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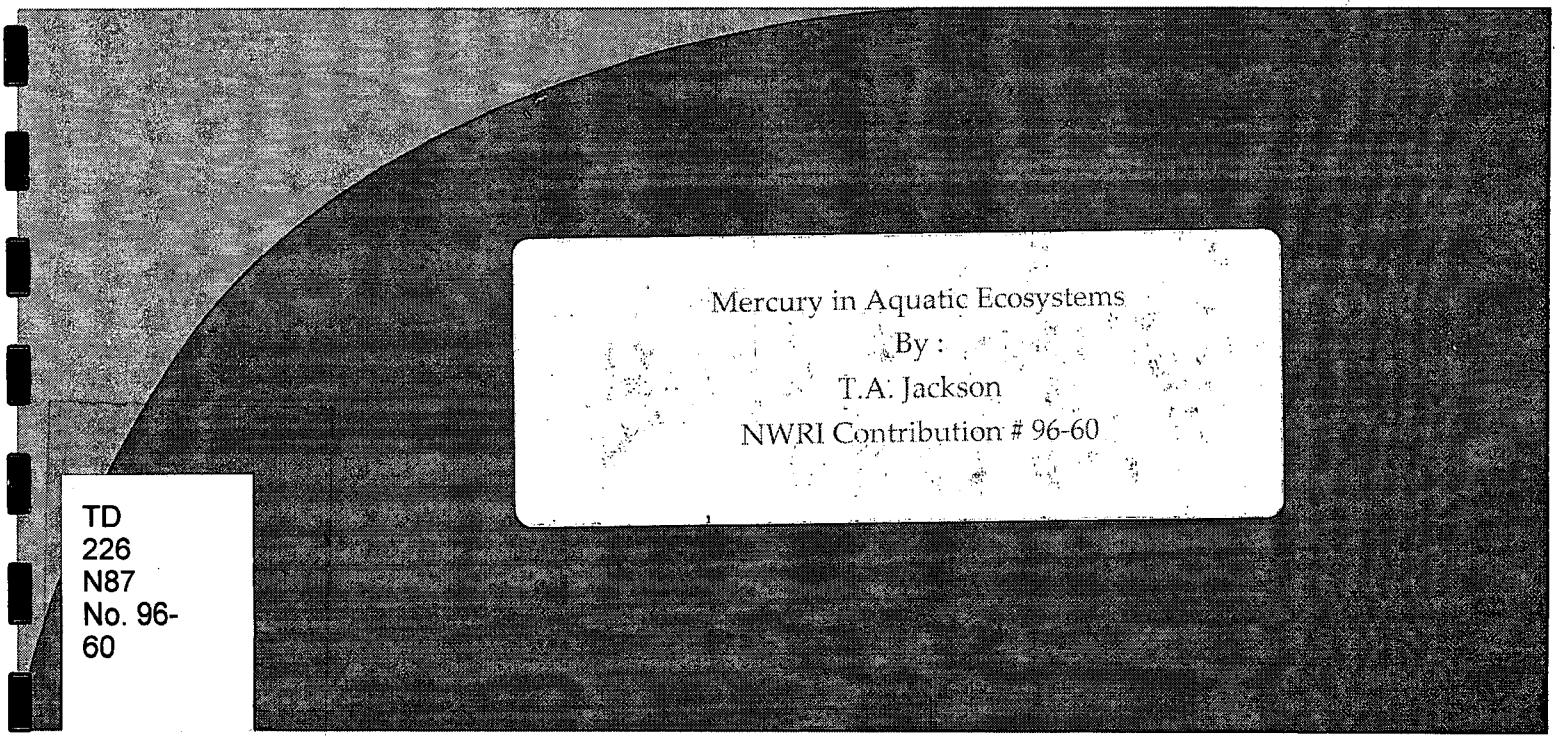

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MERCURY IN AQUATIC ECOSYSTEMS

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"And loathsome canker lives in sweetest bud."

- Shakespeare

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MANAGEMENT PERSPECTIVE

TITLE: MERCURY IN AQUATIC ECOSYSTEMS

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This paper is a review of the biogeochemistry of mercury in aquatic ecosystems. It was written by invitation and, subject to acceptance by the editors, is to be published as a chapter in a forthcoming book on heavy metals in the environment (Langston, W.J. and Bebianno, M. (editors), Metal metabolism in the aquatic environment. Chapman and Hall, London).

Mercury contamination is a serious environmental problem in Canada and many other parts of the world owing to the toxicity of mercury, the accumulation of the toxic, bio-available compound methyl mercury (a by-product of microbial activity) in edible fish and other aquatic organisms in lakes, rivers, reservoirs, and the sea, and the widespread occurrence of the problem. Accumulations of methyl mercury in the flesh of fish consumed by humans pose a public health problem and may lead to outbreaks of Minamata disease (acute or chronic methyl mercury poisoning, which results in permanent nerve and brain damage, leading, in extreme cases, to severe disability or death). Mercury pollution also creates economic hardship for people who earn their living by fishing. Owing to its widespread occurrence as a pollutant and the harm that it has done in many parts of the world, mercury has aroused intense and sustained international concern which has continued to the present day. Moreover, the biogeochemistry of mercury is an extremely challenging subject because it is so complex (involving net effects of countless biological and physicochemical phenomena), and much remains to be learned about it. Consequently, further research is badly needed.

In Canada there have, in the past, been several cases of severe mercury pollution caused by industrial effluents (notably from chlor-alkali plants but from miscellaneous other sources as well) which were discharged into river systems, such as the notorious Wabigoon-English-Winnipeg river system of Northwestern Ontario. However, direct discharge of mercury into aquatic environments from local point sources is far from being the only cause of the merdury problem. Elevated mercury levels in fish are a usual - perhaps universal - side-effect of the impoundment of rivers and flooding of adjacent land to form reservoirs owing to resultant promotion of the growth and activities of methylating microbes, even in essentially pristine areas where only low-level "background" mercury is found, as observed in the hydroelectric reservoirs of northern Manitoba and Québec. Another cause for concern in Canada (mainly in the Canadian Shield), and also in Norway and Sweden, during the past few decades has been a widespread increase in the mercury concentrations in fish inhabiting ill-buffered lakes whose pH levels have been lowered by acid rain. Athough the causes of this large-scale mercury problem are not known and probably involve many factors, there is no doubt that the phenomenon is an effect of long-range atmospheric pollutants, mainly products of the combustion of fossil fuels (especially coal burnt in power plants); these combustion products include not only the sulfur and nitrogen oxides from which the acids of acid precipitation are formed in the atmosphere, but also considerable quantities of mercury, which is concentrated in coal.

This review paper is a comprehensive summary of what is known about the fundamental chemistry, bio-availability, bio-accumulation, toxicity and detoxification, origin, and biogeochemical cycling of mercury in aquatic ecosystems. The topics covered include the fundamental properties (electron configurations, ionisation potentials, polarisability, etc.) and characteristic reactions, speciation (including methylation and demethylation) and complexing, sorption and desorption of mercury, the many environmental and biological variables that control the bio-availability, bio-accumulation, and toxicity of mercury, and the problem of the relative importance of natural and anthropogenic sources and long-range atmsopheric transport of mercury.

MERCURY IN AQUATIC ECOSYSTEMS

T.A. Jackson

Abstract

This paper is a comprehensive review of the biogeochemistry and biological effects of mercury in aquatic ecosystems. The topics dealt with include the following: the basic chemistry (properties and characteristic reactions) of mercury; factors controlling mercury bio-availability and bio-accumulation (speciation and effects of environmental variables and biological activities); toxicity and detoxification; and the biogeochemical cycle of mercury.

(Note: The manuscript does not have an abstract, as it is to be published as a chapter in a book. This abstract was written expressly for the information of NWRI management.)

Introduction.

Mercury (Hg) is one of the most toxic heavy metals. From a biological perspective, it has no redeeming virtue, for, unlike a number of other heavy metals, it is not known to perform any essential biochemical function (Bowen, 1966). Traces of Hg are ubiquitous in soils, natural waters, sediments, organisms, and air (Jonasson and Boyle, 1972), and anomalously high Hg concentrations occur in many ecosystems owing to (1) Hg pollution (a serious, widespread problem), (2) natural Hg enrichment in certain rocks, (3) distinctive properties of Hg, such as its tendency to form highly stable complexes and compounds, including species that are easily taken up by organisms but not readily excreted, (4) natural processes (e.g. methylation) which enhance the bio-availability of Hg, (5) increased bio-availability of Hg due to environmental changes caused by human activities, and (6) efficient accumulation of Hg by organisms and certain natural materials, such as soil organic matter and fine-grained sediments. Moreover, Hg is a relatively volatile element, and this accounts, in large part, for its wide distribution.

Of crucial importance in aquatic ecosystems is microbial conversion of inorganic Hg(II) into the readily bio-accumulated toxic organometallic species methyl Hg (CH_3Hg^+). Unlike inorganic Hg(II), CH_3Hg^+ undergoes biomagnification up the aquatic food chain; hence, most of the Hg in fish consists of CH_3Hg^+, though inorganic Hg predominates in associated water and sediments. Elevated CH_3Hg^+ concentrations in fish are found not only in Hg-contaminated habitats but also in virtually unpolluted ones where conditions favouring CH_3Hg^+ production occur, even if environmental Hg levels are low. CH_3Hg^+ is a health hazard to people who eat contaminated fish, as well as an economic problem for those who fish for a living; and both CH_3Hg^+ and inorganic Hg may poison aquatic organisms. Consumption of fish and shellfish with high CH_3Hg^+ levels has led to outbreaks of Minamata disease, a syndrome of acute or chronic toxic effects, notably irreversible nerve and brain damage leading, in extreme cases, to severe physical and mental disability or death (Takizawa, 1979). Hg has aroused intense and sustained concern because of its toxicity and widespread occurrence as a pollutant.

The purpose of this paper is to review the biogeochemistry and biological effects of Hg in aquatic ecosystems. But to understand these phenomena, we must know the basic properties and characteristic reactions of the element. Therefore, we will begin with a survey of the chemistry of Hg. For brevity, elements and compounds will be represented by their chemical symbols.

The chemistry of Hg.

Properties and reactions. Hg, Cd, and Zn are a family of nontransition heavy metals classed as the Group IIB elements. Heavy metals are defined as metallic elements of specific gravity > $5 g/cm^3$ (Martin and Coughtrey, 1982) and are distinguished by a tendency to form stable complexes (e.g. chelates, sulfides, and hydroxylated species) with partly covalent metal-ligand bonds (Douglas and McDaniel,

1965). But Hg differs strikingly from other heavy metals, including Cd and Zn, in a number of respects.

Within Group IIB, Hg has the highest atomic number and weight, and its divalent cation has the largest ionic radius (Cotton and Wilkinson, 1988). The electron configurations of Hg are $[Xe]4f^{14}5d^{10}6s^2$, the two outermost *s* electrons being the valence electrons. In nature, Hg can exist in any of three interconvertible oxidation states: Hg(0), Hg(I), and Hg(II) (Jonasson and Boyle, 1972). Hg(0) (elemental Hg) has the unique distinction of being a volatile liquid at most earth-surface temperatures (Lide, 1992). It is rather unreactive, and oxidation to HgO by O_2, though thermodynamically favoured, is very slow (Cotton and Wilkinson, 1988); besides, HgO decomposes to Hg(0) + O_2 on exposure to light (Budavari *et al.*, 1989). Therefore, Hg(0) can persist for significant lengths of time in contact with air. Hg(I), which consists of the diatomic cation Hg_2^{2+}, is unstable in most natural environments; it forms no stable aqueous complexes and disproportionates spontaneously to Hg(0) + complexed Hg(II) in the presence of ligands that bind Hg(II) (Jonasson and Boyle, 1972; Beneš and Havlík, 1979; Cotton and Wilkinson, 1988; Douglas and McDaniel, 1965). Thus, the main oxidation states of Hg in nature are Hg(0) and Hg(II). Hg(II), or Hg^{2+}, is the principal form of Hg in aquatic environments. It has a strong tendency to form extremely stable coordination complexes and organometallic compounds whose bonds are mainly covalent, the most stable bonds being those linking the Hg directly to S, N, P, or C. Being rather inert, Hg species do not react readily with O_2 and water (Cotton and Wilkinson, 1988).

The behaviour of Hg is attributable to the electronic configuration and nuclear charge of the Hg atom or Hg^{2+} ion. The valence electrons of a Group IIB metal comprise two *s* electrons situated just outside a filled *d* subshell. Zn has one filled *d* subshell, and Cd has two, but Hg has three of them along with a filled *f* subshell. As the shielding effect of the inner electrons decreases in the order $s > p > d > f$, the nuclear charge is poorly shielded by the *d* and *f* electrons (Sisler, 1963). Therefore, the primary valence electrons and pairs of secondary valence electrons donated by ligands are strongly attracted to the nucleus. Indeed, the primary valence electrons penetrate the inner electron shells, spending part of their time near the nucleus, for such penetration is most readily accomplished by *s* electrons (Sisler, 1963; Douglas and McDaniel, 1965). Because of these effects, the metals form stable, partly covalent bonds with ligands. This tendency is most pronounced in Hg, because Hg, besides having the most *d* orbitals, possesses an *f* orbital and has the highest nuclear charge, exerting the strongest pull on the valence electrons (Douglas and McDaniel, 1965). Thus, Hg has a higher electronegativity and higher stability constant of metal cation hydrolysis than Cd or Zn, has higher first and second ionisation potentials, is much less reactive, and displays the "inert pair" effect (Sillén and Martell, 1964, 1971; Douglas and McDaniel, 1965; Cotton and Wilkinson, 1988; Lide, 1992). Furthermore, Hg^{2+} has a high degree of polarisability (Phillips and Williams, 1965), meaning that its *d* and *f* electron subshells are readily deformed by an applied electric field (Douglas and McDaniel, 1965; Cotton and Wilkinson, 1988). Being

far from the nucleus and unable to get closer by penetration of inner subshells, *d* and *f* electrons are not as securely anchored as *s* and *p* ones and are more easily pushed aside by the repulsive force of electrons in an approaching ligand. Polarisation of Hg^{2+} by a ligand decreases the shielding of the cation's nuclear charge and shortens the Hg-ligand distance, enhancing the stability and covalent character of the bond.

Speciation and complexing of inorganic Hg(II). Owing to its marked ability to attract and retain electrons donated by ligands, Hg(II) forms a variety of very stable complexes whose bonds have a high degree of covalent character, and the formation constants of Hg(II) complexes exceed those of Zn(II) and Cd(II) complexes by orders of magnitude (Cotton and Wilkinson, 1988). Among Hg(II) complexes the most usual coordination number is 2, and the molecular structure is linear, as in $HgCl_2$. The bonds in linear Hg complexes have the highest degree of covalent character, and the dipole moment of such a complex is 0 if the two ligands are identical. The second most common coordination number is 4, as in $HgCl_4^{2-}$; more rarely it is 6, as in $Hg(H_2O)_6^{2+}$, or 3 or 5.

An important consequence of the polarisability of Hg(II) (the "softness" of the Lewis acid Hg^{2+}) is that Hg(II) has a much stronger affinity for large, highly polarisable ligands ("soft" Lewis bases), such as sulfide species, than for smaller, less polarisable ligands ("hard" Lewis bases) such as O-bearing ones (e.g. -COOH) (Douglas and McDaniel, 1965; Williams, 1971; Schuster, 1991). The preferential binding of Hg(II) by soft Lewis bases is due to stabilisation of the resulting complexes by mutual polarisation of the cation and its ligands (Douglas and McDaniel, 1965). In theory, the relative affinities of Hg(II) for electron-donating elements within different groups are as follows: Group VIb: $O << S < Se \approx Te$; Group VIIB: $F << Cl < Br < I$ (Williams, 1971). The Hg(II)-binding capacities of aliphatic complexing agents of similar size decrease in the order $R\text{-}SH >> R\text{-}NH_2 > R\text{-}COOH$ (Reimers and Krenkel, 1974; Reimers *et al.*, 1975), demonstrating that Hg(II) forms more stable bonds with -SH groups than with the harder N- and O-bearing groups (Williams, 1971). In anoxic natural environments, Hg(II) is preferentially bound by sulfides (Gavis and Ferguson, 1972; Jackson (1988b).

Dissolved inorganic Hg(II) readily combines with inorganic sulfide (H_2S, HS^-, and S^{2-}) to precipitate black HgS, which is kinetically favoured over the thermodynamically more stable red HgS (cinnabar) (Cotton and Wilkinson, 1988). Black HgS has a very low solubility product (10^{-54}), but some Hg(II) and sulfide remain in solution as hydrolysis products (Cotton and Wilkinson, 1988). Moreover, Hg(II) forms soluble sulfide and mixed-ligand complexes, including HgS_2^{2-}, $Hg(SH)_2$, $Hg(SH)S^-$, $HgSH^+$, $Hg(S_6)_2^{2-}$, HgOHSH, and HgClSH as well as solid HgS, the proportions of the products depending on the pH and the concentrations of the reactants (Gavis and Ferguson, 1972; Cotton and Wilkinson, 1988; Dyrssen and Wedborg, 1991; Hudson *et al.*, 1994). If Fe(II) is vastly more abundant than Hg(II), as is usual in nature, the Hg(II) coprecipitates with FeS. Hg(II) also forms highly stable bonds with -SH (thiol) groups of organic sulfides, including proteins, cysteine, and "thiols" (mercaptans) formed by putrefaction of

proteins. Aliphatic thiols bind Hg more effectively than inorganic sulfide does (Douglas and McDaniel, 1965; Dyrssen and Wedborg, 1991), as the alkyl chain releases electrons to the S atom, strengthening the Hg-S bond (Roberts and Caserio, 1965). The stability of sulfide complexes depends on the dissolved O_2 level, because oxidation of the ligand releases the bound Hg (Jernelöv, 1972).

Hg(II) has a greater affinity for Se and Te analogues of sulfides than for sulfides (Rimerman *et al.*, 1977; Dyrssen and Wedborg, 1991), because they are more polarisable (Williams, 1971). The solubility products of Hg sulfide, selenide, and telluride decrease in the order HgS > HgSe > HgTe (Björnberg *et al.*, 1988). Hg and Se are closely associated in lake sediments, even at very low or high pH, implying the existence of extremely stable Hg-Se bonds (Jackson, 1991a; Jackson *et al.*, 1980). In nature Se is orders of magnitude less abundant than S; yet both selenides and sulfides play significant parts in the biogeochemistry and toxicology of Hg.

Hg(II) is also complexed by nitrogenous ligands (e.g. R-NH_2) and O-bearing ligands (e.g. R-COO^-, OH^-, and H_2O), including ligands of amino acids and nucleic acids (Douglas and McDaniel, 1965; Gavis and Ferguson, 1972; Ochiai, 1977; Cotton and Wilkinson, 1988). But such ligands, being hard or intermediate between hard and soft, form less stable bonds with Hg(II) than sulfides do (Williams, 1971; Reimers and Krenkel, 1974).

Organic matter - notably humic substances, which are among the most common, abundant, and effective complexing agents in soil, water, and sediments (Aiken *et al.*, 1985) - forms very stable complexes with Hg(II) (Trost and Bisque, 1972; Lindberg and Harriss, 1974; Andren and Harriss, 1975; Ramamoorthy and Kushner, 1975b; Reimers *et al.*, 1975; Khalid *et al.*, 1977; Jackson *et al.*, 1978; Jackson *et al.*, 1980, 1982; Andersson, 1979; Kerndorff and Schnitzer, 1980; Randle and Hartmann, 1987; Semu *et al.*, 1987; Jackson, 1989; Xu and Allard, 1991; Stordal *et al.*, 1996). It has been shown repeatedly that the complexing capacity of humic matter is far greater for Hg than for other heavy metals such as Cd, Zn, Cu and Pb, apparently because it forms the most highly covalent bonds with ligands (Ramamoorthy and Kushner, 1975b; Kerndorff and Schnitzer, 1980; Jackson *et al.*, 1980). The majority of ligands in humic matter are O-bearing ones (-COOH, phenolic [and enolic?] -OH, and >C=O), but nitrogenous ligands (e.g. -NH_2, -NH-, and -N=), along with some S-bearing groups (-SH?), are present as well (Aiken *et al.*, 1985). The S- and N-bearing groups (especially -SH), which probably belong to remnants of biochemical compounds (e.g. proteins), may well bind Hg(II) preferentially even though they make up a minority of the ligands (Bidstrup, 1964; Ochiai, 1977; Ramamoorthy and Kushner, 1975a).

The complexing capacity of organic (e.g. humic) matter for metal cations is minimal under extremely acidic conditions but rises to a maximum with increasing pH within a certain pH range that is characteristic of the metal (Kerndorff and Schnitzer, 1980). Hg(II) binding, while conforming to this rule, is anomalous by virtue of its relative insensitivity to pH, remaining close to peak efficiency

throughout the pH range of natural waters (85-96% even at pH values as low as ~1.0-2.5), increasing with pH and reaching a maximum of ~94-100% within the pH range ~4-7 (Andersson, 1979; Kerndorff and Schnitzer, 1980; Zvonarev and Zyrin, 1982). Similarly, Hg scavenged by organic (largely humic) lake mud was found to be unextractable with HCl up to a strength of 1 M (Jackson *et al.*, 1980). More efficient binding of Hg at higher pH reflects elimination of competing H^+ ions and creation of negatively charged binding sites by dissociation of acidic ligands (Tipping and Hurley, 1992). The same principle applies to acidic ligands in general, including -SH, H_2S, and the -COOH groups of all organic acids that function as chelators. Neutralisation of positively charged, cation-repelling groups like $-NH_3^+$ and $-NH_2^+$- by removal of protons could be a contributing factor. Metal cation hydrolysis, too, may assist the complexing process, as suggested by a correlation between metal-humic acid affinities under weakly acidic conditions (Kerndorff and Schnitzer, 1980) and the stability constants for metal cation hydrolysis (Sillén and Martell, 1964, 1971). However, as the pH rises into the alkaline range, the efficiency of Hg(II) sorption declines somewhat owing to solubilisation of intact Hg-humic complexes (not, as might be supposed, because of the formation of $Hg(OH)_3^-$ anions and negatively charged deprotonated ligands, such as $-COO^-$ and $-O^-$, which repel the anions) (Andersson, 1979; Jackson *et al.*, 1980, 1982; Kerndorff and Schnitzer, 1980; Zvonarev and Zyrin, 1982). In brief, Hg-humic complexes have a high degree of stability which is hardly affected by pH, even extremely acidic or alkaline pH values.

Hg(II) shows a preference for larger organic molecules (e.g. humic acids) in some environments but for smaller ones (e.g. fulvic acids) in others (Lindberg and Harriss, 1974; Andren and Harriss, 1975; Ramamoorthy and Kushner, 1975b; Jackson *et al.*, 1980, 1982; Louchouarn *et al.*, 1993), and the pattern of partitioning between large and small size fractions may vary seasonally too (Jackson *et al.*, 1982). The geographical and temporal variations could reflect differences in source material, environment, and microbial activity (Semu *et al.*, 1987; Schuster, 1991). Preferential scavenging of Hg by large humic molecules in lake mud relative to small ones has been linked to the high electronegativity of Hg, implying that metal-ligand bonds formed by the larger molecules are more stable because they have a higher degree of covalent character (Jackson *et al.*, 1980).

Under reducing conditions organic complexing agents compete with inorganic sulfide for Hg(II) and may solubilise part of the Hg, even in the presence of H_2S (Lindberg and Harriss, 1974; Timperley and Allan, 1974; Khalid *et al.*, 1977; Hallberg, 1978; Jackson *et al.*, 1978; Jackson, 1978, 1979); on the other hand, sulfide may strip Hg(II) from non-thiol organic ligands. In anoxic, H_2S-generating freshwater mud, partitioning of Hg and other metals between sulfide and organic matter may be controlled by the stability of the metal sulfide as represented by either its standard entropy *or* its standard enthalpy of formation, depending on the prevailing conditions (Jackson, 1978, 1979). However, it is safe to assume that Hg associated with organic matter is bound preferentially by thiol groups and that Hg(II) always has

a stronger affinity for both inorganic sulfide and thiols than for non-thiol groups of organic complexing agents (Reimers and Krenkel, 1974; Reimers *et al.*, 1975; Jackson *et al.*, 1978).

In natural waters, any dissolved inorganic Hg(II) not bound to organic or sulfide ligands probably consists mainly of hydroxy and chloride complexes. In the absence of ligands other than H_2O and OH^-, aqueous Hg(II), owing to its strong tendency to be hydrolysed, is mostly in the form of hydroxylated species except under extremely acidic conditions (Hahne and Kroontje, 1973; Leckie and James, 1974; MacNaughton and James, 1974; Farrah and Pickering, 1978; Schuster, 1991; Xu and Allard, 1991). The formation of Hg-OH complexes is a function of pH. In theory, the dominant Hg(II) species at pH $< \sim 2$ or 3 is the "free" Hg^{2+} cation ($Hg(H_2O)_6^{2+}$). But the proportion of the Hg in the form of the OH^- complexes $HgOH^+$ and $Hg(OH)_2$ increases sharply to $\sim 100\%$ as the pH rises from ~ 1 to 4, $HgOH^+$ peaking at pH ~ 3, while $Hg(OH)_2$ predominates over other species throughout the pH range $\sim$3-14, which brackets the range of most natural waters. As the pH rises through the alkaline range, the complex anion $Hg(OH)_3^-$ becomes increasingly significant, but it never exceeds $Hg(OH)_2$.

Hg(II) forms stable complexes with Cl^-, Br^-, and I^- as well as sulfides, organic ligands, and OH^-. Hg halide stability in solution increases in the order of increasing polarisability of the ligand, i.e. $Cl^- < Br^- < I^-$ (Douglas and McDaniel, 1965; Williams, 1971). But in nature most Hg complexes of this class are probably chlorides (Gavis and Ferguson, 1972), as Cl^- is far more abundant than Br^- or I^- and forms the most water-soluble Hg complexes, halide solubility decreasing in the order $HgCl_2 >> HgBr_2 >> HgI_2$ (Cotton and Wilkinson, 1988; Budavari *et al.*, 1989; Lide, 1992). Therefore, competition between Cl^- and OH^- ions plays a significant part in the aqueous chemistry of Hg(II), the proportions of the various possible complexes at equilibrium being dependent on the Cl^- and Hg(II) levels and the pH. Assuming values of these variables that might be expected in freshwater environments, and leaving organic and sulfide ligands out of consideration, $HgCl_2$ (with smaller amounts of Hg^{2+}, $HgCl^+$, $HgCl_3^-$, $HgCl_4^{2-}$, and HgOHCl) predominates under acidic to neutral or mildly alkaline conditions, but $HgOH_2$ (with smaller amounts of $Hg(OH)_3^-$ and HgOHCl) is the most abundant species over all or most of the alkaline pH range (Hahne and Kroontje, 1973; Leckie and James, 1974; MacNaughton and James, 1974; Farrah and Pickering, 1978; Schuster, 1991; Hudson *et al.*, 1994). The critical pH separating the field of Hg chloride predominance from that of Hg hydroxide predominance shifts to higher or lower values as the Cl^- level increases or decreases, respectively. The hybrid species HgOHCl peaks at this pH, approaching $HgCl_2$ and $Hg(OH)_2$ in abundance. In short, $HgCl_2$ and $Hg(OH)_2$ are probably the main inorganic Hg species in oxygenated, sulfide-free fresh waters. But $HgCl_3^-$ and $HgCl_4^{2-}$ become increasingly important with rising Cl^- level, attaining predominance in seawater (Andren and Harriss, 1975).

Inorganic Hg(II) ions (e.g. Hg^{2+}, $HgOH^+$, $HgCl_4^{2-}$, and HgS_2^{2-}) are hydrophilic and water soluble; but uncharged linear complexes (e.g. $HgCl_2$, $Hg(OH)_2$, HgOHCl, $Hg(SH)_2$, HgOHSH, and HgClSH) are

more or less lipophilic owing to their lack of an electric charge and the largely covalent character of their bonds (which limits bond polarity and impedes dissociation in water). In addition, any linear complex whose two ligands are identical (e.g. $HgCl_2$, $Hg(OH)_2$, or $Hg(SH)_2$) has a dipole moment of 0, increasing its lipophilic character (though the individual bonds have polarity). For the same reasons, and also because of its low molecular weight, $HgCl_2$ is slightly volatile at ordinary temperatures (Budavari *et al.*, 1989). Hg salts in general have appreciable volatility (Matheson, 1979).

On the other hand, uncharged Hg(II) species have some degree of hydrophilic as well as lipophilic character and hence are somewhat soluble in water (Budavari *et al.*, 1989). The relative lipophilicity and hydrophilicity of an uncharged species depend on the molecule's dipole moment (if any) and the polarity of its individual bonds, and are critically dependent on the nature of the anions bound to the Hg(II) (Mason *et al.*, 1995b). Thus, $HgCl_2$ is much more lipophilic than $Hg(OH)_2$, its octanol-water partition coefficient (K_{ow}) being two orders of magnitude greater (even though neither species has a dipole moment) (Mason *et al.*, 1995b). This probably indicates that $Hg(OH)_2$, unlike $HgCl_2$, forms H-bonds with water.

In the complexing of Hg(II), Cl^- ions compete with other ligands (even sulfides) and tend to release Hg(II) from them, forming dissolved Hg-Cl^- complexes (Carty and Malone, 1979; Schuster, 1991). Yet different studies have led to quite different conclusions about the effectiveness of Cl^- in releasing Hg from sulfide and organic matter or interfering with the binding of Hg by these substances (Reimers and Krenkel, 1974; Jackson *et al.*, 1980; Randle and Hartmann, 1987; Jackson, 1989; Schuster, 1991), suggesting that reactions between Hg(II) and competing ligands are controlled by an assortment of factors, including environmental variables and the properties and concentrations of the reactants.

Photochemical reactions also play important roles in Hg speciation. Many Hg(II) species are reduced to Hg(I) or Hg(0) by ultraviolet (UV) or visible light, as in Eder's reaction ($HgCl_2 \xrightarrow{\text{oxalate, } h\nu} Hg_2Cl_2$) (Balzani and Carassiti, 1970; Baughman *et al.*, 1973), owing, perhaps, to the high polarisability of Hg(II). Amyot *et al.* (1994) showed that sunlight can induce production of "dissolved gaseous mercury" in lake water, suggesting reduction of Hg(II) to Hg(0) (a plausible inference, though the forms of Hg were not identified). Reactions requiring UV light of wavelength (λ) < 290 nm must be negligible at the Earth's surface but could be significant for volatile Hg(II) species which, on evaporating, migrate into the stratosphere (Kondratyev, 1969). Photochemical reactions of Hg may be promoted by photosensitising agents (e.g. $FeCl_3$, MnO_4^-, Mn^{2+}, Mn and Co oxalates, and fluorescent dyes in Eder's reaction) (Balzani and Carassiti, 1970). These agents absorb light, making its energy available for the reactions, and may enable the reactants to use light of frequencies which could not otherwise be employed: Eder's reaction normally requires UV light of $\lambda < 350$ nm but can be driven by visible (blue) light if photoreactive impurities such as Fe oxalate are present. There are also many substances

that inhibit photochemical reactions; thus, O_2, O_3, H_2O_2, H^+, CrO_4^{2-}, and phenol tend to block Eder's reaction. In nature, Hg photochemistry could be very complex, with promotion and inhibition of different reactions occurring simultaneously. Humic matter, Fe and Mn oxides, and mineral-humic complexes can promote or suppress a variety of photochemical reactions (Baxter and Carey, 1982, 1983; Choudhry, 1984; Langford and Carey, 1987; Zepp, 1988) and may participate in photochemical reactions of Hg (Allard and Arsenie, 1991).

Inorganic Hg is subject to reduction or oxidation by purely chemical or biochemical mechanisms as well as photochemical ones, or by a combination of these processes. Many abiotic reactions occur in the atmosphere; these include oxidation of Hg(0) to Hg(II) by O_3 and reduction of Hg(II) to Hg(I) by aqueous SO_3^{2-}, followed by release of Hg(0) owing to breakdown of the Hg(I) (Lindqvist *et al.*, 1991; Munthe *et al.*, 1991; Schroeder *et al.*, 1991). In water, humic matter may reduce Hg(II) to Hg(0), possibly through donation of electrons by free radicals (Alberts *et al.*, 1974), and the reaction is promoted by light (Allard and Arsenie, 1991; Xiao *et al.*, 1995). H_2O_2 formed photochemically through the agency of humic matter (Baxter and Carey, 1982, 1983), may oxidise Hg(0) to Hg(II) or reduce Hg(II) to Hg(0), depending on the ambient pH (Schroeder *et al.*, 1991). Finally, Hg(II) is converted to Hg(0) by bacteria (including cyanobacteria) and planktonic algae in lakes and in the ocean (Schottel *et al.*, 1974; De Filippis and Pallaghy, 1975; Summers, 1988; Baldi *et al.*, 1989, 1993a; Nakamura *et al.*, 1990; Barkay *et al.*, 1991; Regnell and Tunlid, 1991; Radosevich and Klein, 1993; Mason *et al.*, 1995a). Microbial reduction of Hg(II) to Hg(0) is catalysed by mercuric reductase (Summers, 1988; Baldi *et al.*, 1989; 1991).

Sorption and desorption of inorganic Hg(II). Hg(II) is rapidly and efficiently removed from solution through sorption by fine suspended matter and sediments (Jackson, 1996) and is not readily leached out by mild extractants such as solutions of $CaCl_2$ and the chelator DTPA (Hogg *et al.*, 1978; Jackson, 1984, 1988b, 1996; Jackson and Woychuk, 1980a, 1980b; Jackson *et al.*, 1982). As a rule, the finest particles (colloidal [clay-sized] ones, which are < 2 μm in diameter) have the highest sorption capacities owing to their large specific surfaces (Jackson, 1996), though exceptions occur, as with coarse organic debris (Ramamoorthy and Rust, 1976). The most important sorbents in nature are the following: (1) clay minerals; (2) "amorphous" (short-range order) oxides, hydroxides, and oxyhydroxides ("hydrated" or "hydrous" oxides) of Fe, Mn, and Al (e.g. FeOOH and MnOOH), all of which will, in this review, be termed "oxides" for brevity; (3) amorphous FeS, which occurs only under reducing conditions; (4) particulate humic substances; (5) nonhumic organic matter, including plankton, biofilms, extracellular biogenic colloids, faecal pellets, and moulted exoskeletons of planktonic crustaceans; and (6) composite particles, such as clay and plankton hard parts with coatings of oxide or humic matter, or both (Jackson, 1978; Jackson *et al.*, 1980; Jackson and Bistricki, 1995). The scavenging of Hg and other metals by FeS and oxides commonly occurs by coprecipitation, whereby the metals are sorbed and simultaneously

enclosed in a growing mass of precipitate (Inoue and Munemori, 1979). Environmental processes (e.g. a drop in pH or solubilisation of metals by complexing agents) may result in release (desorption) of sorbed metals; but if the metals are sealed inside a precipitate owing to coprecipitation, they are released only if the precipitate is dissolved or decomposed, as in the reduction and dissolution of MnOOH and FeOOH or the oxidation of FeS. The binding and release of metals by sorbents are controlled by many variables (Jackson, 1996), notably metal properties, characteristics of the sorbent, environmental conditions, competition between different metals for sorption sites, and the concentrations of the reactants. A further complication is that sorption energy varies from one sorption site to another, even within a single particle, and does not bear a consistent relationship with sorption capacity (Jackson, 1996). (Sorption energy doubtless affects the sorption capacity but is not the only factor that does so.)

The mechanisms of metal uptake by particulate matter may be summarised as follows: (1) Rather weak, readily reversible sorption of metal cations occurs at sites of permanent negative charge (cation exchange sites) on the 001 (basal cleavage) faces of clay crystals, where the cations, their hydration spheres intact, are held by ionic bonding reinforced by H-bonding but have no direct contact with the atoms of the mineral surface. But these exchange sites make little contribution to the sorption of heavy metals, as heavy metal cations are easily displaced from them by the far more numerous common cations (Na^+, Ca^{2+}, H^+, etc.) through mass action. (2) Small uncharged metal species are subject to weak, ephemeral sorption to uncharged areas of particle surfaces by van der Waals forces, other dipole interactions, and H-bonds. This mechanism, too, is relatively ineffectual. (3) "Specific sorption," or "surface complexation," of cationic, anionic, and uncharged heavy metal species is the characteristic uptake mechanism of oxides and edge faces of clay. Under suitable conditions (e.g. within a favourable pH range), heavy metals are strongly and preferentially complexed by the various oxygenic ligands (O, OH, O^-, etc.) that make up the mineral surfaces, the result being the formation of stable, partly covalent coordinate bonds linking the metals *directly* to structural units of the mineral. This process involves ligand exchange and some ion exchange (displacement of ligands (e.g. H_2O and OH^-) from dissolved metal species, displacement of H^+ and OH^- ions from the mineral by cations and oxyhydroxy complex anions, respectively, of the metals, etc.). Heavy metals are rapidly and easily bound in this way but may be desorbed only slowly and with difficulty. Depending on the ambient pH, a surface ligand of a mineral may have a transitory negative or positive charge owing to deprotonation or protonation, functioning, respectively, as a cation or anion exchange site; heavy metal ions may be attracted to these sites by coulombic forces initially but end up being fixed to the mineral by partly covalent coordinate bonds, which are more stable than ionic bonds. The process may be augmented somewhat by H-bonding. Moreover, the sorption of heavy metals by FeS and organic particles is due to complexing by surface ligands and is therefore embraced by the term "specific sorption." The discussion of metal complexing

by sulfides and organic matter given in the preceding section is applicable here and need not be repeated. For a detailed review of published information about the binding and release of heavy metals by colloidal minerals, see a forthcoming treatise by Jackson (1996).

Specific sorption is the principal mechanism - and by far the most effective mechanism - for the binding of Hg(II) and other heavy metals whose cations are readily hydrolysed. This phenomenon, however, is highly pH-dependent, often reaching maximum efficiency with rising pH over the pH range in which the free cation becomes hydroxylated. In the absence of Cl^- ions the sorption capacity of Mn oxide (Lockwood and Chen, 1973) or quartz (Leckie and James, 1974; MacNaughton and James, 1974; Schuster, 1991) for Hg(II) is lowest at pH $\leq \sim 1.5$ or 2.5 (at which Hg is chiefly in the form of Hg^{2+}); but sorption efficiency rises sharply to its maximum as the pH is raised to 4 (i.e. as Hg^{2+} is hydrolysed to $HgOH^+$ and $Hg(OH)_2$). (The curve showing this abrupt increase is called the "sorption edge.") Over the pH range ~4 to 6 or 7, in which nearly all the Hg is in the form of $Hg(OH)_2$, the % Hg removed from solution is constant or decreases slightly; and the pH effect is essentially the same for Fe oxide, Mn oxide, and quartz (Forbes *et al.*, 1974; Kooner *et al.*, 1995). But from pH ~6 or 7 to pH 11 there is a decline in sorption efficiency, possibly reflecting the predicted increase in $Hg(OH)_3^-$ concentration. In brief, Hg(II) is most efficiently sorbed by minerals at moderately acidic to neutral pH values and is poorly sorbed under extremely acidic or alkaline conditions. Comparable results have been reported for coprecipitation of Hg(II) with FeOOH, the % bound being highest at pH ~6-8 (Inoue and Munemori, 1979). Data such as these could mean that $HgOH^+$ and $Hg(OH)_2$ are the most efficiently sorbed Hg species (Hahne and Kroontje, 1973; Schuster, 1991). Little Hg^{2+} is sorbed because of competition with H^+ ions, repulsion by positively charged (protonated) sites on oxide surfaces (as would also be true of the edge faces of clay), and possibly interference by H_2O molecules coordinated to the Hg^{2+} ions (Leckie and James, 1974), while $Hg(OH)_3^-$ is not sorbed because it is repelled by negatively charged sites formed by removal of H^+ ions from OH groups of mineral surfaces (and sorption of OH^- ions?). Nevertheless, the exact mechanisms of specific sorption are open to debate (Jackson, 1996). Moreover, specific properties of the mineral surface may play a part. In experiments on the sorption of $Hg(NO_3)_2$ by clay minerals over the pH range ~3-12, Farrah and Pickering (1978) found that illite, kaolinite, and montmorillonite gave qualitatively different results. Only illite approximated the expected pattern of variation with rising pH (i.e. a steady increase in sorption capacity up to a plateau followed by a decline). But the results are mostly inconsistent with data reported by Andersson (1979), who showed qualitatively similar variations for all three minerals. As the clay specimens of Farrah and Pickering had been "finely ground" and subjected to other treatments before being used, the possible occurrence of artefacts cannot be discounted. Coatings or other surface impurities on the clay could also account for the discrepancy.

The Hg(II) sorption capacities of minerals and organic matter usually show qualitatively similar

variations with respect to pH, but there is a major quantitative difference. Under acidic conditions the sorption capacities of mineral particles decline sharply with decreasing pH, whereas organic matter shows only a slight decline (Andersson, 1979; Zvonarev and Zyrin, 1982). Thus, 1 M HCl was unable to leach sorbed Hg from organic lake mud (Jackson *et al.*, 1980), whereas it extracted 10-25% of the Hg sorbed to mineral-rich soils (Hogg *et al.*, 1978). In general, organic matter is the main binding agent for Hg(II) in acidic sulfide-poor environments.

Oxides and humic matter have much higher sorption capacities for Hg(II) than clay minerals do (Andersson, 1979; Schuster, 1991) - even the clay minerals with the highest cation exchange capacities (e.g. montmorillonite); indeed, cation exchange capacity and heavy metal sorption capacity vary independently of each other (Jackson, 1996). Thus, Andersson (1979) reported that the amount of Hg(II) sorbed by soils and soil constituents in the pH range 6-9 decreased in the order hydrated Fe oxide > organic soils > illite-rich clay soil > bentonite (i.e. montmorillonite) > kaolinite. The affinity of Hg(II) for thiol groups probably goes far toward explaining the marked ability of organic matter to sorb Hg, and under reducing conditions both FeS and organic particles containing thiol groups are probably the chief sorbents of Hg(II) (Schuster, 1991). Fe, Mn, and Al oxides differ among themselves in their sorption capacities for heavy metals. But regardless of composition, freshly precipitated amorphous oxide gels have much higher sorption capacities than the well crystallised phases that eventually form from them during ageing (Jackson, 1996), and crystallisation may be accompanied by release of bound Hg(II) (Waslenchuk, 1975). Among common clay minerals, sorption capacity for Hg(II) decreases in the order illite > montmorillonite > kaolinite (Reimers and Krenkel, 1974; Andersson, 1979). This series bears no consistent relation to cation exchange capacity, which decreases in the order montmorillonite >> illite $\geq$ kaolinite (Jackson, 1996); it probably reflects distinctive properties of the edge faces of the clay. Note that clay minerals, despite their limitations as sorbents, play important roles as carriers of Hg and other metals bound to associated oxides and humic matter. Clay crystals, silt and sand grains, and plankton hard parts commonly have Fe and Mn oxide coatings, and both clay and oxide minerals may be coated with humic matter. Such coatings probably play important roles in the biogeochemistry and transport of metals (Jackson, 1989, 1996; Jackson and Bistricki, 1995).

Competition between Hg(II) and other metals for binding sites must also be considered, but the results of comparative studies have been somewhat inconsistent. Organic matter preferentially binds Hg(II) with respect to other metals at low pH, but colloidal minerals may have relatively low binding capacities for Hg(II). Even in the pH range most favourable for sorption of Hg(II) (pH ~4-7), the % sorbed by a mineral (e.g. goethite) is lower for Hg(II) than for other hydrolysable heavy metal cations, such as divalent Cd, Zn, Cu, and Pb (Schuster, 1991). This surprising fact suggests that the largely covalent Hg-OH bond diminishes the stability of the bonds linking Hg-OH complexes to mineral surfaces (Schuster,

1991). In a study mentioned by Siegel and Siegel (1979), the affinities of divalent metals for montmorillonite decreased in the order Pb > Cu > Ca > Ba > Mg > Hg. For kaolinite, sorption energy decreased in the order Hg > Cu > Pb, but calcium replacement decreased in the order Pb > Cu > Hg, signifying an inverse relation between sorption strength and sorption capacity: Hg was the most strongly bound metal, but the quantity of Hg sorbed was smallest. However, Ramamoorthy and Rust (1978) claimed that the "order of cation exchange" in fluvial sediment poor in organic matter was Hg > Pb > Cu > Cd. These results suggest that the outcome of competition for binding sites is hard to predict, as it is the net result of many interacting variables.

A dissolved complexing agent may either hinder or promote the sorption of a heavy metal by particulate matter or have no apparent effect (Jackson, 1996). The net effect depends on the partitioning of "free" and complexed forms of the metal between the solution phase and solid phase. A complexing agent may interfere with metal sorption or enhance desorption by forming a highly soluble metal complex, but it may promote metal sorption if the complex itself is readily sorbed. Fulvic acid has been found to enhance the sorption of Hg(II) by α-Al_2O_3 over a wide pH range (2.5-9.5) (Xu and Allard, 1991), reflecting the tendency of humic matter to form stable associations with mineral colloids (Schnitzer and Khan, 1972). Yet Cl^- ions commonly interfere with the binding of Hg(II) by natural sorbents and complexing agents, and may release Hg(II) from these binding agents by the formation of soluble Hg-Cl complexes which are more weakly sorbed than Hg-OH complexes (Feick *et al.*, 1972; Lockwood and Chen, 1973; Forbes *et al.*, 1974; Leckie and James, 1974; MacNaughton and James, 1974; Reimers and Krenkel, 1974; Newton *et al.*, 1976; Kinniburgh and Jackson, 1978; Ramamoorthy and Rust, 1978; Inoue and Munemori, 1979; Jackson *et al.*, 1982; Wang *et al.*, 1985, 1988, 1991; Schuster, 1991; Chen *et al.*, 1995). As the concentration of dissolved Cl^- increases, the sorption edge of Hg(II) is displaced toward higher pH values, reflecting competition between Cl^- and OH^- for Hg(II) and preferential sorption of hydroxylated Hg species (Leckie and James, 1974; MacNaughton and James, 1974; Andersson, 1979), and the maximum % Hg(II) sorbed is lowered (Leckie and James, 1974; Schuster, 1991). Thus, dissolved Hg-Cl^- complexes are not readily sorbed by suspended organic and mineral particles; and if the particles have a preponderance of negative charges, as is usually the case, they repel anionic Cl^- complexes. As would be expected, Cl^- ions compete more successfully with sorption sites of clay and -COOH groups of organic matter than with -SH and $-NH_2$ groups of organic matter (Reimers and Krenkel, 1974), and solubilises Hg(II) much more readily from clay and silt than from organic matter (Jackson *et al.*, 1982). The Cl^- concentration and Cl^-/Hg ratio, and various environmental factors such as pH, also have important effects (Reimers and Krenkel, 1974). The negative effect of Cl^- ions on sorption is particularly strong at lower pH values, as Hg-OH^- complexes, which predominate at higher pH values, are more readily sorbed than Hg-Cl^- complexes. Occasionally, however, Cl^- promotes the

sorption of Hg by forming anionic Hg-Cl^- complexes which are bound by positively charged sites of oxides or edge faces of clay (Xu and Allard, 1991).

Hg and other heavy metals differ widely in their relative affinities for particular complexing agents and sorbents. For instance, the order of decreasing ability of complexing agents to desorb metals from fluvial sediment poor in organic matter was Hg > Cd >> Pb for Cl^- but was Cd > Hg > Pb in the case of the chelator NTA (Ramamoorthy and Rust, 1978). Moreover, the partitioning of metals between binding agents of water and sediments varies widely from one environment to another. Thus, when Hg and other metals are introduced into lakes by rivers, their relative tendencies to be trapped in lake sediments may correlate with the standard entropy of metal cation hydration in some river-lake systems and on the standard enthalpy in others (Jackson, 1979). Hg tends to be either the most or the least efficiently trapped metal, depending on whether entropy or enthalpy, respectively, controls metal partitioning between water and sediment!

Distilled water with no added Cl^- ions or other ligands is ineffective in desorbing Hg(II) from fluvial sediments (Ramamoorthy and Rust, 1976). Rinsing of Hg(II)-bearing fluvial sediment with Hg-poor river water has been shown to remove at least 50% of the Hg (Bothner and Carpenter, 1973), but the desorption could have been accomplished by complexing agents in the water.

Finally, Hg(II) bound by Fe or Mn oxide is released if the oxide is dissolved by reduction, as happens, for instance, when Hg-contaminated oxides in fluvial suspended matter are deposited in reducing bottom environments of productive riverine lakes (Jackson, 1986, 1993a, 1996; Wang *et al.*, 1989). On the other hand, Hg(II) bound to FeS may be released by oxidation of the sulfide (Jackson, 1996). Hg released by reduction of oxides may be scavenged by sulfides and organic matter, and Hg released by oxidation of FeS may be immobilised by precipitated Fe oxide and organic matter (Jackson, 1996). Such phenomena are controlled jointly by Eh, pH, and other factors, such as complexing agents, and are mediated by microbes.

Organometallic compounds of Hg(II). Because of their highly covalent Hg-C bonds, organometallic Hg(II) compounds are resistant to oxidation and hydrolysis and are quite stable kinetically (though not thermodynamically) in water and O_2 (Cotton and Wilkinson, 1962; Douglas and McDaniel, 1965; Roberts and Caserio, 1965). The naturally occurring organometallic Hg(II) species are methyl Hg and dimethyl Hg (CH_3Hg^+ and $(CH_3)_2Hg$, respectively). The cation CH_3Hg^+ is usually associated with anionic ligands. CH_3Hg^+ species (free CH_3Hg^+ and complexes such as CH_3HgCl, CH_3HgOH, CH_3HgSH, etc.) will be designated collectively as CH_3Hg^+ for convenience when the anion is not specified. The cationic species will be referred to as "free CH_3Hg^+."

CH_3Hg^+ and $(CH_3)_2Hg$ are synthesised mostly by microbial methylation of bio-available inorganic Hg(II) species, a reaction mediated by many different species and strains of free-living bacteria and fungi

(methylating microbes, or methylators), ranging from anaerobes to aerobes, under a wide range of environmental conditions (Jensen and Jernelöv, 1969; Landner, 1971; Fagerström and Jernelöv, 1972; Vonk and Sijpesteijn, 1973; Bisogni and Lawrence, 1975; Hamdy and Noyes, 1975; Blum and Bartha, 1980; Pan-Hou and Imura, 1982; Compeau and Bartha, 1985, 1987; Jackson, 1987, 1989, 1991a, 1991b, 1988b, 1993a, 1993b; Kerry *et al.*, 1991; Mason and Fitzgerald, 1991; Matilainen *et al.*, 1991; Regnell and Tunlid, 1991; Choi and Bartha, 1993; Zhang and Planas, 1994; Matilainen, 1995; Watras *et al.*, 1995). In a number of aquatic ecosystems (e.g. estuaries), SO_4^{2-}-reducing bacteria (e.g. *Desulfovibrio desulfuricans*) are the dominant methylators in sediments and water under anoxic conditions, provided that ambient SO_4^{2-} levels are low enough to be limiting, thus compelling the bacteria to live by fermentation rather than anaerobic respiration (Compeau and Bartha, 1985, 1987; Kerry *et al.*, 1991; Choi and Bartha, 1993; Matilainen, 1995; Watras *et al.*, 1995). When SO_4^{2-} levels are high enough to sustain production of H_2S, methylating activity declines owing to interference by sulfide. Production of CH_3Hg^+ or $(CH_3)_2Hg$ by anaerobes may be accompanied by release of CH_4 (Wood, 1971; Jackson, 1987, 1988b, 1991b), and extracts from methane bacteria have been shown to methylate Hg (Wood *et al.*, 1968; Wood, 1971), but independent studies by different workers have established that methane bacteria are unable to synthesise methyl Hg species (McBride and Edwards, 1977; Compeau and Bartha, 1985; Kerry *et al.*, 1991). Microbes, including *Desulfovibrio desulfuricans*, may also convert CH_3Hg^+ to $(CH_3)_2Hg$ and inorganic Hg(II) (Fagerström and Jernelöv, 1972; Baldi *et al.*, 1993b, 1995). Other organometallic Hg compounds, such as phenyl Hg ($C_6H_5Hg^+$), have been introduced into aquatic environments by pollution (Gavis and Ferguson, 1972; Hintelmann *et al.*, 1995a) but are not known to occur naturally. $C_6H_5Hg^+$, being rather unstable, is readily converted to inorganic Hg(II) or transformed into CH_3Hg^+ by microbes (Gavis and Ferguson, 1972).

Microbial production of CH_3Hg^+ and $(CH_3)_2Hg$ is usually accomplished by enzyme-catalysed and nonenzymatic mechanisms whereby methyl groups are transferred to inorganic Hg(II) by methylated cobalamin (vitamin B_{12}), a common coenzyme among both aerobic and anaerobic microbes (Bertilsson and Neujahr, 1971; Wood, 1971; DeSimone *et al.*, 1973; Vonk and Sijpesteijn, 1973; D'Itri, 1991; Choi and Bartha, 1993; Choi *et al.*, 1994). Methylators exploit various sources of methyl groups (Choi *et al.*, 1994). A different mechanism employing the biosynthetic pathway for methionine, with transfer of the methyl group to Hg complexed by homocysteine, has been proposed for the fungus *Neurospora crassa* (Landner, 1971; also see Jackson and Woychuk, 1980a, 1980b); and certain microbes may use other biochemical pathways, including reactions for biosynthesis of unsaturated hydrocarbons such as ethylene and acetylene (De Filippis and Pallaghy, 1975). Another possible mechanism is microbial methylation of Sn(IV) followed by abiotic transfer of the methyl group to inorganic Hg(II), forming CH_3Hg^+ (Huey *et al.*, 1974). CH_3Hg^+ can also be generated abiotically by humic substances (Rogers, 1977; Nagase *et*

al., 1982; Weber *et al.*, 1985; Weber, 1993) and by acetate ions in the presence of sunlight or UV radiation (Akagi *et al.*, 1977), and CH_3Hg^+ can be transformed abiotically into $(CH_3)_2Hg$ by reaction with H_2S (Craig and Bartlett, 1978). The significance of abiotic mechanisms in nature is unknown (Zhang and Planas, 1994), but there are grounds for believing that the microbially mediated pathways for the synthesis of methyl Hg species are the most important ones, especially in sediments (Jensen and Jernelöv, 1969; Jackson, 1987, 1988b, 1989; Korthals and Winfrey, 1987; Zhang and Planas, 1994). Of course, the "abiotic" mechanisms are indirect consequences of biological activity, as humic matter, acetate, methyl Sn, and H_2S are by-products of the microbial decomposition of the remains of organisms; besides, the apparent role of humic matter could, in fact, be due to extracellular bacterial enzymes associated with the humic matter (Matilainen and Verta, 1995). The effect of humic matter on microbial production of CH_3Hg^+ is equally ambiguous, as both enhancement and inhibition of the process have been reported (Jackson, 1989; Matilainen and Verta, 1995). But there is no contradiction: Humic matter may have many different effects, the *net* effect being either enhancement or inhibition depending on circumstances.

CH_3Hg^+ is the principal methylated form of Hg in aquatic organisms, but both CH_3Hg^+ and $(CH_3)_2Hg$ occur in natural waters, the proportion of the one species to the other varying with environmental conditions (Fagerström and Jernelöv, 1972; Mason and Fitzgerald, 1991). Moreover, the possibility that inadvertent conversion of $(CH_3)_2Hg$ to CH_3Hg^+ by reagents used for extraction of CH_3Hg^+ has led to overestimates of the abundance of CH_3Hg^+ cannot be ruled out (Gavis and Ferguson, 1972).

CH_3Hg^+ and inorganic Hg(II) have similar chemical affinities and form analogous complexes and species, but systematic quantitative differences exist as well. Like inorganic Hg(II), CH_3Hg^+ has a marked preferential affinity for sulfide and thiols, and is strongly fixed by them (Zepp *et al.*, 1974; Ochiai, 1977; Dyrssen and Wedborg, 1991), the formation constants of thiol complexes of CH_3Hg^+ being 10^8 times higher than those of amino complexes (Cotton and Wilkinson, 1988). But, unlike Hg^{2+}, CH_3Hg^+ easily and rapidly exchanges one thiol ligand for another (Rabenstein and Reid, 1984; Cotton and Wilkinson, 1988). In sediments CH_3Hg^+ is bonded to sulfides (e.g. FeS) and thiols (e.g. proteinaceous residues in organic matter). Nonetheless, H_2S volatilises CH_3HgCl (Rowland *et al.*, 1977) by converting it to $(CH_3)_2Hg$ (Craig and Bartlett, 1978), although the CH_3Hg^+ may be partially converted to inorganic Hg(II) (e.g. black HgS) + CH_4 (Baldi *et al.*, 1993b). CH_3Hg^+ also reacts with H_2S and thiols to form low molecular weight complexes such as CH_3HgSH and CH_3HgSR, especially at pH values of 7 and slightly higher (Zepp *et al.*, 1974; Dyrssen and Wedborg, 1991); these could include volatile as well as water-soluble species. In natural waters CH_3Hg^+ is thought to be mostly complexed by inorganic and organic sulfide ligands, or, if these are absent, by OH^- or Cl^- ions, although CH_3Hg^+ may be released from sulfide complexes under acidic conditions or at high Cl^- concentrations (Zepp *et al.*, 1974). At ambient sulfide levels exceeding a critical value, sulfide inhibits Hg methylation, probably by

immobilising inorganic Hg(II) and by converting CH_3Hg^+ to $(CH_3)_2Hg$ (Bartlett and Craig, 1979; Craig and Moreton, 1986). This explains why SO_4^{2-}-reducing bacteria are major CH_3Hg^+ producers only in SO_4^{2-}-poor environments where they are unable to reduce SO_4^{2-} to H_2S.

In theory (Dyrssen and Wedborg, 1991), the affinities of both free CH_3Hg^+ and Hg^{2+} for different ligands decrease in the order $R\text{-}S^- > SH^- > OH^- > Cl^-$, and CH_3Hg^+ and inorganic Hg(II) have about the same affinity for -SH groups (Gavis and Ferguson, 1972). By the same token, CH_3Hg^+ (Hintelmann *et al.*, 1995b) and inorganic Hg(II) react in very similar ways with humic matter. Hintelmann *et al.* (1995b) reported that CH_3Hg^+ forms extremely stable complexes with humic matter and is probably bound preferentially by thiol groups rather than O- and N-bearing groups (Zepp *et al.*, 1974); and the stability constants of CH_3Hg^+-humic complexes were found to lie within the range of those reported for inorganic Hg(II). CH_3Hg^+, as often observed with inorganic Hg(II), was shown to be accumulated preferentially by the higher molecular weight fractions of humic and fulvic acids. As with inorganic Hg(II), the ability of humic matter to bind CH_3Hg^+ declines, but only moderately, as the pH drops from 7 to 3; and the binding capacity of humic matter for CH_3Hg^+ decreases with increasing CH_3Hg^+ concentration.

But despite the similarities between the chemical reactions of CH_3Hg^+ and inorganic Hg(II), systematic quantitative differences exist. Dyrssen and Wedborg (1991) demonstrated that the stability constants of sulfide, OH^-, and Cl^- complexes of CH_3Hg^+ are consistently lower than those of equivalent inorganic Hg(II) complexes; and Hogg *et al.* (1978) showed that the sorption capacities of two soils differing in clay and organic content were lower for CH_3HgCl than for $HgCl_2$. Similar results have been reported for sediments (Regnell and Tunlid, 1991). These differences, and the fact that CH_3Hg^+ easily exchanges thiol groups, probably reflect the tendency of the methyl group to release electrons to its Hg atom, thereby diminishing the positive charge on the Hg and weakening the Hg-ligand bonds. Besides, CH_3Hg^+, unlike Hg^{2+}, can be bound by only one ligand at a time (Gavis and Ferguson, 1972).

As with inorganic Hg(II), aqueous CH_3Hg^+ speciation is largely a function of pH and the concentrations of anionic ligands. Theoretically, in model freshwater systems consisting of CH_3Hg^+ and Cl^- solutions at pH values in the range 2-10 (Faust, 1992), the fraction of the CH_3Hg^+ in the form of CH_3HgOH increases with rising pH over nearly the entire pH range 2-10, levelling off in the range 8-10, whereas the proportions of both CH_3HgCl and free CH_3Hg^+ are constant from pH 2 to pH ~6.5 and then decline sharply with rising pH. The dominant CH_3Hg^+ species at different pH values are as follows: In the pH range 2-10, $CH_3HgCl >>$ free CH_3Hg^+; at pH 2 to ~4.7, $CH_3HgCl >>$ free $CH_3Hg^+ > CH_3HgOH$; at pH ~4.7 to ~7.5, $CH_3HgCl > CH_3HgOH >$ free CH_3Hg^+; and at ~7.5-10, $CH_3HgOH > CH_3HgCl >>$ free CH_3Hg^+. The K_{ow} value of CH_3Hg^+ increases with Cl^- and, at constant Cl^- concentration, decreases with rising pH over the range 2-10 (falling most sharply in the range 7-8) (Major

et al., 1991), as CH_3HgCl is much more lipophilic than CH_3HgOH (Mason *et al.*, 1995b). Free CH_3Hg^+ is undoubtedly the least lipophilic CH_3Hg^+ species because of its charge, but it makes up no more than a minor fraction of the dissolved CH_3Hg^+ at any given pH. In brief, the lipophilicity of CH_3Hg^+ in freshwater environments is apt to be higher under acidic conditions owing to a preponderance of CH_3HgCl over CH_3HgOH, and lower under alkaline conditions owing to a greater abundance of CH_3HgOH. In sulfide-free marine waters, where Cl^- levels are high, CH_3Hg^+ may well be mainly in the form of CH_3HgCl despite the mild alkalinity of seawater.

A number of CH_3Hg^+ species have a much stronger affinity for lipids than for water owing to their stable, largely covalent bonds and the nonpolar character of the methyl group. But CH_3Hg^+ species differ widely among themselves in their degree of lipophilicity, and all of them must have some degree of hydrophilic as well as lipophilic character because of the polarity and dipole moment of the molecule and, when dissociated, its charge. Therefore, CH_3Hg^+ is subject to hydration and is somewhat water soluble (Gavis and Ferguson, 1972; Cotton and Wilkinson, 1988). As with inorganic Hg(II), the relative lipophilicity and hydrophilicity of CH_3Hg^+ depend on its associated anion. CH_3Hg^+ halides (e.g. CH_3HgCl) are among the more lipophilic CH_3Hg^+ species owing to the covalent character of their bonds and hence their tendency to remain undissociated and uncharged in aqueous solution (Cotton and Wilkinson, 1988); thus, they are two orders of magnitude more soluble in nonpolar solvents than in water (Bidstrup, 1964). CH_3Hg^+ sulfate and nitrate have bonds with a greater degree of ionic character (and presumably a greater tendency to dissociate), and are correspondingly more hydrophilic (Cotton and Wilkinson, 1988). Cotton and Wilkinson (1988) imply that CH_3HgOH is predominantly lipophilic, but Mason *et al.* (1995b) have shown that it is, in fact, one of the more hydrophilic species. CH_3HgCl and CH_3HgOH are comparable to their inorganic Hg(II) analogues in their absolute and relative degrees of lipophilic character (Mason *et al.*, 1995b). Thus, their K_{ow} values are of the same order of magnitude as those of the inorganic Hg(II) species, and the K_{ow} value of CH_3HgCl exceeds that of CH_3HgOH by two orders of magnitude. H-bonding between OH groups and H_2O probably enhances the hydrophilicity of CH_3HgOH. However, the K_{ow} value of CH_3HgCl is only about half that of $HgCl_2$, meaning that CH_3HgCl is less lipophilic and more water-soluble - presumably because CH_3HgCl, unlike $HgCl_2$, has a dipole moment. But CH_3HgOH has a slightly higher K_{ow} value than $Hg(OH)_2$; apparently H-bonding of H_2O by the pair of OH groups in $Hg(OH)_2$ makes this species more hydrophilic than CH_3HgOH.

Being small, uncharged, largely undissociated, and weakly hydrated, species such as CH_3HgCl are somewhat volatile (Matheson, 1979). CH_3Hg^+ species in general are more volatile than inorganic Hg(II) compounds (Ochiai, 1977); indeed, the vapour pressure of CH_3HgCl is two orders of magnitude greater than that of $HgCl_2$ (Phillips *et al.*, 1959).

The properties of $(CH_3)_2Hg$ differ radically from those of CH_3Hg^+. $(CH_3)_2Hg$ is extremely lipophilic

and nonpolar, as it possesses two nonpolar groups, is devoid of a dipole moment, and has stable, largely covalent bonds that do not dissociate in water (Fagerström and Jernelöv, 1972; Gavis and Ferguson, 1972; Ochiai, 1977; Cotton and Wilkinson, 1988). $(CH_3)_2Hg$ is also highly volatile (much more so than CH_3Hg^+) and practically insoluble in water (Fagerström and Jernelöv, 1972; Gavis and Ferguson, 1972; Ochiai, 1977; Cotton and Wilkinson, 1988). Hence, $(CH_3)_2Hg$ readily escapes into the atmosphere, whereas CH_3Hg^+ has a greater tendency to be retained by water.

Turning to the destruction of methyl Hg species, we find that in aquatic environments, such as lake sediments, various free-living demethylating microbes, or demethylators, ranging from anaerobes to aerobes, readily decompose (demethylate) CH_3Hg^+ with release of Hg(0) and in some instances CH_4 or $CH_4 + CO_2$, thereby limiting the net rate of CH_3Hg^+ production (Spangler *et al.*, 1973; Schottel *et al.*, 1974; Mason *et al.*, 1979; Shariat *et al.*, 1979; Compeau and Bartha, 1984; Jackson, 1987, 1988b, 1989, 1991a, 1993b; Korthals and Winfrey, 1987; Baldi *et al.*, 1989, 1991; D'Itri, 1991; Matilainen *et al.*, 1991; Oremland *et al.*, 1991; Regnell and Tunlid, 1991; Baldi *et al.*, 1993b; Mason and Fitzgerald, 1993; Pahan *et al.*, 1994; Zhang and Planas, 1994; Matilainen and Verta, 1995). $(CH_3)_2Hg$ may be converted to CH_3Hg^+, and thence to Hg(0) (Mason and Fitzgerald, 1993). Many bacterial strains capable of volatilising CH_3Hg^+ (possibly through demethylation) have been isolated from Hg-polluted sediments (Nakamura *et al.*, 1990). Microbes that demethylate CH_3Hg^+ include methane bacteria and SO_4^{2-} reducing bacteria (though the latter also synthesise CH_3Hg^+) (Oremland *et al.*, 1991). The enzyme organomercurial lyase degrades methyl Hg species, yielding inorganic Hg(II), which is then reduced to Hg(0) by mercuric reductase (Baldi *et al.*, 1991; Pahan *et al.*, 1994); demethylation can supposedly be mediated by cobalamin too (DeSimone *et al.*, 1973), even though this coenzyme is the chief catalyst for methylation. Abiotic decomposition of CH_3Hg^+ by Mn oxide has been observed in experimental aquatic systems, though its significance in nature is unknown (Jackson, 1989). Aqueous CH_3Hg^+ complexes may also be broken down abiotically to inorganic Hg(I), Hg(0), and other products by photochemical reactions on exposure to sunlight ($\lambda \geq 290$ nm at the Earth's surface) or UV light (Baughman *et al.*, 1973; Inoko, 1981), and the process has been detected in lake water (Sellers *et al.*, 1996).

Baughman *et al.* (1973) demonstrated that various aqueous organic and inorganic sulfide complexes of CH_3Hg^+ undergo photochemical decomposition, yielding inorganic Hg products, in the presence of sunlight. The rates of photolysis decreased in the order $CH_3HgS^- >> CH_3Hg^+$-thiol complexes, and the quantum yields were highest in the absence of O_2. The rates of photolysis for CH_3Hg^+ halide and OH^- complexes decreased in the order $CH_3HgI >> CH_3HgBr > CH_3HgCl$, CH_3HgOH, and the authors concluded that CH_3HgCl, CH_3HgOH, and free CH_3Hg^+ are not decomposed appreciably by sunlight at the Earth's surface, although volatile species such as CH_3HgCl may be broken down by UV radiation in the stratosphere (Inoko, 1981). These results show that susceptibility to photochemical decomposition

increases with the polarisability of the ligand and, hence the degree of covalent character of the bond which it forms with the Hg atom. Sellers *et al.* (1996) found that variations in lake water composition (e.g. dissolved organic C content) had no effect on CH_3Hg^+ photolysis in sunlight. As they failed to point out, however, it does not follow that photolysis of CH_3Hg^+ is independent of water chemistry. The work of Baughman *et al.* (1973) and well-known basic principles of photochemistry, invalidates any such inference. Possibly the water samples of Sellers *et al.*, even those that were poorest in organic C, had enough thiol groups to scavenge all the CH_3Hg^+, in which case the variations in water chemistry that fell within the scope of their study were irrelevant.

Sunlight has little or no effect on $(CH_3)_2Hg$ at the Earth's surface (Baughman *et al.*, 1973); but UV light of short wavelength (e.g. 254 nm) decomposes $(CH_3)_2Hg$ with production of Hg(0) (Balzani and Carassiti, 1970; Fagerström and Jernelöv, 1972; Inoko, 1981), implying that gaseous $(CH_3)_2Hg$ is destroyed on reaching the upper atmosphere. In addition, $(CH_3)_2Hg$ in water is spontaneously converted to CH_3Hg^+ under acidic conditions (pH < 5.6) (Wood, 1971; Fagerström and Jernelöv, 1972; Gavis and Ferguson, 1972).

Elemental mercury. Although Hg(II) is the most characteristic oxidation state of Hg in aquatic environments, Hg(0) must also be taken into account, as it has been introduced into natural waters by pollution and natural processes, including *in situ* formation of Hg(0) from Hg(I) and Hg(II). We may infer that strong retention of valence electrons explains why Hg(0) is a liquid at room temperature, is readily vapourised, and is relatively inert: Hg atoms have only a weak mutual attraction, which probably owes more to van der Waals forces than to the sharing of delocalised outer electrons (the characteristic mechanism of bonding in metals (Sisler, 1963)), and they do not readily combine with other substances such as O_2 by sharing or giving up their valence electrons. Being volatile, rather inert, and only slightly soluble in water, Hg(0) tends to escape into the atmosphere as Hg(0) vapour (Budavari *et al.*, 1989; Bidstrup, 1964; Gavis and Ferguson, 1972; Carty and Malone, 1979). As Hg(0) does not react readily with free O_2, it may persist for significant periods of time in the atmosphere or in O_2-saturated water, but it is subject to eventual oxidation to Hg(II) by various biological and abiotic mechanisms (Jonasson and Boyle, 1972; Carty and Malone, 1979; Schroeder *et al.*, 1991). Hg(0) is lipophilic and hence more soluble in nonpolar organic liquids than in water (Bidstrup, 1964; Gavis and Ferguson, 1972; Carty and Malone, 1979).

Bio-availability and bio-accumulation: controlling factors.

In aquatic environments, Hg concentrations in organisms and rates of Hg bio-accumulation (the net result of uptake and excretion) depend on (1) ambient production rates and concentrations of *bio-available* Hg species, which comprise a small, variable proportion of the total Hg content of sediments and water;

(2) physicochemical variables and biological activities which determine the bio-availability of Hg by controlling the speciation, binding, release, distribution, and biogeochemical pathways of Hg in the environment; (3) the total supply of Hg, from which are formed the bio-available species; (4) the nature and activities of the biota and individual organisms within it; and (5) biochemical reactions of Hg inside organisms. It must be borne in mind that what we see in nature is the net effect of many diverse phenomena operating at once.

Hg speciation. The principal bio-available forms of Hg in aquatic ecosystems are CH_3Hg^+ and inorganic Hg(II) species. $(CH_3)_2Hg$ and Hg(0) are less important insofar as direct effects on aquatic organisms are concerned.

CH_3Hg^+ is created primarily by microbial methylation of bio-available inorganic Hg(II). Immediately bio-available inorganic Hg(II) usually makes up only a small percentage of the total inorganic Hg content of sediment or water (Jackson and Woychuk, 1980a, 1980b; Jackson *et al.*, 1982; Jackson, 1988b). Similarly, the CH_3Hg^+ content is generally at least an order (often several orders) of magnitude less than the total Hg inorganic content (e.g. Jackson and Woychuk, 1980a, 1980b, 1981; Jackson *et al.*, 1982; Jackson, 1986, 1988b, 1993a; Bloom and Watras, 1989; Parks *et al.*, 1989; Lee and Iverfeldt, 1991; Wilken and Hintelmann, 1991; Hintelmann and Wilken, 1995). But many aquatic organisms accumulate CH_3Hg^+ preferentially and thus have much higher CH_3Hg^+/total Hg ratios than do the water and sediments of their habitat, although the ratio varies greatly among different organisms, reaching its maximum at the upper end of the food chain. Hg in fish is mostly in the form of CH_3Hg^+, but Hg in sediments, the chief repositories of Hg in aquatic environments, is mainly inorganic (Watras *et al.*, 1994).

CH_3Hg^+ is considered the most baneful form of Hg in aquatic ecosystems, as it is highly toxic, is readily accumulated by organisms, and becomes increasingly concentrated upward through the food chain. Certain inorganic Hg(II) species, too, are taken up easily, but, unlike CH_3Hg^+, they tend to be immobilised immediately after crossing biological membranes and have a more limited ability to spread to different parts of an organism's body, are more rapidly eliminated and less efficiently accumulated, are not subject to amplification up the food chain, and are less toxic (Knauer and Martin, 1972; Westöö, 1973; Bishop and Neary, 1974; Miettinen, 1975; Mortimer and Kudo, 1975; Wobeser, 1975; Ochiai, 1977; Grieb *et al.*, 1990; Boudou *et al.*., 1991; Wright *et al.*, 1991; Watras and Bloom, 1992; Odin *et al.*, 1994; Mason *et al.*, 1995b; Southworth *et al.*, 1995). However, bio-available inorganic Hg(II) species are of key significance, primarily because CH_3Hg^+ is synthesised by methylation of these species (Jackson, 1988b, 1991a, 1993b; Farrell *et al.*, 1990), but also because they themselves may contaminate and poison aquatic organisms to some extent (Knauer and Martin, 1972; Nuzzi, 1972; Alexander, 1974; Wobeser, 1975; Hamdy *et al.*, 1977; Ochiai, 1977; Farrell *et al.*, 1990; Liebert *et al.*, 1991).

The bio-available forms of inorganic Hg(II) consist of $HgOH^+$, $Hg(OH)_2$, HgClOH, $HgCl^+$, $HgCl_2$,

$HgCl_3^-$, and other low molecular weight complexes (Farrell *et al.*, 1990), including thiol and inorganic sulfide species such as $Hg(SH)_2$ and $Hg(SH)S^-$ (Dyrssen and Wedborg, 1991; Gottofrey and Tjälve, 1991; Hudson *et al.*, 1994). The uncharged Hg(II) species display both lipophilicity and hydrophilicity in varying degrees, and each of these qualities, in its way, promotes biological uptake. Hydrophilicity is conducive to solubility and mobility in the aquatic milieu, release of Hg from binding agents (e.g. sediment particles) that compete with organisms for Hg, and retention of Hg in the water rather than loss by volatilisation; thus, it helps to bring the Hg into contact with methylators and other organisms and enhances bio-availability. On the other hand, lipophilicity enables the Hg species to diffuse easily and rapidly through a cell or mucus membrane by dissolving in the membrane's lipid phase, resulting in passive uptake by organisms. Because of its greater lipophilicity, $HgCl_2$ penetrates membranes more readily than $Hg(OH)_2$ does (Farrell *et al.*, 1990; Boudou *et al.*, 1991; Mason *et al.*, 1995b). Ionic species and other strongly hydrophilic species cannot diffuse through membrane lipids but may enter cells by means of active transport and pores in the membrane; however, passive diffusion of uncharged lipophilic species through membranes is by far the principal uptake mechanism (Boudou *et al.*, 1991; Hudson *et al.*, 1994; Mason *et al.*, 1995b). The small dimensions of the bio-available species also facilitate the penetration of membranes, especially in the case of hydrophilic species.

In oxygenated fresh water the bio-availability of inorganic Hg(II) is enhanced in the range of Cl^- levels and pH values at which dissolved inorganic Hg(II) is mostly in the form of the lipophilic species $HgCl_2$ (Farrell *et al.*, 1990; Boudou *et al.*, 1991; Mason *et al.*, 1995b). By the same token, lipophilic thiol and inorganic sulfide complexes such as $Hg(SH)_2$ probably account for much of the bio-availability of Hg under reducing conditions, especially in freshwater environments (Gottofrey and Tjälve, 1991; Hudson *et al.*, 1994). But the bio-availability of Hg is much lower if the dissolved Hg(II) is mostly in the form of ionic complexes or $Hg(OH)_2$ (Ribeyre and Boudou, 1982; Walczak and Hammer, 1986; Ribo *et al.*, 1989; Boudou *et al.*, 1991; Mason *et al.*, 1995b). In brief, inorganic Hg(II) is probably most bio-available in acidic fresh waters in which it is mainly in the form of $HgCl_2$ or $Hg(SH)_2$; it should be less bio-available in weakly acidic or alkaline fresh waters in which $Hg(OH)_2$ exceeds $HgCl_2$ or $Hg(SH)S^-$ exceeds $Hg(SH)_2$, *or* in seawater or brackish water in which $HgCl_3^-$, $HgCl_4^-$, or $Hg(SH)S^-$ prevails. Yet fish can absorb inorganic Hg(II) to some extent directly from seawater (Windom and Kendall, 1979), suggesting uptake by anion transport mechanisms (Boudou *et al.*, 1991). Sea salt levels near those of seawater inhibit methylation of Hg by SO_4^{2-}-reducing bacteria in anoxic estuarine sediments, but this is not due to conversion of inorganic Hg(II) to anionic Cl^- complexes (Compeau and Bartha, 1987). At sufficiently high pH and low Cl^- levels for $Hg(OH)_2$ to exceed $HgCl_2$, the bio-availability of inorganic Hg(II) should be relatively low for *two* reasons: (1) $Hg(OH)_2$ penetrates membranes less easily than $HgCl_2$, and (2) it is more readily sorbed by suspended matter (see above).

Inorganic Hg(II) absorbed by an organism is excreted slowly, as it is strongly retained by -SH groups of proteins (unlike more typical lipophilic substances, which are excreted slowly because they are selectively accumulated by fat) (Miettinen, 1975; Ochiai, 1977; Mason *et al.*, 1995b). On entering an organism by penetration of cell or mucus membranes, inorganic Hg(II) tends to be fixed to proteinaceous components of the membranes, though it is partly distributed elsewhere in the organism's body (Boudou *et al.*, 1991). After exposure of trout to water or food containing $HgCl_2$, the highest inorganic Hg concentrations in the tissues of the fish were found to be in either the gut *or* the gills, depending on whether the Hg came from food or water, respectively, the next highest levels being in the kidney and spleen (Boudou *et al.*, 1991). Following ingestion of Hg-contaminated food, Hg was at least an order of magnitude more abundant in the intestine than in any other organ. Mayfly nymphs yielded comparable results. Similarly, on exposure of a rooted aquatic plant to sediment containing $HgCl_2$, most of the Hg taken up was concentrated in the roots, though Hg was also detected in leaves and stems (Boudou *et al.*, 1991). Thus, in both plants and animals inorganic Hg(II) tends to remain fixed at its points of entry, resisting assimilation into the inner tissues.

CH_3Hg^+ species differ strikingly from analogous inorganic Hg(II) species in their interactions with organisms, although there are basic similarities too. As a rule, organisms absorb CH_3Hg^+ rapidly, both directly from ambient water and from food, and retain it tenaciously, excreting it only very slowly (Miettinen, 1975). CH_3Hg^+ easily penetrates cell and gill membranes (if absorbed from water) and the mucus membrane of the gut (if ingested with food), and is quickly assimilated by cytoplasm and internal tissues. CH_3Hg^+ species do not necessarily differ significantly from their inorganic Hg(II) analogues in membrane penetration kinetics, but they behave quite differently once they get inside (Boudou *et al.*, 1991; Mason *et al.*, 1995b).

Comparison of the membrane penetration kinetics of different Hg species using diatom cells has shown that analogous CH_3Hg^+ and inorganic Hg(II) species cross membranes at comparable rates (Mason *et al.*, 1995b). CH_3HgCl crossed the membranes at virtually the same rate as $HgCl_2$ despite its lower degree of lipophilicity, whilst CH_3HgOH was taken up 2.6 times as fast as $Hg(OH)_2$, although it is only 1.4 times as lipophilic. Apparently the methyl group facilitates membrane penetration irrespective of the lipophilicity of the molecule as a whole. But at the most, the results for analogous CH_3Hg^+ inorganic Hg(II) species differed by far less than an order of magnitude. An experiment on the diffusion of CH_3Hg^+ and inorganic Hg(II) species through model membranes revealed the same broad tendencies, except that CH_3HgCl penetrated the membrane more rapidly than $HgCl_2$ (Boudou *et al.*, 1991). In short, CH_3Hg^+ penetrates membranes at the same rate as its inorganic Hg(II) analogues or somewhat more rapidly. Note, however, that inorganic Hg(II) alters membrane permeability (Ochiai, 1977; Boudou *et al.*, 1991), introducing a degree of ambiguity into membrane penetration data.

Another important observation is that CH_3HgCl passes through membranes much more easily and rapidly than CH_3HgOH. Therefore, the kinetics of CH_3Hg^+ uptake by organisms must be a function of the Cl^- content and pH of the ambient solution, CH_3HgCl predominating over CH_3HgOH in strongly to moderately acidic fresh waters, whereas the reverse is true under weakly acidic to alkaline conditions. The same reasoning applies to sulfide complexes; thus, the bio-available species CH_3HgSH must be prevalent at low pH, changing to the less bio-available species CH_3HgS^- at higher pH values. In acidic fresh water at least two factors favour bio-accumulation of CH_3Hg^+: greater availability of inorganic Hg(II) to methylators *and* more rapid biological uptake of the CH_3Hg^+, because *both* are largely in the form of uncharged lipophilic complexes. On the other hand, CH_3Hg^+ could, conceivably, be more prone to demethylation under these conditions because of enhanced availability to demethylators. In seawater, CH_3Hg^+ is probably taken up rapidly by organisms, as it is mainly in the form of CH_3HgCl, but production of CH_3Hg^+ could be retarded somewhat by the prevalence of $HgCl_3^-$ and $HgCl_4^-$ over $HgCl_2$.

On entering an organism by passage through a membrane, CH_3Hg^+, like inorganic Hg(II), is preferentially complexed by thiol groups of proteins (and peptides and amino acids) and accumulates in proteinaceous material such as the edible muscle tissues of fish (Ochiai, 1977; Boudou *et al.*, 1991; Mason *et al.*, 1995b); it is also bound by nucleic acids, nucleotides, pyrimidines, etc. (Cotton and Wilkinson, 1988). But CH_3Hg^+ spreads much more readily through the internal tissues of both plants and animals than inorganic Hg(II) does, and it shows a far weaker tendency to be retained at the points of entry (Boudou *et al.*, 1991). CH_3Hg^+ is also eliminated far more slowly than inorganic Hg (Ochiai, 1977); its ½-time in mussels, for instance, is 100 times greater than that of inorganic Hg (Miettinen, 1975). Comparing effects of $HgCl_2$ and CH_3HgCl on trout and aquatic plants, Boudou *et al.* (1991) showed that the concentrations in most tissues were much higher for CH_3Hg^+ than for inorganic Hg(II) after exposure; only in the intestines of the fish and the roots of the plant did inorganic Hg(II) predominate. But Mortimer and Kudo (1975) concluded that aquatic plants accumulate $HgCl_2$ and CH_3HgCl with equal ease. Be that as it may, CH_3Hg^+ is much more efficiently accumulated (more rapidly assimilated and more slowly excreted) by many organisms, notably those at higher trophic levels (fish and fish-eating animals) (Westöö, 1973; Bishop and Neary, 1974; Ochiai, 1977; Huckabee *et al.*, 1979; Windom and Kendall, 1979; Grieb *et al.*, 1990; Wright *et al.*, 1991; Watras and Bloom, 1992; Odin *et al.*, 1994; Watras *et al.*, 1994; Southworth *et al.*, 1995). It is reported that organisms at and near the lower end of the aquatic food chain (plankton and benthic invertebrates) have lower CH_3Hg^+/inorganic Hg ratios and more inorganic Hg than CH_3Hg^+ (Jernelöv and Lann, 1971; Koeman *et al.*, 1975; Huckabee *et al.*, 1979; Windom and Kendall, 1979; May *et al.*, 1987; Jackson, 1988a, 1991a), although such observations may be biased by errors due to inorganic Hg in gut contents of invertebrates, nonliving particles associated with plankton, and coatings (e.g. oxide deposits) on hard

parts of organisms (Jackson and Bistricki, 1995). As a rule, CH_3Hg^+ undergoes amplification up the food chain (although at least one exception is on record (Knauer and Martin, 1972)), but inorganic Hg does not (D'Itri, 1972; Huckabee *et al.*, 1979; Windom and Kendall, 1979; May *et al.*, 1987; Jackson, 1991a). Thus, the proportion of CH_3Hg^+ in the total Hg body burden is typically very high (as high as 99%) in fish, especially fish-eating predators.

The contrast between CH_3Hg^+ and inorganic Hg(II) probably reflects the fact that CH_3Hg^+ readily exchanges one thiol group for another, thereby spreading rapidly through the bodies of organisms (Cotton and Wilkinson, 1988), whereas inorganic Hg(II) may be strongly fixed by the first proteins that it encounters, the protein components of membranes. Another factor contributing to the more efficient bio-accumulation of CH_3Hg^+ is that it is less strongly bound by nonliving matter in the environment. Furthermore, the relative stability of CH_3Hg^+ in the presence of water and dissolved O_2 allows the compound to remain in the environment long enough to have a fair probability of coming into contact with organisms, although demethylation limits the net production rates and concentrations of CH_3Hg^+.

As with other lipophilic Hg species, aquatic organisms easily absorb $(CH_3)_2Hg$ and Hg(0) from their environment by passive diffusion through membranes. $(CH_3)_2Hg$, being more lipophilic than CH_3Hg^+ and unable to bind thiol groups, accumulates in fat (Ochiai, 1977) unless it is transformed into CH_3Hg^+ or inorganic Hg inside the organisms (Bidstrup, 1964; Wood, 1971; Gavis and Ferguson, 1972). Because of their great volatility and low solubility in water, however, $(CH_3)_2Hg$ and Hg(0) are not retained effectively by aquatic environments and are readily lost to the atmosphere; thus, they are of secondary importance to the biota despite their bio-availability (Jernelöv and Fagerström, 1972; Baldi *et al.*, 1995).

Owing to the overriding importance of speciation (along with the environmental and biological factors that control it) as the basis of bio-availability, the total Hg content of water or sediment is an unreliable and generally poor guide to the biological effects of Hg - far too crude a parameter except where the grossest comparisons are concerned (e.g. between heavily polluted and pristine environments) (Langley, 1973; Jackson and Woychuk, 1980a, 1980b, 1981; Jackson *et al.*, 1982, 1993; Jackson, 1986, 1988a, 1988b, 1991a, 1991b, 1993a, 1993b; Kelly *et al.*, 1995). Only a small fraction of the total inorganic Hg is readily available for methylation, and its magnitude is a function of physicochemical and biological variables, as are the production and decomposition rates and concentrations of CH_3Hg^+ in ecosystems. CH_3Hg^+ and total Hg in water and sediments are positively correlated in some instances (Jackson *et al.*, 1982; Jackson, 1988b, 1993a; Parks *et al.*, 1989; Hudson *et al.*, 1994; Watras *et al.*, 1995); but within a wide range of total Hg concentrations the ambient CH_3Hg^+ levels and production rates and biological Hg accumulations commonly vary independently of the total supply of inorganic Hg, or correlate much more weakly with it than with environmental and biological factors or, in some cases, are *inversely* related to it. In river systems polluted with Hg from point sources, total Hg levels decrease sharply (as

expected) with distance downstream from the source of pollution, whereas CH_3Hg^+ levels may decrease much more gradually, or show no consistent trend, or even *increase* over a considerable stretch of the river's course (Langley, 1973; Jackson and Woychuk, 1980a, 1980b, 1981; Jackson *et al.*, 1982; Jackson, 1986, 1988b, 1993a, 1993b; Parks and Hamilton, 1987; Parks *et al.*, 1991b). In a long, narrow, highly productive riverine lake characterised by physicochemical and biological gradients extending from a shallow deltaic environment at the inflow end to a deep basin at the outflow end, the total Hg content of the water was found to decrease from the inflow to the outflow as a result of the settling out and dilution of Hg-contaminated fluvial detritus, but the CH_3Hg^+ content increased because environmental conditions became increasingly favourable for the activities of methylating microbes owing to a greater abundance of organic nutrients derived from phytoplankton blooms (Jackson, 1986, 1993a). CH_3Hg^+ and total Hg in the water of a river system may also display inversely related seasonal trends because conditions that maximise total Hg content (e.g. high flow rates resulting in erosion and resuspension of Hg-contaminated sediment during the spring flood) are not favourable for CH_3Hg^+ production, whereas conditions favourable for CH_3Hg^+ production (e.g. low flow rates in the summer and autumn) are not conducive to high total Hg levels (Jackson, 1986; Parks *et al.*, 1986, 1989). Cores of organic sediment taken from a severely Hg-polluted river several years after the discharge of Hg into the river had largely ceased showed that CH_3Hg^+ was most abundant at the sediment-water interface, because microbial activity was most intense there, whereas the total Hg maximum occurred below the interface, reflecting a gradual decline in Hg loading since the cessation of Hg discharges (Jackson and Woychuk, 1980a, 1980b). In general, rates of CH_3Hg^+ production and bio-accumulation may be high where total Hg levels are low if the prevailing conditions enhance the activities of methylating microbes or the bio-availability of inorganic Hg, whilst the rates may be low where total Hg levels are high if the conditions are unfavourable for methylating activity or the release of bio-available inorganic Hg(II) (Langley, 1973; Jackson and Woychuk, 1980a, 1980b, 1981; Jackson *et al.*, 1982; Jackson, 1986, 1993a, 1993b; Kelly *et al.*, 1995). Even in a virtually unpolluted system with no more than low background Hg levels, the Hg content of fish may increase greatly in response to environmental changes that foster microbial production of CH_3Hg^+, as usually occurs when reservoirs are created by the impoundment of river systems and flooding of adjacent land (Bodaly *et al.*, 1984; Jackson, 1987, 1988b, 1991a; Messier and Roy, 1987; Verdon *et al.*, 1991; Morrison and Thérien, 1995).

At extremely low concentrations, total inorganic Hg(II) may, of course, be the limiting factor in CH_3Hg^+ production: CH_3Hg^+ concentrations and production rates increase markedly when a virtually pristine aquatic environment with low background Hg levels is polluted with inorganic Hg. At the opposite extreme, exceedingly high concentrations of inorganic Hg(II) could suppress CH_3Hg^+ production by poisoning the methylators (Jensen and Jernelöv, 1969; Jackson *et al.*, 1982; Jackson, 1991b), and a

large enough build-up of CH_3Hg^+ itself could have this effect (D'Itri, 1991). But over a wide range of ambient total inorganic Hg levels, as in different regions within Hg-polluted river systems, CH_3Hg^+ production varies independently of the total inorganic Hg supply and is controlled, instead, by environmental conditions and biological activities.

The production, decomposition, and bio-accumulation of CH_3Hg^+ are functions of numerous environmental and biological factors, all acting and interacting at once, directly and indirectly. Some factors reinforce each other whilst others tend to cancel each other's effects, and one factor may have multiple effects; moreover, different combinations of environmental variables (e.g. low Eh and high salinity, low pH and high dissolved O_2 concentration, etc.) may lead to quite different results (e.g. Compeau and Bartha, 1984; Jackson, 1987, 1989, 1993b). As the overall result is the *net* effect of many diverse phenomena and conditions, it is hard to interpret in detail or to predict accurately, and the various cause-and-effect relations contributing to it are difficult to disentangle. The complexity of the situation is compounded by the fact that both methylation and demethylation are mediated by many different kinds of bacteria and fungi that differ from one another widely in their ecological requirements and limits of tolerance, besides interacting, it may be assumed, with other microbes in multifarious direct and indirect ways ranging from symbiosis and mutualism to competition and antagonism (e.g. Compeau and Bartha, 1985, 1987; Jackson, 1989, 1991b, 1995a, 1996; Oremland *et al.*, 1991). Besides affecting the bio-availability of inorganic Hg(II) and the overall activity of the microbial community, a change in environmental conditions is apt to modify the species composition of the active part of the microbial community by initiating ecological succession, thereby altering the rates of methylation and demethylation; the result may be a marked increase or decrease, or hardly any change, in the *net* rate of CH_3Hg^+ production (Jackson, 1984, 1989, 1991b). Microbial synthesis and decomposition of CH_3Hg^+ occur under a wide variety of conditions (ranging, for instance, from O_2-rich to highly reducing, from oligotrophic to eutrophic, and from acidic to alkaline) (e.g. Bisogni and Lawrence, 1975; Jackson, 1987, 1989, 1991b); but the net rate of CH_3Hg^+ production is subject to large spatial and temporal (e.g. seasonal) variations related to environmental variations (e.g. Jackson, 1986, 1987, 1988b, 1993a, 1993b). The efficiency of CH_3Hg^+ production depends on (1) microbial growth and activities (which are regulated by factors such as nutrient supply, pH, temperature, and oxidation-reduction conditions) *and* (2) the bio-availability of inorganic Hg(II) (which is limited by inorganic Hg speciation and the sorption and complexing of Hg by various metal-binding agents - especially sulfides - that compete with methylators for inorganic Hg species), as well as loss of Hg through volatilisation. Ideal conditions for the growth and activities of methylating microbes do not necessarily favour maximum availability of inorganic Hg(II) for methylation, and *vice versa*. Thus, different tendencies may offset each other's effects, the net rate of CH_3Hg^+ production representing a compromise between high intensity of methylating activity and low

availability of inorganic Hg(II) or low intensity of methylating activity and high availability of inorganic Hg(II) (Jackson, 1988b; 1993a, 1993b; Mason and Fitzgerald, 1991).

Given such a complex web of effects and relationships, it is difficult to predict or explain pathways of bio-available Hg in detail in any particular ecosystem, each system being a unique and ever-changing complex of physicochemical and biological characteristics that affect the behaviour of Hg in countless direct and indirect ways. Each ecosystem in which Hg is a problem must be investigated comprehensively and in depth with a view to achieving an interdisciplinary synthesis of a wide range of information if the biogeochemistry and environmental impact of Hg in that system are to be adequately understood and dealt with. Nevertheless, from existing knowledge it is possible to formulate a number of widely applicable generalisations about the factors that control the speciation, bio-availability, bio-accumulation, and biogeochemical cycling of Hg, and sophisticated models combining empirical data and theoretical calculations - for example, the Mercury Cycling Model for lakes in northern Wisconsin (U.S.A.) (Hudson *et al.*, 1994) - have been developed. Despite their inevitable limitations (oversimplification, questionable assumptions, lack of sufficient information about natural processes, omission of relevant phenomena that may be important, limited applicability to specific situations, correlations that do not necessarily indicate cause and effect, etc.), such models may assist our interpretation and prediction of phenomena occurring in natural waters and help to narrow down the number of possible explanations for observed phenomena. But a model should never be accepted uncritically at face value, and it is necessary to keep clearly in mind the limits of its usefulness (e.g. the limited ability of theoretical calculations based on the chemistry of simple aqueous solutions at equilibrium to predict Hg speciation in complex natural environments dominated by innumerable microbes, metal-binding agents, and processes subject to kinetic rather than thermodynamic control).

The rest of this section will be devoted to effects of specific environmental factors on the bio-availability and bio-accumulation of Hg.

Organic nutrients, oxygen, sulfides, and selenides. Optimal conditions for the production and bio-accumulation of CH_3Hg^+ in aquatic ecosystems include (1) an ample supply of biodegradable organic substances, such as remains of dead algae or plants, (2) anoxic or O_2-poor (low Eh) conditions, and (3) absence or paucity of sulfides (Fagerström and Jernelöv, 1972; Langley, 1973; Olson and Cooper, 1976; Shin and Krenkel, 1976; Bisogni, 1979; Wright and Hamilton, 1982; Bodaly *et al.*, 1984; Jackson, 1986, 1987, 1988b, 1991a, 1993a, 1993b; Korthals and Winfrey, 1987; Björnberg *et al.*, 1988; Matilainen *et al.*, 1991; Mason and Fitzgerald, 1991, 1993; Regnell and Tunlid, 1991; Regnell, 1994, 1995; Slotton *et al.*, 1995; Watras *et al.*, 1995; Gagnon *et al.*, 1996). These factors are linked, as microbes utilising labile organic matter consume O_2 and generate sulfides.

Labile organic matter matter fosters production of CH_3Hg^+ by furnishing nutrient substrates for direct

utilisation by methylators *and* by promoting heterotrophic microbial growth in general, resulting in anoxic conditions; thus, methylating activity tends to correlate with heterotrophic microbial activity as a whole. Enrichment of lake or river water with labile organic matter, whether it be autochthonous (e.g. the remains of a plankton bloom in a eutrophic lake) or allochthonous (e.g. remains of land plants and soil humus submerged by the waters of a newly formed reservoir), is typically followed by a marked upsurge in the microbial production of CH_3Hg^+ (Bodaly *et al.*, 1984; Jackson, 1986, 1987, 1988b, 1991a, 1993a, 1993b; Scruton *et al.*, 1994; Anderson *et al.*, 1995; Morrison and Thérien, 1995). But decomposition of organic matter also produces sulfides, which interfere with methylation because they bind inorganic Hg(II), rendering it less bio-available (although certain soluble sulfide complexes of inorganic Hg(II) and CH_3Hg^+ are bio-available); production of selenides and organic complexing agents (especially compounds bearing thiol groups) probably have this effect as well. Dissolved O_2 tends to inhibit microbial methylating activity and may deplete the pool of inorganic Hg potentially available for methylation by fostering microbial reduction of inorganic Hg(II) to Hg(0) in well aerated mixed-layer (surface water) environments (Mason *et al.*, 1995a); but O_2 also enhances the release of bio-available inorganic Hg(II) into solution by oxidising sulfides, selenides, and organic matter, thereby compensating somewhat for the negative effect of O_2 on methylation (Jernelöv, 1972; Jackson, 1988b; 1993b).

Microbial CH_3Hg^+ production is commonly concentrated in surface sediments (at the sediment-water interface) because microbial activity is most intense there; but in certain regions of the water column, labile organic matter (e.g. remains of plankton) accompanied by local O_2 depletion, may support a level of CH_3Hg^+ producing activity comparable to that found in surficial sediments, as may be observed in the hypolimnion of a lake just below the thermocline or below the thermocline of the ocean, and even in the epilimnion of an extremely eutrophic lake following a phytoplankton bloom (Fagerström and Jernelöv, 1972; Jackson, 1986, 1993a; Mason and Fitzgerald, 1991, 1993; Matilainen, 1995; Watras *et al.*, 1995). Results of a field experiment suggest that the quantities of CH_3Hg^+ generated each year in the water column in some regions of the sea are comparable to those produced in associated bottom sediments (Topping and Davies, 1981). Methylating activity is likely to be concentrated at the boundary between anoxic and oxygenated zones, e.g. the sediment-water interface where O_2-rich water overlies anoxic sediment (Jackson and Woychuk, 1980a, 1980b; Korthals and Winfrey, 1987; Watras *et al.*, 1995) and the top of an anoxic hypolimnion in a stratified lake (in which case methylating activity in the bottom sediments of the hypolimnion may be relatively insignificant) (Watras *et al.*, 1995). This may reflect the fact that SO_4^{2-}-reducing bacteria methylate Hg mainly under conditions favouring fermentation rather than SO_{42-} reduction; it is also consistent with a role for microaerophilic microbes in CH_3Hg^+ production. As labile organic substances and sulfides in sediments decrease in relation to mineral detritus, the proportion of inorganic Hg(II) weakly sorbed to mineral particles (e.g. clay and oxides) increases; hence, the Hg

becomes correspondingly more exchangeable and more bio-available (Jackson and Woychuk, 1980a, 1980b, 1981; Jackson *et al.*, 1982; Jackson, 1993b). Thus, the bio-availability of inorganic Hg(II) is greatest in detrital mineral sediment situated in a well aerated environment. Possible exceptions, however, have been noted: Comparing vigorously mixed, well aerated riverine lake environments with relatively stagnant, poorly aerated ones, Jackson (1988a) found that aeration enhances the availability of Hg to plankton by promoting decomposition of organic matter and sulfides, leading to release of their bound Hg, but decreases the availability of Hg to benthic invertebrates by causing precipitation of Hg-immobilising Fe and Mn oxides.

As a rule, the rate of Hg methylation or rate of methylation per unit rate of demethylation (the "M/D ratio") in sediments and water is higher under anoxic conditions than in the presence of O_2 (Olson and Cooper, 1976; Bisogni, 1979; Windom and Kendall, 1979; Jackson, 1987, 1988b; Korthals and Winfrey, 1987; Parks *et al.*, 1989), although at least one study showed the reverse of this tendency (Bisogni and Lawrence, 1975), and certain bacterial species methylate Hg more effectively in oxygenated environments than in anoxic ones (Vonk and Sijpesteijn, 1973). Besides lowering the rate of methylation, dissolved O_2 commonly increases the rate of demethylation, helping to account for the relatively low rate of CH_3Hg^+ production in well aerated environments, whereas anoxic conditions promote methylation at the expense of demethylation (Windom and Kendall, 1979; Compeau and Bartha, 1984; Jackson, 1987). CH_3Hg^+ production is likely to be greatest in anoxic sediments at and near the sediment-water interface, because bacterial activity is normally concentrated in that region (Fagerström and Jernelöv, 1972; Jackson and Woychuk, 1980a, 1980b; Korthals and Winfrey, 1987), or a few cm below the interface, if the surface sediment has been oxidised (Gagnon *et al.*, 1996). Korthals and Winfrey (1987) reported that the M/D ratio was highest at the sediment-water interface, even though the rate of demethylation was also maximal there. Matilainen *et al.* (1991) found that methylation rates in lake sediments were highest under anoxic conditions but that demethylation rates in anoxic and oxygenated environments were similar.

The apparent inconsistencies in the effects of dissolved O_2 may reflect the fact that methylation and demethylation are not simple functions of O_2; the role of O_2 is modified by other variables, such as pH and salinity. Jackson (1987) showed that rates of methylation and demethylation in lake sediment amended with organic nutrients were independent of dissolved O_2 levels if the pH was acidic ($\sim$4.5-6.0); but near pH 7.0 the methylation rate was higher and the demethylation rate lower under anoxic conditions (under N_2), whereas the methylation rate was lower and the demethylation rate higher in the presence of O_2 (under air). Without nutrient enrichment, methylation was inhibited under both N_2 and air (equally so in both cases), whereas the rate of demethylation was high under N_2 but low under air. In brief, given an adequate supply of labile organic matter, pH values near 7, and other conditions favourable for heterotrophic microbial activity, lack of O_2 fosters CH_3Hg^+ production (within certain bounds, at least).

by promoting methylation and inhibiting demethylation, whereas O_2 depresses CH_3Hg^+ production by inhibiting methylation and enhancing demethylation. But the effects of O_2 depend on other factors, such as nutrient levels, pH, and salinity, which affect microbial activities and the availability of inorganic Hg. Regarding effects of dissolved salts, Compeau and Bartha (1984) observed that at low Eh methylation in estuarine sediments was fostered by low salinity but inhibited by high salinity, whereas at high Eh methylation was less sensitive to variations in salinity. In contrast, demethylation was suppressed by a combination of low Eh and low salinity, whereas the inhibition was reversed by raising the salinity; but high Eh values promoted demethylation irrespective of the salinity. In estuaries, then, CH_3Hg^+ production as determined by the balance between methylating and demethylating activities is a complex function of at least two independently varying factors, Eh and salinity, and many other variables could be involved as well. In any aquatic environment the rate of CH_3Hg^+ production is the net effect of many variables acting and interacting in different ways.

Owing to their strong preferential binding of Hg, sulfides are of paramount importance as limiting factors in the production and bio-accumulation of CH_3Hg^+ and the biological uptake of inorganic Hg(II). Thus, Hg concentrations in freshwater plankton and at least two species of freshwater fish (lake whitefish and white sucker) that feed on benthic animals, have been found to correlate inversely with the sulfide content of associated sediments, suggesting that sulfides interfered with the Hg uptake (Jackson, 1988a; Jackson *et al.*, 1993). Sulfides, including thiols (e.g. cysteine) as well as H_2S, tend to reduce the rates of Hg methylation and bio-accumulation by decreasing the bio-availability of inorganic Hg(II) (Fagerström and Jernelöv, 1972; Jernelöv, 1972; Blum and Bartha, 1980; Björnberg *et al.*, 1988; Jackson, 1984, 1988a, 1988b, 1991a; Farrell *et al.*, 1990; Jackson *et al.*, 1993). Thus, in sediments from several lakes polluted with heavy metals (including Hg), the lowest CH_3Hg^+/total Hg ratios were associated with the highest free sulfide concentrations (Jackson, 1984). Sulfides may also immobilise CH_3Hg^+ itself, interfering with biological uptake. If, however, other conditions, such as nutrient supply, are highly favourable, rates of CH_3Hg^+ production and bio-accumulation may be relatively high even in the presence of sulfide, as in the anoxic hypolimnion of a lake (Jackson, 1984, 1993a, 1993b; Matilainen, 1995; Watras *et al.*, 1995) - up to a point, at least (Craig and Moreton, 1986), probably because the suppression of CH_3Hg^+ production by sulfides is mitigated somewhat by the fact that some hydrolysed Hg(II) remains in solution even in the presence of excess sulfide, and by the fact that small, uncharged lipophilic Hg thiol and inorganic sulfide complexes are bio-available. Hudson *et al.* (1994) have postulated that passive uptake of the uncharged lipophilic Hg sulfide complexes such as $Hg(SH)_2$ by methylating microbes explains the occurrence of high methylation rates in anoxic environments. As nutrient enrichment and sulfide production go together, a trade-off of positive and negative effects on CH_3Hg^+ production and bio-accumulation can be expected. For these reasons, perhaps, CH_3Hg^+ production in estuarine

sediments increases with rising sulfide concentration up to a critical level and then declines with further increases in sulfide (Craig and Moreton, 1986).

Generally speaking, sulfides (along with the analogous but much less abundant selenides and tellurides) are the principal metal-binding agents that limit the bio-availability of Hg(II) in natural waters (Björnberg *et al.*, 1988). Thus, Jackson (1987, 1991a, 1993b) found that the total Hg/sulfide or Hg/Se ratio of lake sediment is a reliable parameter for estimating the bio-availability of inorganic Hg in the sediment. Jackson calculated the relative rates of CH_3Hg^+ production in sediments from different lakes by (1) measuring microbial methylating activity using a special laboratory assay (Jackson, 1987, 1988b, 1989), (2) determining the Hg/sulfide or Hg/Se ratio of the sediment, and then (3) combining the two sets of data by multiplication. The resulting empirical compound variable (but neither of its two component variables alone) gave a very significant positive correlation with mean Hg levels in populations of walleye (predatory fish at the upper end of the aquatic food chain) inhabiting the lakes. Using the concentrations of 0.5 M $CaCl_2$-extractable Hg in the sediment in place of the Hg/sulfide or Hg/Se ratio to quantify the bio-available inorganic Hg(II) fraction yielded nearly the same results (Jackson, 1987, 1991a), and the same method accurately predicted CH_3Hg^+ concentrations in sediments and water (Jackson, 1987, 1988b). (Unlike $CaCl_2$, neither dilute acetic acid nor the chelator DTPA proved to be a satisfactory extractant for bio-available inorganic Hg(II), suggesting that the formation of soluble Hg-Cl^- complexes accounts for the success of the $CaCl_2$ extraction method (Jackson, 1988b, 1991a).) The results of this research constitute strong evidence for the following conclusions: (1) it is mainly sulfides and selenides that limit the availability of inorganic Hg(II) for methylation; (2) meaningful estimates of relative rates of CH_3Hg^+ production and bio-accumulation can be obtained only if the microbial CH_3Hg^+ generating activity and the supply of inorganic Hg(II) available for methylation are both taken into account (neither variable alone being sufficient); (3) walleye (unlike certain other fish species that were tested) are well suited for whole-lake bioassays of CH_3Hg^+ production; and (4) the methods employed for quantification of CH_3Hg^+ production in sediments are both valid and potentially useful for purposes of research and monitoring, as demonstrated by the strong correlations between the sediment data and independent data for fish.

Owing to the extremely stable bonds that Hg forms with selenides, Se either interferes with the accumulation of Hg in aquatic organisms or is closely associated with Hg in their tissues (probably in the form of Hg-Se or CH_3Hg-Se complexes bound to the -SH groups of proteins (Koeman *et al.*, 1973)), depending on the nature of the organisms. Research by several workers has established that Se (probably in the form of selenides, even if initially in the form of selenite in the environment) can be remarkably effective in blocking the accumulation of Hg by fish and other aquatic animals and may further the elimination of Hg from Hg-contaminated fish (Rudd *et al.*, 1980; Turner and Rudd, 1983; Turner and Swick, 1983; Björnberg *et al.*, 1988; Lindqvist *et al.*, 1991; Paulsson and Lundbergh, 1991). Field

experiments demonstrated that Se in lake water did not affect the uptake of waterborne Hg by fish, whereas Se ingested with food decreased the Hg content of the fish (Turner and Swick, 1983). However, a number of marine and freshwater animals accumulate Hg and Se together, so that an increase in the one element is accompanied by an increase in the other. Thus, there is a highly significant positive correlation between Hg and Se in the tissues of marine mammals (e.g. dolphins, porpoises, and seals), the Hg/Se mole ratio in the tissues being 1:1, and the Hg was found to be tightly bound, strongly suggesting fixation of CH_3Hg^+ by the formation of selenide complexes bound to -SH groups of proteins (Koeman *et al.*, 1973, 1975). Similarly, there is a marked positive correlation between Hg and Se in the flesh of tuna fish, which is also attributed to CH_3Hg-Se-S-protein complexes (Ganther *et al.*, 1972). One study showed that Se increased the Hg body burden of goldfish exposed to inorganic Hg(II) in the form of $HgCl_2$, but it ameliorated the toxicity of the Hg, implying strong fixation of Hg, as in marine mammals (Heisinger *et al.*, 1979). Evidently selenides intervene in the uptake, assimilation, and excretion of CH_3Hg^+, the principal form of Hg in fish and aquatic mammals. Besides affecting Hg accumulation by animals, Se may have complex effects on microbial production of CH_3Hg^+ and other microbial activities in sediments, as demonstrated experimentally using sediment from a lake polluted with smelter fallout (Jackson, 1991b). With increasing Se concentration, CH_3Hg^+ production alternately increased and decreased, forming a series of CH_3Hg^+ maxima (coinciding with CO_2 maxima) superimposed on a downward trend ending in total inhibition at the highest Se levels ($\geq$ 50 μmol/L in the aqueous phase). This complex zigzag pattern of variation was ascribed to systematic changes in the species compositon of the microflora (ecological succession) owing to suppression of Se-sensitive species accompanied by opportunistic flourishing of Se-tolerant species, which were themselves inhibited as the Se continued to rise, the result being alternate upswings and downswings in the net rate of CH_3Hg^+ production.

Finally, it is important to be aware that organic nutrients, O_2, and sulfides have multiple effects, some reinforcing each other whilst others tend to cancel each other. The *net* effect of any one of these three factors, or a combination of them, acting in conjunction with a host of other variables, such as pH, may be to stimulate *or* depress CH_3Hg^+ production, depending on the outcome of a complex trade-off. High primary productivity may promote CH_3Hg^+ production by providing organic nutrient substrates and creating anoxic conditions, while tending to inhibit CH_3Hg^+ production though the formation of sulfide and organic complexing agents (e.g. thiols); and organic matter dispersed in the water may scavenge dissolved CH_3Hg^+, making it less available for uptake by fish (Hudson *et al.*, 1994). In contrast, a well aerated, highly oxidising environment poor in labile organic matter is less favourable for microbial methylating activity but makes inorganic Hg(II) more available for methylation (Jackson, 1988b, 1991a, 1993a, 1993b). Consequently, in a eutrophic lake the net rate of CH_3Hg^+ production may be high in a zone of O_2 depletion because stimulation of the activities of methylating microbes compensates for

immobilisation of inorganic Hg(II) by sulfide; but in a well aerated region of the lake the rate could be equally high because enhanced bio-availability of inorganic Hg(II) compensates for a lower level of methylating activity. These principles are strikingly illustrated by phenomena observed in a chain of extremely eutrophic, Hg-polluted lakes linked by the Qu'Appelle River in the semi-arid prairie region of Saskatchewan, Canada (Jackson, 1986, 1993a, 1993b). In the deepest basins of the lakes the bottom water was poorest in dissolved O_2 and the sediments had the lowest Eh values, highest organic content, highest level of heterotrophic (CO_2-generating) microbial activity, and most intense microbial Hg methylating activity but had the lowest degree of inorganic Hg bio-availability (as estimated by the total Hg/sulfide ratio of the sediment). An analogous trade-off exists in an O_2-depleted zone in ocean water, where a methyl Hg maximum coincides with a minimum in bio-available inorganic Hg (Mason and Fitzgerald, 1991). At the opposite extreme, the most shallow basins of the lakes were richest in dissolved O_2 and had the lowest levels of heterotrophic and methylating activities (despite a high level of primary productivity) but were characterised by the highest degree of inorganic Hg bio-availability. The observed relationship between CH_3Hg^+ production in the sediments and mean Hg concentrations in walleye populations in the lakes revealed that the Hg content of the fish is determined by the combined effect of microbial methylating activity and inorganic Hg(II) availability, not either factor alone. The highest Hg levels in the fish occurred in lakes with deep anoxic basins (or a deep anoxic basin at one end and a shallow, well-aerated basin at the other), because they supported the greatest intensity of methylating and general heterotrophic activity. But in one shallow, well aerated lake (the one situated furthest downstream from the source of Hg pollution), the Hg content of walleye was much higher than might have been expected. The reason for this anomaly is that inorganic Hg(II) in that lake had a high degree of bio-availability, compensating somewhat for a low level of methylating activity. A comparable trade-off was brought to light by comparison of two constrasting basins - one relatively stagnant and poorly aerated, and the other well flushed and aerated by fluvial currents - in Notigi Lake (northern Manitoba, Canada), a natural Boreal forest lake artificially expanded to form a reservoir (Jackson, 1988b, 1991a).

One other example of apparent effects of variations in the abundance of labile organic matter would be instructive. Huge quantities of both Hg and organic particles (wood chips) have been discharged into the Wabigoon River in Northern Ontario (Canada) from a chlor-alkali plant and pulp-and-paper mill (Jackson, 1980; Jackson and Woychuk, 1980a, 1980b, 1981; Jackson *et al.*, 1982; Parks and Hamilton, 1987). Dispersal and dilution of the pollutants in the downstream direction created an environmental gradient characterised by a sharp decrease in the total Hg and organic C content, and a corresponding increase in the natural clay-silt content, of the sediment with distance downstream from the source of pollution. But CH_3Hg^+ levels remained high throughout the river, even *increasing* in the downstream direction over part of the river's course, despite the drop in total Hg (Jackson and Woychuk, 1980a,

1980b, 1981; Jackson *et al.*, 1982; Parks and Hamilton, 1987; Parks *et al.*, 1991b; and the bio-availability of the inorganic Hg (based on the percent extracted with 0.5 M $CaCl_2$ or Ca acetate solution or the amount solubilised per unit concentration of Cl^- ions present as pollutants in the river water) increased in the downstream direction, signifying that Hg sorbed to fine mineral particles was more weakly bound than Hg sorbed to the wood chips (Jackson and Woychuk, 1980a, 1980b, 1981). The results suggest that conditions for CH_3Hg^+ production improved in the downstream direction because the inorganic Hg(II) became more bio-available (and possibly owing to attenuation of toxic pollutants that inhibited bacteria), although this advantage may have been partially offset by the decrease in the abundance of organic matter and inorganic Hg.

The nature of the labile organic matter as well as its gross abundance may have a bearing on CH_3Hg^+ production. Data for the Qu'Appelle River lakes suggest that the species composition of the phytoplankton, which is the main source of organic nutrients for Hg-transforming microbes, affects the rates of Hg methylation and demethylation. Thus, certain species of cyanobacteria appear to promote methylation, but diatoms and chlorophytes apparently foster demethylation (Jackson, 1993b).

As these observations and others (e.g. Jackson, 1987, 1991a, 1993a) illustrate, organic nutrient substrates are required for the growth of demethylators as well as methylators. But the net effect of adding organic matter to an environment relatively poor in organic matter is an upsurge in CH_3Hg^+ production (Jackson, 1988b, 1991a). Thus, a marked increase in the rate of CH_3Hg^+ production leading to a rise in the Hg content of fish is a usual - perhaps universal - side-effect of the creation of reservoirs owing to the introduction of organic matter into the aquatic environment by the flooding of land (Bodaly *et al.*, 1984; Jackson, 1987, 1988b, 1991a); this phenomenon has occurred repeatedly in newly formed reservoirs located in widely separated, environmentally diverse geographical regions where no local point sources of Hg contamination are known to exist. In reservoirs of northern Manitoba, Canada, which have been studied in detail, the main reason for this effect is that the labile terrestrial organic matter of recently submerged land areas stimulated the growth and activities of methylating microbes by providing them with nutrient substrates and, at the same time, creating anoxic conditions (Jackson, 1987, 1988b). However, as the organic content and heterotrophic microbial activity of the sediments increased, production of CH_3Hg^+ in the sediments and concentrations of Hg (mostly CH_3Hg^+) in fish inhabiting the overlying water rose to a maximum and then declined (Jackson, 1991a). By the same token, experimental enrichment of lake and reservoir sediments with organic nutrients accelerated methylation only if the sediment was poor in organic matter to begin with; if it was already rich in organic matter, the nutrient amendment depressed methylation somewhat (Jackson, 1991a). The reduced production and bio-accumulation of CH_3Hg^+ following excessive enrichment in organic nutrients was probably caused primarily by the production of sulfide and organic complexing agents, especially thiols, which lowered

the bio-availability of inorganic Hg(II) and perhaps the bio-availability of CH_3Hg^+ itself (D'Itri, 1971; Jackson, 1991a), although other possible causes include stimulation of demethylating microbes at the expense of methylators (Jackson, 1991a), conversion of CH_3Hg^+ to volatile derivatives such as $(CH_3)_2Hg$ which were then lost to the atmosphere (Rowland *et al.*, 1977; Craig and Bartlett, 1978), and microbial reduction of inorganic Hg(II) to Hg(0) (mainly in the epilimnion), leading to loss through evaporation and depletion of the pool of inorganic Hg(II) available for methylation (Mason *et al.*, 1995a). These conflicting effects of nutrient enrichment may help to reconcile the documented stimulation of microbial CH_3Hg^+ production and bio-accumulation by labile organic matter in eutrophic lakes with the seemingly paradoxical fact that fish in eutrophic lakes commonly have lower Hg levels than fish in oligotrophic lakes with a comparable degree of Hg contamination (Jernelöv *et al.*, 1975; Björnberg *et al.*, 1988). The systematic difference between Hg concentrations in the biota of eutrophic and oligotrophic lakes has been ascribed to greater "biodilution" and "growth dilution" in the more productive lakes, a consequence of their larger biomass and the higher growth rates of their inhabitants (Jernelöv *et al.*, 1975; Björnberg *et al.*, 1988; Meili, 1991). This interpretation is plausible, but Rudd and Turner (1983) and Jackson (1988a, 1991a) found no evidence that biodilution and growth dilution played a significant role in nutrient-enriched systems that they studied, probably because the increase in biological Hg concentrations due to acceleration of CH_3Hg^+ production by the nutrients far outweighed any opposing effect of biodilution and growth dilution.

In the reservoirs of Manitoba and other regions, an increase in the supply of Hg owing to the incorporation of Hg-bearing terrestrial organic matter into the aquatic environment has probably contributed to the increase in the Hg content of the biota following impoundment (Jackson, 1987, 1988b; Louchouarn *et al.*, 1993; Mucci *et al.*, 1995; Rodgers *et al.*, 1995). Jackson (1987, 1988b) considered this to be of secondary importance compared with the large post-impoundment upsurge in the growth of methylating microbes, but it could be significant, as suggested by the next section.

Humic matter. Allochthonous organic matter (notably humic matter) dispersed in runoff water from soils, peat bogs, and wetlands is a vehicle for transporting inorganic Hg(II) and CH_3Hg^+ into lakes in the Boreal forest zone (Lee and Hultberg, 1990; Meili, 1991; Meili *et al.*, 1991; Haines *et al.*, 1994; St. Louis *et al.*, 1994; Rudd, 1995; Branfireun *et al.*, 1996). High concentrations of humic matter in forest lakes are associated with high Hg levels in fish such as the piscivorous species northern pike and lake trout (Håkanson *et al.*, 1988; McMurty *et al.*, 1989; Rask and Metsälä, 1991; Haines *et al.*, 1994). Haines *et al.* (1994) postulated that humic matter promotes bio-accumulation of Hg by furthering the transport of Hg into lakes and retaining Hg in the water column. Humic matter may also stimulate the activities of heterotrophic microbes that generate CH_3Hg^+ (Jackson, 1989, 1995a), while depressing primary production (Jackson and Hecky, 1980), thereby reducing the biodilution of Hg. But Jackson

(1989) observed both positive and negative effects of humic matter on CH_3Hg^+ production in forest lake sediments; and Matilainen and Verta (1995) concluded that methylation in forest lakes was suppressed by humic matter. Moreover, "dissolved organic matter" (possibly composed largely of humic matter) scavenges dissolved CH_3Hg^+, making it less available to fish (Hudson *et al.*, 1994). Evidently humic matter performs diverse functions, and the net effect may be the result of opposing tendencies.

Humic matter may affect the bio-availability and bio-accumulation of Hg by complexing Hg(II) species and influencing microbial activities (Jackson, 1989, 1995a), and by mediating "abiotic" methylation. Though largely resistant to microbial decomposition, humic substances have profound and complex effects, both harmful and beneficial, on the growth and activities of aquatic organisms, including phytoplankton and benthic bacteria (Jackson, 1995a). The experiments of Jackson (1989) revealed that soil humic acid extracts had a number of different effects on microbial transformations of Hg in lake sediments. Humic acid (stripped of associated biochemical compounds by acid hydrolysis and dialysis) caused no immediate change in the rate of microbial Hg methylation and CO_2 production in nutrient-amended, $CaCO_3$-buffered sediment, but after incubation for a few days it increased both CH_3Hg^+ and CO_2 production appreciably. After several more days, however, the humic acid caused a decline in CH_3Hg^+ and CO_2 levels accompanied by an upsurge of CH_4-generating activity. The humic acid also complexed inorganic Hg(II) ($HgCl_2$) strongly, rendering it practically nondialysable. The results indicate that humic acid stimulated methylating microbes, causing a *net* increase in the CH_3Hg^+ production rate even though it probably lowered the rate somewhat as well by decreasing the bio-availability of the inorganic Hg(II); but subsequently the humic acid brought the CH_3Hg^+ level down by stimulating the activities of demethylating microbes. The data suggest that the humic matter altered the course of ecological succession in the microbial community, thereby altering the balance between methylation and demethylation, first in favour of CH_3Hg^+ production and then in favour of CH_3Hg^+ decomposition. In another experiment, in which humic acid was present as a coating on kaolinite, the humic acid inhibited Hg methylation, possibly by masking Fe oxide coatings on the clay (see below), although it enhanced demethylation as before. These results demonstrate that humic substances interacting with different microbial species and different environmental variables, may have complex, variable, and not altogether predictable effects on the microbial production and decomposition of CH_3Hg^+. Considering the wide variety of humic substances, microbial species and strains, and combinations of environmental conditions that may interact in nature, the possible effects could vary enormously, both qualitatively and quantitatively. Humic matter probably has important indirect effects as well (Jackson, 1995a): Depending on the nature of the humic matter (e.g. its molecular size), its abundance, and the ambient conditions, humic matter may either suppress primary production, as in Boreal forest lakes, or promote it, as in some coastal marine waters, and this must influence CH_3Hg^+ production and bio-accumulation

in different ways; besides, humic substances dispersed in water could benefit bacteria by serving as carriers of biodegradable organic matter and extracellular enzymes, and by exerting favourable effects on cell physiology. A general review of such phenomena has been given elsewhere (Jackson, 1995a).

pH and buffering. The pH of natural water, together with related parameters such as alkalinity, hardness, and buffering capacity, is of key importance in the production and bio-accumulation of CH_3Hg^+. The role of pH has attracted much attention in recent years owing to the influence of acid precipitation on the bio-accumulation of Hg in lakes. Widespread acidification of ill-buffered lakes in remote regions, such as the Precambrian shields of Canada and Scandinavia (Schindler, 1988), has been accompanied by a pronounced rise in the Hg content of fish, even though Hg pollution in these lakes has been limited to deposition of trace quantities of Hg transported from distant sources (e.g. coal-burning power plants) by atmospheric circulation (see below). A large body of empirical data produced by extensive field studies and experiments has established the important generalisation that Hg concentrations in freshwater fish and other aquatic organisms (and fish-eating animals) tend to increase as the pH, alkalinity, hardness, conductivity, and acid neutralising capacity of the water decrease (Jernelöv, 1972; Jernelöv *et al.*, 1975; Brouzes *et al.*, 1977; Scheider *et al.*, 1979; HÅkanson, 1980; Wren and MacCrimmon, 1983; Håkanson *et al.*, 1988; Richman *et al.*, 1988; Lathrop *et al.*, 1989, 1991; McMurty *et al.*, 1989; Cope *et al.*, 1990; Grieb *et al.*, 1990; Wiener *et al.*, 1990; Winfrey and Rudd, 1990; Ponce and Bloom, 1991; Rask and Metsälä, 1991; Wren *et al.*, 1991; Watras and Bloom, 1992; Hudson *et al.*, 1994; Simonin *et al.*, 1994; Anderson *et al.*, 1995; Meyer *et al.*, 1995).

The relationship between ambient pH and Hg in fish is neither simple nor completely consistent, and its underlying causes are not well understood. Several possible explanations merit serious consideration, but apparently no one of them, by itself, is sufficient to cover all the facts, suggesting that the observed effect is the net result of a complex interplay of many different physicochemical and biological phenomena involving different effects of pH and interactions of pH with other variables (Wood, 1980; Jackson, 1987; Richman *et al.*, 1988; Winfrey and Rudd, 1990; Ponce and Bloom, 1991; Haines *et al.*, 1994). Two examples of empirical observations should suffice to make the point that a number of different factors must be taken into account: (1) Andersson *et al.* (1995) reported that Hg levels in fish inhabiting acidified lakes peaked at a pH slightly higher than 5.0, decreasing above and below that value, demonstrating that bio-accumulation of Hg was not a simple function of pH. (2) Haines *et al.* (1994) found that the effect of pH on the Hg content of freshwater fish depended on the humic content ("colour") of the water; fish from lakes of high pH had low Hg levels regardless of humic content, but Hg levels in fish from lakes of low pH were quite variable, being highest in lakes of high humic content. A number of hypothetical explanations may be - and have been - invoked to explain the effect of pH and related factors on Hg levels in fish. One possible contributing factor which immediately springs to mind

is the fact that the acids of acid precipitation are accompanied by airborne anthropogenic Hg, since both volatile Hg and acid-generating S and N oxides are released into the atmosphere by the combustion of fossil fuels (see below). Another likely consequence of acidification is that the proportions of lipophilic, highly bio-available aqueous Hg species (e.g. $HgCl_2$ and CH_3HgCl) increase at the expense of less bio-available species (e.g. $Hg(OH)_2$ and CH_3HgOH), with the two-fold result that inorganic Hg(II) is more available for methylation and the CH_3Hg^+ produced is more rapidly and efficiently taken up by aquatic organisms (see above). Lowering the pH also furthers the release of sorbed and complexed inorganic Hg(II) into solution, making it more available for methylation; at higher pH values, aqueous Hg(II) is more efficiently sorbed by particulate matter because a higher proportion of it is in the form of $Hg(OH)_2$. (This would apply mainly to Hg(II) sorbed by colloidal minerals; organic (and probably sulfide) complexes of Hg are relatively insensitive to pH except under extremely acidic conditions (see above). Furthermore, acidic conditions may promote production of CH_3Hg^+ at the expense of $(CH_3)_2Hg$, both by causing spontaneous conversion of $(CH_3)_2Hg$ to CH_3Hg^+ and by promoting the activities of microbes that produce CH_3Hg^+ rather than $(CH_3)_2Hg$ (Wood, 1971; Fagerström and Jernelöv, 1972; Gavis and Ferguson, 1972). An additional factor linked to acid precipitation is increased SO_4^{2-} loading from the air; in anoxic environments this could foster the growth of SO_4^{2-}-reducing bacteria, which, under anoxic, low-SO_4^{2-} conditions, are important CH_3Hg^+ producers, but the effect of this on methylation is uncertain, as SO_4^{2-} concentrations above a certain critical level block the methylating activities of these bacteria (see above). A direct effect of pH on the bio-accumulation of CH_3Hg^+ has been postulated as well, but it has received only limited support from the available evidence and seems to be of no more than minor significance (Bloom *et al.*, 1991; Ponce and Bloom, 1991).

The arguments relating the increased Hg content of fish in acidified lakes to more efficient production of CH_3Hg^+ by microbes are plausible, but research in this area has yielded seemingly contradictory results. Some publications claim that acidification increases the net rate of CH_3Hg^+ production (Jernelöv, 1972; Fagerström and Jernelöv, 1972; Beijer and Jernelöv, 1979; Jackson and Woychuk, 1980a, 1980b, 1981; Miskimmin *et al.*, 1992; Wood, 1980; Xun *et al.*, 1987; Winfrey and Rudd, 1990; Bloom *et al.*, 1991; Matilainen *et al.*, 1991), but others report evidence that acidification tends to inhibit CH_3Hg^+ production (Shin and Krenkel, 1976; Ramlal *et al.*, 1985; Jackson, 1987; Steffan *et al.*, 1988). This paradox probably indicates that the role of pH is complex and can be understood only by examining the combined effects of pH and other factors. Experimental data reported by Jackson (1987) suggest that combined effects of pH and dissolved O_2 may be involved, and observations reported by Jackson and Woychuk (1980a, 1980b, 1981) and Matilainen *et al.* (1991), as well as literature surveyed by Winfrey and Rudd (1990), are consistent with this possibility. Investigation of Hg transformations in lake sediment over a range of ambient pH values under atmospheres of air and N_2 (Jackson, 1987) revealed

that within the pH range ~4.5-8.6 the rates of both methylation and demethylation peaked at pH values close to 7.0 (in the range ~6.0-7.5) under both air and N_2, declining as the pH rose or fell. These results are in agreement with those of Shin and Krenkel (1976). At pH ~7.0, methylating activity was more intense under N_2 than under air, but demethylating activity was stronger under air. Thus, at pH 7.0 anoxic conditions were optimal for CH_3Hg^+ production owing to high rates of methylation combined with low rates of demethylation, whereas exposure to well oxygenated water depressed CH_3Hg^+ production by simultaneously lowering the methylation rate and raising the rate of demethylation. At pH ~4.5-6.0, however, the rates of both methylation and demethylation were the same under air as under N_2. In a well oxygenated lake, therefore, acidification might well increase the net rate of CH_3Hg^+ production. These results are consistent with the possibility that the increase in the Hg content of fish in poorly buffered lakes following acidification may be caused, at least in part, by a combined effect of pH and O_2 which alters the balance between methylation and demethylation, causing a rise in the annual net rates of CH_3Hg^+ production in the lakes.

Miscellaneous physical variables. Various physical characteristics of the aquatic environment are of key importance in CH_3Hg^+ production and the bio-accumulation of Hg because of their effects on biological activities, oxidation-reduction conditions, and water chemistry. Depth of water, thermal stratification, and water dynamics (flushing, turbulent mixing, etc.) are of major significance; and lake volume and maximum depth have an important bearing on Hg levels in fish, probably owing to their influence on water quality and biological productivity (Wren and MacCrimmon, 1983).

Summer stratification isolates the hypolimnion from the well aerated epilimnion, often leading to anoxia and build-up of CH_3Hg^+ in eutrophic lakes. During the autumn turnover, CH_3Hg^+ concentrated in the hypolimnion is brought to the surface and may then be taken up by organisms in surface waters or (in the case of riverine lakes and lakes drained by streams) flushed out through the outflow, contaminating aquatic environments downstream from the lake (Parks *et al.*, 1989). During the spring turnover, algal blooms formed as a result of nutrient recycling may stimulate CH_3Hg^+ production. During the growing season in the temperate zone, the waters of a broad, shallow lake whose well mixed water column is not subject to stable thermal stratification are apt to be warm, well aerated, and rich in nutrients (and possibly resuspended sediment) released from the bottom and continually circulated throughout the water column. The warmth and nutrients probably favour CH_3Hg^+ production, whilst aeration and suspended particles (which limit light penetration besides scavenging Hg) tend to depress it. In river systems, flow rate and discharge are critical, as the biological activity necessary for CH_3Hg^+ production is likely to be greatest in times of slack water, when the flushing and dilution of nutrients and resuspension of bed sediments are minimal (Jackson, 1986; Parks *et al.*, 1989); in the temperate zone, this typically occurs during the summer, when low flow rates and high temperatures maximise microbial activity (Parks and Hamilton,

1987; Parks *et al.*, 1989). A study of seasonal variations in the Hg speciation in the Moose Jaw River, a tributary of the Qu'Appelle River (see above), showed that at the time of minimal discharge (in November) there was phytoplankton bloom resulting in a major upsurge in CH_3Hg^+ levels in the water even though total Hg levels were lowest, whereas during peak discharge (during the spring flood) CH_3Hg^+ levels were nil even though total Hg concentrations were maximal owing to bottom scour and resuspension of particulate Hg (Jackson, 1986). Unfavourable conditions for CH_3Hg^+ production in a river during the spring flood may result not only from the flushing and dilution of nutrients but also from the binding of Hg by sediments and bank material eroded and brought into suspension by fluvial currents (Jackson *et al.*, 1982; Jackson, 1986; Parks *et al.*, 1986).

Water temperature is of central importance, because it affects the production and bio-accumulation of CH_3Hg^+ by regulating the metabolic rates of organisms. Temperature is a function of climate, season, and factors such as the mean depth, surface area, and morphology of a body of water. Thermal stratification is dependent on depth, and its stability depends, too, on factors such as wind-driven circulation and fluvial currents flowing through riverine lakes. With rising temperature (all other things being equal) CH_3Hg^+ production rates and concentrations in aquatic environments increase, and the bio-availability of inorganic Hg in sediments and the concentration of inorganic Hg in the overlying water may increase as well, suggesting mobilisation of inorganic Hg(II) by microbial activities such as the decomposition of Hg-bearing organic matter (Shin and Krenkel, 1976; Jackson *et al.*, 1982; Parks *et al.*, 1986, 1989; Parks and Hamilton, 1987; Jackson, 1988b, 1991a; Bodaly *et al.*, 1993). Thus, Jackson (1988b) found that in lake and reservoir environments of Manitoba the concentrations of both CH_3Hg^+ in water and bio-available inorganic Hg in sediments were higher in August than in June. As a rule, the production and bio-accumulation of CH_3Hg^+ in a lake of the temperate zone are probably maximised in the mid-summer, the height of the growing season (Jackson *et al.*, 1982; Parks and Hamilton, 1987; Jackson, 1988b; Parks *et al.*, 1989); and in a river the combined effects of high temperature and low flow rate would be expected to enhance CH_3Hg^+-generating biological activity in the mid-summer.

In a study of lakes differing in surface area but otherwise similar, Bodaly *et al.* (1993) found that both CH_3Hg^+ production in epilimnetic bottom sediments and the Hg content of several fish species increased with the mean temperature of epilimnetic water, which, in turn, was inversely related to the "size" (i.e. surface area) of the lake. The methylation rate increased with rising temperature, but the demethylation rate decreased; hence, the M/D ratio correlated positively with temperature. The correlation between Hg in fish and epilimnion temperature did not apply to benthivorous fish, probably because they frequent cool bottom waters. The authors ascribed these results to direct effects of temperature on both bacterial activities and the metabolic rates of the fish. Their interpretation, though reasonable as far as it goes, is an oversimplification which ignores alternatives that merit consideration. Possible effects of

temperature and lake size are more complex than Bodaly *et al.* have indicated: They include indirect effects involving related variables, which were not considered (e.g. enhancement of primary production by heat and solar radiation, leading to intensified activity of methylators). Although temperature is known to affect the bio-accumulation of Hg, the relationships described by the authors may be due to variables that correlate with temperature or lake area, or temperature together with other factors, rather than temperature as such or temperature alone (Jackson, 1988a).

Generally speaking, the rise in temperature from winter to summer, or from cold, deep water to warm, shallow water, probably increases the growth rates and metabolic rates of (1) methylating microbes in the epilimnetic zone, (2) primary and secondary producers that provide these microbes with organic nutrients, and (3) fish and other organisms that accumulate CH_3Hg^+. At higher temperatures, aquatic organisms accumulate both CH_3Hg^+ and inorganic Hg(II) more efficiently and transfer CH_3Hg^+ more readily from one trophic level to another (e.g. from phytoplankton to zooplankton) because the metabolic rates of the organisms are elevated (Reinert *et al.*, 1974; Boudou and Ribeyre, 1981; Ribeyre and Boudou, 1982; Jackson, 1988a, 1991a; Bodaly *et al.*, 1993). But the higher rate of CH_3Hg^+ uptake by fish at higher temperatures is offset somewhat by accelerated excretion of CH_3Hg^+ (Ruohtula and Miettinen, 1975). Another complication arises from the fact that rising water temperature may cause the rate of CH_3Hg^+ accumulation by fish to increase until a critical temperature is reached and then decline (Burkett, 1974). Furthermore, the waters of small Boreal forest lakes are commonly enriched in allochthonous humic matter, which affects the production and bio-accumulation of CH_3Hg^+ (see above), whereas in the larger lakes the humic matter is more dilute. Also note that warm conditions do not favour the growth of all bacteria; some species are adapted to cold conditions, as is doubtless the case with bacteria in the sediments and hypolimnetic waters of deep lake basins where the temperature is perpetually low, though rising temperatures and other favourable conditions in the epilimnion may stimulate these microbes indirectly by increasing the supply of plankton-generated organic nutrient substrates that sink to the bottom. It is necessary to add that the effect of temperature may be obscured by that of some other environmental factor; thus, the above-mentioned seasonal maximum in phytoplankton biomass and CH_3Hg^+ content coinciding with minimum discharge in Moose Jaw River water occurred in November, when the temperature of the water was close to the freezing point (1.0-3.3°C.), whereas the concentrations in July, when the temperature was high (18.5°C.), were much lower (comparable to the levels observed during the spring flood) (Jackson, 1986). This implies that variation in methylating activity during the growing season was controlled by the supply of organic nutrient substrates, and therefore by the flow rate, not by water temperature.

Exposure of surface waters to solar radiation (a function of latitude, time of year, and climate) must also be considered because of its relation to temperature and primary production, and because Hg is

subject to photochemical alteration. Effects of sunlight depend on characteristics of individual lakes, such as humic content, suspended matter, surface area, mean depth, trophic status, and the nature of the biota.

Dissolved salts. Salinity is of paramount importance, especially where Cl^-, SO_4^{2-}, and possibly Ca^{2+} are concerned, and it has multiple effects. The results of experiments on the effects of variations in salinity on Hg methylation in $HgCl_2$-spiked slurries composed of anoxic estuarine sediments mixed with sea salt solutions at different concentrations (0.3-24 and 1-30 o/oo) show a decline in methylating activity with rising salinity (Blum and Bartha, 1980; Compeau and Bartha, 1987). Compeau and Bartha (1985) concluded that SO_4^{2-} ions in the sea salt prevented SO_4^{2-}-reducing bacteria from synthesising CH_3Hg^+ by by causing the bacteria to switch from fermentation to SO_4^{2-} reduction, leading to immobilisation of inorganic Hg(II) by H_2S. Evidently the observed effect of salinity was not caused by the formation of anionic Hg-Cl^- complexes (Compeau and Bartha, 1987). Nevertheless, Cl^- ions at concentrations of 0.2-20 o/oo have been found to inhibit microbial CH_3Hg^+ production in soil-water slurries (Shin and Krenkel, 1976), proving that suppression of the methylating activities of SO_4^{2-}-reducing bacteria by SO_4^{2-} ions is not the only possible effect of elevated salinity. Hg in fish from Canadian Shield lakes have been shown to correlate inversely with the conductivity (i.e. salinity) of the water, but this may reflect the influence of variables controlling the pH (e.g. water hardness and alkalinity) rather than salinity as such (Wren and MacCrimmon, 1983; Björnberg *et al.*, 1988). Interactive effects of salinity and Eh on Hg methylation and demethylation (Compeau and Bartha, 1984) have already been discussed.

As explained above, Cl^- ions play an important part in determining the bio-availability of Hg. Owing to the formation of water-soluble, weakly sorbed Hg-Cl^- complexes, Cl^- ions tend to prevent or reverse the complexing or sorption of inorganic Hg(II) by other binding agents, thereby making it more bio-available and more readily methylated. Accordingly, inorganic Hg(II) sorbed to suspended particles transported to the sea by rivers is largely desorbed by Cl^- ions on coming into contact with the salty waters of estuaries (De Groot *et al.*, 1971; De Groot and Allersma, 1975; Newton *et al.*, 1976; van der Weijden, 1990; Chen *et al.*, 1995); by the same token, contamination of Hg-polluted freshwater environments with Cl^- ions (e.g. from road deicing salt and effluents from chlor-alkali plants) results in desorption of sediment-bound Hg (Feick *et al.*, 1972; Jackson *et al.*, 1982). As we have seen, moreover, dissolved Cl^- concentrations and pH values favouring the formation of the uncharged, lipophilic species $HgCl_2$ and CH_3HgCl, enhance the biological uptake of both inorganic and methyl Hg owing to the ease with which they pass through membranes, and this may assist methylation and demethylation of Hg.

Finally, there is evidence consistent with the possibility that dissolved Ca^{2+} ions interfere with the uptake of Hg by fish. Thus, Wren and MacCrimmon (1983) observed an inverse correlation between the Hg content of fish and Ca levels in the surrounding water. As they themselves pointed out, this may simply be an indirect indication of the effect of pH, as water quality variables (e.g. hardness) that

determine the water's buffering capacity are linked to ambient Ca levels; but the relationship is also consistent with the possibility that Ca interferes directly in the biological uptake of CH_3Hg^+, possibly by decreasing gill membrane permeability or by competing with Hg species for cellular binding sites (Wren and MacCrimmon, 1983; Hudson *et al.*, 1994). In any event, the evidence available thus far consists solely of inverse correlations; a cause-and-effect relationship has not been established.

Clay- and silt-sized mineral particles. The binding and release of Hg by fine-grained mineral particles are among the major determinants of the bio-availability of the metal (Jackson, 1995a, 1996). Thus, the sorption or coprecipitation of inorganic Hg(II) by Fe and Mn oxides may interfere with the uptake of Hg by aquatic organisms, such as benthic invertebrates, which have a high proportion of inorganic Hg to CH_3Hg^+ (Jackson, 1988a). There is indirect evidence, too, that Fe and Mn oxides have selective effects on Hg uptake by specific kinds of organisms: The results of research on benthic invertebrates in lake and reservoir sediments suggest that the uptake of inorganic Hg by chironomid larvae is limited by FeOOH, whilst uptake by oligochaetes, nematodes, and pelecypods at the same sampling sites is controlled by MnOOH, implying discrimination between different forms of inorganic Hg(II) both by the oxides and by the animals themselves (Jackson, 1988a).

Clay- and silt-sized mineral particles strongly influence the microbial production of CH_3Hg^+, but the effects are complex, variable, poorly understood, and hard to predict. Inorganic Hg(II) in sediments is less strongly sorbed and hence more available for methylation if it is sorbed to clay, oxides, and silt than if it is bound to organic matter or sulfide (Jackson and Woychuk, 1980a, 1980b, 1981; Jackson *et al.*, 1982; Schuster, 1991; Jackson, 1993b). But clay and silt introduced into lakes by fluvial transport or the erosion of shoreline material inhibits CH_3Hg^+ production in sediments, and both methylation and demethylation may be adversely affected (Jackson, 1987, 1988a, 1988b, 1989; 1991a, 1993a, 1993b, 1995a). Possible reasons include the following: (1) reduced light penetration owing to turbidity, limiting primary production of the organic nutrients needed by microbes; (2) rapid burial and dilution of organic matter and other nutrients; (3) the smothering of microbes by prevention of the exchange of dissolved nutrients and wastes between the sediment and water; (4) scavenging and immobilisation of inorganic Hg(II); and (5) selective inhibitory or stimulatory effects of the minerals on specific kinds of microbes. Regarding selective effects, experiments performed by Jackson (1987, 1989, 1995a) showed that clay had no effect, or a slightly inhibitory effect, on Hg methylation in sediments from a Boreal forest lake but strongly enhanced subsequent demethylation. In contrast, clay strongly inhibited Hg methylation in sediment from a prairie lake but did not stimulate subsequent demethylation. Either of these radically different effects could lower the net rate of CH_3Hg^+ production in an aquatic ecosystem. The disparity between the two sets of observations probably reflects a major difference between the microbial communities of the two unlike lakes. In general, experiments on effects of clay minerals and oxides on

microbial Hg transformations in sediments yielded complex and variable results suggesting selective effects on particular microbes, and therefore involvement of ecological succession in the microbial community, rather than general effects such as suppression of microbial activity as a whole or decreased bio-availability of inorganic Hg(II) owing to sorption. Depending on the nature, abundance, and surface chemistry of the mineral colloid, the experimental conditions, and the source of the sediment (i.e. the species composition of the microflora), the minerals either strongly inhibited or promoted Hg transformations or had little net effect, or exerted a succession of different effects as the experimental conditions (e.g. the abundance of the added colloid) changed or as the incubation time increased (Jackson, 1989, 1995a). Coatings on the mineral particles were of decisive importance. FeOOH tended to enhance methylation, and FeOOH coatings on clay crystals greatly mitigated the inhibitory effect of the clay. Indeed, the extent to which a specimen of clay inhibited methylation was attributable entirely to the amount of FeOOH on the surfaces of the clay crystals, not to the nature of the clay mineral itself (Jackson, 1989, 1995a). Removal of oxide coatings from clay depressed both methylation and demethylation. Furthermore, environmental changes, such as nutrient enrichment, altered the effects of the coatings on the clay: On addition of organic nutrients, oxide coatings promoted methylation and impeded demethylation; but without nutrient enrichment the reverse tended to occur.

The importance of particle coatings and other impurities associated with clay cannot be overemphasised, and failure to recognise it may lead to serious errors. An object lesson recorded in the literature will serve to drive this point home. Specimens of natural silty clay used in some of the experiments of Jackson (1987, 1989, 1995a) contain calcite and dolomite; pH buffering by these carbonates stimulated the activities of Hg methylating microbes in sediments amended with the clay, offsetting the negative effect of the non-carbonate minerals and causing a net *rise* in the rate of CH_3Hg^+ production. To measure the impact of the non-carbonate minerals, it was necessary to eliminate this pH effect by buffering all experimental and control systems with added $CaCO_3$. Meanwhile, Hecky *et al.* (1987, 1991) independently carried out a comparable experiment employing the same clay but neglected to take pH buffering into account (though it was obvious from their own raw data). As in the initial experiments of Jackson, their data showed a favourable effect of the clay on methylation; but, taking no notice of the published findings of Jackson, they failed to realise that their results were attributable solely to buffering by carbonates. Thus, they drew invalid inferences and used their data as a basis for unfounded speculation about effects of clay in nature.

Pollutants other than mercury. Hg in aquatic environments is commonly accompanied by other pollutants which may either exacerbate or ameliorate the undesirable biological effects of Hg. A common and notorious instance of this is the association between the volatile Hg and strong acids introduced into the air by combustion of coal and transported over great distances by winds. As we have seen, the acids

aggravate the adverse effects of the Hg, apparently promoting the accumulation of CH_3Hg^+ by fish.

Synergistic and antagonistic effects of toxic pollutants such as heavy metals other than Hg may occur as well. A study of sediments from lakes polluted with heavy metals showed a strong inverse correlation between Hg methylating activity and the abundance of bio-available (DTPA-extractable) Cd, probably owing to inhibition of methylators by the Cd (Jackson *et al.*, 1993). In contrast, total Cd content, as well as other variables, such as the Eh, pH, and organic content of the sediment, which might be expected to control CH_3Hg^+ production, did not correlate significantly with methylating activity. Hence, bio-available Cd exerted a controlling influence on the Hg content of northern pike in the lakes. Cu and Zn gave comparable results, but Cd, though much less abundant, had by far the strongest inhibitory effect. The order of decreasing inhibition was Cd > Cu > Zn, which is the order of decreasing metal sulfide stability as represented by standard entropy, suggesting that inhibition of methylators resulted from the binding of Cd by -SH groups of enzymes. Also note that low Hg levels have been found in fish inhabiting lakes polluted with Zn (Björnberg *et al.*, 1988). Experiments, too, have shown inhibition of methylating activity by added Cd, Cu, and Zn in lake sediments (Jackson, 1991b). In sediment from an essentially pristine lake, CH_3Hg^+ production simply declined with increasing Cd, Cu, or Zn concentration, revealing an absence of metal-tolerant methylating microbes. But in sediments from metal-polluted lakes methylating activity was alternately inhibited and enhanced, yielding a zigzag pattern of variation, with increasing Cd, Cu, or Zn. Only at the highest metal concentrations was methylation completely suppressed. Surprisingly, within certain ranges of metal concentrations the CH_3Hg^+ yield was higher than in control systems containing no added Cd, Cu, or Zn. These complex results imply ecological succession based on competition between metal-sensitive and metal-tolerant microbes, with tolerant species supplanting sensitive ones as the metal concentration increased, the result being large upswings and downswings in the net rate of CH_3Hg^+ production. As would be expected, metal-tolerant microbes were detected only in metal-contaminated sediments. Moreover, the relative toxicities of different metals apparently depended on the nature of the microbes. For instance, the relative toxicities of Cd and Cu varied in the order Cd > Cu *or* Cd < Cu *or* Cd = Cu, depending on the circumstances.

The effects of organic wastes are complex and variable, and some of them are mutually antagonistic, the net result being either enhancement or suppression of CH_3Hg^+ production. Thus, wood chip deposits in the Wabigoon River (see above) provide nutrients for methylators but restrict the availability of inorganic Hg(II) (Jackson and Woychuk, 1980a, 1980b, 1981). Sewage, too, may play many parts. A lake near near a base metal mine at Flin Flon, Manitoba is the receiving basin for both municipal sewage effluent and tailings pond effluent contaminated with heavy metals (including Cu, Zn, Cd, and some Hg), along with SO_4^{2-} (Jackson, 1978, 1979, 1984). Nutrients in the sewage support the growth of algal blooms, resulting in rapid immobilisation of the metals owing to the scavenging of metals by plankton

and nonliving suspended particles (aided by alkaline conditions due to photosynthesis) followed by sedimentation of the particulate metals and precipitation of metal sulfides by H_2S generated by decomposition of dead algae accompanied by SO_4^{2-} reduction. Hg is more efficiently trapped in the sediments than the other metals because the stability of black HgS, as represented by its standard entropy, is greater than that of any of the other metal sulfides (Jackson, 1978, 1979). Compared with sediments in sulfide-poor lakes in the vicinity, the sediments of this lake were found to have a low CH_3Hg^+/total Hg ratio (Jackson, 1984), indicating net inhibition of CH_3Hg^+ production owing to immobilisation of inorganic Hg(II) by sulfide despite presumed stimulation of methylating activity by the high primary productivity of the lake. An altogether different effect of sewage was seen in lakes of the Qu'Appelle River system (see above). Jackson (1993b) found evidence that nutrients from sewage effluents discharged into one of the lakes favours development of plankton blooms with anomalously high proportions of diatoms and chlorophytes, which apparently foster the growth of demethylators at the expense of methylators (Jackson, 1993b), resulting in relatively weak CH_3Hg^+ producing activity.

Biological factors. The bio-accumulation of Hg is regulated by the characteristics and activities of (1) the microbial community that controls the speciation and bio-availability of the Hg and (2) the aquatic food-chain organisms that accumulate the Hg. An extremely complex, ever-shifting interplay of biological and physicochemical factors is involved in this process, and a list of possible direct and indirect effects, feedback mechanisms, and interactions between different factors would be endless.

As discussed above, the activities of microbial communities in sediments and water are multifarious. Natural microfloras contain many diverse species and strains of both methylating and demethylating microbes and microbes that convert inorganic Hg(II) to Hg(0), together with other kinds of microbes which do not mediate Hg speciation reactions but may affect these processes indirectly by influencing the growth and activities of Hg-transforming species (through mutualism, competition, antagonism, etc.) (Jackson, 1995a). These microbes differ widely in their ecological requirements and limits of tolerance to different conditions, and they interact with each other in various complex ways. In any given environment at any point in time, the microflora is composed of an assemblage of those species that are best adapted to the prevailing conditions. A shift in environmental conditions, either imposed by external events (e.g. an influx of suspended silt or dead algae from a plankton bloom) or caused by the microbes themselves (e.g. when aerobes deplete the local supply of dissolved O_2, creating a favourable environment for anaerobes, or when anaerobes start generating H_2S), leads to a shift in the species composition of the active portion of the microflora (i.e. ecological succession), whereby microbes ill adapted to the new conditions die or become inactive whilst well adapted species replace them. There may also be important changes in overall microbial biomass or activity; thus, enrichment in organic nutrients increases the microbial biomass and the general level of heterotrophic microbial activity besides changing the species

composition of the microflora. Not surprisingly, the nature and activities of the microflora are subject to major spatial and temporal (e.g. seasonal) variations. As we have seen, these variations commonly result in large changes in the rates of Hg methylation and demethylation and in the precarious balance between the two processes (the M/D ratio). An essential role of food-chain organisms, chiefly phytoplankton, is to produce the labile organic matter utilised as nutrient substrates by the microflora. Irrespective of their influence on Hg-transforming microbes, however, the food chain organisms regulate their uptake, retention, and excretion of Hg through an assortment of vital functions that differ from species to species, vary over the lifetime of an individual organism, and are modified by the environment; and different combinations of these biological variables produce different *net* effects (Jernelöv and Lann, 1971; Scott and Armstrong, 1972; Burrows and Krenkel, 1973; Scott, 1974; de Freitas and Hart, 1975; Miettinen, 1975; Norstrom *et al.*, 1976; de Freitas *et al.*, 1977; Huckabee *et al.*, 1979; Windom and Kendall, 1979; Jackson and Woychuk, 1980a, 1980b; Jackson, 1988a, 1991a; Nicoletto and Hendricks, 1988; Richman *et al.*, 1988; Grieb *et al.*, 1990; Cabana *et al.*, 1994; Rodgers, 1994).

A most important general principle of Hg biogeochemistry is the marked tendency of Hg concentrations in the muscle tissue of fish (mature fish, at least) to increase with the size (fork length or weight) of the fish (Scott, 1974; Jackson, 1991a). In some instances, as in newly formed reservoirs following a sudden increase in CH_3Hg^+ production, Hg content and size are poorly correlated, and the correlations may even be negative in the case of small fish with high growth rates (Jackson, 1991a), but these cases are exceptional. The positive correlation between Hg content and size in fish is thought to be primarily an effect of age, which, of course, correlates with size: The older the fish, the greater its cumulative body burden of CH_3Hg^+ because it has been exposed to environmental CH_3Hg^+ for a longer time and because CH_3Hg^+ is usually taken up rapidly but excreted slowly (Huckabee *et al.*, 1979; Windom and Kendall, 1979). However, Scott (1974) inferred that the correlation between size and Hg content reflects interactions between age, growth rate, and condition. Indeed, we can go further and draw the conclusion that CH_3Hg^+ (or total Hg) levels in fish and other organisms are complex functions of many biological variables, including metabolic rate, growth rate, diet, excretory pathways, population biomass, and habitat preference, as well as age and size (Jackson, 1991a). Smaller, younger fish take up CH_3Hg^+ more rapidly than larger, older ones because of their higher rate of metabolism (de Freitas and Hart, 1975), but they also excrete it more rapidly because of their small body size, and growth dilution tends to keep the concentrations low. As with growth dilution, biomass dilution may result in lower Hg concentrations in the tissues of individual fish in the relatively large populations of the more productive lakes (Jernelöv *et al.*, 1975; Björnberg *et al.*, 1988; Rask and Metsälä, 1991), although in some environments its quantitative importance relative to other factors appears to be small (Rudd and Turner, 1983; Jackson, 1988a, 1991a). Retention of CH_3Hg^+ by fish is a function of body size, diet, and species and is not

affected by growth rate (de Freitas *et al.*, 1977). Miettinen (1975) maintains that excretion of CH_3Hg^+ and other forms of Hg becomes more rapid with rising temperature, but de Freitas *et al.* (1977) deny that temperature affects whole-body retention of CH_3Hg^+ by fish. Another consideration is that juvenile fish have different feeding habits than adults of the same species; thus, among piscivorous predators, immature fish feed on small invertebrates, which are likely to have low CH_3Hg^+ concentrations, whereas adults prey on other fish, which are enriched in CH_3Hg^+. Fish that feed on invertebrates generally have lower Hg concentrations than fish that feed on other fish (Jackson, 1991a; Brouard *et al.*, 1994; Rodgers, 1994). In brief, there are many different tendencies controlled by different physiological phenomena, some of them tending to offset each other, but the net result is that larger fish tend to be richer in Hg than smaller ones even though smaller fish, paradoxically, accumulate Hg faster.

Another generalisation of major importance is that CH_3Hg^+ concentrations and CH_3Hg^+/inorganic Hg ratios in aquatic organisms usually increase progressively up the food chain, the result being that the lower organisms (plankton and benthos) have relatively high, though variable, proportions of inorganic Hg, whilst the Hg in fish, especially piscivorous predators, is mostly in the form of CH_3Hg^+ (Jernelöv and Lann, 1971; D'Itri, 1972; Bishop and Neary, 1974; Koeman *et al.*, 1975; Huckabee *et al.*, 1979; Windom and Kendall, 1979; May *et al.*, 1987; Jackson, 1988a, 1991a; Grieb *et al.*, 1990). The longer the food chain, the higher the Hg content of the fish at the upper end of it (Cabana *et al.*, 1994) (which may explain the absence of biomagnification in the short food chain studied by Knauer and Martin (1972)). There is some doubt, however, about the mechanism of biomagnification, and the very concept of it is thought to be misleading: Biomagnification may be no more than an expression of the longer life spans and lower growth rates of animals at the upper end of the food chain (de Freitas *et al.*, 1974; Huckabee et al., 1979). But the fact that animals at higher trophic levels consume food that is richer in CH_3Hg^+ than do animals at lower levels probably helps to account for it too (Jackson, 1991a; Brouard *et al.*, 1994; Rodgers, 1994), as suggested by (1) an observed rise in the Hg content of a whitefish population owing to the inclusion of more fish in their diet (Brouard *et al.*, 1994), (2) higher Hg levels of pike populations that preyed on fish species of higher Hg content (Rask and Metsälä, 1991), and (3) the occurrence of two separate but parallel food chain segments, one linking benthic invertebrates to whitefish and the other linking zooplankton to spottail shiner, implying that anomalously low CH_3Hg^+ levels in the benthos resulted in correspondingly low CH_3Hg^+ levels in the whitefish (Jackson, 1991a). In any case, biomagnification is far from straightforward and simple. Even animals at the same trophic level may differ considerably in Hg content, Hg-fork length relationships, and regional and temporal variations in Hg content (Jackson, 1991a). Walleye and northern pike populations coexisting in reservoirs and a riverine lake were found to differ appreciably in this regard, probably because they differ in their habitat preferences and spatial distributions within the bodies of water that they occupy (Jackson, 1991a).

Owing to their lower metabolic rate, pike prefer to lurk in shallow, weedy waters near the shore, whilst walleye have a greater tendency to venture into open water. Consequently, they differ in their degree of exposure to the regions of most intense Hg methylating activity, which, in recently formed reservoirs, are the near-shore zones of flooded land. Systematic differences in Hg concentrations in two other coexisting fish species at the same trophic level were tentatively ascribed to different spatial variations in diet, rate of food intake, growth rate, metabolic rate, and biomass, resulting in different rates of Hg uptake, elimination, and biodilution (Jackson, 1991a). To take another example from lakes of the Wabigoon River system (see above), Hg in walleye decreased with distance downstream from the source of Hg pollution owing to attenuation of fluvially transported CH_3Hg^+ in surface water, whereas Hg in white sucker increased, reflecting a trend in the CH_3Hg^+ content of sediments and bottom water (Jackson and Woychuk, 1980a, 1980b). Even within a single species, individuals differ among themselves. Females commonly have higher Hg levels than males, and the difference is not related to body size (Nicoletto and Hendricks, 1988); and, as already discussed, smaller, younger fish have lower Hg concentrations than larger, older ones. The mechanism of Hg uptake must also be considered. Animals take up CH_3Hg^+ in two ways: by ingestion with food and direct absorption from water (through the gill membrane in the case of fish) (de Freitas *et al.*, 1974; Norstrom *et al.*, 1976; Gottofrey and Tjälve, 1991; Jackson, 1991a). The proportions of CH_3Hg^+ assimilated by these two pathways appears to vary from one species to another (Jackson, 1991a). According to D'Itri (1991), fish generally take up most of their CH_3Hg^+ with food, but absorption through the gill membrane and body surface is also a significant pathway. Diet is the main source of CH_3Hg^+ for certain predatory fish, and the nature of the diet affects the transfer of CH_3Hg^+ to the fish (see above): Differences in feeding strategy cause differences in the Hg content of fish (Richman *et al.*, 1988).

Some aquatic animals appear to have evolved biochemical mechanisms for transforming and eliminating Hg. In reservoirs where the Hg content of fish was found to be abnormally high owing to effects of impoundment, Hg levels in whitefish peaked early and then declined over time, whilst Hg levels in walleye, pike, and trout remained high (Bodaly *et al.*, 1984; Jackson, 1991a; Anderson *et al.*, 1995; Morrison and Thérien, 1995), suggesting that the biochemical and physiological pathways of Hg in whitefish are fundamentally different from those of the other species, and that they include a special mechanism for excretion of Hg. Compared with other fish species studied, whitefish in northern Manitoba lake and reservoir waters have a weak tendency to accumulate CH_3Hg^+ (although most of the Hg in their flesh is in the form of CH_3Hg^+), and, compared with walleye and pike, they have an anomalously high ratio of liver CH_3Hg^+ to muscle CH_3Hg^+, suggesting, again, a special mechanism of excretion, such as the binding of CH_3Hg^+ by carrier molecules (possibly proteins with -SH groups, or other thiols), creating hydrophilic complexes that are readily eliminated (Jackson, 1991a). The fact that

whitefish feed on benthic invertebrates which, themselves, have a low affinity for CH_3Hg^+ suggests that the hypothetical complexes are formed by the benthos consumed by the fish and are subsequently excreted by the fish. This theory is in agreement with evidence that the CH_3Hg^+ which fish ingest with food is less toxic than CH_3Hg^+ absorbed directly from water (Wobeser, 1974). Experimental results showing that CH_3Hg^+ administered to rainbow trout as a protein complex had a shorter ½-time in the fish than CH_3Hg^+ administered as a nitrate (Ruohtula and Miettinen, 1975) are also consistent with idea of a molecular carrier originating in food consumed by the fish. In any case, the low-CH_3Hg^+ diet of whitefish is surely linked to the low CH_3Hg^+ content of the fish. Habitat preference may be a contributing factor, as whitefish frequent cold bottom waters, where rates of CH_3Hg^+ are relatively low, partly because of the low temperatures and, in reservoirs, partly because organic nutrients are concentrated in the nearshore zone of flooded land (Jackson, 1991a). Demethylation of CH_3Hg^+ in liver or kidney tissues also occurs in certain fish species, including whitefish (Burrows and Krenkel, 1973; Windom and Kendall, 1979).

Toxicity and detoxification.

The chief cause of Hg toxicity is inhibition of enzymes owing to strong binding of their -SH groups by inorganic Hg(II) and CH_3Hg^+ (although Hg(II) may also activate certain enzymes (Bidstrup, 1964; Ochiai, 1977)). Hg(0) and $(CH_3)_2Hg$, too, are toxic, probably as a result of being transformed into inorganic Hg(II) and CH_3Hg^+, respectively, after entering an organism's body (Bidstrup, 1964; Wood, 1971; Gavis and Ferguson, 1972; Carty and Malone, 1979); but because of their high degree of volatility, they are more fugitive in the environment, and hence have a lower probability of being taken up by the aquatic biota. Besides combining with -SH groups of enzymes and other proteins, Hg(II) forms complexes with the -COOH and $-NH_2$ groups of amino acids and proteins and with the nitrogenous bases and phosphate groups of nucleic acids, altering the conformations of the molecules (Ochiai, 1977); it also interferes with the normal functions of biological membranes, including cell membranes of phytoplankton (Ochiai, 1977) and gill membranes of fish (Walczak *et al.*, 1986). CH_3Hg^+, moreover, denatures nucleic acids (Ochiai, 1977; Cotton and Wilkinson, 1988).

Both inorganic Hg(II) and CH_3Hg^+ in aqueous solution are very toxic to a wide range of aquatic organisms, including bacteria (Hamdy *et al.*, 1977; Hamdy and Wheeler, 1978; Ribo *et al.*, 1989; Farrell *et al.*, 1990), yeast (Kidby, 1974), planktonic marine and freshwater algae (Knauer and Martin, 1972; Nuzzi, 1972; Röderer, 1983), and fish (Alexander, 1974; Ruohtula and Miettinen, 1975; Wobeser, 1975; Walczak *et al.*, 1986). Experiments, however, have shown CH_3Hg^+ to be more effective than inorganic Hg(II) in suppressing the photosynthetic activities of marine phytoplankton (Knauer and Martin, 1972). Similarly, CH_3HgCl was found to be almost an order of magnitude more toxic than $HgCl_2$ to rainbow

trout fingerlings (Wobeser, 1975); as $HgCl_2$ and CH_3HgCl penetrate membranes with equal ease (Mason *et al.*, 1995b), the difference in toxicity probably reflects differences in the fate of the two species inside the fish. The greater toxicity of CH_3Hg^+ may arise from the fact that this species more readily exchanges one thiol group for another, rapidly spreading through the contaminated organism's body, impairing the functions of many enzymes in succession (Cotton and Wilkinson, 1988). CH_3Hg^+ and inorganic Hg(II) have qualitatively as well as quantitatively different toxic effects on aquatic organisms (Röderer, 1983).

Wobeser (1974) claimed that certain fish (which he did not identify) are more sensitive to CH_3Hg^+ taken up directly from water than to CH_3Hg^+ ingested with food. Even after long-term consumption of food rich in CH_3Hg^+, there is little evidence of toxicity. Therefore, fish can accumulate large amounts of Hg without suffering detectable adverse effects, whereas predators that prey on the fish are poisoned by the contaminated flesh.

Environmental factors (e.g. Cl^-, sulfides, and pH) that determine the bio-availability of Hg also affect the toxicity of the Hg correspondingly. Experiments with model aqueous systems showed that addition of Cl^- ions increased the toxicity of inorganic Hg(II) to bacteria (Farrell *et al.*, 1990), probably by forming the lipophilic species $HgCl_2$, thereby facilitating uptake by bacterial cells. In contrast, addition of Cl^- to rainbow trout in water initially poor in Cl^- protected the fish against otherwise fatal concentrations of inorganic Hg(II) (Walczak *et al.*, 1986). No interpretation of these results was offered, but conversion of part of the Hg to anionic chloride species that were not readily taken up by the fish is at least one possible explanation. By the same token, the fact that CH_3Hg^+ is more toxic than inorganic Hg(II) to marine phytoplankton (Knauer and Martin, 1972) could be explained, in part at least, by the fact that the lipophilic uncharged species CH_3HgCl crosses cell membranes more easily and rapidly than the hydrophilic anionic species $HgCl_3^-$ and $HgCl_4^{2-}$.

The strong tendency of sulfides and thiols to bind inorganic Hg(II) and CH_3Hg^+ probably has a detoxifying effect except in the case of uncharged, lipophilic, low molecular weight sulfide and thiol complexes, which are bio-available and therefore presumably toxic (see above). Experiments have demonstrated amelioration of the toxicity of inorganic Hg(II) to bacteria in the presence of cysteine (Ribo *et al.*, 1989; Farrell *et al.*, 1990), suggesting (1) strong binding of Hg(II) by the -SH group of the molecule and (2) inability of the cysteine-Hg complex to pass easily through cell membranes because of the hydrophilic character of the amino acid's -COOH and $-NH_2$ groups (especially when they are ionised).

On exposure to bio-available, potentially poisonous Hg species, microbial populations undergo natural selection in favour of Hg-tolerant or -resistant strains (Liebert *et al.*, 1991), including ones that protect themselves by means of biochemical mechanisms for converting the toxic Hg species to less harmful forms (Schottel *et al.*, 1974; Hamdy *et al.*, 1977; Pan-Hou and Imura, 1982; Compeau and Bartha, 1985; Summers, 1988; Baldi *et al.*, 1991, 1993b). Both methylation and demethylation, as well as the other

microbially mediated Hg speciation and Hg-binding reactions described above, are widely regarded as mechanisms of detoxification. The detoxification strategies of microbes include volatilisation of Hg by conversion of inorganic Hg(II) or CH_3Hg^+ to Hg(0), and by transformation of inorganic Hg(II) or CH_3Hg^+ to $(CH_3)_2Hg$, resulting in removal of the Hg from the microbe's immediate vicinity (Schottel *et al.*, 1974; Summers, 1988; Baldi *et al.*, 1991, 1993b). Conversion of inorganic Hg(II) to CH_3Hg^+ is also seen as a detoxification reaction (Hamdy and Noyes, 1975; Hamdy *et al.*, 1977; Pan-Hou and Imura, 1982; Compeau and Bartha, 1985; D'Itri, 1991). (This may seem illogical, since many microbes find it necessary to get rid of CH_3Hg^+ by changing it into more volatile, less water-soluble products, but the fact that CH_3HgCl is more hydrophilic than $HgCl_2$ may help to explain it. Besides, CH_3Hg^+ is more volatile, as well as more water-soluble, and it forms less stable bonds than equivalent inorganic Hg(II) species; hence, it has a greater tendency to diffuse away from the microbes (D'Itri, 1991). Besides, methylation may meet the detoxification requirements of some microbial species, whereas demethylation is more satisfactory for others, or the choice of a detoxification strategy may depend on external conditions. The volatility and relative lipophilicity and hydrophilicity depend on the nature of the ligands bound to the CH_3Hg^+ and Hg^{2+} ions, and on other factors, such as pH. Immobilisation of Hg by production of H_2S or thiols is another possible strategy for preventing Hg toxicity. Accordingly, SO_4^{2-}-reducing bacteria have two protective mechanisms which they use under different conditions: methylation (conversion of inorganic Hg(II) to CH_3Hg^+, and CH_3Hg^+ to $(CH_3)_2Hg$) and production of H_2S (Compeau and Bartha, 1985; Baldi *et al.*, 1993b). The pH of water also has an important bearing on Hg toxicity. The toxicity of inorganic Hg(II) to bacteria was found to be lower at pH 9 than at pH 5 or 6 (Ribo *et al.*, 1989); no doubt the reason for this is that the proportion of $Hg(OH)_2$ to $HgCl_2$ is highest at pH 9 (see above). The same principles apply to the analogous species CH_3HgOH and CH_3HgCl.

There are grounds for suspecting that fish and other aquatic animals, as with microbes, have evolved special mechanisms for protecting themselves against Hg poisoning. The evidence suggesting excretion of CH_3Hg^+ complexed with hydrophilic carrer molecules, the ability of certain fish species to demethylate CH_3Hg^+ in their tissues, and the fact that many fish habitually consume food heavily contaminated with CH_3Hg^+ without suffering untoward consequences all point to the possible existence of specific adaptations designed to protect fish from harmful effects of Hg (see above).

An agent of CH_3Hg^+ and inorganic Hg(II) detoxification which may be of great significance to aquatic organisms is Se in the form of selenides (see above). Se has long been known to be effective in detoxifying heavy metals, including Hg and Cd, leading to the hypothesis that it detoxifies the Hg accumulated by marine mammals. The highly significant positive correlation between Hg and Se, the 1:1 Hg/Se mole ratio, and the apparently strong binding of Hg by Se in liver and brain tissues in marine mammals are consistent with this possibility (Koeman *et al.*, 1973, 1975). Se has also been shown to

abate the acute toxicity of $HgCl_2$ in freshwater fish; interestingly, Se increased the total Hg content of the fish while decreasing its toxicity, strongly suggesting immobilisation of Hg inside the animal by formation of stable Hg-Se complexes (Heisinger *et al.*, 1979). Se in marine fish containing high CH_3Hg^+ concentrations may also protect animals and humans that eat the flesh of the fish (Ganther *et al.*, 1972). The ability of Se to prevent or abate the toxicity of CH_3Hg^+ and inorganic Hg(II) has inspired the idea of deliberately adding Se to Hg-polluted lakes for purposes of remediation (Rudd *et al.*, 1980; Turner and Rudd, 1983; Turner and Swick, 1983). Field experiments designed to test this concept succeeded in demonstrating that Se was effective in reducing Hg concentrations in freshwater fish (Rudd *et al.*, 1980; Turner and Rudd, 1983; Turner and Swick, 1983; Paulsson and Lundbergh, 1991; Lindqvist *et al.*, 1991). Unfortunately, however, Se itself is a potentially toxic element (Lemly and Smith, 1987; Magos, 1991). In natural waters, Se levels as low as 10 μg/L, the legal upper limit for drinking water in Canada (Turner and Rudd, 1983), can be harmful to fish, and Se at concentrations exceeding 2-5 μg/L may undergo biomagnification in food chains, resulting in toxic effects (Lemly and Smith, 1987). The perils of using Se to combat Hg were revealed dramatically by a field experiment in Sweden: In four of eleven lakes treated with Se for detoxification of Hg, the reproduction of fish declined catastrophically (Lindqvist *et al.*, 1991). Thus, although the method has shown some efficacy, further work is needed, and application of such a method cannot be recommended without a guarantee that its potentially disastrous side-effects can be prevented.

The biogeochemical cycle of mercury.

Sources of mercury. Hg is introduced into air, water, and soil by various natural processes and human activities (Nriagu and Pacyna, 1988; Nriagu, 1989; D'Itri, 1991; Lindqvist *et al.*, 1991; Hudson *et al.*, 1995; Jackson, 1995b; Pacyna and Keeler, 1995). The Hg may be derived mainly from local sources or imported from distant sources by atmospheric or fluvial transport. It may come from point sources or diffuse sources, or both, and from secondary sources (e.g. soil organic matter) as well as primary sources (e.g. volcanoes or coal-burning power plants); and it is cycled between different sources and sinks, undergoing chemical transformations by various biological and abiotic pathways. There are continual interchanges between the Hg pools in the lithosphere, hydrosphere, and atmosphere.

Largely owing to the volatility of Hg, major quantities of natural and anthropogenic Hg are released into the atmosphere every year and are conveyed to aquatic and terrestrial ecosystems near and far by atmospheric circulation. Hg is a ubiquitous trace constituent of the atmosphere. Airborne Hg is mostly in the form of gaseous Hg(0) but includes volatile Hg(II) species along with Hg(II) (and traces of Hg(0)) sorbed to dust or dissolved in water droplets (Lindberg, 1987; Brosset and Lord, 1991; Lindqvist *et al.*, 1991). Hg(0) and Hg(II) are transported over thousands of kilometers by global atmospheric circulation,

but dissolved and particulate Hg(II) has a far stronger tendency than Hg(0) to be returned to the Earth's surface by wet and dry deposition, much of which occurs within 100 km of the source (Lindberg, 1987; Lindqvist *et al.*, 1991); at low temperatures Hg(0) too may undergo appreciable dry deposition (Steinnes and Andersson, 1991). The separation of these pathways is never absolute, as Hg(0) and Hg(II) are interconvertible (Lindqvist *et al.*, 1991; Munthe *et al.*, 1991; Schroeder *et al.*, 1991). On a global scale, the natural and anthropogenic contributions to the atmospheric Hg burden are of comparable magnitude, each amounting to thousands of tonnes per year, although there is considerable geographic and temporal variation (Nriagu and Pacyna, 1988; Nriagu, 1989; D'Itri, 1991; Lindqvist *et al.*, 1991; Hudson *et al.*, 1995; Jackson, 1995b). But most estimates of the natural flux may be too high because of failure to take secondary anthropogenic emissions into account (Hudson *et al.*, 1995). Anthropogenic emissions have increased over time (largely owing to combustion of fossil fuels) since the onset of the Industrial Revolution, accelerating in the mid-20th century, and then, in some regions, declining somewhat, whilst continuing unabated elsewhere. The evidence for a temporal increase in the rate of Hg deposition from the atmosphere includes profiles of Hg (and associated pollutants and micro-fossils indicative of fuel combustion) in dated cores of fine-grained sediments representing continuous, undisturbed stratigraphic sequences from remote lakes with no history of local pollution (e.g. Heit *et al.*, 1981; Ouellet and Jones, 1983; Evans, 1986; Johnson *et al.*, 1986; Lockhart *et al.*, 1993; Louchouarn *et al.*, 1993; Engstrom *et al.*, 1994). The cores typically show Hg enrichment in the uppermost (youngest) horizons. Rasmussen (1994) has questioned the quantitative significance of long-range atmospheric transport of anthropogenic Hg, asserting that insufficient attention has been paid to natural sources of Hg and maintaining that the distribution of Hg in cores may be due to postdepositional remobilisation of Hg rather than temporal variation in loading. However, a comprehensive review and synthesis of the literature (Jackson, 1995b) has refuted Rasmussen's arguments. The case against Rasmussen's views is especially convincing because it is based on a large, diverse body of evidence characterised by agreement between different kinds of information amassed by many investigators studying various natural systems in widely separated regions.

The ultimate natural sources of Hg are in the Earth's crust and upper mantle. Volatile Hg is vented into the atmosphere by volcanic activity and other degassing processes, whilst Hg in rocks exposed at the surface is released by weathering (Jonasson and Boyle, 1972; Nriagu, 1989, 1992; D'Itri, 1991; Painter *et al.*, 1994; Friske and Coker, 1995). Hg is widely dispersed as a trace element in various rocks, but anomalously high concentrations of Hg, including Hg ores, are found in mineralised bedrock in localised zones within belts of tectonic activity, notably regions of vulcanism or faulting; and coal and fine-grained sedimentary rocks (e.g. shales, especially those of high organic and sulfide content), are enriched in Hg with respect to other common rocks (Gavis and Ferguson, 1972; Jonasson and Boyle, 1972; Painter *et al.*, 1994; Friske and Coker, 1995). The Hg deposited in mineralised zones is mainly in the form of

cinnabar but may include minor amounts of metacinnabar, calomel, Hg(0), and assorted rare Hg minerals, and occurs as an impurity in other minerals. Primary Hg deposits usually precipitate in faults, fractures, and pores in the host rock (commonly sedimentary rock), or replace the rock, and are deposited in hot springs, through the agency of hydrothermal solutions emanating from subsurface magma. Other phenomena that transfer Hg, directly or indirectly, from natural sources to aquatic ecosystems include soil erosion, forest fires, the formation of aerosols from sea spray, and various microbially mediated and abiotic reactions whereby Hg(II) is converted to volatile species in soil and water (Nriagu, 1989, 1992). Owing to the patchy distribution of Hg-rich materials and the episodic nature of phenomena such as volcanic eruptions, natural Hg levels in Earth surface environments show considerable spatial and temporal variation. Geographic variations in the composition of lake and stream sediments reflect variations in the Hg content of rock formations in their catchment basins (Evans, 1986; Rognerud and Fjeld, 1993; Painter *et al.*, 1994; Friske and Coker, 1995). Some regional Hg anomalies in soil organic matter and marine animals may be of geologic origin (Steinnes, 1994; Wagemann *et al.*, 1995).

The natural background Hg has been enormously augmented by Hg pollution resulting from a variety of human (especially industrial) activities (Gavis and Ferguson, 1972; D'Itri *et al.*, 1978; Lindberg, 1987; Nriagu and Pacyna, 1988; D'Itri, 1991; Lindqvist *et al.*, 1991; Nriagu, 1992). Combustion of coal to generate electricity and for other purposes has been the greatest single cause of atmospheric Hg pollution, incineration of solid refuse being a close second (Nriagu and Pacyna, 1988; Nriagu, 1992; Pacyna and Keeler, 1995). Air pollution due to the burning of coal and other fossil fuels is responsible for Hg contamination and acidification in many lakes hundreds or thousands of kilometers from the sources of pollution (Jackson, 1995b). At many localities industrial and municipal wastewaters containing Hg in the form of Hg(0), inorganic Hg(II), or, in some cases, organometallic Hg(II) compounds have been discharged directly into aquatic environments, usually rivers, which may then transport the Hg (mostly as particulate Hg(II)) over great distances, causing widespread contamination of aquatic organisms and habitats (e.g. Armstrong and Hamilton, 1973; Fimreite and Reynolds, 1973; Bishop and Neary, 1976; Parks, 1976; Parks and Hamilton, 1987; Parks *et al.*, 1991b). Chlor-alkali plants employing Hg(0) electrodes for electrolysis of NaCl have been especially notorious point sources of Hg (Gavis and Ferguson, 1972) and have been a source of airborne Hg too (Lindqvist *et al.*, 1991). Technological changes involving replacement of Hg(0) electrodes with diaphragm cells have abated the problem, resulting in gradual lowering of Hg levels in fish, but harmful effects of past pollution persist for many years (e.g. Armstrong and Scott, 1979; Jackson, 1980; Jackson *et al.*, 1982; Jackson and Woychuk, 1980a, 1980b; Parks and Hamilton, 1987; Parks *et al.*, 1986, 1989, 1991a, 1991b). Many other human activities contribute to Hg pollution. The Hg pollution and consequent mass poisonings by consumption of CH_3Hg^+-contaminated fish and shellfish at Minamata and Niigata, Japan resulted from discharge of

Hg-contaminated effluents from acetaldehyde plants into natural waters (Takizawa, 1979). Recently the use of Hg(0) to extract gold from ore has led to severe pollution of rivers and air in the Amazon region of Brazil (Aula *et al.*, 1994; Palheta and Taylor, 1995).

Biogeochemical pathways of mercury in aquatic ecosystems. Inorganic Hg(II) is the dominant form of Hg in aquatic environments. When introduced into natural waters, the Hg is rapidly and efficiently scavenged by fine-grained suspended particles, and most of it accumulates in clay- and silt-sized bottom sediments, although a small and highly variable proportion of it remains in solution, or is resolubilised, in the form of different ionised and uncharged aqueous species and complexes. The partitioning of Hg between the solid and aqueous phases, and the nature and quantities of the different forms of Hg are subject to continual change in response to varying environmental conditions and microbial activities. As a rule, Hg(II) is strongly and preferentially bound by inorganic sulfides and the thiol groups of humic and nonhumic organic substances (and their much rarer selenide and telluride analogues); if these binding agents are scarce (as in a highly oxidising environment where most of the particulate matter consists of mineral detritus) the Hg(II) is sorbed by mineral particles, principally by Fe and Mn oxyhydroxides. Because most of the Hg is bound to sediments and suspended particles, the dynamics and distribution of Hg in natural waters are largely determined by the same forces that control the erosion, suspension, transport, and deposition of its carrier particles. In river systems, particulate Hg is resuspended from bed and bank deposits during times of high flow rates and bottom scour (e.g. during the spring flood in the temperate zone), is transported in suspension by fluvial currents, and is deposited in basins of deposition such as riverine lakes and marine basins. Fairly deep productive basins characterised by reducing conditions and the formation of H_2S on the bottom tend to trap and accumulate Hg, and a series of riverine lakes or settling ponds, especially ones with reducing conditions at the bottom, helps to purify a river and ameliorate the effects of heavy metal pollution through removal, immobilisation, and burial of the metals (Jackson, 1978, 1979, 1993a, 1993b); wetlands, too, can be effective in trapping riverborne metals (Sinicrope *et al.*, 1992). However, the efficiency of Hg immobilisation, and even the relative tendencies of Hg and other heavy metals to be immobilised, vary greatly from one basin of deposition to another (Jackson, 1979). At best, the process of entrapment is far from absolute, and the Hg deposited and immobilised in sediments is, to a greater or lesser extent, subject to remobilisation and further transport (Jackson and Woychuk, 1980a, 1980b, 1981; Jackson, 1993a); and Hg buried in the sediments of a riverbed or floodplain can be returned to the aquatic environment through erosion and resuspension (brought on by short-term environmental changes such as storms or long-term changes such as a drop in base level causing the river to shift from aggradation to downward cutting). Even in a river with a succession of efficient Hg-trapping basins of deposition, Hg pursues its gradual migration in the downstream direction. For example, Hg sorbed to FeOOH coatings on suspended clay and silt may be

transported by fluvial currents and deposited in an anoxic lake basin rich in sulfides and organic matter, where the FeOOH is reduced and solubilised, liberating the Hg, which is mostly immobilised by sulfide and thiols but is, to some extent, mobilised as dissolved sulfide and thiol complexes, hydrolysis products, etc., and recycled into the water (Jackson, 1993a). Oxidation of the reduced sediments through contact with water containing dissolved O_2 would liberate sulfide-bound Hg by oxidising the sulfide, although part of the Hg might immediately be immobilised again owing to coprecipitation with FeOOH or MnOOH and binding by humic matter. Changes of this kind may occur seasonally. During times of slack flow in a river, there is minimal resuspension of Hg bound to mineral detritus (except during episodic events like storms), but there may be an increase in the concentration of Hg dissolved or associated with dispersed colloidal organic matter in the water, as may occur during the summer (Jackson *et al.*, 1982). When Hg sorbed to fluvial particulate matter is transported into an estuary emptying into the sea, a number of important changes occur owing to the gradational shift from freshwater to marine conditions (Jackson, 1996). The changes include partial desorption and solubilisation of the bound Hg by the formation of water-soluble Hg-Cl^- complexes, as well as flocculation of Hg-bearing clay and humic matter owing to the increase in salinity.

Throughout these processes, Hg is continually in a state of flux owing to biological activities and physicochemical processes controlling speciation reactions and binding and release by various sorbents, complexing agents, and organisms - crucially important reactions because of their relevance to the biological effects of the Hg, even though aqueous Hg species usually comprise only a small percentage of the total Hg supply. In any aquatic ecosystem, a small and highly variable fraction of the total inorganic Hg(II) in the environment consists bio-available inorganic Hg(II) species in solution or loosely sorbed by particles. It is from this pool of reactive inorganic Hg(II) species that the methylated species CH_3Hg^+ and $(CH_3)_2Hg$ are synthesised by various free-living micro-organisms in the surficial sediments and water column. The $(CH_3)_2Hg$ is largely volatilised, but dissolved CH_3Hg^+ gradually diffuses through the water column, where it is readily accumulated by organisms along with some bio-available inorganic Hg(II); but CH_3Hg^+ production is kept in check by the process of demethylation, whereby various micro-organisms decompose CH_3Hg^+, reducing the Hg to Hg(0). Inorganic Hg(II) may also be reduced to Hg(0) by microbes. To some extent, such processes are abiotic (as in photochemical production of Hg(0) from CH_3Hg^+ and inorganic Hg(II) in sunlight), but they are mostly mediated by microbes. In contrast to inorganic Hg(II), the CH_3Hg^+ undergoes biomagnification up the food chain; therefore, it is by far the dominant form of Hg in fish and animals such as marine mammals and aquatic birds that consume fish; at high concentrations in fish CH_3Hg^+ is extremely hazardous to humans and animals that eat the fish. Hg(0) formed in the aquatic environment tends to be lost through volatilisation, although Hg(0) gas, along with inorganic Hg(II) bound to dust, in the atmosphere is also introduced into bodies of water by wet and

dry fallout, and some of it may be oxidised biochemically or abiotically to Hg(II). The net rate of CH_3Hg^+ production depends on the abundance of bio-available inorganic Hg(II) species and the activities of methylating and demethylating microbes. Both the percentage of the total inorganic Hg(II) pool that is bio-available (susceptible to methylation) and the activities of the microbes that produce and destroy CH_3Hg^+ are controlled by a wide range of environmental variables; moreover, the kinetics of CH_3Hg^+ accumulation by the aquatic biota depend not only on the conditions controlling the supply of CH_3Hg^+ but also on the inherent characteristics, behaviour, activities, and stage of development of the organisms themselves. Consequently, net rates of CH_3Hg^+ production and bio-accumulation show enormous variation in response to spatial and temporal variations in environmental conditions. In general, anoxic but not excessively reducing (sulfide-rich) environments of weakly acidic to neutral pH, and a generous supply of labile organic matter that can provide nutrient substrates for microbes, are optimal for CH_3Hg^+ production, but the process occurs to a greater or lesser extent under a wide variety of conditions. Above all, the formation and bio-accumulation of bio-available Hg species such as CH_3Hg^+ are controlled by an infinitely complex interplay of countless biological and physicochemical processes. The biologically reactive unmethylated and methylated species make up only a minor proportion of the total Hg supply, which is a generally very poor and unreliable measure of the ecological effects of Hg. The net result represents the combined effect of all these multifararious spatially and temporally varying processes acting and interacting at the same time (or in succession), directly and indirectly, some processes reinforcing each other's effects whilst others tend to counteract each other. To understand the biological effects of Hg in nature, we must take all these different environmental and biological aspects of the problem into account and achieve an interdisciplinary synthesis. One of the greatest challenges in future biogeochemical research will be to attain an in-depth understanding of this most intricate and multidimensional of subjects - the biogeochemical cycle of mercury.

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