

## Mercury contamination in aquatic ecosystems under a changing environment: Implications for the Three Gorges Reservoir

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Received May 20, 2012; accepted July 20, 2012; published online October 11, 2012

Mercury is one of the primary contaminants of global concern. As anthropogenic emissions of mercury are gradually placed under control, evidence is emerging that biotic mercury levels in many aquatic ecosystems are increasingly driven by internal biogeochemical processes, especially in ecosystems that have been undergoing dramatic environmental changes. Here we review the unique properties of mercury that are responsible for the exceptional sensitivity of its biogeochemical cycles to changes in climatic, geochemical, biological and ecological processes. We show that, due to rapid climate warming, a shift from sources-driven to processes-driven mercury bioaccumulation is already happening in the Arctic marine ecosystem. We further suggest that such a shift might also be operating in the Three Gorges Reservoir due to changes in these biogeochemical processes induced by the damming. As a result, the effectiveness of mercury emission control is expected to be followed by long delays before ensuing reduction is seen in food-web levels, making it all the more pressing to control and reduce mercury emissions to the reservoir. Long-term monitoring and targeted studies are urgently needed to understand how biotic mercury levels in the reservoir are responding to changes in mercury emissions and in biogeochemical processes.

**mercury, bioaccumulation, climate change, environmental change, Arctic Ocean, Three Gorges Reservoir, emission control**

**Citation:** Wang F, Zhang J Z. Mercury contamination in aquatic ecosystems under a changing environment: Implications for the Three Gorges Reservoir. *Chin Sci Bull*, 2013, 58: 141–149, doi: 10.1007/s11434-012-5490-7

Mercury (Hg) is among the first elements discovered and utilized by humans, and its relationship with human society has been a topic of conundrum, controversy, and catastrophe over the past at least 2000 years. Written records of medicinal use of Hg and cinnabar (HgS) in China can be traced back to at least *Shennong Bencao Jing* (“Herbal Classic of Shennong”, ca. 100 A.D.) which stated that cinnabar could cure almost any disease, nurture the “essence spirit”, and, if taken repeatedly, lead to immortality. The latter was fully exploited by the Taoist alchemists in the search of elixir of life. Ancient Egyptians and Greeks used Hg in skin treatments, which may have prompted the application of Hg for dealing with syphilis from about the 15th

century to the mid-20th century [1].

We now know that Hg is a non-essential element, and is not required by any known essential biochemical functions of any life form. On the contrary, acute or chronic exposure to Hg results in adverse biological impacts leading ultimately to death. The medicinal benefits of Hg, if any, are most likely related to its biocidal property. Mercury poisoning was recorded in Paracelsus’ work, and neurotoxic effects were noticed in the 19th century with the erythrim symptom [2]. However, it was not until the epidemics in the mid-20th century did the severity of Hg toxicity start to gain wide-spread attention: first the outbreak of the Minamata Disease in Japan in the 1950s and 1960s and then the grain-related poisoning in Iraq in 1971–1972. In both cases, the toxicity was attributed to the methylated form of Hg,

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methylmercury ( $\text{CH}_3\text{Hg}^+$  and its various complexes; MeHg hereafter). The Japanese outbreak was due to human consumption of local seafood that contained elevated concentrations of MeHg which was formed in the aquatic environment from dumping of industrial Hg waste [3]. The Iraqi outbreak was due to human consumption of bread prepared from seed wheat treated with MeHg-containing fungicide [4]. It is now well established that MeHg is one of a few known developmental neurotoxic substances to humans [5].

With the increasing awareness of the toxicity of Hg, Hg mining and production for industrial use has been greatly reduced since the 1970s. Anthropogenic emission of Hg is now dominated by the so-called “by-product” sectors, with fossil fuel combustion for power and heating accounting for nearly 50% of the total Hg emission to air [6]. The total global anthropogenic Hg emissions to air had been stabilized around 1900 t/year for the period 1990–2005 [6]. Though this number is projected to rise in the next decades [7], international efforts are ramping up to control further Hg emissions, particularly from the “by-product” sectors. In February 2009, the Governing Council of United Nations Environmental Programme (UNEP) agreed on the need to develop a global, legally binding agreement on Hg emission. The intergovernmental negotiations are on going, with the goal of reaching a final agreement in 2013.

Despite increasing efforts in emission controls, Hg remains the primary contaminant of global concern of our time, with elevated MeHg concentrations frequently exceeding safety thresholds—found in many biota worldwide, especially in aquatic predators such as fish and marine mammals, and even in some of the most remote regions on this planet [6]. This seems count-intuitive: why has source control of Hg not resulted in alleviation of global Hg contamination? When, if ever, will we see ecosystems be recovered following source control? These beg for an even more important and timely question: if the ecosystem were not responding, shall we control Hg emission after all?

Based on a large body of studies on Hg contamination in the Arctic marine ecosystem, we recently proposed [8] that, to address the above questions, we need to realize and appreciate a new paradigm in driving Hg contamination: while Hg contamination in many ecosystems in the past centuries

was a direct result of “external” anthropogenic Hg emissions, it is increasingly driven by “internal” processes that are controlling the transformation and biological uptake of the legacy Hg that has been stored in the system from the past emissions. We further proposed that such shift in the paradigm is most obvious where these internal processes have been undergoing drastic changes due to climate change [8].

In this paper, we provide an analysis on the sensitivity of Hg biogeochemistry to changing processes within an aquatic ecosystem. We further argue that, in addition to systems where a shift in the paradigm is driven by climate-induced changes such as in the Arctic Ocean, such a shift from source-driven to process-driven Hg bioaccumulation could also be prompted by drastic environmental changes due to large-scale engineering operations such as the Three Gorges Reservoir on the Yangtze River. Such a change in the paradigm would have major implications for Hg contamination and remediation in the region.

## 1 Sensitivity of Hg biogeochemical cycles to environmental change

Among all the metals, Hg possesses many unique properties, which make its biogeochemical cycles exceptionally sensitive to climatic (e.g., temperature, light, hydrology), geochemical (e.g., pH, pe, complexing ligands), biological (e.g., feeding behavior of an organism) and ecological (e.g., organic carbon flux, microbial processes, and food web structure and dynamics) processes. Some of these are summarized in Table 1 and highlighted below.

(1) Volatility of  $\text{Hg}^0$ . With a melting point of  $-38.8^\circ\text{C}$ , elemental Hg ( $\text{Hg}^0$ ) is the only liquid metal at room temperature and under standard pressure. The high vapor pressure of  $\text{Hg}^0$  also makes it highly volatile with its volatility greatly dependent on temperature. For instance, the Henry's law constant of  $\text{Hg}^0$ , defined as:

$$\text{Hg}^0(\text{aq}) = \text{Hg}^0(\text{g}); K'_H = [\text{Hg}^0(\text{g})]/[\text{Hg}^0(\text{aq})]$$

(dimensionless;  $(\text{ng}/\text{m}^3 \text{ air})/(\text{ng}/\text{m}^3 \text{ water})$ )

has been shown to increase with temperature following the empirical equation [9]:

**Table 1** Unique properties of mercury and implications for its biogeochemistry

Property	Implications
Redox between $\text{Hg}^0$ and $\text{Hg}(\text{II})$	Sensitive to changes in pe and pH; Sensitive to photochemical and microbial processes.
High vapor pressure of $\text{Hg}^0$	Sensitive to changes in temperature; Long range atmospheric transport; A global problem needing global solutions.
$\text{Hg}^{2+}$ ions being one of the softest Lewis acids	Strong affinity to ligands (e.g., reduced sulfides, halogens); Sensitive to changes in organic carbon.
Methylation is primarily microbial, with MeHg being the most bioavailable and toxic	Sensitive to changes in organic carbon, nutrients, redox and microbial processes; Direct source control of MeHg difficult.
MeHg biomagnifies in the food chain	Sensitive to changes in food web structure and dynamics.

$$K'_H = \exp\left(\frac{-2404.3}{T} + 6.92\right)$$

(freshwater or artificial seawater),

where  $T$  is in Kelvin. Within the temperature range of 5–30°C, an increase of 1°C (or 1 K) in temperature would thus increase the Henry's Law constant of  $\text{Hg}^0$ , and thus its tendency to partition into the air, by ~2.8%. The high volatility of  $\text{Hg}^0$ , its increase with rising temperature, and its generally low reactivity are responsible for the transport of  $\text{Hg}^0$  in the global atmosphere, in a fashion bearing some similarity to the grasshopper effect of volatile and semi-volatile persistent organic pollutants [10], making Hg a global contaminant.

(2) Redox. Similar to many other trace metals, Hg is present in the environment in several oxidation states including  $\text{Hg}^0$  and  $\text{Hg(II)}$ . Although trace amounts of  $\text{Hg(I)}$  may be present in the atmosphere, it is an unstable intermediate and tends to be further oxidized to  $\text{Hg(II)}$  or reduced to  $\text{Hg}^0$  [11]. The redox chemistry of Hg in the aquatic and terrestrial environments is typically mediated by microbial processes. Unlike many other trace metals, the redox chemistry of Hg in the atmosphere and surface environment is highly sensitive to UV radiation. Whereas photoreduction of  $\text{Hg(II)}$  to  $\text{Hg}^0$  readily occurs, photooxidation of  $\text{Hg}^0$  to  $\text{Hg(II)}$  occurs primarily via photolytically produced reactive halogen species (e.g., atomic halogens and halogen oxides), making the Hg cycling sensitive to reactive halogen hotspots. The best example is over the polar oceans during the spring time when sea ice related activation of bromine in the marine boundary layer, known as bromine explosion events [12], could completely oxidize tropospheric  $\text{Hg}^0$ , resulting in the so-called mercury depletion events (MDEs) [13].

(3) Affinity of  $\text{Hg}^{2+}$  ions to ligands. Once oxidized,  $\text{Hg(II)}$  readily deposits into the surface environment where it subsequently bioaccumulates. With a highly deformable electron sheath,  $\text{Hg}^{2+}$  ions are among the softest Lewis acids [14], and thus tend to form strong covalent bonds with soft Lewis bases such as sulfides, selenides, and chloride. As a result, there is virtually no free  $\text{Hg}^{2+}$  ions (or more accurately, the aquo complexes  $\text{Hg(H}_2\text{O)}_x^{2+}$ ) in environmental or biological media. Instead,  $\text{Hg(II)}$  speciation is dominated by its complexes with dissolved organic carbon (primarily via its sulphydral function groups) in freshwaters, with chloride in estuarine and marine waters, with sulfide and thiols in anoxic waters [15], and with thiols and thiol-containing proteins in biological systems [16]. Any changes in the type and concentration of these complexing ligands, therefore, will result in major changes in the speciation and bioavailability of Hg.

(4) Methylation. Inorganic Hg is toxic, but it is its methylated form, MeHg, that is responsible for the biomagnification and neurotoxicity of Hg. The binding of  $\text{Hg}^{2+}$  with a methyl group renders MeHg both hydrophilic and

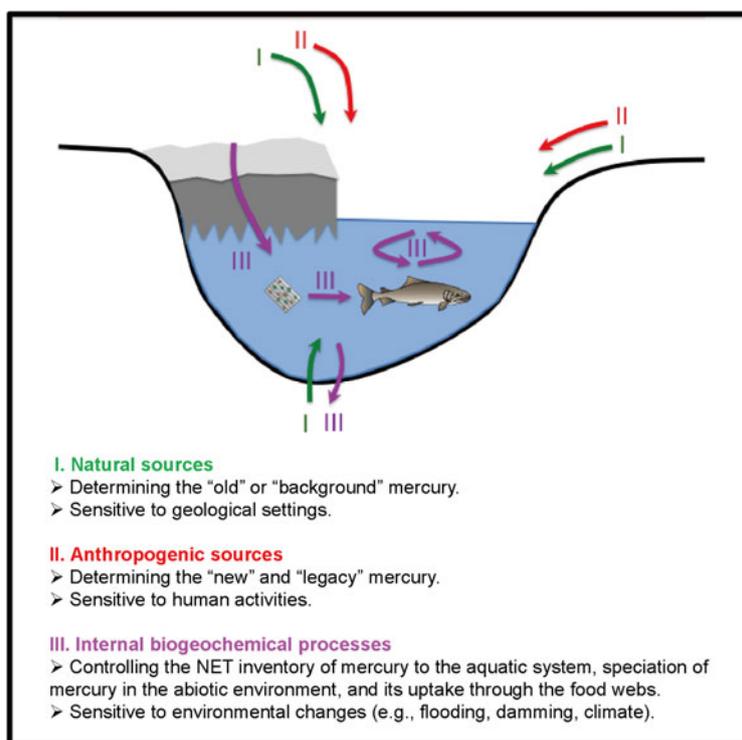
lipophilic, readily passing through boundaries and accumulating within fatty tissues, making Hg one of few trace elements that are known to biomagnify along the food chain. When binding with cysteine, the resulting methylmercuric cysteinate can be transported across the blood-brain barrier and placental barrier [17], leading to its developmental neurotoxicity. Although methylation can occur abiotically, most of the MeHg present in ecosystems is formed in the environment via microbial processes. Several species of sulfate reducing bacteria [18], iron reducing bacteria [19] and methanogens [20] are known to methylate Hg, though other microbes including aerobic ones may also be capable of this conversion [21]. The fact that MeHg, the key chemical species responsible for environmental Hg problems, is formed in situ in the environment after the deposition of inorganic Hg, instead of directly from anthropogenic emissions, poses a major challenge in controlling its levels in the ecosystem.

(5) Biomagnification. Since MeHg biomagnifies along the food chain, Hg concentrations in higher trophic level biota are affected not only by the pool of bioavailable Hg in the abiotic environment, but also by trophic processes that affect biological uptake of Hg. Such processes could be "bottom-up" or "top-down", including [22]: (i) initial MeHg concentrations entering the biota at the bottom of the food web (bottom-up); (ii) species-specific characteristics such as growth rates, age, size, and Hg elimination rates that impact bioaccumulation or biodilution (bottom-up); (iii) the food web structure and dynamics that defines the transfer of Hg among trophic levels and/or between food webs, such as benthic-pelagic coupling (bottom-up); and (iv) predator behavior defining diet and feeding ecology (top-down). Because of biomagnification, MeHg concentration can increase by up to an order of magnitude or more at each successive trophic level. Hence, any changes in these bottom-up or top-down processes would have a major effect on the Hg levels in an ecosystem, particularly in top predators.

## 2 Sources vs processes in driving Hg contamination under a changing environment: Signs from the Arctic Ocean

It becomes clear from the above discussions that the level of Hg in an ecosystem is determined not only by the influx (natural or anthropogenic) of Hg to the system, but also by the processes in the ecosystem that control the transport, speciation, bioavailability and biological uptake of Hg, as shown in Figure 1. Given the strong sensitivity of Hg biogeochemical cycles to a suite of climatic, geochemical, biological and ecological processes (Table 1), any changes in these processes would have the potential to result in major changes in Hg biogeochemical cycles and ultimately in Hg levels in biota.

There is no doubt that the significant increase in Hg

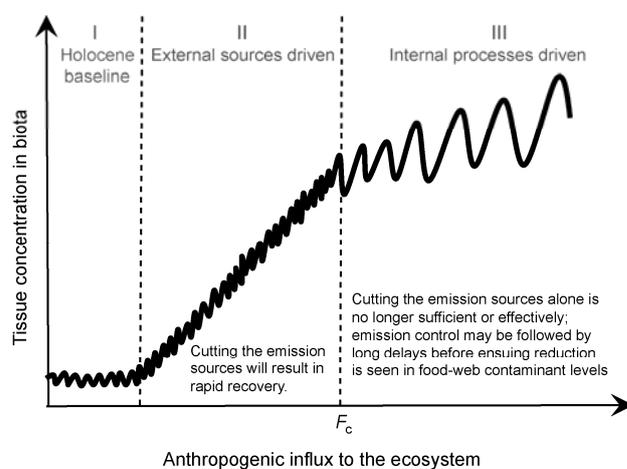


**Figure 1** Sources and processes that drive mercury bioaccumulation in aquatic ecosystems.

concentrations in present-day biota in most ecosystems compared to their pre-industrial counterparts is driven primarily by the increase of anthropogenic Hg emissions. This is supported by the significant increase in anthropogenic Hg depositional flux recorded in Arctic lake sediment cores and glacier ice cores [6] and in the world's oceans [23]. However, as the accumulated mass of Hg in a water body becomes large enough relative to the emission-driven loading rate, the internal biogeochemical processes that control the permanent removal (e.g., degradation and burial) or the recycling of the contaminant into the biosphere would increasingly become the determining steps in bioaccumulation.

This shift from sources-driven to processes-driven bioaccumulation of Hg and other biomagnifying contaminants (e.g., PCBs) was first proposed by Wang et al. [8] and illustrated in Figure 2. Three phases can be distinguished from the figure. During the Holocene and prior to the Anthropocene, the flux of these contaminants was generally low (e.g., Hg) or absent (e.g., PCBs), so were their biotic concentrations (Phase I—"Holocene baseline"). At the onset of the Anthropocene, however, industrialization resulted in a sharp increase in the flux of these contaminants to the otherwise "pristine" environment, and biotic concentrations of these contaminants responded rapidly due to increasing exposure and uptake of these chemicals from a small but growing environmental reservoir (Phase II—"External sources-driven"). Once a reservoir has accumulated sufficient amount of a chemical, say at a critical influx ( $F_c$ ), additional increases in influx become secondary to the recycling of the

chemical that has been stored in the environmental reservoir ("legacy" contaminants) accumulated by years of loading. Bioaccumulation then draws predominantly on the "legacy" contaminants, which are operated on by the internal biogeochemical processes (Phase III—"Internal processes-driven"). Throughout all the three phases, biogeochemical cycling (shown as sine-wave "noise" in Figure 2) determines the speciation, bioavailability, and uptake of the contaminant, but it is in the latter phase that these processes emerge to create a variability that is large enough to obscure downturning or up-turning trends, at least at the decadal scale if not longer [8].



**Figure 2** Change of the paradigms in driving bioaccumulation of mercury in the environment and their implications for remediation strategies. Modified from ref. [8].

Based primarily on a Hg mass balance study on the Arctic Ocean [24], we proposed at that time that Hg bioaccumulation in the Arctic marine ecosystem had reached Phase III in the past 30 years, resulting in “noise” from the processes becoming the main “signal” in the “trend” data for Hg in Arctic marine animals during the recent decades [8]. This proposal is supported by a recent comprehensive, international assessment of Hg in the Arctic [6]. While the Hg concentration in the Arctic troposphere has remained constant or slightly declining since the 1970s [6], a rigorous statistical analysis of all available biotic Hg time series obtained from the past 30 years or so showed no consistent trend across tissues and species of the entire circumpolar Arctic [6]. Of the 83 time-series analyzed, 13 (16%) showed a significantly increasing trend, 5 (5%) showed a significantly decreasing trend, 21 (25%) showed a significant non-linear trend, and the rest 45 (54%) showed no statistically significant trend [6]. For instance, while Hg concentrations in polar bear (> 2 years) hair from east Greenland (Ittoqqortoormiit; 1984–2008) showed a significantly increasing trend, those from west Greenland (Avanersuaq, 1987–2006) and from Svalbard (1995–2008) showed no significant trend [6]. Similarly, whereas Hg concentrations in beluga whales in most part of the Canadian Arctic showed an increasing trend, that cannot be said for seals from the same region [6]. The increasing role of internal processes in driving Hg bioaccumulation in the Arctic is further supported by 8 case studies detailed in the AMAP report [6]: while the signature of atmospheric Hg deposition was visible in a few case studies, all the case studies supported a role of climatic, biological and ecological processes in determining the biotic Hg trend in recent decades.

It is not a coincidence that signs of this change in the paradigm would be most profound in the Arctic Ocean, as rapid climate warming has resulted in dramatic changes in many internal biogeochemical and ecological processes that drive Hg cycling [25]. For instance, the rapid decline in the aerial coverage and thickness of Arctic sea ice and the replacement of multi-year sea ice with first-year ice have the great potential to affect the timing and net deposition of atmospheric Hg via the occurrence and severity of MDEs and via changes in the timing of ice melting. Rising temperature and changes in organic carbon flux would affect the presence and activity of Hg methylators thus changing the locality and pool of MeHg available for biological uptake. Furthermore, any changes in the predator behavior (e.g., habitat use, diet preferences) of an Arctic animal and in the structure and dynamics of Arctic food webs in general would also result in a significance change in the Hg concentration in the animal [26].

### 3 Implications for the Three Gorges Reservoir

The shift from the sources-driven to processes-driven Hg

bioaccumulation does not necessarily require the Hg influx to the system reaching a critical value ( $F_c$  in Figure 2). It could also be initiated by dramatic changes in the internal biogeochemical processes. Such dramatic changes can be induced by rapid climate warming as is the case for the aforementioned Arctic Ocean, but they can also be caused by severe natural events such as major flooding, or by large-scale engineering operations. The recently completed Three Gorges Reservoir (TGR) project on the Yangtze River, China, is the largest hydraulic engineering in the world. The reservoir drains through a region that is geologically enriched in Hg and is among the most Hg contaminated in the world, due to millennia of mining and smelting of Hg and other metals (e.g., zinc) and a rapid increase in coal-burning power plants [27]. The reservoir region is also home to some 16 million people, as well as source water for all the downstream regions. It is thus important and timely to examine how Hg cycles in the reservoir respond to both high Hg emissions from natural and anthropogenic sources and to dramatic changes in internal biogeochemical processes due to the damming.

Water and sediment started to be impounded behind the Three Gorges Dam in June 2003 and the construction of the dam was completed in 2008. The water level of the reservoir reached its designed maximum of 175 m above the sea level (a.s.l.) in October 2010, and it has since been fluctuating between 145 m a.s.l. in summer and 175 m a.s.l. in winter [28]. At its maximum water level, the reservoir stretches some 660 km with a total surface area of 1080 km<sup>2</sup>. The reservoir floods a total area of 630 km<sup>2</sup>, 350 km<sup>2</sup> of which is a seasonally flooded water level fluctuation zone (WLFZ) due to changes in water level [28]. The impoundment of TGR has brought about many environmental concerns including enhanced sedimentation, decreased self-cleaning capacity of the water body, eutrophication, and contamination by chemicals such as Hg and changes in their cycling in the reservoir ecosystem.

(1) Mercury sources to TGR. No mass balance model has been constructed for Hg in TGR, though sporadically available Hg flux data paint a system that has been stressed by Hg from natural and anthropogenic sources. A good portion of the TGR drainage basin is located in Guizhou Province on a mercuriferous belt that has been mined for Hg for more than 2000 years. With more than 12 large and super-large Hg mines, the province is one of the world's largest Hg production centers and has a total reserve of cinnabar deposits of nearly 80000 t (as metal Hg) [27]. Although all large-scale Hg mining activities ceased operations by the beginning of the 21st century, artisanal Hg mining has continued with much less or non-existing measures to reduce Hg emission. These artisanal Hg mines, mining and smelting of other metals from Hg-enriched ores, and the re-emission of legacy Hg stored in mine tailings distinguish Hg dynamics in TGR from many other water bodies in the world, and need to be fully appreciated when addressing the

Hg issues in TGR.

As is the same in the global context [6], coal-fired power plants remain the main source of Hg in the TGR region. A recent study estimated that coal-fired power plants from Chongqing, Sichuan and Guizhou, where the majority of the TGR watershed is located, emit a total of 11 t/year of Hg to air in 2007 [29]. To put this number in context, the entire Arctic Ocean, which has a surface area about 9000 times greater than TGR, receives a similar amount of atmospheric Hg (8.4–98 t/year; [24]). Of course, a fraction of the emitted Hg<sup>0</sup> from the power plants is carried out to other regions, but a significant fraction, especially those in the form of Hg(II) (gaseous or particulate), is deposited in the region and ultimately into the reservoir. The high Hg emission from the power plants is in part due to the elevated Hg concentrations in the coal used in the region [30,31]; with an average Hg concentration of 530 ng/g (ranging from 100–2670 ng/g), coal produced from Guizhou has the highest Hg level in China [31]). As a result, the Hg<sup>0</sup> concentration in ambient air in Chongqing is highly elevated with an annual average of 6.7 ng/m<sup>3</sup> [32], which doubles that in remote mountainous areas in the region (Mount Gongga in Sichuan 3.9 ng/m<sup>3</sup> [33], and Mount Leigong in Guizhou 2.8 ng/m<sup>3</sup> [34]), and more than triples the north hemispheric background values of < 2 ng/m<sup>3</sup>.

A recent study [35] on the metal concentrations in topsoil (0–20 cm) in the main stretches of the TGR area showed that on average Hg concentrations in the region (49 ± 40 ng/g; mean ± s.d.) are comparable with the background levels in China (60 ± 70 ng/g; [36]); however, Hg concentrations as high as 490 ng/g are found in areas that are underlain by sedimentary limestone due to geological enrichment, or are in the vicinity of urban centers due to deposition of atmospheric Hg [35]. Much higher Hg concentrations have

been reported in surface soils in the upstream Guizhou province, with concentrations up to 790000 ng/g near Hg mines [27].

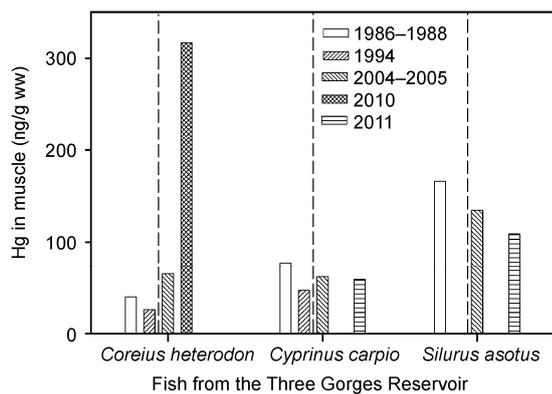
Much less studied are the concentrations and fluxes of Hg in industrial wastewater, domestic sewage and solid waste, as well as the losses of Hg from the system (e.g., sedimentation).

(2) Mercury concentrations in TGR before and after the impoundment. Comparison of Hg concentrations in abiotic and biotic compartments of TGR before and after the impoundment in 2003 is difficult due to a lack of systematic and holistic studies before and after, and due to inconsistent sampling and analytical methods used in different studies. Table 2 and Figure 3 summarize results from a few published studies. Cautions need to be exercised when making any definitive statements; nevertheless, they do provide a first glimpse at what might have been happening since the impoundment. For instance, in most cases the Hg concentrations in the river water and sediment/soil seem to have increased after the impoundment (Table 2).

A thorough search of the literature showed that Hg data for fish before and after the impoundment are only available for three species [41–45]: bronze gudgeon (*Coreius heterodon*), common carp (*Cyprinus carpio*) and Amur catfish (*Silurus asotus*). Although the data are not corrected for fish age, the sizes and weights collected in these studies seemed to be comparable. As can be seen from Figure 3, whereas no significant change has been seen for Hg concentrations in the muscle of common carp and Amur catfish, they have increased considerably in the muscle of bronze gudgeon since the impoundment. Yu et al. [45] further noted that after the impoundment, higher increase was observed in muscle Hg concentrations in fish species that are at higher trophic levels and inhabit in deeper waters. A recent study

**Table 2** Total mercury concentrations in the Three Gorges Reservoir before and after the impoundment

	Before impoundment		After impoundment	
	Concentration	Reference	Concentration	Reference
River water – Total Hg (ng/L)				
Low-water period	18	[37]	68	[37]
High-water period	43	[37]	49	[37]
River water – Dissolved Hg (ng/L)				
High-water period	6–12	[38]	23	[38]
WLFZ soil – Total Hg (ng/g)				
Changshou	46	[39]	57	[40]
Fuling	82	[39]	53	[40]
Fengdu	204	[39]	52	[40]
Zhongxian	62	[39]	103	[40]
Wanzhou	85	[39]	95	[40]
Yunyang	63	[39]	23	[40]
Fengjie	35	[39]	62	[40]
Wushan	34	[39]	73	[40]



**Figure 3** Compilation of available data on Hg concentrations in fish from the Three Gorges Reservoir before and after the impoundment. Data for 1986–1988 are from [41], 1994 are from [42], 2004–2005 are from [43], 2010 are from [44], and 2011 are from [45]. The dashed line indicates the year (2003) when the reservoir was impounded.

found that the Hg concentrations in the muscle of bronze gudgeon from Yibin and Banan in the upper reaches of Yangtze River and in darkbarbel catfish (*Pelteobagrus vachelli*) from Yibin have exceeded the safe limit level (300 ng/g ww) for human consumption [44]. This is alarming as both are important commercial and edible fish in the region. More studies are needed to verify these concentration ranges and to monitor Hg concentrations in other fish species from the reservoir.

(3) Impact of damming on processes driving Hg bioaccumulation in TGR. Reservoirs, particularly recently flooded reservoirs, are known areas of rapid Hg methylation and thus act as MeHg sources for bioaccumulation in aquatic food web [46]. This is due to the influx of “fresh” organic carbon at the oxic-anoxic transition zone which promotes the activities of Hg methylating bacteria [18,19]. While this has been extensively demonstrated in North America, it is not unusual to see very low levels of Hg in freshwater fishes in many reservoirs in China, even in most contaminated regions [47]. This discrepancy can be due to many different processes. Many reservoirs in China have seen extensive past or current aquaculture activities as well as eutrophication, which result in enhanced biodilution of Hg at the base of food-chain due to algal bloom, enhanced biodilution due to fast growth rate of the fish, and lessened biomagnification due to shortened trophic levels [47]. Sustained stratification may also “protect” the fish by limiting them to feed in oxic and low MeHg-containing epilimnion and thus “disconnecting” their habitat from the high MeHg zone in the hypolimnion [47]. Alkaline pH in some of the reservoirs may have also limited the production of MeHg.

Different from small reservoirs such as Baihua Reservoir that have been extensively studied (e.g., [47]), TGR is the second largest reservoir in the world that is formed by damming the Yangtze River, the 4th largest river (in discharge) in the world. As a result, the impact of aquaculture and eutrophication, though occurring in parts of the

reservoir, will not likely simplify the food-web structures to the extent seen in smaller reservoirs, at least not in the foreseeable future. Therefore, the biodilution effect will most likely not be as significant as in other reservoirs, making fish, particularly predator fish, potentially more sensitive to MeHg production in the reservoir.

While damming will have some impact on new sources of Hg to the reservoir, given that the system has been under high Hg loading for decades to centuries, the most important effect of damming on Hg bioaccumulation in the reservoir ecosystem appear to be via changes in internal biogeochemical processes that drive the removal, remobilization and biological uptake of legacy Hg that has already been accumulated in the system. In other words, the dramatic changes in processes due to human engineering would likely shift Hg bioaccumulation from being driven by sources (Phase II, Figure 2) to by internal processes (Phase III), similar to the case of the Arctic Ocean where the shift is prompted by climate warming.

Similar to the Arctic Ocean, damming of the Yangtze River will affect both bottom-up and top-down processes in TGR that will ultimately control the Hg levels in the reservoir ecosystem. Among the most important bottom-up processes that will be affected by the damming is Hg methylation. The recently flooded farmlands and forests would provide a large influx of “fresh” organic carbon which, when fuelled by Hg methylators, will produce MeHg as a by-product. This is particularly the case for the large area of WLFZ which will be seasonally flooded when the reservoir adjusts the water level, providing the ideal redox conditions for the Hg methylators. A good fraction of WLFZ was formerly rice paddy fields which are known to produce MeHg [48].

Other important changes in the processes include: (i) changes in residence time of water and sediment which will affect the critical loading of Hg in the reservoir; (ii) changes in sedimentation rate which will affect Hg removal from the water column; (iii) changes in feeding and habitat selection of biota due to the changes in hydrology among others; and (iv) changes in food web structures and dynamics due to eutrophication, aquaculture and invasive species. While some of these processes tend to increase Hg concentrations in predator fish, others may decrease Hg bioaccumulation, resulting in greater difficulty in predicting Hg trend in biota in the reservoir (Table 3).

## 4 Conclusions

While Hg (and contaminants in general) research and management has so far primarily focused on source reduction, evidence is emerging that the effectiveness of controlling “external” Hg sources is being increasingly modified by changes in “internal” biogeochemical processes in the aquatic ecosystem. Such shift from sources-driven to

**Table 3** Summary of likely impacts of damming on biota Hg levels in the Three Gorges Reservoir<sup>a)</sup>

Process	Likely change	Likely impact on biotic Hg
Atmospheric deposition	+	+
Evasion	+	-
Riverine inputs	+	+
Soil erosion	+	+
Mercury methylation	+	+
Demethylation	±	±
Eutrophication and primary productivity	+	-
Scavenging and sedimentation	+	-
Food-web structure and dynamics	±	±

a) “+” indicates increases in process rates and impact of biotic Hg levels; “-” indicates decreases in rates and impacts; “±” indicates no or unknown change.

processes-driven Hg bioaccumulation has been demonstrated in the Arctic marine ecosystem that has been undergoing dramatic changes due to rapid climate warming.

Located in a region that is geologically enriched in Hg, the TGR area has also received large amounts of anthropogenic Hg from coal-burning power plants, mining and smelting industries and other activities. Following impoundment in 2003, major changes have already been occurring in the reservoir, many of which will have direct influence on the cycling and bioaccumulation of Hg, particularly the legacy Hg that has been stored in the system. Based on the insights from the Hg cycling in the Arctic Ocean, we postulate that Hg bioaccumulation in TGR is increasingly controlled by damming-induced changes in the internal processes, and that emission control of Hg will not result in immediate recovery of the ecosystem. Instead, emission control is expected to be followed by long delays before ensuing reduction is seen in food-web Hg levels. This response lag makes it all the more urgent to reduce or halt further loading of Hg to the system.

Unlikely the Arctic Ocean where intensive studies have resulted in Hg time-series data for many species for the past three decades [6], our ability to project how Hg levels in TGR will change is extremely limited due to a genuine lack of reliable time series of Hg in any biotic or abiotic compartment of the reservoir. Given the major implications of a processes-driven Hg bioaccumulation on pollution prevention and remediation, there is a pressing need to start a long-term monitoring program that will systematically and holistically monitor how Hg levels in the abiotic and biotic compartments are changing. Targeted and hypothesis-driven research should also be carried out, with a focus on key processes involved in the Hg biogeochemical cycles (Table 3). To rectify the lack of data before the impoundment, efforts should be taken to reconstruct the chronology from sediment cores or other abiotic and biotic archives. It is only through such careful and coordinated monitoring and

research that the risk of another major Hg problem can be reduced. This is especially important given the large human population inhabiting the reservoir region and downstream. If there is any lesson that can be learnt from the Hg problem in the Arctic Ocean, that is, when an aquatic ecosystem is polluted by Hg, it will take a very long time to recover, long after the emission sources are placed under control.

*This work was supported by the Natural Science and Engineering Council (NSERC) of Canada (F.W.) and the National High Technology Research and Development Program of China (2012AA101405). We thank Dr. Yong Cai for his kind invitation to write this review.*

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