

Introduction to the WASP Model

The Water Quality Analysis Simulation Program (WASP7) is an enhancement of the original WASP (Di Toro et al., 1983; Connolly and Winfield, 1984; Ambrose, R.B. et al., 1988). This model helps users interpret and predict water quality responses to natural phenomena and man-made pollution for various pollution management decisions. WASP7 is a dynamic compartment modeling program for aquatic systems, including both the water column and the underlying sediment. The model can be used to analyse a variety of water quality problems in such diverse water bodies as ponds, streams, lakes, reservoirs, rivers, estuaries, and coastal waters. The time-varying processes of advection, dispersion, point and diffuse mass loading and boundary exchange are represented in the basic program.

Water quality processes are represented in special kinetic subroutines that are either chosen from a library or written by the user. WASP is structured to permit easy substitution of kinetic subroutines into the overall package to form problem-specific models. WASP7 comes with two general kinetic modules -- TOXI for toxicants and EUTRO for conventional water quality. In addition to the general toxicant module, WASP7 offers a specific mercury module, which is described in a section below. Earlier versions of WASP have been used to examine eutrophication of Tampa Bay; phosphorus loading to Lake Okeechobee; eutrophication of the Neuse River and estuary; eutrophication and PCB pollution of the Great Lakes (Thomann, 1975; Thomann et al., 1976; Thomann et al, 1979; Di Toro and Connolly, 1980), eutrophication of the Potomac Estuary (Thomann and Fitzpatrick, 1982), kepone pollution of the James River Estuary (O'Connor et al., 1983), volatile organic pollution of the Delaware Estuary (Ambrose, 1987), and heavy metal pollution of the Deep River, North Carolina (JRB, 1984). In addition to these, numerous applications are listed in Di Toro et al., 1983.

The flexibility afforded by the Water Quality Analysis Simulation Program is unique. WASP7 permits the modeler to structure one, two, and three dimensional models; allows the specification of time-variable exchange coefficients, advective flows, waste loads and water quality boundary conditions; and permits tailored structuring of the kinetic processes, all within the larger modeling framework without having to write or rewrite large sections of computer code. The two operational WASP7 models, TOXI and EUTRO, are reasonably general. In addition, users may develop new kinetic or reactive structures. This however requires an additional measure of judgment, insight, and programming experience on the part of the modeler. The kinetic subroutine in WASP (denoted "WASPB"), is kept as a separate section of code, with its own subroutines if desired.

The Basic Water Quality Model

The equations solved by WASP7 are based on the key principle of the conservation of mass. This principle requires that the mass of each water quality constituent being investigated must be accounted for in one way or another. WASP7 traces each water quality constituent from the point of spatial and temporal input to its final point of export, conserving mass in space and time. To perform these mass balance computations, the user must supply WASP7 with input data defining seven important categories:

- simulation and output control
- model segmentation
- advective and dispersive transport
- boundary concentrations
- point and diffuse source waste loads
- kinetic parameters, constants, and time functions
- initial concentrations

These input data, together with the general WASP7 mass balance equations and the specific chemical kinetics equations, uniquely define a special set of water quality equations. These are numerically integrated by WASP7 as the simulation proceeds in time. At user-specified print intervals, WASP7 saves the values of all display variables for subsequent retrieval by the post-processor program. These programs allow the user to interactively produce graphs and tables of variables of all display variables.

General Mass Balance Equation

A mass balance equation for dissolved constituents in a body of water must account for all the material entering and leaving through direct and diffuse loading; advective and dispersive transport; and physical, chemical, and biological transformation. Consider the coordinate system shown in

Equation 1-1, where the x- and y-coordinates are in the horizontal plane and the z-coordinate is in the vertical plane.

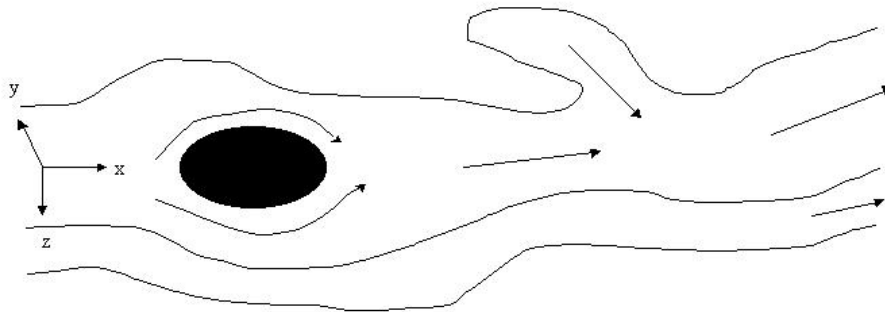


Figure 0-1 Coordinate System for Mass Balance Equation

The mass balance equation around an infinitesimally small fluid volume is:

Equation 1-1 General Mass Balance Equation

$$\begin{aligned} \frac{\partial C}{\partial t} = & -\frac{\partial}{\partial x}(U_x C) - \frac{\partial}{\partial y}(U_y C) - \frac{\partial}{\partial z}(U_z C) \\ & + \frac{\partial}{\partial x}\left(E_x \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(E_y \frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(E_z \frac{\partial C}{\partial z}\right) \\ & + S_L + S_B + S_K \end{aligned}$$

where C is concentration of the water quality constituent, in mg/L or g/m³, t is time, in days, U_x, U_y, U_z are longitudinal, lateral, and vertical advective velocities, in m/day, E_x, E_y, E_z are longitudinal, lateral, and vertical diffusion coefficients, in m²/day, S_L the total direct and diffuse loading rate, in g/m³-day, S_B is the total boundary loading rate (including upstream, downstream, benthic, and atmospheric), in g/m³-day, and S_K is the total kinetic transformation rate (positive is source, negative is sink), in g/m³-day.

By expanding the infinitesimally small control volumes into larger adjoining "segments," and by specifying proper transport, loading, and transformation parameters, WASP implements a finite-difference form of Equation 1-1. This equation represents the three major classes of water quality processes -- transport, loading, and transformation. The model network and the major processes are discussed in the following sections.

The Model Network

The model network is a set of expanded control volumes, or "segments," that together represents the physical configuration of the water body. As Figure 0-2 illustrates, the network may subdivide the water body laterally and vertically as well as longitudinally. Benthic segments can be included along with water column segments. If the water quality model is being linked to the hydrodynamic model, then water column segments must correspond to the hydrodynamic junctions. Concentrations of water quality constituents are calculated within each segment. Transport rates of water quality constituents are calculated across the interface of adjoining segments.

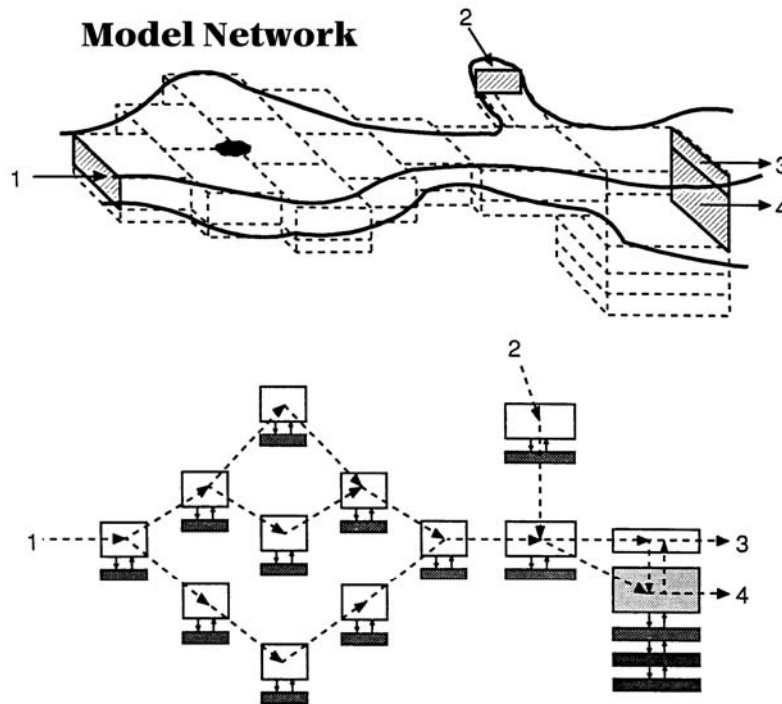


Figure 0-2 Model Segmentation Schematic

Segments in WASP may be one of four types: 1 - epilimnion (surface water), 2 - hypolimnion layers (subsurface), 3 - upper sediment layer, and 4 - lower sediment layers. The segment type plays an important role in bed sedimentation and in certain transformation processes. Specifying vertical segment alignment is important when light needs to be passed from one segment to the next in the water column, or when material is buried or eroded in the bed.

Segment volumes and the simulation time step are directly related. As one increases or decreases, the other must do the same to insure stability and numerical accuracy. Segment size can vary dramatically, dictated more by the spatial and temporal scale of the problem being analysed than by the characteristics of the water body or the pollutant per se. For example, analysing a problem involving the upstream tidal migration of a pollutant into a water supply might require a time step of minutes to an hour. By contrast, analysing a problem involving the total residence time of that pollutant in the same water body could allow a time step of hours to a day.

Overview of the WASP7 Mercury Model

The WASP7 mercury module MERC7 utilizes a subset of the WASP7 general toxic chemical module TOXI7 to simulate mercury cycling and transport through a water body. MERC7 simulates three mercury species, Hg^0 , Hg(II) , and MeHg , as well as one to three solids types (i.e., silt, sand, biotic solids). Simulations are driven by the speciated mercury loadings delivered from the atmosphere, from watershed tributaries, and from point sources. Throughout the simulation period, MERC7 calculates solids and mercury

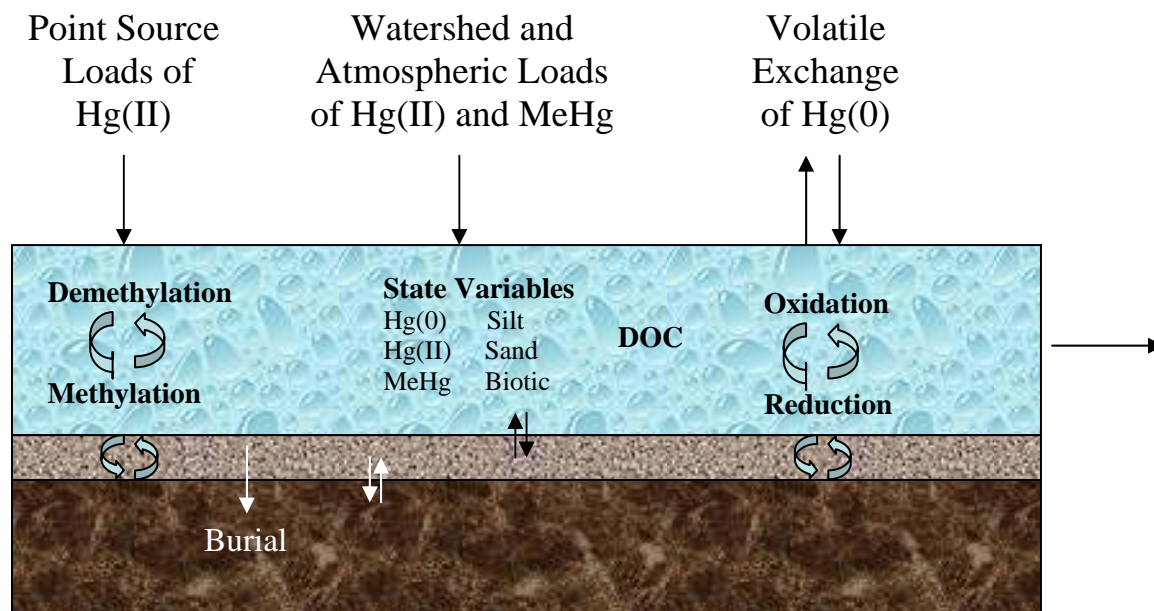


Figure 0-3 Overview of Wasp7 Mercury Module

species concentrations in the water column and sediments of each reach. Hg(II) and MeHg are partitioned to suspended and benthic solids and to dissolved organic carbon (DOC) with user-specified partition coefficients for each sorbent type.

Mercury species are subject to several transformation reactions, including oxidation of Hg^0 in the water column, reduction and methylation of Hg(II) in the water column and sediment layers, and demethylation of MeHg in the water column and sediment layers. These transformation processes are represented as first-order reactions operating on the total pool of the reactants (i.e., no difference in reactivity of recently deposited Hg(II) and that deposited weeks to years earlier) with rate constants that can vary spatially and temperature correction coefficients that adjust the rates with variations in water temperature. Water column reduction and demethylation reactions are driven by sunlight, and so their input surface rate constants are attenuated through the water column using specified light extinction coefficients. Hg^0 is subject to volatile exchange between the water column the atmosphere governed by a transfer rate calculated from velocity and depth, and by its Henry's Law constant. Rate constants can be applied to the dissolved, DOC-complexed, and solids-sorbed phases at varying strengths (0 to 1), as specified by the user.

For this module, mercury concentrations C_i are input in volumetric units of ng/L. These C_i are converted internally to WASP units of mg/L for use in the chemical transport and transformation equations. Particulate and DOC-associated C_i are calculated in units of mg/kg, and are displayed in conventional mercury units of ng/g. Solids and DOC concentrations S_i are input and used in the solids transport equations in units of mg/L. These S_i are converted internally to the equivalent concentrations M_i , in kg/L, for use in the chemical partitioning equations.

Partitioning Equations

Hg(II) and MeHg are partitioned between the dissolved, DOC-complexed, and solids-sorbed phases using a set of partition coefficients and the following linear equations:

$$C_{DOC} = K_{DOC} C_{diss}$$

$$C_{sand} = K_{sand} C_{diss}$$

$$C_{silt} = K_{silt} C_{diss}$$

$$C_{biotic} = K_{biotic} C_{diss}$$

where C_{diss} is the dissolved divalent or methyl mercury concentration, C_{DOC} is the DOC-complexed concentration, C_{sand} , C_{silt} , and C_{biotic} are the sorbed concentrations, K_{DOC} , and K_{sand} , K_{silt} , and K_{biotic} are the partition coefficients to DOC, sand, silt, and biotic solids in mg/kg per mg/L, or L/kg.

Multiplying these chemical concentrations by their respective volumetric phase concentrations (porosity, n , in L_{water}/L, dissolved organic carbon, M_{DOC} , in kg/L, and solids class “s,” M_s , in kg/L) gives the volumetric chemical concentration in each phase. Summing the volumetric chemical concentrations over all phases gives the total chemical concentration. The dissolved, DOC-bound, and sorbed fractions of the total chemical concentration are given by:

$$f_{diss} = \frac{n}{n + K_{DOC} M_{DOC} + \sum_s K_{ps} \cdot M_s}$$

$$f_{DOC} = \frac{K_{DOC} M_{DOC}}{n + K_{DOC} M_{DOC} + \sum_s K_{ps} \cdot M_s}$$

$$f_{ps} = \frac{K_{ps} \cdot M_s}{n + K_{DOC} M_{DOC} + \sum_s K_{ps} \cdot M_s}$$

These fractions are used internally within the WASP7 transport and transformation equations.

Transformation Equations

In the WASP7 mercury module, reaction rates are applied to the dissolved, DOC-complexed, and solids-sorbed phases using a set of process-specific phase multipliers, designated x_{diss} , x_{DOC} , and x_{sorb} in the equations below. These multipliers are generally set equal to 1 for the dissolved and sorbed phases, and equal to 0 for the DOC-bound phase. In the equations below, input rate constants k_i are input in units of day^{-1} , and transformation rates $S_{K,i}$ are calculated in units of $\text{g/m}^3\text{-day}$.

Oxidation – Hg^0 is oxidized in the water column to Hg(II) using the following linear equation:

$$S_{K,ox} = k_{ox} x_{diss} \text{Hg}_{diss}^0$$

where $S_{K,ox}$ is the oxidation rate and k_{ox} is the oxidation rate constant. Rate constants k_{ox} are specified by the user as a spatially-variable model parameter. These constants are for a reference temperature T_R (specified in K), and if the user specifies reaction activation energy E_{ao} (in kcal/mole), the rate constants are adjusted internally for ambient water temperature using the following Arrhenius equation:

$$k_{ox,T} = k_{ox,TR} \cdot \exp\left(1000 E_{ao} \cdot \frac{T_K - T_R}{R T_K T_R}\right)$$

The oxidation rate is subtracted from the Hg^0 derivative and added to the Hg(II) derivative with a specified reaction mass yield coefficient of 1.0.

Reduction – Hg(II) is reduced by sunlight in the water column to Hg^0 using the following linear equation:

$$S_{K,red} = k_{red} \cdot L_N(t) \cdot [x_{diss} \text{Hg(II)}_{diss} + x_{DOC} \text{Hg(II)}_{DOC} + x_{sorb} \text{Hg(II)}_{sorb}] \cdot 10^{-6}$$

where $S_{K,red}$ is the reduction rate and k_{red} is the surface reduction rate constant. $L_N(t)$ is the normalized light intensity over the segment depth, given by:

$$L_N(t) = \frac{L_S(t)}{L_{ref}} \left[\frac{1 - e^{-K_e d}}{K_e d} \right]$$

where $L_S(t)$ is the light intensity at the water surface, L_{ref} is the light intensity corresponding to the measured surface reduction rate constant, K_e is the light extinction coefficient, in meter^{-1} , and d is the depth of the computational segment, in meters. The light extinction coefficient can be specified directly, or calculated internally as a function of solids, chlorophyll a , and DOC:

$$K_e = K_{e,water} + k_{e,solids} S_{tot} + k_{e,DOC} S_{DOC} + k_{e,Chl} Chla^{k_{exp}}$$

where $K_{e,water}$ is the background light extinction coefficient, in meter^{-1} , $k_{e,solids}$ is the solids light extinction multiplier, in L/mg-meter , S_{tot} is total suspended solids concentration, in mg/L , $k_{e,DOC}$ is the light extinction DOC multiplier, in L/mg-meter , S_{DOC} is total dissolved organic carbon concentration, in mg/L , $k_{e,Chl}$ is the light extinction chlorophyll multiplier, in $\text{L}/\mu\text{g-meter}$, $Chla$ is phytoplankton chlorophyll *a* concentration, in $\mu\text{g/L}$, and k_{exp} is the light extinction chlorophyll exponent. Default values for $k_{e,Chl}$ and k_{exp} are 0.0587 and 0.778, respectively.

The surface reduction rate constant k_{red} is specified by the user as a model constant. This light-driven rate is not adjusted for temperature. The reduction rate is subtracted from the Hg(II) derivative and added to the Hg^0 derivative with a specified reaction mass yield coefficient of 1.0.

Methylation – Given proper substrate and environmental conditions, Hg(II) is methylated in the surficial sediment layer to MeHg . With favorable conditions, methylation can also occur in the water column. WASP7 implements this spatially-variable reaction using the following linear equation:

$$S_{K, meth} = k_{meth} \cdot [x_{diss} \text{Hg(II)}_{diss} + x_{DOC} \text{Hg(II)}_{DOC} + x_{sorb} \text{Hg(II)}_{sorb}]$$

where $S_{K, meth}$ is the methylation rate and k_{meth} is the methylation rate constant. Rate constants k_{meth} are specified by the user as a spatially-variable model parameter. Input rate constants are for 20°C , and are adjusted internally for ambient water temperature using the following equation:

$$k_{meth, T} = k_{meth, 20} \cdot Q_{Bac}^{(T-20)/10}$$

where Q_{Bac} is the “Q-10” temperature adjustment factor, which represents the increase in the biodegradation rate constants resulting from a 10°C temperature increase. Values in the range of 1.5 to 2 are common. The methylation rate is subtracted from the Hg(II) derivative and added to the MeHg derivative with a specified reaction mass yield coefficient of 1.07.

Reductive Demethylation – MeHg is reduced by sunlight in the water column to Hg^0 using the following linear equation:

$$S_{K, rdm} = k_{rdm} \cdot L_N(t) \cdot [x_{diss} \text{MeHg}_{diss} + x_{DOC} \text{MeHg}_{DOC} + x_{sorb} \text{MeHg}_{sorb}]$$

where $S_{K, rdm}$ is the reduction rate and k_{rdm} is the surface reduction rate constant. The surface reductive demethylation rate constant k_{rdm} is specified by the user as a model constant. This light-driven rate is not adjusted for temperature. The reductive demethylation rate is subtracted from the MeHg derivative and added to the Hg^0 derivative with a specified reaction mass yield coefficient of 0.93.

Bacterial Demethylation – MeHg is demethylated by bacteria in surficial sediments to Hg(II) using the following linear equations:

$$S_{K,dem} = k_{dem} \cdot [x_{diss} MeHg_{diss} + x_{DOC} MeHg_{DOC} + x_{sorb} MeHg_{sorb}]$$

where $S_{K,dem}$ is the demethylation rate and k_{dem} is the demethylation rate constant. Rate constants k_{dem} are specified by the user as a spatially-variable model parameter. These constants are for a reference temperature T_R of 20°C (specified as 293 K), and if the user specifies reaction activation energy $E_{a,dem}$ (about 10 kcal/mole), the rate constants are adjusted internally to ambient water temperatures using the following Arrhenius equation:

$$k_{dem,T} = k_{dem,TR} \cdot \exp\left(1000 E_{a,dem} \cdot \frac{T_K - T_R}{R T_K T_R}\right)$$

The demethylation rate is subtracted from the MeHg derivative and added to the Hg(II) derivative with a specified reaction mass yield coefficient of 0.93.

Volatilization – In surface water segments, dissolved Hg^0 is exchanged with gaseous atmospheric Hg^0 across the air-water interface using the following linear equation:

$$S_{K,vol} = k_{vol} \cdot \left(Hg_{diss}^0 - \frac{Hg_{atm}^0}{H / RT_K} \right)$$

where $S_{K,vol}$ is the net volatilization exchange rate, k_{vol} is the volatilization rate constant, H is the Henry's Law constant, in atm/molar (e.g., 7.1×10^{-3}), R is the Universal Gas constant, 8.206×10^{-5} atm/molar-K, and T_K is air temperature, in K.

The volatilization rate constant k_{vol} is based on the Whitman two-film resistance model, and can be calculated internally using a variety of options based on wind speed, water current velocity, and segment depth. The computed volatilization rate constant is for a water temperature of 20°C, and is adjusted internally for segment temperature using the equation:

$$k_{vol,T} = k_{vol,20} \cdot \theta_{vol}^{T-20}$$

where $k_{vol,T}$ is the temperature-adjusted volatilization rate constant, $k_{vol,20}$ is the calculated rate constant for 20C, and θ_{vol} is the temperature coefficient.

The net volatilization rate is subtracted from the Hg^0 derivative. Note that if high atmospheric concentrations are specified, this transfer process can become a net source rather than a net sink.

Implementation

These mercury reaction equations contain several constants and parameters that must be specified to implement the WASP7 mercury model. Reaction rates and coefficients are uncertain, and exhibit a significant range of variability among water bodies. As a consequence, site-specific mercury data are needed for model calibration. A good calibration dataset should include filtered and unfiltered samples of total and methyl mercury in the water column and upper sediment layer at different locations and time periods. Measurements or model simulations of atmospheric and watershed loadings are needed to drive the model. Important environmental data include flow rates, temperature, pH, light attenuation, and concentrations of suspended solids and DOC. Important sediment characteristics include size composition, organic fraction, bulk density, redox status, and concentrations of sulfate and sulfide. The model calibration should reproduce as well as possible not only the overall mercury concentration trends in space and time, but also the important internal relationships, including methyl mercury fractions and dissolved mercury fractions in the water column and sediments. Because of the number of model constants and parameters and the limited amount of data usually available for calibration, the resulting mercury fate model will be under-determined.

Table 1. Reaction rate constants and coefficients used in WASP Mercury model.

Variable	Reaction or Coefficient	Range of Values
Hg ⁰	Henry's Law constant, atm-m ³ /mole Oxidation in water, day ⁻¹	7.1×10 ⁻³ 1×10 ⁻³ - 1×10 ⁻¹
Hg(II)	Partition Coefficients, L/kg Sand Silt Biotic Solids DOC Photo-Reduction at water surface, day ⁻¹ Methylation in water, day ⁻¹ Bacterial Methylation in sediment, day ⁻¹	1×10 ³ - 5×10 ⁴ 1×10 ⁵ - 1×10 ⁶ 1×10 ⁴ - 1×10 ⁵ 1×10 ⁴ - 1×10 ⁵ 1×10 ⁻³ - 5×10 ⁻¹ 1×10 ⁻⁵ - 5×10 ⁻² 1×10 ⁻⁵ - 5×10 ⁻²
MeHg	Partition Coefficients, L/kg Sand Silt Biotic Solids DOC Photo-Demethylation at water surface, day ⁻¹ Bacterial Demethylation in sediment, day ⁻¹	1×10 ³ - 5×10 ⁴ 1×10 ⁵ - 1×10 ⁶ 1×10 ⁵ - 1×10 ⁶ 1×10 ⁵ - 1×10 ⁶ 1×10 ⁻³ - 5×10 ⁻¹ 1×10 ⁻⁵ - 5×10 ⁻²