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# Pesticides in Urban/Suburban Water Wells in Milwaukee, Ozaukee, Washington, and Waukesha Counties in Wisconsin

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# PESTICIDES IN URBAN/SUBURBAN WATER WELLS IN MILWAUKEE, OZAUKEE, WASHINGTON,

# AND WAUKESHA COUNTIES IN WISCONSIN

by

# Leslie Bychinski

A Thesis Submitted in

Partial Fulfillment of the

Requirements for the Degree of

Master of Science

in Geoscience

at

The University of Wisconsin-Milwaukee

May 2020

#### ABSTRACT

## PESTICIDES IN URBAN/SUBURBAN WATER WELLS IN MILWAUKEE, OZAUKEE, WASHINGTON, AND WAUKESHA COUNTIES IN WISCONSIN

by

Leslie Bychinski

The University of Wisconsin-Milwaukee, 2020 Under the Supervision of Professor Shangping Xu

The professional lawn care business has developed into a multibillion-dollar industry (Mazareanu, 2019) over the last few decades with a rise in home and garden market sector for urban/suburban use (Atwood & Paisley-Jones, 2017). Some homeowners purchase and apply the pesticides themselves while others hire professional lawn care companies. The US EPA states that "all pesticides are toxic to some degree" and the prevalent, widespread use of pesticides is both a major environmental problem and a public health issue (EPA, 1992). There have been many studies tracing agricultural pesticides application and contamination of public drinking water, and less on (sub)urban, residential pesticide application. This study targets active, private wells within four Wisconsin counties in the Milwaukee metropolitan area: Milwaukee, Ozaukee, Washington, and Waukesha, which consist of large portions of nonagricultural, suburban land use. The groundwater samples collected were tested for seven pesticide compounds that are active ingredients in some of the most commonly applied residential pesticides: 2,4−Dichlorophenoxyacetic Acid (2,4-D), Carbaryl, Dicamba, imidacloprid, Malathion, 2-methyl-4-chlorophenoxyacetic acid (MCPA), and methylchlorophenoxypropionic

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acid (MCPP). Of these seven compounds, only three (2,4-D, Carbaryl, and Dicamba) have health-based enforcement standards, and none of them have a maximum contaminant level.

In this study, 16 active, private wells were sampled; 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 the groundwater collected was representative of residential pesticide application. Samples were collected during June/July, August/September, and November of 2019, and February 2020 and analyzed for 2,4-D, carbaryl, dicamba, imidacloprid, malathion, MCPA, and MCPP. There were seven wells that detected one or more of the targeted pesticides between June and August, no other sampling event resulted in any pesticide detections. The pesticide most frequently detected being 2,4-D, showing up in three separate wells, followed by malathion showing up in two wells; carbaryl, dicamba, MCPA, and MCPP each making an appearance once.





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#### **1. INTRODUCTION**

Pesticides are a class of substances designed to disrupt the growth of weeds, insects, fungi, or any undesirable living organism in both agricultural and (sub)urban settings. (Sub)urban uses include home and garden application, as well as golf course and roadside applications (Hoffman et al, 2000). A survey conducted by the U.S. Environment & Human Health, Inc. (EHHI) suggests that around 72 percent of homeowners have applied pesticides on their lawns (EHHI, 2003). The U.S. Fish and Wildlife Service reported that homeowners used up to ten times more chemical pesticides per acre on their lawns than farmers use for agriculture (USFWS, 2000). It is estimated that more than 60 million pounds of the active ingredients of home and garden pesticides are used in the United States per year (Grube et al, 2011).

The National Water Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) has been monitoring pesticide contamination in drinking water sources in the United States since the early 1990's. Their results show that 97 percent of surface water samples from both agricultural and (sub)urban areas contain one or more pesticides at detectable levels (Giliom et al, 2006). Meanwhile, 55 percent of the shallow groundwater samples from the (sub)urban areas have detectable pesticide levels, which is comparable to that of agricultural areas (61%) (Giliom, 2007). More surprisingly, higher pesticide concentrations exceeding human-health benchmarks have been observed in shallow groundwater in (sub)urban areas than that in agricultural areas (Giliom, 2007). 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 GAO, 1990).

So far, U.S. Environmental Protection Agency (EPA) authorizes over 200 different pesticides to be used for residential purposes, and 30 of them are commonly applied. Many studies over the past few decades have suggested that pesticides may pose adverse health effects, with children, infants, and fetuses being particularly susceptible. A study in 1998 found that exposure to pesticides may cause childhood malignancies, such as neuroblastoma, Wilms' tumor, Ewing's sarcoma and non-Hodgkin's lymphoma (Zahm and Ward, 1998). Other studies have found evidence of kidney and liver damage and neurotoxicity (EHHI, 2003).

Due to this rising concern in pesticide detection nationally, the Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP), the Wisconsin Department of Natural Resources (DNR), and other agencies have implemented groundwater monitoring programs in the state. Groundwater provides drinking water for approximately 2/3 of Wisconsin's population - It is estimated that around 25 percent of Wisconsin residents obtain their drinking water from over 800,000 private wells (DNR, 2017). In the most recent statewide survey provided by the DATCP in 2016, 401 private drinking wells were sampled for pesticide and nitrate analysis (DATCP, 2017). Pesticides and their metabolites were detected in 41.7 percent of the selected wells, which shows a rise from 33.5 percent from the 2007 survey. However, it is important to note that this survey used a stratified random sampling approach that focused its efforts on areas cultivated for agricultural production, while urban and non-agricultural areas were excluded (DATCP, 2017). Limited efforts have been made on suburban/urban areas, leaving incomplete information on the occurrence and impact of residential pesticides on local groundwater supply. This project will aid as a complimentary study to current pesticide

monitoring practices and provide necessary data towards the potential risk of residential pesticide contamination in a local groundwater setting.

## **2. SETTING**

## **Study Area**

The focus of this research occupies Milwaukee (i.e. Wauwatosa and Franklin), Ozaukee (i.e. Mequon and Grafton), Washington (i.e. Hubertus, Germantown and Richfield), and Waukesha (i.e. Muskego and Elm Grove) counties of Southeastern Wisconsin (Figure 1). These four counties incorporate the Milwaukee metropolitan area and consist of large portions of nonagricultural suburban land use (Appendix A) (SEWRPC, 2006).



## **Hydrogeologic Setting**

Glaciation has largely characterized the physiography, topography, and soils of Wisconsin. Southeastern Wisconsin displays evidence of multiple glaciation events, with the last stage ending about 11,000 years ago (SEWRPC & WGNHS, 2002). A variety of complex glacial landforms and features (Appendix B) characterize the surface water drainage patterns of Southeast Wisconsin in 11 watersheds (Appendix C).

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 (Figure 2) (WGNHS, 2020). The first two aquifers collectively are referred to as the "shallow aquifer" and the "deep aquifer" collectively for the latter (SEWRPC & WGNHS, 2002). 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 3) (Bradbury, 2007).



Figure 2: Wisconsin's Aquifers from Shallowest to Deepest (darker shades of each color represent thicker deposits) Brown: Sand and Gravel Purple: Eastern Dolomite Blue: Sandstone Green: Crystalline Bedrock Source: Wisconsin Geological and Natural History Survey



Figure 3: Schematic Cross Section of Relation Well Depths to Rock Units in Southeastern Wisconsin

Source: K.R. Bradbury, Wisconsin Geological and Natural History Survey

#### **Groundwater Availability**

The total use of surface and ground water has been relatively stable in Southeastern Wisconsin (Lawrence and Ellefson, 1982; Ellefson and others, 1987; 1993; 1997). However, there has been an increase in groundwater usage, primarily due to population growth in suburban and rural subdivisions that depend on wells for water supply (SEWRPC & WGNHS, 2002).

Recharge into the groundwater system is almost entirely from precipitation, in the form of rain or snow that infiltrates the land surface downward towards the water table. On average, precipitation brings 32 inches of water to the land surface of Southeastern Wisconsin, however, *approximately 80 percent of that is lost by evapotranspiration* (Cotter et al, 1969). The amount of recharge entering the groundwater system is not uniform and can vary substantially over space and time. Spatial variation is due to differences in surface topography, soil type, and land use while temporal changes are due to annual climatic variability (SEWRPC & WGNHS, 2008). Climate affects recharge in that recharge typically increases with an increase in precipitation, in addition to the intensity and timing of precipitation as well as the temperature (SEWRPC & WGNHS, 2008). Some groundwater recharge models suggest a higher correlation between groundwater recharge and temporal controls (i.e. timing of precipitation and snowmelt) (Dripps et al, 2006).

Groundwater monitoring data typically exhibits isolated, seasonal recharge events, characteristically in the late spring (May-June) due to the spring rains and melting snow.

#### **Pesticide Application Trends**

The EPA reports on the U.S. pesticide industry's expenditures and sales reports on an annual basis. Figure 4 shows total U.S. expenditures by pesticide type and market sector from 2005 to 2012. Within the agricultural sector, herbicides accounted for over 50 percent of the total market in 2009 and 2012. In the industrial/commercial/government, insecticides accounted for 50 percent of the market in 2009 and 2012, while insecticides in the home and garden sector accounted for approximately 80 percent of the total market in 2009 and 2012 (Atwood & Paisley-Jones, 2017). Figure 5 summarizes the total user expenditures on conventional pesticides in the U.S. by market sector (Atwood & Paisley-Jones, 2017) (Appendix D).

In Wisconsin, the main source of pesticides in groundwater is agricultural herbicides and insecticides (WGCC,2016). Current research and monitoring programs have been primarily focusing on the use of agricultural pesticides and assessing groundwater quality in agricultural areas while limited information is available on the occurrence and effects residential pesticides on local groundwater quality. Table 1 shows the most commonly used pesticide active ingredients from the home and garden sector as of 2012 from the EPA market estimates report (Atwood & Paisley-Jones, 2017). Although several pesticides (e.g. 2,4-D, dicamba, malathion) have been used for both residential and agricultural purposes, due to their different end-use purposes, their doses can be relatively different. Thus, their determination in groundwater within agricultural areas does not reflect the risk of residential pesticide groundwater contamination in (sub)urban areas.





Figure 5: Total User Expenditures on Conventional Pesticides in the U.S. by Market Sector Sources: Agricultural Market Research Proprietary Data (2005-2012) Non-Agricultural Market Research Proprietary Data (2005-2012) USDA/NASS Quick Stats



Table 1: Most Commonly Used Pesticide Active Ingredients from the Home and Garden Sector

\*Note: H = Herbicide; I = Insecticide; a dash (-) means no estimate available

Sources: Non-Agricultural Market Research Proprietary Data (2012 and 2009) USDA/NASS Quick Stats

#### **3. OBJECTIVE**

## **Hypothesis**

A majority of Wisconsin homeowners use a professional lawn care company or apply pesticides themselves to their lawns to rid of various pests. Current monitoring programs in Wisconsin have been focusing their efforts on pesticide application in agricultural areas and lack information on the occurrence and subsequent effects of residential pesticides on local groundwater quality. In order to fill this knowledge gap, the focus of this study will be on active, shallow, transient non-community wells in (sub)urban locations.

The wells would be away from agricultural fields, within more densely populated, wellkept, suburban locations, and reside in the sand and gravel aquifer or the slightly deeper dolomite aquifer. Targeting wells away from agricultural fields would ensure that the water sample was representative of residential pesticide application, focusing on populated, wellkept, suburban neighborhoods to have the greatest likelihood of application and frequency of application. The higher permeability of the sand and gravel aquifer increases the overall vertical permeability of the glacial material above the water table (SEWRPC & WGNHS, 2002), and therefore would increase the likelihood of pesticide downward leaching. The dolomite aquifer is often hydraulically connected to the sand and gravel aquifer. Although groundwater flow in the dolomite aquifer is still heavily dominated by fracturing, some studies have also shown that several areas within the dolomite aquifer have behaved as a porous medium and generally control the local-scale bulk hydraulic conductivity (Rovey & Cherkauer, 1994a, b).

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.

We hypothesized that the wells located within criteria previously listed would be subjected to residential pesticide leaching and local groundwater contamination.

#### **Pesticide Selection**

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−Dichlorophenoxyacetic Acid (2,4-D), carbaryl, dicamba, imidacloprid, malathion, 2 methyl-4-chlorophenoxyacetic acid (MCPA), and methylchlorophenoxypropionic acid (MCPP) (Figure 6). These chemicals were selected because of their high-end usage, high water solubility, moderate to low soil organic carbon-water partitioning coefficients ( $K_{\text{OC}}$ ), and relatively long half-life (Table 2) (PAN, 2019). Each of these pesticides has been previously observed in groundwater sources across the globe, especially in shallow groundwater (Howard, 1991; Hill et al., 1996; Buss et al., 2006; Börjesson et al., 2004; Gilliom, 2007; Newhart, 2006; Bonmatin et al., 2015). 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.





**Table 2:** Physical Property Data for Pesticides in this Project

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

## **4. METHODOLOGY**

#### **Collecting Well Information**

The Wisconsin DNR's 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 sent to over 70 home owners 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 initial sampling locations among Milwaukee, Ozaukee, Washington, and Waukesha County (Table 3). See Figure 8 for a Google Earth map image of the locations.



A survey was sent for each of the homeowners concerning the pesticide products used, or the company hired, and the temporal application throughout the year (Appendix E).

#### **Well Sample Collection**

Groundwater samples were collected and handled following the protocols addressed in the DATCP survey (DATCP, 2017) and returned to our analytical lab. They were further prepared under standard EPA and USGS methods.

Each of the samples were chosen based primarily as a function of the location within a well-kept neighborhood in the sand and gravel or dolomite aquifer. All locations except for Well 2, 4, and 8 are less than or equal to a depth of 100 feet. All of the locations, but Well 7 and 15 accredited applying pesticides/insecticides/herbicides to their lawn multiple times a season either personally or through a company. With this in mind, there could be some level of detection for the deeper wells.

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.

#### **Basic Water Chemistry Data**

Initial temperature, pH, conductivity, pressure, and ORP measurements was taken with a YSI probe. Titration calculations with a Hach Manual-Digital Titrator (Model 16900) along with Iron (II) and Total Iron measurements with a Hach Multiparameter Portable Colorimeter were also taken at the time of collection, and then transported to the School of Freshwater Sciences to be prepped for major ion analysis. Titrations were done by taking 20ml of the well sample and titrating with 1.6 N sulfuric acid cartridge. The conversions for the Hach Manual-Digital Titrator were found by downloading Method 10244 from DOC316.53.01308, Table 1 on

page 4. On the Hach Multiparameter Portable Colorimeter, ferrous iron was programed by Method 8146 from DOC316.53.01049 and total iron was programmed by Method 8008 from DOC316.53.01053.

Roughly 30-40 mL of the well sample was filtered through 0.22 μm filter into a 50mL polypropylene centrifuge test tube with the addition of 100 μL of nitric acid to ensure a pH below 2 for major cation analysis using Thermo Scientific Flame Atomic Absorption Spectrometer (AAS) iCE 3000 Series. An additional 20-30 mL of the well sample was filtered through 0.22 μm filter into a 50mL polypropylene centrifuge test tube for the major ion analysis through the ion chromatography (IC) equipped with a conductivity detector (Dionex ICS-1000).

The major cations analyzed are calcium, magnesium, potassium, and sodium. Dilutions of each are based off previous tests conducted on Waukesha wells: Ca 1:50, Mg 1:50, K 1:10, and Na 1:100. The major anions analyzed are chloride, nitrate, phosphate, and sulfate.

See Appendix F for Basic Water Chemistry Data by Well.

## **Pesticide Detection Data**

All samples were tested at the University of Wisconsin Milwaukee (UWM) Kenwood Interdisciplinary Research Center (IRC) using the Shimadzu Triple Quadrupole Liquid Chromatography - Mass Spectrometry (LCMS) 8040. Samples were prepped for the Shimadzu Triple Quad LCMS-8040 by liquid-liquid separation with two organic solvents: Dichloromethane (DCM) and Diethyl Ether. DCM was used for positive ion analysis for carbaryl, imidacloprid, and malathion. Diethyl Ether was used for negative ionization analysis for 2,4-D, dicamba, MCPA, and MCPP. All samples are filtered first through Whatman GF/B (1 μm) filter.

For positive ionization analysis, 250 mL of the sample was measured out and adjusted to a pH between 5.5 and 6 before pouring into a separatory funnel. The equipment used for filtering and measuring the sample was washed with 10 mL each of DCM and added to the separatory funnel. An additional 30 mL of DCM (total of 50 mL) was added into the funnel. Then, the funnel was hand-shook for two minutes and left to settle for ten minutes before transferring the organic layer into a 600 mL nitrogen evaporation flask. Another 30 mL of DCM is added to the funnel and this process repeats for a total of three times. After the third organic layer transfer, the aqueous layer is drained into a waste container. The separatory funnel was washed again with 20 mL of DCM, which is also transferred to the nitrogen evaporation flask.

For negative ionization analysis, 250 mL of the sample was measured out and poured into a separatory funnel. An addition of 3mL of 12N sulfuric acid is added to the sample. The equipment used for filtering and measuring the sample was washed with 10 mL each of diethyl ether and added to the separatory funnel. An additional 30 mL of diethyl ether (total of 50 mL) was added into the funnel. Then, the funnel was hand-shook for two minutes and left to settle for ten minutes before transferring the organic layer into a 600 mL nitrogen evaporation flask. Another 30 mL of diethyl ether is added to the funnel and this process repeats for a total of three times. After the third organic layer transfer, the aqueous layer is drained into a waste container. The separatory funnel was once more with 20 mL of diethyl ether, which is also transferred to the nitrogen evaporation flask.

All samples were placed into a nitrogen evaporation system for roughly 20-30 minutes. Once the solvent was fully evaporated an additional 20 mL of the corresponding organic solvent was added into the 600 mL nitrogen evaporation flask and then transferred into a nitrogen

evaporation vial. Each sample was then evaporated to complete dryness. 100 μL of ACN is added to each vial, swirled for 30-45 seconds, and left to settle for 2-3 minutes. 900 μL of ultradistilled water (type 1 water) is added to each vial, swirled for 30-45 seconds, and left to settle for 2-3 minutes. Lastly, the sample is transferred to an analytical vial for the Shimadzu Triple Quad LCMS-8040.

As shown in Figure 7, the obtained calibration curves indicate acceptable linearity, with  $R<sup>2</sup>$  values greater than 0.99, which would be used for the target pesticide detection in real groundwater samples.



Figure 7: Calibration Curves for Target Pesticide Detection



Figure 7 (cont.): Calibration Curves for Target Pesticide Detection



#### **5. RESULTS AND DISCUSSION**

#### **Selected Wells**

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), up to sixteen by the second sampling event (August), and down to eleven for the third and fourth event (November and February). 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. Not all could be tested due to budget constraints. Wells 1, 4, 6, and 16 were not tested after the second sampling event in August. Figure 8 shows a Google Earth Image of the sample locations by the given Well ID. The well logs for each of these locations by county is shown in Figure 9a-d.



Blue: Washington County Green: Ozaukee County<br>Purple: Waukesha County Orange: Milwaukee Cou **Orange: Milwaukee County** 










## **Water Standards and Health Criteria**

Wisconsin only has a groundwater quality health-based enforcement standard (ES) for 30 pesticides (WI NR 140.10), with even less having a maximum contaminant level (MCL) (WI NR 809.20) regulated in drinking water systems (WGCC, 2018) (Table 4). Pesticides that do not have groundwater quality ES or public drinking water MCL have been detected in drinking water supplies and their health effects are inadequately understood (WGCC, 2018). Several studies have also pointed out that the coexistence of pesticide mixtures can produce augmented health effects because of their synergistic effects (Jaeger et al, 1999; Hayes et al, 2006).



Table 4: Wisconsin Groundwater Standards

The World Health Organization (WHO) reported on the **acute** toxicity of the pure

chemical ingredient to distinguish between the hazardous nature of selected pesticides (Table

5) (2010). The WHO bases its ratings on the lowest lethal dose that kills 50 percent of the tested

rats (Appendix H). The highest hazard ranking is classified as Ia Extremely Hazardous and the lowest is classified as III Slightly Hazardous. The pesticides in this research rank on the lower end of hazardous risk, however, a lack research has left them insufficiently understood, particularly for the health effects caused by long-term exposure.



Table 5: WHO Acute Hazard Rankings by Pesticide

### **Local Water Elevation Data**

The Village of Richfield, Wisconsin installed Wellntel system units in various wells throughout the village designed to create a groundwater measurement network in order to track the spatial distribution of seasonal water level trends (Cherkauer, 2013). Figure 10 and Figure 11 show data collected from two wells in the network. Figure 10 correlates to Well 10 in this study and shows data from January 1, 2017 to March 2, 2020. Figure 11 does not correlate to a groundwater well in this study, but is located approximately 0.06 miles from Well 5, 0.45 miles from Well 6, and 1.44 miles from Well 7. The data varies from year to year, with somewhat of a trend in groundwater recharge during the spring and a lack of infiltration during the summer months.







# **δ <sup>18</sup>O and δ <sup>2</sup>H Isotope Data from Samples**

Each groundwater sample collected was analyzed for oxygen and hydrogen isotopes with the Picarro Cavity Ring Down Spectroscopy (L2130-i) at UW-Milwaukee's School of Freshwater Sciences. The differences in isotopic compositions of groundwater and precipitation stem from the seasonal differences in the ratio of groundwater recharge as a proportion of precipitation (Jasechko et al, 2014). The local meteoric water line (LMWL) (Figure 12) was established for Madison, Wisconsin using precipitation samples between August 1998 and November 1999 (Swanson et al, 2006). The isotopic concentrations between the LMWL and the global meteoric water line (GMWL) contrast as a result of local climatic and geographic characteristics. Summer precipitation is isotopically heavier than winter precipitation values. The process of evaporation leaves waters to plot below the LMWL, which is demonstrated especially for the June and July samples in Figure 12 (Benettin et al, 2018). Figure 12 also illustrates that the summer groundwater is isotopically lighter than the early winter groundwater, showing that there is a lag in groundwater recharge from summer precipitation infiltration.



# **Pesticide Detection Results**



### **Round 2: August-September 2019**



#### **Round 3: November 2019**



**Round 4: February 2020**



~ No Detection

Table 6: Pesticide Detection Results from the Shimadzu Triple Quad LCMS-8040 at UW- Milwaukee



Table 6-a: Limit of Quantitation for Pesticide Detection from the Shimadzu Triple Quad LCMS-8040 at UW- Milwaukee

Pesticide detection only occurred within the first and second sampling events from June to August 2019, which takes place through Wisconsin's growing season (mid May to early October), and when pesticides are actively applied. There were no pesticides detected, at least above ppb levels, in the wells during the months of November and February. 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 2). Somewhat higher concentrations of the pesticides were detected in the early summer months compared to late summer months. Lawn care companies commonly follow a five or six step application process, others as low as two to three step application process (Table 7). Typical, over-thecounter 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.

Overall, 2,4-D was the most frequently detected, 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 (Table 1) (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 2, 2,4-D is very highly water soluble (27,600 mg/L) and has a low soil organic carbon-water partitioning coefficient (K<sub>OC</sub>) (46 L/kg) (PAN, 2020). Wells 9, 12, and 15 detected concentrations under 0.0592 ppb, which is well under the Wisconsin health-based enforcement standard (ES) of 70 ppb (WI DNR, 2020). Wells 9, 12, and 15 have variable levels of clay content (Figure 9b-2, 9c, and 9d).

Dicamba was also detected in the first sampling event in June at Well 5 at 2.18 ppb, substantially below the Wisconsin health-based enforcement standard (ES) of 300 ppb. Dicamba is highly water soluble (27,200 mg/L) and has a very low  $K_{OC}$  (5 L/kg) (Table 2) (PAN, 2020). According to the EPA sales and market data, Dicamba ranks as the eighth most commonly used pesticide in the home and garden market sector (Table 1) (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's health-based ES is 40 ppb, considerably above the detection in Well 2 (WI DNR, 2020). MCPA does not have a health-based ES, but it does meet the WI DATCP reporting limit standard of 0.05 ppb (2017). Carbaryl is the least water soluble of the pesticides targeted in this research, nonetheless is still fairly soluble (116 mg/L) (Table 2) (PAN, 2020). It has the highest  $K_{OC}$  of the pesticides at 375 L/kg (Table 2) (PAN, 2020). Carbaryl is ranked the fifth most common pesticide in the home and garden sector (Table 1) (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 (Table 1) (Atwood & Paisley-Jones, 2017) and is frequently found in products designed to rid of dandelions and other general weed management products (UC IPM, 2019).





Table 7: 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.

Imidacloprid and malathion were detected together at Well 13 during July. Imidacloprid was detected at 0.04 ppb. Imidacloprid does not have a health-based ES and the reporting limit for the WI DATCP is 0.05 ppb (WI DNR, 2020) (WI DATCP, 2017). Imidacloprid is quite water soluble (514 mg/L) and has a moderate  $K_{OC}$  (262 L/kg) (Table 2) (PAN, 2020). 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 also does not have a health-based ES and a reporting limit for the WI DATCP at 0.05 ppb (WI DNR, 2020) (WI DATCP, 2017). It is water soluble (125 mg/L) and has a moderate  $K_{\text{OC}}$  (291 L/kg) (Table 2) (PAN, 2020). It is ranked as the tenth most common pesticide in the home and garden sector (Table 1) (Atwood & Paisley-Jones, 2017) and targets lawn insects and mosquitoes (UC IPM, 2019). Trace amounts of Malathion (0.03 ppb) were also detected in Well 14 during the month of August.

Well 9 also showed a 0.01 ppb detection of MCPP at the end of August. MCPP does not have a health-based ES and a reporting limit of 0.055 ppb (WI DNR, 2020) (WI DATCP, 2017). It ranks third most popular home and garden pesticide (Table 1) (Atwood & Paisley-Jones, 2017). MCPP is water soluble (734 mg/L) and has a low  $K_{OC}$  (26 L/kg) (Table 2) (PAN, 2020). MCPP is used in a variety of products targeting various lawn weed, such as clovers and dandelions (UC IPM, 2019).

#### **One or More Pesticide Detection**

#### Reference Appendix G for Complete Survey Results

Well 2 (Figure 9a) 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 homeowner's have lived there between seven to ten years and have hired a landscape company with a five-step application program for their lawn (Table 7). 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 (Figure 9b-1) is drilled 67 feet down into the sand and gravel aquifer with no clay presumably present. The homeowner's have lived at this location for over ten years. They hire a lawn care company that has a six-step application program (Table 7) and apply their own spot treatment, mostly insecticides. Higher levels of dicamba were detected in June. This correlates to the spring and early summer pesticide application. The all sand and gravel pathway permit pesticide leaching.

Well 9 (Figure 9b-2) is 52 feet deep into the sand and gravel aquifer. The homeowner's have lived there between four and seven years and apply pesticides themselves. This includes 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 (Figure 9c) 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 lived at this location for over 10 years and have hired multiple lawn care companies over the years. Each, however, each having a five-step application program throughout the growing season (Table 7). 2, 4-D was detected in early July and correlates with the heavy spring/early summer weed control application.

Well 13 (Figure 9d) is 40 feet into the sand and gravel aquifer with a rather significant clay layer taking up the first 23 feet. The homeowner's have lived at this location between seven and ten years and apply pesticides themselves. This includes 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 (Figure 9d) 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 homeowner's have lived here between one to three years and hire a lawn care company with a five-step application program (Table 7). Even with the presence of thick clay layers, malathion was detected in the groundwater at the end of August. This likely is due to an application right before the sample was taken.

Well 15 (Figure 9d) 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.

Wells in the sand and gravel aquifer show the highest potential for pesticide leaching. Of the twelve wells that reside in the sand and gravel aquifer, six showed detectable pesticide levels. Of the four wells that reside in the dolomite aquifer, one resulted in pesticide detection. Table 8 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. Table 9 shows the number of wells with pesticide detection by the percent of clay content. Pesticide were detectable in wells that varied from 0 to about 75 percent clay content. Table 10 shows the means of application from the wells that had one or more pesticide detection. All but one had pesticide detections relating to their application. The unoccupied home had pesticide detection and can likely attribute this detection to any of the surrounding neighbors.



Table 8: Number of Detections by Well Depth



Table 9: Number of Wells with One or More Pesticide Detection by Percent Clay Content



Table 10: Means of Pesticide Application from Wells with One or More Pesticide Detection

### **No Pesticide Detection**

Reference Appendix G for Complete Survey Results

 Well 1 (Figure 9a) is drilled 100 feet into the dolomite aquifer with clay mixed into sandy layers. The homeowners have lived at this location for over ten years and have hired two professional lawn care companies with five-step application programs, along with selfapplication. Due to a personal concern, the homeowners were not able to allow a sample collection after August.

Well 3 (Figure 9a) is drilled 185 feet into the dolomite aquifer. Clay makes up the first 73 feet, with another 29-foot clay layer before the well screen. The homeowners did not disclose any information in the survey. However, most home in the area hire a professional lawn care companies that have a five-step application program.

Well 4 (Figure 9a) is located 86 feet into the dolomite aquifer. A 30-foot clay layer caps a 23-foot clay and gravel layer and the dolomite/limestone aquifer. The homeowners have lived there for over ten years and have hired a professional lawn care company every year. They did not disclose which company but did confirm application processes happened three times a season.

Well 6 (Figure 9b-1) is drilled 50 feet into the sand and gravel aquifer. The well is mostly gravel, with a little bit of clay present in the middle. The homeowners have lived at this location between seven and ten years. From 2014-2018 they hired a professional lawn care company with a five-step application program. However, in 2019 they applied pesticides themselves.

Well 7 (Figure 9b-1) is drilled 98 feet into the sand and gravel aquifer with only a fivefoot clay cap. The homeowners have lived there for seven years and have never applied pesticides to their lawn. It is important to note that this location was added late and did not have any groundwater samples tested in June or July.

Well 8 (Figure 9b-1) is located 178 feet into the dolomite aquifer with clay mixed into the top layers. There is no specific homeowner that resides here. The lawn is managed by a professional lawn care company that comes three times a season. This location was also added in August and was not tested in June or July.

Well 10 (Figure 9b-2) is drilled 221 feet into the sand and gravel aquifer with a sandy clay mixture making up 120 feet in the middle. The homeowners have lived at this location for over ten years. They apply pesticides themselves once a season but will call a professional animal control company as needed and not consecutively. This location was added late and missed the first round of sampling in the late spring/early summer.

Well 11 (Figure 9c) is 180 feet into the dolomite aquifer and is capped by 40 feet of clay. The homeowners have lived here over ten years and have hired two different professional lawn care companies over the years. In 2019, they made the switch from a company with a five-step application program to one with a two to three step application program. They also will apply pesticides themselves as needed.

Well 16 (Figure 9d) is drilled 77 feet into the sand and gravel aquifer. Almost the entire well is drilled through stony clay. The homeowners have lived at this location for more than ten years. They do not hire a lawn care company and self-apply three times a season.

### **Pesticides and Nitrate Detection**

Each groundwater sample from each sampling event was tested for nitrate (as nitrate) (Appendix F) and the results are shown below in Table 11. 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). This table shows evidence to support in-situ degradation of pesticides in the aerobic conditions (Table 2) of the vadose zone, even if downward leaching is occurring (i.e. movement of nitrate).

It is 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).



1 or More Pesticides Detected

NO<sub>3</sub> Detected, No Pesticides Detected

Table 11: Nitrate and Pesticide Detections for Groundwater Samples

### **6. CONCLUSION**

There is no real correlation or trend between the hydrology, chemical properties, and/or application of chemicals to the wells in this study. However, even with the limited data set of this study, it is observed that groundwater is the most susceptible to 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 the late spring and early summer. Continuing research and testing should make sure to take into account this seasonal variability. All of the pesticides detected showed results in parts per billion (ppb) and did not exceed any known health standards. 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.

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**APPENDIX A**

**LAND USE TRENDS OF SE WISCONSIN FROM 1963-2000**

**(SEWRPC, 2006)**



Source: SEWRPC.

#### LAND USE IN THE REGION: 1963, 1970, 1980, 1990, AND 2000



<sup>a</sup> Off-street parking is included with the associated land use.

# **A-3**

#### LAND USE IN MILWAUKEE COUNTY: 1963, 1970, 1980, 1990, AND 2000



<sup>a</sup>Off-street parking is included with the associated land use.

LAND USE IN OZAUKEE COUNTY: 1963, 1970, 1980, 1990, AND 2000



"Off-street parking is included with the associated land use.

### **A-5**

#### LAND USE IN WASHINGTON COUNTY: 1963, 1970, 1980, 1990, AND 2000



<sup>a</sup>Off-street parking is included with the associated land use.

LAND USE IN WAUKESHA COUNTY: 1963, 1970, 1980, 1990, AND 2000

	<b>Existing Land Use</b>									
	1963		1970		1980		1990		2000	
Land Use Category <sup>a</sup>	Acres	Percent of Total	Acres	Percent of Total	<b>Acres</b>	Percent of Total	<b>Acres</b>	Percent of Total	Acres	Percent of Total
Urban										
	28,148	7.6	35,476	9.5	50.745	13.7	59,247	15.9	75.221	20.2
	1,197	0.3	1,831	0.5	2.754	0.7	3,827	1.0	5,351	1.4
	924	0.2	1,758	0.5	2,747	0.7	3,802	1.0	5,525	1.5
Transportation, Communication,										
	16,079	4.3	18,545	5.0	21.867	5.9	22,805	6.1	30,001	8.1
Governmental and Institutional	2.550	0.7	3,587	1.0	4.037	1.1	4.215	1.1	4.887	1.3
	3,311	0.9	4.605	1.2	5.756	1.5	6.465	1.7	8.253	2.2
Unused Urban Land	8,509	2.3	8.516	2.3	8.017	2.2	7.025	1.9	7,806	2.1
<b>Subtotal Urban</b>	60,717	16.3	74.319	20.0	95,923	25.8	107.386	28.7	137,045	36.8
Nonurban										
<b>Natural Areas</b>										
	16,076	4.3	16,461	4.4	16,753	4.5	16,878	4.5	16,892	4.5
	52,588	14.2	51,660	13.9	51.233	13.8	51,978	14.0	52,661	14.2
	31,181	8.4	30,818	8.3	29,472	7.9	29,584	8.0	28,932	7.8
<b>Subtotal Natural Areas</b>	99,846	26.9	98,939	26.6	97,458	26.2	98,439	26.5	98,484	26.5
	200.242	53.9	184.389	49.6	161.558	43.5	142.429	38.4	112,611	30.4
Unused Rural and Other Open Land	10.786	2.9	13,943	3.8	16.651	4.5	23.336	6.4	23.397	6.3
<b>Subtotal Nonurban</b>	310,873	83.7	297,271	80.0	275,668	74.2	264,205	71.3	234,492	63.2
<b>Total</b>	371,591	100.0	371,591	100.0	371,591	100.0	371,591	100.0	371,537	100.0

<sup>a</sup>Off-street parking is included with the associated land use.

**APPENDIX B**

# **PHYSIOGRAPHIC FEATURES OF SE WISCONSIN**

**(SEWRPC, 2002)**



Source: SEWRPC.
**APPENDIX C**

## **WATERSHEDS AND SURFACE WATER RESOURCES OF SE WISCONSIN**

**(SEWRPC, 2006)**



Source: SEWRPC.

**APPENDIX D**

# **USER EXPENDITURES ON CONVENTIONAL PESTICIDES IN THE U.S. BY PESTICIDE TYPE AND MARKET SECTOR – 2012, 2009, 2007, AND 2005 ESTIMATES**

**(Atwood & Paisley-Jones, 2017)**



#### Table 2.2. User Expenditures on Conventional Pesticides in the United States by Pesticide Type and Market Sector - 2012, 2009, 2007, and 2005 Estimates

Sources: Agricultural Market Research Proprietary Data (2005-2012). Non-Agricultural Market Research Proprietary Data (2005-2012) USDA/NASS Quick Stats (http://www.nass.usda.gov/Quick Stats/)

Note: Includes the cost of insecticides, herbicides, fungicides, and other pesticides, excluding the cost of custom application. Insecticide and fungicide values include seed treatment uses. Totals may not be exact due to rounding.

- "Sulfur and Oil" includes sulfur, petroleum distillate, and petroleum oil.
- $2^{\circ}$ "Other" includes chemicals used as pesticides which are not primarily produced as pesticides for the agricultural market (e.g., sulfuric acid and phosphoric acid) as well as rodenticides and repellant use in the home and industrial markets. It does not cover specialty biocides or wood preservatives.
- 3 USDA/NASS data incorporated into agricultural expenditures to account for malathion expenditures in the Boll Weevil Eradication Program (BWEP).
- $\overline{4}$ Due to lack of data, the values presented for 2009 for the Industrial/Commercial/Government category are an average of the 2012 and 2007 values. This value may over or underestimate actual 2009 usage, due to fluctuations in annual usage.
- Updated values for 2007 and 2005 presented for continuity. See Data Reporting Changes. \*

**APPENDIX E**

**PESTICIDE SURVEY SENT OUT TO PARTICIPATING HOMEOWNERS**



 **College of Letters and Science**

*Department of Geosciences*

 **Leslie Bychinski** Graduate Student Department of Geosciences bychins4@uwm.edu

- 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)



**APPENDIX F**

## **BASIC WATER CHEMISTRY DATA BY WELL**





# **F-2: WELL 2**













#### **F-5: WELL 5**



	Fe II	<b>Fe Total</b>	Fe III	$Ca2+$	$\overline{\text{Mg}}^{2+}$	$Na+$		HCO <sub>3</sub>	<b>CI</b>	SO <sub>a</sub> <sup>2</sup>	NO <sub>3</sub>
Sample Date						mg/L					
11-Jun-19	n.a.	n.a.	n.a.	226.91	63.34	274.74	3.45	n.a.	137.68	12.24	11.23
28-Aug-19	0.01	0.03	0.02	90.74	40.95	117.82	2.29	515.00	183.11	17.98	17.90
21-Nov-19	0.04	0.10	0.06	160.45	77.97	126.08	0.24	485.00	170.90	18.22	16.90
6-Feb-20	0.00	0.61	0.61	99.21	42.16	110.19	1.54	425.00	179.74	17.29	16.42

**F-6: WELL 6**











# **F-8: WELL 8**









# **F-10: WELL 10**



#### **F-11: WELL 11**





#### **F-12: WELL 12**



# **F-13: WELL 13**





#### **F-14: WELL 14**





### **F-15: WELL 15**





#### **F-16: WELL 16**



**APPENDIX G**

**SURVEY RESULTS FOR EACH WELL**

# **G-1: WELL 1 SURVEY**

How long have you lived at this location?

10+ Years

How many times a season do you use pesticides?

Yes, 2 times a season (spring, summer, fall)

Do you hire a lawn care company or self apply?

NatureScape® Lawn and Landscape Care (5 Step Application

# Program)

Aptive Environmental



### **G-2: WELL 2 SURVEY**

How long have you lived at this location?

7-10 years

How many times a season do you use pesticides?

3 times a season; spring, summer, fall

Do you hire a lawn care company or self apply?

La Rosa Landscape Company, Inc (5 Step Application Program)



# **G-3: WELL 3 SURVEY**

How long have you lived at this location?

How many times a season do you use pesticides? Not stated

Do you hire a lawn care company or self apply?

Not stated





# **G-4: WELL 4 SURVEY**

How long have you lived at this location?

10+ Years

How many times a season do you use pesticides?

Yes, 3 times a season (spring, summer, fall)

Do you hire a lawn care company or self apply?

Hire a company - Not stated Self Application (as needed)



# **G-5: WELL 5 SURVEY**







# **G-6: WELL 6 SURVEY**

How long have you lived at this location?

7-10 Years

How many times a season do you use pesticides?

Yes, 3 times a season (spring, summer, fall)

Do you hire a lawn care company or self apply?

Schoofs GreenWorks,LLC



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# **G-7: WELL 7 SURVEY**

How long have you lived at this location?

4-7 Years

How many times a season do you use pesticides?

No, never

Do you hire a lawn care company or self apply?

N.A.





# **G-8: WELL 8 SURVEY**

How long have you lived at this location?

10+ Years

How many times a season do you use pesticides?

Yes, 3 times a season (spring, summer, fall)

Do you hire a lawn care company or self apply?

HMB Lawn & Landscape





# **G-9: WELL 9 SURVEY**



Self apply



## **G-10: WELL 10 SURVEY**

How long have you lived at this location?

10+ Years

How many times a season do you use pesticides?

Yes, 1 time a season (spring, summer, fall)

Do you hire a lawn care company or self apply?

American Animal Control® LLC

Self Application (as needed)



# **G-11: WELL 11 SURVEY**

How long have you lived at this location?

10+ Years

How many times a season do you use pesticides? 3 times a season (spring, summer, fall)

Do you hire a lawn care company or self apply?

NatureScape Lawn and Landscape Care (Previously) (5 Step Application Program) Sunburst Environmental Services (2019) (2-3 Step Application Program)



# **G-12: WELL 12 SURVEY**



10+ years

How many times a season do you use pesticides?

1 time a season; spring, summer, fall

Do you hire a lawn care company or self apply?

Naturescape (most consistent) (5 Step Application Program NaturaLawn & Happy Lawns (for 1 year)



# **G-13: WELL 13 SURVEY**



7-10 years

How many times a season do you use pesticides?

2 times a season; spring, summer, fall

Do you hire a lawn care company or self apply?

Self apply



# **G-14: WELL 14 SURVEY**

How long have you lived at this location?

1-3 years

How many times a season do you use pesticides?

2 times a season; spring, summer, fall

NatureScape Lawn and Landscape Care (5 Step Application Program) Do you hire a lawn care company or self apply?



#### **G-15: WELL 15 SURVEY**

How long have you lived at this location?

1-3 years (Not lived in - Under Renovation)

How many times a season do you use pesticides?

N.A.

Do you hire a lawn care company or self apply?

N.A.



# **G-16: WELL 16 SURVEY**

How long have you lived at this location?

10+ Years

How many times a season do you use pesticides? Yes, 3 times a season (spring, summer, fall)

Do you hire a lawn care company or self apply?

Hire a company - Not stated

Self Application (as needed)







**APPENDIX H**

# **WORLD HEALTH ORGANIZATION ACUTE HAZARD RANKINGS BASED OFF RAT LD<sup>50</sup> (WHO, 2010)**



Reference: *The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification 2004*, World Health Organization, May 2010