Toward the next generation of air quality monitoring: Mercury

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HIGHLIGHTS

- Atmospheric Hg monitoring is now occurring on a global scale for the first time.
- Mercury research priorities are identified and described.
- Modelling advances give insight into the deposition and biota concentration links.
- The current level of monitoring is inadequate for regulatory purposes.
- Knowledge of fundamental atmospheric Hg chemistry processes needs to be improved.

ARTICLE INFO

ABSTRACT

Mercury is a global pollutant that is ubiquitous in the environment. Enrichment of mercury in the biosphere as the result of human activities and subsequent production of methylmercury (MeHg) has resulted in elevated concentrations in fish, wildlife and marine mammals globally.

Elemental mercury (Hg^0) is the most common form of mercury in the atmosphere, and the form that is most readily transported long distances from its emission source. Most mercury deposition from the atmosphere is in the highly soluble, oxidised inorganic form Hg^{II}. Thus, understanding atmospheric transport and oxidant distribution is essential for understanding mercury inputs to ecosystems. Methylmercury (MeHg) is the most toxic form of mercury that accumulates in aquatic food web and can cause a variety of negative health effects such as long-term IQ deficits and cardiovascular impairment in exposed individuals. Humans are predominately exposed to MeHg by consuming fish.

Hg^0 emitted from anthropogenic sources has a long (6 months–1 year) atmospheric residence time allowing it to be transported long distances in the atmosphere. It is eventually oxidised to the highly soluble Hg^{II} (likely by atomic Br and/or OH/O_3) and rapidly deposited with precipitation. Some of the mercury deposited to terrestrial and marine ecosystems is converted to MeHg, which is the only form that bioaccumulates in aquatic food webs. Recent studies suggest that there is a first-order relationship between the supply of inorganic mercury to ecosystems and production of MeHg, thus implying that declines in deposition will translate directly into reduced concentrations in biota and human exposures. However, one of the major uncertainties in this cycle is the time scale required for these changes to take place and this is known to vary from years to centuries across different environmental compartments depending on their physical and biogeochemical attributes. Thus, a key challenge in the case of mercury pollution is understanding the link between the magnitude of mercury emissions and the concentrations found in the fish that we consume.

For air quality monitoring, priorities include expanding the existing data collection network and widening the scope of atmospheric mercury measurements (elemental, oxidised, and particulate species as well as mercury in precipitation). Presently, the only accurate indicators of mercury impacts on human and biological health are methylmercury concentrations in biota. However, recent advances in analytical techniques (stable mercury isotopes) and integrated modelling tools are allowing greater understanding

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of the relationship between atmospheric deposition, concentrations in water, methylation and uptake by biota. This article recommends an expansion of the current atmospheric monitoring network and the establishment of new coordinated measurements of total mercury and methylmercury concentrations in seawater and concurrent concentrations and trends in marine fish.

1. Background and objective

The toxicity of mercury and its compounds for humans such as ataxia, constriction of vision, impaired hearing and death was first described in 1865 (Grandjean et al., 2010). Mercury mining and use in products continues to the present day. Consumer products still containing mercury include button cell batteries, fluorescent bulbs, and some cosmetics (McKelvey et al., 2011; Streets et al., 2011). However, most mercury emitted to the atmosphere since the beginning of the Industrial Revolution has been as a result of coal combustion, and to a lesser extent metal smelting and more recently cement production and waste disposal through incinerator plants (Nriagu and Pacyna, 1988; Pirrone et al., 1996, 2010).

Most non-occupational human exposure to mercury is from fish and marine seafood containing MeHg (e.g. Sunderland, 2007; Mahaffey et al., 2004, 2009). MeHg is a potent neurotoxin that causes a variety of reproductive and developmental disorders at high concentrations (Clarkson and Magos, 2006). New research has also suggested a link between MeHg exposure and cardiovascular health in adults, although conflicting results have been reported across epidemiological studies (Mozaffarian et al., 2011; Roman et al., 2011; Valera et al., 2011; Wennberg et al., 2012). Unlike Hg^{II}, MeHg is absorbed efficiently from food (>90%) and readily crosses the blood—brain and placental barriers. Gaseous Hg^0 is also efficiently absorbed when inhaled, although concentrations in the atmosphere, even next to point sources such as coal-fired utilities, are far below levels of toxicological concern (Clarkson and Magos, 2006). Occupational exposures to Hg^0 (which can also cross the blood—brain barrier) associated with artisanal gold mining and due to vaporisation of quicksilver used in products and other uses can cause severe health effects such as kidney failure and central nervous system impacts (Mergler et al., 2007).

Atmospheric mercury exists in three forms: Gaseous elemental mercury (GEM), gaseous oxidised mercury (Hg^{II}) compounds (GOM), and mercury associated with particulate matter (Hg^P). Oxidised mercury compounds are emitted from anthropogenic sources and readily transferred to aquatic and terrestrial receptors by dry deposition processes and wet scavenging by precipitation. Oxidised mercury compounds are much less volatile, and most are more water soluble than Hg^0. The precise chemical nature of these compounds is still not known and thus the term GOM is used to describe all forms of mercury sampled from the atmosphere using a KCl-coated denuder and analysed by CVAAFS (Landis et al., 2002). There is some debate however over the efficiency of the commonly used sampling techniques, and indeed what they sample, although alternative techniques are being developed (Lyman et al., 2010b; Ambrose et al., 2013; Gustin et al., 2013). Mercury associated with particulate matter can be emitted from anthropogenic sources, active volcanic eruptions and evaporation of cloud/aerosol droplets that contained mercury compounds. These particles are generally part of the fine aerosol fraction and their transport and deposition characteristics are defined by particle properties. Mercury in this form is thought to be mostly insoluble.

All three forms are released by anthropogenic sources, primarily combustion processes, as well as by a variety of natural sources and processes. Natural sources include crustal degassing, volcanoes, a component of the reemitted mercury from soils and aquatic surfaces, weathering processes of the Earth's crust and some forest fires (Pirrone et al., 2010). On a global scale, the dominant component of the mercury released from terrestrial and oceanic systems is previously deposited anthropogenic mercury rather then geogenic sources (Streets et al., 2011). Contributions from natural sources and processes vary geographically and over time depending on a number of factors including meteorological conditions, the presence of volcanic or geothermal activities, the presence of Hg bearing minerals such as cinnabar, the magnitude of exchange processes between waters and the atmosphere, the re-emission of previously deposited Hg from top soils and plants, and also the occurrence of forest fires (Mason, 2009; Friedli et al., 2009; Pirrone et al., 2010).

In addition to anthropogenic mercury emissions (≈ 2000 Mg yr^{-1}), reemitted mercury from soils and aquatic ecosystems presently contribute approximately 2/3 of global emissions to the atmosphere (Corbitt et al., 2011). Pirrone et al. (2010) estimated that mercury evasion from terrestrial surfaces is about 2430 Mg yr^{-1} and that from surface waters (oceans and lakes) is about 2780 Mg yr^{-1}. The latest simulations based on data from GEOS-Chem global biogeochemical mercury model show similar estimates with emissions from land at 2100 Mg yr^{-1} and 3100 Mg yr^{-1} from the ocean (Streets et al., 2011). On an areal basis, re-emissions from the land (surface 1.46×10^8 km^2) are higher than those from the ocean (surface 3.49×10^8 km^2), and the majority of anthropogenic mercury appears to accumulate in the subsurface and deep ocean. Biomass burning estimates range between 200 and 675 Mg yr^{-1} (Friedli et al., 2009; Holmes et al., 2010), whereas desert and non-vegetated zones emit 546 Mg yr^{-1}, followed by tundra and grassland with 448 Mg yr^{-1}, forest with 342 Mg yr^{-1} and contaminated sites with 200 Mg yr^{-1} (Pirrone et al., 2010).

Mercury in ocean waters is present as elemental mercury (Hg^0), monomethyl mercury (MeHg), dimethyl mercury (Me$_2$Hg), aqueous divalent mercury (Hg^{II}), colloidal mercury, and particulate mercury (Mason et al., 2012). Globally, total Hg concentrations in the ocean mixed layer are generally <1 pM (1 pM = 10^{-12} mol l^{-1}) (Soerensen et al., 2010) and slightly greater than 1 pM in the upper 1000 m of the water column (Mason et al., 2012). In the early 1980s, values as high as 9.6 pM were measured and may provide evidence for a historical decline in some ocean basins (Gill and Fitzgerald, 1987; Soerensen et al., 2012).

Mercury air—sea exchange is primarily driven by

(i) the concentration gradient of Hg^0 between top-water microlayer and the air above,
(ii) solar irradiation, which is responsible for photo-mediated redox processes,
(iii) wind speed and temperature at the air—water interface,
(iv) and the supply of reducible Hg^{II} available for reduction to Hg^0 and the intensity of other processes that affect this supply such as scavenging by particulate organic matter

(Pirrone et al., 2003; Soerensen et al., 2010). Evasion of Hg^0 competes with methylation for the available substrate of mercury in seawater and is thus a critical loss process affecting biological MeHg concentrations (Mason et al., 2012).

Measurements of atmospheric and aquatic concentrations of mercury have now been performed on a sampling campaign basis in a number of parts of the world, and in some areas repeatedly (Sprovieri et al., 2009; Soerensen et al., 2012). Exceptions include the Southern Hemisphere and most oceans, where data are still patchy. Long-standing monitoring networks only exist in Europe and the North American continent, although a recent initiative from the EU is setting up a global monitoring network for mercury as part of the Global Mercury Observation System (GMOS) project (www.gmos.eu).

Guidelines for exposure to mercury include: 1 $\mu g\ L^{-1}$ for Hg in water, 1 $\mu g\ m^{-3}$ for air (annual average) and 0.2 $\mu g\ m^{-3}$ for long-term inhalation of exposure to elemental mercury vapour (FAO/WHO, 2007). The U.S. EPA reference dose for daily intake of MeHg that is without an appreciable increase in risk of adverse effects over a lifetime is 0.1 $\mu g\ kg^{-1}$ body weight per day. Acceptable exposures to MeHg are continually being refined with the discovery of effects of MeHg on the central nervous system at lower levels (Grandjean et al., 2010). Other governmental agencies have developed MeHg intake levels to protect public health that range from 0.10 to 0.47 $\mu g\ kg^{-1}$ body weight per day, UNEP (see Table 4.1 of 2002). Last year the EFSA Panel on Contaminants in the Food Chain (CONTAM) established a Tolerable Weekly Intake (TWI) of 1.3 $\mu g\ kg^{-1}$ body weight (EFSA, 2012) less than the TWI of 1.6 $\mu g\ kg^{-1}$ body weight recommended by the Joint FAO/WHO Expert Committee on Food Additives (FAO/WHO, 2007). Differences in safe recommended intakes relate to methods used to estimate exposure considered to be without adverse effects (extrapolation of measured dose response relationships for IQ and MeHg exposure) rather than exposures producing effects (Mahaffey et al., 2011).

In Europe, environmental target levels that are safe for both humans and the environment have been established by a legislative framework (i.e. Environmental Quality Standards Directive, 2008/105/EC). In particular, either Environmental Quality Standards (EQSs), which represent thresholds that should not be exceeded, or Environmental Assessment Criteria (EACs), which are long-term objectives close to Background Concentrations, have been adopted for different marine sediment, water and biota. Regulatory levels have been also established in community legislation for protection of public health. Following guideline levels formerly established within the Codex Alimentarius (FAO/WHO, 1995), maximum levels of mercury in certain foods have been established by Commission Regulation (EC) No 1881/2006. Maximum levels for mercury in fish range from 0.2 ppm to 1.0 ppm depending on the agency. These levels are generally derived from the above safe intake levels for humans and depend on the assumed magnitude of fish consumption in a given population that will maintain intakes below the safety threshold. State governments in the U.S. have issued advisories for populations that are assumed to eat large quantities of fish (e.g. Minnesota), while international standards set by different federal governments tend to be between 0.3 ppm (U.S.) and 1.0 ppm. Contaminants in fish and other seafood influence both the health of the consumer and the sustainable use of marine resources (Oken et al., 2012).

This article makes recommendations for improved atmospheric Hg monitoring and modelling strategies to better link emission sources to human health impacts. Since most human exposure to Hg results from consuming MeHg in seafood, we discuss possibilities for establishing a coordinated atmospheric–ocean Hg measurement strategy. Such a strategy would allow us to better assess the temporal response of marine ecosystems to reductions of mercury emissions to the atmosphere from anthropogenic sources, and future changes in the global mercury cycle that may occur as the result of variability in reemissions from soils and the ocean and driven by climate.

2. Overview of existing monitoring systems and indicators

2.1. Ground-based monitoring networks

Systematic long-term direct measurements of mercury in the atmosphere provide valuable information about the impact of emission controls on the global budget of atmospheric mercury and offer insight into source-receptor transboundary transport of mercury. Additional mercury species measurements such as oxidized and particle-bound mercury compounds can help to improve the understanding of local atmospheric chemistry and short-term oxidation processes regarding the removal of mercury from the atmosphere. Harmonized Standard Operating Procedures (SOPs) and QA/QC protocols for monitoring ambient concentrations of all mercury species are needed in order to assure a full comparability of site specific observational datasets with that obtained inside and outside existing monitoring networks. SOPs and QA/QC protocols should be in accordance with measurement practice adopted in well established monitoring networks and based on the most recent literature. State-of-the-art SOPs and QA/QC protocols have been developed in the frameworks of several programs including EMEP, CEN-TC 264, NADP, AMNet, CAMNet, GMOS. A large number of activities have been carried out to characterise the levels of mercury (Hg) species in ambient air and precipitation, in order to understand how they vary over time and how they depend on meteorological conditions. Monitoring of ambient mercury is focused on the three primary forms of mercury in the atmosphere: GEM, GOM, Hg^P. The measurement of atmospheric GEM is now routine, and can be easily implemented due to its relatively high concentration and chemical inertness. Uncertainties, detection limits and ruggedness are well established (Brown et al., 2010; Steffen et al., 2012; Gay et al., 2013). In contrast, the measurement of the atmospheric mercury species GOM and Hg^P are more challenging and uncertain due to their extremely low concentrations, more complex chemical reactivity and analytical challenges related to coated and non-coated glassware, heated filters, vials and tubings. However, GOM and PBM measurements are critical to help define and model the fate and transport of atmospheric mercury. The atmosphere provides the main environmental pathway for redistribution of Hg around the globe, and based on the existing data, there is a scientific consensus about the current global background concentration of airborne Hg which is considered to be in the range of 1.5–1.7 ng m^{-3} in the Northern Hemisphere and 1.1–1.3 ng m^{-3} in the Southern Hemisphere (Lindberg et al., 2007; Sprovieri et al., 2010b; Slemr et al., 2011). Due to its *global nature*, it is critically important to quantify the transfer of Hg from the air to the Earth's surface via wet and dry deposition and analyse the global long-term trends of mercury in the atmosphere and in precipitation. To date a lack of legislation at national as well as international levels has resulted in limited long-term measurements, the exceptions being some sites in Europe and the Arctic (Ebinghaus et al., 2011; Cole and Steffen, 2010; Cole et al., 2013). Measurement data is particularly limited in the Southern Hemisphere. There is the need to coordinate activities at the global level to ensure that future research provides the maximum benefits in terms of assessing global and regional trends in Hg concentration. The Group on Earth Observations (GEO, http://www.earthobservations.org/about_geo.shtml) has established the Task HE-02-C1 "Global Mercury Observation System" for the work plan 2012–2015, which is a continuation of the activity initiated in the GEO Work Plan (2009–2012). This task supports the achievement of the goals of GEOSS http://www.earthobservations.org/geoss.shtml and other on-going international programs such as the UNEP Mercury Program and international conventions dealing with large-scale transboundary transport of mercury such as the

United Nations Economic Council for Europe Convention on Long-range Transboundary Air Pollution (UNECE-CLRTAP, http://www.unece.org/env/lrtap/welcome.html).

Table 1 provides a summary of the existing networks for measuring mercury in ambient air and precipitation. A number of regional monitoring networks have been in operation for many years in North America and Northern Europe. Measurements have also been collected at a few sites in Asia and in the Arctic region. However, in many parts of the world, especially the Southern Hemisphere, such extensive measurement networks do not exist. Given the mostly ad hoc nature and spatially heterogeneous distribution of the efforts to monitor and measure atmospheric Hg species, it has become clear that a coordinated global monitoring network is needed to provide information for a global assessment, and for global and regional model evaluation and extrapolation (Pirrone et al., 2008).

The European Monitoring and Evaluation Program (EMEP) under the UNECE-LRTAP convention was the first international measurement network for mercury, with Swedish measurements dating from 1980 and other European sites, located mostly in the northern, western and central parts of Europe starting in 1990 (Tørseth et al., 2012). Several of the EMEP sites are also part of other regional networks such as that related to the marine Conventions OSPARCOM and HELCOM, and the Arctic Programme AMAP.

Long-term monitoring of atmospheric Hg with high time resolution started at Alert, Canada in 1995, which was the first milestone in the development and set up of the Canadian Atmospheric Mercury Network (CAMNet) established in 1996, which currently includes, 11 TGM monitoring sites. More recently, some sites within CAMNet have been measuring atmospheric Hg species in addition to TGM.

The Arctic Monitoring and Assessment Programme (AMAP) represents a coordinated air monitoring program (AMAP, 2011) established in 1991 and covering the circum-Arctic areas of North America and Eurasia (Cole et al., 2013; Goodsite et al., 2013). A regional network for atmospheric mercury measurements has not yet been established in Antarctica, and as a result there is less information on spatial and temporal trends in atmospheric mercury is available. However the Norwegian site at Troll has been measuring atmospheric Hg concentrations since 2007 (Pfaffhuber et al., 2012). Since 2012 the GAW French-Italian monitoring Station, Dome Concordia, on the Antarctic Plateau and for the GAW coastal Antarctic French Research Station, Dumont d'Urville, are performing atmospheric measurements as part of GMOS.

In Asia there are no formally coordinated regional networks for monitoring atmospheric Hg species and deposition. However, Cape Hedo in Japan has been running continuously since 2007, and a number of sites in China have been used repeatedly for measurement campaigns, some of which lasted for more than 12 months. A review of Hg measurements in Asia was recently published by Fu et al. (2012a). Measurements are also regularly performed in Korea and at the Lulin Observatory in Taiwan (Seo et al., 2012; Ahn

Table 1
Worldwide monitoring networks for Hg measurements in ambient air and wet deposition.

Location	Program	Region	Ambient Hg duration	Ambient Hg measurements	Wet Hg duration	Wet Hg measurements	References
Europe	EMEP	Continental	1980-	Automated and manual TGM	From 1987-	Weekly to monthly; bulk and wet-only collection	Wängberg et al. (2007) Tørseth et al. (2012) Aas and Breivik (2012)
Europe	OSPARCOM CAMP	Continental/Marine	1992	Automated and manual TGM	From 1990	Weekly to monthly; bulk and wet-only collection	
Europe	HELCOM	Continental/marine	1998	Automated and manual TGM	From 1998	Weekly to monthly; bulk and wet-only collection	Bartnicki et al. (2011)
USA/Canada	NADP-AMNet	National	2009-	Automated speciation			
Canada	CAMNet	National	1994—2010	Automated TGM			Blanchard et al. (2002) Kellerhals et al. (2003) Temme et al. (2007)
Canada	CAPMoN	National	2010-	Automated TGM	From 1998	Weekly; wet-only collection	Prestbo and Gay (2009) Risch et al. (2012b)
USA	UMAQL	Midwest	1999—2009	Manual TGM and Hg[p]; automated speciation			Landis et al. (2002); Lynam and Keeler (2005) Lynam and Keeler (2006); Liu et al. (2007) Liu et al. (2010)
USA	NADP-MDN	National	From 1999	Weekly; wet-only collection			Butler et al. (2008) Prestbo and Gay (2009) Risch et al. (2012b)
USA	UMAQL	Midwest and Northeast	From 1992	Daily-event; wet-only collection			Burke et al. (1995); Landis et al. (2002) Keeler and Dvonch (2005); Keeler et al. (2006) White et al. (2009); Gratz et al. (2009) Gratz and Keeler (2011)
USA	UMAQL	Florida	1995 2008—2010	Daily-event; wet-only collection			Dvonch et al. (1998, 1999) Dvonch et al. (2012)
Polar Regions	AMAP	Arctic Circle	1992-	Automated and manual TGM[a]	1996-	Weekly to monthly; bulk and wet-only collection	AMAP (2011) Berg and Aas (2007)
Global	GMOS	Global	2011-	Automated TGM/GEM and speciation	From 2011	Weekly; wet-only and bulk collection	Sprovieri et al. (2012)
Asia[b]		Japan China[c]	2007- Intermittent	Automated TGM/GEM Automated TGM/GEM			Suzuki et al. (2009) Fu et al. (2012a,b)

[a] The measurement site at Alert also measures GOM.
[b] Measurements are not made within formal Programs, but are included for completeness.
[c] The measurements are not continuous but a number of sites have been used repeatedly.

et al., 2011; Sheu et al., 2010) Since 2012 atmospheric Hg measurements are being continuously performed at the Ev-K2-CNR Pyramid (5050 m asl) near the Everest Base Camp in the Sagarmatha National Park, Nepal, and three sites in China on Mount Waliguan, Mount Changbai, and Mount Ailao have also been running continuously since 2012 (almost real-time data from these sites can be seen at http://sdi.iia.cnr.it/geoint/publicpage/GMOS/gmos_monitor.zul. The mountain sites in China measure provide background data in the northwest, northeast, southwest of the country.

The GMOS project, funded by the European Commission, but with a global perspective began in November 2011. The GMOS network consists of 38 remote background monitoring sites at both high altitude and sea level locations. Some are existing sites, such as EMEP and AMAP sites, and also Cape Point in South Africa, which have been monitoring concentrations of atmospheric mercury for many years and can offer an important historical measurement record to the project/network. New sites have been established in India, Amsterdam Island, Antarctica, Suriname, Brazil and Argentina.

2.2. Mountain sites

Long distance transport of Hg^0 occurs mostly above the planetary boundary layer, and therefore measurements of atmospheric composition at high altitude sites, which are regularly in the free troposphere are of great use in pollution transport studies. Studies at Mount Bachelor in Oregon (Weiss-Penzias et al., 2007) and Storm Peak in Colorado (Obrist et al., 2008) have provided a fascinating insight into long distance transport to North America. Studies have also been performed for extended periods at Mt Leigong and Mt Waliguan in China (Fu et al., 2012a,b), and Mt Lulin in Taiwan (Sheu et al., 2010). As part of GMOS there is a high altitude measurement site on Dome Concordia in Antarctica, and at the EvK2CNR Pyramid International Laboratory at an altitude of just over 5400 m a.s.l. on K2 in Nepal.

These regional and global initiatives will allow policy makers and scientists in the near future to fulfil the international need highlighted over the last 20 years for monitoring temporal changes in Hg concentrations at a global scale. This information will allow us to assess deposition at remote locations and will provide high quality data for regional and global scale model evaluation. Ultimately, this will reduce model uncertainty and allow better understanding of the impacts of emissions reductions on atmospheric mercury deposition under different policy scenarios.

2.3. Aircraft campaigns

Aircraft campaigns give a snapshot of the spatial and extremely importantly the vertical distribution of mercury compounds in the atmosphere. There have been a few one-off airborne campaigns (Ebinghaus and Slemr, 2000; Banic et al., 2003; Friedli et al., 2003; Murphy et al., 2006), and some projects in which aircraft measurements were repeated during intensive measurement campaigns such as Intex-B (Swartzendruber et al., 2008; Talbot et al., 2007, 2008), and ACE-Asia (Pan et al., 2006, 2007; Friedli et al., 2004). It is only recently that techniques have been developed which have permitted the measurement of GOM compounds rather than TGM or solely GEM (or Hg associated with particles (Murphy et al., 2006). Lyman and Jaffe (2012) for the first time made speciated measurements of mercury in the region of the tropopause over the North Atlantic, their results indicate that mercury is short-lived in the stratosphere. Another approach to obtaining data from aircraft has been the CARIBIC (Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container) project (http://www.caribic-atmospheric.com/). An automated

analyser for total gaseous mercury has been included in the instrument container on board Lufthansa flights since 2005, and there are typically 4 intercontinental flights per month between Frankfurt and destinations in Asia, Africa and North and South America (Slemr et al., 2009). The results from CARIBIC indicate a longer lifetime for Hg than suggested by the results obtained by Lyman and Jaffe (2012), underlining the importance of undertaking more campaigns of this type.

2.4. Offshore measurements

Oceanic evasion of mercury is equivalent to anthropogenic emissions each year and driven by a combination of factors, as described above, including atmospheric mercury deposition to the surface ocean and the supply of mercury in subsurface ocean waters. Despite the importance of air—sea exchange on a global basis for the biogeochemical mercury cycle, there are limited cruise observations of Hg^0 concentrations in the marine boundary layer and even sparser measurements of speciated mercury, including MeHg, in seawater. These data limitations make it difficult to interpret long-term trends in atmospheric concentrations and the role of oceanic processes. Recently, simultaneous measurements of atmospheric at the air—water interface and dissolved Hg^0 in the top-water microlayer and in the water column have been performed at several ocean and sea locations in the world (Ferrara et al., 2000; Sprovieri et al., 2003; Gårdfeldt et al., 2003; Hedgecock et al., 2003; Andersson et al., 2007). Such measurements would be extremely useful in refining global estimates of air—sea exchange and factors controlling spatial and temporal variability in concentrations but need to be extended to cover a greater range of physical and chemical conditions. Subsurface seawater data are also needed to accurately model air—sea exchange on a global basis since entrainment of the mixed layer can enhance the supply of Hg^{II} for reduction and subsequent evasion (Soerensen et al., 2010, 2012). Such measurements are extremely difficult to collect and should be prioritised as part of other ongoing seawater sampling efforts (e.g. GEOTRACES, GMOS, MEDOCEANOR, CLIVAR, IPY) (Mason et al., 2012).

A recent study by Weiss-Penzias et al. (2012) has shown that fog water on the Californian coast has significant concentrations of MeHg, and that the fog water deposition could be the major source of MeHg to coastal land surfaces. The coastal fog forms as marine air masses move onshore, and the authors hypothesise that the high levels concentrations (and MeHg to total Hg ratio) are due to the seawater being enriched in dimethyl Hg as a result of upwelling. More investigation of the Hg species present in coastal waters, and their temporal variation with upwelling cycles, temperature, and season is required in order to understand the provenance of MeHg in fog water. One possible approach to aid the determination of the source of MeHg is stable isotope analysis. This technique is discussed further in section 4.

2.5. Models

Recent monitoring data on atmospheric mercury trends show a worldwide decline in concentrations that appears inconsistent with global emissions trends (Slemr et al., 2011). These and other findings reinforce the importance of coupling longer lived mercury reservoirs in terrestrial ecosystems and the ocean to model simulations of atmospheric concentrations and deposition (Soerensen et al., 2012). Air—sea exchange and land—air exchange of GEM exert a large influence on global emissions each year and can affect temporal trends in atmospheric concentrations by delayed re-release of previously deposited anthropogenic mercury to the atmosphere (Streets et al., 2011). Mechanistic data on how mercury dynamics in oceanic and terrestrial ecosystems change as a

function of environmental conditions are therefore needed to improve model representations of the full biogeochemical mercury cycle and time scales of terrestrial and oceanic responses to changes in anthropogenic emissions.

Chemical transport models that include atmospheric mercury consider the emission (natural, anthropogenic and legacy mercury), transport and transformation, and eventual deposition of mercury and its compounds. While there are still many uncertainties in the detailed mechanisms of processes influencing the fate of atmospheric mercury, most models are in broad agreement (Pirrone et al., 2010), and the ever increasing amount of observational data available continue to refine the parametrisations used to describe the more important of these processes. The redox chemistry of atmospheric mercury remains the subject of some debate, however consensus is growing that homogeneous reactions with atomic bromine and bromine containing radicals are the most important atmospheric oxidation processes even at mid-latitudes and not just in the Arctic (Hedgecock and Pirrone, 2004; Holmes et al., 2010; Sprovieri et al., 2010a; Obrist et al., 2011). The heterogeneous oxidation of mercury in the atmosphere is less well understood, as are the reactions that reduce oxidized mercury compounds, although it is generally agreed that reduction occurs predominantly in cloud water, two recent reviews by Subir et al. (2011, 2012) give a thorough overview of some of the uncertainties in atmospheric mercury chemistry.

Over the last four or five years ocean and atmosphere models have been coupled to provide a more comprehensive insight into the ocean—atmosphere cycle of mercury (Selin et al., 2007; Sunderland, 2007; Soerensen et al., 2012). This has been an important step forward due to the importance of the oceans as a receptor for mercury deposition, and their role in air—sea exchange of mercury. The importance of coupling ocean and atmospheric models is not limited to furthering the understanding of the exchange processes which occur, it is the mercury deposited to oceans which eventually makes its way into the food web, and deep ocean sediments are where mercury is sequestered in the long-term from actively cycling surface reservoirs.

3. Regional and global considerations

3.1. Emissions

Most anthropogenic mercury emissions occur in the northern hemisphere (Pacyna et al., 2010; Pirrone et al., 2010; Pirrone and Keating, 2010), and the lifetime of atmospheric mercury (Hedgecock and Pirrone, 2004; Corbitt et al., 2011) is such that this is reflected in the difference in the background concentration of mercury in the northern and southern hemispheres. North of the equator observed ambient Hg concentrations are around 1.7 ng m^{-3}, while in the southern hemisphere these values are around 1.2 ng m^{-3}. Most anthropogenic emissions are linked to large-scale industrial facilities, particularly coal fired electricity generation, cement production and metallurgical industries (Pirrone and Mason, 2009; Pirrone et al., 2010). Emissions control technology and coal types burned at these facilities often vary between nations so it is not always possible to use Emission Factors measured at one installation to another in a different area. One of the most important factors concerning mercury emissions is the speciation of mercury emitted (GEM, GOM and Hg^P), because the proportion of GOM and Hg^P dictates the extent of local deposition. The nature of a region's anthropogenic emissions is important because it will influence the proper choice of indicators, as discussed below. Natural emissions, emissions from biomass burning, and legacy emissions from previously deposited mercury are primarily as the Hg^0 form and can thus be distributed globally.

3.2. Long-range transport

The global nature of mercury pollution needs to be taken into account when considering a future monitoring network. Experience gained from measurements in the Arctic and Antarctica show that regions with close to zero anthropogenic emissions are nonetheless susceptible to mercury pollution (Pfaffhuber et al., 2012; AMAP, 2011; Dommergue et al., 2009; Sprovieri et al., 2002). Long-range transport to the Arctic has been studied not only in terms of mercury pollution but numerous other atmospheric pollutants as well, and it has been shown that the source regions impacting the Arctic ecosystem depend on a number of variables (e.g. Shindell et al., 2008; Law and Stohl, 2007). The importance of a source region changes with season and can also vary with large scale climatic phenomena such as the North Atlantic Oscillation (Eckhardt et al., 2003). In planning the sites for a monitoring network in a given region it will be necessary to take into consideration the potential routes of mercury transport into the region. In regions with large natural or anthropogenic emission fluxes the monitoring network should be planned so that regional outflow can be estimated with reasonable precision. Considering that the chemical transformation of GEM to more soluble oxidized forms that can readily transferred to aquatic and terrestrial receptors, it is important to establish monitoring sites at locations such as the MBL and at high altitudes where the oxidation processes of GEM is primarily driven by the presence of strong oxidants including halogens and OH radicals. Ad-hoc profile measurements on board aircraft that would allow measurements of mercury species in the upper troposphere—lower stratosphere (UTLS) would help to better constrain global and regional atmospheric models.

3.3. Indicators

Identifying appropriate indicators that can be used to quantify the risk posed to human health by mercury varies widely by region, as a consequence of the amount of seafood in peoples diet and their species selection preferences. Even within small areas it is possible to find a large variation as coastal communities traditionally rely more on fish as a source of protein than inland communities. For example, Mahaffey et al. (2009) showed that coastal residents in the U.S. consumed significantly more fish and as a result had higher blood mercury levels than their inland counterparts. Individuals also consume a combination of locally derived fish from nearby water bodies as well as globally harvested seafood sold in the commercial market. Commercial marine fish account for >90% of mercury exposure in the U.S. (Sunderland, 2007; Carrington et al., 2004), with the majority of the mercury coming from migratory, pelagic marine fish (mainly tuna). This means that human exposures reflect the global burden of mercury in addition to local sources and resulting contamination in regional water bodies. Additional information on the geographic origins of seafood consumed by different populations is therefore critical for establishing the link between changes in mercury emissions, atmospheric deposition and concentration in fish.

3.4. Measures to support policy making

On regional scales it is extremely important to understand the chemical characteristics of all the anthropogenic mercury emissions within the region. Reducing atmospheric mercury deposition to ecosystems hinges on both reducing mercury emissions globally and from nearby sources. The relative impact of local emissions reductions on deposition will depend on their relative magnitude compared to the global pool and speciation of mercury emissions

sources. It is therefore of paramount importance that emission sources are well characterised as in some regions the benefits of local emission reductions could be very significant even in the relatively short term. However the links between local/regional emissions and exposure are not direct, as mentioned above, because exposure will depend on dietary habits and the specific characteristics of the local fish market (i.e. import of sea food from more sensitive regions) which provides seafood consumed by a given population. The propensity for long-range transport of mercury means a population's exposure to mercury may derive from a number of geographical regions.

The general public is the main stakeholder of the environment, responsible for exploitation of its geological and living resources on one side, and for its management based on ecological economy concepts. In recent years the policy making process has paid greater attention to data gathering and analysis, and also to their quality. This has been to ensure that state of the art knowledge, regarding the fate of mercury in the global environment and its impact on human health, is taken into account in the preparation of specific requirements of resulting legislation and its future implementation. This is why the GMOS participates in the Global Earth Observation System of Systems (GEOSS) initiative through the GEO Task HE-02 "Tracking Pollutants". GEOSS is aimed to enhance the relevance of Earth observations to global issues, by connecting the producers of environmental data and decision-support tools with the end users of these products. The mercury task under GEOSS deals with the sharing of data from GMOS, allowing access to comparable and long-term data from a large number of ground-based and off-shore sites, helping understand temporal and spatial patterns of mercury transport, deposition to, and evasion from, terrestrial and aquatic ecosystems. The data produced through state of the art interoperable systems based on GEO data sharing principles, will support the evaluation of regional and global atmospheric mercury models for use in the analysis of different policy options for reducing mercury pollution impacts on human health and ecosystems. The data sets, evaluated models and interoperable system produced within this task will support the policy making process of the future Minamata Convention on Mercury. The task builds upon the contributions of, among others, the GMOS project, UNEP Fate and Transport Partnership Area that is part of the UNEP Mercury Programme, the Hemispheric Transport of Air Pollutants Task Force (TF HTAP) that is part of the UNECE-CLRTAP, and other national and international programs.

4. 'State of the art' technical aspects of monitoring, and research needs

4.1. Techniques

Current technology permits the measurement of the concentration of atmospheric elemental mercury with a time resolution of 5 min, oxidized mercury compounds with a time resolution of 2–4 h, and mercury concentration in precipitation on a rainfall event basis or better. The capacity to automatically monitor the extremely low concentrations of mercury and its compounds in the atmosphere with precision and at reasonable temporal scales exists. There has been some debate regarding the efficacy of the KCl denuder technique used to sample GOM compounds (Gustin et al., 2013), however alternatives are being developed and tested (Lyman et al., 2010b,a). The cost of current automated atmospheric Hg sampling and measuring instruments, as well as their technical requirements in terms of power, carrier gas supply and trained personnel, does mean however that their deployment on a large scale is problematic.

One outstanding problem is the determination of the nature and proportions of the chemical compounds which make up GOM. It is probably fair to say that techniques which could do this would revolutionise understanding of the atmospheric Hg cycle. The potential for improvement of atmospheric Hg modelling, given a knowledge of what GOM is, and how its composition changes in time and space, is enormous.

4.1.1. Passive sampling techniques

The use of automated systems for atmospheric mercury species measurements implies a large financial investment ('000s of dollars) as well as trained technical staff on location or relatively nearby, and continuous operating costs. Recently, however, there has been a research push towards the development of passive samplers for GEM and also for GOM. These samplers are simple to deploy, require no power supply or special gases and can be analysed at a central laboratory. They do not have the same time resolution as automated analysers and in fact GOM samplers would usually remain in the field for a week. However this does allow them to be placed in relatively remote areas. Testing and development of these devices is still going on, but it is possible to foresee a time when they can be used to provide high spatial monitoring coverage, the results of which would be extremely useful in deciding which locations in a region would provide the most useful data using an automated system (Lyman et al., 2010a; Brown et al., 2012; Peterson et al., 2012; Zhang et al., 2012). Passive techniques are working well for the monitoring of a number of Persistent Organic Pollutants (see companion paper by Hung et al. 2013). Another recent development which is also a 'passive' technique and which could make a great difference to atmospheric mercury monitoring are dry deposition collectors. Where precipitation is not very frequent dry deposition of mercury could account for the greater part of mercury deposited to ecosystems, however there have been very few attempts to measure it due to the practical difficulties involved. The use of surrogate surfaces to sample mercury deposition has begun to be used only in the last few years and as measurements improve the results should give a better insight into deposition loading (Marsik et al., 2007; Lyman et al., 2009; Peterson et al., 2012). The amount of mercury deposited to woodland soils as a result of trees shedding their leaves in autumn is another unknown in the mercury cycle, and the NADP has begun sampling litterfall at some appropriate sites in its network (Risch et al., 2012a).

It should be noted that passive sampling techniques have as yet never been employed for long-term monitoring. Another important point to make at this point is that not only are there no standard methods for measuring the concentrations of gas phase oxidised Hg species in the atmosphere, but there are no accepted standards for calibrating the instruments/methods currently in use to sample oxidised Hg species.

4.1.2. Satellite monitoring

In principle, mercury monitoring by satellite remote sensing should technically be feasible, however, Hg is present at very low concentrations in the troposphere. Satellite spectra, such as those obtained by SCIAMACHY (one of the instruments on the ENVISAT satellite) currently measure wavelengths 240 nm–1700 nm. Although Hg absorption lines for this particular range exist, there is a strong absorption at 254 nm, interference from O_2 and O_3 could make interpretation of the spectra difficult. Another and possibly more important technical problem arises from insufficient resolution of the spectrographs (SCHIAMACHY has a resolution of 0.2–0.5 nm for example). Existing satellite systems are used to detect spectra from molecules rather than atoms in the atmosphere. Molecular spectra have broader absorption bands than atoms and a resolution of around 0.001 nm would be necessary to detect mercury atomic absorption lines.

4.1.3. Stable isotope techniques

While not strictly a monitoring technique the use of stable isotope analysis to study Hg in different environmental compartments has the potential to become a powerful tool for the elucidation of some aspects of the Hg cycle which are still not clear. Mercury has seven stable isotopes and modern techniques can distinguish their relative abundances even in the very low concentrations typical of environmental samples. Mercury exhibits both mass dependent fractionation and mass-independent fractionation. The former occurs during a number of biotic and abiotic chemical processes, while the latter occurs during radical pair reactions (Blum, 2012). A review of the application of stable isotope techniques to environmental Hg studies can be found in Blum (2012) and a review of recent advances in Sonke and Blum (2013). A recent study by Tsui et al. (2012) of total Hg and MeHg in a river and adjacent river in California showed noticeable differences in δ^{202} Hg for MeHg and Hg^{II} in the forest ecosystem but not the in the river. The authors suggest that from the evidence of their study that the forest ecosystem is more impacted by MeHg deposition in precipitation, whereas MeHg in the riverine ecosystem is predominantly derived from in-situ methylation. Employing these techniques on a regular and long-term basis, say for example for precipitation samples, has the potential to reveal much information on Hg atmospheric pathways and MeHg sources in environmental systems.

4.2. Monitoring networks

As mentioned in above (section 4.1) there are some inherent difficulties in basing an extensive monitoring network on current automated atmospheric Hg instruments. However, their capabilities are such, that any future network would probably need to include a significant number. To expand monitoring beyond a limited number of sites will require the development of new techniques which are simpler to use and to deploy, less costly but nonetheless reliable. Currently the most promising possibility would appear to be passive sampling techniques. Frankly the high time resolution of available instruments is not necessary for monitoring purposes, where even daily averages would provide extremely useful additional information. It is important to recall that the greatest lack in terms of monitoring for atmospheric Hg is spatial coverage, and that the temporal resolution, and to an extent the detection limit are secondary concerns. There is no long term monitoring data for much of Asia, Africa or South America, there is also very little campaign data. Apart from some oceanographic campaign data there is effectively no atmospheric Hg measurement data between Southern Italy and Cape Point in South Africa, or between the Middle East and China, there have been a number of measurements (usually campaigns) between the Gulf of Mexico and Cape Horn (e.g. Hachiya et al. (1998); de la Rosa et al. (2004); Higueras et al. (2005); Fostier and Michelazzo (2006); Müller et al. (2012)). Thus although there are global emissions estimates (UNEP/AMAP, 2013) of Hg to the atmosphere vast areas have no measurement data at all. It is therefore imperative that research efforts are channelled into looking for solutions which are cost-efficient, reasonably uncomplicated and robust, even if their temporal resolution is not particularly high. Recent advances in passive sampling techniques could also lead to their application for both GOM and GEM (i.e. Peterson et al. (2012), for other references see section 4.1.1).

Monitoring Hg in precipitation presents difficulties that are likely to be harder to address than those regarding atmospheric Hg sampling. The extremely low concentrations of Hg in precipitation mean that contamination is a problem which needs to very carefully avoided. The procedures typically required are described in US-EPA (1996, 2002). The extension of precipitation monitoring will require a concerted effort to establish accredited laboratories in areas where they are lacking as the practice of sending samples to far away laboratories would become unfeasible beyond a certain number of monitoring sites.

4.3. Modelling – to link observations to impacts

The indirect link between most atmospheric Hg measurements which are routinely preformed, and the impact of Hg on human means that atmospheric measurements cannot be used directly as indicators. However, these observations when coupled with modelling techniques can provide estimates of ecosystem Hg fluxes. Thus changes in emissions can be linked to changes in fluxes and to ecosystem loadings. The challenge then is link those ecosystem loadings to impacts.

The recent establishment of new monitoring sites for atmospheric mercury and mercury in precipitation is a major step forward for those involved in modelling the emission, transport and deposition of mercury. This is particularly true of the establishment of monitoring sites in the southern hemisphere and around the equator, where until now there has been little if any data with which modelled atmospheric mercury concentrations and deposition fluxes could be compared. Long term monitoring at sites not overly influenced by local emissions is useful for the study of long-range atmospheric transport patterns, and how these are influenced by large scale climatic variations. The evaluation of global scale modelling studies reliable long-term monitoring data is extremely important as it will determine the confidence that can be placed in modelling results when future emission/climate scenarios are simulated. Modelling at the global scale has proved to be a useful tool in refining a number of the parametrisations used to describe a number of the processes which influence the concentration and distribution of atmospheric mercury, and therefore also mercury deposition, see for example Ryaboshapko et al. (2007); Lohman et al. (2008); Jung et al. (2009); Durnford et al. (2010); Soerensen et al. (2010); Amos et al. (2012) and references therein. The large-scale distribution of mercury (and its compounds) in the atmosphere depends on rates of emission, transformation, transport and deposition. Models assist in formalising our best available understanding of processes affecting mercury dynamics and help to identify key gaps in our knowledge and research priorities. Another benefit of models is extrapolation of the results of site specific observations in space and time. For mercury this includes estimates of the rates of exchange across air−sea and terrestrial−atmospheric interfaces and magnitudes of reservoirs in different ecosystems at the global scale. Based on the most sensitive parameters identified in modelling studies, experiments and/or observations can then be designed specifically to improve our understanding of mercury dynamics at the regional and global scale. The lack of understanding of the chemical composition of GOM remains a major hurdle in atmospheric Hg modelling. There is a great need for the developments of techniques which can distinguish the individual compounds which make up GOM.

One goal of mercury modelling for policy applications is to quantify the relationship between anthropogenic emissions of mercury and resulting concentration in seafood consumed by humans. As mentioned earlier, coupling of surface reservoirs (land, atmosphere, ocean) to describe the biogeochemical cycling of mercury (e.g. Selin et al., 2008) has been a major step forward. Recent work (Streets et al., 2011), shows that deposition estimates and overall responses of ecosystems are also highly sensitive to longer time scale reservoirs in terrestrial ecosystems and the ocean as well. Thus, fully coupled biogeochemical models and their link to biological dynamics in food-webs are needed for future policy

analysis. Such models will provide estimate of the magnitude and timing of changes in mercury concentrations in fish in response to changes in anthropogenic emissions. The very fact that models of this type are beginning to be discussed is, however, a measure of the progress which has been made in the mercury modelling field in the last decade.

4.4. Data management

A major challenge in numerous fields of earth system science is the ever increasing amount of Earth Observations and how this data can be managed and used in order to provide the greatest range of benefits to a wide range of potential users. The Group on Earth Observations was set up specifically to address this issue, see http://www.earthobservations.org/about_geo.shtml. It is fundamental that data sources be coherent in terms of metadata provision, data harmonisation, the adoption of standards and consistent (geographically and over time). The vast amounts of data generated by modern measurement techniques requires specialised high performance infrastructure. Such cyber-infrastructures enable, and enhance, data collection, validation, query, discovery, and access. They are also used to provide services such as export, brokering, metadata management (Cinnirella et al., 2012; D'Amore et al., 2012). The cyber-infrastructure can also be used to provide tools for data analysis and mapping and visualisation, all of which add significant value to datasets.

5. Recommendations for next generation mercury monitoring

There is a general consensus that to improve our ability to adequately evaluate the source–receptor relationships and the relative contribution of anthropogenic sources vs. natural processes/sources in terms of Hg, there is a need for a global monitoring network. This must necessarily be a concerted international effort as part of the implementation phase of the policy process that is going to be undertaken with the next diplomatic conference to be held in Japan in October 2013. One of the limiting factor of current technologies and methodologies is their high investment and running costs that often does not allow their use in continuous monitoring program, especially at remote locations. The next generation of air quality monitoring in terms of Hg will necessarily require a two-fold effort, a significant effort in developing new low cost sensors and an expansion in the number of permanent Hg monitoring sites worldwide, especially in the southern hemisphere and in those regions whose economies are growing the fastest. The Southern Hemisphere with the exceptions of South Africa and Antarctica is practically unexplored territory in terms of atmospheric Hg monitoring. The next generation of monitoring must absolutely address this lack given the global nature of Hg contamination. The most commonly used instruments currently employed in atmospheric Hg monitoring networks are accurate and have high time resolution, they do however require a carrier gas supply and a stable electrical supply. The development of simpler and less expensive methods needs to higher on the Hg research community's agenda. The monitoring of oxidised Hg compounds in the atmosphere, and of Hg in precipitation presents a different set of difficulties at the moment. For precipitation samples the difficulty lies in the fact that clean rooms are needed for both preparation and analysis, therefore direct measurements in the field are not possible. This situation seems likely to persist for some time. There are no standards with which to calibrate instruments that collect and determine the concentrations of oxidised Hg compounds in the atmosphere, and therefore there is some doubt concerning sampling efficiency. Not knowing exactly which oxidised Hg compounds are present in the atmosphere clearly adds to the difficulties of resolving these problems.

At present it is possible to identify a number of important points which need to be addressed as soon as possible.

- Only about a third of the Hg currently emitted to the atmosphere is derived from point and other identifiable anthropogenic sources.
- The remainder of emissions are associated with reemissions from oceans and terrestrial ecosystems. Many of these processes have been exacerbated by human activity (e.g. biomass burning, forest fires) and most of the Hg emitted from terrestrial and oceanic sources had an original anthropogenic source.
- Recent estimates suggest that about a third of the current total Hg emissions to the atmosphere from natural processes are due to the pre-industrial (natural) emission component and the remainder is recycled (previously deposited) Hg. However, the most recent studies using a fully coupled ocean–atmosphere model and all-time emissions (including emissions prior to 1850) suggest that 60% of emissions are from legacy, 14% natural and the rest anthropogenic (Streets et al., 2011).
- Changes in atmospheric Hg concentrations over time have been detected in some locations, in particular in the northern hemisphere (Soerensen et al., 2012). Slemr et al. (2011) have analysed global data since 1995 and find a decreasing trend in atmospheric Hg that is not simply explained, they suggest that the legacy of previous anthropogenic emissions plays an important role. Importantly they conclude "*And last but not least: more extensive mercury monitoring especially south of 40–60°N is needed to confirm the reported trend of the atmospheric mercury burden and to follow its future development.*"
- There is the need to coordinate activities at the global level to ensure that future research provides the maximum benefits in terms of assessing global and regional trends in Hg concentration. The current level of measurements and evaluation is inadequate for determining the extent of temporal and spatial changes in atmospheric Hg concentrations.
- There is a need for a permanent global monitoring network to ensure that atmospheric Hg concentration trends may be established unambiguously. Data from such a network could also be used for model testing and evaluation, and enhance confidence in the results of modelling evaluations of future emission scenarios.
- The chemical form of GOM is not actually known. It is operationally defined as oxidized Hg compounds, but what those compounds are is not well understood. There is a need to develop more capable technique to identify and quantify specific Hg compounds in ambient air. The recent developments in passive sampling techniques look promising from this point of view.
- Redox reaction rates for Hg with atmospheric oxidants need further investigation. There is still no consensus on which oxidants are important, although recent studies suggest that Br (and possibly Br containing compounds) are a large contributor. More work is needed to understand the relative importance of these redox reactions as well as to determine temperature dependent rate constants.
- The parameters that determine the rates of exchange of Hg compounds at air–sea, air–soil, and air–vegetation are not fully understood, but an improved understanding of these parameters is needed in order to improve existing Hg models.

Looking beyond the most probable developments in Hg monitoring, a number of possibilities for future intensive measurement campaigns on land or at sea deserve mentioning. In order to better

understand long-range transport and source–source receptor relation-ships, coordinated upper tropospheric studies to better understand the vertical distribution of Hg species would be of great use, particularly for model studies as such data is scarce. Focused pro-cess studies, particularly on the exchange of Hg at environmental interfaces would reduce modelling uncertainty, and would be instrumental in improving model evaluations of future emission scenarios. In particular these studies would be of benefit to improve estimates of environmental compartment response times to changes in deposition fluxes. The link between atmospheric mer-cury deposition, methylation, and uptake by living organisms is a very important area for further investigation. Therefore an improved knowledge of Hg concentrations in biota and particularly fish, by region, species and size (age) would be invaluable. Long term data for Hg in oceanic biota are available but often not shared in an interoperable form despite their importance as an exposure source for humans. The extension of Hg measurements to begin to regularly measure stable isotope concentrations and MeHg partic-ularly in precipitation samples is something that could be already be proposed. This information as well as being of scientific interest could lead to greater understanding of how particular regions and ecosystem types become contaminated with Hg.

Acknowledgements

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