Dose-response function for zinc obtained from a four-year exposure programme in Switzerland

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Dose-response functions for zinc were obtained from a four-year exposure programme within Switzerland. Material loss for zinc was investigated at seven sites in Switzerland. The exposure sites were chosen near the stations of the National Air Pollution Monitoring Network (NABEL), where climatic and air pollution data are measured. Material loss was investigated gravimetrically after one, two and four years of exposure.

The resulting dose-response function shows a critical contribution of ozone in addition to sulphur dioxide to the corrosion of zinc. The growing demand for environmental protective actions has led to lower atmospheric sulphur levels as a result of the use of cleaner heating oil and sophisticated gas emission controls. This has increased the relative importance of other atmospheric pollutants like ozone or nitrous oxide for the corrosion of metallic materials. The calculated amount of zinc in runoff is about 60 % of the total material loss through corrosion after four years of exposure.

Introduction

One of the most important effects of air pollution on materials is the accelerated corrosion of metals. Atmospheric corrosion of metals is known to be an electrochemical process governed by several factors, among others: the time of wetness and the chemical composition of the atmosphere. Atmospheric pollutants reach the surface of exposed materials, including dry

and wet deposition and incorporate into the overlying moisture layer. Dry deposition involves adsorption of gases on the surface of exposed materials and impaction of particulate material. Wet deposition involves removal of gases and aerosols from the atmosphere and deposition over exposed materials by precipitation [1]. Dose-response functions (DRFs) correlate climatic and air pollution parameters with the corrosion of metals [2]. Laboratory and outdoor exposure investigations give clues about the corrosiveness of single and combined atmospheric and climatic parameters [3, 4, 5, 6].

In the UN/ECE Programme, effects of air pollution on materials and buildings, including historic and cultural heritage, have been investigated for 39 sites in Europe, Canada and the United States [7]. DRFs, which were developed within this investigation, can be applied on sites within Switzerland. Calculated material losses obtained with the DRFs form the UN/ECE programme don't give a very accurate prediction of the real material loss within Switzerland, which are presented in this paper. And vice versa, dose-response functions for Switzerland are not applicable for the whole of Europe, because they give very inaccurate predictions for sites with high SO_2 pollution level. Therefore, dose-response functions for the special pollution and climatic situation of Switzerland were developed. The goal of the present paper is a) to present results of total corrosion loss and material loss in runoff for zinc metal during a four-year exposure programme in Switzerland; b) to present and discuss dose-response functions obtained from this four-year exposure programme.

Methods

Exposure sites
Field exposure sites were chosen near the Swiss National Pollution Monitoring Network (NABEL) [8]. Air pollutants and climatic parameters are continuously measured at these sites. Urban (Bern), suburban (Dübendorf), rural (Payerne, Sion, Cadenazzo), forest (Lägern, Davos) and sites close to highways (Härkingen) have been chosen all over Switzerland to cover a variety of environmental conditions. Samples were exposed in the immediate vicinity of the air pollution monitoring stations.

The average pollutant concentrations for the first year of exposure are given in *Table 1*. The average pollutant concentrations for the two- and four-year exposure periods are given in *Table 2* and *3* respectively. Time of wetness is defined as the time when the rel. humidity $>80\%$ and the tem-

mean 1993	SO₂ µg/m³	NO₂ µg/m³	O₃ µg/m³	tempe- rature °C	rel. humidity %	wind velocity m/sec	time of wetness/ exposure time
Dübendorf	8	33	33	9.8	76	1.3	0.431
Lägern	2.8	15	60	7.9	79	2.2	0.410
Härkingen	10	40	22	9.4	79	2.2	0.497
Bern	8	57	8	9.7	74	1.9	0.406
Payerne	3	18	44	9.3	78	2.1	0.456
Sion	4	34	32	10.3	68	2.3	0.235
Cadenazzo	9	26	38	10.9	73	1.6	0.395
Davos	1.4	5.2	66	3.7	68	1.9	0.246

Table 1: Environmental conditions at the different test sites for the two-year exposure period (mean values for the respective test periods).

mean 1993– 1994	SO₂ µg/m³	NO₂ µg/m³	O₃ µg/m³	tempe- rature °C	rel. humidity %	wind velocity m/sec	time of wetness/ exposure time
Dübendorf	7	32	35	10.5	76	1.3	0.458
Lägern	2.8	15	60	8.7	80	2.2	0.436
Härkingen	9.5	41	23	10.2	64	2.2	0.515
Bern	7.5	58	9	10.5	74	1.9	0.415
Payerne	2.5	17	46	10.0	79	2.1	0.495
Sion	4	35	31	10.8	70	2.3	0.283
Cadenazzo	8.5	25	39	11.6	73	1.6	0.424
Davos	1.3	5.0	67	4.3	69	1.9	0.252

Table 2: Environmental conditions at the different test sites for the four-year exposure period (mean values for the respective test periods).

mean 1993– 1994	SO₂ µg/m³	NO₂ µg/m³	O₃ µg/m³	tempe- rature °C	rel. humidity %	wind velocity m/sec	time of wetness/ exposure time
Dübendorf	6.8	33	36	9.9	77	1.2	0.439
Lägern	2.9	16	60	8.1	79	2.1	0.414
Härkingen	8.3	39	26	10.1	70	2.1	0.468
Bern	7	57	11	10.1	74	1.9	0.384
Payerne	2.3	18	48	9.5	79	2.1	0.480
Sion	3.5	35	33	10.4	70	2.2	0.297
Cadenazzo	7.8	25	42	11.8	72	1.7	0.427
Davos	1.3	4.9	68	3.8	70	1.9	0.261

Table 3: Environmental conditions at the different test sites for the four-year exposure period (mean values for the respective test periods).

perature $>0\,°C$. For our calculations we used the parameter TOW, which is the ratio of time of wetness over exposure time.

Exposed materials
Zinc plates $(99,99\%)$ 5×10 cm in size and 1 mm in thickness were used. The samples were degreased in petrol and glass blasted before exposure. After exposure corrosion products were removed using an adequate pickling solution [4, 5].

Investigation methods
The evaluation is based on gravimetric measurements of the samples. The mass of corrosion products retained on the surface and material loss were determined by weighing test specimens before exposure, after exposure and after removal of the corrosion products. Chemical composition of the corrosion products was determined by X-ray diffraction (XRD) [9].

Dose-response functions
a) Choice of environmental parameters
The measured environmental data include the following parameters: temperature, rel. humidity, wind velocity and time of wetness/exposure time; gaseous pollutants: SO_2, NO_2 and O_3. Not all of these were used in the final dose-response functions. A Spearman Rank correlation was done to investigate correlation between environmental parameters [10]. The correlation matrix (Table 4) shows a strong negative correlation for NO_2 and O_3. NO_2 was therefore excluded from the further statistical analysis [7].

The general knowledge of atmospheric corrosion together with the results of the statistical analysis (pair correlation coefficient, stepwise regression analysis) prove that SO_2, TOW and ozone are the important factors of the corrosion of zinc.

	SO_2	NO_2	O_3	tempe-rature	rel. humidity	wind velocity	TOW
SO_2	1	0.75	−0.76	0.63	−0.09	−0.19	0.38
NO_2	0.75	1	−0.99	0.56	−0.16	0.05	0.2
O_3	−0.76	−0.99	1	−0.55	0.15	−0.05	−0.2
temperature	0.63	0.56	−0.55	1	−0.27	−0.16	0.1
rel. humidity	−0.09	−0.16	0.15	−0.26	1	−0.08	0.51
wind velocity	−0.19	0.05	−0.05	−0.08	−0.77	1	−0.04
TOW	0.38	0.2	−0.2	0.51	0.51	−0.04	1

Table 4: Spearman Rank correlation matrix for environmental data for the four-year exposure period 1993–1996.

b) Choice of mathematical form for dose-response relations
It was argued that a response function must rely primarily on physicochemical factors and their combination. This means in other words, that DRFs should reflect the physicochemical nature of atmospheric corrosion and the contribution of each individual parameter to the overall effect. In fact, DRFs in which the level of SO_2 and time of wetness/exposure time (TOW) are considered as independent parameters and those where the corrosion effect is treated as their combined action SO_2*TOW give various results on SO_2 corrosiveness [11]. SO_2 as a corrosive agent on zinc is highly depending on the relative humidity or TOW at that time, we believe that a statistical analysis (multiple linear regression) should be done with the combination of SO_2 and TOW or RH respectively.

c) Time dependence of dose-response relations *(Table 5)*
The time dependence of the corrosion loss of zinc was expressed by exponential functions $ML=a*t^b$, where «a» corresponds to the idealised one year mass loss, 'b' is a measure for the degree of passivation and «t» is exposure time in years. The lower the value of b the higher the decrease for the degree of the mass loss rate with longer exposure time.

Exposure time t (years):	1	2	4	a	b	R^2
Dübendorf	1.27	1.78	2.72	1.25	0.55	0.99
Lägern	1.03	1.49	2.40	1.01	0.61	0.99
Härkingen	2.25	3.66	5.57	2.27	0.66	0.99
Bern	1.25	1.74	2.55	1.23	0.52	0.99
Payerne	1.41	1.88	2.56	1.4	0.43	0.99
Sion	1.55	2.21	2.55	1.61	0.36	0.94
Cadenazzo	2.20	3.17	4.86	2.17	0.57	0.99
Davos	0.82	1.38	1.78	0.86	0.56	0.96

Table 5: Time dependence of corrosion loss in μm after 1, 2 and 4 years of exposure, corrosion loss $= a*t^b$; t = time (years), R^2 = correlation coefficient.

Results and discussion

The results of material loss for zinc for 1, 2 and 4 years of exposure are presented in *Table 6*. Material loss was determined gravimetrically.

Material loss
After four years of exposure material loss is between $12,7 g/m^2$ and $39,8 g/m^2$ *(Table 6)*. Highest material losses for zinc were found in Härkingen, where the SO_2 concentration is highest (Table 1–3). A lowest corrosion loss was found for Davos, where a low SO_2 concentration is combined

with a low rel. humidity. In the first year of exposure material loss per year is much higher than in the following years. This is true for all test sites.

Material Exposure duration (years)	Zn 1	2	4
Dübendorf	9.07	12.71	19.43
Lägern	7.35	10.61	17.12
Härkingen	16.05	26.14	39.80
Bern	8.89	12.40	18.24
Payerne	10.03	13.43	18.28
Sion	11.08	15.77	18.22
Cadenazzo	15.68	22.63	34.70
Davos	5.89	9.85	12.71

Table 6: Corrosion loss in g/m² of zinc plates after 1, 2 and 4 years exposure.

Runoff of zinc metal

To estimate the ecological influence of zinc corrosion we need to know the effective runoff of metallic material to the environment. After four years of exposure $8-24$ g/m² of zinc metal are washed away into the environment *(Table 7)*. These amounts correspond to about 60% of the total amount of corrosion products. The left over corrosion products are held back on the metal plate. The runoff metallic material was calculated by comparing the held back corrosion products to the theoretical amount of corrosion products. The corrosion products were identified as hydrozincite $Zn_5(CO_3)_2 (OH)_6$. With this information the theoretical amount of corrosion products can be calculated from the total corrosion loss of metallic zinc. The mass of held back corrosion products was determined by weighing test specimen before pickling and after pickling.

Material Exposure duration (years)	Zn 1	2	4
	g/m² (%)	g/m² (%)	g/m² (%)
Dübendorf	4.29 (47)	7.11 (56)	12.32 (63)
Lägern	3.54 (48)	5.81 (55)	10.98 (64)
Härkingen	7.08 (44)	13.67 (52)	23.79 (60)
Bern	3.34 (38)	6.08 (49)	10.49 (58)
Payerne	3.91 (39)	6.80 (51)	10.60 (58)
Sion	4.82 (43)	7.90 (50)	10.72 (59)
Cadenazzo	7.40 (47)	12.99 (57)	22.48 (65)
Davos	2.24 (38)	5.03 (51)	7.93 (62)

Table 7: Runoff of corroded zinc into the environment after 1, 2 and 4 years exposure; in g zinc/m² of exposed material and in (%) of total corrosion loss.

Dose-response functions

In general the material loss is continually increasing during the four years of outdoor exposure. The corrosion rate is not linear in time *(Table 5)*. The corrosion of zinc is highly depending on the SO_2 concentration combined with a high TOW parameter [14]. Wind velocity in combination with SO_2 and TOW is a further parameter that has an influence on the atmospheric corrosion of zinc [10]. Ozone and sulphur dioxide show a strong synergistic effect if SO_2 concentration in the atmosphere is low [14]. But the corrosiveness of SO_2 combined with ozone is also depending on the rel. humidity. In 70 % rel. humidity the synergistic effect is much smaller compared to 95 % rel. humidity [14]. Svensson, Johansson and Oesch [5, 14] reported small or negligible effects of ozone on zinc. Therefore we didn't consider ozone as an addend in the dose-response function DRF Nr. 1. NO_2 was ignored in the following dose-response functions for the following reasons: Ozone and NO_2 are strongly anticorrelated *(Table 4)*. Therefore the influence of NO_2 on the corrosion of steel can mathematically be described by the influence of the ozone parameter. The chemical reason for this strong anticorrelation is the following reaction: $NO + O_3 \rightarrow NO_2 + O_2$. [12, 13].

Nr	Dose-response function	R²
1	ML (µm) = 0.33 +0.38*SO_2*TOW*v*$t^{0.53}$ – 0.5* SO_2*TOW*$t^{0.53}$ + 0.00007* SO_2*O_3*RH* $t^{0.53}$	0.87
2	ML (µm) = 0.64 + 0.28*SO_2*TOW*SO_2*4 + 0.000035* $t^{0.53}$*O_3*RH*$t^{0.53}$	0.69
3	ML (µm) = 0.93 + 0.395*SO_2*TOW*$t^{0.53}$	0.63

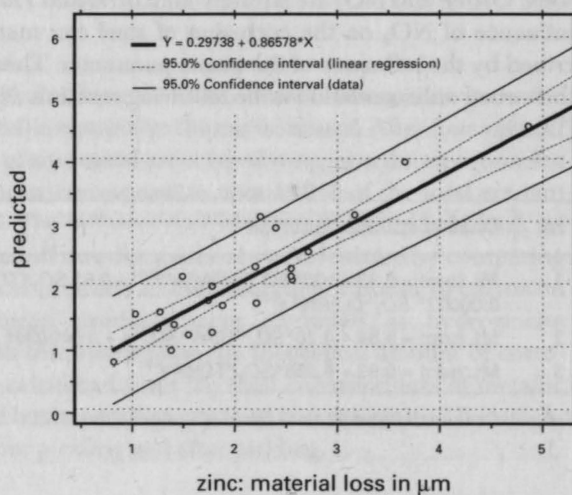*Table 8: Dose-response functions for total material loss (ML).*

As it is shown in DRF Nr. 1 *(Table 8)* material loss for zinc can be quite accurately predicted with a correlation coefficient of $R^2 = 0.87$ *(Figure 1)*. The question is therefore, whether a simpler function, which considerates less parameters, could do as well as DRF Nr. 1. If the wind velocity is disregarded, we get DRF Nr. 2. The influence of the wind velocity seems to be quite important. Dose-response function Nr. 2 predicts material loss less accurately than DRF Nr. 1 with a correlation coefficient of $R^2 = 0.69$ instead of $R^2 = 0.87$ (DRF Nr. 1).

If the addend SO_2*O_3*RH* $t^{0.53}$ and the wind velocity are disregarded, we get DRF Nr. 3 with a correlation coefficient of $R^2 = 0.63$. The correlation of observed versus predicted material loss is less accurate compared to DRF Nr. 1 and 2. This finding proves the influence of the synergetic effect of SO_2 combined with O_3 and RH.

Conclusions

The resulting dose-response functions show a critical contribution of ozone in addition to sulphur dioxide to the corrosion of zinc. The growing demand for environmental protective actions has led to lower atmospheric sulphur levels as a result of the use of cleaner heating oil and sophisticated gas emission controls. This has increased the relative importance of other atmospheric pollutants like ozone or nitrous oxide for the corrosion of metallic materials after four years of exposure. The monitoring of dose-response predictions can serve as a confirmation of the correctness of reduction strategies for pollutants. The amount of zinc in runoff is between 58 – 65 % of the total material loss through corrosion after four years of exposure.

Figure 1: Effective material loss for zinc in µm versus predicted material loss, calculated with dose-response function DRF Nr. 1; for all investigated test sites and exposure times (1, 2, 4 years).

Plot legend:
Y = 0.29738 + 0.86578*X
95.0% Confidence interval (linear regression)
95.0% Confidence interval (data)

Y-axis: predicted
X-axis: zinc: material loss in µm

Acknowledgements

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