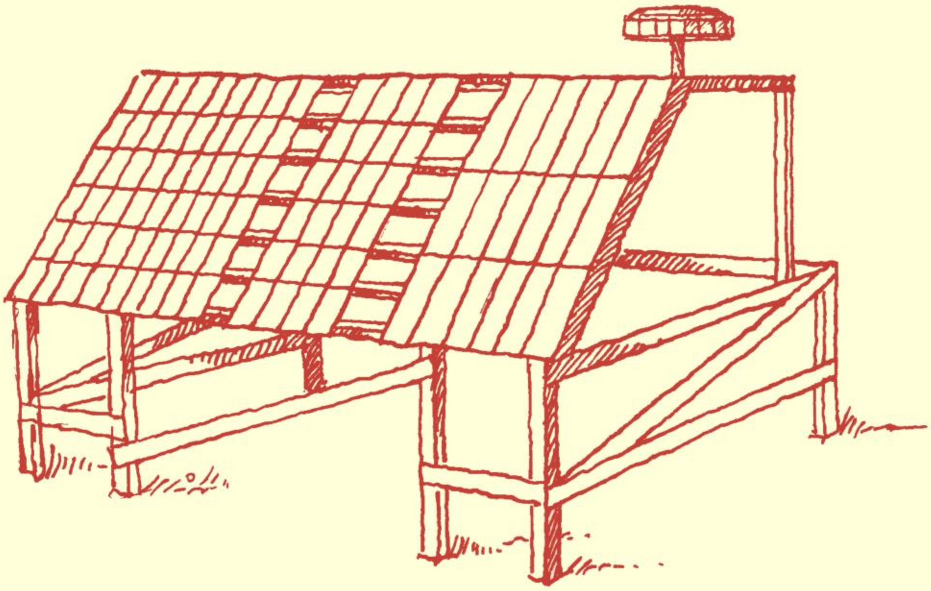
CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

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



Report No 64:

Validity of dose-response functions for different climatic conditions

November 2010

PREPARED BY THE MAIN RESEARCH CENTRE

swerea KIMAB Swerea KIMAB AB, Stockholm, Sweden

CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION
INTERNATIONAL CO-OPERATIVE PROGRAMME
ON EFFECTS ON MATERIALS,
INCLUDING HISTORIC AND CULTURAL MONUMENTS

ICP Materials
http://www.corr-institute.se/ICP-Materials

Report No 64
Validity of dose-response functions for different climatic conditions

Compiled by
Johan Tidblad[1], Daniel de la Fuente[2], Markus Faller[3], Katerina Kreislova[4*] and Tim Yates[5*]

[1]Swerea KIMAB AB, Stockholm, Sweden
[2]National Centre for Metallurgical Research, Madrid, Spain
[3]Swiss Federal Laboratories for Materials Testing and Research (Empa), Dübendorf, Switzerland
[4]Svuom Ltd., Prague, Czech Republic
[5]Building Research Establishment Ltd. (BRE), Watford, United Kingdom
[*]To be confirmed

http://www.swereakimab.se/

Contents

1 Introduction

The International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments (ICP Materials) started in 1985. It was initiated in order to provide a scientific basis for new protocols and regulations developed within the Convention on Long-range Transboundary Air Pollution. One of the aims of ICP Materials is to

> “Perform a quantitative evaluation of the effects of multi-pollutants such as S and N compounds, O_3 and particles as well as climate parameters on the atmospheric corrosion and soiling of important materials, including materials used in objects of cultural heritage”

ICP Materials have developed dose-response functions for the situation dominated by sulphur dioxide and for the multi-pollutant situation, based on corrosion, pollution and climate data from the temperate climate zone, mainly Europe. With the expected global climate change and targets developed for 2050, when these changes can be substantial, it is important to verify the robustness of dose-response functions for different climatic conditions. Also, the evaluation of robustness of dose-response functions and measured corrosion effects is a common work plan item for all ICPs. Previously experimental and random error for corrosion were reported in 2007, ECE/EB.AIR/WG.1/2007/3 and soiling in 2008, ECE/EB.AIR/WG.1/2008/3. Possible systematic errors based on independent data have, however, previous to this report not been reported.

The aim of the present report is to present and compare observed and predicted values based on ICP Materials dose-response functions for different situations using independently derived corrosion data. The material is presented as separate case studies based on individual exposures or investigations in separate countries.

2 Dose-response functions and overview

Dose-response functions recommended from ICP Materials for mapping are given in the UNECE Mapping Manual, chapter 4 where further details are given. Two sets of dose-response functions have been derived, functions for the SO_2 dominating situation and functions for the multi-pollutant situation.

Dose-response functions for the SO_2 dominating situation are based on results from the 8-year exposure within ICP Materials (1987-1995).

Dose-response functions for the multi-pollutant situation are based on 4-year results from the exposure within ICP Materials (1997-2001) complemented with environmental measurements of HNO_3 and particulate matter (2002-2003).

Materials, dose-response functions and case studies included in the report are summarised in table 1.

Table 1. Included dose response functions (SO_2 dominating situation and/or multi-pollutant situation) for case studies (countries) and materials. Dose-response functions are not available for carbon steel for the SO_2 dominating situation and for weathering steel, copper and aluminium for the multi-pollutant situation.

	SO_2 dominating situation	**Multi-pollutant situation**
Weathering steel	Switzerland	N/A
Carbon steel	N/A	Spain, Asia/Africa
Zinc	Switzerland, Spain, Asia/Africa	Asia/Africa
Copper	Switzerland, Asia/Africa	N/A
Bronze	United States	United States
Aluminium	Spain	N/A
Limestone	Asia/Africa	Asia/Africa

3 Validation of dose-response functions

3.1 Switzerland

The following case study is based on Leuenberger-Minger et al (2002). An exposure programme including weathering steel, copper and zinc after 1, 2 and 4 years of exposure was performed during 1993-1996 at 8 test sites in Switzerland (Dübendorf, Lägern, Härkingen, Bern, Payerne, Sion, Cadenazzo and Davos). Environmental data were collected for the parameters SO_2, NO_2, O_3, temperature (T), relative humidity (Rh) wind velocity and time of wetness. Based on the environmental data the sites can be grouped into three categories

- Davos with low temperature (3-5 ^{o}C) and low SO_2 pollution (1-2 µg m^{-3})
- Lägern, Payerne and Sion with normal temperature (8-11 ^{o}C) and medium SO_2 pollution (2-4 µg m^{-3})
- Dübendorf, Härkingen, Bern and Cadenazzo with with normal temperature (8-11 ^{o}C) and elevated SO_2 pollution (7-8 µg m^{-3})

Dose-response functions for the SO_2 dominating situation are available for all these metals and involve SO_2, temperature and relative humidity for all materials, and in addition O_3 (for copper) and amount and pH of precipitation (for copper and zinc). Of these, amount and pH of precipitation are not available. For zinc, a dose-response function for the multi-pollutant situation is available including in addition the HNO_3 concentration. This parameter can according to the mapping manual be calculated from NO_2, O_3, temperature and relative humidity, which are all available. However, for this data set, predicted values using the dose-response function for the SO_2 dominating situation and the dose-response function for the multi-pollutant situation are very similar and thus we only show results from the dose-response function for the SO_2 dominating situation.

Observed and predicted values are shown in figure 1. Except for copper where the observed values are about 1 µm higher than expected, the agreement is good. Worth mentioning is that the samples were glass blasted before exposure. This may result in increased corrosion attack not necessarily equal for the different materials. The extent of this sensitization were not quantified.

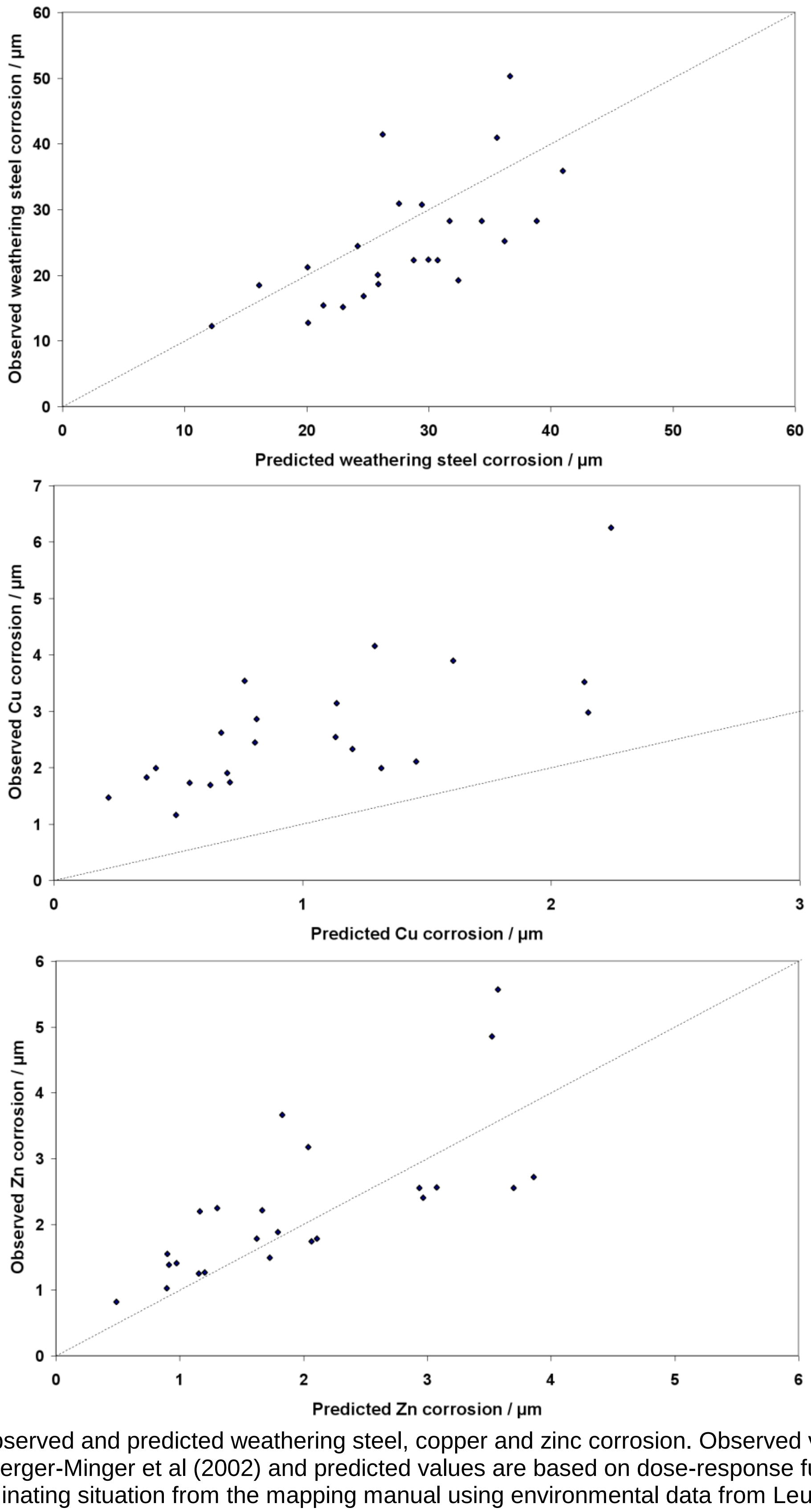


Figure 1. Observed and predicted weathering steel, copper and zinc corrosion. Observed values are from Leuenberger-Minger et al (2002) and predicted values are based on dose-response functions for the SO_2 dominating situation from the mapping manual using environmental data from Leuenberger-Minger et al (2002).

3.2 Spain

This case study is based on Spanish data collected from different exposure programs (MICAT, ISOCORRAG, Spanish Corrosion Map, Regional Corrosion Maps, etc.) De la Fuente (2010). Therefore, the data is not homogeneous regarding the used methodology. Temperature, relative humidity, SO_2 and chloride deposition are available as environmental parameters for carbon steel, zinc, copper and aluminium. In addition, estimated precipitation values in mm based on number of rain days are available. The original database contained 149 cases/test sites spread all of over Spain. However, since the ICP Materials dose-response functions do not contain chloride deposition and are in fact based on sites with relatively low chloride deposition a selection was made using only cases with $Cl^- < 1{,}5$ mg m^{-2} day^{-1} leaving only 35 unique cases. Of these, six had high precipitation levels (> 1000 mm $year^{-1}$).

Dose-response function functions are available for all these metals. However, the dose-response function for copper involves ozone (together with SO_2) and therefore it is not possible to estimate copper corrosion based on this data. Dose-response functions for the SO_2 dominating situation are available for zinc and aluminium while dose-response functions for the multi-pollutant situation are available for carbon steel and zinc. The zinc dose-response function for the multi-pollutant situation involves HNO_3, which is not available, and therefore the function for the SO_2 dominating situation is selected for zinc. All the tested functions involve precipitation and acidity/chloride concentration, which is not available and, in addition, the function for carbon steel involves PM10, which is also not available. Therefore, predicted values are based on SO_2, temperature and relative humidity only.

Observed and predicted values are shown in figure 2. The measured carbon steel corrosion is higher than predicted while there are no obvious systematic differences for zinc and aluminium. For all materials the high precipitation sites show as expected or higher values than predicted.

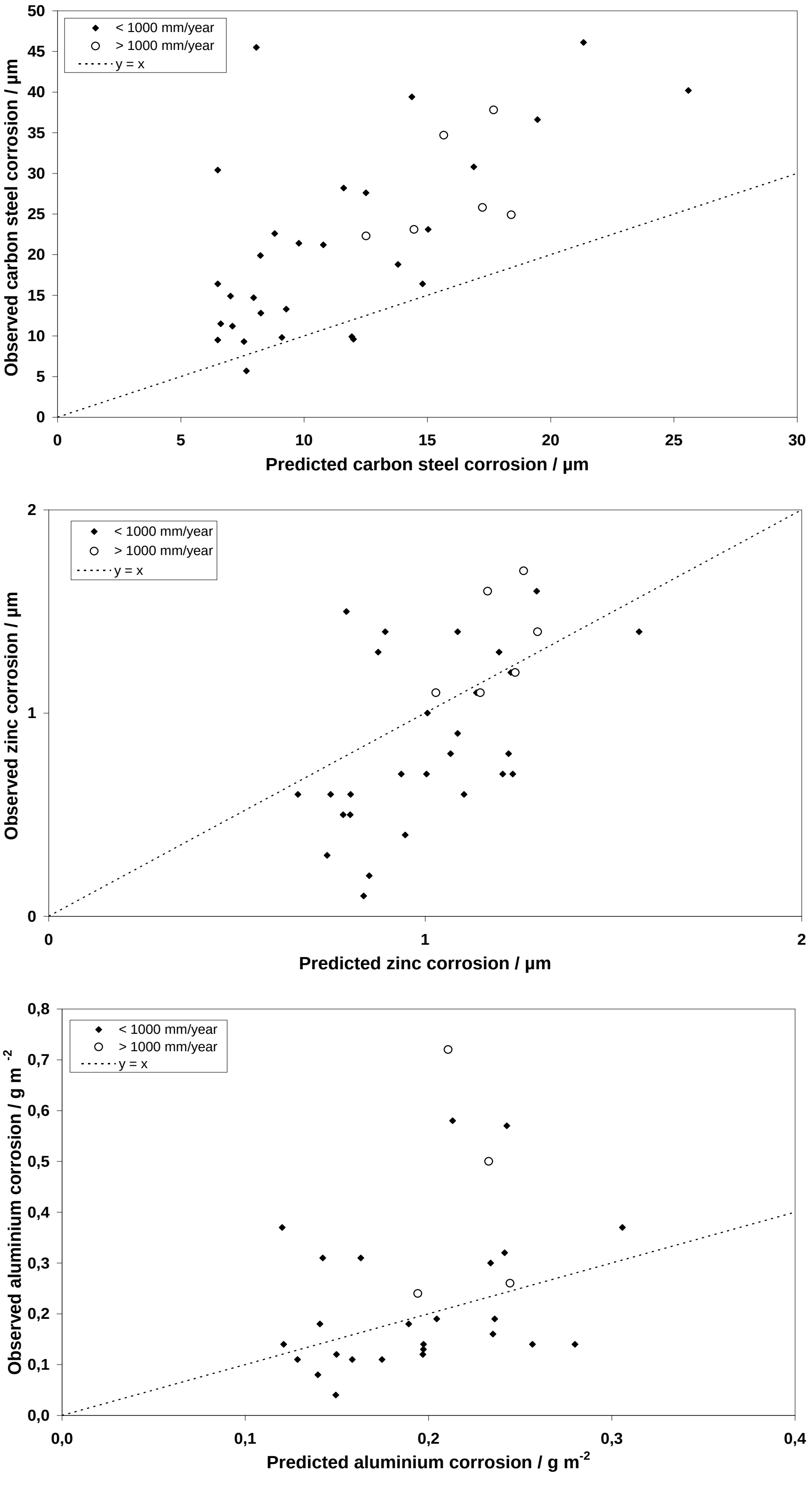


Figure 2. Observed vs predicted carbon steel, zinc and aluminium corrosion. Observed values are from De la Fuente (2010) and predicted values are based on dose-response functions for the multipollutant situation (carbon steel) and the SO_2 dominating situation (zinc and aluminium) from the mapping manual using environmental data from De la Fuente (2010).

3.3 United States

The following case study is based on Tidblad et al (2009).

The Hiker figure, sculpted by Theo Alice Ruggles Kitson at the turn of the 19th century, represents an infantry soldier from the Spanish American War (1898–1902), the United State's first overseas conflict.

Fifty-two replicates of a single-figure bronze statue known as "Kitson Hikers" (figure 3) were cast by the Gorham Bronze Company and placed in cities across the United States in the 1920–1950s. They were consistently made with regard to composition and method. Of these, thirty four statues were in sufficiently good conditions and did not receive conservation treatment thus providing an excellent opportunity to verify relationships between environment and corrosion on real cultural heritage.

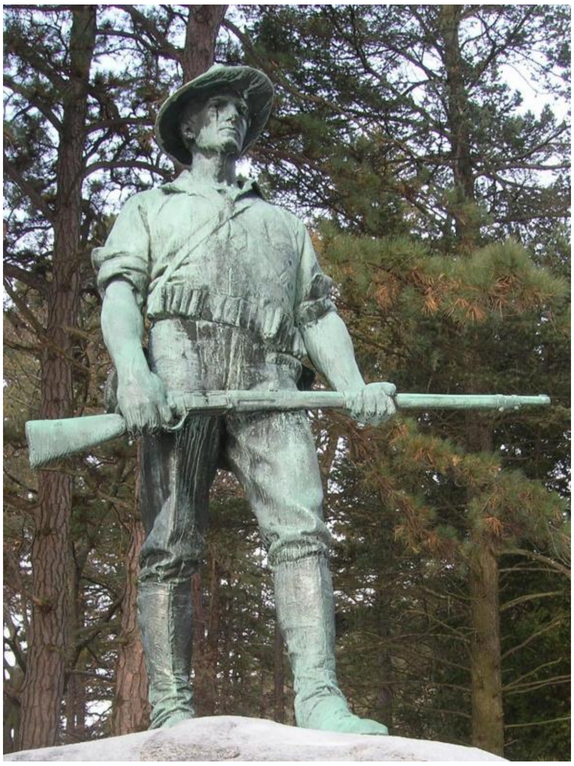


Figure 3. A selected Kitson Hiker statue with *verdigris* corrosion (see text).

Kitson Hikers are found in nearly every climate zone in the continental United States, which covers Desert to Alpine regimes. Hikers have seen pollution levels rise and fall dramatically, peaking in the 1930s and 1950s. All the Hikers pre-date the United States Clean Air Act of 1970, which caused air pollution levels in all cities to drop further by at least 50% and in some cases by an additional factor of 5–10.

The ‘‘greening’’ or verdigris patina formation on copper roofs is a well known corrosion phenomenon. 'Verdigris' is a translation from the Latin and originates from 'viride Hispanus', Spanish green. This was the name of an imported inorganic green dye from Spain in the middle Ages. Common synonyms were Span green, copper green, copper rust and many more. It dealt with green coloured copper salts, mostly with basic acetates, also often with sulphates (Krummenacher, 1997).

Bronze corrosion rates calculated for the locations were the statues were situated using ICP Materials dose-response functions result in highly plausible corrosion rates for the statues typically within the range 2 to 4 μm year^{-1}. Figure 4 shows a comparison of predicted and measured values based on the bronze dose-response functions for the SO_2 and multi-pollutant situation. Not surprisingly, considering that the statues were exposure during the high pollution era, the SO_2 model works best while the multi-pollutant model tends to overestimate corrosion when SO_2 is high (> 15 μg m^{-3}).

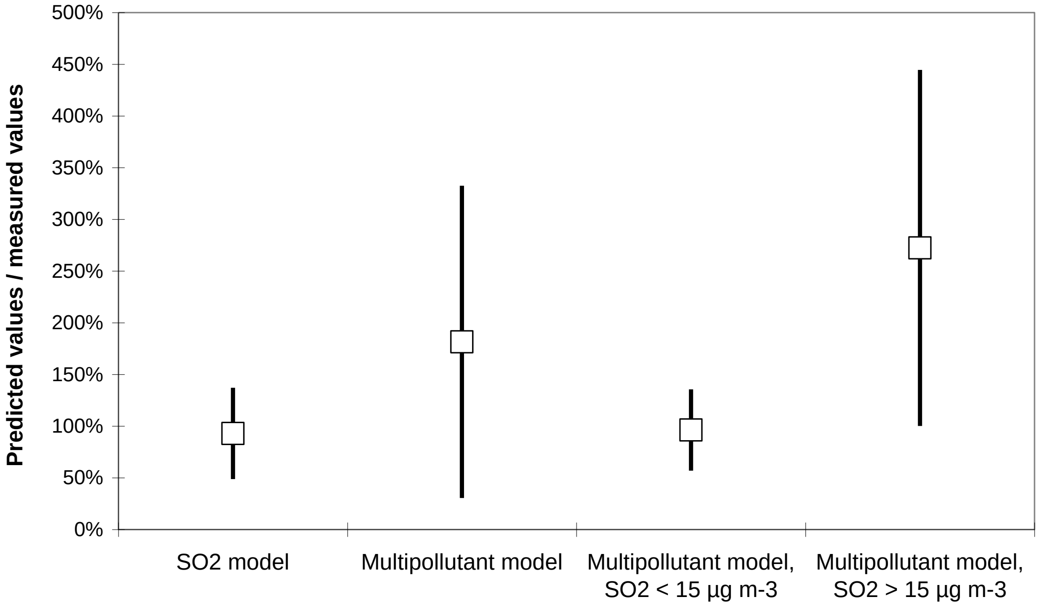


Figure 4. Hiker pit depth measurements relative to corrosion predicted by dose-response functions.

3.4 Asia and Africa

The high pollution levels combined with the elevated temperature levels and high amount of precipitation observed in many developing sub-tropical and tropical countries may result in higher corrosion rates than previously observed in Europe, Canada and the United States. However, available data and exposure programs in sub-tropical and tropical regions have in the past either limited environmental characterization or short exposure times.

In order to fill this gap a network of test sites was developed in Asia and Africa under the framework of the 2001-2004 Swedish International Development Cooperation Agency (Sida) funded program on Regional Air Pollution in Developing Countries (RAPIDC). Corrosion data after 1, 2 and 4 years of exposure have been published from this program (Tidblad et al, 2008). Comparison of absolute values from ICP Materials and RAPIDC are given in figure 5. For zinc, the median is slightly lower in Asia/Africa while for copper and carbon steel the median is slightly higher. Note that in Europe, copper values are generally lower than zinc values but this is not the case for Asia/Africa. For painted steel, the median is about the same but there are some extreme values in Asia/Africa not seen in Europe. Limestone shows the highest difference with significantly higher values in Asia/Africa, the median is about three times higher.

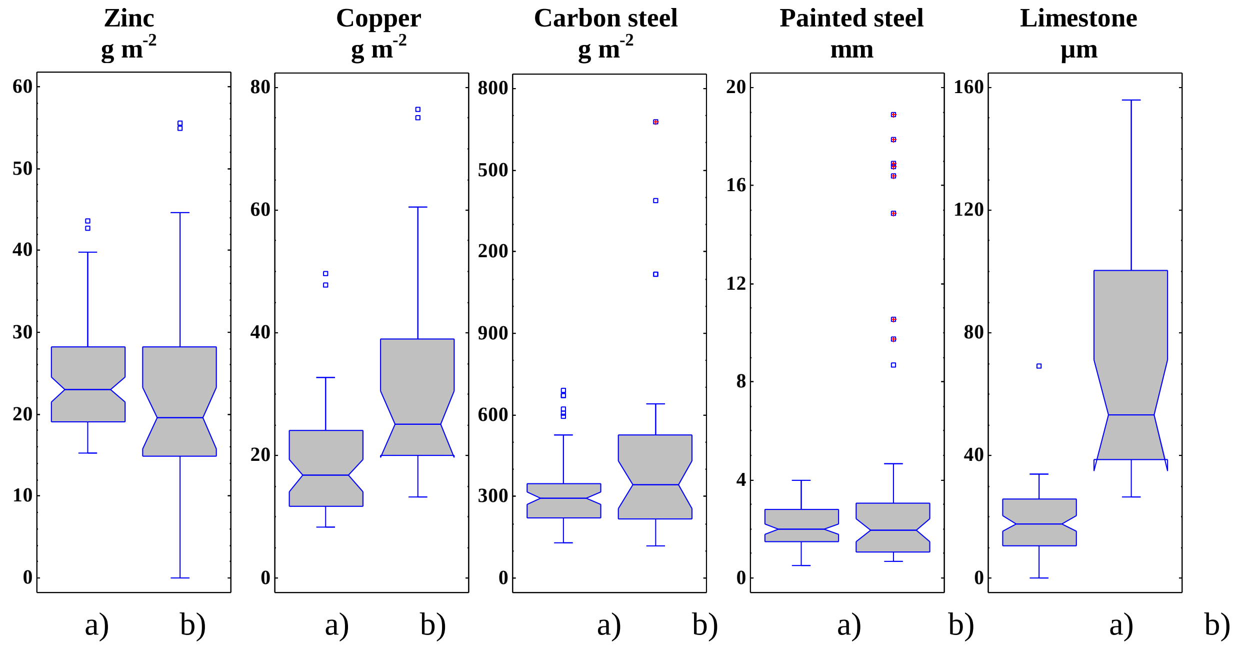


Figure 5. Comparison of data after 4 years of exposure: a) ICP Materials; b) RAPIDC

For carbon steel, zinc, copper and limestone all required environmental parameters are available. Therefore, all available dose-response functions are tested.

Observed and predicted values for carbon steel and copper are given in figure 6. There are no large systematic differences.

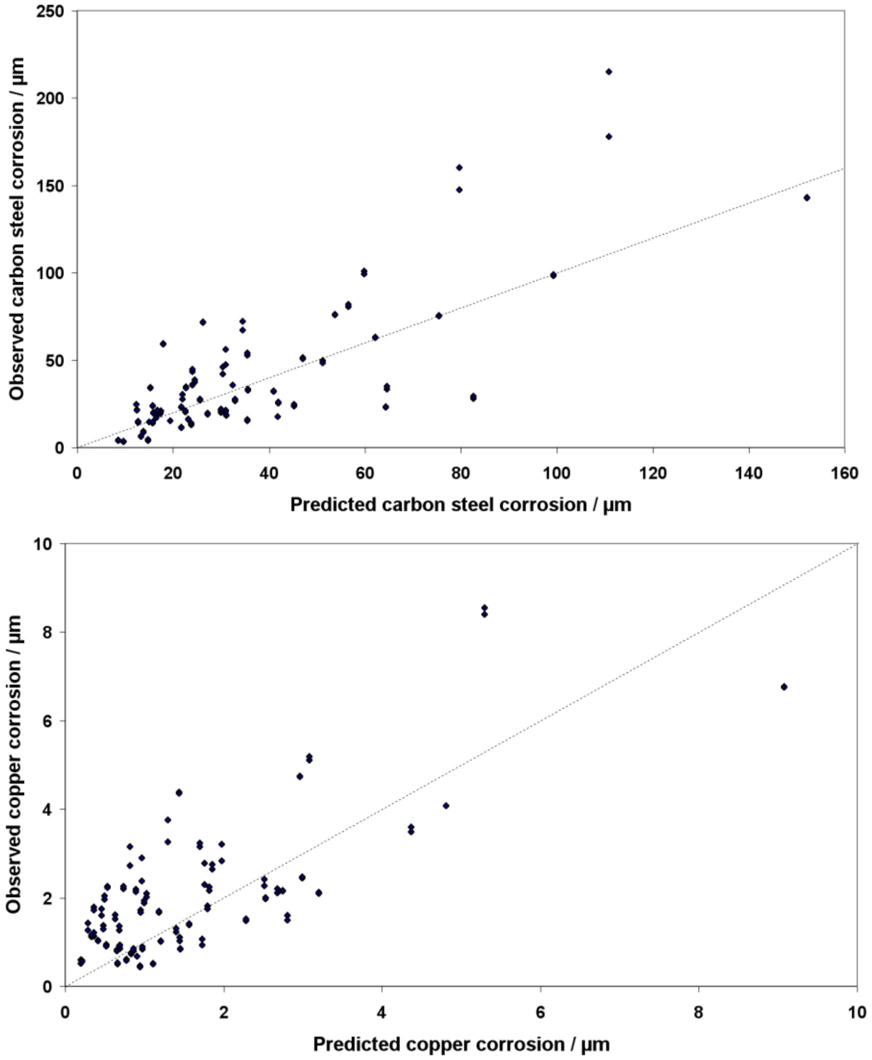


Figure 6. Observed and predicted carbon steel and copper corrosion (RAPIDC data from Asia/Africa). Predicted values for carbon steel are based on the dose-response function for the multi-pollutant situation while predicted values for copper are based on the dose-response function for the SO_2 dominating situation.

Figure 7 shows observed and predicted values for zinc. The function for the SO_2 dominating situation works very well, which is not surprising considering the high SO_2 levels (up to 100 µg m^{-3}) in the RAPIDC programme. The function for the multi-pollutant situation show similar results as for bronze in the Kitson Hiker study with higher elevated predicted values in many cases (compare figure 4).

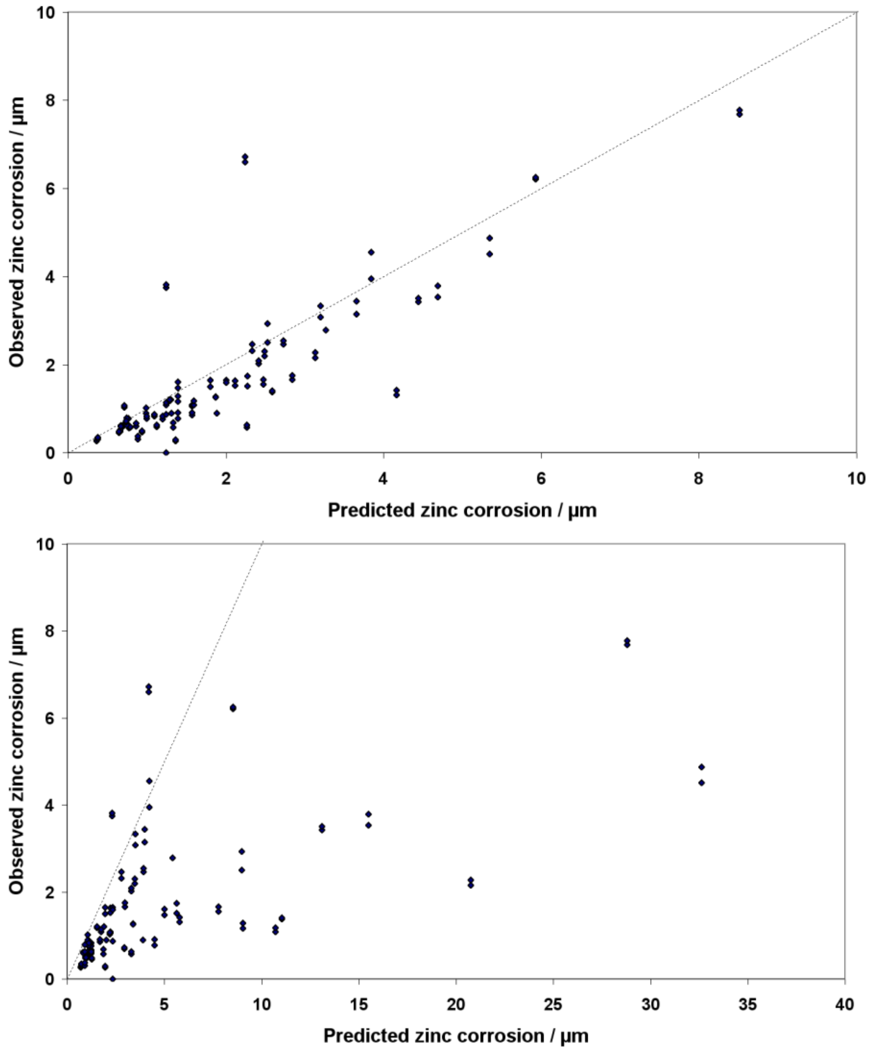


Figure 7. Observed and predicted zinc corrosion (RAPIDC data from Asia/Africa). Predicted values are given for the SO_2 dominating situation (top) and the multi-pollutant situation (bottom).

Figure 8 shows observed and predicted values for Portland limestone. The observed values are much higher than those predicted based on the function for the SO_2 dominating situation, which in principle should be the best selection considering the SO_2 levels. The reason for the discrepancy is probably related to the effect of temperature. In the SO_2 dominating function the temperature dependence was negative, i.e. higher temperatures gives lower predicted corrosion. When the SO_2 function was derived this was interpreted in terms of increasing sensitivity of the stone around 0 ^{o}C due to freeze-thaw cycles. Obviously, this dependence can not be extrapolated to the high temperatures in the RAPIDC data set (20-30 ^{o}C). The function for the multi-pollutant situation has no temperature dependence but still predicts too low values. Based on both RAPIDC and ICP Materials data the temperature dependence, if any, should be slightly positive.

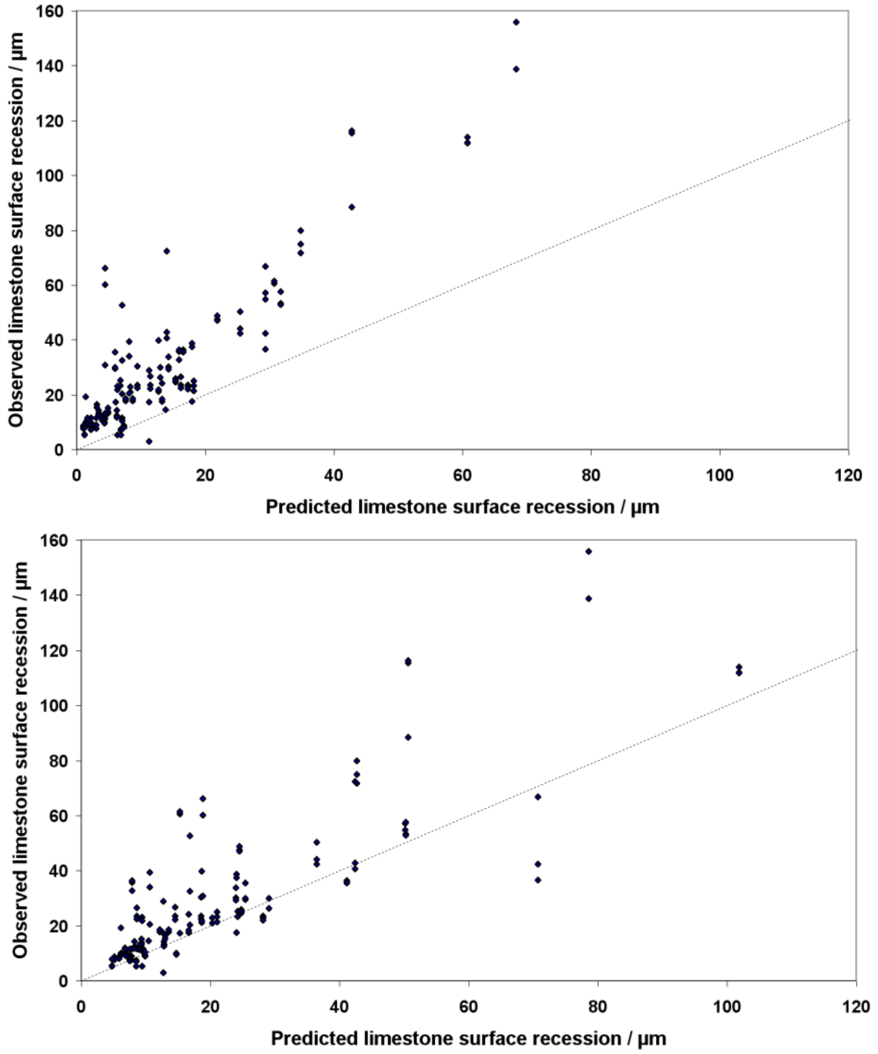


Figure 8. Observed and predicted limestone surface recession (RAPIDC data from Asia/Africa). Predicted values are given for the SO_2 dominating situation (top) and the multi-pollutant situation (bottom).

4 Summary

Table 2 shows an overview of the systematic differences presented in section 3 organised in the same format as table 1.

Table 2. Included dose response functions (SO_2 dominating situation and/or multi-pollutant situation) for case studies (countries) and materials. Results of comparison of observed and predicted values are shown in brackets (0: no systematic differences; +: observed values higher than predicted; -: observed values lower than predicted; ++: observed values much higher than predicted).

	SO_2 dominating situation	**Multi-pollutant situation**
Weathering steel	Switzerland (0)	N/A
Carbon steel	N/A	Spain (+), Asia/Africa (0)
Zinc	Switzerland (+), Spain (0), Asia/Africa (0)	Asia/Africa (-)
Copper	Switzerland (++), Asia/Africa (0)	N/A
Bronze	United States (0)	United States (-)
Aluminium	Spain (0)	N/A
Limestone	Asia/Africa (++)	Asia/Africa (+)

For the functions for the SO_2 dominating situation higher values than expected are in Switzerland for zinc and much higher for copper. This could be explained by the special surface treatment (glass blasting) used for these materials. Much higher values than predicted are also experienced for limestone and the explanation for this is the temperature dependence as discussed previously.

For the functions for the multi-pollutant situation lower observed values are observed for zinc and bronze and this is not surprising considering that the situation in reality is SO_2-dominating (see corresponding entry for the SO_2 dominating situation). For carbon steel in Spain the observed values are higher than predicted but two effects are not included in the function due to lack of data: acid rain and particulate deposition. For limestone in Asia/Africa the observed values are higher than the predicted and again this is most likely related to the effect of temperature.

5 Conclusions and recommendations

A comparison of observed and predicted values based on ICP materials dose-response functions and independent data has been performed with the aim of identifying possible systematic differences. The analysis provides further information regarding the robustness of the functions compared to previous analyses that focussed on random errors. The comparison permits the following specific conclusions:

- No high systematic differences related to environmental conditions are evident and the general recommendations regarding the selection of functions, with the exception of limestone, is still valid
- For limestone, the function for the SO_2 dominating situation is not recommended for use at elevated temperatures (20-30 ^{o}C), even if the SO_2 concentration is high, since the predicted values will be much lower than the observed.

6 References

De la Fuente D, 2010: personal communication

Krummenacher B 1997: Verdigris, Green Lion and Vitriol: The Basis of the Philosopher's Stone. URL: http://www.triad-publishing.com/stone20e.html. Reprinted from Issue 20 of The Stone, May-June, 1997.

Leuenberger-Minger A U, Buchmann B, Faller M, Richner P and Zöbeli M 2002: Dose-response functions for weathering steel, copper and zinc obtained from a four-year exposure programme in Switzerland. Corrosion Science v 22, pp 675-687.

Tidblad J, Kucera V, Hicks K, Kuylenstierna J, Dawei Z, Ng K W, Saha D, Das S N, Zandi M, Galang R, Ramiz A M, Pradhan B B, Arachchi W R, Chantra W, Lien L T H, Foax L J, Dombo G, Chissico M L, Lungu C and Mmmari A G, 2008: Atmospheric corrosion effects of air pollution on materials and cultural property in Asia and Africa. *Proc. 17th International Corrosion Congress*, Las Vegas, USA.

Tidblad J, Kucera V and Sherwood S 2009: Corrosion, pp 53-103, in “The effects of air pollution on cultural heritage”, Watt J, Tidblad J, Kucera V and Hamilton R, Eds., Springer, New York, USA.