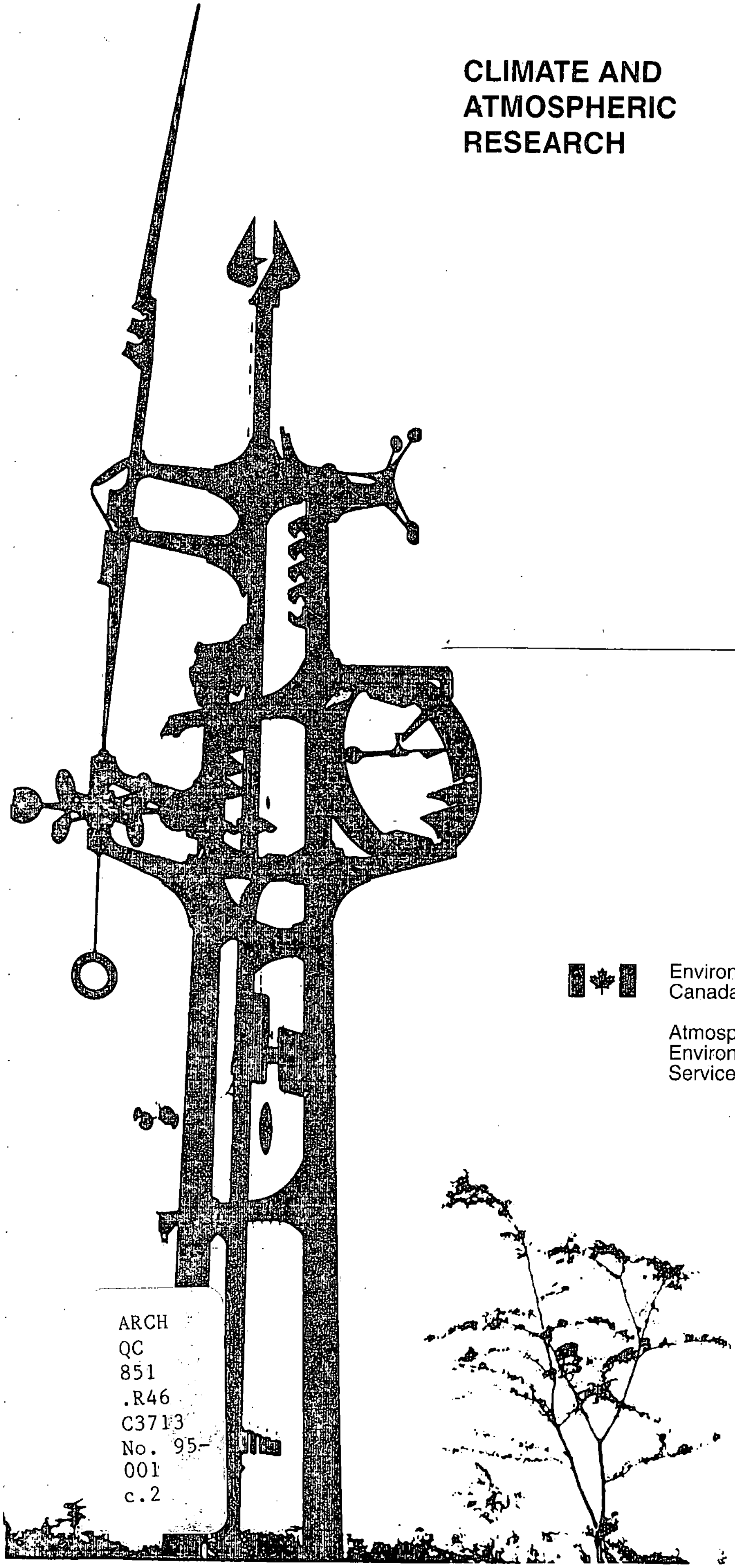


CLIMATE AND ATMOSPHERIC RESEARCH

RECHERCHE ATMOSPHÉRIQUE ET CLIMATIQUE

Environment Canada
Atmospheric Environment Service

Environnement Canada
Service de l'environnement atmosphérique

CARD Report No. CARD-95-001

AIR TOXICS PROGRAM

October 1994

INDEX

INTRODUCTION

Ann C. McMillan

The Air Toxics Program represents, perhaps, the dark horse among the issues dealt with by the Atmospheric Environment Program. Whether they are grouped as heavy metals, organochlorines (OC's), persistent organic pollutants (POPs) or hazardous air pollutants (HAPs), there are a group of substances present in the environment that are being shown to affect human and ecosystem health even in trace amounts. These substances are characterized by a number of properties:

- they are persistent in the environment;
- they bioaccumulate;
- commonly exposure to them is greatest through food consumption;
- they are transported, sometimes on global scales, by the atmosphere; and
- evidence is mounting that they cause effects ranging from neurological changes to estrogenetic effects to cancer.

The Air Toxics Program has become a national effort with programs underway in the Regions as well as at AES/Downsview. This research supports the Regional Flagship Ecosystem Programs, the Arctic Environmental Strategy, the development of related policies, the development of as national HAPs program under the CCME and associated international programs including the proposed development of a protocol on Persistent Organic Pollutants by the UN-ECE. In addition to carrying out measurements of these chemicals in the atmosphere and associated research on sampling and analysis, the research program continues to explore exchange processes between air and water and air and soil. Understanding these processes is essential if we are to be able to accurately describe and assess the movement of these chemicals in the environment. Finally a program of air toxics modelling is under development. In addition to modelling the processes involved with chemical transport, models at all scales are beginning to be applied to a variety of air toxics problems.

Perhaps the finest interdisciplinary research team in the world has been assembled and developed within this Canadian program. Currently resource limitations are having major impacts on the program of this group. Although various schedules are slipping and we are likely to lose our leadership position in this program over the next little while, the following report attests to the drive and dedication of the scientists who have produced some of the new knowledge we require to develop more effective ways of managing chemicals in our environment.

PACIFIC REGION: 1993 MONITORING PROGRAM - PRELIMINARY REPORT

Wayne Belzer

PSL Toxics

Sampling was performed at four sites within the GVRD area. Samples were taken for PCBs, PAHs, phthalate esters (PEs) and for metals. Samples were taken in the summer of 1993.

The data are in the analyses stage, but should be completed soon. Initial results again show that PCBs are not a problem in the GVRD area. Metals continue to be low in airborne concentrations. PAHs are at levels similar to those monitored in previous years. The data for phthalate esters was inconclusive. As this was the first time they have been sampled, there were problems with blanks and laboratory procedures. However, some of the data appears to be useful.

A continuation of this sampling program is proposed for the winter of 1994/95.

Dioxins and Furans

A joint sampling program with Health Canada was done at Campbell River, B.C. to measure dioxins, furans and PAHs in ambient air. Emissions were from hog fuel fired boilers. Data is currently being evaluated.

PRAIRIE & NORTHERN REGION: JASPER WOOD SMOKE STUDY

Renata Bailey, Air Issues Team

A joint preliminary study between Canadian Heritage, Parks Canada of Jasper National Park and Environment Canada, Air Issues Team of Prairie and Northern Region on the effects of wood smoke in the Whistlers Campground of Jasper National Park ran from September 9, 1992 to October 18, 1992. Due to the high levels of wood smoke in the Whistlers Campground during 1992 the study was extended for the period from May 7, 1993 to October 11, 1993. The preliminary study showed an average value of 104.6$\mu g/m^3$ and a maximum value of 252.6$\mu g/m^3$ for total suspended particulate with 47.4% of days sampled in 1992 over the acceptable level of 120$\mu g/m^3$. In order to reduce the amount of wood burned in the Campgrounds, Parks Canada of Jasper National Park initiated the selling of wood in 1993 in the Whistlers and Wapiti Campgrounds. During the 1993 camping season wood was sol.d by SBC Firemaster in the Whistlers and Wapiti Campgrounds of Jasper National Park. During this period average levels of total suspended particulate were 19.4$\mu g/m^3$ with a maximum of 89.5$\mu g/m^3$ and there were no days over the acceptable level of 120$\mu g/m^3$ for a 24-hour average sample. Average particulate levels in 1993 dropped 81.5% from those measured in 1992 in the Whistlers Campground.

Analysis of polycyclic aromatic hydrocarbons (PAHs) by Atmospheric Environment Service, Downsview, showed high levels of PAHs, particularly indeno(1,2,3-cd) pyrene, benzo(b)fluoranthene and benzo(a)pyrene, even though particular levels had dropped significantly (20-40$\mu g/m^3$). These levels of PAHs have been observed in other areas such as Whitehorse, but only during wood smoke episodes where levels of particulate are > 120$\mu g/m^3$. The relative distribution of the individual PAHs in Jasper National Park samples was also found to be different than other areas with high levels of wood smoke suggesting that other sources may be contributing to PAH loading in the atmosphere of Jasper National Park. No background samples, or samples from other potential source regions were taken for particular PAH analysis,m and consequently the contribution of wood smoke to PAH loading could not be estimated. An executive report and more detailed technical report summarizing the results of the first two years of the study are available on request from Renata Bailey of Air Issues Team in Prairie and Northern Region (403) 951-8626. Other publications include:

Renata Bailey and Allan Stendie, Should Campgrounds have Campfires?, Research Links, Canadian Parks Service, Western Region, Vol. 1, No. 1, 1993, pg. 3 and 7.

Renata Bailey, Wood Smoke Particulate Levels in the Whistler's Campground of Jasper National Park, Clean Air Views, Alberta Lung Association, Vol. 3, Issue 1, April 1994.

In order to ensure that the wood selling initiative is maintaining levels of PM10 below 50$\mu g/m^3$ in Whistlers Campground, sampling for PM10 took place in the 1994 camping season from August 24 to October 12. This sampling also only took place in the late afternoon-evening period as it was determined from the Whistlers Campground Survey in 1993 that the majority of wood burning takes place after 4:00 pm.

The study was also expanding in 1994/95 to include sampling of polycyclic aromatic hydrocarbons in the Jasper-Hinton area and is a joint effort of Air

Issues Team in Prairie and Northern Region, Parks Canada Jasper National Park, and Atmospheric Environment Service in Downsview. Sampling will take place in the January-March period of 1995 and sample analysis will be done by Chemistry Division, Environmental Technology Centre in Ottawa. Some of the samples taken during the 1994 camping season will also be analyzed for PAHs.

PAH, PCDD/PCDF sampling will also be taking place over the next year at a number of sites in the Prairies through the semi-volatile organics monitoring program lead by Tom Dann, Pollution Measurement Division, Environment Protection, Ottawa. Similar methods will be used for PAH sampling for the Jasper Wood Smoke Stud and are being coordinated with Tom Dann.

Karen McDonald of the Air Issues Team in Prairie and Northern Region will be joining the HCH Modelling Group (L. Barrie lead) to provide chemical modelling expertise on the air-surface exchange processes and atmospheric transformations in an attempt to model the temporal distributions and fate of an annual fresh pulse of HCH emissions on the 1992 global background.

Renata Bailey of the Air Issues Team in Prairie and Northern Region is a member of the Northern Contaminants Air Monitoring Group (L. Barrie lead). A paper examining the first six months of data for PCCs (toxaphene) at Tagish in comparison to observations at Alert for the same time period is available. The changes in air concentrations were related to air trajectory analysis which shows periods of relatively high concentrations of PCCs at Tagish have been associated with air masses that originate over western United States.

Bailey, R., L. Barrie, D. Dougherty, P. Fellin, B. Grift, D. Muir and D. Toom, 1994, Preliminary measurements of PCCs in air at Tagish, Yukon, Proceedings of the Yukon Contaminants Committee Workshop, Feb. 1994, Whitehorse, Yukon.

QUEBEC REGION:

ATMOSPHERIC CONTRIBUTION TO THE ST. LAWRENCE RIVER POLLUTION (On-Going Research)

Laurier Poissant, Jean-Francois Koprivnjak and Bruno Harvey

Contents

1- Reviews of our Objectives

2- Actions in 1994-95

3- Results from Villeroy (1992)

1- Our Objectives

Within the St.Lawrence Vision 2000 Action Plan, Environment Canada, has initiated studies assessing the atmospheric toxic contribution to the contamination of the St.Lawrence River.

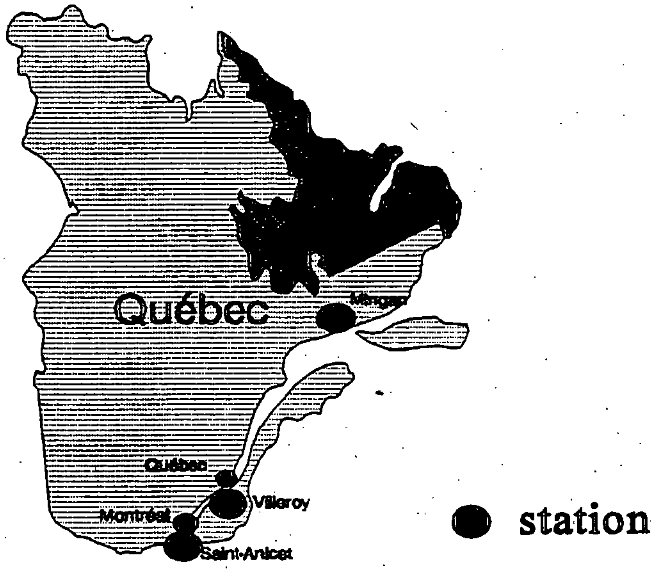
Four objectives have been addressed in order to give information to decision-makers, namely:

- determine the concentration of 20 organic and 8 inorganic toxic species in air and precipitation;
- estimate their annual deposition (spatio-temporal) along the St.Lawrence River;
- determine their probable origins;
- and finally to evaluate the atmospheric contribution of these toxic to the chemical contamination of the St.Lawrence River.

2- Actions in 1994-95

i- Completed the airborne toxic network along the St.Lawrence River:

- ***Villeroy is running since in 1992;***
- ***Saint-Anicet started in April 1994;***
- ***Mingan has started in June 1994.***



Airborne toxic network

Figure 1- Airborne toxic network along the St.Lawrence River

ii- improvements of the Analytical procedures

⇨ ***Université de Montréal*** *has changed its analytical procedures: Using GC-MS (for all analysis) and uses isotopic tracers (e.g. fluoranthene (d_{10}), α-HCH (d_6)) as internal Stds, triphenylamine was already used as external Std.*

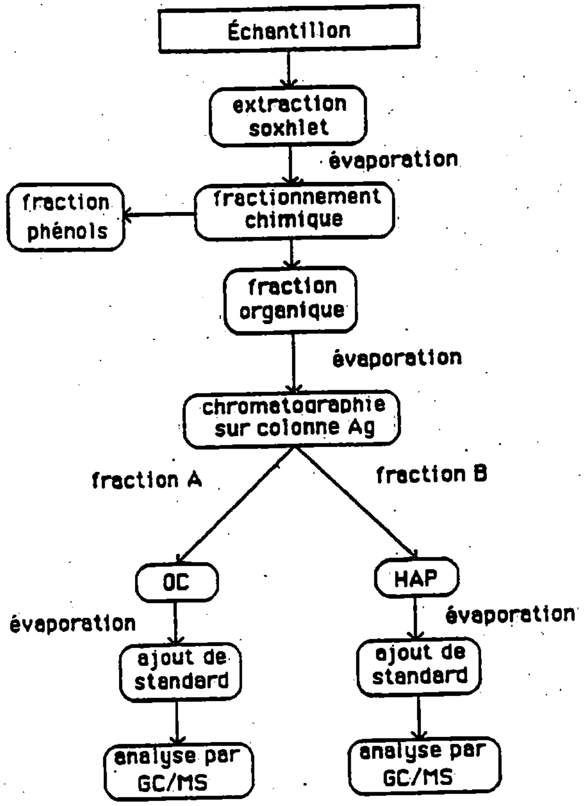


FIGURE 1: Schéma de traitement préparatif des échantillons

⇨ ***Université Laval*** *got a new Electrothermic Atomizer Graphite Furnace (EAGF) with Zeeman effect correction (Background).*

iii- Harmonization of the species with CSL

in 1992

(inorganic)

Parameter
pH
Conductivity
Calcium
Magnesium
Potassium
Sodium
Zinc
Sulphate
Nitrate
Chloride
Cadmium
Copper
Lead
Selenium

(Organic)

Phenanthrene
Anthracene
Fluoranthene
Pyrene
B(a)P
PCB 3
PCB 26
PCB 28
PCB 66
PCB 77
PCB 126
PCB 169
PCB 180
α-BHC
γ-BHC
HCB
γ-Chlordane
p,p' DDE
p,p' DDT
Mirex

in 1993-94

⇨

+ NH4, Al, Fe, Mn, As

⇨

Suite of PCBs has been changed as: 77, 105*, 118*,126 128*, 138*, 169 and 180

* new

iv- Study the Representativity of the stations (Dry fraction)

⇨ Villeroy (January 94)

Operated two sampling sites in the area of Villeroy
- ***At the permanent site***
- ***At a satellite site (5 Km from the permanent one)***

⇨ Saint-Anicet (March 94)

Operated two sampling sites in the area of Saint-Anicet
- ***At the permanent site***
- ***At a satellite site (15 Km from the permanent one, on the other river shore side (Left Shore))***

v- Study on breakthrough (For Organic)

⇨ Villeroy (Jan-Feb 94)

Hi-Vol PS-1 (Filter & PUF)
Two samplers in parallel

Sampler A	Sampler B
300 m3	300 m3
300 m3	200 m3
300 m3	500 m3

vi- Research grants (4) 50 K (May 94)

1) (15K) Prof. Michèle Heitz, Université de Sherbrooke
Subject: Emission of Zn and Cd from electrolytic industries.

2) (15K) Prof. Joseph Zayed, Université de Montréal
Subject: Integration of the airborne toxic measurements from urban and rural sites in Québec.

3) (10K) Prof. Jean-Pierre Schmit, UQAM
Subject: Vertical flux measurements of inorganic particles along the St.Lawrence river.

4) (10K) Prof. James Agbebavi, UQTR
Subject: Expert system development for industrial airborne toxic fallout.

⇨ *Seeding money about 115K (with partners):*

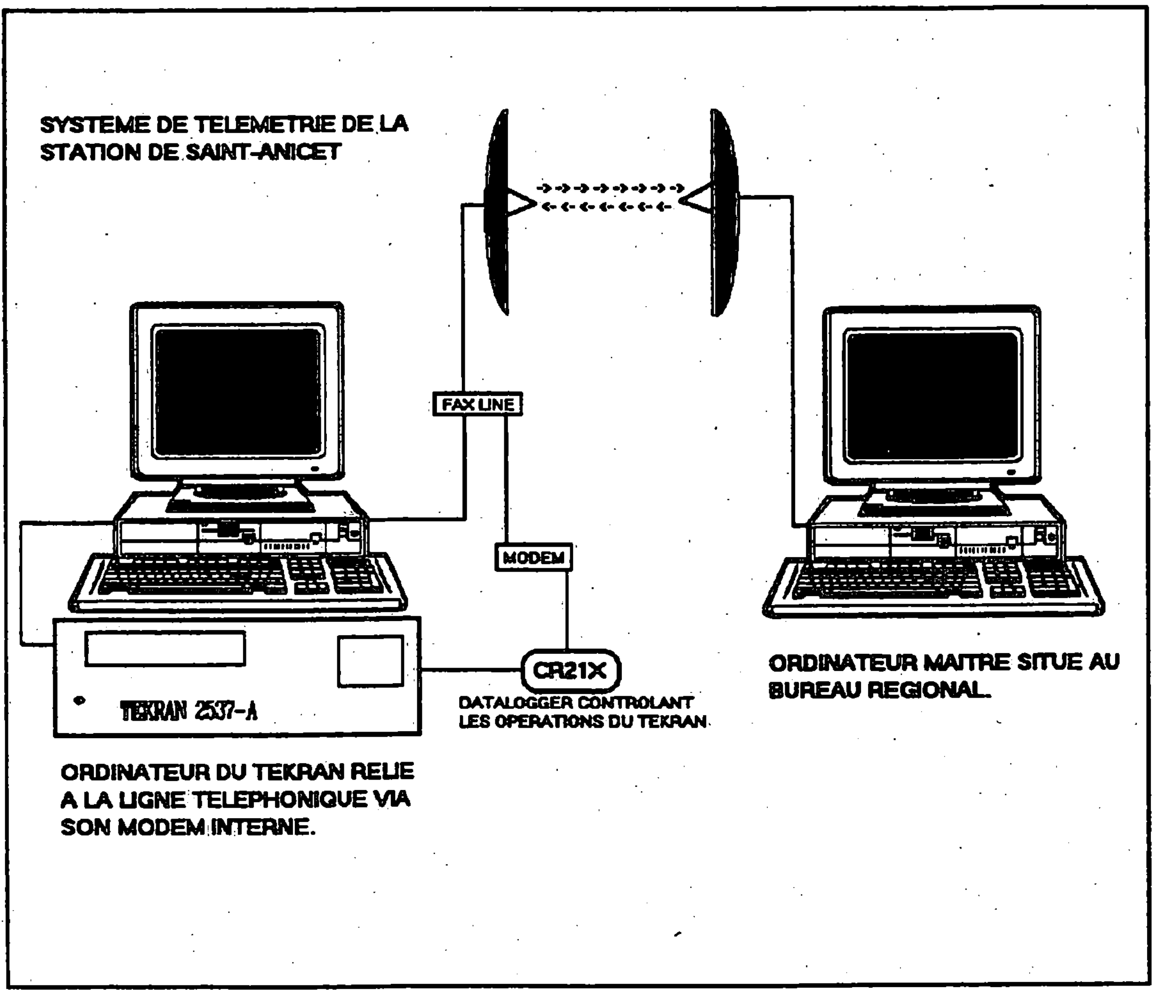
- *. Zinc Electrolytic of Canada*
- *. Ethyl Corp.*
- *. Canadian Institute of petroleum products*
- *. Ministère de l'Environnement et de la Faune (Québec)*

⇨ *All of these researches will be presented to the 7th Symposium on Toxic Substance in 1996.*

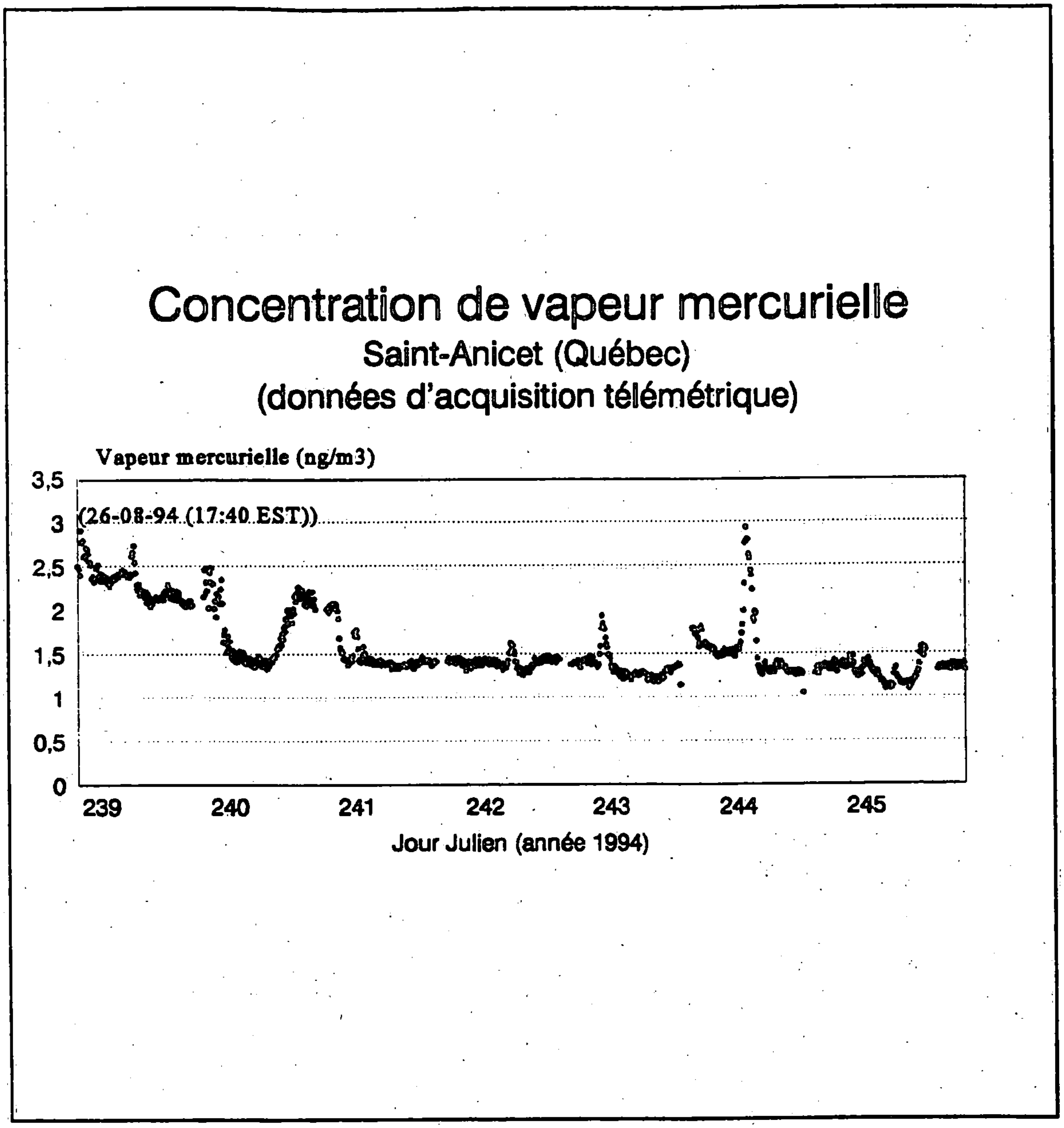
vii- Atmospheric Mercury Study in Québec

Continuous Measurements at Saint-Anicet with Tekran instrument

⇨ *Aims:* ***assess the mercury flux along the St.Lawrence river: Soil-air and water-air exchange studies.***



Telemetry Lay-out



Time series of atmospheric vapour mercury measured at Saint-Anicet (Qc) between August 26th and September 3td 1994.

viii- Reportings

reports (4)

1- Mingan: Description du site et aspects météorologiques.
2- Saint-Anicet: Description du site et aspects météorologiques
3- Rapport sur la caractérisation et l'évaluation de l'analyseur de vapeur mercurielle Tekran 2537-A
4- Reference guide on organic and inorganic airborne toxic

Proceedings (3)

1- 6e Colloque sur les substances toxiques (Montréal, Mai 94)
2- Transport et pollution de l'air (Avignon (France), June 94)
3- Atmospheric Contribution to the St.Lawrence river pollution (Québec, Canada): On Going Research. (This Mid-Term Review)

Article (1)

Mesures en continu de la vapeur mercurielle atmosphérique en milieu rural au sud du Québec, Canada. submitted to: S&TE.

3- Results from Villeroy (1992)

i- Results (Villeroy)

1992 data-set (Villeroy)

Table 3 and 4 give the statistical summary (N, Means and the Coefficient of Variation) for all compounds in wet and dry fraction and their comparison with other values (from literature) of rural sites in North America. Most of the parameters measured in precipitation and air at Villeroy have their means within the bracket of the North America comparison. However, three compounds found in precipitation are in excess, namely cadmium, DDE and anthracene. Mean fluoranthene value measured in air is also out of range. At this moment we cannot speculate on these discrepancies. Further measurements and investigations are needed to confirm these trends, since no historical data-sets exist.

Table 3 - Statistical Summary of chemical species measured in precipitation at Villeroy (Qc) for 1992 and comparison with others rural sites in North America

Inorganic

Compounds	N°	Arith. means	CV%	Frequency of detection (%)	Rural Sites North America (1)
pH	50	4.2	5.9	100	-
conductivity (µS/cm)	51	22.9	59.7	100	-
Ca (ppb)	50	188.2	51.3	100	-
Mg (ppb)	51	39.2	61.8	100	-
K (ppb)	52	70.9	77	100	-
Cd (ppb)	51	0.28	115.8	100	0.04 - 0.12
Cu (ppb)	51	0.88	122.4	100	0.7 - 3.0
Pb (ppb)	51	2.24	141.9	100	0.1 - 7.0
Se (ppb)	52	0.35	74.4	100	-
Zn (ppb)	48	8.08	93.7	100	1.8 - 15

(1) Poissant & Koprivnjak (1994)
* Sample integrated over 6 days

Table 3 (Rest)

PAH

Compounds	N*	Arith. Means	CV%	Frequency of detection (%)	Rural Sites North America (1)
Phenanthrene (ng/L)	8	27.5	98.9	100	1.6 - 132
Anthracene (ng/L)	8	19.8	173.8	100	0.2 - 3
Fluoranthene (ng/L)	8	1.32	62.3	100	1.2 - 150
Pyrene (ng/L)	8	7.9	66.5	100	0.9 - 100
B(a)P (ng/L)	8	1.47	103	75	0.4 - 3.0

Organochlorines

Compounds	N*	Arith. Means	CV%	Frequency of detection (%)	Rural Sites North America (1)
α-BHC (ng/L)	8	7.12	191.5	100	0.82 - 17.4
Lindane (ng/L)	8	2.62	191.2	38	0.25 - 6.7
p,p' DDT (ng/L)	8	0.50	87.9	75	< 0.44
p,p' DDE (ng/L)	8	0.49	124.9	63	0.02 - 0.13
γ-Chlordane (ng/L)	8	0.26	99	88	0.01 - 0.18
Mirex (ng/L)	8	N.D.	-	-	-
HCB (ng/L)	8	0.04	66	75	0.01 - 3.8
PCB 3 (ng/L)	8	0.08	168	50	-
PCB 26 (ng/L)	7	0.19	89.9	86	-
PCB 28 (ng/L)	7	1.27	59	100	-
PCB 66 (ng/L)	7	0.17	112	57	-
PCB 77 (ng/L)	8	N.D.	-	-	-
PCB 126 (ng/L)	8	-	-	13	-
PCB 169 (ng/L)	8	N.D.	-	-	-
PCB 180 (ng/L)	8	N.D	-	-	-

(1) Poissant & Koprivnjak (1994)
* Sample integrated over monthly period

Table 4 - Statistical Summary of air quality at Villeroy (Qc) and comparison with other rural sites in North America

Inorganic

Compounds	N	Arith. Mean	CV%	Frequency of detection (%)	Rural Sites North America
TSP (mg/m^3)	58	0.022	77.9	100	0.02[1]
Cd (ng/m3)	58	0.38	87.3	100	0.4 - 1000[2]
Pb (ng/m3)	58	5.41	94.4	98	2 - 1700[2]
Se (ng/m3)	58	1.28	79.6	100	0.01 - 3.0[2]

1- Bidleman (1988)
2- Schroeder <u>et al.</u> (1987)

PAH

Compounds	N	Arith. Means	CV%	Frequency of detection (%)	Rural Sites North America (1)
Phenanthrene (vapour) (pg/m3)	59	2795.5	126.1	100	1750-2650
Fluoranthene (vapour) (pg/m3)	59	438.9	166.4	100	174-280
Pyrene (vapour) (pg/m3)	59	224.6	231.8	100	150-332

(1) Poissant & Koprivnjak (1994)

Table 4 (rest)

Organochlorines

Compounds	N	Arith. Means	CV%	Frequency of detection (%)	Rural Sites North America (1*)
α-BHC (vapour) (pg/m3)	56	30.72	45.65	100	81-310
Lindane (vapour) (pg/m3)	58	37.64	171.8	100	15-60
p,p' DDT (vapour) (pg/m3)	58	N.D.	-	-	<20
Mirex (vapour) (pg/m3)	58	N.D.	-	-	0.35
HCB (vapour) (pg/m3)	56	27.8	55.35	100	31-189
PCB 3 (vapour) (pg/m3)	N.D.	-	-	-	-
PCB 26 (vapour) (pg/m3)	42	14.1	167.9	100	-
PCB 28 (vapour) (pg/m3)	45	25.2	72.9	100	-
PCB 66 (vapour) (pg/m3)	58	4.56	159.1	100	-
PCB 77 (vapour) (pg/m3)	58	N.D.	-	-	-
PCB 126 (vapour) (pg/m3)	58	N.D.	-	-	-
PCB 169 (vapour) (pg/m3)	58	N.D.	-	-	-

(1) Poissant & Koprivnjak (1994)

* totals (vapour + aerosol)

ii- Sources-Receptors Modelling: Lindane Case Study

Lindane is used in Canada as seed dressing (insecticide), namely for corn seed (as a mixture of diazinon, captan and lindane). About 4 metric tons are used for this function in Québec.

There is two types of lindane in the international market: pure lindane (γ-HCH 99%), is one of the top 10 insecticides used in Canada (McConnell *et al.* 1993); and the HCH technical grade which is an isomeric mixture (55-80% α, 5-14% γ, 2-16% δ and 3-5% ε-HCH). The latter has been banished in Canada and USA since the 60's, but is still used in some third world countries.

The annual time series of both isomers and their ratio indicate a North American source of lindane (Fig.2). Furthermore, a five-day-back-trajectory (at 925mb level) on May 20th shows that the air masses have not travelled a long distance. Therefore long range transport might not be involved in this high lindane concentration measured at Villeroy since the lifetime of lindane in the atmosphere is about 3-4 days.

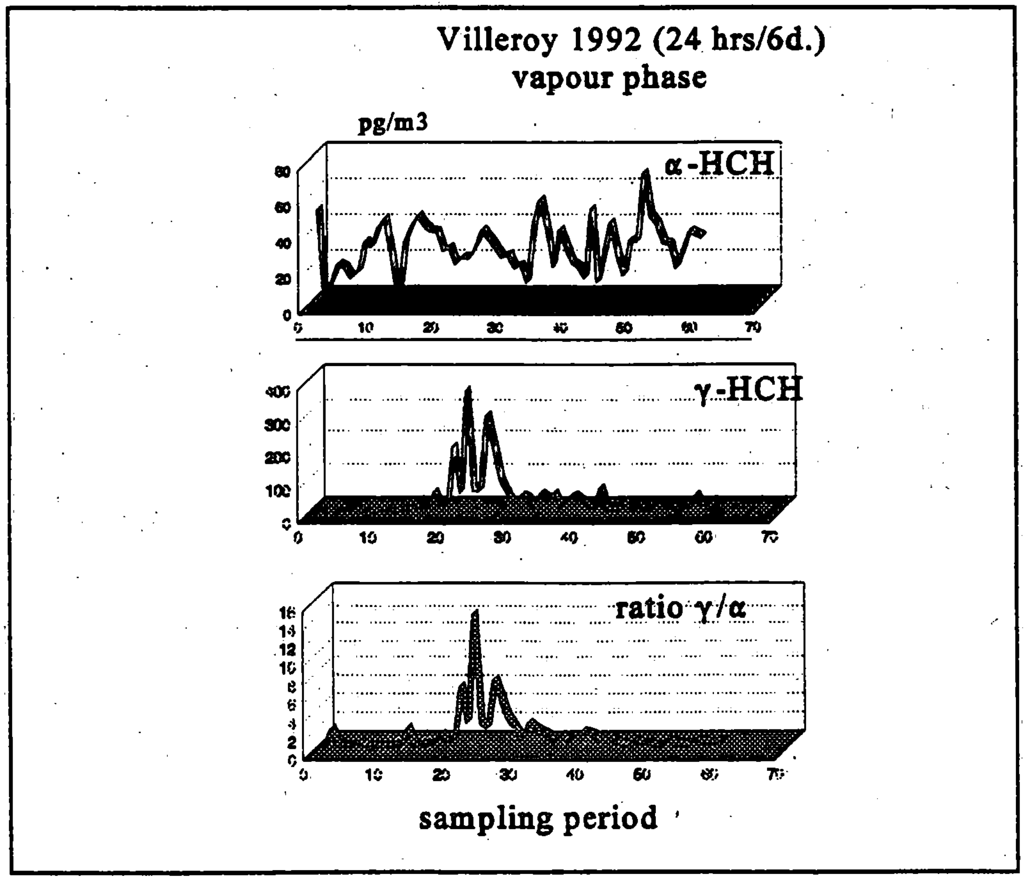
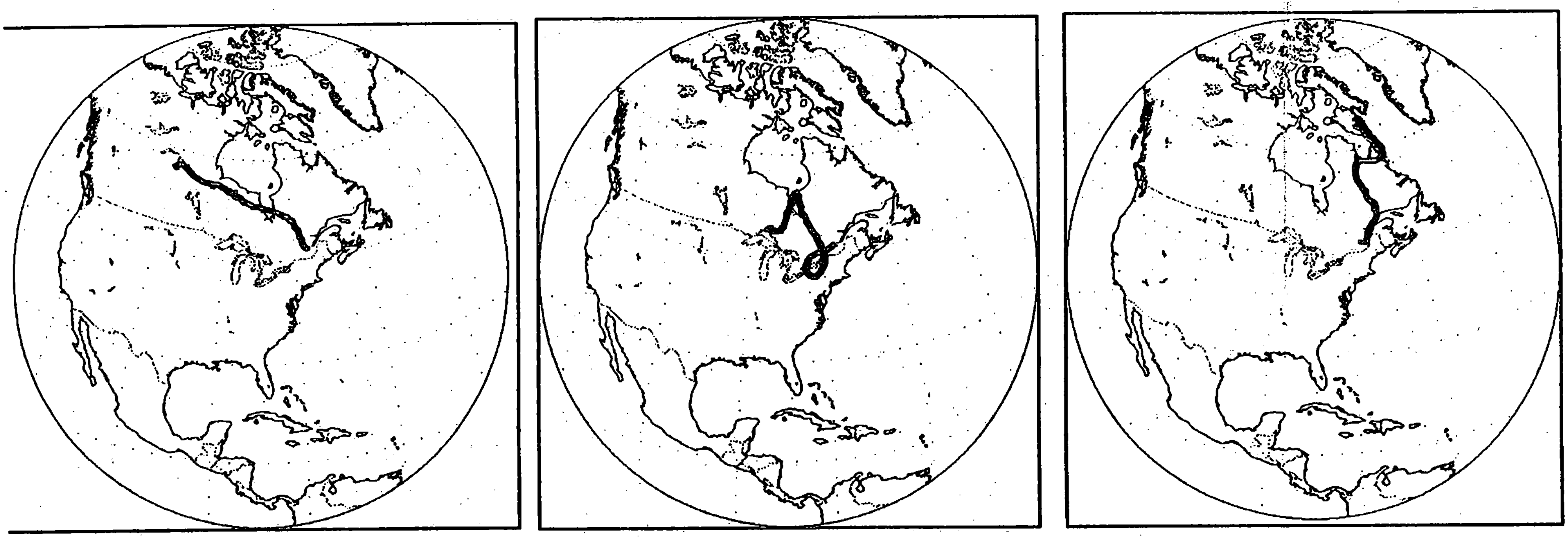


Figure 2- Time series of α and γ-HCH (pg/m3) and their ratio measured at Villeroy (Qc) in 1992



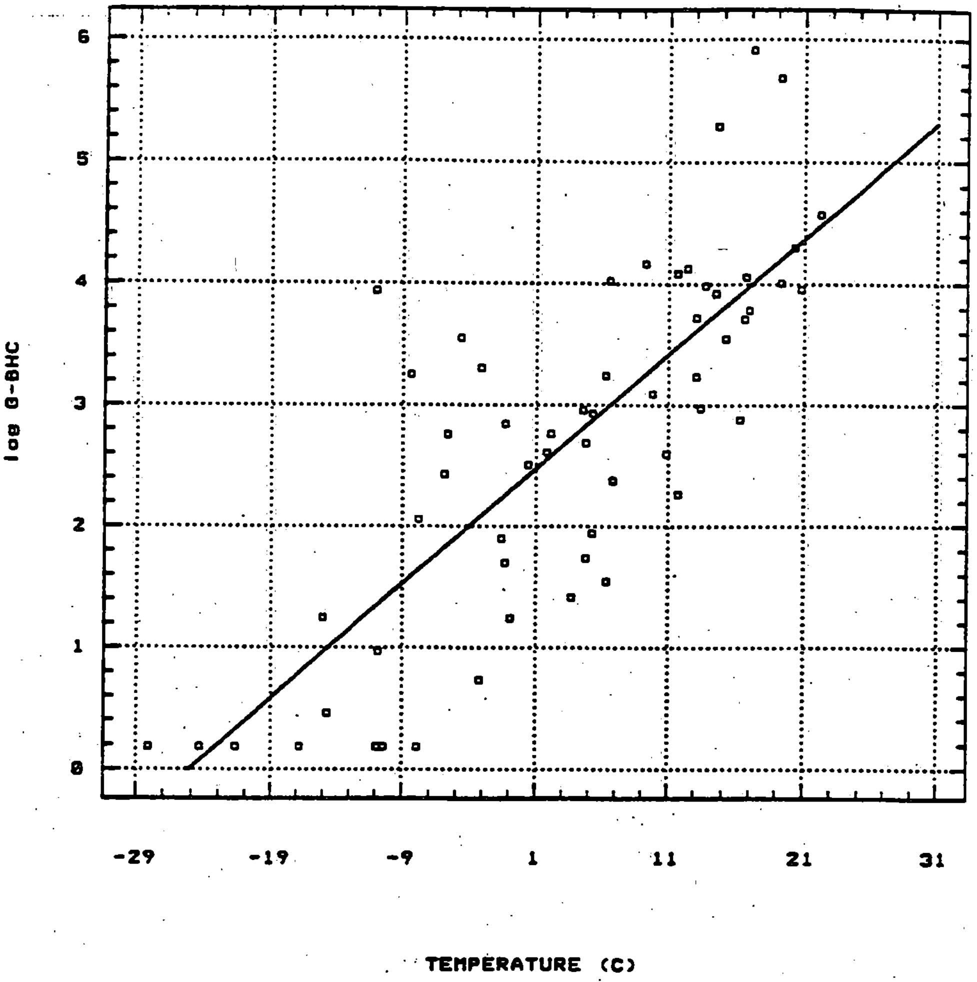
May 14, 1992
γ-HCH= 55 pg/m3
α-HCH= 21 pg/m3

May 20, 1992
γ-HCH=367 pg/m3
α-HCH=25 pg/m3

May 26, 1992
γ-HCH=64 pg/m3
α-HCH=24 pg/m3

Figure 3- Five-day-back-trajectories (925mb) at Villeroy before, during and after the highest measured concentration (May 20th,1992)

Correlation of mean daily ambient temperature measured at Villeroy with lindane concentrations (log scale) (R=0.79) shows that desorption mechanisms and fresh injection of lindane into the atmosphere are both acting in the concentration build-up of lindane at Villeroy (Fig. 4).



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B0:  2.3805     SE:  0.12369      T:  19.245

B1:  0.094637  SE:  0.0098028  T:    9.6541

CORR:  0.79036   MSE:  0.82672   DF:  56

POINTS DELETED:
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Figure 4- Correlation between ambient daily temperature and lindane concentrations (Log scale) measured at Villeroy (Qc) in 1992.

Conceptual modelling of lindane

Figure 5 shows the conceptual model of the atmospheric lindane in the atmosphere at Villeroy. Agricultural activities, namely seeding of corn, are responsible of the atmospheric release of lindane. About 375, 000 ha of land are used for this crop activity in Quebec, and the period of seeding appears to be concomitant with the highest peak of atmospheric lindane. Relationship of lindane with temperature shows that desorption mechanisms are an important process in the atmospheric lindane build-up. This volatilization might come from soil or through water desorption and might involve old as well as fresh lindane. The overall lifetime of lindane in the free environment is about 3 years.

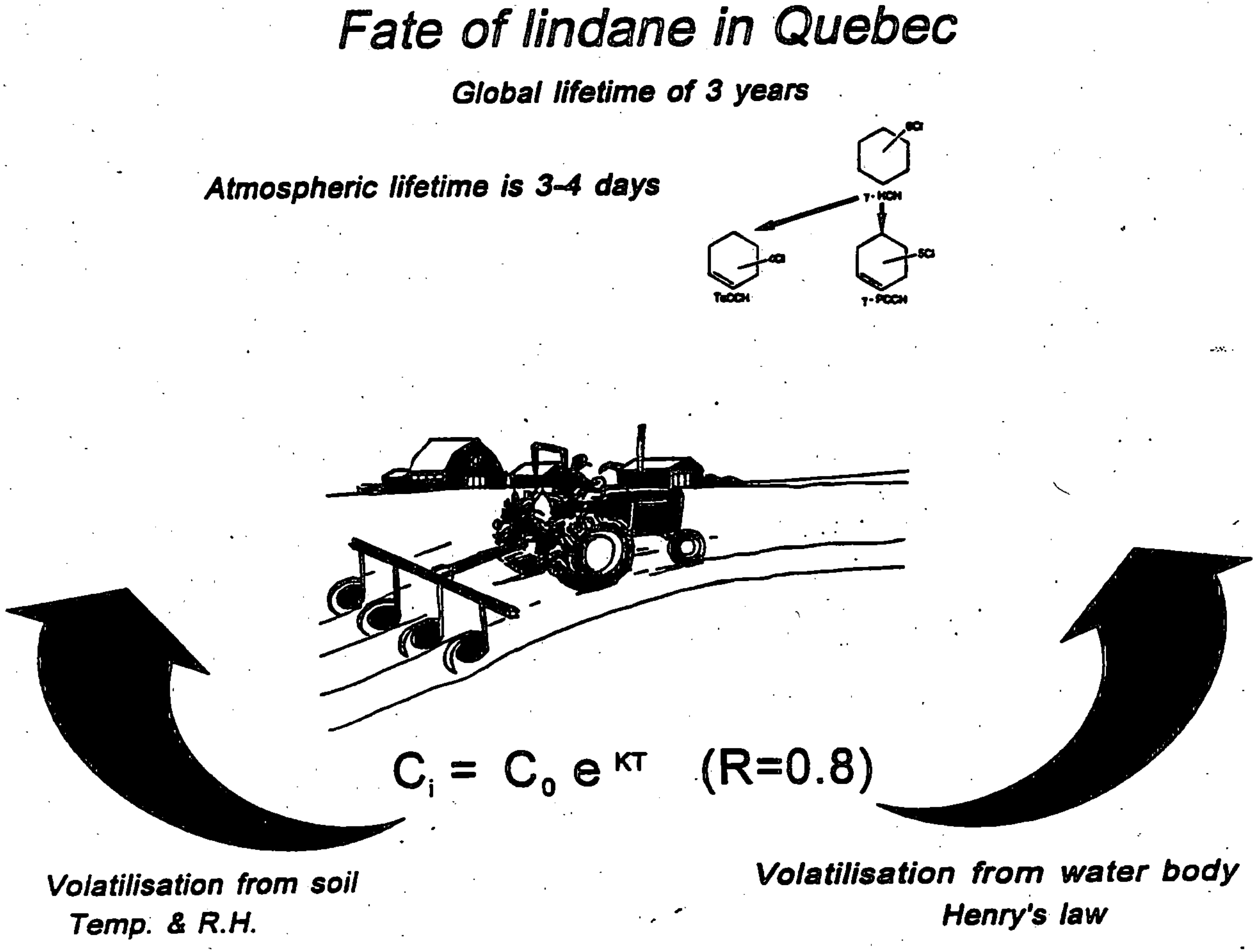

Figure 5- Conceptual model of atmospheric lindane in Québec

Conclusions

This first year of operation has permitted to determine some rough trends concerning airborne toxic in Québec. However, these trends have to be confirmed with longer time series since no historical data-sets are available. Furthermore, this 1992 data-set has permitted to initiate some conceptual modelling concerning the source-receptor relationship of lindane. Within this 5 year project, we expect to bring forth more information to decision-makers about all 20 organic and 8 inorganic toxic species.

References

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ATLANTIC REGION: AIR TOXICS PROGRESS

Stephen Beauchamp

A regional air toxics proposal to initiate a 3-5 year monitoring program for trace inorganics (metals) and organics (PAHs, PCDDs, PCDFs) was not supported outside of the region by either EPB or AES. Regional capital funds were used to purchase sampling equipment but there were insufficient resources to conduct field operations or support analytical costs in 94/95.

A cooperative PAH, PCDD, PCDF sampling program is currently being discussed with T. Dann, however, resources for the operational field component of this program are required. AEB may consider another proposal for 95/96 to support this program when project details are defined.

The long-range transport and deposition of trace organics and metals into the Atlantic region is still considered to be a high profile issue by federal and provincial governments in eastern Canada as well as the northeastern U.S. states. Several meetings have been held with representatives from these agencies (e.g. Acid Deposition to the Gulf of Maine, Atlantic Regional Oxidants Working Group, Gulf of Maine Council) and the lack of air toxics data has repeatedly been identified as an issue. The transboundary transport and deposition of air toxics to the Atlantic region has also been identified by representatives of the IJC air board as a high regional priority.

The current level of effort/support to air toxics research and monitoring in the Atlantic region by responsible government agencies is widely viewed as inadequate. However, the level of interest and potential for productive partnerships remains high.

The Gulf of Maine Council has recently been approached to develop and coordinate an air toxics monitoring program for the Gulf of Maine (including the watershed) which encompasses a large segment (but not all) of the southern Atlantic region where the problem is expected to be the greatest. The Council supports this in principle but their role would likely be limited to coordination and integration. Environment Canada Atlantic region is represented on the council and will pursue this in the future.

Mercury continues to be a high profile issue primarily due to the fish consumption/human health aspect of this issue. The high public profile, potential economic impact on the recreation/tourism industry of the Atlantic region and subsequent political fallout should place this issue high on the federal air issues agenda, especially since there is a potential linkage to interprovincial and international transboundary transport of mercury compounds directly into the region or mercury mobilization as an indirect consequence of soil and watershed acidification (also a federal LRTAP issue).

Atlantic region is also currently unable to effectively respond to other regional issues. For example, concern over the volatilization of toxic organic compounds from pulp mill effluent near federal lands (native peoples reserve) has put pressure on Environment Canada (EC) to set up a monitoring program to test for toxins (PCDD, PCDF) in fog water droplets and air.

The effects of the federal government's program review, S&T review and plans to terminate the Green Plan will put additional pressures on research programs nationally and regionally. There is a need to define priorities on a national and regional basis and develop cooperative strategies to address these issues. EC Atlantic region has established excellent working relationships with the Atlantic provinces, eastern U.S. states and various committees therein and is well positioned to integrate air toxics R&M programs. We feel that there needs to be better cooperation on air toxics research and monitoring issues between national and regional levels and between EPB, ECB and AES at the national level.

IADN OPERATIONS
Ray M. Hoff

The Integrated Atmospheric Deposition Network has been in operation since November 1988 at Point Petre and Egbert, and from January 1992 at Burnt Island, Ontario. Now into its fifth year of obtaining data, only during the last six months has that data been synthesized between the agencies involved (AES, Ontario Ministry of Environment and Energy, National Water Research Institute, Inland Waters Directorate and the Illinois State Water Survey). The results of the sample analyses will be reported by Ken Brice and the results of the QA/QC work will be reported by Sylvia Cussion.

In June, a workshop was held in Windsor, Ontario, to review the IADN data and provide updated loading estimates to the Great Lakes. The results of that workshop have been written up in a draft article which will appear in Environmental Science and Technology(1). The conclusions to that study state:

> Updated estimates of the loadings of PCBs, 11 OC compounds, four metals, and four PAHs have been made for the five Great Lakes, using data primarily from the IADN network. The results provide improved estimates of the loadings on a seasonal basis to each of the lakes from previous estimates made by Eisenreich and Strachan. In particular, the inclusion of a gas transfer term in the loading equation makes it clear that this process cannot be neglected in atmospheric loading assessments. The data for dieldrin, α-HCH, HCB and PCBs show that the fluxes are dominated by gas transfer. For the lower molecular weight PAHs phenanthrene and pyrene, the gas transfer term is at least as important as wet and dry deposition. For DDT, there is indication that the gas term can be greater than the wet deposition flux, yet poor resolution of lakewide water concentrations make the determination of the gas flux tenuous at best. Clearly, integrated air-water assessments of the gas term are needed on each lake.

The workshop summary will also appear in fuller detail in a workshop report to be available in January.

In addition, a data summary report is available for the AES Trace Element data from IADN, a data summary report is available from ISWS for their OC, PCB and PAH analyses from their four stations, and an AWMA paper is available summarizing dry deposition of metals to the lakes(2).

(1)Hoff, R.M., S.Cussion, W.M.J.Strachan, T.A.Bidleman, R. Falconer, L. Jantunen, M.Shackleton, C.H.Chan, J.Ridal, E. Voldner, D. Gatz, M. Neilson, J. Bode, T. Holsen, C. Sweet, J.-F Koprivnjak, W.H. Schroeder, S.J. Eisenreich, D.L. Leister, J.E. Baker, D.M. Dolan, D. Long, A.C. McMillan, K.A. Brice. An Update of the Deposition of Toxic Chemicals to the Great Lakes, Environ. Sci. & Technol. (in press).

(2)Hoff, R.M. and K.A. Brice, 1994. Atmospheric Dry Deposition of PAHs and Trace Metals to Lake Ontario and Lake Huron, Paper 94-RA110.04, Air and Waste Management 87th Annual Meeting, Cincinnati, OH.

ORGANICS ANALYSIS LABORATORY

K.A. Brice, N. Alexandrou, K.V. Su, L. Liao, M. Shoeib

Overview of Project Activities

The primary responsibility of the Organics Analysis Laboratory (OAL) during the past twelve months has continued to be the provision of an in-house service for the determination of trace organic chemicals in air samples collected as part of AES activities under Annex 15 of the GLWQA, with emphasis on a set of target species [PCB congeners (PCBs), organo-chlorine pesticides (OCs) and polycyclic aromatic hydrocarbons (PAHs)] identified for "semi-routine" determination. In addition, OAL controls the external contracts for the determination of trace elements (using INAA and ICP-ES) in samples of atmospheric particulate matter collected at the three Canadian Integrated Atmospheric Deposition Network (IADN) sites.

OAL has also been very active in following its "research" mandate to develop and ultimately implement new or improved analytical methods for organic contaminants, with two projects currently at an advanced stage:

- determination of co-planar PCBs by multi-dimensional gas chromatography (GC-EC);
- extraction of air sample filter media (GFF) by supercritical fluid (SFE).

A further project just initiated will investigate the determination of toxaphene congeners using electron-capture negative chemical ionization-mass spectrometry (ECNCI-MS).

OAL has participated fully in Phase 2 of the IADN Interlaboratory Study with results being reported for PCBs, OCs, PAHs and trace elements.

Overall, progress with all in-house work has continued to be hampered by a lack of suitable space to deploy and operate available instrumentation. The move of OAL to new facilities in the "Downsview South" laboratory building is now tentatively planned for January 1995, which will finally remove this limitation. Because of the current space constraints, there has been only limited consideration given to the purchase of new analytical instrumentation and equipment during this FY. However, considerable improvements to the existing procedures for chromatographic data reduction are expected to derive from the acquisition of the HP ChemServer system (deferred from FY 1993/94 because of funding problems). Installation in the new building will allow very convenient connection of all existing GC/LC/MS acquisition systems and the provision of fast data reduction workstations networked to the server.

Status of IADN Sample Analysis for PCBs, OCs and PAHs

The backlog of unanalyzed samples from the network continues to be a major issue. Attempts to accelerate in-house analytical progress have been hindered by the ongoing space limitations of the laboratory, which essentially limits the number of activities which can be conducted simultaneously and prevents all the available equipment and instrumentation from being efficiently utilised. The use of external contractors to assist with tasks such as sample extraction, drying and volume reduction had to be discontinued because of budget difficulties at the end of FY 1993/94 and insufficient funds were allocated for FY 1994/95 to permit this approach. Over the past twelve months, good progress has been made with the analysis of samples for PAHs, while the task of PCBs/OCs determination remains resistant to any significant acceleration because of its inherent complexity and need for experienced manual interpretation and confirmation.

In an effort to reduce the incremental loading of samples submitted for analysis, a decision was taken in April 1994 to move to a 1-in-12 day sampling frequency, reducing the number of samples collected annually at each site by a factor of 2. Furthermore, to provide the fastest possible route to obtaining some form of seasonal coverage for all sites, it has been proposed to move to a similar 1-in-12 day analytical frequency for Point Petre from 1993 onwards and potentially for CARE and Burnt Island retroactively to 1990 and 1992, respectively. The selection of samples for analysis will also be guided by a desire to overlap with the sampling schedules utilised by ISWS at the US sites. Using such an approach will, at least, rapidly improve the temporal coverage provided by the AES data set, allowing improved interpretation of seasonal cycles and year-to-year trends.

(a) Point Petre Samples

Tables I and II illustrate the current analytical status of PUF (vapour-phase) and GFF (particle phase) samples collected at Point Petre since 1990.

For 1990, the tasks of extraction, cleanup and instrumental analysis for PCBs/OCs and PAHs are essentially complete for all the PUF samples collected on the 1-in-6 day cycle by the three replicate samplers (C,L and M). For GFF, PAHs determination is complete for all the samples, whereas PCBs/OCs are approximately 70% complete. The low levels of PCBs and OCs observed in the GFF samples presents a real analytical challenge; even by combining the extracts from the three replicate samplers and using a lower (0.5 cm^3) final volume, most of the components of interest are still very close to instrument detection limit (IDL).

For 1991, a decision was made early in the year to switch to the use of duplicate samplers (L and C) only, with samples from C being archived and those from L being submitted for analysis. The tasks of extraction, cleanup and instrumental analysis for PCBs/OCs and PAHs are complete for all the PUF samples collected by sampler L. For GFF, all samples have been extracted, but the determination of PAHs has been completed for only 81% of the samples submitted. For PCBs/OCs, clean-up and analysis has only been completed for 21% of the GFF samples; clearly, with the revised sampling format, combination of replicates is no longer feasible, which results in most of the target analytes being reported as "not-detected".

For 1992, sampler M was deployed for a series of 96h samples to provide some overlap with the schedule used by the Ontario Ministry of Environment collocated at Point Petre: the determination of PAHs and PCBs/OCs has been completed for 100% of these samples (PUF and GFF). Unfortunately, due to a field error, the actual sample flow rate was not correctly adjusted to reflect the increased sampling period, with the result that these samples are probably influenced by appreciable vapour-phase "breakthrough". For samples collected on the "routine" schedule by sampler L, PUF and GFF extraction are 74% and 25% complete, respectively. Actual analysis is 32% complete for PCBs/OCs and PAHs.

For 1993, a small number (5) of 96h samples from sampler M were taken early in the year. For the PUF component, the analysis has been completed for PCBs/OCs and PAHs, whereas for GFF only 2 samples from the set have been processed. For samples collected by sampler L, no extraction has taken place for PUF or GFF.

(b) Egbert (CARE) and Burnt Island Samples

A high priority has been placed upon the development of a high quality data-set from the Point Petre Master Station possessing the maximum time-coverage feasible (given resource limitations) for comparison to other collocated agencies. In consequence, it has not been possible to dedicate extensive resources to the samples being collected at CARE and Burnt Island.

For CARE, a single sampler has operated since 1990: to date, only a limited set of 12 GFF samples from 1992 covering the annual cycle have been extracted, with analysis being completed for PAHs only.

For Burnt Island, a single sampler has operated since 1992: to date, some 12% of the PUF samples collected in 1992 have been extracted and analysed for PCBs/OCs.

Status of IADN Sample Analysis for Trace Elements

High-volume air sample filters for particulate matter trace element determination have been collected at the three AES IADN sites on a 1-in-6 day sampling frequency up to the end of 1993. In 1994, the sites moved over to a 1-in-12 day sampling frequency for these components. After collection, the filters are cut into four equal portions: two of these are archived and the other two are submitted for determination of trace elements to two contract laboratories using different analytical procedures. Dr. Sheldon Landsberger at the University of Illinois performs instrumental neutron activation analysis (INAA) on one of the filter portions, while inductively coupled plasma emission spectroscopy (ICP-ES) analysis is provided by Environmental Protection Laboratories, Inc.

Sampling at Point Petre and CARE was initiated in 1989. To date, the analysis of all samples from 1989, 1990, 1991 and 1992 has been completed. Because of budget limitations, a 1-in-12 day <u>analytical</u> frequency has been adopted for the 1993 samples, aligning the dates with ISWS as far as possible, with the analysis of the selected samples currently underway. If funds are available, it is hoped to submit some samples from 1994 before the end of FY 1994/95.

Sampling at Burnt Island did not commence until 1992. Analysis of 1992 samples has been completed. As for Point Petre and CARE, samples from 1993 are currently being analyzed on a 1-in-12 day frequency.

Application of Multi-dimensional GC-EC to Measurements of Co-planar PCBs in Archived Air Sample Extracts

There is currently much interest in the determination of "co-planar" PCB congener species in ambient samples. The term "co-planar" refers to the similarity of the molecule dimensionally and sterically to the highly toxic 2,3,7,8 TCDD, allowed by the absence (non-ortho) or presence of only one (mono-ortho) chlorine atom in an ortho-substituted position on the biphenyl skeleton. Such species (e.g. PCB 77, 126, 169) have been found to have high inherent toxicities.

Reliable analytical data for these co-planar PCBs are not feasible using the conventional single-column, or dual column, capillary GC-EC methods utilised for the "routine" analysis of the IADN air sample extracts. This is due to the complex co-elutions of PCBs that occur and possible interferences by non-PCB species, with the co-planars typically constituting the minor portion of such "merged" peaks.

A multi-dimensional GC-EC system (Siemens 2-8) was acquired by OAL in April 1992 with the intention of pursuing improved data on PCB congener distributions, in particular for the co-planar species. During FY 92/93 and FY 93/94, with PDF support, methods were developed using DB5 and DB17 columns for full resolution and accurate determination of co-planar pcbs.

During the past year, an in-house contractor has applied these methods to the re-analysis of combined, archived extract fractions from replicated air samples (vapour phase and particle-bound) taken at Point Petre during 1990: 12 typical sampling periods were selected for this re-analysis in an attempt to generate a "snapshot" of seasonal trends and partitioning behaviour. Data analysis has been completed and a full report and journal publication is in preparation. The measurement of these species at the low levels typical of "background" air constitutes a somewhat unique dataset, since previously available data relate primarily to urban "polluted" air. Intriguingly, the results show that the co-planar species display a clearly elevated tendency to partition into the particulate phase compared to mono-ortho and di-ortho chlorinated PCBs belonging to the same homologue group. Furthermore, a seasonal cycle in the partitioning behaviour is also apparent for the co-planars, with higher particulate phase components of the airborne total being observed in the winter months. Such experimental findings are consistent with the theoretical predictions of Bidleman and Falconer (1994) based upon observed/predicted vapour pressures. The atmospheric consequence of this finding is an increased tendency for these species to be removed by particle dry deposition or precipitation scavenging.

Further Evaluation and Implementation of Supercritical Fluid Extraction (SFE) Techniques for Extraction of Exposed Glass Fibre Filters (GFF) and Subsequent Determination of PAHs, PCBs, OCs

Present methods for the extraction of trace organic species from air sample collected on filters or adsorbent cartridges are time-consuming, labour-intensive and utilise large volumes of solvents, with consequent storage and disposal problems. Extraction using supercritical fluids (SFE) offers the potential for faster, semi-automated procedures while minimising usage of hazardous solvents.

In FY 91/92 a Dionex 703 multi-cell extractor was purchased, with a 703M modifier addition module being added in FY 92/93. In FY 93/94, some limited funding ($13K) was made available to support initial investigations of applying the technique to AES sample extraction requirements. Some OAL operational funds were also dedicated to allow an extension to the work program. With the support of an in-house contractor, a working method has been established for extraction of GFF using CO_2 modified by the addition of 5% dichloromethane (DCM). Good recoveries were obtained using spiked GFF in packed extraction cells, and the method has been tested against the standard Soxhlet method using a limited number of "real" air sample filters. The results obtained for PAHs compared very favourably. For PCBs/OCs, the comparison was complicated by the intrinsically low levels found on the filters. In addition, a background pump contamination (from a lubricant used on the pump seal) produced significant interference with many of the target PCB/OC analytes. The AES 703 pump module was eventually returned to Dionex to undergo a "special cleaning" and the testing program commenced again in September using this clean module. Pending satisfactory results from an extended series of SFE/Soxhlet comparisons, it is hoped to adopt SFE as the method of choice for GFF extraction before the end of this year.

TABLE I

ORGANICS ANALYSIS LABORATORY PROGRESS SUMMARY SEPTEMBER 29th 1994

SEMI–VOLATILE ORGANICS IN AIR AT POINT PETRE PUF (VAPOUR PHASE)

YEAR	1990	1990	1990	1991	1991	1991	1992	1992	1992	1993	1993	1993
SAMPLER	L	C	M	L	C	M	L	C	M	L	C	M
Sampling Frequency	6d	6d	6d	6d	6d	6d	6d	6d	14d	6d	6d	14d
Sampling Period	24h	24h	24h	24h	24h	24h	24h	24h	96h	24h	24h	96h
No. of Samples Collected	73	73	73	73	73	12	73	73	28	73	73	5
No. of Samples to be Submitted	73	73	73	73	Archive	12	73	Archive	28	73	Archive	5
No. of Samples Extracted	73	73	73	73	NR	NIL	54	NR	28	NIL	NR	5
PCBs/OCs												
Florisil Cleanup	73	73	73	73	NR	NIL	28	NR	28	NIL	NR	5
GC–EC Analysis	73	73	73	73	NR	NIL	23	NR	28	NIL	NR	5
Completion Level*	100%	100%	100%	100%	NR	NIL	32%	NR	100%	NIL	NR	100%
PAHs												
Silica/Alumina–N SPE Cleanup	73	73	73	73	NR	NIL	23	NR	28	NIL	NR	5
HPLC–FLD–UV Analysis	73	73	73	73	NR	NIL	23	NR	28	NIL	NR	5
% Complete*	100%	100%	100%	100%	NR	NIL	32%	NR	100%	NIL	NR	100%
COMMENTS	1990 COMPLETED			LARRY 100% COMPLETE								

TABLE II

ORGANICS ANALYSIS LABORATORY PROGRESS SUMMARY SEPTEMBER 29th 1994

SEMI–VOLATILE ORGANICS IN AIR AT POINT PETRE GFF (PARTICLE PHASE)

YEAR	1990	1990	1990	1991	1991	1991	1992	1992	1992	1993	1993	1993
SAMPLER	L	C	M	L	C	M	L	C	M	L	C	M
Sampling Frequency	6d	6d	6d	6d	6d	6d	6d	6d	14d	6d	6d	14d
Sampling Period	24h	24h	24h	24h	24h	24h	24h	24h	96h	24h	24h	96h
No. of Samples Collected	73	73	73	73	73	12	73	73	28	73	73	5
No. of Samples to be Submitted	73	73	73	73	Archive	12	73	Archive	28	73	Archive	5
No. of Samples Extracted	73	73	73	73	NR	NIL	18	NR	28	NIL	NR	2
PCBs/OCs												
Florisil Cleanup	52	52	51	15	NR	NIL	NIL	NR	28	NIL	NR	2
GC–EC Analysis	50	50	50	15	NR	NIL	NIL	NR	28	NIL	NR	2
Completion Level*	69%	69%	69%	21%	NR	NIL	NIL	NR	100%	NIL	NR	40%
PAHs												
Silica/Alumina–N SPE Cleanup	73	73	73	68	NR	NIL	NIL	NR	28	NIL	NR	2
HPLC–FLD–UV Analysis	73	73	73	59	NR	NIL	NIL	NR	28	NIL	NR	2
% Complete*	100%	100%	100%	81%	NR	NIL	NIL	NR	100%	NIL	NR	40%
COMMENTS	PAHs 1990 COMPLETED PAHs 1991 81%											

QA/QC UPDATE

Sylvia Cussion

IADN Quality Assurance Program Plan (QAPP)

- Canadian agencies (AES, NWRI, IWD & MOEE) completed a final review in August 1993.
- Bi-national workshop was held in November 1993 for a final review.
- All final updates and revisions were completed at the end of February 1994.
- Final document was recommended for approval by AES, MOEE & GLNPO (US-EPA) in May 1994 and signed by "The Parties" on May 19, 1994.
- Printing and distribution to all Canadian agencies was completed in September 1994.

AES Air Toxics QAPP

- Air Toxics QAPP addresses Annex 15 activities of the Great Lakes Water Quality Agreement.
- Specifically applies to Semi-Routine Monitoring Project (SRMP) and other related projects and Special Studies.
- Final internal review almost completed as of October 6, 1994.
- Future goal: adapt QAPP to other Air Toxics programs (eg. Arctic).

SRMP Quality Assurance Project Plan (QAPP)

- SRMP is AES's contribution to Integrated Atmospheric Deposition Network (IADN).
- QAPP details specific QA/QC activities undertaken to meet the goals of the Quality Assurance Program Plans (QAPPs).
- Revised and updated in winter of 1994, primarily based on revisions in AES and IADN QAPPs.
- Some information is missing for data processing and approval.
- "Incomplete" version printed and distributed at AES March 31, 1994.

IADN/Air Toxics Internal Audits

- Technical Systems Audits of SRMP Field sites and laboratories providing IADN data:

Field Sites:	CARE (Egbert)	August 1993
	Burnt Island	October 1993
	Pt. Petre	October 1993
Laboratories:	AES Organics Lab	February 1994
	NWRI Organics Lab	November 1993 & March 1994
	NLET (for IWD) Labs	March 1994
	EPL (AES Contractor)	March 1994
	Concord Environmental (AES Contractor)	September 1994

Interlaboratory Studies in Support of IADN

Final reports available for the following:

- Interlaboratory Study 92-1: PCB Isomers
- Interlaboratory Study 92-2: Polycyclic Aromatic Hydrocarbons
- Interlaboratory Study 92-3: Organochlorine Pesticides
- Interlaboratory Study 92-4: Trace Metals

- Interlaboratory Study 93-1: Trace Metals
- Interlaboratory Study 93-2: Organochlorine Pesticides

- Interlaboratory Study 93-3: PCB Isomers undergoing final peer review and approval for publishing; should be available end of October or early November 1994.

- Interlaboratory Study 93-4: Polycyclic Aromatic Hydrocarbons just had table of results distributed; final report to be written and completed by December 1994.

- 1994 studies plan spiked matrix samples.

- Target Trace Metals on filters (ambient air) and spiked precipitation for end of October 1994.

- Target Organics on spiked filters (ambient air) with all three compound groups (PCBs, OCs and PAHs) plus a split extract from a bulk real sample for mid-November 1994.

- Target Organics in spiked precipitation passed through collection columns for all three compound groups (PCBs, OCs and PAHs) for end of November 1994.

Other QA/QC Activities

- AES Organics laboratory annual OC data report outline developed; data being collated by lab staff but not quite ready to be assembled into a report.

- Participation in IADN Data Review Workshop, Windsor, Ontario, June 1994.

- "The IADN Quality Assurance Program and Related Interlaboratory Studies" presented at POPS Measurements in Northern Environments Workshop, Waterloo, Ontario, June 1994.

Example of Findings from Interlaboratory Studies

- Showed examples of improvement in agreement in second Trace Metals study (93-1) compared to first study (92-4).

- Showed examples of improvement in agreement with target in second OC study (93-2) compared to first study (92-3).

- Showed examples of good agreement between laboratories for injection standards for OCs compared to greater spread in results for solutions processed through analytical Clean-up (Study 93-2).

- Showed examples of comparison of results between the first PCB study (92-1) and the second study (93-3); examples of maintenance of performance, improvement in performance, and shift from high to low bias.

RDMQ - TOXICS

W. Sukloff

Software Development

- Extensive testing was performed in co-ordination with G.B. Skelton Technical Services Inc.

- RDMQ was used to quality control the first 3 months of the 1994 CAPMoN precipitation chemistry data.

- The 1st draft of the User Manual was completed and distributed for comments. The final version will be completed within a few weeks.

AES Toxics

- Databases have been created for: PCB/OC's, PAH's, NAA trace elements, and ICP trace elements.

- Statistical and graphical reporting programs have been written.

- Field blank-correction programs have been written for each of the databases.

- Programs have been written to produce the annual and seasonal summary statistics as specified in the Quality Assurance Program Plan (Appendix L).

- Initial training has been provided to Jim Woods at CARE. Additional training will be provided after the manual has been completed.

EPA Toxics

- A $50k grant has been provided to AES to implement RDMQ at GLNPO (EPA).

- A contract is in place to enhance RDMQ and apply quality control checks and flag their data.

Work in Progress

- Enhancements to the lab datasets will streamline the transfer of data into RDMQ.

- The change-over to the UNIX-based lab analysis software by the AES lab will require changes to the data management procedures. We will take this opportunity to further integrate RDMQ into the lab data management activities.

- The implementation of RDMQ at GLNPO will help AES in the development of data flags and quality control procedures.

NAtChem - TOXICS DATABASE DEVELOPMENT

R. Vet, W. Sukloff, C. Ro, D. Ord - Contractor

NAtChem (The National Atmospheric Chemistry Database System)

- The Canadian facility for regional scale atmospheric deposition data.
- Currently: only precipitation chemistry data.
- Future: the toxic data.

Objectives

(1) To combine different network data.
(2) To archive the QA/QC data with standard format.
(3) To produce data analyses.

Data Group

(1) AES Air Organics Data
(2) AES Air Metals Data
(3) NWRI Precipitation Organics Data
(4) NWRI Precipitation Metals Data
(5) IWD Precipitation Organics Data
(6) OMEE Air Organics Data
(7) OMEE Air Metals Data
(8) OMEE Precipitation Organics Data
(9) OMEE Precipitation Metals Data

Tasks

(1) Interview with Four Network Managers.

(2) Functional Specifications.

(3) Network Information Database:

- operation, component groups monitored, instrument descriptions, format, documents, and laboratory.

(4) Site Information Database:

- operation, component groups monitored, instrument descriptions, site environs, and nearby monitoring stations.

(5) Chemistry Database:

(1) Air:
- Organics (PCB, PEST, PAH, TOC, TSP)
- Metals

(2) Precipitation:
  - Organics (PCB, PEST, PAH)
  - Metals

(6) Summary Database (Seasonal, Annual).

(7) Summary Tables:

Data Completeness, Distribution Test, Concentration Statistics, Volume/P-W Mean Concentration Wet/Dry Deposition, Average Volume/Total Precipitation

(8) Graphical Analysis Routines:

QC Cart, Histograms, Time-series, Frequency, Contour

(9) Complete DB:

March 31, 1995

AIR-WATER EXCHANGE PROCESSES
Bill Schroeder

The scientific objective of this project is to determine directly (in situ) the magnitude and the direction of fluxes of volatile organic compounds, VOCs (and subsequently of semi-volatile organic compounds, SVOCs) across the air-water interface of the Great Lakes under various environmental conditions. The ongoing work, which is being performed through a 2-year professional services contract, is the second phase of a multi-year work plan consisting of 3 phases. The first phase, consisting of the design, fabrication, and initial testing of prototype versions of an in-situ sparger device and a flux chamber for directly determining chemical mass transfer ("fluxes") across the air-water interface, have been successfully completed (see Ref. 5).

Significant modifications and improvements have been made to the prototype devices which have been subjected to laboratory-based tests as well as recent field trials in Hamilton Harbour. An important component of this project has been the development, evaluation and application of reliable methods of sampling and analysis of VOCs at low concentrations in water and in ambient air. Carbotrap 300 multi-bed sorbent tubes and Tenax TA sorbent tubes are showing considerable promise during preliminary experiments. The target compounds selected for this project are a sub-set of the priority chemicals considered in Annex 15 of the Great Lakes Water Quality Agreement and include: chloroform, toluene, di-chloro-benzenes, naphthalene, hexachlorocyclohexanes, hexachlorobenzene and 2,4,6-trichlorobiphenyl. Different sampling techniques and trapping media are necessary for efficient collection of OCs and SVOCs.

PUBLICATIONS & PRESENTATIONS:

Schroeder, W.H., D. Mackay, A. Cassamalli, Y.-Z. Tang, Q. Tran, P. Fellin, S. Eisenreich and D. Achman. Testing and Evaluation of two Prototype Devices for Direct Measurements of Air-Water Transfer Processes involving Toxic Chemicals. In: Proceedings of the EPA/A&WMA Symposium on Measurement of Toxic and Related Air Pollutants, Air & Waste Management Association, Pittsburgh, PA, 1993. pp. 263-268.

AIR/WATER EXCHANGE

Bryan Kerman, Jeff Ridal, Louise Durham, Denis Roy, K. Muthuramu

Gas Exchange Studies

From April to October 1994, personnel from the AES Lake Meteorology Lab, sailing on the Lauzier, conducted a weekly observational program which measured both the concentration of basic gases. (N_2, O_2, Ar) and a pesticide (HCH) at three sites in Lake Ontario. Measurements were made at about six or more depths at the three stations spaced evenly along the lake's central axis. In addition air concentration of HCH was measured using a hi-vol samplers under appropriate wind conditions as the ship proceeded. A mass-spectrometer carried on-board was used to analyze the water samples for the basic gases. The organo- chlorine samples were extracted into a solvent and analyzed at the Canada Centre for Inland Waters.

Organochlorines

Measurements of HCH in air over Lake Ontario are consistently less than those reported in 1990. No comparison is possible with the IADN site due to sampling difficulties associated with breakthrough there. Nevertheless, a clear trend to decreasing in time is seen in our data, both air and water, as well as in Arctic studies. The atmospheric transport of α-HCH is relatively steady throughout the warm season whereas lindane (γ-HCH) increases during May, June and July.

Gas Fluxes of Organochlorines

The flux of the α isomer is weakly depositional in the spring and early summer, changing sign with the formation of the thermocline and becoming volatilizational by mid summer. The γ isomer remains depositional until the late summer. Hence the loss experienced by the lake for at least the γ isomer must be occurring in the non-stratified period which suggests that convective exchange may play a significant role.

Lo-Vol Sampler

A new sensor is under development, based on the basic design of hi-vol samplers, but simplified and much more cost effective. The new sensors accumulate about 300 m^3 during a week, then are sealed ahead and after the PUF plug, and another sensor within a manifold is then opened for another week's sampling. All monitoring and switching will be controlled by a small computer. A similar system is planned for water sampling using XAD resin collectors.

Basic Gases

After an examination of the calibration procedures and results, it was determined that the deep water which remains unaffected by seasonal mixing in the ten's of metres could be used to provide reliable concentration ratios. Combined with the absolute measurements of O_2 using the Winkler method, reliable absolute measurements were obtained for the other gases. Estimates of gas fluxes were determined from vertically integrated differences between cruises. Results show a flux out of the water during the summer and a large flux in as the convective regime is re-established.

Mixed Layer Dynamics

The gas entrainment rate (gas flux normalized by the air to water concentration potential) is of the same order as the heat entrainment rate predicted from classical mixing layer theory. The results are in good agreement with a previous analysis of data from the IFGYL experiment.

Primary Productivity

The existence of a biological supply of O_2 associated with the fixation of carbon during photosynthesis in the epilimnion was studied using gas ratios. It was found that the ratio of Ar to N_2 remains very nearly constant at all depths despite the large losses during the season in the epilimnion. However, the ratio O_2/N_2 increased significantly in the May-June period in the epilimnion. The biological production was estimated from this ratio. The inferred primary production agrees well with other methods such as C14 uptake. An anomalous increase of oxygen in late winter - early spring in the hypolimnion has been hypothesized to be associated with shallow primary production transported downward convectively near thermal bars associated with riverine warming of the littoral zone.

Eco-Buoy Development

A large 12m buoy is being outfitted as an ecological monitoring station and real-time laboratory. The buoy is being insulated for all season operation, and AC powered by diesels, as well as refurbished. An internal well is being constructed through which water will be drawn up from about 20 depths using a multiple hose assembly. Plans call for an on-board mass-spectrometer to measure basic gases, a CO_2 sensor, a low-vol sampler for air concentration of selected organochlorines, an equivalent sample for organochlorines in the water, as well as radiation, fluorescence and C14 measurements. Other plans call for studies of the particle load and size distribution in the water column. It is expected that the buoy will be deployed and evaluated in 1995.

SMOG CHAMBER STUDIES AT YORK UNIVERSITY

Douglas Lane

The basic objective of this work was to continue to elucidate the reaction mechanisms and products of the reaction of the OH radical with naphthalene in the smog chamber at York University.

Work on elucidating the products and rate of production of the individual products has continued in cooperation with Dr. Bunce and his graduate students from the University of Guelph. We have now identified approximately 19 products of the above reaction. These include oxidation products, nitration products and ring opening products. Of particular interest is the identification of both the hydroxy nitro and hydroxy dinitro derivatives of naphthalene since these products are known to be highly mutagenic. Since naphthalene is found in the atmosphere of Ontario in much higher concentrations (between 100 and 150 ng/m^3, or, between 10 and 100 times!) than all the other PAH put together, it would be prudent to look for these species in air extracts.

This project requires the identification of unknown products of a complex atmospheric reaction. In order to identify these products, one must first separate the individual products (gas chromatography or/and liquid chromatography) and then analyze them (mass selective detection). At present, we have only a gas chromatograph (GC) at the smog chamber facility. Although we have access to a high resolution mass spectrometer at Nova-Mann, unique mass determination via a high resolution mass spectrometer is feasible only after some basic information is known about the compound of interest (i.s. through low resolution mass spectrometry). In other words, we can separate the products but we cannot determine what they are. Access to a high resolution mass spectrometer is a moot point.

I have expanded the sphere of collaboration by including Dr. Brian McCarry (McMaster University) who is carrying out biodirected analyses on several of the extracts obtained from chamber studies.

When we installed the HP GC last fiscal year, we had some intermittent incompatibility problems between the HPIB board for the GC and the computer which was being used. Over the next 10 months, the incompatibility problems became regular and frequently caused the abortion of entire runs. It was finally proven that the fault was with the computer, not the HPIB interface board. As a result a new computer was purchased. All problems vanished when the new computer arrived.

Last fiscal year, I submitted a capital request which included $45K for a mass selective detector for our GC, and $14K for a new computer and software for the MSD. We were granted $38K total. Thus far we have obtained the computer and the MSD software. We are now, looking for approximately $16K to purchase the MSD. Without it, the work by AES scientists must be halted and we must rely on other groups to do the analyses and hope that they will share their results with us. This is a highly undesirable situation.

At the present time, my role in the chamber studies is that of a facilitator, assisting cooperative work amongst other scientists but doing none of the research myself.

No O&M was granted for this project.

Publications and Presentations:

Douglas A. Lane and Hongmao Tang, "Photochemical Degradation of Polycyclic Aromatic Compounds. I. Naphthalene". Polycyclic Aromatic Compounds 5(1-4), 131-138 (1994).

D.A. Lane, "Smog Chamber Studies on the Reaction of Naphthalene with the OH Radical" to the Indoor Environmental Program of the Environment, Health and Safety Division of the Lawrence Berkeley Laboratory, August 19, 1994.

GAP SAMPLER MODIFICATIONS AND SAMPLING

Douglas Lane

The objective of this project is to improve gas/particle partition measurement instrumentation and techniques.

The GAP sampler developed by AES and ORTECH scientists is recognized as the most accurate and precise denuder based system for gas/particle partition measurements of semivolatile organic compounds in the atmosphere. The GAP sampler comprises two samplers, one which yields the total loading of a compound (the gas and particle phase) and a second (which contains the denuder to remove the gas phase component) which yields the particle phase component. The vapour phase loading is determined by subtracting the denuder sampler result from that of the total sampler. The basic objection to the unit, apart from its size, is that the gas phase component must be determined by a difference measurement.

A new technique to coat small (30 cm) single channel denuders with XAD-4 has been developed by scientists at the Lawrence Berkeley Laboratory of the University of California at Berkeley and is in the process of being patented. Their system has been called the IOVAPS or Integrated Organic Vapour and Particle Sampler and has been used in gas and particle partition measurements of the components of environmental tobacco smoke. The IOVAPS normally samples for up to 5 hours at 5 Lpm. They have been requested by their supporters to scale up their denuders to match the accuracy and efficiency of the GAP sampler (which typically samples for 40 hours at 16.7 Lpm). A collaborative effort was initiated to combine the two technologies to produce a new denuder based sampler which would permit a direct measurement of both the gas and particle components of atmospheric PAH. After the modifications are made, the samplers will be evaluated in experiments to determine the gas/particle partitioning of PAH and nitrosamines in both environmental tobacco smoke samples and in atmospheric samples. The results will be compared with those of the IOVAPS.

Two GAP samplers and denuders were shipped to the LBL in early August. In order to make the modifications to the GAP denuders (which were considerably larger (41 times greater surface area) than the IOVAPS denuders used a LBL) new coating procedures had to be developed.

The LBL procedure requires that the denuders be sandblasted before applying the XAD-4. The nature of the pitting of the surface of the glass is dependant on the size of the carborundum grit used. To determine the optimum size grit (i.e. the one yielding the greatest loading of XAD-4) glass discs were ground with a variety of grit sizes and then coated with XAD-4 according to the prescribed procedures. The mass of XAD-4 coated on each disc was determined as a function of grit size used to sandblast the disc. Once the optimum grit size was determined, two GAP denuders were sandblasted by the LBL resident glassblower. The sandblasting was not entirely successful as the sandblasting was not uniform and some patches were apparently not sandblasted at all. This was particularly true of the inside surface of some of the annuli. Nevertheless, we successfully coated the denuders with the XAD-4. If more denuders are sandblasted, alternative sources will be sought. The first objective has been achieved.

LBL scientists were subsequently trained in the operation of the GAP sampler and, over the next 4 months while I am back at AES, will carry out some preliminary assessments of the effectiveness of the newly coated denuders. When I return to LBL in the spring, we will carry out a brief atmospheric sampling program.

Presentations:

L.A. Gundel, V.C. Lee, K.R.R. Mahanama, J.M. Daisey and D.A. Lane, "Phase Distribution of Polycyclic Aromatic Hydrocarbons and Other Semi-Volatile Compounds" at the Fifth International Conference on Carbonaceous Particles in the Atmosphere, August 23-26, 1994, Berkeley, CA.

AERIAL APPLICATION OF PESTICIDES
R. Mickle

In 1989, the Interdepartmental Task Force on Pesticide Drift was established to develop new regulatory drift guidelines in the registration of pesticides by assessing the potential for drift associated with a given use strategy. In essence, these new guidelines would include predictions centred on the use of models and/or a data base. The outcome of the evaluation would be an assessment of the expected environmental concentrations which, in association with the environmental toxicology data already supplied by the applicant, could be used to determine the environmental significance of the predicted drift and if necessary to estimate buffer zones as mitigative measures. In 1992, the data base on the aerial application of pesticides within a forestry context was completed. It presently contains over 200 spray trials associated with 48 field experiments. Presently, the data base is being used to verify a series of models which will be used to predict drift for operational and meteorological cases that do not exist within the data base. The contract on model intercomparison is to be completed by the end of this fiscal year. Utilizing the data base, a generic approach for setting buffer zones has been developed. The approach will be linked at a later date to models to establish buffer zones associated with specific pesticides and proposed use strategies. The approach incorporates, for the first time, a scientific rational to the size of buffer zones and at the same time allows for the incorporation of application technologies that will reduce the potential for off-target drift. As a spin off from the generic approach, deposit variability within the target block was shown to be influenced by application strategy and meteorology and hence could be minimized. Optimized spray programs could lead to improved deposit and hence the potential for reduced pesticide usage. The generic approach has been applied to the results from the vortex study in New Mexico showing that the use of the upwind wing results in substantially reduced buffer zones which translates into reduced environmental impact outside of the target block. Presentations on the generic approach have been made to industry, federal departments responsible for the registration of pesticides (both in Canada and the USA) and to the provincial pest control officers who are responsible for the regulation of the use of pesticides in Canada.

Collaborative research with Forestry Canada continued this past year in field trials for an alternate product for the control of gypsy moth. Further testing of an aircraft spray monitor has permitted detailed logging of the location and amounts of pesticide being applied. Models have been used to predict the ultimate fate of the released pesticide from the on-board logging and the results compared against population reduction data. A strong correlation between predicted deposit and population reduction has emerged clearly indicating those parts of the spray block that received less than the target application rate and subsequently had elevated population levels. The results have generated potential collaboration with provincial jurisdictions for the equipment to be used to monitor spray programs both aerially and on the ground. Future collaboration will address the usefulness of the procedure in predicting the levels of pesticides depositing outside the target area.

TOXAPHENE, PCB'S

Terry Bidleman, Renee Falconer, Liisa Jantunen

Research on atmospheric transport and cycling of organochlorine compounds (OCs) in the Arctic and Great Lakes is being carried out in the three areas described below.

Toxaphene in the Arctic: Atmospheric Delivery & Transformation in the Lower Food Chain

Toxaphene and other chlorobornane (CHB) products were heavily applied to cotton and other crops in the U.S. until 1986, and are still used in several tropical and subtropical countries. Atmospheric transport is responsible for widespread contamination of the Arctic with CHBs, where they are the most abundant pesticide residues in fish and whale blubber. Elevated levels of CHBs have led to closure of a commercial fishery on Lake Lebarge, Yukon. This study, supported by DIAND, has the following objectives: a) Determine the physico-chemical properties of CHBs that affect atmospheric transport and deposition, b) Compare air-water gas exchange of CHBs and hexachlorocyclohexane (HCH) in arctic waters, and c) Characterize changes in the CHB profile that accompany transfer from air to water to plankton. In the 1992-94 summers we collected air and water samples at Resolute Bay (1992), on the U.S.-Russian cruise in the Bering-Chukchi (B-C) seas (1993) and on the Canada-U.S. Arctic Ocean Sections (AOS) cruise (1994) to determine levels of OCs and air-sea gas exchange.

Results from the Resolute study are given in two papers (Bidleman et al., 1994a; Falconer et al., 1994a, both in press). Concentrations of CHBs in air and seawater were 3-4 times lower than found at the Ice Island in 1986-87. Still, CHBs ranked in abundance over chlordanes, DDTs, and dieldrin. The chromatographic profiles of CHBs in air and water were similar, implying gas exchange of compounds having similar Henry's law constants. Fugacity gradient calculations indicated net gas-phase deposition of CHBs and volatilization of α-HCH and trans-chlordane (TC) during the summer. Concentrations of α-HCH in air at Resolute and the B-C seas (see below) have declined three-fold since 1988-90, which has led to oversaturation of α-HCH in the surface water. Volatilization of TC may be tied to the seasonal cycle of chlordane isomers in arctic air. Several studies, including those at Resolute and Alert, show that ratios of TC to cis-chlordane (CC) are 0.3-0.4 in summer, 0.5-0.7 in spring, and close to 1.0 in winter. Summertime depletion of TC in air may trigger outgassing of the TC that has been deposited over winter.

Two papers are in press or submitted from the B-C work (Bidleman et al., 1994b; Jantunen and Bidleman et al., 1994). Both papers discuss revolatilization of HCHs caused by a long-term decline in tropospheric HCH levels. From B-C and Resolute measurements, the concentration of α-HCH in arctic air is now about 100 pg/m^3 -- three times lower than in the late 1980s. These results agree with independent measurements at Alert. In the last five years the air-sea gas flux direction of α-HCH has reversed, from deposition to volatilization, and γ-HCH has changed from deposition to near-equilibrium (zero net flux). The Resolute Bay and B-C studies are the first to demonstrate volatilization of OCs from arctic waters. As more and more countries ban OCs, a consequence of declining emissions from source regions will be remobilization from oceanic reservoirs to the atmosphere.

Other OCs measured on the 1993 B-C cruise include TC, CC, CHBs, dieldrin, and endosulfan. Air concentrations of these agree excellently with measurements at Alert for the same period in 1992. Future work will involve determining Henry's law constants and vapor pressures of CHB congeners, examining plankton extracts for CHBs, and completing the analysis of the 1994 AOS cruise samples.

Preferential Sorption of Coplanar PCBs to Urban Aerosols

Coplanar PCBs are minor but highly toxic components of commercial PCB fluids which have modes of action similar to polychlorinated dibenzodioxins and dibenzofurans (PCDDs, PCDFs). When expressed as "dioxin-like" toxic equivalents (TEQ), the contribution from coplanar PCBs often outweighs PCDDs and PCDFs in birds, marine mammals, fish, and human milk. The most important of these PCBs are congeners 77, 81, 126, and 169 (non-ortho) and 105, 118, and 156 (mono-ortho). This project, funded by the U.S. EPA, tests the hypothesis that non- and mono-ortho PCBs are preferentially sorbed to atmospheric particles. Association with particles leads to more efficient atmospheric delivery to lakes by wet and dry deposition. Objectives are to: a) Obtain vapor pressures for PCBs as a function of temperature and ortho-chlorine substitution, b) Compare the particulate fraction of PCBs in urban air for congeners having different numbers of ortho-chlorines and c) Determine particle/gas partition coefficients for PCBs to urban aerosols in laboratory experiments.

A capillary GC method was used to estimate liquid-phase vapor pressures for 180 PCB congeners as a function of temperature. Within a homolog group (e.g., pentachlorobiphenyls) congeners with fewer ortho-chlorines have lower vapor pressures. Consequently, greater fractions of coplanar PCBs on aerosols are predicted from the Junge-Pankow model (Falconer and Bidleman, 1994). Ambient air samples from 1988 and 1989 collections in Chicago were analyzed for PCBs, including the coplanars. Non- and mono-ortho congeners were associated with particles to a greater extent than congeners with two or more ortho-chlorines. Sorption of non-ortho PCBs 77 and 126 was slightly greater than attributable to lower vapor pressure alone, suggesting that planarity of the molecule also exerted an effect. Chicago aerosols were equilibrated with gas-phase PCBs in a controlled laboratory system. Particle/gas partition coefficients increased in the order: di-ortho PCBs < mono-ortho PCBs < non-ortho PCBs. A multiple linear regression model using vapor pressure and the dihedral angle between the two biphenyl rings explained 98% of the variance in sorption.

Our conclusion is that coplanar PCBs are preferentially sorbed to urban aerosols. This was a major part of Renee Falconer's Ph.D. research, for which she won the Hydrolab student award at the June IAGLR meeting. Her paper on this work has been submitted (Falconer et al., 1994b). Future investigations will explore the interaction between gas-phase organics and aerosols, especially to distinguish a<u>d</u>sorption from a<u>b</u>sorption mechanisms. Tom Harner from University of Toronto has recently joined us to continue this work. He will measure air/octanol partition coefficients of PCBs as a surrogate for sorption into an organic liquid film on aerosols, and carry out field and laboratory experiments to examine differences in sorption of planar and non-planar compounds.

Chiral Pesticides as Tracers of Biogeochemical Processes

Like amino acids, certain pesticides have right- and left-handed forms. Commercial pesticides are racemic mixtures in which the ratio of the two mirror-image molecules (enantiomers) is 1:1. Enantiomers have identical physical and chemical properties in all respects <u>except</u> toxicology and enzymatic breakdown. Because enzymes are themselves chiral ("handed") molecules, they have the ability to react selectively with one of the pesticide enantiomers. In the last few years the development of chiral-phase capillary GC has enabled the separation of pesticide enantiomers that cannot be resolved on conventional columns. Since then, several articles have appeared which document selective metabolism of one enantiomer by birds, mammals, and marine bacteria. Some of the common chiral OC pesticides are α-HCH, TC, CC, heptachlor, heptachlor epoxide, oxychlordane, o,p'-DDT, o,p'-DDE, and many CHBs. Our work, supported by the Keeping Toxics out of the Environment thrust, has the following objectives: a) Test chiral-phase columns for their ability to separate pesticide enantiomers, b) Examine pesticide residues in agricultural soils for evidence of enantioselective metabolism, and c) Determine the potential for volatilization of enantiomers from soils and changes in the proportion of enantiomers that may constitute an "old source" signature.

Several chiral OC pesticides have been run on two columns obtained from Supelco: Betadex-120 and Gammadex-120 (20% permethylated beta- or gamma-cyclodextrin in polydimethylsiloxane) and a 30% BSCD column (tert-butyldimethylsilylated beta-cyclodextrin in 7% phenyl 7% cyanopropyl polydimethylsiloxane) from BGB Analytik AG in Switzerland. These columns give us the ability to resolve the enantiomers of α-HCH, TC, CC, and o,p'-DDT. Most of our work has been with α-HCH in lake water, air, snow, and soils, using electron capture detection (GC-ECD) and negative ion mass spectrometry (GC-NIMS). The order of α-HCH elution is reversed on the different columns. On Betadex (+)α-HCH elutes first, whereas on Gammadex and BSCD (-)α-HCH elutes first. These reversals provide excellent confirmation on environmental samples.

Water, air, and snow samples were collected at Resolute Bay and Amituk Lake (Cornwallis Island, N.W.T.) to investigate the enantioselective breakdown of α-HCH. The enantiomeric ratios (ER = (+)α-HCH/(-)α-HCH) in air and snow were racemic (1.00 and 0.98, respectively). Selective degradation of (+)α-HCH was found in Amituk Lake at 20 m depth, where the ER = 0.77. ERs of influent streams changed over the melting period, being closest to racemic (0.9) at the beginning of snowmelt and decreasing to 0.6-0.8 near the end of the flow period. We were able to trace the stream runoff over the surface of the lake by differences in the ER of surface and deep lake water. This is the first evidence of a biological degradation pathway for an OC pesticide in arctic waters, and suggests that the ability of arctic microbial systems to break down organic contaminants is greater than commonly thought. A paper on this work has been submitted (Falconer et al., 1994c).

We are cooperating with Dr. Jeff Ridal, University of Montreal, in his investigation of α-HCH enantiomers in Lake Ontario. Here (+)α-HCH is also selectively degraded, but to a lesser extent than in Amituk Lake. Lake Ontario ERs range from nearly racemic in the Niagara River to 0.86 in the open lake.

A study has been initiated in cooperation with Dr. Sunny Szeto, Agriculture Canada, to determine the enantiomeric composition of pesticide residues in soils from the Fraser Valley, B.C. Farms in this region used large quantities of DDT, chlordane, heptachlor, and technical HCH in the 1970s, and high levels persist in some organic-rich soils. We found selective breakdown of (-)α-HCH in muck soils, where ER = 1.2 - 1.3, a reversal from Amituk Lake ERs! TC and CC residues from all soils were racemic (ER = 1.00), indicating no enantioselective degradation.

Future work will include examination of soils from the "cotton belt" in the U.S., with an emphasis on characterizing the enantiomeric composition of o,p'-DDT and o,p'-DDE residues. Air samples are being collected from August - December, 1994 in Columbia, SC to determine concentrations and ERs of OC pesticides in air from the southeastern U.S. We are attempting to obtain soil samples or extracts from India and southeast Asia, where vast quantities of technical HCH and DDT have been applied for decades. We have identified three farms in B.C. where the ERs of α-HCH are significantly different from racemic. In the coming year we plan to collect air samples at various heights above these soils to determine if volatilization of α-HCH residues can be traced by the ER.

Publications

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ATMOSPHERIC MERCURY

Bill Schroeder, A. Tham

Previous atmospheric mercury measurements conducted in the Great Lakes Basin -- at Egbert during late winter and early spring, and at the Pt. Petre master research station during the fall of 1990) have culminated in a peer-reviewed journal publication (Ref. 1).

Last fall, AES co-ordinated an international atmospheric mercury measurement methods intercomparison study in Windsor, Ontario. Scientists from four leading laboratories participated in this field study: Ontario Ministry of the Environment and Energy (OMEE), Ontario Hydro (OH), University of Michigan Air Quality Laboratory (UMAQL), and the GKSS Research Centre (near Hamburg, Germany). Manual methods of sampling and analysis (by UMAQL & GKSS) were employed along with two Tekran mercury vapour analyzers (operated by OMEE and OH). Short-term sampling (2- and 3-hour intervals) as well as longer-term sampling (6- to 16-hour intervals) was used in the manual methods, while the Tekran analyzers were operated with 5-minute sample integration times. The results generated from this study were presented at the International Mercury Conference held at Whistler, B.C., in July (Ref. 2). Of the 13 runs comprising this study, 8 produced meaningful results. For these 8 runs, all measurement results were in reasonably good agreement. The maximum deviation of individual results from the arithmetic mean of all 8 sets was about 35%. Considering the difficulties inherent in making ultra-trace environmental mercury measurements, this degree of agreement is quite satisfactory. For further details the reader is directed to Reference 2.

The results from our 1-year time series of (weekly integrated) gas phase atmospheric mercury measurements at Alert, NWT, from August 1992 to August 1993, were presented in a second paper at the 1994 Whistler Mercury Conference (Ref. 3). These data are helping to define continental background concentrations of total gaseous mercury (TGM) in the Canadian Arctic. During that time, monthly-integrated samples were also collected (on quartz-wool plugs) at Alert, on a trial basis, for subsequent determinations of particulate-phase mercury. The lack of appropriate clean-room facilities and trained personnel at AES at this time has necessitated sending these samples to another laboratory (U. of Connecticut) for chemical analysis. Results for particulate-phase mercury concentrations at Alert are expected to be available before the end of the current fiscal year.

With funding from DIAND (Northern Contaminants Program/Arctic Environmental Strategy), we are currently assessing the suitability of the Tekran mercury vapour analyzer (Model 2537A) for possible future use in making TGM measurements in the Canadian Arctic. It is of considerable interest to investigate the temporal/seasonal variability of atmospheric mercury concentrations in the Arctic environment (initially at Alert). The laboratory-based testing and evaluation phase of the Tekran analyzer was successfully completed at AES over the summer months. A field trial was carried out in September 1994, during which 2 Tekran analyzers operated by AES were compared against the (traditional) manual measurement method, as performed by C. Lamborg (of W. Fitzgerald's group;University of Connecticut). Initial results from this field study (at a remote site in North-Central Wisconsin) appear to be very encouraging.
If resources permit, the Tekran analyzer will be tested at Alert during the winter of 1994/95.

During the spring of 1994, B. Schroeder was part of an Inter-national Expert Panel which was convened by a diverse group of institutions to review and evaluate the current state of knowledge regarding the role of the atmosphere in the environmental cycling of mercury. The report prepared by this panel was distributed in September 1994 (Ref. 4).

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NORTHERN CONTAMINANTS AIR MONITORING

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OBJECTIVE: To measure the occurrence of selected organochlorines and polycyclic organic hydrocarbons in the Arctic atmosphere for a period of several years thereby providing insight into sources, transport, transformation and surface exchange processes as well as data for validation of models of toxics pathways in the northern environment.

PROJECT DESCRIPTION:

Since January 1992, measurements of persistent organic pollutants including herbicides, pesticides, synthetic industrial compounds and polycyclic aromatic hydrocarbons(PAHs) have been made on a weekly basis in the Canadian and Russsian Arctic(Figure 1). This research was supported by the Arctic Environmental Strategy Northern Contaminants Greenplan Program and the Department of External Affairs.

In 1993, a hivolume air sampler placed at Alert(N.W.T.), Tagish(Yukon), C. Dorset(Baffin I.) and at the mouth of the Lena River on Dunay Island in Russia was used to collect particulate and gaseous fractions of these airborne pollutants on filters. The filters were subsequently extracted in organic solvents and analyzed for more than 80 organochlorines and for 20 PAHs by gas chromatographic techniques. The sampling schedule is shown in the following Table(the past ,light arrows and the future, bold arrows).

SITE	1992	1993	1994	1995	1996	1997
ALERT	<test>|<------------------------>|<-->					
TAGISH	|<------------------------>|<--|					
DUNAY I.		|<-------------->|<-------------->|				
C. DORSET		|<---->|<------------------------->|				
W. RUSSIA				|<------------------------------->|		

RESULTS

At Alert in 1992, 18 PAHs and 29 OCs plus many PCB congenors were measured. A principal component analysis of the PAH and OC data(not including PCB) showed that 9 components that explained 90% of the variance in the data set. The groupings are shown in Table 1.

COMPONENT	MAJOR CONSTITUENTS	MINOR CONSTITUENTS
1.	ppDDT, opDDT, ppDDE, ppDDD, MIREX	opDDE, opDDD, TOXAPHENE
2.	DIELDRIN, ENDOSULFAN HEPTACHLOR EPOXIDE	OXYCHLORDANE, TOXAPHENE, PCB118
3.	α-HCH	γ-HCH, PCA
4.	METHOXYCHLOR	TRICHLOROVERATROLE, PCB187, TOXAPHENE
5.	TOT-PAH PLUS CONSTITUENTS*	HEPTACHLOR, PENTA-CHLOROBENZENE
6.	OCTACHLOROSTYRENE	
7.	4-Cl-VER	
8.	TRIFLURALIN	
9.	ENDRIN	

* Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, BaAnthracene, Chrysene, BkFluorene, BaP, BeP, Iso-Pyrene, Dibenzoanthracene, Benzoperylene

These components actually indicate groups of substances that have similar seasonal cycles in the arctic troposphere. The seasonal cycle is affected by seasonal variations in sources, in transport to the arctic, in removal from the atmosphere and in atmosphere-Earth surface exchange. In Figure 2, the seasonal cycle of the first six components is illustrated using representative constituents at Alert, namely, total DDT(op and pp), dieldrin, total HCH(α plus γ), methoxychlor(MeOCl), Total PAH and Octachlorostyrene.

The chlordanes had anomalously high field blanks until June of 1992. Therefore only results for the last half of 1992 can be shown(Figure 3). The cis-chlordane peaks in summer over trans-chlordane. This observation is consistent with shorter term observations in the Arctic made previously in the Arctic and likely reflects a relatively greater rate of degradation of trans- over cis- in the summer.

Toxaphene is a problem pesticide in the Canadian arctic being responsible for the closure of commercial fisheries in some large lakes in the Yukon. At Alert(Figure 3) it has a peak early in the year between March and early July and a minimum in late summer fall and winter. Prelimary data from Tagish and Alert(Bailey et al, 1994) from January to May 1994(Figure 4) show that Alert and Tagish are not very different and that the Alert observations in 1993 are reproducible in 1994.

Finally, Figure 5 shows that the seasonal variation of the ratio of γ-HCH/α-HCH peaks in May and June. Lindane(γ-HCH) is the active pesticide while α-HCH is its degradation product as well as a contaminant in technical lindane(~55-70% α and 10-18% γ-HCH) which in former times was widely used when awareness of the deleterious effects of persistent organic substances in the environment was poor. Today, lindane rich mixtures are used. The spring peak likely reflect fresher mixtures of HCH as a result of spring time applications and tilling.

Publications, Presentations and Reports:

Barrie, L. A., T. Bidelman, D. Dougherty, P. Fellin, N. Grift, D. Muir, B. Rosenberg, G. Stern and D. Toom, 1993, Atmospheric toxaphene in the high Antic, Chemosphere, 27, 2037-2046.

Bailey, R., L. Barrie, D. Dougherty, P. Fellin, B. Grift, D. Muir and D. Toom, 1994, Preliminary measurements of PCCs in air at Tagish Yukon, Proceedings of the Yukon Contaminants Committee Workshop, Feb 1994, Whitehorse Yukon.

Fellin, P., L. Barrie, D. Dougherty, D. Muir, N. Grift, L. Lockhart and B. Billeck, 1993, Air monitoring at Alert: results for 1992 for organochlorines and PAH's Proc. In Symp. "Ecological Effects of Antic Airorne Contaminants", October 4-8, Reykjavik, Iceland, Eds. Christie and Martin, USA CRREL Rep. 93-23.

Fellin, P. et all Technical and Operating Manual for The Canadian Antic Air Toxics Network, Concord Environment Report, J3034.

NORTHERN CONTAMINANTS NETWORK

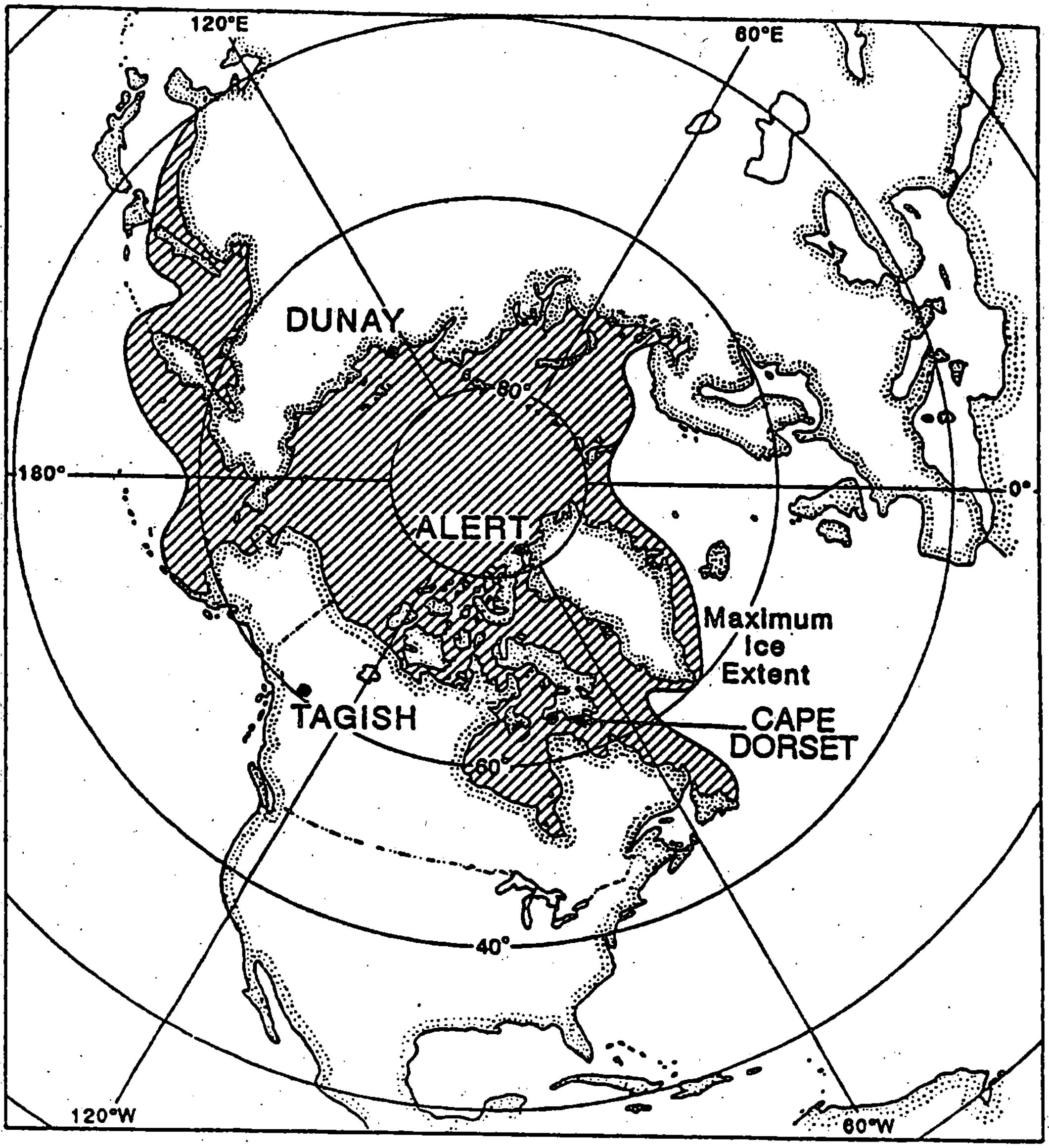


Figure 1

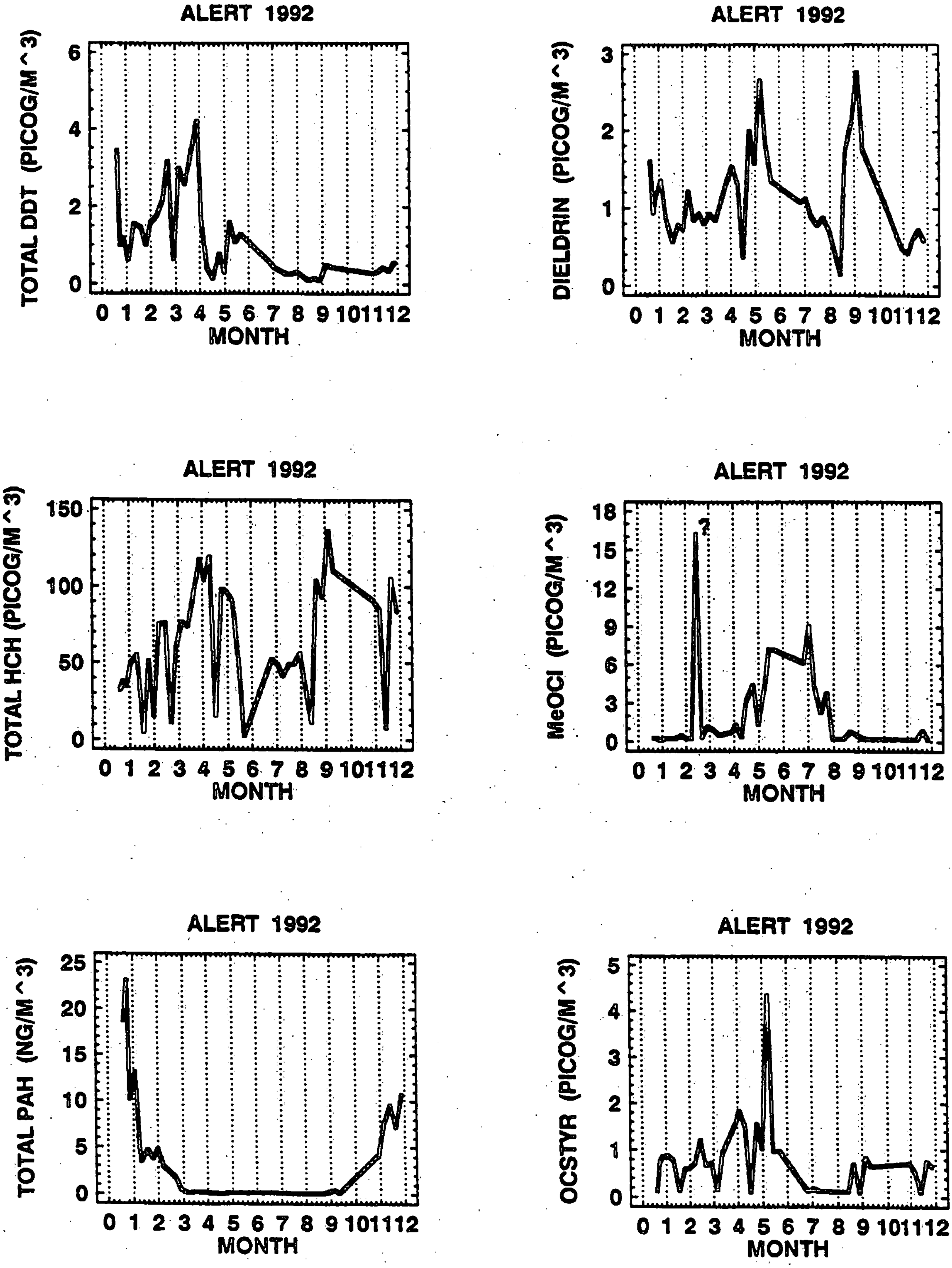
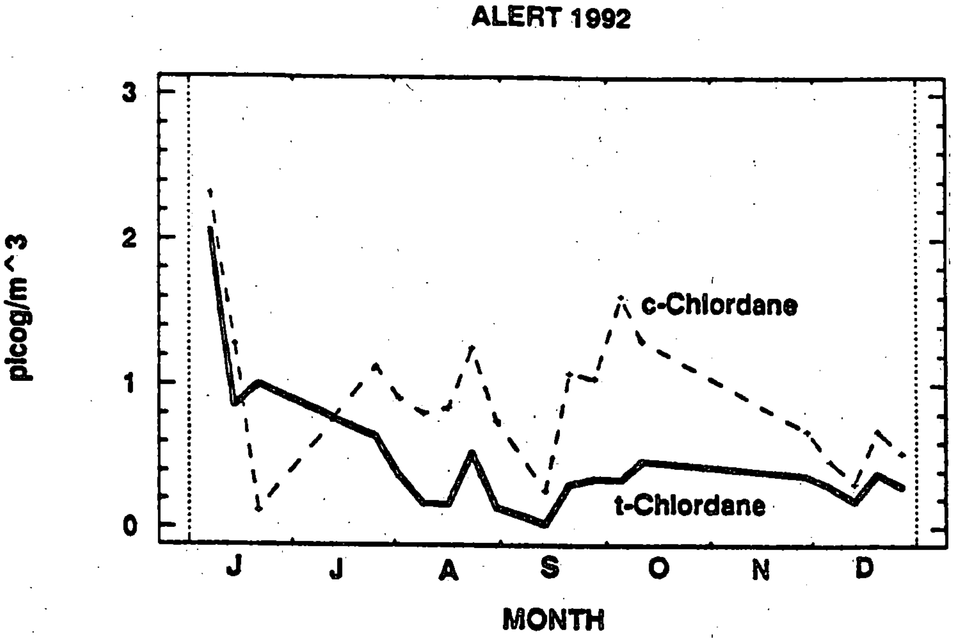

ALERT 1992
TOTAL DDT (PICOG/M^3)
0
2
4
6
0 1 2 3 4 5 6 7 8 9 10 11 12
MONTH
ALERT 1992
DIELDRIN (PICOG/M^3)
0
1
2
3
0 1 2 3 4 5 6 7 8 9 10 11 12
MONTH
ALERT 1992
TOTAL HCH (PICOG/M^3)
0
50
100
150
0 1 2 3 4 5 6 7 8 9 10 11 12
MONTH
ALERT 1992
MeOCl (PICOG/M^3)
?
0
3
6
9
12
15
18
0 1 2 3 4 5 6 7 8 9 10 11 12
MONTH
ALERT 1992
TOTAL PAH (NG/M^3)
0
5
10
15
20
25
0 1 2 3 4 5 6 7 8 9 10 11 12
MONTH
ALERT 1992
OCSTYR (PICOG/M^3)
0
1
2
3
4
5
0 1 2 3 4 5 6 7 8 9 10 11 12
MONTH

Figure 2


ALERT 1992
picog/m^3
3
2
1
0
c-Chlordane
t-Chlordane
J
J
A
S
O
N
D
MONTH

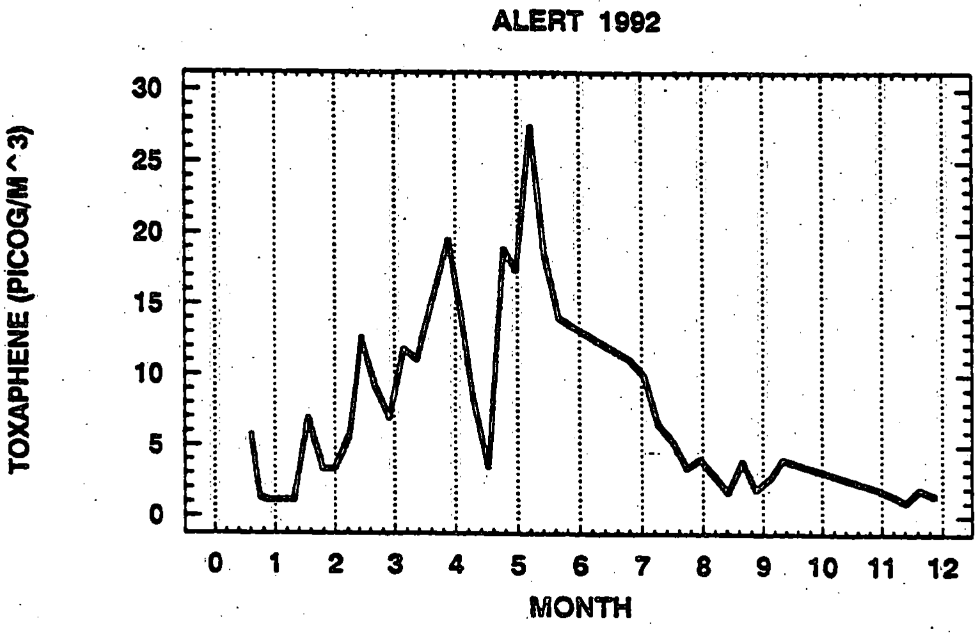

ALERT 1992
TOXAPHENE (PICOG/M^3)
30
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8
9
10
11
12
MONTH

Figure 3

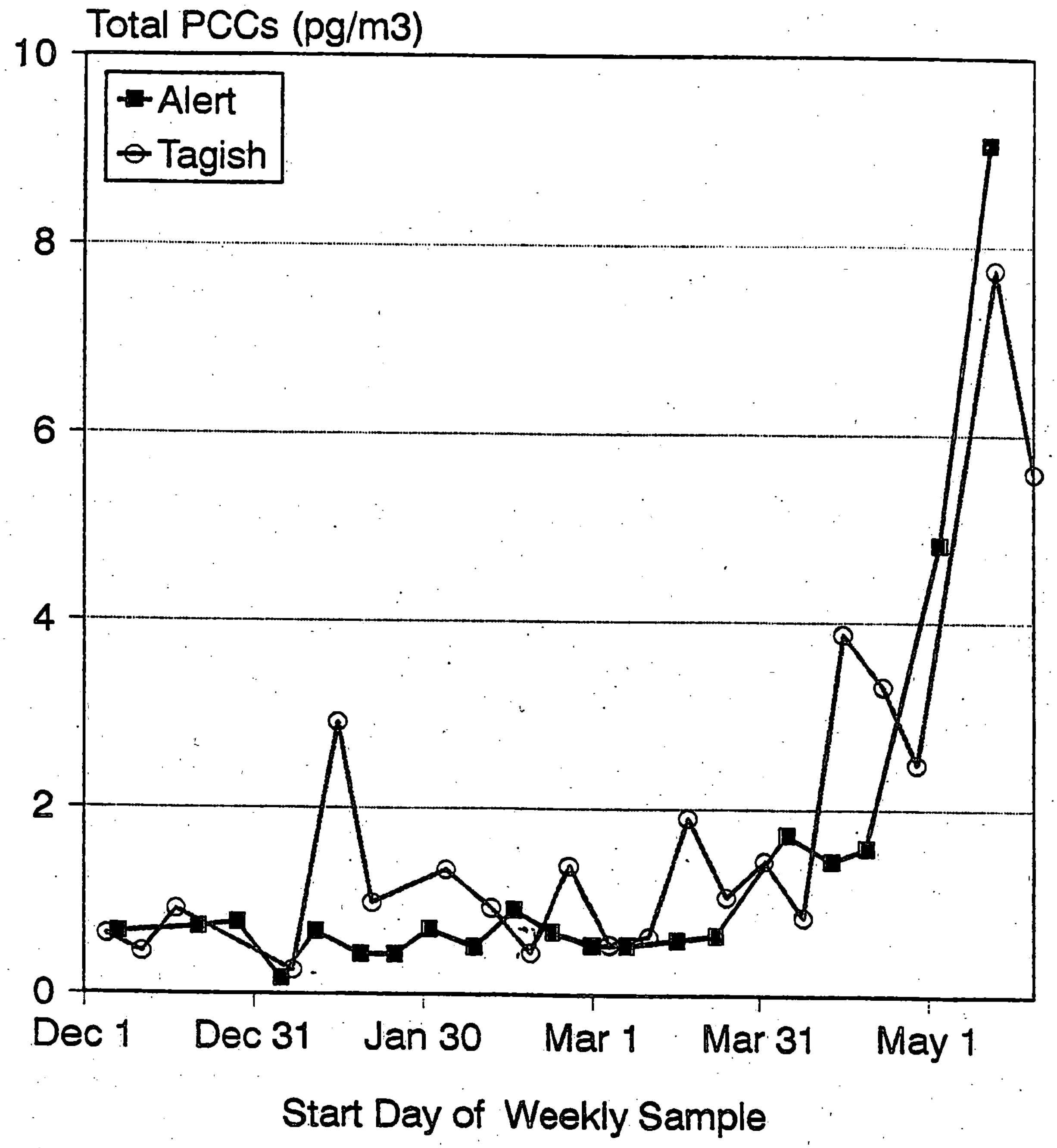


Figure 4: Air Concentrations of Total PCCs at Tagish, Yukon and Alert , NWT (Dec 1992 - May 1993)

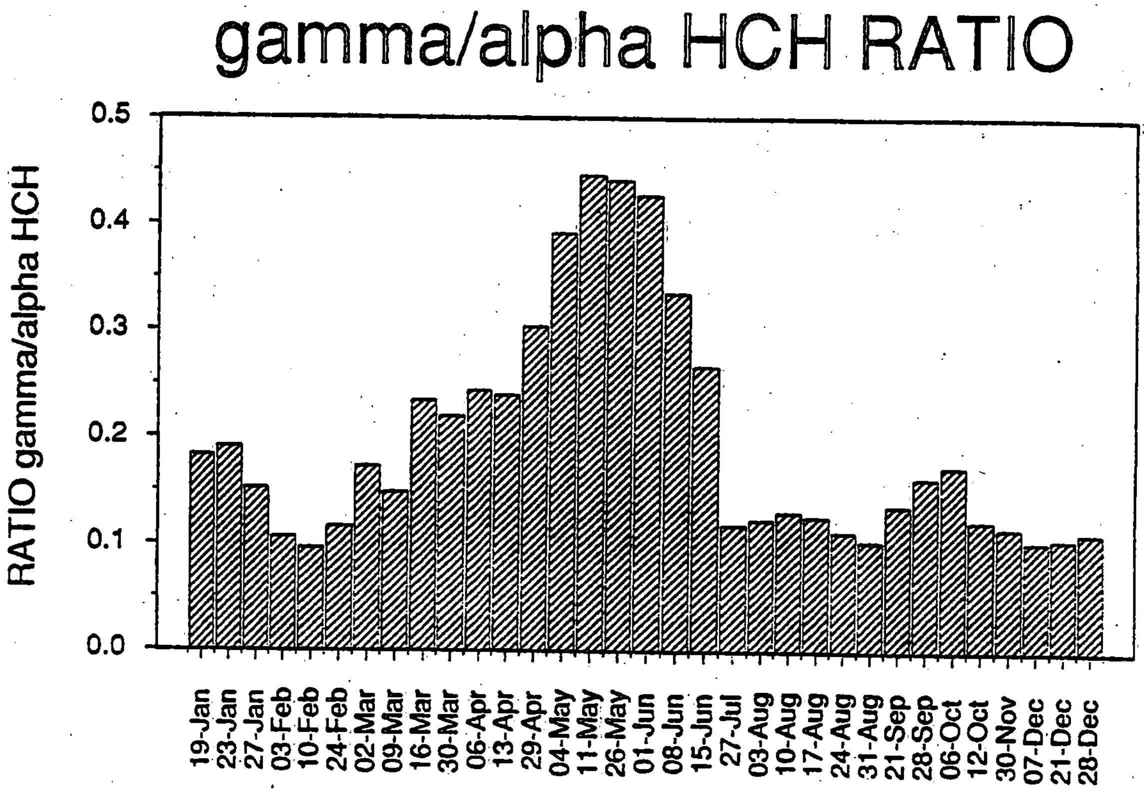

gamma/alpha HCH RATIO
RATIO gamma/alpha HCH
0.0
0.1
0.2
0.3
0.4
0.5
19-Jan
23-Jan
27-Jan
03-Feb
10-Feb
24-Feb
02-Mar
09-Mar
16-Mar
30-Mar
06-Apr
13-Apr
29-Apr
04-May
11-May
26-May
01-Jun
08-Jun
15-Jun
27-Jul
03-Aug
10-Aug
17-Aug
24-Aug
31-Aug
21-Sep
28-Sep
06-Oct
12-Oct
30-Nov
07-Dec
21-Dec
28-Dec

Figure 5

MODELLING OF AIR TOXICS

Ann C. McMillan

Introduction:

The movement of toxic chemicals in the atmosphere is a concern at all time and space scales. Instantaneous releases of large amounts of toxic chemicals may be fatal to those near by. Exposure over a lifetime to a contaminated diet elevates levels of some chemicals in the bodies of the Inuit even though emissions of these chemicals may be hundreds or thousands of kilometres away.

In order to develop and assess management strategies to deal with toxic chemicals, models can give insight into the physical and chemical properties involved, the source/receptor relationships and the probable consequences of various control activities. There are as many applications for modelling in describing air toxics as in all other air quality issues combined. It is the objective of ARQI to provide modelling systems to allow for a range of applications by a variety of clients. Our clients so far include the Regions, the Department of Indian and Northern Affairs, the Atomic Energy Control Board, Health Canada and CMC.

Clearly it is not possible to address all issues at once. The strategy being used is to use existing approaches and models wherever possible and to develop new techniques and models for selected priority problems only. A schematic of the needs and the ongoing modelling effort follows and indicates the type of work ongoing. A sampling of some of this goal-oriented, niche research is presented in the following.

In addition to air toxics modelling, the back trajectory package routinely available has been used extensively to interpret the measurements of air toxics.

In order to support modelling of air toxics, emissions inventories are required. Such inventories have not been compiled locally, regionally, nationally or globally. For some classes of compounds such as pesticides, even the methodologies required to compile such inventories have not been developed. AES is supporting the development of a Canadian Global Emissions Inventory Center in cooperation with ORTECH in order to move forward in this area.

OVERVIEW OF MODELS AVAILABLE

Space scale	**Model Description**
short space scale	AQPAC (available) Short range emergency response model which runs quickly on a PC. Can also be run to do assessment work for longer time periods.
	MC2 (available but must be coupled with chemical modules) Canadian Community meso scale model. Designed for incident simulation.
	BLFMESO (under development) Meso scale model designed for emergency response. Work station compatible.
	CANERM (available) Large scale emergency response model for short time scales.
long space scale	Global tracer model (available) For transport over long distances (eg to the Arctic). Can run on observed data or on spectral model output.

Note: Research is also underway on emissions inventories and modelling, modelling of exchange processes, effects of topography, boundary layer parameters, and turbulent mixing.

MIXING HEIGHT MODELS FOR STABLE AND UNSTABLE ATMOSPHERES

C. S. Matthias

The mixing height is the thickness of a turbulent layer of air between the surface and calmer air aloft. The mixing height is important for the calculation of air pollution concentrations and for estimating convective turbulence intensities. It is an important input variable for both short term and long term concentration models.

The most common model for calculating daily maximum mixing heights was published in the mid 1960's by George Holzworth. It is valid only during unstable or convective conditions during which the upper air temperature profile is being warmed from below by surface heating. The data required are daily upper air soundings and hourly surface temperature. The results have been used to generate climatological statistics. Of more importance is their use in regulatory air pollution models for the calculation of hourly concentrations. For optimum results, the atmosphere should be nearly homogeneous on a regional scale.

Model shortcomings are as follows:

(1) Model accuracy is not well defined, even for ideal conditions.

(2) If the morning upper air potential temperature profile is near neutral, a small error in hourly surface temperature makes a large difference in calculated mixing height.

(3) Advection of a warmer air mass to the station causes an overestimate of mixing height.

(4) Advection of a colder air mass to the station causes an underestimate of mixing height.

(5) The upper air sounding is an instantaneous description of the T - z conditions in the air. Similarly, the surface temperature is a short time average (1 minute). The model would work better with an ensemble average or a longer term mean.

(6) Because the radiosonde network is sparse, the spatial resolution of maximum mixing height across the country is low. It would be very useful if surface data alone (dense network) could be used to generate mixing heights.

(7) Little work has been done to adapt these schemes for finding hourly mixing heights.

When surface heating becomes less important than shear stress in generating turbulence, the boundary layer is generally statically stable - as at nighttime. Various formulae have been developed for the nighttime or minimum mixed layer height but comparisons between theory and experiment show much scatter. This is primarily due to the difficulty in representing a non-stationary and inhomogeneous boundary layer with a simple diagnostic model. Estimates of model bias and standard deviation will be made.

Most effort will concentrate on the unstable boundary layer. 'Measured' mixing heights are made with morning and afternoon measured profiles. Various analytical schemes for the mixing height will be compared to these measurements. The most elaborate scheme contains net radiation and surface energy balance models.

STUDIES ON MESOSCALE METEOROLOGICAL PROCESSES OVER COMPLEX TERRAIN

Ying Qi

In this presentation, studies on mesoscale meteorological processes are overviewed and it is noticed that mesoscale processes over complex terrain depend on larger-scale airflows. When the larger-scale airflow is stable,the mesoscale process over terrain is mainly induced by orographic forcing. When the larger-scale flow is in the state of instability and a synoptically-induced mesoscale system appears, the mesoscale process over terrain actually depends on the effect of topography on the synoptically-induced mesoscale system and sometimes it can be very complicated and is often related to orographically-forced flows. Until now, we have not known much about it. In fact, even for orographically-forced flows, the knowledge is also quite finite. Major patterns in the mesoscale orographically-forced flow should be composed of waves, vortices and turbulence, so it is one of the most complicated flows in fluid mechanics. Until now, many phenomena in the flow are still unknown. However, understanding the complicated flow is one of the prerequisites for us to analyze or predict air pollutants over complex terrain.

In this presentation, one way to investigate the complicated flow over mesoscale terrain is proposed. It is pointed out that the patterns in orographically dynamically-forced flow, thermally-forced flow and the atmospheric boundary layer are different. Therefore, the mechanism of formation for the complicated flow can be studied through discussing the interaction among different patterns in orographically dynamically and thermally forced-flows and the atmospheric boundary layer.

Based on this consideration, we did a lot of numerical experiments respectively for different topographies by our mesoscale numerical model with second-order turbulent closure to discover some universal mechanism of formation for the complicated flow over mesoscale terrain:

(1) Turbulent mixing in the atmospheric boundary layer,particularly in the convective boundary layer always suppress the development of mountain waves in orographically dynamically-forced flows.

(2) Thermal circulations forced by topography are favourable to the transition from vertical waves to interface waves, particularly favourable to the development of the interface waves at the top of the convective boundary layer or residual layer and can even cause the interface waves to break up. In some situations, thermal circulations can also augment the development of vortices in dynamically-forced flows, such as a blocking vortex.

(3) Mountain waves and vortices in orographically dynamically-forced flows can affect thermal circulations principally by advecting the thermal source formed in the atmospheric boundary layer as well as by advecting momentum.

(4) Turbulent structure strongly depends on the patterns in mesoscale terrain flow.

AQPAC AND MESOSCALE MODELLING

S.M. Daggupaty

AQPAC

The air quality package of programs for environmental emergency response has been transferred to private industry and it is being marketed all over the world. One of the counties of Ohio State, USA is using PC-AQPAC for air quality emergency response. The package is known for its use in planning, mitigation, response and clean-up operations of emergencies associated with hazardous chemical spills into the environment.

Fruits of its very modest funding over the past few years are successfully beginning to show by the way of revenue generation to the Government of Canada.

The Candu Nuclear reactor operators group (COG) initiated a dispersion model validation study. Several models are being examined against a field experimental data set of tracer releases over a forest region. We are participating in the study with our AQPAC's plume dispersion model.

Mesoscale Modelling

The paper describing BLFMESO (Boundary Layer Forecast Model for Mesoscale Dispersion Studies) is in press and is to be published in the Journal of Boundary Layer Meteorology.

Presently the model is undergoing modifications to be operational on the workstation for any user opted window region of the North American Continent. It is also being coupled with regional finite element model's forecast data, for time-dependent boundary conditions. Periodic updating of mesomodel data with objectively analyzed data will aid in the long term simulation studies. This feature of BLFMESO with an air pollution module such as CALGRID (California Air Quality Model) and UAM (Urban Airshed Model) will be of use to study impact of air pollution on regions like Hamilton Harbour and others in the vicinity of Great Lakes.

The mesoscale air quality project is being funded jointly by AECB, Health Canada and Emergency Response Division of CMC/DOE.

EMISSIONS INVENTORIES

Arthur Y.F. Li

The Canadian Global Emissions Inventory Center has been participating in a number of international activities, such as Global Emissions Inventory Activities (GEIA), to establish global inventories of SO_x, NO_x, VOCs, lead, and organochlorine pesticides.

An air/soil exchange model has been developed under contract to ORTECH. This model has been used to estimate annual average emissions factors for some 96 pesticides following their application by spraying, soil incorporation or in furrow placement with fertilizer or seeds. We are going to calculate the global emissions of selected pesticides in the near future using this model and a variety of other data.

Three Dark Figures
Making the Weather
In Folk, in Myth, in Legend,
A threefold test.
Shiva, Vishnu, Brahmin.
Father, Son, Holy Ghost.
Body, Mind, Spirit.
Triune, Triumvirate, Tribunal.
One is Isolate
Two is divisive
Three is Peace.
Three is Torment.
Three is Potent.
Power, Power, Power.
Air, Fire, Water.
Three Dark Figures,
Making the Weather.

Ron Baird, Sculptor