REPORT TO THE U.S. ENVIRONMENTAL PROTECTION AGENCY

on

ATMOSPHERIC DEPOSITION WORKSHOP ON ORGANIC CONTAMINANT DEPOSITION

TO THE GREAT LAKES BASIN

held at the UNIVERSITY OF MINNESOTA, MINNEAPOLIS

20-21 NOVEMBER, 1985

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"IT IS OFTEN NECESSARY TO MAKE A DECISION BASED

ON INFORMATION WHICH IS SUFFICIENT FOR ACTION

BUT INSUFFICIENT TO SATISFY THE INTELLECT"

Emmanual Kant ,1786

" Critique of Pure Reason"

EXECUTIVE SUMMARY

An "Atmospheric Deposition" Workshop was held at the University of
Minnesota, Minneapolis on 20-21 November, 1985 under the support and
auspices of the Great Lakes National Program Office (GLNPO) of the
U.S. Environmental Protection Agency (EPA). Participants at the
workshop included distinguished scientists knowledgeable in
atmospheric processes from the U.S. and Canada, representatives of the
Canadian and U.s. organizations conducting monitoring studies and
staff of the GLNPO. The objectives of the workshop were two-fold:
(1) to review the Great Lakes atmospheric deposition network (GLAD)
presently operated by EPA; and (2) to make recommendations as to the
design and strategy for a new or modified network capable of assessing
atmospheric deposition of selected toxic chemicals to the Great lakes,
identify sources and quantify source strengths. These objectives are
meant to assist in the successful achievement of the goals stated in
EPA's five-year stategy relative to atmospheric deposition: (1) to
determine the portion of total loadings of critical toxic pollutants
by atmospheric deposition; (2) to recommend the extent to which
additional remedial programs and international activities are needed
to control atmospheric sources; and (3) to provide source information
for immediate regulatory action.

A thorough review of the present GLAD network and accumulated data on
precipitation concentrations conclusively showed that the GLAD network
as presently constituted is not adequate to provide needed data on
atmospheric inputs of toxic chemicals to the Great Lakes. This
conclusion was based on siting, sample collection and data analysis

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A detailed discussion of the processes of wet deposition, dry particle deposition and vapor exchange at the air-water interface was held to acquaint all present with the state-of-the-art in these areas. These discussions led to the generation of recommendations on the structure and design of a monitoring network capable of assessing atmospheric inputs of toxic chemicals to the Great Lakes. The design strategy for the network is to combine both deposition measurement and modeling to assess atmospheric deposition. It would have relatively few sites (e.g., 16) at which collection of wet precipitation, air particles and meteorological data necessary for the modeling effort would occur. Two to four of these sites would be designated as master sites where calibrations, intercomparison studies and research would be carried out. Sites would be distributed in such a way as to estimate "regional" deposition (half of the sites) and "urban" deposition since it is believed that intense episodes of localized inputs occur in areas adjacent to population centers. If possible, monitoring stations should be located on in-lake islands. A complete list of instrumentation common to all sites is provided in the text but includes wet-only precipitation samplers capable of isolating the analyte in the field, multiple Hi-Vol samplers operating to provide directional data on atmospheric concentrations, and a suite of sensors to measure meteorological parameters such as temperature profiles, relative humidity, total suspended particulates (TSP), and wind speed and direction. Additional instrumentation to be located at the master sites are cascade impactors and any necessary to support the research

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component. Toxic organic species to be monitored are polychlorinated biphenyls (PCBs), routine organochlorine pesticides and industrial chemicals, polycyclic aromatic hydrocarbons (PAHs), Hg, Pb and Cd, toxaphene and generic chlorinated dioxins and furans. Analysis of these toxic chemicals will require considerable analytical support. It is anticipated that this network would largely replace the larger GLAD network. The research component of this network should include a significant effort to quantify dry deposition and vapor exchange or both inorganic and organic toxic species through a combination of sampling and modeling of over-lake processes. Other methods of assessing atmospheric inputs should be continued (e.g., mass balance; small lake studies; sediment and peat profiles). Every attempt should be made to integrate the U.s. network with Canadian efforts using similar samplers and stratagies, inter-calibrations and co-located sampling sites to implement an "Integrated Atmospheric Deposition Network". A rigorous QA/QC system need be instituted at the outset of the project to ensure the quality of the data.

It is proposed that a multi-investigator study be performed in the summer and winter of 1988 to integrate deposition data generated at the master sites with intensive over-lake measurements involving wet deposition, dry deposition, vapor exchange and source reconciliation.

2.0 Workshop Objectives

The Great Lakes National Program Office (GLNPO) of the U.S. Environmental Protection Agency (EPA) presently operates a 36 site atmospheric monitoring network (GLAD), of which 10 sites are equipped with bulk samples for assessing organic contaminant deposition to the Great Lakes.

The atmospheric deposition program for the next five years has three objectives as stated in EPA's 5-year strategy document (1):

(1) to determine the portion of total loadings of critical toxic pollutants by atmospheric deposition;

(2) to recommend the extent to which additional remedial programs and international activities are needed to control atmospheric sources;

(3) to provide source information for immediate regulatory action.

The objectives of the "Atmospheric Deposition" workshop held at the University of Minnesota on the 20 and 21 November 1985 under the auspices of the GLNPO of EPA were:

(1) to review the atmospheric deposition monitoring network (GLAD) operated by the GLNP;

(2) to make recommendations as to the design and strategy for a new or modified atmospheric deposition network capable of assessing atmospheric deposition of selected toxic organic contaminants to the Great Lakes, identify sources and quantify source strengths.

Essential to this discussion was a thorough review of the feasibility and limitations of assessing wet and dry deposition. To these ends, the first part of the workshop dealt with an overview of the present GLAD network by T.C. Murphy (DePaul University) and D. Gatz (Illinois State Water Survey). Based on a study recently completed for EPA, T.C. Murphy outlined requirements for a new Great Lakes atmospheric and sources (GLAIS) network. These presentations were followed by detailed discussions on the processes of atmospheric deposition led by J. Pankow (Oregon Graduate Center) on wet deposition of organic species, A. Andren (University of Wisconsin) on dry particle deposition of organic species, M. Weseley (Argonne National Laboratory) on meteorological aspects of dry deposition, and T. Bidleman (University of South Carolina) and S. Eisenreich (University of Minnesota) on vapor-particle partitioning in the atmosphere and volatilization, respectively. The remainder of the workshop involved generating specific recommendations for measurement and assessment of atmospheric deposition of organic contaminants to the Great Lakes.

Specific questions addressed throughout the workshop were:

(1) What is the relative importance of atmospheric deposition compared to other input pathways for specific contaminants in the Great Lakes Basin and specific Great Lakes?

(2) What are the important deposition processes and how could they be quantified?

(3) What of the thousands of organic chemicals produced and released to the environment need be measured and how?

(4) What are the atmospheric sources and source strengths for specific organic contaminants?

(5) What are the characteristics of an atmospheric deposition network

which is adequate to provide needed data?

(6) What are the research needs to support the atmospheric deposition network?

3.0 Atmospheric Deposition Processes

Atmospheric organic chemicals exist in the vapor phase and adsorbed to suspended particles (TSP). The processes by which trace organic contaminants are removed from the atmosphere (wet and dry deposition) and the quantity ultimately deposited on the water/land surface depend on the distribution between the vapor and particle phases. Partitioning between the gas and aerosol phase depends on contaminant vapor pressure, size and surface area of the aerosol, temperature, and the organic carbon content. The less volatile the compound, the higher the affinity for TSP. Theoretical considerations and laboratory and field measurements indicate that PCBs, DDT, Hg, low molecular weight (MW) hydrocarbons, and low MW PAHs exist primarily in the gas phase in "clean" airsheds, while the more chlorinated PCB congeners, high MW PAHs and dioxins occur primarily in the particle phase. In "dirty" or urban/industrial airsheds, a greater fraction of the total atmospheric burden for a particular chemical will occur in the particle phase. Particle size plays a significant role in the removal efficiency of aerosol-bound contaminants. Organic species tend to concentrate in the submicron particle-size fraction (i.e.,

aerosol) and will be primarily removed by precipitation scavenging
(>70 %) while larger particles will have a greater fraction removed by
dry particle deposition.

Wet Deposition

The mechanisms of wet removal from the atmosphere are very
different for particle-associated compounds than for gas phase
compounds. The relative importance of these two processes depends on
the distribution of the organic compound between vapor and aerosol,
particle-size distribution and Henry's Law Constant (H). Non-reactive
organic gases will be scavenged by rain according to H if equilibrium
between the gas and aqueous phases is achieved (2,3). Henry's Law
constant, H, is the ratio of the compound's vapor pressure to its
solubility for low solubility compounds. In the absence of chemical
reactions occurring in the droplet, an atmospheric gas should attain
equilibrium with a falling raindrop in about ten meters of fall. The
position of equilibrium defined by H is a function of temperature as
it increases by about 2 for each 10°C rise in temperature (3).

The total extent of organic compound scavenging by falling
precipitation may be given as:

$$W_T = W_g (1 - \phi) + W_p \phi$$

where W_T = overall scavenging efficiency

$$W_T = \frac{[rain, T]}{[air, T]}$$

W_g is the gas scavenging efficiency

$$W_g = \frac{[rain, diss]}{[air, gas]}$$

W_p is the particle scavenging efficiency

$$W_p = \frac{[\text{rain, part.}]}{[\text{air, part.}]}$$

and ϕ is the fraction of the total atmospheric concentration occurring in the particle phase.

An atmospheric gas attaining equilibrium with a falling raindrop is scavenged from the atmosphere inversely proportional to H:

$$W_g = \frac{RT}{H} = \alpha$$

where R is the universal gas constant, T = temperature, H = Henry's Law Constant, and α = solubility coefficient. Surface flux then becomes:

$$F_g = \alpha \cdot J \cdot C_g = W_g \cdot J \cdot C_g$$

where J = rainfall intensity, and C_g = concentration of organic gas in the atmosphere. Field determined W_T values are generally larger than W_g values based on H for some organic compounds suggesting particle scavenging by precipitation is an important flux term. Ligocki et al. (3) have reported gas scavenging efficiencies for a variety of nonpolar organic compounds measured in the field in Portland, OR. Tables 1 and 2 from their paper compares the field-determined W_g values to those estimated from consideration of H and ambient temperatures. They obtained W_g values ranging from 3 to 10^5, and which were underestimated by factors of 3 to 6 using H data at 25°C. Correcting published H values for ambient temperatures of 5 to 9°C, equilibrium between the atmospheric gas and dissolved constituent of

Table 3. Mean dissolved rain concentrations (ng $\ell^{-1} \pm 1$ s), mean gas phase concentrations (ng m$^{-3} \pm 1$ s), correlations between rain and air data and gas scavenging ratios

Compound	Mean concentrations Rain	Air	Correlation (r^2)	$\overline{W}_g$ (meas) 8°C*	α (lit) 25°C	Ref.†
Tetrachloroethene	4.6±3.4	1200±690	0.97	3.6±1.1	1.0	2
Trichloroethene	5.6±5.6	1500±1300	0.81	3.7±1.3	2.4	2
Mesitylene	5.1±2.5	430±220	0.82	12±3	4.5	2
Toluene	88±75 (5)‡	3800±2400	0.97	22±5 (5)	3.7	1
Durene	2.9±1.3	120±70	0.73	26±9	1.0	2
1,2,4-Trimethylbenzene	30±14	1300±800	0.33	27±9	4.2	2
Ethylbenzene	34±21	1300±700	0.75	27±11	3.7	1
m+p-Xylene	110±73	3400±2000	0.68	33±17	3.5‖	2
o-Xylene	45±31	1300±690	0.79	35±15	4.8	2
1,4-Dichlorobenzene	4.8±1.2	120±32	0.21	39±10 (6)	8.2	1
1,2-Dichlorobenzene	0.26±0.20 (5)	5.8±2.3	0.91	46±13 (5)	12	1
1,2,4-Trichlorobenzene	0.25±0.17 (3)	3.8±0.4	—§	66±51 (3)	11	1
C$_2$-naphthalenes	17±6	91±35	0.87	190±32	66¶	2
Naphthalene	100±32	450±220	0.37	250±73	59	2,3
2-Methylnaphthalene	45±16	200±120	0.67	250±78	48	2
1-Methylnaphthalene	29±11	96±54	0.78	330±100	56	2
Dibenzofuran	17±6	19±5	0.69	930±180		
Acenaphthene	5.4±2.0	5.5±1.9	0.16	1000±310	250	3,4
Fluorene	14±4	9.5±2.4	0.16	1500±390	350	3,4
Acenaphthylene	37±13	28±16 (4)	0.28	1600±500 (4)	72	3,4
Anthracene	5.1±2.0	2.8±1.0	0.48	1900±600	680	3,4
Methylphenanthrenes	30±8	13±3	0.09	2500±800		
Dibenzothiophene	41±2.1	1.6±0.5	0.59	2500±900		
Phenanthrene	90±26	27±7	0.36	3400±740	1100	3,4
Benzo[e]pyrene	0.37±0.20 (2)	0.03±0.01 (5)	—	5800 (1)		
Pyrene	39±13	6.8±1.9	0.09	5900±1800	2900	3,4
Fluoranthene	48±17	7.8±2.0	0.20	6300±2000	2400	3,4
Benzo[b+j+k]fluoranthene	1.6±1.9 (2)	0.11±0.14 (5)	—	7400±1300 (2)	1300**	1
9-Fluorenone	79±21	7.0±1.7	0.52	11,000±2200		
Benz[a]anthracene	3.3±1.0	0.28±0.07	0.06	12,000±4900	4300	3,4
Chrysene	7.9±2.8	0.45±0.07	0.00	18,000±6500	23,000	1
Diethylphthalate	59±30	2.7±0.4 (4)	0.03	20,000±12,000 (4)	21,000	1
Dioctylphthalate	2.6±0.8 (6)	0.39±0.39 (5)	—	20,000±20,000 (4)		
9,10-Anthracenedione	67±26	2.5±0.8	0.64	27,000±7000		
α-HCH	11±3	0.34±0.05	0.48	31,000±6900	4200	1
Dibutylphthalate	46±10	0.37 (1)	—	110,000 (1)	87,000	1

*Average temperature during sampling. †1 = Mabey *et al.* (1982), 2 = Mackay and Shiu (1981), 3 = Sonnefeld *et al.* (1983). 4 = Pearlman *et al.* (1984). ‡Number of samples, if other than seven. §Correlation not computed for fewer than four points. ‖Average of the values for m-xylene and p-xylene. ¶Value for 1-ethylnaphthalene. **Average of the values for benzo[b]fluoranthene and benzo[k]fluoranthene.

Table 4 Comparison of field W_g values to temperature-dependent α values* for polycyclic aromatic hydrocarbons

Compound		2/12–2/13 8 C	2/14–2/15 6°C	2/20–2/21 5°C	2/23–2/24 7°C	2/29–3/1 9°C	3/16–3/20 9°C	4/11–4/12 8°C	Average $W_g/α$
Naphthalene	W_g	160	340	240	290	140	270	290	
	α	190	220	240	200	170	170	190	
	$W_g/α$	0.86	1.6	1.0	1.5	0.81	1.6	1.5	1.3
Fluorene	W_g	1200	2200	1500	1300	930	1500	1500	
	α	1200	1400	1500	1300	1100	1100	1200	
	$W_g/α$	1.0	1.6	1.0	1.0	0.84	1.4	1.2	1.1
Phenanthrene	W_g	2900	3400	3900	4100	2100	4000	3300	
	α	3600	4300	4700	3900	3300	3300	3600	
	$W_g/α$	0.81	0.80	0.84	1.1	0.62	1.2	0.91	0.90
Anthracene	W_g	1000	2100	1800	2100	1400	2700	2000	
	α	2300	2700	2900	2500	2200	2200	2300	
	$W_g/α$	0.43	0.78	0.60	0.84	0.63	1.2	0.85	0.76
Fluoranthene	W_g	5100	6000	6900	7000	3500	9900	5400	
	α	6000	7100	7600	6500	5600	5600	6000	
	$W_g/α$	0.85	0.85	0.91	1.1	0.63	1.8	0.90	1.0
Pyrene	W_g	5000	6200	6600	7000	3000	8600	4800	
	α	9800	12,000	13,000	11,000	8700	8700	9800	
	$W_g/α$	0.51	0.52	0.51	0.64	0.34	0.99	0.49	0.57
Benz[a]anthracene	W_g	11,000	14,000	22,000	13,000	8000	9400	7300	
	α	8700	9800	10,000	9300	8200	8200	8700	
	$W_g/α$	1.3	1.4	2.2	1.4	0.98	1.1	0.84	1.3

*α values were calculated from the data of May *et al.* (1978) and Sonnefeld *et al.* (1983).

precipitation was demonstrated for several PAHs. Based on these results, temperature-corrected W_g values may be used to estimate organic gas concentrations in the atmosphere or temperature-specific H values.

Precipitation scavenging of particles containing sorbed organic species (W_p) permit the calculation of surface fluxes:

$$F_p = W_p \cdot J \cdot C_p$$

where F_p is the particle flux and C_p is the concentration of atmospheric particulate organic compound. Depending on particle size, precipitation intensity and type of meterological event, W_p may equal 10^4 to 10^6. The higher value implies that the aerosol is readily incorporated into cloud water and is hygroscopic. The lower value implies a non hygroscopic, probably carbonaceous particle that is not readily incorporated into cloud water. Below cloud particle scavenging efficiencies of 10^3 to 10^5 for 0.01 to 1.0 µm particles have been reported. The most comprehensive study of particle scavenging by precipitation was conducted by Ligocki et al. (4). Tables 3 and 4 list W_p values of 10^2 to 10^5 for a series of PAHs, alkanes and phthalates and compares W_p to W_g values. In general, W_p values were consistent with below-cloud and in-cloud scavenging for PAHs, in which the compounds with higher scavenging ratios were associated more frequently with large particles. To adequately predict W_p's, detailed information on particle-size distribution, organic concentrations in particle-size ranges and meteorological parameters are needed.

Table 3. Particle scavenging ratios for neutral organic compounds during rain events in Portland, Oregon in 1984

		W_p						
Compound	MW	2/12–2/13 frontal cyclone	2/14–2/15 weak storm	2/20–2/21 showers	2/23–2/24 cold front	2/29–3/1 warm front	3/16–3/20 showers	4/11–4/12 cold front
Polycyclic aromatic hydrocarbons and derivatives								
Dibenzofuran	168	NA*	4900	23,000	NA	9300	5500	NA
Fluorene	166	NA	NA	34,000	NA	8200	2400	NA
9-Fluorenone	180	29,000	NA	NA	9000	17,000	1900	18,000
Phenanthrene + Anthracene	178	19,000	2500	38,000	5600	17,000	15,000	22,000
Methylphenanthrenes	192	19,000	NA	15,000	3400	11,000	NA	NA
Fluoranthene	202	4500	2400	15,000	3500	12,000	23,000	18,000
Pyrene	202	2600	1700	13,000	3600	10,000	20,000	14,000
9,10-Anthracenedione	208	1700	NA	2600	1400	3900	NA	NA
Benz[a]anthracene	228	640	410	1300	400	2300	2600	1100
Chrysene	228	1700	1100	3500	1200	4500	3800	2400
7-Benz[de]anthracenone	230	560	NA	1100	900	2700	NA	NA
Benzo[b+j+k]fluoranthene	252	1300	430	2700	3200	4900	2100	900 ·
Benzo[e]pyrene	252	1400	430	3000	2800	4500	1700	290
Benzo[a]pyrene	252	580	180	2500	1200	3900	NA	NA
Perylene	252	630	NA	2600	920	3000	NA	NA
Benzo[ghi]perylene	276	1300	NA	4200	3900	5800	NA	290
Coronene	300	2000	NA	1800	NA	14,000	NA	NA
Average of PAHs with MW <	202	15,000	2900	24,000	5000	12,000	11,000	18,000
Average of PAHs with MW >	202	1200	510	2500	1800	5000	2600	1000
Alkanes								
Eicosane	282	21,000	NA	15,000	89,000	44,000	NA	32,000
Heneicosane	296	14,000	NA	16,000	76,000	46,000	10,000	12,000
Docosane	310	15,000	NA	12,000	63,000	34,000	NA	6300
Tricosane	324	27,000	3900	16,000	29,000	44,000	NA	13,000
Tetracosane	338	10,000	NA	18,000	NA	27,000	NA	6400
Pentacosane	352	47,000	5000	11,000	26,000	29,000	NA	22,000
Hexacosane	366	NA	3300	14,000	NA	36,000	NA	7000
Average of alkanes		22,000	4100	15,000	57,000	37,000	10,000	14,000
Phthalate esters								
Butylbenzylphthalate	298	1000	NA	13,000	10,000	NA	NA	NA
Bis[2-ethylhexyl]-phthalate	391	9100	NA	37,000	15,000	NA	NA	NA
Dioctylphthalate	391	29,000	NA	15,000	65,000	NA	35,000	25,000
Average of phthalates		13,000	NA	22,000	30,000	NA	35,000	25,000

Table 4 Mean particle scavenging ratios, mean gas scavenging ratios*, and overall scavenging ratios for neutral organic compounds

Compound	Mean ϕ†	Mean W_p	Mean W_g	Mean W‡	Dominant scav. mech.§
α-HCH	0.0	NA‖	31,000	31,000	g
Diethylphthalate	0.0	NA	20,000	20,000	g
Dibenzofuran	0.008	11,000	930	1000	g
Fluorene	0.009	15,000	1500	1600	g
Phenanthrene + Anthracene	0.011	17,000	3300	3500	g
9-Fluorenone	0.021	15,000	11,000	11,000	g
Methylphenanthrenes	0.027	13,000	2500	2800	g
Fluoranthene	0.053	11,000	6300	6600	g
Pyrene	0.071	9300	5900	6100	g
Eicosane	0.14	40,000	NA	5600	p
9,10-Anthracenedione	0.21	2400	27,000	22,000	g
Heneicosane	0.41	32,000	NA	13,000	p
Dioctylphthalate	0.56	36,000	20,000	30,000	p
Docosane	0.61	27,000	NA	17,000	p
Chrysene	0.71	2600	18,000	7000	g
Benz[a]anthracene	0.75	1300	12,000	4000	g
Benzo[e]pyrene	0.97	2000	5800	2100	p
Benzo[a]pyrene	0.98	1700	NA	1700	p
Benzo[b+j+k]fluoranthene	0.98	2200	7400	2300	p
Perylene	1.0	1800	NA	1800	p
Tricosane	1.0	22,000	NA	22,000	p
Tetracosane	1.0	16,000	NA	16,000	p
Pentacosane	1.0	23,000	NA	23,000	p
Hexacosane	1.0	15,000	NA	15,000	p
Bis[2-ethylhexyl]phthalate	1.0	20,000	NA	20,000	p
Benzo[ghi]perylene	1.0	3100	NA	3100	p
Coronene	1.0	5900	NA	5900	p

*Mean gas scavenging ratios from Ligocki et al. (1985). †ϕ = [aerosol]/[vapor + aerosol]. ‡$W = W_p\phi + W_g(1 - \phi)$. §g = gas; p = particle. ‖NA = not available

The total wet surface flux of organic compounds in the atmosphere may be estimated from:

$$F_T = W_T \cdot C_{air} = W_g(1-\phi)C_{air} + W_p\phi C_{air}$$

$$= (\frac{RT}{H})(1-\phi)C_{air} + W_p\phi C_{air}$$

Dry Particle Deposition

The dry deposition of particle-bound organic compounds onto a receptor surface depends on the type of surface, resistance to mass transfer in the deposition layer, particle size, and macro- and micrometeorology. Particles are delivered to surfaces by Brownian diffusion (mmd < 0.3 μm), inertial impaction-interception (mmd = 0.5-5 μm) and gravitational settling (mmd > 5 μm). Because Brownian diffusion increases below 0.3 μm and inertial impaction-interception increases as particle size increase above 0.5 μm, the minimum deposition velocity (V_d) is in the range of 0.3 to 0.5 μm. As stated earlier, nonpolar organic compounds in the atmosphere tend to concentrate on the small, carbon-rich, high surface area particles.
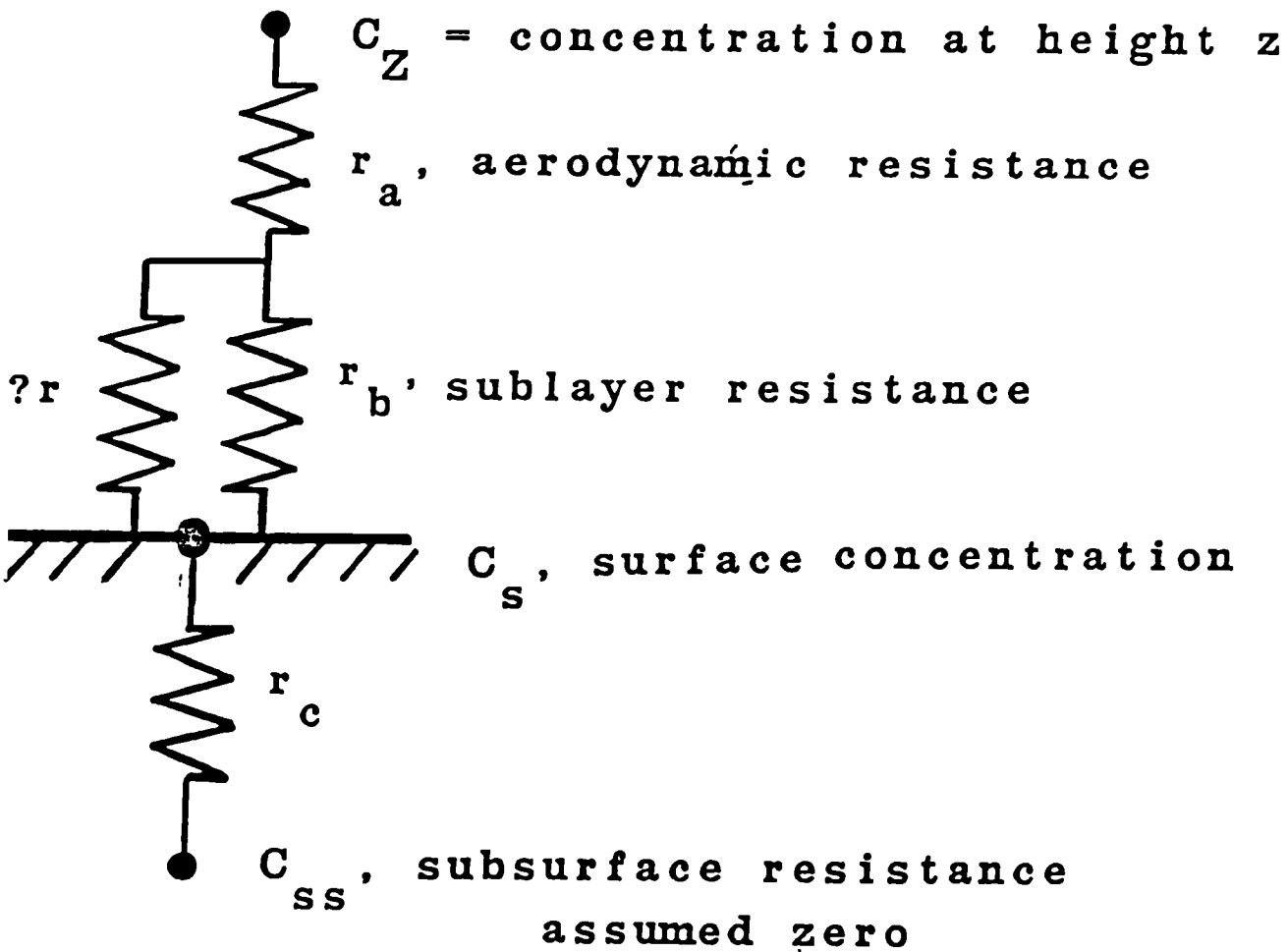
In the simplified case, the flux of particles to a receptor surface is:

$$F_{p,dry} = V_d \cdot C_p$$

where $F_{p,dry}$ is the surface flux of particle-bound chemical, V_d is the deposition velocity and C_p is the organic concentration in the particulate phase. The particle deposition velocity, V_d, may be viewed as the result of a series of resistances in transfer from the well-mixed atmosphere to the surface (Figure 1).

Figure 1. Simplified Model of Dry Deposition (from M. Weseley, ANL)

v_d, deposition velocity

$= -F/C_z$

$= 1/(r_a + r_b + r_c)$

C_z = concentration at height z

r_a, aerodynamic resistance

r_b, sublayer resistance

C_s, surface concentration

r_c

C_{ss}, subsurface resistance assumed zero

All resistances are for conceptual horizontal layers.

$$V_d = F/C_{p,z}$$

$$V_d = 1/(r_a + r_b + r_c)$$

where r_a, r_b, r_c are aerodynamic, sublayer and subsurface resistances, respectively and $C_{p,z}$ is the particulate concentration at a reference height. If r_c is assumed to be zero, then the aerodynamic resistance components r_a, r_b may be roughly estimated from local measurements of $\bar{u}_z$, mean wind speed at a specified height; and σ_θ, a measure of atmospheric stability. V_d ($1/(r_a + r_b)$) estimates for the Great Lakes based on seasonal atmospheric stabilities varied with season with values of 0.5 to 1.0 cm/sec in summer to 1.7 cm/sec in the colder months. M. Wesley (Argonne) and A. Andren (University of Wisconsin) point out that the following measurements or data are essential to adequately predict ('mouel") dry particle deposition:

C(r); concentration as a function of particle size;

u(z); wind velocity at a reference height;

T_s-T_A; surface and atmospheric temperatures;

R_H; relative humidity;

$\rho(r)$; particle density as a function of particle size;

D(r); molecular diffusivity as a function of particle size;

OC(TSP); organic carbon content;

TSP; total suspended particulate concentrations.

These parameters may be used in a variety of dry deposition models (5,6) to quantify particle deposition.

Particle deposition velocities have been estimated from deposition to artificial surfaces (grass; trees; filter paper; glass or Al plates; plates coated with hydrophilic substances such as

ethylene glycol). For a number of nonpolar chlorinated hydrocarbons thought to associate with fine particles, V_d values of 0.1 to 1.0 cm/sec were observed. These values are similar to estimates for reactive gas and aerosol deposition to soils, grass, trees, agricultural crops and snow.

A. Andren suggested that measurements required to assess dry deposition needed to occur on an event basis during unstable atmospheric periods and also on a regular periodic basis. This assumes that particle deposition tends to concentrate during intense, episodic periods; however, field measurements are few. Measurements should be performed in a few rural areas representative of "regional" deposition and more intensively in major source areas. It is always preferable to make the measurements over the lake than on the shoreline. Atmospheric organic contaminants should be measured with both high volume and low volume samples. It is advisable to determine particle size distributions as well as a measure of total C_p and TSP. Denuders may be of some value in isolated situations. These sampling procedures are severely restricted by analytical detection limits.

T. Murphy (DePaul University) has suggested that although most of the atmospheric burden of nonpolar organic compounds may be in the gas phase, and these contaminants are concentrated on fine particles, dry deposition especially near sources, may be dominated by large particle deposition. Gravitational settling velocities for large particles are greater than 2 cm/sec while submicron-sized particles may have deposition velocities much less than 1 cm/sec. Urban and industrial centers bordering the Great Lakes may contribute to regional emissions

and deposition as well as intense localized deposition (e.g., Chicago, IL - Gary, IN ; Detroit, MI; Hamilton, Ont.).

The relative importance or wet versus dry deposition (R) depends on the proportion of atmospheric organic concentration in the gas and particle phases (ϕ), and the relative efficiency with which each phase is removed by wet and dry deposition. In general,

$$R_{w/d} = \frac{[(W_g \cdot J \cdot C_g) + (W_p \cdot J \cdot C_p)]\Delta t_w}{(V_d \cdot C_p)}$$

Based on atmospheric fluxes of Al, Pb, and Pb-210 to Crystal Lake, Wi, A. Andren (Table 5) concluded that 70-80% of the Pb and Pb-210 flux was due to wet deposition, while <40% of the Al flux was attributed to wet inputs. The major difference is that Pb and Pb-210 are associated with submicron aerosol and effectively removed only by precipitation scavenging, Al is derived from large soil particles that have high V_d's. In contrast, atmospheric inputs of PCBs to Lake Michigan are likely due to scavenging of particulate PCBs by rain with small contributions from gas scavenging and dry particle deposition.

Transfer of organic vapors across the air-water interface can oftentimes be predicted from a two-film diffusion model (4-6). In this model, the rate of gas transfer between the well-mixed air and water reservoirs across the stagnant films at the interface is assumed to be governed by molecular diffusion and is driven by the concentration gradient between the equilibrium concentrations at the interface and bulk reservoirs. For steady-state transfer, the flux (F), is given by:

TOTAL ATMOSPHERIC FLUXES AT CRYSTAL LAKE

ELEMENT	WET[1]	DRY[2]	TOTAL	SED. RATE	UNITS
AL	3.6	6.9(66)[3]	10.5	11.1	μg $-$ cm^{-2} $-$ yr^{-1}
PB	0.8	0.2(20)[3]	1.0	1.2[4]	μg $-$ cm^{-2} $-$ yr^{-1}
PB-210	1.58	0.21(12)[3]	1.79	1.86	dpm $-$ cm^{-2} $-$ yr^{-1}

[1]BASED ON RAIN DEPOSITION ONLY.

[2]UNCERTAINTY IS ABOUT $\pm$ 20% (TALBOT, 1981)

[3]INDICATES % DRY INPUT.

[4]EDGINGTON AND ROBBINS (1976) ESTIMATE 1.5 FOR LAKE MICHIGAN
   (STA. 17).

$$F_o = K_{oL}(C-P/H)$$

$$\frac{1}{K_{oL}} = \frac{1}{K_L} + \frac{RT}{HK_g}$$

where F = flux in moles/m^2 · hr; K_L, K_g = liquid and gas-phase mass

transfer coefficients (m/hr); C = solute concentration in liquid phase

(moles/m^3), P = solute partial pressure in atm.; T = absolute

temperature in ^oK, and R = gas constant. The volatilization rate may

be controlled by resistance to mass transfer in the liquid phase, gas

phase or a combination of the two. At typical values of K_L and K_g (20

cm/hr and 2000 cm/hr, respectively), resistance to mass transfer

occurs > 95% in liquid phase for H $\geq$ 4.4 x 10^{-3} atm m^3/mole, and > 95%

in gas phase for H $\leq$ 1.4 x 10^{-5} atm m^3/mole. Considering the range of

H values for PCB congeners, 60 to 90% of the resistance occurs in the

liquid phase at 25-C. This implies that, in general, slightly soluble

PCBs with H > 10^{-4} atm m^3/mole tend to volatilize from water; however

transfer direction is established by the concentration gradient.

Examples of compounds where this occurs are PCBs, many CHs including

pesticides, chlorinated benzenes and tetrachloroethylene.

Theoretical and experimental methods to estimate mass transfer

coefficients in the field for gas and liquid-phase controlled organic

compounds have been developed. Mackay and Yeun (8) have suggested

equations relating environmental mass transfer coefficients based on

Schmidt number (Sc) and windspeed at a reference height of 10 m (U_{10};

m/sec):

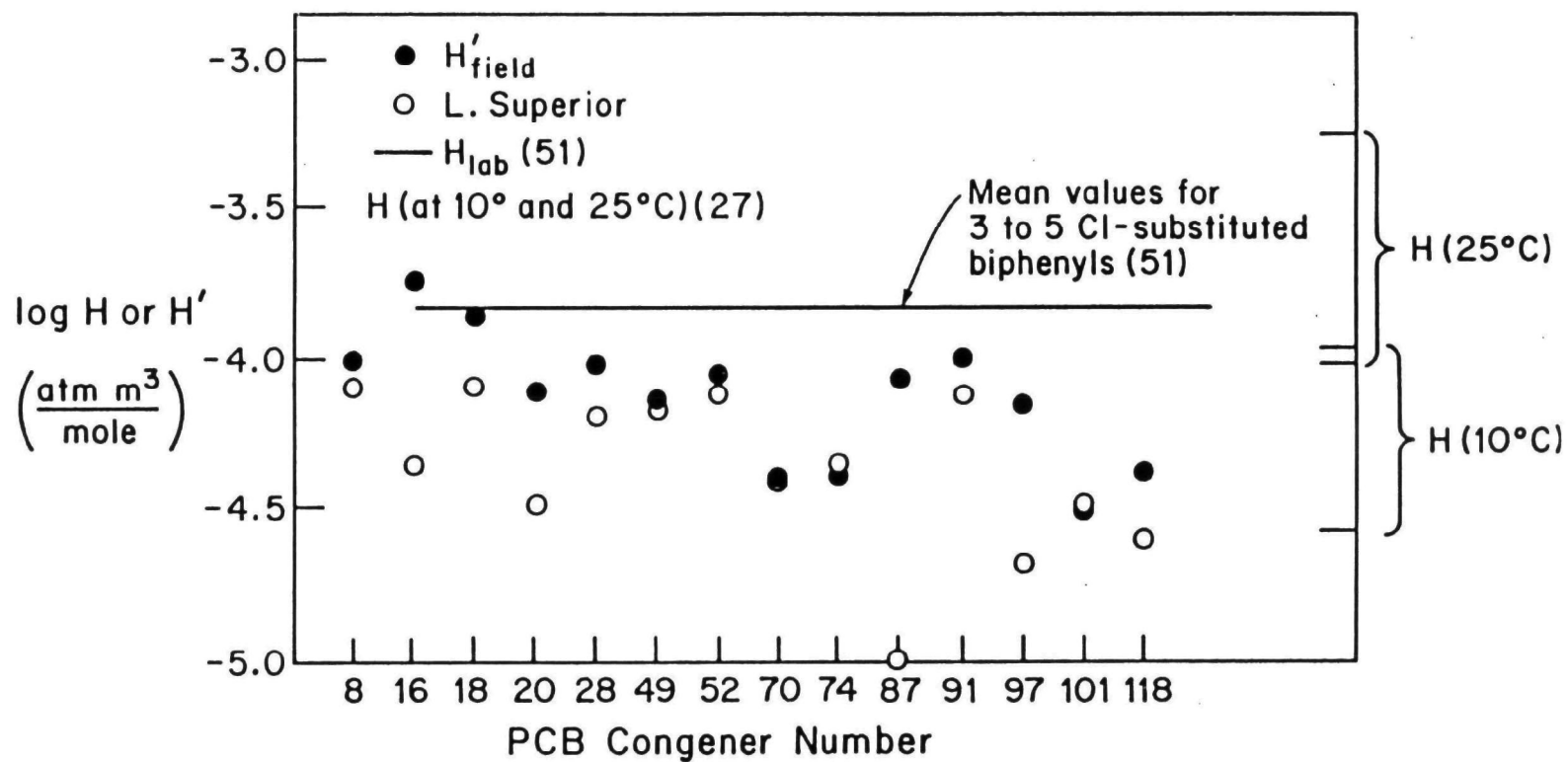$$K_g = 1.0 \times 10^{-3} + 46.2 \times 10^{-3} U^* Sc_o^{-0.67}$$

Figure 2. Henry's Law Constants (H) and Air–Water Partition
Coefficients (H') for PCB Congeners Measured
in Air (vapor) and Water (filtrate) in Lake
Superior – 1980 (Ref. 13).

$$K_L = 1.0 \times 10^{-6} + 34.1 \times 10^{-4} \ U^* \ Sc_L^{-0.5} \quad (U^* > 0.3)$$

$$K_L = 1.0 \times 10^{-6} + 144 \times 10^{-4} \ U^{*2.2} \ Sc_L^{-0.5} \quad (U^* < 0.3)$$

$$U^{*1}(env) = 6.1 + 0.63 \ U_{10})^{0.5} \ U_{10}$$

where U^* = air-side, friction velocity (m/sec). Results suggest that environmental mass transfer coefficients will generally be lower than those measured in the laboratory. Annual integrated K_L values for liquid-phase controlled organic compounds determined from mass balance calculations on large lake systems are 0.2 to 0.25 m/day, or about 50 to 100% smaller than predicted from laboratory experiments: (Table 6).

Table 6. K_L Values Determined from Mass Balance Calculations

Lake	Compound	K_L (m/day)
Zurich	1,4-dichlorobenzene	0.24
Saginaw Bay, Lake Huron	PCBs	0.2
Lake Superior	PCBs	0.24
Great Lakes	PCBs	0.10

(modified from Ref. 13)

Estimating volatilization of PCBs, for example, is complicated by the inability to accurately determine the concentration of the dissolved, unassociated species in equilibrium with the atmospheric vapor. An example of this phenomenon is presented in Figure 2, where Henry's Law Constant (H) or air-water partition coefficients (H') for several PCB congeners are compared to apparent air-water partition coefficients (H') determined from measurements of atmospheric PCBs in

the vapor phase and dissolved PCBs in two surface water samples from Lake Superior (13).

The apparent H' values are lower than the range or H values for the 3 to 5 substituted PCB congeners at 25°C but similar to H values at 10°C, much closer to the ambient temperature of Lake Superior. The temperature dependence on H for PCBs (9) suggests that gas-phase PCBs may be absorbed into the lake at colder temperatures and lost via volatilization at warmer temperatures. For bodies of water such as Lake Superior, PCB_{gas} absorption may be important for 9 or 10 months of the year.

Air-Transfer Scenario: PCBs as an Example

Figure 3 depicts our present understanding of the relative importance of air-water transfer processes for hydrophobic organic cycling in large lakes. The dominant input pathway is the scavenging of particles from the atmosphere containing sorbed organic species, with dry particle deposition being much less important. Particles thus reaching the lake equilibrate with the new aqueous environment, and partition between the dissolved phase and other biotic and abiotic particle phases. PCBs in the dissolved phase equilbrate with the atmospheric gas phase or or mixed downward. Several important observations can be made. The major input is through precipitation scavenging of particles and the major losses are through volatilization and sedimentation. It is conceivable that measurement of PCB flux to the atmosphere via volatilization may be more than counterbalanced by atmospheric inputs on particles. Mackay and Paterson (9) describe this phenomenon as a dynamic, steady-state but

Figure 3. PCB Air-Water Transfer Scenario (Ref. 13)

WET DEPOSITION

DRY DEPOSITION

VAPOR   PARTICLE

VAPOR EXCHANGE

AIR

WATER

P_1

D

P_2

P_{res}

SEDIMENT
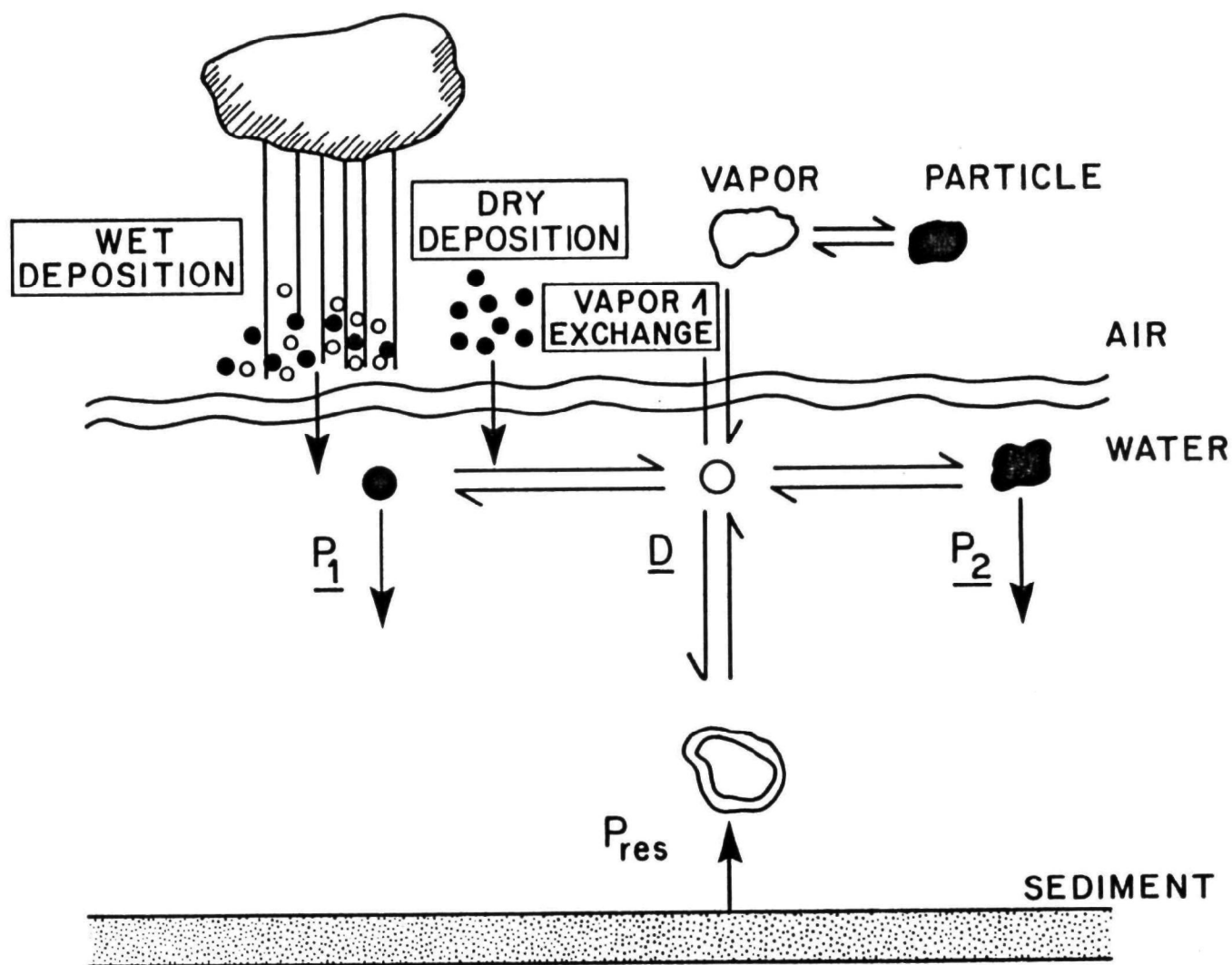
D = Dissolved – phase concentrations

P = Particle – phase concentrations

non-equilibrium process whereby the input (particle scavenging) is connected to loss (volatilization) by the equilbrium partitioning of hydrophobic species. This model also suggests that airborne concentrations of organic contaminants over the lakes are partially or wholly derived from in-lake processes. Compounds such as PCBs may cycle between water and air with intermittent periods of intense deposition followed by slower but prolonged volatilization.

4.0   Great Lakes Atmospheric Deposition (GLAD) Network

T. Murphy (DePaul University) thoroughly reviewed the present GLAD network as to whether it fulfilled its overall mission to quantify atmospheric inputs of nutrients, metals and toxic organic contaminants to the Great Lakes. He concluded that the GLAD network as presently constituted is not adequate to provide needed data on atmospheric loading rates of trace metals and toxic chemicals. This conclusion was based on evaluation of GLAD using criterea based on siting, sample collection methodology and solute analysis. Figure 4 shows the locations of the 36 stations comprising the GLAD network and 15 stations on the Canadian side. Each GLAD site is equipped with weekly-integrating, wet/dry automatic precipitation samplers. Until recently, 28 sites had been equipped with three bulk colectors. The bulk collectors have now been discontinued such that the 36 sites collect integrating wet-only precipitation samples for nutrient and trace metal analysis. There is presently no sampler dedicated to
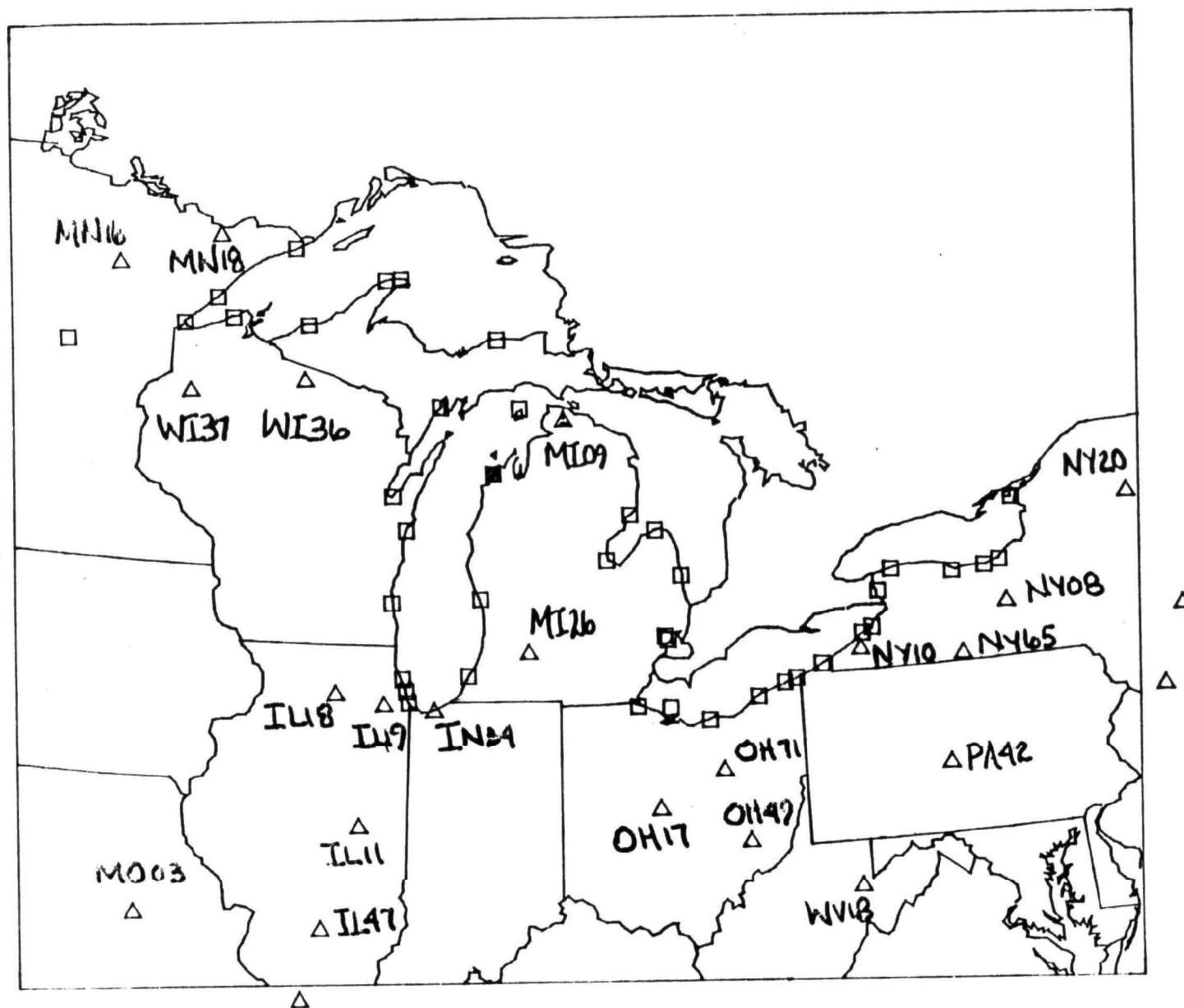
organic monitoring studies. Murphy applied a set of criterea developed by EPA to sites listed in Table 7. Siting criterea relate to obstructions nearby, distance between samplers, orientation of samplers, nature of ground cover, use of rain gauges and distance to nearest local contaminating sources such as roads, etc. More than 50 % of the sites are located in areas directly impacted by urban/industrial sources; most are within 0.5 km of the shoreline and many are located on roofs. A few sites are located on islands in the lakes, but none collect samples on or over the lake.

D. Gatz (Illinois Water Survey) examined the chemical data collected at GLAD sites in 1982 and compared them to data similarly collected at regional National Atmospheric Deposition Program (NADP) and National Trend Network (NTN) sites. The NADP sites shown in Figure 5 are located away from the lakes and localized sources, and may be considered representative of regional deposition. GLAD sites are more closely aligned with urban areas and lake shorelines. A comparison of ion balances for 11 NADP sites and 36 GLAD sites for 1982 precipitation show the GLAD data routinely exhibit cation deficits (Figure 6). This behavior suggests problemns in quality assurance and control at the analytical laboratory.

Spatial distributions portrayed using median concentration isopleths for sulphate, nitrate, pH, ammonium and calcium showed close agreement between NADP concentrations and NADP + GLAD concentrations in similar areas. The GLAD sites added spatial resolution and coverage in urban areas. Cumulative frequency distributions for the same ions at paired sites in GLAD and NADP consistently showed

Figure 5. NADP/GLAD Site Map
(D. Gatz, Ill. State Water Survey)

△ -- NADP
☐ -- GLAD

COMPARISON OF ION BALANCES, 1982

11 NADP SITES AND 37 GLAD SITES

100*(SUM A − SUM C)/(SUM A + SUM C)

□   NADP (448 Sa)   △   GLAD (367 Sa)
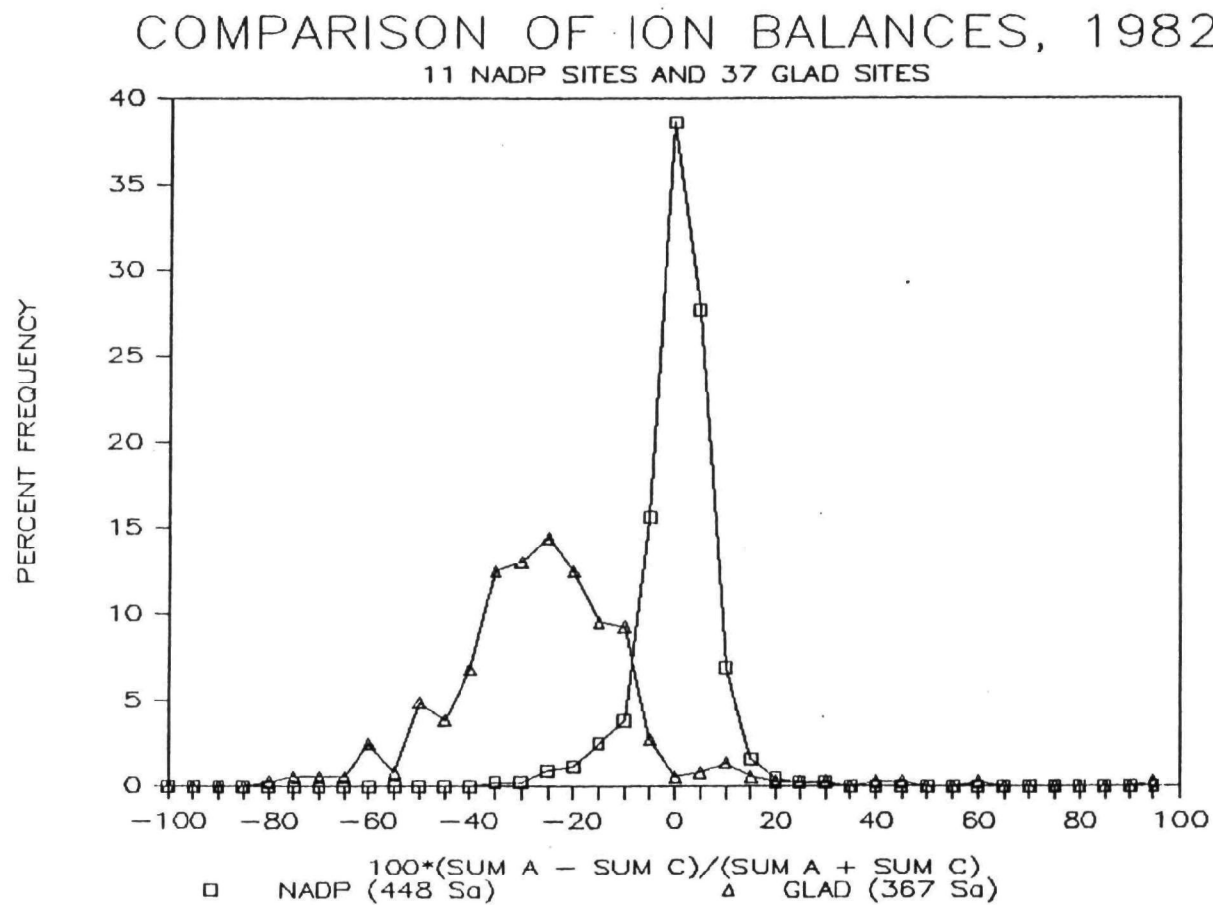
Figure 6. Comparison of Ion Balances, 1982 in the
GLAD/NADP Networks
(D. Gatz, Ill. State Water Survey)

WET COLLECTOR SITES (36)

X = CANADIAN Collection Sites (15)
□ = GLAD Bulk Collection Sites (28)

LAKE SUPERIOR

LAKE HURON

LAKE MICHIGAN

LAKE ONTARIO

LAKE ERIE

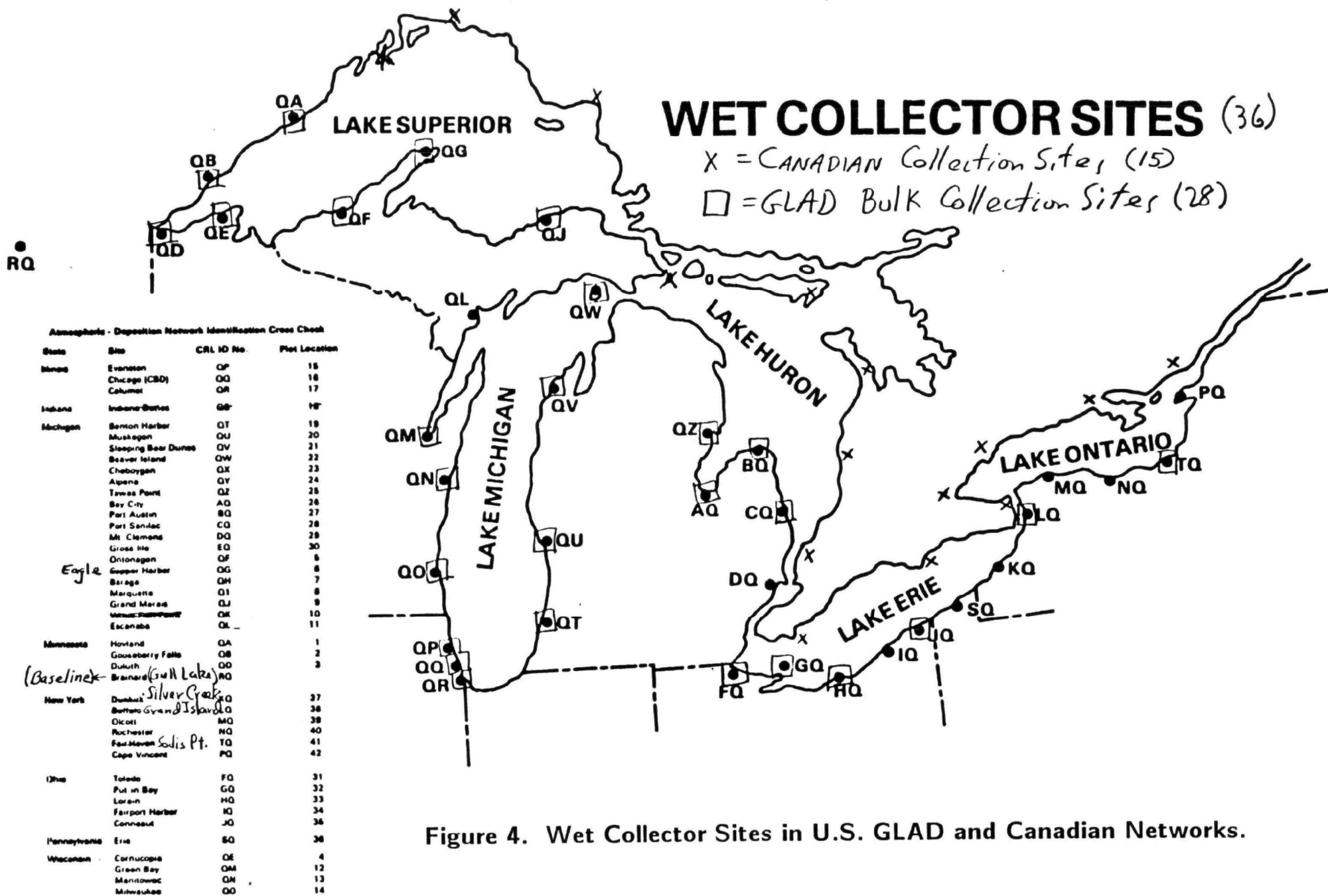| Atmospheric - Deposition Network Identification Cross Check			
State	**Site**	**CRL ID No.**	**Plot Location**
Illinois	Evanston	QP	15
	Chicago (CBD)	QQ	16
	Calumet	QR	17
Indiana	Indiana Dunes	QS	18
Michigan	Benton Harbor	QT	19
	Muskegon	QU	20
	Sleeping Bear Dunes	QV	21
	Beaver Island	QW	22
	Cheboygan	QX	23
	Alpena	QY	24
	Tawas Point	QZ	25
	Bay City	AQ	26
	Port Austin	BQ	27
	Port Sanilac	CQ	28
	Mt Clemens	DQ	29
	Gross Ile	EQ	30
	Ontonagon	QF	5
Eagle	Copper Harbor	QG	6
	Baraga	QH	7
	Marquette	QI	8
	Grand Marais	QJ	9
	Whitefish Point	QK	10
	Escanaba	QL	11
Minnesota	Hovland	QA	1
	Gooseberry Falls	QB	2
	Duluth	QO	3
(Baseline)	Brainerd (Gull Lake)	RQ	
New York	Dunkirk Silver Creek	LQ	37
	Buffalo Grand Island	LQ	38
	Olcott	MQ	39
	Rochester	NQ	40
	Fair Haven Sodis Pt.	TQ	41
	Cape Vincent	PQ	42
Ohio	Toledo	FQ	31
	Put in Bay	GQ	32
	Lorain	HQ	33
	Fairport Harbor	IQ	34
	Conneaut	JQ	35
Pennsylvania	Erie	SQ	36
Wisconsin	Cornucopia	QE	4
	Green Bay	QM	12
	Manitowoc	QN	13
	Milwaukee	QO	14

Figure 4. Wet Collector Sites in U.S. GLAD and Canadian Networks.

differences between the site populations (Figure 7) for sulphate and calcium median concentrations. These data show that major element concentrations and deposition generated in the NADP network adequately describe regional inputs. GLAD sites may more properly describible urban inputs.

D. Gatz concluded that GLAD network laboratory measurements of pH are biased low, major ion concentrations are similar but generally higher that NADP/NTN values, and wet deposition demonstrates the influence of local urban loading effects. The GLAD network adds resolution to the other network sites located in the Great Lakes vicinity.

5.0 Recommendations for a Great Lakes Atmospheric Inputs and Sources (GLAIS) Network.

5.1 General Recommendations

The most important recommendation is that the relevant U.S. and Canadian agencies cooperate in the formation of an "Integrated Atmospheric Deposition Network". The relative importance of the atmospheric deposition pathway compared to other input pathways is a matter of conjecture. In the Upper Lakes, especially Lake Superior, inputs of PCBs, DDT, PAHs, and chlorinated dioxins and furans are derived primarily from atmospheric deposition (7, 11-13). In the Lower Lakes, atmospheric inputs may dominate for some compounds but riverine sources dominate in most cases. For example, atmospheric Pb input to Lake Michigan is accounted for by accumulation in bottom sediments. In contrast, PCBs are about equally loaded from

Compliance of GLAD Sites to Criteria

Key to Column Headings in Table

(from T. Murphy, DePaul University)

Rf = Are collectors on a roof?
Rg = Does the site have a recording rain gauge?
Sp = Is the site located at a Waste Water Treatment Plant (POTW)?
Tr = Are trees obstructing the site (angle >45° above horizon)?
Rd = Is there a frequently used road within 100m of the site?
Co = Are the collectors located too close to one another?
So = Is a local source adversly affecting the site?
Ob = Are objects obstructing the site (angle >45° above horizon)?

Siting criteria from *EPA Quality Assurance Manual for Precipitation Measurement Systems (1985).*

1 = Obstructions subtend an angle less than 30° with the horizon.
2 = The distance between samplers or rain gages is >2m.
3 = Routine air, ground or water traffic is more than 100m distant.
4 = There are no overhead wires that affect the collectors.
5 = Open storage of agricultural products, fuels or other foreign materials are not be within 100m of the collectors.
6 = The ground surface is grass or gravel, and is firm.
7 = wet/dry collectors are oriented parallel to the prevailing winds with the wet bucket upwind.
8 = The rain gage is oriented parallel both to the collector and to the prevailing wind
Cl = Station Classification

Class I: Station satisfies criteria 1-8;
Instrumentation includes: automatic precipitation collector recording rain gauge; pH and Cond. meters; Wind speed and dir sensors; SO_2 and NO_x analyzers.

Class II: Station satisfies criteria 1-8;
Instrumentation includes: automatic precipitation collector recording rain gauge; pH and Cond. meters.

Class III: Station satisfies criteria 1-8;
Instrumentation includes: automatic precipitation collector non-recording rain gauge; pH and Cond. meters.

**Class IV**: Station does **not** satisfy all 8 criteria;
Instrumentation identical to Class I station.

Class V: Station does **not** satisfy all 8 criteria;
Instrumentation identical to Class II station.

Table 7B: Compliance of GLAD Sites to Criteria
(from T. Murphy, DePaul University)

SM	GL#	Name	Rf	RG	SP	Tr	Rd	Co	So	Ob	1	2	3	4	5	6	7	8	Cl
288a	QP	Evanston	Y	N	N	N	N	N	Y	N	Y	Y	Y	Y	Y	Y	Y	NA	
7a	QQ	Jardine Plant	Y	y	N	N	N	N	N	N	Y	Y	Y	Y	Y	Y	Y	NA	II
0a	QR	So. Water Plant	Y	y	N	N	N	N	N	N	Y	Y	Y	Y	Y	Y	Y	NA	II
291a	AQ	Bay City	Y	Y	N	N	N	Y	N	N	Y	N	Y	Y	Y	Y	Y	Y	U
2a	QW	Beaver Island	N	Y	N	N	N	N	N	N	Y	Y	Y	Y	Y	Y	Y	Y	II
3a	QT	Benton Harbor	Y	Y	N	N	Y	N	N	N	Y	Y	Y	Y-	Y	Y	N	Y	II
5a	QG	Eagle Harbor	N	Y	N	Y	Y	Y	N	N	N	Y	N	Y	Y	Y	y	N	U
206a	QV	Empire	N	Y	N	N	N	Y	N	N	Y	N	Y	Y	Y	Y	Y	Y	U
7a	QL	Escanaba	Y	Y	N	N	Y	N	Y	N	Y	Y	N	Y	Y	Y	N	N	U
8a	QJ	Grand Marais	N	Y	N	N	Y	Y	N	Y	N	N	N	Y	Y	N	N	N	U
299a	DQ	Mt. Clemens	Y	Y	N	N	N	N	N	Y	Y	N	Y	N	Y	Y	Y	Y	U
1a	QU	Muskegon	Y	Y	N	N	N	Y	N	N	Y	N	Y	Y	Y	Y	Y	Y	U
2a	QF	Ontonagon	N	Y	N	Y	Y	Y	Y	N	N	N	N	Y	N	N	Y	N	U
303a	BQ	Port Austin	Y	Y	N	N	Y	N	N	N	Y	Y	N	Y	Y	Y	Y	Y	U
4a	CQ	Port Sanilac	N	Y	N	Y	N	Y	N	N	N	N	Y	Y	Y	Y	Y	N	U
5a	QZ	Tawas Point	N	Y	N	Y	Y	Y	N	N	N	N	N	Y	Y	Y	Y	N	U
6a	QD	Duluth	Y	Y	N	N	N	Y	N	N	Y	Y	Y	Y	Y	Y	Y	N	U
307a	QB	Gooseberry Fls	N	N	N	N	N	Y	N	N	Y	Y	Y	Y	Y	Y	Y	NA	
8a	RQ	Gull Lake	N	N	N	Y	N	N	N	N	Y	Y	Y	Y	Y	Y	Y	NA	
9a	QA	Hovland	N	Y	N	N	N	Y	N	N	Y	N	Y	Y	Y	Y	N	N	U
310a	PQ	Cape Vincent	N	N	N	Y	Y	N	N	N	N	Y	N	Y	Y	Y	Y	NA	
1a	KQ	Silver Creek	N	N	Y	Y	Y	N	N	N	Y	Y	N	Y	Y	Y	Y	NA	
a	TQ	Sodus Point	N	N	N	N	Y	Y	N	N	Y	N	N	Y	Y	N	Y	NA	
313a	LQ	Grand Island	N	N	Y	N	N	N	Y	N	Y	N	Y	Y	Y	Y	N	NA	
314a	MQ	Olcott	Y	N	Y	Y	Y	N	Y	N	Y	Y	N	Y	Y	Y	Y	NA	
5a	NQ	Rochester	Y	N	Y	N	N	N	Y	N	Y	Y	Y	Y	N	Y	Y	NA	
6a	JQ	Conneaut	Y	y	N	N	N	Y	N	N	Y	N	Y	Y	Y	Y	Y	N	U
317a	IQ	Fairport Harbor	Y	N	N	N	N	N	N	N	Y	Y	Y	Y	Y	Y	Y	NA	
8a	HQ	Lorain	Y	N	N	Y	N	N	N	N	Y	Y	Y	Y	Y	Y	Y	NA	
9a	GQ	Put-In-Bay	N	Y	N	Y	Y	Y	N	N	Y	N	Y	Y	Y	Y	N	Y	U
320a	FQ	Toledo	N	N	Y	N	Y	Y	Y	N	Y	N	N	Y	Y	Y	N	NA	
1a	SQ	Erie	Y	Y	N	N	N	N	N	N	Y	Y	Y	Y	Y	Y	N	N	U
2a	QE	Cornucopia	N	Y	N	N	N	N	N	N	Y	Y	Y	Y	Y	Y	Y	Y	II
323a	QM	Green Bay	N	N	N	N	N	N	N	N	Y	Y	Y	Y	Y	Y	Y	NA	
324a	QN	Manitowoc	Y	Y	N	N	Y	N	N	N	Y	Y	Y	Y	Y	Y	N	Y	II
5a	QO	Milwaukee	Y	Y	N	N	Y	N	N	N	Y	Y	Y	Y	Y	Y	Y	Y	I
10		Hammond Bay	N		N	N	N		N	N	Y		Y	Y	Y	Y		NA	
502	CDN	Rossport	N	N	N	N	Y	N	N	N	Y	Y	N	Y	Y	Y	Y	NA	
13	CDN	Wawa	N	N	N	N	Y	N	N	N	Y	Y	N	Y	Y	Y	Y	NA	
14	CDN	Sault Ste Marie	N	Y	N	N	Y	N	Y	N	Y	Y	N	Y	Y	Y	Y	Y	U
508	CDN	Sarnia	N	N	N	Y	Y	N	?	N	Y	Y	N	Y	Y	Y	N	NA	
11	CDN	Niagara ot Lake	N	N	N	Y	N	Y	N	Y	N	N	Y	Y	Y	Y	Y	NA	

C-3

CUMULATIVE FREQUENCY DISTRIBUTION
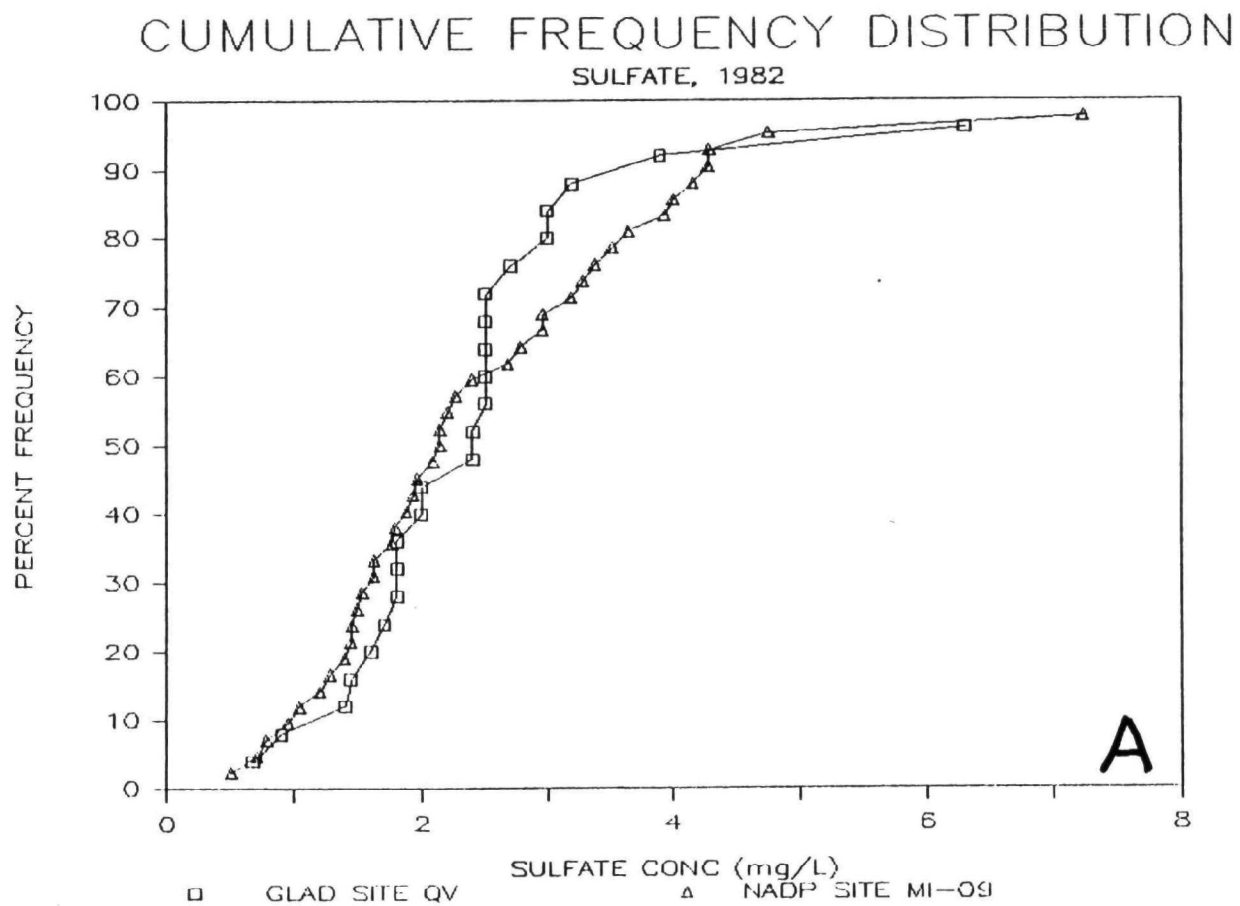
SULFATE, 1982

Figure 7. Cumulative Frequency Distributions for
GLAD and NADP Networks:
A. Sulfate;   B. Calcium
(D. Gatz, Ill. State Water Survey)

CUMULATIVE FREQUENCY DISTRIBUTION

CALCIUM, 1982

□   GLAD SITE QV   △   NADP SITE MI-09
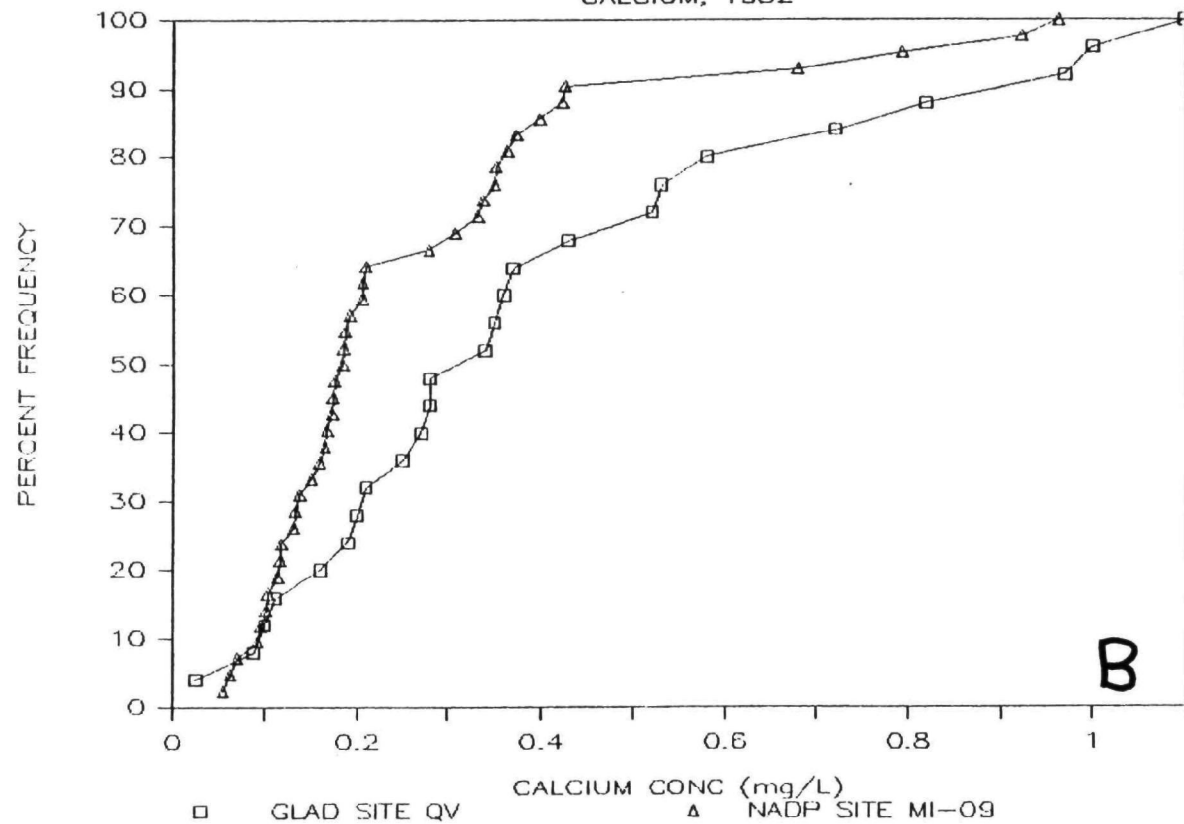
atmospheric and riverine sources (12). The chlorinated hydrocarbon burden of Lake Ontario and Lake Erie sediments can only be explained by dominating inputs from the Niagara River and Detroit River, respectively. Urban and industrial centers bordering the Great Lakes may also support intense, localized atmospheric inputs to the nearshore area (30 km) of unknown magnitude. Thus, atmospheric deposition of organic contaminants to the Great Lakes is impacted by regional deposition of pollutants transported some distance from their source, and localized deposition of pollutants transported short distances from sources. To complicate the issue, regional deposition is impacted by both regional sources and sources outside of the Great Lakes Basin. The GLAIS network must take into account these differing deposition patterns.

The processes controlling atmospheric inputs of specific organic contaminants are wet depositon (scavenging of gases and particles by rain and snow), dry particle deposition and vapor-exchange at the air-water interface. The relative importance of each process depends on the distribution of the chemical between the gas and particle phase and the efficiency of removal for each phase. In general, chemical-physical properties of the organic contaminant (e.g., H; Sol; P_V; K_{ow}) may be combined with mass transfer parameters (J; U_z; V_d; RH) and atmospheric concentrations to estimate deposition using simple (rain) or complex (particle or gas dry deposition) models. The GLAIS network should include the measurement of these parameters if it is to be successful.

The organic contaminants which have been frequently measured in the Great Lakes ecosystem include the PCBs, chlorinated pesticides and chlorinated compounds which are by-products of industrial activities (e.g., HCB; octochlorostyrene). In addition, some measurements of PAHs and chlorinated dioxins and furans have been reported (R. Hites, Indiana University, personal comm.). The new GLAIS network should monitor a suite of frequently encountered toxic chemicals as well as search for new chemicals introduced into the environment, especially via emerging technologies such as municipal waste incineration.

The new GLAIS network must incorporate a rigorous sampling protocol and QA/QC program to ensure the validity of the data. This protocol must describe the development status for each contaminant to be considered in terms of its concentration, precision, accuracy and validity (i.e., compliance with assumptions made in analytical methodology). Care should be taken to provide analytical detection limits corresponding to expected concentrations. U.S. and Canadian efforts should be closely coordinated in terms of goals, and sampling and analytical protocols.

As conceptualized by the workshop participants, the GLAIS network would encompass about 6 to 8 sampling sites per lake for "routine" deposition monitoring (2 to 4 in U.S. and Canada each), and 1 or 2 "master" stations per lake which incorporate research and cooperative studies (1 in Canada; 1 in U.S.). The sites should be evenly distributed between U.S. and Canadian territory (except for Lake Michigan). Perhaps 4 of the 8 routine stations should be located to assess regional inputs and the remaining 4 to assess more localized

urban inputs. The sites should be located, where posssible, on in-lake islands (e.g., Beaver Island; Isle Royale) and upwind and downwind relative to the prevailing wind direction. Every effort should be made to incorporate over-lake sampling and a strong research component to the new network. The routine stations would be equipped with sufficient wet samplers, air particle samplers and equipment necessary to collect meteorological data required for modeling atmospheric deposition.

Alternate methods of estimating total and atmospheric inputs of organic contaminants to the lakes should be continued. These include snow-coring, where possible, to obtain integrated winter loading rates, obtaining dated lake sediment and peat cores and mass balance studies.

5.2   Specific Recommendations.

5.2.1   Sampling Sites

* Routine Monitoring Sites

    * 6 to 8 per lake (divided between U.S. and Canada)

    * 3 to 4 per lake in dominant urban areas

    * 4 to 5 in rural areas differing in land-use

    * In-lake islands and on-lake sites are

      preferable to shoreline sites.

* Master Sites

    * 1 or 2 per lake (divided between U.S. and Canada)

    * Rural and urban area(s)

    * Co-located with Canadian sites.

5.2.2   Measurement at Routine Monitoring Sites

* Wet Deposition

    * (1) Wet-only integrating samplers

    * 2 week sampling period

    * In-situ separation of particulate and idssolved organic species

    * In-situ isolation of dissolved species

    * Collector surface area > 0.2 m^2

    * Samplers suitable for all-weather operation

* Dry Deposition

    * (2) Hi-Volume air samplers equipped with filter and backup adsorbent operated directionally.

    * Sampling frequency of 24 hours every 3 days

    * (1) Low-volume cascade impactor

* Climatological/Meteorological Parameters

    * Continuous recording of rain intensity, temperature, wind direction and velocity, and relative humidity.

5.2.3 Measurement at Master Sites

* Wet Deposition

    * (2) Wet-only integrating precipitating samplers

    * (1) Event precipitation sampler

    * In-situ separation of particulate and dissolved species

    * In situ isolation of dissolved species

    * Collector surface area > 0.2 m^2

    * All-weather operation

* Dry Deposition

* (3) Hi-volume air samplers equipped with filter and backup adsorbent

* Sampling frequency - every 24 hours

* Hi-Vols operated in concurrence with wind vectors (directional sampling)

* (1) Low flow cascade impactor with backup adsorbent

* (1) Hi-Vol dedicated to TSP and OC measurement

* Climatological/Meteorological Parameters

  * Same as for routine monitoring sites

  * Meteorological tower for measurement of atmospheric gradients (e.g., $T_{surface} - T_{air}$; etc.).

5.2.4 Chemical Measurements

* Routine

  * PCBs (total; congeners)

  * Chlorinated pesticides and other common ClCs.

  * PAHs

  * Pb, Cd

* Resarch Component (Master Site)

  * Toxaphene

  * Chlorinated dioxins and furans

  * Hg

* Other

  * TSP; OC (TSP); density and mmd of size-differentiated particles.

5.2.5 Quality Control/Quality Assurance

;ampling protocols

inalytical protocols

)lers at U.S. and Canadian sites

 sample replication; exchange between

)oratories.

inalytical detection limits.

itinuing) Deposition Methods

itudies

)r winter burdens

;n peat cores (atmosphere only)

l/or remote island studies

·iation

mpling

ds of specific sources

lysis

onment

earch Component to Monitoring Study

tmospheric inputs of organic contaminants

 at the air-water interface may result in

rganic gases or volatilization of organic

. Research needs are:

nstants (h) for organic contaminants

pendence of H

hodology to distinguish vapor and

ecies in the atmosphere, and dissolved

and non-dissolved species in the water

* Development/implementation of time-dependent model describing air-water interactions

* Methodology to estimate environment-dependent mass transfer coefficients

5.3.2 Detailed study to establish importance of urban vs. nonbpoint, intensive, localized deposition

5.3.3 Development/implementation of of dry particle deposition models

5.3.4 Development/implementation of _field_ measurements over lake and at the master site describing dry particle deposition models.

5.3.5 Identification of non-routine chemical substances in atmospheric deposition offering potentially adverse impacts on ecosystem health.

5.3.6 Implementation of research to "calibrate" dry particle deposition to artificial surfaces.

5.3.7 Conduct research to quantify the relative importance of atmospheric versus riverine contaminant inputs.

5.3.8 A _major field_ experiment should be conducted in the summer and winter of 1988 to integrate atmospheric data generated at the rural and urban master sites with those generated concurrently from an intensive over-lake study involving a meteorological tower and surface ship. The objectives of the multi-investigator study are to quantify the absolute atmospheric inputs, the relative importance of the various

input processes, reconcile sources, and to verify
atmospheric deposition models. Two potential locations
are southern Lake Michigan near Chicago and western
Ontario near Toronto.

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