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# TOXIC CONTAMINANTS IN RAINFALL IN CANADA: 1984

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## EXECUTIVE SUMMARY

Replicate rain samples for the bulk of the wetfall periods were collected from four widely separated sites in Canada — Cree Lake in northern Saskatchewan, an island (Caribou) in eastern Lake Superior, a shoreline station downwind from Caribou Island (Agawa) and a site on the Atlantic coast at Kouchibouguac. Concentrations and loadings of a number of polychlorinated biphenyls and organochlorine pesticides were determined and comparisons made among the sites and with results from other years. The conclusions from this part of an on-going study is that these compounds are widely dispersed in the atmosphere and that all of Canada, as well as elsewhere, is subjected to the effects of these compounds. Long range transport of contaminants must be considered a major factor in their environmental behaviour and distribution.

RESUME - GESTION

Des échantillons de pluie en plusieurs exemplaires pour la plus grande partie des périodes de précipitations ont été recueillis à quatre endroits très éloignés les uns des autres du Canada, soit le lac Cree dans le nord de la Saskatchewan, l'île Caribou dans l'est du lac Supérieur, une station sur la rive sous le vent par rapport à l'île Caribou (Agawa), ainsi qu'à un emplacement sur la côte de l'Atlantique, à Kouchibougouac. Les concentrations et les charges d'un certain nombre de biphényles polychlorés et de pesticides organochlorés ont été mesurées et on a comparé les résultats obtenus aux divers sites et d'une année à l'autre. Les conclusions de cette partie d'une étude en cours sont que ces composés sont très répandus dans l'atmosphère et que tout le Canada, comme tous les autres pays, est soumis aux effets de ces composés. Le transport à grande distance des contaminants doit être considéré comme un facteur important de leur comportement et de leur distribution dans l'environnement.

# Contaminants toxiques dans la pluie au Canada en 1984

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## Introduction

Le dépôt atmosphérique de polluants toxiques sur les eaux superficielles a été identifié depuis longtemps comme une "voie" du cycle ervironnemental de ces produits chimiques. Des rapports déjà anciens portant sur des échantillons d'eau de pluie britanniques soulignaient la présence de lindane et de dieldrine, ainsi que de DDT (Abbott et al., 1965; Wheatley et Hardman, 1965; Tarrant et Tatton, 1968). Ces observations, ainsi que des observations subséquentes directes de contamination atmosphérique, de même que des rapports portant sur les mêmes substances dans des régions éloignées (Peterle, 1969; Clausen et al., 1974; Bowes et Jonkel, 1975) indiquent une dispersion globale de ces substances et de leur dépôt. D'autres indices du transport à grande distance de ces polluants atmosphériques ont été signalés dans les Antilles et dans les eaux libres de l'Atlantique (Risebrough et al., 1968; Seba et Prospero, 1971; Harvey et Steinhauer, 1974; Bidleman et Olney, 1974, 1975), ainsi qu'à l'intérieur de la partie continentale des É.-U. (Cohen et Pinkerton, 1966; Antommaria et al., 1965).

Dans les Grands Lacs, des informations sur les concentrations de polluants dans les eaux de pluie sont disponibles depuis le milieu des années 70. Le premier rapport portant sur la présence de ces composés organiques dans l'atmosphère indiquait leur présence dans des échantillons de pluie (Sanderson et Frank, 1976), dans lesquels on a mesuré des concentrations de 10-100 mg/L de PCB.

Par la suite, Murphy et Rzeszutko (1977), Swain (1978), ainsi que Strachan et Huneault (1979) ont signalé la présence de concentrations semblables de PCB dans la pluie et la neige dans cette région, le dernier rapport indiquant également la présence d'un certain nombre de pesticides organochlorés. Eisenreich et al. (1981) ont fait un compte rendu d'une bonne partie de ces données, ainsi que d'autres documents.

En 1983, des échantillons de deux îles du lac Supérieur (l'île Royale à l'ouest et l'île Caribou à l'est) ont été étudiés. On a observé, par ordre de concentration décroissante l'a-BHC, le lindane, des PCB et du méthoxychlore, ainsi que des traces d'autres composés organochlorés (Strachan, 1985). On a observé une diminution d'ouest en est (direction des principaux vents de la région) dans les concentrations, qu'on attribue à l'écoulement dans les eaux libres sans remplacement. En 1984, deux autres aspects des contaminants des eaux de pluies ont été étudiés, soit les différences entre les concentrations dans les eaux du lac et sur les rivages, ainsi que la possibilité d'élargir l'échantillonnage à d'autres parties du Canada. Les résultats de ces études sont présentés ici.

# Toxic Contaminants in Rainfall in Canada: 1984

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## Introduction

Atmospheric deposition of toxic pollutants to surface waters has long been established as a "pathway" in the environmental cycling of such chemicals. Early reports for British rainfall samples noted lindane and dieldrin as well as DDT (Abbott et al.,1965; Wheatley and Hardman, 1965; Tarrant and Tatton, 1968). These and subsequent direct observations of atmospheric contamination, together with reports of the same substances in remote areas (Peterle, 1969; Clausen et al., 1974; Bowes and Jonkel, 1975) are indicative of a global dispersion of these substances and of their deposition. Other evidence of the long range transport of these atmospheric pollutants has been reported for the West Indies and the open Atlantic (Risebrough et al., 1968; Seba and Prospero, 1971; Harvey and Steinhauer, 1974; Bidleman and Olney, 1974, 1975) and within the continental U. S. (Cohen and Pinkerton, 1966; Antommaria et al., 1965).

In the Great Lakes, information on pollutant concentrations in rainfall has been available since the mid 1970's. The first atmospheric-related report for these organic compounds was in rain samples (Sanderson and Frank, 1976) where PCBs were reported at 10-100 ng/L. Subsequent to that, Murphy and Rzeszutko (1977), Swain (1978) and Strachan and Huneault (1979) reported similar levels of PCBs in rain and snow in the region with the latter report including a number of organochlorine pesticides as well. Eisenreich et al. (1981) provided an extensive review of much of this and other material.

In 1983, samples from two islands in Lake Superior (Isle Royale in the

west and Caribou Island in the east) were investigated . In order of decreasing concentrations, a-BHC, lindane, PCBs and methoxychlor were observed with trace levels of other organochlorine substances also being found (Strachan, 1985). A west to east decrease (the direction of the prevailing winds in this region) in concentration levels was observed, attributed to washing-out without replacement over the open water. In 1984, two further aspects of contaminants in rainfall were investigated — the differences between overlake and shoreline concentrations, and, an expansion of the sampling to other parts of Canada. The results of these studies are reported here.

## Experimental

Triplicate samples were collected for most of the rain period from Caribou Island (eastern Lake Superior, 47°22'N, 85°49'W), Agawa Bay (Lake Superior Provincial Park, 47°21'N, 84°42'W) and Cree Lake (Environment Canada atmospheric research station in northern Saskatchewan, 57°30'N, 106°30'W); duplicates were obtained from Kouchibouguac (National Park, New Brunswick, 46°50'N, 65°0'W). An outline map of these locations is given in Figure 1. The sampling procedures and analytical methodology have been presented in previous papers (Strachan and Huneault 1984; Strachan, 1985). Collection and concentration of neutral, hydrophobic compounds is on XAD-2 resin; cleanup and analysis of samples is according to the methods of Environment Canada's Inland Waters Directorate (1979 and subsequent revisions).

For the comparison between open lake (Caribou Island) and shoreline sampling (Agawa), resin columns were changed when approximately 100 mm rain (20 litres) had fallen. These changes were co-ordinated so that new columns, from the same batches of resin, were put on the automated samplers

on the same dates. Samples from Kouchibouguac and Cree Lake were also obtained when roughly 100 mm of rain had fallen. The dates of the sample periods, and the mean levels of chemicals observed are given in Tables 1 through 4. In addition to the compounds listed, others were looked for but not found with any consistency; these (and their approximate detection limits, ng/L) were: o,p'-DDT (0.02), mirex (0.02), endosulfans (0.02 ea.), chlordanes (0.02 ea.) and toxaphene (2.).

Loadings via rain (and snowfall with certain assumptions) are calculated and presented as Table 5. Estimates for 1976/77 are from concentrations averages of single samples representing approximately 25 % of the rainfall; all others are from volume weighted averages of triplicate (duplicate for Kouchibouguac) samples covering the bulk of the wetfall season. A "nd" was assigned a value of half the detection limit for these calculations and snowmelt concentrations were considered equal to rain for PCBs and to 10 % of the rain values for other substances. For Lake Superior, the rainfall is the average of data from Thunder Bay and Sault Ste. Marie. "Loadings" for Cree Lake and Kouchibouguac during 1984 are given for comparison; they correspond to an area equivalent to the surface of Lake Superior.

## Results and Discussion

The data from tables 2 and 3 permit an examination of the impact of shoreline on over-lake concentrations in the rain. Caribou Island and Agawa are locations separated by approximately 100 km due east-west, the direction of the prevailing winds in the area. The former is representtive of over-lake conditions, the latter is both downwind and a shoreline (ca. 150 m inland) location. The sample columns at both sites were changed at the same time for four time periods and results, by chemical, were tested

were made for Cree Lake and Kouchibouguac using an area comparable to Lake Superior.

Examination of Table 5 (and the supporting results in Tables 1-4) show that the same 11 compounds occur in the rain in all four of the sample locations. It also shows that, with a few exceptions, the loadings were similar at all four sites — despite the fact that they are separated by up to 3500 kms and are "fed" by different air masses (Arctic in the one case). Indeed, even the concentrations are similar. These observations are in keeping with the contention that, at least for these compounds, long range transport is responsible for their presence in these atmospheric samples and could even be construed as indicative of global pollution.

Table 5 also indicates a few apparent site differences in the 1984 loadings of individual compounds. alpha-HCH and lindane were lower (ca. 40%) at Cree Lake and higher (ca. 260 %) at Kouchibouguac than in the Lake Superior region. PCBs, along with heptachlor epoxide and methoxychlor, were high in the Lake Superior region when comparwed with both Cree Lake (62, 7 and 4 % respectively) and Kouchibouguac (57, 4 and 5 % respectively). There are other differences indicated in the table but it is debatable whether the data base on which they are founded is sufficiently firm to allow more than speculation on their significance. Since the use patterns of these compounds are unknown to this author, it is uncertain whether any of these differences are due to local consumption added to a global "ambient" level.

The data base for Lake Superior covers a longer period than the other areas. In Table 5, it appears that there has been a reduction in PCB loadings in the Lake Superior region over the 7-8 years of sampling noted here. This conclusion is somewhat speculative since the 1977 and 1981

sampling periods were less comprehensive than 1983 and 1984 (some 25 % of the rainfall) and since the 1981 value is so largely off the indicated trend. Further sampling is an obvious requirement.

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Table 1: Cree Lake Rain Data - 1984

| Compound | May 16-Jun 29 | Jun 29-Sep 7 | Sep 7-Sep 27 |
|---|---|---|---|
| | - - mean value in ng/L (percent rel. std. dev.)- - | | |
| a-BHC | 3.9 (11) | 0.89(22) | 53. (3) |
| Lindane | 4.3 (12) | 0.46(39) | 14. (22) |
| Hept.Ep. | 0.08(40) | 0.03(57)# | nd* |
| Dieldrin | nd | nd | 4.4(23)# |
| Endrin | nd | 0.44(36) | nd |
| pp'-DDE | 0.04(15) | 0.10(31) | nd |
| pp'-DDD | 0.09(45) | nd | 1.8(29)# |
| M'ychlor | 0.25(18) | nd | nd |
| PCB's | 0.61(28)# | 2.5 (4)# | 17. (14) |
| HCB | nd | 0.01(16)# | nd |
| Rain(L) | 20.8 | 31.4 | 5.0 |
| (mm) | 99.7 | 150. | 23.9 |

* - not detected # - duplicate

Table 2: Caribou Island Rain Data - 1984

| Compound | May1-May31 | May31-Jul5 | Jul5-Aug14 | Aug14-Sep21 | Sep21-Oct29 |
|---|---|---|---|---|---|
| | - - - - mean value in ng/L (percent rel. std. dev.)- - - - - | | | | |
| a-BHC | 3.9 (21) | 3.5 (10) | 7.1 (7) | 3.7 (22) | 12. (16) |
| Lindane | 2.3 (26) | 2.3 (16) | 2.8 (31) | 3.5 (24) | 3.7 (7) |
| Hept.Ep. | 0.15(42)# | 0.51(10) | 0.39(16) | 0.25(27) | nd* |
| Dieldrin | 0.49(55) | 1.0(47) | 0.91(28) | 1.3 (17) | 0.80 (5)# |
| Endrin | nd | nd | nd | 0.30(14) | nd |
| pp'-DDE | 0.49(56) | 0.20(17) | 0.22(29) | 0.15(37) | nd |
| pp'-DDT | 1.2 (58)# | 0.36(40) | 0.54(38) | nd | 0.70(10)# |
| pp'-DDD | nd | nd | 0.27(41)# | nd | nd |
| M'ychlor | 1.2 (32)# | 2.5 (48) | 0.56(11) | 1.8 (29) | 0.78(10)# |
| PCB's | nd | 2.6 (45) | 2.9 (21)# | 3.9 (56)# | 1.3 (0)# |
| HCB | nd | 0.03(13) | 0.23(38) | 0.13(74)# | nd |
| Rain(L) | 5.7 | 19.2 | 19.8 | 18.4 | 19.9 |
| (mm) | 27.2 | 91.8 | 94.8 | 88.0 | 95.4 |

* - not detected # - duplicate

Table 3: Agawa Bay Rain Data - 1984

| Compound | May31-Jul5 | Jul5-Aug14 | Aug14-Sep21 | Sep21-Oct29 |
|---|---|---|---|---|
| | - - - mean value in ng/L (percent rel.std.dev.) - - - - | | | |
| a-BHC | 2.9 ( 8) | 4.3 (11)# | 2.7 (24) | 14.9 (22) |
| Lindane | 1.7 (17) | 1.8 (11)# | 2.9 (42) | 4.7 (14) |
| Hept.ep. | 0.15(47) | 0.32(28) | 0.29( 2)# | nd* |
| Dieldrin | 0.21(23)# | 0.57(37) | 0.72(41) | 0.92(33) |
| Endrin | nd | nd | 0.13(29)# | 0.16(27) |
| pp'-DDE | 0.15(22) | 0.13( 2) | 0.11(41) | nd |
| pp'-DDT | 0.08(20)# | 0.37(55)# | nd | nd |
| pp'-DDD | nd | nd | nd | nd |
| M'ychlor | 0.43(35)# | 0.60(22)# | 1.5 (68) | nd |
| PCB's | 2.2 ( 9)# | 5.0 (70)# | 4.2 (21) | 1.7 (33) |
| HCB | 0.03(24)# | 0.11(19)# | nd | nd |
| Rain (L) | 21.4 | 21.6 | 20.8 | 26.2 |
| (mm) | 102.4 | 103.5 | 99.4 | 125.5 |

* - not detected # - duplicate

Table 4: Kouchibouguac Rain Data - 1984#

| Compound | May8-Jun19 | Jun19-Aug 29 | Aug29-Sep5 | Sep5-Oct29 |
|---|---|---|---|---|
| | - - - mean value in ng/L (percent rel. std. dev.)- - - | | | |
| a-BHC | 1.8 (14) | 5.9 (26) | 1.2 (47) | 66. (53) |
| Lindane | 1.0 (32) | 2.8 (40) | 0.48(71) | 34. (38) |
| Hept.Ep. | 0.03(35) | 0.18(84) | nd* | nd |
| Dieldrin | 0.07(46) | nd | nd | 1.6 (24) |
| Endrin | nd | nd | 4.8(123) | nd |
| pp'-DDE | 0.06(16) | 0.10(42) | 0.13(18) | nd |
| pp'-DDT | nd | 0.50(55) | nd | nd |
| pp'-DDD | nd | nd | nd | 0.89(55) |
| M'ychlor | 0.07(64) | nd | nd | nd |
| PCB's | nd | 0.74(11) | 1.7(104) | 7.3 (46) |
| HCB | 0.01(28) | 0.12 (5) | nd | 0.12(28) |
| Rain(L) | 42.6 | 49.7 | 18.0 | 20.3 |
| (mm) | 203.7 | 238.0 | 86.2 | 97.1 |

* - not detected # - all values are for duplicates

Table 5: Mean Rain Concentrations(1) and Mean Loadings(2) of Observed Contaminants

| Compound | 1977(3,4) Lake Superior ng/L | 1977(3,4) Lake Superior kg/yr | 1981(3) Lake Superior ng/L | 1981(3) Lake Superior kg/yr | 1983(3) Lake Superior ng/L | 1983(3) Lake Superior kg/yr | 1984(3) Lake Superior ng/L | 1984(3) Lake Superior kg/yr | 1984 Kouchibouguac ng/L | 1984 Kouchibouguac kg/yr | 1984 Cree Lake ng/L | 1984 Cree Lake kg/yr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| a-HCH | 13. | 850. | 17. | 770. | 17. | 870. | 6.2 | 320. | 13. | 1150. | 6.5 | 170. |
| Lindane | 6.5 | 425. | 6.0 | 270. | 5.9 | 300. | 3.0 | 160. | 6.7 | 590. | 1.2 | 32. |
| Hept.ep. | nd(5) | - - | nd | - - | 0.35 | 18. | 0.23 | 12. | 0.07 | 0.8 | 0.02 | 0.53 |
| Dieldrin | 0.39 | 25. | 0.26 | 12. | 0.56 | 29. | 0.78 | 41. | 0.27 | 24. | 0.38 | 10. |
| Endrin | nd | - - | 0.065 | 2.9 | 0.085 | 4.3 | 0.049 | 2.6 | 0.66 | 58. | 0.24 | 6.3 |
| pp'-DDE | } | | nd | - - | 0.12 | 6.1 | 0.13 | 6.8 | 0.02 | 1.8 | 0.07 | 1.8 |
| pp'-DDT | }0.62 | 41. | 0.15 | 6.8 | 0.11 | 5.6 | 0.23 | 12. | 0.19 | 17. | nd | - - |
| pp'-DDD | } | | nd | - - | 0.11 | 5.6 | tr(5) | - - | 0.14 | 12. | 0.19 | 5.0 |
| M'ychlor | 1.7 | 111. | nd | - - | 2.4 | 120. | 0.98 | 51. | 0.02 | 1.8 | 0.09 | 2.4 |
| PCB's | 23. | 1500. | 1.7 | 97. | 6.0 | 400. | 2.9 | 210. | 1.1 | 130. | 3.1 | 120. |
| HCB | 2.2 | 143. | nd | - - | 0.075 | 3.8 | 0.065 | 3.4 | 0.07 | 6.2 | 0.01 | 0.3 |
| Rain (mm) | 782. | | 543. | | 607. | | 618. | | 1050. | | 307. | |
| Snowmelt(mm) | 249. | | 164. | | 214. | | 263. | | 377. | | 176. | |

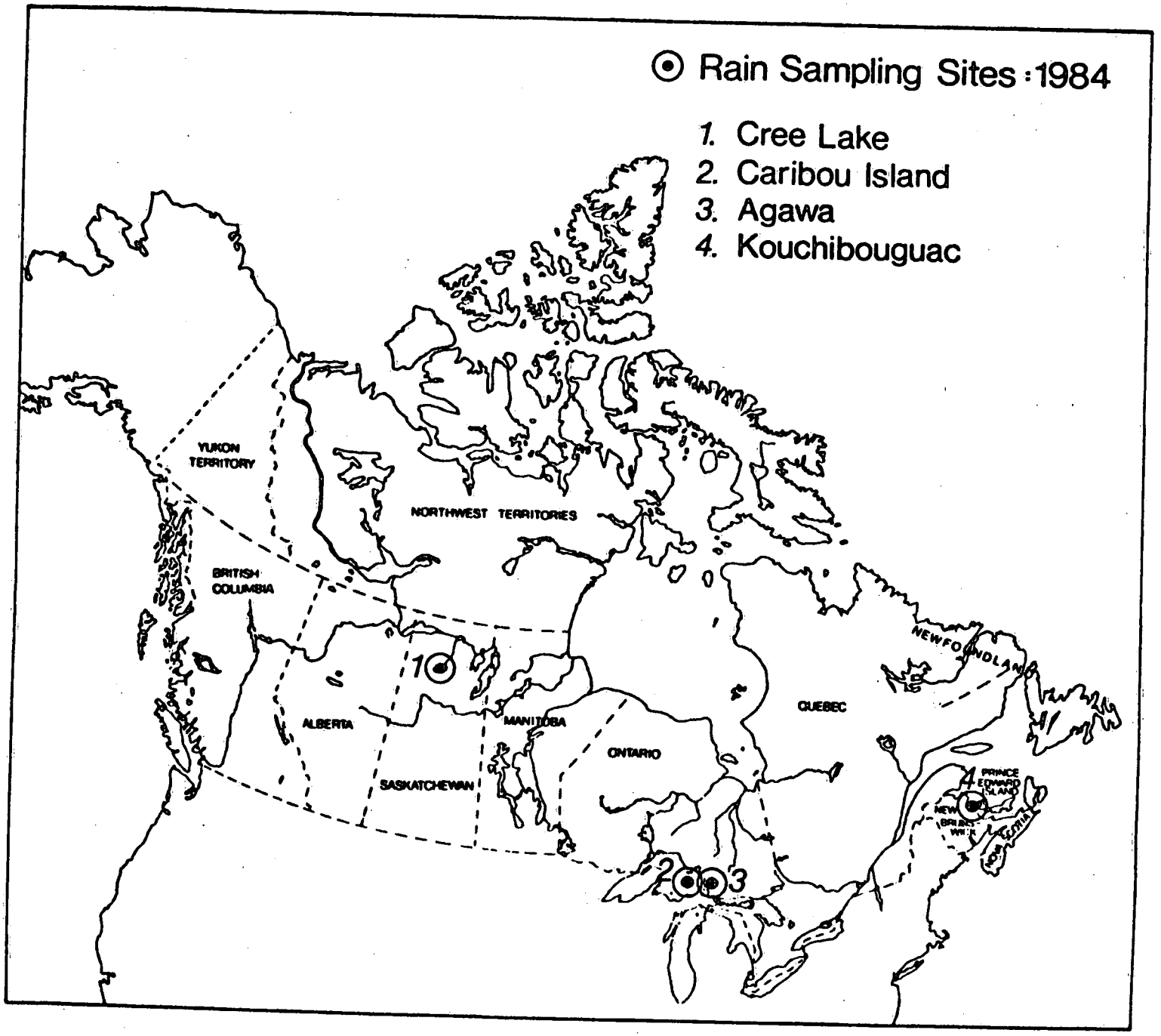
(1) - 1983 and 1984 concentrations from full wet season sampling; others from part season sampling.

(2) - loadings assume: area of 81,200 $km^2$ (Lake Superior), rain and snow for the sites are for the indicated year (L. Superior = average of Thunder Bay and Sault Ste. Marie), snowmelt concentrations are 10 % of rain concentrations except for PCBs (100 %).

(3) - Lake Superior sites: 1977 - Sibley and Batchawana (Strachan and Huneault, 1979); 1981 - Turkey Lake, near Batchawana (Strachan and Huneault, 1984); 1983 - Isle Royale and Caribou Island (Strachan, 1985); 1984 - Caribou Island and Agawa (this paper).

(4) - from averages of single samples using less sensitive analytical methodology.

(5) - nd: not detected, tr: trace (< ca. 0.02 ng/L).


Rain Sampling Sites : 1984
1. Cree Lake
2. Caribou Island
3. Agawa
4. Kouchibouguac
YUKON TERRITORY
NORTHWEST TERRITORIES
BRITISH COLUMBIA
ALBERTA
SASKATCHEWAN
MANITOBA
ONTARIO
QUEBEC
NEWFOUNDLAND
PRINCE EDWARD ISLAND
NEW BRUNSWICK
NOVA SCOTIA
1
2
3
4