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Reasoned use of chemical parameters for the diagnostic evaluation of the state of preservation of waterlogged archaeological wood

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ABSTRACT

Waterlogged archaeological wood undergoes decay processes that depend on both the burial conditions and the constituting species, and which cause the depletion of the structural components of wood cells. To quantitatively assess the state of preservation of the decayed material, specific parameters are usually measured by means of both chemical and physical analyses. In this paper an innovative approach in the use of the data obtained from these kinds of measurements is developed. A series of 132 archaeological wood samples of different wood species, burial times and states of preservation, and coming from different sites in Italy, was analysed. Their residual chemical composition, maximum water content and basic density were measured, and a reasoned use of these parameters was carried out through their elaboration, with the aim of both evaluating eventual incongruence or anomalies in the raw physical and chemical data (which has never been accomplished so far) and directly comparing in a reliable way the analytical results obtained from archaeological samples with very different states of preservation. This approach allowed defining the effective values of chemical parameters related to wood decay according to a same reference basis of calculation among the various data. By this way, it was possible to state that lignin can be also attacked by the agents causing biotic decay, and that in hardwoods its decay is more related to the burial conditions than to the wood species. Instead, the mechanism of polysaccharide depletion is diversified: conifers showed a uniform behaviour whereas hardwoods were more species-dependent. Moreover, in addition to the chemical composition, also anatomical factors influence the carbohydrate rate of decay in waterlogged wood.

1. Introduction

Wood findings of archaeological interest recovered in recent times in Italy are numerous. Their typology is extremely varied and ranges from the hulls and planking of shipwrecks, like those found in Pisa, Naples and near Comacchio, to the wood objects pertaining their shipload and life on board (Bruni, 2002; Fede Berti, 1990; Giampaola et al., 2005), to small objects of everyday life, like carved stairs (Bellini et al., 2007). Moreover, recent studies on the stability of some historic buildings in Venice gave the opportunity of investigating on their wood foundation piles, submerged in the lagoon (Biscontin et al., 2011).

All these findings are dated in a large time-span ranging from Eneolithic to XVIII cent. Furthermore, while part the objects were discovered in submerged contexts, most of them were collected during terrestrial archaeological excavations, where they have been preserved embedded in sediments below the water table. In waterlogged conditions, the rate of wood decay is related to its constituting species and, mostly, to the burial conditions (Jordan, 2001; Rowell and Barbour, 1990). These latter are due to the different characteristic of soils. Composition, granulometry and interstitial water content are the main parameters responsible for creating different microenvironments where nature of salts, pH, organic matter and oxygen availability favour the degradation of wood (Huisman et al., 2008a; Kretshmar et al., 2008). However, the agents provoking the wood decay process are generally of biological origin (Björdal et al., 1999). Although some bacteria, such as erosion bacteria, seem to live even at low oxygen content (Björdal et al., 2000), in general oxygen is essential for decay. Moreover, recent studies demonstrated that the action of microorganisms in the soil is also accelerated by other substances, such as nitrogen and phosphorous compounds (Huisman et al., 2008b). The decay process implies a series of structural modifications in wood, in terms of chemical composition and cell morphology. Fungi and bacteria

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act depleting mainly the polysaccharidic content, and leaving a partially oxidized lignin, which is commonly considered quantitatively similar to the original one (Fengel, 1991; Hedges, 1990). As a result, wood becomes a sort of "new material" with chemical, physical and mechanical properties very different from those at the fresh state. These differences are normally considered more related to decay level than to the different species (Schniewind, 1990). Generally, the state of preservation of waterlogged archaeological wood is assessed thus to help in conservation. Only in a few cases, data regarding the burial conditions are collected, because archaeological excavations are mostly carried out in emergency situations, and all efforts are mainly focused towards the recovery of artefacts. To assess the state of preservation of waterlogged archaeological wood different analytical approaches are currently followed. They are useful to both identify the agents of decay and to evaluate the present state of preservation of wood cells, and include physical and chemical measurements and micro-morphological examination (Capretti et al., 2008; Macchioni, 2003; Pizzo et al., 2010). Micro-morphological analysis leads to verify the diffusion and in depth extension of cell wall decay, and moreover to distinguish the biological agents responsible of the attack (Kim and Singh, 2000). Physical evaluation lets to know the global effect of the decay by setting the mass loss of the wood and the consequent increase of porosity and of water content (Jensen and Gregory, 2006). Chemical analysis allows quantitatively determining the residual components of wood cells and thus understanding the final effect of decay on the material (Giachi et al., 2003). The results of this integrated approach contribute in developing some strategies in planning the conservation of wood findings (Giachi et al., 2010, 2011).

In this paper an innovative approach in the use of data usually obtained from chemical and physical analyses is presented. A series of 132 archaeological wood samples were analysed, and their level of decay was estimated by means of a reasoned use of the measured parameters, also involving some mathematical elaborations of the same parameters. It is shown how a more effective assessment of the wood decay can be obtained through this approach, and how the effects of wood species and of burial contexts on the degradation of structural biopolymers constituting wood cell walls can be accurately evaluated.

2. Material and methods

A series of 132 archaeological wood samples coming from some excavations carried out in Italy were analysed in this work, their brief description being reported in Tables 1 and 2. In most of the samples, micro-morphological analysis evidenced the attack of erosion bacteria and less frequently of soft rot fungi. Collected samples are representative of a large range of conditions and time of burial during waterlogging, as well as variability of wood species. The amount of material for the analyses was variable, depending on the sampling availability. Usually, parallelepipeds of approximately 2–4 cm^2 in section and 3–5 cm in length were used.

Chemical analysis of fossil wood was carried out according to the procedures described in the specific Tappi standards or with well-established methodologies, which are briefly described in the followings. All samples were firstly dried and thereafter milled; then, meals were sieved, and the fraction 40–60[1] mesh was collected for the analysis. The parameters measured on the meals were:

- moisture content at the initial moment of the analysis, by maintaining the samples in an oven at 103 °C until constant weight (at least 24 h). By this way, all results were referred to the anhydrous weight of wood;
- content of organic extractives (OE), by means of Soxhlet extraction according to Tappi T204-cm07, but using a mixture of toluene and ethanol (2:1 v/v) as extracting solvents. Each sample was extracted for at least 25 cycles;
- content of aqueous extractives (AE), carried out on the previously extracted meal by using deionised water in a Soxhlet extractor. Even in this case, each sample was extracted for at least 25 cycles;
- lignin amount (L), measured on the extracted meal according to the Klason's method (Tappi T222-om02);
- ash content (A), according to Tappi T211-om02.

The remaining part, constituting the holocellulose (Fengel and Wegener, 1989) was evaluated in percentage by the arithmetic difference with the sum of all the other chemical components (considered as 100% in the original amount of wood meal) according to the following equation:

$$H = 100 - (L + \mathrm{OE} + \mathrm{AE} + A) \quad (\text{all values in } \%). \tag{1}$$

In this expression, the generic parameter P (that is: L, OE, AE, A) was given by:

$$P = \frac{M_P}{M_{\mathrm{ANHYDR}}} \quad [\%]. \tag{2}$$

where M_P is the mass of the considered parameter and M_{ANHYDR} the mass of the anhydrous wood sample.

It is also possible to directly measure the holocellulose amount, for example by using the method of Norman and Jenkins (Browning, 1967). However, it was shown previously that this method underestimates the real quantity of holocellulose (Pizzo et al., 2010), and therefore only the calculated values were used in present case.

Furthermore, chemical composition of recent wood of the same species as for archaeological material was also assessed. Measurements were carried out with the same procedure described for the archaeological samples.

Prior to carry out the chemical analysis, some physical parameters were measured on the same samples. More specifically, both Maximum Water Content (MWC) and Basic Density (BD) were evaluated, according to the following equations:

$$\mathrm{MWC} = 100 \cdot \frac{M_{\mathrm{WET}} - M_{\mathrm{ANHYDR}}}{M_{\mathrm{ANHYDR}}} \quad [\%] \tag{3}$$

$$\mathrm{BD} = \frac{M_{\mathrm{ANHYDR}}}{V_{\mathrm{WET}}} \quad \left[\mathrm{g/cm^3}\right] \tag{4}$$

where M_{WET} and V_{WET} are the mass and the volume of the waterlogged sample, respectively. The condition of fully waterlogged wood was assured by maintaining samples in water between sampling and the analyses. It is worth noticing that MWC and BD are correlated by the simple expression: $\mathrm{BD} = 100/(\mathrm{MWC} + 67)$ (Schniewind, 1990; Tsoumis, 1991).

For each sample, if the BD value is compared with that one of the same species in fresh conditions (reported in Table 2 and obtained from literature: Giordano, 1981), the Residual Basic Density (RBD) can be calculated as:

$$\mathrm{RBD} = \frac{\mathrm{BD}_{\mathrm{sample}}}{\mathrm{BD}_{\mathrm{fresh\ wood}}}. \tag{5}$$

[1] In a few cases the use of a wider granulometric interval was necessary because of the very limited quantity of available material.