MARTOB

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

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2			
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Contents

1 Executive Summary

The general objectives of the Work Package 3 were the design and development of the proposed treatment methods at laboratory scale and with computer simulation, the assessment of the environmental, biological, economical, risk and safety aspects and the evaluation of subsequent long-term effect of the individual methods on the marine ecosystems. The Work Package consists of eleven different Tasks. Six tasks deals with various treatment technologies. Economic and environmental performance, assessment of direct and indirect environmental aspects and evaluation of corrosion risk of the treatment methods are also included in the work plan.

The test trials were held at Newcastle University in early June 2002, in the facilities provided by the University of Newcastle including the following technologies: high temperature thermal treatment, oxicide treatment, ultraviolet light, ultrasound and ozone methods, de-oxygenation, Advanced Oxidation Method and combinations of the above technologies as the hurdle technology. Sampling and analysis were carried out by University of Newcastle and Fisheries Research Services according to the biological assessment protocol developed in Work Package 2. In addition to the biological assessment, corrosion characteristics measurements were carried out during the test trials in Newcastle.

High Temperature Thermal Treatment

High thermal treatment offers one solution if short heating duration is required for the effective elimination of unwanted marine organisms. Treatment during ballasting and treatment at exit during deballasting are two possible options. The treatment at exit allows us to treat the water when deballasting, before discharging it overboard. It doesn't require the water to be pumped from one tank to the other for treatment, or additional tanks to be installed, both of which can cause problems with stability of a vessel and/or reduction of the cargo space. There is also no risk of cross-contamination of the treated ballast water, once treated water will be discharged. A possible problem for this system is that the equipment reliability is critical as the water is not stored and there is therefore no backup.

The high temperature treatment option would avoid the voyage duration limitation, encountered by the low temperature option. In theory, exposure to high temperature treatment for a few seconds would be sufficient to cause the de-naturation of all organisms in ballast water. Furthermore, it has the added advantage of either intake or in-transit or exit treatment. However, a pre-requisite for high temperature treatment option would be requirement of steam.

The effects of temperature on phytoplankton and zooplankton have successfully been tested under laboratory conditions. This has allowed us to obtain a correlation between kill rate and temperature for *Acartia tonsa*, *Nereis virens* and *Tisbe battagliai*, the zooplankton species used in the tests. For the phytoplankton *Alexandrium tamarense* and *Thalassiosira pseudonana,* it was stated that all the temperatures that were used for thermal treatment resulted in a reduction of chlorophyll *a*. However, experiments carried out at lower temperatures (40 and 45^{o}C) resulted in a significantly lower reduction of chlorophyll *a*. It would therefore appear that temperatures of 50^{o}C and above were more effective at reducing phytoplankton biomass. However, it would also appear that there is no significant effect between the results for treatments at 55, 60 and 65^{o}C "Touch and Go", which would seem to indicate that increasing the temperature above 55^{o}C does not result in a corresponding reduction of chlorophyll *a*. Combining the results from the zooplankton and phytoplankton we have been able to deduce a treatment temperature for the high temperature thermal treatment system of 55°C.

Since the heater is followed by a cooler and is located at the discharge of ballast water, no risk of corrosion increase or risk with respect to coating and gaskets has been identified.

Biological de-oxygenation

Biological de-oxygenation is based on the fact that addition of nutrients to ballast water will stimulate the growth of the indigenous bacteria in the ballast water. The solubility of oxygen in water is low, and the bacterial growth will consume the dissolved oxygen. When the ballast water becomes anoxic, organisms that require a steady supply of oxygen will die. The aim of the studies reported here was to develop a de-oxygenation process that could be applied in large scale, and to test the efficiency towards selected organisms in the meso-scale trials in Newcastle.

In a series of laboratory studies performed in 3 liter fermentors with seawater from the Trondheim Fjord, a promising nutrient solution for biological de-oxygenation was composed. However, it may still be necessary to slightly modify the composition to prevent excessive formation of H_2S. The time it takes to consume all the oxygen in seawater decreases with increasing temperature. At 4 °C it takes 3-4 days, at 10-20 °C 1-2 days, and above 20 °C less than 1 day to obtain anoxic conditions.

In Newcastle, biological de-oxygenation was tested in meso-scale in 50 liter polypropylene vessels covered with black plastic bags to simulate the darkness in a ballast tank. 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), and two species of phytoplankton; the dinoflagellate *Alexandrium tamarense*) and the diatom *Thalassiosira pseudonana*.

Biological de-oxygenation of the seawater killed all the added zooplankton species. The killing rate increased with increasing time under anoxic conditions. After 4-6 days of anoxia, more than 95 % of all the tested zooplankton species were dead.

De-oxygenation of seawater had little effect on the survival of the two added species of phytoplankton. A slight decline in the concentration of the dinoflagellate was observed as a function of incubation 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 incubation in darkness seemed to have little effect on the survival within the time-frame studied.

Corrosion effect estimated with FMECA analysis allowed to pay attention to the following aspects: a slight decrease of pH with possible consequences on metal corrosion, coatings and gaskets, a slight increase in CO_2 concentration with possible consequences on metal corrosion and gaskets, the production of H_2S with possible consequences on metal corrosion, coatings and gaskets, the addition of inorganic substances with possible consequences on metal corrosion, coatings and gaskets, the addition of organic substances with possible consequences on coatings, and a significant increase in the concentration of bacteria with possible consequences on metal corrosion, coatings and gaskets.

Ultraviolet light, ultrasound and ozone treatments

Ultraviolet light, ultrasound and ozone methods were tested in two test phases. The preliminary test phase was carried out in Espoo, Finland, in April-May 2002. The aim of the preliminary test trials was to establish the operational parameters to the Newcastle test trials and study the effectiveness of the methods against *Artemia salina*. The second test phase took place in Newcastle as part of the collective test trials.

The ultraviolet light device and ultrasonic devices were built in the same test rig in order to test single technologies and also to test the combination of ultrasound and ultraviolet light as part of hurdle technologies. The ozone device was a stand-alone device. The test arrangements included flow and pressure meters and required sampling taps before and after treatment process.

In Espoo trials artificial sea water with salinity of 30-35 ppt and average temperature of 18 °C was used. Centrifugal pump was utilised when the water was introduced to the treatment process. Achieved total reduction of *Artemia* was 43-60 % with ozone treatment. The contact times were short enough to affect only on activity rates but not on mortality rates of *Artemia*. With ultrasound treatment total reduction rates of 84-100 % were achieved and with ultraviolet treatment, maximum reduction rate of 78 % was achieved. Also the combination of ultrasound and ultraviolet light was tested as a part of hurdle technology. The result of total reduction of *Artemia* was 82-99 %. Each test run was carried out only once, hence the results should be regarded as indicative.

During the first three and a half days in the Newcastle trials the centrifugal pump was used but after realising that the pump itself was eliminating all the zooplankton, a gravity system to supply the water was used. For zooplankton the mortality attained by the ultrasound treatment was always below 40 %. The ultraviolet method did not inactivate more than 56 % of the zooplankton. The highest value for the ozone treatment was 89 %, eliminating *Nereis*. In terms of hurdle technology, a better performance from the Filter (125 microns) + ultrasound + ultraviolet test compared to the ultrasound + ultraviolet seemed apparent, mainly for *Acartia* and *Tisbe*.

Phytoplankton results indicated that ozone were the most effective at reducing chlorophyll *a* levels with reduction rate of 97 %. The highest reduction rate of pheophytin level attained with ultrasound was 67 % and the highest reduction rate with chlorophyll *a* levels achieved was 71 %. With ultraviolet light treatment, the highest reduction rate of chlorophyll *a* level achieved was 56 % and the highest reduction rate of pheophytin level was 33 %. The hurdle technology, ultrasound combined with ultrasound, achieved reduction rate of 68 % with chlorophyll *a* levels and 46 % reduction of pheophytin level. The combination of filter, ultrasound and ultraviolet light achieved the reduction rate of 57 % of chlorophyll *a* level and 52 % reduction rate of pheophytin level at its best.

After the pump was replaced with the gravity water supply it was noticed that the bends, valves and long pipes could cause a source of error. Since the flow rate with gravity supply system was much lower that with the pump, it was concluded that some of the species were accumulated into the points with low velocity, thus altering some results. Both living and dead organisms were found to be hidden in the treatment systems. After the problem was noticed, it was decided to flush the systems after each test run, and some of the zooplankton species were detected from the samples. This arrangement could slightly remedy the source of error but there are still concerns regarding the accuracy of analysis.

The system configuration was designed for the macro scale testing. Therefore the available amount of water was insufficient in order to enable a designed function of the devices. Preliminary test phase in Espoo and the Newcastle test trials showed that the apparatus were working as designed when enough water was available. Also the lack of pressure caused alterations to the design principles.

In addition to the biological effectiveness of the methods, also possibly modification of the ballast water properties and contents by the treatment method was identified. Ultraviolet light causes a slight increase of the Redox potential (short term effect) with possible consequences on metal corrosion, coatings and gaskets. Regarding the ultrasound method no risk of corrosion increase or risk with respect to coating and gaskets was identified. Ozone method causes a significant increase of the Redox potential (short term effect) with possible consequences on metal corrosion, coatings and gaskets. Also the production of O_3 (short term effect) with possible consequences on metal corrosion, coatings and gaskets was identified.

Along with the biological effectiveness and corrosion related matters the economical aspects, environmental and risk and safety effects were evaluated. Regarding the economical issues the estimated cost for ultraviolet light was 0.11, ultrasound 0.28 and for ozone 0.22 €/m^3 treated ballast water. Ultrasound treatment increased the water temperature about 5-6 °C. None of the discharges of the methods will in-

clude substances identified as "priority hazardous substances". Ultraviolet light and ultrasound treatments require additional pipe lines that may cause breaks and ballast water leaks. Ultraviolet lamps contain mercury that would result in damages in case of breakage. The possible hazard with ozone treatment would encompass larger area since the ballast water is treated in the ballast tanks.

The results from Espoo and Newcastle test trials were partly promising and encouraging but also partly difficult to explain. Therefore ultrasound and ultraviolet systems need to be tested with continuous flow and with duration long enough and also with various pressure levels. Ozone treatment needs to be studied with longer contact times to determine mortality rates versus ozone dosage and contact time. Larger scale test trials are inevitable to find out proper limits for adjustments and efficiency, otherwise the scaling to the full-scale dimension would be very difficult.

Oxicide treatment

Hydrogen peroxide is an oxidising compound and can be produced in-situ by means of an electrochemical conversion of dissolved oxygen. This new process, the Oxicide process, is carried out in an especially designed and patented electrochemical reactor. H_2O_2 destructs plankton and micro-organisms in the ballast water. Hydrogen peroxide is known to be of limited risk to humans, especially at low concentrations. It decays within a period of days or a few weeks, resulting in harmless compounds: water and oxygen. Hydrogen peroxide has various applications, among others treatment of swimming pool water, as alternative to chlorine based disinfectants.

A first design of the Oxicide cell has been build and tested under laboratory conditions at a scale of 100 dm^3 water per hour. It contained three Oxicide cells in series, each with contactors for supplying oxygen to the seawater, the source of which is either pure oxygen or air. The seawater runs along a 3 dimensional electrode (cathode), where the oxygen is transformed to hydrogen peroxide. The anode compartment is fully separated from the seawater compartment by means of a conducting membrane. It was found that the maximum achievable concentration of hydrogen peroxide in seawater is determined by kinetics and depends on the concentration of dissolved oxygen, temperature, electrical current and cell voltage. The H_2O_2 concentration follows a logarithmic trend in batch operation. The highest concentration of H_2O_2 achieved at ambient condiments is approx. 400 mg per litre (using pure oxygen gas) or 150-180 mg per litre (using air). The initial current efficiency (CE) is 70-80%. The pH of the seawater decreases because of some migration of H+ ions from the anode compartment through the membrane. The maximum observed pH drop in a batch operated Oxicide cell was from pH 8.4 to pH 6.5. The 3-dimensional electrode of the Oxicide module showed no plugging or irreversible retention of particles in tests with kaolin, wheat flour and algae, i.e. particles < 100 μm.

The Oxicide process is a promising treatment technology for ballast water. The tests at the premises of UNEW show that H_2O_2 is efficient against selected organisms: 100% of *Nereis virens* and ≥ 90% of *Acartia tonsa* were removed in all experiments at 10-15 mg H_2O_2/dm^3. *Tisbe battagliai* proved more difficult, but was also removed by at least 85% at higher concentrations of H_2O_2 (> 28 mg/dm^3). Furthermore, at least 50% of the phytoplankton is removed by Oxicide treatment at 10-15 mg/dm^3, although some of the other test results with phytoplankton were inexplicable. Elevated temperature (up to 35° C) seems to improve the efficiency of H_2O_2, especially zooplankton. A literature study and additional tests revealed that some organisms need much larger concentrations (>100 mg H_2O_2/dm^3) to be destructed or inactivated; this especially holds for large organisms.

Electrochemically produced H_2O_2 had the same efficiency in killing *Skeletonema* sp. algae as a technical solution. This indirectly shows that probably no significant amounts of byproducts (e.g. chlorine) are formed.

In summary, various organisms are destructed or inactivated at relatively low concentrations of hydrogen peroxide (10-30 mg H_2O_2/dm^3). A treatment time of at least 24 hrs is required for H_2O_2 to take full effect. However, a combination of Oxicide with other techniques should be considered, because of the relative high resistance of some organisms to hydrogen peroxide.

In terms of corrosion assessment, the production of H_2O_2 and the significant increase of the Redox potential of the water (several hours to a few days) may have consequences for the metal corrosion, coatings and gaskets. In addition, it is recommended to pay attention to the electric isolation of the DC equipment, because of the risk of unexpected current return paths and significant local metal corrosion.

Oxidation method

The oxidation technology is based on an Advanced Oxidation Technology (AOT) consisting of a combination of ozone, UV and catalysts, and has been developed by BenRad Marine Technology. Thus Ozonolytic / Photolytic / Photocatalytic Redox Processes are operating simultaneously within a titanium reactor to generate large amounts of radicals, mainly hydroxyl radicals, within BenRad's water purifier. These radicals will destruct and/or eliminate micro organisms. This technology has successfully been used in land-based applications such as purification of swimming pool water, drinking water, water used for irrigation in green houses and water used in fish breeding.

The water was circulated through the water purifier. Tests were taken after 1 – 10 cycles. Some tests were done with 100 μm filter upstream of the water purifier. Some tests were done with turbid water. In the 10 litres taken out before treatment a lot of organisms were found alive when the water was clear. When the water was turbid a large amount of organisms were dead or not found. Therefore the turbid tests are not included in the results.

The combination of BenRad Marine Technology water purifier and the 100 μm filter achieved a killrate of zooplankton over 95 %. When both the water purifier and the filter were used, the fraction of recovered zooplankton, dead or alive, was low (1.4 - 17 % of the number initially subjected to the treatment), indicating that organisms were caught in the filter. Also when only the water purifier was used (i.e. without filter), the fraction of recovered zooplankton was low (down to 3.8 % of the number initially subjected to the treatment). This indicates that organisms were eliminated by the water purifier. Some of the added organisms may have been left behind in the pipes or in the tank, but in controls where the water with the organisms was pumped trough the system, but not treated, the fraction of recovered zooplankton was 35-52 %.

The combination BenRad Marine Technology water purifier together with the 100 μm filter achieved 40-70 % reduction in chlorophyll *a* compared to samples taken before treatment. This indicates that there has been a reduction in the phytoplankton biomass. It is possible that the filter caught some of the phytoplankton.

In terms of corrosion assessment a moderate increase of the Redox potential (short term effect) with possible consequences on metal corrosion, coatings and gaskets and a slight increase of CO_2 with possible consequences with respect to metal corrosion and coatings were recommended to pay attention to.

Hurdle Technologies

Combining disinfecting technologies offer the option of eliminating the limitations of individual techniques as well as the advantage of using the synergy of different methods. From food industry it is known that combinations of two disinfecting techniques have more effect than the sum of individual conserva-

tion methods. One well known application of hurdle technology in ballast water treatment is the combination of filter technology (hydrocyclons) and UV disinfection.

During the Newcastle trials various combinations were tested based on the expected synergistics effects, i.e. the combination of mechanical filter + US + UV, filter + UV + oxicide (H_2O_2), H_2O_2 + UV, thermal treatment + de-oxygenation and H_2O_2 + heat treatment. From the results of the hurdle technologies, the treatment that worked better was the thermal + deoxygenation, which had a 100% efficiency for *Tisbe battagliai* and *Nereis virens*, and 97 % for *Acartia tonsa*. Because there were no replicates, the results must be interpreted with care. Comparing the efficiency of UV+H_2O_2 with and without filter (150µm), the results showed that the filter did affect the survival of the organisms, as the percentage of organisms removed increased for *Acartia tonsa* and *Nereis virens* when the filter was used. The combination of US and UV achieved a 68 % reduction of chlorophyll *a* levels compared to samples taken before treatment. The combination of filter, US and UV achieved a 57 % reduction of chlorophyll *a* level.

The combination of US and UV was also tested in the Espoo triails carried out by VTT. The result of total reduction of *Artemia salina* was 82-99 %. In terms of hurdle technology, a better performance from the filter (125 µm) + US + UV test compared to the US + UV seems apparent, mainly for *Acartia tonsa* and *Tisbe battagliai*.

Regarding the phytoplankton results, it is difficult to be certain which of the combinations of technologies are the most effective. It would appear that combinations of heat with deoxygenation or H_2O_2 were not effective at reducing chlorophyll *a*. The remaining four treatments were all based on combinations of UV and H_2O_2, sometimes with the added combination of a filter. On two occasions this reduced the chlorophyll *a* by over 70 %, on another occasion the reduction was less than 20 % and the fourth run resulted in an increase in chlorophyll *a*. It is therefore impossible to say with any certainty whether this combination of technologies is effective.

In conclusion, the results obtained don't support a combination unambiguously. Results from some combinations and process parameters showed improvement, where others combinations gave poorer results.

Environmental Impacts, Risk and Safety, and Economic Aspects of Ballast Water Treatment Methods

The economic, environmental, and risk and safety effects of ballast water treatment methods tested in work package 3 of the MARTOB project were evaluated. Information from the laboratory scale test reports and from information provided by system designers for ballast water treatment on a case study ship formed the basis of the evaluation. Evaluation criteria developed in task 2.6 were used to assess each of these effects. To provide a consistent basis for comparing the individual ballast water treatment techniques, a theoretical case study approach was used. Data on the case ship and sample voyage was specified and provided to the technical developers in the project, as well as a list of data needed for assessing cost, environmental effects, and hazards.

Risk and safety effects

For the risk and safety assessment of ballast water treatment methods, hazard identification was carried out and some recommendations for potential risk control measures were provided. Hazards can be considered from the perspective of safety/survivability of the vessel and safety of the crew during ship operations. Categories of hazards related to operation of the ballast water treatment methods 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. The major hazards associated with most of the treatment methods, including thermal treatment, UV, US, BenRad, and Oxicide, were confined to the location of the equipment installation. None of the on-board treatment methods have the po-

tential to threaten ship structural integrity in the manner of empty-refill ballast exchange. For biological de-oxygenation and ozone, ballast water is treated in the ballast tanks, so the hazard would encompass a larger area of the ship.

Most of the ballast water treatment methods, with the exception of biological de-oxygenation and ozone, require the ballast water to be pumped through treatment systems. This additional piping means that there is an additional risk for pipe breaks and leaks in areas of the ship where there was previously no risk of ballast water leaks. However, this is expected to be a minor risk as most additional pipe work would be in a very localized area.

Other hazards associated with ballast water treatment include the potential for a spill of hazardous material stored or being used within the treatment. The UV and BenRad treatment systems both use UV lamps that contain mercury or amalgamated mercury. The oxicide method uses nitric acid as an anolyte and requires sodium nitrate salt to be stored on board. All of these could result in damages if accidentally released.

With all methods, there is the potential to reduce risks through appropriate training and safety procedures. If these systems are installed on new ships additional safety features could be considered during ship design.

Environmental Effects

Environmental impact categories used to assess the effects of each of the ballast water treatment technologies tested in WP3 of the MARTOB project included:

- Direct Impact through Discharge to Receiving Water:
    - Discharge of water with altered quality with respect to the following parameter types:
        - Physical parameter
        - Metals
        - Nutrients/Oxygen Demand, Low D.O.
        - Biocide residuals
    - Discharge of surviving organisms
    - Discharge of solids (organisms and sediments)
- Other Environmental Impacts
    - Energy Consumption (treatment systems, additional pumping, filtration)
    - Potential for Spill of treatment chemicals
    - Materials use (both for consumables and for construction of treatment equipment)

Although some of the treatment methods will result in the discharge of ballast water with altered quality, none of the discharges will include substances that are identified as ‘priority hazardous substances’ (under the European Union’s Water Framework Directive), or that have the potential to bio-accumulate. Ballast water quality will undergo the most changes with the biological oxygen removal method, which will produce a discharge that is low in dissolved oxygen and that has increased concentrations of nutrients and bacteria. The oxicide and BenRad method will both lower the dissolved oxygen concentration of the ballast water. Increased temperature of the ballast water discharge will occur after thermal treatment (10˚ C temperature increase) and ultrasound treatment (estimated range of 5-6 ˚ C temperature increase occurred during the laboratory scale tests). UV treatment has no effect on ballast water quality.

All methods will result in organic matter in the discharge in the form of dead organisms, but this will vary depending on filtration use, treatment type, and the concentration of organisms in the intake ballast water. The potential impact of this would be much less than if live non-indigenous species are released, but

could be of minor concern in eutrophic waters. 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. Methods using the filter as pre-treatment will need to discharge the filtered material to the receiving environment, which could cause some turbidity.

All treatment methods require the use of some energy, and this will result in environmental effects from fuel consumption and associated emissions. Energy use is lowest for biological oxygen removal and high temperature thermal treatment is the most energy intensive method (although the energy used is dependent on the selected treatment temperature and the temperature of the ballast water before treatment).

Stainless steel and titanium are the most commonly used materials for the treatment systems. Materials used for construction of the treatment equipment will be further refined in the next phase of the project (WP4) when the treatment systems are constructed for full scale testing. It should then be possible to have more detailed information to assess life cycle impacts of the methods.

Economic Aspects

Installation of an on-board ballast water treatment system will lead to changes in a ships' capital costs, changes in annual operating costs, and possibly will lead to extra training and management costs and economic benefits or disadvantages. Generally, the cost calculation results highly depend on some basic data associated with shipping trade and ballast water treatment. This may include 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, number of ballast pumps and their capacities, type of fuel used, type of treatment and treatment capacity. Costs can be easily compared when they are calculated based on the same type of dependants mentioned above. The theoretical case study approach provided a consistent basis upon which to compare costs.

From the preliminary cost calculations it can be concluded that there are still some data gaps to be filled in. For some treatment methods the potential cost and cost factors are already quite transparent, for some other systems there is still a lot of data to be estimated. The differences are partly related to the status of development of the method. It is expected that during up-scaling of the systems and the large-scale trials in WP4 more data will become available. In addition more research into tank cleaning costs, cost of corrosion control, certification cost, average wages of on-board personnel, total shipping cost to be able to calculate the impact of ballast water treatment on the total cost of shipping, needs to be done. During WP4 the cost calculations will be further improved and refined.

The preliminary cost of treatment of ballast water on "the case study ship" varies considerably, ranging from €0.10/m^3 up to €2.34/m^3. Nevertheless, it should be kept in mind that not all data were available for the techniques, and some were preliminary.

Biological assessment

The purpose of the shore based trials carried out at the University of Newcastle was to carry out a series of experiments using a standard test sea water containing a representative mix of phytoplankton and zooplankton. These experiments were designed to assess the biological efficiency of the different treatment methods.

Zooplankton
Following the MARTOB laboratory-scale trials, a protocol for assessing ballast water treatment methods has been used successfully. The 'soup' designed was simple to use, highly reliable and effective. The control test showed that organisms in the soup survived for 24 hours. Hence a meaningful and reliable means

to assess and compare different ballast water treatment methodologies has been identified. Based on the percentage kill of animals in the test soup the results indicated which of the methodologies were the most effective and which had more potential for ballast water treatment. Unfortunately only some of the tests had replications, and it was only on these that a more rigorous statistical analysis could be carried out, and the results interpreted with confidence.

The mortality of the different species varied depending on the treatment tested, *Nereis virens* usually being the most sensitive organism and *Tisbe battagliai* the most resistant. Sometimes the numbers obtained from the after-treatment samples were very low. This could have been due to the fact that some of the equipment had long pipes with corners where possibly organisms could have hidden. Moreover during the first three and a half days a pump was utilised as a means to introduce the water into one of the systems. After it was shown that the pump itself was eliminating all the zooplankton, a gravity system was used to supply the water. For future tests these aspects should be considered and the redesign of some of the treatment systems and their sampling points is therefore recommended.

Phytoplankton
The results showed that there was great natural variability of the phytoplankton cell numbers within the control samples, which made it difficult to interpret some of the results of the treatments as many of the experiments were not replicated. The heat treatment method showed consistent reductions in chlorophyll *a* and pheophytin but the cell count data were more variable. The results from the oxidation treatment were somewhat ambiguous and there was no clear treatment effect. The ozone treatment showed reductions in chlorophyll *a* but again the cell count data did not show such a clear effect. The results for the ultrasound technique were compromised by the fact that much of the water being treated remained in the equipment and a further flushing step had to be added, which resulted in an increased reduction of chlorophyll *a.* Again, the cell counts for this treatment were not so clear, with reductions of *Alexandrium tamarense* but more variable results from *Thalassiosira pseudonana* counts. The ultraviolet and a combination of ultraviolet and ultrasound treatments also had to have a flushing step added. For these treatments there was a reduction in chlorophyll *a* but again the cell counts did not show consistent reductions. The deoxygenation treatment resulted in reductions of chlorophyll *a* and some reductions in cell numbers but there were some high cell count results that did not correspond with high levels of chlorophyll *a* and were difficult to explain. The advanced oxidation technique generally showed reductions in chlorophyll *a* but the lack of replication made it difficult to determine which of the treatments was the most effective. The cell counts were also more variable and there was no clear treatment effect. The results of the hurdle technologies were difficult to explain as there was no replication at all and there did not seem to be any pattern to the results. It was therefore difficult to determine whether there was a treatment effect.

Overall, the results showed that some of the treatments produced a consistent decline in chlorophyll *a* levels, which indicates that there was a treatment effect. However, the more variable cell count data needs to be taken into account as well. It is possible that some of the cell count data may have included counts of cells that looked normal and undamaged but had actually been killed. It had been intended to use a flow cytometer to count and assess viability of the cells but this was not possible owing to circumstances beyond our control. The counts were therefore carried out on preserved samples where it is more difficult to assess whether a cell was alive before preservation.

Evaluation of corrosion risk of the treatment methods

In ships, an important problem is the corrosion of the hull structure, the piping system and the ballast water handling equipment. Therefore it has been decided to identify if the installation and operation on board of the considered in the MARTOB project ballast water treatment systems will modify the water properties in such a way that it could increase the corrosion risk of the ship structure and ballast water piping network.

The target of this task is not to performed a detail analysis of the corrosion risk link to each system which will require to know all details about the ship on which they will be installed, but to provide a warning to the designers and classification societies which will have to approve the installation on board, on the main possible new risks with respect to corrosion attached to each system. This approach was carried out utilising FMECA grid support and ranking tables developed by the expert group.

The parameters considered in the analysis with indication of the variation or consequences which induces a corrosion risk increase were water properties, water content and circuit content. The resistance list for the chosen coating is important. It appears that the manufacturers of the coatings, linings, seals, Dresser couplings, pumps, etc. should be asked to provide a resistance list for their product. The coating maker will have to investigate the resistance of the coating where the ballast tanks contain treated water.

Therefore, it is possible that the chosen ballast water treatment method needs to be specified first so that the materials with the best corrosion resistance and coatings compatible with the water content can be chosen for the detailed specification of coating, piping, pump, valve, seals, alloys etc., based on the treatment method.

All risk increases are acceptable with respect with today knowledge and can be managed for new ship design with existing techniques and methods. Referring existing ships, some treatment systems may be not acceptable due to the treated water characteristics incompatibility with the existing piping, gaskets or coatings materials.

Strategy for large/full scale test trials

Strategy for full scale is based on the experience gained from laboratory scale test trials. High Temperature Thermal Treatment, de-oxygenation and oxidation technologies will be tested onboard a vessel. Ultraviolet light, ultrasound, ozone and oxicide methods will be tested with large scale facilities.

In the large scale onshore test trials the duration of test runs with US and UV will be longer as in laboratory scale tests in order to minimise the technical sources of errors, i.e. piping, fittings, valves and small amount of water. The use of sea water enables the access to unlimited amount of water and the link to the actual marine environment is evident. Regarding the ozone method the contact time will be extended with modification of the device in order to monitor ozone dosage per amount of water versus contact time. Various ozone dosages and contact times will be studied.

The first-generation of the Oxicide module performed well, but the conversion of dissolved oxygen was rather low. A second-generation Oxicide cell have been pre-designed; changes include other dimensions of the Oxicide cell for better consumption of dissolved oxygen and the spatial separation of the oxygen transfer unit and the electrochemical cell. In addition, it will be tried to substantially increase the hydrogen peroxide production per unit area of electrodes.

In view of up-scaling the Oxicide treatment method to large-scale or even full size ship application, several environmental economic aspects are of interest. In task 3.5.2, the main aspects of interest were defined, selected and (partly) assessed, i.e.:

- Pressure in the Oxicide cell: atmospheric, small overpressure or pressurised;
- Source of primary material, oxygen, in the electrochemical cell: air or pure oxygen;
- Power consumption of the Oxicide cell and its impact on total power consumption of the ship;
- Capacity of the Oxicide cell;
- Efficiency of H_2O_2-production;

- Formation of by-products, its harmfulness and ways to handle them during the generation of H_2O_2 in the Oxicide cell;
- Differences of installation and use of the Oxicide technology between existing and new ships;
- Sizing and costing of full scale Oxicide technology;
- Full versus partial treatment of ballast water.

In co-operation with the designer and the manufacturer of the Oxicide technology, it will be decided which of the aspects described above will be further assessed in WP4..

2 Detailed design of the thermal treatment system with computer simulation and demonstration of the system

2.1 Introduction

The use of ballast water as a vector for translocation of marine species has led to the need for an onboard treatment system, which can kill these organisms cheaply and with the least impact on the environment. The objective of this report is to present the state of the art high temperature thermal treatment system, to compare it to the existing low temperature thermal treatment systems and to present the steps undertaken in the design process of the high temperature system.

The effects of temperature on zooplankton and phytoplankton are presented, followed by the laboratory scale design and testing and the full size design. The report finishes with a look at corrosion problems and operational considerations.

2.2 High Temperature Thermal Treatment Laboratory tests

The laboratory tests were run over a period of two weeks in the beginning of June 2002, to ensure that these tests would represent the real world conditions experienced by the ballast water system; deionised water was mixed with the required salts in the right proportions to form “pure” seawater. Three different types of zooplankton and two types of phytoplankton were added to the water, these species were chosen as they were considered to be some of the most resilient species available and the most widely encountered in ballast water.

The laboratory scale treatment system evolved from a simple single heater, single cooler system, following preliminary testing, when it was found that the system would not give us enough control of the temperature and that high temperatures would not be possible. The system which was used in the experiments contained a pre-heater as well as the heater and cooler. The heat exchangers used glass coils immersed in insulated baths. The pre heater used an 11-spire coil and the heater a 22-spire coil, with ports to allow the use of thermocouples for temperature measurement. The insulated baths where heated using re-circulating heaters, 2 for the pre-heater and 1 for the heater. The soup was circulated through the system by gravity (using a header tank) to avoid the use of a pump, which would have a detrimental effect on the plankton and would interfere with the test, and was adjusted using a needle-valve flowmeter.

Three repetitions of the same test were used to eliminate any errors and the soup was treated at temperatures going from 35 to 65°C in 5°C steps.

2.3 Laboratory Test Results

2.3.1 Zooplankton

Following each test run the zooplankton was filtered out and stained with a special dye, which only reacts to ATP, live plankton would therefore be stained red, and the proportions of live and dead animals could be determined. As the phytoplankton was much smaller than the filter used, a 10-litre sample was collected post-filtering, for the Chlorophyll and Phaeophytin values to be determined. The results for the biological effectiveness of the treatment against the phytoplankton were obtained at the end of august. These show that the treatment is effective from around 50°C upwards, with a 100% killrate.

2.3.2 Phytoplankton

All the temperatures that were used by UNEW resulted in a reduction of chlorophyll a. However, experiments carried out at lower temperatures (40 and 45oC) resulted in a significantly lower reduction of chlorophyll a. It would therefore appear that temperatures of 50oC and above were more effective at reducing phytoplankton biomass. However, it would also appear that there is no significant effect between the results for treatments at 55, 60 and 65oC "Touch and Go", which would seem to indicate that increasing the temperature above 55oC does not result in a corresponding reduction of chlorophyll *a*.

There is no clear indication from these results as to whether the "Touch and Go" method or the longer exposure method was more efficient. From these results it would appear that an increased exposure time at 55^{o}C to 30 seconds led to a less effective reduction in the chlorophyll a level than the same experiment run at shorter exposure times. However, without the same experiment being repeated at different temperatures it is difficult to conclude whether this would always be the case or whether there were some other variables influencing the result. The experiments at 55^{o}C were run using two different cultures, which may have had an effect on the results.

There were some different effects between the two phytoplankton species used, the *Alexandruim* sp. was reduced in 22 out of the 24 tests whereas there was a reduction in Thalassiosira sp. cell numbers in 18 of the 24 tests. The results for *Thalassiosira* sp. were more variable and showed reductions and increases when subjected to the same treatment. However, the overall finding was that there was no significant difference for either species in the mean change between the eight treatment methods. This indicates that there is a requirement for further investigation as to whether the cells are surviving the treatment or whether the cell counts are picking up cells that look normal but are actually dead. The results from the chlorophyll a indicate that there may have been a reduction in the number of cells that were alive.

2.4 Assessment of the environmental and corrosion risks caused by the HTTT system

The treatment system on board ship will comprise of two Alfa Laval heat exchangers, one pre-heater/recuperator and one treatment heater. The pre-heater will be heated by the treatment heater outlet water and will therefore reduce the temperature of the water been discharged overboard, limiting any environmental damage.

All the heating will be done in the system, using the titanium heat exchangers and there are therefore no increased corrosion risks to the ballast system or vessel.

2.5 System Simulation and Design

2.5.1 Static Simulation

Using Microsoft Excel a simulation program was designed which could give the required heat exchanger areas for given treatment and ballast water temperatures and de-ballasting and steam flowrates. This was done from first principles and therefore didn't reflect what was achievable in on board ship.

To remedy to this a database of heat exchangers (both pre- and treatment exchangers) was created using CAS 2000, the program used by Alfa Laval to design its heat exchangers. This was then modelled using neural networks and inserted into a Labview virtual instrument (VI), giving us a static model.

2.5.2 Dynamic Simulation

The dynamic model was based on the same VI but took into account the dynamics and interactions of the pre-heater/heater system. This model allows us to vary all the parameters for the system: pre-heater and heater areas, the ballast water and steam inlet temperatures and the steam and de-ballasting flow rates, to give us the treatment and overboard temperatures, the energy used and the capital and running costs of the system.

This simulation program allows us to select the required pre-heater and treatment heaters to obtain the required treatment temperature for a given ship and sea route. It also allows us to choose the areas to minimise capital expenditure, running costs or to balance both costs.

2.6 Conclusions

With the problem of non-indigenous species being transported by ballast water gaining more attention and the problems associated to mid-ocean ballast water exchange, different ballast water treatment systems have been investigated by various parties. Thermal treatment has been a very promising solution, with the onboard trials of the low temperature treatment systems giving good results, but being limited by the long duration required achieve the temperature and the incapacitation of the organisms. This is a problem for short voyages and for partial de-ballasting and re-ballasting when the nutrient rich treated water is mixed with new seawater.

To combat these problems, high temperature treatment at exit must be used. By using high temperatures, the organisms are killed with a much shorter duration, which allows for shorter voyages and treatment at exit. Treatment at exit allows us to treat only the water which is being discharged, which eliminates cross contamination and any increased corrosion problems in the ballast tanks.

The effects of temperature on phytoplankton and zooplankton have successfully been tested under laboratory conditions. This has allowed us to obtain a correlation between kill-rate and temperature for *Acartia*, *Nereis*, *Tisbe*, *Alexandrium* and *Thallasiosira*, five of the plankton species most commonly found in ballast water. From these tests we have been able to deduce a treatment temperature for the high temperature thermal treatment system of between 55 to 60°C.

Finally from the design program presented in this paper, the heat exchangers required by the system will be sized and chosen. This will be done once the particulars of the ships and their routes on are obtained. With the proper design practices, there should be no extra corrosion problems, and the only remaining task would be to decide whether a fully automated control system would be used or if manual control is adequate.

3 Biological de-oxygenation

3.1 Introduction

The idea behind biological de-oxygenation 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 main objective of the studies in Work Package 3 was to develop a de-oxygenation process that could be applied in large scale, and to test the efficiency towards selected organisms in the meso-scale trials in Newcastle.

3.2 Laboratory studies at SINTEF

The primary aim of the laboratory studies at SINTEF was to develop a suitable nutrient solution for biological de-oxygenation. The experiments were performed in small (1.7-3 litre) fermentors with magnetic stirring. The fermentors were filled almost to the top with fresh surface seawater from the Trondheim Fjord. Thereafter nutrients were added and the fermentors closed to prevent air exchange with the surroundings. Temperature, dissolved oxygen and pH were recorded continuously with electrodes, and samples taken at intervals for analysis with respect to turbidity and/or viable bacteria.

The result of the studies was a promising nutrient solution that was later employed in the meso-scale studies in Newcastle. The water became anoxic within 1-2 days at 10-20 ºC, and the formation of H_2S upon extended incubation (1-2 weeks) was low (<1 µmol/litre). Because biological de-oxygenation depends upon the activity of the indigenous bacteria in the water, the time it takes to obtain anoxic conditions will increase with decreasing temperature (Figure 3.1).

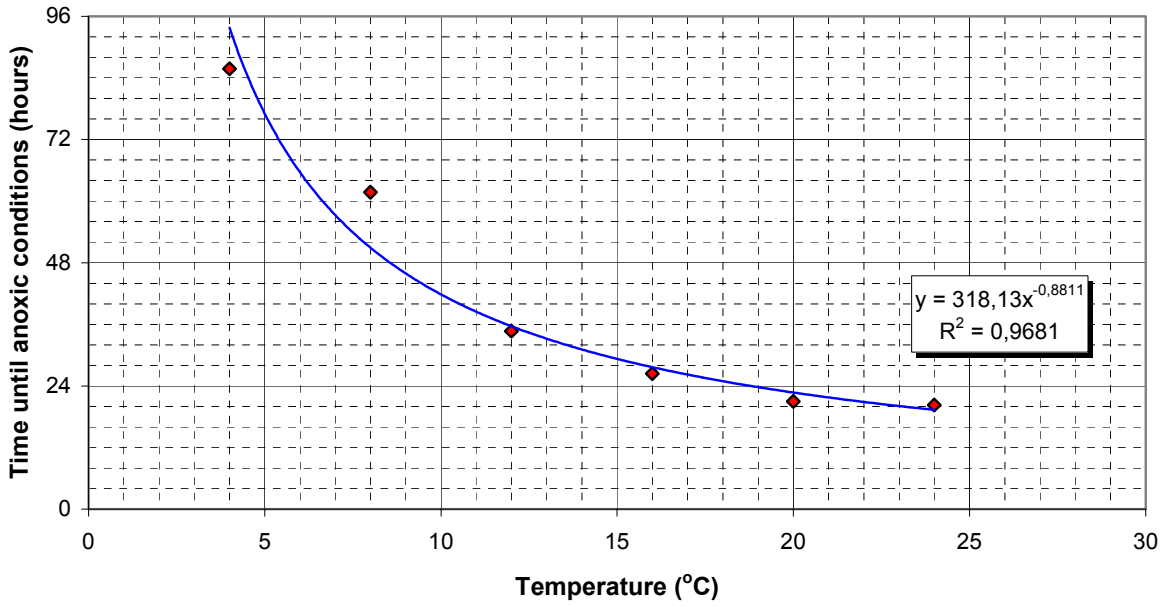


Figure 3.1. Effect of temperature on the time it takes to obtain anoxic conditions.

3.3 Meso-scale studies in Newcastle

In Newcastle eight 50 litre polypropylene vessels were used as ”ballast tanks” (Figure 2). To each tank 5 litres of filtered (5.0 µm) “real” seawater was added as a source of bacteria for the de-oxygenation process. Then 47.5 litres of artificial seawater with added zoo- and phytoplankton species were added. Finally, nutrient solution was added to five tanks, while the three others were used as non-treated controls. The tanks were incubated at ambient temperature, *i.e.* 17.5-18.5 °C.

Figure 3.2. Polypropylene vessel used as ”ballast tank”. The vessel was closed with a silicon rubber stopper, through which an oxygen electrode was inserted into the water to measure dissolved oxygen, and covered with a black plastic bag to minimise exposure to light.

During the incubation, samples were taken at intervals for analysis with respect to turbidity, viable bacteria, and pH. Dissolved oxygen was measured with an oxygen electrode at intervals. At the beginning and end of the experiment, the concentration of H_2S in the water was determined. Before and after treatment the water was analysed for live and dead phyto- and zooplankton as described in Section 8.

3.3.1 Microbiological and chemical changes during the experiment

The concentration of viable bacteria increased from $3 \cdot 10^5$ to $3 \cdot 10^7$ cfu/ml during the first 24 hours in the tanks with added nutrients, and then remained relatively constant. In the control without added nutrients, the concentration varied between $1 \cdot 10^5$ and $2 \cdot 10^6$ cfu/ml during the study.

In the control tanks the dissolved oxygen declined slightly from around 90 % of saturation at start to around 80 % at the end of the experiment. In tanks with added nutrients, the dissolved oxygen started to decline rapidly after about 20 hours, and the water became anoxic after about 30 hours. Thereafter the tanks remained anoxic until about 72 hours after start. Then the dissolved oxygen level started to increase, somewhat varying from tank to tank, but in some cases up to a maximum of around 20 % after about 96 hours. Then the dissolved oxygen again started to decrease and the water became anoxic again after about

120 hours, and remained so for the rest of the experiment. An increase in the dissolved oxygen level after a period of anoxia had also been observed in laboratory experiments at SINTEF, and may be due to oxygen leakage into the tanks. The leakage may occur all the time, but as long as the metabolic activity of the bacteria in the water is high, any oxygen that enters the tank is immediately consumed. However, when the carbon-sources have been consumed, the bacterial activity declines and eventually becomes so low that oxygen starts to accumulate. This theory explains why dissolved oxygen starts to increase, but not why it declines again. A possible explanation for the decline is that when an increase in dissolved oxygen is observed, the operator becomes aware of the possibility of leakage, and extra effort is made to prevent leakage.

pH in the control tanks was 8.2-8.3 throughout the experiment, while pH decreased from 8.2-8.3 to around 6.7 during the first 48 hours in the tanks with added nutrients. Thereafter it decreased slowly to pH 6.5-6.6 at the end of the experiment.

In anoxic seawater sulphate-reducing bacteria may start to reduce sulphate in the water to hydrogen sulphide (H_2S), which is a corrosive and extremely toxic gas. In all tanks at the start of the experiment, and also at the end of the experiment in the control tanks, the concentration of H_2S was 0.02-0.4 µmol/litre. In the treated tanks the concentration increased during the incubation. After 122-123 hours the concentration varied from 0.2-1 µmol/litre, and after 170 hours it was approx. 5 µmol/litre. Only the last value can be considered significantly higher than the background.

3.3.2 Effect of de-oxygenation on the survival of zooplankton

Three species of zooplankton were added to the tanks: the calanoid copepod *Acartia tonsa*, the harpacticoid copepod *Tisbe battagliai* and nectochaete larvae of the polychaete *Nereis virens*.

Both the larvae of *N. virens* and the copepod T. *battagliai* survived the mixing into the artificial seawater, the transfer to the polypropylene vessels, and the stay in the control tanks very well (Figure 3.3). For the copepod *A. tonsa*, however, the process of mixing and transfer to the polypropylene vessels was stressful, and around 60 % of the added individuals died within 48 hours in the control tanks. Those who survived the first phase, however, also survived for the rest of the period.

In tanks with added nutrients, the water became anoxic after about 30 hours. The first two tanks, one with nutrients and one control, were harvested after 50 hours, *i.e*. after 20 hours of anoxic conditions in the treated tank. In the treated tank about 10 % of the examined individuals of *A. tonsa* were still alive, compared with 35 % in the control, while around 60 % of the examined individuals of both *N. virens* and *T. battagliai* were still alive, compared with 95-100 % in the control. The next two tanks were harvested after 98 hours, *i.e*. 38 hours of anoxic conditions in the treated tank. Here almost 30 % of the examined individuals of *A. tonsa* were still alive in the treated tank, compared with 42 % in the control. However, only 13-14 % of the examined individuals of *N. virens* and *T. battagliai* were still alive, compared with 95 % in the control. After 122-123 hours two tanks with added nutrients and one control tank were harvested. None of the examined individuals of *A. tonsa* were alive in the treated tanks, compared with 39 % in the control tank. About 4 % of the examined individuals of *N. virens* were still alive, compared with 92 % in the control, and around 5 % of the examined individuals of T. *battagliai* were still alive, compared with 76 % in the control. The last tank with added nutrients was harvested after 170 hours, *i.e.* after 140 hours of anoxic conditions. For this tank there was no control tank. None of the examined individuals of *A. tonsa* or *N. virens* were alive, but 4 % of the examined individuals of *T. battagliai* were still alive.

Theoretically, each tank should have contained 136 individuals of *A. tonsa* and 54 each of *T. battagliai* and *N. virens* from start. However, the total numbers of recovered individuals, dead or alive, were always

lower than this. On average, the number of individuals recovered from tanks with added nutrients was 28 % of the expected number for *A. tonsa*, 40 % of the expected number for *T. battagliai*, and 15 % of the expected number for *N. virens*. In the control tanks the average recoveries were significantly higher: 78 % of the expected number for *A. tonsa*, 87 % of the expected number for *T. battagliai*, and 33 % of the expected number for *N. virens*. This may indicate that the actual killing rate in the treated tanks was higher than the value obtained by counting live and dead individuals. Possibly, some of the dead zooplankton in the treated tanks had, at the time of harvest, been degraded beyond recognition, or even disintegrated so much that the residues passed through the plankton filter. The bacterial activity in the treated tanks was much higher than in the non-treated tanks, and the degradation of dead zooplankton is therefore likely to have been much faster in the treated tanks than in the control tanks.

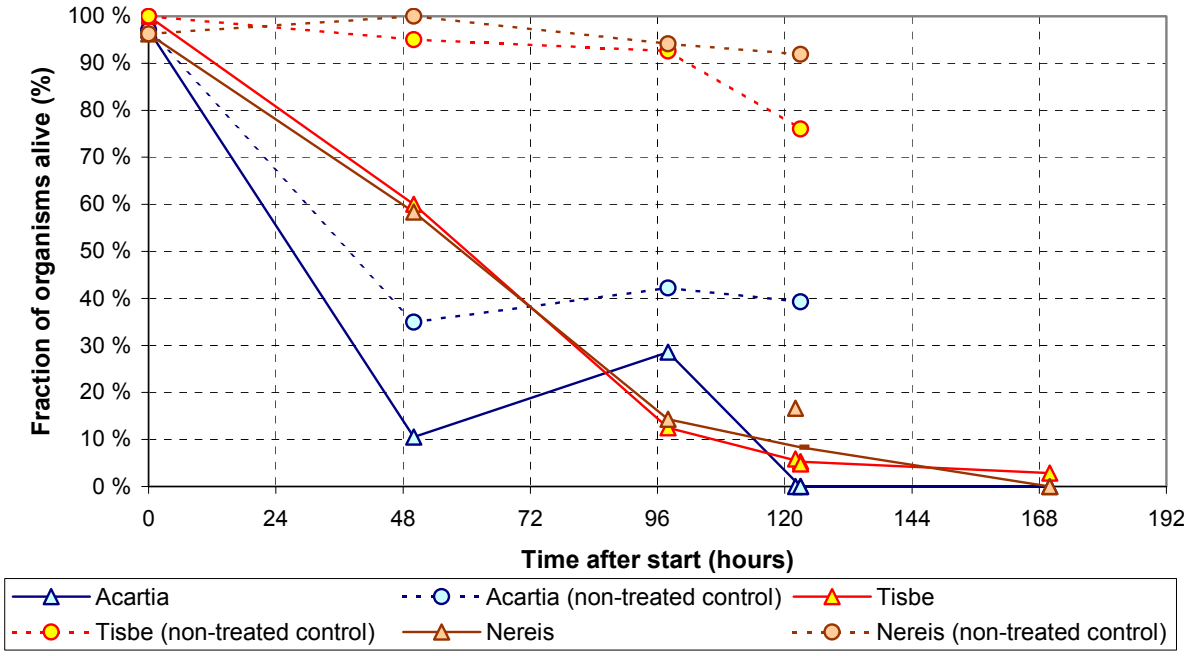


Figure 3.3. Survival of zooplankton as function of the storage time. In the treated tanks, the water became anoxic after approx. 30 hours. The studied organisms were the calanoid copepod Acartia tonsa, the harpacticoid copepod Tisbe battagliai and nectochaete larvae of the polychaete Nereis virens. The survival is calculated based on the recovered individuals from the tanks [living / (living + dead], but the number of recovered individuals varied considerably between different tanks and species (see text).

3.3.3 Effect of de-oxygenation on the survival of phytoplankton

Two phytoplankton species were added to the artificial seawater; the dinoflagellate *A. tamarense* and the diatom *T. pseudonana*. The concentration of the phytoplankton species did not change dramatically during the incubation period (Figure 3.4), neither in the control tanks nor in the treated tanks. The concentration of *A. tamarense* seemed to decrease slightly as a function of incubation time, while there was no significant change in the concentration of *T. pseudonana* during the study. Furthermore, there were no significant differences between the treated tanks and the controls.

Also the concentration of chlorophyll *a* and pheophytin (results not shown) seemed to decrease slightly during the incubation period, but again there was no significant difference between the treated tanks and

the controls. There was no significant change in the ratio of pheophytin to chlorophyll *a* before and after the treatment.

Taken together the phytoplankton results indicate that de-oxygenation did not affect the survival of the added species. The slight reduction in the concentration of the dinoflagellate as a function of incubation time may be due to the fact that the cells were incubated in darkness. For the diatom even the incubation in darkness seemed to have little effect on the survival during the study.

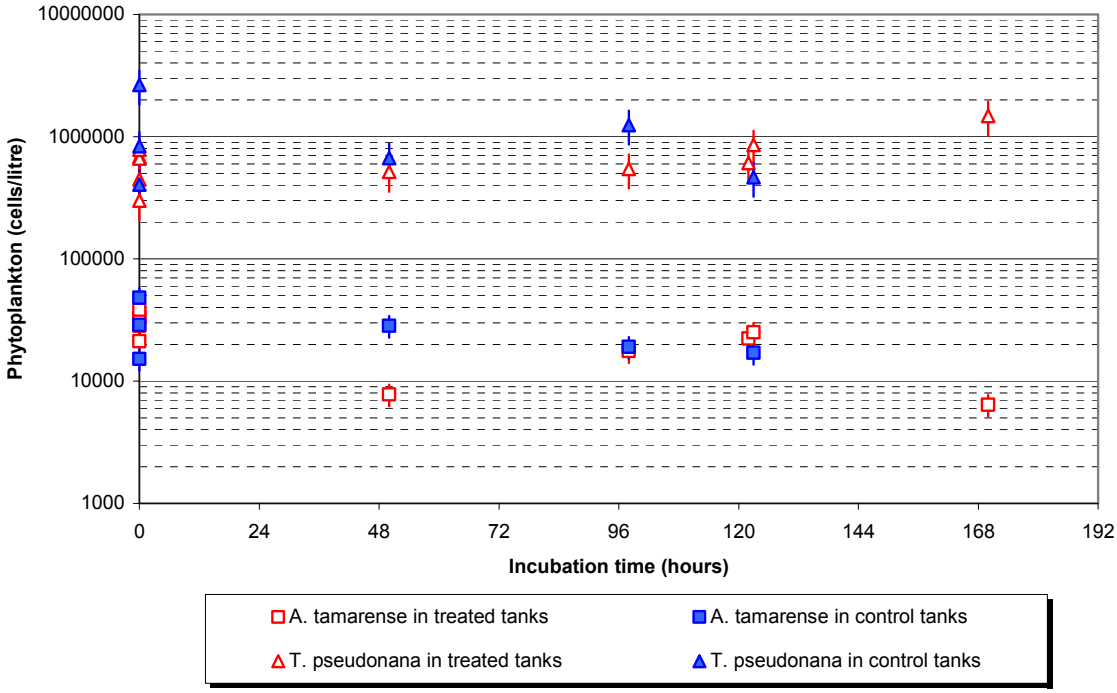


Figure 3.4. Concentration of the dinoflagellate A. tamarense and the diatom T. pseudonana in the treated tanks and the control tanks as a function of incubation time. Approximate standard deviations of ±20 % for A. tamarense and ±31 % for T. pseudonana are indicated.

3.4 Conclusions

A promising nutrient solution for biological de-oxygenation has been designed. However, it may still be necessary to slightly modify the composition to prevent excessive formation of H_2S.

The rate of biological de-oxygenation is dependent upon the temperature. At 4 °C it takes 3-4 days, at 10-20 °C 1-2 days, and above 20 °C less than 1 day to obtain anoxic conditions.

Biological de-oxygenation of the seawater in the trials at Newcastle killed the added zooplankton species. The killing rate increased with increasing time under anoxic conditions. After 4-6 days of anoxia, more than 95 % of the tested organisms were dead.

De-oxygenation of the water had little effect on the survival of the two added species of phytoplankton. A slight decline in the concentration of the dinoflagellate was observed as a function of incubation time, but this was most likely due to the fact that the water was incubated in darkness, and not to the removal of the oxygen. For the diatom even the incubation in darkness seemed to have little effect on the survival within the time-frame studied.

4 Ultraviolet light, Ultrasound and Ozone methods

4.1 Introduction

The main objectives for the laboratory scale test trials in Work Package 3 were to design and development of the proposed methods and demonstrate their effectiveness against the selected organisms. Ultraviolet light, ultrasound and ozone methods were tested in two test phases. The preliminary test phase was carried out in Espoo, Finland, in April-May 2002. The aim of the preliminary test trials was to establish the operational parameters to the Newcastle test trials and study the effectiveness of the methods against *Artemia salina* and algae. The second test phase took place in Newcastle, UK, in June 2002, as part of the collective test trials, in the facilities provided by Newcastle University. The test arrangements were the same than in Espoo trials, excluding the composition of the artificial sea water and the utilisation of the centrifugal pump. The test platform was designed in order to enable the test trials with all three devices without any major re-modification of the system. Ultrasound and ultraviolet light devices were installed in the same aggregate in order to enable the test trials of the combination of ultrasound and ultraviolet as part of the hurdle technologies.

4.2 Ultraviolet light technology

Ultraviolet light irradiation is used for the disinfection of potable, process, aquaculture and waste waters. It achieves disinfection by inducing photochemical changes of biological components within micro-organisms, and more specifically by breaking chemical bonds at the DNA and RNA molecules and proteins in the cell. In the majority of UV disinfection applications, low-pressure mercury arc lamps have been chosen as the source of UV radiation. Approximately 85 % of the output from these lamps is monochromatic at a wavelength (λ) of 253.7 nm. This corresponds to the short wave portion of the UV spectrum which in all spans from 200-280 nm, and is referred as UV-C. The sensitivity of micro-organisms to UV radiation depends on the wavelength. Micro-organisms are sensible to UV radiation between 210 and 320 nm, with a peak at 265 nm.

Ultraviolet light device used in the laboratory test trials was provided and manufactured by Berson Milieutechniek BV, 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 gas discharge lamp and its electric power is 230 V, 50 Hz, 4.0 A. The UV output is 200-400nm or germicidal UV output is 210-320 nm. UV output power is 58 W and operation gas pressure is 2-3 bar. The UV-C output of the lamp remains constant in the temperature range 0-70 °C.

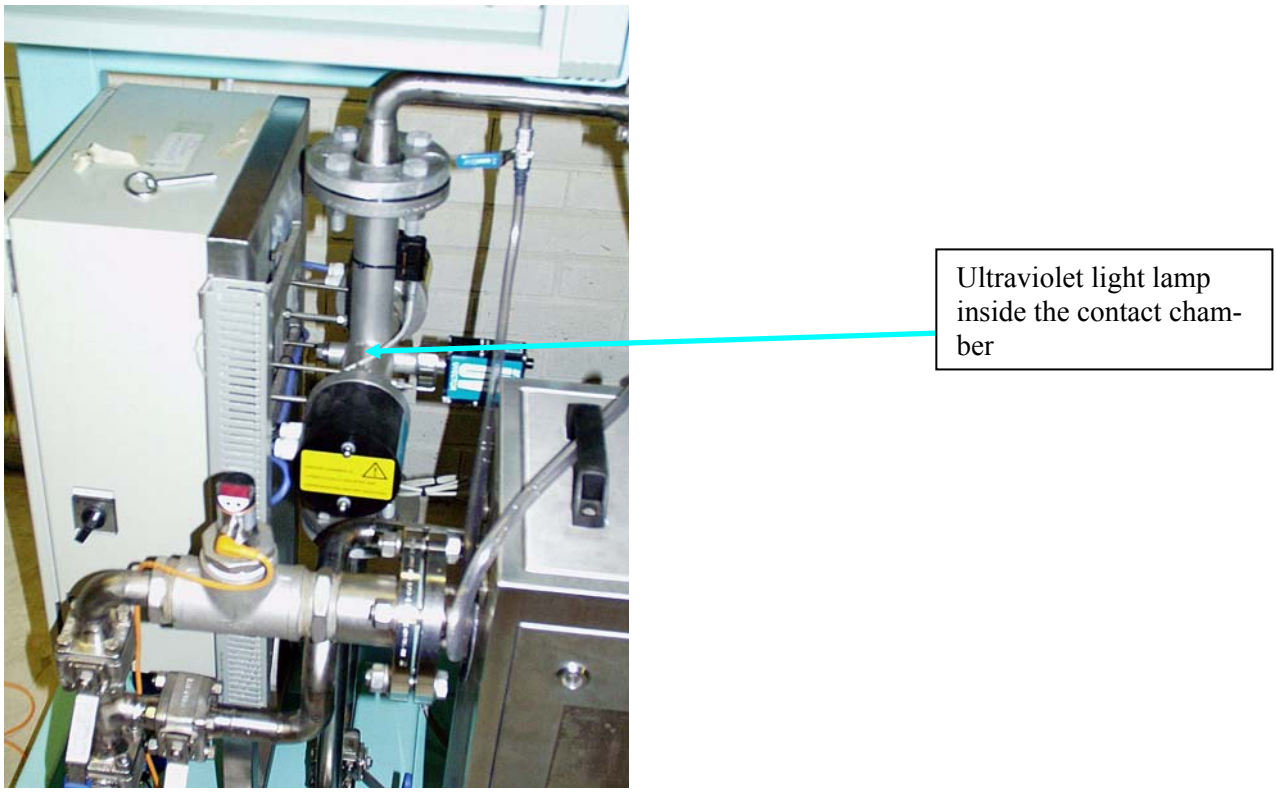


Figure 4.1. The ultraviolet light and the ultrasound devices were mounted in the same aggregate.

4.3 Ultrasound technology

Ultrasonic treatment is relatively new technology in ballast water treatment. Two types of ultrasound exists, low intensity, which is not used to disinfection, and power ultrasound. Ultrasound is generated by transducer, which convert the mechanical or electrical energy into high frequency vibration. The effect of ultrasound is based on physical and chemical changes, destruction of organisms and rupture of cell membranes, resulted from cavitation. The cavitation is influenced by frequency, power density, exposure time and properties of the treated water.

The ultrasound device used in test trials is designed and constructed by Acomarin Engineering Ltd, Naantali, Finland, see Figure 2. The device is equipped with dr. Hielscher UIP 2000 Ultrasonic Processor with effective output power of 2 kW and operating frequency of 20 kHz. The processor includes generator, transducer and sonotrode, which is made of titanium. The processor is 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.

Figure 4.2. The ultraviolet light and ultrasonic devices mounted in the same aggregate. Ultrasound transducer is mounted inside the stainless steel box.

4.4 Ozone technology

Ozone has been used for the disinfection of water supplies since 1886. Marine applications of ozone include depuration of shellfish, oxidation of colour producing organics and toxins, improvement of filtration, control of microbiological contamination in aquaria and aquaculture, and control of biofouling in cooling water systems. Ozone is a fairly powerful but unstable, oxidising agent which rapidly destroys viruses and bacteria, including spores, when used as a disinfectant in conventional water treatment. Ozone is more effective biocide than chlorine and is being used increasingly in the place of chlorine in the treatment of domestic and industrial water supplies. Salt-water ozone reactors are currently used for salt-water aquariums and fish hatcheries.

The three modules of an ozone treatment system are a generator, ozone contact chamber, and ozone destructor. The contact chamber is where the ozone is introduced to the water stream. The biological effectiveness is a function of concentration (equates to energy) and exposure period. The more ozone in the water, the higher is the micro organism mortality. The longer the ozone-contact time, the higher is mortality. In the test device ozone is produced by the reaction of an oxygen molecule and an oxygen atom with the principle of silent electrical discharge from a gas containing oxygen, in this case ambient air. The ozone device is designed and manufactured by ProMinent Dosiertechnik GMBH, Germany, and the maximum ozone dose is 5 g/h. Ozone device was mounted to the metal stand, see Figure 3.

Figure 4.3. The ozone device during the laboratory trials.

4.5 Test Results

In Espoo trials *Artemia salina* and algae was used as the target organisms. Artificial sea water with salinity of 30-35 ppt and average temperature of 18 °C was used. Centrifugal pump was utilised when the water was introduced to the treatment process. Achieved total reduction of *Artemia* was 43-60 % with ozone treatment. The highest reduction rate was achieved on the slowest flow rate and on maximum ozone dosage (150 l/h, ozone dosage of 5.0 g/h). The contact times were short enough to affect only on activity rates but not on mortality rates of *Artemia*. Mortality rates increased rapidly with increasing contact time. With ultrasound treatment total reduction rates of 84-100 % were achieved, best result with flow rate of 200 l/h and with 50 % of maximum transducer amplitude. Regarding ultraviolet treatment, maximum reduction rate of 78 % was achieved with flow rate of 200 l/h and with ultraviolet dose of 562.5 mJ/cm^2.

Also the combination of ultrasound and ultraviolet light was tested as a part of hurdle technology. The result of total reduction of *Artemia* was 82-99 %, best results achieved with flow rate of 400 l/h and with maximum ultrasound amplitude and ultraviolet dose of 281.25 mJ/cm^2. Each test run was carried out only once, hence the results should be regarded as indicative. The algae culture used in the test trials was corrupted, thus the results were abandoned.

In the Newcastle trials standard seawater was prepared for all tests using de-ionised water added with Tropic Marine salt and the target organisms, i.e. *Nereis virens, Acartia tonsa, Tisbe battagliai, Alexan-*

drium tamarense and *Thalassiosira pseudonana*. During the first three and a half days centrifugal pump was used but after realising that the pump itself was eliminating all the zooplankton, a gravity system to supply the water was used. The mortality attained by the ultrasound treatment was always below 40 % for all the tests. The ultraviolet method did not inactivate more than 56 % of the zooplankton. The highest value for the ozone treatment was 89 %, eliminating *Nereis*. In terms of hurdle technology, a better performance from the Filter (125 microns) + ultrasound + ultraviolet test compared to the ultrasound + ultraviolet seems apparent, mainly for *Acartia* and *Tisbe*. As an overall observation, excluding the use of the filter, *Acartia* was the most resistant of the three species and *Nereis* the least.

Phytoplankton results showed that ozone were the most effective at reducing chlorophyll *a* levels with reduction rate of 97 % (flow rate 200 l/h, ozone dosage of 5,0 g/h). Ultrasound achieved the highest reduction rate of pheophytin level, 67 %, with flow rate of 400 l/h and amplitude of 50 % with after flushing sample. The highest reduction rate with chlorophyll *a* levels, 71 %, with ultrasound were also achieved with flow rate of 400 l/h and with amplitude of 100 %. With ultraviolet light treatment, the highest reduction rate of chlorophyll *a* level, 56 %, was achieved with flow rate of 300 l/h and with ultraviolet dose of 375 mJ/cm^2. The highest reduction rate of pheophytin level, 33 %, was achieved with flow rate of 900 l/h and with ultraviolet dose of 125 mJ/cm^2, in after flushing sample. The hurdle technology, ultrasound combined with ultrasound, achieved reduction rate of 68 % with chlorophyll *a* levels and 46 % reduction of pheophytin level (flow rate 300 l/h, US amplitude 100 %, UV dose 375 mJ/cm^2). The combination of filter (125 microns), ultrasound and ultraviolet light achieved the reduction rate of 57 % of chlorophyll *a* level and 52 % reduction rate of pheophytin level (flow rate 300 l/h, US amplitude 100 %, UV dose 375 mJ/cm^2) at its best.

During the first few days in the Newcastle trials a centrifugal pump was utilised for supplying the artificial sea water to the treatment process. The preliminary results indicated that the pump itself was eliminating most of the zooplankton and therefore it was replaced with a gravity supply system for the rest of the tests. Consequently, it was noticed that the bends, valves and long pipes could cause a source of error for ultraviolet light, ultrasound and ozone technologies. Since the flow rate with gravity supply system was much lower that with the pump, it was concluded that some of the species were accumulated into the points with low velocity, thus altering some results. Both living and dead organisms were found to be hidden in the treatment systems. After the problem was noticed, it was decided to flush the systems after each test run, and some of the zooplankton species were detected from the samples. This arrangement could slightly remedy the source of error but there are still concerns regarding the accuracy of analysis.

In addition to the biological effectiveness of the methods, also possibly modification of the ballast water properties and contents by the treatment method was identified. Ultraviolet light causes a slight increase of the Redox potential (short term effect) with possible consequences on metal corrosion, coatings and gaskets. Regarding the ultrasound method no risk of corrosion increase or risk with respect to coating and gaskets was identified. Ozone method causes a significant increase of the Redox potential (short term effect) with possible consequences on metal corrosion, coatings and gaskets. Also the production of O_3 (short term effect) with possible consequences on metal corrosion, coatings and gaskets was identified.

Along with the biological effectiveness and corrosion related matters the economical aspects (preliminary cost calculations), environmental (impacts through discharge to receiving water, energy consumption, chemical spills, materials used) and risk and safety effects were evaluated. Regarding the economical issues the estimated cost for ultraviolet light was 0.11, ultrasound 0.28 and for ozone 0.22 €/m^3 treated ballast water. Ultrasound treatment increased the water temperature about 5-6 °C. None of the discharges of the methods will include substances identified as "priority hazardous substances". Ultraviolet light and ultrasound treatments require additional pipe lines that may cause breaks and ballast water leaks. Ultraviolet lamps contain mercury that would result in damages in case of breakage. The possible hazard with ozone treatment would encompass larger area since the ballast water is treated in the ballast tanks.

4.6 Discussions

When considering the results from the preliminary Espoo trials, it must keep in mind that there were no repetitions hence all of these results are based on only one test run. It is therefore not possible to make any final conclusion of the differences in the efficiency between the three treatments. Compared to the Newcastle trials, more water for each test runs was available, hence the error caused by the piping system might be less notable than in Newcastle trials. Also the higher concentration of the organisms in the test water enabled the utilisation of the centrifugal pump in Espoo trials. Although part of the organisms was eliminated by the pump, still enough organisms survived from the pump and entered to the treatment process. In that respect it might be worthwhile to consider using higher concentrations of target organisms in the test water than it appears in the natural marine environment. When utilising pumps in the test arrangements, it would imitate the real situation where pumps are used during ballasting and de-ballasting.

Of all the treatments tested during the Newcastle trials the experiments carried out with the ozone treatment were the most effective at reducing chlorophyll *a* levels. However, there has to be some caution when examining these results as the initial six ozone experiments were carried out with a pump to transfer the water into the treatment system and this was shown to have the effect of killing all the zooplankton. It is unlikely that the phytoplankton would have been affected as much as the zooplankton by the pump and the following six experiments, which bypassed the pump all together, also show a reduction in chlorophyll *a*. This treatment method would therefore appear to be efficient at reducing phytoplankton biomass. The cell counts showed that the larger *Alexandrium* sp. generally showed a reduction after treatment with ozone but that the counts of the smaller *Thalassiosira* sp. were much more variable and showed some large increases in cell number after treatment. It is possible that there were some differences in the ways in which each species was affected by the ozone. However, there was no significant difference in the average change in cell counts of either species between the four treatments, i.e. ozone, ultrasound or ultraviolet light treatment. Further experiments would have to be carried out to investigate whether there are differences in the effect of the treatment on different species.

Previous studies on ozone have concluded that it may have some potential for ballast water treatment but that pre-treatment such as filtering would be required and that it is likely to be ineffective against difficult taxa such as dinoflagellate cysts. Difficult to kill taxa are likely to require greater doses of ozone for longer periods of time, which raises issues of corrosion and depletion of sacrificial anodes within the ballast tank. A ship board study concentrated on bacteria initially but had no data with respect to phytoplankton. It is therefore difficult to compare the results of these experiments as they have been run under very different circumstances. The results from the Newcastle tests are promising but it will be necessary to test the equipment further in order to investigate how it copes with heavy sediment loads and a greater range of organisms.

The results from the ultrasound experiments are more ambiguous as the effect of the flushing is much more evident in these experiments. For the experiments where the test water was not flushed out of the equipment and sampled in the same way as the test water, the chlorophyll *a* levels are very low and do not demonstrate much change after treatment. However, once the equipment was flushed there is a marked improvement in the reduction of chlorophyll *a*. Two of the experiments resulted in >50% reduction and these were both run at higher flow rates and maximum amplitude so it would appear that these factors could have an influence on the efficiency of the ultrasound. However, it is difficult to draw any firm conclusions as the first 9 (out of 12) runs were not subject to the further flushing of the equipment and this is likely to have had an effect on the results. Again, there are generally reductions in the cell counts for *Alexandrium* sp. but the results for *Thalassiosira* sp. are much more variable and show large increases and decreases in cell numbers.

The effect of the flushing is also apparent in the results of the ultraviolet experiments. Previous experiments have found chlorophyll *a* concentrations 18 hours after treatment could be reduced by 60% in comparison to controls after treatment with UV and that for specific species such as *Tetrasemis* spp. and *Prorocentrum minimum* removal rates of 89 and 92% have been found. Montani et al. found that UV treatment affected the germination of cysts differently, with some species such as *Chattonella* spp. more sensitive than species such as *Scrippsiella* spp. The cell counts for the four experiments carried out generally show a reduction for both species (*Thalassiosira* sp. shows a small increase in one experiment), which would seem to indicate that the ultraviolet light treatment did not affect each species differently. However, in the experiments that combined the ultrasound and ultraviolet the *Thalassiosira* sp. cell counts are much more variable and show large increases after some experiments.

The variability of different experiments, the flushing and the different treatment methods make it very difficult to draw any firm conclusions regarding these results. The chlorophyll *a* and *Alexandrium* sp. cell counts would seem to indicate that some of the treatments have an effect on phytoplankton but the results from the cell counts of *Thalassiosira* sp. are much more variable and do not follow any pattern. Further replicated experiments to examine the effect of the treatments on different species are required.

During the first few days in the Newcastle trials a centrifugal pump was utilised for supplying the artificial sea water to the treatment process. The preliminary results indicated that the pump itself was eliminating most of the zooplankton and therefore it was replaced with a gravity supply system for the rest of the tests. Consequently, it was noticed that the bends, valves and long pipes could cause a source of error for ultraviolet light, ultrasound and ozone technologies. Since the flow rate with gravity supply system was much lower that with the pump, it was concluded that some of the species were accumulated into the points with low velocity, thus altering some results. Both living and dead organisms were found to be hidden in the treatment systems. After the problem was noticed, it was decided to flush the systems after each test run, and some of the zooplankton species were detected from the samples. This arrangement could slightly remedy the source of error but there are still concerns regarding the accuracy of analysis.

The results from biological analysis indicate inconsistency in some level. Logically thinking, if the flow rate is constant and the treatment efficiency is increased, i.e. higher ozone dosage or higher ultrasound amplitude, the reduction rate should also be higher. In that respect, some of the results were confusing and interpretation was difficult. During the test trials in Espoo and in Newcastle the testing devices were working as they were designed. The small amount of water presented uncertainty to the results, since the apparatus were designed for a larger amount of water. The organisms were strong enough to oppose the low flow rates and were able to accumulate to the treatment system. The results from both phytoplankton and zooplankton analysis support that argument. Therefore it is inevitable to conduct large scale onshore test trials to determine operational limits for adjustments and efficiency before any full scale testing.

4.7 Recommendations for large scale test trials

Strategy for large scale test trials is based on the experience gained from laboratory scale test trials. The large scale test phase will be carried out utilising the Baltic Sea marine environment. Duration of test runs with ultrasound and ultraviolet light treatments must be long enough in order to minimise the technical sources of errors, i.e. piping, fittings, valves and small amount of water. The utilisation of real sea water enables the access to unlimited amount of water and thus the error caused by small amount of water can be reduced. Also the link to the actual marine environment is evident. Ultrasound treatment should also be tested with a turbulent flow, since turbulence increases the efficiency of ultrasound treatment.

Regarding the ozone treatment, instead of the flow-through arrangement the contact time will be extended by introducing ozone to a contact tank in order to monitor ozone dosage per amount of water versus contact time. Various ozone dosages and contact times will be studied, possibly also long term test runs

might be carried out. Sampling will be conducted before and after the treatment to monitor the organisms concentrations and species and the alterations induced by the treatment.

5 Oxicide treatment

5.1 Background and objectives

Many water organisms are destroyed when exposed to an oxidative environment, such as hydrogen peroxide. Hydrogen peroxide can be produced in-situ from dissolved oxygen in seawater by means of an electrochemical reaction. This process, the Oxicide process, is carried out in an especially designed and patented electrochemical reactor. Seawater is led through a 3-dimensional electrode (cathode) where hydrogen peroxide is formed by the reaction:

$$O_2 + 2e + 2H^+ \rightarrow H_2O_2$$

The other electrode (anode) is separated from the seawater by a membrane. A special liquid is recirculated over the anode to enhance the reaction rate; basically, the liquid (anolyte) needs no replacement. The membrane in the electrochemical cell prevents the migration of chloride in the seawater to the anode and hence no chlorine gas or other chlorine compounds are formed by the Oxicide treatment. The main reaction at the anode is:

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e$$

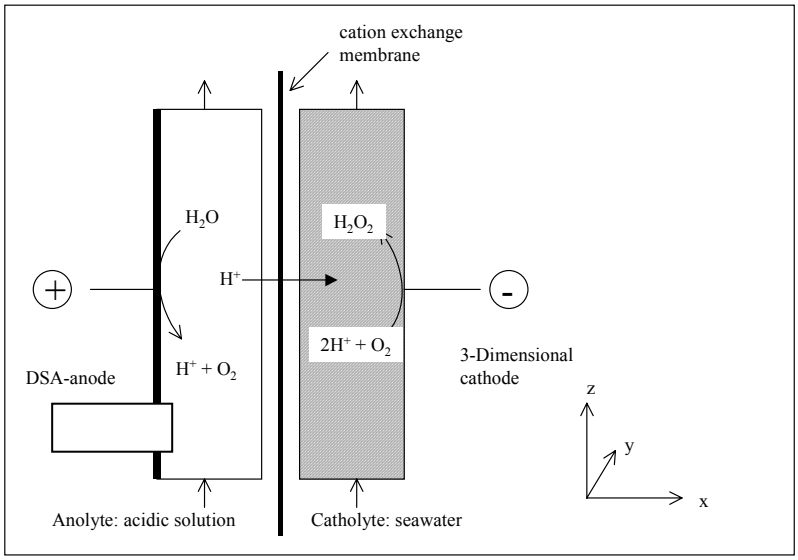


Figure 5.1. The principle of H_2O_2 production by the Oxicide method.

The main objectives of the work in WP3 were:

- realisation of the proof-of-principle of the Oxicide process on a 100 dm^3/h scale;
- a first evaluation of the effectivity against biology in seawater and feasibility of the technology;
- collecting data needed for designing the pilot test in MARTOB WP4 and evaluation of the operating aspects of the Oxicide method.

The Oxicide reactor and test facility was designed and built by TNO and Van den Heuvel Watertechnology. The influence of various operating parameters was determined in laboratory experiments, followed by assessment of the biological efficacy of hydrogen peroxide. Oxicide was also tested in joint experiments at the premises of UNEW in Newcastle (UK), according to the MARTOB test-protocol.

5.2 Hydrogen peroxide production in the Oxicide module

A first-generation design of the Oxicide cell has been tested under laboratory conditions, see figure 5.2. The installation contained three Oxicide cells in series, each with a 3-dimensional cathode for generating hydrogen peroxide and a membrane unit (Transversal Flow Module) for supplying oxygen to the water. The following findings result from laboratory tests.

- The maximum achievable concentration of hydrogen peroxide in seawater is determined by kinetics and depends on the concentration of dissolved oxygen, temperature, electrical current and cell voltage. The H_2O_2 concentration follows a logarithmic trend during batch operation. The highest concentration of H_2O_2 achieved in tests is ca. 400 mg/dm3 (20 degC). The initial current efficiency (CE) is up to 70-80%. The highest H_2O_2 production rate achieved in the laboratory scale Oxicide module is 1 g/h.
- In single pass mode the current Oxicide module (three cells in series) is able to produce up to 10 mg/dm3 H_2O_2 in seawater at a flow rate of 100 dm^3/h and a CE of 80% (production rate = 900 mg/h). The production rate and H_2O_2 concentration in the seawater is influenced by the flow rate through the Oxicide cell.
- The trends of H2O2 production are the same when air is used in stead of oxygen gas, but production rates and limiting concentrations are 3 to 5 times lower.
- It is possible to produce H_2O_2 in seawater that contains a variety of organisms (zooplankton and phytoplankton). The production takes place with the same efficiency and rates compared to when no organisms are present.
- The pH of the seawater at the outlet of the module is influenced by the composition of the liquid in the anode compartment (anolyte), due to H+ diffusing through the membrane of the Oxicide cell. The maximum observed pH drop was almost 2 pH-units during a recirculation test (from pH 8.4 to pH 6.5)
- The Oxicide module shows no irreversible retention of particles < 100 μm, whether it be inert Kaolin (inorganic), flower (organic) or algae, in tests with 50 dm^3 of suspension and 1 g/dm^3 of solids.

Figure 5.2: Set up of laboratory installation with first generation Oxicide cell

5.3 Biological efficacy of the Oxicide technique

- Hydrogen peroxide shows good promise as a disinfectant in seawater. At relatively low concentrations (10-30 mg H_2O_2/dm3) various organisms are killed efficiently and in a short period of time (<48 hrs). Some organisms need larger concentrations to be killed in a short time (>100 mg/dm3). A contact time of 24 hrs or more is needed for the H_2O_2 to take full effect.
- Electrochemically produced H_2O_2 and a technical H_2O_2 solution show the same efficiency in killing marine organisms. This is also an indication that no harmful by-products are formed.
- Hydrogen peroxide shows promising results against zooplankton at relatively low concentrations (10-15 mg/dm3). The tests at UNEW show that H_2O_2 is very efficient against *Nereis* (100% kill rate in all experiments) and reasonably efficient against *Acartia* (≥ 90% kill rate in all experiments). Tisbe proves more difficult to kill with H_2O_2, but at higher concentrations H_2O_2 (> 28 mg/dm3) *Tisbe* is also killed at efficiencies > 85%. Elevated temperature seems to improve the efficiency of H_2O_2.
- Hydrogen peroxide showed promising results against phytoplankton during some tests at TNO, but the joint tests in Newcastle were not conclusive. The TNO tests with among others a *Skeletonema* culture resulted in fast removal of the organisms at concentrations levels of approx 15 mg H_2O_2/l, see table 5.1. In Newcastle no significant treatment effect was detected in the percentage change in chlorophyll a (see figure 5.3). Although treatments 3 and 4 consistently resulted in reduction and increase, respectively, in chlorophyll a, the other treatments, 1 and 2, produced inconsistent results. For the first run of treatment 1 there was a reduction in chlorophyll a after treatment but for second there was a small increase. In the case of treatment 2, there was a reduction of 31.6% for the first test run, an increase of 1.5% for the second and an increase of 87.3% for the third.

Table 5.1. Summary of test results of experiments with Skeletonema with technical and electrochemical-produced hydrogen peroxide (TNO tests); LC50 is the concentration that is lethal to 50% of the population

	Bottle		Electrochemical cell	
Time	**LC50**	**R_2**	**LC50**	**R_2**
1:45 h	17.2 mg/l	0.91		
2:30 h			21.7 mg/l	0.89
3:15 h	14.2 mg/l	1.00		
3:40 h			16.5 mg/l	0.90
4:45 h	8.5 mg/l	0.98		
5:25 h			14.0 mg/l	1.00

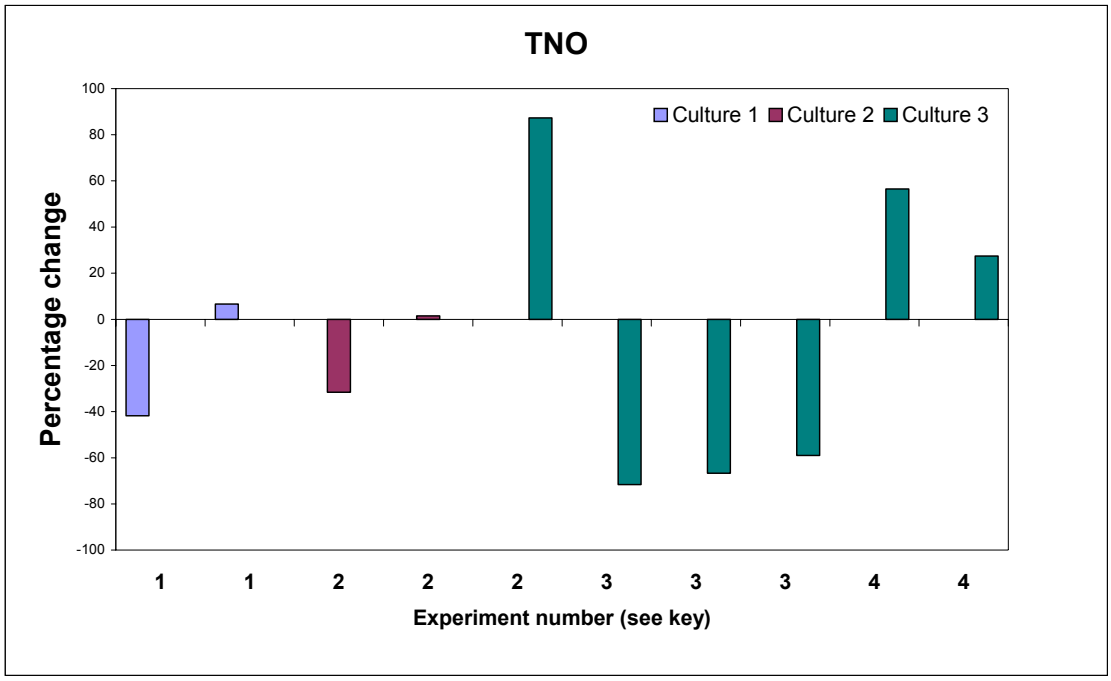


Figure5.3. Percentage changes in chlorophyll a levels after Oxicide treatment (Newcastle tests).
Key: 1) Hydrogen peroxide added to the standard sea water to a final concentration of 13.3 and 13.1 mg/l. **2)** Experiments run at elevated temperatures of 35, 30 and 30 ^{o}C with final concentrations of 9.1, 14.5 and 16.5 mg/l of hydrogen peroxide (ordered sequentially in figure). **3)** Hydrogen peroxide produced in the test seawater to investigate the influence of organisms on the production of hydrogen peroxide. The final concentrations of hydrogen peroxide were 10.6, 13.8 and 14.1 mg/l (listed sequentially). **4)** High concentrations (28 and 64 mg/l respectively) of hydrogen peroxide were added to the standard seawater.

5.4 Operation and design of the Oxicide module

The first design of the Oxicide module performed well and stable over a period of approx. 200 hours and the process shows promise as a treatment technology for ballast water. However, the design is not yet optimal in relation to the production rate. Based on the current Oxicide cell design, the treatment of 1000 m^3/h of ballast water would need an electrochemical module of 37.5 m^3 or more. This would result in considerable economical investment and use of space. Issues for the next generation Oxicide cell have been considered, including:

- Improved and simplified design of the oxygen transfer unit;
- Dimensions and an improved electrode configuration, resulting in:
  - higher utilisation of oxygen in the water;
  - increased production rate per m3 of module volume
- These changes will result in substantial lower costs for Oxicide than now estimated (see paragraph 7).

5.5 Ballast water treatment configuration

Highest production rates and current efficiencies are achieved at the lowest concentration of hydrogen peroxide. The likely method of treatment will be the treatment of a side stream of the ballast water upon intake (10% of the full stream) and subsequent treatment of circulating ballast water during the voyage, from the ballast tank through the Oxicide plant back to the ballast tank. Further development of the Oxicide technology will be directed towards this scenario.

5.6 Economic environmental aspects of interest related to up-scaling the treatment system

In view of up-scaling the Oxicide treatment method to large-scale or even full size ship application, several environmental economic aspects are of interest. In task 3.5.2 the main aspects of interest were defined, selected and (partly) assessed, i.e.:

- Pressure in the Oxicide cell: atmospheric, small overpressure or pressurised;
- Source of primary material, oxygen, in the electrochemical cell: air or pure oxygen;
- Power consumption of the Oxicide cell and its impact on total power consumption of the ship;
- Capacity of the Oxicide cell;
- Efficiency of H_2O_2-production;
- Formation of by-products, its harmfulness and ways to handle them during the generation of H_2O_2 in the Oxicide cell;
- Differences of installation and use of the Oxicide technology between existing and new ships;
- Sizing and costing of full scale Oxicide technology;
- Full versus partial treatment of ballast water.

Many of the aspects of interest were covered by the experimental work. In co-operation with the designer and the manufacturer of the Oxicide technology, it will be decided which of the aspects described above will be further assessed in WP4.

5.7 Further research (work package 4)

More experimental work needs to be carried out to be conclusive about some of the findings in T3.5:

- effect of Oxicide on phytoplankton
- effect of flow rate and electrical currents on production rate

Additional work is suggested on:

- effect of Oxicide on other organisms than those tested
- cell geometry and electrode material
- oxygen transfer options
- the options and considerations for on-board installation

- the option to improve performance (production and/or biological efficiency) by using slightly increased temperatures

For pheophytin there was a significant difference ($p<0.01$) in the percentage change due to the different treatments (see Figure 5.4). The effects of treatments 3 and 4 were significantly different, with treatment 3 giving an average decrease of 70% and treatment 4 giving an average increase of 99%.

This treatment resulted in very variable responses in terms of the changes in cell counts of the phytoplankton, even allowing for substituted samples (see Table 3.4). The percentage changes in cell counts of *Alexandrium* sp. varied between -96% and +438% as seen in Figure 6.2. The corresponding changes for *Thalassiosira* sp. varied between -18% and +460% (see Figure 6.3). Runs of the same form of the treatment also provided very variable outcomes. The extremes quoted for *Thalassiosira* sp. arose from consecutive runs of the same treatment on the same culture and day.

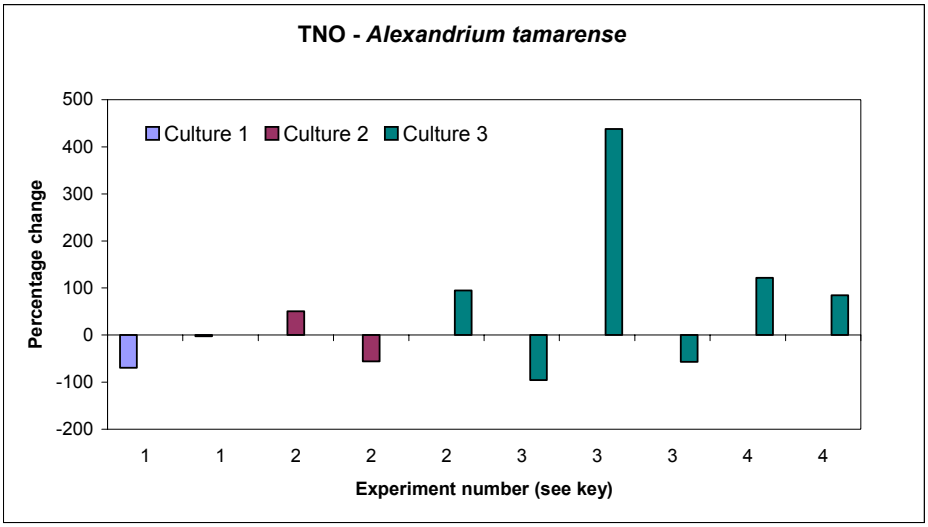


Figure 5.4. Alexandrium tamarense. Percentage change in cell count.

Key: 1) Hydrogen peroxide added to the standard sea water to a final concentration of 13.3 and 13.1 mg/l. **2)** Experiments run at elevated temperatures of 35, 30 and 30 ^{o}C with final concentrations of 9.1, 14.5 and 16.5 mg/l of hydrogen peroxide (ordered sequentially in figure). **3)** Hydrogen peroxide produced in the test seawater to investigate the influence of organisms on the production of hydrogen peroxide. The final concentrations of hydrogen peroxide were 10.6, 13.8 and 14.1 mg/l (listed sequentially). **4)** High concentrations (28 and 64 mg/l respectively) of hydrogen peroxide were added to the standard seawater.

6 Hurdle Technology

6.1 Introduction

Combining disinfecting technologies offer the option of eliminating the limitations of individual techniques as well as the advantage of using the synergy of different methods. From food industry it is known that combinations of two disinfecting techniques have more effect than the sum of individual conservation methods. One well known application of hurdle technology in ballast water treatment is the combination of filter technology (hydrocyclons) and UV disinfection.

To assess the effectiveness of combinations of techniques a number of individual techniques being tested at Newcastle were combined based on the combined synergistic effect.

6.1.1 Materials and Methods

Since the single techniques (e.g. heat treatment) being tested can be used as a point of reference, the following combinations were not tested as a duplicate set of experiments. Some of the techniques present in Newcastle (e.g. UV) were also tested not in combination with other techniques, as these were not present in the programme.

Techniques combined:

- Ultrasound (US) + Ultraviolet (UV): from a tank the water was gravity fed through a US device, followed by a UV unit. The effluent was collected for micro biological analysis.
- Mechanical filter (MF) + US/UV: the same set-up as for US+UV was used, but now a 125µm filter cloth was inserted in the exit from the sample tank.
- Thermal treatment (TT) + de-oxygenation (DO): the water was treated by the thermal treatment method (continuous process) and collected. After completion of the batch it was held in a container for the de-oxygenation treatment.
- UV + H_2O_2: A batch of hydrogen peroxide was prepared, then fed through the UV system.
- MF + UV/H_2O_2: The same procedure as UV + H_2O_2 with a 125µm filter cloth installed.
- H_2O_2 + TT: A batch of hydrogen peroxide was prepared, followed by thermal treatment.
- UV: a batch was treated, to obtain the performance of the single technique.
- US: a batch was treated, to obtain the performance of the single technique.
- MF: “real”sea water was used to be treated by the MF, rather than the artificial “soup”.

For a detailed description of the individual techniques, refer to the respective chapters.

With some of the preliminary results known, the parameters for the individual techniques were chosen not to kill 100%. So after the first technique some of the animals survived, as to be treated by the second technique.

The following table lists the process parameters set for the individual techniques.

Table 1. process conditions of individual techniques during Hurdle testing.

treatment method	sample i.d.	flow [l/h]	power [kW]	T10 [% @ 254nm]	T [°C]	C [mg/l]	mech. filter [μm]	remarks
US+UV	3/12/1	100	2.4	94	17			
US+UV	3/12/2	300	2.4	94	17			
MF+US/UV	3/12/3	100	2.4	94	17		125	
MF+US/UV	3/13/1	300	2.4	92			125	
TT+DO	6/12/1	100			40			
TT+DO	6/12/1							after treatment
TT+DO	6/14/1	100			45			
UV	3/13/2	300	0.4	95				short piping
UV+H_2O_2	6/13/1	300	0.4	93		3.1		
UV+H_2O_2	6/14/2	300	0.4	91		17.2		
MF+UV/H_2O_2	6/13/2	240	0.4	93		4.5	125	
MF+UV/H_2O_2	6/14/3	300	0.4	91		14.9		
H_2O_2+TT	6/14/4				40	15		
UV		290	0.4	96				micro biological
MF	6/14/5						125	real seawater, filter blocks after 5 litres of seawater

6.2 Results and Discussion

6.2.1 Thermal treatment and de-oxygenation

No valid results were obtained for the treatment at 40°C, as the sample before treatment already showed a 100% mortality. The mortality by thermal treatment at 45°C shows 90% for *Acartia*, 50% for *Tisbe* and 30% for *Nereis*. De-oxygenation has 100% mortality for *Acartia* and *Nereis* and 97% for *Tisbe*. The combination of techniques shows 100% mortality for *Tisbe* and *Nereis* and 92% for *Acartia*. The combination has no improvement for *Nereis* over the individual technique (de-oxygenation or thermal treatment at 50°C). The improvement for *Tisbe* from 97 to 100% can be accounted for as an insignificant increase. In case of *Acartia* the combination performs less than the individual techniques, which is related to the overall accuracy of the measurements.

The main advantage of the combined techniques is that the treatment period for de-oxygenation decreases significantly. As the process is completed when the oxygen concentration dropped to 0%, for the individual technique in the same time frame it is still 80%.

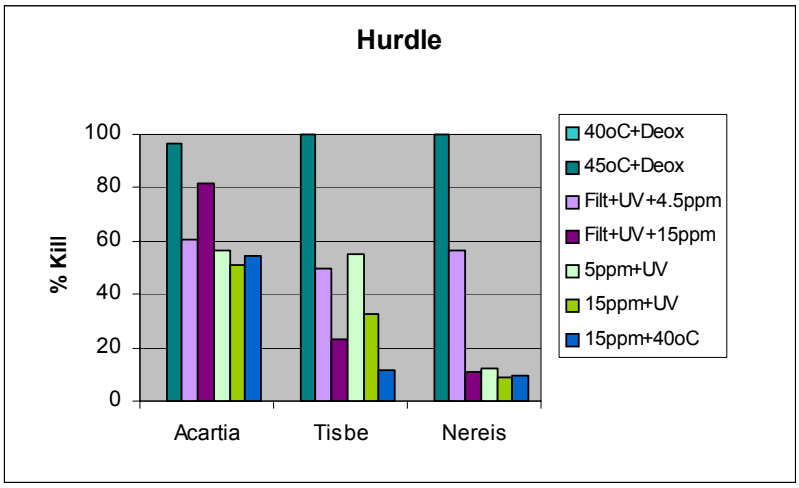


***Fig 1**. % Kill of the 3 different species of zooplankton depending on the treatment applied.*
Note: There are no data for the '40°C + De-oxygenation' treatment. The before sample for this treatment had a 100% of mortality for all three species. Therefore the invalidation of the after treatment sample was necessary.

6.2.2 UV + Hydrogen peroxide

Hydrogen peroxide treatment results is in 93% mortality of *Acartia*, 47% of *Tisbe* and 99% of *Nereis*. Then combined with UV the mortality of *Acartia* drops to 50% (for both 3.1 and 17.2 mg/l) and 10% for *Nereis*. For *Tisbe* 55% (3.1 mg/l) and 30% (17.2 mg/l) are recorded. At 300l/h the UV mortality is 25-30% for all three organisms. So the combination of techniques does not improve the performance as possibly obtained by one of the individual techniques. This can be explained in this way that the UV reduces the amount of H_2O_2 by the formation of OH radicals. Apparently the organisms are susceptible to hydrogen peroxide rather than OH radicals.

6.2.3 UV + Hydrogen peroxide and mechanical filter

The addition of a 125µm filter to the process above, improves the mortality towards Acartia, not for Tisbe and Nereis. The overall performance of the combination is less than for hydrogen peroxide as a single technique.

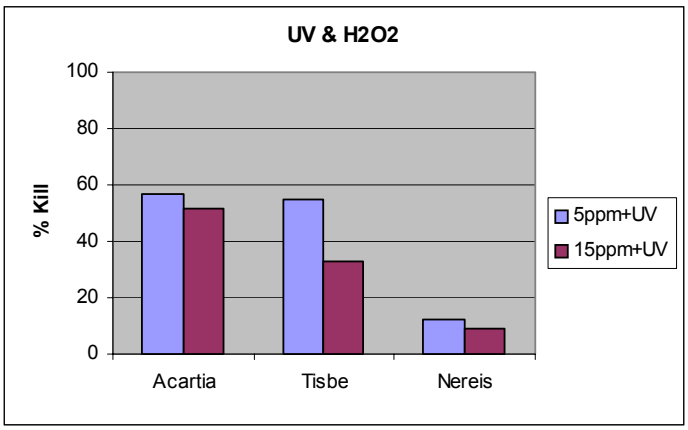


***Fig. 2** % Kill for the UV+H_2O_2 hurdle technology, comparing 2 different concentrations.*

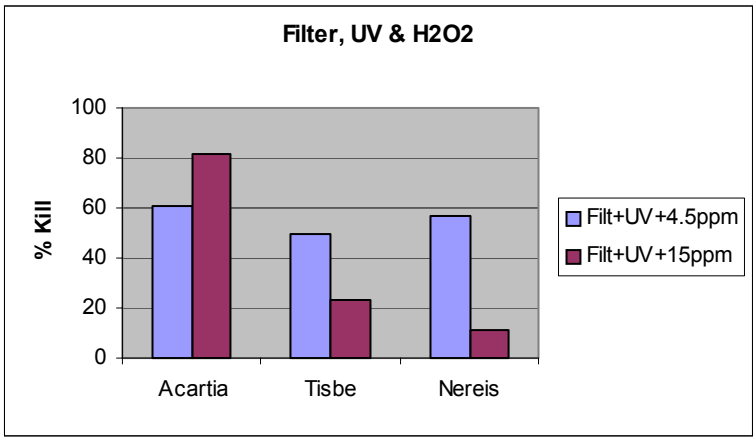


Fig. 3. *% Kill of organisms for hurdle technology of Filter+UV+H_2O_2, with 2 different concentrations.*

6.2.4 Hydrogen peroxide + thermal treatment

Addition of 15mg/l +H_2O_2, prior to thermal treatment at 40°C shows improved performance towards Acartia and Nereis and similar performance for Tisbe. But only in relation to the single technique of thermal treatment, not compared to the single treatment with hydrogen peroxide. The results do not match logic reason.

6.2.5 Ultrasound + Ultraviolet

Where the individual techniques show a mortality of around 10-20% for both US and UV, the combination shows none for *Acartia* and *Tisbe*, 5% for *Nereis* at low water flow and none for *Acartia*, 10% for *Tisbe* and 40% for *Nereis* at high flow. The results are not unanimous, which could relate to the pipework of the pilot installation. The addition of a 125µm filter improves the performance.

6.2.6 Additional tests

The UV system was operated as a single treatment and analysed for micro biological effect. The water used was derived from the de-oxygenation test, which has for certain a large amount of micro organisms, which are added together with nutrients and allowed to grow in number. The UV reduced a log 7 (e.g from 1×10^9 to 1×10^2) as most probable number (MPN).

Seawater taken from the nearby shore was tested on a mechanical filter. The particles (sand, organic materials) present in the water block the 125µm filter after flushing 5 litres of seawater through this 3 cm diameter filter.

6.3 Conclusion

None of the combinations of techniques tested under hurdle techniques show a significant qualitative improvement. The combination of thermal treatment and de-oxygenation benefits from the reduced time to reach a 0% oxygen level, which helps in the process of ballast water treatment.

However the mechanical filter is not contributing to the performance in a uniform way, the results from Benrad do benefit from adding a filter to the process.

The pilot unit for UV/US treatment will be subject to treatment of larger flows of seawater in continued test in Finland.

7 Environmental Impacts, Risk and Safety, and Economic Aspects of Ballast Water Treatment Methods

7.1 Introduction

Economic aspects, environmental impacts, and risk and safety effects of ballast water treatment methods tested in work package 3 of the MARTOB project were evaluated. Information from the laboratory scale test reports and from information provided by system designers for ballast water treatment on a case study ship formed the basis of the evaluation. Evaluation criteria developed in task 2.6 were used to assess each of these effects. To provide a consistent basis for comparing the individual ballast water treatment techniques, a theoretical case study approach was used. Data on the case ship and sample voyage was specified and provided to the technical developers in the project, as well as a list of data needed for assessing cost, environmental effects, and hazards.

7.2 Risk and safety effects

For the risk and safety assessment of ballast water treatment methods, hazard identification was carried out and some recommendations for potential risk control measures were provided. Hazards can be considered from the perspective of safety/survivability of the vessel and safety of the crew during ship operations. Categories of hazards related to operation of the ballast water treatment methods 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. The major hazards associated with most of the treatment methods, including thermal treatment, UV, US, BenRad, and Oxicide, were confined to the equipment location. For biological de-oxygenation and ozone, the hazard would encompass a larger area of the ship because ballast water is treated in the ballast tanks.

Most of the ballast water treatment methods, with the exception of biological de-oxygenation and ozone, require the ballast water to be pumped through treatment systems. This additional piping means that there is an additional risk for pipe breaks and leaks in areas of the ship where there were previously no risks of ballast water leaks. However, this is expected to be a minor risk as most additional pipe work would be in a very localized area. For the Oxicide method the ballast water being pumped into the tanks will contain hydrogen peroxide so this could increase problems from a spill. For BenRad, the treated water will have a low dissolved oxygen concentration and will be more corrosive. For thermal treatment, if there is a pipe break within the heat exchanger system, there could be a discharge of hot water.

Other hazards associated with ballast water treatment include the potential for a spill of hazardous material stored or being used within the treatment. The UV and BenRad treatment systems both use UV lamps that contain mercury or amalgamated mercury. The Oxicide method uses nitric acid as an anolyte and requires sodium nitrate salt to be stored on board. All of these could result in damages if accidentally released.

With all methods, there is the potential to reduce risks through appropriate training and safety procedures. If these systems are installed on new ships additional safety features could be considered during ship design.

7.3 Environmental Effects

Environmental impact categories used to assess the effects of each of the ballast water treatment technologies tested in WP3 of the MARTOB project included:

- Direct Impact through Discharge to Receiving Water:
  - 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)
- Other Environmental Impacts
  - Energy consumption (treatment systems, additional pumping, filtration)
  - Potential for spill of treatment chemicals
  - Materials use (both for consumables and for construction of treatment equipment)

Although some of the treatment methods will result in the discharge of ballast water with altered quality, none of the discharges will include substances that are identified as 'priority hazardous substances', or that have the potential to bio-accumulate. Ballast water quality will undergo the most changes with the biological oxygen removal method, which will produce a discharge that is low in dissolved oxygen and that has increased concentrations of nutrients and bacteria. The BenRad method will lower the dissolved oxygen concentration of the ballast water. The Oxicide method will lower the dissolved oxygen concentration temporarily. Increased temperature of the ballast water discharge will occur after thermal treatment (10˚C temperature increase) and ultrasound treatment (estimated range of 5-6˚C temperature increase was observed at laboratory scale). UV treatment has no effect on ballast water quality.

For all methods, the ballast water discharge will include some form of organic matter in the form of dead organisms, but this will vary depending on filtration use, treatment type, and the concentration of organisms in the intake ballast water. The potential impact of this would be much less than if live non-indigenous species are released, but could be of minor concern in eutrophic waters. All but two of the treatment methods would be operated using a filter as pre-treatment. Methods using the filter as pre-treatment will need to discharge the filtered material to the receiving environment, which could cause some turbidity.

All treatment methods require the use of some energy, and this will result in environmental effects from fuel consumption and associated emissions. Energy use is lowest for biological oxygen removal and high temperature thermal treatment is the most energy intensive method.

Stainless steel and titanium are the most commonly used materials for the treatment systems. Materials used for construction of the treatment equipment will be further refined in the next phase of the project (WP4) when the treatment systems are constructed for full scale testing. It should then be possible to have more detailed information to do a life cycle assessment of the methods.

7.4 Economic Aspects

Installation of an on-board ballast water treatment system will lead to changes in a ships' capital costs, changes in annual operating costs, and possibly will lead to extra training and management costs and economic benefits or disadvantages. Generally, the cost calculation results highly depend on some basic data associated with shipping trade and ballast water treatment. This may include 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, number of ballast pumps and their capacities, type of fuel used, type of treatment and treatment capacity. Costs can be easily compared when they are calculated based on the same type of dependants mentioned above. The theoretical case study approach provided a consistent basis upon which to compare costs.

From the preliminary cost calculations it can be concluded that there are still some data gaps to be filled in. For some treatment methods the potential cost and cost factors are already quite transparent, for some other systems there is still a lot of data to be estimated. The differences are partly related to the status of development of the method. It is expected that during up-scaling of the systems and the large-scale trials in WP4 more data will become available. In addition more research into tank cleaning costs, cost of corrosion control, certification cost, average wages of on-board personnel, total shipping cost to be able to calculate the impact of ballast water treatment on the total cost of shipping, needs to be done. During WP4 the cost calculations will be further improved and refined.

The preliminary cost of treatment of ballast water on "the case study ship" varies considerably, ranging from €0.10/m^3 in the case of biological de-oxygenation up to €2.34/m^3 for Oxicide, see Table 7.1.

Table 7.1. Preliminary cost calculations.

Cost Type	**Details**	**Thermal Treatment**	**Biological Oxygen removal**	**UV**	**US**	**Ozone**	**Oxicide**	**AOT (average)**
Capital costs		€	€	€	€	€	€	€
TOTAL capital costs (for 10 years)	one time investment costs (including investment, installation, testing and commissioning)	110,000	50,000	60,500	130,000	105,000	1,552,000	125,000
Capital costs / year	10 year depr. at 8 % interest	16,393	7,451	9,016	19,374	15,648	231,294	18,629
Operational Costs		€/year	€/year	€/year	€/year	€/year	€/year	€/year
Material costs	Costs of all materials needed in the course of system operation, including fuel	38,764	2,629	1,434	1,672	3,501	2,837	2,943
Maintenance costs	Including materials and labour	0	0	75	7,000	2,200	0	1,813
Training and management costs	Including training, management, certification	0	0	200	200	575	360	75
Total costs (€ / year)	All costs annualised	**55,157**	**10,081**	**10,726**	**28,245**	**22,124**	**234,491**	**23,459**
Costs per m3 BW (€/m^3 BW)	All costs calculated towards costs per tonne ballast water treated	0,55	0,10	0,11	0,28	0,22	2,34	0,23

Nevertheless, it should be kept in mind that not all data were available for the techniques, and some were preliminary.

8 Assessment of biological effectiveness

8.1 Introduction

The purpose of the laboratory-scale testing phase of the MARTOB project was to test a range of ballast water treatment methods using a standard mixture of seawater and target organisms. Specifications for the seawater/organism mixture were developed within the MARTOB project. The test organisms included three species of zooplankton and two species of phytoplankton. By using a standard mixture and analysis method it was possible to measure the biological effectiveness of all methods and to make basic comparisons. In June 2002, laboratory scale testing of selected ballast water treatment methods was carried out at the School of Marine Science and Technology at the University of Newcastle upon Tyne.

In addition to assessing biological effectiveness of the treatment methods, information on safety, corrosion, costs, and potential environmental 'side-effects' is being collected for each method. It is important that the methods are practical, safe for the ship and its crew, environmentally friendly, and economically viable. These characteristics are in addition to the primary requirement that the methods have to be effective at controlling the spread of alien species.

8.2 Materials and Methods

Standard seawater was prepared for all tests 24 hours before use. Deionised water (supplier) was added to Tropic Marine salt (35g/l) (Aquatics Unlimited, Bridgewater, Wales) in 4 mesocosms of 250 or 450l. Following the addition of water, the mixture was agitated continuously for 24h using compressed air to ensure that all the salt had dissolved. Salinity was checked using a refractometer.

Cultures were supplied in bulk, zooplankton every 2 days and phytoplankton every 5 days. They were stored in CT rooms in the aquarium suite at the Ridley Building, University of Newcastle, at 10 and 15^{o}C respectively.

Information on supplied plankton density was available from the suppliers. Samples were measured out directly from the cultures, each species being stored in a separate bottle. The organisms were mixed with 70l of seawater that had been pumped into a tank, to create a sample of test organisms, the 'soup' (Table 1). This was the agreed minimum volume to be used in the experiments that would be statistically significant regarding the density of the organisms added as well as being cost effective. However this volume can always be increased in the case larger experiments are wanted to be conducted. After pouring the samples into the prepared seawater the bottles used to carry them were rinsed twice in the same water and added to the mixture.

Prior to pumping the soup into test rigs the mixture was gently agitated to ensure a homogeneous mixture. Following pumping to the test rigs the tank was rinsed with clean seawater to ensure removal of any residual organisms.

Before initiating the treatments, a 10 l initial sample was collected from each test rig for laboratory analysis (see below). Treatments were carried out and on completion a 60l sample was taken for analysis.

A control tank containing one sample was set up and left at room temperature. Sub-samples were taken at intervals to monitor background mortality (Table 1). Three replicates were made during three consecutive days (12-14th June).

Table 1. Times after set-up and sample sizes used for control soup sampling.

Time of sampling	Size of sample
0 min	10l
30 min	3l
1h	3l
2h	3l
3h	3l
4h	3l
5h	3l
6h	3l
24h	Rest

8.3 Sampling and Test Protocols

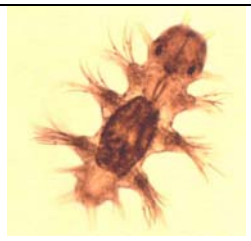
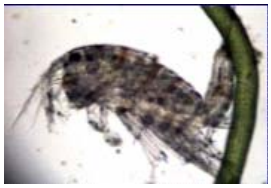
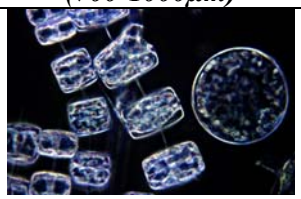
Within the MARTOB project it was necessary to assess the performance of various ballast water treatment techniques. A standard test protocol was therefore required. Because the standards under discussion at IMO were not finalised, it was necessary to develop a test protocol specifically for this project. The developed protocol is to some extent based on the draft standards, but also other suggested protocols were taken into account. The sampling and test protocol provided standards for:

- water quality,
- species to be used for laboratory tests,
- composition of the test mixture,
- how to assess the biological effectiveness

The water quality standard specifies the quality and quantity of the artificial seawater (ASW), including salinity, turbidity, pH and temperature. The chosen salinity was 33-35, achieved by adding “Tropic Marine seasalt” to distilled water. Seawater may be turbid due to both inorganic and organic particles. Kaolin was used to simulate the former, while flour was used to simulate the latter. The pH of the ASW was around 8.3, i.e. close to the normal pH of seawater. The temperature was 10-15 °C to ensure the survival of the introduced marine organisms.

Five different species, three zooplankton species and two phytoplankton species, were selected as test organisms, and added to the ASW. The zooplanktons were a polychaete (nectochaete larvae of Nereis virens), a harpacticoid copepod (Tisbe battagliai), and a calanoid copepod (Acartia tonsa). The phytoplanktons were a diatom (Thalassiosira pseudonana) and a dinoflaggelate (Alexandrium tamarense). Densities of the species are given in Table 2.

Table 2. Artificial Sea Water or MARTOB Soup.

Selected Species	Maximum field densities (indivs /m^3)	Standard mix composition (indivs/ m^3)	Standard mix composition of a 70 litre test solution
 Benthic nectochaete larvae **Nereis virens** ***(700-800µm)***	740	1100	80
 Harpacticoid copepod **Tisbe battagliai** ***(700-800µm)***	807	1100	80
 Calanoid copepod **Acartia tonsa** ***(700-1000µm)***	159,659	2500	200
 Diatom **Thalassiosira pseudonana** ***(4-5µm)***	30×10^8	50×10^7	30×10^6
 Dinoflagellate **Alexandrium tamarense** ***(25-30µm)***	75×10^6	40×10^6	24×10^5

The mix used did not include any fish eggs or larvae. In many countries, including the UK, experiments involving vertebrates require special licenses. For this reason we excluded them from the standard test mix and would propose that separate trials of a mix containing fish eggs and larvae (probably salmon or turbot) be conducted, under licence for the most promising techniques identified in the trials with the standard mix. The mixture composition describes the density of the species to be included in the test mixture. The premise here is that densities should reflect the top end of the natural range for each taxa.

Figure 1. Preparation of MARTOB soup.

The effectiveness of each individual treatment technique was assessed by determining the number of live and dead organisms of each species after the treatment. This was done by fixing and staining the organisms in a manner that allowed living and recently dead material to be easily distinguished. This will allow the efficiency, expressed as %kill, of each technique for each group of organisms to be reported.

During the first few days of testing, UV, US and Ozone techniques used a high pressure pump for supplying artificial seawater into the treatment system. Analysis of preliminary results showed that the pump itself was eliminating almost all of the zooplankton; therefore a gravity system was used to supply the water for the rest of the tests. Consequently, it was observed that large number of bends, valves and long pipes could contribute as a source of error for these technologies. Since ASW flowrate was now much lower than original pump, it was concluded that some of species were gathered into the slow velocity points, thus altering some of the results. Both living and dead organisms were found to be hidden in the systems. It was therefore decided to flush these systems after each test run, when some of zooplankton species were detected from the sample. This could slightly remedy the source of error but there are still concerns regarding the accuracy of analysis.

8.4 Zooplankton

8.4.1 Zooplankton Fixation and Staining

All samples were filtered through a 63µm sieve. The zooplankton was rinsed from the sieve with clean seawater into labelled pots. Zooplankton samples were stained with 0.1% Neutral Red solution in the ratio of 3ml stain/100ml sample. After staining for 60 min, 4 ml of 1N 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). Thereafter all samples were stored overnight at 5°C prior to counting.

Following the overnight storage and before examination of the samples, 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. During the counting procedure the sample was kept in water. After counting organisms were preserved in 4% Formalin.

Live copepods stained immediately prior to fixation turned a deep magenta after acidification, whereas dead specimens were light pink to white. Nereis had to be more carefully observed, as dark staining did not guarantee viability. Some treatments affected the staining in such way that 'live' organisms varied in colour from magenta to orange. Therefore the assessment of individuals also included a morphological examination. For the counting procedure whole organisms as well as bits were taken into account. The quantity of organisms delivered by the suppliers was a range between two densities therefore we dealt with volumes and not with exact number of organisms to make the soup samples. The percentage of mortality was calculated as the number of dead animals divided by the sum of dead and alive animals found in the after treatment samples. When no material or no whole animals only bits were found a 100% in mortality was recorded.

8.4.2 Zooplankton results

The control tank showed that the zooplankton organisms survived successfully for 24 hours. Below is the summary of the results of the zooplankton analysis for each of the treatments tested. A lack of replication led to uncertainty in some of the results.

Heat treatment

There were no differences in the levels of mortality for the different species in the instant exposures temperatures. All the treatments above 55^{o}C were effective at killing *Tisbe* sp. and *Nereis* sp. For *Acartia* sp. the highest mortality achieved was 88.5%, however no significant difference was found in the % kill of *Acartia* sp. and the other two species. There was no difference in the effectiveness with increasing time of exposure.

Oxicide treatment

Of the three species *Tisbe* sp. was significantly the least affected, while *Nereis* sp. was the most sensitive for this treatment, achieving 100% mortality in all cases. *Acartia* was reduced above 95% in all but one case. *Tisbe* achieved a 96% kill in one of the treatments, however for all other tests it was always below 88%. Total mortality appeared to increase with increasing H_2O_2 (hydrogen peroxide) concentration, reaching a plateau at 28mg/l. Greater mortality was also observed with temperature increases from 30 to 35 ^{o}C. However these two latter results are not significant due to a lack of replicates.

Ozone, ultrasound (US) and ultraviolet (UV) treatments

The combination of filter (125 µm), US and UV achieved a removal that was always higher than 98%. However none of the other treatments did (UV, US, ozone and the combination of US+UV). From the methodologies tested on their own, ozone appeared to achieve the best results, at least for *Nereis* sp. However the lack of replicates makes these results not reliable. As an overall observation for this treatment (excluding the use of the filter), *Acartia* sp. and *Tisbe* sp. were the most resistant and *Nereis* sp. the least of the three species.

Deoxygenation

The deoxygenation treatment, when nutrients were added into the tanks had a high efficacy from the fifth day for *Acartia* sp. (above 95% mortality), whereas *Tisbe* sp. and *Nereis* sp. did not achieve effective reductions until day 7 (97% and 100%, respectively). There was a difference between treatments, with and without nutrients, for the three organisms. *Tisbe* sp. was the least sensitive species out of the three. *Acartia* sp. was the most sensitive species out of the three, even when no nutrients were added to the bacteria culture.

Advanced oxidation

The oxidation method was very effective (always above 98%) when using the 100µm filter. However, when the system was tested on its own, the kill rate never achieved more than 80% (i.e. for *Acartia* sp. after 10 passes through the system). For the treatment without filter, there seemed to be some improvement in the efficiency with increasing the number of passes through the system, for *Acartia* sp. This trend was not observed for the other two species.

Hurdle technologies

The most effective combination was the Thermal and Deoxygenation treatment, which had 100% efficiency for all three species. A comparison of the efficiency of UV and H_2O_2 with and without the filter (150µm) showed that the filter did affect the survival of the organisms. The percentage removal for *Acartia* (principally), *Tisbe* and *Nereis* increased when the filter was used. An increase in H_2O_2 concentration did not seem to have any marked effect.

8.4.3 Conclusions

Following the MARTOB laboratory-scale trials, a protocol for assessing ballast water treatment methods has been used successfully. The 'soup' designed was simple to use, highly reliable and effective. The control test showed that organisms in the soup survived for 24 hours. Hence a meaningful and reliable means to assess and compare different ballast water treatment methodologies has been identified.

Based on the percentage kill of animals in the test soup the results indicated which of the methodologies were the most effective and which had more potential for ballast water treatment. The high temperature thermal treatment was the most effective technology, followed by deoxygenation, hydrogen peroxide (oxicide treatment) and the hurdle technology combining high temperature with deoxygenation. Unfortunately only some of the tests had replications, and it was only on these that a more rigorous statistical analysis could be carried out, and the results interpreted with confidence.

The mortality of the different species varied depending on the treatment tested, *Nereis virens* usually being the most sensitive organism and *Tisbe battagliai* the most resistant. Sometimes the numbers obtained from the after-treatment samples were very low. This could have been due to the fact that some of the equipment had long pipes with corners where possibly organisms could have hidden. Moreover during the first three and a half days a pump was utilised as a means to introduce the water into one of the systems. After it was shown that the pump itself was eliminating all the zooplankton, a gravity system was used to supply the water. For future tests these aspects should be considered and the redesign of some of the treatment systems and their sampling points is therefore recommended.

Difficulties also arose concerning attempts to provide turbid samples. The turbidity caused problems for filtration and for counting. The particles of kaolin (used to simulate inorganic turbidity) tended to aggregate, therefore clogging the filter and impeding the observation of any organism in the turbid samples. This point also needs some thought before further tests are carried out.

8.5 Phytoplankton

8.5.1 Overview

The basis of each test run was the preparation of a standard sea water containing a known quantity of each of the representative species. The phytoplankton used were *Alexandrium tamarense* and *Thalassiosira pseudonana*. Samples of the standard sea water were taken before and after treatment in order to assess how effective each treatment was at inactivating or removing the organisms. In addition to the treatment tanks, control tanks were set up and sampled at intervals over the period of the trial.

The test procedure was based on a series of robust criteria developed earlier in the MARTOB project and the aim of the trials was to assess the biological efficiency of each of the treatment methods. For the phytoplankton this was achieved by the following means:

- Measuring chlorophyll *a* levels in the water before and after treatment, which would give an overview of the change in phytoplankton biomass after treatment.
- Carrying out direct cell counts to investigate whether there were differences in the survival of the two phytoplankton species used in the experiments.

8.5.2 Results

Difficulties arose when interpreting the results of the treatments as the results from the control tanks showed that there was great natural variability of the phytoplankton cell numbers. Taking this into account as well as the fact that many of the experiments lacked replication means some of the results were difficult to interpret. An outline of the main results for each treatment is given below:

Heat treatment

The heat treatment method showed consistent reductions in chlorophyll *a* but the cell count data are more variable. The levels of chlorophyll *a* reduction indicated that temperatures of 50^{o}C and above were more effective at reducing phytoplankton biomass. It was not clear whether increased exposure time was any more efficient at killing the phytoplankton. The cell counts for *Alexandrium* sp. showed a more consistent reduction in cell numbers than for *Thalassiosira* sp. However, there was no significant difference for either species in the mean change in cell numbers between the experiments.

Oxicide treatment

The results from the oxicide treatment are somewhat ambiguous. The results from both the chlorophyll *a* and cell counts are very variable and there is no clear treatment effect. This may be due to several reasons, there may have been variations in the cell density of the culture used in separate experiments, the cell counts may have included cells that looked normal but were in fact dead and these experiments had to rely on substitute “before” treatment samples. The substitute samples were used because the hydrogen peroxide was produced in the test water and it was not possible to take a direct sample. Also, the equipment is still at the bench scale of testing and it is possible that small variations in flow through the cell that produced the hydrogen peroxide may have resulted in variable retention of cells.

Ozone, ultrasound and ultraviolet treatments

The ozone treatment resulted in consistent reductions in chlorophyll *a* but the corresponding cell count data did not show such a clear treatment effect. Although *Alexandrium* sp. cell counts were generally reduced after ozone treatment the counts for *Thalassiosira* sp. were much more variable and showed some large increases in cell numbers after treatment. Another factor that has to be taken into account with these treatments was the fact that because much of the test water remained in the pipes and hoses of the equipment a second flushing stage had to be added. The effect of this is clear in the ultrasound results, as there is a greater reduction in the chlorophyll *a* levels once the test water has been flushed out. However, the cell counts for the ultrasound experiments show that although *Alexandrium* sp. cell counts are generally reduced after treatment the results for *Thalassiosira* sp. are much more variable. Treatments with ultraviolet and with a combination of ultrasound and ultraviolet show consistent decreases in chlorophyll *a* levels. The cell counts for both species also generally decrease after treatment with ultraviolet alone but the *Thalassiosira* sp. cell counts are much more variable after the combined treatment.

Deoxygenation

The deoxygenation treatment resulted in reductions of chlorophyll *a* and some reductions in cell numbers but there were some high cell count results that did not correspond with high levels of chlorophyll *a* and were difficult to explain. The levels of chlorophyll *a* showed no significant difference between the four different treatment trials for this method. However, the cell counts may have been influenced by the fact that once preserved it is difficult to ascertain whether a cell that looks normal was viable before preservation. The initial results of this treatment method indicate that the method has potential to reduce phytoplankton biomass but the method needs to be refined further to achieve greater reductions.

Advanced oxidation

The advanced oxidation technique generally showed reductions in chlorophyll *a* but the lack of replication made it difficult to determine which of the treatments was the most effective. The cell counts show that *Alexandrium* sp. is reduced to some extent after all the treatments but that the cell counts for *Thalassiosira* sp. are more variable and show some increases after treatment. It is possible that the filter may have resulted in reductions in the phytoplankton present in the samples taken after treatment. As the filter was used it would have become more clogged and this may have reduced the amount of phytoplankton present in the test tank.

Hurdle technologies

It is difficult to be certain which of the combinations of technologies are the most effective at reducing phytoplankton. It would appear that combinations of heat with deoxygenation or hydrogen peroxide were not effective at reducing chlorophyll *a*. Other combinations had variable results and showed both decreases and increases in chlorophyll *a* for the same combinations of treatments. The cell count data was also extremely variable and there was no clear pattern to the results.

8.5.3 Conclusions

Many of the results that were obtained from the Newcastle tests are difficult to explain. As many of the experiments were not replicated it is difficult to be certain whether any effect is due to the treatment or the natural variation in the phytoplankton cultures used. For those treatments that do show a consistent reduction in chlorophyll *a* the corresponding cell counts do not always demonstrate the same level of reduction and in some cases show a large increase in cell numbers. For some treatments there did seem to

be different effects on each of the species, with the dinoflagellate *Alexandrium* sp. generally showing reductions in cell numbers and the diatom *Thalassiosira* sp. having a more variable response. This is unexpected in that the dinoflagellate is the more robust of these two species and would be expected to be able to withstand more severe conditions than the diatom.

The methods used to obtain the cell counts should also be taken into account, it had been intended to use a flow cytometer to count and assess the viability of the phytoplankton but owing to circumstances beyond our control this was not possible. The counts were therefore carried out on preserved samples where it is more difficult to assess whether the cells were viable before preservation. In some cases a cell may look normal and be counted as having been alive before preservation but may in fact have been a dead cell.

Another factor that may have affected the results is the different scale of the equipment, some were bench scale and others were closer to full scale. This led to problems such as having to flush extra water through equipment to remove the treated water from the pipes and hoses. The oxidation technique also had problems with a variable flow through the hydrogen peroxide producing cell, which may have affected the results.

However, the results do indicate which treatments show potential and which may require some modifications in order to operate more consistently. The results of the shore based tests have demonstrated the problems of working with natural cultures and also the importance of an experimental design that includes replicates and control samples. If such tests were to be carried out in the future it would be necessary to have a well planned experimental design that included replication and controls and took account of the natural variability within plankton cultures. It would also be necessary to further refine methods to count and assess the viability of the cells.

9 Evaluation of corrosion risk of the treatment methods

9.1 Introduction

The on board ballast water treatment systems act on the water and consequently may modify the ballast water properties and contents.

In ships, an important problem is the corrosion of the hull structure, the piping system and the ballast water handling equipment. Therefore it has been decided to identify if the installation and operation on board of the considered in the MARTOB project ballast water treatment systems will modify the water properties in such a way that it could increase the corrosion risk of the ship structure and ballast water piping network.

The target of this task is not to performed a detail analysis of the corrosion risk link to each system which will require to know all details about the ship on which they will be installed, but to provide a warning to the designers and classification societies which will have to approve the installation on board, on the main possible new risks with respect to corrosion attached to each system.

As the task concerns the identification of a corrosion risk increase within the scope of a classification society concept approval, it has been decided to consider valid an Expert group opinion, opinion formalised by using a FMECA grid support. The FMECA grid and the ranking tables have been developed by the Expert group.

The ballast water corrosive action has been considered on the ship and piping steel components, ship frame and piping coatings and piping network gaskets.

The Expert group has been working on the data provided by the ballast water treatment systems developers following a format fixed by the Expert group and on the water characteristics measurements performed by TNO during the tests in UNEW laboratory.

The required and provided data by the treatment system developers are:

- Principle sketch of the circuit with ballast water flow and equipment
- On the circuit sketch, point of water treatments: filtration, actions, additives, etc...
- For each treatment point a short description of the actions on the ballast water and:
  - ⇒ equipment materials
  - ⇒ water content before and after
  - ⇒ water properties changes

presented following an unified format.

The report provides in the following: the list of the considered parameters for the Expert group analysis, a global view of the corrosion problems on board a ship, the points to be addressed when designing and approving the installation of each treatment system on board of a particular ship. The annexes provide the FMECA rules and results and the provided descriptions by the developers for each treatment system.

9.2 Considered parameters

The following parameters are considered in the analysis with indication of the variation or consequences which induces a corrosion risk increase:

Water properties:

− Conductivity:	increase
− Hardness	decrease for steel, increase for aluminium
− PH	decrease
− Redox potential	increase
− Temperature	increase

Water content

− O2 content	increase
− O3 content (ozone)	increase
− CO2 content	increase
− H2S content	increase
− H2O2 content	increase
− Added inorganic substances	increase (but not for all materials)
− Added organic substances	increase
− Increase of bacteria concentration	increase

Circuit content

− New added materials	battery effects
− DC (Direct Current) equipment	current return paths

9.3 Corrosion risks global view

The following remarks aims to help the designing and approval teams when developing or verifying the drawing and justification notes concerning the installation of a ballast water treatment system on board of a particular ships.

The ballast water comes in across the grid in the sea chest. The sea chest grid and the sea chest itself is coated by antifouling product. Many types of antifouling products are available with various components and therefore with various compatibility to water contents.

There is the possibility that the seawater passes through a coarse strainer. The basket can be made of stainless steel with the housing and cover by steel, probably with an internal lining with its particular resistance characteristics.

The ballast piping, if made of steel is mostly protected by some coatings. There are several types of coatings suitable for ballast piping. Larger pipes can also be neoprene lined, for example. Some of these linings do not require gaskets between the flanges, because the lining acts like gasket. There is also an increasing use of glass fibre reinforced piping for the ballast systems.

When stainless steel, AISI 316L type or equivalent is used, it should be noted that stainless steel AISI 316L, although commonly used for seawater applications, may suffer from severe and rapid failure by pitting and crevice corrosion in aerated at moderated temperatures (T around 30°). Numerous pitting and crevice corrosion problems have been reported in piping system carrying seawater. Need for high alloy stainless steel may be therefore justified in such case, specifically those with high chromium and molybdenum content (super duplex stainless steel for instance, having a higher PREN or pitting resistance equivalent number).

In the ballast system there are for example so-called "Dresser couplings" that allow for expansion/contraction/movements of pipes. Normally there are a couple of "O" rings and a gland that can be tightened, that ensures the Dresser coupling is not leaking. The "O" ring material can vary.

The next is the ballast tank valves. Those can be metallic - brass - stainless steel - or a combination of materials. There is the spindle material that will be some stainless steel quality, probably the lowest cost version. The valve housing can be some steel quality, possibly cast material. There are several gaskets or seals of varying materials in the valves. Then there is the possibility that the valve housing is covered internally by a renewable lining providing disk seal and flange gaskets on both flanges. If this lining is good there is no contact inside the valve between the seawater and the valve housing.

Flange gaskets can also be made of a range of materials ranging from rubber to fibre of various types.

Then there is the ballast pumps. The shaft is normally of a low cost stainless steel type, the impeller is either bronze or even non metallic in some cases. The ballast pumps have often mechanical seals around the rotating shaft. There can be various metals involved as well as "O" rings.

There are also the ballast eductors that can range form bronze/stainless steel combinations to ultra cheep cast iron types made in the Far East in accordance with copied drawings from reputable makers.

There is the ballast tank level gauges to consider. Some use bubble systems where the piping can be stainless steel, copper or non-metallic.

There is the gas sampling systems for when the ballast tanks are empty and the tanker loaded. Materials, gas analysers, etc..., are complicated installations.

Then, finally the ballast tank coating itself. That is where the corrosion problems start; when the coating starts to fail. It is only the paint makers (perhaps) that can give a realistic answer to their resistance to water characteristics changes.

It is well known that transported products can be not compatible with structural materials and coatings. As an example we can mention that recently a new crude oil tanker with the cargo tanks coated in top and bottom had the opportunity to take a cargo of Gas oil for it's maiden voyage. However, the cargo had to be turned down because the coating used for crude oil could not take gas oil.
In conclusion, the resistance list for the chosen coating is important. It appears that the manufacturers of the coatings, linings, seals, Dresser couplings, pumps, etc should be asked to provide a resistance list for their product. Finally, the coating maker will have to investigate the resistance of the coating where the ballast tanks contain treated water.

Therefore, it is possible that the chosen ballast water treatment method needs to be specified first so that the materials with the best corrosion resistance and coatings compatible with the water content can be chosen for the detailed specification of coating, piping, pump, valve, seals, alloys etc, based on the treatment method.

9.4 FMECA results

The review of the FMECA analysis results given in annex 1, allows recommending paying attention for the on board ship installation to the following points:

BenRad Oxidation method

A moderate increase of the Redox potential (short term effect) with possible consequences on metal corrosion, coatings and gaskets.

A slight increase of CO2 (order of mg/l) with possible consequences with respect to metal corrosion and coatings.

Oxicide method

The use of DC equipment with possible non expected current return paths and possible localised significant metal corrosion.

A significant increase of the Redox with possible consequences on metal corrosion, coatings and gaskets.

The production of H2O2 with possible consequences on metal corrosion, coatings and gaskets

Biological de-oxygenation method

A slight decrease of the pH with possible consequences on metal corrosion, coatings and gaskets.

A slight increase of CO2 (order of mg/l) with possible consequences on metal corrosion and gaskets.

The production of H2S (order of mg/l) with possible consequences on metal corrosion, coatings and gaskets.

The addition of inorganic substances with possible consequences on metal corrosion, coatings and gaskets.

The addition of organic substances with possible consequences on coatings.

A significant increase of the bacteria concentration with possible consequences on metal corrosion, coatings and gaskets.

High temperature method

Due the fact that the heater is followed by a cooler and is located at the discharge of ballast water, no risk of corrosion increase or risk with respect to coating and gaskets has been identified

Ultraviolet method

A slight increase of the Redox potential (short term effect) with possible consequences on metal corrosion, coatings and gaskets.

Ultrasound method

No risk of corrosion increase or risk with respect to coating and gaskets has been identified.

Ozone method

A significant increase of the Redox potential (short term effect) with possible consequences on metal corrosion, coatings and gaskets.

The production of O3 (short term effect) with possible consequences on metal corrosion, coatings and gaskets.

In conclusion, all risk increases are acceptable with respect with today knowledge and can be managed for new ship design with existing techniques and methods. Referring existing ships, some treatment systems may be not acceptable due to the treated water characteristics incompatibility with the existing piping, gaskets or coatings materials.

10 Oxidation Method

10.1 Introduction

The BenRad Marine Technology is based on an Advanced Oxidation Technology (AOT) consisting of a combination of ozone, UV and catalysts. Thus Ozonolytic / Photolytic / Photocatalytic Redox Processes are operating simultaneously within a titanium reactor. The unique combination is designed to generate large amounts of radicals, mainly hydroxyl radicals, within the reactor. It is these radicals that destruct / eliminate microorganisms.

This water purifier has successfully been used in land-based applications such as purification of swimming pool water, drinking water, water used for irrigation in green houses and water used in fish breeding.

The aim is to find out the efficiency and feasibility of the method for purifying ballast water and to compare it with the other technologies that will be evaluated in WP3.

10.2 The technique

Recently there has been great interest in the use of advanced oxidation technology (AOTs) to effectively destroy hazardous organics. The 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.

BenRad water purifiers have been tested for elimination of several microorganisms. The following bacteria were tested: *Eschericia coli, Streptococcus (Enterococcus) faecalis, Salmonella enteritidis, Campylobacter jejuni and Legionella pneumophila.* The conclusion of the report is: "The BenRad water purifier has a very marked bacteria-reducing effect on the bacteria being tested in water".

Reduction of *Cryptosporidium parvum* have been tested in water circulating through a BenRad water purifier. The report concludes: "The BenRad device effectively destroys *Cryptosporidium parvum* oocysts with a reduction of *Cryptosporidium parvum* oocysts of 99.98% after 3.5 hours exposure".

The destruction of poliovirus was tested and the report concludes: "The capacity of BenRad water purifier to inactive poliovirus has been tested in one type of experiment which was repeated twice. In three out of four samples tested no virus could be detected, but in one sample a small amount of virus was traced. However, in all four samples the reduction of live poliovirus was more than 4.60 Log_{10} $^{-10}$".

10.3 Test trials in Newcastle

BenRad Marine Technology used a small mobile testing unit consisting of a tank, pump, filter and water purifier, as can be seen in Figure 10.1.

Figure 10.1. Mobile testing equipment.

The water flow for the testing device was 6 litres/min. The filter was a cartridge filter, 100 µ.

10.4 Materials and Methods

70 litres with artificial seawater was mixed with five different organisms. According to the salesmen every jar with zooplankton that was mixed in the water contained approximately 200 pcs. of Acartia, 80 pcs. of Tisbe and 80 pcs. of Nereis. The phytoplankton Alexandrium and Thalassiosira were cultured and 200 – 250 ml of the species was added to the water. The organisms were not counted before mixed in the water. For analysis 10 litres was taken from the mixed 70 litres before treatment to make sure that the organisms were alive. Remaining 60 litres were used for treatment in the water purifier.

After every test the tank and water purifier was cleaned first with municipal water and then with distilled water several times. The UV-lamps were also cleaned after every test with acid and the filter was rinsed. The turbid water was a mixture of organic (flour) and inorganic (kaolin) matters, 1 g / litre. The turbid mix did not clog the filter.

For analysing of zooplankton the organisms were counted under microscope. For analysing phytoplankton a fluorescence method was used. The concentration of chlorophyll and pheophytin were measured. A reduction in chlorophyll would indicate that there had been a reduction in the phytoplankton biomass.

10.5 Results

The water was circulated through the pump and the water purifier. Tests were taken after 1 – 10 cycles. Some tests were done with the 100 µ filter. Some tests were done with turbid water. In the 10 litres taken out before treatment a lot of organisms were found alive when the water was clear. When the water was turbid a large amount of organisms were dead or not found. Therefore the turbid tests are not included in the results.

In the first test the treated water was sampled through the drain of the water tank. Since complete circulation of all the water through the water purifier may not be the case I did not include that result. All the other samples were taken from the outlet of the water purifier.

The zooplankton results obtained with the BenRad Marine Technology water purifier together with the 100 µ filter are shown in Figure 10.2, below. Elimination is calculated as the number of dead organisms divided by the sum of dead and alive organisms found in the after treatment samples. When no organisms or parts of organisms were found, a 100 % elimination was recorded.

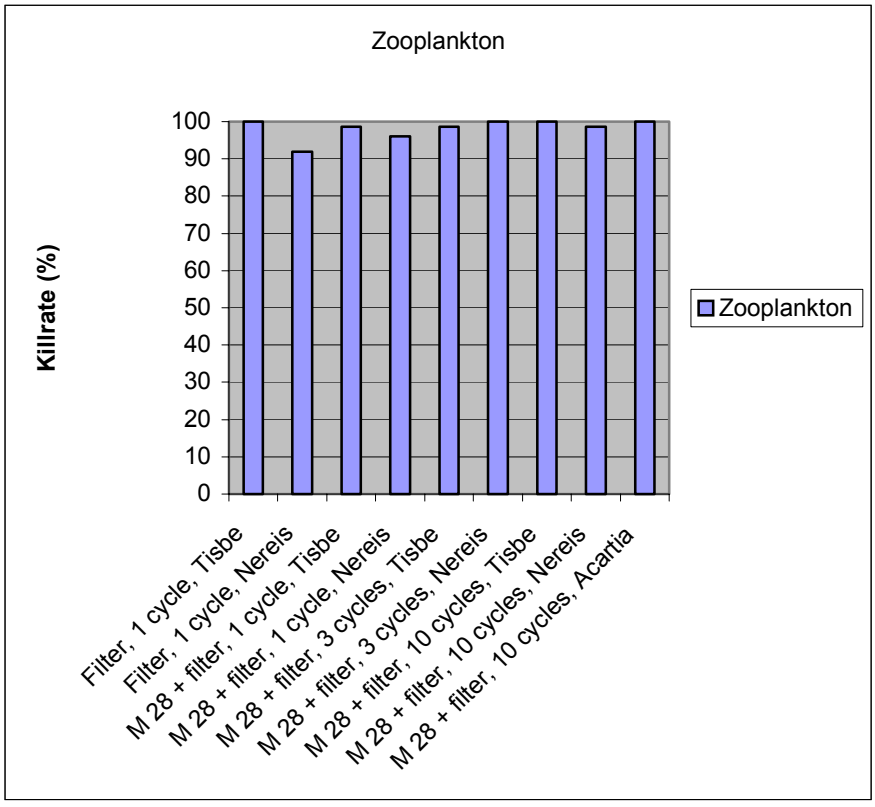


Figure 10.2. Killrate of Zooplankton in BenRad Marine Technology water purifier + 100 µ filter.

The combination BenRad Marine Technology water purifier together with the 100 µ filter achieved a ell-imination of zooplankton over 95 %. Naturally the filter has a major part of this reduction.

The results of the amount of organisms, dead and alive, after treatment is listed in Table 10.1, below. "Diff" is the difference between how many organisms it was supposed to be and how many actually found. The %-difference is calculated as the amount of plankton in the 60 litres treated water divided by the supposed amount before treatment (200 pcs. of Acartia, 80 pcs. of Tisbe and 80 pcs. of Nereis) minus the ones in the 10 litres.

Test	Cycles	Treat-ment	Acartia			Tisbe			Nereis		
			Alive	Dead	Diff	Alive	Dead	Diff	Alive	Dead	Diff
1)	1	M 28	67 (+ 3 child)	22	68 %	10	2	16 %	9	0	13 %
2)	2	M 28	60	9	38%	4	0	5.1%	2	1	3.8%
3)	4	M 28	35	33	37%	9	6	23 %	5	0	6.6%
4)	10	M 28	-	-	-	2	1	3.8%	6	3	12 %
5)	10	M 28	7	28	18 %	9	2	18 %	63	3	*
6)	1	filter+ M28	-	-	-	1	0	1.4%	2	0	17 %
7)	3	filter+ M 28	-	-	-	1	1	2.7%	0	0	**
8)	10	filter + M 28	0	0	***	0	0	***	1	0	1.4%
9)	1	Filter	-	-	-	0	0	***	1	1	17 %
10)	3	only pump	43	22 (hurt)	37%	28	4	52 %	20	5	35 %

Table 10.1. Amount of organisms after treatment

* Higher number of organisms after the treatment indicates higher initial values than estimated.
** All the 80 plankton were found in the 10 litres taken before treatment (it was even 85 plankton in the 10 litres)
*** No plankton found

The phytoplankton results obtained with the BenRad Marine Technology water purifier are shown in Figure 10.3, below. Percentage reduction is calculated as the amount of chlorophyll before in the 10 litres multiplied with 6 divided by the amount of chlorophyll found in the after treatment samples.

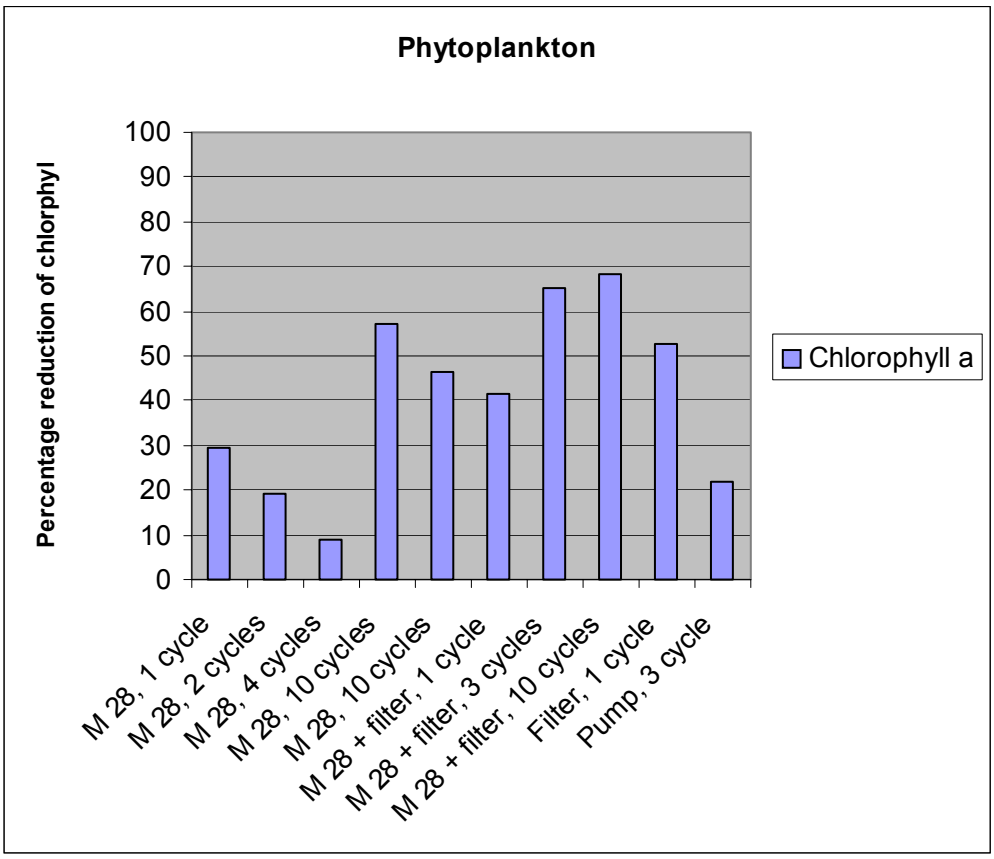


Figure 10.3. Percentage reduction of Chlorophyll a in BenRad Marine Technology water purifier.

10.6 Conclusions and Discussion

The combination BenRad Marine Technology water purifier together with the 100 µ filter achieved an elimination rate of zooplankton over 95 %. The filter has of course a major part of this reduction.

Since the tests were not considering the amount, live/dead ratio before treatment /between filter and end treatment it is impossible to make any certain conclusions. From tests and installations mentioned in the introduction it is proven that the BenRad units kills microorganisms. Tests have been done with bacteria, viruses and cryptosporidium (size 4-8 µ).

In the samples after treatment with water purifier and filter the number of dead and alive zooplankton are low (1.4 - 17 % of the number supposed to be included in test water). Organisms are obviously caught in the filter.

Also in the samples after treatment with the water purifier and no filter the number of zooplankton are low (down to 3.8 % of the number supposed to be included in test water). This indicates that organisms are eliminated. However, such elimination of the organisms is not measured in this study. It could also be that some organisms are left in the pipes or in the tank. But compared to the number of zooplankton left after the pump (35-52 % of the number supposed to be included in test water) indicates that some are lost somewhere.

Results obtained in the present study are not easy to interpret. The concentration of the zooplankton in the water before it was treated by the BenRad unit is unclear.

The combination BenRad Marine Technology water purifier together with the 100 μ filter achieved a reduction in chlorophyll with 40-70 %. This indicates that there has been a killrate in the phytoplankton biomass. It is possible that the filter caught some of the phytoplankton. Cell counting do not show any major reduction of biomass at the end treatment.

Analysis performed in a marine station in Sweden (Fiskebäckskil) clearly shows that a very high kill rate can be achieved without actually changing the chlorophyll rate. This is therefore not a good method to measure the kill rate performance. These analysis is done with microscope and incubation. Dinoflagelates can be counted live/dead directly and other may have to be incubated. When considering other tests performed this seems to be the only available methods for accurate performance tests.

Further studies must be done before conclusions can be drawn on the reduction efficiency of the BenRad unit on organisms used in this study.

11 Conclusions and Discussions

The main objectives for the laboratory test trials in the Work Package 3 were to design and development of the proposed treatment technologies and demonstrate their efficiency against the selected organisms. While the project proceeded it was decided that all the equipment will be tested in the facilities provided by the University of Newcastle, UK. Before the Newcastle trials various partners conducted preliminary test trials in their own laboratories in order to define operational parameters for their devices and also to determine the efficiency of their technology against different organisms than used in the Newcastle trials.

The framework for evaluation utilised during the Newcastle trials was defined in the Work Package 2. Previously there was no standards to comply with and hence wide variety of ways to report the results were available. The objective for the framework for evaluation, i.e. the test and sampling protocol and the standards for evaluation, was to provide a common and fair basis for comparison and evaluation of different ballast water treatment options. The matter has been one of the most important issues at the International Maritime Organisation's (IMO) Marine Environmental Protection Committee (MEPC) and therefore closely watched.

The sampling and test protocol provides standards for water quality, species to be used for laboratory tests, composition of as test mixture and how to assess biological effectiveness of the different treatment methods. The protocol was used for the first time during the Newcastle trials and therefore unexpected problems occurred. Number of phytoplankton cells on the final test water is difficult to estimate, since phytoplankton cultures are continuously growing due to the changes in temperature and light. A better approach could be to estimate a range of concentrations for phytoplankton and also to incorporate a standard method to measure this. The suitable method should be rapid in order to enable the calculation of the cell densities and the correct dosing of the culture to the test water. The utilisation of a flow cytometer and the further refinement of the methods for counting and assessing the viability of the cells could be considered. Also the importance of replicates and control samples is evident.

The number of samples to be analysed was higher than expected and caused an exhausting work load to the biologists, since this type of shore base test trials was not originally planned. This also hindered the biologists to deal with other matters arisen during the trials, i.e. problems with mixing and filtering. Hence there was a long delay before the final results were available. The analysis of turbid samples was extremely difficult and time-consuming and in some cases the "lost individuals" in zooplankton analysis, probably disintegrated during the treatment process, caused problems. In many cases the results were unexpected and difficult to explain. Since many of the experiments were not replicated it is difficult to make any final conclusions if the effect was due to the treatment or the natural variation in the cultures used. The framework for evaluation will be useful in the test work of any new technology to be carried out in the future and could be considered as a first step towards a standard.

While there was no definition of a treatment capacity of a laboratory scale test unit, the different scale of the equipment affected the results. Also the individual test runs could not be repeated and therefore the results should be considered as indicative. The different developing stages of the test methods make the comparison even more difficult. The data provided for the economical assessment varied a lot depending on the development stage of the method. Therefore some of the data were not available and was partly preliminary. Hence the results must not be compared directly with each other, since the aim of the laboratory scale test trials was to develop proposed treatment, not verify them.

The artificial sea water (ASW) with defined concentration of species, salinities, temperatures and turbidity was utilised through the test trials and the framework of evaluation provides a good approach to estimate the performance of each technology. In the real marine environment, where the ballast water intake occurs, the composition of the water differs substantially from ASW. The presence of organic material,

small particles, micro-organisms etc. will have a significant effect to the water properties in respect to ballast water treatment. Therefore it is important to keep in mind that the results indicated more how well the configuration of a treatment system performed in the test set-up rather than what is the capability of a treatment in respect to ballast water treatment. The further test trials will be required in order to obtain more extensive results from various marine environments.

During the laboratory scale test trials a lot of valuable experience was gained in testing and analysing process. This knowledge should be transferred to the realisation of the onshore and full scale test trials to be conducted in the Work Package 4. Besides the knowledge should be utilised when any kind of new test trials with ballast water treatment technologies will be planned. The cooperation between engineers and biologists will be essential in order to understand the design principles of various technologies, the behaviour of organisms and the interpretation of the results. When the knowledge and expertise of different expert fields can be integrated, an interdisciplinary way to find solution will be possible.

12 Contact Information

In the following Table 12.1 is indicated the contact information regarding each paragraph of this report in case of further information request.

Parag. Number	Description of the Work / Task	Organisation	Contact
2	Detailed design of the thermal system with computer simulation and demonstration of the system	University of Newcastle upon Tyne, UK	Ehsan Mesbahi School of Marine Science and Technology Armstrong Building, University of Newcastle Newcastle upon Tyne NE1 7RU UK Email: Ehsan.Mesbahi@ncl.ac.uk
3	Biological de-oxygenation	SINTEF, Norway	Kjell Josefsen SINTEF Applied Chemistry N-7465 Trondheim Norway Email: Kjell.D.Josefsen@sintef.no
4	Ultraviolet light, ultrasound and ozone methods	VTT Industrial Systems, Finland	Jukka Sassi or Jorma Rytkönen VTT Industrial System PO Box 1705 FIN-02044 VTT, Finland Email: jukka.sassi@vtt.fi Email: jorma.rytkonen@vtt.fi
5	Oxicide treatment	TNO Environment, Energy and Process Innovation, the Netherlands	Jan-Willem Assink TNO, Department of Chemical Engineering TNO-MEP P.O.box 342 7300 AH Apeldoorn Email: J.W.Assink@mep.tno.nl
6	Hurdle technology	Berson Milieutechniek B.V., the Netherlands	Leon Janssen Berson UV Techniek B.V. 90, 5670 AB Nuenen De Huufkes 23 5674 TL Nuenen The Netherlands Email: leon.janssen@bersonuv.com
7	Environmental Impacts, Risk and Safety, and Economic Aspects of Ballast Water Treatment Methods	SSPA Sweden AB, Sweden	Joanne Ellis SSPA Sweden AB Chalmers Tvaergata 10 40022 Gothenburg Sweden Email: joanne.ellis@sspa.se
8	Assessment of biological effectiveness		
8.4	Zooplankton analysis	University of Newcastle upon Tyne, UK	Gemma Quílez-Badia or Margaret Gill Dove Marine Laboratory School of Marine Science and Technology University of Newcastle upon Tyne Cullercoats

			Tyne and Wear NE30 4PZ UK Email: Gemma.Quilez-Badia@newcastle.ac.uk Email: M.E.Gill@newcastle.ac.uk
8.5	Phytoplankton analysis	Fisheries Research Services, UK	Tracy McCollin Coastal Hydrobiology Fisheries Research Services Marine Laboratory PO Box 101 375 Victoria Road, Torry Aberdeen, UK, AB11 9DB Email: mccollint@marlab.ac.uk
9	Evaluation of corrosion risk of the treatment methods	Bureau Veritas, France	Michel Huther Bureau Veritas 17 bis place des reflets - La Défence 92077 Paris La Défence Cedex France Email: michel.huther@bureauveritas.com
10	Oxidation method	BenRad, Sweden	Lena Blomqvist or Sara Gorton Wallenius Wilhelmsen P.O. Box 38193 Swedenborgsgatan 19 SE-100 61 Stockholm Sweden E-mail: lena.blomqvist@2wglobal.com E-mail: Sara.Gorton@walleniuslines.com

Table 12.1. Contact information regarding the paragraphs in the Completion Report of the Work Package 3.