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Distribution of mercury, methyl mercury and organic sulphur species in soil, soil solution and stream of a boreal forest catchment

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Abstract. Concentrations of methyl mercury, CH_3Hg (II), total mercury, Hg_{tot} = CH_3Hg (II) + Hg (II), and organic sulphur species were determined in soils, soil solutions and streams of a small (50 ha) boreal forest catchment in northern Sweden. The CH_3Hg (II)/Hg_{tot} ratio decreased from 1.2–17.2% in the peaty stream bank soils to 0.4–0.8% in mineral and peat soils 20 m away from the streams, indicating that conditions for net methylation of Hg (II) are most favourable in the riparian zone close to streams. Concentrations of CH_3Hg (II) bound in soil and in soil solution were significantly, positively correlated to the concentration of Hg_{tot} in soil solution. This, and the fact that the CH_3Hg (II)/Hg_{tot} ratio was higher in soil solution than in soil may indicate that Hg (II) in soil solution is more available for methylation processes than soil bound Hg (II). Reduced organic S functional groups (Org-S_{RED}) in soil, soil extract and in samples of organic substances from streams were quantified using S K-edge X-ray absorption near-edge structure (XANES) spectroscopy. Org-S_{RED}, likely representing RSH, RSSH, RSR and RSSR functionalities, made up 50 to 78% of total S in all samples examined. Inorganic sulphide [e.g. FeS_2 (s)] was only detected in one soil sample out of 10, and in none of the stream samples. Model calculations showed that under oxic conditions nearly 100% of Hg (II) and CH_3Hg (II) were complexed by thiol groups (RSH) in the soil, soil solution and in the stream water. Concentrations of free CH_3Hg^+ and Hg^{2+} ions in soil solution and stream were on the order of 10^{-18} and 10^{-32} M, respectively, at pH 5. For CH_3Hg (II), inorganic bi-sulphide complexes may contribute to an overall solubility at concentrations of inorganic sulphides higher than 10^{-9} M, whereas considerably higher concentrations of inorganic sulphides (lower redox-potential) are required to increase the solubility of Hg (II).

Abbreviations: CH_3Hg (II) – methyl mercury with oxidation state + II, Hg (II) – inorganic mercury with oxidation state + II, Hg_{tot} – total mercury, N_{tot} – total nitrogen, Org-S_{RED} – reduced organic sulphur, PSOC – potential soluble organic carbon, S_{tot} – total sulphur, SOM – soil organic matter, TOC – unfiltered total organic carbon in aqueous phase, XANES – X-ray absorption near-edge structure spectroscopy.

Introduction

Fish in about 40 000 of Sweden's 83 000 lakes contain Hg_{tot} exceeding the recommended consumption advisory of 0.5 mg Hg kg^{-1} (Håkanson 1996). Main mercury

sources in aquatic systems are direct atmospheric deposition of Hg (II), and Hg_{tot} transported from soils and wetlands. A net production of CH_3Hg (II) in wetlands and discharge areas of upland forest soils is of major importance for the methyl mercury concentration in lakes and streams (St. Louis et al. 1994; Hurley et al. 1995), and not at least, for concentration of mercury in fish Downs et al. (1998).

The composition of mercury species is crucial for the bioavailability of Hg_{tot} and its accumulation in aquatic food webs. Biotically mediated transformations of the two major mercury forms in soils and waters, such as demethylation of CH_3Hg (II) and methylation of Hg (II), are assumed to involve uptake of neutral mercury species by microorganisms (Hudson et al. 1994). Benoit et al. (1999) suggested that methylation of Hg (II) in reduced sediments involves uptake of HgS^0 (aq) by sulphate reducing bacteria. Concentrations of neutral Hg species, as well as most other CH_3Hg (II) and Hg (II) species, are extremely low and vary with environmental factors such as pH, organic ligand concentration, sulphur speciation and redox potential. Knowledge about these factors and how they influence the speciation of Hg is therefore needed before we can understand processes such as methylation of Hg (II) and demethylation of CH_3Hg (II).

For many reasons, the biogeochemistry of Hg_{tot} is linked to sulphur. Recent findings using X-ray absorption spectroscopy (Xia et al. 1999; Hesterberg et al. 2001; Qian et al. 2002) show that both CH_3Hg (II) and Hg (II) bind to reduced organic S, rather than to O and N functional groups, in soil and aquatic organic substances. Therefore, the mobility and retention of mercury in soil will be highly dependent on the solubility of natural organic matter (NOM) and its densities of reduced organic S functionalities. X-ray absorption near-edge structure (XANES) spectroscopy has been successfully employed to quantitatively estimate oxidation states of S in marine sediments (Vairavamurthy et al. 1994), as well as in soil humic and fulvic acids (Morra et al. 1997; Xia et al. 1998). Under anoxic conditions dissolved bi- and poly-sulphides may control the solubility of CH_3Hg (II) and Hg (II) (Jay et al. 2000; Tossell 2001). Furthermore, sulphate has been shown to promote biotic methylation of mercury by sulphate-reducing bacteria in sediments (Gilmour et al. 1992) and peat soils (Branfierun et al. 2001).

Based on empirical correlations, the ratio between CH_3Hg (II) and Hg_{tot} has been suggested to be a better predictor of the rate of Hg accumulation in fish than the absolute concentration of CH_3Hg (II) in lake water (Lee and Iverfeldt 1991). Hurley et al. (1995) reported the CH_3Hg (II)/Hg_{tot} ratio to be higher in streams draining wetlands and forested catchments in northern Wisconsin than in agricultural areas. They suggested that a higher ratio during fall reflected a higher net methylation rate than during springtime. Similarly, data on the CH_3Hg (II)/Hg_{tot} ratio along hydrological pathways in soils, draining into surface waters, might be used to identify soil conditions and sites favourable for methylation processes. At this point data on CH_3Hg (II) bound in soils are few, and most of them have been obtained using a distillation method (Horvat et al. 1993), which may be subjected to errors due to an artefact formation of methyl mercury (Bloom et al. 1997; Hintelmann et al. 1997). In order to avoid this problem, Qian et al. (2000) developed solvent extraction methods for soil bound methyl mercury.

The aims of this study are; 1) to describe the distribution of CH_3Hg (II), Hg (II) and reduced organic S functionalities in the compartments soil, soil solution and stream, and 2) to model the speciation of CH_3Hg (II) and Hg (II) in these three compartments along a short hydrological gradient in a small forested catchment.

Materials and methods

Study area and its soils

The 50 ha Nyänget catchment, located at Svartberget in northern Sweden (64°14′ N, 19°46′ E), was selected as the study site. The catchment is covered by mature stands of Scots Pine (*Pinus sylvestris*) on higher ground and Norway Spruce (*Picea abies*) in low-lying areas. The field vegetation is dominated by the shrubs *Vaccinium vitis-idaea* (under pine) and *Vaccinium myrtillus* (under spruce), with some patches of the grass *Deschampsia flexuosa*. Feather mosses covering the ground is dominated by a mixture of *Hylocomnium splendens*, *Pleurozium schreberi* and *Dicranum spp*. Adjacent to the stream wetter conditions are encountered, reflected by patches of the mosses *Sphagnum spp*. and *Polytrichum spp*.

Two streams drain the catchment: Kallkällebäcken and Västrabäcken (Figure 1). Kallkällebäcken is draining 83% of the catchment; including an 8 ha open mire (peatland with no tree cover) at the upper end, and Västrabäcken drains the remaining 17%. Slopes from the upland down to the stream range from 5 to 10%. Several meters of locally derived glacial till, overlying gneiss bedrock, covers the catchment. The southern half of the catchment is located below the highest limit for the Quaternary coastline. Much of the riparian zone along both tributaries is covered by peat, more than 50 cm in depth at Kallkällebäcken and 20–50 cm in depth at Västrabäcken. Both tributaries were straightened and deepened by man in the 1930's. Kallkällebäcken stream banks consist almost completely of peat, whereas at Västrabäcken the peat in the stream bank is partly mixed with mineral soil. Communities of *Sphagnum spp*. cover the stream banks at both tributaries. Soils and streams were sampled at the mire outlet (Site M), along a transect 700 m downstream the mire outlet at Kallkällebäcken (Site K), and along a transect at Västrabäcken (Site V), Figure 1.

Spodosols (Typic Cryorthods, Soil Survey Staff (1997)) are developed in mineral soils not covered by peat. In places where the peat layer is less than approximately 20–30 cm thick, a weak E horizon underlain by a weak Bs horizon indicates vertical podsolization processes. Where the peat is deeper, the mineral soil is bleached and mixed with organic substances down to the ground-water table. The hydrology is highly driven by events such as spring flooding and heavy rains, which raise the ground-water table. This in turn gives rise to a lateral flow, since the transmissivity of the soil profile is greater towards the surface. Because the laterally moving water passes through the peat and the stream bank before entering the stream, chemical and biological processes at these sites are assumed to highly af-

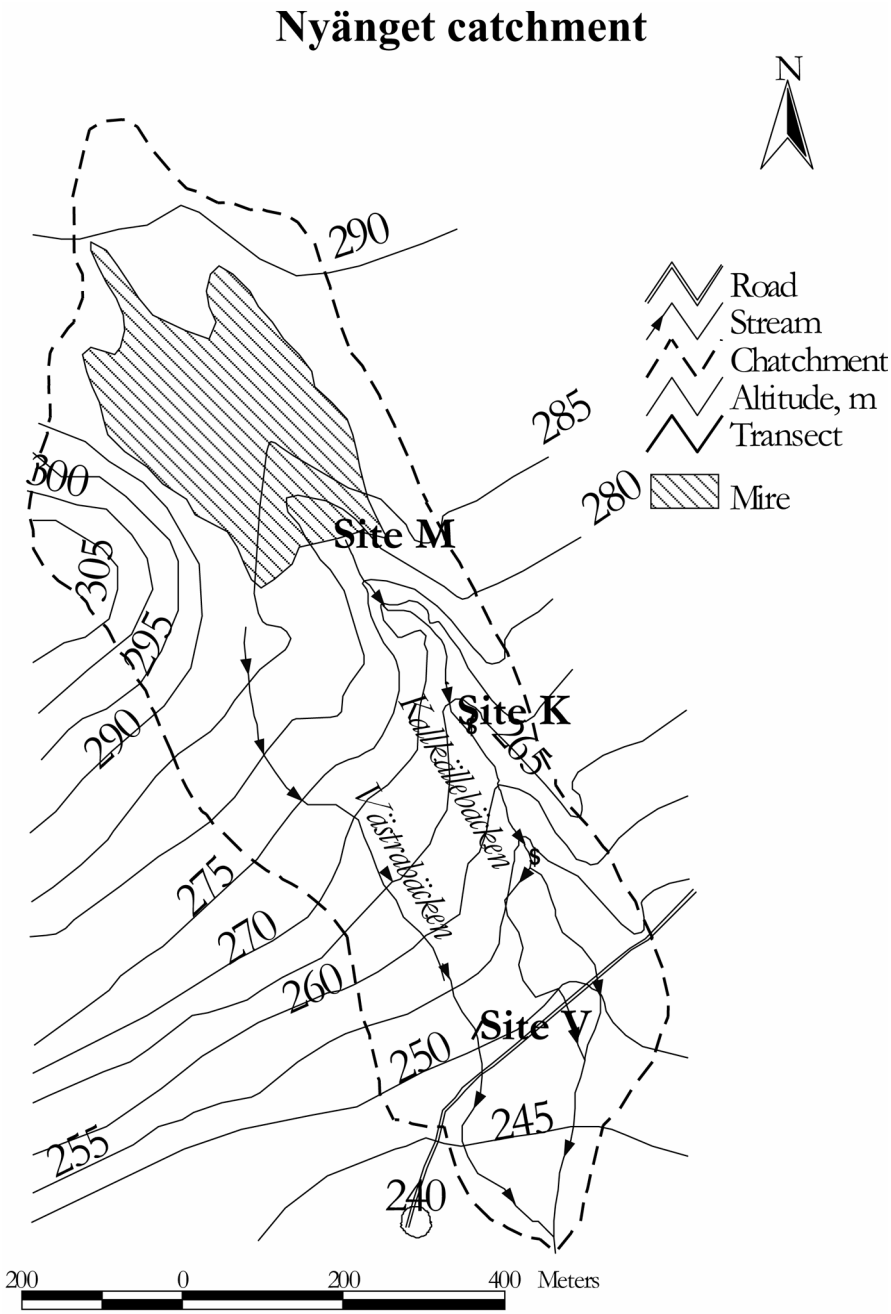

Figure 1. Map over the Nyänget catchment with Site M and transects at Site K and V inserted (modified from (Bishop et al. 1995a)).

fect the chemistry in the stream during high flow events (Bishop et al. (1995a, 1995b)).

Sampling of soils and streams

Soil, soil solution and stream water were sampled at Sites M, K and V on June 2, 1998. At site M, soil samples were collected above and below the ground water table of the open peatland as well as at the point where water from the mire emerges and initiates Kallkällebäcken (Site M stream bank). Six soil samples were collected along each of the transects at Site K and V: in the stream banks and at approximately 2 and 20 m away from each of the two streams. To obtain soil samples with a high likelihood of reflecting the chemistry in run-off at the sampling occasion, samples were taken just above and below the ground water table. Stream bank samples were taken just above and below the water surface of the stream. Streams were sampled downstream at each of the two transects. One litre of stream water was collected in a Teflon® flask. A sub-sample was acidified and saved for mercury analyses, another sub-sample was saved for analyses of general chemistry. Twenty-five litres of stream water was collected in 1 to 4 containers for subsequent flocculation and collection of stream organic matter for S *K*-edge XANES analyses. Additional sampling of soils and streams was conducted Aug. 3, 1998 (Site K stream), May 17, 1999 (Sites M, K and V streams and 3, 2 and 2 soils from the three sites), Sept. 3, 1999 (Sites M and K streams, the stream bank from Site M and 5 soils from Site K) and Nov. 12, 1999 (Sites K and V streams). All samples were collected following protocols for clean sampling procedure. Soil samples were sealed in double plastic bags and stored at 4 °C. Within 24 h soil samples were centrifuged at 22 100 g (Beckman J2-21M/E model, JA.14 rotor) for 15 minutes. No precautions were undertaken to avoid contact with atmospheric oxygen. The supernatant was decanted and divided into one aliquot that was acidified and stored in Teflon® flasks in darkness at 4 °C until analysed for mercury, and another aliquot saved for general chemical analyses.

Flocculation of stream organic matter and extraction of soil organics

To each container with 25 litres of stream water, 10.0 g $Al(NO_3)_3$ was added immediately after sampling. The mass of $Al(NO_3)_3$ needed for an optimal flocculation, was determined in a separate experiment. During transport to Umeå the stream water + added Al was mixed and organic substances in the stream water were flocculated. After 12 hours of settling in darkness at 6 °C, the supernatant was decanted from the flocculated sediment. The flocculate was separated from solution by centrifugation at 22 100 g for 15 min. Excess salt was removed by three successive equilibrations of the flocculates with 100 mL Millipore® water for 30 min. The flocculates were freeze-dried until analysed for S_{tot}, N_{tot}, organic C, and S *K*-edge XANES. Using the above procedure, 33 to 48% of the stream organic C was collected in June-98 and May-99 and 70 to 72% in September-99.

Potentially soluble organic carbon (PSOC) was extracted from one selected soil sample at Site K with a modified version of the method used by Adams and Byrne (1989). A metal-chelating resin was used to release PSOC from soil. To ten 500 mL polycarbonate centrifuge bottles with 30 g moist soil each, 5.0 g of Chelex 20 (Biorad) and 250 mL Millipore water was added. After 12 h of gentle shaking, the brown-coloured supernatant was separated from soil and resin by centrifugation at 22 100 g. The supernatant of each sample (pH between 5.9 and 6.1) was collected in a 500 mL centrifuge bottle and added $Al(NO_3)_3$ (under 5 min of stirring) to give a total Al concentration of 2 mM. After 55 min of sedimentation in darkness, the formed Al-organic matter flocculate was separated from the clear solution by centrifugation. Excess salt was removed by three successive equilibrations of the flocculates with 100 mL Millipore water for 30 min. The precipitates were collected and freeze-dried as one sample. On average 98% of PSOC were re-flocculated by $Al(NO_3)_3$ as determined by absorption at 254 nm.

Chemical analyses of samples from soil, soil solution and stream

pH was measured in stream samples and in centrifuged soil solutions by an Orion 610 digital ion analyser coupled to an Orion 8103 SC Ross combination electrode (Orion Research, Cambridge, MA). Total organic carbon (TOC) in soil solutions and streams was measured on a TOC-5000 (Shimadzu Company, Tokyo, Japan). The dissolved metals Na, K, Mg, Ca, Al and Fe were determined by ICP-AES (Perkin-Elmer Plasma 2000, Norwalk, CT). Concentrations of Cl^-, SO_4^{2-} and NO_3^- were determined by IC-Dionex 4000i (Dionex Corporation, Sunnyvale, CA). Total organic C and total N were determined on an elemental analyser (Perkin-Elmer, 2400 CHN, Norwalk, CT). Total S in soil samples was determined on a LECO analyser (LECO Corporation, MI). Total S in PSOC and stream organics was determined after digestion of 30 mg soil in 5.0 mL concentrated HNO_3 + 0.5 mL concentrated $HClO_4$ at 100 °C for 3 h until all solution had evaporated. Ten mL Millipore water was added and S was analysed by ICP/AES (Perkin-Elmer Plasma 2000, Norwalk, CT). The method gave comparable results as the LECO analyser for some selected organic soil samples.

Determination of CH_3Hg (II) and Hg_{tot}

Extraction and derivatisation procedure for the determination of methyl mercury
CH_3Hg (II) in soil was determined by gas chromatography, microwave induced plasma, atomic emission spectrometry (GC-MIP-AES) after solvent extraction and *in situ* ethylation following Qian et al. (2000). CH_3Hg (II) in soil solution and stream was also determined by GC-MIP-AES after solvent extraction and *in situ* ethylation (Qvarnström et al. 2000). Some modifications were introduced in the extraction part. Briefly, CH_2Cl_2 was added to soil solution or stream water, followed by drop-wise addition of 4 mol L^{-1} HCl until the pH was below 2. The sample was shaken for half an hour and the CH_2Cl_2 phase was then separated. The above extraction procedure was repeated 3 times and the organic phases were combined.

Methyl mercury in the CH_2Cl_2 was back extracted into water, followed by ethylation, GC separation and MIP-AES detection. The absolute detection limits for CH_3Hg (II) is around 0.5 pg.

Digestion and determination of Hg_{tot}

Soil samples were digested with a mixture of HNO_3 and HCl in a microwave system (Qian et al. 2000). Due to technical problems with this system, some of the samples were treated as follows: 4 mL of HNO_3 and 4 drops of HCl were added to 200 mg of soil. The samples were left over night on a clean bench. After this 10 drops of H_2O_2 were added and the samples were subsequently heated to 80 °C for 8 hours. Four mL of H_2O were added and after centrifugation the clear solution was used for quantification by cold vapour atomic absorption spectrometry (CVAAS) using $SnCl_2$ and the amalgamation technique at the 254 nm mercury line (FIMS, Bodenseewerk Perkin Elmer, Uberlingen, Germany) The accuracy of results was tested by standard addition of Hg as $Hg(Cl)_2$ or as CH_3HgCl.

Soil solution and stream water samples (30 mL) were added HNO_3 (3 mL) and HCl (0.5 mL) in quartz flasks, which thereafter were subjected to UV radiation for seven hours. After complete digestion, 5 mL of a solution containing 30% $SnCl_2$ and 5% H_2SO_4 was added to the quartz flasks. The Hg^0 formed was detected by CVAAS as described above. The absolute detection limit for Hg_{tot} is lower than 0.1 ng. The accuracy of the entire procedure was validated by analysing certified reference materials (BCR light sandy soil CRM 142 R, marine sediment NRC Mess 2) and by using the method of standard addition

Sulphur speciation using S K*-edge XANES*

Sulphur K-edge XANES data for selected samples from streams, soils and PSOC were collected on beamline X19A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (Upton, NY, USA). The incident X-ray energy was scanned over the range of 2462 to 2500 eV with a step size of 0.2 eV. Sodium sulphate was used as reference and the energy was calibrated at 2482 eV with this compound. The energy drift between samples was corrected by setting the energy of the sulphate peak to 10.0 eV above that of elemental S (2472 eV) (Huffman et al. 1991; Waldo et al. 1991). All XANES spectra were recorded in fluorescence mode using a Stern-Heald ionisation detector filled with He gas and positioned 90° to the incident beam (Lytle et al. 1984). The monochrometer was detuned 70% at the S K-edge in order to reduce fluorescence induced by high-order harmonics. Depending on the data quality, 3 to 12 scans were collected for each sample. The computer program SOLVER (Microsoft Excel) was used to deconvolute the average spectrum for each sample into pseudo-components by a least-square fitting procedure, described in detail by Xia et al. (1998). In the oxidized end of the spectrum, sulphates (formal oxidation state + 6, peak maximum 10.0 eV above elemental S), sulphonates (+5, 8.0–8.5 eV), sulphones/sulphites (+4, 6.2–7.4 eV) and sulphoxides (+2, 2.7–4.3 eV) were quantified. In the reduced end of the spectrum (formal oxidation state −1–0, 0–1.9 eV), thiols (RSH), dithiane (RSSH), organic

sulphides (RSR), organic disulphides (RSSR) and thiophenes are more difficult to separate. Therefore, in line with Xia et al. (1998), reduced organic S functionalites with a peak maximum of 0–2 eV relative to elemental S were summarized and designated Org-S_{RED}. This definition of Org-S_{RED} was used by Skyllberg et al. (2000), but it differs slightly from the one used by Qian et al. (2002).

Mercury speciation modelling in soil and stream at Nyänget

We used data on TOC, ionic strength and concentrations of CH_3Hg (II), Hg_{tot}, measured inorganic ligands (Cl^-, OH^-) and estimated concentrations of complexing organic ligands to calculate the most important mercury and methyl mercury species. This was done for the pH range 3.5 to 6.5. Concentrations of functional groups associated to the solid phase of soils were related to the volume of soil solution based on average water contents in soil (approximately 85% of fresh weight). Neither electrostatic effects, nor organic matter heterogeneity were considered in the modelling.

Chemical modelling was performed on two systems: 1) a soil – soil solution system, and 2) a stream water system. In the stream only one phase was considered (since the stream water and soil solutions were not filtered, colloids and possible particles were considered as a part of the aqueous phase). In both systems free concentrations of Hg^{2+}, CH_3Hg^+ and their organic and inorganic complexes were calculated. In the stream system total aqueous concentrations of Hg (II) and CH_3Hg (II) were used as input data, whereas in the soil – soil solution system total concentrations of Hg (II) and CH_3Hg (II) in the soil were used as input data. Total concentrations of Hg (II) and CH_3Hg (II) in soil solution was modelled, and was used to evaluate the model by comparison with actual measured data in soil solution.

Critical stability constants for all inorganic complexes and dissociation constants were taken from Smith and Martell (1993). As model compounds for carboxylic groups associated to TOC in soil solution and in SOM we used oxalic acid (pKa_1 = 3.60, pKa_2 = 1.16) for the complexation of Hg^{2+} and acetic acid (pKa = 4.76) for the complexation of CH_3Hg^+ (constants for larger carboxylic molecules were not found). Concentrations of carboxylic groups in SOM were estimated from a base-titration of organic soils from Site V (Skyllberg and Magnusson 1995) and in stream and soil solution organics from base-titration of organics in Site K stream (Hruska et al. 2001). As model compound for amino groups in stream and SOM we used methylamine (pKa = 10.43) and its complexation of both mercury forms. We assumed the concentration ratio amino groups:carboxylic groups to be 1:10 in soil, soil solution and stream. The concentration of amino groups in the aqueous phase of soils obtained in this way corresponds fairly well with the range given by Stevenson (1994).

Based on a combination of S XANES with Hg EXAFS, Qian et al. (2002) found that 29% of Org-S_{RED} (37% with the definition of Org-S_{RED} used by Qian and coworkers) in soil, 24% of Org-S_{RED} in PSOC and 16% of Org-S_{RED} in stream organics at Site K may be taken as a representation of RSH. The constant for the

complexation of Hg^{2+} to SOM in a bi-dentate mode with one thiol and one carboxyl group (log K_1 = 31.8), reported by Skyllberg et al. (2000), was used for both soil and stream organics. Acidity constants (pKa) were 9.96 (thiol) and 3.44 (carboxyl), as in mercaptoacetic acid. Skyllberg et al. (2000) determined constants at native Hg concentrations (pM) in humus layers and peat soils in fair agreement with bi-dentate complexation of Hg^{2+} to one thiol and one carboxyl group in mercaptoacetic acid (Basinger et al. 1981). The constant for a mono-dentate complexation of CH_3Hg^+ to RS^- (log K_1 = 16.5) was taken from Qian et al. (2002). This value is in agreement with stability constants (log K_1 = 15.1–17.8) reported for thiol – methyl mercury associations in a range of proteins (Carty and Malone 1979). The pKa for the thiol was set to 9.96, as in mercaptoacetic acid.

Results and discussion

Factors affecting pH and dissolved organic carbon in soil and stream

The Nyänget catchment is typical for large parts of northern Scandinavia. It is covered by Histosols (peat), close to streams, and by Spodosols developed in sandy glacial till originating from gneissic and granitic mineralogy. Typical for boreal forest catchments, the chemistry of streams changes quite dramatically during a year. During spring-flow conditions streams become more acidic due to superficial flow through organic-rich surface horizons. Thus, the pH-value was 4.35 in the outlet from the mire (Site M) in May-99, 4.53 and 4.52 in the Site K stream during June-98 and May-99, and 4.63 and 4.67 in the Site V stream in June-98 and May-99. Summer and early autumn base-flow through deeper, mineral soil horizons increased pH to 6.18 in the mire outlet and 6.28 in Site K stream in September-99.

Another important factor for the stream and soil solution chemistry in this catchment is the formation of organic-Al complexes in discharge areas, close to the streams. Skyllberg and Magnusson (1995) showed that a high Al-saturation of oxygen-containing functional groups in SOM was the major controlling factor of both pH and TOC in the stream bank soil solution at Site V. In this study we found that the Al/TOC quotient was substantially higher in soil solutions and in the stream at site V, as compared to Site K (Table 1). Thus, a higher Al-saturation of organic substances in Site V soils, most probably due to the fact that Site V peat soils are shallower than at Site K, may explain why the Site V soil solutions and its stream generally have lower concentrations of TOC, a higher pH and higher concentrations of dissolved Al than those from Site K. Weekly sampling from January to December 1993 (Pettersson et al. 1995) showed that TOC concentrations at all occasions except three were lower in the stream at Site V (range: 8–25 mg L^{-1}) than at Site K (range: 20–40 mg L^{-1}).

With one exception, C/N-tot ratios in peat soils at Sites K and V ranged between 22 and 27 (Table 2). The C/N ratio was 30 and above in the mineral soils at Site V with SOC less than 5%. For mosses (dead and alive) in the open mire (Site M) and

Table 1. Samples taken in stream and above (A) and below (B) the ground water table (GWT) in soils at Site M, K and V in June-98. pH, total organic carbon in aqueous phase (TOC) and Al saturation of TOC refer to aqueous phase and concentrations of methyl mercury (±SD), total mercury (±SD) and their ratio refer to solid phase of soil.

Sampling site	Soil No.	Depth (cm)	GWT (A/B)	pH	TOC mg L^{-1}	Al / TOC mmol g^{-1}	CH_3Hg (II) / Hg_{tot} (%)	CH_3Hg (II) (ng g^{-1})	Hg_{tot} (ng g^{-1})
Site M									
Stream bank	1	0–20	A/B	4.06	47	0.19	5.8	3.21 ± 0.39	55 ± 5
50 m from outlet	2	0–5	B	4.00	68	0.04	3.4	2.86 ± 0.03	85 ± 6
50 m from outlet	3	5–25	B	3.88	42	0.05	5.2	1.41 ± 0.10	27 ± 4
Site K									
Stream				4.53	19	0.43			
Stream bank	4	0–10	A	4.15	32	0.50	17.2	13.38 ± 0.62	78 ± 11
Stream bank	5	10–25	B	4.56	50	1.04	9.0	10.18 ± 0.68	113 ± 15
2 m from stream	6	10–20	A	3.70	59	0.41	1.6	1.73 ± 0.19	106 ± 3
2 m from stream	7	30–50	B	3.93	117	0.26	3.6	4.08 ± 0.64	114 ± 17
20 m from stream	8	10–20	A	3.63	67	0.18	0.8	0.60 ± 0.15	77 ± 7
20 m from stream	9	30–50	B	3.74	109	0.10	0.4	0.33 ± 0.04	77 ± 15
Site V									
Stream				4.63	10	1.33			
Stream bank	10	0–10	A	4.75	21	1.71	2.1	0.87 ± 0.05	41 ± 5
Stream bank	11	10–25	B	4.34	23	1.26	1.2	1.18 ± 0.17	95 ± 8
2 m from stream	12	25–45	A	4.04	58	0.93	0.7	0.68 ± 0.08	101 ± 5
2 m from stream	13	45–60	B	4.60	22	2.05	1.7	0.58 ± 0.05	35 ± 1
20 m from stream	14	35–45	A	5.09	17	3.24	0.7	0.11 ± 0.01	15 ± 1
20 m from stream	15	45–60	B	5.35	28	4.54	< 0.5	Below DL	10 ± 2

the stream bank of Site K, the C/N ratio, as expected, was substantially higher than in the more decomposed organic matter in soils. In the Site K stream the C/N ratio was higher than in its peat soils during both spring sampling occasions (43 and 40). Also at Site V, the stream had a higher C/N ratio (37) than its soils. This indicates that superficial flow in springtime results in a significant transport of organics from surface peat and stream bank mosses (with a high C/N ratio) into streams. This conclusion is in agreement with findings reported by Bishop et al. (1995a, 1995b) at Nyänget, using several other methods to determine the origin of stream organics.

Variation in CH_3Hg (II)/Hg_{tot} ratio in soil, soil solution and stream

The CH_3Hg (II)/Hg_{tot} ratio varied between 0.3 and 17.2% in the soils, between 1.6 and 8.5% in soil solutions and between 2.4 and 10.3% in the streams of this study (Tables 1 and 3). For a comparison, Hurley et al. (1995) reported a range of 0.4 and 11.1% CH_3Hg (II) (of Hg_{tot}) in streams draining northern wetlands and forest soils in Wisconsin. Very few data have been reported for organic soils. In a Canadian boreal bog peat, Heyes et al. (2000) found 3.1% of Hg_{tot} to be CH_3Hg (II) in hollows and 0.7% in hummocks. In the pore water of these peat soils, CH_3Hg (II) varied between 1 and 26% of Hg_{tot}.

In June 1998, soils at Sites K and V were systematically sampled. Samples were also taken at the mire outlet and 50 m out on the open mire (Site M). Figure 2 depicts the soil transect at Site K. Concentrations of CH_3Hg (II) and the CH_3Hg (II)/Hg_{tot} ratio were highest in the stream bank soils, and decreased with increasing distance from the stream. A similar, but less obvious, pattern was found also at Site V and Site M (Table 1). At the following sampling occasions fewer samples were taken, but still the highest CH_3Hg (II) concentrations and CH_3Hg (II)/Hg_{tot} ratios were found in the stream bank soils (Table 3). There was no positive correlation between concentration of CH_3Hg (II) and organic-C content ($r = 0.001$, $n = 27$), nor between CH_3Hg (II)/Hg_{tot} ratio and organic-C ($r = 0.001$, $n = 27$). Apparently distance to the stream was more important for CH_3Hg (II) concentrations and CH_3Hg (II)/Hg_{tot} ratios than content of organic matter.

The hypothesis by Bishop et al. (1995a) that the output of CH_3Hg (II) from soils into streams at Nyänget is controlled by biogeochemical processes in the riparian zone, is further supported by our determinations of soil bound CH_3Hg (II). It is a consensus that wetlands and organic rich soils, subjected to flooding and variable ground water levels, can act as sources of CH_3Hg (II) at a catchment scale (Hurley et al. 1995; St. Louis et al. 1994). More specifically, inundation of labile soil organic matter and litter have been shown to be important factors for the production of CH_3Hg (II) in boreal peat soils (Heyes et al. 2000), as well as in tropical soils (Roulet et al. 2001). High concentrations of CH_3Hg (II) and CH_3Hg (II)/Hg_{tot} ratios in the stream bank soils at Nyänget may therefore be an effect of enhanced net methylation rates owing to highly variable ground water levels close to the streams.

In agreement with higher CH_3Hg (II)/Hg_{tot} ratios in stream bank soils at Site K, as compared to Site V, (Table 1), the CH_3Hg (II)/Hg_{tot} ratio in the stream was twice as high as at Site K, as compared to Site V, in May-99 and November-99 (Table 3).

Table 2. Dry weight based percentage of organic carbon (Org-C), total nitrogen (N_{tot}) and total sulfur (S_{tot}), C/ N_{tot} and C/ S_{tot} ratios in soils and stream dissolved organic matter (DOM) sampled at different occasions at the three sites. Soil samples have numbers and were taken above (A) and below (B) the ground water table (GWT).

Sampling occasion	No.	GWT (A/B)	Soil and stream sample	Org-C (%)	N_{tot} (%)	C/ N_{tot}	S_{tot} (%)	C/ S_{tot}
Site M soil & mire outlet								
June–98	1	A/B	Stream bank 0–20 cm	49.2	1.34	37	1.00	49
	2	B	50 m from outlet 0–5 cm, mosses	46.6	1.31	36	0.38	123
	3	B	50 m from outlet 5–25 cm, mosses	47.3	0.47	101	0.18	263
May–99			Site M outlet DOM	35.3	1.48	24	0.41	86
	16	A/B	Stream bank 0–20 cm	42.7	1.97	22	0.43	99
	17	B	50 m from outlet 3–15 cm, mosses	42.9	0.44	98	0.18	238
	18	B	50 m from outlet 15–22 cm, mosses	43.0	0.65	66	0.17	253
Site K soil & stream								
June–98			Site K Stream DOM	43.1	1.01	43	0.34	127
	4	A	Stream bank 0–10 cm	33.0	1.38	24	0.37	89
	5	B	Stream bank 10–25 cm	30.3	1.23	25	0.42	72
	6	A	2 m from stream 10–20 cm	49.3	1.83	27	0.41	120
	7	B	2 m from stream 30–50 cm	46.9	1.82	26	0.50	94
	8	A	20 m from stream 10–20 cm	56.5	1.71	33	0.26	217
	9	B	20 m from stream 30–50 cm	54.9	2.37	23	0.64	86
			PSOC of Soil 6	48.0	2.22	22	0.52	92
Aug.–98			Site K Stream DOM	44.2	0.80	54	0.32	138
May–99			Site K Stream DOM	42.7	1.07	40	0.42	102
	19	A	Stream bank, mosses	40.7	0.59	69	0.08	509
	20	B	Stream bank 30–40 cm	27.1	1.05	26	0.18	151
Site V soil & stream								
June–98	10	A	Stream bank 0–10 cm	13.0	0.54	24	0.08	163
	11	B	Stream bank10–25 cm	19.7	0.79	25	0.09	219
	12	A	2 m from stream 25–45 cm	33.1	1.40	24	0.29	114
	13	B	2 m from stream 45–60 cm	4.2	0.12	35	0.05	84
	14	A	20 m from stream 35–45 cm	2.4	0.08	30	0.03	80
	15	B	20 m from stream 45–60 cm	0.6	0.02	30	0.03	20
May–99			Site V Stream DOM	40.3	1.08	37	0.34	119
	21	A	Stream bank 0–15 cm	29.1	1.22	24	0.17	171
	22	B	Stream bank 15–25 cm	13.9	0.61	23	0.15	93

Table 3. Methyl mercury (±SD) and total mercury (±SD) concentrations and their ratios in streams, soil solutions and soils at Sites M, K and V.

No.	Sampling site and depth	Stream			Soil Solution				Soil				
		TOC mg L^{-1}	CH_3Hg (II) / Hg_{tot}%	CH_3Hg (II) ng L^{-1}	Hg_{tot} ng L^{-1}	TOC mg L^{-1}	CH_3Hg (II) / Hg_{tot}%	CH_3Hg (II) ng L^{-1}	Hg_{tot} ng L^{-1}	OC %	CH_3Hg (II) / Hg_{tot}%	CH_3Hg (II) ng g^{-1}	Hg_{tot} ng g^{-1}
	May–99												
	Site M outlet	13.8	9.78	0.88	9.0								
16	Stream bank 5–15 cm					48.4	1.6	0.64	39	42.7	12.0	7.21 ± 0.51	60 ± 2
17	50m from outlet 3–15 cm					41.3	4.0	0.62	15.5	42.9	0.88	0.25 ± 0.02	29 ± 4
18	50m from outlet 5–22 cm					62.8	8.5	1.1	12.9	43.0	1.5	0.45 ± 0.07	30 ± 1
	Site K stream	16.8	10.32	0.96	9.3								
19	Stream bank mosses					14.3	4.3	0.79	18.3	40.7	0.39	0.41 ± 0.08	104 ± 2
20	Stream bank 30–40 cm					28.7	7.4	2.04	27.4	27.1	1.5	1.48 ± 0.14	100 ± 5
	Site V stream	14.8	4.65	0.4	8.6								
21	Stream bank 0–15 cm					34.6	5.0	2.11	42.6	29.1	11.9	8.12 ± 2.28	68 ± 3
22	Stream bank 15–25 cm					29.8	2.8	0.93	32.9	13.9	1.4	1.53 ± 0.06	110 ± 3
	Sept.–99												
	Site M outlet	20.7	7.10	0.71	10								
23	Stream bank 5–15 cm					35.1	4.2	0.56	13.2	26.7	1.7	1.10 ± 0.10	65 ± 2
	Site K stream	16.0	6.52	0.60	9.2								
24	Stream bank 0–10 cm					32.0	6.0	0.96	15.9	36.9	3.8	3.58 ± 0.59	95 ± 5
25	Stream bank 10–20 cm					32.3	4.0	0.58	14.6	32.5	2.6	2.57 ± 0.01	97 ± 6
26	Stream bank 20–30 cm					100	3.7	0.74	19.8	42.5	3.6	3.45 ± 0.45	95 ± 2
27	2m from stream 50–60 cm					196	4.7	0.38	8.1	55.0	0.34	0.23 ± 0.02	66 ± 5
28	20m from stream 70–80 cm					131	2.3	0.22	9.4	52.9	0.30	0.16 ± 0.01	53 ± 0
	Nov.–99												
	Site K stream	29.4	5.5	0.35	6.4								
	Site V stream	13.2	2.4	0.13	5.4								

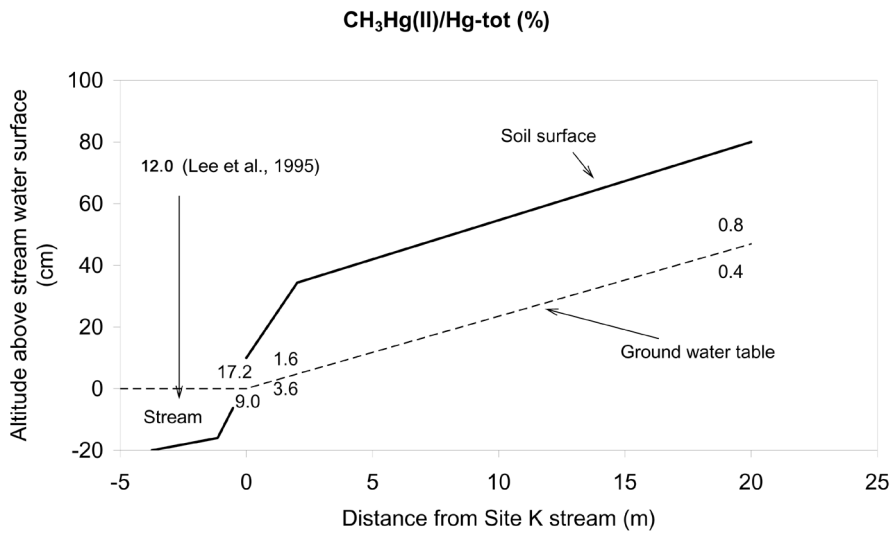

Figure 2. The CH_3Hg (II) / Hg-tot ratio (%) in soils located along hydrological pathways at Site K stream (June-98). Annual average data from the stream are taken from Lee et al. (1995). The ground water table represents the level at the sampling occasion. Note that all soils along the Site K transect were highly organic (> 30% org-C).

This difference between the two streams was maintained also on an annual basis in 1993. An annual average calculation based on weekly sampling showed that 12% of Hg_{tot} was in the form of CH_3Hg (II) in stream K and 6% in stream V (Lee et al. 1995). Except possible differences in ground water fluctuations and redox-conditions (not determined) marked differences in soil solution and stream chemistry (pH, Al, TOC) between the two sub-catchments, indirectly or directly, may have an effect on the net production of CH_3Hg (II).

With the exception of two soil samples (16 & 21), CH_3Hg (II)/Hg_{tot} ratios increased along the sequence of the compartments; soil – soil solution – stream at site M, K and V (Table 3). Further away from the streams (2–20 m), a much lower ratio was found in soils (0.30–0.34%, Site K, September-99) as compared to soil solutions (2.3–4.7%, Site K September-99). Similarly, the ratio was 0.88–1.5% in the peat soil 50 m from the Site M mire outlet (May-99), whereas the ratio in soil solution was 4.0–8.5%. These observations may indicate that methylation preferentially takes place in the aqueous phase of these soils. In addition, the concentration of Hg_{tot} in soil solution was significantly, positively correlated with both the concentration of CH_3Hg (II) in soil solution ($r^2 = 0.40$, $p < 0.021$, $n = 13$), as well as with CH_3Hg (II) bound to soil ($r^2 = 0.63$, $p < 0.001$, $n = 13$). In contrast, Hg_{tot} and CH_3Hg (II) bound to soil showed no significant relationship ($r^2 = 0.089$, $n = 27$). This may be taken as an indication that Hg^{2+} in solution is a source for methylation, and that soil bound Hg^{2+} is not (at least in a shorter time perspective).

Distribution of sulphur species in soil, soil solution and stream

In Table 4 the organic S speciation, as determined by XANES, is presented for Site M, K and V streams, stream banks and the complete soil transect at Site K. Based on the S K-edge XANES spectra, six different groups (the sum of sulphones/sulphites and sulphoxides is given in Table 4) of S functionalities in organic substances, were quantified. Note that inorganic sulphides (e.g. FeS-colloids) were only detected in one of the soil samples.

During spring (May–June), flocculated organics from all three streams showed quite uniform S speciation, with similar relative concentration of Org-S_{RED}. The only significant deviations were enhanced concentrations of sulphoxides + sulphones in Site V stream and sulphate esters in site M outlet. The sample taken in Site K stream under base-flow conditions in August was different with higher relative concentration of Org-S_{RED} and lower concentration of sulphonates. Normalized to organic C, reflecting the average composition of organic substances, Org-S_{RED}/C did not show any seasonal variation in the Site K stream. In soils the relative composition of S varied more than in streams. Interesting to note is that the Org-S_{RED}/C ratio was consistently higher below the ground water table, as compared to above, along the Site K soil transect. Even if data are few, it can be noted that the Site M stream had a relatively high Org-S_{RED}/C ratio in both the stream and in the stream bank, and that comparatively low Org-S_{RED}/C ratios were found in the stream bank at Site V.

A comparison of S composition of organic substances in the three compartments; soil – soil solution – stream is not straightforward since we do not have any data for true soil solutions (due to very low concentrations of S_{tot} in soil centrifugates). If PSOC from soil 6 is taken as a representative of soil solution, it's Org-S_{RED}/C ratio of 0.61 can be compared to 0.51 for soil 6. The Org-S_{RED}/C ratio of 0.45 in Site K stream in June 1998 in turn fall in the range of Org-S_{RED}/C ratios (0.26–0.99) along the Site K soil transect.

In general Org-S_{RED} in both soils and streams at Nyänget is higher than in soils along upland-peat soils transects in northern Minnesota (30–52% of S_{tot}, Skyllberg et al. (2000)), in extracts of humic and fulvic acids from soils and from the Suwannee River (15–55%, Xia et al. (1998)), as well as in a hydrophobic fulvic acid fraction (47–58%) and in a hydrophilic fulvic acid fraction (32–36%) Hundal et al. (2000).

Both Site K and Site V soils are situated below the highest Quaternary coastline limit, and most likely pyrite (FeS_2) is present in the mineralogy in the C-horizon in the soils (not determined). This is the case in most soils in the coastal area of northern Sweden (e.g. Öborn (1989)). Even though inorganic S was only detected in one organic soil sample, an active incorporation of inorganic sulphides into organic S under partly reducing conditions (Brown 1986), may contribute to a variation in the C/S ratio in soils. The C/S ratio varied much more in the Site K and V soils than did the C/N ratio (Table 2). Furthermore, Urban et al. (1999) explained decreasing C/S ratios with depth in lake sediments with biotic and/or abiotic incorporation of inorganic S into organic substances. A similar process may explain de-

Table 4. Total S (% of dry mass) and S speciation (% of total S), as determined by XANES (Xia et al. 1998), in dissolved organic matter of streams, organic soils and extracted organics from soil 6. The error for each S species is estimated to be ± 5–10% of the given values. ND = not detected. * Peask maxima for listed S-species are given in Material and Methods section.

Sampling occasion	No.	Above / below GWT	Soil and stream sample	S_{tot} (%)	Inorganic sulphide (%)	Org-S_{RED} (%)	Sulphox-ide + Sul-phone (%)	Sulpho-nate (%)	Sulphate (%)	Org-S_{RED}/C (%)
May–99			Site M outlet DOM flocculate	0.41	ND	55	3	19	23	0.65
May–99			Site V Stream DOM flocculate	0.34	ND	55	11	19	15	0.50
May–99			Site K Stream DOM flocculate	0.42	ND	57	4	22	17	0.56
June–98			Site K Stream DOM flocculate	0.34	ND	59	4	20	17	0.45
Aug.–98			Site K Stream DOM flocculate	0.32	ND	70	3	10	17	0.51
June–98	1	A/B	Site M Stream bank 0–20 cm	1.00	ND	78	5	11	6	1.59
	4	A	Site K Stream bank 0–10 cm	0.37	ND	70	8	12	10	0.78
	5	B	Site K Stream bank 10–25 cm	0.42	ND	71	2	17	9	0.99
	6	A	Site K 2 m from stream 10–20 cm	0.41	ND	61	7	17	14	0.51
	6	A	Extracted organic substances of Soil 6	0.52	ND	56	8	17	19	0.61
	7	B	Site K 2 m from stream 30–50 cm	0.50	ND	71	8	12	10	0.76
	8	A	Site K 20 m from stream 10–20 cm	0.26	ND	57	8	18	17	0.26
	9	B	Site K 20 m from stream 30–50 cm	0.64	ND	76	4	13	7	0.89
	10	A	Site V Stream bank 0–10 cm	0.08	ND	60	5	29	7	0.37
	11	B	Site V Stream bank 10–25 cm	0.09	ND	50	8	20	23	0.23
May–99	20	B	Site K Stream bank 30–40 cm	0.18	11	56	6	16	12	0.37

creasing C/S ratios with depth in the soils at Sites K and V (Table 2), as well as higher Org-S_{RED}/S and Org-S_{RED}/C ratios below than above the ground water table at Site K (Table 4).

Mercury speciation modelling in soil and stream at Nyänget catchment

Chemical speciation modelling is essential because absolute concentrations of different mercury and methyl mercury species are of crucial importance for biotic and abiotic transformations and cycling of mercury in soils and waters. In our approach it is assumed that activities of Hg^{2+} and CH_3Hg^+ in soil solution are in chemical equilibrium with complexes at soil surfaces, as well as with complexes in the aqueous phase. Particles (and colloids) in streams and complexes formed at their surfaces were not separated from dissolved species in this study. Input data for the model are given in Table 5 and the model output is illustrated as logarithmic concentration – pH diagrams in Figures 3 and 4 for the soil/soil solution and stream at Site K.

It is obvious from the diagrams that complexes with RS^- (thiol) groups control the speciation of Hg (II) and CH_3Hg (II) in both soil/soil solution and stream. In principle, 100% of Hg (II) and CH_3Hg (II) form thiol-complexes, either at the soil surface or in solution. At a water content of 85%, concentrations of Hg (II) and CH_3Hg (II) complexes with RS^- pertaining to the solid phase of soils are approximately 3.3 orders of magnitude higher than complexes with RS^- in solution (Figures 3 and 4). This modelled distribution of Hg (II) between the soil and soil solution is somewhat higher than the actual ratio of approximately 2.9 orders of magnitude, as determined in acid digest of soil and in soil centrifugate. A similar difference also holds for measured CH_3Hg (II) where the soil solid phase had 2.8 orders of magnitude higher concentrations than soil solution. In absolute terms the model predicted 4.8 x 10^{-11} M of total Hg (II) and 1.3 x 10^{-12} M CH_3Hg (II) in soil solution, as compared to determined 11 x 10^{-11} M of total Hg (II) and 4.5 x 10^{-12} M CH_3Hg (II).

The enhanced solubility of Hg (II) and CH_3Hg (II) in measured, as compared to modelled soil data, might be due to an omission of relevant soluble ligands in the model. Inorganic sulphides and bi-sulphides and/or high-affinity organic ligands, not completely reflected by Org-S_{RED} are two possibilities. Since concentrations of CH_3Hg (II) on average are about 6 to 7, and Hg (II) on average 5 to 6 orders of magnitude lower than the concentration of Org-S_{RED} in all compartments (soil, soil solution and stream), even very low concentrations of high-affinity ligands/sites are of importance for the chemical speciation. Another possibility is that chemical equilibrium is not completely attained between aqueous and solid (surface) phases.

Methyl mercury forms weaker complexes with organic substances than Hg^{2+}. This results in higher concentrations of free CH_3Hg^+ in both soil solution and stream (Figure 4), as compared to free concentration of Hg^{2+} (Figure 3). The concentration of free CH_3Hg^+ is approximately one order of magnitude lower in soil solution (10^{-17} to 10^{-20} M) than in the stream (10^{-16} to 10^{-19} M), in the pH range 3.5 to 6.5. In contrast to Hg (II), chloro and hydroxyl complexes with CH_3Hg (II)

Table 5. Concentrations of ligands and complex formation constants used in chemical equilibrium calculations performed by MINTEQA2.

Inorganic mercury	Soil/Soil Solution Concentrations mol kg^{-1} (ads) and mol L^{-1} (aq)	Stream	Complex formation reaction	$LogK_1$	Model compound	Reference
pH	3.5 – 6.5	3.5 – 6.5				
TOC(mg L^{-1})	60.5	17.8				
Ionic Strength	0.001	0.001				
[≡RS/RCOO]tot	0.12		Hg^{2+} + ≡RS^- /$RCOO^-$ = ≡RSHgOOCR≡ (ads)	31.8	Soil organic matter	Skyllberg et al. (2000)
[≡RNH_2]tot	0.095		Hg^{2+} + ≡RNH_2 = ≡RNH_2Hg^{2+} (ads)	8.7	Methylamine	Bjerrum (1972)
[≡RCOO]tot	0.95		Hg^{2+} + ≡$RCOO^-$ = ≡$RCOOHg^+$(ads)	9.7	Oxalic acid	Perrin (1979)
[Hg(II,ads)]tot	4.8×10^{-7}					
[RS/RCOO(aq)]tot	1.2×10^{-5}	3.0×10^{-6}	Hg^{2+} + RS^- + $RCOO^-$ = RSHgOOCR (aq)	31.8	Soil organic matter	Skyllberg et al. (2000)
[RNH_2(aq)]tot	5.2×10^{-5}	1.5×10^{-5}	Hg^{2+} + RNH_2 = RNH_2Hg^{2+} (aq)	8.7	Methylamine	Bjerrum (1972)
[RCOO(aq)]tot	5.2×10^{-4}	1.5×10^{-4}	Hg^{2+} + $RCOO^-$ = $RCOOHg^+$ (aq)	9.7	Oxalic acid	Perrin (1979)
[Cl^-]	3.0×10^{-5}	3.0×10^{-5}	Hg^{2+} + $2Cl^-$ = $HgCl_2$ (aq)	13.22		Smith and Martell (1993)
[Hg(II,aq)]tot	modelled	4.6×10^{-11}				
Methyl mercury						
pH	3.5 – 6.5	3.5 – 6.5				
TOC(mg L^-)	60.5	17.8				
Ionic Strength	0.001	0.001				
[≡RS/RCOO]tot	0.12		CH_3Hg^+ + ≡RS^- = ≡$RSHgCH_3$ (ads)	16.5	Soil organic matter	Qian et al. (2002)
[≡RNH_2tot	0.095		CH_3Hg^+ + ≡RNH_2 = ≡$RNH_2HgCH_3^+$(ads)	7.57	Methylamine	Rabenstein et al. (1974)
[≡RCOO]tot	0.95		CH_3Hg^+ + ≡$RCOO^-$ = ≡$RCOOHgCH_3$ (ads)	3.20	Acetic acid	Jawaid and Ingman (1978)
[CH_3Hg(ads)]tot	1.4×10^{-8}					
[RS(aq)]tot	1.2×10^{-5}	3.0×10^{-6}	CH_3Hg^+ + RS^- = $RSHgCH_3$ (aq)	16.5	Soil organic matter	Qian et al. (2002)
[RNH_2 (aq)]tot	5.2×10^{-5}	1.5×10^{-5}	CH_3Hg^+ + RNH_2 = $RNH_2HgCH_3^+$ (aq)	7.57	Methylamine	Rabenstein et al. (1974)
[RCOO(aq)]tot	5.2×10^{-4}	1.5×10^{-4}	CH_3Hg^+ + $RCOO^-$ = $RCOOHgCH_3$ (aq)	3.20	Acetic acid	Jawaid and Ingman (1978)
[Cl^-]	3.0×10^{-5}	3.0×10^{-5}	CH_3Hg^+ + Cl^- = CH_3HgCl (aq)	5.25		Smith and Martell (1993)
[CH_3Hg(II,aq)]tot	modelled	2.9×10^{-12}				

*(ads) and ≡ represents species in the solid (surface) phase of soil and (aq) means species in aqueous phase in soil solution and stream.

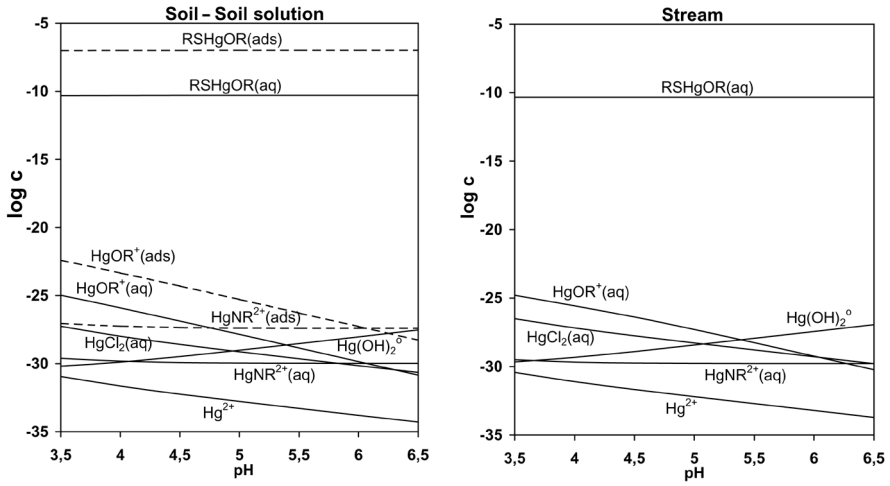

Figure 3. Calculated equilibrium concentrations of mercury species in the soil-soil solution equilibrium system and in stream water at Site K. Possible inorganic sulphide complexes are not taken into consideration.

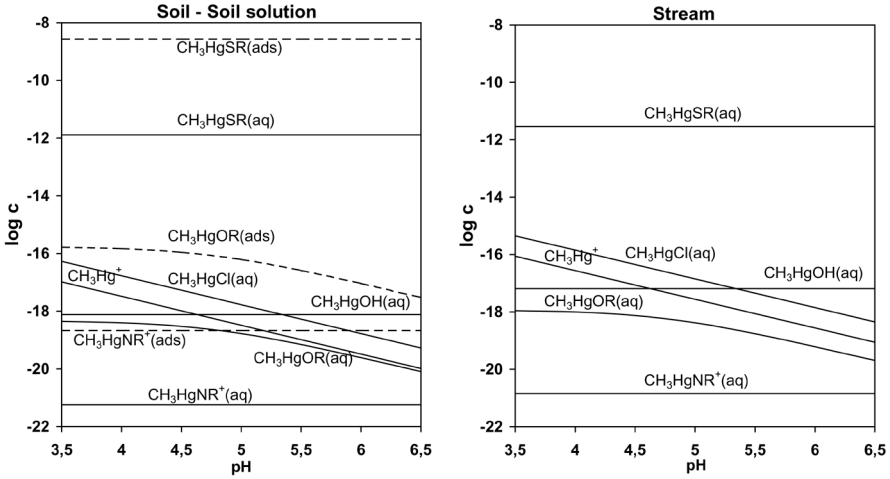

Figure 4. Calculated equilibrium concentrations of methyl mercury species in soil-soil solution system and in stream water at Site K. Possible inorganic sulphide complexes are not taken into consideration.

dominate over aqueous phase carboxyl and amino complexes. Phenols (not included in the model) may form much stronger complexes with CH_3Hg^+ than acetate (Carty and Malone 1979), but as in the case with methylamine, lower concentrations and much higher pKa-values of phenols results in lower concentrations of phenol – CH_3Hg (II) complexes in comparison with the weaker acetate – CH_3Hg (II) complexes. For Hg (II), on the other hand, amino – Hg complexes have concentrations on the similar order of magnitude as carboxyl complexes at pH 6 and above. Complexes of Hg^{2+} with carboxyl groups modelled by oxalate show concentrations on

the order of 10^{-22} to 10^{-27} M. If oxygen and amino groups are situated close enough, they may form bi-dentate co-ordinations with Hg^{2+}. Data for such a model compound are, however, lacking. If EDTA (log K_1 = 23.5) is used as a model compound for a chelating agent involving 1–2 carboxyl (+1–2 amino) groups, the concentration of the EDTA – Hg (II) complex would be 10^{-16} M in the stream, and in soil solution. It is, however, questionable whether EDTA is a relevant model compound for organic substances in soils and streams.

Our modelling approach is only valid for a situation when inorganic sulphides do not control the speciation of Hg (II) and CH_3Hg (II). Under increasing anoxic conditions, dissolved inorganic sulphide, bi- and/or poly-sulphide complexes will contribute to the solubility of Hg^{2+} and CH_3Hg^+. When the concentration of reduced inorganic S, S (-II), reaches a certain value the solubility and speciation of Hg (II) is controlled by HgS (s). At pH 5.0 the crucial concentration of S (-II) (= [H_2S (aq)] + [HS^-] + [S^{2-}]) for precipitation of HgS (s) is approximately 10^{-9} M (pK_{SP} HgS (s) = 51). This corresponds to a redox potential of −34 mV (pe = −0.58), at the sulphate concentrations determined in soil solution at Nyänget (0.077 mM). With 10^{-9} M of S (-II), and in the absence of HgS (s), the predominating aqueous sulphide complexes $Hg(SH)S^-$ and $Hg(SH)_2^0$ still have concentrations 6 orders of magnitude lower than RSHgOR (aq) at pH 5.0, using constants from Smith and Martell (1993). This result is in opposition to Hudson et al. (1994), who reported $Hg(SH)S^-$ and $Hg(SH)_2^0$ to out-compete stream organics in lakes by almost 4 orders of magnitude at pH 5.0 and similar redox conditions.

Constants used by Hudson et al. (1994) to model the complexation of Hg (II) to stream organics are much weaker than the ones we have used in our model. Hudson and co-workers refer to the work of Dyrssen and Wedborg (1991), whom estimated the log K_1 constant (22.1) for the reaction: $Hg^{2+} + RS^- = HgSR^+$, by use of a mathematical model. In environments with natural organic matter, a bi-dentate complexation between Hg^{2+} and one thiol and one carboxyl (or amine) is more likely than a mono-denate, positively charged complex. This has been confirmed indirectly by binding affinity data from organic soils (Skyllberg et al. (2000), as well as directly by spectroscopic data for organic soils and dissolved organics from soils (Xia et al. 1999; Hesterberg et al. 2001). A few thiol groups may even be situated close enough for a bi-dentate complexation of Hg^{2+}, but not likely to an extent sufficient to complex all Hg^{2+}. Also in marine environments thiol groups seem to determine the speciation of Hg^{2+}. Data from Guentzel et al. (1996) indicated that Hg^{2+} binds to seawater organic colloids in a bi-dentate mode including at least one thiol.

Aqueous bi-sulphides are more competitive for CH_3Hg (II), than for Hg (II), as compared with organic S ligands. With S (-II) concentrations of 10^{-9} M, the concentration of the aqueous complex CH_3HgSH^0 would be only 1.5 orders of magnitude lower than the organic complex CH_3HgSR (aq) at pH 5.0, and the complex CH_3HgS^- would be 3.5 orders of magnitude lower. Thus, with slightly higher concentrations of S (-II) than 10^{-9} M, bi-sulphide complexes will significantly contribute to the overall solubility of methyl mercury. As mentioned above, presence of

bi-sulphides at relatively low concentrations might be one explanation for the observed slightly higher solubility in the soils, as compared modelling results.

As for Hg^{2+}, our constants for the complexation of CH_3Hg^+ to stream organics are greater than constants incorporated in the model by Hudson et al. (1994). Using dialysis, Hintelmann et al. (1997) determined a constant for the complexation of CH_3Hg^+ to a humic acid only slightly smaller than the one we use (Qian et al. 2002). Similar to our modelling results, Hintelmann and co-workers calculated that the concentration of CH_3HgSH^0 (aq) was lower than the methyl mercury complex with humic acid at total sulphide concentration below 10^{-10} M and pH values below 7.

It has been suggested that passive transport of neutral, inorganic complexes over cell membranes is the main uptake mechanism for suggested Hg-methylating, sulphur reducing bacteria (Benoit et al. 1999). If this is true, these bacteria need to utilize concentrations of $HgCl_2^0$ and $Hg(OH)_2^0$ on the order of 10^{-27} M, if inorganic sulphides are absent, to methylate Hg (II) in streams and soils at Nyänget. Under anoxic conditions $Hg(SH)_2^0$ may be used. At pH 5 and 10^{-9} M of S (II) the concentration of $Hg(SH)_2^0$ would be 10^{-16} M. Concentrations of $HgCl_2^0$ and $Hg(OH)_2^0$ are 11 orders of magnitude lower than the ones calculated by the mercury cycling model (Hudson et al. 1994), and five orders of magnitude lower for $Hg(SH)_2^0$. Higher concentrations of neutral species, including dissolved HgS^0, may be present in reduced sediments with cinnabar (Benoit et al. 1999). There is, however, still some controversy about the identity of inorganic Hg-S species that in reality may form in solution under anoxic conditions (Tossell 2001).

Using S *K*-edge XANES we could only detect an inorganic sulphide phase in one of the soils of this study. At this point we can only speculate as to what extent the seasonally fluctuating water table in the peat soils at Nyänget, especially near the streams, will result in varying redox conditions in soils and streams. The fact that our modelling results, based on thiol complexation, were not significantly different from measurements of Hg_{tot} in the soil and soil solution, may indicate that the soils studied did not contain any HgS (s). More research is needed in order to establish the relative importance of inorganic and organic S for the speciation control of Hg (II) and CH_3Hg (II) in northern forest soils and streams.

Conclusions

The ratio of CH_3Hg (II) to Hg_{tot} decreased from 1.2 to 17.2% in stream bank soils to 0.4 to 0.8% in peat and mineral soils further away from streams. This may indicate that active methylation of Hg (II) in the discharge area close to streams (stream bank) is a major source of CH_3Hg (II) in streams.

The concentration of Hg_{tot} in soil solution was significantly, positively correlated with CH_3Hg (II) in both soil solution and soil. This, and the fact that the ratio of CH_3Hg (II) to Hg_{tot} was higher in soil solution than in soil may indicate that Hg (II) in soil solution is more available for methylation processes than Hg (II) in soil.

Between 50 and 78% of total S in peat soils, stream organics and potentially soluble organic matter from soil at the Nyänget catchment was in the form of reduced organic S functional groups. Normalized to organic C, concentrations of reduced organic S were consistently higher below than above the ground water table. Inorganic S colloids were only detected in one soil sample out of 10, and in none of the streams.

Chemical speciation modelling showed that practically 100% of Hg (II) and CH_3Hg (II) were complexed by thiol (RSH) groups, both in the soil – soil solution system and in stream water. This holds for oxic and slightly reduced conditions. If methylating bacteria take up neutral Hg (II) species they need to utilize concentrations of $HgCl_2^0$ and $Hg(OH)_2^0$ on the order of 10^{-27} M in the absence of inorganic sulphide complexes. Under anoxic conditions $Hg(SH)_2^0$ may be used. At pH 5 and 10^{-9} M of reduced inorganic S the concentration of $Hg(SH)_2^0$ would be 10^{-16} M.

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