# Corrosion behaviour of structural metals in respect to long-term changes in the atmospheric environment

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## Summary

Corrosivity of the atmospheres in Europe as same as in other industrial developed countries in the past was very high due to high level of acidic pollution, mainly $SO_2$. In the last 20 years it decreased as a result of applied legislative, economic and technological measures. The trends of changes in atmospheric corrosivity were systematically evaluated in respect to short-term and long-term corrosion rate of structural metals in the frame of exposure program UN ECE ICP *Effect of Materials* at atmospheric test sites with different environment. In relatively steady general climate, the effect of $SO_2$ air concentration on the corrosion rate of carbon steel, zinc and copper was analysed. In this paper the results of exposures ´programs in different environmental situations and corrosion rate response on the corrosivity changes are presented. The use of these results for application of long-term corrosion prediction was proposed.

## 1 Introduction

Metallic materials are damaged by basic climatic factors as temperature and relative humidity at atmospheric environments. The corrosion stress is increased by air pollution – gaseous and/or solid. The complex effect of atmospheric environments onto atmospheric corrosion is very difficult to quantify due to variability of its parameters. The decisive effect of sulphur dioxide ($SO_2$) on metal corrosion has been shown in many field exposures [1 - 4].

Emissions of air pollutants derive from almost all economic and societal activities. In Europe, policies and actions at all levels have greatly reduced anthropogenic emissions [5]. Emissions of the main air pollutants in Europe have declined significantly, in recent decades, greatly reducing exposure to $SO_2$.

The $SO_2$ pollution had been started to measure systematically since 70ties. The European mean of the annual mean $SO_2$ concentrations has decreased from 55 $\mu g/m^3$ to 20 $\mu g/m^3$ between 1978 and 1993 [1]. The $SO_2$ had been measured in the frame of exposure program UN ECE ICP *Effect of Materials* on 16 test sites (selected test sites from program) for 25 years – Figure 1 [6, 7]. In the Czech Republic the measurement of environmental parameters including $SO_2$ concentration and field exposure of metal panels started in 1969 at the atmospheric test site Kopisty located in the one of the most industrial part of the Czech Republic (previous measurements were not systematic).

In the last years, however, a synergistic corrosive effect of $SO_2$ and $NO_2$ and later of $SO_2$ and $O_3$ has been discovered first in laboratory exposure; this has been confirmed later on by field exposure studies. They enhance the corrosive effect of $SO_2$ by promoting its oxidation to sulphate. This underlines the necessity to treat the deterioration of materials taking into account the interrelated role of $SO_2$, $NO_2$ and $O_3$ in a contemporary multi-pollutant situation.

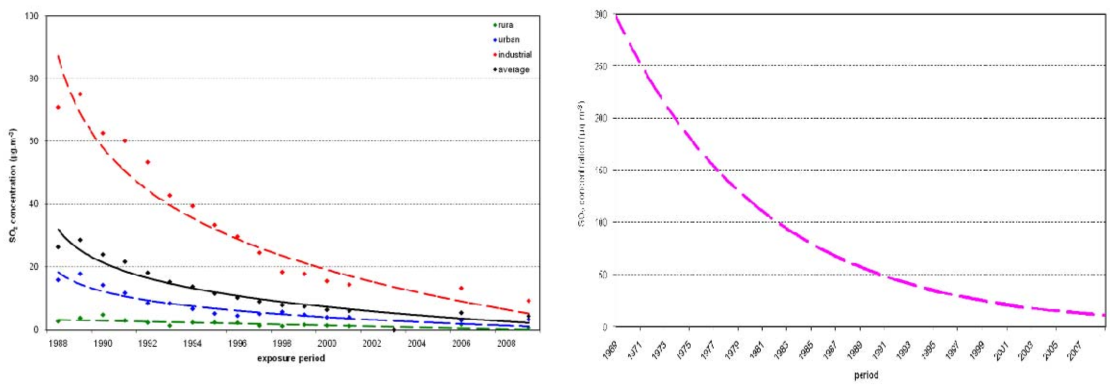


**Figure 1:** $SO_2$ average yearly concentration decreasing at European test sites (ICP program) and at Czech industrial test site Kopisty (No 03)

Together with decreasing $SO_2$ concentration, the pH of precipitation changed - Figure 2. Except industrial test sites, there is evident trend of significant increasing till some value and since 2000 the pH value seems to be increased only negligible. The pH value is still increasing at industrial test sites.

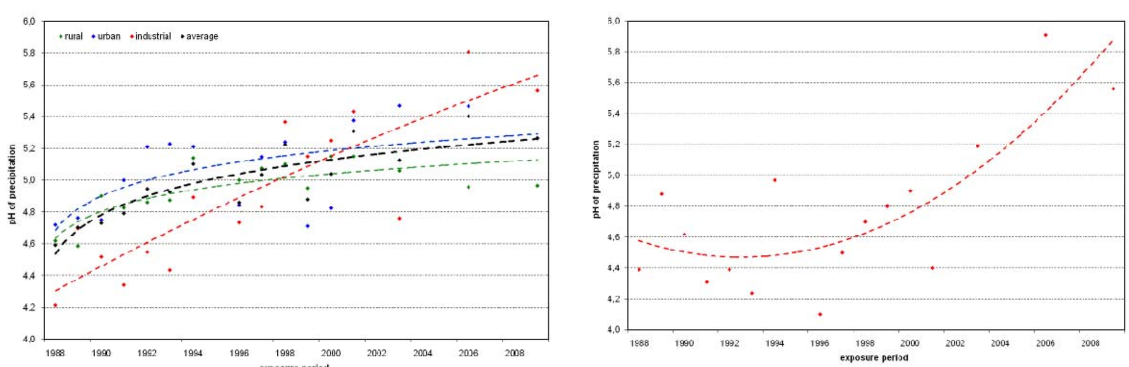


**Figure 2:** pH average yearly value decreasing at European test sites (ICP program) and at Czech industrial test site Kopisty (No 03)

## 2 One-year corrosion loss of structural metals

During the last decades, several field exposure programs have greatly contributed to enhancement of the present state of knowledge on the effects of acidifying air pollutants on materials. UN ECE ICP *Effect of Materials* is one of the largest and longest exposure programs.

In this program the samples of structural metals were exposed in standard conditions – at atmospheric test sites on racks in open atmosphere according to ISO 8565. The corrosion losses had been estimated by gravimetric evaluation after removal of corrosion product layers by pickling according to ISO 8407.

### 2.1 Carbon steel

Standard flat samples with dimension 100 x 150 x 1 mm are made from carbon steel 1.0338 according to EN 10130 (C < 0,08 %, P < 0,03 %, Mn < 0,40 %, S < 0,03 %).

The trend in yearly corrosion loss of carbon steel was estimated for 16 test sites included into program UN ECE ICP *Effect of Materials* since 1987 – Figure 3. In period 1987 – 2009 nine repeated one-year exposures were performed. The trend of decreasing of yearly corrosion loss of carbon steel is exponential except for rural test sites where it is linear. The most significant decreasing trend of yearly corrosion loss of carbon steel occurred for industrial test site where the decreasing of $SO_2$ pollution had been more radical (see Figure 1).

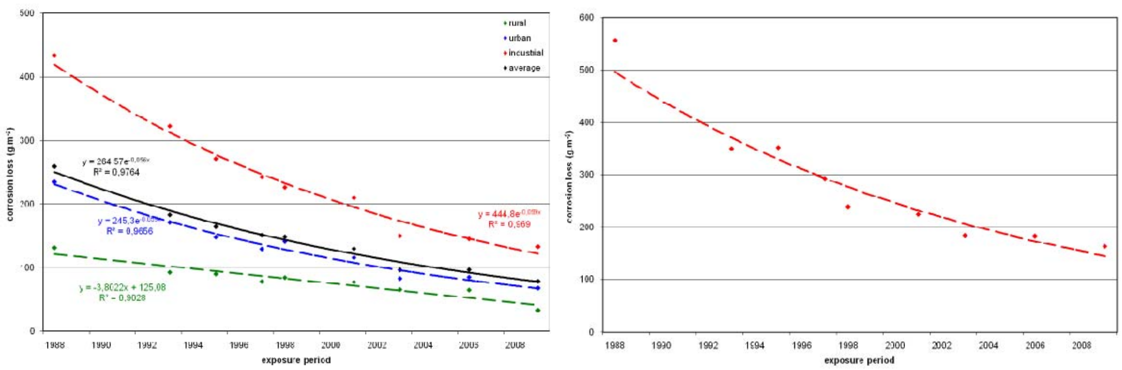


**Figure 3:** Yearly corrosion loss of carbon steel decreasing at European test sites (ICP program) and at Czech industrial test site Kopisty (No 03)

In contrast to other materials, carbon steel is less sensitive to other pollutants like $O_3$ and $HNO_3$. This makes it an ideal material for assessing in more detail the concept of tolerable $SO_2$ levels. The relationship between $SO_2$ concentration and yearly corrosion loss of carbon steel is evident from Figure 4. The significance of $SO_2$ for corrosion loss of carbon steel degreased together with this trend. The relationship is not linear as for past exposure periods but exponential one and $R^2$ value of this regression equation is lower. In this environmental situation the $SO_2$ air pollution is not dominant factor for carbon steel corrosion but the effect of other environmental factors become more significant. This change affected the dose-response function which was derived from database based on data from period with higher $SO_2$ pollution.

### 2.2 Zinc

Standard flat samples with dimension 100 x 150 x 1 mm are made from cold rolled zinc sheet (98.5 w %).

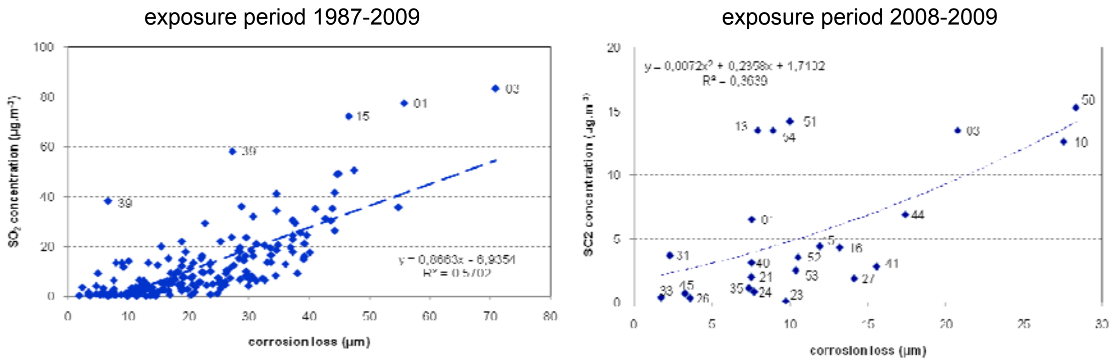


**Figure 4:** The plot of $SO_2$ concentration and yearly corrosion loss of carbon steel (all test sites)

The trend in yearly corrosion loss of zinc was estimated for 16 test sites included into program UN ECE ICP *Effect of Materials* since 1987 – Figure 5. In period 1987 – 2009 seven repeated one-year exposures were performed. The data are less systematic because the $SO_2$ is not the only dominant factor for corrosion of zinc, mainly for one-year exposure. In this short period the effect of humidity condition is very important too. The trend of decreasing of yearly corrosion loss of zinc was exponential.

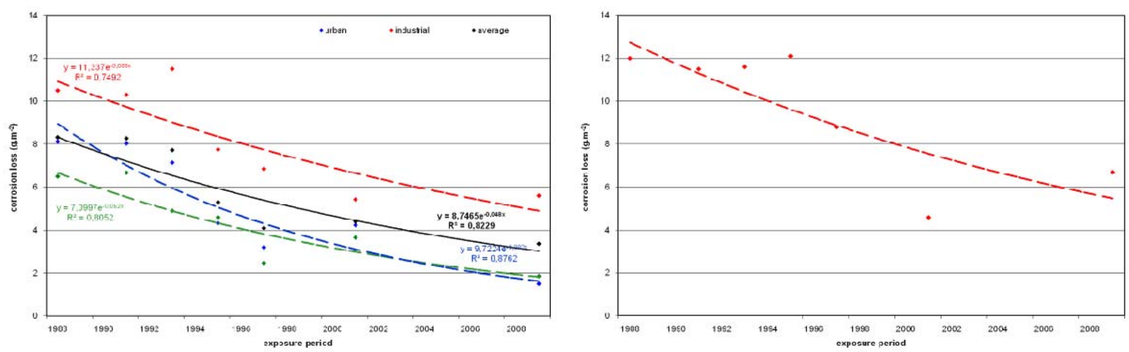


**Figure 5:** Yearly corrosion loss of zinc decreasing at European test sites (ICP program) and at Czech industrial test site Kopisty (No 03)

The relationship between $SO_2$ concentration and yearly corrosion loss of zinc is evident from Figure 6. All values which are above the trend line belong to data from industrial test sites in the periods with high $SO_2$ pollution. For contemporary environmental situation there are not enough data for similar relationship estimation.

## 2.3 Copper

Standard flat samples with dimension 100 x 150 x 1 mm are made from cold rolled copper sheet (99,8 w %).

In period 1987 – 2009 only two repeated one-year exposures were performed, and one other exposure was performed at the Czech atmospheric test sites in frame of national program. The trend in yearly corrosion loss of copper was estimated for 16 test sites included into program UN ECE ICP *Effect of Materials* since 1987 – Figure 7. The results are affected by limited number of corrosion loss data.

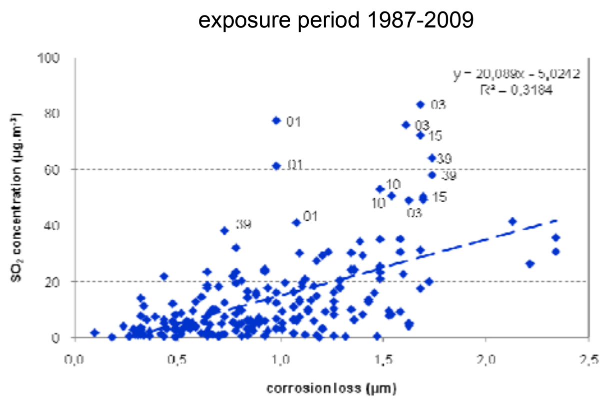


**Figure 6:** The plot of $SO_2$ concentration and yearly corrosion loss of zinc (all test sites)

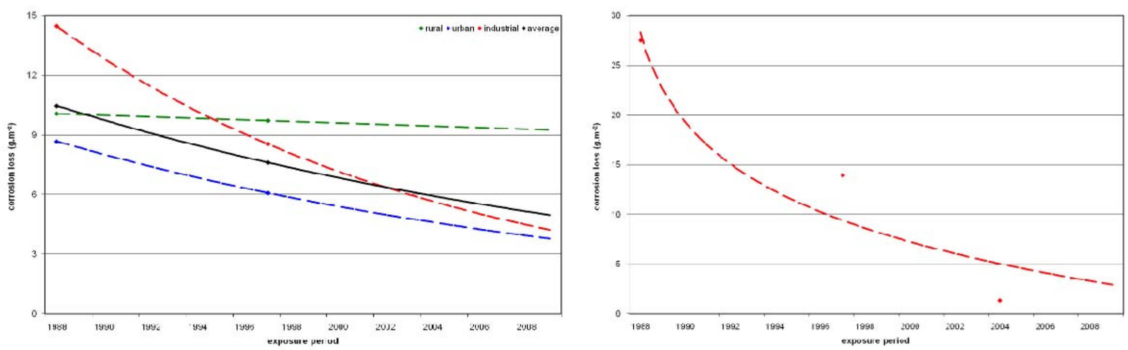


**Figure 7:** Yearly corrosion loss of copper decreasing at European test sites (ICP program) and at Czech industrial test site Kopisty (No 03)

# 3 Long-term corrosion loss of structural metals

The decreasing of corrosion loss was estimated not only for yearly values but for long-term exposure too. The number of long-term exposure of structural metals exposed at changed environmental conditions is limited. The zinc and copper had been exposed in the frame of UN ECE ICP *Effect of Materials* but only for 8 resp. 4 years and carbon steel had not been exposed. The Czech national programs give more data for comparison and evaluation of the trends for all structural metals, especially at industrial atmospheres.

## 3.1 Long-term corrosion loss of structural metals in stable environment

During 90ties the changes of $SO_2$ concentration in the Czech Republic were very significant and rapid and the pollution situation was not stable. Since 2000 the decreasing of $SO_2$ is practically stopped. In contemporary stabilised environmental situation the 5 years´ exposure had been evaluated only yet. The long-term corrosion loss of carbon steel and copper has logarithmic behaviour and after decreasing of $SO_2$ concentration the slope of a curve aproximates to linear behaviour – Figure 8.

The long-term corrosion loss of zinc has linear behaviour. The long-term corrosion loss of structural metals is compared for 3 Czech atmospheric test sites in stable pollution situation before and after $SO_2$ reduction.

### 3.2 Long-term corrosion loss of structural metals in changing environment

The actual corrosion rate of structural metals quickly reacts on decreasing of $SO_2$. The surfaces exposed in high polluted environment slowed the corrosion rate in case of $SO_2$ pollution had been reduced in atmosphere.

In period 1970 – 1990 test site Kopisty was affected by air pollution from industrial plants, mainly $SO_2$. At the test site Kopisty the zinc and copper had been exposed for 20 and 25 years from 1981 to 2006. The environmental parameters were relatively stable for this period with exception of $SO_2$ air pollution and pH of precipitation which followed the changes in air pollution of $SO_2$. During this period the yearly value of $SO_2$ air pollution decreased from 145 $\mu g.m^{-3}$ to 11 $\mu g.m^{-3}$ in 2003, respectively 19 $\mu g.m^{-3}$ in 2006 (Table 1) [8].

**Table 1**: The yearly average values of environmental parameters at test site Kopisty

| year | T (°C) | RH (%) | $SO_2$ ($\mu g.m^{-3}$) | $NO_x$ ($\mu g.m^{-3}$) | rain (mm) | pH of precipitation |
|---|---|---|---|---|---|---|
| 1980 | 7,6 | 75,4 | 145,2 | - | 519,8 | - |
| 1990 | 9,7 | 70,8 | 67,4 | 31,7 | 397,8 | 4,9 |
| 2000 | 10,2 | 76,3 | 15,8 | 27,6 | 486,2 | 4,7 |
| 2006 | 8,9 | 76,4 | 14,8 | 25,7 | 405,5 | 6,0 |

The corrosion losses of this exposure started at environment with high $SO_2$ pollution and ca in the middle of exposure the $SO_2$ pollution significantly deceased in 2 – 3 years. During the exposure period the corrosion rate of exposed metals decreased as a result of decreasing $SO_2$ (Figure 9) and in comparison to previous periods shown significant visual change. The results show that the metals quickly react on decreasing of $SO_2$. They also show that not only the new exposed metals but the surfaces exposed in high polluted environment slowed the corrosion rate in case of $SO_2$ pollution had been reduced in atmosphere. It is very important for prediction of service life of existing structures or objects.

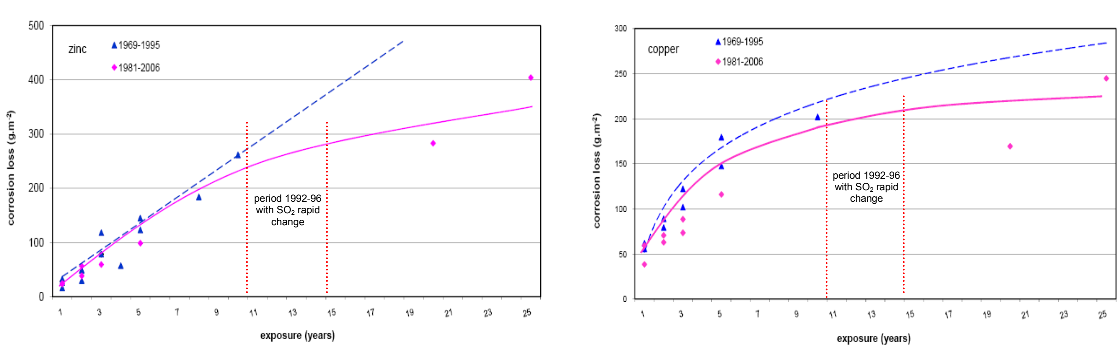


**Figure 9:** Changes in long-term corrosion behaviour of zinc and copper in atmosphere with changing

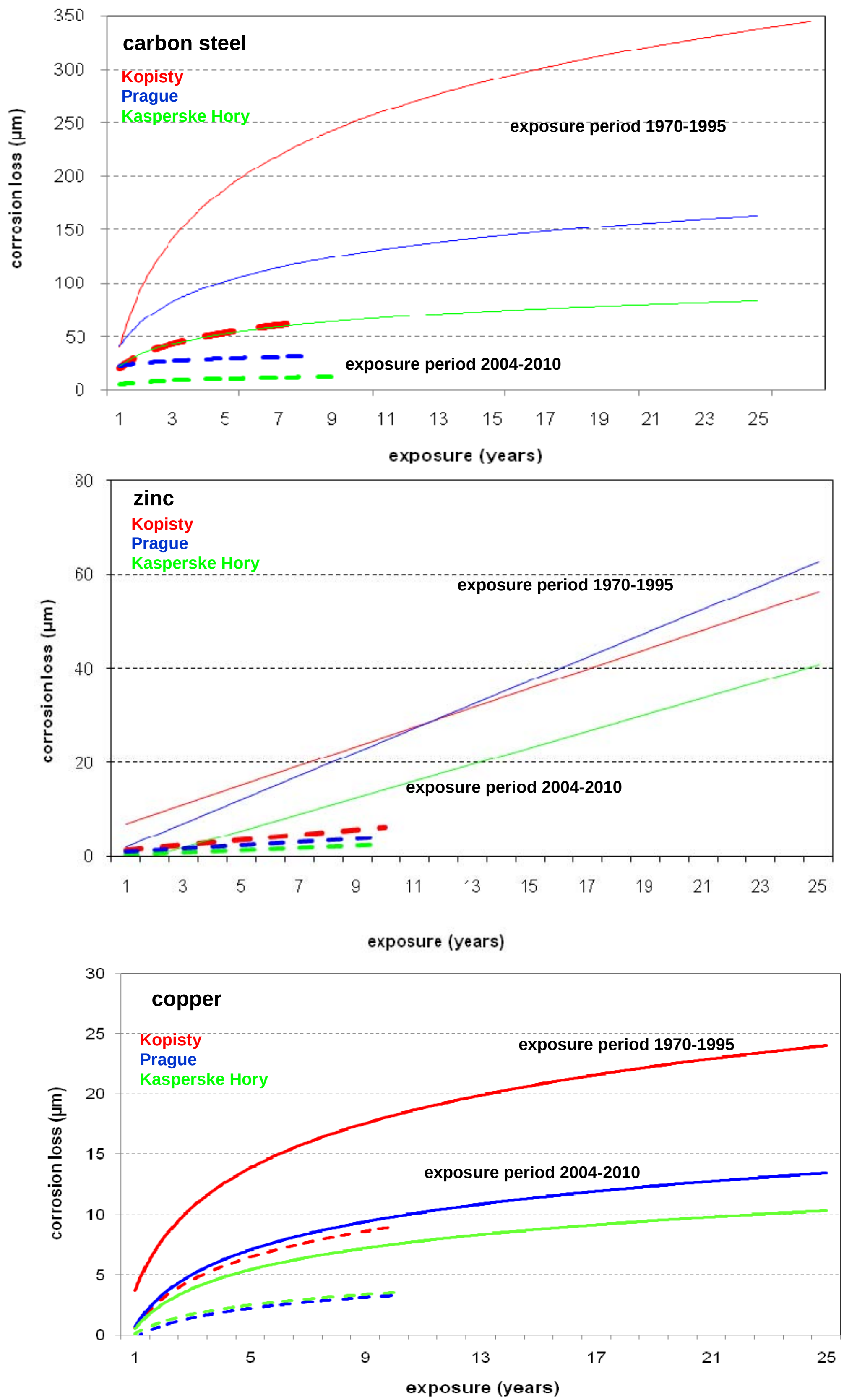


**Figure 8:** Trend of long-term corrosion loss of structural metals at Czech test sites

## Conclusion

The data from UN ECE ICP *Effect of Materials* and other programs had been used for dose-response functions derivation for atmospheric corrosion loss [9]. All these functions had been derived in environmental situation with higher $SO_2$ air concentration.

In Table 2 the comparison of 1, 3 and 5 years exposure values for carbon steel, zinc and copper is given for values determinated from standard specimens (exposure period 2004-2010 at Czech atmospheric test sites) and various calculation methods.

**Table 2:** The comparison of real and calculated corrosion loss of carbon steel, zinc and copper (2004-2010) at Czech atmospheric test sites

| test site | exposure period (years) | corrosion loss (µm) | | |
|---|---|---|---|---|
| | | determination on standard specimens according to ISO 9226 | calculated according to ISO 9223 and ISO 9224 equations | calculated according to UN ICP equations |
| ***carbon steel*** | | | | |
| Prague | 1 | 12,8 | 18,3 | * |
| | 3 | 17,8 | 22,7 | * |
| | 5 | 23,6 | 29,6 | * |
| Kopisty | 1 | 23,3 | 32,6 | * |
| | 3 | 36,2 | 41,4 | * |
| | 5 | 59,1 | 54,1 | * |
| ***zinc*** | | | | |
| Prague | 1 | 0,45 | 1,00 | 1,21 |
| | 3 | 0,95 | 2,61 | 3,00 |
| | 5 | 1,52 | 4,18 | 4,61 |
| Kopisty | 1 | 1,28 | 1,25 | 1,23 |
| | 3 | 2,22 | 2,88 | 3,69 |
| | 5 | 3,63 | 4,39 | 5,29 |
| ***copper*** | | | | |
| Prague | 1 | 0,31 | 0,62 | 0,79 |
| | 3 | 0,75 | 5,54 | 2,49 |
| | 5 | 1,30 | 9,34 | 4,30 |
| Kopisty | 1 | 1,34 | 0,82 | 0,98 |
| | 3 | 2,97 | 8,01 | 3,49 |
| | 5 | 5,52 | 12,09 | 5,38 |

Note: ISO equations are given in ISO/FDIS 9223 and ISO/FDIS 9224. For carbon steel no dose-response function was derived from UN ECE ICP *Effect of Materials.* Into Table 2 the statistical uncertainty is not included, in general it is ca 2 – 5 % for estimated values and 30 – 50 % for calculated values.

In contemporary European atmospheres the $SO_2$ air pollution is not dominant factor for structural metals´ corrosion but the effect of other environmental factors become more significant. Field studies have shown that exist limiting value of $SO_2$ pollution above which the $SO_2$ effect is dominant – Figure 10. This value is different for carbon steel and for zinc (there are limited values for copper). Probably the dose-response functions for prediction of atmospheric corrosion loss should be modified for two $SO_2$ values similar as it is derived for temperature.

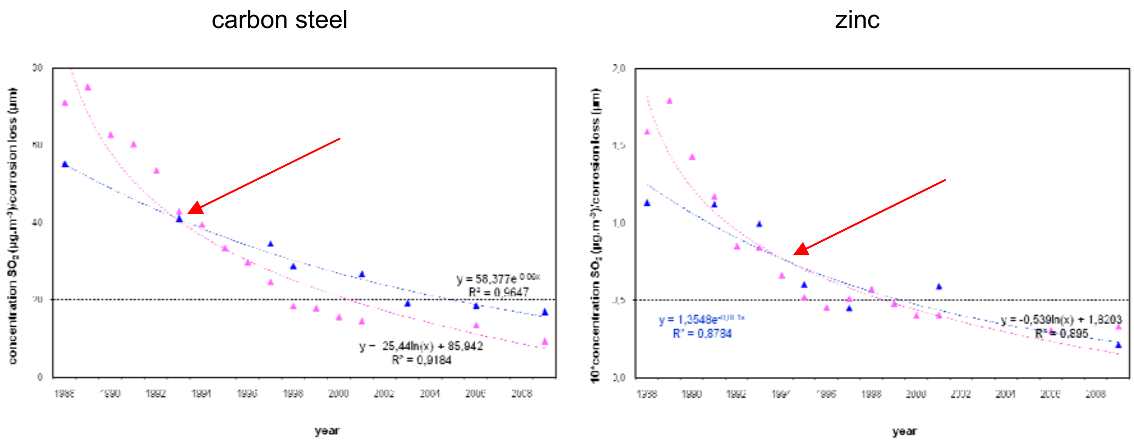


**Figure 10:** The trend of $SO_2$ concentration and yearly corrosion losses of carbon steel and zinc

These dose-response functions - mathematical functions - are of limited use to describe the short-term and long-term atmospheric corrosion which is non-linear process depending on various environmental parameters. It is necessary to obtain large set of corrosion and environmental data for conditions with low $SO_2$ air pollution.

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