Mass budgets of methylmercury in Kongsfjorden, Svalbard

Jihee Kim, Seunghee Han*
School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, Republic of Korea

Abstract

Methylmercury (MeHg) is a neurotoxin that bioaccumulates in aquatic food chains and human can be exposed to MeHg through fish consumption. While MeHg concentrations in Arctic seawater are relatively higher than lower latitudes, major sources of MeHg in arctic seawater remain uncertain. In the current study, we calculated mass budgets for MeHg in the Kongsfjorden, Svalbard, based on reference values and measurement data obtained from the 2016 and 2017 Svalbard cruise. We found out that significant MeHg production occurs in the water column through in-situ methylation, and input from sediment diffusion is the second largest source. The MeHg input from external sources, such as river and glacier, was relatively low. The result of mass flux estimation agreed well to the spatial distribution pattern of MeHg in this region, showing higher concentrations (0.07-0.17 pM) at surface 0-50 m and lower at deeper depths (0.06-0.13 pM, 100-250 m). We also found two components of fluorescent dissolved organic matter (FDOM) from the surface seawater using a PARAFAC (parallel factor analysis) model: component 1 is biological organic matter like amino acid (i.e., tyrosine or tryptophan) and component 2 is terrestrial humic matter. The MeHg concentration was revealed to be higher in the C1-dominant seawater and lower in the C2-dominant seawater. Currently, we are measuring methylation (K_m) and demethylation rate constants (K_d) of Kongsfjorden seawater to find out how K_m and K_d are associated with environmental variables such as FDOM components.

Introduction

❖ Methylmercury (MeHg) in the Arctic ocean

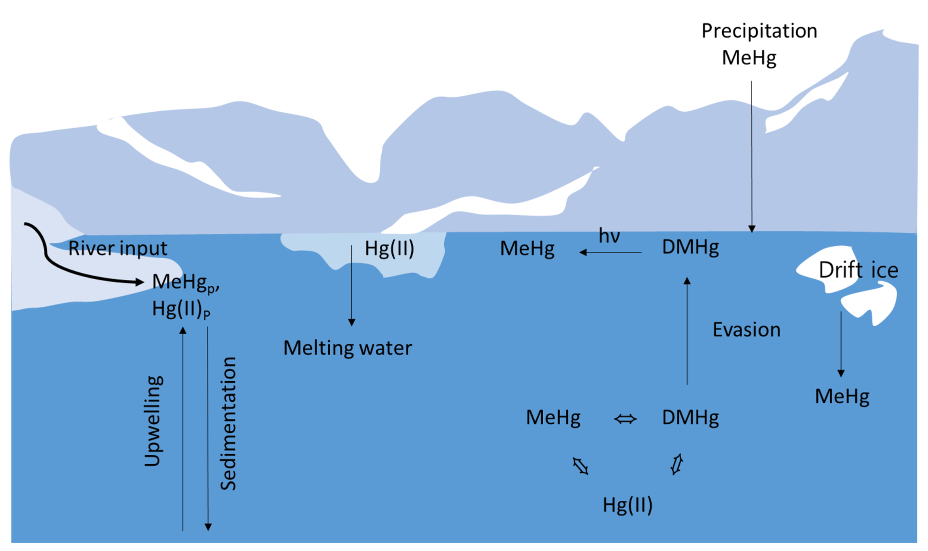


Figure 1. The cycle of MeHg in the Arctic ocean

- The MeHg in Arctic ocean is strongly affected by riverine inputs (Lehnherr, 2014). The depth profiles of MeHg showed an increase of concentration in the subsurface water, suggesting that MeHg source is likely a water column production (Kirk et al. 2008, Lehnherr, 2014).
- In the marginal sea ice zone (81°N, 85°N), one feature of MeHg profile was that the MeHg maxima were located at shallow depth (150-200 m, Heimbürger et al., 2015). Only small fractions of methylated Hg species were found in the benthic sediment unlike total Hg (Soerensen et al.,2016)

❖ The properties of Kongsfjorden, Svalbard (Svendsen et al., 2012)

Figure 2. Map of Kongsfjorden

- There is a well-marked inner fjord with relatively shallow water less than 100 m depth and a deeper fjord (volume is 29.4 km^3).
- Four main sources of freshwater run-off are glacier ablation, snowbelt, summer rainfall and ice calving.
- Sediment accumulation rates decline by one order of magnitude from the glacier front to the second sill in the central part.

Acknowledgement

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (NRF-2015R1A2A2A01003774).

Sampling & Methods

❖ Sampling in Kongsfjorden

Figure 3. The marine sampling sites in Kongsfjorden

❖ The mass budgets of methylmercury

Evasion: K_w * [C_{Me2Hg} - ($C_{Me2Hg\ air}$/H)]	
K_w (cm/hr)	A*(windspeed^2)*($ScMe_2Hg/ScCO_2$)^(-0.5)
H (K)	Exp [(-2512.43/K_{temp})+7.27]
$C_{Me2HgL1}$ (ng/L)	0.009975
$C_{Me2Hgair}$ (ng/m^3)	0.0038
Settling: C_{MeHgL1} * $Fraction_{PMeHg}$ * V	
Fraction $_{PMeHg}$	1 - [1/(1 + K_D * C_{SPM})]
V (m/yr)	V_s *60*60*24*365
Diffusion: D_w * ([Peak $C_{MeHg(L2)}$ - Peak $C_{MeHg(L1)}$] / [Peak depth (L2) - Peak depth (L1)])	
Peak $C_{MeHg(L2)}$ (ng/L)	0.0255
Peak $C_{MeHg(L1)}$ (ng/L)	0.0349
Dw (m^2/s)	$0.8*10^{-4}$
Deposition: $C_{MeHg\ precipitation}$ * precipitation rate	
$C_{MeHgprecipitation}$(ng/L)	0.038
Precipitation rate (mm/d)	28.8
Photodemethylation: C_{MeHg} * PAR * $K_{photodem}$ * depth	
C_{MeHg} (ng/L)	0.020592
PAR (E/m^2)	0.000058
$K_{photodem}$ (m^2/E/d)	0.001
Depth (m)	140
Freshwater discharge: Discharge rate * $C_{MeHg\ river}$ / Basin area	
Stream C_{MeHg} (ng/L)	0.0384
Red River C_{MeHg} (ng/L)	0.02847
Glacier (Drift ice) C_{MeHg} (ng/L)	0.0238
Basin area (m^2)	$2.245*10^9$
River discharge rate (m^3/yr)	$3.6 * 10^8$
Glacier (Drift ice) discharge rate (m^3/yr)	$1.016 * 10^9$

Results

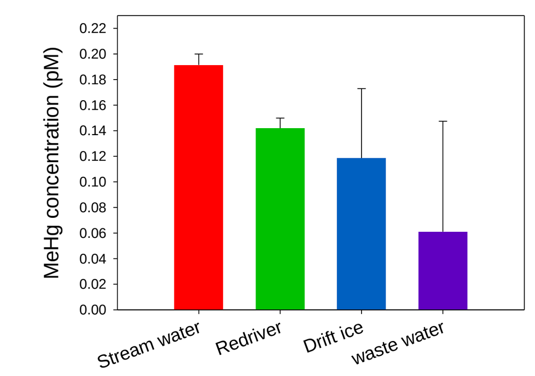


Figure 4. MeHg concentration of stream water, Red River water, drift ice, and wastewater

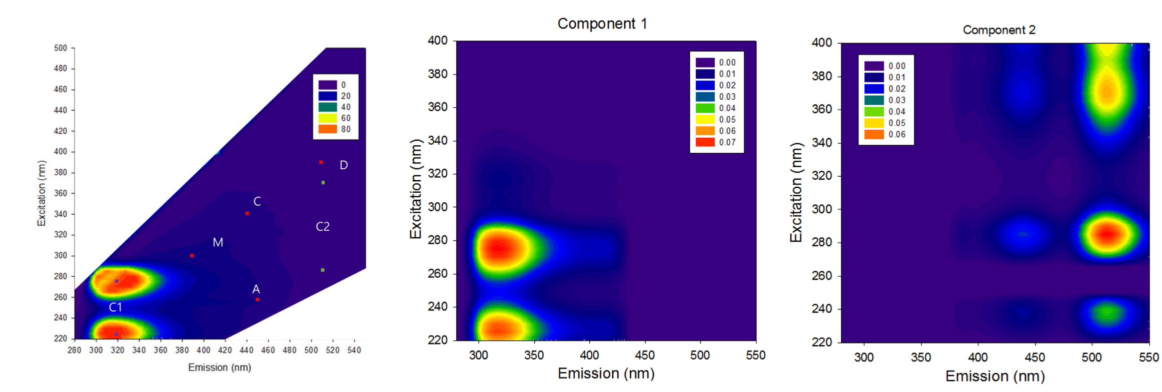
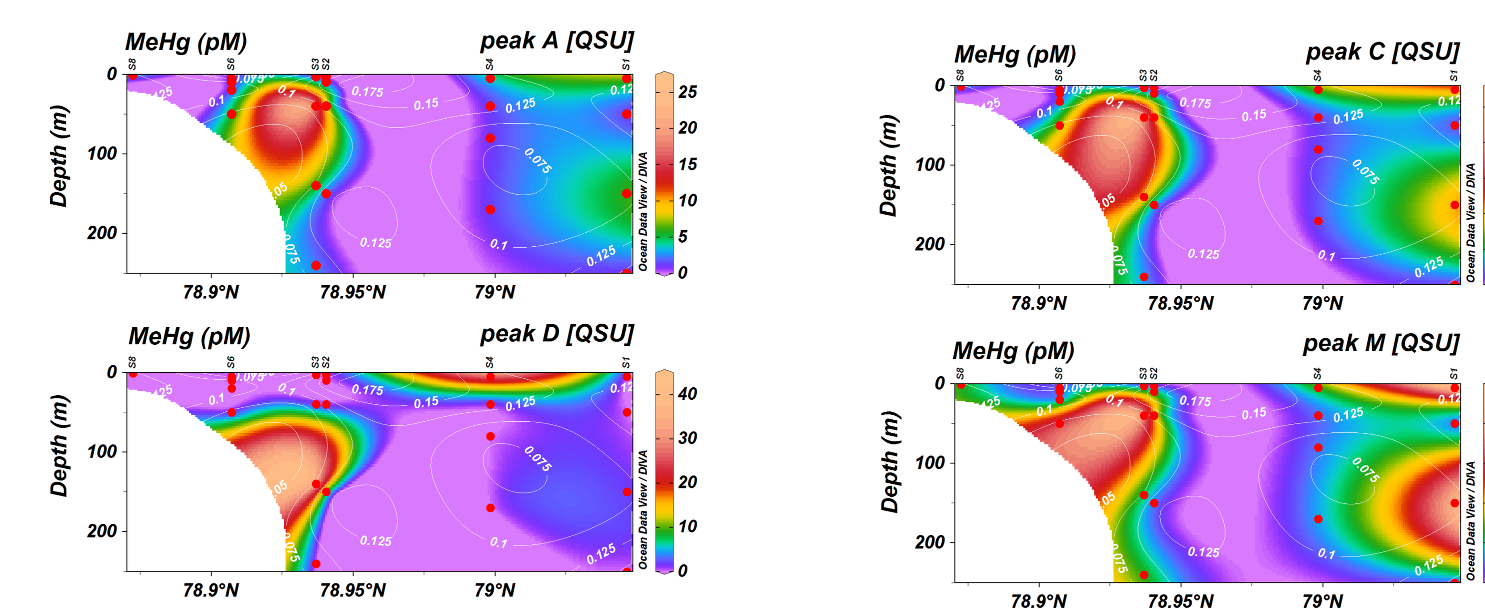


Figure 5. The EEM fluorescence intensities of DOM components (C1 and C1 from PARAFAC).

Component	Ex_{max} (nm)	Em_{max} (nm)	Properties
C1	225, 275	318	Free amino acid or amino acid combined withprotein, similar to tyrosine or tryptophan
C2	285 (240), 370	514 (440)	Terrestrial humic matter
Peak A	260	450	Relative amount of “humic-like” DOM
Peak C	340	440	Relative amount of “humic-like” DOM
Peak D	390	510	Relative amount of soil “fulvic-like” DOM
Peak M	300	390	Relative amount of “marine-like” DOM



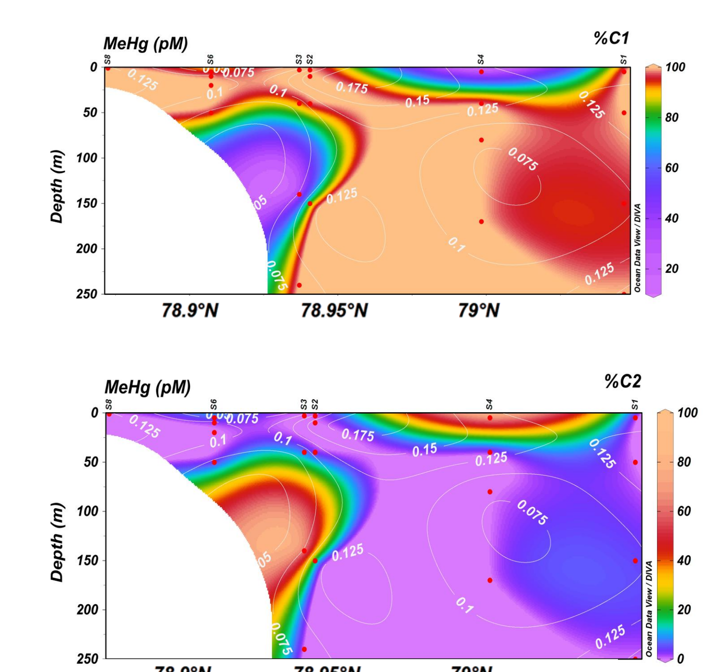


Figure 6. The relationship between FDOM component and MeHg

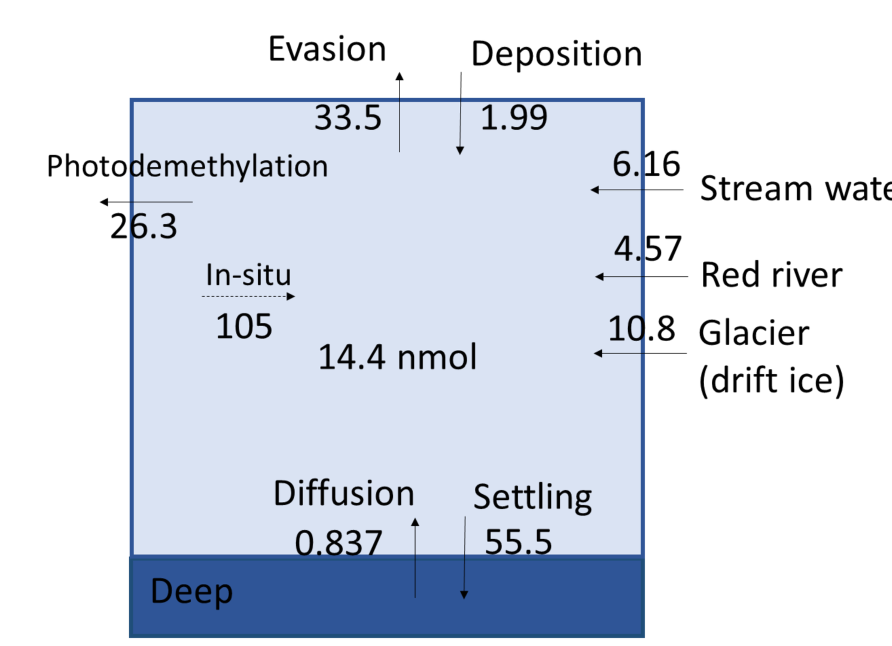


Figure 7. The preliminary mass budgets of MeHg in Kongsfjorden (unit: nmol/m2/yr)

Conclusions

- The average MeHg concentration in Kongsfjorden was 0.11±0.03 pM (0.053-0.17 pM). The highest concentration was found to be 0.17 pM at 10 m depth of site 2. The high MeHg concentrations were commonly observed in the surface water.
- The relationship between terrestrial organic matter (C2 and D) and MeHg was positive, indicating that microbial decomposition of soil organic matter may promote MeHg production.
- In-situ methylation was a major source of MeHg in water column, according to the mass budget results. Further studies are needed to connect the methylation rate constants and FDOM components.