UNITED NATIONS **E**

Economic and Social Council

Distr.
GENERAL

EB.AIR/WG.1/2005/7
22 June 2005

Original: ENGLISH

ECONOMIC COMMISSION FOR EUROPE

EXECUTIVE BODY FOR THE CONVENTION ON
LONG-RANGE TRANSBOUNDARY AIR POLLUTION

Working Group on Effects
(Twenty-fourth session, Geneva, 31 August–2 September 2005)
Item 5 (iii) of the provisional agenda

FINAL RESULTS FROM THE MULTI-POLLUTANT PROGRAMME INCLUDING DOSE-RESPONSE FUNCTIONS ON EFFECTS ON MATERIALS

Report prepared by the Programme Centre of the International Cooperative Programme on Effects of Air Pollution on Materials, including Historic and Cultural Monuments (ICP Materials)

Introduction

1. The multi-pollutant programme of ICP Materials consisted of 1-, 2- and 4-year exposures of materials during 1997–2001. Additional environmental measurements of particulate matter and nitric acid (HNO_3) were carried out during the European Union (EU) project MULTI-ASSESS that started in 2002. One of the aims was to develop dose-response functions for the multi-pollutant situation. This report gives an overview of the final results from the multi-pollutant and MULTI-ASSESS exposure programmes, which are inextricably intertwined. The new dose-response functions are compared with the functions obtained in the original 8-year (1987–1994) exposure programme of ICP Materials.

GE.05-31536

I. OVERVIEW OF MULTI-POLLUTANT EXPOSURE PROGRAMME

2. The ICP Materials network included 30 test sites in 16 European countries, Israel, Canada and the United States. The targeted network of the MULTI-ASSESS programme included sites in London, Prague, Rome, Athens, Krakow and Riga with a special aim to study the local urban situation and to quantify soiling effects.

3. The evaluation of corrosion effects on materials was done by standardized or well-established procedures. The evaluation of materials was performed at dedicated sub-centres, each responsible for a material, or group of materials, and for performing all corrosion analyses of this material regardless of where it was exposed. Environmental data were continuously measured at or nearby each site. These included gaseous pollutants, precipitation and climatic parameters. The environmental characterization was more extensive compared to the original exposure programme (1987–1994). All environmental measurements were compiled and reported by the Norwegian Institute for Air Research. The overview of the measured parameters is in table 1.

Table 1. Measurements of environmental parameters, corrosion attack and soiling in the multi-pollutant / MULTI-ASSESS exposure programmes

Environmental parameters	**Corrosion materials**	**Soiling materials**
Climate	Structural metals	Plastic materials
- Temperature	- Carbon steel	- Hard white ultraviolet
- Relative humidity	- Copper	radiation (UV) stable
- Sun radiation	- Cast bronze	- Filter materials
- Amount of precipitation	- Zinc	- Millipore Isopore
Gaseous pollutants	Stone materials	Stone materials
- SO_2	- Portland limestone	- Portland limestone
- NO_2	- Carrara Marble	
- O_3	- Baumberger sandstone	Paint coatings
- HNO_3	- Gotland sandstone	- Steel panel with alkyd
	- Saaremaa dolomite	
Particulate matter	- Concrete	Glass materials
- Total deposition		- Modern glass
- Chemical composition #	Paint coatings	
	- Steel panel with alkyd	
Wet deposition		
- pH and conductivity	Glass materials	
- Chemical composition	- Glass of medieval composition	

Includes quantification of the ions SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, Ca^{2+}, Mg^{2+} and K^+

4. The new programme included soiling, which had not been evaluated earlier. Glass materials were also included in the multi-pollutant programme with withdrawals after three and four years of exposure. Carbon steel was previously only included as a trend material, that is, exposed only for one year. The results of corrosion of unsheltered carbon steel are shown in figure I.

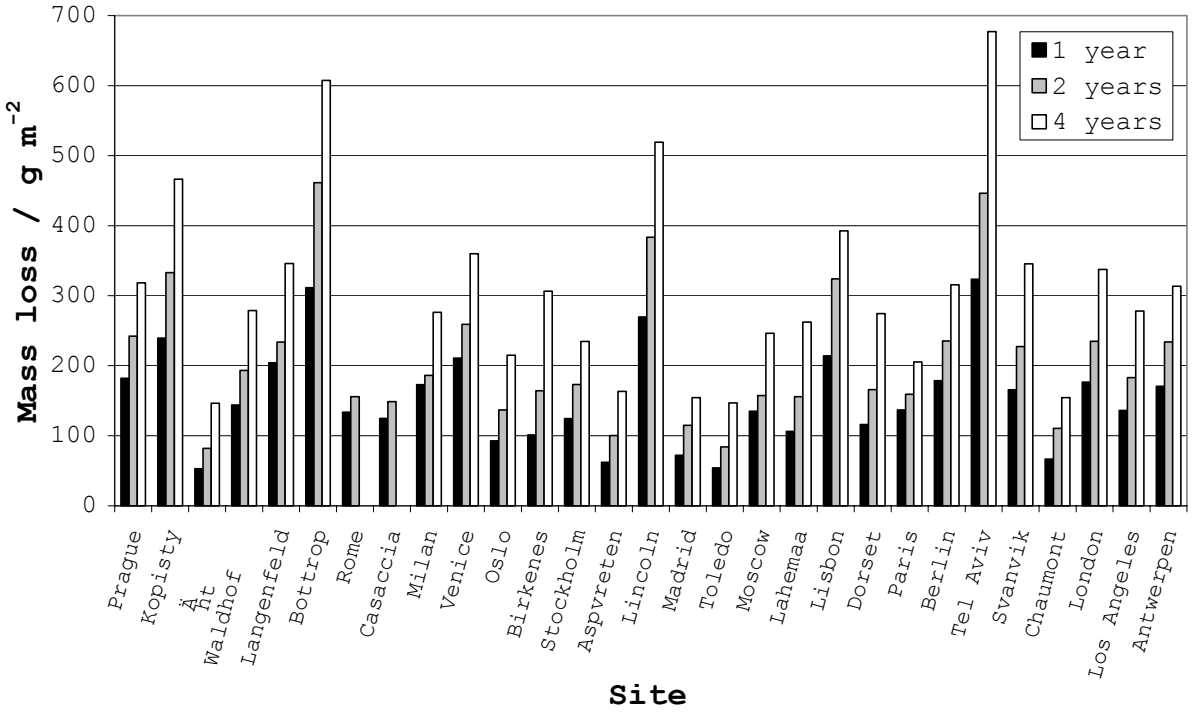

Figure I. Corrosion attack of unsheltered carbon steel in the multi-pollutant exposure programme

II. DOSE-RESPONSE FUNCTIONS OF CORROSION

5. The statistical analysis was based on corrosion values of carbon steel, zinc, copper, bronze and limestone after 1, 2 and 4 years of exposure in the multi-pollutant programme. One important criterion for the dose-response functions was that they should be suitable for mapping areas with increased risk of corrosion. Therefore the environmental parameters for the final dose-response functions were restricted to easily available ones (table 2). Possible exceptions were the new parameters HNO_3 and total particulate matter (PM) deposition (PM_{dep}), however, these were possible to relate to or calculate from other easily available parameters.

Table 2. Environmental parameters included in the final dose-response functions

Parameter description	**Abbreviation**	**Unit**
Temperature	T	°C
Relative humidity	Rh	%
Amount of precipitation	Rain	mm $year^{-1}$
pH of precipitation	pH	decades (dimensionless)
Acidity of precipitation #	$[H^+]$	mg l^{-1}
SO_2 concentration	$[SO_2]$	µg m^{-3}
NO_2 concentration	$[NO_2]$	µg m^{-3}
O_3 concentration	$[O_3]$	µg m^{-3}
HNO_3 concentration	$[HNO_3]$	µg m^{-3}
Total PM deposition	PM_{dep}	g m^{-2} $year^{-1}$

Calculated directly from pH

6. The statistical evaluation was a combination of linear and non-linear regression performed at the Main Research Centre and an analysis using automatic generation and selection of non-linear models developed at the Swiss sub-centre for zinc. The result of the analysis is summarized in table 3.

Table 3. Pollution parameters used in the dose-response functions

Material	**pH**	**SO_2**	**O_3**	**HNO_3**	**PM_{dep}**
carbon steel	X	X			X
zinc	X	X		X	
copper	X	X	X		
bronze	X	X			X
limestone	X	X		X	X

7. The climatic parameters (T, Rh and Rain) were included in almost all of the functions. Both pH and SO_2 were in all of the new and previous functions. NO_2 was not included in any of the functions directly as it was closely related to the HNO_3 concentration. Inclusion of the remaining parameters depended on material. The function for copper was very similar to the previously developed 8-year function, which also included ozone. A complete list of the new functions will be presented in the Acid Rain 2005 conference (Prague, June 2005).

8. The effects of HNO_3 (zinc and limestone) and PM (carbon steel and bronze) were new and are discussed below using carbon steel and limestone as examples.

A. Dose-response function for carbon steel

9. No dose-response function for carbon steel was derived in the 8-year exposure programme of ICP Materials. However, a recently developed function based on work within the International Standard Organization resulted in the following equation describing the corrosion attack after one year of exposure:

$$r_{corrFe} = 1.77\ [SO_2]^{0.52}\ e^{0.020Rh}\ e^{f(T)} + g(Cl^-, Rh, T) \quad (1)$$

where r_{corr} is measured in µm, f(T) = 0.15 (T–10) when T<10°C and otherwise –0.05 (T–10), and g(Cl^-, Rh, T) is a function describing the effect of dry deposition of chloride. The temperature interval used in the derivation of this function was from –20°C to +30°C. The multi-pollutant database only included values from 0°C to +25°C and since the data set did not disagree with this temperature function, the same function was used in the resulting multi-assess function (R^2 = 0.88):

$$ML_{Fe} = 29.1 + t^{0.6}\ (21.8 + 1.38\ [SO_2]^{0.6}\ Rh_{60}\ e^{f(T)} + 1.29\ Rain\ [H^+] + 8.11\ PM_{dep}) \quad (2)$$

where ML was the mass loss measured in g m^{-2}, t was the time in years, RH60 was equal to (Rh–60) when Rh>60% and otherwise 0, and f(T) = 0.15 (T–10) when T<10°C and otherwise –0.05 (T–10). The observed and predicted values are shown in figure II.

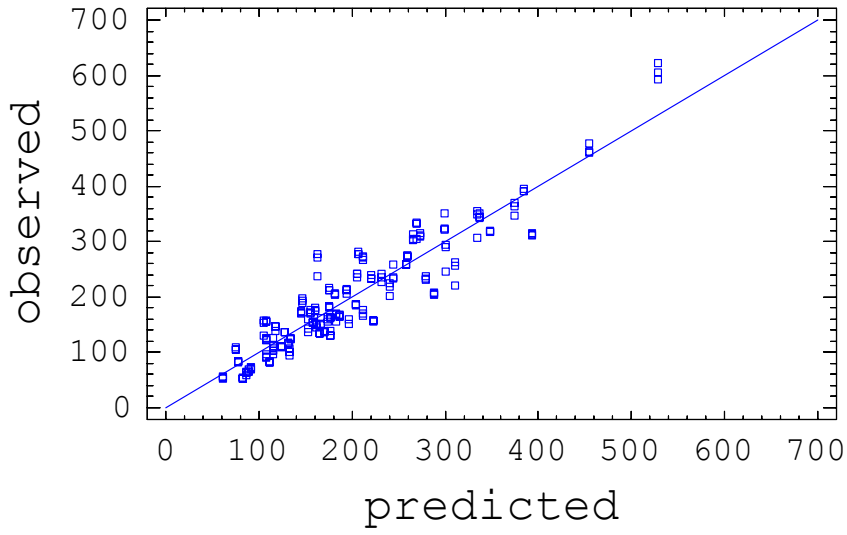

Figure II. Observed (vertical) and predicted (horizontal) values (mg m^{-2}) of corrosion attack of unsheltered carbon steel in the multi-pollutant exposure programme based on equation 2

10. In the dose-response function for carbon steel the deposited mass (PM_{dep}) was measured with a passive particle collector developed and used for the first time within the multi-pollutant / MULTI-ASSESS programme. Therefore this parameter could not be used directly for producing corrosion maps. However, PM_{10} concentrations were obtained from 14 sites and the deposited mass (PM_{dep}) correlated well with the PM_{10} concentration at 11 of these (fig. III). The slope of the regression line corresponded to a deposition velocity of 2.3 mm s^{-1}. The other three sites were all close to roads with heavy traffic and gave higher deposition velocities. The dose-response function was modified to include PM_{10} instead of PM_{dep}.

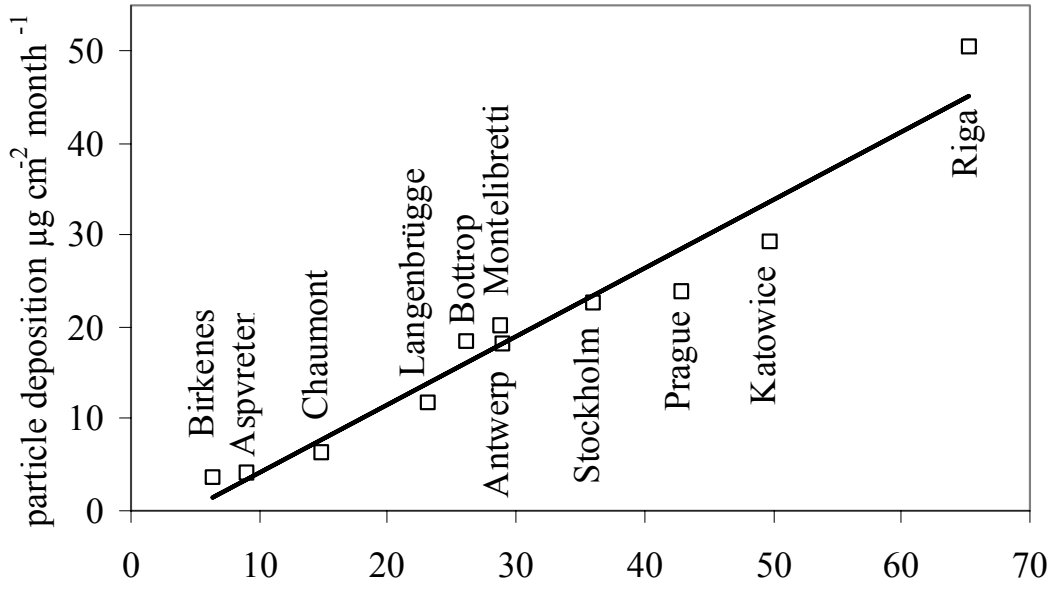

Figure III. Particulate matter deposition to the surrogate surface (PM_{dep}) in wind-exposed positions as a function of particle air concentration (PM_{10})

B. Dose-response function for limestone

11. The dose-response function from the 8-year ICP Materials exposure programme was:

$$R_{8\text{-year}} = 2.7\,[SO_2]^{0.48}\, e^{-0.018T}\, t^{0.96} + 0.019\,\text{Rain}\,[H^+]\, t^{0.96} \qquad (3)$$

where R was surface recession at open exposure measured in µm.

12. The updated function from the multi-pollutant programme includes SO_2, wet deposition, HNO_3 and particles($R^2 = 0.66$):

$$R_{multipol} = 3.1 + t \cdot (0.85 + 0.0059\,Rh_{60}\,[SO_2] + 0.078\,Rh_{60}\,[HNO_3] + 0.054\,\text{Rain}\,[H^+] + 0.36\,PM_{dep}) \qquad (4)$$

13. The equation predicted that at equal concentrations the effect of HNO_3 was about 13 times higher than that of SO_2. The HNO_3 concentrations typically varied between 0 and 2.0 µg m^{-3} (fig. IV). They were low in northern Europe and high in southern Europe. Comparisons of urban and rural stations close to each other (Oslo-Birkenes, Stockholm-Aspvreten, Madrid-Toledo and Rome-Casaccia) showed HNO_3 concentrations were higher in the cities.

14. These qualitative observations were summarized in an equation predicting the annual HNO_3 concentration:

$$HNO_3 = 5.0\ 10^2\ e^{-3400\ /\ (T+273)}\ (Rh\ [O_3]\ [NO_2])^{0.5} \qquad (5)$$

15. The observed and predicted values of $[HNO_3]$ are given in figure V. The most important parameter influencing the HNO_3 concentration was NO_2, followed by T, O_3 and Rh.

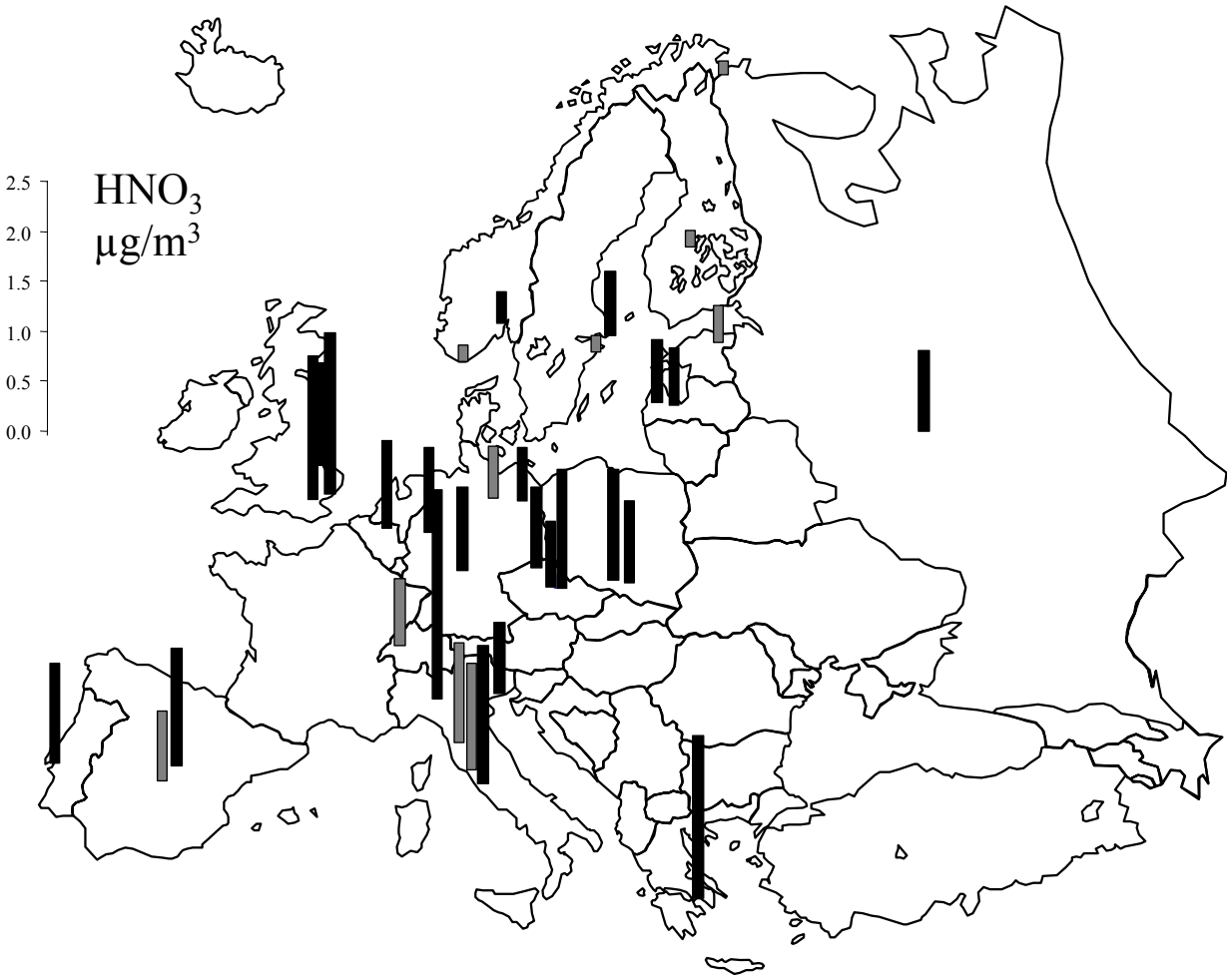

Figure IV. Annual HNO_3 concentration (December 2002–November 2003) at the test sites. Grey and black bars indicate rural and urban stations, respectively

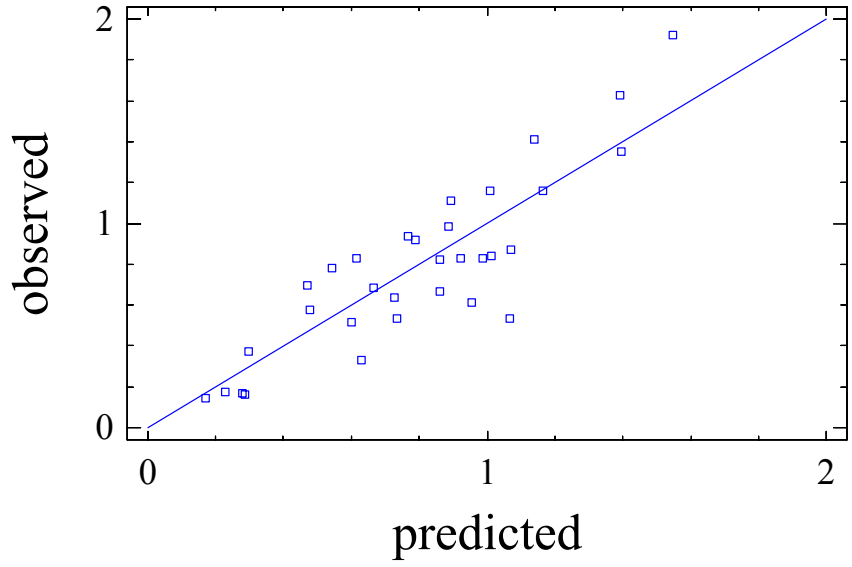

Figure V. Observed (vertical) and predicted (horizontal) HNO_3 concentrations (µg m^{-3}) based on equation 5

III. DOSE-RESPONSE FUNCTIONS OF SOILING

16. Particles can damage materials both by enhancing the rate of degradation and by soiling. A number of earlier studies examined the relationship between the concentration of particulate matter and the rate of soiling. The existing dose-response functions for soiling usually linked reflection measurements with measurements of particulate elemental carbon. Some initial empirical soiling rates were published as well as theoretically derived equations, but there was no consensus on a generally applicable rate. More recent studies have highlighted the importance of particulate material derived from traffic emissions, especially those from diesel fuel. It was clear that particulate material matter was much more complex than gaseous pollutants since their corrosion and soiling potential depended on the emission source. It was necessary to express the soiling as a function of the concentration of particles for policy related purposes such as mapping and cost calculations. PM_{10} was preferred as it was available from the EMEP monitoring network and it was also included in the European Communities Council Directive 1999/30/EC relating to limit values of air pollutants.

17. The soiling experiments were performed at ICP Materials sites, where passive samplers for particles were exposed, and at the targeted sites of the MULTI-ASSESS project in Athens, Rome, London, Prague and Krakow. The soiling rates of the following surrogate materials were recorded (table 1):

(a) White stone (Portland limestone) and painted steel representing real (white) materials used in cultural heritage objects;

(b) Ultraviolet radiation (UV) stable white plastic as an inert surface for soiling without corrosion reactions;

(c) A polycarbonate membrane mounted on UV-stable white plastic providing continuous soiling measurement of the material used in the passive samplers;

(d) Modern silica-lime floating glass as a soiling sensor for materials due to its transparency.

18. The reflectance results were analysed using various model approaches. Preliminary analyses gave dose-response functions for the first three materials:

$$\Delta R/R_0 = 1 - e^{-k\,CPM10\,t} \qquad (6)$$

where $\Delta R/R_0$ is the relative loss of reflectance (%), k is a soiling constant, C_{PM10} is the concentration of PM_{10} ($\mu g\ m^{-3}$) and t is the time.

19. The task of identifying an acceptable level of soiling relied on detailed knowledge of two factors:

(a) Public perception of what constitutes acceptable soiling. The recent EU project CARAMEL indicated that a 35% loss in reflectance triggers significant adverse public reaction;

(b) Assessment of the period of time for which the building could remain without cleaning and an economic evaluation of the maintenance options. For cultural heritage objects a period of 10–15 years was considered to be appropriate.

20. These factors together with the dose-response functions were used to estimate the maximum ambient air quality to which a building can be exposed before the level of soiling becomes unacceptable.

21. By inserting $\Delta R/R_0 = 0.35$, an acceptable level of soiling of 35%, into equation 6 allowed an evaluation of the relationship between critical levels of particulate matter ($C_{PM10,crit}$) and time (t_{crit}). A cleaning periodicity of 10–15 years was assumed. The critical level of PM_{10} for the first three materials resulted in a $C_{PM10,crit}$ of 12–22 $\mu g\ m^{-3}$. This is illustrated for limestone in figure VI.

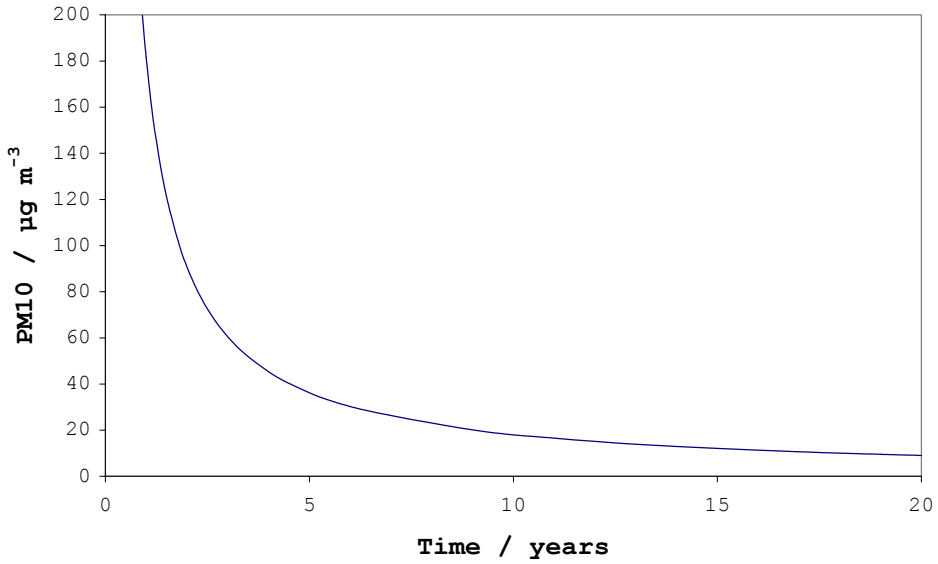

Figure VI. Critical PM_{10} concentration vs. exposure time based on equation 6 and an acceptable soiling level of 35%. The curve is calculated for limestone

IV. CONCLUSIONS

22. The multi-pollutant programme covered a wide range of materials including the effects of both corrosion and soiling together with an extensive environmental characterization of climate, gaseous pollutants, particulate matter and wet deposition.

23. Dose-response functions for corrosion were developed for carbon steel, zinc, copper, bronze and limestone. The pollutant parameters pH, SO_2, O_3, HNO_3 and PM deposition were included. The equations described the corrosion effects on materials in a multi-pollutant situation.

24. A relationship was established between PM deposition and PM_{10} concentrations that enabled mapping of areas with increased risk to corrosion due to particulate matter.

25. A relationship was established between HNO_3 concentrations and NO_2, O_3, relative humidity and temperature that enabled mapping of areas with increased risk to corrosion due to HNO_3.

26. Dose-response functions for soiling were developed for limestone and plastic materials that enable the quantification of acceptable soiling levels as a function of exposure time and PM_{10} concentration.