Antifoulant Model to Predict Environmental Concentrations (MAMPEC V2.0)

Technical background additional features of MAMPEC version 2.0

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I Introduction

MAMPEC (Marine Antifoulant Model to Predict Environmental Concentrations) is a generic chemical fate model specifically developed for the prediction of antifoulant concentrations in the environment. The MAMPEC model provides a state-of-the-art prediction of environmental concentrations of antifouling products in five generalised ‘typical’ marine environments (open sea, shipping lane, estuary, commercial harbour, yachting marina). The user can specify different environment dimensions and properties. Based on these user-defined conditions, different hydraulic water exchange scenarios are calculated.

The first proto-type version of the MAMPEC model (version 1.2) was issued in 1999 as part of a study, commissioned by the European Paint Makers Association (CEPE) within the project "Utilisation of more environmental friendly antifouling products” of the Antifouling Working Group of the European Paint Makers Association (CEPE), sponsored by the European Commission (DG XI; Contract # 96/559/3040/ DEB/E2). Based on the experiences of users with the first version of the model, it was decided to upgrade the model to make it more flexible to regional country settings, to adapt some of the default exposure scenarios, to add an interactive module for concentrations in sediments, to revise and extend the help files, and to add a separate short manual. The MAMPEC model has been or is considered to be used in admission procedures in different European countries. During 2001 and 2002 a second version of the model (version 1.4) was prepared under contract to CEPE (2001-02-02).

In 2005, in close co-operation with members of the CEPE Antifouling Working Group, additional features have been defined and implemented in version 2.0. These new features are related to extensions in the user-defined functionality and chemical process formulations.

In summary these new extensions includes:

- additional fields in the database to accommodate the new functionalities;
- wind driven exchange;
- extension of environmental scenarios;
- correction zero-tidal exchange formulation;
- export compounds / environments & emissions (to new dbase format)
- import compounds / environments & emissions (from new dbase format)
- photolysis module
- concentrations in the area outside the harbour (for new runs)
- automatic update of previous database to accommodate the new features (consequence: if you back-up your database before you install the new version, then copy your database back to the MAMPEC directory and start MAMPEC, the database will be converted to the new format while retaining all your previous data)
This report describes the technical background of some of the extensions and adaptations of the new features implemented in version 2.0 of the MAMPEC model. Chapter 2 describes the wind–and low tide exchange between of marina. In chapter 3 the implemented new photolysis module is described and compared with results of EXAMS. In Chapter 4 the mixing and exchange in some additional new marina geometries are discussed.
2 Exchange under low tidal conditions

2.1 Introduction

In general, the exchange of water between a harbour basin and an estuary/sea is caused by three phenomena (Eysink and Verinaas, 1983; Eysink, 1988):

1. filling and emptying by the tide;
2. horizontal eddy generated in the harbour entrance by the passing main flow;
3. vertical circulation currents in the harbour generated by density differences between the water inside and outside the basin.

These three processes are included in the MAMPEC model (Hattum et al., 2002). Based on either default or user defined parameters the model calculates the water exchange between harbour/marina and the environment. The exchange volume can be manually changed by the user.

Under specific conditions of low tidal conditions, small currents and no density differences, other physical processes can become important in the exchange caused by:

- non-tidal water level changes
- wind induced currents

These processes are not explicitly included in the MAMPEC (version 1.3) model but are implemented schematically in the current version 2.0. For the derivation of suitable descriptions of these exchanges, the Finnish Uittamo marina has been selected as an appropriate test case and described in the following sections.

Table 2.1 shows the dimensions and properties of the ‘default Marina’ in the MAMPEC program and the user defined Finnish Uittamo marina. It is clear that in the case of Uittamo, where the tidal amplitude is zero, the density exchange is zero and the flow velocity is very low (1 cm/s) the other exchange processes should be considered.

Table 2.1: Dimensions and settings of the default MAMPEC marina and the Uittamo marina

<table>
<thead>
<tr>
<th>Parameter</th>
<th>default marina</th>
<th>Uittamo</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>400</td>
<td>420</td>
<td>m</td>
</tr>
<tr>
<td>Width</td>
<td>400</td>
<td>140</td>
<td>m</td>
</tr>
<tr>
<td>Depth</td>
<td>3.5</td>
<td>2.2</td>
<td>m</td>
</tr>
<tr>
<td>Width Mouth</td>
<td>100</td>
<td>420</td>
<td>m</td>
</tr>
<tr>
<td>Mouth depth</td>
<td>3.5</td>
<td>2.2</td>
<td>m</td>
</tr>
<tr>
<td>Tidal period</td>
<td>12.41</td>
<td>12.41</td>
<td>h</td>
</tr>
<tr>
<td>Tidal amplitude</td>
<td>1</td>
<td>0</td>
<td>m</td>
</tr>
<tr>
<td>Flow velocity</td>
<td>1.0</td>
<td>0.01</td>
<td>m/s</td>
</tr>
<tr>
<td>Density difference</td>
<td>0.1</td>
<td>0</td>
<td>kg/m³</td>
</tr>
</tbody>
</table>
### 2.2 Water exchange by horizontal eddy in harbour entrance

A current passing the entrance of a basin generates an eddy in this entrance. Steep velocity gradients generate an exchange of water by turbulence. Through this mechanism water from the outside penetrates the eddy and from there further into the harbour. The rate of this mechanism depends on flow velocities in front of the harbour basin, the size of the entrance and the tidal prism. The rate of “horizontal water exchange” can be approximated by the formula (Graaf and Reinalda, 1977):

$$ Q_h = f_1 h b u_0 - f_2 Q_t $$

- $Q_h$ = rate of horizontal water exchange
- $Q_t$ = filling discharge due to rising tide
- $f_1$, $f_2$ = empirical coefficients depending on geometry of the basin
- $h$ = depth of entrance
- $b$ = width of entrance
- $u_0$ = main flow velocity due to rising tide ($h b u_{tide}$)
- $u_{tide}$ = tidal in and out flow velocities in the entrance

The formula is valid for rivers ($Q_t=0$) and in tidal areas during flood. $Q_h$ is almost negligible during ebb. Hence in tidal areas substitution of $h = h_0 - \eta \cos \omega t$ and $u_0 = u_{0,\max} \sin \omega t$ and integration over the flood period ($t=0$ to $T/2$) yield the total volume per tide by horizontal exchange:
\[ V_h = f_1 h_0 b u_{0,\text{max}} \frac{T}{\pi} - f_2 V_t \]

where:
- \( V_h \) = total water exchange volume per tidal period by horizontal exchange
- \( h_0 \) = depth in entrance relative to mean sea level
- \( u_{0,\text{max}} \) = maximum flow velocity during tidal period
- \( T \) = tidal period
- \( V_t \) = tidal prism of harbour

Typical values for coefficients \( f_1 \) and \( f_2 \) are generally within ranges 0.01-0.03 and 0.1-0.25 respectively. The current version of MAMPEC assumes the existence of a tidal period so this formula is incorporated in MAMPEC. However in the absence of tide the formula reduces to:

\[ V_h = f_1 h_0 b u_{0,\text{avg}} T \]

\( u_{0,\text{avg}} \) = average flow velocity in front of harbour entrance

### 2.3 Non-tidal water level changes

The Finnish marina is assumed to be situated on the south or south west coast of Finland. The coast is assumed to have an archipelago as it is outside Turku (south-west Finland) and Helsinki. The average tidal amplitude is zero. In the absence of tide, water level differences still occur based on large scale water movement or wind related water setup. Due to the large (spatial) scale of these processes they are difficult to model with a ‘local scale’ model such as MAMPEC.

To estimate the importance of non-tidal water level changes in this specific area, the water level measurements at the Turku station (see Figure 2.2) have been analysed.

The Turku measurement location is at 60°26’ N 22°06’ E.
Daily average water level measurements (based on hourly measurements), together with the daily minimum and maximum values have been obtained from the Finnish Institute of Marine Research for a 5-year period (1998-2002). During that period the average daily difference between low and high water level was 14.4 cm. The minimum daily difference is 3 cm, the maximum 77 cm. Like tide, water level changes will give an exchange between marina and the sea.

Based on the average daily difference an exchange volume can be estimated:

\[ V_t = h_{\text{daily \_avg}} \cdot \text{width} \cdot \text{length} \cdot \frac{T}{24} \]

- \( V_t \) = exchange volume per tidal period
- \( h_{\text{daily \_avg}} \) = average difference between daily maximum and minimum water level
- \( \text{width} \cdot \text{length} \) = area harbour
- \( T \) = tidal period

In this approach the maximum difference in water levels over a 24 hour period is taken and then normalized to tidal frequency. It does assume that on average over 24 hours the water level fluctuates and approaches a maximum height difference only once. The water level changes are non tidal and most likely caused by large scale wind and atmospheric pressure effects, which are relatively slow processes (i.e. scale of days, not minutes/hours). It is therefore expected that the frequency of water level fluctuations will be in the same order of magnitude. In order to validate this approach hourly water level measurements at Turku for 2002 (8759 data points) have been analysed.

Based on the daily minimum and maximum water levels the average daily water level difference in 2002 was 14.3 cm. Based on the hourly measurements of the fluctuations in 2002 the daily average water level difference amounts to 17.7 cm. This value is quite close to the one based on the daily minimum and maximum values (approximately 20 % higher). The estimate based on the daily maximum difference seems therefore a reasonable approach, requiring much less data than with hourly measurements. The daily maximum difference approach slightly underestimates the actual exchange (20 % in case of Turku).

In the present version 2.0 of MAMPEC the daily non-tidal water level difference is an user input to estimate the non-tidal exchange volume. It should be noted that if one has reason to assume a much higher frequency of water level fluctuations, one should make a proper estimation, based on hourly measurements.

For the Uittamo marina, using the daily maximum water level difference, a non-tidal water exchange of 4.370 m³/tidal period is estimated.

### 2.4 Wind effect on exchange

When wind blows over a water surface, interaction of wind and water consists of shear stress at the surface and sometimes a normal pressure component on a wavy surface. Internal friction exists both in the air flow as in the water flow, as well as friction between
water and bed-layer and walls. These interactions cause various phenomena which are relevant for the marina – sea exchange:

1. Vertical wind velocity profile
Wind velocity at the actual water surface and water velocity are identical. Generally the wind velocity at surface level is much lower than at some meters above the surface. The vertical wind velocity profile over a water body is generally estimated to be of logarithmic shape. The velocity at the water surface is in the order of 3 – 3.5 % of the wind speed at 10m.

2. Vertical water velocity profile
In an originally stagnant water system the wind causes a surface current velocity \( u_s \) by shear stress. The internal shear stress in the water gives rise to a vertical velocity profile, mostly of logarithmic shape near the water surface.

Given:
- \( U \) = depth averaged velocity (due to wind only)
- \( D \) = Water depth (in m)
- \( z_b \) = bottom roughness height (in m)
- \( W \) = Wind force (in m/s)

The velocity profile (velocity as function of \( z \) – height) is given as:

\[
u(z) = \kappa^{-1} u_s \ln \left\{ \left( \frac{h - z}{z_b} \right) / \left( \frac{h - z}{z_b} \right) \right\} + u_b / \kappa \ln \left( \frac{z}{z_b} \right) \quad \text{For } z_b \leq z \leq h - z_s
\]

\[
= 0 \quad \text{For } 0 \leq z \leq z_b
\]

\[
= u_s \quad \text{For } h - z_s \leq z \leq h
\]

With:
- \( u_s \) = Wind driven velocity at water surface (usually 3-3.5 % * \( W \)) (m/s)
- \( z_s \) = Surface roughness height (m)
- \( \kappa \) = Von-Karmans constant = 0.41
- \( u_b \) = bottom stress velocity (m/s)
- \( \kappa_b \) = (\( \kappa \) * \( D \) - \( u_s \)) / \left( \ln \left( \frac{h}{z_b} \right) - 1 \right)
- \( u_{s,*} \) = Surface stress velocity (m/s)
- \( C_d \) = Wind drag coefficient = 6.3e-4 * (1 + 0.1 * ABS(\( W \)))

If the wind direction drives the water flow parallel to the harbour entrance, this results in a flow velocity which is included in the MAMPEC model as input. The selected setting for the Finnish marina of 0.01 m/s is a lower estimate, based on local current measurements which are in the order of several centimetres per second. The effect of this parallel flow is included in the MAMPEC model.

However when the wind is perpendicular to the harbour entrance, the surface flow in the harbour would cause a bottom return flow. In order to estimate the effect of wind on the harbour exchange flow and to derive schematised formulations, a 3D model of the MAMPEC marina schematisation has been set up.
**Detailed 3D model**

A schematic 3D model has been set up to calculate the depth integrated exchange flow in a harbour basin as a result of inland wind and a minor alongshore current (0.01 m s\(^{-1}\)). The model is schematic in the sense that only the basic flow conditions were simulated. The water body has been assumed to be homogeneous and any eddies in the horizontal plane that may occur in the basin have not been verified. Furthermore, some assumptions with respect to the wind setup along the open boundaries were made for running of the model (see below for details). The model was setup using Delft3D-FLOW modelling tool (WL, 2005a).

The grid used is shown in Figure 2.3. The boundaries are chosen far enough from the area of interest (the harbour entrance), so that any circulations that may appear along the open boundaries do not affect the solution. The grid size in the harbour is a uniform 14 m by 10 m. Further away from the area of interest the grid sizes increase.

![Hydrodynamic grid](image)

Figure 2.3: Hydrodynamic grid

The bathymetry in the model is schematised by a uniform depth of 2.2 m. Bottom roughness is incorporated in the model by means of a Chezy bottom friction coefficient with a value of 65.0 m\(^{1/2}\) s\(^{-1}\).

The background flow in the model is 0.01 m s\(^{-1}\), flowing from the left to the right (using Figure 2.3 as a reference). This is done by prescribing this velocity on the right hand side boundary and prescribing the gradient of the water level on the left hand side open boundary (Neumann type boundary). On the upper boundary, a fixed water level is prescribed. The other boundaries are closed.

<table>
<thead>
<tr>
<th>Boundary section</th>
<th>Type</th>
<th>Prescribed value</th>
</tr>
</thead>
<tbody>
<tr>
<td>left</td>
<td>water level gradient</td>
<td>-0.486 ( \times 10^5 )</td>
</tr>
<tr>
<td>right</td>
<td>velocity (logarithmic)</td>
<td>0.01 m s(^{-1}) (depth averaged)</td>
</tr>
<tr>
<td>upper</td>
<td>water level</td>
<td>1.81 ( \times 10^{-5} ) m to 0.0 m</td>
</tr>
<tr>
<td>lower</td>
<td>closed</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: At the upper boundary section the water level is interpolated linearly from the left (1.81 \( \times 10^{-5} \) m) to the right (0.0 m).
For the vertical eddy viscosity, the k-epsilon turbulence closure is used. For horizontal eddy viscosities, the Horizontal Large Eddy Simulation (HLES) feature of Delft3D is applied. This feature allows for the calculation of flow separation and eddy generation by sharp bends in the geometry.

Four runs with corresponding wind speeds of 0.0 m s\(^{-1}\), 2.0 m s\(^{-1}\), 5.0 m s\(^{-1}\) and 10.0 m s\(^{-1}\) have been conducted with this model. This direction of the wind in those four runs was inland perpendicular to the harbour entrance. In Figures 2.4 to 2.7 the cross sectional flow velocities are presented for the four scenarios. The bottom return flow is clearly observed. The net depth averaged exchange flow has been calculated by adding up all the fluxes perpendicular to the interface between the harbour and the ambient water body over the vertical. This has been done separately for both the positive and negative fluxes, thereby yielding the exchange flows:

<table>
<thead>
<tr>
<th>Wind speed at 10 m (m/s)</th>
<th>Additional exchange flow at entrance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 m/s</td>
<td>0.9 m(^3)/s</td>
</tr>
<tr>
<td>5.0 m/s</td>
<td>2.8 m(^3)/s</td>
</tr>
<tr>
<td>10.0 m/s</td>
<td>6.8 m(^3)/s</td>
</tr>
</tbody>
</table>

Figure 2.4: Flow velocity in harbour – cross sectional view, open boundary is on the right; 0 m/s

Figure 2.5: Flow velocity in harbour – cross sectional view, open boundary is on the right; 2 m/s
Based on these results a generic formulation for the wind exchange has been derived and tested for the Uittamo marina. As such, the actual wind distribution for several locations along the south – south-western coast of Finland (Figure 2.8) are given in the Table 2.4 (Drebs, A., A. Nordlund, P. Karlsson, J. Helminen, P. Rissanen; 2002). The wind distribution has been calculated from four daily observations 0, 6, 12, 18 UTC. The Table contains the percentages and average speeds of the 10-minute-observation-hour mean winds, divided into eight principal directions over the period 1971 – 2000.

Table 2.4 Wind distribution and velocities 1971-2000

<table>
<thead>
<tr>
<th>Station name</th>
<th>N m/s</th>
<th>N %</th>
<th>NE m/s</th>
<th>NE %</th>
<th>E m/s</th>
<th>E %</th>
<th>SE m/s</th>
<th>SE %</th>
<th>S m/s</th>
<th>S %</th>
<th>SW m/s</th>
<th>SW %</th>
<th>W m/s</th>
<th>W %</th>
<th>NW m/s</th>
<th>NW %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maarianhamina lentoasema</td>
<td>4.4</td>
<td>17</td>
<td>3.6</td>
<td>7</td>
<td>3.4</td>
<td>6</td>
<td>4.4</td>
<td>9</td>
<td>5.4</td>
<td>20</td>
<td>4.5</td>
<td>15</td>
<td>3.8</td>
<td>8</td>
<td>4.7</td>
<td>10</td>
</tr>
<tr>
<td>Korppoo utö</td>
<td>6.7</td>
<td>11</td>
<td>6.1</td>
<td>8</td>
<td>6.8</td>
<td>9</td>
<td>6.2</td>
<td>10</td>
<td>6.8</td>
<td>15</td>
<td>7.2</td>
<td>19</td>
<td>6.6</td>
<td>14</td>
<td>7.1</td>
<td>14</td>
</tr>
<tr>
<td>Kotka ranki</td>
<td>4.5</td>
<td>11</td>
<td>4.8</td>
<td>10</td>
<td>5.7</td>
<td>10</td>
<td>5.0</td>
<td>9</td>
<td>5.8</td>
<td>13</td>
<td>6.5</td>
<td>22</td>
<td>5.3</td>
<td>15</td>
<td>4.3</td>
<td>10</td>
</tr>
<tr>
<td>Inkoo Bågaskär</td>
<td>5.0</td>
<td>11</td>
<td>3.2</td>
<td>9</td>
<td>7.1</td>
<td>11</td>
<td>6.2</td>
<td>8</td>
<td>6.2</td>
<td>11</td>
<td>6.3</td>
<td>21</td>
<td>5.2</td>
<td>18</td>
<td>4.2</td>
<td>9</td>
</tr>
<tr>
<td>Hanko Russarö</td>
<td>5.9</td>
<td>10</td>
<td>5.6</td>
<td>8</td>
<td>6.5</td>
<td>12</td>
<td>5.4</td>
<td>8</td>
<td>6.6</td>
<td>13</td>
<td>6.7</td>
<td>19</td>
<td>5.6</td>
<td>16</td>
<td>5.5</td>
<td>12</td>
</tr>
<tr>
<td>Rauma kaukajokari</td>
<td>5.7</td>
<td>10</td>
<td>4.1</td>
<td>9</td>
<td>4.3</td>
<td>10</td>
<td>4.5</td>
<td>15</td>
<td>5.8</td>
<td>15</td>
<td>6.7</td>
<td>16</td>
<td>6.5</td>
<td>10</td>
<td>6.9</td>
<td>13</td>
</tr>
<tr>
<td>average</td>
<td>5.4</td>
<td>12</td>
<td>4.9</td>
<td>9</td>
<td>5.6</td>
<td>10</td>
<td>5.3</td>
<td>10</td>
<td>6.1</td>
<td>15</td>
<td>6.3</td>
<td>19</td>
<td>5.5</td>
<td>14</td>
<td>5.5</td>
<td>11</td>
</tr>
</tbody>
</table>
The relevant wind direction for the wind to be perpendicular to the marina entrance depends obviously on the exact situation of the harbour. For harbours along the coast, perpendicular winds are from the S to W. Winds from these directions average about 5.3 – 6.3 m/s. Occurrence depends on the location and varies from 8 % (for both W and SE winds) to 22% (for SW winds).

A tentative assumption that 10 % of the time the wind is directed more or less perpendicular to the harbour entrance, with an average wind speed of 5 m/s, leads for the Uittamo marina to an additional wind-driven exchange of 2.8 m$^3$/s (or 12,500 m$^3$/tidal period). The actual exchange due to wind effects would also depend on the actual layout of the harbour and the free fetch area in front of the harbour. The way the harbour is schematised for the Uittamo marina (harbour entrance as wide as the harbour itself), leads to a maximal wind driven exchange. Under less favourable conditions we can assume a smaller wind driven exchange effect. Taking the exchange at a wind speed of 2 m/s as a lower estimate this would give a wind driven exchange of approx 4,000 m$^3$/tidal period.

The formulation of the additional wind driven exchange is implemented in version 2.0 of MAMPEC by defining a percentage of time the wind is perpendicular to the entrance and by the associated wind velocity.

### 2.5 Concluding remarks

MAMPEC calculates the exchange between harbours and their environment based on the occurrence of horizontal flow, tide and/or density differences. In general these processes determine the exchange. Under conditions of very low flow, no density differences and no tide, other processes become important which are schematically included in the current version 2.0 of MAMPEC. An overview of the implications compared to the previous version 1.4 for an example case of the Uittamo marina in Finland, is given in the Table below.
Table 2.5  Exchange volumes (m³/tide) in example case study of Uittamo marina.

<table>
<thead>
<tr>
<th>Process</th>
<th>MamPec 1.4 Uittamo default settings</th>
<th>MamPec 2.0, corrected for low tide conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal flow exchange</td>
<td>2.628</td>
<td>8.250</td>
</tr>
<tr>
<td>Non tidal water level exchange</td>
<td>not taken into account</td>
<td>4.370</td>
</tr>
<tr>
<td>Wind driven exchange</td>
<td>not taken into account</td>
<td>4.000 to 12.500 (8.250 avg)</td>
</tr>
</tbody>
</table>
3 Photolysis module

Photolysis refers to any chemical reaction in which a compound is broken down by light. The direct process is defined as the interaction of one photon interacting with one target molecule. In the previous versions of MAMPEC this process was implemented as a first order photolytic degradation rate. In order to allow a more comprehensive description of this chemical process, an extension of the formulations has been implemented in version 2.0 based on the formulations applied in EXAMS (Burns, 2004) and briefly described in section 3.1.

During the implementation two aspects were addressed that may affect the effects of photolysis:

- The water systems to be applied in MAMPEC may be more or less stratified. If they are stratified, the concentration of the substances that influence the light climate may have a marked vertical profile. This would in turn impact the photolysis of the anti-fouling agents. But we do not want to burden the user with estimating the type and degree of stratification in his or her system, unless it is unavoidable (see section 3.2).
- The EXAMS manual describes the algorithm in detail; however the some coefficients that EXAMS uses differ significantly from the coefficients used by water quality models such as Delft Hydraulics’ DELFT3D-WAQ (see section 3.3).

3.1 Short description of photolysis in MamPec

As stated above, the treatment of photolysis as implemented in MAMPEC closely follows the implementation in EXAMS (Burns, 2004):

- The extinction of light due to chlorophyll, dissolved organic matter and suspended inorganic matter as well as the natural background is computed for a number of narrow wave length bands from 280 to 800 nm. For the dependency of the specific extinction coefficients on the wave length, the table found in the EXAMS manual is used.
- For the chemical in question the user can supply the spectral absorption coefficient and the quantum yield. These are then used, together with the environmental parameters (depth and concentrations of chlorophyll, DOC and suspended solids) to calculate the photolysis rate.

The only simplification with respect to EXAMS is that in MAMPEC the substance is considered only in its neutral form (no distinction is made between the various ions that can be formed in aqueous solutions). It is also assumed that the substance is not present in the bottom sediment.
The formulae are:

- Extinction ($\varepsilon$) due to pure water ($\varepsilon_0$), chlorophyll and phaeophytin (C), dissolved organic carbon (D) and suspended inorganic solids (S):

$$\varepsilon = \varepsilon_0 + a_C C + a_D D + a_S S$$

(The specific extinction coefficients $\varepsilon_0, a_C, a_D, a_S$ all depend on the wave length.)

- Depth-averaged light intensity (due to extinction):

$$I = I_0 \frac{1 - \exp(-d\varepsilon H)}{dH}$$

($d$ is a correction for the optical path length and $H$ the water depth)

- The photolysis rate ($K$) is related to the light intensity through:

$$K = \alpha q I$$

($q$ the quantum yield of the photolysis reaction and $\alpha$ the absorption coefficient for the chemical. The quantum yield measures the chance an absorbed photon will lead to disintegration of the molecule)

Since all the coefficients are in principle and in practice a function of the light’s wave length, the above formulae are integrated numerically over the spectrum running from 280 nm to 800 nm:

$$K_{\text{total}} = \int \frac{1 - \exp(-d\varepsilon(\lambda) H)}{d\varepsilon(\lambda) H} \alpha(\lambda) q I_0(\lambda) \, d\lambda$$

In the EXAMS manual no mention is made of the computation of the solar irradiation. However, to get a better agreement between the photolysis rate computed by EXAMS and that computed by MAMPEC it turned out to be necessary to incorporate the extensive algorithms used in EXAMS to compute the contribution of each wave length band to the total irradiation. The formulae are rather involved and are therefore not repeated here.

The line of reasoning in the computation is this: The angle under which the sunlight enters the water is computed using a straightforward geometrical model of the rotation of the Earth around the Sun and its own axis. The irradiation just below the surface is computed using a description of the passage of the light through the atmosphere and the reflection at the water surface. Finally, the average irradiation for the whole year is computed. It is this average (as a function of the wave length) that is substituted in the above formulae. (For details we refer to the source code of EXAMS, which can be found at: http://www.epa.gov/ceampubl/swater/exams/exams29804.htm.)
The computation of the irradiation just below the surface (resulting in $I_0$ as a function of the wave length) takes the latitude as its only external parameter. The cloudiness is currently ignored (assuming a clear sky).

### 3.2 Effect of stratification on photolysis

In order to examine the likely effect of stratification on photolysis, a simplified conceptual model and some numerical tests with the following assumptions has been made:

- The water body consists of two layers that are each well-mixed (no vertical variation of the concentrations of chlorophyll, DOC and suspended solids)
- These two layers exchange matter due to turbulence and diffusion at a constant rate
- The anti-fouling agent is decaying due to light at a constant but different rate for each of the layers.

In general, the upper layer (layer 1) will be brighter than the lower layer (layer 2), so that the photolysis rate in the upper layer will be higher. Due to the vertical mixing the substance will enter the lower layer and experience a different light climate, making it survive longer. As a consequence, the effect of the vertical mixing has to be analysed.

Mass balance for each layer, yield the following formulae:

$$\frac{dC_1}{dt} = -\frac{a_1}{H_1} C_1 - \frac{D}{H_1 + H_2} (C_1 - C_2) + L_1$$

$$\frac{dC_2}{dt} = -\frac{a_2}{H_2} C_2 - \frac{D}{H_1 + H_2} (C_2 - C_1) + L_2$$

where:

- $C_1, C_2$ - concentration in layer 1, respectively layer 2 (kg/m$^3$)
- $H_1, H_2$ - thickness of layer 1, respectively layer 2 (m)
- $a_1, a_2$ - photolysis in layer 1, respectively layer 2 (1/s)
- $L_1, L_2$ - release rate of the substance in layer 1, respectively layer 2 (kg/m$^2$s)
- $D$ - the vertical diffusion coefficient (m$^2$/s)

Solving these equations yields a solution of the form:

$$C = A e^{-b_1 t} + B e^{-b_2 t}$$

where the coefficients $b_1, b_2$ represent the rates at which the substances decays.

The actual solution will depend on how much is released in the upper layer and how much is released in the lower layer, but for this examination the most important aspect is: what is the slowest decay rate?

The decay rate $b_1, b_2$ can be determined with some elementary analysis as:
\[ b_{1,2} = \frac{(a_1 + d_1 + a_2 + d_2)}{2} \pm \frac{1}{2} \sqrt{(a_1 + d_1 - a_2 - d_2)^2 + 4d_1d_2} \]

\[ d_1 = \frac{D}{H_1 (H_1 + H_2)} \]

\[ d_2 = \frac{D}{H_2 (H_1 + H_2)} \]

To get more insight in the effect of these formulae, some extreme cases are examined:

**No photolysis in the lower layer**

If the upper layer is thick or the light attenuation (extinction) is large, light can not penetrate in the lower layer and the photolysis rate may be almost zero. Furthermore, assume the thickness of both layers is comparable. In that case the formula reduces to:

\[ b_{1,2} = \frac{(a + 2d)}{2} \pm \frac{1}{2} \sqrt{a^2 + 4d^2} \]

For a substance that decays very fast (in comparison to the vertical mixing), we get:

\[ b_1 = a + d + d^2/a \]
\[ b_2 = d - d^2/a \]

the first coefficient is due to substances released in the upper layer and decaying before the vertical mixing can transport it to the lower layer and the second is due to substances released in the lower layer and being transported (slowly) to the upper layer via the mixing processes where they decay.

The coefficient that is most important here is \( b_2 \) – assuming the substance is released in comparable amounts in both layers. If by far the most of the substance is released in the upper, the other coefficient will be important even though it will decay quickly there (there simply is no time for the substance to be transported to the lower layer in this case).

**Fast vertical mixing with respect to photolysis**

If, instead, the mixing processes are relatively fast, the formula can be reduced to (assuming only photolysis in the upper layer and equal thicknesses):

\[ b_1 = \frac{\sqrt{a}}{4} a + 2d + a^2/8d \]
\[ b_2 = \frac{\sqrt{a}}{4} a - a^2/8d \]

The first coefficient indicates the rate by which the initial concentration differences between the two layers disappear and the second indicates the mean rate by which the substance in both layers decays (note the slight correction on the intuitive value \( \sqrt{a} \) for this mean rate).
From this analysis the following can be observed:

- If the vertical mixing in the presence of stratification is still considerably faster than the photolysis, the mean rate by which the substance decays is approximately the same as it would be in case of no stratification.
- If, however, the vertical mixing is slow compared to the photolysis, the resulting mean rate depends on the vertical distribution of the substance:
  - If nearly all of the substance is present in the upper layer, then the decay rate is determined by the conditions in the upper layer.
  - If it is not the case, then the vertical mixing determines the mean decay rate.

A simple computation of the mean light intensity for typical environmental conditions using the Lambert-Beer equation, shows that the above assumption of no photolysis in the lower layer is a fair approximation (Table 3.1).

Table 3.1: Light attenuation for various schematized conditions

<table>
<thead>
<tr>
<th>Thickness of layers (m)</th>
<th>Extinction (1/m)</th>
<th>Secchi disk depth (m)</th>
<th>Mean light attenuation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Upper</td>
</tr>
<tr>
<td>Upper</td>
<td>Lower</td>
<td></td>
<td>Upper</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>5.2</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>0.5</td>
<td>5.2</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>0.5</td>
<td>5.2</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2.6</td>
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<tr>
<td>1</td>
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<td>2.6</td>
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<td>10</td>
<td>1</td>
<td>2.6</td>
</tr>
<tr>
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<td>3</td>
<td>0.5</td>
<td>5.2</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.5</td>
<td>5.2</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0.5</td>
<td>5.2</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>1</td>
<td>2.6</td>
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<tr>
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<td>1</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>1</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Only when the water is fairly shallow (less than 10 m) and the light penetrates more than, say, 5 m, the ratio of the mean light intensity larger than 0.2.

To put these conclusions in a more concise way:

- If the photolysis rate is much lower than the vertical mixing, the water column appears well-mixed as far as photolysis is concerned. As a rule of thumb:
  - If the half life due to photolysis is longer than a few days, the water column may be treated as well-mixed.
- If the photolysis rate is much larger than the vertical mixing, the two water layers can be regarded as independent. To prevent an underestimation of the concentration, the model should use a corrected water depth (that is the thickness of the layer that receives most of the substance) rather than the total water depth.

---

1 Computed as 2.6/extinction.
3.3 Comparison of light extinction coefficients

In EXAMS the following coefficients to describe the light extinction or attenuation are used (see paragraph 3.2.2 of Burns (2004)):

- Extinction due to suspended solids: $0.34 \text{ m}^{-1}/(\text{mg SS/l})$
- Extinction due to chlorophyll and phaeophytine: $55.7 \text{ m}^{-1}/(\text{mg Chlf+Phaeo/l})$
- Extinction due to dissolved organic matter: $0.86 \text{ m}^{-1}/(\text{mg DOC/l})$
- Extinction due to water: $0.24 \text{ m}^{-1}$

The last two values are the averages of the coefficients over the spectral range 280-850 nm.

In commonly used general water quality models such as the Delft3D-WAQ model (WL, 2005) typically used coefficients are:

- Extinction due to suspended solids: $0.025 \text{ m}^{-1}/(\text{mg SS/l})$
- Extinction due to chlorophyll (depends on species): $0.2 \text{ m}^{-1}/(\text{mg C/l})$
- Extinction due to detritus: $0.10 \text{ m}^{-1}/(\text{mg C/l})$
- Extinction due to water: $0.08 \text{ m}^{-1}$

However, DELFT3D-WAQ does not distinguish these coefficients as function of the light wavelength. Instead for most processes in DELFT3D-WAQ (certainly the processes concerning primary production), the photo-active radiation (PAR) is the only important component of the total irradiation. If we limit the averaging mentioned above the range 400-700 nm, roughly the range for PAR, then the figures for EXAMS become:

- Extinction due to suspended solids: $0.34 \text{ m}^{-1}/(\text{mg SS/l})$
- Extinction due to chlorophyll and phaeophytine: $12.07 \text{ m}^{-1}/(\text{mg Chlf+Phaeo/l})$
- Extinction due to dissolved organic matter: $0.33 \text{ m}^{-1}/(\text{mg DOC/l})$
- Extinction due to water: $0.065 \text{ m}^{-1}$

The background extinction coefficient due to pure water is quite comparable now. The extinction due to chlorophyll and phaeophytine requires some further conversion to arrive at quantities that can be compared. To convert mg C as a measure for living algae to mg chlorophyll: 1 mg C means approximately 0.025 mg chlorophyll, though the value depends on the species of algae. Detritus and phaeophytine are loosely related, assuming the same relation for this comparison, the specific extinction become:

Extinction due to living algae: $0.2 \text{ m}^{-1}/(0.025 \text{ mg Chlf/l}) = 8 \text{ m}^{-1}/(\text{mg Chlf/l})$
Extinction due to detritus: $0.1 \text{ m}^{-1}/(0.025 \text{ mg Chlf/l}) = 4 \text{ m}^{-1}/(\text{mg Phaeo/l})$

These numbers are not exactly comparable to the EXAMS values, but they are of the same order of magnitude, especially considering the distinction between various species, each having their own values of the C/Chlorophyll ratios and the specific extinction coefficients.

The main discrepancy in the applied coefficient is the extinction due to suspended solids. This could be due to the difference in the spectral ranges, however no information is available on the dependency of the extinction coefficient from the wavelength. In a review by C. Gallegos (Gallegos et al.) it is mentioned that various surveys yield a rather wide range for this particular coefficient. In that light, it would seem that no significant discrepancy exists, though the value reported in the EXAMS manual is rather high. The
same holds for the value of the specific extinction due to DOC – the order of magnitude in DELFT3D-WAQ is 0.1 m\(^{-1}\)/(mg C/l), well within the range reported by Gallegos, but the value in EXAMS seems relatively large.

In (WL, 2003) the performance of several relations is investigated for determining the extinction coefficient with respect to available measurements for the Dutch North Sea coast. From this study it was concluded that the existing relations were not sufficiently accurate for all data points. Instead they devised a formula that distinguishes two situations: a concentration of inorganic suspended solids below 15 mg/l and a concentration above 15 mg/l. The reason for this distinction is that high concentrations usually indicate the presence of coarse material, which has very different optical properties.

### 3.4 Computed photolysis in MAMPEC and EXAMS

In order to evaluate the photolysis implementation in MAMPEC produces similar photolysis rates as EXAMS, some test computations for the substance “pyrithione” has been performed. The results including the half life time are shown in Table 3.2 below.

<table>
<thead>
<tr>
<th>Environmental conditions</th>
<th>Chlorophyll ((\mu{\text{g}}/l))</th>
<th>DOC (mg/l)</th>
<th>Suspended solids (mg/l)</th>
<th>Depth (m)</th>
<th>MAMPEC Half-life (h)</th>
<th>EXAMS Half-life (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>1</td>
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<td>0</td>
<td>10</td>
<td>0.94</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1</td>
<td>0</td>
<td>3</td>
<td>0.41</td>
<td>0.31</td>
</tr>
<tr>
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<td>1.18</td>
<td>0.90</td>
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<td>1</td>
<td>0</td>
<td>3</td>
<td>0.52</td>
<td>0.39</td>
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<td></td>
<td>30</td>
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<td>0</td>
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<td>1.61</td>
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</tr>
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<td></td>
<td>10</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>0.67</td>
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<td></td>
<td>10</td>
<td>3</td>
<td>0</td>
<td>10</td>
<td>2.08</td>
<td>1.43</td>
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<td>1</td>
<td>3</td>
<td>0.53</td>
<td>0.41</td>
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<td>1</td>
<td>10</td>
<td>1.72</td>
<td>1.31</td>
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<td>1</td>
<td>10</td>
<td>10</td>
<td>4.87</td>
<td>3.53</td>
</tr>
</tbody>
</table>

The following can be observed from the results:
- In EXAMS the minimum concentration of DOC that one can set is 1.0 mg/l.
- After a computation the concentration of suspended solids in EXAMS that started as 0, is set to 0.001 mg/l.
- There is an almost constant ratio of 1.3 (up to 1.45) between the estimated half-lifes for MAMPEC and EXAMS. This difference is caused by the numerical implementation on how the absorption over the wave-length spectrum is integrated. MAMPEC uses linear interpolation while in EXAMS a constant absorption over the band width intervals is applied. Furthermore MAMPEC uses a yearly averaged radiation while in EXAMS monthly averaged values are applied. At least the half-lifes as estimated by MAMPEC are somewhat larger, so that the predicted concentrations will be larger.
4 Extension of harbour layout

The MAMPEC model provides a state-of-the-art prediction of environmental concentrations of antifouling products in generalized ‘typical’ marine environments. In the previous versions of the MAMPEC model (versions 1.0-1.6.03) the implemented prototype environments consist of rectangular shaped harbour basins and ‘open waters’ in which the user can specify different dimensions and area properties (see Figure 4.1). Structures such as jetties screening off harbour entrances and moorings in the river or estuary are often seen phenomena in harbour geometries that are not explicitly implemented in MAMPEC (Figure 4.2).

![Figure 4.1: Implemented prototype environments in MAMPEC version 1.0-1.6.03](image1)

<table>
<thead>
<tr>
<th>Commercial/estuarine harbour</th>
<th>Marina</th>
<th>Shipping Lane/ Open Sea</th>
</tr>
</thead>
</table>

Figure 4.2: Examples of harbour geometry (obtained from GoogleEarth)
In order to evaluate to what extent it is possible and feasible to implement an option which allows the user to add such structures to the currently implemented prototype environments, various numerical experiments have been carried out with a detailed schematised hydrodynamic model (Delft3D-Flow). These experiments focus on the exchange volume of water between the harbour and the estuary/river since that primarily determines the concentration of antifoulants.

In general, the exchange of water between a harbour basin and an estuary/river is caused by three phenomena (see Figure 4.3). That is by:

1. filling and emptying by the tide,
2. the horizontal eddy generated in the harbour entrance by the passing main flow, and
3. vertical circulation currents in the harbour generated by density differences between the water inside and outside the basin.

The exchange of water due to 2 and 3 are complex hydrodynamic processes. In MAMPEC these exchanges are approached by empirical formulas which are derived from measurements of several test cases with complex geometries such as the Botlek harbour and the Europoort (see Figure 4.4 and 4.5). In these formulations the deviations in harbour geometry from the rectangular generalized geometry such as implemented in MAMPEC are implicitly accounted for.
In order to get a better grip on the relative contribution of the processes responsible for the exchange of water, a 2DH hydrodynamic model of a prototype harbour used in MAMPEC
was set-up with the Delft3D software package. Several numerical simulations were made to analyse the effect of changes in geometry, hydrological forcing and model parameters on the exchange volume of water due to 1 & 2. In Figure 4.6 some illustrative examples are presented to demonstrate the complex behaviour of a conservative tracer released in the harbour basin.

As a result of eddy generated fluxes, the calculated exchange volumes of water over the harbour entrance by Delft3D for a number of runs are compared with the volumes calculated with the simplified formulations implemented in MAMPEC.

From these simulations the following observations are made:

- the exchange of water due to complex eddies generated by a passing main flow is not so easily trapped in a generic model, due to a large sensitivity to geometry and process parameters.
- the exchange of water over the harbour entrance due to eddies generated by a passing main flow can be very large, but it is not easily determined to what extent these transports contribute to the advection of antifouling products (longer residence times in the back of the harbour than near the entrance).

Considering this and the fact that the MAMPEC empirical formulations have already proven their value in the past it is stated other geometry of harbour basins can be defined by the dimensions of the current implemented shapes (volume exchange is covered by the MAMPEC formulations). “Outside” jetties breakwater can be included by defining the appropriate harbour entrance (see Figure 4.7).

---

**Figure 4.7 Proposed approach for accounting for the effect of structures outside the harbour entrance.**
5 Concluding remarks

The current version 2.0 of MAMPEC has been extended with some new features. These additional features include:

*Exchange under low tide conditions*
Under specific conditions of low tidal conditions, small currents and no density differences, other physical exchange mechanism caused by non-tidal water level changes and wind induced currents (return flow near bottom) will become important in determining the concentration distribution of antifoulants. Based on detailed 3D numerical model experiments these processes are implemented schematically with a minimum of required user input in the current version 2.0. The additional user input consist of the daily non-tidal water level differences, wind speed and the percentage of time the wind is blowing perpendicular to the harbour entrance.

*Photolysis module*
The implementation of the photolysis degradation process has been substantially extended according to the formulations used in EXAMS. The required additional user input is implemented in the graphical user interface. In order to avoid underestimation of the photolysis rate in case of (stratified) conditions where the photolysis rate is much larger than the vertical mixing time, it is advised to use a corrected water depth (that is the thickness of the layer that receives most of the substance) rather than the total water depth.

*Harbour extensions*
From various detailed numerical experiments is concluded that the exchange of water due to complex eddies generated by a passing main flow is not easily trapped in a generic model, due to a large sensitivity to geometry and process parameters. The exchange of water over the harbour entrance due to eddies generated by a passing main flow can be very large, but it is not simply determined to what extent these transports contribute to the advection of antifouling products (longer residence times in the back of the harbour than near the entrance). Based on this and the fact that the MAMPEC empirical formulations have already proven their value in the past it is recommended that other geometry of harbour basins can be defined by the appropriate dimensions of the current implemented shapes.
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