



Article Characterizing the Preservation Potential of Buried Marine Archaeological Sites

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Abstract: The preservation potential of sediments from a submerged prehistoric site buried in a full marine environment was assessed using a combination of direct in situ measurements, measurements on extracted sediment cores and laboratory mesocosm experiments. The results show that first and foremost it is paramount to ascertain the state of preservation of the materials in the seabed—in this case wooden artifacts—that are to be preserved in situ. The results suggest that dissolved oxygen and sulfide are good parameters to measure in situ to assess the general oxidizing or reducing nature of the environment. If it is possible to take sediment core samples, it is similarly important to measure dissolved oxygen and hydrogen sulfide in the core and extract pore water to assess for sulfate content. Sediments should be characterized for particle size, water content (porosity) and organic content. In this way, we show that dissolved oxygen was rapidly depleted in the first few centimeters of sediment, thereafter sulfate reduction dominated the geochemical processes. Coarser sediment types with high porosity and low organic content have lower rates of organic material turnover, indicating better preservation conditions.

Keywords: assessment; underwater cultural heritage; in situ preservation; deterioration; marine environment

1. Introduction

Current international trends favor in situ preservation as a means to manage marine archaeological sites that, for economic or other reasons, are not excavated, raised and conserved [1,2]. In situ preservation implies a structured and controlled approach to ensuring the survival of archaeological sites until such time as the archaeologists and conservators have the capacity, research questions and desire to investigate these sites in the future. Since the early 1990s European Heritage management has focused upon in situ preservation and there have been numerous projects that addressed material deterioration [3,4], monitoring [5] and stabilization [6] of marine archaeological sites. The current author [7] has previously discussed five fundamental steps necessary to ensuring the successful and responsible in situ preservation and management of archaeological sites in general. These are:

- The extent of the site to be preserved;
- The most significant physical, chemical and biological threats to the site;
- The types of materials present on-site and their state of preservation;
- Strategies to mitigate deterioration and stabilize the site from natural impacts; and
- Subsequent monitoring of the site and the implemented mitigation strategies.

As part of the three-year EU-funded SASMAP (Development of Tools and Techniques to Survey, Assess, Stabilize, Monitor and Preserve Underwater Archaeological Sites) project [8], tools and methods for the characterization of the potential preservation of the marine environment were developed. These

included proof of concept in situ data logging devices, which could characterize the environment of marine archaeological sites both in open water and sedimentary environments, and a diver-held vibracorer to sample sediments from archaeological sites. Using this developed equipment, guidelines were produced [9] for best practice methods to characterize the preservation potential of sediments on marine archaeological sites, as will be discussed in the following paragraphs.

2. Scientific Background

Deterioration of Organic Material in Marine Sediments

Buried waterlogged environments provide unique conditions for archaeological organic materials, such as wood, bone, antler, textile, skin and plant remains, preserving these materials for millennia, partly due to the low oxygen levels. Conditions in open seawater can, in the absence of wood boring organisms (see http://wreckprotect.eu), also preserve these materials for many hundreds of years. However, deterioration of organic material can occur in low or oxygen free (anoxic) environments due to the activity of anaerobic bacteria. This is because nearly all biogeochemical processes in young (i.e., during early diagenesis) sediments are directly or indirectly connected with the degradation of organic matter [10]. Organic matter may be produced by algae and other organisms in open water, and it subsequently sinks to the seabed and becomes incorporated within the sediment. It may also consist of the remains of plant material, such as eelgrass or seaweed, or archaeological material deposited within the sediment. The utilization of any organic matter by organisms within sediments involves oxidation–reduction (redox) reactions [11]. These reactions follow a well-documented succession (Figure 1) with various chemical species (electron acceptors) being utilized based on the amount of energy they yield [12].



Figure 1. Use of chemical species (electron acceptors) within marine sediments (after [12]).

From the pool of potential electron acceptors, the microbial community selects the one that maximizes energy yield from the available substrate. This is partly due to metabolic regulation within a single population and partly due to the competition between several populations with diverse metabolic capabilities. In marine sediments, the sequence of electron acceptor utilization can be observed spatially in horizontal layers of increasing depth. In typical coastal marine sediment, only the first few millimeters of the sediment are oxygenated, though bioturbation by invertebrates and advection may extend this oxygenated zone downward. For a few centimeters under the oxygenated zone, nitrate serves as the electron acceptor, followed by manganese and iron oxides. Below this, sulfate is the principal electron acceptor and sulfate reduction is often the dominant process in shallow marine sediments due to the high concentrations of sulfate in seawater. Methanogenesis is usually

confined to the sulfate-depleted deeper sediment layers, though the generated methane may diffuse upward into the zone of sulfate reduction. Thus, the deterioration of organic matter still occurs in anoxic environments due to the activity of anaerobic organisms, albeit at a slower rate.

Assessing the preservation characteristics of marine sediments containing archaeological materials does, however, pose other questions. What is the state of preservation of the material that we are trying to preserve in situ? Does the material in fact resemble "fresh" material and is it still possible for it to be degraded if it remains buried in these waterlogged and low oxygen environments?

3. Materials and Methods

The submerged prehistoric site of Tudse Hage was used for sampling and trialing of equipment. It is a shallow (2–4 m deep) site, is very close to the coast and is in an area that is subject to heavy coastal and seabed erosion. The site was discovered in the 1950s and finds from the site include log boats, fish traps, fishing gear, butchered animal bones and numerous worked flint artifacts from the Mesolithic period [13]. Investigations in the 2000s sought to locate the prehistoric coastline and a series of small trenches were excavated for this purpose. The sampling and measuring strategy outlined below was based around these excavations in undisturbed areas adjacent to the trenches that were known to contain cultural layers from the seabed surface down to the underlying glacial moraine.

3.1. Characterizing the Preservation Potential of Archaeological Material in Marine Sediments

Research into characterizing the environment for marine archaeological purposes has been carried out since the mid-1990s [3–7,14]. Many of these methods have focused upon taking sediment core samples, assessing pore water and characterizing sediments in the laboratory. Part of the challenge in the first instance is to be as non-destructive to the archaeological site as possible and, secondly, to ensure the quality of sediment cores. Thus it was thought desirable that key parameters could be assessed in situ on the seabed in as non-destructive a manner as possible. Sediment cores are often taken using gravity corers dropped from the surface to the seabed. This is not particularly specific in terms of the precise location of the cores, and often the uppermost sediments at the seabed–seawater interface are disturbed. Thus, it is desirable to be able to use diver-held corers to be able to carefully select where cores should be taken and to take them in such a way that they cause as little destruction to the site as possible and yield undisturbed sediment cores. The strategy for characterizing the preservation potential of organic archaeological material in marine sediments was thus as follows:

• Characterizing the environment to assess whether it is oxic or anoxic and determine the dominant process ongoing in the sediments. This was done both through in situ profiling using an in situ sediment profiling data logger and ex situ, using sediments taken with a diver-held vibracorer. The parameters assessed are listed in Tables 1 and 2.

Parameter	In Situ (Sediment Profiler)	Ex Situ (Sediment Core)	
Dissolved oxygen		Х	
pН	(X)	Х	
Sulfide content	Х	Х	
Redox potential	Х	Х	
Sulfate content		X (pore water)	

Table 1. Sediment parameters measured in situ using a sediment profiler and measured ex situ in a sediment core taken with a vibracorer.

• Laboratory mesocosm studies with broadly different sediment types (e.g., sand, gytje and "polluted" (high organic content) harbor sediments) to see if there was a difference in the rates of turnover of material.

Sediment Parameter		
Visual characterization		
Water content		
Particle size analysis		
Porosity		
Organic content		

Table 2. Sediment parameters characterized on sections from a core.

3.2. Characterizing the Burial Environment to Determine whether It Is Oxic or Anoxic

3.2.1. In Situ Sediment Profiler

The in situ sediment profiler was designed to measure environmental parameters (pH, sulfide, redox potential) in sediment profiles in situ using a diver-based data logging system to a depth of 50 cm within the seabed (Figure 2). The sediment profiler was manufactured by Unisense; it uses a hollow spear that can be hammered into the sediment to the desired depth, after which sensors are placed into and passed through a silicon membrane to take the desired measurements (Figure 3). Needle-type sensors and electrodes from Unisense were used for the spear application and were calibrated following Unisense's standard methods [15].



Figure 2. Data logger for characterizing environmental parameters in sediments. The logger has four channels and was developed to measure sulfide, pH, redox potential and dissolved oxygen.

3.2.2. Ex Situ Assessment (Sediment Cores) Using a Diver-Held Vibracorer

The prototype of the vibracorer device uses a compressed air-driven vibrating head that is attached to an 8 cm-diameter polycarbonate tube with 5 mm thick walls. The cores are driven into the seabed and the frequency of the vibracorer is such that it does not cause disturbance of the uppermost sediments at the seabed–seawater interface. Core depths of 85 cm were obtained, which was the depth to the underlying clay moraine. Retrieval of the cores is facilitated by the use of a cushion that can be filled with compressed air. This is attached to metal jaws that firmly grip the polycarbonate coring tube. As air is pumped into the cushion it expands vertically and the metal jaws pull the sediment core up from the seabed in ca. 10 cm intervals. The metal jaws are opened and air is released from the cushion to deflate it; the process is repeated until the corer is almost free from the seabed. In the case at Tudse Hage, the underlying natural moraine served as the perfect "seal" to the end of the coring tube, thus preventing loss of sediment upon retrieval of the core. This device saved overexertion from the diver and avoided the use of winching from the surface or the use of airbags underwater to

remove the core. Once back on land, laboratory-based Unisense micro-sensors for hydrogen sulfide, dissolved oxygen, pH and redox were applied to characterize the spatial distribution of the chemical parameters inside the sediments. Micro-sensor analyses were performed in a horizontal position using a micromanipulator on a stand in order to position the micro-sensors with high accuracy near the center of the core through 3 mm wide openings made with a drill (Figure 4).



Figure 3. Diver taking profile measurements in situ. Sensors are attached to orange cables, one of which the diver is seen preparing prior to inserting into the profiling spear (vertical metal spear in front of diver's left hand). Photo: Anne Marie Hoier Eriksen

The core measurements were performed at a 5 cm spatial resolution at depth gradients from 5–60 cm in Core #1 and 10–60 cm in Core #2. Due to the very coarse sediment characteristics in the uppermost core regions, it was not possible to carry out micro-sensor measurements at shallower sediment depths. Micro-sensors were prepared with a pointed tip design and an approximate tip diameter of 250 μ m in order to facilitate the deep sensor positioning inside the core without breakage.

Following profiling with the micro-sensors, pore water was sampled at the same depth in the core using Rhizon pore water samplers (Figure 5); the samples subsequently frozen to prevent further microbial sulfate reduction. Sulfate was analyzed in the laboratory using an ion chromatograph and the results complemented the sulfide sensor results, i.e., as sulfate is utilized, sulfide evolves.

3.3. Sediment Characterisation

In the laboratory, the core section from the archaeological site (Core #2) was sectioned using an angle grinder, cleaned and geologically characterized. A selection of five appropriate wooden fragments found at various depths (-18 cm, -23 cm, -33 cm, -48 cm and -68 cm below the seabed) within the core was taken out and sampled for carbon-14 dating. The core was then sectioned into 2 cm sections and samples were taken for particle size, water content and organic content analysis.



Figure 4. Profiling cores with sulfide sensor. A: Micromanipulator enabling insertion of microsensor. B: 500 µm tipped sulfide sensor



Figure 5. Rhizon pore water samplers, which filter pore water from the core using a blood-sampling vacuum tube.

Particle size analysis was only carried out on the loose sand gravel sediments (0–10 cm), the underlying sandy gytje layer (10–20 cm) and the sandy layer underlying the lowest layers of gytje (60–70 cm) above the moraine clay sediment (natural). An attempt was made to take a sample of the gytje at –45 cm (ca. midway in the core) but, due to the very high organic content matter, this location did not yield enough inorganic material after drying to test for particle size. This was generally a problem when working with such a small sample size (2 cm sections) and highly organic materials.

3.4. Mesocosm Studies of Organic Turnover in Different Sediment Types

The mesocosms were used to examine different sediment types often encountered on archaeological sites, namely sand, organic rich gytje and loose organic rich harbor sediments. Sub samples of the different sediments were used in mesocosm experiments where, under controlled laboratory conditions, the turnover of organic material in the different sediments was assessed. The mesocosms consisted of 100 g of sediment placed into separate 100 mL incubation jars, which were then filled to the top of the jar with water from the Tudse Hage site and kept at a constant temperature of 20 °C (Figure 6). A range of sensors mounted on the screw caps with epoxy resin continually measured hydrogen sulfide development (as a result of sulfate reduction), redox potential and dissolved oxygen. A hypodermic needle was glued into the cap as well so that water samples from the mesocosm could be taken in order to measure sulfate concentration. The temporal dynamics of the chemical environment inside the incubations were monitored continuously with sensors for hydrogen sulfide and redox potential. Dissolved oxygen was measured using a Presense oxygen optode sensor, and was fully depleted within six days of closing the jars. Concentrations of hydrogen sulfide were measured with Unisense hydrogen sulfide micro-sensors constructed with 500 µm tips.



Figure 6. Mesocosm setup showing (**A**) hydrogen sulfide and redox datalogger (upper). (**B**) Mesocosm jars (red caps) in water bath. Redox, sulphide and hypodermic needle for water sampling were glued into the caps with epoxy resin.

4. Results

4.1. Characterizing the Environment to Determine whether It Is Oxic or Anoxic: In Situ Profiling

Sediment profiles for hydrogen sulfide and redox were characterized successfully from depths of 10–60 cm with a spatial resolution of 10 cm. With some variation, the overall profile trends where measurements were taken were similar, with increasing hydrogen sulfide concentrations and decreasing redox levels as a function of sediment depth (Figure 7). Both of these factors indicate reducing and anoxic conditions that are beneficial for the preservation of organic archaeological materials.



Figure 7. Sediment distributions of hydrogen sulfide and redox measured in situ with micro-sensors using the spear application the Tudse Hage at site.

4.2. Ex Situ Assessment (Sediment Cores)

4.2.1. Microsensor Profiling

Profiles from the core in Tudse Hage are shown in Figure 8.



Figure 8. Spatial distribution of hydrogen sulfide, redox, pH and O₂ at the Tudse Hage site.

The measured hydrogen sulfide levels were very high, with a gradually increasing concentration as a function of depth and maximum concentrations of 2194 μ M. pH levels declined throughout the core, reaching a value of < 6.8 at the deepest point. The sediment redox levels, from 10 cm depth and below, varied between -70 to -145 mV, indicating reducing conditions. Dissolved oxygen showed zero oxygen already at -5 cm depth. This was to be expected, as the high organic content of this sediment type (data not shown) would mean that microorganisms would rapidly utilize any oxygen that may have been present in the sediment, thus making the environment anoxic. The hydrogen sulfide, redox and dissolved oxygen values all indicate that sediment conditions are anoxic.

4.2.2. Pore Water Analysis

The sulfate results taken from the pore water are shown in Figure 9, along with the sulfide profile measurements.



Figure 9. Sulfate and sulfide profiles (x axis arbitrary) showing the decrease in sulfate with a concomitant increase in sulfide.

From the profile, it is apparent that there may be a natural variation in the salinity of the seawater, which has, through diffusion and/or convection, affected the sulfate levels within the seabed; one would not necessarily expect to see an increase in sulfate. However, from -25 cm in the seabed and below, sulfate reduction could be seen with a general decrease in sulfate concentrations down to a depth of -60 cm. This indicates that even though the conditions are anoxic, there was still turnover of organic material at these depths due to sulfate reduction. This trend generally corresponds well with the ex situ micro sensor profiles (Figure 8), where an increase in sulfide evolution was seen after 10 cm depth.

4.2.3. Sediment Characterization

The core is shown below (Figure 10) with the description of the cultural layers alongside it.





Characterization of the physical properties of the sediment layers (every 2 cm) are shown in Figures 11–13, and particle size analysis is given in Table 3.

	Weight%		
	0–10 cm	10–20 cm	60–70 cm
Silt and clay (<0.063 mm)	0.66	11.90	14.34
Sand, fire (0.0063–02 mm)	5.54	25.49	41.92
Sand, medium (0.2–0.6 mm)	29.12	38.81	29.76
Sand, coarse (0.6–2 mm)	16.62	14.19	6.17
Gravel (>2 mm)	48.07	9.60	7.81

Table 3. Particle size analysis.



Figure 11. Particle size, water content and porosity within the core from the Tudse Hage site.

Figure 11 shows that the water content and porosity of the sediment core were lower in the upper 10 cm, where the sediments consisted of gravel and sand. As the sediments became more organic (gytje) in nature with depth, the water content increased (10–20 cm below the seabed). This was also reflected in the particle size of the sediments, with lower amounts of coarser grained sediments. The water content and porosity dropped off around 55–60 cm within the seabed, corresponding to the slightly sandier nature of the gytje; this relates to the suspected re-deposition of sediments, which may indicate a previous coastal area. Unfortunately, particle size analysis was not carried out in this specific layer. The water content and porosity increased between -60 and -68 cm, as the sediment became more organically rich again, before finally decreasing as the underlying moraine was reached. Again, particle size analysis showed a higher proportion of fine-grained sediments (sands). The results for the particle size analysis are also shown in Table 3.



Figure 12. Organic and inorganic contents % w/w (dry weight) within the core at Station #2, Tudse Hage site.

Figure 12 shows the organic and inorganic contents of the core. The results reflect the water content and porosity of the sediments, with generally lower organic matter in the less porous sediment (sand) and vice versa.

Organic matter can be labile, i.e., it is degradable by microorganisms; or it can be refractive, i.e., it has been utilized and is difficult to degrade further by the microbial community. The results represent the amount of labile and refractive organic material as a percentage of the total organic material (Figure 13).

Generally, the organic material present within the cores had a higher percentage of labile, i.e., degradable, carbon, than refractive carbon. This corresponds with the sulfate and sulfide measurements in the cores, which showed that microorganisms are active through sulfate reduction. Notably, at areas where there are high organic contents (ca. -34 cm, -44 cm and -68 cm), the majority of the carbon was still labile. An exception to this was at -54 cm where the carbon present was more refractory in nature. Considering this in light of the sulfate and sulfide measurements, an increase in the rate of sulfate

reduction was seen at this point. However, sulfide levels decreased whereas one may have expected an increase in the sulfide levels if sulfate was being reduced.



Figure 13. Labile and refractory organic matter amounts.

4.2.4. Mesocosm Studies

The overall performance of the hydrogen sulfide sensors that were used during the mesocosm experiments was worse than expected. The primary issues experienced were: (1) signal noise during on-line monitoring, which became increasingly problematic over time; and (2) loss of sensitivity towards hydrogen sulfide. This limited the overall quality of the experimental data.

The hydrogen sulfide dynamics inside the mesocosms were monitored for a 28-day period (Figure 14).

The mesocosm results suggested the presence of highly variable hydrogen sulfide dynamics within the three sediment types. For each sediment type, the results for the two replicate measurements showed that there is a reasonable level of agreement between the dynamic trends in hydrogen sulfide concentrations measured during the initial 28-day incubation period and the end-point measurements after 71 days (see Table 4). In summary, the results showed that there was a high rate of hydrogen

sulfide production in the polluted harbor samples, a low accumulation level in sand and very little net accumulation of hydrogen sulfide in the samples with gytje.



Figure 14. Hydrogen sulfide dynamics in mesocosms during the initial 28-day incubation period measured continuously with hydrogen sulfide sensors. Samples with harbor (**A**,**B**), sand (**C**,**D**) and gytje (**E**,**F**).

Table 4. Physical parameters of the sediment types used in the mesocosm experiments. Values are given as %. L: labile carbon; R: refractive carbon.

Sediment Type	Particle Size (mm)	Harbur	Sand	Gytje
Silt & Clay	< 0.063	43.1	0.4	84.8
Sand, Fine	0.063-0.2	44.3	80.4	5.0
Sand, Medium	0.2-0.6	9.5	17.2	9.1
Sand, Coarse	0.5–2	1.5	1.5	1.2
Gravel	> 2	1.5	0.6	0.0
Water content (%)		64.3	17.5	56.3
Organic Content (%)		6.7 (L: 2.8 R: 3.9)	0.5 (L: 0.1 R: 0.4)	11.5 (L: 5.8 R: 5.6)
Inorganic content (%)		93.3	99.5	88.5
Sulfide content (µMoles)		1927	43.5	0.7

Further to the hydrogen sulfide measurements, redox potential was logged continually. The results from the mesocosm study after 71 days indicated an anoxic and reducing environment (confirming the preliminary dissolved oxygen measurements, which showed a complete loss of oxygen in the mesocosms within 6 days; data not shown) as shown in Figure 15.



Figure 15. Redox potentials logged during the microcosm studies.

The potentials shown for all sediment types look very realistic for highly reducing conditions and are more than likely related to the sulfate–sulfide or carbon dioxide–methane redox couples, both of which are around 200 to -250 mV. Notably, there was variation over time, which potentially shows that redox potential is perhaps best logged rather than taking spot measurements as was the case with the in situ spear logger. Looking at the slopes of the data in Figure 15, sensors appear to have stabilized within the harbor and gytje sediments but those in sand do not appear to have stabilized even after over two months. Whether this is due to the particle size (porosity) or organic content may be worthy of further study; however, redox potential is a notoriously difficult parameter to measure reliably.

When the sulfide and redox measurements were compared with the physical characteristics of the sediment, particle size and organic content, the results also reflected what was seen in the results from the ex situ studies of the core, whereby finer grained sediments had a higher water content (porosity) and generally higher organic contents. The physical parameters for the sediments used in the mesocosm study along with the final sulfide concentrations are shown in Table 4.

When looking at the evolution of the hydrogen sulfide in the mesocosms (Figure 14), it can be seen that Harbor sediments produced the most, followed by gytje and sand, which produced very little. When considering the organic content of the sediments from the mesocosms, the gytje had higher organic content but was almost equal parts labile and refractive. Explanations may be that the higher rates of sulfide evolution are simply due to the higher numbers of microorganisms respiring in the harbor sediments, or that the labile fraction of the organic carbon is less easily degraded in the gytje.

4.2.5. Carbon-14 Dating of Wood and Organic Fragments from Tudse Hage Core

The positions and resulting dates of the five fragments of wood, along with those of the wood analyzed for deterioration, are presented graphically in Figure 16. The results show that the formation of the overall archaeological deposits took ca. 400 years, between 5990 and 6390 (\pm 30) years Before Present (BP).



Figure 16. Positions of wood for characterization of deterioration and carbon-14 dating. The evolution of the archaeological layers from just above the natural moraine to the top of the youngest gytje deposits is ca. 400 years.

Looking at the age differences between the carbon-14 datings, it can be hypothesized that deposition times of the various layers have varied quite drastically. For example, between -18 and -23 cm, 90 years; between -23 and -33 cm, 70 years; between -33 cm and -48 cm, 30 years, and between -48 to -66 cm, 210 years. Of course, one has be cautious due to the limited data and accuracy of the results, but an important observation, certainly on submerged prehistoric landscapes, is that the formation of the site is extremely important when considering the deterioration of organic materials as well as their future preservation in situ: are the materials fully degraded for the environment they currently lie in? All the above samples showed a total degradation of the cellulose and hemicellulose rich cell wall components, which were exclusively caused by bacterial decay (unpublished results). This decay form (erosion bacteria) requires an environment that is very low in oxygen, which is too low for fungal activity by soft rot. The degree of microbial degradation has probably reached its final stage and as long as an anaerobic–anaerobic environment is maintained, it will be unlikely to undergo further deterioration.

5. Discussion

5.1. Dissolved Oxygen

Oxygen was characterized using both the in situ profiler and the measuring profiles in sediment cores taken using the diver-held sediment corer. Both sets of results show that dissolved oxygen was utilized within the overlying few centimeters of sediments—this is as would be expected based on similar studies of near coastal sediments carried out by marine biologists and ecologists [14].

5.2. Sulfate Reduction and the Measurement of Hydrogen Sulfide

When in anoxic environments, below the layer of where oxygen is present, other biogeochemical processes will dominate and, in shallow coastal sites, this will usually consist of the action of sulfate reduction bacteria that produce hydrogen sulfide [16].

Hydrogen sulfide was measured using the in situ profiler and ex situ cores. Although the in situ sulfide measuring system may need to be further developed, results from both the in situ profiling and profiling ex situ showed the sulfate reducing zone at the Tudse Hage site. The overall oxic or anoxic state of the environment can, in theory, be characterized by measuring the redox potential. However, caution is required when taking spot measurements, such as with the in situ data logger, as a stable measurement may not be achieved in the typical time durations a diver can work underwater. Our laboratory mesocosm studies in different sediment types showed that there is a relatively long stabilizing time of the redox probes (i.e., months rather than minutes), so this is not necessarily recommended unless long term in situ logging is possible.

5.3. Physical Characterisation of Sediment Type and Ongoing Processes

Using the ex situ cores, sediments were characterized using general methods for assessing the turnover of organic material, including particle size, water content (porosity), organic content (labile and refractive) and analysis of pore water content. These are relatively simple parameters for the majority of archaeological and conservation laboratories to measure in terms of the equipment required. Results showed that in general, coarser grained sediments with a lower porosity and lower organic material content exhibited lower turnover rates. Specific turnover rates in a range of sediments (sand (medium porosity and low organic content), polluted harbor sediments (high porosity and high organic content) and "archaeological sediment" (gytje from the site of Tudse Hage, with high porosity and high organic content)) were not possible to determine from the mesocosm studies as had been hoped due to problems with the sulfide sensors. Nonetheless, they did show this general relationship to be true, as did the profiling results and characterization of the sediments from the ex situ core.

However, again, it cannot be stressed enough that the paramount importance is to determine the state of preservation of the material to be preserved. In the case of the wood from Tudse Hage, as long as the wood is buried in the present low-oxygen and sulfate-reducing conditions, it should be safe for the future as there is insignificant material remaining that can be degraded under waterlogged environmental conditions. Furthermore, this is why it is also important to understand the overall ongoing physical processes at a site, as it is these processes that may cause the erosion of sediments.

6. Conclusions

A four-pronged approach was taken to characterizing the burial environment:

- 1. In situ classification of sediments;
- 2. Ex situ classification of sediments;
- 3. Laboratory microcosm studies examining turnover rates in different sediments;
- 4. Characterization of the actual state of preservation of archaeological wood and dating.

In summary, it was found that it is of paramount importance to obtain samples of the material (in this case wood) in order to assess their state of preservation, so as to determine whether future deterioration in the environment is likely. Wood fragments taken from the Tudse Hage site were shown to be extensively degraded and, should the conditions remain the same, it is unlikely that further deterioration will occur due to the ecological constraints on the microorganisms that could cause further deterioration (i.e., the microorganisms cannot survive).

These results also highlight the importance of understanding the post-depositional formation processes on archaeological sites in general (i.e., how were artifacts deposited and incorporated in a site). Again, from the analysis of the wooden fragments it is apparent that deterioration had occurred

long ago—no significant difference was seen in the state of preservation of the wood regardless of depth (increasing age) within the sediment. When this was correlated with carbon-14 dating, it was found that the formation of the site took place between 6390 and 5990 (\pm 30) years BP, i.e., over 400 years, and as stated no significant difference was found in the overall state of preservation of the wood.

Thus, in terms of the archaeological wood analyzed here, it could be argued that it is irrelevant to monitor the sedimentary environment, as the wood was totally degraded by those microorganisms that could survive. This reiterates the importance of characterizing the material to be preserved in situ, as contrary to the case of Tudse Hage, wood is not always fully degraded. Nonetheless, if these results are to be relevant to other sites and archaeological wood that is in a better state of preservation, characterization of the environment is still relevant. The main factors affecting the deterioration of organic materials in marine sediments are related to the amount of oxygen in the environment (oxic or anoxic) and the ongoing processes that are related to the physical characteristics and organic contents of the sediments in which the material is buried. Flow diagrams for the generic best practice for characterizing site environments in relation to the preservation of archaeological wood at underwater sites both in situ and ex situ are given in Figures 17 and 18.



Figure 17. In situ profiling for characterizing whether a site is oxic or anoxic.



Figure 18. Ex situ assessment of sediment cores for the assessment of the preservation potential of archaeological sites.

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References

- European Convention on the Protection of the Archaeological Heritage (Revised). 1992. Available online: https://rm .coe.int/CoERMPublicCommonSearchServices/DisplayDCTMContent?documentId=090000168007bd25 (accessed on 15 July 2020).
- 2. UNESCO. Unesco Convention on the Protection of the Underwater Cultural Heritage. 2001. Available online: http://www.unesco.org/new/en/culture/themes/underwater-cultural-heritage/2001-convention/official-text/ (accessed on 15 July 2020).
- 3. Gregory, D.J. Environmental Monitoring of the re-burial trenches 2007–2009. In *Reburial and Analysis of Archaeological Remains. The RAAR Project: Phase II—Results from the 4th Retrieval in 2009 from Marstrand, Sweden*; Godfrey, I.N., Bergstrand, T., Petersson, H., Eds.; Bohusläns Museum: Uddevalla, Sweden, 2011; Volume 28.
- 4. Manders, M. Protecting common maritime heritage. The Netherlands involved in two EU-projects: MoSS and BACPOLES. In *Mediterraneum*; Maniscalco, F., Ed.; Massa Editore: Naples, Italy, 2004; pp. 279–292.

- 5. Manders, M. MACHU—Managing Cultural Heritage Underwater. 2010. Available online: https://www.ma chuproject.eu/ (accessed on 15 July 2020).
- 6. Björdal, C.G.; Gregory, D. Wreck Protect: Decay and Protection of Archaeological Wooden Shipwrecks; Archaeopress: Oxford, UK, 2012.
- Gregory, D. In situ preservation of marine archaeological sites: Out of sight but not out of mind. In *In Situ Conservation of Cultural Heritage: Public, Professionals and Preservation;* Richards, V., Mckinnon, J., Eds.; Flinders University: Adelaide, Australia, 2009; pp. 1–16.
- 8. SASMAP Project Home Page. Available online: http://www.sasmap.eu (accessed on 15 July 2020).
- Gregory, D.; Manders, M. Best Practices for Locating, Surveying, Assessing, Monitoring and Preserving Underwater Archaeological Sites. SASMAP Guidel. Man. 2016, 2. Available online: http://sasmap.eu/fileadm in/user_upload/temasites/sas_map/pdf/SASMAP_guideline_02_LR.pdf (accessed on 18 July 2020).
- 10. Rullkötter, J. Organic Matter: The Driving Force for Early Diagenesis. In *Marine Geochemistry*; Schulz, H.D., Zabel, M., Eds.; Springer: Berlin, Germany, 2000; pp. 129–153.
- Schulz, H.D. Redox Measurements in Marine Sediments. In *Redox: Fundamentals, Processes and Applications;* Schüring, J., Schulz, H.D., Fischer, W.R., Böttcher, J., Duijnisveld, W.H.N., Eds.; Springer: Berlin, Germany, 2000; pp. 235–246.
- Froelich, P.N.; Klinkhammer, G.P.; Bender, M.L.; Luedtke, N.A.; Heath, G.R.; Cullen, D.; Dauphin, P.; Hammond, D.; Hartman, B.; Maynard, V. Early Oxidation of Organic Matter in Pelagic Sediments of the Eastern Equatorial Atlantic: Suboxic Diagenesis. *Geochim. Cosmochim. Acta* 1979, 43, 1075–1090. [CrossRef]
- 13. Lotz, P. Tudse Hage—An underwater settlement on Sjælland. Marit. Archaeol. Newsl. Rosk. Den. 2000, 14, 8–13.
- 14. Richards, V. In situ preservation and monitoring of the *James Matthews* shipwreck site. *Conserv. Manag. Archaeol. Sites* **2012**, *14*, 169–181. [CrossRef]
- 15. Available online: https://www.unisense.com/manuals/ (accessed on 15 July 2020).
- Jørgensen, B.B. Mineralisation of Organic Matter in the Sea Bed—The Role of Sulphate Reduction. *Nature* 1982, 296, 643–645. [CrossRef]



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