

4 Mapping of Effects on Materials

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4.1 Introduction

4.1.1 Aims

Atmospheric pollution is an important factor in material deterioration including the degradation of systems used for material protection and of cultural heritage materials. Due to pollution, the lifetime of technological products is shortened. Buildings and other structures, as well as objects of cultural heritage that are exposed to the atmosphere deteriorate more rapidly. The resulting physicochemical and economic damage can be significant - not to mention the loss of unique parts of our cultural heritage and the hazards due to compromised reliability of complicated technological devices. Therefore, as a result of weathering, in particular due to acidifying pollutants, a significant part of metals used in constructions and products are emitted to the biosphere with a potential hazard to the environment. Last, air pollution induces the soiling of glass and other materials (stone, coatings, painted surfaces etc.) that requires either a frequent potentially expensive cleaning, or maintenance operations.

This part of the Manual provides methods used to assess the impact of atmospheric pollution on materials in terms of corrosion and soiling. These methods are based on studies carried out by ICP Materials since 1987. The approach initially proposed was based on results obtained after an 8-year field exposure (1987-1995, Tidblad et al., 2001). It was revised in 2005, following a multi-pollutant exposure programme (1997-2003, Kucera et al., 2007). Since then, a series of trend exposures each third year including several materials for the evaluation of soiling effects have been performed and these new results together with practical experiences in mapping areas of increased risk of corrosion has led to the present update, which mainly consist of new functions for soiling (4.2.3) and how they should be used for mapping (4.4) (2021).

This chapter considers the corrosive and soiling effects of gaseous SO₂, NO_x, O₃, HNO₃, particulate matter and acid rainfall in combination with climatic parameters. The chapter also aims to define procedures for mapping values of pollutants acceptable for buildings and materials and tolerable values for cultural and historical monuments in an analogous way to the methods defined elsewhere for critical levels and loads for natural ecosystems.

4.1.2 Definitions

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 as "acceptable" or "tolerable", based on technical, economic and social 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. The term "acceptable" is reserved for materials

used in technical constructions while “tolerable” is used in connection with degradation of cultural heritage. Thus, in the following, “acceptable” can be replaced by “tolerable” when considering cultural heritage specifically.

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 may be defined as the corrosion, which is considered "acceptable" based on technical and economic considerations and is in principle material and application dependent. For the purpose of development or assessment of policies within the LRTAP Convention, the concept can, however, be simplified (see 4.3.3 below).

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 by using a dose-response function that relates corrosion rate to pollutant and climate exposure.

4.2 Dose-response functions

4.2.1 Introduction

Deterioration rates can be calculated using dose-response functions. The functions recommended have been derived from the field research programmes undertaken as part of the UN ECE ICP Materials Exposure Programmes and are developed primarily by taking into account the need of the LRTAP Convention to quantify effects of pollution. However, if other functions of the same or of other form are considered more suitable, then they can be used as an alternative.

This could for example, be in particular areas where pollution is not considered the main cause of corrosion. In any case, the range of values over which the dose-response function is derived must be considered. Two sets of dose-response functions described in the following have been derived, functions for the SO₂ dominating situation and functions for the multi-pollutant situation. For glass soiling, only the multi-pollutant situation was considered.

4.2.2 Dose-response functions for corrosion of materials

4.2.2.1 Dose-response functions for the SO₂ dominating situation

The following equations are based on 8-year results from an exposure carried out within ICP Materials (1987-1995). They reflect the increased level of the physico-chemical understanding of the corrosion mechanisms including the synergistic effects of SO₂ and O₃ in the case of copper. The equations are valid for unsheltered exposure of materials (Tidblad et al., 2001), and r² denotes the explained variability and N the number of observations used in the statistical analysis.

Structural metals

r² N

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%)

$$ML = 34[SO_2]^{0.13} e^{\{0.020Rh+f(T)\}t^{0.33}} \quad 0.68 \quad 148 \quad (4.1)$$

f(T) = 0.059(T-10) when T≤10°C, otherwise -0.036(T-10)

Zinc

$$ML = 1.4[SO_2]^{0.22} e^{\{0.018Rh+f(T)\}t^{0.85}} + 0.029Rain[H^+]t \quad 0.84 \quad 98 \quad (4.2)$$

f(T) = 0.062(T-10) when T≤10°C, otherwise -0.021(T-10)

Aluminium

$$ML = 0.0021[SO_2]^{0.23} Rh \cdot e^{\{f(T)\}t^{1.2}} + 0.000023Rain[Cl^-]t \quad 0.74 \quad 106 \quad (4.3)$$

f(T) = 0.031(T-10) when T≤10°C, otherwise -0.061(T-10)

Copper

$$ML = 0.0027[SO_2]^{0.32}[O_3]^{0.79} Rh \cdot e^{\{f(T)\}t^{0.78}} + 0.050Rain[H^+]t^{0.89} \quad 0.73 \quad 95 \quad (4.4)$$

f(T) = 0.083(T-10) when T≤10°C, otherwise -0.032(T-10)

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

$$ML = 0.026[SO_2]^{0.44}Rh \cdot e^{\{f(T)\}t^{0.86}} + 0.029Rain[H^+]t^{0.76} + 0.00043Rain[Cl^-]t^{0.76} \quad 0.81 \quad 144 \quad (4.5)$$

$f(T) = 0.060(T-11)$ when $T \leq 11^\circ\text{C}$, otherwise $-0.067(T-11)$

Stone materials

Limestone

$$R = 2.7[SO_2]^{0.48}e^{\{-0.018T\}t^{0.96}} + 0.019Rain[H^+]t^{0.96} \quad 0.88 \quad 100 \quad (4.6)$$

Sandstone (White Mansfield dolomitic sandstone)

$$R = 2.0[SO_2]^{0.52}e^{\{f(T)\}t^{0.91}} + 0.028Rain[H^+]t^{0.91} \quad 0.86 \quad 101 \quad (4.7)$$

$f(T) = 0$ when $T \leq 10^\circ\text{C}$, otherwise $-0.013(T-10)$

Paint coatings

Coil coated galvanised steel with alkyd melamine

$$L = \left[\frac{5}{0.084[SO_2] + 0.015Rh + f(T) + 0.00082Rain} \right]^{1/0.43} \quad 0.73 \quad 138 \quad (4.8)$$

$f(T) = 0.040(T-10)$ when $T \leq 10^\circ\text{C}$, otherwise $-0.064(T-10)$

Steel panels with alkyd

$$L = \left[\frac{5}{0.033[SO_2] + 0.013Rh + f(T) + 0.0013Rain} \right]^{1/0.41} \quad 0.68 \quad 139 \quad (4.9)$$

$f(T) = 0.015(T-11)$ when $T \leq 11^\circ\text{C}$, otherwise $-0.15(T-11)$

where

ML = mass loss, g m^{-2} , *NOTE: see section 4.2.2.3*

R = surface recession, μm

t = exposure time, years

L = maintenance interval (lifetime), years

Rh = relative humidity, % - annual average

T = temperature, $^{\circ}\text{C}$ - annual average

$[SO_2]$ = concentration, $\mu\text{g m}^{-3}$ - annual average

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

$Rain$ = amount of precipitation, mm year^{-1} - annual average

$[H^+]$ = concentration, mg l^{-1} - annual average

$[Cl^-]$ = concentration, mg l^{-1} - annual average

NOTE: the unit for $[H^+]$ is not the normal one (M) used for this denomination and the relation between pH and $[H^+]$ is therefore here $[H^+] = 1007.97 \cdot 10^{-pH} \approx 10^{3-pH}$

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

The functions for paint coatings are expressed as lifetime equations. These lifetimes can be mapped but the functions cannot at present be used for calculating acceptable levels using the concept of acceptable corrosion rates since tolerable lifetime has not yet been established for these materials.

For all these materials, and also electric contact materials and tin, data for exposure in sheltered positions are available but are of less general validity for mapping at the UNECE level since actual corrosion rates are highly dependent on the particular sheltering conditions.

4.2.2.2 Dose-response functions for the multi-pollutant situation

The following equations are based on 4-year results from the exposure within UN ECE ICP on Materials (1997-2001). These were complemented with environmental measurements of HNO_3 and particulate matter as a result from the extra effort connected to the MULTI-ASSESS project in 2002-2003. Later data of HNO_3 and particulate matter show no significant trend. They reflect the increased level of the physico-chemical understanding of the corrosion mechanisms including the effect SO_2 and acid rain for all materials, the effect of nitric acid for zinc and Portland limestone and the effect of particulate matter for carbon steel, cast bronze and Portland limestone. The functions were first derived with an inclusion of time as an independent variable, Kucera et al., 2007. However, discussions within the ICP Materials Task Force have concluded that the mapping of areas with increased risk of corrosion and calculation of acceptable levels of pollution

should be based on one-year exposure. Therefore, the functions are to be only over periods of one year. Time-dependent corrosion rates are necessary for the calculation and the mapping of costs caused by atmospheric corrosion. They are described below, in the cost section (4.4).

Carbon steel

$$R = 6.5 + 0.178[SO_2]^{0.6}Rh_{60}e^{f(T)} + 0.166Rain[H^+] + 0.076[PM_{10}] \quad (4.10)$$

$$f(T) = 0.15(T-10) \text{ when } T < 10^\circ\text{C}, \text{ otherwise } f(T) = -0.054(T-10)$$

Zinc

$$R = 0.49 + 0.066[SO_2]^{0.22}e^{0.018Rh+f(T)} + 0.0057Rain[H^+] + 0.192[HNO_3] \quad (4.11)$$

$$f(T) = 0.062(T-10) \text{ when } T < 10^\circ\text{C}, \text{ otherwise } f(T) = -0.021(T-10)$$

Cast Bronze

$$R = 0.15 + 0.000985[SO_2]Rh_{60}e^{f(T)} + 0.00465Rain[H^+] + 0.00432[PM_{10}] \quad (4.12)$$

$$f(T) = 0.060(T-11) \text{ when } T < 11^\circ\text{C}, \text{ otherwise } f(T) = -0.067(T-11)$$

Portland limestone

$$R = 4.0 + 0.0059[SO_2]Rh_{60} + 0.054Rain[H^+] + 0.078[HNO_3]Rh_{60} + 0.0258[PM_{10}] \quad (4.13)$$

where

Rh_{60} = $Rh - 60$ when $Rh > 60$, 0 otherwise

$[HNO_3]$ = annual average concentration, $\mu\text{g m}^{-3}$

$[PM_{10}]$ = annual average concentration, $\mu\text{g m}^{-3}$

And other symbols as in the previous section.

4.2.2.3 Units for corrosion attack of metals

Mass loss and surface recession, the two units of corrosion attack proposed, have been denoted as ML (g m⁻²) and R (µm). It is recommended that all maps for metals are produced with the unit R (µm) with the exception of aluminium, where it is recommended to use ML (g m⁻²). For aluminium the corrosion is localised, and it would therefore be misleading to express the results in µm since this is not reflecting the depth of local attack. For the purpose of conversion from ML to R the following densities should be used: steel (7.8 g cm⁻³), zinc (7.14 g cm⁻³), copper (8.93 g cm⁻³) and bronze (8.8 g cm⁻³).

4.2.2.4 Direct effects of ozone

The effect of ozone (O₃) on corrosion of materials is complex and there are still today serious gaps of knowledge to characterise it. Both O₃ and NO₂ have a direct effect on corrosion and degradation of especially some organic materials. In recent years the synergistic effect of SO₂ in combination with O₃ and NO₂ 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 SO₂ and O₃ has been shown in the UN ECE exposure programme, and only for copper as can be inferred from the dose-response functions.

4.2.3 Dose-response functions for soiling of materials

Soiling is the visual effect resulting from the darkening of exposed surfaces following the deposition and accumulation of atmospheric particles. It can be assessed by the change of optical properties of different materials, generally, as the loss of reflectance for opaque materials (such as stones, concrete, painted steel, etc.), and as the loss of transparency, i.e. transmittance, for transparent materials (such as glass). Most of the measurements were carried out on samples that were exposed in vertical position under sheltered conditions to avoid recurring washing by rain.

For non-transparent materials, several dose-response functions were defined (Watt et al., 2008). They relate the loss of reflectance ΔR to the PM₁₀ concentration ([PM₁₀] in µg m⁻³) and time (t in days):

White painted steel

$$\Delta R = R_0 [1 - e^{-3.96 \cdot 10^{-6} [PM_{10}] t}] \quad (4.14)$$

White plastic

$$\Delta R = R_0 [1 - e^{-4.43 \cdot 10^{-6} [PM_{10}] t}] \quad (4.15)$$

Polycarbonate membrane

$$\Delta R = R_0 [1 - e^{-3.47 \cdot 10^{-6} [PM_{10}] t}] \quad (4.16)$$

where

ΔR = loss of reflectance, %

R_0 = reflectance from uncovered surface, %

$[PM_{10}]$ = annual average concentration, $\mu\text{g m}^{-3}$

t = exposure time, days

There is no DRF for Portland limestone as the correlation with PM_{10} was too poor to predict a relationship with any confidence.

For transparent material, such as float glass, two kinds of dose-response functions were developed:

- (1) The first one is based on multilinear regression where haze is a temporal trend whose amplitude is controlled by $[SO_2]$, $[NO_2]$ and $[PM_{10}]$ (in $\mu\text{g m}^{-3}$) (Lombardo et al., 2010):

$$H = \frac{0.2529[SO_2] + 0.1080[NO_2] + 0.1473[PM_{10}]}{1 + \left(\frac{382}{t}\right)^{1.86}} \quad (4.17)$$

where

H = haze, %

t = exposure time, days

And other symbols as in the previous section.

- (2) The second one is based on a neural network approach (Verney-Carron et al., 2012). It corresponds to a pure statistical model that uses a non-linear parametric regression with a hyperbolic tangent function. Once set up, this function is easy to use:

$$H_{est} = 4.81H_{norm} + 5.27 \quad (4.18)$$

$$H_{norm} = 3.951 - 39.193 \tan(S_1) + 44.067 \tan(S_2) \quad (4.19)$$

$$S_1 = -1.498 - 0.145 \left(\frac{t - 387.18}{275.17} \right) + 0.031 \left(\frac{[SO_2] - 9.7}{11.82} \right) + 0.297 \left(\frac{[NO_2] - 33.29}{19.37} \right) + 0.280 \left(\frac{[PM_{10}] - 28.93}{15.68} \right) \quad (4.20)$$

$$S_2 = -1.45 - 0.073 \left(\frac{t-387.18}{275.17} \right) + 0.033 \left(\frac{[SO_2]-9.7}{11.82} \right) + 0.281 \left(\frac{[NO_2]-33.29}{19.37} \right) + 0.261 \left(\frac{[PM_{10}]-28.93}{15.68} \right) \quad (4.21)$$

where

H_{est} = estimated haze, %

H_{norm} = normalized haze, %

S_1, S_2 = 2 neurons

And other symbols as in the previous section.

The range of use of this model must be within the range of the data used to parameterize the function: a duration less than 1638 days, $[SO_2]$ less than $51.1 \mu\text{g m}^{-3}$, $[NO_2]$ between 1.3 and $90.1 \mu\text{g m}^{-3}$ and $[PM_{10}]$ between 5.4 and $84.3 \mu\text{g m}^{-3}$. This model can therefore be used in rural, urban and traffic areas.

4.3 Use of dose-response functions for mapping "acceptable corrosion rates" and "acceptable levels" for pollutants

4.3.1 Recommendations regarding the selection of functions

For the following materials, two sets of functions have been given, one for the SO_2 dominating situation and one for the multi-pollutant situation:

- Zinc
- Cast bronze
- Portland limestone.

It is not possible to exactly define the SO_2 dominating situation and the multi-pollutant situation. However, it is possible to specify the recommended use of the functions:

- The multi-pollutant functions are the preferred choice. This is especially true when making maps of future scenarios and comparing the situation of today with those in the future arising from different pollution scenarios.

- The SO₂-dominating functions may be used if it can be shown that effects of other pollutants besides SO₂ and acid rain are not contributing significantly to the general appearance of maps or to conclusions. This could for example be the case when showing the significant improvements made in the past for Europe or when mapping areas of the world where SO₂ values are very high.

4.3.2 Recommendations regarding the use of environmental data

Any user who is considering producing maps on pollution effects of materials based on procedures specified in this chapter should also consult the general chapters of this manual, Chapter 1 Introduction, Outline and General Considerations and, especially, Chapter 2 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 protons ($Rain[H^+]$) is not mentioned explicitly in chapter 2 but it should be noted that the recommendation “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 valid also for H⁺.

Annual averages of environmental parameters shall always be used in the dose-response functions but could be based either on measured or modelled values. Data valid for longer periods may also be used depending on the purpose. For example, when climatic data for a particular year is missing or when the purpose is to isolate the effect of pollutants it is possible to use long term average data for climatic parameters, for example 30-year averages, so called “climate normals”.

Values of climatic and pollution data can usually be obtained from national or international meteorological centres, international organisations e.g. (WMO), international research programmes (e.g. EMEP) or national organisations or authorities responsible for environmental protection.

4.3.2.1 Supporting function for the calculation of HNO₃

Nitric acid is a parameter that is not measured within dense monitoring networks very frequently. The availability of data is therefore limited. The following empirical function, which has been derived within the MULTI-ASSESS project (MULTI-ASSES final report), gives a good possibility of calculating the nitric acid concentrations from NO₂, O₃, relative humidity (Rh) and temperature (T).

$$HNO_3 = 516e^{\frac{-3400}{T+273}} \cdot ([NO_2][O_3]Rh)^{0.5} \quad (4.22)$$

4.3.3 Recommendations regarding selection of intervals for mapping corrosion attack

The acceptable rate of corrosion or deterioration (R_a), expressed in μm , or the acceptable soiling (S_a), expressed in %, was defined as being dependent on the technical and economic considerations for the particular material and application. In reality, it is not considered practical in the context of Convention policy to do this for each individual material and for each individual application separately. Instead, it is recommended that the acceptable corrosion rate is expressed as a multiple of a constant, material dependent, “background corrosion”. ICP Materials has calculated reference levels representing the background corrosion or deterioration rate (R_b) as the lower 10 percentile of observed corrosion rates in the materials exposure programme, which started in 1987 and ended in 1995. Acceptable corrosion rates can then be expressed as a multiple (n) of the background corrosion or rate:

$$R_a = n \cdot R_b \quad (4.23)$$

An appropriate n value still has to be selected based on technical/economic consideration but will then be independent of material.

Acceptable rate of corrosion can be used to produce maps. They will show where corrosion exceeds the acceptable deterioration rate (R_a) for simple samples of material. Thus, no correction is implemented for the form in which the material is used (e.g. the type of component). Practical n values 1.5, 2.0 and 2.5 are recommended following discussion at the 24th meeting of the Task Force (2008), and corresponding R_a values are given in table 4.1. Targets for protecting materials of infrastructure and cultural heritage monuments for 2050 and 2020 have been given in “Indicators and targets for air pollution effects” (ECE/EB.AIR/WG.1/2009/16) corresponding to $n=2.5$ (2020) and $n=2.0$ (2050).

Table 4.1. Recommended class boundaries to be used for mapping corresponding to n values of 1.0 (background corrosion rate), 1.5, 2.0 and 2.5.

Material	$n = 1.0$	$n = 1.5$	$n = 2.0$	$n = 2.5$	
Limestone	3.2	5.0	6.4	8	μm , first year exposure
Sandstone	2.8	4.0	5.5	7	μm , first year exposure
Copper	0.32	0.5	0.64	0.8	μm , first year exposure
Bronze	0.25	0.4	0.5	0.6	μm , first year exposure

Zinc	0.45	0.7	0.9	1.1	μm , first year exposure
Carbon steel and weathering steel	8.5	12	16	20	μm , first year exposure
Aluminium [#]	0.09	0.14	0.18	0.22	g m^{-2} , first year exposure

[#]Aluminium undergoes localised corrosion, but the corrosion rates were calculated as uniform corrosion. Maximum pit depth is a better indication of potential damage, but this characteristic cannot be evaluated after the first year of exposure.

Most sites of Europe today have corrosion values in the range corresponding to those given in Table 4.1. However, intervals for higher corrosion attack also need to be specified in order to map corrosion in areas with high levels of pollution, in or outside Europe or to map situations observed in the past. The ISO standard 9223 specifies intervals of corrosion values for the following metallic materials: carbon steel, zinc, copper and aluminium, see Table 4.2. Although these intervals correspond to different n values the variation is not so large and the corresponding approximate n values are 5.0, 10 and 20. Therefore, it is recommended to use these n values for mapping high corrosion values for materials other than carbon steel, zinc, copper and aluminium. For carbon steel, zinc, copper and aluminium the C classes given in Table 4.2 are recommended when mapping areas with high corrosion rates.

Table 4.2 ISO 9223 corrosivity categories.

Material	C1	C2	C3	C4	C5	CX	
Carbon steel	< 1,3	1,3-25	25-50	50-80	80-200	200-700	μm , first year exposure
Zinc	<0,1	0,1-0,7	0,7-2,1	2,1-4,2	4,2-8,4	8,4-25	μm , first year exposure
Copper	<0,1	0,1-0,6	0,6-1,3	1,3-2,8	2,8-5,6	5,6-10	μm , first year exposure
Aluminium [#]		<0,6	0,6-2	2-5	5-10	>10	g m^{-2} , first year exposure

[#]Aluminium undergoes localised corrosion, but the corrosion rates were calculated as uniform corrosion. Maximum pit depth is a better indication of potential damage, but this characteristic cannot be evaluated after the first year of exposure due to passivation effects and decreasing corrosion rates.

4.3.4 Recommendations regarding grid size

It is recommended that countries make use of best available data and generate information at appropriate national scales. It is advisable to produce maps with high resolution (small grid size), preferably 1 km² or smaller, especially for mapping of effects in urban areas. Such resolution enables taking into account differences between urban and rural conditions in levels of pollution, in relevant climatic characteristics (such as temperature and relative humidity) and may include both long-range transported pollutants and local emissions.

However, for regional European assessments, pollutant effects on materials may be mapped using EMEP grid areas (0.1° x 0.1° Lat-Long currently). It is thus advisable to use a grid network that coincides with the EMEP network or, preferably, a smaller network that is a fraction of the EMEP size.

4.3.5 Recommended maps

Several maps may be used to illustrate the effects of air pollution on materials:

- Maps showing the geographical distribution of some of the most important environmental parameters and their combinations used in the dose-response functions: [SO₂], [O₃], T, Rh, Rain, pH, Cl⁻, Rain[H⁺].
- Maps showing combinations of important parameters illustrating important effects related to materials damage but not possible to express in terms of a specific material. This could for example be time of wetness (TOW), calculated as a combination of temperature and relative humidity parameters (Tidblad et al., 2000) or other “heritage climatology” parameters such as the number of freeze-thaw cycles (Brimblecombe, 2010).
- Materials damage maps for selected materials should preferably be produced using the recommendations in 4.3.3. These maps will enable the identification of areas exceeding acceptable/tolerable corrosion rates.
- Maps can also be made showing the contribution of wet deposition to the total corrosion effect or ratio between corrosion effect of wet and dry deposition.

Maps showing acceptable/tolerable pollution levels/loads of individual pollutants (SO₂, O₃, HNO₃, PM₁₀, H⁺) can be made but levels of other pollutants need to be specified. A common approach is to assume that these are unchanged.

Another possibility is to use target values. These inform on the pollutant deposition that would lead to a given (chosen) acceptable level of corrosion or soiling for a given year (the target). For example, if we assume that PM_{10} levels are below $20 \mu\text{g m}^{-3}$ annual mean (as recommended by WHO Air quality guidelines, global update 2005) and that pH levels are equal to those in 2000, it is possible to calculate acceptable SO_2 levels for carbon steel using equation 4.11 for 2020 ($R=20 \mu\text{m}$) and 2050 ($R=16 \mu\text{m}$). Assisting maps of temperature, relative humidity and precipitation (long-term averages) and pH (for the year 2000) would be needed.

4.4 Use of dose-response functions for mapping "acceptable soiling rates"

For the mapping of soiling rates and costs, a background rate and suggested tolerable and acceptable rates (thresholds) in the years 2020 and 2050 can be used.

For non-transparent materials (white painted steel and plastic, and polycarbonate membrane (Equations 4.14 to 4.16) the lifetimes are calculated until 30% loss of reflection, for a selected PM_{10} background scenario, and it is suggested to use threshold cleaning intervals of 10 years (in year 2020) and 15 years (in 2050). The cleaning interval in the background is expected to, typically, be between 30 and 40 years. The threshold of tolerable soiling of 30% loss of reflection is suggested based on the research of Brimblecombe and Grossi (2005), and on the following considerations:

- The threshold is chosen to protect buildings sensitive to soiling of light colour.
- The threshold represents a perceived reflectance where about 30% of respondents find the surface dirty.
- The unprompted dirtiness response is expected to be considerably lower (than 30% of the respondents).

For glass soiling, both functions can be used provided that the concentration ranges are respected for the neural network DRF.

For the soiling of modern glass, it is recommended to use a lifetime between cleaning in the background of 1500 days (\approx 4 years), and a threshold lifetime for 2050 calculated from a haze value of 1% for cultural heritage (and in sensitive situations), and from a haze value of 3% for technical constructions and the general stock of buildings. In instances when a haze value of 3% is never reached by Equations (4.14, 4.15 or 4.16), or only reached at cleaning intervals longer than 1500 days, the cleaning interval is set to 1500 days and the rate and cost over background is set equal to zero (Grøntoft et al., 2019). Depending on the pollution, 1% haze would, typically, be reached in some months up to a year, whereas 3% haze was found to be reached in one year for the average of the ICP stations between 2002 and 2014.

4.5 Use of dose response functions for calculation and mapping of costs resulting from corrosion

One additional important 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

$$\Delta C = C \cdot S \cdot (L_{S1}^{-1} - L_{S2}^{-1}) \quad (4.25)$$

where ΔC is the cost difference, C is the cost per surface area of material for maintenance/replacement/cleaning, S is the surface area of material, L_{s1} is the maintenance interval (lifetime) for scenario 1 and L_{s2} is the maintenance interval for scenario 2. If Equation 4.16 is to be used for estimating the cost of corrosion or soiling due to pollutants in the present situation it is 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 Equations 4.1 - 4.7, which means $t^{0.85}$ for zinc and $t^{0.86}$ for bronze in the multi-pollutant situation. For carbon steel a time dependence of $t^{0.54}$ is recommended. For the paint coatings it is not recommended to use Equations 4.8 - 4.9 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 the only ones available today but these have not been verified by ICP Materials. A UN/ECE Workshop on economic evaluation of air pollution abatement and damage to buildings including cultural heritage took place in Stockholm on 23-25 January 1996 (Proc. UNECE Economic Workshop, 2007). 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 and Cowell and ApSimon, 1996. In the ECOTEC study of 1986, building identikits for Birmingham (UK), Dortmund and Cologne (Germany) were compiled. 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. Later, Tidblad et al., 2010 made an updated review on economic assessment of corrosion and soiling of materials including cultural heritage including references to several national studies and also the EU projects REACH, ExternE and ExternE Transport, and CULT-STRAT. The CULT-STRAT project resulted in a book "The effects of air pollution on cultural heritage" with a chapter on economic evaluation (Watt et al., 2009a).

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 change in the rate of deterioration can be used to estimate the cost associated with the deterioration and furthermore to undertake a cost benefit analysis of pollutant emission reduction scenarios in the mapping area.

4.5.1 Assessment of stock of materials at risk

Materials have so far not been included in integrated assessment modelling and are not included in the multi-pollutant protocol. Part of the explanation for this may be the lack of stock at risk data. Several stock at risk studies have, however, been performed during the years, the most intensive period being from 1990 to 1996 with several important studies in individual countries that in the end enabled the estimate of Cowell and ApSimon (1996) on the cost of damage to buildings by atmospheric pollution in Europe. These studies, many others and an overview of methodologies for assessing stock at risk were recently presented in the ICP Materials report 61 “Assessment of stock of materials at risk including cultural heritage”, Tidblad et al., 2010. Furthermore, the CULT-STRAT book mentioned above also included a chapter on stock at risk (Watt et al., 2009b)

4.5.2 Sources of uncertainty

The main sources of uncertainty for estimation of corrosion costs will result from

- assessment of the stock of materials at risk;
- 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;
- characterisation of reduced service lifetime and quantification of costs associated with reduced service lifetime;
- 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; and
- use of yearly mean values of pollution parameters which do not take into account the effect of fluctuations of pollutant levels.

4.6 Concluding remarks

Mapping atmospheric corrosivity was first done in the past to identify effect of emission on metals in the vicinity of industrial emission sources. These maps could be done simply by plotting SO₂ isolines, which would be almost identical to corrosion isolines. With more knowledge and changing pollution situation more parameters have successively been added to dose-response functions including the effect of climate (time of wetness, temperature, relative humidity), precipitation (acid rain), other gaseous pollutants (O₃, HNO₃) and particulate pollution.

Corrosivity maps are useful for material selection and for appropriate selection of protection methods in industrial applications for bare as well as coated metals. Furthermore, the use of indicator materials can show potential effects on cultural heritage as is illustrated in the “Guidance document on health and environmental improvements using new knowledge, methods and data” (ECE/EB.AIR/2013/8) giving materials corrosion and soiling risks for individual countries in the ECE region.

It is our hope that this document will stimulate further mapping of corrosion by using a standardised methodology also outside Europe to facilitate comparison of maps produced at different geographical resolution, geographical scales and time scales.

4.7 References

- Brimblecombe P. and Grossi C. M., 2005. Aesthetic thresholds and blackening of stone buildings, *Science of the total environment* 349, 175-189.
- Brimblecombe P., 2010: "Heritage Climatology", in *Climate change and cultural heritage*, Proc. Ravello Int. Workshop, ISBN 978-88-7228-601-2, Edipuglia, Italy.
- Cowell and Apsimon H., 1996: "Estimating the cost of damage to buildings by acidifying atmospheric pollution in Europe", *Atmos. Env.*, Vol. 30, pp. 2959-2968.
- Ecotec (1986) *Identification and Assessment of Materials Damage to Buildings and Historic Monuments by Air Pollution*. Report to the UK Department of the Environment. Ecotec Consulting Ltd., Birmingham.
- Grøntoft T., Verney-Carron A., and Tidblad J. (2019) *Cleaning Costs for European Sheltered White Painted Steel and Modern Glass Surfaces due to Air Pollution since the Year 2000*. *Atmosphere* 10, 167, 31 pp.
- Kucera V., Henriksen J., Knotkova D., and Sjöström C., 1993: "Model for Calculations of Corrosion Costs Caused by Air Pollution and its Applications in three Cities", Proc. 10th European Corros. Congr., Barcelona.
- Kucera V., J. Tidblad, K. Kreislova, D. Knotkova, M. Faller, D. Reiss, R. Snethlage, T. Yates, J. Henriksen, M. Schreiner, M. Melcher, M. Ferm, R.-A. Lefèvre and J. Kobus, "UN/ECE ICP materials dose-response functions for the multi-pollutant situation," *Water, Air, & Soil Pollution: Focus*, vol. 7, 2007, pp. 249–258.
- Lombardo T., Ionescu A., Chabas A., Lefèvre R.-A., Ausset P. and Candau Y., 2010. Dose–response function for the soiling of silica–soda–lime glass due to dry deposition, *Science of the total environment* 408, 976-984.
- MULTI-ASSESS final report, <http://www.corr-institute.se/MULTI-ASSESS/>
- Tolstoy N., Andersson G., Sjöström C and Kucera V. 1989: "External building materials – quantities and degradation." Statens institut för byggnadsforskning, Gävle. ISBN 91-540-9315-5.
- Tidblad, J., Mikhailov, A.A. and Kucera, V., 2000. Model for the prediction of the time of wetness from average annual data on relative air humidity and air temperature. *Protection of Metals (Russia)*, 36(6), 533-540.

- Tidblad, J., Kucera, V., Mikhailov, A. A., Henriksen, J., Kreislova, K., Yates, T., Stöckle, B. and Schreiner, M., 2001. UN ECE ICP Materials. Dose-response functions on dry and wet acid deposition effects after 8 years of exposure. *Water, air and soil pollution*, 130(1-4 III), 1457-1462.
- Tidblad J., T. Yates, S. Doytchinov, M. Faller, and K. Kreislova, UNECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No 61 Assessment of stock of materials at risk including cultural heritage., Swerea KIMAB AB, Stockholm, Sweden., 2010.
- Tidblad J., Faller M., Grøntoft T., Kreislova K., Varotsos C., De la Fuente D., Lombardo T., Doytchinov S., Brüggerhoff S. and Yates T., 2010: UNECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No 65 Economic assessment of corrosion and soiling of materials including cultural heritage, Swerea KIMAB AB, Stockholm, Sweden.
- UN/ECE Economic Workshop, 1997: “Economic Evaluation of Air Pollution Damage to Materials.” Proceedings of the UN ECE Workshop on Economic Evaluation of Air Pollution Abatement and Damage to Buildings including Cultural Heritage, Eds V. Kucera, D. Pearce and Y.-W. Brodin, Report 4761, Swedish Environmental Protection Agency, Stockholm, Sweden, 1997.
- Verney-Carron A., Dutot A.L., Lombardo T., Chabas A., 2012. Predicting changes of glass optical properties in polluted atmospheric environment by a neural network model, *Atmospheric Environment* 54, 141-148.
- Watt J., Jarrett D. and Hamilton R., 2008. Dose-response functions for the soiling of heritage materials due to air pollution exposure, *Science of the total environment* 400, 415-424.
- Watt J., Navrud S., Slizkova Z. and Yates T., 2009a: “Economic Evaluation”, in *The effects of air pollution on cultural heritage*. Springer (book chapter), pp. 189-214.
- Watt J., Doytchinov S., Lefevre R.-A., Ionescu A., Dela Fuente D., Kreislova K and Screpanti A., 2009b: ”Stock at risk”, in *The effects of air pollution on cultural heritage*. Springer (book chapter), pp. 147-188.