THE CHEMICAL CYCLE AND BIOACCUMULATION OF MERCURY

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ABSTRACT

Because it is very toxic and accumulates in organisms, particularly in fish, mercury is an important pollutant and one of the most studied. Nonetheless we still have an incomplete understanding of the factors that control the bioconcentration of mercury. Elemental mercury is efficiently transported as a gas around the globe, and even remote areas show evidence of mercury pollution originating from industrial sources such as power plants. Besides elemental mercury, the major forms of mercury in water are ionic mercury (which is bound to chloride, sulfide, or organic acids) and organic mercury, particularly methylmercury. Methylmercury rather than inorganic mercury is bioconcentrated because it is better retained by organisms at various levels in the food chain. The key factor determining the concentration of mercury in the biota is the methylmercury concentration in water, which is controlled by the relative efficiency of the methylation and demethylation processes. Anoxic waters and sediments are an important source of methylmercury, apparently as the result of the methylating activity of sulfate-reducing bacteria. In surface waters, methylmercury may originate from anoxic

543

layers or be formed through poorly known biological or chemical processes. Demethylation is effected both photochemically and biologically.

INTRODUCTION

Mercury is a pervasive pollutant that accumulates in organisms and is highly toxic. As a result, it is probably the most studied of all trace elements in the environment. Known in mythology for its fleet-footedness, mercury rapidly spreads all over the earth from its natural and anthropogenic sources. It is also elusive, and the ways by which it is transformed in the environment and bioaccumulated remain perplexing.

In this review, after a brief overview of the global mercury cycle, we focus on the transformations of mercury in aquatic systems, for it is ultimately the accumulation of mercury in fish that is of concern to us. Even in remote regions, methylmercury in fish is often near to and sometimes exceeds the concentration deemed safe for human consumption (0.5–1 ppm). The question is straightforward, even if the answer is not: How do concentrations of parts per trillion of mercury in water yield concentrations of parts per million in fish? To begin to answer this question we do not provide an extensive review of the immense literature on mercury in the environment. Rather, we examine what is known of the chemical and biological mechanisms that effect the transformations of mercury in water and ultimately control its bioaccumulation in fish.

THE GLOBAL CYCLE OF MERCURY

The only metal to be liquid at room temperature, elemental mercury Hg^0 (1) is also a gas, Hg^0 (g), with little tendency to dissolve in water (57, 65). Natural waters are usually supersatured in Hg^0 (aq) compared to the air above, and volatilization thus results in a flux of Hg^0 from the water into the atmosphere (see Figure 1) (28). This supersaturation is maximal during summer days, when photoreduction of Hg(II) in surficial waters is at its peak (5, 6, 8, 67, 83). In the atmosphere, where approximately 95% of total mercury is in the elemental state, Hg^0, it is slowly oxidized to the mercuric (+II) state, Hg(II). Most of this oxidation occurs at the solid-liquid interface in fog and cloud droplets. Ozone is probably the main oxidant in this process, with HClO, HSO_3^-, and $OH^\bullet$ being also significant (54–56). Gas-phase oxidation reactions of Hg^0 by O_3, Cl_2, and H_2O_2 may sometimes be important, although large uncertainties exist regarding their rates (70). Some of the Hg(II) produced in the atmosphere is re-reduced by mechanisms involving either SO_3^- as the reductant (56), or photoreduction of $Hg(OH)_2$ (84).
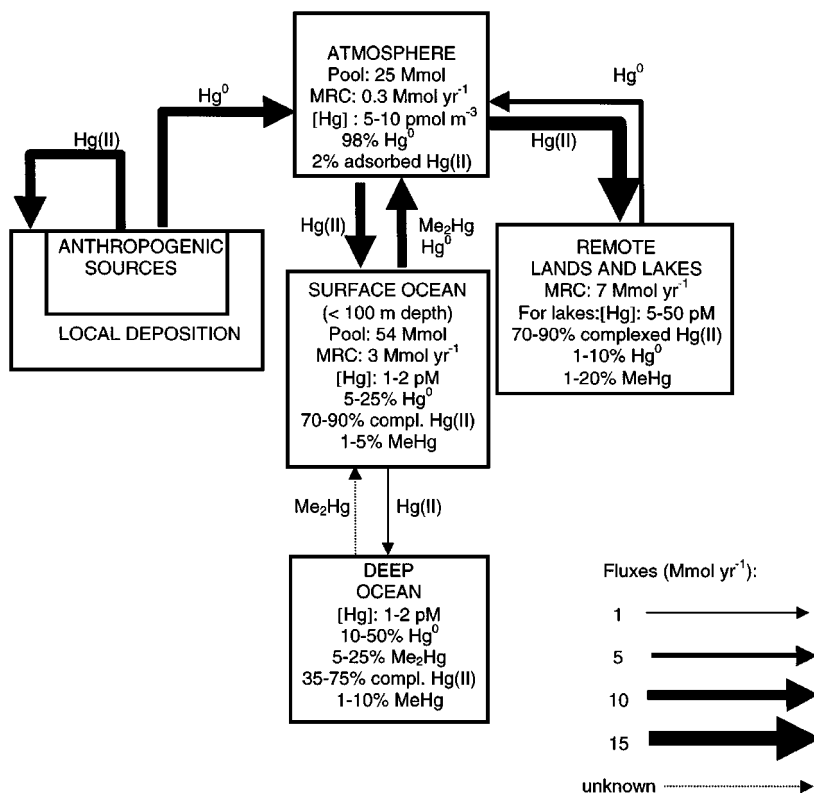
Figure 1 Global Hg cycle. The width of the *arrows* corresponds to the importance of the different fluxes, and are estimated from Mason et al (46). Main Hg species contributing to these fluxes are identified. MRC stands for modern rate of change for global reservoirs (35). Concentrations and species distributions are average from different sources, in particular Fitzgerald & Mason (27) and Meili (49). Caveat: The MRC estimates from Hudson et al (35) correspond to less evasion from land and reduced deposition compared to the fluxes from Mason et al (46).

   The return of mercury from the atmosphere to the Earth's surface occurs chiefly via wet precipitation of dissolved Hg(II). Adsorption of mercury on aerosols such as soot also promotes its deposition, especially over land (46), where aerosols are abundant. Because Hg^0 reoxidizes relatively slowly to the mercuric state Hg(II), its residence time in the atmosphere is on the order of a year (27) or perhaps less (SE Lindberg, personal communication). This is sufficient time for atmospheric mercury to be distributed over the entire planet before returning to the land, lakes, sea, and ice. As a result, while the principal emissions of mercury are from point sources concentrated in industrial

regions, mercury pollution is truly global, affecting the most remote areas of the planet (see Figure 1). Historical records from lake sediments provide the most compelling evidence that remote areas receive significant inputs of anthropogenic Hg by long-range atmospheric transport (26).

Once oxidized, 60% of atmospheric mercury is deposited to land and 40% to water, even though land represents only 30% of the Earth's surface (46). The greater proportion of Hg deposition on land presumably reflects the proximity of its sources since water precipitation is three times less on land than on the oceans. In oceanic waters, after it undergoes a complex set of chemical and biological transformations, most of the Hg(II) is reduced to Hg^0 and returned to the atmosphere; only a small fraction is permanently exported to the sediments (46). Thus the mercury inventories in the atmosphere and surface seawater are tightly coupled by an effective precipitation/volatilization cycle driven by oxidation/reduction reactions. In lakes, the main loss mechanisms for mercury are sedimentation and gas evasion. The relative importance of each is still the subject of debate and seems to be a function of the concentration of reducible Hg in the epilimnion (28). Similar processes occur on land, resulting apparently in a smaller return of reduced mercury to the atmosphere and a greater permanent burial in soils. In the case of uncontaminated soils, net dry-weather Hg deposition (dry deposition > gas evasion) is sometimes observed, about three times less frequently than net emission (dry deposition < gas evasion) (42). Contaminated sites, however, consistently display important net emission fluxes (30, 42). Compared to its atmospheric flux, little mercury is transported by rivers.

Anthropogenic sources of mercury come from metal production, chlor-alkali, and pulp industries, waste handling and treatment, and coal, peat, and wood burning (43). Natural inputs to the atmosphere include degassing and wind entrainment of dust particles from land, notably from mercuriferous areas, volcanic eruptions, forest fires, biogenic emissions of volatile and particulate compounds, and degassing from water surfaces (63). Among those sources, degassing from natural mercury-rich geological formations may have been underestimated in the past (30, 31, 63). Based on lake sediment records (77), it is estimated that the atmospheric inputs of mercury have tripled over the past 150 years (46). This indicates that two thirds of the mercury now in the atmosphere, and hence in surface seawater, is of anthropogenic origin, and one third is from natural sources (see Figure 1).

THE CHEMISTRY OF MERCURY IN SURFACE WATERS

Chemical Speciation in Oxic Waters

In oxic surface freshwaters from uncontaminated sites, mercury at concentrations of 5–100 pM ($= 5$–100×10^{-12} mol/L $= 1$–20 parts per trillion) occurs in several physical and chemical forms (see Figures 1, 2, and 3). The
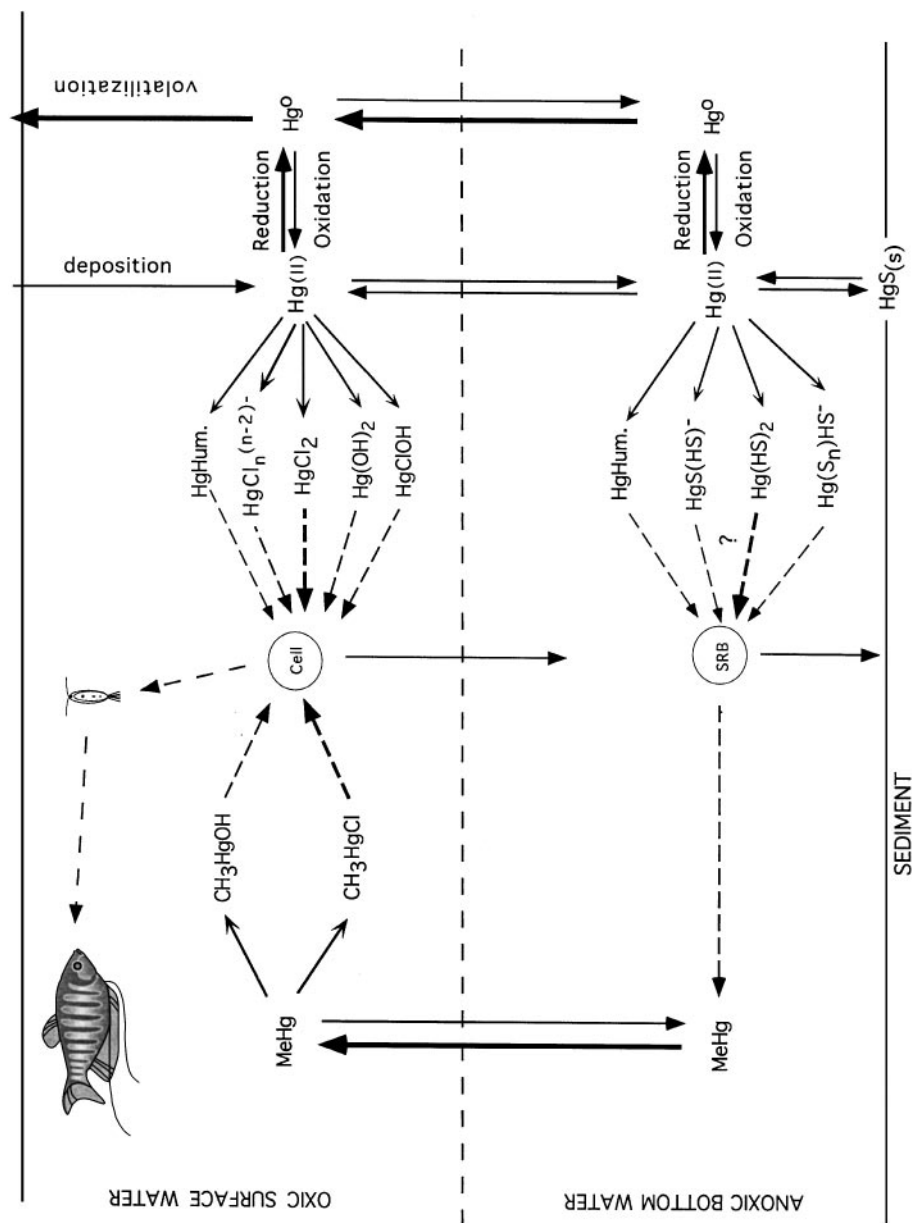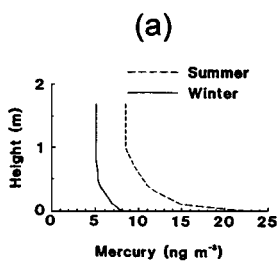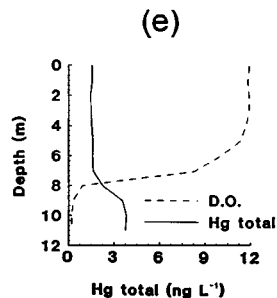
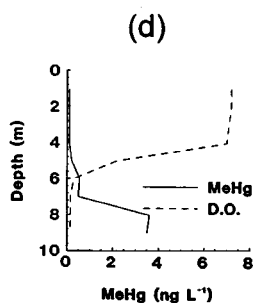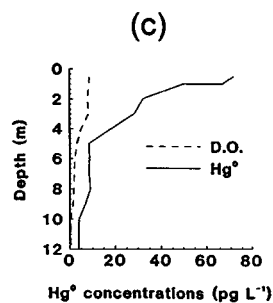*Figure 2*   Aquatic cycle of mercury. See text for details. SRB = Sulfate-reducing bacteria.

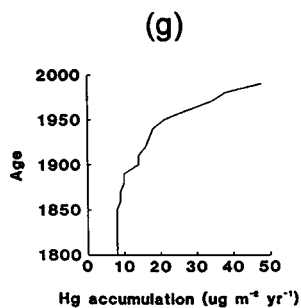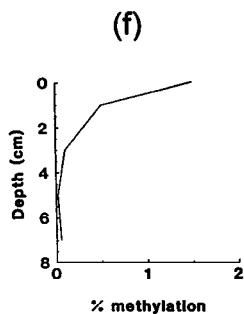**AIR**

(a)

WATER

(b)

(c)

(d)

(e)

SEDIMENTS

(f)

(g)
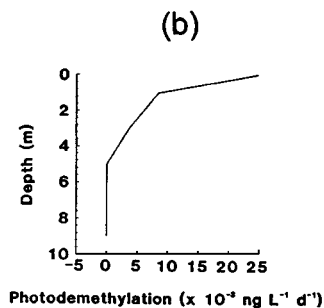
partitioning of Hg between the dissolved, colloidal and particulate phases varies widely spatially, seasonally and with depth in the water column. Some of this variation seems to be related to temporal changes in living particulate matter, mostly phytoplankton and bacteria (23, 36). The concentration of particulate Hg per unit particle weight is relatively constant reflecting perhaps a sorption equilibrium between dissolved and particulate phases (49). The exact chemical form of particulate mercury is unknown, although most of it is probably tightly bound in suspended organic matter. Adsorption of Hg to oxyhydroxides may also be important in lakes. In fact, the commonly observed enrichment of MeHg and Hg(II) in anoxic waters of lakes may result from the sedimentation of mercury-laden oxyhydroxides of iron and manganese from the epilimnion and their dissolution in the anoxic hypolimnion (49).

Dissolved Hg is distributed among several chemical forms: elemental mercury ($Hg^0_{(aq)}$), which is volatile but relatively unreactive, a number of mercuric species (Hg(II)), and organic mercury, chiefly methyl (MeHg), dimethyl (Me_2Hg), and some ethyl (EtHg) mercury.[1] In general, and particularly in stratified systems, concentrations of Hg^0 are higher near the air-water interface whereas levels of total Hg and MeHg are higher near the sediments (see Figure 3). An operationally defined fraction of total Hg (the sum of particulate and dissolved mercury), the so-called "reactive" Hg (measured after a $SnCl_2$ reduction step), is considered to be a good predictor of the naturally reducible Hg (28). It probably corresponds to the inorganically bound fraction of Hg(II).

According to thermodynamic calculations (74), the divalent mercury in surface waters, Hg(II), is not present as the free ion Hg^{2+} but should be complexed

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[1]The simultaneous presence of Hg^0 and Hg(II) in natural waters, both oxic and anoxic, brings up the question of the possible formation of Hg(I), the mercurous form of Hg, which is only stable in water as the dimer Hg_2^{2+}. Simple calculations based on the constants in Table 1 show that a negligible fraction of either Hg(II) or Hg(0) may be present as Hg(I) in natural waters when the concentrations are below 0.1 nM. Stabilization by an unknown ligand with much higher affinity for Hg_2^{2+} than for Hg^{2+} seems highly improbable. Note, however, that in many laboratory experiments performed with mercury concentrations in excess of 1 nM, and where Hg^0 may be present by design or as a contaminant, the formation of Hg_2^{2+} may be a complicating and easily overlooked factor.

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Figure 3 Vertical profiles of mercury species concentrations and of transformation rates in air, water, and sediments. (*a*) Hg^0 height profile over the surface of a contaminated pond in summer and winter (10); (*b*)–(*e*) depth profiles of mercury photodemethylation (71), Hg^0 (8), MeHg (14), and total Hg (7) levels in different remote temperate forested lakes; (*f*) depth profile of mercury methylation in profundal lake sediments, expressed as percentage of total added mercury methylated after 24 h (40); (*g*) ^{210}Pd-dated depth profile of mercury accumulation rates in a western Minnesota lake (25).
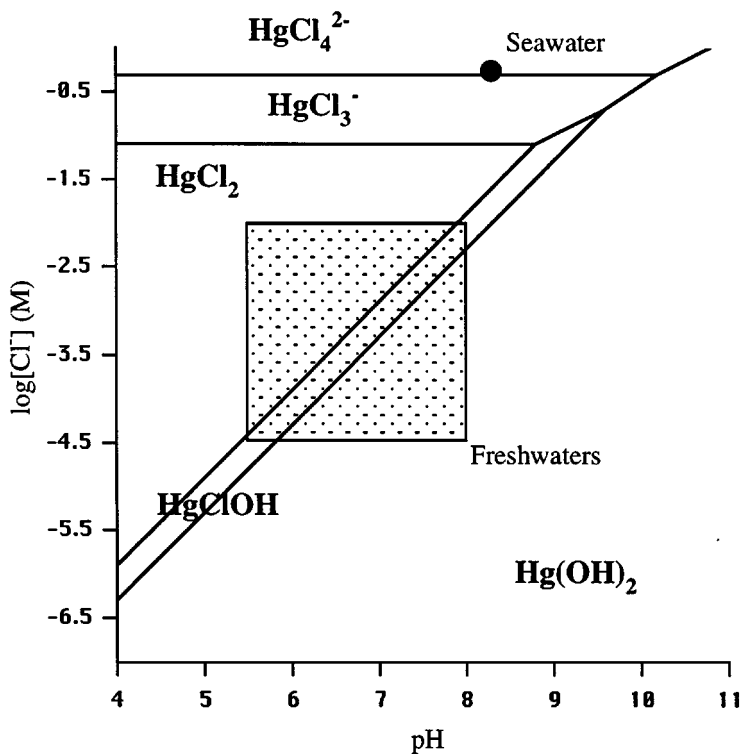
Figure 4   Dominance diagram of hydroxo- and chloro-complexes of Hg(II) as a function of pH
and chloride concentrations (see Table 1). Ionic strength corrections were neglected. Seawater has
a pH of 8.3 and a chloride concentration of 0.55 M. The pH and chloride concentration range of
freshwaters was taken from Davies & DeWiest (24).

in variable amounts to hydroxide ($Hg(OH)^+$, $Hg(OH)_2$, $Hg(OH)_3^-$), and to
chloride ($HgCl^+$, $HgClOH$, $HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$) ions depending on the
pH and the chloride concentration (see Figure 4 and Table 1). It is also possible
that, even in oxic surface waters, some or much of Hg(II) might be bound to
sulfides (S^{2-} and HS^-; see Table 1), which have been measured at nanomo-
lar concentrations in surface seawater (45). In addition, an unknown fraction
of Hg(II) is likely bound to humic acids, the assemblage of poorly defined
organic compounds that constitute 50–90% of the dissolved organic carbon
(DOC) in natural waters. According to Meili (49), nearly 95% of inorganic ox-
idized mercury in lakes is bound to dissolved organic matter. The nature of the
chemical moieties responsible for the binding of Hg(II) and the thermodynamic

Table 1 Relevant acidity and thermodynamic constants for Hg_2^{2+}, Hg^{2+}, and CH_3Hg^+

Dissolution & Volatilization of Hg^0

$Hg^0(1) = Hg^0(aq)$	$K = 3.30\ 10^{-7}$ mol/L	[Clever et al (22)]
$Hg^0(g) = Hg^0(aq)$	$K = 2.56 \cdot 10^{-3}$ mol.l^{-1}.atm^{-1}	[Sanemasa (65)]

Dismutation of Hg(I)

$Hg^{2+} + Hg^0(aq) = Hg_2^{2+}$	$K = 10^{8.46}$	[Hietanen & Sillen (33)]

Acidity constants

Acid/base couple	H_2S/HS^-	HS^-/S^{2-}	$Hg(SH)_2/Hg(SH)S^-$	$Hg(SH)S^-/HgS_2^{2-}$
pKa	7.02	14.6	6.33	8.72

Hg(I) complexes

Complex	Hg_2Cl_2
log K	12.4

Hg(II) complexes

Complex	$HgCl^+$	$HgCl_2$	$HgCl_3^-$	$HgCl_4^{2-}$	$HgOH^+$	$Hg(OH)_2$	$Hg(OH)_3^-$	HgClOH
log K	7.2	14	15.1	15.4	10.6	21.8	20.9	18.1

Complex	$Hg(SH)_2$	$Hg(SH)S^-$	HgS_2^{2-}	$Hg(S_n)HS^-$	HgS (red)	HgS (black)
log K	36.6	46.8	52.6	−3.7	53.3	52.7

MeHg complexes

Complex	CH_3HgCl	CH_3HgOH	CH_3HgS^-
log K	5.5	9.6	21.5

Constants are given as logarithms of the overall formation constants for complexes (e.g. for the reaction M + nL = ML$_n$, where M is Hg^{2+} or CH_3Hg^+ and L is a ligand). For solids (HgS$_{(s)}$), the constant corresponds to the precipitation reaction. For the mercury polysulfide complex, $Hg(S_n)HS^-$, the constant K is given for HgS (cinn) SH$^-$ + (n − 1) S^0(rhom) = $Hg(S_n)HS^-$. All constants are given at ionic strength I = 0 and are taken from Smith & Martell (72), except for $Hg(S_n)HS^-$ (58), Hg_2Cl_2 (59, 60), and those otherwise indicated in the table.

properties of the complexes have been little studied (34, 44). Through its binding to DOC, Hg can be mobilized from the drainage basin and transported to lakes (50, 51, 81). The reactions of ionic mercury are relatively fast, and it is thought that the various species of Hg(II), including those in the particulate phase, are at equilibrium with each other.

In the organometallic species of mercury, the carbon-to-metal bonds are stable in water because they are partly covalent and the hydrolysis reaction (see below), which is thermodynamically favorable (and makes the organometallic species of most others metals unstable), is kinetically hindered. As a result, the dimethyl mercury species, Me_2Hg ($= CH_3HgCH_3$), is unreactive. The monomethylmercury species, MeHg, is usually present as chloro- and hydroxo-complexes (CH_3HgCl and CH_3HgOH) in oxic waters (see Figure 5 and Table 1).

Reduction of Hg(II)

The processes that transform mercury between its elemental and ionic or organic forms determine how much mercury is in the elemental state, thus how
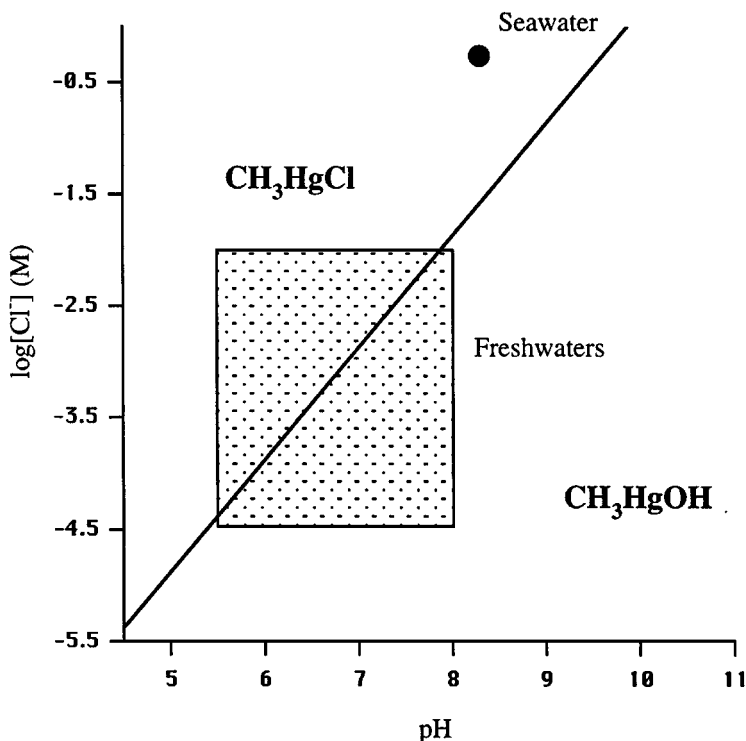
Figure 5   Dominance diagram of hydroxo- and chloro-complexes of methylmercury MeHg as a function of pH and chloride concentrations (see Table 1). Ionic strength corrections were neglected. Seawater has a pH of 8.3 and a chloride concentration of 0.55 M. The pH and chloride concentration range of freshwaters was taken from Davies & DeWiest (24).

quickly it volatilizes and, ultimately, how much total mercury remains in the water (see Figures 1 and 2). These processes are beginning to be understood. Reduction of ionic to elemental mercury may be effected by biological or chemical processes. Some published data show that most of the Hg(II) reduction in incubation bottles is linked to the presence of particles, implicating microorganisms (47). More recent data, however, show that, in many cases, photoreduction rather than microbial reduction is the principal mechanism (6, 8, 41). While it is likely that there are variations in time and space in the relative importance of these two processes, the explanation for this apparent contradiction may lie in the differences between experimental conditions. The experiments showing microbial Hg(II) reduction were conducted with additions of Hg(II) of 0.3–0.9 nM (47). These concentrations are above the threshold value of ca 50 pM, which

is now known to induce the *mer*-operon[2] in bacteria (62; I Schaperdoth and FMM Morel, unpublished data). Microbial reduction via induction of the *mer*-reductase likely explains these data. In contrast, the experiments showing the dominance of photoreductive mechanisms were conducted at Hg(II) concentration of 3–20 pM, below the threshold for induction of the reductase. The efficiency of the photoreduction depends on levels of reducible Hg(II) complexes and radiation wavelength and intensity. When present at high concentrations, DOC seems to act as a competitive inhibitor for solar radiation, scavenging UV radiation before it can photoreduce Hg(II). As a result, higher photoreduction rates have been observed in clear, low-DOC lakes (6).

The mechanism for this photoreduction is still uncertain. Photoreduction of Fe, Mn, or humic acids may be implicated. The reduced metals [Fe(II), Mn(II)] or organic moieties (hydroquinones and semiquinones) formed photochemically could, in turn, reduce Hg(II) when they reoxidize, as they are known to do for other elements (39). Alternatively, direct photoreduction of $Hg(OH)_2$, $Hg(HS)_2$ (73), or DOC-bound mercury is possible (85). Part of the light dependence of the reduction may result from the activity of photosynthetic phytoplankton and cyanobacteria. Ben-Bassat & Mayer (13) noted that reduction of Hg(II) to Hg^0 was accelerated by illumination of *Chlorella* cells. In their study, formation of Hg^0 decreased in concert with inhibition of photosynthesis. These authors suggested that light increased the amount of leakage from the cells of a metabolite capable of reducing Hg. Several studies have also shown that phytoplankton can externally reduce various species of Cu(II) and Fe(III) by cell-surface enzymatic processes that are inhibited by photosynthetic inhibitors (37, 38, 61). Such enzymatic processes also probably contribute to Hg reduction in the photic zone. Since photoreduction of Hg has been observed in uncontaminated environments under diverse conditions (pH: 4.5–8.3; DOC: 1–32 mg/L; total Hg: 2–20 pM; salinity: <1–30‰) and was induced by visible and UV radiation, it is likely that more than one of those processes are involved (5–8).

At the natural mercury concentrations in the low picomolar range, reduction thus seems to be effected chiefly by photochemical processes, whereas in polluted waters, when the mercury concentration exceeds 50 pM, microbial reduction via the MerA reductase likely becomes the predominant mechanism of Hg(II) reduction.

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[2]The *mer*-operon, one of the best studied metal resistance mechanisms in bacteria, consists of a series of enzyme-encoding genes whose transcription is de-repressed by Hg(II). These enzymes include a MerT membrane protein that transports Hg(II) into the cell and a MerA reductase that reduces Hg(II) to Hg^0. Some *mer* also contain the gene for a MerB lyase that hydrolyzes organomercury compounds. The *mer*-operon is usually encoded on a plasmid and has been shown to be transferable among bacterial species (66, 76).

Oxidation of Elemental Mercury

Until very recently, it was thought that the oxidation of Hg^0 to Hg(II) in natural waters was negligible or inexistent. However, recent data show that this may not be true in seawater (87). The presence of high chloride concentrations and of appropriate particle surfaces catalyze the oxidation of Hg^0 by oxygen, resulting in rates as high as 10% per hour in natural seawater (5). This oxidation may be more important in coastal areas, where particulate matter loadings are higher. One should note that an effective surface for the catalysis of Hg^0 oxidation is that of liquid mercury (M Amyot, unpublished). Thus, pools or droplets of liquid mercury that may be present in oxic seawater as a result of some human activity should be oxidized relatively efficiently.

Demethylation Reactions

As mentioned above, the hydrolysis reaction of MeHg,

$$CH_3\text{-}Hg^+ + H^+ \rightarrow CH_4 + Hg^{2+},$$
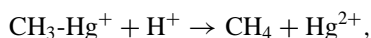
is thermodynamically favorable but kinetically hindered, and MeHg is thus stable in aqueous solution. However, the kinetic hindrance of this reaction can be overcome by enzymatic or photochemical mechanisms, and methylmercury has been shown to be degraded by some bacteria and by light.

Some *mer* operons (see above) carry a gene, MerB, for an organomercury lyase that confers bacterial resistance to organomercury compounds. The MerB enzyme catalyzes the hydrolysis reaction shown above, leading to the formation of Hg(II). The Hg(II) ion formed is then reduced to Hg^0 by the mercuric ion reductase MerA (53). There are no direct field data quantifying the importance of this mechanism in nature, but one may infer from the involvement of the MerA reductase that it may be induced in polluted water only when the Hg concentration exceeds 50 pM.

MeHg has been shown to be photodegraded in oxic waters in lakes and seawater (71, 75; see Figure 3). The reaction rate is first-order with respect to MeHg concentration and sunlight radiation, and is not associated with the particulate phase (71). Singlet oxygen generated by photochemical reactions is likely responsible for this degradation (75). Photodegradation is probably the main degradation pathway for methylmercury in oxic water bodies with low mercury concentrations (<50 pM).

Sources of Methylmercury in Surface Waters

Methylation is believed to occur mainly in anoxic waters and sediments; in most lakes, the MeHg at the surface originates from the anoxic water below, whence it is transported by diffusion and advection (see Figure 2). However, significant MeHg levels in the surface waters of the oceans and Great Lakes, for

which transport of MeHg from deep waters is negligible, clearly indicate that there may be some MeHg production in oxic waters. The mechanism for the methylation is still uncertain, although most of the reaction is probably driven by microbial processes similar to those observed near the sediments (49). However, in lakes some of it may result from dark (82) or photochemical processes involving humic acids (see below). In the oceans, some MeHg could be formed by the partial demethylation of $(Me)_2Hg$ upwelled from deep waters, where it is itself formed by unknown biological mechanisms (27). In some rare cases, the atmosphere may be a significant source of MeHg, although most surface waters are a source rather than a sink for atmospheric organic mercury.

THE CHEMISTRY OF MERCURY IN ANOXIC WATERS AND SEDIMENTS

Chemical Speciation in Anoxic Waters

The mercuric ion exhibits extremely high affinity for sulfide. This property controls the chemistry of mercury in anoxic waters and sediments. The speciation of dissolved Hg(II) in sulfidic waters is completely dominated by sulfide and bisulfide complexes (HgS_2H_2, HgS_2H^- and HgS_2^{2-}), even at total sulfide, S(−II), concentrations as low as 1 nM (see Figure 6 and Table 1). The only important sulfide complex of MeHg is CH_3HgS^- (see Figure 7). Two forms of solid mercuric sulfide, HgS(s), are known: the black form (metacinnabar) is metastable at room pressure and temperature, and in solution, it spontaneously evolves into the red form (cinnabar) over days. Both cinnabar and metacinnabar have a very low solubility product (see Table 1), and HgS(s) is thought to be the particulate mercury species that is buried in sediments and controls Hg(II) solubility in anoxic waters. It is difficult, however, to ascertain analytically the exact chemical nature of the traces of mercury present in natural sediments, and it is possible that, rather than being precipitated as HgS(s), sedimentary mercury is bound to particulate organic matter or even to inorganic particles such as iron oxides (78). Recently, authigenic submicron crystals of metacinnabar [black HgS(s)] have been identified in contaminated soils, using various electron microscopy techniques (11).

Although the solubility product of cinnabar is extremely low, its actual solubility increases at high S(−II) concentrations, due to the formation of the dissolved sulfide and bisulfide mercuric complexes (see Figure 6). For example, at pH = 7, the dissolved mercury concentration of a water body at equilibrium with HgS(s) increases from 3 pM for S(−II) = 1 μM to 3 nM for S(−II) = 1 mM. This increasing solubility of mercury with sulfide concentration undoubtedly plays a role in the high dissolved mercury concentrations observed in many
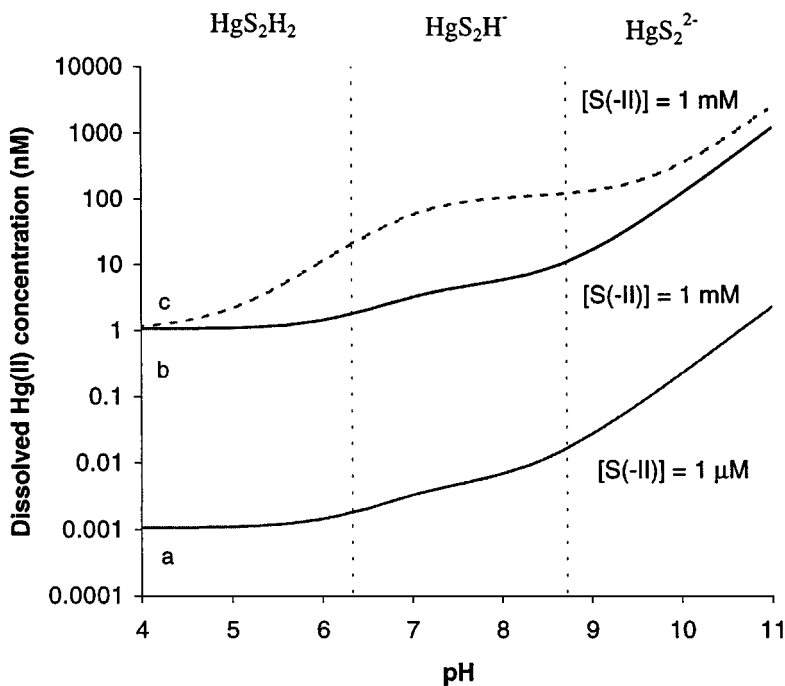
Figure 6 Calculated dissolved Hg(II) concentrations at equilibrium with HgS(s) [$K_s = 10^{52.1}$; $I = 0$; Schwarzenbach & Widmer (68)] in the presence of added sulfides (see Table 1); [Cl$^-$] = 1 mM. (*a*) and (*b*) (*solid lines*): no elemental sulfur is present. (*c*) (*dotted line*): the solution is at equilibrium with $S^0_{8(\text{rhom.})}$; in that case, the dominant mercury complex is Hg(S_n)HS$^-$ for pH > 5. The *vertical lines* delimit the predominance regions of the sulfide and disulfide complexes.

anoxic waters. There is also recent evidence for the formation of polysulfide mercury complexes, Hg(S_n)SH$^-$ (n = 4–6) in the presence of elemental sulfur S(0) (58). Significant S(0) concentrations have often been measured in anoxic waters (58), and polysulfide complexes could in some cases dominate mercury speciation and increase its solubility even further (see Table 1, Figure 6).

In addition, we note that cinnabar, which is a semiconductor, can be dissolved by visible light. The dissolution rate increases at high sulfide concentrations and leads to the production of Hg^0 (AML Kraepiel and FMM Morel, unpublished data).

Reduction of Hg(II) in Anoxic Waters

As in oxic waters, Hg(II) can be reduced in anoxic waters by the activity of bacteria carrying the *mer*-operon, if the Hg levels are sufficiently high.
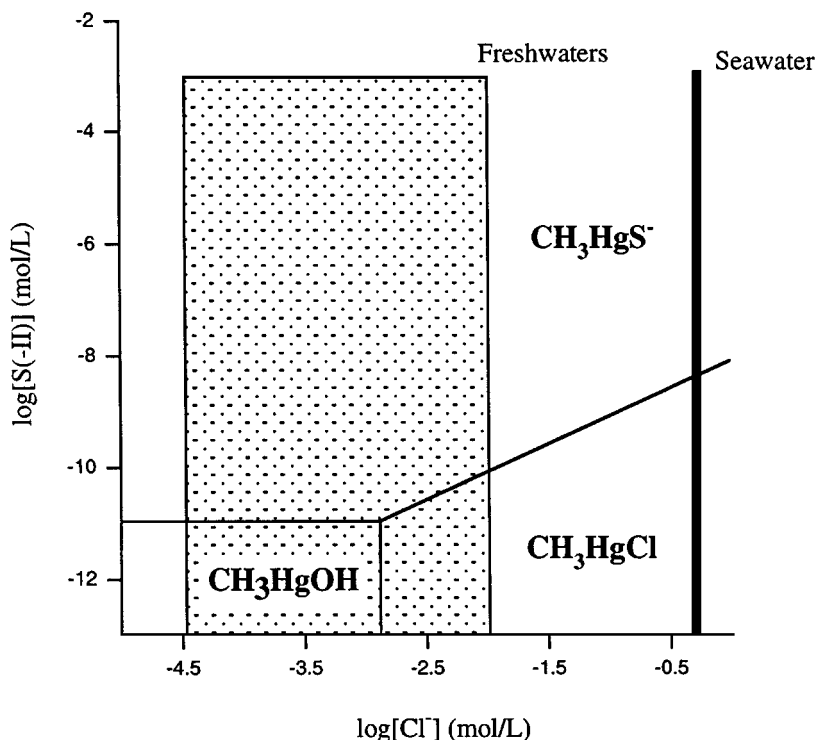
Figure 7   Dominance diagram of hydroxo-, chloro- and sulfide complexes of MeHg at pH $= 7$ as a function of chloride and total sulfide S($-$II) concentrations (see Table 1). Ionic strength corrections were neglected. Seawater has a pH of 8.3 and a total sulfide concentration varying from 1 nM to 1 mM. The chloride concentration range of freshwaters was taken from Davies & DeWiest (24), and the total sulfide concentration was taken to vary from 1 nM to 1 mM.

Alternatively, abiotic reduction of mercury in the dark may be effected by humic substances (3, 9). According to Allard & Arsenie (4), this process is optimal in the absence of chloride and at pH circa 4.5. These authors have suggested that the formation of a complex between Hg and humic acids was necessary in order for the reduction to take place. A similar dark reduction process has been studied for other metals such as iron (79).

The Methylation of Mercury

Methylation of a metal—i.e. the transfer of a methyl group from an organic compound to the metal ion—is not a facile chemical reaction, at least in aqueous solution. It ultimately requires the transfer of an alkyl anion group (such

as CH_3^-), a strong base highly unstable in water. Thus, methylation reactions either are the result of photochemical processes or need to be catalyzed by microorganisms. It is possible that photochemical reactions involving, for example, acetate or humic acids may lead to the formation of methylmercury in natural waters. Laboratory data have shown that Hg(II) is photomethylated in the presence of acetate (1, 2), but there are no direct field data implicating photoproduction of MeHg. As discussed above, field studies show a net photochemical demethylation in oxic surface waters. In anoxic waters with sufficient light penetration (like those that support the growth of green and purple sulfur bacteria), it is conceivable that, in the absence of species such as singlet oxygen, net photomethylation would be observed. However, the methylmercuric sulfide ion (CH_3HgS^-), which is the dominant form of methylmercury in anoxic water (see Figure 7), has been shown to be readily decomposed by sunlight to CH_4 and HgS (12). Nonetheless, a balance of photochemically induced methylation and demethylation reactions may be important in maintaining low levels of MeHg in some natural waters (such as the surface of deep lakes and oceans).

There has long been massive circumstantial evidence that sulfate-reducing bacteria are responsible for the bulk of mercury methylation in natural waters (29): Sulfate-reducers in cultures are effective at methylating mercury; methylation rates are observed to correlate in time and space with the abundance and activity of sulfate-reducers; and the addition to natural samples of molybdate, a specific inhibitor of sulfate reduction, inhibits mercury methylation.

Recently, mechanistic evidence has been obtained to support the dominant role of sulfate-reducers in mercury methylation. In laboratory cultures with very elevated mercury concentrations (0.5 mM), the bacterium *Desulfovibrio desulfiricans* was shown to produce large amounts of MeHg (18, 19). The methylation of Hg(II) is enzymatically mediated in the presence of cobalamin (20). The higher methylation rates observed during fermentative growth compared to sulfate-reducing conditions may be due to the presence of pyruvate, which is necessary for the functioning of the enzyme. The nature of the enzyme has still to be investigated to resolve whether mercury methylation is the result of a specific process or of an aberrant side reaction of the enzyme at high mercury concentrations.

Although model sediment studies and pure culture studies are clearly showing the importance of sulfate-reducing bacteria in mercury methylation, its importance in the field, at natural concentrations, has yet to be demonstrated as convincingly. In particular, field observations and experiments with natural samples show that methylation increases with the sulfate concentration up to 200–500 μM and decreases at higher concentrations (29). Thus, sulfate

concentrations in estuaries and seawater may be too high for methylation by sulfate-reducing bacteria to be efficient.

MICROBIAL UPTAKE OF MERCURY

To be methylated by sulfate-reducing bacteria or to enter the aquatic food chain via phytoplankton or bacteria, mercury must first be transported across the lipid membrane that surrounds unicellular organisms. The microbial uptake of mercury is thus a key step both in its methylation and its bioaccumulation.

Most metals enter cells via specialized transmembrane cation transporters, or they "leak" through the transporters of other metals. Indeed, at high concentrations, Hg(II) is transported into *mer*-carrying bacteria via a specialized MerT transport protein. At low concentrations, however, the cellular uptake of mercury, unlike that of other cationic metals, such as zinc or cadmium whose coordination properties are similar, appears to be effected chiefly by diffusion through the lipid membrane of lipid-soluble mercury complexes. The chemical bonding in the dichloro mercuric complex, $HgCl_2$, is largely covalent rather than ionic, such that the uncharged complex is relatively nonpolar and has fair lipid solubility. Lipid solubility is generally quantified by the "octanol-water partition coefficient," K_{ow}, which measures the relative solubilities of a compound in octanol and water and ranges from near zero for very hydrophilic molecules to 10^8 for very hydrophobic ones (69). The K_{ow} of $HgCl_2$ is 3.3, showing almost equal solubility in both solvents. Like other lipid-soluble species, this complex diffuses rapidly through lipid bilayers (32), leading to an efficient cellular uptake of mercury. This is, of course, not true of the charged chloride complexes such as $HgCl^+$ or $HgCl_3^-$. $Hg(OH)_2$, although uncharged, has a lower K_{ow} (= 0.5) than $HgCl_2$ and diffuses very slowly through membranes (32). The net result is that the chloride concentration and the pH (see Figure 3) greatly affect the cellular uptake of mercury in oxic waters, and all of its direct and indirect consequences such as toxicity or methylation.

While it seems clear that $HgCl_2$ is the key chemical species determining cellular uptake of inorganic mercury in oxic waters, the question remains of what species may play a similar role in anoxic waters, where most of the methylation occurs. A possible candidate is the uncharged di-bisulfide-mercury complex, $Hg(Hs)_2$, which dominates the speciation of Hg(II) at pH < 6.3 (see Figure 6). Except for the higher methylation rates observed at lower pHs (52, 64, 86), there are no reported experiments that directly or indirectly implicate $Hg(HS)_2$ in microbial uptake or methylation, however, and its K_{ow} is unknown. Perhaps the species of mercury that are important for bacterial uptake are the putative polysulfide complexes HgS_n, which carry no net charge. Some may have a low polarity and diffuse efficiently through cellular membranes. If this were

the case, the presence of polysulfides might be an important factor determining the methylation rate in natural waters. One should note, however, that the only published study on mercury-polysulfide complexes (58) reports the existence of $Hg(S_n)HS^-$ complex but shows no evidence of an uncharged HgS_n species.

Like that of inorganic mercury, the microbial uptake of methylmercury is effected by diffusion of its uncharged chloride complex, CH_3HgCl. The lipid solubility of CH_3HgCl is similar to that of $HgCl_2$, and its permeability through cellular membrane is also similar ($K_{ow} = 1.7$). The accumulation of methylmercury in the food chain should thus be favored by conditions that maximize the formation of the CH_3HgCl species, namely low pH and high chloride concentration (see Figure 5). Field data generally support this conclusion (48).

Other nonpolar mercury species such as $(CH_3)_2Hg$ and Hg^0 also diffuse rapidly through lipid membranes. They are not bioaccumulated, however, as discussed below.

Biomagnification of Mercury in the Food Chain

To yield high concentrations in fish, mercury must not only be taken up efficiently by the microorganisms that are at the bottom of the food chain, it must also be retained by these organisms and passed on to their predators. Many trace metals are efficiently accumulated in planktonic bacteria and microalgae, but most are not biomagnified: Their concentrations in the biomass do not increase (they often decrease) at higher levels in the food chain. A key to understanding mercury bioaccumulation is provided by the contrast between Hg^0, Hg(II), and Me_2Hg, which are not bioaccumulated, and MeHg, which is. Hg^0 and $(CH_3)_2Hg$ are not bioaccumulated, simply because they are not reactive and thus are not retained in phyto- or bacterio-pico-plankton: They diffuse out as readily as they diffuse in. (Note that intracellular oxidation of Hg^0 may be effected by catalase and hydrogen peroxide, as has been shown in red blood cells and brain cells; 21).

The difference between bioaccumulation of Hg(II) and MeHg is more subtle. As we have seen, $HgCl_2$ and CH_3HgCl diffuse through membranes at about the same rate. Both are also reactive with cellular components and are efficiently retained by microorganisms. Laboratory experiments show, however, that the efficiency of transfer between a marine diatom and a copepod is four times greater for MeHg than for Hg(II) (48). This is explained by the fact that Hg(II) becomes bound chiefly to particulate cellular material (membranes) of the diatoms which are excreted rather than absorbed by the copepod. In contrast, MeHg is associated with the soluble fraction of the diatom cell and is efficiently assimilated by the copepod (see Figure 8; 48). Field data indicate that this difference in the efficiency of transfer between Hg(II) and MeHg is applicable to other unicellular microorganisms and their predators (80).
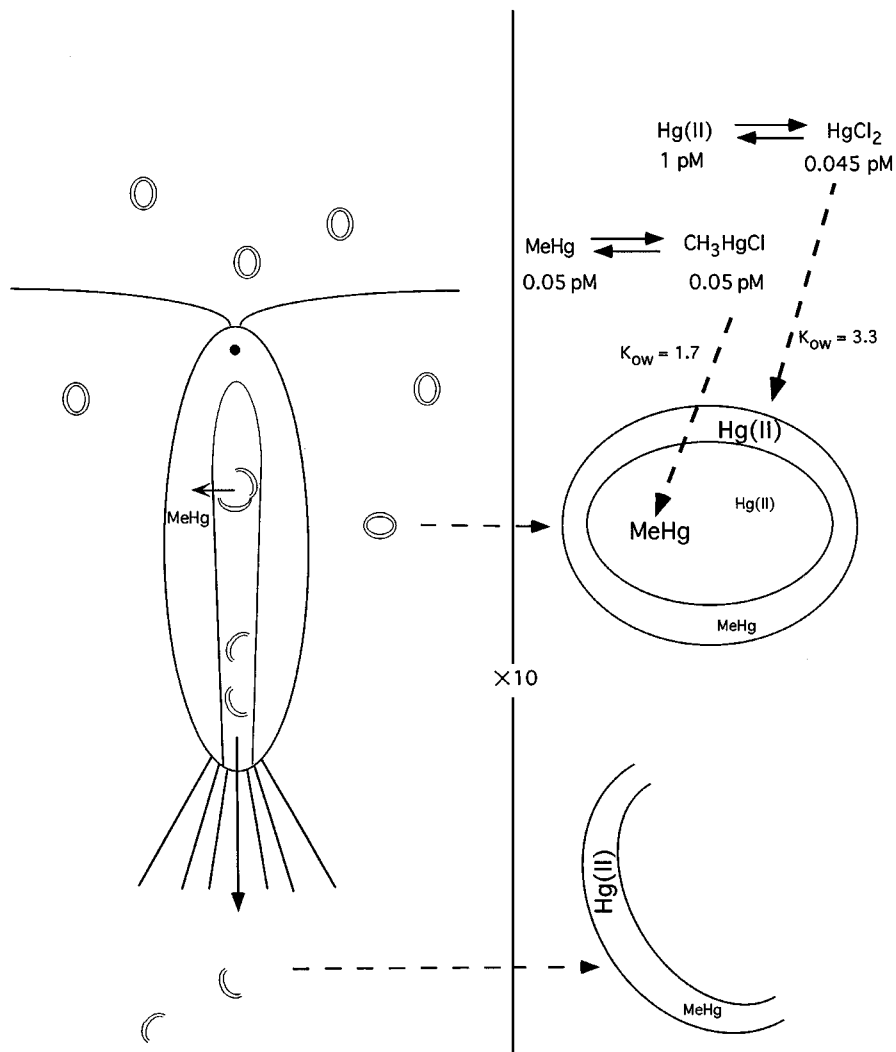
Figure 8   Bioaccumulation of mercury in the first steps of the food chain. Hg(II) and MeHg concentrations are estimates for average seawater (27); HgCl$_2$ and CH$_3$HgCl concentrations are calculated (see Table 1). See text for explanations.

To quantify the difference in the bioaccumulation of inorganic and organic mercury in the first steps of the food chain, we need to take into account three factors: the relative concentrations of Hg(II) and MeHg, the proportion of each that is in a lipid-permeable form, $HgCl_2$ and CH_3HgCl, and the relative efficiency of assimilation by grazers. As seen in Figure 8, even in seawater, where the excess of Hg(II) over MeHg is particularly large, organic mercury should be (and is) more bioaccumulated in grazers than is inorganic mercury.

Further efficient transfer of methylmercury through higher levels of the food chain seems to result from the lipid solubility of CH_3HgCl, which allows it to be partly retained in the fatty tissue of animals. In fish, however, MeHg burden in muscle tissue is more important than in lipids, clearly showing that bioaccumulation cannot be explained solely by MeHg liposolubility (15). In the case of fish, there seems to be a high specificity of the intestine wall toward MeHg absorption. In contrast, inorganic Hg is adsorbed at the microvilli interface, resulting in a very low uptake rate (15). As a result, the average proportion of MeHg over total Hg increases from about 10% in the water column to 15% in phytoplankton, 30% in zooplankton, and 95% in fish (80).

The accumulation of MeHg in higher organisms results mainly from the ingestion of MeHg-containing food rather than direct uptake of MeHg from the water. The structure of the foodweb determines the efficiency of transfer from algae to top predators. The number of trophic levels between predators and prey is critical, as shown by studies that correlate $\delta^{15}N$ (the normalized proportion of ^{15}N in biomass, a measure of trophic level) and Hg bioaccumulation (16, 17). In North American lakes, it has been observed (16, 17) that the presence of certain planktivores, such as lake herring, rainbow smelt, or mysids, which increases the number of trophic levels in the aquatic ecosystem, leads to higher mercury concentrations in top predators.

CONCLUSIONS

Over the past dozen years, much has been learned about the cycle of mercury in the environment. We now have good analytical data for the concentration of various mercury species in a number of environmental settings. We also have reasonable estimates for the various fluxes in the global mercury budget as well as in budgets for particular water bodies. The chemical and biological processes that control those fluxes are very difficult to ascertain and quantify, however, because of their complexities and the very low concentrations involved. Nonetheless, we are beginning to understand the redox mechanisms that control the exchange of mercury between natural waters and the atmosphere and the chemical/biological processes that control the bioaccumulation of mercury in the food chain. Less well understood are the mechanisms that control

the removal of mercury from water to sediments. Most critical of all is the elucidation of the processes that determine the extent of mercury methylation in the environment, particularly the processes that control methylmercury concentrations in surface seawater and the nature of the chemical species that are available to the methylating bacteria in anoxic waters.

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CONTENTS