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Evaluating the effects of linseed oil treatments applied to waterlogged archaeological wood from the CSS *Neuse*

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Abstract

During the 1970s in eastern North Carolina, linseed oil was a popular conservation treatment for waterlogged wood. The largest use of the treatment was for the CSS *Neuse*, an early ironclad gunboat from the American Civil War. The *Neuse* was eventually scuttled and burned by the Confederates to prevent it from being used by the Union. The 1930s showed renewed interest in the vessel by the local population and efforts were made to have it relocated from the river in 1961 by three local citizens.

During storage on the riverbank, the *Neuse* went through several cycles of drying and a conservation treatment was implemented a year after the recovery. Initial treatments included a spray application of a five percent solution of pentachlorophenol and polyethylene glycol with later tests utilizing linseed oil. In addition to the treatment of the vessel, over 15,000 artifacts were recovered for conservation. The *Neuse* is currently managed by the North Carolina Department of Cultural Resources and is available to the public through display in a newly constructed museum located in Kinston, North Carolina. This research seeks to identify the stability and condition of the wood and the success of the linseed oil treatment.

Keywords: linseed oil, waterlogged wood, CSS *Neuse*, Civil War, FTIR, SEM

Introduction

The fascination of underwater cultural heritage has captured the attention of the public and treasure seekers for hundreds of years. As technology progressed that allowed us to discover and research submerged sites more frequently, so did the desire to share these finds with the public through the recovery of small finds and, in some cases, the entire vessel. Within the United States, several sites or artifacts have been investigated that include partial to total recovery and preservation of the wood hull. A complete international database is in the process of development that lists additional large wooden artifact conservation projects (Fix 2013).

When it was realized that several objects and entire shipwrecks were being successfully conserved in Europe and Scandinavia, there was an increase in wooden hulled vessels in the United States being raised from the seabed and brought on shore for display and preservation. In the 1960s, shipwreck sites were being discovered and salvaged at an accelerated rate in North Carolina waters and the North Carolina Department of Archives and History appropriated funds in 1963 to construct a conservation facility at historic Fort Fisher. The archaeologist working in this early laboratory on maritime archaeological materials utilized the information outlined in Plenderleith's, *Conservation of Antiquities and Works of Art* (1972) to experiment on and conserve the materials from the *Modern Greece* and others. As funding became available, additional staff was hired, but with still severely limited resources (Lawrence 2011). The CSS *Neuse* is of particular interest as it was the only ship to undergo a continuous linseed oil treatment.

Linseed oil is obtained from the flax plant and after a process of drying, the seeds of the plant are cold pressed similar to the methods used to produce olive oil. The oil is then heated in combination with minerals to produce a drying oil which has properties making it suitable for utilitarian applications such as a binding agent in paints and a furniture varnish or finish which acts as a preservative. While the popularity of linseed oil as a wood preservative has diminished in recent times, it continues to be touted as a conservation treatment for waterlogged wooden artifacts by several avocational websites providing information on "do-it-yourself" conservation. Conservators are now left with the task of determining how linseed oil specifically interacts with maritime archaeological materials and the long-term preservation concerns.

History of the CSS *Neuse*

April 1861 was the beginning of the American Civil War, and the Confederacy faced a large disadvantage of manpower and supplies. On October 17, 1862, the shipbuilding firm of Howard & Ellis began constructing the CSS *Neuse* from Southern yellow pine for the hull and iron plating for the casemate. In an effort to keep her commission a secret from the Union she was built in White Hall, North Carolina. After a lengthy and problematic construction process the *Neuse* was finally given orders on March 4, 1864 to sail to New Bern to recapture the port from the Union. The *Neuse* ran aground on a sandbar and, instead of sailing to New Bern once freed, the ship settled back in the moorings in Kinston.

During the remainder of the war, the *Neuse* was stationed in Kinston until March 12, 1865, when her own crew to prevent the Union from capturing her and her artillery sank it in the battle of Wyse Fork. After the initial salvage of usable materials, she sat at the bottom of the Neuse River in Kinston, North Carolina for one hundred years.

In 1961 serious excavation began on the *Neuse*. Three local businessmen who had no experience in archaeology or artifac conservation conducted the project. They used tools such as shovels, picks, tractors and backhoes to excavate the ship. The Neuse was cut into three pieces in order to be removed from the riverbed. The chain of events that took place in excavating the ship led to state involvement that greatly changed the way archaeology was done in North Carolina by prompting lawmakers to create laws that prevented amateur archaeological digs on public property. The CSS *Neuse* became state property during the 1960s and thousands of dollars were allocated for the remainder of the ships recovery and conservation. The remains of the ship were moved to the current location of the Richard Caswell Memorial and CSS *Neuse* State Historic Site.

This location was its home until the summer of 2012 when it was moved to a new permanent home in a museum located in downtown Kinston. The CSS *Neuse* is one of the largest artifacts owned by North Carolina and make up the largest collection of artifacts associated with a commissioned Confederate Ironclad.

Conservation history of the *Neuse*

Leslie Bright, employed by the North Carolina Department of Cultural Resources, was the lead conservator responsible for treating the CSS *Neuse* (Bright, Rowland and Baron 1981). Conservation notes kept during the project highlight only essential information, leaving future conservators questioning some treatments and conclusions.

The conservation process began when the ship arrived in Caswell Park. It was mounted on oak supports and pressure washed to remove sand, mud, and other debris. The ship was initially treated by a private company with a 5% solution of pentachlorophenol (w/v) and polyethylene glycol (PEG) (v/v) in water. As the wooden hull dried, it continued to shrink and large sections began to delaminate. At this point the state conservators assumed responsibility of the ship's treatment.

To determine the best possible treatment method, blocks of wood were selected from various portions of the ship for analysis. It was determined that although the surface of these samples appeared relatively dry, the core contained a large quantity of moisture.

In order to find a suitable treatment, Bright (1969) experimented with four treatment methods including two different solutions of PEG 400, linseed oil, and Hydrozo. Based on these experiments, raw linseed oil was chosen to treat the ship.

Test results indicated that the entire surface area of the ship would require treatment. Plans for application were as follows:

- first application - 50% v/v linseed oil with mineral spirits, 20% w/v (aq) pentachlorophenol,
- second application - 50% v/v linseed oil with mineral spirits,
- third application - 100% linseed oil.

Once the ship was clean of debris, conservators focused their attention on the ship's iron spikes and pins. To treat the iron spikes within the wood, conservators cleaned the visible portions of the metal pieces and then coated them with products described in the reports as Manganese-Phospholene #7 by Western Reserve Laboratories®, as a rust remover, and Dimetcote #4 by Amercoat®, as a final coating. It is important to note this treatment because it has leached into the surrounding wood.

Once the treatment of the metal pieces was complete, the next step was to treat the wood with linseed oil. Portions of the ship, which appeared to be extra dry, received a larger quantity than other areas. Conservators allowed one week for evaporation of the excess mineral spirits before applying a second coat, which was applied in the same manner as the first. The third application was begun after waiting two weeks for the linseed oil to penetrate and the mineral spirits to evaporate. Pure linseed oil was then applied. Nine weeks were allowed for maximum penetration and evaporation of the mineral spirits. The ship was then sprayed with a wood sealer diluted with 25% v/v mineral spirits.

In his report, Bright (n.d.) noted that in many cases no "fool-proof method" of preservation could be found or financially afforded and that the linseed oil treatment should stabilize the ship for approximately ten years before additional treatments would be required. State employed conservators continued the linseed oil treatment and vacuuming periodically every few years until at least 1994, when the decision was made to switch to Tim-bor®. This decision came after a state conservator published a general conservation assessment of the *Neuse*. In the report, she concluded that the linseed oil treatments had not been effectively penetrating the wood, and that fungal growth was responsible for further deterioration of the ship (Davis 1996). It is unclear what application methods and concentrations of Tim-bor® were used to treat the ship.

Most recently, the ship was vacuumed during the summer of 2012 in preparation for its move to the CSS *Neuse* Civil War Interpretive Center in downtown Kinston, North Carolina. Many of the globules of yellow and white encrustations that had been noted during display in its previous locations had been removed before sampling could be conducted.

Analysis

The process of analysis for archaeological wood can be varied and complex due to the inconsistencies between samples and the nature of wood chemistry, even if in similar locations. The main goal in the analysis of samples from the CSS *Neuse* was to provide a baseline of condition utilizing scientific methods on which future studies could be built. In order to accomplish this goal, local analytical resources were utilized at East Carolina University through Fourier Transform Infrared (FTIR) Spectroscopy in the Department of Chemistry and Scanning Electron Microscopy (SEM) in the Department of Biology. The samples were examined using both techniques, which provided a visual basis for the wood condition and a qualitative understanding of the presence of various organic compounds, namely linseed oil.

Linseed oil is a mixture of unsaturated fatty acids and contains linolenic acid, oleic acid, linoleic acid, palmitic acid and stearic acid. The presence of linolenic acid is primarily responsible for the oxidation process that causes the linseed oil to "cure" or polymerize. Another product that was important to this research was Tim-bor®, a water-soluble insecticide and fungicide. Both products were obtained locally in an effort to reproduce how the original materials would have been located and used. These were used as reference samples to compare results.

Samples

Sixteen samples were collected from the *Neuse* in February 2013 after it had been located to the newly renovated interpretation center and museum in downtown Kinston. Locations for sampling were selected based on unique visible features, which represented a variety of locations along the 48 m length of the vessel. The most important set of samples were taken with a forestry corer, Sample 4 through Sample 8, from Timber 4 between frames, indicated as Bay 5, on the port side mid-ship (Figure 1). The samples were divided into two sets (set A and set B). Set A was used in the SEM, and set B was used with the FTIR. The core ranged from light brown to dark brown and red in color with several areas of variation in color and consistency. The surface has a pH of 3 to 3.5 measured with ColorpHast pH strips. During sampling, the core produced solid wood sections as well as fragments (Figure 2). The orientation of the samples was maintained as best as possible and they were further separated and labeled according to their position within the core. For example, Sample 4 was located closest to the exterior of the ship and Sample 7 (fragments) and Sample 8 (solid core) were located closest to the interior of the ship.

Fourier Transform Infrared Spectroscopy method

Fourier Transform Infrared (FTIR) Spectroscopy was utilized in an effort to evaluate the presence or absence of linseed oil

Figure 1. *Morris Bass, CSS Neuse Interpretive Center and Gov. Richard Caswell Memorial operations manager, removing the core from Timber 4 in Bay 5.*

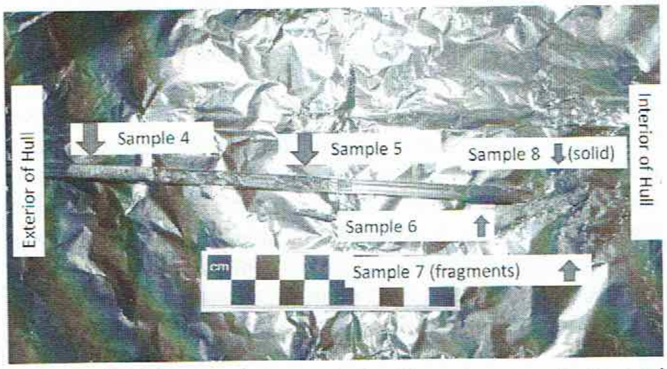

Figure 2. *Extracted core indicating the locations and condition of Sample 4 to Sample 8.*

and Tim-bor® and possibly identify depth of penetration. Infrared spectroscopy uses infrared radiation to analyze materials and determine their chemical composition. If a molecule absorbs infrared radiation then the bonds in the molecule undergo vibrational transitions. We can measure the light absorbed and hence the vibrational frequencies, which are specific for every different chemical compound. Small differences in chemical composition will result in a different absorption spectrum. The wood samples were ground into a fine powder using a mortar and pestle and pressed between a sapphire anvil and a diamond crystal to obtain intimate contact between the wood and the crystal. The fine powder was then analyzed using a single bounce Attenuated Total Reflectance (ATR) unit with a diamond internal reflection element. A total of 64 scans were collected for each spectrum on a Nicolet 6700 spectrometer using a DTGS detector. Spectra were then straight line corrected in the region 2000-2500 cm^{-1} and normalized.

Scanning Electron Microscopy method

To assist in the microscopy for this research project, a FEI Quanta 200 Mark 1 Scanning Electron Microscope with an Oxford Inca x-act Energy Dispersive (EDX) Microanalysis Elemental detector was used for imaging of the various wood samples collected from the CSS *Neuse*.

Each of the subsamples described above was mounted on an SEM platform prepared with carbon tape and photographed using a Leica EZ4 HD microscope. These pictures provided researchers with color images of the wood samples, and revealed the amber colored resin that was coating some of the wood samples. After the samples were properly mounted, they were placed in the SEM under low vacuum and examined at a variety of magnifications using backscatter imaging.

Results and discussion

The use of visual analysis followed by chemical characterization identified the current condition of the wood and provided an indication of the presence or absence of linseed oil and Tim-bor®. Results were compared to determine the cause of deterioration and depth of penetration of the applied treatments.

Fourier Transform Infrared Spectroscopy results

The results obtained from FTIR analysis identified a generic profile of the core. When interpreting FTIR spectra, the region 1900-2500 cm^{-1} is the location of carbon dioxide and other atmospheric gases and is excluded. Also, there are two regions on a spectrum, the functional group and the fingerprint region. The functional group can tell researchers about the classification of a chemical, but the fingerprint region provides specific details about the chemical composition of a sample.

The standard for linseed oil contained a strong absorption in the carbon-hydrogen stretching region 2800-3000 cm^{-1} (Figure 3). Also, a very strong signal at close to 1750 cm^{-1} is typically indicative of a carbonyl organic function group (C=O) (Figure 4). These are the indicators that researchers used to identify linseed oil within the wood samples.

In the standard for Tim-bor®, it is important to note the very strong absorbance at around 1325 cm^{-1} (Figure 5). If Tim-bor® is present in the wood there should be a strong absorption signal in this region in the spectra of the wood.

Once the standards were measured, the wood samples were run through the spectrometer. After each sample the machine was cleaned thoroughly and reset to standard to ensure accurate measurements were being recorded.

Figure 5 shows the spectra containing all of the samples from the wood core taken from the CSS *Neuse* (Sample 4 to Sample 9) compared to the standard for Tim-bor®. There are clearly many differences in the fingerprint region and the strong broad absorption area. This would indicate that infrared spectroscopy could not detect the presence of Tim-bor® specifically in any of these wood segments.

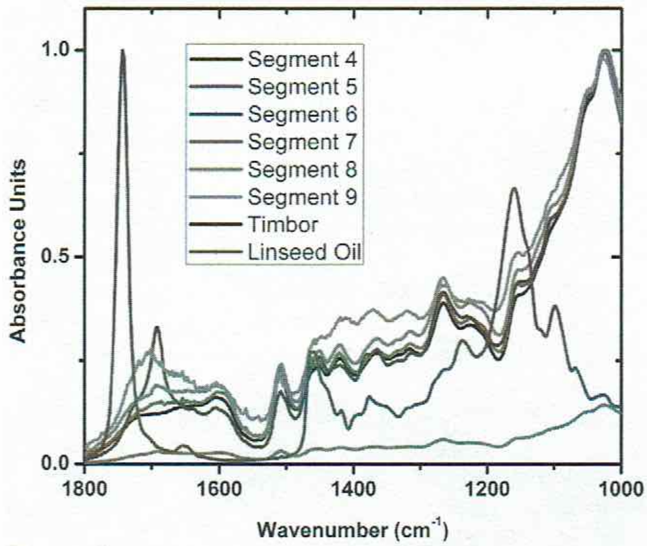

***Figure 4**. The fingerprint region of FTIR spectra showing Sample 4 to Sample 9 compared to a linseed oil standard.*

Next, the wood samples were compared with the standard for linseed oil. If there were significant concentrations of linseed oil in the wood we would expect a very sharp strong absorption in the spectra at about 1750 cm^{-1}. Although we don't see this sharp absorption, the wood samples do absorb some light in this region (Figure 4). Based on this evidence and the presence of the sharp spectral feature in the carbon-hydrogen region it does appear as though the wood contains some linseed oil (Figure 3). The samples of the core (Sample 4 through Sample 8) were also analyzed individually revealing several details:

- Sample 4, closest to the exterior of the hull, appears to have the lowest concentration of linseed oil. This may be due to the fact that the exterior surface was either treated well with Tim-bor®, which flushed out the linseed oil, or

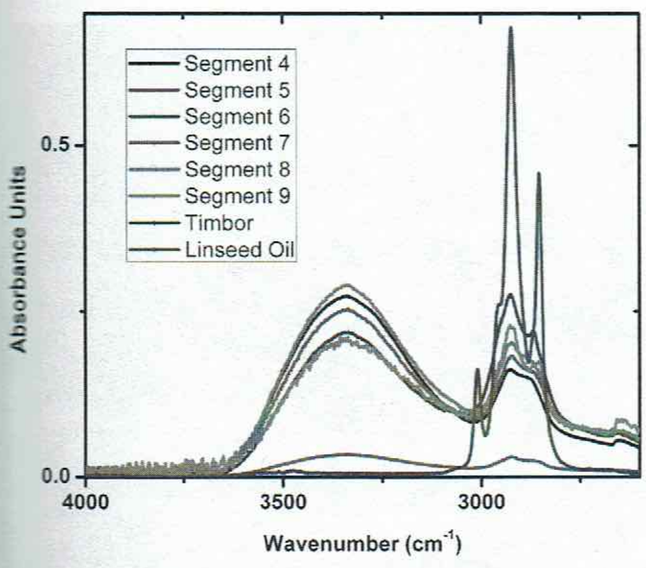

***Figure 3**: The functional group region of FTIR spectra showing Sample 4 to Sample 9 compared to a linseed oil standard showing strong absorption below 3000cm^{-1}.*

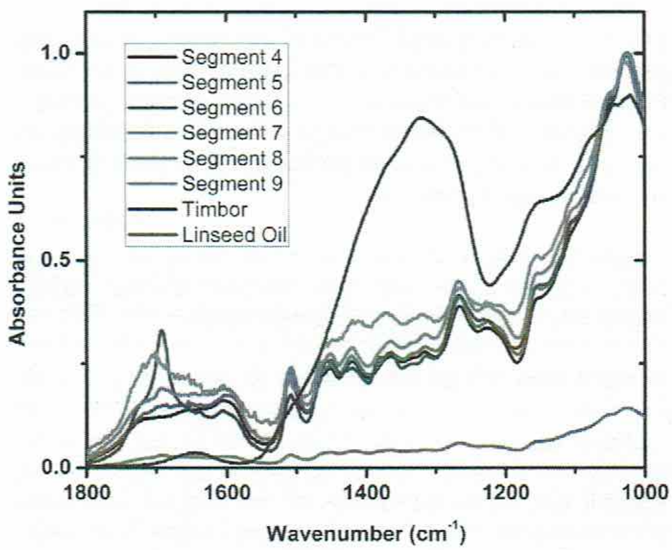

***Figure 5**. The fingerprint region of FTIR spectra showing Sample 4 to Sample 9 compared to Tim-bor.*

environmental exposure has removed the majority of the oil.

- Sample 5, fragments from the center of the timber, appear to contain more linseed oil than Sample 4, indicating that the oil certainly appears to have penetrated beyond the surface of the wood and it has not been completely removed from this area.

- Sample 6, a core section from the center of the timber, also contains a relatively high concentration of linseed oil, again indicating that the oil has penetrated deep within the wood.

- Sample 7, fragments towards the interior of the hull, show the weakest signal for linseed oil, and the sharp features associated with linseed oil or similar chemicals are not as evident.

- Sample 8, a core section close to the interior, shows a higher concentration of linseed oil than Sample 4. This may be due to the fact that the surface has not been exposed to the same environmental factors as the exterior surface or that Tim-bor® treatment in this area was not effective in flushing the linseed oil out.

It should be noted that due to the fragmentary nature of the core sample, it may be possible that the Sample 7 fragments were located further towards the interior of the vessel than Sample 8, but became dislodged during sampling. In conclusion, these results indicate that linseed oil penetrated the core of the wood and remained in situ despite the efforts to flush it out with Tim-bor®. Lower or absent amounts of linseed oil towards the surfaces of the timber indicate that some removal of the linseed oil was successful, but whether that is due to flow of the linseed oil over time or exposure to the elements is unknown.

Scanning Electron Microscopy results

Coupled with chemical analysis, the SEM revealed the general condition of the wood in several areas of the core. Figure 6 demonstrates a cross section of the tracheid cell walls with pits clearly visible in Sample 4. The walls themselves demonstrate limited bacterial and fungal decay of the primary and middle lamella cell wall.

Sample 5 in Figure 7 shows the brittle nature of the wood cells. The primary wall and middle lamella remain structurally intact and pits are clearly visible.

Figure 8 from Sample 6 illustrates two planes of wood, the transverse and radial. In the transverse cross section, the tracheids are clearly visible. They appear ovular due to the method of sectioning. Several inclusions are also visible as granular features on the surface and the lumen area of some of the tracheids are filled with an unknown organic substance. This is consistent with the FTIR analysis indicating the possibility of linseed oil being present. The labels indicate areas that were analyzed using x-ray diffraction (XRD).

***Figure 6**. SEM image of Sample 4 at x525.*

Sample 7, illustrated in Figure 9, clearly shows the distinction between the primary cell walls of the tracheids and the middle lamella with no indication of bacterial or fungal decay. The secondary walls also appear intact.

Lastly, Sample 8 in Figure 10 demonstrates the severely degraded nature of the ray cells traveling transversely through the wood. The primary walls and middle lamella are present, but the secondary walls appear delaminated possibly due to bacterial action. The cells are structurally weak. The tracheid walls are visible on either side indicating these are less affected structurally.

Results from these images indicate that the wood core samples are degraded in certain areas. The cell walls are thin

***Figure 7**. SEM image of Sample 5 at x525.*

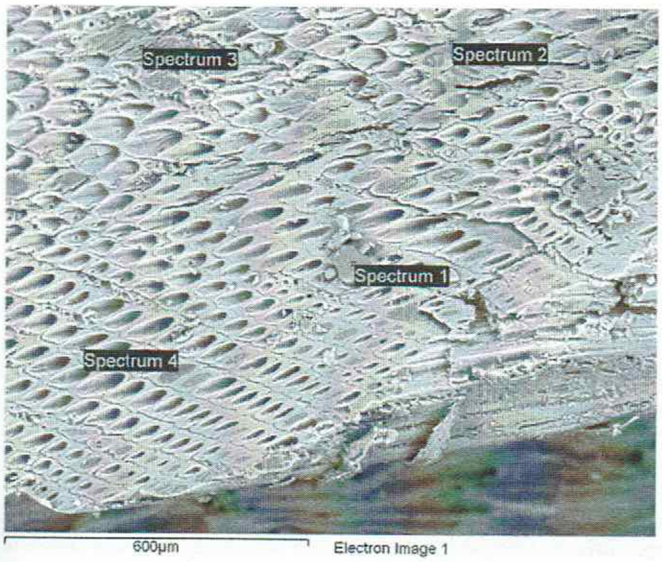

Figure 8*. SEM image of Sample 6 at x400.*

and the shape is malformed in some cases. The wood is delaminating in thin sheets and the structure of the wood is very fragile. This condition appears to be due to chemical damage caused by the cocktail of chemicals used to treat the ship as opposed to bacterial or fungal degradation that is more commonly seen on waterlogged wood samples.

Elemental analysis was also performed to identify unique granular features on the wood samples. The majority of samples were composed of carbon and oxygen indicating their organic nature, but it should be noted that energy-dispersive X-ray spectroscopy (EDX) is not a reliable tool for measuring organic components. The most interesting sample that was examined includes Sample 4ac, which is the third quarter of Subsample 4a and is closer to the interior of the core. The EDX results of this sample include weight percentages of: Na 1.56%, Si 0.15%, Cl 0.40%, K 0.29%, Ca 0.21%, and Fe 10.62%. Other samples evaluated also

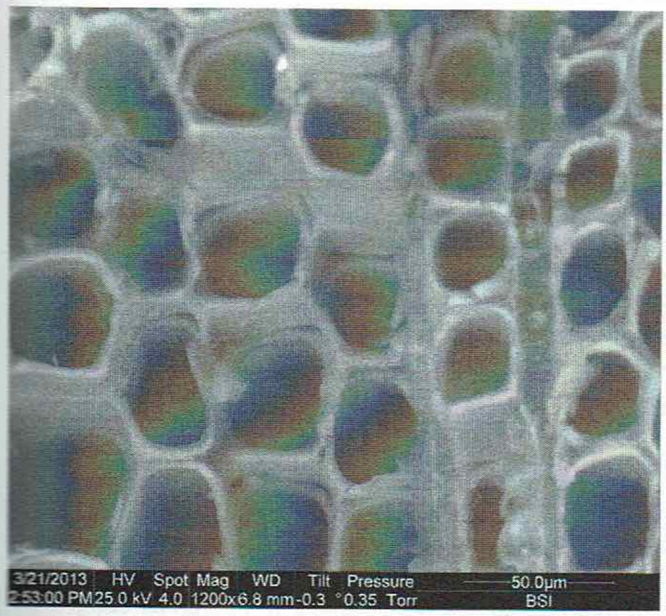

Figure 9*. SEM image of Sample 7 at x1200.*

Figure 10*. SEM image of Sample 8 at x2625.*

contained Magnesium, Nickel, and Aluminum in low amounts, which indicate contaminants from the sample preparation.

Elemental analysis on Sample 6 was performed on areas with unique features, namely a bulbous product on the surface of the wood seen in Figure 8 (Spectrum 1) and in the areas of the tracheids that were filled (Spectrum 3). Spectrum 1 showed a higher amount of carbon and oxygen levels than on the wood cells alone (Spectrum 4) indicating the bulbous feature is also organic in nature. Spectrum 3 also demonstrated higher levels of organic material when compared to the wood cells alone, but also included trace amounts of iron. This suggests that iron ions are present in the material filling the tracheids.

Overall, the SEM images demonstrated that the primary wall and middle lamella of the wood cells remains structurally stable and there is a distinct lack of biologically induced degradation, except for the potential absence of a secondary cell wall in some areas. There does appear to be extensive chemical damage present, which is indicated in samples by defibration and delamination of the tracheid features that is also evident on a macroscopic scale.

Conclusion

The FTIR analysis coupled with the imagery produced using the SEM allowed researchers to evaluate the effectiveness of the linseed oil treatment and provided a baseline on which to identify future research questions and conduct more complex analysis.

In conclusion, the evidence suggests that the linseed oil has penetrated further into the wood than previously thought. Also, the Tim-bor® has not been an effective treatment for penetrating into the wood to flush out the linseed oil.

New treatments should be considered for the CSS *Neuse,* though these should focus on mitigating any negative effects the previously applied treatments may have had. Since the ship is now in a climate-controlled facility, it is critical that careful monitoring be undertaken for the next three to five years. Site managers should note changes that take place. The hull of the *Neuse* is badly chemically degraded and additional chemicals could potentially harm the wood structure. While spectroscopy has its limits, future work could be conducted including the extraction of the wood samples, in particular the cores discussed above, with analysis by Gas Chromatography/Mass Spectrometry to quantitatively identify the previous treatments that had been applied and determine the degree of penetration.

Acknowledgments

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Questions and answers

K. Tran: Susanne, very interesting presentation. Is Tim-bor a pentachlorophenol?

S. Grieve: Yes.

K. Tran: So I'm surprised by such a high concentration.

S. Grieve: Of Tim-bor?

K. Tran: You mentioned 20%.

S. Grieve: I don't know that I had a percent. Oh, you mean at the beginning.

K. Tran: It's incredible--such a high concentration of pentachlorophenol, which is a very toxic biocide.

S. Grieve: You mean from the Tim-bor? Yes, this decision was made because the state conservator felt like it was a bacterial or fungal degradation of the wood so they used it because it was cheap. And the conservators, as far as I understand, were applying it by mixing it in water and applying it with a garden sprayer. But this treatment stopped in 1999.

K. Tran: And you didn't detect the Tim-bor? Not even the chlorine?

S. Grieve: Not using FTIR analysis, no. And, I think my opinion differs a bit from my colleagues on our interpretation, but the feeling was that FTIR analysis was not an effective tool to measure to this. But we did not see a large presence of Tim-bor. But we did it as a standard so of course it's a mixture of compounds so it's not going to be easily detected if it's a mixture using FTIR. It needs to be pretty pure. No, this is helpful, I appreciate your input. We no longer use Tim-bor because of the health and safety issue and the fact that it's not necessary. Thank you, Khoi.

K. Tran: If such high concentrations were used, you have to be aware about the toxicity for workers touching the ship.

S. Grieve: Yes, and I think they were using it above 100% probably.

A. Pournou: Tim-bor is not pentachlorophenol. It's not the same. Tim-bor is a boric product.

S. Grieve: I completely misunderstood.

A. Pournou: Yes, Tim-bor is borax. It's used widely as a fungicide. Disodium octoborate tetrahydrate. But this is not my question. Tim-bor is not toxic. There are health and safety regulations and it's been banned from Europe but it's not toxic. It's a salt. So, my question is....