##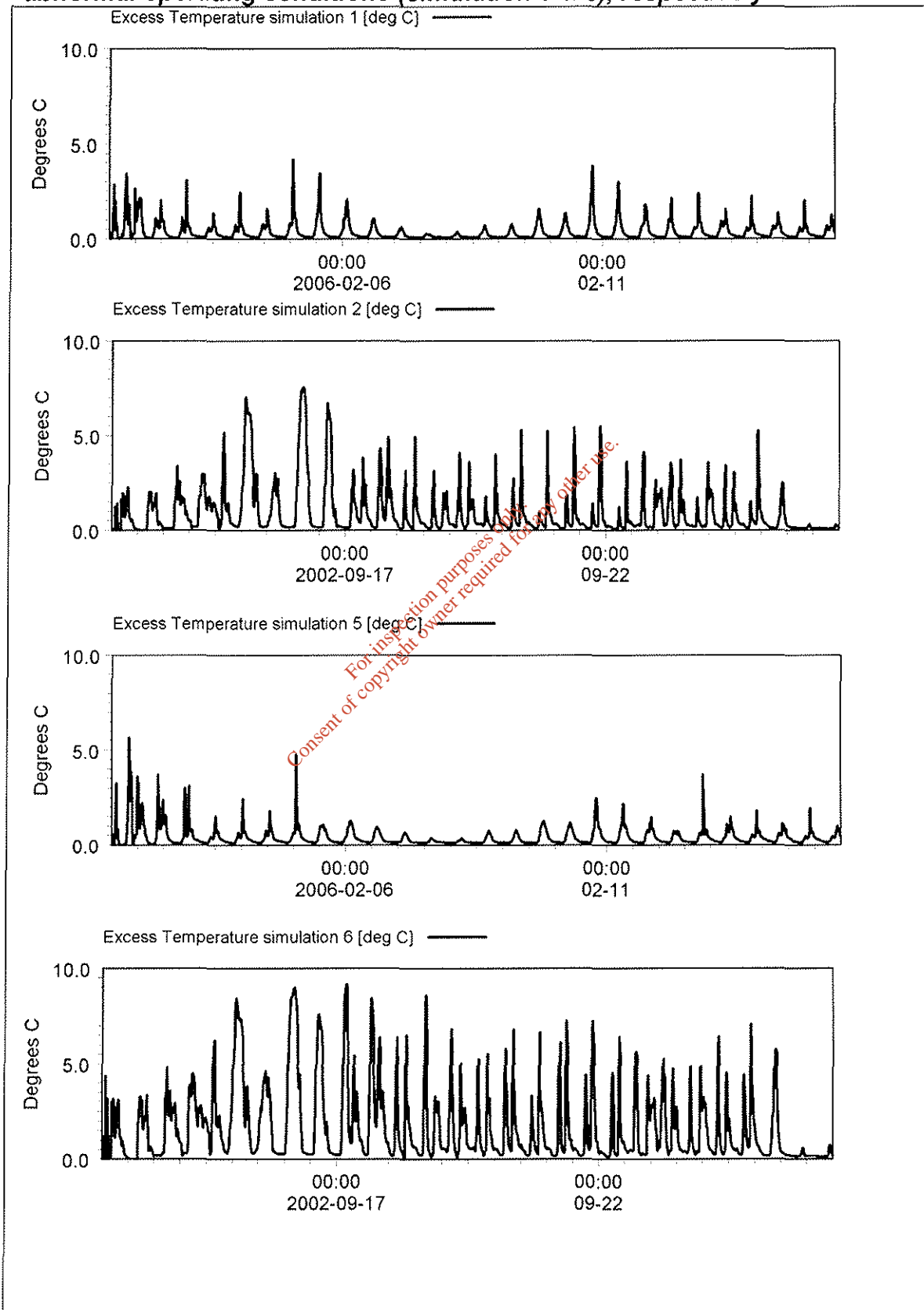 Time series of excess temperature at surface approximately. 50 m from outfall for high, low river flow, normal operating conditions (simulation 1 & 2), high, low and abnormal operating conditions (simulation 5 & 6), respectively.

y:\ced reports\ced 2006-reports\53749 dublin waste to energy
project\eis final version 08062006\53749 dublin wte project -
appendix 12-1.doc

DHI Water & Environment

APPENDIX 12.1H

MIKE 3 Flexible Mesh Description

y:\ced reports\ced 2006-reports\53749 dublin waste to energy
project\eis final version 08062006\53749 dublin wte project -
appendix 12-1.doc

DHI Water & Environment

MIKE 3/21 FLOW MODEL FM

Hydrodynamic and Transport Module

Short Description

DHI Water & Environment
Agern Allé 5
DK-2970 Hørsholm
Denmark

Tel: +45 4516 9200
Fax: +45 4516 9292
E-mail: dhi@dhi.dk
Web: www.dhi.dk

DHI Software 2004

DHI Water & Environment

PLEASE NOTE

COPYRIGHT

This document refers to proprietary computer software, which is protected by copyright. All rights are reserved. Copying or other reproduction of this manual or the related programs is prohibited without prior written consent of DHI Water & Environment (DHI). For details please refer to your 'DHI Software Licence Agreement'.

LIMITED LIABILITY

The liability of DHI is limited as specified in Section III of your 'DHI Software Licence Agreement':

'IN NO EVENT SHALL DHI OR ITS REPRESENTATIVES (AGENTS AND SUPPLIERS) BE LIABLE FOR ANY DAMAGES WHATSOEVER INCLUDING, WITHOUT LIMITATION, SPECIAL, INDIRECT, INCIDENTAL OR CONSEQUENTIAL DAMAGES OR DAMAGES FOR LOSS OF BUSINESS PROFITS OR SAVINGS, BUSINESS INTERRUPTION, LOSS OF BUSINESS INFORMATION OR OTHER PECUNIARY LOSS ARISING OUT OF THE USE OF OR THE INABILITY TO USE THIS DHI SOFTWARE PRODUCT, EVEN IF DHI HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY TO CLAIMS OF PERSONAL INJURY TO THE EXTENT PERMITTED BY LAW. SOME COUNTRIES OR STATES DO NOT ALLOW THE EXCLUSION OR LIMITATION OF LIABILITY FOR CONSEQUENTIAL, SPECIAL, INDIRECT, INCIDENTAL DAMAGES AND, ACCORDINGLY, SOME PORTIONS OF THESE LIMITATIONS MAY NOT APPLY TO YOU. BY YOUR OPENING OF THIS SEALED PACKAGE OR INSTALLING OR USING THE SOFTWARE, YOU HAVE ACCEPTED THAT THE ABOVE LIMITATIONS OR THE MAXIMUM LEGALLY APPLICABLE SUBSET OF THESE LIMITATIONS APPLY TO YOUR PURCHASE OF THIS SOFTWARE.'

PRINTING HISTORY

July 2003...Edition 2002

June 2003..Edition 2003

September 2004 ....Edition 2004

DHI Water & Environment

CONTENTS

MIKE 3/21 FLOW MODEL FM
SHORT DESCRIPTION

i

1 INTRODUCTION

The MIKE 3/21 Flow Model FM is a general hydrodynamic flow modelling system aimed at applications within oceanographic, coastal and estuarine environments. The system comprises both two-dimensional vertically averaged equations (MIKE 21) and three-dimensional hydrostatic equations (MIKE 3).

The discretization in solution domain is performed using a finite volume method on an unstructured mesh.

This note provides the mathematical and numerical background for MIKE 3/21 Flow Model FM[1].

---

[1] *The finite volume option in MIKE 3/21 will be release in September 2004*

DHI Water & Environment

2 GOVERNING EQUATIONS

2.1 Shallow Water Equations

The model is based on the solution of the three-dimensional incompressible Reynolds averaged Navier-Stokes equations, subject to the assumptions of Boussinesq and of a hydrostatic pressure. The equations are solved using a vertical σ-transformation where the transformation $\sigma = (z - \eta)/D$

The local continuity equation is written as

$$\frac{\partial \eta}{\partial t} + \frac{\partial Du}{\partial x} + \frac{\partial Dv}{\partial y} + \frac{\partial \omega}{\partial \sigma} = 0 \tag{2.1}$$

and the two horizontal momentum equations for the x- and y-component, respectively

$$\frac{\partial Du}{\partial t} + \frac{\partial Du^2}{\partial x} + \frac{\partial Duv}{\partial y} + \frac{\partial \omega u}{\partial \sigma} = $$
$$-gD\frac{\partial \eta}{\partial x} - D\frac{\partial}{\partial x}(p_A/\rho_o) + fDV + \frac{\partial}{\partial \sigma}(v_T \frac{\partial u}{\partial \sigma}) + A_X - B_X \tag{2.2}$$

$$\frac{\partial Dv}{\partial t} + \frac{\partial Duv}{\partial x} + \frac{\partial Dv^2}{\partial y} + \frac{\partial \omega v}{\partial \sigma} = $$
$$-gD\frac{\partial \eta}{\partial y} - D\frac{\partial}{\partial y}(p_A/\rho) - fDU + \frac{\partial}{\partial \sigma}(v_T \frac{\partial v}{\partial \sigma}) + A_Y - B_Y \tag{2.3}$$

where

η	:	elevation above mean sea level
u, v, w	:	velocities in x,y,z directions
σ	:	vertical transformed co-ordinate
D	:	total water depth
ρ	:	density
g	:	acceleration due to gravity
f	:	Coriolis parameter
v_t	:	turbulent eddy viscosity
p_A	:	atmospheric pressure
$A_X A_Y$	:	horizontal stress terms
$B_X B_Y$	:	baroclinic pressure gradients

DHI Water & Environment

The horizontal stress terms are described using a gradient-stress relation, which is simplified to

$$A_X = \frac{\partial}{\partial x}(DK_{XY}\frac{\partial u}{\partial x}) + \frac{\partial}{\partial y}(DK_{XY}\frac{\partial u}{\partial y}) \qquad (2.4)$$

and similarly for A_Y where K_{XY} is an eddy viscosity.

Depth averaging of the local equations reads for the continuity equation

$$\frac{\partial \eta}{\partial t} + \frac{\partial UH}{\partial x} + \frac{\partial VH}{\partial y} = 0 \qquad (2.5)$$

The transport equations for salt, temperature and turbulence are solved after the free surface and the velocity field.

2.2   Transport Equations for Salt and Temperature

The transports of salt or temperature follow the general transport-diffusion equations as

$$\frac{\partial Dc}{\partial t} + \frac{\partial Duc}{\partial x} + \frac{\partial Dvc}{\partial y} + \frac{\partial \omega c}{\partial \sigma}$$
$$= \frac{\partial}{\partial x}\left(\Gamma_{XY}\left(D\frac{\partial c}{\partial x} - \frac{\partial D}{\partial x}\sigma\frac{\partial c}{\partial \sigma}\right)\right) + \frac{\partial}{\partial y}\left(\Gamma_{XY}\left(D\frac{\partial c}{\partial y} - \frac{\partial D}{\partial y}\sigma\frac{\partial c}{\partial \sigma}\right)\right) \qquad (2.6)$$
$$+ \frac{\partial}{\partial \sigma}(\Gamma_z\frac{\partial c}{\partial \sigma}) + S$$

where c can be salinity or temperature, Γ_{XY} and Γ_Z are the diffusivity in horizontal and vertical directions and S are additional source terms, e.g. point sources, heat exchange with the atmosphere or contributions from precipitation.

The temperature and salinity variations are linked to the hydrodynamics using an equation of state, here the UNESCO equation is used.

2.3   Turbulence Model

The turbulence is modelled assuming isotropic turbulence following a gradient-stress or gradient-flux relation. Several options as constant viscosity or vertically parabolic viscosity exist, the most complete being a standard k-ε model (Rodi, 1984), where the eddy-viscosity is derived from turbulence parameters k and ε as

$$v_T = C_v k^2 / \varepsilon \tag{2.7}$$

The turbulent kinetic energy k is estimated from a transport equation as

$$\frac{\partial Dk}{\partial t} + \frac{\partial Duk}{\partial x} + \frac{\partial Dvk}{\partial y} + \frac{\partial \omega k}{\partial \sigma}$$
$$= A_{XY} + \frac{\partial}{\partial \sigma}(\Gamma_z^k \frac{\partial k}{\partial \sigma}) + v_T (S^2 / D + N^2 / \sigma_T) - D\varepsilon \tag{2.8}$$

and the dissipation of TKE from

$$\frac{\partial D\varepsilon}{\partial t} + \frac{\partial Du\varepsilon}{\partial x} + \frac{\partial Dv\varepsilon}{\partial y} + \frac{\partial \omega \varepsilon}{\partial \sigma}$$
$$= A_{XY} + \frac{\partial}{\partial \sigma}(\Gamma_z^\varepsilon \frac{\partial \varepsilon}{\partial \sigma}) + \frac{\varepsilon}{k}(v_T (C_{1\varepsilon} S^2 / D + C_{3\varepsilon} N^2 / \sigma_T) - C_{2\varepsilon} \varepsilon D) \tag{2.9}$$

where σ_T is a turbulent Prandtl number, A_{XY} are horizontal dispersion terms and S is the vertical shear, which can be written in tensor notation as

$$S^2 = \left(\frac{\partial u}{\partial \sigma}\right)^2 + \left(\frac{\partial v}{d\sigma}\right)^2 \tag{2.10}$$

and N^2 the Brunt-Vaisala frequency

$$N^2 = \frac{g}{\rho}\frac{\partial \rho}{\partial \sigma} \tag{2.11}$$

For the horizontal stress terms, can be used a Smagorinsky sub-grid scale eddy coefficient, which is calculated as

$$K_{XY} = c_s l^2 |S| \tag{2.12}$$

where c_s is a constant and l is the linear extent of the element.

DHI Water & Environment

3   NUMERICAL SOLUTION

3.1   *Spatial Discretization*

The discretization in solution domain is performed using a cell-centered finite volume method. In the horizontal domain, an unstructured mesh is used. The spatial domain is discretized by subdivision of the continuum into non-overlapping elements. The elements can be of arbitrarily shaped polygons, however, here only triangles and quadrilateral elements are considered. In the vertical domain a layered mesh is applied (see Figure 3.1). The dependent variables of the system are represented as piecewise constants within each element.

The convective fluxes are calculated using Roe's approximative Riemann solver.
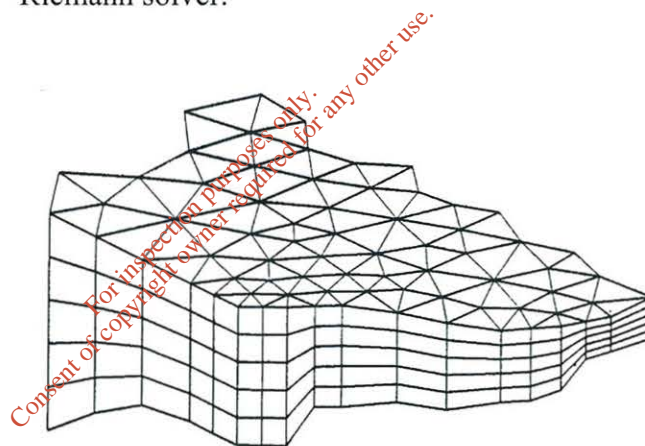

Figure 3.1   Principle of meshing

3.2   *Time Integration*

The time marching is semi-implicit using a procedure where horizontal terms are treated explicitly and vertical terms treated implicitly.

DHI Water & Environment

4 BOUNDARY CONDITIONS

4.1 Closed Boundaries

Along closed boundaries (land boundaries) normal fluxes are forced to zero for all variables. For the momentum equations this leads to full-slip along land boundaries.

4.2 Open Boundaries

The open boundary conditions can be specified either in form of a unit discharge or as the surface elevation for the hydrodynamic equations. For transport equations either a specified value or a specified gradient can be given.

4.3 Flooding and Drying

The approach for treatment of the moving boundaries (flooding and drying fronts) problem is based on the work by Zhao et al. (1994) and Sleigh et al. (1998). When the depths are small the problem is reformulated and only when the depths are very small the elements are removed from the calculation. The reformulation is made by setting the momentum fluxes to zero and only taking the mass fluxes into consideration.

4.4 Resistance

Several options exist for parameterization of the bed friction:

- Constant linear drag where $\tau_B = \rho C_B U_B$
- Quadratic drag $\tau_B = \rho C_B U_B^2$
- Chezy's formula $\tau_B = \dfrac{g}{C_z^2} U_B^2$
- Manning's formula $\tau_B = \dfrac{\rho g}{M^2 D^{4/3}} U_B^2$
- Bed roughness height, using the logarithmic law of the wall to derive the resistance

Here U_B is the velocity in the lowermost element, C_B is a drag coefficient, C_Z is the Chezy number and M is the Manning number.

4.5   Wind Friction

Drag forces from wind on the surface are related to the standard wind speed 10 m above the ground using an empirical relation

$$\tau_W = \rho_{AIR} C_W W_{10}^2 \qquad (4.1)$$

where ρ_{AIR} is the density of air, W_{10} is the wind speed 10 m above the ground and C_W is a drag coefficient, which depends on the wind speed as

$$
\begin{aligned}
C_W &= C_1 \quad W < W_1 \\
C_W &= (C_2 - C_1)/(W_2 - W_1)(W - W_1) \quad W_1 < W < W_2 \\
C_W &= C_2 \quad W_2 < W
\end{aligned}
\qquad (4.2)
$$

where C_1, C_2, W_1 and W_2 are empirical factors.

DHI Water & Environment

5   REFERENCES

Rodi, W. (1984), Turbulence models and their applications in hydraulics, IAHR, Delft, the Netherlands.

Sleigh, P.A., Gaskell, P.H., Bersins, M. and Wright, N.G. (1998), An unstructured finite-volume algorithm for predicting flow in rivers and esturies, Computers & Fluids, Vol. **27**, No. 4, 479-508.

Zhao, D.H., Shen, H.W., Tabios, G.Q., Tan, W.Y. and Lai, J.S. (1994), Finite-volume 2-dimensional unsteady-flow model for river basins, Journal of Hydraulic Engineering, ASCE, 1994, **120**, No. 7, 863-833.

DHI Water & Environment

APPENDIX 12.1I

ECOLab Description

y:\ced reports\ced 2006-reports\53749 dublin waste to energy
project\eis final version 08062006\53749 dublin wte project -
appendix 12-1.doc

DHI Water & Environment

ECO Lab
- a numerical laboratory for
ecological modeling

DHI WATER & ENVIRONMENT

Ecological modeling made easy, open and flexible

With **ECO Lab** you can combine the power of a differential equation solver (like MATLAB™) with DHI's powerful flow models. You get access to the best of both worlds – you can define the ecosystem exactly to the degree of complexity required and still be able to transport and disperse material and substances in a highly accurate manner. **ECO Lab** thus provides the basis for accurate spatial predictions of any aquatic ecosystem response - regardless of the size and structure.
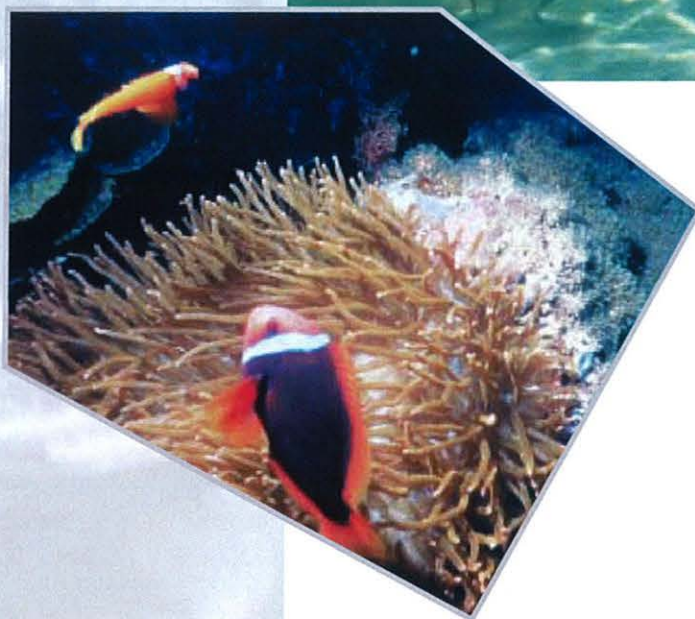
Designed for ecological modeling

Ecological modeling is an immature discipline. It deviates fundamentally from hydrodynamic modeling as the substances and elements in the system may have or take different forms. Therefore it is necessary to operate with networks of interacting subsystems exchanging the substance or element in its different forms with other subsystems. All ecosystems are not equal. Each ecosystem should be evaluated individually for the factors that are most important to the particular ecosystem.

ECO Lab is an equation solver designed for ecological modeling and designed to make the development of tailor-made models easy. Via a modern, user-friendly interface you can adjust and apply simple or complex ecological models – designed by you or based on predefined ecosystem models called **ECO Lab** Templates.

One of the preconditions for ecological modeling is an accurate flow model for the area of interest. DHI's large family of 1D, 2D and 3D models serve this purpose and can be fully integrated with **ECO Lab**.

Predefined models

ECO Lab Templates are predefined ecosystem descriptions ready to be used for ecological modeling or serve as the basis for developing your own templates. An **ECO Lab** template contains eg the mathematical description of a complete ecosystem or simple decay processes.

DHI's expertise and know-how on ecological modeling is made available through the DHI Supported Templates. The DHI Supported Templates include models corresponding to the classical

environmental modules of **MIKE 11**, **MIKE 21** and **MIKE 3** as well as a range of new environmental modules developed on the basis of the most up-to-date discoveries within ecosystem processes.

ECO Lab – a knowledge-sharing environment

Since **ECO Lab** models are open, they can easily be exchanged between users and researchers around the world. DHI supports free and open knowledge-sharing by making **ECO Lab** available to universities and research organizations, which choose to contribute to the development of new knowledge of ecosystems and ecosystem modeling.

Application potential

The transparent and flexible **ECO Lab** technology provides you with the possibility of choosing the exact level of complexity necessary for analyzing a particularly water body. **ECO Lab** therefore enables a wide range of studies to be carried out, ranging from detailed site-specific water quality studies to large-scale, holistic ecosystem descriptions.

ECO Lab enables the user to modify and adjust the equations during the course of the study. The tool even enables the user to develop completely new ecological models that describe site-specific characteristics and are adapted to local standards and regulatory requirements.

To water managers, **ECO Lab** is an indispensable tool for impact and remediation studies in which a number of scenarios can be tested for their consequences on the water environment.

ECO Lab will enable you to make the best use of your resources.

ECO Lab is a numerical modeling laboratory with which you can develop the most appropriate ecological model for your specific task. It works in combination with some of the most recognized flow models in the world – DHI's 1D, 2D and 3D modeling packages. No ecological problem is too simple or too complicated for **ECO Lab**. Even if you don't have a comprehensive process overview, **ECO Lab** can still help you focus on those areas where improved process knowledge matters for your overall understanding of the ecosystem.
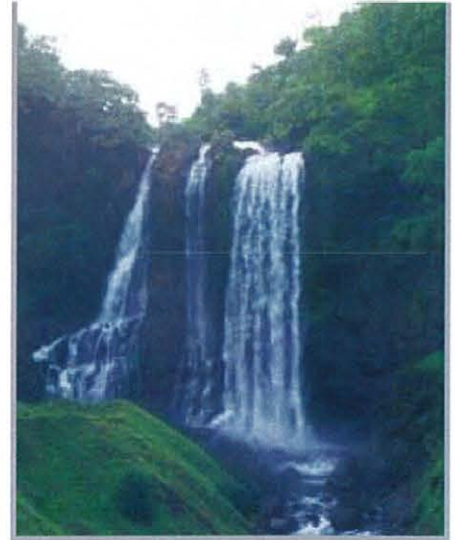
River and wetland applications

In some cases rivers can be considered as simple carriers of pollutants and the ecological interest can be limited to the transport of substances to the downstream recipient. **ECO Lab** and DHI's standard water quality templates for the decay of pollutants, BOD-dissolved oxygen relationships and retention of nutrients are often sufficient, when applied together with the standard flow model, **MIKE 11**.

Site-specific ecological conditions or local regulations will often point towards specific requirements for ecological modeling. In such cases, **ECO Lab** enables engineers and ecosystem experts to develop models tailored to the local conditions.

The retention and removal of nutrients and pollutants in wetlands (such as meadows, floodplains, reed swamps and engineered wetlands) have long been considered an energy-efficient treatment system. Simple or expanded descriptions of the wetland biology coupled to the actual hydrology can readily be developed and modeled using **ECO Lab**.

Lake and reservoir applications

Many lakes and reservoirs suffer from eutrophication. Other lakes may be affected by discharges of substances dangerous to the environment such as metals, oil constituents or pesticides.

There is a growing interest in restoring and controlling the damages to these waters and reliable prediction tools are needed. In combination with DHI's eutrophication template **ECO Lab** forms an excellent instrument for ecological modeling of lakes and reservoirs. The flow models to be integrated with **ECO Lab** are **MIKE 11** or **MIKE 21** for shallow water systems, and for deeper or stratified systems **MIKE 21** or **MIKE 11** Reservoir/ **MIKE 3**.

Estuarine applications

Estuaries are some of the world's most productive areas with high biological diversity. They are characterized by a large variety of habitats, including soft muddy sediments to hard-packed sandy sediments, sea grass meadows, macroalgae, mangrove forests and coral communities. **MIKE 21** and **MIKE 3** with **ECO Lab** allow engineers and biologists to collaborate on the development of more knowledge about these vulnerable habitats and to develop innovative and efficient solutions to the many environmental problems that threaten them.

Coastal water and sea applications

Marine waters are in many cases under environmental pressure. Regional eutrophication problems with algae blooms and oxygen depletion as well as poor water quality near beaches are examples hereof. Analysis of these problems are typical tasks for **MIKE 21** and **MIKE 3** with **ECO Lab**. **ECO Lab** is also the perfect tool for marine environmental impact assessments and for planning and permitting studies, eg in connection with aquaculture.
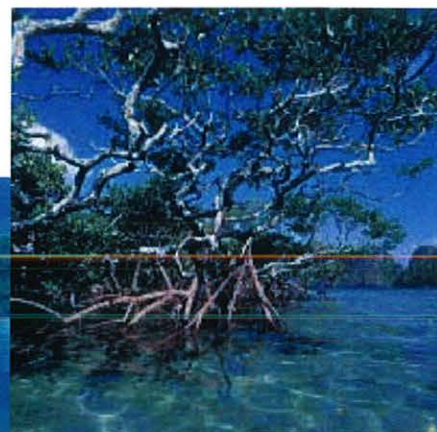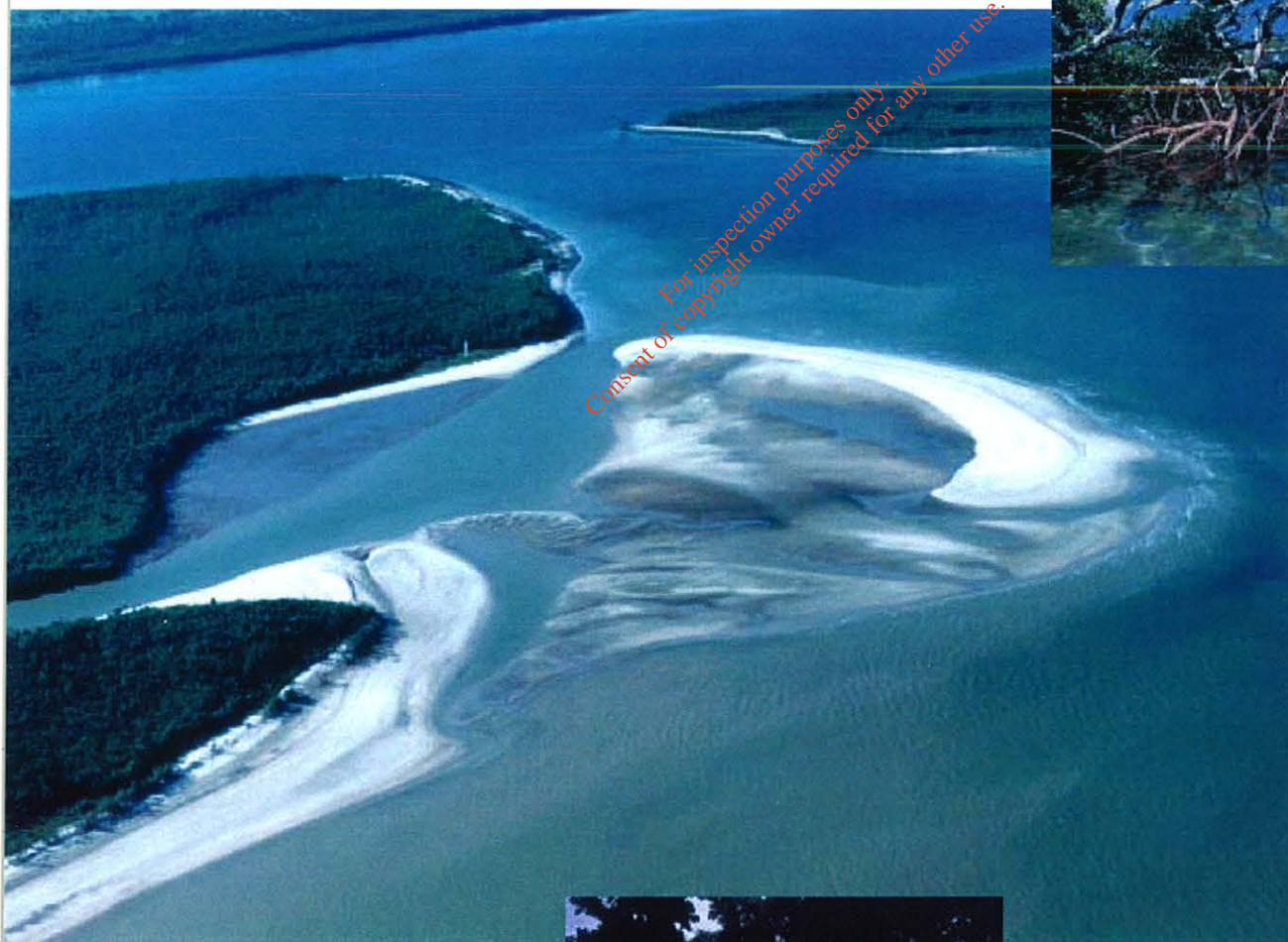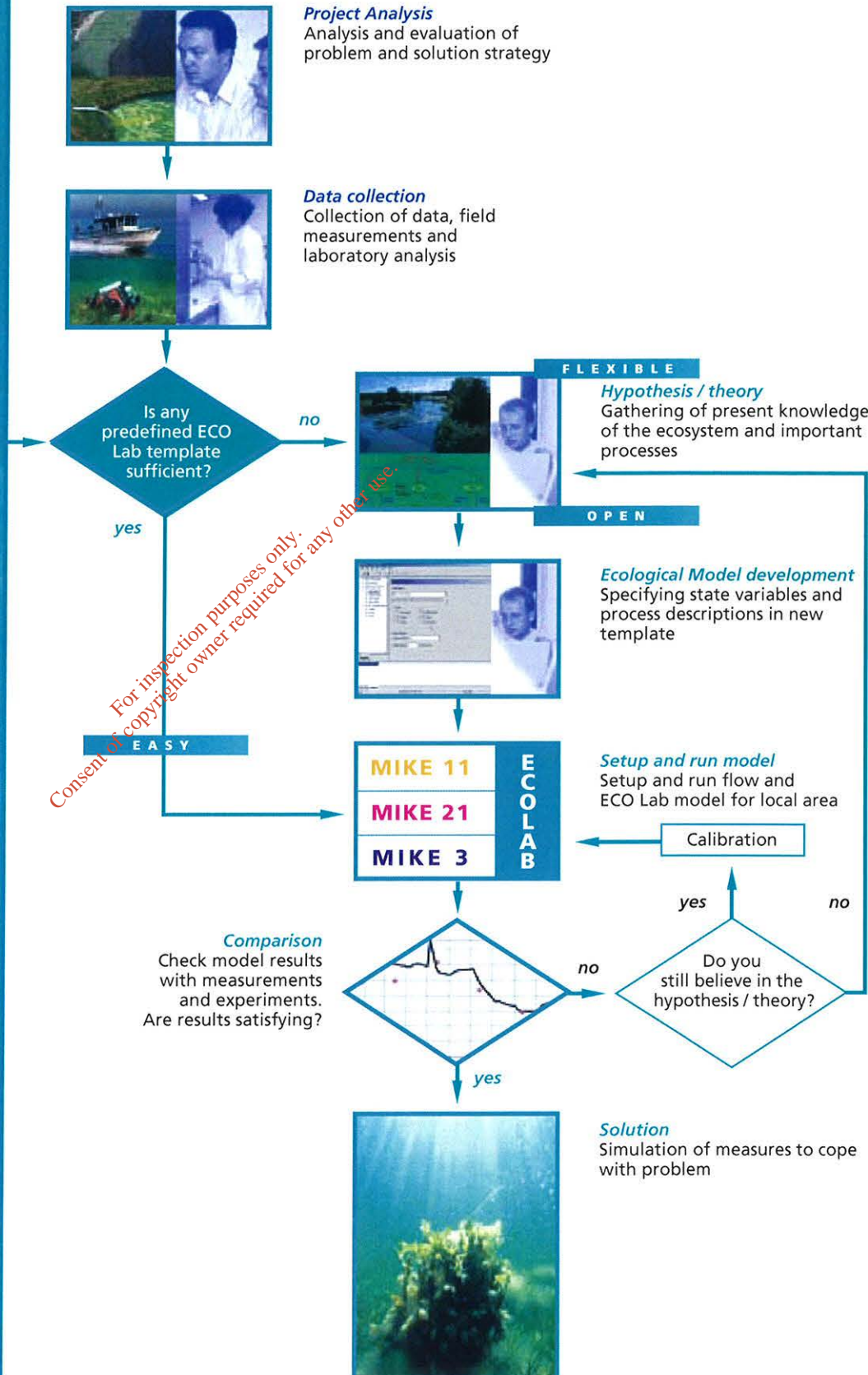
Predefined ecosystem models

Examples of DHI supported ECO Lab templates:

- **Water Quality Templates** - describe the survival of bacteria, degradation of organic matter, resulting oxygen conditions and excess levels of nutrients in water bodies. Templates cover simple combinations of variables such as BOD-DO and more complex combinations, including the most significant inorganic forms of nitrogen and phosphorus.
- **Eutrophication Template** - describes nutrient cycling, phytoplankton and zooplankton growth, growth and distribution of rooted vegetation and macro algae in addition to simulating oxygen conditions. Simulation results describe the concentrations of phytoplankton, chlorophyll-a, zooplankton, organic matter (detritus, organic and inorganic nutrients, oxygen and area-based biomass of benthic vegetation over time. In addition, a number of derived variables are stored: primary production, total nitrogen and phosphorus concentrations, sediment oxygen demand and secchi disc depth.
- **Heavy Metal Template** - describes the adsorption/desorption of metals to suspended matter, the sedimentation of sorbed metals to the seabed as well as resuspension of settled metals. It also includes the exchange of metal between the particulates of the seabed sediment and interstitial waters of the bed. The diffusive exchange of metal in dissolved form in the water and in the interstitial waters is also described. A number of derived values are calculated, eg the total concentration of metal in the water and in the bed sediment and potential concentration of metal in algae and plants and in biota like filter feeders (mussels) and fish.

For complete list of DHI Supported templates, see www.dhisoftware/ecolab

Project Analysis
Analysis and evaluation of problem and solution strategy

Data collection
Collection of data, field measurements and laboratory analysis

Is any predefined ECO Lab template sufficient?

no

yes

FLEXIBLE

Hypothesis / theory
Gathering of present knowledge of the ecosystem and important processes

OPEN

Ecological Model development
Specifying state variables and process descriptions in new template

EASY

MIKE 11

MIKE 21

MIKE 3

E C O L A B

Setup and run model
Setup and run flow and ECO Lab model for local area

Calibration

yes   no

Comparison
Check model results with measurements and experiments. Are results satisfying?

no

Do you still believe in the hypothesis / theory?

yes

Solution
Simulation of measures to cope with problem

6

Eutrophication template

1. Production, phytoplankton
2. Sedimentation, phytoplankton
3. Grazing
4. Mortality, phytoplankton
5. Excretion, zooplankton
6. Mortality, zooplankton
7. Respiration, zooplankton
8. Mineralisation of suspended detritus
9. Sedimentation of detritus
10. Mineralisation of detritus
11. Accumulation in sediment
12. Production, benthic vegetation
13. Mortality, benthic vegetation
14. Exchange with surrounding waters
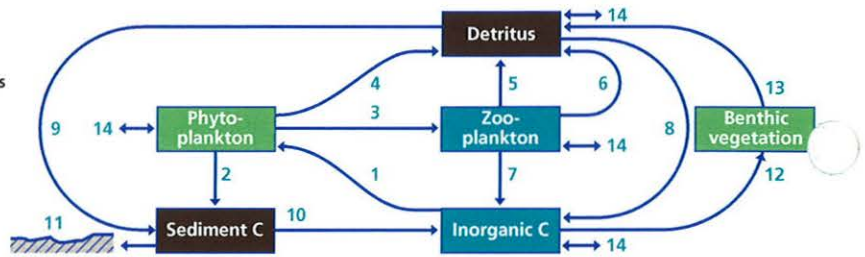
Using predefined ecosystem models / DHI supported templates

The **ECO Lab** GUI provides a logical sequence of steps with easily explained dialogs for specification of input and output.

Benefits

- the DHI supported templates cover a wide range of applications
- the templates have been applied in many studies
- the templates are well-documented
- the templates are easy to use. It is possible, with short notice, to set up and apply models to studies efficiently

Create your own ecosystem templates

The **ECO Lab** interface for developing new templates has been designed with emphasis on a logical and user-friendly interface without compromising on flexibility and functionality. In order that **ECO Lab** can manage that interactions take place only at locations where state variables or processes are defined and available, you must specify the scope and spatial variation. The scope defines where a state variable or process can be found in the water environment (water surface,

water column, on the bottom or in the sediments), and the spatial variation describes the variation pattern that can be expected for the variable (none, horizontal, horizontal and vertical). These attributes are used in the compilation in which combinations of arguments are checked against Semantic Rules and during simulation in order to avoid wasting computer memory and redundant calculations.

To make it simple **ECO Lab** is equipped with libraries of built-in constants, forcings and functions. To give an overview while developing a model or to help navigate through expressions, a number of tools such as a Process Matrix are available.

Benefits

- save many days of painstaking and highly specialized coding work
- test your ideas – faster than ever before
- improve the predictions of potential impacts
- make better evaluations of measures to cope with problems
- facilitate stakeholders participation
- exchange templates with others and stimulate your professional development and networking

Modifying predefined ECO Lab templates

DHI supported templates can be used for developing your own tailor-made ecosystem model. With the **ECO Lab** editor you can add or change the variables and characteristics already specified. The model is interpreted by the MIKE system during the model setup procedure, and you will be prompted for the input to drive the process models - such as model coefficients or functions (temporally and spatially varying external data).

Benefits

- take full advantage of your knowledge and experience
- save time when you need to develop tailor-made models
- adopt models to take full advantage of measurements
- expand your capability to respond professionally to new challenges

Language support

Many DHI Software products are available in several languages. Please check www.dhisoftware.com for details regarding availability of DHI Software products in languages other than English.

Introduction to the DHI Software products are given regularly via the internet - please refer to our web site under webinars.

Hardware and software requirements

All DHI Software products are PC tools working under Windows. All products have state-of-the-art Graphical User Interfaces.

Support and maintenance

The DHI Software products include comprehensive documentation: a *Short Introduction and Tutorial*, a *User Guide*, a *Reference Manual* and an online help system. The products come with a 12-month warranty that includes hotline support and a free version update. Extended support and updates are available by subscription to a maintenance program.

Regional support centers in Europe, North America and Australia provide hotline technical support in all time zones. Other support centers provide assistance in local languages.

User groups and conferences

DHI software user groups meet frequently in many countries. Regional and global user conferences that gather hundreds of users from all over the world are arranged at regular intervals.

Training and courses

Courses are offered regularly in Europe, North America and Australia/ New Zealand. Furthermore courses can be arranged on request at other locations. For detailed information on courses and schedules, please consult www.dhi.dk/courses.

Regional Support Centers

DHI Denmark
Tel: +45 4516 9333
software@dhi.dk
www.dhisoftware.com

DHI USA
Tel: + 1 215 504 8497
software@dhigroup.com
www.dhigroup.com

DHI Australia
Tel: +61 2 4334 6621
software@dhiaust.com
www.dhiaust.com

DHI
WATER & ENVIRONMENT

Agern Allé 5
DK-2970 Hørsholm
Denmark

Tel: +45 4516 9200
Fax: +45 4516 9292
dhi@dhi.dk
www.dhisoftware.com

DHI Software

is the brand name for quality computational models and hydroinformatics systems applicable to the solution of engineering and environmental problems related to water. DHI offers the following products:

- **MIKE 11** - for modeling inland surface waters such as rivers, channels, estuaries and reservoirs, flows, flooding, water quality and sedimentation

- **MIKE 21** - 2D modeling of free-surface flow, water quality, sediment and waves in rivers, estuaries, coastal waters and seas

- **MIKE 3** - 3D modeling free-surface flows and water quality in estuaries, coastal waters and seas

- **LITPACK** - integrated modeling of littoral processes and coastline kinetics

- **MIKE BASIN** - GIS-based decision support tool for integrated water resources management and planning

- **MIKE View** - results presentation tool for MOUSE, MIKE SWMM, MIKE NET and MIKE 11

- **MIKE SHE** - integrated hydrological modeling of the entire land phase of the hydrological cycle

- **MOUSE** - for modeling hydrology, hydraulics, water quality and sediment transport in urban drainage and sewer systems

- **MIKE NET** - for modeling water distribution systems. Based on the EPANET numerical engine

- **MIKE SWMM** - for modeling urban hydrology, wastewater and stormwater networks. Based on the EPA SWMM numerical engine

- **EFOR** - for modeling the processes inside wastewater treatment plants

- **MIKE INFO Coast** - GIS-based information management tool for coastal systems

- **MIKE Animator** - advanced animations of DHI Software model results

- **MIKE C-MAP** – a general tool for extracting depth data and tidal information from electronic sea charts

- **MIKE URBAN** – a powerful GIS-embedded modeling tool for water utilities. Includes EPA-NET, SWMM5 and MOUSE engines and integrates with ESRI ArcGIS. One town - one tool!

Photos:
pp2,6,5 DHI, p8 Polfoto, pp2,5 Ole Søndergaard, p4 BAM, pp2,5 Scanpix, pp1,2,3,6 Peter Bondo Christensen, pp4,7 Bjarne Moeslund, p4 Lennert Carlsen, p6 Christian Nørgaard

APPENDIX 12.1 J

Assessment of Biocides

y:\ced reports\ced 2006-reports\53749 dublin waste to energy
project\eis final version 08062006\53749 dublin wte project -
appendix 12-1.doc

DHI Water & Environment

DUBLIN WASTE TO ENERGY
Assessment of biocides

Elsam Engineering

Report 2006

DUBLIN WASTE TO ENERGY
Assessment of biocides

Appendix report
June 2006

Client		Client's representative			
Elsam Engineering		Peter Rom Poulsen			
Project		Project No			
DUBLIN WASTE TO ENERGY		53749			
Authors		Date			
Dorte Rasmussen		June 2006			
		Approved by			
		H. Jacob Vested			
01	Appendix report	DOR	HJV	HJV	09/06/06
Revision	Description	By	Checked	Approved	Date

Key words	Classification
Biocide Cooling Water System Waste to Energy EIS	☐ Open ☐ Internal ☒ Proprietary

Distribution		No of copies
Elsam	Peter Rom Poulsen	1 pdf
DHI	KIG, HJV, DOR	3 pdf

CONTENTS

1 ASSESSMENT OF CHEMICAL IMPACT DUBLIN WTE

1.1 Principles

The impact on the ecosystem caused by the emission of chemicals should be minimised by applying the best available technique (BAT). Relevant (for this chapter) techniques for the reduction of emissions to surface water due to the application of cooling water are (European Commission 2001):

- Selection of less hazardous cooling water chemicals

- Optimised application of cooling water chemicals (optimal dosage plan)

In this chapter, the assessment of the environmental impact of different possible chemicals and dosage plans is described. The results of this assessment can be used in the process of selecting the optimal dosage plans and chemicals.

The chemicals used to prevent scaling and fouling may constitute a risk to the ecosystem. The risk of the chemicals to the environment was assessed following the principles of the EU Technical Guidance Document (TGD) (EU 2003). The TGD describes the principles on how to carry out risk assessment of chemicals in support of the Commission Directive 93/67/EEC on risk assessment for new notified substances, the Commission regulation (EC) 1488/94 on risk assessment for existing substances and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market.

The environmental impact was assessed by calculating the risk quotient defined as the ratio of the Predicted Environmental Concentration (PEC) to the Predicted No Effect Concentration (PNEC). If the risk quotient is above 1, then it cannot be excluded that the chemicals may exhibit a risk to the ecosystem.

The PEC is the concentration of the chemical in the water. This concentration will vary with time and in space.

The PNEC can be described as the highest concentration in the water, at which no effects on the aquatic organisms are expected at a long-term exposure.

The exposure (PEC) and effects (PNEC) were divided into 2 groups:

1. More or less continuous exposure. The average calculated concentration was compared with chronic PNEC - values, which are the highest concentrations in the environment at which no effects are expected even at a continuous exposure.

2. Acute exposures. The maximum calculated concentration was compared with $PNEC_{Acute}$ - values (PNEC for acute toxicity), which was found by multiplying PNEC by 10. This is in accordance with the principles of the TGD (EU 2003).

1.1.1 PEC

The PEC of each chemical was determined on the basis of dosage and the spreading, dispersion and fate of the chemical additives (described in Section 2.1.1). The relevant fate processes of the different chemicals were identified and incorporated in the ECO Lab system, which is an open modelling system for simulation of chemical processes in combination with the DHI hydraulic models. More desription of the ECO lab can be found at http://www.dhigroup.com/Software/WaterResources/ECOLab.aspx.

1.1.2 PNEC

The estimation of PNEC was based on the European principles described in the revised Technical Guidance Document (TGD) on Risk Assessment revised in 2003 (EU 2003). The method uses a series of assessment factors to compensate for the uncertainties, e.g. extrapolation from laboratory to the field, short-term to long-term studies, interspecies variation, and the quality of the data etc.

Preferably, toxicity data on three trophic levels are required (algae, crustaceans and fish) and, if possible, two more trophic levels (molluscs and echinoderms) to determine the PNEC for a compound.

The PNEC is derived on the basis of the lowest reliable effect concentration divided by the assessment factor. The principles of setting the assessment factors as suggested in the TGD were used.

2 BIOCIDES

Two main categories of biocides exist: oxidizing and organic biocides.

2.1.1 Oxidizing biocides

Examples of useful oxidizing biocides are halogens such as chlorine (Cl_2), chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2), ozone.

Hypochlorite is typically dosed by electrolysis of seawater, whereby chlorine gas (Cl_2) is formed. Cl_2 reacts immediately with water and forms hypochlorite.

Chlorine dioxide is also generated on the site. Most commercial generators use sodium chlorite (NaClO2) as the common precursor feedstock chemical to generate chlorine dioxide for drinking water application. Recently, production of chlorine dioxide from sodium chlorate (NaClO3) has been introduced as a generation method where in NaClO3 is reduced by a mixture of concentrated hydrogen peroxide (H2O2) and concentrated sulfuric acid (H2SO4).

H_2O_2 is a very strong oxidizing agent and an effective biocide at very low levels over a wide pH range. The product actively generates oxygen from solution when reacted with certain organic matter. H_2O_2 is generally not used for the treatment of cooling waters because of its high cost and reactivity. It reacts with most materials in cooling systems (such as wood and metals), so that very little residual is left in large systems. In case hydrogen peroxide can be found suitable, low discharge concentrations are expected, due to the highly reactive nature of H_2O_2. H_2O_2 does not degrade as rapidly as chlorine,

and in general it does not form toxic degradation products contributing to the risk quotient.

Ozone (O_3) is also formed on the site. Ozone is thermally unstable and explosive in the gas, liquid, and solid phases. It is a strong oxidising agent and is considered an excellent disinfectant. It has several applications, e.g. in the treatment of cooling-tower water.

2.1.2 Organic biocides

Glutaric aldehyde, bronopol, Sodium pyrithione, quaternary ammonium salts, isothiazolin and glutaric aldehyde are organic based biocides and were included in the initial assessments.

2.2 Fate properties

2.2.1 Sodium hypochlorite

Hypochlorous acid (pK_a = 7.49) and sodiumhypochlorite are strong oxidising agents. Hypochlorous acid reacts very quickly with bromide (Br^-) (reaction times within seconds) and forms hypobromous acid (HOBr) (pK_a = 8.6). The reaction with bromide is almost complete - meaning that all bromide present will be oxidised into hypobromous acid if sufficient hypochlorous acid is present. Both acids will be partly dissociated at the pH of the water. The undissociated part of the acids is generally more reactive than the dissociated part.

The sum of these compounds is often named CPO (Chlorine Produced Oxidants):

$$CPO = HOCl + {}^-OCl + HOBr + {}^-OBr$$

Hypobromite will react in the same pattern as hypochlorite both with inorganic and organic compounds in the water. In general, hypobromite is more reactive than hypochlorite.

In batch experiments, in which chlorine is added to water, a general degradation pathway is observed. Initially, a very rapid removal of the oxidants is followed by a slower and continuous degradation of the oxidant.

The initial rapid degradation is generally assigned to the oxidation of organic compounds (producing, among other species, CO_2), reaction with hydrogen peroxide and with ammonium, of which the latter reaction produces halogenated amines (e.g. mono- and dichloroamine, monobromoamine).

The slower degradation pathway is assigned both to a photochemical decomposition of the oxidants and reactions with organic compounds, with which halogenated organics (AOX) to some extent are formed. Compounds like trihalomethanes (THM), halophenols, mono-, di- and trihaloacetic acids and halogenated small alkanes are of importance.

THM are compounds defined by any possible combination of CHXYZ (where X,Y, Z are the halogens chlor, brom and iod). The quantitatively most important THMs are the combinations of $CHCl_NBr_{(3-N)}$, e.g. bromoform and chloroform. THMs are formed by a

DHI Water & Environment

stepwise halogenation of for example fulvus and humus acids, which are naturally occurring in the water. Between 0.05 and 5.0% of the initial amount of free chlorine will eventually occur as halogenated organic compounds and halogenated amines. The halogenated organic compounds actually formed depend strongly on the concentration and type of organic matter present in the seawater.

The formation of THM takes place as a stepwise halogenation reaction of methyl groups in an organic molecule. The first halogenation step is the slowest and therefore rate determining for the formation of THM. The formation of THM increases with increasing pH (up to a certain level), halogen concentration and temperature. The formation of THM from humus acid has been found to be a first order reaction with respect to the concentration of humus acid.

Within the group of THMs, only the formation of chloroform and bromoform is considered. The other possible THMs might also be formed but, for simplicity, they are not considered. If the predicted amounts of formed chloroform and bromoform are significant, the other possible THMs will also be produced. Other halogenated compounds (mono-, di- and trihaloacetic acids and halogenated small alkanes) will also be formed.

In a survey on the fate of hypochlorite, it was concluded that approximately 1-3% of CPO is converted into AOX and that the ratio of the formed THM to AOX is around 10-30% (Rasmussen 1998). This results in a conversion of hypochlorite into THM of, maximum 0.9%. The formation of THM is a maximum assumed to be between 1-3% of the CPO.

Halophenols were selected as being one of the most important groups of halogenated organics formed from hypochlorite. The formation of halophenols was assumed to be 0.04% of the degraded CPO. This ratio was estimated by assuming the same rate constant for the formation of halophenols and THMs, and by assuming that the amount of formed THMs and halophenols respectively is proportional to the matter, from which its is formed (THM: DOC; halophenols: phenols). Also the formation of haloacetic acids and haloamines was considered. Approximately 1% of the degraded CPO was assumed to be transformed into each of these substances (between 0.05 and 5% of the initial amount of free chlorine will occur as halogenated organic compounds and halogenated amines).

Kinetics
The degradation pathways for chlorine in seawater are very complex, and it is necessary to make simplifications in order to estimate the concentration profiles of CPO, THM and halophenols. Halophenols may be formed in relatively high concentrations.

The simplified pathways are illustrated in Table 2.1.

DHI Water & Environment

Table 2.1   Assumed degradation pathways for hypochlorite

Reaction	Assumed kinetics	Description
$HOCl + Br^- \rightarrow HOBr + Cl^-$	Instant reaction is assumed. The presence of Br^- determines the degree of reaction.	1 mole of Br^- produces 1 mole of hypobromous acid CPO_{Br}.
$X + CPO \rightarrow$ oxidised compounds + halide ions $CPO = CPO_{Cl} + CPO_{Br}$	First order both with respect to X and CPO. X is the sum of all compounds in seawater, which are readily reacting with CPO. The oxidation of X accounts for the first very rapid removal of CPO (halogen oxidants). The reaction rate of bromine and chlorine based oxidants respectively is assumed to be identical.	$\dfrac{dCPO}{dt} = k_1 \cdot X \cdot (CPO_{Br} + CPO_{Cl})$ The background level in normal seawater of X was set to 3.4 mg /L. k_1 is set to: $k_1 = 0.004$ [L/(mg·s)]
$CPO \rightarrow$ halide ions	The slower part of the destruction of the CPO is assumed to follow a second order reaction.	$\dfrac{d[CPO_{Cl}]}{dt} = -k_2 \cdot [CPO_{Cl}]^2$ $\dfrac{d[CPO_{Br}]}{dt} = -k_2 \cdot [CPO_{Br}]^2$ $k_2 = 0.0002$ [mg/(L·s)]
$CPO_{Cl} + DOC \rightarrow CHCl_3$	A first order reaction with respect to the CPO_{Cl} and DOC concentration is assumed. DOC is the concentration of dissolved organic carbon.	2 (1-3) % of the degraded CPO was assumed to be transformed into THM
$CPO_{Br} + DOC \rightarrow CHBr_3$	A first order reaction with respect to the CPO_{Br} and the DOC concentration is assumed. DOC is the concentration of dissolved organic carbon.	
$CPO_{Br} / CPO_{Cl} +$ phenol halogenated phenols	A first order reaction with respect to the CPO_{Br} and the phenol concentration is assumed.	0.04% of the degraded CPO was assumed to be transformed into halophenols
$CPO_{Br} / CPO_{Cl} \rightarrow$ haloacetic acids		0.3% of the degraded CPO was assumed to be transformed into trichloroacetic acid
$CPO_{Br} / CPO_{Cl} + NH_3/NH_4^+ \rightarrow$ haloamines		1% of the degraded CPO was assumed to be transformed into monochloroamine

DHI Water & Environment

2.2.2 *Chlorine dioxide*

Byproducts from the use of chlorine dioxide include chlorite, chlorate, and organic halogenated compounds.

Chlorite and chlorate are produced in varying ratios as end products during chlorine dioxide treatment and subsequent degradation.

Chlorine dioxide generally produces fewer organic DBPs than chlorine. In some studies, a production of THMs could not be monitored. Chlorine dioxide produces only a small amount of total organic halide (TOX).

80% of the degraded chlorine dioxide was assumed to be converted into chlorite and 6% of the formed chlorite was assumed to be converted into chlorate.

The degradation rate of the chlorine dioxide as assumed to follow the following pattern:

$$\frac{dClO_2}{dt} = (2045 \cdot ClO_2^2 + 144 \cdot ClO_2) \cdot ClO_2 \text{ (mg per L per day)}$$

This equation was derived on the basis of data given in (EPA, 1999).

2.2.3 *Hydrogen peroxide (H₂O₂)*

Hydrogen peroxide (H_2O_2) is generally considered an ecologically desirable pollution-control agent because it does not form toxic by-products and yields only water and oxygen on decomposition.

H_2O_2 is a strong oxidising agent. It is an acid with a pKa of 11.75 (Kirk-Othmer 2003). It is completely miscible with water and has a low Henry's law constant of $7.04 \cdot 10^{-9}$ atm m³/mol at 25°C (HSDB 2003). Therefore, H_2O_2 does not tend to evaporate from water solution.

Surface water levels of H_2O_2 range from 0.34 to 109 μg/m³ (Kirk-Othmer 2003). In the environment, H_2O_2 can be decomposed by various oxidation or reduction processes to oxygen or water at rates that depend on pH, temperature, the presence of cataytic material (ions of transition metals, solid metals, activated carbon, enzymes, etc.) alkaline conditions, organic substances, heat and sunlight. The half-life of H_2O_2 in seawater samples from the Bay of Biscay (filtered 0.2 μm) was 60 hours (IUCLID 2000). The half-life of H_2O_2 in freshwater (initial concentration 3.4 μg/L) was 7.8 hours (unfiltered) and 31 hours (filtered, 1 μm) (IUCLID 2000). Laboratory studies on water from the River Saone (France) showed that H_2O_2 degradation kinetics were of first order and that the half-life is influenced by the initial H_2O_2 concentration (IUCLID 2000). It could be shown that the size of the microbial population in water has a significant effect on the degradation rate (IUCLID 2000).

H_2O_2 occurs naturally as a result of photochemical processes involving free radicals, organic matter and molecular oxygen. In the absence of light, H_2O_2 may be formed in water through the oxidation of iron and copper (Weiss mechanism). The actual concentration of H_2O_2 in the environment results from a dynamic equilibrium between its production and consumption caused by other degradation reactions. The rate of forma-

tion and degradation of H_2O_2 in seawater varies widely from 0.34–17 µg/L/hour. Similar rates, 2–12 µg/L/hour were found in fresh water. Endogenous H_2O_2 levels in plant tissues are relatively high. It has been found that blue–green algae produce H_2O_2 at a rate of 1–50 µg/L/hour under light irradiation; for *Nostoc muscorum* the rate was 0.9 nM/µL cells. *Hymenomonas carterae* (phytoplankton) formed H_2O_2 at 0.034–0.068 µg/L/hour (IUCLID 2000).

Kinetics

A first order degradation rate was assumed in the present study. As already mentioned, the decomposition rate depends on the presence of impurities such as metals and organic matter. According to the above, the highest degradation rate is thus found in unfiltered water, and it is probably higher in fresh water than in seawater (about a factor of 2 according to the reported half-lives of 60 hours in seawater and 31 hours in fresh water, respectively). In the present study a half-life of 15.6 hours was used corresponding to twice the observed half-life in fresh water (7.8 hours).

DHI Water & Environment

2.2.4 Ozone

Ozone (O_3) is an allotropic form of oxygen. Ozone is thermally unstable and explosive in the gas, liquid, and solid phases. It is a strong oxidising agent and is considered an excellent disinfectant. It has several applications, e.g. in the treatment of cooling-tower water.

Ozone has a water solubility of 1.1 g/L and has a Henry's law constant following the equation (Kirk-Othmer 2003):

ln H (kPa L/Mol) = -2297/T + 2.659·I - 688·I/T + 16.808,

where

T   is the temperature (Kelvin)

I   is the molar ionic strength.

Henry's law constant is estimated to be 0.08 atm m^3/mol at an ionic strength of 0.18 mol/L and a temperature of 20°C. Volatilisation of ozone from the water column may thus be an important removal mechanism.

Ozone decomposes with a complex radical chain mechanism, initiated by hydroxyl ion (OH$^-$) and propagated by O_2^- radical ions and HO radicals. The decomposition in natural water can also be initiated by trace metal ions, e.g. Fe^{2+}, promoted by impurities such as organic matter, and inhibited by HO radical scavengers, e.g. carbonate and phosphate.

Ozone may oxidise halide ions. The oxidation increasing with the atomic number of the halide. Fluoride is unreactive; chloride reacts slowly, ultimately forming chlorate; bromide is readily oxidised to hypobromite (O_3 + Br$^-$ → O_2 + BrO$^-$) (Kirk-Othmer 2003). As iodide is not present in surface water at high concentrations (the most abundant form of iodine in seawater is iodate), oxidation of iodide is not expected to be significant in the Dublin Bay. Hypohalites and halides may be formed from the chlorate and bromate as well.

Photolysis of ozone in the aqueous phase can initially produce hydrogen peroxide. At high pH, at which the concentration of free ammonia is higher, ozone may oxidise ammonia to nitrate (4 O_3 + NH$_3$ → H$^+$ + NO$_3^-$ + H$_2$O + 4O$_2$, k ≈ 5 L/Mol·s) but this reaction is not considered to be a quantitatively important reaction. Ozone also oxidises mercaptans, thioethers, disulphides, primary aminocompounds, nitrocompounds etc. These reactions are, however, not considered quantitatively important either.

Kinetics
The degradation reactions considered the most important for ozone are shown in Table 2.2. The degradation rate expressions and constants are shown in the table as well.

DHI Water & Environment

Table 2.2   Degradation of ozone. Kinetics primarily from Kirk-Othmer 2003

Reaction	Kinetics
Decomposition: $O_3 + OH^- \rightarrow HO_2 + O_2$	$\dfrac{dO_3}{dt} = -k_{O_3,OH^-} \cdot [OH^-] \cdot [O_3]$ $k_{O_3,OH^-} = 70 \, L/(Mol \cdot s)$
$O_3 + Br^- \rightarrow O_2 + BrO^-$	$\dfrac{dO_3}{dt} = -k_{O_3,Br^-} \cdot [Br^-] \cdot [O_3]$ $k_{O_3,Br^-} = 160 \, L/(Mol \cdot s)$
$O_3 + BrO^- \rightarrow 2\,O_2 + Br^-$	$\dfrac{dO_3}{dt} = -k_{O_3,BrO^-} \cdot [BrO^-] \cdot [O_3]$ $k_{O_3,BrO^-} = 330 \, L/(Mol \cdot s)$
$O_3 + ClO^- \rightarrow 2\,O_2 + Cl^-$	$\dfrac{dO_3}{dt} = -k_{O_3,ClO^-} \cdot [ClO^-] \cdot [O_3]$ $k_{O_3,ClO^-} = 100 \, L/(Mol \cdot s)$
$O_3 + BrO^- \rightarrow 2\,O_2 + BrO_3^-$	$\dfrac{dO_3}{dt} = -k'_{O_3,BrO^-} \cdot [BrO^-] \cdot [O_3]$ $k'_{O_3,BrO^-} = 100 \, L/(Mol \cdot s)$
$O_3 + ClO^- \rightarrow 2\,O_2 + ClO_3^-$	$\dfrac{dO_3}{dt} = -k'_{O_3,ClO^-} \cdot [ClO^-] \cdot [O_3]$ $k'_{O_3,ClO^-} = 30 \, L/(Mol \cdot s)$
Volatilisation: $O_3(water) \rightarrow O_3$ (air) (Only considered to take place in the upper layer)	$\dfrac{dO_3}{dt} = \dfrac{-k_{vola} \cdot [O_3]}{dz}$ $k_{vola} = \dfrac{1}{\dfrac{1}{k_w} + \dfrac{1}{k_a \cdot \dfrac{H}{R \cdot T}}} \, (m/s)$ $k_w = 3.3 \cdot 10^{-6} + 3.3 \cdot 10^{-7} \cdot U \,(m/s)$ $k_a = 0.001 \cdot U + 0.0016 \,(m/s)$ U is the wind speed (m/s)

Consent of copyright owner required for any other use.

Pilot calculations using the above equations showed that

- The volatilisation and decomposition reactions are of minor importance

- The ozone is almost completely converted into hypobromite, in the situation, where the concentration of ozone (mole/L) is below about 1% of bromide concentration [mole/L] (see Figure 2.1)

- That the formation of hypobromite reaches steady-state very quickly and that the concentration of hypobromite is approximately 36% of the bromide concentration, when ozone is added in very much higher concentrations than the bromide concentration
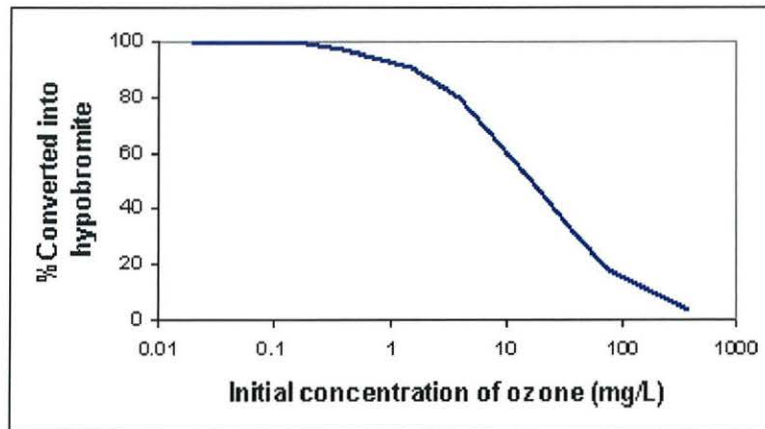
Figure 2.1   Calculated conversion of the ozone into hypobromite. Bromide concentration was fixed a 65 mg/L.

As the concentration of ozone in the receiving water body is expected to decrease down to concentrations below 1% of the concentration of bromide in the water very quickly (corresponding to an ozone concentration of approximately 0.4 mg/L), all ozone is assumed instantaneously to be converted into hypobromite. In this case the degradation and dilution pattern follows the degradation and dilution pattern of hypochlorite (Section 2.2).

2.2.5   Glutaric aldehyde

Glutaric aldehyde (CAS-RN: 111-30-8) is an organic compound identified as being readily biodegradable (IUCLID 2000). It has a low log K_{OW} (below zero) and is thus not suspected of being bioaccumulative or of sorbing to organic matter. It is miscible with water and has a vapour pressure of 0.3 mmHg at 30°C and, therefore, it does not tend to evaporate from a water solution.

Kinetics

Biodegradation is considered to be the most important removal process of glutaric aldehyde (Table 2.3). The degradation rate expression and constant are shown in the table as well.

Table 2.3   Degradation of glutaric aldehyde

Reaction	Comments	Kinetics
Biodegradation Glutaric aldehyde (GI) → degradation products	The value recommend by the TGD (EU 2003) for readily biodegradable compounds used	$\dfrac{d[GI]}{dt} = -k_{GI} \cdot [GI]$ $k_{GI} = 0.014 \ d^{-1}$

2.2.6   Quaternary ammonium salts

Several different quaternary ammonium salts exist. In this study benzalkonium chloride (ADMBAC) was selected as the model compound:

DHI Water & Environment

The substance is involatile and will not evaporate from the water column.

The biodegradability of (ADMBAC) decreases with the length of the alkyl chain length, where the biodegradation is very limited at chain length above 14. In this study, a chain length of 12-14 was assumed.

The substance can be characterised as readily biodegradable at aerobic conditions but it is not biodegradable at anaerobic conditions (Madsen et al. 2001).

Due to its positive charge, the compound will adsorb strongly to suspended matter and sediment.

The compound has a log K_{OW} close to 5 and is therefore possibly also bioaccumulative.

Biodegradation and sedimentation are considered to be the most important removal processes of quaternary ammonium salts (Table 2.4). The degradation rate expressions and constants are shown in the table as well.

DHI Water & Environment

Table 2.4   Degradation of quaternary ammonium salts (model compound ADMBAC)

Reaction	Comments	Kinetics
Biodegradation ADMBAC → degradation products	The value recommend by the TGD (EU 2003) for readily biodegradable compounds used	$$\frac{d[ADMBAC]}{dt} = -k_{ADMBAC} \cdot [ADMBAC]$$ $$k_{ADMBAC} = 0.014\ d^{-1}$$
Sedimentation		$$\frac{d[ADMBAC]}{dt} = -k_{Sed,ADMBAC} \cdot [ADMBAC]$$ $$k_{Sed,ADMBAC} = \frac{V_s \cdot K_D \cdot SS}{dz \cdot (1 + SS \cdot K_D)}$$ SS = concentration of suspended matter V_s = sedimentation rate (kg/day/m^2) dz = thickness of the "box" K_D = 10 m^3/kg (set to a high value)

2.2.7 Isothiazolin

The studied isothiazolin is a mixture of two compounds: 5-Chloro-2-methyl-4-isothiazolin-3-one (CAS-RN : 26172-55-4) and 2-Methyl-4-isothiazolin-3-one (CAS-RN : 2682-20-4).

2-Methyl-4-isothiazolin-3-one is considered not readily but inherently biodegradable (Bashir 1998a). As it has an estimated log K_{OW} of -0.83 (US EPA 2000), it is not considered a bioaccumulative or sorbing compound. It is highly soluble in water (estimated water solubility above 500 g/L) and a low estimated Henry's law constant ($<10^{-7}$ atm m^3/mol) and therefore, volatilisation from the water column is not considered an important removal process.

5-Chloro-2-methyl-4-isothiazolin-3-one is not readily biodegradable (Bashir 1998b), as the substance did not pass the requirements of 60% degradation within a 10 - day window. In a test for readily biodegradability, 62% were biodegraded within 28 days. As it has a log K_{OW} of -0.71 (IUCLID 2000), it is not considered a bioaccumulative or sorbing compound. It is highly soluble in water (water solubility above 5 g/L (IUCLID 2000)) and as it has a low estimated Henry's law constant ($<10^{-7}$ atm m^3/mol), volatilisation from the water column is not considered an important removal process.

Kinetics

Biodegradation is considered the most important removal process of the two isothiazolines (Table 2.2). The applied degradation rate expressions and constants are shown in the table as well.

DHI Water & Environment

Table 2.5   Degradation of isothiazolines

Reaction	Comments	Kinetics
Biodegradation 2-Methyl-4-isothiazolin-3-one (Iso$_1$)→ degradation products	The value is recommend by the TGD (EU 2003) for readily biodegradable but failing 10 - day window compounds applied. The compound does not fulfil this criteria but is assumed too conservative to assume no biodegradation of the compound.	$\dfrac{d[Iso_1]}{dt} = -k_{ISO_1} \cdot [Iso_1]$ $k_{Iso_1} = 0.0046 \ d^{-1}$
5-Chloro-2-methyl-4-isothiazolin-3-one (Iso$_2$) → degradation products	The value is recommend by the TGD (EU 2003) for readily biodegradable but failing 10 - day window compounds	$\dfrac{d[Iso_2]}{dt} = -k_{ISO_2} \cdot [Iso_2]$ $k_{Iso_2} = 0.0046 \ d^{-1}$

2.2.8   *Bronopol*

Bronopol is only inherently biodegradable. It releases formaldehyde, which is a biocide as well. Due to is relatively poor degradability, high dosage rate needed and relatively low PNEC-value (see next section), it was not further studied.

2.2.9   *Sodium pyrithione*

The most important degradation pathway for sodium pyrithione is photolysis with a measured photolytic half-life of 0.25 hours (is dependent of time of the year, lattitude, cloudiness).

2.2.10   *Simulation of biocides*

The above process (kinetics) descriptions for Hypochlorite and Clorine dioxide were implemented in the MIKE 3 Ecolab equation module and solved simultaneously with the hydrodynamic transport equations thus taking into account production of by products, degradation in the environments and hydrodynamic dilution.

2.3   **Effects**

The ecotoxicity data for the substances are summarized below. They were collected from AQUIRE (http://www.epa.gov/ecotox/), IUCLID (http://ecb.jrc.it/ESIS/)). The data set includes freshwater as well as marine species.

The ecotoxicological profiles of the chemicals and their main degradation products are given in Table 2.6.

The effect data used to derive the PNEC-values are given in Table 2.7. In all cases, the lowest available LC/EC50 value for each of the five previously mentioned trophic levels (algae, crustaceans and fish, molluscs and echinoderms) has been selected and, if possible, also the NOEC value. The lowest of all values on each compound (indicated in boldface in Table 2.7) was used for the determination of PNEC.

Table 2.6 *Ecotoxicological profile of the chemicals and their main degradation products. The numbers in brackets are the CAS-RN of the compounds. Substances in italics are degradation products.*

Substance (parent substance in bold, degradation products in italic)	PNEC (µg/L)	Potential for bio-accumulation	Persistency
Sodium hypochlorite [10022-70-5, 7681-52-9]	0.003	Not expected to bioaccumulate	Very reactive, does not persist in water
Bromoform [75-25-2]	2.9	Not expected to bioaccumulate	Is expected to evaporate from the water column. Anaerobic biodegradation may also occur but aerobic biodegration is not expected to be significant
Chloroform [67-66-3]	5.6	Not expected to bioaccumulate	Is expected to evaporate quickly from the water column
Chloroacetic acid [79-11-8]	0.0028	Not expected to bioaccumulate	Will not persist in water
Dichloroacetic acid [79-43-6]	10.6	Not expected to bioaccumulate	Will not persist in water
Trichloroacetic acid [76-03-9]	0.12	Not expected to bioaccumulate	Is not expected to degrade rapidly in water, so some persistency can be expected
Chloramine [10599-90-3]	0.0012	Not expected to bioaccumulate	Very reactive, does not persist in water
Halophenols. 2,4-dichlorophenol [120-83-2] was selected as model compound for the group	0.1	Some of the formed halophenols may bioaccumulate	Some halophenols are persistent (the persistency increases with the number of halogens in the molecule)
Hydrogen peroxide [7722-84-1]	0.09	Not expected to bioaccumulate	Very reactive, does not persist in water
Ozone [10028-15-6]	0.93	Not expected to bioaccumulate	Very reactive, does not persist in water
Hypobromite and the same degradation products as for hypochlorite will be formed.		Some halophenols may bioaccumulate	Very reactive, does not persist in water
Chlorine dioxide [10049-04-4]	0.04	Not expected to bioaccumulate	Very reactive, does not persist in water
Chlorite [7758-19-2]	0.9	Not expected to bioaccumulate	

DHI Water & Environment

Substance (parent substance in bold, degradation products in italic)	PNEC (µg/L)	Potential for bio-accumulation	Persistency
Chlorate [7775-09-9]	1.0	Not expected to bioaccumulate	
Glutaric aldehyde [111-30-8]	0.061	Not expected to bioaccumulate	As readily biode-gradable, it is not expected to persist in the water ecosys-tems
5-chloro-2-methyl-4-isothiazolin-3-one [26172-55-4]	0.0021	Not expected to bioaccumulate	As inherently bio-degradable, it is not expected to persist in the water ecosys-tems
2-Methyl-3(2H)-isothiazolone [2682-20-4]	0.005	Not expected to bioaccumulate	As readily biode-gradable, it is not expected to persist in the water ecosys-tems
Quaternary ammonium salt (ADMBAC)	0.002	May bioaccumulate	As readily biode-gradable, it is not expected to persist in the water ecosys-tems
Bronopol	0.05	Not expected to bioaccumulate	Only inherently bioddegradable
Sodium pyrithione	0.015	Not expected to bioaccumulate	Fast photolytic deg-radation

Table 2.7   Ecotoxicity data for selected chemicals. The numbers in the brackets are the CAS-RN of the chemical. The data selected for deriving the PNEC value are indicated in bold. The sub-stances in bold are degradation products. Data from Aquire and IUCLID.

Compound	Species	Parameter	Exposure period	Acute/ Chronic	Value (mg/L)
Sodium hypochlorite [10022-70-5, 7681-52-9]	**Algae**				
	Dunaliella	EC50	24 h	Acute	0.11
	Crustacean				
	Ceriodaph-nia Dubia	**LC50**	**24 h**	**Acute**	**0.005**
	Ceriodaphnia dubia	NOEC	11 d	Chronic	0.048
	Fish				
	Oncorhyn-chus mykiss	LC50	96 h	Acute	0.059
	Mollusc				
	Dendraster sp.	EC50	5 min	Acute	0.002

DHI Water & Environment

Compound	Species	Parameter	Exposure period	Acute/ Chronic	Value (mg/L)
Bromoform [75-25-2] log K_{OW} = 2.4	**Algae**				
	Skeletonema costatum	EC50	96 h	Acute	12.3
	Crustacean				
	Daphnia magna	LC50	48 h	Acute	46
	Fish				
	Cyprinodon variegatus	LC50	96 h	Acute	7.1
	Cyprinodon variegatus	**NOEC**	**96 h**	**Acute**	**2.9**
Chloroacetic acid [79-11-8] log K_{OW} = 0.22	**Algae**				
	Scenedes- mus sp.	**EC50**	**48 h**	**Acute**	**0.028**
	Crustacean				
	Daphnia magna	EC50	48 h	Acute	77
	Daphnia magna	NOEC	21 d	Chronic	32
	Fish				
	Pimephales promelas	LC50	96 h	Acute	145
Dichloroacetic acid [79-43-6] log K_{OW} = 0.92	**Algae**				
	Scenedes- mus sp.	EC03	7 d	Chronic	1,485
	Crustacean				
	Daphnia magna	**EC50**	**24 h**	**Acute**	**106**
Trichloroacetic acid [76-03-9] log K_{OW} = 1.33	**Crustacean**				
	Streptoce- phalus sp.	**LC50**	**24 h**	**Acute**	**1.2**
	Fish				
	Trout	LC50	96 h	Acute	1,050
Trichloromethane [67-66-3] log K_{OW} = 1.97	**Algae**				
	Selenastrum	EC50	5 d	Acute	1.0
	Selenastrum	**NOEC**	**5 d**	**Chronic**	**0.56**
	Crustacean				
	Daphnia magna	EC50	48 h	Acute	51.6
	Daphnia magna	NOEC	21 d	Chronic	6.3
	Fish				
	Lepomis	LC50	96 h	Acute	13.3
	Oncorhyn- cus mykiss	NOEC	96 h	Acute	42
2,4 dichlorophe- nol [120-83-2] log K_{OW} = 3.06	**Algae**				
	Chlorella vulgaris	EC50	96 h	Acute	9.2
	Crustacean				
	Daphnia magna	EC50	48 h	Acute	1.4

Compound	Species	Parameter	Exposure period	Acute/ Chronic	Value (mg/L)
	Allorchestes compressa (marine)	NOEC	**21 d**	**Chronic**	**0.05**
	Fish				
	Carassius auratus	LC50	96 h	Acute	1.24
	Oncorhyn-chus mykiss	NOEC	85 d	Chronic	0.1
Chloramine [10599-90-3] log K_{OW} = -1.19 (estimated)	Mollusc				
	Corbicula manilens	LC50	48 h	Acute	0.078
	Crustacean				
	Ceriodaph-nia dubia	**LC50**	**24 h**	**Acute**	**0.012**
	Fish				
	Oncorhyn-chus mykiss	LC50	96 h	Acute	0.053
Chlorine dioxide [10049-04-4] log K_{OW} = -3.22 (estimated)	Algae				
	Clado-phora	NR	24 h	Acute	2.6
	Crustacean				
	Daphnia Pulex	EC50	48 h	Acute	1.8
	Fish				
	Paralabrax sp.	NR	48 h	Acute	2.5
	Mollusc				
	Dreissena polymorpha	**LC50**	**96 h**	**Acute**	**0.35**
	Echinoderm				
	Strongylo-centrotus sp.	LC50	48 h	Acute	2.5
Chlorite [7758-19-2]	Algae				
	Pseudo. subcapitata	**EC50**	**96 h**		**0.9**
	Crustacean				
	Daphnia Magna	EC50	48 h	Acute	0.9
	Fish				
	Cyprinodon variegatus	LC50	96 h	Acute	75
	Mollusc				
	Dreissena polymorpha	NR	24-96 h	Acute	5
	Fungi				
	Trichoderma hamatum	NOEC	48 h	Acute	48
Chlorate [7775-09-9]	Algae				
	Pseudo. sub-capitata	EC50	72 h		133
	Ectocarpus variabilis	**NOEC**	**14 d**		**1.5**
	Crustacean				

DHI Water & Environment

Compound	Species	Parameter	Exposure period	Acute/ Chronic	Value (mg/L)
	Daphnia magna	LC50	48 h		3162
	Fish				
	Oncorhynchus masou	LC50	96 h	Acute	1100
	Insect				
	Asellus hilgendorfi	LC50	96 h	Acute	2424
	Fungi				
	Penicillium verrucosum	NOEC	48 h		796
5-Chloro-2-methyl-4-isothiazolin-3-one [26172-55-4] log K_{OW} = -0.71	**Algae**				
	Skeletonema Costatum	**EC50**	**72 h**	**Acute**	**0.021**
	Crustacean				
	Daphnia magna	EC50	48 h	Acute	0.021
	Fish				
	Oncorhynchus mykiss	LC50	96 h	Acute	0.19
	Mollusc				
	Crassostrea	EC50	96 h	Acute	89
Hydrogen peroxide [7722-84-1]	**Algae**				
	Blue green	**EC50**	**22 h**	**Acute**	**0.9**
	Crustacean				
	Daphnia magna	EC50	48 h	Acute	2.4
	Fish				
	Oncorhynchus mykiss	LC50	96 h	Acute	22
	Mollusc				
	Dreissena polymorpha	LT50	28 h	Acute	30
2-Methyl-4-Isothiazolin-3-one [2682-20-4] log K_{OW} = -0.83	**Algae**				
	Skeletonema costatum	**EC50**	**72 h**	**Acute**	**0.05**
	Crustacean				
	Acartia tonsa	LC50	48 h	Acute	0.056
	Fish				
	Oncorhynchus mykiss	LC50	96 h	Acute	0.07
Ozone [10028-15-6]	**Fish**				
	Oncorhynchus mykiss	**LC50**	**96 h**	**Acute**	**9.3**

2-18

Compound	Species	Parameter	Exposure period	Acute/ Chronic	Value (mg/L)
Glutaric aldehyde [111-30-8] log K_{OW} = -0.18 (estimated)	**Algae**				
	Scenedes-mus sp.	EC50	72 h	Acute	0.61
	Crustacean				
	Daphnia magna	EC50	48 h	Acute	0.75
	Fish				
	Oncorhyn-chus mykiss	LC50	96 h	Acute	3.5
	Mollusc				
	Crassostrea	EC50	96 h	Acute	0.78
ADMBAC log K_{OW} ≈ 5	**Algae**				
	Scenedes-mus sub-spicatus	EC50	72 h	Acute	0.024 (C8-18)
	Crustacean				
	Daphnia magna	LC50		Acute	0.057 (C8-18)
	Fish				
	Lepomis macrochirus	LC50	96 h	Acute	0.31 (C8-18)

2.4 Selection of biocides

Table 2.8 shows the profile of the biocides. The approximate required dilution to reach PNEC –neglecting degradation - is also shown.

Apparently, ozone requires the lowest dilution. According to the BREF, "ozone is successfully applied in relatively smaller volumes of recirculating wet systems, but they require specific process conditions and can be quite costly. The use of ozone needs pretreatment of the make-up water and needs special materials. The application needs special care, is expensive and not applicable in all situations". Due to these consideration, ozone was not included in the assessments.

Chlorine/hypochlorite and chlorine dioxide requires a much higher dilution factor than ozone. But these substances are quickly degraded in the environment. Therefore the actually required dilution will be much lower.

Of the organic biocides, only glutaraldehyde requires a dilution below 5000. For the initial assessments, this substance was not included, but it could be an option for further considerations.

The remaining organic biocides were excluded for further studies, as they have a high persistency in the environment and requires a high dilution factor.

DHI Water & Environment

Table 2.8   Profile of biocides

Biocides	Dosage mg/L	Duration hours	PNEC ug/L	Dilution required
Chlorine/NaCl/ hypochlorite	1-5	24	0.005	600000
Chlorine dioxide	1-5	24	0.04	75000
Ozone (O3)	500 – 1000 0.02-0.2	24	0.91	220
H2O2/peracetic acid	1-5	24	0.09	55556
Bronopol	10-100	1	0.05	45833
Glutaraldehyde	20-100	0.08	0.061	3279
Na-Pyrithione	200-400	2	0.015	1666667
Quaternary ammonium	3-50	2	0.002	125000
Isothiazolone	50-250	6	0.003	4166667

3   REFERENCES

AQUIRE (2003): On-line database: http://www.epa.gov/ecotox/

Bashir M (1998a): Covance laboratories Inc., Madison, WI.Rohm and Haas. Technical Report No. TR-97-076.

Bashir M (1998b): Covance laboratories Inc., Madison, WI.Rohm and Haas. Technical Report No. TR-97-15.

BREF. European Commission (2001): Integrated Pollution Prevention and Control (IPPC). reference Document on the application of Best Available Techniques to Industrial Cooling Systems.

European Commission (2003): Technical Guidance Document on risk assessment in support of Commission Directive 93/67/EEC on risk assessment for new notified substances and Commission Regulation (EC) no 1488/94 on risk assessment for existing substances and Directive 98/8/ECof the European Parliament and of the Council concerning the placing of biocidal products on the market.

IUCLID (2000): Public data on high volume chemicals. Joint research centre, European Chemicals Bureau. Ispra, Italy. Year 200 edition. 2000 CD-ROM.

IUCLID (2003): On-line database: http://ecb.jrc.it/ESIS/

Kirk-Othmer (2003). Online handbook: http://www.mrw.interscience.wiley.com/kirk/

DHI Water & Environment

Madsen T, Boyd HB, Nylen D, Pedersen AR, Petersen G, Simonsen F (2001): Environmental Project No. 615, Danish Environmental Protection Agency, Ministry of Energy and Environment, Copenhagen, pp.201

Rasmussen D. (1998): Evaluation (review) of literature on the effects of hypochlorite on the environment. Report to the Danish EPA.

US EPA (1997): EPA Guidance manual. Alternative Disinfectants and Oxidants.

US EPA (2000): EPI Suite. Down-loaded from:
http://www.epa.gov/oppt/exposure/docs/episuitedl.htm

DHI Water & Environment