

DYNAMICS OF MERCURY POLLUTION  
ON REGIONAL AND GLOBAL SCALES:  
Atmospheric Processes and Human  
Exposures Around the World

# DYNAMICS OF MERCURY POLLUTION ON REGIONAL AND GLOBAL SCALES: Atmospheric Processes and Human Exposures Around the World

Edited by

Nicola Pirrone  
CNR-Institute for Atmospheric Pollution, Rende, Italy

and

Kathryn R. Mahaffey  
U. S. Environmental Protection Agency, Washington, DC, USA



Springer

Library of Congress Cataloging-in-Publication Data

Dynamics of mercury pollution on regional and global scales : atmospheric processes and human exposures around the world / edited by Nicola Pirrone and Kathryn R. Mahaffey.

p. cm.

Includes bibliographical references and index.

ISBN-10: 0-387-24493-X (alk. paper) -- ISBN-10: 0-387- 24494-8 (e-book)

ISBN-13: 978-0387-24493-8

ISBN-13: 978-0387-24494-5

1. Mercury—Environmental aspects. 2. Mercury—Health aspects. 3. Environmental policy. I. Pirrone, Nicola, 1960- II. Mahaffey, Kathryn R., 1943-

TD196.M38D96 2005

363.738'49—dc22

2005043442

© 2005 Springer Science+Business Media, Inc.

All rights reserved. This work may not be translated or copied in whole or in part without the written permission of the publisher (Springer Science+Business Media, Inc., 233 Spring Street, New York, NY 10013, USA), except for brief excerpts in connection with reviews or scholarly analysis. Use in connection with any form of information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed is forbidden.

The use in this publication of trade names, trademarks, service marks and similar terms, even if they are not identified as such, is not to be taken as an expression of opinion as to whether or not they are subject to proprietary rights.

Printed in the United States of America.

9 8 7 6 5 4 3 2 1

SPIN 11054696

springeronline.com

## TABLE OF CONTENTS

<b>PREFACE</b>	xi
<b>CHAPTER-1:</b>	
<b>Where we stand on mercury pollution and its health effects on regional and global scales</b>	1
<i>Nicola Pirrone and Kathryn R. Mahaffey</i>	
<b>PART-I: INTERNATIONAL AND REGIONAL PERSPECTIVES</b>	
<b>CHAPTER-2:</b>	
<b>Global mercury production, use and trade</b>	25
<i>Peter Maxson</i>	
<b>CHAPTER-3:</b>	
<b>Mercury emissions from anthropogenic sources: estimates and measurements for Europe</b>	51
<i>Jozef M. Pacyna, John Munthe, Kari Larjava and Elisabeth G. Pacyna</i>	
<b>CHAPTER-4:</b>	
<b>Legislation and policy concerning mercury in the European Union</b>	65
<i>Neil Emmott and Martin Slayne</i>	
<b>CHAPTER-5:</b>	
<b>The DG Research perspective-research on Hg supported by the European Commission</b>	81
<i>Hartmut Barth</i>	
<b>CHAPTER-6:</b>	
<b>Perspective on mercury: progress through cooperation</b>	91
<i>Marilyn Engle</i>	
<b>PART-II: MONITORING AND ANALYTICAL METHODS</b>	
<b>CHAPTER-7:</b>	
<b>The monitoring and modelling of Hg species in support of local, regional and global modelling</b>	123
<i>Matthew S. Landis, Mary M. Lynam, Robert K. Stevens</i>	

**CHAPTER-8:**

- Determination of mercury and its compounds in water, sediment, soil and biological samples** 153  
*Milena Horvat*

**PART-III: CHEMICAL AND PHYSICAL PROCESSES****CHAPTER-9:**

- Environmental chamber studies of mercury reactions in the atmosphere** 193  
*Ann L. Sumner, Chester W. Spicer, Jan Satola, Raj Mangaraj, Kenneth A. Cowen, Matthew S. Landis, Robert K. Stevens and Thomas D. Atkeson*

**CHAPTER-10:**

- Air-sea exchange and marine boundary layer atmospheric transformations of Hg and their importance in the global mercury cycle** 213  
*Robert P. Mason*

**CHAPTER-11:**

- Terrestrial Hg fluxes: is the next exchange up, down, or neither?** 241  
*Mae S. Gustin and Steven E. Lindberg*

**CHAPTER-12:**

- Chemical transformation of gaseous elemental Hg in the atmosphere** 261  
*Parisa A. Ariya and Kirk A. Peterson*

**CHAPTER-13:**

- Modelling chemical and physical processes of Hg compounds in the marine boundary layer** 295  
*Ian M. Hedgecock and Nicola Pirrone*

**CHAPTER-14:**

- Modelling transport and transformation of Hg and its compounds in continental air masses** 319  
*Russell Bullock*

**PART-IV: HUMAN EXPOSURE****CHAPTER-15:**

**Exposure to mercury in the Americas** 345

*Kathryn R. Mahaffey*

**CHAPTER-16:**

**Exposure to Hg in the general population of Europe and the Arctic** 385

*Lars Barregård*

**CHAPTER-17:**

**Methylmercury exposure in general populations of Japan, Asia and Oceania** 405

*Mineshi Sakamoto, Akira Yasutake and Hiroshi Satoh*

**CHAPTER-18:**

**Mercury Pollution from artisanal gold mining in Block B, El Callao, Bolivar State, Venezuela** 421

*Marcello M. Veiga, Dario Bermudez, Heloisa Pacheco-Ferreira, Luiz Roberto Martins Pedroso, Aaron J. Gunson, Gilberto Berrios, Ligia Vos, Pablo Huidobro and Monika Roeser*

**CHAPTER-19:**

**An ecosystem approach to describe the mercury issue in Canada: from mercury sources to human health** 451

*Marc Lucotte, René Canuel, Sylvie Boucher de Grosbois, Marc Amyot, Robin Anderson, Paul Arp, Laura Atikessé, Jean Carreau, Laurie Chan, Steve Garceau, Donna Mergler, Charlie Ritchie, Martha J. Robertson and Claire Vanier*

**CHAPTER-20:**

**The GEF/UNDP/UNIDO global mercury project - environmental and health results from a small-scale gold mining site in Tanzania** 467

*Appleton D., Drasch G., Böse O'Reilly S., Roider G., Lister R., Taylor H., Smith, B., Tesha A. and Beinhoff C.*

**CHAPTER-21:**

**Development of programs to monitor methyl-mercury exposure and issue fish consumption advisories** 491

*Henry A. Anderson and Jeffrey D. Bigler*

**CHAPTER-22:**

- Health effects and risk assessment** 511  
*Philippe Grandjean, Sylvaine Cordier, Tord Kjellström, Pål Weihe and  
 Esben Budtz Jørgensen*

**PART-V: REGIONAL CASE STUDIES****CHAPTER-23:**

- Dynamic processes of atmospheric Hg in the  
 Mediterranean region** 541  
*Nicola Pirrone, Francesca Sprovieri, Ian M. Hedgecock,  
 Giuseppe A. Trunfio and Sergio Cinnirella*

**CHAPTER-24:**

- Spatial and temporal variability of atmospheric  
 Hg in North-Western and central Europe-observations  
 on different time scale** 581  
*Ralf Ebinghaus, Hans. H. Kock, John Munthe and I. Wängberg*

**CHAPTER-25:**

- Atmospheric Hg: a decade of observations in the  
 Great Lakes** 611  
*Gerald J. Keeler and Timothy J. Dvonch*

**CHAPTER-26:**

- Recent trends in Hg emissions, deposition, and biota in the  
 Florida everglades: a monitoring and modelling analysis** 637  
*Thomas D. Atkeson, Curtis D. Pollman and Donald M. Axelrad*

**CHAPTER-27:**

- Mercury pollution in China - an overview** 657  
*Xinbin Feng*

**CHAPTER-28:**

- Mercury pollution in the Arctic and Antarctic regions** 679  
*Francesca Sprovieri and Nicola Pirrone*

**CHAPTER-29:**

- EMEP Regional/Hemispheric mercury modelling:  
 achievements and problems** 707  
*Alexey Ryaboshapko, Sergey Dutchak, Alexey Gusev,  
 Ilia Ilyin and Oleg Travnikov*

**ACRONYMS**

735





## PREFACE

This book brings together authors with expertise in a wide range of fields to provide an up to the minute overview of the most important problems relating to mercury in the environment. The book reflects growing concern over the likelihood of harmful effects to human health and sensitive ecosystems posed by mercury in the light of increasing fossil fuel combustion, mercury use in a range of manufactured goods, and the lack of emission control policies. Concern has been expressed at local, national, and international levels; in the last three years both the European Commission and UNEP have published reports on mercury in the environment. Growing concern has led to an increased effort to understand the fate of mercury in the environment, including primary production and trade in mercury, emissions from manufacturing and power generation, natural emissions and re-emission, atmospheric transport and transformation, deposition patterns, uptake by biota, and eventual health impacts on living organisms. The increasing specialisation, and amount of research in the numerous scientific fields associated with the study of the fate of mercury in the environment, make the publication of this book both necessary and timely. For experts, and non-experts, who require both the broader picture, as well as an awareness of the latest progress in the fields relevant to mercury research, this book provides the most comprehensive and up to date overview available.

The book has five sections. The first section covers '*International and Regional Perspectives*', looking firstly at mercury production, trade and use over the last ten years and future trends. Current and projected industrial emissions of mercury, and their assessment methods are presented. The last part of this section describes the European Union and the United States Environmental Protection Agency perspectives and activities regarding the limitation of risk to human health.

The second section addresses '*Monitoring and Analytical Methods*', that is the determination of the concentration of mercury and mercury compounds in the atmosphere, and in aquatic and terrestrial ecosystems, including biological samples. The problems involved and precautions required when measuring trace concentrations in complex media are described.

The third section deals with the '*Chemical and Physical Processes*' which determine the partitioning of mercury between environmental interfaces, air-sea, water-sediment, air-soil, soil-plant, canopy-air, and the role these have

in the global biogeochemical mercury cycle. Recent advances in the understanding of mercury kinetics in the atmosphere are described.

The fourth section includes six studies on 'Human *Exposure*', reviewing studies reports on different populations from around the world, as well as methods for assessing mercury exposure. The major risks associated with high and extreme cases of mercury exposure are described.

The last section provides seven '*Regional Case Studies*', for regions where substantial research on the fate of mercury in the environment has been carried out including, the Mediterranean Basin, North and North-Eastern Europe, the Polar regions, the Great Lakes and the North-Eastern U.S., Florida, Asia (particularly China), and the area covered by EMEP, the UNECE-Long Range Transport Convention reference area for Europe.

**Nicola Pirrone**

*CNR-Institute for Atmospheric Pollution, Division of Rende, 87036 Rende, Italy*

**Kathryn R. Mahaffey**

*Office of Science Coordination and Policy, United States Environmental Protection Agency,  
Washington, D.C. 20640, USA*

# **Chapter-1**

## **WHERE WE STAND ON MERCURY POLLUTION AND ITS HEALTH EFFECTS ON REGIONAL AND GLOBAL SCALES**

Nicola Pirrone<sup>1</sup> and Kathryn R. Mahaffey<sup>2</sup> \*

<sup>1</sup> *CNR-Institute for Atmospheric Pollution, Division of Rende, 87036 Rende, Italy*

<sup>2</sup> *Office of Science Coordination and Policy, United States Environmental Protection Agency, Washington, D.C. 20640, \* see disclaimer below.*

### **INTRODUCTION**

It is widely accepted in the scientific community that mercury (Hg) contamination of ecosystems and subsequent human exposure remains a serious environmental hazard. The ability of Hg to distribute globally via the atmosphere has received increasing attention in recent years and has emphasized the need for a global perspective in both research, monitoring and policy making. The aim of this chapter is to provide an overview of our understanding of the mercury pollution problem in relation to both its global cycle and its negative effects on human health.

### **MERCURY IN THE GLOBAL ENVIRONMENT**

It is well known that mercury is released to the global environment from a multitude of natural and anthropogenic sources. Once released to soil, water and atmospheric ecosystems it is re-distributed in the environment through a complex combination of chemical, physical and biological processes that can

---

\* *Disclaimer:* The statements in this publication are the professional views and opinions of the author and should not be interpreted to be the policies of the United States Environmental Protection Agency.

act with different time scales. Recent estimates indicate that natural sources (volcanoes, surface waters, soil and vegetation) contribute with 2700 tonnes of mercury released annually to the global atmosphere, whereas the contribution from major industrial sources account for 2250 tonnes per year (Pirrone et al., 1996; Pirrone et al., 2001; Pacyna et al., 2003). Mercury emissions in Europe and North America contribute less than 25% to the global atmospheric emissions, where Asia account for about 40% of global total. The majority of the emissions originate from combustion of fossil fuels, particularly in the Asian countries (i.e., China, India). Combustion of coal is and will remain in the near future as the main source of energy in these countries. The emissions from stationary combustion of fossil fuels (especially coal) and incineration of waste materials accounts for approximately 70% of the total quantified atmospheric emissions from significant anthropogenic sources. As combustion of fossil fuels is increasing in order to meet the growing energy demands of both developing and developed nations, mercury emissions can be expected to increase accordingly in the absence of the deployment of control technologies or the use of alternative energy sources.

Once released to the atmosphere, mercury and its compounds can be transported over long distances before being removed by particle dry deposition and wet scavenging by precipitation (i.e., Pirrone et al., 2000; Pirrone et al., 2003a; 2003b; Hedgecock and Pirrone, 2001; 2004). The temporal and spatial scales of mercury transport in the atmosphere and its transfer to aquatic and terrestrial receptors depends primarily on the chemical and physical forms of mercury which drive their interactions with other atmospheric contaminants and with surface marine waters as well. Gaseous elemental mercury ( $\text{Hg}^0$ ) is relatively inert to chemical reactions with other atmospheric constituents, and is only sparingly soluble in pure water. Therefore, once released to the atmosphere, mercury can be dispersed and transported for long distances over hemispheric and global scales before being deposited to terrestrial and aquatic receptors. The concentration of  $\text{Hg}^0$  in ambient air is mainly determined by the background concentration of around  $1.5\text{--}1.8\text{ ng m}^{-3}$  in the Northern Hemisphere and  $0.9\text{--}1.5\text{ ng m}^{-3}$  in the Southern Hemisphere (see Table I). Oxidised mercury ( $\text{Hg(II)}$ ) and mercury bound to particulate matter ( $\text{Hg(p)}$ ) are typically present in concentrations less than 1 % of the  $\text{Hg}^0$  (Table I).

Studies carried out in the last decade have shown that mercury is transported and deposited to very remote locations such as the Arctic as well as the Antarctica (i.e., Schroeder et al., 1998; Ebinghaus et al., 2002; Lindberg et al., 2002; Sprovieri et al., 2002). The mechanism that primarily influence the transfer of mercury from the atmosphere to snow and ice pack is known as “Mercury Depletion Event (MDE)”, this event or mechanism takes place (high deposition rate of mercury to the surface) primarily during the first few months of the Polar sunrise. The mercury depletion happens at the same time as the

surface-level ozone depletion (a separate phenomenon from the better known ozone depletion in the stratosphere). The net atmospheric input to Polar ecosystems resulting from this phenomena is not known in detail. Re-emissions of mercury occur from the snow surface and during snowmelt, but the depletion events may still result in significant input to the aquatic environment. In case this phenomenon shows up to be resulting in higher yearly mercury deposition rates in the Polar regions than in other regions of the world, this could mean that the Polar regions serve as “mercury cold traps” collecting an unproportionally high part of the global mercury emissions. This would fit well with the observed high mercury concentrations in the Arctic aquatic environment. Mercury depletion has now been observed in Alert, Canada (Schroeder et al., 1998; Lu et al., 2001), in Barrow, Alaska, USA (Lindberg et al., 2002), Svalbard (Berg et al., 2003; Sprovieri et al., 2005, see also Chapter 28), in Greenland (Skov, 2002) as well as in the Antarctic (Ebinghaus et al., 2002), and can thus be described as a generally occurring polar phenomena which may influence the total input to Polar ecosystems.

Atmospheric deposition to marine waters is primarily driven by particle dry deposition and wet scavenging by precipitation mechanisms. Generally, the relative contribution of wet deposition accounts for about two thirds of the overall mercury budget entering to the marine system compared to particle dry deposition. However, in warm and dry region (i.e., Mediterranean) dry deposition was found to account for nearly 50% of the total flux (Pirrone et al., 2003a). Gas exchange of gaseous mercury between the top water microlayer and the atmosphere is considered the major mechanisms driving gaseous mercury from the seawater to the air (e.g., Pirrone et al., 2001b; Pirrone et al., 2003a).

Once released to marine waters, it undergoes a number of chemical and physical transformations (i.e., Mason et al., 2001).  $\text{Hg}^0$  is found in the mixed layer and in deeper waters of the ocean with concentrations generally ranging from 0.01 to 0.5 pM (e.g., Horvat et al., 2003). Gas exchange via Hg reduction and volatilization is the major loss term for marine Hg. Due to the low solubility of  $\text{Hg}^0$  in water, almost all the aqueous mercury is present as  $\text{Hg(II)}$  in the inorganic form and organic methylmercury. Mercury levels in fish constitute a long-standing health hazard and this environmental problem relates predominantly to the conversion of inorganic Hg to neurotoxic monomethylmercury (MMHg) and dimethylmercury (DMHg) (e.g., IARC, 1994).

Table 1. Typical concentrations of mercury species in the Planetary Boundary Layer (PBL).

Species	Concentration	Location	References
Hg <sup>0</sup> (ng m <sup>-3</sup> )	0.5 – 1.2	Atlantic air, southern hemisphere	UNEP, 2002
	1.1 – 1.8	Atlantic air, continental background, northern hemisphere	Wängberg et al., 2001 EC, 2001
	0.8 – 2.2	Mediterranean air	Sprovieri et al., 2003
	1.5 – 15	Continental air, urbanized, industrial	Pirrone et al., 2001; 2003a
	0.1 – 1.4	Arctic	Sprovieri et al., 2000
	0.1 – 1.1	Antarctica	Sprovieri et al., 2002
	1.7 – 4.1	United States	Ebinghaus et al., 2002
			Keeler et al., 1995 Landis et al., 2002
Hg(II) (pg m <sup>-3</sup> )	< 30	Background air	Sprovieri et al., 2003
	up to 40	marine and continental	Pirrone et al., 2001; 2003a
	5 – > 50	near sources	Wängberg et al., 2003
	up to 200	Antarctica and Arctic	Sprovieri et al., 2002
Hg(p) (ng m <sup>-3</sup> )	0.1 – 5	Background air	Sprovieri et al., 2003
	0.1 – 25	Marine (Mediterranean) air	Pirrone et al., 2001; 2003a
	5 – >50	Continental background, higher near sources.	Wängberg et al., 2003
	up to 100	Antarctica and Arctic	Sprovieri et al., 2002
CH <sub>3</sub> HgX (pg m <sup>-3</sup> )	0.1 – 10	Background air	Lee et al., 2003
(CH <sub>3</sub> ) <sub>2</sub> Hg (pg m <sup>-3</sup> )	< 5	Background air	Lee et al., 2003
	-30	Marine polar air	
Hg(II) in precip. (ng L <sup>-1</sup> )	1 – 20	Background / marine locations	Wängberg et al., 2001 Keeler et al., 1995

Anthropogenic activities presumably increased the surface water marine Hg concentration by a factor three, an increase which resulted amongst others in elevated Hg concentrations in marine fishes (e.g., Amyot et al., 1997; Horvat et al., 2001). It is currently thought that most of the methylated Hg found in the

water column and the biota of the marine waters is generated by *in-situ* production, though the reaction mechanisms are not yet clearly understood (e.g., Mason et al., 2002; Hintelman et al., 1997).

Once entered to terrestrial ecosystems, mercury is accumulated in forest soils (Steinnes et al., 1993) from where it is only slowly transported to surface and deep waters. In aquatic ecosystems, a fraction of the mercury directly deposited and transported from surrounding catchments is transformed into methylmercury compounds which are readily taken up and bioaccumulated in aquatic food-chains.

Industrial discharges of mercury directly to water systems will have the same effect. Accumulation of mercury in forest soils may also lead to adverse effects on soil micro-organisms, which has a potential impact on mineralisation processes (Pirrone et al., 2001 and ref. herein).

## Mercury in the Technosphere

Mercury is a natural component of the Earth, with an average abundance of approximately  $0.05 \mu\text{g g}^{-1}$  in the Earth's crust, with significant local variations. Mercury ores that are mined generally contain about 1% mercury, although the strata mined in Spain typically contain up to 12-14% mercury. While about 25 principal mercury minerals are known, virtually the only deposits that have been harvested for the extraction of mercury are cinnabar. Mercury is also present at very low levels throughout the biosphere. Its absorption by plants may account for the presence of mercury within fossil fuels like coal, oil and gas, since these fuels are conventionally thought to be formed from geologic transformation of organic residues. As described in detail by Maxon (this volume – Chapter 2) the mercury available on the world market is supplied from a number of different sources, including:

- Mine production of primary mercury either as the main product of the mining activity, or as by-product of mining or refining of other metals (such as zinc, gold, silver) or minerals;
- Recovered primary mercury from refining of natural gas (actually a by-product, when marketed, however, is not marketed in all countries);
- Reprocessing or secondary mining of historic mine tailings containing mercury;
- Recycled mercury recovered from spent products and waste from industrial production processes. Large amounts (reservoirs) of mercury are "stored" in society within products still in use and "on the users shelves";

- Mercury from government reserve stocks or inventories;
- Private stocks (such as mercury in use in chlor-alkali and other industries), some of which may later be returned to the market.

Since the industrial revolution, due to its unique physico-chemical properties (i.e., high specific gravity, low electrical resistance, constant volume of expansion), mercury has been employed in a wide variety of applications (i.e., manufacturing, dentistry, metallurgy). As a result of its use the amount of mercury mobilised and released into the atmosphere has increased compared to the pre-industrial levels. In the past, a number of organic mercury compounds were used quite widely, for example in pesticides (extensive use in seed dressing among others) and biocides in some paints, pharmaceuticals and cosmetics. While many of these uses have diminished in some parts of the world, organic mercury compounds are still used for several purposes. Some examples are the use of seed dressing with mercury compounds in some countries, use of dimethylmercury in small amounts as a reference standard for some chemical tests, and thimerosal (which contains ethylmercury) used as a preservative in some vaccines and other medical and cosmetic products since the 1930's. As the awareness of mercury's potential adverse effects to health and the environment has been rising, the number of applications (for inorganic and organic mercury) as well as the volume of mercury used have been reduced significantly in many of the industrialised countries, particularly during the last two decades. Therefore as metal, mercury uses (just to cite few applications and uses) are (UNEP, 2003; see also Chapter-2 herein):

- for extraction of gold and silver
- as a catalyst for chlor-alkali production
- in manometers for measuring and controlling pressure
- in thermometers
- in electrical and electronic switches
- in fluorescent lamps
- in dental amalgam fillings

As chemical compounds (among others):

- in batteries (as a dioxide)
- biocides in paper industry, paints and on seed grain
- as antiseptics in pharmaceuticals
- laboratory analyses reactants
- catalysts
- pigments and dyes (may be historical)



- detergents (may be historical)
- explosives (may be historical)

## HEALTH EFFECTS

Both humans and wildlife are adversely affected by multiple chemical forms or chemical species of mercury, although specific changes within the organ system predominantly affected differs with the chemical form of mercury. For example, renal or kidney dysfunction accompanies exposure to inorganic mercury, but the nervous system is adversely affected by all three major forms of mercury found in the environment: mercury vapor, inorganic mercury, and methylmercury. It is important, however, to recognize that the specific types of neurological damage produced following mercury exposures differ with the chemical form of mercury. For all three forms the severity of the damage varies with the intensity and duration of exposure (i.e., the dose).

Adverse human health effects range from those detectable only with specialized testing protocols and sophisticated instruments to gross, clinically evident abnormalities, as well as death. It is unclear at this time the extent to which neurological damage produced by concurrent exposure to multiple forms of mercury produces additive or cumulative neurological damage. Concurrent exposures to both mercury vapor, inorganic mercury, and methylmercury have been identified in people living in artisanal mining areas with long-term environmental contamination secondary to mercury in mining wastes. Within these regions bioaccumulation of methylmercury by the aquatic food chain causing elevated methylmercury accumulation among fish-consuming workers and their families who live in these geographic areas has been found.

The effects of mercury on organ systems in addition to the nervous system include the cardiac, immune, and endocrine functions. Although described in the medical literature, these adverse effects have not yet been incorporated into risk assessments used by countries and world public health organizations in setting regulatory standards or policies aimed to protect public health.

Vulnerability to effects of methylmercury in particular depends on age, in addition to dose and duration of exposure. Specifically methylmercury adversely affects the developing fetal brain at far lower exposures than adversely affect the adult's nervous system. This was first observed in Minamata, Japan during the major outbreak in the 1960s where women who themselves were minimally symptomatic gave birth to infants with substantial neurological problems (Harada, 1977). This difference reflects methylmercury's interference with fetal brain development.

Neurological development during fetal life must progress in an exquisitely

programmed series of steps that must occur in a timed sequence for normal neurological outcomes. A number of mechanisms through which methylmercury impairs *in utero* development have been identified (Rice and Barone, 2000). It is not entirely clear which of these is the “most critical”, but it is clear that there are many opportunities for methylmercury to impair neurological development.

## METHYLMERCURY

What makes methylmercury important to wildlife and human health is that it bioaccumulates in the aquatic food chain. Some wildlife are obligate piscivores consuming only fish and shellfish. Examples, include other fish, birds, and mammals. Methylmercury (released from other organomercurials) which had been added to seed grains in the 1950s and 1960s as a preservative resulted in death of birds in Europe and the United States (US EPA, 1997). Methylmercury is now understood not simply to kill birds at high doses and produce overt symptoms at lower doses, but also to prevent reproduction in wild birds including the common loon (Barr, 1986) and common tern (Fimreite, 1974) and cause neurological damage (Henny et al., 2002).

Fish which are generally thought of as a source of methylmercury to piscivores, including humans. However, as additional toxicology information has been obtained in the past decade, fish are no longer simply regarded as a source of methylmercury, but are themselves adversely impacted by methylmercury exposure as shown by reduced growth in walleye (Freidmann et al., 1996) and reduced reproduction of fish species including the fathead minnow (Hammerschmidt et al., 2002) through alteration of reproductive endocrinology (Drevnick and Sandheinrich, 2003). Because effects of methylmercury on wildlife reproduction and health are complex and publication of significant key studies occur at a rapidly accelerating pace, no attempt has been made to include these in this volume despite their importance.

Because methylmercury exposure is so closely linked to consumption of fish and shellfish, nutritional considerations are a major issue, particularly in geographic regions with few choices in available food resources (Mahaffey, 2004). Fish and shellfish supply protein, omega-3 fatty acids, vitamins and minerals (IOM/NAS, 2002). Omega-3 fatty acids, in particular, are critical to normal development of the fetal nervous system (IOM, 2002). A complex epidemiological situation is emerging in which the same variable (i.e., fish and shellfish consumption) is associated with both beneficial (e.g., omega-3 fatty acids) and adverse (e.g., methylmercury) effects on neurological development. Although affected by both of these constituents of fish, different domains of

neurological function are affected by these chemicals. Recognizing that fish provide important nutrients, actions to control pollution that preserve fish and shellfish resources for both wildlife and people are essential.

Although environmental releases of inorganic mercury and mercury vapor raise great concern for human health and wildlife because these are methylated and bioaccumulate in the aquatic food web, humans also are directly exposed to additional forms of mercury. Multiple uses of mercury in products that may be sold to the general population, such as cosmetics and both regulated and unregulated “medical” remedies, can result in exposures to both inorganic mercury and organo-mercurials. Occupational exposures to mercury vapor and inorganic mercury through industry and mining (particularly Artisanal gold mining) dramatically increase the risk of mercury toxicity for part of the population. Combined with methylmercury exposure the risk of mercury toxicity is further increased.

## **RISK ASSESSMENTS**

Most risk assessments for methylmercury are based on damage to the fetal nervous system as the most sensitive health endpoint (Table 2). Many government regulations and public health decisions rely on these risk assessments. The World Health Organization’s assessment in 1990 indicated that there was a 5% risk of damage to fetal neurological development when maternal mercury exposures resulted in maternal hair mercury concentrations exceeding 10 ppm (WHO, 1990). Subsequent to this assessment, a series of epidemiological studies have been carried out using both longitudinal and cross-sectional approaches. Most of these investigations are still active and continue to yield new data. There has been a clear trend in the past decade to adoption of more public health protective standards for methylmercury.

Comparison of risk assessments for methylmercury developed during the past decade emphasizes differences in the accepted margins between exposures that produce recognized adverse effects and those judged to be an accepted level of exposure. These differences, frequently referred to as “uncertainty factors” are intended to protect members of the population by allowing for variability and uncertainty in toxicodynamics and toxicokinetics of methylmercury. Uncertainty factors broadly reflect two areas: variability between individuals and/or groups, and effects or differences that simply are not recognized at the time the assessment is made.

Dealing first with variability described as differences in toxicodynamics and toxicokinetics. Generally person-to-person variability in toxicodynamics is under-described and risk assessments often need to rely on default values which

are typically not data-derived for the specific assessment (Reference Dose/Reference Concentration Technical Panel, 2002). Toxicokinetic factors are more frequently data derived (Reference Dose/Reference Concentration Technical Panel, 2002). Typically the data-derived component of toxicokinetic factors substantiates the range of person-to-person variability, or when fetal risk is the health end-point of concern maternal/fetal pair-maternal/fetal pair variability. Occasionally an area of variability may be known qualitatively and only as data are assessed through more advanced statistical procedures can the magnitude of the variability be better described. An example of this is the concentration of methylmercury across the placenta from maternal blood to cord blood.

Uncertainty factors are present to reflect effects that are only partially understood and/or differences that there are not yet data sufficient to provide quantitative estimates of variability. Examples for methylmercury include the possible effects of methylmercury on coronary heart disease (Salonen et al., 1995; Guallar et al., 2002; Yoshizawa et al., 2002), as well as methylmercury's effects on the endocrine and immune systems. Over time, as evidence for the effect of a chemical on an organ system accumulates, such data may change the basis of risk assessments. An example was seen for inorganic lead between the 1970s and the 1980s. During the 1970s almost public health screening programs and risk recommendations for health intervention to protect children against lead poisoning were based on changes in the hematopoietic pathway, specifically increases in free erythrocyte protoporphyrin (Centers for Disease Control, 1978). Free erythrocyte protoporphyrin increased exponentially with increasing blood lead concentration with an apparent threshold effect at a blood lead concentration between about 15 and 18  $\mu\text{g Pb/dL}$  whole blood (Piomelli et al., 1982). This strategy was used in public health screening programs for children at a time when the neurobehavioral effects of lead were thought to occur if blood lead concentrations exceeded 30  $\mu\text{g/dL}$  (Centers for Disease Control, 1978). After approximately the mid-1980s as the effects of early childhood lead exposure on intellectual development associated with blood lead exposures near 10  $\mu\text{g Pb/dL}$  whole blood became clear, risk assessments shifted in two ways. The assessments were based on inorganic lead's impact on intelligence in young children rather than on impaired hematopoiesis. The second change was that rather being concerned about exposures producing blood lead concentrations in the range of 25  $\mu\text{g/dL}$  (associated with hematopoietic changes), exposures producing blood lead concentrations of  $\sim 10$   $\mu\text{g/dL}$  became of concern because of neuro-behavioral effects (United States Centers for Disease Control, 1991).

What will the future holds for risk assessments of methylmercury? Inclusion of cardiac effects and/or adult neurotoxicity as sensitive health endpoints would greatly modify the size of the population of immediate concern. It is also

possible that as complex, highly adaptable organ systems - of particular interest, mercury's effects on the immune system and on the endocrine system - are more thoroughly evaluated, these may respond adversely to methylmercury at exposure levels even lower than those currently of concern as adversely affecting fetal neuro-development.

It is abundantly clear that fish, shellfish, and other constituents of the aquatic food web are extraordinarily important food sources of high quality protein, omega-3 fatty acids, vitamins, and minerals. Maintaining low methylmercury concentrations in food sources that supply these nutrients is needed for the well being of all. Continued contamination of these aquatic food sources with methylmercury will further diminish the food supply of this planet.

## GAPS IN OUR UNDERSTANDING

Although our understanding of the global atmospheric cycle including its interfaces with land, water and vegetation has improved greatly in recent decades, we are not yet at a scientific level where we can explain observations of Hg levels in different ecosystems globally or precisely predict the benefit of different scenarios of emission reduction.

In assessing the relative contribution of different patterns/mechanisms affecting the cycle of mercury within and between different ecosystems and its impact on ecosystems and human health, a number of questions, though significant improvement have been made in recent years, still remain to be answered, these questions are briefly reported below.

With reference to the *Retention of Mercury in the Ecosystems*:

- How much of atmospherically-deposited Hg is returned in ecosystems in short-term and in long-term?
- Can we better predict rates of volatilisation of deposited Hg?
- Can we better understand the difference between levels of deposition and re-emission for different ecosystem types?
- Is there any development of watershed budgeting methods for Hg including significant but poorly understood influences such as forest fires?

Table 2. Exposure Limits for Methylmercury.

	Date	Recommended Limits	Critical Effects and Target Group
US FDA	1970s	Acceptable Daily Intake = 0.4 $\mu\text{g/kgbw/day}$	Paresthesia in adults. 200 $\mu\text{g Hg/L}$ whole blood. 50 ppm Hg in hair.
Health Directorate Canada	1990	0.47 $\mu\text{g/kgbw/day}$ .	General population. Same as US FDA 1970.
World Health Organization	1990	0.48 $\mu\text{g/kgbw/day}$  Maternal hair mercury levels in the 10 ppm - 20 ppm range	Paresthesias in adults. Same as US FDA 1970.  5% risk of neurological deficits in the child following fetal exposure secondary to maternal ingestion of methyl-mercury sufficient to produce maternal hair mercury levels in the 10 ppm - 20 ppm range.
US-EPA	2000	Reference Dose = 0.1 $\mu\text{g/kgbw/day}$	Maternal/fetal pair. BMDL of 11 ppm in hair. UF of 10. Fetal/cord blood [Hg] of 58 $\mu\text{g/L}$ . Delays and deficits in neuropsychological development and neuromotor function following <i>in utero</i> methylmercury exposure.
US Agency for Toxic Substances and Disease Registry	1999	Minimal Risk Level = 0.3 $\mu\text{g/kgbw/day}$	Maternal/fetal pair. Delays and deficits in neuropsychological development and neuromotor function following <i>in utero</i> methylmercury exposure.
Health Canada - Health Protection Branch	1998	Provisional Tolerable Daily Intake = 0.2 $\mu\text{g/kgbw/day}$	Maternal/fetal pair. BMDL of 11 ppm in hair. UF of 5.
Kommission "Human-Biomonitoring" des Umwelbundesamtes (Germany)	1999	Recommended limit values for inorganic and organic mercury for general populations, occupationally exposed groups, and sensitive subpopulations.  HBM I of 5 $\mu\text{g/L}$ for organic mercury among women of reproductive age: corresponds to maternal hair mercury concentration of 1.5 $\mu\text{g/g}$ using a 1:300 conversion	Fetal nervous system. HMB I of 5 $\mu\text{g/L}$ in blood or hair of 1.5 ppm mercury. HMB II of 15 $\mu\text{g Hg/L}$ blood or ~ 4 to 5 ppm Hg in hair.  HMB I: Women whose blood mercury exceeds these levels are advised to restrict fish consumption and/or restrict the use of methylmercury-containing pharmaceuticals. HMB II: Additional interventions recommended.
Joint Expert Committee on Food Additives	2003	1.6 $\mu\text{g/kgbw/day}$ Provisional Tolerable Weekly Intake (PTWI). JECFA Committee utilized a mean maternal hair: blood ratio of 250 and a factor of 2 for likely inter-individual variability. For inter-individual pharmacokinetic variability, a UF of 3.2 was used in converting maternal blood concentration to a steady-state dietary intake.	PTWI considered sufficient to protect the developing fetus. Committee calculated a composite hair mercury from Faroes and Seychelles of 14 mg/kg maternal hair to be without appreciable adverse effects in the offspring. Total UF of 6.4 (2 x 3.2).

With reference to the *Ecosystem Sensitivity*:

- How can we predict/understand the wide variability among lakes/ivers in biotic Hg concentrations?
- Have the effects of watershed manipulation (i.e., fishery, agriculture) on fish Hg levels been adequately understood?

With reference to the *Ecosystem Toxicity*:

- What are the key receptors?
- What environmentally concentrations are of key importance to be monitored?
- What impact do elevated fish Hg concentrations have on fish and on their predators?
- What appropriate Hg threshold values to protect soil micro-biota under different ecological conditions?

With reference to the *Ecosystem Response Time*:

- How much time is needed for environmental concentrations to respond to changes in atmospheric Hg depositions?

With reference to the *Human Health*:

- What are the toxic effects of different levels and combined species of inorganic and organic Hg?
- Are there known mixture effects of mercury exposure and exposure to other neurotoxicants commonly found in fish and shell fish?
- What are the long-term effects of low dose exposure at critical life stages in addition to the recognised neurotoxic effects of mercury and methylmercury exposure?

To answer these questions, there is a need to fill existing gaps in our understanding of different chemical and physical mechanisms involved in the dynamics of mercury within and between atmospheric, marine and terrestrial ecosystems. The following may represent the most significant questions in relation to atmospheric and marine processes:

- what are the variations in the regional and global mercury cycle between atmospheric, marine and terrestrial ecosystems over time that can occur with changes in emissions of mercury and other atmospheric contaminants (e.g., NO<sub>x</sub>, SO<sub>2</sub>) as well as with climate change. The

effects driven by climate change on the global mercury cycle has not received a great attention, though on short- and long-term, it is believed to represent the major driving mechanism that may influence the redistribution of mercury on global and regional scales. The effects of climate change can be classified as primary and secondary effects. Primary effects account for an increase in air and sea temperatures, wind speeds and variation in precipitation patterns, whereas secondary effects are related to an increase in O<sub>3</sub> concentration and aerosol loading, to a decrease of sea ice cover in the Arctic and changes in plant growth regimes. All these primary and secondary effects may act with difference time scales and influence the atmospheric residence time of mercury and ultimately its dynamics from local to regional and global scale;

- recent research suggests that through consideration of the role of halogen and OH radical chemistry involving Hg compounds in the marine boundary layer (MBL) better deposition estimates of Hg (and its compounds) could be obtained;
- gaseous Hg exchange at the air-water interface is primarily driven by chemistry in the lower layer of the atmosphere, chemical and biological processes in the marine system and water wave dynamics; the combination of these three mechanisms and their relative magnitude are still unclear;
- in order to develop global assessment models for mercury, there is a need to promote a global mercury monitoring network aimed to assess long-term changes in mercury concentrations in the atmosphere, marine and freshwater reservoirs with reference to primary ecological and public health indicators;
- although stocks of different Hg compounds in the marine system are relatively well quantified, translocations of Hg from one compartment to the other remain largely unknown. In addition the role of sediments and micro-organisms in the biogeochemical cycling of Hg is not yet completely understood;
- qualitative as well as quantitative information about complexing ligands for Hg that act as carriers from one compartment to another (water to plankton, plankton to higher trophic level) as well as from one ecosystem to another is scarce and requires a further investigation;
- bacterially mediated production of organomercury compounds is recognised as an important control function of the Hg introduction in the food chain. Preliminary studies have also shown that demethylation may also occur in seawater (due to photodegradation) or in sediments (due to bacterial activity), simultaneously with the methylation process. A better



understanding of these factors/mechanisms will certainly help improve our capabilities in modeling the fate of mercury in the marine system.

## INTERNATIONAL ACTIONS ON MERCURY

Past and on-going initiatives aimed to reduce the impact of mercury pollution on the environment and human health, including waste management practices, have been taking place at national and international levels (see UNEP, 2003; EC, 2003). Detailed information on regional and global agreements, instruments, organisations and programmes tackling aspects of the mercury problem is provided in detail elsewhere (UNEP, 2003; EC, 2004; Chapters 4, 5, 6 of this volume), therefore, only a brief overview of the main initiatives is given here.

- *The 1998 Protocol on Heavy Metals under the UNECE Convention on Long-Range Transboundary Air Pollution (LRTAP)*. Provisions of the protocol require parties to reduce total annual emissions of mercury into the atmosphere, secure application of the best available techniques for stationary sources, and consider applying additional product controls. The protocol entered into force on 29 December 2003.
- *The OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic*. The Convention's objective of preventing and eliminating pollution is reflected in a strategy on hazardous substances, agreed in 1998. This has the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances (such as mercury) and close to zero for man-made synthetic substances, with every endeavour to be made to move towards the target of cessation of discharges, emissions and losses of hazardous substances by 2020.
- *The Helsinki Convention on the Protection of the Marine Environment of the Baltic Sea Area*. The Convention aims to prevent and eliminate pollution in order to promote the ecological restoration of the Baltic Sea Area and the preservation of its ecological balance. Its objective is to prevent pollution by continuously reducing discharges, emissions and losses of hazardous substances towards the target of their cessation by 2020. The ultimate aim is to achieve concentrations in the environment near background values for naturally occurring substances and close to zero for man-made synthetic substances.
- *The UNEP Mediterranean Action Plan (MAP)*. MAP is an effort involving 21 countries bordering the Mediterranean Sea, as well as the

EU. There are three protocols which control pollution to the sea, including the input of hazardous substances.

- *The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal.* The Convention strictly regulates the transboundary movements of hazardous wastes and establishes obligations for parties to ensure such wastes are managed and disposed of in an environmentally sound manner. Any waste containing or contaminated by mercury or its compounds is considered hazardous waste and is covered by the provisions of the Convention. Hazardous wastes may not be exported from the EU or OECD for disposal, recovery or recycling in other countries.
- *The Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade.* The Convention establishes the principle that export of specified chemicals and pesticides can only take place with the prior informed consent of the importing party. At present, mercury compounds used as pesticides are covered by the PIC procedure, but mercury and its compounds intended for industrial use are not.
- *The Arctic Council Action Plan to Eliminate Pollution of the Arctic (ACAP).* The Arctic Council is a high-level intergovernmental forum that provides a mechanism to address the common concerns and challenges faced by the Arctic governments and peoples. Planned activities include identification and quantification of major point sources, with the aim of implementing concrete emission reduction pilot projects.
- *The Nordic Environmental Action Programme 2001-2004.* This programme establishes environmental priorities within the framework of Nordic cooperation in the fields of nature and the environment. It follows up on commitments in a Nordic sustainable development strategy, which has as one of its objectives the discontinuation within 25 years of discharges of chemicals posing a threat to health and the environment.
- *International action relating to artisanal gold mining.* A number of international bodies have worked on this issue, including the International Labour Organisation, the World Bank, and the United Nations Industrial Development Organisation.
- *UNEP Mercury Programme.* As widely referred to in this paper considerable work has been undertaken under the auspices of UNEP Chemicals in the context of the Global Mercury Assessment.

The brief overview reported above, shows that a considerable range of measures have been implemented at the national and regional levels to deal with

mercury and mercury compounds. Through such measures, a number of countries have achieved substantial reductions in emissions and releases of mercury from products and industrial processes. In addition, a number of coordinated regional approaches, both binding and non-binding have supported national measures and contributed to additional reductions beyond national borders.

Despite these successful national and regional initiatives (see UNEP, 2003 for details), some countries consider that they might not be sufficient to ensure adequate protection of human health and the environment from the adverse effects of mercury, and are calling for the consideration of coordinated initiatives at the international level. If it is found that there are global problems related to mercury that should be addressed, it might be essential to the effectiveness of any reduction measures for the substantive commitments to be discussed and agreed at the international level. Any specific regional or national considerations may be addressed taking into account common but differentiated responsibilities within the commitments agreed to.

## REFERENCES

- Agency for Toxic Substances and Disease Registry (US). Toxicological profile for mercury. Atlanta: Centers for Disease Control and Prevention. (<http://www.atsdr.cdc.gov/toxprofiles/tp46.html>)
- Amyot, M., Gill, G.A., Morel, F.M.M. Production and loss of dissolved gaseous mercury in coastal sea water. *Env. Sci. Technol.*, 31, 3606 – 3611, 1997.
- Barr, J.F. Population dynamics of the common loon (*Garvia immer*) associated with mercury-contaminated waters in north-wester Ontario. Occasional Paper 56. Canadian Wildlife Service, Ottawa, Ontario. Canada.
- Berg, T., Sekkesæter, S., Steinnes, E., Valdal, A-K., Wibetoe, G. Arctic springtime depletion of mercury in the European Arctic as observed at Svalbard. *Sci. Tot. Env.*, 304, 43-51, 2003.
- Drevnick, P.E., Sanheinrich M.R. Effects of dietary methylmercury on reproductive endocrinology of fathead minnows. *Env. Sci Technol.*; 37, 4390-96, 2003.
- Ebinghaus, R., Kock, H.H, Temme, C., Einax, J.W., Lowe, A.G., Richter, A., Burrows, J.P., Schroeder, W.H. Antarctic springtime depletion of atmospheric mercury. *Env. Sci. Technol.*, 36, 1238-1244, 2002.
- European Commission (EC) Consultation Document on Development of an EU Mercury Strategy, EC-DG Environment (ENV.G., ENV.G.2), draft released on 15 March 2004.
- Fimreite, N. Mercury contamination of aquatic birds in northwestern Ontario. *J. Wildlife Management*, 38, 120-131, 1974.
- Food and Agriculture Organization of the United Nations. World Health Organization. Joint FAO/WHO Expert Committee on Food Additives. Summary and Conclusions of the Sixth-First meeting. 10-19 June 2003. <<ftp://ftp.fao.org/es/esn/jecfa/jecfa/jecfa61sc.pdf>>
- Friedmann, A.S., Watzin, M.C., Brinck-Johnsen, T., Leiter, J.C. Low levels of dietary methylmercury inhibit growth and gonadal development in juvenile walleye (*Stizostedion vitreum*). *Aquatic Toxicology*, 35, 265-278, 1996.
- Guallar, E., Sanz-Gallardo, M.I., van't Veer, P., Bode, P., Aro, A., Gomez-Aracena, J., Kark, J.D., Riemersma, R.A., Matin-Moreno, J.M., Kok, F.J. Heavy Metals and Myocardial Infarction Study Group. Mercury fish soils, and the risk of myocardial infarction. *New England J. Medicine*, 347, 1747-54, 2002.
- Hammerschmidt, C.R., Sandheinrich, M.B., Wiener J.G., Rada R.G. Effects of dietary methylmercury on reproduction of fathead minnows. *Env. Sci Technol.* 36, 877-83, 2002.
- Harada Y. Congenital Minamata Disease. In: Tsubaki T., Irukayama K. Editors. Minamata Disease. Elsevier, Amsterdam, 209-39, 1977.
- Health Protection Branch, Bureau of Chemical Safety (Canada). Review of the Tolerable Daily Intake for Methylmercury. Ottawa: Health Canada: 1998 Apr 27.
- Hedgecock, I., Pirrone, N., Sprovieri, F., Pesenti, E. Reactive Gaseous Mercury in the Marine Boundary Layer: Modeling and Experimental Evidence of its Formation in the Mediterranean. *Atmos. Environ.*, 37, S1, 41-50, 2003.
- Hedgecock, I.M., Pirrone, N. Chasing Quicksilver: Modeling the Atmospheric Lifetime of  $Hg^0_{(g)}$  in the Marine Boundary Layer at Various Latitudes. *Env. Sci. Technol.*, 38, 69-76. 2004.
- Henny C.J., Hill, E.F., Hoffman, D.J., Spalding, M.G., Grove, R.A. Nineteenth century mercury: hazard to wading birds and cormorants of the Carson River, Nevada. *Ecotoxicology*, 11, 213-31, 2002.
- Hintelmann, H.; Falter, R.; Ilgen, G., Evans, R.D. Determination of artifactual formation of

- monomethylmercury in environmental samples using stable Hg(II) isotopes with ICP/MS detection: calculation of contents applying species specific isotope addition. *Fresenius J. Anal. Chem.*, 358, 363-370, 1997.
- Horvat, M., Kotnik, J., Fajon, V., Logar, M., Zvonaric, T., Pirrone, N. Speciation of Mercury in Waters of the Mediterranean Sea. In: *Mat. Geoenv.*, Hines, M., Horvat, M., Faganeli, J. (Editors). Proceedings of the *International Workshop on Mercury in the Northern Adriatic Sea*, May 13-15, 2001, Portoroz, Slovenia, Vol. 48, 241-252, 2001.
- Horvat, M., Kotnik, J., Fajon, V., Logar, M., Zvonaric, T., Pirrone, N. Speciation of Mercury in Surface and Deep Seawater in the Mediterranean Sea. *Atmos. Environ.*, 37, S1, 93-108, 2003.
- IARC Evolution of Carcinogenic Risk to Humans. Vol. 58. Mercury and Mercury Compounds. Lyon, France, 1994.
- IOM (Institute of Medicine). National Academy of Sciences. Dietary fats, total fats, and fatty acids. In: dietary Reference Intakes for Energy, Carbohydrates, Fiber, Fatty Acids, Cholesterol, Protein, and Amino Acids. Part 1. Summary and Chapters 1 through 9. Food and Nutrition Board. Panel on Macronutrients. National Academy Press. Washington, D.C. pp. 8-1-9-97 (prepublication copy; unedited proofs) (Chapter 8), 2002.
- Keeler, G.J., Glinsorn, G., Pirrone, N. Particulate Mercury in the Atmosphere: Its Significance, Transport, Transformation and Sources. *Water, Air Soil Pollut.*, 80, 159-168, 1995.
- Kommission "Human-Biomonitoring" des Umweltbundesamtes. Stoffmonographie Quecksilber-Referenz-und-Human-Biomonitoring-Werte (HBM). Berlin. Kommission "Human-Biomonitoring" des Umweltbundesamtes, 1999.
- Landis, M.S., Stevens, R.K., Shaedlich, F., Prestbo, D.E.M. Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air. *Env. Sci. Technol.*, 36, 3000-3009, 2002.
- Lee, Y.H., Wängberg, I., Munthe, J. Sampling and analysis of gas-phase methylmercury in ambient air. *Sci. Tot. Env.* 304,107-113, 2003.
- Lindberg, S.E., Brooks, S., Lin, C.J., Scott, K.J., Landis, M.S., Stevens, R. K., Goodsite, M., Richter, A. Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Env. Sci. Technol.*, 36, 1245-1256, 2002b.
- Lu, J. Y., Schroeder, W. H., Barrie, L. A., Steffen, A., Welch, H. E., Martin, K., Lockhart, L., Hunt, R. V., Boila, G., Richter, A., Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. *Geophys. Res. Lett.* 28, 3219-3222, 2001.
- Mahaffey, K.R. Fish and shellfish as dietary sources of methylmercury and the  $\omega$ -3 fatty acids, eicosahexaenoic acid and docosahexaenoic acid: risks and benefits. *Environ. Res.* 95, 414-428, 2004.
- Mason, R.P., Lawson, N.M., Sheu, G.R. Mercury in the Atlantic Ocean: factors controlling air-sea exchange of mercury and its distribution in the upper waters. *Deep-Sea Research II*, 48, 2829-2853, 2001.
- Mason, R.P.; Sheu, G.-R. *Global Biogeochem. Cycles*, 16, 1093, doi:10.10229/2001GB001440, 2002.
- Munthe, J., Wangberg, I., Pirrone, N., Iverfeld, A., Ferrara, R., Ebinghaus, R., Feng, R., Gerdelt, K., Keeler, G.J., Lanzillotta, E., Lindberg, S.E., Lu, J., Mamane, Y., Prestbo, E., Schmolke, S., Schroder, W.H., Sommar, J., Sprovieri, F., Stevens, R.K., Stratton, W., Tuncel, G., Urba, A. Intercomparison of Methods for Sampling and Analysis of Atmospheric Mercury Species. *Atmos. Environ.*, 35, 3007-3017, 2001.
- Piomelli S, Seaman, C, Zullow, D, Curran, A, Davidow, B. Threshold for lead damage to

- heme synthesis in urban children. *Proc Natl Acad Sci USA*. 79, 3335-39, 1982.
- Pirrone, N., Keeler, G.J., Nriagu, J.O. Regional Differences in Worldwide Emissions of Mercury to the Atmosphere. *Atmos. Env.*, 30, 2981-2987, 1996.
- Pirrone, N., Hedgecock, I., Forlano, L. The Role of the Ambient Aerosol in the Atmospheric Processing of Semi-Volatile Contaminants: A Parameterised Numerical Model (GASPAR). *J. Geophys. Res.*, 105, D8, 9773-9790, 2000.
- Pirrone, N., Munthe, J., Barregård, L., Ehrlich, H.C., Petersen, G., Fernandez, R., Hansen, J.C., Grandjean, P., Horvat, M., Steinnes, E., Ahrens, R., Pacyna, J.M., Borowiak, A., Boffetta, P., Wichmann-Fiebig, M. EU Ambient Air Pollution by Mercury (Hg) - Position Paper. Office for Official Publications of the European Communities, 2001.
- Pirrone, N., Costa, P., Pacyna, J.M., Ferrara, R. Atmospheric Mercury Emissions from Anthropogenic and Natural Sources in the Mediterranean Region. *Atmos. Environ.*, 35, 2997-3006, 2001a.
- Pirrone, N., Pacyna, J.M., Barth, H. Atmospheric Mercury Research in Europe. Special Issue of Atmospheric Environment, volume 35 (17), Elsevier Science, Amsterdam, Netherlands, 2001b.
- Pirrone, N., Ferrara, R., Hedgecock, I.M., Kallos, G., Mamane, Y., Munthe, J., Pacyna, J.M., Pytharoulis, I., Sprovieri, F., Voudouri, A., Wangberg, I. Dynamic Processes of Atmospheric Mercury Over the Mediterranean Region. *Atmos. Environ.*, 37, S1, 21-40, 2003a.
- Pirrone, N., Pacyna, J.M., Munthe, J., Barth, H. Dynamic Processes of Mercury and Other Atmospheric Contaminants in the Marine Boundary Layer of European Seas. Special Issue of Atmospheric Environment, volume 37 (S1), Elsevier Science, Amsterdam, Netherlands, 2003b.
- Reference Dose/Reference Concentration (RfD/RfC) Technical Panel. Risk Assessment Forum. A Review of the Reference Dose and Reference Concentration Processes. EPA/630/P-02/002F. December 2002. Final Report. <http://cfpub2.epa.gov/ncea/raf/>
- Rice D, Barone, S. Jr. Critical periods of vulnerability for the developing nervous system: evidence from humans and animal models. *Environ. Health Perspect*, 108 (Suppl 3), 511-33, 2000.
- Salonen, J.T., Seppanen, K., Nyyssonen, K., Korpela, H., Kauhanen, J., Kantol, M., Tuomilehto, J., Esterbauer H., Tatzber F., Salonen, R. Intake of mercury from fish, lipid peroxidation, and the risk of myocardial infarction and coronary, cardiovascular, and any death in eastern Finnish men. *Circulation*, 91, 645-55, 1995.
- Schroeder, W. H., Anlauf, K.G., Barrie, L.A., Lu, J.Y., Steffen, A. Arctic springtime depletion of mercury. *Nature* 394, 331-332, 1998.
- Skov, H. Personal communication, NERI, Denmark, 2002.
- Sprovieri, F., Pirrone, N. A Preliminary Assessment of Mercury Levels in the Antarctic and Arctic Troposphere. *J. Aerosol. Sci.*, 31, 757-758, 2000.
- Sprovieri, F., Pirrone, N., Hedgecock, I. M., Landis, M., Stevens, B, K. Intensive atmospheric mercury measurements at Terra Nova Bay in Antarctica during November and December 2000. *J. Geophys. Res.* 107, D23, 4722-4729, 2002.
- Sprovieri, F., Pirrone, N., Gardfeldt, K., Sommar, J. Atmospheric Mercury Speciation in the Marine Boundary Layer along 6000 km Cruise path over the Mediterranean Sea. *Atmos. Environ.*, 37/S1, 63-72, 2003.
- Sprovieri, F., Pirrone, N., Landis, M., Stevens, B, K. Mercury depletion events in the Arctic during the Intensive Spring 2003 campaign. *Environ. Sci. Technol.* (submitted), 2005.
- Steinnes, E., Andersson, Jakobsen. E.M. Atmospheric deposition of mercury in Norway. In Allan and Nriagu (eds.) Proceedings of the International Conference of Heavy Metals in the Environment, Toronto, September 1993, 70-73, 1993.
- UNEP Global Mercury Assessment (GMS) report. United Nations Environment Programme,