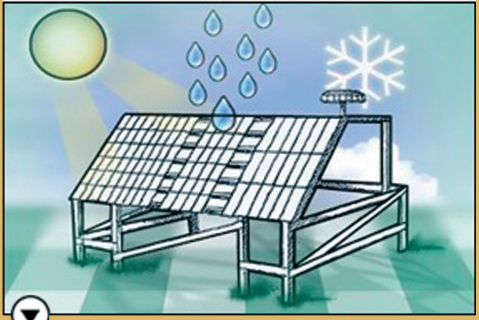
4 Mapping of Effects on Materials

Mapping Manual
2004

International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments



UNECE CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

ICP Materials is one of several effect oriented International Co-operative Programmes (ICPs) within the United Nations Economic Commission for Europe (UN ECE) and its Environment and Human Settlements Division.
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. To develop the necessary international co-operation in the research on and the monitoring of pollutant effects, the Working Group on Effects (WGE) was established under the Convention.
For further information about the ICP, see the home page www.corr-institute.se/ICP-Materials

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www.icpmapping.org

4.1 Introduction - objectives, definitions and general remarks

Atmospheric pollution is an important factor in material deterioration including degradation of systems used for material protection. Due to pollution, the lifetime of technological products is shortened. Buildings, other structures, as well as objects of cultural heritage exposed to the atmosphere deteriorate more rapidly. The resulting physico-chemical and economic damage can be significant - not to mention the loss of unique parts of our cultural heritage and hazards due to endangered reliability of complicated technological devices.

devices. Also, as the result of weathering due to especially acidifying pollutants, a significant part of the metals used in constructions and products are emitted to the biosphere with a potential hazard to the environment.

This part of the manual was revised in connection with the UNECE Workshop on Mapping Air Pollution Effects on Materials, Including Stock at Risk, held in Stockholm, Sweden on 14-16 June 2000 (UNECE 2000). The present revision has been performed by the UNECE ICP on Materials with support from ICP Modelling and Mapping, based on results obtained at evaluation of deterioration of materials after 8-year field exposure (Tidblad, Kucera, Mikhailov 1998) his chapter considers the corrosive effects of gaseous SO_2, NO_x, ozone and acid rainfall in combination with climatic parameters. It aims to define procedures for mapping "acceptable values" of pollutants for buildings and materials including cultural and historical monuments in an analogous way to the methods defined elsewhere for critical levels and loads for natural ecosystems.

Because atmospheric deterioration of materials is a cumulative, irreversible process, which proceeds even in the absence of pollutants, "critical" values are not as easily defined as for some natural ecosystems. Some rate of deterioration must be defined which may be considered "acceptable" based on technical and economic considerations. This approach provides the basis for mapping "acceptable areas" for corrosion and deriving areas where the acceptable pollution level/load is exceeded, in an analogous way to the maps produced for natural ecosystems.

Acceptable load/level. The "acceptable level or load" of pollutants for buildings and materials is the concentration or load which does not lead to an unacceptable increase in the rate of corrosion or deterioration.

Acceptable rate of corrosion or deterioration (K_a) may be defined as the corrosion, which is considered "acceptable" based on technical and economic considerations. In reality this may not be considered practical. Therefore, it is recommended that the acceptable corrosion rate should be expressed in terms of average corrosion rates in areas with "background" pollution. Within the UNECE ICP on Materials it was decided to recommend the background corrosion or deterioration rate (K_b) as the lower 10 percentile of the observed corrosion rates in the materials exposure programme which started in 1987 and ended in 1995. Acceptable corrosion rates are then defined as a multiple (n) of the background corrosion rate

(4.1)

$$K_a = n \cdot K_b$$

It is possible to relate such rates of corrosion to the "lifetimes" or economic values of materials.

Dose-response function. The relationship between the corrosion or deterioration rate and the levels or loads of pollutants in combination with climatic parameters.

Using the above definitions it is possible to calculate the acceptable pollution level from the acceptable corrosion rate and a dose-response function which relates corrosion rate to pollutant and climate exposure.

4.2 Mapping “acceptable corrosion rates” and “acceptable levels/loads” for pollutants

4.2.1 Introduction

Deterioration rates can be calculated using dose-response functions. The functions recommended have been derived from the field research programme undertaken as part of the UNECE ICP Materials Exposure Programme. However, if other functions of the same or of other form are considered more suitable, then they can be used as an alternative. The range of values over which the dose-response function is considered valid must be considered. At this time, scientific evidence from field exposure is limited, in contrary to laboratory experiments. Even if NO_x is not included in the dose-response functions included in this manual it may be included for some materials in the future.

The following equations are based on 8-year results from the exposure within UNECE ICP on Materials. They reflect the increased level of the physico-chemical understanding of the corrosion mechanisms including the synergistic effects of SO_2 and O_3 in the case of copper. The calculation of an acceptable level for sulfur dioxide and ozone for materials where the synergistic effect with SO_2 is included in the dose-response function is described in 4.2.3.

The impact of wet deposition of acidic species on sensitive materials is in this revision of the Mapping Manual considered as an effect of the total load of H^+ deposition. The calculation and mapping of the acceptable load for materials where the H^+ load is included in the dose-response function is described in 4.2.3.

4.2.2 Dose-response functions

The equations for the following materials are at present available for mapping purposes. The equations are valid for unsheltered exposure of materials (Tidblad, Kucera, Mikhailov 1998, see also the ICP website: www.corrinstitute.se/ICPMaterials).

Structural metals	r^2	N	eq.
Weathering steel (C<0.12%, Mn 0.3-0.8%, Si 0.25-0.7%, P 0.07-0.15%, S<0.04%, Cr 0.5-1.2%, Ni 0.3-0.6%, Cu 0.3-0.55%, Al<0.01%)			
$ML = 34[SO_2]^{0.33}exp\{0.020Rh34[SO_2]^{0.13}exp\{0.020Rh + f(T)\}t^{0.33}$	0.68	148	(4.2)
f(T) = 0.059(T-10) when T≤10°C, otherwise -0.036(T-10)			
Zinc			
$ML = 1.4[SO_2]^{0.22}exp\{0.018Rh + f(T)\}t^{0.85} + 0.029Rain[H^+]t$	0.84	98	(4.3)
f(T) = 0.062(T-10) when T≤10°C, otherwise -0.021(T-10)			
Aluminium			
$ML = 0.0021[SO_2]^{0.23}Rh\cdot exp\{f(T)\}t^{1.2} + 0.000023Rain[Cl^-]t$	0.74	106	(4.4)
f(T) = 0.031(T-10) when T≤10°C, otherwise -0.061(T-10)			
Copper			
$ML = 0.0027[SO_2]^{0.32}[O_3]^{0.79}Rh\cdot exp\{f(T)\}t^{0.78} + 0.050Rain[H^+]t^{0.89}$	0.73	95	(4.5)
f(T) = 0.083(T-10) when T≤10°C, otherwise -0.032(T-10)			

Bronze (Cu Sn6Pb7Zn5, ISO/R 1338 (Cu 81%, Sn 5.8%, Pb 6.7%, Zn 4.5%, Ni 1.6% + trace elements)

$ML = 0.026[SO_2]^{0.44} Rh \cdot exp\{f(T)\} t^{0.86} + 0.029 Rain[H^+] t^{0.76}$

$+ 0.00043 Rain[Cl^-] t^{0.76}$ 0.81 144 (4.6)

f(T) = 0.060(T-11) when T≤11°C, otherwise -0.067(T-11)

Stone materials

Limestone

$R = 2.7[SO_2]^{0.48} exp\{-0.018T\} t^{0.96} + 0.019 Rain[H^+] t^{0.96}$ 0.88 100 (4.7)

Sandstone (White Mansfield dolomitic sandstone)

$R = 2.0[SO_2]^{0.52} exp\{f(T)\} t^{0.91} + 0.028 Rain[H^+] t^{0.91}$ 0.86 101 (4.8)

f(T) = 0 when T≤10°C, otherwise -0.013(T-10)

Paint coatings

Coil coated galv. steel with alkyd melamine

$L = [5 / (0.084[SO_2] + 0.015 Rh + f(T) + 0.00082 Rain)]^{1/0.43}$ 0.73 138 (4.9)

f(T) = 0.040(T-10) when T≤10°C, otherwise -0.064(T-10)

Steel panels with alkyd

$L = [5 / (0.033[SO_2] + 0.013 Rh + f(T) + 0.0013 Rain)]^{1/0.41}$ 0.68 139 (4.10)

f(T) = 0.015(T-11) when T≤11°C, otherwise -0.15(T-11)

where

ML = mass loss, $g\ m^{-2}$
R = surface recession, μm
t = exposure time, years
L = maintenance interval (life time), years
Rh = relative humidity, % - annual average
T = temperature, $°C$ - annual average
$[SO_2]$ = concentration, $\mu g\ m^{-3}$ - annual average
$[O_3]$ = concentration, $\mu g\ m^{-3}$ - annual average
$Rain$ = amount of precipitation, $m\ year^{-1}$ - annual average
$[H^+]$ = concentration, $mg\ l^{-1}$ - annual average
$[Cl^-]$ = concentration, $mg\ l^{-1}$ - annual average

The equations are valid for regions without strong influence of sea salts with a chloride content in precipitation < 5 $mg\ l^{-1}$ approx.

The functions for paint coatings are expressed as lifetime equations. These lifetimes can be mapped but the functions can not be used for calculating acceptable levels/loads using the concept of acceptable corrosion rates.

For all these materials, however, also equations for exposure in sheltered positions are available. Also equations are available for glass materials representative of medieval stained glass windows, for paint coatings and for the electric contact materials nickel and tin (Tidblad, Kucera, Mikhailov 1998).

The preferably recommended value of the background corrosion rate for individual materials is given in Table 4.1. In order to simplify the procedure of obtaining acceptable levels/loads as described in section 4.2.3 the rates in Table 4.1 are expressed for a 1-year exposure period. An analysis of the dose-response functions shows that using longer exposure periods than 1 year leads in principle to very similar acceptable levels/loads.

Table 4.1: Background corrosion rates K_b, expressed for a 1-year exposure period (1997-98), for different materials based on results from the UNECE ICP Materials exposure programme after 1, 2, 4 and 8 years of exposure.

Material	1-year background corrosion rate, K_b
Weathering steel	72 g m^{-2}
Zinc	3.3 g m^{-2}
Aluminium	0.09 g m^{-2}
Copper	3.0 g m^{-2}
Bronze	2.1 g m^{-2}
Limestone	3.2 µm
Sandstone	2.8 µm

4.2.3 Calculation and mapping of acceptable levels/loads and their exceedances

Mapping will produce a map which depicts the mapping units that exceed the acceptable deterioration rate (K_a) for simple samples of material used in particular locations expressed in a number of defined classes. It makes no correction for the form in which the material is used (e.g. the type of component). At present it is recommended that n values 1.5, 2.0 and 2.5 are used (see eq. 4.1). It should, however, be emphasised that lower n values can be used for, e.g. areas with valuable objects of cultural heritage.

The data requirements are annual mean SO_2 and O_3 concentrations in $\mu g\ m^{-3}$, the temperature in °C, the relative humidity in %, the total rainfall in mm $year^{-1}$, and the concentration of H^+ and Cl^- in mg/l for each mapping unit (e.g. the EMEP grid size 50 x 50 km or smaller, preferably as a fraction of the EMEP size). In addition, the value for the background corrosion rate is required. The values are then used to calculate the corrosion rate and the corrosion rate as a ratio of the background corrosion rate. All mapping units that exceed the acceptable corrosion rate $(n \cdot K_b)$ are then identified.

In each mapping unit that exceeds the acceptable corrosion rate, the same data sets and dose-response functions are then used to calculate the

- SO_2 concentration
- O_3 concentration (for copper)
- H^+ load

that keeps this rate at an acceptable level.

The equations have the following form, illustrated on the example of copper. For the other materials the equations for SO_2 concentration and H^+ load are created from the dose-response relations in an analogous way, except that O_3 is not included in the functions. The basis for the calculations should be one year of exposure $(t=1)$ since K_b is expressed for this period.

(4.11)

$$[SO_2]_{accCu} = [(3.0 \cdot n - 0.050Rain[H^+]) / (0.0027[O_3]^{0.79}Rh \cdot \exp\{f(T)\})]^{1/0.32}$$

(4.12)

$$[O_2]_{accCu}[O_3]_{accCu} = [(3.0 \cdot n - 0.050Rain[H^+]) / (0.0027[SO_2]^{0.32}Rh \cdot \exp\{f(T)\})]^{1/0.79}$$

(4.13)

$$(Rain[H^+])_{accCu} = (3.0 \cdot n - 0.0027[SO_2]^{0.32}[O_3]^{0.79}Rh \cdot \exp\{f(T)\}) / 0.050$$

where

$[SO_2]_{accCu}$ = acceptable concentration for corrosion of copper at given values of other parameters, $\mu g\ m^{-3}$

$[O_3]_{accCu}$ = acceptable concentration for corrosion of copper at given values of other parameters, $\mu g\ m^{-3}$

$Rain[H^+]_{accCu}$ = acceptable value of H^+ load for corrosion of copper at given values of other parameters (product of amount of precipitation, $mm\ year^{-1}$, and concentration of H^+, $mg\ l^{-1}$)

n = $\dfrac{\text{acceptable corrosion/deterioration rate (see eq. 4.1)}}{\text{background corrosion/deterioration rate}}$

and the other symbols as in point 4.2.2.

The values of the climatic and pollution data for each grid square can usually be obtained from national or international meteorological centres, international organisations e.g. (WHO), international research programmes (e.g. EMEP) or national organisations or authorities responsible for environmental protection.

When data on ozone concentrations are not available, but concentrations of NO_2 are known, a crude approximation of ozone values can be obtained using one of the following empirical equations, which are based on data from the UNECE ICP Materials Programme:

	r^2	n
(4.14)		
$[O_3] = 57 \cdot \exp\{-0.012[NO_2]\}$	0.70	103
(4.15)		
$[O_3] = (38 + 0.013Sun) \cdot \exp\{(-0.022+$ $-0.000005Sun)[NO_2]\}$	0.78	132

where

$[O_3]$ = average annual concentration, $\mu g\ m^{-3}$

$[NO_2]$ = average annual concentration, $\mu g\ m^{-3}$

Sun = sunshine duration, $h\ year^{-1}$

Eq. 4.14 is based on values from the five first years of exposure (1987-1992) while eq. 4.15 is based on values from all eight one-year exposure periods (1987-1995). Eq. 4.15 is preferred but 4.14 may be used if data on sunshine duration is not available. It should be stressed that the equations are empirical and obtained in the absence of a theory from which a relation between ozone and nitrogen dioxide concentrations could be derived. More importantly, the equations are based on a set of NO_x and ozone concentration data that include inner-city data. The latter are characterised by very high NO_x and low O_3 , which is a situation not found in rural/remote areas that are of most interest for the other parts of the mapping programme and in the general framework of the Convention on Long-range Transboundary Air Pollution. If only those values typical for rural/remote areas were used, a different relationship between O_3 and NO_x would emerge. Note that, according to eq. 4.14, a long-term average ozone concentration larger than 57 $\mu g\ m^{-3}$ would not be possible; however, this is a relatively low value in rural/remote areas.

4.2.4 Calculations and mapping of costs resulting from corrosion

The ultimate goal of the mapping activities in the field of materials is the calculation of cost of damage caused by air pollutants to materials. While it is not recommended to assess the absolute cost, it is possible to estimate the difference in cost between two alternative scenarios using the equation

(4.16)

$$\Delta C = C \cdot S \cdot (L_{s1}^{-1} - L_{s2}^{-1})$$

where ΔC is the cost difference, C is the cost per surface area of material, for maintenance/replacement, S is the surface area of material, L_pL_{s1} is the maintenance interval (life time) in polluted areas and L_c for scenario 1 and L_{s2} is the maintenance interval for scenario 2. If eq. 4.16 is to be used for estimating the cost of corrosion due to pollutants in the present situation it is in clean areas. recommended to use the present pollution situation as scenario 1 and the background corrosion as scenario 2. When calculating the lifetime from the background scenario it is recommended to use the time dependence from the dry deposition term given in eqs. 4.2 - 4.8, for example $t^{0.85}$ for zinc. For the paint coatings it is not recommended to use eqs. 4.9 - 4.10 for cost calculations since the evaluation are based on damage from an intentionally made scratch, which may be regarded as a form of accelerated testing.

Instead the practical functions described in Kucera et al. (1993) are recommended.

A UNECE Workshop on economic evaluation of air pollution abatement and damage to buildings including cultural heritage took place in Stockholm on 23-25 January 1996 (UNECE 1997). The proceedings of the workshop summarised the state of the art, and is given in the reference list together with a selection of other important publications (Kucera et al. 1993, ECOTEC 1986, Tolstoy et al. 1989, Cowell, Apsimon 1996). In the ECOTEC study of 1986, building identikits for Birmingham (UK), Dortmund and Koeln (Germany) were compiled (ECOTEC 1986). For Stockholm (Sweden), Sarpsborg (Norway), and Prague (Czech Republic) statistically based inventories of outdoor material surfaces were compiled by Kucera et al. (1993). These studies include percentage values of the most common construction materials and their distribution, which in absence of stock at risk data may provisionally be used as default values.

Mapping of cost of damage will be similar to mapping of acceptable levels/loads but will include data on the stock of material in each mapping unit and the economic costs associated with deterioration of these materials (e.g. replacement or repair costs). The classes to be used are based on multiples of the Background Deterioration Rate. The change in the rate of deterioration can be used to estimate the cost associated with the deterioration. This can be used to estimate the costs resulting from the deterioration and to undertake a cost benefit analysis of pollutant emission reduction scenarios in the mapping area.

In addition to the data required for mapping acceptable levels/loads estimates of the total area of the respective building material in each mapping unit and the cost for replacement and/or maintenance of the material is required.

4.2.5 Sources of uncertainty

The main sources of uncertainty will result from

- use of yearly mean values of pollution parameters which do not take into account the effect of fluctuations of pollutant levels,
- use of dose-response functions, which may be further developed i.a. after the evaluation of results of the ongoing “multi-pollutant” exposure in ICP Materials,
- assessment of environmental data and their extrapolation to each mapping square taking into account the importance of the difference in local environment in populated and rural areas,
- translation of dose-response functions obtained by exposure of test specimens to damage functions taking into account the exposure situation on a construction and rational maintenance practice.
- assessment of the stock of materials at risk,
- characterisation of reduced service lifetime, and
- quantification of costs associated with reduced service lifetime.

4.3 Direct effects of ozone

The effect of ozone on corrosion of materials is complex and there are today serious gaps of knowledge. Both ozone and NO_2 have a direct effect on corrosion and degradation of especially some organic materials. In recent years the synergistic effect of SO_2 in combination with O_3 and NO_2 has been shown to lead to severely increased corrosion on several inorganic materials in laboratory exposures. In field exposures so far only the synergistic effect of SO_2 and O_3 has been shown in the UNECE exposure programme.

Recent studies of historical ozone measurements indicate that background tropospheric ozone concentrations over Europe have approximately doubled since the end of the 19th century. This change is due to increased emissions of precursor compounds from human activities in form of NO_x and VOC (volatile organic compounds). In urban areas the ozone concentrations are suppressed due to local emissions of NO_x primarily from motor vehicle exhausts. Motor vehicle emission controls will serve to reduce local emissions of NO_x and as a consequence ozone concentrations in urban areas will increase. Over the last decade the background ozone concentrations have increased by up to a few percent per year over northern and central Europe and are at present approximately 30 ppb. For sensitive organic materials exposed to outdoor atmospheres an acceptable level for ozone is proposed to be 20 ppb as an annual mean. It may provisionally represent a acceptable above which unacceptable shortening of the material lifetime will result. It should, however, be emphasised that for protection of sensitive organic materials in e.g. museums, galleries and archives much lower levels for ozone are recommended.

4.4 Data and mapping procedure

Any user who are considering to produce maps on effect of materials based on procedures specified in this chapter should also consult the general chapters of this manual, Chapter 1 Introduction and, especially, Chapter 2 Guidance on Mapping Concentration Levels and Deposition Loads. In chapter 2 the general methods of mapping, their underlying assumptions and data requirements are given for many of the parameters needed for mapping effects on materials. Regarding the wet deposition parameters it should be noted that the term $Rain[Cl^-]$ given in this chapter is identical to the chloride wet deposition parameter described in chapter 2. Deposition of protones $(Rain[H^+])$ is not mentioned explicitly in chapter 2 but it should be noted that the recommendation that maps of annual wet deposition should not be drawn by interpolating measured wet deposition but instead by combining maps of interpolated solute concentrations and precipitation amounts separately is vialid also for H^+.

For materials damage the following types of maps are recommended. For recommended n values see 4.2.3.

Assisting maps

These maps illustrates the geographical distribution of some of the most important environmental parameters and their combinations used in the dose-response functions:

- $[SO_2]$
- $[O_3]$
- T
- Rh
- $Rain$
- pH
- Cl^-
- $Rain[H^+]$

Material damage maps (for each selected material)

Maps for present value of corrosion effects (based on dose-response functions):

- Exceedance of acceptable corrosion rate quantifying the degree of exceedance in classes $K_a/(n \cdot K_b)$, preferably for n = 1.5, 2.0 and 2.5.
- Contribution of wet deposition to the total corrosion effect or ratio between corrosion effect of wet and dry deposition

Maps for different scenarios:

- Comparison between present corrosion rate with the rate at different levels of $[SO_2]$, $[O_3]$ and $[H^+]$

Acceptable pollution levels/loads maps (for each selected material)

- Acceptable SO_2 levels for present level of $[O_3]$ and $[H^+]$
- Acceptable O_3 levels for copper for present level of $[SO_2]$ and $[H^+]$
- Acceptable H^+ loads for present level of $[SO_2]$ and $[O_3]$

Maps for different scenarios:

- Acceptable SO_2, O_3 (for copper) levels or H^+ loads for different levels/loads of the two other pollutant parameters.

4.4.1 Data and scale of mapping

It is recommended that countries make use of best available data and generate information at appropriate national scales. These data when incorporated into European maps will be mapped for EMEP grid areas (50 km currently). It is thus advisable to use a grid network which coincide with the EMEP network or if smaller (which is preferable) is a fraction of the EMEP size.

4.4.2 Urban and rural areas

It is recognised that urban areas differ from rural especially in levels of pollutants. Also relevant climatic data as temperature and relative humidity may show variations between urban and rural areas. Having in mind that corrosion of materials is affected both by long-range transported pollutants and by more local emissions it is advisable to produce maps with considerably smaller grids especially for mapping of effects in urban areas.

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