Global Change and Mercury

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More than 140 nations recently agreed to a legally binding treaty on reductions in human uses and releases of mercury that will be signed in October of this year. This follows the 2011 rule in the United States that for the first time regulates mercury emissions from electricity-generating utilities. Several decades of scientific research preceded these important regulations. However, the impacts of global change on environmental mercury concentrations and human exposures remain a major uncertainty affecting the potential effectiveness of regulatory activities.

Mercury is naturally abundant in heavy-metal–rich geologic deposits and coal. Since antiquity, humans have intentionally (mining) and unintentionally (fossil-fuel combustion) liberated mercury from these stable long-lived reservoirs (1). Global mercury releases increased steeply during the 16th-century silviculture rush in Spanish America, and increased during the late–19th-century gold rush in North America (1, 2). Over the past century, anthropogenic mercury releases have been dominated by atmospheric emissions from fossil-fuel combustion, particularly coal-fired power plants (2). Artisanal and small-scale gold mining in developing countries has recently replaced coal combustion as the largest anthropogenic mercury emission source globally (3). This often unrecognized industry employs at least 10 to 15 million people globally and poses severe health risks to the miners due to inhalation of concentrated elemental mercury during gold recovery (3).

Most mercury released to the atmosphere is in the gaseous elemental (Hg0) form, which has a long atmospheric lifetime (6 to 12 months), allowing hemispheric-to-global mixing and transport before deposition. Elemental mercury reacts with atmospheric oxidants such as bromine to form the mercury oxides (Hg2+) that is rapidly deposited to terrestrial ecosystems, and oceans.

Mercury concentrations in the atmosphere and oceans are affected not only by anthropogenic emissions but also by climate and ecosystem change.

Mercury is reduced back to Hg0 and reemitted to the atmosphere; the remainder cycles through soils and the oceans over time scales ranging from decades to many centuries until it is resequestered in the lithosphere (4).

Sedimentary records of historical pollution provide evidence of a three- to fivefold increase in global atmospheric concentrations since the mid-1800s (5). Assessments that account for releases since antiquity suggest that humans have increased background atmospheric concentrations and deposition by a factor of 7 to 10 worldwide (1, 4). Modeling and observations also provide evidence of human-driven changes in seawater mercury concentrations (4, 6). A shift in global anthropogenic mercury releases from North America and Europe to Asia in recent years can be linked to decadal-scale decreases in mercury concentrations in the Atlantic Ocean and contrasting increases in the Pacific Ocean (6).

Methylation of inorganic mercury in wetlands, lakes, rivers, and seawater leads to the formation of methylmercury, a potent neurotoxin. Methylmercury is the only species of mercury to become concentrated with each successive level in the food chain, reaching levels in predatory fish that are about a million times higher than in seawater (6, 7). Fish are the main methylmercury exposure source for most wildlife and humans. Experimental data show that methylation of inorganic mercury responds proportionally to changes in mercury inputs (8), suggesting that reductions in human and wildlife exposures are achievable with declines in environmental releases over the long-term (6, 7). Epidemiological studies show long-term neurocognitive deficits in children exposed to methylmercury and some evidence for impaired cardiovascular health in adults (9).

Currently, human activities result in mercury emissions of ~2000 metric tons per year. Global anthropogenic emissions scenarios for 2050 range from a best-case decrease from present levels to 800 metric tons per year (driven by mercury-specific control technology and co-benefits from climate mitigation strategies) to an increase to 3400 metric tons per year under a business-as-usual scenario (10, 11). Present-day human sources consti-
tute ~30% of atmospheric emissions each year, with the remainder attributed to terrestrial and oceanic emissions that originate from legacy anthropogenic and natural mercury sources (3). Terrestrial and oceanic mercury reservoirs will continue to grow and release more mercury under all but the most stringent emissions controls scenarios, meaning that aggressive emissions reductions are required to stabilize background concentrations in the atmosphere and global oceans (4). However, future emissions trajectories are highly uncertain and depend on changes both in the global economy and in technology penetration.

Global biogeochemical cycling of mercury will also be affected by rapid climate change (see the figure). Weaker global circulation and elevated temperatures will affect atmospheric oxidation rates and patterns of deposition globally. Increased precipitation intensity and incidence of extreme storm events are likely to lead to increased mercury inputs to aquatic systems through direct deposition, run off, and erosion. Terrestrial soils are the largest global mercury reservoirs (4) and atmospheric mercury sequestration will likely increase in areas where ecosystem primary productivity is stimulated by increases in precipitation and elevated atmospheric CO₂ (12).

Furthermore, increases in the frequency, scale, and intensity of wildfires are likely to mobilize vast stores of mercury in terrestrial soils (4). Changes in ocean circulation, productivity, and growth of oxygen minimum zones will likely alter rates and patterns of methylmercury formation in seawater (6). In polar regions, higher temperatures and declining sea ice could enhance oceanic mercury losses through elevated evasion of Hg⁵. However, changes in primary productivity and species composition in Arctic ice-free waters have also been associated with an increase in biological mercury concentrations due to differences in feeding preferences (13). Many studies have suggested that climate change will exacerbate methylmercury production and bioaccumulation in aquatic ecosystems, but improved understanding of impacts on global mercury biogeochemistry is necessary for anticipating future human and wildlife exposures and risks.

Mercury cycling and bioaccumulation is also affected by other human-driven changes (see the figure). For example, increased ozone concentrations since preindustrial times are thought to have increased the residence time of mercury in the atmosphere by 66% through interactions with bromine (4). This change, coupled with greater emissions, has promoted an overall increase in the worldwide distribution and accumulation of anthropogenic mercury. Widespread nutrient enrichment of coastal ecosystems is likely to increase methylmercury formation in many ecosystems (6). Increasing consumption of lower-mercury containing fish from aquaculture (particularly in China) and fishing pressure that has decreased the size and trophic level of fish consumed in many regions, have partially offset increases due to rising pollution levels.

The links between environmental mercury cycling and major global change drivers (warming, hydrology, and emission controls) are reasonably understood. However, it remains challenging to forecast a future environment driven by multiple synergistic and antagonistic drivers operating simultaneously. New and rapidly developing scientific tools such as the application of high-resolution mass spectrometry to fingerprint sources and key processes (14) and genetic markers for the capacity to methylate mercury (15) will help to improve understanding of the cycling and health impacts of environmental mercury.

References

MATERIALS SCIENCE

A Coat of Many Functions

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Smart coatings are designed to be sensitive to various external and internal stimuli, thereby enhancing the surface functionality of materials.

The past decade has seen great interest in the development of smart materials with autonomic functionalities. Among them smart coatings have a special niche, filling the position at the interface between bulk solid substrate and liquid or gaseous external environment. This makes them uniquely well suited for such applications as corrosion protection, detection and delivery of bioactive species, and anti fouling. They can provide either autonomic response to fluctuations and variations of the coating integrity (disruption, melting) or stimulated response to changes in the external environment (magnetic or electromagnetic fields). The response action depends on the functionalities that the coatings attain during their preparation. The main challenges are to introduce these improvements, maintain them through all manufacturing steps and material life cycle, and use them efficiently when demanded.

The development of smart coatings possessing rapid or sustained feedback activity in response to external impacts will be an enabling technology for the fabrication of high-tech products with multifunctional surfaces. In general, the coatings combine passive properties inherited from classical coating design (barrier, color, adhesion) and engineered active parts, which are sensitive to instant or gradual impacts occurring either in the coating matrix (pH changes, cracks) or in the environment surrounding the coating (light, temperature, humidity). After exposure to certain impact(s), the active part of the smart coatings responds in order to restore the coating functionality, thus reducing the negative effect of the impact on the coating (self-healing concept) or launching additional properties of the coating interface (bioactivity, detection). The coatings should also have several passive and active functionalities (e.g., antireflection, antifungal, anti-corrosion) exhibiting synergistic effects, thus