Water, Air, & Soil Pollution

BULK DEPOSITION OF PESTICIDES IN A CANADIAN CITY: PART 2. IMPACT OF MALATHION USE WITHIN CITY-LIMITS.

--Manuscript Draft--

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Full Title:	BULK DEPOSITION OF PESTICIDES IN A CANADIAN CITY: PART 2. IMPACT OF MALATHION USE WITHIN CITY-LIMITS.
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Abstract:	Malathion is an organophosphate insecticide registered for use in cities throughout North America to control adult mosquitoes. The objective of this study was to determine the impact of urban malathion applications on the levels of malathion detected in bulk deposition. In 2010, malathion was applied by the City of Winnipeg's Insect Control Branch for a total amount of 6,632 kg in the city, as well as by the general public in relatively small amounts. In 2011, no malathion was applied by the city. Malathion was detected in 41% of the samples in 2010 with deposition rates ranging from 0.5 to 107.7 µg/m2/week. Only 9% of the samples contained malathion in 2011 with deposition rates always being < 0.4 µg/m2/week. Between 6 to 25% of the samples in 2010 exceeded the toxicological threshold levels of malathion to a range of freshwater amphipods, water fleas and stoneflies, including Daphnia magna which is a bioindicator of good environmental health. The weekly maximum malathion concentration detected in this study (5.2 µg/L for a week in June 2010) was at least 26 times greater than the maximum concentration of malathion reported in other atmospheric deposition studies. For the two insect management areas (7.4 and 37.6 km2) where the bulk deposition samplers had been placed, calculations suggested that between 1.2 to 5.1% of the malathion applied by the city became bulk deposition. Percutaneous absorption by humans of malathion in rainfall is unknown.
Response to Reviewers:	BULK DEPOSITION OF PESTICIDES IN A CANADIAN CITY: PART 2. IMPACT OF MALATHION USE WITHIN CITY-LIMITS Reply to the questions of the reviewer. Reviewer #1: Interesting manuscript, well-written and easy to read. The objective stated in introduction is met and well supported with good data. A few minor issues: 1.Any reference for the City of Winnipeg 2014 citation on p.3? We have added the following reference to the reference list: City of Winnipeg. (2014). Nuisance Mosquito Fogging Program. [Online]. http://www.winnipeg.ca/publicworks/bugline/mosquitoes/fogging.stm. Accessed 1 October, 2014. 2.Malaoxen or malaoxon, on p.4?

	It is malaoxon. We corrected this on page 4. 3.Figure 4: X-axis caption : whch should be which. The reviewer means the X-axis caption in figure 2 and we modified "whch" to "which" in this figure. 4.References: Borras(p. 11) or Borrasa (reference section)? University of Hertfordshire: 2011 or 2013? Guilherminoa or Guilhermino? Eichelberg and Lichtenberg 1971 or 1974? •It is Borrás and we corrected the reference list. •It is 2013 and we corrected the reference. •It is Guilhermino and we corrected the spelling of this reference in the main text. •It is Eichelberg and Lichtenberg 1971 and we corrected the reference list.
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Question	**Response**
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If yes, how is this research significant to furthering worldwide knowledge on this topic	Malathion is an organophosphate insecticide registered for use in cities throughout North America to control adult mosquitoes. Mosquitoes are vector-hosts to a number of diseases including the West Nile virus. There were more than 5,000 recorded clinical cases of West Nile virus in Canada between 2002 and 2012 and an estimated 780,000 clinical cases in the United States between 1999 and 2010. Malathion has been used in North American cities to minimize West Nile virus clinical cases. There are concerns about the exposure of the general public to malathion and hence there have been discussions through the scientific literature and social media about the use of malathion in an urban environment. Malathion is also applied in cities for the nuisance control of adult mosquitoes. Also this use of malathion is frequently debated in the popular media. The study examines relationships between weekly rainfall amount and weekly malathion deposition and this is relevant to the pollution problem of malathion in other locations. The study also provides evidence that malathion dry deposition occurs, which is relevant to better understanding the fate of malathion in the environment. The study compares weekly malathion concentrations in rainfall to the toxicological threshold levels of malathion to a range of species. In our study, the weekly maximum concentration detected was 5,208 ng/L which is at least 26 times larger than the previously detected maximum malathion concentration in rainwater. The study thus directly demonstrates that urban application is a significant source of malathion contamination in the environment. A limited amount of studies have previously examined for malathion in bulk deposition, particularly in urban environments. This is the first study to estimate the percentage of malathion applied in a city to the amount of malathion deposited. We estimate that between 1.2 to 5.1% of the malathion applied in the city becomes bulk deposition. Such information is relevant to decision-makers in other cities, as this allows them to estimate the approximate amount of malathion that can be deposited given the mass of malathion applied by city-officials. We prefer to publish this study in Water, Air, & Soil Pollution because it is an open access journal and in addition to the scientific community, this would allow the general public (e.g., urban residents) to get immediate access to the scientific findings.
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BULK DEPOSITION OF PESTICIDES IN A CANADIAN CITY: PART 2. IMPACT OF MALATHION USE WITHIN CITY-LIMITS

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Abstract

Malathion is an organophosphate insecticide registered for use in cities throughout North America to control adult mosquitoes. The objective of this study was to determine the impact of urban malathion applications on the levels of malathion detected in bulk deposition. In 2010, malathion was applied by the City of Winnipeg's Insect Control Branch for a total amount of 6,632 kg in the city, as well as by the general public in relatively small amounts. In 2011, no malathion was applied by the city. Malathion was detected in 41% of the samples in 2010 with deposition rates ranging from 0.5 to 107.7 $\mu g/m^2$/week. Only 9% of the samples contained malathion in 2011 with deposition rates always being < 0.4 $\mu g/m^2$/week. Between 6 to 25% of the samples in 2010 exceeded the toxicological threshold levels of malathion to a range of freshwater amphipods, water fleas and stoneflies, including *Daphnia magna* which is a bioindicator of good environmental health. The weekly maximum malathion concentration detected in this study (5.2 µg/L for a week in June 2010) was at least 26 times greater than the maximum concentration of malathion reported in other atmospheric deposition studies. For the two insect management areas (7.4 and 37.6 km^2) where the bulk deposition samplers had been placed, calculations suggested that between 1.2 to 5.1% of the malathion applied by the city became bulk deposition. Percutaneous absorption by humans of malathion in rainfall is unknown.

Keywords: Malathion, mosquitoes, urban application, bulk deposition, concentration in rainfall, non-target species

Introduction

Malathion is an organophosphate insecticide that is registered for use in Canada and the USA to control adult mosquitoes. Mosquitoes are vector-hosts to a number of diseases including the West Nile virus. There were 5,094 recorded clinical cases of West Nile virus in Canada between 2002 and 2012 (Public Health Agency of Canada, 2013) and an estimated 780,000 clinical cases in the United States between 1999 and 2010 (Petersen et al. 2012). Malathion was used in New York City, USA to minimize West Nile virus clinical cases in 1999-2000 (McCormick and Whitney, 2013) and it was used for the same purpose in the City of Winnipeg, Canada in 2005. West Nile virus clinical cases are drastically reduced in areas where malathion is applied (Carney et al. 2008).

In Winnipeg, malathion has been used for decades for the nuisance control of adult mosquitoes. Applications take place along residential streets and lanes, in golf courses, parks, and other areas within the city limits. Decisions to spray are based on the size of mosquito populations which are monitored in 51 Insect Management Areas (IMAs) in the city. The 51 IMAs range in size from 2.5 to 37.6 km^2 with 44 IMAs being smaller than 11.9 km^2, and the remaining IMAs being larger than 18.0 km^2. The total number of malathion applications reported for these IMAs combined was 222 in 2007, 171 in 2008, 103 in 2009, 237 in 2010, no applications in 2011 and 2012, and 31 in 2013 (City of Winnipeg 2014). Malathion was not applied in 2011 and 2012 because the adult mosquito densities were below the threshold which the city uses to determine if malathion should be applied. Malathion has also been used for the nuisance control of mosquitoes in a number of other North American cities, such as Brandon, Manitoba in 2013. There are concerns about the exposure of the general public to malathion (Tickner 2002, McCormick and Whitney 2013), particularly when there is exposure to other pesticides at the same time (Hohenadel et al. 2011, Hernández et al. 2013).

Malathion has been detected in rainfall and bulk deposition samples collected in urban and rural sites (Charizopoulos and Papadopoulou-Mourkidou 1999, Majewski et al., 1999; Coupe et al., 2000; Grynkiewicz et al., 2003; Raina et al., 2010). Malathion transport in the atmosphere is influenced by factors such as its atmospheric degradation and deposition rates, as well as wind speed and direction. In the atmosphere, malathion is oxidized to malaoxon due to reactions with ozone, OH radicals or nitrate radicals (Brown et al. 1993, Masten et al. 2001, Liu et al. 2012). In California, USA, following aerial applications of malathion, the deposition rate of malathion per unit area was found to be a few hundred times larger than malaoxon (Brown et al.1993).

The objective of this study was to determine the impact of malathion application in a city on the levels of malathion detected in bulk deposition.

Materials and Methods

Malathion application. Malathion applications were made by the City of Winnipeg's Insect Control Branch. The City of Winnipeg uses Malathion (PRO ® Malathion ULV ® Insecticide Concentrate, Agrium Advanced Technologies RP Inc., Brantford, ON, registration number 14597). The City of Winnipeg applies malathion using ultra-low volume ground applications with a maximum recommended malathion application rate of 6.08 kg/km^2 (Health Canada 2003).

Sampling stations and analysis. The study sites were located in two insect management areas in southern Winnipeg. Site Whyte Ridge (Ridge) (49° 48'N latitude, 97° 12'W longitude) was located approximately 7 km west of site St. Vital (Vital) (49° 47'N latitude, 97° 6'W longitude). Weekly bulk deposition samples were collected for 18 weeks from May 18 to September 21, during 2010 and 2011. Precipitation and temperature were recorded using a meteorological station (Watch Dog 2700 Weather Station, Spectrum Technologies Inc., Plainfield, IL) installed next to the bulk deposition sampler. During the 2010 sampling season, temperatures ranged from 4.6 to 31°C with 487 mm of total rainfall. During 2011, temperatures ranged from -3.7 to 37.2°C with 182 mm of total rainfall. The thirty-year normal for rainfall from May to September (1971-2000) in Winnipeg is 354 mm (Environment Canada, 2012). Average annual temperature extremes are from –45.0 to 40.6 °C.

Bulk deposition samples were collected in a 1m by 1m galvanized sheet metal pan that emptied into a 23L glass carboy shaded by plywood to minimize pesticide photodegradation. If no rainfall occurred during the week, the pan was rinsed with 500 mL of deionized water, and the sample was considered a dry deposit. The pan was also rinsed if there was precipitation during the week. In 2010 rainfall occurred during collection twice (11%) at Ridge and once (6%) at Vital. In 2011 rainfall occurred during collection three (17%) times at Ridge, twice (12%) at Vital. If it was raining during collection, the sheet metal pan was not rinsed.

Rain water collected in the carboy was mixed thoroughly before taking a subsample with maximum volume of 1L. The subsamples in an amber glass bottle with a Teflon sealed cap were shipped in an ice packed cooler to a commercial laboratory on the same day they were collected. Upon arrival subsamples were stored at 4°C and analyzed within 7 days. The commercial laboratory is the Environmental Analytical Services department of Alberta Innovates Technology Futures (AITF), Edmonton, Alberta. The laboratory is accredited by the Canadian Association for Laboratories Accreditation through the Standards Council of Canada.

The AITF method PESTE-EM443 for the analyses of pesticides in water was used to extract and quantify malathion in water. This is a multi-residue method and the results of the other pesticides in the samples are reported in Farenhorst et al. (2014). Briefly, samples were acidified with phosphoric acid to a pH of 2 and then extracted by liquid-liquid partitioning with methylene chloride. Extracts were dried through acidified sodium sulphate. Extracts were reduced to approximately 300 μl under nitrogen gas. Any acidic compounds were esterified with diazomethane. The final volume (250 μl) was analyzed on a Varian 2200 GC/Iontrap mass spectrometer with a Varian 3400 autosampler and a DB-5 30m column. As part of QA/QC protocols, for every batch of 11 samples, a laboratory blank was included, and a standard curve was run for calibration. Deuterated surrogates were added to water samples to determine percent recovery. All compounds were identified and quantified using retention times and compound specific ions of specific mass and charge. The method detection limit for malathion is 50 ng/L. For samples that contained malathion at concentrations below the method detection limit, malathion concentrations were estimated as long as malathion met the identification criteria.

Results and Discussion

Comparison of detections between the two years suggests that the source of the malathion was mainly that applied by the city. There were 237 malathion applications by the city in 2010 and total seasonal deposition of malathion was 151 μg/m^2 (Ridge) and 274 μg/m^2 (Vital). In contrast, when there were no malathion applications by the city in 2011, total seasonal deposition was only 0.69 μg/m^2 (Ridge) and 0.03 μg/m^2 (Vital). Some of the detected malathion in either year could have been the result of applications made by city residents. It is unlikely that the malathion detections were due to agricultural use. Typically, less than 400 kg of malathion is used per year on the 104,802 km^2 of agricultural land in Manitoba, with no use reported in any of the townships (93.2 km^2) adjacent to Winnipeg. Several other studies concluded that urban use is the main reason why malathion is detected in rain or bulk deposition (Nations and Hallberg 1992, Majewski et al.1999, Coupe et al., 2000).

Malathion was always detected in bulk deposition samples in the weeks in which malathion was applied by the city (Figure 1). For these detections, the deposition rates ranged from 13.6 to 88.1 μg/m^2/week in Ridge and from 2.42 to 107.7 μg/m^2/week in Vital. Malathion deposition was particularly large when it was applied twice in the same week (Figure 1). The weekly deposition rate in Ridge ($r= -1.00$, $P=0.008$), but not Vital, was significantly negatively correlated with the number of days from the previous malathion application (Figure 2). In the weeks that malathion was applied, neither Ridge nor Vital showed a significant association between the weekly amount of rainfall and malathion deposited.

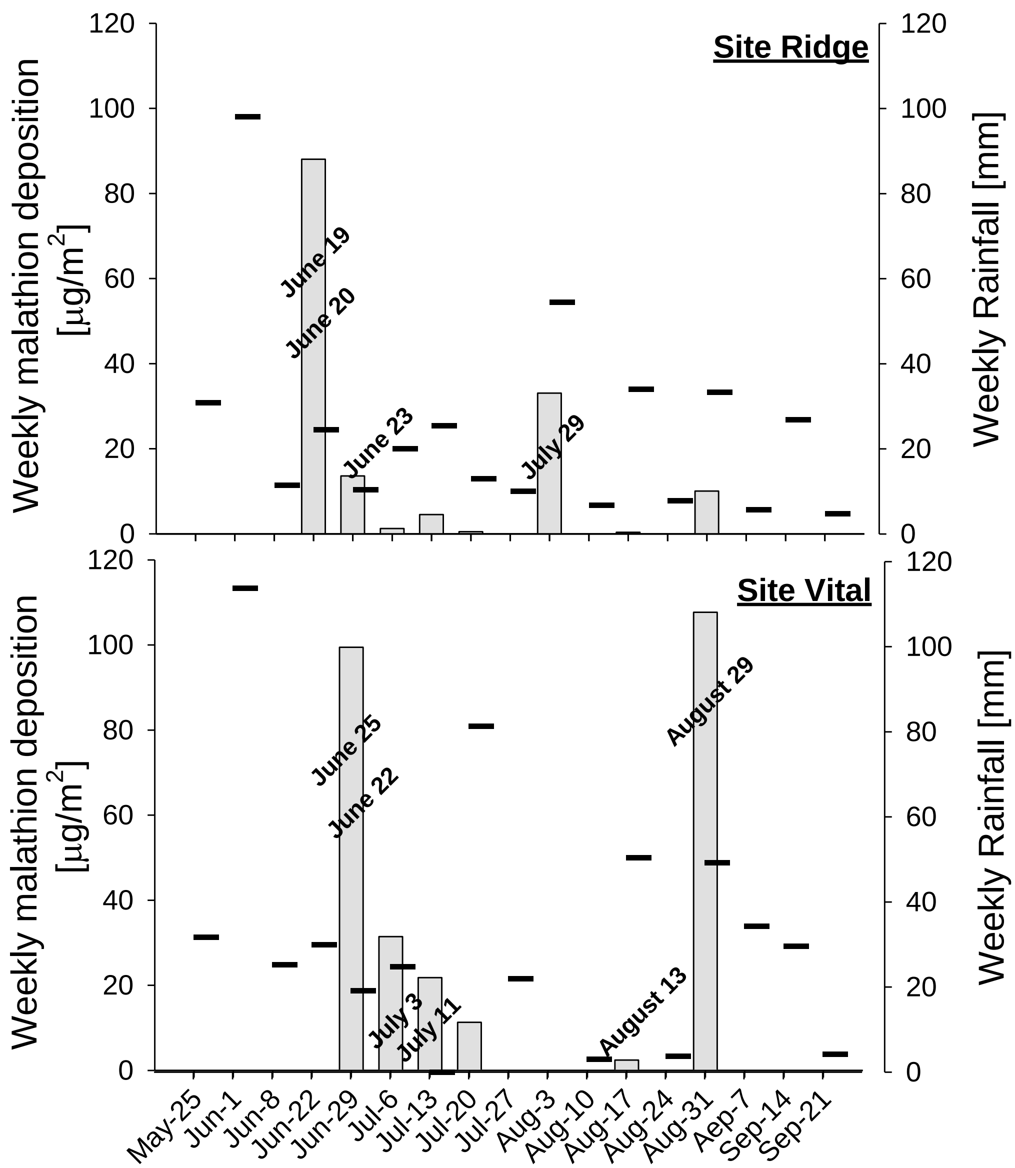

Figure 1. Weekly amounts of malathion detected from May 18 to September 21, 2010. Dates in bold refer to ultra-low volume ground applications by the City of Winnipeg. For the Vital site, malathion was also applied on July 28th, 2010 but the bulk deposition sample of Vital was not analyzed for that week (ending Aug 3) because the sample bottle was accidentally dropped.

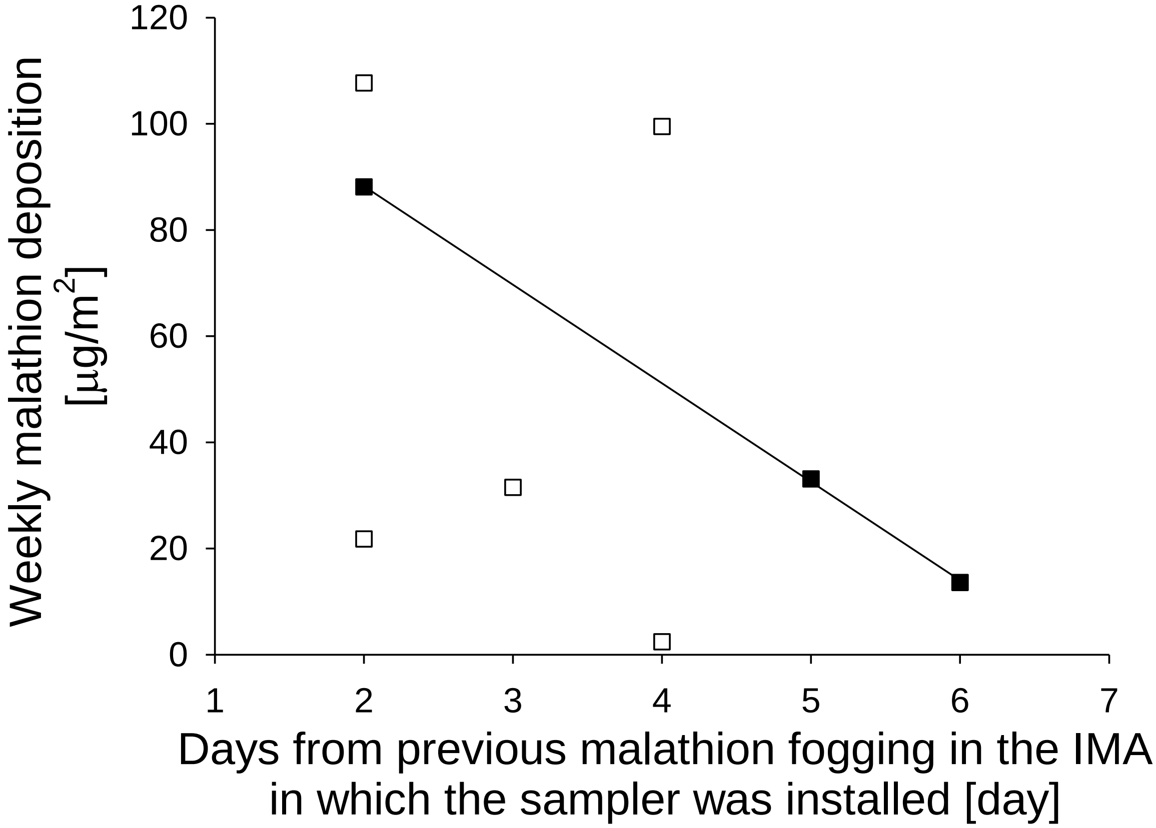

Figure 2. Weekly amounts of malathion detected as a function of time [days] from previous malathion fogging by city officials in the Insect Management Area (IMA) in which the samplers were installed. Solid squares are detections at the Ridge site, for which the linear regression equation was significant (Y = -18.56X+125.35, R^2 = 1.00, $P<0.01$). Open squares are detections at Vital site for which the linear regression equation was not significant at $P<0.05$.

In 2010, malathion was also detected in weeks that no malathion was applied in the IMA's of Ridge and Vital (Figure 1). Malathion was detected in four weeks in Ridge and there was a significantly association between weekly rainfall and weekly malathion deposition (r= 0.95, P=0.046) (Figure 3). In Vital, malathion was detected only once in weeks with no malathion applications by the city (Figure 1). The detection at Vital was at a relatively high level (11.3 μg/m^2/week), possibly because it occurred in a week with much rainfall (81.3 mm), relative to the average weekly rainfall (32.7 mm) from May 18 to September 21, 2010.

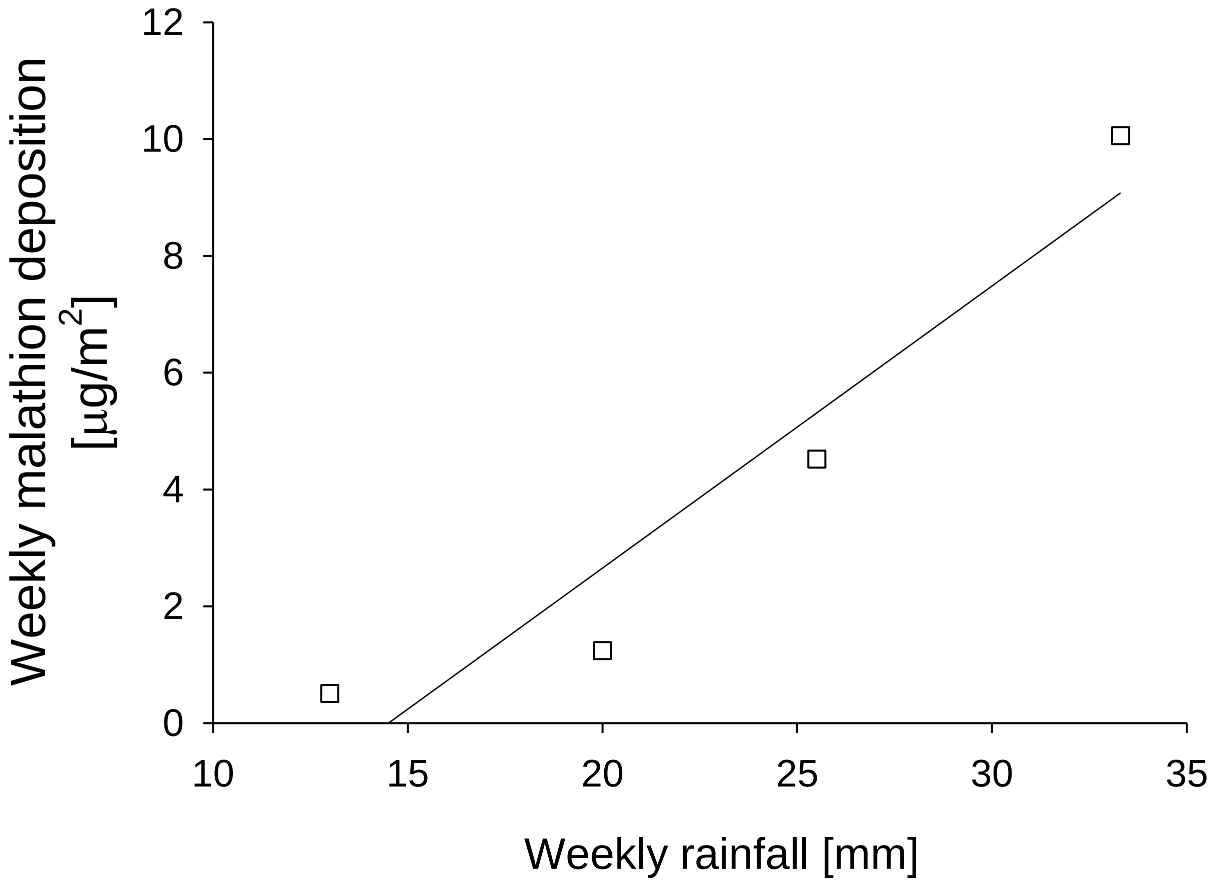

Figure 3. Data refer to the weekly amounts of malathion detected at the Ridge site in weeks that malathion was not applied. The linear regression between the weekly amount of rainfall and the weekly amount of malathion deposited was significant ($y = 0.48X-7.00$, $R^2 = 0.95$, $P<0.05$).

Malathion was only detected on three occasions in 2011 and these weekly levels were less than 0.4 μg/m^2/week. In contrast, in weeks without malathion applications by the city in 2010, the malathion deposition ranged from 0.5 to 11.3 μg/m^2/week. In weeks without applications in 2010, malathion was detected in Ridge at two to four weeks after the last ULV ground application in this IMA, and in Vital ten days after the last ULV ground application in its IMA. It is likely that malathion was persistent in air from previous applications in Ridge or Vital. The atmospheric half-life of malathion has been estimated to range from a few days to three weeks (Brown et al. 1993, Meng et al. 2010). It is also possible that malathion was transported to Ridge and Vital following applications in other IMAs, and that city residents used more malathion in their gardens in 2010 then 2011.

Malathion was detected (21.8 μg/m^2/week) in one week when there was no rainfall (Vital – July 7 to 13, 2010 sample) (Figure 1). This was likely due to the deposition of atmospheric particulate matter onto which malathion is sorbed. Malathion has a high Koc value (1800 mg/g) (University of Hertfordshire, 2013) and has been previously detected in the atmosphere in association with particulate matter (Borrás et al., 2011). It could have additionally resulted from application drift because an application in the Vital IMA had occurred on July 11, 2010.

Assuming that the deposition rate was consistent across the IMAs, an estimated 2.02 kg (Vital=7.4 km^2) and 5.69 kg (Ridge=37.6 km^2) was deposited between May 18 to September 21, 2010. Since the surface area of application within IMAs is unknown, we attempted two different calculation scenarios to estimate the percentage of the applied malathion in the IMAs of Ridge and Vital that was deposited as bulk deposition (Table 1). These calculations suggested that between 1.2 to 5.1% of the applied malathion was deposited. If these percentages are applied to the total amount of malathion applied in the city in 2010 (6,632 kg), the amount of malathion deposited in the City of Winnipeg would be between 80 and 338 kg.

Table 1. Estimated percentage of the applied malathion being deposited as bulk deposition in the IMA of Ridge and Vital from May 18 to September 21, 2010. Calculations were performed using two different methods. In these equations, the following numbers were used: 6,632 = the kg of malathion used by the city in 2010, 237 = the number of applications the city made in 2010, 2,220 = the maximum size of the potential spraying area in km^2.

Method[1]	Amount of malathion applied (kg)		% malathion deposited	
	Ridge	Vital	Ridge	Vital
I.	449	132	1.3	1.5
II.	112	168	5.1	1.2

[1]Method I: 6,632/2,220 × *SA* × *FE*, where *SA* is the surface area of the IMA of Ridge (37.6 km^2) or Vital (7.4 km^2), and *FE* is the number of fogging events in Ridge (4) or Vital (6), respectively. Method II: 6,632/237 × *FE*

Weekly malathion concentrations (weekly malathion mass divided by weekly rainfall volume) ranged from 10 to 5,208 ng L^{-1} in 2010 and from 6 to 96 ng L^{-1} in 2011. The maximum weekly malathion concentration of 5,208 ng/L (June 23 to 29, 2010) was at least 26 times greater than the maximum concentration of malathion reported in other atmospheric deposition studies. Previously reported maximum concentrations of malathion in rainfall and bulk deposition samples have been 10 ng L^{-1} in Grynkiewicz et al. (2003), 24 ng L^{-1} in McConnell et al. (1998) and 200 ng L^{-1} in Charizopoulos and Papadopoulou-Mourkidou (1999). In our study, 25% of the samples collected in 2010 exceeded 200 ng L^{-1}. The weekly concentration of malathion was not significantly correlated with the number of days from the previous malathion application, nor with weekly rainfall amount.

The Canadian Water Quality Guideline for malathion in drinking water is 190 μg/L (Canadian Council of Ministers of the Environment, 2013). This is well above the maximum concentration (5.21 μg/L) detected in our study. There are no other Canadian Water Quality Guidelines set for malathion (e.g., for the protection of aquatic life). Only in 2010 did the weekly malathion concentrations in rain exceed toxicological threshold values of a range of non-target species (Table 2), including the keystone species *Daphnia magna*. *Daphnia magna* is as a bioindicator of good environmental health (Poynton et. al., 2007) and has been suggested for use as a prescreening tool to provide evidence of toxicity to mammals (Guilhermino et. al .2000).

Table 2. Selected toxicological reference data and the % of samples in 2010 exceeding the threshold concentrations stated. Unless otherwise indicated, toxicological reference data are from various studies as summarized in Mulla et al. 1981.

Species	Habitat	Toxicological reference	% Samples exceeding
Freshwater amphipods			
Gammarus fasciatus	Streams, rivers and freshwater lakes.	0.76 µg/L (96h LC50)[1]	16
Gammarus lacustris	Mountain and glacier lakes, and other lakes provided summer temperatures stay below 20°C.	1.00 µg/L (96h LC50)	16
Water fleas			
Daphnia carinata	Water bodies ranging from huge lakes down to very small temporary pools, such as rock pools and seasonally flooded depressions	0.2 µg/L (48-50h LC50)	25
Daphnia magna	As above	0.9 µg/L (48-50h LC50)	16
Simocephalus serrulatus	Ponds and small lakes	3.5 µg/L (48h LC50)	6
Stoneflies			
Pteronarcys badia	Streams and rivers	1.1 µg/L (96h LC50)	16
Claassenia sabulosa	Streams and rivers	2.8 µg/L (96h LC50)	6

[1]Mayer and Ellersieck 1986 as reported in McConnell et al. 1998

None of the malathion concentrations calculated in this study exceeded the LC50 or EC50 parameters measured for fish species (Mulla et al. 1981). In addition, in 2010, the weekly amount of malathion deposited in the bulk deposition samplers (maximum 107.7 μg/m^2/week) did not exceed malathion dermal LD50 values determined for predatory insects such as *Adonia variegata* (ladybird) (dermal LD50 250 μg/m^2), *Nabis americoferus* (Common Damsel Bug) (dermal LD50 460 μg/m^2) and *Chrysopa carnea* (common green lacewing) (dermal LD50 1,200 μg/m^2) (Mulla et al. 1981). In humans, the percutaneous absorption of malathion ranges from 0.9 for the palm to 4.2 for the armpit, with the forearm (1.0) being the reference region (Mulla et al. 1981). Percutaneous absorption by humans of malathion in rainfall is unknown.

Photodegradation of malathion may have occurred on the collection tray but this is unlikely a significant process of malathion loss because the insecticide has a half-life of more than 40 days when exposed (in distilled water) to wavelengths greater than 290nm (Wolfe et al. 1977). Chemical and biological degradation of malathion may have occurred in the glass carboy that was shielded from light, and if so, the weekly deposition rates and concentrations stated in this paper may have been underestimated. The extent of malathion degradation in water is affected by particulates in the water, and other factors such as temperature (Eichelberger and Lichtenberg, 1971, Wolfe et al. 1977). For example, malathion at an initial concentration of 10 μg/L in glass containers was 100% persistent in distilled water for 3 weeks but was reduced to a concentration of 2.5 μg /L after seven days when the glass containers held river water (Eichelberger and

Lichtenberg, 1971). Particulates in the water and other factors such as temperature would have varied throughout our sampling season.

Conclusion

Total malathion deposition from May 18 to September 21, 2010 was 151 μg/m^2 at Ridge and 274 μg/m^2 at Vital, suggesting that bulk deposition accounted for about 1.2 to 5.1% of the applied malathion. During the same time frame in 2011, which was a year without malathion applications by the city, total malathion deposition was only 0.69 μg/m^2 (Ridge) and 0.03 μg/m^2 (Vital). It was during 2010 that the weekly malathion concentrations in rain sometimes exceeded toxicological threshold values of non-target species, including freshwater amphipods, water flies and stone flies species. This included 16% of the weekly samples exceeding thresholds for *Daphnia magna* which is a keystone species important to preserving an ecological structure in the environment. As such, the use of malathion in cities as part of West Nile virus mosquito control programs or nuisance control of mosquitoes should be further evaluated in terms of its impact on the urban ecosystem.

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