

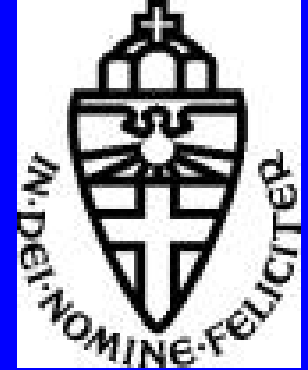
**Better biocide delivery to fouling surfaces:
reaching the interface from within**

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Objectives

- ▶ **Different fouling control methods**
- ▶ **Chlorine vs Mussels**
- ▶ **Evaluation of porous ceramic surfaces in relation to fouling control**
- ▶ **Porous ceramic surfaces – Pros and Cons**



Biofouling

Biofouling - the unwanted growth of plants and animals on the surfaces

Note: Ships collect biofouling on their hulls largely during their stay in ports and harbours; fouling build-up during transit is generally minimal, owing to shear forces.

Major biofouling species (East Coast)

Green mussels (*Perna viridis* and
P. perna)

Barnacles (*Megabalanus tintinnabulum*
and *Balanus reticulatus*)

Oysters (*Crassostrea madrasensis*)

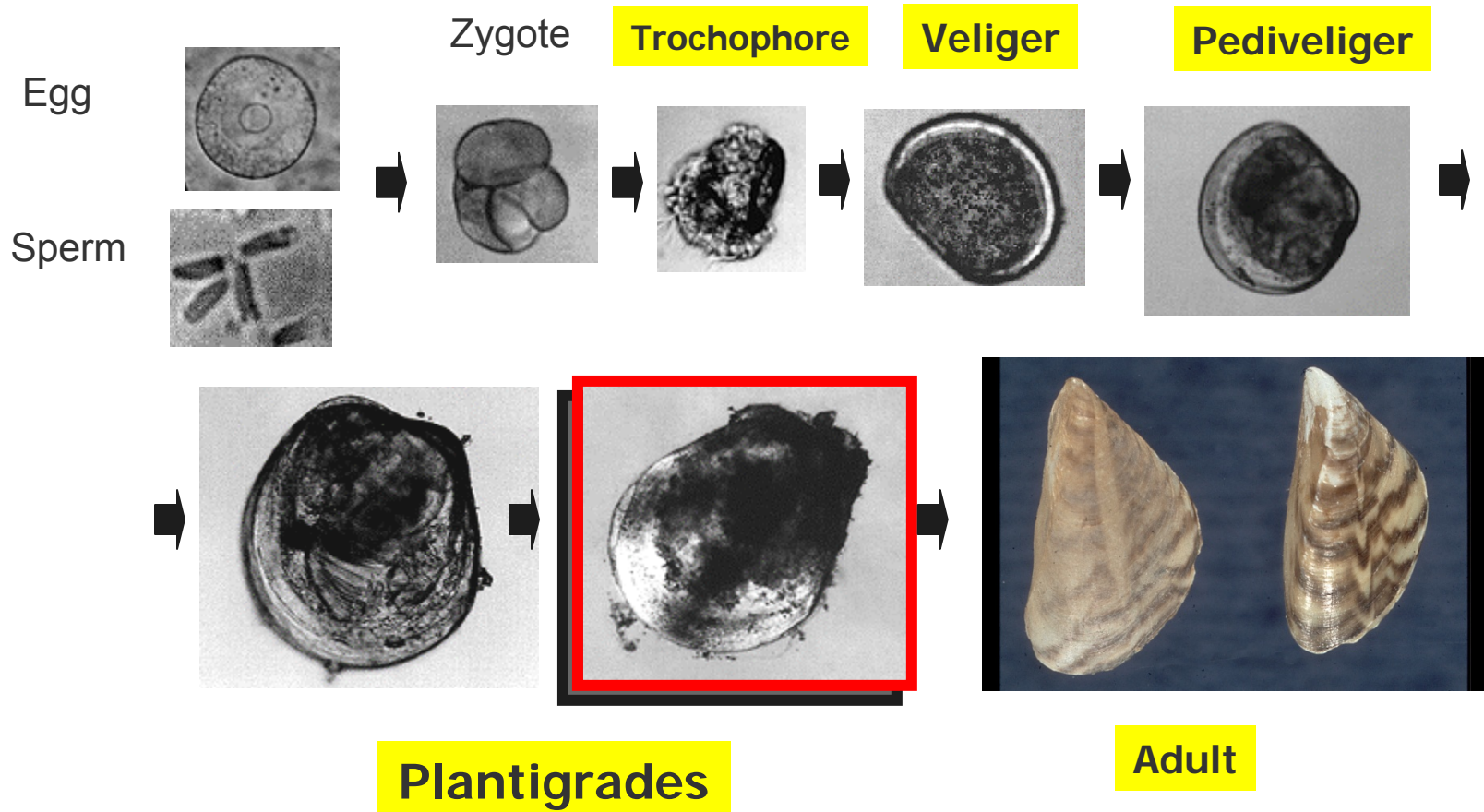
Other bivalves (*Mytilopsis sallei*,
Brachidontes & *Modiolus* spp.)

IMPORTANCE OF FLOW FOR MUSSELS

Water flow is required for:

- 1) Supplying larvae to the substratum**
- 2) Reaching food to attached organisms**
- 3) Higher growth rate**
- 4) Oxygen replenishment**
- 5) Waste removal**

MUSSEL: LIFE HISTORY STAGES



BIOFOULING CONTROL

MUSSEL
CONTROL

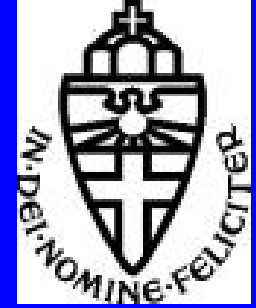
Physical

Chemical

Biological

Heat
Treatment

Chlorination



What is ideal antifoulant ?

The **ideal antifoulant** would prevent fouling from a wide variety of marine organisms **without causing harm to non-target organisms**

CHLORINATION - ADVANTAGES

Chlorination - best available technique (BAT) in anti-fouling

- **proven efficacy**
- **large industrial experience**
(time & instrumentation)
- **relative costs**
- **no or minor ecological consequences**
(Pulse-Chlorination[®])
- **rapid decay in the outlet area**

Optimisation: reduction in environmental impact and costs is possible

Acute toxic effects

Freshwater: acute toxicity level at 10 min. dosing time ~ 0.3 mg/L (FO) = about dosing level for mitigation zebra mussel (*Dreissena polymorpha*) in the Netherlands

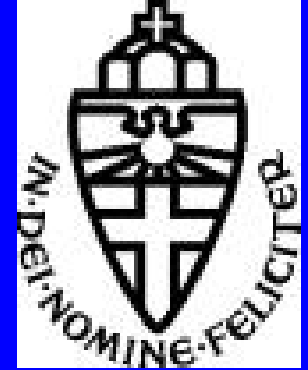
Seawater: acute toxicity level at 10 min. dosing time ~ 0.35 mg/L (TRO) = lower concentration level at Pulse-Chlorination. Long-term effects at < 0.20 mg/L (TRO)



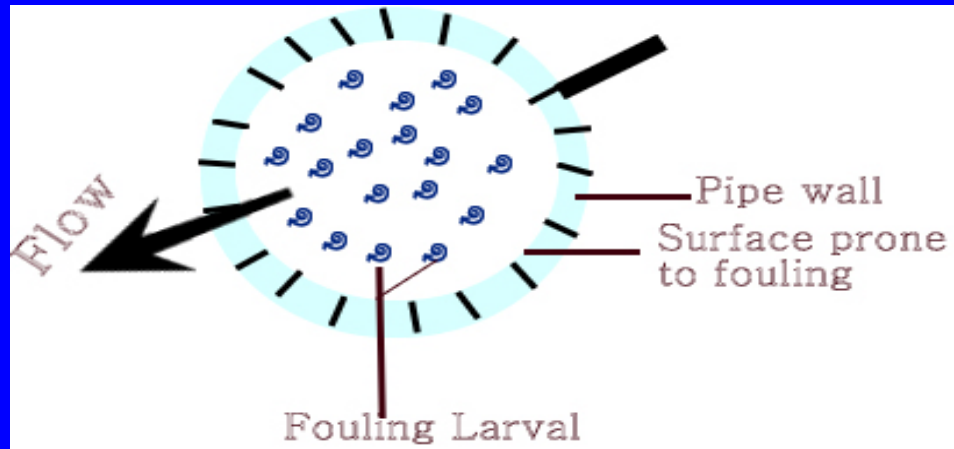
Methodology

- We used porous surfaces to serve as a biocide delivery vehicle
- Porous ceramic surfaces - new class of materials - produced from a variety of starting materials and processed in different ways to yield products with a broad range of physical-chemical characteristics and an equally large range of applications
- The robust character of ceramic membranes enables them to withstand broad pH and temperature ranges, elevated pressures, organic solvents, and chemical and heat sterilization
- Pore size can be controlled in these materials

Note: Ceramic based delivery vehicles are successfully being used for application of sparingly soluble biocides such as ozone

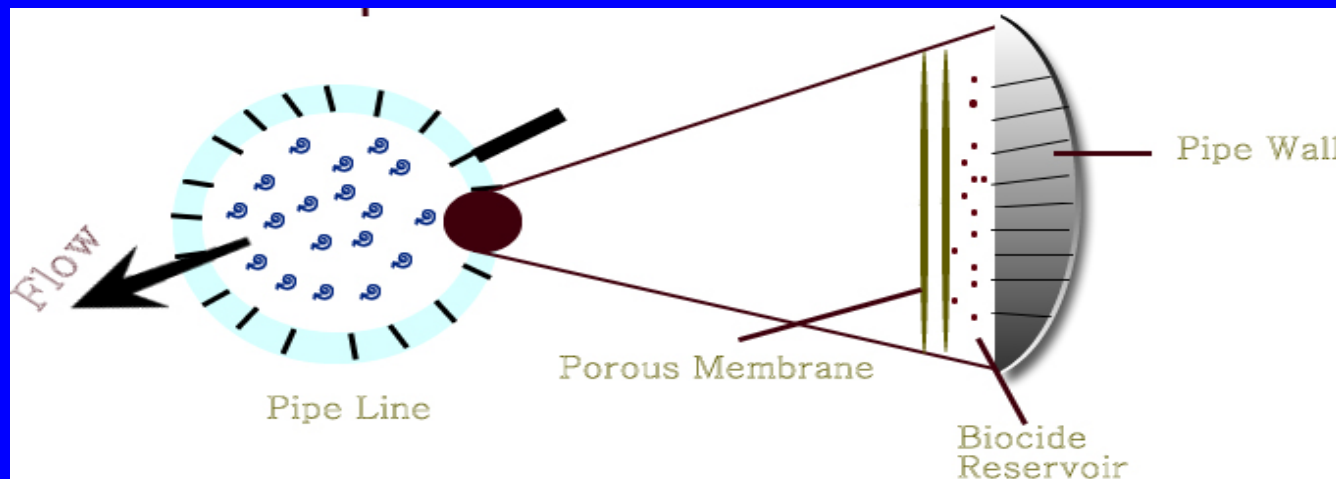
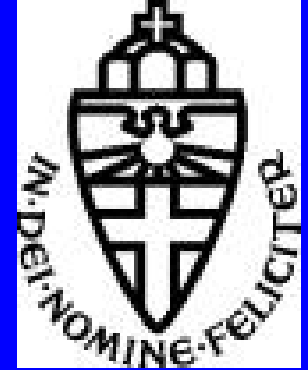


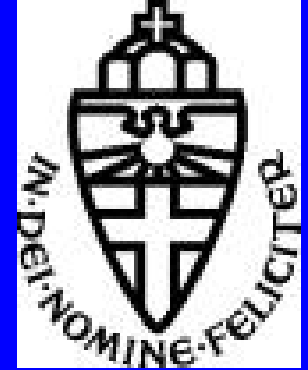
Biofouling and seawater pipe



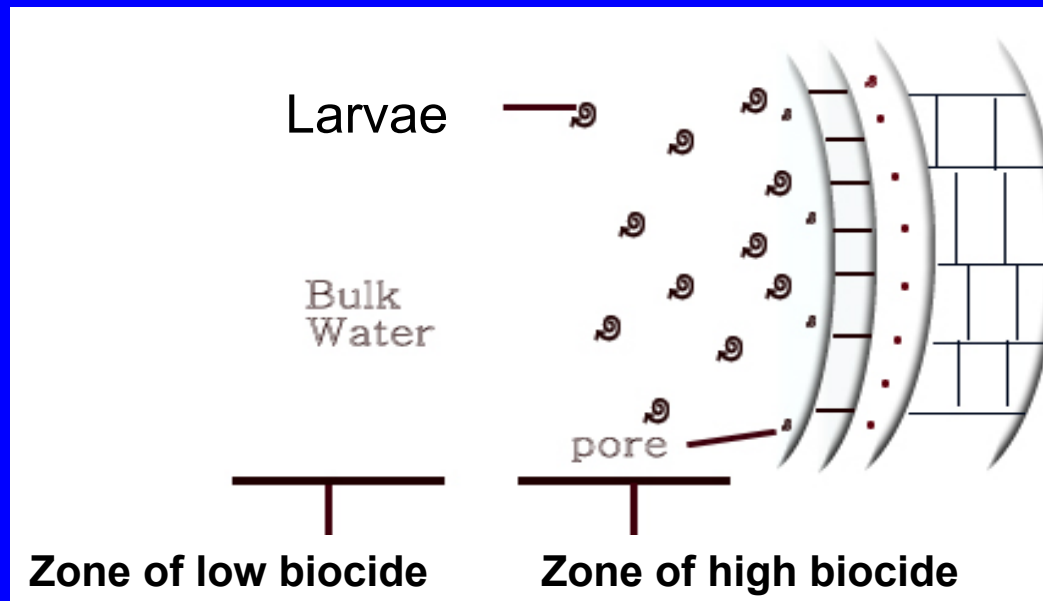
- 1) The surface alone needs to be protected
- 2) This can be done by repelling larvae close to the surface
- 3) No need to treat bulk water!

Porous Membrane



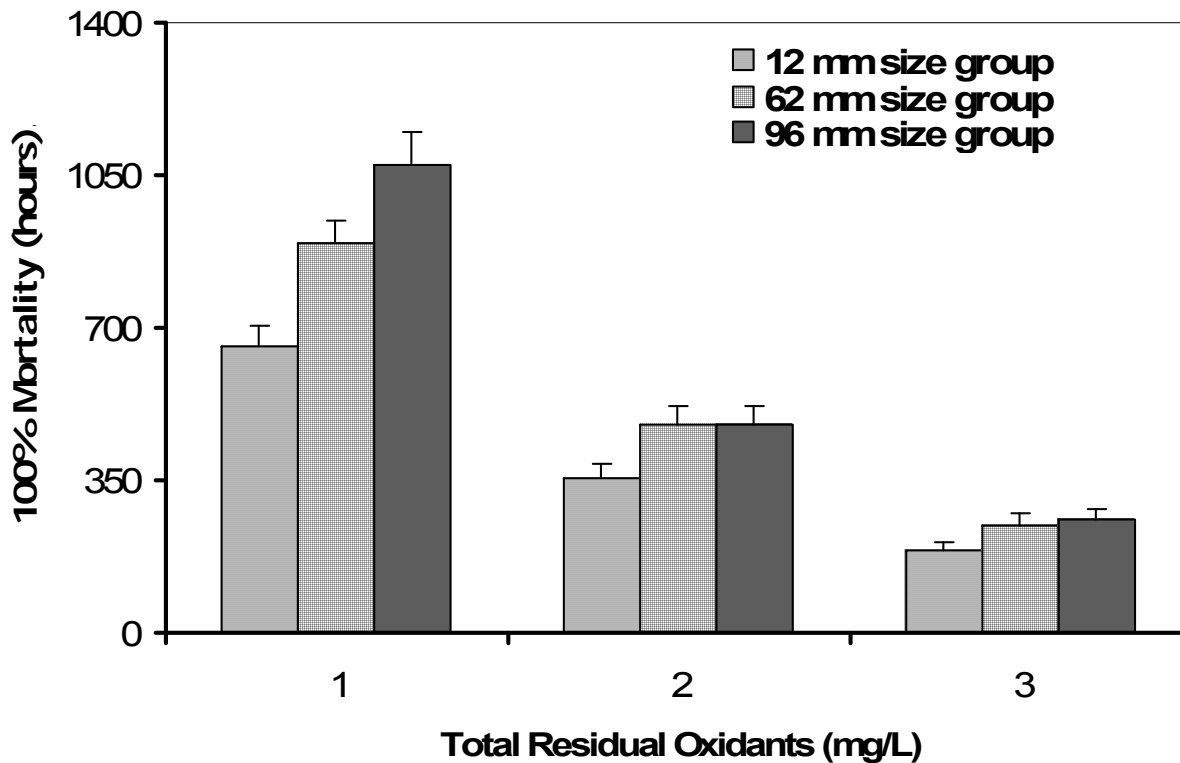


Mechanism of action



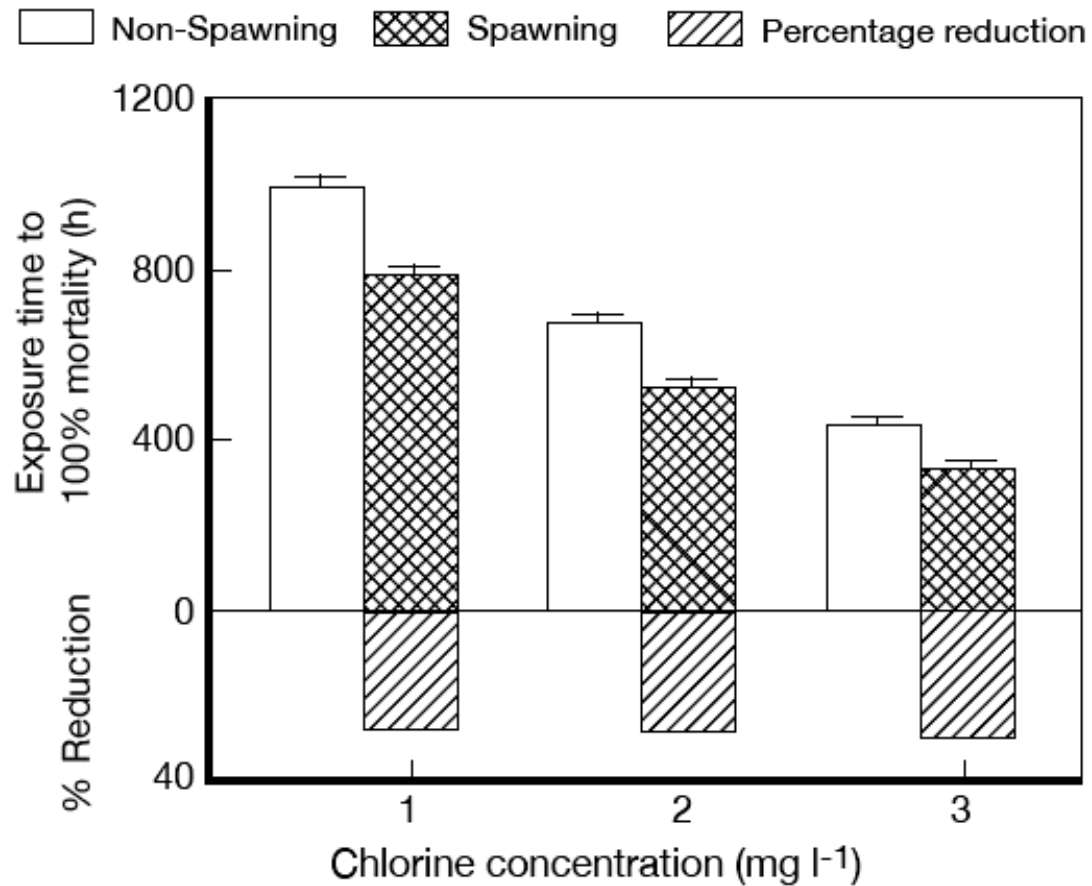
Types of Experiments

- ▶ **Conventional chlorination**
- ▶ Porous ceramic surfaces with chlorine
- ▶ Porous ceramic surfaces and Pulse-Chlorination®

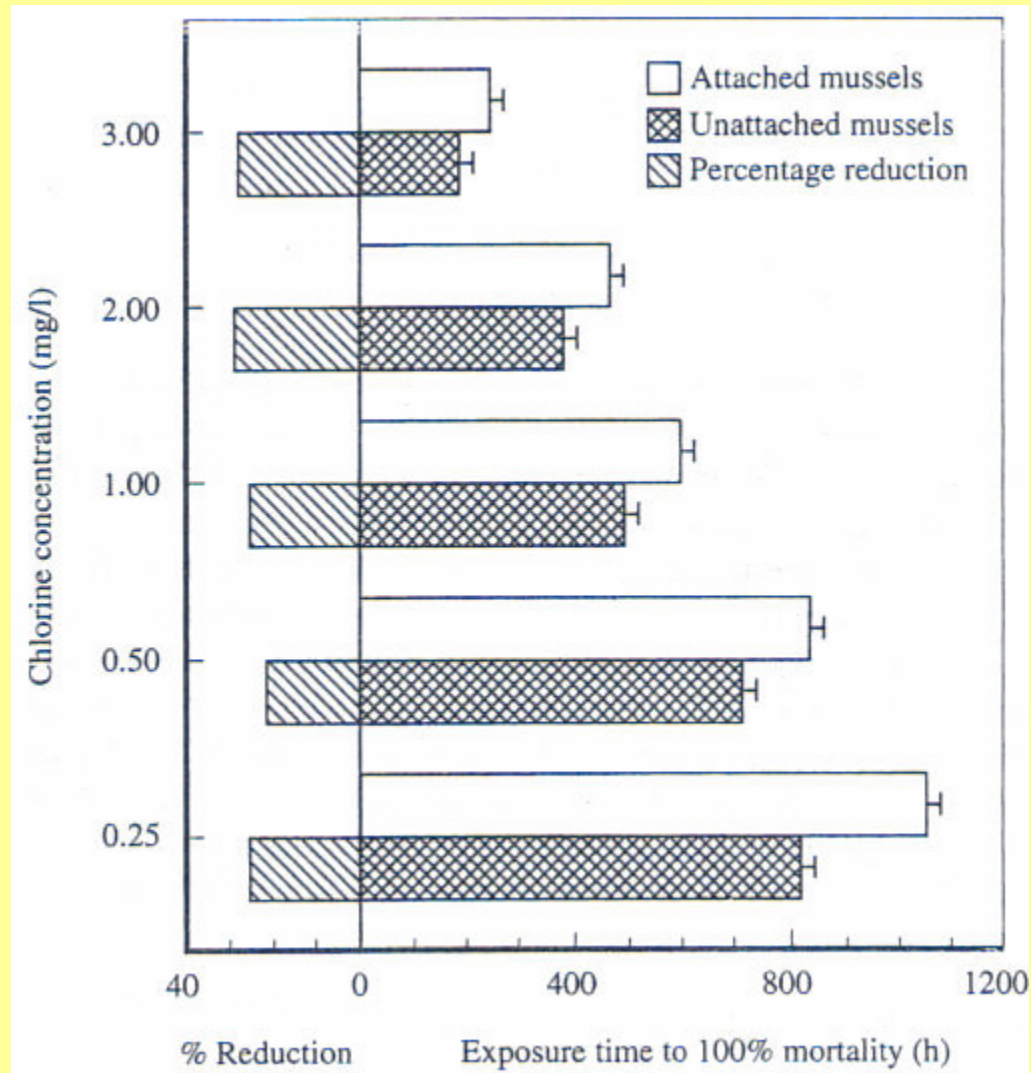


Time required for 100% mortality of different size groups of the green mussel, *Perna viridis* to different chlorine concentrations

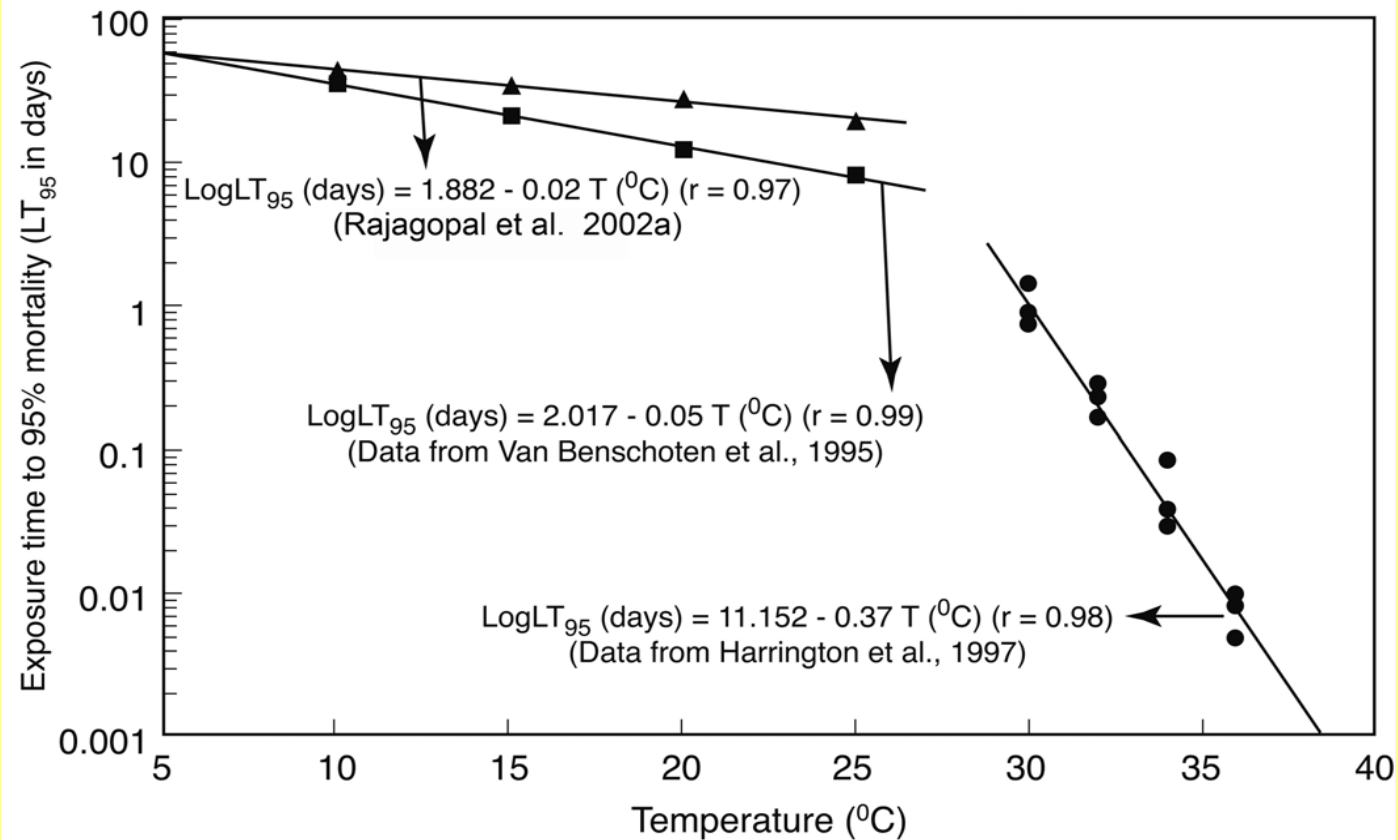
Spawning vs Non-spawning



Attached vs Unattached Mussels



Dreissena polymorpha: Chlorine and Temperature



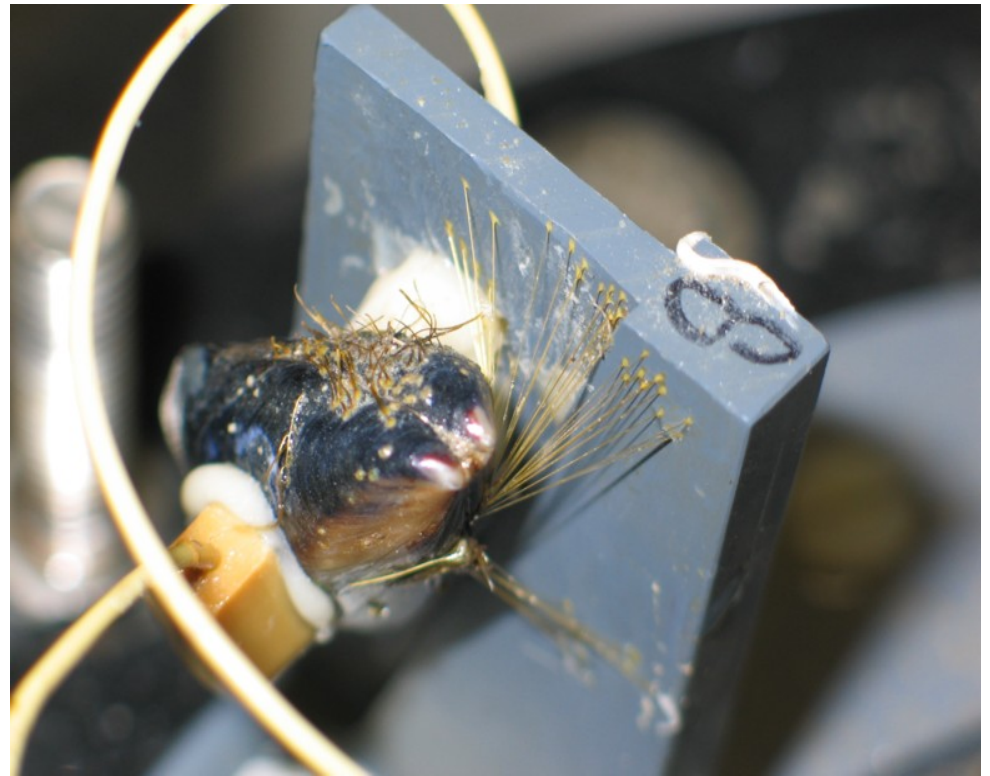
Pulse-Chlorination®

The Dutch Power Industry contracted KEMA to investigate alternatives chlorination procedures to **reduce** the amount of chlorine, **without loss of effectiveness** in fouling control

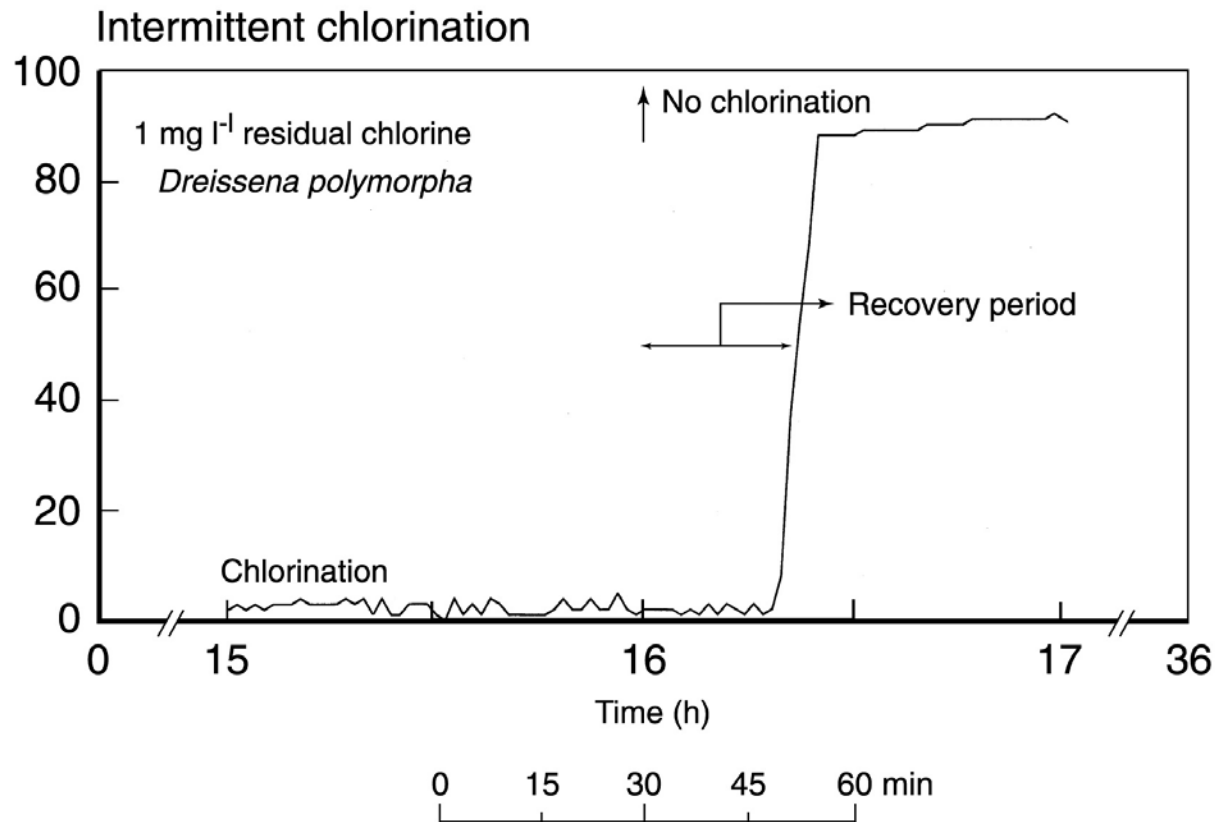
Pulse-Chlorination®

- Pulse-Chlorination® is based on short successive periods with and without chlorine
- Forces a deterioration of the physiological condition of the bivalves; switching aerobic to anaerobic and vice versa
- After exposure to a chlorination period, bivalves show a recovery period before full opening and start filtration

MusselMonitor[®] (Biological Early Warning System)

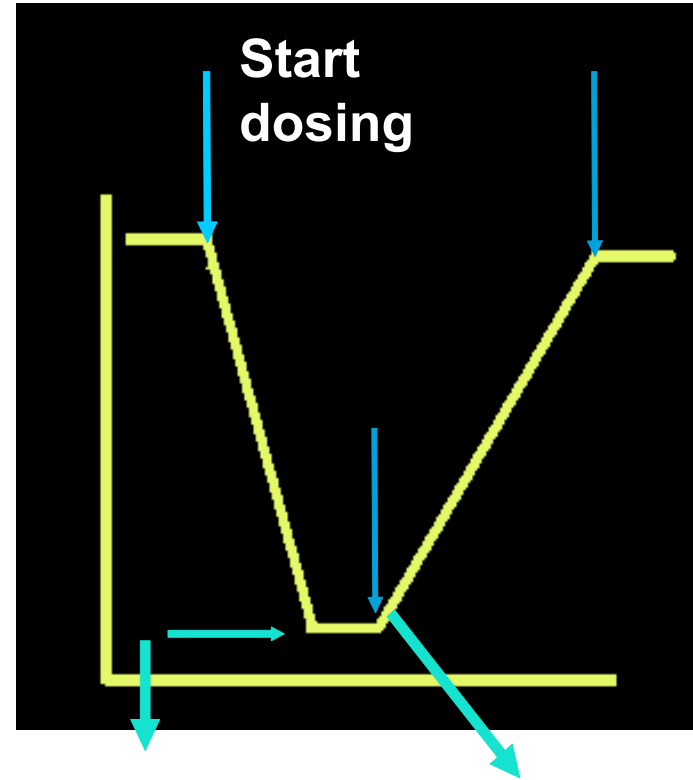


Pulse chlorination



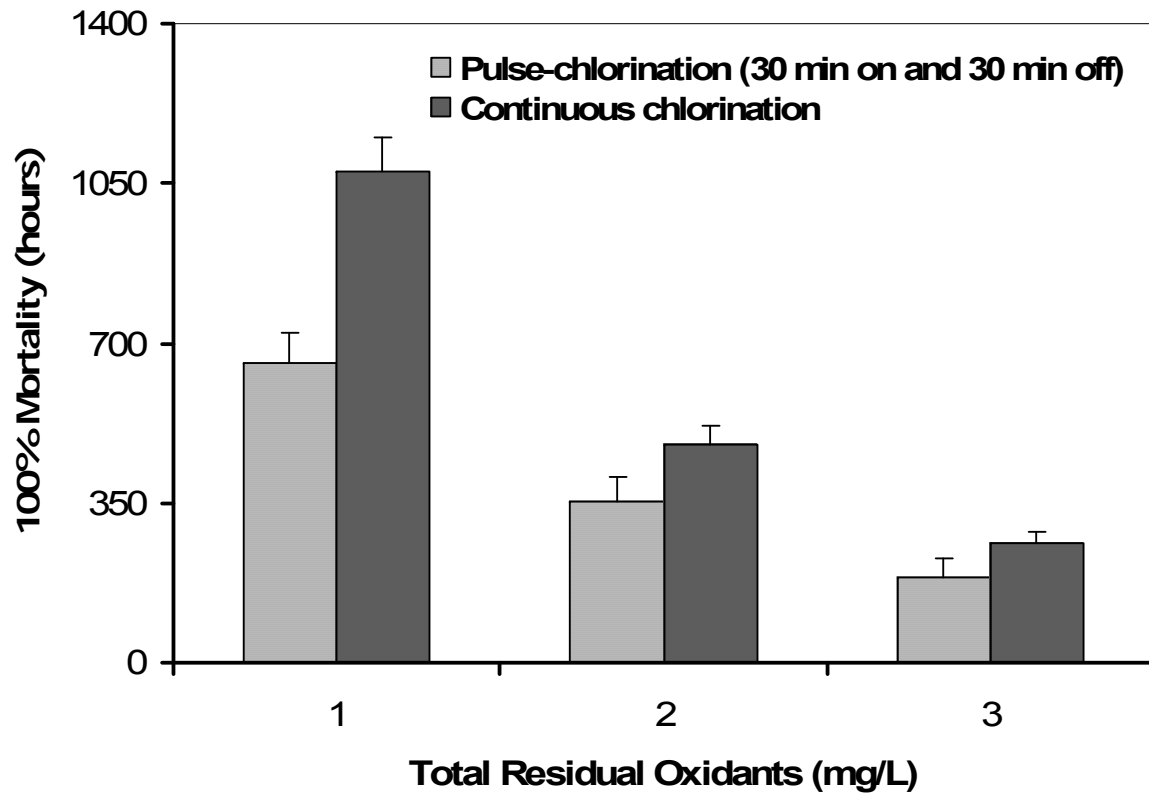
General reaction patterns of bivalves

In- (ciliated) & exhalent siphons



Stop
dosing

No dosing traject
= method profit



Comparison of exposure time to reach 100% mortality of *Perna viridis* (96 mm size group mussels) under Pulse-chlorination (30 min on and 30 min off) and continuous chlorination regimes

Pulse Chlorination®

Best Available Technique (BAT):

- Information from the European Commission (2000)
- Integrated Pollution Prevention and Control (IPPC)
- BAT Reference Document (BREF = guideline)



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Institute for Prospective Technological Studies (Seville)
Technologies for Sustainable Development
European IPPC Bureau

Conventional vs Porous

Chlorine

Chlorine Dose - 1 mg/L TRO

100% Mortality

- Conventional - 32 days
- Porous - 31 days

ANOVA: p > 0.05

Conventional vs Porous

Chlorine requirement for

Chlorine Dose - 1 mg/L TRO

Can be reduced from 45% to 60% to attain
100% Mortality of mussels by using Porous

SNK tests: p < 0.001

Conventional vs Porous

Chlorine requirement for

Chlorine Dose - 1 mg/L TRO

Can be reduced from 45% to 60% to
attain 100% Mortality of mussels by
using Porous

Porous with Pulse-Chlorination®

About from 60% to 75% chlorine can be
reduced

Conventional vs Porous

Chlorine requirement for

Chlorine Dose - 1 mg/L TRO

Can be reduced from 45% to 60%

To attain 100% Mortality of mussels by using porous ceramic surfaces

Pulse-Chlorination®

At least from 65% to 70% chlorine can be reduced – depending on the species and effective application.

Time of application

For example: During spawning season – from 25% to 35%

Conclusion:

About 60 – 75% chlorine can be reduced – by using proper control strategies.

COST BENEFIT

Power station	=	600 MWe
Cooling water	=	25 m ³ /sec
Application period	=	6 months (May – Oct)
Chlorine dose (intake)	=	1 – 2 mg/L TRO
Chlorine requirement	=	4,000 tons
Cost per 1 ton	=	Euro 150
Cost per 4,000 ton	=	Euro 600,000
Pulse-chlorination	=	Euro 300,000 (50%)
Porous surfaces	=	Euro 270,000 – 360,000 (45 – 60%)
Porous + Pulse	=	Euro 180,000 – 210,000 (65 – 70%)
Spawning Season	=	Euro 150,000 – 180,000 (70 – 75%)

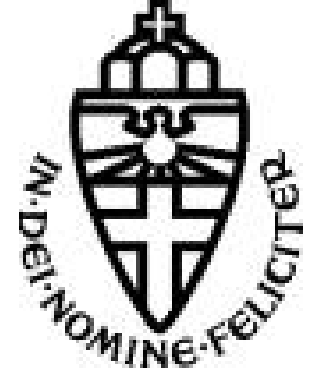
Conclusion:

About 60 – 75% chlorine can be reduced – by using proper control strategies



Advantages

- ▶ **Reduced biocide inventory**
- ▶ **Reduced environmental discharge**
- ▶ **Better fouling control**



Disadvantages

The present data – Basic experimental results and have only limited application

To finalise operating porous ceramic surfaces in real power station cooling circuit and shipping industries will require additional data and will also need more technical details for specific application.

Project Output



Editor of the Books

Book Title: **The Zebra Mussel in Europe** (to be published in February 2009)

Editors: Gerard van der Velde, Sanjeevi Rajagopal & Abraham bij de Vaate

Publishers: **Backhuys Publishers BV, Leiden, The Netherlands**

Book Title: **Environmental Consequences of Large Industrial Cooling Water Applications** (to be published in 2009)

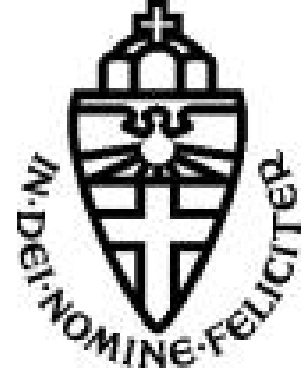
Editors: Sanjeevi Rajagopal, Henk A. Jenner & Vayalam P. Venugopalan

Publishers: **Springer, New York, USA**

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5. Van der Velde G, Rajagopal S, bij de Vaate A (2009) From zebra mussels to quagga mussels: an introduction to the Dreissenidae. In: *The Zebra Mussel in Europe* (edited by G. van der Velde, S. Rajagopal & A. bij de Vaate). Backhuys Publishers BV, Leiden, The Netherlands.
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7. Rajagopal S, G. van der Velde, H A Jenner (2009) Zebra mussel and industrial cooling water systems. In: *The Zebra Mussel in Europe* (edited by G. van der Velde, S. Rajagopal & A. bij de Vaate). Backhuys Publishers BV, Leiden, The Netherlands.

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8. Rajagopal S, VP Venugopalan, HA Jenner (2009) Operational and environmental consequences of large industrial cooling water systems: general overview. In: Operational and environmental consequences of large industrial cooling water systems (edited by S. Rajagopal, H. A. Jenner & V.P. Venugopalan). Springer, New York, USA (In press).
9. Jenner HA, S Rajagopal, M Khalanski (2009) Biofouling in cooling water intake systems: ecological aspects. In: Operational and environmental consequences of large industrial cooling water systems (edited by S. Rajagopal, H. A. Jenner & V.P. Venugopalan). Springer, New York, USA (In Press).
10. Rajagopal S, Venugopalan VP, Van der Velde G, Jenner HA (2009) Chlorination and biofouling control in industrial cooling water systems. In: Operational and environmental consequences of large industrial cooling water systems (edited by S. Rajagopal, H. A. Jenner & V.P. Venugopalan). Springer, New York, USA (In Press).
11. Rajagopal S, Venugopalan VP, Van der Velde G, Jenner HA (2009) Biofouling control: alternatives to chlorine. In: Operational and environmental consequences of large industrial cooling water systems (edited by S. Rajagopal, H. A. Jenner & V.P. Venugopalan). Springer, New York, USA (In Press).
12. Rajagopal S, Van der Velde G (2009) Invasive species: implications for industrial cooling water systems. In: Operational and environmental consequences of large industrial cooling water systems (edited by S. Rajagopal, H. A. Jenner & V.P. Venugopalan). Springer, New York, USA (In press).
13. Venugopalan VP, HA Jenner, S Rajagopal (2009) Operational and environmental consequences of large industrial cooling water systems: synthesis. In: Operational and environmental consequences of large industrial cooling water systems (edited by S. Rajagopal, H. A. Jenner & V.P. Venugopalan). Springer, New York, USA (In press).

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14. Rajagopal S, Venugopalan VP, van der Velde G, Jenner HA (2009) Mussel control in industrial cooling water systems: comparative efficacy of intermittent vs. pulse chlorination. **Water Research**.
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Abstract

16. Rajagopal S., Van der Velde G (2008) Biofouling and its control in European power stations: an overview. In: Symposium on Operational and Environmental Issues concerning use of Water as Coolant in Power Plants and Industries (OPENWAC 2008), 16 December 2008, Kalpakkam, India.
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