DATCP 2019-1

Assessment of Pesticide Contamination in Suburban Drinking Water Wells in Southeastern Wisconsin

Final Report Prepared by Yin Wang and Shangping Xu

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PROJECT SUMMARY

Title: Assessment of pesticide contamination in suburban drinking water wells in Southeastern Wisconsin

Project I.D.: 19-01

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Background/Need: The wide use of pesticides for agricultural and residential activities has a significant impact on groundwater quality in the United States. Currently, the occurrence of pesticides in groundwater has been monitored in Wisconsin with an emphasis on agricultural land by multiple agencies. However, limited efforts have focused on monitoring residential (e.g., home and garden) pesticides in groundwater in suburban areas, where a substantial portion of the land is for non-agricultural use. Considering the commonly over use of home and garden pesticides, and the widespread presence of private drinking water wells in suburban areas, the impact of residential pesticide on groundwater quality in suburban areas remains insufficiently evaluated.

Objectives: The primary objective of this project was to evaluate the impact of home and garden pesticides on local groundwater quality in suburban areas in Southeastern Wisconsin. Specifically, we used Milwaukee metropolitan area as the model study area because of the substantial portion of non-agricultural land and the large population in the suburban area that use groundwater as the drinking water source.

Methods: Groundwater samples were collected from 16 active private wells in the Milwaukee metropolitan area: including two in Milwaukee County, four in Ozaukee County, six in Washington County, and four in Waukesha County. These wells were selected primarily based on their location within well-kept, more densely populated, suburb neighborhood away from agricultural fields to ensure that the groundwater collected was representative of residential pesticide application. Four sampling events were performed during June 2019 to February 2020 to capture seasonal dynamics. Groundwater samples were analyzed for seven representative home and garden pesticides, including four herbicides (2,4-dichlorophenoxyacetic acid (2,4-D), methylchlorophenoxypropionic acid (MCPP), dicamba, and 2-methyl-4-chlorophenoxyacetic acid (MCPA)), and three insecticides (carbaryl, malathion, and imidacloprid). These pesticides were selected based on their popular use, relatively high water solubility, low soil affinity and long half-life. The pesticide concentrations in groundwater were determined using liquid-liquid extraction, followed by liquid chromatography tandem mass spectrometry (LC-MS/MS) measurement.

Results and Discussion: One or more of the targeted pesticides have been detected in groundwater in seven of the sixteen wells during the four sampling events. Specifically, there were six and two wells that detected one or more of the targeted pesticides during the June/July 2019 and August 2019 sampling events, respectively. No pesticides were detected in any wells during the November 2019 and February 2020 sampling events. Results suggested a seasonal trend of residential pesticide occurrence in groundwater. The most frequently detected pesticide was 2,4-D, showing up in three separate wells, followed by malathion showing up in two wells; carbaryl, dicamba, imidacloprid, MCPA, and MCPP each making an appearance once. The concentrations of all detected pesticides were below any known groundwater standards, indicating a relatively low risk of residential pesticide contamination in private drinking water wells.

Conclusions/Implications/Recommendations: This study suggested that groundwater may be more susceptible to residential pesticide contamination during the late spring and early summer months. This time frame is when homeowners and professional lawn care companies apply the most pesticides to lawns. Recharge into the local groundwater also typically takes place during this time. However, this study did not observe any strong correlation or trend between the hydrology, chemical properties and/or chemical application to the wells. Although the severity and frequency of detection does not compare to those done in an agricultural setting, testing for residential pesticides should continue to be monitored for historical trends and potential health-based implications. Specifically, long-term monitoring activities are recommended to fully evaluate the seasonal variability of residential pesticide occurrence in groundwater.

Related Publications: Bychinski, Leslie, "Pesticides in Urban/Suburban Water Wells in Milwaukee, Ozaukee, Washington, and Waukesha Counties in Wisconsin" (2020). *Theses and Dissertations*. 2358. https://dc.uwm.edu/etd/2358

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Final Report: A final report containing more detailed information on this project is available at the Wisconsin Department of Agriculture, Trade and Consumer Protection. For more information, phone 608/224-4503, or email stan.senger@wisconsin.gov

INTRODUCTION

Pesticides are a class of substances to control the growth of weeds, fungi and insects in both agricultural and residential settings. Residential uses (e.g., home and garden), primarily in urban and suburban areas, account for about 25% of total pesticide use in the United States (Grube et al., 2011). A survey conducted by the U.S. Environment & Human Health, Inc. (EHHI) suggests that ~72% of homeowners have used pesticides on their lawns (EHHI, 2003). The U.S. Fish and Wildlife Service reported that homeowners used up to 10 times more chemical pesticides per acre on their lawns than farmers use on crops (USFWS, 2000). So far, U.S. Environmental Protection Agency (EPA) permits over 200 different pesticides to be used for residential purposes, and 30 of them are commonly applied. It is estimated that more than 60 million pounds of the active ingredients of home and garden pesticides (herbicide + insecticide + fungicide) are used in the United States per year (Grube et al., 2011).

Pesticides and their metabolites may pose adverse health effects, with children, infants and fetuses being particularly susceptible. For example, Zahm and Ward (1998) found that exposure to pesticides may cause childhood malignancies, such as neuroblastoma, Wilms' tumor, Ewing's sarcoma and non-Hodgkin's lymphoma (NHL). Other studies have found evidence of kidney and liver damage and neurotoxicity (EHHI, 2003). Currently, the State of Wisconsin has set health-based enforcement standards for about 30 pesticides in groundwater (WI NR 140.10), and a smaller number of pesticides have been regulated in drinking water (WI NR 809.20). However, some of the commonly used residential pesticides (e.g., methylchlorophenoxypropionic acid (MCPP), 2-methyl-4-chlorophenoxyacetic acid (MCPA)) have not been regulated in groundwater or drinking water, and their health impact is insufficiently understood. More importantly, the coexistence of multiple pesticides in a source water may lead to increased health concerns because of their synergistic effects (Hayes et al., 2006).

Pesticide contamination in drinking water sources has been widely observed in the United States. A decadal assessment by the National Water Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) has shown that 97% of the surface water samples from both agricultural and (sub)urban areas contain one or more pesticides at detectable levels (USGS, 2006). Meanwhile, 55% of the shallow groundwater samples from the (sub)urban areas have detectable pesticide levels, which is comparable to that of agricultural areas (61%) (USGS, 2006). More surprisingly, higher pesticide concentrations have been observed in shallow groundwater in (sub)urban areas than that in agricultural areas (i.e., 4.8% and 1.2% of shallow groundwater samples have at least one pesticide concentration greater than the human-health benchmark level for urban and agricultural areas, respectively). A separate survey suggests that 17 of the 30 commonly used home and garden pesticides have been detected in groundwater, and 23 have potential to contaminate groundwater (US General Accounting Office, 1990).

Groundwater is a major drinking water source in Wisconsin that it serves ~2/3 of Wisconsin's population. In particular, it is estimated that around 25% of Wisconsin residents get drinking water from over 800,000 private wells. Due to the rising concern of groundwater contamination by pesticides in Wisconsin, the Department of Agriculture, Trade and Consumer Protection (DATCP), the Department of Natural Resources (DNR), and other agencies have implemented groundwater monitoring programs since 1983. A statewide survey has been repeated every several years to continuously monitor the groundwater quality and to guide the agricultural practices (Wisconsin Groundwater Coordinating Council, 2016). In a statewide survey conducted in 2016, a total of 401 private drinking water wells were sampled for analysis of agricultural pesticides and nitrate (DATCP, 2017). Pesticides and their metabolites were detected in 41.7% of the tested wells, showing an increasing trend in comparison to the previous survey conducted in 2007 (33.5% of the wells contained at least one pesticide or its metabolite). A stratified random sampling approach was used in the survey based on the percentage of area cultivated for agricultural production, and thus the sampling practices primarily focused on the agricultural field. In contrast, only limited efforts have focused on agri-urban area, and urban and non-agricultural areas were excluded from sampling.

While current monitoring programs have primarily been focusing on the use of agricultural pesticides, and have mainly assessed drinking water wells in agricultural area, limited information is available on the occurrence and impact of residential pesticides on local groundwater quality in (sub)urban areas. Although several pesticides (e.g., 2,4-D, dicamba, malathion) have been used for both residential and agricultural purposes, their doses can be quite different because of the different end-use purposes and varied product ingredients. Thus, their determination in groundwater within the agricultural area does not reflect the risk of residential pesticide leaching into groundwater in (sub)urban areas. To fill the knowledge gap, this project aimed to evaluate the impact of home and garden pesticides on local groundwater quality in suburban areas in Southeastern Wisconsin. This project serves as a complimentary study to current pesticide monitoring practices and provides necessary data towards the potential risk of residential pesticide contamination in a local groundwater setting.

PROCEDURES AND METHODS

Site selection and groundwater sampling

The focus of this research occupies Milwaukee, Ozaukee, Washington, and Waukesha counties of Southeastern Wisconsin. These four counties incorporate the Milwaukee metropolitan area and consist of large portions of non-agricultural suburban land use (SEWRPC, 2006). Wisconsin has four main aquifers, from shallowest to deepest: the sand and gravel aquifer, the eastern dolomite aquifer, the sandstone aquifer, and the crystalline bedrock aquifer (WGNHS, 2020). The first two aquifers collectively are referred to as the “shallow aquifer” and the “deep aquifer” collectively for the latter. Private, residential wells are commonly drilled into the “shallow aquifer” from <100 to roughly 300 feet into unlithified glacial material of the sand and gravel aquifer or into the fractured dolomite aquifer (**Figure 1**) (Bradbury, 2007).

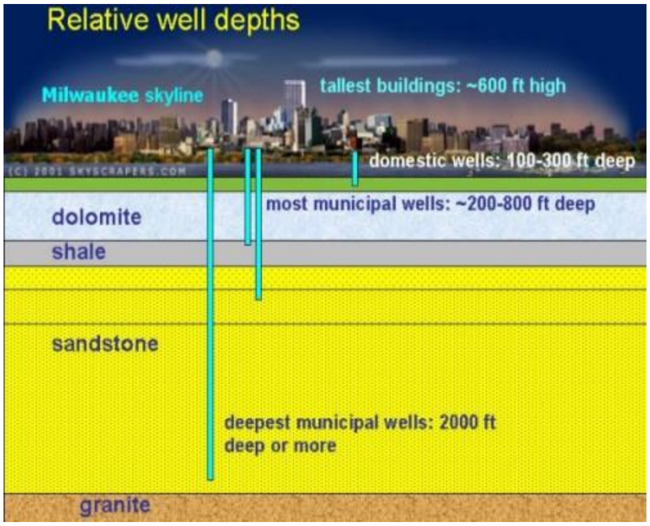

Figure 1. Schematic cross section of relation of well depths to rock units in Southeastern Wisconsin. Source: K.R. Bradbury, Wisconsin Geological and Natural History Survey.

In this project, we focused on active, shallow, transient non-community wells in (sub)urban locations. The wells are away from agricultural fields, within more densely populated, well-kept, suburban locations, and reside in the sand and gravel aquifer or the shallow dolomite aquifer. Additionally, in the selection of the sampling wells, efforts were made to exclude wells that are either along lake shorelines and/or had thick clay or hardpan layers. Clayey deposits are the least permeable deposits and can hinder local, downward leaching. Wells along lake shorelines likely draw more water from the lake and would more so reflect the lake water chemistry. Our hypothesis was that wells selected based on the abovementioned criteria may be more vulnerable to residential pesticide leaching. Thus, our approach would allow us to develop a conservative assessment of groundwater contamination by residential pesticides.

Candidate wells were identified based on information documented in Wisconsin DNR. Briefly, Wisconsin DNR provides multiple Well Inventory search engines by inputting criteria such as WI Unique Well Numbers, County, Well Use, Well Status, etc. Searching active, non-transient non-community wells within each county queried a table of the unique well numbers and well depth. With the help of Google Maps and trial and error, each address on the well construction report was searched for its comparative suburban location as well as its geologic significance. A formal letter was then sent to over 70 homeowners in ideal or close to ideal locations for approval, in hopes that at least 15 would respond. Inaccurate address inputs on well construction reports proved to be more of an issue than initially intended, as several of them were sent back. In the end, ten homeowners participated. A few of them knew other interested homeowners and resulted in 16 sampling locations among Milwaukee, Ozaukee, Washington, and Waukesha County (**Figure 2**). The well logs for individual wells are shown in Figure A1 (Appendix B). For each of the participated homeowners, a survey was sent concerning the pesticide products used, or the company hired, and the temporal application throughout the year (Appendix B).

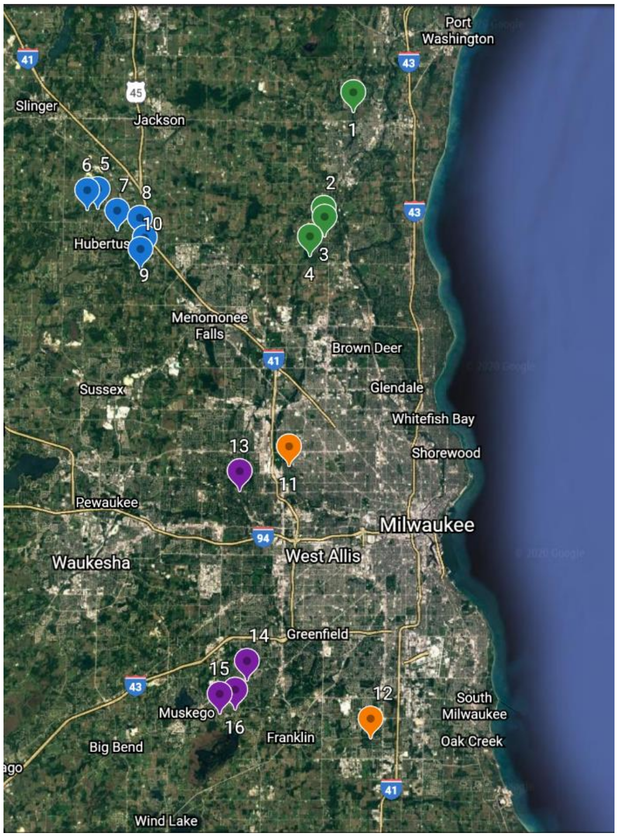

Figure 2. Sample well locations (Blue: Washington County; Green: Ozaukee County; Purple: Waukesha County; Orange: Milwaukee County)

A total of 16 wells were sampled for pesticides from June 2019 to February 2020 over four sampling events: thirteen participated in the first round (June/July 2019), sixteen by the second sampling event (August/September 2019), and down to eleven for the third (November 2019) and fourth (February 2020) events. The eleven selected wells in the third and fourth sampling event were the wells that showed previous pesticide detection or were in ideal suburb locations that better highlighted the focus of this study. For all sampling events, groundwater samples were collected and handled following the protocols addressed in the DATCP survey (DATCP, 2017) and returned to our analytical lab. Briefly, samples were collected from the spigot right before the water pump within each of the homeowner's basements into two 1-liter amber glass bottles. As extra precaution, each bottle was wrapped in tin foil, and transported for further testing in a cooler. Water quality parameters that include temperature, pH, conductivity, pressure and oxidation reduction potential (ORP) were measured during sample collection using a YSI probe. Concentrations of total iron, other major cations (calcium, magnesium, potassium and sodium), and major anions (chloride, nitrate, phosphate and sulfate) were measured using standard methods at UW-Milwaukee.

Pesticide selection and measurement

Among the 30 most popular residential pesticides from EPA sales and market data, this project analyzed seven commonly used home and garden pesticide active ingredients that include: 2,4-D, carbaryl, dicamba, imidacloprid, malathion, MCPA, and MCPP (**Figure 3**). These chemicals were selected because of their high-end usage, high water solubility, moderate to low soil organic carbon-water partitioning coefficients (K_{OC}), and relatively long half-life (**Table 1**) (PAN, 2019). Each of these pesticides has been previously observed in groundwater sources across the globe, especially in shallow groundwater (Gilliom, 2007; Hill et al., 1996; Newhart, 2006). It is worth mentioning that the soil sorption characteristic constants for each of the pesticides may vary based on different references, soil properties, and environmental matrices. Therefore, reported values may not fully reflect the affinity between a given pesticide and soil (Ahmed and Rahman, 2009), and a case-by-case investigation is required to determine the pesticide leaching potential to local groundwater sources.

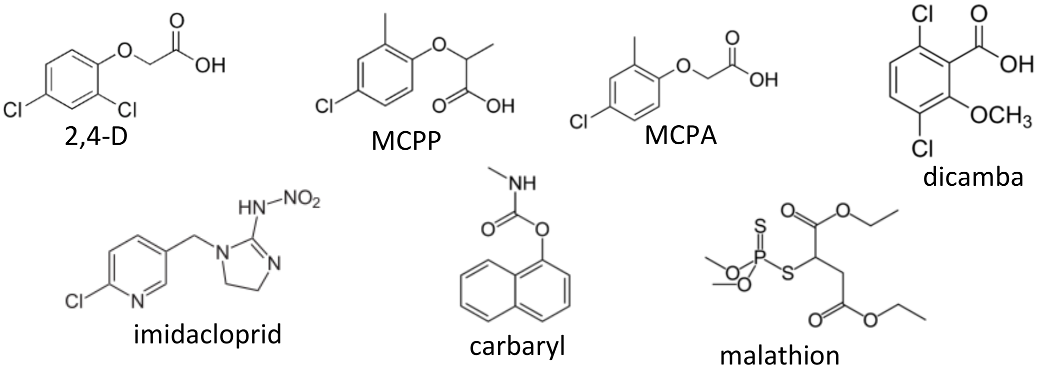

Figure 3. Home and garden pesticides monitored in this project.

Pesticide concentrations in groundwater samples were determined using a liquid-liquid extraction method followed by liquid chromatography – tandem mass spectrometry (LC-MS/MS) measurement developed in our lab. Two organic solvents, namely dicholoromethane (DCM) and diethyl ether were used to extract pesticides for positive (i.e., carbaryl imidacloprid and malathion) and negative (i.e., 2,4-D, dicamba, MCPA and MCPP) ionization analyses, respectively. Briefly, two 250-mL water samples were extracted using DCM and diethyl ether 3 times using a separatory funnel, respectively. Each extract was then evaporated to dryness using a nitrogen evaporation system (Labconco) and reconstituted in an acetonitrile:water (10%:90%) mixture to a final volume of 1 mL.

Table 1. Physical property data for the residential pesticides monitored in this project.

pesticide	Avg. water solubility (mg/L)	K_{oc} (L/kg)	Avg. hydrolysis half-life ($t_{1/2}$, d)	Avg. aerobic soil $t_{1/2}$ (d)	Avg. anaerobic soil $t_{1/2}$ (d)
2,4-D	27,600	46	39	34	333
dicamba	27,200	5	30	10	88
MCPA	29,390	74	N.A.	15	N.A.
MCPP	734	26	31	13	541
carbaryl	116	375	12	6	87
malathion	125	291	6	3	30
imidacloprid	514	262	30	997	27

All values are cited from PAN Pesticide Database at http://www.pesticideinfo.org/

Pesticide concentrations in the extract were determined using an ultra-high-performance liquid chromatograph (UHPLC, Shimadzu Nexera X2) coupled with a triple quadrupole mass spectrometer (MS/MS, Shimadzu LCMS-8040). Chromatography was performed using an EVO-C18 column (Kinetex® 1.7 µm, 100 Å, 100 x 2.1 mm, Phenomenex). The mobile phase consisted of (A) ultrapure water (resistance > 18.2 MΩ) and (B) acetonitrile (Optima LCMS grade, Fisher Scientific), each amended with 0.1% formic acid (Fisher Scientific). Samples were injected at 50-µL volume with a loading pump delivering 0.6 mL/min of the mobile phase consisting of 10% B. The column temperature was held constant at 45 ºC. Mass spectrometry (MS) analysis was performed using the triple quadrupole MS with dual ESI/APCI ion source operated either in a negative polarity mode (SIM-) or a positive polarity mode (SIM+). MS operating conditions were as follows: capillary voltage at 4.5kv, desolvation temperature at 250 ºC, source block temperature at 400 ºC. Nitrogen (>99.99% purity, Airgas) will be used as the desolvation gas and nebulizing gas with flow rates of 15 L/min and 2 L/min, respectively. The collision energy for each pesticide was optimized (Table A1 in Appendix B). The dwell time was set at 60 ms for each transition. LabSolutions V6.82 (Shimadzu) was used for instrument control, acquisition and mass analysis. Overall, our method has a sample recovery in the range of 70 - 102% (except for carbaryl), and limit of quantification (LOQ) in the range of 0.001 – 0.032 µg/L, depending on the type of pesticide (**Table 2**).

Table 2. Pesticide extraction and measurement method limit of quantification (LOQ) and recovery.

Target analyte	Method LOQ (µg/L)	Method recovery (%)
2,4-D	0.004	85 – 102
Carbaryl	0.032	61 – 107
Dicamba	0.006	71 – 76
Imidacloprid	0.030	73 – 99
Malathion	0.008	79 – 91
MCPP	0.002	75 – 91
MCPA	0.001	70 – 98

RESULTS AND DISCUSSION

Results of pesticide detection

Four sampling events were performed from June 2019 – February 2020 to investigate pesticide occurrence at different seasons. Overall, pesticides were only detected within the first and second sampling events from June to September 2019 (**Figure 4**), which took place through Wisconsin's growing season (mid May to early October), and when pesticides were actively applied. There were no pesticides detected in the wells during the months of November and February, even in the sub-ppb level. This is to be expected from the absence of lawn application during the non-growing season, as well as the environmentally short-lived soil sorption characteristics of the pesticides (**Table 1**). Higher concentrations of the pesticides were detected in the early summer months (June/July) compared to late summer months (August/September). Lawn care companies commonly follow a five or six step application process, others as low as two to three step application process (Table A2 in Appendix B). Typical, over-the-counter lawn care products also follow this multistep application process. Each application process consistently applies pesticides during the spring months to allow pre-emergent pesticide control to be effective throughout the growing season. Summer month applications are typically spot treatments.

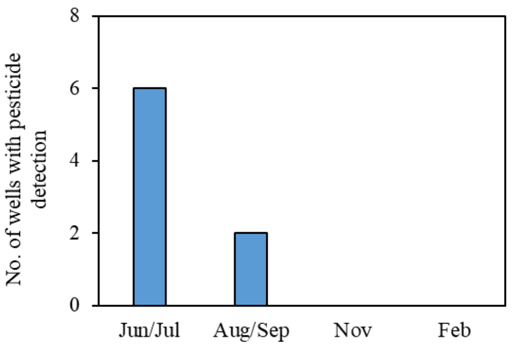

Figure 4. Number of wells with pesticide detection during the four sampling events.

The detailed pesticide detection results are shown in Table A3 (Appendix B). Notably, the newly developed LC-MS/MS-based method (with pre-extraction) allows us for the detection of pesticide under sub-ppb (i.e., ng/L) level. Overall, all of the seven pesticides have been detected at least in one well during one of the sampling events. Most of the detected pesticides were under sub-ppb level, and the concentrations of all detected pesticides were below any known groundwater standards. Specifically, 2,4-D was the most frequently detected pesticide, appearing the most in June and July. 2,4-D is ranked as the number one most commonly used pesticide active ingredient in the home and garden sector (Atwood & Paisley-Jones, 2017). 2,4-D is an herbicide used to eliminate a variety of grasses and broadleaf weeds (UC IPM, 2019). From the physical property data on **Table 1**, 2,4-D is highly water soluble (27,600 mg/L) and has a low soil organic carbon-water partitioning coefficient (K_{OC}) (46 L/kg). During the first sampling event, 2,4-D was detected in three wells (i.e., Wells 9, 12, and 15) with concentrations up to 0.059 ppb.

Dicamba was also detected in the first sampling event in June at Well 5 at 2.18 ppb. According to the EPA sales and market data, Dicamba ranks as the eighth most commonly used pesticide in the home and garden market sector (Atwood & Paisley-Jones, 2017). Dicamba is an herbicide commonly found in products targeting dandelions and poison oak (UC IPM, 2019). Carbaryl was detected during mid-June at Well 2 (1.93 ppb) along with MCPA (0.16 ppb). Carbaryl is ranked the fifth most common pesticide in the home and garden sector (Atwood & Paisley-Jones, 2017). It is found in products that target a range of lawn insects and mites (UC IPM, 2019). MCPA is the ninth most common home and garden pesticide (Atwood & Paisley-Jones, 2017) and is frequently found in products designed to rid of dandelions and other general weed management products (UC IPM, 2019). Imidacloprid and malathion were detected together at Well 13 during July. Imidacloprid was detected at 0.043 ppb. It did not rank in the top ten for the most common pesticides in the home and garden sector for the EPA market and sales report, but it is commonly used as the active ingredient designed to rid of common lawn insects and mites, as well as cockroaches, carpenter ants, and fleas (UC IPM, 2019). Malathion was detected at 0.27 ppb. It is ranked as the tenth most common pesticide in the home and garden sector (Atwood & Paisley-

Jones, 2017) and targets lawn insects and mosquitoes (UC IPM, 2019). Trace amount of Malathion (0.03 ppb) were also detected in Well 14 during the second sampling event. Well 9 also showed a 0.01-ppb detection of MCPP during the second sampling event. It ranks third most popular home and garden pesticide (Atwood & Paisley-Jones, 2017), and is used in a variety of products targeting various lawn weed, such as clovers and dandelions (UC IPM, 2019).

Pesticide detection and well setting

Overall, we found that wells in the sand and gravel aquifer showed higher potential for pesticide leaching and detection, compared to those in dolomite aquifer. Of the twelve wells that reside in the sand and gravel aquifer, six (50%) showed detectable pesticide levels. In contrast, of the four wells that reside in the dolomite aquifer, one (25%) resulted in pesticide detection. **Table 3** shows the number of detections by well depth. The majority of the samples were between 50–150 foot range and had the greatest number of detections. Meanwhile, there was no apparent correlation between pesticide detection and clay content of the well location. For the seven wells with one or more pesticide detection, detailed information and discussion on the well settings is provided below.

Table 3. Number of pesticide detection by well depth.

Well depth (feet)	No. of sample locations	No. of pesticide detections						
		MCPP	**MCPA**	**dicamba**	**2,4-D**	**carbaryl**	**imidacloprid**	**malathion**
under 50	3				1		1	1
50 – 150	8	1		1	2			1
over 150	5		1			1		

Well 2 is drilled 225 feet down into the dolomite aquifer. It has a rather thick clay layer (78 feet) followed by a 7-foot hardpan layer. The homeowners have hired a landscape company with a five-step application program for their lawn. Carbaryl and MCPA were detected in the early summer which correlates to the spring and early summer weed and insect control application. The presence of a thick clay layer did not completely hinder downward pesticide leaching. Well 5 is drilled 67 feet down into the sand and gravel aquifer with no clay presumably present. The homeowners have hired a lawn care company that has a six-step application program and apply their own spot treatment, mostly insecticides. A relatively high level of dicamba was detected in June. This correlates to the spring and early summer pesticide application. The all sand and gravel pathway permit pesticide leaching. Well 9 is 52 feet deep into the sand and gravel aquifer. The homeowners have applied pesticides themselves, including a Stein's Garden and Home four-step lawn treatment, as well as multiple herbicides and insecticides. This well detected 2,4-D in July and MCPP in August. 2,4-D and MCPP are both active ingredients in Stein's Garden and Home four-step lawn treatment. Clay content varies within a sand and gravel layer; it does not hinder leaching potential. Well 12 resides in the sand and gravel aquifer, 88 feet deep. Clay appears through most of the well with a clay-rich layer occupying 52 feet between to sandy layers. The homeowners have hired multiple lawn care companies over the years. 2, 4-D was detected in early July and correlates with the heavy spring/early summer weed control application. Well 13 is 40 feet into the sand and gravel aquifer with a rather significant clay layer taking up the first 23 feet. The homeowners have applied pesticides themselves, including various weed and grass killers, along with insecticides. Well 13 detected imidacloprid and malathion early July. This correlates to the time insecticides are frequently applied. Well 14 is drilled 87 feet into the sand and gravel aquifer. Clay makes up the first 28 feet and is mixed into larger grained intervals. The homeowners have hired a lawn care company with a five-step application program. Even with the presence of thick clay layers, malathion was detected in the groundwater at the end of August. This possibly was due to an application right before the sample was taken. Well 15 resides in the sand and gravel aquifer at a depth of 43 feet. Clay layers make up the first 22 feet as well as another 10 feet just above the bottom of the well. The home was under construction and subsequently unoccupied since the start of sample collection. The detection of 2,4-D at this well in June would likely be the result of neighboring application methods. Nonetheless, it correlates to the spring/early summer weed control application patterns.

Pesticide occurrence and nitrate detection

Each groundwater sample from each sampling event was also tested for nitrate (as nitrate) and the results are shown in **Table 4**. The rate and amount of leaching of nitrate in groundwater can be linked to physical characteristics such as well depth and sediment structure. It is also linked to water quality characteristics that reflect biological and geochemical conditions, such that nitrate is stable in aerobic conditions (Burow et al., 1998). There is no clear relation between pesticide and nitrate detection, which may imply that *in situ* degradation of pesticides might occur in the aerobic conditions of the vadose zone after application, even if downward leaching is occurring (i.e. movement of nitrate). It is also important to note the source of nitrate contamination versus pesticide contamination. Pesticides are applied as single events, multiple times a season and therefore show up in groundwater in pulses. The detection of nitrate can be caused by excessive fertilizer application, but also improper manure management or leaking septic tanks, resulting in a more continual contamination source (Wick et al., 2012).

Table 4. Nitrate and pesticide detections in groundwater samples.

Well	Event 1		Event 2		Event 3		Event 4	
	Jun/Jul 2019 NO_3^- (mg/L)	pesticide detection yes/no	Aug/Sep 2019 NO_3^- (mg/L)	pesticide detection yes/no	Nov 2019 NO_3^- (mg/L)	pesticide detection yes/no	Feb 2020 NO_3^- (mg/L)	pesticide detection yes/no
1	0	no	0	no	N.A.	N.A.	N.A.	N.A.
2	11.0	yes	15.1	no	14.7	no	15.0	no
3	0	no	0	no	N.A.	N.A.	0	no
4	0	no	0	no	N.A.	N.A.	N.A.	N.A.
5	11.2	yes	17.9	no	16.9	no	16.4	no
6	24.6	no	36.3	no	N.A.	N.A.	N.A.	N.A.
7	N.A.	N.A.	34.3	no	34.5	no	34.6	no
8	N.A.	N.A.	1.9	no	3.3	no	2.7	no
9	13.0	yes	14.6	yes	17.1	no	17.0	no
10	N.A.	N.A.	0	no	0	no	N.A.	N.A.
11	0.8	no	0.2	no	1.2	no	0.3	no
12	0	yes	0	no	0	no	0	no
13	0	yes	0	no	0	no	0	no
14	0	no	0	yes	0	no	0	no
15	0	yes	0	no	0	no	0	no
16	0	no	0	no	N.A.	N.A.	N.A.	N.A.

Darker yellow represents wells with one or more pesticides detected; lighter yellow represents wells with nitrate detected but no pesticide detected.
N.A.: not sampled or analyzed

CONCLUSIONS AND RECOMMENDATIONS

This project evaluated the occurrence of seven common residential pesticides in groundwater in suburban areas in Southeastern Wisconsin based on four sampling events. A seasonal trend was observed on pesticide detection in private wells, suggesting that groundwater may be more susceptible to residential pesticide contamination during the late spring and early summer months. This time frame is when homeowners and professional lawn care companies apply the most pesticides to lawns. Recharge into the local groundwater also typically takes place during this time. However, this study did not observe any strong correlation or trend between the hydrology, chemical properties and/or chemical application to the wells. Additionally, most of the detected pesticides were under sub-ppb level, and the concentrations of all detected pesticides were below any known groundwater standards.

This study presents the first investigation of residential pesticide contamination in groundwater in suburban areas in Southeastern Wisconsin. Although the severity and frequency of residential pesticide detection does not compare to those done in an agricultural setting, testing for residential pesticides should continue to be monitored for historical trends and potential health-based implications. Specifically, future research efforts are recommended in the following directions: (1) long-term monitoring activities over several years to fully evaluate the seasonal variability of residential pesticide occurrence in groundwater, and (2) investigation of the relation between pesticide application activities and their occurrence in groundwater, particularly for wells in the shallow sand and gravel aquifer.

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APPENDIX A

List of patents and publications

- Bychinski, Leslie, "Pesticides in Urban/Suburban Water Wells in Milwaukee, Ozaukee, Washington, and Waukesha Counties in Wisconsin" (2020). *Theses and Dissertations*. 2358. https://dc.uwm.edu/etd/2358

List of presentations

N.A.

List of awards

N.A.

List of students

- Dulay Trujillo, MS student (2018 – present), dulay@uwm.edu
- Leslie Bychinski, MS student (2018 – 2020), bychins4@uwm.edu, graduated, now work in AECOM as a hydrogeologist
- Xiaopeng Min, PhD student (2015 – present), xmin@uwm.edu

Impact of work

This monitoring project focuses on an important but overlooked issue, groundwater contamination by home and garden pesticides in non-agricultural land and/or agri-urban area. Residential pesticides have been frequently detected in groundwater in multiple states in the U.S. and other countries, while the risk of groundwater contamination by residential pesticides in Wisconsin remains insufficiently understood. This project directly evaluates the impact of residential pesticides on local groundwater quality in Southeastern Wisconsin, using Milwaukee metropolitan area as a model study area. Our results suggest that groundwater may be more susceptible to residential pesticide contamination during the late spring and early summer months, which lies within pesticide application seasons. Results of this project can provide useful guidance to stakeholders, such as homeowners of private wells, regarding pesticide application practices and water use. Specifically, we have engaged with homeowners and discussed our findings with them throughout the project. Although the concentrations of detected pesticides were below groundwater standards, homeowners are advised to use groundwater with caution after residential pesticide application activities.

APPENDIX B

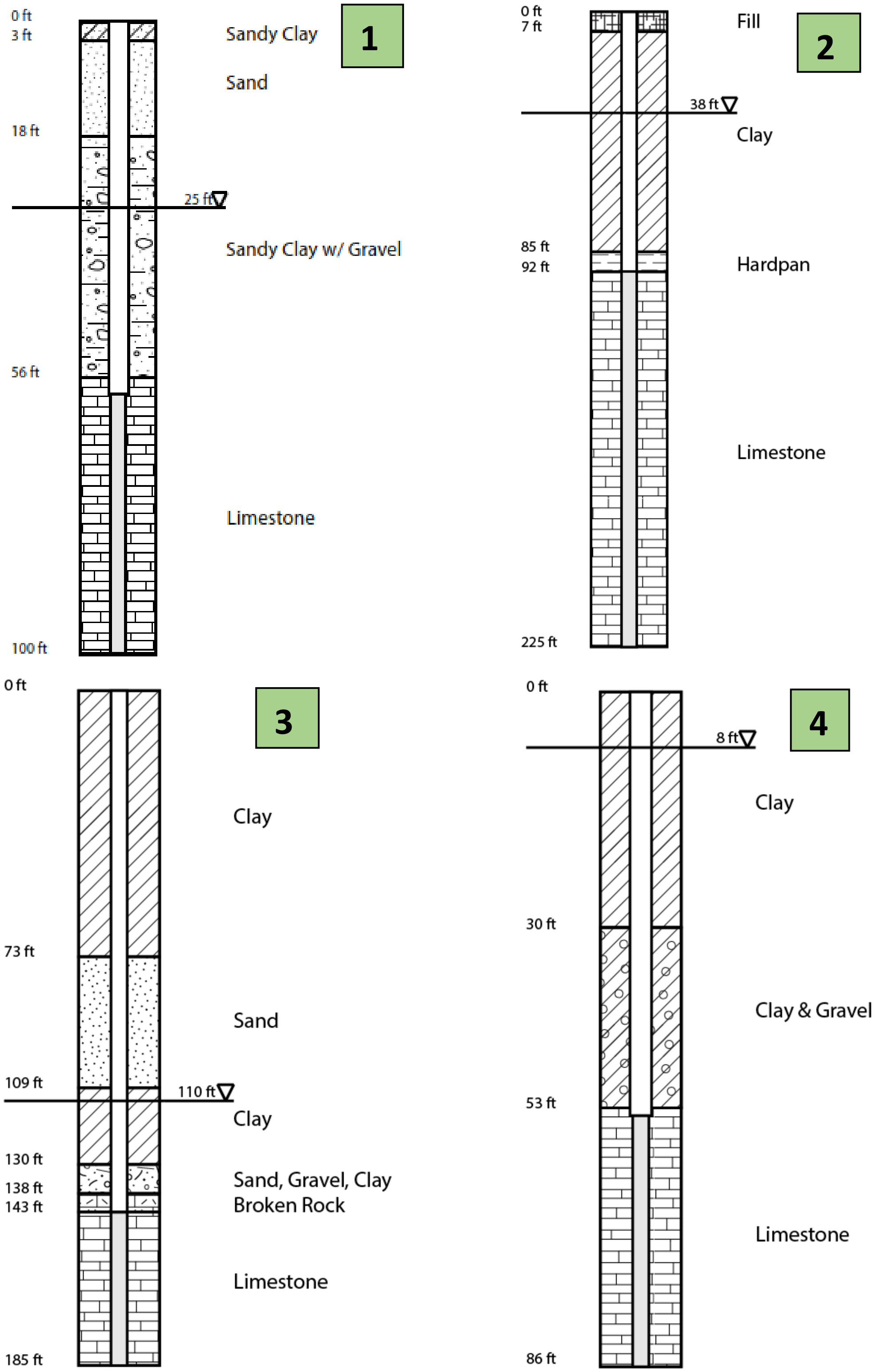

Figure A1a. Well Logs for Ozaukee County. Well ID 1, 2, 3, 4.

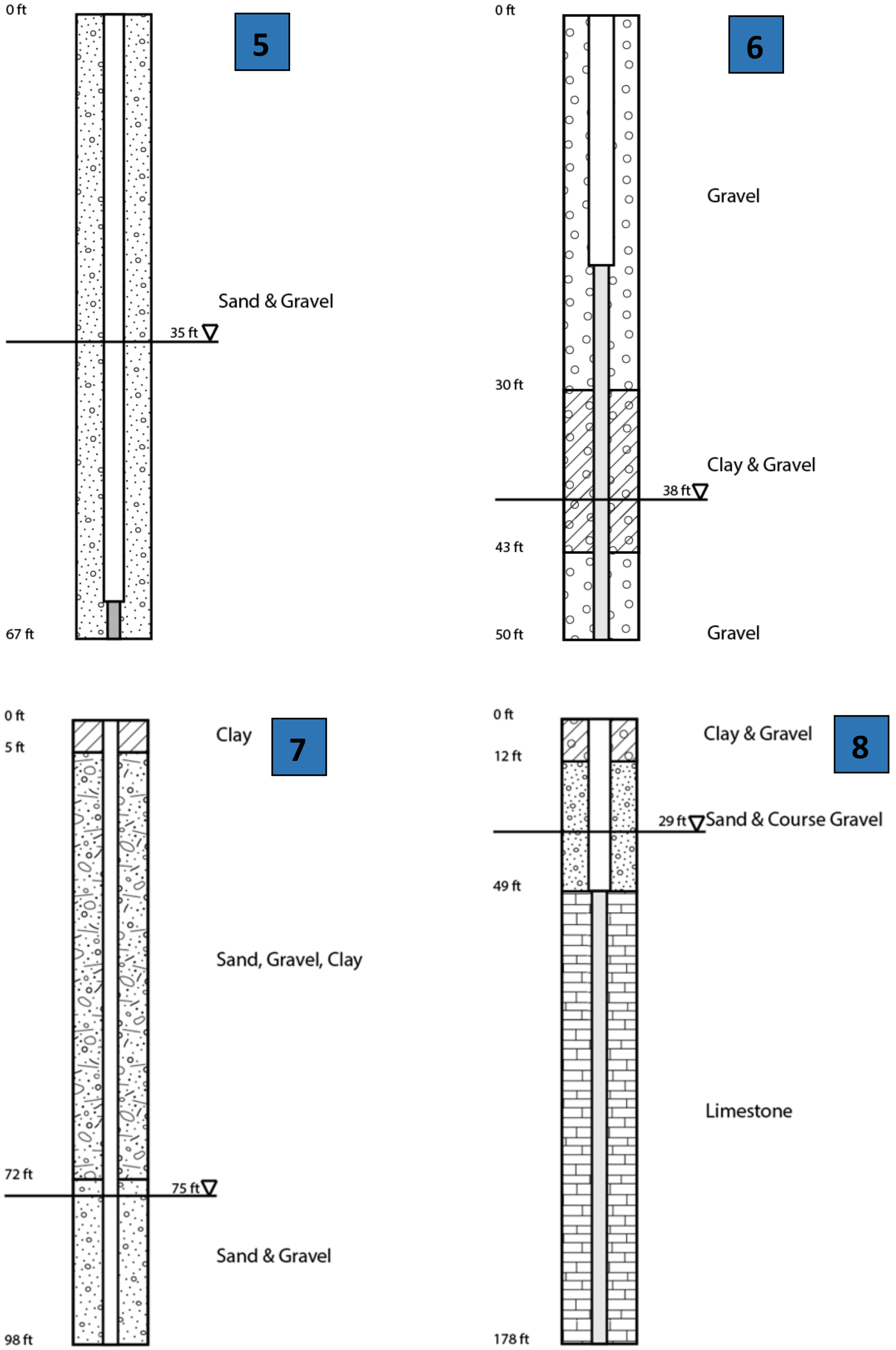

Figure A1b-1. Well Logs for Washington County. Well ID 5, 6, 7, 8.

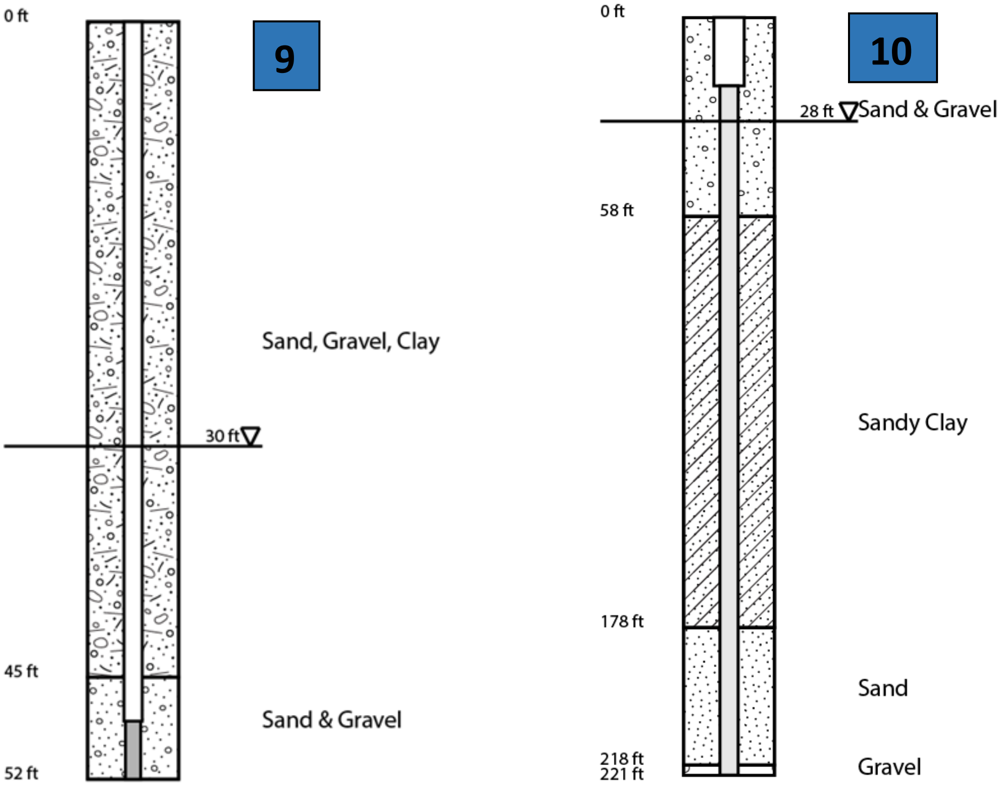

Figure A1b-2. Well Logs for Washington County. Well ID 9, 10.

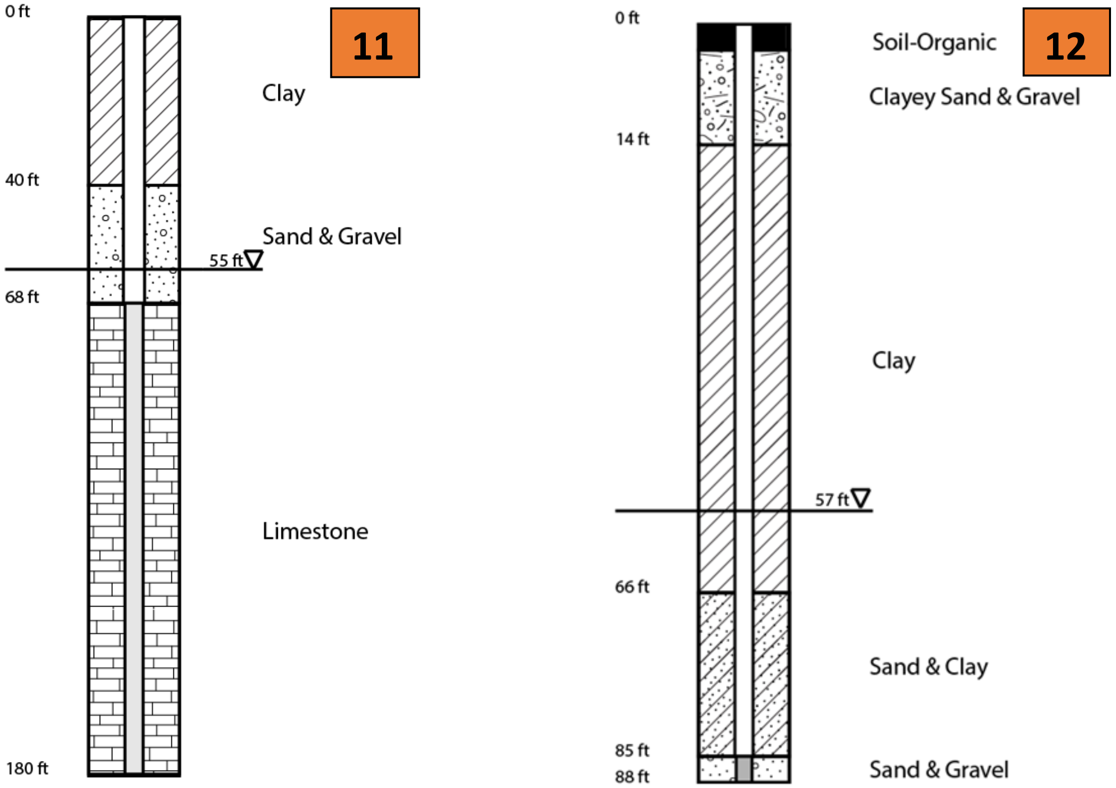

Figure A1c. Well Logs for Milwaukee County. Well ID 11, 12.

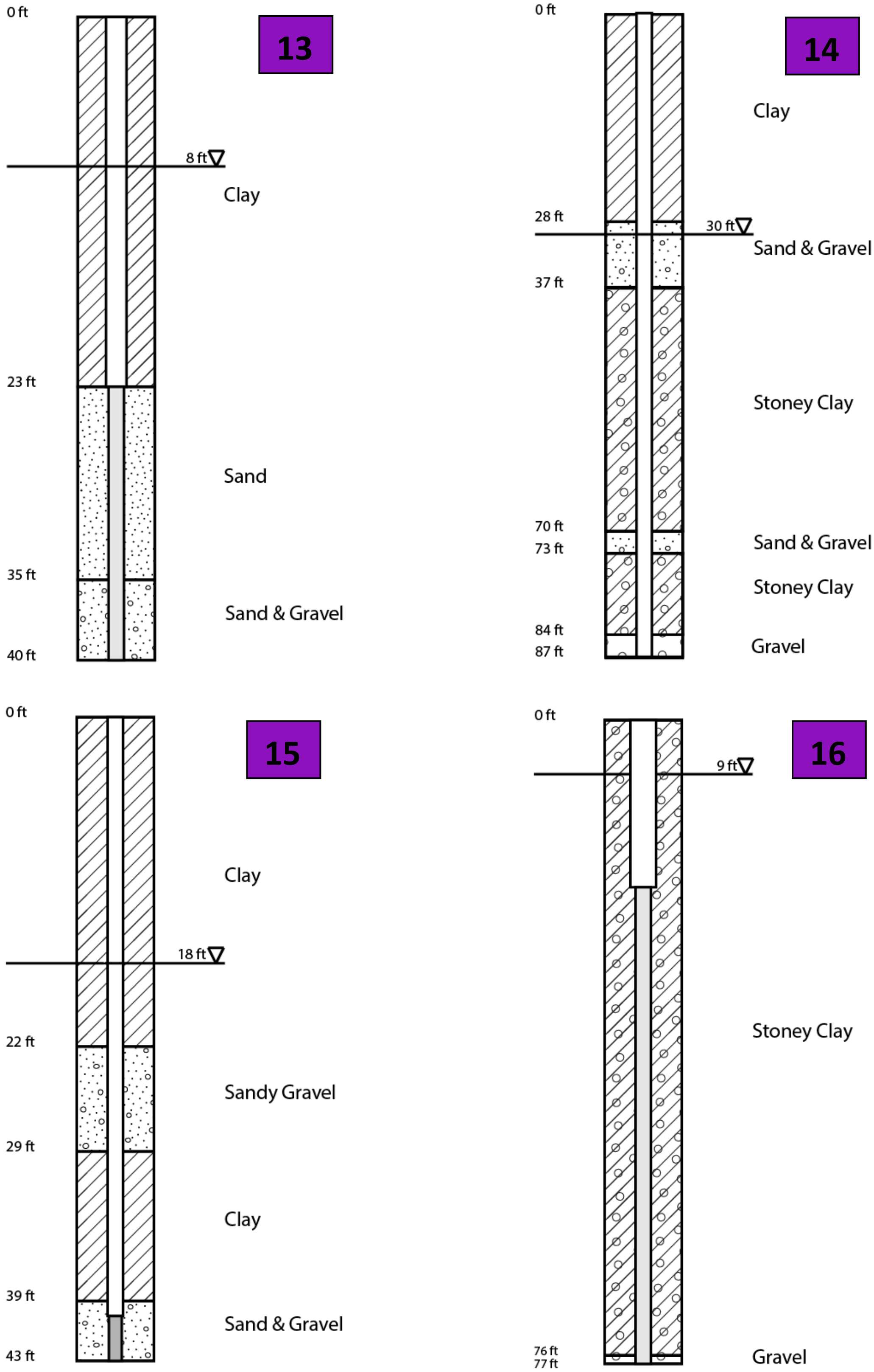

Figure A1d. Well Logs for Waukesha County. Well ID 13, 14, 15, 16.

Table A1. LC-MS/MS data acquisition parameters

	Analyte		Retention Time (min)	Precursor Ion	Product Ion	Collision Energy (V)
Target Analyte	1	Carbaryl	2.75	201.5	142.2	-11.0
	2	Imidacloprid	1.75	255.5	209.0	-14.0
	3	Malathion	3.60	330.5	127.05	-13.0
	4	MCPA	2.80	199.2	141.1	12.0
	5	MCPP	3.10	213.2	141.1	13.0
	6	2,4-D	2.80	219.1	161.0	12.0
	7	Dicamba	2.40	219.1	175.1	8.0

Table A2. Common multistep weed control and fertilization application programs. Source: Naturescape® Lawn and Landscape Care; La Rosa Landscape Co, Inc.; GreenWorks LLC.; Sunburst Environmental Services Inc.

5-6 Step Application Program			
Step	**Season**	**Months**	**Process**
1	Spring	Mar/Apr	Crabgrass/Broadleaf Weed Control, Fertilizer
2	Spring	Apr/May	Broadleaf/Blanket Weed Control, Fertilizer
3	Summer	Jun/Jul	Spot Weed Control/ Insect Control Application, Slow Release Nitrogen
4	Summer	Jul/Aug	Spot Weed Control/ Insect Control Application, Fertilizer
5	Fall	Sept/Oct	Blanket Weed Control, Fertilizer
6	Fall	Oct/Nov	Winterization Fertilization

2-3 Step Application			
Step	**Season**	**Months**	**Process**
1	Spring	Mar-May	Pre-Emergent Crabgrass & Broadleaf Weed Control, Post-Emergent Broadleaf Control, Fertilization
2	Mid-Late Summer	Jul/Aug	Broadleaf Weed Control, Fertilizer
3	Fall	Sept-Oct	Low-Rate Fertilizer

Table A3. Pesticide detection results.

Round 1: June-July 2019

Well Study #	Sample Date	*Concentration of 1L Sample (ppb)*						
		MCPP	**MCPA**	**DICAMBA**	**2,4-D**	**Carbaryl**	**Imidacloprid**	**Malathion**
1	1-Jul	~	~	~	~	~	~	~
2	18-Jun	~	0.16	~	~	1.9312	~	~
3	24-Jun	~	~	~	~	~	~	~
4	12-Jun	~	~	~	~	~	~	~
5	11-Jun	~	~	2.1824	~	~	~	~
6	11-Jun	~	~	~	~	~	~	~
9	22-Jul	~	~	~	0.0256	~	~	~
11	23-Jul	~	~	~	~	~	~	~
12	3-Jul	~	~	~	0.0592	~	~	~
13	4-Jul	~	~	~	~	~	0.0432	0.27
14	19-Jun	~	~	~	~	~	~	~
15	19-Jun	~	~	~	0.008	~	~	~
16	12-Jun	~	~	~	~	~	~	~

Round 2: August-September 2019

Well Study #	Sample Date	*Concentration of 1L Sample (ppb)*						
		MCPP	**MCPA**	**DICAMBA**	**2,4-D**	**Carbaryl**	**Imidacloprid**	**Malathion**
1	21-Aug	~	~	~	~	~	~	~
2	10-Sep	~	~	~	~	~	~	~
3	16-Aug	~	~	~	~	~	~	~
4	23-Aug	~	~	~	~	~	~	~
5	28-Aug	~	~	~	~	~	~	~
6	19-Aug	~	~	~	~	~	~	~
7	30-Aug	~	~	~	~	~	~	~
8	28-Aug	~	~	~	~	~	~	~
9	28-Aug	0.0112	~	~	~	~	~	~
10	27-Aug	~	~	~	~	~	~	~
11	27-Aug	~	~	~	~	~	~	~
12	26-Aug	~	~	~	~	~	~	~
13	19-Aug	~	~	~	~	~	~	~
14	29-Aug	~	~	~	~	~	~	0.032
15	29-Aug	~	~	~	~	~	~	~
16	26-Aug	~	~	~	~	~	~	~

Round 3: November 2019

Well Study #	Sample Date	*Concentration of 1L Sample (ppb)*						
		MCPP	**MCPA**	**DICAMBA**	**2,4-D**	**Carbaryl**	**Imidacloprid**	**Malathion**
2	26-Nov	~	~	~	~	~	~	~
5	21-Nov	~	~	~	~	~	~	~
7	13-Nov	~	~	~	~	~	~	~
8	14-Nov	~	~	~	~	~	~	~
9	22-Nov	~	~	~	~	~	~	~
10	22-Nov	~	~	~	~	~	~	~
11	20-Nov	~	~	~	~	~	~	~
12	8-Nov	~	~	~	~	~	~	~
13	12-Nov	~	~	~	~	~	~	~
14	11-Nov	~	~	~	~	~	~	~
15	11-Nov	~	~	~	~	~	~	~

Round 4: February 2020

Well Study #	Sample Date	*Concentration of 1L Sample (ppb)*						
		MCPP	**MCPA**	**DICAMBA**	**2,4-D**	**Carbaryl**	**Imidacloprid**	**Malathion**
2	14-Feb	~	~	~	~	~	~	~
3	14-Feb	~	~	~	~	~	~	~
5	6-Feb	~	~	~	~	~	~	~
7	2-Feb	~	~	~	~	~	~	~
8	6-Feb	~	~	~	~	~	~	~
9	12-Feb	~	~	~	~	~	~	~
11	10-Feb	~	~	~	~	~	~	~
12	3-Feb	~	~	~	~	~	~	~
13	4-Feb	~	~	~	~	~	~	~
14	3-Feb	~	~	~	~	~	~	~
15	3-Feb	~	~	~	~	~	~	~

~	No Detection

Pesticide survey sent out to participating homeowners

UNIVERSITY of WISCONSIN
UWMILWAUKEE

College of Letters and Science

Department of Geosciences

Leslie Bychinski
Graduate Student
Department of Geosciences
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1. How long have you lived at this location? (circle one)
   a. Less than 1 year
   b. 1-3 years
   c. 4-7 years
   d. 7-10 years
   e. More than 10 years

2. Do you use pesticides, herbicides, insecticides, etc. of any kind? And in what season (circle all that apply)
   a. Yes, 1 time a season (Spring, Summer, Fall)
   b. Yes, 2 times a season (Spring, Summer, Fall)
   c. Yes, 3 times a season (Spring, Summer, Fall)
   d. No, never

3. Do you use any of these products (see back of page and circle all that apply)? If you hire a company to do so, please indicate in the space below.

4. Are you willing to allow us to take a water sample from your well? (see attached note for further information)

Producer	**Commercial Name**	✓
HERBICIDE		
Bayer	DuraZone® Weed and Grass Killer	
Bayer	Bayer Advanced® Weed Killer for Lawn	
Bonide	Weed Beater® Ultra Weed Killer	
Gordon's	Speed Zone® Lawn Weed Killer	
Lebanon Seaboard Corporation	Preen® Garden Weed Preventer	
Scotts	Ortho® Weed B Gon	
Scotts	Roundup® Max Control 365 Weed Killer	
Scotts	Ortho®Weed B Gon Max Plus Crabgrass Control	
Spectrum Brand	Spectracide® Weed and Grass Killer	
Vigoro	Vigoro® Concentrate Weed and Feed	
INSECTICIDE		
Ambrands	Amdro® Quick Kill Lawn and Landscape Insect Killer	
Bayer	Bayer Advanced® Concentrate Tree and Shrub Protect with Feed	
BlackFlag	Black Flag® Spider and Scorpion Killer	
GardenTech Inc.	Sevin® Dust Garden Insect Killer Shaker Canister	
Scotts	Ortho® Home Defense Max Ready-to-Use Insect Killer Granules	
PF Harris	Harris® Asian Lady Beetle and Box-Elder Bug Killer	
Spectrum Brand	Triazicide® Concentrate Lawn and Landscape Insect Killer	
United Industries Corporation	HotShot Cutter® Bug Free Backyard Hose End Sprayer	
Woodstream Corporation	Safer Brand® Tomato & Vegetable Insect Killer	