MERCURY DISTRIBUTION IN SOILS AND STREAM SEDIMENTS OF CENTRAL INDIANA, USA

Carrie Lynn Hatcher

Submitted to the faculty of the University Graduate School in partial fulfillment of the requirements for the degree

Master of Science in the Department of Earth Sciences

Indiana University

July 2009

	Accepted by the Faculty of Indiana University, in partial fulfillment of the requirements for the degree of Master of Science.		
		Gabriel M. Filippelli, Ph.D., Chair	
Master's Thesis Committee			
		Kathy Licht, Ph.D.	
		Pierre-Andre Jacinthe, Ph.D.	

DEDICATION

Earning a masters degree is about more than just learning how to observe, study, and experiment to describe and explain natural phenomena. It includes the development of an individual from being the hesitant student to the confident scientist. Along this path we encounter people who facilitate this development – people who will be remembered as teachers. One of the most influential teachers I must credit is Rosalice Buehrer.

As the biogeochemistry lab manager, she's tasked with overseeing graduate students and aiding in their learning of how to run laboratory procedures. She was witness to my success through my own trials and frustration; she put my failures into perspective. Rosalice always found the time to offer support whether work or personal. Never hesitating to drop whatever she is doing to listen, understand, and give advice about lab work, looking at research papers, analyzing data, personal life, and other difficulties of being a student. She takes it in and guides in a warm and realistic manner, not only giving answers, but asking pointed questions.

ACKNOWLEDGEMENTS

Rudy Banerjee, Meghna Babbar-Sebens, Bob Barr, Rosalice Buehrer, Julie Crewe, Gabriel Filippelli, Bob Hall, Vince Hernly, Pierre-Andre Jacinthe, Kathy Licht, Brice Mabry, Debbie Morrison, Angela Robertson, Alex Rowan, and Erdal Yilmaz.

ABSTRACT

Carrie Lynn Hatcher

Mercury Distribution In Soils and Stream Sediments of Central Indiana, USA

An investigation of mercury (Hg) in soils and stream sediments was conducted to understand the impact of urbanization on Hg deposition and accumulation on the upper west fork of the White River watershed in central Indiana. Samples were collected to the north and east (i.e., downwind) of emission sources to understand the anthropogenic influences on Hg distribution in soil. Stream sediment sampling was designed to characterize the riverine particulate deposition of Hg through Indianapolis and to predict the potential for stream sediments with high Hg to become sources of methylmercury (MeHg). Spatial analysis revealed that soil Hg was elevated downwind of known industrial emission sites, indicating a local footprint of Hg deposition in central Indiana. Hg in streambank sediments was generally low in up-river sites to the northeast of Indianapolis, and increased markedly as the White River flowed through downtown, with high Hg persisting to downstream rural locations far to the south approximately 40 miles.

The stream sediment results also revealed variations in total Hg ($Hg_{(T)}$) as a function of local depositional sources, sub-watershed location, combined sewer outflows (CSOs), and impoundments along the White River. Low Hg values were recorded where the White River flow rate increased south of the 16th street dam at the confluence of the Fall Creek, where bankside industry and development confine the river. Three tributaries feeding into the White River were included in this study site, all having CSOs. Fall

Creek and Pleasant Run have higher values of Hg with Lick Creek having lower values in comparison to the White River and other tributaries. The highest values occur right before confluences to the White River where the flow rate slows and drops sediment. Mercury values typically increased immediately downstream of dams and impoundments. $Hg_{(T)}$ deposition and transport processes pose a problem to anglers fishing south of Indianapolis who may not be aware of the potential dangers related to elevated stream sediment Hg values and the greater potential for MeHg production from these sediments.

Gabriel M. Filippelli, Ph.D., Chair

TABLE OF CONTENTS

Introduction

Introduction	1
Objectives	1
Background	
Depositional Sources.	2
Anthropogenic Atmospheric Emissions Sources	2
Waterway Transport in Urban Areas	3
Human Exposure Risk	3
Cell Energy and Hg	4
Hg Chemistry and Cycling	5
Aqueous Phase	5
Deposition Processes	6
Waterway Transport and Methyl-Mercury Production	7
Study Area and Methods	
Study Area	
Site Description	9
Stream Flow Rates of the White River and Tributaries	10
Industrial Sources of Hg	10
Emissions Data	11
Wind Data	11

Methods

	Field	
	Soil	11
	Bankside Sediments	12
	Survey Methods	13
	Sampling Approach	13
	Sample Analysis	14
	Reproducibility	15
Resul	s ·	
	Spatial Distribution	15
	Geospatial Analysis Results	16
	Relationships Between Soil Hg-Sources-Win	d17
	Other Sources of Hg to Soil	17
	Linear Patterns of Hg	
	Bankside Sediments Hamilton County (Nob	lesville) to Marion17
	Bankside Sediments South of Marion County	y18
	Tributaries East and West of White River	
	Fall Creek	19
	Pleasant Run Creek and Citizens Coke	20
	Lick Creek	20

Stream Sediments as a Monitor of Transport Processes and Fisheries Risk

Creeks West of the White River......20

Explanation of Hg Normalization......20

Relationship of Stream Sediment Values to Landscape Use	21
Northeast to Southwest Increase	21
Grain Size Analysis	22
Analysis of 5 Sample Transect	22
Angler Survey	22
Results of Survey	23
Discussion	
Patterns of Hg Deposition Relative to Airborne Emitters	23
Soil Retention in Soil	23
General Soil Hg Distribution	23
Hg in Bankside Sediment	24
Impacts of Wastewater and CSOs, City-Urban	24
Factors Affecting Sediment Hg _(T)	25
Watershed Soil Hg _(T) Values Versus Sediment Hg _(T) Values	25
Risk to angler	26
Southern Push of Hg to Rural Areas	26
Limitations and Advantages of Sampling Method	26
Conclusions	27
Table Captions	
Tables	
Table 1. Global Budgets	28
Table 2. Anthropogenic Hg Emissions	29
Table 3 Indiana Ha Polluting Power-Plants	30

Table 4. Top 10 Emitters in Central Indiana	31
Table 5. Standard Error	32
Table 6. Sampling Reproducibility	33
Table 7. Wind Statistics	34
Table 8. Soil and Sediment Ratio	35
Table 9. Hg _(T) , Hg(norm.), and OM Values Based on Impoundment	36
Figure Captions	
Figures	
Figure 1. Bankside Sediment Sampling Area	37
Figure 2. Soil Sampling Area	38
Figure 3. CSO, Impoundment, Water Flow, and Industrial Locations	39
Figure 4. Sampling Strategy	40
Figure 5. Soil Hg _(T) Concentrations	41
Figure 6. Soil Hg _(T) Concentrations of Sites South	42
Figure 7. Map of Soil Hg Concentrations and Median Wind Direction	43
Figure 8. Soil Hg _(T) Concentration and Ordinary Krige Prediction	44
Figure 9. Soil Concentration Map Ordinary Krigged Prediction Error Map)45
Figure 10. Normal QQPlot	46
Figure 11. Log- Histogram	47
Figure 12. Semi-variogram Cloud	48
Figure 13. North to South Overview of Bankside Sediment Sampling Sites	49
Figure 14. Banksediment Hg Values Normalized	50
Figure 15. Bankside Sediment and Total Hg (ppb)	51

Figure 16. Grain Size Analysis	52
Figure 17. Analysis of Sample Transects	53
Figure 18. Grain Size, Hg _(norm.,) and OM Compared	54
Appendices	
Appendix A. Mercury Chemistry and Cycling	
Table A3. Species of Hg and Transformations	55
Table A4. Species of Hg and Solubility Constants	56
Figure A1. Conceptual Biogeochemical Mercury Cycle	57
Figure A2. Chemical Cycling	58
Appendix B. Hydro-geological Background	
Table B4. Stream Flow Rates	59
Figure B1. Location of Study Site Watershed	60
Figure B2. Hydromorphic Regions	61
Figure B3. Land-use	62
Figure B5. Visual Description of Deposition at Lowhead Dams	63
Appendix C. Survey	
Figure 1. Survey	64
References	74
Curriculum Vitae	