Influence of usage and chemical–physical properties on the atmospheric transport and deposition of pesticides to agricultural regions of Manitoba, Canada

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HIGHLIGHTS

► 14 pesticide residues analyzed in prairie atmosphere and in dry and wet deposition.
► 8 herbicides were all frequently detected (92–100%) in the air samples.
► Total bulk deposition ranged from 0.009 to 2.3 $\mu g\ m^{-2}$ for the 12 pesticides detected.
► Dry deposition contributed up to 51% of total deposition.
► Pesticide use and physico-chemical properties explained detected concentrations.

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ABSTRACT

This study quantified the masses of 14 pesticides deposited as wet (precipitation) versus dry (gaseous and particle) atmospheric deposition at a research farm in southwestern Manitoba, Canada. The concentration in air of these pesticides was also measured. Total bulk deposition amounts (wet + dry) ranged from 0.009 to 2.3 $\mu g\ m^{-2}$ for the 12 pesticides detected, and for the six pesticides with both wet and dry deposition detections, dry deposition contributed 12–51% of the total deposition over the crop growing season. Although not applied at the site, eight herbicides registered for use in Canada, as well as lindane (γ-HCH), were all frequently detected (92–100%) in the 12 air samples analyzed during the crop growing season, with by-product isomer α-HCH (75%), clopyralid (50%) and atrazine (8%) detected to a lesser extent. The chemical's physicochemical properties and the relative mean mass of each agricultural pesticide applied in the province of Manitoba and in a 13 km radius were significant parameters in explaining the trends in the concentrations of pesticides detected in our samples. The important contribution of dry deposition to total pesticide deposition warrants greater attention in arid and semi-arid areas such as the Prairie Region of Canada, also because under a changing climate this region is estimated to experience more severe droughts while the more favorable conditions predicted for pest infestations could lead to increased pesticide applications in agricultural and urban areas.

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1. Introduction

Wetlands of the Prairie Pothole Region of North America are among the most productive ecosystems in the world, providing habitats for a wide variety of flora and fauna such as 50–80% of the continent's duck population (Batt et al., 1989). Prairie wetlands in Canada are contaminated with a suite of pesticides (Donald et al., 2001; Anderson et al., 2002; Waite et al., 2002) with an estimated 9–24% of the wetlands in the province of Saskatchwan having levels exceeding the Canadian guidelines for the protection of aquatic life (Donald et al., 1999). Pesticide loadings to prairie wetlands can be caused by atmospheric sources such as pesticide wet (precipitation) and dry (gaseous and particle) deposition (Waite et al., 1995; Jantunen et al., 2008; Messing et al., 2011). Pesticides enter the atmosphere through application drift (Caldwell, 2007), post-application vapor losses (Grover et al., 1985) or on wind eroded soil (Larney et al., 1999).

Atmospheric deposition of pesticides is typically measured using samplers that collect precipitation only (Hall et al., 1993; Belzer et al., 1998; Rawn et al., 1999) or through bulk (dry and wet combined) deposition samplers (Waite et al., 1995; Hill et al., 2001). Bulk deposition has been shown to vary spatially in

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the prairies depending on the intensity of local and regional pesticide use (Hill et al., 2003).

To our knowledge, Canada is the only country worldwide to have compared simultaneous measurements of pesticide wet versus dry deposition. This work has been limited to one study site in the province of Saskatchewan (Waite et al., 2005). Using the Waite–Banner Atmospheric Dry/Wet Deposition Sampler (Waite et al., 1999), this single study demonstrated that total seasonal dry deposition may account for up to ~85–100% of the total bulk deposition mass (wet + dry) of triallate, trifluralin, 2,4-D, bromoxynil, dicamba, and MCPA (Waite et al., 2005). Prior to this Canadian study, it was reported that dry deposition contributed only to a minor extent of the total deposition of pesticides (Siebers et al., 1994).

In Manitoba, approximately 2 million kg of agricultural pesticides are applied annually encompassing ~60 different active ingredients (Wilson, 2012). Quantifications of the concentrations of pesticides in air and atmospheric deposits in Manitoba have been limited to three studies: (1) high-volume air and rainwater (using a wet-only sampler) samples collected at a site near Miami (49°19′28″N, 98°21′50″W) between 1993 and 1996 (Rawn et al., 1999), (2) bulk deposition samples collected at a site near Minnedosa (50°14′39″N, 99°50′34″W) in 2000 and 2001 (Hill et al., 2003), and (3) high-volume air and bulk deposition samples collected at a site near Brandon (50°03′07″N, 99°55′26″W) in 2008 (Messing et al., 2011).

The objectives of this study were to quantify, in an agricultural field site typical of the Prairie Pothole Region near Brandon, Manitoba, the relative amounts of 14 pesticides deposited as dry versus wet atmospheric deposition, and to relate their detections to airborne levels measured at the same site.

2. Materials and methods

2.1. Sampling location

The Manitoba Zero-Tillage Research Association (MZTRA) research site (260 ha) is located in south central Canada ~20 km north of Brandon (50°03′07″N, 99°55′26″W), Manitoba. Ambient air temperatures are highly variable with extremes ranging from −46.7 to 43.3 °C (Brandon Airport). The warmest month is July (daily mean of 18.9 °C) and the coldest month is January (daily mean of −17.9 °C) (Environment Canada, 2012). Mean annual precipitation is 474 mm of rainfall and 1014 mm of snowfall. Mean wind speeds in the area are 15.2 km h^{-1} (Environment Canada, 2012).

2.2. Sampling devices and pesticides analyzed

A high volume air sampler (Model PS-1, General Metals Works, Village of Cleves, OH) and the Waite–Banner Atmospheric Dry/Wet Deposition Sampler (Waite et al., 1999) were installed at the field site adjacent to a meteorological station that has been operational since April, 2007 through the Manitoba Ag-Weather Program. Samples were collected in the summer of 2007 and analyzed for 11 currently-used herbicides and three pesticides no longer registered for use in Canada. During the sampling period none of the analyzed chemicals were applied on the research farm but both MCPA and clopyralid were applied the previous year. The currently-used herbicides included three active ingredients with vapor pressures larger than 9 mPa (ethalfluralin, triallate, and trifluralin) and eight other active ingredients with vapor pressures below 2 mPa (Table 1). The legacy pesticides included lindane (γ-HCH), its by-product isomer α-HCH, and alachlor. In Canada, producers were able to use lindane stocks until the end of 2002. α-HCH was a

manufacturing by-product in technical lindane only prior to 1971 (Tuduri et al., 2006). Lindane was primarily used on the prairies on canola seed (Waite et al., 2001) with 94% of total usage applied from 1970 to 2000 at approximately 8.5 million kg (Li et al., 2004). The herbicide alachlor was de-registered in 1985 (Health Canada, 2012).

2.3. Sampling frequencies

The air samples were collected weekly for 12 weeks beginning on May 23 and ending on August 15, 2007. Air was sampled continuously throughout the week with the high volume air sampler field calibrated on set up and monitored daily during operation by integral Venturi/Magnahelic assemblies for a flow rate of 2000 m^3-week^{-1}. The sampling head consisted of a 10.2 cm diameter glass fiber filter (Graseby, GMW) for particle collection and XAD-2 resin sandwiched between polyurethane foam for vapor phase collection. The filter and cartridge were extracted together as described below to obtain a 7 d total pesticide concentration per volume.

Weekly dry and wet deposition samples were collected for 8 weeks beginning on May 23 and ending on July 18, 2007 using the Waite–Banner Atmospheric Dry/Wet Deposition Sampler. A detailed description of the sampler can be found in Waite et al. (1999). To summarize the unique sampling device and protocol, dry atmospheric depositions are collected on a sheet of water continuously flowing down a stainless steel tray that is 0.5 m × 1 m to simulate an open water surface. The water consisted of 18-megohm deionised water acidified to a pH of ~1 with concentrated trace metal grade sulfuric acid (Fisher Scientific Ltd., Montreal, Quebec). Any particles or gases that partition into the sheet of water are swept into the sampler to pass through a glass fiber and XAD-2 resin sampling cartridge removing any organics (including the pesticides) from the water before being re-circulated back to the surface of the tray. The XAD-2 resin cartridge was removed and replaced by another each week and extracted to obtain a 7 d composite dry deposition sample. Prior to replacement the sampler was refilled with 18-megohm deionised acidified water to replace the water that evaporated during the week. After replacement, the machine was run for 30 min through a XAD-2 clean-up column (identical to the sample columns) to ensure that no contaminants were present and to remove any that may have been in the water. A 1 L background water sample was then taken, extracted, and analyzed. The sampler collects rainfall separately as rain triggers a sensor that both stopped the water flow and redirected any rainwater falling onto the steel tray to a separate stainless steel collection container outside of the sampler. The revolatilization of pesticides from rainwater collected in the container was minimized because the container was closed off from air as soon as the rainfall stopped. After the 7 d sampling period the rainwater container was well mixed and a subsample was taken in a 1 L amber glass bottle with a Teflon sealed cap. Rainfall samples were preserved with the addition of 5 mL of concentrated trace metal grade sulfuric acid immediately following sample collection. The sampler is prone to breakdown which occurred in the week ending June 20 (weekly sample not taken) and it malfunctioned after July 18, leaving seven weeks of data available. Similar challenges with the equipment were reported in Waite et al. (2005).

2.4. Pesticide extraction and quantification

All reagents were reagent grade. Solvents (acetone, dichloromethane, ether and hexane) were pesticide grade and were obtained from Caledon Laboratories (Georgetown, Canada). Pesticide standards were 98% purity or greater and were obtained from ChemService (West Chester, USA) and Riedel-de Haen (Seelze,

Table 1
Mass of active ingredients applied in MB and in a 13 km radius around study site (2004–2006 average) (Shymko et al., unpublished data) and their physicochemical properties (The Pesticide Properties Database, 2012).

Active ingredient	Mass applied in MB (kg)	% of Total of all applied in MB	Rank out of the 59 A.I.s used in MB	Mass applied in a 13 km radius	Water solubility 20 °C (mg L^{-1})	Vapor pressure at 25 °C (mPa)	Henry's law constant at 25 °C (Pa m^3 mol^{-1})	Koc (mL g^{-1})	Kow at pH 7, 20 °C
MCPA	439 470	21	2	10 880	29 390	0.4	5.50×10^{-05}	74	1.55×10^{-01}
Bromoxynil	168 146	8	4	3453	90	0.17	5.30×10^{-04}	174	1.10×10
2,4-D	148 936	7	5	6731	23 180	0.0187	1.30×10^{-05}	56	1.48×10^{-01}
Ethalfluralin	93 126	4	6	817	0.01	12	18	5356	1.29×10^{05}
Trifluralin	41 683	2	10	83	0.221	9.5	10.2	8765	1.86×10^{05}
Dicamba	20 537	1	16	260	250 000	1.67	1.0×10^{-04}	12	1.32×10^{-02}
Clopyralid	19 655	1	15	579	143 000	1.36	1.80×10^{-11}	5	2.34×10^{-03}
Atrazine	18 171	1	17	0	35	0.039	1.50×10^{-04}	100	5.01×10^{02}
Triallate	7194	0	23	542	4.1	12	0.89	4301	1.15×10^{04}
Mecoprop	5008	0	25	199	250 000	1.6	2.20×10^{-04}	31	6.46×10^{-01}
Metolachlor	194	0	48	0	530	1.7	2.40×10^{-03}	200	2.51×10^{03}
Lindane	0	0	NA	0	8.52	4.34	1.50×10^{-01}	1100	4.90×10^{03}
α-HCH	0	0	NA	0	2.0	5.99	0.43–2.16[c]	1888	6.61×10^{03}
Alachlor	0	0	NA	0	240	2.9	3.20×10^{-03}	124	1.23×10^{03}

NA (not applicable) – Not registered for use in Canada.

Germany). Deuterated pesticide standards were obtained from C/D/N Isotopes (Pointe Claire, Quebec). 2,4-D CAA (2,4-dichlorophenyl acetic acid) was obtained from Sigma–Aldrich (Oakville, Ontario) to act as a surrogate.

All samples were analyzed at the Prairie & Northern Laboratory for Environmental Testing, Environment Canada, Edmonton, Alberta (AB), Canada. Samples were shipped in an ice packed cooler from Manitoba to Alberta on the day of collection and then stored at 4 °C in the dark prior to extractions which occurred within 10 d of collection.

The PUF/XAD-2 resin cartridge and glass fiber filter from the PS-1 high volume air sampler were Soxhlet extracted with 500 mL acetone for 24 h as described by Waite et al. (2005). One mL of acetone containing 1 µg 2,4-D CAA was added to the PUF in the laboratory to each sample prior to extractions. Acetone extracts were concentrated with rotary evaporation, methylated with three 2 mL aliquots of ethereal diazomethane and concentrated with a stream of pure nitrogen gas after each addition. The final concentrate was then made up to a final volume of 10 mL using hexane for the analytes quantification by gas chromatography-mass spectrometry.

For the extraction of the XAD-2 column from the dry/wet deposition sampler, the same 2,4-D CAA solution was added in the laboratory to the sampling inlet end of the column and flushed onto the column with 250 mL of reagent water. The reagent water that eluted from the column was discarded and a vacuum was applied to the outlet end of the column to remove any excess water which was also discarded. The XAD-2 column was extracted by back flushing it with 1000 mL of acetone as described by Waite et al. (2005). The acetone extract was concentrated using rotary evaporation until an aqueous phase remained from the water remaining in the column after the vacuum had been applied. The aqueous phase was transferred to a separatory funnel, combined with 100 mL of reagent water and acidified to a pH of 2 with 0.5 mL of concentrated sulfuric acid. The entire volume was extracted with three 40 mL aliquots of dichloromethane. The dichloromethane extract was dried by passing through 30 grams of acidic sodium sulfate, and concentrated by rotary evaporation. Samples were then methylated and exchanged into hexane to a final volume of 10 mL, as described above.

The same 2,4-D CAA solution was added in the laboratory to the rainfall and background water samples from the dry/wet deposition sampler. Sodium chloride (150 g) was dissolved in each sample and samples were acidified to pH 2 with sulfuric acid and then extracted by liquid–liquid partitioning with three 60 mL aliquots of dichloromethane, as described in Cessna et al. (1985). The dichloromethane extract was then dried and concentrated as described above, after which the samples were methylated and exchanged into hexane to a final volume of 10 mL, also as described above.

Quantification was performed using an Agilent Technologies (Palo Alta, CA) model 6890 gas chromatograph (GC) interfaced with a Waters (Manchester, UK) model Quattro Micro GC triple-quadrupole mass spectrometer operated in electron impact ionization mode using multiple reaction monitoring. The GC column used was a HP-5 ms 30-m × 0.25-mm internal diameter, film thickness 0.25 µm of 5% phenyl-95% dimethylpolysiloxane. Helium was used as the carrier gas with a flow rate of 1 mL min^{-1}. Extract aliquots (2 µL) were injected into the GC with an Agilent model 7683 automatic liquid sampler. Minimum detection limits (MDLs) were 0.01 µg sample^{-1} for all analytes with the exceptions of 2,4-D, atrazine, ethalfluralin, and trifluralin that had MDLs of 0.05 µg sample^{-1}. The accuracy of the calibration standards were verified by comparison to external standards obtained from an independent chemical supplier. In addition to 2,4-D CAA, an internal standard (0.1 µg 4,4′Dibromooctafluorobiphenyl in 0.1 mL of hexane) was added just prior to instrumental analysis.

QA/QC protocols also included the use of field and laboratory blank matrices as well as matrix spikes. Field blanks consisted of two PUF/XAD-2 resin cartridges, two XAD-2 columns and two 1 L 18-megohm deionised water samples. The laboratory blanks included PUF/XAD-2 resin cartridges, XAD-2 columns and dechlorinated Edmonton, AB drinking water. Matrix spikes included samples of clean matrix fortified prior to extraction with 1.0 µg of each of the analytes of interest including the surrogate. Matrix spikes and matrix blanks were analyzed throughout the study period at a frequency of at least 10% of the samples analyzed. Recovery values typically ranged from 82 to 124% for the water spikes, 88–118% for the XAD-2 column spikes, and 75–113% for the PUF/XAD-2 resin cartridges spikes. However, XAD column spike recoveries for ethalfluralin and trifluralin were generally lower (37.9–75%). Blanks for all media and water background samples were below levels of detection with the following exceptions: 0.03 µg MCPA was found in XAD Column Method Blanks 1 and 2 and 0.01 µg of dicamba found in XAD Column Method Blank 2.

3. Statistical analysis

Pearson product-moment correlation and multiple linear regression analyses were performed on log$_{10}$ transformed data in Data Desk 6.3 (Data Description Inc., Ithaca, NY, USA) to determine correlations and predictions of the physicochemical properties

(vapor pressure, water solubility, Henry's law constant) (The Pesticide Properties Database, 2012), meteorological conditions (temperature and rainfall) and/or pesticide use data (mass applied within a 13 km radius of the research site, mass applied in Manitoba) versus pesticide air concentrations and atmospheric deposits. The 13 km radius was chosen because the pesticides applied in this area would likely be able to transport to the study site given the known chemical half-lives of some pesticides in air and average wind speeds in the area. The 13 km radius is a conservative estimate as the atmospheric half-life for many of these chemicals is unknown.

4. Results

4.1. Currently-used herbicides

Metolachlor was not detected in any of the matrices. Except for atrazine, all other active ingredients were frequently detected (50–100%) in the air, with their detection generally being highest from May 30th to mid July (Table 2). Weekly air concentrations ranged from 0.00 to 1.23 ng m^{-3} with ethalfluralin detected at the highest concentration. Ethalfluralin, triallate, MCPA, bromoxynil, trifluralin, dicamba, 2,4-D, and mecoprop were all detected in 92–100% of the air samples collected (Table 2). The mean air concentration of pesticides detected over the study period was strongly positively associated with their masses applied in a 13 km radius of the site and in Manitoba (Table 3). Among the regressions investigated, the mean air concentration was best predicted by a combination of the relative use of these active ingredients in Manitoba and their vapor pressures: mean air concentration = 1.032 active ingredient use in Manitoba + 0.509 vapor pressure − 3.498, $R^2 = 0.83$; with the p-values being 0.0003 for the active ingredient use in Manitoba, and 0.01 for the active ingredient vapor pressure.

All active ingredients were frequently detected in the dry deposition samples except atrazine, and trifluarilin. Largest deposition rates occurred from May 30th to June 27th and then fell to lower levels or below detection limits throughout the remaining season except for a concentration increase of most herbicides in the week ending in the July 18th sample (Table 4). Ethalfluralin had the greatest rates of dry deposition followed by 2,4-D, MCPA, Triallate, and bromoxynil (Table 4). The total dry deposition of pesticides detected over the study period was strongly positively associated with their mass applied in Manitoba and to a lesser extent with those applied in a 13 km radius of the site (Table 3). Among the regressions investigated, total dry depositions are best predicted by the relative use of these active ingredients applied in Manitoba ($R^2 = 0.68$, Fig. 1).

Six herbicides were detected in wet depositions in 14–86% of the samples (Table 5). Wet deposition rates were highest in the samples collected throughout most of June and in the week ending in July 11th (Table 5). Ethalfluralin, triallate, and trifluralin, all having vapor pressures larger than 9 mPa (Table 1), were not detected (Table 5). The total wet deposition of pesticides detected over the study period was strongly positively associated with their mass applied in a 13 km radius of the site and to a lesser extent with the mass applied in Manitoba. There was also a weaker positive correlation to water solubility and negative association with Kow (Table 3). Among the regressions investigated, total wet deposition of detected pesticides (excluding those which partition to the air and were not found in the wet deposition samples) was best predicted by the annual mean mass of each pesticide applied in a 13 km radius surrounding the farm: total wet deposition of detected pesticides = 0.841 active ingredient use in a 13 km radius + 0.082, $R^2 = 0.98$, $p \leqslant 0.0001$. For the three most frequently detected herbicides (all as mixtures in 86% of the samples), larger weekly wet deposition rates are predicted in weeks of greater precipitation (Fig. 2).

For those pesticides with both wet and dry deposition detections, dry deposition contributed 12–21% of the total deposition over the sampling period, except for mecoprop for which dry deposition accounted for 51% of total deposition (Table 5). Total bulk deposition amounts (wet + dry) ranged from 0.009 to 2.3 µg m^{-2} with 2,4-D and MCPA accounting for the greatest mass deposited (Table 5). The total bulk deposition of pesticides detected over the study period was well correlated with their detected mean air concentrations ($r = 0.75$). The total bulk deposition of pesticides detected over the study period was strongly associated with both the masses applied in a 13 km radius of the site and in Manitoba (Table 3). Among the regressions investigated, the total deposition was best predicted by a combination of the relative use of these active ingredients applied in a 13 km radius from the site and their vapor pressures: total deposition = 0.465 active ingredients applied in a 13 km radius − 0.223 vapor pressures + 2.007; $R^2 = 0.88$; 13 km radius p-value $\leqslant 0.0001$; vapor pressure p-value = 0.04.

4.2. Pesticides no longer registered for use in Canada

Alachlor was not detected in any of the matrices. Air concentrations of Lindane and α-HCH remained relatively consistent throughout the season (Table 2). Lindane was more frequently detected in the dry deposits than α-HCH (Table 4). Lindane and α-HCH were not detected in the wet deposition samples (Table 5).

5. Discussion

As none of the monitored pesticides were applied on the research farm, the detectable concentrations must have resulted from application drift (Caldwell, 2007), post-application vapor

Table 2
Atmospheric concentrations of herbicides (ng m^{-3}) including detection frequencies and maximum concentrations (bold values are the maximum weekly concentrations).

Date	30-May	7-June	13-June	20-June	27-June	4-July	11-July	18-July	25-July	1-August	8-August	15-August	Detection frequency (%)	Max. conc. (ng m^{-3})
Ethalfluralin	0.63	**1.23**	1.00	0.82	0.49	0.26	0.42	0.43	0.14	0.21	0.16	0.19	100	1.23
Triallate	0.12	0.15	**0.46**	0.19	0.26	0.17	0.10	0.13	0.09	0.07	0.07	0.05	100	0.46
MCPA	0.02	0.12	0.23	0.20	0.13	0.10	**0.46**	0.05	0.04	0.03	0.01	0.01	100	0.46
Bromoxynil	0.03	0.16	**0.32**	0.20	0.23	0.14	0.12	0.05	0.05	0.04	0.02	0.01	100	0.32
2,4-D	ND	0.18	**0.21**	0.16	0.14	0.10	0.11	0.05	0.10	0.10	0.04	0.04	92	0.21
Trifluralin	0.07	0.15	**0.21**	0.18	0.15	0.20	0.14	0.06	0.07	0.08	0.10	0.08	100	0.21
Mecoprop	ND	0.02	0.02	0.03	0.02	0.03	**0.14**	0.04	0.06	0.04	0.02	0.02	92	0.14
Dicamba	0.01	0.02	0.03	0.03	0.03	0.02	**0.11**	0.02	0.04	0.03	0.02	0.01	100	0.11
Clopyralid	ND	0.05	0.05	0.03	0.05	**0.06**	**0.06**	ND	ND	ND	ND	ND	50	0.06
Atrazine	ND	ND	**0.04**	ND	ND	ND	ND	ND	ND	ND	ND	ND	8	0.04
Lindane	0.02	0.03	**0.04**	0.03	0.03	0.03	0.03	0.02	0.03	**0.04**	0.03	0.02	100	0.04
α-HCH	0.01	0.02	ND	**0.02**	**0.02**	**0.02**	**0.02**	ND	0.01	ND	**0.02**	**0.02**	75	0.02

ND = No detection.

Table 3
Correlation coefficients of log-transformed data between pesticides average air concentration, total wet deposition, total dry deposition, and total bulk deposition and physicochemical properties and pesticide use data.

	Mean air conc.	Dry dep.	Wet dep.[*]	Bulk dep. (wet + dry)
Mass applied in MB	0.79[B]	0.82[B]	0.78[B]	0.88[A]
Mass applied in a 13 km radius of the site	0.81[B]	0.69[C]	0.99[A]	0.89[A]
Water solubility 20 °C (mg L^{-1})	ns	ns	0.52[D]	ns
Vapor pressure at 25 °C (mPa)	ns	ns	ns	ns
Henry's law constant at 25 °C (Pa m^3 mol^{-1})	ns	ns	ns	ns
Koc (mL g^{-1})	ns	ns	ns	ns
Kow at pH 7, 20 °C	ns	ns	−0.79[B]	ns

ns: Not significant.
[*] Excluding those active ingredients which partition to the air and were not found in the wet deposition samples.
[A] p-Value: <0.001.
[B] p-Value: <0.01.
[C] p-Value: <0.05.
[D] p-Value: <0.1.

Table 4
Herbicide dry deposition rate (ng m^{-2} d^{-1}) and average temperatures including detection frequencies, maximum deposition rate, and total mass of dry depositions (bold values are the maximum weekly mass deposited).

Date Avg. temp. (°C)	30-May 8.6	7-June 14.2	13-June 15.6	27-June 17.0	4-July 16.5	11-July 18.7	18-July 17.5	Detection Frequency (%)	Max. deposition (ng m^{-2} d^{-1})	Total dry Deposition (ng m^{-2})
Ethalfluralin	218.79	**414.43**	93.04	98.20	19.34	ND	74.37	86	414.43	918.17
2,4-D	64.24	**122.97**	55.19	120.09	ND	ND	33.64	71	122.97	396.12
MCPA	32.05	87.71	48.56	**112.03**	7.79	11.51	38.23	100	112.03	337.88
Triallate	47.76	**51.52**	11.64	46.66	10.70	3.99	17.34	100	51.52	189.61
Bromoxynil	12.41	47.47	18.85	**88.70**	7.82	3.11	9.12	100	88.70	187.46
Clopyralid	11.96	**24.53**	6.94	23.63	ND	ND	7.14	71	24.53	74.20
Atrazine	**31.82**	18.16	ND	11.72	ND	ND	ND	43	31.82	61.71
Dicamba	11.41	11.96	5.04	**13.98**	2.20	2.63	4.81	100	13.98	52.04
Mecoprop	6.59	**8.34**	4.25	7.19	ND	2.43	ND	71	8.34	28.80
Trifluralin	ND	**17.42**	ND	11.37	ND	ND	ND	29	17.42	28.79
Lindane	**8.43**	6.29	4.72	4.80	ND	ND	4.41	71	8.43	28.65
α-HCH	**5.82**	ND	ND	ND	ND	ND	3.62	29	5.82	9.44

ND = No detection.

losses (Grover et al., 1985) or on wind eroded soil (Larney et al., 1999) associated with off-farm pesticide applications. This dispersion and subsequent deposition of pesticides may contaminate non-target areas including biologically important ecosystems such as the numerous wetlands that are pervasive within the PPR. The detected air concentrations and depositions of pesticides were significantly correlated to estimates of the masses and physicochemical properties of pesticides applied. Levels of pesticide use are generally lacking for Canada as well as other countries (Boyd, 2001; Brimble et al., 2005). Physicochemical data for pesticides can be derived from sources such as the IUPAC Footprint data base (The Pesticide Properties Database, 2012). Our study provides direct evidence of well established theories that pesticides will more likely be associated with the water-phase (rain) when they have relatively small Kow values and with the vapor-phase (air) when they have relatively large vapor pressures.

Donald et al. (2001) have previously proposed that applied pesticides are lost to the atmosphere and evenly distributed over the regional landscape within the province of Saskatchewan. The current study gives further indication that pesticides are dispersed throughout the landscape from their areas of application. In our study, the masses of pesticide wet deposition were more strongly associated with the masses of pesticides applied in a 13-km radius surrounding the site than with the masses of pesticides applied in Manitoba as a whole; in contrast, the masses of pesticide dry deposition were more strongly associated with the masses of pesticides applied in Manitoba as a whole than with the masses of pesticides applied in a 13-km radius surrounding the site. This suggests that currently-applied pesticides move relatively short distances before being deposited by rainfall but that they are also transported over
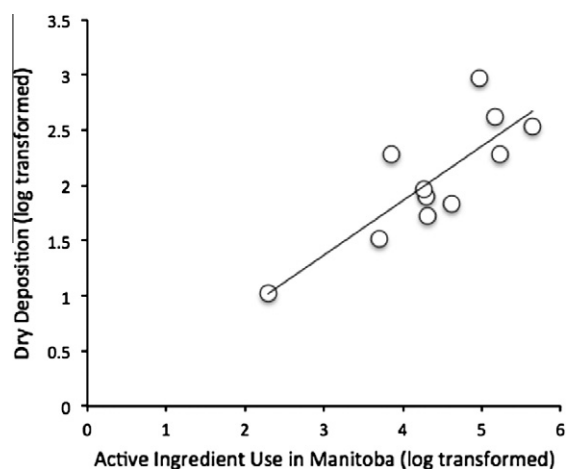

Fig. 1. Total dry deposition of detected pesticides plotted against the relative use of these active ingredients applied in MB. Regression equation: total dry deposition mass = 0.493 active ingredient applied in Manitoba − 0.111, R^2 = 0.68, p < 0.002.

longer distances particularly when in the gas phase or associated with dust particles. Dry deposition followed similar trends to the air concentrations and total dry deposition shared similar correlations with the same physicochemical properties as the average air concentrations.

Drinking, Aquatic and Irrigation Water Quality guidelines in Canada are set for some individual pesticides, but not for pesticide mixtures which were commonly found in the current study. In all

Table 5
Herbicide wet deposition rate (ng m^{-2} d^{-1}) and weekly precipitation (mm) including detection frequencies, total wet deposition, total (wet + dry) deposition, and dry deposition contribution to total deposition (bold values are the maximum weekly concentrations).

| Date	30-May	7-June	13-June	27-June	4-July	11-July	18-July	Detection Frequency (%)	Max. deposition (ng m^{-2} d^{-1})	Total wet Deposition (ng m^{-2})	Total (wet + dry) Deposition (ng m^{-2})	Dry deposition Contribution to total (%)
Precipitation (mm)	9.0	25.2	21.8	19.6	1.6	18.0	3.8					
2,4-D	ND	**939.81**	932.61	ND	ND	ND	ND	29	939.81	1872.42	2268.55	17.46
MCPA	ND	**685.50**	549.72	60.58	2.57	139.41	8.22	86	685.50	1446.00	1783.88	18.94
Bromoxynil	ND	343.06	**582.05**	83.93	4.34	31.42	9.59	86	582.05	1054.39	1241.85	15.10
Clopyralid	ND	161.81	**246.93**	88.93	4.86	26.14	7.51	86	246.93	536.19	610.38	12.16
Dicamba	ND	52.37	58.79	ND	3.03	**86.34**	ND	57	86.34	200.53	252.57	20.60
Mecoprop	ND	ND	ND	ND	ND	**27.99**	ND	14	27.99	27.99	56.79	50.72
Ethalfluralin	ND	ND	ND	ND	ND	ND	ND	0	0.00	0.00	918.17	100.00
Triallate	ND	ND	ND	ND	ND	ND	ND	0	0.00	0.00	189.61	100.00
Atrazine	ND	ND	ND	ND	ND	ND	ND	0	0.00	0.00	61.71	100.00
Trifluralin	ND	ND	ND	ND	ND	ND	ND	0	0.00	0.00	28.79	100.00
Lindane	ND	ND	ND	ND	ND	ND	ND	0	0.00	0.00	28.65	100.00
α-HCH	ND	ND	ND	ND	ND	ND	ND	0	0.00	0.00	9.44	100.00

ND = No detection.
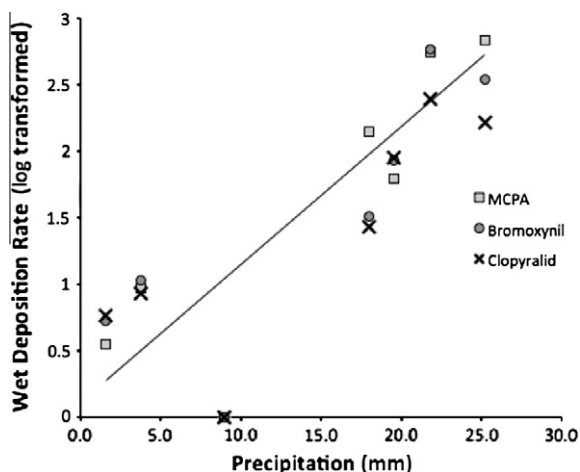
Fig. 2. Wet deposition rate plotted against precipitation. Regression equation is wet deposition rate = 0.077 precipitation (mm) + 0.5773, R^2 = 0.86, $p \leqslant 0.0001$.

of the samples that contained detectable levels of pesticides, at least three pesticides were detected. Of the pesticides screened in this study, Canadian Environmental Quality Guidelines (Canadian Council of Ministers of the Environment, 2012) for the Protection of Aquatic Life (Freshwater), Water Quality Guidelines for the Protection of Agriculture (Irrigation/Livestock), Air Quality Guidelines for the Protection of Human Health and the Environment are available for 9, 5/9, and 0 of pesticides respectively. The Guidelines for Canadian Drinking Water Quality are published by Health Canada (2010) and of the number of pesticides screened in this study 6 are available. The detected concentrations of individual pesticides never exceeded the respective Water Quality guidelines.

Ethalfluralin and triallate were detected at the highest air concentrations among the pesticides studied because these active ingredients have high vapor pressures and low water solubilities (Table 1). Ethalfluralin was detected at higher concentrations than triallate because it is more frequently used in the province of Manitoba (Table 1). Trifluralin is used in larger quantities in the Province of Manitoba than triallate, but the concentrations detected were less than that of triallate because of its lower vapor pressure. MCPA, bromoxynil and 2,4-D have vapor pressures ranging from 0.02 to 0.4 mPa but are widely applied in Manitoba and were within the top five maximum air concentrations (Table 2). Other studies have demonstrated that pesticides that have relatively low vapor

pressures are present in the atmosphere partitioned in the gas phase or sorbed to atmospheric particulates (Rawn et al., 1999; Waite et al., 2005; Yao et al., 2008). Although mecoprop and dicamba were frequently detected in the air, their concentrations were lower than the other frequently detected pesticides, likely due to the lower amounts applied within Manitoba.

Although the highest concentrations of pesticides in wet deposition were found with low rainfall events, as previously discussed by Hill et al. (2003), greater total deposition was found with greater precipitation, at least this was evident for the pesticides frequently detected as wet deposits (MCPA, bromoxynil, and clopyralid; Fig. 2). Evidence for this was also found by Donald et al. (2005) who reported the frequent detection of some herbicides in wetlands (e.g., MCPA, 2,4-D, and dicamba) resulted most likely from direct atmospheric wet deposition rather than herbicide rainfall runoff from agricultural soils. Using the same sampler as the current study, Waite et al. (1999), also found positive correlations between precipitation and wet deposition concentrations of several herbicides (2,4-D, dicamba, and lindane) but no such correlations were found in a later study by Waite et al. (2005).

For those pesticides with both wet and dry deposition detections Waite et al. (2005) found that dry deposition contributed approximately 90% to the total herbicide deposition for 2,4-D, Bromoxynil, Dicamba, and MCPA. This is more than the proportional dry deposits observed in our study (12–51%) for these and other pesticides. The proportional greater amount of dry deposits observed by Waite et al. (2005) is likely due to their study site being located in Saskatchewan, a province which typically receives less precipitation than Manitoba. Only 48 mm of rainfall was measured in the five weeks of the study by Waite et al. (2005) compared to 99 mm of rainfall in the seven weeks in the current study.

The pesticides no longer registered for use in Canada were found at very low concentrations in both the air and dry deposition samples suggesting that these chemicals with moderately high vapor pressures are still persistent in our environment at near background levels.

6. Conclusion

Monitoring studies often focus on precipitation only and may miss quantitatively important dry deposits, contributing 12–51% of the total deposition in the current study. Air concentrations and dry and wet deposition rates of pesticides were found to correlate to the mass and physicochemical properties of pesticide

applied. In addition, an increasing amount of weekly rainfall demonstrated increasing masses of wet deposition by those pesticides more often detected in rainfall. This study represented only a small portion of the commonly-used herbicides in the Prairie region, but all were frequently detected. Other pesticides applied in the region would contribute to greater total pesticide air concentrations and atmospheric depositions and further contribute to the chemical mixtures found in the environment. In order to reduce agricultural pesticide loadings to the atmosphere and to surface waters by subsequent atmospheric deposition, farm extension efforts designed to minimize spray drift and post-volatilization losses should operate at the regional-scale.

Acknowledgments

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