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Atmospheric flows of semi-volatile organic pollutants to the Great Lakes estimated by the United States' Integrated Atmospheric Deposition and Canada's Great Lakes Basin Monitoring and Surveillance Networks

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ABSTRACT

We calculated the wet and dry deposition, vapor absorption, and volatilization flows (in kg/yr) of seven polychlorinated biphenyls (PCBs), nine organochlorine pesticides, and two polycyclic aromatic hydrocarbons (PAHs) into and out of the Great Lakes during 2010–2015 (inclusive). Particle, vapor, and precipitation concentrations from five rural and remote stations (one site on each lake) and two urban sites, operated by the United States and Canada, were used for the flow calculations. Output from the water to the air was the most important process for PCBs, chlordanes, and *p,p′*-DDE. The flows of endosulfan, *p,p′*-DDT, and phenanthrene were dominated by vapor absorption from the air to the water. The flow of benzo[*a*]pyrene was controlled by wet and dry deposition to the water. The flows of the hexachlorocyclohexanes (HCHs) into and out of the lakes were about equal, indicating air-water equilibrium for these compounds. Among the lakes, Lakes Superior and Erie had the highest input and output flows. The input and output flows for the five lakes were decreasing with halving times of 1–10 years and 10–40 years, respectively. Most chemicals had seasonal variations in their flows, with maximum inputs in the summer and maximum outputs in the fall. The flows of PCBs and PAHs into Lakes Michigan and Erie were associated with Chicago and Cleveland, respectively. Combining our data with previous data over the period 1992–2015, we estimated that the input flows of most of these chemicals have significantly decreased, but the output flows do not show consistent trends.

Introduction

In 1990, to support the commitments of the Great Lakes Water Quality Agreement (U.S. EPA, 2012), the United States and Canada established the Integrated Atmospheric Deposition Network (IADN) to measure the atmospheric concentrations of semi-volatile organic pollutants to the lakes. These measurements were standardized by collaborations between these two national programs (Wu et al., 2009). Later, Canada's part of IADN was renamed the Great Lakes Basin (GLB) Monitoring and Surveillance Network. The primary goals of these programs were measuring semi-volatile organic pollutant concentrations in air and precipitation, estimating their atmospheric flows into the lakes, and examining spatial and temporal trends of both concentrations and atmospheric flows (Buehler and Hites, 2002; Shunthirasingham et al., 2016). The pollutants included in this study are polychlorinated biphenyls (PCBs), organochlorine pesticides, and polycyclic aromatic hydrocarbons (PAHs).

Extensive studies using IADN and GLB data have reported on the spatial and temporal trends of PCB, pesticide, and PAH concentrations in Great Lakes air and precipitation (Buehler et al., 2002; Cortes et al., 1998; Hillery et al., 1997; Liu et al., 2014; Salamova et al., 2015; Shunthirasingham et al., 2016; Strandberg et al., 2001; Sun et al., 2007, 2006a, 2006b, 2006c; Venier and Hites, 2010b; Venier et al., 2016). According to these studies, atmospheric concentrations of semi-volatile organic pollutants, such as PCBs, chlordanes, and dichlorodiphenyltrichloroethanes (DDTs), current use pesticides, such as endosulfan, and unintentionally produced pollutants, such as PAHs, have been decreasing with halving times of about 10–15 years. The exceptions are the hexachlorocyclohexanes (HCHs), the concentrations of which have been decreasing with halving times of 3–4 years (Venier and Hites, 2010b). In general, the concentrations of all of these

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compounds were higher in urban than in rural areas with the exception of the HCHs and endosulfans.

By maintaining a master station on each of the Great Lakes, IADN and GLB are able to measure the atmospheric deposition of selected pollutants to the lakes (Buehler et al., 2001), and the networks have, in fact, produced flow estimates using data from 1992 through 2012 (Blanchard et al., 2008, 2004; Buehler et al., 2001; Galarneau et al., 2000; Hillery et al., 1998; Hoff et al., 1996; Shunthirasingham et al., 2016). According to these atmospheric flow estimates, during 1993–1994 (Hillery et al., 1998), the flows of most pesticides and lower molecular weight PAHs were primarily controlled by the air-water exchange process, and their deposition to the lakes was roughly balanced by their output from the lakes. In the flow estimates for the years 1995–2005 (Blanchard et al., 2008, 2004; Buehler et al., 2001; Galarneau et al., 2000), the deposition of PCBs and most pesticides to the lakes continued to decline and the outputs from the lakes exceeded their inputs. The exceptions were endosulfan and some PAHs. The inputs of the current-use pesticide endosulfan exceeded its outputs; and the inputs of PAHs were significant, but their outputs were small. A more recent study based on IADN and GLB data collected between 1992 and 2012 focused only on Lakes Huron and Ontario (Shunthirasingham et al., 2016). This study noted the continuously decreasing inputs of pesticides and PCBs and pointed out that PCB inputs were decreasing slower than those of pesticides. Other recent studies on atmospheric flows into the Great Lakes have focused on a limited number of analytes, on a limited number of lakes, or on a limited time period (Khairy et al., 2014; Liu et al., 2016; McDonough et al., 2014; Melymuk et al., 2011).

This study updates the spatial and temporal trends of atmospheric flows of PCBs, organochlorine pesticides, and PAHs to all of the five Great Lakes based on published and recent IADN and GLB chemical concentration measurements. To make the discussion tractable, we have selected a set of 18 semi-volatile pollutants: seven PCB congeners, nine pesticides, and two PAHs. The time frame of this study is 2010–2015 (inclusive). Seventy-two monthly deposition flows for wet and dry deposition and for vapor transfer at the air-water interface are calculated. Seasonal trends, differences among the lakes, and urban effects are also examined. Yearly flows during 2010–2015 are compared to earlier estimates to determine temporal trends over the period 1992–2015. This study is the most up-to-date estimate of the atmospheric flows of PCBs, pesticides, and PAHs to the Great Lakes.

This paper focuses only on the air-water interface and transfers across this interface. Because it is outside the scope of this paper, we are not including deposition processes to and from the sediment, which can be significant (Rossmann, 2005; Guo et al., 2017). In addition, we are not including inputs from tributaries, which, at least for PCBs in Lake Michigan, are not large (Guo et al., 2017). Neither are we including outputs through the St. Lawrence River.

Methods

Sampling and sample pretreatment

The sampling sites for air are shown in the Electronic Supplemental Material (ESM: Fig. S1). The sampling sites are part of the United States' Integrated Atmospheric Deposition Network and Canada's Great Lakes Basin Monitoring and Surveillance Network (ECCC, 2010). Flows of semi-volatile organic pollutants into the lakes are estimated based on the concentrations measured at the five master stations, one per lake. The master stations on Lakes Erie (Sturgeon Point, STP), Michigan (Sleeping Bear Dunes, SBD), and Superior (Eagle Harbor, EH) are operated by Indiana University (IU) via a cooperative agreement with the U.S. Environmental Protection Agency (EPA). Environment and Climate Change Canada (ECCC) operates the master stations on Lakes Huron (Burnt Island, BNT) and Ontario (Point Petre, PPT) (Blanchard et al., 2008). The satellite stations in Chicago (CHI) and Cleveland (CLEV), representing the urban influences on Lake Michigan and Lake Erie, respectively, are also operated by IU. Sampling at BNT stopped in March 2013.

Details on the protocols used to sample precipitation and air (both particulate and vapor phases) are given in their corresponding Standard Operating Procedure (SOP) manuals for each participating agency (ECCC, 2002; Harrison, 2005; U.S. EPA, 2011). IADN and GLB both use modified high volume samplers with filter and absorbent combinations to sample the organic compounds in air. In general, air was sampled for 24 h every 12 days. IU and ECCC use quartz and glass fiber filters, respectively, to collect particulate-phase organic compounds. These filters are followed in the airstream by absorbents to collect the vapor-phase compounds. ECCC uses polyurethane foam with a sample volume no higher than 400 m^3 to minimize breakthrough of the more volatile species during warm summer months. In January 2010, sampling of the vapor phase at PPT was changed to include two polyurethane foam disks in series to reduce breakthrough. IU uses XAD-2 resin, which allows for a sample volume of 815 m^3. All master and satellite stations collected precipitation using Meteorological Instruments of Canada samplers (MIC-B, Thornhill, Ontario, Canada), which are triggered to open only during a precipitation event. In the IU samplers, the precipitation flows through an XAD-2 resin packed column, and the water is discarded. The ECCC precipitation samplers use an on-site dichloromethane solvent extraction system in which dichloromethane is added to the sample bottles in the field for stabilization. After the monthly sample collection, liquid/liquid extraction with dichloromethane takes place on the whole sample in the laboratory. Precipitation samples are integrated on a monthly basis.

Detailed sample preparation information about these vapor, particle, and precipitation samples has been previously published (Wu et al., 2009; Salamova et al., 2015; Shunthirasingham et al., 2016; Venier et al., 2016). The sample preparation procedures in the U.S. and in Canada are different. In the U.S., the samples (vapor, particle, and precipitation) are spiked with surrogates and Soxhlet extracted for 24 h with 1:1 (v:v) hexane in acetone. The extracts are then cleaned-up on water deactivated silica gel columns, concentrated, and analyzed (see below). In Canada, the vapor phase samples were Soxhlet extracted with hexane, and the particle samples were extracted with 7:3 (v:v) hexane in acetone using accelerated solvent extraction. The precipitation samples were spiked with recovery standards and liquid-liquid extracted using a separatory funnel or a Goulden Large Sample Extractor. The extracts were reduced in volume by rotary evaporation, fractionated on silica or Florisil columns, concentrated, and analyzed (see below). Data for the concentrations of the compounds of interest in open Great Lakes' water samples, collected in 2011 and 2012, have been previously published (Venier et al., 2014).

Instrumental analysis

The target chemicals in this study include seven PCBs (congeners 28, 52, 101, 118, 138, 153, and 180), two PAHs (phenanthrene and benzo[*a*]pyrene), and nine organochlorine pesticides. The latter are two DDTs (*p,p′*-DDT and *p,p′*-DDE), three chlordanes (α-chlordane, γ-chlordane, and *t*-nonachlor), two endosulfans (α-endosulfan and β-endosulfan), and two HCHs (α-HCH and γ-HCH). For the IU samples, PCBs and pesticides were analyzed by gas chromatography on Hewlett-Packard and Agilent instruments equipped with ^{63}Ni electron capture detectors (GC-ECD) and with DB-5 (J&W Scientific) 60-m columns (250 μm i.d., 0.1 μm film thickness). Pesticide analyses were confirmed by GC-ECD using 60-m DB-1701 columns (250 μm i.d., 0.1 μm film thickness); the reported pesticide concentrations are the minimum of the two measurements. The PAHs were measured on an Agilent 6890 gas chromatograph coupled to an Agilent 5973 mass spectrometer (MS) operating in the electron impact ionization mode with a DB-5 column (J&W Scientific, 30-m, 250-μm i.d., 0.25-μm film thickness). Quantitation