Canadian Pesticide Air Sampling Campaign

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Introduction

Pesticides are widely used in Canada, however little is known about the presence, distribution and fate of currently used pesticides (CUPs) in the Canadian atmosphere. The Canadian Pesticide Air Sampling Campaign was initiated in 2003 through funding from the Environment Canada (EC) Pesticide Science Fund (PSF). The goal of this project is to provide information on air and precipitation levels of CUPs across Canada, create pesticide emission inventories and identify important pesticide issues regarding environmental fate, exposure and risk assessment. All of this will help to develop a sound national policy towards pesticides.

Materials and Methods

The 3-year national air surveillance program was conducted through two complementary approaches: 1. The implementation of the Canadian Atmospheric Network for Currently Used Pesticides (CANCUP) and 2. An intensive field study in the Canadian Prairies (Prairie Study). Two sampling campaigns were undertaken during the spring to summer of 2003 and the spring to fall of 2004, respectively. The first field campaign was conducted at 8 sampling sites across Canada including 3 sites in the Prairies. For the second year, one more site (Vineland) was added. Sites are indicated in Fig.1 that also shows main agricultural regions in Canada.

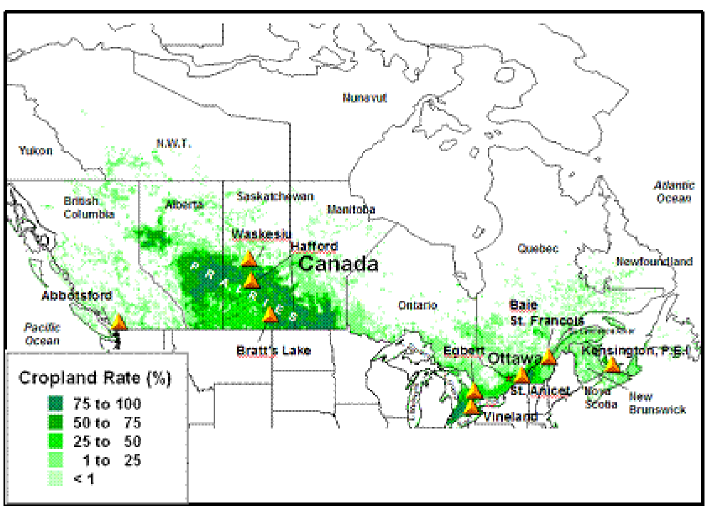

Fig. 1. Sampling sites of CANCUP and Prairie Study across Canada.

Air samples were collected weekly using high volume PS-1 samplers with PUF/XAD sandwiches (gas-phase) and glass fibre filters (particle-phase). Precipitation samples were collected monthly using MIC samplers equipped with XAD columns. At Bratt's Lake site, air samples were further collected at 1, 10 and 30 m heights on a sampling tower to investigate pesticide vertical profiles. Dry and wet depositions were collected separately and combined to get the total deposition. Furthermore, passive air samplers with PUF disks were deployed at most sites for sampling periods of 1 to 3 months. Sample analysis was performed by several external laboratories. Target pesticides were selected based on available knowledge of use, the priority list of the Pest Management Regulatory Agency (PMRA) and analytical capabilities of the participating laboratories.

Results and Discussion

2003 Campaign

Sampling under CANCUP in 2003 occurred late in the summer in July-September. Results will therefore not reflect pesticides that are used early in the growing season (e.g. pre-emergent herbicides). Fig. 2 shows results for chlorothalonil and endosulfans in air. The monthly average air levels of chlorothalonil ranged from 1,900 to11,900 pg m^{-3} with highest levels at Kensington, PEI. This is likely related to its high use for potato production on the island. Results for clorothalonil are in general much higher than those reported by James et al.[1] around the Great Lakes (30-100 pg m^{-3}) in 1996.

Endosulfan is a chlorinated insecticide used widely in Canada on fruits and vegetables. Technical endosulfan contains two isomers, α-endosulfan and β–endosulfan in approximately a 7:3 ratio (ca. 2.3). Endosulfans were detected at all CANCUP sites with the highest monthly average air concentrations at Kensington (α-endosulfan: 5,710 pg m^{-3}, β–endosulfan: 1,960 pg m^{-3}) (Fig. 2). The ratio of these two isomers (2.9) is close to the technical mixture, suggesting fresh application in the region during sampling.

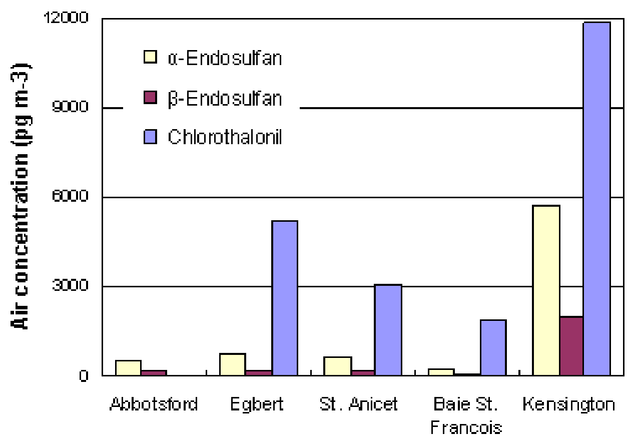

Fig. 2. Concentrations of chlorothalonil and α-/β–endosulfans in air at CANCUP sites, 2003.

Other insecticides such as chlorpyrifos, malathion and carbofuran were also detected from air samples at high levels. Chlorpyrifos was found in air across Canada with the highest level (768 pg m^{-3}) at St. Anicet, QC. Malathion was detected in British Columbia, Ontario and Québec. The highest concentration (2,500 pg m^{-3}) was measured at Abbotsford, BC. In addition, lindane (γ-HCH) was detected at all the sampling sites ranging from 10 to 92 pg m^{-3} for air samples and 0.5 to 18.2 ng L^{-1} for rainfall samples. Good correlation between air and precipitation concentrations was observed for lindane (Fig. 3). Furthermore, pyrethroids (permethrin, cypermethrins and cyfluthrins) were successfully detected in BC air samples. Several herbicides such as alachlor, metolachlor and trifluralin were detected from most of the Ontario and Québec air and rainfall samples. Ethalfluralin, dicamba and atrazine were also detected in air while linuron was only detected at St. Anicet.

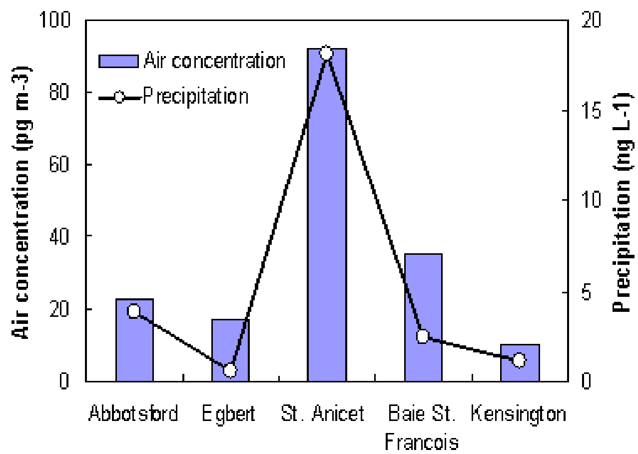

Fig. 3. Concentrations of lindane in air and precipitation at CANCUP sites, 2003.

In the Prairie Study which spanned the entire growing season, 11 target pesticides were monitored and most were detected from air samples with most frequent detections for triallate (97%), bromoxynil (95%), MCPA (93%), 2,4-D (90%), dicamba (90%) and lindane (83%). Highest concentrations were observed for triallate and probably associated with its relatively high vapour pressure[2]. Good correlations between air concentration trends and dry deposition trends were found for triallate, 2,4-D, MCPA, dicamba and bromoxynil. Figs 4-5 show the time trends of 2,4-D concentrations in air and dry deposition at Bratt's Lake and the comparison of the time trends at the 3 prairie sites. The uniformity of air concentrations with height and occurrence at all sites suggests that 2,4-D is well dispersed in the regional atmosphere. The same is true for MCPA, dicamba and bromoxynil. Despite a Canadian ban on lindane use in the prairies that became effective in 2003, lindane was still detected in air but at much lower concentrations than previous years[3]. This air burden is likely due to soil-air transfer of residual lindane.

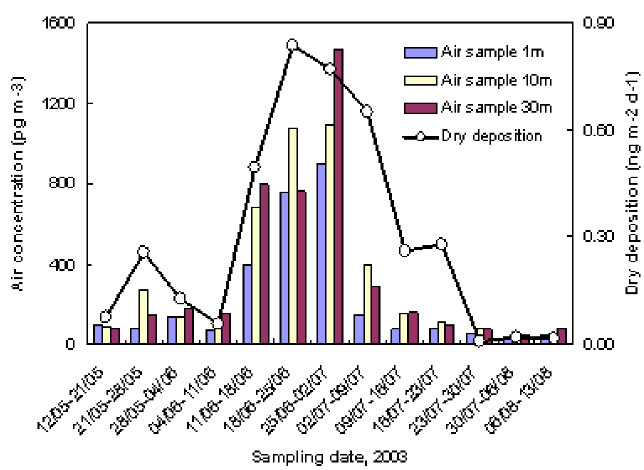

Fig. 4. Time trends of 2,4-D concentrations in air and dry deposition at Bratt's Lake, SK, 2003.

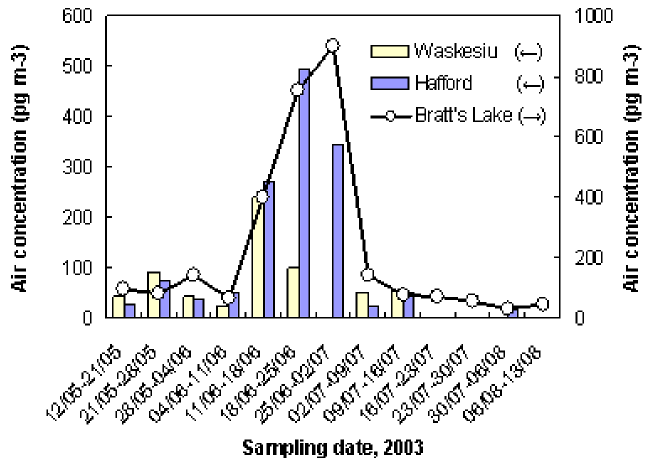

Fig. 5. Time trends of 2,4-D air concentrations at Bratt's Lake, Hafford, and Waskesiu, SK, 2003.

2004 Campaign

Sampling during 2004 was more closely linked with pesticide application times in each region. Preliminary results are available for 26 organochlorine pesticides (OCPs), 4 organophosphorous pesticides (OPPs), 8 acid herbicides, and several triazines that have been measured in active and passive air samples. Fig. 6 shows the average air concentrations of 11 OCPs. Highest OCP levels were observed at Abbotsford, BC and Vineland, ON and are probably associated with heavy past-use of OCPs in these regions. Results from the passive samplers (not shown) were similar, indicating the capability and potential of passive sampling for these compounds.

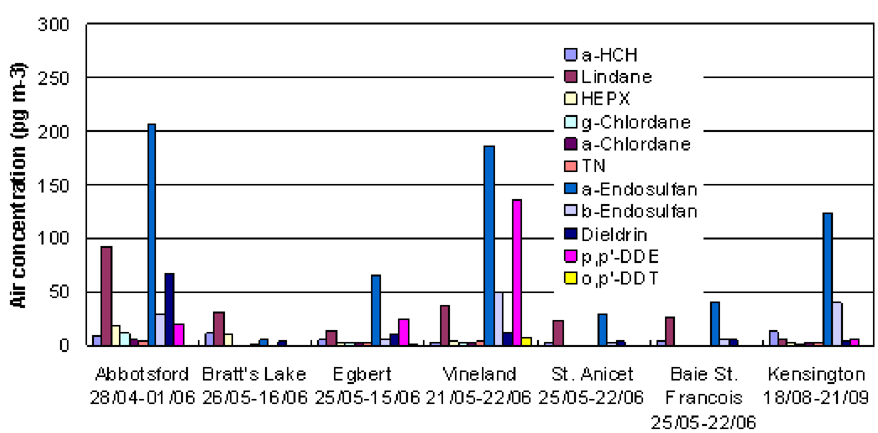

Fig. 6. Average air concentrations of OCPs across Canada, summer 2004.

As a result of air sampling under CANCUP starting earlier in the growing season in 2004, many additional pesticides were successfully detected. For OPPs, diazinon and parathion were found at high levels with average concentrations of 443,000 pg m^{-3} and 1,230 pg m^{-3} at Abbotsford and Vineland, respectively. For acid herbicides, bromoxynil, MCPA and 2,4-D were detected at most CANCUP sites. In case of triazines, atrazine was detected in BC, ON and QC samples with the highest concentration (3,500 pg m^{-3}) at St. Anicet. As expected, triallate was only detected in the Prairies with an average concentration of 3,840 pg m^{-3} at Bratt's Lake in 2004, similar to the 4,510 pg m^{-3} measured during the same period in 2003.

Emission Modeling

To address the lack of CUP usage data, emission modeling using the Simplified Gridded Pesticide Emission and Residue Model (SGPERM) is being conducted. So far, maps of total lindane usage in Canada for the past 30 years ($1/6^{o} \times 1/4^{o}$ latitude/longitude resolution), lindane emissions in North America for 2000 ($1^{o} \times 1^{o}$ latitude/longitude resolution, Fig. 7), and annual atrazine usage in Ontario for 2000 ($1/6^{o} \times 1/4^{o}$ latitude/longitude resolution) have been completed. Results for lindane emissions agree well with passive air sampler (PAS) derived air concentrations[4] over the same time period (Fig. 7).

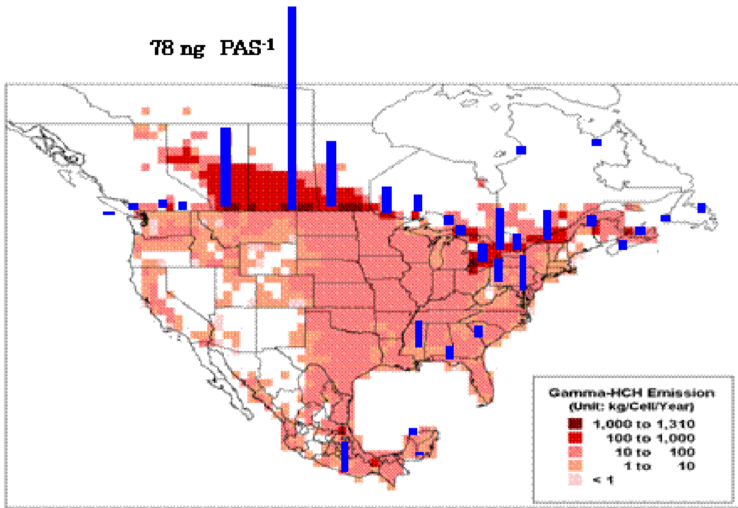

Fig. 7. Lindane emissions in North America for 2000 with $1^{o} \times 1^{o}$ latitude/longitude resolution. Overlaid bars represent passive air sampler (PAS) derived air concentrations of lindane for a 1-year deployment during 2000-2001[4].

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