



2.3. Development of dose-response functions for historic plastic materials

The study of degradation processes in plastic artefacts is a complex analytical problem and it represents a challenging area of research. This is because of the extreme variability of plastic materials, but also because environmental agents of degradation are many and they can have synergistic/antagonistic effects.

Environmental conditions (i.e., climate and atmospheric pollution) can exacerbate or retard degradation of synthetic materials. As for all materials, elevated temperature accelerates the rate of decay, however, much less is known about the susceptibility of individual types of historic plastic materials to humidity and pollutants. Understanding and prioritisation of agents of deterioration leading to degradation of plastic objects is essential in order to develop suitable preservation strategies. The aim of this research was therefore to obtain quantitative data on environmental effects on plastics degradation, principally discolouration, identifying the factors that play the most significant role.

Considering the number of potentially significant agents of degradation: temperature (T), relative humidity (RH), visible light (VIS), pollutant concentration (nitrogen dioxide, sulfur dioxide and ozone) to list those that might be seen as most important agents indoors, it is immediately apparent that a well-controlled laboratory experiment taking into account various possible combinations of the above agents would be extremely complex, if at all possible. Therefore, an alternative approach is needed.

Considering that most plastic materials are moderately stable with a few exceptions where degradation is noticeable in a matter of weeks or months, some method of acceleration of the degradation processes is necessary in order to reduce experimental times to an





acceptable level. The usual method of accelerated degradation in a climate chamber would not allow for variation of all the relevant agents of deterioration.

Moderate acceleration of degradation can be achieved by exposing indoor heritage materials in the external environment. Care needs to be taken that agents of deterioration that are not relevant indoors are excluded, particularly contact with water and ultra violet radiation, that can easily be achieved by exposure in sheltered conditions, i.e., well sheltered from direct sunlight and rainfall. Since externally, the agents of deterioration cannot be controlled, they need to be continuously monitored, so that data, needed for the development of dose-response functions, is available. Environmental parameters: temperature, relative humidity and visible light intensity were constantly monitored with Onset HOBO U12 data loggers and concentrations of traffic-generated pollutants, i.e., ozone (O_3), sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), were monitored every three months using Gradko passive samplers. A representative variety of plastic materials was selected and subjected to accelerated natural ageing.

Regular assessment of change in colour using non-destructive colorimetry and multivariate data analysis allows for summing up the obtained results in an easily presentable format, providing crucial information about the synergistic effects of environmental parameters on the decay of plastics. The samples were selected from the ResinKit™ collection, the SamCo and the UCL Centre for Sustainable Heritage historic plastics collection. With few exceptions, most of the samples were not artificially colored.

Additionally, in order to assure sufficient variation in combinations of agents of deterioration, the samples were exposed in 11 different environments across Europe and Egypt (Figure 49), so that different climates (variation in temperature: $-10 - 50^\circ\text{C}$; variation in relative humidity: 10-95%; variation in illuminance: $0 - 12000 \text{ lx}$) and different levels of pollution (SO_2 max – 1.8 ppb; NO_2 max – 31 ppb; O_3 max – 60 ppb) were taken into account. This also covers the entire expected range of climate and pollution level in indoor situations in most museums.

On a 3 monthly basis, colour changes were measured using CIE $L^*a^*b^*$ colorimetry with an X-Rite 500 Series portable spectrodensitometer, and both CIE76 ΔE_{ab} and Δb (Robertson 1990) were calculated.

Multivariate analysis of data was used in order to be able to understand the complex effect of multiple environmental variables (agents of degradation) on colour change of plastic samples. The relationship between colour change and the various environmental





Location	Description	Heat	Pollution	Humidity	Light
London, UK	Urban, ext	0	1	1	0
London, UK	Suburban, ext	0	-1	1	0
London, UK	Urban, int	1	-1	-1	-1
Bilbao, ESP	Suburban, ext	1	1	0	1
Ljubljana, SI	Suburban, North facing, ext	-1	-1	1	-1
Ljubljana, SI	Suburban, South facing, ext	1	-1	1	1
Ljubljana, SI	Suburban, int	1	0	0	-1
Florence, IT	Urban, ext	1	1	1	1
Rome, IT	Urban, ext	1	1	0	1
Zurrieq, MT	Rural, ext	1	1	1	1
Cairo, EGY	Suburban, ext	1	1	-1	0

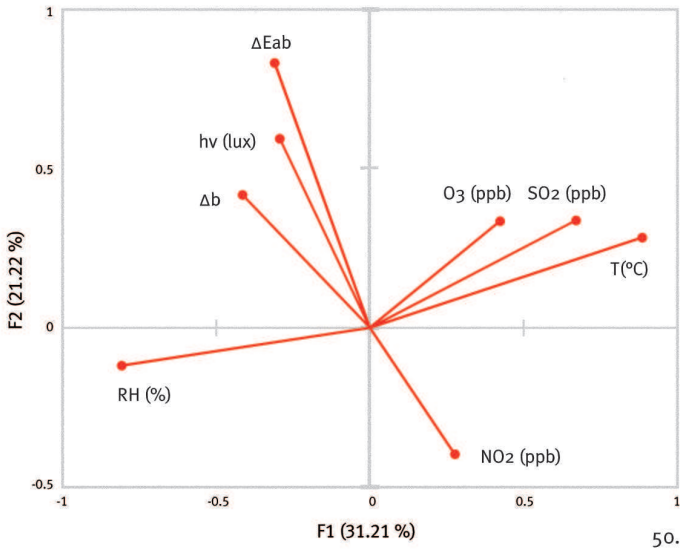
Figure 49. Exposure sites and their environmental characteristics: “-1” – low; “0” – medium; “1” – high; “ext” – external; “int” – internal

parameters, i.e., different variables in the complex degradation experiment, can be statistically examined using multivariate analysis (Brereton, 2003). Principal component analysis (PCA) is a data visualisation technique, where the observed experimental data with a number of “variables” (i.e., colour change, T , RH, light dose and concentrations of SO_2 , NO_2 and O_3) is re-plotted using a few non-correlated “principal components” so that the first principal component explains the most variability in the data set and each consecutive one progressively less. Thus, if most variation in the dataset is explained by the first two principal components (PC1 and PC2), we can explore the weight of original “variables” contributing to the two PCs in a simple two-dimensional diagram called a “loading plot”. In such a plot, the distance from the origin represents the weight of a particular variable, however, the position is also revealing: if two factors are positioned close to each other in the plot, they are correlated, if they are positioned opposite to each other across the origin, they are anti-correlated, and if they are positioned at an angle of 90° , they are not correlated.

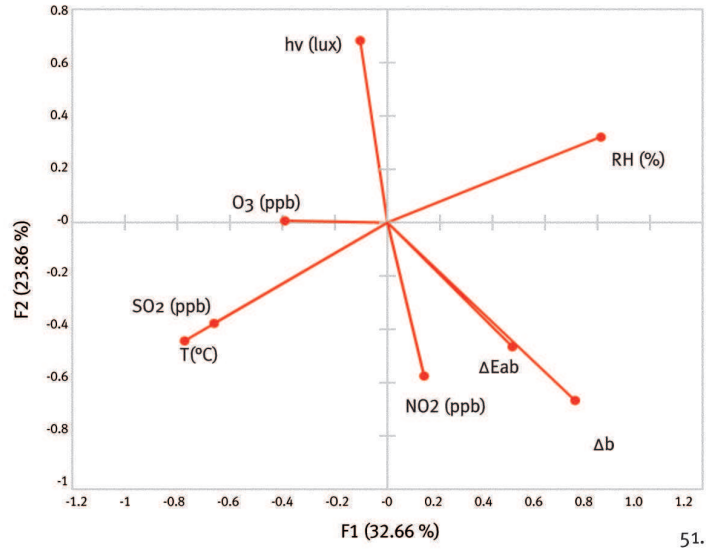
Discolouration of samples, principally yellowing, was a generally observed phenomenon, depending on whether the samples were exposed to lower or higher concentrations of airborne pollutants and on the different levels of light intensity, suggesting that these environmental agents might be the most significant degradation factors out of those measured and monitored. However, it is also very evident that different samples behave differently.

As it is shown in Figure 50, discolouration measured as total colour difference ΔE_{ab} and yellowing measured as Δb of CA were mostly correlated with light intensity, while colour changes were not affected by T , RH, SO_2 or O_3 , and higher NO_2 concentration led to less discolouration. MIPS (Figure 51) behaves very differently: colour changes are due mainly to high concentration of NO_2 , while light has a bleaching effect, i.e., contrary to NO_2 , T , RH, SO_2 or O_3 do

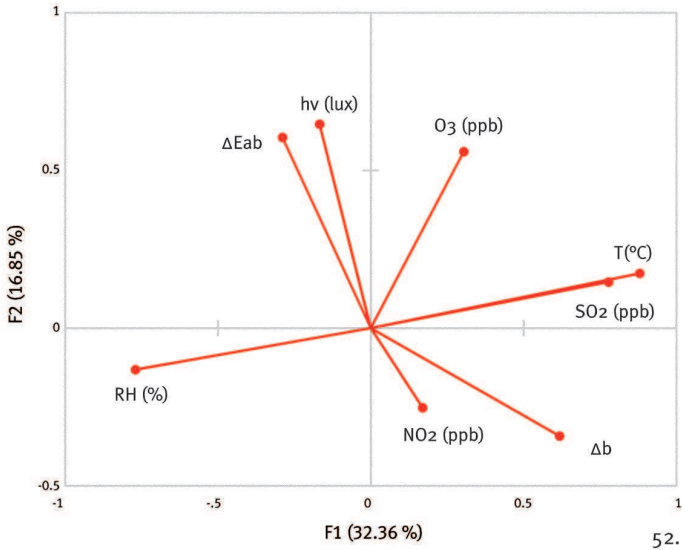




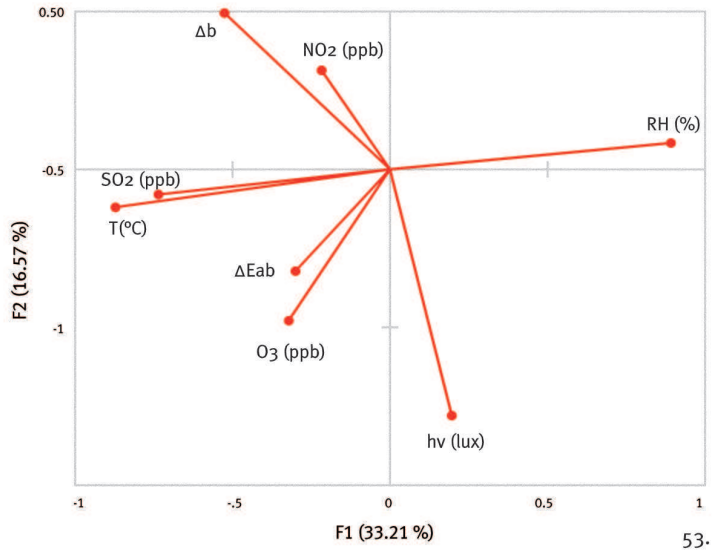
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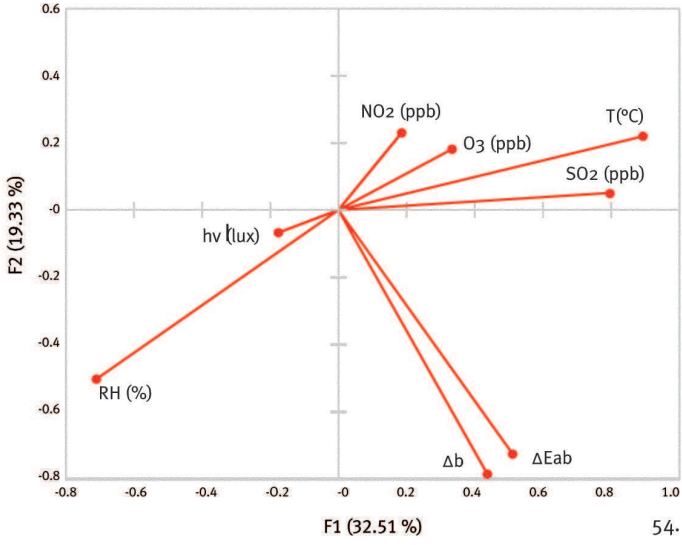
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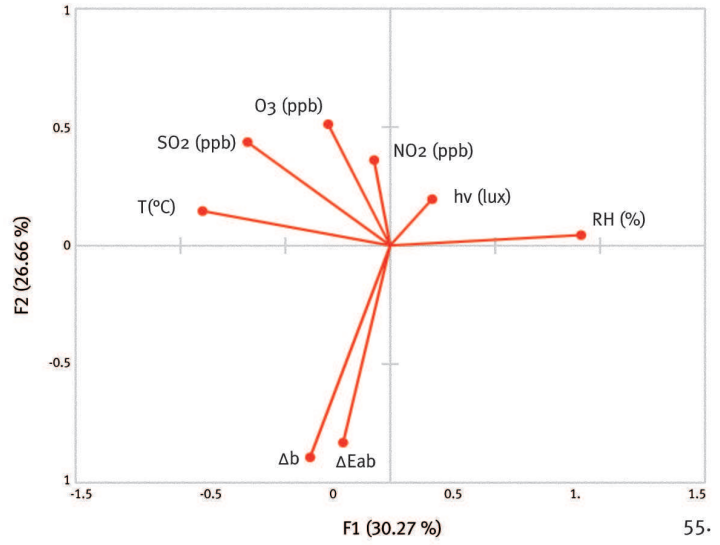
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not affect colour change to a great extent. For LDPE (Figure 52) and rigid PVC (Figure 53), total discoloration was affected by light and O_3 , while NO_2 mainly affected yellowing, and the effect of T , RH, and SO_2 was of lesser importance. In some cases, such as GPPS (Figure 54) and PF (Figure 55), there are no strong correlations between colour change and environmental parameters. The colour of these materials did also not change appreciably during the 2-year experiment, which explains the lack of any correlation.

It is thus evident that light, NO_2 and O_3 are the most important agents of deterioration leading to colour change of plastic materials, while T , RH and SO_2 are of less importance. It is important to stress that different materials, even of the same general chemical composition, may react differently, i.e., their level of response may be different.

This research has important implications for display and storage of historic plastic materials, particularly where aesthetic values are of importance and where colour changes might be seen as particularly negative.

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Figure 50. Loading plot showing PCA results for CA

Figure 51. Loading plot showing PCA results for MIPS

Figure 52. Loading plot showing PCA results for LDPE

Figure 53. Loading plot showing PCA results for rigid PVC

Figure 54. Loading plot showing PCA results for GPPS

Figure 55. Loading plot showing PCA results for PF

