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ORIGINAL RESEARCH

Atmospheric Concentrations of Captan and Folpet in the Lower Fraser Valley Agricultural Region of Canada

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Abstract: Two N-trihalomethylthio fungicides were detected in the atmosphere in the Lower Fraser Valley agricultural region of Canada. Captan was detected in both the particle and gas phase with a dominant particle phase fraction observed in both 2005 and 2006 (only total captan atmospheric concentrations were available for 2004). This provides the first evidence of particle transport as a significant atmospheric transport pathway for captan in an agricultural region in Canada. Weekly captan air concentrations reached maximum levels of 13.2 ng m^{-3} in June 2006, while for folpet total atmospheric levels were lower with maximum reaching 1.7 ng m^{-3} in August 2004 and generally <1 ng m^3 in 2005 and 2006. Folpet is detected in the atmosphere although not previously reported in usage inventories. In the three years examined (2004–2006) captan concentrations observed a seasonal maximum in atmospheric concentrations during spring to early summer coinciding with expected peak usage period on crops in the Lower Fraser Valley agricultural region located in British Columbia, Canada. No usage data is available in Canada beyond 2003 but these seasonal trends show that captan remains a dominant pesticide used in this agricultural region with no decline in atmospheric concentrations during 2004–2006.

Keywords: fungicides, atmospheric transport, particle and gas phase partitioning, captan, folpet

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Introduction

Pesticides are used in agricultural areas to protect plants from pests and diseases and allow for increased crop production. Numerous laboratory and epidemiological studies have suggested that certain pesticides are associated with carcinogenesis, immunitoxicity, neurotoxicity, behavioural impairment, reproductive dysfunction, endrocrine disruption, developmental disabilities, skin conditions and respiratory diseases. Captan, folpet and captafol are N-trihalomethylthio fungicides used to control diseases on many fruit, ornamental and vegetable crops. Folpet and captafol have been shown to produce cancer in test animals, while there is strong evidence that captan can also cause cancer in female mice and male rats at high doses.[1–3] Captan is classified as a category I toxicant[1] and has a short half-life in human blood[4] and consequently EPA has classified it as not likely to be a human carcinogen expect for prolonged high-level exposures.[5] Human exposure and regulations exist for fruit and vegetation residue and also for workers occupational exposures for 8- or 10-hr time-weighted-average exposure of 5 mg/m.[3,6] As with many of the currently used pesticides in Canada, there are currently no regulations for atmospheric concentrations of captan or folpet.

Captan and folpet are of interest in our 3-year research study due to their known or suspected use as agricultural fungicides in the Lower Fraser Valley (LFV) of British Columbia (BC), Canada. They are primarily used on berry fruit (e.g. raspberries, strawberries, blueberries) with over 75% of BC acreage or crop treated dominantly in the Lower Mainland Region 2.[7–8] Little information on atmospheric levels of fungicides is available in North America. Captan has also been used for apple scrab control. No pesticide usage information is available for the period of the study of 2004–2006 or subsequent years, but 2003 usage data indicates 25,500 kg of captan was sold in BC, making it one of the top 20 pesticides in use in the province. The major products sold include Agrox Seed Treatment Powders, Maestro, and Captan.[7–8] Captan usage has remained significant in the region with reported sales between 25,500 and 29,160 kg from 1991 through to 2003; consequently it would be expected to have a similar usage level in 2004–2006. No folpet or captafol information is available in BC or the United States inventories, however folpet has been used previously for fruit rot on cranberries in BC and was listed in the berry production guide for commercial growers (Folpan 50 WP) for use on cranberries.[8] The 2003 BC inventory lists folpet as an active ingredient that has been replaced with chlorthalonil and copper oxychloride, but it was still identified as an active ingredient present in domestic pesticides sold in BC.[7] Captafol is registered for used in the United States, has potential for long range atmospheric transport to this region of Canada so was included in the analytical method but was not detected in any samples. Captan is also used in the United States on fruit and berry crops (see pesticide usage maps)[9] with a higher density of usage in the eastern United States where it is the second most widely applied fungicide on apples and peaches.[10] Its use in western US is mainly on berry crops particularly in Washington, the largest raspberry production area in the US, for control of common fungi that cause fruit rot and primocane lesions. Captan residue studies have also been carried out in other agricultural applications[7] and have detected residues on fruits and vegetables, which can be a significant contributor to public and occupational exposures.[11,12]

The Lower Fraser Valley (LFV) of British Columbia is an important fruit and berry production region with the largest concentration of farmland in Canada, an estimated 6,000 farms spread amongst urban centers within an area of approximately 100,000 ha.[13] More recent studies in this region have identified organochlorine (OCs), organophosphorus pesticides (OPs), common acid herbicides, and triazines either in farm ditches[13] or atmospheric samples[14–19] but did not include N-trihalo methyl thio fungicides. A published report of atmospheric captan levels in 1996 indicated a maximum concentration of 6.5 ng m^{-3} along with detection in dry deposition and rainfall.[20]

The purpose of this study is to identify recent trends in N-trihalo methyl fungicides (captan, folpet, captafol) atmospheric levels in agricultural region of the LFV. No usage information is available in BC beyond 2003 so atmospheric measurements provide the only indication of current usage trends in the region. The study was expanded to include both particle and gas phase measurements in 2005 and 2006 to provide insight on the transport pathway and potential influence of local versus long-range atmospheric transport sources. In a previous study we developed a new large volume injection cold on-column (COC) gas chromatography-mass spectrometry-negative chemical ionization (GC-MS-NCI) method that permits detection of ~2–4 pg m^{-3} of these fungicides in air samples[21] which enabled lower levels of detection than in the 1996 studies for improved seasonal variation analysis as well as expansion to other N-methyl trihalo fungicides such as folpet and captafol.

Experimental

Materials

All standards were purchased from Chem Service Inc. (West Chester, PA). The pesticide standards included captan (N-[trichloromethylthio]-4-cyclohexene-1, 2-dicarboximide, CAS RN [133-06-02], 100 μg mL^{-1} intoluene); captafol (N-[1,1,2,2-tetrachloroethylthiol]-4-cyclohexene-1,2-dicarboximide, CAS RN 2425-06-1, 100 μg mL^{-1} in toluene); and solid folpet (N-[trichloromethylthio] phthalimide, CAS RN [133-07-3]. Deuterated internal standard, parathion diethyl-d_{10} (O,O-diethyl-O-p-nitrophenyl phosphorothioate (diethyl-d10), and surrogate, diazinon (diethyl-d_{10}) at 100 μg mL^{-1} in n-nonane, were also purchased from Chem Service Inc. Individual stock solutions were prepared from solids dissolved in pesticide grade hexane (Fisher Scientific) to 100 μg mL^{-1}. Standard mixtures at 1.0 μg mL^{-1} were prepared in pesticide grade hexane from individual stock solutions and were stored at 4 °C. Suitable calibration standards were prepared by dilution of a standard mixture and internal standard (IS) with pesticide grade hexane with final concentration of IS parathion-d_{10} of 10 μg L^{-1} in all standards and samples. The calibration range was 2.5–100 μg L^{-1}. All final diluted standards and samples were prepared on the day of analysis. All organic solvents used in standard preparation and extraction (hexane, methanol, acetone, ethyl acetate) were pesticide grade (Fisher Scientific).

Polyurethane foam plugs (PUFs), 2.54 and 5.08 cm lengths, and glass fiber filters (10.2 cm diameter) were obtained from Pacwill Environmental (Grimsby, ON, Canada); and sorbents were Amberlite XAD-2 from Supelco (Oakvile, ON, Canada) and Tenax-TA, 60/80 mesh, from Mandel Scientific Co. Inc. (Guelph, ON, Canada). All PUF and sorbent materials were cleaned with the same method described in the sample collection and preparation of air extracts section.

Sample Location and Collection

The Agriculture Canada/Environment Canada/ Greater Vancouver Regional District (GVRD) (AQ Station T034) field station located in Abbotsford is in the middle of the Lower Frasey Valley (LFV). It is located in Region 2 (Lower Mainland), the region with the highest pesticide sales of captan in BC (90% of 2003 sales). From May 5, 2004 through to the end of December, 2005 7-day samples were collected using a PUF PS-1 sampler in order to assess the seasonal variation of fungicide levels in the LFV. Sampling began near the start of the agricultural season in 2004. In 2006, the 7-day samples were only collected between mid-June and end of the year. All sampling heads with the filter and PUF/sorbent materials were prepared in a class 1000 cleanroom laboratory. Gravimetric analysis was conducted on the filters (±3 μg) to determine total suspended particulate (TSP) concentrations using a microbalance enclosed in a glovebox purged with nitrogen to allow for humidity control.

Sample Preparation

The methods for preparation and analysis of air samples for fungicides has been previous described[21] and summarized herein. Air samples were extracted using an accelerated solvent extraction system (Dionex, ASE100 or ASE300) with the following extraction program: temperature 100 °C; static mode time 30 min; 2 static cycles; 60% flush volume; purge time with nitrogen (UHP) at end of 600 sec. Ethyl acetate was used for all extractions reported here. A second extraction with acetone was also tested and showed no presence of these fungicides in the extracts. The extract volume was reduced to approximately 3–5 mL in a Visiprep solid phase extraction apparatus, extract transferred to 15 mL vial, further dried to near dryness, and then re-dissolved in 0.5 mL or 1.0 mL of 50/50 v/v% acetone/hexane (pesticide grade) and stored at –4 °C.

C18 (ENVI-18, 6 cc, 1 g, Supelco) solid phase extraction (SPE) tubes were conditioned with 4 mL ethyl acetate, followed by 4 mL methanol. Sample extract (0.25–0.5 mL) was loaded onto the preconditioned tubes, followed by surrogate standard (diazinon-d_{10}), and 1 mL methanol. The eluted solvent was collected into fraction F0 and was observed to contain no fungicides of interest. The fungicides were eluted in fraction F1 with 4 mL ethyl acetate. A Visiprep solid phase extraction vacuum manifold (Supelco) was used to process the SPE tubes and the Visiprep drying attachment (Supelco) was also used to evaporate and concentrate eluted extracts from SPE (and from ASE) to near dryness with nitrogen (UHP). The dried ethyl acetate fraction was re-dissolved in 0.50 mL pesticide grade hexane/acetone (50/50% v/v) and stored at −4 °C. A subset of this sample was diluted with pesticide grade hexane (typically 10 μL sample extract in total volume of 250 or 500 μL) with addition of internal standard, parathion-d_{10} for GC-MS analysis.

GC-NCI-MS Conditions

The GC-MS system consisted of an Agilent HP6890 GC coupled to a quadrupole mass spectrometer (5973 Network) with negative chemical ionization capability (turbo performance pump). The GC system was equipped with a cold on-column inlet with solvent vapor exit accessory. The cold on-column inlet was connected to a 5 m × 0.53 mm ID (Siltek™ or IP deactivated guard column, Chromatographic Specialties, Inc., Brookville, ON, Canada). This was connected with a Siltek™ straight connector to a retaining pre-column of approximately 2 m × 0.25 mm, Siltek™. The retaining pre-column was then connected with the solvent vapor exit (50 μm bleed restrictor, Agilent) and to the analytical column (DB5MS, poly-5% diphenyl-95% dimethylsiloxane, 60 m × 0.25 mm ID and 0.25 μm film thickness (J&W Scientific, Folsom, CA, USA) with a Siltek™ angled Y connector. The oven temperature program was 60 °C for 5 min, 25 °C min^{-1} to 290 °C hold for 5 min, 25 °C min^{-1} to 320 °C hold for 5 min. The carrier gas was helium (UHP) at a column flow rate of 1.1 mL min^{-1}. The cold on-column inlet temperature was set to follow the oven temperature program, with split vent held open for 0–30 seconds. Chemical ionization (CI) gas was methane (99.99%) at 2 mL min^{-1}, ion source temperature 150 °C, quadrupole temperature 150 °C, interface temperature 280 °C. CI tuning with PFDTD (perfluoro-5,8-dimethyl-3,6,9-trioxidodecane). Spectra were obtained at 70 eV, dwell time of 100 msec in SIM NCI mode. The ions selected for identification and quantification in NCI SIM mode for captan, folpet, captafol, and parathion (diethyl-d_{10}) were m/z of 150 (151), 146 (148), 150 (151), and 301 (303).[21]

Results and discussion

In 2004 all filters and PUFs/sorbents were extracted together for determination of total captan air concentrations. However in early 2005 for a few samples the filters and PUF/sorbent were extracted separately for determination of both particle and gas phase concentration of captan. As the presence of captan was observed in the particle phase, the samples in 2005 and 2006 were analyzed for both particle and gas phase concentrations. Other CUPs such as atrazine have been shown to have a significant particle and gas phase fraction.[21] Weekly total air concentrations of captan during 2004–2006 are shown in Figure 1. Captan concentrations were higher in 2006 than in 2005 and 2004 and reached levels as high as 13.2 ng m^{-3} for the June 27, 2006 sampling period, which exceeded previously reported 1996 atmospheric captan maximum concentrations of 6.5 ng m^{-3}.[20] This shows that captan is still heavily used in this agricultural region and usage or atmospheric levels are not declining. These maximum concentrations are comparable or higher than other regions which are typically in the low ng/m^3 range to nondetectable.[22–24] In 2004 sampling began in May at the start of the agricultural season, but a number of weekly periods were missed due to motor repairs and power issues so it is possible that some of the high concentration periods were missed in spring-summer. Figure 1 shows consistently that the spring to early summer period is when the highest concentrations

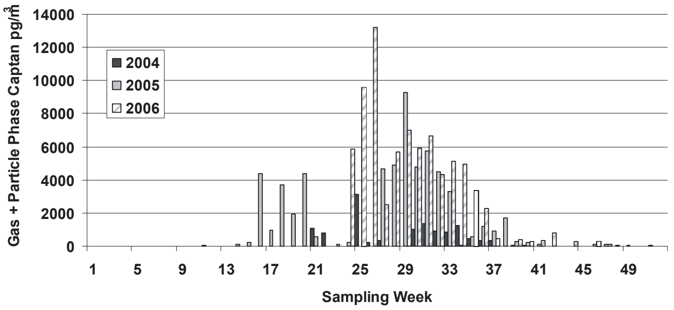

Figure 1. Weekly Total (Gas + Particle Phase) Captan Atmospheric Concentrations at Abbotsford, BC during 2004–2006. Total captan concentrations as determined from extracts of the PUF/sorbent and filter collected for a one-week period with a PS-1 sampler. Individual weekly total captan concentrations shown with nondetectable levels as zero-level concentrations.

of captan are observed coinciding with spraying of captan for protection of the blossoms and developing fruit on raspberry crops from the fungus Botrytis which leads to rot and loss of yield. Atmospheric levels of captan in July and August decrease as usage is expected to decrease with termination of usage near harvest. Captan is not recommended for application within 2 days of harvest.

Particle and gas phase air concentrations of captan during 2005 through 2006 are shown in Figure 2. Particle phase captan air concentrations were generally higher than gas phase concentrations with maxima during the spring-summer coinciding with peak air concentrations of captan. In the spring-summer when captan levels are maximum there are weekly sampling periods where both particle and gas phase concentrations are high, while for other periods the captan is mainly observed in the particle phase (see Fig. 2A and B). Tests on the potential loss of captan from the PUF/sorbent material to filter during a weekly sampling period in spring/summer field conditions did not show any transfer of captan from the PUF/sorbent to the filter. Levels during the winter were generally nondetectable.

A more urban site where captan was measured observed captan predominately in the gas phase,[25] indicating that this partitioning of captan observed

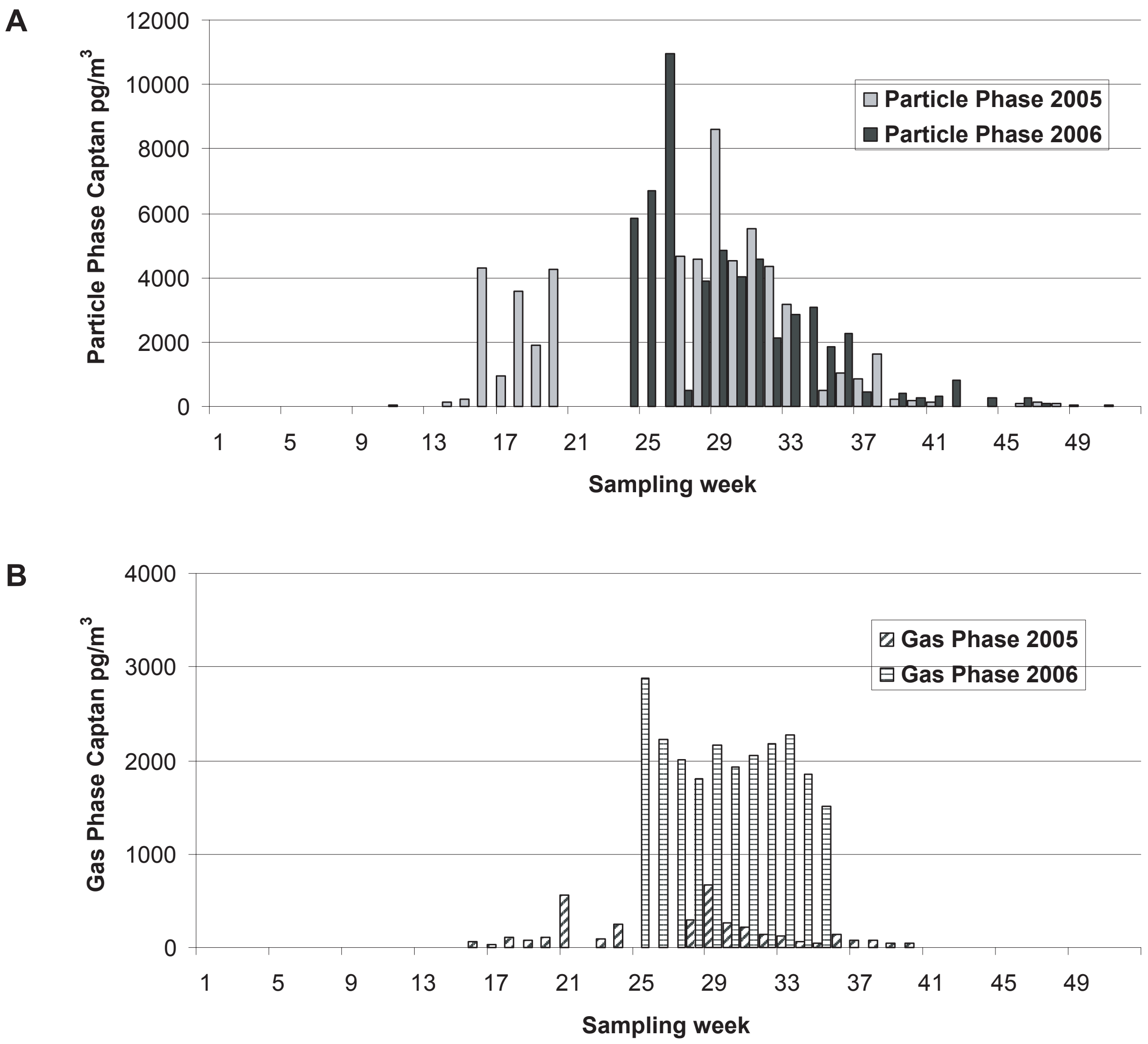

Figure 2. Weekly Captan Atmospheric Concentrations at Abbotsford, BC during 2005–2006. **A**) Particle Phase; **B**) Gas Phase. Particle phase concentrations are determined from levels of captan in extracts obtained from the filters, while gas phase captan concentrations are determined from levels of captan from the PUF/sorbents collected over a one-week sampling period with a PS-1 sampler. (Separate analyses of PUF/sorbent and filter levels were not available for 2004).

at Abbotsford, BC is related to a regional to local partitioning of captan close to the source region. Studies on organic marker compounds in surface soils of crop fields from the San Joaquin Valley in California also suggest that fugitive dust can play a significant role in source contributions of airborne particulate matter.[26,27] Atmospheric measurements at urban and rural sites in France also suggest captan is adsorbed after changing of phase directly into the atmosphere during transport from pesticide application regions where it is predominately in the vapor phase.[23] Other pesticides also indicate a favouring of particle phase partitioning with distance from application region.[28]

Captan particle concentrations are strongly correlated with air temperature. The natural logartithm of particle captan concentration versus inverse air temperature (K^{-1}) shows a negative slope and strong correlation (Fig. 3A, $r^2 = 0.72$ for data in 2005–2006 were both particle and gas phase concentrations are available) as expected with higher predicted concentrations during July–August (week 28–32) at Abbotsford. Gas phase concentrations are not as strongly correlated with inverse temperature ($r^2 = 0.45$). This relationship does not predict the higher atmospheric concentration of captan in the spring—early summer of 2006 (week 24–28, Fig. 2). The Clausius-Clapeyron plots (ln P versus 1/T) have been used to suggest the relative importance of short-versus long-range atmospheric transport.[29] The strong correlation with temperature and slopes for Abbotsford would suggest short-range transport (local or regional sources) is more important to the LFV. However the variation in particle/gas phase ratios suggest that there are multiple application regions surrounding the monitoring site with some in much closer proximity leading to higher vapour phase concentrations. The Abbotsford field station is located in region 2, mainland region, of LFV where 90% of 2003 BC sales of captan were reported.[7] In this localized region between 75 to 100% of acreage with berry crops are expected to have application

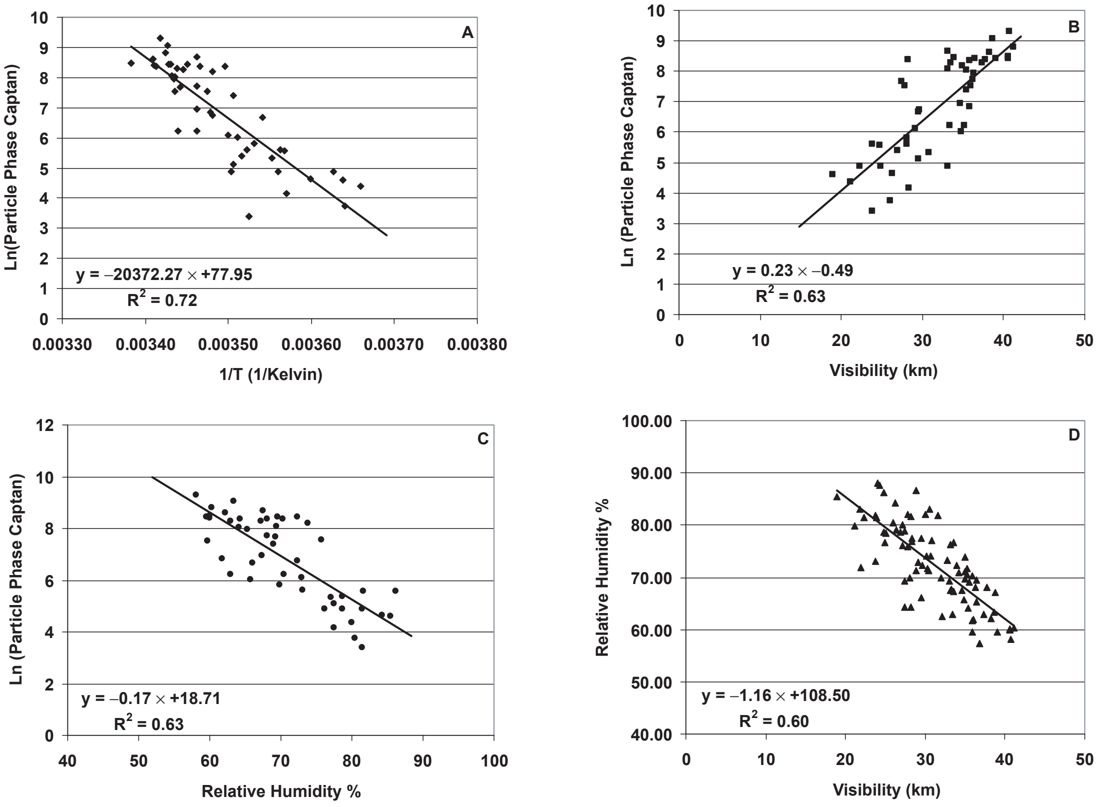

Figure 3. Trends of Climatic Conditions at Abbotsford, BC during 2005–2006. **A**) Natural logarithm of particle phase captan concentration with inverse temperature; **B**) natural logarithm of particle phase captan concentration with visibility; **C**) natural logarithm of particle phase concentration with percentage relative humidity; **D**) percentage relative humidity with visibility. Climate data are averages for sampling period taken from hourly measurements. Particle phase captan concentrations determined from extracts of the filter. 2004 not included as particle phase captan concentrations were not available.

of captan. No pesticide usage data is available for 2004–2006 period or beyond.

TSP (total suspended particulate) atmospheric concentrations (measured from mass of particles on glass fiber filter collected with PUF PS-1 sampler) at Abbotsford are variable generally between 10 to 40 μg m^{-3} with generally lowest levels observed during the winter months. While particle phase captan concentrations were poorly correlated with TSP levels we found that the natural logarithm of particle phase captan concentrations were strongly correlated with visibility and relative humidity ($r^2 = 0.63$ for both) as shown in Figure 3B and C. Relative humidity measurements at most monitoring sites do not show a strong correlation with atmospheric pesticide concentrations, however this site has a strong relationship between visibility and relative humidity ($r^2 = 0.60$, Fig. 3D) with lower visibility with increasing relative humidity. Soil water content rather than relative humidity would provide a better indication of hydrolysis of captan which is in the order of hours but was not available for this study. Of interest for future studies in addition to air temperature is also the relationship to soil water content as it has been found that these are the strongest environmental influences on respirable dust production from agricultural operations in California.[30] The fact that visibility correlates with captan concentration in the particle phase would indicate that small particles play a key role in the atmospheric transport process. Captan in the vapour phase is also rapidly degraded by hydroxyl radicals such that particle transport is a major route of movement of captan in the environment from application region to nonexposed regions.

Although there is usage of captan in the west coast of United States such as in Washington on rasperberries, regional usage in LFV is expected to be more significant. Potential future studies on these N-trihalo methyl fungicides should examine geographic differences between the LFV and Okanagan Valley, where usage of captan is lower. This will help to provide insight into the potential contributions from local/regional and long range atmospheric transport from different geographic regions. As particle levels are relatively uniform in the LFV (as compared to other Canadian agricultural regions such as the prairies) the large variation in ratio of particle/gas phase concentrations is expected to be related to proximity of sampling site to farmland applications. Recent applications in close proximity to the field station may be exhibiting higher gas phase concentrations, however these individual events are difficult to identify as the site is surrounded in all directions by acreages with raspberries. The data does indicate that captan is transported in the atmosphere significantly in the particle phase which differs from many other currently used pesticides (CUPs) and this enhanced particle phase partitioning warrents further investigation as a potential significant pathway of movement of CUPs.

Figure 4 shows total atmospheric concentrations of folpet at Abbotsford, BC during 2004–2006. Folpet air concentrations are lower than captan and year to year variations are smaller. Maximum concentrations occur in spring-summer period but can also be high during latter summer months as observed in 2004. Folpet sales and usage are not well documented. It is known to be present in domestic products and has been used previously as a fungicide on cranberries (Folpan). Although the most recent pesticide sales inventory (2003) indicates that it has been replaced by other active ingredients,[5,6] the significant atmospheric concentrations and spring-early summer maximum concentrations would indicate that it is still used in the region. There are no significant reported uses of folpet in western United States that would indicate a potential for long-range atmospheric transport source of folpet. Residues of folpet have been reported on food products in the United States, but its main

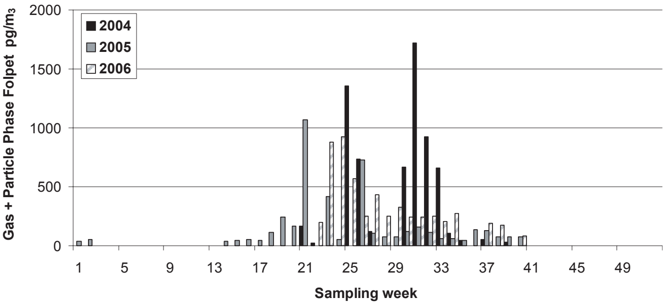

Figure 4. Weekly Total (Gas + Particle Phase) Folpet Atmospheric Concentrations at Abbotsford, BC during 2004–2006. Total folpet concentrations as determined from extracts of the PUF/sorbent and filter collected for a one-week period with a PS-1 sampler. Individual weekly total folpet concentrations shown with nondetectable levels as zero-level concentrations.

permitted food application is on avocados in Florida. Both captan and folpet are also used in manufacturing of paints and coatings.

Conclusions

This study on atmospheric samples collected at Abbotsford, BC during 2004–2006 and analyzed at the University of Regina, Trace Analysis Facility (TAF) provide the first evidence of importance of particle transport pathway in the atmosphere for captan in the LFV agricultural region of western Canada. In 2004–2006 a seasonal maximum in captan concentration was observed in spring to early summer period coinciding with its expected high usage period on berries. Folpet was also observed in the atmosphere although not reported in the 2003 usage inventory but has been previously used in the region such as for cranberries. Levels of folpet in the atmosphere between 2004–2006 have decreased and are significantly lower than captan. In winter when there was no farming activity atmospheric levels were nondetectable.

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Disclosure

The authors report no conflicts of interest.

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