MARTOB

On Board Treatment of Ballast Water (Technologies Development and Applications) and Application of Low-sulphur Marine Fuel

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EXECUTIVE SUMMARY

The work planned for this period consisted of a full or pilot scale set up of each individual ballast water treatment system, developed in WP3, onboard ship or on land based laboratories. Once the systems were installed the biological, environmental, risk and safety and economical assessments were carried out.

Due to system and ship constraints only two systems were installed onboard ship. These were High Temperature Thermal Treatment (HTTT) and Biological De-Oxygenation Treatment (DEOX). The Ultraviolet Light (UV), Ultrasound (US), Ozone and Oxicide Treatments were all tested onshore (full/pilot scale).

The ballast water treatment systems
In the HTTT it is the high temperature that kills the organisms. The ballast water is heated to a set temperature (55-80 ºC) in a heat exchanger and immediately cooled down again. The water temperature is within 5 ºC of the set temperature for 1-2 seconds and at the set temperature for a fraction of a second.

In the DEOX treatment it is lack of oxygen that kills the organisms. Nutrients are added to the ballast water to stimulate the growth of the indigenous bacteria in the water. Their growth consumes the oxygen and makes the water anoxic after 1-2 days. Because some aquatic organisms can tolerate a period without oxygen, anoxia has to be maintained for 3-5 days for the method to be effective.

In the UV treatment it is ultraviolet radiation that kills the organisms. The ballast water passes through an irradiation chamber where the water receives an UV dose of 140-560 mJ/cm^2 depending on the flow rate.

In the US treatment it is cavitations created by the ultrasound that destroys the organisms. The ballast water passes through an ultrasound chamber where the water receives US energy (19 and 20 kHz) of 0.4-2.3 Wh/L depending on the flow rate and the output of the US device.

In the ozone treatment it is the oxidising effect of ozone (O_3) that kills the organisms. Ozone is produced on-site and the organisms are subjected to a concentration of 7-17 mg/L for 1-24 hours.

In the Oxicide treatment it is the oxidising effect of hydrogen peroxide (H_2O_2) that kills the organisms. The hydrogen peroxide is produced on-site in an Oxicide reactor to a concentration of approx. 15 mg/L. The organisms are subjected to this concentration for 24-48 hours during the trip.

The onboard feasibility installation analysis
This analysis was performed in parallel with the corrosion risk assessment (WP3) and the onboard installation design and the sea trials reporting. The requirements for the systems concept approval were presented. All systems obtained the design concept approval.

Risk and safety issues

The preliminary hazard identification and "what if" questions developed in WP3 formed the starting point for the analysis of the safety aspects of the ballast water treatment methods. Each method was re-evaluated in light of the experience gained from the large scale trials. In addition, further recommendations for potential risk control measures were provided. Hazards were considered from the perspective of safety/survivability of the vessel and safety of the crew during ship operations.

For most of the treatment methods, including thermal treatment, UV, and US the hazard would be confined to the equipment location. For the DEOX method there is the potential for the generation of toxic hydrogen sulphide gas to be produced in the ballast tanks if the water remains in the tank for extended periods beyond the recommended 7-day treatment time. In this case the hazard would encompass a much larger area of the ship. Ozone treatment requires the ozone (which is hazardous) to be piped into the ballast tanks: hazards could exist along the length of the piping and in areas of the tank if the gas accumulates in air spaces within the tanks. The potential of ballast water and vapours leaking out of the tanks and into adjacent areas of the ship could also be a concern. For the Oxicide method, there will be some hydrogen peroxide residual in the ballast water when it is returned to the tanks after treatment. The UV lamps contain mercury, and there is the potential for the mercury from UV lamps to be released if the lamps are broken. The Oxicide method uses diluted nitric acid as an anolyte. This could potentially be spilled if there is a pipe break. Sodium nitrate salts are also required for the Oxicide method (to be stored for addition to the anolyte). Another concern with the Oxicide method is the possible generation of chlorine gas if there is leakage across the cell and seawater comes in contact with the anolyte. One final hazard common to all systems is that the additional workload placed on the crew may contribute to unsafe conditions due to stress and fatigue.

Environmental impacts

The categories used to assess the effects of each of the ballast water treatment technologies tested included the discharge of water with altered quality, the discharge of surviving organisms, the discharge of solids (organisms and sediments), the energy consumption during operation, the potential for spill of treatment chemicals and the materials use (both for raw materials for construction of treatment equipment and consumables used during operation of the system). From a life cycle perspective, impacts during system operation were dominant for all treatment methods. Emissions to air resulting from fuel use for energy production represented more than 95% of the total. This is similar to the life cycle of a ship as a whole, with the majority of impacts occurring during the operations phase, and primarily related to energy use, with some impacts from maintenance. None of the treatment methods result in the discharge of substances that are identified as 'priority hazardous substances', or that have the potential to bio-accumulate. All methods will result in organic matter in the discharge in the form of dead organisms. The methods using a filter as pre-treatment will need to discharge the filtered material to the receiving environment, which could cause increased turbidity. Possible impacts on receiving waters include potential impacts from accidental spills of substances used in the treatment process. The Oxicide method uses nitric acid anolyte and requires sodium nitrate to be stored on board. The DEOX method requires nutrient solution to be stored on board, and UV treatment uses lamps containing small amounts of mercury.

Economic aspects
Cost calculations were viewed much more from the standpoint of the ship owners and not only of the producers or developers of the treatment systems. This means that the treatment systems are compared not only by costs per treated m^3 ballast water, but also by looking at cost behaviour under different external data. The following cost components were specified: capital costs, operational costs, training and management costs and economic benefits or disadvantages.

For some of the treatment systems personnel costs, extra maintenance costs, cleaning costs and costs of corrosion control are not quite clear yet. If better estimates are available, they can be substantial to the operational costs. Some of the systems cannot treat ballast water during intake or during discharge. When treatment during a trip is necessary, one has to think about ballast water tanks with a piston to keep treated ballast water apart from non treated ballast water (recommended only for new ships). The total annual costs per treatment system for 50 trips (100,000 m^3 treated ballast water) ranges from € 10,000 to € 60,000. For some intercontinental ships this equals the total costs to "run" that ship for 1 to 6 days.

Biological assessment
The sampling procedure, statistical analysis, methods and materials are described. Comments on the practicality of the tests are made.

The International Maritime Organisation (IMO) recently (13.2.2004) adopted a new ballast water performance standard that probably will become mandatory for ships over the next 5-10 years. According to this standard, ships conducting ballast water management shall discharge less than 10 viable organisms per m^3 larger than 50 µm, i.e. mainly zooplankton, and less than 10 viable organisms per ml between 10 and 50 µm, i.e. mainly phytoplankton. In addition, limits are set for the concentration of three indicator bacteria: *Escherichia coli* (<250 colony forming units (cfu)/100 ml), intestinal enterococci (<100 cfu/100 ml), and toxicogenic *Vibrio cholerae* (O1 and O139) (<1 cfu/100 ml or <1 cfu/g zooplankton (wet weight)). Although the standard was in draft form at the when the trials were carried out, attempts were made to collect the samples in such a way as to allow some assessment of whether the treatments would have achieved the IMO standard.

The ballast water treated by the HTTT contained approximately 1100 zooplankton per m^3, almost exclusively copepods and nauplii. The concentration of viable zooplankton after treatment ranged from 82 to less than 1 organisms per m^3 depending mainly on the age of the ballast water. The longer the organisms had been in the ballast tanks, the fewer survived the HTTT. However, a significant fraction of the zooplankton, sometimes more than 90 %, was killed in the control samples, probably by the pressure fluctuations in the fire pump during transport from the ballast tanks to the heat exchanger on deck. The killing rate of the HTTT was therefore due to a combination of the heat treatment and the killing during transport. It is not possible to determine exactly the effect of the heat treatment alone, but the results indicate that the heat treatment killed at least 90 % of the zooplankton, and probably considerably more.
Due to the low starting concentration of phytoplankton in the ballast water (<1 per ml) and their low chlorophyll content, it was not possible to assess the biological efficiency of the HTTT towards this group. In order to make any reliable judgements

it would be necessary to repeat the experiments with ballast water that contained a higher concentration of phytoplankton from the start.

The concentration of viable bacteria in the ballast water was $1 \cdot 10^4$ GU (growth units[1]) per ml. The HTTT reduced the concentration by approximately 95 %. Surprisingly, there was no significant increase in the kill rate with increasing treatment temperature (55-80 ºC). The concentration of the indicator bacteria in the new IMO standard was not determined, but the results indicate that, if present, the concentration of viable *E. coli* and *V. cholerae* would have been reduced by at least 95 %. Whether or not this is enough to achieve the IMO standard depend upon the starting concentration of the indicator bacteria. In most cases a reduction in the viability of the indicator bacteria by two orders of magnitude is likely to be sufficient, but in extreme cases a higher reduction may be required. Because some intestinal enterococci are fairly heat resistant, the efficiency of the HTTT towards these bacteria is difficult to predict from the above results, and further studies are required.

The DEOX treatment significantly reduced the concentration of zooplankton in the ballast water. From start the ballast water contained approximately 2600 zooplankton per m^3, mainly copepods and nauplii, and at the end of the treatment (7 days) this was reduced to an average of 27 zooplankton per m^3. The IMO standard relates specifically to viable organisms, but because the sampling via the fire pump killed a substantial fraction of the zooplankton in the samples, sometimes more than 90 %, it was not possible to estimate the viable fraction in the ballast water. The concentration of viable organisms in the treated water must have been less than 27 per m^3, but probably not below the new IMO standard (max. 10 per m^3). In addition, the starting concentration in the sea trial was towards the low end of the range of the zooplankton concentrations that can be expected in near shore sea- and brackish water ($10^3 – 10^5$ org/m^3). The concentration of zooplankton decreased during the trial also in the untreated control tanks, possibly because the ballast water temperature increased from 16-17 to 28-29 ºC during the trial, but the average concentration at the end of the study; 411 org/m^3, was 15 times higher than in the treated water.

From start the ballast water contained only around 1 phytoplankton cell (diatoms + dinoflagellates) per ml, i.e. well below the new IMO standard. The effect of the DEOX treatment on the survival of phytoplankton is unclear. The analyses of the concentration of diatoms and dinoflagellates, and the analyses of the concentration of chlorophyll *a* produced conflicting results. The former indicated around 90 % reduction while the latter indicated no effect. Because the viability of the phyto-plankton cells was not determined it was not possible to resolve these conflicting results. The fate of the indicator bacteria, if present, was not studied in the DEOX sea trial.

The UV, US and ozone treatments were tested onshore in Finland with water from Baltic Sea. The results with considerable reliability for ultraviolet light treatment were 94-99 % for copepods, 78-100 % for copepods nauplii and 98-100 % for rotifers. For the ultrasound technology the achieved mortality rates were 94-99 % for copepods, 86-99 % for copepod nauplii, 95-98 % for cladocerans, 80 % for rotifers and 97 % for

[1] Growth units correspond approx. to colony forming units.

barnacle nauplii. For the combination of ultrasound and ultraviolet light the mortality rates were between 97-100 % and the combination of ultraviolet light and hydrogen peroxide achieved the mortality rates of 94-100 %. UV combined with hydrogen peroxide seemed to be effective, although our data is deficient in respect of cladocerans and barnacle nauplii, which were not present in the study area at the time of the experiments. It must be noted that only limited number of different treatment combinations was tested and some of the potential combinations based on the laboratory scale test trials must have been excluded.

The results with considerable reliability for ozone treatment with ozone dosage of 17 mg/L were 96-100 % for copepods, 98-100 % for copepod nauplii and for rotifers 99-100 %. When ozone dosage was 7 mg/L, the results were 95-100 % for copepods, 96-100 % for copepod nauplii, 97-100 % for rotifers and 99-100 % for barnacle nauplii. The volumes of the contact tanks were 60 L for the ozone dosage of 17 mg/L and 360 L for dosage of 7 mg/L. The ozone dosages were kept constant throughout the trials. The effect on phytoplankton and bacteria was not studied with UV, US and ozone treatments.

Compared to the results attained from the laboratory scale tests conducted in WP3, the results confirmed that the UV, US and ozone equipment were working as designed. The decision to perform onshore test trials instead of full scale onboard trials seems justified as most of the error sources that occurred during the laboratory scale test phase could be avoided, and the results achieved were more reliable and logical. The results also provided basis for the up-scaling of UV, US and ozone treatment processes.

The total concentration of zooplankton during the studies performed in Finland with UV, US, US+UV, UV + H_2O_2 and ozone, ranged from 30 000 to 150 000 organisms per m^3, dominated by copepods and copepods nauplii. Thus, 99 % kill rate corresponds to 300-1500 viable organisms per m^3 after treatment. It should also be noted that maximum 60 litres of water was examined after treatment. Thus even in those cases where 100 % mortality was observed, less than 10 viable organisms per m^3 after treatment was not necessarily achieved.

The Oxicide treatment was tested onshore in the Netherlands. During the first trials in August, the concentration of phytoplankton in the North Sea was very low, most likely due to a long period of extremely warm weather. The biological efficiency of the system could therefore not be studied during the test period. Instead, the experiments focused on the H_2O_2 production rate of the Oxicide pilot. The newly designed generation-2 and generation-3 electrochemical cells showed an important increase in peroxide production rate compared to the cell used in WP3, from 14 g/m^2 of cell membrane per hour up to 60 g/m^2h. During the large scale onshore tests in October and November the Oxicide pilot functioned very well. An endurance test of 4 days revealed that the specific production rate remained stable at approx. 60 g/m^2h for two cells in parallel and at a flow rate of 400 L/h. Due to this substantial gain in production rate the size of an Oxicide system onboard a ship can be reduced by a factor of 4 compared to the design in WP3. This will reduce the cost of the system by almost the same factor (subsequently the cost per m^3 of ballast water treated will go down). The results provided basis for the up-scaling of the Oxicide treatment process.

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INTRODUCTION

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Due to system and ship constraints only two systems were installed onboard ship. These were High Temperature Thermal Treatment (HTTT) and Biological De-Oxygenation Treatment (DEOX). The Ultraviolet Light (UV), Ultrasound, Ozone and Oxicide Treatments were all tested at full scale onshore.

The onboard feasibility installation analysis of the different systems is explained in chapter 1. This analysis was performed in parallel with the corrosion risk assessment (WP3) and the onboard installation design and the sea trials reporting. The requirements for the systems concept approval are also given in this chapter.

The preliminary hazard identification and "what if" questions developed in WP3 formed the starting point for the analysis of the safety aspects of the ballast water treatment methods. Each method was re-evaluated in light of the experience gained from the large scale trials. In addition, further recommendations for potential risk control measures were provided. Hazards were considered from the perspective of safety/survivability of the vessel and safety of the crew during ship operations.

Environmental impact categories used to assess the effects of each of the ballast water treatment technologies tested included the discharge of water with altered quality, the discharge of surviving organisms, the discharge of solids (organisms and sediments), the energy consumption during operation, the potential for spill of treatment chemicals and the materials use (both for raw materials for construction of treatment equipment and consumables used during operation of the system).

Cost calculations were viewed much more from the standpoint of the ship owners and not only of the producers or developers of the treatment systems. This means that the treatment systems are compared not only by costs per treated m3 ballast water, but also by looking at cost behaviour under different external data. The following cost components were specified: capital costs, operational costs, training and management costs and economic benefits or disadvantages.

The above mentioned economic aspects, environmental impacts, and risk and safety effects of ballast water treatment methods tested onboard or at large scale are discussed in chapter 2. Information provided by system developers on the onboard and large scale test reports and from scaled-up designs from a case study ship formed the basis of the evaluation. This evaluation was developed in WP2 and was used in WP3.

In chapter 3 details are given for the full scale tests as well as information for the biological assessment. The sampling procedure, statistical analysis, methods and materials are explained. Comments on the practicality of the tests are also presented there.

The risk and safety issues, environmental impacts, economical aspects, biological assessment and details (manufacture/operation) for each system are given in chapters 4 to 9. The high temperature thermal treatment is discussed in chapter 4, the de-oxygenation treatment in chapter 5, the ultraviolet and ultrasound treatments in chapter 6, the ozone treatment is explained in chapter 7, the Oxicide treatment in chapter 8 and the BenRad treatment in chapter 9.

Combinations of techniques (UV - hydrogen peroxide and UV - US) were also tested at full scale and are discussed in chapter 10. For the combination treatments only the biological assessment was performed. The other impacts are assumed to be a combination from the individual treatments.

1 CONCEPT APPROVAL

The onboard feasibility installation analysis of the different systems concerns the compliance with the existing rules and regulations and with respect to the State of the Art of ship design. The analysis has been performed following the scheme for ship equipment or installation Concept Approval of Bureau Veritas.

The concept approval provides a confirmation of the project technical feasibility considering both the current state of art and the applicable rules. These applicable rules may be either the Classification Society's rules or other appropriate regulation, in particular SOLAS and IMO requirements.

The MARTOB systems review with respect to onboard feasibility installation have been performed in parallel with the corrosion risk assessment (DTR 3.8), the onboard installation design for sea trials (DTR 3.9) and the sea trials reporting (DTR 4.2 to 4.7).

1.1 GENERAL SCHEME

The concept approval includes three different stages:

1. **Basic approval:** it can be issues as soon as pilot studies are completed and refers to the project qualitative studies. It confirms that its outlines are consistent with both the state of art and the applicable rules.
2. **Design approval:** it can be performed as soon as the project developing studies are sufficiently advanced and can be issued on the basis of the project development chart and the first quantitative studies. The design approval states that the design of the project is consistent with the rules or criteria taken into account and listed in the Certificate.
3. **Final approval:** it is the step prior to classification or certification. It can be issued when all steps specified in the development chart should have been satisfactorily performed, when all limitations liable to interfere with either the manufacturing process or the use of the system or its maintenance should properly mentioned. Restrictions to the use of the system are sated, for instance, ship limitation in size or deflection, sea state or wind speed which may not be exceeded.

For the issuance of concept approval, documents have to be provided for review and approval by the Classification Society. The typical list of documents required for approval is given in Table 1.1.

For a particular system the exact list of required document and the acceptance criteria are defined on a case by case basis by the Classification Society, in agreement with the system developer.

Table 1.1: Typical list of data for concept approval

Document for approval	Basic approval	Design approval	Final approval
Project description	X	X	X
Definition of the design criteria	X	X	X
Definition of material & equipment specifications	X	X	X
Material selection	X	X	X
Appraisal of material properties		X	X
Methods of calculation of design loads		X	X
Identification of singularities		X	X
Review of individual safety margins		X	X
Review of feasibility test results on prototype		X	
List of calculations & tests for design confirmation		X	X
Review of final calculation & test results			X
Review of return experience, if any			X
Safety & reliability assessment of the system			X
Material & equipment purchase specifications			X
Definition of the operating field			X
Definition of the quality assurance program			X
Definition of the acceptance tests			X

1.2 MARTOB WBT SYSTEM CONCEPT APPROVAL REQUIREMENTS

Concerning the systems developed within MARTOB the following list of required documents and data has been defined by the Classification Society:

Table 1.2: List of data for WBT systems concept approval

Document and data	Reference number	Approval level
Project description	1	DCA
Definition of the design criteria	2	DCA
Definition of material & equipment specifications	3	DCA
Appraisal of material properties	4	DCA
Biological efficiency evaluation in laboratory	5	DCA
Prototype on-board ship installation	6	DCA
Full scale prototype biological efficiency tests	7	DCA
Review of return experience, if any	8	FCA
Safety & reliability assessment of the system	9	FCA
List of calculations & tests for ship installation design	10	FCA
Onboard installation specification	11	FCA
Material & equipment purchase specifications	12	FCA
Definition of the operating field	13	FCA
Definition of the acceptance tests	14	FCA
Generic Water Ballast Management Plan	15	FCA

(DCA: required for Design and Final Approval – FCA: required for Final Approval)

When full scale applications on-board of ships exist, a final concept approval may be granted from the review of the provided technical documentation and return experience review (reference number 8), without need of the documentation reference number 9 to 14.

1.3 CHECKED ITEMS AND CRITERIA

The required documents and data to obtain the system concept approval have to be provided by the system developers and contain the following:

1. Principle sketch of the circuit with ballast water flow and equipment
2. On the circuit sketch, indication of the points where the water is treated: filtration, actions, additives, etc...
3. For each treatment point a short description providing information on:
   - components of the equipment
   - materials of the equipment components, use of DC (Direct Current)
   - type of water treatment
   - addition or extraction of substances in the water
   - water parameters changes after treatment:
     - Water properties: conductivity, hardness, PH, redox potential, temperature
     - Water content: O_2, O_3 (ozone), CO_2, H_2S, bacteria concentration
4. Justification and calculation notes concerning:
   - the necessary power
   - the time duration of the water treatment
   - the efficiency of the water treatment
5. Drawings for a typical ship installation showing
   - Water ballast piping, equipment location and fixation, circuits for additives if any,
   - Power supply with characteristics if any,
   - Command, safety and monitoring circuits
   - Additive storage system and location if any
6. A draft of the ballast water management plan

The concept approval checks the conformity with the IMO Resolution 868 (20). The circular MEPC/Circ.389 dated 21/03/2002 should also be taken into account. It is also verifies that the BW Treatment method should not affect in any case the conformity of the vessel with SOLAS Regulation, in particular for safety of crew or passengers. Depending of the type of vessel, attention is given to specific regulation, such as MARPOL for oil tankers, IGC Code for gas carriers, IBC Code for chemical tankers.

The conformity to the above regulations is ensured by the compliance with the relevant BV rules for classification of steel ships. The following areas are taken into account:

1. **Stability criteria:** in case the loading condition of the vessel is changed during the treatment procedure, the intact stability will have to be checked: the criteria of IMO A.167 should be complied with at any time of the treatment phase. The criteria for minimum forward draught of the vessel (criteria which is in relation with risk of slamming) should also be complied with when emptying the ballast tanks.
   BV RULES Pt B, Ch 3, Sec 2

2. **Visibility:** in case the loading condition of the vessel is changed during the treatment procedure, the visibility will have to be checked: the treatment equipment should not decrease the visibility of the master of the vessel. In particular, the criteria given by SOLAS chapter V, reg.22 should be complied with. This could be sensible in case of large equipment on deck or in case of big change of trim during the treatment operations.
   SOLAS chapter V, reg.22

3. **Longitudinal strength of the vessel:** in case the loading condition of the vessel is changed during the treatment procedure, the longitudinal strength will have to be checked: for the same reason as point 1 above, in particular in ballast loading conditions (for example if the system requires to empty one ballast tank), it should be checked that the vessel will remain within the admissible bending moments and shear forces used for the vessel design.
   BV RULES Pt B, Ch 6, Sec 2

4. **Overpressure in ballast tanks:** it should be checked that the treatment system will not create any overpressure in the ballast tanks. Otherwise additional calculations should be done to check the structural strength of the ballast tanks under this overpressure.
   BV RULES Pt B, Ch 7

5. **Liquid motions in ballast tanks:** if the treatment requires to partly empty the ballast tanks, it should be verified whether it will not create dynamic effects and sloshing problems. For example, this can be sensible for the ballast holds of bulk carriers.
   BV RULES Pt B, Ch 5

6. **Piping:** every piping systems used for BW treatment should be in conformity with BV Rules
   BV RULES Pt C, Ch 1, Sec 10

7. **Risk of fire:** in case of risk of fire, due to chemicals or other inflammable products which can be involved in BW treatment, BV Rules should be applied.
   BV RULES Pt C, Ch 4

8. **Material:** every material involved in BW treatment should be approved by Bureau Veritas.
   BV RULES Pt D

1.4 MARTOB WBT SYSTEMS CONCEPT APPROVAL STATUS

The required information and data for the concept approval has been provided by the various reports edited during the project development. This includes reports in WP3 and WP4 as well as other documents which have been provided by the technology developers. Due to the project context and developer status, mainly research centres, the provided documents have not covered the reference number 9 to 15 of Table 1.2. Therefore the certificates are limited to Design Concept Approval.

Four of the systems have been submitted to large scale on-shore tests. Such tests are not considered providing information about the feasibility of installation onboard a ship, nor about the behaviour in a ship environment, in particular motions and accelerations. Therefore they are not considered eligible for Final Concept approval.

The detailed review of each system is given in chapters 4 to 9.

1.5 DISCUSSION

Within the Bureau Veritas, Marine Division, Concept Approval Scheme, **Design Concept Approval certificates** have been granted to all developed systems.

Only two systems have been tested full scale onboard a ship:

- Water Ballast Treatment by High Temperature Thermal Treatment
- Water Ballast Treatment by Biological De-Oxygenation

The systems may obtain a Final Concept Approval without main difficulty. To obtain the Final Concept Approval, additional works and documents covering the points 9 to 15 of Table 1.2 have to be submitted for review to the Classification Society.

One system has been installed onboard a ship and is operated since 2003, but without biological efficiency measurements:

- BenRad Ballast Water Treatment

The BenRad method may obtain a Final Concept Approval when additional works and documents covering the points 7 to 15 of Table 1.2 will have been submitted for review to the Classification Society.

The other systems have been tested in laboratory and onshore at large scale:

- Ultraviolet Water Ballast Treatment (UV)
- Ultrasound Water Ballast Treatment (US)
- Ozone Water Ballast Treatment
- Oxicide Water Ballast Treatment

The UV and US systems may not obtain a Final Concept Approval if used alone but jointed together, except if future works demonstrate their biological efficiency alone.

The UV plus US, ozone and Oxicide method may obtain a Final Concept Approval when additional works and documents covering the points 7 and 9 to 15 of Table 1.2 will have been submitted for review to the Classification Society.

2 RISK, SAFETY, ENVIRONMENTAL AND ECONOMICAL ISSUES

The ballast water treatment technologies were tested at large scale or onboard a RoRo car carrier within the MARTOB project and were assessed with respect to:

- **Risk and safety issues:** related to operation of the ballast water treatment system on board a vessel, and recommendations for safety equipment, procedures, or measures to mitigate these concerns.
- **Environmental impacts:** including direct impacts on receiving water quality and indirect impacts occurring during the life cycle of a ballast water treatment process. The main impacts assessed included energy consumption and associated emissions to air, materials use for equipment construction, and consumables used during operations.
- **Economic aspects:** such as capital costs, operating costs, training costs, management costs, and economic advantages and disadvantages. In addition a sensitivity assessment of the effects of number of treatments per year was carried out.

Information used to carry out the assessments was obtained from the following sources:

- Data obtained from the large-scale and onboard tests, and from the associated reports in WP4.
- Information provided by the developers of each technology for a case study ship. The case study ship was the same as that used for WP3. System developers updated information for their systems after having conducted testing in WP4. Information provided included required size of their equipment, energy consumption, use of materials and consumables, approximate composition of equipment (materials), and estimations of the cost related to the onboard installation of the treatment technologies.
- Additional supplemental data from literature sources, including life cycle inventory information for the main materials used in the treatment systems.

The evaluation categories defined as part of WP2 served as the basis for this assessment, which is described in the following sections.

2.1 CASE STUDY SHIP

As was done in WP3, a theoretical case study approach was used as part of the assessment of economic aspects, safety, and environmental effects of the treatment methods because it provided a consistent basis to scale up the treatment methods to allow comparisons. Each technology developer had provided details of a scaled-up version of their treatment system for WP3. This scaled-up system was to be capable of treating the volume of water required for the case study ship. In WP4, the system developers provided updated information on their scaled-up systems, based on information collected and modifications made during the large scale testing.

The case study ship selected was similar to the vessel used for the onboard large scale testing. The vessel selected was a roll-on roll-off pure car and truck carrier (RoRo

PCTC). Specific information about the ship used to develop the case information is provided below.

2.1.1 SHIP INFORMATION

General vessel information:

- Ship type: PCTC (Pure Car and Truck Carrier)

Ship dimensions:

- Breadth: 32.26 m
- Length overall: 199.1 m
- Length between perpendiculars: 190.5 m
- Depth up to freeboard deck: 14.05 m
- Depth up to upper deck: 33.48 m
- Deadweight at design draft: 14841 tonne

Ballast water system information:

- Total volume of ballast tanks: 8076 m^3 (but maximum amount to be treated on one voyage is 2000 m^3). This vessel would take on a maximum of 2000 m^3 of ballast water at a time as it always operates with some ballast water within the tanks to allow for trimming of the vessel. System developers were therefore requested to base their design calculations on the requirement to treat 2000 m^3 during each visit to port.
- Piping for ballast water system: 250A

Ballast water pump:

- Capacity: 500 m^3/hr
- Total head: 25 m

Drawings and additional information:

The following additional information was provided for the case ship:

- General arrangement plan of the vessel
- Capacity plan
- Piping diagram of the ballast system
- Pump curve for the ballast and bilge pump

2.1.2 BALLASTING ACTIVITIES DURING AN ACTUAL OR TYPICAL VOYAGE

A sample voyage was selected to serve as the basis for calculations such as energy use, treatment time, operating costs, etc. The following information was provided on ballasting activities:

- Amount of ballast water taken on and discharged during the voyage: Amount of water to be treated is 2000 m^3 (this is 25% of the total ballast water capacity

of the ship). It was to be assumed that this would be taken on or discharged while the ship is in port.
- Approximate sailing time and distance between the ports: 6 to 7 days
- Amount of time spent at port (amount of time available to treat and discharge the ballast water): 12 hours (minimum)

Technology developers were asked to provide a conceptual design for the application of their system onboard the case ship.

2.2 RISK AND SAFETY ISSUES

Potential hazards associated with ballast water treatment methods can be assessed with respect to their potential impact on two main safety perspectives:

- Safety of the vessel (ship survivability): stability, structural strength, visibility
- Safety of the crew (ship operations):
  - Operational: physical equipment hazards: chemical, electrical, or biological hazards
  - Chemical storage
  - Safety/contamination of living spaces

For the methods tested within MARTOB, almost all potential impacts would be related to ship operations issues. Ship survivability issues such as stability and structural strength are only a problem with ballast water management methods that involve changing the amount of ballast water in the tanks while the ship is at sea, such as the sequential ballast water exchange method. The Oxicide method is the only one tested within MARTOB that requires ballast water to be pumped from the tanks through the treatment system while the ship is at sea.

Categories of hazards assessed for the methods tested include physical, chemical, electrical, and biological, depending on the specific treatment method. A summary of the main categories of safety issues is as follows:

- Operational issues:
  - Use of hazardous chemicals (on-site generation and storage)
  - Equipment hazards (relating to heating equipment, UV, electrical, etc.)
- Storage and handling of chemicals and residuals: potential spills, vapour release,
- Potential for unintentional release of treated ballast water containing residuals: from ballast tanks or piping systems.

The safety issues of each of the ballast water treatment systems tested in WP4 are discussed in chapters 4 to 9 in this report.

2.2.1 HAZARD ASSESSMENT

For the ballast water treatment methods tested a preliminary hazard assessment and a preliminary “what if?” approach were used to identify categories and types of hazards. This type of approach was used in WP3, and the work conducted in WP4 was a continuation and update based on experiences gained by system developers during the onboard and large scale testing.

The ballast water treatment methods are still in a development phase, so the preliminary hazard assessment techniques were considered the most appropriate. The preliminary hazard analysis method is useful for carrying out a broad identification and overview of hazards (Milstein, 1999). This method focuses on major components such as hazardous materials used in the process, operating environment, and major equipment hazards. Categories of hazards that were considered for each ballast water treatment method include physical, chemical, electrical, and biological.

That 'What-if ' checklist approach was also used to assess potential safety issues with the ballast water treatment methods. The technique is very flexible and can be directed towards equipment, process, raw materials, storage, management practices, materials flows, products, etc. Because it is a loosely structured technique, it can be used for preliminary development phases as well as for established processes that have been in regular operation. A 'What if' analysis is conducted by collecting descriptive information about the process (as detailed as possible). The review team then uses brainstorming techniques to generate a list of questions about the process to help determine potential consequences. Examples of questions include:

- What if too much treatment chemical is added?
- What if the chemical feed hose ruptures?
- What if the storage tank leaks?

After some "what-if" questions were developed for each method, systems designers were able to recommend risk reduction and safety measures that could be implemented. Once full scale systems are designed, detailed investigations would need to be carried out on a ship-specific basis prior to installation of any ballast water treatment system.

2.2.2 DISCUSSION

Hazards associated with operation of treatment equipment include physical hazards such as heat, electrical hazards, ultraviolet or ultrasound radiation hazards, and chemical hazards from gases or hazardous liquids used or generated during treatment. For most of the treatment methods, including high temperature thermal treatment, UV, and US the hazard would be confined to the equipment location. For the biological de-oxygenation method there is the potential for the generation of toxic hydrogen sulphide gas to be produced in the ballast tanks if the water remains in the tank for extended periods beyond the recommended 7-day treatment time. In this case the hazard would encompass a much larger area of the ship. Ozone treatment requires the ozone (which is hazardous) to be piped into the ballast tanks: hazards could exist along the length of the piping and in areas of the tank if the gas accumulates in air spaces within the tanks. The potential of ballast water and vapours leaking out of the tanks and into adjacent areas of the ship could also be a concern. For the Oxicide method, there will be some hydrogen peroxide residual in the ballast water when it is returned to the tanks after treatment.

Other hazards associated with ballast water treatment include the potential for a spill of hazardous material stored or being used within the treatment system. The UV lamps contain mercury, and there is the potential for the mercury from UV lamps to be released if the lamps are broken. The Oxicide method uses nitric acid as an

anolyte. This could potentially be spilled if there is a pipe break. Sodium nitrate salts are also required for the Oxicide method (to be stored for addition to the anolyte). Another concern with the Oxicide method is the possible generation of chlorine gas if there is leakage across the cell and seawater comes in contact with the anolyte.

One final hazard is that the additional workload placed on the crew may contribute to unsafe conditions due to stress and fatigue.

Table 2.1 summarises the information on hazards associated with each of the ballast water treatment methods tested at large scale or on board during WP4 of the MARTOB project. The information is an update from WP3, using new information and experience gained during the WP4 tests.

Table 2.1: Hazards associated with ballast water treatment methods

Hazard Categories and Description	Thermal Treatment	Biological Oxygen removal	UV	US	Ozone	Oxicide
Equipment Operation Hazards						
Electrical		No	230 Volts AC, 50 Hz	400 Volts AC, 50 Hz	230 Volts AC, 50 Hz	Required for equipment
Heat	Steam to and from system, hot water circulated	No	Heat generated by UV lamps	Heat generated within equipment	Heat generated during ozone production process	Some heat generated in the power supply
UV or US Radiation	No	No	UV-C Radiation	Ultrasonic Radiation (20 Hz)	No	No
Substances generated and/or added to ballast water during operation	None	Nutrient solution	None	None	Ozone Gas	H_2O_2 generated, possible Cl_2 and H_2 formation
Hazardous Substances Contained in Equipment	None	No	Mercury in UV lamps (100 mg per lamp)	None	No (but during operation ozone gas)	Nitric Acid as Anolyte
Potential for Leakage from Tanks or Piping System						
Additional Piping?	Yes	No	Yes	Yes	Yes	Yes
Residual in Ballast Water in Piping?	Heat (max. measured + 7˚ C)	Discharge of low O_2, elevated nutrient content ballast water H_2S was below detection	Heat (+2.1˚ C max. increase measured during large-scale trials)	Heat (+2.0˚ C max. increase measured during large-scale trials)	No	H_2O_2 in ballast water pumped from the Oxicide unit to ballast water tank.
Residual in Ballast Water in Tanks?	No	low O_2 elevated nutrient content ballast water H_2S below detection	Slight temp. incease. Small increase in redox potential of ballast water identified in WP3	Slight temperature increase	Ozone in tanks for the required contact time, increased redox potential	H_2O_2; no or low concentrations of H_2O_2 in the discharge
Storage / Handling of Chemicals and Residuals	No	Nutrient Solution	Storage of spare UV lamps	No	No	$NaNO_3$ to replenish nitric acid anolyte.
Filtration Pre-Treatment	Yes	No	Yes	No	Yes	Yes

2.3 ENVIRONMENTAL IMPACTS

Although the goal of ballast water treatment systems is to have a net positive impact on the environment through reducing the risk of introducing non-indigenous species to new environments, the systems may have some negative impacts. These environmental impacts vary depending on the treatment method, but can be grouped into two general categories: direct impacts through discharges to receiving waters and indirect impacts resulting from energy use, emissions and materials use. There can also be the potential for impacts from accidental spills of substances used in the treatment process. Impacts occur throughout the life of the treatment process – from construction of the equipment, through the operational phase, and finally during scrapping of obsolete equipment and components. Previous work within the MARTOB project included summarising and assessing information from the literature on possible effects and consequences of ballast water treatment methods, and assessing impacts using information collected during the laboratory-scale testing phase of the project.

Work in WP4 builds on previous work by including information obtained during the large scale and onboard testing phase provided by the system developers and information obtained from the literature. The approach taken was to collect information relating to impacts from each phase of the life cycle of the ballast water treatment process but to focus on the impact categories that are considered important within transport or that have been identified as potential concerns with ballast water treatment.

Impact categories based on the OECD's core indicators for life cycle assessment of transports, with modifications to reflect impacts and information available for marine transport (Fet et al., 2000) include:

- Energy Consumption
- Emissions to air, with its consequences:
  - Climate change: emissions of CO_2, CH_4, N_2O
  - Acidification: emissions of SO_2, NO_x, NH_3 from additional fuel combustion
  - Eutrophication: nutrients, forms of nitrogen and phosphorous
  - Local air pollution: emissions of particulates
- Eco-toxicity: quantities of toxic contaminants discharged as residuals, or as process treatment waste

These were considered when collecting information on the potential environmental impacts of the ballast water treatment methods tested shipboard or at large scale within MARTOB.

2.3.1 LIFE CYCLE CONCEPT FOR ASSESSMENT OF BALLAST WATER TREATMENT METHODS

Life Cycle Assessment (LCA) is an environmental assessment method that studies a certain product's or activity's environmental impact "from the cradle to the grave". A detailed LCA includes the whole life cycle of a process or product, from the

environmental impacts of raw material extraction to the final disposal. This includes all steps outlined in ISO 14040 and is a complex process requiring detailed information on all inputs and outputs to the process or product being studied. Life cycle concepts can also be applied in cases where information is limited or when the product is under development: in these cases it may be more appropriate to qualitatively assess environmental issues across the life cycle. A streamlined LCA falls somewhere in between, and involves limiting the extent of the study, the detail of the information collected, or the types of environmental issues to be addressed (Environmental Resource Management, 2002). For the MARTOB project, the assessment began with a qualitative investigation of the types of impacts that could occur across the life cycle of each ballast water treatment method. Quantitative information was then collected where available and the assessment discussion focused on those environmental issues considered to be of the most concern.

When assessing environmental issues across the life cycle of a ballast water treatment process, the major inputs and outputs during production, operation, and scrapping should be considered, as shown in Figure 2.1. Each of these phases and the relative contribution of a ballast water treatment system to the whole life of a ship are discussed in more detail below.

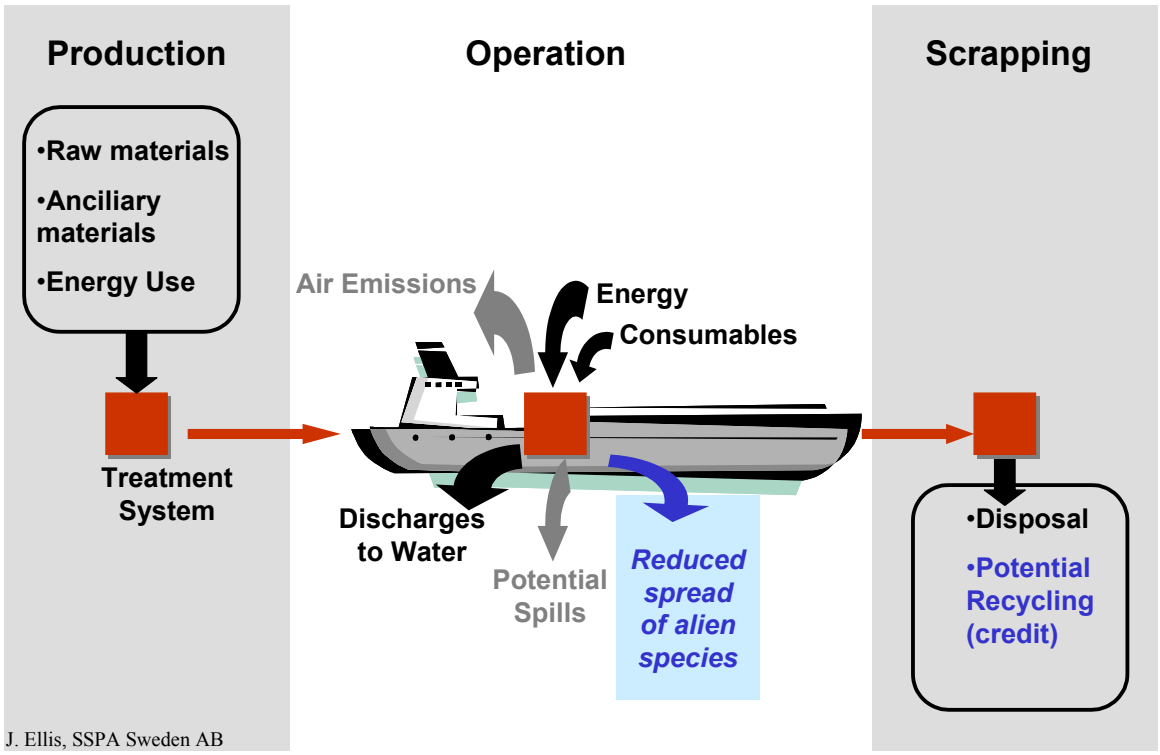

Figure 2.1: Life cycle of ballast water treatment processes

Equipment Production

Many of the inputs and outputs for the ballast water treatment process add only incremental increases to those that already occur during the life cycle of a ship. For example materials use, energy use, and related emissions during construction of the treatment equipment are of the same type as those that result from ship construction, as the majority of the materials used are the same. For the treatment methods tested in

WP4, steel, stainless steel, and iron accounted for the largest weight components. All of these materials are used extensively in ship construction. Table 2.2 shows a summary of the main materials used to construct each treatment system. Note that the summary table shows only the materials for the treatment systems themselves. For UV, ozone, and Oxicide treatment methods, a filter would have to be installed to filter the ballast water before it passes through the treatment system (optional for HTTT). The estimates of materials for the filter have not been included.

Table 2.2: Summary of materials estimates for construction of BW treatment systems tested

Treatment Method / Material Type	Weight (kg)	% of Total Weight
High Temperature Thermal Treatment: Materials to construct the pilot system tested (Capacity 50 m^3/hr, could treat 800 tonnes ballast water in 16 hours)		
Steel	951.1	73.8
Mild Steel	148.8	11.5
Stainless Steel	13.5	1.1
Cast Iron	66.1	5.1
Titanium	90.6	7.0
Aluminum	5.9	0.5
Others (rubber, plastic, rockwool, etc.)	13.0	1.0
Total:	***1289***	***100***
Biological Deoxygenation System, Capacity: 2000 m^3 per voyage (based on Case Study Vessel)		
Stainless Steel (Nutrient solution storage tank)	1000	100
Total:	***1000***	***100***
Ultraviolet Light Chamber and Equipment, Capacity 2000 m^3 per voyage (based on Case Study Vessel), major components only provided		
Stainless Steel (UV Chamber)	100	~ 18
Steel (Power Control Module)	450	~ 82
Others (UV lamps, electrical wiring components, etc.)	Unspecified	
Total:	***550 plus***	
Ultrasound, Capacity 2000 m^3 per voyage (based on Case Study Vessel)		
Stainless steel	240	~ 69
Painted steel	50	~ 14
Titanium	60	~ 17
Others (wiring, etc.)	Unspecified	
Total:	***350 plus***	
Ozone Generator, Capacity 2000 m^3 per voyage (based on Case Study Vessel)		
Stainless steel, steel for cabinet	2000	~ 100
Others (wiring, etc.)	Unspecified	
Total:	***2000 plus***	
Oxicide Method, Capacity: 2000 m^3 over 24 hours (based on Case Study Vessel), but could treat up to 2500 m^3		
Steel (Equipment and piping)	250	16.2
Polypropylene (Equipment and piping)	250	16.2
PVC (Equipment and piping)	5	0.3
Carbon Electrodes (Oxicide Cell)	400	26.0
Carbon Felt (Oxicide Cell)	10	0.6
Ion Conducting Membrane (Oxicide Cell)	5	0.3
Copper Wiring (Oxicide Cell)	20	1.2
External Electrical Equipment (material unspecified)	600	39.0
Total:	***1540***	***100***

Operations

For the operations phase of the treatment equipment's life cycle, energy use and related emissions will add an incremental increase to those already occurring during ship operations. Fuel consumption and the related emissions during operations account for the largest environmental impacts during shipping. Johnsen and Fet (1998), in their LCA for the Ro/Ro vessel M/V Color Festival, found that the impacts occurring during the operation phase were dominant in the main environmental impact categories. This is consistent for transport in general. Ellingsen et al. (2002) stated that "energy consumption and related emissions are the most important environmental effects of transport." Many of the ballast water treatment systems will also require replacement parts, materials (consumables) and maintenance throughout the operation phase, similar to the ship in general.

Another potential negative impact occurring during the operations phase of a ballast water treatment system is direct discharges to receiving waters, which will occur for those systems that discharge ballast water with altered quality. This type of impact generated a lot of concern from environmental agencies and groups at a recent ballast water treatment symposium. It is a new impact category for the ship operations phase, although ships have other routine direct discharges to coastal waters, such as treated sewage and cooling water. Because of the concerns due to discharge of ballast water with altered quality, this type of impact received additional attention during the MARTOB study.

Ballast water treatment systems that require chemicals to be stored on-board also have the potential for a spill to the environment. This type of environmental impact is not accounted for in most life cycle assessment methods, as it is not an expected impact. For the methods tested in WP4, this type of impact was noted but was not quantified in terms of an estimate of probability.

All ballast water treatment systems should have a very large positive environmental impact during their operation phase – the prevention of the introduction of non-indigenous species. This cannot be quantified using existing life cycle techniques. This is an obvious positive impact but it doesn't fit into the indicator categories used for LCA environmental impacts. "Biodiversity" is perhaps the most applicable category in an LCA, but in the short term introduction of a new species may increase biodiversity. In the long term, there could well be a decrease if local species are out-competed. For the MARTOB project, it can be qualitatively stated that all ballast water treatment systems will have a positive environmental impact with respect to reducing the risk of introduction of non-indigenous species. The relative effectiveness of each method in terms of the percentage reduction for representative species types is discussed in the MARTOB reports describing the biological effectiveness testing carried out for each method.

Scrapping

The disposal/recycle phase of ballast water treatment equipment starts when the equipment is taken off the ship or when the ship itself is scrapped. If the equipment is scrapped together with the ship, it will add only an incremental value to the impact resulting from the ship itself. If some of the materials used for the equipment can be recycled, it will be a "credit" in the life cycle assessment against material used. When treatment system design is being finalised consideration should be given to

determining how larger components or materials can be recycled to reduce the overall impact

2.3.1.1 APPLICATION OF THE LIFE CYCLE CONCEPT TO MARTOB TREATMENT SYSTEMS

A life cycle assessment includes the following components (US EPA, 2001):

- Goal definition and scoping
- Inventory analysis
- Impact assessment
- Interpretation

A general explanation of the approach taken for each of these components to assess the ballast water treatment systems tested in WP4 of the MARTOB project is provided below. Specific information collected for each system is provided in chapters 4 to 9.

2.3.1.2 GOAL DEFINITION AND SCOPING

The intent behind assessing the environmental issues across the life cycle of the ballast water treatment methods tested within the MARTOB project was to contribute information towards the decision-making process for selecting an appropriate treatment method. The specific goals were:

- To investigate the environmental impacts of each of the treatment methods from a life cycle perspective
- To help identify stages where there are larger impacts, so that efforts can be directed towards them during the method development phase.

The assessment also focused on determining how the ballast water treatment methods may contribute to those categories of impacts where transport in general and shipping in particular is trying to reduce the overall impact.

Because the methods are all currently in the development and testing phase, detailed information was not always available. The goal, therefore, was not to carry out a detailed assessment but rather to identify and assess those areas considered to have the most significant impacts. For the production phase of the life cycle, the major materials required for production were considered. For the operations phase, an emphasis was placed on energy use and direct discharges to water. For scrapping, it was assumed that the equipment would be scrapped with the ship. Most ship breaking is done in third world countries and detailed information on the impacts of this is not available for inclusion in a life cycle assessment.

To collect similar life cycle data for each treatment system evaluated within MARTOB, it was assumed they would be operated on the same type of vessel. It was assumed that the system would be installed on a RoRo vessel, similar to that used to test the treatment systems in WP4. The total ballast water capacity is approximately 8000 m^3, but the system is only required to treat 2000 m^3 of ballast water for each port call because the vessel always operates with some ballast water in the tanks for trim.

It is assumed that the vessel would make 40 port calls each year where it would be required to treat the ballast water. The system life is estimated at 20 years.

2.3.1.3 INVENTORY ANALYSIS

The purpose of the inventory analysis phase is to identify and quantify energy, materials use, emissions to water and air, and solid waste throughout the life of the product or treatment system (US EPA, 2001). Stages in the life cycle of a ballast water treatment system could include the following:

- Extraction of raw materials
- Transport of raw materials
- Manufacture/Production of the ballast water treatment equipment
- Transport and installation of the equipment to ship
- Operation Phase (maintenance and consumables)
- Scrapping of equipment

Extraction of raw materials can be described as removal of raw materials and energy sources from the earth. These materials are then used for production of steel, iron, titanium, and other materials required in the production of the equipment. Information was collected on the quantity of the major materials (by weight) used in the prototype treatment system or as required to produce equipment to treat 2000 m^3 of ballast water. Production of the equipment itself was not included. This was due to lack of information for all systems, and also the degree of uncertainty with systems still in a prototype phase. The process used to produce a prototype is generally not the same as the one that will be used to produce an item that is in full production. Producing a prototype is usually labour intensive and may go through some iterations. Also, it was not possible to get information on the energy used to produce the prototype. Most methods are still at a stage where the quantity and source of materials, and manufacturing process and location still needs to be determined. For this reason, selected open life cycle inventory data from production sources in Europe was used for emissions and energy use for the major materials. Sources of the data for specific material types are shown in Table 2.3.

Table 2.3: Sources of LCA data for materials production

Material Type	Data Source and Type
Steel	Sunér, 1996. Life cycle data for production of Steel in Sweden
Polypropylene	Boustead, 1999. Eco-profile data for polypropylene resin produced in selected Western European Countries.
Fertilisers (Biological De-oxygenation method)	Davis and Haglund, 1999. Life cycle inventory of fertiliser production for fertilisers used in Europe.
Sugar (Biological de-oxygenation method)	Nielsen et al., 2003. Life cycle data for basic food in Denmark.

Transport of the equipment to the ship, and installation on board was not included in the assessment. This would vary considerably depending on the specific ship being assessed. New ships would have the equipment installed on board at the shipyard where the ship was being constructed. For existing ships, the installation may occur when the ship was in dry dock undergoing regular maintenance. Depending on the system, the installation time would vary but likely more time would be required than what would be available during a routine call at port.

For the operations phase, the focus was placed on energy use and discharges to receiving waters for methods where this was applicable. For energy use, it was assumed that the ship's engines were used to produce the required energy, and that the fuel was marine diesel with a 3% sulphur content. The environmental impact from energy production can vary considerably depending on the source. Before the energy can be produced on board, the fuel must first be extracted and transported. It must then be transported to the point where it is loaded on to the vessel. It is then ready to be used for energy production. So there is already an impact even before combustion of the fuel takes place. Fuel quality and composition can vary widely by country, resulting in a wide variation of emissions values (Jun et al., 2002). For the MARTOB assessment, default emission values from the Intergovernmental Panel on Climate Change and values from a study carried out by Lloyd's Register Engineering Services in the Marine Exhaust Emissions Research Programme (Carlton et al., 1995) were used. These emission factors are shown in Table 2.4.

Table 2.4: Air emissions per tonne of fuel burned

Emissions	**Emissions, kg per tonne fuel, Marine Diesel Engine**
CO_2	3140 (1)
CO	7.4 (2)
CH_4	0.3 (3)
N_2O	0.08 (3)
NO_x (as NO_2 for Lloyd's)	72 (3)
NMVOCs	2.1 (3)
SO_2	60 (4)
Hydrocarbons (HC)	2.4 (2)
PM10	4.4 (2)

Sources:

1. From IPCC Default Emission Factors for European Diesel Engine Ships on Inland Waters, Table 1-47, IPCC Reference Manual, as reported in Jun et al. (2002).
2. Carlton et al. (1995) as reported in (Corbett and Fischbeck, 1998). Note that the emission for PM10 is an average of the values provided for slow speed and medium speed diesel engines. For CO and HC the same value was provided for both speeds.
3. From IPCC Default Emission Factors for Diesel Engine Ocean Going Ships (IPCC Reference Manual), as reported in (Jun et al., 2002)
4. Estimated based on a fuel with a sulphur content of 3%, which is recommended by IPCC as a default value for marine bunker fuels. The sulphur content of the fuel is the main factor for the emission of SO_2. Using a low or high-sulphur fuel would yield different results of emission of SO_2.

To summarise, the main life cycle stages considered for the ballast water treatment systems tested in MARTOB were:

- Production of equipment:
  - Raw materials extraction
  - Production of materials required for the equipment/process
- Operation:
  - Use of energy
  - Consumables

2.3.1.4 IMPACT ASSESSMENT AND INTERPRETATION

The impact assessment phase includes an assessment of the potential human health and ecological effects of the energy and material usage identified in the inventory. The focus within the assessment carried out in MARTOB was on global impacts in terms of greenhouse gas emissions and global warming, and local impacts in terms of acidification and direct discharges to receiving water bodies. Some of the relevant inventory data for the global warming impact category included:

- Carbon dioxide (CO_2)
- Nitroous Oxide (N_2O)
- Methane (CH_4)

Emissions were converted to CO_2 equivalents. For acidification, sulfur oxides (SO_x) and nitrogen oxides (NO_x) are relevant parameters. Discharges to receiving waters and their associated impacts are described in the next section.

2.3.2 WATER QUALITY IMPACTS

Large volumes of ballast water are transported and discharged at ports all over the world. There are concerns about possible environmental effects that would result if this ballast water were treated prior to discharge. The available information on the quantity of ballast water discharged to ports is rather limited, as described in the report by Gollasch and Leppäkoski (DTR 2.2). Only 6 European countries could provide estimates on the total annual amount of ballast water discharged to their waters (see Table 2.5). This table also presents estimates of ballast water discharges for other countries and regions, as found in the literature. Gollasch and Leppäkoski (DTR 2.2) reported that the method of data collection and recording varies by country.

Table 2.5: Estimates of annual BW discharges to selected locations worldwide

Location	Annual Amount Discharged	Reference Source
Worldwide	3 – 5 billion tonnes	IMO, 2002, in Reynolds and Endresen, 2002
Australian Ports	150 million tonnes	CRIMP (2001)
New Zealand	3.7 to 5 million	Hay et al., 1997, in Reynolds and Endresen, 2002
US Coastal Ports (excluding Great Lakes)	44.7 million tonnes	Reeves (1999)
Canadian Coastal Ports (excluding Great Lakes)	49.7 million tonnes	Reeves (1999)
Great Lakes	720,000 tonnes (originating from outside the Lakes)	Reeves (1999)
Selected European Countries (DTR 2.2)		
France	22 million tonnes	Year 2000, Masson, pers. Comm.
Germany	8 million tonnes	1996 (Gollasch, 1996)
Ireland	2 million tonnes	1995 (Minchin & Sheehan)

Netherlands	7.5 million tonnes	
Sweden	23 million m^3	1997 (SSPA, 1998)
United Kingdom	42.5 million tonnes	1994 (Macdonald (1994), Laing (1995)

The annual volumes of ballast water discharged appear quite large, so it can be useful to compare them to other discharges to the same region. A Swedish Report (SSPA, 1998) provides an estimate of ballast water discharged into Swedish coastal areas and inland waterways. The area of the North Sea referred to as the Kattegat (approximately from Halmstad to Göteborg, including the Port of Göteborg) received the largest amount of ballast water. It was estimated that a total of 7.8 million m^3 of ballast water was discharged to this area by tankers and cargo ships. By comparison, the annual discharge from sewage and industrial sources to this same waterbody was estimated to be 173,000 million tonnes (OSPAR Commission, 1999). Ballast water is only 0.005% of these sources, and represents only a very small loading to the receiving environment. In addition, it is not discharged continuously and the discharge location is not fixed. It is discharged at a number of harbours along the coast, and at different berths within these harbours. Ballast water is also discharged at approaches to the ports.

Water quality impacts resulting from direct discharge of treated ballast water can be caused by:

- Discharge of water with altered quality:
  - Physical parameter changes
  - Metals
  - Nutrients/Oxygen Demand, Low D.O.
  - Biocide residuals
- Discharge of surviving organisms
- Discharge of solids (organisms and sediments)

The magnitude of the impacts of the discharge of ballast water with altered quality will vary greatly depending on the sensitivity of the receiving environment. Because of different local conditions and concerns, receiving water quality guidelines for ports around the world also vary. There are currently no standards or regulations for the quality of ballast water discharged. The ballast water convention approved in February 2004 by the IMO has set standards pertaining to the allowable concentrations of viable organisms (zooplankton and phytoplankton) and bacteria but not for water quality parameters. It seems reasonable, therefore, to compare ballast water quality to relevant parameter limits that are currently permitted for urban and industrial wastewater discharges. Ballast water discharges are a much smaller volume than most wastewater discharges, and they are intermittent, so using these limits can be considered a conservative approach. The quality of the ballast water discharged from the treatment systems tested within MARTOB was compared to the following standards:

Table 2.6: Standard for Ballast Water Discharge

Water Quality Standard	Relevant Parameter Limits
IMO, Annex IV of MARPOL 73/78 (Standards for discharge from on-board sewage treatment facilities)	Suspended solids (max 100 mg/l above water used for flushing), BOD_5 (max. 50 mg/l), Faecal Coliforms (max 250 MPN / 100 ml),
EU Urban Waste Water Directive	BOD_5 (max. 25 mg/l), COD (125 mg/l),

(91/271/EEC)	TSS (60 mg/l), (2000 to 10,000 pop. Equiv.) 2 mg/l P, 15 mg/l N (for populations of 10,000 to 100,000 discharging to 'sensitive areas')
EU Dangerous Substances Directive (76/464/EEC)	(Specific emission values for 18 substances – none of these would be in ballast water discharges treated using methods tested as part of the MARTOB project)

2.3.3 DISCUSSION

The environmental impacts of the ballast water treatment methods tested in WP4 were investigated using information from the on-board and shore-based large scale test results. Updated estimates for materials and energy use over the life cycle of the treatment systems was provided based on optimised system operational parameters. The assessment focussed on potential impacts resulting from:

- Materials use during system production
- Use of energy and consumables over the operational life of the treatment system (resulting in emissions to air)
- Direct discharges to receiving waters

From a life cycle perspective, impacts during system operation were dominant for all treatment methods. Emissions to air resulting from fuel use for energy production represented more than 95% of the total. This is similar to the life cycle of a ship as a whole, with the majority of impacts occurring during the operations phase, and primarily related to energy use, with some impacts from maintenance.

Direct discharges to water also occurred during operation of the treatment methods. The methods tested within MARTOB had an effect on the following water quality parameters:

- Temperature (maximum 7°C increase above background was measured during the tests): high temperature thermal treatment, UV, and US methods had an effect on water temperature
- Lowered pH (6.8 is the lowest estimated): biological de-oxygenation method resulted in a lower pH
- Potential higher redox potential and possibility for increased metal concentration from increased corrosion (Fe, Zn, Al): biological de-oxygenation and the Oxicide method have the potential to result in increased corrosion
- Very low dissolved oxygen (D.O.) concentration: biological de-oxygenation method resulted in ballast water with a D.O. of essentially zero, the Oxicide method is expected to produce ballast water with a D.O. concentration of less than 5 mg/l
- Elevated nitrogen and phosphorus concentrations in ballast water treated with the biological de-oxygenation method, but these would still be below concentrations specified in the EU urban wastewater directive
- Possible hydrogen peroxide residual in ballast water treated with the Oxicide method.

None of the treatment methods result in the discharge of substances that are identified as 'priority hazardous substances', or that have the potential to bio-accumulate. All methods will result in organic matter in the discharge in the form of dead organisms. All but two of the methods would be operated using a filter as pre-treatment. Biological de-oxygenation and ultrasound treatment do not require the use of a filter and this is optional for HTTT. Methods using the filter as pre-treatment will need to discharge the filtered material to the receiving environment, which could cause some turbidity.

In terms of the effects of organisms surviving the treatments, further investigations are required to determine effectiveness against phytoplankton, bacteria, and viruses. The actual environmental effects of survival of specific species cannot be determined as it would depend on the specific environmental conditions of donor and receiving ports, and would be outside the scope of this assessment.

Other possible impacts on receiving waters include potential impacts from accidental spills of substances used in the treatment process. The Oxicide method uses nitric acid anolyte and requires sodium nitrated to be stored on board. The de-oxygenation method requires nutrient solution to be stored on board, and UV treatment uses lamps containing small amounts of mercury.

Table 2.7 summarises the environmental impacts for each ballast water treatment method, as determined using information from the large scale trials or from re-design and optimisation that occurred as a result of the large scale testing.

Table 2.7: Summary of environmental impacts associated with BW treatments tested

Environmental Impact Categories	HTTT	Biological De-oxygenation	UV	US	Ozone	Oxicide
Direct impact through discharge to receiving water						
Discharge of surviving organisms	Effective against zooplankton during trials, phytoplankton results inconclusive	Concentration of bacteria about 10 times higher than control (1 million cfu/ml compared to 100000 cfu/ml, survival of some phytoplankton and resting stages likely	Effective against zooplankton during trials, no phytoplankton results	Higher energy levels and low flow rates resulted in effective zooplankton kills, no phytoplankton results	Higher concentrations and contact times resulted in effective zooplankton kills, no phytoplankton results	Laboratory tests showed effectiveness against zooplankton species tested, no large scale testing results available
Discharge of water with altered quality						
Physical parameter changes	Temperature 6˚C higher (min. 4, max. 7)	Reduced pH (pH 6.8 – 7.0) compared to pH 7.9 – 8.1 in control tanks	Temp. increase ranging from 0.2 to 2.1˚C measured	Temp. about 1˚C higher (min. 0.3, max. 2.0)	Higher redox potential estimated during WP3 corrosion assessment	Higher redox potential estimated during WP3 corrosion assessment
Metals	No change expected	Possible increased metals (Fe, Zn, Al) due to higher corrosivity	No change	No change	Possible increase (Fe, Zn, Al) from corrosion	Possible increase (Fe, Zn, Al) from corrosion
Nutrients/Oxygen Demand, Low Dissolved Oxygen (D.O.)	No change	Very low D.O., N 2.5 g/m^3, P 0.071 g/m^3	No change	No change	No change	D.O. less than 5 mg/l (temporarily)
Biocide residuals	None	None	None	None	None	Possible H_2O_2 residual
Discharge of solids (organisms and sediments)	Dead organisms; solids from filtration	Dead organisms, increased concentration of organic matter	Dead organisms; solids from filtration	Dead organisms	Dead organisms; solids from filtration	Dead organisms; solids from filtration

Table 2.7 (Cont.): Summary of environmental impacts associated with BW treatments tested

Environmental Impact Categories	HTTT	Biological De-oxygenation	UV	US	Ozone	Oxicide
Other Environmental Impacts						
Energy Consumption, treatment, estimated to treat 2000 m^3 of ballast water	323 kg. of marine diesel	V. small amount to pump nutrient solution into ballast tanks (but was not pumped during shipboard trials)	15.3 kg of marine diesel to produce energy for UV lamps	27.2 kg of marine diesel to produce energy for US system	118.5 kg of marine diesel to produce energy for ozone generator	85.5 kg of diesel to produce energy for Oxicide cell, compressor, and anoltye/catholyte pumps
Energy Consumption due to additional pumping to move water through treatment unit	Required	Not Required	Required	Required	Not Required	Required
Potential for Spill of treatment chemicals	No	Nutrient solution	Mercury from UV lamps	No	No	Nitric Acid (Anolyte), Sodium Nitrate Salt solution
Materials Use, consumables		Nutrient solution	UV lamps (mercury and quartz)			Sodium Nitrate Salt solution
Materials Use, equipment construction	See summary Table 2.2					

2.4 ECONOMIC ASPECTS

In WP3 one case ship was defined and cost data of the prototypes of onboard ballast water treatment systems were used to calculate costs per m^3 of treated ballast water. Last year, large-scale prototypes were tested on shore or on board ship. The main objective of the on shore tests and see trials was to test the treatment effectiveness, but technical moderation of the treatment systems also result in changes in economic data. In that way this chapter is an update of the work done in WP3. However, in the current work done, costs were viewed much more from the standpoint of the ship owners and not only of the producers or developers of the treatment systems. This means that the treatment systems are compared not only by costs per m^3 of treated ballast water, but also by looking at cost behaviour under different external data.

As mentioned in previous report economic aspects of the treatment systems can be shown by determining changes in ships capital costs, changes in annual operational costs and man-hours needed. One can also take into account possible extra costs of training and management, as well as economic benefits or disadvantages on other (non-treatment) activities on board.

Besides data associated with ballast water treatment, cost calculations depend on ship data, like type and characteristic of the vessel, sailing and trading pattern, including aspects like route, distances, speed, sailing and harbour time, and number of voyages per year, volume of ballast water to be treated, number of ballast pumps and their capacities and type of fuel used.

2.4.1 COST COMPONENTS

The following cost components were specified: capital costs, operational costs, training and management costs and economic benefits or disadvantages.

Capital costs

Capital costs reflect the one-time costs incurred to implement a treatment alternative. This may include, among others the total costs to purchase the treatment system (investment costs), and costs for installation, testing and commissioning. Using an interest rate of 8% and a depreciation period (economic lifetime) of 10 years annualises these one-time costs.

Operational costs

Operational costs: reflect the on-going costs that incur per annum throughout the economic life span of the treatment equipment. Operational costs can be specified into personnel costs, material costs and maintenance costs.

Personnel costs: include costs of personnel involvement (man-hours) to run the treatment system. The amount of personnel hours involved during ballast water treatment and the status of the personnel have to be specified. In view of comparison of the cost calculation results, the personnel costs have to be based on a fixed rate per hour for a specific personnel status. For none of the onboard ballast water treatment techniques extra personnel is needed, all handling can be done by the current crew on-board. Most of the developers specified the involvement of current personnel on board as “negligible” or as “no additional personnel”. Therefore, personnel involvement is

only described in the text but not included in the cost calculations yet (average man-hour costs).

Material costs: include cost of all material needed in the course of system operation, this involves energy costs and costs of consumables. Almost all treatment systems require energy to operate, with exception of de-oxygenation. The ballast water pumps also require energy to operate. The amount of fuel to produce this energy is also included in the cost calculations. Energy use is specified into kWh. Based on the energy requirement of treatment systems, energy use of the ballast water pumps, energy content of fuel and energy conversion factors, the amount of fuel consumed by the ballast water treatment system and the pumps is calculated.

Maintenance costs: are divided into material costs and personnel costs. Treatment systems can require TAM (Turn Around Maintenance), refurbishment, or total overhaul, involving the use of spare parts, after some time. It is necessary to know at what time interval regular maintenance is needed and what wear and tear maintenance is expected.

Training and management costs
The installation of some of the treatment systems will lead to extra training for personnel on-board. Training ranges from a one-hour explanation of the system to a three-day instruction course of how to operate the system, health and safety precautions and how to register data. Training costs are specified into total costs, hours and personnel involved. Management costs include cost for obtaining certification, cost related to the development of a specific management system or costs to prepare of a safety manual. Those costs can be one-time costs or cost that will return every few years. Training and management costs are annualised over the lifetime of the equipment.

Economic benefits or disadvantages
Costs of non-treatment activities on-board can be affected by implementation of a treatment technique. Increased or reduced tank cleaning costs, costs of corrosion control, increased maintenance, loss of cargo space, delay in harbour or during trip caused by the treatment of ballast water are specified. These economic benefits and disadvantages must be attributed to the implemented technique. Most of these costs are related to the number of trips per year.

2.4.2 NON-TREATMENT SYSTEM DATA

Data external to the treatment techniques that determine annual treatment costs include (some of the) ship data, energy related data and costs per man-hour.

Comments on case ship data
The most determinant (or sensitive) factor to the annual operational costs for each of the treatment systems is the total amount of treated m^3 ballast water per year. In the spreadsheets, this total amount is the outcome of the number of trips per year multiplied by the amount of ballast water treated per trip. So, the average number of trips per year must be interpreted as “trips per year on which ballast water must be treated”. Changing this number in the spreadsheets, one can easily recalculate and compare the total costs of one treatment system between different “usages” of the

system. In section 2.4.3 a figure is drawn (Figure 2.2), which shows the cost behaviour of all treatment systems under different number of trips per year, c.q. different amounts of treated m^3 ballast water per year.

Table 2.8: Case ship data

Case ship data		**Unit**
Ship type	RoRo, PCTC	
DWT	14,841	tonnes
Total ballast water capacity	8,076	m^3
Ballast water to be treated on one voyage	2,000	m^3
Average number of trips per year	50	trips
Average duration per trip		days/trip
Average sailing speed	20	naut miles/h
Number of ballast pumps	4	
Ballast water pump capacity	500	m^3/h
Total ballast water pump capacity	2,000	m^3/h
Power requirement of ballast pump	50	kW/pump
Type of fuel for ballast pumps	diesel	
Average personnel cost per hour	25	€/man-hour
Shadow costs of space	100	€/m^3

Table 2.9: Basic energy data

Basic energy data		**Unit**
MJ to kWh	3.6	MJ/kWh
Conversion rate diesel to electricity	30%	
Conversion rate diesel to steam	66%	
Energy content diesel	42.5	MJ/kg
Price diesel	0.40	€/kg

Table 2.10: Electricity production data

Electricity production		**Unit**
energy requirement	100	kWh
kWh to MJ (electricity)	360	MJ (electricity)
MJ (electricity) to MJ (diesel)	1,200	MJ (diesel)
MJ to kg (diesel)	28.24	kg (diesel)
Energy costs (diesel)	11,29	€ (28.24 kg)
Energy costs electricity	0.113	€/kWh

Table 2.11: Steam production data

Steam production		**Unit**
Ballast water to be treated per trip	2,000	M^3/trip
Steam requirement per m^3 BW	10	kg/m^3 BW
Total steam requirement	20,000	kg/trip
Energy needed to produce one kg of steam	0.0025	GJ/kg steam
Total energy needed for steam per trip	50.0	GJ/trip
Energy needed	2.5	MJ/kg steam
Energy needed	0.69	kWh/kg steam
Total energy needed for steam per trip	**13,889**	**kWh/trip**
Diesel, energy content	42.5	MJ/kg
Use of diesel (100% conversion efficiency)	1,176.5	kg diesel
Use of diesel (66% conversion efficiency)	**1,782.5**	**kg diesel**
Energy costs steam (66% conversion rate)	0.89	€/kg

Comments on energy data
Basic energy data and electricity production data are applied to all systems. Steam production data are only relevant for thermal treatment. It is assumed that on-board production of energy (electricity or steam) is not limited, that is, existing generators can produce any amount of energy that is needed.

2.4.3 DISCUSSION

From the cost calculations it can be concluded that the large part of the needed data is available. For some of the treatment systems personnel costs, extra maintenance costs, cleaning costs and costs of corrosion control are not quite clear yet. If better estimates are available, they can be substantial to the operational costs.

Some of the treatment systems cannot treat ballast water during intake or during discharge. When treatment during a trip is necessary, one has to think about ballast water tanks with a piston to keep treated ballast water apart from non treated ballast water (recommended only for new ships).

The total annual costs per treatment system for 50 trips (100,000 m^3 treated ballast water) ranges from € 10,000 to € 60,000. For some intercontinental ships this equals the total costs to "run" that ship for 1 to 6 days.

Figure 2.3 shows for all of the treatment methods the annual capital and operational costs per m^3 of treated ballast water in the (static) case of treating 100,000 m^3 ballast water a year.

Ballast water is treated mostly during long (intercontinental) trips. As mentioned earlier, the number of trips should be interpreted as to determine the amount of m^3 of ballast water treated. To show what the influence is of changing the yearly number of trips on costs per m^3 of treated ballast water the next figure is drawn.

Treating less cubic metres ballast water will lead to relative higher costs per m^3 treated ballast water, mainly because of spreading the same annualised capital costs over less cubic meters, and vice versa. But there is more: the higher the annualised capital costs compared to other systems; the steeper the curve will be and the more expensive the treatment method will be compared to the other systems at fewer trips a year (or relatively cheaper in case more m^3 ballast water is treated). By comparing the two figures it is easily seen that this is the case for ultrasonic, Oxicide, and for advanced oxidation treatments.

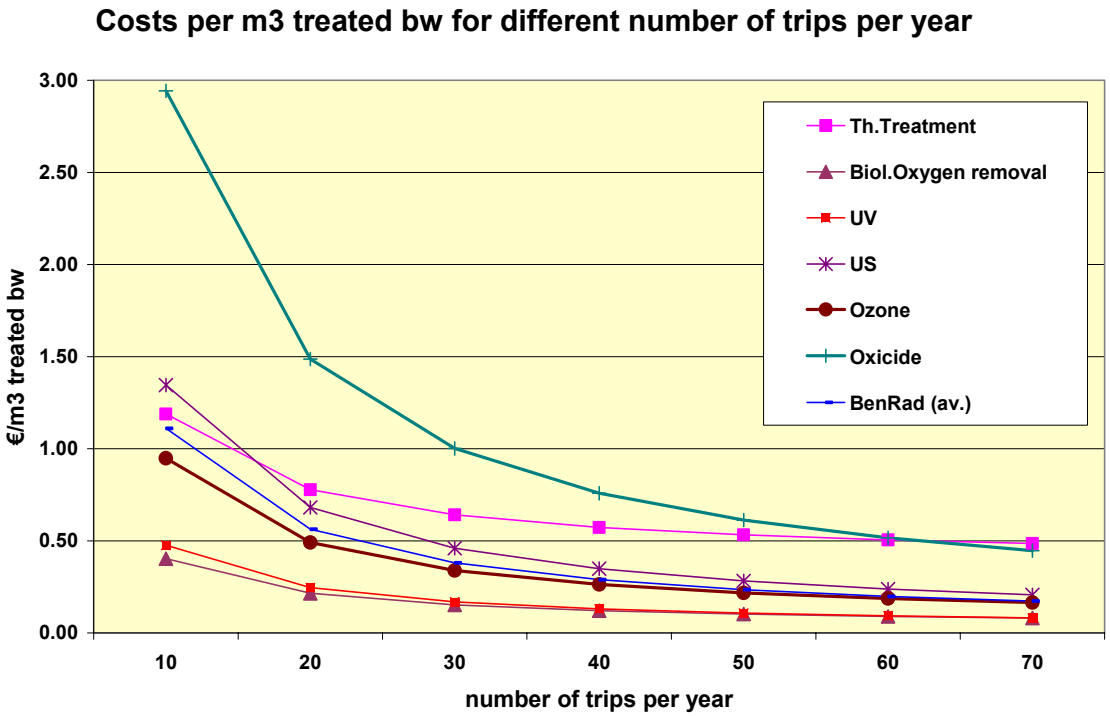

Figure 2.2: Cost per m^3 for different number of trips per year

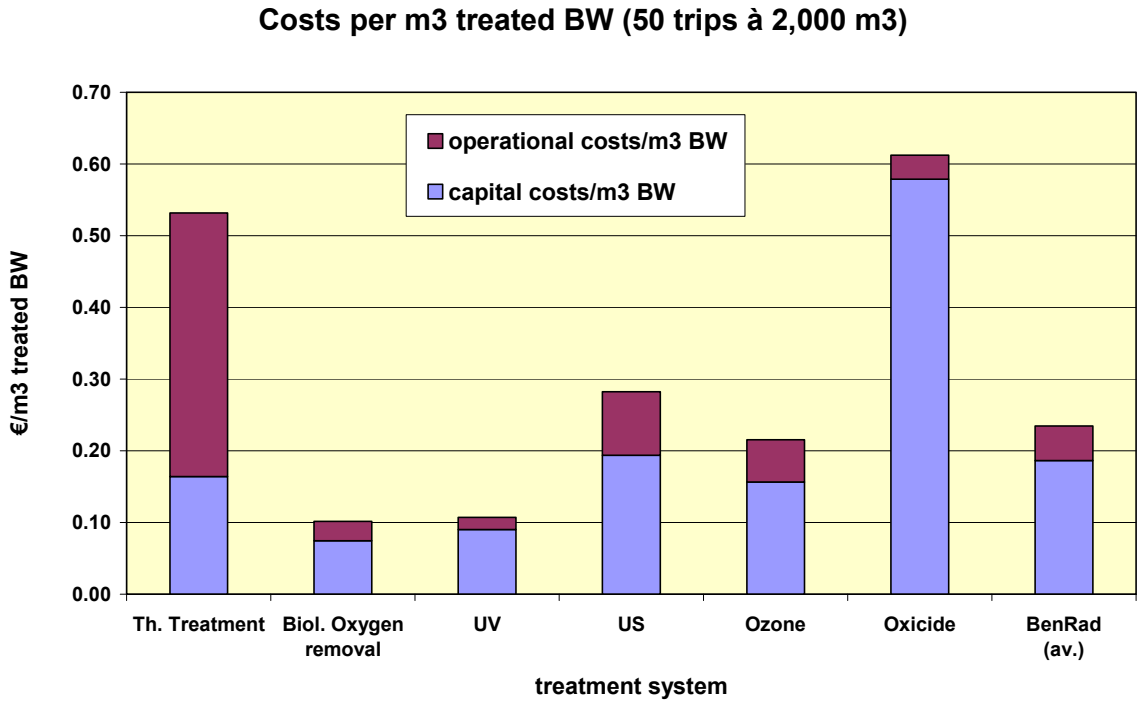

Figure 2.3: Cost per m^3 of treated BW

3 BIOLOGICAL ASSESSMENT

The biological assessment of each ballast water technology, at full scale, was performed in WP4. All the methods had previously been tested during the small scale shore based trials, which took place in Newcastle in June 2002. The full scale trials therefore offered an opportunity to test whether the treatment methods could be scaled-up to work during normal ship operations and also to assess the biological efficiency of the methods.

3.1 IMO BALLAST WATER PERFORMANCE STANDARD

The sampling methodology was influenced by the discussion at the International Maritime Organisation (IMO) regarding the ballast water management standard. Although the standard was in draft form at the time when the trials were carried out and had undergone frequent changes, attempts were made to collect the samples in such a way as to allow some assessment of whether the treatments would have achieved the IMO standard. The ballast water performance standard, adopted by consensus at a Diplomatic Conference at IMO in London on Friday 13 February 2004 reads as below[2].

1. "Ships conducting ballast water management shall discharge less than 10 viable organisms per cubic metre greater than or equal to 50 micrometers in minimum dimension and less than 10 viable organisms per milliliter less than 50 micrometers in minimum dimension and greater than or equal to 10 micrometers in minimum dimension; and discharge of the indicator microbes shall not exceed the specified concentrations.
2. The indicator microbes, as a human health standard, include, but are not be limited to:
    a) Toxicogenic *Vibrio cholerae* (O1 and O139) with less than 1 colony forming unit (cfu) per 100 milliliters or less than 1 cfu per 1 gram (wet weight) zooplankton samples;
    b) *Escherichia coli* less than 250 cfu per 100 milliliters;
    c) Intestinal Enterococci less than 100 cfu per 100 milliliters.

As the sampling methodology had been developed with the IMO standard in mind the results were used to ascertain whether the treatment methods would have achieved the standard.

3.2 SEA TRIALS

The sea trials were carried out on board the M/V Don Quijote (gross weight 56 893 MT) owned by the Swedish shipping company Wallenius Lines. It has a capacity of 5 850 cars or a combination of 3 000 cars and 475 trucks on 13 car decks. The overall length is 199.15 meters, the width 32.26 meters, and the height to the weather deck is 33.48 meters. The maximum speed is 20.5 knots.

Two treatment methods were tested onboard Don Quijote; High Temperature Thermal Treatment (HTTT) (see chapter 4) and Biological De-Oxygenation (DEOX)

[2] More information is available on http://globallast.imo.org.

Treatment (see chapter 5). The HTTT method was evaluated during the voyage from Suez (Egypt) to Zeebrugge (Belgium) between the 27th May and 5th June 2003. The DEOX method was tested from 21st to 28th June 2003 during the vessel's journey from Southampton (UK) to Manzanillo (Panama).

3.2.1 SAMPLING AND ANALYSIS

During the study, the ballast water was analysed at intervals for live and dead zooplankton, phytoplankton, viable bacteria, hydrogen sulphide, temperature, pH, and dissolved oxygen. The analysis of zooplankton was done at Newcastle University, the analysis of phytoplankton was done at FRS Marine Laboratory and all the other analysis was performed onboard by SINTEF. At the end of the experiment samples for nutrient analysis were taken and frozen for later analysis at SINTEF.

For both treatments, samples for zooplankton, phytoplankton and bacteria were collected by pumping water with the help of the ship's own fire pump and through ship pipes from the ballast tanks to the HTTT unit located on deck (for details see DTR 4.2). Figure 3.1 shows the sampling system after the HTTT unit.

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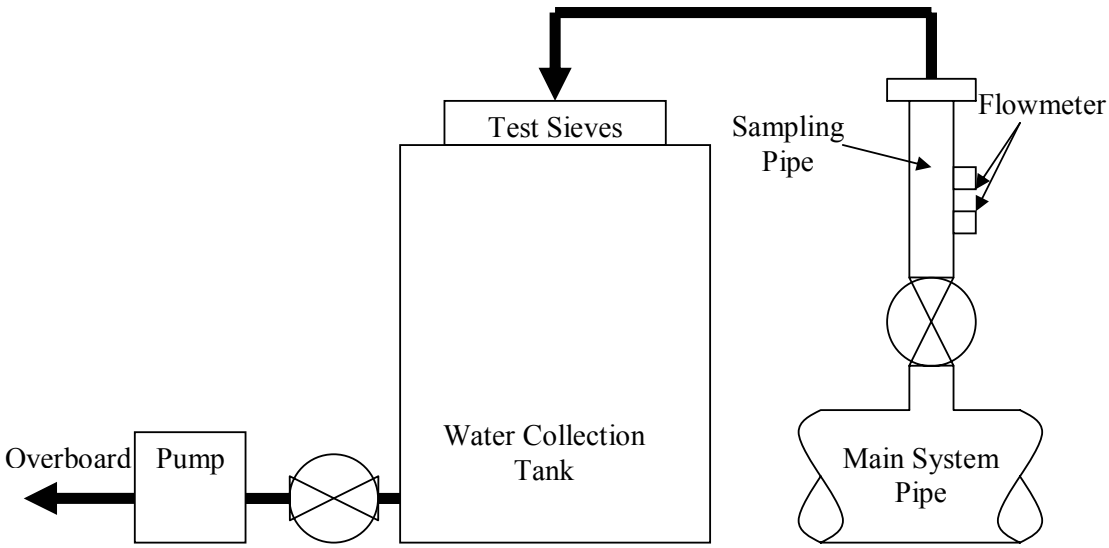


Figure 3.1: Test sampling system

The flow rate was measured with a flow meter and used to calculate the collected volume. The flow rate was usually 55 to 85 litres per minute. During the HTTT trials, the pipes were flushed for approximately 15 minutes before each new tank was sampled to ensure that the water was from the required ballast tank and not water remaining in the sampling pipes. However, as the density of plankton collected was not as high as expected this procedure was not carried out on the 2nd June in order to check whether the zooplankton were avoiding the pumps. During the first two sampling days of the DEOX trial, the same flushing operation was applied. However, from the 26th June observations indicated that around 5-10 tonnes of water (depending on the position of the tank sampled) should have been run to waste in order to ensure that water from the intended tank was being sampled and the amount of water flushed was adjusted accordingly from this date.

Samples were also taken directly from the tanks through the sounding pipe. This method was used for small samples from the DEOX treated tanks. Silicon tubing with a metal tube connected to the end as a weight, was lowered down through the sounding pipe (diameter approx 3 cm) until it hit the bottom of the ballast tank. It was then hoisted up again 20-50 cm, and water sucked up with a peristaltic pump into a 1 litre plastic bottle (Figure 3.2). The samples were used for analyses of bacteria, chlorophyll (only 1 or 2 parallels), pH, temperature, and H_2S.

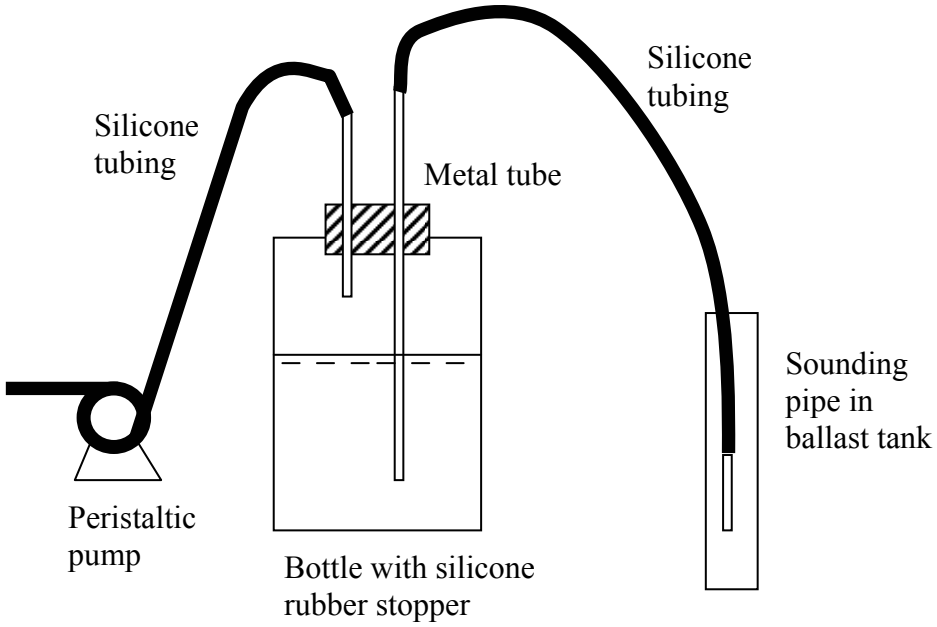


Figure 3.2: Sampling system for small water samples through the sounding pipe.

3.2.1.1 ZOOPLANKTON

The zooplankton samples consisted of the organisms present in 1 tonne of water. In the HTTT trials two sets of samples were collected, one prior to treating the water and the other after heating it. In the DEOX trials, the same water sampling system was used without heat treating the water. Initially, the water was filtered through three different size sieves: 250, 150 and 50µm (ENDECOT) to prevent clogging of the sieves by pre-filtering larger organisms. However, after the first 9 tonnes were sampled during the HTTT trials it was apparent that the densities filtered would not clog the sieves, therefore only the 50µm sieve was used for the rest of the trials.

Once filtered, each sample was rinsed into a bottle with filtered seawater that was made freshly each day and contained in a 90 litre tank. The sample was then stained with 0.1% Neutral Red solution in the ratio of 3ml stain/100ml sample. After staining for 30 min, 4ml of 1M Sodium Acetate solution was added per 100ml of sample. The specimens were then fixed with 4% Formalin in a volume equal to that of the sample (50/50) and stored overnight at 5°C. Thereafter, the samples were kept at room temperature until the end of the trials. This staining procedure was based on Omori and Ikeda methodology (Omori and Ikeda, 1984).

On return to the Dove Marine Laboratory in Newcastle (UK) and before examination, Glacial Acetic Acid was added dropwise to each sample, until the colour of the solution changed to magenta. The sample was filtered through a 48µm sieve and

washed with tap water. For the counting analysis and the taxonomic identification, the samples were kept in a Petri dish in water and sorted using a Nikon 90729 stereomicroscope. For those samples containing high numbers of organisms, sub-samples were taken. The volume of the sub-sample varied depending on the amount of specimens encountered for the main taxon (i.e. copepods and nauplii). Each sub-sample contained at least 100 individuals of one of these groups. The numbers were then scaled up to the whole volume of the sample. After counting organisms were preserved in 4% Formalin.

Live organisms stained immediately prior to fixation turned a deep magenta after acidification, whereas dead specimens were light pink to white or transparent (when having an exoskeleton or shell). The assessment of individuals also included a morphological examination. For the counting procedure whole organisms as well as identifiable body parts were taken into account.

Zooplankton was identified to the level of subclass or class, to ensure the availability of the results promptly.

3.2.1.1.1 Statistical Analysis for High Temperature Thermal Treatment

For the HTTT experiment, samples from before (control) and after treating the ballast water were taken. Mortalities for both types of samples were calculated. The mortality for the control samples (*Mort Bef*) was calculated as the dead organisms divided by the total number of organisms counted (dead plus alive). The mortality for the treated samples (*% Mort*) was calculated based on the supposed total input obtained from the control samples, and assuming that the missing organisms had been killed and destroyed by the treatment.

Two-way ANOVA test was used to analyse the mortality from the control samples over time and between life stages, for the treated samples (apart from the last day, which was analysed by Kruskal-Wallis test), to see if there were any differences in the efficiency between the different temperatures tested and over time, and between control and treated samples. It should be noted that two-way ANOVA was conducted even when the assumptions could not be followed, therefore caution was required when interpreting the results.

To check the disappearance of the organisms in the ballast tanks over time, one-way ANOVA was used. To analyse the number of viable (live) organisms between tanks and over time, one-way ANOVA (or Kruskal-Wallis) was applied.

3.2.1.1.2 Statistical Analysis for the De-Oxygenation Treatment

In the DEOX trials, two tanks were used as controls while nutrients were added to two other tanks. Samples were collected on the following dates: 21/6, 24/6, 26/6 and 28/6.

The mortality on day 0 (21/6) was calculated the same way as the mortality for the control samples in the HTTT trials (*Mort Bef*). Mortality for the other days was calculated in the same way as for the treated samples in the HTTT trials (*% Mort*). However, instead of using the control sample numbers to estimate the amount of organisms present in the tanks, the numbers used were those found in each of the tanks on the first day. For example, for calculations in tank 3UP on the 28th the

concentration found in the same tank on the 21st were used as reference for the concentration of organisms present at the beginning.

To analyse the mortality over time, between tanks and between treatments (treated and control), three-way nested ANOVA was conducted (tank was nested to treatment). However, the data were not following the assumptions for ANOVA (even after transforming them by means of squaring the raw data), therefore a careful interpretation of the results was required.

The analysis of the disappearance rate between treated and control tanks over time for copepods and nauplii was undertaken by means of a three-way nested ANOVA (tank being nested to treatment). When normality was not attained, a Box-Cox or a Log+1 (when 0 values where present) transformation was performed, however sometimes the data were still not normal but despite this the test was used, the results were therefore interpreted with care.

To compare the sensitivity between copepods and nauplii towards the treatment, one-way ANOVA or Kruskal-Wallis were performed. To check if there were any differences with regards to the concentration of viable organisms between the treated and control tanks and over time, three-way nested ANOVA test was applied, even when the data were not normal.

3.2.1.2 PHYTOPLANKTON

The phytoplankton sampling consisted of collecting samples of the ballast water for two types of analyses: chlorophyll *a* analysis and direct cell counts.

For the chlorophyll *a* analysis, approximately 5 litres of ballast water were filtered, to remove larger pieces of dirt and rust, through a 250µm mesh into a bucket. After mixing the collected water thoroughly, 2 litres were collected in a white HDPE plastic bottle. This was then divided into three replicates of 500ml which were vacuum filtered using a Whatman GF/F glass fibre filter (0.7µm) for the HTTT samples and GF/A glass fibre filters (1.6µm) for the DEOX samples. Each of these filters was folded in on itself once and wrapped with a labelled foil square and frozen immediately. These samples were stored at –20°C until the end of the sampling trials. The samples were stored in dry ice for transport to the FRS Marine Laboratory and were transferred to a -20ºC freezer immediately on arrival. Fluorometric chlorophyll *a* analysis was carried out based on an acetone extraction method (Arar and Collins, 1997).

For the direct cell count samples the water from the tanks was directed from the sample pipe through the 250µm and 100µm sieves. The filtrate was collected in buckets. During the HTTT trials, 90 litres of water were collected each time. However, from the second sampling day of the DEOX trial (day 3) the volume collected was reduced to 60 litres to reduce the time required for the next step of filtration. The buckets were divided into three replicates of 30 litres or 20 litres (depending on whether the volume collected was 90 or 60 litres). Each of the replicates was filtered through 10µm plankton net. The sample was rinsed into a bottle with the filtered water and preserved with Lugol's iodine (approximately 2ml was added in each sample). The samples were then stored in a cool dark place until the trials finished.

The cell counts were carried out using standard counting procedures based on the Uterm ̄hl sedimentation method and using an inverted microscope (Uterm ̄hl, 1958). The counts were very broad taxonomically, phytoplankton were only counted to the level of class i.e. Bacillariophyceae (diatoms) and Dinophyceae (dinoflagellates), in order to ensure the results of the analyses would be available quickly. Enough of the sample was examined to ensure that a minimum of 100 cells from each class was counted.

3.2.1.2.1 STATISTICAL ANALYSIS FOR HIGH TEMPERATURE TREATMENT

For the HTTT trials a total of 78 samples were collected before (control) and after treatment of the ballast water. Unfortunately, the majority of the samples had no chlorophyll *a* present, hence nothing could be stated from these results. With regard to the cell counts, for both diatoms and dinoflagellates one-way ANOVA was used to analyse differences in cell concentration between days, tanks and temperatures. When one-way ANOVA could not be used, i.e. when the data were not normal (checked by the Anderson-Darling test) or the variances were not homogeneous (checked by the Levene's test) even after transforming them (by means of a Box-Cox transformation), the Kruskal-Wallis test was used instead.

3.2.1.2.2 STATISTICAL ANALYSIS FOR DE-OXYGENATION TREATMENT

Two tanks were used as control and two were treated in the DEOX trial. Samples were collected via the fire pump from all tanks on the following dates: 21/6, 24/6, 26/6 and 28/6. In addition further samples were taken via the sounding pipe on the 23/6, 25/6 and 27/6 from the treated tanks. However, on the 27/6 only one replicate was obtained. The chlorophyll *a* samples were all filtered using a GF/A filter (1.6µm). For those samples taken via the fire pump a GF/F filter (0.7µm) was also used (this size of filter was also used in the HTTT trials).

To analyse if there was any difference in chlorophyll *a* and phaeophytin concentration or in cell concentrations (dinoflagellates and diatoms) between treated and control tanks and over time, two-way ANOVA tests were carried out even when data were not normal (see explanation in Section 3.2.1.1.1).

To test differences between particular days or between particular tanks, one-way ANOVA or a Kruskal-Wallis test (when data were not normal or homogeneous, even after conducting a Box-Cox transformation) was used.

To check whether there were differences between the samples taken via the fire pump system and those taken via the sounding pipe, a one-way ANOVA or a Kruskal-Wallis test were performed.

A Kruskal-Wallis test was used to see if there were any differences between the samples collected with GF/A and GF/F filter.

3.2.1.3 BACTERIA

Seawater samples for bacterial analysis were collected in sterile polypropylene bottles (100ml or 1 litre) and stored cool until they could be processed further (usually within a few hours).

Samples for bacterial analysis during HTTT trials were collected in 100ml bottles from water pumped via the fire pump. The bottles were filled from the tube flushing the water over the zooplankton sieve. The samples were always taken during the last of the replicates of 1 tonne for zooplankton analysis, except on June 3 from DB4S. On this date a sample was taken during each of the three replicates of the before treatment samples, and in addition an extra before treatment sample was taken during each treatment from a tap just before the water entered the heat treatment unit. Immediately after this sample bottle had been filled, a second bottle was filled with treated water from the tube flushing treated water over the zooplankton sieve.

Samples for bacterial analysis during the DEOX trial were either collected in 100ml or 1 litre bottles. The 100ml bottles were from the tube flushing water over the zooplankton sieve as described above, always from the last of the three replicates, but on some occasions also from other replicates. On those days that zooplankton samples were not taken, a 1 litre sample was pumped up from the treated tanks through the sounding pipe (for details see DTR 4.3).

The concentration of viable bacteria in the samples was determined by a most probable number technique. The seawater was diluted in a tenfold dilution series in filtered (Whatman glass microfibre filter GF/A), heat sterilised (120ºC, 20min) sea-water. Five times 0.1ml aliquots from selected dilutions were mixed with 0.1ml medium in 5 wells in a pre-sterilised 96 well microtiter plate. The medium contained per litre: peptone (Oxoid), 10.0g; yeast extract (Oxoid), 2.0g; NaCl (Norsk Medisinaldepot), 15.0g; $K_2HPO4 \cdot 3\ H_2O$ (Riedel-de Häen), 20mg; phenol red (Sigma), 60mg; filtered (glass microfibre filter GF/A) seawater, 500ml, distilled water, 500ml, pH 8.1 ± 0.1. The medium was heat sterilized (120ºC, 20min.). The inoculated microtiter plates were incubated at room temperature (22 ± 3ºC) for 1-2 weeks. Positive cultures were scored by visible turbidity, and the most probable number determined from the tables given in Appendix II in the US Food & Drug Administration's Bacteriological Analytical Manual online (Blodgett, 2001).

3.2.1.4 OTHER ANALYSES

3.2.1.4.1 HYDROGEN SULPHIDE

The concentration of H_2S was assessed by a spectrophotometric method (Cline's method) as described by Fonselius *et al*. (1999).

3.2.1.4.2 DISSOLVED OXYGEN

Dissolved oxygen was measured with an oxygen electrode (InPro 6050/120 O2 Sensor, Mettler Toledo, Switzerland). The electrode measured dissolved oxygen as percentage of saturation, and was calibrated with air as 100 %. However, it was not possible to dip the electrode directly into the ballast water in the ballast tanks. Instead, a thick-walled plastic bottle (1 litre) was filled to the rim with water from the ballast tank, either collected during sampling for zooplankton (via the fire pump), or directly from the ballast tank via the sounding pipe. The bottle was closed immediately after it had been filled, and taken to the "laboratory" on the ship. There the cap on the bottle was removed, an oxygen electrode placed in the bottle, and the bottle opening sealed as well as possible with aluminium foil. The reading of the oxygen electrode was followed until it seemed to have stabilised, normally 0.5-1 hour.

3.2.1.4.3 pH

pH was determined with PHM 80 Portable pH meter (Radiometer, Copenhagen) equipped with a pHC2005-7 "red rod" combined pH electrode (Radiometer, Copenhagen). The electrodes were calibrated with buffer solutions (pH 7.00 and pH 4.00, JT Baker) prior to measurement.

3.2.1.4.4 Mineral Nutrients

The concentration of mineral nutrients in the ballast water at the end of the study was determined according to NS (Norwegian Standard) 10304 (nitrate), NS 1189 (ortho-phosphate), and a modification of NS 4746 (ammonium).

3.2.2 Results and Discussion

The results of the sea trials are presented in details in chapter 4 (HTTT) and chapter 5 (DEOX). Below the biological results are discussed.

3.2.2.1 Flora and Fauna in the Ballast Water

The ballast water for the HTTT was from the Mediterranean Sea off the coast of Egypt and was pumped into the ballast tanks during the night between the 28th and 29th of May. The depth was from 839 to 2809 m during the filling of the tanks.

The ballast water for the DEOX treatment was from the English Channel and was pumped into the tanks during the night and early morning on June 21. The depth was from 50-62 m during the filling of the tanks.

In both ballast waters copepods and nauplii constituted 98 % of the zooplankton, but a number of other taxa were also found (Table 3.1). The total concentration of zoo-plankton was relatively low. The average concentration in the ballast water for the HTTT was 1064 organisms per m^3, while the average concentration in the water for the DEOX treatment was 2570 organisms per m^3 from start. In the ballast water for the HTTT the concentration of zooplankton remained relatively constant throughout the study (6 days), while the concentration in the untreated control tanks in the DEOX trial decreased significantly to an average of 411 organisms per m^3 at the end of the study (7 days).

Table 3.1: Taxa found in the water from the ballast tanks during the study and their frequency of occurrence

Organism	Fraction of total number of individs (%)	
	HTTT	DEOX
Copepods (adults)	57	38
Copepods (nauplii)	41	60
Cirriped larvae	<1	<1
Zoea	<1	<1
Ostracods	<1	0
Cladocerans	<1	0
Eggs (copepods and other crustaceans)	<1	1
Bivalve larvae	<1	<1
Echinoderm larvae	<1	0
Polychaete larvae	<1	<1
Nematodes	<1	<1
Tintinnids	<1	0
Hydroids	<1	<1

Gastropod larvae	<1	<1
Chaetognath	<1	0
Appendicularia or Ascidian larvae	<1	<1

Both ballast waters contained few phytoplankton cells (diatoms + dinoflagellates), particularly as the samples were taken in the summer when higher cell concentrations would be expected. The ballast water for the HTTT contained an average of 0.6 cells/ml and the concentration of chlorophyll *a* was mostly below the detection limit (0.02 µg/L). The ballast water for the DEOX trial contained from start an average of 0.9 cells/ml and the average concentration of chlorophyll *a* was 0.23 µg/L. The cell concentrations remained relatively constant in the untreated controls in both ballast waters during the study (6-7 days), but the concentration of chlorophyll a decreased to around the detection limit in the control tanks in the DEOX trial.

The concentration of viable bacteria was approximately $1 \cdot 10^4$ cfu/ml in the ballast water for the HTTT throughout the study. The concentration of viable bacteria in the ballast water for the DEOX trial was approximately $1 \cdot 10^4$ cfu/ml from start, but increased in the untreated control tanks to $1 \cdot 10^5$ cfu/ml at the end of the study.

3.2.2.2 HIGH TEMPERATURE THERMAL TREATMENT

3.2.2.2.1 ZOOPLANKTON

When measured as live (viable) zooplankton after treatment, the HTTT treatment was very effective for all temperatures tested (55-80ºC) for both nauplii and adult copepods. Only in two cases for copepods and four cases for nauplii, was 95% inactivation not achieved, but only one of these situations (copepods in tank AP on the 30/05 at 65ºC) had a significantly lower mortality than the rest. However, the high mortality in the control samples indicates that a significant fraction of the zooplankton was killed before they reached the heat treatment unit, most likely by the fire pump. This makes it difficult to determine how much of the killing effect was due to the HTTT. For copepods there was no significant difference between the mortality in the treated and the control samples, while for nauplii the mortality was significantly higher in the treated samples. Copepods may be up to forty times bigger than nauplii and therefore probably more sensitive to the fire pump. This may also explain that significantly higher mortality was found for copepods than nauplii.

Due to practical limitations 60 and 65ºC were the only temperatures tested in all tanks on every sampling day. The other treatment temperatures (55, 70, 75 and 80ºC) were only applied to water from some of the tanks on particular days. No significant differences in the killing rate were found between the different treatment temperatures throughout the study, hence between the tanks. These results indicate that increasing the temperature above 60ºC did not improve the treatment effectiveness.

The total concentration of copepods and nauplii (i.e. both live and dead) in the tanks did not change over time, but the mortality of nauplii in the control samples increased significantly from the first day, indicating that there was an increment in mortality as a function of the time they had been in the ballast tank.

Even though there was no significant difference in the mortality of copepods between treated samples and controls, the concentration of copepods, as well as of nauplii,

were significantly lower in the treated water than in the control samples. The sudden increase in the temperature as the organisms entered the HTTT unit must therefore have destroyed physically a considerable fraction of the organisms. This also indicates that if the organisms had not been killed by the fire pump before the treatment, they would have been killed by the HTTT. The mortality rates achieved after the combination of fire pump and HTTT may therefore not be much higher than what could have been achieved by HTTT alone.

An alternative way of evaluating the killing effect of the HTTT is to look at the concentration of surviving zooplankton in the water samples. In the control samples the average concentration of viable zooplankton decreased from 479 org/m^3 on the first day of the trials, i.e. around 1.5 days after ballasting, to 33 org/m^3 on the last day of the trials, i.e. between 5 and 6 days after ballasting. The total concentration of zooplankton, i.e. both live and dead, remained relatively constant during the trials with an average of 1064 ± 419 org/m^3. This indicates that either a significant fraction of the zooplankton in the ballast tanks died (but did not degrade) during the trials, or, perhaps more likely, the stress of residing inside the ballast tank increased over time the susceptibility of the zooplankton to the pressure fluctuations in the fire pump.

The average concentration of viable zooplankton in the HTTT treated samples ranged from 12-82 org/m^3 on the first day of the trials, and decreased to <1-13 org/m^3 on the last day of the trials. The large variation range is due to a number of factors, including treatment temperature and fluctuations in the total concentration of zooplankton in the samples reflecting an inhomogeneous distribution of the organisms in the ballast tanks and pipelines. Assuming, as the results indicate, that the treatment temperature had relatively little importance within the range studied, we can divide the results into two groups; HTTT treated samples and not HTTT treated samples (controls). The organisms in the former had been subjected to the killing effect of both the fire pump and the HTTT, while the organisms in the second group had only been subjected to the fire pump. The logarithmic average[3] concentration of viable zooplankton in the HTTT treated samples was 9% of the concentration of viable zooplankton in the control samples from the same day. This indicates that the HTTT killed roughly 90% of the zooplankton individuals that had survived the fire pump. The survivors from the fire pump are likely to be among the hardiest individuals, and the result therefore indicates that the HTTT alone would have killed at least 90% of the zooplankton, and probably considerably more.

Our results are in accordance with the experiments carried out on the ship *Iron Whyalla*, where 90-100% of the phyto- and zooplankton did not survive after using waste engine heat to treat the ballast (35-38°C) (Rigby *et al.*, 1999). Other options with additional heat exchangers at higher temperatures tested on the *Sandra Marie* and the *Union Rotoma* ships, yielded 80-90% plankton mortality (Thornton, 2000 in Rigby and Taylor, 2001) and a total destruction of the *Crassostrea calamaria* larvae (Mountfort *et al.*, 1999 in Rigby and Taylor, 2001).

[3] Because of the large variation in the concentration of organisms (more than one order of magnitude) the logarithmic average gives a better description of the situation than the arithmetic average, which in this case gives 13%.

Regarding the IMO standard (see section 3.1) the sum of live copepods and nauplii, hence organisms greater than 50µm, were less than 10 per m^3 for all temperatures tested except one (70ºC) on the 3rd June in tank DB4S, on the 2nd June in tank DB4P for all the temperatures applied, and on the 31st May at 60ºC. The treatment temperatures that yielded a significantly lower number of live organisms were 75 and 80ºC. All the aforementioned indicates a high effectiveness of the HTTT in this study, enhanced by the effect of time.

3.2.2.2.2 PHYTOPLANKTON

The phytoplankton results from the samples taken during the HTTT experiments show no treatment effect in comparison to controls. However, the ballast water loaded into the tanks at the start of the trial had a very low concentration of phytoplankton owing to the time and location at which ballasting took place. Due to the low starting concentration it is difficult to assess the biological efficiency of the HTTT. In order to make any reliable judgements it would be necessary to repeat the experiments with ballast water that contained a higher concentration of phytoplankton from the start.

3.2.2.3 DE-OXYGENATION TREATMENT

3.2.2.3.1 ZOOPLANKTON

The most striking feature of the zooplankton results from the DEOX trial is the decrease in the concentration as a function of time both in the treated and the control tanks. During the 7 days the trial lasted the concentration of zooplankton in the water samples decreased from an average of around 2600 organisms per m^3 to around 400org/m^3 in the control tanks and around 30org/m^3 in the treated tanks. A similar decrease in the zooplankton concentration in the water samples during the HTTT trial, which lasted 5 days, was not observed. We have no explanation for the difference but it may be related to the type of species present in the ballast water from start. During the DEOX trial the temperature in the ballast water increased from around 17-18°C at intake to almost 30°C at the end of the trial as the ship travelled south (DTR 4.3). It is possible that for many of the zooplankton species from the English Channel, this temperature increase was very stressful. The temperature in the ballast water was not measured during the HTTT trials, but the species in the Mediterranean were probably adapted to higher temperatures than those in the English Channel, and the ship was travelling north towards cooler waters.

The zooplankton may have disappeared from the water samples because they died and disintegrated. In the treated tanks, the bacterial concentration was about 1000 times higher than in the control tanks, so it is likely that the bacterial degradation of zooplankton in the treated tanks was more rapid than in the control tanks. Because the samples were pumped out from the tanks from sampling points close to the bottom, sedimentation would have tended to increase the concentration of organisms in the samples, but if the zooplankton rather than swimming freely in the water, started to cling to structures in the ballast tanks, or accumulate towards the water surface, *i.e.* far away from the sampling point, the same decline in the concentration would have been observed. In the treated tanks, in particular, zooplankton may have responded to lack of oxygen by swimming towards the surface. On the other hand, it is known from laboratory experiments (DTR 3.2) and the literature (DTR 2.5, for a review) that

zooplankton dies under anoxic conditions. Dead zooplankton is likely to sink towards the bottom, or if the mixing is strong, drift with the current until they degrade.

As in the HTTT trials, a considerable fraction of the zooplankton was apparently killed by the fire pump during transport from the ballast tank to the sampling point, and this complicates the evaluation of the killing effect of the DEOX process. Because of the killing in the fire pump the concentration of live zooplankton in the collected samples will be lower than in the water in the ballast tanks, leading to an overestimate of the killing effect of the DEOX treatment. An alternative is to base the evaluation of the treatment on the concentration of zooplankton in the collected samples regardless of whether they were alive or not. This approach is likely to underestimate the killing effect of the treatment as it is likely that a larger fraction of the zooplankton was dead in the treated than in the untreated water. Below both approaches have been evaluated.

An evaluation of the treatment efficiency based on the concentration of zooplankton in the samples is based on the assumption that the organisms disappeared because they died. When individuals in a population die due to a treatment, a logarithmic decrease in the number of survivors with increasing treatment time is common, and this is what is observed both in the treated and the control tanks. The disappearance rate in the treated tanks was higher than in the controls, and the total concentration of zooplankton in the treated water was significantly lower than in the untreated water after 5 and 7 days. Moreover, the effect of the de-oxygenation increased the longer the organisms were left inside the ballast water.

The total concentrations of zooplankton in the treated water after 5 days (average 45org/m^3) and 7 days (average 27org/m^3) were both significantly lower than in the untreated water; 429org/m^3 after 5 days and 402org/m^3 after 7 days, but still higher than the new IMO standard (<10 viable org/m^3 larger than 50µm). As we do not know the viable fraction, it is not possible to conclude from the total concentration results whether or not the treatment achieved new IMO standard.

The average concentrations of *viable* zooplankton in the treated water samples, which are the result of a combination of the DEOX treatment and the killing effect of the fire pump, were 1org/m^3 after 5 days and 2org/m^3 after 7 days. Both results are below the IMO standard. For comparison, the average concentrations of viable zooplankton in the untreated water samples were 87org/m^3 after 5 days and 24org/m^3 after 7 days. Therefore the combined treatment achieved the requirement of less than 10 viable organisms per cubic metre, but it is not possible to determine how much of the killing that was due to the DEOX treatment alone. However, the viability data in combination with the total zooplankton results discussed above, clearly indicate that the DEOX treatment at least must have yielded results close to the new IMO standard.

No differences were found in the mortality between treated and control tanks for either copepods or nauplii. However, it is possible that this result reflects the high degree of killing in the fire pump, which may have overshadowed a treatment effect. As mentioned above, there were significant differences in the total concentration of zooplankton between the treated and the untreated water at the end of the trial.

In the water samples taken during the DEOX trials mortality higher than 95% was achieved from the fifth day for both nauplii and copepods. However, we do not know if this could have been achieved earlier, as the sample from the third day (24/6) had to be discarded because it was not known where the water had come from within the ballast system.

In the water sample taken on the first day (21/6) the mortality of copepods was significantly lower than on the other days, indicating an effect over time. Only on one occasion, tank 3UP (treated) on the 21st, was the copepod mortality significantly lower than in the other tanks on the same day. Regarding nauplii, none of these effects were apparent.

Apart from two cases (21/6 in tank 3UP (treated) and 26/6 in tank DB3S (control)), no significant differences were observed between the mortality for copepods and nauplii. This indicates that these two life stages were equally sensitive to de-oxygenation.

Tamburri *et al.* (2002) studied the effect of de-oxygenation as a treatment for ballast water while also reducing ship corrosion. For the larvae of three species (3 day larvae of *Ficopomatus enigmaticus* (serpulid polychaete), first-stage zoea larvae of *Carcinus maenas* (common European green shore crab) and 3-day-old veligers of *Dreissena polymorpha* (zebra mussel)) they found that 79% of *F. enigmaticus*, 97% of *C. maenas* and 82% of *D. polymorpha* larvae did not survive the low oxygen environment (below 0.8 mg/l) after 3 days.

With regard to the IMO standard, the viable zooplankton concentration (>50µm) was less than 10 viable organisms per m^3 in all the treated samples taken after the 21st June, finding on this particular day significantly higher numbers of alive individuals. This was, however, expected as the DEOX treatment takes time and the water in the treated tanks had not become anoxic on the first day.

3.2.2.3.2 PHYTOPLANKTON

The phytoplankton results from the samples taken during the DEOX treatment experiments show no clear treatment effect. The cell counts show that there were fewer cells in the treated tanks on the last day of treatment compared to controls, which would seem to indicate that the treatment had been successful in reducing the number of diatoms and dinoflagellates in the ballast tanks. However, the chlorophyll *a* results show a higher level of chlorophyll *a* in the treated tanks than in the controls, which would seem to indicate that although the cells were present in lower numbers those that were present contained a greater level of chlorophyll.

This anomaly could be explained by the fact that the cell count analysis could not distinguish between live and dead cells so the high cell counts in the control tanks could include dead cells. This would appear to be confirmed by the ratio of degradation products, which showed that the control samples had a greater proportion of phaeophytin than the treated samples. However, another explanation for the fact that there were fewer cells in treated samples could be that the high concentration of bacteria in the treated water increased the speed at which the dead cells were degraded. Dead and degraded cells would not be included in the cell counts, which would lead

to lower cell counts in comparison to the control samples. This emphasises the need for development of methods to ascertain the viability of the cells.

The presence of extra nutrients in the treated water may have affected the way in which the cells responded to being in the dark ballast tank. The way in which cells react to being in the dark is complex as phytoplankton has a cell cycle that is keyed to a light/dark cycle. This cycle will continue for some time even in complete darkness and is usually expressed for a longer period when the cells are subject to continuous darkness than when in continuous illumination (Falkowski and Raven, 1997). Initially, cells are able to react to being in the dark by producing more chlorophyll to ensure that when conditions improve they are able to photosynthesise to ensure further growth. They are also able to utilise lipid reserves to survive prolonged periods of darkness (Falkowski and Raven, 1997). However, the presence of the extra nutrients used in this treatment method may mean that the cells were able to utilise these in order to prolong further their survival in the dark tank. It is difficult to make any firm conclusions from these data but it would seem unlikely that de-oxygenation is an effective method of reducing diatoms and dinoflagellates.

Only a broad indication can be given as to whether the treatment methods would have achieved the IMO ballast water treatment standard. The IMO standard specifies that the viability of the cells should be taken into account and the analytical methods used during these trials were not able to ascertain the viability of the cells. Also, only diatoms and dinoflagellates were counted during these trials but other classes of phytoplankton may have been present in these samples which were not counted. It is therefore probable that the cell counts are underestimates.

All the cell counts were below the IMO standard (<10 viable cells per ml) after treatment but the average cell counts were very low to begin with and would have been below this standard from the start of the experiment. This highlights the fact that several ship based trials would be required to ensure that the treatments were tested over a range of concentrations of plankton.

3.2.2.4 PRACTICAL EXPERIENCES FROM THE ONBOARD TRIALS

The current study is one of the few ballast water treatment studies that have been performed onboard a ship, and it may therefore be of interest to summarize some of the practical experiences from this study.

3.2.2.4.1 SAMPLING OF BALLAST TANKS

Ballast tanks on modern ships are often not easily accessible during the voyage. Zooplankton analyses, especially, require large volumes of water (several tonnes). Therefore, the use of the fire pump system to withdraw water samples from the ballast tanks seemed a good option. However, the results clearly indicate that the fire pump killed a substantial fraction of the zooplankton in the samples, sometimes more than 90%, and this made it difficult to evaluate the effect of the treatments as discussed earlier. We believe that the main reason for the killing was pressure fluctuations in the pump. These may have been especially large on the car carrier because it is a very tall vessel and the ballast water had to be lifted 10-20 metres to the sampling point on deck. However, also on lower ships this may be a problem, and the use of the fire pump can not be recommended in future studies. Other sampling methods have to be

developed. The observation that a ”nasty” pump may kill a substantial fraction of the zooplankton, and presumably also larger organisms, is however interesting and may deserve to be followed up. However, it should be noted that the pressure fluctuations are not expected to have any significant effect on the survival of phytoplankton and bacteria.

The concentration of organisms in the samples taken from the ballast tanks, particularly the concentration of zooplankton, varied considerably between successive samples taken within an hour from the same tank. In the DEOX trial, for example, the concentrations of zooplankton in the three 1 tonne samples taken from the control tank DB3S on the 26th June were 1109, 518 and 330org/m^3, i.e. a factor of 3.4 between the highest and the lowest number. The concentrations of phytoplankton (dinoflagellates + diatoms) in the same samples were 391, 251 and 566 cells per litre, i.e. a factor of 2.3 between the highest and the lowest number. It should be noted that these are not extreme examples, for zooplankton a factor of more than 10 between the highest and lowest concentration was occasionally observed. This indicates that the organisms are not evenly distributed in the ballast water. A better understanding of how the organisms are distributed in the ballast tanks is needed, and in particular how the concentration of various groups of organisms varies in the water during discharge of ballast water. Does zooplankton in particular, try to avoid the outlet so that the highest concentration will be found in the discharged water towards the end of the emptying of a tank? This has important implications for how sampling should be carried out to test for compliance with the new IMO standard.

3.2.2.4.2 Analytical Methods for Determining Viability

The new IMO standard (section 3.1) refers to viable organisms. In an onboard trial one is limited to methods that are suitable for field work. The viability of the zooplankton was determined by a staining technique combined with microscopic examination. This is a very laborious method, and it took months before the results became available. The viability of phytoplankton was not assessed at all. The samples were preserved and the only way of deducing something about their ”health status” was from their chlorophyll and phaeophytin content, and changes in the concentration as a function of the treatment (assuming that ”missing” cells were dead). Only for bacteria methods for determination of viable cells seem available (plate count, etc.) that require moderate amounts of work and are suitable for use onboard ships. However, even these methods require an incubation period of several days before the results become available. There is therefore an urgent need for rapid methods for assessing the viability of different groups of marine organisms on board ships if the new IMO standard shall become the tool it is intended to be in the prevention of spreading of invasive species.

3.3 Onshore Trials

The land based tests were performed in the Tvärminne Zoological Station (University of Helsinki) which is located on the south coast of Finland, about 100 km west from Helsinki, in a corner of the Hanko peninsula, the southernmost tip of continental Finland (Figure 3.3). The area is characterised by exceptionally high diversity in its physical appearance, a number of different biotopes and species richness (it harbours about 15 % of the endangered species of Finland) thus fulfilling one of the most demanding criteria for a biological field station.

The first test phase with ultraviolet light (UV), ultrasound (US) and ozone (O_3) methods was carried out in September-October 2002 and the second test phase in August-September 2003. During the second test phase, also the combinations of US+UV and UV+hydrogen peroxide (H_2O_2) were included in the test programme in addition to the technologies mentioned above.

The marine environment of the Baltic Sea is extraordinary in many ways. This semi-enclosed basin forms one of the largest brackish water areas in the world, although the mean depth is only 55 m. Hydrodynamics of the Baltic Sea are characterized by steep thermal and salinity stratification. Salinity, regulated by river discharge and pulses of saline water from the North Sea, gradually decreases towards north in the Bothnian Sea and east in the Gulf of Finland. Furthermore, seasonality in weather and food conditions is pronounced; cold winters with partial ice cover are typical, and growing seasons remain short. The species in the northern Baltic are, to a large degree, either of marine or fresh water origin. Due to the harsh environmental conditions, most of the species live at the limits of their tolerance. The number of taxa is relatively small (Finnish Institute of Marine Research, 2003) and the food webs are typically less complex than in the oceans. The study area is situated in the archipelago of Hanko Peninsula, at the entrance to the Gulf of Finland. Thermocline is formed during the warm summer months but upwelling events may frequently mix the water column. There is no permanent halocline in the study area. Salinity in the surface waters is around 6 psu.

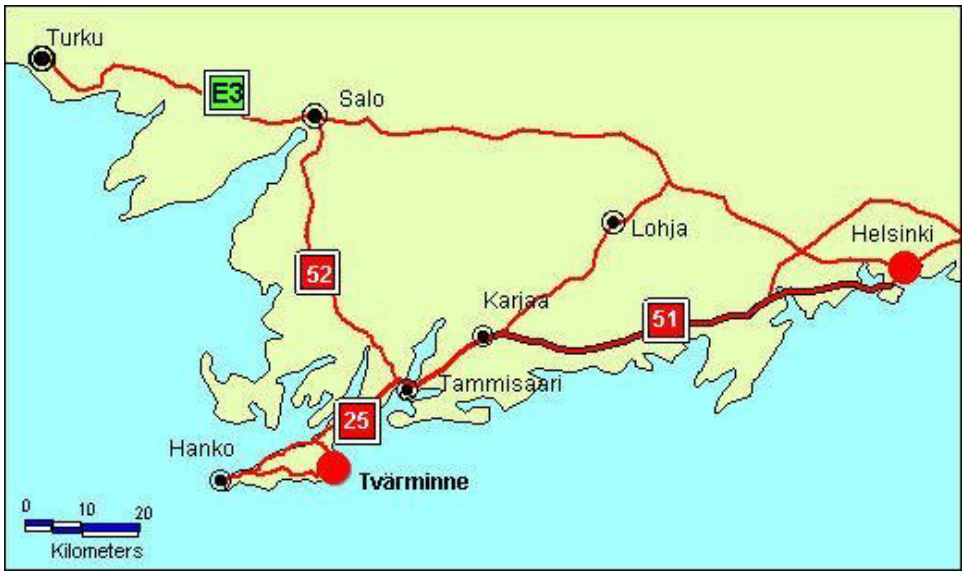


Figure 3.3: The location of the Tvärminne Zoological Station in the southern Finland

Mesozooplankton, feeding on nano- and microplankton and being food for fish in turn, forms a key group linking the classic grazing food chain to microbial loop (Rudstam *et al.* 1992, Turner and Roff 1993). In the northern Baltic, copepods (Copepoda) generally dominate the biomass of mesozooplankton, other main groups being cladocerans (Cladocera) and rotifers (Rotifera). The dynamics of the mesozooplankton community are mainly regulated by changes in salinity and temperature, and show large seasonal fluctuation (Viitasalo et al. 1995).

The size range of mesozooplankton species in general (0,2-20 mm) is somewhat bigger than the size range of species studied here (100–1000 μm), reflecting the common feature of the species inhabiting the Baltic Sea. The largest species included in this study, the spiny water flea *Cercopagis pengo*i, is a newcomer of the 1990's, introduced by ballast water transport (Uitto *et al.* 1999).

The utilisation of natural sea water enabled the access to unlimited amount of water and thus the error caused by small amount of water could be reduced. Also the link to the actual marine environment was evident. The water intake pipe was placed at the depth of 0.5 m and a peristaltic pump (type Watson-Marlow 604 U/R) was utilised to feed the water to the treatment process. For the higher flow rates with ultrasound and ultraviolet light devices (800 and 1600 L/h), a membrane pump (type Yamada NDP-20-BST) was utilized. Significant mortality rates were not observed during the trials due to the utilization of the pumps. No filter was used in the end of the inlet pipe.

3.3.1 ZOOPLANKTON SAMPLING AND ANALYSIS

In this part of the study, the objective was to compare and quantify effects of the different treatments described above on natural mesozooplankton assemblage in the northern Baltic Sea. The treatment effects were studied on four dominating groups of mesozooplankton species – copepods (adults and copepodite stages), copepod nauplii (larvae), water fleas (cladocerans) and rotifers. In addition, barnacle (*Balanus improvisus*) larvae (nauplii) and mussel (Lamellibranchiata) larvae (veligers), though meroplankton[4], were occasionally present in plankton in considerable numbers, and were included in the analysis.

In order to guarantee wider generality of the results with regard to changing seasons with changes in the plankton community, it was decided to conduct the experiments during two separate periods of the two following years (i.e. September-October 2002 and August-September 2003). In all experiments, unfiltered inshore seawater was conducted through the devices. Since zooplankton species composition shows large annual fluctuations (Viitasalo *et al.* 1995), the water sample was taken bi-daily from the sea, in the average, to check the ambient composition of the mesozooplankton community. The species present can be regarded as typical for the study area and the season (late summer-autumn). Dominating groups were copepods (*Eurytemora affinis, Acartia bifilosa*) and rotifers (*Keratella cochlearis*, *Synchaeta balthica*).

An initial sample of 10-15 L was taken before the treatment (near the inlet) and a final sample of 15-60 L (depending on the ambient zooplankton density) after the treatment (near the outlet). In UV+H_2O_2 treatments, the final samples after UV treatment were poured in 30 L containers in which hydrogen peroxide (15 or 30 mg/L) was added and incubated for 48 h (option A in Figure 3.4). Alternatively, water was first conducted in a 360 L tank from which the initial sample (10 L) was immediately taken. H_2O_2 was then added in the tank and water was run through the UV device. The final samples (30 L) were incubated for 48 h before further handling, as in section A (option B in Figure 3.4). In ozone treatments, as well, water was conducted in a tank

[4] Meroplankton = organisms that spend part of their life cycle, usually the larval or egg stages, as plankton.

(60 or 360 L) in which we immediately took an initial sample (10 L). After 1-24 h incubation time the final samples (10-60 L) were taken.

Sample water was gently sieved using a 100 µm sieve and washed to 0.9 L plastic containers with 10 µm filtered, aerated sea water. Containers were immediately transferred to a temperature controlled room (+ 13 ºC). After a recovery time of 2-5 h samples were studied under stereo microscope. Live individuals of mesozooplankton species were counted and classified into the following groups: Copepoda (adults and copepodides), Copepoda nauplii, Cladocera, Rotifera, *Balanus improvisus* nauplii and Lamellibranchiata veliger larvae. Actively swimming and damaged individuals were counted separately. Judgement between active and damaged individuals was done on the basis of swimming modes and morphological characters.

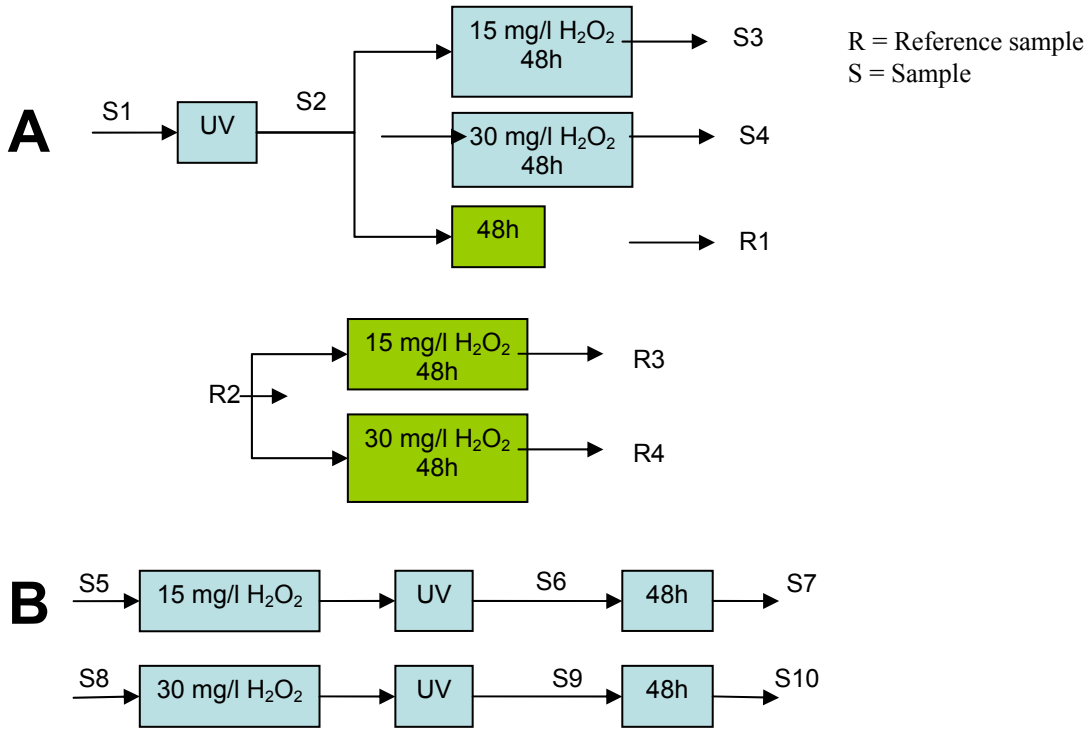


Figure 3.4: The schematic layout of the test arrangements with the combination of UV and H_2O

Three replicates were conducted for each treatment (only two replicates in UV+H_2O_2 and US 4 kW treatments). However, since the water used in the experiments was directly taken from the sea, the plankton assemblage conducted through the devices showed some variation. In order to get representative samples and guarantee a reasonable reliability of the results, only species groups with the minimum density of 1 ind / L in the initial sample were included in the analysis. Due to this, in some cases (i.e. species groups present in low natural densities) the final number of replicates is less than 3. To check mortality or loss of individuals in devices without treatment, we conducted controls following the same procedure as with treatments (but with zero doses). The percentage of killed individuals (death rate; hereafter kill %) in UV, US, UV+US and UV+H_2O_2 treatments was calculated as follows:

$$Kill\% = 1 - \frac{N_3 / N_2}{N_1 / N_0}$$

Where, N_0 = density of live individuals before control
N_1 = density of live individuals after control
N_2 = density of live individuals before treatment
N_3 = density of live individuals after treatment

In ozone treatments, as well, the treatment efficacy is presented as a kill % after different contact times. Since no mortality could be observed during the control incubations, natural mortality in treatment tanks was assumed to be 0 %. Therefore, the actual mortality observed in treatment incubations (the reduction in the number of alive individuals) was interpreted to directly represent the kill %.

In UV+H_2O_2 treatments, on the other hand, the kill % is presented as the percentage killed by UV alone (S2 in option A), the percentage killed by UV combined with H_2O_2 and a incubation time of 48 h (S3 and S4), the percentage killed by UV with the same incubation time of 48 h but without H_2O_2 (R1), the percentage killed by H_2O_2 alone (in 48 h) (R3 and R4), the percentage killed by H_2O_2 combined with UV (S6 and S9 in option B), and the percentage killed by H_2O_2 combined with UV (48 h incubation time) (S7 and S10) (see Figure 3.4).

The difference in kill % between species groups and different treatment parameters were tested. In ozone treatments, difference in proportion of live individuals between control and treatment tanks was tested. We used parametric Student's *t*-test or analysis of variance (ANOVA) in case data followed normal distribution and variances were homogenous. When these premises were not filled, Mann-Whitney U-test or Kruskall-Wallis non-parametric analysis of variance was used instead.

3.3.2 DISCUSSION

The procedure for biological analysis consisted of live sample studies (method also used by Sutherland *et al.* 2001) instead of staining with preserving used in some previous studies (Waite *et al.* 2003), due to certain difficulties related to staining methods (i.e. difficulties in making judgement between alive and dead individuals). In addition, live sample studies allowed us to count active and damaged individuals separately. This method, however, is time consuming, demanding long analysing times before final results. Therefore, development of an easier method for zooplankton analysis would be essential in terms of full-scale testing. Flow cytometry can only be used in studies with unicellular organisms. Instead, measuring ATP-activity could be an optional method to be used in the future (Waite *et al.* 2003), although development work is still required.

The heterogeneous nature of field conditions and natural zooplankton assemblage evidently forms an essential source of variation, observed in some of the results. The initial zooplankton densities varied between replicates conducted during different test phases, in general, densities were higher in 2003 than the year before. Also, initial densities varied from one species group to another, generally being highest for rotifers and copepod nauplii and lowest for cladocerans. Density dependent effects can not be precluded: for example, in high zooplankton densities shading can reduce the efficiency of UV irradiation. Instead, the effect of US has been suggested to increase as density of organisms increases (Batelle 1998).

To avoid sticking of animals into the twisting pipe system of the US and UV devices, the pipe work was simplified after the trials conducted in autumn 2002. Moreover the pipe network was always flushed for 1 h between treatments and replicates. Due to the longer flushing time of the pipe work in each experiment with ultrasound and ultraviolet light, the technical source of error caused by the piping during the laboratory scale test trials could be reduced significantly. Despite these efforts made, however, some individuals seemed to get stuck to the system. This sticking effect, combined with a patchy distribution of zooplankton in the sea, evidently causes variation between replicates. These factors may also explain the illogical response of organisms to counter pressure in US 2 kW treatments (800 L/h). However, while the water was extracted directly from the Baltic Sea, the limitations due to the amount of water could be avoided. Also the link to the real marine environment was evident.

In ozone treatments, a mechanical mixer was used in order to ensure efficient ozone gas mixing and homogeneous organism distribution in the water column. Zooplankton density, however, tended to increase during control incubations. This might be due to the possibly tendency of organisms to avoid the outlet of the contact tank. This can be regarded as an indication of incomplete mixing, causing additional error source. Sample water was conducted near the bottom of the tank, allowing live plankters remain in the surface layer of the water column. This can be seen in the results of the 24 h ozone experiment, conducted in a 360 l tank: mortality rates were low during the first hour but approached gradually 100 %. The differences in densities of live individuals between control and treatment incubations, however, are clear enough to give evidence of real treatment effects.

With respect to all treatments tested, an error source caused by an insufficient number of replicates especially concerns cladocerans and barnacle nauplii. Despite the fact that statistically significant differences between treatment effects at different parameters were found in only few cases, an increasing amount of variation between replicates can be interpreted as an indication of depressing treatment effect. However, as the efficiency reduces and variation increases, judgement of real kill percents becomes difficult if not impossible. Therefore, the most reliably data concerns treatments with high kill percents and low variation between replicates.

3.3.2.1 Species Group Specific Responses to Different Treatments

Some differences can be seen in the effects of the different treatments tested on different species groups. A few reasons for this are suggested. Firstly, cladocerans appeared to tolerate at least to some extent all other treatments except US. The susceptibility of cladocerans to US is likely due to their considerable big size and tough carapace, liable to be crushed by US. On the other hand, carapace can offer protection against chemical substances such as H_2O_2 and O_3. As regards to UV treatment, planktonic cladocerans are considered as surface community species (Viitasalo *et al.* 1995), inhabiting the uppermost layer of the water column. Due to this, they probably are better adapted to solar ultraviolet irradiation than other species, i.e. copepods.

Copepod nauplii seemed to be more susceptible than adults and copepodide stages to all the treatments, with UV as the only exception. Rotifers, as small in size, were

evidently most tolerant of US, as compared to the other groups. But, recognisably they could not tolerate other treatments.

Barnacle nauplii form an equivocal group, with varying responses to different treatments. In US treatment, their susceptibility increased gradually with increasing power, the kill % being under 70 with the lowest power but approaching 100 with the highest power. It must, however, be emphasized that no replicates for barnacles could be included in the analyses. In O_3 treatments, barnacle nauplii seemed to be more susceptible than cladocerans but more tolerant than rotifers or copepods of different life stages. In UV treatments, the response of barnacles was particularly inconsistent, with apparently the lowest vulnerability with intermediate dosage (i.e. flow rate). This obvious artefact can, in part, be explained by the deficiency of replicates.

3.3.2.2 RESULTS WITH RESPECT TO PREVIOUS STUDIES

Naturally, care must be taken in direct comparisons of results from different studies, due to different test regimes and different species in question. A general overview can still be done.

Efficiency of ozonation as a means for ballast water treatment has been questioned (Oemcke and Leeuwen 1998), due to relatively long contact times required. Crecelius (1979) reported that bromate at 30 mg/L, corresponding to ozonation at 50 mg/L min (contact time 30 min), resulted in 50 % mortality for larvae of Pacific oyster (*Crassostrea gigas*). However, Kuzirian *et al.* (1990) reported ozonation at 2,2 mg/L in only 12,8 min to have a fatal impact on larvae of nudibranchs. In the present study, ozonation at 1 g/h (17 mg/L) proved to kill nearly 100 % of organisms, exluding cladocerans, in two hours. On the other hand, experiment in a larger water volume (360 L) revealed the same treatment at 2,5 O_3 g/h (7 mg/L) to have a weaker effect: a considerably longer time period (8 h) was required to eliminate organisms (cladocerans were not eliminated in 24 h). Probably with better mixing the effect of ozone could be increased.

Ultrasonication (12 kW) has been found efficient on eliminating veliger larvae of zebra mussels (*Dreissena polymorpha*) at flow rates as high as 2200 L/min (Battelle 1998). In our experiments, US (4 kW with counter pressure) had a detrimental effect on copepods and rotifers at 800 L/h but the efficiency was somewhat reduced when the flow rate was doubled (the difference was not statistically significant but variation in kill % was much higher at 1600 L/h).

In previous studies concerning ballast water treatment with UV irradiation, greatly higher flow rates have been used (Sutherland *et al.* 2001, Waite *et al.* 2003). At a flow rate of 350 m^3/h (2,5 kW), Sutherland *et al.* (2001) found a considerable effect of UV on some diatom species. UV also appeared to have an impact on copepods although no statistical tests were done due to low initial densities. At a flow rate of 5,7 m^3/min (60 mW/s cm^2), on the other hand, Waite *et al.* (2003) failed to find any effect of UV on zooplankton (Copepoda). A clear effect on bacteria was reported, instead. In our experiments, UV had a clear effect on copepods at flow rates of 200-400 L/h (corresponding to 562-281 mJ/cm^2), although this effect depressed as flow rate increased.

Kuzirian *et al.* (2001) reported hydrogen peroxide at even as low concentrations as 1 mg/L to efficiently kill zooplankton in only 30 min. In this respect, concentrations used in this study were considerably high (15 and 30 mg/L) and incubation times long (48 h). An effect of H_2O_2 treatment was also found on germination of dinoflagellate cysts but only at very high concentrations (5000 mg/L) (Bolch and Hallegraeff 1993).

4 HIGH TEMPERATURE THERMAL TREATMENT

The objectives for WP4 were to run full (or pilot) size tests of the technologies tested in the laboratory during WP3. This included the design and manufacture of large-scale version of the test system, to test the system in "real" conditions; i.e. onboard ship or shore side and to prove the effectiveness of the system against a wide variety of plankton.

The High Temperature Thermal Treatment (HTTT) was successfully tested in the Jones Laboratory during WP3 and was also tested in full scale onboard ship during WP4.

4.1 PRELIMINARY DESIGN

The purpose of the ballast water treatment system is to purify the ballast water and limit the translocation of non-indigenous species. This was achieved, in this case, by heating the ballast water to about 55-65° C.

The average ballast capacity for a ship is 40000m^3, with the ballast water at a temperature of between 15 and 20° C. To treat this water properly, its temperature has to be raised by between 45 and 50° C by a steam heat exchanger, which will require the following amount of energy:

$$energy = \left(mass \times c_p\right) \times T_{increase} = \left(40 \times 10^6\, kg \times 4.186\right) \times 50 = 8372 \times 10^6\, kJ = 8.372 \times 10^6\, MJ$$

There are two disadvantages of using a single heat exchanger:

- The water after treatment is too hot to discharge
- A single heat exchanger requires too much energy

These problems can be remedied by using a pre-heater. This will reduce the post-treatment water temperature to a more acceptable level and allow it to be discharged overboard, but more importantly heat the water up to 40-50°C. The water temperature will only need to be raised 15-25°C using steam, reducing the energy consumption:

$$energy = \left(mass \times c_p\right) \times T_{increase} = \left(40 \times 10^6\, kg \times 4.174\right) \times 25 = 4174 \times 10^6\, kJ = 4.174 \times 10^6\, MJ$$

The heat exchangers to be used in the full size test system were supplied by Alfa Laval, who also supplied their heat exchanger performance program CAS200. This enabled the generation of a performance map of heat exchangers, which was inserted via a genetic algorithm into a LabVIEW program to dynamically simulate the pre-heater and treatment heater interactions (Figure 4.1).

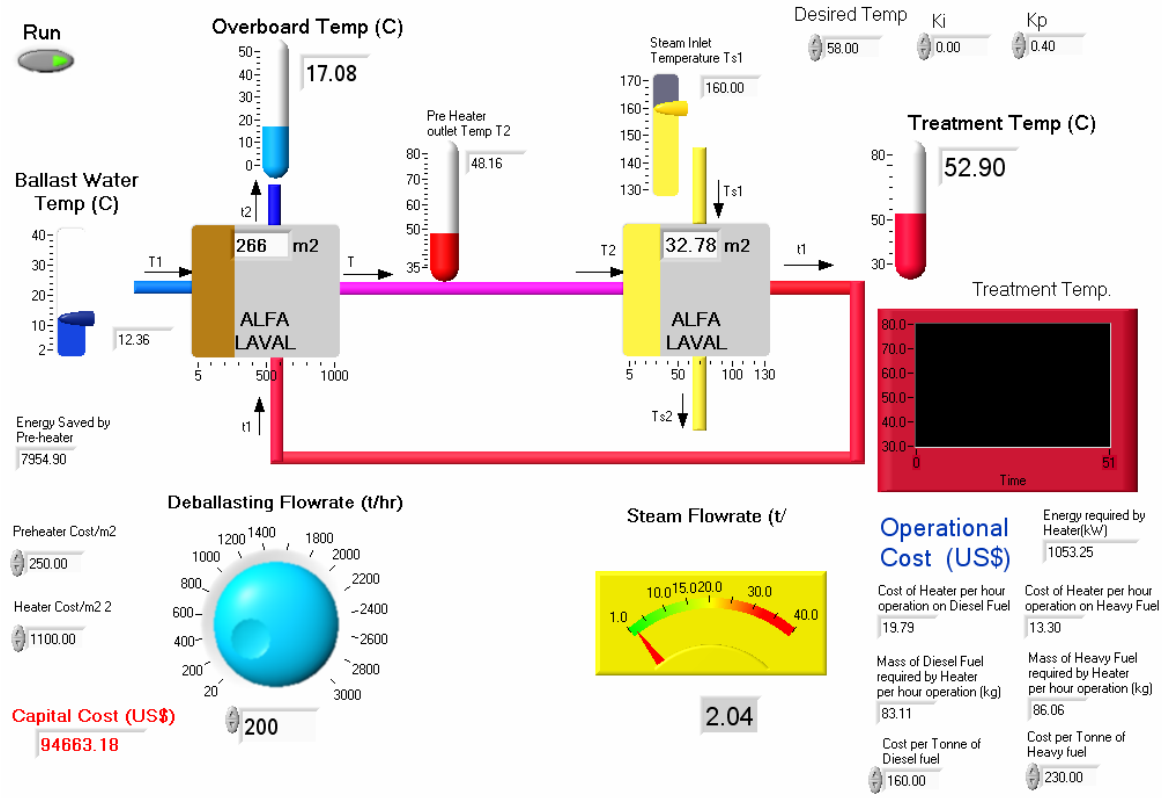


Figure 4.1: Front panel view of the dynamic model for HTTT programme

Using the dynamic simulation program it was possible to size the heat exchangers and simulate the behaviour of the system under various operating conditions. It quickly became apparent that the system was unstable and non-linear. Past a certain threshold, the treatment temperature would increase very rapidly for only a small increase in the steam flowrate. Reducing the steam flowrate back to the initial level would not yield the starting temperature due to the non-linear behaviour. This was remedied by using a PID controller in the simulation program and a steam control valve in the full size system.

4.2 General Arrangement

It was decided that the system would be self-contained, with all the components mounted on a frame, which gave extra flexibility as the module would be easier to transport and install onboard the ship.

Using the dynamic simulation program in conjunction with the CAS200 program it was possible to accurately size the heat exchangers for the onboard application. To enable the system to be mounted in the largest number of ships possible it was decided to use a pilot scale system with the steam requirement limited to 1.5 tons per hour. It was then possible to decide and order the relevant heat exchangers and the 2-D drawings were sent to us (Figure 4.2).

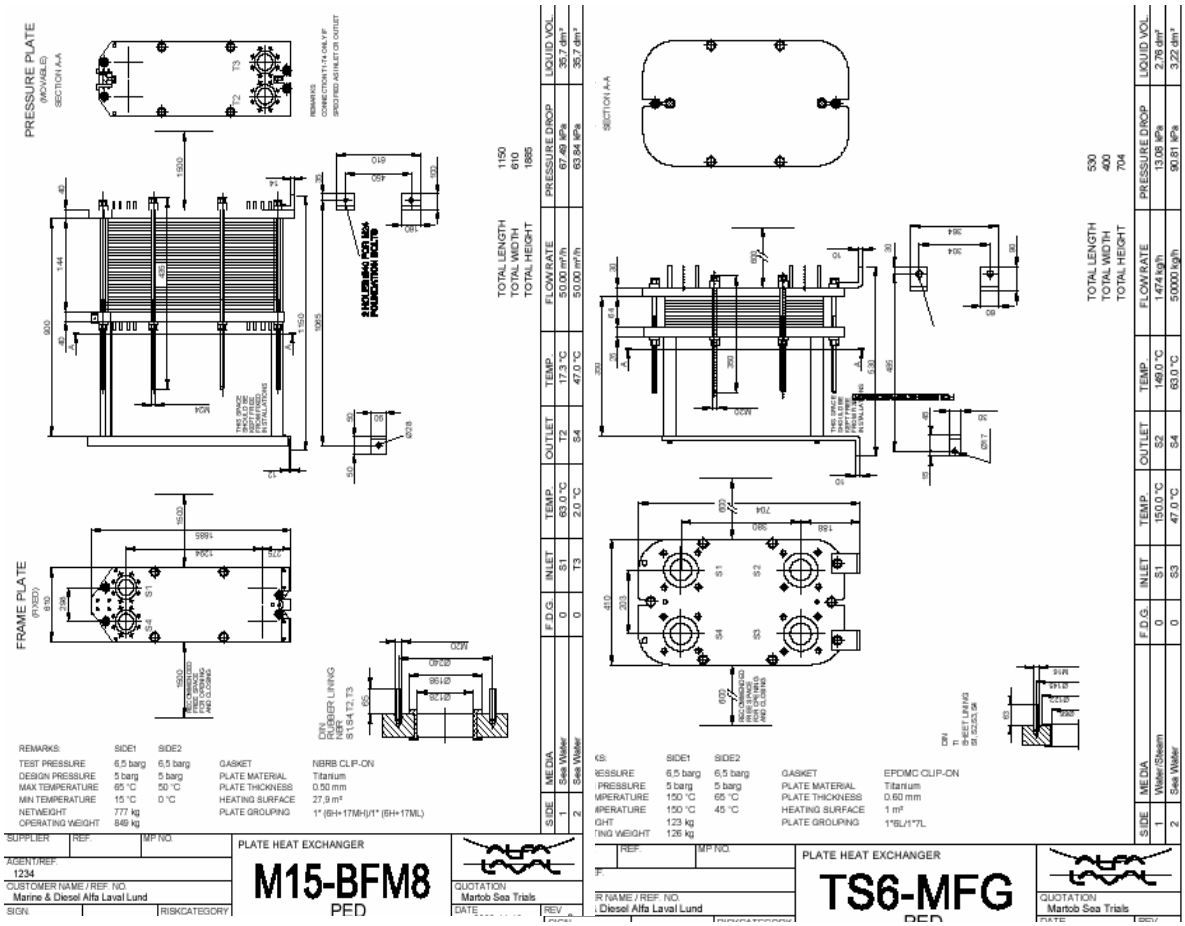


Figure 4.2: 2-D drawings of pre-heater (left) and treatment heater (right)

The drawings were then translated into 3-D AutoCAD drawings to allow for a greater understanding of the geometry of the heat exchangers and their relative positioning on the system (Figure 4.3).

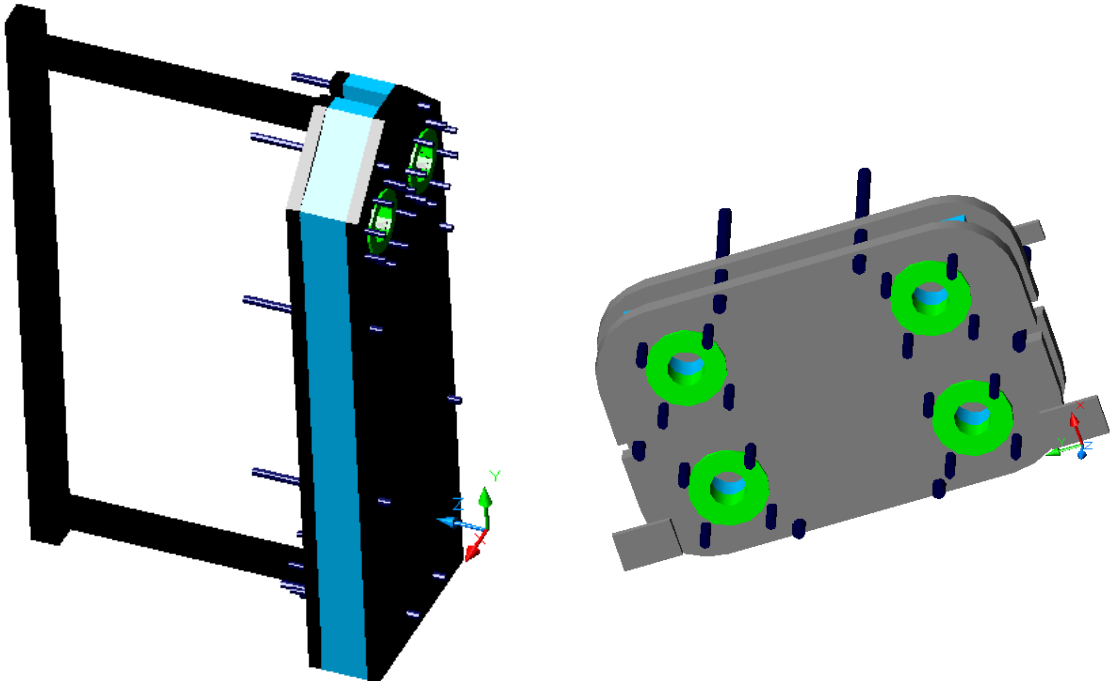


Figure 4.3: 3-D Drawings of pre-heater (left) and treatment heater (right)

This allowed us to position the heat exchangers in order to simplify the pipework as much as possible. The ports from the two the exchangers were aligned as much as possible to reduce the amount of bends in the pipework and simplify the construction and reduce the weight of the unit.

The following diagram gives the finished general arrangement (Figure 4.4)

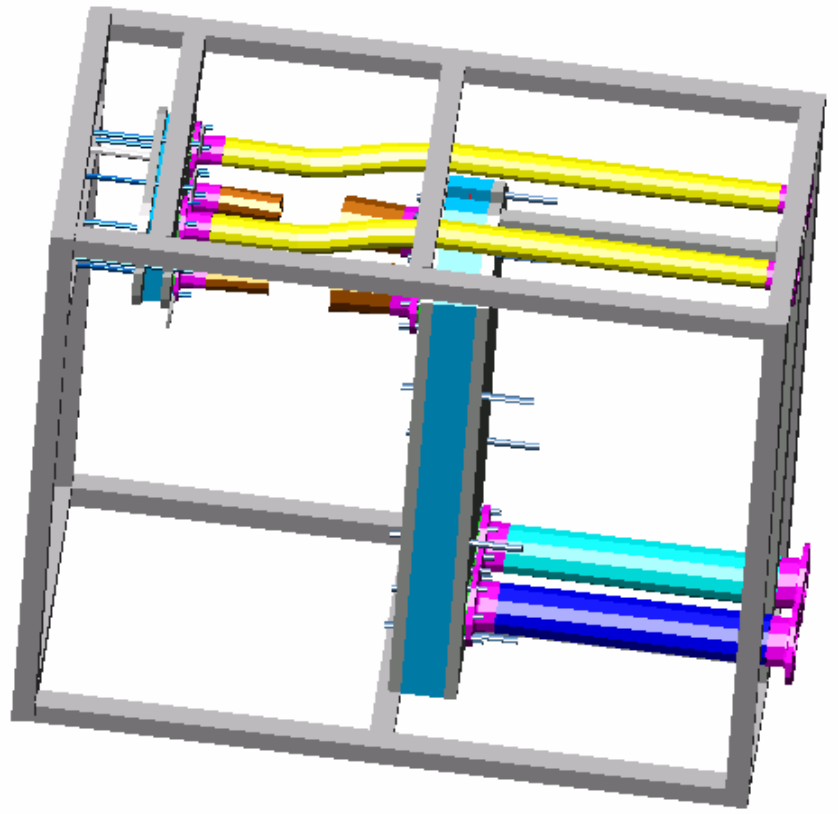


Figure 4.4: 3-D rendition of the system.

The fact that system was turned into a self contained module meant that the framework design would be very important in terms of structural strength to ensure that the system was safe in transport and operation.

4.3 Structural Design of the Framework

Once the general design of the frame was finished, the structural design could be undertaken to ensure the frame would be strong enough to support the loads imposed by the operation of the system and by its transport and installation. A further consideration was that the frame should not be too heavy as that would hinder its ease of installation and would possibly have adverse effects on the ship it was installed on. PTC pro engineer and pro mechanica were used to model the frame in 3D and run the finite element structural analysis. The design was done under close collaboration with Bureau Veritas, following their rules and regulations. Their help was invaluable, especially when it came to the worst case scenario, with extra accelerations applied to the frame.

The first design of the frame was made up of members welded together. The members are 120mm x 80mm box section with 10mm wall thickness steel (Corus S355), these were chosen as a starting point as it was almost certain that the frame would be strong

enough to withstand the forces applied to it without being too complex and difficult to manufacture. It would then be easy to modify the frame to reduce its weight and increase its complexity.

To make the members on pro engineer, the 120 x 80 x 10 shape was extruded to the right length and 45° cuts at either end were made for the members to mate properly together. All the members (or parts) were then assembled together and constrained in the proper way using the assemble components function on pro engineer. Finally to prepare the model for the structural analysis, the last step was the definition the shell idealisation for all the members of the frame and the welding idealisation for all component junctions.

The basis of the structural analysis on pro engineer was to apply a set of constraints and a set of loads on the structure and to analyse its behaviour when subjected to those loads. These loads came from the two heat exchangers to be mounted in the frame, the pre-heater weighing 849kg and the heater weighing 128kg. Due to the geometry of these heat exchangers, it was decided that the front legs of the pre-heater would be supporting ¾ of the weight (636.75kg) with the rear leg accounting for ¼ of the weight (212.25kg). In the same way the heater front legs would be supporting 4/5 of the weight (102.4kg) and the rear leg 1/5 (25.6kg).

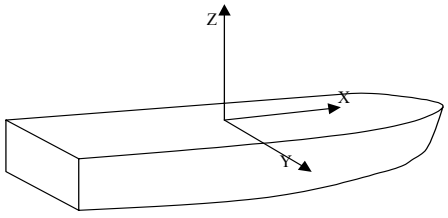
In this case it was decided to separate the analysis into tree different cases; the standard load, worst case and lifting load.

- **Standard Load**

The standard load case reflects the system onboard ship with the ship at rest. The constraints are applied to the placement of the feet, i.e. each corner and midway down the side beams under the vertical members.

- **Worst-Case**

Following talks with Bureau Veritas, it was clear that the frame should be designed following Classification Society rules, as it would ensure the system would be able to withstand the rigors of the sea. Furthermore, this would add to the confidence of the shipping companies when asked to allow us to install the system onboard their vessel. For the worst-case scenario, the frame would be subjected to the maximum accelerations, simultaneously, in all three directions. The maximum accelerations were given to us by Bureau Veritas, and are presented in Figure 4.5.



Accelerations:
X= 0.2g
Y= 0.5g
Z= 1.6g

Figure 4.5: Maximum accelerations to be applied to the frame

The analysis had to satisfy the above criteria as the worst-case scenario.

- **Lifting Load**

Finally the lifting load was analysed to ensure the frame could safely be craned onboard a vessel to be installed in the required position. The constraints applied this time were different and consisted of two constraints, one on each top horizontal member of the frame, in the centre of that same member. The loads applied were the same as the standard load case.

The results from the structural analysis of the first frame design made from 120 x 80mm box section with 10mm wall thickness, found it to be over specified with very little stress being applied to the frame. The design was found to be allowing too large deflections during the lifting and the worst case scenarios. Finally with a weight of 750kg, it was felt the frame would weigh too much.

The design was therefore revised to include cross-bracing to reduce the deflections and a smaller section to reduce weight. Following many iterations of the analysis program, the final design was decided. The frame used 50 x 50mm box section with 5mm wall thickness, with an approximate frame weight of 275kg. It was possible to reduce the size of the members further, but this would increase the complexity of the frame even more and would therefore make the frame more time consuming to manufacture. One of the results of the structural analysis on the final design is shown in Figure 4.6 below.

The stress results were below the maximum allowable stress (355 MPa) for all the cases and therefore the frame will perform in the right way.

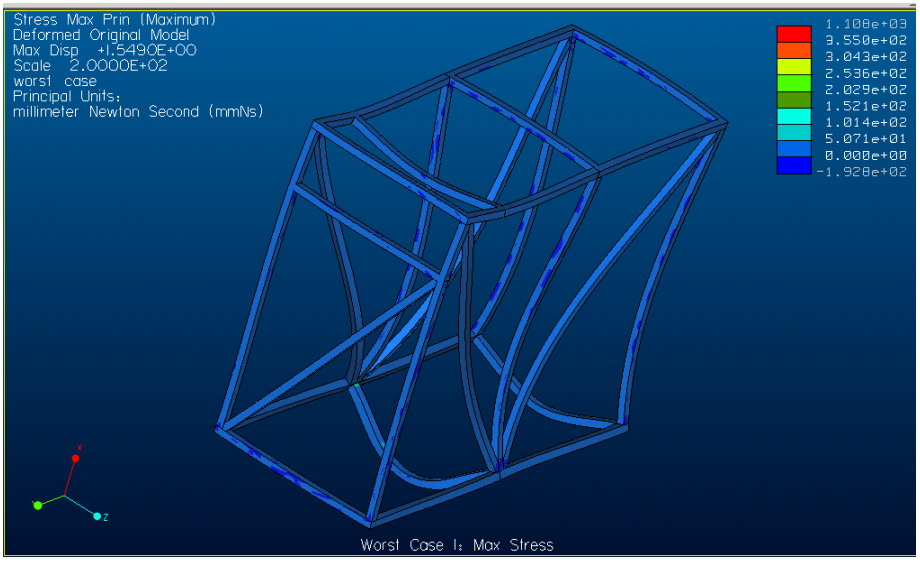


Figure 4.6: Result of the structural analysis for the worst-case loading condition.

4.4 PIPEWORK DESIGN

The pipework had to be designed to transport water from the ship to the pre-heater, from the per-heater to the treatment heater then back to the ship, via the pre-heater again, for discharge. Steam pipework to feed the treatment heater and a condensate

line to return the used steam to the ships boiler was also required. All the necessary valves had to be included as well as more specialised items:

- Seawater flowmeter on the pre-heater inlet.
- Steam flowmeter linked to a volume totaliser on the treatment heater inlet.
- Steam control valve linked to thermocouple (see below) and controller unit.
- Thermocouple between treatment heater and pre-heater to measure treatment temperature.
- Strainer on the steam pipework.
- Strainer and steam trap on condensate line.

The ports between the pre-heater and treatment heater were not perfectly aligned and to simplify the junction it was decided to use convoluted stainless steel pipe which is flexible and would enable an easy and quick connection and would help with disassembly for maintenance.

The pipework manufacturing drawings were produced in AutoCAD and an overview of the pipework is presented below (Figure 4.7).

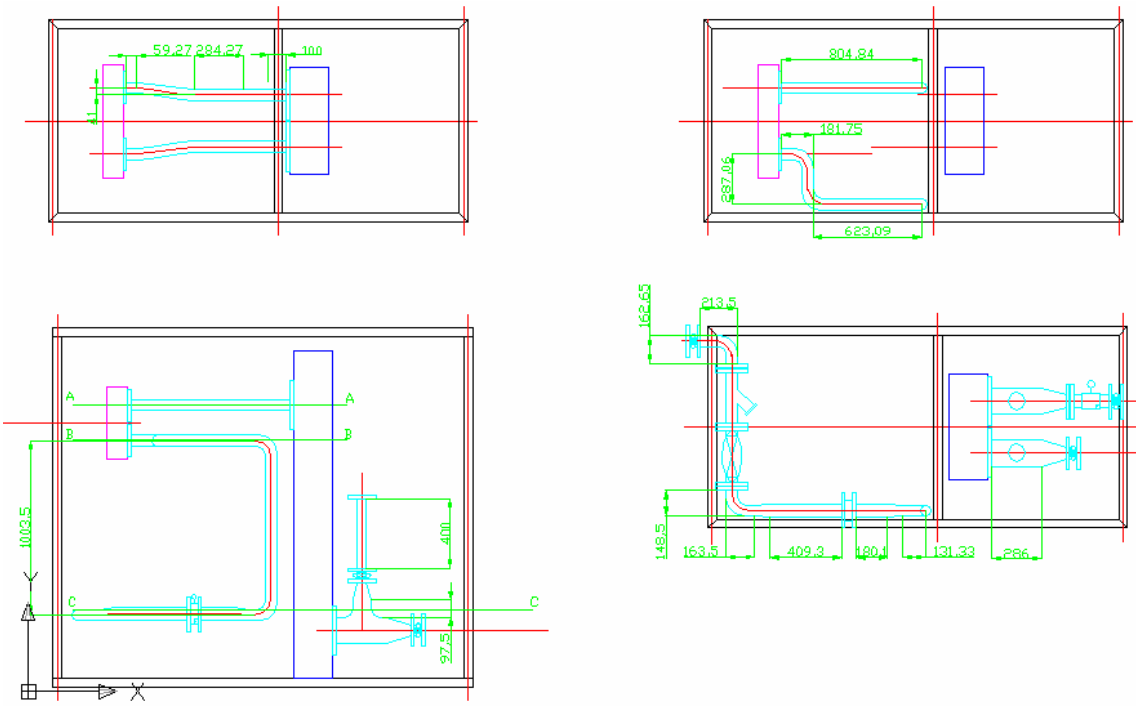


Figure 4.7: Overview of the system pipework

4.5 MANUFACTURE

The system was manufactured in the Jones Engine Test Laboratory, at Newcastle University during February-March 2003. The S355 box section was ordered from Corus, and once delivered, was cut to the right size and welded according to the manufacturing drawing.

The heat exchangers were then lifted and bolted into place and the pipework manufacture could start following the pipework drawings (Figure 4.7). All the

dimensions from the drawing were checked on the actual frame before the pipework was tack welded into place and checked. Once the pipework was deemed satisfactory, it was butt-welded. The pipework was then pressure checked and painted before final assembly. All the steam pipework was lagged to reduce heat losses and increase safety for the system operators.

The control system and the flow meters were then connected before the calibration could start. The system was then run with water only to check and calibrate the seawater side. Finally a test run and calibration of the steam side was done before the system was tested with both the seawater and steam sides working.

The complete system can be seen in the Figure 4.8 below.

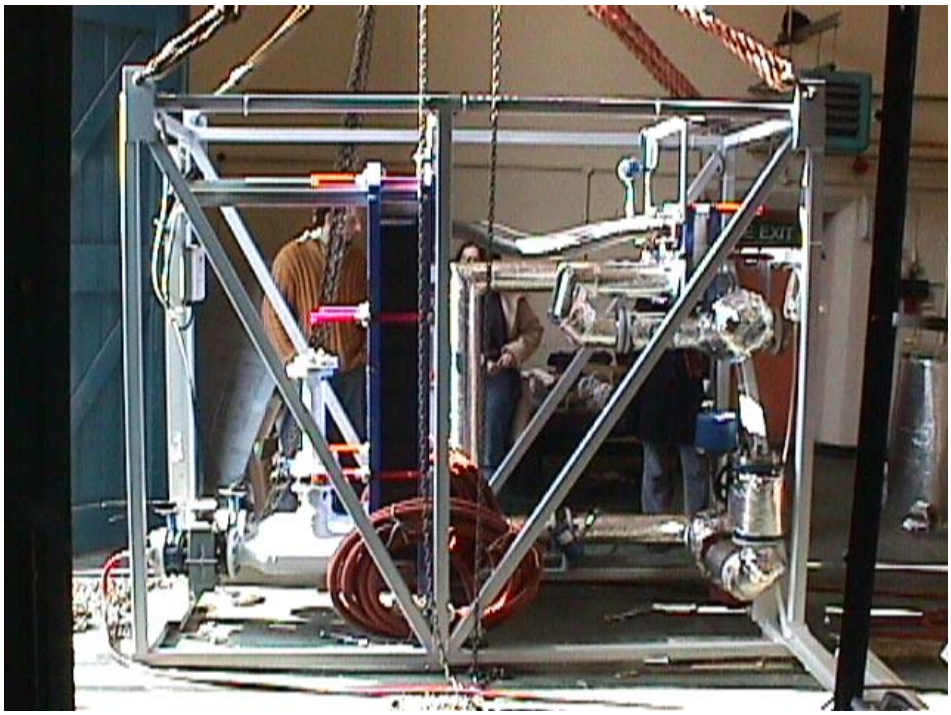


Figure 4.8: Finished system in the Jones Engine Test Laboratory.

4.6 ONBOARD TESTING

The system was installed aboard M/V Don Quijote, a 199m long car carrier, to run the testing phase. Due to space restrictions in the engine room and to reduce the risk of seawater damage to the cargo, the system was placed on the starboard side deck amidships. Using fire hose connections, the fire pump and fire main were used to supply ballast water to the system at up to 90 tonnes per hour. The steam pipe was connected to the steam supply in the adjacent air conditioning room using flexible steam hoses. Electricity was also supplied from the air conditioning room.

The testing period for the high temperature thermal treatment system ran from the 27th of May 2003 to the 5th of June 2003 from Suez (Egypt) to Zeebrugge (Belgium).

Three ballast tanks were used in the testing; 2 double bottom tanks, DB4 Port (DB4P) and DB4 Starboard (DB4S) and the Aft Peak (AP) tank. For each tank, 3 before treatment samples and 3 after treatment samples were taken. A total of six different

treatment temperatures from 55 to 80 ºC were tested, but only 60 and 65 ºC were tested every time (Table 4.1).

Table 4.1: Summary of treatment temperatures employed in the study

Date	Tank	Treatment temperature (ºC)					
		55	60	65	70	75	80
30.5	AP	X	X	X			
31.5	DB4P	X	X	X			
	DB4S	X	X	X			
2.6	AP		X	X	X		
	DB4P		X	X	X		
3.6	DB4S		X	X	X	X	X

4.7 CONCEPT APPROVAL

The installation scheme providing a global view of the components and links with the ship installation is given below.

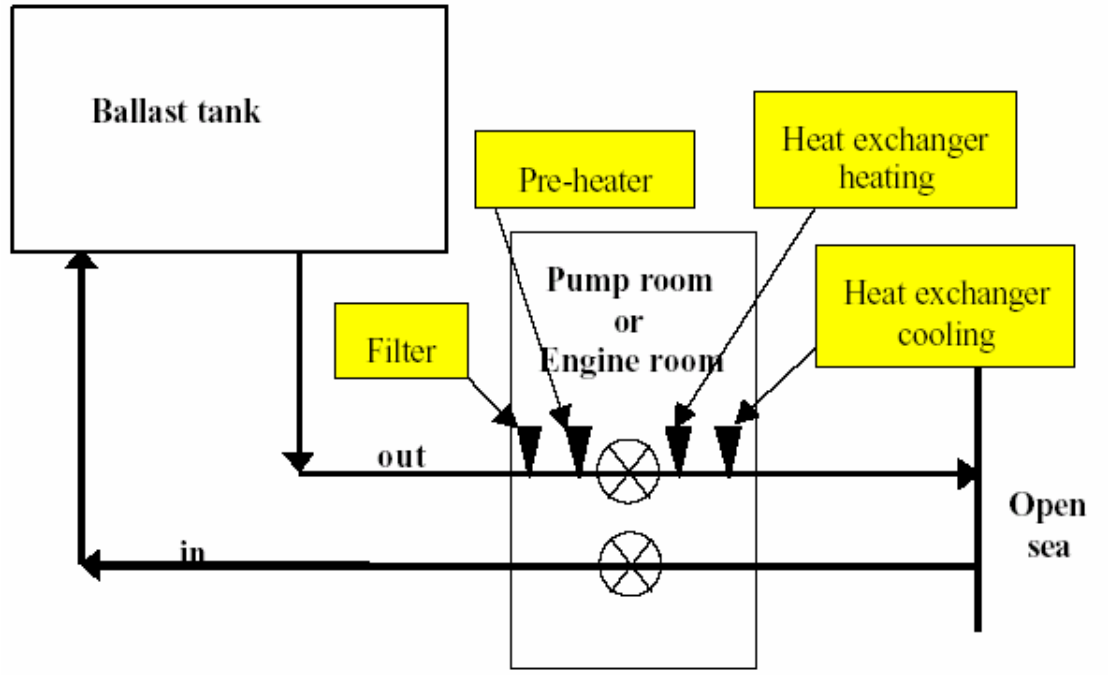


Figure 4.9: HTTT system diagram

The system is connected to the ballast water piping and uses components which exist on the ship and are well known ship equipment and have the following characteristics:

- Filter (optional): Alfa Laval filter
- Pre-heater (heating): Alfa Laval water-to-water heat exchanger
- Heat Exchanger (Heater): Alfa Laval water-to-steam plate heat exchanger (Titanium plates)
- Heat Exchanger (Cooling): Alfa Laval water-to-water heat exchanger

The review of the defined criteria in chapter 1 leads to the following conclusions shown in Table 4.2.

Table 4.2: HTTT criteria results

Criteria	Review Results
Stability	No tank filling different than those of the operational ship loading cases. No impact on stability.
Visibility	No modification of the loading cases, so of the trim, at sea. No impact on visibility.
Longitudinal strength of the vessel	No tank filling different than those of the operational ship loading cases. No impact on the hull girder strength.
Overpressure in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of overpressure.
Liquid motions in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of sloshing.
Piping	Use of well known marine equipment on ballast piping. No increase of risk.
Risk of fire	No specific non common equipments nor products. No increase of the risk of fire.
Material and products	Use of well known marine equipment on ballast piping. No particular risks.
Ballast water composition	No addition to the water. No particular risk.
Biological efficiency	Good laboratory test results. Good onboard full scale test results, complying with under discussion IMO standard.

The system analysis does not show any particular difficulty with respect to normal ship design and building. The biological efficiency has been proven acceptable. Considering the documents submitted, the system is granted with a Design Concept Approval.

To obtain the Final Concept Approval there is no identified difficult points, it will be granted after submission of the required documents reference number 9 to 15 of Table 1.2 (see chapter 1).

4.8 Risk and Safety Issues

A conceptual diagram of the ballast water flow through a thermal treatment system that would be installed as a full-scale system is shown in Figure 4.10 below. The water may be filtered prior to HTTT to protect the heat exchanger plates. Ballast water would be treated during de-ballasting operations, and the discharged ballast water would have a temperature a maximum of 10°C above the temperature of the ballast water in the tanks.

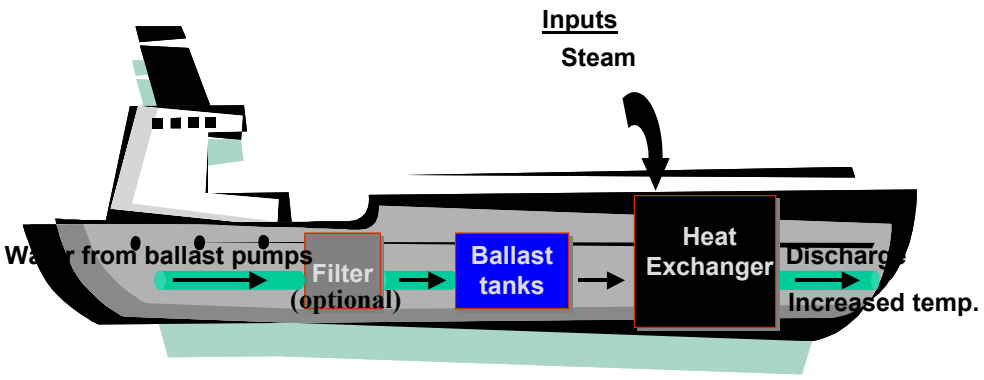


Figure 4.10: Simplified presentation of ballast water flow through the HTTT system

4.8.1 HAZARDS

Hazards identified in WP3 were physical heat hazards from steam, hot water, and heated surfaces of pipes and equipment. No additional hazards were identified during the onboard testing carried out in WP4, and there were no incidents resulting from contact with steam or hot water. Exposed hot-water pipework was covered with insulation.

For a full-scale installation, potential damages can result if the following occur:

- Rupture of steam pipe with release of steam
- Rupture of pipe containing heated ballast water with subsequent spill
- Rupture of pipe containing inlet ballast water or cooled ballast water, with subsequent spill
- Release of ballast water that has not been sufficient cooled

The consequences on ship machinery and equipment resulting from a release of steam or ballast water will depend on the location of the treatment system. Heated seawater within the treatment system is more corrosive than seawater at ambient temperature, so there is the potential for stresses and cracks to develop within the piping system. The steam will be contained within a closed system so corrosion would not be increased within the steam system.

Both steam and heated water have the potential to cause scalds and burns to any crew member that comes in contact with it. The target temperature of 55° C would produce third-degree scald burns in about 30 seconds (Bynum, 2001). The risk of scalding increases exponentially with temperature.

4.8.2 OTHER POTENTIAL HAZARDS

If a filter is used the sediment material removed by the filter could potentially be a biohazard if the ballast water is taken on in polluted waters and if the material removed by the filter requires handling. It is likely that a filter with a backwash cycle would be used, and there would be no handling of filtered material and thus no hazard.

4.8.3 "WHAT-IF" ASSESSMENT

"What if" questions considered during WP3 included the following:

- What if the steam pipe ruptures?
- What if a pipe containing heated ballast water ruptures?
- What if the manual or automatic control system within the water re-circulation system doesn't work and temperature and pressure increases within this piping system?
- What if there is a break in the inlet or outlet ballast water piping system?

The consequences resulting from the events described by the "what if" questions would be ship specific, and influenced by the location within the ship where the high temperature thermal treatment system/heat exchanger was installed. In some cases, there may be the potential for damage of equipment or injury to crew if a lot of water is released.

4.8.4 POTENTIAL RISK REDUCTION MEASURES

Risk reduction measures to address the "what if" questions include:

- Containment systems or shut off valves to limit the release of hot water
- Regular inspection of hot water pipes to check for corrosion damage
- Control system and valves to ensure shut off of steam if pipe breaks
- Control system/valve system to shut down pump and flow of ballast water if there is a pipe failure
- Control or warning system to notify if temperature of treated water exceeds the maximum treatment value
- Control systems to ensure that the ballast water is sufficiently cooled before discharge

4.9 ENVIRONMENTAL IMPACTS

The prototype for HTTT system tested onboard a Ro/Ro vessel was designed to treat a flow rate of 50 m^3/hr. Data was provided by the system designer on the materials used during construction of this prototype, energy use during operation, and measurements of the temperature of the water that was discharged. Environmental impacts resulting from operation and use of the HTTT system, based on the protoype tested in WP4, are discussed here.

4.9.1 PRODUCTION PHASE

A detailed list of parts and materials used for manufacture of the HTTT system were specified for each of the main components, including the main heater, the pre-heater, valves, flow meters, and pipe work. A summary of total weights for each of the main materials used is shown in Table 4.3.

Note that for a full scale version of the HTTT system an optional filtration unit may be installed for pre-treatment. The purpose of the filtration unit is to provide longer operation of the heat exchanger plates. A filtration unit was not used during the prototype testing so materials for this were not included in the summary table.

Table 4.3: Summary of materials used to construct the HTTT test unit

Material Type	Weight (kg)	% of Total Weight
Steel	951.1	73.8
Mild Steel	148.8	11.5
Stainless Steel	13.5	1.1
Cast Iron	66.1	5.1
Titanium	90.6	7.0
Aluminum	5.9	0.5
Others (rubber, plastic, rockwool, etc.)	13.0	1.0
Total:	***1289***	***100***

Steel, mild steel, stainless steel, and cast iron make up approximately 90% of the total weight of the equipment. These materials are all produced from the mining and smelting of iron ore. The heater and main heater were produced in Sweden and contain a majority of the steel required (about 800 kg out of the total 951 kg required). Life cycle inventory data for Swedish steel production was obtained from a report by Sunér (1996). Air emissions and energy use for production of the prototype was

estimated from this data. The weights of steel, mild steel, stainless steel, and cast iron were combined, and the inventory data for steel production was used as a proxy to estimate emissions and energy use for the other types of steel/iron products. Although this is a simplification, it was considered acceptable given that the data from other parts of the assessment are also at a rather preliminary stage. In addition, steel represents approximately 74% of the materials, and the other steel/iron products have similar process trees up until the blast furnace iron is produced from the blast furnace stage of steel production, so much of the process tree is similar. For example raw iron produced in the blast furnace is an input to the steel works. The blast furnace also produces pig iron. Table 4.4 shows the estimate of energy use to produce the steel, mild steel, stainless steel, and cast iron used in the production of the prototype.

Table 4.4: Estimate of gross energy requirement to produce the HTTT system

Energy Summary Categories	Requirements (MJ)
Electricity	2034
Oil Fuels	2002
Other Fuels	5190
Total	9225

Emissions to air resulting from productions of these same materials were also estimated. Emissions categories included gases that contribute to global warming (greenhouse theme), gases that contribute to acidification (acidification theme), and gases that contribute to the formation of tropospheric ozone (tropospheric ozone precursors theme). Table 4.5 shows the amounts of the major types of emissions according to these "themes", and also shows the equivalents totals for each of these themes. Equivalents were estimated by multiplying by standard conversion factors, which are shown in Table 4.5. The equivalents used are as follows:

- Greenhouse theme: CO_2 equivalent
- Acidification theme: Potential Acid Equivalent (PAE)
- Tropospheric Ozone Precursors Theme ((TOFP)

Table 4.5: Emissions from the production phase of HTTT

Theme	Type of Emission	Amount (kg)	Conversion Factor	Equivalent Value
Greenhouse	CO_2	1170	1	1170
	CH_4	2.82	23	65
	N_2O	0.008	296	2
Total CO_2 equivalents(kg)				1237
Acidification	NO_x	1.8	1/46	0.04
	$SO_2 + SO_x$	2.9	1/32	0.09
	NH_3	0.001	1/17	0.00006
Total Potential Acid Equivalent (kg PAE)				0.13
Tropospheric Ozone Precursors	NO_x	1.8	1.22	2.22
	CO	0.28	0.11	0.03
	CH_4	2.82	0.014	0.04
Tropospheric Ozone Forming Potentials (kg TOFP)				2.29

Notes: Conversion factors for greenhouse gases to CO2 equivalents from IPCC 2001
Conversion factors for PAE and TOFP from Hass (2002).

4.9.2 OPERATIONS PHASE

Fuel is required to heat the steam used in the heat exchangers and also to operate the pumps for pumping ballast water through the heat exchanger system. Emissions related to fuel will vary with engine type and fuel type. It was assumed that marine diesel fuel was used and the IPCC standard emission values shown in Table 2.4 (see chapter 2) were used for this assessment.

Lymberopoulos (2003) from the University of Newcastle provided energy estimates for treating 800 m^3 of ballast water with the prototype system. An average inlet water temperature of 26°C was used, and measurements taken during the onboard testing showed that the water had a temperature of 51°C when it exited the treatment system. It was estimated that 2592 MJ was required for each treatment operation. For this report, it was assumed the average inlet water temperature should be 15°C, and further that the water exiting the pre-heater would be 41°C (although this has not been confirmed with field testing). Based on this assumption, the energy required is 5472 MJ per 800 m^3 of ballast water treated. If diesel fuel is used, with a heating value of 42.5 MJ/kg, then 129 kg of fuel is required. For the life cycle assessment, it is estimated that the ship makes 25 voyages per year where the 800 m^3 of ballast water is treated. The life cycle of the equipment is estimated as 20 years. Using these assumptions, a total of 64.5 tonnes of fuel would be used over the life of the equipment. Emissions associated with this fuel use are shown in Table 4.6.

Table 4.6: Emissions over life cycle operation of thermal treatment system.

Theme	Type of Emission	Amount (kg)	Conversion Factor	Equivalent Value
Greenhouse	CO_2	205,356	1	205,356
	CH_4	19.6	23	451
	N_2O	5.2	296	1549
			Total CO_2 equivalents(kg)	207,356
Acidification	NO_x	4709	1/46	102
	$SO_2 + SO_x$	3924	1/32	123
			Total Potential Acid Equivalent (kg PAE)	225
Tropospheric Ozone Precursors	NO_x	4709	1.22	5745
	CO	484	0.11	53
	CH_4	20	0.014	0.3
			Tropospheric Ozone Forming Potentials (kg TOFP)	5708

Notes: Conversion factors for greenhouse gases to CO2 equivalents from IPCC 2001
Conversion factors for PAE and TOFP from Hass (2002).

4.9.3 COMPARISON OF EMISSIONS BY LIFE CYCLE STAGE

Emissions values for both the equipment production and operations phase of the thermal treatment equipment is presented in Table 4.7. For all three categories considered the operations phase is dominant, accounting for more than 99% of emissions during the life cycle.

Table 4.7: Emissions over production and operation phase of HTTT system

Theme	Production		Operation	
	kg	% life cycle	kg	% life cycle
Greenhouse theme: Total CO_2 equivalents	1237	0.6	207,356	99.4

Acidification: Total Potential Acid Equivalent (kg PAE)	0.13	0.1	225	99.9
Tropospheric Ozone Forming Potentials (kg TOFP)	2.29	0.1	5708	99.9

4.9.4 DIRECT IMPACTS THROUGH DISCHARGE TO RECEIVING WATER

Discharge of water with altered quality

The only expected change to ballast water quality undergoing HTTT is an increase in water temperature. The temperature of the ballast water discharged from the process was measured during the on-board trials of the system. The increase in water temperature ranged from 4°C to 7°C.

There are currently no standards for thermal discharges from ships. Ships discharge cooling water on a regular basis, and there have not been any documented impacts from these types of discharges. As discussed in WP3, there have been studies showing that large, continuous thermal discharges from facilities such as power plants can have impacts on receiving environments within the mixing zone. These discharges produce a zone with an elevated temperature that remains elevated for a continuous (more or less) period of time. Ballast water discharges, however, are intermittent, and the mixing zone location would likely be different for each ship. Under these conditions an area of elevated water temperature would only be established for a short time, and it is unlikely that any permanent impacts would be apparent, particularly for a temperature increase in the range of 4°C to 7°C.

As stated in WP3, if thermal treatment from ballast water is widely adopted, ports that receive large discharges of ballast water may need to model or monitor temperature to determine if there is an adverse effect. A survey of the number of ships, ballast water volumes, times and locations of discharges would be helpful for conducting a preliminary estimate.

Impact from surviving non-indigenous organisms

The results of the on-board testing for biological effectiveness of HTTT showed a high degree of inactivation of zooplankton by heat treatment (DTR-4.7). Results for phytoplankton testing were considered to be inconclusive due to the low concentrations of phytoplankton in the ballast water. If further testing confirms good effectiveness against phytoplankton, it is expected that there would be few surviving organisms and minimal impacts.

Discharge of solids (organisms and sediments)

In full scale operations, the ballast water may be filtered prior to passing through the heat exchangers. If the filtration takes place prior to de-ballasting, sediments would have to be returned to the ballast tanks or disposed of at sea to prevent discharging non-indigenous organisms to the arrival port. If the filtration takes place during ballasting the sediments could be discharged to the origin port. This could result in localised areas of increased turbidity. Turbidity increase would depend upon the amount of sediments present in the ballast water.

The treated ballast water would contain organic material in the form of dead organisms. The amount of organic matter would be dependent on the concentration of

organisms taken on with the ballast water, with the larger organisms being removed by filtration. Impacts would vary depending upon the sensitivity of the receiving environment, with organics loading being more of a concern in eutrophic waterbodies.

4.10 ECONOMIC ASPECTS

4.10.1 CAPITAL COST

The approximate investment costs for the system is € 95,500 for the two heat exchangers (including filter if used), approximately € 4,500 for the framework. Total investments are € 100,000. The approximate installation costs are 10% of the system costs, i.e. € 10,000. There are no testing or commissioning costs expected.

4.10.2 OPERATIONAL COSTS

Treating the ballast water at 200 m^3 per hour with the pre-heater, the steam heater system requires 2 tonnes of steam per hour. The discharge of 2,000 m^3 ballast water will take 10 hours, which results in a steam use of 20 tonnes to treat the ballast water. Detailed steam production calculations are shown Table 2.11 (see chapter 2).

Table 4.8: Electricity use by the BW pump

Electricity use pump (ballast water)		**Unit**
electricity requirement per hour (pump)	50	kW per pump
working hours for pump per trip	4	hours per trip
electricity use per trip (pump)	200	kWh per trip
electricity use per year (pump)	10,000	kWh per year

Table 4.9: Electricity use by the system

Electricity use treatment system		**Unit**
energy use treatment system (per hour)	1,389	kW
treatment time per trip (hours)	10	hours during discharge
treatment capacity per hour	200	m3 BW/hour
steam requirement per m3 BW	10	kg/m3 BW
steam requirement per hour	2,000	kg/hour

Table 4.10: Total energy use

Total energy use		**Unit**
for steam production	13,889	kWh per trip
kWh > MJ (steam)	50,000	MJ (steam)
MJ (steam) > MJ (diesel)	75,758	MJ (diesel)
MJ >kg (diesel)	1,783	kg (diesel)
for electricity production	200	kWh per trip
kWh > MJ (electricity)	720	MJ (electr.)
MJ (electricity) > MJ (diesel)	2,400	MJ (diesel)
MJ >kg (diesel)	56	kg (diesel)
total diesel use per trip	1,839	kg (diesel)
energy costs per trip (diesel)	735.60	€/trip
total energy costs per year (diesel)	**36,780**	**€/year**
working hours per year (treatment)	500	hours per year
energy use per year (treatment)	694,444	kWh per year

Apart from diesel no other *consumables* are used during treatment. *Personnel* involvement for the operation of the system is negligible. The system is self-contained,

self-cleaning and generally self-sufficient. Estimations on *maintenance costs* related to regular or incidental maintenance (materials and personnel involved) are not available yet and therefore not included in the calculations.

To inform the crew onboard about the system and provide them *some training* in using the system only an hour familiarisation is needed. Costs related to this are not included in the calculations. There are no *management costs*, like certification costs, and development of safety manuals, expected.

4.10.3 COST AND BENEFITS ASPECTS

Influence on tank cleaning costs and corrosion control costs are expected to be negligible. There is no delay in harbour or during the trip expected related to the HTTT system. No extra maintenance costs are expected. An estimation of the size of the equipment required onboard is 8 m^2 and 2.8 m high. Total weight of the (empty) equipment is 7,150 kg and consists of titanium (5,600 kg), stainless steel (1,200 kg) and steel (350 kg). Installation of the system will not result in cargo space reduction.

The next table (Table 4.11) shows detailed calculation results for thermal treatment.

Table 4.11: HTTT economic results

Cost type	Description	€ (euro)	Comments
Capital Costs		**€ (euro)**	
Investment	investment costs	100,000	two heat exchangers, filters
Installation	installation costs	10,000	10% of investment costs
Testing	testing costs	0	not expected
Commissioning	commissioning costs	0	not expected
	total investment	**110,000**	**€**
Depreciation factors	depreciation period	10	years
	interest rate	8%	
	annual capital costs	**16,393**	**€/year**
Operational Costs		**€/year**	
Personnel	personnel during treatment	p.m.	negligible
Energy	energy (diesel)	36,780	€/year
Materials	additives use	0	
Maintenance	TAM (maintenance euro)	0	
	additional maintenance	0	
Training and management	training costs	0	only familiarisation
	certification costs	0	no costs expected
	health and safety issues	0	
Cost and benefits	tank cleaning costs	0	no influence
	corrosion costs	0	no influence
	costs of delay	0	no delay
	increased maintenance	0	
	loss of cargo space	0	no loss of cargo space
	annual operational costs	**36,780**	**€/year**
Total annual costs		**53,173**	**€/year**
Costs per treated m3 ballast water	**50 trips / 100,000 m3**	**0.5317**	**€/treated m3 BW**

4.11 BIOLOGICAL ASSESSMENT

The original plan for the sea trials was to test different treatment temperatures on ballast water from three different tanks (DB4S, DB4P, and AP), and also as a function of the age of the ballast water. However, it later became clear that too little ballast water had been flushed through the pipelines between changes from one ballast tank to the next. In the study only 1-2 tonnes of ballast water was flushed through the pipes, while later studies during the DEOX trial revealed that 5-10 tonnes of water (depending on the position of the tank sampled) should have been run to waste in order to ensure that water from the intended tank was being treated. Thus, water samples treated towards the end of a test series were probably from the intended tank, but samples treated in the beginning of a test series were probably from the previous tank or the pipelines. It is possible that in some cases not enough water was let run to reach the intended tank even when the third sample was taken. The two ballast tanks DB4S and DB4P were filled simultaneously and should therefore contain the same concentration of organisms and species composition from start. The last tank, AP, was filled a few hours later and in somewhat deeper sea (2400-2800m versus 800-1100m for DB4S/P), and may have contained a slightly different concentration of organisms and species composition. However, the results indicate that the differences between the tanks were small. We may therefore treat the samples as all originating from the same ballast water, and evaluate the effect of the treatment temperature and the age of the ballast water, but the possibility of evaluating tank to tank variations is lost. For practical reasons, the designation of the samples with the intended ballast tank is kept.

4.11.1 ZOOPLANKTON RESULTS

4.11.1.1 CONTROL SAMPLES

To provide a measure of comparison between the survival of the treated and untreated organisms, 1-2 non-treated control samples were taken on all sampling days. The mortality in these samples was surprisingly high and varied from 40 to almost 100%. The high mortality already a few hours after the water had been pumped into the ballast tank is not likely to be due to the short stay in the tank, and must therefore be due to the pumping of the water into the ballast tanks and/or the pumping of the water from the ballast tank to the HTTT unit on the upper deck. When water passes through a pump, organisms in the water will risk damage due to the moving parts of the pump and pressure fluctuations. The latter may have been especially strong in the case of the fire pump, which had to lift the water from the ballast tanks and 10 to 20 meters to the upper deck. The ship's ballast pumps are much larger than the fire pump, which should reduce the risk of mechanical damage to the organisms, and in addition the ballast pumps do not have to pump the water against a high backpressure.

The total concentrations of copepods and nauplii in the control samples, i.e. both live and dead, on the different sampling days are shown in Figure 4.11. The concentration varied considerably between different sampling days, but did not change significantly as a function of time.

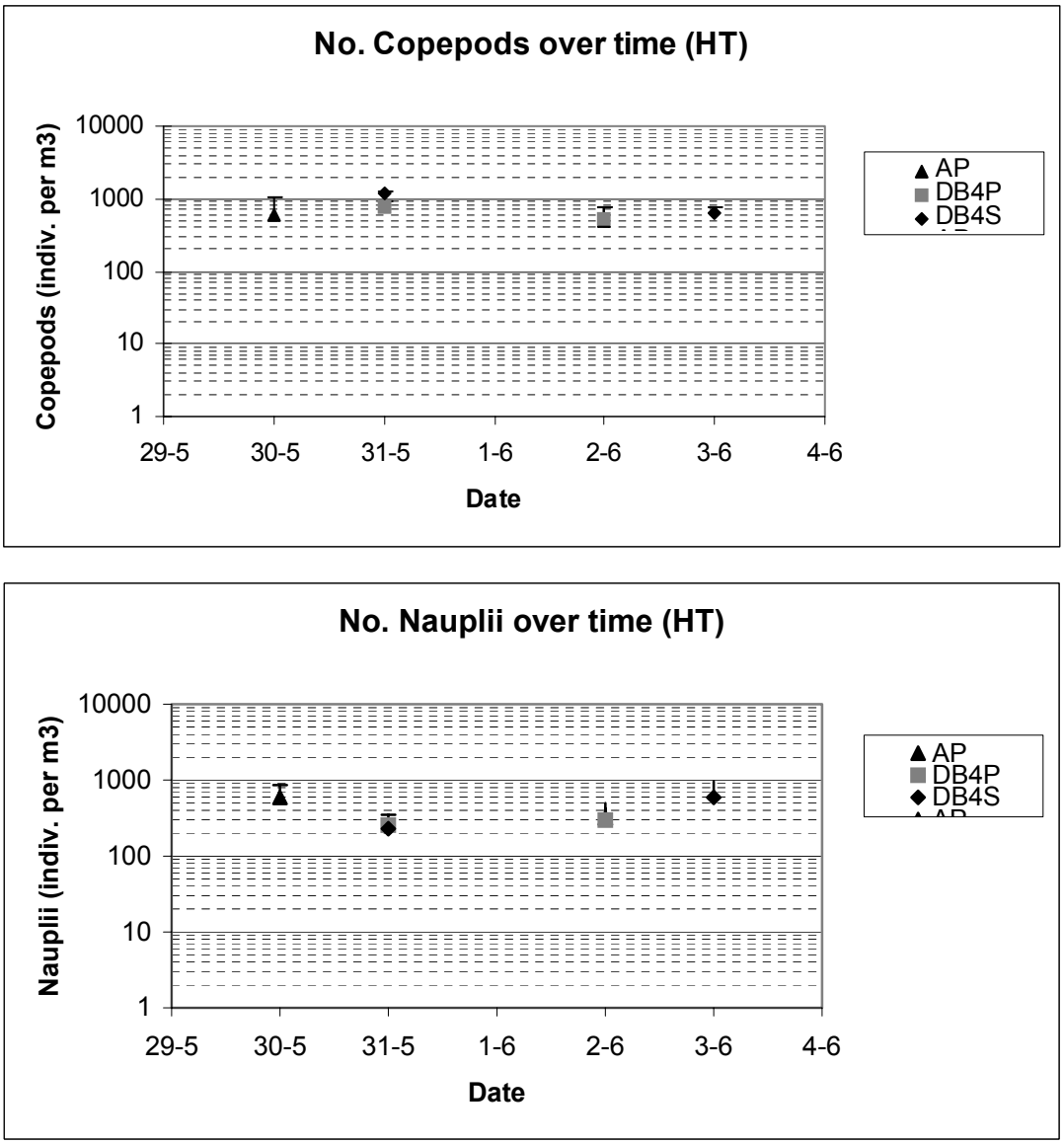


Figure 4.11: Total concentration of copepods and nauplii in the ballast water samples as a function of storage time during the HTTT

In the control samples there were no significant differences in copepod mortality over time. For nauplii, significant lower mortality was found on day 30/5 moreover the mortality on day 31/5 was also significantly lower than on the 3/6 (one-way ANOVA, $p<0.001$).

Significant differences were found between life stages and over time. The mortality encountered on the first day (30/5) was significantly lower than on the following days (two-way ANOVA, $p<0.001$). Copepods had significantly higher mortality than nauplii (two-way ANOVA, $p<0.001$). The mortality of nauplii on day 30/5 was significantly the lowest (two-way ANOVA, $p=0.001$).

4.11.1.2 HEAT TREATED SAMPLES

Six different temperatures were tested: 55, 60, 65, 70, 75 and 80°C on water from three different tanks, AP, DB4P and DB4S (Table 6). Two temperatures, 60 and 65ºC,

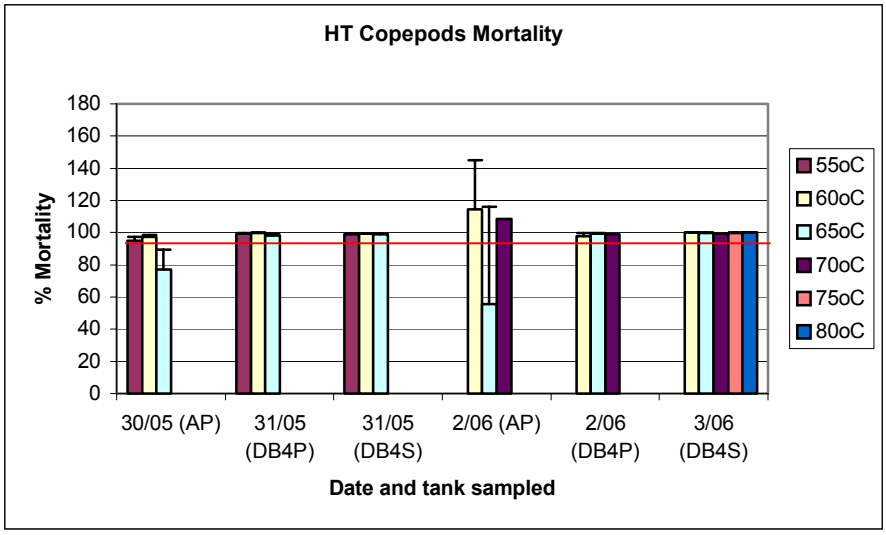
were applied every time the experiments were carried out, while 55ºC was tested on the first two days (30/5 and 31/5) on water from all tanks and 70ºC was tested on the 2/6 and the 3/6 on water from all tanks. The two highest treatment temperatures, 75 and 80ºC, were applied on the last day (3/6) on water from tank DB4S.

Figure 4.12 shows the mortality of copepods and nauplii after treating the ballast water at different temperatures from different tanks and on different days.

Significantly lower copepod mortality (77%) was found when the water was treated at 65ºC on the 30/5 compared to treatment at 55 or 60ºC during the first two days (two-way ANOVA, $p<0.001$ for temperature, day and different temperatures on different days). However, no significant differences were found between 60 and 65ºC throughout all the days. Similarly, 60, 65 and 70ºC had no significantly different effect on the mortality on the last two days and the same happened when comparing 60, 65, 70, 75 and 80ºC on the last day. Therefore, an increase of temperature above 60ºC did not make the treatment more effective towards the copepods.

In most cases the kill rate for copepods was higher than 95% (see the red line in Figure 4.12). Only when the water in the AP tank was treated at 65ºC on the 30/5 and the 2/6 (with a standard deviation of ±60%) was this value not achieved.

Significantly higher nauplius mortality was found at 60ºC than at 65ºC (two-way ANOVA, $p<0.05$). However, no significant differences were found over the days or between these two temperatures on a particular day. Moreover, as the data were not normal and the result not highly significant ($p=0.039$) it should be treated with caution. Furthermore, when comparing the mortality at 55, 60 and 65ºC on the first two days, at 60, 65 and 70ºC on the last two days, and at 60, 65, 70, 75 and 80ºC on the last day, no significant differences were found in the nauplius killing rate. Consequently, increasing the temperature above 60ºC did not increase the killing rate for nauplii.



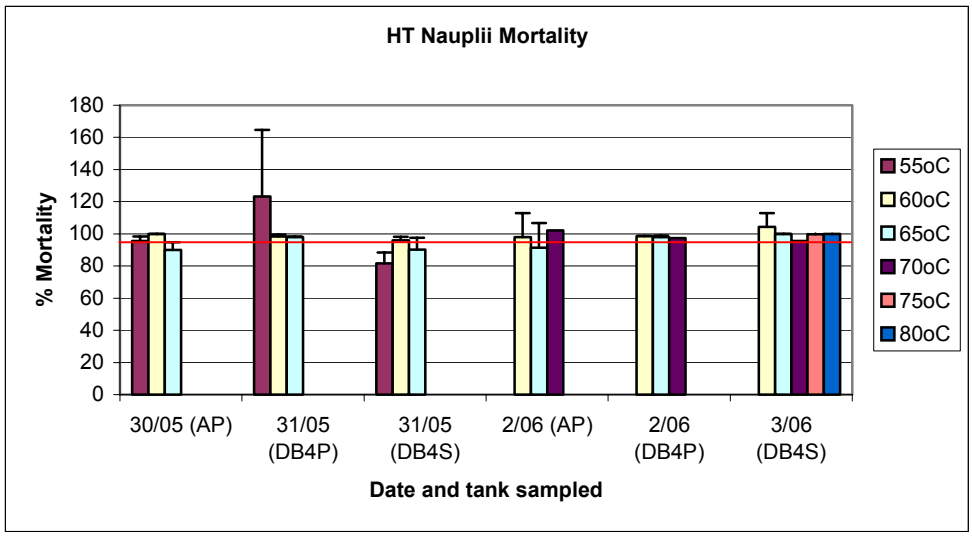


Figure 4.12: Copepod and nauplius mortality at different treatment temperatures
The columns and error bars represent sample means and standard deviations based on three observations. Note: the red line shows 95% kill efficiency.

In four cases (65 ºC on the 30th and the 2nd in water from tank AP, 55 and 65ºC on the 31st in water from tank DB4S) the 95% kill rate was not achieved. In all other cases, more than 95% of the nauplii were killed (see red line in Figure 4.12).

In most cases there were no significant differences in the efficiency of the HT treatment towards copepods or nauplii. On the 30th in water from tank AP treated at 60ºC the kill rate for copepods (97%) was significantly lower than for nauplii (100%) (one-way ANOVA, $p<0.05$). On the other hand nauplii had significantly lower mortality (82% compared to 99% for copepods) on the 31st in water from tank DB4S treated at 55ºC (Kruskal-Wallis, $p<0.05$). The overall conclusion is therefore that these two life stages have the same sensitivity for heat.

When comparing the mortality in the control samples and the treated samples no significant differences were found for copepods. Nauplii, on the other hand, had significantly lower mortality in the control samples and on the first day, compared to the treated samples (two-way ANOVA, $p<0.001$).

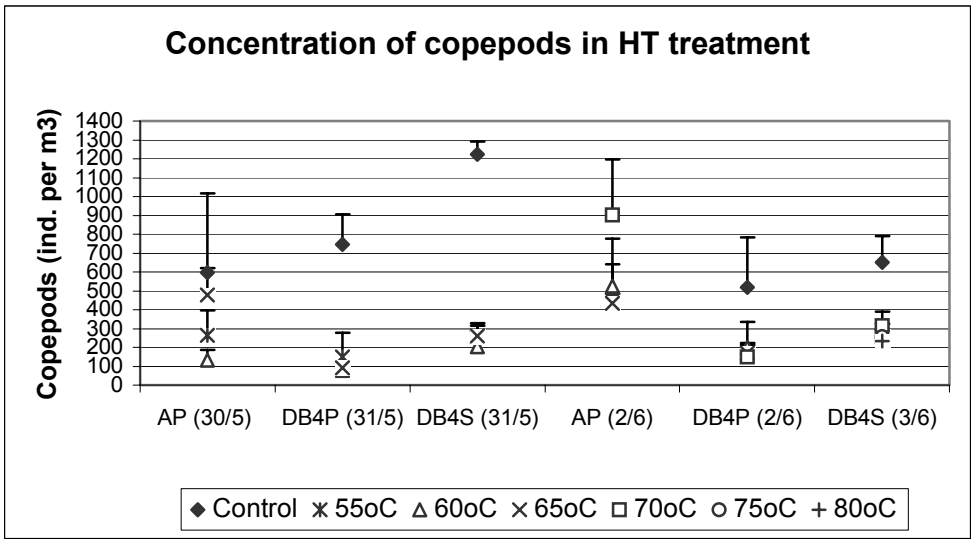
The total concentrations of copepods and nauplii, i.e. both live and dead, (Figure 4.13) were significantly lower in the treated samples than in the untreated controls (one-way ANOVA, $p<0.001$ for copepods and Kruskal-Wallis, $p<0.01$ for nauplii).

4.11.1.3 Comparison with IMO Standards

The new IMO standard (see section 3.1) specifies that the ballast water upon discharge shall contain no more than 10 viable organisms per cubic metre greater than or equal to 50µm in size. In the current study a 50µm sieve was used to collect the zooplankton. The concentration of live (counted as viable) zooplankton found in the controls and HTTT treated samples is presented in Figure 4.14.

The HTTT achieved the IMO standard on the 3rd June in tank DB4S at all temperatures tested apart from 70ºC, on the 2nd June in tank DB4P at all temperatures tested and on the 31st May at 60ºC. More live organisms were found on 30th May than

on 2nd and 3rd of June (one-way ANOVA, $p<0.05$) from the control samples, but no differences were found between tanks. Significant differences were found for the different temperatures tested (75 and 80ºC were the temperatures with fewer live organisms, one-way ANOVA, $p<0.001$). The tank AP had the highest numbers of live copepods (Kruskal-Wallis, $p<0.001$) and on 3rd June the numbers encountered were the lowest compared to the other days (one-way ANOVA, $p<0.001$). Significantly lower concentration of live organisms were found in the after treatment samples compared to the controls (one-way ANOVA, $p<0.001$).



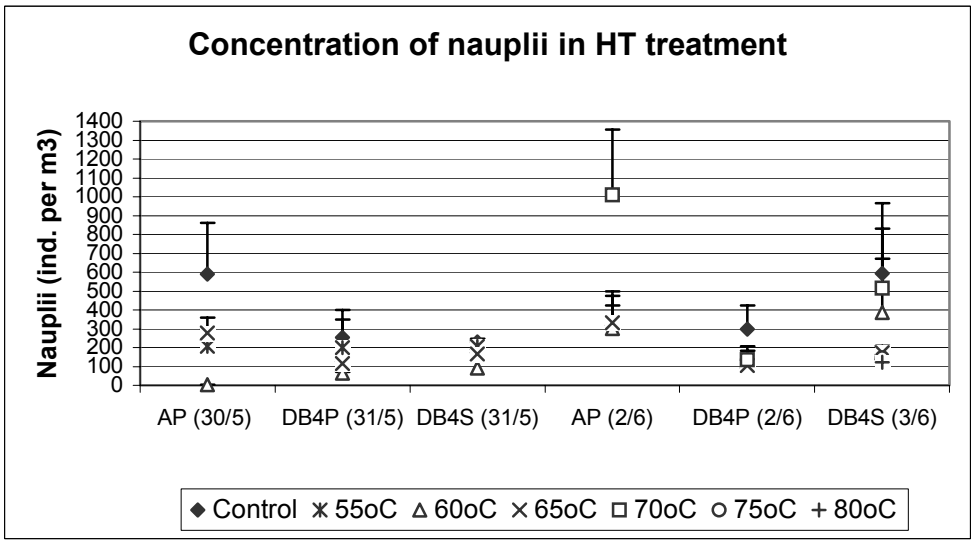


Figure 4.13: Copepod and nauplius total concentrations from the control and treated samples. The points and error bars represent sample means and standard deviations based on three observations.

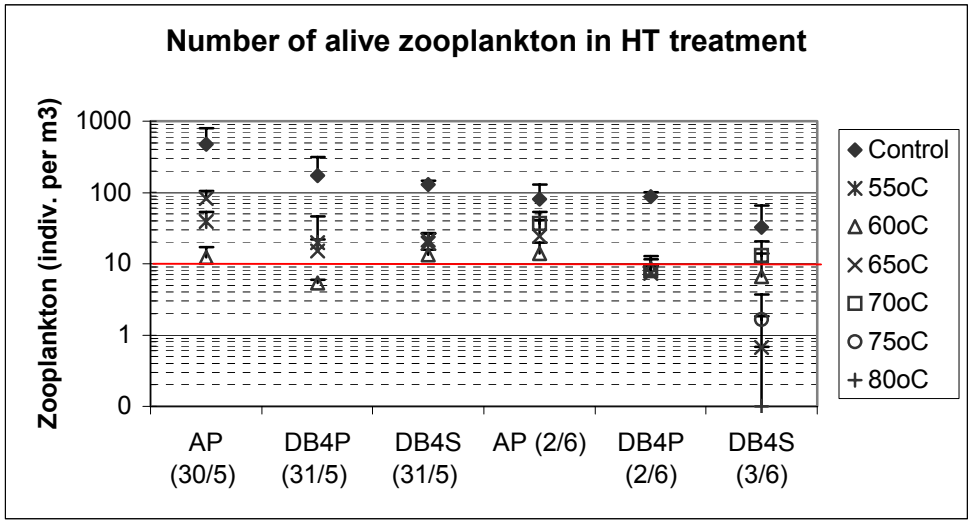


Figure 4.14: Concentration of viable zooplankton present in the samples from the HTTT. The columns and error bars represent sample means and standard deviation based on three observations. Note: the red line indicates the IMO limit of 10 viable organisms per m^3 greater than 50μm

4.11.2 PHYTOPLANKTON RESULTS

A total of 78 chlorophyll samples were collected during the HTTT trials. During sampling it was noted that there did not seem to be much plankton present in the water. The water did not have a strong green colour and filtered very easily even through a very fine 10μm mesh. On carrying out the chlorophyll analysis, very few of the samples contained any detectable chlorophyll *a*. This was owing to the fact that the water contained very little phytoplankton (see below) and the amount of water filtered was not enough to detect the very low levels of chlorophyll *a* present. The results from this analysis could therefore not be used.

In total, 82 phytoplankton samples were collected during the trials. The cell counts for the ship board trials were carried out on preserved samples and there was therefore no way of assessing cell viability. Figure 4.15 shows the cell counts for dinoflagellates and diatoms. The concentrations were low probably owing to a number of factors, such as the location and the time of day the ballast water was originally loaded. The ballast water was loaded during the night as the vessel left port and entered deeper waters and there would be fewer phytoplankton cells present in the deeper waters away from the coast. Other factors could also play a role in how much chlorophyll *a* was present in the cells. For comparison, typical cell counts for phytoplankton samples collected in June from the Stonehaven sampling station near Aberdeen would be in the range of 12,000 cells per litre for dinoflagellates and 100,000 cells per litre for diatoms.

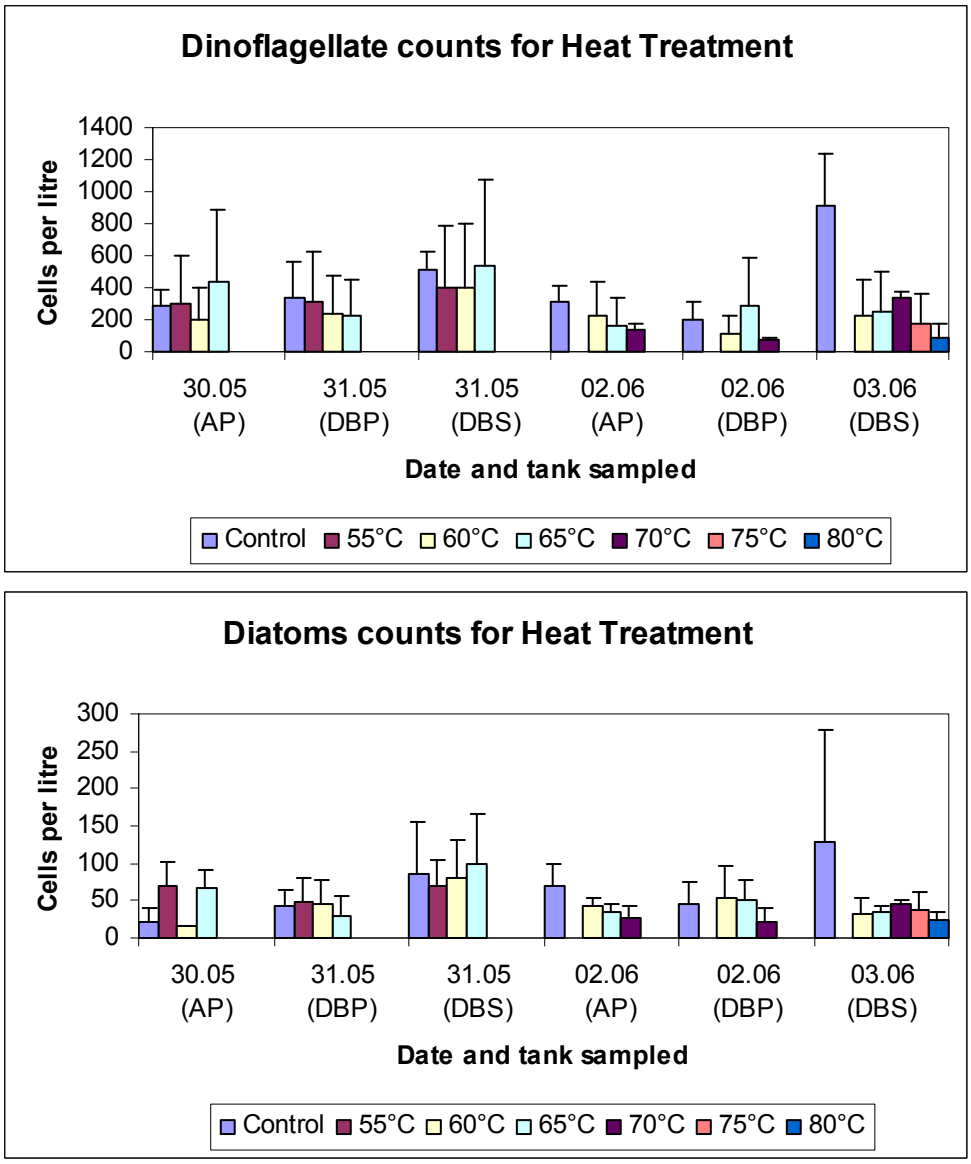


Figure 4.15: Dinoflagellate and diatom cell counts for samples collected with a 10µm mesh The columns and error bars represent sample means and standard deviations based on three observations

The water was treated at 55ºC on three occasions, once on 30th June and twice on 31st June. The results for the first run show that the cell counts for both dinoflagellates and diatoms were higher in comparison to the control samples. For the second run the dinoflagellate cell counts were slightly lower than the control but the diatom counts were slightly higher. For the third run the counts for both dinoflagellates and diatoms in the treated samples were lower than the control sample cell counts. However, statistical analysis showed no significant differences between the treated and untreated samples.

Six test runs were carried out at 60ºC. For these tests the dinoflagellate counts were always lower in the treated samples than in the control samples. The diatom counts for the treated samples were lower than the controls on four occasions (30th, 31st (DB4S), 2nd (AP) and 3rd (DB4S)) and had equal or slightly higher counts on the remaining two occasions. None of the results from the treated samples were

significantly different from the untreated samples except for the samples taken on the 3rd where the untreated sample had a significantly higher number of dinoflagellates in comparison to the treated sample (Kruskal-Wallis, $p<0.05$).

Six test runs were carried out at 65ºC. For both dinoflagellates and diatoms three test runs had higher counts in comparison to the control samples (for samples on the 30th, 31st (DB4S) and 2nd (DB4P)). However, there were no significant differences between the treated and untreated samples.

Three tests were carried out at 70ºC. All the counts for diatoms and dinoflagellates were lower in comparison to the control samples. There were no significant differences between the treated and untreated samples apart from the dinoflagellate samples taken on the 3rd, where the untreated sample had a significantly higher number of dinoflagellates compared to the treated sample (Kruskal-Wallis, $p<0.05$).

Only one test each was carried out at 75 and 80ºC. The cell counts for both these tests were lower in comparison to the control from the same day (3rd June). The difference was significant for the dinoflagellates (Kruskal-Wallis, $p<0.05$).

On the last day of sampling (3rd), the control sample had a much higher cell count than on any of the previous days. It should be remembered that these counts do not take account of viability and could include dead cells. If the results are all taken together only the dinoflagellate cell count for the untreated sample on the 3rd is significantly different from all the other samples (1-way ANOVA, $p<0.001$). For the remainder of the cell count results there are no significant differences between the treated and untreated samples.

4.11.3 BACTERIA RESULTS

The water pumped into the tanks in the Mediterranean Sea contained about $1 \cdot 10^4$ growth units[5] (GU) per ml before treatment (Figure 4.16). There were no significant differences between ballast water from different tanks or changes as a function of the time the ballast water was stored in the tanks.

The HTTT reduced the bacterial concentration in the ballast water by approximately 95% (Figure 4.17). Surprisingly, there was no significant increase in the killing rate with increasing treatment temperature. The killing of bacteria with heat is a well-known technology, and the killing rate always increases with increasing temperature under otherwise equal conditions. With the large temperature range tested in this study (55 to 80ºC) an effect of temperature should have been observed. A possible explanation is that the remaining 5% consisted of bacterial endospores. Bacterial endospores are very heat resistant and require much higher temperatures than vegetative cells to be killed, usually more than 100ºC for several minutes. Possibly, almost all vegetative bacterial cells were killed already at the lowest treatment temperature (55ºC), while the remaining endospores were not affected within the temperature range tested. However, as the bacterial endospore concentration in the ballast water was not determined, no firm conclusions can be drawn.

[5] One growth unit can consist of one bacterial cell, but if several bacterial cells are clumped or linked together, they will be counted as one unit.

The IMO ballast water performance standard stipulates limits for some specified indicator bacteria (*E. coli*, *V. cholerae*, and intestinal enterococci) in discharged ballast water (see section 3.1). None of these indicator bacteria are spore formers and should therefore be relatively easy to kill by heating. However, some intestinal enterococci are relatively heat resistant and may require temperatures of 75-80 ºC for the viability to be significantly reduced within seconds. The study indicates that the HTTT would have reduced the viability of *E. coli* and *V. cholerae* by at least 95%, and possibly much more if the remaining viable bacteria in the ballast water after the HTTT originated from bacterial endospores. Whether or not this is enough to achieve the IMO standard depends upon the starting concentration of the indicator bacteria. In most cases a reduction in the viability of the indicator bacteria with two orders of magnitude is likely to be sufficient, but in extreme cases a higher reduction in viability may be required. The effect of the HTTT on the viability of intestinal enterococci is more difficult to predict and may need to be tested in practical experiments.

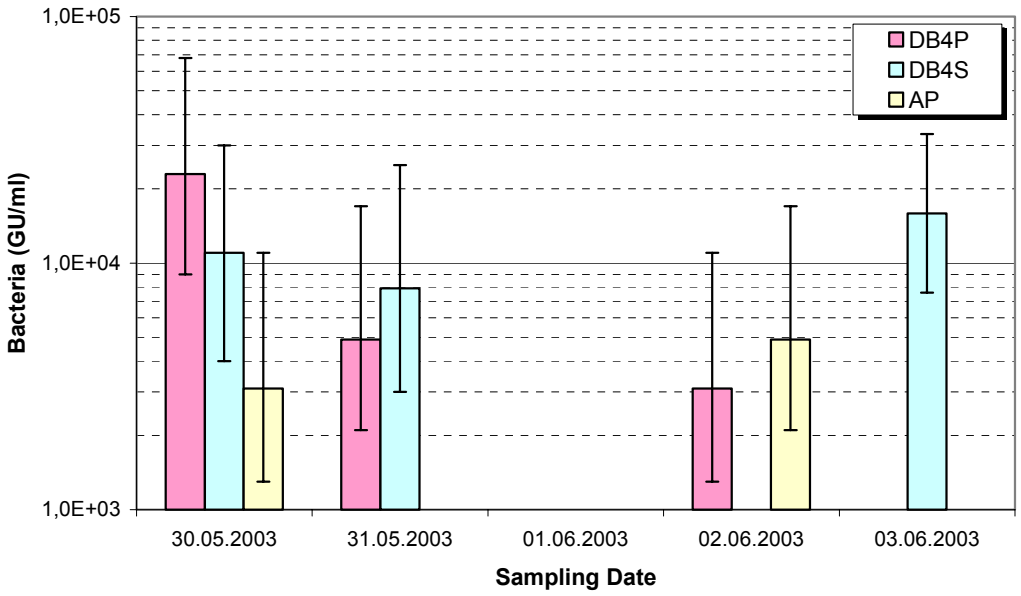


Figure 4.16: Viable bacteria in the BW before the HTTT
A theoretical 95% confidence interval as given by Blodgett (2001) is shown for all the ballast tank samples and dates where only one bacterial analysis was performed. On June 3 a total of eight samples of untreated ballast water were collected during the day, and here the actual 95% confidence interval is shown

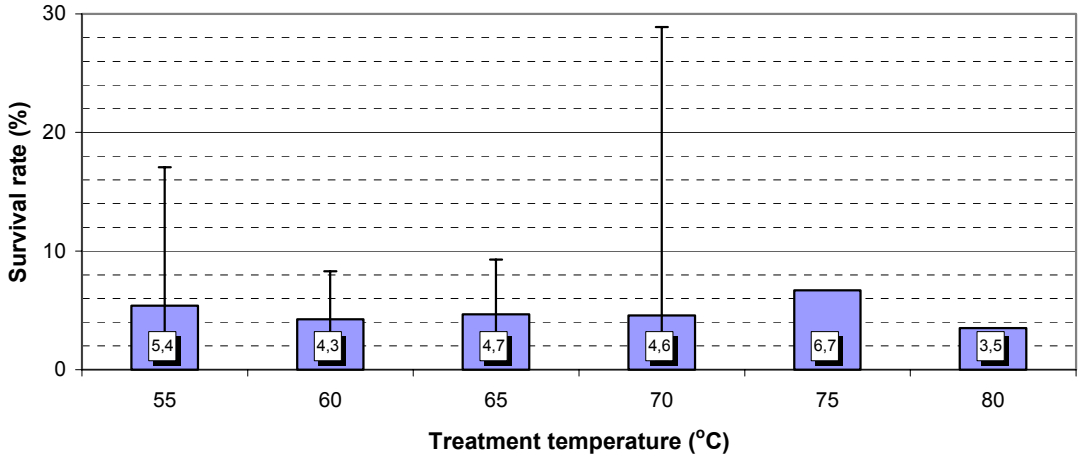


Figure 4.17: Logarithmic average survival rate for bacteria in BW
The standard deviation is indicated in those cases where three or more experiments were performed.

5 BIOLOGICAL DE-OXYGENATION TREATMENT

The idea behind biological de-oxygenation (DEOX) is to stimulate the growth of the indigenous bacteria in the ballast water so that they consume the available oxygen in the water. This is achieved by adding nutrients to the ballast water. When the ballast water becomes anoxic, organisms that require a steady supply of oxygen will die.

The solubility of oxygen in water is low, and decreases both with increasing temperature and increasing salinity. In distilled water at 10 °C the saturation level is 11.3 mg/L, in seawater (35 S) at 25 °C, 6.8 mg/L. Hypoxic water is often defined as water containing less than 2.9 mg/L, while anoxic water contains no oxygen.

5.1 DISSOLVED OXYGEN IN BALLAST WATER

Despite the low solubility of oxygen, ballast water does not usually become anoxic during transport. In a study of ballast water arriving at the Sture oil terminal on the west coast of Norway, water from 30 vessels from all major geographic areas were examined (Botnen *et al*. 2000). The age of the ballast water was from 2 to 18 days, and the oxygen content ranged from 6.8 – 14.0 mg/L. The temperature and salinity ranged from 5.5 – 23.4 °C and 1 – 37 S, respectively. No correlation between the age of the ballast water and the oxygen content was observed. Most of the examined ballast waters were supersaturated when the temperature and salinity of the waters were taken into account, with an average saturation level of 110 ± 16 %.

5.2 ANOXIC TOLERANCE OF AQUATIC ORGANISMS; LITERATURE REPORTS AND PREVIOUS STUDIES IN THE MARTOB PROJECT

The anoxic tolerance of aquatic species as reported in the literature is discussed in a previous report (DTR 2.5). A short summary is given below.

Most fish species will die if deprived of oxygen for more than a few minutes or hours. The most tolerant species, such as some flatfishes, show 50 % mortality (LT_{50}) after exposure to anoxia for around 24 hours. The sensitivity of fish eggs and fish larvae to low oxygen levels does not seem to be very different from the sensitivity of adult fishes.

The ability to survive anoxia varies considerably within the invertebrate macrofauna. Molluscs in particular can often tolerate long periods of anoxia (LT_{50} = 4-85 days). However, the larvae are much more sensitive, with a LT_{50} in the range of 10-50 hours depending on the development stage and body size. Next to the outstanding ability of molluscs (and some specialists of other taxa) to resist anoxia, come some annelids (worms) (LT_{50} = <55-120 hours) and echinoderms (LT_{50} = 35-90 hours), while crustaceans are most sensitive (LT_{50} = 1-91 hours).

Some invertebrates produce cysts or other resting bodies and these can survive long periods of anoxia (months to years).

In Newcastle, biological de-oxygenation was tested in meso-scale in 50 litres polypropylene vessels covered with black plastic bags to simulate the darkness in a ballast tank (DTR 3.2). The efficiency of the treatment was tested against three

species of zooplankton; the copepods *Acartia tonsa* and *Tisbe battagliai*, and the polychaete *Nereis virens* (nectochaete larvae). After 4-6 days of anoxia, more than 95 % of all the tested zooplankton species were dead.

Microorganisms include bacteria, microalgae (phytoplankton) and fungi. In relation to ballast water, the focus of much of the research has been on the transfer of microalgae such as dinoflagellates that can cause toxic blooms. Microalgae are primarily photo-trophic, but some species can grow heterotrophically in the dark. However, this usually requires oxygen, and most algae will not grow under dark, anoxic conditions. How long they survive is another question. In the Newcastle trials, de-oxygenation of the water had little effect on the survival of the two added species of phytoplankton; the dinoflagellate *Alexandrium tamarense* and the diatom *Thalassiosira pseudonana*. The concentration of the dinoflagellate seemed to decline slightly as a function of time, but this was most likely due to the fact that the water was incubated in darkness, and not the removal of the oxygen. For the diatom even the lack of light seemed to have little effect on the survival within the time-frame studied (up to 6 days of anoxia).

5.3 ONBOARD TESTING

The sea trials were carried out on board the car carrier M/V Don Quijote (see section 3.2). The ship left Southampton in the evening on the 20th of June and headed southwest across the Atlantic, passed to the west and within sight of the Azores, went through the "Canal de la Mona" between Puerto Rico and The Dominican Republic into the Caribbean Sea, and ended in Manzanillo on the west coast (north coast) of Panama on the 30th of June. The weather was nice and calm throughout the voyage. The testing period for the DEOX treatment was from the 21st to 28th June 2003.

Four ballast tanks were used in the study, two treated tanks: Tank no. 3 upper port (3UP) (285 m^3) and Tank no. 3 upper starboard (3US) (326 m^3), and two control tanks: Double bottom tank no. 3 port (DB3P) (513 m^3) and Double bottom tank no. 3 starboard (DB3S) (513 m^3). The ship left Southampton in the evening of June 20, and the ballast water in the tanks was exchanged for new water from the English Channel during the early hours of June 21. The control tanks were filled first (Table 5.1). The weather during the filling was nice and calm. The depth of the sea in the area was around 50-60 meters (DTR 4.7).

Table 5.1: Filling of the ballast tanks in the English Channel.

Date and time	Position	Filling of ballast tanks[1]
June 21, 01.00 a.m.	N 50 ° 26' W 001° 24'	Start DB3P and S
June 21, 02.00 a.m.	N 50 ° 21' W 001° 38'	Finished DB3P and S, start 3UP and S
June 21, 02.50 a.m.	N 50 ° 14' W 002° 01'	Finished 3UP and S

[1] S = starboard, P = port.

5.4 ADDITION OF NUTRIENTS TO THE BALLAST WATER TANKS

The nutrient solution was made on the ship from chemicals brought onboard. The composition of each batch is given in Table 5.2. Three or two batches were mixed together in 25-30 litre plastic cans. When the ballast tanks had been emptied, the nutrient solution was added to the tanks through the sounding pipe. Six batches were added to 3US, while 5 batches plus 2 litres extra were added to 3UP. The nutrient

solution was added to the tanks at 2 a.m. in the morning of the 21st of June, and the filling of the tanks with new ballast water started immediately after that.

Table 5.2: Batch composition of nutrient solution employed onboard "Don Quijote"

Compound	Producer/Supplier	Amount
Sucrose	Table sugar bought in a shop in Southampton	3.15 kg
Glucose · H_2O	Norsk medisinaldepot	1.25 kg
NH_4NO_3	Riedel-de Häen	0.60 kg
KNO_3	Riedel-de Häen	0.60 kg
$Na_2HPO_4 \cdot 2\ H_2O$	Riedel-de Häen	0.195 kg
Ship's tap water (hot)	-	4.40 litres

5.5 CONCEPT APPROVAL

The installation scheme providing a global view of the components and links with the ship installation is given on Figure 5.1 below.

The treatment takes place in the ballast water tank. The nutrient solution may either be added directly to the ballast water tank or into the ballast water pipeline at some point in the pump room or between the pump room and the ballast water tank.

The volume of nutrient solution required is approx. 1/10000 of the volume of ballast water and will therefore not significantly change the water volume after the point of addition. The pipes and pump for addition of the nutrient solution may be any existing marine equipment.

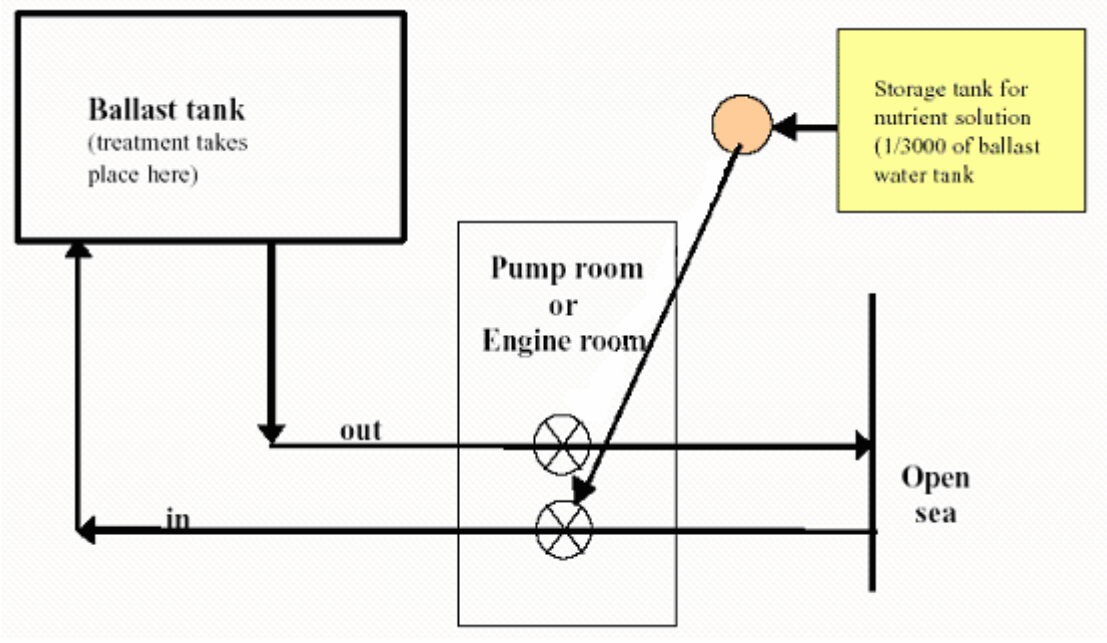


Figure 5.1: De-Oxygenation treatment diagram

The review of the defined criteria in chapter 1 leads to the following conclusions shown in Table 5.3.

The system analysis does not show any particular difficulty with respect to normal ship design and building. The biological efficiency has been proven acceptable in

laboratory. The results of the full scale onboard test present uncertainties which must be clarified. Considering the documents submitted, the system is granted with a Design Concept Approval.

Table 5.3: De-Oxygenation criteria results

Criteria	Review Results
Stability	No tank filling different than those of the operational ship loading cases. No impact on stability.
Visibility	No modification of the loading cases, so of the trim, at sea. No impact on visibility.
Longitudinal strength of the vessel	No tank filling different than those of the operational ship loading cases. No impact on the hull girder strength.
Overpressure in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of overpressure.
Liquid motions in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of sloshing.
Piping	Use of well known marine equipment on ballast piping. No increase of risk.
Risk of fire	No specific non common equipments. No increase of the risk of fire.
Material and products	Use of well known marine equipment on ballast piping. Use of nutrient but without risk for the crew.
Ballast water composition	Nutrient addition to the water. No risk for the crew. Possible increased risk of corrosion but acceptable.
Biological efficiency	Good laboratory test results. Uncertainties on results for the onboard full scale test.

To obtain the Final Concept Approval the efficiency of the on-board full scale application will have to be re-assessed and the required documents reference number 9 to 15 of Table 1.2 (see chapter 1) must be provided.

5.6 Risk and Safety Issues

Figure 5.2 shows a conceptual diagram of a biological de-oxygenation treatment system for ballast water. Ballast water is pumped into the ballast water tanks as would be done for normal operations. A nutrient solution is added to the ballast water tanks, and treatment occurs during the voyage. The system developer estimates minimum treatment time should be 5-7 days depending on the temperature. After treatment, ballast water is pumped out. The water would have a low dissolved oxygen concentration and elevated concentrations of nutrients and bacteria.

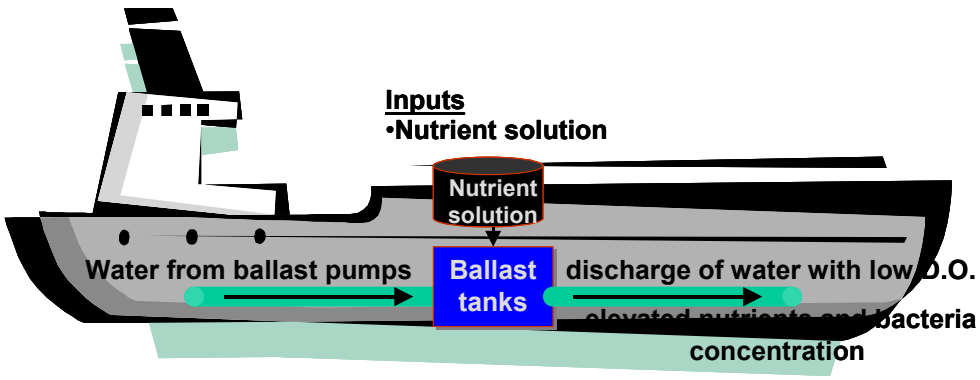


Figure 5.2: Simplified presentation of biological de-oxygenation treatment system

5.6.1 HAZARDS

As described in WP3, the most serious hazard with this method is the potential for the formation of hydrogen sulphide gas (H_2S), which is corrosive and very toxic. During the onboard testing, H_2S measurements were taken and concentrations were always below detection (less than 1 micromole/litre). Odours were noticed by the crew and sampling assistants during the onboard tests. However, it was the opinion of the system developer that the smell was more "rotten" than H_2S. It was also noted that the odours were only noticed during sampling, and not at discharge or from the closed tanks.

When oxygen is removed from ballast water by any method there is the potential for hydrogen sulphide production, as there are sulphate ions in seawater that can be converted to hydrogen sulphide by sulphur-reducing bacteria. If produced, this gas could represent a very serious health and safety hazard to the crew. H_2S is a colourless gas that is heavier than air, and can cause death at higher concentrations (loss of consciousness at 500-1000 parts per million (ppm) in air, collapse and death at 1000-2000 ppm (cited in Fischer et al., 2000)). Because hydrogen sulphide is heavier than air, if it is produced there is the potential for it to accumulate in confined spaces, such as at the bottom of tanks. The 'no observable adverse effect level' (NOAEL) of H_2S in air is between 2 and 10 ppm (Fischer et al., 2000) and even long term exposure to concentrations below 10 ppm is not thought to produce toxic effects, as it is rapidly detoxified in the body at this level.

The low oxygen content of the ballast water can also potentially be a hazard. Extra care would need to be taken with ventilating ballast tanks prior to entry for cleaning and inspection, although proper confined space entry procedures should be followed before entering any tank.

5.6.2 "WHAT-IF" ASSESSMENT

"What if" questions considered during WP3 included the following:

- What if the nutrient solution has been prepared with too much ammonium as compared to nitrate nitrogen? (would hydrogen sulphide gas be produced?)
- What if more nutrient solution than required is added to the tank?
- What if the ballast water has a higher than normal nutrient level (because it is taken on in polluted waters, for example)?
- What if there is a leak or rupture in the pipe when treated ballast water is being pumped out of the ship?
- What if the treated ballast water is left in the tanks for an extended period of time (for 6 months, for example)?
- What if H_2S gas is produced?

5.6.3 POTENTIAL RISK REDUCTION MEASURES

Some of the "what if" questions would not result in any concern. For example the system developer states that the addition of excess nutrient solution should not result in any problems. If the ballast water taken on has higher than normal nutrient levels there should not be any problems either. The nutrient solution is being optimised to prevent the formation of H_2S gas. The aim is to keep the concentration of H_2S below

1 µmol/litre, and an upper acceptable limit will be 10 µmol/litre. This corresponds to a equilibrium air concentration (at 20 °C, 1 atm) of roughly 10 ppm and 100 ppm, respectively.

Risk reduction measures to address the other "what if" questions include:

- Quality control systems for the production of the nutrient solution, and testing to ensure that concentrations of all relevant components of the solution fall within the "safe" range.
- Careful monitoring to ensure ballast water is not left in the ballast tanks after the treatment time. There is a possibility that this may lead to the formation of H_2S gas.
- Until it is certain that the production of H_2S is not a problem, H_2S gas portable gas monitors and alarms could be used adjacent to the ballast tanks undergoing treatment. Self-contained breathing apparatus and safety training could be provided to crew members that may have to respond to any incident where H_2S gas may be present. When entering empty ballast tanks that have been used for biological de-oxygenation, confined space entry procedures should be followed, including thorough ventilation of the space, use of gas detectors (both to warn for presence of H_2S and also to ensure that there is sufficient oxygen) and availability of positive-pressure self-contained breathing apparatus.

5.7 ENVIRONMENTAL IMPACTS

Data was provided by the system designer on water quality parameters measured during the test, and on the amounts of materials used. Environmental impacts resulting from the biological de-oxygenation method, based on data collected during onboard testing, are discussed below.

5.7.1 PRODUCTION PHASE

The biological de-oxygenation process requires very little equipment. The system developer (SINTEF) states that a stainless steel holding tank may be used to store the nutrient solution. The tank weight would be approximately 1 tonne.

Emissions to air resulting from production of steel were estimated. Emissions categories included gases that contribute to global warming (greenhouse theme), gases that contribute to acidification (acidification theme), and gases that contribute to the formation of tropospheric ozone (tropospheric ozone precursors theme). Table 5.4 shows the amounts of the major types of emissions according to these "themes", and also shows the equivalents totals for each of these themes.

Table 5.4: Emissions resulting from production of steel for nutrient solution storage tank

Theme	Type of Emission	Amount (kg)	Conversion Factor	Equivalent Value
Greenhouse	CO_2	992	1	992
	CH_4	2.4	23	55
	N_2O	0.006	296	2
			Total CO_2 equivalents(kg)	1049
Acidification	NO_x	1.5	1/46	0.03
	$SO_2 + SO_x$	2.5	1/32	0.08
	NH_3	0.0009	1/17	0.00

			Total Potential Acid Equivalent (kg PAE)	0.11
Tropospheric Ozone Precursors	NO_x	1.5	1.22	1.88
	CO	0.2	0.11	0.03
	CH_4	2.4	0.014	0.03
			Tropospheric Ozone Forming Potentials (kg TOFP)	1.94

5.7.2 OPERATION PHASE

The nutrient solution added to the ballast water tanks to encourage bacteria growth and oxygen consumption consisted of glucose, sucrose, ammonium nitrate fertiliser, potassium nitrate fertiliser, and monobasic sodium phosphate. Based on the amounts used in the onboard trials, quantities were estimated to treat 2000 m^3 of ballast water on a case study ship. Total amounts required over a 20-year life cycle, assuming that the ballast water is treated during 25 voyages, are shown in Table 5.5.

Table 5.5: Materials required for production of nutrient solution

Material	Amount required to treat 2000 m^3 (kg)	Amount estimated for 20-year life cycle (tonnes)
Glucose (nutrient)	42	21
Sucrose (sugar)	116	58
Ammonium nitrate (NH_4NO_3)	21	10.5
Potassium nitrate (KNO_3)	21	10.5
Monobasic Sodium Phosphate (Na_2HPO_4)	7	3.5

The estimated emissions produced from the production of the components of the nutrient solution are shown in Table 5.6. Data on the emissions for ammonium nitrate and potassium nitrate were obtained from a report by Davis and Haglund (1999) on life cycle inventory of fertiliser products used in Sweden and Western Europe. Data for western Europe was used. Data could not be obtained for monobasic sodium phosphate, so inventory information for single superphosphate was used instead (Davis and Haglund (1999)). For sucrose, summary data for Danish sugar was used (Nielsen et al., 2003). Information was only available for the greenhouse theme and for acidification. For glucose, the inventory data for sucrose was used. Glucose can also be crystallized from sugar cane and sugar beets, so it was considered that it was a reasonable approximation.

Table 5.6: Emissions resulting from production of the nutrient solution

Theme	Type of Emission	Amount (kg)	Conversion Factor	Equivalent Value
Greenhouse	CO_2	21887	1	21887
	CH_4	24.5	23	563
	N_2O	97	296	28712
	CO_2 equivalents (glucose/sucrose)	102700	1	102700
			Total CO_2 equivalents (kg)	153862
Acidification	NO_x	138	1/46	3
	$SO_2 + SO_x$	502	1/32	15.7
	NH_3	0	1/17	0.0
			Total Potential Acid Equivalent (kg PAE)	18.7
Tropospheric Ozone Precursors	NO_x	138	1.22	168
	NMVOC	22	1	22
	CO	11	0.11	1
	CH_4	24	0.014	0
			Tropospheric Ozone Forming Potentials (kg TOFP)	192

5.7.3 COMPARISON OF EMISSIONS BY LIFE CYCLE STAGE

Emissions values for both the equipment production and operations phase of the biological de-oxygenation treatment process is presented in Table 5.7. For all three categories considered the operations phase is dominant, accounting for 99% or more of emissions during the life cycle.

Table 5.7: Emissions over production and operation phase of DEOX process

Theme	Production		Operation	
	amount	% life cycle	amount	% life cycle
Greenhouse theme: Total CO_2 equivalents	1049 kg	0.7	153862 kg	99.3
Acidification: Total Potential Acid Equivalent (kg PAE)	0.11 kg	0.6	18.7 kg	99.4
Tropospheric Ozone Forming Potentials (kg TOFP)	1.94 kg	1.0	192 kg	99.0

5.7.4 DIRECT IMPACTS THROUGH DISCHARGE TO RECEIVING WATER

Discharge of water with altered quality

Information provided by SINTEF on the quality of ballast water discharged from the treatment tanks is shown in Table 5.8. The concentration in the control tanks is also shown for comparison. Both the nitrogen and phosphorus concentrations are lower than what was estimated in WP3, based on the laboratory scale tests.

Table 5.8: Water quality as measured in ballast tanks at the time of discharge

Ballast tank	Concentration (g/m^3 ballast water)					
				NH_4^+ (as N)	NO_3^- (as N)	PO_4^{2-} (as P)
	pH	D.O.	H_2S	June 28	June 28	June 28
3US	6.8 – 7.0	Approx. 0	< 1 µM/l	2.47	0.036	0.071
3UP	6.8 – 7.0	Approx. 0	< 1 µM/l	2.03	0.027	0.068
Control 1	7.9 – 8.1	80%	n.d.	<0.05	0.026	<0.005
Control 2	7.9 – 8.1	79%	n.d.	<0.05	0.024	<0.005

n.d.: No data,
µM/l: micro mole per litre
D.O.: Dissolved oxygen (% of saturation)

There are currently no guidelines for these parameters for ship discharges. The nitrogen and phosphorus concentrations are both below the EU Urban Waste Water Directive (91/271/EEC) for discharges to sensitive areas. The discharge may still potentially be a concern in waterbodies with eutrophication problems, because the nutrients and organic materials would be an additional loading. To assess this potential problem, an example calculation was carried out for hypothetical ballast water discharges to the Kattegatt area of the west coast of Sweden. It was assumed that 25% of all ballast water discharged was treated with the biological de-oxygenation method. This percentage was chosen because it is likely that not all ships will use the same ballast water treatment technology. In addition, some of the ballast water discharged may be arriving from areas within the same waterbody or region and treatment may not be necessary. The estimated nitrogen and phosphorus loadings from ballast water were compared to land based sources. This example was chosen because it is one of the few areas where both ballast water discharges and nutrient

loadings from direct land discharges are available. Table 5.9 shows results from the estimate.

Table 5.9: Comparison of Nitrogen and Phosphorus loadings from hypothetical BW sources with land-based sources

Discharge Source to Kattegatt	Annual Discharge (tonnes)	Phosphorus Loading, as PO_4-P (kt)	Nitrogen Loading, as Total N (kt)
Ballast Water Loading, assuming 25% of ballast water discharged is treated using biological de-oxygenation method	7.8 million	0.000137	0.0049
Annual Sewage and Industrial Discharge	173 000 million	0.02	2.1

The results of the estimate show that potential increased loading from ballast water would be very small: in the order of 0.2% for nitrogen, and 0.7% for phosphorus.

Other potential discharges to water resulting from the biological de-oxygenation method may result if there is increased corrosion in the ballast tanks. If the treatment method causes increased corrosion, there may be elevated metals levels (iron from the steel tanks, zinc and/or aluminium from sacrificial anodes) in the ballast water to be discharged. The concentrations of metals would depend on the condition of the coating of the ballast water tanks.

Impact from surviving non-indigenous organisms
There would be an increased concentration of bacteria. During the onboard testing, the concentration of bacteria in the treated ballast water was about 10 times higher than that in the control tanks (1 million cfu/ml compared to 100000 cfu/m). Results of the testing to determine phytoplankton survivability were inconclusive (DTR 4.3). However, it would appear that not all phytoplankton are inactivated by low dissolved oxygen. Also, some resting cysts and resting stages of organisms can tolerate low dissolved oxygen levels.

Spill Potential
The case ship, a maximum of 2000 litres of nutrient solution would be stored onboard the ship. There is a potential for this to be accidentally spilled during loading or in the event of damage to the ship and the tank. The nutrient solution would cause problems in receiving waters that are eutrophic, as it would contribute to increased productivity. The problem would be short term and would not have lasting effects on the environment.

5.8 ECONOMIC ASPECTS

5.8.1 CAPITAL COSTS

A preliminary estimation of equipment and installation cost of a tank with a holding capacity of 2,000 litre nutrient solution is € 50,000. This tank size will be sufficient for the treatment of 2,000 m^3 per trip. There are no testing or commissioning costs expected.

5.8.2 OPERATIONAL COSTS

Treating ballast water by biological oxygen removal does require a negligible amount of energy use (only a short time use of small pumps). Only the ballast water pumps to pump the water in and out of the ship use energy, i.e. 200 kWh per trip.

Table 5.10: Total energy use

Total energy use		Unit
energy requirement per trip	200	kWh/trip
kWh > MJ (electricity)	720	MJ (electricity)
MJ (electricity) > MJ (diesel)	2,400	MJ (diesel)
MJ >kg (diesel)	56	kg (diesel)
energy costs per trip (diesel)	22.59	€/trip
total energy costs per year (diesel)	**1,129.41**	**€/year**

The *consumables* used for treatment are a nutrient solution. Per 10 m^3 ballast water, 1 litre nutrient solution is needed, i.e. 200 litres per trip. This cost about € 0.015/m^3 ballast water, i.e. € 30 per trip or € 1,500 per year.

Handling the system will mainly be in closed systems. It is expected that *personnel* involvement for the operation of the system is negligible. Estimations of *maintenance costs* related to regular or incidental maintenance (materials and personnel involved) are not available yet and therefore not included in the calculations.

Training and *management costs*, like certification costs and development of safety manuals, are not expected.

5.8.3 COST AND BENEFITS ASPECTS

As the ballast water discharged after treatment will contain an increased content of bacteria and other organic material (a rough estimate is 10 mg per litre ballast water) increased tank cleaning costs can be expected. At this time no estimation of the costs is available. The nutrient solution should be less corrosive than seawater; this might affect the cost of corrosion control. No estimation on the cost is available. There is no delay in harbour or during the trip expected related to the ballast water treatment. No extra maintenance costs are expected. A preliminary estimation of the size of the equipment required on-board is 1 square metre, 2.12 metres high. The equipment has a weight of 2.6 tonnes (if completely filled). It is expected that installation of the system will not result in cargo space reduction.

The next table (Table 5.11) shows detailed calculation results for de-oxygenation.

Table 5.11: De-oxygenation economic results

Cost type	Description	€ (euro)	Comments
Capital Costs			
Investment	Investment costs	50,000	2,000 litre tank
Installation	installation costs	0	included in investment costs
Testing	testing costs	0	
Commissioning	commissioning costs	0	
	total investment	**50,000**	**€**
Depreciation factors	depreciation period	10	years
	interest rate	8%	

Cost type	Description	€ (euro)	Comments
	annual capital costs	**7,451**	**€/year**
Operational Costs		**€/year**	
Personnel	personnel during treatment	p.m.	negligible
Energy	energy (diesel)	1,129	€/year
Additives	additives use	1,500	
Maintenance	TAM (maintenance euro)	0	
	additional maintenance	0	
Training and management	training costs	75	no costs expected
	certification costs	0	no costs expected
	health and safety issues	0	
Cost and benefits	tank cleaning costs	0	increased sediments in tank (cost estimates not available)
	corrosion costs	0	no influence
	costs of delay	0	no delay
	increased maintenance	0	
	loss of cargo space	0	no loss of cargo space
	annual operational costs	**2,704**	**€/year**
Total annual costs		**10,156**	**€/year**
Costs per treated m^3 ballast water	**50 trips / 100,000 m^3**	**0.1016**	**€/treated m^3 BW**

5.9 PROCESS ASSESSMENT

In order to evaluate the technical performance of the process and the biological killing efficiency, a number of samples were taken from the ballast tanks during the onboard trial. Samples were taken on the 21st, 24th, 26th and 28th of June by pumping water from the ballast tanks via the fire pump system to the upper deck. In addition, small samples of about 1 litre were taken through the sounding pipe from 3US and 3UP on the 22nd, 23rd, 25th and 27th. These samples were too small to be used for analysis of zooplankton, but were used for bacterial and chemical analyses.

After sampling on the 24th it became clear that too little water had been flushed through the fire pump system between the samples, and it was therefore not possible to determine from which ballast tank the water in the samples originated. These samples were therefore excluded from further analysis. The samples taken on the 21st would also have been affected by this, as we used the same procedure as on the 24th, but because the water on the first day essentially should have been the same in all tanks as well as in the main pipelines, we still consider the values useful.

On the 26th and 28th, on-site pH measurements were used to ensure that the water was from the correct ballast tank. The pH in the treated tanks were considerably lower than in the control tanks (see section 5.9.5), and by altering the sampling between treated and non-treated tanks and measuring pH at intervals until it stabilized, it was ensured that the water was from the intended ballast tank.

5.9.1 TEMPERATURE

The temperature in the ballast water increased during the voyage (Figure 5.3). The temperature immediately after the water was pumped into the tanks was not recorded, but was probably between 16 and 18 ºC, and increased to an estimated 28-29 ºC after seven days. The temperature increase is probably mainly due to the fact that the ship sailed into steadily warmer waters.

The large temperature difference between the samples taken through the sounding pipe and the samples taken via the fire pump, particularly in the beginning, shows that when samples were taken via the fire pump the water was heated during the transport from the ballast tanks to the sampling point on the upper deck. As the temperature in the ballast tanks increased during the voyage, the increase during pumping became smaller, probably because the temperature difference between the water in the ballast tanks and the rest of the ship became smaller.

In all previous laboratory studies, including the meso-scale experiment in Newcastle, the temperature was kept relatively constant throughout the experiment.

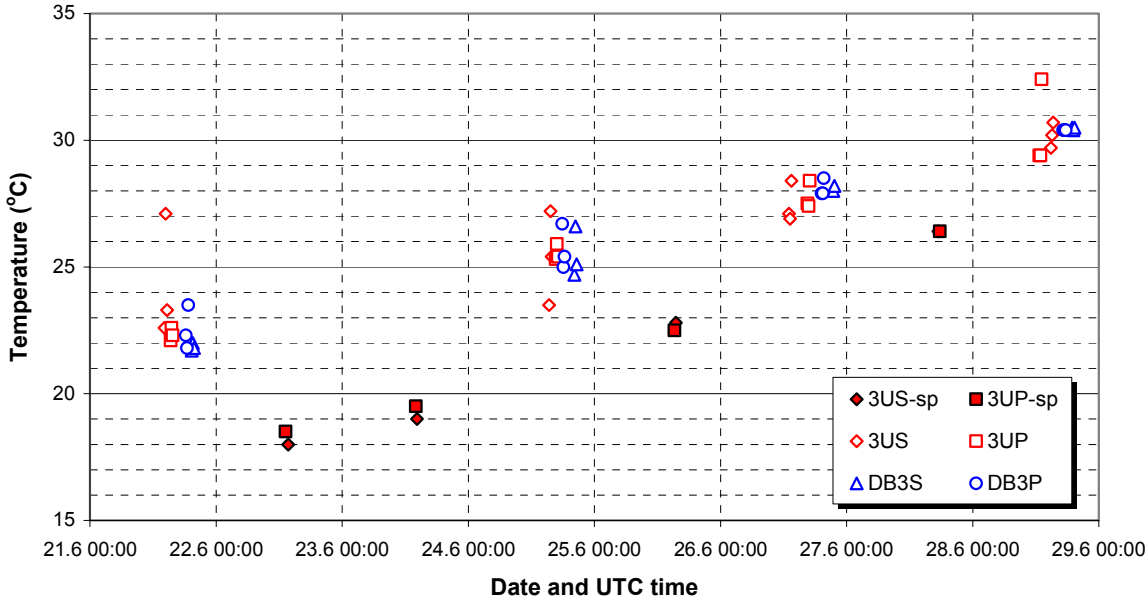


Figure 5.3: Temperature measurement for water samples taken by sounding pipe and by fire pump

5.9.2 Mineral Nutrients in Treated Ballast Water

The nutrient solution added to the ballast water (see section 5.4) contained glucose, sucrose, ammonium, nitrate and phosphate (Table 5.12). At the end of the trial, the treated tanks contained slightly more ammonium than added at the start (105-128 % of the original addition), less than 1 % of the original addition of nitrate, and 10-11 % of the original addition of phosphate. The sugar content of the ballast water at the end of the trial was not analysed, but based on previous studies nothing is left at the end of a DEOX treatment. The fact that there was no increase in the bacterial concentration after the first two days, despite that the water contained available N- and P-sources, also indicates that all the added sugar had been consumed.

The difference between the added mineral nutrients and the observed concentration at the end of the study is 2.9-3.4 g N per m^3 and 0.58 g P per m^3. The difference has probably been built into biomass, mainly bacteria. If we assume 12 % (of dry weight) N and 2 % P in bacteria, the missing N corresponds to 24-28 g bacteria (dry weight) per m^3 and the missing P corresponds to 29 g bacteria per m^3. Assuming a bacterial weight of $2\text{-}3 \cdot 10^{-13}$ g/cell, the measured maximum bacterial concentration in the treated water, $6 \cdot 10^7$ GU/ml (see below), corresponds to 12-18 g bacteria per m^3. This

is a minimum value because one growth unit may consist of more than one bacterial cell.

Table 5.12: Concentration of nutrient solution added to BW

Ballast tank	Concentration (g/m^3 ballast water)									
	Glucose[1]		Sucrose[1]		NH_4^+ (as N)		NO_3^- (as N)		PO_4^{2-} (as P)	
	Added on the 21st	Conc. on the 28th	Added on the 21st	Conc. on the 28th	Added on the 21st	Conc. on the 28th	Added on the 21st	Conc. on the 28th	Added on the 21st	Conc. on the 28th
3US	20.9	n.a.	58.0	n.a.	1.93	2.47	3.46	0.036	0.65	0.071
3UP	20.9	n.a.	58.1	n.a.	1.94	2.03	3.47	0.027	0.65	0.068
DB3S	0	n.a.	0	n.a.	0	<0.05	0	0.026	0	<0.005
DB3P	0	n.a.	0	n.a.	0	<0.05	0	0.024	0	<0.005

n.a. = not analysed
[1] The concentration of glucose and sucrose in the ballast water on the 28th was not determined, but previous studies have shown that in treated water at this stage the concentration is less than 1 g/m^3.

The increase in the concentration of ammonium relative to the addition at the start is probably mainly due to denitrification. Under anoxic conditions, bacteria may convert nitrate to nitrite, which may then either be converted to ammonia, or further reduced to nitric oxide, nitrous oxide, and finally nitrogen gas. In addition, decomposing organic material may yield ammonium. Under anoxic, carbon limited conditions, ammonium will be relatively stable and tend to accumulate. Nitrate reduced to nitrogen gas will be lost from the system.

In conclusion, the discharged water contained around 2-2.5 g N/m^3 as ammonium and a similar amount of organic N in bacteria and other organisms. The concentration of phosphate (as P) was around 70 mg/m^3, while the rest of the added P, around 0.6 g/m^3, must have been discharged as organic P in biomass.

5.9.3 CONCENTRATION OF VIABLE BACTERIA

The concentration of viable bacteria in the treated tanks increased, as expected, rapidly, from around $1 \cdot 10^4$ GU (growth units)/ml a few hours after filling of the tanks to around $6 \cdot 10^7$ GU/ml after about 48 hours (Figure 5.4). This is the same level as in the meso-scale experiments in Newcastle (DTR 3.2). However, whereas the concentration remained at this level for the rest of the study (up to 7 days) in the Newcastle experiments, the concentration of viable bacteria in the treated ballast tanks started to decline after about 5 days, and ended at a level of around $8 \cdot 10^5$ GU/ml at the end of the experiment. The reason for this decrease is not known. It may be that the bacterial flora started to shift towards obligate anaerobic bacteria, i.e. the aerobic and facultative anaerobic bacteria started to die and were replaced by obligate anaerobic bacteria, which would not be registered by the applied analytical method. However, in earlier laboratory experiments obligate anaerobic have only constituted a small fraction of the flora. Another possible explanation for the decrease is that the bacteria started to aggregate. This has been observed in some laboratory experiments, where the optical density sometimes decreased upon extended incubation. The MPN-method measure viable units that may consist of one or more bacterial cells and aggregation will lead to an apparent decrease in the bacterial concentration. A third possible explanation for the decrease is predation by facultative or obligate anaerobic protozoa

that increased in the ballast water in response to the increased concentration of bacteria.

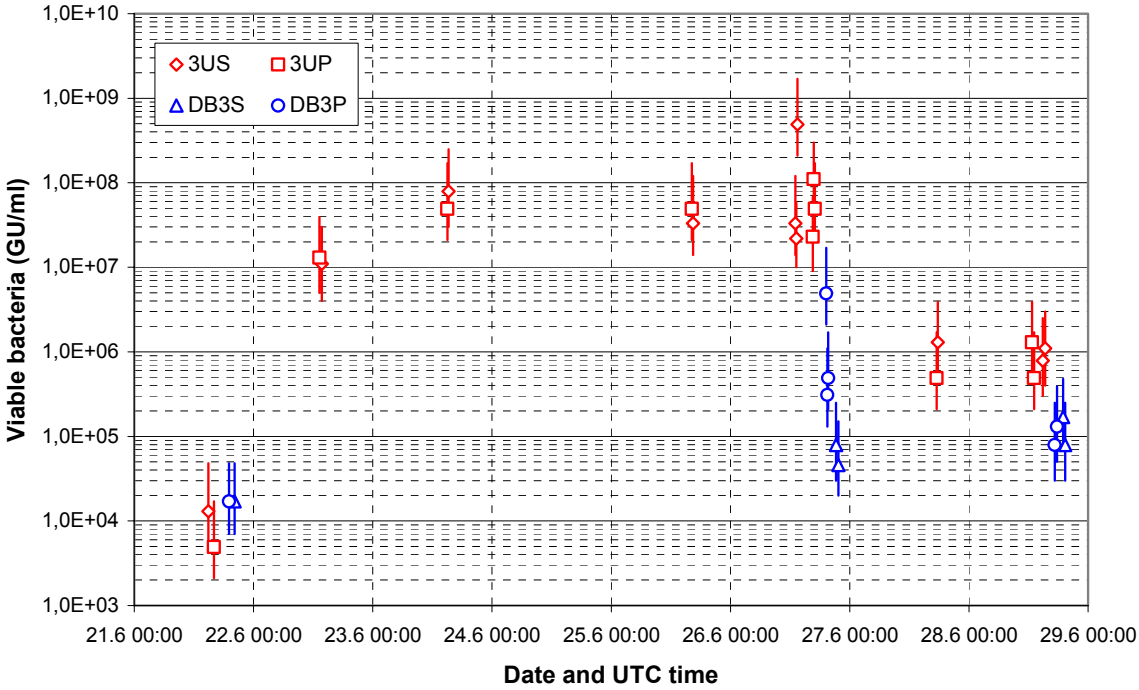


Figure 5.4: Concentration of viable bacteria in the ballast tanks
The control tanks were filled with new seawater at 2 a.m. on the 21st of June and the treated tanks were filled at 3 a.m. The samples on the 22nd, 23rd, 25th and 27th were taken via the sounding pipe, the rest via the fire pump.

The bacterial concentration also increased in the control tanks during the study, but considerably less than in the treated tanks. From a starting point of around $1 \cdot 10^4$ GU/ml it increased about 10 times to around $1 \cdot 10^5$ GU/ml at the end of the study. The extraordinary high concentration of $5 \cdot 10^6$ GU/ml in one of the control samples from DB3P on the 26th, is probably due to contamination with water from the previous sampling of the treated tanks.

The reason for the increase in the bacterial concentration in the control tanks is not known, but other analyses (see section 5.10.1) indicate that a considerable fraction of the zooplankton died in the control tanks during the voyage. Their death and degradation would release nutrients that could be utilized by bacteria.

5.9.4 DISSOLVED OXYGEN

The concentration of dissolved oxygen (D.O.)in the ballast water was determined with an oxygen electrode in one litre water samples withdrawn from the ballast tanks. Contamination of the samples with oxygen during sampling was unavoidable, but was expected to be low and of little consequence for the overall evaluation. However, the results (Table 5.13) show an unexpected high level of dissolved oxygen in the water samples, with three notable exceptions, both samples on the last day (28th) and the sample from 3UP on the 26th. Thus, either the contamination of the water samples during sampling was higher than expected, or the ballast water in the treated tanks did not become anoxic until the last day.

Table 5.13: Measured concentration of D.O. in water samples taken from the ballast tanks

Sample date	Ballast tank			
	3US	3UP	DB3S	DB3P
	Measured dissolved O_2 (%)			
23.06.2003	17	30	-	-
25.06.2003	20	26	-	-
26.06.2003	31	5[A]	88	92
27.06.2003	22	31	-	-
28.06.2003	0	0	80	79

[A]Incubated for 2 hours before reading.

When an oxygen electrode is inserted into a water sample, it takes some time before the reading stabilises. Normally, the reading decreases rapidly at first and then slowly levels out at the dissolved oxygen concentration in the sample. The reading was therefore normally recorded after 0.5-1 hour, when the reading seemed to have stabilised. On the 26th the electrode was, by accident, left in the water bottle for 2 hours before the reading was recorded, and the result may indicate that although the reading appeared to have stabilised after 0.5-1 hour, it was still slowly declining. On the 28th, the readings in both water samples declined rapidly and reached zero after 1 hour in the sample from 3UP, and 2.5 hours in the sample from 3US. In these samples the readings were clearly decreasing until they reached zero. We may therefore be very confident that the ballast water in the treated tanks was anoxic on the last day of the study, but it is not possible to conclude from the analyses whether or not the ballast water in the treated tanks was anoxic before the last day. Based on previous laboratory studies, the treated water was expected to become anoxic after around 30 hours.

5.9.5 pH

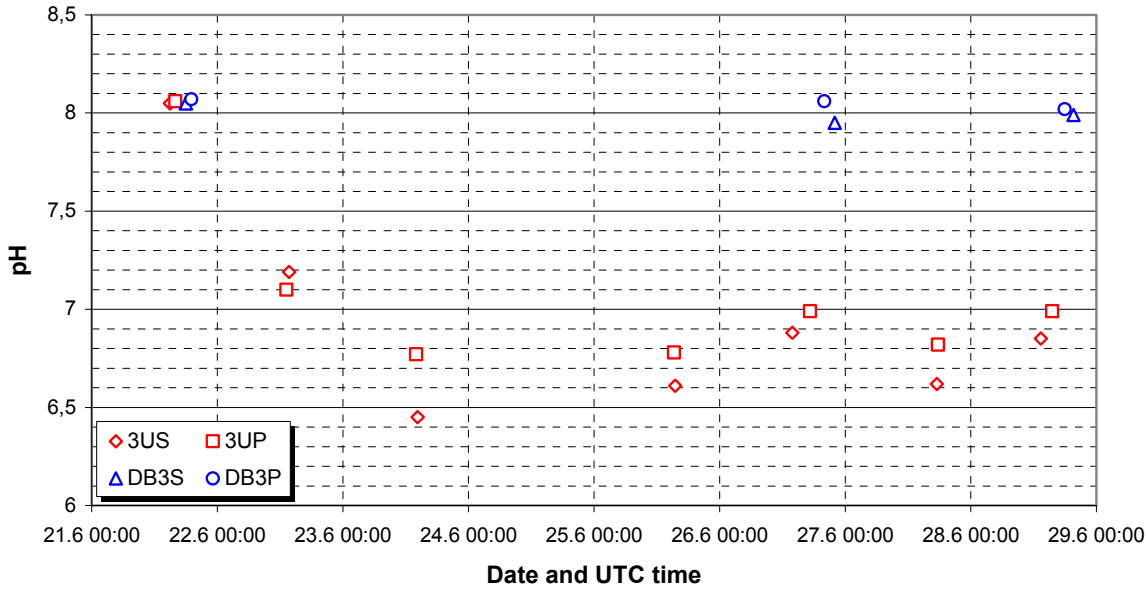


Figure 5.5: pH in the treated and control tanks as a function of time.
The control tanks were filled with seawater at 2 a.m. on the 21st of June, while the treated tanks were filled with seawater at 3 a.m. The samples on 22nd, 23rd, 25th and 27th were taken through the sounding pipe, the rest via the fire pump.

The pH in most surface seawater in equilibrium with the atmosphere is 8.2 ± 0.1 (Millero & Sohn, 1992). The bacterial growth in the treated tanks, as expected, lead to a decrease in pH, while it remained constant in the control tanks (Figure 5.5). The decrease was somewhat lower than observed in previous laboratory experiments, where pH normally decreased to between 6 and 6.5, but comparable to the pH decrease in the meso-scale studies in Newcastle. Both in the laboratory experiments and the meso-scale studies in Newcastle pH remained relatively constant after the initial decrease, but in the treated tanks onboard Don Quijote pH increased slightly after the initial decrease.

5.9.6 HYDROGEN SULPHIDE

When seawater becomes anoxic, sulphate-reducing bacteria in the water may start to reduce sulphate in the seawater to hydrogen sulphide (H_2S), which is a corrosive and extremely toxic gas. However, this process can be controlled by adding nitrate to the water, and the added nutrient solution was composed to minimise H_2S formation.

The water from the treated tanks started to smell after some days, but in the opinion of the system developer, it was more of a generally rotten smell, than a typical H_2S smell. No significant amounts of H_2S were detected in any of the analysed samples. Because the analyses were performed under field conditions, an exact concentration could not be determined, but it was well below 1 μmol per litre.

5.10 BIOLOGICAL ASSESSMENT

The aim of the biological assessment was to evaluate the killing efficiency of the DEOX process during the onboard trial.

5.10.1 ZOOPLANKTON RESULTS

A large number of different species and taxa were found in the ballast tank samples, but copepods (crustaceans of the subclass *Copepoda*) and nauplii (a larval form of many crustaceans, usually the first stage of development after leaving the egg) dominated and constituted 38.5 and 59.9 %, respectively, of the total numbers of identified zooplankton in the samples. The samples (3 x 1 tonne) were analysed with respect to total concentration of zooplankton and, by a staining technique, for the fraction that was alive at the time of sampling.

5.10.1.1 MORTALITY

Surprisingly, in the samples taken 12-18 hours after the new seawater had been pumped into the ballast tanks, 70-90 % of the copepods and nauplii were already dead, both in the samples from the treated and the control tanks (Figure 5.6). In the control tanks, 20-30 % of the copepods and nauplii disappeared daily, and if we assume that it took about a day from the organisms died until they disappeared due to degradation, settlement, or otherwise, an observed mortality[6] of 20-30 % in the first samples could be possible. An observed mortality of as high as 70-90 % must be due to factors during sampling: most likely the pumping of the ballast water from the ballast tanks via the fire pump system to the sampling point. When water passes through a pump, organisms in the water will risk damage due to the moving parts of the pump and pressure fluctuations. The latter may have been especially strong in the case of the fire

[6] Observed mortality = 100 % x (number of dead zooplankton / total sum of zooplankton in the sample)

pump, which had to lift the water from the ballast tanks and 10-20 meters to the upper deck. The ship's ballast pumps are much larger than the fire pump, which should reduce the risk of organisms hitting moving parts, and in addition the ballast pumps do not have to pump the water against a high backpressure. However, the ballast pumps will also probably kill a fraction of the zooplankton passing through them, and it may be possible to improve the killing rate by selecting the right pump.

The mortality was also high in later samples from both the treated and control tanks (Figure 5.7), and this also indicates that the fire pump is mainly to blame.

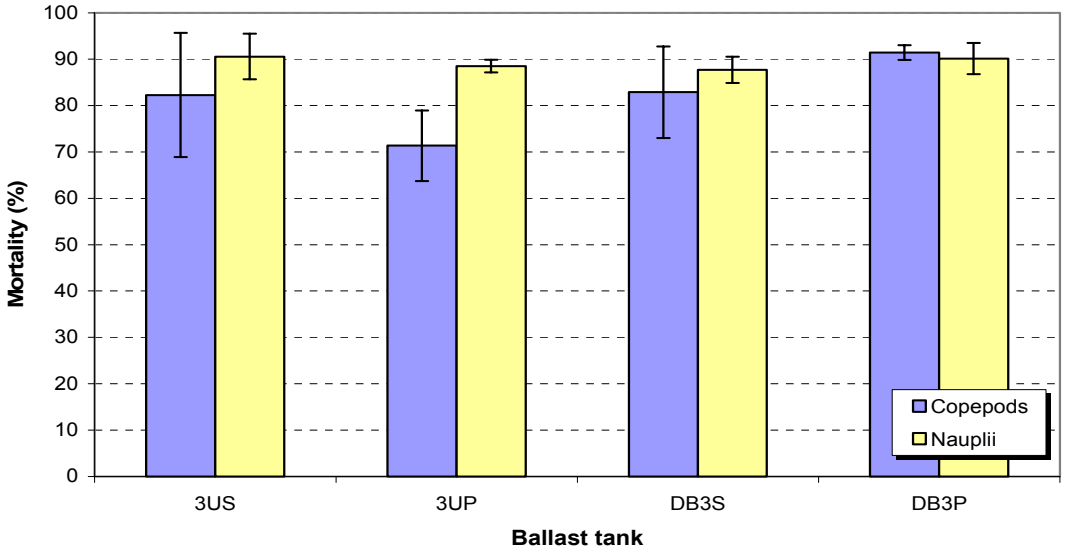


Figure 5.6: Observed mortality in samples collected after 12-18 hours
The results are the average of three parallels and standard deviations are indicated.

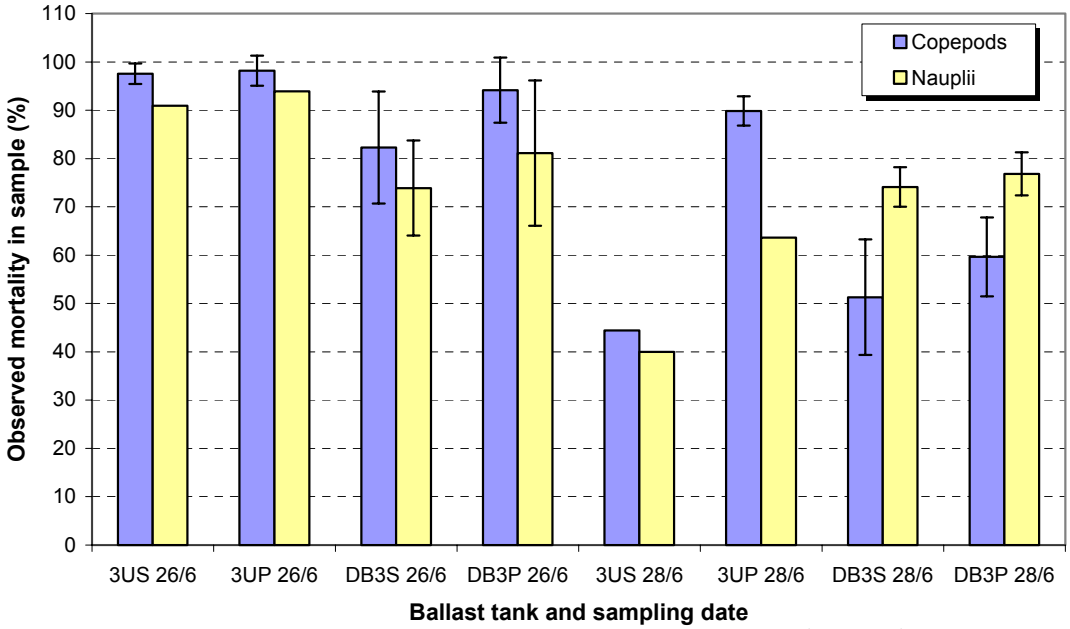


Figure 5.7: Observed mortality in samples collected on the 26th and 28th
The standard deviation is indicated in those cases where the total number of copepods or nauplii, both live and dead, in 3 tonnes of ballast water exceeded 100 individuals. In these cases the mortality rate was calculated for each of the three one tonne parallels, and the average ± standard deviation is shown in the figure. If the total number of individuals was less than 100, the mortality rate was calculated by combining the results from all three parallels.

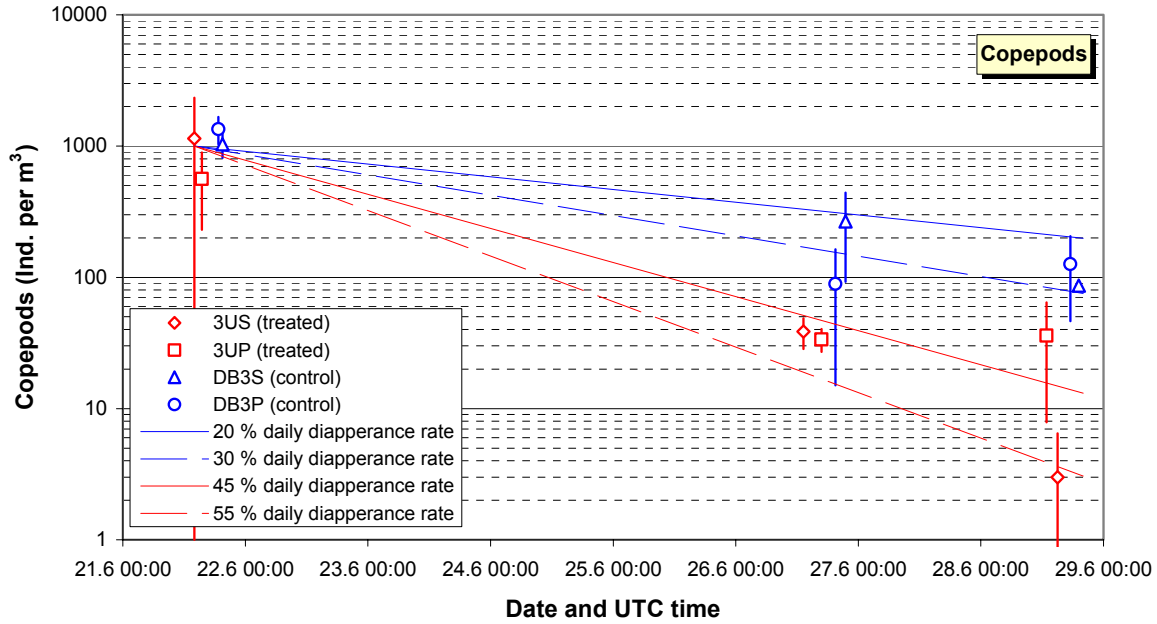
5.10.1.2 CONCENTRATION

Because of the unforeseen killing effect of the fire pump, it is difficult to evaluate the treatment by comparing mortality rates. Instead, we have to base our conclusions on the concentration of zooplankton in the ballast water. The concentration decreased during the process both in the treated and the control tanks, but the decrease was more rapid in the treated tanks (Figure 5.8). After 5 and 7 days the concentrations of both copepods and nauplii in the treated water were significantly lower (Student's t test, $p<0.001$) than in the water from the control tanks.

When individuals in a population die due to a treatment, a logarithmic decrease in the number of survivors with increasing treatment time is a reasonable first assumption. If we assume that the copepods and nauplii disappeared because they died, which is by no means the only possible explanation, the disappearance rate in the control tanks seems to be in the range of 20-30 % of the population per day for both copepods and nauplii; while in the treated tanks it seems to be 45-55 % per day for copepods and 50-65 % per day for nauplii (Figure 5.8). However, it is likely that for the first 1-2 days, before the oxygen concentration in the treated tanks became too low, the disappearance rate in the treated tanks was comparable to the disappearance rate in the control tanks, and therefore that the disappearance rate once the water became anoxic was considerably higher than the overall rate estimated in Figure 5.8.

Copepods and nauplii may disappear from the ballast water samples because they die and settle on the bottom or are degraded by their own enzymes and/or bacteria in the water. In the treated tanks, the bacterial concentration was about 1000 times higher than in the control tanks, and it is likely that the bacterial degradation of zooplankton in the treated tanks was more rapid than in the control tanks. The samples were pumped out from the ballast tanks from sampling points close to the bottom, and sedimentation should therefore tend to increase the concentration of organisms in the samples, although stringer decks in the ballast tank would catch some of the settling organisms and prevent them from reaching the bottom of the tank. Because of the ship's movements, the water would have been moving in the ballast tanks. Particularly towards the end of the study, when several tens of tonnes of water had been removed from the tanks due to sampling, it is likely that there was considerable movement and mixing in the ballast tanks and this may have prevented significant settling during the study.

The zooplankton did not have to die in order to disappear from the samples. The same decline in the samples would have been observed if the copepods and nauplii rather than swimming freely in the water, started to cling to structures in the ballast tanks, or accumulate towards the water surface, i.e. far away from the sampling point. In the treated tanks in particular, the zooplankton may have responded to lack of oxygen by swimming towards the surface. On the other hand, we know from laboratory experiments (DTR 3.2) and the literature (DTR 2.5, for a review) that zooplankton dies under anoxic conditions, and dead zooplankton are likely to sink towards the bottom, or if the mixing is strong, drift with the current until they degrade.



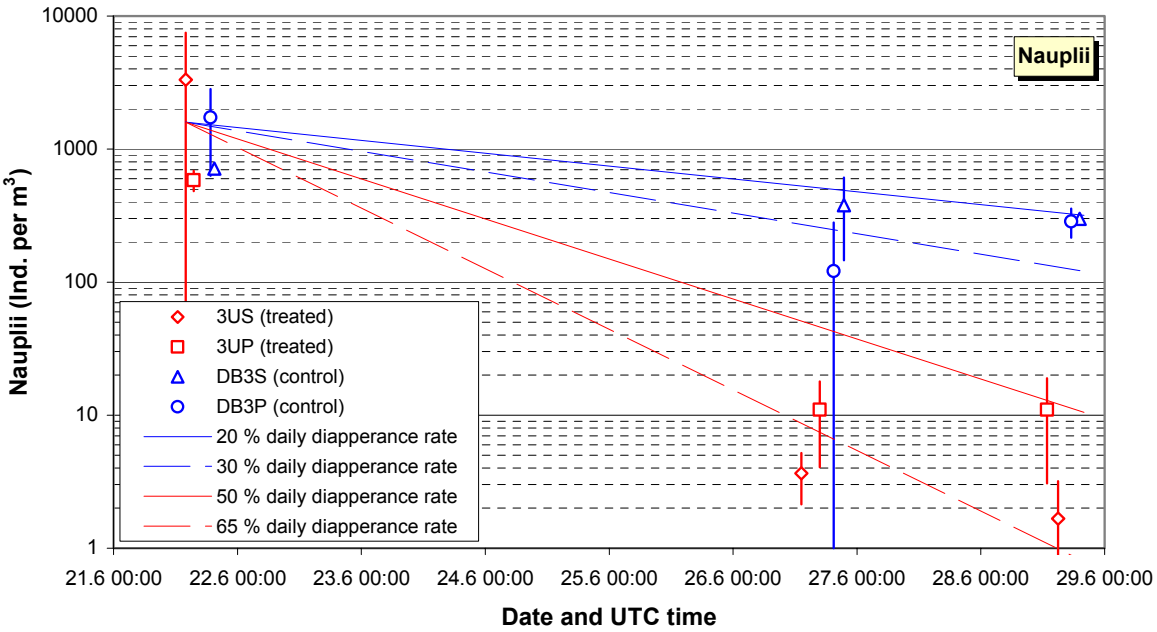


Figure 5.8: Concentration of copepods and nauplii in the BW samples
The control tanks were filled with new seawater at 2 a.m. on the 21st of June, while the treated tanks were filled at 3 a.m. The disappearance rates indicated in the figures are based on the assumption that a given percentage of the zooplankton individuals in the ballast tanks disappears every day. The average concentration in the samples on the 21st is used as starting level.

5.10.1.3 Comparison with IMO Standards

Figure 5.9 shows the concentration of live zooplankton per m^3 in the samples collected during the DEOX treatment. This treatment achieved the IMO standard (i.e. <10 viable organisms ≥ 50µm) after 5 and 7 days in the treated tanks (3US and 3UP).

On the 21st June, the number of live, i.e. viable, organisms was significantly higher compared to the other days (three-way nested ANOVA, $p<0.001$). More live

organisms were found in the samples from the control tanks than in the treated ones (three-way nested ANOVA, $p<0.001$).

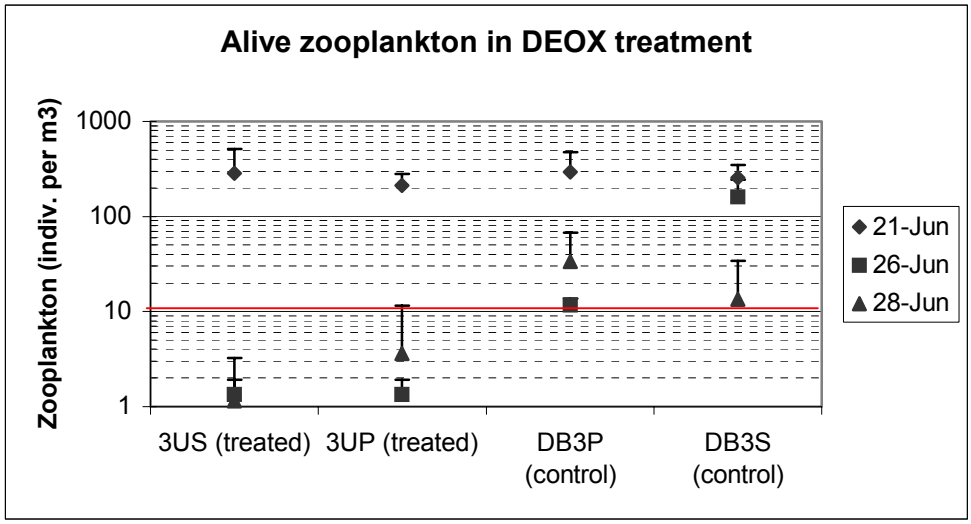


Figure 5.9: Concentration of viable zooplankton in the samples
Note: the red line indicates the IMO limit of 10 viable organisms per m^3 greater than 50µm.

5.10.2 PHYTOPLANKTON RESULTS

The fate of the phytoplankton in the ballast tanks was assessed by analysis of chlorophyll a and phaeophytin, and by direct count of phytoplankton cells. The latter was restricted to dinophyceae (dinoflagellates) and bacillariophyceae (diatoms).

5.10.2.1 CHLOROPHYLL A AND PHAEOPHYTIN

Chlorophyll *a* is the primary photosynthetic pigment in phytoplankton, and a reduction in the concentration of chlorophyll *a* after treatment would indicate that the treatment had reduced the phytoplankton biomass. Phaeophytin is a degradation product of chlorophyll *a*, but also a component of the photosynthetic system and will therefore always be present. However, an increase in the ratio of phaeophytin to chlorophyll *a* indicates that degradation products are becoming an increasing part of the pigment pool and thus that the population is not healthy.

In the treated tanks, the concentration of chlorophyll *a* seemed to increase the first days after the filling of the tanks (Figure 5.10). The reason for this is not known. Among microalgae a common cellular response to decreasing light intensity is to increase chlorophyll *a* and other light-harvesting pigments (Hu, 2004), and it may be this effect that was observed. In contrast to the control tanks, the ballast water in the treated tanks had a large surplus of easily available mineral nutrients (N, P) and could support a much higher production rate than the water in the control tanks. After a day or two the phytoplankton cells run out of intracellularly stored carbon reserves (lipids, carbohydrates) and the pigment production ceased. Alternatively, the access to sugar and nutrients may have allowed heterotrophic growth of the phytoplankton. However, most microalgae are obligate photoautothrophs (Grobbelaar, 2004). A third possibility is that the seawater pumped into the treated tanks contained more phytoplankton than the water pumped into the control tanks. However, the cell counts do not indicate more phytoplankton in the treated tanks than the controls from start (Figure 5.11).

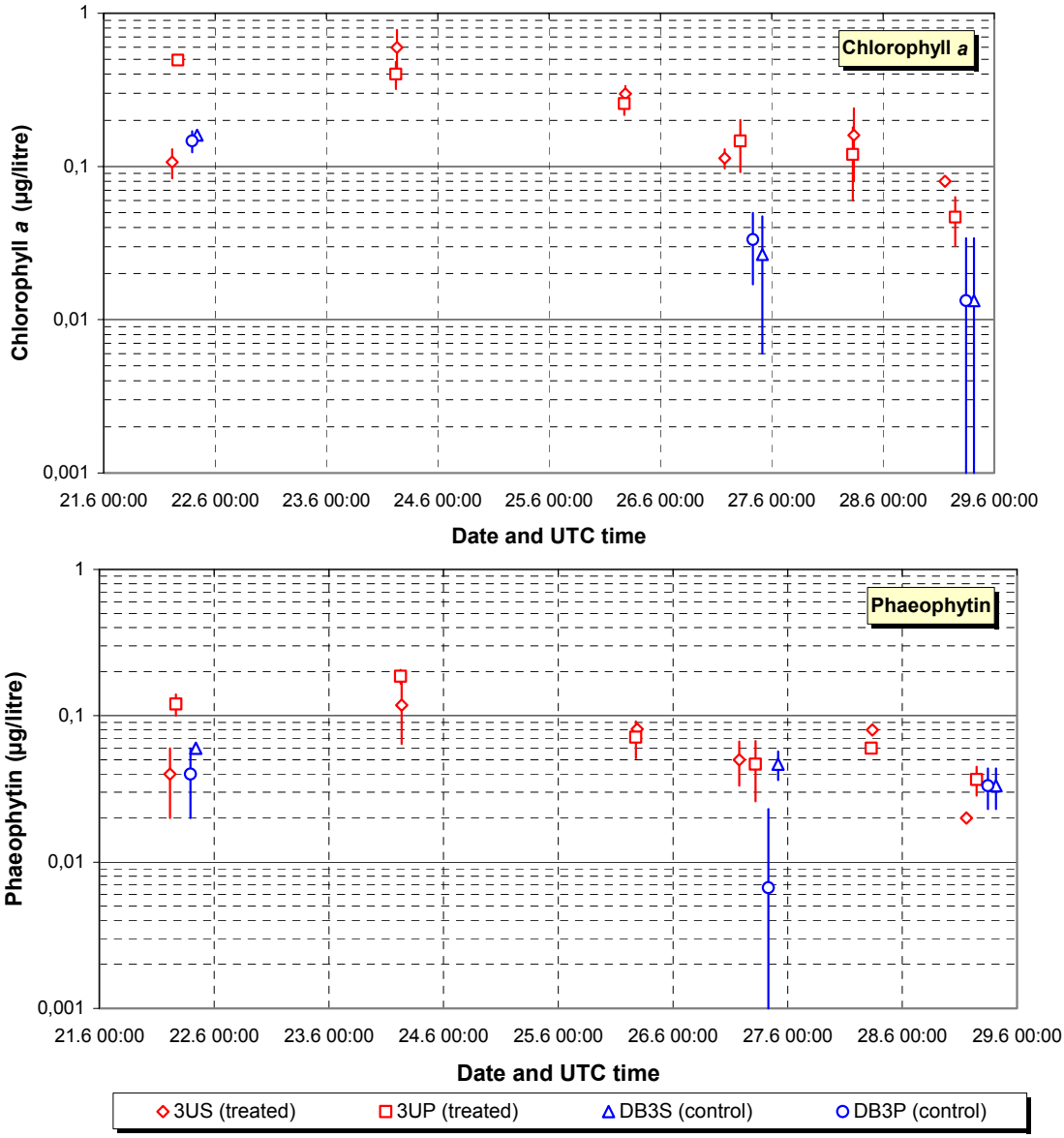


Figure 5.10: Chlorophyll *a* and phaeophytin from the treated and control tanks
The control tanks were filled with seawater at 2 a.m. on the 21st of June, while the treated tanks were filled at 3 a.m. The results are the average of 1-6 parallels, and standard deviations are indicated. The samples on the 23rd, 25th and 27th were taken via the sounding pipe, the others via the fire pump.

In the control tanks, the concentration of chlorophyll *a* seemed to remain relatively constant the first days after the filling of the tanks, but because we lost the samples on the 24th, it is not possible to draw a firm conclusion.

After a few days, the concentration of chlorophyll *a* started to decrease. The concentration was in this phase reduced by a factor of two approximately every 1.5 days, both in the treated and the control tanks.

The concentration of phaeophytin remained relatively constant in the control tanks throughout the study (Figure 5.10). The ratio of phaeophytin to chlorophyll *a* increased from about 0.3 on day 1 to about 2.5 on day 7 (Figure 5.12), indicating an increase in degradation pigments in the phytoplankton population in the control tanks.

In the treated tanks, the concentration of both phaeophytin and chlorophyll *a*, seemed to increase initially, before they started to decline. The ratio of phaeophytin to chlorophyll *a* increased only slightly from about 0.3 on day 1 to about 0.5 on day 7. In the meso-scale studies at Newcastle, the ratio of phaeophytin to chlorophyll *a* was 0.2-0.3 throughout the study, both in treated and untreated water (DTR 3.2).

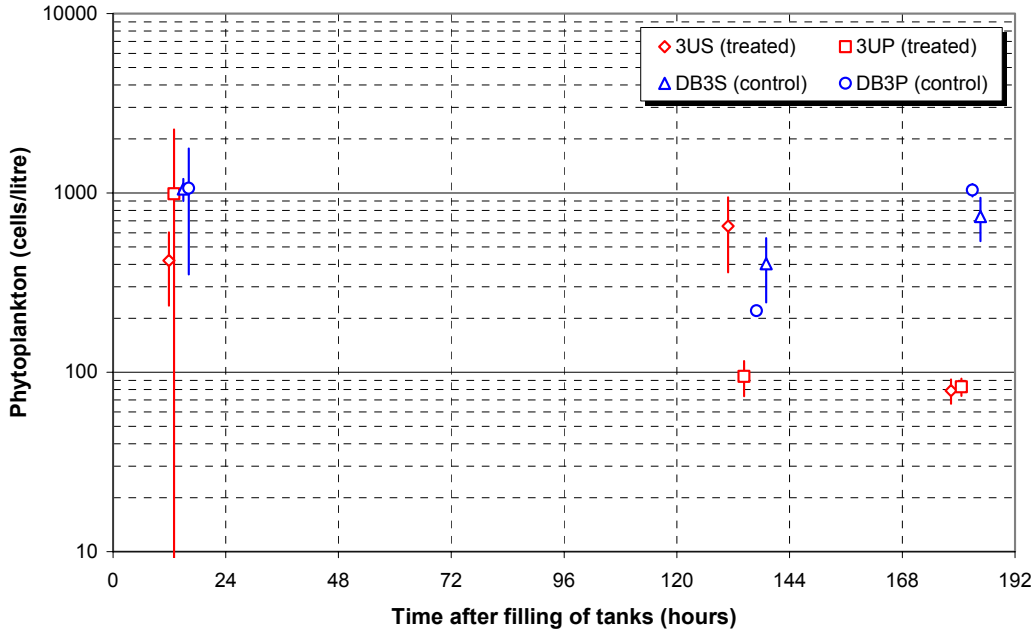


Figure 5.11: Concentration of counted phytoplankton cells
For comparison, the most stringent of the suggested IMO standards require that discharged ballast water must contain no more than 1000 viable phytoplankton cells per litre. All samples were taken via the fire pump.

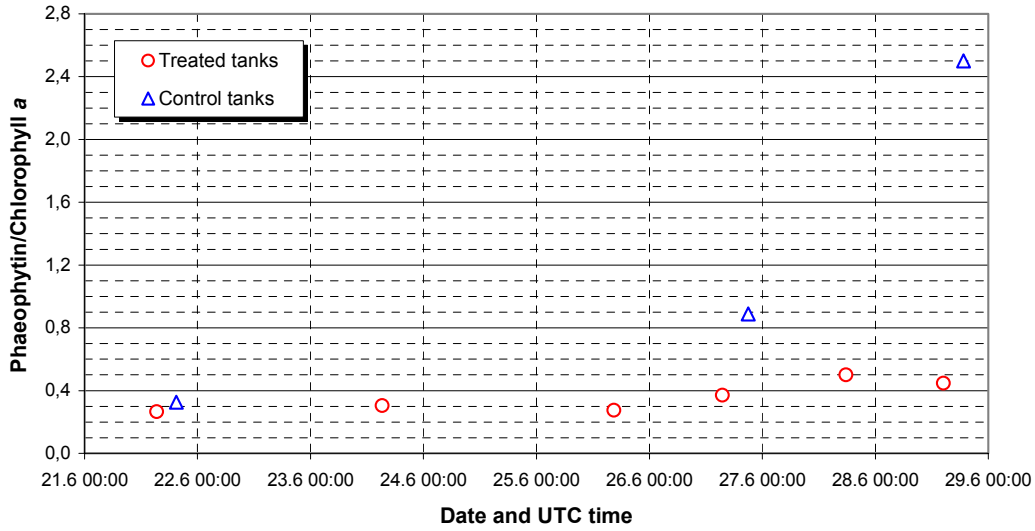


Figure 5.12: Phaeophytin relative to chlorophyll *a* in samples
The figure shows the sum of the phaeophytin contents in all samples from the sampling day from the treated tanks and the control tanks, divided by the sum of chlorophyll a contents in all samples from the same day from the treated tanks and the control tanks.

5.10.2.2 PHYTOPLANKTON CELL COUNTS

The direct cell counts of phytoplankton (Figure 5.11 and Figure 5.13) show considerable variation both between parallels from the same tank taken on the same day, and between averages from the same tank on different days. However, the overall impression is that the cell concentration decreased in the treated tanks, but remained relatively constant in the control tanks. Thus, while the chlorophyll *a* analyses and the phaeophytin to chlorophyll *a* ratio indicated that the phytoplankton concentration was lowest and the cells in the poorest condition in the control tanks, the direct cell counts give the opposite impression.

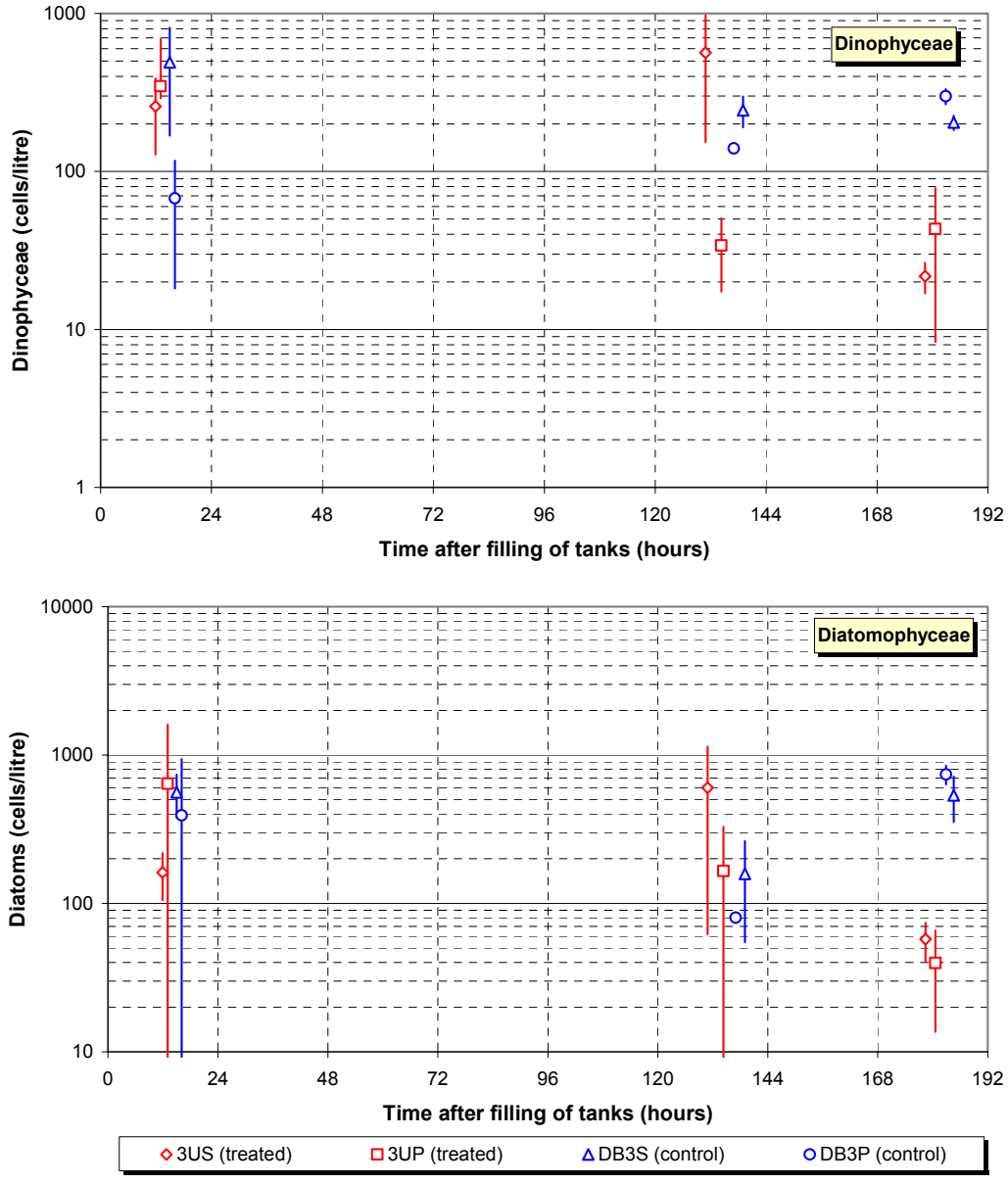


Figure 5.13: Concentration of dinoflagellates and diatoms per litre
All samples were taken via the fire pump.

A possible explanation is that in the control tanks dead phytoplankton cells remained intact, while the high concentration of bacteria lead to a rapid degradation of dead cells in the treated tanks. Dead, but still intact phytoplankton cells would be included

in a direct count, and may contain degraded chlorophyll, while degradation of the dead cells will remove the degraded chlorophyll and the ratio of phaeophytin to chlorophyll *a* will not change. The concentration of chlorophyll *a* decreased by roughly a factor of ten in both the treated and the control tanks during the study, and this reduction is comparable to the reduction in the direct cell count in the treated tanks.

6 ULTRAVIOLET LIGHT AND ULTRA SOUND TREATMENTS

The onshore test trials were conducted utilising the facilities provided by the Tvärminne Zoological Station in Finland. The trials were carried out in two phases, September-October 2002 and August-September 2003. The test water was extracted directly from the sea without filtering to ensure water volume large enough for the test execution and to maintain the link to the local marine environment (see also chapter 3.3 for general arrangements). Various flow rates and two ultrasound transducers were included in the test programme. In addition to the single techniques, also the combinations of ultrasound and ultraviolet light and ultraviolet light and hydrogen peroxide were tested as part of the hurdle experiments (see chapter 10).

The aggregate where UV and US devices were mounted was modified in order to minimise the source of error caused by the dead-end pipes, valves and bends. Duration of test runs was longer, typically 1 h with each combination of parameters, in order to minimise the technical sources of errors, i.e. piping, fittings, valves and too small amount of test water. The parameters and flow rates used during the trials are indicated in the Tables 6.3 and 6.13.

6.1 ULTRAVIOLET LIGHT DEVICE

Ultraviolet light device used in the onshore test trials was provided and manufactured by Berson Milieutechniek BV, in The Netherlands. The Berson InLine 5 UV disinfection unit has one 316L stainless steel irradiation chamber with a total length of 460mm. The internal diameter is 56mm. Inside the chamber, one B410 Berson MultiWave® lamp is mounted perpendicular to the flow and enclosed by a quartz sleeve. The lamp is a medium pressure mercury gas discharge lamp manufactured by Berson Milieutechniek BV. Its electric power is 350W. The UV output is 200-400 nm or germicidal UV output is 210-320 nm. The output spectrum of the lamp is indicated in (Figure 6.1). UV output power is 58 W and operation gas pressure is 2-3 bar. The UV-C output of the B410 Berson MultiWave® lamp remains constant in the temperature range 0-70 °C. A sensor within the chamber constantly checks the water temperature. If this parameter reaches a pre-set maximum level, the lamp is automatically switched off. The irradiation chamber is standard fitted with a non-aging UV-sensor, type UVector.

The power supply for the B410 Berson MultiWave® lamp is housed in the same painted steel cabinet as the control system. It includes the power supply for the B410 Berson MultiWave® lamp and the ECtronic control system. The ECtronic control system includes a "lamp-on" indicator to indicate if the UV-C lamp is operating correctly and "Power" indication to visualise that the electric supply is switched on. Alarm signals are visualised by means of LED indicators and potential free contacts are used for remote signaling. The unit is also equipped with hour counter. The technical specification of the UV chamber and power module is shown in the Tables 6.1 and 6.2 (Berson Milieutechniek BV, 2002).

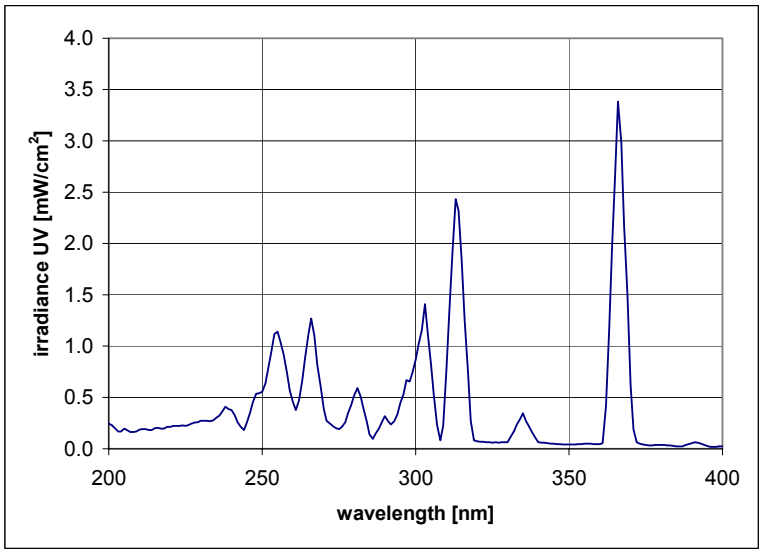


Figure 6.1: The UV output spectrum of the B410 Berson MultiWave® lamp

Table 6.1: Technical specification of UV chamber of Berson InLine 5 disinfection unit

UV chamber HXK1	
Type	BersonInLine®
Material	Stainless steel 316L, ac. to AISI
Internal finish	Dairy (Ra_{max} 1.0 μm)
Connections	NW40 DIN2576
Number of lamps	1* B410, BersonMultiWave® UV lamp
Sample tap connections	no
Drain plug	yes
Air relieve valve	no
UV sensor	yes
Cleaning mechanism	no
Degree of protection	IP54
Pressure test	15Bar
Pressure operational	10Bar
Dimensions (H x W x D)	460 x 390 x 300 mm
Weight dry	10kg
Weight wet	12kg

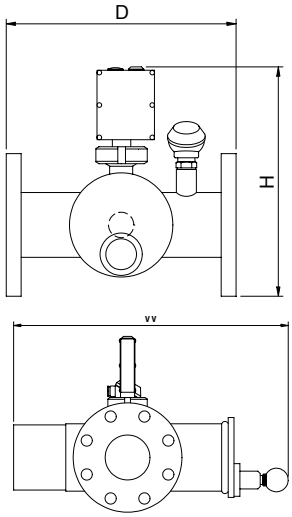


Table 6.2: Technical specification of power/control module of Berson InLine5 disinfection unit

Power/control module 410VL1ECU	
Material	painted steel
Degree of protection	IP54
Dimensions (H x W x D)	600 x 380 x 210 mm
Weight	15kg
Required power supply	230V/50Hz
Connected power	500 W
Safety door switch	yes
UV intensity indication	yes
UV alarm with relay	yes
Temperature control	no
Cabinet temp. control	yes
Hour counter	yes
Energy control	no

The 2 kW US device and UV device were installed in the same aggregate to enable flexible test arrangements of the combination of US and UV (Fig. 6.2 and 6.3).

Figure 6.2: The UV light and US devices (2 kW) mounted in the same aggregate US transducer is mounted inside the stainless steel box.

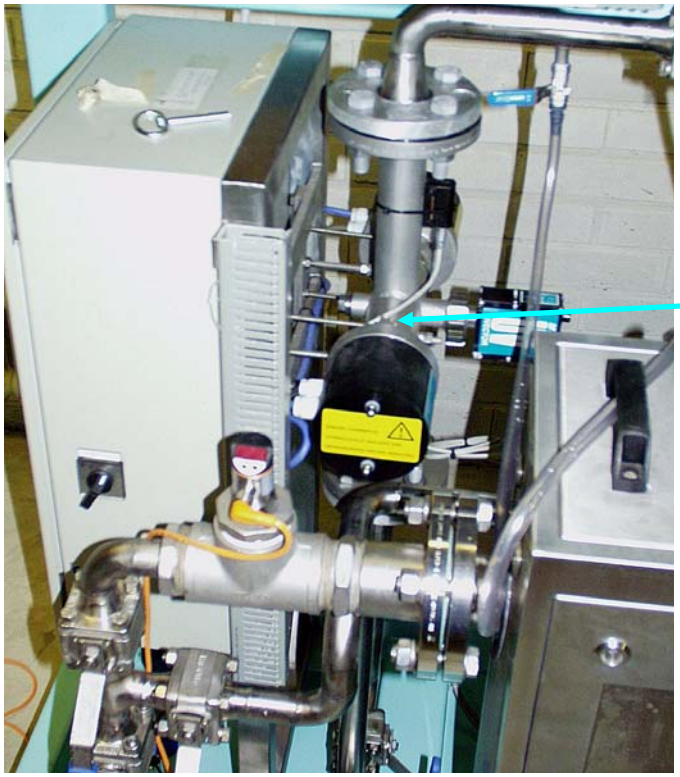


Figure 6.3: Ultraviolet light device in the test rig

The parameters and flow rates used during the trials with UV light technology are presented in the Table 6.3. The temperature of the sea water during the first test phase was lower than during the second test phase. The Total Suspended Solid analyses were conducted during the second test phase (August - September 2003) once a day, accordingly to the standard SFS-EN 872 (1996) with filter paper Schleicher & Schuell GF52. The temperatures were measured with Fluke 51 K/J Thermometer.

Table 6.3: The operational parameters with UV light treatment

Flow rate [L/h]	**UV dose** [mJ/cm^2]	**T_{sample}** before / after [°C]	**ΔT** [°C]	**Total Suspended Solids** (TSS) [mg/L]	**Test phase**		**Comments**
					Sept.-Oct. 2002	Aug.-Sept. 2003	
200	562	6,6 / 7,6	1,0	-	x		
		19,4 / 21,4	2,0	3,9		x	
		20,0 / 22,1	2,1	3,9		x	
400	281	6,7 / 7,3	0,6	-	x		
		19,2 / 20,3	1,1	3,9		x	
		19,3 / 20,3	1,0	3,9		x	
520	216	6,7 / 7,2	0,5	-	x		
		19,3 / 20,2	0,9	3,9		x	
		19,6 / 20,4	0,8	3,9		x	
800	141	14,7 / 14,9	0,2	4,7		x	Conducted as part of UV + H2O2 experiment

The spectrum was measured with a Shimadzu UV-2101PC spectrophotometer, which has the resolution of 0.1 nm and wavelength accuracy of ±0.3 nm. The spectral bandwidth was 2 nm. The measurement was done with a deuterium lamp. The photometric accuracy is ±0.3% T in transmittance. The sample was filtered particle free and measured in 10 mm quartz cuvette. Distilled water was used as absorbance control. The water samples were taken before the UV treatment (Figure 6.4).

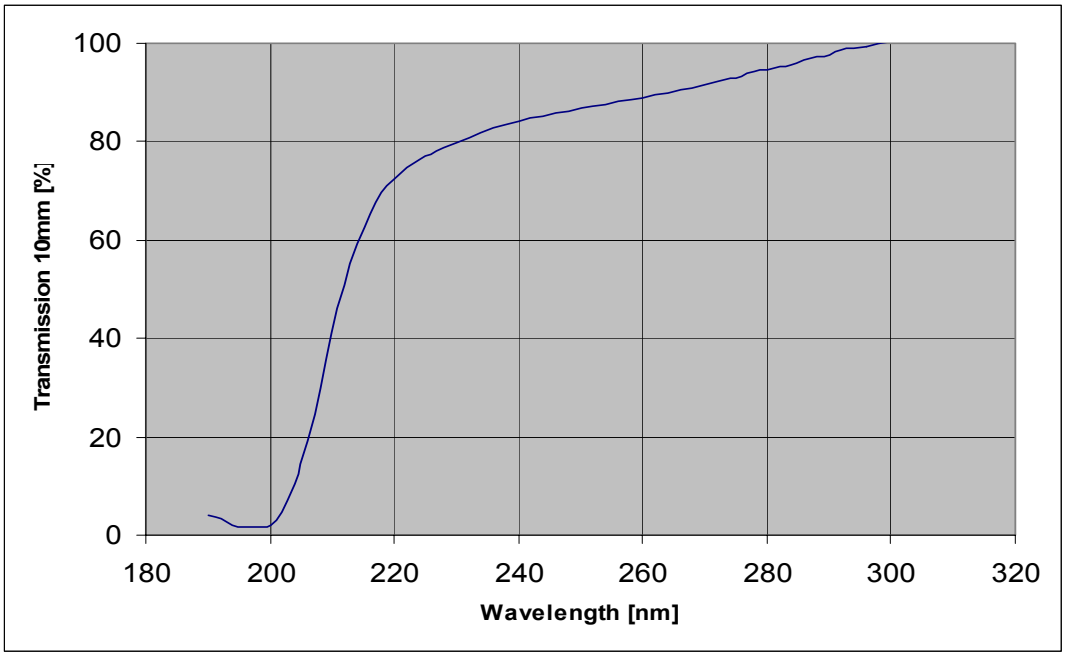


Figure 6.4: UV spectrum for the Baltic Sea water during the tests in September 2003

6.1.1 CONCEPT APPROVAL

The installation scheme providing a global view of the components and links with the ship installation is given below.

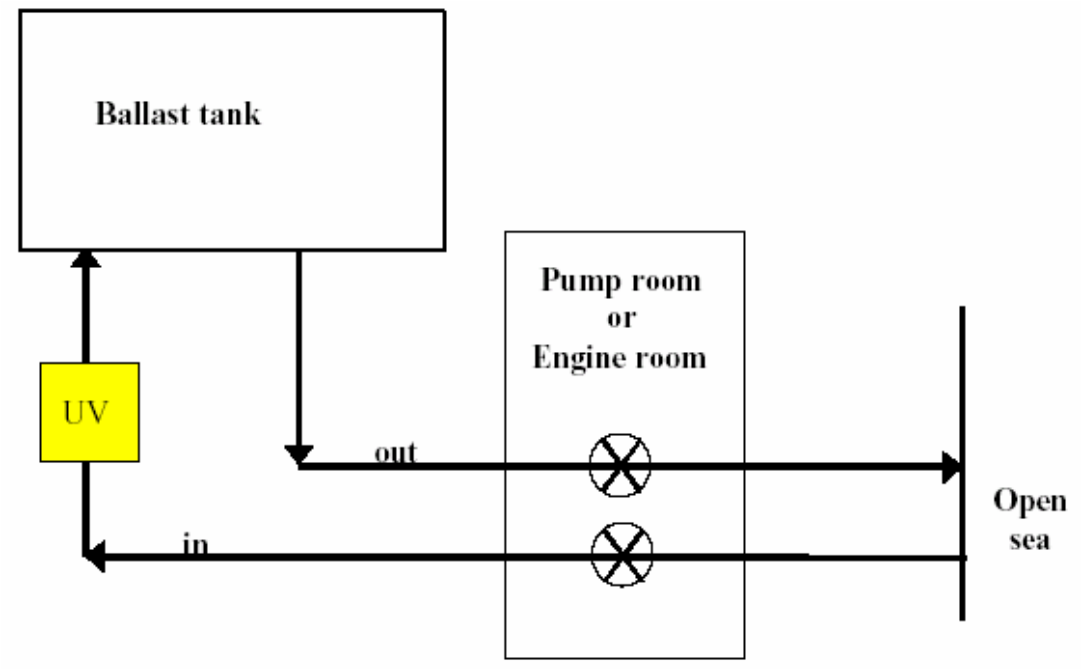


Figure 6.5: UV system diagram

The system is connected to the ballast water piping and uses components which exist on the ship and are well known ship equipment and have the following characteristics:

- UV-lamp with power supply of 380 V AC
- A contact chamber in stainless steel (AISI 316 or equivalent), quartz sleeve, viton seals, teflon
- A control console, modular unit, to be placed outside ballast tanks.

The review of the defined criteria in chapter 1 leads to the following conclusions shown in Table 6.4.

Table 6.4: UV criteria results

Criteria	Review Results
Stability	No tank filling different than those of the operational ship loading cases. No impact on stability.
Visibility	No modification of the loading cases, so of the trim, at sea. No impact on visibility.
Longitudinal strength of the vessel	No tank filling different than those of the operational ship loading cases. No impact on the hull girder strength.
Overpressure in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of overpressure.
Liquid motions in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of sloshing.
Piping	Use of well known marine equipment on ballast piping. No increase of risk.
Risk of fire	No specific non common equipments. No increase of the risk of fire.

Material and products	Use of well known marine equipment on ballast piping. No particular risks.
Ballast water composition	No addition to the water. No particular risk.
Biological efficiency	Good laboratory test results. Selective efficiency in on-shore large scale tests. No onboard scale test results.

The system analysis does not show any particular difficulty with respect to normal ship design and building. The biological efficiency has been proven acceptable but selective versus species. Considering the documents submitted, the system is granted with a Design Concept Approval.

To obtain the Final Concept Approval of the system alone does not seem possible due to the selectivity versus species. As such it seems necessary to combine at least another system with UV. The Final Concept Approval will be granted after submission of the required documents reference number 7 and 9 to 15 of Table 1.2 (see chapter 1).

6.1.2 Risk and Safety Issues

For an onboard installation, the UV system would be installed in a line between the pump intake and the ballast water tank. Although no filtration was used in the large scale tests, it is expected that a filter would be installed with the onboard system. Spare UV lamps, each containing 100 mg of mercury, would need to be stored on board. Figure 6.6 shows a simplified presentation of a UV system installed onboard.

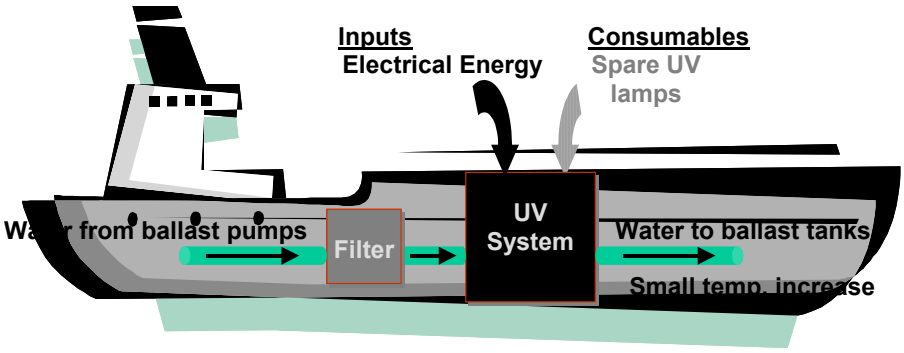


Figure 6.6: Simplified presentation of UV treatment system

6.1.2.1 Hazards

Hazards identified in WP3 were UV radiation, electrical hazards resulting from the equipment, and potential hazards associated with overheating of equipment and possible spill of mercury contained within the UV lamps if they are dropped and broken. Another potential hazard is the sediment material removed by the filter if the ballast water is taken on in polluted waters and if solid material needs to be handled. If the filters operate using a backwash cycle and no handling of filtered material is required then there would be no hazard. A more detailed description of each of the hazards was provided in report DTR-3.5. No incidents resulting from these hazards occurred during the large-scale testing carried out in WP4.

The hazards associated with the UV treatment system would be confined to the equipment itself and the storage area for the lamps. There is no potential for contamination of crew spaces, or of contaminated ballast water as the quality of the

ballast water is essentially unchanged. UV treatment systems have been used in many applications and the equipment is designed with safety features to minimise risk of exposure to UV radiation and electrical hazards.

6.1.2.2 "WHAT-IF" ASSESSMENT

"What if" questions considered during WP3 included the following:

- What if there is a break or crack in the cabinet shielding the lamps?
- Is it possible for safety systems to be turned off and the lamps turned on without shields in place?
- What if a lamp is dropped and broken, or breaks during storage?

6.1.2.3 POSSIBLE RISK REDUCTION MEASURES

Risk reduction measures to address the "what if" questions and other potential safety issues included:

- The UV equipment used for the large scale testing had a sensor installed within the chamber to continuously check the water temperature. A maximum allowable temperature was pre-set, and if this value was reached then the lamp would automatically be switched off.
- The UV treatment system would have shields in place to prevent potential UV exposure to personnel.
- The equipment used in the large-scale test was equipped with a number of safety features. These included an indicator to show if the UV-C lamp is operating correctly, and a lamp to indicate when the electric supply is switched on. As well there were alarms to indicate problems with the UV system. The power control module of the UV disinfection unit was housed in an enclosure rated "IP54", which means that it is protected against solid objects greater than 1 mm, and that it is protected against splashing water. More detailed information on the equipment is provided in report DTR-4.4.
- As standard the equipment is labelled not to be operated without flow of water through the system. There are also labels to indicate the UV radiation hazard and warning labels to not open lamp covers before switching off the UV system.
- Training of crew who would be operating the equipment will help make them aware of the hazards of exposure to UV radiation.
- The system operator should be made aware of the hazards associated with mercury and there should be appropriate clean-up equipment available in the event of lamp breakage. In addition there should be procedures for disposal of used lamps, and spare lamps should be stored in an appropriate manner.

6.1.3 ENVIRONMENTAL IMPACTS

Data was provided by the system designer on water quality parameters measured during the test. For materials and energy use, quantities estimated for the case study work were used. Environmental impacts resulting from the ultraviolet irradiation method, based on data collected during large scale testing and from the case study estimates, are discussed below.

6.1.3.1 PRODUCTION PHASE

The system developer, VTT, provided estimates for materials use for a UV chamber and associated equipment to treat 2000 m^3 of ballast water. The estimated materials use was as follows:

- UV chamber: stainless steel 316 L, weight, dry: 100 kg, weight, wet: 175 kg, number of UV-lamps: 8,
- Power control module: weight: 450 kg, painted steel

The UV lamps contain quartz and approximately 100 mg each of mercury. For a full-scale onboard installation a filtration unit would be required for pre-treatment. Materials use for this unit was not available.

Emissions to air resulting from production of steel for the UV chamber and control module (total 550 kg) were estimated. Emissions categories included gases that contribute to global warming (greenhouse theme), gases that contribute to acidification (acidification theme), and gases that contribute to the formation of tropospheric ozone (tropospheric ozone precursors theme). Table 6.5 shows the amounts of the major types of emissions according to these "themes", and also shows the equivalents totals for each of these themes.

Table 6.5: Emissions resulting from production of steel for UV chamber and equipment

Theme	Type of Emission	Amount (kg)	Conversion Factor	Equivalent Value
Greenhouse	CO_2	545.5	1	545.5
	CH_4	1.3	23	30.2
	N_2O	0.0035	296	1
			Total CO_2 equivalents(kg)	576.8
Acidification	NO_x	0.85	1/46	0.02
	$SO_2 + SO_x$	1.35	1/32	0.04
	NH_3	0.0005	1/17	0.00
			Total Potential Acid Equivalent (kg PAE)	0.06
Tropospheric Ozone Precursors	NO_x	0.85	1.22	1.03
	CO	0.13	0.11	0.01
	CH_4	1.32	0.014	0.02
			Tropospheric Ozone Forming Potentials (kg TOFP)	1.07

6.1.3.2 OPERATIONS PHASE

Fuel is required to generate energy to operate the UV treatment system. As for other treatment systems, it was assumed that marine diesel fuel was used and the IPCC standard emission values per tonne of fuel, as shown in Table 2.4 (see chapter 2), were used for this assessment.

For the life cycle assessment, it is estimated that the ship makes 25 voyages per year where the 2000 m^3 of ballast water is treated. The power consumption for each treatment is estimated at 54 kWh, which requires 15.3 kg of diesel fuel to produce. The life cycle of the equipment is estimated as 20 years. Using these assumptions, a total of 7.7 tonnes of fuel would be used over the life of the equipment. Emissions associated with this fuel use are shown in Table 6.6.

Table 6.6: Emissions related to energy use over life cycle operation of UV system

Theme	Type of Emission	Amount (kg)	Conversion Factor	Equivalent Value
Greenhouse	CO_2	24032	1	24032
	CH_4	2.3	23	53
	N_2O	0.6	296	181
Total CO_2 equivalents(kg)				24266
Acidification	NO_x	551	1/46	12
	$SO_2 + SO_x$	459	1/32	14
Total Potential Acid Equivalent (kg PAE)				26
Tropospheric Ozone Precursors	NO_x	551	1.22	672
	CO	57	0.11	6
	CH_4	2	0.014	0.03
Tropospheric Ozone Forming Potentials (kg TOFP)				679

Notes: Conversion factors for greenhouse gases to CO2 equivalents from IPCC 2001
Conversion factors for PAE and TOFP from Hass (2002).

6.1.3.3 COMPARISON OF EMISSIONS BY LIFE CYCLE STAGE

Emissions values for both the equipment production and operations phase of the UV Irradiation treatment system is presented in Table 6.7. For all three categories considered the operations phase is dominant, accounting for more than 97% of emissions during the life cycle.

Table 6.7: Emissions over production and operation phase of UV system

Theme	Production		Operation	
	kg	% life cycle	kg	% life cycle
Greenhouse theme: Total CO_2 equivalents	577	2.3	24266	97.7
Acidification: Total Potential Acid Equivalent (kg PAE)	0.06	0.2	26	99.8
Tropospheric Ozone Forming Potentials (kg TOFP)	1.07	0.2	679	99.8

6.1.3.4 DIRECT IMPACTS THROUGH DISCHARGE TO RECEIVING WATER

Discharge of water with altered quality

The only expected change is a slight temperature increase. For the large scale tests carried out, the measured temperature increase ranged from 0.2 to 2.1˚C. The larger temperature increases were recorded for the lowest flow rates. If ballast water is treated during ballasting the difference in water temperature upon discharge would be negligible. Even for de-ballasting, this temperature increase would not be considered a problem for an intermittent discharge.

Discharge of solids (organisms and sediments)

For a full scale installation the ballast water would be filtered prior to passing through the UV treatment system. Filtration would take place during ballasting. Discharge of sediments in localised turbidity increases – this would depend upon the amount of sediments present in the ballast water.

The treated ballast water would contain organic material in the form of dead organisms. This would vary depending on the concentration of organisms taken on with the ballast water. Impacts would vary depending upon the sensitivity of the

receiving environment, with organics loading being more of a concern in eutrophic waterbodies.

Impact from surviving non-indigenous organisms
The UV system was tested with four flow rates as part of large-scale test program for WP4. The mortality rates were highest for the lower flow rates. In general mortality rates were high, but there were some differences among different zooplankton groups (DTR-4.4).

Some researchers (Buccholz *et al*, 1998) have identified a possible risk of genetic mutation of organisms surviving the UV treatment process. However, they state that it is expected that most of the damaged and surviving organisms would fail to procreate. The study of this potential effect was not within the scope of the MARTOB project.

6.1.3.5 OTHER ENVIRONMENTAL IMPACTS

Spill potential
There is the potential for low-level mercury from the lamps to be released to the environment if they are broken or not disposed of properly. There is 100 mg in each lamp used, and spare lamps would also be carried onboard. Mercury is on a list of 11 substances or groups of substances identified as "priority hazardous substances" listed in the European Union's Water Framework Directive (2000/60/EC), which was adopted in September 2000.

6.1.4 ECONOMIC ASPECTS

6.1.4.1 CAPITAL COSTS

The investment costs for the system are approximate € 58,000; this includes UV system, auto-wipe (cleaning system) and UV sensor. The approximate installation costs are € 1,500; this includes welding and two NW300 valves. Testing costs for the first start-up of the system are estimated to be € 1,000 (one day, including travel).

6.1.4.2 OPERATIONAL COSTS

Treating the amount of ballast water from one voyage, i.e. 2,000 m^3, with the UV treatment system requires 54 kWh. The ballast water pumps use 200 kWh per trip.

Table 6.8: Total energy use

Total energy use		Unit
energy requirement per trip	254	kWh
kWh > MJ (electricity)	914	MJ (electricity)
MJ (electricity) > MJ (diesel)	3,048	MJ (diesel)
MJ >kg (diesel)	72	kg (diesel)
energy costs per trip (diesel)	28.69	€/trip
total energy costs per year (diesel)	**1,434.35**	**€/year**

No other *consumables* are used during treatment. No additional *personnel* will be involved running the system. Personnel involvement of the crew on-board is not specified. TAM (Turn Around *Maintenance*) is expected after 8000 hours of operation. Material costs will be € 3,000 (i.e. € 1.50 for 4 hours (1 trip) or € 75 per year). There is no extra maintenance required.

It is envisaged that no *training* is needed. Safety and health issues are addressed in the standard operational manual. *Certification costs* will be € 2,000.

6.1.4.3 COST AND BENEFITS ASPECTS

No increased tank cleaning or corrosion control costs are expected, no delay in harbour or during trip is expected. The footprint of the equipment is about 1.5 square metres (power control module 2000x800x800 mm (HxWxD), UV chamber 590x920x550 mm (HxWxD)). There will be no cargo space reduction. The weight of the system in operation is about 625 kg (UV chamber: stainless steel 316 L, dry: 100 kg, wet: 175 kg, 8 UV lamps, and power control module 450 kg).

The next table shows the detailed calculation results for ultraviolet irradiation.

Table 6.9: UV economic results

Cost type	Description	€ (euro)	Comments
Capital Costs			
Investment	investment costs	58,000	UV system, auto wipe (cleaning system) and UV sensor
Installation	installation costs	1,500	including welding and two NW300 valves
Testing	testing costs	1,000	one day work including travel
Commissioning	commissioning costs		
	total investment	**60,500**	**€**
Depreciation factors	depreciation period	10	years
	interest rate	8%	
	annual capital costs	**9,016**	**€/year**
Operational Costs		**€/year**	
Personnel	personnel during treatment	p.m.	€/year
Energy	energy (diesel)	1,434	€/year
Additives	additives use	0	
Maintenance	TAM (maintenance euro)	75	
	additional maintenance	0	
Training and management	training costs	0	no training involved
	certification costs	200	certification costs € 2.000
	health and safety issues	0	no separate H&S manual
Cost and benefits	tank cleaning costs	0	no influence
	corrosion costs	0	no influence
	costs of delay	0	no delay
	increased maintenance	0	
	loss of cargo space	0	no loss of cargo space
	annual operational costs	**1,709**	**€/year**
Total annual costs		**10,726**	**€/year**
Costs per treated m^3 ballast water	**50 trips / 100,000 m^3**	**0.1073**	**€/treated m^3 BW**

6.1.5 BIOLOGICAL ASSESSMENT

The effect of UV was tested at four flow rates (200, 400, 520 and 800 L/h). High mortality rates (80-100 %) were found, with only few exceptions (i.e. cladocerans and barnacle nauplii) (Figure 6.7). Cladocerans appeared to be the most tolerant group, although low numbers of cladocerans allowed no statistical analysis. Some differences in the kill % between the different groups and different flow rates were

found (at a flow rate of 400 L/h, *Balanus* nauplii differed from other groups; Kruskall-Wallis: x^2=27,413, df=12, p=0,007). As in the US treatments, mortality rates increased with decreasing flow rates (copepod nauplii: Kruskall-Wallis: H=8,6, df=3, p=0,035; rotifers: Kruskall-Wallis: H=8,512, df=3, p=0,037).

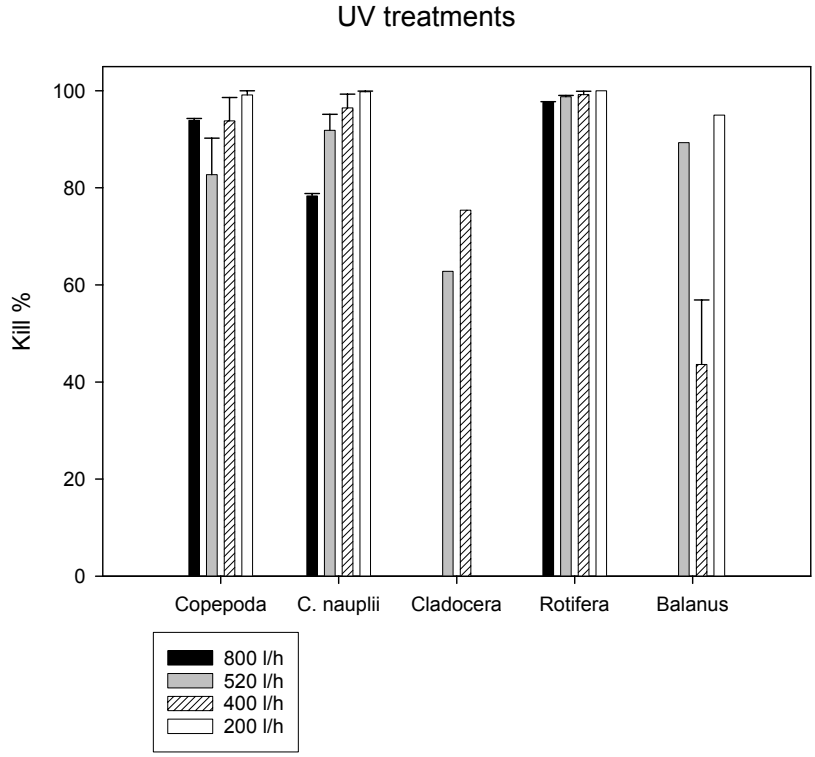


Figure 6.7: Treatments with ultraviolet light.

The Total Suspended Solid (TSS) values seems to have no effect on the UV treatment for the relative large species, but higher TSS values (> 10 mg/L) will limit the performance of the UV treatment on micro organisms since lower log reductions can be achieved at higher TSS values.

6.1.5.1 TEMPERATURE MEASUREMENTS

Temperature measurements indicated that the temperature rise is depending on the flow rate and also on the water temperature before the treatment. During the first test trials (September - October 2002) the sea water was colder that during the second trials. Therefore the heat energy generated by the ultraviolet lamp (58 W) increased the temperature more during the second trials with the slowest flow rate (200 L/h). With the higher flow rates the differences between the two trials were smaller (Table 6.10).

Table 6.10: The maximum rise of temperatures measured with UV system

Flow rate [L/h]	**UV dose** [mJ/cm^2]	**T_{sample}** before / after [°C]	**ΔT** [°C]
200	562	19,4 / 21,4	2,0
400	281	19,2 / 20,3	1,1
520	216	19,3 / 20,2	0,9
800	141	14,7 / 14,9	0,2

The increased temperature levels generated by the ultraviolet treatment fit into the daily variation of the water temperatures in the Baltic Sea at the time scale of the test trials and therefore have no significant effect to the mortality rates.

6.2 ULTRASOUND DEVICES

The ultrasound devices used in the onshore test trials were designed and constructed by Acomarin Engineering Ltd, Naantali, Finland (Fig. 6.2 and 6.8, Acomarin Engineering Ltd., 2003). The different ultrasound devices, 2 kW and 4 kW, were used during the trials. The 2 kW device is equipped with dr. Hielscher UIP 2000 Ultrasonic Processor, including generator, transducer and sonotrode, which is made of titanium. Sonotrode is a mechanical component, which transmits the ultrasonic vibrations from the transducer to the material to be sonified. Transducer is an electro-mechanical component, which converts electrical oscillations into mechanical vibrations. The electrical oscillations are generated by the generator. The mechanical vibrations are transmitted to the sonotrode.

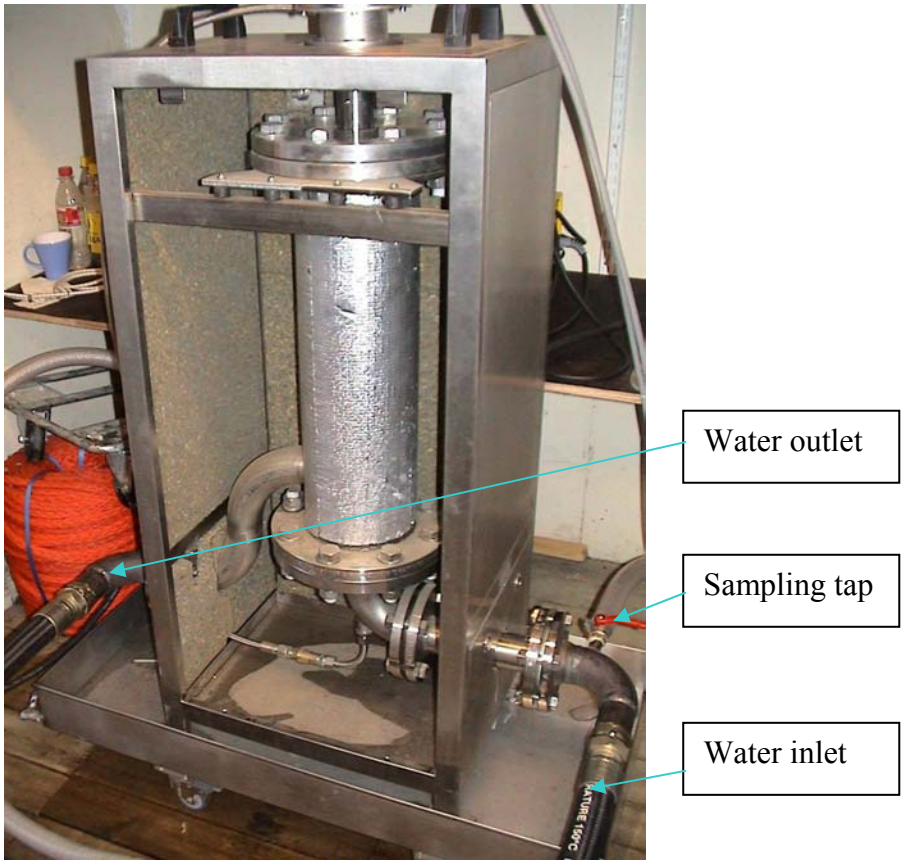


Figure 6.8: The 4 kW ultrasound device during the onshore test trials

The processor is exclusively designed for the purposes of disintegration (e.g. cell disruption, emulsifying, homogenising), thermoplastic molding, coating-lacquer removal, intensive surface cleaning, wire cleaning, cutting, drilling, lapping and compressing, used by industry or sonochemistry laboratories. The amplitude is adjustable and equipped with automatic frequency scanning system. Generator and transducer are housed separately and processor is dry running protected. The technical specifications of the 2 kW processors are shown in Table 6.11 (Acomarin Engineering Ltd., 2002).

Table 6.11: The technical specification of UIP2000 Ultrasonic Processor

Power supply	3 AC 400 V, AC ±10 %, 10A, 48 ... 63 Hz
Fuse	10 A time-lag primary (generator), 2A fan processor
Effective output power	2000 W
Efficiency	> 85 %
Power control range	20 % to 100 % continuously adjustable
Operating frequency	20 kHz
Freq. control range	± 1 kHz
Operational safety	cont. operational proof, even within air
Safety classification / Degree of protection	Generator: I, earthened equipment Processor: IP65
R.F.I. suppression / suspectibility	complies to EN 55011 complies to EN 50082-2
Permissible environmental conditions	operational temperature + 5 to + 40 °C 10 to 90 % relative humidity non-condensing
Weight	approx. 15 kg
Dimensions (W x H x D, max.)	Processor: 475 x Ø115 mm Generator 600 x 400 x 550 mm

The 4 kW processor generates longitudinal mechanical oscillations of a frequency of 19,000 cycles per second (19 kHz). The cascade sonotrode mounted to the electroacoustic transducer is made of titanium alloy. Designed as λ/2-oscillators it boost the longitudinal oscillation and radiate the sonic energy with increased density via its front face into the medium to be processed (Fig. 6.8 and 6.9, Acomarin Engineering Ltd., 2003). The technical specifications of the processor is indicated in the Table 6.12 (Acomarin Engineering Ltd., 2003).

Figure 6.9: The power control unit of the 4 kW Ultrasound device

Table 6.12: The technical specifications of the UIP4000 Ultrasonic Processor

Power supply	400V~3Phase, 48–63 Hz
Fuse	3x25 A
Effective power	4000 W
Efficiency	>85 %
Power control range	50-100 % continuous control
Operating frequency	19 kHz
Frequency control range	±1 kHz
Operational safety	steady state proof, even within air
Safety classification / degree of protection	generator: I, grounded transducer: IP 65
R.F.I. suppression	complies to EN 55011 and EN 50082-2
Operational temperature	5-40 °C
Environment humidity	10-90 % relative humidity, non-condensing
Weight	ca. 45 kg

The CE mark on this product complies with the directives of FunkStörG, EMVG, 1. GSGV.

The ultrasonic processor can work without a commonly necessary enforced cooling and is even continuous operation proof. A frequency scanning feature ensures secure oscillation startup of the sonotrode, even if it is worn out by the cavitation after longer terms of operation. With advanced wear or a not properly mounted sonotrode the processor automatically turns to the pulse mode operation. It will switch off after several seconds of pulse mode.

The oscillation amplitude is continuously adjustable. The value, once set, remains constant under all operation conditions. Thus, operation in air is possible, too. All sonotrodes are power adapted and reach their maximum amplitude at 100 % amplitude setting. Amplitude limits to certain values do not apply. The combination of several processors to groups, e.g. for high efficiency flow cells is possible. The generators controlling the processors are always remote. They can be manually operated or, in slave mode, be remotely controlled. Due to the strong cavitation, the sonotrode is subject to wear. This can even result in cracks and therefore the sonotrode has to be checked visually every 5000 hours of operation (Acomarin Engineering Ltd., 2003).

The operational parameters used during the trials with ultrasound are presented in the Table 6.13. The noise levels of ultrasound device were measured with Integrating Impulse Sound Level Meter, Brüel & Kjaer, type 2226, at 1 m distance from the device. The temperatures were measured with Fluke 51 K/J Thermometer. The temperature of the sea water during the first test phase was lower than during the second test phase.

Table 6.13: The operational parameters with ultrasound treatment.

Average flow rate [L/h]	**Amplitude** [%]	**Effective output power of US device** [kW]	**Actual energy exposed to water** [kW]	**Noise level** [dB]	**T_{sample}** before / after [°C]	**ΔT** [°C]	**Test phase**		**Comments**
							Sept.-Oct. 2002	Aug.-Sept. 2003	
200	25	2	0,185	-	10,9 / 11,7	0,8	x	x	No counter pressure
200	50	2	0,230	-	10,7 / 11,7	1,0	x	x	No counter pressure
200	75	2	0,350	-	10,7 / 12,2	1,5	x	x	No counter pressure
200	100	2	0,420	-	10,7 / 12,5	1,8	x	x	No counter pressure
400	50	2	0,230	-	9,2 / 9,7	0,5	x	x	No counter pressure
400	100	2	0,370	-	9,1 / 9,9	0,8	x	x	No counter pressure
520	50	2	0,360	-	7,7 / 8,3	0,6	x	x	No counter pressure
520	100	2	0,600	-	7,7 / 8,7	1,0	x	x	No counter pressure
800	50	2	0,280	-	16,3 / 16,6	0,3		x	Counter pressure 0,6 - 1 bar
			0,370	86	15,5 / 15,9	0,4			Counter pressure 0,6 - 1 bar
			0,460	88	15,8 / 16,3	0,5			Counter pressure 0,6 - 1 bar
800	100	2	0,700	-	16,5 / 17,3	0,8		x	Counter pressure 0,6 - 1 bar
			0,650	93	15,8 / 16,5	0,7		x	Counter pressure 0,6 - 1 bar
			0,830	93	15,7 / 16,6	0,9		x	Counter pressure 0,6 - 1 bar
			0,830	82	15,7 / 16,6	0,9		x	No counter pressure
			1,020	91	8,6 / 9,7	1,1		x	Counter pressure 1,3 - 1,7 bar
			1,390	91	8,7 / 10,2	1,5		x	Counter pressure 1,3 - 1,7 bar
800	100	4	1,850	86	13,4 / 15,4	2,0		x	No counter pressure
			1,670	86	13,4 / 15,2	1,8		x	No counter pressure
1600	100	4	0,740	84	13,5 / 13,9	0,4		x	No counter pressure
			1,480	84	13,3 / 14,1	0,8		x	No counter pressure
			1,850	94	8,9 / 9,9	1,0		x	Counter pressure 1,2 - 1,7 bar
				94	9,4 / -	-		x	Counter pressure 1,2 - 1,7 bar

The effective output power indicates the nominal output power level of the ultrasound device. The actual energy exposed to the water to be treated has been calculated based on the flow rates and temperature rises. In addition the water temperature, media, amplitude and sonotrode type has an influence to the actual energy input. The recorded output power levels varied between 0,7 - 3,4 kW during the trials with the 4 kW unit. The values in Table 6.13 represent the values at the time when the samples after the treatment were taken. The changes in the temperatures (before treatment) arose from the different test phase.

6.2.1 CONCEPT APPROVAL

The installation scheme providing a global view of the components and links with the ship installation is given below.

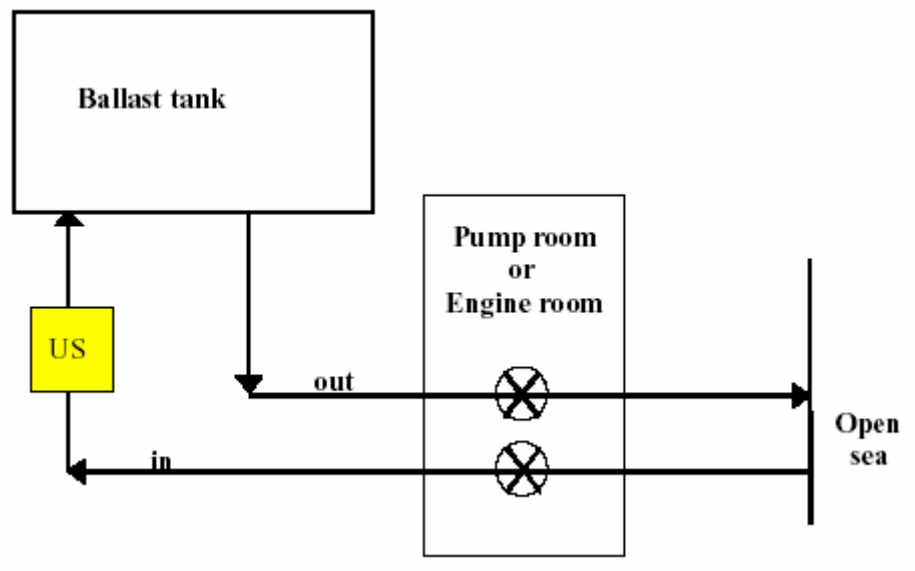


Figure 6.10: US system diagram

The system is connected to the ballast water piping and uses components which exist on the ship and are well known ship equipment and have the following characteristics:

- US transducer, stainless steel (AISI 316 or equivalent)
- Counter pressure valve: stainless steel (AISI 316 or equivalent)
- A control console, modular unit, to be placed outside ballast tanks.

The review of the defined criteria in chapter 1 leads to the following conclusions shown in Table 6.14.

Table 6.14: US criteria results

Criteria	Review Results
Stability	No tank filling different than those of the operational ship loading cases. No impact on stability
Visibility	No modification of the loading cases, so of the trim, at sea. No impact on visibility
Longitudinal strength of the vessel	No tank filling different than those of the operational ship loading cases. No impact on the hull girder strength
Overpressure in	No tank filling different than those of the operational ship loading

ballast tanks	cases. No increase on the risk of overpressure
Liquid motions in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of sloshing
Piping	Use of well known marine equipment on ballast piping. No increase of risk
Risk of fire	No specific non common equipments. No increase of the risk of fire
Material and products	Use of well known marine equipment on ballast piping. No particular risks
Ballast water composition	No addition to the water. No particular risk
Biological efficiency	Good laboratory test results. Selective efficiency in on-shore large scale tests. No onboard full scale test results

The system analysis does not show any particular difficulty with respect to normal ship design and building. The biological efficiency has been proven acceptable but selective versus species. Considering the documents submitted, the system is granted with a Design Concept Approval.

To obtain the Final Concept Approval of the system alone does not seem possible due to the selectivity versus species. As such it seems necessary to combine at least another system with US. The Final Concept Approval will be granted after submission of the required documents reference number 7 and 9 to 15 of Table 1.2 (see chapter 1).

6.2.2 Risk and Safety Issues

A description of the ultrasound devices used during full scale testing was provided by VTT. For an onboard installation ballast water would be treated during ballasting. The units would be installed after the ship's ballast pumps, and filtration would not be required. The treatment results in an increase in temperature. The increase in temperature varies with flow rate and energy of the system, temperature increases recorded during the trials ranged from a minimum of 0.3˚C to a maximum of 2.0 ˚C. This is the only expected change in water quality. Figure 6.11 shows a simplified presentation of an ultrasound system installed onboard.

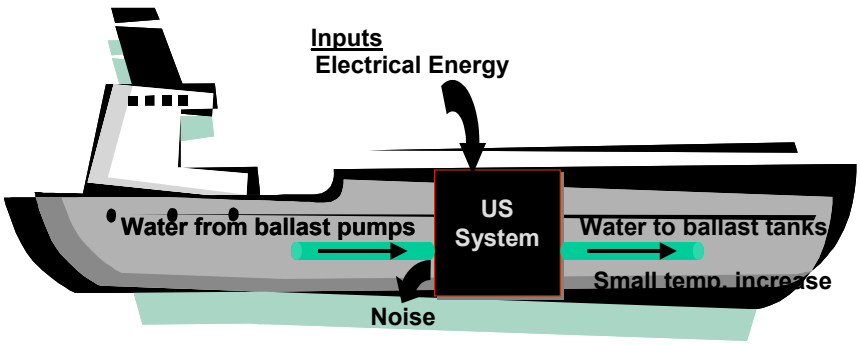


Figure 6.11: Simplified presentation of US treatment system

6.2.2.1 Hazards

Hazards identified in WP3 were included ultrasonic radiation, electrical hazards, heat hazards, and hazards associated with additional piping.

Equipment used to generate ultrasonic radiation can present both a hazard from accidental contact exposure and can also generate high sound-pressure levels in the air

in the sonic and ultrasonic range. To investigate possible concerns about noise from operation of the ultrasound equipment, noise levels were measured by VTT during the large scale testing (DTR 4.4). Measurements were taken at a 1 m distance from the device. The measured noise levels ranged between 84 dB and 94 dB. A comparison of the noise level limits by the Finnish government for allowable noise levels on vessels, and IMO's "Code on Noise Levels on Board Ships" was also performed. The Finnish government guidelines require that an announcement of noise and requirements for hearing protection be posted at the entrance to spaces where the noise level exceeds 85 dB. The IMO guidelines also require hearing protection to be worn when the noise level exceeds 85 dB.

Other hazards include potential hazards associated with the high voltage electricity (400 Volts) needed to power the ultrasonic transducer. Hazards related to this equipment would be similar to other equipment requiring high-voltage electricity. There is also the potential for heat to build up in the transducer, resulting in a potential hazard for burns from heated surfaces, or fire.

The hazards associated with the US treatment system would be confined to the equipment itself and the additional piping required. There is no potential for contamination of crew spaces, or of contaminated ballast water within the tanks as the only change to the ballast water is a slight temperature increase.

6.2.2.2 "WHAT-IF" ASSESSMENT

"What if" questions developed during WP3 and WP4 included the following:

- What if the equipment overheats?
- What if there is a pipe break within the ultrasonic treatment unit?
- What if the sonotrode cracks due to excessive wear due to cavitation?

6.2.2.3 POSSIBLE RISK REDUCTION MEASURES

Risk reduction measures to address the "what if" questions and other potential safety issues included:

- The equipment used in the large-scale test was equipped with a number of safety features. The ultrasonic processor was housed in an enclosure rated "IP65", which means that it is "dust-tight" (no ingress of dust will occur), and that it is protected against water jets. This means that water projected from a nozzle against the enclosure shall not have harmful effects. More detailed information on the equipment is provided in the report DTR-4.4
- If the sonotrode experiences advanced wear or is not properly mounted, the processor switches to pulse mode operation, and then switches off after several seconds in pulse mode.
- The sonotrode should be checked visually every 5000 hours of operation because it is susceptible to wear due to high cavitation.
- Crew will require some familiarization and training with the equipment to ensure they understand potential noise issues and are familiar with the safety features of the equipment.

- Hearing protectors should be worn in the vicinity of the ultrasound equipment when it is in operation.
- Signs should be placed at the entrance to the equipment space where the ultrasound is located, warning of excess noise levels and stating the need for hearing protectors.

6.2.3 ENVIRONMENTAL IMPACTS

The system designer provided information on water quality parameters measured during the test. For materials and energy use, quantities estimated for the case study work were used. Environmental impacts resulting from the ultrasound method, based on data collected during large scale testing and from the case study estimates, are discussed below.

6.2.3.1 PRODUCTION PHASE

The estimates provided for materials use for ultrasound treatment equipment to treat 2000 m^3 of ballast water was as follows:

- Stainless steel: 240 kg
- Titanium: 60 kg
- Painted steel: 50 kg

Emissions to air resulting from production of steel for the ultrasonic equipment (290 kg steel) were estimated. Emissions categories included gases that contribute to global warming (greenhouse theme), gases that contribute to acidification (acidification theme), and gases that contribute to the formation of tropospheric ozone (tropospheric ozone precursors theme). Table 6.15 shows the amounts of the major types of emissions according to these "themes", and also shows the equivalents totals for each of these themes.

Table 6.15: Emissions resulting from production of steel for US system

Theme	Type of Emission	Amount (kg)	Conversion Factor	Equivalent Value
Greenhouse	CO_2	287.6	1	287.6
	CH_4	0.7	23	15.9
	N_2O	0.002	296	0.5
			Total CO_2 equivalents(kg)	304.1
Acidification	NO_x	0.45	1/46	0.01
	$SO_2 + SO_x$	0.71	1/32	0.02
	NH_3	0.0003	1/17	0.00002
			Total Potential Acid Equivalent (kg PAE)	0.03
Tropospheric Ozone Precursors	NO_x	0.45	1.22	0.55
	CO	0.07	0.11	0.008
	CH_4	0.69	0.014	0.01
			Tropospheric Ozone Forming Potentials (kg TOFP)	0.563

6.2.3.2 OPERATIONS PHASE

Fuel is required to generate energy to operate the ultrasound treatment equipment. As for other treatment systems, it was assumed that marine diesel fuel was used and the IPCC standard emission values per tonne of fuel, as shown in Table 2.4 (see chapter 2), were used for this assessment. For the life cycle assessment, it is estimated that the

ship makes 25 voyages per year where the 2000 m^3 of ballast water is treated. The power consumption for each treatment is estimated at 96 kWh, which requires 27.2 kg of diesel fuel to produce. The life cycle of the equipment is estimated as 20 years. Using these assumptions, a total of 13.6 tonnes of fuel would be used over the life of the equipment. Emissions associated with this fuel use are shown in Table 6.16.

Table 6.16: Emissions related to energy use over life cycle operation of US system

Theme	Type of Emission	Amount (kg)	Conversion Factor	Equivalent Value
Greenhouse	CO_2	42767	1	42767
	CH_4	4	23	94
	N_2O	1	296	323
Total CO_2 equivalents(kg)				43183
Acidification	NO_x	981	1/46	21
	$SO_2 + SO_x$	817	1/32	26
Total Potential Acid Equivalent (kg PAE)				47
Tropospheric Ozone Precursors	NO_x	981	1.22	1196
	CO	101	0.11	11
	CH_4	4	0.014	0.1
Tropospheric Ozone Forming Potentials (kg TOFP)				1207

Notes: Conversion factors for greenhouse gases to CO2 equivalents from IPCC 2001
Conversion factors for PAE and TOFP from Hass (2002).

6.2.3.3 COMPARISON OF EMISSIONS BY LIFE CYCLE STAGE

Emissions values for both the equipment production and operations phase of the ultrasound treatment system is presented in Table 6.17. For all three categories considered the operations phase is dominant, accounting for more than 99% of emissions during the life cycle.

Table 6.17: Emissions over production and operation phase of US system.

Theme	Production		Operation	
	kg	% life cycle	kg	% life cycle
Greenhouse theme: Total CO_2 equivalents	304.1	0.7	43183	99.3
Acidification: Total Potential Acid Equivalent (kg PAE)	0.03	0.1	47	99.9
Tropospheric Ozone Forming Potentials (kg TOFP)	0.563	0.05	1207	99.95

6.2.3.4 DIRECT IMPACTS THROUGH DISCHARGE TO RECEIVING WATER

Discharge of water with altered quality

Ultrasound treatment is expected to result in a slight increase in the temperature of the ballast water. During the large scale testing carried out during WP4, the water temperature was measured before and after treatment. The increase in temperature varied with flow rate and energy of the system; temperature increases recorded during the trials ranged from a minimum of 0.3˚C to a maximum of 2.0 ˚C. This is the only expected change in water quality. If the ballast water is treated during ballasting it would cool in the ballast water tanks prior to discharge.

Discharge of solids (organisms and sediments)

The treated ballast water would contain organic material in the form of dead organisms. This would vary depending on the concentration of organisms taken on with the ballast water. Impacts would vary depending upon the sensitivity of the receiving environment, with organics loading being more of a concern in eutrophic waterbodies.

Impact from surviving non-indigenous organisms
Two different ultrasound devices were tested during the large scale trials conducted in WP4 (DTR 4.4). For the 2 kW device, four flow rates were tested at four different amplitudes. Kill rates increased with increasing amplitude and decreasing flow rates. In most cases kill rates above 90% were achieved. For rotifers, kill rates were somewhat lower. For the 4 kW device, two flow rates were tested at the maximum amplitude. The rotifers were again the group of zooplankton least affected by the treatment.

6.2.4 ECONOMIC ASPECTS

6.2.4.1 CAPITAL COSTS

The investment costs for the system are approximately € 125,000, including six processors (4 kW each), six sonotrodes and tube type flow vessels. Installation costs for installing all six units will be approximately € 4,000. Testing costs for the first start-up and testing of the system are estimated to be € 1,000. There are no commissioning costs expected.

6.2.4.2 OPERATIONAL COSTS

Treating the amount of ballast water of 2,000 m^3 per trip will require 96 kWh of energy. The 4 ballast water pumps together use 200 kWh per trip.

Table 6.18: Total energy use

Total energy use		Unit
energy requirement per trip	296	kWh
kWh > MJ (electricity)	1,066	MJ (electricity)
MJ (electricity) > MJ (diesel)	3,552	MJ (diesel)
MJ >kg (diesel)	84	kg (diesel)
energy costs per trip (diesel)	33.43	€/trip
total energy costs per year (diesel)	**1,671.53**	**€/year**

No chemicals or other *consumables* are used during US treatment. No additional *personnel* will be involved running the system. TAM (Turn Around *Maintenance*) is expected at a three month interval. Every three months, one day maintenance is expected resulting in TAM cost of € 3,500 per year. It is also expected that every year one sonotrode has to be replaced within a period of ten years, costing € 35,000 in ten years, which is € 3,500 per year.

It is expected that no specific *training* is needed. Safety and health issues are addressed in the standard operational manual. *Certification costs* are estimated to be € 2,000.

6.2.4.3 COST AND BENEFITS ASPECTS

There is no expected effect on tank cleaning costs and cost of corrosion control. There is no delay in harbour or during trip and no extra maintenance expected. An estimation of the footprint of the equipment required on-board is 5 m^2. It will be maximum 2 m high and has a weight of 350 kg. The treatment system will be installed in the engine room implying no effect on cargo space.

The next table shows the detailed calculation results for ultrasonic irradiation.

Table 6.19: US economic results

Cost type	Description	€ (euro)	Comments
Capital Costs			
Investment	investment costs	125,000	including 6 processors (4 kW each), 6 sonotrodes and tube type flow vessels
Installation	installation costs	4,000	installation of all 6 units
Testing	testing costs	1,000	one day work including travel
Commissioning	commissioning costs		
	total investment	**130,000**	**€**
Depreciation factors	depreciation period	10	years
	interest rate	8%	
	annual capital costs	**19,374**	**€/year**
Operational Costs		**€/year**	
Personnel	personnel during treatment	p.m.	€/year
Energy	energy (diesel)	1,672	€/year
Additives	additives use	0	
Maintenance	TAM (maintenance euro)	3,500	replacement of 1 sonotrode (€ 3,500) per year
	additional maintenance	3,500	labour costs
Training and management	training costs	0	no training involved
	certification costs	200	certification costs € 2.000
	health and safety issues	0	no separate H&S manual
Cost and benefits	tank cleaning costs	0	no influence
	corrosion costs	0	no influence
	costs of delay	0	no delay
	increased maintenance	0	
	loss of cargo space	0	no loss of cargo space
	annual operational costs	**8,872**	**€/year**
Total annual costs		**28,245**	**€/year**
Costs per treated m^3 ballast water	**50 trips / 100,000 m^3**	**0.2825**	**€/treated m^3 BW**

6.2.5 BIOLOGICAL ASSESSMENT

US treatments were conducted with two devices, hereafter referred to as US 2 kW and US 4 kW treatments. In US 2 kW treatments, four flow rates combined with four different amplitudes were tested: 200 L/h (25 %, 50 %, 75 % and 100 % of the maximal amplitude), 400 and 520 L/h (50 % and 100 %) and 800 L/h (100 %). The kill % achieved for the various organisms groups are presented in Figures 6.12-6.16.

The results show that kill % tended to increase (i) with increasing amplitude and (ii) with decreasing flow rate. Rotifers were the least affected group, whereas high kill % (above 90 % in most cases) was observed in other groups. Due to large variation,

again, statistical differences could only be found between rotifers (at 50 %, 520 L/h) and all other groups (Kruskall-Wallis: x^2=57,113, df=31, p=0,003). At the highest flow rate (800 L/h), counter pressure was used to intensify the treatment effect. In these experiments, however, counter pressure appeared to weaken the effect of US (Figure 6.17) although the difference was not statistically significant (Student's *t*-test for copepods: *t*=2,374, df=4, p=0,077; for c. nauplii: *t* =1,155, df=4, p=0,312; and for rotifers: *t* =1,389, df=4, p=0,237).

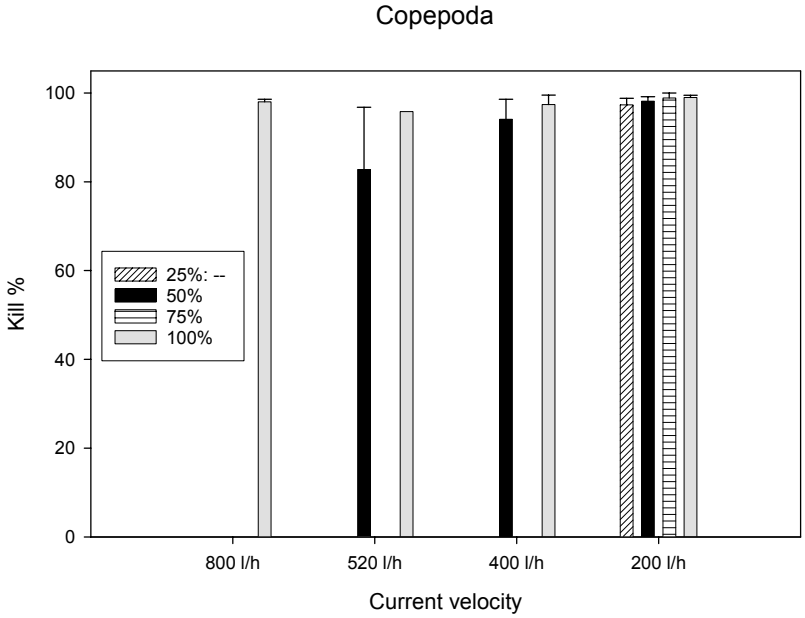


Figure 6.12: Kill % (Copepoda) in US 2 kW treatments with four flow rates

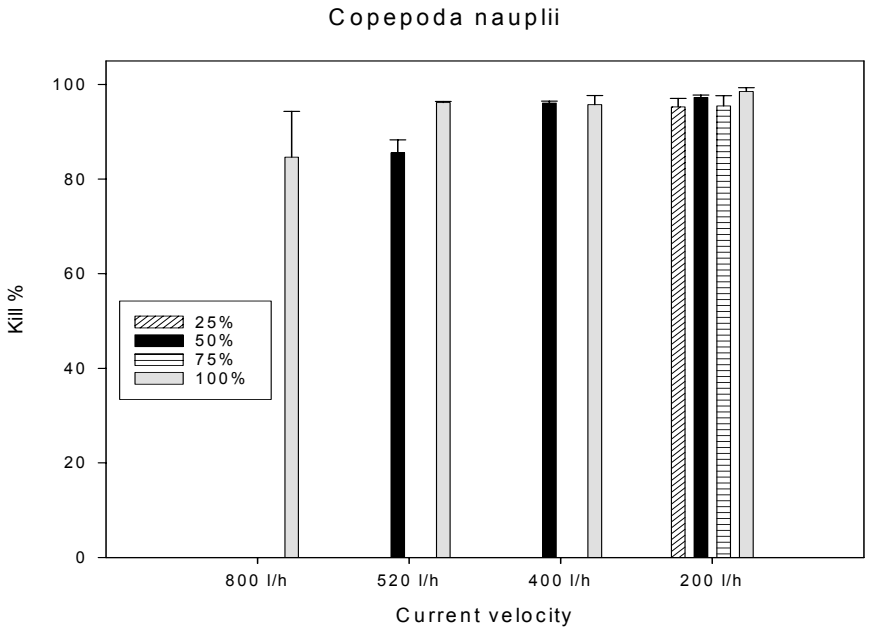


Figure 6.13: Kill % (Copepoda nauplii) in US 2 kW treatments with four flow rates

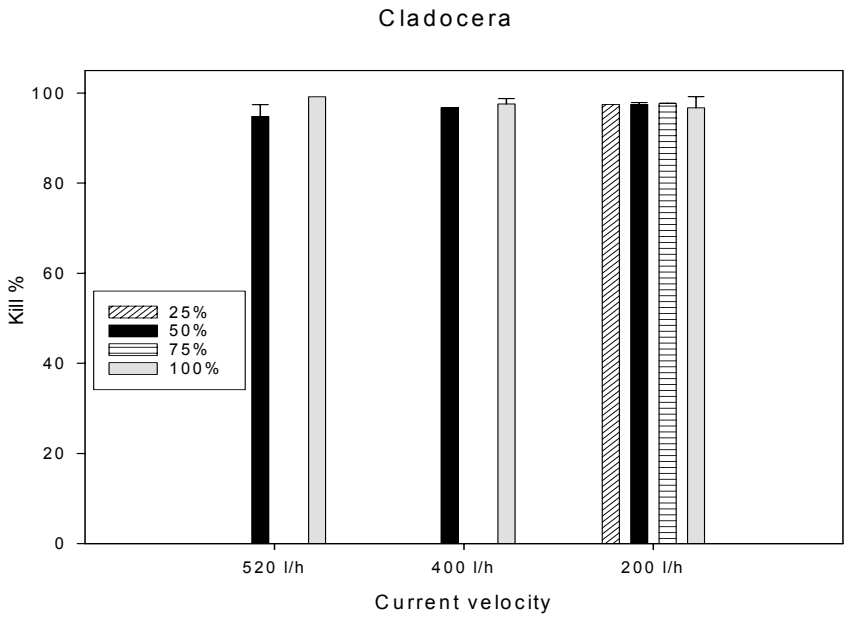


Figure 6.14: Kill % (Cladocera) in US 2 kW treatments with four flow rates

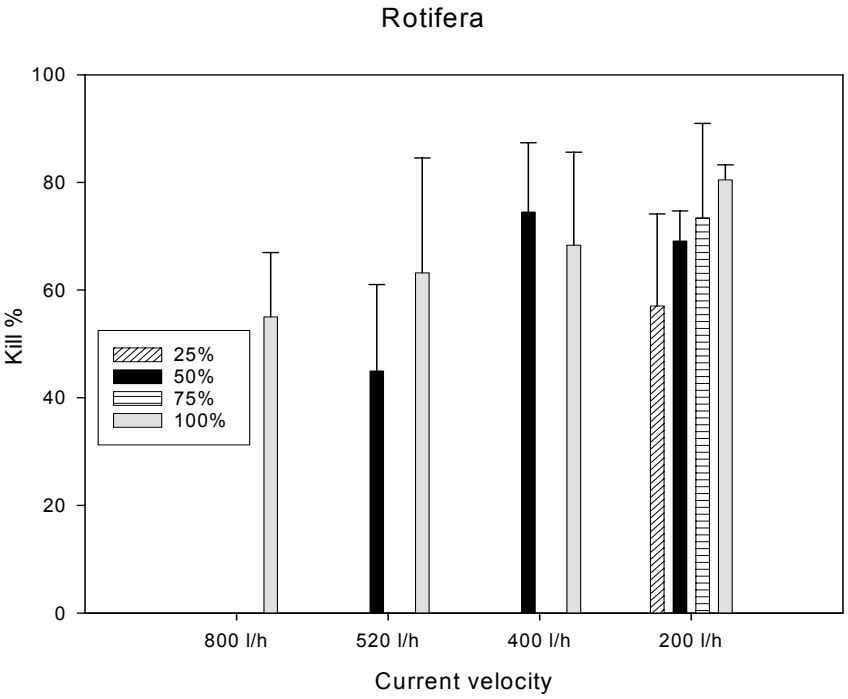


Figure 6.15: Kill % (Rotifera) in US 2 kW treatments with four flow rates

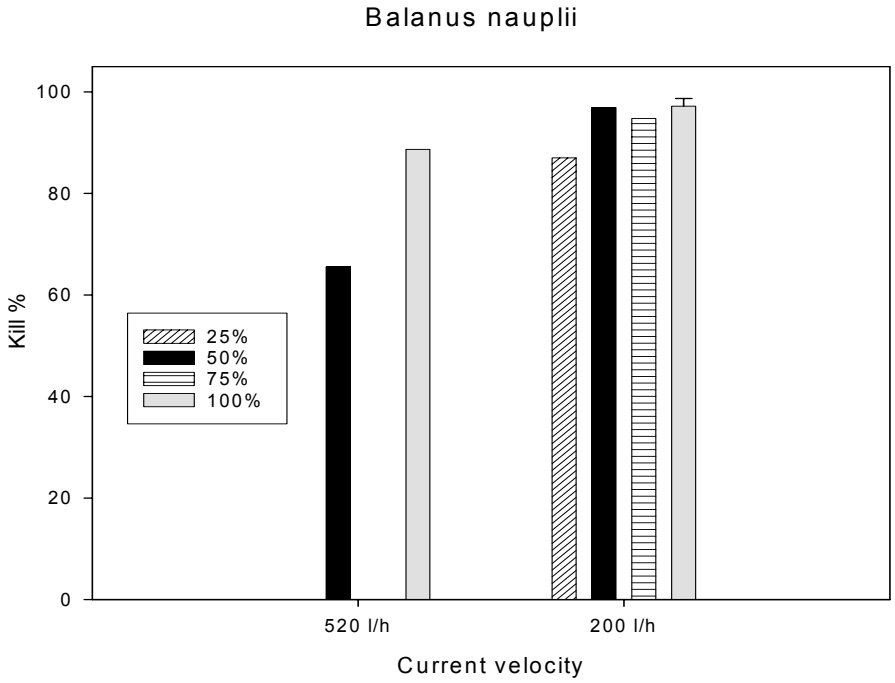


Figure 6.16: Kill % (Balanus nauplii) in US 2 kW treatments with four flow rates

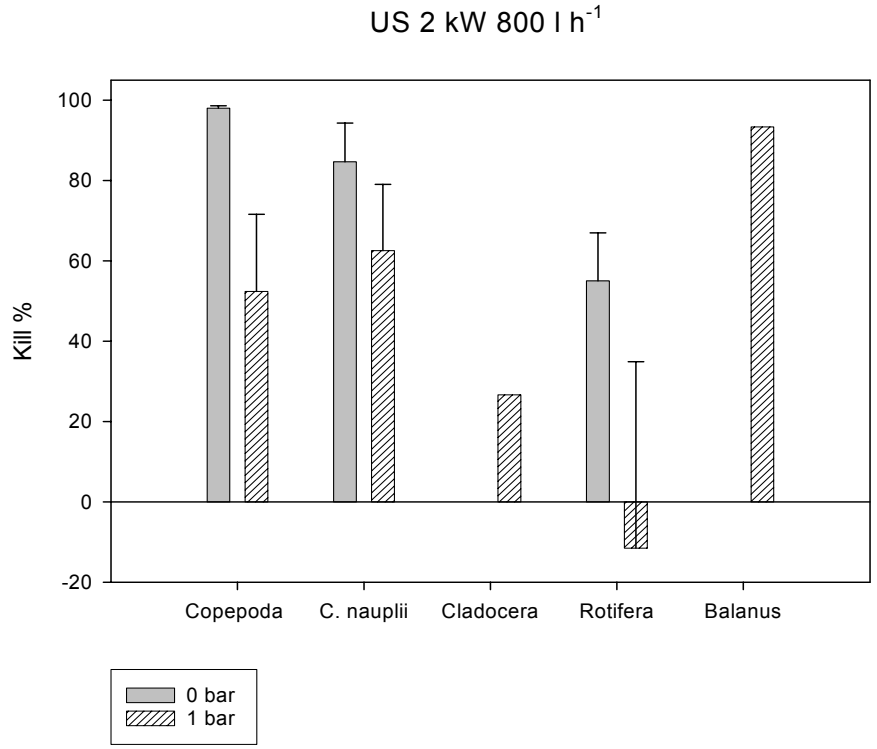


Figure 6.17: Kill % in US 2 kW at a flow rate of 800 L/h

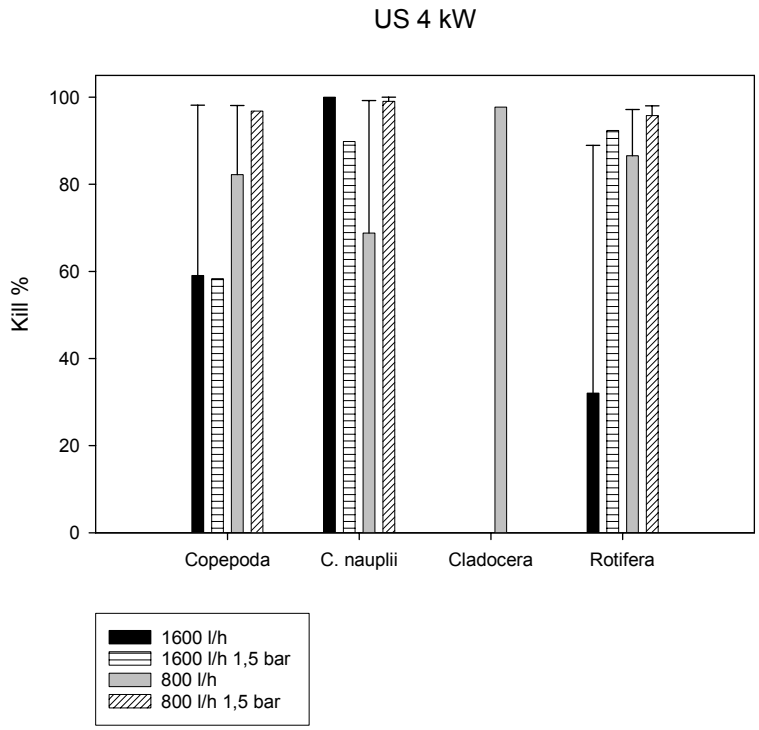


Figure 6.18: Kill % in US 4 kW at two flow rates

In US 4 kW treatments, the effect of two flow rates (800 and 1600 L/h) at maximal amplitude (100 %), both with and without counter pressure, was tested (for operational parameters, see Table 6.13). Small number of replicates and large variation caused difficulties in finding statistical differences between treatments (Kruskall-Wallis: x^2=4,635, df=6, p=0,591). Nevertheless, a tendency of increasing treatment effect with (i) counter pressure and (ii) decreasing flow rate could be observed (Figure 6.18). The highest kill percents (approaching 100 %) were found with the combination of slower flow rate (800 L/h) and counter pressure. No statistically significant difference was found between the effects of US 2 kW and US 4 kW (at 800 L/h) on mesozooplankton (Mann-Whitney U-test for copepods: U=3, 0, p=0,7; for copepod nauplii U=3,0, p=1,0; for rotifers U=1,0, P=0,127). Evidently, ultrasound had a mechanical cutting effect on the organisms (Figure 6.19).

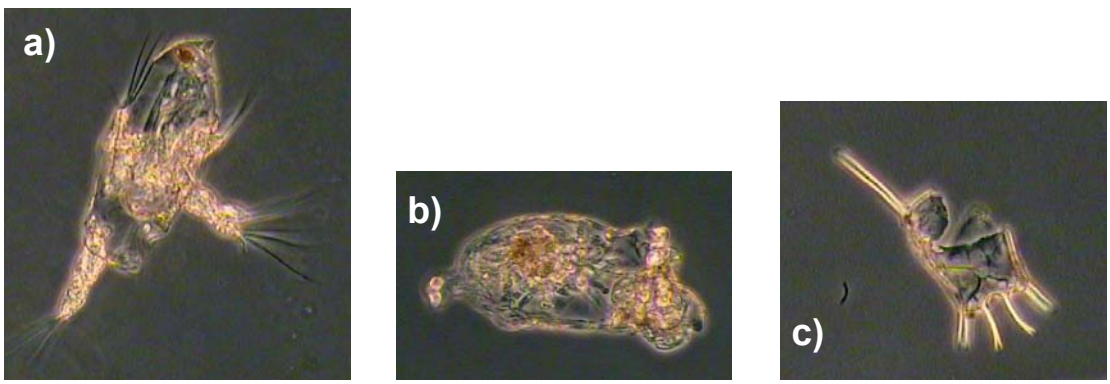


Figure 6.19: Organisms after US treatment.
a) *Acartia bifilosa* nauplius, b) *Sychaeta balthica*, c) *Keratella quadrata*.

6.2.5.1 NOISE LEVEL MEASUREMENTS

Regarding the noise levels measured near the ultrasound device (Table 6.13), the levels seem to be depending on the counter pressure level and on the effective power of the device. The measured noise levels varied from 84 dB to 94 dB. The highest values were detected with the 4 kW (frequency 19 kHZ) device and with counter pressure of 1,2 - 1,7 bar. Also the 2 kW (frequency 20 kHz) device generated a noise level of 93 dB with counter pressure of 0,6 - 1 bar. According to the guidelines approved by the Finnish Government, the following maximum values for A-weighted noise levels must be adapted when designing and constructing a vessel in Finland:

Table 6.20: Guidelines from the Finnish Government

	Tonnages of a vessel			
	65 - <400	400 - < 2.000	2.000 - < 10.000	> 10.000
Engine control room	70 dB	70 dB	70 dB	70 dB
Workshops	85 dB	85 dB	80 dB	75 dB
Galleys	80 dB	75 dB	70 dB	65 dB
Premises intended for continuous working in cargo room and on deck, such as operation position of winches	80 dB	80 dB	80 dB	80 dB
Radio rooms (radio switched off)	70 dB	65 dB	60 dB	60 dB
Offices	75 dB	70 dB	65 dB	60 dB
Navigating bridge wings	75 dB	75 dB	70 dB	70 dB
Navigating bridge and chartrooms	70 dB	65 dB	65 dB	65 dB

In a vessel, which is operating in ice or is on the run for a short period of time during a day, for example a harbour craft, values can be exceeded by 10 dB. In cases where a noise level of 85 dB will be exceeded in the interior premises of > 400 tonnes vessel, a permanent announcement of noise and a demand for use of hearing protection must be displayed on the way or in the door of those premises (Government of Finland, 1981).

The IMO guidelines "Code on Noise Levels on Board Ships" (Resolution A.468(XII)) applies to new ships of 1.600 tons gross tonnage and over, and should be applied to new ships less than 1.600 tons gross tonnage as far as reasonable and practicable. The code do not apply to dynamically supported craft, fishing vessels, pipe-laying barges, crane barges, mobile offshore drilling units, pleasure yachts not engaged in trade, ships of war and troopships and to ships not propelled by mechanical means.

Normally the national guidelines are applied onboard vessels. The control procedures of the health and safety matters are different depending on the flag state of a vessel, for example in the vessels under the Finnish flag the control is on the responsibility of the Ministry of Social Affairs and Health. (Kuusela, 2003).

Since the ultrasound transducers will be installed into the ballast water pipeline and the control unit in the engine room, the harmful effect of noise generated by the transducer can be reduced in the premises where the member of the staff needs to work most of the time. Also proper isolation of the cabinet where transducers are installed reduces the noise levels. When working near the transducers, proper hearing protectors should be used.

6.2.5.2 TEMPERATURE MEASUREMENTS

Temperatures measured before and after US treatment indicated that amplitude, flow rate and effective power level affected the increased temperature. The observed temperature increase during the trials did not exceed 2 °C (Table 6.21).

Table 6.21: The maximum rise of temperature measured with US system

Average flow rate [L/h]	**Amplitude** [%]	**Effective power of US device** [kW]	**T_{sample}** before / after [°C]	**ΔT** [°C]	**Pressure level**
200	100	2	10,7 / 12,5	1,8	No counter pressure
400	100	2	9,1 / 9,9	0,8	No counter pressure
520	100	2	7,7 / 8,7	1,0	No counter pressure
800	100	2	8,7 / 10,2	1,5	Counter pressure 1,3 - 1,7 bar
800	100	4	13,4 / 15,4	2,0	No counter pressure
1600	100	4	8,9 / 9,9	1,0	Counter pressure 1,2 - 1,7 bar

The differences in the measured temperatures (before and after treatment) are due to the different test phase. The increase of the temperature equals to the energy level exposed to the water (Table 6.13). The increased temperature levels generated by the US treatment fit into the daily variation of the water temperatures in the Baltic Sea at the time scale of the test trials.

7 OZONE TREATMENT

The test trials with ozone were conducted simultaneously with the trials of UV and US. The general arrangements of the onshore test trials have been described in chapters 3 and 6. Instead of the flow-through arrangement used previously in laboratory trials (DTR 3.3), the contact time was extended by introducing ozone to two contact tank of different size, 60 L and 360 L. The aim was to monitor the ozone dosage per water volume versus contact time. During the laboratory scale test trials in WP3 it was noticed that with the flow-through arrangement the contact times were too short in order to achieve contact time effective enough. Therefore various ozone dosages and contact times were studied and also long term test runs (24 h) were carried out.

Ozone gas was fed to the bottom of the tank with plastic pipe (inside diameter 4 mm) from ozone generator, and a diffuser was installed at the end of pipe in order to generate smaller bubbles. The contact tanks were stored indoors in order to keep them warm enough (around 6 - 12 °C) during the night time. The contact tanks were equipped with mixer (speed around 200 rpm in the smaller tank, around 57 rpm in the larger tank). The operational parameters during the trials are presented in the Table 7.1. The ozone dosages per water volume [mg/L] were constant during each test run.

Table 7.1: The operational parameters during the trials with ozone treatment

Contact time [h]	**Ozone dose** [mg/L]	**Water volume** [L]	**Total Organic Carbon** (TOC) mg/L	**T_{sample}** [°C]	**Test phase**	
					Sept.-Oct. 2002	Aug.-Sept. 2003
1	17	60	3,3 3,0	10,9 18,2	x	x
2	17	50		10,5 18,0	x	x
3	17	40		10,1 17,9	x	x
4	17	30		9,7 17,6	x	x
5	17	20		9,5 -	x	x
6	17	10		9,0 17,4	x	x
1	7	360		11,1	x	
2	7	300		10,7	x	
3	7	240		10,8	x	
5	7	180		10,8	x	
8	7	120		10,9	x	
24	7	60		10,4	x	

The Total Organic Carbon (TOC) values were analysed during the trials August - September 2003, once a day before the treatment, accordingly to the standard SFS-EN 1484 (1997), guideline "Total Organic Carbon Analyzer ASTRO Model 2001".

7.1 OZONE DEVICE

Ozone was generated from the ambient air by the ozone device "Ozonfilt® OXVa, Type 1", manufactured by ProMinent Dosiertechnik GMBH (ProMinent Finland, 2002), Germany. Ozone is produced by the reaction of an oxygen molecule and an oxygen atom with the principle of silent electrical discharge. The gas is passed through an electronic field produced between two electrodes. The air is treated to ensure it is dry and free from dust particles. Part of the oxygen in the air is converted into ozone in the electrical field. The air stream, which now contains ozone, is then fed to the contact tank for dissolving in water requiring disinfection. The device requires cooling water (tap water quality), pressured air for ozone production and electricity for function. Ozone device was mounted to a metal stand (Figure 7.1). The technical specifications of the ozone device are given in Table 7.2 (ProMinent Finland, 2002).

Figure 7.1: The ozone device during the onshore test trials

Table 7.2: Technical specifications of the Ozonfilt® OXVa, Type 1 device

Electrical connections	
Power consumption for ozone generation	< 0.15 kW
Power factor	0.7 cos f
Mains power supply	230 V / 50 Hz
Enclosure rating	IP 43
Switch input, pause (XPs)	Isolated, load: +15 V/max. 10 mA
Switch input, ozone warning device (XOz)	Isolated, load: +12 V/max. 1.5 mA
Standard signal input, Ozone reference value (XmA)	Isolated, resistance +1.7 V at +20 mA, input current
Alarm output (XUsr)	Isolated, change-over: 230 V/max. 8 A, free contact
Mixing equipment module	
Flow volume for OZVa, Type 1	0.5 - 3 m³/h
Raw water connector for OZVa Type 1	DN 32
Raw water temperature	< 35 °C
Pressure range in raw water pipe	0.2 - 2 bar
Total dimensions	
Width	1190 mm
Height	1300 mm

Depth	305 mm
Weight	70 kg
Compressor accessor	
Compressor mains power supply	230 V / 50 Hz
Average power consumption at max. operating pressure	0.18 kW

7.2 CONCEPT APPROVAL

The installation scheme providing a global view of the components and links with the ship installation is given below.

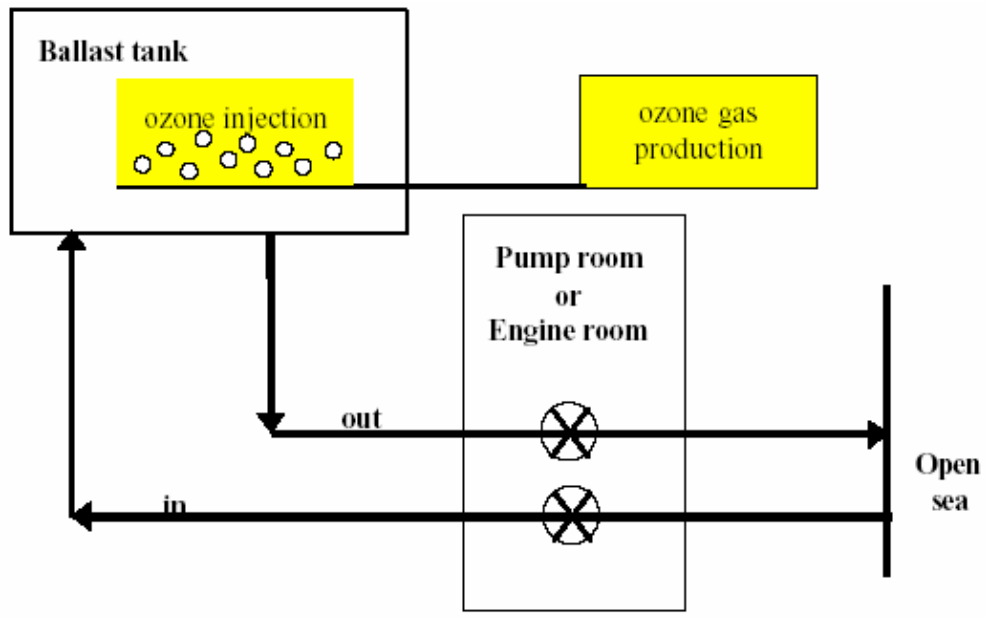


Figure 7.2: Ozone system diagram

The system is connected to the ballast water piping and uses components which exist on the ship and are well known ship equipment, except for the ozone generator, and have the following characteristics:

- Ozone generator and control console: modular installed outside ballast tank
- Diffusers and diffuser pipes in PVC or stainless steel, (AISI 316 or equivalent)
- Pumps: stainless steel, for example AISI 316, or equivalent,
- Counter pressure valve: stainless steel, for example AISI 316 or equivalent
- Power supply: 380 V AC

The review of the defined criteria in chapter 1 leads to the following conclusions shown in Table 7.3.

Table 7.3: Ozone criteria results

Criteria	Review Results
Stability	No tank filling different than those of the operational ship loading cases. No impact on stability.
Visibility	No modification of the loading cases, so of the trim, at sea. No impact on visibility.
Longitudinal strength of the vessel	No tank filling different than those of the operational ship loading cases. No impact on the hull girder strength.

Overpressure in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of overpressure.
Liquid motions in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of sloshing.
Piping	Use of well known marine equipment on ballast piping. No increase of risk.
Risk of fire	No specific non common equipments. No increase of the risk of fire.
Material and products	Use of well known marine equipment on ballast piping. No particular risks.
Ballast water composition	Modification of the water properties by the ozone water. Possible increased risk of corrosion but acceptable.
Biological efficiency	Good laboratory test results. Good results for onshore large scale test results. No onboard full scale test results.

The system analysis does not show any particular difficulty with respect to normal ship design and building. The biological efficiency has been proven in laboratory and for the large scale onshore tests. Considering the documents submitted, the system is granted with a Design Concept Approval.

To obtain a Final Concept Approval it is necessary to define the onboard required concentration and verify the full scale onboard feasibility. The Final Concept Approval will be granted after submission of the required documents reference number 6 and 9 to 15 of Table 1.2 (see chapter 1).

7.3 Risk and Safety Issues

A description of the system used for the large scale shore-based tests was provided by VTT. For an onboard installation, an ozone generator would be installed near the ballast water tanks. A filtration unit is required for primary treatment of the ballast water. The water would be filtered during ballasting. Ozone quickly decomposes to oxygen, so there would be no ozone residual in the ballast water that is discharged from the tanks. Figure 7.3 shows a simplified presentation of an ozone system installed onboard.

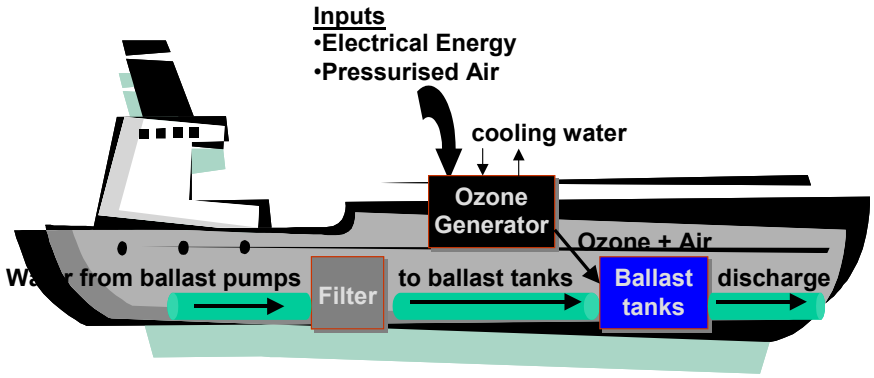


Figure 7.3: Simplified presentation of ozone treatment system

7.3.1 Hazards

As described in WP3, the most serious hazard associated with ozone treatment of ballast water is that of the ozone gas, which is a corrosive gas that can cause extreme irritation of the respiratory system. A very small leak of gas can result in unacceptable ambient ozone levels. There is the possibility in the event of an equipment or piping

failure for ozone to be released near the ozone generator or at any point along the piping system leading to the ballast tanks. The ozone will be pumped into the ballast tanks but there is also the potential for it to accumulate in air spaces within the tanks if mixing within the ballast water is not complete. Other hazards include electrical hazards associated with the ozone generation equipment, potential overheating of the equipment (fire), and possible biohazards if solids from the filtration unit need to be handled (DTR 3.5).

The hazards associated with the ozone treatment system would be present within the vicinity of the ozone generator, the piping system carrying the ozone gas to the ballast tanks, and the tanks themselves before the ozone decomposes. There is the potential for contamination of other areas of the ship if there is a leak in the ballast water tank or if the ozone gas accumulates in the head space above the ballast tanks and leaks to other parts of the ship.

7.3.2 "WHAT-IF" ASSESSMENT

"What if" questions developed during WP3 and WP4 included the following:

- What if the pipe from the ozone generator to the ballast tank breaks or develops leaks?
- What if there is a leak of ozone from the ozone generator?
- What if there is a leak from the ballast tanks when the water contains ozone?
- What if ozone accumulates in the head space above the ballast tanks and leaks to other areas of the ships?
- What if the ozone generator overheats?
- What if the ozone detector is not maintained or malfunctions?
- What if the activated carbon filters aren't maintained regularly?
- What if the cooling water piping system leaks?

7.3.3 POSSIBLE RISK REDUCTION MEASURES

Risk reduction measures to address the "what if" questions and other potential safety issues included:

- Equipment safety features: The ozone generator to be used for ballast water treatment has been developed according to applicable to EU and national guidelines and has many safety features to minimise risks. These include:
  - detectors to ensure the cooling water flow is above a minimum value
  - a non-return valve to prevent the ozone from passing back out of the generator
  - valves to control pressure, emergency shut-off switches and temperature regulators.
- Installation of alarms and ozone detectors in the room housing the ozone generator.
- Appropriate ventilation in the location of the ozone generating equipment.
- A control unit and alarm systems for the generator would be placed in the engine room.

- The ballast tanks would be equipped with activated carbon filters to remove excess ozone and would also have ozone monitors connected to the alarm system.
- Pipes, particularly those carrying ozone, should be inspected regularly.
- Operator training should be implemented to ensure the hazards are well understood and that there are established procedures for maintenance and for ensuring detectors and alarm systems are working properly.
- Emergency procedures should be put in place for dealing with leaks and alarms.

7.4 ENVIRONMENTAL IMPACTS

Results from the full scale tests were provided by the system designer. For materials and energy use, quantities estimated for the case study work were used. Environmental impacts resulting from the ozone treatment method, based on data collected during large scale testing and from the case study estimates, are discussed below.

7.4.1 PRODUCTION PHASE

The system developer, VTT, provided estimates for materials use for ozone treatment equipment to treat 2000 m^3 of ballast water. The estimated materials use was as follows:

- weight: 2,000 kg: approximate materials composition:
  - ozone generator, stainless steel
  - control unit: painted steel

Emissions to air resulting from production of steel for the ozone generator and control unit (2000 kg steel) were estimated. Emissions categories included gases that contribute to global warming (greenhouse theme), gases that contribute to acidification (acidification theme), and gases that contribute to the formation of tropospheric ozone (tropospheric ozone precursors theme). Table 7.4 shows the amounts of the major types of emissions according to these "themes", and also shows the equivalents totals for each of these themes.

Table 7.4: Emissions resulting from production of steel for ozone generator and control unit

Theme	Type of Emission	Amount (kg)	Conversion Factor	Equivalent Value
Greenhouse	CO_2	1984	1	1984
	CH_4	5	23	110
	N_2O	0.013	296	4
Total CO_2 equivalents(kg)				2098
Acidification	NO_x	3.1	1/46	0.07
	$SO_2 + SO_x$	4.9	1/32	0.15
	NH_3	0.002	1/17	0.0001
Total Potential Acid Equivalent (kg PAE)				0.22
Tropospheric Ozone Precursors	NO_x	3.1	1.22	3.76
	CO	0.5	0.11	0.05
	CH_4	4.8	0.014	0.07
Tropospheric Ozone Forming Potentials (kg TOFP)				3.88

7.4.2 OPERATIONS PHASE

Fuel is required to generate energy to operate the ultrasound treatment equipment. As for other treatment systems, it was assumed that marine diesel fuel was used and the IPCC standard emission values per tonne of fuel, as shown in Table 2.4 (see chapter 2), were used for this assessment. For the life cycle assessment, it is estimated that the ship makes 25 voyages per year where the 2000 m^3 of ballast water is treated. The power consumption for each treatment is estimated by VTT to be 420 kWh, which requires 118.5 kg of diesel fuel to produce. The life cycle of the equipment is estimated as 20 years. Using these assumptions, a total of 59.3 tonnes of fuel would be used over the life of the equipment. Emissions associated with this fuel use are shown in Table 7.5.

Table 7.5: Emissions related to energy use over life cycle operation of US system

Theme	Type of Emission	Amount (kg)	Conversion Factor	Equivalent Value
Greenhouse	CO_2	186121	1	186121
	CH_4	17.8	23	409
	N_2O	4.7	296	1404
			Total CO_2 equivalents(kg)	187934
Acidification	NO_x	4268	1/46	91
	$SO_2 + SO_x$	3557	1/32	111
			Total Potential Acid Equivalent (kg PAE)	204
Tropospheric Ozone Precursors	NO_x	4268	1.22	5207
	CO	439	0.11	48
	CH_4	18	0.014	0.25
			Tropospheric Ozone Forming Potentials (kg TOFP)	5255

Notes: Conversion factors for greenhouse gases to CO2 equivalents from IPCC 2001
Conversion factors for PAE and TOFP from Hass (2002).

7.4.3 COMPARISON OF EMISSIONS BY LIFE CYCLE STAGE

Emissions values for both the equipment production and operations phase of the ozone treatment system is presented in Table 7.6. For all three categories considered the operations phase is dominant, accounting for more than 98.9% of emissions during the life cycle.

Table 7.6: Emissions over production and operation phase of ozone system

Theme	Production		Operation	
	kg	% life cycle	kg	% life cycle
Greenhouse theme: Total CO_2 equivalents	2098	1.1	187934	98.9
Acidification: Total Potential Acid Equivalent (kg PAE)	0.22	0.1	204	99.9
Tropospheric Ozone Forming Potentials (kg TOFP)	3.88	0.1	5255	99.9

7.4.4 DIRECT IMPACTS THROUGH DISCHARGE TO RECEIVING WATER

Discharge of water with altered quality

No water quality measurements were taken during the large scale testing. The only direct change to water quality is an increase in ozone concentration in the treatment tanks. Ozone is highly reactive, and it is expected the residual would be negligible. Ozone decomposes to biatomic oxygen (O_2) at normal temperatures. The corrosion study carried out during WP3 noted that a significant increase in redox potential is

expected as a result of the treatment. The increased corrosiveness of the ballast water may result in elevated metals levels (iron from the steel tanks, zinc and/or aluminium from sacrificial anodes) in the ballast water to be discharged. The concentrations of metals would depend on the condition of the coating of the ballast water tanks.

Discharge of solids (organisms and sediments)
In a full scale onboard application, the ballast water would be filtered prior to ozone addition. Discharge of sediments could result in localised areas of increased turbidity. Turbidity increase would depend upon the amount of sediments present in the ballast water.

The treated ballast water would contain organic material in the form of dead organisms. The amount of organic matter would be dependent on the concentration of organisms taken on with the ballast water, with the larger organisms being removed by filtration. Impacts would vary depending upon the sensitivity of the receiving environment, with organics loading being more of a concern in eutrophic waterbodies.

Impact from surviving non-indigenous organisms
Different contact times and dosages were tested during the large scale trials. Both the 6-hour contact time with a dosage of 17 mg/l and the 24-hour contact time with a dosage of 7 mg/l achieved greater than 95% kill rates. Cladocerans were more tolerant of the ozone treatment than other types of zooplankton (DTR-4.4).

7.5 ECONOMIC ASPECTS

7.5.1 CAPITAL COSTS

The total investment costs for the Ozone system are approximately € 94,000, i.e. € 70,000 for the ozone generator (ozone production: 720 g/h), control unit and ejector pumps, € 20,000 for piping and diffusers, € 2,000 for the alarm system, and € 2,000 for the activated carbon filters. Installation of the ozone generator, control unit and piping will cost € 10,000. Testing costs for the first start-up and testing of the system are estimated to be € 1,000. There are no commissioning costs expected.

7.5.2 OPERATIONAL COSTS

The power requirement of the ozone system is 35 kW. Treating the amount of ballast water of 2,000 m^3 per trip will take 12 hours of the ozone system, resulting in an energy use of 420 kWh. The 4 ballast water pumps use together 200 kWh per trip. Per year 31,000 kWh will be used related to ballast water treatment.

Table 7.7: Total energy use

Total energy use		**Unit**
energy requirement per trip	620	kWh
kWh > MJ (electricity)	2,232	MJ (electricity)
MJ (electricity) > MJ (diesel)	7,440	MJ (diesel)
MJ >kg (diesel)	175	kg (diesel)
energy costs per trip (diesel)	70.02	€/trip
total energy costs per year (diesel)	**3,501.18**	**€/year**

No chemicals or other *consumables* are used for ozone treatment. No additional *personnel* will be involved running the system. It is expected that running the system

will take 5 man-hours per trip. This will be a crewmember with normal maintenance qualification. Costs related to this are not included in the calculations as for only a few of the other treatment systems involvement of the current crew onboard is specified.

TAM (Turn Around *Maintenance*) is expected at a yearly interval. Every year, one-day maintenance is expected resulting in TAM cost of € 1,000 per year. It is also expected that once in a ten year period extra maintenance is needed, resulting in € 12,000 material and personnel cost per ten years, i.e. € 1,200 per year.

It is expected that safety training is needed for 2 persons, total 15 hours. With an hourly rate of € 25, this leads to € 375 training costs per year. Handling safety and health issues lead to € 1,000. Certification costs are estimated to be € 1,000.

7.5.3 COST AND BENEFITS ASPECTS

There is no expected effect on tank cleaning costs. Cost of corrosion control is expected to increase. At this time no estimation could be made of % of increase in corrosion control cost. There is no delay in harbour or during trip expected. Installation of the system will lead to extra maintenance cost related to the replacement of PVC components, € 200 per year.

A preliminary estimation of the footprint of the equipment required onboard is 3 m^2. The equipment is 2.15 m high and has a weight of 2 tonnes. It is expected that installation of the ozone treatment system will have no effect on cargo space.

The next table shows the detailed calculation results for ozone.

Table 7.8: Ozone economic results

Cost type	Description	€ (euro)	Comments
Capital Costs			
Investment	investment costs	94,000	ozone generator, control unit, piping, alarm system and filters
Installation	installation costs	10,000	ozone generator, control unit and piping
Testing	testing costs	1,000	testing and start-up
Commissioning	commissioning costs		not expected
	total investment	**105,000**	**€**
Depreciation factors	depreciation period	10	years
	interest rate	8%	
	annual capital costs	**15,648**	**€/year**
Operational Costs		**€/year**	
Personnel	personnel during treatment	p.m.	€/year
Energy	energy (diesel)	3,501	€/year
Additives	additives use	0	
Maintenance	TAM (maintenance euro)	1,000	
	additional maintenance	1,200	material and labour costs
Training and management	training costs	375	2 persons, 15 hours total
	certification costs	100	certification costs € 1,000
	health and safety issues	100	handling H&S issues
Cost and benefits	tank cleaning costs	0	no influence
	corrosion costs	0	no influence
	costs of delay	0	no delay

	increased maintenance	200	replacement PVC
	loss of cargo space	0	no loss of cargo space
	annual operational costs	**6,476**	**€/year**
Total annual costs		**22,124**	**€/year**
Costs per treated m^3 ballast water	**50 trips / 100,000 m^3**	**0.2212**	**€/treated m^3 BW**

7.6 BIOLOGICAL ASSESSMENT

Ozone treatments were conducted in a 60 L tank (max. contact time 6 h) or in a 360 L tank (max. contact time 24 h) with 1 g O_3 / h or 2,5 g O_3 / h, respectively (Table 7.1).

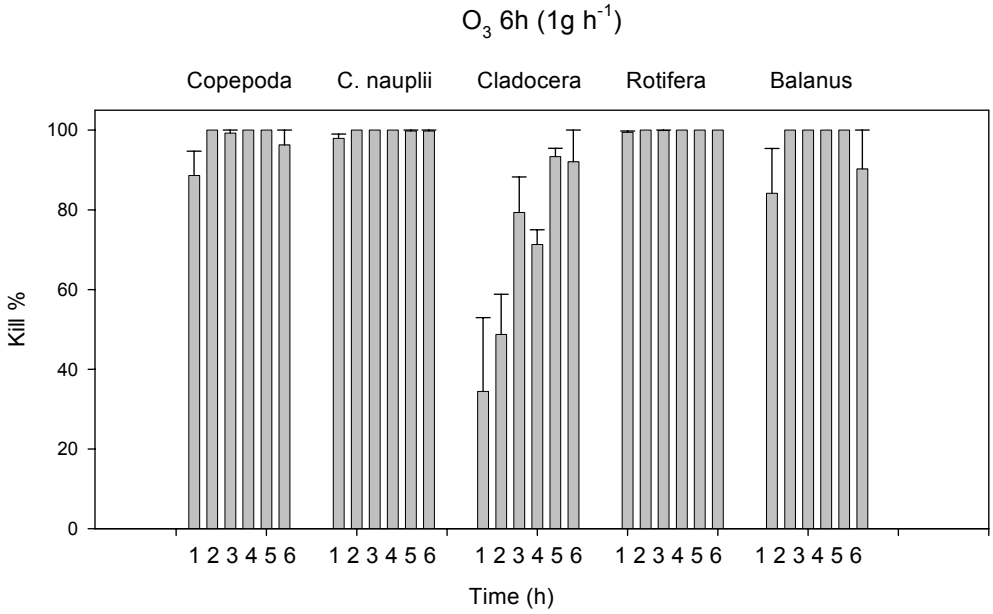


Figure 7.4: 6 h experiment (dosage 1 g O_3 / h, 17 mg/L).
Bars indicate the kill % after time periods of 1-6 h contact time (mean with S.E.).

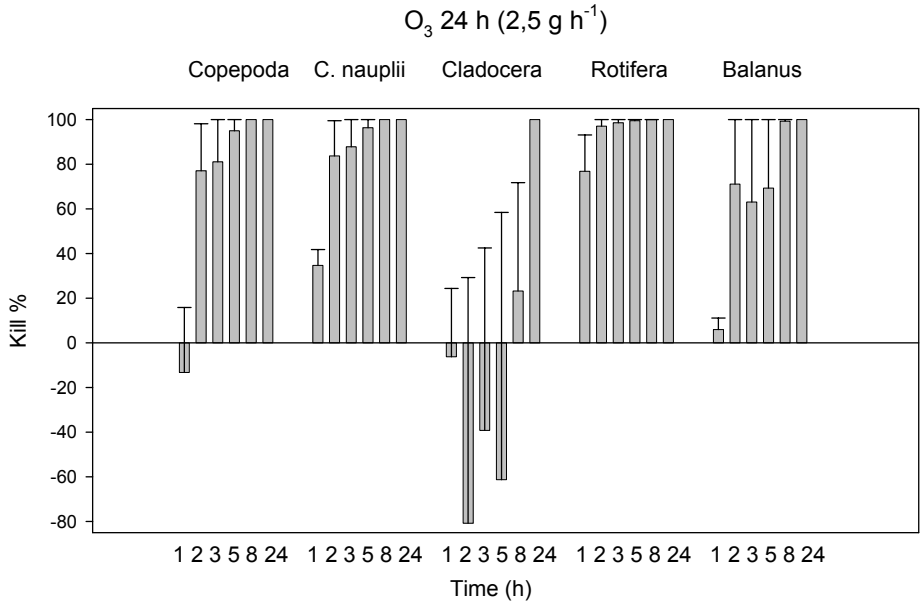


Figure 7.5: 24 h experiment (dosage 2,5 g O_3 / h, 7 mg/L).
Bars indicate the kill % after time periods of 1, 2, 3, 5, 8 and 24 h contact time (mean with S.E.).
Negative values in kill % indicate lower death rates as compared to initial samples (before treatment).

In most cases, total elimination of all mesozooplankton by the end of the experiment was achieved (Figure 7.4 and 7.5). In the shorter experiment the ozone dosage per litre was more than twice as high as in the longer experiment, in order to study acute toxicity versus long time exposure. The results are quite similar in both 6 and 24 h experiments, only the time required to kill organisms differ, being shorter in the shorter experiment. In the 6 h experiment, high death rates were observed already after the first hour and almost total elimination of zooplankton in 2 h (excluding cladocerans). In the 24 h experiment, 8 h was required to eliminate zooplankton (24 h for cladocerans). Ozone treatments seemed to have the most pronounced effect on rotifers, almost totally eliminated in the first hour in the 6 h experiment and in two hours in the 24 h experiment. Also copepod adults and copepodites as well as copepod naulpii were considerably susceptible to ozone. Barnacle nauplii, on the other hand, were not as drastically affected, although only two replicates were made in the 24 h experiment. The most tolerant group was cladocerans, surviving longest and being not totally eliminated by the end of the 6 h experiment. In statistical analysis, cladocerans differed from the other groups in the 6 h experiment (Kruskall-Wallis: H=56,519, df=29, p=0,002). In the 24 h experiment, however, no statistical differences were found, presumably due to large variation and small number of replicates.

In addition to killing mesozooplankton, ozone treatment also damaged live individuals. Figures 7.6 and 7.7 show the percentage of damaged individuals (if any) of total number of live individuals before treatment and after different incubation times.

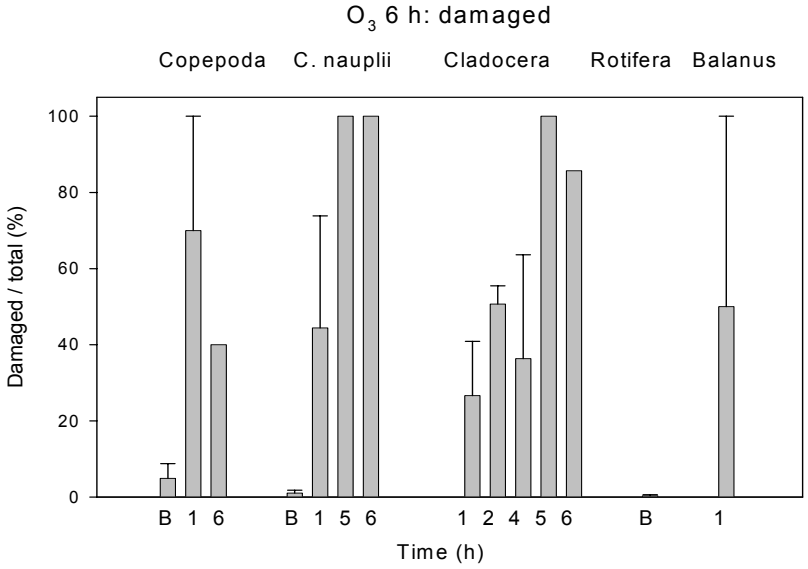
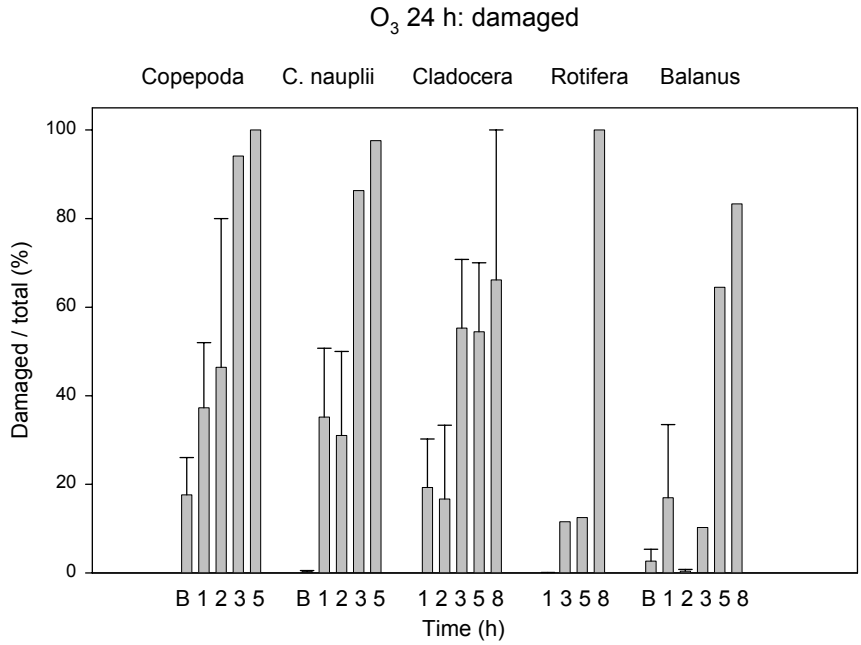


Figure 7.6: Percentages of damaged individuals, 6 h treatment.
B = situation before treatment (initial sample). Missing bars indicate either absence of damaged individuals (all living individuals were active) or absence of living individuals (all were dead).



Figures 7.7: Percentages of damaged individuals, 24 h treatment.
B = situation before treatment (initial sample). Missing bars indicate either absence of damaged individuals (all living individuals were active) or absence of living individuals (all were dead).

Obviously, the majority of individuals were actively swimming before treatment (low bars above letter B in Figures 7.6 and 7.7). However, in the course of the incubations, the percentage of damaged individuals tends to increase. The range of damages was wide, though; some individuals had only slight morfological injuries while others hardly noticeably moved. However, as damaged individuals have weaker escaping responses, they become more susceptible to predation. Therefore, even a minor decrease in the swimming ability will affect the survival of a plankter in field. The effect of any injury may thus be even as detrimental as total elimination.

8 OXICIDE TREATMENT

The results with the electrochemical cell in WP3 of the MARTOB project showed that only a very small part of the oxygen is converted into hydrogen peroxide. Therefore it was decided to design and built a new electrochemical reactor cell (generation 2 cell). Laboratory experiments with this new reactor cell were carried out to assess the best operating conditions for the production of hydrogen peroxide in artificial seawater.

It was decided to make a further change to the electrochemical cell design, in advance to the construction of the pilot (generation 3 cell, see section 8.2.3). The pilot-scale Oxicide set-up was designed and build with two generation 3 cells, which can be operated in parallel and in series. The pilot setup was tested on an onshore location in the harbour of Den Helder (the Netherlands). Results of the onshore tests are evaluated on the basis of hydrogen peroxide production, electrical efficiency, capacity and biocidal efficiency.

8.1 TECHNOLOGY DESCRIPTION

Since in work package 4 no changes were made to the fundamental process of the hydrogen peroxide production we refer to the report prepared for WP3 for the technology description paragraph (DTR-3.4).

8.2 OXICIDE EXPERIMENTAL SET-UP

8.2.1 CELL DESIGN

The design of a new Oxicide reactor is based on the results obtained during the previous work package. The main changes with respect to the first generation reactor and the expected advantages of these changes are:

- Improved oxygen feed to the sea water by using a cell gard system in front of the electrochemical cell. The commercially available Cell gard system makes it possible to easily reach high oxygen concentrations (40 mg/l or more at 20°C and P_{oxygen}= 1 bar).
- Larger dimensions of both the graphite felt electrode (cathode) and the dimensional stable anode (DSA). This should increase the oxygen reduction efficiency and thus increase the hydrogen peroxide production rate.
- The increased dimensions also make it possible to have a higher throughput of the system.

The re-designed electrochemical cell for the hydrogen peroxide production was manufactured by Van den Heuvel Watertechnologie in the Netherlands. The cell was received at TNO early April. First tests revealed that the cell was leakage proof but that the anode had to be modified to obtain the desired dimensional stable anode (DSA). This delayed the first electrochemical experiments by two weeks. The picture in Figure 8.1 shows the two cell parts (left anode, right cathode) of the generation-2 design.

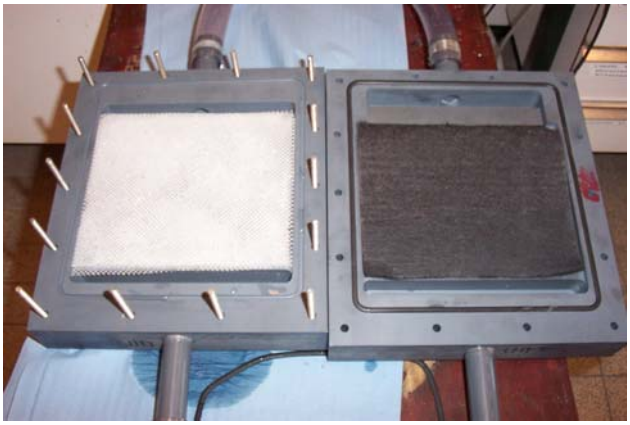


Figure 8.1: Picture of the generation-2 electrochemical cell.
Left the anode compartment, Right the cathode compartment, showing the graphite felt.

8.2.2 LABORATORY SET-UP AND EXPERIMENTAL CONDITIONS

The description of the laboratory setup for the production of hydrogen peroxide with the generation-2 cell design is discussed in DTR-3.4.

All laboratory experiments were performed batch wise, using artificial sea salt dissolved in tap water as catholyt and a 0.1M nitric acid solution as anolyt. Experiments were run in a galvanostatic mode, i.e. using a constant electrical current on the electrochemical cell. The production of peroxide is measured using the spectrophotometer method described in WP3.

8.2.3 PILOT SET-UP AND EXPERIMENTAL CONDITIONS

A new Oxicide cell (generation-3) was defined for the pilot, because results from the laboratory experiments gave rise to the suspicion that the electrical contact with the 3-D carbon felt electrode was limiting the production rate in the scale-up cell of the 2nd generation. For that reason contacts for the graphite felt were made on both sides in the generation-3 cell; also cell dimensions were changed a little.

The pilot setup is build with two Oxicide modules both build up from one Cell gard module in series with an electrochemical cell. The two Oxicide modules can be run both in series and parallel. In the parallel mode the throughput (flow) is highest while the series mode can be used to obtain the highest output concentration of hydrogen peroxide. The setup makes it also possible to run with only one of the two Oxicide modules (both possible).

Both the generation-3 cells and the pilot setup were built by Van den Heuvel Watertechnologie in the Netherlands. Due to a delay in delivery of the hose pump the pilot setup was delayed for more than a month. This delay made it impossible to test the pilot setup before going to the onshore testing location. Figures 8.2 and 8.3 depict the pilot setup on location in Den Helder. The pilot setup is 2m in height, 1.2m in width and 0.6m in depth. The pilot is electrically connected to the 380V (16A) AC mains.

The seawater was obtained from a constant flow of water that was pumped up from about 7 meters deep at the end of a pier in the middle of the naval harbour of Den Helder. The harbour has an open, direct connection with the North Sea. The seawater

enters the Oxicide pilot in the 100 litre stock vessel. From here the water is pumped through a 150µm filter towards the Oxicide modules, using a hose pump (maximum flow 800 litres/hour).

The oxygen flow through the in series connected Cell gard modules is controlled using an adjustable gas flow meter. The oxygen is obtained from a 50 litres oxygen gas cylinder connected to the pilot rig.

The peroxide production is measured using an in-situ peroxide sensor (Dulcometer D1C from Prominent). The sensor continuously measures the peroxide concentration in parts per million (ppm □mg/l) in the sea water which leaves the Oxicide modules. Figure 8.2 shows the peroxide sensor setup. Beside the concentration of peroxide also the oxygen concentration and the temperature of the seawater are continuously monitored.

For safety reasons the pilot setup is build above a drip tray with a leakage detector that turns-off the electrical circuit and electrolyte pumps when a large volume is spilled. Another safety measure was a chlorine detector placed just above the spill tray. Chlorine can be formed when the chloride ions in the seawater come in contact with the anode. This might happen when there is leakage through the membrane. The chlorine detector turns-off the electrical system and pumps when the chlorine concentration in the air is higher than 10 ppm.

Figure 8.2: Pictures of the Oxicide pilot setup on location in Den Helder.
The picture on the left shows the front of the complete setup. The picture on the right shows in more detail the aeration-modules (bottem) and the electrochemical cells (top).

Figure 8.3: Picture of the on-line hydrogen peroxide sensor unit.
In the measuring vessel also the temperature and oxygen concentration are measured

The effect of hydrogen peroxide and the Oxicide treatment on zooplankton was assessed in the tests performed in TNO laboratories and in Newcastle during WP3. The results on phytoplankton were much less clear, especially during the Newcastle trials. With this in mind and knowing that there were no fundamental changes in the Oxicide technology in WP4, it was concluded that follow-up work should be focused on phytoplankton removal efficiency. Originally, it was anticipated to do onshore tests in Finland, where a team of experts would be available to perform the bio-assays. Due to a delay in delivery of the pilot setup the tests were postponed and replaced to an onshore site in the Netherlands. Limited facilities were available for bio-assays, it was decided to focus on chlorophyll counts and activity measurements because phytoplankton results of WP3 were not unambiguous. These measurements were performed using a Moldaenke BBE 1-Hz-Kuvetten-Fluorometer at the TNO-Environment, Energy and Process Innovation location in Den Helder. To determine the effect of the Oxicide method the seawater was sampled after leaving the Oxicide system. Reference samples of the fresh seawater were taken from the 100 litre stock vessel. No samples were conserved, for phytoplankton counts by external labs were anticipated.

8.3 LAB SCALE RESULTS

Figure 8.4 shows the influence of different types of graphite felt used as cathode material on the hydrogen peroxide production. In these experiments a 5 litre artificial sea water batch is circulated over the Oxicide reactor. The electrochemical cell is operating under a constant electrical current of 4.5 A.

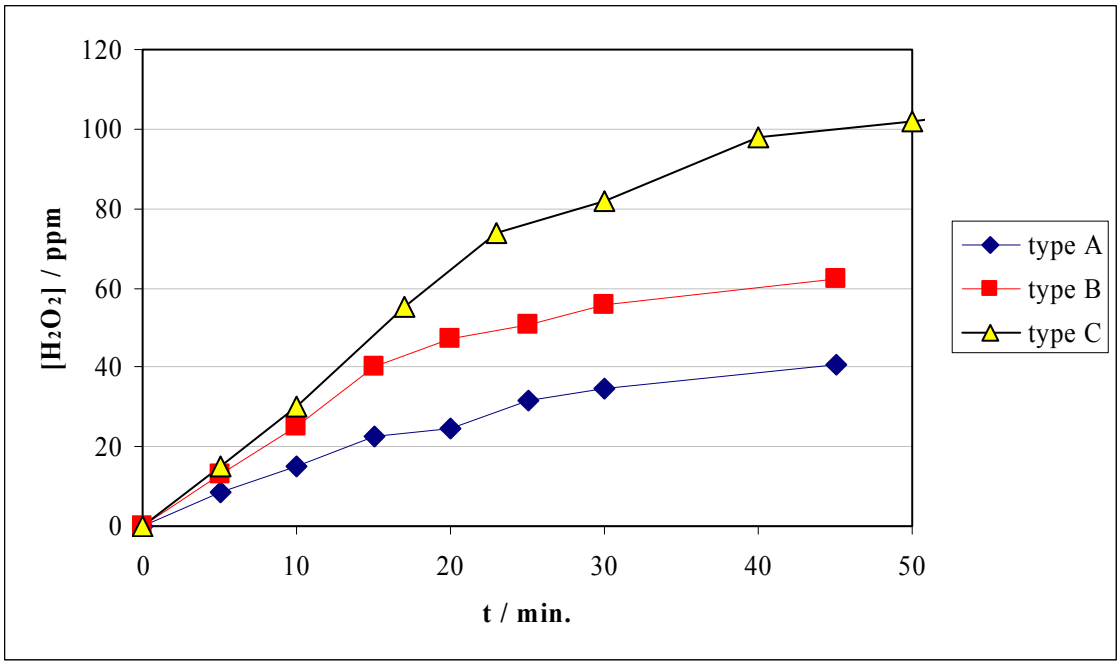


Figure 8.4: Influence of the type of graphite felt (A,B,C)on the production rate of H_2O_2

The plots clearly show the different production behaviour of the three types of felt (type A < type B < type C).

Two values obtained from these curves are of importance. First, the value of the end concentration, obtained after approximately 1 hour. This value indicates the maximum concentration that can be obtained with this Oxicide configuration in a recirculation system. Second, the value of the slope of the production curve at t=0. This value corresponds to the production rate for this configuration for a system operating with peroxide free seawater.

The production rate measured from the slope of the production curve at t=0 will be used in this report to evaluate the different configurations and variations of the Oxicide system tested in this work package. The value is noted in grams produced hydrogen peroxide per square meter cell membrane per hour (g/m^2h) in order to compare the production rate of the system with other Oxicide cells.

Table 8.1 shows a summary of the laboratory experiments performed. Variations were made in the type and thickness of the graphite felt, oxygen concentration, current density and the salt concentration of the catholyte. All these experiments were performed with a catholyte flow rate of 200 l/h. For a comparison the value for the *maximum* production rate obtained in WP3 is added (14 g/m^2h). Several conclusions are drawn up from the experiments in Table 8.1.

Table 8.1: Overview of the laboratory experiments with the generation-2 electrochemical cell.

Exp	Current A	Graphite felt	O2 in ppm	O2 out ppm	salt *) g/l	prod.rate g/m2h
WP3(max)						14
A	2.9	C	37.4	29.9	33	23.2
B	4.5	C	39	31.5	33	39
C	6	C	40.9	31.4	33	36.3
D	4.5	C	40	32.6	6	42
E	4.5	C	39.8	31.1	0	34.5
F	4.5	A	38.8	29.8	33	17.3
G	4.5	B	39.9	34.6	33	26.7
H	4.5	C (1.5x)	40.6	31.1	33	17.6
I	4.5	C	25.5	18.6	33	25.2

O2-in represents the oxygen concentration in the catholyte with the current switched off (no peroxide production). O2-out represents the oxygen concentration measured 10 minutes after the electrochemical cell is switched on. Accuracy range of the productions rates is ± 5-10%.
*) sea salt added to tap water (containing approx. 0,1 g/l salt)

The production rates of the generation-2 cell show a large improvement compared to the first generation cell used in WP3. The production rate is increased from a maximum of 14 g/m^2.h in WP3 to a maximum of 42 g/m^2.h with the generation-2 electrochemical cell. This improvement by a factor 3 shows that the new cell design and the change in operating conditions are successful.

Experiments A, B and C show the influence of the cell current on the production rate. The increase in peroxide production found when increasing the current from 2.9A (exp A) to 4.5A (exp B) is not followed by a further increase when the current is raised from 4.5 A to 6A (exp C). The slight decrease in the 6A experiment (exp C) can be explained by the observation of gas bubbles in the catholyte flow leaving the electrochemical cell. This indicates that part of the electrons is used to produce hydrogen gas at these high electrical currents.

$$2H^+ + 2e^- \rightarrow H_2\,(g)$$

The gas bubbles produced at the felt might cause a blockage of the graphite felt surface for reduction of oxygen to peroxide and therefore slightly decrease the production rate of H_2O_2.

Experiments D and E were performed to investigate the influence of the sea salt concentration in the catholyte on the hydrogen peroxide production rate. This experiment was performed because it was expected to do the onshore pilot tests in Finland; the Baltic Sea has substantial lower salt concentrations than the normal 33 g/l in oceans. The data of exp. B, D and E shows no remarkable difference between the three salt concentrations. Also no difference was measured in the voltage over the electrochemical cell. This indicates that the conduction in the electrochemical cell is not limiting to the process. The conduction in tap water may be contributed to the protons, which are supplied by the anolyte (HNO_3).

It is clearly shown that the type of graphite felt has a large impact (exp. F and G compared with exp. B). These three types of felt were chosen after contacting two

suppliers and research via the worldwide web. The standard type C felt proofs to have the highest production rate.

To investigate the influence of the thickness of the felt a 50% thicker felt of the same type was used in experiment H. The production rate of this felt showed to be much lower than that of the standard 5mm thick felt. A plausible explanation for this behaviour could be the increase potential drop over the felt with increased thickness. Due to the enlarged potential drop unwanted side reaction, such as the reduction of oxygen to form water (see below), become more favourable leading to a lower hydrogen peroxide production.

While all the experiments described above were performed with the highest possible oxygen concentration (~40 ppm) in the catholyte, experiment I shows the effect of a much lower oxygen concentration (25 ppm). Clearly, the higher concentration gives the higher output of hydrogen peroxide. Only a small part of the oxygen is reduced in both cases, because the effluent contains still ~75 % of the influent oxygen concentration.

From the measured H_2O_2 production rate we calculate that approximately 40 to 60% of the decrease in the oxygen concentration, equalling to approximately 9ppm, is used for the production of hydrogen peroxide. The other oxygen consumption in the cell is due to the reduction of oxygen with protons to form water:

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O_2$$

As a result, only 10 – 15% of the oxygen in the influent is used to produce peroxide. Further improvements of the Oxicide process are considered possible, since ~75% of the oxygen leaves the cell without being reduced.

From the raw data (not shown here) we calculate a value for the initial current efficiency of the generation-2 system between 20 - 35%. This is rather low and indicates that a substantial part of the electrical current is used for competing reactions like water production, HO_2^- reduction and - at high currents- hydrogen gas formation. For that reason it once again concluded that further improvements of the process should be possible.

Because of the positive results obtained with the generation-2 cell design it was decided to make only a minor adjustment to the cell design to be used in the pilot setup. The generation-3 cells have the possibility to contact the graphite felt on both sides (in and outlet side) of the electrochemical cell instead of only on the inlet side with the generation-2 design.

8.4 ONSHORE TEST RESULTS

8.4.1 FIRST SESSION (AUGUST 2003)

The start of the pilot tests was delayed by approximately 6 weeks, due to late delivery of some major parts and serious start-up problems with the catholyte hose pump. As a consequence, no time was available to do preliminary laboratory tests; it was decided to bring the pilot plant straight away to test location in Den Helder (the Netherlands).

Several (small) problems with the pilot installation and the hydrogen peroxide sensor were observed, which delayed the actual testing for another couple of days.

The pilot uses new generation-3 electrochemical cells. During the first tests extremely low production rates of less than 0.6 mg/l (<5 g/m^{2}h) were found for these cells both in parallel and series configuration. This forced us to perform substantial trouble shooting work in order to find the cause of the low production (see section 8.4.2). The various parts of the cell including the graphite felt, spacer and membranes were checked and replaced one by one. All systematic changes showed no improvement of the production rate.

With some small changes to the in and outlet construction of the generation-2 cell it was possible to fit this cell into the pilot. The generation-2 cell was tested in Den Helder producing approximately 6.5 mg/l hydrogen peroxide. This production was reached with a catholyte flow of 250l/h in single cell, once-through mode, and a cell current of 4.5A. The output of 6.5 mg/l equals a production rate of 55 g/m^{2}h even higher than that obtained in the laboratories experiments described above. The dissolved oxygen concentration was 30.4 mg/l with the cell switched off and 18.1 mg/l with the cell switched on. The pilot functioned very well during these tests.

Figure 8.5 shows the production curve of an experiment with the generation 2 cell and a cell current of 4.5A. In this experiment, 94 litres of seawater is circulated over the system with a flow rate of 200 l/h. The seawater, which is contained in a buffer tank, is not shielded from the light.

The curves show the same shape as those obtained in the laboratory experiments previously described. With this one cell and the 94 litres a concentration of approximately 10 mg/l is reached within 30 minutes.

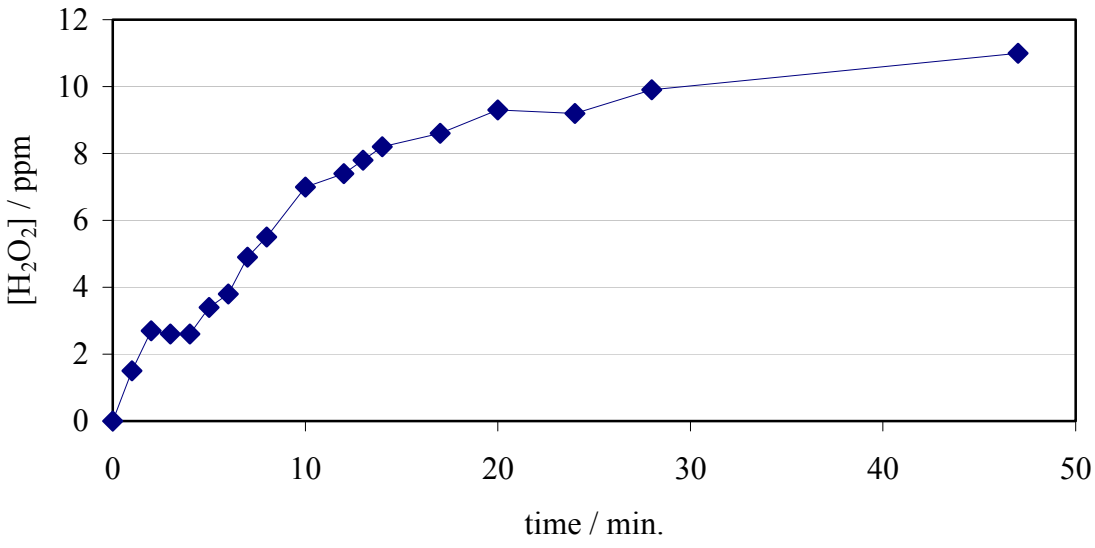


Figure 8.5: H_2O_2 production curve for 94 litres of seawater

The search for the reason of the low production rate in the generation-3 cells was continued for some days in sessions of operation with Van den Heuvel Water Technology, but without success. This ended the first onshore tests in Den Helder in August.

8.4.2 LABORATORIES COMPARISON GENERATION-2 AND 3 CELL DESIGN

To investigate the odd behaviour of the generation-3 cell, both the 2nd and 3rd generation were tested in the laboratories of TNO Apeldoorn. One of the possible reasons for the difference could be a different coating on the dimensional stable anode (titanium). Figure 8.6 shows the hydrogen peroxide production curves of the two anodes in the same generation 2 cell as an example to the search for the origin of the odd behaviour. No difference in production rate can be observed. The firm who coated the titanium electrode also confirmed that the coatings on the anodes were identical.

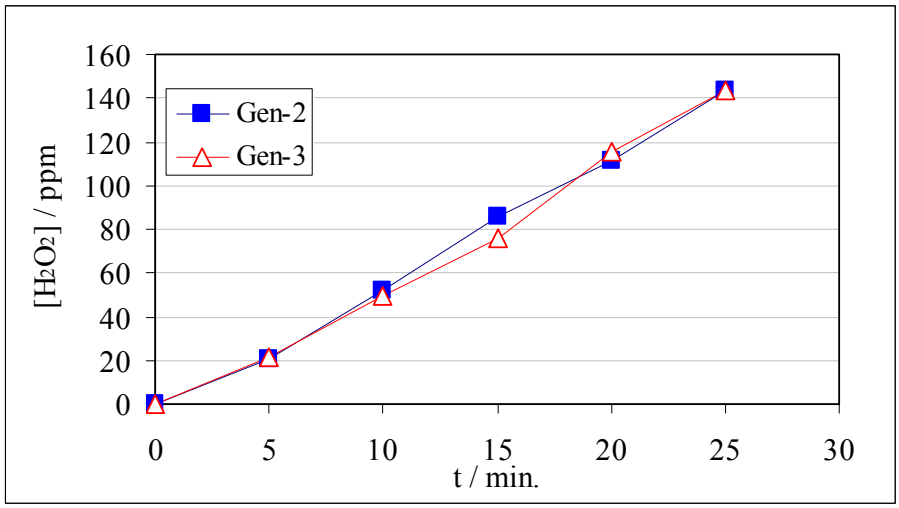


Figure 8.6: production curves measured in the generation-2 electrochemical cell. Blue: using the gen-2 anode; Red: using the gen-3 anode.

Subsequently experiments were performed in which the different membranes, felts and spacers were tested in one cell setup. All these experiments showed results similar to those in Figure 8.6. In other words, the very low production rates observed in the pilot test with generation 3 cells could not be reproduced in the laboratory.

8.4.3 SECOND SESSION PILOT TESTS (OCTOBER 2003)

In October 2003 a second test series was performed in Den Helder. The pilot setup was now run with both a generation-2 and a generation-3 cell. Both cells now performed well and showed a very similar hydrogen peroxide production rate. Previous results of the pilot tests with 3rd generation cell therefore remain unexplained.

Similar to the first session the phytoplankton activity was still too low to measure (which is normal in this time of year). Therefore only the peroxide production of the Oxicide pilot was monitored.

Figure 8.7 shows the results of experiments in which we varied the flow rate and the cell electrical current. The hydrogen peroxide output concentration of the pilot is

given at different cell currents for 5 different situations. The legends show the configuration, two cells parallel or series, and the total catholyte flow rate.

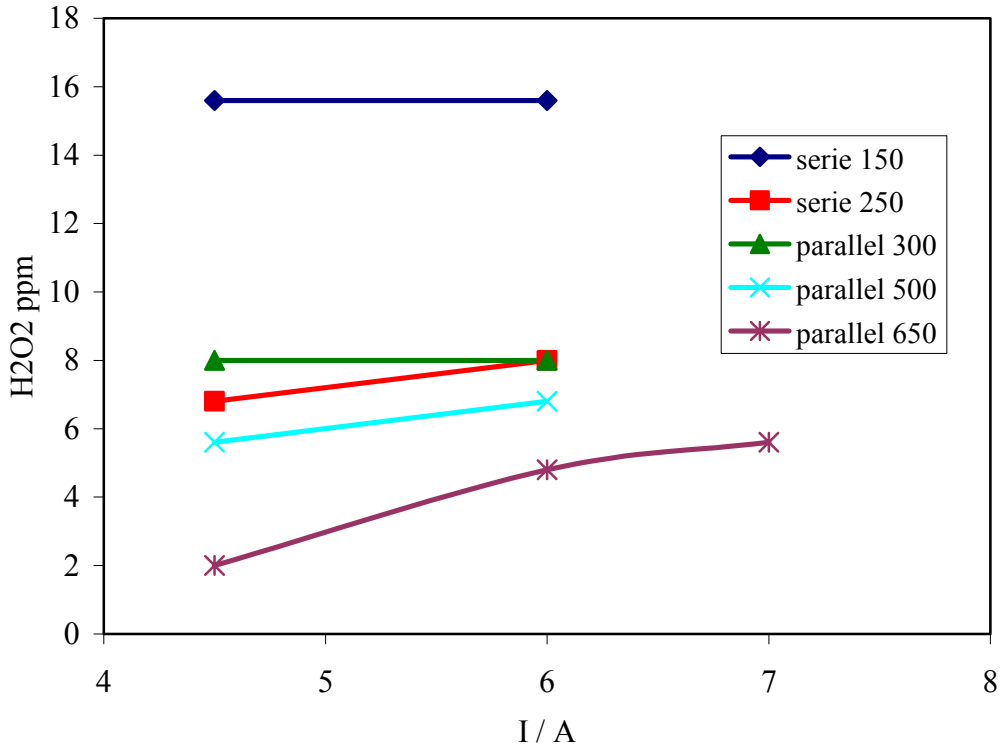


Figure 8.7: Output concentration of the pilot installation as function of the electrical current
The legend shows the configuration of the setup (cells parallel or in series) and the total flow rate in l/h.

As expected, the highest H_2O_2 concentrations are obtained for in series connected cells with a low flow rate (150 l/h) of seawater.

The values in the figure above are recalculated to the normalized production rate in grams per square meter of cell membrane per hour and plotted in Figure 8.8. Due to the low flow rate c.q. the high final concentration, the 150 l/h-serial cells experiment can now be found in the middle of the graph. The highest production rate is observed for two cells connected in parallel with a high flow rate of 500 or even 650 l/h. The data even suggest that for this configuration higher electrical currents might be possible to give an even higher production rate.

This can also be observed in Figure 8.9, which shows an overview of the current efficiency of these experiments. As expected, the two experiments with a high flow rate and parallel cells show the highest current efficiencies.

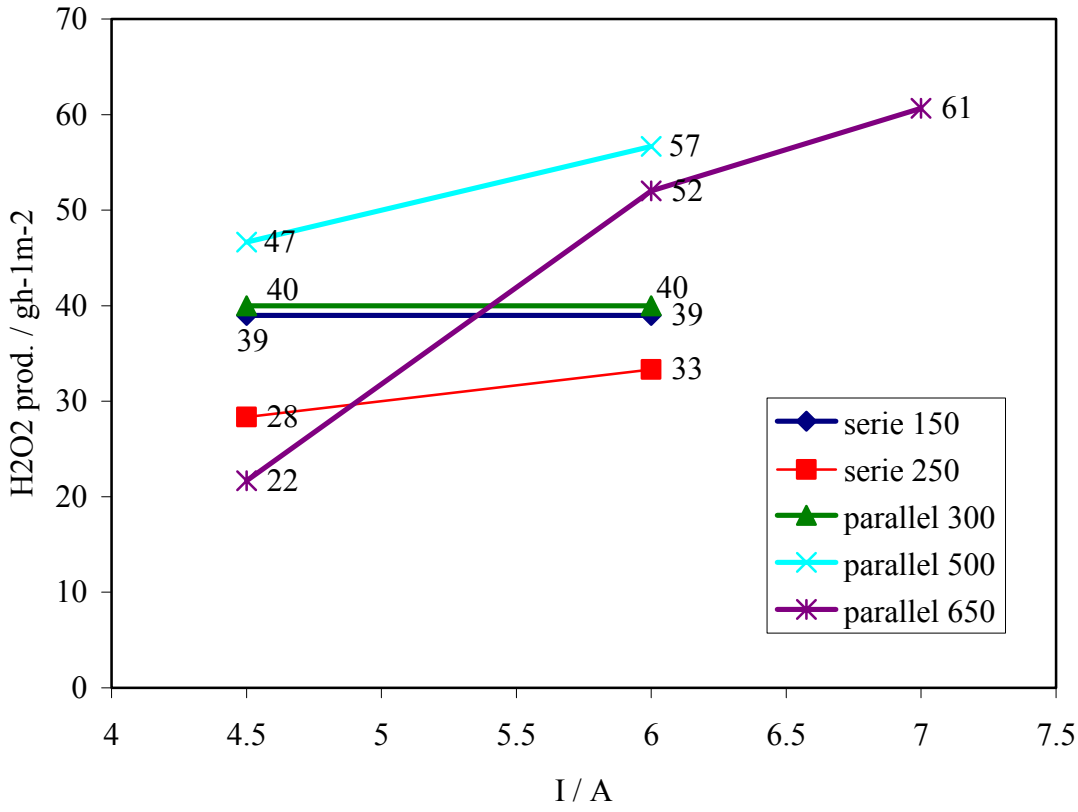


Figure 8.8: H_2O_2 specific production rates, calculated from the data in Figure 8.7.
The legend shows the configuration of the setup (parallel or series) and the total flow rate in l/h.

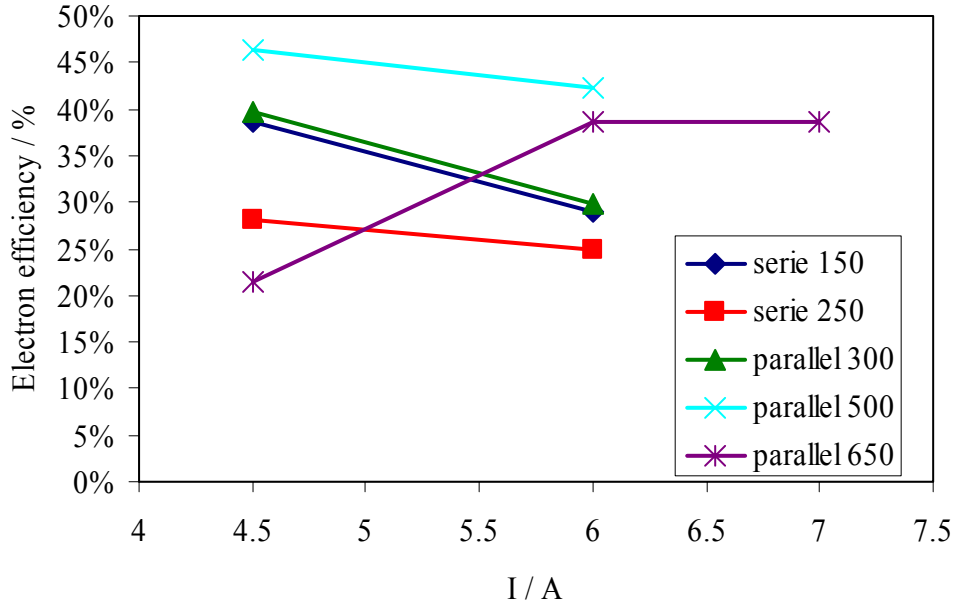


Figure 8.9: Current efficiency, calculated from the data shown in Figure 8.7.
The legend shows the configuration of the setup (parallel or series) and the total flow rate in l/h.

8.4.4 ENDURANCE TEST (NOVEMBER 2003)

A full continuous duration test was started in the first week of November 2003. The experimental conditions were set to:

- Two parallel Oxicide cells
- Constant current mode 4.5A
- Catholyte (seawater) flow rate 400 l/h, equalling to 200 l/h per cell
- Anolyte flow rate 400 l/h (200 l/h per cell)

The pilot produced hydrogen peroxide for the planned period (4 days), but was interrupted in two occasions. One was due to a general blackout of the electricity supply. This caused the Oxicide pilot to stop for about 12 hours. The second interruption was due to an empty oxygen cylinder, which had to be replaced. In this occasion the production was stopped for a few hours. The peroxide production, which was recorded approximately 2 times a day, was remarkable stable over the test period (see Figure 8.10). The sensor was calibrated before and after the experiment using a standard 100ppm solution, prepared from a concentrated hydrogen peroxide stock solution (Merck 30% p.a.).

The output of approximately 9 mg/l hydrogen peroxide corresponds to a specific production rate of almost 60 g/m^{2}h, the highest value obtained so far.

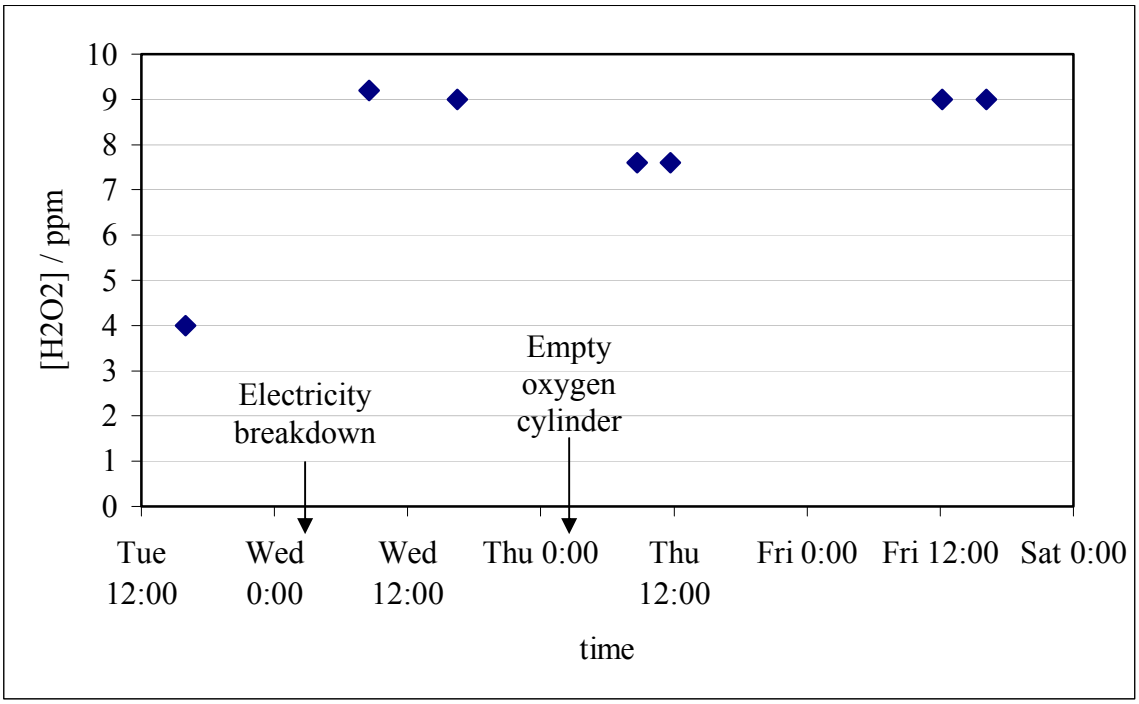


Figure 8.10: 4 day's duration test of the Oxicide pilot on location.
Start up: Thursday afternoon

8.5 CONCEPT APPROVAL

The installation scheme providing a global view of the components and links with the ship installation is given below.

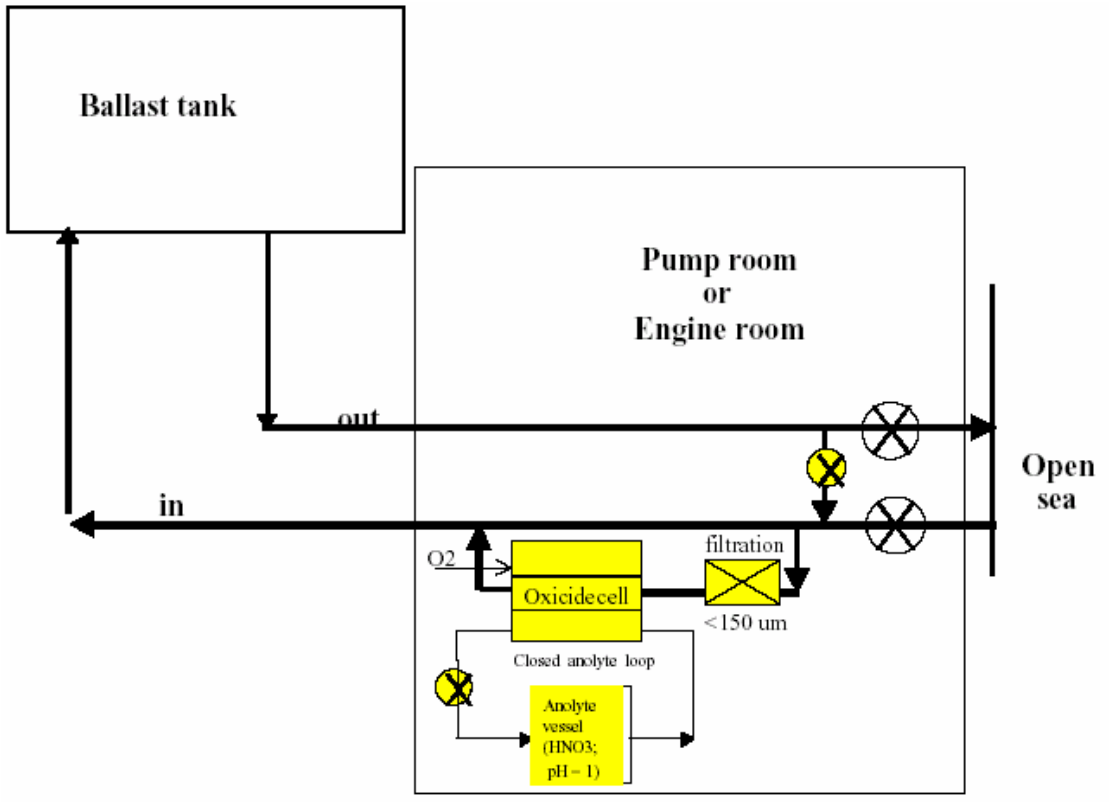


Figure 8.11: Oxicide system diagram

The system is connected to the ballast water piping and uses components which exist on the ship and are well known ship equipment, except the hydrogen peroxide generator, and have the following characteristics:

- Filter: capable of removing particles > 150 um.
- Oxicide cell: a chamber in PVC/Polycarbonate with polymeric fibre membranes (DAM) plus a 3-dimensional carbon felt cathode
- DC power supplier: for electrochemical cell (3-4 V per cell), depending on the amount of cells in series, up to a maximum of 100 V DC.
- Anolyte vessel: est. 500-1000 dm3, containing the anolyte. In the anolyte compartment diluted (0.1 N HNO_3) nitric acid is circulated. This compartment is completely separated from the seawater by a cation exchange membrane (Nafion).
- Compressor: for pumping compressed air or in case of oxygen a compressed oxygen container
- Piping/pumps: chemical resistant pump, preferably centrifugal

The review of the defined criteria in chapter 1 leads to the following conclusions shown in Table 8.2.

Table 8.2: Oxicide criteria results

Criteria	Review Results
Stability	No tank filling different than those of the operational ship loading cases. No impact on stability.
Visibility	No modification of the loading cases, so of the trim, at sea. No impact on visibility.

Longitudinal strength of the vessel	No tank filling different than those of the operational ship loading cases. No impact on the hull girder strength.
Overpressure in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of overpressure.
Liquid motions in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of sloshing.
Piping	Use of well known marine equipment on ballast piping. Use of direct current requiring known precautions.
Risk of fire	No specific non common equipments. No increase of the risk of fire.
Material and products	Use of well known marine equipment on ballast piping. Use of non conventional products requiring specific procedures and protection.
Ballast water composition	Modification of the water properties by the ozone water. Possible increased risk of corrosion but acceptable.
Biological efficiency	Good laboratory test results. No results for on-shore large scale tests. No onboard scale test results.

The system analysis does not show any particular difficulty with respect to normal ship design and building. The biological efficiency has been proven only in laboratory; large scale onshore tests efficiency has not been measured. Considering the documents submitted, the system is granted with a Design Concept Approval.

To obtain a Final Concept Approval it is necessary to re-assess the large scale tests and conduct a full scale onboard test. The Final Concept Approval will be granted after submission of the required documents reference number 7 and 9 to 15 of Table 1.2 (see chapter 1).

8.6 Risk and Safety Issues

Figure 8.12 shows a simplified presentation of an Oxicide system installed onboard. Ballast water needs to be filtered before being passed through the Oxicide unit – this could either take place during ballasting activities or before the water is passed through the cells.

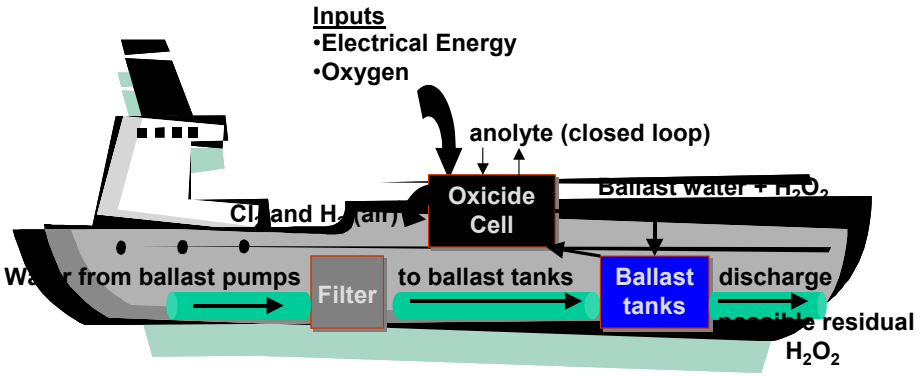


Figure 8.12: Simplified presentation of Oxicide treatment system

8.6.1 Hazards

During WP4, it was determined that chlorine gas could be formed if the chloride ions in the seawater come in contact with the anode. This could potentially occur if there is leakage through the cell membrane. Other hazards associated with the Oxicide method of ballast water treatment, as identified during WP3, include chemical hazards related to nitric acid (anolyte), hydrogen peroxide, and sodium nitrate. Nitric acid (0.1

N) is classified as a corrosive substance and can cause burns in contract with the skin. Inhaled vapours can cause irritation of the nose and throat and damage to the mucous membranes and upper respiratory tract. Sodium nitrate crystals are classified as an oxidizer (Class 5.1, UN Number 1498). It can cause irritation to skin, eyes, and the respiratory tract. It is a strong oxidizer and should be stored away from combustible materials. The maximum target concentration of ballast water of 20 g/m^3 hydrogen peroxide (this is approximately 0.002% by weight of hydrogen peroxide) to be produced during the treatment process is not considered an oxidizer or classified as dangerous goods.

There are also electrical hazards associated with the equipment; possible biohazards if solids from the filtration unit need to be handled; and hazards related to the potential of spills from additional piping. In addition, ballast water will be moved between tanks during the voyage – if there is a change in the volume of ballast water in specific tanks this could affect stability. A more detailed description of hazards is provided in DTR-3.5.

8.6.2 "WHAT-IF" ASSESSMENT

"What if" questions developed during WP3 and WP4 included the following:

- What if levels of chlorine gas build up near the electrochemical cell?
- What if the piping containing treated ballast water (with a maximum concentration of 20 g/m3 of hydrogen peroxide) leaks or breaks?
- What if ballast water containing hydrogen peroxide leaks from the ballast tanks?
- What if the anolyte tank (containing nitric acid), piping system, or pump leaks or ruptures?
- What if there is a spill of $NaNO_3$?
- What if there is an electrical problem with the equipment?
- What if there is a break in the inlet of the ballast water piping system?

8.6.3 POSSIBLE RISK REDUCTION MEASURES

Risk reduction measures to address the "what if" questions and other potential safety issues included:

- The room containing the treatment equipment should be well ventilated.
- There should be detectors and alarms in place for chlorine and hydrogen gas. For the shore based trial a chlorine detector was placed above a spill tray that was located under the cell. If chlorine was detected at concentrations above 10 ppm the electrical system and pumps would be automatically turned off (DTR-4.5).
- The complete anolyte system (tank, pump and piping) would be build above a save-all drip tray. A level switch in the tray would to detect leakage, send an alarm to personnel, and switch off the Oxicide system.
- The NaNO3 solution would also be placed in a drip tray including a level switch which can alarm the personnel in case of leakage.
- Procedures for ballast water exchange should be checked to ensure that ship stability is not compromised by the movement of ballast water.
- Training procedures for crew responsible for operating the equipment to make them aware of the hazards

- Development of proper procedures and equipment for dealing with spills in the event of an accidental release.

8.7 ENVIRONMENTAL IMPACTS

Oxicide treatment was tested at a shore based installation for WP4. Results from this testing were provided by the system designer. For materials and energy use, quantities estimated for the case study work were used. Based on the work carried out in WP4, the Oxicide cell was re-designed and updated estimates were provided for the case study vessel. Environmental impacts resulting from the Oxicide treatment method, based on data collected during large scale testing and from the case study estimates, are discussed below.

8.7.1 PRODUCTION PHASE

The system developer, TNO, provided updated estimates for materials required to construct an Oxicide treatment system as required to treat 2000 m^3 of ballast water. The estimated materials use is shown in Table 8.3.

Table 8.3: Summary of materials required to construct the Oxicide system

Material Type	Weight (kg)	% of Total Weight
Steel (Equipment and piping)	250	16.2
Polypropylene (Equipment and piping)	250	16.2
PVC (Equipment and piping)	5	0.3
Carbon Electrodes (Oxicide Cell)	400	26.0
Carbon Felt (Oxicide Cell)	10	0.6
Ion Conducting Membrane (Oxicide Cell)	5	0.3
Copper (Oxicide Cell)	20	1.2
External Electrical Equipment (material unspecified)	600	39.0
Total:	***1540***	***100***

A full scale installation of an Oxicide treatment system would require a filtration unit for pre-treatment of the ballast water and an air compressor to provide air to the Oxicide cell. The materials for these units were not included in the materials estimate.

Emissions to air resulting from production of steel (250 kg) and polypropylene (250 kg) were estimated. Together these two materials account for 53% of the weight of the specified materials. Emissions data for steel are from Sunér (1996) and data for polypropylene are from Boustead (1999). Emissions categories for production of these two materials included gases that contribute to global warming (greenhouse theme), gases that contribute to acidification (acidification theme), and gases that contribute to the formation of tropospheric ozone (tropospheric ozone precursors theme). Table 8.4 shows the amounts of the major types of emissions according to these "themes", and also shows the equivalents totals for each of these themes.

Table 8.4: Emissions resulting from production of steel and polypropylene for Oxicide system

Theme	Type of Emission	Amount (kg)	Conversion Factor	Equivalent Value
Greenhouse	CO_2	723	1	723
	CH_4	0.6	23	14
	N_2O	1.5	296	452
Total CO_2 equivalents(kg)				1189

Acidification	NO_x	2.8	1/46	0.06
	$SO_2 + SO_x$	3.9	1/32	0.12
	NH_3	0.0002	1/17	0.00001
Total Potential Acid Equivalent (kg PAE)				0.18
Tropospheric Ozone Precursors	NO_x	2.8	1.22	3.4
	CO	0.8	0.11	0.03
	CH_4	2.1	0.014	0.03
Tropospheric Ozone Forming Potentials (kg TOFP)				3.46

8.7.2 OPERATIONS PHASE

Fuel is required to generate energy to operate the Oxicide treatment equipment. As for other treatment systems, it was assumed that marine diesel fuel was used and the IPCC standard emission values per tonne of fuel, as shown in Table 2.4 (see chapter 2), were used for this assessment. For the life cycle assessment, it is estimated that the ship makes 25 voyages per year where the 2000 m^3 of ballast water is treated. The power consumption for each treatment is estimated by TNO to be 302.4 kWh for the Oxicide cell and air compressor. This requires 85.5 kg of diesel fuel to produce. The life cycle of the equipment is estimated as 20 years. Using these assumptions, a total of 42.8 tonnes of fuel would be used over the life of the equipment. Emissions associated with this fuel use are shown in Table 8.5.

Table 8.5: Emissions related to energy use over life cycle operation for Oxicide system (20 years/500 voyages)

Theme	Type of Emission	Amount (kg)	Conversion Factor	Equivalent Value
Greenhouse	CO_2	134297	1	134297
	CH_4	13	23	295
	N_2O	3	296	1013
Total CO_2 equivalents(kg)				135605
Acidification	NO_x	3079	1/46	67
	$SO_2 + SO_x$	2566	1/32	80
Total Potential Acid Equivalent (kg PAE)				147
Tropospheric Ozone Precursors	NO_x	3079	1.22	3757
	CO	316	0.11	35
	CH_4	13	0.014	0.2
Tropospheric Ozone Forming Potentials (kg TOFP)				3792

Notes: Conversion factors for greenhouse gases to CO2 equivalents from IPCC 2001
Conversion factors for PAE and TOFP from Hass (2002).

Other materials required during the operation of the Oxicide cell are approximately 1000 litres of 0.1 N nitric acid (HNO_3,) for the anolyte solution. $NaNO_3$ (sodium nitrate) salt would be carried onboard as it may be required to replenish the anolyte of the electrochemical cell. Approximately one jerry can of 20 litres concentrated solution of 10N would be stored onboard. This would be expected to last 10 to 100 trips.

8.7.3 COMPARISON OF EMISSIONS BY LIFE CYCLE STAGE

Emissions values for both the equipment production and operations phase of the Oxicide treatment system is presented in Table 8.6. For all three categories considered the operations phase is dominant, accounting for more than 99% of emissions during the life cycle.

Table 8.6: Emissions over production and operation phase of Oxicide system

Theme	Production		Operation	
	kg	% life cycle	kg	% life cycle
Greenhouse theme: Total CO_2 equivalents	1189	0.9	135605	99.1
Acidification: Total Potential Acid Equivalent (kg PAE)	0.18	0.1	147	99.9
Tropospheric Ozone Forming Potentials (kg TOFP)	3.46	0.1	3792	99.9

8.7.4 DIRECT IMPACTS THROUGH DISCHARGE TO RECEIVING WATER

Discharge of water with altered quality

Measurements of selected water quality parameters were taken for the water being discharged from the cell during the shore based tests. Dissolved oxygen concentrations were 20 mg/l as a result of the oxygen that was being added to increase hydrogen peroxide (H_2O_2) production. It is expected that further optimization of the system will result in the use of a mixture of air and oxygen for a full scale installation, thus dissolved oxygen concentrations would probably be less than 5 mg/l. The pH of water leaving the cell ranged from 7 to 8. Hydrogen peroxide concentration was between 10 and 20 g/m3. Because of slow decay of hydrogen peroxide into water and oxygen, the concentration of hydrogen peroxide in the ballast water is expected to be very low at the time of discharge, although there may be some residual. This would have minimal impact on the receiving environment, as it would be diluted and quickly break down to harmless products.

A corrosion assessment carried out during WP3 (DTR 3.8) projected a significant increase in redox potential as a result of the treatment. The increased corrosiveness of the ballast water may result in elevated metals levels (iron from the steel tanks) in the ballast water to be discharged. The concentrations of metals would depend on the condition of the coating of the ballast water tanks.

Discharge of solids (organisms and sediments)

The ballast water would be filtered prior to treatment with hydrogen peroxide. Discharge of sediments could result in localised areas of increased turbidity. Turbidity increase would depend upon the amount of sediments present in the ballast water.

The treated ballast water would contain organic material in the form of dead organisms. The amount of organic matter would be dependent on the concentration of organisms taken on with the ballast water, with the larger organisms being removed by filtration upon intake of ballast water or within 24 hours. Impacts would vary depending upon the sensitivity of the receiving environment, with organics loading being more of a concern in eutrophic waterbodies.

Impact from surviving non-indigenous organisms

The biological effectiveness of Oxicide treatment was not investigated during WP4. The report for WP3 provides details of the effectiveness determined during laboratory scale testing.

Spill potential

There is the potential for nitric acid and sodium nitrate spills in the event of an accident (<100kg HNO_3 resp. <10kg $NaNO_3$). Also, ballast water containing hydrogen peroxide could potentially be spilled if an accident occurs while the ballast water still contains hydrogen peroxide residual.

8.8 ECONOMIC ASPECTS

8.8.1 CAPITAL COSTS

The total investment costs for the Oxicide system will be about four times smaller than was estimated in WP3. The new generation system, including cells, pumps e.g., is € 387,500. Installation costs are included in the total investment costs. Testing cost in relation to certification is not exactly known. It is expected that it will be sufficient to take samples of the treated ballast water and analyse them for the content of hydrogen peroxide. This should be done onboard by a certification organisation. This will take about 2 days of work (excluding travel time). In the calculations those costs are estimated to be € 1,000.

8.8.2 OPERATIONAL COSTS

The Oxicide system will add approximately 15 – 20 g Hydrogen Peroxide per m^3 ballast water. For the 2,000 m^3 per trip to be treated, this means a production of (up to) 40 kg hydrogen peroxide, i.e. 2,000 kg per year. Treatment time per trip is 24 hours, which means a production rate of 1.67 kg HP per hour.

Table 8.7: Total energy use

Total energy use		Unit
energy requirement treatment system per trip	328.8	kWh
energy requirement BW pumps per trip	200	kWh
total energy requirement per trip	**528.8**	**kWh**
kWh > MJ (electricity)	1,904	MJ (electricity)
MJ (electricity) > MJ (diesel)	6,346	MJ (diesel)
MJ >kg (diesel)	149	kg (diesel)
energy costs per trip (diesel)	59.72	€/trip
total energy costs per year (diesel)	**2,986.16**	**€/year**

The current crew of the ship can do the operational work in approximately 1 hour per trip. The treatment program of the Oxicide unit will partially run automatically. *Personnel* will be required to switch on the equipment, to choose between some treatment options and to supervise the treatment progress. The personnel involved should be qualified to operate the system (high school level). Costs related to this are not included in the calculations as for only a few of the other treatment systems involvement of the current crew onboard is specified.

Turn around *maintenance* (TAM) is limited to periodically back rinsing of the cell (based on pressure drop indicators), and will depend on the amount of suspended solids in the ballast water. In the best case the cleaning frequency is estimated to be once per 20 trips, in the worst case more than once a trip. This should be an automatic run, reducing personnel time to less than 10 minutes. Occasionally, the anolyte liquid should be replaced. In theory this is not necessary, however the liquid could become contaminated over a long period. Replacement frequency is (conservatively) set to once per two years. The amount is approx. 20 litres of an acidic salt solution (pH = 1

– 2, approx. 0.5 M $NaNO_3$); this needs to be treated on site or disposed off in a proper way (neutralisation, removal of precipitates by filtration, recovery of the liquid with the nitrate salt). If this 'regeneration' is done onboard of a ship it would require approximately 4 hours and the appropriate equipment (sensors, dosing equipment, filtration).

Next to the TAM, extra maintenance is expected. The main parts of electrochemical cell (membrane, electrodes) could require replacement once or twice in the lifetime of the equipment (once in 5 to 10 years). It is envisaged that the supplier offers this service, by replacing the complete cell. The replacement should preferably be done in conjunction with other major services to the ship (e.g. inspection and cleaning of the ballast tanks). The costs for replacing the cell encompasses the transport costs of the cells and maintenance personnel, the actual replacement onboard of the ship (approx. 1 day, 2 persons) and the cleaning and refurbishing of the old cell (approx. 10 man days, material cost and about € 500 for waste handling and disposal). The same holds for other parts of the installation (e.g. electrical feed, pumps and valves), but the frequency of replacement are expected to be lower and – as a result - these costs are probably marginal to the costs for replacement of the electrochemical cell. Useful estimations of the cost related to regular or incidental *maintenance* (materials and personnel involved) are not available yet and therefore not included in the calculations.

To the opinion of the developer at least 3 persons should be able to operate the Oxicide cell. A full training would require approximately 3 days, and assumes the trainee has some general knowledge of ballasting/deballasting and of electrical circuits. In the calculations the costs related to the training are estimated to be € 3,600. It is estimated that this 3-day training course is needed once every ten years. In view of possible changes in personnel onboard this estimation is quite optimistic. No cost estimates can be provided yet on management cost like certification, writing of safety manuals and a general training for the crew on HSE aspects.

8.8.3 COST AND BENEFITS ASPECTS

The cost and benefits aspects are only described qualitatively. No cost estimations could be made at this point of time.

Tank cleaning will be reduced, also because of the pre-filtration on approx. 100 μm. The reduction is difficult to estimate because it depends on the place of the filter (in the feed line to the ballast tank is most efficient) and the cut-off size. A rough estimate is that the Oxicide treatment reduces cleaning frequency by 30% -60%. The associated reduction in costs could be substantial.

We expect increased costs for *corrosion control*, because of the corrosion risk of Oxicide. At this time no estimation of the cost can be provided. *No delay* is expected during a trip, assuming ballast water can stay at least 36 h onboard, before it is pumped overboard. If the ship is assumed to make short trips (much less than 36 h), Oxicide is not an attractive solution (if ballast water treatment is needed on short trips), because it would require a (very) large installation to generate the total amount of peroxide in this short period of time.

Increased maintenance of ballast water pump could arise, when these are not resistant to the slightly increased redox potential of the ballast water.

The footprint of the equipment is approximately 6.0 m^2. Another 4.4 m^2 is needed for piping and crew space. Depending on the available space to install the system this might influence cargo space. The following table lists the weight of the Oxicide components and the weight of materials used.

Table 8.8: Weight of the Oxicide components and weight of materials used

Weight		**Unit**
empty Oxicide cell, piping	940	kg
ballast water	300	kg
anolyte vessel	300	kg
anolyte	1,000	kg
external electrical equipment	600	kg
total weight equipment in operation	4340	kg
Materials use		**Unit**
PVC	5	kg
PP	250	kg
steel (additional piping not included)	250	kg
carbon felt	10	kg
carbon electrodes	400	kg
ion conducting membrane (ca. 30m^2)	5	kg (ca.)
wiring (copper)	20	kg
total weight materials (equipment)	940	kg

The next table shows the detailed calculation results for Oxicide.

Table 8.9: Oxicide economic results

Cost type	**Description**	**€ (euro)**	**Comments**
Capital Costs			
Investment	investment costs	387,500	
Installation	installation costs	0	included in inv. costs
Testing	testing costs	1,000	analyse samples of treated BW in relation to certification; two days work in addition to travel time and costs
Commissioning	commissioning costs		not expected
	total investment	**388,500**	**€**
Depreciation factors	depreciation period	10	years
	interest rate	8%	
	annual capital costs	**57,898**	**€/year**
Operational Costs		**€/year**	
Personnel	personnel during treatment	p.m.	€/year
Energy	energy (diesel)	2,986	€/year
Additives	additives use	0	
Maintenance	TAM (maintenance euro)	0	
	additional maintenance	0	material and labour costs
Training and management	training costs	360	training course (€ 3.600) every 10 years
	certification costs	0	
	health and safety issues	0	
Cost and benefits	tank cleaning costs	0	no influence
	corrosion costs	0	no influence
	costs of delay	0	no delay

	increased maintenance	0	
	loss of cargo space	0	no loss of cargo space
	annual operational costs	**3,346**	**€/year**
Total annual costs		**61,244**	**€/year**
Costs per treated m^3 ballast water	**50 trips / 100,000 m^3**	**0.6124**	**€/treated m^3 BW**

8.9 BIOLOGICAL ASSESSMENT

The pilot tests were scheduled for August 2003 in Den Helder (the Netherlands). There it was planned to test the biological efficiency of Oxicide by measuring phytoplankton and chlorophyll concentrations. However, the chlorophyll concentration of phytoplankton in the seawater was extremely low during the tests period (< 2 µg/l). Photoluminescence of the fresh seawater, which is a measure for the activity of the phytoplankton, was often not measurable or only just above the detection limit. The low concentration of active phytoplankton is attributed to a long period of high seawater temperature (> 20°C).

The low concentrations of active phytoplankton made it impossible to measure the biocidal efficiency of Oxicide. Instead, it was decided to focus on the hydrogen peroxide production rate of the pilot system.

9 BENRAD SYSTEM TREATMENT

The Advanced Oxidation Technologies (AOTs) are defined as processes that involve the generation of OH radicals that can effectively destruct organics.

The definition of a radical is as follows: A radical is any species - atom or molecule - capable of independent existence and which contains one or more unpaired electrons.

Hydroxyl radicals have one unpaired electron. As soon as the radicals are generated they try to steal one electron from other molecules. They are short-lived (nanoseconds) and aggressive. New radicals are formed by the loss or by the gain of a single electron from a non-radical.

The destruction of microorganisms by radicals is considered as an oxidation reaction. The membrane of the microorganism is the first site of attack. Beyond the membrane/cell wall, radicals destroy nuclear materials within the cell/virus/spore. The destruction reactions of most microorganisms occur within seconds. Hydroxyl radical is a strong oxidant, its electric potential of oxidation/reduction is 2.85 V, which is less than fluorine (2.87 V) and more than Ozone (2.07 V). All of them, and OH radicals in particular, have pronounced ability to kill microbes and viruses.

In the BenRad AOT two different wavelength spectra, 185 and 254 nm are used. At 185 nm some ozone is produced in the water. A catalyst is coated on the inside of the unit and exposed to UV-light. The unit is made of titanium.

Hydroxyl radicals are generated in three ways:

1. UV-light hits the catalyst surface. An electron is exited which leads to radical formation
2. Ozone in water generates hydrogen peroxide which breaks down to radicals
3. UV-light hits ozone in water. Ozone breaks down to singlet oxygen and oxygen. Singlet oxygen can then form radicals in water.

The BenRad water purifier units always have filters upstream to prevent particles in the contaminated water to enter the unit.

Figure 9.1 shows the system installed on board the ship.

Figure 9.1: BenRad system

9.1 CONCEPT APPROVAL

The installation scheme providing a global view of the components and links with the ship installation is given below.

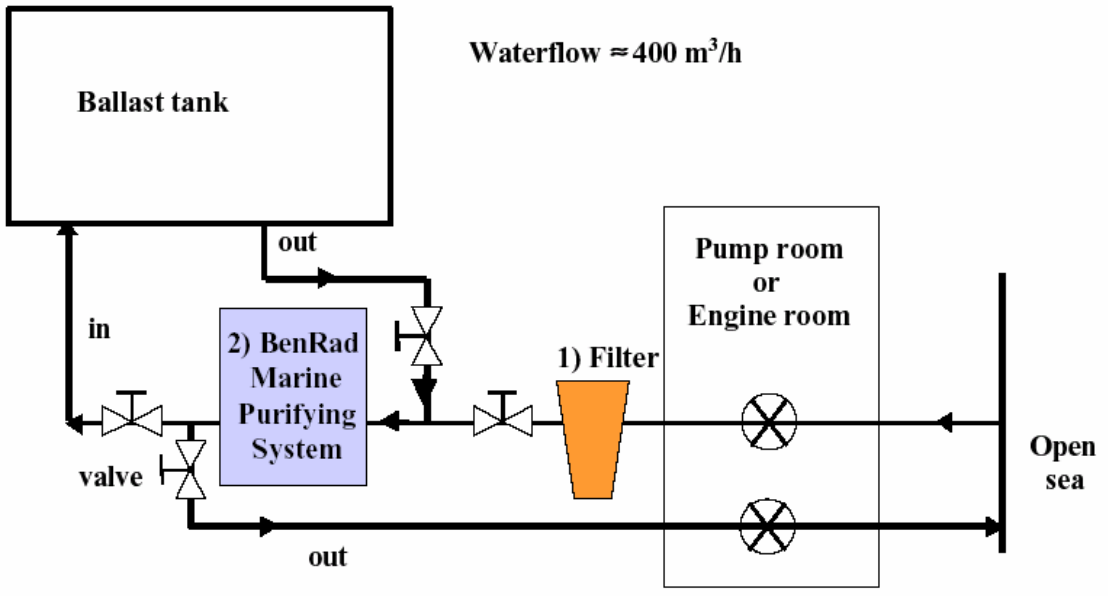


Figure 9.2: BenRad system diagram

The system is connected to the ballast water piping and uses components which exist on the ship and are well known ship equipment and have the following characteristics:

- Filter: Selfcleaning backflush, stainless steel
- Effect: 0,09 kW - Power: 3 x 230V / 50Hz
- Purifying system: House, titanium gr 2
- UV lamps - Effect: 3 kW - Power: 230V / 50-60Hz

The review of the defined criteria in chapter 1 leads to the following conclusions shown in Table 9.1.

Table 9.1: BenRad criteria review

Criteria	Review Results
Stability	No tank filling different than those of the operational ship loading cases. No impact on stability.
Visibility	No modification of the loading cases, so of the trim, at sea. No impact on visibility.
Longitudinal strength of the vessel	No tank filling different than those of the operational ship loading cases. No impact on the hull girder strength.
Overpressure in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of overpressure.
Liquid motions in ballast tanks	No tank filling different than those of the operational ship loading cases. No increase on the risk of sloshing.
Piping	Use of well known marine equipment on ballast piping. No increase of risk.
Risk of fire	No specific non common equipments. No increase of the risk of fire.
Material and products	Use of well known marine equipment on ballast piping. No particular risks.
Ballast water composition	No addition to the water. Possible increased risk of corrosion but acceptable.
Biological efficiency	Good laboratory test results. No onboard full scale test results.

The system analysis does not show any particular difficulty with respect to normal ship design and building. The biological efficiency has been proven acceptable in laboratory. Considering the documents submitted, the system is granted with a Design Concept Approval.

To obtain the Final Concept approval the efficiency of the onboard full scale application will have to be assessed and the required documents reference number 8 and 10 to 15 of Table 1.2 (see chapter 1) must be provided.

9.2 ECONOMIC ASPECTS

9.2.1 CAPITAL COSTS

The investment costs for the water purifier ranges from € 35,000 to € 50,000 (estimated costs based on a commercial product), the filter from € 30,000 to € 70,000, and cleaning from € 5,000 to € 20,000. Total investment costs range from minimum € 70,000 to maximum € 140,000. Installation costs for the water purifier, filter and cleaning will be € 10,000 - € 30,000. There are no testing or commissioning costs expected.

9.2.2 OPERATIONAL COSTS

The water purifier prototype requires 8 kW per hour and needs 2 x 4 hours for the treatment of 2,000 m^3 ballast water, resulting in an energy use of 64 kWh per trip (treatment during both ballasting and deballasting). Cleaning the system will take 18 kWh per trip and backflushing 0.1 kWh per trip. The ballast water pumps use 200 kWh per trip. That makes total energy use per trip 282.1 kWh.

Table 9.2: Total energy use

Total energy use		**Unit**
energy requirement per trip	282.1	kWh
kWh > MJ (electricity)	1,016	MJ (electricity)
MJ (electricity) > MJ (diesel)	3,385	MJ (diesel)
MJ >kg (diesel)	80	kg (diesel)
energy costs per trip (diesel)	31.86	€/trip
total energy costs per year (diesel)	**1,593.04**	**€/year**

The yearly costs for cleaning chemicals will lead to *consumable costs* of € 1,200 - 1,500 which are used during treatment. No extra *personnel* are needed. The system can be operated by, e.g., a machinist. It will take approximately 2 man-hours per trip to operate the system. TAM (Turn Around *Maintenance*) is expected. The UV lamps have to be replaced after 9,000 working hours. Quartz sleeves may be broken and sealing may need to be changed. Material costs per year are calculated to be approximately € 1500 and 10 – 15 personnel hours are needed for this maintenance, i.e. € 250 - € 375 (average € 313), resulting in total TAM € 1,750 - € 1,875. There is no extra *maintenance costs* expected related to the use of the water purifier. There is no information available on TAM and extra maintenance related to the use of the filter and cleaning.

Two persons, first officer and chief engineer, should be trained in 1 - 2 hours. Using the average personnel cost of € 25 per hour, this leads to (average) € 75 *training cost*. There are also *certification cost* expected, but no estimation could be provided yet.

9.2.3 COST AND BENEFITS ASPECTS

A reduction in the tank *cleaning costs* is expected due to the use of the filter. The filter will at least be 100 micron; this will result in reduced sediment. Next to this a reduction in the cost of corrosion control is expected. The system reduces the concentration of oxygen. No bio-film is expected since the water purifier eliminates bacteria. No estimation of the benefits related to those aspects, reduced cleaning costs and reduced corrosion costs, are available yet.

There is no delay in harbour or during the trip expected related to the ballast water treatment system. No extra maintenance costs are expected. A preliminary estimation of the size of the equipment required onboard is 4-7 m^2 (water purifier 1 m^2, 2 – 5 m^2 for the filter and 1 m^2 for the cleaning equipment), 2.5 m high. It is expected that the system will be installed in the engine room and will therefore not result in cargo space reduction.

The next table shows detailed calculation results for the BenRad advanced oxidation technology.

Table 9.3: BenRad economic results

Cost type	Description	€ (euro)	Comments
Capital Costs		**average**	
Investment	investment costs	105,000	water purifier, filter and cleaning
Installation	installation costs	20,000	
Testing	testing costs		not expected
Commissioning	commissioning costs		not expected
	total investment	**125,000**	**€**
Depreciation factors	depreciation period	10	years
	interest rate	8%	
	annual capital costs	**18,629**	**€/year**
Operational Costs		**€/year**	
Personnel	personnel during treatment	p.m.	€/year
Energy	energy (diesel)	1,593	€/year
Additives	cleaning chemicals	1,350	1,200 - 1,500 €/year
Maintenance	TAM (maintenance euro)	1,813	
	additional maintenance	0	material and labour costs
Training and management	training costs	75	
	certification costs	0	
	health and safety issues	0	
Cost and benefits	tank cleaning costs	0	no influence
	corrosion costs	0	no influence
	costs of delay	0	no delay
	increased maintenance	0	
	loss of cargo space	0	no loss of cargo space
	annual operational costs	**4,831**	**€/year**
Total annual costs		**23,460**	**€/year**
Costs per treated m^3 ballast water	**50 trips / 100,000 m^3**	**0.2346**	**€/treated m^3 BW**

9.3 BIOLOGICAL ASSESSMENT

The system has been fitted onboard the M/V Don Quijote and the biological analysis was planned for May and June 2003. Unfortunately due to unavoidable practical issues it was not possible to perform the tests and as such these have been postponed for a later opportunity.

10 HURDLE TECHNOLOGY

The major goal for combining individual techniques is to achieve an improved efficiency for the overall treatment. This can be either a qualitative improvement, where the second technique has an effect on part of the organisms that the first one does not affect. It can also be that it reduces the effort in e.g. energy or operational costs to achieve the same level of treatment.

From the combinations of techniques tested in WP3 at laboratory scale, the only combination to benefit seemed to be high temperature thermal treatment followed by de-oxygenation. This is because of the increased rate of oxygen consumption at elevated temperatures, which will reduce the treatment time for the de-oxygenation process. Some doubt was raised for the results of the tests with combinations of ultrasound and ultraviolet, as the treatment capacity of the pilot equipment was relative large compared to the volume of ballast water ("MARTOB soup") to be treated and relative large errors occurred in the results. Therefore, the combination of ultrasound and ultraviolet technology was planned to be tested at large scale in Finland. Additionally, test trials with combinations of hydrogen peroxide and ultraviolet light were carried out.

During the laboratory scale test trials in the WP3 also other combinations were tested, i.e. thermal treatment + de-oxygenation and hydrogen peroxide + thermal treatment. Since thermal treatment and de-oxygenation technologies were tested onboard a vessel, due to the logistical reasons it was not possible to test the combinations in larger scale. Also the different primary treatment options (filtering, cyclons etc.) were excluded from the trials since they were not included in the work program of the MARTOB project.

10.1 COMBINATION OF ULTRASOUND AND ULTRAVIOLET LIGHT

Regarding the combination of US+UV the general test arrangements were the same as with the test trials of the single technologies, i.e. 1 h of continuous flow before samples were taken. The design of the aggregate where the US and UV devices were installed enabled flexible testing arrangements. The operational parameters with the combination of ultrasound and ultraviolet light are summarised in Table 10.1.

Table 10.1: Operational parameters with the combination of US+UV

Flow rate [L/h]	**Amplitude** [%]	**UV dose** [mJ/cm^2]	**T_{sample}** before / after [°C]	**ΔT** [°C]	**Test phase**	
					Sept.-Oct. 2002	Aug.-Sept. 2003
520	50	216	7,0 / 8,1	1,1	x	
	50		19,2 / 20,5	1,3		x
	50		19,6 / 20,8	1,2		x
	100		7,1 / 8,4	1,3	x	
	100		18,3 / 19,8	1,5		x
	100		19,7 / 20,1	0,4		x

10.2 COMBINATION OF ULTRAVIOLET LIGHT AND HYDROGEN PEROXIDE

The combinations of UV + H_2O_2 and H_2O_2 + UV were tested according to Figure 3.4 (see section 3.3.1). In the Option "A" the sea water was first treated with ultraviolet light (average flow rate 800 L/h) and after that the hydrogen peroxide (0,045 ml/L and

0,09 ml/L of 30 % hydrogen peroxide) was injected to the water in order to obtain the required concentrations (15 mg/l and 30 mg/l respectively). The tanks with water treated with ultraviolet light and peroxide were stored for 48 h before analysis.

In the option "B" 1000 L of seawater were pumped with membrane pump (average flow rate 800 L/h) to the tank and hydrogen peroxide (45 ml and 90 ml of 30 % H_2O_2 to obtain the concentration of 15 mg/L and 30 mg/L respectively) was added to the water. After the injection of hydrogen peroxide the water was pumped through the UV device and water volume of 60 L (2 x 30 L) was analysed after 48 h incubation time. The operational parameters with the combination of UV and hydrogen peroxide become clear from Table 10.2. The Total Suspended Solids (TSS) values were analysed during the trials August - September 2003, once a day before the treatment, accordingly to the standard SFS-EN 872 (1996), filter paper Schleicher & Schuell GF52.

Table 10.2: Oerational parameters with combinations of UV + H_2O_2 and H_2O_2 + UV

Flow rate [L/h]	**UV dose** [mJ/cm^2]	**H_2O_2 concentration** [mg/L]	**Total Suspended Solids** (TSS) [mg/L]
800	141	15	4,4
800	141	30	4,1

10.3 BIOLOGICAL ASSESSMENT

The large scale onshore test phase for hurdle technologies was carried out utilising the Baltic Sea plankton assemblage as a target system. The test trials were conducted in the facilities provided by Tvärminne Zoological Station and the combinations tested were US+UV and UV+hydrogen peroxide (H_2O_2).

10.3.1 ULTRASOUND WITH ULTRAVIOLET LIGHT

The combination of US and UV was tested at one flow rate (520 L/h), at two US amplitudes (50 and 100 %). Kill percents approached 100 % in all cases (copepods with US dosage of 100% forms the only exception, but obviously is an artefact caused by small initial densities and lack of replicates) (Figure 10.1). No difference in death rates was observed between the treatments or species groups (Kruskall-Wallis x^2=7,749, df=5, p=0,171). Unfortunately cladocerans were not present but veliger larvae of bivalves were abundant and were included in the study, instead.

In order to evaluate the efficiency of combining techniques, the results are compared with the results of the single techniques at the same parameter settings (flow rate, energy input). Copepods, C.Nauplii, Rotifers and Barnacles were tested with the combination of US+UV (Table 10.3). For both single use of US and single use of UV Copepods, C. Nauplii and Rotifers were tested. These results can be used for comparing the effectiveness. Results are summarised in Table 10.3.

For the combination of US+UV it is shown that the combination improves the overall effect for Copepods and Nauplii. No effect could be shown for Rotifers, because of high kill rates with individual treatments.

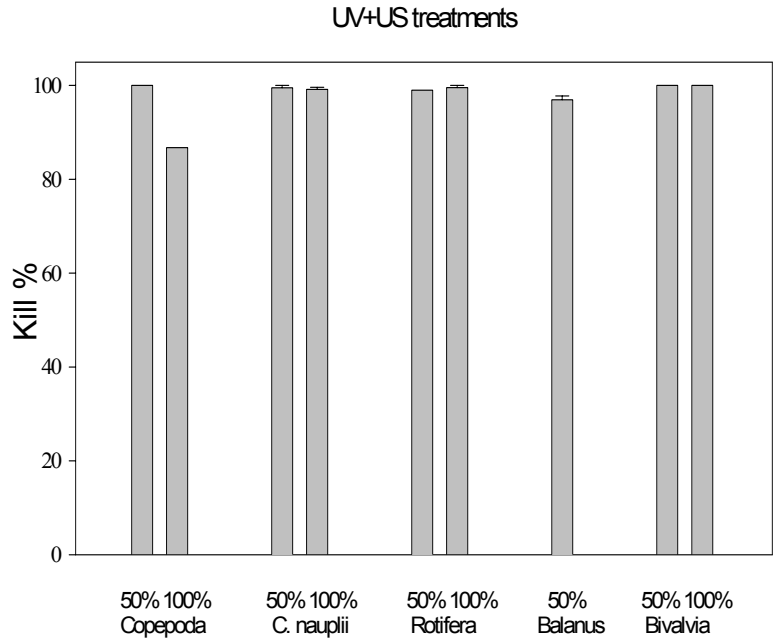


Figure 10.1: Treatments with US+UV.

Table 10.3: Summary of results of using single and combination of US and UV

	Treatment (parameter)				
Species group	UV (520 l/h)	US 50%	US 100%	UV (520) + US (50%)	UV (520) + US (100%)
Copepods	94	n.a.	97	100	n.a.
C.Nauplii	92	86	96	100	99
Rotifers	99	n.a.	96	99	100

10.3.2 ULTRAVIOLET LIGHT WITH HYDROGEN PEROXIDE

The overall effect of the combination of UV and H_2O_2 was highly powerful (Figures 10.2 to 10.4). Experiments included two options (Figure 3.4, see section 3.3.1). In the option A, UV treatment was followed by an addition of hydrogen peroxide in the sample water. In the option B, instead, H_2O_2 was initially added to untreated water followed by UV treatment. Two concentrations of hydrogen peroxide were used (15 and 30 mg/L), flow rate in UV treatment was always 800 L/h.

In all cases, no live individuals were found after 48 h incubation period, either with or without addition of H_2O_2 (Figures 10.2 to 10.4). Thereby, the final kill % was 100 in every case. No effect of different H_2O_2 concentrations could thus be observed. For copepod nauplii, the effect of UV alone in section A was not as powerful as the effect of other combinations (Kruskall-Wallis: x^2=14,738, df=7, p=0,04).

As single treatment techniques UV and H_2O_2 were tested for Copepods, C. Nauplii and Rotifers. For combination of UV with H_2O_2 improvement is made for Copepods, Nauplii and Rotifiers, when compared to the single UV technique. However the H_2O_2 single application shows 100% mortality already at the tested doses after 48 h of incubation time, even at a low H_2O_2 dose of 15 mg/L. This is better than expected from previous work.

From the results for test series B (Figure 10.4) the incubation time of 48 hours seems essential to achieve a 100% rate when applying hydrogen peroxide.

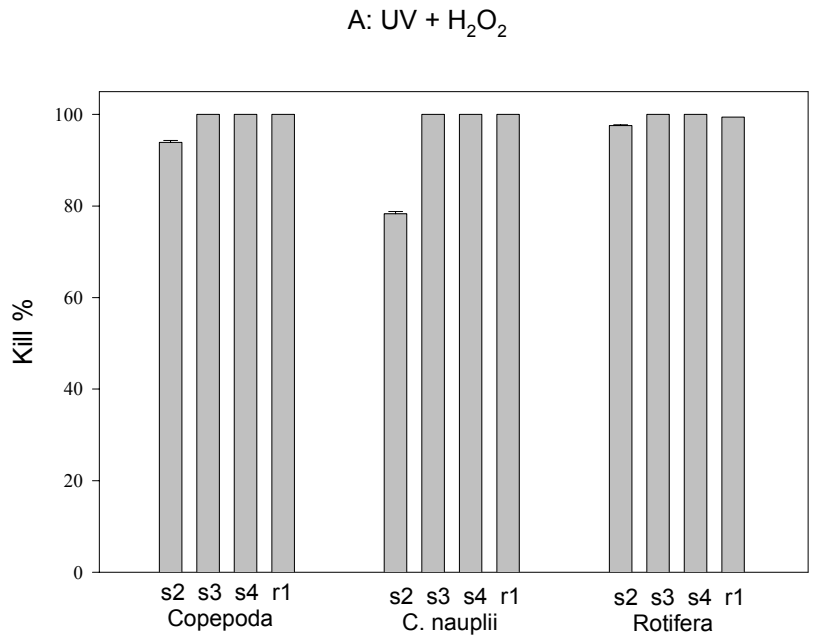


Figure 10.2: The combination of UV + H_2O_2.

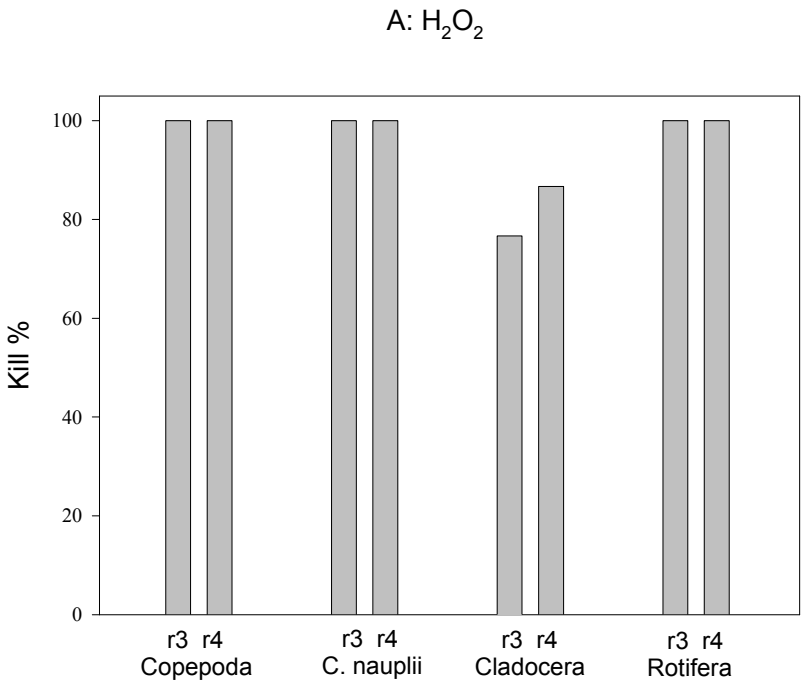


Figure 10.3: H_2O_2 treatment only.

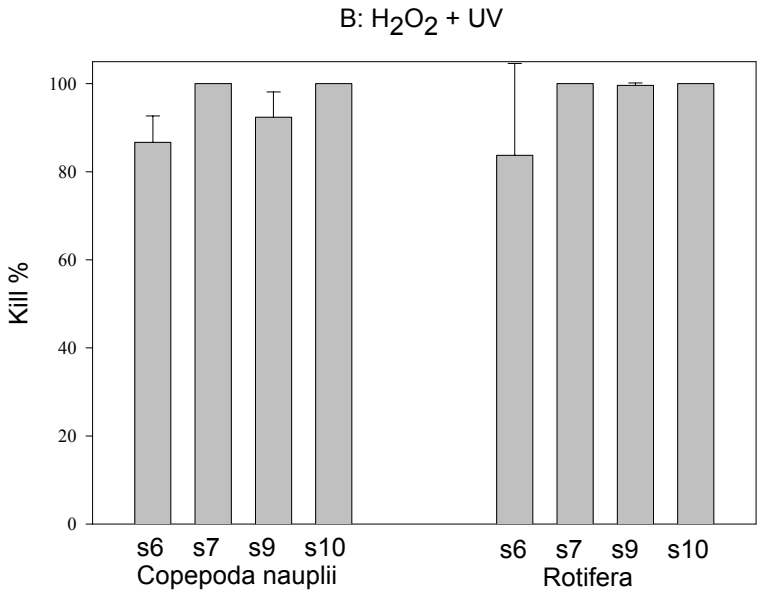


Figure 10.4: Treatment with and H_2O_2 + UV

CONCLUSIONS

High Temperature Thermal Treatment (HTTT)

The onboard HTTT tests were a success on the technical side as the system performed as designed. The only limitation was that the ballast water supply was through a fire hose that could only provide a maximum of about 9t/hr of ballast water. The steam control system performed adequately when the steam supply was constant, but any perturbations in the steam supply led to oscillations in the treatment temperature as the control valve could not respond fast enough. This was further hampered by the fact that the valve did not have a variable feed rate and would often over-compensate.

The concentration of zooplankton in the ballast water was around 1100 organisms per m^3. After treatment the concentration of viable zooplankton ranged from 82 to less than 1 organisms per m^3 depending mainly on the age of the ballast water. The longer the organisms had been in the ballast tanks, the fewer survived the HTTT. The treatment temperature (55-80 ºC) had less effect. A significant fraction of the zooplankton, sometimes more than 90 %, was killed in the control samples, probably by the pressure fluctuations in the fire pump during transport from the ballast tanks to the heat exchanger on deck. The killing rate of the HTTT was therefore due to a combination of the heat treatment and the killing during transport. It is therefore impossible to determine exactly the effect of the heat treatment alone, but the results indicate that the heat treatment killed at least 90 % of the zooplankton, and probably considerably more.

Due to the low starting concentration of phytoplankton in the ballast water (<1 cell/ml) and their low chlorophyll content, it was not possible to assess the efficiency of the HTTT towards this group.

The average concentration of viable bacteria in the ballast water was $1 \cdot 10^4$ GU/ml, and the HTTT reduced this with approximately 95 %. The concentration of the indicator bacteria in the new IMO standard was not determined, but the results indicate that, if present, the concentration of viable *E. coli* and *V. cholerae* would have been reduced with at least 95 %. Whether or not this is enough to achieve the IMO standard depend upon the starting concentration of the indicator bacteria. In most cases a reduction in the viability of the indicator bacteria with two orders of magnitude is likely to be sufficient, but in extreme cases a higher reduction in viability may be required. Because some intestinal enterococci are fairly heat resistant, the efficiency of the HTTT towards these bacteria is difficult to predict from the above results, and further studies are required.

Biological De-oxygenation (DEOX) Treatment

During the DEOX treatment the concentration of viable bacteria increased within the first 48 hours from around $1 \cdot 10^4$ to $6 \cdot 10^7$ GU/ml in the treated water. As a result of the bacterial growth, pH decreased from around pH 8 to around pH 6.5. The dissolved oxygen measurements gave a more ambiguous result, and only on the last day of the study (day 7) did they clearly indicate that the ballast water was anoxic. This may be due to practical problems with the dissolved oxygen measurements. The biological results indicate that the treated water became anoxic no later than 2-3 days after start. In the control tanks the dissolved oxygen concentration was high throughout the

experiment. No significant amounts of H_2S were formed in the treated ballast water. Due to the treatment the discharged water was enriched in nitrogen (N) and phosphorous (P).

The effect of the DEOX treatment on the survival of phytoplankton is unclear. At the start the ballast water contained an average of 0.9 phytoplankton cells (diatoms + dinoflagellates) per ml. In the treated water the concentration decreased to around 10 % of the initial concentration. In the controls, the decrease, if any, was much smaller. On the other hand, the concentration of chlorophyll *a* decreased to around 10 % of the initial value in the control tanks, but decreased only slightly in the treated tanks. Because the cell count was restricted to diatoms and dinoflagellates, and the viability of the cells was not determined, it is not possible to resolve these conflicting results, but the results indicate that the effect of the DEOX treatment on the viable phyto-plankton population is limited.

The DEOX treatment significantly reduced the concentration of zooplankton in the ballast water. From start the ballast water contained an average of 2570 zooplankton per m^3, mainly copepods and nauplii, and at the end of the treatment (7 days) this was reduced to 27 zooplankton per m^3. The IMO standard relates specifically to *viable* organisms, but because the sampling via the fire pump killed a substantial fraction of the zooplankton in the samples, sometimes more than 90 %, it was not possible to estimate the viable fraction in the ballast water. The concentration of viable organisms in the treated water must have been less than 27 per m^3, but probably not below the new IMO limit of 10 viable organisms per m^3.

Ultraviolet light (UV), Ultrasound (US), Ozone and Combination Treatments
The brackish water (6 psu) used in these trials contained from 30 to 150 thousand organisms per m^3, mostly dominated by copepods and copepod nauplii. The UV treatment killed 94-99 % of the copepods, 78-100 % of the copepod nauplii and 98-100 % of the rotifers. The US treatment killed 94-99 % of the copepods, 86-99 % of the copepod nauplii, 95-98 % of the cladocerans, 80 % of the rotifers and 97 % of the barnacle nauplii. For the combination of US and UV the mortality rates were between 97-100 % and the combination of UV and hydrogen peroxide achieved mortality rates of 94-100 %. UV combined with hydrogen peroxide seemed to be effective, although our data are deficient with respect to cladocerans and barnacle nauplii, which were not present in the study area at the time of the experiments. It should be noted that only a limited number of different treatment combinations were tested and some of the potential combinations based on the laboratory scale test trials had to be left out.

Ozone treatment (17 mg/L) killed 96-100 % of the copepods, 98-100 % of the copepod nauplii and 99-100 % of the rotifers. When the ozone dosage was 7 mg/L, the results were 95-100 % for copepods, 96-100 % for copepod nauplii, 97-100 % for rotifers and 99-100 % for barnacle nauplii. The volume of the contact tank was 60 L for the ozone dosage of 17 mg/L and 360 L for dosage of 7 mg/L. The ozone dosages were kept constant throughout the trials.

It must be emphasized that only moderate flow rates were used. In addition, in some cases, an insufficient number of replicates make further conclusions difficult. Fortunately, high mortality rates were achieved in many cases to draw a general

conclusion of the killing power of UV, US, ozone and combination treatments. Thus, it is suggested that a combination of the treatments tested would be effective in eliminating mesozooplankton from ballast water.

The study confirmed that the equipment was working as designed. The decision to conduct test trials onshore instead of onboard a ship seems justified as most of the error sources that occurred during the laboratory scale test phase could be avoided and the results were more reliable and logical. The results also provided basis for the up-scaling of ultraviolet, ultrasound and ozone treatment processes.

Oxicide Treatment
During the first onshore trials in August for the Oxicide treatment, the concentration of phytoplankton in the North Sea was very low, most likely due to a long period of extremely warm weather, and the biological efficiency of the system could therefore not be studied. Instead, the experiments focused on the H_2O_2 production rate of the Oxicide pilot. The newly designed generation-2 and generation-3 electrochemical cells showed an important increase in the peroxide production rate compared to the cell used in WP3, from 14 grams/m^2 of cell membrane per hour up to 60 g/m^2h. During the large scale onshore tests in October and November the Oxicide pilot functioned very well. An endurance test of 4 days revealed that the specific production rate remained stable at approx. 60 g/m^2h for two cells in parallel and at a flow rate of 400 L/h. Due to this substantial gain in production rate, the size of an Oxicide system onboard of a ship can be reduced a factor of 4 compared to the design in WP3. This will reduce the cost of the system with almost the same factor and thus the cost per cubic metre of ballast water treated.

Risk, Safety, Environmental Impacts and Economical aspects
The major hazards associated with the HTTT, UV and US are confined to the equipment location. For DEOX, Oxcide and Ozone, the hazard will encompass a larger area of the ship because ballast water is treated in the ballast tanks or is returned to the tanks with a residual amount of disinfectant. For all treatment methods there is a potential to reduce risks through appropiate training and safety procedures.

Excluding spills and accidents, the environmental impact will be through (1) direct discharge to receiving water, (2) consumption of energy and other consumables during operation, and (3) energy and raw materials for construction of treatment equipment. From a life cycle perspective, impacts during operation were dominant for all treatment methods. Emissions to air resulting from fuel use for energy production represented more than 95 % of the total.

For a ship with a need to treat 2000 m^3 each time and 50 trips per year, the estimated cost per m^3 treated for the different methods ranged from € 0.1 to € 0.6. With the exception of HTTT, where operational costs constituted around 69 % of the total costs, capital costs dominated and constituted 69-95 % of the total costs.

For the comparison details of risk and safety issues see Table 2.1, for environmental impacts see Table 2.2 and for economical aspects see Figure 2.2 and 2.3 all given in Section 2.

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