Original research or treatment paper

The effect of dust particles on cellulose degradation

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This study focuses on the changes in properties of cellulose-based paper, which can take place as a consequence of its contamination by dust particles. The PM1 (fine) and PM10 (coarse) fractions of the dust particles from archival repositories were collected on cellulose filters Whatman 41, polytetrafluorethylene, and quartz filters. The latter two types of samples were subsequently analyzed gravimetrically, with ion chromatography, PIXE, and the thermal–optical transmission method, giving mass, ionic, elemental carbon, and organic carbon concentrations. After artificial aging, the viscosity-average degree of polymerization of cellulose (DP_v) was measured. It was confirmed that cellulose-based paper can undergo substantial changes when contaminated by dust particles and artificially aged. The decrease of the DP_v of cellulose showed a negative correlation with the deposited mass of sulfate ions in the dust particles. Considering the particle size fraction, the results suggest the decisive importance of the fine (PM1) particles. The results provide better understanding of how particulate matter contributes to the chemical degradation of cellulose-based paper. Such knowledge is of importance when considering appropriate conservation measures in archives, libraries, and galleries.

Keywords: Cellulose, Paper, Dust, Particulate matter, Degradation, Ammonium sulfate

Introduction

The importance of air quality control in archives, libraries, and related institutions was acknowledged as early as the 1970s (Hatchfield, 2002). For decades the adverse effects caused by gaseous pollutants gained the most attention, although a high risk of contamination by particulate matter was also assumed. The discussion regarding this issue mostly focused on paper soiling, the possibility of surface abrasion, or microbiological infestation (Brimblecombe, 1990; Wilson, 1995; NPS, 1999; Hatchfield, 2002; NAFA, 2004). With regard to the chemical degradation of artifacts, the most frequently mentioned problem associated with this type of pollution was the hygroscopicity and acidity of the fine particles (NPS, 1999; Hatchfield, 2002). Particles embedded in paper were also suspected to enhance the sorption of harmful gaseous pollutants and to react with them, yielding harmful products (Wilson, 1995; NPS, 1999, NAFA, 2004).

There have been several attempts to specify the maximum 'acceptable' levels of contamination of cellulose-based materials by particulate matter (Brimblecombe, 1990; Wilson, 1995; Hatchfield, 2002; ISO 11799, 2003; NAFA, 2004). Furthermore, after developing the concept of the lowest observable adverse effect dose, the LOAED values have also been tabulated for paper objects (Tétreault, 2003). However, the basis on which those suggestions were formulated is not always apparent and the recommended values vary significantly. The main reason for this is that the way in which particulate matter contributes to chemical degradation of cellulose and the relative importance of this contribution is still not well understood.

This study aims to contribute to filling this gap. The work was focused on the changes in the properties of cellulose-based paper that took place as a consequence of its contamination by dust particles, followed by artificial aging. By comparing the degree of the cellulose degradation with various characteristics of the dust particles (size, chemical composition), it was possible to obtain more detailed insights into the issue. The results showed not only the importance of the problem, but also its complex and often non-intuitive nature.

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Methods

Deposition of dust particles

In order to obtain relevant results, dust particles were collected directly in selected repositories. Sampling was carried out in the State Regional Archives in Třeboň and the Research Library of South Bohemia in Zlatá Koruna (Czech Republic). While the Regional Archives is located in a Renaissance castle in the centre of a small tourist town, Zlatá Koruna represents a rural region of Bohemia. In both repositories, the possibilities of control of indoor air quality are very limited. Ventilation is provided by opening windows, which facilitates the exchange of air pollutants between indoor and outdoor environments. Sampling was carried out in the winter of 2011 and in the spring, summer, and autumn of 2012.

Particulate matter fractions PM1 (particles with aerodynamic diameter ≤ 1 μm) and PM10 (particles with aerodynamic diameter ≤ 10 μm) were collected on cellulose filters Whatman 41. This filter was selected as representative of pure cellulose paper since it contains only very low amounts of metals and ash and no additives or sizing agents which could affect the viscosity-average degree of polymerization (DP_v) measurement. Of course, the same properties make it somewhat less representative of common archival and library material.

Sampling was performed by means of single-filter gravimetric samplers Leckel LVS-3 (Sven Leckel Ingenieurbüro, Germany), positioned on the floor in the proximity of bookshelves (Fig. 1). The sampler consisted of a vacuum pump with flow rate controlled by a microprocessor, filter holder, and a PM1 or a PM10 sampling head. In this case, the flow rate was set to $2.3\,m^3/h$ and the sampling period was 24 hours, in the course of which 7–61 $\mu g/cm^2$ was deposited on the filters, depending on the concentration of particulate matter in the air. This way it was possible to collect samples representing the airborne particles in the larger volume of repository environment in a short period of time. This approach was chosen to suppress the possible interfering effect of the exposure of samples to gaseous pollutants and different light and climate conditions during the sampling. The negligible contribution of gaseous pollutants when using this experimental setup was confirmed in the course of our preliminary tests.

Figure 1 Sampling in the repository of the State Regional Archives in Třeboň employing Leckel LVS-3 devices.

In parallel, the same size fractions were collected on polytetrafluorethylene (PTFE) and quartz filters for subsequent analysis of the chemical composition. Two sets of specimens were prepared at both locations during each campaign.

Sources of pollution

For the determination of possible sources of air pollution, the particle number concentration and the size distribution of indoor and outdoor particulate matter was measured using Ultrafine Particle Monitor (TSI, USA, model 3031) and Aerodynamic Particle Sizer (TSI, USA, model 3321). Sampling was carried out indoors and outdoors simultaneously, the range of the sampled particulate matter covered an interval of 20–20 000 nm.

Analyses of dust particles

The dust particles collected on PTFE and quartz filters were analyzed gravimetrically (Sartorius M5P Microbalance, Data Weighing Systems, USA), by ion chromatography (Dionex ICS-5000, Thermo Scientific), particle induced X-ray emission (PIXE, 3MV Tandetron Accelerator) and the thermal-optical transmission method (EC/OC Field Analyser, Sunset Laboratory, USA, EUSAAR II temperature protocol). Using this approach, mass, ionic, elemental, organic, and elemental carbon concentrations were obtained.

The composition of particulate matter deposited on Whatman 41 filters was recalculated considering the volume flow rate, the total time of sampling and the concentration of components (μ/gm^3) obtained from analyses of particles deposited on PTFE and quartz filters. For characterization of particulate matter, six aerosol components were considered: organic aerosol, elemental carbon, sulphates, ammonium ions, nitrates, and crustal matter (Chan *et al.*, 1997; Turpin *et al.*, 2000; Maenhaut *et al.*, 2002).

Deposition of ammonium sulfate

The results of analyses suggested the importance of the presence of ammonium sulfate in deposited dust. Therefore, a known mass (0.29–6.75 μg/cm^2) of pure ammonium sulfate (purity ≥99.5%, Fluka, Germany) was deposited on Whatman 41 filters under laboratory conditions. The particles with mean diameter 200 nm were generated by spraying the aqueous solution of ammonium sulfate employing aerosol generator AGK 2000 (Palas, Germany) and subsequent drying. The prepared samples were later subjected to accelerated degradation in the same manner as the other samples. In this way, a relative contribution of this compound to the total degradative effect of the dust particles could be verified.

Measurement of changes in cellulose properties

The changes in paper properties resulting from its exposure to dust were expected to be rather gradual. Therefore, before comparing their properties, all the samples were degraded for 28 days at 80°C and 65% relative humidity, according to the standard ISO 5630-3:1986. An environmental test chamber (Espec PR-2KP, Japan) was used, with the samples laid horizontally with the uncontaminated side down in semi-closed glass Petri dishes. Several unexposed Whatman 41 filters were degraded in the same way and were later used as reference samples.

From a practical point of view, the determination of the changes in mechanical properties would be of the greatest interest. However, due to the small dimensions of the samples, it was impossible to carry out such tests. Therefore, the extent of degradation was expressed as a decrease in the DP$_v$ of cellulose. For pure cellulose-based materials, the relation between mechanical properties and DP$_v$ is well established (Feller *et al.*, 1986; Zou *et al.*, 1994; Zervos, 2010; Bílková, 2012;).

The DP$_v$ was calculated on the basis of limiting viscosity number [η] which was determined viscometrically in cupriethylenediamine solution. Prior to the measurement, the solubilized samples were passed through a polyvinylidene fluoride filter with nominal particle size retention of 0.45 μm. The determination of the limiting viscosity number itself was carried out according to the standard ISO 5351:2010 employing the semi-automatic viscometer (TV2000AKV, Tamson Instruments, Netherlands). The value of the average degree of polymerization DP$_v$ was calculated following the Mark-Houwink equation, which, for the pair of cellulose and cupriethylenediamine, can be written in the form $DP_v^{0.85} = 1.1\ [\eta]$ (Evans & Wallis, 1987).

Results and discussion

Chemical composition of dust particles

As follows from the analyses, the most abundant components of indoor PM1 fraction were elemental carbon, organic aerosol, ammonium ions, and sulfates. The crustal elements were found predominantly in a particle fraction of a diameter of 1–10 μm. The contribution of coarse (1–10 μm) particles to the total mass of deposited dust was rather small (Tables 1 and 2).

The accompanying measurement of the particle number concentration and the size distribution of indoor and outdoor PM revealed that the indoor aerosol pollution reflected the variability of outdoor

Table 1 Concentrations of six aerosol components of PM1 and PM10 samples, collected in the archival repositories in Třeboň during the period winter–autumn 2012*

Date (2012)	PM fraction	SO_4^{2-}	NO_3^-	NH_4^+	Elemental carbon	Organic matter	Crustal elements	Total mass
31.1.	PM1	3.6	1.6	1.8	3.8	15.1	0.4	35.1
2.2.	PM1	0.9	0.2	0.4	2.0	5.4	0.1	11.7
24.4.	PM1	0.5	0.1	0.2	1.4	21.2	0.2	29.0
25.4.	PM1	0.2	0.1	0.1	1.2	21.1	0.3	30.2
18.7.	PM1	0.8	0.0	0.4	2.2	5.2	1.3	13.0
19.7.	PM1	0.8	0.1	0.4	0.9	2.2	0.3	6.6
24.10.	PM1	13.6	1.0	5.4	5.5	10.0	1.1	54.1
25.10.	PM1	7.5	0.2	3.1	4.9	12.2	1.0	34.1
31.1.	PM10	3.9	1.9	1.8	4.0	23.5	1.9	45.2
2.2.	PM10	1.2	0.4	0.5	2.2	7.4	0.8	15.9
24.4.	PM10	0.8	0.1	0.3	1.5	22.3	1.2	31.5
25.4.	PM10	0.2	0.0	0.1	1.3	20.7	0.8	31.1
18.7.	PM10	0.5	0.0	0.2	1.2	7.6	2.1	11.1
19.7.	PM10	0.9	0.2	0.4	1.0	5.1	1.5	10.5
24.10.	PM10	15.3	1.6	6.0	4.6	13.3	2.6	61.1
25.10.	PM10	8.9	0.6	3.6	5.6	11.8	2.7	42.2

* Concentrations are in μg/cm^2.

Table 2 Concentrations of six aerosol components of PM1 and PM10 samples, collected in the archival repositories in Zlatá Koruna during the period winter–autumn 2012*

Date (2012)	PM fraction	SO_4^{2-}	NO_3^-	NH_4^+	Elemental carbon	Organic matter	Crustal elements	Total mass
24.1.	PM1	0.5	0.1	0.3	1.9	10.0	0.3	15.7
26.1.	PM1	2.0	0.3	0.9	2.0	14.4	0.2	22.9
17.4.	PM1	1.4	0.0	0.6	1.8	8.3	0.3	18.6
18.4.	PM1	1.7	0.2	0.7	1.6	11.5	0.3	19.0
24.7.	PM1	4.3	0.1	1.7	1.5	10.4	0.5	27.0
25.7.	PM1	3.2	0.3	1.2	1.0	11.7	0.5	25.6
30.10.	PM1	0.6	0.1	0.3	1.6	10.2	1.3	17.7
31.10.	PM1	1.4	0.0	0.6	2.9	13.7	2.8	26.4
24.1.	PM10	0.9	0.4	0.4	1.9	13.4	0.4	19.8
26.1.	PM10	1.6	0.1	0.7	1.3	10.1	0.6	16.8
17.4.	PM10	1.3	0.3	0.5	1.6	8.3	0.8	19.6
18.4.	PM10	2.2	0.3	0.8	2.1	18.4	1.2	27.5
24.7.	PM10	3.8	0.1	1.5	1.6	14.3	2.0	32.6
25.7.	PM10	3.0	0.3	1.1	1.1	12.9	1.0	27.7
30.10.	PM10	0.8	0.1	0.3	1.4	11.7	2.1	19.2
31.10.	PM10	2.0	0.3	0.8	2.9	15.2	3.9	28.9

*Concentrations are in µg/cm^2.

conditions, such as the immediate meteorological situation and human activities. Therefore, the main source of pollution was presumably of outdoor origin. The fine organic aerosol and elemental carbon particles are typical products of combustion processes, i.e. vehicle exhaust and heating (Hatchfield, 2002; Gaffney & Marley, 2005; Andělová *et al.*, 2010). Ammonium and sulfate ions were predominantly present in the form of ammonium sulfate. Both ions were detected in the same size fraction (0.1–1.0 µm), i.e. among the particles that penetrated the most easily from the outdoor environment to indoors. The ammonium sulfate is a product of the neutralization reaction between ammonia and sulfuric acid, which takes place in the atmosphere and is known to be one of the most common components of fine atmospheric particles (Seinfeld & Pandis, 1998; Finlayson-Pitts & Pitts, 1999; Tétreault, 2003; Gaffney & Marley, 2005).

Effect of deposited dust on cellulose properties

The results confirmed that Whatman 41 filters can undergo substantial changes when contaminated with dust particles and degraded. As expected, DP$_v$ decreased with increased mass of the deposited dust particles (Fig. 2). Considering the particle size fraction, the results obtained for the parallel PM1 and PM10 samples never differed significantly. This strongly suggests that fine particles play a decisive role within the studied size range of particles. Although the coarse particles may be important from an esthetic point of view or with respect to possible abrasion of the surface of the paper, their contribution to the chemical degradation of cellulose seems to be negligible.

Of course, the PM mass, deposited using Leckel LVS-3 samplers was higher then could be expected under conditions of passive deposition in the course of 24 hours. For rough comparison, the total mass of sulfates, which were passively deposited in the same repositories in the course of one year was 0.3 µg/cm^2 and 0.1 µg/cm^2 in Třeboň and Zlatá Koruna, respectively. Therefore, the prepared samples simulated long-term storage of documents in a polluted environment.

However, the dependence of the decrease of DP$_v$ on the mass of the deposited particles was not straightforward. Apparently, the degradation of cellulose was caused by specific chemical compounds, which were present both in PM1 and PM10 samples. A clue for

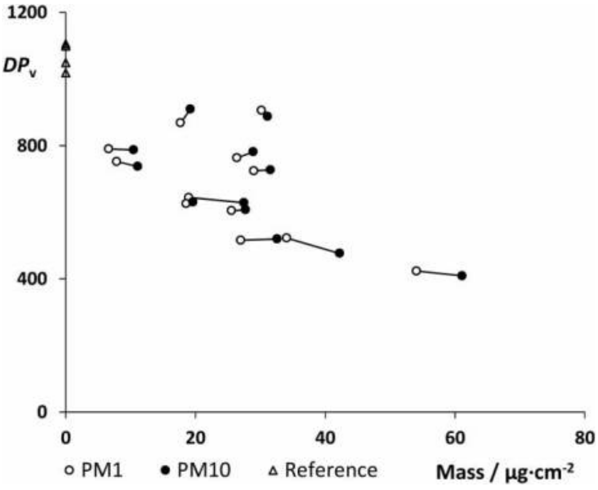

Figure 2 **DP$_v$ of cellulose in relation to the total deposited PM1 and PM10 mass. The parallel PM1 and PM10 samples are connected by a line. Reference = unexposed aged filters.**

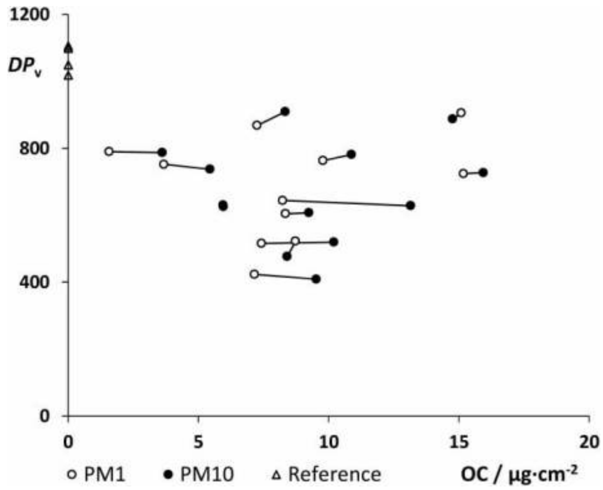

Figure 3 DP_v of cellulose in relation to the deposited organic carbon mass. The parallel PM1 and PM10 samples are connected by a line. Reference = unexposed aged filters.

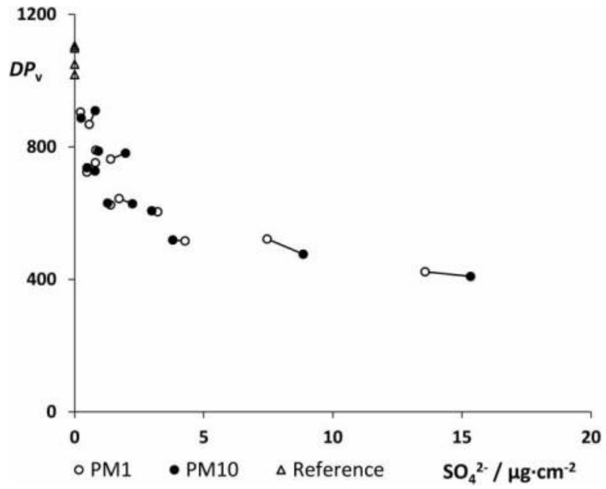

Figure 5 DP_v of cellulose in relation to the deposited sulfate anion mass. The parallel PM1 and PM10 samples are connected by a line. Reference = unexposed aged filters.

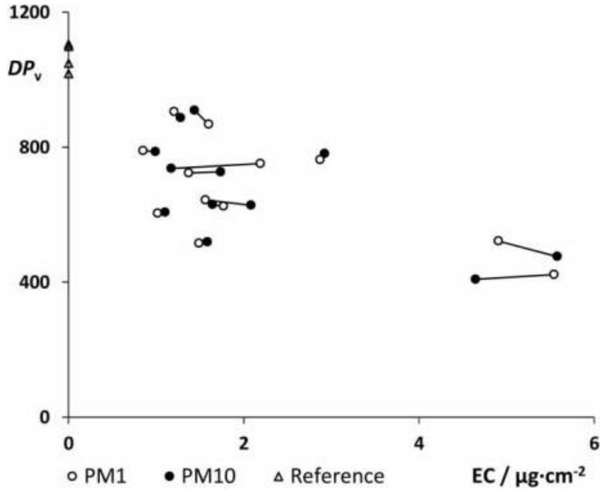

Figure 4 DP_v of cellulose in relation to the deposited elemental carbon mass. The parallel PM1 and PM10 samples are connected by a line. Reference = unexposed aged filters.

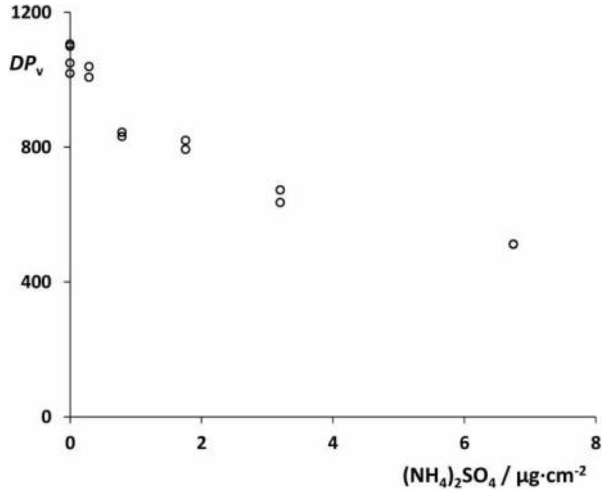

Figure 6 DP_v of cellulose in relation to the deposited pure ammonium sulfate mass. Reference = unexposed aged filters.

estimation of the degradative effect of the particular components of dust was provided by relating the measured DP_v values to the deposited mass of the most abundant components of the fine particles, i.e. organic carbon, elemental carbon, and sulfates (Figs. 3–5).

The most convincing correlation was found in the case of sulfate ions (Fig. 5), which suggests the importance of ammonium sulfate to cellulose degradation. Of course, the observed correlation does not necessarily imply causality. In order to verify the possible degradative effect of this compound on cellulose, special samples with deposits of pure ammonium sulfate were aged and measured as well.

Effect of ammonium sulfate on cellulose

The results confirmed that during accelerated degradation, ammonium sulfate contributes to degradation of cellulose (Fig. 6). However, the mechanism of this phenomenon is not clear. The degradative effect of an application of an aqueous solution of ammonium sulfate was reported in the case of Whatman 1 filter paper (Antušková, 2013) and wooden construction objects (Kučerová *et al.*, 2010). Because of its hygroscopicity and slight acidity of its aqueous solutions, some authors suspect it to increase the rate of acid hydrolysis of the cellulose (Le Van & Winandy, 1990; Antušková, 2013). However, this hypothesis is not generally accepted. The opponents point out that the solutions of ammonium sulfate are not acid enough to justify the idea (Kučerová *et al.*, 2010). The phenomenon is currently under investigation.

As already mentioned, ammonium sulfate is a common component of fine secondary aerosols. It means that its importance is not limited to specific locations of Třeboň or Zlatá Koruna, and the presented results could be of more general importance.

Conclusions

Dust particles collected in the State Regional Archives in Třeboň and the Research Library of South Bohemia in Zlatá Koruna (Czech Republic) consist predominantly of organic aerosol, elemental carbon, crustal elements, and ammonium, sulfate, and nitrate ions. These components are commonly found both in urban and rural environments.

It was confirmed that the contamination of Whatman 41 filters by such dust particles can substantially contribute to its degradation in the course of accelerated degradation. The degradative effect of the dust particles depends on their chemical composition rather than solely on their total mass.

The decrease in the degree of polymerization of cellulose showed a negative correlation with the content of sulfate ions in the dust particles. The possible degradative effect of fine sulfate particles was also confirmed in the case of samples with a deposit of pure ammonium sulfate. However, the mechanism behind its degradative effect and its relative importance in repository conditions still needs to be clarified.

With regard to particle size fraction, the results obtained for PM1 and PM10 samples did not differ significantly, which suggests the decisive importance of the fine particles.

The results indicate that the deposition of dust particles presents not only an esthetic problem, but can also contribute to chemical degradation of paper.

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References

Andělová, L., Smolík, J., Ondráčková, L., Ondráček, J., López-Aparicio, S., Grøntoft, T. & Stankiewicz, J. 2010. Characterization of Airborne Particles in the Baroque Hall of the National Library in Prague. *e-Preservation Science*, 7: 141–6.

Antušková, V. 2013. Vliv anorganických sloučenin užívaných pro ochranu dřeva na celulosu. Diploma Thesis, Vysoká škola chemicko-technologická v Praze.

Bílková, L. 2012. Application of Infrared Spectroscopy and Thermal Analysis to the Examination of the Degradation of Cotton Fibers. *Polymer Degradation and Stability*, 97: 35–9.

Brimblecombe, P. 1990. The Composition of Museum Atmospheres. *Atmospheric Environment*, 24B: 1–8.

Chan, Y.C., Simpson, R.W., McTainsh, G.H., Vowles, P.D., Cohen, D.D. & Bailey, G.M. 1997. Characterisation of Chemical Species in PM2.5 and PM10 Aerosolos in Brisbane, Australia. *Atmospheric Environment*, 31(22): 3773–85.

Evans, R. & Wallis, A.F.A. 1987. Comparison of Cellulose Molecular Weights Determined by High Performance Size Exclusion Chromatography and Viscometry. *Proceedings of the Fourth International Symposium on Wood and Pulping Chemistry*. Paris: International Symposium on Wood and Pulping Chemistry.

Feller, R.L., Lee, S.B. & Bogaard, J. 1986. The Kinetics of Cellulose Deterioration. In: H.L. Needles & S.H. Zeronian eds. *Historic Textile and Paper Materials. Advances in Chemistry*. Washington, DC: American Chemical Society.

Finlayson-Pitts, B. & Pitts, J., Jr. 1999. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*. San Diego, London: Academic Press.

Gaffney, J.S. & Marley, N.A. 2005. *Urban Aerosols and Their Impacts*. Washington, DC: American Chemical Society, ACS Symposium Series.

Hatchfield, P.B. 2002. *Pollutants in the Museum Environment*. London: Archetype Publications Ltd.

ISO 11799. 2003. *Information and Documentation – Document Storage Requirements for Archive and Library Materials*. Switzerland: International Standard Organization.

Kučerová, I., Ohlídalová, M., Frankl, J., Kloiber, M. & Michalcová, A. 2010. Defibring of Historical Roof Beam Caused by Ammonium Sulphate and Ammonium Phosphates Based Fire Retardants. In: J. Gril, ed. *Proceedings of Wood Science for Conservation of Cultural Heritage*. Braga: Firenze University Press, pp. 281–6.

Maenhaut, W., Schwarz, J., Cafmeyer, J. & Chi, X. 2002. Aerosol Chemical Mass Closure During the EUROTRAC-2 AEROSOL Intercomparison 2000. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 189(1–4): 233–7.

National Air Filtration Association. 2004. *The NAFA Guidelines–Libraries, Archives and Museums*. Virginia Beach: National Air Filtration Association.

National Park Service. 1999. Chapter 4: Museum Collections Environment. In: *NPS Museum Handbook*, Part I [accessed 28 November 2014]. Available at: <http://www.nps.gov/museum/publications/MHI/mushbkI.html>

Seinfeld, J.H. & Pandis, S.N. 1998. *Atmospheric Chemistry and Physics, From Air Pollution to Climate Change*. New York: John Wiley & Sons, Inc., pp. 491–544.

Tétreault, J. 2003. *Airborne Pollutants in Museums, Galleries, and Archives: Risk Assessment, Control Strategies, and Preservation, Anagement*. Ottawa: Canadian Conservation Institute.

Turpin, B.J., Saxena, P. & Andrews, E. 2000. Measuring and Simulating Particulate Organics in the Atmosphere: Problems and Prospects. *Atmospheric Environment*, 34(18): 2983–3013.

Le Van, S.L. & Winandy, J.E. 1990. Effects of Fire Retardant Treatments on Wood Strength: A Review. *Wood and Fiber Science*, 22(1): 113–31.

Wilson, W.K. 1995. NISO TR01–1995; *Environmental Guidelines for the Storage of Paper Records*. Bethesda: National Information Standards Organization.

Zervos, S. 2010. Natural and Accelerated Ageing of Cellulose and Paper: A Literature Review. In: A. Lejeune & T. Deprez, eds. *Cellulose: Structure and Properties, Derivatives and Industrial Uses*. New York: Nova Science Publishers, Incorporated, pp. 155–203.

Zou, X., Gurnagul, N., Uesaka, T. & Bouchard, J. 1994. Accelerated Aging of Papers of Pure Cellulose: Mechanism of Cellulose Degradation and Paper Embrittlement. *Polymer Degradation and Stability*, 43: 393–402.