Mercury transformations in wetland soils in relation to C, S and Fe biogeochemistry

Ulf Skyllberg[A]

[A]Department of Forest Ecology and Management, Swedish University of Agricultural Sciences SE-90883 Umeå, Sweden,
Email ulf.skyllberg@sek.slu.se

Abstract

Net production of the toxic and bioaccumulating methyl mercury (MeHg) molecule in wetlands is a major environmental health issue. In this paper factors and processes in control of MeHg net production in wetlands are covered. Of major importance are methylation, demethylation and photo-induced redox processes. All these reactions are linked to the biogeochemistry of C, S and Fe via an intricate interplay with iron(III) and sulphate reducing bacteria. A special focus is put on the link between the chemical speciation of Hg(II) and uptake of bioavailable forms of Hg(II) by methylating bacteria. A key role is played by organic substances. They control the transport of Hg(II) and MeHg, as well as the bioavailability of Hg(II) and the energy source for methylating bacteria. Research needs are identified. In particular, limited fundamental knowledge about demethylation processes may restrict society to make correct decisions regarding e.g. restoration efforts of wetlands.

Background

Mercury (Hg) is one of the most toxic elements and there is currently a worldwide concern about negative health effects, in particular in human populations highly dependent on fish consumption (Mergler *et al.* 2007). On a global scale, the major source of Hg is emission of elemental $Hg^0(g)$ as a consequence of combustion of fossil fuels. The residence time of Hg^0 in the atmosphere is about one year, resulting in a long-range transportation from industrial areas to areas without significant local Hg sources. The pool of atmospheric $Hg^0(g)$ is gradually oxidized and the product, Hg(II), is deposited in association with particles or dissolved in precipitation. In arctic areas, atmospheric mercury depletion events have been reported to result in locally relatively high concentrations of Hg(II) (Steffen *et al.* 2008). Once deposited, Hg(II) may undergo a number of biogeochemical reactions. From a human health perspective, processes directly and indirectly involved in the production and degradation of the most abundant toxic and bioaccumulating form of organic Hg; monomethyl mercury (MeHg) is of greatest concern. Together with marine environments, hypolimnetic waters and lake sediments, wetlands are known to be environments in which MeHg is net produced. Most research focus has been on wetlands in temperate areas, but also in sub-tropic and tropic wetlands the formation of MeHg is an issue. It is well-established, by laboratory experiments and by studies in the field, that MeHg formation can be linked to the activity of iron(III) and sulphate reducing bacteria (FeRB and SRB, respectively) (Benoit *et al.* 2003). This means that factors stimulating the activity of these groups of bacteria, such as the availability of electron donors and acceptors, may result in an increased net MeHg production. However, because these groups of bacteria obviously affect the chemistry of sulphur and iron geochemistry, there is an intricate interplay with both the chemical speciation and transformations of Hg(II) and MeHg that need to be fully understood.

The objective of this paper is to provide an overview of the current knowledge about the link between mercury and organic carbon, sulphur and iron biogeochemistry in wetland environments. Special focus is put on the link between chemical speciation, mobility of Hg(II) and MeHg and the transformation of Hg(II) to MeHg.

Chemical speciation of mercury in wetland soils

Complexation with organic thiols

In order to be able to discuss important transformation processes of Hg(II) and MeHg, the chemical speciation of these two forms under natural conditions in wetlands needs to be understood. Because of the "soft" properties of mercury, it forms exceptionally strong bonds with sulphur. Under oxic conditions, complexes with organic thiols (RSH) highly dominate the chemical speciation of both Hg(II) and MeHg in organic rich environments such as wetlands (Skyllberg 2008). The binding to organic thiols is strong enough to out-compete Cl^- and Br^- also in marine or estuarine wetlands. Organic thiol functional groups are associated to natural organic matter (NOM) both in the solid and aqueous phases (pore water) of soils. In the aqueous phase low molecular mass (LMM) thiols may occur. Concentrations up to 250 nM have been reported for LMM thiols like cysteine and thioglycolic acid in wetlands (Zhang *et al.* 2004). This concentration of RSH would be equal to the concentration of thiol groups associated with DOM in a water containing 2 mg DOC/L, if we assume that RSH in NOM corresponds to 0.15 % of OC, as reported from spectroscopic determinations (Skyllberg 2008). Assuming that the affinity of Hg(II) and MeHg for LMM thiols and thiol groups associated to NOM is the same, this suggests that Hg(II) and MeHg are mainly associated to NOM in wetland pore waters (having DOC > 2 mg/L). Adsorption of Hg(II) and MeHg to other solid phases (e.g. iron oxyhydroxides or clay minerals) than NOM is insignificant under oxic conditions.

Suboxic conditions

Under suboxic conditions, FeRB, SRB and sulphide oxidizing bacteria (SOB) are active, which results in the formation of Fe(II), inorganic sulphides (H_2S, HS^-) and elemental S. Elemental S, which may be formed by the activity of SOB and SRB (e.g. 6), reacts with HS^- under the formation of polysulphides (S_n^{2-}). Hg(II) and MeHg form complexes with HS^- having a quite similar chemical stability as complexes with organic thiols (Skyllberg 2008). In wetlands with significant minerogenic influence, amorphous FeS(s) can be expected to control the concentration of HS^-, via the reaction $FeS(s) + H^+ = Fe^{2+} + HS^-$ (Rickard and Luther 2007). This reaction therefore, indirectly, affects the chemical speciation of Hg(II) and MeHg in the aqueous phase. Chemical speciation modelling of Hg(II) in a wetland soil (pH 4-7) showed that concentrations of dissolved complexes with organic thiols [$Hg(SR)_2(aq)$] and with inorganic sulphides [$Hg(SH)_2^0(aq)$, HgS_2H^-, HgS_2^{2-}] were approximately equal at 0.5 µM of S(-II) and 50 mg DOC/L (Skyllberg 2008). At the same conditions, concentrations of MeHg complexes with organic thiol [MeHgSR(aq)] and inorganic sulphide [$MeHgSH^0(aq)$, $MeHgS^-$] were approximately equal. However, if polysulphides are formed, organic thiols and inorganic sulphides are out-competed. For MeHg stability constants with polysulphides are unknown.

Anoxic conditions

With increasing anoxic conditions, elemental S and polysulphides will be reduced to inorganic sulphides, making the speciation of Hg(II) in the aqueous phase somewhat less complicated. In the solid phase, however, amorphous metacinnabar [HgS(s)] may form. It is known that organic substances on one hand diminish the aggregation and crystallinization of metacinnabar (Ravichandran *et al.* 1999), but on the other hand organic molecules stabilize amorphous nanoparticles of HgS(s) (Deonarine and Hsu-Kim 2009). Thermodynamic modelling suggests that metacinnabar is stable at a concentration of HS^- exceeding ~10 µM at neutral pH in organic soils (Skyllberg 2008). Below this concentration, complexes with organic thiols associated to NOM are the dominant form of Hg(II) in the solid phase. Recent spectroscopic studies have shown that Hg(II) reacts with FeS(s) to form metacinnabar, and that organically complexed Hg coexist with HgS(s) in the solid phase of organic soils. At increasing anoxic conditions (i.e. increasing concentrations of HS^-), the solubility of Hg(II) increases and $Hg(SH)_2^0(aq)$, HgS_2H^-, HgS_2^{2-} and $MeHgSH^0(aq)$, $MeHgS^-$ completely dominates the chemical speciation of Hg(II) and MeHg in solution.

Biogeochemical transformations in wetland soils with focus on MeHg net production

With focus on the formation of MeHg, the two perhaps most important biogeochemical transformation reactions of mercury in wetlands are the methylation and demethylation processes. The current consensus is that the former process is biotic (intracellular) and linked to the activity of FeRB and SRB, whereas the latter is known to be both biotic and abiotic (Benoit *et al.* 2003). Also redox reactions involving Hg(II), Hg(0) and MeHg need to be considered, as these processes will indirectly affect the formation of MeHg.

Influence of C, S and Fe biogeochemistry on methylation processes

The following factors are generally considered to be in control of methylation rates: 1) the concentration of Hg(II) in bioavailable form, and the availability of 2) electron-donors (energy source) and 3) electron-acceptors [Fe(III) and sulphate] for methylating bacteria.

Organic C is in indirect control of 1) and in direct control of 2). One reason for northern wetland – forested regions to be high risk environments for MeHg net production and bioaccumulation is its production of recalcitrant, soluble humic substances. The transportation of Hg(II) with humic substances from upland, forested environments to methylation "hot-spots", such as certain types of wetlands, is a key process for MeHg net production. Similarly, dissolved humic substances transport MeHg from methylation "hot-spots" to streams and surface waters with biota that accumulate MeHg. In addition, LMM organic C molecules (e.g. acetate, propionate, lactate, fatty acids) serve as electron-donors to methylating bacteria. Several studies of different reducing environments highlight the importance of LMM organic molecules for MeHg production (e.g. Benoit *et al.* 2003; Drott *et al.* 2007).

Sulphur containing ligands (HS^-, S_n^{2-}, and RSH) highly affect methylation processes by controlling the solubility and concentrations of bioavailable forms of Hg(II). There is currently little consensus regarding the forms of Hg(II) taken up by methylating bacteria. A number of laboratory and field studies indicate that a passive uptake of neutral forms of Hg(II) by methylating bacteria may limit the net production of MeHg. Given the dominance of the $Hg(SH)_2^0$ molecule under anoxic conditions in wetlands, this species is the most reasonable candidate to be taken up by SRB (Benoit *et al.* 2003; Drott *et al.* 2007). The suggestion that the species $HOHgSH^0$ is the predominant form of neutral Hg-sulphides (Benoit *et al.* 2003) is controversial because it builds on an unreasonably large stability constant for the formation of this complex (Skyllberg 2008). Under suboxic conditions neutral forms of polysulphides (e.g. HgS_5) have been suggested (but not confirmed) to be bioavailable (Jay *et al.* 2002). A recent study shows that LMM Hg(II)-thiols are actively taken up by FeRB (Schaefer and Morel 2009). This is reasonable given that FeRB are active under redox condition under which neutral Hg(II) complexes (e.g. $Hg(SH)_2^0$) show very low concentrations. Even if there is not a consensus regarding which forms of Hg(II) that are bioavailable for methylating bacteria (and mechanism for their uptake), there is no doubt that all reasonable candidates involve inorganic or organic S as major ligands.

Sulphur (in form of the sulphate ion) acts as an electron acceptor for SRB. Several studies have shown that amendments of sulphate to wetlands result in increased concentrations of MeHg. This may be caused by an increased methylation, indicating that SRB were limited by sulphate. If, however, only the pore water concentration of MeHg is measured (which unfortunately has been the case in several studies), increased concentration of MeHg may simply be an effect of HS^- formation (reduction of sulphate) and a subsequent increased solubility of MeHg by formation of $MeHgSH^0(aq)$ and $MeHgS^-$. Because of this, there are only a few studies in support of sulphate limitation of the methylation process.

Iron has two major effects on the methylation processes. Under sub- and anoxic conditions, FeS(s) is in control of the concentration of HS^- (and indirectly of the concentration of $Hg(SH)_2^0$). Furthermore, Fe(III) is an electron acceptor for FeRB. In both of the two studies in which Fe(II) and Fe(III) compounds has been amended to wetlands, a decrease in MeHg net production has been observed (Mehrotra and Sedlak 2005). This has been interpreted as indirect inhibitory effect by formation of FeS(s) and decrease in the concentration of presumably bioavailable $Hg(SH)_2^0$.

Demethylation and photo-induced redox processes

Biotic demethylation may be either reductive or oxidative. Reductive demethylation is a detoxification process (it costs energy) involving the mercury resistance *mer* operon (Barkay *et al.* 2003), degrading MeHg to Hg^0 and CH_4. This process is believed to be induced by relatively high concentrations of Hg(II), and is used by a broad spectrum of bacteria. During oxidative demethylation MeHg is degraded to Hg^0 and CO_2. This process is assumed to be part of microbial metabolism (e.g. SRB) and is believed to be the dominant process at less contaminated sites (Marvin-DiPascale *et al.* 2000). There is currently very little knowledge about the variability in demethylation rates among different environments (e.g. different types of wetlands) and even less knowledge concerning the influence of external factors (e.g. C, S and Fe biogeochemistry). This is one of the most urgent research needs to be filled in the near future. Some new results will be presented at the symposium, suggesting that certain types of wetlands may act as sinks for MeHg because of high demethylation rates.

Photo-degradation of MeHg is an important demethylation process in water columns of lakes (Sellers *et al.* 1996), and the importance of this process needs to be investigated in open wetlands. Photo-reduction of Hg(II) to Hg(0) and photo-oxidation of Hg(0) to Hg(II) are important processes occurring in open wetlands. It has been shown that chromophoric groups associated to DOM plays an important role in the electron transfer in both these processes. Also the redox-couple Fe(II)-Fe(III) has been indicated to be involved (Zhang 2006).

Research needs for mercury biogeochemistry in wetlands

Not all types of wetlands are net sources for MeHg. One of the most urgent research need is to identify sites, processes and environmental factors in control of MeHg demethylation. Limited knowledge on how different types of wetlands respond to human activities (e.g. restoration efforts), as well as to climate change, restrict society from making correct decisions.

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