Atmospheric Contribution to the St. Lawrence River Pollution (Québec, Canada): On-Going Research

by

Laurier Poissant, Jean-François Koprivnjak and Bruno Harvey

Atmospheric Environment Directorate
Environment Canada
Québec Region

Extensive abstract

Introduction

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.

To achieve these objectives three measurement sites were deployed in rural areas along the St.Lawrence river, namely at Villeroy, Saint-Anicet and Mingan. Villeroy has started the monitoring of chemical airborne toxic in 1992 and Saint-Anicet and Mingan in 1994.

The aims of this paper are to present the results of the first year of operation (1992) at Villeroy (Qc) and to point out the source-receptor relationship of lindane and its conceptual fate modelling in Québec.

Methods

The station of Villeroy is located in a rural setting along the St.Lawrence river between Trois-Rivères and Québec city (46°26' North latitude and 71°56' West longitude) (Fig.1). The instruments are installed on a plate-form (30'X30') located at a height of 1 meter. Air pollution and meteorological instruments are both used (Table 1). The data-set from 1992 included inorganic and organic species in both components (wet and dry) (Table 2). Some of these species are toxic and some others not. The latter are used as complementary species for better characterization of the air masses carrying the toxic. Analytical procedures are described elsewhere (Barbeau *et al.* 1991 and El Khoury *et al.* 1991).

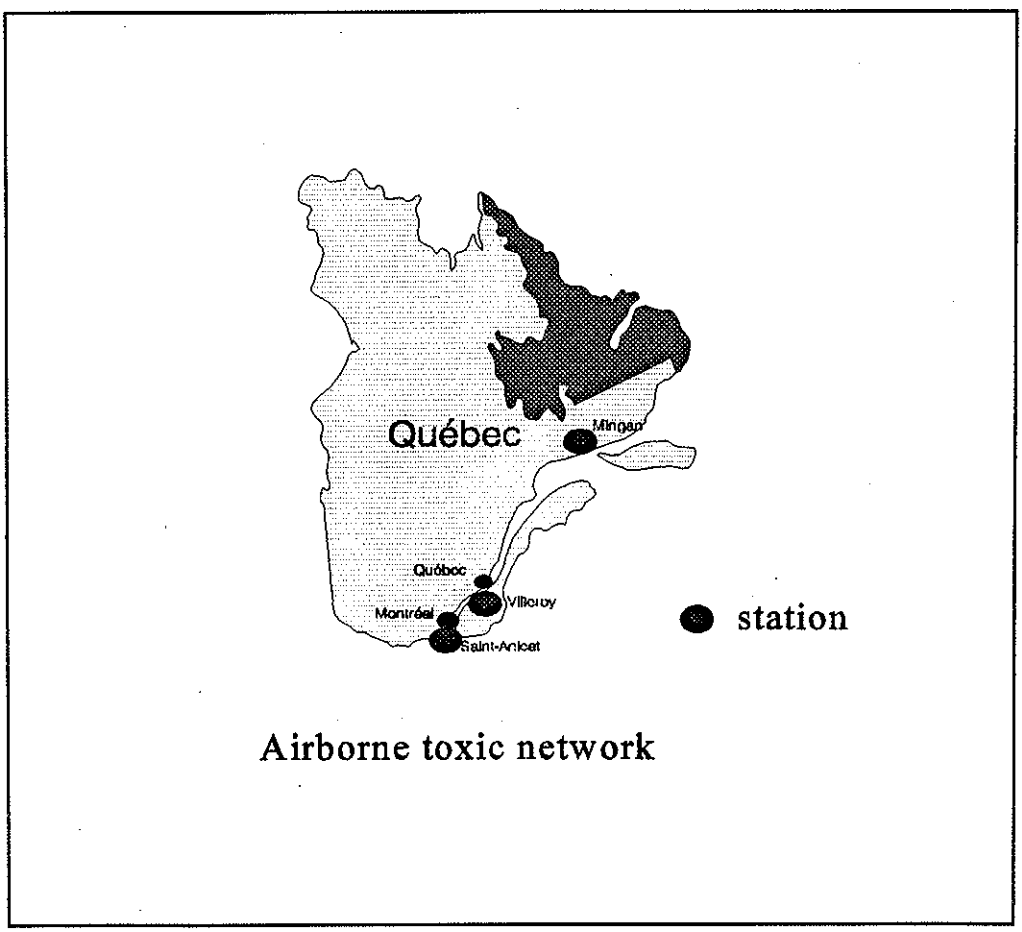


Figure 1- Airborne toxic network along the St.Lawrence River

Table 1-List of instruments at Villeroy

Meteorological	Chemical
precipitation rain- gauge	Hi-Vol PS-1 (organic (dry))
Anemometer	MIC B-100 (organic (wet))
Hygrometer	Hi-Vol (inorganic (dry))
Thermometer (3 levels)	MIC B-200 (inorganic (wet))

Table 2-List of parameters, instruments and their limits of detection

(inorganics)

Parameter	Instrument	Limit of detection
pH	Orion	0.01 unit
Conductivity	Cole Parmer	0.1 µS/cm
Calcium	Atomic Abs. (flamme)	0.01 ppm
Magnesium	" "	0.01 ppm
Potassium	" "	0.01 ppm
Sodium	" "	0.01 ppm
Zinc	" "	0.01 ppm
Sulphate	(Dionex I.C.)	0.03 ppm
Nitrate	(Dionex I.C.)	0.01 ppm
Chloride	(Dionex I.C.)	0.01 ppm
Cadmium	Atomic abs (graphite): Perkin-Elmer 305	0.02 ppb
Copper	" "	0.04 ppb
Lead	" "	0.05 ppb
Selenium	" "	0.05 ppb

Table 2- (Rest)

(Organics)

Parameters	Instrument	Limit of detection
Phenanthrene	GC-FID	100 ng
Anthracene	GC-FID	100 ng
Fluoranthene	GC-FID	100 ng
Pyrene	GC-FID	100 ng
B(a)P	GC-FID	100 ng
BPC 3	GC-ECD	0.4 ng
BPC 26	GC-ECD	0.4 ng
BPC 28	GC-ECD	0.4 ng
BPC 66	GC-ECD	0.4 ng
BPC 77	GC-ECD	0.4 ng
BPC 126	GC-ECD	0.4 ng
BPC 169	GC-ECD	0.4 ng
BPC 180	GC-ECD	0.4 ng
α-BHC	GC-ECD	0.4 ng
γ-BHC	GC-ECD	0.4 ng
HCB	GC-ECD	0.4 ng
γ-Chlordane	GC-ECD	0.4 ng
p,p' DDE	GC-ECD	0.4 ng
p,p' DDT	GC-ECD	0.4 ng
Mirex	GC-ECD	0.4 ng

1- Precipitation has been analyzed by GC-MS
(Limit of detection 0.8 ng)
2- Confirmation done by GC-MS: limit of detection 0.8 ng

3- Results and discussion

1992 data-set

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

Inorganics

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	115.9	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 on 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	19.9	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

Inorganics

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 et al. (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)

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.

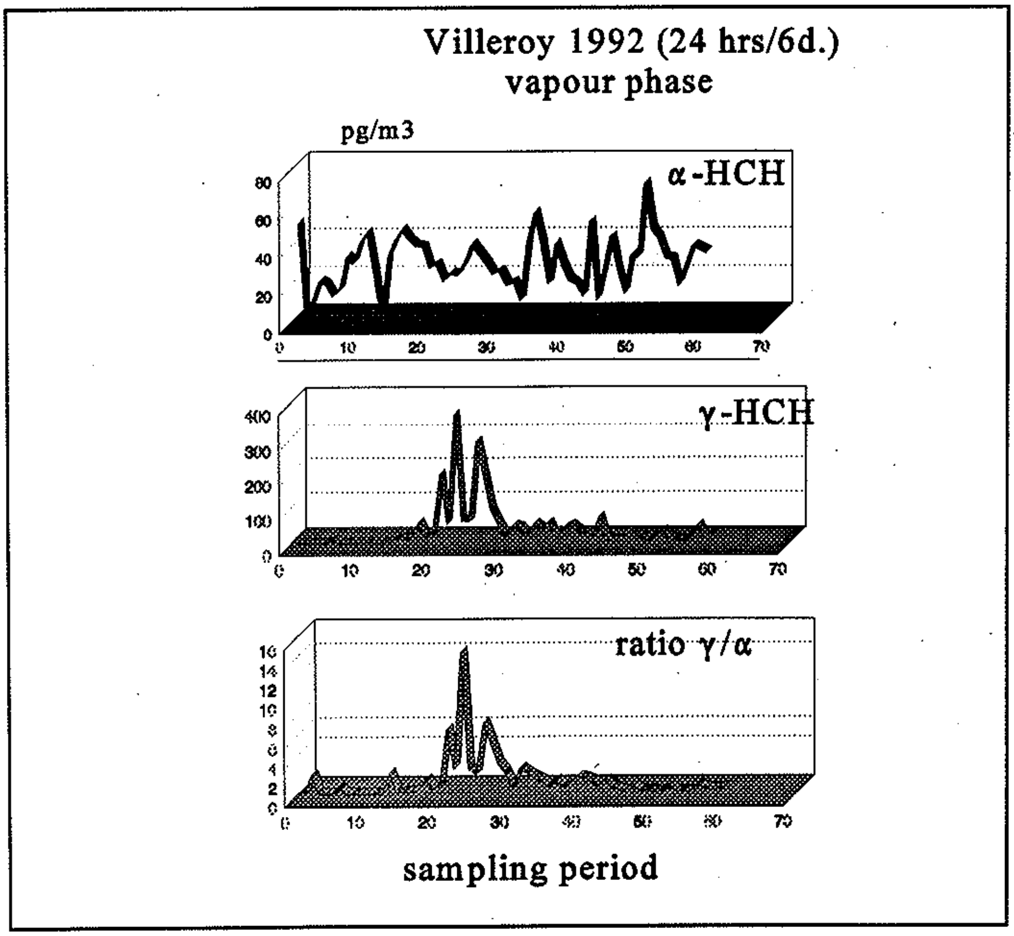


Figure 2- Time series of α and γ-HCH (pg/m3) and their ratio measured at Villeroy (Qc) in 1992

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

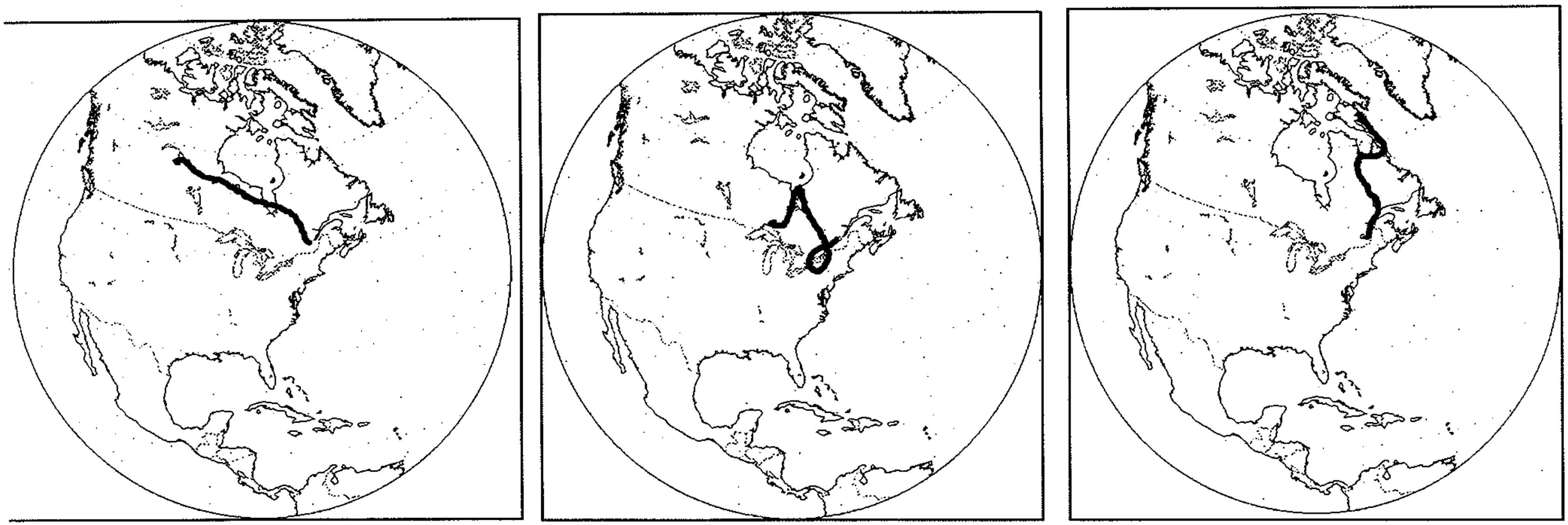
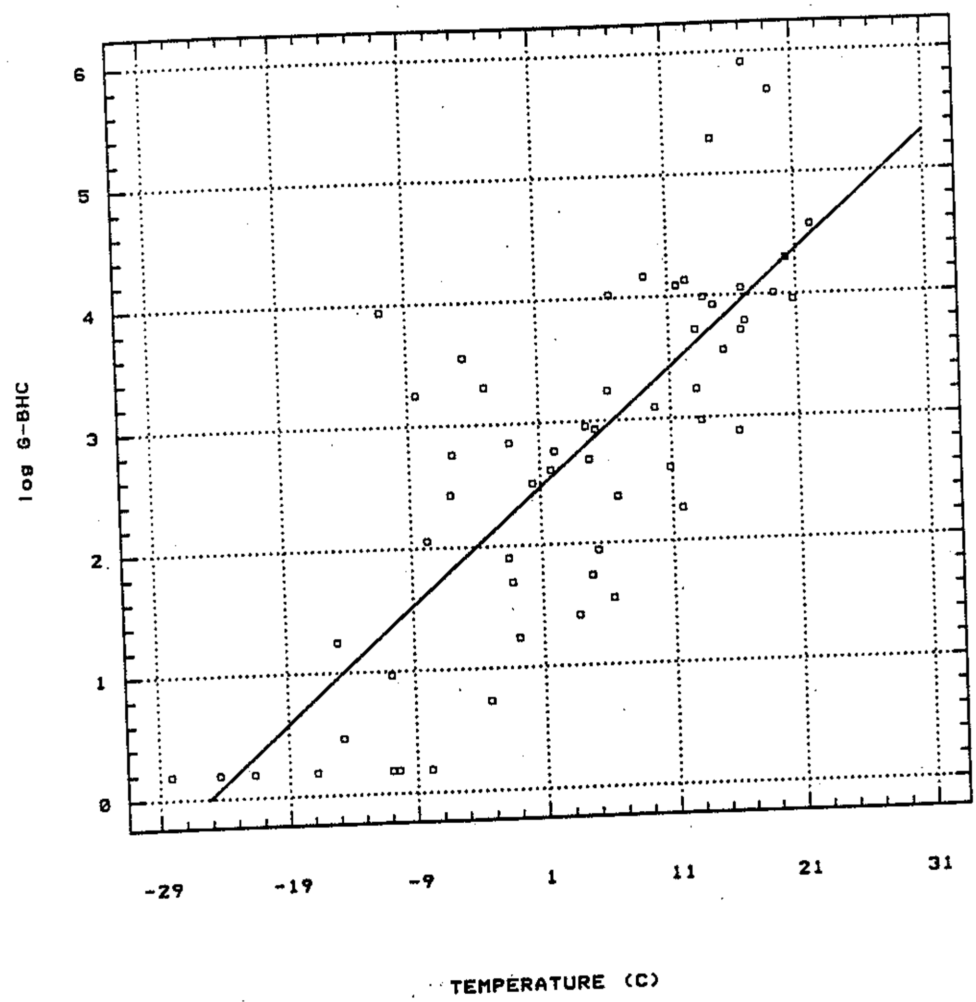


Figure 3- Five-day-back-trajectories (925mb) at Villeroy
before, during and after the highest measured concentration (May 20th,1992)

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).



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:

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 Québec, 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.

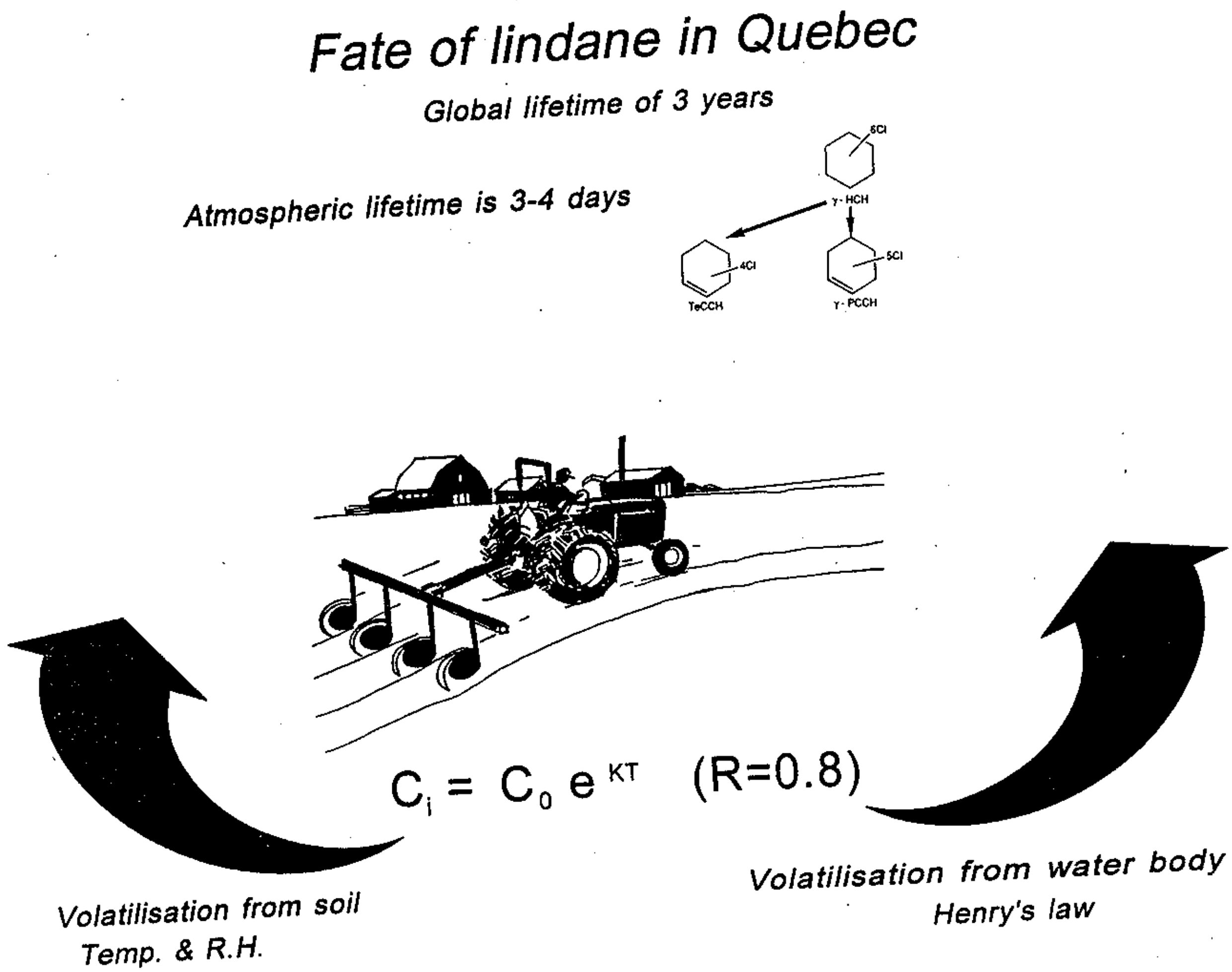


Figure 5- Conceptual model of atmospheric lindane in Québec

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

Barbeau C., Turcotte J., Fraser E. et Paré S. (1991) Échantillonnage et analyse des composés inorganiques toxiques aéroportés (bassin hydrographique du fleuve Saint-Laurent), Département de chimie, Université Laval, 58 p.

Bidleman T.F. (1988) Atmospheric processes: wet and dry of organic compounds are controlled by their vapour-particle partitioning, Environ. Sci. Technol., Vol. 4, p 361-367.

El Khoury M. et Bertrand M.J. (1991) Apport atmosphérique de certains composés organiques toxiques dans la composition chimique du fleuve Saint-Laurent et quelques-uns de ses tributaires- Protocole d'échantillonnage et d'analyse, Département de chimie Université de Montréal, 42 p.

Poissant L. and Koprivnjak J.F. (1994) Reference guide on organic and inorganic airborne toxic contaminants. Scientific Report, Services scientifiques, Direction de l'Environnement Atmosphérique, Environnement Canada, 105 p.

McConnel, L., Cothan W.E. et Bidleman T.F. (1993)- Gas Exchange of Hexachlorocyclohexane in the Great Lakes, Env. Sc. & Technol., 27, 1304-1311.

Schroeder W.H., Dobson M., Kane D.M. et Johnson N.D. (1987)- Toxic trace elements associated with airborne particle matter: A review, APCA, Vol 37, no 11 p 1267.