Latest results from testing seven different technologies under the EU MARTOB project- Where do we stand now?

Ehsan Mesbahi

On behalf of MARTOB Consortium
http://www.marinetech.ncl.ac.uk/research/martob/

School of Marine Science and Technology,
Armstrong Building,
University of Newcastle upon Tyne,
Newcastle upon Tyne, NE1 7RU, UK
Tel: +44 (0191) 222 6723
Fax: +44 (0191) 222 5491
Email: Ehsan.Mesbahi@ncl.ac.uk

1 Introduction

MARTOB is a three-year project funded through the Transport and Energy Directorate of the European Commission (GROWTH Programme). The MARTOB project began in April 2001, and it has the dual aims of developing methods for treating ballast water on-board ships and for developing recommendations of best practice for verification and monitoring of compliance of a sulphur cap for marine fuels. Both of these aims are directed towards making shipping operations more environmentally friendly.

The main work components to be carried out as part of the MARTOB project are as follows:

- Collection and assessment of data and information on ballast water management methods and existing relevant legislation, and a review and update of alien species introductions in European waters,
- Development of selected methods for on-board treatment of ballast water through lab-scale testing and in-depth analysis,
- Large and full-scale testing of selected ballast water treatment methods,
- Assessment of the financial, technical and operational effects of a sulphur cap on marine bunker fuel in European waters.

The first phase of the project related to ballast water management was completed in early 2002. This included collection of information on ballast water management methods that are currently used, that have been tested on board ships, or that are in an advanced stage of development. In addition to collecting information on biological effectiveness, information was collected on the safety of methods, environmental effects, and costs. Information was also collected on existing and proposed regulations, to give an indication of future directions for ballast water management requirements.

2 Techniques tested within the MARTOB project

High temperature Thermal Treatment: This method uses heat to incapacitate and kill organisms in ballast water. Low temperature treatment requires a long time and will not be effective against bacteria and some of the hardier organisms, but will be cheaper to implement as it uses waste heat. High temperature treatment is more expensive as in most cases it needs a dedicated heating system, but is potentially more effective at killing the organisms and requires a much shorter exposure time.

De-oxygenation Treatment:: De-oxygenation of ballast water can be achieved mechanically by gas sparging, chemically by adding reducing chemicals, and biologically by adding nutrients. In MARTOB only the latter method has been studied in detail. By adding nutrients into the ballast water, the growth of the naturally occurring bacteria in the water will be stimulated. During the growth they consume oxygen, and the oxygen in the water will be depleted.

Ultraviolet Treatment: Ultraviolet (UV) lamps are used to irradiate the organisms in the ballast water. The UV radiation will induce photochemical changes in the organism; i.e. it will break the chemical bonds in DNA. This can lead to problems should the organisms survive, as it may carry mutations. Furthermore, there is a requirement for pre-treatment of the ballast water, as the performance of the system decreases with the turbidity of the water. Ultraviolet Treatment is well established and proven as a disinfectant in the wastewater treatment sector.

Ultrasonic Treatment: Ultrasound is generated by a transducer, which converts mechanical or electrical energy into high frequency vibration. The ultrasound generates cavitation in liquid (in this case ballast water), which can lead to the cells of organisms rupturing. It has been shown to be effective with bacteria, plankton and other larger organisms. However, ultrasound may have an adverse effect on ship/tank coatings and ship structure and would, therefore, need to be tested. Ultrasonic treatment has been successfully used in water treatment and the food industry to control microorganisms.

Ozonation Treatment: The Ozonation system introduces ozone into the ballast water. As ozone is unstable at atmospheric pressure it must be generated in situ. Ozone has been used in onshore applications, such as swimming pools, disinfecting drinking water and controlling microbiological contamination in various areas. In these applications it has proven to be very effective and a more powerful biocide than chlorine, which has traditionally been used. Ozone is toxic and therefore it will have to be used with care. There is also concern that it may cause increased corrosion in the tanks and pipes.

Oxicide Treatment: The Oxicide method is an electrochemical method, which generates hydrogen peroxide from the oxygen present in the ballast water. This decline in the concentration of oxygen and the presence of hydrogen peroxide is enough to significantly reduce the number of organisms present in the water. It also decomposes in water and will therefore not cause any problems to the environment. Hydrogen peroxide is an irritant and it will have to be used with care and it could possibly lead to increased corrosion.

Advanced Oxidation Technology: Advanced Oxidation Technology (AOT) consisting of a combination of ozone, UV and catalysts. Thus Ozonolytic / Photolytic / Photocatalytic Redox processes are operating simultaneously within a 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.
Hurdle Technology: Hurdle technology uses a combination of two or more treatment methods to reduce the number of microorganisms present. This may increase the effectiveness of the treatment and if chosen properly, can also eliminate some of the disadvantages of using the treatment methods alone.

3 Timeframe of the project

MARTOB project, (On Board Treatment of ballast water (Technologies Development and Applications) and Application of Low-sulphur Marine Fuel, partially funded by European Commission by contract number GRD1-2000-25383, started in April 2001 for a period of 36 months under the coordination of University of Newcastle upon Tyne.

4 Aims and objectives:

MARTOB's main objectives are:

- To investigate methodologies and technologies for preventing the introduction of non-indigenous species through ships' ballast water.
- To develop design tools and treatment equipment to be used in the further development of ballast water treatment techniques.
- To assess the effectiveness, safety and environmental and economic aspects of current and newly developed methods.
- To develop cost-effective (capital and operating), safe, environmentally friendly on board ballast water treatment methods, which have a minimum impact on ship operations.
- To produce guidelines for crew training and criteria for selecting appropriate ballast water management method.
- To assess the financial, technical and operational effects of sulphur cap on marine bunker fuel in European waters, and propose a verification scheme ensuring compliance with a sulphur cap from all players in the market.
- To help to facilitate the introduction of an important sulphur emission abatement measure without unintentional distortion of competition in the shipping market.

5 Research methods, test protocols and experimental design:

5.1 Laboratory-Scale Testing of Ballast Water Treatment Methods

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.

5.2 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 10l 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

5.3 Biological Assessment: 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.

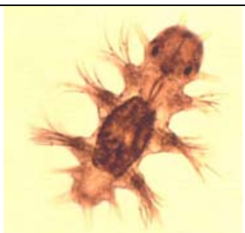
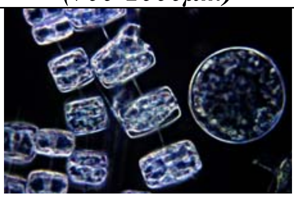
The sampling and test protocol provided standards for:

- 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.

***Zooplankton Fixation and Staining*:** All samples were filtered through a 63µm sieve. The zooplankton was rinsed from the sieve with clean seawater into labeled 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.

5.4 Framework of Evaluation

Environmental assessment: Environmental assessment includes evaluation of the direct environmental impact resulting from the discharge of treated ballast water and consideration of the indirect environmental impact. Direct impacts on receiving waters can result from discharges of the ballast water systems including that with altered quality, discharge of solids from physical separation methods, and discharge of living organisms that have survived treatment. The treated ballast water will be sampled on discharge for those parameters that are expected to change as a result of the treatment. Data from testing for biological effectiveness will give an indication of the types of organisms that will survive the treatment and be discharged. Indirect environmental effects of ballast water management will be assessed by estimating energy use, and calculating amounts of materials used during both operation and construction of the treatment equipment. Waste generated during operation or through disposal of worn out components and equipment will also be assessed.

Safety assessment: The assessment of safety aspects of treatment methods within the MARTOB project will be based on an evaluation of operational aspects. These include use of hazardous chemicals (either generated or stored on site), hazards related to operation of the equipment, aspects related to the storage and handling of chemicals and residuals required for, or resulting from, the on-board treatment of ballast water; and aspects related to unintentional release on board the vessel of treated ballast water containing residuals. The safety assessment of each method will also consider possible accident scenarios.

Economic assessment: In order to assess the economic viability of treatment options, two basic cost components are relevant, i.e. capital costs and operational costs. An interest rate of 8% over a period of 10 years is recommended to depreciate the investment costs, which fall under capital costs. Material costs, personnel costs and maintenance costs all fall under operational costs and these must be estimated in details for each treatment option. Other cost components like those resulting from training and management issues and those from the economic benefits and disadvantages of treatment options all need to be estimated in detail for each treatment option. All these cost components mentioned above must be estimated based on the same basic data e.g. ship type, ballast water capacity, number of voyages per year, number of ballast pumps, ballast pump capacities etc.

Technical and operational applicability: With respect to on-board ship applicability of treatment options, the options, alongwith their space requirements, capacity, flow rate and time, should be checked on the vessel for effects on stability, visibility, longitudinal strength, overpressure in the ballast tanks, liquid motions in the ballast tanks, thermal stresses, aggressiveness versus materials, corrosion, pressure drop in pumping system, modification of the piping and pumping system, safety of the crew and compatibility with trip duration and crew working load.

5.5 Objective Assessment

Assessment of ballast water treatment technologies have not been limited to their biological effectiveness only, other criteria such as their compatibility with a particular ship and her route, overall cost, safety, crew, life cycle assessment, corrosion effects and many other factors have been considered here as ranking criteria with their individual weighting in the final assessment. MARTOB has also developed a comprehensive IT based technology to determine attractiveness of a particular ballast water management system for an individual ship travelling at a particular route. Details of the developed objective assessment methodology have been illustrated in Fig.2.

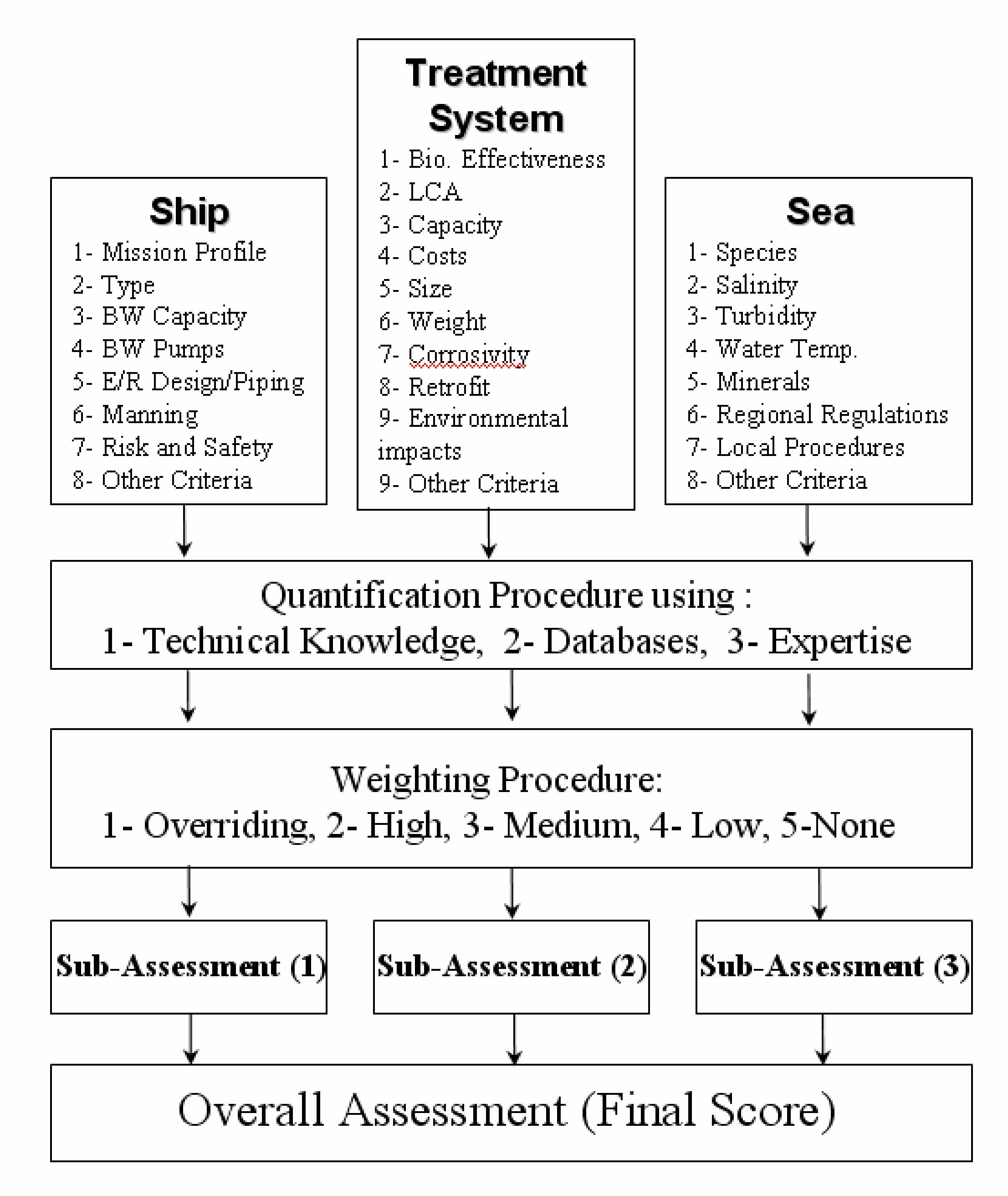


Figure 2. Objective assessment flowchart

6 Results: Biological effectiveness

6.1 ***High Temperature Thermal Treatment*****:** Offers one solution if short heating period is required for the effective elimination of unwanted marine organisms. Treatment during ballasting and treatment at exit (deballasting) are two possible options. The treatment at exit does not require the water to be pumped from one tank to the other for treatment, or additional tanks for storage, 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 is 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.

Figure 3. High Temperature Thermal Treatment, Laboratory Scale

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* sp., *Nereis* sp. and *Tisbe* sp., three zooplankton species commonly found in ballast water. For the phytoplankton *Alexandrium* sp. and *Thalassiosira* sp., 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 55^{o}C and above were more effective at reducing phytoplankton biomass. However, there was no significant effect between the results for treatments at 55, 60 and 65^{o}C, 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 between 55 to 60°C. Fig. 3 shows laboratory scale equipment for High Temperature Thermal Treatment.

6.2 ***Biological de-oxygenation*****:** the solubility of oxygen in water is low. 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 growth of the bacteria will consume the available oxygen in the water, and when the ballast water becomes anoxic, organisms that require a steady supply of oxygen will die. The aim of the studies was to develop a de-oxygenation process that could be applied in large scale, and to test the efficiency towards selected organisms in the mesoscale trials in Newcastle. See Fig. 4.

Figure 4. Laboratory scale De-oxygenation technique

The time it takes to consume all the oxygen in seawater decreases with increasing temperature. At 4°C it will take 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 was tested in meso-scale in 50 litre 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, two copepods (*Acartia tonsa* and *Tisbe battagliai*) and one polychaete (nectochaete larvae of *Nereis* virens), and two species of phytoplankton, a dinoflagellate (*Alexandrium tamarense*) and a 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 organisms were dead.

The killing effect on phytoplankton of de-oxygenation was limited as measured by the change in the concentration of chlorophyll a. On average, the chlorophyll concentration decreased by 33%, but there was no significant difference between the treated tanks and the non-treated controls. The reduction in chlorophyll may therefore be due to the fact that the micro algae in all cases were incubated in darkness.

Corrosion effect estimated with FMECA analysis identified the following issues: a slight decrease of the pH with possible consequences on metal corrosion, coatings and gaskets, a slight increase of CO_2 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 of the bacteria concentration with possible consequences on metal corrosion, coatings and gaskets.

6.3 ***Ultraviolet light treatment (UV):*** UV 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 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. Microorganisms are sensible to UV radiation between 210 and 320 nm, with a peak at 265 nm. See Fig. 5.

Figure 5. Laboratory scale equipment for UV and US systems

Maximum reduction rate of 78% with phytoplankton was achieved and regarding zooplankton the UV method did not inactivate more than 56%. With UV treatment, the greatest percentage change of chlorophyll *a* concentration achieved was a 56% reduction.

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

6.4 ***Ultrasound treatment (US):*** Ultrasonic treatment is a relatively new technology in ballast water treatment. Ultrasonic liquid treatment uses high frequency energy to cause vibration in liquids to produce physical or chemical effects. Ultrasound, from 20 kHz to 10 MHz, is generated by a transducer that converts mechanical or electrical energy into high frequency acoustical (sound) energy. The sound energy is then fed to a horn that transmits the energy as high frequency vibrations to the liquid being processed. The action of ultrasound is thought to be mediated through various responses that may be fatal to marine organisms. These are heat generation, pressure wave deflections, cavitation and possibly the degassing effect of ultra-sound causing removal of much of the oxygen. Cavitation, the formation of gas cavities within liquids, is affected by the frequency of the ultrasonic, power level, volume of water, temperature of the water and concentration of dissolved matter and gases. Higher frequencies, warmer temperatures and lower concentrations of dissolved matter have been found to increase the effect of ultrasound pulses. Plankton mortality has also been observed in the presence of ultrasound and is considered in part to be attributable to the cavitation process.

The mortality attained by the US treatment was always below 40% for zooplankton for all the tests. The highest percentage change of chlorophyll *a* levels achieved with US was a 71% reduction.

No risk of increased corrosion with respect to coating and gaskets was identified regarding the US method.

6.5 ***Ozone treatment***: O_3 is the triatomic form of oxygen which is a gas at room temperature. 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 agent which rapidly destroys viruses and bacteria, including spores, when used as a disinfectant in conventional water treatment. 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. In the contact chamber ozone is introduced to the water stream. Biological effectiveness is a function of concentration and exposure period. The longer the ozone-contact time, the higher the mortality. Industrial systems use a "bubble contractor" chamber that maximises ozone exposure. A bubble system was also selected to the ozone device utilized in the Martob project. See Fig. 6.

Figure 6. Laboratory Scale Ozone treatment

Mortality rates increased rapidly with increasing contact time. The highest value for the O_3 treatment was 89%, eliminating *Nereis*. Phytoplankton results showed that O_3 reduced chlorophyll *a* levels with a 97.2 percentage change against samples taken before treatment.

O_3 method caused a significant increase of the Redox potential (short term effect) with possible consequences on metal corrosion, coatings and gaskets. The production of O_3 (short term effect) with possible effects on metal corrosion, coatings and gaskets was also identified.

6.6 ***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 a specially designed and patented electrochemical reactor. H_2O_2 destructs plankton and microorganisms 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 an alternative to chlorine based disinfectants. A first design of the Oxicide cell has been built 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 sea-water, 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 was approx. 400 mg per liter (using pure oxygen gas) or 150-180 mg per liter (using air). The initial current efficiency (CE) was 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. See Fig. 7.

Figure 7. Laboratory scale Oxicide treatment system

H_2O_2 is efficient against selected organisms: 100% of *Nereis* and ≥ 90% of *Acartia* were removed in all experiments at 10-15 mg H_2O_2/dm^3. *Tisbe* proved more difficult, but was also removed by at least 85% at higher concentrations of H_2O_2 (> 28 mg/dm^3). Furthermore, a reduction in chlorophyll *a* levels of 50% was achieved 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 higher concentrations (>100 mg H_2O_2/dm^3) to destruct or inactivate; this especially holds for large organisms.

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 relatively 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 consider the electric isolation of the DC equipment, because of the risk of unexpected current return paths and significant local metal corrosion.

6.7 ***Advanced Oxidation Technology (AOT)*****:** AOT consists of a combination of ozone, UV and catalysts. Thus Ozonolytic / Photolytic / Photocatalytic Redox processes are operating simultaneously within a titanium reactor to generate large amounts of radicals, mainly hydroxyl radicals, which will destruct and/or eliminate microorganisms. 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 carried out with 100μ filter upstream the water purifier. The combination of AOT and the 100 μ filter could achieve over 95% killrate of zooplankton. See Fig. 8.

Figure 8. Laboratory Scale Advanced Oxidation Technique

In the samples after treatment with the water purifier and filter the number of dead and alive zooplankton are low (1.4 - 17% of the number initially 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 4% of the number included in test water). This indicates that organisms are eliminated by the water purifier. It could be that some organisms are left in the pipes or in the tank. But compared to the number of zooplankton left after a test with only the pump (35-52% of the number included in test water) some may have been lost.

The combination oxidation technology together with the 100µ filter achieved a 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 for careful scrutiny.

6.8 ***Hurdle Technology***: 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 the 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.

During the MARTOB trials various combinations were tested, based on the expected synergistic 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 best was the low temperature thermal treatment (40^{o}C) + de-oxygenation, which had 100% efficiency for *Tisbe* and *Nereis*, and 97% for *Acartia*.

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 removal increased for *Acartia* and *Nereis* 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.

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 low heat with de-oxygenation or hydrogen peroxide were not effective at reducing chlorophyll *a*. The remaining four treatments were all based on combinations of UV and hydrogen peroxide, 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.

7 Results: Environmental impacts, Risk and Safety and Economic aspects

In the laboratory testing phase of the MARTOB project, 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 within the MARTOB project were used to assess each of these effects for each of the methods tested at laboratory scale. 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 were 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.

Table 2: Case study Ship details

Basic Ship Information		
Ship type	Pure Car and Truck Carrier (PCTC)	
DWT (Dead Weight Tonnage)	14841	
Length Overall	199.1 m	
Voyages per year	50	
Route	Southampton – New York	
Ballast water capacity	8076 m^3 (total volume of all ballast water tanks)	
Volume of Ballast Water to be treated per trip	2000 m^3	
Number of ballast pumps	4	
Capacity of ballast pumps	500 m^3/h	
Additional Data Selected for Economic Assessment		
Parameter	**Details**	**Specified for case study**
Power consumption of pumps	Energy use per hour per pump	50 kW
Fuel Type	Fuel type used for BW pumps	MDO
Energy content of fuel	Standard factor	42.5 MJ/kg
Fuel notional costs	Have to be standard for all comparative calculations	0.4 €/kg
Fuel conversion efficiency (diesel to electricity)	Standard factor	30 %
Fuel conversion efficiency (diesel to steam)	Standard factor	66 %
Depreciation period	period in years used to annualise capital costs	10 year
Interest rate	Interest rate used to annualise capital costs	8%
Fuel cost	Cost per litre MDO	0.4 €/kg
Personnel cost	Average cost per hour	25 €/h

7.1 *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 tested in MARTOB 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, Oxidation, and Oxicide, were confined to the location of the equipment installation. None of the on-board treatment methods have the potential 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 of treated or untreated ballast water. 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 system. The UV and AOT 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.

7.2 ***Environmental Effects***: Environmental impact categories used to assess the effects of each of the ballast water treatment technologies tested in 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 parameters
        - 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 change 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 advanced oxidation methods will both lower the dissolved oxygen concentration of the ballast water. Increased temperature of the ballast water discharge will occur after thermal treatment and ultrasound treatment. 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 whether filtration is used, treatment type, and the concentration of organisms within the intake ballast water. The potential 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. 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 constructing the treatment systems. Materials used for construction of the treatment equipment will be further refined in the next phase of the project 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 these methods.

7.3 ***Economic Aspects***: Installation of an on-board ballast water treatment system will lead to changes in 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 scaling-up of the systems and the large-scale trials 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.

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

Table 3. Preliminary calculations for costs

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 m^3 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

8 Results: 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 study was not to perform a detailed analysis of the corrosion risk link to each system which will require information 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 MARTOB's expert group.

The parameters considered in the analysis with indication of the variation or consequences which induce 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 and alloys etc., based on the treatment method.

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

9 Full/Large Scale 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 Care and Truck Carrier. Ultraviolet, ultrasound, ozone and oxicide methods will be tested with large scale facilities.

In the large scale test phase of US and UV the duration of test runs will be longer 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 thus the error caused by the small amount of water can be reduced. Also the link to the actual marine environment is evident. The strategy with ozone has also been changed. 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, and long term test runs might also be carried out.

To assess biological effectiveness of treatment systems, similar procedures as laboratory tests will be followed. Standard sieves of size ranging from 10µm (for phytoplankton) to 50µm (for zooplanktons) will be used onboard the ship. A large volume of Ballast Water (1000 litres) will be tested at each sampling period to ascertain true representative of individual Ballast Water tanks. The effect of time spent in the ballast water tank on species' survival will also be studied.

10 Conclusions and Recommendations

During last two years, MARTOB has gained valuable expertise in the field of Ballast Water treatment technology, assessment of biological effectiveness (large and small scale), development of test protocols and procedures and overall objective assessment.
MARTOB believes that all key criteria in the development of Ballast Water technologies should be weighted and considered accordingly.

MARTOB believes that given time and adequate funding, there are technologies which have the capability of reaching high standards for Ballast Water treatment. Setting up a high standard of "No harmful discharge" and deciding on realistic time horizons to achieve such goal, could urge technology developers to seek more effective solutions. Considering the existing level of expertise, a primary standard of "No discharge of live species larger than 50µm" seems justifiable. More stringent standard (i.e. No discharge of 10-20µm live species) could be introduced in a 3 or 5 year time and after re-visiting the level of technological developments.

During last few years, significant progress has been made by various projects all around the world; MARTOB strongly suggests that additional Research and Development funds through appropriate channels at national, continental and international levels should be provided to enable technologists and scientists proceed with further development.

11 MARTOB Partners

University of Newcastle upon Tyne (Coordinator, UK) Abo Akademi University (FIN) VTT Industrial Systems (FIN) Environment, Energy and Process Innovation (NL) Institute for Applied Environmental Economics (NL) SINTEF Applied Chemistry (NO) Fisheries Research Services (UK) French Research Institute for the Exploitation of the Sea (F) Association of Bulk Carriers (UK) Alfa Laval AB (S) Berson Milieutechniek B.V. (NL) Environmental Protection Engineering S.A. (EL) V/den Heuvel Watertechnologie BV (NL)	The International Association of Independent Tanker Owners (UK) Souter Shipping Ltd. (UK) SSPA Sweden AB (S) Three Quays Marine Services (UK) International Chamber of Shipping (UK) Bureau Veritas (F) (MARINTEK) Norwegian Marine Technology Research Institute (NO) Shell Marine Products (NO) Wallenius Wilhelmsen Lines (SW and NO) MAN B&W (DK) Fueltech AS (NO) Norwegian Shipowner Association (NO)

12 Acknowledgements

MARTOB is partly funded by the European Commission under the 5th Framework Programme for Research, Technological development and Demonstration activities, Programme GROWTH, and is managed by the Direction-General for Energy and Transport.

13 References

All materials presented in this paper are extracts from publicly available MARTOB reports.

Please visit our website:

http://www.marinetech.ncl.ac.uk/research/martob/Public%20Reports.htm

where all detailed technical and scientific references may be found.