

ATMOSPHERIC TRANSFER OF AGROCHEMICALS¹

GREAT LAKES WATER QUALITY INITIATIVES

Final Report

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1. RATIONALE AND OBJECTIVES

Atmospheric transport is considered to be a significant input pathway of toxic chemicals to the Great Lakes. Confidence in the measurements of vapour fluxes of agrochemicals between soil, air and water surfaces suffers from uncertainties associated with the measuring techniques. A reliable measuring technique was therefore needed to assess the impact of soil and crop management on atmospheric loading of agrochemicals.

Until recently, the only micrometeorological technique used to measure the vapour flux of agrochemicals was the aerodynamic gradient technique. Four to six measuring levels were used to determine the concentration profile. This technique required the estimation of the turbulent exchange coefficient, K , which introduced considerable uncertainties. Since agrochemical analysis is very time consuming, a measuring technique requiring fewer samples was highly desirable. The relaxed eddy-accumulation technique offered this opportunity, in addition to the fact that it was a more direct approach for measuring fluxes. It was also the only technique that could be used for regional flux measurements with an aircraft.

The objectives of this study were:

- a) To develop methods based on the eddy-accumulation technique to quantify the emission and surface deposition rates of agrochemicals and other toxic substances.
- b) To measure the atmosphere-surface exchange of agrochemicals used in the Great Lakes region using two tower-based systems having different trapping devices.
- c) To measure the atmosphere-surface exchange of agrochemicals in the Great Lakes region using an aircraft-based system.

2. METHODOLOGY

A- DEVELOPMENT OF THREE NEW FLUX MEASURING SYSTEMS

The relaxed eddy-accumulation (REA) technique is a relatively new technique to measure trace gas fluxes. It is based on the conditional sampling of updrafts and downdrafts in reservoirs for later analysis of mean concentration. By using fast-response sampling valves, it avoids the need for a fast-response trace gas analyzer required for the eddy-correlation technique (EC).

$$F_C = A s_w (\overline{\rho_C^+} - \overline{\rho_C^-}) \quad (1)$$

In the REA technique (Businger and Oncley, 1990), the flux of a gas (F_C , $\mu\text{g m}^{-2} \text{s}^{-1}$) is expressed as the product of an empirical coefficient (A), the standard deviation of the vertical wind velocity (s_w , m s^{-1}) and the difference in the mean concentration of the gas (ρ_C , $\mu\text{g m}^{-3}$) associated with updrafts and downdrafts:

where the plus and the minus signs denote updrafts and downdrafts, respectively, and overbar denotes the mean value over the sampling period. The coefficient "A" can be calculated for each period using simultaneous computation of either evaporation rate or carbon dioxide flux by EC and REA (Pattey *et al.*, 1993). Technical difficulties have limited the number of experimental results obtained using the REA technique (MacPherson and Desjardins, 1991; Baker *et al.*, 1992; Majewski *et al.*, 1993, Oncley *et al.*, 1993). However, recent field experiments carried out by Pattey *et al.* (1993) have demonstrated a system which showed an excellent agreement between CO_2 fluxes measured by the EC and the REA techniques. This trace gas measuring system is using bags as reservoirs and cannot be used to collect pesticides.

Agrochemicals need to be adsorbed on a trapping medium prior to analysis by gas chromatography. The selection of a trapping medium for specific agrochemicals depends on its trapping and recovery efficiency. Polyurethane foam plugs (PUF) have been successfully used to collect trifluralin and triallate due to their high trapping efficiency (Turner and Glotfelty, 1977). They permit high flow rates during sampling, compared to solid particulate sorbents but they need extensive solvent cleaning, before sampling. The recovery of pesticides is done by solvent desorption (Cessna and Kerr, 1993). Resins can also be used to adsorb agrochemicals, which can be thermally desorbed before quantification on a gas chromatograph. Two tower-based systems were developed, one using PUF and the other one using mini-tubes filled with Tenax-TA as trapping media.

The tower-based systems were developed and tested through several field experiments:



* Fall 1989: Description in Majewski *et al.* (1993).

Comparison of a REA system with an aerodynamic-gradient system, both employing polyurethane foam plugs to trap trifluralin and triallate.

* Summers 1991 & 1992: Description in Pattey *et al.*, (1992, 1993).

Development of software to control the conditional sampling system and to compute fluxes. Evaluation of some corrections involved in the calculation of agrochemical fluxes and of the accuracy of the REA technique compared to the EC technique. Several improvements have been incorporated into the REA measuring system that was used in the fall 1989 herbicide flux experiment (Majewski *et al.*, 1993). These include digital filtering of the vertical wind velocity (W), reduced delays for controlling valves, heated inlet teflon tubes, and development of a stand-by position. In addition, computation, sampling valve control and trapping media selection have all been automated.

* Summer 1992: Description in Cessna and Kerr, (1993).

Evaluation of the trapping and recovery efficiency of the mini-tube (MT) technology (Canadian Centre for Advanced Instrumentation, Saskatoon, Sask., Canada) which used Tenax-TA sorbent for collecting trifluralin and triallate. The mini-tube technology includes the mini-tube samplers and an automated thermal desorption unit (ATDU) developed in cooperation with industry.

* Fall 1992: Description in Pattey *et al.*, (1994).

Development of two REA systems for measuring agrochemical fluxes one using PUF and the other one using MT filled with Tenax-TA. Comparison of the two REA systems carried out in the field by trapping trifluralin and triallate. The PUF medium requires more time and effort to perform the extraction and to concentrate the extract prior to gas chromatography (GC) analysis, whereas the MT technology allows for direct analysis of the entire sample by coupling a thermal desorption unit to a GC.

The third measuring system was developed for an aircraft. It requires high flow rate capabilities and it was tested over four experimental seasons:

* Summers 1990 & 1991: Description in MacPherson and Desjardins (1991).

Adaptation of the data acquisition software to operate the conditional sampling and to compute fluxes. Comparison of the REA technique with the EC technique, based on CO₂ flux measurements by flying over forests near Ottawa and from Moosonee to Ottawa.

* Summers 1992 & 1993.

The Twin Otter of the Flight Research Laboratory (National Research Council of Canada) was used for the flux measurements. It is instrumented to measure the three orthogonal components of atmospheric motion over a frequency range from 0 to 5 Hz. The wind computation methods and a description of the data acquisition system is given by MacPherson (1990). Vertical wind velocity, computed in real time, is used to control three solenoid valves that divert air through one of two herbicide absorbers depending on the direction of W , or directly to the pump when $-0.1 < W < 0.1 \text{ ms}^{-1}$. Air flows through a large duct at 45 m s^{-1} and is then passed through a PUF plug at a rate of 646 L min^{-1} . The PUF plugs (6-cm diameter, 2.5-cm high), which are used to trap agrochemicals, were inserted in commercially available glass cartridges (Andersen Samplers inc., Atlanta, Georgia). During sampling, the cartridges were inserted into an aluminum holder connected to the sampling channels. After sampling, the cartridges were unloaded immediately and the PUF plugs were placed in clean sample jars and refrigerated. They were covered with thick aluminum foil to protect them from photodegradation. The samples were stored at approximately $-5 \text{ }^\circ\text{C}$ until analyzed.

B- MEASUREMENT OF AGROCHEMICAL VAPOUR FLUX UNDER FIELD CONDITIONS.

The vapour flux of herbicides were measured during several field experiments. These experiments were carried out at Agriculture Canada's Greenbelt farm in Ottawa on soils similar to those of the Great Lakes area. Thus, the results obtained in Ottawa should be directly applicable to the Great Lakes basin.

* Fall 1989: Majewski *et al.* (1993).

The experiment was carried out between September 20th and 25th 1989 on a 20-ha field. The soil type was Dalhousie clay. A 150-m-radius circular plot (7.1 ha), approximately in the centre of the field, was treated with trifluralin and triallate at rates of 2.66 and 3.37 kg ha^{-1} , respectively. These compounds were chosen because of their very high volatility potential based on their vapour pressures. Moreover, trifluralin is commonly used in the Great Lakes region. The herbicides were sprayed on the surface as an aqueous emulsion and not incorporated into the soil as is the usual practice in order to test the trapping media with a wider range of vapor fluxes. Air and soil samples were analyzed for herbicides on a gas chromatograph equipped with an electron capture detector.

* Fall 1992: Pattey *et al.*, (1994).



The field sampling was performed from September 24th to 28th 1992. The experiment was carried out on a 29-ha fine sandy loam field (North Gower). A 150-m-radius circular plot was sprayed with an aqueous emulsion of trifluralin and triallate at rates of 1.15 and 1.70 kg a.i. ha⁻¹, respectively. The physical properties of the herbicides are reported in Jury *et al.* (1983). The circular area was used to ensure the same fetch irrespective of the wind direction. Again, the herbicides were not soil-incorporated as recommended in order to compare the results with a previous experiment (Majewski *et al.*, 1993). The soil was a loam (45.3% sand, 16.7% clay and 38.0% silt; 2.36% organic matter) and had a pH of 6.1.

* Spring and Summer 1993.

The field sampling lasted from June 4th to 11th and from July 6th to the 18th 1993. The experiment was carried out on a 22-ha loam field. Metolachlor and metribuzin were selected because they are used in the Great Lakes area and they are recommended for soybean and corn in preplanting. They were analyzed with a Nitrogen-Phosphorus detector on a gas chromatograph. The two herbicides were sprayed simultaneously to the surface as an aqueous emulsion at a rate of 0.5 a.i. kg/ha for metribuzin and 2.4 a.i. kg/ha for metolachlor. The herbicides were incorporated as is the usual practice at a depth of 5 to 7.5 cm, right after being sprayed on the bare soil. The soil was a loam (41.7% sand, 26.8% clay and 31.6% silt; 1.9% organic matter) and had a pH of 5.9.

Herbicide concentrations in soil were determined in order to establish the mass balance of herbicides and to determine the fraction of herbicides available for volatilization. The field was divided into 6 sectors (at directions 0°, 60°, 120°, 180°, 240°, 300° from the North), each sector was split into three (radii of 25, 75, 125 m), giving 18 sites. For each site, ten closely spaced cores of soil with depth up to 27 cm (2.5 cm diameter) were sampled. This depth should include all the herbicides in the soil, for calculating the mass balance of the herbicides. To quantify the herbicide amount available for volatilization, soil samples taken on 23 June were split into three pieces along their depth (0-2.5 cm, 2.5-10 cm, 10-27 cm) to determine the herbicide concentration profile. The samples were collected into clean glass jars and transported to the laboratory. Stones and organic materials were removed. The soil samples were mixed thoroughly and subsampled with a sample splitter and were either analyzed immediately or stored in freezer at -20°C.

C- ESTIMATION OF REGIONAL ATMOSPHERE-SURFACE EXCHANGE OF AGROCHEMICALS IN THE GREAT LAKES REGION

* Summer 1993.

Regional flux measurements of atrazine and metolachlor were obtained at an altitude of 150 m along two transects of approximately 400 km between Ottawa and London (Ontario).

The PUF plugs collected during the conditional sampling were warmed to room temperature and then Soxhlet-extracted with 600 mL of hexane (glass distilled grade, Caledon) for 24 h. The Soxhlet extracts were concentrated to 2 mL with a rotary evaporator, then cleaned and fractionated with florisil columns (8 g florisil for each column). Four organic solvents were used to elute herbicides from florisil columns: 1) 38 mL hexane; 2) 37 mL 15% dichloromethane (DCM) in hexane, 3) 40 mL 60% DCM in hexane and 40 mL DCM; 4) 50 mL acetone. The elutes were concentrated to 2 mL with the rotary evaporator and were brought to 1 mL with the nitrogen flow evaporator. The herbicides in the samples were identified with a GC-MS (HP) of the AES, Environment Canada. A DB-5 column (30 m, 320 μm) was used in the GC-MS.

Quantification of the herbicides in the florisil elutes was conducted on a GC (Varian 3600) equipped with a thermionic selective detector (TSD) and a DB-5 column (30 m, 530 μm). The carrier gas (Helium UHP) flow rate was 8 mL min⁻¹ and the detector make-up gas (Helium UHP) flow rate was 22 mL min⁻¹. For the TSD, the flow rate of air was 175 mL min⁻¹, and 4 mL min⁻¹ for hydrogen. Since herbicide concentrations of the sample were very low (<5 pg μL^{-1} for metolachlor), mini-tubes were fortified with the herbicide extracts and thermodesorbed by the ATDU in order to concentrate the samples of herbicides injected into the GC. The sensitivity of the system could be increased up to 50 times by using the ATDU. The column oven temperature program of the GC system was as follows: 70°C for 16 min, then 10°C min⁻¹ to 250°C, and hold for 5 min.

3. FINDINGS

A- DEVELOPMENT OF THREE NEW FLUX MEASURING SYSTEMS

The relaxed eddy accumulation technique was demonstrated to be an excellent technique to measure the flux of agrochemicals using both tower- and aircraft-based systems. The following technical details were found:

- The vertical wind velocity has to be filtered in real-time to remove any bias over the averaging period before activating the valves involved in the conditional sampling (MacPherson and Desjardins, 1991; Pattey *et al.*, 1993).
- The time lag between the sign change of the vertical wind velocity and the effective conditional sampling of air has to be kept as short as possible (Pattey *et al.*, 1993).



-The empirical coefficient, in the REA technique, can be calculated from either temperature or water vapour signals (Pattey *et al.*, 1993).

-A deadband on the vertical wind velocity can be used to increase the difference in agrochemical concentration between the updraft and downdraft if its normalized value does not exceed ± 0.2 (Pattey *et al.*, 1993).

-In most situations, the agrochemical vapour fluxes do not need to be corrected for air density fluctuations (Pattey *et al.*, 1992).

-In order to minimize deposition of agrochemicals on the tubing of the conditional sampler the inlet tube needs to be heated at 75°C (Pattey *et al.*, 1994).

-The mini-tube filled with resin needs to have a continuous flow rate for use in a conditional sampler (Pattey *et al.*, 1994).

-The background peaks of thermally conditioned mini-tubes increased somewhat after 8 weeks of storage at room temperature in a carousel wrapped in aluminium foil (Cessna and Kerr, 1993).

-For quantitation of small amounts of agrochemicals using mini-tubes, the time intervals between thermal conditioning and air sampling and analysis should be kept as short as possible (Cessna and Kerr, 1993).

-Cross-contamination was minimal between mini-tubes stored at room temperature for two weeks in a carousel wrapped in aluminium foil (Cessna and Kerr, 1993).

-Relative humidity had little effect on the breakthrough of trifluralin or triallate through the Tenax-TA resin (Cessna and Kerr, 1993).

-Since all the analytes trapped on a mini-tube are thermally desorbed onto the GC column, sensitivity was enhanced compared to the PUF plug analytical procedure (Cessna and Kerr, 1993).

-The mini-tube sampling system was more sensitive to adsorption/desorption effects than the PUF plug system (Cessna and Kerr, 1993).



-Because the herbicide concentrations of the aircraft-based samples were relatively low (approximately 5 pg/uL for metolachlor), an automatic thermal desorption unit (ATDU) was used to increase the amount of herbicide injected into the GC. With the ATDU, it was possible to increase the sensitivity of the analysis by up to 50 times.

B- MEASUREMENT OF AGROCHEMICAL VAPOUR FLUX UNDER FIELD CONDITIONS.

* Fall 1989.

OBJECTIVE: To measure the vapour fluxes of triallate (3.37 kg a.i./ha) and trifluralin (2.66 kg a.i./ha) applied at high rates and not incorporated in the soil. (Majewski *et al.*, 1993)

-The highest herbicide vapour fluxes were observed during the first 4 hours after spraying and after the first hours of rain.

-Trifluralin and triallate had a similar pattern of volatilization.

-Diurnal pattern of volatilization tended to follow the moisture content of the top layer of the soil.

-The dissipation of herbicides in soil followed a log-linear relationship. The soil half-lives were 9.8 days for triallate and 7.0 days for trifluralin.

* Fall 1992

OBJECTIVE: To measure the vapour fluxes of triallate (1.70 kg a.i./ha) and trifluralin (1.15 kg a.i./ha) applied at recommended rates but not incorporated in the soil. (Pattey *et al.*, 1994)

-Herbicide vapour fluxes were highly synchronized with latent heat fluxes, but regulated by the dryness of the soil surface.

-Maximum fluxes occurred on the day of herbicide application and were $0.64 \mu\text{g m}^{-2} \text{s}^{-1}$ for trifluralin and $0.86 \mu\text{g m}^{-2} \text{s}^{-1}$ for triallate, which represents about 10% of the amount applied. If the herbicides had been incorporated, the vapour flux losses on the first day would have been about 2 to 3%.

-Fluxes on the day after spraying were approximately three times less than the previous day.

-Soil analyses indicated that the total herbicide dissipation over the experiment exceeded the cumulative vapour losses for both herbicides. The difference is explained by the removal of straw residues from the soil samples and by the photodegradation susceptibility of trifluralin.

* Spring and summer 1993.

OBJECTIVE: To measure the vapour fluxes of two herbicides used in the Great Lakes region: metolachlor and metribuzin incorporated into the soil, for two separate periods (in June and July).

-Vapour fluxes of metolachlor were most of the time below $10 \text{ ng m}^{-2} \text{ s}^{-1}$, with maximum values close to $30 \text{ ng m}^{-2} \text{ s}^{-1}$, when soil surface was wet. Metribuzin showed vapour fluxes below $1 \text{ ng m}^{-2} \text{ s}^{-1}$ and was very difficult to detect. The cumulative volatilization represented less than 1% of what was applied.

-The volatilization lasted for an extensive period of time and was driven by latent heat flux and soil moisture content at the surface.

-Metribuzin volatilization losses were minimal. The concentrations were too low most of the time and occasionally the GC analysis showed interference from another compound.

-The tower-based system was capable of measuring very small fluxes; 100 times smaller than those of fall 1992.

OBJECTIVE: 1) To establish the mass balance of herbicides and 2) to determine the fraction of herbicides available for volatilization.

-During the first 33 days, the first order decay rate of extractable metribuzin was $0.44 \text{ mg m}^{-2} \text{ d}^{-1}$; the decay of extractable metolachlor was higher order, and it averaged to $1.50 \text{ mg m}^{-2} \text{ d}^{-1}$.

-19 days after spraying, metribuzin concentration in the top layer of soil (0-2.5 cm) accounted for 56% of the total amount remaining in the soil, while metolachlor in the top layer accounted for 60%.

-Between 19 and 47 days after spraying, extractable metribuzin in the top layer decayed from 3.4 to 2.1 mg m⁻², at a rate of 0.011 mg m⁻² d⁻¹, while extractable metolachlor in the top layer decayed from 50 to 34 mg m⁻², at a rate of 0.57 mg m⁻² d⁻¹.

C- ESTIMATION OF REGIONAL ATMOSPHERE-SURFACE EXCHANGE OF AGROCHEMICALS IN THE GREAT LAKES REGION

* Summer 1993.

OBJECTIVE: To measure the emission or deposition of atrazine and metolachlor over the Great Lakes region.

-With 7 to 10 m³ of air passing through both PUFs, measurable concentrations and fluxes of atrazine and metolachlor were obtained from the aircraft-based samples. These samples were collected at 150 m above agricultural and non-agricultural regions in Ontario. A greater volume of air would be required to cumulate measurable concentrations of EPTC, butylate and trifluralin which were detected with the ground-based systems at Point Petre and Egbert. This could be achieved by either sampling for longer periods or increasing the sampling rate.

-The large variation of concentrations and fluxes of atrazine indicates a strong local influence for this chemical. Metolachlor, which has a much higher vapour pressure than atrazine, can persist in the air much longer than atrazine. The small variation of its concentration along various flight paths indicates that the local influence is of minor importance and that metolachlor is well mixed in the atmosphere and transported long distances (Zhu *et al.*, 1994).

4. STUDY CONCLUSIONS

A- DEVELOPMENT OF THREE NEW FLUX MEASURING SYSTEMS

Three new systems for measuring the exchange of agrochemicals above land surfaces were developed: two tower-based systems for field-scale measurements and an aircraft-based system for estimation of regional fluxes. These systems are based on the relaxed eddy-accumulation technique. The advantages of this technique are the following:

- It is based on a sound theoretical basis;
- In the case of the tower-based system, it requires air sampling at only one level as opposed to 4 to 6 levels with the more traditional aerodynamic gradient technique, thereby considerably reducing the need for laboratory analysis;
- In the case of the aircraft-based system, it is the only technique that can be used for flux measurements of agrochemicals.

The tower-based system was developed and tested through several field experiments:

* Fall 1989.

OBJECTIVE: Test of a REA system prototype and comparison of results from this new system to results from existing techniques.

- i) Herbicide vapour fluxes measured by REA system were lower than those measured by the gradient technique;
- ii) Design problems were identified such as slow valve controlling system and deposition of chemicals on tubing walls.

* Summer 1991.

OBJECTIVE: Test of the REA technique for the measurement of carbon dioxide fluxes.

- i) The measurements of CO₂ fluxes by REA compared well with the eddy-correlation technique. This was an independent validation of the accuracy of REA for the measurement of gas fluxes.
- ii) The REA sampling system could be modified to measure the flux of agrochemicals.

* Fall 1992.

OBJECTIVE: Tests of a new device for trapping agrochemicals in air samples were carried out.

- i) Use of mini-tubes filled with Tenax-TA resin considerably shortened the time for the determination of chemical concentration in air samples and increased the accuracy of the analysis.

- ii) The deposition of chemicals on the tubing walls had a strong impact on flux calculations because of the low flow rates through the mini-tubes (caused by higher resistance to air flow). Improved heating system of inlet tubing walls solved this problem.

The aircraft-based system was developed and tested during several test flights.

* Summers 1990 & 1991.

OBJECTIVE: Theoretical validation of the aircraft-based REA.

- i) CO₂ fluxes calculated by REA and eddy correlation using fast-response analyzer data were in close agreement.

* Summers 1992 & 1993.

OBJECTIVE: Test of an aircraft-based REA system prototype.

- i) Measurements of low background concentration of agrochemicals in the lower troposphere indicated that very high sampling flow rates were needed for aircraft-based REA system.

- ii) A high-volume sampler (646 L min⁻¹) was able to collect measurable quantities of atrazine and metolachlor at 150 m above agricultural regions during flights lasting approximately one hour.

B- MEASUREMENT OF AGROCHEMICAL VAPOUR FLUX UNDER FIELD CONDITIONS.

Vapour fluxes of herbicides were measured during several field experiments:

* Fall 1989.

OBJECTIVE: To measure the vapour fluxes of triallate (3.37 kg a.i./ha) and trifluralin (2.66 kg a.i./ha) applied at high rates and not incorporated in the soil.

i) Highest vapour fluxes occurred just after spraying and after rainfall. Smaller peaks coincided with dew evaporation.

ii) After 24 hours, 11 and 15% of the applied triallate and trifluralin were volatilized, and after four days, the volatilization losses accounted for 30% of the applied chemicals.

iii) The measurements were used to evaluate the results obtained by the air-soil exchange model of Scholtz and Voldner (1992, 1993).

* Fall 1992

OBJECTIVE: To measure the vapour fluxes of triallate (1.70 kg a.i./ha) and trifluralin (1.15 kg a.i./ha) applied at recommended rates but not incorporated in the soil.

i) After 24 hours, 10 and 9% of the applied triallate and trifluralin were volatilized, and after four days, the volatilization losses accounted for 21 and 13% of the applied chemicals.

ii) The measurements were compared to the results obtained by the air-soil exchange model of Scholtz *et al.*, (1994) and they agreed reasonably well.

* Spring and summer 1993.

OBJECTIVE: To measure the vapour fluxes of two herbicides used in the Great Lakes region: metolachlor and metribuzin incorporated in the soil, for two separate periods (in June and July).

i) Vapour fluxes were small but persisted long after the application. However, the cumulative losses represented less than 1% of the applied amount.

ii) Difficulties were encountered for detecting metribuzin concentrations.

iii) The capability of our tower-based systems to measure very small fluxes was successfully tested in this experiment.

C- ESTIMATION OF REGIONAL ATMOSPHERE-SURFACE EXCHANGE OF AGROCHEMICALS IN THE GREAT LAKES REGION

* Summer 1993.

OBJECTIVE: To measure the emission or deposition of atrazine and metolachlor over the Great Lakes region.

i) The results from a return flight between Ottawa and London, Ontario demonstrated that the aircraft-based sampling system can be used to quantify regional fluxes of agrochemicals. Metolachlor and atrazine, the two herbicides used in largest quantities in Ontario, were found in all samples except one. The concentration of atrazine was higher than that of metalochlor and the concentrations of both chemicals were higher over the more intensive agricultural areas. An upward flux was observed over intensive agricultural areas and a downward flux over less intensive areas (Zhu *et al.*, 1994).

ii) A test flight was also done over Lake Ontario but because of the smaller vertical wind over the lake that day (more than 82% of the time) the sampler was in the deadband region, where no sample is collected. Therefore, less than 1 m³ of upward and downward moving air was collected by each PUF plug and no chemicals were detected in this relatively small volume of air. In the future the deadband region should be considerably smaller over a lake.

iii) These aircraft-based results are based on a very limited data set. More measurements of this type are required to evaluate the technique more fully.

5. NEW TECHNOLOGIES AND BENEFITS

Many new technologies have been developed. Three new systems for measuring the air surface exchange of agrochemicals were developed: two tower-based systems for field-scale measurements and an aircraft-based system for estimation of regional fluxes. These systems are based on the relaxed eddy-accumulation technique. A new thermal desorption unit, developed with industry, was shown to simplify the analysis of agrochemicals and improve the accuracy of the measurements considerably.

These new technologies provide a better knowledge of the magnitude of the exchange of agrochemicals between agricultural lands and the atmosphere. Previously accurate measurements of such vapour fluxes under field conditions were lacking. The new measuring systems developed in this project provide the scientific community with a much needed tool for quantifying the volatilization of agrochemicals under field conditions. Volatilization subroutines in models simulating the fate of agrochemicals in the environment can now be validated.

The measurement of the volatilization of agrochemicals under a wide range of conditions has the potential to provide the guidelines for selecting the management practices which minimize atmospheric contamination.

6. IMPLICATIONS FOR THE GREAT LAKES ECOSYSTEM

A- VOLATILIZATION LOSSES OF AGROCHEMICALS

Volatilization losses of agrochemicals from agricultural fields are transported in the atmosphere and deposited elsewhere. The study of the impact of atmospheric transfer of agrochemicals on the Great Lakes ecosystem cannot, therefore, be limited to the Great Lakes basin since the amount of agrochemicals deposited is dependent on the amount that was emitted.

Measuring the losses from all individual sources (fields) is impossible. However, measurements of the volatilization of the most important substances under a wide range of agricultural management practices are needed in order to:

- i) validate simulation models that can later be used for obtaining large area emission estimates;
- ii) select management strategies which minimize atmospheric contamination.

The tower-based measuring systems that were developed in this project are the first systems based on the REA approach.

With the new REA measuring systems, the volatilization losses of four herbicides were measured after their field application. The soil texture and structure on which the experiments were carried out are similar to those of the Great Lakes basin. These results were successfully used to validate model estimates of vapour fluxes.

B- ATMOSPHERIC DEPOSITION OF AGROCHEMICALS

The atmospheric deposition of agrochemicals into the Great Lakes basin is affected by several factors such as the atmospheric concentration of agrochemicals, the atmospheric conditions, and the surface conditions. These factors are highly variable resulting in a large spatial variability of the deposition rates. Regional estimates of the atmospheric deposition rates can be best obtain using aircraft-based measurement techniques which integrate local variability. REA is the only technique that can be used for flux measurements of agrochemicals using an aircraft-based system because of the lack of fast-response analyzer for most substances and the fact that observations at one level preclude the use of gradient techniques.

In this project, an aircraft-based REA system was developed and measurements obtained for the first time. This new measuring facility represents important progress in our capability for measuring regional exchange of agrochemicals. However, the difficulties encountered in the development process were significant and the resulting delays prevented us from carrying out as many field experiments in the Great Lakes area as had been originally planned.

7. TECHNOLOGY TRANSFER POTENTIAL

The relaxed eddy-accumulation technique is now well known within the micrometeorological community. The real challenge for anyone who wants to use REA is to build a measuring system that respects the principles of the technique and that performs reliably. The systems that we developed are unique for the measurement of volatile compounds for which no real-time gas analyzer exists. The air samples are trapped in either Tenax-TA resin or polyurethane foam which are later analyzed in the laboratory. After three years of improvements, we have now reached a degree of reliability and automation which, we believe, makes it attractive for commercial development. We have developed programs to automate the measurements of the flux of agrochemicals over a wide range of scales. The analysis system of the mini-tube is now available commercially and we collaborated with the Canadian Centre for Advanced Instrumentation, to improve their mini-tube technology.

8. GAPS/NEEDS FOR FUTURE RESEARCH

- More measurements of the exchange rates of agrochemicals above agricultural fields are needed i) to develop and validate simulation models of the volatilization of agrochemicals and ii) to make recommendations to reduce the atmospheric contamination by agrochemicals.
- Measurements of the volatilization of the most frequently used substances under a wide range of agricultural management practices are needed at the scale of a field (mostly for pesticides applied on crop canopies), to make recommendations for remedial actions.
- A tower-based system should be run in the Great Lakes region to monitor the agrochemical deposition over selected areas during intensive application periods, in order to quantify the sources.
- Aircraft-based flux measurements should be carried out above and around the Great Lakes in order to quantify the fluxes (emission and deposition) of agrochemicals as a function of land use. There is a great need to have such data to evaluate regional and long-range transport models, which are used to quantify the contribution of agricultural activities to the contamination of the Great Lakes basin.
- Systems with higher sampling rates and improvement in the agrochemical determination are required for more accurate measurements of background level deposition with both the tower- and aircraft-based systems.

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