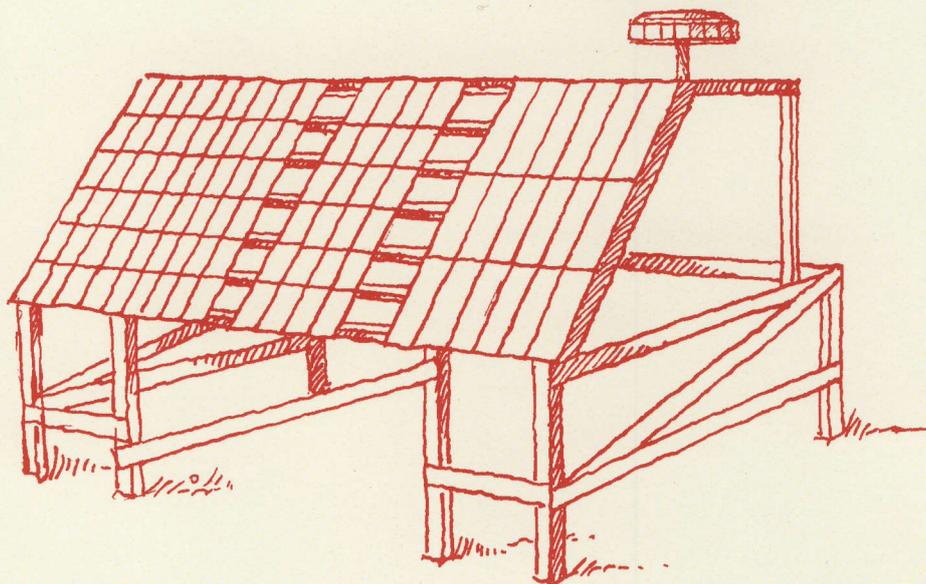


CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

UN/ECE INTERNATIONAL CO-OPERATIVE PROGRAMME
ON EFFECTS ON MATERIALS, INCLUDING HISTORIC
AND CULTURAL MONUMENTS



Report No 59:

Soiling of exposed materials and dose-response
functions for modern glass

June 2009

PREPARED BY THE SUB-CENTRE FOR SOILING



Laboratoire Interuniversitaire des Systèmes
Atmosphériques (LISA), Paris, France

Report no 59

**Soiling of exposed materials and dose-response functions
for modern glass**

Tiziana Lombardo¹, Anda Ionescu²



1. Laboratoire Interuniversitaire des Systèmes Atmosphérique, UMR
CNRS Universités Paris 12 et Paris 7
61, Avenue du Général de Gaulle, 94010 Créteil Cedex, France



2. Centre d'Etudes et de Recherche en Thermique, Environnement et
Systèmes, Université Paris 12
61, Avenue du Général de Gaulle, 94010 Créteil Cedex, France

CONTENTS

Summary.....	5
1. Introduction.....	6
2. Experimental data.....	9
2.1 <i>Glass soiling sensors.....</i>	9
2.2 <i>Measurement of soiling through the Haze.....</i>	9
2.3 <i>Field exposure campaigns.....</i>	10
2.4 <i>Selection of environmental parameters.....</i>	11
2.5 <i>Initial database for soiling.....</i>	13
3. Establishment of a dose-response function.....	15
3.1 <i>General procedure.....</i>	16
3.2 <i>Temporal trend.....</i>	17
3.3 <i>Amplitude function.....</i>	21
3.4 <i>Summary and conclusion.....</i>	25
4. Conclusion.....	28
5. Acknowledgments.....	29
6. Bibliographic references.....	29
Annexes.....	33

Summary

The International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments (ICP Materials) started in 1985. Its main goal was to provide a scientific basis for new protocols and regulations developed within the Convention on Long-range Transboundary Air Pollution. The main goal of the programme is to perform a quantitative estimation of the effect of multi-pollutants (SO₂, NO_x, O₃, HNO₃, Particles...) and meteorological parameters on the degradation (corrosion, soiling) of key materials, including materials used in object of cultural heritage. This quantification is usually performed by establishing dose-response functions and trends. Dose-response functions represent a quantitative approach to summarizing results. They are mathematical expressions that attempt to express the rate of material degradation as a function of several different variables which are responsible for it. Dose-response functions can be used to quantify the benefits of different pollution-control policies.

This report shows the main results concerning the soiling of glass materials based on several exposure campaigns of silica-soda-lime float glass performed in 31 European sites (and 1 in Canada). Dose-response functions, established for samples exposed in sheltered condition, are reported. These functions are the first attempt performed to quantify the impact of atmospheric pollutant on transparent materials, such as glass, which are largely used in modern buildings as well as in Heritage artefacts. Statistical analyses show that PM10 is not the only parameter responsible for the soiling of glass materials, indeed SO₂ and NO₂ atmospheric concentrations seem to be responsible for the optical impairment of glass surfaces, expressed as haze%.

1. Introduction

Wet and dry deposition of gaseous pollutants on material surfaces are the cause of two kinds of damage. The first type involves chemical reactions between the pollutants and the materials itself leading to a structural damage whose extent and typology depend on the nature of the material (e.g. corrosion for metal and glass, dissolution for stone...). The second kind of damage - the soiling - consists in the deposition of pollutants. Despite the fact that there is no direct modification of the material structure, this phenomenon is very effective in terms of optical degradation of all kind of materials (stone, glass, painted surface, metals...) (Figure 1.1).



Figure 1.1. Soiling of glass. Detail of a glass window affected by soiling on its left side and opened at the right side

Haynie (1986) defined soiling as “a surface degradation that can be undone by cleaning”, a definition that implies that soiling is “reversible”. Nevertheless soiling of materials, especially of stone, might lead to the formation of black crusts whose withdrawal might result in a severe loss of material. Also, it has been shown that soiling appears on surfaces exposed to the direct effect of rain indicating that rain washing is not totally effective (Lombardo et al., 2005a). Additionally, the definition of Haney neglects the fact that particle deposition, i.e. soiling, can indirectly influence the chemical attack of materials. Indeed, particles can retain moisture (e.g. deliquescent salts) or promote the adsorption of critical species at the materials surfaces (e.g. soot can act as catalyst of the oxidation of gaseous pollutants or they simply adsorb VOC...); as a consequence of this interaction, soiling, can lead to structural modifications of materials. Anyhow, the “reversibility” of soiling involves high maintenance costs (Stritt, 1993; Rabl 1999, Watt et al., in press) and has a strong impact in term of economic (increase of cost of maintenance and cleaning...), sociological (perception of aesthetical impairment of building façades and monuments...) and politic (including the effect of pollutants on materials in emission reduction strategies) concerns.

Studies on soiling carried out in the past decades have largely described this phenomenon and its consequences on different materials in term of: loss of reflectance, lightness (L^*), percentage of covered surface for opaque materials (stones, concretes, plastics, woods, asphalt shingles) - (Lanting, 1986; Haney, 1986, Creighton et al., 1990; Mansfield and Hamilton, 1989; Hamilton and Mansfield, 1993; Pio et al., 1998, Viles et al., 2002, Grossi et al. 2003, Viles and Gorbushina, 2003, O’hanlon et al., 2005, Watt et al. 2008); haze, transparency loss and percentage of covered surface for glass

(Sharples et al., 2001; Adams et al., 2002; Chabas and Lefèvre, 2002; Lombardo et al., 2005a, b; Favez et al., 2006; Ionescu et al., 2006).

Some of these studies have also established an empirical model through the statistical treatment of environmental and weathering data issued from field exposure or road tunnel tests (table 1.1). These studies permitted the establishment of dose-response functions for several materials. Although they differ in detail, a fairly consistent overall picture emerges. In most cases, dose-response functions for soiling have shown a correlation between particle content in the air - in term of TPM (Total particulate matter), PM10, PEC (Particulate Elemental Carbon), black carbon and suspended particles - and soiling of stone (Lating, 1986; Grossi et al., 2003; Pio et al., 1998, Kucera, 2007), acrylic materials (Beloin and Haney, 1975; Watt et al. 2008) and painted surfaces (Haynie, 1986; Watt et al. 2008).

Materials	Dose-Response Function	Reference
Glossy painted surfaces	$R/R_0 = e^{-\sigma kp^{2L}}$	Lating (1976)
Painted wood, concrete, brick, limestone and window glass	$R = 1.413\sqrt{C_{TSP}t}$	Beloin and Haney (1975)
Stone (Limestone and Dolostone)	$L_t^* = L_i^* - k\sqrt{C_{TSP}t}$	Grossi et al. 2003
Painted Wood	$R = 100 - 0.0663\sqrt{C_{PM10}t}$	Pio et al., 1998
Portland Stone	$R = 100 - 0.0876\sqrt{C_{DS}t}$	
	$R = 100 - 0.234\sqrt{C_{BC}t}$	
	$R = 100 - 0.0838\sqrt{C_{PM10}t}$	
	$R = 100 - 0.111\sqrt{C_{DS}t}$	
	$R = 100 - 0.296\sqrt{C_{BC}t}$	
Painted steel White plastic Polycarbonate membrane	$\Delta R = R_0[1 - \exp(-C_{PM10} \times t \times 3.96 \times 10^{-6})]$ $\Delta R = R_0[1 - \exp(-C_{PM10} \times t \times 4.43 \times 10^{-6})]$ $\Delta R = R_0[1 - \exp(-C_{PM10} \times t \times 3.47 \times 10^{-6})]$	Watt et al. 2008
		Haynie, 1986
Where: R= Reflectance after exposure R ₀ = Initial reflectance L _t [*] = Lightness after exposure L _i [*] = Lightness before exposure K = soiling constant σ = absorption coefficient of PEC (Particulate Elemental Carbon) L = length of a column of air from which PEC is deposited per unit of time C _{TSP} = Concentration in Total Suspended Particles C _{PM10} = Concentration in PM10 C _{DS} = Concentration in Dark smoke C _{BC} = Concentration in Black carbon t = time		

Table 1.1: Dose-response functions for soiling of materials.

In the case of glass, a dose-response function exists to describe the weathering of low-durability glasses (Melcher and Schreiner, 2004), nevertheless concerning durable for durable glass are sparser. Only the equations found by Lating (1986) and Beloin and Haney (1975) for several materials apply to the soiling of this kind of substrate. Furthermore, these two studies use as response a modification in reflectance. As reflectance considers only light absorption, it is not the most appropriate parameter

in the case of transparent materials, such as glass, whose optical impairment is due to both absorption (by elemental carbon) and scattering of light (by salts) (Lombardo et al., 2005b, Favez et al., 2006), as confirmed by a previous study (Saucier and Sansone, 1972). For this reason, in the present report, soiling of durable glass is assessed using haze as a response. In addition, the previous studies consider as doses only the particle content and the exposure time and neglect other parameters, which, from a physico-chemical point of view, can contribute to soiling. Indeed, it might be affirmed that quantitative reconciliation of data of durable glass soiling should be deeply explored. This report constitutes an attempt to relate soiling of glass (using haze as a response) and environmental parameter (PM and other doses) in order to make a step forward in the domain of material weathering.

2. Experimental

2.1 Glass soiling sensors

Float silica-soda-lime glass (Planilux®) has been used for this experiment as a sensor for soiling. This glass is a durable industrially produced glass, normally used for windows and building facades, as well as for stained glass window protective glazing. Previous studies (Lombardo et al. 2005a, c) demonstrated that, because of its chemical inertia, its flat surface, the absence of open porosity and the low surface roughness, this glass is a satisfactory substrate to study dust deposition and, therefore, to understand soiling.

Depending on the campaigns, one or several *glass soiling sensors* of $10 \times 10 \times 0.2$ cm in dimension were prepared for exposure. Prior to exposure samples were submitted to a 3-step cleaning procedure, using in order: compressed air (to remove coarse particles), de-ionised water (to dissolve soluble species) and ethanol (in order to eliminate organic species). After cleaning, glass samples are dried and stored in desiccators until their exposure, in case of samples exposed in the Paris area, or to their shipment, for samples sent abroad. These latter, after reception, are put in a desiccators until their exposure. At each step, gloves were used in order to avoid any contamination of the surface.

2.2. Measurement of soiling through the Haze

As defined by the ASTM D 1003 norm (ASTM, 2007), sample haze has been accessed using the following formula:

$$\text{Haze\%} = \frac{Td}{TL} * 100 \quad (2.1)$$

where Td is the diffuse transmitted light and TL the direct transmitted light.

Measurements have been carried out using a UV-VIS spectrophotometer Lambda 650 (Perkin Elmer) equipped with a 60 mm integrated sphere and via a D65 light reference. Light is provided by a tungsten-halogen lamp. The measurements are performed in a light tight box.

Following the ICI 1931 standards (CIE, 1932) the measurement are performed by acquiring a spectra between 380-780 nm (1-nm step), the transmittance of the sample is obtained after the integration of the spectrum. A personal computer drives all the measurements. The accuracies on Td and TL is 0.1 unit.

Analyses are performed on samples before and after exposure. In the latter case, samples are previously preconditioned. Indeed, the edges and the face opposite to the one directly exposed are carefully cleaned using a paper imbibed with de-ionised water. In this way, only the deposit on the directly exposed face is considered. After cleaning, samples are placed in desiccators at least during 24h.

2.3 Field exposure campaigns

Several exposure campaigns of silica-soda-lime float glass were performed in 31 European sites (and 1 in Canada) in order to understand, quantify and model the phenomenon of soiling.

Concerning the exposure conditions, although some differences exist (see tables 2.2), glass samples have been exposed in sheltered and unsheltered condition in agreement with the protocol developed during the ICP-Materials Program (Tidblad et al., 2001). These two contrasted exposures allow determining the relative contribution of wet and dry deposition to soiling process. However, due to the complication induced by rain washing, the present study focuses on sheltered samples. These latter are generally placed in vertical position, in boxes equipped with openings at the bottom and at the four sides, except in few cases, where they were placed under metal rain shield hanged on a wall and allowing free air circulation on 3 sides.

For each campaign, a cluster of samples have been exposed and withdrawn at a pre-fixed exposure time and not replaced. In such a way samples can be considered statistically independent.

Parallel to the sample exposure, a continuous survey of several meteorological (temperature, relative humidity, rain amount...) and pollution (PM, SO₂, NO_x, HNO₃, O₃... ambient concentrations) parameters has been carried out during the campaigns. It has to be noticed that these parameters are measured directly on site or very close to it (maximum hundreds of meters away), and only exceptionally data have been obtained from station with same environmental characteristics and located few km away. For air pollution parameters, generally, data are measured by the local air quality survey network using active equipments, in some cases (indicated in table 2.2) measurements are performed using passive samplers (diffusion tubes) (Ferm et al., 2005, 2006).

Specifically for particles, both active and passive measurements refer to PM₁₀. Although measurement performed with passive tubes does not allow determining the particle cut-off diameter, it is possible to estimate PM₁₀ concentration using the deposition velocity as shown by Ferm et al. (2006).

Exposure sites were located in 16 European countries (except one exposed at Dorset, Canada) and several of them situated in France (Paris area). They correspond to a large range of environmental and climatic conditions.

Table 2.2: List of the test sites within the different exposure campaigns, showing the type of environment, and the exposure details.

PROGRAMME	SITES	ENVIRONMENT	OBSERVATIONS
AERO	Gonesse	urban, neighbouring airport	Field campaign was performed from June 2004 to June 2005. Samples were exposed under rain shields. Glass withdrawal at 3, 6, 9 and 12 months. Further details to be found at http://www.airparif.asso.fr/airparif/pdf/Rsuies.pdf
	Bobigny	urban	
	Paray Vieille Poste	urban, neighbouring airport	
	Issy les Moulineaux	urban	
	Fontainebleau	rural	
MULTI-ASSESS	Athens	urban (heavy traffic)	Field campaign was performed from winter 2002 to winter 2004. Sample were exposed inside boxes. Glass withdrawals were generally performed at 3, 6, 9, 12, 15, 18, 21, 24, 27 months. [SO ₂] and [PM ₁₀] at all sites are measured by passive samplers. Further details to be found in: Kucera V. (2005); Favez et al., (2006) and Ionescu et al., 2006.
	Cracovie	urban (heavy traffic)	
	Prague	urban (traffic)	
	Rome - Monte Libretti	rural	
ICP - MATERIALS	Prague Lethany	urban (traffic)	Field campaign lasted from fall 2005 to fall 2006. Samples were exposed inside boxes. Glass withdrawals were performed after 1year exposure. [PM] were measured by passive samplers at: Prague, Kopisty, Stockholm, Aspveten, Madrid, Toledo, Dorset, Berlin, Svanvik and Chaumont. [SO ₂] and [NO ₂] were measured by passive samplers at: Strockholm, Aspveten and Riga. Further details to be found in: ICP-Materials (1989, 2007); Kucera et al. (2007)
	Kopisty	industrial	
	Bottrop	industrial	
	Rome	urban (heavy traffic)	
	Casaccia	rural	
	Milan	urban (heavy traffic)	
	Venice	urbain (traffic)	
	Oslo	urban (background)	
	Birkenes	rural	
	Stockholm	urban (heavy traffic)	
	Aspveten	rural	
	Madrid	urban (heavy traffic)	
	Toledo	rural	
	Lahemaa	rural	
	Dorset	rural	
	Paris	urban (background)	
	Berlin	urban (traffic)	
	Svanvik	rural	
Chaumont	rural		
Katowice	urban		
Athens	urban (heavy traffic)		
Riga	urban (heavy traffic)		
SCG	Paris	urban (background)	Field campaigns lasted from June 2004 to June 2008 for SCG; from June 2005 to June 2008 for Serie K and from August 2000 to August 2002 for ATMOGLASS. Samples were exposed inside boxes. Glass withdrawals were performed at various intervals varying from 1 month up to 4 years. Further details to be found in: Lombardo et al., 2005b; Chabas et al., 2008.
Serie K			
ATMO-GLASS			
VIDRIO	Troyes	urban (background)	Field exposure lasted from October 2002 to October 2003 in Troyes and from November 2003 to November 2004 in Cologne. Samples were exposed inside boxes. Glass withdrawals were generally performed at 4, 5, 6, 8 and 12 months. Further details to be found in: Lefèvre et al. (2005).
	Cologne	urban (background)	

2.4. Selection of environmental parameters

As indicated in section 2.2., a large range of environmental parameters have been measured during the different campaigns. It has to be noticed that this variety of parameters is mainly due to the fact that in most campaigns several types of materials were exposed in parallel (metals, stones, glass...). Some of these parameters, that should not have a physico-chemical influence on soiling, have not been

considered in the statistical treatment. This section expresses the reasons underlying the parameter selection to establish the dose-response function.

From a physical point of view, soiling is mainly caused by the particle deposition. Different physical processes can be accounted for particle deposition-adsorption (Camuffo, 1998; Bernardi, 2003), all of them depending on thermo-hygrometric condition of the interface air/substrate (Bernardi, 2003). The description of soiling in terms of the involved physical processes is therefore highly complicated and would need the set up of laboratory experiments were all critical parameters are controlled. In the present case, samples have been exposed in the field, and although, several parameters were measured, some others as particle size distribution, size resolved particle concentrations and nature, particles aerodynamic factors...were not. For these reasons, a statistical approach (dose-response function) taking into account the most relevant parameters – among the measured ones - have been preferred in the present study. All the parameters presenting a potential to influence soiling from a physico-chemical point of view were considered in the statistical treatment and, finally, only the statistical relevant ones were kept to explain soiling variability. In the following paragraphs, it will be described how different parameters can influence soiling, in the light of its mechanism.

Generally, deposition is described in terms of number of particles, with a given diameter, ($N(d)$) deposited on a surface. At first approximation this phenomenon is controlled by the depositional velocity (v_d), particle concentration (C) and size distribution according to the formula:

$$N(d) = v_d * C(d) \quad (2.3)$$

Thus, taking into account this formula, soiling cannot only be described in terms of particle concentration, as it is the case of the existing models, but all the parameters controlling particle deposition should be taken into account. Indeed, particle deposition depends on the temperature gradient, the water vapour in the air, the air turbulence and the characteristic of the surface (roughness, electrostatic properties...). As glass roughness is very low, it is possible to use a simplified approach for the description of glass soiling, neglecting the intrinsic parameters and performing a statistical treatment taking into account only pertinent environmental parameters.

The most obvious of these parameters is the particle concentration; the other parameters have to be chosen between those having a physical meaning. Because of their influence on depositional deposit, temperature and relative humidity should be taken into account for the statistical treatment. Furthermore, it has to be noticed that deposition rate depends on the equilibrium between the deposit and the remobilisation processes. In other terms, a particle induces soiling only if it stays on the surface (“particle capture”). Therefore, wind speed should be used as parameter to describe soiling, nevertheless, although wind speed was measured at some exposure sites, samples were not submitted to the direct impact of wind as they were exposed in a box. Therefore in the present attempt, wind speed has been neglected. But, particle capture also depends on the presence of a film of condensed water on the surface and it is known that deposition is enhanced on a wet surface compared to a dry one. Condensation on a non-porous surface (such as glass) takes place when its temperature is lower than the dew point temperature of the surrounding environment (T_d). Indeed, according to equation 2.4, which is a simplified version of the Magnus formula, condensation depends on the ambient temperature (T) and the relative humidity (RH):

$$T_d = \frac{b\gamma(T, RH)}{a - \gamma(T, RH)} \quad (2.4)$$

where $\gamma(T, RH) = \frac{aT}{b+T} + \ln(RH / 100)$ with a and b being constant values.

Condensation is a common phenomenon in outdoor environment during night time due to the cooling of the surface by infrared emission. Indeed, a glass surface can be covered by a film of water for a certain time and during this time particle capture can be improved. This constitutes a reason to introduce dew point temperature as possible doses, but it has to be reminded that surface temperature is not known and, thus, condensation episodes are not definitely detectable. Furthermore, relative humidity can also play an indirect role in the soiling, as it controls the deliquescence of salts. Indeed salts can form at certain humidity depending on their hygroscopicity. Therefore, according to their chemical composition at a precise level of humidity, salts can act as condensation nuclei favouring the condensation and consequently enhancing soiling.

Finally, experimental evidences show that particles can also form on the surface itself by reaction of gaseous pollutants, dissolved in a film of water, and the cations carried out by atmospheric particles. The morphology of sulphate salts observed on glass deposit testifies of their in situ formation (Chabas et al., 2008; Lombardo et al. 2004). Additionally, it is known that the reaction of SO₂ with stone surface takes place in case of presence of a film of water, inducing a sulphation phenomenon (see extensive bibliography in Sabbioni, 2003). By similarity to a stone substrate, it might be inferred that the same happens on a glass surface. These proofs encourage us to include the SO₂ concentrations as a possible dose. Finally, experimental data (Chabas et al., 2008; Favez et al. 2007, Lombardo et al. 2004) revealed the presence of nitrate salts on the glass surface indeed, by similarity with sulphur dioxide, NO₂ concentrations have also been included on the statistical treatment.

In conclusion, beside the particle concentrations (PM₁₀), which are considered in other models describing soiling, we select as potential doses the other pollutions parameters, SO₂ and NO₂, as well as temperature, relative humidity and dew point temperature. Finally, soiling time evolution has already been revealed by previous studies (Lombardo, 2005; Ionescu, 2006); this variable is a key one, in the dose-response to be built.

2.5. Initial database for soiling

The domain of investigation of the initial data submitted to statistical treatment is summarized on table 2.3.

Data have been gathered during 8 field campaigns in the frame of 7 scientific national and international programs.

Field campaign duration varies between 1 to almost 4 years. Sample withdrawal intervals are spread from 1 month up to several years.

Concerning the type of site, the 31 sites represents a large variety of environment, from rural (10 sites), to urban (19 sites), to industrial (2 sites).

It is somehow important to strike that the two sub-urban sites are located very close to the two major airport of Paris area, respectively close to Charles de Gaulle airport for Bobigny and to Orly airport in the case of Paray Vieille Poste.

Finally, as for the environmental parameters they show a quite large interval for all pollutant concentrations, while the climate parameters are less spread especially in the case of relative humidity. It is important to notice that all the potential doses given in this table represent moving averages calculated over all the exposure period, while the response corresponds to the value measured on sample withdrawn at a precise moment.

Table 2.3: Summary of the dose and response database used for the present study.

	DOSES							RESPONSE
	time (days)	[SO ₂] µg m ⁻³	[NO ₂] µg m ⁻³	PM10 µg m ⁻³	T (°C)	RH (%)	Dew Point (°C)	haze (%)
average	372	9	34	28	11	73	7	5
st.deviation	248	11	18	15	5	6	4	5
min	31	0.1	2	7	-5	56	-7	1
max	1454	51	90	84	21	88	14	32

3. Establishment of a dose-response function

A first study on glass soiling (Lombardo et al., 2005a, b) focused on a single site (Paris), where four parameters characterising soiling have been measured. Despite a rather short exposure (2 years), a general temporal trend could be modelled. This trend was very similar for the four parameters, one of them being the haze. The fitted model was described through the Hill equation, which is a model including a saturation level. If compared to the decreasing exponential, another model characterised by an asymptote for saturation, and which represents the solution of a first-order differential equation describing linearly the deposit and the removal, the Hill equation offers more degrees of freedom than the previous one, allowing thus the description of non linear phenomena for the kinetics of deposit and removal. In addition, it results in a curve with a second asymptote, at the beginning of the exposure.

We remind here the general form of the Hill equation that can be expressed as:

$$Y(t) = B + \frac{K}{1 + \left(\frac{M}{t}\right)^H} \quad (3.1)$$

where:

B (Bottom): initial level of response or, more generally, level of response in the absence of dose; in most of the cases is considered *a priori* null;

K (Span): Top-Bottom, where Top is the value of the soiling parameter corresponding to the maximum curve asymptote (saturation), or level of response produced after infinite soiling;

M (Half life): time (dose) when the response is halfway between the *Top* and *Bottom*; it corresponds to the curve inflection;

H (Hill slope): maximum slope of the dose-response curve at time *M*; it is used as a measure of the evolution rate.

This model has been then tested on data obtained from exposure driven on other four European sites (Ionescu et al., 2006). The model fitted reasonably well, indicating that the trend revealed from the Paris exposure could be generalised for the other sites (Krakow, Athens, Rome and Prague). It was interesting to notice that the saturation level predicted by the Hill's model, fitted on each series apart, was different from a site to another, and, at a first glance, related to the general level of pollution characterising each site. Another important remark consisted that the function's coefficients (*M* and *H*: mi-saturation time and maximum soiling rate), other than those describing soiling's magnitude (e.g. *B* and *K*) were rather constant for all sites, proving that a general trend could be highlighted, but with a different amplitude (*B+K*) from a site to another.

These results sustain our approach to search a dose-response function for soiling containing a common temporal trend for all the sites and characterised by a saturation level whose amplitude can be further explained via the environmental parameters of each site. The procedure will be presented in the next section.

It has to be noticed that, although we had a previous knowledge about the temporal trend for the durable glass soiling, some other models have been tested to fit to temporal trend (decreasing exponential, Gaussian). Either in terms of temporal trend or in terms of results predicted by the final

dose-response function corresponding to each temporal trend, we obtained, from a statistical point of view, a similar quality or inferior.

3.4.1 . Forme générale de la fonction doses-réponse

3.1. General Procedure:

As already mentioned, within the dose-response formulation, the response is the haze, and potential doses are environmental and meteorological parameters: pollutant concentrations of PM₁₀, SO₂ and NO₂, temperature, relative humidity and the calculated dew point temperature. We remind that the haze values are issued from measurements of samples exposed during certain duration, while the doses have been averaged over the period of exposure. Averages have been calculated generally from hourly values.

Based- on our previous studies, and taking into account the reasons invoked in the introduction of this section, the general form of the dose-response function to be fitted is:

$$\text{Response} = \text{Amplitude(doses)} * \text{Trend}(t), \quad (3.2)$$

and in particular :

$$\text{Haze} = \mathbf{A}(\text{environment, meteo}) * \mathbf{g}(t), \quad (3.3)$$

where the function $\mathbf{g}(t)$ represents the temporal trend for soiling, which has to be similar for all the sites and whose formulation must include an asymptote (a saturation level for long-time exposures) and the function A represents the amplitude, different from a site to another, obtained from the environmental and meteorological doses.

In this purpose, the dose-response function has been calculated via a 2-step procedure:

- firstly, all the time series which were at least 1-year long have been normalised, in order to fit a temporal trend $\mathbf{g}'(t)$; for example the coefficients B, K, M, H have to be determined :

$$\text{NormalisedHaze} = B + \frac{K}{\left(1 + \frac{M}{t}\right)^H} = \mathbf{g}'(t) \quad (3.4)$$

- once $\mathbf{g}'(t)$ determined, the resulting saturation level is ignored and considered to be 1 in the formulation of $\mathbf{g}(t)$; within this stage, a more general saturation is expressed, this time, by a function, \mathbf{A} , depending on the environmental and meteorological doses.

For the same example, corresponding to the Hill's equation, the function $\mathbf{g}(t)$ will be :

$$\mathbf{g}(t) = \frac{1}{\left(1 + \frac{M}{t}\right)^H} \quad (3.5)$$

where the coefficients M and H have been previously determined. They describe the general trend, common for all the sites of exposure.

Technically, the first stage requires fitting a non linear function of a single variable, i.e. time, which can be achieved by a classical non linear regression. The amplitude function can be reached by a multiple linear regression, if a cumulative effect of the doses is considered, based on the following development:

$$\begin{aligned} \text{Haze} &= A(\text{SO}_2, \text{NO}_2, \text{PM10}, T, \text{RH}, \text{DewPoint}) \cdot g(t) \\ &= (a_1 \cdot \text{SO}_2 + a_2 \cdot \text{NO}_2 + a_3 \cdot T + \dots) \cdot g(t) \\ &= a_1 \cdot (\text{SO}_2 \cdot g(t)) + a_2 \cdot (\text{NO}_2 \cdot g(t)) + a_3 \cdot (T \cdot g(t)) + \dots \end{aligned} \quad (3.6)$$

Thus, the coefficients a_1, a_2, \dots can be obtained using a Multiple Linear Regression. Each value of haze in equation (3.6) corresponds to a specific time t , known, i.e. time is not a variable in equation (3.6), it is fixed.

The **normalisation** consists in dividing a temporal series by a same constant. This constant has to be chosen in order to scale the different series to a common range. Two types of normalisation have been tested:

- by the haze value measured after a 1-year exposure;
- by the predicted saturation level, when an individual Hill model could be adjusted to a time series.

The results obtained for the temporal trend fit are presented in section 3.2 and the amplitude function, in section 3.3.

3.2. Temporal trend

Following the procedure described in section 3.1, the temporal trend, obtained for the two normalisations are presented.

- Temporal trend obtained when the time series were normalised by the 1-year value of haze.

All the haze time series corresponding to a haze evolution during at least one year long were normalised by the 1-year haze value, and the $g'(t)$ function obtained for this normalised haze is indicated in eq. 3.7 and represented in figure 3.1:

$$\text{NormalisedHaze} = 0.14 + \frac{2}{\left(1 + \left(\frac{382}{\text{Days}}\right)^{1.86}\right)} \quad (3.7)$$

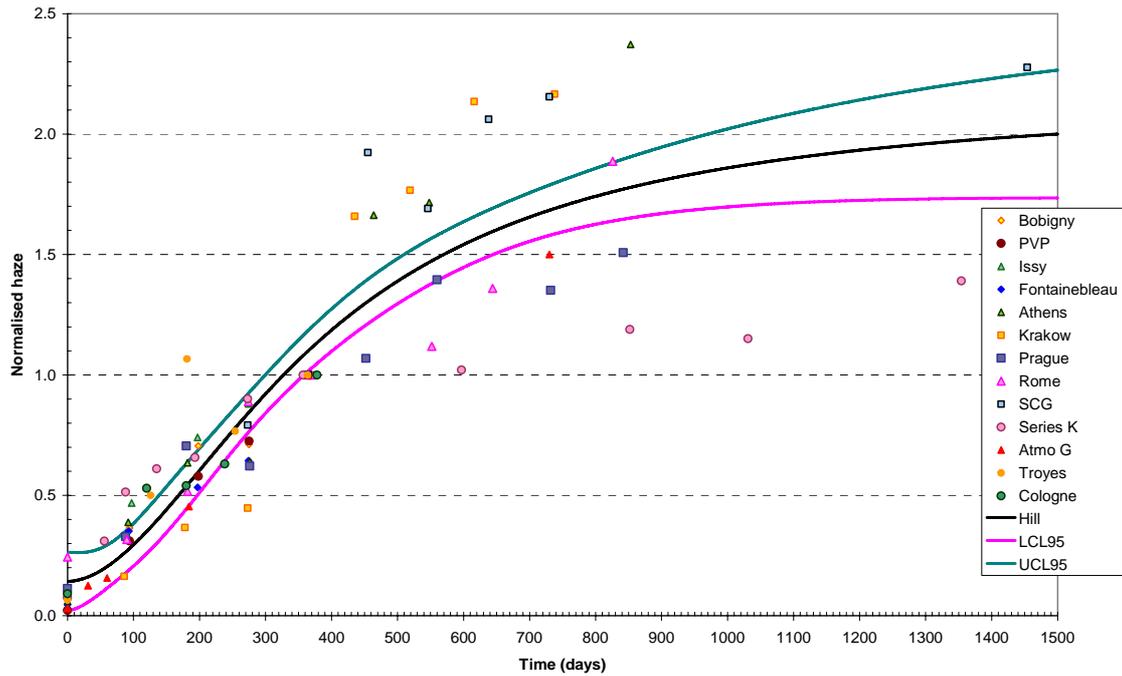


Figure 3.1.: Temporal trend for the normalised haze values in the case of the 1-year value normalisation, using a Hill equation (eq. 3.7). The different time series correspond to haze measurements presented in Table 1.1, which were normalised and are represented by points on the graph. The continue lines correspond to the fitted model (Hill) and its prediction band at a 95% confidence level (LCL95 and UCL95).

The fitted normalised haze is plotted versus the measured normalised haze in the figure 3.2, which shows a rather moderate dispersion: $R^2=0.83$.

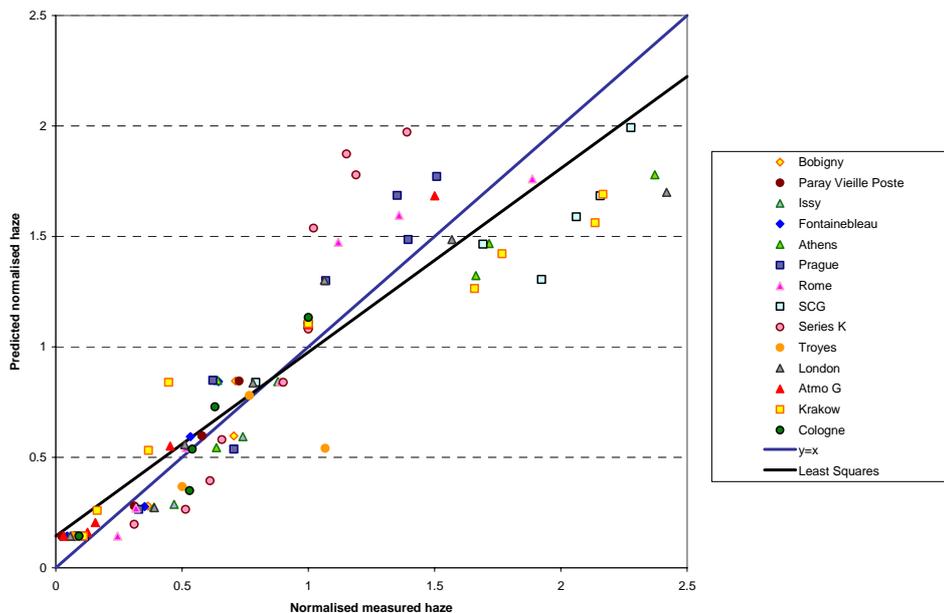


Figure 3.2: Predicted normalised haze versus normalised measured haze ($R^2=0.83$); 1-year value normalisation and Hill's model (eq. 3.7).

- Temporal trend obtained when the time series were normalised by the saturation level

The second type of normalisation that has been tested in this study consisted in dividing each time series by its saturation level (B+K), obtained by fitting an individual Hill model to each series, independently.

The corresponding $g'(t)$ function is :

$$NormalisedHaze = \frac{1}{\left(1 + \left(\frac{438}{Days}\right)^{1.63}\right)} = g'(t) \quad (3.8)$$

and the results are presented in figures 3.3. and 3.4.

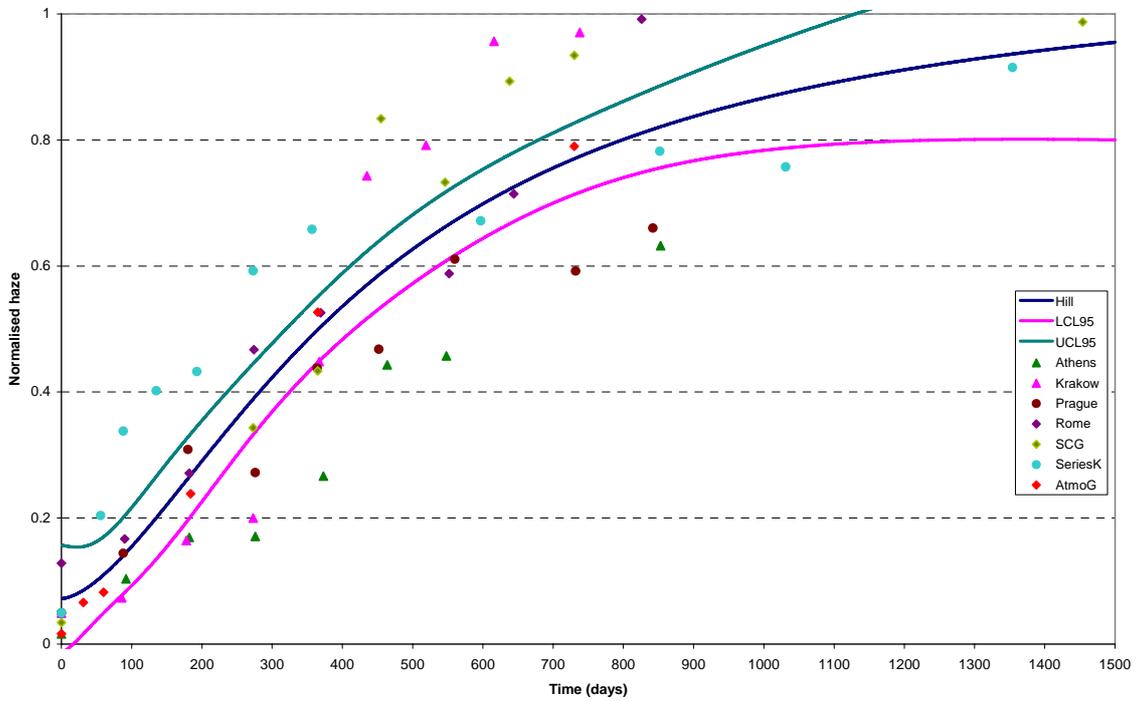


Figure 3.3: Temporal trend for the normalised haze values in the case of the (B+K)-value normalisation, using a Hill equation (eq. 3.8). The different time series correspond to haze measurements presented in Table 1.1, which were normalised and are represented by points on the graph. The continue lines correspond to the fitted model (Hill) and its prediction band at a 95% confidence level (LCL95 and UCL95).

The fitted normalised haze is plotted versus the measured normalised haze ($R^2=0.83$) in figure 3.4.:

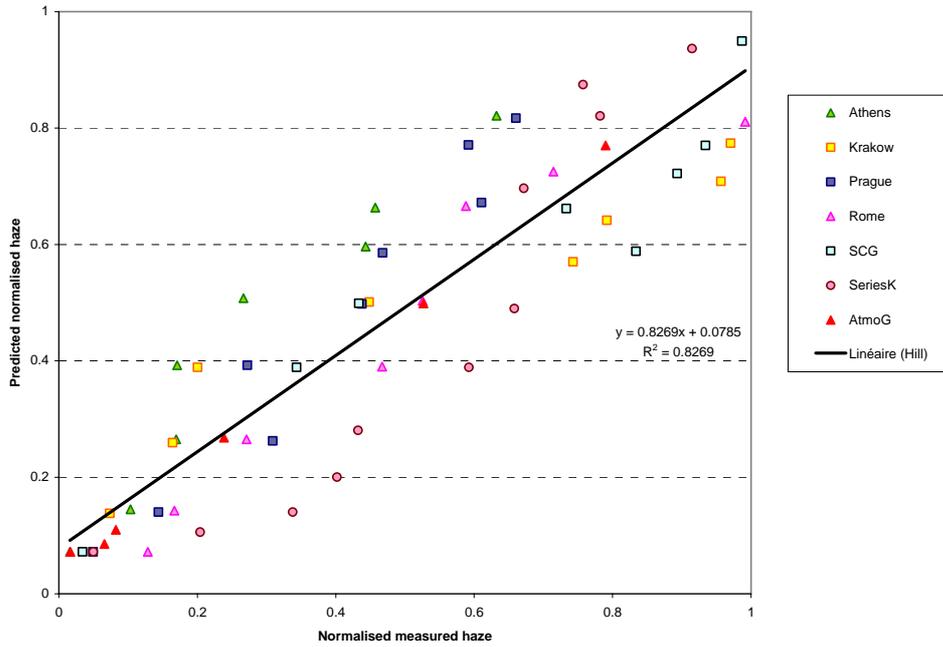


Figure 3.4: Predicted normalised haze versus normalised measured haze ($R^2=0.83$); $(B+K)$ -value normalisation and Hill's model (eq. 3.8).

One can notice that the number of time series available in the case of the second normalisation is lower, because it has not been always possible to fit an individual model to a time series, especially for the cases when the latter were rather short (1-year long).

Comparing the results obtained with the two types of normalisation, the results were very similar, at a temporal level, but also, when the two temporal trends were used within the final dose-response function; this quasi-equivalence has been considered essentially by comparing the predictions of the two models, but one can notice, also, that the two model coefficients sets are very close.

Finally, we decided to focus our further presentation on a single temporal trend, based on the Hill's model and applied to data normalised by the 1-year haze value, due to the fact that this normalisation permits to use a higher number of temporal series than the second one and also because it is based on experimental data (1-year value) instead of the individual saturation levels which arise from the statistical treatment and are not error free. Nevertheless, it is good to remark that similar results were obtained for different functions, proving the robustness of the approach.

To resume, the function corresponding to the temporal trend further used is given in equation (3.9), deriving from equation (3.7):

$$g(t) = \frac{1}{\left(1 + \left(\frac{382}{Days}\right)^{1.86}\right)}. \quad (3.9)$$

3.3. Amplitude function

Environmental and meteorological data are collected within the frame of different campaigns and the measurement protocol is not always strictly the same; a first difference to be noticed is that pollutant concentration measurement are different. Indeed, in the case of PM₁₀ concentrations sometimes active values are given, other times, passive ones (value obtained with diffusive tubes) (cf. section 2.2). A conversion has been applied to values obtained by passive samplers to transform them in equivalent values obtained with active ones, but this operation is not error-free. Therefore, when building up the dose-response function we preferred to start by using *only the active measurements*.

At this stage, the relevance of the different doses has not been evaluated yet, so we started by using all of them (namely SO₂, NO₂, PM10, T, HR, Dew Point Temperature), but in this case the database has been slightly restrained, as all the doses were not available at each site.

a) Amplitude function based only on active measurements of pollutant concentrations and meteorological parameters

In order to select the most important doses explaining the haze variance, an ascending procedure, including the different doses step by step, has been performed. Results are summarized in table 3.1.

First of all, one can notice that only the temporal trend explains, by itself, 33% of the haze variance ($R^2=0.33$). When adding pollutant concentrations, the percentage of variance explained rises to 52% for PM10 concentration, 57% for SO₂ and 61% for NO₂. It as to be noticed that these three parameters might possess a common source (e.g. engine exhausts for PM and NO₂) and therefore these coefficients might be strongly affected.

The dew point temperature alone is not an explicative variable for haze, neither the ambient temperature, the relative humidity or their combination.

The cumulative effect of two pollutants increases the explained percentage of haze up to 62%, 65% or 69% when using all three pollutants: PM₁₀, SO₂ and NO₂. Nevertheless, it has to be notice that, although from the statistical point of view using in the same equation parameters which are correlated, as is the case of PM₁₀ and NO₂, is not recommended, from the physico-chemical point of view it was important to fit all of these parameters in the same equation. Indeed, soiling of glass is not only due to the particle deposition but also to the deposition of gaseous species (NO₂ and SO₂) which form specific salts at the surface of the glass by gas-particle conversion.

If any other meteorological parameter is added to this combination, there is no benefit neither when used as a cumulative effect, nor as an interaction (different product such as SO₂*RH).

Table 3.1: Performance of dose-response functions based on different doses: relevance of doses.

Doses	R ²	Doses	R ²
Time g(t)	0.33	(SO ₂ , NO ₂ , PM10, DewPoint)*g(t)	0.69
PM ₁₀ *g(t)	0.52	(SO ₂ , NO ₂ , PM10, T)*g(t)	0.69
SO ₂ *g(t)	0.57	(NO ₂ , PM ₁₀ , T)*g(t)	0.62
NO ₂ *g(t)	0.61	(SO ₂ , PM ₁₀ , T)*g(t)	0.65
Dew point temperature*g(t)	0.22	(SO ₂ , NO ₂ , PM ₁₀ , T)*g(t)	0.68
T*g(t)	0.32	(SO ₂ , RH)*g(t)	0.63
RH*g(t)	0.28	(SO ₂ , PM ₁₀ , RH)*g(t)	0.65
(T, RH)*g(t)	0.33	(SO ₂ , NO ₂ , RH)*g(t)	0.67
(T*RH)*g(t)	0.29	(NO ₂ , PM ₁₀ , RH)*g(t)	0.69
(PM ₁₀ , SO ₂)*g(t)	0.65	(SO ₂ , NO ₂ , PM ₁₀ , RH)*g(t)	0.69
(PM ₁₀ , NO ₂)*g(t)	0.62		
(SO ₂ , NO ₂)*g(t)	0.68	(PM ₁₀ , NO ₂ RH, SO ₂ RH)*g(t)	0.65
(SO ₂ , NO ₂ , PM ₁₀)*g(t)	0.69	(PM ₁₀ , NO ₂ , SO ₂ RH)*g(t)	0.68
		(PM ₁₀ , NO ₂ RH, SO ₂ RH)*g(t)	0.65
		(PM ₁₀ , NO ₂ RH, SO ₂ RH, TC)*g(t)	0.67
		(PM ₁₀ , NO ₂ RH, SO ₂ RH)*g(t)	0.65

This analysis reveals the impact of environmental parameters on the haze amplitude: PM₁₀, SO₂ and NO₂ concentrations. Meteorological parameters can not explain any further haze variance; despite the physical explanation, this is not very surprising, because these parameters interfere punctually, and their values that could really be explicative are, anyhow, smoothed by the fact that we are using average values.

The best results can be formulated by the following dose-response function:

$$Haze = (0.2524 * [SO_2] + 0.1182 * [NO_2] + 0.131 * [PM_{10}]) \cdot \frac{1}{\left(1 + \left(\frac{382}{Days}\right)^{1.86}\right)} \quad (3.10)$$

The pollutant concentrations are given in $\mu\text{g}\cdot\text{m}^{-3}$ and Haze in %.

These results were obtained when using the database including data from the following sites: Gonesse, Issy, Athens (Multi-Assess), Krakow, Prague (Multi-Assess), Rome-Monte Libretti ((Multi-Assess), Paris (Series K, Atmo Glass, Self Cleaning Glass), Troyes, Oslo, Lahemaa, Paris (ICP-Materials) and Athens (ICP-Materials).

The determination value obtained when plotting measured haze versus predicted one is 0.69 for the complete dataset. We remind that all these sites correspond to value sets including only active measurements for PM₁₀ concentrations and all the meteorological values. This could be the case of Bottrop site, which has been considered as outlier (very low values of haze for high doses). When including the Bottrop site value, the dose-response function based on the same doses, is characterised by a determination coefficient of 0.65.

b) Amplitude function based only on active measurements of doses representing only pollutant concentrations

The previous analysis showed that the meteorological parameters (averaged over the exposure period) are not important to explain haze variance. Therefore, the database considered to fit the dose-response function can be enhanced, including also the Fontainebleau site measurements.

On this new database, the dose-response function was recalculated:

$$Haze = (0.2529 * [SO_2] + 0.1080 * [NO_2] + 0.1473 * [PM_{10}]) \cdot \frac{1}{\left(1 + \left(\frac{382}{Days}\right)^{1.86}\right)} \quad (3.11)$$

and the determination coefficient obtained in this case was of 0.695. The results obtained through this new equation are plotted in figure 3.5. The obtained coefficients are only slightly different compared to the previous ones.

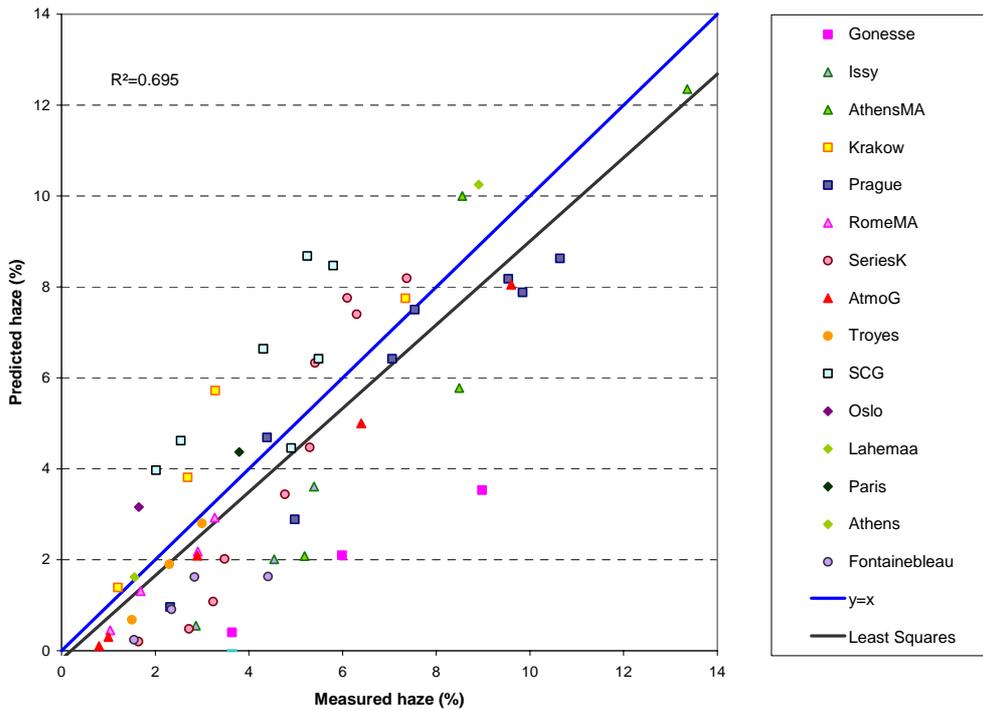


Figure 3.5: Predicted haze versus measured haze using the dose-response function eq. 3.11.

- Contribution of different doses

Starting from this dose-response function (eq. 3.11), the contribution of each dose explaining either predicted or measured haze can be estimated via the formula:

$$Contribution[\%] = \frac{a_i [Dose_i] \cdot g(t)}{HazeValue} \cdot 100 \quad (3.12)$$

where a_i represents the coefficient obtained by multiple linear regression for dose i and the HazeValue corresponds either to the measured or to the predicted haze.

The contributions obtained for each set of values are presented in annexe 2. A summary of these contributions is given in the table 3.2.

Table 3.2: Contribution (in %) of the different doses to the measured and predicted haze by eq. 3.11

	% of Predicted Haze explained by:			% of Measured Haze explained by:		
	SO ₂	NO ₂	PM ₁₀	SO ₂	NO ₂	PM ₁₀
mean	19.2	38.6	42.5	16.8	32.4	35.0
median	16.9	42.3	41.3	14.5	31.5	33.9
st.dev	9.04	9.7	12.0	13.5	21.2	20.4
min	5.2	12.3	23.7	1.8	3.7	3.7
max	43.7	52.3	71.9	54.2	91.3	96.3

It appears clearly that for the predicted values of haze, PM₁₀ accounts for the highest contribution (~42%), followed by NO₂ (~39%) and SO₂ (~19%). The same results are highlighted in the case of the contributions to the measured values: PM₁₀ (~35%) > NO₂ (~32%) > SO₂ (~17%).

The contributions of the different doses can vary from site to site and are different for each sample (cf. annexe 2). The sum of contribution of all parameters to the measured value of haze is generally close to 100% for samples exposed at least one year long; haze values corresponding to shorter durations are usually underestimated.

- Test of the dose-response function (obtained using only active measurements), on value sets corresponding to passive measurements for PM₁₀ concentrations

The following ICP Materials sites : Prague Lethany, Kopisty, Stockholm, Aspvreten, Madrid, Toledo, Svanvik, Chaumont, Katowice, Athens, Birkenes could be used for testing the dose-response function obtained using only active measurements (eq. 3.11), on value sets corresponding to passive measurements for PM₁₀. The determination coefficient of the obtained dataset is R²=0.32. Plotting the predicted versus the measured haze values, it appears a great difference in the case of the Katowice site; if the latter is excluded from the database, the determination coefficient increases significantly to R²=0.65, not far to the performance obtained with the last dose-response function.

These close performances obtained without Katowice site encouraged us to test another dose-reponse function, including in the database also the following sites: Prague Lethany, Kopisty, Stockholm, Aspvreten, Madrid, Toledo, Svanvik, Chaumont, Athens and Birkenes.

c) Amplitude function based on active and passive measurements of pollutant concentrations

In this configuration, the dose-response function based on active and passive measurements of pollutant concentrations can be expressed by the following formula:

$$Haze = (0.2215 * [SO_2] + 0.1367 * [NO_x] + 0.1092 * [PM_{10}]) \cdot \frac{1}{\left(1 + \left(\frac{382}{Days}\right)^{1.86}\right)} \quad (3.13)$$

The predicted versus the measured haze obtained in this new try is presented in figure 3.6. Dispersion of the data is very similar to the one obtained with equation 3.11, and the determination coefficient is rather similar $R^2=0.69$.

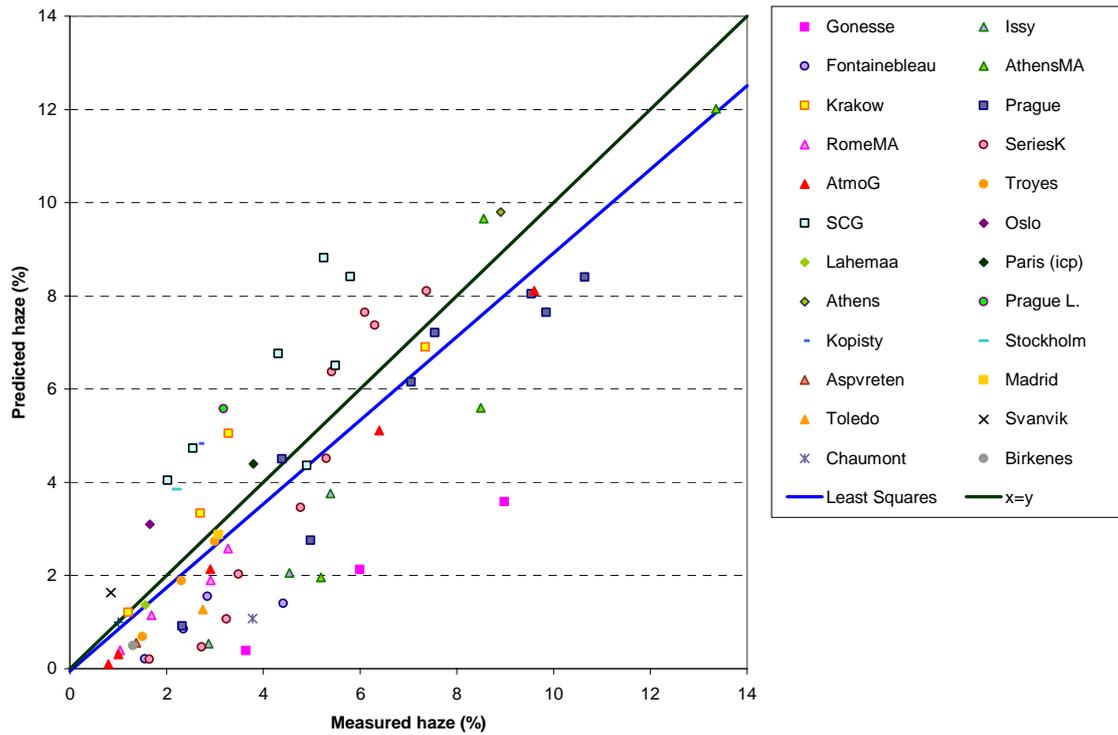


Figure 3.6: Predicted haze versus measured haze using the dose-response function eq.3.13.

3.4. Summary and conclusions

The 2-step statistical treatment described in this section permitted the establishment of several dose-response functions to quantify soiling of glass materials. The procedure consisted in finding separately the kinetics of the phenomenon ($g(t)$) and the amplitude of the response expressed in terms of environmental parameters.

The kinetics (temporal trend) required to normalise the different time series within the same range. Two different normalisations have been tested, leading to a similar quality statistical fit, and finally the normalisation by the 1-year measured haze value has been retained. For the temporal trend analytical form, the Hill's model was preferred to other functions giving also statistically good results, for reasons of previous knowledge acquired on the soiling time evolution. The analytical formulation is given in equation (3.9), deriving from the complete model given in equation (3.8) and reminded here:

$$g(t) = \frac{1}{\left(1 + \left(\frac{382}{Days}\right)^{1.86}\right)}$$

After establishing the temporal trend, several attempts to obtain a complete dose-response function were performed, they are summarised in table 3.3. Each of the dose-response function applied to a different initial data-set chosen in agreement with the several prerequisite.

The first attempt was realised on the database containing all the potential doses measured by active techniques (namely SO₂, NO₂, PM₁₀, T, HR, Dew Point Temperature). This first attempt (eq. 3.10, see table 3.3) showed the importance of pollution concentrations, while, despite their possible physico-chemical involvement in the process of soiling, climate parameters were found have a negligible contribution. These remarks result from a step-by-step multiple linear regression, where the different doses has been introduced progressively.

Table 3.3: Summary of the dose-response functions and their R² fitted on different databases: *a*, *b*, *c* are respectively the SO₂, NO₂ and PM₁₀ coefficients from the amplitude function. The temporal trend is given by equation 3.9.

D-R function	<i>a</i>	<i>b</i>	<i>c</i>	R ²
Eq. (3.10)	0.2524	0.1182	0.131	0.690
Eq. (3.11)	0.2529	0.1080	0.1473	0.695
Eq. (3.13)	0.2215	0.1367	0.1092	0.685

This finding allowed extending the database by including another site (Fontainebleau) characterised by active measurements (this site had been initially ignored because meteorological data were missing). On this second database, a new dose-response function has been fitted (3.11); the coefficients (table 3.3) and the predicted haze were very similar to the first attempt, suggesting that the last included site respects the same trend predicted by the first dose-response function. The two first dose-response functions (3.10 and 3.11) explained 69% of the haze variance.

The function (3.11) has been applied to a test database, consisting of all the sites characterised by passive measurement of pollutants. After excluding an outlier, 65% of the haze variance for the test database could be explained by the function (3.11).

The last database has been extended including the test database (without outlier) and a third function (eq. 3.13) has been obtained (cf. table 3.3). This function explained 69% of the variance of the haze for the database containing active and passive measurements.

It appears clearly that dose-response coefficients are very similar in the case of active measurements (eq. 3.10 and 3.11); they only slightly differ when passive measurements are taken into account. The same remark can be made for the determination coefficients corresponding to the different functions.

Finally, we propose the (3.11) equation as a dose-response function for durable glass soiling:

$$Haze = (0.2529 * [SO_2] + 0.1080 * [NO_2] + 0.1473 * [PM_{10}]) \cdot \frac{1}{\left(1 + \left(\frac{382}{Days}\right)^{1.86}\right)}$$

which is obtained from the largest database where active and passive measurements for PM₁₀ concentrations were not mixed.

Further, using equation (3.11), it has been possible to calculate the contribution of each dose to the haze (both predicted and measured) of samples. It appears that PM₁₀ concentrations show the highest contribution to the haze, followed by NO₂ and SO₂ (see Table 3.2)

In conclusion, this study permitted to develop a dose-response function from data collected from several field campaigns, in different environments, considering the same temporal trend for all soiling evolution and explaining the soiling amplitude through different doses characterising the environment of each site. This analysis revealed that only the pollutant concentrations could effectively explain the haze variance (~70%) no additional information could be brought by the meteorological parameters.

4. Conclusion

A dose-response function for soiling of glass materials has been developed from data issued from several field exposures in various environments (industrial, urban and rural areas) with duration variables between 1 month and almost 4 years.

The function, presented as follow, was obtained by a 2-step procedure, where the temporal trend is expressed by the Hill equation, and the amplitude of the soiling measurement (expressed in term of haze%) is explained via the environmental parameters of each site.

$$Haze = (0.2529 * [SO_2] + 0.1080 * [NO_2] + 0.1473 * [PM_{10}]) \cdot \frac{1}{\left(1 + \left(\frac{382}{Days}\right)^{1.86}\right)}$$

It shows that particulate concentration (expressed in term of PM_{10}), NO_2 and SO_2 concentrations, have to be taken into account to predict soiling variation. Despite their possible physical influences on soiling processes, meteorological parameters (temperature, relative humidity and dew point temperature) did not explain any further variance. This is probably due to the use of averaged values which smooths the occurrence of condensation episodes. Further studies, in more contrasted environmental conditions should be carried out to better understand the role of meteorological parameters.

The function was established using only active measurements of pollutants and allows explaining 69% of the haze variance. Statistical treatment shows that it can be successfully applied on site characterised by doses measured by passive methods ($R^2=0.65$), showing the robustness of this approach.

It has to be reminded that the dose-response function concerns only data from sheltered exposure, which are not the normal exposure condition of a building façade. Therefore, the values obtained have to be considered as the highest values that could be attained on a building which is regularly submitted to a partial rain washing.

This function is the first attempt to quantify the soiling of transparent materials, such as durable glass. It constitutes a first important step towards the establishment of maps of increased risk of soiling and for calculating maintenance cost.

Finally, further studies on the impact of each pollution parameters, and in particular on the different parts of the particulate phase (soluble salts, black and organic carbon, insoluble fractions...) should be carried out, in order to built up a dose-response function which will be useful in the process of decision making in the domain of environmental policies (e.g. reduction strategies).

5. Acknowledgments

The authors address a special thank to Vladimir Kucera, Johan Tidblad, Adriana Bernardi, Philippe Espiard and Leticia Rancourel coordinators of EU projects MultiAssess, Vidrio and Self-Cleaning glass and UN-ECE ICP-Materials Program, as well as to all colleagues involved in these projects. They also thank AirParif for their financial and scientific support during the AERO project. The European commission and the ADEME are gratefully acknowledged for the financial support of this research.

6. Bibliographic References

- Adams, S.J., Kibrya R., Brimblecombe P., 2002. A particle accumulation study during the reconstruction of The Great Cour, British Museum. *Journal of Cultural Heritage* 3, 283-287.
- ASTM D1003, Haze and Luminous Transmittance of Transparent Plastics, November 2007.
- Beloin, N.J., Haynie, F.H., 1975. Soiling of building materials. *Journal Air Pollution Control Association* 25, 393-403.
- Bernardi A., 2003, *Conservare opera d'arte: Il microclima negli ambienti museali*. Eds Il Prato, Padova, 143 pp.
- Camuffo D., 1998, *Microclimate for Cultural Heritage*, Elsevier, Amsterdam, 415 pp.
- CIE (1932). *Commission Internationale de l'Eclairage proceedings, 1931*. Cambridge University Press, Cambridge.
- Chabas, A., Lefèvre, R.-A., 2002. Soiling of soda-lime float glass in the polluted atmosphere of Paris. *Glass Technology* 43C, 79-83.
- Chabas A., Lombardo T., Cachier H., Pertuisot M.H., Oilonomou K., Falcone R., Verità M., Geotti-Bianchini F., 2008. Behaviour of self-cleaning glass in urban atmosphere, *Building and Environment*, 43, 2124-2131.
- Creighton, P.J., Liroy, P.J., Haynie, F.H., Lemmons, T.J., Miller, J.L., Gerhart, J., 1990. Soiling by atmospheric aerosols in an urban industrial area. *Journal of Air and Waste Management Association* 40, 1285-1289.
- Favez O., Cachier H., Chabas A., Ausset P., Lefèvre R., 2006. Crossed optical and chemical evaluations of modern glass soiling in various European environments. *Atmospheric Environment*, 40, 7192-7204.
- Ferm M., Watt J., O'Hanlon S., De Santis F., Varotsos C., 2006. Deposition measurement of particulate matter in connection with corrosion studies. *Analytical Bioanalytical Chemistry*, 384, 1320-1330.
- Ferm M., De Santis F., Varotsos C., 2005. Nitric acid measurement in connection with corrosion studies. *Atmospheric Environment*, 39, 6664-6672.
- Grossi, C.M., Esber, R.M., Diaz-Pache, F., Alonso, F.J., 2003. Soiling of building stones in urban environments. *Building and Environment* 38, 147-159.
- Hamilton, R.S., Mansfield, T.A., 1993. The soiling of materials in the ambient atmosphere. *Atmospheric Environment* 27A, 8, 369-1374.
- Haynie F.H., 1986, The theoretical model of soiling of surfaces by airborne particles. In: Lee S.D., Schnider T., Grant L.D., Verkerk P.J. editors, *Aerosols*. Boca Raton: Lewis Publisher, 961-959.
- ICP-Materials, 1989. Report n. 2 of the International co-operative programme on materials, including historic and cultural monuments: Description of sites, 25 pp.
- ICP-Materials, 2007, Report n. 52 of the International co-operative programme on materials, including historic and cultural monuments: Environmental data report. 62 pp.
- Ionescu A., Lefèvre R., Chabas A., Lombardo T., Ausset P., Candau Y., Rosseman L., 2006. Modeling of soiling based on silica-soda-lime glass exposure at six European sites. *Science of the Total Environment*, 369, 246-255.

- Kucera V., 2005. Publishable final Report of the EU Contract Multi-ASSESS “Model for multi-pollutant impact and assessment of threshold levels for cultural heritage”, <http://www.corr-institute.se/MULTI-ASSESS/> 52 pp.
- Kucera V., Tidblad J., Kreislova K., Knotkova D., Faller M., Reiss D., Snethlage R., Yates T., Heriksen J., Schreiner M., Melcher M., Ferm M., Lefèvre R.A., Kobus J., 2007. UN/ECE ICP Materials Dose-response functions for the multi-pollutants situation. *Water, Air, Soil Pollution: Focus* 7, 249-258.
- Lanting, R.W., 1986. Black smoke and soiling. In: Lee, S. D., Schneider, T., Grant, L. D., Verkerk, P.J., (Eds), *Aerosols*. pp. 923-932. Lewis Publisher, Chelsea, Michigan, USA.
- Lefèvre R.A., Ionescu A., Ausset P., Cachier H., Chabas A., Favez O., Lombardo T., Oikonomou K., 2005. In the field experimental simulation using glass soiling sensors and modelling of the atmospheric particle deposition on stained-glass windows with protective double-glazing. *Rivista della Stazione Sperimentale del Vetro*, 3, 41-48.
- Lombardo, T., Lefèvre, R.-A, Chabas, A., Ausset P., H. Cachier, Ionescu A., 2004. Characterisation of particulate matter deposition inducing soiling of modern glass. In Saiz-Jimenez, C. (Ed.), *European Commission International Workshop Air Pollution and Cultural Heritage*, Seville, Spain. Balkema, A.A. Publisher, Leiden, The Netherlands, 209-214.
- Lombardo T., Chabas A., Ionescu A., Lefèvre R.-A., 2005a. Modelling the soiling of float glass in a polluted atmosphere. *Glass Technology*, 46(2), 192-196.
- Lombardo T., Ionescu A., Lefèvre R.-A., Chabas A., Ausset P., Cachier H., 2005b: Soiling of silica-soda-lime float glass in urban environment: measurements and modelling. *Atmospheric Environment*, 39, 989-997.
- Lombardo T., Chabas, A., Lefèvre, R.A., Verita, M. & Geotti-Bianchini, F. 2005c. Weathering of float glass exposed outdoors in an urban area. *Glass technology* 46(3): 271-276.
- Melcher, M., Schreiner, M., 2004. Statistical evaluation of potash-lime-silica glass weathering. *Analytical and Bioanalytical Chemistry* 379, 628-639.
- Mansfield T.A. and Hamilton R.S., 1989. The soiling of materials: models and measurement in a road tunnel in Man and his ecosystem. *Proceedings of the 8th World Clean Air Congress*, L.J. Brassier and W.C. Mulder Eds, Elsevier Science Publisher B.V. Amsterdam, The Netherlands, 353-357.
- O’Hanlon S., Watt J., Hamilton R., 2005. The soiling of Cultural Heritage materials. *Cultural Heritage in the City of tomorrow: developing policies to manage the continuing risks from air pollution*. Proceeding of a MULTI-ASSESS Workshop, London 10-11, 2004, Kucera V., Tidblad J., Hamilton R. Eds., Korrosioninsitutet, Stockholm. 201-212.
- Pio, C.A., Ramos, M.M., Duarte, A.C., 1998. Atmospheric aerosol and soiling of external surface in urban environment. *Atmospheric Environment* 32, vol. 11, 1979-1898.
- Rabl A. 1999. Air pollution and building: an estimation of damage costs in France. *Environ. Impact Assess. Rev.*, 19, 361-385.
- Sabbioni C., 2003, Mechanisms of air pollution damage to stone, In: *The effects of air pollution on the built environment*, P. Brimblecombe Ed., Imperial College Press, London, 289-334.
- Saucier J.Y. and Sansone E.B., 1972, The relationship between transmittance and reflectance measurement of “soiling index”. *Atmospheric Environment* 6, 37-43.
- Sharples, S., Stewart, L., Tregenza, P.R., 2001. Glazing daylight transmittances: a field survey of windows in urban area. *Building and Environment* 36, 503-509.
- Stritt M.A., 1993. Cost of soiling of building caused by road traffic: methodological aspects and empirical results for the town of Neuchâtel (Switzerland). *The Science of the Total Environment*, 134, 1-3, 31-38.
- Tidblad J., Kucera V., Mikhailov A.A., Heriksen J., Kreislova, K., Yates T., Stöckle B., Schreiner M., 2001, UN-ECE ICP materials: dose-response functions on dry an wet acid deposition effects after 8 years of exposure. *Water, Air and Soil Pollution*, 130, 1457-1462.
- Viles H.A., Taylor M.P., Yates T.J.S, Massey S.W., 2002, Soiling and decay of N.M.E.P. limestone tablets, *The Sciences of the Total Environment*, 292, 215-229.
- Viles H.A. and Gorbushina A.A., 2003, Soiling and microbial colonisation on urban roadside limestone: a three year study in Oxford, England, *Building and Environment*, 38, 1217-1224.

- Watt J. and Hamilton R., 2002, The soiling of buildings by air pollution, In: The effects of air pollution on the built environment, P. Brimblecombe Ed., Imperial College Press, London, 289-334.
- Watt J., Jarrett D., Hamilton R., 2008, Dose-response functions for the soiling of heritage materials due to air pollution exposure, *The Sciences of the Total Environment*, 400, 1-3, 415-424.
- Watt et al., *The effect of Air pollution on Cultural Heritage – A Reference Manual*, John Watt and Ron Hamilton Eds., Springer, 2008, in press.

ANNEXES

Annexe 1: Haze measured at different sites, and predicted via different Dose-response functions (1/2).

Site	Measured Haze	Haze predicted by:		
		D-R Function eq. 3.10	D-R Function eq. 3.11	D-R Function eq. 3.13
Gonesse	3.6	3.6	0.4	0.4
Gonesse	6.0	6.0	2.1	2.1
Gonesse	9.0	9.0	3.6	3.6
Issy	2.9	2.9	0.6	0.5
Issy	4.5	4.5	2.0	2.1
Issy	5.4	5.4	3.7	3.8
AthensMA	5.2	5.2	2.0	2.0
AthensMA	8.5	8.5	5.7	5.6
AthensMA	8.6	8.6	10.0	9.7
AthensMA	13.4	13.4	12.5	12.0
Krakow	1.2	1.2	1.3	1.2
Krakow	2.7	2.7	3.6	3.3
Krakow	3.3	3.3	5.5	5.1
Krakow	7.3	7.3	7.5	6.9
Prague	2.3	2.3	0.9	0.9
Prague	5.0	5.0	2.8	2.8
Prague	4.4	4.4	4.6	4.5
Prague	7.1	7.1	6.3	6.2
Prague	7.5	7.5	7.2	7.2
Prague	9.8	9.8	7.7	7.6
Prague	9.5	9.5	8.1	8.0
Prague	10.6	10.6	8.5	8.4
RomeMA	1.0	1.0	0.4	0.4
RomeMA	1.7	1.7	1.3	1.2
RomeMA	2.9	2.9	2.1	1.9
RomeMA	3.3	3.3	2.9	2.6
SeriesK	1.6	1.6	0.2	0.2
SeriesK	2.7	2.7	0.5	0.5
SeriesK	3.2	3.2	1.1	1.1
SeriesK	3.5	3.5	2.1	2.0
SeriesK	4.8	4.8	3.5	3.5
SeriesK	5.3	5.3	4.5	4.5
SeriesK	5.4	5.4	6.4	6.4
SeriesK	6.3	6.3	7.5	7.4
SeriesK	6.1	6.1	7.8	7.6
SeriesK	7.37	7.4	8.2	8.1
AtmoG	0.8	0.8	0.1	0.1
AtmoG	1.0	1.0	0.3	0.3
AtmoG	2.9	2.9	2.1	2.1
AtmoG	6.4	6.4	5.1	5.1
AtmoG	9.6	9.6	8.1	8.1
Troyes	1.5	1.5	0.7	0.7
Troyes	2.3	2.3	1.9	1.9
Troyes	3.0	3.0	2.8	2.7
SCG	2.0	2.0	4.0	4.0
SCG	2.5	2.5	4.7	4.7
SCG	4.9	4.9	4.6	4.4
SCG	4.3	4.3	6.7	6.8
SCG	5.3	5.3	8.6	8.8
SCG	5.5	5.5	6.5	6.5
SCG	5.8	5.8	8.5	8.4

Annexe 1: Haze measured at different sites, and predicted via different Dose-response functions (2/2).

Site	Measured Haze	D-R Function eq. 3.10	Haze predicted by:	
			D-R Function eq. 3.11	D-R Function eq. 3.13
Oslo	1.6	1.6	3.1	3.1
Lahemaa	1.6	1.6	1.6	1.4
Paris	3.8	3.8	4.4	4.4
Athens	8.9	8.9	10.2	9.8
Fontainebleau	1.55		0.2	0.2
Fontainebleau	2.4		0.9	0.9
Fontainebleau	2.8		1.6	1.6
Fontainebleau	4.4		1.6	1.4
Prague Lethany	3.2			5.6
Kopisty	2.7			4.8
Stockholm	2.2			3.9
Aspvreten	1.4			0.6
Madrid	3.1			2.9
Toledo	2.7			1.3
Svanvik	0.9			1.6
Chaumont	3.8			1.1
Athens	8.9			9.8
Birkenes	1.3			0.5
Katowice	2.2			

Annexe 2: Measured and predicted haze value, corresponding doses and their contributions, i.e. equivalent haze values explained by the different doses via the dose-response function (eq. 3.11), given in percentage of respectively predicted and measured haze (1/2)

Site	Predicted Haze	Measured Haze	Time	Doses			Equivalent haze value explained by:			%of Predicted haze explained by:			% of Measured haze explained by:		
				SO ₂ *g(t)	NO ₂ *g(t)	PM10*g(t)	HazeSO ₂ *g(t)	HazeNO ₂ *g(t)	HazePM10*g(t)	%HazeSO ₂ tmod	%HazeNO ₂ tmod	%HazePM10tmod	%HazeSO ₂ tmeas	%HazeNO ₂ tmeas	%HazePM10tmeas
Gonesse	0.41	3.6	94	0.3	1.4	1.2	0.09	0.15	0.17	21.019917	37.701204	41.625919	2.4	4.2	4.7
Gonesse	2.13	6.0	198	1.8	9.1	4.5	0.46	0.98	0.67	21.535020	45.982248	31.357339	7.7	16.4	11.2
Gonesse	3.55	9.0	275	3.2	15.1	7.4	0.80	1.63	1.09	22.503991	45.915617	30.583716	8.9	18.2	12.1
Issy	0.56	2.9	97	0.4	2.2	1.4	0.09	0.24	0.21	16.250793	43.027012	37.860686	3.2	8.4	7.4
Issy	2.04	4.5	197	1.4	9.2	4.5	0.34	1.00	0.66	16.741078	48.852967	32.502448	7.5	22.0	14.6
Issy	3.68	5.4	274	2.4	17.8	7.3	0.62	1.92	1.08	16.810460	52.303007	29.373437	11.5	35.7	20.1
AthensMA	2.04	5.2	92	3.4	5.4	4.3	0.85	0.58	0.63	41.590346	28.431506	30.955564	16.4	11.2	12.2
AthensMA	5.74	8.5	182	8.7	18.1	11.0	2.19	1.95	1.62	38.137777	33.979417	28.152027	25.8	23.0	19.0
AthensMA	10.04	8.6	276	17.4	29.1	16.7	4.39	3.14	2.46	43.749423	31.281851	24.538693	51.3	36.7	28.8
AthensMA	12.45	13.4	373	21.1	37.7	20.0	5.34	4.07	2.95	42.854568	32.704356	23.693864	39.9	30.5	22.1
Krakow	1.33	1.2	86	1.8	2.0	4.9	0.47	0.22	0.72	35.135782	16.583862	54.499707	38.8	18.3	60.2
Krakow	3.64	2.7	178	4.8	6.2	13.1	1.23	0.67	1.93	33.665055	18.401966	53.072575	45.5	24.9	71.7
Krakow	5.49	3.3	273	7.0	10.2	19.3	1.78	1.10	2.84	32.408097	20.073191	51.649671	54.2	33.6	86.4
Krakow	7.47	7.3	367	9.6	14.6	25.4	2.42	1.58	3.75	32.420567	21.146126	50.170199	33.0	21.5	51.0
Prague	0.92	2.3	88	0.7	3.3	2.9	0.17	0.35	0.43	18.591693	38.560088	46.687635	7.4	15.3	18.5
Prague	2.8	5.0	180	1.8	9.6	9.5	0.46	1.04	1.39	16.288460	37.075466	49.768447	9.2	20.9	28.0
Prague	4.6	4.4	276	2.8	16.4	15.0	0.72	1.77	2.22	15.548395	38.520631	48.165350	16.3	40.4	50.5
Prague	6.25	7.1	364	4.0	22.1	20.5	1.00	2.39	3.02	16.003640	38.186727	48.245310	14.2	33.8	42.7
Prague	7.24	7.5	452	5.1	26.0	23.1	1.28	2.81	3.40	17.689211	38.840760	46.933797	17.0	37.3	45.1
Prague	7.69	9.8	560	5.1	28.8	23.6	1.29	3.11	3.48	16.726087	40.378673	45.253334	13.1	31.5	35.4
Prague	8.08	9.5	732	5.3	31.7	23.2	1.34	3.42	3.42	16.634171	42.342564	42.286483	14.1	35.9	35.8
Prague	8.48	10.6	842	6.3	31.7	24.5	1.60	3.42	3.61	18.854587	40.328262	42.540876	15.0	32.1	33.9
RomeMA	0.42	1.0	90	0.1	1.2	2.0	0.02	0.13	0.30	5.578294	29.992650	70.935747	2.3	12.1	28.7
RomeMA	1.28	1.7	182	0.3	3.0	6.2	0.07	0.33	0.92	5.819570	25.646851	71.850488	4.4	19.4	54.5
RomeMA	2.13	2.9	274	0.6	4.7	10.3	0.14	0.51	1.52	6.553441	24.043880	71.398458	4.8	17.6	52.3
RomeMA	2.87	3.3	369	0.7	6.7	13.8	0.17	0.73	2.04	5.972906	25.281540	70.914511	5.2	22.2	62.2

Annexe 2: Measured and predicted haze value, corresponding doses and their contributions, i.e. equivalent haze values explained by the different doses via the dose-response function (eq. 3.11), given in percentage of respectively predicted and measured haze (2/2)

Site	Predicted Haze	Measured Haze	Time	Doses			Equivalent haze value explained by:			% of Predicted haze explained by:			% of Measured haze explained by:		
				SO ₂ *g(t)	NO ₂ *g(t)	PM10*g(t)	HzSO ₂ *g(t)	HzNO ₂ *g(t)	HzPM10*g(t)	%HzSO ₂ tmod	%HzNO ₂ tmod	%HzPM10tmod	%HzSO ₂ tmeas	%HzNO ₂ tmeas	%HzPM10tmeas
SeriesK	0.22	1.6	56	0.1	0.8	0.6	0.03	0.09	0.09	15.732714	39.912455	42.097292	2.1	5.3	5.6
SeriesK	0.48	2.7	88	0.3	1.8	1.4	0.08	0.19	0.20	15.897115	39.639324	41.635212	2.8	7.0	7.3
SeriesK	1.1	3.2	135	0.7	4.4	2.9	0.17	0.48	0.43	15.329354	43.642290	39.413124	5.2	14.8	13.4
SeriesK	2.05	3.5	193	1.5	8.5	4.9	0.38	0.92	0.72	18.673691	44.723136	35.028647	11.0	26.3	20.6
SeriesK	3.48	4.8	273	2.7	14.5	8.1	0.69	1.57	1.19	19.818786	45.106880	34.294558	14.5	32.9	25.0
SeriesK	4.5	5.3	357	3.5	18.9	10.5	0.88	2.04	1.54	19.494679	45.392783	34.210456	16.6	38.5	29.0
SeriesK	6.4	5.4	597	4.4	26.9	15.7	1.11	2.91	2.31	17.359868	45.452226	36.104023	20.5	53.8	42.7
SeriesK	7.46	6.3	852	4.6	30.5	20.0	1.17	3.29	2.95	15.709659	44.158811	39.503339	18.6	52.3	46.8
SeriesK	7.77	6.1	1031	5.0	30.4	21.8	1.26	3.29	3.21	16.268874	42.310774	41.312349	20.7	53.9	52.6
SeriesK	8.18	7.37	1354	4.6	33.0	23.5	1.16	3.56	3.46	14.120179	43.536382	42.272433	15.7	48.3	46.9
AtmoG	0.09	0.8	31	0.1	0.4	0.2	0.01	0.04	0.03	16.111939	46.534854	32.576303	1.8	5.2	3.7
AtmoG	0.3	1.0	60	0.2	1.4	0.7	0.04	0.15	0.10	14.833844	48.701049	33.071220	4.5	14.6	9.9
AtmoG	2.13	2.9	184	1.8	9.4	4.2	0.46	1.02	0.62	21.502361	47.784621	29.058073	15.8	35.1	21.3
AtmoG	5.08	6.4	365	4.3	22.2	10.3	1.09	2.40	1.52	21.503632	47.226801	29.861908	17.1	37.5	23.7
AtmoG	8.1	9.6	730	6.9	33.7	18.1	1.74	3.64	2.67	21.439621	44.915127	32.951265	18.1	37.9	27.8
Troyes	0.68	1.5	126	0.2	3.2	1.9	0.06	0.35	0.28	8.339293	51.460265	41.043074	3.8	23.3	18.6
Troyes	1.9	2.3	254	0.4	8.2	6.2	0.11	0.89	0.91	5.969164	46.643271	47.835466	4.9	38.5	39.5
Troyes	2.81	3.0	364	0.6	11.4	9.6	0.16	1.23	1.42	5.537817	43.814890	50.507304	5.2	41.0	47.3
SCG	3.95	2.0	273	3.9	17.0	7.8	0.98	1.84	1.14	24.835880	46.609633	28.931001	48.6	91.3	56.7
SCG	4.65	2.5	365	3.3	21.0	10.3	0.83	2.27	1.51	17.774397	48.875350	32.471766	32.4	89.2	59.3
SCG	4.55	4.9	455	2.9	16.8	13.0	0.73	1.82	1.91	16.018132	39.941077	41.952158	14.9	37.1	39.0
SCG	6.73	4.3	546	4.6	29.7	15.4	1.17	3.21	2.26	17.362679	47.665718	33.612962	27.1	74.5	52.5
SCG	8.64	5.3	638	8.3	37.1	17.5	2.11	4.00	2.58	24.405110	46.320493	29.865021	40.2	76.2	49.1
SCG	6.46	5.5	730	4.7	28.0	15.0	1.19	3.02	2.21	18.473873	46.734926	34.151273	21.7	55.0	40.2
SCG	8.48	5.8	1454	5.7	34.2	22.6	1.44	3.69	3.33	16.934782	43.498166	39.275268	24.8	63.6	57.4
Oslo	3.09	1.6	371	0.6	13.1	10.8	0.16	1.41	1.59	5.169346	45.679302	51.416102	9.7	85.6	96.3
Lahemaa	1.55	1.6	365	1.9	1.8	6.4	0.48	0.19	0.94	31.213575	12.329918	60.448995	31.1	12.3	60.1
Paris	4.42	3.8	363	3.1	18.7	10.6	0.79	2.02	1.57	17.964323	45.680872	35.445431	20.9	53.2	41.3
Athens	10.15	8.9	367	11.1	32.2	26.9	2.80	3.48	3.97	27.553647	34.276856	39.074479	31.4	39.1	44.5
Fontainebleau	0.24	1.55	93	0.1	0.5	1.0	0.03	0.06	0.15	14.099093	24.083861	61.589456	2.2	3.7	9.5
Fontainebleau	0.91	2.4	197	0.5	2.9	3.2	0.11	0.32	0.46	12.509816	34.724757	51.003842	4.8	13.4	19.8
Fontainebleau	1.62	2.8	274	1.0	5.6	5.2	0.27	0.60	0.77	16.365739	37.274280	47.660603	9.3	21.3	27.2