Xenobiotics

MIKE ECO Lab Template

Scientific Description

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1 Introduction

MIKE ECO Lab is a numerical lab for Ecological Modelling. It is a generic and open tool for customising aquatic ecosystem models to describe for instance water quality. DHI's expertise and know how concerning ecological modelling has been collected in predefined ecosystem descriptions (MIKE ECO Lab templates) to be loaded and used in MIKE ECO Lab. So the MIKE ECO Lab templates describe physical, chemical and biological processes related to environmental problems and water pollution. The following is a description of the DHI supported xenobiotic template.

It is an extension of the former heavy metal template.

The xenobiotic template is used in investigations of xenobiotics spreading and potential accumulation in sediment. The xenobiotic template can be applied in environmental impact assessments concerning:

- spreading of xenobiotics from urban and/or industrial discharges

- leakages of xenobiotics from disposal sites (fly ash disposals, cinders disposals, metal or chemical land dump sites etc.)

- spreading of xenobiotics from dumping/waste disposal activities at sea

- accumulation of xenobiotics in sediment and potentially in biota

- release or leakage of xenobiotics formerly dumped or accumulated in the sediment resulting in further spreading and 'dilution' of the sediments.

- dredging and other operations disturbing the sediment leading to a re-introduction of the sorbed xenobiotics into the water.

The xenobiotic template describes the adsorption/desorption of xenobiotics to suspended matter, the sedimentation of sorbed xenobiotics to the seabed as well as resuspension of settled xenobiotics. It also includes the exchange of xenobiotic between the particulates of the bed sediment and the interstitial waters of the bed. The diffusive exchange of xenobiotics in dissolved form in the water and in the interstitial waters is also described.

A number of derived values are calculated for instance the total concentration of xenobiotics in the water and in the bed sediment (the sum of dissolved and adsorbed xenobiotic).

The various xenobiotics behave very differently. The template is therefore designed as a general model with the relevant processes included and then with a number of xenobiotic specific parameters. Once the parameters for a xenobiotic have been settled this set-up can be said to be a model for this specific xenobiotic.

The model results are the concentrations of dissolved xenobiotic, adsorbed xenobiotic and of suspended matter in the water (per volume) and the dissolved xenobiotic in interstitial waters of the bed sediment, the xenobiotic adsorbed to particles in the bed sediment and finally the mass of the considered sediment layer. In addition to this the above mentioned derived values are stored.

The data required are concentrations at model boundaries, flow and concentration from pollution sources, environmental conditions like temperature, pH, salinity and redox potential, a number of parameters describing the sediment characteristics and the xenobiotic specific model parameters.

The xenobiotic template is integrated with the advection-dispersion module, which describes the physical transport and spreading processes at each grid point covering the area of interest.

2   Theoretical Aspects of Xenobiotic Spreading

Xenobiotics in the aquatic environment will be found dissolved in the water or attached to suspended matter. The extent to which a xenobiotic is bound to the suspended matter differs from xenobiotic to xenobiotic and it also depends on the nature of the suspended particles. The adsorption to suspended matter leads to sedimentation of xenobiotic, which will often look like a disappearance. It is rather just a transport out of the water column into the sediment. This apparent cleaning of the water is often called "scavenging" (Nyffeler et.al., 1986).

The xenobiotics will reappear in the sediment together with the sedimented particles. Xenobiotics can remain in the sediment attached to the particles even long time after the pollution has stopped (de Bruijn et.al., 1989).

In the sediment the conditions for adsorption are very different from the water phase conditions, due to differences in particle concentration. The xenobiotic concentration in the pore water of the sediment will therefore differ from the water column concentration resulting in diffusive transport between sediment and water. This is one of the mechanisms by which xenobiotics are transported from polluted sediment to more clean water. The other mechanism is resuspension of the sediment.

The consequences of discharging xenobiotic into the aquatic environment or the mobility of xenobiotic from formerly polluted sediment can be predicted by modelling the mechanisms governing the transport of xenobiotics. On a molecular level these mechanisms are numerous, but in a macroscopic scale a limited number of overall processes seems to be governing (Honeyman & Santschi, 1988; Anderson et.al., 1987):

1. The adsorption and desorption of xenobiotic
2. The sedimentation and resuspension of particulate xenobiotic
3. The diffusive transport of dissolved xenobiotic at the sediment/ water interface
4. Biodegradation
5. Photolysis
6. Hydrolysis.
7. Evaporation of dissolved xenobiotic
8. The transport of dissolved and particulate xenobiotic in the water column by advection and dispersion.

The Xenobiotic MIKE ECO Lab template itself accounts for the first 7 mentioned overall processes, whereas the advection-dispersion process is calculated in the software product that has MIKE ECO Lab implemented: for instance MIKE 11 or MIKE 21. So the scientific documentation for the advection-dispersion process must be found in the manuals for the used product.

In the Xenobiotic Template a kinetic approach to describe the distribution of xenobiotics between water and particles has been chosen for two reasons.

First, the time to reach equilibrium between water and particles has turned out to be in the range 'day to week' when the measuring is based on natural sediment (Honeyman & Santschi, 1988; Nyffeler et.al.,1986). This is contradictory to results of measurements based on artificial sediment composed of a limited number of minerals. Here the adsorption and desorption rates were found to be too fast to have significant influence on the scavenging (DiToro et.al., 1986). As the residence time of particles in the water column of shallow waters is usually within the range mentioned above (day to week), the time to reach equilibrium may

be longer than the residence time of the particles. In this case the equilibrium assumption is not valid.

Secondly, the only rational way to account for the diffusive transport of dissolved xenobiotics at the sediment/water interface is to use the kinetic approach. Otherwise, several consecutive iteration schemes must be introduced to fulfil the equilibrium constraint and describe the diffusive transport (Chapman, 1982).

The terms "sorption", "adsorption" or "desorption" are here generic terms used to describe the transport of solute from the solution phase to a contiguous solid phase or reverse. In principle an aqueous solute (be it dissolved xenobiotic) may react with a preexisting solid phase by three main processes (Honeyman & Santschi, 1988):

- adsorption (attachment at the interface without development of a three-dimensional molecular arrangement),

- absorption (the incorporation of chemical solute into the solid phase),

- surface precipitation.

In this model these terms are viewed as one overall process. The rates of the above listed individual processes and the relevance of each of them are not considered.

The sorption of the xenobiotics depends on the nature of the particulate matter due to varying mechanisms (from xenobiotic to xenobiotic) for the sorption.

The sorption of xenobiotics depends on the characteristics of the water as well as on the sediment. The most important parameters for the dependency of water conditions are pH, redox potential, salinity and temperature. The observed effects differ from xenobiotic to xenobiotic.

Adsorption and desorption are reverse reactions for the transition of xenobiotic between solute (C_w, concentration in water, g/m3) and solid (C_s, concentration on solid, g/g) phases:

$$C_w \underset{\leftarrow}{\overset{\rightarrow}{}} C_s \qquad (2.1)$$
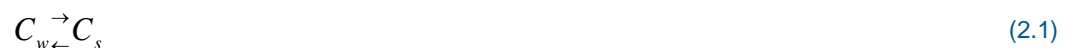
where the forward reaction ($\rightarrow$) is the adsorption and the reverse reaction ($\leftarrow$) is the desorption.

Due to differences in the characteristics of the particulate matter in the water column and the sediment, the adsorption and desorption processes can be different in the sediment and the water column respectively.

The suspended matter and the xenobiotic attached to it can settle and be resuspended depending on the hydraulic conditions. This exchange of particles between water and sediment is one way of exchanging xenobiotic. The other is the diffusive transport between water and pore water due to concentration differences (Santschi,1988).

The balance for suspended solids in the water phase includes settling, resuspension and production of particles (e.g. detritus (degrading biomass) or micro algae).

The direct exchange of xenobiotics between water and pore water is assumed to be a diffusive process, driven by the concentration gradient over a thin stagnant water layer at the water/sediment interface (Jørgensen, 1979; Nyffeler et.al.,1986; Santschi et.al.,1987).

The effects on adsorption/desorption of variations in pH, redox conditions, salinity and temperature are modelled by multiplying the adsorption/desorption constants by functions describing the dependence of each of these four parameters. Since the dependence on environmental conditions varies between xenobiotics there is no general function for all xenobiotics.

Both the heavy metal template and the xenobiotics template share the same description of adsorption and desorption to suspended solids, but the xenobiotics template also includes degradation processes of the chemical: Biodegradation, photolysis, hydrolysis. Besides also evaporation of the chemical is included.

3 Mathematical Formulations

In the following all symbols for state variables distinguish between soluble S and particulate X.

The considered dependent state variables in the model are:

1. SXE   Dissolved Xenobiotic conc. in the water [gXe/m3 bulk]
2. XXE   Adsorbed Xenobiotic conc. in the water [gXe/m3 bulk]
3. XSS   Suspended solids conc. in the water [g DW/m3 bulk]
4. SXES   Dissolved Xenobiotic conc. in sediment [gXe/m2]
5. XXES   Adsorbed Xenobiotic conc. in sediment [gXe/m2]
6. XSED   Mass of sediment [g DW/m2]

The theoretical basis and the assumptions connected with the mathematical formulations of the involved processes for the xenobiotics are outlined above. Furthermore, it is necessary to introduce some assumptions concerning the sediment layer.

The part of the sediment layer included in this model is the top 10 centimeters or so, being homogeneous (Nyffeler, 1984). It is assumed that the composition of the sediment concerning porosity and density of particles and pore water is constant in time. The consequences of sedimentation or resuspension are not a change in concentration of particles in the sediment, but a change in sediment layer thickness.

Xenobiotic dissolved in the water S_{XE}.

$$\frac{dS_{XE}}{dt} = -adsorption + desorption + diffusion - biodecay - hydrolysis$$
$$- photolysis - evaporation$$

(3.1)

$$\frac{dS_{XE}}{dt} = -adss + dess + difwc - biow - hydw - phot - evap$$

Adsorption
The partitioning coefficient K_d can be described as the relation between xenobiotic content in the suspended matter and concentrations in the water phase at steady state.

The xenobiotics are mostly bound to the organic part of the suspended matter, therefore the K_d partitioning coefficient is estimated from of the organic carbon partitioning coefficient for the xenobiotic in question, and the fraction of organic carbon in the suspended matter:

$$K_d = f_{OC} \cdot K_{OC}$$

(3.2)

Where:
f_{OC} Fraction of organic carbon in the suspended solids (mg/mg).
K_{OC} Organic Carbon Partitioning coefficient [l / kg DW]. K_{OC} is the key parameter in the xenobiotic template, and it is different for each xenobiotic. It is also dynamic, and depends on temperature, pH, salinity, and pe. Therefore the user should give K_{OC} values based on measurements at the conditions in the model regarding temperature, pH,

salinity, and pe. If these measurements do not exist the K_{OC} is a calibration parameter.

The adsorption and desorption rates are assumed to be related relative to each other according to the equilibrium partitioning coefficient K_d for the xenobiotic in question:

$$K_d = \frac{k_a}{k_w} \qquad (3.3)$$

Where:

k_w	Desorption rate in water [d^{-1}]
k_a	Adsorption rate [m^3 H$_2$O /g DW / d]
K_d	Partitioning coefficient for xenobiotic chemical between particulate matter and water [m^3 H$_2$O / g DW]

Therefore it is only necessary to know one of the sorption rates and the partitioning coefficient to estimate the opposite sorption rate. This has been used in the following to exclude the adsorption rate k_a from the equations and replace it by k_w and K_d.

The following assumption has been made: m^3 H$_2$O ≈ m^3 bulk

$$adss = k_w \cdot K_d \cdot S_{XE} \cdot X_{SS} \qquad \left[\frac{gXe}{m^3 bulk \cdot d} \right] \qquad (3.4)$$

Where:

k_w	Desorption rate in water [d^{-1}]
K_d	Partitioning coefficient for metal between particulate matter and water [m^3 H$_2$O / g DW]
S_{XE}	Dissolved xenobiotic conc. in the water [g Xe/m^3 bulk] ≈ [g Xe/m^3 H$_2$O]
X_{SS}	Suspended solids conc. in the water [g DW/m^3 bulk]

Desorption

The adsorbed heavy metals can be desorbed from the adsorbed phase to the dissolved phase in the water column.

$$dess = k_w \cdot X_{XE} \qquad \left[\frac{gXe}{m^3 bulk \cdot d} \right] \qquad (3.5)$$

Where:

k_w	Desorption rate in water [d-1]
X_{XE}	Adsorbed xenobiotic conc. in the water [g Xe/m^3 bulk]

Diffusion

According to Fick's law, gradients in concentration fields can cause diffusion. In this template diffusion can take place between dissolved heavy metals in the water column and in the porewater of the sediment.

$$difv = \frac{fbiot \cdot difw \cdot \left(\frac{S_{XES}}{pors \cdot dzs} - S_{XE} \right)}{(dzwf + dzds) \cdot dz} \qquad \left[\frac{gXe}{m^3 bulk \cdot d} \right] \qquad (3.6)$$

Where:

fbiot	Factor for diffusion due to bioturbation [dimensionless]
difw	*D*iffusion coefficient in water is estimated from the metals moleweight [m²/d]
S_{XE}	Dissolved xenobiotic conc. in the water [g Xe/m³ bulk] ≈ [g Xe/m³ H₂O]
S_{XES}	Dissolved xenobiotic conc. in sed. porewater [g Xe/m²]
dzwf	Thickness of water film [m]
dzds	Thickness of diffusion layer in sediment [m]
dz	Thickness of actual layer in computational grid [m]

Biodecay

The organic xenobiotics can be degraded by biological decay biow in the water. The biodecay rate is dependent on the temperature and a Michaelis Menten expression.

$$biow = kbw \cdot \frac{S_{XE}}{S_{XE} + hsdw} tetb^{temp-20} \cdot S_{XE} \qquad \left[\frac{gXe}{m^3 bulk \cdot d}\right] \qquad (3.7)$$

Where:

kbw	Biodecay rate in water [per day]
S_{XE}	Dissolved xenobiotic conc. in the water [g Xe/m³ bulk] ≈ [g Xe/m³ H₂O]
hsdw	Halfsaturation concentration [g XE/m³ bulk]
tetb	Arrhenius temperature coefficient [dimensionless]
temp	Temperature [deg. Celcius]

Hydrolysis

Hydrolysis is a chemical reaction or process in which a molecule is split into two parts by reacting with a molecule of water.

$$hydw = khac \cdot 10^{-phw} + (khne + khal) \cdot 10^{phw-14} S_{XE} \qquad (3.8)$$

Where:

khac	Hydrolysis constant, acid [l/mol/day]
khne	Hydrolysis constant, neutral [l/mol/day]
khal	Hydrolysis constant, alkaline [l/mol/day]
phw	pH, water [dimensionless]
S_{XE}	Dissolved xenobiotic conc. in the water [g Xe/m³ bulk] ≈ [g Xe/m³ H₂O]

Photolysis

Photolysis is a chemical process by which molecules are broken down into smaller units through the absorption of light.

$$phot = kpho \cdot \frac{i_o}{i_{os}} S_{XE} \qquad \left[\frac{gXe}{m^3 bulk \cdot d}\right] \qquad (3.9)$$

Where:

kpho	Photolysis rate at surface [/day]
io	Solar Radiation actual layer[E/m²/day]
ios	Solar Radiation at water surface [E/m²/day]
S_{XE}	Dissolved xenobiotic conc. in the water [g Xe/m³ bulk] ≈ [g Xe/m³ H₂O]

Evaporation

Evaporation is a process moves the xenobiotics from the water column to the atmosphere.

$$evap = \frac{kevt}{dz} S_{XE} \qquad \left[\frac{gXe}{m^3 bulk \cdot d} \right] \qquad (3.10)$$

Where:
kevt   Evaporation constant [m/day]
dz   Thickness of actual layer [m]
S_{XE} Dissolved xenobiotic conc. in the water [g Xe/m^3 bulk] ≈ [g Xe/m^3 H$_2$O]

Xenobiotics on suspended matter X$_{XE}$

$$\frac{dX_{XE}}{dt} = adsorption - desorption - sedimentation + resuspension \qquad (3.11)$$

$$\frac{dX_{XE}}{dt} = adss - dess - sev + resv \qquad \left[\frac{gXe}{m^3 bulk \cdot d} \right]$$

Adsorption

See also description of adsorption for S$_{XE}$.

$$adss = k_w \cdot K_d \cdot S_{XE} \cdot X_{SS} \qquad \left[\frac{gXe}{m^3 bulk \cdot d} \right] \qquad (3.12)$$

Where:
k_w Desorption rate in water [d^{-1}]
K_d Partitioning coefficient for metal between particulate matter and water [m^3 H$_2$O / g DW], see table 1
S_{XE} Dissolved xenobiotic conc. in the water [g XE/m^3 bulk]
X_{SS} Suspended solids conc. in the water [g DW/m^3 bulk]

Desorption
The adsorbed xenobiotic chemical can be desorbed from the adsorbed phase to the dissolved phase in the water column.

$$dess = k_w \cdot X_{XE} \qquad \left[\frac{gXe}{m^3 bulk \cdot d} \right] \qquad (3.13)$$

Where:
k_w Desorption rate in water [d^{-1}]
X_{XE} Adsorbed Xenobiotic conc. in the water [g Xe/m^3 bulk]

The unit of *dess* is g xenobiotic per cubic meter volume bulk.

Sedimentation
The adsorbed xenobiotics will be transported with the suspended solid, that normally are affected by a sedimentation process. The sedimentation of suspended solids is described with a settling velocity.

$$sev = \frac{vsm \cdot X_{XE}}{dz} \qquad \left[\frac{gXe}{m^3 bulk \cdot d} \right] \qquad (3.14)$$

Where:
vsm	Settling velocity of SS [m/d]
X_{XE}	Adsorbed Xenobiotic conc. in the water [gXe/m³ bulk]
dz	Thickness of actual layer in computational grid [m]

Resuspension

The adsorbed xenobiotics in the sediment can be resuspended if the suspended matter is brought into suspension in the water column. This can occur when the current speed exceeds a critical value.

$$\text{if } (\text{cspd} > \text{ucrit}):$$

$$resv = \frac{resrat \cdot \dfrac{X_{XES}}{X_{SED}}}{dz} \qquad \left[\frac{gXe}{m^3 bulk \cdot d}\right] \qquad (3.15)$$

Where:
cspd	Current Speed adjusted for sediment build up [m/s]
ucrit	Critical current speed for resuspension of SS [m/s]
resrat	Resuspension rate of SS [gDW/m²/day]
X_{XES}	Adsorbed xenobiotics. in the sediment [g Xe/m²]
X_{SED}	Mass of sediment [g DW/m²]
dz	Thickness of actual layer in computational grid [m]

Suspended matter or solids in the water X_{SS}

$$\frac{dX_{SS}}{dt} = production – sedimentation + resuspension \qquad (3.16)$$

$$\frac{dS_{SS}}{dt} = prss - sessv + ressv \qquad \left[\frac{gDW}{m^3 bulk \cdot d}\right]$$

Production

Suspended matter can be produced in the water column by primary production. The rate of particle production is specified as a fixed coefficient parpro:

$$prss = \frac{parpro}{dz} \qquad \left[\frac{gDW}{m^3 bulk \cdot d}\right] \qquad (3.17)$$

Where:
parpro	Particle production rate [gDW/m²/day]
dz	Thickness of actual layer in computational grid [m]

Sedimentation

The suspended matter is affected by a sedimentation process. The sedimentation of suspended solids is described with a settling velocity.

$$sessv = \frac{vsm \cdot X_{SS}}{dz} \qquad \left[\frac{gDW}{m^3 bulk \cdot d}\right] \qquad (3.18)$$

Where:

vsm	Settling velocity of SS [m/d]
X_{SS}	Suspended solids conc. in the water [g DW/m^3 bulk]
dz	Thickness of actual layer in computational grid [m]

Resuspension

The sediments can be resuspended when the current speed exceeds a critical value.

$$\text{if } (cspd > ucrit):$$

$$ressv = \frac{resrat}{dz} \qquad \left[\frac{gDW}{m^3 bulk \cdot d} \right] \qquad (3.19)$$

Where:

cspd	Current Speed adjusted for sediment build up [m/s]
ucrit	Critical current speed for resuspension of SS
resrat	Resuspension rate of SS [gDW/m^2/day]
dz	Thickness of actual layer in computational grid [m]

Dissolved xenobiotic in the sediment S_{XES}

$$\frac{dS_{XES}}{dt} = - \text{adsorption} + \text{desorption} - \text{diffusion} - \text{biodecay} - \text{hydrolysis} \qquad (3.20)$$

$$\frac{dS_{XES}}{dt} = -adsa + desa - difa - bios - hyds$$

Adsorption

The adsorption and desorption rates are assumed to be related relative to each other according to the equilibrium partitioning coefficient K_d for the xenobiotic chemical in question:

$$K_{ds} = \frac{k_a}{k_s} \qquad \qquad [m^3 \text{ H}_2\text{O / g DW}] \qquad (3.21)$$

Where:

k_s	Desorption rate in sediment [d^{-1}]
k_a	Adsorption rate [m^3 H$_2$O /g DW / d]
K_{ds}	Partitioning coefficient for xenobiotic chemical between particulate matter and water [m^3 H$_2$O / g DW]

Therefore it is only necessary to know one of the sorption rates and the partitioning coefficient to estimate the opposite sorption rate. This has been used in the following to exclude the adsorption rate k_a from the equations and replace it by k_s and $K_{ds.}$

$$adsa = k_s \cdot K_{ds} \cdot S_{XES} \cdot \frac{X_{SED}}{dzs \cdot por_s} \qquad \left[\frac{gXe}{m^2 \cdot d} \right] \qquad (3.22)$$

Where:

k_s	Desorption rate in sediment [d^{-1}]

K_{ds}	Partitioning coefficient for xenobiotic chemical between particulate matter and water [m^3 H$_2$O / g DW]
S_{XES}	Dissolved Xenobiotics conc. in the sediment [gXe/m^2]
dzs	Sediment layer thickness [m]
X_{SED}	Mass of sediment (g DW/m^2)
por_s	Porosity of sediment [m^3 H$_2$0 / m^3 bulk], assumed constant

Desorption
The adsorped xenobiotics in the sediment can be desorbed from the adsorbed phase to the dissolved phase in the pore water.

$$desa = k_s \cdot X_{XES} \qquad \left[\frac{gXe}{m^2 \cdot d} \right] \qquad (3.23)$$

Where:

k_s	Desorption rate in sediment [d^{-1}]
X_{XES}	Adsorbed Xenobiotics in the sediment [g Xe/m^2]

Sedimentation
The suspended matter is affected by a sedimentation process. The sedimentation of suspended solids is described with a settling velocity.

$$sea = vsm \cdot X_{XE} \qquad \left[\frac{gXe}{m^2 \cdot d} \right] \qquad (3.24)$$

Where:

vsm	Settling velocity of SS [m/d]
X_{XE}	Adsorbed xenobiotic conc. in the water [gXe/m^3 bulk]

Resuspension
The adsorbed xenobiotics in the sediment can be resuspended if the suspended matter is brought into suspension in the water column. This can occur when the current speed exceeds a critical value.

$$\text{if } (cspd > ucrit):$$
$$resa = \frac{resrat \cdot X_{XES}}{X_{SED}} \qquad \left[\frac{gXe}{m^2 \cdot d} \right] \qquad (3.25)$$

Where:

$cspd$	Current Speed adjusted for sediment build up [m/s]
$ucrit$	Critical current speed for resuspension of SS
$resrat$	Resuspension rate of SS [gDW/m^2/day]
X_{XES}	Adsorbed Xenobiotics in the sediment [g Xe/m^2]
X_{SED}	Mass of sediment [g DW/m^2]

Diffusion
According to Fick's law, gradients in concentration fields can cause diffusion. In this template diffusion can take place between dissolved xenobiotics in the water column and in the porewater of the sediment.

$$difa = \frac{fbiot \cdot difw \cdot \left(\dfrac{S_{XES}}{por_s \cdot dzs} - S_{XE} \right)}{dzwf + dzds} \qquad \left[\frac{gXe}{m^2 \cdot d} \right] \qquad (3.26)$$

Where:

fbiot	Factor for diffusion due to bioturbation [dimensionless]
difw	Diffusion coefficient in water is estimated from the moleweight [m^2/d]
S_{XE}	Dissolved xenobiotic conc. in the water [g Xe/m^3 bulk] ≈ [g Xe/m^3 H$_2$O]
S_{XES}	Dissolved Xenobiotics conc. in the sediment [gXe/m^2]
dzwf	Thickness of water film
dzds	Thickness of diffusion layer in sediment
dzs	Sediment layer thickness [m]
por_s	Porosity of sediment [m^3 H$_2$0 / m^3 Bulk]

Biodecay

The organic xenobiotics can be degraded by biological decay bios in the water. The biodecay rate is dependent on the temperature and a Michaelis Menten expression.

$$bios = kbs \cdot \frac{S_{XES}}{S_{XES} + hsds} tetb^{temp-20} \cdot S_{XES} \qquad (3.27)$$

Where:

kbs	Biodecay rate in water [per day]
S_{XES}	Dissolved Xenobiotics conc. in the sediment [g Xe/m^2]
hsds	Halfsaturation concentration [g XE/m^2]
tetb	Arrhenius temperature coefficient [dimensionless]
temp	Temperature [deg. Celcius]

Hydrolysis

Hydrolysis is a chemical reaction or process in which a molecule is split into two parts by reacting with a molecule of water.

$$hydw = khac \cdot 10^{-phs} + (khne + khal) \cdot 10^{phs-14} S_{XES} \qquad (3.28)$$

Where:

khac	Hydrolysis constant, acid [l/mol/day]
khne	Hydrolysis constant, neutral [l/mol/day]
khal	Hydrolysis constant, alkaline [l/mol/day]
phs	pH, sediment [dimensionless]
S_{XES}	Dissolved Xenobiotics conc. in the sediment [gXe/m^2]

Xenobiotic attached to sediment X_{XES}

$$\frac{dX_{XES}}{dt} = adsorption-desorption+sedimentation-resuspension \qquad (3.29)$$

$$\frac{dX_{XES}}{dt} = adsa - desa + sea - resa$$

Adsorption
The adsorption and desorption rates are assumed to be related relative to each other according to the equilibrium partitioning coefficient K_d for the xenobiotic chemical in question:

$$K_{ds} = \frac{k_a}{k_s} \qquad \text{[m}^3 \text{ H}_2\text{O / g DW]} \qquad (3.30)$$

Where:

k_s	Desorption rate in sediment [d^{-1}]
k_a	Adsorption rate [m^3 H$_2$O /g DW / d]
K_{ds}	Partitioning coefficient for xenobiotic chemical between particulate matter and water [m^3 H$_2$O / g DW]

Therefore it is only necessary to know one of the sorption rates and the partitioning coefficient to estimate the opposite sorption rate. This has been used in the following to exclude the adsorption rate k_a from the equations and replace it by k_s and K_{ds}.

$$adsa = k_s \cdot K_{ds} \cdot S_{XES} \cdot \frac{X_{SED}}{dzs \cdot por_s} \qquad \left[\frac{gXe}{m^2 \cdot d}\right] \qquad (3.31)$$

Where:
k_s	Desorption rate in sediment [d^{-1}]
K_{ds}	Partitioning coefficient for xenobiotic chemical between particulate matter and water [m^3 H$_2$O / g DW] , see table 1
S_{XES}	Dissolved Xenobiotics conc. in the sediment [gXe/m^2]
dzs	Sediment layer thickness [m]
X_{SED}	Mass of sediment (g DW/m^2)
por_s	Porosity of sediment [m^3 H$_2$0 / m^3 bulk], assumed constant

Desorption
The adsorbed xenobiotics in the sediment can be desorbed from the adsorbed phase to the dissolved phase in the pore water.

$$desa = k_s \cdot X_{XES} \qquad \left[\frac{gXe}{m^2 \cdot d}\right] \qquad (3.32)$$

Where:
k_s	Desorption rate in sediment [d^{-1}]
X_{XES}	Adsorbed Xenobiotics in the sediment [g Xe/m^2]

Sedimentation
The suspended matter is affected by a sedimentation process. The sedimentation of suspended solids is described with a settling velocity.

$$sea = vsm \cdot X_{HM} \qquad \left[\frac{gXe}{m^2 \cdot d}\right] \qquad (3.33)$$

Where:
vsm	Settling velocity of SS [m/d]
X_{XE}	Adsorbed xenobiotic conc. in the water [g Xe/m^3 bulk]

Resuspension

The adsorbed xenobiotics in the sediment can be resuspended if the suspended matter is brought into suspension in the water column. This can occur when the current speed exceeds a critical value.

$$\text{if } (cspd > ucrit):$$
$$resa = \frac{resrat \cdot X_{XES}}{X_{SED}} \qquad \left[\frac{gXe}{m^2 \cdot d}\right] \qquad (3.34)$$

Where:
cspd	Current Speed adjusted for sediment build up [m/s]
ucrit	Critical current speed for resuspension of SS
resrat	Resuspension rate of SS [gDW/m²/day]
X_{XES}	Adsorbed Xenobiotics in the sediment [g Xe/m²]
X_{SED}	Mass of sediment [g DW/m²]

Mass of sediment X_{SED}

$$\frac{dX_{SED}}{dt} = sedimentation - resuspension \qquad (3.35)$$
$$\frac{dX_{SED}}{dt} = sessa - ressa \qquad \left[\frac{gDW}{m^2 \cdot d}\right]$$

Sedimentation

The suspended matter in the water column is affected by a sedimentation process. The sedimentation of suspended solids is described with a settling velocity.

$$sessa = vsm \cdot X_{SS} \qquad \left[\frac{gDW}{m^2 \cdot d}\right] \qquad (3.36)$$

Where:
vsm	Settling velocity of SS [m/d]
X_{SS}	Suspended solids conc. in the water [g DW/m³ bulk]

Resuspension

The sediments are resuspended when the current speed exceeds a critical value.

$$\text{if } (cspd > ucrit):$$
$$ressa = resrat \qquad \left[\frac{gDW}{m^2 \cdot d}\right] \qquad (3.37)$$

Where:
cspd	Current Speed adjusted for sediment build up [m/s]
ucrit	Critical current speed for resuspension of SS
resrat	Resuspension rate of SS [gDW/m²/day]

4   Data Requirements

- Basic Model Parameters
  - Model grid size and extent
  - Time step and length of simulation
  - Type of output required and its frequency

- Bathymetry and Hydrodynamic Input

- Combined Advection-Dispersion Model
  - Dispersion coefficients

- Initial Conditions
  - Concentration of state variables

- Boundary Conditions
  - Concentration of state variables

- Pollution Sources
  - Discharge magnitudes and concentration of relevant state variables

- Process Rates
  - Size of coefficients governing the process rates. Some of these coefficients can be determined by calibration. Others will be based on literature values or found from actual measurements and laboratory tests.

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