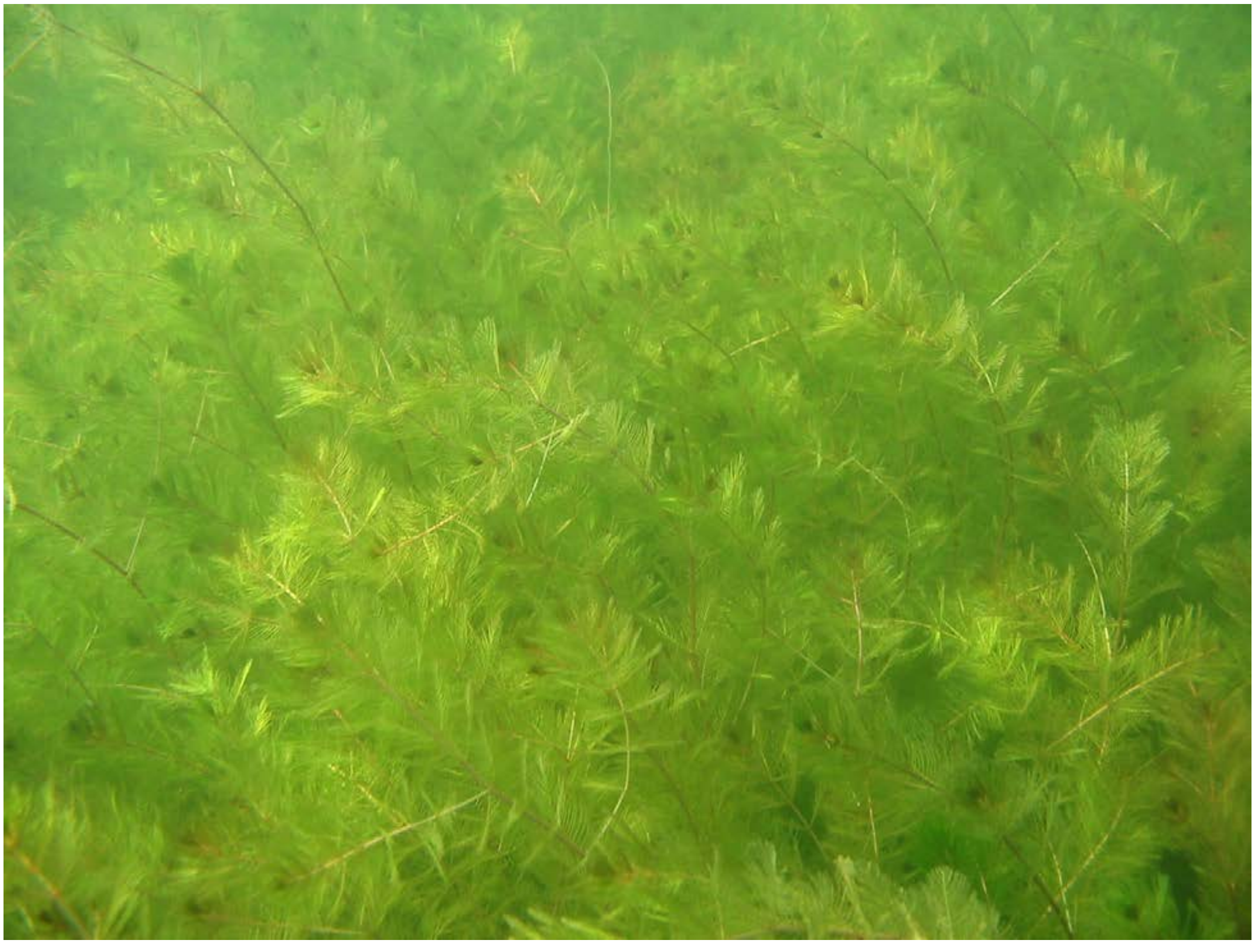
Analysis of 2,4-D and Endothall Residues from Michigan Drinking Water Wells



John D. Madsen

Geosystems Research Institute, Mississippi State University, Mississippi State, MS 39762

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John D. Madsen, Associate Professor[1]
Geosystems Research Institute, Mississippi State University, Mississippi State, MS 39762

Introduction

Aquatic plant management in the United States relies heavily on herbicides labeled by the US EPA for aquatic use. In Michigan, two of the products widely used to manage invasive aquatic weeds like Eurasian watermilfoil (*Myriophyllum spicatum* L.) and curlyleaf pondweed (*Potamogeton crispus* L.) are 2,4-D and endothall. While liquid formulations are available for both, granular formulations of 2,4-D have been more commonly used for Eurasian watermilfoil control . The potassium salt of endothall is also available as a granular formulation. Regulatory agencies raised the concern of granular formulations possibly increasing the potential of herbicide groundwater infiltration. The following presents the results of long-term monitoring of groundwater wells for the presence of 2,4-D and endothall, in response to restrictions imposed on the use of granular products.

2,4-D. The herbicide and plant growth regulator 2,4-dichlorophenoxyacetic acid (or 2,4-D, as it is more commonly known) is a widely used product for both agricultural and nonagricultural environments, with both terrestrial and aquatic applications (Gervais et al. 2008). 2,4-D is a selective broadleaf herbicide, and has been widely used in agronomic applications for cereal or grass crops, weed control in turf, and control of Eurasian watermilfoil (*Myriophyllum spicatum* L.) in aquatic environments (Gervais et al. 2008, Madsen 2014). 2,4-D is available in several different formulations of the ester, amino acid, and acid. The dimethylamine salt and the ester combined account for around 95% of all formulations sold globally. 2,4-D was first used in the United States in the 1940’s, and was last evaluated by the U.S. EPA through re-registration in 2005. Approximately 46 million pounds of 2,4-D are used each year in the US (2000 data, Gervais et al. 2008).

Depending on the formulation, 2,4-D has a low acute oral toxicity (639 to 1747 mg/kg in rats; Gervais et al. 2008). In all three evaluations by US EPA for carcinogenic effects, US EPA concluded that there was no link between 2,4-D exposure and cancer, but they have refrained from finally classifying 2,4-D due to epidemiological studies which involve mixtures of 2,4-D and dioxin.

While 2,4-D typically has a low half-life in soils (1 to 14 days, median value of 2.9 days), the half-life of the ester formulation in aquatic sediments has been measured to be as high as 186 days (Gervais et al. 2008). Degradation is predominantly by microbial activity. The half-life in aerobic water is typically 15 days, and in anaerobic water it ranges from 41 to 333 days. The half-life in water is sensitive to pH, with degradation occurring more rapidly at pH above 8, and more slowly at pH below 5.

[1]Current Contact Information: Dr. John D. Madsen, Research Biologist, USDA ARS EIWRU, University of California-Davis, Plant Sciences Department, 1 Shield Avenue, 274 Robbins Hall, Davis, CA 95616, E-mail: jmadsen@ucdavis.edu or john.madsen@ars.usda.gov, Ph. 530-752-7870, Cell: 662-722-0157.

Extremely sensitive analytical techniques have found traces of 2,4-D in 49.3% of treated water supplies and 53.7% of untreated water samples, with detections from 1.1 to 2400 ppb (parts per billion, or µg/L; Gervais et al. 2008). US EPA has set the maximum contaminant level (MCL) in drinking water at 70,000 ppt, or 70 ppb (parts per billion, or µg/L). Based on this concentration, the common detection of trace levels of 2,4-D in water supplies is not a significant concern for human health.

Groundwater Contamination. Relatively little publicly-available research has been done on the transport of 2,4-D to groundwater from aquatic treatments. Studies in British Columbia measured 2,4-D residues in the water and sediment following granular 2,4-D treatments (BC 1980). They found persistence of 2,4-D residues in hydrosoils from one to eleven months, and to a depth of no more than 30 cm. They conclude that it was unlikely for 2,4-D to contaminate the groundwater. Additional studies in British Columbia found that no 2,4-D residues were found 50 days after treatment with granular 2,4-D (Kangasniemi and Nagpal 1982). In a three-pond study performed in Florida, Georgia, and Missouri, ponds were treated with liquid 2,4-D rather than granular 2,4-D. Pond sediment maximum 2,4-D residues ranged from 42 to 170 ppb, and decreased to below detection in 56 to 112 days (Schultz and Harman 1974). Given the low concentrations in sediments, it seems unlikely that significant infiltration to groundwater would occur. In lake sediments, 2,4-D is microbially-degraded (Aly and Faust 1964). Lakes treated repeatedly with 2,4-D build up a microbial flora that more rapidly degrade 2,4-D.

The potential for groundwater contamination is a compelling concern for state natural resource and public health agencies. In addition to propagating potential contamination to other locations through a medium with a slow but persistent transport, the states are given the primary role of protecting drinking water resources through the Federal Safe Drinking Water Act (SDWA) of 1974. The SDWA provides primary and secondary drinking-water standards to protect drinking water sources (US EPA 2004). The maximum contaminant level for drinking water is 70 ppb (US EPA 1990a). According to the drinking water regulations, the reference dose for an adult is 10 µg/kg/day, meaning that an adult can consume 10 µg for every kg of body weight every day without an appreciable risk of adverse effects.

In 1990, the US EPA (1990b) released the results of the National Pesticide Survey, which sampled 1300 community well systems and rural domestic wells for 101 pesticides, 25 pesticide degradates, and nitrate – a total of 127 analytes per sample. The most common analyte detected was nitrate, found in 53% of community wells and 57% of rural domestic wells. In contrast, pesticides were much less common. Only 12 of the 126 pesticides or pesticide degradates were detected above the minimum analytical level. Approximately 10.4% of community well systems and 4.2% of rural domestic wells had at least one pesticide contaminant, though not necessarily above the minimum contaminant level. The most common pesticide found was atrazine, which was detected in 1.7% of community water systems and 0.7% of rural domestic wells. Of interest here, 2,4-D was not one of the pesticides detected in drinking water wells, despite being a widely-used herbicide.

The best study available was for Bashan Lake in Connecticut (Bugbee et al. 2003). In this study, variable-leaf watermilfoil (*Myriophyllum heterophyllum* Michx.) was treated with granular 2,4-D (BEE formulation) at a rate of 144 kg/ha. Lake water residues were below the 100 ppb irrigation and 70 ppb drinking water levels within 3 days after treatment (DAT). Five shallow wells (less than 5 m or 15 feet deep) were monitored for 73 DAT. No 2,4-D residues were found in well water samples at detectable levels throughout the study.

Endothall. Endothall is a contact herbicide used primarily in aquatic and ditch bank applications (Wilson and Ju 2012). It is widely used either alone or in combination with 2,4-D to control Eurasian watermilfoil (Parsons et al. 2004, Skogerboe and Getsinger 2006). Research on the low-temperature activity of endothall has led to its widespread use for early spring treatments to control curlyleaf pondweed before native plant growth is initiated (Netherland et al. 2000, Poovey et al. 2002). Despite its reputation as a broad-spectrum contact herbicide, proper rate selection and timing allows significant selectivity in managing some invasive species (Skogerboe and Getsinger 2001, 2002). Development of low-dose metering technology (Sisneros et al. 1998) and establishment of food tolerances through the IR-4 program have also opened a new use for endothall in treating weeds in irrigation canals (Netherland 2014).

Endothall is available as two different salts, which confers different toxicity and efficacy for management: the dipotassium salt (sold as Aquathol K or Cascade) and the dimethylalkylamine salt (sold as Hydrothol 191 or Teton). Since the target of sampling in this study was the dipotassium salt (Aquathol K), discussion will focus on the dipotassium salt and not other endothall salts. The oral LD_{50} for rat ingestion is 198 mg/kg (Ahrens 1994, in MacDonald et al. 2003). Endothall is not teratogenic, mutagenic, or carcinogenic; nor does it affect reproductive processes or specific organs (Extoxnet 1996).

Endothall is highly mobile in soil, creating some potential for infiltration to groundwater (Extoxnet 1996). However, it is rapidly degraded in the soil by microbial degradation, which limits leaching. Endothall degrades in soil in 7 to 21 days. The half-life in soils ranges from 4 days in clays to 9 days in organic soils. The half-life in surface waters is from 4 to 7 days at 72F, but can range from 14 to 21 days at 45F to 36 hours at 80F (Cody Gray, UPI, pers. comm.).

Langeland and Warner (1986) treated two ponds in North Carolina with 2 ppm endothall as a liquid formulation of the dipotassium salt. The half-life of endothall was 14 days.

The maximum contaminant level (MCL) for endothall is 100 ppt, or 0.1 ppb (Extonet 1996). Endothall was not detected in 3 surface water and 604 groundwater samples from STORET in 1988 (US EPA 1989).

Groundwater contamination. The risk of endothall contamination to surface and groundwater was considered low in the most recent re-registration review (US EPA 2005). A review of data from the National Contaminant Occurrence Database indicated that only 7 of more than 27,000 groundwater samples and 8 of more than 5,000 surface water samples had detectable endothall levels. For these assessments, the detection level was 10 ppb, well below the 100 ppb maximum contaminant level (MCL). The reviewers suggested that the low number of detections were more likely statistical outliers than significant contamination events. The Safe Drinking Water Information System (SDWIS) recorded only 2 occurrences of endothall residues in excess of the MCL (US EPA 2005).

Much less published information is available on endothall than on 2,4-D, which has the distinction of being the most studied herbicide. The State of Washington Department of Ecology examined the dissipation and breakdown characteristics, and concluded that endothall does not pose a significant threat to groundwater (WA DOE 2001).

Background. The current study was undertaken in response to an initial study by the Michigan Department of Environmental Quality over concerns from applying 2,4-D and endothall to waters adjacent to groundwater wells. According to an interoffice memo (Brown 1996a), a study was conducted by the Michigan Department of Environmental Quality on behalf of the Michigan Aquatic Managers Association in 1988. Although a 2" monitoring well was placed only 7' from shore, and a 4" pumping well placed only 15' from shore at a depth of only 8' deep, the samples had only traces of 2,4-D for 2 to 4 weeks after treatment and traces of endothall 2 days after treatment. According to current well code, a well casing must extend at least 25' belowground (MDEQ 1994). These two study wells were clearly not constructed to a reasonable facsimile of operational wells. The traces of 2,4-D and endothall were below detectable limits, but the 1988 study only used a detection limit of 100 ppb. The maximum contaminant level (MCL) for 2,4-D is below this, at 70 ppb. In addition, the study in 1988 used an application rate of 6.0 ppm for both 2,4-D and endothall, which is twice the normal application rate concentration, and above the maximum label rate. For Aquathol-K, the maximum allowed label rate is 5.0 ppm and the maximum contaminant level (MCL) is 0.1 ppm (UPI 2011). For 2,4-D DMA, the maximum allowed rate is 4.0 ppm, with an MCL of 70 ppb (Dow AgroSciences 2013). With these results, the MDEQ recommended repeating the study with some alterations. Given that US EPA had established a trigger concentration of one-half the MCL for increased monitoring, the MDEQ proposed looking for these trigger events. A subsequent memo (Brown 1996b) confirmed an agreement to initiate a second study on July 9, 1996.

The 1996 study once more used study wells that did not meet well construction standards (MDEQ 1996). The pumping well was constructed of 5" casing, only 12' from the lake edge and extending 12' deep into soil. Two observation wells were constructed, one 16' from the lake edge and one 6' from the lake edge. The wells were placed in a fine sand glacial till, above a clay lens. The pump well was pumping at a rate of 2.4 gal/min, pulling water from the lake into the well. Herbicides were applied in this study at the rates typically used by applicators in the region. In this study, endothall was detected in the lakewater, pumping and observation well samples for 30 days. The highest value in the pumping well was 20 ppb, which is below the MCL. The observation well peaked at 130 ppb, which is above the MCL. 2,4-D was detected in the lake water and observation wells for 33 days, consistently from 400 to 600 ppb. These values greatly exceeded the MCL of 70 ppb. The pumping well only reached 400 ppb, but continued to have levels exceeding the MCL for 50 days. The conclusion of the report authors is that the study demonstrates the potential for treated lake water to enter the groundwater. Rather than await peer review, the authors released the results in published proceedings articles (Lovato et al. 1998) and a briefing paper.

The results were strongly criticized by both industry and researchers, with comments centered on the fact that the study wells are well below drinking well standards for the state (Armbruster 1996). The shallow wells used, perched above a clay layer in the soil, and continuous pumping set up a shallow soil flow that drew water directly from the lake into the sampling well. Given that wells constructed to code would only take water below the clay layer, requiring water to infiltrate a greater depth of soil.

Beginning in 1997, permits for application of granular formulations of 2,4-D and endothall included a limitation of not applying within 75 feet of any well, or within 250 feet of wells less than 30 feet deep (Witte 1997). In addition, the permittee was responsible for locating water wells and observing appropriate setback requirements. These requirements were reinforced in a 1998 memo (Klemans 1998).

The initiative for a new study originated in an e-mail from Ernie Maier of Environmental Lake Management (Maier 1998). His initial plan, developed in conjunction with Dick Pinagel, was to take five well samples per lake in four different lakes that had a history of 2,4-D treatments. Soon after, Lake and Water Management Division and Drinking Water and Radiological Protection Division members met to discuss a new study (Brown 1998). The study initially included four counties, with lakes between 10 and 100 acre. A list of lakes for which 2,4-D treatments were issued was used to develop a study well list.

The current study was developed to assess 2,4-D and endothall residue samples from wells near lakes treated with 2,4-D and endothall, respectively.

Materials and Methods

Sample Design. Public and private wells were selected that were near lakes treated with 2,4-D and endothall throughout the state of Michigan, and sampling times were dispersed throughout the year to ensure that both rapid and slow infiltration of herbicides would be detected.

Analytical Methods. Water samples were analyzed at the State of Michigan, Michigan Department of Environmental Quality Drinking Water Laboratory in Lansing, Michigan. The DWL is the laboratory certification authority for the State of Michigan. Samples were analyzed using GC/MS (gas chromatography / mass spectrophotometry).

Sample Population. A total of 15,539 2,4-D samples were collected from wells and drinking water sources in Michigan over the study period. Of these, 14,609 were analyzed with a detection limit of 0.002 ppm, and 367 were analyzed with a detection limit of 0.0001 ppm. The remainder did not state the detection limit. Samples were collected from all 83 counties in Michigan (Table 1). Samples were collected across eighteen years, from 1997 to 2013, though the sampling was not uniformly distributed by year (Table 2, Figure 1). Samples were taken across the calendar year, though the timing of these samples was also not evenly distributed (Table 3, Figure 2).

A total of 193 samples were collected to be analyzed for endothall residues. The samples were collected from 34 different counties (Table 4). Samples were taken across an eleven year span (1997-2007), with almost one-half (95 of 193) taken in 1997 (Table 5). Samples were collected across the year, with more than half taken in either August or September (Table 6). Despite this intensive sampling, all residues were below detection limits (0.01 ppm or 10 ppb). Since the

MCL for endothall is 100 ppb, any residues close to violating the MCL should have been detected.

Statistical Analysis. The data were assessed using histograms of the timing and distribution of samples, and for the frequency of specific value ranges. No statistical tests per se were conducted.

Results and Discussion

2,4-D. Of the 15,539 samples analyzed for 2,4-D over an 18 year period of time, 99.8% had no detectable amount of 2,4-D. Of the remaining 0.2%, one-half that number (or 0.1%, 16 samples) had a trace amount that was not quantifiable. The remaining 13 samples had 2,4-D concentrations that were quantifiable (Table 7, Figure 3).

The detection limit for these analyses was largely at the 0.002 ppm (2 ppb) level. This means that quantifiable amounts of 2,4-D must be above 2 ppb. A finding of trace amount is often recorded as one-half the detection limit, or 1 ppb in most instances. The maximum contaminant level for 2,4-D is established as 70 ppb for drinking water. Trace value samples pose no threat to human health, based on US EPA standards (US EPA 1990a).

Thirteen samples (out of more than 15,000) had a quantifiable amount of 2,4-D (Table 8, Figure 4). Two of these samples exceeded one-half the MCL, and only one exceeded the MCL (133 ppb). Both of these samples were taken from Calhoun County, on April 26, 1999 (Table 8, Figure 5). A third sample collected from Calhoun County on the same date had a quantifiable amount of 2,4-D. The sample date for these three samples, April 26, 1999, would be early for an aquatic treatment with 2,4-D. Most permits are issued in the late spring for Eurasian watermilfoil treatments, with treatments put out in May or June, when Eurasian watermilfoil is actively growing. Eight quantifiable samples were collected in Clare County from early January to late February 1997. These samples are also questionable given the time of year that detections occurred. With so many samples analyzed, the likelihood of external contamination during sample collection or in the laboratory during analysis of a standard curve is significant.

Given that only one sample out of 15,539 (or 0.006% of samples) exceeded the Maximum Contaminant Level for 2,4-D in drinking water samples, contamination of drinking water wells is not occurring in a systematic manner. Treatments with granular 2,4-D in Michigan lakes is not resulting in significant contamination of wells with 2,4-D. Further, studies at other locations, including the study by Bugbee and others (2003) indicate that contamination of shallow drinking water wells do not occur from aquatic treatments with 2,4-D. Current setbacks are too restrictive, and are not necessary to reduce 2,4-D infiltration to groundwater.

Endothall. Despite collecting 193 samples for analysis across 35 counties and spread over 11 years, no endothall residues were detected. This substantiates previous observations and analytical estimates that endothall does not pose a threat to groundwater (US EPA 1989, 2005, WA DOE 2001).

Summary. Only 29 samples had detectable levels of 2,4-D out of more than 15,000 analyzed. Of these, more than half were not quantifiable. Thirteen samples had a quantifiable amount of 2,4-D. Only one sample exceeded the MCL, and this (along with two samples that were detectable) was measured in April, which would be too early for an aquatic herbicide treatment. These results would indicate that the use of granular 2,4-D is not a significant threat to groundwater.

None of the 193 samples collected for endothall analysis were detectable, much less quantifiable. Since no endothall was detected in groundwater, endothall likewise does not pose a significant threat to groundwater.

For reasons other than pesticide contamination, homeowners should be encouraged to build private wells in compliance with Michigan law. Shallow wells can be contaminated with other more mobile chemical contaminants, including nitrates and septic discharges, which are a more common risk to human health derived from drinking water.

Acknowledgements

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A Note on Units

1 ppm (parts per million) is the same as 1 mg/L (milligrams per liter)
1 ppm is the same as 1,000 ppb (parts per billion) or 1,000 µg/L (microgams per liter)
1 ppm is the same as 1,000,000 ppt (parts per trillion) or 1,000,000 ng/L (nanograms per liter)

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Table 1. 2,4-D sample distribution by Michigan county.

County Name	Frequency	Percent
Alcona	48	0.3
Alger	70	0.5
Allegan	489	3.1
Alpena	43	0.3
Antrim	139	0.9
Arenac	42	0.3
Baraga	28	0.2
Barry	207	1.3
Bay	43	0.3
Benzie	147	0.9
Berrien	428	2.8
Branch	107	0.7
Calhoun	316	2
Cass	160	1
Charlevoix	162	1
Cheboygan	95	0.6
Chippewa	59	0.4
Clare	60	0.4
Clinton	210	1.4
Crawford	72	0.5
Delta	73	0.5
Dickinson	71	0.5
Eaton	196	1.3
Emmet	365	2.3
Genesee	589	3.8
Gladwin	63	0.4
Gogebic	49	0.3
Grand Traverse	308	2
Gratiot	174	1.1
Hillsdale	114	0.7
Houghton	51	0.3
Huron	152	1
Ingham	381	2.5
Ionia	234	1.5
Iosco	59	0.4
Iron	107	0.7
Isabella	149	1
Jackson	364	2.3

Table 1. 2,4-D sample distribution by Michigan county.

County Name	Frequency	Percent
Kalamazoo	332	2.1
Kalkaska	40	0.3
Kent	528	3.4
Keweenaw	33	0.2
Lake	58	0.4
Lapeer	160	1
Leelanau	211	1.4
Lenawee	327	2.1
Livingston	728	4.7
Luce	58	0.4
Mackinac	57	0.4
Macomb	219	1.4
Manistee	131	0.8
Marquette	197	1.3
Mason	89	0.6
Mecosta	154	1
Menominee	85	0.5
Midland	82	0.5
Missaukee	65	0.4
Monroe	99	0.6
Montcalm	387	2.5
Montmorency	41	0.3
Muskegon	218	1.4
Newaygo	132	0.8
Oakland	1661	10.7
Oceana	166	1.1
Ogemaw	72	0.5
Ontonagon	45	0.3
Osceola	133	0.9
Oscoda	37	0.2
Otsego	137	0.9
Ottawa	218	1.4
Presque Isle	78	0.5
Roscommon	152	1
Saginaw	96	0.6
Sanilac	143	0.9
Schoolcraft	25	0.2
Shiawassee	227	1.5
St Clair	156	1
St Joseph	259	1.7
Tuscola	192	1.2

Table 1. 2,4-D sample distribution by Michigan county.

County Name	Frequency	Percent
Van Buren	337	2.2
Washtenaw	345	2.2
Wayne	85	0.5
Wexford	120	0.8
Total	15539	100

Table 2. Distribution of 2,4-D sample collections by year collected.

Year	Freq	Percent
1997	858	5.5
1998	1370	8.8
1999	856	5.5
2000	986	6.3
2001	1609	10.4
2002	827	5.3
2003	796	5.1
2004	1574	10.1
2005	744	4.8
2006	732	4.7
2007	1029	6.6
2008	573	3.7
2009	685	4.4
2010	1661	10.7
2011	528	3.4
2012	628	4
2013	83	0.5
Total	15539	100

Table 3. Distribution of 2,4-D sample events by month of the year.

Month	Frequency	Percent
JAN	676	4.4
FEB	786	5.1
MAR	1153	7.4
APR	951	6.1
MAY	1044	6.7
JUN	1677	10.8
JUL	1731	11.1
AUG	2188	14.1
SEP	2549	16.4
OCT	685	4.4
NOV	801	5.2
DEC	1298	8.4

Table 4. Endothall sample distribution by Michigan county.

County	Frequency	Percent
Allegan	2	1
Arenac	2	1
Baraga	3	1.6
Barry	1	0.5
Bay	5	2.6
Benzie	10	5.2
Berrien	6	3.1
Branch	1	0.5
Calhoun	2	1
Cass	5	2.6
Clare	2	1
Grand Traverse	4	2.1
Gratiot	3	1.6
Huron	6	3.1
Ingham	2	1
Ionia	1	0.5
Isabella	1	0.5
Kalamazoo	1	0.5
Kent	12	6.3
Lapeer	2	1
Leelanau	22	11.5
Lenawee	8	4.2
Manistee	4	2.1
Mecosta	6	3.1
Monroe	3	1.6
Montcalm	5	2.6
Newaygo	4	2.1
Oakland	21	10.9
Oceana	6	3.1
Ottawa	7	3.6
Presque Isle	8	4.2
St Joseph	3	1.6
Van Buren	13	6.8
Washtenaw	6	3.1
Wayne	5	2.6
Total	192	

Table 5. Endothall sample distribution by year.

Year	Frequency	Percent
1997	95	49.5
1998	8	4.2
1999	17	8.9
2000	15	7.8
2001	10	5.2
2002	8	4.2
2003	27	14.1
2004	8	4.2
2005	3	1.6
2007	1	0.5
Total	192	100

Table 6. Endothall sample distribution by month.

Month	Frequency	Percent
January	2	1
February	8	4.2
March	2	1
April	0	0
May	4	2.1
June	27	14.1
July	6	3.1
August	52	27.1
September	74	38.5
October	6	3.1
November	4	2.1
December	7	3.6
Total	192	99.9

Table 7. Analytical results of well and drinking water analyses for the presence of 2,4-D, from 1997 to 2013, in Michigan.

Analytical Result	Frequency	Percent
No detection	15509	99.8
Trace	16	0.1
Measureable	13	0.1
Total	15538	100

Table 8. Quantifiable test results of 2,4-D concentration from over 15,000 samples taken from Michigan wells, in mg/L and ppb (µg/L).

Sample Code	County	Date Collected	2,4-D (ppm)	2,4-D (ppb)	Test Detection Limit (ppm)
LC1997009511	Clare	02-Jan-97	0.018	18	0.002
LC1997009512	Clare	02-Jan-97	0.005	5	0.002
LC1997010355	Clare	14-Jan-97	0.018	18	0.002
LC1997010356	Clare	14-Jan-97	0.003	3	0.002
LC1997011629	Clare	25-Jan-97	0.017	17	0.002
LC1997011630	Clare	28-Jan-97	0.004	4	0.002
LC1997012762	Clare	07-Feb-97	0.016	16	0.002
LC1997014132	Clare	25-Feb-97	0.006	6	0.002
LC1998002691	Montcalm	20-Oct-97	0.005	5	0.002
LC1999027584	Calhoun	26-Apr-99	0.039	39	0.002
LC1999027586	Calhoun	26-Apr-99	0.133	133	0.002
LC1999027590	Calhoun	26-Apr-99	0.018	18	0.002
LC1999040583	Ingham	14-Jul-99	0.012	12	0.002

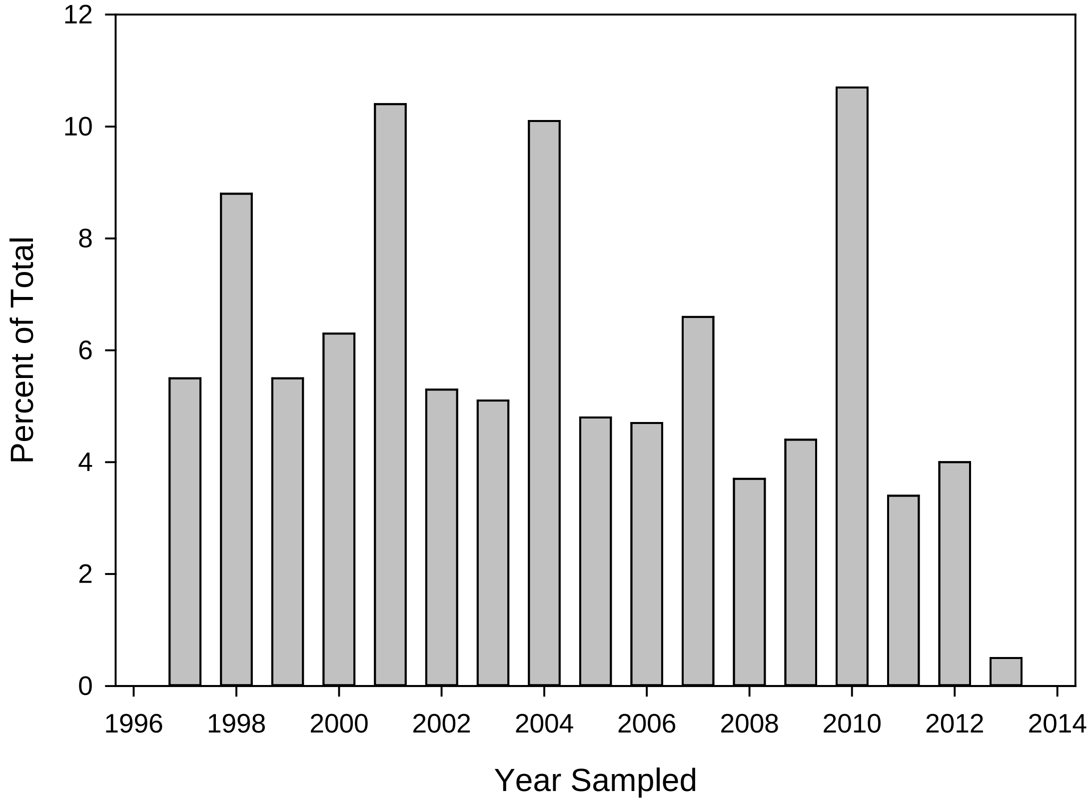

Figure 1. The percent of 2,4-D samples taken each year of the Michigan well study, from 1997 to 2013.

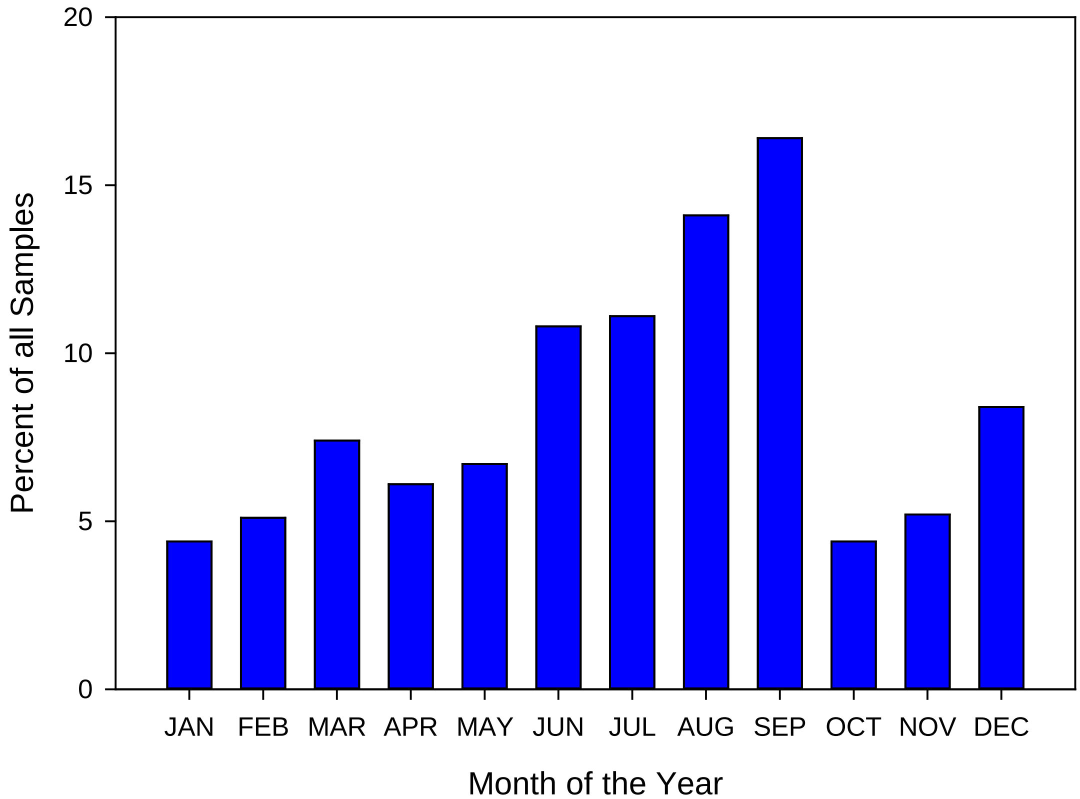

Figure 2. Distribution of 2,4-D sample collection timing by month of the year in which samples were taken, for the Michigan well study 1997-2013.

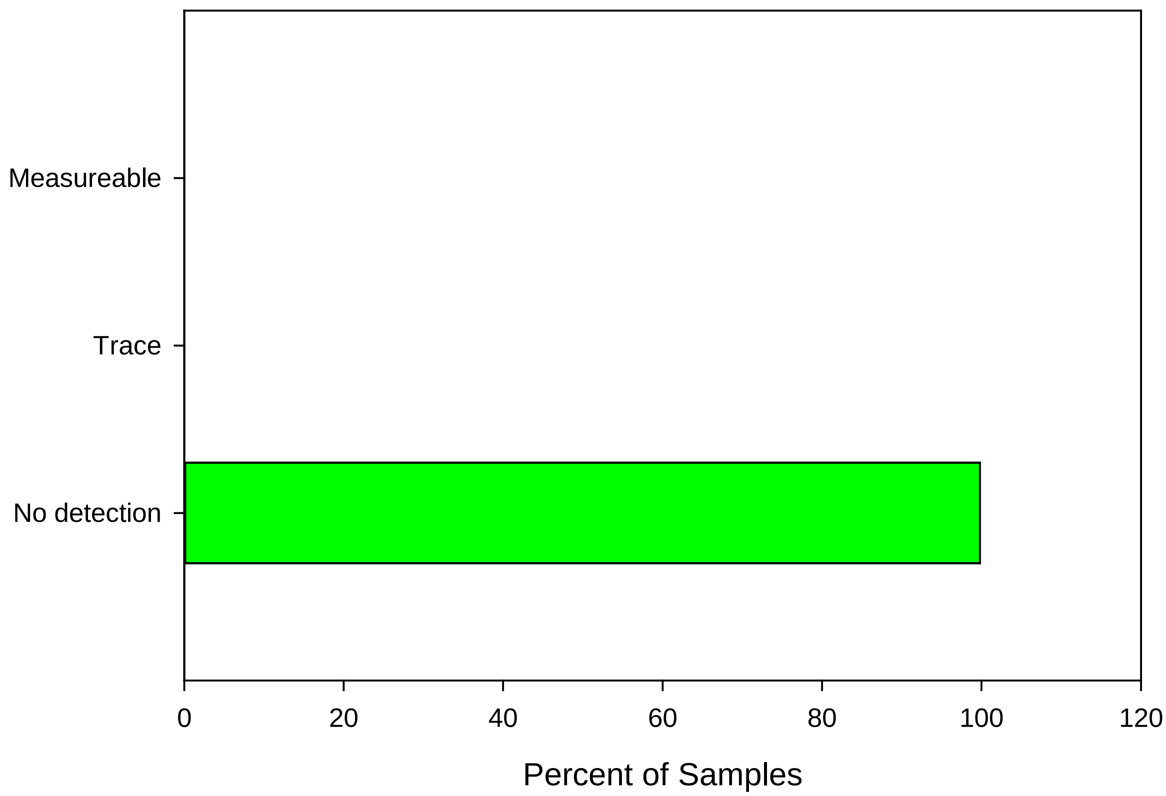

Figure 3. The analytical results of the analysis of over 15,000 samples from Michigan for 2,4-D over an 18 year period. Y axis categories are no detection, trace amount, and measurable amount. Trace and measurable amounts are both 0.1% of samples.

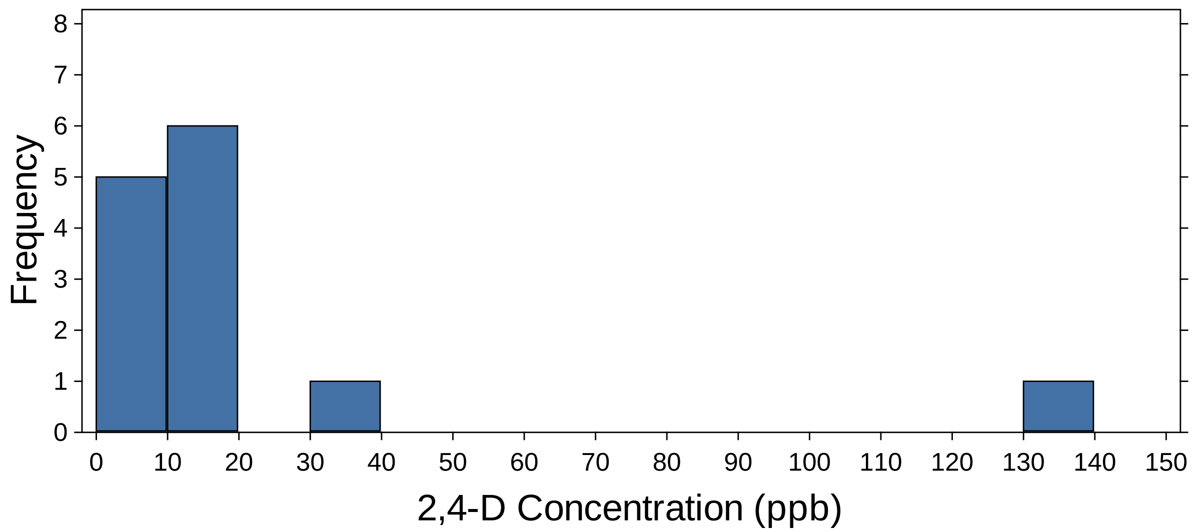

Figure 4. Histogram of the thirteen quantifiable tests of 2,4-D out of over 15,000 tests from Michigan wells from X to Y, in ppb (ug/L).

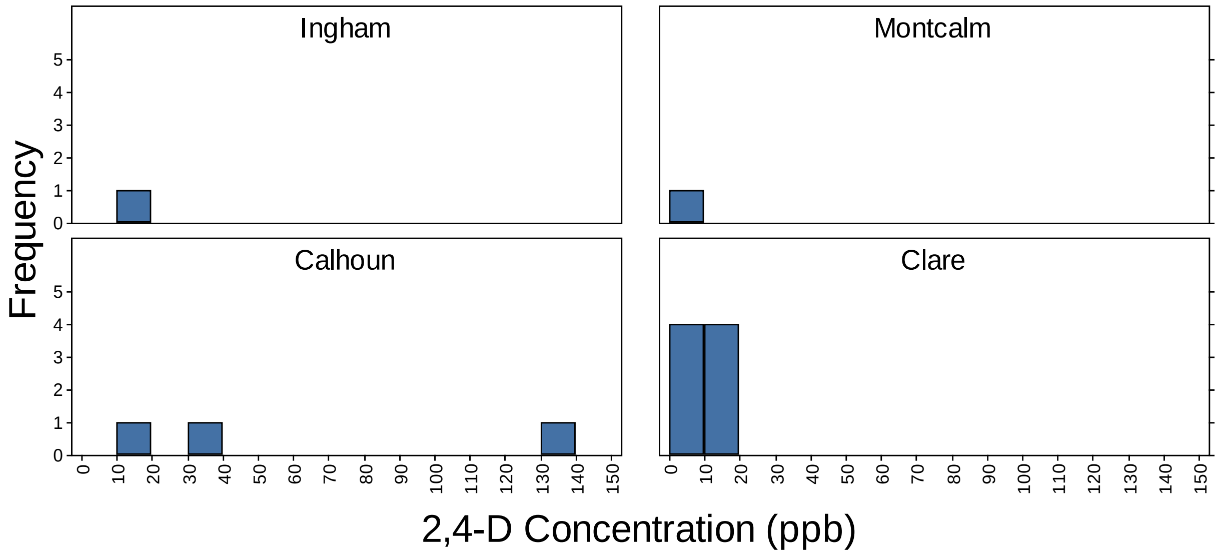

Figure 5. Frequency of quantifiable 2,4-D samples (N=13) from over 15,000 samples taken in Michigan wells over an eight year period, sorted by county. The y axis is the number of samples per county that were detectable in a given concentration range, and the x axis is the concentration range of 2,4-D quantified in ppb (µg/L). The maximum detectable concentration for irrigation is 100 ppb, and the maximum contaminant level for drinking water is 70 ppb.