The Role of Air-Water Exchange of PCBs in Whole-Lake Cycling

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Introduction

Toxic organic compounds are ubiquitous in the global atmosphere as a result of historical and present anthropogenic emissions, and their continued mobilization from aquatic and terrestrial reservoirs[1,2]. Polychlorinated biphenyls (PCBS) are persistent, bioaccumulative organic chemicals that are globally distributed and contribute to wide-scale environmental problems[3]. Wet deposition, dry particle deposition and gas exchange are the three major depositional pathways for atmospheric delivery of PCBs to aquatic systems[4,5]. Measurements and modeling suggest that wet deposition is important over long- and short-range scales[1]. Dry particle deposition is, by comparison, poorly quantified but improved measurement and modeling strategies have improved estimates of atmospheric deposition. By comparison, air-water exchange of PCBs in aquatic systems has only recently been quantified with sufficient certainty to suggest that air-water exchange dynamics frequently dominate PCB fluxes in several types of aquatic systems[6]. This presentation will highlight the important processes of air-water exchange, summarize quantification strategies, and provide evidence for its relative importance in especially susceptible aquatic ecosystems such as the Great Lakes of North America.

Process of Air-Water Exchange of Gaseous PCBs

Air-water exchange refers to the transfer of a chemical across an air-water interface driven by the concentration or chemical potential gradient from the atmospheric turbulently-mixed layer to an aquatic mixed layer and a mass transfer coefficient. The chemical potential gradient depends on the instantaneous atmospheric gas-phase and aquatic dissolved-phase concentrations of PCBs, the molecular volume of the chemicals, and the temperature-dependent Henry's Law constants. The mass transfer coefficient is a function of the extent of turbulent mixing in the surface water, most often derived from wind speed correlations[7]. The actual selection of the transfer model is not as critical as selecting an appropriate strategy for estimating mass transfer coefficients as a function of wind speed, especially using gas tracers such as SF_6. Once instantaneous coefficients are estimated, then the challenge is to aggregate them over temporal and spatial regimes, and to couple them to temporal and spatial variations in measured or modeled air and water concentrations. These dynamic models are only now being developed. The challenges also include the necessity of measuring or predicting atmospheric gaseous and aquatic dissolved PCB concentrations over time and space which actively partition between dissolved/gaseous and particle phases. The temporal signal of atmospheric PCBs is reasonably known over land[8,9], but over water characterization is uncertain[10-12]. The temporal and spatial signals of dissolved-phase concentrations of PCBs are largely unknown although variations may not be as large as expected.

Air-Water Exchange Fluxes of Σ-PCBs

Methodologies to quantify air-water exchange fluxes of PCBs include construction of mass budgets [13-16], using available data on air and water concentrations linked to average meteorological and water *conditions*[1,17] and simultaneous measurements of air and water concentrations linked to timely meteorological measurements with model extension to seasonal and annual fluxes[6,10,11,18]. Table 1 lists published *net* air-water exchange fluxes for PCBs mostly related to the North American Great Lakes.

Taken as a whole, the air-water exchange fluxes of PCBs support the following conclusions:

- *Net* air-water exchange fluxes of Σ-PCBs are approximately + 30 to + 100 ng/m^2 d for most of the lakes averaged across the seasons in the last decade.
- *Net* air-water exchange fluxes reflect *net* volatilization, whether in pristine or impacted lakes, whether near or far from sources, whether big or small, and whether eutrophic or oligotrophic.
- Absorption fluxes dominate in Spring; volatilization fluxes dominate in Autumn.
- *Net* air-water exchange fluxes reflect *net* Σ-PCB absorption over extended temporal and spatial scales only when the lake is proximate to urban-industrial centers such as southern Lake Michigan and the local emissions are transported to the lake by the winds.
- Remote lakes also exhibit *net* volatilization fluxes on an annual basis due to focused atmospheric inputs from the lake's watershed.
- The dominant effect of trophic status is to reduce the importance of the volatilization pathway.
- Shallow, warm, and impacted aquatic systems such as Green Bay, Lake Michigan and Chesapeake Bay exhibit high net volatilization fluxes partially due to intimate contact with contaminated sediments.
- Air-water exchange fluxes of Σ-PCBs are important contributors to whole-lake inventories, water column residence times and ecosystem response times.
- Air-water exchange dynamics of PCBs may support chemical burdens in phytoplankton, thereby supporting the aquatic food chain.

The best of the air-water exchange fluxes of Σ-PCBs reported in Table 1 exhibit uncertainties of ~ 50 to 100%. This is inadequate to model lake response times to changing inputs from other sources and to estimate the role of air pollution on water quality. A strategy which couples a dynamic measurements program with dynamic models of air-water exchange are needed to reduce uncertainties and respond to control and regulatory scenarios.

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Table 1. Air-Water Exchange Fluxes of PCBs (+ = net volatilization; - = net absorption)

Lake	Σ-PCB Flux ng/m² d	Reference
Superior-1986	+ 19 (Still air) +141 (5 m/s)	19
Superior-1986 -1992	+ 63 + 17	15
Superior-1986	+ 63	17
Superior-1992	+ 8	10
Siskiwit Lake-1986	+ 23	13
Superior-1992	+ 57	1
Green Bay-1989 Lake Michigan	+ 65 to + 195	6
Michigan-1986	+ 240	17
Michigan-1986	+ 15	20
Michigan-1992 North 75%	+ 34	11
Michigan-1992	+ 130	1
Michigan-1994 South 25%	- 50	18
Erie-1992	+ 45	1
Ontario-1986	+ 97	17
Ontario-1989	+ 81	14
Ontario-1992	+ 46	1
ELA Lake 110-1994 Oligotrophic	+ 13	16
ELA Lake 227-1994 Eutrophic	+ 9	16
Chesapeake Bay	+ 370	21