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DEVELOPMENT OF A MULTI-MEDIA MODEL FOR SCREENING EMERGING CHEMICAL IN THE GREAT LAKES BASIN

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ABSTRACT: We have undertaken the development of a physically-based, multi-media model (GLMOD) that will help to establish a screening-level quantitative relationship between the sources, transport, ultimate fate, and effects of emerging chemicals in the Great Lakes Basin. This presentation will explore the feasibility and utility of this type of model, which is still in the prototype development phase, as a tier 2 screening tool to address many of the research, monitoring and management questions for chemicals of emerging concern in the basin.

KEY TERMS: multi-media modeling, Great Lakes, exposure assessment

INTRODUCTION

Many "chemicals of emerging concern" that pose potential threats to human and ecological health have been identified in the Great Lakes (Manchester-Neesvig et al. 2001; Luross et al. 2002; Dodder et al. 2002; Hale et al. 2003; Daughton 2004; Boulanger, et al. 2005; Carlson and Swackhamer 2006; Li, A. et al. 2006; Muir, et al. 2006). To appropriately assess and manage these emerging persistent, bioaccumulative, and toxic chemicals, it is necessary to establish a quantitative relationship between their sources, transport within the environment, ultimate fate in the ecosystem, particularly their concentrations in fish, and effects of emerging chemicals in the Great Lakes Basin. In order to assist Great Lakes resource managers in this task, we have undertaken the development of a physically-based, multi-media model (GLMOD). The purpose of this model is to help managers anticipate basin-wide relative potential exposure and effects from emerging chemicals of concern based on emissions (e.g., wastewater effluents, atmospheric emissions, combined sewer overflows, watershed inputs as a result of various land uses such as pesticide application) and known or estimated properties of those chemicals. It will also help managers prioritize monitoring programs in terms of what chemicals to monitor, what media to focus on, and what geographic locations within the basin are likely to experience the highest concentrations in various media.

Considerable multi-media modeling of organic chemicals of concern has already been accomplished (Fenner, et al. 2005; Scheringer, et al. 2004; Gouin, et al. 2000; Palm, et al. 2002; MacLoed, et al. 2002: Breivik and Wania, 2003). Fenner, et al. and Scheringer, et al. provide very good review and comparison of a suite of popular evaluative and box models. However, these multi-media model applications to date have all been for generic or continental and global scale systems. Recently, there have been some multi-media model applications to the Great Lakes basin (Zhang, et al. 2003; Luo and Yang 2007); however, these models have only resolved the region at the whole-lake scale. Our model builds on these previous multi-media models; but it provides added value to existing modeling tools by incorporating a finer scale spatial resolution for the Great Lakes and by linking sources to human exposure and associated risk. Thus, limited resources can be focused on those chemicals and in those locations that pose the biggest threat to the Great Lakes ecosystem and human health.

Given the more physically-based configuration of our model to the Great Lakes, we believe that GLMOD can provide a higher-level screening tool (i.e., tier 2) than those that simply compare chemical properties (e.g., Muir and Howard 2006) for prioritizing research, monitoring, and pollution prevention and reduction actions in the Great Lakes. Specifically, the model could inform resource managers in their effort to address many management needs, including:

- Assess the potential basin-wide and location-specific impact of emerging chemicals and assist in prioritizing research and monitoring programs for determining chemical properties, measuring sources, evaluating exposure pathways, evaluating trends, and identifying hotspots;

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- Compare the potential exposure pathways and risks of emerging chemicals in the Great Lakes in order to prioritize and plan for source reduction;
- Assess the relative contributions of sources inside and outside of a given Great Lake watershed, including atmospheric sources outside the entire basin;
- Assess progress toward achievement of specific risk reduction targets of emerging chemicals in the Great Lakes;
- Assess how changes in emissions of emerging chemicals will affect trends in receptor concentrations throughout the Great Lakes (i.e., understand the relative importance of exposure pathways within the basin);
- Estimate concentrations of bioaccumulative in sport fish and compare them to toxicity benchmarks and to anticipate fish consumption advisories; and
- Support the development of TMDLs for chemicals in lakes or lake basins for which a significant fraction of the current loading is coming from outside the watershed (atmospheric transport, upstream lakes).

This paper will present the development of the GLMOD framework and explore approaches for its application in a screening mode for chemicals of emerging concern in the Great Lakes basin.

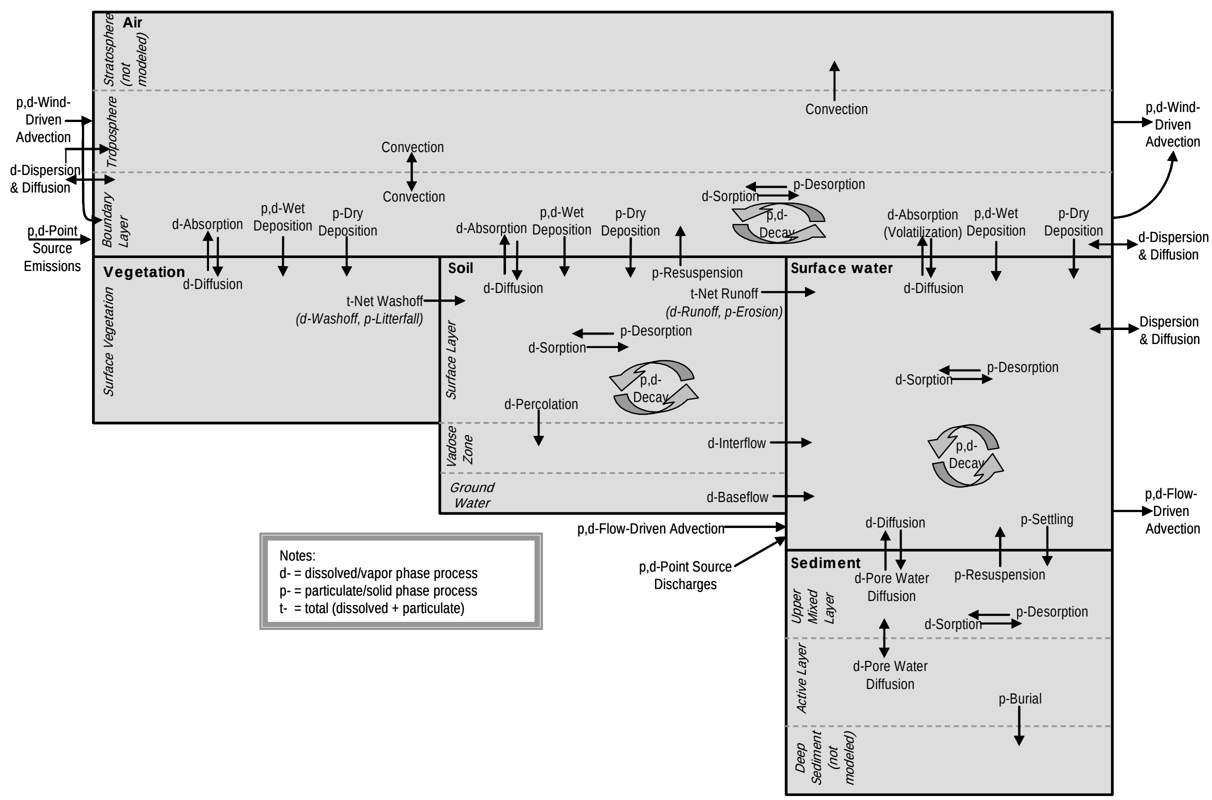

Figure 0. Schematic diagram of intra- and inter-compartmental processes included in GLMOD.

MODEL DEVELOPMENT

GLMOD is constructed by coupling sub-models for three different media – air, water, and watershed (land, vegetation, and stream network) – into a single, integrated model framework that allows dynamic feedback between compartments within these media where appropriate on a spatially and temporally specific basis. This integrated model will include all of the intra-compartmental and inter-compartmental transport and transformation processes of importance for describing organic chemical transport and fate in the Great Lakes basin. Figure 1 depicts a conceptual model diagram of the processes included in the framework.

The watershed sub-model of GLMOD is constructed using a combination of existing and customized simulation algorithms. The hydrologic/hydraulic simulation of the watershed is based on algorithms available from the Large Basin Runoff Model

(LBRM), developed for the 119 watersheds of the Great Lakes (Croley 2002; Croley and He 2005, Croley, et al. 2005). GLMOD includes each of these 119 watersheds as a separate land model segment (see Figure 2). The source, fate and transport processes depicted in Figure 1 have been added to the LBRM hydrology to comprise the watershed chemical mass balance sub-model. As shown in Figure 1, the watershed sub-model will contain both a soil layer and a vegetation layer.

The surface water-sediment sub-model is derived from the many emerging chemical mass balance models that have been developed for individual Great Lakes (e.g., Bierman, et al. 1992; LimnoTech, Inc. 2004; U.S. EPA 2006); the source, fate, and transport processes depicted in Figure 1 are included in this sub-model. The entire Great Lakes basin water/sediment system is segmented into completely-mixed water column segments as shown in Figure 2. There will be two sediment segments (an upper mixed layer and an active layer below the mixed layer) below each water column segment. To provide exposure concentrations for the effects sub-models, we will use empirical- or QSAR-derived BAF or BSAF for various fish species in various locations that might be consumed by either fish-eating fauna or humans.

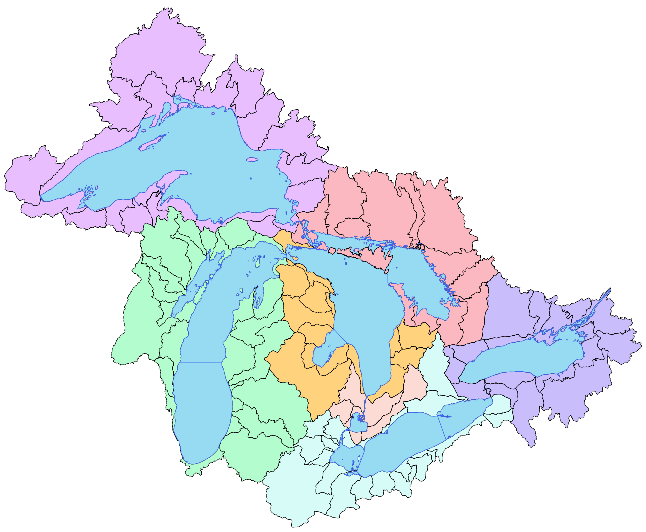

Figure 0. Watershed and water column segmentation for GLMOD

The air sub-model is comprised of a rectilinear horizontal grid 50 km on a side that overlays the entire Great Lakes basin. Each 2500 km^2 grid cell is comprised of two vertically stacked layers that will be actively modeled – a lower boundary layer and an overlying troposphere layer – and the lower layer of each grid cell will interact with the appropriate area of vegetation, soil, and/or water according to the processes shown in Figure 1. In addition to atmospheric emission within the basin, the air sub-model may also receive chemical inputs form outside the basin via wind-driven loads of specified boundary concentrations.

MODEL APPLICATION

Model Calibration and Prototype Demonstration

We intend to calibrate and field test the GLMOD using PCBs because we have a wealth of data on PCBs in various media throughout the Great Lakes basin (Hornbuckle et al. 2005; Carlson and Swackhamer 2006; Sun, et al. 2007). We can best constrain inter-media mass transfer rates (e.g., air-water or air-plant exchange rates, solids settling and resuspension rates, etc.) using PCBs in water, air, sediments and biota throughout the basin, particularly in capturing the long-term decline trends that have been observed from the 1980s forward following banning of PCB production. Then these same mass transfer rate coefficients can then be used when modeling other chemicals for which we have less concentration data but have basic chemical property data.

Model Screening Application

Following the calibration of GLMOD, we are in the process of applying it to several PBDE congeners as a means of demonstrating its feasibility and utility as a screening tool for addressing some of the management needs listed above.

For many of the potentially high priority compounds (e.g., PBDEs, PCDEs, PCNs, phthalate esters, synthetic musks, chlorinated paraffins, etc.), it is anticipated that quantitative emission estimates are unavailable. In this event, we can still obtain value from this model by using a combination of two diagnostic approaches for comparing chemicals. The first approach will be to run the model for each chemical using a unit emission (e.g., 1 kg/year/sq-mile) to compare chemical attributes such as: distribution among compartments (air, water, sediments, fish, etc.); overall residence time in the Great Lakes environment; transport distance (long range transport potential); geographic location of exposure "hotspots"; rate of decline in fish and water and air once emissions are eliminated; and others.

The second approach will be to use GLMOD along with estimated ecological and/or human health effect thresholds for chemicals of concern to determine the amount of emissions necessary to achieve that estimated threshold concentration (i.e., the critical release amount). It is important to note that the spatial resolution of the GLMOD model allows this approach to be used to determine when the critical concentration is exceeded in <u>any</u> of the model cells, allowing for sensitivity or vulnerability of certain geographic areas to be assessed. Combined with the possibility of using population-weighted emissions, this will allow for a much more refined estimate of when critical effect thresholds would be exceeded than would result from a coarser modeling approach.

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REFERENCES

Bierman, V.J. Jr., J.V. DePinto, T.C. Young, P.W. Rodgers, S.C. Martin, and R.Raghunathan. 1992. Development and validation of an integrated exposure model for toxic chemicals in Green Bay, Lake Michigan. Final Report for EPA Cooperative Agreement CR-814885, ERL-Duluth, Large Lakes and Rivers Research Branch, Grosse Ile, MI, 350 pp. (September, 1992).

Boulanger, B. A.M. Peck, J.L. Schnoor, and K.C. Hornbuckle. 2005. Mass Budget of Perfluorooctane Surfactants in Lake Ontario. *Environ. Sci. Technol.* 39:74-79.

Breivik, K. and F. Wania. 2003. Expanding the Applicability of Multimedia Fate Models to Polar Organic Chemicals. Environ. Sci. Technol. 37:4934-4943.

Carlson, D.L. and D.L. Swackhamer. 2006. Results from the U.S. Great Lakes Fish Monitoring Program and effects of lake processes on contaminant concentrations. *J. Great Lakes Research.* 32:370-385.

Croley II, T.E. 2002. Large basin runoff model. Chapter in: *Mathematical Models of Large Watershed Hydrology*. V.P. Singh and D.K. Frevert (eds). Water Resources Publications, LLC. Highlands Ranch, CO.

Croley II, T. E., and He, C. 2005. Distributed-parameter large basin runoff model I: model development. *J. Hydrologic Engineer*. 10: 173-181.

Croley II, T. E., He, C. and Lee, D.H. 2005. Distributed-parameter large basin runoff model II: application. *J. Hydrologic Engineer.* 10: 182-191.

Daughton, C.G. 2004. “PPCP’s in the environment: Future research – beginning with the end always in mind.” In: *Pharmaceuticals in the Environment.* Kummerer, K. (ed), 2nd edition, Springer.

Dodder, N. G., B. Strandberg and R. A. Hites (2002). "Concentrations and spatial variations of polybrominated diphenyl ethers and several organochlorine compounds in fishes from the northeastern United States." *Environ. Sci. Technol.* 36(2): 146-51.

Fenner, K., M. Scheringer, M. MacLoed, M. Matthies, et al. 2005. Comparing Estimates of Persistence and Long-Range Transport Potential among Multimedia Models. Environ. Sci. Technol. 39(7):1932-1942.

Gouin, T. and T. Harner. Modelling the environmental fate of the polybrominated diphenyl ethers, Environment International, Volume 29, Issue 6, September 2003, Pages 717-724

Gouin, T., D. Mackay, E. Webster and F. Wania, Screening chemicals for persistence in the environment. Environ. Sci. Technol. 34 (2000), pp. 881–884.Luross, J. M., M. Alaee, D. B. Sergeant, C. M. Cannon, D. Michael Whittle, K. R. Solomon and D. C. G. Muir (2002). "Spatial distribution of polybrominated diphenyl ethers and polybrominated biphenyls in lake trout from the Laurentian Great Lakes." *Chemosphere* 46(5): 665-672.

Hornbuckle, K. C., D. Carlson, D. L. Swackhamer, J. E. Baker and S. J. Eisenreich (2005). PCBs in the Great Lakes: Legacy Contaminant, Still a Concern. *Contaminants in the Great Lakes*. R. A. Hites (ed). American Chemical Society, Washington, DC.

Li, A., K.J. Rockne, N. Sturchio, W. Song, J.C. Ford, D.R. Buckley, and W.J. Mills. 2006. Polybrominated Diphenyl Ethers in the sediments of the Great Lakes. 4. Influencing factors, trends, and implications. *Environ. Sci. Technol.* 40:7528-7534.

Limno-Tech, Inc. 2004. LOTOX2 Model Documentation in Support of Development of Load Reduction Strategies and a TMDL for PCBs in Lake Ontario. Prepared for the New England Interstate Water Pollution Control Commission, Lowell, MA and EPA-Region 2, New York, NY. Limno-Tech, Inc., Ann Arbor, MI.

Luo, Y. and X. Yang. 2007. A multi-media model of chemical distribution: fate, transport, and uncertainty. *Chemosphere*. 66:1396-1407.

Luross, J. M., M. Alaee, D. B. Sergeant, C. M. Cannon, D. Michael Whittle, K. R. Solomon and D. C. G. Muir. 2002. "Spatial distribution of polybrominated diphenyl ethers and polybrominated biphenyls in lake trout from the Laurentian Great Lakes." Chemosphere 46(5): 665-672.

Manchester-Neesvig, J. B., K. Valters and W. C. Sonzogni (2001). "Comparison of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in Lake Michigan salmonids." *Environ. Sci. Technol.* 35(6): 1072-1077.

MacLeod, M.J., D. Woodfine, J. Brimacombe, L. Toose, and D. Mackay 2002. A dynamic mass budget for Toxaphene in North America. Environmental Toxicology and Chemistry. 21(8):1628–1637.

Muir, D.C. and P.H. Howard. 2006. Are there other persistent organic pollutants? A challenge for environmental chemists. *Environ. Sci. Technol.* 40(23): 7157-7166.

Muir, D.C., M. Alaee, and B. Scott. 2006. Identifying potential and emerging chemical contaminants in the Great Lakes. Paper in: *Expert Consultation on Emerging Issues of the Great Lakes in the 21st Century*. International Joint Commission report of an IJC, Great Lakes Science Advisory Board Conference in Racine, WI, February 5-7, 2003. P. Boyer, A. Jones, and D. Swackhamer (eds). IJC Great Lakes Regional Office, Windsor, Ontario.

Palm, A., I.T. Cousins, D. Mackay, M. Tysklind, C. Metcalfe and M. Alaee, Assessing the environmental fate of chemicals of emerging concern: a case study of the polybrominated diphenyl ethers. Environ. Pollut. 117 (2002), pp. 195–213.

Scheringer, M., F. Wegmann, and K. Hungerbuhler. 2004. Investigating The Mechanics Of Multimedia Box Models: How To Explain Differences Between Models In Terms Of Mass Fluxes? Environ. Sci. Technol, 23(10):2433–2440.

Sun, P., I. Basu, P. Blanchard, K.A. Brice, and R.A. Hites. 2007. Temporal and spatial trends of atmospheric polychlorinated biphenyl concentrations near the Great Lakes. *Environ. Sci. Technol.* 41:1131-1136.

U.S. Environmental Protection Agency. 2006. Results of the Lake Michigan Mass Balance Project: Polychlorinated Biphenyls Modeling Report. EPA-600/River-04/167, Large Lakes and Rivers Forecasting Research Branch, Mid-Continent Ecology Division, Grosse Ile, MI. 579 pp. (December 2006).

Zhang, Q., J.C. Crittenden, D. Shonnard, and J.R. Michelcic. 2003. Development and evauation of an environmental multimedia fate model CHEMGL for the Great Lakes region. *Chemosphere.* 50:1377-1397.