# **Table of Contents**

		Page
List of table	s	xvi
List of figur	'es	xxiii
Preface		xxxii
Foreword		xxxiii
Acknowledg	yments	xxxiv
Executive S	-	XXXV
1.	Introduction	
	1.1 Major Conclusions and Recommendations	
2.	Mercury Inputs to the Global Atmosphere	
3.	Mercury Cycling within the Atmospheric Reservoir	
4.	Mercury Processes and Modelling Studies	
PART-1:	Sources of Mercury released to the Global Atmosphere	
Chapter 1	Global Mercury Emissions to the Atmosphere from Natural and Anthropogenic Sources	
	Summary	1
1.1	Introduction	1
1.2	Mercury emissions from natural sources	2
	1.2.1 Volcanoes and geothermal activities	3
	1.2.2 Water surfaces	3
	1.2.3 Rocks, soils and vegetation	4
	1.2.4 Biomass burning	5
1.3	Mercury emissions from anthropogenic sources	6
	1.3.1 Anthropogenic emissions by sources category	7
	1.3.2 Anthropogenic mercury emissions by region	22
	1.3.2.1 Europe	22
	1.3.2.2 North and Central America	23
	1.3.2.3 Russia	23
	1.3.2.4 China	24
	1.3.2.5 Australia	25
	1.3.2.6 India	26
	1.3.2.7 South Africa	26
1.4	1.3.2.8 South America	27
1.4	Global Assessment	27
1.5	Further Research	30
1.6	References	31
Chapter 2	Mercury Emissions from Coal Combustion in China	
	Summary	37
2.1	Introduction	37
2.2	Results and Discussion	37

	2.2.1 Coal use trends, 1995-2005	37
	2.2.2 Mercury in coal	39
2.3	Mercury released to the atmosphere	40
2.4	Mercury emission trends in China	41
2.5	Future mercury emissions from coal combustion	44
2.6	Future Research and Policy Implications	45
2.7	References	46
Chapter 3	Mercury Emissions from Industrial Sources in China	
	Summary	47
3.1	Introduction	47
3.2	Mercury emission factors from different industrial sources in China	48
3.3	Speciation of mercury compounds from different industrial sources in China	50
3.4	Mercury emissions from different industrial sources in China in 1999	50
3.5	Mercury emission trends from 1995 to 2003	52
3.6	Uncertainties	53
3.7	Future Research and Policy Implications	54
3.8	References	54
Chapter 4	Mercury Emissions from Industrial Sources in India and its Effects in the Environment	
	Summary	57
4.1	Introduction	57
4.2	Results	61
	4.2.1 Coal combustion	62

4.2	Results	01
	4.2.1 Coal combustion	62
4.3	Iron and Steel Industry	64
	4.3.1 Non-ferrous metallurgical industry in India	65
	4.3.1.1 Production of metals by different processes and emissions of mercury	65
	4.3.2 Chlor-alkali industry in India	66
	4.3.2.1 Chlorine and caustic soda production	66
4.4	Cement Industry	68
4.5	Wastes	69
	4.5.1 Municipal Solid Waste (MSW)	69
	4.5.2 Medical wastes	71
	4.5.3 Electronic waste (E-waste)	71
4.6	Biomass burning	72
4.7	Miscellaneous	73
	4.7.1 Brick industry	73
	4.7.2 Instruments, batteries and thermometers	73
4.8	Mercury in the Indian Environment and the cycling in the bio-geosphere	74
4.9	Discussion	75
4.10	Future directions	78

4.11	References	79
Capter 5	Mercury Emissions from Point Sources in South Africa	
	Summary	83
5.1	Introduction	83
5.2	Current understanding of mercury emissions and levels in South Africa	84
	5.2.1 Priority areas identified for monitoring air pollution in South Africa	84
	5.2.2 Mercury emissions inventory for South Africa	86
	5.2.2.1 Coal Combustion: Power Plants	87
	5.2.2.2 Coal Combustion: Coal Gasification Process	88
	5.2.2.3 Crude Oil Refining and Minerals Processing	89
	5.2.2.4 Cement production	89
	5.2.2.5 Ferrous Metal Production - Iron and Steel	90
	5.2.2.6 Coal Combustion: Residential Heating	90
	5.2.2.7 Non-Ferrous Metal Production: Primary Metals	90
	5.2.2.8 Consumer Products, Waste Deposition (landfills) and Incineration	91
	5.2.2.9 Artisanal and Small-Scale Gold Mining Activities	91
5.3	Monitoring Hg emissions in South Africa	92
5.4	Gaps in our current understanding	92
5.5	Research needs	93
5.6	References	93
Chapter 6	World Emissions of Mercury from Artisanal and Small Scale Gold Mining	e
	Summary	96
6.1	Introduction	97
	6.1.1 Why mercury is used	98
	6.1.2 How mercury is released to the Environment	100
	6.1.2.1 Whole ore amalgamation	100
	6.1.2.2 Amalgamation of a concentrate	102
6.2	Where ASGM is Occurring	102
6.3	Amount of Mercury Used in ASGM	109
	6.3.1 Indonesia	110
	6.3.2 Brazil	111
	6.3.3 Other Countries with Documented Estimates	111
	6.3.4 Other Countries – Direct Anecdoctal Information	111
	6.3.5 Remaining Countries – Indirect Anecdotal Information	112
6.4	Reported Trade in Mercury and Gold	112
	6.4.1 Using gold production to estimate mercury consumption in ASGM	118
6.5	Knowledge Gaps about Mercury in ASGM	118
	6.5.1 River Siltation in ASGM	120

vii

6.6	Reducing Mercury Use in ASGM	121
	6.6.1 Reducing Emissions	121
6.7	Conclusions	124
6.8	References	125
Chapter 7	Mercury Emissions from Natural Processes and their Importance in the Global Mercury Cycle	
	Summary	130
7.1	Introduction	130
7.2	Estimates of oceanic evasion	133
7.3	Estimates of net terrestrial evasion	135
7.4	References	141
Chapter 8	Mercury Emissions from Global Biomass Burning: Spatial and Temporal Distribution	1
	Summary	145
8.1	Introduction	146
	Global distribution of vegetation	146
	8.1.2 Biogeochemistry of mercury in forests	147
	8.1.3 Mercury distribution in vegetation and organic soil by region	147
	8.1.4 Mercury release from burning biomass and organic soil in different landscapes	148
	8.1.5 Estimation of mercury emissions from biomass burning	149
	8.1.6 Carbon emission model	149
	8.1.7 Mercury emission factors	152
8.2	Results and discussion	155
	8.2.1 Global Distribution of Carbon Emissions	155
	8.2.2 Global Distribution of Mercury Emissions	156
	8.2.3 Regional Estimates of Carbon and Mercury Emissions	158
	8.2.2 Inter-annual Variability of Mercury Emissions	159
	8.2.3 Global Hg emissions using global CO emission estimates	160
	8.2.4 Comparison with other regional emission estimates	161
8.3	Future work	163
8.4	Policy implications	164
8.5	Aknowledgments	164
8.6	References	164
PART-2:	Spatial Coverage and Temporal Trends of Mercury Measurements	
Chapter 9	Spatial Coverage and Temporal Trends of Land-Based Atmospheric Mercury Measurements in the Northern and Southern Hemispheres	
	Summary	168
9.1	Introduction	168

	9.1.1	Quality of Data / Field intercomparisons	169
9.2	Measu	urements of air concentrations in North America	170
	9.2.1	Measurements of air concentrations in Canada	170
		9.2.1.1 Remote locations	170
		9.2.1.2 Urban locations (including mining areas)	170
		9.2.1.3 Temporal Trends at single locations	171
		9.2.1.4 Monitoring networks and trend	171
		9.2.1.4.1 Trend analysis	174
		9.2.1.4.2 Comparison between air data and wet deposition of mercury in North America	175
		9.2.1.5 Mercury speciation analysis	177
		9.2.1.6 Mercury measurements (incl. air craft) related to emissions, and source attribution	180
	9.2.2	Measurements of air concentrations in United States	181
		9.2.2.1 Remote locations	182
		9.2.2.2 Urban locations (including mining areas)	184
		9.2.2.3 Temporal Trends at single locations	185
		9.2.2.4 Monitoring networks and trends	187
		9.2.2.5 Mercury speciation analysis	190
		9.2.2.6 Mercury measurements related to emissions, and source attribution	193
	9.2.3	Measurements of air concentrations in Mexico	195
		9.2.3.1 Remote locations	196
		9.2.3.2 Urban locations (including mining areas)	197
9.3	Measu	urements of air concentrations in South America	197
	9.3.1	Urban locations (including mining areas)	197
	9.3.2	Mercury measurements (incl. air craft) related to emissions, and source attribution	198
9.4	Measu	urements of air concentrations in Europe	199
	9.4.1	Remote locations	199
	9.4.2	Urban locations (including mining areas)	199
	9.4.3	Temporal Trends at single locations	200
	9.4.4	Monitoring networks and trends	200
	9.4.5	Mercury speciation analysis	202
	9.4.6	Mercury measurements (incl. air craft) related to emissions, and source attribution	208
9.5	Measu	urements of air concentrations in Asia	209
	9.5.1	Remote locations	209
	9.5.2	Urban locations (including mining areas)	209
	9.5.3	Temporal Trends at single locations	210
	9.5.4	Mercury speciation analysis	210
	9.5.5	Mercury measurements (incl. air craft) related to emissions, and source attribution	211
9.6	Measu	urements of air concentrations in Africa	211
	9.6.1	Monitoring networks and trends	211

	9.6.2 Mercury measurements (incl. air craft) related to emissions, and source attribution	212
9.7	Summary and Conclusion	212
9.8	References	214
Chapter 10	Spatial Coverage and Temporal Trends of Atmospheric Mercury Measurements in Polar Regions	
	Summary	220
10.1	Introduction	220
10.2	Results and discussion	222
	10.2.1 Methods	222
	10.2.1.1 Definitions	222
	10.2.1.2 Atmospheric measurements in cold regions	222
	10.2.2 Atmospheric mercury in the Arctic	223
	10.2.2.1 Introduction	223
	10.2.2.2 Atmospheric Mercury Depletion Events in the Arctic	223
	10.2.2.3 Temporal trends of atmospheric mercury and comparisons between sites	226
	10.2.3 Atmospheric Mercury in the Antarctic	227
	10.2.3.1 Introduction	227
	10.2.3.2 Atmospheric measurements on the Antarctic Region	228
	10.2.3.3 Temporal trends of atmospheric mercury in Antarctica	229
	10.2.3.3.1 Coastal sites	230
	10.2.3.3.2 Sites on the Polar Plateau	232
	10.2.3.4 Antarctica vs Arctic	233
	10.2.4 The role of snow surfaces on atmospheric Hg trends	234
	10.2.4.1 Role of snow in emission and deposition processes	234
	10.2.4.1.1 Snowpacks as promoters of atmospheric Hg deposition	234
	10.2.4.1.2 Snowpacks as promoters of Hg evasion	235
	10.2.4.2 Potential influence on local, regional and global mercury levels.	236
	10.2.4.2.1 Local scale	236
	10.2.4.2.2 Regional and global scale	236
10.3	Gap of knowledge, future Research and Policy Implications	237
10.4	References	238
Chapter 11	Spatial Coverage and Temporal Trends of Over-Water, Air- Surface Exchange, Surface and Deep Sea Water Mercury Measurements	
	Summary	243
11.1	Introduction	243
11.2	Over-water Mercury Measurements	245
	11.2.1 Atlantic Ocean	246
	11.2.2 Pacific Ocean	252

ter 12	Monitoring and Modeling Projects for Fate of Mercury	
11.5	References	281
	11.4.3 Mediterranean Sea	275
	11.4.2 Pacific Ocean	273
	11.4.1 Atlantic Ocean	272
11.4	Surface and Deep Sea Water Mercury Measurements	271
	11.3.4.3 Baltic Sea	271
	11.3.4.2 North Sea	270
	11.3.4.1 Arctic Ocean	269
	11.3.4 Other Oceans	269
	11.3.3 Mediterranean Sea	261
	11.3.2 Pacific Ocean	259
	11.3.1 Atlantic Ocean	258
11.3	Air-Water Mercury Exchange	256
	11.2.3 Mediterranean Sea	253

## Chapter 12 Monitoring and Modeling Projects for Fate of Mercury Species in Japan

	Summary	288
12.1	Introduction	288
12.2	Monitoring Project for ambient atmospheric mercury and other heavy metals in remote Background Area	289
	12.2.1 Project site for the field measurement	289
	12.2.2 Methods of sampling and analysis	290
	12.2. 3 Measurement results	290
12.3	Fate analysis of mercury species for the monitoring data using multimedia environmental fate model	293
	12.3.1 Outline of the model	294
	12.3.2 Results and comparison to the monitoring outputs	295
12.4	Future direction	295
12.5	References	296

# Chapter 13 The Need for a Coordinated Global Mercury Monitoring Network for Global and Regional Models Validation

	Summary	297
13.1	Introduction	297
13.2	Existing Global Monitoring Programs	299
	13.2.1 Ambient measurements	299
	13.2.2 Mercury Measurements at Altitude	299
	13.2.3 Episode-based Measurement Intensives	300
	13.2.4 Meteorological Measurements	300
	13.2.5 Atmospheric Deposition	300
13.3	Measurements and Model Development	301
	13.3.1 General evaluation of model transport and photochemistry	301

xi

	13.3.2 Source-receptor relationships: Long-range transport versus local sources	302
	13.3.3 Evaluation of photochemical processes	305
	13.3.4 Evaluation of gas-particle partitioning	306
	13.3.5 Evaluation of emission inventories	306
	13.3.6 Evaluation of past/future changes and effectiveness of control strategies	307
	13.3.7 Proposed Measurements to Enhance Model Development	307
13.4	Establishment of the coordinated global mercury monitoring network (CGMMN)	308
	13.4.1 Key Components of a Coordinated Long-Term Network	308
	13.4.2 Mercury Measurement Methods	309
13.5	Coordinated monitoring and modeling	310
	13.5.1 Importance of establishing boundary conditions	311
	13.5.2 Identification of key measurements parameters and species	311
	13.5.3 Four-D Data Assimilation	312
	13.5.4 Observation-based Apportionment Methods for Emission Inventory Reconciliation	313
	13.5.5 Case Study of coordinated measurement/modeling in the Mediterranean	315
13.6	References	318
PART-3:	Understanding Atmospheric Mercury on Hemispheric and Global Scales	
PART-3: Chapter 14		
	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces	322
Chapter 14	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary	322 322
<b>Chapter 14</b> 14.1	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary Introduction	322
Chapter 14	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary Introduction Homogeneous Gas phase Transformation	322 323
<b>Chapter 14</b> 14.1	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary Introduction Homogeneous Gas phase Transformation 14.2.1 Field Observations	322 323 323
<b>Chapter 14</b> 14.1	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary Introduction Homogeneous Gas phase Transformation 14.2.1 Field Observations 14.2.2 Kinetic of Homogeneous Gas Phase Reactions	<ul><li>322</li><li>323</li><li>323</li><li>324</li></ul>
<b>Chapter 14</b> 14.1	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary Introduction Homogeneous Gas phase Transformation 14.2.1 Field Observations 14.2.2 Kinetic of Homogeneous Gas Phase Reactions 14.2.2.1 Terminology	
<b>Chapter 14</b> 14.1	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary Introduction Homogeneous Gas phase Transformation 14.2.1 Field Observations 14.2.2 Kinetic of Homogeneous Gas Phase Reactions 14.2.2.1 Terminology 14.2.2.2 Thermodynamics	<ul> <li>322</li> <li>323</li> <li>323</li> <li>324</li> <li>324</li> </ul>
<b>Chapter 14</b> 14.1	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary Introduction Homogeneous Gas phase Transformation 14.2.1 Field Observations 14.2.2 Kinetic of Homogeneous Gas Phase Reactions 14.2.2.1 Terminology	<ul> <li>322</li> <li>323</li> <li>323</li> <li>324</li> <li>324</li> <li>326</li> </ul>
<b>Chapter 14</b> 14.1	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary Introduction Homogeneous Gas phase Transformation 14.2.1 Field Observations 14.2.2 Kinetic of Homogeneous Gas Phase Reactions 14.2.2 I Terminology 14.2.2.2 Thermodynamics 14.2.2.3 Experimental Approaches	<ul> <li>322</li> <li>323</li> <li>323</li> <li>324</li> <li>324</li> <li>326</li> <li>326</li> </ul>
<b>Chapter 14</b> 14.1 14.2	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary Introduction Homogeneous Gas phase Transformation 14.2.1 Field Observations 14.2.2 Kinetic of Homogeneous Gas Phase Reactions 14.2.2.1 Terminology 14.2.2.2 Thermodynamics 14.2.2.3 Experimental Approaches 14.2.2.4 Ab-Initio Thermochemistry	<ul> <li>322</li> <li>323</li> <li>323</li> <li>324</li> <li>324</li> <li>326</li> <li>326</li> <li>326</li> </ul>
<b>Chapter 14</b> 14.1 14.2	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary Introduction Homogeneous Gas phase Transformation 14.2.1 Field Observations 14.2.2 Kinetic of Homogeneous Gas Phase Reactions 14.2.2 Kinetic of Homogeneous Gas Phase Reactions 14.2.2.1 Terminology 14.2.2.2 Thermodynamics 14.2.2.3 Experimental Approaches 14.2.2.4 Ab-Initio Thermochemistry Specific Reaction Systems	<ul> <li>322</li> <li>323</li> <li>324</li> <li>324</li> <li>326</li> <li>326</li> <li>326</li> <li>326</li> <li>327</li> </ul>
<b>Chapter 14</b> 14.1 14.2	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary Introduction Homogeneous Gas phase Transformation 14.2.1 Field Observations 14.2.2 Kinetic of Homogeneous Gas Phase Reactions 14.2.2 Kinetic of Homogeneous Gas Phase Reactions 14.2.2.1 Terminology 14.2.2.2 Thermodynamics 14.2.2.3 Experimental Approaches 14.2.2.4 Ab-Initio Thermochemistry Specific Reaction Systems 14.3.1 Hg(0) - O3	<ul> <li>322</li> <li>323</li> <li>324</li> <li>324</li> <li>326</li> <li>326</li> <li>326</li> <li>327</li> <li>327</li> </ul>
<b>Chapter 14</b> 14.1 14.2	Global Scales Or Current Understanding of Major Chemical and Physical Processes Affecting Mercury Dynamics in the Atmosphere and at the Air-Water/Terrestrial Interfaces Summary Introduction Homogeneous Gas phase Transformation 14.2.1 Field Observations 14.2.2 Kinetic of Homogeneous Gas Phase Reactions 14.2.2.1 Terminology 14.2.2.2 Thermodynamics 14.2.2.3 Experimental Approaches 14.2.2.4 Ab-Initio Thermochemistry Specific Reaction Systems 14.3.1 Hg(0) - O3 14.3.2 Hg(0) + OH	<ul> <li>322</li> <li>323</li> <li>324</li> <li>324</li> <li>326</li> <li>326</li> <li>326</li> <li>327</li> <li>327</li> <li>329</li> </ul>

	14.3.3.3 Hg + BrO	334		
	14.3.3.4 Hg(0) + NO3	335		
14.4	14.4 Gas Phase Oxidation: Issues and Uncertainties			
14.5	Mercury Chemistry in the Atmospheric Aqueous Phase	335		
	14.5.1 Redox reactions	336		
	14.5.2 Does reduction actually occur in the aqueous phase?	336		
	14.5.3 Speciation	337		
	14.5.4 Is aqueous phase chemistry important compared to gas phase oxidation?	337		
	14.5.5 The Sea Salt Aerosol	338		
14.6	The Uncertainty due to Hg Chemistry in Atmospheric Models			
14.7	Deposition Processes			
14.8	References			
Capter 15	Mercury Chemical Transformation in the Gas, Aqueous and Heterogeneous Phases: State-of-the-Art Science and Uncertainties			
	Summary	345		
15.1	Introduction	345		
15.2	Atmospheric oxidation and reductions			
15.3	Theoretical evaluation of kinetic data	360		
15.4	Reactions at interfaces: Heterogeneous reactions	363		
	15.4.1 Lake surface	363		
	15.4.2 Surface of oceans	364		
	15.4.3 Snow surface	365		
	15.4.4 Soil surface	366		
	15.4.5 Vegetation surface	366		
	15.4.6 Carbon (fly ash, charcoal)	367		
15.5	Open questions and future directions	368		
15.6	Acknowledgements	369		
15.7	References	369		
Chapter 16	Importance of a Global Scale Approach to Using Regional Models in the Assessment of Source-Receptor Relationships for Mercury			
	Summary	377		
16.1	Introduction	378		
16.2	Previous Testing and Application	379		
	16.2.1 Introduction of Dynamic Global Modeling for Boundary Conditions	380		
16.3	Testing Model Sensitivities to Intercontinental Transport	383		
16.4	Future Research and Policy Implications	386		
16.5	References	387		

17.2	Model Description		
17.3	7.3 Results and Discussion		
17.4	4 Uncertainties and Future Research		
17.5	References	398	
Capter 18	The GEOS-CHEM Model		
	Summary	401	
18.1	Introduction	401	
18.2	Model Description		
18.3	Results / Discussion	404	
	18.3.1 Reference Simulation	404	
	18.3.2 Response of deposition to anthropogenic emission reductions	405	
	18.3.3 Response of land and ocean emissions	408	
18.4	Uncertainties in Model Results and Future Research	409	
18.5	References	410	
Capter 19	The ECHMERT Model		
	Summary	411	
19.1	Introduction	411	
19.2	Model description	412	
19.3	Results/Discussion	414	
	19.3.1 Sensitivity Analysis of the Chemical Mechanism	414	
	19.3.2 Model Evaluation	417	
	19.3.3 Tracer transport studies	419	
	19.3.4 Emission Reduction Experiment	425	
19.4	Future Research and Policy Implications	426	
19.5	References	427	
Capter 20	The EMEP/MSC-E Mercury Modeling System		
	Summary	428	
20.1	Introduction	428	
20.2	Model Description	428	
20.3	Results and Discussion		
204			
20.5	References	437	
Capter 21	The AER/EPRI Global Chemical Transport Model for Mercury (CTM-HG)		

**Global Mercury Modelling at Environment Canada** 

Summary

Capter 17

Summary

21.1	Description of the CTM-Hg	440
21.2	Emission Inventory	441
21.3	Atmospheric Chemistry of Mercury	442
21.4	Model Performance Evaluation	443
21.5	Source/Receptor Relationships	445
21.6	Conclusion	447
21.7	References	448