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Feasibility study of an indicative Ballast Water Tester

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Technical Report

Feasibility study of an indicative Ballast Water Tester

By

LITEHAUZ

01th of March 2012

Project supported by the Danish Ministry of Environment

Executive summary

Once the Ballast Water Management Convention enters into force, one of the main concerns is how the Port State Control (PSC) is to determine whether a ship is in compliance with the requirement of the Convention. According to Article 9.1 any inspection aiming to determine this, is limited to verify the validity of certificates, inspecting the ballast water record book (BWRB), and sampling of the ship's Ballast Water.

Regarding the latter two issues, this project have desk-top tested a series of rapid measurable or readily available parameters for their feasibility as indicators of ballast water conditions. Amongst the assessed simple parameters were salinity, dissolved oxygen, turbidity, temperature and pH and as a bit more complicated parameters were chlorophyll *a* and particle size distribution.

Three basic parameters have been selected as viable key parameters for the rapid ballast water assessment system:

- salinity (for basic verification of the Ballast Water Record Book),
- particle size distribution (for use as an indictor of organisms, i.e. system malfunction), and
- phytoplankton chlorophyll *a* (live organism indication through active photosystem II measurements)

These indicative parameters will assist the port state control in deciding whether the ship is free to discharge ballast water or whether "clear grounds" exist to continue with detailed analysis and stop the ship from emptying its ballast water tanks.

The parameters have been included in an example of a tool, which can be used by port state control or ship owners for monitoring ballast water conditions. Strong options exist for using existing databases of meteorological data in combination with position data to develop indicators for port (uptake) water conditions for several parameters.

Technology is available that allows particle size distribution and other robust and simple parameters to be added and used as a self-monitoring system that can accurately measure "before and after" conditions related specifically to the installed system. Preliminary tests have been carried out to substantiate this (found in confidential annex).

Further developments of the project may be along one or both of two routes:

1. Develop port state control tool, in particular the "port conditions" on-line database access.
2. Develop the self-monitoring device, algorithms and on-line access further through test in the field and in the laboratory.

In terms of commercial potentials option 2 would be the first choice for a continued development project. There is a considerable synergy for option 1 in developing the on-line application for option 2.

Preface

This report was conducted by Frank Stuer-Lauridsen, Svend Overgaard and Jens A. Jacobsen of Litehauz ApS during 2011 and early 2012. A number of individuals and companies have been consulted or directly involved in the study and we are grateful for the time you have donated and/or equipment or facilities we were allowed to borrow. In particular, this includes Aquasense, Bollfilter, DHI, NERI and DTU.

The project has been supported and partly funded under the subsidy scheme of environmentally efficient technology under the auspices of the Danish Ministry of Environment. A steering committee with members from the Danish Nature Agency, the Danish EPA, the Danish Maritime Authority and the Danish Shipowners Association has followed the project and provided valuable insights and proposals.

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List of abbreviations and definitions

Expression/Abbreviation	Explanation
AOC	Assimilable organic carbon
BDOC	Biodegradable Dissolved Organic Carbon
BOD	Biological Oxygen Demand
BLG	IMO sub-committee on Bulk liquid and gasses
BW	Ballast Water
BWMS	Ballast water management system
BWRB	Ballast Water Record Book
cfu	Colony forming units
COD	Chemical Oxygen Demand
D-1 Standard	Ballast water exchange compliance
D-2 Standard	Ballast water treatment to eliminate biological pollution
Detailed anlysis	Measurement of a viable organism concentration in the ballast water discharge which is directly comparable to the D-2 standard, i.e. number of viable organisms per volume[1] within the two size categories.
DOC	Dissolved Organic Carbon
EMSA	European Maritime Safety Agency
Environmental Distance	Differences in environmental parameters, salinity, climate, prior considered sufficient to avoid invasive species.
Indicative analysis	A direct or indirect measurement of a sample of a ballast water discharge. Direct measurements are directly related to the D-2 standard, i.e. determination of viable organism concentrations in the two size categories. The indirect measurement may include parameters that do not provide a value directly comparable to the D-2 standard.
NOAA	National Oceanic and Atmospheric Administration
NODC	National Oceanographic Data Centre
POC	Particulate organic carbon
PSC	Port State Control
Remote sensing	The use of satellite to obtain data
Self monitoring	Onboard monitoring of the BWMS during operations.
SOP	Standard operating procedure
std dev	Standard Deviation
TEU	Twenty-foot Equivalent Unit – the standard container size
TOC	Total Organic Carbon

1 Objectives

The purpose of this project is to test the feasibility of a series of parameters for indicative analysis of ballast water to assist port state control (PSC) in the assessment of compliance.

Being indicative the level assessed is “gross exceedance”; a level that is not yet defined by IMO, but would be defined as the level that establish “clear grounds” for intervention or vice versa provides grounds for not intervening. The parameters considered are also chosen based on their applicability in a practical situation.

This report does consider indicative methods with regards to the D-2 size and viability criteria, but not the bacteria requirements since it is assessed that methods to test the latter will require several days of testing and access to land-based facilities for a foreseeable future.

2 Background

Ballast water are used in ships for stability reasons and the ballast water are normally taken up or discharged during loading or de-loading of cargo operations in or close to the port. Ships ballast water has been demonstrated to be an important vector for introduction of alien invasive species.

2.1 Compliance requirements

In order to comply with the requirements of the Convention (IMO, 2004) the ballast water need to be managed. This can be done other either by exchange of the ballast water in offshore waters (D-1)[1] or by treatment of the ballast water (D-2). Regulation D-2 stipulates the requirements for ballast water quality with regards to maximum number of viable organisms, which is allowed in the discharge water. Organisms sized ≥ 50 µm are mainly zooplankton and organisms between 10 µm and < 50 µm are mainly phytoplankton. An overview over the regulated size categories and bacteria is presented in Table 1.

Table 1. The Conventions D-2 discharge requirements for Ballast water.

Organism category	Standard
Organisms ≥ 50 µm	< 10 viable organisms/m3
Organism size: ≤ 10 µm < 50 µm	< 10 viable organisms /mL
Vibrio cholerae	< 1 cfu/100 mL
Escherichia coli	< 250 cfu/100 mL
Enterococci	< 100 cfu/100 mL

2.2 Methods of compliance

Compliance to regulation D-1 is done by ballast water exchange in mid-ocean waters according to the guidelines for ballast water exchange (G6). Minimum requirements are: 50 nautical miles from the nearest land and in water which at least has a depth of 200 meters or in exchange areas designated by the flag state when the distance from the nearest land or depth requirements cannot be met.

In order to comply with the D-2 discharge requirements, treatment of the ballast water is typically done. The majority of the BW treatment systems (see Figure 1) comprise a solid-liquid separation unit and a disinfection unit which are used prior to storage of the water in the ballast tank. Some systems also treat upon discharge and many have a neutralisation step, which is initiated during de-ballasting to remove the disinfectants before the ballast water is discharged. The treatment systems are subject to an evaluation process by GESAMP under the auspices of IMO and systems employing active substances must be approved by MEPC. All ballast water treatment systems are subject to a national type approval process and notification of IMO before a system can be commercialised[2] for ballast water treatment with regards to regulation B-4.

[1] Depending on the ship's date of construction D-1 is applicable for some ships until 2014 or 2016 . After the dates all ships must eventually comply with D-2.

[2] Only Type Approved technologies that can be commercialised to compliance treatment requirements of ballast water

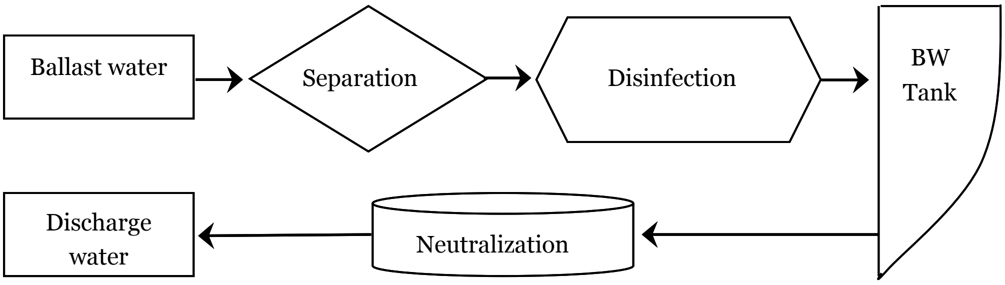
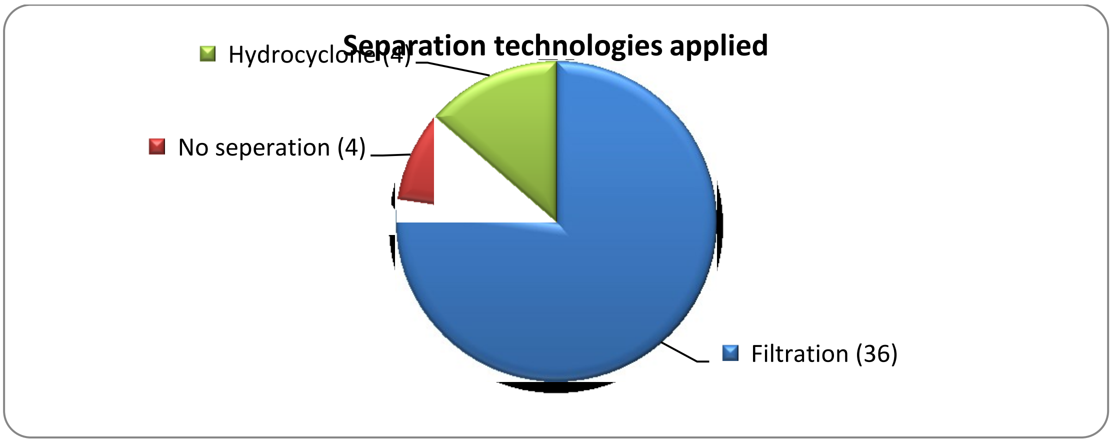


Figure 1. Example of ballast water treatment system with neutralization step

According to IMO, there are 40 systems in various level of approval as of August 2011.[3] 17 systems have Type Approval with ten of these using active substances. 20 systems have Final Approval and another 15 only with Basic Approval at this point. Of these systems 36 uses filtration and four hydrocyclone as solid-liquid separation technology. Four systems do not apply any separation. For the disinfection step, a number of different technologies are used for the disinfection step. See figures below.



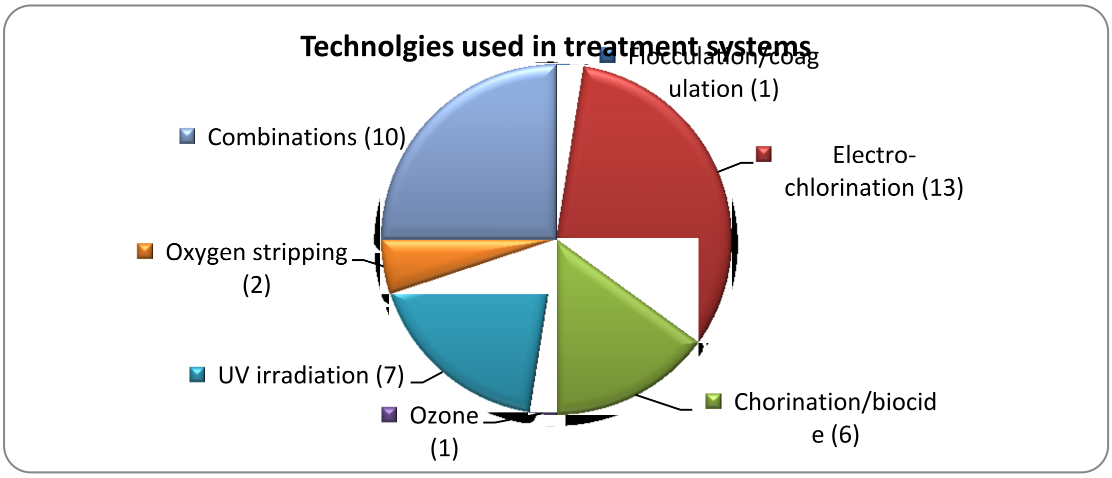


Figure 2. Summary of treatment technologies. (a) Physical solid-liquid separation, and (b) disinfection. "Combined" treatments include the number of systems, which uses more than one type of technology to disinfect.

[3]http://www.imo.org/OurWork/Environment/BallastWaterManagement/Documents/table%20updated%20in%20August%202011.pdf

Ten systems use combinations of two or more technologies. These combinations are presented in Figure 3.

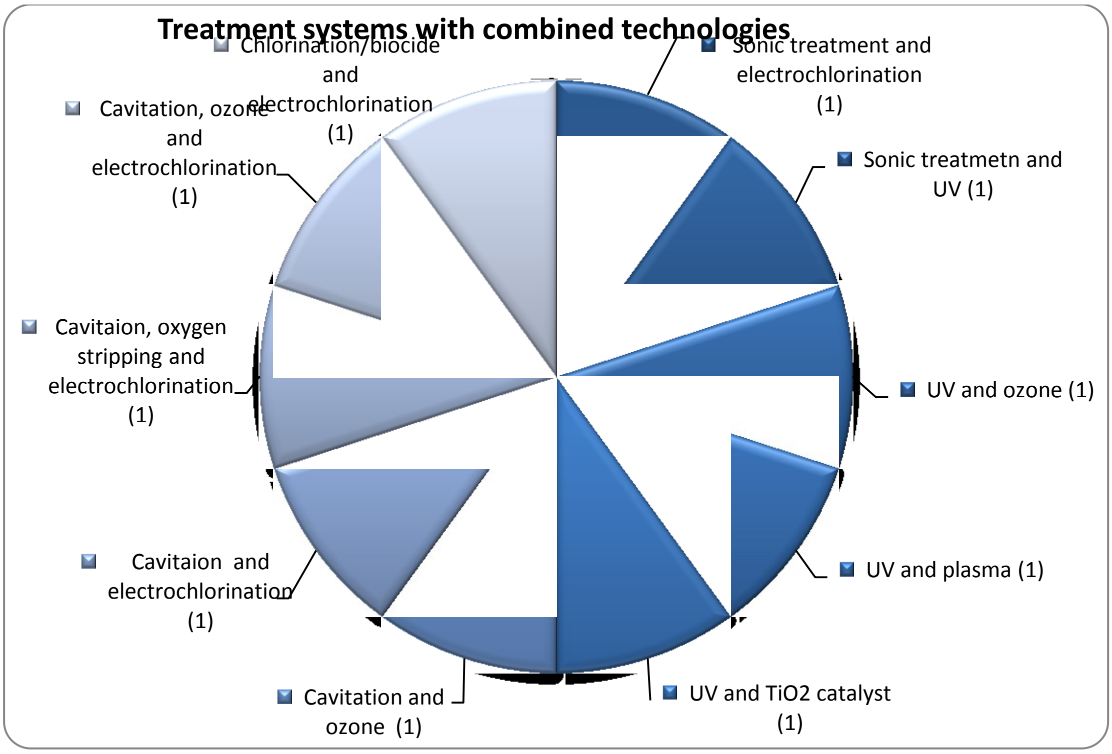


Figure 3. Systems which uses a combination of different technologies, (number of systems within each category).

2.3 Port state control

The BWMS is subject to port state control (PSC) just like other installed equipment on-board, to monitor if the discharge water complies with the D-2 requirements. A PSC is conducted as a part of a routine or random check on arrival in a port or if foul play is suspected. PSC compliance testing according to regulation D-2 requires a detailed analysis conducted after the IMO Guideline 2 (G2), which can take up to several days with the technology available today. A detailed analysis is a direct measurement of a viable organism concentration in the ballast water discharge, which is directly comparable to the D-2 standard, i.e. number of viable organisms per volume[1] within the two size categories.[4]

The crux of the matter is to perform such analysis in a fast and reliable way and that is not possible presently. The options for carrying out detailed analysis without causing undue delay are limited and no immediate technologies for detailed analysis have emerged which can be handled with limited technical experience and give results within the short timeframe available when the ship is in port.[5] As a consequence the immediate focus regarding on-board tests has been to establish a technological regime of indicative analysis methodologies and the general belief is, that indicative analysis for a foreseeable time will be the only practical way forward[6].

[4] The samples need also to be “representative” (se BLG 16 document for more information on this topic) as opposed to indicative analysis methods
[5] Merchant ships often have a short turnaround in ports of only 6-18 hours.
[6] Pers. Comm. with instrument developers and key actors within the ballast water management area at the GloBallast R&D conference in Istanbul - 2011.

Consequently, several tiered decision frameworks have been presented at BLG 16 on how a PSC can be conducted (a combined model can be seen in Figure 2). The procedure for a PSC inspection can be described in four stages where clear grounds can be determined at each stage when non-compliance with the convention is assumed (BLG 16, 2011).

1. Initial inspection of records and assurance that an officer is responsible for the ballast water management system on board the ship and that the officer is sufficiently trained to operate it.
2. Operation of the BWMS is checked and the BWMS is assessed for adequate operation.
3. Sampling and indicative analysis[7].
4. Detailed analysis and full-scale sampling to detect compliance/non-compliance with the D-2 standard.

Step 1. and 2.; inspection of the ships documents and verification of adequate personnel training regarding the BWMS is a straightforward process.

Step 3.; The sampling and indicative analysis methods in step three have been presented in the EMSA report on representativeness and methods for indicative analysis (Gollasch and David, 2010), the BLG 15 document and the recent BLG 16 document. The suggested indicative analysis methods are more qualitative than quantitative in nature and are used as indication of gross exceedance of compliance requirements. Indicative analysis can be either a direct or indirect measurement of a sample of a ballast water discharge. Direct measurements are directly comparable to the D-2 standard, i.e. determination of viable organism concentrations, however the sample needs not to be representative and can have a large confidence interval (e.g. +- 50 organisms per volume stated in the D-2 standard). The indirect measurement may include parameters that do not provide a value directly comparable to the D-2 standard, such as dissolved oxygen levels, residual chlorine levels, Adenosine triphosphate (ATP), Deoxyribonucleic acid (DNA), Chlorophyll *a*, pulse amplitude-modulated (PAM) fluorescence, etc.

Step 4.; When step three indicates non-compliance, a detailed analysis can be initiated.

[7] The present study does not address "representative" analysis or sampling methods and points to the extensive work currently undertaken in this area by working groups under IMO and EMSA. It is for simplicity assumed that the final sampling methodology decided upon by IMO is implementable for the parameters suggested here.

Flow Chart Proposal for PSC inspection (BLG 16, 2011)

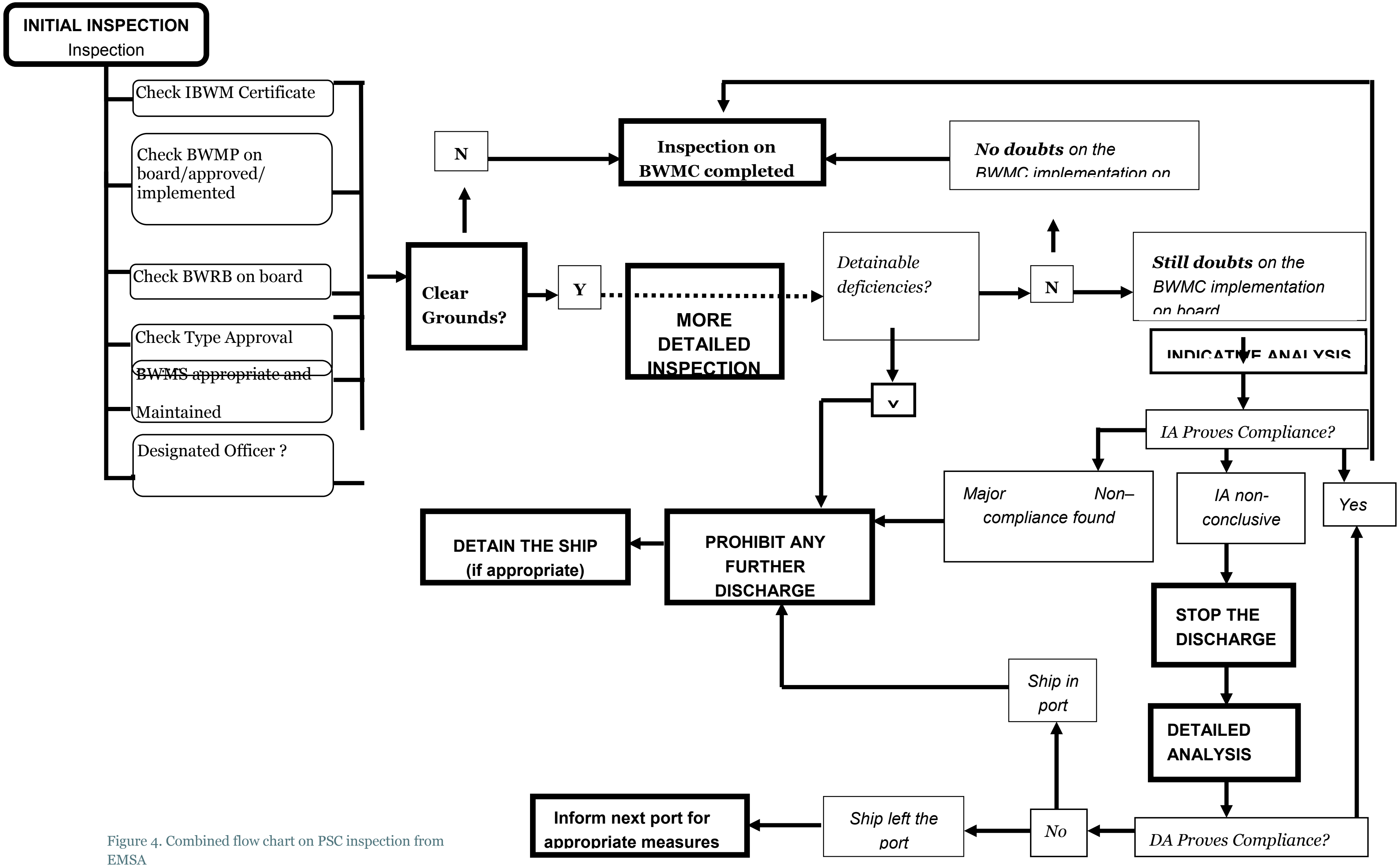


Figure 4. Combined flow chart on PSC inspection from EMSA

2.4 Assessing the feasibility of the indicative parameters

The parameters assessed in this report comprise salinity, dissolved oxygen, turbidity, temperature and pH, chlorophyll *a* and particle size distribution and concentration. All the parameters falls under step three of the PSC procedure.

The chemical composition of the ballast water with regards to salinity, dissolved oxygen, turbidity, temperature and pH are assessed for discrepancies from the expected based on the Ballast Water Record Book (BWRB), which establishes the location of where the ballast water was taken.

The parameters chlorophyll *a* and particle size distribution are assessed as to whether the BWMS is performing to standard with regards to number of viable organism. Chlorophyll *a* relates indirectly to D-2 parameters, however, particle size distribution is not listed as a parameter for indicative analysis in the BLG 16 document (2011) and is therefore regarded as a parameter for indirect indicative analysis. The indicative parameters and in which categories the fall are presented in Table 2

Table 2. Parameters and categories

Category	Parameter
Chemical parameters	Salinity Dissolved oxygen Turbidity Temperature pH
Organisms and viability	Chlorophyll *a* Particle size distribution

In order to assess the feasibility of using the parameters for indicative analysis, they are assessed with regards to robustness on influences from natural factors as well as influences from BWMS. Within both areas, the parameters are also assessed on stability during the holding time in the tanks.

Effects from natural influences is understood as how stable the parameters are over time when they are exposed to e.g. sun, rain, temperature etc. The natural ranges in which the parameters can be found are presented in Appendix 1.

With regards to influences from the BWMS, there is a range of different systems to disinfect the ballast water prior to discharge. Some of the technologies applied in the treatment processes could have an effect on the parameters. The treatment systems are mostly based on proven technologies within separation and disinfection processes suitable for use in ballast water. The main technologies presented in Figure 5, can be separated in a solid-liquid separation step and a disinfection step, which is chemical or physical based.

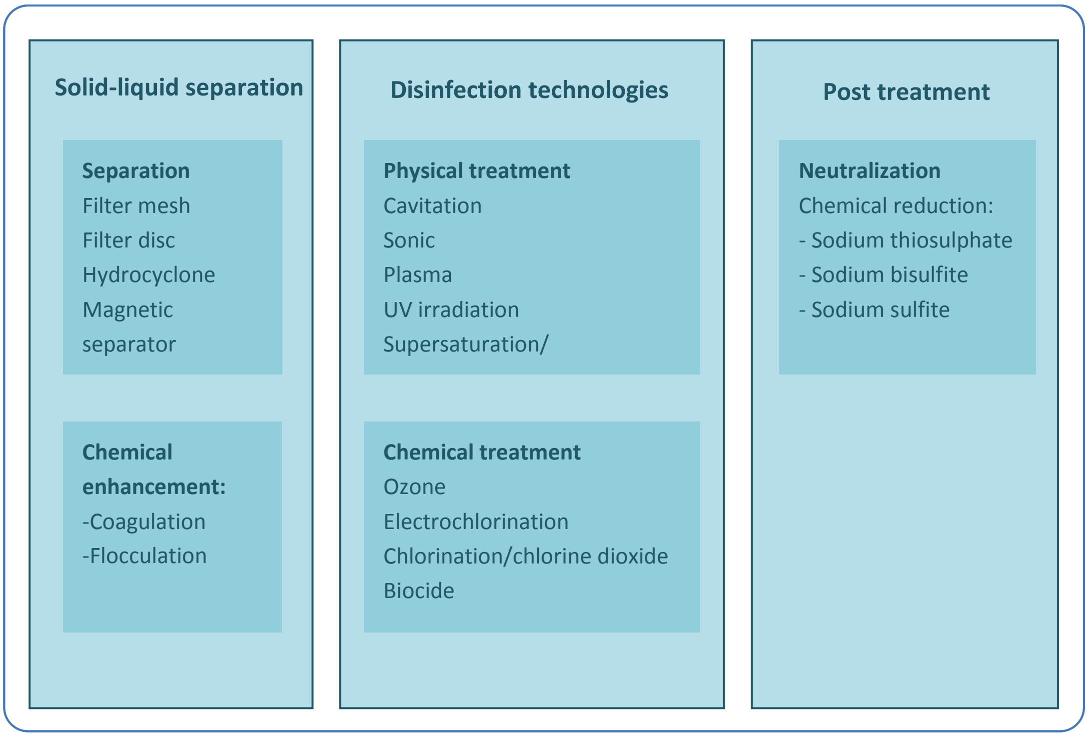


Figure 5. Main processes and technologies applied for ballast water treatment

3 Ballast water characteristics - no treatment

In the following, the proposed parameters are assessed under the following headings

- *Measurement methodology*
- *Parameter Robustness and stability*

with regard to general data availability, natural influences and stability when stored in the tank in a no BW treatment scenario and for each parameter a *Conclusion* is given.

3.1 Salinity

The salinity of the ballast water is a key parameter which can be used to estimate if the origin of the ballast water as stated in the BWRB is consistent with the expected salinity at uptake location. This is possible, as the variations in salinity are dependent on the proximity to coast and precipitation in the area. In coastal regions the salinity may vary from freshwater to marine water due to natural influences, such as tides, currents, rainwater runoffs, rivers, and river proximity. In certain arid regions surface water salinity can reach more than 52 psu due to evaporation (Awad et al 2004). For ocean waters the salinity is very stable at around 35 psu.

Measurement methodology
A salinity measurement is simple and used routinely around the world. The measurement is based on accurate conductivity (platinum electrodes measuring the voltage), temperature measurements and knowledge of the seawater composition (Cox et al., 1967). There are several cheap and modern instruments on the marked with a precision better than 0.005psu..

Parameter Robustness and stability
The salinity of the ballast water does not change when it is stored in a ballast tank and it is therefore considered a stabile parameter. Salinity can be used to do an indirect indicative analysis of whether the measured salinity in the ballast tank correlates with the expected salinity based on the uptake and discharge history given in the BWRB.

Apart from the BW log it is therefore crucial to know the salinity in the area where ballast water is taken up and the temporal and spatial salinity variances seen over the year. The smaller the variation in salinity, the higher degree of certainty. and thus a more reliable basis on which to determine if the measured salinity is consistent with the location(s) logged in the BWRB. If real time data of local salinity where ready available under a PSC in form of a continuous updated database this would provide a robust way to assess discrepancies.

A number of ways to obtain local salinity information exists. One way could be to use the quality assured data available through the National Oceanographic Data Centre[8] (NODC) where the salinity of the water bodies of the world are given for a 1° grid (approximately 110 x110km grid). The data is available on a monthly basis and as real time data for selected locations. Data on salinity can also be obtained on a

[8] An organization under the US National Oceanic and Atmospheric Administration (NOAA)

daily basis by remote sensing[9] (observation by satellites). Sea and coastal areas are scanned by satellites providing a resolution down to a global 4x4 km grid. Areas of higher resolution exist (260x260m), however, these are dependent on the satellite orbit and applied technology. Satellite data can be further developed by regional point data gathered from different applications, hereunder; buoys, Expendable Bathy Thermographs (XBT), and scientific monitoring projects.

The GloBallast Monograph series[10] offers another point of reference, as it contains seasonal variations for salinity[11] for 225 ports, which is among some of the busiest ports in the world. Out of the 225 ports, approximately half show salinity variances of less than 10%, especially ports from arid zones like the Mediterranean Sea, the Persian Gulf, and in some cases ports having oceanic proximity like Singapore and several ports in Brazil. The majority of low variance ports listed in GloBallast Monographs are high salinity ports, and only a few ports have zero to brackish water salinity. Low variance ports can obviously also be found in riverine environment with low or no salinity variance, however, the majority of these are typically not used for oceanic transport of goods, and is therefor not included in the GloBallast Monograph ports. The variations in salinity found in the GloBallast Monograph series can be seen in Figure 6.

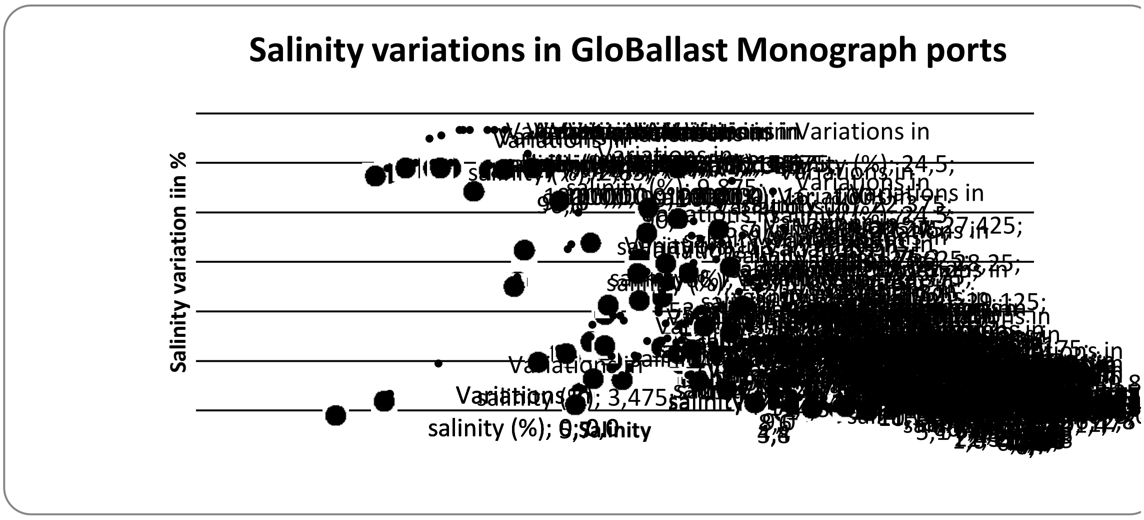


Figure 6. Variation in salinity from minimum and maximum values recorded over a year in 225 ports (Awad *et al.* 2004).

The ports listed in the GloBallast Monograph ports comprise some of the busiest ports in the world. These are of interest, as the shipping frequency is high and the overall chances of conducting a PSC on these are therefore the highest. As can be seen in Figure 7, many of the busiest ports are located at transshipment or break-of-bulk points.[12] The top container ports are in Southeast Asia, Northwest Europe, and the West Coast of the United States. Notable is also that the main recipients of BW are ports of export as e.g. oil terminals in the Gulf area or export ports in Asia (China, Taiwan, Hong Kong, and Singapore). The illustration reflects the main patterns of global trade between locations of production and consumption.

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[9] http://oceancolor.gsfc.nasa.gov/

[10] http://globallast.imo.org/index.asp?page=monograph.htm&menu=true

[11] Amongst others also seasonal ranges of temperature, tidal ranges and port proximity to rivers and size of river catchment.

[12] The point at which a cargo is unloaded and broken up into smaller units prior to delivery

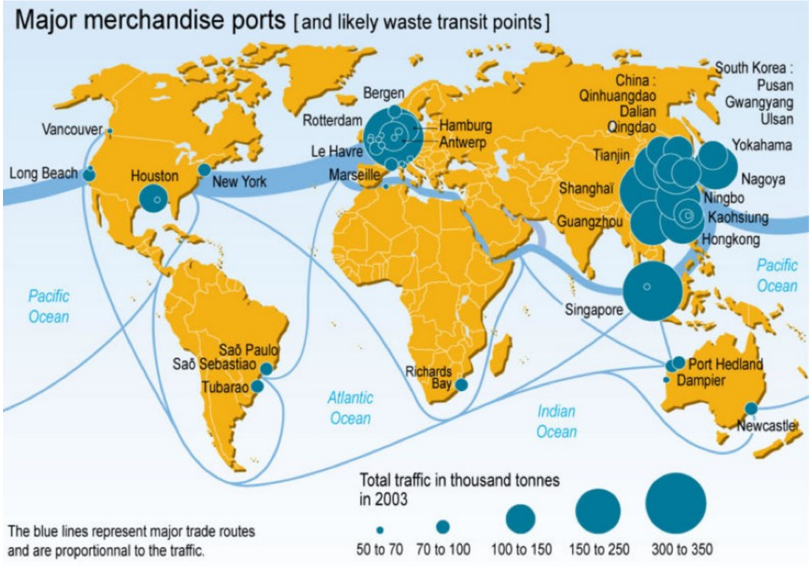
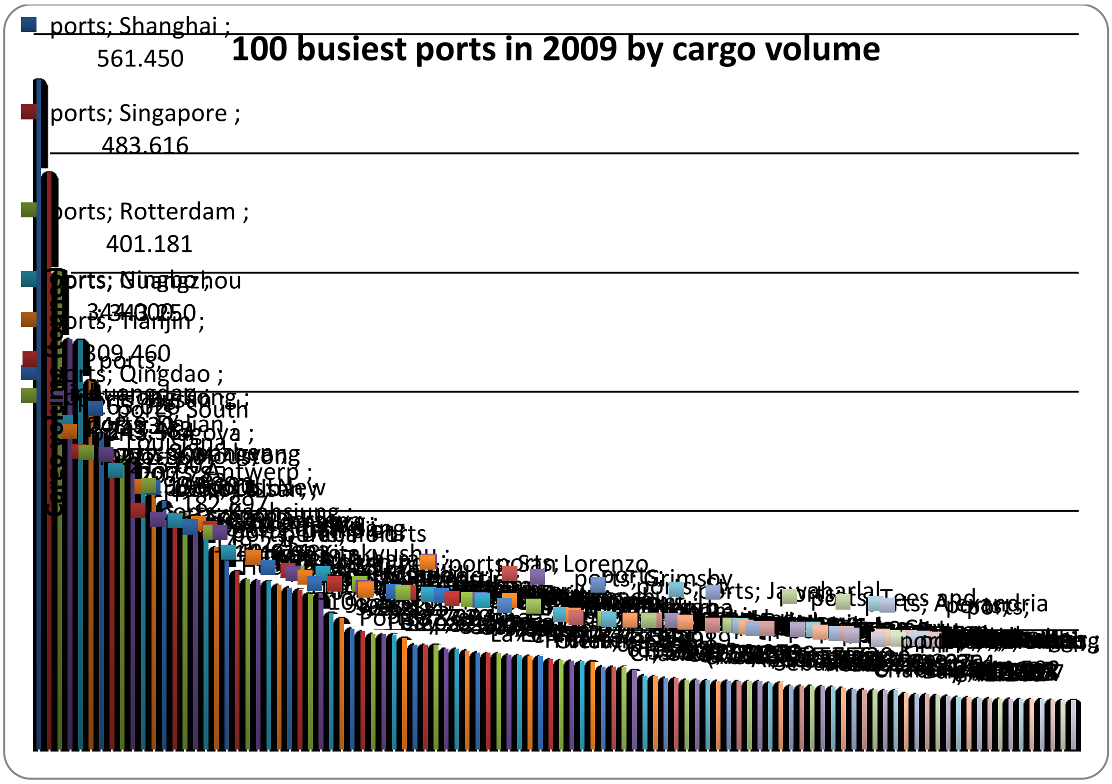


Figure 7. Major shipping ports and shipping routes of the World 2003. (Source: https://qed.princeton.edu/index.php/User:Student/Major_Merchandise_Ports_and_Likely_Waste_Transit_Points,_2003)

The 100 busiest ports in 2009 by size of bulk volume handled[13] are presented in Figure 8. If the GloBallast Monographs were used as information basis for salinity variance, 32% of the cargo volume handled within these ports would be from ports with salinity variances less than 10%. The full list of the 100 busiest port together with salinity variances can be found in Appendix 2.



[13] In metric tons

Figure 8. Top 100 busiest ports in the world by cargo volume in metric tons (Only displaying every 4th name).

Conclusion
In conclusion, the information that can be derived from a salinity measurement may prove useful indication of the origin of the BW in approximately half of the GloBallast Monograph ports (less than 10% variance in salinity).[14] As one third of the handled cargo at the 100 busiest ports is done in ports with salinity variances of less than 10% (GloBallast Monographs ports), it is therefore considered a fairly robust parameter, which can be used to correlate to the entries in the BWRB on uptake location of ballast water and not only as a feasible D-1 compliance parameter. It should be noted that the usefulness currently is highly dependent on origin of uptake where the salinity variance is low. Within its limitations regarding data accuracy and availability, it is assessed to be a rugged and cost effective analytical method.

3.2 Dissolved oxygen

According to BLG 15/5/4, dissolved oxygen (dO) is not considered for use in indicative analysis of either D-1 or D-2 requirements. It is, however, assessed here to establish if it is feasible to be used in connection with information derived from the BWRB to establish uptake location or duration of voyage.

Dissolved oxygen is a dynamic parameter influenced by biology and by the mixing and state of equilibrium with the atmospheric oxygen (the gas phase). The level of dissolved oxygen follows Henry´s Law with warmer water holding less oxygen than colder water. The chemical and biological oxygen production and consumption in the water, naturally have a profound influence. In ports, oxygen levels shows variations due to algal primary production in the daytime and biological consumption during the night.

Measurement methodology
The level of dissolved oxygen in water can be determined with electrodes, which measure the flux of oxygen across a membrane. As oxygen is consumed in the process the membrane in traditional instruments needs to be flushed continuously with new water to replace the oxygen consumed. Membrane-based instruments need special care in maintenance and calibration to maintain stability and accuracy in the system. However new technologies are available such as Rapid Pulse or luminescent based sensors[15], which need no calibration, are independent on water flow and have low or no maintenance requirements.

Parameter robustness and stability
The robustness of dO with regards to natural influences is assessed on the basis of detailed dO monitoring in the San Diego Bay as well as the stability of the dO levels in the tank.

In average the monthly dissolved oxygen is reported to vary in the range of 6 to 10 mg/L (Unified Port of San Diego, 2010a). The measured amount of chlorophyll *a* was found to rise 300% within a four hour interval for one sample point however only a 50% increase for another sample point (Unified Port of San Diego, 2010b), which significantly will influence the level of dO. A spot sample may therefore show highly variable levels of dissolved oxygen dependent on both time and location, even within a reasonably limited area.

In addition, uptake of BW extends over the entire period of time when cargo is unloaded. This can take between 2-9 hours and is dependent on ballast water capacity and weight of the unloaded cargo. Thus, the level of dO in the BW is an integrated level over a duration of time. However, data,on oxygen are normally only spot samples taken at one specific time during the day at one location when available, and

[14] Salinity is only regarded as a parameter for D-1 compliance testing in BLG 15/5/4 (2010)
[15] E.g the Optical Dissolved Oxygen Sensor (ROX) from YSI

this will not suffice to represent the actual level of dO in the BW tank.

Once the untreated ballast water is inside the BW tanks, oxygen levels will decrease close to zero in six to nine days (Seiden et al., 2010; Klein et al., 2009) due to bacterial activity within the tanks (Biological oxygen demand (BOD)), see Figure 9.

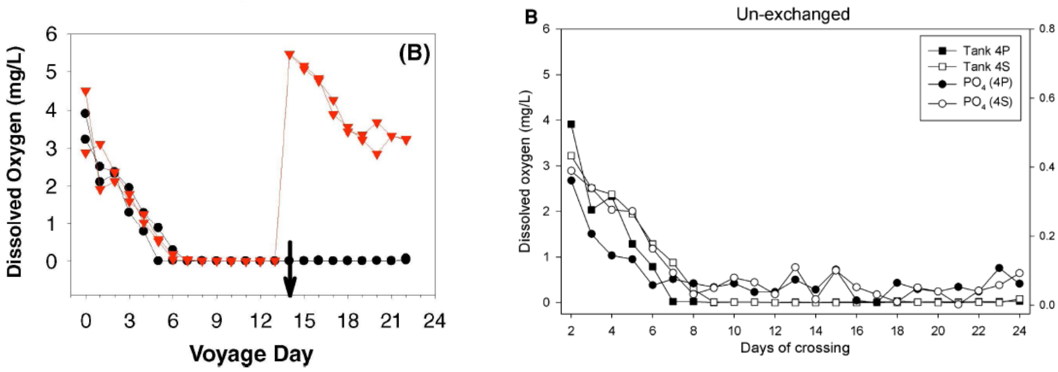


Figure 9. (Left) Oxygen depletion in BW tanks with no treatment. Arrow indicates Mid Ocean Exchange of BW (Seiden et al., 2010; Klein). (Right) Oxygen depletion in BW tanks with no treatment, no exchange (Klein et al., 2009)

Conclusion

In conclusion, the levels of oxygen at intake vary both on a temporal and spatial scale and with the general lack of environmental port data on dO levels, it difficult to obtain a comparable reference. As the dO levels furthermore decreases in the tank within a relative short time interval the usefulness of the parameter is low.

3.3 Acidity (pH)

The acidity in form of pH measurements are not considered in BLG 15/5/4 (2019) as a parameter for indicative analysis of compliance to either D-1 or D-2 requirements. It is, however, included in this assessment to determine if it is a feasible parameter to be used in an indicative analysis of BW.

Seawater pH ranges from approximately 7.4 to 8.4 and have seasonal variances mostly dependent on meteorological factors, such as acid precipitation, which can increase the pH. Changes in the pH of seawater are in general buffered by carbonate system as seen below in Figure 10. Freshwater pH is more variable and may be of more value as a parameter.

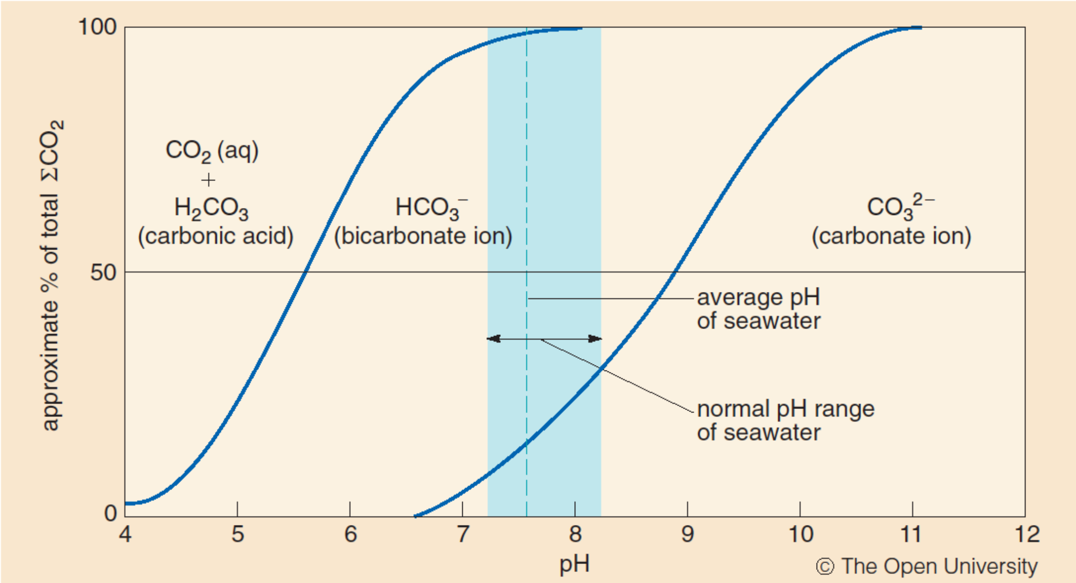


Figure 10. pH range of seawater. (Source: http://www.cambridge.org/resources/0521538432/1488_218437.pdf)

Measuring methodology

The acidity of a solution is determined on the basis of the hydrogen ion activity by a probe and a pH meter. The methodology is well established and results are rugged when temperature is taken into consideration. Before pH can be measured any probe needs to be calibrated in a known water buffer solution.

Parameter robustness and stability

Seawater pH is influenced by seasonal variances within a narrow band due to the carbonate buffer system and no usable information can be derived to determine the origin of the seawater on acidity. The parameter is considered stabile during holding time in the tanks.

Conclusion

In conclusion, acidity is not a feasible parameter for indicative analysis.

3.4 Water temperature

According to BLG 15 (2010), water temperature is not considered to relate to either a D-1 or D-2 indicative analysis, but is mentioned in connection with salinity measurements, as these are interdependent. In present report the parameter is evaluated for, if it is robust enough to correlate water temperature at uptake location with temperature of ballast water at discharge and it is therefore an indirect indicative analysis that relates to entries in the BWRB as well as supportive parameter for salinity measurements.

Seawater temperature changes mainly with longitude with the coldest water near the poles (approx. -2°Celsius) and the warmest near equator (approx. 36°Celsius). There are profound influences on local seawater temperature from the major current systems. Data on temperature is available as a monthly mean in a 1° grid global mesh.[16] After ballast water uptake the tank temperatures adapt to ambient temperatures following the gradient of the ambient temperatures and the heat transmission coefficient for materials between the ambient seawater and the tanks (steel & air and paints)

Measurement methodology

[16] Can be obtained from the American National Oceanographic Data Center (NODC)

Temperature measurement is a trivial and well-described technique with high degree of precision. Cheap hand held instruments, which measures with an accuracy of better than ±0.05 degree Celsius are available on the market.

Parameter robustness and stability

Seiden et al. (2010) has described the temperature dynamics of a common BW tank system with 4 tanks on a typical oceanic passage. Two tanks were exchanged at sea and two were kept un-exchanged. The experiment showed that the temperature changed at a rate of approximately 1°C per day with a maximum of 2°C per day. However, the tanks also rose above ambient oceanic temperatures, See Figure 11.

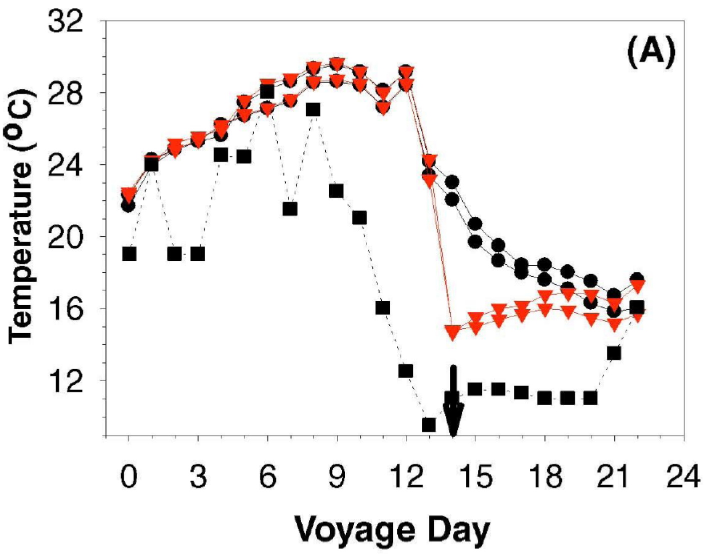


Figure 11. Temperature measurements in four BW tanks and in the ambient seawater on a three-week voyage across the Pacific Ocean. Temperatures shown: Black Squares (ambient); Triangles (BW with exchange); and Circles (BW without exchange) . Arrow indicates BW exchange in two of the tanks (Seiden et al., 2010).

From the data in presented in Figure 11, it is apparent that there are other influences on BW temperature than the ambient seawater. The influences can most likely be ascribed to energy influx from e.g. the sun, temperature difference between ballast water and cargo, ambient air and engine room. These parameters are highly variable and the thermodynamic relationship consequently becomes very difficult to determine, as comprehensive knowledge on cargo composition and location and in- depth knowledge of ambient air temperature and influx of energy from the sun would be needed in order to encompass all influential parameters.

Conclusion

In conclusion, the temperature has a low robustness and it is not found suited as a parameter for indicative analysis. The temperature, however, will still need to be measured in order to determine salinity.

3.5 Turbidity

According to BLG 15/5/4 (2010), turbidity is considered to be an indicator to describe distance to shore. Turbidity is in aquatic samples the cloudiness of that sample. It is measured as Nephelometric Turbidity Units (NTU) with a turbidimeter. The causes of turbidity are in general algal growth (phytoplankton), organic particles or inorganic particles, which derives from natural or human activities. The turbidity is highly variable due to run-of, proximity to river mouths, sea floor composition, depth of intake etc.

Measurement methodology
The turbidity is measured on the degree of light deflection. A light source is pointed at the water sample and a detector measures the amount of light that is deflected. The measurements not only depend on concentration but also the properties of the solids, related to shape, size, colour, and reflective capacity. Thus, the method is unspecific in the sense that it cannot determine the composition of the substances, which are causing the turbidity. Though turbidity measurements are fairly rugged, the output is repeatable only when the same suspension is used for the measurement.

Parameter robustness and stability
The majority of BW intake is conducted close to or in harbours and the turbidity of the water on uptake depends primarily on coastal proximity. Furthermore, turbidity also changes over time and variations can be substantial during the day due to algae growth and in influx of particles and organic matter. Local data of turbidity development are thus needed; data, which are not readily available for ports on a general basis. It is possible to obtain satellite information in a daily 4x4 km grid snapshot with worldwide coverage[17], however, quantification on satellite data would have to be cross referenced with meteorological and tide data, proximity to river mouths, bottom composition etc.

The turbidity also changes during holding time in the tank due to settling of suspended solids. The settling rate follows Stokes law and is dependent on particle density and size relative to the salinity and viscosity of the ballast water. The loss in concentration of total suspended solids (TSS) from five days of settling in ballast tanks is typically around 50% (Data from MEPC Basic and Final Approval applications). Particles that have settled might also re-enter the water phase due to ship movements.

Conclusion
In conclusion, turbidity is not considered a feasible parameter for indicative analysis. This is primarily based on the facts that a considerable amount of local data on bottom composition, runoff and rain are needed in order to determine if the measured turbidity is consistent with expected turbidity of uptake location. As the suspended solid also settles to a degree during the voyage and the turbidity is dependent on the reflection properties of the specific particle suspended, the total uncertainty is very high. The turbidity can, however, as noted in the BLG 16/4 (2011), be used as an indication of D-1 compliance since the oceanic water is not turbid (<1 NTU in open sea areas (Shi & Wang, 2010)).

3.6 Chlorophyll *a*

Chlorophyll *a* is considered an indicator for compliance with the D-2 Standard in BLG 15/5/4 (2010) where the detection of chlorophyll *a* may be taken as evidence of live photosynthetic organisms in the typical size range of 10 to 50 μm.

Chlorophyll *a* is a green pigment found in most phytoplankton using oxygenic photosynthesis to harvest energy from light. Chlorophyll exists in three forms with the main pigment being chlorophyll *a* and the accessory pigments chlorophylls *b* and *c*.

Measurement methodology
The use of light excitation of chlorophyll *a* to measure the fluorescence is a well-accepted methodology to assess and monitor water quality and provide an indirect measure of algal biomass (Chapman D., 1996). The commonly applied measurement methods do not, however, take into account whether the fluorescence is coming from live or recently dead algae. As this differentiation is crucial with regards to D-2 requirements, the only chlorophyll-based technology, which gives a useful output, is the Pulse-Amplitude Modulated (PAM) fluorometer technique.

[17] http://oceancolor.gsfc.nasa.gov/

The PAM fluorometer measures the photochemical efficiency of what is known as the photosystem II in live phytoplankton. The methodology uses four different excitation wavelengths to separate the fluorescence contributions from different groups of phytoplankton and calculate the different concentrations on the basis of a reference register of common phytoplankton by which fluorescence response is known. In situ detection limits are around 10-100 ng/L.

The PAM-fluorometer needs frequent calibration (before each analysis) and a measurement takes approximately 30 minutes for a sampling batch. The measurement should be conducted no later than six hours after sampling.

Parameter robustness and stability
Data on chlorophyll *a* based on satellite monitoring world-wide is available on a daily basis. However, the phytoplankton primary production is highly variable both on a temporal and spatial scale. During holding time in the tank, the chlorophyll *a* will degrade but the degradation rate is dependent on e.g. species, water temperature and light and chlorophyll can be measured from a couple of hours after treatment up to several days. [18]

With regards to PAM fluorometer measurements, it only gives a qualitative indication of the photosynthetic activity from live organisms. A semi-quantification of the PAM fluorometer output has been developed to estimate the number of viable phytoplankton in the size range 10 µm to 50 µm, suggesting that when the PAM 'health' condition (cell viability) indicator level is above 0.300 the number of organisms is 20 and above (Gollasch and David, 2010).[19] It should be noted that though larger phytoplankton (>50µm) may occur in the measured samples, a clear correlation to the number of viable smaller phytoplankton in the size range 10 µm to 50 µm is still seen (Gollasch and David, 2010).

Conclusion
The available chlorophyll *a* data on uptake locations is currently not considered sufficient to be able to correlate to measured amount of chlorophyll in the tank due to both spatial and temporal variations at uptake location, which are impossible to determine, and chlorophyll degradation in the tank dependent on several factors.

The detection limit of the PAM fluorometer is sufficiently low for the methodology to be used on the algae concentrations found in ballast water. As the PAM measurement can be translated into a semi-quantitative result which correlates lower D-2 size range, the method is considered to an indirect indicative analysis robust enough as indicator of non compliant BWM.

3.7 Particle size distribution

Characterisation of particle size distribution and particle concentration is a way to detect and quantify organisms and other particulate matter. The parameter can be used as an indirect indicative analysis that relates to the D-2 size ranges 10-50 µm and >50µm. However, without identification it is not possible to determine whether the particle measured is an organism, live or dead or other organic or inorganic matter. Particle size distribution without an identification element is therefore not listed in BLG 15/5/4. The majority of phytoplankton species are typically sized between 10 and 50 µm and the zooplankton above 50 µm.[20] Therefore, the quantification of size ranges can also be used to assess the efficiency of the solid-liquid separation step found in most BW treatment technologies.

[18] Pers. comm. Guillaume Drillet (DHI) February 2012, and email correspondence with Aurore Trottet (DHI) of February the 20th 2012.
[19] Included in the BLG document 15/5/4 (2010)
[20] Some large phytoplankton species are also found outside the 10-50 µm size range, however this is considered insignificant with respect to determination of gross exceedance.

Measurement methodology

Characterisation of particle size distribution can be achieved in several ways. One technology, which has been featured at BLG, is the FlowCam® from Fluid Imaging Technologies. This technology uses flow cytometry in connection with photo analysis to identify selective types of organisms based upon their shape and aspect ratio (width/length). Other and simpler technologies to determine particle size distribution are also available such as electro-resistance or laser diffraction/blocking. A commonly known electro-resistance based instrument is the Coulter counter.

A technology, which uses laser blocking, is the PAMAS S4031 GO. The instrument is a mobile seawater version for particle counting and quantitative assessment of filtration and cleaning control systems. The unit has been used in connection with the efficacy testing of the Hydrocyclone technology to validate the compliance requirements for separation of particles in ballast water. Dependent on the specific particle sensor installed in the PAMAS GO it can define particle distribution in the size range of 1-100 up to 1-400 μm with a measuring flow rate between 10 and 25 ml/minute.

Parameter robustness and stability

The determination of particle concentrations in the D-2 size ranges can support an enumeration of concentrations of phytoplankton and zooplankton. With regards to D-2 requirements, the critical point is viability of the measured organisms. The FlowCam® can determine viability when staining methods is applied, however, it can be a challenge for untrained personnel. The other methodologies (electro-resistance and laser diffraction/blocking) do not differentiate between live-dead and may therefore only provide an indication of a maximum organism concentration. Considering the fact that inorganic and inactive particles will settle in the tank over time and active phytoplankton will stay suspended, determination of particle size distribution is considered as a potentially useful parameter for performance of BWMS with a separation step. With regards to D-1 requirements, the methodology can aid to in the assessment to determine level particle concentration and thus if it is likely that a ballast water exchange has been conducted in mid ocean.

Conclusion

Particle size distribution can be used in indicative analysis with regards to both D-1 and D-2 requirements. Considering that the particle concentration in the lower size range in addition can be combined with PAM fluorometer measurements of chlorophyll *a*, to strengthen the estimation of number of viable phytoplankton, the particle size distribution is considered a feasible indicative parameter.

3.8 Summary of ballast water characteristics - no treatment

Of the seven parameters assessed, three parameters are found useful and robust enough with regards to natural influences and stability when stored in the tank to be used as indicators of ballast water quality or origin of ballast water. The parameters are:

- Salinity
- Particle size distribution/concentration
- Chlorophyll a (PAM fluorescence)

The main assessment elements and conclusions of the all the parameters are presented in the table below.

Table 3. Summary of the parameters feasibility to be used as indication of ballast water quality or determination of origin uptake.

Parameter	Robustness	Conclusion
Salinity	Salinity is a stable parameter which can be used to indicate origin of uptake location	Feasible indicative parameter of assessment of uptake origin
Dissolved oxygen	Due to lack of data and variance at uptake site, dissolved oxygen has a low robustness.	Not a feasible indicative parameter
Temperature	The temperature has a low robustness and it is not found suited as an indicative parameter, however, the temperature will still be measured in order to determine salinity.	Monitored
pH	No usable information can be derived to determine the origin of seawater on the basis of pH.	Not a feasible indicative parameter
Turbidity	Water turbidity on location of uptake and expected turbidity on discharge is not possible to adequately compare.	Not a feasible indicative parameter
Chlorophyll *a*	Useful to assess presence of viable phytoplankton	Feasible indicative parameter for insufficient treatment
Particle size distribution	Useful to address insufficient treatment	Feasible indicative parameter for insufficient treatment

4 Effect on parameters from ballast water treatment systems

The filter, hydrocyclone, and flocculation treatment technologies are assessed hereunder with regard to influence on the proposed indicative parameters. Data on level of influences for salinity and dissolved oxygen are presented in Appendix 3. The particle size distribution is further assessed with regards to particle concentration. The robustness of the parameters is assessed on the basis of a number of BWMS that holds final approval. The list of BW treatment assessed can be found in Appendix 4.

4.1 Separation technologies

4.1.1 Filters and hydrocyclone

The majority of the treatment systems utilize a process where solids are separated from the liquid phase. Two basic separation principles exists; filter based method such as a mesh, wedge wire or disks and centrifugal separation i.e. hydrocyclone technology. Selected separation technologies are presented in the figures below.

Figure 12. Disk filtration (Picture: Hyde Guardian using disk from Arkal filtration systems.
(Source: hydemarine.com)

Figure 13. Wedge wire candle filter (Bollfilter)

(Source: Bollfilter)

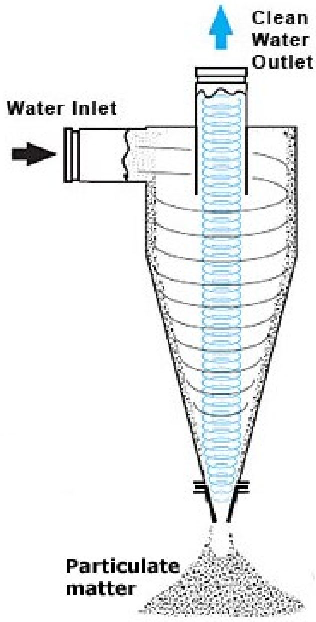


Figure 14. Hydrocyclone technology.

(Source: Modified from waterrenewaltech.com)

There are several filter-based technologies available, which all works by holding back particles of a certain size. The choice of filtration materials, like e.g. stainless steel, polypropylene or nylon and the specific functional layout influences the efficiency of the technology. The smaller the filter dimension the larger the pressure build up resulting in need of more regularly back flush to ensure continuous high flux over the filter.

The choice of filter size is thus a balance between size separation efficiency, flux and energy consumption. The typical particle size cut off value is approximately 50 μm. In Table 4 are a number of filters commonly used in ballast water treatment systems presented. To obtain a cut off of particles of at least 50 μm, filter pore sizes from 30 μm are applied. In general, the smaller the nominal filter size, the more efficient the reduction in particles above 50μm.

Table 4. Filter and hydrocyclone efficiencies of a selection of filters applied in BWMS[21]

Producer	Technology	Nominal size (μm)	Efficiency (%)	Particle load /m^3	Particles after filtration /m^3	Efficiency (%)	Particle load /mL	Particles after filtration /m^3
			> 50 μm			10< X < 50 μm		
Filtersafe	-	40	98.0000	1000000	20000	37	10000	6300
Bollfilter	Wire mesh	30-40	99.9988	1000000	12	50	10000	5000
Bollfilter	Wire mesh	40	99.8222	1000000	1778	50	10000	5000
Bollfilter	Wire wedge	50	74.3260	1000000	256740	50	10000	5000
Arkal	Spin Disc	-	80	-	-	-	-	-
			> 20μm			10 < 20 μm		
-	Hydrocyclone	-	100	-	0	80	-	-

The reduction in particles is, apart from the differences seen between filter types and manufacturer, also relative to the amount of particles suspended in the water upstream from the filter. It is therefore not possible directly to quantify the particle size distribution and particle concentration after filtration without knowing the amount and size distribution beforehand. This makes it critical to have a high removal rate, and as can be seen in Table 4, only the 30-40 μm wire mesh is close to the compliance levels.

The other basic principle, the hydrocyclone, uses centrifugal force to separate particles from the liquid phase by pushing sediments and other organisms to the outer portion of an intake pipe. The effectiveness of the separation depends upon the difference in density of the particle and the surrounding water, particle size, speed of rotation and residence time. The hydrocyclone used in ballast water systems is reported to hold back all particles above 20 μm and in addition it also lowers the particle concentration of high-density particles and particles in the size range 10-20μm considerably.

In conclusion, there is no affect on salinity, pH and temperature when using a filtration or hydrocyclone technology, but relative high influence with a decrease in turbidity, chlorophyll *a* species and change in both particle size distribution and concentration.

4.1.2 Coagulation and flocculation

Another methodology to target particles and organisms is to ad a magnetic coagulant to form larger agglomerate called flocs. The flocs can then be removed by a magnetic separation module. Two other salts are used; poly aluminium chloride (PAC) in concentrations of 5 mg/L and poly acrylamide sodium acrylate (PASA) in 1 mg/L concentration. When the technology is sued in connection with an additional filtration unit (apart from the magnetic separation) removal efficiency of 98% of suspended solids has

[21] The exact filter type for Bollfilter technologies are known by Litehauz, however, the information is confidential and not presented here.

been reported.

In conclusion, there is no notable affect in salinity as the raise in conductivity from the charged reagents added are a factor 7,000 lower than that of marine water. There is, however, a considerable effect on all the particle-based parameters.

4.2 Physical disinfection

4.2.1 Cavitation and sonic treatment

Both cavitation and sonic treatment processes disinfects through collapse of micro bubbles at the surface of the microorganism, which leads to a disruption of the cell wall. The process fragments cell colonies rendering more organisms available for further disinfection processes. Some cavitation systems additionally apply a shearing force to disrupt cell membranes, a force that arises when the ballast water is forced through a narrow passage such as a venturi tube.

Both the cavitation and ultra sonic processes have no influence on the salinity, however, they will have an influence on particle based parameters; chlorophyll *a*, turbidity and particle size distribution/concentration. The process results in an increase in the low size range concentrations and a decrease in number of larger particles.

4.2.2 Plasma

The plasma technology works by applying high voltage and current between two electrodes in a reactor to create an ionized high-energy plasma arc. The energy field causes a rapid rise in pressure, temperature and density flow and generates a pressure shockwave killing organisms either by damaging cell membranes or by micro-eddies created inside the cell. The process additionally generates hydroxyl radicals, UV-radiation and electric fields, which aids the disinfection process.

The plasma technology has no influence on the salinity. The damaged cell membranes will, however, have an influence on chlorophyll *a*, turbidity and particle size distribution/concentration with an increase in the low range size concentration to fragmentation of organisms.

4.2.3 Ultraviolet irradiation

The treatment of ballast water by ultraviolet irradiation (UV) is typically done wavelengths and intensities, however the exact range and intensity depends on the particular system. It is effective against a wide range of microorganisms, but relies on good UV transmission through the water. To provide greater oxidative power some UV systems are enhanced by combining reagents such as ozone, hydrogen peroxide and titanium dioxide or by the use of plasma technology.

The UV technology has no influence on the salinity or particle size distribution/concentration. The chlorophyll generating species is expected to die, however, it is possible to measure chlorophyll *a* some time after the UV disinfection is applied. The length of time after treatment where chlorophyll *a* can be found is dependent on e.g. temperature and species and can last from only a couple of hours to several days[22].

4.2.4 Gas super-saturation / oxygen stripping

The gas super-saturation technology strips the ballast water from oxygen with an inert gas, typically nitrogen. When the inert gas is injected the ballast water is supersaturating and the naturally dissolved

[22] The information has been identified regarding the length of time chlorophyll *a* can be measured after killing the chlorophyll *a* producing organism is based on interview with experts from DHI.

oxygen is released from the water column, leaving the ballast water in a hypoxic condition where organisms dependent on oxygen for their survival cannot survive under these conditions.

The technology has no influence on salinity, turbidity, and particle distribution/particle concentration.

4.3 Chemical disinfection

Chemical disinfection comprise a range of technologies, hereunder:

- Ozonation
- Electrochlorination
- Chlorine dioxide / chlorination
- Biocides

4.3.1 Ozonation

Ozone is a strong oxidizing agent, which reacts in water containing bromide ions (Br^-) to oxidize Br^- to form HOBr/OBr (hypobromous acid) and bromate ions, The treatment technologies that use ozone generates the active substance in situ and no chemicals are stored on board.

The use of ozone have no influence on salinity, turbidity, particle size distribution or particle concentration, however the majority of the chlorophyll *a* generating species are expected to die and no or very low levels of fluorescence is expected.

4.3.2 Electrochlorination

The electrochlorination technologies utilizes electrolysis by applying a direct current between an anode and a cathode to generate free hydroxyl- and oxygen radicals and through generation of hypochlorous acid acts as disinfectants. The treatment technologies that use electrochlorination generate the active substance in situ and no chemicals are stored on board and

Electrochlorination has no influence salinity, turbidity, particle size distribution or particle concentration, however the majority of the chlorophyll *a* generating species are expected to die and no or low fluorescence is thus expected.

4.3.3 Chlorine dioxide

The disinfection process can also work by administering chlorine dioxide or chlorinate directly. These technologies do not differ in ways of disinfection from electrochlorination although less formation of corrosive species is reported.

Adding chlorine dioxide as disinfection agent has only marginal influence (less than 1% on salinity) and the change is therefore negligible as the uncertainties associated with natural variations are considerably higher. No change is seen in turbidity, particle size distribution or particle concentration, however the majority of the chlorophyll *a* generating species are expected to die and no or low fluorescence is consequently expected.

4.3.4 Biocides

Two biocides are also used for chemical disinfection; Seakleen® and Peraclean® Ocean,. Seakleen® is a quinone-based chemical, which utilizes the biocidal effect from vitamin K to disinfect the ballast water. Peraclean® Ocean is an oxidizing agent based on peracetic acid, hydrogen peroxide and acetic acid.

The biocides applied in ballast water treatment have only a marginal influence on the indicative parameters. The change seen in salinity is less than 1% and thus considerably less than the uncertainty connected to natural variances. Moreover, biocides have no influence on turbidity, particle size distribution or particle concentration. Only a decrease in fluorescence is expected, as the majority of the chlorophyll *a* generating species will be killed.

4.4 Neutralization

Some of the treatment technologies that have residual TRO present in the ballast water after treatment apply a neutralization process in order to decrease TRO concentration to the IMO requirement level of 0.2 mg/L (as Cl_2). The neutralization process is in general conducted immediate prior to discharge.

Neutralization agents used are:

- Sodium thiosulfate
- Sodium bisulfite
- Sodium sulfite

The neutralization agent is closely dependent on the level of residual TRO in the treated ballast water and a maximum of 15 mg/L is found in the systems assessed. Hence the contribution of ions is a factor 1000 lower than that the salinity of brackish water and the neutralization process will have no measurable influence on the salinity. The process also has no influence on the particle-based parameters or chlorophyll *a*.

4.5 Summary of parameter feasibility

The assessment on the influence of the BW treatment on the indicative parameters shows that there is a correlation between the treatment applied and the potential changes for the parameters salinity, particle distribution/concentration and chlorophyll *a*. As the changes can be quantified or qualified the parameters are still considered feasible to be used for indicative analysis.

Table 5. Summary

	Filters	Hydrocyclone	Coagulation/ flocculation	Cavitation/ultra sonic	Plasma	Ultraviolet irradiation	Gas super-saturation / oxygen stripping	Ozone	Electrochlorination	chlorine dioxide	Biocide	Neutralization
Salinity	No change	No change	No change	No change	No change	No change	No change	No change	No change	No change	No change	No change
pH	No change	No change										
Temperature	No change	No change	No change					No change	No change	No change	No change	No change
Turbidity	Decrease	Decrease	Decrease	Change in turbidity is expected	Change in turbidity is expected.	No change	No change	No change	No change	No change	No change	No change
Chlorophyll *a*	Decrease	Decrease	Decrease	All chlorophyll generating species are expected to die.	All chlorophyll generating species are expected to die.	All chlorophyll generating species are expected to die.	All chlorophyll generating species are expected to die..		The majority of the chlorophyll *a* generating species are expected to die	The majority of the chlorophyll *a* generating species are expected to die	The majority of the chlorophyll *a* generating species are expected to die	No change
Particle size distribution	Performance is dependant on type of filter Theoretical cut off value are 50 µm	Theoretical cut off value is 20 µm	n.a.	General lowering of particles sizes.	General lowering of particles sizes.	No change	No change	No change	No change	No change	No change	No change
Particle concentration	General decrease above filter cut	General decrease above	Decrease of suspended	Increase in low range size	Increase in low range size	No change	No change	No change	No change	No change	No change	No change

	off value of 99.9%. 50% decrease in particle size range 10 to 50 μm.	filter cut off value is 100%. Approximately 80% decrease in particle size range 10 to 20 μm, with highest reductions in high density particles m.	solids of 98%.	concentration and a decrease in high range size concentration.	concentration and a decrease in high range size concentration.							

The robustness of all seven indicative assessment parameters with regards to robustness was assessed in chapter 3, which lead to an exclusion of the parameters; temperature, dissolved oxygen, and pH due to influence from natural variances, which made them unfeasible for indicative analysis.

A summary of the findings in chapter 3 and 4 are presented in Table 6. The terms used are explained in the following: "Variable" are used for water parameters before uptake and indicates that they change over time due to natural influences. Consequently, the values of these parameters are difficult determine for uptake location. "Stable" are used for parameters that due not change over time. "Change" is apparent and used for parameters that change over time. The arrow inserted after indicates the direction of the value. "Zero" is used for viability

Table 6. Qualification of parameter robustness, port dynamics and influence from BWMS and storage.

Change by step / Parameter	General aquatic behaviour	Water port dynamics	BW No treatment	BW treatment	BW Storage	BW Neutralisation
Salinity	Stable	Variable in estuarine and riverine over time Stable in seawater	Stable	Stable	Stable	Stable
Dissolved oxygen	Dynamic atmospheric eq. at surface	Variable	Change ↓	Change↓↑	Change ↓	Change ↓
pH	Dynamic Buffer	Stable	Stable	Change↓↑	Stable	Change
Temperature	Dynamic	Variable	Stable	Change	Change ↓↑	Stable
Turbidity	Dynamic	Variable	Change ↓	Change ↓	Change ↓	Stable
Chlorophyll *a*	Dynamic	Variable	Stable	Change ↓	<10 /100mL	<10 /100mL
10< Particles <50	Dynamic	Variable	Stable	Change ↓	Stable	Stable
Particles > 50	Dynamic	Variable	Stable	Change ↓	Stable	Stable

5 Parameter algorithms for decision making

The three parameters found feasible to be used in an indicative analysis are:

1. Salinity
2. Particle size distribution/concentration
3. Chlorophyll *a*

The salinity may be used to verify or dismiss uptake locations as entered in the BW record book, the particle distribution and concentration as an indication of filter performance and live chlorophyll *a* response as an indication of live phytoplankton. The basic use of the parameters is presented here as decision trees together with appertaining algorithms.

The algorithms are included in a BWMS Performance kit developed in Excel and exemplified in the Example boxes in each of the following sections.

5.1 Salinity

Salinity is relevant for assessment of D-1 compliance or to establish if there is gross exceedance of expected salinity based on uptake location. The decision tree of salinity is comprised of three basic elements: the uptake location(s) entered in the BWRB, the measured salinity in the tank, and the expected salinity range at the uptake location. The two first elements are given by information obtained onboard the ship. The third element, information on the expected salinity range, with which the measured salinity is compared to, is obtained e.g. from satellite data as described in paragraph 3.1. The basic decision tree for salinity is shown in Figure 15.

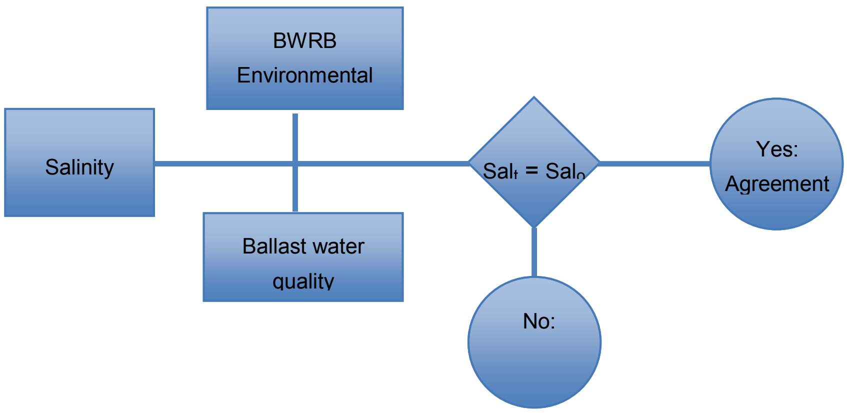


Figure 15. Decision tree for salinity where Sal_t is measured salinity in tank and Sal_o is salinity at uptake location.

The algorithm determines the degree of agreement between measured salinity and expected salinity based on uptake location entered in the BWRB. The resulting output is given as a positive or negative; "salinity within range" or "salinity outside range" together with a quantification (in percentage) of the deviation, Dev_{sal}, from the upper and lower range limits. Obviously this methodology only works for uptake locations where ranges of salinity are defined. The deviation is given by the equation:

$$Dev_{sal} = (Sal_{max,min} - Sal_{measured})/Sal_{max,min}$$

The GloBallast Monograph data shows that the higher the salinity in uptake location, the lower the standard deviation and hence a more reliable comparison of measured and expected salinity. In the below example the GloBallast Monograph data are used to illustrate the methodology for a scenario with only one uptake location.[23]

Example box 1. BW uptake: port of Fredericia

1. The port code for Fredericia is entered in the *uptake port code* field:

Uptake port code	DKFRC

2. The salinity of the BW tank is measured

In situ measurements	
Salinity (psu)	28

3. The measured salinity is checked against database

Input check against database			
Min psu	**Max psu**	**Outside min. range**	**Outside max. range**
18.0	24.0	NO	YES

4. The result is assessed applying the model of calculation:

$$Dev_{sal} = (24\ psu - 28\ psu)/24\ psu = 0.167 = 16.7\%$$

Assessment		
Display	**Deviation from expected**	**Estimated uncertainty**
Salinity outside expected range	16.7%	5%

The example shows that the measured salinity of 28 psu is above max psu range for the specific port. The calculated value of deviation is 16.7 % above maximum. The estimated uncertainty covers sampling- analysis- and instrument uncertainty.

5.2 Particle size distribution and concentration

The particle size distribution measurement relates to the D-2 size categories of 10-50 µm and 50µm and above. Dependent on the specific separation technology applied, removal efficiencies of particles of 50µm and above and between 10-50 µm are between 80-100% and 50% respectively. As the altered particle distribution after treatment is relative to the particle load in the ballast water, the optimal scenario would comprise knowledge of the specific particle concentrations of the uptake location. However, only data on turbidity can be obtained on a day-to-day basis (remote sensing by satellite), and this is insufficient to determine the particle size distribution.

[23] Currently, data for ports do not allow modeling of time and space defined salinities or calculation of 95% confidence intervals

The sensible approach would be to self-monitor onboard before and after treatment to obtain real time separation performance and such results could be made available for the PSC. As this methodology is not in place an other approach is to create a benchmark for a worst-case water quality scenario which can act as a default for initial particle concentration for all cases assessed. The benchmark is in lack of available data and for demonstration purposes based on the challenged water requirements in land-based testing (IMO guideline G8 for approval of ballast water management system). The water before treatment is therefore as default assumed to contain 10^6 particles greater than or equal to 50 µm per m^3 and 10^4 particles greater than or equal to 10 µm and less than 50 µm per mL.

The decision tree for particle size distribution and concentration comprise two basic elements: the measurement of the particle size distribution/concentration after treatment, and the separation efficiency based on the actual type of separation technology applied in the BW treatment system. The algorithm basically compares the measured particle size distribution and concentration with the expected distribution and concentration after filtering. For obvious reasons, it is not possible to apply this methodology for BWT systems where no separation unit is applied. For systems using venturi or shearing force after separation, the altered size distribution can be taken into account.

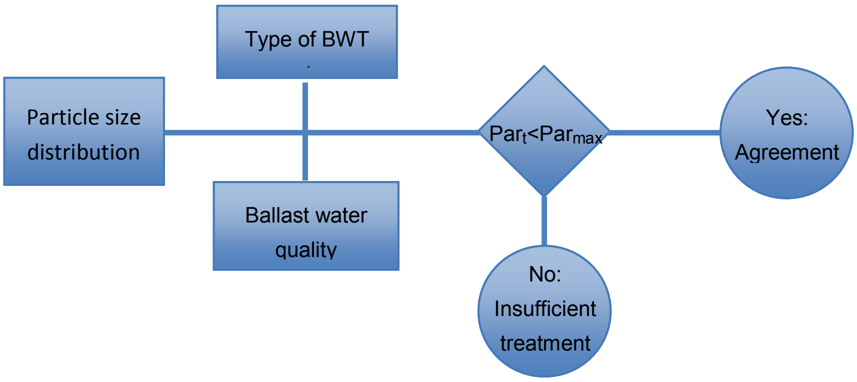


Figure 16. Decision tree for particle size distribution where Par_t is measured particle size distribution in tank, and Par_{max} is the maximum load expected after reduction, which is dependent on type of BWT system applied.

In the currently approved BWMS, the efficiency of the filter-based system is mostly monitored on the basis of backpressure on intake side of the filter. As particles accumulate on the intake side during operation the pressure rises leading to a difference in pressure to the other side of the filter. This triggers an automatic back flush, which cleans the filter. This approach may not detect a torn or perforated filter as the pressure build up only will be slower and resemble water with little suspension load. As described in section 3.7m the removal efficiencies are quantified for the most common solid-liquid separation technologies and by using this information it would detect a malfunctioning filter not identified by monitoring backpressure. The particle size distribution and particle concentration can therefore act as a useful indicator of how well the solid-liquid separation element of a BWMS performs.

When high amounts of particles are found in the ballast water at discharge[24], it could be indication of three things:

1. That the solid-liquid separation element of the BWMS is not working to standard.
2. That ballast water intake has been conducted in an area of high turbidity. High turbidity areas are typically river mouths or estuaries with a large runoff from the land, which carries suspended organic and inorganic materials to the sea. A higher number of bacteria are often found in water of high turbidity than in non-turbid water. By using a high load benchmark, the factors of regrowth and potential presence of bacteria is taken into account.
3. That regrowth of e.g. phytoplankton has taken place. This could be the case when the disinfection

[24] Only systems applying a separation unit

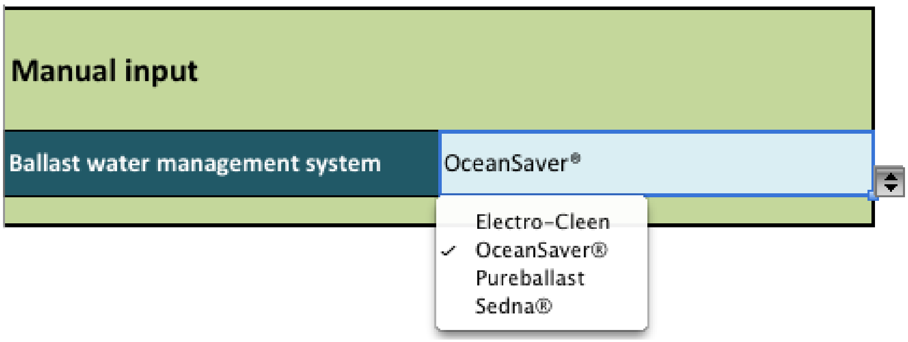
step is not working to standard, potentially leading to higher levels of particles in the size range 10-50 µm

The primary uncertainty of the algorithm is the lack of original particle load giving a result that is very conservative. In addition, two other potential scenarios add to the uncertainty of using particle size distribution. In scenario one suspended particles not withheld by the filtration unit might settle and disappear out of the water column, leaving the impression that the separation is more efficient than is the case. The speed of settling in water follows Stokes law and is dependent on particle density and size relative to the salinity of the ballast water. In the second scenario previously settled particles might re-enter the water phase due to ship movements. Without before and after monitoring data these two additional scenarios are not included in the algorithm, as the uncertainty associated with the constructed benchmark is considerably higher than the uncertainty connected to settling and re-entering.

An example of the filter performance assessment using the algorithm can be seen in
Example box 2.

Example box 2. Filter performance assessment

1. The applied BWMS is selected from the dropdown menu in the spreadsheet and the underlying database identifies the current filter type used for the chosen application (see bullet three).



2. The measured particle size distribution data is compiled into the two size ranges 10-50µm and >50µm and concentration is calculated.

In situ measurements	
Particle concentration > 50µm /m³	**Particle concentration 10<x<50 /mL**
800	6000

3. The number of particles, which can be expected at applied filter efficiency at max load, are listed and compared to the calculated particle concentrations. Results are given as whether the particle concentrations are within the max limit of expected value or not.

Evaluation of input parameters against database		
Filter type	**Max number of particles > 50 µm**	**Above expect value for >50um**
Bollilter	1000	NO
	Max number of particles 10 ≤ x ≤ 50	**Above expected value for 10<x<50**
	500	YES

4. Deviations are calculated by comparing measured and maximum particles and are published as factors, thus positive values will mean exceeding the filter specs and negative values that value are within the expected range. The values are not referring to D-2 standards – only to expected filter performance.

Evaluation of input parameters against database	
Display > 50	**Deviation from expected**
Filter not performing to standard	-10%
Display 10 < x < 50	**Deviation from expected**
Filter performing to standard	-20%

5.3 PAM measurements.

The PAM measurement is based on detection of the in-situ fluorescence of chlorophyll *a* from live organisms (photosystem II), as described in section 3.6. The photosynthetic activity is related to the size fraction between 10 and 50 µm where the vast majority of phytoplankton is found.

With the D-2 requirements in mind, it would be favourable to be able to estimate when more than 10 viable phytoplankton per mL is encountered; however, due to detection limits of the PAM instrument the uncertainty makes that unfeasible. A higher semi-quantitative limit of 20 viable phytoplankton suggested by Gollasch and David (2010) is used for the basic decision tree and algorithm.

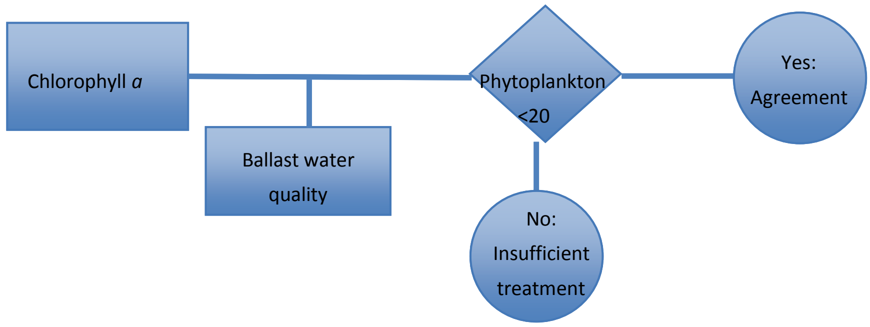


Figure 17. Decision three for PAM fluorescent measurement of photosynthetic activity.

The algorithm is based on the three resulting variables given by the PAM fluorescence instrument; the biomass (f0) and viability (fv/fm).

$$f_0 > 20 \wedge fv/fm > 0.3 \Rightarrow \text{number of viable phytoplankton per mL} > 20$$

Example box 3. Calculation of whether the viable number of phytoplankton is over 20 or not.

1. The samples are measured with a PAM fluorescence instrument resulting in biomass (f0) and viability (fv/fm) output.

In situ measurements		
Sample	**f0**	**fv/fm**
1	250	0.538

2. The resulting output is assessed applying the model of calculation:

$$\text{When } f0 > 20 \wedge fv/fm > 0.3 \Rightarrow \text{number of phytoplankton} > 20$$

Calculating number of viable phytoplankton			
Sample	Viable organism detected	**Display**	**Deviation**
1	YES	Viable organism detected	1150%

PAM fluorescence can also be combined with Particle size distribution though the particle concentration is a “blind” measurement and do not differentiate between live/dead organisms and other particles. If all particles are considered to be organisms the particle concentrations can act as an enumeration of possible number of organisms in the respective size categories. This is a conservative position, but considering the fact that inorganic particles to a certain degree will settle over time and active phytoplankton will stay suspended this is considered a navigable approach for monitoring on discharge. To obtain a clear indication that the BWMS do not operate according to the Ballast Water Management Plan and accommodating a potential degree other particulate matter an exceedance of 10 times the D-2 regulation is used (>100 viable organisms).

The selection of data points from PAM measurements and viable phytoplankton (Gollasch and David, 2010) presented in Figure 18, indicates that in order to have more than 100 organisms/mL the product of f0 and fv/fm must have a value 75. This assumption applies only for measurement where f0 > 20 and fv/fm is above 0.300.

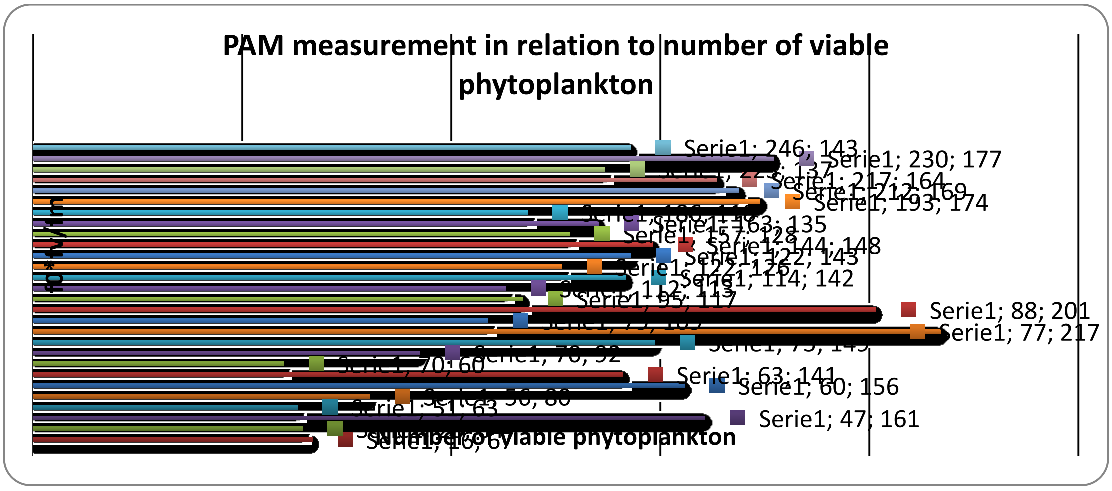


Figure 18. The PAM measurement output seen in relation to number of viable phytoplankton. Data from Gollasch and David (2010).

The basic decision tree of the combined PAM and particle size distribution measurement can be seen in Figure 19 and an example of the algorithm is presented in Example box 4. When the two measuring techniques PAM and particle size distribution are combined a more rugged indication analysis to establish a clear D-2 exceedance is obtained.

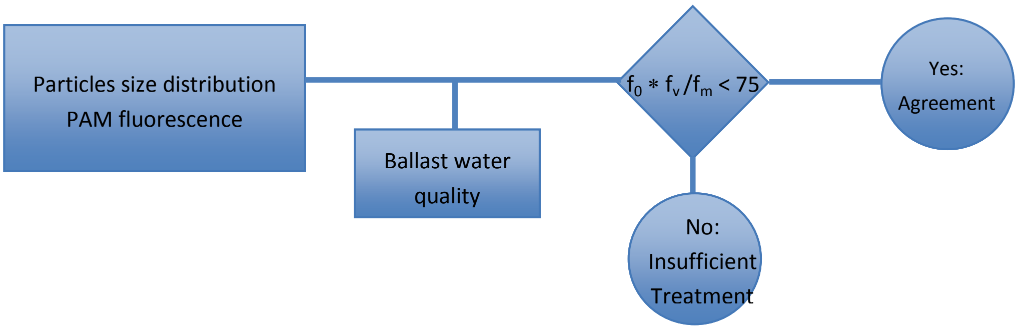


Figure 19. Decision tree for combined particle size distribution and PAM fluorescent measurement. F_0 is bulk biomass and f_v/f_m is viability.

Example box 4. PAM fluorescence and particle size distribution measurements combined.

1. The product of the PAM-fluorescence measurement output f0 and fv/fm is calculated and compared to the number of particles measured (in the size category 10-50 µm) above the maximum expected. When the product of PAM results are over 75 and the number of particles exceeding the expected value are above 100, it is assumed that there is above 100 viable phytoplankton per mL in the ballast water.

Evaluation of PAM and separation results				
$f_0 * f_v/f_m$	No. particles above expected (10-50um)	$f_0 * f_v/f_m > 75$	Deviation (>75)	Display
134.5	1000	YES	34.5%	Above 100 viable phytoplankton/mL

5.4 Final results

The results are envisaged presented in a combined screen that gives an easy overview over the assessment results and deviation from the boundary values (see Figure 20). The results can then act as a supportive foundation on which to decide if a detailed analysis should be conducted.

SALINITY	Salinity outside expected range	16.7%
PHYTOPLANKTON	Viable organisms detected	1150.0%
SEPARATION PERFORMANCE (>50µm)	Filter performing to standard	-20.0%
SEPARATION PERFORMANCE (10 < x < 50µm)	Filter not performing to standard	20.0%
COMBINED PAM - SEPARATION PERFORMANCE	Phytoplankton > 100/mL	34.5%

Figure 20. Result screen with deviations from boundary values.

6 Technology overview

A number of indicative methods with regards to D-2 compliance requirements have been debated in the IMO and the following types of methods are currently on the agenda[25]:

1. Indication for presence of organisms
   a. deoxyribonucleic acid (DNA)
   b. ribonucleic acid (RNA), and
   c. oxygen production
2. Indication of viability
   a. adenosine triphosphate (ATP),
   b. chlorophyll *a* (algae bulk biomass), and
   c. staining for esterase activity with e.g. calcein AM (acetomethoxy derivate of calcein) or fluorescein diacetate (FDA)
3. Physical and automatic counting methods
   a. stereomicroscopy (for organisms > 50µm), and

[25] In BLG 15/5/4, BLG 16/4 and EMSA, 2010b.

b. flow cytometry combined with digital imaging

Three indicative analysis methods relating to the D-1 criteria are presented in BLG 15/5/4. These are visual counts or stereomicroscopy of organisms >50 μm, dissolved inorganic nutrients and colored dissolved organic matter (CDOM).

With regards to measuring methodology, four new instruments which makes use of both previously covered technologies and new technologies within the field of indicative analysis of ballast water has been identified during the research for this study. These methodologies are briefly introduced:

1. Hach Rapid Ballast Water Compliance Test Kit (Hach)
2. BallastCAM® (Fluid imaging technologies)
3. BD Accuri® C6 Flow Cytometer (BD biosciences)
4. Spectro::lyser (S::CAN)

Common for Hach and BallastCAM is that they have been introduced as technologies to conduct indicative analysis on site to assess whether the tested ballast water displays gross exceedance of D-2 requirements. BD Accuri and the Spectro::lyser has not specifically been developed with ballast water testing in mind are presently used in enumeration of cells/bacteria and monitoring of waste water respectively. The four applications will briefly be described in the following sections.

6.1 Fluorescein diacetate - Hach Rapid Ballast Water Compliance Test Kit

Recently the Hach Rapid Ballast Water Compliance Test Kit was introduced, which offers a direct indicative analysis to determine gross exceedance of D-2 requirements with regards to viable biomass. The technology is based on recent work by Welschmeyer and Maurer (2011) and makes use of fluorescein diacetate (FDA) for cell-specific determination of viability. The test kit is sensitive to all living organisms in the 10 μm to 50 μm size class and gives a result within an hour. The kit is reportedly developed to be handled by non-technical personnel, e.g. at PSC.

FDA is a non-fluorescent reaction compound, which is hydrolyzed to the fluorescent fluorescein by biological enzyme activity, although some non-biological conversion has been found to occur. Neither FDA nor the reaction product fluorescein are chemically bound within the cell and diffuse freely through cell membranes. As a consequence the FDA method has been subject to criticism because 1) the efflux of fluorescein results in rapid fading of a fluorescent cellular signature making the need of a fast numerical analysis paramount in the success of the method and 2) the non-biological conversion of FDA give rise to false positives.

The claim by Hach for their newly developed FDA method is that they have solved these issues and developed a reagent buffer mixture, which prevents non-biological conversion of FDA and identified a linear correlation between the amount of fluorescein in the extra-cellular fluid and the bulk biomass. When applying simple fluorometric analysis of fluorescein in the extra-cellular fluid the bulk biomass can be quantified.

The Hach test kit is developed for event such as PSC or self-monitoring after treatment, and is dependent on mechanisms to obtain representative samples. Reportedly, the cost of reagents is high.

6.2 Flow cytometry - BallastCAM®

The use of flow cytometry has previously been addressed at BLG 15 with the FlowCAM from Fluid Imaging Technologies. As an instrument that requires some expertise in handling the manufacturer has developed a 2nd generation version recently, the BallastCam®, which offers an easier manageable way to conduct indicative analysis with regard to D-2 parameters. The technology interrelates two methodologies, total particle concentration and an image-based approach for determining treatment efficacy on organism.

The particle count uses an in-build feature, which can identify selective types of particles based upon their shape and aspect ratio (width/length) scatterplot in the size range 3-2000µm. The BallastCam has a flowrate of 20mL/min and a 200 µm x 2000 µm flow cell. The sizes of the samples used for the BallastCam are between 1-12 mL. The samples are sucked through the flow cell where the imaging is conducted and a full sample sequence and subsequent software analysis is conducted in less than 10 minutes.

The particle concentration is a "stand alone" parameter in the sense that it indicates the efficacy of the solid liquid separation part of the BW treatment, but it provides no indication of viability. This is addressed by the imaging part of instrument, which works together with a large database with photos of organisms. To determine viability, the BallastCam® uses "*gray-scale*" attributes such as intensity, sigma intensity (contrast) and apparent blue instead of staining to demonstrate a rise in organism transparency after treatment. The more transparent the organisms are, the less viable the organisms are considered.

Figure 21. BallastCam© from Fluid Imaging Technologies, developed to conduct indicative sampling and analysis onboard the ship.

The combination of flow cytometry and digital imaging have the disadvantage that the high complexity of constituents in the water leads to small sample sizes to be able to generate species specific results with low uncertainty. Another issue is the maximum particle density, which for high-density waters will entail dilution of samples prior to running the BallastCam©.

6.3 BD Accuri® C6 Flow Cytometer (BD biosciences)

The BD Accuri® C6 is a portable flow cytometer comprising three parameters to be used in an indicative analysis; Flow cytometry, chlorophyll *a* determination and particle size distribution.

The instrument can be used to detect particles, bacteria, algae, virus, chlorophyll, as well as various blood cells and has an optimum detection capability around 5 – 40 µm, a lower limit of 0.5 µm when special considerations are taken. Furthermore, it is possible to distinguish between dead and alive cells using staining dyes. The system can handle more than 10,000 events per second with concentrations of $5x10^6$ events/mL sample sizes of minimum of 50 µL are needed.

The BD Accuri methodology does, as such, not contribute with new technologies but is a combination of technologies already described in present report.

6.4 Ultraviolet-visible spectrometry

The various indicative analysis methods requires different approaches for the respective organism groups in focus (bacteria, >10 µm and <50 µm (phytoplankton) and, >50 µm (zooplankton) with regards to D-2 requirements. Consequently one method might not indicate exceedance of the D-2 requirements for one type of organism while the level at the same time might too high for another. The full potential exceedance will only show if one or several methods covering all organism groups are applied. Any indicative methodology, which accommodates more than one organism group is therefore of interest.

One technology, which holds the potential to address both concentration and size distribution of particles between 10 and 50 µm and above 50 µm, and at the same time indicate viability is ultraviolet-visible (UV-Vis) spectrometry. The viability can be qualified in form of the level of blue sheen after the influence of a treatment step, which makes the organisms more transparent. The optical instruments existing today are applied in many types of in water quality measurement applications from monitoring drinking water to wastewater treatment facilities. Traditionally, optical instruments measures one or two wavelengths in the visible or UV range of the spectrum, but lately more advanced instruments has emerged that measure absorbance in the full range of UV and visible light in high resolution. These advanced spectrometer probes are able to exploit that chromophores absorb radiation at a well-defined wavelength and combined with algorithms are able to quantify multiple parameters simultaneously in real time (this would include the Coloured Dissolved Organic Matter, CDOM).

A range of individual parameters can be quantified based on algorithms, see Table 7 for examples, or spectral alarms can be set up based on expected spectral absorbance fingerprints. The optical path length can be adjusted from 2-100 mm to accommodate different water qualities from ultra pure waters (DOC > 10 µg/L) up to concentrated wastewaters with a COD of several 1000 mg/L.

Table 7. Based on spectrum fingerprint and algorithms, quantitative information on the a range of parameters can be deducted e.g:

Parameters quantified				
TSS	COD	DOC	BOD	TOC
Turbidity	AOC	Colour	H_2S	O_3

The UV-Vis spectrometry is a rugged methodology, which is used in a wide variety of applications today to establish water quality or identify specific substances or organisms in a fluid. Though only limited information on the how the absorbance spectrum for compliant and non-compliant ballast water exists at this point, it is estimated that the technique is promising and more in depth information should be obtained.

7 Conclusions

This project has desk-top tested a series of rapid measurable or readily available parameters for their feasibility as indicators of ballast water conditions. Amongst the assessed simple parameters were salinity, dissolved oxygen, turbidity, temperature and pH and as a bit more complicated parameters were chlorophyll *a* and particle size distribution.

Three basic parameters have been selected as viable key parameters for the rapid ballast water assessment system:

- salinity (for basic verification of the Ballast Water Record Book),
- particle size distribution (for use as an indictor of organisms, i.e. system malfunction), and
- phytoplankton chlorophyll *a* (live organism indication through active photosystem II measurements)

These indicative parameters will assist the port state control in deciding whether the ship is free to discharge ballast water or whether "clear grounds" exist to continue with detailed analysis and stop the ship from emptying its ballast water tanks.

The parameters have been included in an example of a tool, which can be used by port state control or ship owners for monitoring ballast water conditions. Strong options exist for using existing databases of meteorological data in combination with position data to develop indicators for port (uptake) water conditions for several parameters.

Technology is available that allows particle size distribution and other robust and simple parameters to be added and used as a self-monitoring system that can accurately measure "before and after" conditions related specifically to the installed system. Preliminary tests have been carried out to substantiate this (found in confidential annex).

Further developments of the project may be along one or both of two routes:

3. Develop port state control tool, in particular the "port conditions" on-line database access.
4. Develop the self-monitoring device, algorithms and on-line access further through test in the field and in the laboratory.

In terms of commercial potential option 2 would be the first choice for a continued development project. There is a considerable synergy for option 1 in developing the on-line application for option 2.

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