Atmospheric Deposition of Toxic Chemicals

Formerly indicator #117

Overall Assessment

Status: Fair

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

Rationale: Fair because different chemical groups have different trends and rates of decline over time. Levels of toxic chemicals in urban areas can be much higher than in rural areas.

Levels of persistent bioaccumulative toxic (PBT) chemicals in air tend to be lowest over Lake Superior, Lake Huron, and northern Lake Michigan, but their surface area is larger, resulting in a greater importance of atmospheric inputs (Strachan and Eisenreich 1990; Kreis 2005). Connecting channels inputs dominate for Lake Erie and Lake Ontario, which have smaller surface areas.

While concentrations of some toxic chemicals 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.

Atmospheric deposition of chemicals of emerging concern, such as brominated flame retardants and other compounds that may currently be under the radar, could be future stressors to the Great Lakes. Efforts are being made to screen for other chemicals of potential concern.

Lake-by-Lake Assessment

Each lake was categorized with a not assessed status and an undetermined trend, indicating that assessments were not made on an individual lake basis.

Purpose

- To determine temporal trends in concentrations of PBT chemicals in the atmosphere over the Great Lakes
- To estimate the annual average loadings of PBT chemicals from the atmosphere to the Great Lakes
- 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

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.

Ecological Condition

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

PCBs

Total PCBs (ΣPCBs) is a suite of congeners that make up most of the PCB mass and that represent the full range of PCBs. Concentrations of gas-phase ΣPCBs have generally decreased over time at the master stations (Figure 1, Sun *et al*. 2007, Venier and Hites 2010a, Venier and Hites 2010b), but the rate of change is remarkably slow considering that the manufacture of PCBs was banned in North America over 30 years ago. Some increases are seen during the late 1990s and early 2000s that remain unexplained. There is some evidence of connections with atmospheric circulation phenomena such as North Atlantic Oscillations (NAO) or El Nino events (Ma *et al*. 2004a); however, similar increases were not seen for other compounds making this perhaps an unlikely explanation (Venier and Hites 2010b). PCB measurements in precipitation samples were stopped at the rural master stations after 2005 because concentrations were nearing levels of detection.

The Lake Erie site consistently shows relatively elevated ΣPCB 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 ΣPCB concentrations at urban satellite stations in Chicago and Cleveland are about fifteen and ten times higher, respectively, than the remote master stations at Eagle Harbor (Lake Superior), Sleeping Bear Dunes (Lake Michigan) and Burnt Island (Lake Huron) and the rural master station at Point Petre (Lake Ontario).

In comparison to other PBT chemicals measured by IADN, PCBs have a long halving time (13 to 17 years) and are generally showing the slowest rate of decline (Venier and Hites 2010a, Venier and Hites 2010b). The slow rate of decline, despite PCBs being banned in the US in 1976, is likely due to large amounts of PCBs still in transformers, capacitors, and other electrical equipment and in storage and disposal facilities. It is assumed that PCB concentrations will continue this slow decline in the future.

Organochlorine Pesticides

In general, concentrations of banned or restricted pesticides measured by IADN are decreasing over time in air and precipitation (Sun *et al*. 2006a; Sun *et al*. 2006b; Venier and Hites 2010a, Venier and Hites 2010b). Concentrations of endosulfans, DDT, chlordane, α-HCH and γ-HCH in all phases are decreasing steadily (Figure 3). The fastest rates of decline are in α-HCH and γ-HCH, which have halving times of 3 to 4 years in all phases (Venier and Hites 2010a, Venier and Hites 2010b). The slowest rate of decline is for endosulfans, which has a halving time of 11 to 14 years (Venier and Hites 2010a, Venier and Hites 2010b). This is not surprising as endosulfans are still used in agriculture with a complete phase-out scheduled in the U.S. in 2016. Until the phase out is complete, the slow rate of decline is expected to continue.

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 (Figure 4). Dieldrin and ΣDDTs show similar increases in urban locales.

Polycyclic aromatic Hydrocarbons (PAHs)

Concentrations of PAHs, such as phenanthrene and chrysene, have been slowly decreasing in all phases at the master and urban stations and are decreasing more rapidly than PCB concentrations (Venier and Hites 2010b). Concentrations of PAHs 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 (Venier and Hites 2010a). In general, PAH concentrations in Chicago and Cleveland are about ten to one hundred times higher than at the rural master stations.

Dioxins and Furans

Concentrations of dioxins and furans have decreased over time (Figure 5) with the largest declines in areas with the highest historical concentrations (unpublished data, T. Dann, Environment Canada 2006). Data collected as part of the IADN program between 2004 and 2007 show no significant changes in concentration of dioxins and furans which is not surprising given the short time scale (Venier *et al*. 2009). Data do suggest that urban and industrial areas act as source of these chemicals to the atmosphere.

Mercury

An analysis of data from the Mercury Deposition Network (MDN) through 2005 show that concentrations of mercury in precipitation were decreasing for nearly half of the network's sites, particularly across Pennsylvania and into the Northeast. However, the sites in the Great Lakes region do not generally show this decreasing trend, except for 1 site in Indiana (Prestbo and Gay 2009).

A recent analysis of annual and weekly mercury concentrations, precipitation depths, and mercury wet deposition in the Great Lakes region found that mercury wet deposition was mostly unchanged from 2002 to 2008, with any small decreases in concentration offset with increases in precipitation (Risch et al. 2011).

Flame Retardants (FRs)

There does not appear to be any strong trend for flame retardants in the atmosphere around the Great Lakes (Figure 6), with a few notable exceptions. With the voluntary phase-out of the penta- and octa-BDE formulations by the only U.S. manufacturer in 2004, concentrations of these congeners appear to be decreasing, with an overall halving time in the atmosphere of about 6 years (Salamova and Hites 2011). These rates of decline are much faster than those for other persistent organic pollutants such as PCBs (~17 years), PAHs (~10 years), and sum-DDTs (~9 years) indicating that the production restrictions are having immediate benefits. The overall concentrations don't appear to be changing in the graphic because concentrations of other flame retardants that are still in production are not yet decreasing. For example, deca-BDE, which is still in production, is not yet decreasing. Deca-BDE accounts for about 25% of the total flame retardant concentrations. However, deca-BDE contributes a relative large fraction of the total flame retardant concentrations at Cleveland and Sturgeon Point, indicating that there may be a local source in the vicinity of Cleveland (Venier and Hites 2008, Salamova and Hites 2011). Perhaps, when restrictions on production and use of Deca-BDE go into effect after 2013, its concentration will start to decline. It should be noted, though, that even when these commercial mixtures will be completely retired from the market, large amounts of flame retardants will still be present in the environment since they have been used in a variety of consumer products that have a long life (i.e. mattresses, sofas, electronics, and upholstery).

Similar observations were found at the two Canadian master stations as described above for the U.S. stations (see

Figure 7). Figure 7 shows the trend plots and halflives in the atmosphere derived for PBDE congeners 47 and 99 for Point Petre and Burnt Island in the gas and particle phases. BDE-47 and 99 appear to be decreasing. Their halflives at Point Petre (3 and 3.1 years, respectively) are both shorter than at Burnt Island (13 and 5.2 years, respectively). Due to proximity of Point Petre to urban areas, the decline is reflective of both reduction in use and environmental removal processes from the atmosphere (e.g. degradation and partitioning into other media). Burnt Island is more remote, and therefore, the decline observed probably reflects mainly environmental removal.

Figure 7 also shows the trend plots and halflives derived for BDE-209 in the gas and particle phases. For BDE-209, BNT showed halflife of 7.3 years, but PPT showed increasing trend (doubling every 12 years). This increasing trend may be attributed to the proximity of PPT to urban locations and the continued usage of DecaBDE technical mixture.

Recently, IADN and tree bark data was also used to identify the source(s) of dechlorane plus (another recently identified flame retardant in the environment) in Niagara Falls, New York (Qiu and Hites 2008, Salamova and Hites, 2010).

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 γ-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/air2/iadn/reports/IADN_Toxics_Deposition_Thru_2005.pdf. To receive a hardcopy, please contact one of the agencies listed at the end of this report.

Summary

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.

Linkages

Atmospheric deposition of toxic chemicals is the primary pathway by which PBTs reach the Great Lakes. Increases in the concentration and loadings of atmospheric PBTs may result in increased contamination in sediment, toxic chemicals in offshore waters and contaminants in whole fish and waterbirds. Bioaccumulation of these PBTs in fish may result in fish consumption advisories.

Management Challenges/Opportunities

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 because fish consumption advisories for PCBs exist for all five Great Lakes.

In terms of in-use agricultural chemicals, further restrictions on the use of these compounds may be warranted. Recently the agricultural chemical lindane was phased out in the U.S. and Canada and endosulfans are scheduled to be phased out in the U.S. by 2016 (Federal Register 2010). These restrictions will hopefully result increased rate of decline in their concentrations in the atmosphere.

PAH inputs to the Great Lakes may be reduced through controls on the emissions of combustion systems, such as those in factories and motor vehicles.

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 recently added routine monitoring of PBDEs and some non-PBDE flame retardants to the IADN program. Screening and method development for additional non-PBDE flame retardants is currently under way. 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

Data Characteristics	Strongly Agree	Agree	Neutral or Unknown	Disagree	Strongly Disagree	Not Applicable
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

Author:

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, Michelle Craddock, Oak Ridge Institute for Science and Education Research Fellow, appointed to the U.S. Environmental Protection Agency, Great Lakes National Program Office, Sum Chi Lee, IADN Research Manager, Environment Canada, Science and Technology Branch, and Hayley Hung, IADN Principal Investigator, Environment Canada, Science and Technology Branch,, (2011).

Contributors:

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IADN Contacts:

Hayley Hung, IADN Principal Investigator, Environment Canada, Science and Technology Branch, 4905 Dufferin Street, Toronto, Ontario, M3H 5T4, hayley.hung@ec.gc.ca, 416-739-5944.

Todd Nettesheim, IADN Program Manager, Great Lakes National Program Office, U.S. Environmental Protection Agency, 77 West Jackson Boulevard (G-17J), Chicago, IL, 60604, nettesheim.todd@epa.gov, 312-353-9153.

Link to IADN data: http://www.on.ec.gc.ca/natchem/Login/Login.aspx, or contact Helena Dryfhout-Clark, IADN Data Manager, Environment Canada, Science and Technology Branch, 6248 Eighth Line, Egbert (Ontario) L0L

1N0, Helena.Dryfhout-Clark@ec.gc.ca, 705 458-3316.

Link to IADN websites: http://www.ec.gc.ca/rs-mn/, and http://epa.gov/greatlakes/monitoring/air2/index.html

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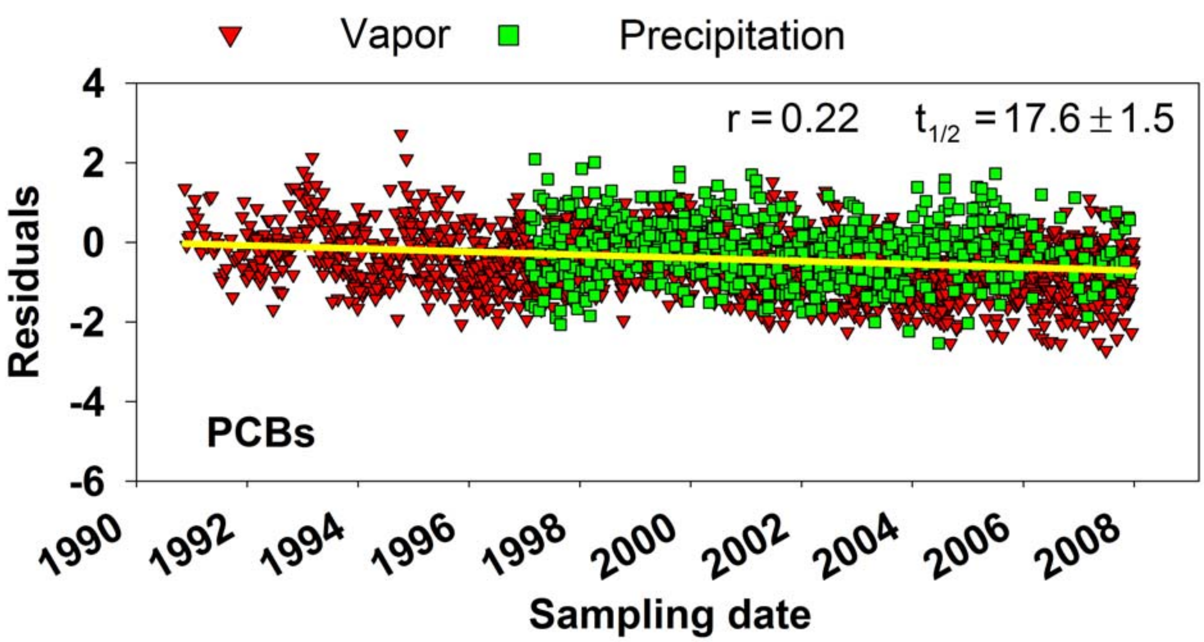


Fgure 1. Partial residuals versus sampling date for vapor and particle phase PCBs. (The partial residual analysis identifies the relationship between time and the natural logarithm of concentration.) Source: Venier and Hites 2010b.

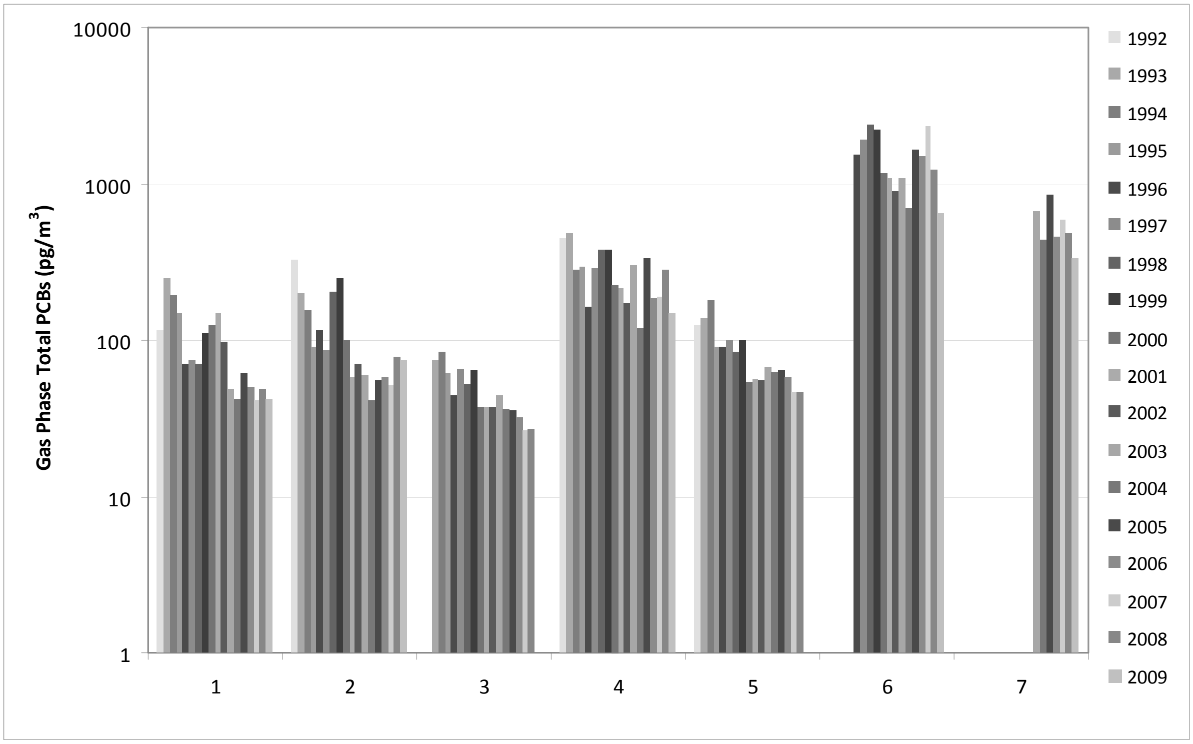


Figure 2. Annual average gas phase concentration of total PCBs at rural and urban IADN stations. Source: IADN Steering Committee, unpublished, 2011.

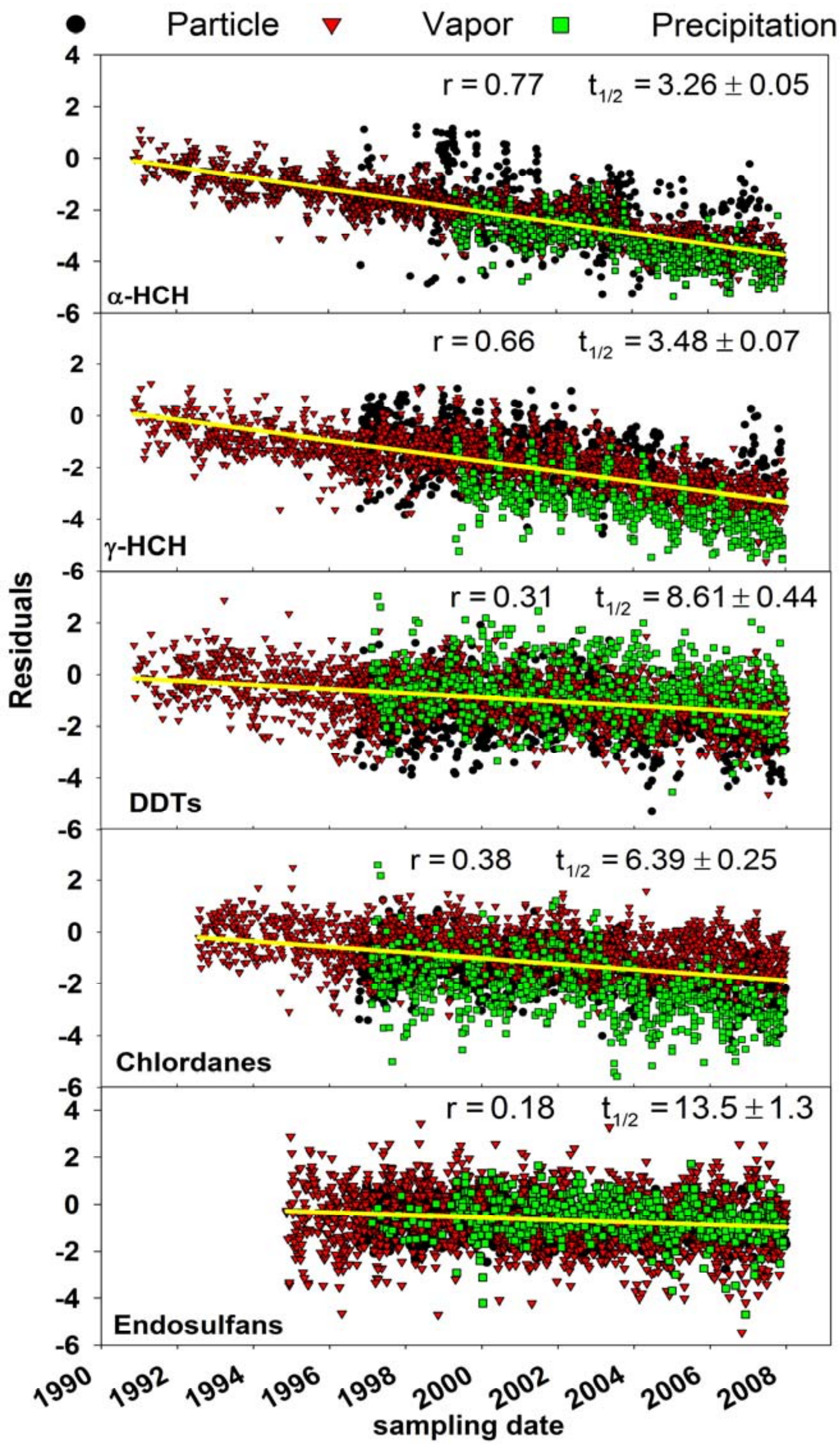
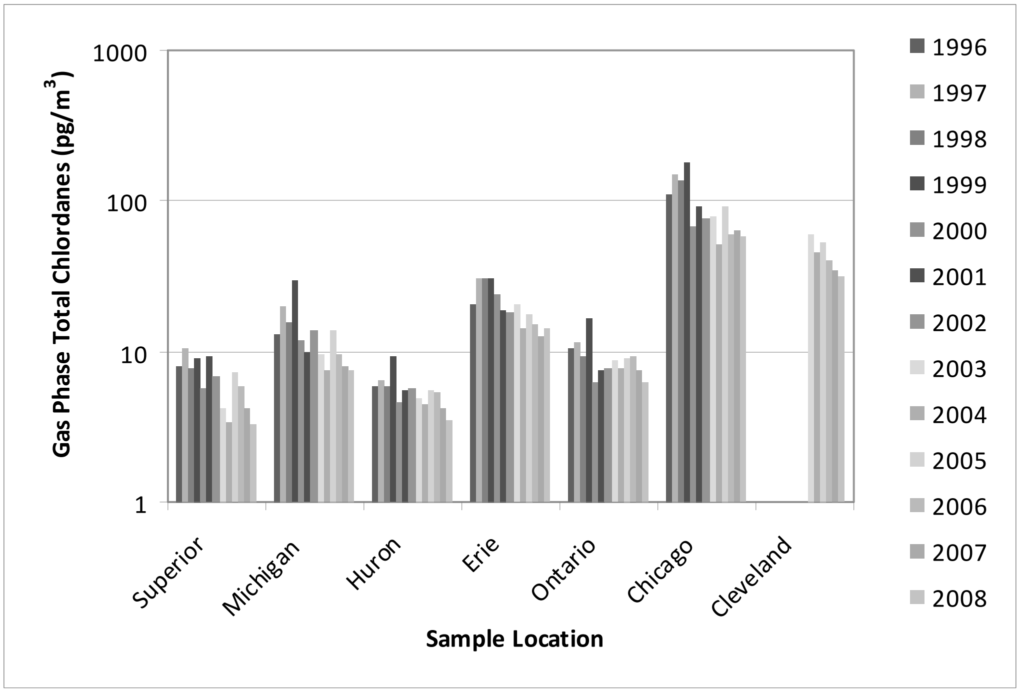


Figure 3. Partial residuals versus sampling date for vapor and particle phase organochlorine pesticides. (The partial residual analysis identifies the relationship between time and the natural logarithm of concentration.) Source: Venier and Hites 2010b.



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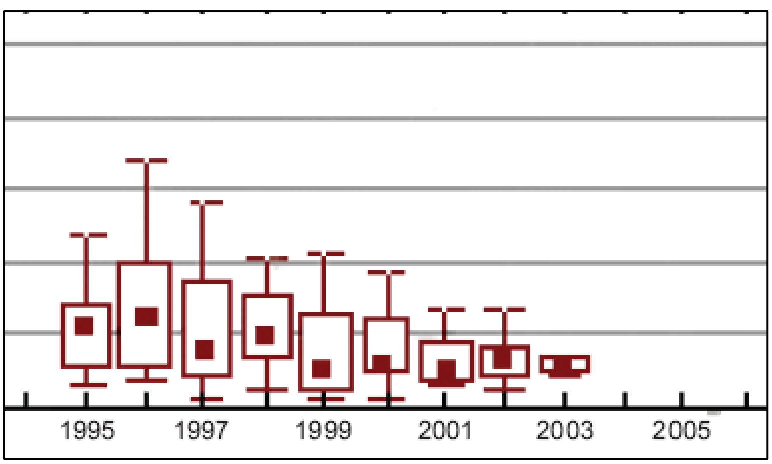

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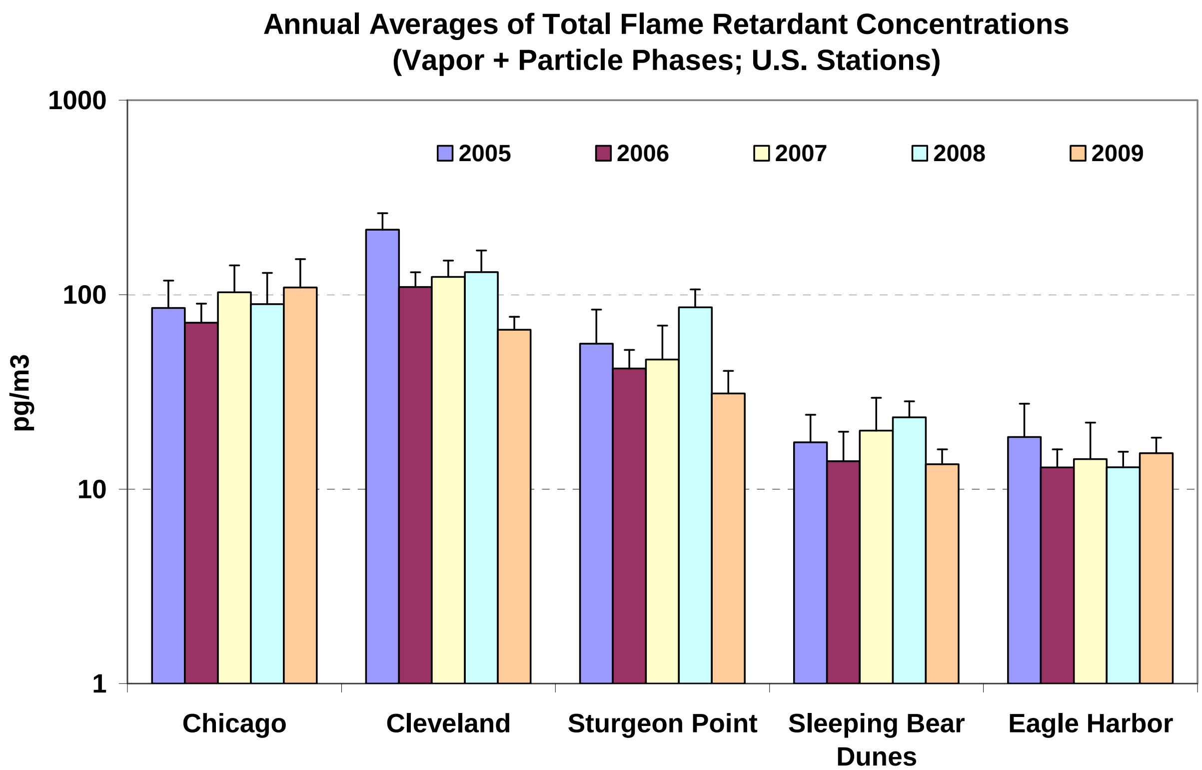

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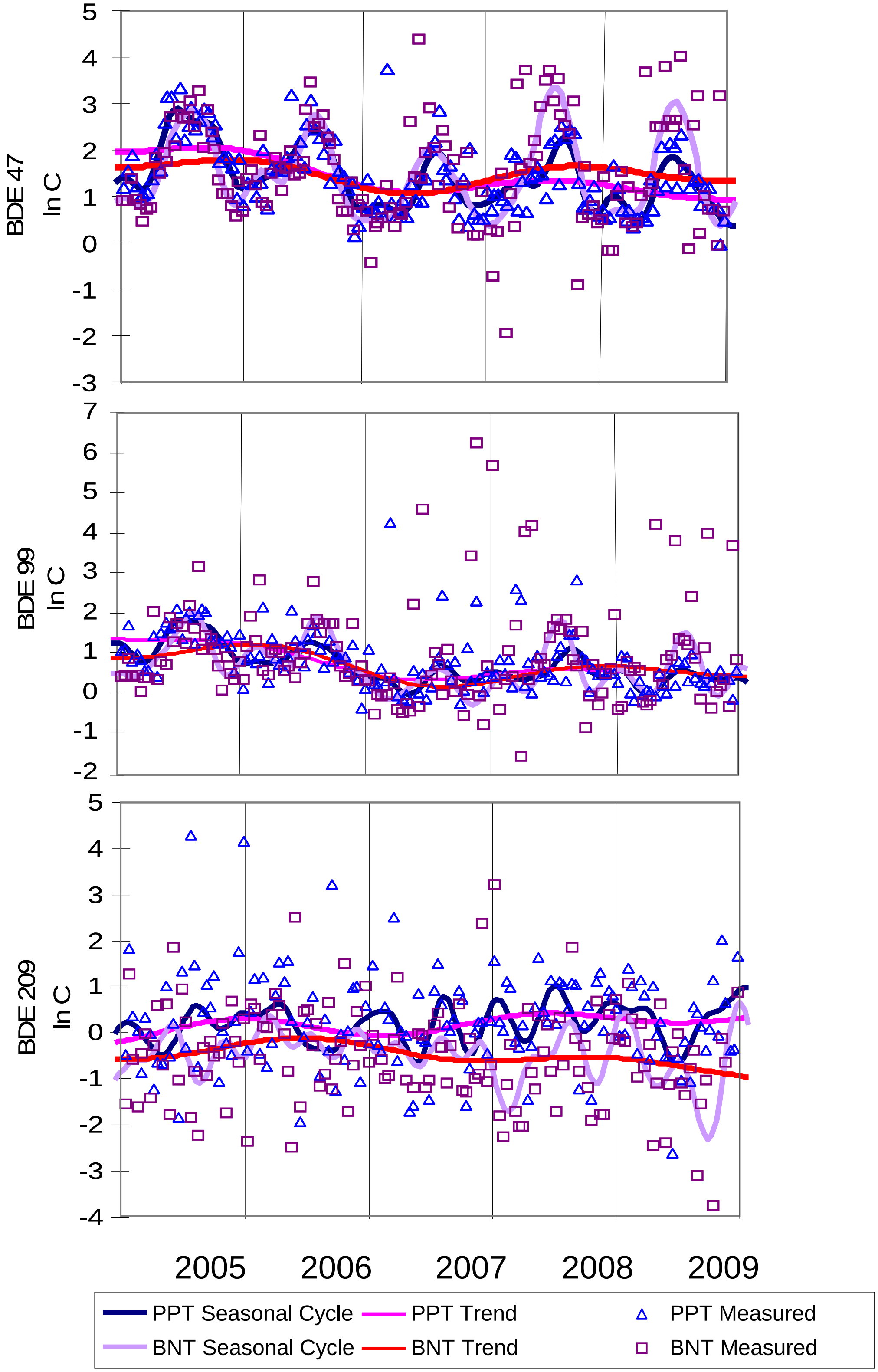

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