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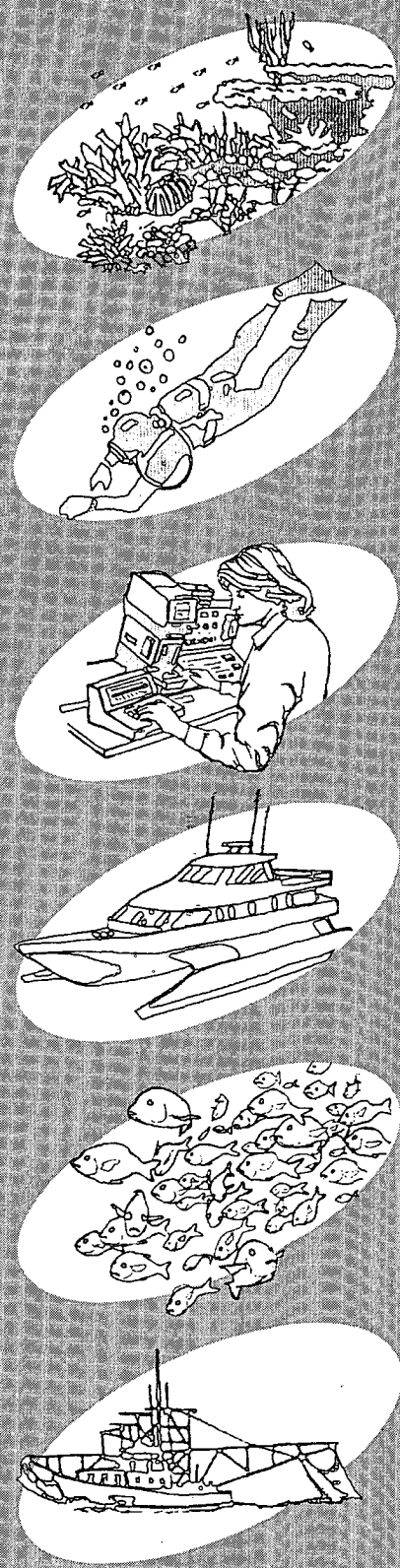
CRC REEF RESEARCH

TECHNICAL REPORT



CHEMICAL AND PHYSICAL CHARACTERISTICS OF BALLAST WATER: IMPLICATIONS FOR TREATMENT PROCESSES AND SAMPLING METHODS

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CRC Reef Research Centre

PORTS CORPORATION QUEENSLAND

Project Funded by the CRC Reef Research Centre
In association with the Ports Corporation Queensland

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CHEMICAL AND PHYSICAL CHARACTERISTICS OF BALLAST WATER: IMPLICATIONS FOR TREATMENT PROCESSES AND SAMPLING METHODS

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The centre, established in 1993, undertakes an integral program of applied research and development, training and education, aimed at increasing opportunities for ecologically sustainable development of the Great Barrier Reef and providing an improved scientific basis for reef management and regulatory decision making.

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FOREWORD

The Ports Corporation of Queensland has provided funding, operational support and an industry focus for this research into the very important question of how to minimise the spread of exotic organisms via ships' ballast water. The Corporation believes that it is necessary for ballast water treatment to be rigorously evaluated using the best techniques available, both to determine the treatments that are likely to be successful as well as those that are not. This work by Mr. Oemcke and Prof van Leeuwen at the Cooperative Research Centre for the Ecologically Sustainable Development of the Great Barrier Reef, based in Townsville, Queensland, is among the first research of its kind and has led to a synthesis of important data and the development of new ideas. It provides the shipping and ports industries with high quality, relevant data, which can be used as a basis for proceeding towards the treatment of ballast water in an environmentally responsible and economical manner. Particularly, this report provides insights into the design requirements for ballast water treatment plants and the practical difficulties associated with the exchange of ballast water at sea.

The Ports Corporation of Queensland is operationally focused and does not usually provide financial support for fundamental research but, in this case, takes the view that this strategic research is of substantial long-term benefit and should lead to the further practical development of ballast water treatment systems by other organisations. The Corporation encourages national and international maritime industries to take this work into consideration as they further address ways of reducing the adverse impacts that have occurred, and are still occurring, as a result of ballast water being discharged into ports throughout the world. The Corporation commends the CRC Reef Research Centre for also supporting this research.

Derek Andrews
Chief Executive Officer
Ports Corporation of Queensland

1. SUMMARY

The Ballast Water Treatment project at the CRC Reef Research Centre, funded by the Ports Corporation of Queensland, aims to test technologies or techniques which can be used to remove exotic organisms from ships' ballast water. Techniques currently being examined for their potential to disinfect ballast water are ozonation, ultraviolet irradiation (UV) and filtration. To develop treatment systems for ballast water, it is necessary to understand some of the chemical and physical characteristics of the water to be treated.

The aims of the ballast water sampling program were to:

1. Determine the sizes of solids and organisms present in ballast water and analyse the effectiveness of filtration both as a pretreatment to disinfection and as a disinfectant.
2. Determine if ballast water, as landed after a voyage, had any characteristics which would impact adversely on filtration, UV irradiation or ozonation.
3. Investigate the potential for chemical and physical characterisation of ballast water as a tool to verify that ballast water exchange had been conducted effectively.
4. To develop sampling methods for determining the chemical and physical characteristics of ballast water.

Ballast water samples were taken from a number of vessels entering North Queensland ports during 1995 and 1996. Water, sludge and sediment samples were analysed for a range of physical and chemical characteristics which will affect filtration, UV irradiation and ozonation, and which may be useful for determining if ballast exchange at sea had been conducted.

Filtration may be necessary to reduce suspended solids prior to ozonation or UV irradiation. Only pilot testing can determine if it is necessary or effective. Without flocculation, screens of 20 to 30 μm would probably be necessary. Filters can also be used as a disinfection treatment for some organisms. 50 μm screens could be used as a stand alone treatment to remove zooplankton from ballast water and 20 μm screens should remove dinoflagellate hypnocysts, which are an important species of concern in ballast water. Viruses, bacteria, and many amoebae, protozoans, diatoms and dinoflagellate algae will not be affected by 20 μm screening.

UV irradiation may be limited to shipboard treatment, as the iron levels in ballast discharges may cause iron precipitation on UV lamps if UV is used after vessels deballast. Shipboard UV treatment of ballast water during ballasting, before iron from the ballast tanks contaminates the

ballast water, will be unaffected by iron introduced from the ballast tanks. Shorebased treatment plants, where ballast is treated at the end of a voyage, will require pre-oxidation and clarification prior to UV irradiation. Newer vessels and vessels with good corrosion protection, will not contain such high levels of iron. Ozone is unlikely to be appropriate for ship board treatment of ballast water, due both to the possibility of increased corrosion of ballast tanks and the difficulty of maintaining a disinfection residual in an area high in dissolved iron and areas of sludge and sediment which are high in organic material.

The results of the sampling indicate that at least 14% of vessels which reported ballast exchange at sea had either done so ineffectively or failed to do so. It is possible that up to 57% had exchanged ineffectively, based on a chemical characterisation process, which compares the composition of ballast water with what would be expected from oceanic water. Problems with this type of comparison is re-contamination of the oceanic water by unexchanged sediments and water remaining in ballast tanks, even after the exchange process, and the effect that the presence of iron in some ballast tanks may have on measurements. Additional research is needed to determine the effectiveness of characterisation as a way of monitoring the exchange process.

The method used to sample ballast water, and the sample location have a substantial effect on the measured characteristics of the water collected. Problems with sampling methods and ways to overcome them are described.

2. INTRODUCTION

2.1 Ballast Water

It is estimated that in 1991 there were 121 million tonnes of ballast water discharged into Australian ports as a result of over 4,500 international ship visits (Kerr 1994). This ballast water is carried by ships to ensure that the propeller is kept at an optimum depth when no cargo is carried and to adjust trim and draft to suit prevailing sea and cargo conditions.

Ballast water is recognised internationally as a vector for the translocation of marine species across biogeographical boundaries. Examples include toxic dinoflagellate algae (Hallegraeff & Bolch 1991), macroalga (Ribera 1995), *Vibrio cholerae* (McCarthy & Khambaty 1994) and a range of zooplankton (eg. Carlton 1985). Of the 76 known introduced marine animals and plants in Australia, ballast water is considered a potential vector for around 35% (Richard Martin, Centre for Research on Introduced Marine Pests *pers. comm.*).

Gymnodinium catenatum, a toxic dinoflagellate species introduced to Australia in ships' ballast water, was responsible in 1986, 1987 and 1991 for the closure of shellfisheries in southern Tasmania for periods of up to 6 months (Hallegraeff 1992). In the Great Lakes of North America the zebra mussel, *Dreissena polymorpha*, introduced in ballast water, is estimated to have cost $5 billion by blocking water intakes at power plants, water treatment plants and heavy industry and fouling fishing nets, boat hulls and buoys (Ribera 1995, Lamarre 1991). The Northern Pacific Seastar, *Asterias amurensis*, introduced to Southern Tasmania via ships' ballast, has become a dominant benthic species in the Derwent River estuary, posing a threat to yields in the scallop industry (Sutton & Bruce 1996). Not all introduced species have had such severe impacts, but these and other examples have galvanised concern about ballast water in many countries.

Strategies being investigated for the control of these species introductions include ballast water exchange at sea and several treatment technologies. Locke *et al.* (1993) and Rigby & Hallegraeff (1992*a*,*b*) found that ballast exchange at sea can be used to reduce the risk of exotic species introductions, but not effectively enough for complete control. Several treatment technologies have been experimentally tested (Lloyd's 1995, Bolch & Hallegraeff 1993, Ichikawa *et al.* 1992) resulting in the rejection of a number of treatment alternatives and further research on others. Options currently being researched include ultraviolet irradiation (Jorstad &

Jelmert 1998, this project), ozone (this project), filtration (Cangelosi 1997) and the flushing of hot water from the salt water engine cooling circuit through the ballast tanks (Hallegraeff *et al.* 1997, Rigby 1994).

The aims of the ballast water sampling program were to:

1. Determine the sizes of solids and organisms present in ballast water and analyse the effectiveness of filtration both as a pretreatment to disinfection and as a disinfectant.
2. Determine if ballast water, as landed after a voyage, had any characteristics which would impact adversely on filtration, UV irradiation or ozonation.
3. Investigate the potential for chemical and physical characterisation of ballast water as a tool to verify that ballast water exchange had been conducted effectively.
4. To develop sampling methods for determining the chemical and physical characteristics of ballast water.

2.2 Ballast Treatment

To develop treatment systems for ballast water it is necessary to understand some of the characteristics of the water to be treated. There is very little data available on the chemical and physical characteristics of ballast water with which to make treatment plant design decisions, other than dissolved oxygen, temperature, pH and salinity, as researchers have been primarily focused on organisms (eg. Hay *et al.* 1996, Rigby & Hallegraeff 1994, McCarthy & Khambaty 1994, Locke *et al.* 1993, Rigby, *et al.* 1990, Howarth 1981, Medcof 1975). This lack of adequate physical and chemical data is a constraint to making informed decisions on ballast water treatment (Gutteridge Haskins and Davey 1993, Laughton *et al.* 1992).

2.2.1 Characteristics which will affect ballast water filtration

Prefiltration of ballast water may be necessary prior to biocidal treatment, or as a treatment in its own right. The effectiveness of prefiltration or even the type of prefilter cannot be determined from water quality analysis alone, and pilot testing is required. The filtration experiments currently being conducted in the USA (Cangelosi 1997) may provide some answers in this area.

Turbidity, total suspended solids, particle size distribution and target organism sizes will help to determine both the need for prefiltration prior to biocidal treatment, and the organisms which will be removed by various types of filters.

2.2.2 Characteristics which will affect the UV treatment of ballast water

Grasso *et al.* (1996) listed only UV transmittance (λ=254), suspended solids and target organism concentrations as necessary water quality criteria for the design of UV treatment plants. They also mention the importance of iron and calcium precipitation as a cause of lamp fouling.

The size of the suspended solids is also important for UV treatment, as particles substantially larger than the target organisms will cause shading and large flocs with organisms enmeshed within will protect the organisms from the UV. The interaction between the size of a target organism and the size and nature of suspended solids will determine the importance of the suspended solids, although little information on these interactions is available from the literature.

2.2.3 Characteristics which will affect the ozonation of ballast water

Hoigné (1994) published what is considered to be a minimum set of water quality data to be collected to ensure that results from ozonation experiments can be generalised. The parameters relevant to the ozonation of ballast water are temperature, pH, Alkalinity, dissolved organic carbon (DOC), absorbance (λ=255nm), nitrite, iron(II), manganese(II), bromide, ammonia and turbidity. Table 1 summarises the effect of these properties on ballast water ozonation.

2.2.4 Determining if ballast has been exchanged

Characteristics which could be used to indicate whether vessels had exchanged their ballast at sea in compliance with the Australian Quarantine and Inspection Service voluntary guidelines for the exchange of ballast at sea (Australian Quarantine and Inspection Service 1995) were measured during the sampling program. Oceanic water criteria were defined for salinity, pH, Alkalinity, dissolved organic carbon, total organic carbon, nitrite, nitrate, ammonia, phosphate, chlorophyll *a* and pheophytin from a sample of literature (Dickson & Wheeler 1993, Millero & Sohn 1992, Furnas 1991, Furuya 1990, Legendre *et al.*. 1988, Furnas & Smayda 1987, Le Bouteiller & Herbland 1984, Burton & Liss 1976, Eppley *et al.* 1973, Strickland & Parsons

1972). The above characteristics were all sampled and compared to the oceanic water criteria to determine if effective ballast water exchange had been conducted. Total nitrogen and phosphorus were also sampled, although there is inadequate data in the literature referenced to use them for determining ballast exchange efficiency.

Table 1. Water properties which will affect ballast water ozonation

Parameter	Effect
temperature	• increase in temperature decreases ozone solubility • increase in temperature increases reaction rates with contaminants
pH	• pH above 7.5 increases ozone radical chain decomposition • deprotonation of weak acids which affects their reactions with ozone
Alkalinity	carbonate and bicarbonate scavenge hydroxyl radicals
dissolved organic carbon	• some highly reactive organic material consumes ozone almost instantly • organic material can inhibit or accelerate radical chain decomposition of ozone • formation of by-products
absorbance (λ=254nm)	can be used as a surrogate for dissolved organic carbon (DOC)
turbidity	turbidity can interfere with disinfection by offering partial protection of organisms, or by consuming ozone
nitrite	instantaneous reaction with ozone (Hoigné *et al.* 1985) $O_3 + NO_2^- \rightarrow NO_3^- + O_2$
iron(II)	instantaneous reaction with ozone (Hoigné *et al.* 1985) $2Fe^{2+} + O_3 + H_2O \rightarrow 2Fe^{3+} + O_2 + 2OH^-$
manganese(II)	instantaneous reaction with ozone (Pouvreau 1984 in Langlais *et al.* 1991) $Mn^{2+} + O_3 + H_2O \rightarrow MnO_2 + O_2 + 2H^+$
bromide	fast cyclic decomposition of ozone (Von Guten & Hoigné 1994) $O_3 + Br^- \rightarrow O_2 + OBr^-$ $O_3 + OBr^- \rightarrow 2O_2 + Br^-$ $2O_3 + OBr^- \rightarrow 2O_2 + BrO_3^-$ $OBr^- + H^+ \Leftrightarrow HOBr$ $O_3 + HOBr \rightarrow$ No reaction $HOBr + DOC \rightarrow$ Brominated organics
ammonia	slow reaction with ozone (Haag *et al.* 1984) $4O_3 + NH_3 \rightarrow NO_3^- + 4O_2 + H_2O + H^+$ fast reactions with bromide (Von Guten & Hoigné 1994) $HOBr + NH_3 \rightarrow NH_2Br + H_2O$ $3O_3 + NH_2Br \rightarrow 2H^+ + NO_3^- + Br^-$ $NH_3 + H^+ \Leftrightarrow NH_4^+$ The reactions of ammonia bromide slow the cyclic decomposition of ozone (Von Gunten & Hoigné 1992) Bromamines are also good disinfectants (Johannesson 1958)

2.3 Sampling Program

Sampling to determine the chemical and physical characteristics of ships' ballast water was conducted during visits to North Queensland ports during 1995 and 1996. Ports visited were Mourilyan (bulk sugar and molasses), Lucinda (bulk sugar), Abbot Point (bulk coal), and the Port of Townsville (sugar and general cargo terminals). The Ports Corporation of Queensland is responsible for the provision of services at Mourilyan, Lucinda and Abbot Point. Ten vessels ranging in size from 2,700 to 75,100 DWT (Deadweight tonnage) were sampled. They were mostly bulk carriers but included a molasses tanker and two container vessels. Most vessels reported that they had exchanged their ballast water at sea, the source of the ballast of one is unknown, one contained semi permanent ballast (the source of which was unknown) and two were Australian coastal vessels, which could not exchange ballast at sea.

The ballast water samples were collected from sounding pipes, a ballast hatch, a pressure gauge connection, with a Van Dorn bottle and by standing on a wharf onto which ballast was being discharged. Collection from ballast tank hatches was not generally attempted because of the interference with normal deck operations of the vessels.

A total of thirteen water samples were collected from nine vessels. On some vessels it was possible to obtain multiple samples, once the methods became routine and familiar. Two sludge samples (and the associated supernatant from one) were collected from one of those vessels and sediment samples were collected from a tenth vessel. The water samples were collected from topside, double bottom, topside/double bottom and fore peak tanks. The sludge was collected from a fore peak tank, and the sediment from the bottom of a topside/double bottom tank.

Water samples were analysed for pH, salinity, temperature, turbidity, suspended solids, dissolved organic carbon, total organic carbon, total iron, dissolved iron, Alkalinity, absorbance and %transmittance at λ=254nm, redox potential, chlorophyll *a*, pheophytin, nitrite, nitrate, ammonia, total nitrogen, phosphate and total phosphorus. One dissolved oxygen measurement was conducted. Sludges were analysed for pH, salinity, suspended solids, total iron and particle size distribution. The sludge supernate was analysed for pH, salinity, absorbance & %transmittance (λ=254nm), turbidity, suspended solids, chlorophyll *a* and pheophytin. The sediment was analysed for particle size distribution.

To determine the sizes of organisms which might be removed by filtration a literature review was conducted. The sizes of the organisms were compared with commercial data on filtration system capabilities.

3. METHODS

3.1 Sampling methods

A summary of sample collection method, location and vessel details are shown in table 2. All equipment used in the collection of samples was washed in phosphate free detergent, deionised water and soaked in 8% HCl for at least 72 hours then rinsed with Milli-q water. Inorganic nitrogen and phosphorus and dissolved iron samples were syringe filtered with 0.45 μm cellulose acetate membrane filters (sartorius) during sample collection. Acidification of iron samples was conducted in the laboratory. All samples were placed on crushed ice in an insulated container immediately upon sampling and taken for storage as recommended for each sample (Greenberg *et al.* 1992). The period between sampling and laboratory storage was typically less than two hours and never more than eight hours. Salinity, pH, redox potential and temperature were sampled in line, minimising any interference of external conditions, eg. contact with the air. The samples were stored in glass or plastic containers which had been prepared as recommended in Greenberg *et al.* (1992). The volume of water collected was only that necessary to obtain sufficient volume for accurate chemical analysis and did not amount to more than 5L per sample.

The apparatus for the peristaltic pump samples, listed as "sounding pump" in table 2, consisted of a 12V battery operated peristaltic pump, 30 cm silicon flexible tubing and 10m of teflon lined PVC tubing (ISCO). The teflon lined tubing was pushed into the sounding tube as far as it would go, connected to the silicon tubing and pumped until any initial colour in the water had disappeared. It was then pumped to sample bottles for storage or subsampling. Samples from sounding pipe overflows were taken by opening the sounding pipe cover and taking samples as it overflowed. A sounding pipe access from the deck is shown in plate 1 in figure 1 and the bottom of the sounding pipe, at the bottom of the ballast tank, is shown in plate 2. The sample from the access hatch was taken by opening the hatch and sampling approximately 30 cm from the top of the water column. The cargo hold sample was taken by dropping a Van Dorn sampling bottle from the deck into the cargo hold and subsampling on deck. The sample from the main ballast pump was taken by removing the pressure gauge and allowing the water to

flow through. The ballast discharge sample was taken standing on a wharf as a vessel discharged ballast. Sediment samples were scraped from the bottom of the topside/double bottom tank of a bulk carrier.

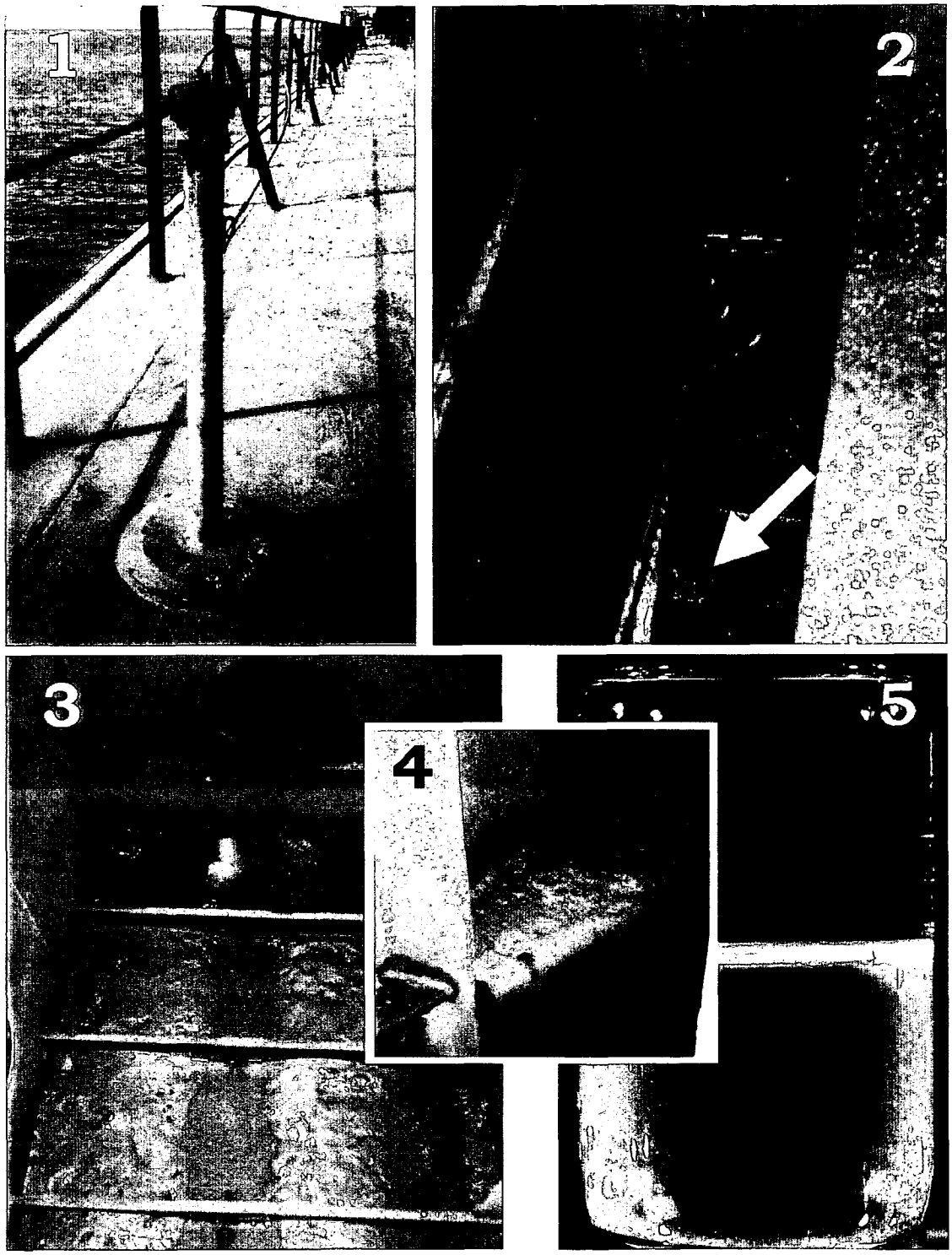

Figure 1. Plate 1. Deck level sounding pipe access, Plate 2. Bottom of sounding pipe in a fore peak tank (bottom indicated by arrow), Plate 3. Sediments in the bottom of a topside/double bottom tank, Plate 4. Sediment on a stringer (horizontal bracing), Plate 5. Sludge pumped from the bottom of a fore peak tank of a container vessel (after settling).

3.2 Analytical methods

All analytical methods conform with *Standard Methods for the Examination of Water and Wastewater* (Greenberg *et al.* 1992), with the exception of absorbance and transmittance at 254 nm. Chemical analysis was conducted at the Australian Centre for Tropical Freshwater Research and the Advanced Analytical Centre at James Cook University, with the exception of pH, salinity, temperature, redox potential, absorbance, transmittance and size distribution of solids.

Salinity was measured by electrical conductivity with a TPS meter. The pH was measured with a Hannah Instruments HI9023C portable pH meter and combination glass electrode with separate temperature probe. Redox potential was measured using a Hannah HI3131 platinum combination ORP electrode. Turbidity was measured nephelometrically with a Hach Portable Turbidimeter. Dissolved oxygen was measured with a TPS model LC182A portable membrane electrode dissolved oxygen meter.

Total Suspended Solids was measured by filtration on GF/C filter paper (Whatman). Total and dissolved organic carbon (TOC and DOC) were determined using a Shimazdu TOC 5000 carbon analyser with DOC samples filtered through a GF/C filter paper (Whatman). Alkalinity measurements were conducted by end point titration.

Chlorophyll *a* and pheophytin concentrations were determined by spectrophotometry. Iron was analysed by microwave assisted digestion in a Zeeman Graphite Furnace. Particle sizing was conducted with a Malvern Instruments Mastersizer X which uses a light blockage system. Beam length and lens size were selected to suit the size distribution of the solids by trial and error. Sonicated samples were exposed to ultrasound for 15 seconds prior to size analysis.

All nutrients were analysed using an Alpkem Flow Solution II Autoanalyser. Nitrite and nitrate were determined by spectrophotometry (Greiss-ilosvay and automated cadmium reduction respectively), ammonia by the automated phenate method, phosphate by automated ascorbic acid reduction, total N by the persulphate method and total P by the persulphate digestion method.

Absorbance and transmittance at λ=254 nm were measured in a Varian 635 UV-Vis spectrophotometer using split beam and fitted with 10 mm pathlength matched pair quartz cells.

For the experimental work on redox potentials, dissolved oxygen was measured with an Orion model 830 membrane electrode dissolved oxygen meter, redox potential was measured using a Hach model 50230 ORP electrode on the Hannah Instruments HI9023C portable pH meter and the ferrous sulphate (hydrated) was AR grade (Ajax chemicals).

Table 2. Location of ballast samples, collection method and ballast water exchange details.

Ship No.	Cargo	Size DWT[1]	Sample No. and type	Sample location[2]	Collection method	Exchange at sea?
1	sugar	28,900	1 (water)	TST	sounding overflow	yes
2	sugar	30,000	2 (water)	DBT	sounding overflow	yes
2	sugar	30,000	3 (water)	TST	access hatch	yes
3	sugar	16,000	4 (water)	Cargo	Van Dorn bottle	yes
4	container	2,700	5 (water)	DBT 3	sounding pump	semi-permanent
4	container	2,700	6 (water)	DBT 4	sounding pump	yes
4[3]	container	2,700	7 (sludge)	FPT	sounding pump	no[4]
5	sugar	44,500	8 (water)	DBT	engine room	yes
6	container	2,700	9 (water)	DBT 3	sounding pump	unknown
4[3]	container	2,700	10 (sludge)	FPT	sounding pump	yes
7	coal	73,500	11 (water)	TS/DB 4	sounding pump	yes
7	coal	73,500	12 (water)	TS/DB 1	sounding pump	yes
7	coal	73,500	13 (water)	FPT	sounding pump	yes
8	molasses	6,800	14 (water)	FPT	sounding pump	no[5]
9	sugar	24,100	15 (water)	TST	ballast discharge	yes
10	ore	75,100	16 (sediment)	TS/DB	scraped	no[5]

1. DWT = Deadweight Tonnage, which is the maximum carrying capacity of the vessel.
2. TST = topside tank, DBT = double bottom tank, FPT = fore peak tank, TS/DB = topside/double bottom tank. Tank number is given where known.
3. Vessel 4 sampled on a second occasion to obtain an adequate sludge sample for analysis.
4. Semi-permanent ballast.
5. These vessels trade on the Australian coast.

4. RESULTS

4.1 Results of water analysis

Table 3 summarises the analytical results for the water samples. Sample 2 was taken from the overflow of a sounding pipe and had a distinct red-orange colour. It was subsequently found to be extremely high in iron. It was not included with the other samples for any analysis as the

extremely high iron is due to sampling from the top of the sounding pipe without inserting tubing and pumping until the initial colour had disappeared.

Table 3. Characteristics of the ballast water samples. Sample 2 is treated separately due to very heavy contamination with iron at the top of the sounding pipe.

Characteristic	Range and (mean)[1]	n[2]	Sample 2
Water quality			
pH	7.0 - 8.6 (7.9)	11	7.0
Salinity (‰)	22.9 - 33.3 (29.7)[3]	11	32
Temp (°C)	30.1 - 32.5 (31.5)	10	
Turbidity (NTU)	0.7 - 52 (10.4)	13	1550
Total Suspended Solids (mg/L)	1.7 - 26 (12.2)	13	714
Total Organic Carbon (mg/L)	0.9 to 8.8, 14.7[4]	12	
Dissolved Organic Carbon (mg/L)	0.8 to 2.8, 10.5[4]	8	
Alkalinity (mg/L as $CaCO_3$)	30.5 to 139	11	
Redox potential (mV)	-360 to 60	9	-58
absorbance (λ=254nm)	0.01 to 0.26	11	
% Transmittance (λ=254nm)	54.8 to 99.9	11	
Dissolved oxygen (mg/L)	6.3	1	
Dissolved iron (µg/L)	see table 8	9	
Total iron (µg/L)	see table 8	12	298,000
Nutrients and productivity			
Chlorophyll a (µg/L)	nd[5] to 2.1	11 (4)	
Pheophytin (µg/L)	nd to 2.9	11 (8)	
Nitrate (µg/L)	<0.5 (nd) to 592	8 (7)	
Nitrite (µg/L)	0.6 to 29.9	8	
Ammonia (µg/L)	<0.5 (nd) to 351	8 (7)	
Total N (µg/L)	73.7 to 1204	10	
Phosphate (µg/L)	0.3 to 13	8	
Total P (µg/L)	2.3 to 47.2	10	

1. Mean only shown where informative
2. Number in parenthesis is the number of samples which were above the limit of detection
3. Only two samples below 31‰ (‰ = parts per thousand)
4. The highest DOC and TOC values were from the cargo hold of a sugar carrier
5. nd = Not detectable

After the high iron observed in sample 2 all samples from sounding pipes were pumped until any visible iron contamination, which varies in colour from red to black, had been eliminated. Table 4 shows the effect on suspended solids and turbidity of pumping from a sounding pipe until after the water was visibly clear. A ballast tank on vessel 4 (DBT4) was specifically sampled to examine this effect. Sample t_o was taken immediately after pumping from the sounding tube commenced and sample t_x was taken after the water was clear to the naked eye.

Table 4. The effect of a period of pumping from the bottom of a sounding pipe on the total suspended solids and turbidity (vessel 4 DBT4). Salinity was 22.9‰.

Parameter	Sample t_o	Sample t_x
Turbidity (NTU)	69	12.9
Total Suspended Solids (mg/L)	478	14
%transmittance	42.8	85.3

4.2 Results of sludge and sediment analysis

The sludge and supernatant shown in table 5 came from two visits to the same vessel (ship 4) and are taken from the fore peak tank. This water was reported as being from Port Moresby. The supernatant was decanted after settling overnight. Figure 1 plate 5 shows a sample of the sludge taken from this vessel after settling for 2 weeks.

Table 5. Ballast sludge and supernatant characteristics (Source: Port Moresby).

Parameter	Sludge	n	Supernatant	n
pH	6.65	2	6.62	1
Salinity (‰)	21.4	2	19.5	1
Total Suspended Solids (mg/L)	33,700	2	161	1
Turbidity (NTU)	#		18	1
% Transmittance	#		93.2	1
Alkalinity (mg/L as $CaCO_3$)	#		53	1
Total N (µg/L)	2,076	1	#	
Total P (µg/L)	241	1	#	
chlorophyll *a* (µg/L)	8.5	1	15.4	1
Pheophytin (µg/L)	<2.0	1	7.7	1
Iron (µg/L)	see table 8			

not done

The size distribution of solids in the sludge and sediment samples are shown in figure 2 . Plate 3, figure 1 shows a sample of the sediment on the bottom of the ballast tank and plate 4 shows the sediment on a stringer.

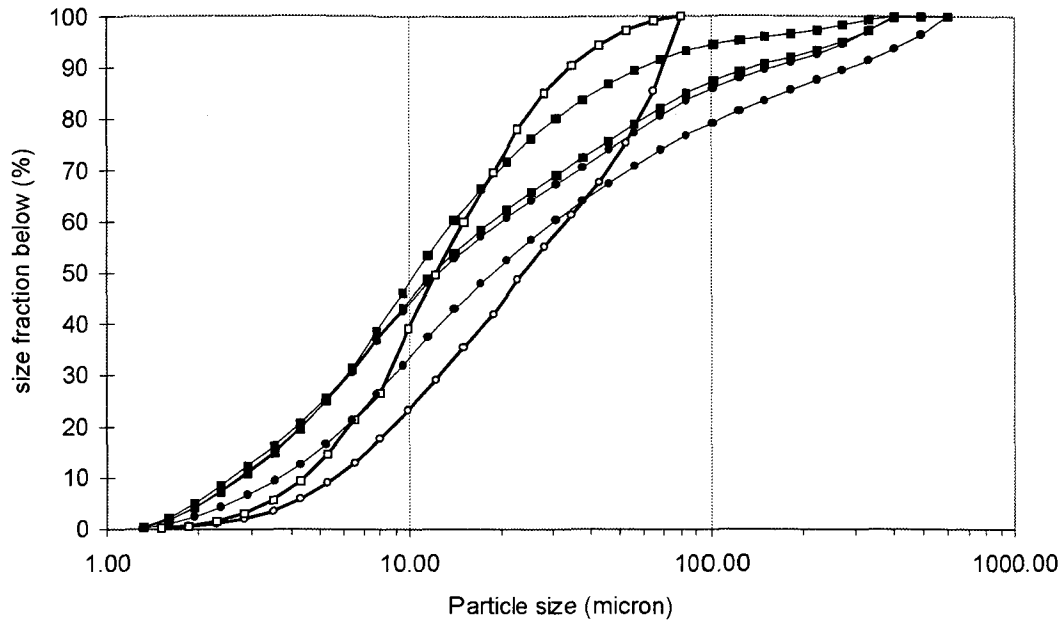

Figure 2. Particle size distribution of the sediment samples. Closed symbols (●, ■) represent the sludge from vessel 4, the open symbols (□, ○) represent the sediment from vessel 10. Circles (○, ●) are not sonicated and squares (□, ■) are sonicated.

5. DISCUSSION

5.1 Characteristics affecting filtration

5.1.1 Size distribution of sludge and sediment solids

Care needs to be taken interpreting the data from particle size analysis (figure 2) as the analytical method will reduce the aggregate size of any flocs present. Seawater is a natural coagulant due to charge destabilisation by high ionic strength waters (Sawyer & McCarty, 1978) and it is likely that the sludge and sediment is naturally flocculated. The particle sizer uses freshwater to deliver the solids to the laser for measurement which may cause some destabilisation of the flocs, and hence underestimation of particle size.

Sediment samples from the bottom of ballast tanks represents many years of accumulation of settleable material on the bottom of ballast tanks. The particle size may also be affected by flocculation processes during transit and will not necessarily reflect the particle size as pumped aboard. This size distribution data is therefore only useful to guide design and for analysis of

pilot testing, not for determining the impact on treatment. The actual levels of solids entering ballast tanks may be negligible in terms of impact on disinfection processes.

For the sediment and sludge samples two sets of data are presented in figure 2. One is samples as they arrived in the lab and the other is samples which have been sonicated prior to size analysis. The sonicated samples give the minimum particle size distribution whereas the unsonicated samples will contain many more flocs. The effect of floc destabilisation on reducing particle size is particularly apparent in the sludge samples.

The data shows that there could be a reduction of turbidity and suspended solids present in the water by filtration of 20 to 30 μm, but that anything larger will have little effect on solid material in the ballast water. Pilot testing would be required to draw any more substantial conclusions for the effectiveness of filtration.

Smaller organisms such as bacteria and small microalgae will require filtration to 20 μm or less prior to treatment to reduce shadowing during UV irradiation or protection during ozonation. However for the majority of ballast water this may not be necessary and pilot scale testing is necessary to determine the importance of the settleable material for disinfection processes.

5.1.2 Sizes of Organisms

The sizes of organisms are important for determining the effectiveness of various filtration options against target organisms. Sizes of microorganisms are described below with examples of macroorganisms, mostly zooplankton, shown in table 6. The size of organisms and filtration options are then represented graphically in figure 3.

Viruses range from 18 nm in diameter 1400 nm long (Bridson 1993). Bacteria typically range in size from 0.5 μm wide to 3 μm long though they can be as small as ≤0.1 μm and as large as 10 x 33 μm (Starr & Schmidt 1981). For example *Vibrio cholerae*, has dimensions of 0.38 x 1.5 μm for the vegetative stage and 0.2-0.4 μm diameter for the viable, non-culturable form (Colwell & Spira 1992).

Free living protozoans range in size from 2 to 2,000 μm (McKane & Kandel 1996). Protozoan agents of shellfish disease are as small as 2 μm with spores as small as 3 μm (Bower 1995).

Table 6. Sizes of transportable stages of selected macroorganisms.

Species	stage	size	reference
Undaria pinnatifida[2,3,4] (Japanese giant kelp)	zoospore gametophyte	5 µm 30-100µm (L)	Munday *et al.* (1993)
Dreissena polymorpha[1] (zebra mussel)	larvae	70-290 µm (L)	Laughton *et al.* (1992)
Asterias amurensis[2,3,4] Northern Pacific seastar	fertilised egg to bipinarria	>100 µm (D)[5]	Kasyanov (1988)
Pseudopolydora paucibranchiata[2,4] (polychaete)	3 setiger larvae	>100 µm (L)	(Levin, 1984).
Boccardia proboscidea[2,4] (polychaete)	3 setiger larvae	>200 µm (L)	Blake & Kudenov (1981), Woodwick (1977)
Lepeophtheirus salmonis (metazoan)	nauplii	160 µm (W) 450 µm (L)	Johannessen (1978) Schram (1993)
Pyromaia tuberculata[2,4] spider crab	zoea	0.65 mm (CL) 1.9 mm (L)	Webber & Wear (1981)
Carcinus maenas[2,3,4] European shore crab	zoea to megalopa	0.47-1.18 mm (CL)	Rice & Ingle (1975)
Acanthogobius flavimanus[2,4] Yellowfin Goby	larvae	4.6-12 mm (L)	Dotu & Mito (1955)

L= length, CL= carapace length, W= width, D= diameter

1. Introduced species via ballast water, Great Lakes USA (Hebert *et al.* 1991)
2. Introduced Species, Australia (Furlani 1996)
3. Australian Ballast Water Management Advisory Council Pest Status
4. Suspected of introduction to Australia in ballast water CRIMP (1995)
5. Munday *et al.* (1993) estimate that after taking plasticity into account, a 50 µm filter would be effective for the removal of fertilised eggs of *Asterias amurensis*.

Unicellular algae can be as small as 2 µm in diameter and diatom resting spores and vegetative cells as small as 3 µm (Hargraves & French 1983). The brown tide microalga *Aureococcus anophagefferens* has vegetative cells as small as 2-3 µm in diameter (Buskey & Stockwell 1993). Dinoflagellates range in size from 2 µm to 2,000 µm and typically 20-200 µm (Taylor 1987). Resting cysts of toxin producing species range from 20 to 75 µm in diameter (Denn *et al.* 1993, Faust 1993). The fish predator *Pfiesteria piscicida* has various motile and spore stages ranging from as small as 5 µm (Steidinger *et al.* 1996).

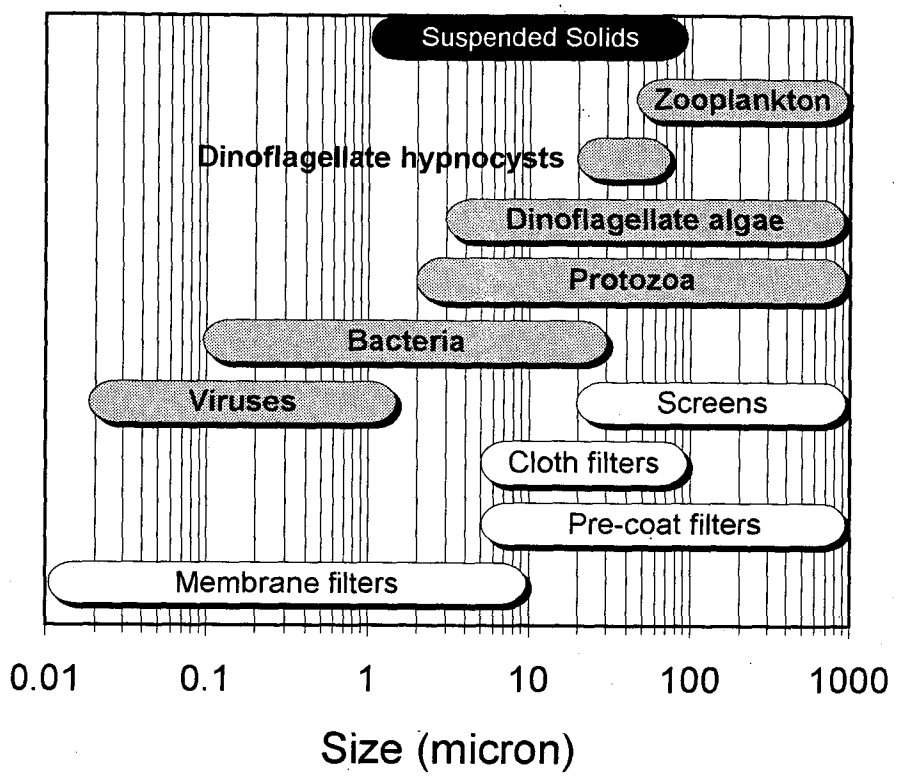

Figure 3. Sizes of organisms and particle removal sizes for filters.

5.1.3 Filtration technologies

Methods for direct filtration include slow sand filtration, rapid sand filtration, screening, cloth screens/filters, precoat filtration and a range of membrane filters. Sand filtration is not an option for shipboard ballast treatment and probably not even for port based treatment due to the space required. Representative removal sizes for the other filtration technologies are shown in figure 3.

Membrane filters are capable of removing any organism in water depending on what is required. A typical unit for removal of bacteria from water has an effective size of 0.2 μm although much smaller membranes are used in some applications (Mallevialle *et al.* 1996). Membrane filters have much higher maintenance, space, pressure and prefiltration requirements than screens or precoat filters and are unlikely to find application in ballast water treatment.

Self cleaning stainless steel screens can filter down to about 10 to 20 μm (eg. Filtomat, Amaid) depending on the quality of the source water. Self cleaning cloth filters can clean down to 3 μm (eg.filtomat). Cloth filters will probably require prefiltration to protect them from excessive

wear. Diatomaceous earth precoat filters are capable of removing down to between 5 and 17 μ m and other precoat media are capable of removing down to 1 μm (McIndoe *et al.* 1988). As the effective diameter of the filter material decreases the capital, operating and maintenance costs tend to increase, and the plant size ("footprint") required to meet ballast water flow rates will increase.

It appears that 50 μm filtration is likely to be effective for the removal of most or all zooplankton and 20 μm is likely to remove dinoflagellate cysts. Laughton *et al.* (1992) also conclude that 50 μm filters would be adequate for the removal of most zooplankton. These may be effective options for the removal of these organisms although other treatment systems currently being researched such as UV irradiation, ozone or heat may be more effective. Simple filtration technologies are unlikely to be useful for treatment of *Undaria pinnatifida*, some important microalgae, protozoans, bacteria and any free viruses.

5.2 Characteristics affecting UV treatment

The %transmittance (λ=254nm) is well within acceptable limits for UV treatment. Total suspended solids is also low and not of particular concern. The effect of total suspended solids on UV treatment will depend on the size of the solids and the size of the target organism. Organisms of about the same size as particulate material should not be shaded by them during UV treatment. Smaller particles could be partially protected from UV disinfection.

The tendency of water to precipitate iron or calcium is important for the maintenance of UV lamps. The Alkalinity indicates that calcium will not be a major problem but the dissolved iron levels are high and iron is likely to precipitate onto quartz or teflon sleeves. This is likely to restrict the application of UV to treatment during ballasting. If UV is used at deballasting, either a heavy cleaning schedule or pretreatment to remove the iron will be necessary.

5.3 Characteristics which could affect ozonation

5.3.1 Temperature

The high temperatures recorded are moderately counter-indicative for the use of ozone to treat ballast water in the tropics as it will be more difficult to dissolve ozone. Reactions which consume ozone and ozone produced oxidants will also be reasonably fast. Water temperature,

however, will be dependant on the temperature of the water through which the ship has recently travelled. Howarth (1981) recorded temperatures ranging from 5.6 to 35°C.

5.3.2 pH

The pH levels are generally in the high range for ozonation. These levels mean that reactions with hydroxide will be an important pathway for consuming ozone. Reactions with bromide will also produce lower concentrations of hypobromous acid (HOBr) at these high pH values, further reducing the effectiveness of ozonation. Reducing pH to below 7.5 would improve the efficacy of ozonation.

5.3.3 Salinity

Bromide concentrations can be determined from salinity as the ratio of bromide to salinity is stable for marine waters and about 1.915 mg/L per ‰S (Millero & Sohn 1991). The bromide concentrations for all vessels sampled would be greater than 40 mg/L. Reactions with bromine will dominate the ozonation process for all vessels sampled. It is expected, in the absence of ballast water exchange at sea, that salinity could vary from 0 to 36‰.

5.3.4 Alkalinity

The Alkalinity levels are generally what would be expected from seawater, although the lower levels are surprising. These moderate to high levels mean that hydroxyl radical chain reactions will be restricted by carbonate and bicarbonate (Hoigné 1995).

5.3.5 Ammonia, nitrite and iron(II)

Ammonia levels are quite low and will probably not have an effect on ballast water ozonation. Where ammonia is present it may slightly improve ozonation. The levels of nitrite are quite low and will not present a problem for ozonation.

The high dissolved iron levels and the low redox potentials indicate that ozone demand from iron(II) will be modest. If ozone treatment was to be used there would be an ozone demand from the reduced iron which would need to be satisfied before an ozone residual would form.

5.3.6 Dissolved organic carbon

The dissolved organic carbon levels are all quite low. There will be some formation of brominated organics but probably not excessive. The levels of organics measured would probably not cause much ozone demand. Sediments, however, will exert high ozone demand due to entrained organic matter, which will deplete ozone residuals locally, protecting organisms near sediments from the effects of ozonation.

5.3.7 Turbidity

The turbidity is quite high for some of the samples and this will necessitate the pre-clarification of water prior to ozonation. The turbidity appears to be correlated strongly with the iron content of the water (figure 6) so it is possible that only treatment during ballast discharge or in-transit will be affected by the iron levels. In samples with high turbidity it will be necessary to pre-clarify the water for ozonation.

5.3.8 Use of absorbance as a surrogate for dissolved organic carbon

From figure 4 it is clear that there is no relationship between dissolved or total organic carbon and absorbance (λ=254nm). Absorbance, as suggested by Hoigné (1994), could not be used as a surrogate for organic carbon in the samples used to obtain this data.

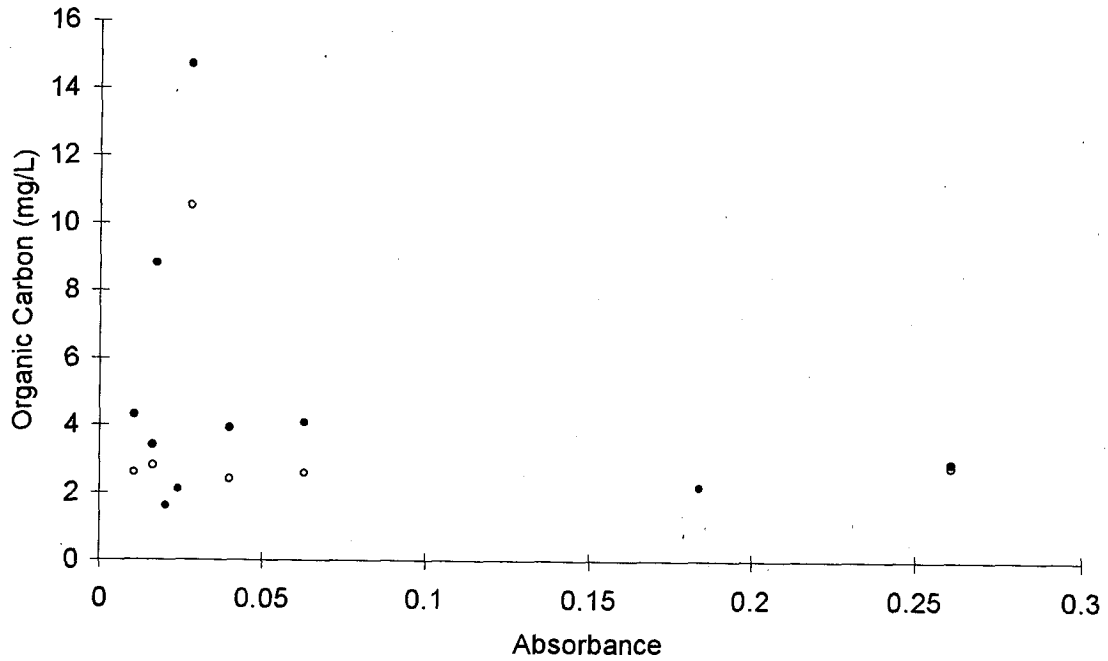

Figure 4. Relationship between organic carbon levels and absorbance (λ=254nm). Total organic carbon(●), dissolved organic carbon (O).

5.4 Implications for ballast exchange at sea

Of the 9 vessels from which water samples were taken, one was a coastal vessel (ship 8), which cannot exchange ballast at sea, and the ballast exchange status of one is unknown (ship 6). One vessel reported it had not exchanged two of the sampled tanks and reported the other sampled tank as exchanged at sea (ship 4). Six vessels reported exchange at sea of all tanks sampled and a total of seven vessels reported exchange at sea of at least one tank. These results are summarised in table 2.

The coastal vessel (ship 8) reported that it had taken all ballast aboard at Adelaide. However it had a salinity of 23.9 ‰, and the water near the inner harbour at Adelaide had a salinity of 37‰ at around the time it was ballasting (John Cugley, SA Dept. of the Environment, *pers. comm.*). The tank sampled was the fore peak tank and it is possible that the tank was not fully empty upon arrival in Adelaide due to the role of this tank in maintaining trim.

The vessel which reported one tank exchanged, one semi-permanent and one unexchanged had a salinity of 22.9‰ in DBT4 which was reported as exchanged at sea. This tank was either poorly exchanged or not exchanged at all. All other vessels had acceptable salinities, but the levels of other characteristics on some vessels was counter-indicative for ballast exchange at

sea. Table 7 shows how the values of these criteria can be compared to the values expected of oceanic water to determine whether they were different than would be expected from oceanic water.

Two of the vessels shown in table 7 (ships 1 and 5) have salinity, pH and Alkalinity which suggest seawater and the levels of the characteristics which fail to meet the oceanic level, do not fail by much. Failure to meet the oceanic water criteria is probably due to material retained in the ballast tanks during the exchange process and material contained in sediments and sludges retained in the ballast tanks. Plates 3, 4 and 5 in figure 1 show sludge and sediments retained in ballast tanks which could affect such results.

Vessel 3 has acceptable salinity and pH (Alkalinity was not measured) as well as acceptable levels of nitrite, ammonia, phosphate, chlorophyll *a* and pheophytin. The levels of DOC, TOC and nitrate, however, exceed the oceanic levels. This sample was taken from a cargo/ballast hold and the previous cargo was sugar which is probably the cause of the elevated levels of organic material and nitrate. This demonstrates the importance of the previous condition of the ballast tank in contributing to the chemistry of the ballast water.

Vessels 2, 6 and 7 all have levels of pH and Alkalinity which fail to meet the oceanic criteria, although in vessel 7 this varies between tanks. They also fail to meet the oceanic criteria in one or more of the organic material, nutrient and chlorophyll *a* + pheophytin criteria. These vessels have probably either exchanged ballast inefficiently or failed to do so. The variability in vessel 7 may be due to inefficient exchange as the tanks sampled are double bottom and fore peak tanks. The double bottom tanks can contain considerable sediments and are likely to be difficult to exchange properly (see plate 3, figure 1 for sediments at the bottom of a ballast tank and plate 5 for a sludge pumped from a fore peak tank). The very high levels of total nitrogen and phosphorus, chlorophyll *a* and pheophytin of the sludges and supernatant shown in table 5 indicate that the sludges, supernatants and sediments can be major sources of contamination. Additionally Rigby & Hallegraeff (1994) observed that half of the sediments inspected in one of their trials was organic in nature.

Table 7. Selected characteristics for determining whether vessels had exchanged ballast at sea. Values which do not meet the oceanic water criteria are marked in bold.

Parameter	Oceanic water criteria[a]	Vessel No 1 TST	5 DBT	3 Cargo	2 TST	6 DBT	7 DBT1	7 DBT4	7 FPT
Salinity (‰)	³30‰[b]	32.2	32.3	32.1	32	33.3	31.0	31.2	32.5
pH	7.8-8.3[1,2]	8.06	8.2	7.91	**7.05**	**7.75**	8.22	8.39	**7.7**
Alkalinity (mg/L as $CaCO_3$)	105-126[1,2]	111	109	-	**86**	**59**	**27**	**46**	120
DOC (mg/L)	<2.0[1,3]	**2.8**	**2.6**	**10.5**	**2.6**	**2.4**	-	-	-
TOC (mg/L)	<2.5[3]	**3.4**	**4.3**	**14.7**	**4.1**	**3.9**	2.1	2.2	1.6
Nitrate (µg/L)	<1.4[2], 24[4]	nd	**31**	**42.7**	-	**45.6**	**592**	6.8	**510**
Nitrite (µg/L)	<2.1[4,5]	0.6	**8.1**	1.7	-	**6.2**	**29.9**	0.5	**112**
Ammonia (µg/L)	<10[2,5]	6.3	**16.4**	2.1	-	**10.2**	**351**	**423**	0
Phosphate (µg/L)	<20[2,4,5,7]	0.3	2.7	2.0	-	0.9	2.7	5.8	13
Chlorophyll *a* (pheophytin) (µg/L)	chlorophyll *a* + pheophytin. <0.5[4-9]	**nd (0.9)**	**0.2 (0.4)**	nd	**nd (0.8)**	**0.3 (0.8)**	nd (0.3)	nd (nd)	nd (nd)

References:
1. Millero & Sohn 1992, 2. Furnas 1991, 3. Burton & Liss 1976, 4. Legendre *et al.* 1988, 5. Furuya 1990, 6. Furnas & Smayda 1987, 7. Eppley *et al.* 1973, 8. Le Bouteiller & Herbland 1984, 9. Dickson & Wheeler 1993.
Notes:
a. values from the indicated literature for the top 50m or less of oceanic samples.
b. Criteria used by Locke *et al.* (1993) for determining if water in ballast tanks was seawater.
nd; Not detected
- not measured

It may be possible to use a chemical test based on some of these or similar characteristics to determine if a particular ballast water is high risk or not, though this would require additional research. A more complete review of literature may help to improve the oceanic water criteria and databases such as W.O.O.D. (1998) or National Oceanographic Data Center (NODC) (eg. Chai *et al.* 1996) could also be used to refine the oceanic water criteria.

An important concern with the oceanic water criteria is the often high chlorophyll *a* and pheophytin levels which may be due to a problem with the criteria, although a brief examination of the W.O.O.D. (1998) database suggests that the levels used here are sensible. It is also possible that the measured levels are affected by entrained macrophyton, or are due to the presence of microalga within sediments. This criteria needs further evaluation. It is also possible for pH and Alkalinity to be moderatley affected by the presence of iron.

Of the seven vessels sampled which reported ballast exchange at sea, between one and four (14-57%) had either done so incompletely or not at all, according to the chemical criteria used here. The vessel which reported its ballast was from Adelaide appears to have had ballast from another location in its fore peak tank.

It is important to note that this is a small sampling from predominantly small vessels (average size 25,500 DWT) with little attempt to representatively sample different tank types, so the conclusions need to be subjected to further testing. The method of ballast exchange, ie. flow through or empty-refill (see National Research Council 1996, Rigby 1995 or Rigby 1994), was not recorded, and this information may have assisted in understanding the causes of vessels failing to meet the oceanic criteria. More detailed information on ballast history would be useful in interpreting the results.

It may be possible to use chemical criteria to monitor ballast exchange at sea, although the effect of residual, unexchanged, ballast water in the composition of the water needs to be investigated.

5.5 Iron levels

Table 8 shows details of the measured iron levels in the ballast water, sludge and sediment samples. Dissolved iron was not analysed for samples which had been exposed to the atmosphere as oxidation is likely to affect the results. Rigby *et al.* (1990) found very low levels (<1μg/L) of particulate iron in samples taken from the M.V. Iron Whyalla, in contrast to the high levels found in this sampling. This tends to suggest that well maintained, relatively young (9 years at sampling) vessels will produce low levels of iron, and may not cause iron precipitation problems for UV treatment, even if it were conducted after ballast water was discharged.

5.5.1 Interaction between iron levels and sampling location

There is a very important important relationship between sampling method and the iron level detected. Overall the samples taken from sounding pipes have much higher iron levels, particularly when the sample tubing does not reach the bottom of the sounding pipe. This data gives some reason to carefully consider whether or not it is appropriate to take samples from sounding pipes for certain types of sample. Figures 5 to 9 show the effect of iron on other parameters. The samples which were not taken from sounding pipes have an average total iron level of 520 μg/L which represents low levels of corrosion within the ballast tanks. It approximates to an average corrosion level of less than 1 μm/year across the steel work of a vessel.

Table 8. Iron levels in ballast water tanks showing the effect of sample location on iron level.

Sampling method	Sample No.	Sample type	Dissolved Iron (µg/L)	Total Iron (µg/L)
sounding pipe overflow	1,2	water		482, (298,000)[1]
sounding pipe pump[2]	7,9,14	water	70, 105, 106	970, 1306, 4905
sounding pipe pump[3]	11,12,13	water	33, 206, 1200	1103, 2860, 3716
open hatch	3	water	85	1495
grab sample	4	water	52	392
engine room pump	8	water	48	218
ballast discharge	15	water		241, 252
sounding pipe pump	5/10	sludge		$70x10^3$
Average of all water samples (excludes 2)			212	1495
Av. of water samples (excludes sounding pipes)			62	520

1. Sample from vessel 2, not included in further analysis.
2. Sample tube extended to bottom of sounding pipe.
3. Sample tube did not extend to bottom of the sounding pipe.

5.5.2 Data affected by iron

The iron levels are cause for concern about the reliability of some of the measurements. Iron is likely to affect the results of turbidity, absorbance, transmittance and suspended solids measurements. Iron levels will affect the redox potential and may influence the Alkalinity and pH. Iron will not affect measurements of salinity, temperature, chlorophyll *a*, pheophytin , nitrite, nitrate, ammonia, phosphate, total N, total P, dissolved organic carbon and total organic carbon, except where the concentrations are high enough for the colour to interfere with colorimetric determinations.

5.5.3 Sources of iron

The major sources of iron are likely to be from humid corrosion when the ballast is empty, galvanic corrosion when full and adsorbed to colloids in sediments. It is likely that the iron came from within the ballast tanks, particularly within the sounding pipes which are difficult to protect from corrosion.

Characteristics which are indicative of the presence of particulates in the source waters are total organic carbon, particulate organic carbon, total phosphorus and total suspended solids. Figure 5 shows the relationship between total iron levels and total organic carbon, particulate

organic carbon and total phosphorus. Figure 7 shows the relationship between total suspended solids and total iron.

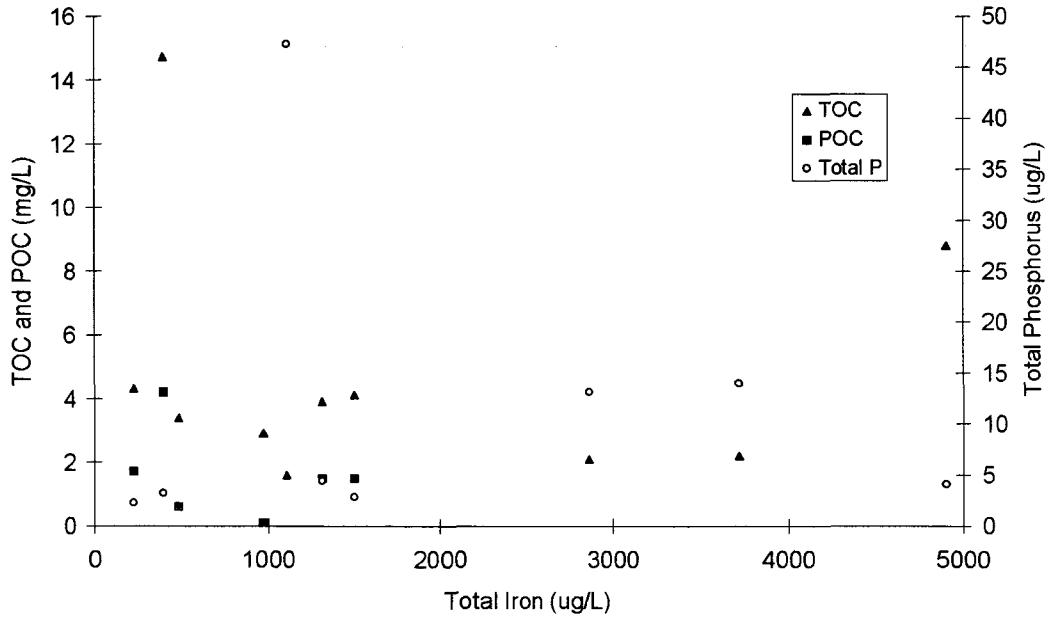

Figure 5. Relationship between total iron, total organic carbon (TOC), particulate organic carbon (POC) and total phosphorus.

The lack of correlation between total iron and total suspended solids, organic carbon and total phosphorus suggests that the iron present in the samples is from within the tanks and not adsorbed to particulates.

5.5.4 Effect of iron on turbidity

Iron precipitates such as ferrous hydroxide, ferric hydroxide and ferrous sulphide will affect turbidity measurements. The precipitation reactions are shown in equations 1, 2 and 3. These precipitates will scatter light in a nephelometer, contributing to the measured turbidity.

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \quad (1)$$

$$Fe^{2+} + HS^- \rightarrow FeS + H^+ \quad (2)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (3)$$

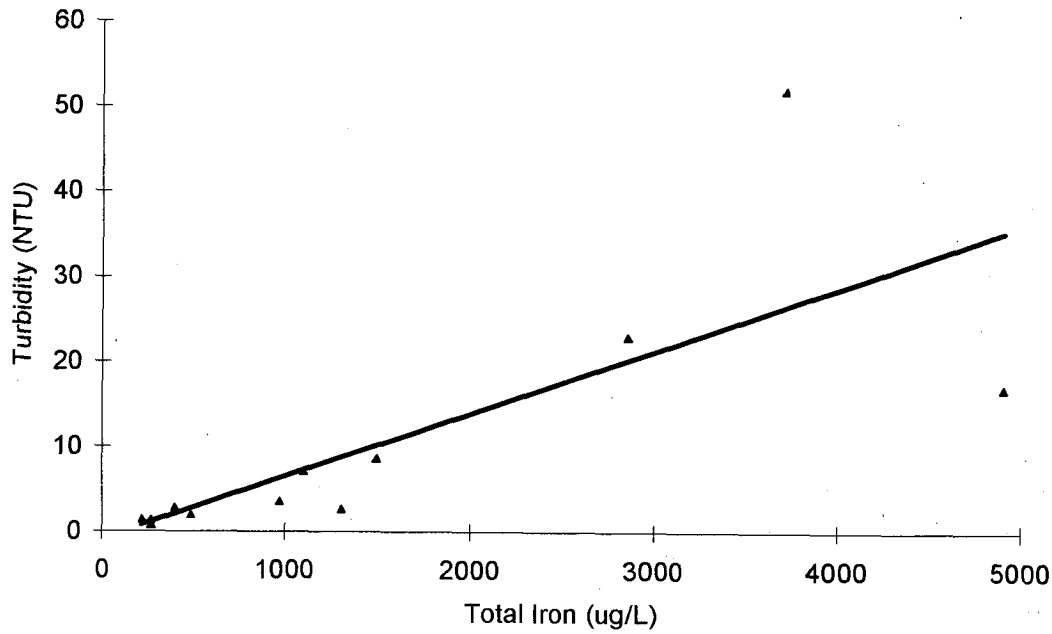

Figure 6. Relationship between total iron and turbidity. ($r^2 = 0.57$).

Figure 6 shows a good correlation between total iron and turbidity. The turbidity is probably caused to a very large extent by the presence of the iron.

5.5.5 Effect of total iron on total suspended solids

Iron can affect suspended solids by the same pathways as for turbidity. The correlation is not expected to be as strong as for turbidity because total suspended solids is measured by filtering the sample through GF/C filter paper. This only retains particles larger than 1.2 μm and is based on a dry weight measurement. Nephelometric turbidity measurement will register the effect of much smaller particles.

The data in figure 7 shows there is no correlation between total iron levels and suspended solids. This is most likely due to both the small size of iron flocs and the low ratio of mass to surface area of flocs. Particles with such a low ratio of mass to surface area will register a strong response in a nephelometer but a small response in suspended solids measurement.

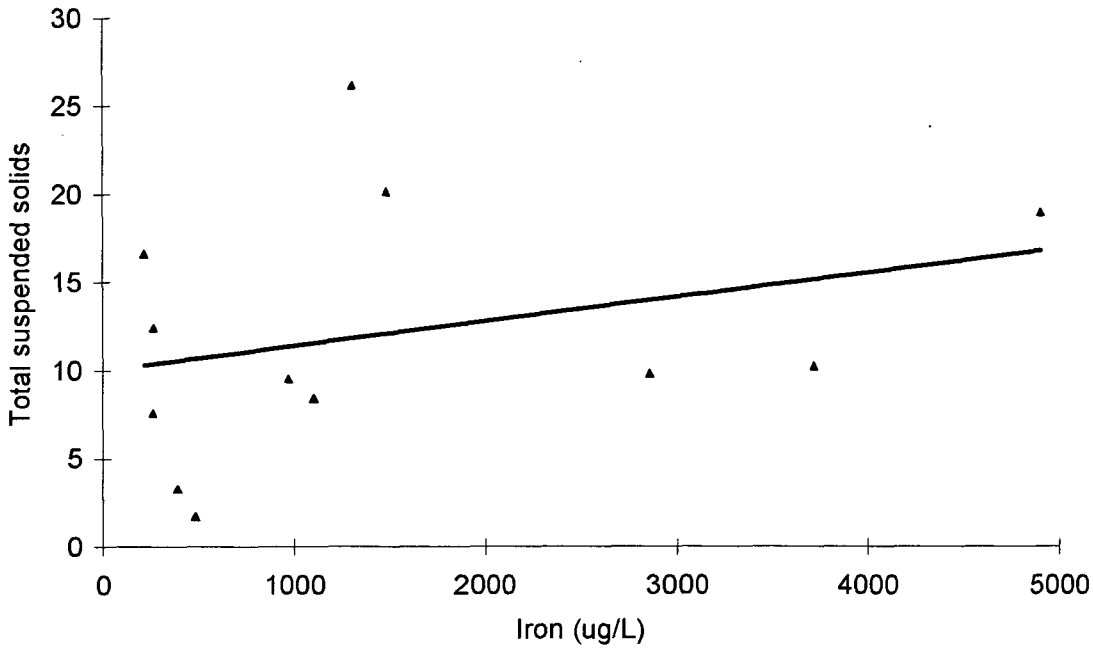

Figure 7. Relationship between total iron and total suspended solids (mg/L). (r^2=0.09).

5.5.6 Effect of iron on absorbance and transmittance

The effect of iron on absorbance (λ=254nm) or %transmittance (λ=254nm) is identical to that for turbidity. The only difference between the measurement of turbidity and absorbance or transmittance is that turbidity is based on the amount of light scattered by the sample and absorbance and transmittance are based on the amount of light which passes through the sample.

Figure 8 shows the relationship between total and dissolved iron and transmittance. The hollow data points are suspected of being low due to precipitation of iron onto the cuvettes during measurement and are not included in the analysis.

Dissolved iron has no effect on transmittance. Transmittance is correlated with total iron, when the suspect data is removed from the linear regression.

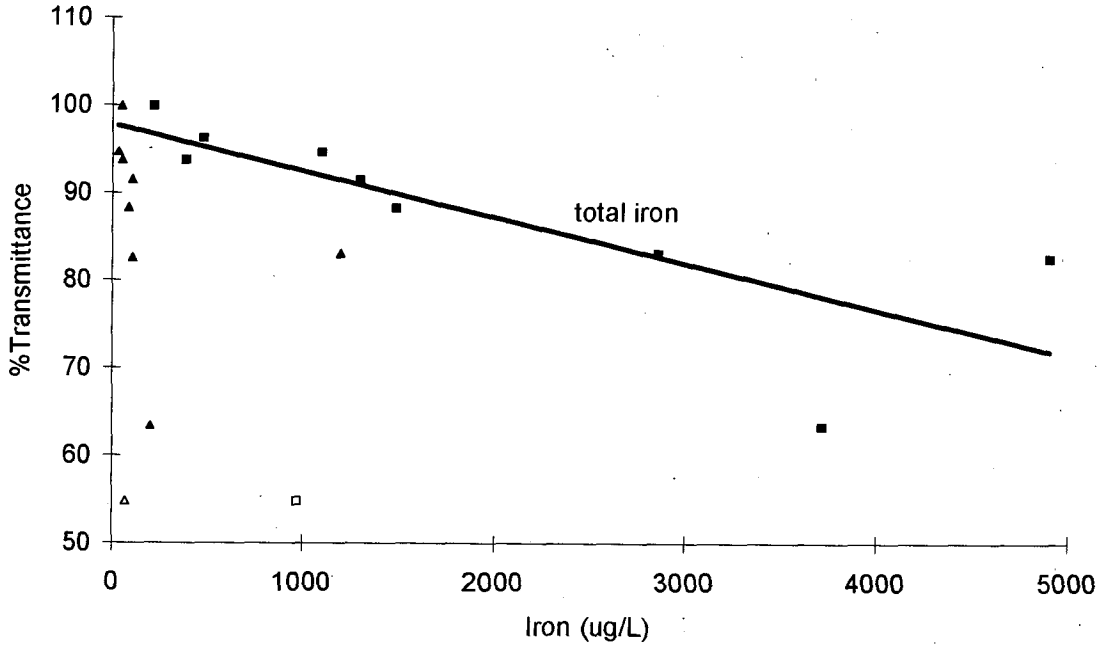

Figure 8. Effect of total and dissolved iron concentration on %transmittance (λ=254nm). The hollow symbols represent suspected outliers which have been removed from the analysed data. Total iron ■ $r^2 = 0.63$, dissolved iron ▲ $r^2 = 0.07$ (regression line not shown).

5.5.7 Relationship of iron with pH and Alkalinity

It is difficult to determine the effect that iron will have on pH as it depends on chemical oxidation of iron, iron precipitation, sulphate reducing bacteria and sulphur oxidising bacteria (Brock *et al.*, 1984). The reactions which dominate depends on starting conditions in the ballast tank and the ballast water. The effect of organic matter, dissolved oxygen levels and heterotrophic activity add another layer of complexity. The actual changes in pH caused by any of these reactions is probably relatively small and as shown in figure 9 there is no correlation between pH and total or dissolved iron. Alkalinity is affected in a similar manner to pH and there in no correlation with iron level (not shown).

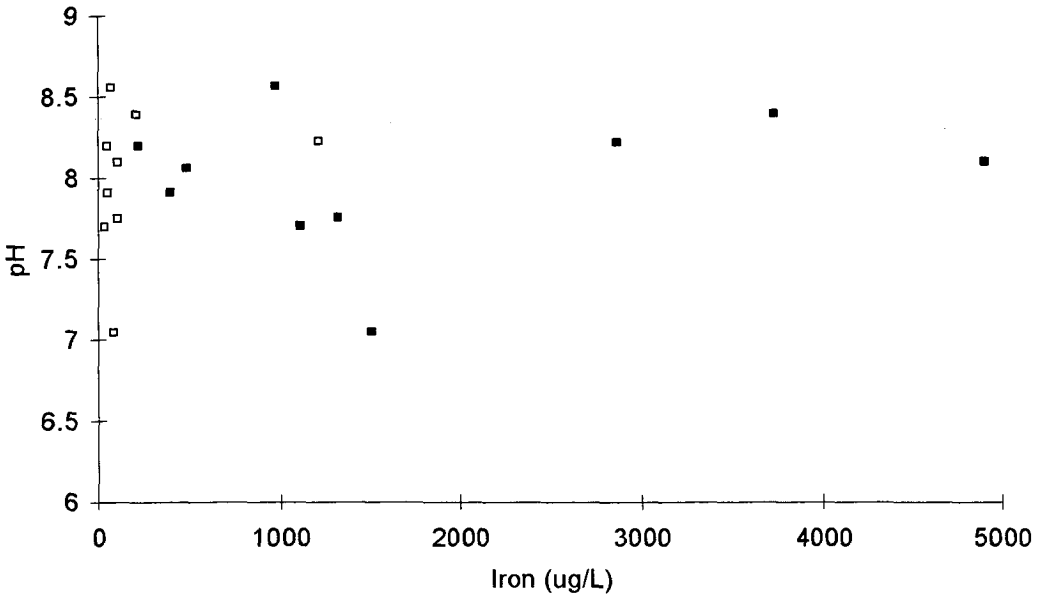

Figure 9. Relationship between iron level and pH. Total iron ■ and dissolved iron □.

5.5.8 Redox potential

The low redox potentials may tend to suggest that the waters sampled are anoxic at the time of sampling (Millero and Sohn 1981), which is partially supported by the presence of nitrite and dissolved iron in all samples. However, this conclusion does not correlate with published dissolved oxygen data, which gives a range of values from saturated to depleted, with the majority of samples having high dissolved oxygen levels (Rigby & Hallegraeff 1994, Howarth, 1981, Medcof 1975). On one occasion Rigby and Hallegraeff (1994) found that dissolved oxygen declined to less than 0.5 ppm in a stagnant ballast tank with a high biomass of diatoms.

The only dissolved oxygen sample (sample 1) taken during this sampling program was 6.3 mg/L (saturated), which had a redox potential of 42.7 mV, which would normally suggest anoxia (Millero & Sohn 1981). However, iron (II) can cause low redox potential in seawater without depleting dissolved oxygen, depending on the speciation of the iron(II) present, slow reactions between iron(II) and oxygen in seawater, and the inhibitory presence of organic complexes (Stumm & Morgan 1996, Wetzel 1983, Kester *et al.* 1975). This suggests that dissolved iron may be responsible for the low ORP levels, not low dissolved oxygen. In experiments, low additions of iron(II) (200-1,000 µg/L) to stirred beakers reduced ORP to as low as -27 mV, without depleting dissolved oxygen.

The low redox potentials in the ballast water samples may be caused by oxygen depletion due to reactions with dissolved organic material and biological corrosion, or the iron(II) levels may have affected the redox potential without affecting dissolved oxygen. It is possible that iron(II), not dissolved oxygen is the cause of the low redox potential in at least some samples.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Implications for Water treatment

6.1.1 Filtration

Analysis of the particle size distribution of solids cannot be used to make any decision on the need for clarification but can be used to determine an approximate size for filters. Unassisted filtration above 50μm would be useless for clarification, filters of between 20 and 30μm are likely to be effective. Flocculation prior to filtration would significantly improve the performance of filter clarification. Pilot testing is necessary to fully determine the effectiveness of filtration to clarify the water.

For direct removal of zooplankton 50μm filters are likely to be effective. 20 μm filtration will be required for direct removal of dinoflagellate hypnocysts and even smaller filters would be required for other algae, some protozoa and bacteria. Smaller pore size filters require higher pressure for operation, and need for prefiltration, both of which increase their costs. Constraints on filter size may be determined in tests being conducted in the USA (Cangelosi 1997).

Characteristics which are essential for assessing pilot filtration both on the inflow and permeate side of the system are turbidity and total suspended solids. Particle size distribution is important for interpreting the effect of filtration on these parameters. If the filtration is a pretreatment for UV then %transmittance(λ=254nm) should also be measured.

6.1.2 UV Disinfection

UV treatment during ballasting is the only system which is unaffected by the iron in ballast tanks and the most attractive UV option. The results from this data collection exercise are not useful for assessing UV treatment during ballasting as they were all taken at ballast discharge

where absorbance and turbidity were affected by iron. The importance of total solids and particle size will not be able to be determined without pilot testing and will depend on the concentration and size of target organisms. For UV treatment after deballasting the high iron levels may cause precipitates which coat teflon or quartz sleeves in UV lamps, preventing the passage of light into the water and necessitating frequent cleaning of the sleeves. The iron levels mean that water must be oxidised and/or clarified before UV can be used, or an intense cleaning schedule must be implemented. Unassisted filtration will not remove the iron.

For a pilot UV treatment system, measurement of only %transmittance (λ=254nm) is essential. Turbidity and suspended solids will help to interpret factors causing changes in transmittance. If UV treatment was conducted after ballast discharge the total and dissolved iron and pH would be required. Redox potential would be helpful, but not necessary.

6.1.3 Ozone Disinfection

The salinity levels of the ballast waters were all in the range where reactions with bromide will dominate the disinfection process, making ozone less effective than would be expected in the absence of bromide. The generally high pH levels mean that less disinfectant will be formed than at a lower pH. The ammonia levels are generally insignificant which also leads to the formation of less hypobromous acid. Modification of pH to about 7 would improve the production of disinfectant for a set ozone dose at relatively low cost. The high temperatures at tropical ports may have a modest effect by reducing the solubility of ozone in water.

Iron in ships is likely to be oxidised by ozone and hypobromous acid (HOBr). This may limit the application of ozonation due to corrosion concerns on vessels. The oxidation of iron(II) produced by galvanic corrosion will also consume ozone and HOBr, which may limit the disinfectant residual to low, possibly useless levels. Organic material in sediments will also exert an ozone and HOBr demand, reducing residuals to ineffective levels in the region of sediments to useless levels. It is likely that ozone will be limited to shore based plants where the iron can be dealt with by preoxidation and/or clarification.

For an ozone pilot plant the sampling required is complex. Salinity, pH, temperature, turbidity, ammonia, dissolved oxygen, total and dissolved iron monitoring are essential. Total suspended solids, dissolved organic carbon and nitrite are useful for understanding the system.

Absorbance (λ=254nm) cannot be used as a proxy for the measurement of dissolved organic carbon in waters from ballast tanks.

6.1.4 Other oxidising biocides

Other oxidising biocides such as chlorine, chlorine dioxide and bromine will have some of the same problems as ozone particularly the high oxidant demand in discharged ballast water due to iron(II), the presence of reducing organic material in sediments and corrosion concerns.

6.2 Ballast exchange at sea

Seven of the nine of the vessels sampled reported ballast exchange at sea. Two had either failed to do so or exchanged inadequately on the basis of salinity. On a further three vessels some of the chemical characteristics and nutrient levels were suggestive of non-oceanic water. The effective compliance with voluntary guidelines to exchange ballast at sea was therefore between 43 and 86% . It may be possible to develop tests based on multi-parameter analysis to determine whether vessels had exchanged their ballast water at sea, although a considerable amount of dedicated research is required to test this possibility. The issue of interferences which would not occur in nature, such as elevated iron levels in ballast tanks, would need to be carefully considered when selecting the criteria to measure.

Problems which may be encountered with the use of chemical characteristics to monitor ballast exchange at sea are the presence of sediments in tanks and the presence of iron in some areas of many tanks. Sediments will act as a reservoir of contaminants such as organic carbon, nutrients, chlorophyll *a* and iron, which will resuspend as new ballast is taken aboard, lifting levels above what would be expected for uncontaminated seawater. For ballast in cargo holds, the characteristics will be affected by the previous cargo.

Iron levels affect measures of turbidity, absorbance, transmittance and redox potential, and possibly dissolved oxygen. This effect will probably be more marked on older or poorly maintained vessels.

6.3 Recommendations for future sampling

6.3.1 Sampling Method

The method of sampling from ballast tanks, for chemical analysis, is important as it is essential not to oxidise some of the chemical species or strip dissolved gases which will affect the levels of other parameters. To ensure that water is not aerated it should be pumped through a manifold containing probes for pH, temperature, salinity, and dissolved oxygen. Probes are also available for turbidity measurement. Care also needs to be taken with the sampling of turbidity, %transmittance, nitrite and particularly iron to minimise oxygenation of the sample. Properly cleaned teflon lined tubing is essential if iron is being measured as only teflon can be properly cleaned between sampling in a high iron environment to prevent cross contamination.

When taking samples with methods where the chemistry cannot be controlled like taps, removed gauges, and from overboard discharge, the measured chemistry will not reflect the ballast tank chemistry. Use of Van Dorn bottles for cargo/ballast tanks is not ideal as the samples are oxygenated during subsampling.

6.3.2 Location of Sampling

If ballast tanks are being sampled for treatment technology it is important to be aware that the water characteristics will vary with location within the ballast tank and therefore with method of sampling. For example sounding pipes are areas of high iron, probably due to poor corrosion protection in this area.

Samples which do not go to the bottom of sounding pipes should be avoided and all samples from sounding pipes should be pumped for a period of time. The use of portable turbidity probes would be helpful for determining when the turbidity level had stabilised which will indicate that the contamination from the sounding pipes has been pumped through. The use of a turbidity probe removes the need for judgement by eye or pumping for a set period of time.

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