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# ATMOSPHERIC DEPOSITION IN THE GREAT LAKES

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## EXECUTIVE SUMMARY

The Swedish National Environmental Protection Board and the United Nations Economic Commission for Europe hosted a workshop in Stockholm (March 12-14, 1990) entitled "Long-Range Transport of Organic Pollutants". The particular purpose of this meeting was to (a) provide a forum for exchange of information on the topic among researchers and policy makers in Europe, and (b) acquaint Scandinavian and other European researchers with existing and potential activities concerning atmospheric transport and deposition of persistent toxic organics, especially the organochlorines. A number of North American investigators in the field were invited and their papers, including this one, will appear in a published proceedings of the workshop.

This particular paper was intended to describe the development of the concern over atmospheric deposition in the Great Lakes and to describe the investigations in that area and what progress has been achieved to date. Here and in the workshop, the stress has been on the global nature of the transport and dispersal of the persistent organochlorine group of chemicals.

## RÉSUMÉ

Le Conseil national de protection de l'environnement de la Suède et la Commission économique pour l'Europe des Nations Unies ont organisé un colloque sur le transport à distance des polluants organiques, à Stockolm, du 12 au 14 mars 1990. Les objectifs principaux de cette rencontre étaient de permettre aux chercheurs et aux décideurs européens d'échanger des renseignements au sujet de ce phénomène et de mettre au courant les chercheurs scandinaves et autres chercheurs européens des activités actuelles et éventuelles touchant le transport et les dépôts de matières organiques toxiques persistantes, notamment de substances organochlorées. Un certain nombre de chercheurs américains oeuvrant dans ce domaine ont été invités à la rencontre, et leurs présentations, tout comme la présente, seront publiées dans le procès-verbal du colloque.

Ce document décrit l'évolution des préoccupations qui ont été soulevées au sujet des dépôts d'origine atmosphérique dans les Grands Lacs ainsi que les travaux et les progrès réalisés à ce jour. Tant dans ce document que pendant le colloque, on a mis l'accent sur le fait que le transport et la dispersion des substances organochlorées persistantes étaient devenus des phénomènes mondiaux.

# ATMOSPHERIC DEPOSITION IN THE GREAT LAKES

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## The Great Lakes Water Quality Agreements

Much of the efforts concerning toxic chemicals in the Great Lakes of North America has come from the Great Lakes Water Quality Agreements between the governments of Canada and the United States. It was these Agreements, and the infra-structure developed to ensure that they were carried out, which resulted in the development of a number of monitoring programs (International Joint Commission, 1986a) and the public reporting of the results of these. The first Agreement, signed in 1972, primarily dealt with the problems of cultural eutrophication and in particular, those arising from excessive phosphorous loadings to these freshwater lakes. The second Agreement was signed in 1978 and a major revision to this version took place in 1987; these had toxic chemical reductions in the system as their main goal.

There are two aspects of the Agreements related to sampling which have been particularly relevant to the long-range transport of toxic chemicals issue. The first was the emphasis on the water column to the exclusion of other compartments and subcompartments which was present in the first Agreement was changed in the second one. The Agreement of 1978 (and the Protocol of 1987) deliberately included all waters of the drainage basin as well as introducing the concept of `ecosystem'. This meant that activities in support of (and funded by) the Agreement could include those which were not directly addressing the water column -- including atmospheric loadings of toxic chemicals to the lakes.

The second concern -- analytical detection limits -- was perhaps not only a consequence of the Agreements although activities in support of them failed to provide necessary levels until recently. This resulted in monitoring efforts for the persistent organic contaminants directed towards measurements in biota and to a lesser extent sediments,. Our analytical capabilities have improved greatly today but because of this historic direction, there is a paucity of data on the basic compartments and few new efforts underway to improve the situation.

These shortcomings have been recognized recently, to no small extent because of a workshop held in late 1986 (International Joint Commission, 1987) and an entire Annex of the 1987 Protocol revised Agreement is devoted to Airborne Toxic Substances. This, together with a `Plan for Assessing Atmospheric Deposition to was Great Lakes' (International Joint Commission, 1988a) gives some promise of a more rational and predictive era of dealing with toxic chemicals in the Great Lakes. It still preserves, however, the traditional division of monitoring media and it seems that there is less of a concerted attack on the problem than there should be. Unbalanced efforts to develope the atmospheric component of the toxic chemicals monitoring program may not serve their intended purpose if the other compartments do not see a concurrent increase in effort.

## Modeling Toxic Chemicals in the Great Lakes

There are a number of models (International Joint Commission, 1986b) of the physical aspects of the Great Lakes -- ones which provide considerable description of changes to specific parameters in specific parts of the system at specific times. Some of them are quite reliable. There are also other models (International Joint Commission, 1988b) which aim at describing what happens to a chemical when it is released anywhere in the environment. These tend to be non-specific in predicting concentrations and are referred to as generic models.

For the Atmospheric Deposition Workshop mentioned, a simple accounting model or budget of the fate of chemicals in individual lakes was developed by Eisenreich and co-workers. This was used to evaluate the relative importance of the atmospheric route in loading chemicals to the Great Lakes (Strachan and Eisenreich, 1988). Efforts for this were focussed on the International Joint Commisssion's list of `Critical Pollutants' (Table 1). This Canada-U.S. body administers the Agreements and is the co-ordinating and evaluating mechanism whereby progress under the Agreements is assessed.

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Table 1: I.J.C.'s Water Quality Board's Critical Pollutants

Metals: Pb, Hg, Cd, As

Industrial Organics: B(a)P#, PAHs*, PCBs, TCDD, HCB#, Mirex, Kepone*

Pesticides: Dieldrin, Lindane (g-HCH), a-HCH#, DDT, Toxaphene

# - added to list for the workshop
* - deleted from the list for the workshop

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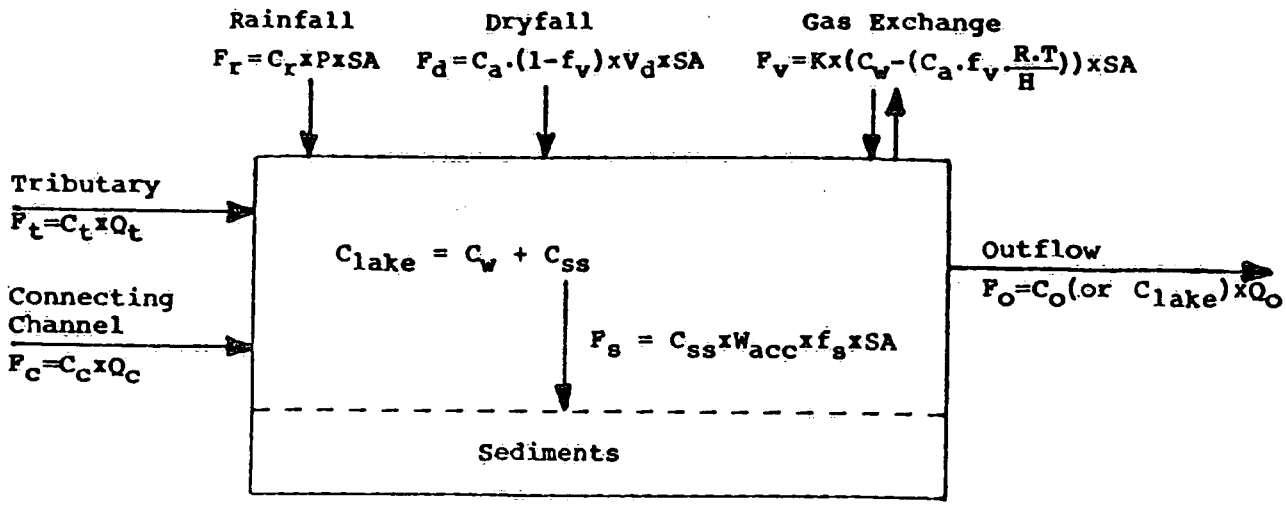
For each of these compounds for each of the lakes, the literature was examined and evaluated for utility in the mass balance model. The model framework is represented in Figure 1. In this, it can be seen that all processes are considered as "first order" which requires that data be available for each compartment and that the significant process rate constants must be known. It is also noted that, at the time of the workshop, no provisions were put in for the degradation rates. This latter assumption was not deemed to be a major problem for the substances for which there were concentration data for the compartments but it is a major problem if the model is to be applied generally for other chemicals.

Of all the chemicals examined from the Critical Pollutant List, only the polychlorinated biphenyls (total), DDT residues (including p,p'-DDT, p,p'-DDE and p,p'-DDD [TDE]), benzo(a)pyrene and lead had data bases adequate to attempt a mass balance. Table 2 summarizes the results. For all of the chemicals in this table, the atmosphere is indicated as an important if not dominant factor in the overall loading to individual lakes. Lower percentages in the lower lakes (Erie and Ontario) are the consequence of high inputs in the upstream

Figure 1: Framework for Mass Balance Calculations




Data Requirements:

- Q's - flows in tributaries and connecting channels
- C's - concentrations in rain, air (vapour plus particulate), water (dissolved), suspended solids(or sediments), tributaries and connecting channels (total)
- $f_v$ - fraction of atmospheric contaminant present as vapour
- $f_s$ - fraction of lake area with significant deposition
- P - precipitation to lake surface
- SA - surface area of the lake
- $V_d$ - particulate deposition velocity
- $W_{acc}$ - sediment accumulation rate for depositional zones

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connecting channels. The table also indicates that volatilization to the atmosphere is a major mechanism of removal of some of the same compounds. These conclusions are limited by the quality of the data which, for the purposes addressed here, is not high. They are often taken from different years and sometimes more than ten years separates concentration determinations in different compartments; some values used were debatable as to whether they were representative of a particular lakewide subcompartment since only a few determinations had been made. Despite these caveats, the results represent the best and most current data available at the time of the workshop and the estimates should be indicative of the importance of the several processes affecting the distribution of these chemicals.

## The Plan for Assessing Atmospheric Deposition in the Great Lakes

About the same time as the workshop was being prepared, the I.J.C. commissioned a group to draw up a plan to assess the extent and significance of atmospheric deposition in the system. A report was prepared which provides for a three-phase development of a network of sampling stations collecting precipitation and air samples on a bi-weekly basis (International Joint Commission, 1988a). A number of equipment decisions are still required as well as criteria for siting and several analytical problems. There were also a number

Table 2: Mass Balance Estimates of Chemical Sources and Fates in the Great Lakes

| CHEMICAL/ Lake | INPUTS: Atmospheric Direct | Atmospheric Indirect | Tributary Inputs | Connecting Channel# | OUTPUTS: Volaliz'n | Sediment'n | Export |
|---|---|---|---|---|---|---|---|
| | percentages | | | | | | |
| **PCBs** | | | | | | | |
| Superior | 90 | -- | 9 | -- | 87 | 11 | 2 |
| Michigan | 58 | -- | 42 | -- | 68 | 31 | 1 |
| Huron | 63 | 15 | 8 | 7 | 75 | 19 | 6 |
| Erie | 7 | 6 | 17 | 70 | 46 | 45 | 9 |
| Ontario | 6 | 1 | 12 | 81 | 53 | 30 | 17 |
| **DDT** | | | | | | | |
| Superior | 97 | -- | 3 | -- | 89 | 9 | 2 |
| Michigan | 98 | -- | 2 | -- | 44 | 54 | 2 |
| Huron | 71 | 26 | 3 | tr | 62 | 34 | 4 |
| Erie | 10 | 12 | tr | 78 | 26 | 68 | 6 |
| Ontario | 23 | 8 | 1 | 68 | 39 | 45 | 16 |
| **B(a)P** | | | | | | | |
| Superior | 96 | -- | 4 | -- | 19 | 78 | 3 |
| Michigan | 86 | -- | 14 | -- | 6 | 92 | 2 |
| Huron | 63 | 17 | 18 | 2 | 3 | 96 | 1 |
| Erie | 66 | 13 | 18 | 3 | 2 | 97 | 1 |
| Ontario | 40 | 32 | 20 | 8 | 3 | 91 | 6 |
| **Lead** | | | | | | | |
| Superior | 97 | -- | 1 | -- | -- | 99 | 1 |
| Michigan | 99+ | -- | tr | -- | -- | 98 | 2 |
| Huron | 94 | 4 | tr | tr | -- | 93 | 7 |
| Erie | 40 | 7 | tr | 53 | -- | 90 | 10 |
| Ontario | 51 | 23 | tr | 26 | -- | 80 | 20 |

# - excluding the portion due to the atmosphere which is exported from the upstream lake.

of research questions which were identified as essential information in either the operation of the network or the interpretation of the data. These several requirements are indicated in Table 3.

At present, Canada and the United States are engaged in implementing Phase 1 of the overall plan. This consists of building and operating a "master" station on each side of the border. Canada has constructed its station at Point Petrie on Lake Ontario while the United States has placed their's temporarily at Green Bay on Lake Michigan although they have stated an intention to move it next year to the Keewenaw Penninsula on Lake Superior. For two years, there is to be replicate biweekly sampling for organics and some metals in rainfall (or

snow depending on the season) and air. The questions in Table 3 are all to be addressed during this period and new stations identified -- a total of one master station and five satellite stations on each lake plus a station "upwind" and another "downwind" of the basin. The master stations are to serve as investigation sites as well as provide statistical data for the network while the satellites are to fill out the geographical resolution of the data.

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Table 3: Problems For the "International Atmospheric Deposition Network"

For Monitoring

1. Select chemicals for monitoring purposes;
2. Develop samplers particularly for vapour and particulates;
3. Determine the significance of overlake versus overland sampling;
4. Decide on the spatial and temporal sampling regimes;
5. Agree on local and areal siting criteria;
6. Develop routine analytical methods as needed and determine a sampling quality assurance program;
7. Assess indirect indicators of atmospheric input;
8. Identify sources and emissions;
9. Apply meteorological data in evaluating for source regions and other aspects of interpretation.

For Research and Interpretation

1. Determine the partition coefficients for airborne particles and vapour state by size fraction;
2. Determine particle deposition velocities by size fraction;
3. Determine the coefficients for mass transfer in the vapour state across the air-water interface;
4. Determine the partition coefficients for waterborne particles and the dissolved state;
5. Determine the scavenging (washout) coefficients of vapour and adsorbed state by rain and snow.

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The program has just commenced (January, 1990) although considerable preliminary work has led to the setting up of the two master stations mentioned and the establishment of a co-ordinating committee between the two countries to ensure comparability of data. To date, the two countries have:

- agreed that IJC plan was basically appropriate and forms a suitable basis for their programs addressing the Atmospheric Annex to the Agreement;

- agreed to develop a common QA/QC protocol (by October 1990) and to achieve compliance (October 1991);

- have selected the chemicals to be monitored at the master stations during Phase 1 (PCBs, the HCHs, Pb, benzo(a)pyrene, DDT residues, heptachlorepoxide, chlordane and nonachlor, methoxychlor, dieldrin, the endosulfans, HCB and endrin);

- have further identified several substances requiring methods development (toxaphene, Hg and unspecified PAHs) and others requiring evaluation as candidate substances for atmospheric concern (co-planar PCBs, Dioxins and furans and agrochemicals including the triazines and alachlor/metalachlor.

- agreed to master and satellite station facilities and sampling regimes (biweekly, air sampling 2 days in 14).

Because of the global nature of the transport of toxic chemical problem, those involved with the Great Lakes atmospheric program welcome the initiative undertaken by the Swedish Environmental Protection Board and the U. N. Economic Commission for Europe and hope that some integrated efforts along the lines indicated by `the plan' can be undertaken and hence that better estimates of the ways to control the spread of this type of pollution identified.

References

[Depending upon availability, reports of the International Joint Commission can be obtained free of charge from: International Joint Commission (Regional Office), 100 Ouellette Ave., Windsor, Ontario, Canada, N9A 6T3]

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