



## Atmospheric Deposition of Toxic Chemicals

Indicator #117

### Overall Assessment

Status: **Mixed**

Trend: **Improving (for PCBs, banned organochlorine pesticides, dioxins and furans) / Unchanging or slightly improving (for PAHs and mercury)**

Rationale: **Mixed since different chemical groups have different trends over time; levels in cities can be much higher than in rural areas.**

Levels of persistent bioaccumulative toxic (PBT) chemicals in air tend to be lower over Lake Superior and Lake Huron than over the other three Great Lakes (which are more impacted by human activity), but their surface area is larger, resulting in a greater importance of atmospheric inputs.

While concentrations of some of these substances are very low at rural sites, they may be much higher in “hotspots” such as urban areas. Lake Michigan, Lake Erie, and Lake Ontario have greater inputs from urban areas. The Lake Erie station tends to have higher levels than the other remote masters stations, most likely since it is located closer to an urban area (Buffalo, NY) than the other master stations. It may also receive some influence from the East Coast of the U.S..

In general for PBT chemicals, atmospheric inputs dominate for Lake Superior, Lake Huron, and Lake Michigan due to their large surface areas (Strachan and Eisenreich 1991; Kreis 2005). Connecting channels inputs dominate for Lake Erie and Lake Ontario, which have smaller surface areas.

### Purpose

- To estimate the annual average loadings of PBT chemicals from the atmosphere to the Great Lakes
- To determine trends over time in contaminant concentrations
- To infer potential impacts of toxic chemicals from atmospheric deposition on human health and the Great Lakes aquatic ecosystem
- To track the progress of various Great Lakes programs toward virtual elimination of toxic chemicals to the Great Lakes

Tracking atmospheric inputs is important since the air is a primary pathway by which PBTs reach the Great Lakes. Once PBTs reach the Great Lakes, they can bioaccumulate in fish and other wildlife and cause fish consumption advisories.

### Ecosystem Objective

The Great Lakes Water Quality Agreement (GLWQA, United States and Canada 1987) and the Binational Toxics Strategy (Environment Canada and U.S. Environmental Protection Agency 1997) both state the virtual elimination of toxic substances in the Great Lakes as an objective. Additionally, GLWQA General Objective (d) states that the Great Lakes should be free from materials entering the water as a result of human activity that will produce conditions that are toxic to human, animal, or aquatic life.

### State of the Ecosystem

The Integrated Atmospheric Deposition Network (IADN) consists of five master sampling sites, one near each of the Great Lakes, and several satellite stations. This joint United States-Canada project has been in operation since 1990. Since that time, thousands of measurements of the concentrations of PCBs, pesticides, PAHs and trace metals have been made at these sites. Concentrations are measured in the atmospheric gas and particle phases and in precipitation. Spatial and temporal trends in these concentrations and atmospheric loadings to the Great Lakes can be examined. Data from other networks are used here to supplement the IADN data for mercury, dioxins and furans.

#### PCBs

Concentrations of gas-phase PCBs ( $\Sigma$ PCB) have generally decreased over time at the master stations (Figure 1, Sun *et al.* 2007).  $\Sigma$ PCB is a suite of congeners that make up most of the PCB mass and that represent the full range of PCBs. Some increases are seen during the late 1990s for Lake Michigan and Lake Erie and during 2000-2001 for Lake Superior. These increases remain unexplained, although there is some evidence of connections with atmospheric circulation phenomena such as El Nino (Ma *et al.* 2004a). Levels decreased again by 2002. It is assumed that PCB concentrations will continue to decrease slowly. PCBs in precipitation samples at the rural master stations are nearing levels of detection.

The Lake Erie site consistently shows relatively elevated  $\Sigma$ PCB concentrations compared to the other master stations. Back-trajectory analyses have shown that this is due to possible influences from upstate New York and the East Coast (Hafner and Hites 2003). Figure 2 shows that  $\Sigma$ PCB concentrations at urban satellite stations in Chicago and Cleveland are about fifteen and ten times higher, respectively, than at the remote master stations at Eagle Harbor (Lake Superior) and Sleeping Bear Dunes (Lake Michigan).

#### Pesticides

In general, concentrations of banned or restricted pesticides measured by the IADN (such as hexachlorocyclohexane ( $\alpha$ -HCH) and DDT) are decreasing over time in air and precipitation (Sun *et al.* 2006a; Sun *et al.* 2006b). Concentrations of chlordane are about ten times higher at the urban stations than at the more remote master stations, most likely due to the use of chlordane as a termiticide in buildings. Dieldrin levels show a similar increase in urban locales. This pesticide was also used as a termiticide until 1987, after all other uses were banned in 1974. Current-use pesticide endosulfan shows mixed trends, with significant decreases at some sites in some phases, but no trends at other sites. Concentrations of endosulfan were generally higher in the summer, following application of this current-use pesticide (Sun *et al.* 2006b). An investigation of atrazine, a current-use herbicide, concentrations at 3 Canadian IADN sites from 1996 to 2002 also yielded similar results with concentrations highest in the spring and early summer (Yao *et al.* 2007). Concentrations of atrazine also varied spatially with the highest concentrations occurring in Egbert and the lowest in Burnt Island. This is the pattern that would be expected if local usage is contributing to the levels observed at these sites (Yao *et al.* 2007).

#### PAHs

In general, concentrations of polycyclic aromatic hydrocarbons (PAH) can be roughly correlated with human population, with highest levels in Chicago and Cleveland, followed by the semi-urban site at Sturgeon Point, and lower concentrations at the other remote master stations. In general, PAH concentrations in Chicago and Cleveland are about ten to one hundred times higher than at the master stations.

Concentrations of PAHs in the particle and gas phases are decreasing at Chicago, with half-lives ranging from 3 to 10 years in the vapor phase and 5 to 15 years in the particle phase. At the other sites, most gas phase PAH

concentrations showed significant, but slow long-term decreasing trends (greater than 15 years). For most PAHs, decreases on particles and in precipitation were only found at Chicago (Sun *et al.* 2006c, Sun *et al.* 2006d).

An example of a PAH is benzo[ $\alpha$ ]pyrene (BaP), which is produced by the incomplete combustion of almost any fuel and is a probable human carcinogen. Figure 3 shows the annual average particle-phase concentrations of BaP.

#### Dioxins and Furans

Concentrations of dioxins and furans have decreased over time (Figure 4) with the largest declines in areas with the highest historical concentrations (unpublished data, T. Dann, Environment Canada 2006).

#### Mercury

Data from the Canadian Atmospheric Mercury Measurement Network (CAMNet) for the IADN stations at Egbert, Point Petre, and Burnt Island show decreases in total gaseous mercury (TGM) concentrations of 2.2%, 16.6%, and 5.1%, respectively from 1996 (1998 for Burnt Island) to 2005 (Temme *et al.* 2007). A large decrease in median concentrations from 2001 to 2002 dominates these overall trends for combined data at Egbert, Point Petre, and St. Anicet – all rural sites that are impacted by urban areas of Toronto or Montreal (Figure 5).

Data from the Mercury Deposition Network show that concentrations of mercury in precipitation are decreasing for much of the U.S., but there is no visible trend for the stations in the upper Midwest (Gay *et al.* 2006).

#### PBDE

Total PBDE concentrations in the Great Lakes atmosphere during 2004-2006 were in the single pg/m<sup>3</sup> range for the rural master stations and in the 50 to 100 pg/m<sup>3</sup> range for the urban stations (Venier 2008). This is lower than total PCB levels, which are generally in the 10s to 100s of pg/m<sup>3</sup> range at the rural master stations. On a congener by congener basis, the atmospheric concentrations of BDE-47 and BDE-99 (but not of BDE-209) appear to be generally declining (Figure 6). This reflects their historical usage with U.S. manufacturers having phased out production of penta- and octa- PBDEs in 2004, and deca-PBDE still being produced. However, 3 years worth of data is limited and future data will confirm whether levels of PBDEs increase or decrease in the air of the Great Lakes.

#### Loadings

An atmospheric loading is the amount of a pollutant entering a lake from the air, which equals wet deposition (rain) plus dry deposition (falling particles) plus gas absorption into the water minus volatilization out of the water. Absorption minus volatilization equals net gas exchange, which is the most significant part of the loadings for many semi-volatile PBT pollutants. For many banned or restricted substances that IADN monitors, net atmospheric inputs to the lake are headed toward equilibrium; that is, the amount going into the lake equals the amount volatilizing out. Current-use pesticides, such as  $\gamma$ -HCH (lindane) and endosulfan, as well as PAHs and trace metals, still have net deposition from the atmosphere to the Lakes.

A report on the atmospheric loadings of these compounds to the Great Lakes for data through 2005 is available online at: <http://www.epa.gov/glnpo/monitoring/air/iadn/iadn.html>. To receive a hardcopy, please contact one of the agencies listed at the end of this report.

#### **Pressures**

Atmospheric deposition of toxic compounds to the Great Lakes is likely to continue into the future. The amount of compounds no longer in use, such as most of the organochlorine pesticides, may decrease to undetectable levels, especially if they are phased out in developing countries, as is being called for by international agreements.

Residual sources of PCBs remain in the U.S. and throughout the world; therefore, atmospheric deposition will still be significant at least decades into the future. PAHs and metals continue to be emitted and therefore concentrations of these substances may not decrease or will decrease very slowly depending on further pollution reduction efforts or regulatory requirements. Even though emissions from many sources of mercury and dioxin have been reduced over the past decade, both pollutants are still seen at elevated levels in the environment. This problem will continue unless the emissions of mercury and dioxin are reduced further.

Atmospheric deposition of chemicals of emerging concern, such as brominated flame retardants and other compounds that may currently be under the radar, could also serve as a future stressor on the Great Lakes. Efforts are being made to screen for other chemicals of potential concern, with the intent of adding such chemicals to Great Lakes monitoring programs given available methods and sufficient resources.

### **Management Implications**

In terms of in-use agricultural chemicals, such as lindane, further restrictions on the use of these compounds may be warranted. Transport of lindane to the Great Lakes following planting of lindane-treated canola seeds in the Canadian prairies has been demonstrated through models (Ma *et al.* 2004b). On 1 January 2005, Canada withdrew registration of lindane for agricultural pest control. Agricultural uses of lindane in the U.S. will end in 2009 (Federal Register 2006).

Controls on the emissions of combustion systems, such as those in factories and motor vehicles, could decrease inputs of PAHs to the Great Lakes atmosphere.

Although concentrations of PCBs continue to decline slowly, somewhat of a “leveling-off” trend seems to be occurring in air, fish, and other biota as shown by various long-term monitoring programs. Remaining sources of PCBs, such as contaminated sediments, sewage sludge, and in-use electrical equipment, may need to be addressed more systematically through efforts like the Canada-U.S. Binational Toxics Strategy and national regulatory programs in order to see more significant declines. Many such sources are located in urban areas, which is reflected by the higher levels of PCBs measured in Chicago and Cleveland by IADN, and by other researchers in other areas (Wethington and Hornbuckle 2005; Totten *et al.* 2001). Research to investigate the significance of these remaining sources is underway. This is important since fish consumption advisories for PCBs exist for all five Great Lakes.

Progress has been made in reducing emissions of dioxins and furans, particularly through regulatory controls on incinerators. Residential garbage burning (burn barrels) is now the largest current source of dioxins and furans (Environment Canada and U.S. Environmental Protection Agency 2003). Basin and nationwide efforts are underway to eliminate emissions from burn barrels.

Regulations on coal-fired electric power plants, the largest remaining source of anthropogenic mercury air emissions, will help to decrease loadings of mercury to the Great Lakes.

Pollution prevention activities, technology-based pollution controls, screening of in-use and new chemicals, and chemical substitution (for pesticides, household, and industrial chemicals) can aid in reducing the amounts of toxic chemicals deposited to the Great Lakes. Efforts to achieve reductions in use and emissions of toxic substances worldwide through international assistance and negotiations should also be supported, since PBTs used in other countries can reach the Great Lakes through long-range transport.

Continued long-term monitoring of the atmosphere is necessary in order to measure progress brought about by toxic reduction efforts. Environment Canada and U.S. EPA are currently adding dioxins and PBDEs to the IADN as funding allows. Mercury monitoring at Canadian stations is being conducted through the CAMNet. Additional urban monitoring is needed to better characterize atmospheric deposition to the Great Lakes.

**Assessing Data Quality**

Insert “x” under the statement that best corresponds with each data characteristic

<b>Data Characteristics</b>	<b>Strongly Agree</b>	<b>Agree</b>	<b>Neutral or Unknown</b>	<b>Disagree</b>	<b>Strongly Disagree</b>	<b>Not Applicable</b>
1. Data are documented, validated, or quality-assured by a recognized agency or organization	X					
2. Data are traceable to original sources	X					
3. The source of the data is a known, reliable and respected generator of data	X					
4. Geographic coverage and scale of data are appropriate to the Great Lakes basin		X				
5. Data obtained from sources within the U.S. are comparable to those from Canada	X					
6. Uncertainty and variability in the data are documented and within acceptable limits for this indicator report		X				
Clarifying Notes:						

**Acknowledgments**

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This report was prepared on behalf of the IADN Steering Committee by Todd Nettesheim, IADN Program Manager, U.S. Environmental Protection Agency, Great Lakes National Program Office.

Contributors:

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Link to IADN data: [http://www.msc.ec.gc.ca/iadn/data/form/form\\_e.html](http://www.msc.ec.gc.ca/iadn/data/form/form_e.html)

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Source: Integrated Atmospheric Deposition Network (IADN) Steering Committee, unpublished, 2008

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Source: IADN Steering Committee, unpublished, 2008

Figure 3. Annual Average Particulate Concentrations of Benzo(a)pyrene.

Source: IADN Steering Committee, unpublished, 2008

Figure 4. Concentrations of dioxins and furans expressed as TEQ (Toxic Equivalent) in fg/m<sup>3</sup> in Windsor, Ontario.

Source: Environment Canada National Air Pollution Surveillance (NAPS) network, unpublished, 2006

Figure 5. Median TGM concentrations and upper and lower quartiles (1997-2005): Comparison of significant year-by-year changes (arrows) to the overall linear regression (dotted line) obtained from daily averages after seasonal decomposition.

Source: Temme *et al.* (2007)

Figure 6. Temporal trends of total PBDEs, BDE-47, and BDE-209 (gas and particulate concentrations) in pg/m<sup>3</sup> at 5 IADN stations

Source: Venier and Hites (2008)

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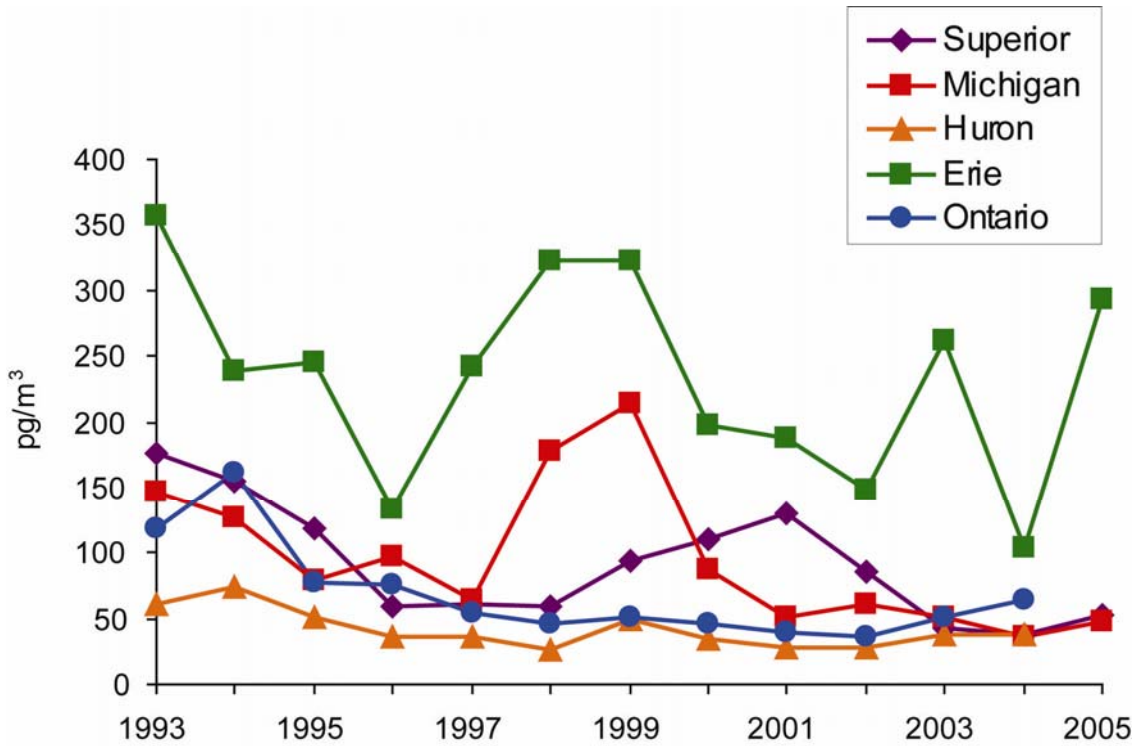


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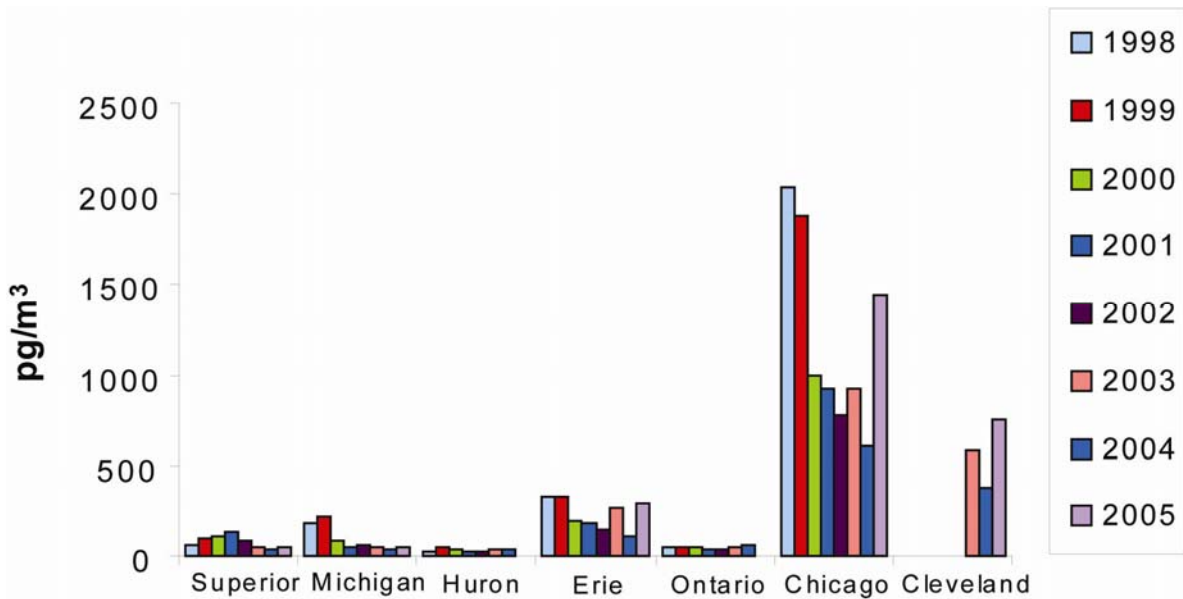


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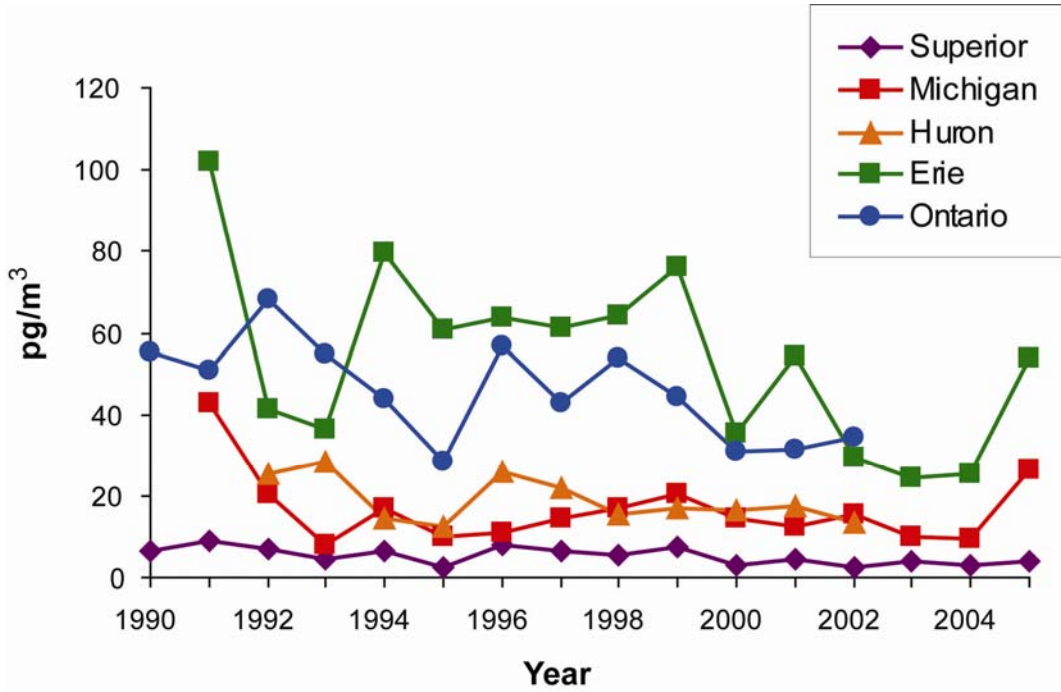


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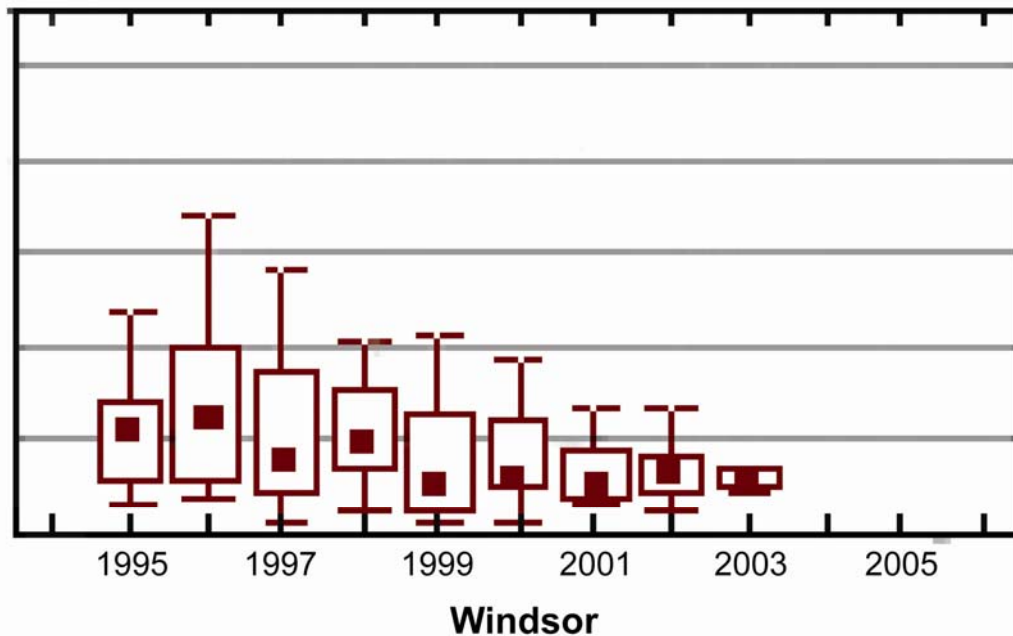


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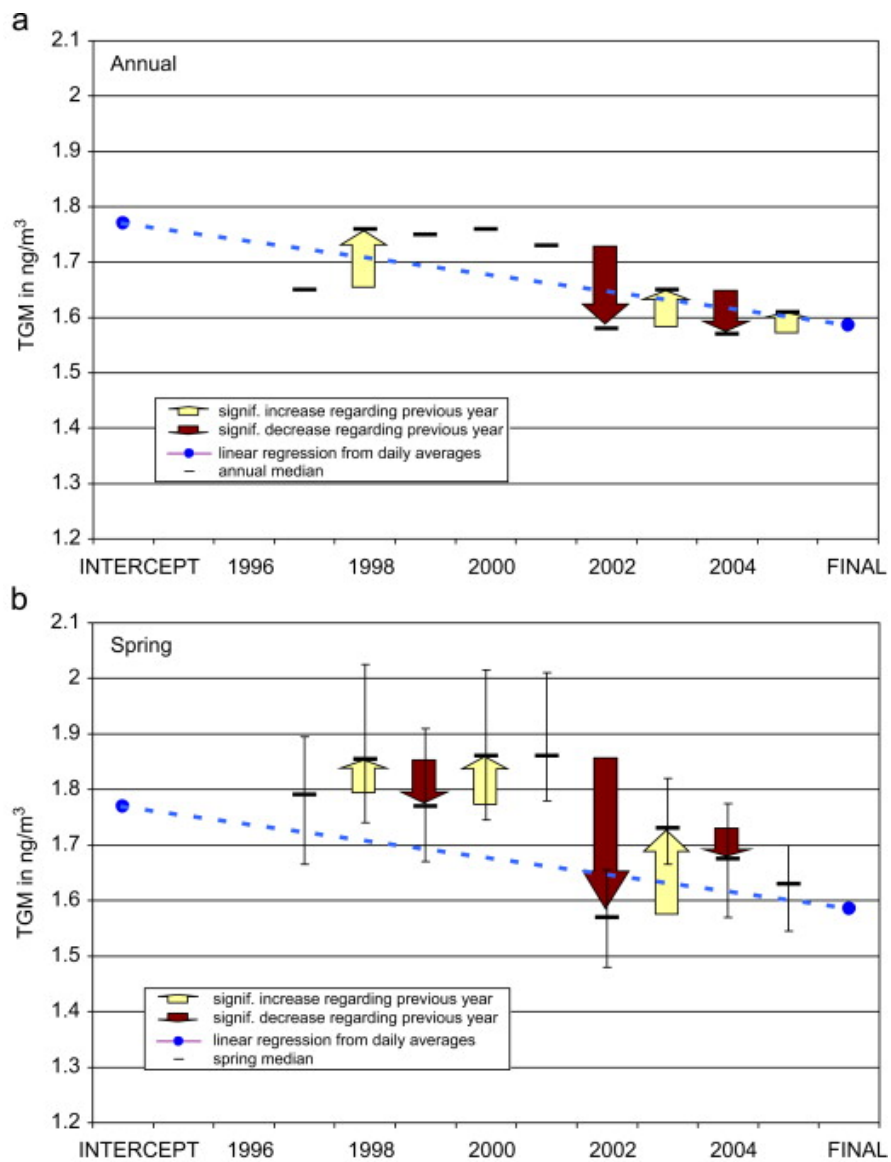


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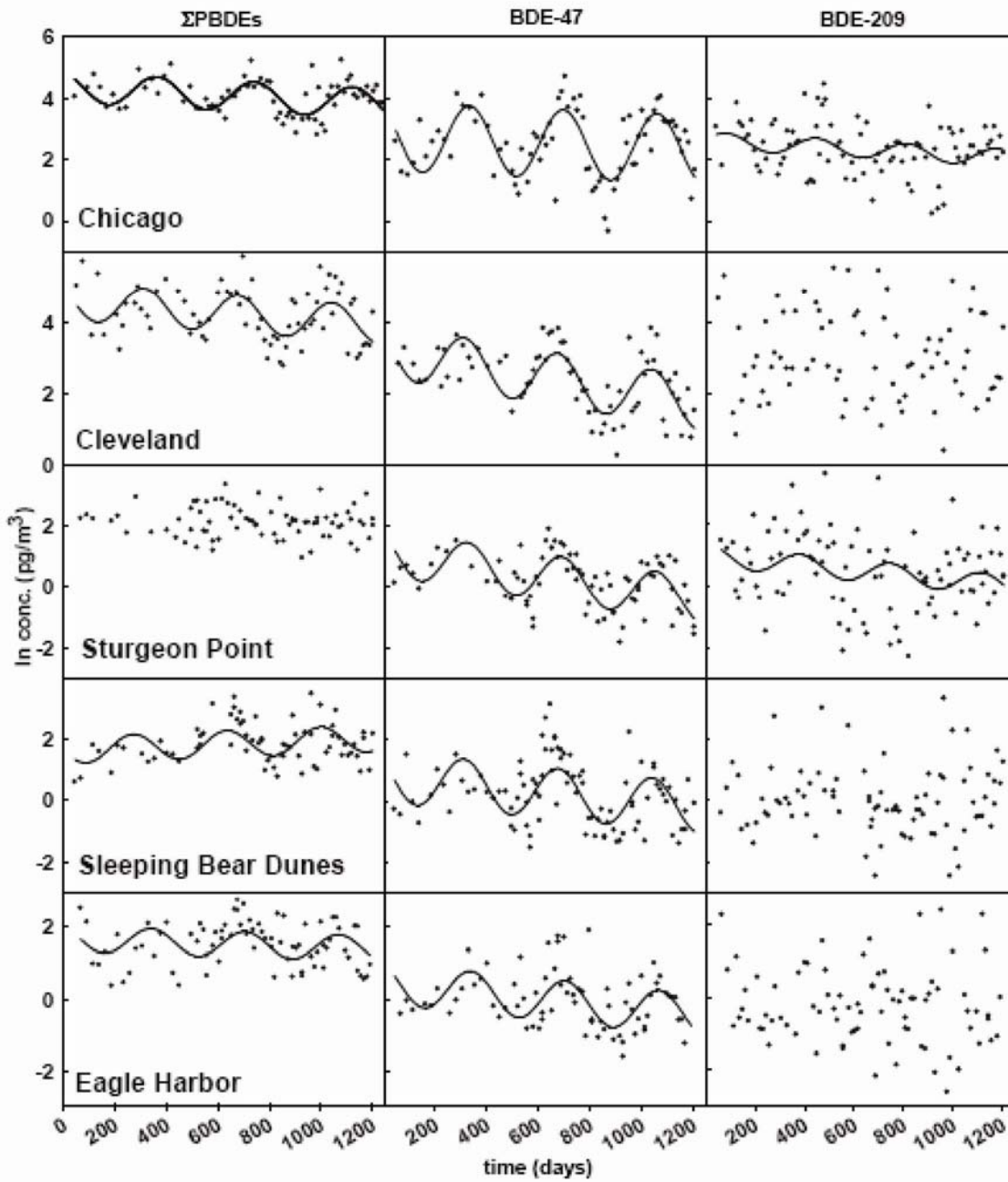


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