

2.2 *In-situ* Monitoring and Stabilisation of the *James Matthews* Shipwreck Site

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Abstract

Reburial of underwater archaeological sites is becoming increasingly common practice. Reburial may be an appropriate means of stabilizing and decreasing the deterioration rate of a site, however, there needs to be a holistic approach to the study of the environment, before and after reburial, to gain a full understanding of the changes that are occurring on the site and determine the effectiveness of the technique.

In the last few years, the *James Matthews*, wrecked in 1841 on Woodman Point, south of Fremantle, Western Australia has been identified as being under considerable threat from increased site exposure due to natural near-shore sedimentary processes and industrial activity in the immediate area. In 2000, an extensive on-site conservation survey was carried out to establish the state of preservation of the wreck. In 2003 it was confirmed that further exposure of the site was occurring at an alarming rate and devising a suitable *in-situ* management plan, including an extensive conservation monitoring programme was of paramount importance. A number of different reburial techniques are currently being evaluated and geological, physico-chemical and microbiological changes in the burial environment monitored over time. The results of these experiments will assist in implementing the most appropriate mitigation strategy for the long-term preservation of this wreck site.

Keywords: *in-situ* preservation, reburial, shipwrecks, marine environment, monitoring, sediment

Introduction

Over the past few decades, the archaeological community has been slowly moving away from the more traditional methods of excavation and recovery of underwater cultural heritage towards a less intrusive management approach, essentially involving the preservation of sites *in-situ*. International conventions, such as the ICOMOS Charter for the Protection and Management of the Archaeological Heritage (ICOMOS 1996) and the yet to be ratified UNESCO Convention on the Protection of the Underwater Cultural Heritage (UNESCO 2001) both state as a fundamental principle that "the preservation of underwater cultural heritage in situ should be considered as a first option". There are a number of different remediation strategies that have been utilised in order to protect underwater heritage sites *in-situ* and most of the techniques or combinations thereof, involve reburial of sites (Manders et al. in press). Reburying an archaeological site may be an appropriate means of stabilising and decreasing the overall deterioration rate of the site, however, there is often little, if any subsequent monitoring to determine the effectiveness of the applied technique (Gregory 1999). A holistic approach to the study of the pre- and post reburial environment is necessary to gain a full understanding of the changes occurring in the local environment and the associated deterioration

of the archaeological material. This in turn, will allow accurate assessment of the adopted mitigation strategy on the long-term preservation of the site (Caple 1994, Hogan et al. 2002).

Notably, a few of the more recent reburial projects have included very extensive on-site environmental monitoring programmes as an integral part of their overall *in-situ* management plans. Some excellent examples were the European Commission funded projects, Bacpoles (Bacpoles 2002, Klassen 2005) and MoSS (MoSS 2001, Cederlund 2004), the ongoing Scandinavian funded RAAR project (RAAR 2002, Godfrey et al. 2004, Bergstrand et al. 2005, Nyström-Godfrey & Bergstrand 2007) and the Western Australian Museum funded *James Matthews* project (Richards 2001, 2003, Godfrey et al. 2004, Godfrey et al. 2005, Winton & Richards 2005). This paper will concentrate on presenting the results of the more recent reburial experiments currently being trialled on the *James Matthews* site.

The *James Matthews* was a relatively small (24.3m x 6.4m x 3.5m), copper sheathed, wooden hulled vessel, fastened with a combination of copper alloy fastenings, iron deck knees and wooden treenails, constructed in France in the late 1700s. During the 1830s, registered under the name *Don Francisco*, it operated in the illegal slave trade between Africa and America until it was captured by the British in 1837. At that time condemned slavers were normally destroyed but this vessel was sold, re-registered and taken into general trading as the *James Matthews*. In 1841 the ship sailed for the Swan River colony in Fremantle, Western Australia but one day after arrival, a violent storm struck the port and the vessel was wrecked on 22 July 1841 (Henderson 1976, 1980). The *James Matthews* has been identified as historically and archaeologically important not only because of its significance to the early colonial history of Western Australia but because the near-complete starboard side of the vessel remains intact. As most of these types of vessels were destroyed when captured under the anti-slave trade legislation of the time, it is one of the world's best preserved examples of a 19th century purpose-built illegal slaver. However, in more recent times the site has been under considerable threat from increased exposure due to natural near-shore sedimentary processes and localised industrial activity in the immediate area. Therefore, devising a comprehensive, appropriate and cost-effective remediation strategy to significantly reduce the continued deterioration of this historic shipwreck site is of paramount importance.

Background

The *James Matthews* was discovered in 1973 about 12km south of Fremantle and lies on the north side of Woodman's Point in Owen Anchorage about 100m off shore (Figure 1) on a north-west/south-east axis in approximately 2m of water. Prior to the commencement of archaeological investigations, the site was extensively covered with seagrass meadows and very little of the wreck was visible above the sediment prior to excavation (Henderson 1976). Four seasons of excavation, approximately three months each in duration, were carried out between 1973 and 1977. At the completion of each excavation period the vessel remains were reburied by backfilling with the original overburden to minimise the destructive effects of marine organisms and the physical damage caused by water and sand movement (Baker & Henderson 1979). No post depositional environmental monitoring was undertaken after these reburial periods. The site appeared to be relatively stable albeit devoid of seagrass and remained essentially buried for many years.

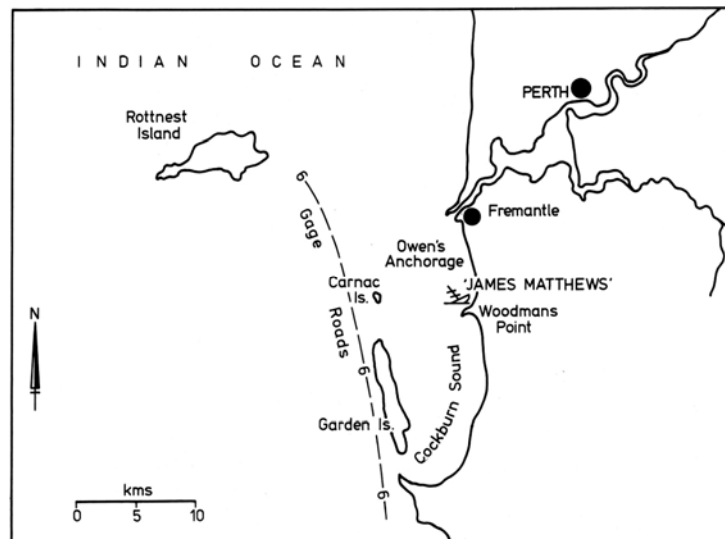


Figure 1. The location of the *James Matthews* wreck site (Burgh & Henderson 1979, p. 7).

A visit to the site in early 2000 however, indicated that there had been extensive scouring and exposure of the vessel remains and therefore, from August to December 2000, a comprehensive on-site conservation survey was conducted with a primary objective to recover the hull remains for stabilisation and eventual display. It involved a limited excavation of the site, which consisted of dredging six 2m³ test trenches (TT) at various positions on the site (Figure 2). The survey included a full corrosion survey of the iron fittings on the starboard side of the wreck, pH profiles, maximum water contents (U_{max}) and wood species identification of the structural timbers located in each test trench and physico-chemical and microbiological analyses of the surrounding sediments. The survey results are published in full in Heldtberg et al. (2004) and Godfrey et al. (2005) but basically, the results of the survey showed that the site had been previously exposed to a depth of ~30cm for an extended period of time, the exposed timbers exhibited active and extensive marine borer damage whilst the timbers buried to a depth greater than 30cm were in good condition. As the majority of the structural hull remains were buried it was concluded that the vessel could be recovered, however the estimated cost of recovery and conservation was prohibitive (in excess of 450M €) and hence, the idea was abandoned. Remediation of the exposed wreck site however, still needed to be addressed. The results from the survey by design, also provided important information on the physico-chemical and biological nature of the environment prior to the implementation of any mitigation strategy.

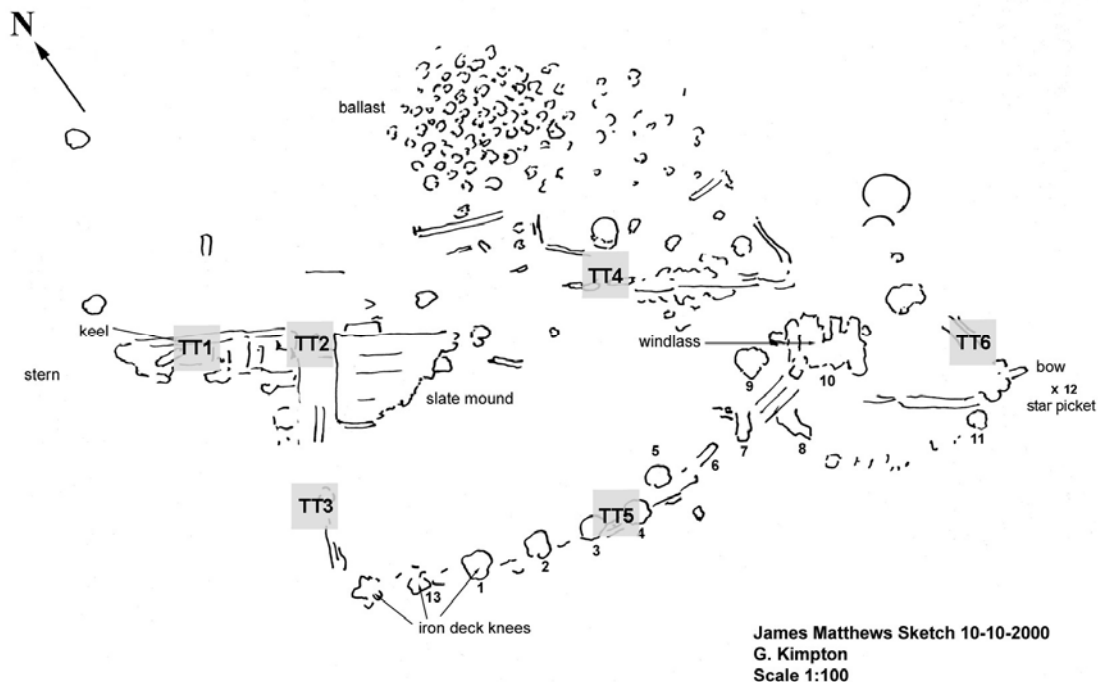


Figure 2. Sketch plan of the James Matthews wreck site indicating the extent of site exposure in 2000 and the position of the test trenches.

Concurrent to the on-site conservation survey, another study was conducted, which examined the broader scale sedimentary processes affecting the site. The purpose of this study was to understand the forces that had shaped the current day configuration of the site and from that understanding, be able to predict the impact and likely success of any *in-situ* preservation strategies considered to protect the exposed elements of the wreck. The results of this study, published in Winton & Richards (2005), concluded that the local coastal and sedimentary changes caused by artificial constructions at Woodman's Point and industrial dredging in Cockburn Sound had altered the natural longshore processes and the net effect was sediment mobilisation away from the immediate area resulting in an overall reduction in sand coverage over the site. More importantly, the results indicated it was unlikely that significant sediment accumulation would occur naturally in the future.

In April 2001, the more traditional method of sandbagging was used to temporarily stabilise the areas that were exposed or were only covered with thin layers of sediment (< 1cm). The canvas sandbags degraded very rapidly and after only three months very little textile remained. After six months there was, on average, only about 1cm of sand coverage over these remediated areas. Unfortunately, subsequent visits to the site at irregular intervals until 2004 confirmed the results of the coastal processes study. It was observed that the site was becoming increasingly more exposed every year. Obviously some form of remediation was of paramount importance to alleviate or, at least reduce, the major physico-chemical and biological degradative forces acting on this site.

Depth of burial has been found to be a very important parameter when relating the degree of wood decay to the local environment. Many authors have shown that the extent of biological degradation of organic materials decreases considerably with burial depths greater than 50cm and this is directly related to the decrease in oxygen diffusion, which adversely affects the activity of micro-organisms, such as fungi and bacteria (Gregory 1999, Nilsson 1999, Björdal 2000, Björdal & Nilsson 1999, 2002). However, recent studies have indicated that to decrease degradation of organic materials to almost negligible levels the depth of burial may need to be significantly greater than 50cm (RAAR 2002, Nyström-Godfrey & Bergstrand 2007). Similarly, the biological results from the analysis of the *James Matthews* sediments obtained in 2000 were reasonably consistent with these observations (Godfrey et al. 2005).

Therefore, based on past and present research and the results from the on-site conservation survey and the coastal processes study any proposed remediation strategy has to maintain sediment coverage of at least 50cm over the entire site. This is especially important around the periphery of the site where the extent of hull exposure is most extensive, to ensure that the degradation rate of the wreck is significantly reduced. Most importantly, this depth of sand coverage must be maintained in the long-term under sediment transport conditions that work counter to this objective and the chosen technique must not adversely affect the wreck material and/or the micro-environment.

Reburial Experiments

A variety of traditional and more innovative covering techniques were considered for the long-term preservation of this site. However, the traditional sandbag approach, utilising UV stabilised, reinforced polymeric recycling bags (~500) was used in March 2004 as an interim preservation measure while more permanent stabilisation strategies were examined. As expected, this technique had limited success. The results from the analysis of the structural timbers in test trench 2 covered by the different sand bagging methods will be discussed.

Mechanical dumping of rock and gravel was considered as one of the more permanent preservation strategies but then future access to the site, which was one of the archaeological requirements of the management plan, becomes problematic due to the difficulty in removing this type of overburden. There was also the potential risk of damage to the underlying wreck remains by compression. Another strategy considered was dumping sand on the site and then stabilising the burial mound with geotextile fabrics or polymeric matting. The problem with this option is as the dumped sand hits the seabed, the sediment is laterally dispersed and the depth of coverage is significantly reduced. Therefore in order to gain full coverage of greater than 50cm over the entire site, especially at the periphery where exposure is extensive, the reburial area would need to be significantly larger than the actual wreck itself.

It was obvious that we required some form of cofferdam arrangement surrounding the site to confine the deposited sand and minimise the reburial area and sediment mobilisation. Cofferdams are usually constructed from timber, which would deteriorate rapidly in this marine environment or steel plate, which would corrode and could adversely affect the delicate balance of the wreck ecosystem. In late 2002, Winton (2002) proposed the use of chemically and environmentally inert, interlocking medium density polyethylene 'crash barrier' units (Figure 3a). This innovative approach would utilise approximately 80 of these units, interlocked into a ring-like arrangement using a pin and hinge system, around the periphery of the wreck site, subsequently filled with dredged sand to the required depth (~1m in total). The minimum depth of sand would need to be at least 80cm. That is, the average current extent of timber exposure above the sediment (~30cm) plus 50cm. The surface area within the confines of the cofferdam would then be covered with a marine grade geotextile, such as Terram 4000 (Pournou et al. 1999) to minimise sediment loss during periods of storm wave conditions. It was thought that this ring wall arrangement would be structurally very stable, withstand wave loading, scouring and maintain this depth of sand coverage over time.

In March 2003, a field trial of the 'test square' (Figure 3b) was initiated on another shipwreck site subjected to greater wave loading than the *James Matthews* to assess the logistics of deployment, stability of the structure, the effect on the local seabed topography and sediment movement within the barrier arrangement. After two years this approach, after some modifications, had shown the concept to be effective. The results of this study are presented in Winton & Richards (2005) and demonstrated that the road crash barrier arrangement was structurally very stable, could withstand short period wave loading, did not result in significant changes to the local seabed topography and with a shade cloth covering on the backfilled sediment inside the test square, maintained this depth of sand coverage over time. Therefore, in early 2005, based on the success of the pilot study, another 'test square' was placed adjacent to the *James Matthews* wreck site. The usual sediment and seabed response is being monitored within and around the test square with changes in the micro-environment (i.e. dissolved oxygen, redox potential, pH, total sulphide, nutrient levels, biological activity) of the sediment inside the test square monitored at regular intervals.



Figure 3. a) Crash barrier unit with enclosed holes; b) Example of assembled crash barrier units prior to experimental deployment.

Concurrently, other techniques used to actively trap and confine sediment without recourse to dredging or dumping sediment onto the site are also being investigated. Polymeric netting/shade cloth mats (50% density) had been previously trialled on the bow section of the wreck with some limited success. Unfortunately after three months there was no appreciable sediment accretion under the netting, the cloth was heavily colonised with a thick algal mat that caused the netting to sink and the section covering the high profile, heavily concreted iron fittings was severely damaged. However, it was interesting to note that when the shade cloth was removed the surface sediment was quite grey, indicating that under the fouled shade cloth, conditions were reducing (lower oxygen levels) probably due to a decrease in the diffusion of oxygen through the thick algal mat and degradation of organic matter.

Although the result of this experiment was essentially negative, observing the reducing environment under the shade cloth was encouraging. Therefore two more shade cloth mats were redeployed in early 2005: one on the bow section (Figure 4a) and the other adjacent to the wreck, 20m off site (Figure 4b); with some simple modifications: small fishing buoys were attached to keep the shade cloth suspended in the water column and concreted fittings in the bow area were covered in sandbags to minimise damage to the cloth. Increasing the density of the shade cloth (80%) was considered in order to decrease the failure rate of the weave over time but based on the results of the 2000 conservation survey the sediment in this area is medium to coarse grain (average 700μ) calcareous sand and therefore, it was decided to continue to use the cloth with a mesh size closest to the average particle size of this sediment.



Figure 4. a) Shade cloth mat on bow in-situ; b) Shade cloth mat off site in-situ.

At the same time, two other types of mats were trialled. One was an artificial seagrass mat using polyvinyl chloride bunting to simulate the natural seagrass leaves (Figure 5a) and the other utilised the same bunting material attached to the 50% density shade cloth mentioned above (Figure 5b). All materials used to manufacture the mats were polymeric in nature and UV stabilised polymeric sandbags were used to anchor the mats to the seabed. A monitoring programme similar to that being used to measure changes in seabed response and micro-environment for the test square has also been implemented.



Figure 5. a) Artificial seagrass mat in-situ; b) Artificial seagrass attached to shade cloth mat in-situ.

The site was revisited after two months and the mat that combined both systems was absent. It was assumed that it had been displaced by pleasure craft anchors, therefore, this system will not be discussed further. The results from the other reburial experiments will be presented in this paper and used to finalise the design of the full scale *in-situ* preservation strategy for the site and assist in establishing a long-term, post-reburial monitoring programme.

Experimental

Wood Analyses

In-situ pH profiles of selected structural timbers in test trench 2 (Figure 2) were obtained. Samples of these measured timbers were collected for wood identification, microscopic analysis, maximum water content (U_{max}) determinations and sulphur K-edge x-ray absorption near-edge spectroscopic (XANES) analysis. *In-situ* pH profiles were determined using a BDH GelPlas flat surface pH electrode connected to a Cyberscan 200 pH meter sealed inside a custom-built plexiglass waterproof housing. The procedure for measuring the pH was to drill into the timber at approximately 1cm depth intervals using a ground down 20mm wood bit driven by a pneumatic drill powered from a SCUBA tank. Immediately after removal of the drill bit the pH electrode was inserted and held against the wood surface until the minimum pH reading was recorded. The depth of penetration into the wood was then accurately measured with a vernier calliper. The maximum depth of measurement was limited by the length of the pH electrode shaft (13cm). Therefore, this procedure was repeated until the entire width of the timber was traversed, the drill could not penetrate any further due to the wood hardness or the limiting depth of the probe was reached. Core samples of the measured structural timbers were collected, sectioned and the maximum water content (U_{max}) determined by the standard method described in Pearson (1987, p. 66). The samples provided for wood identification were sectioned, polished to a 1200 grit finish and then examined using transmission microscopy.

In 2005 two subsamples were taken for microscopic analysis, one each from the exterior and interior of the measured timber samples. Samples were infiltrated with O.C.T. (Tissue Tek ®) embedding medium (50% aqueous solution), frozen to -20°C and sectioned using a cryo-microtome. They were then rinsed in water to remove the embedding medium and were dehydrated in 25, 50, 75, 95 and 100% ethanol series for 10 minutes each. Following dehydration, sections were critical point dried and coated with gold. Observations of deterioration in the sections were made using a Hitachi S-3500N scanning electron microscope (SEM).

One core sample from frame 2 was recovered in 2002, sub-sectioned and analysed for total sulphur content using combustion of the weighed samples in tin capsules, followed by gas chromatographic sulphur dioxide detection (Mikrokemi 2002). Another core sample recovered from frame 2 in 2004 was analysed by the sulphur K-edge XANES technique. The core sample (5mm diameter; 175mm total length) was stored in argon filled tubes and sectioned at various depths into 3mm sub-samples. Sulphur K-edge XANES spectra were collected in fluorescence mode on wiggler beamline 6-2 at the Stanford Synchrotron Radiation Laboratory (SSRL) under dedicated conditions of 3.0 GeV and 75-99 mA of current. The x-ray energy was varied using Si(III) double-crystal monochromator and a nickel-coated mirror to reject higher-order harmonics. The beam path and sample chamber were in a helium atmosphere. The samples, stored and handled in an inert atmosphere in a glove box, were filed to fine particles and mounted as a thin layer on a sulphur-free covered $6\mu\text{m}$ polypropylene film. The emitted x-ray fluorescence, proportional to the x-ray absorption in the sample was measured at 90° using a nitrogen filled Lytle detector. The energy scale was calibrated against the first peak position of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) set to 2472.0 eV (Sandström et al. 2003).

Sediment Analyses

Physical and Chemical Analyses

A set of five sediment core samples [clear, polycarbonate (PC) cylinders (50mm diameter) 30 or 60cm in length] were collected from under each of the experimental mats [*bow shade cloth mat* (5 x 30cm); *seagrass mat* (5 x 30cm); *shade cloth mat* (5 x 30cm) and the *test square* (5 x 60cm)]. One set of reference core samples were collected 20m north-west of the stern section (5 x 60cm). The corers were mechanically pushed into the sediment column using a pneumatic hammer chisel powered by a SCUBA tank with a specially designed attachment that fitted over the PC corer (Figure 6) until the top of the corer was level with the seabed. The top of the corer was sealed with a tight fitting rubber bung. The corer was slowly withdrawn from the sediment assisted by a muffler clamp attached to the top of the sample tube until the base of the corer breached the sediment surface then simultaneously the top bung was removed whilst the bottom bung was pushed rapidly and firmly into the base of the corer. The top bung was then replaced. The removal of the top bung released the vacuum in the corer and minimised, but did not always totally alleviate, upwelling of bulk seawater through the sediment from the base of the core. The cores were stored vertically on-site in a specifically designed crate until transferred to the support vessel.



Figure 6. Polycarbonate sediment corer with hammer chisel and attachment.

In the support vessel, the core samples were sealed at both ends with electrical tape followed by polyvinyl chloride (PVC) plumbers tape, ensuring agitation was kept to a minimum. The cores were transferred to the WA Museum and stored in the fridge at 4°C overnight before transportation to Geotechnical Services, Welshpool, WA for analysis. Each of the five sediment cores were divided into the following size fractions using a polycarbonate extruder specifically designed for this purpose: [for 30cm core – (0-10cm), (10-20cm), (>20cm); for 60cm core - (0-10cm), (10-20cm), (20-30cm), (30-40cm), (40-50cm), (>50cm)]. The size fractions from each of the five sediment cores were then combined and stored in high density polyethylene (HDPE) jars at 4°C until the pore water was extracted (less than 24 hours). The entire contents of each jar was transferred to the cylinder of the Millipore leachate filtration apparatus. The cylinder was flushed with nitrogen gas before the lid was fixed on. Nitrogen gas pressure was applied and the displaced pore water was collected in a 125 ml polyethylene terephthalate (PET) bottle.

Subsamples (15ml) were taken for determination of sulphide immediately after collection and were preserved with zinc acetate solution and sodium hydroxide solution then refrigerated until the analysis was performed. The pH was determined on the remaining water and then the bottles were flushed with nitrogen and refrigerated awaiting analysis for sulphate, total sulphur, ammoniacal nitrogen, nitrate nitrogen, total nitrogen, total phosphorus and orthophosphate phosphorus.

Following pore water extraction, the sediment was removed from the Millipore apparatus and spread on plastic-film-lined aluminium baking trays. These were allowed to air-dry for several days and were then heated in a fan-forced drying oven at approximately 45°C for 8 hours. The dry sediment was transferred from the tray to HDPE jars, in which it was mixed by manual end-over-end rolling. A representative portion (~250ml) of the dry, mixed sediment was sieved (63µm, 125 µm, 250 µm, 500 µm, 1000 µm, 2000 µm and 4000µm sieves) with mechanical shaking. Each size fraction collected was weighed, then recombined with the bulk of the sediment sample in the HDPE jar and remixed. A representative portion (~100ml) of the dry, mixed sediment was sieved (2mm) to remove stones, shells and weed. The portion passing the sieve was crushed in a steel ring-mill. Separate subsamples of the crushed sediment were analysed for dichloromethane-extractable organic matter (by extraction/gravimetry) and for total sulphur content (by Leco combustion).

Microbiological Analyses

One sediment core sample [PVC cylinder (50mm diameter) 30 or 60cm in length] was collected from under each of the experimental mats (30cm) and from within the test square (60cm). Two separate reference core samples (60cm) were collected 20m north-west of the stern section and 20m south-west of deck knee 1 (Figure 2). The sampling procedure is outlined above. On recovery, the sediment samples were sealed with electrical and PVC tape and then placed in their outer PVC casings (60mm diameter). Each outer casing had a plug of steel wool in the base. After placing the sediment core in the casing, 250ml of 12.5% acetic acid was added. The casing was then capped and taped. This was to ensure the core samples remained in an anaerobic environment until analysed. The samples were delivered to Promicro, Hillarys, WA the same day and stored at 5°C until analysed. Each core sample was sub-sectioned and examined at 10cm intervals. The bacteria and fungi in the sediment sub-samples were isolated to pure culture status using aerobic, microaerophilic and anaerobic cultures. Individual organisms were identified to genus and where possible, species status.

Microelectrode Analyses

One sediment core sample [PC cylinder (50mm diameter) 30 or 60cm in length] was collected from under each of the experimental mats (30cm) and from within the test square (60cm). Two separate reference core samples (60cm) were collected 20m north-west of the stern section and 20m south-west of deck knee 1 (Figure 2). The sampling procedure is outlined above. The cores were transferred to the WA Museum where they were stored vertically at 4°C up to a maximum of 5 days prior to analysis. Prior to measurement the residual seawater in the head space of the sample tubes was displaced by pressing a machined PC rod of slightly smaller diameter into the corer until the surface of the sediment was reached. An o-ring, which was fitted around its circumference, was then pressed into the junction between the rod and the corer and sealed with electrical tape. This prevented any lateral movement of sediment when the core was mounted horizontally and fixed to the bench with electrical tape prior to measurement. Holes (3.5mm in diameter) were then drilled into the PC sample tube at 1cm intervals for the first 10cm, then every 5cm until the nearest 5cm interval was reached near the base of the cylinder followed by 1cm intervals until the end of the sediment core. After each hole was drilled it was sealed with a piece of electrical tape to prevent leakage of pore water. This tape was then removed and in the following order: pH, dissolved oxygen content, sulphide and redox potential were measured using the appropriate microelectrodes (Figure 7). After each measurement, the microelectrodes were inspected under a magnifying glass and any superfluous material removed with a wetted cotton bud, then rinsed with deionised water.

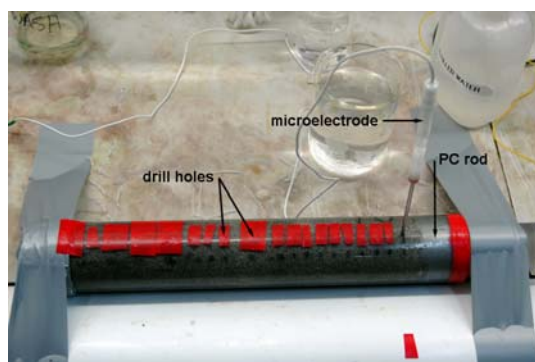


Figure 7. Example of the procedure for microelectrode measurement of the sediment cores.

The pH microelectrode was a Microelectrode Inc (<http://www.microelectrodes.com/>) combination type sensor, MI-411-P with a bevelled needle fitting connected to a Cyberscan 200 pH meter. The microelectrode was calibrated using pH 7 and pH 10.01 buffer solutions. The redox microelectrode was a Microelectrode Inc combination type sensor, MI-800-P with a bevelled needle fitting connected to a high impedance digital multimeter (Finest 100). The microelectrode was calibrated in pH 4 and pH 7 buffer solutions saturated with quinhydrone. The dissolved oxygen and sulphide microelectrodes were Unisense (<http://www.unisense.com/>) needle type micro-sensors, OX-N and H₂S-N, respectively coupled to a Unisense PA 2000 picoammeter. The dissolved oxygen microelectrode is a miniaturised Clark-type sensor with an internal reference and a guard cathode and is calibrated by using a two-point calibration curve: 100% saturation was achieved by bubbling air through distilled deionised water with an aquarium pump and 0% saturation was achieved by bubbling argon through distilled, deionised water for 1 hour. The sulphide microelectrode is a miniaturised amperometric sensor with an internal reference and a guard anode and is calibrated by using a five-point calibration curve between concentrations of H₂S of ca. 0 - 0.13mM following the manufacturers instructions.

Results and Discussion

General

The average pH of the seawater on the *James Matthews* site measured at irregular intervals from 2000 to 2007 was 8.24 ± 0.06 , the average redox potential was $0.234 \pm 0.045V$, the average salinity was 35ppt and the average dissolved oxygen content was $7.88 \pm 0.04ppm$ (92% saturation at 24°C). These measurements indicate that the site is an open circulation, oxidising marine environment typical of this area. The pH and redox potential of the sediment directly adjacent to deck knee 1 (Figure 2) was also measured at irregular intervals over this seven year period by simply pushing the flat surface pH and platinum working electrodes directly into the sediment to average depths of 5cm and 15cm, respectively. Based on more than 30 measurements, the average pH of the sediment was 8.01 ± 0.10 and the redox potential was $-0.001 \pm 0.080V$. Despite the well known problems associated with measuring redox potential with platinum electrodes in sediments (Matthiesen et al. 2004), the average values indicate that the surface sediment is only slightly more acidic than the surrounding seawater column and is neither strongly oxidising nor reducing in nature. This may well have some repercussions for the long-term decomposition of reburied materials on the site as it is well known that less oxygenated, more reducing conditions are more conducive to the preservation of wreck remains and the associated artefacts (Bergstrand et al. 2005, Nyström-Godfrey & Bergstrand 2007).

Another important factor to consider is the shallow nature of the site. The water temperature varies quite markedly and ranges from 15°C in winter to 25°C at the height of summer. This would significantly increase biological activity on this wreck site, subsequently increasing the degradation rate of exposed organic materials and the corrosion rate of metals. Another disadvantage of the shallow conditions is the increase in total water and sand movement with decreasing water depth. This would increase the amount of physical damage caused to exposed wooden structural features on the site and the corrosion rates of metal fittings due to an increase in the oxygen flux to the surfaces.

Biological, chemical and physical degradation of wood occurs to some extent on all shipwreck sites, however, biodeterioration, especially from marine borers and physical damage from wave and sand movement are the major causes of degradation of exposed timbers. When a site is disturbed either by dredging, excavation, scouring, etc the concomitant increase in oxygen, nutrient and water contents will almost certainly lead to a more aggressive environment. Consequently, wood and other organic materials will be exposed to increased marine borer and aerobic fungi and bacterial activity. With time, however microbial processes within the sediment will consume the oxygen and less aerobic environments will be established excluding marine borers and other obligate aerobic micro-organisms (Björdal & Nilsson 1999). However, soft rot fungi (ascomycete and fungi imperfecti) and tunnelling bacteria are able to tolerate lower oxygen levels and can attack remaining sound wood under less aerobic conditions (Nilsson 1999, Björdal & Nilsson 2002). As the oxygen concentration in the sediment decreases further to near anaerobic conditions, wood will only be subjected to the relatively slow action of erosion bacteria (Nilsson 1999). Furthermore, Florian (1987, p.15) has reported that anaerobic bacteria only survive to a depth of approximately 60cm and laboratory experiments carried out by Nilsson (1999) suggest that no degradation of wood occurs in the complete absence of oxygen. Hence, it is obvious that depth of burial is one of the important factors to consider during reburial.

Sandbagging Methods

General

Despite the limited success of the sandbagging method as a long-term preservation strategy, discussions regarding its use as an interim remediation measure are important. Hence, the effect of this technique on the extent of degradation of the timbers in test trench 2 is presented below.

The results from the analyses (pH profiles, U_{max}) of the timbers in test trench 2 (Figure 2) (Godfrey et al. 2005) conducted during the inaugural 2000 conservation survey prior to the deposition of any sand bags were used as a baseline comparison for subsequent analyses (pH profiles, U_{max}) carried out in 2003 after stabilisation with canvas sand bags since April 2001 and in 2005 (U_{max} , microscopic analysis), after coverage with UV stabilised reinforced polymeric sand bags for one year. The positions of the measured structural timbers in test trench 2 are shown in Figure 8. All timbers were white oak with the exception of the outer planking 2 which was elm. The approximate dimensions of the major structural timbers measured on-site were as follows: frames (18cm wide x 12cm thick), outer planking (25 x 5cm), inner planking (20 x 4cm) and the keelson (33 x 20cm).

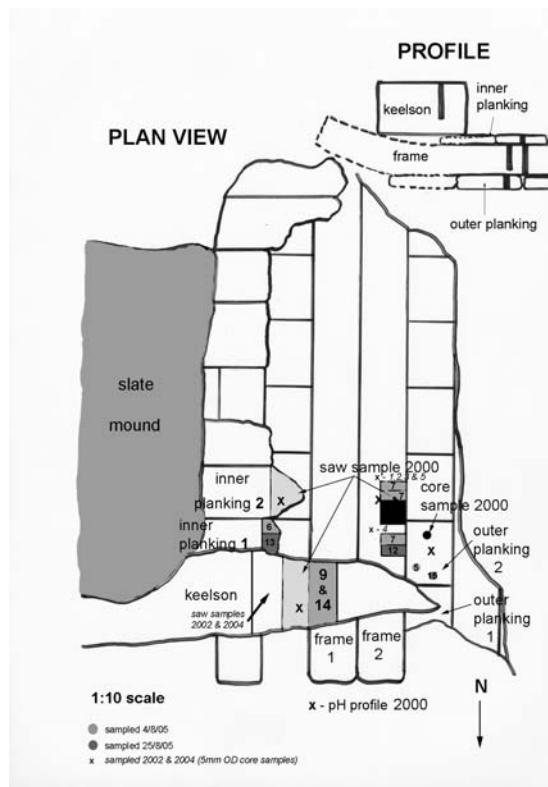


Figure 8. Sketch plan of the sampled structural timbers in test trench 2.

In 2000, there was evidence of past biological depredation of the buried timbers to an average depth of 20cm under the sediment. It was also at this depth where the timbers and surrounding sediment possessed the usual black discolouration associated with anaerobic micro-environments. These observations suggested that the site had been previously exposed to a greater extent than observed during the 2000 survey. It is possible that this damage occurred during the seasonal excavation periods in the 1970s when the site was exposed for extended periods of time because it appears that the site is not subjected to seasonal burial and exposure cycles based on visual observations of the site over the past seven years.

In general, from 2000 to 2005, it was observed that the extent of exposure and biodeterioration of the keelson had increased significantly over this period. The sediment coverage on the inner planking, frames and outer planking varied over the years and with the method of sandbagging. In 2003, two years after stabilisation with the canvas sand bags, where the textile only survived three months, the inner planking was totally exposed and frame 2 was only covered by a thin layer (<1cm) of sediment. The outer planking 2 however, remained covered with about 10cm of sediment and dead seagrass. In 2004, the test trench 2 area was even more exposed than observed in 2003, therefore in early March the area was covered with the polymeric sand bags. In August 2005, one year after stabilisation the sandbags had partially concreted together, essentially protecting the exposed timbers from physical deterioration but there had been no significant sand accretion as previously reported when this technique was applied in other reburial projects. There was only about 2cm of sand covering the inner planking and frame 2 but it was well packed and light grey in colour. The outer planking remained buried to a depth of approximately 15cm. After the sampling period in 2005, the excavated test trench area was backfilled with dredged local sediment to a depth of approximately 30cm, covered in shade cloth and anchored with polymeric sand bags.

pH Profiles

The pH profiles of the timbers measured in 2000 during the initial conservation survey and in 2003, two years after stabilisation with canvas sand bags are shown in Figure 9.

The pH profiles of the timbers measured in 2000 (solid points in Figure 9) followed a typical sigmoidal relationship. That is, the pH of the wood near the upper, more exposed surfaces was high then as the timbers were vertically traversed there was a decrease in pH that tended to plateau with increasing depth. The normally acidic nature of undegraded waterlogged wood, albeit more alkaline than undegraded, seasoned wood of the same species, becomes progressively more alkaline with increasing degradation due to the inward diffusion of alkaline seawater into the void spaces of the more degraded wood cells. Therefore, the higher pH values generally observed near the timber surfaces denoted the areas of greater deterioration.

The decreasing trend in pH as the core depth increased was indicative of a gradual decrease in the extent of degradation towards the interior of the timbers until the pH reached a minimum that represented the area of least deterioration.

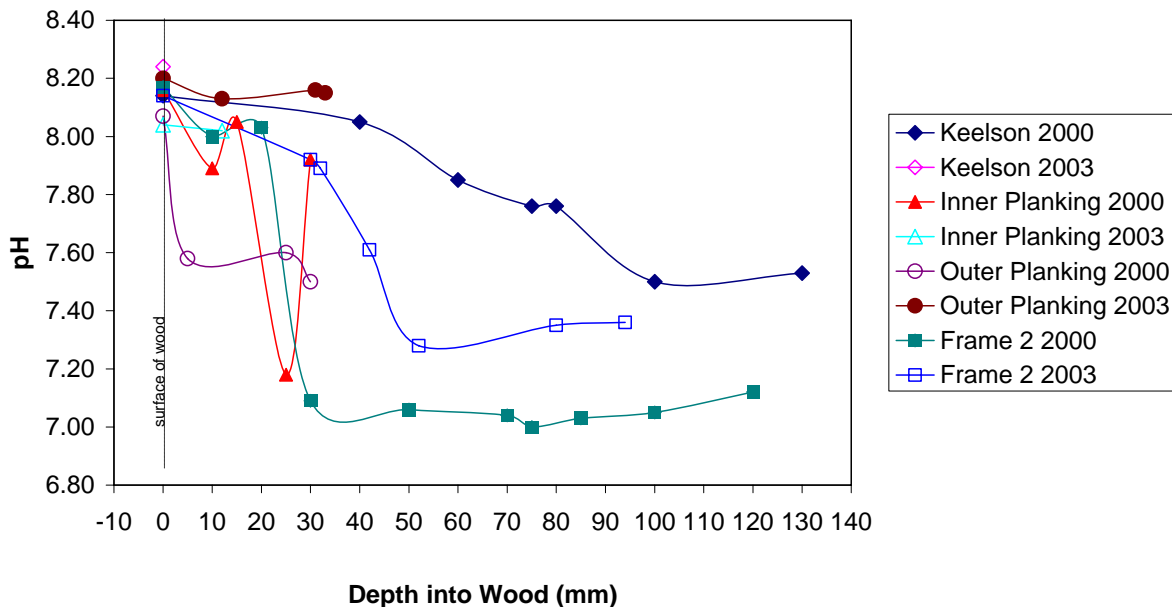


Figure 9. pH profiles of structural timbers measured in test trench 2.

Prior to the commencement of the 2000 baseline survey, the keelson and inner planking were partially exposed and the upper surfaces extensively deteriorated by teredo worm whilst the frames and the outer planking were buried and subjected to a less oxygenated micro-environment. Based on the pH profiles for 2000 (solid points in Figure 9), the keelson was the most degraded of the timbers in this test trench. The pH values for the keelson were much higher than those recorded for the other timbers, denoting more extensive degradation throughout the entire width of the timber. Similarly the upper and lower surfaces of the inner planking were very degraded with a relatively small undegraded core indicated by a dramatic decrease in pH at a depth of 2.5cm. The frame and the outer planking were in considerably better condition indicated by the more acidic pH measurements recorded throughout the inner regions of the timbers. The pH profile of frame 2 represented a timber possessing a relatively degraded outer surface, about 2cm thick, overlying an essentially large, undegraded core. The profile for the outer planking indicated that this timber was less degraded than the exposed timbers but considerably more degraded than the white oak frame. It would be expected that the outer planking would be less degraded as it was buried to a greater extent than the frame but one of the reasons for the apparent increase in the extent of degradation of this timber may be that it only has a total width of 4cm and this would allow easier and more rapid penetration of sea water into the wood structure. In addition, from other studies it has been shown that elm is more permeable and more susceptible to biodeterioration than oak (Bergstand et al. 2005). Another possible explanation is that the outer planking had suffered more deterioration during the service life of the vessel prior to the wrecking event.

In comparison, the pHs of the timbers measured in 2003 (outlined points in (Figure 9) increased considerably indicating a significant increase in the extent of deterioration of all timbers in test trench 2 since the initial conservation survey in 2000. This is not surprising as most of the timbers, with the exception of the outer planking, were essentially exposed or were only covered with relatively thin layers of sediment until 2004. For example, by 2003 the keelson and inner planking were so degraded by marine borers that after the initial surface measurements, the timbers disintegrated and no further measurements could be obtained. The extent of deterioration of the outer surface of the frame had increased from 2cm to 5cm then the pH decreased to an average of 7.33 ± 0.04 compared to 7.06 ± 0.04 in 2000 indicative of a general increase in degradation. The outer planking was degraded relatively uniformly throughout its entire width indicated by an average pH of 8.16 ± 0.03 . This is interesting in the fact that this timber was almost always covered with sediment, however obviously the oxygen concentration in the sand layer was not low enough to prevent continued degradation.

Maximum Water Contents

The U_{max} results obtained in 2000 during the conservation survey, 2003 after canvas sandbagging in 2001 and in 2005, one year after stabilisation with the polymeric bags are presented graphically in Figures 10a, b, c and d.

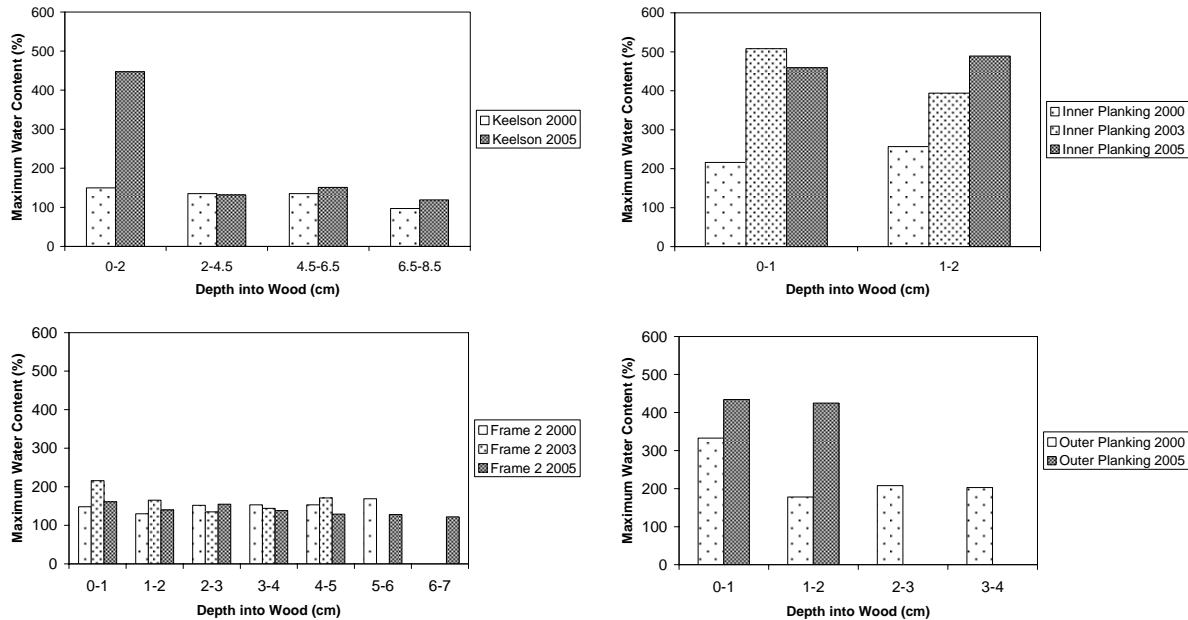


Figure 10. Percentage maximum water contents of the a) keelson, b) inner planking, c) frame 2 and d) outer planking in test trench 2.

The results of the maximum water contents for the timbers support, in part, the results obtained from the *in-situ* pH profiles. The keelson (Figure 10a) had been subjected to extensive depredation by marine borers by 2005 and calcium carbonate lined the bore holes. The maximum water contents of this timber indicated that it was relatively undegraded, however, from visual examination of the sample, it was obvious that this was not the case. The presence of large quantities of calcium carbonate had significantly increased the dry weight, artificially decreasing the maximum water contents. Therefore, this measurement cannot be used as an indicator of the extent of wood deterioration for timbers with extensive marine borer attack. However, the pH profiles can provide a good indication of the state of degradation if the wood does not disintegrate during the measurement procedure.

The extent of deterioration of the inner planking increased almost linearly with exposure time and by 2005 the average U_{max} was $470 \pm 21\%$ indicating extensive degradation (Figure 10b). This is not unexpected as these timbers were either totally exposed or only ever covered with a few centimetres of sand. The extent of deterioration of the exterior of the outer planking increased significantly from 2000 to 2005 (Figure 10d). Only the first 2cm of the timber was measured in 2005 because the recovered core sample did not traverse the entire width of the timber (~5cm) therefore, it is not possible to ascertain if there was any further increase in the deterioration of the inner regions of this timber with this method. The extent of degradation of the outer surfaces of the frame (Figure 10c) increased from 2000 to 2003 when it was only covered in a thin layer of sand, however by 2005 it appeared that the rate of deterioration had decreased significantly and the U_{max} appeared to remain relatively steady from 2003 to 2005 when it was covered with the UV stabilised sand bags, which encouraged sediment build up of approximately 2cm and more anoxic conditions beneath the sand bags.

Microscopic Analysis

The results from the microbiological analyses carried out on samples recovered in August 2005, one year after coverage with the UV stabilised sand bags are in general agreement with the results from the pH profiles and the maximum water contents.

The wood samples collected from frame 2 (Figure 11a and b) and the outer planking (Figure 11c and d) showed the exterior of the samples were highly degraded while the interior zones were less deteriorated. Much of the decay observed in the exterior of frame 2 and the outer planking was due to bacterial degradation, resulting in a complete collapse of the secondary cell walls. Bacteria had made numerous

minute cavities throughout the secondary cell walls. Cellulose and hemicelluloses that predominantly make up the secondary cell walls were degraded leaving behind a loose matrix of lignified secondary wall material as well as the middle lamella between cells. The interior zone of the samples was largely free of appreciable decay. However, some fungal soft rot cavities were observed in the cell walls of this area. Due to marine fungi requiring higher oxygen concentrations for metabolic processes, this fungal attack was likely to have occurred before the wood was buried in sediment. Environmental changes that occurred as the depth of sediment increased over the years appear to have made conditions non-conducive to decay by soft rot fungi. Instead, bacterial erosion and tunnelling became the dominant forms of cell wall attack. A progression of limited soft rot followed by bacterial degradation took place over time. In the outer regions of the wood, conditions allowed extensive degradation by bacteria to occur and the soft rot attack that was once present was masked by the advanced stages of bacterial attack. Most probably, the size of the frame 2 (12cm) and the increasing depth of burial for both the frame and the outer planking over the past five years have allowed the inner regions of these timbers to remain relatively free of degradation.

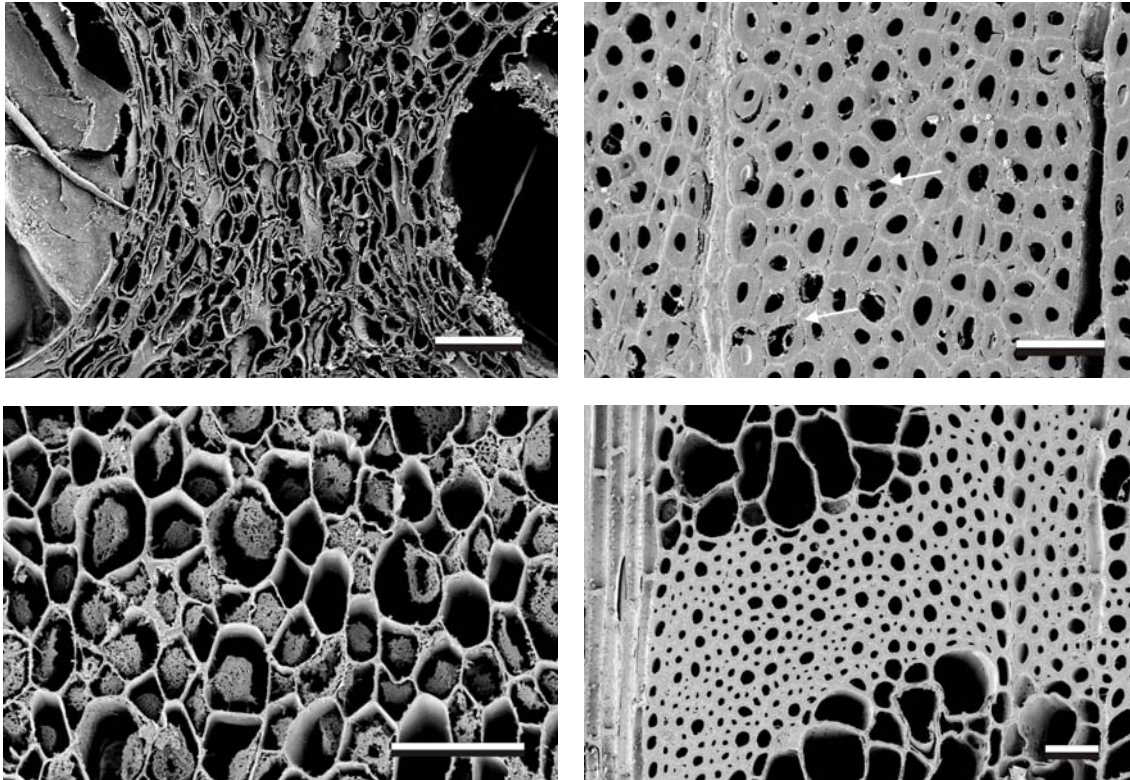


Figure 11. Scanning electron micrographs of wood samples from frame 2 (top photos) and a core sample from the outer planking in test trench 2 (bottom photos) showing the condition of the wood cells. a) Upper left, Extensive bacterial degradation and complete collapse of the wood cell walls in a sample from the exterior wood surface. b) Upper right, Interior region of the wood showing a relatively intact cell wall structure. Close examination shows several isolated soft rot cavities are present in these cells (arrows). c) Lower left, Exterior wood cell walls showing extensive bacterial degradation. The secondary cell wall is severely degraded and only a matrix of eroded cell wall material is left. An intact middle lamella, which is highly lignified, remains between cells. d) Lower right, Interior wood cells showing relatively sound wood structure.

Sections from the inner planking reveal deteriorated wood cells throughout the sample (Figure 12a and b). The cell walls were heavily degraded by bacteria and large strength losses were evident. Over the past five years this timber was either totally exposed or only covered in thin layers of sediment (<1cm) and therefore, subjected to conditions conducive for wood destroying bacteria to colonize and attack this entire structural member. The keelson also showed exterior wood that was degraded more than the interior regions (Figure 12c and d). Although some bacterial degradation was seen, soft rot cavities were pronounced. The extent of exposure of this timber increased over the years and hence, it has been subjected to a more aerobic micro-environment, which allowed a greater period for soft rot to occur.

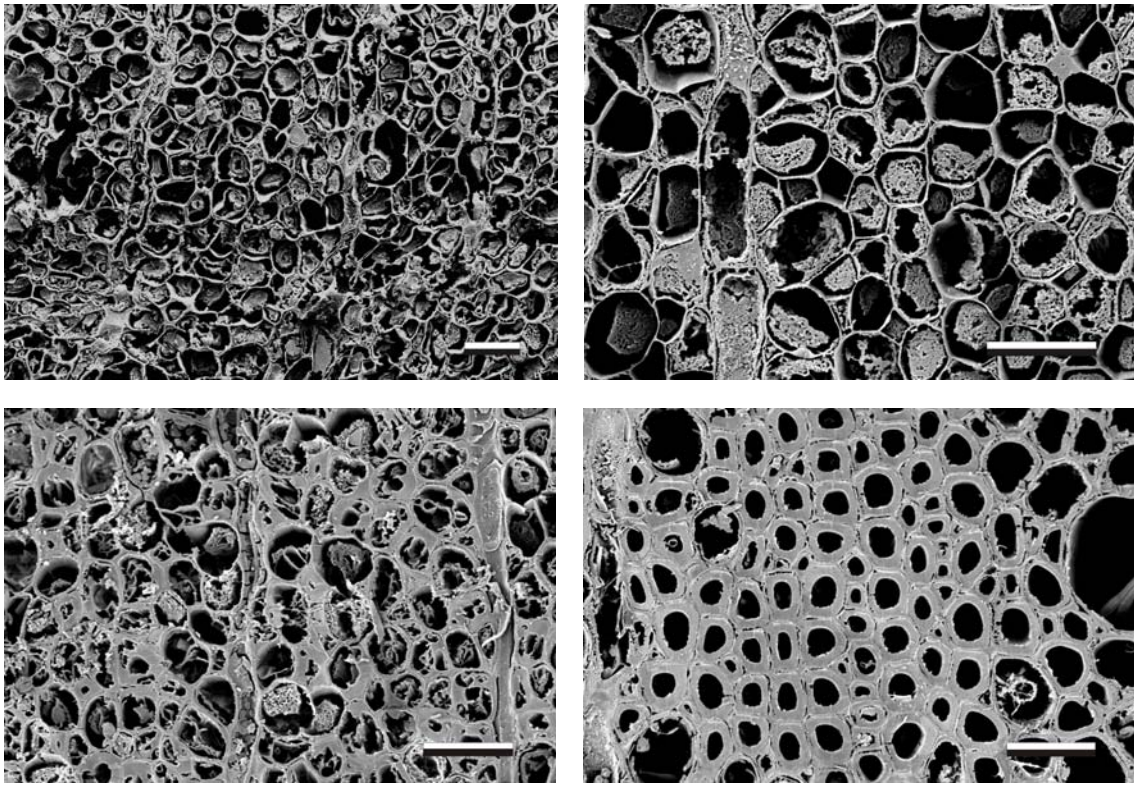


Figure 12. Scanning electron micrographs of samples taken from the inner planking (top photos) and keelson (bottom photos) from test trench 2. **a) Upper left**, Exterior wood showing attack by bacteria. The secondary wall is extensively degraded and a fragile middle lamella remains between cells. **b) Upper right**, Advanced bacterial degradation extending into the interior portion of the sample showing the advanced decay with only a matrix of degraded cell wall material left between cells. **c) Lower left**, Exterior wood of sample showing extensive soft rot and bacterial degradation. Some cell walls have soft rot cavities while others have degraded cell walls caused by bacteria. **d) Lower right**, Wood from the interior portion of the keelson sample showing relatively intact cell walls. Only a few cells show soft rot cavities or evidence of bacterial degradation.

These results have shown that different forms of microbial degradation were present in the timbers and varying depths of burial influenced the dominant type of micro-organisms present, their duration of attack and the extent and type of degradation that occurred. Undoubtedly, the bacteria and fungi responsible for the wood decay are still present in the timbers. Therefore, if the micro-environmental conditions are favourable for microbial growth, fungal soft rot and bacterial degradation of the wood, or a combination of the two will continue well into the future.

Total Sulphur and XANES Analyses

Despite the fact that the remains of the *James Matthews* will not be recovered and conserved in the near future it was decided to analyse one of the timbers in the test trench for total sulphur concentration and with sulphur K-edge XANES in order to possibly provide some information regarding the micro-environmental conditions prevalent in test trench 2. The total sulphur content and preliminary XANES spectra for sections of the core recovered from frame 2 are presented graphically in Figures 13 and 14a and b, respectively. It should be noted that the XANES spectra have not been normalised and therefore, can only be used as a qualitative indication of the ratio between reduced and oxidised sulphur species. However, the spectra show characteristic features that allow identification of the dominant sulphur compounds in the sample.

The entire core sample was found to contain intermediate sulphur concentrations ranging from 0.32 to 0.78% with an average value of $0.58 \pm 0.17\%$, with the inner regions containing less total sulphur in comparison to the exterior areas (Figure 13). The raw XANES spectra (Figure 14a and b) showed two major peaks corresponding to elemental sulphur (S_8), thiols (R-SH) and disulphides (R-S-S-R) at 2473.0eV and sulphate (SO_4^{2-}) at 2482.6eV (Sandström et al. 2003). However, the intensity maximum of the sulphate peak is approximately a factor of 3 times greater than that of elemental sulphur for the same sulphur concentration. Therefore, the spectra showed that reduced sulphur species were the dominant form, especially in the inner regions of the core sample where almost no sulphate is present because oxygen would be limited due to the

thickness of the timber (Figure 14b). On the other hand, the presence of the sulphate peak in the surface sample (0-8mm) spectrum (Figure 14a), albeit relatively small when the intensity factor difference was taken into account and the emergence of a small peak at 2481.4eV corresponding to sulphonates ($R-SO_3^-$) (Sandström et al. 2003) indicated that some oxidation of the reduced sulphur species had occurred in the upper surface of the frame when it was exposed to a more oxygenated environment. There was a very small emerging pre-peak at about 2470.5eV (Figure 14a) that was believed to be a pyrrhotite-like FeS_x phase (Sandström et al. 2002), however to reveal and distinguish this peak from the reduced sulphur peak at 2473.0eV requires careful analysis.

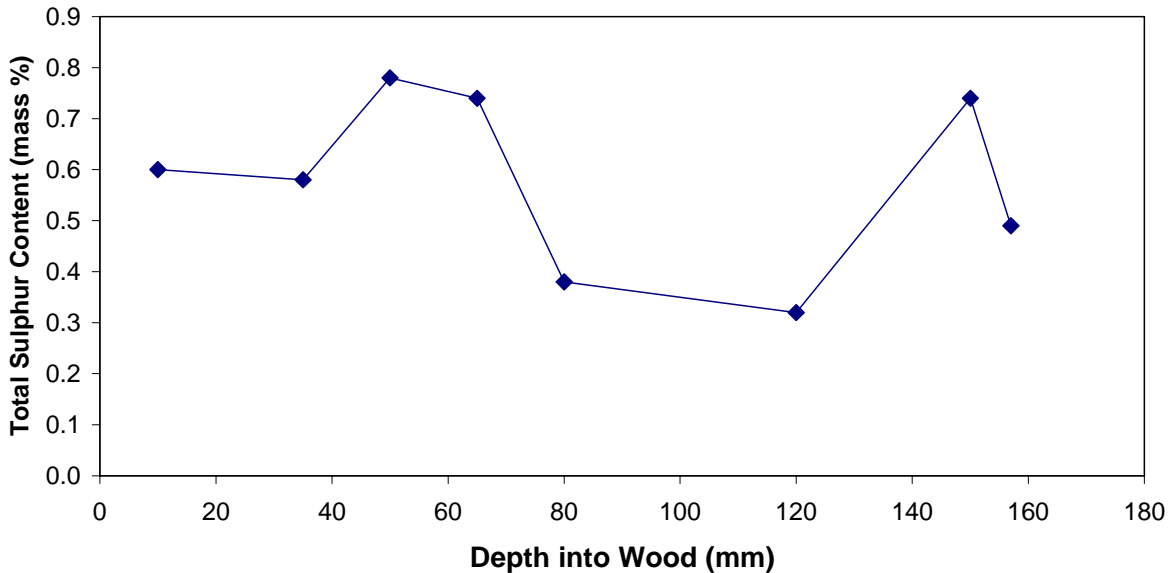


Figure 13. Depth profiles of total sulphur in frame 2.

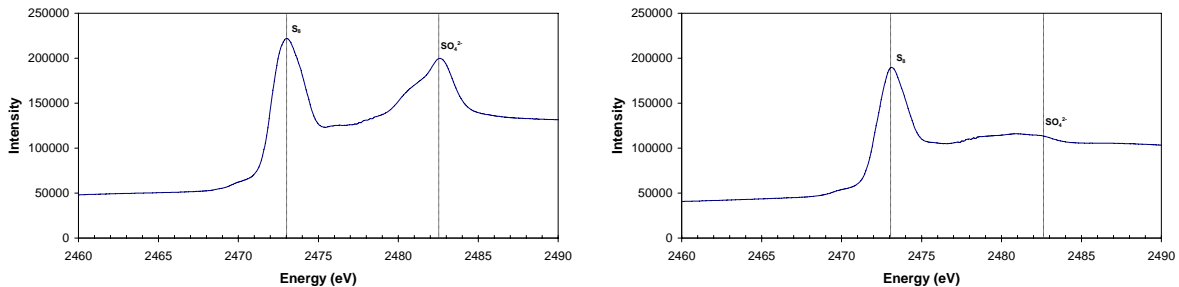


Figure 14. Sulphur K-edge XANES spectra from a) exterior frame 2 (0-8mm core section) and b) interior frame 2 (77-80mm core section).

These results correspond well to the initial stages of diagenesis in marine sediments where hydrogen sulphide produced by sulphate reducing bacteria in anaerobic environments, reacts with active sites in organic compounds present in humic matter, carbohydrates, etc forming reduced organo-sulphur species and elemental sulphur. These reduced sulphur species can then be oxidised in a step-wise process to more oxidised sulphur compounds, such as sulphate under more aerobic conditions. Iron ions are also known to catalyse these reactions. Therefore based on these results, prior to 2000 the frame had been subjected to an anaerobic, strongly reducing micro-environment for an extended period of time producing reduced sulphur species within the wood structure. The presence of more oxidised sulphur species in the outer surface of the frame suggests that the frame has been subjected to a more oxygenated environment more recently, which is in good agreement with the other analytical results previously discussed.

Conclusions

Comparisons of the results obtained from the analyses of these timbers indicated that since the initial conservation survey in 2000, there has been a significant increase in the extent of deterioration of all structural members in test trench 2. All timbers, but especially the keelson and inner planking, have been subjected to a more oxygenated and hence, aggressive environment for an extended period of time and the extent of deterioration increased over the five year period despite the use of sand bags. The extent of

degradation of the timbers increased considerably by 2003 indicating that canvas sand bags are totally unsuitable even as an interim remediation strategy, but there may have been some small decrease in the rate of deterioration with the use of the polymeric sand bags.

However, based on these trials, it was obvious that the type of polymeric sand bags chosen for stabilisation and the method of deployment was very important. The most effective method for obtaining maximum coverage with the least quantity of bags was to half fill the bags with sand and then seal the bags with cable ties near the opening so there was an air space between the sand and the top of the bag. Prior to the bags being positioned *in-situ*, the sand was distributed evenly throughout the bags so the maximum rectangular area was covered. This was where the choice of bag was important. Some of the proprietary laminated polymeric bags were so well reinforced that they were not permeable to seawater and when the half filled bags were placed on-site the increase in pressure compressed the air and the material collapsed around the sand. This made it impossible to evenly distribute the sand within the bag and maximum coverage could not be attained. Therefore, it is important to trial the type of bags prior to purchase to ensure that they are permeable enough to allow the trapped air to escape and the pressure to equalise at that water depth.

Although the results using this technique were encouraging, it could not be recommended as an acceptable method for the medium to long-term preservation of a wreck site. Hence, it will be interesting to analyse (pH profiles, U_{max} and microscopic investigations) another similar set of timber samples from test trench 2 in order to ascertain the success of the mitigation strategy (reburial with local sediment (30cm) then stabilisation of the burial mound with shade cloth) used to protect the timbers after the final sampling period in August 2005.

Sediment Trapping and Containment Methods

General

The exact positions and orientation of the two shade cloth mats, one placed off-site (*shade cloth mat*) and the other positioned over the bow region of the wreck (*bow shade cloth mat*), the artificial seagrass mat (*seagrass mat*) and the test square (*test square*) are shown in Figure 15.

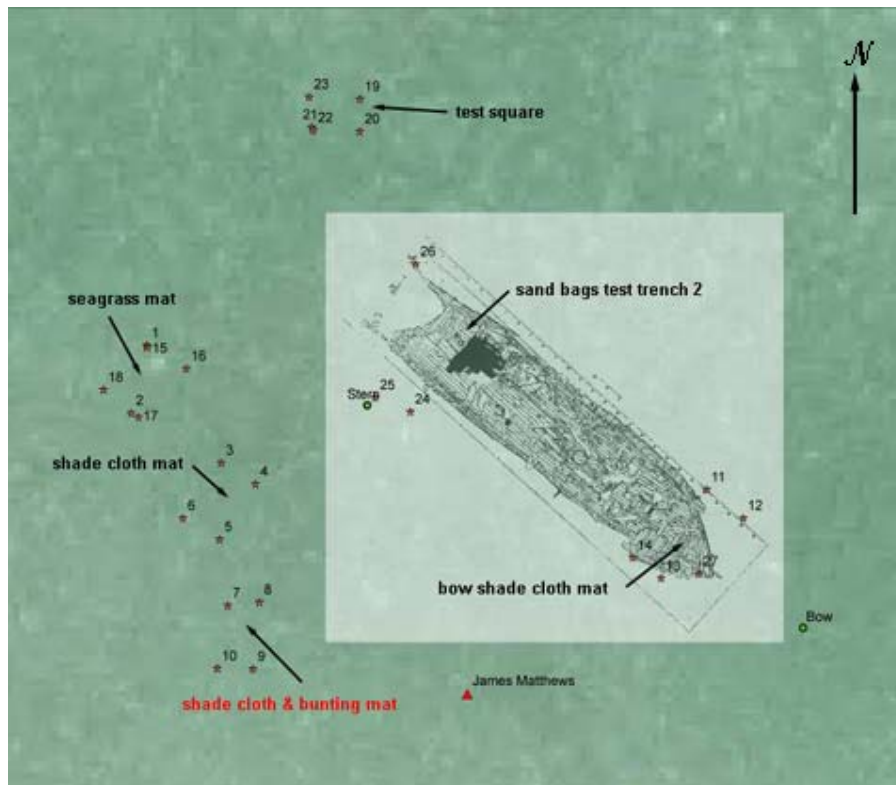


Figure 15. Positioning and orientation of the mats and the test square on the James Matthews site.

The mats were placed about 20m SW of the wreck site, orientated lengthwise in the same direction as the local sand ripples on the seabed (NE/SW transit) and approximately 10m apart in a staggered arrangement to minimise any inter-mat influences. Another shade cloth mat was deployed on the bow in order to ascertain

if there were any discernible environmental differences caused by the iron and wood located in this area. The test square was placed on a N/S-W/E axis, about 20m north of the site to minimise any effects the wreck may have on sediment movement. The three mats (4m length x 3m width) and the test square (2m² x 1m depth) were deployed in April 2005 and monitored photographically at irregular intervals over the next two years.

All mats were pre-prepared at the WA Museum, rolled up and tied with small gauge nylon rope with three lead weights attached to one leading edge of the mat prior to transportation to the site by boat. On arrival, the mats were placed in the water and if necessary, further weighed down with chain in order to sink the mats. Once on the seabed, the mats were placed in the correct orientation (lengthwise edges NE/SW transit), the weighted leading edge (SW edge) anchored with polymeric sand bags, then the nylon ties cut and the mats unfurled. All edges of the mats were then anchored with more sand bags in the manner described above for sandbagging test trench 2.

The shade cloth mats were anchored in such a way that there was excess material within the internal rectangular area of the mat, where twelve small fishing buoys were attached, evenly spaced in three rows of four (Figure 4a & b). The function of the buoys was to keep the shade cloth floating in the water column even when the mesh was heavily colonised with algae during the summer months. The suspended shade cloth would continue to trap sediment particles for a longer period of time and greater sediment accretion would occur under the mats. Unfortunately, after only one month the weight of the algal mat on the shade cloth was greater than the increased buoyancy caused by the fishing buoys and the mats had sunk to the seabed. Despite this problem, after three months there was some build up of sediment along the SW and SE edges but no appreciable sediment accretion along the NW and NE edges of both shade cloth mats (Figure 16a). In addition, toe scouring had occurred around the southern corners of the mats, exposing bivalve mollusc shells. Over the next two years, the extent of sediment build up under the mats increased until the maximum average depth along the SW edge was about 40cm, progressively decreasing to a minimum average depth of 10cm around the NE edge (Figure 16b). This gradual sediment depth differential was probably caused by the predominantly southerly movement of sediment during periods of high water movement from the north in winter causing more sand accretion towards the southern ends of the mats.



Figure 16. Sediment accretion under the shade cloth mat deployed off site after a) three months and b) two years.

The seagrass mat was anchored flush with the seabed surface (Figure 5a). After three months, there was extensive algal growth on the fronds but they maintained enough buoyancy to allow free movement in the water column. There were appreciable quantities of dead seagrass trapped under the mat but no notable sediment accretion (Figure 17a). There was also some toe scouring around the NE edge of the mat. After two years, the amount of colonisation on the fronds increased significantly and this added weight interfered with the movement of the fronds in the water column. There was more dead seagrass present and extensive scouring had occurred under the centre of the mat (Figure 17b).

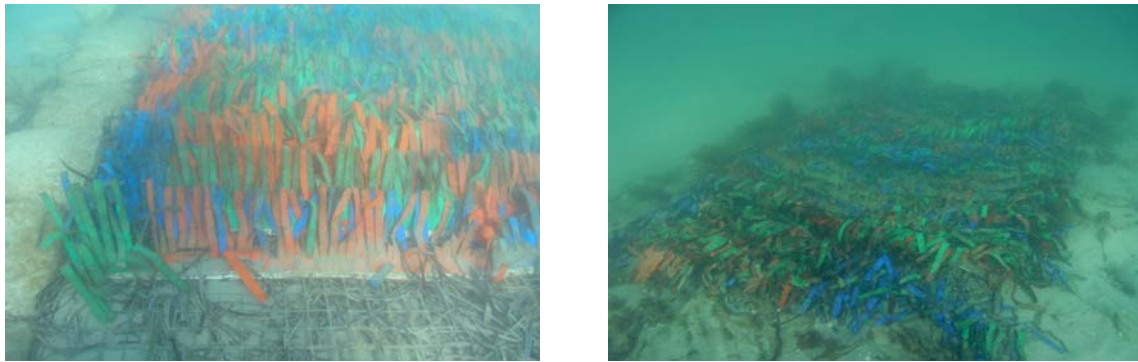


Figure 17. The artificial seagrass mat deployed off site after a) three months and b) two years.

The preparation and deployment procedure for the test square has been previously described in Winton and Richards (2005). After the test square was positioned on-site in April 2005, it was backfilled with local sediment, which was then covered with shade cloth and anchored with polymeric sand bags. After three months, the depth of sediment within the confines of the test square had diminished significantly and by 2006, it was totally devoid of sand and only the shade cloth covering and the sand bags were present in the bottom of the test square (Figure 18a). It was obvious that the sediment had been leaking from the corners of the test square. The test square was refilled in May 2007, but this time prior to backfilling, heavy gauge black polyethylene sheeting was draped over the interior of each corner to prevent any sediment loss through these gaps. It is important note that the shade cloth and sand bags in the base of the test square were not removed prior to the second refilling. After three months, there was no significant change in sediment level within the confines of the test square (Figure 18b).



Figure 18. The test square after a) one year with significant sediment loss and b) three months after refilling.

In mid 2007 sediment core samples were collected from under the SW edges of each mat (30cm in length) and within the test square (60cm in length) for microbiological and physico-chemical analyses via wet chemical techniques and ex-situ, utilising dissolved oxygen, sulphide, pH and redox microelectrodes. Baseline sediment core samples (60cm in length) were also collected for comparative assessment. The results of these analyses will be presented below.

Physical Analyses

The simplest method of presenting particle size distribution data of sediments is in graphical form by means of a histogram, where $\phi = -\log_2$ of the grain size diameter (mm). These even divisions are referred to as the phi scale, where the intervals from (-1)-0 to 4-5 represent decreasing grain size intervals ranging from very coarse sand to silt, respectively (Figure 19). The results of the particle size distribution analyses for the redeposited sediments in the test square and under the experimental mats are similar, despite differences in the total length of the core samples, therefore only the histograms of the two 60cm sediment cores from baseline 20m NW and the test square will be shown as examples (Figures 19 and 20, respectively).

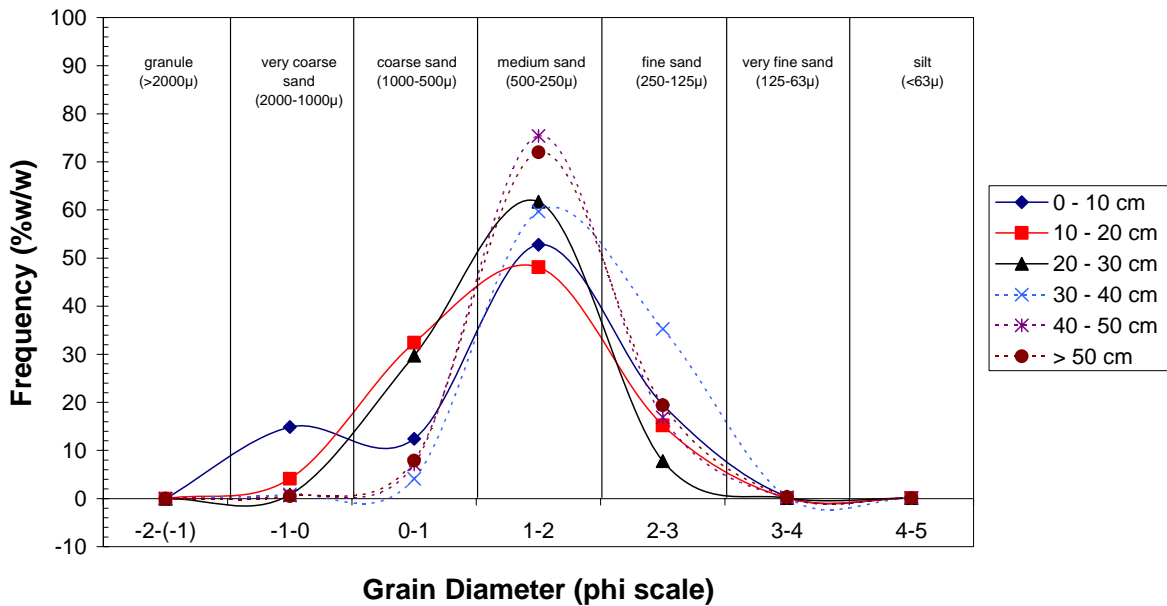


Figure 19. Histogram of particle size distribution of the baseline 20m NW sediment.

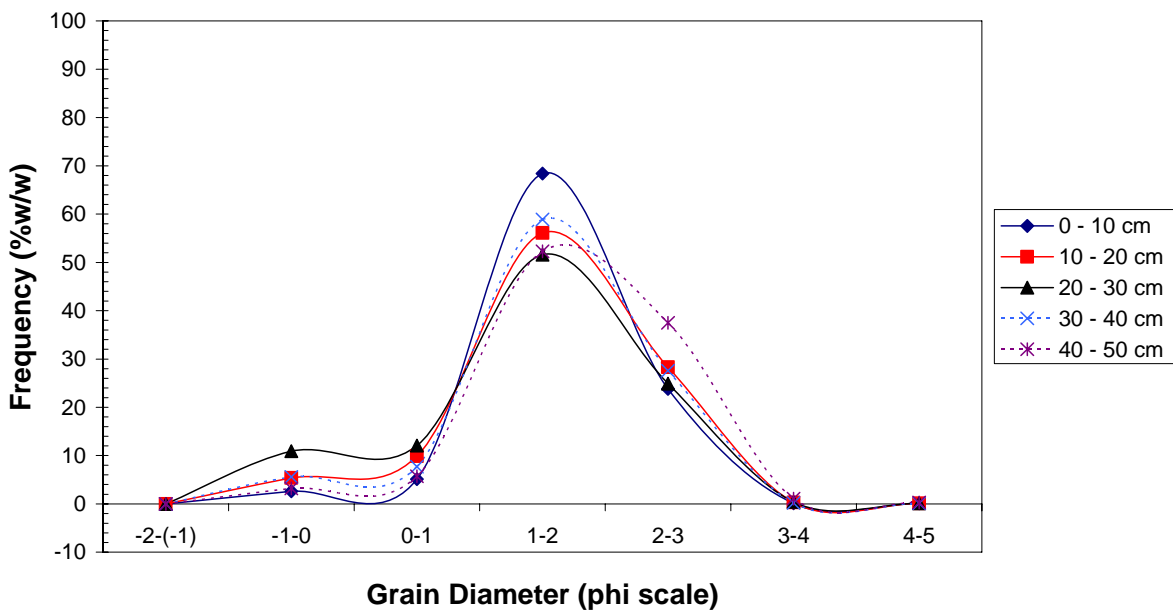


Figure 20. Histogram of particle size distribution of the test square sediment.

The sediment around the *James Matthews* site is predominantly calcareous in nature with a low siliceous content (Godfrey et al. 2005). In general, the baseline sediment consisted largely of medium (250-500µ) skeletal and detrital lithoclastic sands with some coarser grained inter-beds of predominantly skeletal grains representing gastropods and bivalves in the upper 20cm of the sediment column (Figure 19). Sorting is dependent on grain size and gives an indication of the effectiveness of the depositional medium in separating grains of different classes. The mean particle size of the baseline sediment decreased marginally with increasing sediment depth and demonstrated a trend for sorting to increase gradually from moderately well sorted to moderately well sorted as the sediment depth increased. This is consistent with sand-sized sediments, which are more easily transported and reworked by water movement. Hence, the sediments on beaches and shallow shelf areas, similar to this site, will tend to be better sorted than sediments that are deposited rapidly.

Skewness is a measure of the symmetry of the distribution and reflects the depositional process. If the distribution has a coarse "tail", i.e. excess coarse material, then the sediment is said to be negatively or coarsely skewed; if there is a fine "tail", then the skew is positive or fine. If the distribution is symmetrical then

there is no skew (Friedman 1961). The level of skewness of the baseline sediment gradually increased from negative to more positive with increasing sediment depth. This change indicated that there was more coarse grained sand in the surface sediment (0-10cm), then the distribution became more symmetrical with increasing depth until there was a slight increase in the amount of finer grained sand in the lower stratigraphic fraction (>50cm). The negative skewness of the surface sediment is typical of winnowing, where fine components have been removed by persistent wave action, however the decrease of coarser grained sand below this depth is indicative of a very stable near shoreline bed load, which is consistent with the mean grain size and sorting results for the baseline sediment.

The redeposited sediments were predominantly medium (250-500 μ) grained sands but with higher proportions of coarser grained sands throughout the sediment column compared to the baseline sample (Figure 20). In general, all stratigraphic fractions of the redeposited sediments were moderately sorted and sorting decreased marginally with increasing sediment depth. All redeposited sediments were less well sorted than the baseline sample and this is a direct consequence of the more rapid and recent deposition. All grain size intervals at all depths were strongly coarsely skewed indicating that the finer particulates had been preferentially removed by the deposition processes. In the test square this would have occurred during dredging as the finer material was mobilised into the water column and only the coarser, more dense sand would be deposited within the test square. Similarly, during periods of high water movement, the fines would again be suspended in the water column and kept in suspension by fluid turbulence allowing these finer particles to flow over the shade cloth mats whilst the coarser grained sands in the bed load were preferentially trapped. Finally, scouring has caused the preferential loss of fines under the seagrass mat. This is supported by the fact that the lower fraction (>20cm) in this sediment core was less coarsely skewed than the shallower fractions.

These results indicate that the redeposited sediments under the shade cloth mats and even in the test square, that was only refilled 3 months previously, are stable and reflect the major grain size distribution of the bed load in the immediate surrounds albeit with some loss of finer particulates due to the deposition process. The sediment under the seagrass mat is subjected to scouring and therefore, would probably not be a viable option for trapping and containing sediment on this particular site.

Chemical Analyses

During the initial conservation survey in 2000, sediment core samples were collected from the test trenches on the *James Matthews* site (Figure 2). At this time, the sediment and the elutriation waters, obtained by extracting the pore water from the sediment fractions with a known volume of seawater, were subjected to a large range of chemical analyses and the results are detailed in Godfrey et al. (2005). Based on these published results and more importantly, monetary constraints it was decided to significantly reduce the number of chemical analyses performed on the sediment core samples recovered in 2007 from the reburial experiments. In addition, since the concentration and composition of analytes in elutriation waters differ significantly from those measured directly in pore waters it was decided to remove the pore water from the sediment fractions without recourse to extraction with seawater. This of course, means that direct comparison of the pore water results with the elutriation water results obtained in 2000 is not feasible, however these more recent analytical results should provide more relevant information regarding the pore water chemistry in the sediments at different depths and hence, the effects on reburied materials.

The sediment fractions were analysed for total sulphur and extractable organic matter (EOM) content and the pore waters for pH, sulphide, sulphate, total sulphur and nutrients (ammoniacal nitrogen (NH₃), nitrate nitrogen (NO₃⁻), total nitrogen, soluble reactive phosphorus, total phosphorus). The average results for each sediment core are shown in Tables 1 and 2.

The average pore water recovery was 12% of the initial mass and the average water loss on drying was 12% giving a total average water content of 24% for the redeposited and baseline sediments. These results were in agreement with the moisture contents of the core samples measured in 2000, which were on average 20%. The water content of freshly settled sediment increases with decreasing particle size. For example, the water content of freshly settled medium grained sand (250-500 μ) is 45.0% (Pearson 1987, p. 9), which is considerably less than clays (1-4 μ) (~86%). In addition, chemical processes and the downward pressure of surface sediments as sorting increases, compresses and consolidates the sediment particles, causing the upward advection of water, leading to lower moisture contents as sediment depth increases. The average water content of these sediment samples was relatively low indicating that the redeposited sediments are stable and relatively well-sorted.

There appeared to be no significant differences between the pH profiles of the reburial sediments and the baseline sample (Table 1). Generally, lower pHs were measured in the 0-10cm surface fractions of all sediments compared to the surrounding seawater and this is not unusual as this is the region where most

biological activity and redox reactions occur, which tends to produce hydrogen ions and more acidic degraded organic matter. After this minimum there was a general trend towards more alkaline pHs as the sediment depth increased indicative of a decrease in biological activity. However, it should be noted that there may be some contamination of the lower sediment fractions with bulk seawater due to the upwelling effect outlined in the experimental section despite careful attempts to minimise this particular sampling problem.

Table 1. Average concentrations of sulphur species, organic components and pH in the sediments and pore waters measured in 2007.

Parameter	Pore Water				Sediment	
	pH	Sulphide (mg/l)	Sulphate (mg/l)	Total Sulphur (mg/l)	Total Sulphur (%)	EOM (mg/kg)
Seagrass mat	7.92±0.10	0.39±0.35	2800±61	915±20	0.21±0.02	48±28
Shade cloth mat	8.03±0.08	0.16±0.02	2700±233	892±51	0.22±0.05	90±23
Bow shade cloth mat	8.00±0.10	0.24±0.01	2863±72	926±8	0.23±0.01	73±8
Test square	7.90±0.08	1.45±2.88	2728±118	891±28	0.20±0.01	57±13
Baseline 20m NW	7.90±0.13	0.07±0.01	2773±206	893±53	0.20±0.01	52±23
Seawater	8.00	0.06	2790	915	na ¹	na

¹ Not applicable

Extractable organic matter (EOM) includes all particulate and dissolved organic matter including degraded plants, animals and organic chemicals from anthropogenic sources. Generally, as would be expected, the levels of EOM were greatest in all surface sediments where particulate organic matter (POM) and dissolved organic matter (DOM) concentrate as it settles through the water column (Table 1). The concentrations then decreased with increasing sediment depth. There appeared to be slightly more EOM in the 0-20cm fraction of the mat sediments compared to the test square and the baseline samples. This is not unexpected due to the extended length of time (2 years) these experiments had been deployed, the very dense algal mats that colonised both the shade cloth surfaces and seagrass fronds and the presence of any residual detrital plant material in the seagrass sediment not removed prior to extraction. The test square sediment column had an EOM concentration profile similar to the baseline sample but the levels increased markedly after about 30cm. This increase can be directly attributed to the presence of decaying organic matter on the shade cloth and sand bags left *in-situ* when the test square was refilled in May 2007 for the second time. Overall the baseline sample had the lowest concentrations of EOM but there were unusually high levels in the 40-50cm fraction indicating that there was some form of extraneous organic matter in this area. In 2000, dead rhizome and seagrass had been identified at this depth interval in other sediment cores sampled in this area (Godfrey et al. 2005). It is well known that higher levels of organic matter can lead to increased microbial activity even in deeper sediments (Muraoka 1966, Libes 1992, Nyström- Godfrey & Bergstrand 2007, Richards & MacLeod 2007).

The total sulphur content includes any sulphates, sulphides and naturally occurring sulphur-containing compounds, such as mercaptans, etc. The test square and baseline sediments possessed the lowest total sulphur contents and the distribution was relatively uniform throughout the sediment column (Table 1). The test square was refilled only three months prior to sampling with dredged local sediment that was in relatively close proximity (~10m) to the sampling position of the baseline sample, therefore it is not surprising that the total sulphur contents were similar. The sediments under the mats had higher total sulphur contents than the test square and baseline samples, especially in the surface fractions (0-10cm) where the concentration of organic matter and biological activity are highest. After this depth, the concentration of total sulphur in the seagrass and off site shade cloth sediments decreased to baseline levels, however the total sulphur contents of the bow shade cloth sediment increased. This increase may have been caused by the presence of an iron chain buried near the sediment sampling site. Some anaerobic and facultative bacteria are known to increase iron corrosion rates in sediments and dependent on the bacteria type and metabolic mechanism, form different sulphur-containing compounds and corrosion products (Pearson 1987, p. 15, Richards & MacLeod 2007).

Marine sediments are sites of many chemical reactions, such as sulphate reduction, as well as mineral precipitation and dissolution, any of which can alter the major ion ratios. As a result, the chemical composition of pore water is usually quite different from that of seawater (Libes 1992). The pore water samples had similar average total sulphur values to that of the bulk seawater and the distribution was relatively uniform in the upper 30cm of the sediments (Table 1). The deeper fractions in the baseline and test square samples however, showed slight decreases in the total sulphur content. The total sulphide concentrations in the pore waters of the redeposited sediments were generally very low but significantly higher than the baseline sample, which had similar values throughout the sediment column to that of the bulk seawater (0.06mg/l). With the exception of the bow shade cloth mat sample where sulphide levels remained

relatively uniform throughout the entire sediment column, the sulphide distribution in the redeposited sediments appeared to decrease marginally with increasing depth. The seagrass mat sample had comparatively higher concentrations of sulphide present in the surface fraction (0-10cm) (0.79mg/l), which may be attributed to the large quantities of dead seagrass present to a depth of about 15cm. There was also an extremely high level of sulphide (6.60mg/l) in the surface fraction of the test square sediment sample that appeared anomalous because after this depth interval, the average concentration in the pore water throughout the sediment column decreased to about 0.2mg/l. Possibly there was some contamination of the pore water sample with extraneous material containing high levels of sulphides. The average amount of sulphate in all pore waters was similar to the sulphate concentration in the bulk seawater. The distribution of sulphate was relatively uniform throughout the sediment columns and there was no discernible difference between the redeposited samples and the baseline sediment.

The results of the nutrient analysis of the bulk seawater indicated elevated levels of total nitrogen (N) (0.51mg/l) and total phosphorus (P) (0.13mg/l) when compared with the Environment Australia (2002) standards (Table 2). As dissolved inorganic nitrogen and phosphorus are biolimiting elements that may, at least partly control or limit phytoplankton growth, the levels of inorganic P (0.01mg/l) and inorganic N (0.04mg/l) in the bulk seawater may cause increased algal growth as the levels are equal to or exceed the quoted nuisance values (P = 0.01mg/l; N = 0.03mg/l) (Environment Australia 2002). In support of this, a large proportion of the total N and P in the seawater was in organic form possibly indicating an increase in phytoplankton assimilation of the dissolved inorganic carbon (C), N and P species resulting in an increase in the production of particulate organic matter (POM). This increase in POM will stimulate the growth of heterotrophic organisms, such as aerobic bacteria and fungi in the water column, which could significantly increase the deterioration rates of any exposed wreck material on site.

Table 2. Average nutrient levels (mg/l) in the pore waters extracted from the sediments in 2007.

Parameter	Ammonium Nitrogen	Nitrate Nitrogen	Organic Nitrogen	Total Nitrogen	Soluble Reactive Phosphorus	Organic Phosphorus	Total Phosphorus
Seagrass mat	2.7±2.1	0.09±0.13	1.45±0.22	4.27±1.75	0.07±0.03	2.27±1.92	2.33±1.89
Shade cloth mat	4.5±0.7	0.06±0.08	2.03±0.74	6.60±0.26	0.06±0.03	2.30±1.56	2.36±1.57
Bow shade cloth mat	3.3±1.0	0.02±0.02	1.68±0.42	5.03±1.45	0.08±0.02	0.79±0.20	0.87±0.21
Test square	6.9±4.9	0.02±0.02	0.38±0.54	7.34±4.41	0.07±0.06	1.34±2.29	1.41±2.29
Baseline 20m NW	0.5±0.6	0.06±0.05	1.30±0.73	1.89±1.24	0.09±0.02	0.91±1.28	1.00±1.25
Seawater	0.029	0.01	0.47	0.51	0.01	0.12	0.13

The results from the pore water analyses showed significantly higher average concentrations of nutrients in comparison to the seawater (Table 2). Significant amounts of total N and P were present in the surface sediments and at depths where there were larger quantities of extractable organic matter (EOM) (Table 1). This is to be expected as nutrients are closely associated with particulate organic matter (POM), especially on the sediment-seawater interface where most biological activity occurs.

A high proportion of the total N in the reburial sediments was present as total dissolved inorganic nitrogen (DIN), comprised of ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-) ions formed by the bacterial oxidation of dissolved organic nitrogen (DON) whereas a higher proportion of the total nitrogen flux in the baseline sample was present as organic nitrogen, indicative of less heterotrophic bacterial activity in this sediment. Generally, in the upper sediment fractions the levels of nitrate/nitrite nitrogen (nitrate N) increased with decreasing concentrations of ammonium nitrogen (ammonium N), which is consistent with the marine nitrogen cycle (Libes 1992) where ammonium ions are oxidised in a step-wise manner (nitrification) by specific aerobic heterotrophic bacteria.

In the baseline sample, the total N content decreased and the proportion of organic N to DIN increased with increasing depth, which is consistent with the gradual decrease in the amount of extractable organic matter in the sediment with depth and the marine nitrogen cycle. That is, the presence of larger concentrations of ammonium N in the surface sediments is due to the remineralisation of particulate organic nitrogen (PON) and the subsequent degradation of the DON by ammonification. Ammonium ions will also be produced by nitrogen fixing of some benthic heterotrophic bacteria and cyanobacteria that are abundant in coastal regions. The subsequent decline in ammonium N levels after the first 10cm of the sediment and the corresponding higher levels of nitrate N levels persisting to greater depths into the sediment column is also consistent with the nitrification of ammonium ions by heterotrophic bacteria.

Similarly, the distribution of total N, organic N and DIN in the seagrass mat sediment mimicked that of the baseline sample, except in the surface sediment (0-10cm), which contained significantly higher

concentrations of total N with a higher proportion of DIN to organic N. These higher levels would be a result of microbiological degradation of the dead seagrass trapped directly under the mat.

The sediments under the shade cloth mats had very high concentrations of total N throughout, with most of the N present as DIN in the surface sediments (0-10cm) and in the deeper >20cm fractions. The DIN levels were lowest in the mid (10-20cm) fractions. This anomaly can be simply explained by the sedimentary deposition process that occurred under the shade cloth. These mats were placed directly on the seabed surface where biological activity and hence, the concentrations of POM, total N and DIN were already highest. Over the next two years, the sediment slowly accumulated under the mats but there remained a significant store of POM and DIN in the original seabed surface sediment, which subsequently became the "deeper" fractions when buried under the 30cm of trapped sediment.

The test square sediment sample had only slightly higher total N levels in the first 20cm as compared to the baseline sample but a significantly higher proportion of this was present as DIN, indicating that the microenvironment under the shade cloth and sand bags used to confine the sand inside the test square was more conducive to microbial activity than that of the surrounding sediment in the local area. However, the total N content of the test square sample increased exponentially after 30cm with most of the N present as DIN indicating strong microbiological activity at these lower depth intervals. The large increases in N levels would be directly associated with the microbial decay of the large quantities of particulate organic matter attached to the surfaces of the sand bags and shade cloth left in the base of the test square prior to refilling in May 2007. Even in less oxygenated, deeper sediments, anaerobic and facultative micro-organisms will utilise nitrates to oxidise organic material producing ammonium ions (denitrification) if there are considerable stores of particulate organic matter.

The levels and distribution of the phosphorus (P) in the sediments were consistent with the nitrogen results (Table 2). That is, in the sediment fractions containing large quantities of decaying organic material there were correspondingly high concentrations of total P with most of it present in organic form associated with or bound to the particulate organic matter consistent with the marine phosphorus cycle (Libes 1992).

The results from the chemical analyses indicate that the redeposited sediments contain significant stores of organic matter and nutrients that will directly influence biological activity. The sediments also possess relatively low concentrations of sulphides and concomitant high levels of sulphates, which tends to suggest that the sediments are not very reducing in nature. This may have an effect on the deterioration rates of organics and metals buried via these remediation methods.

Microbiological Analyses

The main biodegrading organisms of wood found in marine environments are the wood boring molluscs and crustaceans, the lignicolous fungi and cellulose digesting marine bacteria. Marine fungi and bacteria can degrade wood surfaces in the sea. The resulting soft wood surface is often quickly removed by marine borers, causing extensive decay of exposed timbers. As timbers or parts of timbers become buried in the sediments they will be degraded by organisms that require less oxygen until they will only be subjected to the relatively slow action of near anaerobic erosion bacteria (Fazzani et al. 1975, Björdal 2000, Björdal & Nilsson 2002).

From the aforementioned microscopic analysis results of wood samples recovered from structural timbers in test trench 2, it is obvious that wood borers, soft rot fungi and tunnelling, cavitation and erosion bacteria are active on the *James Matthews* site. The speciation of the bacteria responsible for wood degradation still remains unknown despite concerted efforts to isolate and identify these micro-organisms (Daniel & Nilsson 1997, Helms & Kilstrup 2002). The scientific reasoning behind the microbiological analyses of the sediment samples was to identify the different fungi and bacteria present at different depths in the reburial sediments in order to better understand the synergistic relationship between sediment chemistry and microbial activity and possibly, in the future, their effects on reburied wreck materials. At no time was there any attempt to specifically isolate and speciate the wood degrading bacteria. The results of the microbiological analyses of the core samples collected from the reburial experiments and the two reference areas off site are summarised in Table 3.

Table 3. Comparison of organisms identified in the sediments at increasing depth intervals.

ORGANISMS	Seagrass Mat	Shade Cloth Mat	Bow Shade Cloth	Test Square	Baseline (20m SW)	Baseline (20m NW)
FUNGI						
<i>Kloekera apiculata</i>					0-10	
<i>Rhodotorula rubra</i>		0-30				
<i>Saccharomyces sp</i>					30-60	
<i>Debaryomyces hansenii</i>				20-60		
Mould (unidentified)		0-30				
BACTERIA						
<i>Bacillus sp</i>	0-10					
<i>Nitrobacter</i>	+	+	+	+	+	+
<i>Nitrosomonas</i>	+	+	+	+	+	+
<i>Pseudomonas sp</i>	0-10; 20-30		+	0-20	0-10; 30-60	0-10
<i>Rhodopseudomonas capsulata</i>	+	+	+	+	+	+
Sulphate Reducing Bacteria	20-30			+	0-20	0-20; 50-60
<i>Thiobacillus denitrificans</i>						
<i>Thiobacillus feroxidans</i>						
<i>Vibrio sp</i>						
Iron Precipitating Bacteria						
<i>Desulfovibrio sp</i>						
<i>Clostridium sp</i>						
Enterobacteriaceae (<i>Klebsiella</i>)		0-10			0-10	

+ = present at all depths
shaded areas = no growth

The organisms identified in these sediment samples are typical of seawater, seagrass beds and/or marine sediments (Jones et al. 1976, Libes 1992). There were a variety of organisms identified throughout the sediment samples including fungi, aerobic bacteria, facultative aerobes and anaerobes and obligate anaerobes. Some of these organisms were distributed throughout the entire sediment core (0-60cm), indicating the likelihood that aerobic and anaerobic microzones exist in very close proximity to each other (Muraoka 1966).

Soft rot fungi (e.g *Lulworthia*, *Halosphaeria*, *Pleospora*) are very common degraders of wood in oxygenated marine environments and cause cellular changes, which considerably weaken the wood structure. The fungi and yeasts (a sub-class of fungi) identified in these sediments are ubiquitous in the marine environment but none of these organisms cause soft rot. Moulds and yeasts tend to utilise nutrients within the ray parenchyma cells and tracheid lumina but do not have the ability to degrade wood cell walls (Blanchette et al. 1990, Blanchette & Hoffmann 1994, Björdal & Nilsson 1999, 2002, Björdal 2000, Blanchette 2000). Interestingly, some fungal species were identified in the deeper sediments where oxygen was limited. *Rhodotorula rubra* is microaerophilic and could exist in the deeper fractions, however as the vegetative state of most fungi requires oxygen to survive and multiply, it is more likely they were present in these deeper sediment fractions as spores and growth was initiated in the laboratory when the appropriate aerobic culture produced conditions conducive to microbial growth.

Bacillus sp. were present in the first 10cm of the seagrass sediment and can be either aerobic or facultative organisms. *Pseudomonas sp.* were identified in every sediment sample at most depths with the exception of the sediment under the shade cloth mat. Most of these organisms are strict aerobes, except for those species that can use denitrification as a means of anaerobic respiration. They are common inhabitants of marine water environments where their activities are important in the remineralisation of organic material. *Bacillus sp.* and *Pseudomonas sp.* are examples of cellulolytic wood colonising bacteria, which are commonly found in seawater and marine sediments. Some micro-organisms, such as *Bacillus cereus* and *Bacillus circulans* are able to degrade the non-lignified pectin membranes in bordered pits and ray parenchyma cells, leading to increased permeability, but they do not directly affect wood strength (Dunleavy et al. 1973, Fazzani et al. 1975, Libes 1992, Björdal 2000).

Rhodospseudomonas capsulata was identified throughout all sediment core depths. They are phototrophs, however, some species can carry out oxidative metabolism in the dark under microaerophilic conditions. These organisms can also fix nitrogen, producing ammonium ions, which can stimulate fungal and bacterial growth. They are abundant in polluted waters and are often found in mud and stagnant water.

Nitrosomonas sp. and *Nitrobacter sp.* were also found in all sediments at all depth intervals, which is not surprising as they are ubiquitous in the marine environment and play an important role in the marine nitrogen cycle through nitrification. Ammonium ions produced by heterotrophic bacteria through ammonification of dissolved organic nitrogen stimulates the growth of *Nitrosomonas sp.*, which oxidise the ammonium ions to nitrite ions. Decreasing concentrations of ammonium limit the growth of *Nitrosomonas sp.* and increased levels of nitrite stimulates the growth of *Nitrobacter sp.*, which can then oxidise the nitrite to nitrate. Nitrification is a strictly aerobic process, however nitrification and denitrification are tightly coupled in the sediments due to redox heterogeneity. For example, organic-rich faecal particles form anoxic microzones in the surface sediments. Conversely irrigating activities of macrofauna, such as marine worms produce oxic microzones below the redox boundary. Therefore, nitrification can occur at greater depths than would normally be expected based on dissolved oxygen flux in the sediments.

Klebsiella sp. were identified in the surface fractions of the shade cloth mat and the baseline 20m SW sample. They are facultative anaerobic bacilli and can exist in both aerobic and anaerobic environments. These organisms can reduce nitrate to nitrite and can also fix nitrogen forming ammonium ions, stimulating soft rot activity.

Sulphate reducing bacteria were found at different depth intervals in all sediments, with the exception of both shade cloth mats. Attempts were made to identify them to genus, such as *Vibrio sp.* and *Desulfovibrio sp.* but they were not positively identified. They are usually strict anaerobes but as described previously, anoxic microzones can exist in more oxygenated surface sediments. Sub-surface bacteria, like *Desulfovibrio sp.*, are responsible for much plant decomposition, such as seagrass, and utilise sulphate as an electron acceptor instead of oxygen under anaerobic conditions. Some species, such as *Desulfovibrio desulfuricans* have been associated with deterioration of cellulosic materials by possibly degrading non-lignified cellulosic materials in ray parenchyma cells and pit membranes, however, to this point, no anaerobic cellulose degrading bacteria have accomplished conclusive degradation of wood cell walls (Björdal 2000; Florian et al. 1977).

More importantly, these sulphate-reducing bacteria can promote iron corrosion, which is the second most abundant material type on the *James Matthews* site after wood. They continuously depolarise the cathodic region by removing molecules of hydrogen and use this to reduce sulphate in solution to reduced sulphur species. There can also be a symbiotic relationship between more aerobic micro-organisms and sulphate-reducing bacteria, which can cause increased corrosion of iron under more oxygenated conditions. For example, aerobic cellulolytic bacteria cannot directly corrode iron but they utilise oxygen during remineralisation of organic matter, producing a more anoxic microenvironment under the bacterial slime where sulphate reducing bacteria can multiply and promote corrosion of the iron substrate. In addition, as most iron on shipwrecks is associated with structural timbers, degradation of the non-lignified cellulosic materials in wood by these types of bacteria increases the permeability, allowing the reduced sulphur species and iron corrosion products formed by the microbial corrosion of iron to more readily diffuse into the wood cell structure. The post conservation problems associated with the oxidation of these reduced sulphur species is a well known phenomenon (Sandström et al. 2002, 2003).

It is evident that a wide range of aerobic, microaerophilic, facultative and anaerobic micro-organisms were present in these sediments and there was very little difference observed between the redeposited and baseline sediments. True wood degrading bacteria are those that can degrade ligno-cellulosic material. Some of the bacteria identified in these sediment samples may be scavenging bacteria, which utilise simple sugars associated with the bacterial slime in the amorphous residual material formed during bacterial degradation of wood but they are not true wood degraders (Florian et al. 1977, Blanchette et al. 1990, Nilsson 1999, Björdal 2000). The inter-relationships between micro-organisms in the sediment and other agents of wood destruction in marine environments are extremely complex and more research is required in order to better understand the synergistic effects they have on the reburial environment and the long-term preservation of different material types.

Microelectrode Analyses

Regular monitoring of the physico-chemical environment of the reburial experiments is very important in order to quantitatively assess the changes that occur in the sediment so the effect of the experiments on the long-term preservation of the wreck material may be predicted. Wet chemical analysis of the sediment core samples is labour intensive and ultimately, very expensive. This means that the number of samples that can

be analysed by these methods is limited. Therefore, ex-situ measurement of sediment cores with microelectrodes provided an alternative analytical regime that was much less expensive and could be carried out at more regular intervals. The results of the dissolved oxygen and sulphide contents and the pH and redox potentials measured in the reburial and baseline sediment cores are shown in Figures 21a and b and 22a and b, respectively. All results from the microelectrode analyses were anomalous with no discernible trends consistent with well established natural biogeochemical processes. Obviously there were significant problems associated with the use of the microelectrodes in these types of sediments and this will be the focus of subsequent discussions.

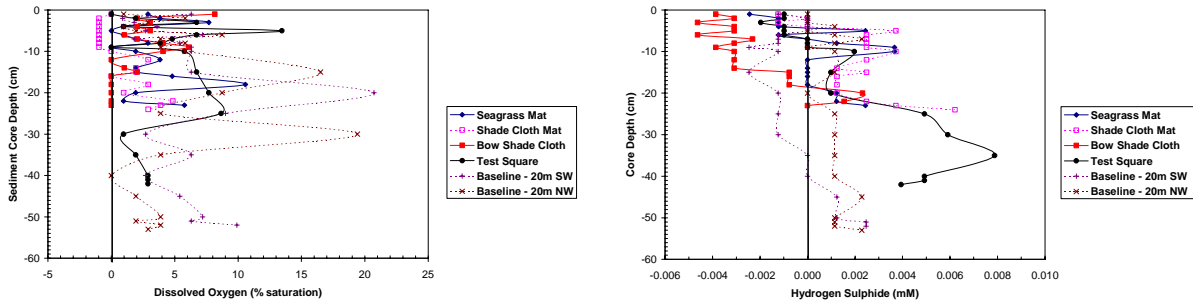


Figure 21. Profiles of a) dissolved oxygen and b) sulphide with increasing sediment depth.

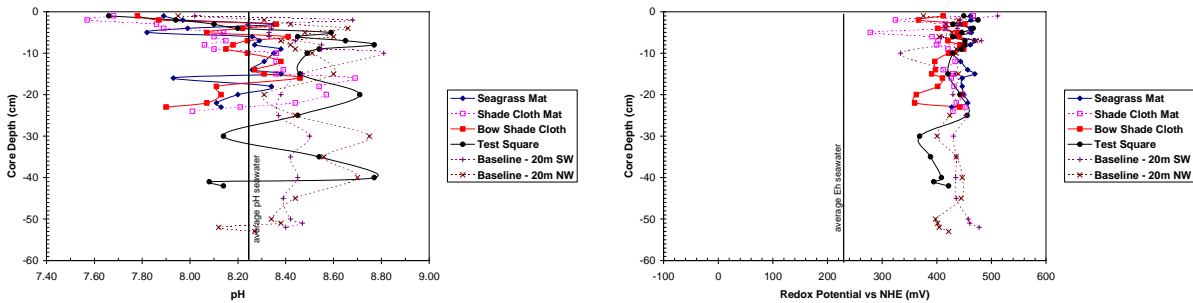


Figure 22. Profiles of a) pH and b) redox potential with increasing sediment depth.

Based on the results of other studies (Matthiesen et al. 2004, Gregory 2007) the concentration of dissolved oxygen should be highest in the surface fractions and then decrease sharply with increasing sediment depth. The dissolved oxygen contents varied considerably (0-20%) throughout these sediment cores (Figure 21a) and there appeared to be no noticeable trends emerging with increasing depth. The variability in the measurements could be attributed to a number of factors, the most important of which would be the low moisture contents of these moderately well sorted, medium grain calcareous sediments, affecting the performance of the microelectrode. The oxygen microprobe is a miniaturised Clark-type oxygen sensor and the design relies on the external partial pressure of oxygen in the sample to drive oxygen through the silicone membrane on the sensor tip, which is then reduced at the gold cathode surface producing a measurable current. However, if there is very little interstitial water in the area of measurement then the diffusion of oxygen through the membrane may be disrupted leading to erroneous results that do not accurately represent the ambient conditions.

Generally, these core samples appeared to have significantly less pore water in the mid fractions compared to the surface sediments (1-3cm) and the last few centimetres of the core. This problem may have been exacerbated by the vertical storage of the sediment cores in the fridge prior to measurement, allowing the pore waters to migrate towards the base of the core sample. This vertical migration of pore water affected the surface sediments to a lesser extent as there was a column of seawater in the head space above the sediment column. The increase in the dissolved oxygen concentration towards the base of the samples (Figure 21a) may be due to a combination of this downward migration of pore water and the upwelling effect caused by the core sample collection procedure described previously.

The sulphide profiles for the sediment cores are shown graphically in Figure 21b. Many of the measurements indicated negative concentrations of sulphide in the sediments. Some of the dissolved oxygen contents (Figure 21a) were also negative. These anomalies are directly related to the sensitivity of the sensors to temperature and salinity. The dissolved oxygen and sulphide microelectrodes were calibrated at higher temperatures (20°C) and in lower salinity solutions (distilled deionised water or pH 4.0 buffer solution, respectively) compared to the sediment samples (T = 4°C and salinity = ~36ppt). However, if the absolute

values are ignored, the profiles indicate that the concentration of sulphide increases with increasing depth, which is to be expected as more suboxic and reducing conditions usually occur with increasing depth into sediments.

The pH measurements for all sediment cores varied significantly and many of the results were considerably higher than the pH of bulk seawater (Figure 22a). This is contrary to the general understanding of pH changes in sediment through marine biogeochemistry studies (Libes 1992). These large increases in pH would be a direct consequence of drilling into the polycarbonate cores prior to measurement. Despite the fact that extreme care was taken not to penetrate the sediment with the drill bit, the drilling action probably caused some mechanical dissolution of finely divided calcium carbonate into the interstitial water and hence, a localised increase in pH was observed.

The redox potential measurements produced the worst results with average readings between 400mV and 450mV (relative to NHE) across all depth fractions, all significantly higher than the average redox potential of aerobic seawater in the immediate vicinity of 234 ± 45 mV. This belies the visual observations of the sediment cores that ranged from very light grey on the surface becoming progressively darker with depth. The platinum working electrode became poisoned very quickly and required considerable rinsing in running water after only a couple of measurements in order to attain the pre-measurement potential in distilled deionised water. One possible solution to this problem may be to catalytically decompose the organic complex chemisorbed onto the poisoned platinum electrode surface in peroxide solution. Another solution would be to manufacture a redox electrode that utilises a rhodium working electrode, which is not prone to poisoning with sulphides and organic complexes.

Another more general problem is that the calibration of all microelectrodes was performed at room temperature but the cores were measured almost directly after removal from the storage fridge. Calibration of the microsensors at a constant temperature of 4°C may be difficult to maintain, therefore the alternative would be to store the core samples at room temperature and measure as soon as possible after retrieval. Another improvement would be to calibrate the microsensors at the same salinity as the samples using a 36ppt salinity standard as the base for making up all calibration solutions. In addition, horizontal storage of the core samples immediately upon recovery may minimise the migration of the interstitial waters. If horizontal storage does not improve this migration problem, we may have to consider rewetting the sediments with a few drops of seawater collected from the site to improve the electrical connectivity in areas where there is minimal interstitial water.

Obviously more method development is required before any meaningful results can be obtained with the microelectrodes in these types of calcareous sediments. Hopefully in the future, the microelectrodes can be used to measure these important environmental parameters directly in sediments without recourse to expensive wet chemical techniques and provide important information on the general processes ongoing in the reburial sediments and hence, their suitability for long-term archaeological preservation.

Conclusions

It is a well known fact that better preservation of archaeological material occurs in more stable environments, characterised by anoxic, highly reducing, near neutral pH conditions with minimal biological activity.

The results of the physical analyses indicated that the reburial sediments were stable with moderately well sorted medium grained calcareous sediments. However, the sediment under the seagrass mat was subjected to scouring and therefore, would probably not be a viable option for trapping and containing sediment on this particular site.

The results from the chemical analyses indicated that the redeposited sediments contained significant stores of organic matter and nutrients that could directly influence biological activity. In addition, there was a wide range of micro-organisms identified in the reburial sediments but there was little difference when compared to those present in the baseline sediments. More importantly, there were no true wood degraders identified in any of the sediments. However, the results from the microscopic analyses of some structural timbers indicated the presence of lignocellulosic degrading bacteria in the buried wood.

The low levels of total sulphides in the reburial sediments suggest that these sediments are not very reducing in nature. This may have an effect on the deterioration rates of organics and metals buried via these remediation methods. Unfortunately, the results from the microelectrode analyses were erroneous and could not be compared with the results of the wet chemical analyses. More method development is required before this less expensive technique can provide reliable additional information regarding the primary processes occurring in the reburial sediments. Then, in conjunction with the physico-chemical and biological

analyses, a better understanding of the effects of the environment on the ongoing deterioration of reburied archaeological materials may be ascertained.

Conclusions and Future Research

The results obtained during this research project initiated in 2005 can be summarised as follows:

- The site is an open circulation, oxidising marine environment typical of this area.
- Wood borers, soft rot fungi and lignocellulosic degrading bacteria are active on the *James Matthews* site.
- There had been a significant increase in the extent of deterioration of all structural members in test trench 2 over the past five years despite the use of sand bags.
- Despite extensive algal growth on the surface of the shade cloth, the extent of sediment build up under the SW edge of the shade cloth mats was about 40cm progressively decreasing to a minimum average depth of 10cm around the NE edge.
- Large quantities of dead seagrass were trapped under the seagrass mat and extensive scouring had occurred.
- After some modifications, the test square successfully contained the backfilled sediment over time.
- The redeposited sediments were very stable, only slightly more acidic than the surrounding seawater column and were neither strongly oxidising nor reducing in nature.
- The results from the pore water analyses showed significantly higher average concentrations of nutrients in the redeposited sediments in comparison to the seawater and local surrounding sediment. Significant amounts of total nitrogen and phosphorus were present in the surface sediments and at depths where there were larger quantities of extractable organic matter.
- The micro-organisms identified in the sediments were typical of the local marine environment and there were no significant differences in the organisms detected in the redeposited sediments compared to the baseline samples. Aerobic and anaerobic microzones existed throughout the sediment columns.
- All results from the microelectrode analyses were anomalous and no discernible trends were evident consistent with well established natural biogeochemical processes. More method development is required.

It is difficult to predict the effect a particular reburial environment may have on the deterioration of different archaeological material types as there are many synergistic, symbiotic and opposing processes occurring within the redeposited sediment column and at this point in time, their inter-relationships remain unclear. However, some recommendations can be made based on these research results.

Canvas sand bags are totally unsuitable even as an interim remediation strategy, but polymeric sand bags may be used for short term preservation of a wreck site. However, to minimise deterioration the type of polymeric sand bags chosen for stabilisation and the method of deployment is very important.

The use of artificial seagrass mats could not be recommended as a means of stabilising the *James Matthews* wreck site. On the other hand, the shade cloth mats were quite successful in trapping sediment but the gradual sediment depth differential under the mats could prove to be problematic. Correct orientation of the shade cloth is very important in order to gain maximum sediment coverage (>60cm) over the exposed sections of the shipwreck. This may prove difficult in some areas on the wreck site and therefore, the use of the road crash barriers remains the preferred reburial option. This innovative management approach would utilise approximately 80 of these units, interlocked into a ring-like arrangement around the periphery of the wreck site, filled with sand to a depth of 0.8m, then covered with polymeric sheeting and sand bags to minimise sediment loss. However, considerable funds are required to establish this management strategy and therefore, research will continue into the shade cloth sediment trapping technique as it is a relatively inexpensive alternative to the road crash barrier containment method.

More research is required in order to verify whether the introduction of extraneous organic matter into the reburial environments and increased nutrient levels is deleterious to the long-term preservation of archaeological materials. It is also important to ascertain whether the naturally occurring increased levels of nitrogen and phosphorus present on the seabed surface will increase the rate of degradation of different material types at this depth even after they are reburied under centimetres of trapped sediment. Hence, physico-chemical and biological monitoring of the sediment environment under the established shade cloth and seagrass mats will continue, however longer sediment cores (60cm) will be collected and sacrificial wood (oak and pine) and iron alloy (cast iron and steel) samples will be inserted into the redeposited sediment column under the shade cloth mats for subsequent analysis.

In addition, the test square will be emptied, the previous reburied shade cloth and sand bags removed, sacrificial samples mounted at different depth intervals then the test square refilled. Finally a new shade cloth mat will be deployed including sacrificial samples mounted under the shade cloth in an attempt to emulate reburial of the wreck by this particular method. Negative controls will also be mounted in the seawater column and in the surrounding baseline sediment for comparison. Sufficient numbers of samples will be deployed so they can be removed at regular intervals and analysed by physical, instrumental and microscopic techniques to monitor the impact of the different reburial environments and deposition mechanisms on the deterioration of the wood and iron alloys over time.

The results of all these analyses will eventually provide information regarding the suitability of the reburial environments for the long-term preservation of the different materials types tested. Subsequently this information will be used to finalise the design of the full scale *in-situ* preservation strategy for the *James Matthews* site and assist in establishing a post-reburial monitoring programme that will measure the success of the adopted remediation technique.

Despite the many questions and uncertainties that surround reburial of archaeological materials it is likely to play an increasingly important role in the *in-situ* preservation of underwater cultural heritage. Hence, more research projects that include extensive monitoring programmes need to be initiated in order to provide information that will ultimately lead to a better understanding of the associated advantages and disadvantages of this technique.

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