ATMOSPHERIC DEPOSITION OF SELECTED CHEMICALS IN CANADA

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Abstract

The deposition of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCs) has been observed in the rainfall and some snow samples throughout Canada since before 1980. The concentrations and areal fluxes of these compounds indicate that the atmosphere is perhaps the most important source of such substances in the aquatic and terrestrial parts of Canada as well as elsewhere. Results of investigations with PCBs, the hexachlorocyclohexanes, dieldrin, DDT and hexachlorobenzene in rain between 1983 and 1986 are presented. Estimations of the loadings arising from the observed wetfall concentrations are made and continent-wide similarities in concentrations and loadings are noted. Rainfall concentration trends in the Great Lakes area in particular are described.

Keywords: rain, atmosphere, pollution, organochlorine, pesticide, PCB

DÉPÔT ATMOSPHÉRIQUE DE CERTAINS PRODUITS CHIMIQUES AU CANADA

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Résumé

Le dépôt de biphényles polychlorés (BPC) et de pesticides organochlorés (OC) a été observé dans les échantillons de pluie et dans certains échantillons de neige, partout au Canada, dès avant 1980. Les concentrations et les flux surfaciques de ces composés montrent que l'atmosphère est peut-être la source la plus importante de ces substances dans les milieux aquatiques et terrestres du Canada et dans d'autres endroits. On présente les résultats de recherches sur les BPC, les hexachlorocyclohexanes, la dieldrine, le DDT et l'hexachlorobenzène dans les pluies, entre 1983 et 1986. On procède à des estimations des charges provenant des concentrations observées dans les précipitations et, enfin, on note les similitudes dans

les concentrations et les charges à l'échelle du continent. L'évolution des concentrations pluviales dans la région des Grands Lacs fait l'objet d'une description particulière.

Mots-clés : pluies, atmosphère, pollution, organochloré, pesticide, BPC

Introduction

Toxic chemicals from the atmosphere have been noted in environmental samples for many years dating back to the mid '60s [1-3]. Most of the reports pertain to persistent organochlorine pesticides in common use up to the late '70s and early '80s. Even now, however, compounds which were banned in Canada and the United States continue to be observed in rain and other atmosphere related samples.

In Canada, official interest in toxic organic compounds in the atmosphere started about 1975 following the observation of some 10-100 ng PCBs/L in the rainfall of southwestern Ontario [4]. Sampling of rain and snow undertaken by the author in the Great Lakes basin found similar levels of PCBs as well as a number of other organochlorine compounds during the period 1976-7 [5]. Investigators on the U. S. side of the lakes also found PCBs in rain and snow and reported these at the 1976 conference of the International Association for Great Lakes Research and subsequent publications [6,7].

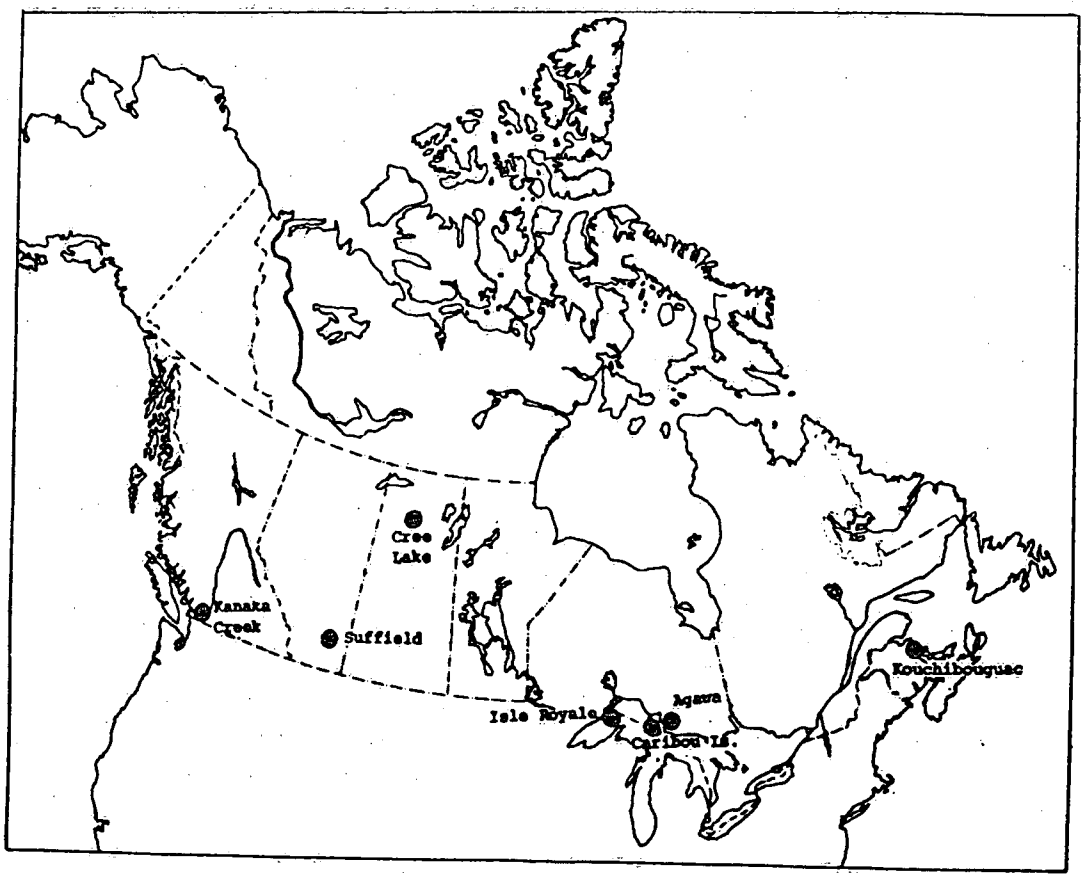
Following these earlier activities, Environment Canada modified an existing sampler and situated them at approximately twenty locations across Canada. The results from this network were only semi-quantitative since the collection area of the sampler did not generally permit samples of sufficient size to be obtained for the analytical detection limits of the time. Where sufficient samples were obtained, however, they tended to confirm the pattern and levels of those observed earlier in the Great Lakes region. Results were reported at an earlier ACS meeting and published as a government report [8]. The results reported here are a continuation of this concern over atmospherically transported and deposited organic chemicals in the Canadian environment.

Experimental

A consequence of the earlier efforts was the development of a wetfall-only rain sampler specifically designed for collection of organics. A description of its constructionand the associated analytical procedures and recoveries have been reported elsewhere [9]. Briefly, the collection funnel area is 0.2 m^2 (1 cm rainfall produces 2 L sample) and the lid opening is controlled by a sensor responding to wetfall precipitation. The sample passes through an all-teflon column containing XAD-2 resin and exits via a U-tube which serves to ensure that the resin remains wet at all times. All funnel surfaces in contact with the sample are teflon coated.

Based on earlier experiences with rain sampling, and recognizing the natural variability of environmental samples of this sort, it was decided to place these samplers as replicate sets of three at selected locations. During the period 1983-86, they were deployed at a number of sites across Canada. The locations of these sitings are indicated in Figure 1; not all stations were operated during all years. During 1985, Environment Canada also established a network around the Great Lakes with single samplers to enable them to provide better geographical coverage and respond to the requirements of the Great LAkes Water Quality Agreement (1978). These locations are indicated in Figure 2.

The samplers were installed early during each wetfall season (usually in


Cree Lake
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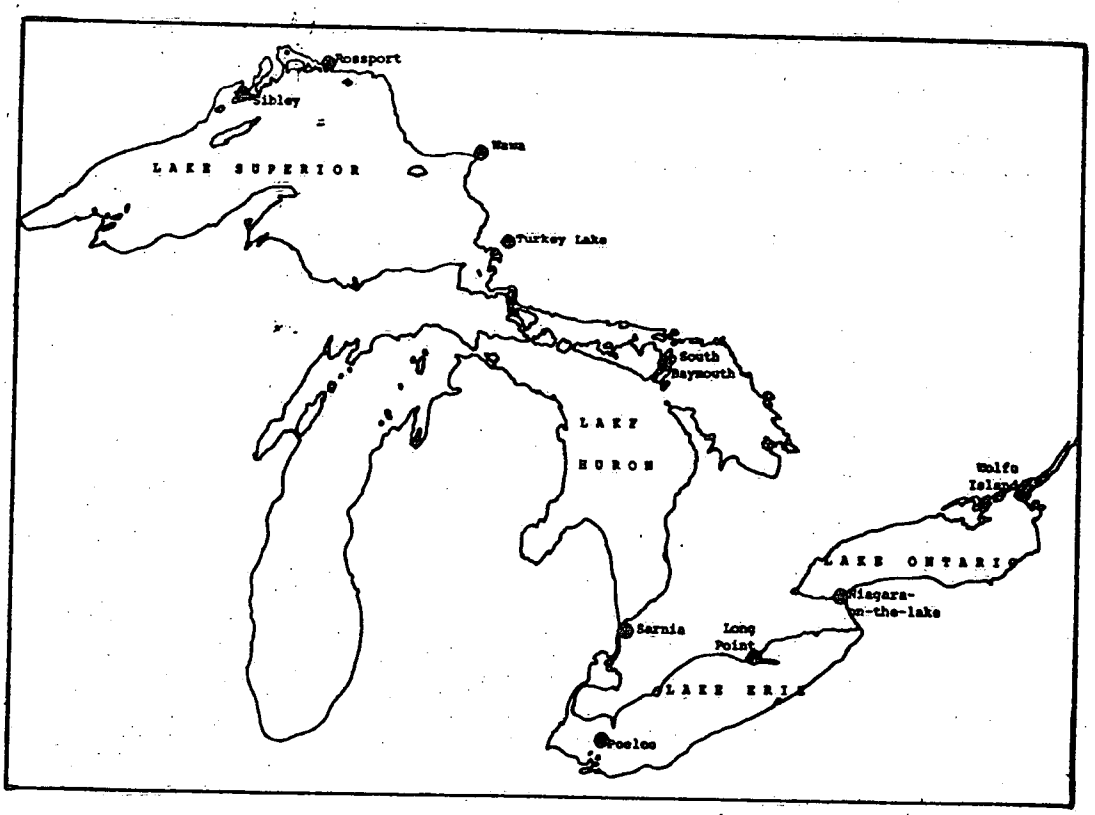
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South Baymouth
LAKE HURON
Wolfe Island
LAKE ONTARIO
Niagara-on-the-lake
Sarnia
Long Point
LAKE ERIE
Proctor

May) and were operated until near freeze-up (variously from the end of September to November) at locations remote from any probable sources of the analytes or evidence of urban activity. In the case of the replicate sampling stations, the sites were mainly in provincial or national parks but two were at research stations of the Atmospheric Environment Service and a third was on a Coast Guard lighthouse station. Samples in these cases corresponded to approximately 100 mm rain (20 litres) and this resulted in 3-5 replicated samples for the wetfall period. At the Great Lakes Network sites, the samplers were approximately 50% at federal or provincial agency locations (and manned by their technical staff), and 50% on private property usually well removed from any obvious activities or potential sources of the analytes. These latter samples were collected on a monthly basis for the rain season.

When the columns were removed from the samplers, they were immediately replaced, the exposed ones sealed with teflon caps and mailed to the author; the process was reversed with clean, conditioned columns. The resin was extracted and analysed for a range of organochlorine pesticides and PCBs; results are corrected for blank values determined for each batch of resin. Compounds investigated included those reported here and in addition: heptachlor, heptachlor epoxide, aldrin, the chlordanes, other forms of DDT and its transformation products, methoxychlor, the endosulfans, endrin and mirex. The detection limit for each of these was approximately 0.02 ng/L. A number of these were found in individual samples (in each of the replicates) but they were not consistently found at most sample locations nor throughout the sampling period; when observed, their levels were usually less than 0.5 ng/L. These other compounds are not reported on in this paper. Mention is made of the pesticide methoxychlor since it was found in most Lake Superior samples at concentrations exceeding 1 ng/L; it was not found, however, in samples elsewhere. It is also noted that the current analytical protocol aims at determining PCBs as individual congeners and has added the balance of the chlorobenzenes and is attempting to include the polynuclear aromatic hydrocarbons (PAHs). Some of the later two items are found frequently but no attempt to report on these is made here.

Results and Discussion

Mean annual concentrations of contaminants found at the various replicate station locations over the four years are presented in Table 1. These means were determined by weighting the various replicate sample means for the amount of rain falling during the sample period. The six compounds noted are the most commonly observed being found in at least 90 percent of the samples and being consistent within the replicate sample set for each collection period.

The relative concentrations of the six reported compounds are similar for all of the locations and years reported in Table 1. The most prominent ones are always the hexachlorocyclohexanes (alpha-HCH and lindane, the gamma-isomer) which together had an overall annual mean concentration of 21. ng/L. PCBs had the second highest concentrations of the six commonly observed contaminants and these are found at a mean annual level of 3.6 ng/L. This class of compounds, as well as the remaining pesticides, accumulate in fishes and other aquatic biota [10] and are responsible, in large part, for the present concern over the whole family of organochlorine pesticides. The remaining compounds from Table 1 have mean annual concentration levels of: dieldrin, 0.29 ng/L; DDE, 0.09 ng/L; and, hexachlorobenzene (HCB), 0.12 ng/L.

Table 1: Mean Annual Concentrations of Contaminants in Canadian Rain

	--L. Superior--		Kouch.	--Cree Lake--		Suffield	--Kanaka Cr.--	
	1983	1984	1984	1984	1985	1985	1985	1986
# Samples	8	9	4	3	3	3	3	3
	- - - - - - concentrations in nanograms per Litre - - - - - -							
a-BHC	26.	6.6	13.	6.5	22.	14.	29.	14.
Lindane	6.4	3.0	6.7	1.2	6.5	5.9	5.0	2.9
Dieldrin	0.43	0.79	0.27	0.38	0.04	0.10	0.27	0.02
pp'-DDE	0.13	0.13	0.02	0.07	0.04	0.03	nd	0.02
PCB's	6.0	2.9	1.1	3.1	3.5	5.5	nd	0.62
HCB	0.07	0.06	0.07	tr	tr	0.84	nd	0.03

§ - nd = not detected; tr = trace (below "detection")

It is interesting to also examine what the significance of these depositions might be with regard to loadings to the surface water and terrestrial parts of the ecosystem. This approach has the advantage of normalizing the comparisons to account for differences in amount of precipitation that falls at any particular location although neither it nor the concentration estimations can give any indication of the influence of intensity and number of events. These latter may be important factors governing the quantities of chemicals removed from the atmosphere via the rain. Table 2 presents these loadings for the replicate stations. The mean annual concentrations are assumed to maintain throughout the seasons with those for snow being ten percent of the levels in rain except for PCBs which are deemed to be the same as the rain [5]. The means for Lake Superior for 1983 and 1984 are derived by averaging the annual means found for the two sets of locations sampled in those years.

Table 2: Contaminant Loading Rates from Rainfall

	--L.Superior--		Kouch.	--Cree Lake--		Suffield	--Kanaka Cr.--	
	1983	1984	1984	1984	1985	1985	1985	1986
Rain (mm)	607	618	1050	307	274	208	1241	1651
Snow (mm)	214	263	377	176	207	98	56	34
	- - - - - - loadings in micrograms/m^2/annum - - - - - - -							
a-HCH	16.	4.3	14.	2.1	6.5	3.3	36.	22.
Lindane	4.0	1.9	7.3	0.39	1.9	1.3	6.2	4.8
Dieldrin	0.27	0.51	0.30	0.12	0.01	0.022	0.34	0.03
pp'-DDE	0.083	0.084	0.02	0.02	0.01	0.007	- -	0.03
PCB's	4.9	2.6	1.6	1.5	1.7	1.2	- -	1.0
HCB	0.04	0.04	0.08	- -	- -	0.18	- -	0.05

A similar pattern is seen for the loadings as was observed with the concentrations. A somewhat higher loading of the HCH isomers is observed on the west coast (Kanaka Creek) than at the other sites in the same years or at any of the sites during other years. This may be the consequence of high usage in parts of Asia [11] coupled with long range atmospheric transport; this sort of transport is indicated by studies on the global movement of the Chernobyl radionuclides in 1986 [12] and by deposition of the same materials in Japan [13] and Hawaii [14]. Studies by Peakall [15] and by Cohen and Pinkerton [16] have also demonstrated this possibility, at least for continental distances.

The deposition of the persistent organochlorine compounds mentioned has been a particular concern in the Great Lakes region. There, the Canada- U. S. Great Lakes Water Quality Agreement and the International Joint Commission that administers it have been concerned over the same compounds which are also found there accumulated in the adipose tissues of resident biota [10] including humans [17]. The rain concentrations for 1985 and 1986 are given in Tables 3 and 4, respectively and show no significant difference from those obtained at other locations in Canada and reported in Tables 1 and 2. As with the replicate sampling for these and other years, the pattern of compounds is qualitatively the same; alpha-HCH and lindane are found at greatest concentrations and the other four pesticides are observed at similar levels as at other locations.

Table 3: Mean Contaminant Concentrations in Great Lakes Rain: 1985

Lake:	Superior	Huron	Erie	Ontario
# Sites	4	2	2	2
# Samples	15	7	6	8
	- - - concentrations in nanograms per litre† - - - -			
a-HCH	25.	6.5	16.	11.
Lindane	4.6	2.0	5.5	3.7
Dieldrin	0.36	0.71	0.86	0.48
p,p'-DDE	tr	0.03	nd	0.06
PCBs	0.51	1.6	2.3	2.5
HCB	tr	0.06	nd	0.04

† - nd = not detected; tr = trace (below "detection")

Lake Superior data are the only ones collected for a sufficient period to consider possible trend determinations. The period 1983-6 does not show any consistent trend although the difference between the concentrations of the 1983-86 period and the earlier 1975-6 results [5] indicates a substantial drop for PCBs and DDT residues. This observation, however, is speculative since changes in analytical procedures between the present and those done earlier make comparisons dubious. The apparent lack of trend in the rain data is in contrast with that found in some biota from the Great Lakes [18]. While data for herring gull eggs, collected annually since 1974, show a steady downward trend with a half-life of clearance from this material of approximately six years, fish data are more ambiguous over the same period [19].

Table 4: Mean Contaminant Concentrations in Great Lakes Rain: 1986

Lake:	Superior	Huron	Erie	Ontario
# Sites	4	2	2	2
# Samples	16	9	10	10
	- - - concentrations in nanograms per litre† - - - -			
a-HCH	12.	5.9	7.1	11.
Lindane	4.9	3.9	4.7	5.9
Dieldrin	0.06	0.18	0.27	0.08
p,p'-DDE	0.02	0.15	0.28	0.26
PCBs§	0.82	0.34	0.41	1.4
HCB	0.03	0.22	0.04	tr

† - tr = trace (below "detection")
§ - high blank values

The compounds reported here represent a group for which sensitive analytical techniques are available — using a gas chromatograph with an electron capture detector. There are many other compounds potentially present in the atmosphere and potentially hazardous because of their known toxic effects and persistence. These latter should be the subject of method development followed by application in the field. In addition, research is sorely needed on the processes affecting the levels in the atmosphere including volatilization from the water compartment, washout by rain and snow, partioning between vapour and particle adsorbed states in the atmosphere and deposition of particle-bound contaminants. All of these affect the concentrations and ultimately the loadings to both the terrestrial and the aquatic environments; all of them are poorly understood.

References

1. Wheatley, G. A., Hardman, J. A.; Nature, (1965), 207, 486-487.

2. Risebrough, R. W., Huggett, R. J., Griffin, J. J., Goldberg, E. D.; Science, (1968), 159, 1233-1236.

3. Peterle, T. J.; Nature, (1969), 224, 620.

4. Sanderson, M., Frank, R.; cited in Report of the Task Force on PCB to the Joint Department of Environment and National Health and welfare Committee on Environmental Contaminants, Envir. Canada Report EPS-CCB-77-1, (1977), 66.

5. Strachan, W. M. J., Huneault, H., Schertzer, W. M., Elder, F. C.; In Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, (1980) ed. Afghan, B. K., Mackay, D. (Plenum Press, New York), 387-396.

6. Murphy, T. J., Rzeszutko, C. P.; J. Great Lakes Res., (1977), 3, 305-312.

7. Swain, W. R.; J. Great Lakes Res., (1978), 4, 398-407.

8. Brooksbank, P. L.; The Canadian Network for Sampling Organic Compounds in Precipitation, Environment Canada, Inland Waters Technical Bulletin 129, (1983).

9. Strachan, W. M. J., Huneault, H.; Envir. Sci. & Tech., (1984), 18, 127-130.

10. International Joint Commission, (1983), Report on Great Lakes Water Quality. Appendix: Great Lakes Surveillance,

11. Kaushik, C. P., Pillai, M. K. K., Raman, A., Agarwal, H. C.; Water, Air & Soil Poll., (1987), 32, 63-76.

12. Joshi, S. R.; J. Environ. Radioactivity, 1988, 6, 203-211.

13. Marahiro, O., Takahisa, H.; Environ. Pollut., (1975), 9, 283-288.

14. Benvenue, A., Ogata, J. N., Hylin, J. W.; Bull. Env. Cont. Tox., (1972), 8, 238-241.

15. Peakall, D. B.; Atmos. Envir., (1976), 10, 899-900.

16. Cohen, J. M., Pinkerton, C.; In Organic Pesticides in the Environment, ed. Gould, R. F., ACS Advances in Chemistry Ser., (1966), 60, 163-176.

17. Mes, J., Davies, D. J., Turton, D.; Bull. Env. Cont. Tox., (1982), 28, 97-104.

18. Mineau, P., Fox, G. A., Norstrom, R. J., Weseloh, D. V., Hallett, D. J., Ellenton, J. A.; In Toxic Contaminants in the Great Lakes, (1984), ed. Nriagu, J. O., Simmons, M. S. (Wiley), 425-452.

19. Great Lakes Water Quality Board; 1987 Report on Great Lakes Water Quality, November 1987, International Joint Commission, Windsor, Ontario, 236 pgs.