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ΘΑΛΗΣ: Ενίσχυση της Διεπιστημονικής ή/και Διιδρυματικής έρευνας και καινοτομίας με δυνατότητα προσέλκυσης ερευνητών υψηλού επιπέδου από το εξωτερικό μέσω της διενέργειας βασικής και εφαρμοσμένης έρευνας αριστείας

Τίτλος υποέργου:
Διερεύνηση των επιδράσεων των περιβαλλοντικών παραγόντων στα οργανικά υλικά τεκμήρια φυσικής και πολιτιστικής κληρονομιάς
(MIS 376986)

ΠΕ.1: Σύνθεση - Αξιολόγηση των αποτελεσμάτων - Δημοσιότητα

Υποδράση 6.1: Μελέτη τεχνητής γήρανσης και συσχέτιση με πραγματικά δεδομένα. Διερεύνηση των μηχανισμών διάβρωσης και αποδόμησης με στόχο τη περιγραφή λειτουργικών μοντέλων φθοράς. Αξιολόγηση των αποτελεσμάτων της επίδρασης του περιβάλλοντος στο υλικό των αντικειμένων.

Παραδοτέο: 6.1 Επιστημονικές δημοσιεύσεις/ανακοινώσεις

Δημοσίευση στο περιοδικό «ΜΟΥΣΕΙΟ»

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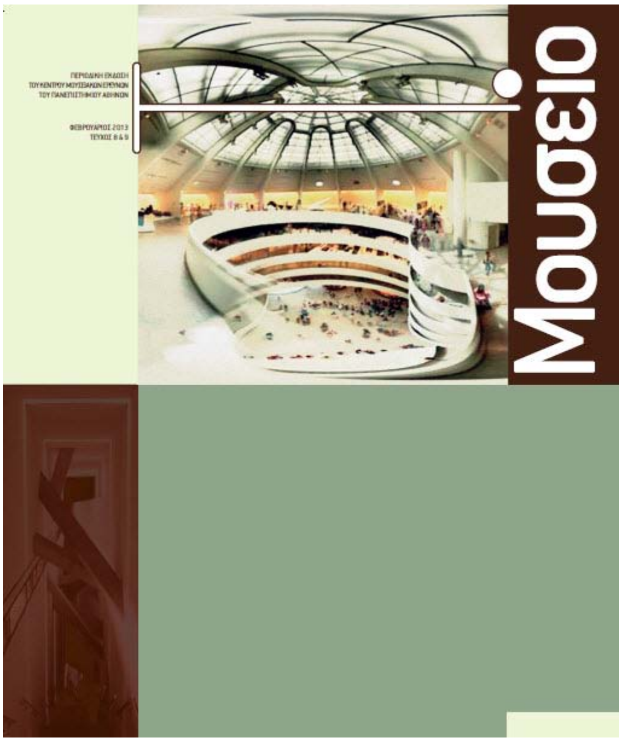
<u>Εισαγωγή</u>

Στο παρόν παραδοτέο παρατίθεται το κείμενο που υποβλήθηκε και εγκρίθηκε προς δημοσίευση στο περιοδικό «Το Μουσείο», το οποίο αποτελεί περιοδική έκδοση του Κέντρου Μουσειακών Ερευνών του Εθνικού και Καποδιστριακού Πανεπιστημίου Αθηνών.



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Investigation of the non-treated organic materials degradation process in museum environment

Διερεύνηση των μηχανισμών διάβρωσης και αποδόμησης μη επεξεργασμένων οργανικών υλικών τεκμηρίων πολιτιστικής κληρονομιάς

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Abstract

The paper reports results on the artificial ageing of bones and wood. Data were collected under a specific fractional experimental design for 5 binary factors, namely duration, humidity levels, sulfur dioxide (SO2) and nitrogen oxides (NOx) exposure and the order of such exposure. The effect of all the factors in different aspects like the color, the gloss characteristics, the mechanical properties and the composition and chemical stability was examined using an analysis of variance approach. The finding show that for the bones duration is not significant while humidity and the pollutants are significant for some of the characteristics. For the wood duration is significant.

1. INTRODUCTION

The current paper presents preliminary findings from the project INVENVORG which aims to carry out the artificial aging of non treated organic materials (parchment, woolen textile, bone, wood and paper) under individual environmental factors such as relative humidity (RH), sulfur dioxide (SO2), nitrogen oxides (NOx) and the order this was applied to the material. It is clear that other factors may affect ageing but it was selected to work due to time and cost restriction with only those. It is important to mentioned that in contrast to the inorganic materials of cultural heritage, organic materials have been subjected to less systematic research.

At the same time, these materials were also studied in real museum environments in which the air gases, the climatic factors, the air particles and the bioaerosol will be measured. So, in addition to artificial ageing, natural ageing was also part of the project. However in the present paper we present results only for the artificial ageing process and not the natural one which will be reported elsewhere when the experiments finish.

The quantitative and qualitative condition assessment of aged and non-aged samples, as this is determined through the study of the structure and of the chemical composition of organic materials, was achieved by modern diagnostic techniques (macroscopic, microscopic, nanoscopic, chemical analytical and mechanical), aiming at recording qualitative and quantitative changes in physical, chemical or even intangible features. It is therefore considered necessary to include in this study, representative samples from various organic materials instead of an in depth investigation of only one kind of material.

One of the important aspects of the project is that the data were collected under specific experimental conditions and in order to maximize the information flow we designed a statistically appropriate experimental design in order to test the optimal combinations of the experimental conditions of interest and hence to maximize the information collected. More on this can be found in the next section. We emphasize that while it has been recognized the importance for well designed experiment in the natural heritage scientific field there are very few such works (see the review in Dellaportas et al, 2014)

In this article we focus on the bone and wood experiment. The remaining of the paper proceeds as follows. Section 2 explains the experimental design setting used for the experiment. Brief descriptions of the procedures applied to bones will be described in section 3. Results based on ANOVA model will be shown in section 4 for different bone and wood characteristics. Concluding remarks and summary of the findings can be seen in section 5.

2. Experimental Designs

2.1 General considerations

The field of experimental designs is an important element of statistical science, since proper experimental designs allow for the collection of the necessary information for deriving statistically valid conclusions. The central idea of experimental designs is that since in most cases we are interested on examining the effect of different factors upon a certain response of interest, we need to apply them in a proper and predefined manner such as to optimize some criterion. A well designed experiment can reduce the number of replications (experiments) needed in order to derive statistically valid conclusions and hence to minimize the cost without loss of information. Experimental designs have been the cornerstone for the development of statistical methodology.

In its simplest form, an experiment aims at predicting the outcome by introducing a change of the preconditions, which is reflected in a variable called the predictor. The change in the predictor is generally hypothesized to result in a change in the second variable, hence called the outcome variable. Experimental design involves not only the selection of suitable predictors and outcomes, but planning the delivery of the experiment under statistically optimal conditions given the constraints of available resources.

To make the situation clearer, in our experiment we wanted to check for the effect of different predictors like the humidity and the duration for example. A natural question is how many experiments and under what circumstance, i.e. humidity and duration levels the researcher should experiment in order to be able to detect differences (if any). It is apparent that restriction on time and cost do not allow for a huge number of experiments and hence the statistician has to work under the challenge of minimizing the number of experiment without sacrificing the statistical validity.

Statistical literature offers several types of design to optimize the information flow depending on the number of available experiments (how many samples we can collect and the factors to be tested). The literature is vast and refers to different criteria. In our case the problem was a challenging one since 5 factors were examined and hence interactions between the factors should be able to be considered (being estimable in the statistical jargon).

We emphasize that an experiment deliberately imposes a treatment on a group of objects or subjects in the interest of observing the response. This differs from an observational study, which involves collecting and analyzing data without changing existing conditions. Because the validity of a experiment is directly affected by its construction and execution, attention to experimental design is extremely important.

2.2 Full factorial designs

A full factorial experiment is an experiment whose design consists of two or more factors. Each factor has a number of discrete possible values (levels), and whose experimental units take on all possible combinations of these levels across all such factors. Another name for a full factorial design is a fully crossed design because all the levels of all factors are crossed together. Such an experiment allows the investigator to study the effect of each factor on the response variable, as well as the effects of interactions between factors on the response variable. However in order to be able to investigate interactions the replication for each combination is needed which can lead to a large number of experimental combinations and hence to a large number of replications.

For the vast majority of factorial experiments, each factor has only two levels. This was also true for our design. For example, with two factors each taking two levels, a factorial experiment would have four treatment combinations in total, and is usually called a 2×2 factorial design. In our experiment with 5 binary factors we need 32 combinations.

If the number of combinations in a full factorial design is too high to be feasible, a fractional factorial design may be done, in which some of the possible combinations (usually at least half) are omitted. This was the case for our experiment on artificial ageing.

2.3 Fractional factrorial designs

Fractional factorial designs are experimental designs consisting of a carefully chosen subset (fraction) of the experimental runs of a full factorial design. The challenge lies on selecting this fraction, since there are several different designs that can be produced. The subset is chosen so as to exploit the “sparsity-of-effects” principle to expose information about the most important features of the problem studied, while using a fraction of the effort of a full factorial design in terms of experimental runs and resources.

An important property of a fractional design is its resolution or ability to separate main effects and low-order interactions from one another. This means that we are able to estimate the main effects and some (the most important) interactions, while sacrificing the ability to estimate all interactions. Typically some interactions that are considered less important are sacrificed in order to reduce the number of replications and hence reduce time and cost issues.

3. The experimental conditions for the artificial ageing.

When materials are exposed to the atmosphere in a museum environment, they are subjected to damage not only from exposure to light, moisture, and heat, but also from interactions with gaseous pollutants (such as SO_2 and NO_x). Damage occurs due to dry and/or wet deposition of the pollutants onto the surface of a material and subsequent formation of an electrolytic solution in water present on the surface. The materials’ damage may be physicochemical, potentially affecting materials’ durability, or may be purely aesthetic, affecting only their appearance.
In the case of bone, the influence of the atmospheric pollutants has not been studied yet. Bone is a "hard" proteinaceous material, while wood is a lignocellulosic one. In both cases inadequate environmental conditions can cause physical, chemical and biological deterioration, depending on the environment in which they are located.
Although, there have been many studies conducted regarding the aging and thermal effects on bone, there has been no focused research approach to documenting, through its results, the degradation mechanisms of bones in museum environment (Cronyn, 1990; Weintraub and Wolf, 1995; Hedges, 2002).
In the case of wood, the main abiotic factors in a museum environment affecting wooden artifacts preservation are heat, radiation, relative humidity, and particulate and gaseous pollution (Rivers and Umney, 2005; George *et al.*, 2005; Yidiz *et al.*, 2006). Literature on the effect of gaseous pollution on wood and its synergistic action with other environmental factors is scare. Gaseous pollutants, such as O_3, NO_2 and SO_2, have been studied mostly for surface treated wood (Grontoft & Raychaudhuri, 2004) or for wood coatings and it has showed that pollutants surface deposition velocities are highly dependent to relative humidity (RH).

The investigation of the degradation mechanisms of the materials constituting the cultural and natural heritage, despite the progress made, has a long way still to go. The most common way followed for the determination of these mechanisms is the application of physicochemical methods after accelerated ageing. The disadvantage of this practice is the inability to control the effect of the combination of degradation factors in real time and in real conditions as it happens in burial environment, in museum environment or in open-air conditions. This problem is getting even worse in the case of organic materials that are characterized by a variety in structure and composition, and that are extensively sensitive in many environmental factors, such as bone and wood. The need for understanding the decay process resulted to the standardization of diagnostic techniques and of the accelerated ageing protocols (ASTM, 2010, 2011, 2013).

According to the literature cited above, the main abiotic factors in a museum environment affecting bone and wood material preservation are i) temperature, ii) relative humidity (RH) and iii) air pollution (NO_2 and SO_2).

The desirable levels, in terms of human comfort, of these factors in a museum are in the intervals of 15-20^{o}C for the temperature and 45-55% for the relative humidity (Ashrae, 2011). As far as the pollutants, their concentrations are usually those met in the area of the museums. According to the standards in Greece the level of alarm for the concentrations of these two pollutants are 200 μg/m^3 (0.10 ppm) and 350 μg/m^3 (0.18 ppm) for NO_2 and SO_2, respectively (ΦΕΚ 125/5.6.02). The levels of the aforementioned factors that do not influence the artifacts remain to be concluded.

In general, during artificial or accelerated ageing extreme environmental conditions are used, in order to simulate the natural ageing process in shorter periods of time (Porck, 2000). The purpose of this experiment is to produce artificially aged samples using specific environmental conditions (temperature, relative humidity and air pollutants) that simulate naturally aged samples, so then to assess the impact of specific environmental conditions on the physical and structural integrity of the bone material.

As bone samples metapodials of modern deers (roe deers - *Capreolus*) from Denmark were used. They were chosen because the bones of this animal have about the same length and thickness, and so similar sized samples can be generated.

As wood samples pieces of a light color softwood (Pinus spp) and a dark color hardwood were used (Quercus spp). In this way it was possible to study the effect of environmental factors on different species of wood, and thus to link to their different anatomical, physical and chemical properties.

According to the experimental design, the properties showed in Table 1 were determined.

Table 1. Properties and physicochemical methods, which are envisaged by the experimental design to be performed on the bone and wood samples.

Property	Method	Institution of implementation
Physicochemical alterations of collagen	HPLC	TEI-A
	FTIR	TEI-A
	ELISA	UoI
Physicochemical alterations of hydroxyapatite	SEM/EDAX	TEI-A
	XRD-XRF	TEI-A
Evaluation of the microstructure	CT - Scanning	NTUA
Alteration of mechanical properties	Three-point bending	NTUA
	Janka Hardness test	NTUA
Degree of pollutants penetration	Chemical mapping RAMAN	UoP
Examination of materials morphology	Visual observation	TEI-A
	SEM	TEI-A
	Optical microscopy	TEI-A
Examination of optical properties (surface gloss and color)	Three angle gloss meter	TEI-A
	CIE L*a*b* colour	TEI-A
FE modeling	Computational mechanical analysis	NTUA

4. The used experimental design

The experimental design has taken into account the ageing of both the organic part of the bone and wood, as well the inorganic part of the bone. As mentioned above a fractional factorial design with replication was constructed in order to maximize the collected information. 5 binary factors were considered

- Duration of the ageing procedure (two levels, 24 and 48 days)
- Relative humidity while ageing (two levels 45% and 70%)
- Pollution with sulfur dioxide (SO2), (two levels in ppm, 100 and 300)
- Pollution with nitrogen oxides (NOx) (two levels in ppm, 100 and 300)
- The order of pollution (two levels S/N and N/S)

Note that since we use 5 binary factors a full factorial design implies 2^5 =32 experiments. The usage of fractional factorial design led to 2^4 =16 different experimental conditions. For each condition we had a replication of 3 samples for the bones leading to a total number of 48 sample points for the analysis and 2 samples for the wood leading to 32 observations.

The design can be seen in Table 2.

Table 2: the experimental designed used for the ageing.

Experiment	Duration in days	Relative humidity (%)	Nox in ppm	Sox in ppm	Pollutant order
1	14	45	100	300	N/S
2	28	70	300	100	N/S
3	28	70	100	300	N/S
4	28	70	100	100	S/N
5	14	70	300	300	N/S
6	28	45	300	100	S/N
7	14	70	100	100	N/S
8	28	45	300	300	N/S
9	28	45	100	300	S/N
10	28	70	300	300	S/N
11	28	45	100	100	N/S
12	14	45	300	100	N/S
13	14	70	100	300	S/N
14	14	45	300	300	S/N
15	14	45	100	100	S/N
16	14	70	300	100	S/N

5. Statistical methodology

5.1. Data processing

As mentioned in a previous section the samples after the ageing procedure were undertaken certain procedures in order to examine a variety of different characteristics. Before statistical analysis careful pre-processing of the data was made to ensure the correctness of the values reported, checking for spurious observation and missing data. Missing data were found for some characteristics and it was verified that there were not measurements for that samples. No outliers or inadmissible values were detected. Descriptive statistics were also checked with the existing literature to verify that the reported values are plausible. No particular problems were found.

5.2. Statistical methods

A very common and typical model for such experimental data is the analysis of variance model. This also relates to the classical regression model if dummy variables are considered.

To keep the notation minimum the ANOVA model for the simplest case of two factors can take the form

$$Y_{ijk} = a + \beta_j + \gamma_k + \varepsilon_{ijk} \ ,$$

where

Y_{ijk} is the i-th observation for the combination of the level j of the first factor and k for the second factor

α is an overall mean effect

β_j is the effect of the j-th level of the first factor

γ_k is the effect of the k-th level of the second factor and finally

ε_{ijk} is some error term following as usual a normal distribution with mean 0 and constant variance

The model does not assume any interaction, no interactions were considered. Since the model can be seen as a standard linear model, significance of factor can be considered by the significance of the relevant coefficients of the dummy variables.

Note that in our case 5 factors were considered. the above model acan be easily extended for five factors but the notation will be more messy.

Also note that no interaction terms were considered. First of all not all the interactions were estimable due to the fractional design, but also since no main effects were deemed significant for most of the models we decided that further investigation of interactions would not be useful. However all the interaction plots were created for further insight.

Checks based on the residuals for the assumptions for the models were done, no particular deviations were detected.

Data analysis was run using SAS software.

6. Results

6.1 Bones

We present the results for the different characteristics measured on the bones, namely color properties (Table 3), gloss characteristics (Table 4) , Composition and chemical stability (Table 5) , Vickers hardness (Table 6) , mechanical properties (Table 7). For each Table we present the basic response variable considered, the general p-value for the hypothesis that all factors are not significant versus that at least one is significant. then for each response we present the mean values under the different levels of each experimental condition together with their standard errors (the first line contains the overall mean) and the p-value corresponding to this factor. All tests were deemed significant at a=5%.

For example for Table 1 we can see the three different responses for the color properties, namely the quantities L, a and b. For L, the overall p-value is 0.021 indicating that at least one factor is not zero (hence it is significant). The overall mean value is 79.2 and the standard deviation 6.5. Looking each factor separately we see that for the duration the mean value for duration equal to 14 days is 80.6 while the standard deviation is 4.2 for this duration. the p-value 0.098 indicates that at level a=5% we do not reject the hypothesis that the factor duration is not important and hence we cannot say that the duration is significant for the response L. the rest of the entries can be read in the same manner.

Note that there are some more characteristics for which the investigation is still ongoing and thus we do not report here

Table 3. ANOVA models for color properties

Main effect	Level	L *(p=0.021)*		a *(p<0.001)*		b *(p=0<0.001)*	
		Avg(std)	*p-value*	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*
OVERALL		79.2 (6.5)		2.8 (1.8)		24.1 (5.3)	
Duration	14	80.6 (4.2)	0.098	3.0 (1.8)	0.45	24.8 (5.8)	0.17
(Days)	28	77.8 (8.0)		2.7 (1.8)		23.5 (4.8)	
Relative Humidity	45	80.7 (3.9)	0.092	2.9 (1.9)	0.82	24.7 (6.2)	0.25
% (RH)	70	77.7 (8.1)		2.8 (1.7)		23.6 (4.3)	
Concentration SOx	100	79.5 (4.7)	0.69	3.4 (1.6)	0.0029	24.7 (4.0)	0.31
(ppm)	300	78.9 (7.9)		2.2 (1.8)		23.6 (6.4)	
Concentration NOx	100	80.6 (6.8)	0.11	1.9 (1.6)	<.0001	22.6 (5.9)	0.0037
(ppm)	300	77.8 (5.9)		3.8 (1.5)		25.7 (4.2)	
Pollutant order	N/S	77.1 (7.3)	0.016	3.5 (1.5)	0.0005	27.9 (4.2)	<.0001
	S/N	81.3 (4.7)		2.1 (1.8)		20.4 (3.3)	

From Table 3 one can see that for the color properties the significant factors are the pollutants and their order whiel humidity and duration are not significant. For gloss characteristics (Table 4) no factor is significant. Relative humidity is significant (p-value =0.028) for *[Pro-Ser(OBzl)-Gly]n antibodies (Table 5)*

Table 4. ANOVA models for gloss characteristics (60^o)

Main effect	Level	Side_A (p=0.45)		Side_B (p=0.43)		Side_C (p=0.71)	
		Avg(std)	*p-value*	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*
OVERALL		2.49 (0.46)		2.69 (0.39)		2.56 (0.41)	
Duration	14	2.58 (0.52)	0.22	2.64 (0.38)	0.4	2.52 (0.42)	0.44
(Days)	28	2.40 (0.38)		2.73 (0.40)		2.61 (0.40)	
Relative Humidity	45	2.55 (0.50)	0.4	2.65 (0.41)	0.48	2.54 (0.40)	0.71
% (RH)	70	2.43 (0.42)		2.73 (0.37)		2.59 (0.43)	
Concentration SOx	100	2.56 (0.53)	0.28	2.70 (0.30)	0.74	2.57 (0.42)	0.92
(ppm)	300	2.42 (0.37)		2.67 (0.47)		2.56 (0.41)	
Concentration NOx	100	2.56 (0.49)	0.31	2.75 (0.38)	0.23	2.57 (0.49)	0.97
(ppm)	300	2.42 (0.43)		2.62 (0.39)		2.56 (0.33)	
Pollutant order	N/S	2.52 (0.50)	0.69	2.77 (0.46)	0.15	2.65 (0.41)	0.15
	S/N	2.46 (0.42)		2.60 (0.29)		2.48 (0.41)	

Table 5. ANOVA models for Composition and chemical stability

Main effect	Level	*Collagen antibodies (p=0.39)*		*[Pro-Ser(OBzl)-Gly]n antibodies (p=0.021)*	
		Avg(std)	*p-value*	*Avg(std)*	*p-value*
OVERALL		0.29 (0.18)		0.41 (0.18)	
Duration	14	0.33 (0.18)	0.14	0.36 (0.19)	0.037
(Days)	28	0.25 (0.17)		0.46 (0.15)	
Relative Humidity	45	0.28 (0.20)	0.69	0.36 (0.15)	0.028
% (RH)	70	0.30 (0.16)		0.46 (0.19)	
Concentration SOx	100	0.30 (0.20)	0.79	0.37 (0.17)	0.084
(ppm)	300	0.29 (0.15)		0.45 (0.18)	
Concentration NOx	100	0.28 (0.18)	0.78	0.41 (0.15)	0.98
(ppm)	300	0.30 (0.17)		0.41 (0.20)	
Pollutant order	N/S	0.25 (0.17)	0.11	0.44 (0.16)	0.15
	S/N	0.33 (0.18)		0.38 (0.19)	

For Vickers Hardness only the order of the Pollutants is significant (p-value=0.018). Finally from Table 7, for the mechanical properties only humidity was found significant for the Mesh evaluation (p-value=0.011)

Table 6. ANOVA models for Mechanical property: Vickers hardness

Main effect	Level	*Mean VH (p=0.067)*	
		Avg(std)	*p-value*
OVERALL		74.47 (11.20)	
Duration (Days)	14	75.00 (11.25)	0.81
	28	73.95 (11.38)	
Relative Humidity % (RH)	45	71.15 (11.28)	0.039
	70	77.79 (10.31)	
Concentration SOx (ppm)	100	75.10 (12.14)	0.65
	300	73.85 (10.42)	
Concentration NOx (ppm)	100	75.41 (12.18)	0.62
	300	73.54 (10.32)	
Pollutant order	N/S	78.47 (5.92)	0.018
	S/N	70.81 (13.57)	

Table 7. ANOVA models for mechanical properties

Main effect	Level	Mesh evaluation (mean vol. el.) *(p=0.025)*		Strain Energy Density *(p=0.083)*		Volume *(p=0.25)*	
		Avg(std)	*p-value*	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*
OVERALL		0.70 (0.20)		938.0 (1033)		9184 (1542)	
Duration (Days)	14	0.66 (0.17)	0.18	724.8 (360.0)	0.14	9043 (1517)	0.53
	28	0.73 (0.23)		1151 (1399)		9325 (1586)	
Relative Humidity % (RH)	45	0.63 (0.19)	0.011	1190 (1384)	0.082	9496 (1267)	0.16
	70	0.77 (0.19)		686.3 (368.8)		8872 (1746)	
Concentration SOx (ppm)	100	0.72 (0.20)	0.28	779.3 (415.8)	0.267	8939 (1580)	0.27
	300	0.67 (0.21)		1097 (1399)		9429 (1496)	
Concentration NOx (ppm)	100	0.72 (0.19)	0.47	1119 (1404)	0.21	9063 (1719)	0.58
	300	0.68 (0.21)		757.1 (379.8)		9305 (1369)	
Pollutant order	N/S	0.75 (0.20)	0.053	729.5 (329.5)	0.15	8815 (1509)	0.098
	S/N	0.64 (0.19)		1146 (1408)		9553 (1516)	

A summary of the findings can be found in Table 8. Here we have collected all the results from the previous tables and note with an X the statistically significant results for a=5%. It is interesting that the duration was not found significant for any of the characteristics tested. The pollutants were significant only for the color properties while humidity was found significant for some of the mechanical and stability properties.

Table 8. Summarizing the Results

	Color properties			Gloss characterícts (60o)			Stability Properties			Mechanical Properties		
	L	a	b	Side A	Side B	Side C	Collagen antibodies	[Pro-Ser(OBzl)-Gly]n antibodies	Vickers hardness	Mesh evaluation (mean vol. el.)	Strain Energy Density	Volume
Duration												
Humidity								X	X	X		
Sox		X										
Nox		X	X									
Pollutant Order		X	X						X			

6.2 Wood

The wood experiments were somewhat different. First of all two types of wood were considered: soft and hard wood. In addition for each sample two different sections were evaluated, radial and tangential. In total for each case we had two replications, i.e. 32 samples for each combination of wood and way for chopping it.

For wood we have measurements only on the color, gloss characteristics and Vickers hardness. Tables are the same as those for the bones, with the average and standard deviation for each case together with the p-value for the ANOVA test.

Table 9. ANOVA models for color properties – Hardwood- Tangerial measurements

Main effect	Level	L *(p=0.0008)*		a *(p=0.053)*		b *(p=0.0069)*	
		Avg(std)	*p-value*	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*
OVERALL		56.72 (3.49)		12.67 (1.09)		28.02 (1.43)	
Duration (Days)	14	57.65 (2.45)	0.13	12.19 (1.12)	0.0028	27.75 (1.43)	0.24
	28	55.78 (4.16)		13.16 (0.84)		28.30 (1.43)	
Relat. Humidity % (RH)	45	57.39 (3.43)	0.26	12.54 (0.96)	0.36	28.32 (1.45)	0.22
	70	56.04 (3.51)		12.81 (1.22)		27.73 (1.39)	
Concent. SOx (ppm)	100	57.79 (3.10)	0.078	12.35 (1.22)	0.039	27.71 (1.28)	0.19
	300	55.64 (3.61)		12.99 (0.88)		28.34 (1.54)	
Concent. NOx (ppm)	100	57.16 (4.39)	0.46	12.19 (1.21)	0.0029	27.46 (1.32)	0.022
	300	56.28 (2.34)		13.15 (0.71)		28.59 (1.35)	
Pollutant order	N/S	57.12 (3.75)	0.50	12.79 (1.09)	0.45	27.92 (1.68)	0.64
	S/N	56.31 (3.27)		12.56 (1.12)		28.13 (1.18)	

Table 10. ANOVA models for color properties – Hardwood- Radial measurements

Main effect	Level	L (p=0.0008)		a (p=0.053)		b (p=0.0069)	
		Avg(std)	*p-value*	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*
OVERALL		58.72 (2.57)		12.49 (1.05)		28.54 (1.27)	
Duration (Days)	14	59.17 (2.02)	0.28	11.99 (1.08)	<0.001	28.04 (1.20)	0.0095
	28	58.28 (3.03)		12.99 (0.75)		29.03 (1.17)	
Relat. Humidity % (RH)	45	59.61 (2.66)	0.037	12.25 (1.05)	0.04	28.44 (1.40)	0.60
	70	57.84 (2.23)		12.73 (1.03)		28.63 (1.17)	
Concent. SOx (ppm)	100	59.21 (3.20)	0.24	12.20 (1.06)	0.016	28.19 (1.20)	0.064
	300	58.24 (1.71)		12.78 (0.98)		28.88 (1.28)	
Concent. NOx (ppm)	100	59.69 (3.20)	0.024	11.93 (0.99)	<0.001	27.93 (1.03)	0.0022
	300	57.76 (1.22)		13.05 (0.78)		29.14 (1.22)	
Pollutant order	N/S	59.02 (3.24)	0.47	12.68 (0.85)	0.100	28.65 (1.23)	0.54
	S/N	58.43 (1.73)		12.30 (1.21)		28.43 (1.34)	

Table 11. ANOVA models for color properties – Softwood- Tangerial measurements

Main effect	Level	L (p=0.0008)		a (p=0.053)		b (p=0.0069)	
		Avg(std)	*p-value*	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*
OVERALL		62.60 (4.87)		14.66 (1.52)		32.78 (2.13)	
Duration (Days)	14	64.43 (3.95)	0.02	14.33 (2.04)	0.19	32.63 (2.00)	0.64
	28	60.77 (5.12)		14.99 (0.63)		32.93 (2.30)	
Relat. Humidity % (RH)	45	61.14 (6.01)	0.059	14.99 (1.77)	0.18	31.70 (2.40)	0.002
	70	64.05 (2.90)		14.32 (1.19)		33.86 (1.05)	
Concent. SOx (ppm)	100	62.88 (5.64)	0.7	14.27 (1.34)	0.13	33.14 (1.68)	0.26
	300	62.31 (4.12)		15.04 (1.63)		32.42 (2.50)	
Concent. NOx (ppm)	100	64.05 (6.09)	0.061	14.14 (1.99)	0.042	32.19 (1.82)	0.072
	300	61.15 (2.74)		15.18 (0.51)		33.38 (2.31)	
Pollutant order	N/S	61.51 (5.95)	0.15	14.90 (1.80)	0.32	32.47 (2.34)	0.33
	S/N	63.68 (3.34)		14.41 (1.19)		33.10 (1.91)	

Table 12. ANOVA models for color properties – Softwood- Radial measurements

Main effect	Level	L *(p=0.0008)*		a *(p=0.053)*		b *(p=0.0069)*	
		Avg(std)	*p-value*	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*
OVERALL		64.97 (3.88)		14.37 (1.42)		32.40 (2.17)	
Duration (Days)	14	66.11 (3.63)	0.035	14.12 (1.79)	0.28	32.43 (2.07)	0.95
	28	63.83 (3.89)		14.61 (0.91)		32.38 (2.33)	
Relat. Humidity % (RH)	45	64.47 (4.69)	0.34	14.60 (1.60)	0.3	31.16 (2.10)	0.0005
	70	65.47 (2.93)		14.13 (1.23)		33.65 (1.41)	
Concent. SOx (ppm)	100	66.01 (3.65)	0.051	13.95 (1.05)	0.079	32.68 (1.61)	0.38
	300	63.93 (3.93)		14.78 (1.65)		32.13 (2.64)	
Concent. NOx (ppm)	100	67.11 (3.38)	0.0003	13.86 (1.73)	0.033	31.81 (1.80)	0.067
	300	62.84 (3.15)		14.87 (0.81)		33.00 (2.39)	
Pollutant order	N/S	64.19 (3.73)	0.14	14.68 (1.43)	0.17	32.25 (2.43)	0.63
	S/N	65.75 (3.98)		14.05 (1.39)		32.56 (1.94)	

Table 13. ANOVA models for gloss characteristics – Hardwood – Tangerial measurements

Main effect	Level	20o (p=0.11)		60o (p=0.24)		75o (p=0.12)	
		Avg(std)	*p-value*	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*
OVERALL		2.11 (0.50)		3.79 (0.59)		10.82 (1.45)	
Duration (Days)	14	2.32 (0.46)	0.018	3.99 (0.48)	0.051	11.01 (1.73)	0.43
	28	1.91 (0.46)		3.58 (0.63)		10.63 (1.14)	
Relative Humidity % (RH)	45	2.11 (0.48)	0.92	3.87 (0.64)	0.41	11.47 (1.47)	0.012
	70	2.12 (0.53)		3.70 (0.53)		10.16 (1.15)	
Concent. SOx (ppm)	100	2.23 (0.46)	0.17	3.90 (0.52)	0.25	10.62 (1.76)	0.43
	300	2.00 (0.52)		3.67 (0.64)		11.01 (1.09)	
Concent. NOx (ppm)	100	2.05 (0.48)	0.4	3.69 (0.60)	0.35	10.58 (1.71)	0.32
	300	2.18 (0.51)		3.88 (0.57)		11.06 (1.15)	
Pollutant order	N/S	2.03 (0.50)	0.3	3.78 (0.54)	0.91	10.82 (1.36)	0.98
	S/N	2.20 (0.49)		3.80 (0.64)		10.81 (1.59)	

Table 14. ANOVA models for gloss characteristics – Hardwood – Radial measurements

Main effect	Level	20° (p=0.21)		60° (p=0.076)		75° (p=0.053)	
		Avg(std)	*p-value*	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*
OVERALL		2.20 (0.42)		4.22 (0.58)		12.00 (2.80)	
Duration (Days)	14	2.33 (0.37)	0.094	4.26 (0.53)	0.65	11.76 (2.13)	0.6
	28	2.08 (0.44)		4.18 (0.65)		12.23 (3.39)	
Relat. Humid. % (RH)	45	2.22 (0.42)	0.77	4.28 (0.65)	0.55	12.27 (3.27)	0.54
	70	2.18 (0.43)		4.16 (0.52)		11.72 (2.30)	
Concent. SOx (ppm)	100	2.31 (0.38)	0.15	4.42 (0.64)	0.046	12.66 (3.33)	0.15
	300	2.10 (0.44)		4.02 (0.46)		11.33 (2.04)	
Concent. NOx (ppm)	100	2.19 (0.39)	0.91	4.41 (0.68)	0.048	13.35 (3.04)	0.005
	300	2.21 (0.45)		4.03 (0.40)		10.65 (1.74)	
Pollutant order	N/S	2.09 (0.40)	0.13	4.08 (0.52)	0.16	11.69 (2.51)	0.5
	S/N	2.31 (0.42)		4.36 (0.62)		12.30 (3.11)	

Table 15. ANOVA models for gloss characteristics – Softwood – Tangerial measurements

Main effect	Level	20° (p=0.22)		60° (p=0.10)		75° (p=0.027)	
		Avg(std)	*p-value*	*Avg(std)*	*p-value*	*Avg(s td)*	*p-value*
OVERALL		2.43 (0.58)		5.89 (1.01)		14.90 (2.40)	
Duration (Days)	14	2.59 (0.53)	0.13	6.22 (0.80)	0.051	15.63 (2.33)	0.057
	28	2.28 (0.61)		5.55 (1.10)		14.17 (2.31)	
Relat. Humid. % (RH)	45	2.36 (0.50)	0.49	6.18 (0.99)	0.085	16.01 (2.45)	0.006
	70	2.50 (0.67)		5.59 (0.96)		13.79 (1.80)	
Concent. SOx (ppm)	100	2.61 (0.49)	0.084	6.04 (0.93)	0.35	14.98 (2.41)	0.84
	300	2.25 (0.63)		5.73 (1.08)		14.83 (2.46)	
Concent. NOx (ppm)	100	2.50 (0.59)	0.51	6.09 (0.82)	0.22	15.43 (1.92)	0.16
	300	2.36 (0.59)		5.68 (1.15)		14.37 (2.76)	
Pollutant order	N/S	2.53 (0.59)	0.35	6.01 (0.92)	0.47	15.00 (2.30)	0.79
	S/N	2.34 (0.58)		5.77 (1.10)		14.80 (2.56)	

Table 16. ANOVA models for gloss characteristics – Softwood – Radial measurements

Main effect	Level	20° (p=0.43)		60° (p=0.90)		75° (p=0.78)	
		Avg(std)	*p-value*	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*
OVERALL		2.55 (0.62)		6.57 (1.74)		16.87 (4.58)	
Duration (Days)	14	2.65 (0.52)	0.38	6.45 (1.48)	0.73	16.10 (4.33)	0.37
	28	2.45 (0.70)		6.68 (2.01)		17.65 (4.82)	
Relative Humidity % (RH)	45	2.47 (0.50)	0.46	6.79 (1.72)	0.5	17.71 (4.45)	0.33
	70	2.63 (0.72)		6.35 (1.79)		16.03 (4.68)	
Concentration SOx (ppm)	100	2.73 (0.52)	0.11	6.81 (1.57)	0.46	16.96 (4.12)	0.92
	300	2.37 (0.66)		6.33 (1.92)		16.79 (5.13)	
Concentration NOx (ppm)	100	2.63 (0.62)	0.47	6.78 (1.76)	0.53	17.31 (4.78)	0.61
	300	2.47 (0.62)		6.36 (1.75)		16.44 (4.48)	
Pollutant order	N/S	2.62 (0.58)	0.53	6.50 (1.67)	0.83	16.37 (4.88)	0.55
	S/N	2.48 (0.67)		6.64 (1.86)		17.38 (4.35)	

Table 17. ANOVA models for Mechanical property: Brinnel's hardness

Brinnel's hardness		Hardwood – Tangerial (p=0.80)		Hardwood – Radial (p=0.012)		Softwood – Tangerial (p=0.13)		Softwood – Radial (p=0.18)	
Main effect	**Level**	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*	*Avg(std)*	*p-value*
OVERALL		4.38 (0.87)		3.65 (0.46)		2.08 (0.25)		2.28 (0.34)	
Duration (Days)	14	4.43 (0.84)	0.74	3.82 (0.46)	0.018	2.19 (0.23)	0.013	2.39 (0.29)	0.074
	28	4.33 (0.93)		3.48 (0.40)		1.97 (0.23)		2.18 (0.36)	
Relative Humidity % (RH)	45	4.29 (1.00)	0.57	3.75 (0.52)	0.19	2.08 (0.20)	0.99	2.30 (0.28)	0.77
	70	4.47 (0.74)		3.56 (0.38)		2.08 (0.30)		2.27 (0.40)	
Concentration SOx (ppm)	100	4.33 (0.92)	0.75	3.59 (0.42)	0.36	2.10 (0.27)	0.67	2.30 (0.33)	0.72
	300	4.43 (0.85)		3.72 (0.49)		2.07 (0.23)		2.26 (0.36)	
Concentration NOx (ppm)	100	4.47 (0.89)	0.56	3.78 (0.42)	0.071	2.14 (0.24)	0.19	2.39 (0.37)	0.062
	300	4.28 (0.87)		3.53 (0.47)		2.03 (0.25)		2.17 (0.28)	
Pollutant order	N/S	4.19 (0.88)	0.25	3.49 (0.37)	0.023	2.06 (0.25)	0.55	2.23 (0.34)	0.4
	S/N	4.57 (0.85)		3.82 (0.48)		2.11 (0.25)		2.33 (0.34)	

Note that for some few cases, we found some statistically significant effect even if the overall model is not significant. Such results should be interpreted with care since it can be attributed to spurious observations and violations of the underlying assumptions for the ANOVA model.

We summarize our findings in Tables 18 and 19.

Table 18: Summary Table for findings from ANOVA models for Hard-wood

Hard wood	Color properties						Gloss characteristics						Brinnel's hardness	
	Tangerial			Radial			Tangerial			Radial			Tangerial	Radial
	L	a	b	L	a	b	20°	60°	75°	20°	60°	75°		
Duration		X			X	X								X
Humidity				X	X									
Sox		X			X									
Nox		X		X	X	X								
Pollutant Order														X

For hard wood all factors are found significant for some characteristic. Humidity was significant only for the color properties of the radial measurements. Duration is significant for color properties in both tangerial and radial measurements and Brinnels' hardness. Pollutants were significant for color properties only while the order was found significant only for hardness.

Table 19: Summary Table for findings from ANOVA models for soft-wood

Soft wood	Color properties						Gloss characteristics						Brinnel's hardness	
	Tangerial			Radial			Tangerial			Radial			Tangerial	Radial
	L	a	b	L	a	b	20°	60°	75°	20°	60°	75°		
Duration	X			X										
Humidity			X			X			X					
Sox														
Nox				X										
Pollutant Order														

Less significant results were found for soft wood. Now the order was never significant. NOx pollutant was found only for color properties in radial measurements, while SOx pollutant was not significant in any case. Duration and humidity were found significant mainly for color properties.

6.3 Remarks

In the present paper we present results from simple ANOVA models without interaction. Since some of the measurements are correlated MANOVA models could have been also used. However since the interest lies in the particular properties themselves and not general properties we presented the findings per different variables without putting together some of them .

7. Concluding Remarks

INVENVORG project examined the ageing behavior of wood and for the first time the ageing behavior of bones under experimental conditions. Five factors were examined based on a fractional factorial experimental design aiming at revealing the factors that influence the ageing. Duration checked in 24 and 48 days was not significant for any of the characteristics considered, while pollutants and humidity appeared to play role in some of the properties.

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