Date:** HP: 1.00
**Manufacturer:** Berkeley
**Pump Type:** Submersible
**Model Number:** 20SP4E02-MG
**Pump Capacity:** 20 GPM
**Drop Pipe Length:** 86.00 ft.
**Drop Pipe Diameter:** 1.25 in.
**Drill Down Seal Used:** Yes
**Draw Down Test Used:** No
**Pressure Tank Installed:** Yes
**Pressure Tank Type:** Diaphragm/bladder
**Manufacturer:** Amtol
**Model Number:** WX-302
**Tank Capacity:** 29.0 Gallons
**Pressure Relief Valve Installed:** Yes

**Static Water Level:** 32.00 ft. Below Grade

**Well Yield Test:**
Fumping level 83.00 ft. after 1.00 hrs. at 22 GPM

**Formation Description**
<table>
<thead>
<tr>
<th>Description</th>
<th>Thickness</th>
<th>Depth to Bottom</th>
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</thead>
<tbody>
<tr>
<td>Sand</td>
<td>23.00</td>
<td>23.00</td>
</tr>
<tr>
<td>Clay hard sticky</td>
<td>56.00</td>
<td>61.00</td>
</tr>
<tr>
<td>Sand medium</td>
<td>5.10</td>
<td>56.00</td>
</tr>
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</table>

**Screen Diameter:** 5.00 in.
**Filter Packed:** Yes
**Blank:** Above
**Screen Material Type:** Stainless steel slotted
**Slot Length:** 20.00 ft.
**Set Between:** 5.00 ft.
**61.00 ft. and 66.00 ft.**

**Fittings:** None

**Well Grouded:** Yes
**Grouting Method:** Grout pipe outside casing
**Grouting Material:** Bags Additives Depth
Bentonite slurry: 5.05 None 0.00 ft. to 7.00 ft.

**Wellhead Completion:** Fittings adapter, 12 inches above grade

**Nearest Source of Possible Contamination:**
Septic tank 150 ft. Northwest

**Drilling Machine Operator Name:** Russ Beckley
**Employment:** Employee
**Pump Installer:** Chat & Tim

**Contractor Type:** Water Well Drilling Contractor
**Reg No:** 03-2342
**Business Name:** Koops Well Drilling
**Business Address:** 1811 56th Street, Holland, MI 49423

**Water Well Contractor's Certification**
This well was drilled under my supervision and this report is true to the best of my knowledge and belief.

**Signature of Registered Contractor**

**General Remarks:** 300# Gravel Pack

**Other Remarks:** Coordinate Source: Google maps address geocoding

---

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APPENDIX E

Summary of Groundwater Chemistry
<table>
<thead>
<tr>
<th>Well</th>
<th>pH</th>
<th>Conductivity (us)</th>
<th>H$_2$S (mg/L)</th>
<th>SO$_4^{2-}$ (mg/L)</th>
<th>Cl$^-$ (mg/L)</th>
<th>NO$_3^-$-N (mg/L)</th>
<th>Total Alkalinity (mg/L)</th>
<th>Fe$^{2+}$ (mg/L)</th>
<th>Mg$^{2+}$ (mg/L)</th>
<th>Ca$^{2+}$ (mg/L)</th>
<th>NH$_4^+$-N (mg/L)</th>
<th>K$^+$ (mg/L)</th>
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</thead>
<tbody>
<tr>
<td>W-1</td>
<td>7.1</td>
<td>1519</td>
<td>&lt; 0.56</td>
<td>5.17</td>
<td>289.26</td>
<td>-</td>
<td>665.91</td>
<td>9.65</td>
<td>25.37</td>
<td>72.52</td>
<td>13.49</td>
<td>5.99</td>
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<tr>
<td>W-2</td>
<td>7.45</td>
<td>739</td>
<td>-</td>
<td>24.23</td>
<td>116.2</td>
<td>-</td>
<td>468.02</td>
<td>3.65</td>
<td>14.13</td>
<td>46.6</td>
<td>10.10</td>
<td>3.59</td>
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<tr>
<td>W-3</td>
<td>7.08</td>
<td>1819</td>
<td>&lt; 0.56</td>
<td>57.59</td>
<td>337.57</td>
<td>-</td>
<td>573.56</td>
<td>5.83</td>
<td>25.83</td>
<td>158.55</td>
<td>13.15</td>
<td>3.86</td>
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<td>W-4</td>
<td>7.14</td>
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<td>&lt; 0.56</td>
<td>59.19</td>
<td>136.62</td>
<td>-</td>
<td>485.62</td>
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<td>18.23</td>
<td>54.45</td>
<td>5.45</td>
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<td>W-5</td>
<td>7.06</td>
<td>-</td>
<td>&lt; 0.48</td>
<td>191.51</td>
<td>-</td>
<td>504.31</td>
<td>4.72</td>
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<tr>
<td>W-6</td>
<td>7.18</td>
<td>-</td>
<td>&lt; 0.56</td>
<td>80.06</td>
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<td>56.43</td>
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<tr>
<td>W-7</td>
<td>8.05</td>
<td>-</td>
<td>-</td>
<td>23.25</td>
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<td>-</td>
<td>168.23</td>
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<td>5.89</td>
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<td>&lt; 1</td>
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<td>W-8</td>
<td>7.38</td>
<td>-</td>
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<td>&lt; 0.48</td>
<td>82.14</td>
<td>-</td>
<td>437.85</td>
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<td>19.5</td>
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<td>642</td>
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<td>76</td>
<td>36.62</td>
<td>7.8</td>
<td>162.76</td>
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<td>22.01</td>
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<td>4.27</td>
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<td>36.81</td>
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<td>3.38</td>
<td>13.04</td>
<td>&lt; 1</td>
<td>0.71</td>
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(-) sample not analyzed for parameter
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<tr>
<th>Well</th>
<th>Na⁺ (mg/L)</th>
<th>DOC (mg/L)</th>
<th>CH₄ (mg/L)</th>
<th>δ¹⁸O (%)</th>
<th>δ²H (%)</th>
<th>δ¹⁵N-NH₄ (%)</th>
<th>δ¹⁵N-NO₃ (%)</th>
<th>δ¹⁸O-NO₃ (%)</th>
<th>δ¹⁴C-CH₄ (cal. yr B.P.)</th>
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