Dose-resp onse Functions as a Basis for Assessment of Acceptable Levels

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Air pollutants in combination with climatic parameters accelerate the corrosion and deterioration of many materials. Dose-response functions separating the effects of dry and wet deposited pollutants have been developed within the UN ECE Convention on Long-range Transboundary Air Pollution. These functions can be used for assessment of acceptable pollution levels, for mapping of areas with elevated rates of corrosion and for cost-benefit analysis at different pollution scenarios. The ultimate goal is to apply dose-response for derivation of threshold pollution levels for materials in the multipollutant situation and to include them in the EC Air Quality Directives for protection of areas with important objects of European cultural heritage.

Les polluants de l´air en combinaison avec des paramètres climatiques accélèrent la corrosion et la dégradation de beaucoup de matériaux. Des fonctions dose-réponse séparant les effets des polluants des depôts secs et humides ont été developées dans le cadre de la Convention UN ECE sur de la pollution atmosphérique transfrontière à longue distance. Ces fonctions peuvent être utilisées pour la prédiction de seuils acceptables, pour la détermination de zones à corrosion elevée et pour l´analyse des coûts associés à la pollution atmosphérique. Le but final est d´appliquer les fonctions dose-reponse à la définition de limites de pollution acceptable pour les materiaux dans le cadre d´une situation multi-polluants; ceci afin de les inclurent dans les directives de la qualité de l´air de la Commission européenne pour la protection de zones comportant un grand nombre d´objets figurant au patrimoine culturel européen.

Air pollutants emitted at combustion of fossil fuels have since a long time been acknowledged as responsible for increased atmospheric corrosion of several metallic and non-metallic materials. An important task in the preservation of the European cultural heritage is the quantification of the effects of air pollutants. This knowledge is essential for the efforts to reach a balance between costs and benefits in the strategies for reduction of pollution. In this process the dose-response (DR) functions play a central role. This presentation will illustrate how the DR functions are obtained and how they can be used, based primarily on the activity of the UN ECE International co-operative programme on effects on materials (ICP Materials) within the Convention on Long-Range Transboundary Air Pollution.

1. Effect of pollutants in the multi-pollutant situation

The decreasing sulphur dioxide levels in most parts of Europe and the increasing car traffic causing elevated levels of nitrogen compounds, ozone and particulates has created a new multi-pollutant situation. This has been acknowledged i.a. in the activities within the UN ECE Convention on long-range transboundary air pollution (CLRTAP), where a multi-pollutant, multi-effect protocol has recently been adopted. This changed pollution situation must be taken into account in the development of an improved model for the effects of pollutants on the deterioration of important material groups.

There are many parameters that can influence the damage to materials in the atmosphere, it is an interplay between chemical, physical and biological parameters. This presentation will focus on the aspects specific to the urban situation, i.e., man-made pollutants and their interplay with natural climatic factors. It is, however, important to recognise that corrosion is a process that occurs even in the absence of pollutants and it is important to quantify to which extent urban conditions affects and accelerates the ”natural” or background corrosion of materials.

Sulphur and nitrogen compounds including secondary pollutants and particulates are the most important pollutants acting as corrosive agents. Systematic laboratory exposures in the 1930’s demonstrated the corrosive effect of SO_2 on metals. This was later also proved by field exposures and SO_2 was for a long time considered to be the main corrosive pollutant.

In the last decade a synergistic corrosive effect of sulphur dioxide and nitrogen dioxide and later also of sulphur dioxide and ozone has been discovered. With decreasing levels, SO_2 is no longer regarded as the only important corrosion stimulator. Instead, its effect in combination with other gaseous pollutants such as NO_2, O_3, and their reaction products needs to be considered. A multi-pollutant situation has arisen where also two other pollutants deserve special attention, nitric acid and particles. They are both potentially harmful to materials used in objects of cultural heritage and they are both less studied than other pollutants in the field of atmospheric corrosion.

In contrast to SO_2, the effects of O_3 and N compounds are not well documented and in particular the total effects of car traffic. This is especially true for nitric acid (HNO_3), a secondary pollutant formed by the oxidation of NO_2. HNO_3 can reach appreciable concentration levels in urban areas – reports usually are in the interval 1-7 $\mu g/m^3$ but in some cases the concentration can be above 10 $\mu g/m^3$. HNO_3 is a strong acid with a high deposition velocity that is relatively independent of the relative humidity, which makes it relatively more harmful for dry and warm climates. Another effect of HNO_3 formation is that acidity of precipitation is significantly increased. The magnitude of its effect relative to other pollutants such as SO_2 is so far not investigated for most materials.

Particles can damage materials both by enhancing the rate of degradation and by soiling. Anthropogenic particles can be divided into primary and secondary. The primary particles which are directly emitted from combustion, have a relatively short life span and deposit near the source. Secondary particles are smaller, less than two micrometers, long-lived, and are the result of chemical reactions amongst other pollutants i.a. SO_2, NO_2, volatile organic compounds and ammonia. The effect of particles on corrosion can be either direct or indirect. Particles containing NH_4NO_3, $(NH_4)_2SO_4$ and NH_4HSO_4 play an important role in atmospheric corrosion related to their ability to increase the time of wetness due to their hygroscopic properties. In addition to the prolonging of the time of wetness, ionic particles enhance the corrosion by providing or adsorbing corrosion stimulators. Particles may in some cases also decrease the corrosion rate if they are basic by neutralising the surface water film formed on the degraded material. Inert particles can reduce the active surface of the corroding material and individual particles may initiate nucleation of corrosion products.

2. Quantification of effects – dose-response functions

A DR function is an equation which express the corrosion attack as a function of environmental parameters. For unsheltered positions the materials damage is usually discussed in terms of dry and wet deposition. Wet deposition includes transport by means of precipitation and dry deposition transport by any other process. One important task is to estimate the relative contribution of dry and wet deposition to the degradation of materials. Therefore, and also because it makes sense from a mechanistic point of view, DR functions have been developed where the corrosion attack, K, is described in terms of dry and wet deposition effects separated as additive terms

$$K = K_{dry}(SO_2, NO_2, O_3, Rh, T) + K_{wet}(Rain, H^+)$$

The dry deposition term is presently quantified in terms of the parameters SO_2, NO_2, O_3, relative humidity and temperature whereas the wet deposition in terms of total amount of precipitation and precipitation acidity.

3. UN ECE ICP Materials

ICP Materials is one of several effect oriented International Co-operative Programmes (ICPs) within the United Nations Economic Commission for Europe (UN ECE). Early in the discussions on the Convention on Long-range Transboundary Air Pollution (CLRTAP) it was recognised that a good understanding of the harmful effects of air pollution was a prerequisite for reaching agreement on effective pollution control. Consequently an extensive field exposure programme was started in September 1987. It involved 39 exposure sites in 12 European countries and in the United States and Canada. A task Force is organising the programme (ICP Materials) with Sweden as lead country and the Swedish Corrosion Institute serving as the main research centre. Sub-centres in the Czech Republic, Germany, Norway, United Kingdom, Sweden and Austria have been responsible for evaluation of individual groups of materials including structural metals, stone materials, paint coatings, electric contact materials, glass and polymer materials. The aim of the programme was to perform a quantitative evaluation of the effects of sulphur pollutants in combination with NO_x and other pollutants as well as climatic parameters on the atmospheric corrosion of important materials. This was achieved by measuring gaseous pollutants, precipitation and climatic parameters at or nearby each test site and by evaluating the corrosion effects on the materials. ICP Materials is an on-going research activity. A finalised part, however, is the extensive 8-year field exposure programme that was started in September 1987 and the results presented here are based on this 8-year programme. For further details on this programme see ref. 1.

4. Dose-response functions for unsheltered materials

A list of all dose-response functions obtained within ICP Materials, including temperature functions, for exposure of unsheltered materials is given in Tab. 1. A detailed discussion on the individual groups of materials can be found elsewhere (2). In addition functions have been obtained for weathering steel, zinc, copper, bronze, nickel, tin and glass M1 representative of medieval stained glass windows exposed in sheltered positions (1).

Table 1. List of dose-response functions, including temperature function, for unsheltered materials. The corrosion attack is expressed as mass loss (ML in g m^{-2}) for metals, surface recession (R in µm) for stone materials, ASTM D 1150-55 rankings (1 to 10 where 10 means a fresh sample and 1 a completely degraded) for paint coatings or depth of leached layer (LL in nm) for glass. The environmental parameters included are expressed as annual mean averages and are time in years (t), temperature in °C (T), relative humidity in % (Rh), SO_2, NO_2 and O_3 concentration in µg m^{-3}, amount of precipitation in mm (Rain) and H^+ and Cl^- concentration of precipitation in mg l^{-1}.

Material N = number of observations R^2 = explained variability	Dose-response function Temperature function
Weathering steel (N=148, R^2=0.68)	$ML = 34[SO_2]^{0.33}\exp\{0.020Rh + f_{Ws}(T)\}t^{0.33}$ $f_{Ws}(T) = 0.059(T-10)$ when $T \leq 10°C$, $-0.036(T-10)$ otherwise
Zinc (N=98, R^2=0.84)	$ML = 1.4[SO_2]^{0.22}\exp\{0.018Rh + f_{Zn}(T)\}t^{0.85} + 0.029Rain[H^+]t$ $f_{Zn}(T) = 0.062(T-10)$ when $T \leq 10°C$, $-0.021(T-10)$ otherwise
Aluminium (N=106, R^2=0.74)	$ML = 0.0021[SO_2]^{0.23}Rh \cdot \exp\{f_{Al}(T)\}t^{1.2} + 0.000023Rain[Cl^-]t$ $f_{Al}(T) = 0.031(T-10)$ when $T \leq 10°C$, $-0.061(T-10)$ otherwise
Copper (N=95, R^2=0.73)	$ML = 0.0027[SO_2]^{0.32}[O_3]^{0.79}Rh \cdot \exp\{f_{Cu}(T)\}t^{0.78} + 0.050Rain[H^+]t^{0.89}$ $f_{Cu}(T) = 0.083(T-10)$ when $T \leq 10°C$, $-0.032(T-10)$ otherwise
Cast Bronze (N=144, R^2=0.81)	$ML = 0.026[SO_2]^{0.44}Rh \cdot \exp\{f_{Br}(T)\}t^{0.86} + 0.029Rain[H^+]t^{0.76} + 0.00043Rain[Cl^-]t^{0.76}$ $f_{Br}(T) = 0.060(T-11)$ when $T \leq 11°C$, $-0.067(T-11)$ otherwise
Portland limestone (N=100, R^2=0.88)	$R = 2.7[SO_2]^{0.48}\exp\{f_{Pl}(T)\}t^{0.96} + 0.019Rain[H^+]t^{0.96}$ $f_{Pl}(T) = -0.018T$
White Mansfield sandstone (N=101, R^2=0.86)	$R = 2.0[SO_2]^{0.52}\exp\{f_{Ms}(T)\}t^{0.91} + 0.028Rain[H^+]t^{0.91}$ $f_{Ms}(T) = 0$ when $T \leq 10°C$, $-0.013(T-10)$ otherwise
Coil coated galvanised steel with alkyd melamine (N=138, R^2=0.73)	$(10-ASTM) = (0.0084[SO_2] + 0.015Rh + f_{Cc}(T))t^{0.43} + 0.00082Rain \cdot t^{0.43}$ $f_{Cc}(T) = 0.040(T-10)$ when $T \leq 10°C$, $-0.064(T-10)$ otherwise
Steel panels with alkyd (N=139, R^2=0.68)	$(10-ASTM) = (0.033[SO_2] + 0.013Rh + f_{Sp}(T))t^{0.41} + 0.0013Rain[H^+]t^{0.41}$ $f_{Sp}(T) = 0.015(T-11)$ when $T \leq 11°C$, $-0.15(T-11)$ otherwise
Glass M1 representative of medieval stained glass windows (N=46, R^2=0.56)	$LL = 0.013[SO_2]^{0.49}Rh^{2.8}t$

5. Use of dose-response functions

The ICP Materials dose-response functions are at present the best available functions to apply for mapping procedures and for calculation of costs of damage on both national and European scales. Mapping of corrosion attack and of exceedances of acceptable levels at a national scale is possible using environmental parameters obtained from national and international meteorological centres, international organisations (e.g. WHO), international research and monitoring programmes (e.g. EMEP) or national organisations or authorities responsible for environmental protection. This has already been carried out at scales varying between 50 km and 1 km squares. The mapping procedure can be an important tool for identifying areas with elevated risk of corrosion and for selection of materials to be used in a particular area. Stock-at-risk data are an essential part of any estimate of the extent of damage to materials and the associated costs, and the potential benefits of pollution abatement. In the future, effort needs to be concentrated on the collection of data on the geographical distribution and quantity (stock) of the materials at risk which applies especially for objects of cultural heritage.

6. Acceptable levels of pollution

Atmospheric corrosion and deterioration of materials is a cumulative, irreversible process which proceeds even in the absence of pollutants. The critical loads/level approach used for the effects of acid deposition on ecosystems has to be modified in relation to degradation of materials as even the lowest concentration of pollutants causes an increase in the deterioration rate. This leads to the well-established concept of acceptable corrosion rates and pollution levels defined in the UN ECE Convention on Long-Range Transboundary Air Pollution report “Manual on methodologies for mapping critical loads/levels” (3).

The acceptable corrosion rate is determined by technical and economic considerations based on the specific application of a material. For model calculations, however, and for the purpose of comparing different materials with respect to their pollution sensitivity, different levels of acceptance can be defined by relating the corrosion rate to corrosion rates in areas with ‘background’ pollution. It has proven to be useful to define a dimensionless number, n

$$n = K_{acc} / K_b$$

where K_{acc} is the acceptable corrosion rate and K_b is the background corrosion rate. The use of a specified acceptable corrosion rate in the dose-response function implicitly describes an acceptable (acc) multi-pollutant situation

$$K_{acc} = K_{dry}(SO_{2,acc}, NO_{2,acc}, O_{3,acc}, Rh, T) + K_{wet}(Rain, H^{+}_{acc})$$

It is possible to reach an acceptable situation from an unacceptable in several ways and there is, consequently, not possible to derive threshold levels directly and uniquely. It is, however, possible to assess different *scenarios* based on reasonable assumptions and to analyse the results of the assessments together with a sensitivity analysis in order to propose reasonable threshold levels for most important pollutants for special areas containing objects of cultural heritage, taking into account existing directives for threshold levels in general. For example, consider the equation for copper given previously. If an acceptable ML value is specified and it is assumed that O_3 and pH levels will be constant, then it is possible to calculate an acceptable SO_2 level as

$$[SO_2]_{acc} = [\ (ML - 0.050Rain[H^{+}]t^{0.89})/(0.0027[O_3]^{0.79}Rh \cdot \exp\{f(T)\}t^{0.78})\ ]^{1/0.32}$$

In this way the synergistic effect of SO_2 and O_3 can be assessed in the multipollutant situation. The acceptable levels of SO2 for some materials and n values using this concept are given in Tab.2.

Table 2. Acceptable levels of SO_2 in μg/m^3 calculated from UN ECE ICP Materials dose-response functions

	n = 1.5	**n = 2.0**
Weathering steel	5	45
Zinc	12	49
Aluminium	10	39
Copper	7	33
Bronze	5	12
Limestone	7	12

7. Present state and need for future action

The development of dose-response relations, which quantify the effects of pollutants in combination with climatic parameters on the deterioration and soiling of different materials in the multipollutant situation, constitutes a necessary condition for prediction of damage and for establishment of threshold levels. The results of this highly innovative research which is performed as a combined effort of the UN ECE LRTAP Convention and the research activities within EU 5FP are planed to be fed into air quality policy for the next decades. A comparison of threshold pollution levels for human health and for ecosystems in the EU Air Quality Directive, see Tab.3, with the accepted pollution levels for materials shows that materials are more sensitive to air pollution than people, animals and vegetation. This highlights the need to obtain well-established pollution thresholds for effects on materials and to incorporate them into the EU Directives on urban air quality. This would be an efficient tool for authorities, organisations and individuals responsible for the care of cultural heritage in the efforts to preserve objects of cultural heritage and to reduce the cost for maintenance. It could be mentioned in this connection that steps in this direction have already been taken in individual member countries as illustrated by the environmental targets for pollution levels in Sweden, Tab.4.

Table 3. Limit values of pollutants, μg/m^3, in Air Quality Directive 99/30/EC (4).

	SO_2	NO_2	PM10
Urban zones - health effects			
Hourly limit value	350	200	
Daily limit value	125		50
Annual limit value		40	40
Rural areas - ecosystems			
Annual limit value	20	30	

Table 4. Environmental targets for pollution levels in Sweden (5).

Pollutant	Target concentration annual value, μg/m^3	Implementation date
Gases		
NO_2	20	2010
SO_2	5	2005
O_3	50*	2020
Particulates		
PM 10 (health)	15	2020
Soot (materials)	10	2020

* March to October

8. Conclusions

The following main conclusions can be listed:

- UN ECE dose-response functions permit the quantification and separation of the effect of dry and wet deposition of pollutants. They include primarily the SO2 levels and rain acidity, which have the dominating pollutants in the past.
- The research is now directed to development of dose-response functions describing the multipollutant situation with decreasing levels of SO_2, taking into account synergistic effects with NO_2 and O_3 and including the effect of particulates and HNO_3.
- The dose-response functions developed are suitable for mapping, for cost-benefit analysis and for planning of abatement strategies using the concept of acceptable levels of corrosion attack and of pollution levels.
- One of the ultimate goals is the inclusion of threshold pollution for materials for protection of important objects of cultural heritage in the EC Air Quality Directives, which would greatly strengthen the efforts to safeguard the European cultural heritage.

9. References

[1] Tidblad J., Kucera V. and Mikhailov A. A., 1997: Report No 30. Statistical analysis of 8 year materials exposure and acceptable deterioration and pollution levels. Swedish Corrosion Institute, Stockholm, Sweden.

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[3] Mapping Manual, 2001: Manual on methodologies and criteria for mapping critical levels/loads and geographical areas where they are exceeded, UN ECE Convention on Long-range Transboundary Air Pollution, International Co-operative Programme on Modelling and Mapping, URL: www.icpmapping.com.

[4] Council Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air, Official Journal L 163, 29/06/1999 P. 0041 – 0060.

[5] Objectives and targets for the Swedish Environment, 2000: Swedish Environmental Protection Agency, Report 5046, Stockholm, Sweden.

Speakers biography

Graduated in 1960 at the Chemical-Technical University in Prague, where also obtained the Ph.D. degree in corrosion science in 1966. Spent a post-doc. year at the Royal Institute of Technology in Stockholm. Since 1969 at the Swedish Corrosion Institute as scientist, as director of research and since 1999 as deputy managing director. Special research interest in the field of atmospheric corrosion and effects of acidification on technical materials and objects of cultural heritage. Chairman of UN ECE ICP Materials since 1985, responsible for several international projects, co-ordinator and participant in projects and activities within EU DG Research and DG Environment. Organiser of national and international congresses and workshops. Author of numerous scientific and technical publications and reports.