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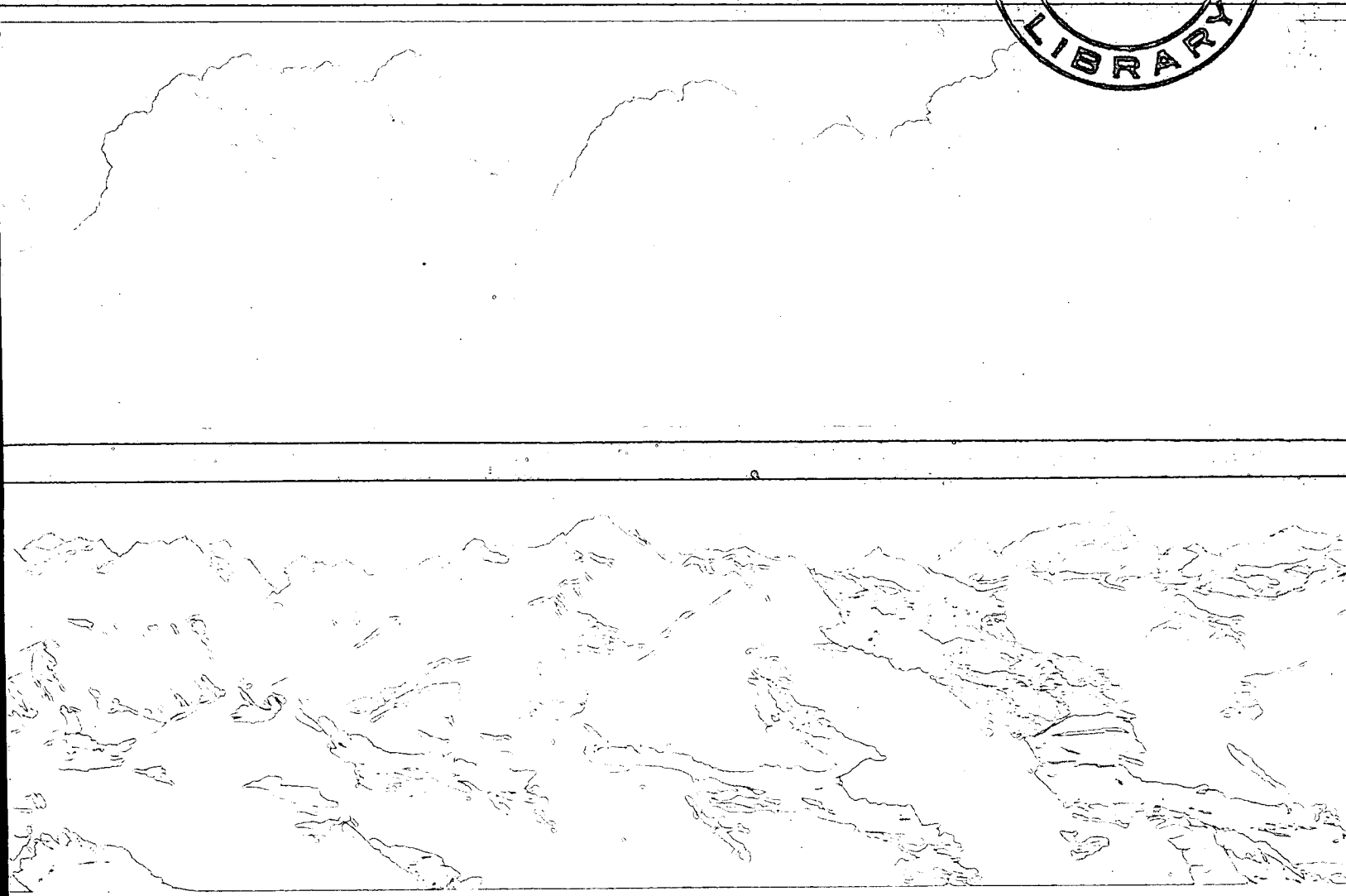
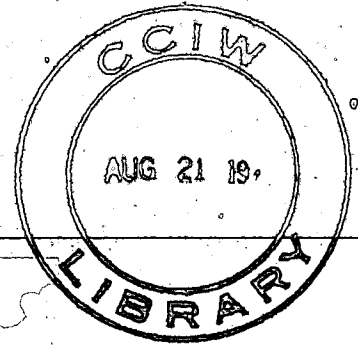


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Atmospheric Bulk Precipitation in the Lake Erie Basin

K.W. Kuntz



REPORT SERIES NO. 56
(Résumé en français)

INLAND WATERS DIRECTORATE, ONTARIO REGION,
WATER QUALITY BRANCH,
BURLINGTON, ONTARIO, 1978.

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Abstract

A wide variety of chemical constituents of atmospheric bulk precipitation in the Lake Erie Basin have been analyzed on a monthly basis since 1970.

Data are compared on the basis of summer months (April to November inclusive) and winter months (December to March inclusive) and on the basis of sampler type. Concentrations for specific conductance, total Kjeldahl nitrogen, total phosphorus, and potassium are significantly higher in summer samples as a result of contamination by soil particles, insects, bird feces and windblown debris. Variations between samplers showed that in summer only sodium was significantly higher in the "Type A" samplers, probably because of the use of a glass wool prefilter from 1970 to July 1974. In winter, nitrate-nitrogen, extractable zinc, sodium and sulphate are significantly higher and total phosphorus is significantly lower in the "Type A" samplers. These high concentrations of sodium and sulphate and the low concentrations of total phosphorus are also attributed to the use of the glass wool prefilter.

From these data, atmospheric loading estimates to the lake surface are calculated and compared with those of an independent analysis and also with 1975 Detroit River loadings to Lake Erie. This comparison shows that the atmosphere is a significant source of nitrogen for Lake Erie.

Résumé

On a effectué tous les mois depuis 1970 des analyses sur une grande variété de composés chimiques des précipitations atmosphériques globales dans le bassin du lac Érié.

On a comparé les données des mois d'été (avril à novembre inclusivement) et des mois d'hiver (décembre à mars inclusivement), compte tenu du type d'échantillonneur. Les concentrations correspondant à la conductivité spécifique, à l'azote total (méthode Kjeldahl), au phosphore total et au potassium sont beaucoup plus élevées dans les échantillons d'été en raison de la contamination par les particules du sol, les insectes, les excréments d'oiseaux et les débris amenés par le vent. D'après les variations présentées par les divers échantillonneurs en été, seule la concentration du sodium était beaucoup plus élevée dans les dispositifs de type «A», parce que l'on avait vraisemblablement utilisé un filtre en laine de verre de 1970 à juillet 1974. En hiver, les échantillonneurs de type «A» ont fourni des concentrations d'azote à l'état de nitrate, de zinc extractible, de sodium et de sulfate nettement plus élevées, contrairement au phosphore total dont les concentrations étaient beaucoup plus faibles. On peut également attribuer à l'utilisation d'un filtre en laine de verre ces fortes concentrations de sodium et de sulfate, ainsi que les faibles concentrations de phosphore total.

D'après ces données, on a pu calculer l'apport des particules atmosphériques à la surface du lac Érié et comparer les résultats à ceux d'une autre analyse, ainsi qu'à l'apport des particules transportées par la rivière Détroit jusqu'au lac Érié en 1975. Cette comparaison indique que l'atmosphère constitue une importante source d'azote pour le lac Érié.

Atmospheric Bulk Precipitation in the Lake Erie Basin

K.W. Kuntz

INTRODUCTION

The Precipitation Chemistry Program of the Canada Centre for Inland Waters (CCIW) was initiated in 1969 as a result of a requirement of the International Joint Commission on the Pollution of Lake Erie, Lake Ontario and the International Section of the St. Lawrence River for information on the atmospheric input to the chemical budget of the Lower Great Lakes. Since 1970, three stations have been operated on a regular basis in the Lake Erie Basin at the locations shown in Figure 1.

Two types of bulk precipitation samplers have been used throughout this study. The first type of sampler, shown in Figures 2 and 3, is similar to that used by Gambell and Fisher (1966) in their studies in North Carolina and Virginia. It will be referred to as a "Type A" sampler in this presentation. It employs a glass collection funnel, and in the early stages of the program a prewashed glass wool pre-filter was used in the bottom end of the funnel to filter out insects and large particulates. However, after July 1974, the use of this filter was discontinued because elevated concentrations of Ca, Mg, Na, and SO_4 and reduced concentra-

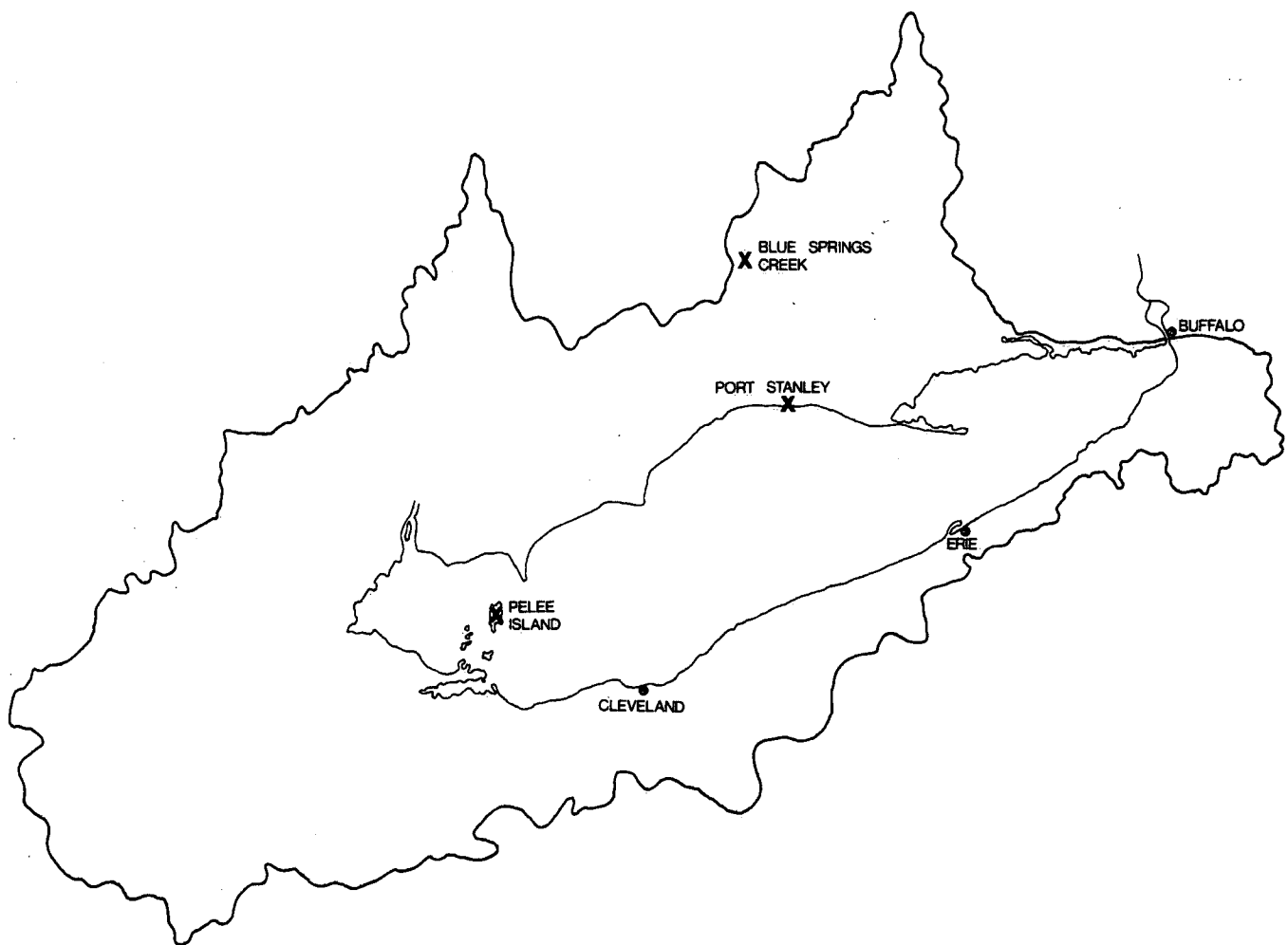


Figure 1. Lake Erie bulk precipitation sampler locations.

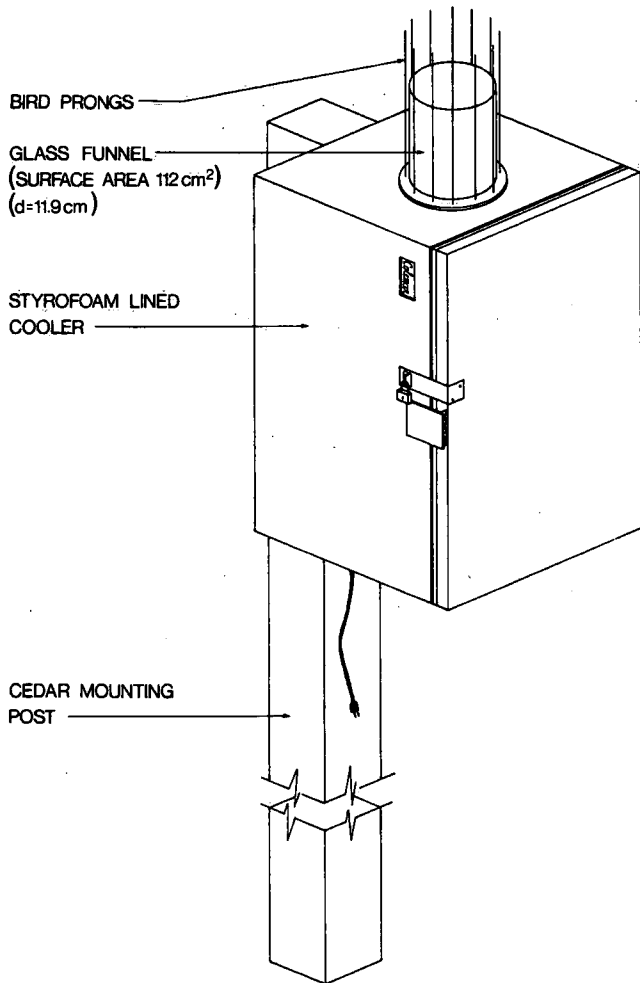


Figure 2. Bulk precipitation Type A sampler.

tions of NH_3 , total P, Zn and Cl were observed because of its use.

The second type of bulk precipitation sampler, which was originally designed to sample for snow, will be referred to as a "Type B" sampler. It was used to collect both snow and rain. It is shown in Figure 4 and consists of a large hollow cylinder with a plastic bag liner surrounded by an "Alter" shield. This type of sampler has been used since August 1972.

All samples were collected on a monthly integrated basis and sent to CCIW for chemical analysis. No preservative was used in the collection bottles. The samples were analyzed for conductivity, major ions, nutrients and trace elements. Detailed discussions of the analytical methodologies have been summarized by Philbert and Traversy (1973).

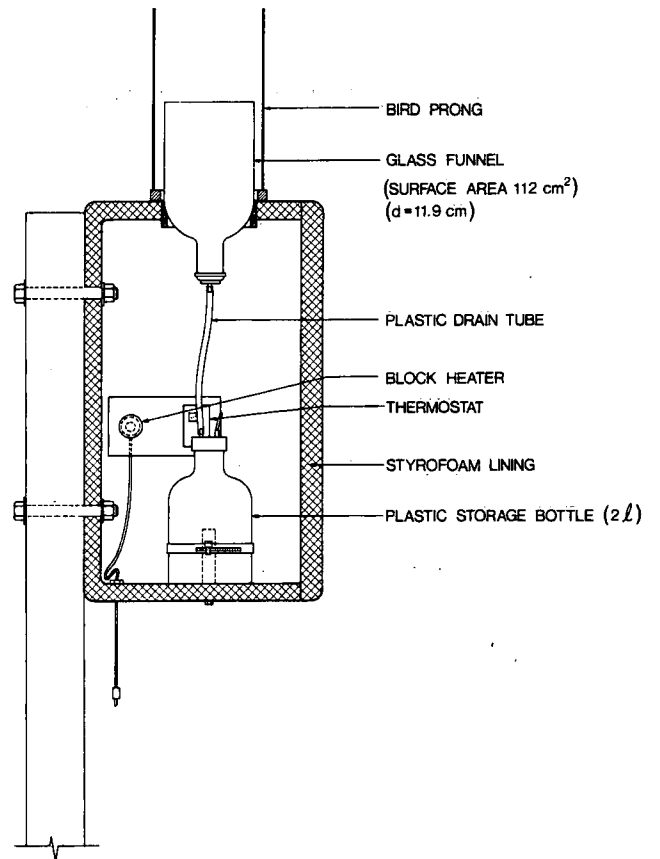


Figure 3. Bulk precipitation Type A sampler interior.

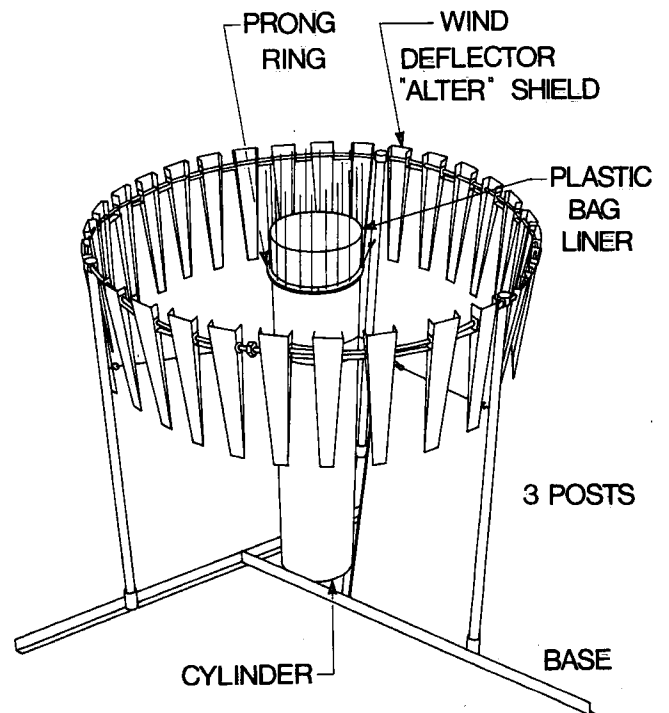


Figure 4. Bulk precipitation Type B sampler.

SEASONAL VARIATIONS

It is apparent that seasonal variations in rain chemistry exist (Acres Consulting Services, 1975, 1977). Hence, our data were grouped into two sets: summer (April to November, inclusive) and winter (December to March, inclusive). Seasonal variations in concentration (mg/l) between summer and winter months are shown for the Type A samplers in Table 1 and for the Type B samplers in Table 2.

Significant (at the 95% confidence level) seasonal variations were observed in several parameters. Specific conductance, total Kjeldahl nitrogen, total phosphorus, and potassium were significantly higher in both samplers in summer. These significantly different means are in italic type in Tables 1 and 2.

Contamination by soil particles, insects, bird feces, and windblown vegetation is a major contributor to the high summer concentrations in both samplers. This problem

Table 1. Lake Erie Type A Sampler Concentrations (mg/l)

Parameter	Summer		Winter	
	No. Observations	Geometric Mean	No. Observations	Geometric Mean
Spec. cond. (20°C), μ mho	119	<i>54</i>	48	<i>45</i>
NH ₃	128	<i>0.61</i>	62	<i>0.42</i>
NO ₃	130	<i>1.06</i>	63	<i>1.17</i>
Total Kjeldahl N	48	<i>1.56</i>	19	<i>0.62</i>
Total P	132	<i>0.068</i>	62	<i>0.018</i>
Cd, ext. *	90	0.001	46	0.001
Cu, ext.	124	0.004	51	0.003
Fe, ext.	121	0.012	55	0.013
Pb, ext.	116	0.006	53	0.007
Zn, ext.	125	0.062	55	0.056
Ca	127	3.43	60	2.89
Mg	127	0.57	60	0.50
Na	116	0.97	58	0.84
K	128	<i>0.42</i>	60	<i>0.18</i>
SO ₄	127	<i>7.60</i>	58	<i>7.24</i>
Cl	128	1.11	60	1.44
% catch	126	<i>74</i>	57	<i>51</i>

* Ext. = extractable.

Table 2. Lake Erie Type B Sampler Concentrations (mg/l)

Parameter	Summer		Winter	
	No. Observations	Geometric Mean	No. Observations	Geometric Mean
Spec. cond. (20°C), μ mho	30	<i>56</i>	32	<i>37</i>
NH ₃ (F)*	34	<i>0.59</i>	21	<i>0.37</i>
NO ₃ (F)	33	<i>0.87</i>	21	<i>0.79</i>
Total Kjeldahl N	40	<i>1.39</i>	18	<i>0.59</i>
Total P	39	<i>0.112</i>	37	<i>0.028</i>
Cd, ext. † (F)	30	<0.001	17	<0.001
Cu, ext. (F)	34	0.003	20	0.002
Fe, ext. (F)	34	0.008	19	0.009
Pb, ext. (F)	31	0.007	19	0.009
Zn, ext. (F)	34	0.026	20	0.029
Ca (F)	33	4.47	21	2.48
Mg (F)	33	0.53	21	0.37
Na (F)	29	0.29	19	0.34
K (F)	34	<i>0.54</i>	22	<i>0.14</i>
SO ₄ (F)	34	<i>8.81</i>	18	<i>4.93</i>
Cl (F)	34	1.00	20	1.02
% catch	27	<i>93</i>	13	<i>57</i>

* (F) = filtered.

† Ext. = extractable.

is greatly reduced in winter because of snow cover, and lack of insects, birds and vegetation.

VARIATIONS BETWEEN TYPE A AND TYPE B SAMPLERS

Summer and winter variations in concentration between the Type A and Type B samplers are shown in Tables 3 and 4, respectively.

Only specific conductance (20°C), total nutrients, major ions and percentage catch were compared between the Type A and Type B samplers in summer because the

total nutrients were not filtered in both cases. The filtering of Type B samples would not affect the major ion concentrations, since they are soluble, unreactive chemical species. As shown in Table 3, in summer only sodium was significantly higher (at the 95% confidence level) in the Type A samplers. This high concentration of sodium is attributed to the use of the prewashed glass wool prefilter from 1970 to July 1974 in the Type A samplers. Similarly, Galloway and Likens (1976) have reported that glass collection vessels increased the concentration of sodium in their samples.

Specific conductance (20°C), nutrients, extractable trace metals, major ions and percentage catch were com-

Table 3. Sampler Variations in Summer (mg/l)

Parameter	Type A samplers		Type B samplers	
	No. Observations	Geometric Mean	No. Observations	Geometric Mean
Spec. cond. (20°C), μ mho	119	54	30	56
Total Kjeldahl N	48	1.56	40	1.39
Total P	132	0.068	39	0.112
Ca	127	3.43	33*	4.47*
Mg	127	0.57	33*	0.53*
Na	116	0.98	29*	0.29*
K	128	0.42	34*	0.54
SO ₄	127	7.60	34*	8.81*
Cl	128	1.11	34*	1.00*
% catch	126	74	27	93

* Filtered samples.

Table 4. Sampler Variations in Winter (mg/l)

Parameter	Type A samplers		Type B samplers	
	No. Observations	Geometric Mean	No. Observations	Geometric Mean
Spec. cond. (20°C), μ mho	48	45	32	37
NH ₃	62	0.42	21	0.33
NO ₃	63	1.17	22	0.77
Total Kjeldahl N	19	0.62	18	0.59
Total P	62	0.018	37	0.028
Cd, ext.*	46	0.001	18	<0.001
Cu, ext.	51	0.003	21	0.002
Fe, ext.	55	0.013	22	0.014
Pb, ext.	53	0.007	22	0.009
Zn, ext.	55	0.056	22	0.025
Ca	60	2.89	22	3.35
Mg	60	0.50	21	0.62
Na	58	0.84	22	0.28
K	60	0.18	21	0.13
SO ₄	58	7.24	19	4.90
Cl	60	1.44	22	1.34
% catch	57	51	13	57

* Ext. = extractable.

pared between the two types of samplers in winter. As shown in Table 4, nitrate-nitrogen, extractable zinc, sodium and sulphate were significantly higher (at the 95% confidence level) in the Type A samplers, and total phosphorus was significantly lower in the Type A samplers in the winter. The high concentrations of sodium and sulphate and the low concentration of total phosphorus in the Type A samplers are attributed to the use of the glass wool filter from 1970 to 1974 and in the case of sodium, the glass collection vessel (Galloway and Likens, 1976). We have no ready explanation for the high concentrations of nitrate-nitrogen and extractable zinc in the Type A samplers.

Loading Calculations

The precipitation chemistry data were used to calculate loadings to Lake Erie in three different ways.

In the first type of calculation, selected concentration data are multiplied by a theoretical volume of rainfall to obtain an areal loading that is termed "theoretical" loading. It can be represented as:

$$L_T = C_s \times V_c \quad (1)$$

where L_T = theoretical loading in g/m^2 , C_s = geometric mean concentration of selected data in mg/l , and V_c = calculated volume of rainfall. This is calculated by multiplying the actual measured rainfall by the surface area of the sampler. Loadings calculated by this method tend to be overestimates in summer because of sample evaporation, but are more reasonable in winter, when catch efficiency is low.

A second type of loading estimate has been calculated and is termed "measured" loading. This loading calculation is represented as:

$$L_m = C_s \times V_m \quad (2)$$

where L_m = measured loading in g/m^2 , C_s = same as in Equation 1, and V_m = measured volume of rainfall retained in the sample collected. This calculation was carried out in two ways: first, using only selected data as in the theoretical loading calculation and second, using all available data.

It was decided not to tabulate the selected "measured" loading data when the number of samples was less than 30, because the variation was too large. However, the selected "theoretical" loading data were tabulated for

comparison with the "measured" loadings calculated using all the data.

When data were selected, the most conservative concentrations were used. This approach has been suggested by Kramer *et al.* (Acres Consulting Services, 1975, 1977) as being valid, since most of the significantly higher concentrations result from contamination, evaporation or some type of sampler problem. The selection approach followed here is summarized below.

Since ammonia-nitrogen, total Kjeldahl nitrogen, total phosphorus, and potassium concentrations are significantly lower in winter than in summer, only winter data are used to calculate their loadings. Copper, iron, lead, calcium, magnesium and chloride did not vary significantly seasonally or between sampler types, so all data were used to calculate their loadings. Because sulphate was significantly lower in the winter Type B samplers, only winter Type B sampler data were used to calculate loadings for this parameter. Nitrate-nitrogen, sodium and zinc showed significantly lower concentrations in the Type B samplers than in the Type A samplers, so only Type B sampler data were used to calculate their loadings.

The results of all three calculations are presented in Table 5. Most significant is the fact that the "theoretical" loadings using selected data are always greater than the "measured" loadings using selected data. Since the only term to change in the loading equation is the volume term, the calculated volume is always larger than the measured volume. This is always true because of sample evaporation in summer and poor catch in winter. Hence measured loadings should be used in summer and theoretical loadings (assuming that the collected sample is representative of all the precipitation) should be used in winter.

Comparison of the measured loadings (all data) from this report with those of Kramer *et al.* (Acres Consulting Services, 1977) shows excellent agreement for some parameters (SO_4 , Na, total P) and very poor agreement for others (total Fe, total N and total Pb). This presumably reflects the large errors currently inherent in atmospheric bulk precipitation chemistry data.

"Theoretical" atmospheric loading to Lake Erie using selected data is compared with 1975 Detroit River loading (Great Lakes Water Quality, 1975) and expressed as a percentage of Detroit River loading in Table 6. Even allowing for a 50% overestimate by use of the "theoretical" loading calculation, it is apparent that ammonia-nitrogen and nitrate-nitrogen from atmospheric bulk precipitation are very important sources of nitrogen to Lake Erie.

Table 5. Atmospheric Loadings to Lake Erie (tonnes/yr)

Parameter	Theoretical loadings*		Measured loadings*		Measured loadings (ALL DATA)		Acres 1977
Total P	470	(89)‡	240	(76)‡	730	(233)‡	800
NH ₃	8 600	(75)	5 000	(62)	8 500	(194)	—
NO ₃ †	22 000	(26)			17 000	(198)	—
Total Kjeldahl N†	13 000	(30)	6 200	(31)	18 000	(105)	—
Total N †	35 000				35 000		19 000
Cu, ext. §	83	(188)	66	(179)	66	(179)	—
Cu, total	140	(32)	120	(30)	120	(30)	330
Fe, ext.	280	(190)	210	(179)	210	(179)	—
Fe, total	2 700	(33)	2 600	(31)	2 600	(31)	5 900
Pb, ext.	150	(182)	110	(172)	110	(172)	—
Pb, total	300	(33)	260	(31)	260	(31)	2 200
Zn, ext.	470	(25)			1 000	(184)	—
Zn, total	910	(13)			1 000	(30)	—
Ca	75 000	(201)	54 000	(191)	54 000	(191)	23 000
Mg	12 000	(200)	9 200	(191)	9 200	(191)	6 600
Na	6 300	(21)			14 000	(176)	13 000
K	3 800	(73)	2 300	(61)	5 200	(192)	22 000
SO ₄	99 000	(16)			120 000	(189)	120 000
Cl	26 000	(201)	20 000	(192)	20 000	(192)	—

* Only selected data used:

All data 1970-76 — Cu, Fe, Pb, Ca, Mg, Cl.

Winter 1970-76 — NH₃, total Kjeldahl N, total P, K.

All data 1970-76 — Type B samplers only, NO₃, Zn, Na.

Winter 1970-76 — Type B samplers only, SO₄.

† NO₃ + total Kjeldahl N = total N.

‡ Parentheses indicate number of data points used.

§ Ext. = extractable.

Table 6. Bulk Precipitation Loadings as Percentage of Detroit River Loadings

Parameter	Theoretical atmospheric loading to Lake Erie (tonnes/yr)	1975 Detroit River loading* to Lake Erie (tonnes/yr)	Theoretical atmospheric loading as % of Detroit River loading
Total P	470	1.21×10^4	4
NH ₃	8 600	2.77×10^4	31
NO ₃	22 400	7.38×10^4	30
Fe, total	2 700	8.58×10^4	3
Dissolved solids	222 000†	3.39×10^7	<1
Cl	26 400	3.15×10^6	<1

* From Great Lakes Water Quality, 1975, Surveillance Subcommittee Report, Appendix B.

† Includes Ca, Mg, Na, K, SO₄ and Cl loadings.

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