Receptor Modeling and Wet Deposition Measurements

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Presented by Robert K. Stevens – Florida DEP

Some Elements of Research Presented were conducted by Matthew Landis & Gary Norris (EPA ORD) Gerald Keeler, Emily Christianson, & J. Timothy Dvonch (University of Michigan)

Evolution of Receptor Modeling

- Initially Used for Particulate Matter (PM) Research
- EPA & Others Experimented with Correlation, Factor, and Principal Component Analysis
- Identified Sources of Visibility Degradation and Ambient PM Exposures
- Statistical Methods Quickly Evolved
 - Chemical Mass Balance Model
 - Multivariate Models





Linear Regression and Factor Analysis Models

- These Models Have Been Used By EPA to Determine Fine And Coarse PM Contributions
- Great Smoky Mountains
- Shenandoah Valley and Abastumani Mountains in Georgia, USSR
- ➢ Houston, TX And Philadelphia, PA
 - See Publications by Tom Dzubay et al



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Example Contemporary Study

> Objective

- Determine the impact of local/regional coal combustion sources on mercury deposition in the Ohio River Valley

Time Line

- Study designed in 1999
- Work being conducted cooperatively with the University of Michigan
- Data collection completed end of 2007
 - 2-years of wet deposition data analysis and modeling completed (2003 and 2004)
 - Keeler et al., 2006 ES&T 40, 5874-5881





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Mercury Source Apportionment Demonstration Project

- Comprehensive State-of-the-Art Measurement & Analyses
 - Aerosols Integrated and Continuous
 - Wet Deposition Daily Event
 - Gases Continuous
 - Meteorology Continuous
- Receptor Modeling
 - EPA Implemented Unmix, and PMF
 - Hybrid Modeling (Regional Transport)





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Wet-Only Precipitation Collection



* Landis and Keeler *Environ. Sci. Technol.*, **1997**, 31, 2610-2615



Insert - Flexible Configurations

- No Significant Splash (in or out) -





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High Resolution ICP-MS Analysis

Low Resolution

- Li, Be, Rb, Sr, Y, Mo, Ag, Cd, In, Sn, Sb
 Cs, Ba, La, Ce, Nd, Sm, Gd, Dy, W, Tl,
 Pb, Bi, Th, U
- Medium Resolution
 - Na, Mg, Al, P, S, Ca, Sc, Ti, V, Cr
 Mn, Fe, Co, Ni, Cu, Zn
- High Resolution
 - K, Ge, As, Se
- Stable Isotope Ratios
 - Pb





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Overview of Source Apportionment

Source apportionment relates sources and environmental concentrations

- Approaches to source apportionment
 - Deterministic modeling (e.g., CMAQ) source to receptor
 - Requires emission inventory, chemistry, and meteorology
 - Models emission source impacts on predicted concentrations
 - Receptor modeling receptor to source
 - Requires comprehensive environmental measurements
 - Statistically identifies sources impacting measured concentrations

Approaches are independent and complementary



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Multivariate Receptor Modeling

- Identify Major "Factors" by Statistical Analysis of an Element Measurement Matrix
- Relate "Factors" to Source Type (e.g., coal combustion) Using Presence and Absence of Tracer Compounds
- Example Tracer Compounds
 - Coal Combustion S, Se
 - Oil Combustion Ni, V
- Requires Many Samples (150 or more)
- Steubenville Study
 - Applied both positive matrix factorization (PMF) and Unmix models
 - Estimated source contributors to measured wet Hg deposition



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Steubenville PMF Apportionment Results 2003 & 2004

Analyte	Source 1 Iron/Steel Production	Source 2 Oil & Incineration	Source 3 Crustal	Source 4 Coal Combustion	Source 5 Phosphorous	Source 6 Molybdenum
Mg	187	*	558	*	101	*
AI	51	80	355	37	*	52
Р	7.8	*	*	*	63.8	*
S	*	*	642	11299	197	*
CI	267	20480	*	584	*	771
V	2.9	1.1	*	*	*	*
Cr	2.5	*	*	*	*	*
Mn	54.4	*	34.1	*	15.4	*
Fe	344	102	17	37	27	*
Ni	*	3.19	*	*	0.68	*
Cu	1.8	14.0	*	18.4	2.7	7.0
Zn	4.0	44.1	6.1	10.7	5.3	15.6
As	*	0.81	0.10	0.49	0.05	0.27
Se	*	0.97	*	1.73	*	1.30
Rb	*	0.25	0.15	0.20	0.29	0.08
Sr	0.48	3.30	5.64	0.95	1.61	*
Мо	*	*	*	*	*	4.02
Cd	0.09	0.27	*	0.31	0.02	0.23
La	*	0.13	0.63	*	*	0.04
Ce	0.02	*	1.23	*	*	*
Hg	0.01	*	*	0.15	< 0.01	*
Pb	1.10	6.59	0.59	3.62	0.36	1.13
NO ₃	*	8639	1501	4532	314	*
% Hg	6	*	*	73	2	*

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Annualized Steubenville Source Apportioned Mercury Wet Deposition Results (μg m⁻² y⁻¹)

	Measured	PMF Estimated CFUB* Contribution	UNMIX Estimated CFUB* Contribution
2003	13.5	Mean = 9.1 (5-95% Cl ^Ω) = (6.4 – 14.7)	Mean = 9.9 (5-95% CI ^Ω) = (5.9 – 15.1)
2004	19.7	Mean = 13.1 (5-95% Cl ^Ω) = (9.3 – 21.4)	Mean = 15.5 (5-95% Cl ^Ω) = (9.1 – 23.1)

*Coal-fired Utility Boiler ^Ω Confidence Interval





Location of Surrounding CFUBs





Local Source Impacts?



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Summary of Steubenville Receptor Modeling

- Hg wet deposition at Steubenville
 - $\sim 80\%$ is attributable to local/regional anthropogenic sources
 - \sim 70% is attributable to coal combustion
 - ~ 20% from reemission/global background
- A significant portion of total Hg wet deposition is driven by a few local coal combustion dominated precipitation events
 - In 2004, >8% of total wet Hg deposition occurred during one event



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USEPA Receptor Modeling Web Site

http://www.epa/heasd/products/unmix.htm
 http://epa.gov/products/pmf.htm



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