

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

Report No 30:
Statistical analysis of
8 year materials exposure
and acceptable deterioration and pollution levels

Compiled by the
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1 Introduction

This report summarizes all results obtained from an extensive field exposure programme within the United Nations Economic Commission for Europe (UN ECE). It was started in September 1987 and involves 39 exposure sites in 12 European countries and in the United States and Canada.

The aim of the programme is to perform a quantitative evaluation of the effect of sulphur pollutants in combination with NO_x and other pollutants as well as climatic parameters on the atmospheric corrosion of important materials. This is achieved by measuring gaseous pollutants, precipitation and climate parameters at or nearby each test site and by evaluating the corrosion effects on the materials.

A Task Force is organizing the programme with Sweden as lead country and the Swedish Corrosion Institute serving as the Main research centre. Subcentres in different countries have been appointed, each responsible for their own group of materials, including structural metals, stone materials, paint coatings, electric contact materials, glass materials and polymer materials. Figure 1 shows a map of the test sites located in Europe.

It would not have been possible to complete the programme without the efforts and financial supports of individual countries. Throughout the programme, many individuals have contributed to the programme, listed by country as follows:

Austria

Mr Manfred Schreiner
Mr Gebhard Woisetschläger

Canada

Mr Jean Jaques Hechler

Czech Republic

Mrs Dagmar Knotkova
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United Kingdom

Mr Tony Coote
Mr Roy Butlin
Mr Tim Yates
Mr Geoffrey Ashall
Mr Stephen Massey

USA

Mr J W Spence

This report comprises three main parts. The first part, sections 2-5, gives a summary of the results of corrosion and environmental data obtained and a description of the uniform statistical evaluation of data after 8 years of exposure. Section 2 summarizes decisions made on procedures for statistical analysis and section 3 gives an overview of experimental data. Section 4 describes the uniform statistical analysis and includes the final dose-response functions for mapping and calculation of costs. Finally, section 5 shows the application dose-response functions for calculation of acceptable deterioration and pollution levels. The second part, section 6, summarizes results and analyses performed at the sub-centres. A number of substantial reports have been produced within the programme and an executive summary of each final report is presented. The third part, section 7, summarizes the evaluation of trends of pollution and material deterioration during the eight year period.

Country	No Site
Czech Republic	1 Prague-Letnany
	2 Kasperske Hory
	3 Kopisty
Finland	4 Espoo
	5 Ähtäri
	6 Helsinki-Vallila
Germany	7 Waldhof-Langenbrügge
	8 Aschaffenburg
	9 Langenfeld-Reusrath
	10 Bottrop
	11 Essen-Leithe
12 Garmisch-Partenkirchen	
Italy	13 Rome
	14 Casaccia
	15 Milan
	16 Venice
Netherlands	17 Vlaardingen
	18 Eibergen
	19 Vredepeel
	20 Wijnandsrade
Norway	21 Oslo
	22 Borregard
	23 Birkenes
Sweden	24 Stockholm South
	25 Stockholm Centre
	26 Aspvreten
United Kingdom	27 Lincoln Cathedral
	28 Wells Cathedral
	29 Clatteringshaws Loch
	30 Stoke Orchard
Spain	31 Madrid
	32 Bilbao
	33 Toledo
Russian F.	34 Moscow
Estonia	35 Lahemaa
Portugal	36 Lisbon
Canada	37 Dorset
USA	38 Research Triangle Park
	39 Steubenville

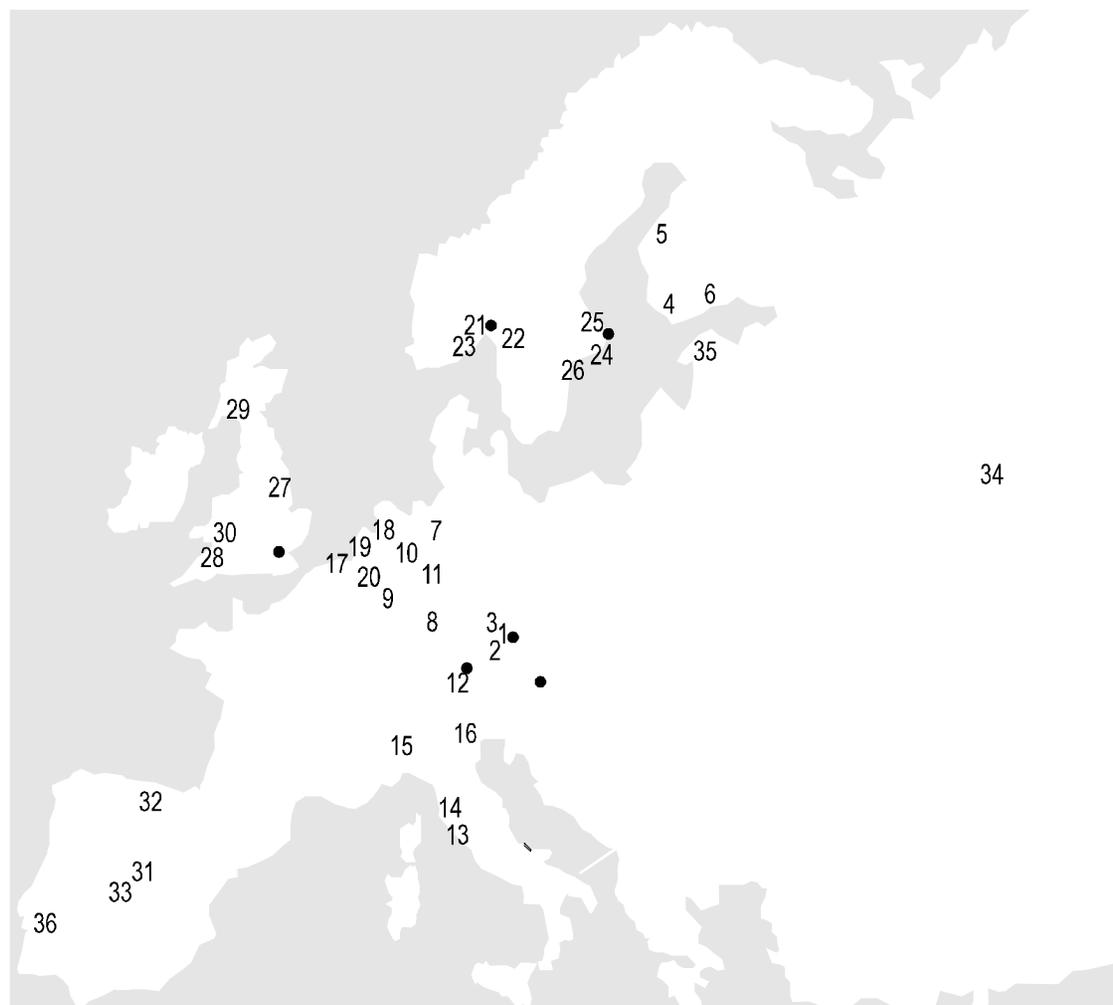


Figure 1 List of sites and map showing the approximate locations of European sites in the UN ECE exposure program. The research centers, responsible for the evaluation, are also indicated (●).

2 Guidelines for statistical evaluation

This section contains a summary of general guidelines for the statistical treatments performed at the individual subcentres. They are based on decisions made at the “Workshop on Joint Final Evaluation”, held in Garston, Watford, United Kingdom, January 13-15, 1997 and the thirteenth meeting of the Programme Task Force, held in Rome, Italy, May 20-22, 1997.

2.1 Descriptive statistics for corrosion data

All corrosion data were described in tables including mean values of triplicates and standard deviation of triplicates, if applicable. Values based on duplicates or single values were clearly indicated.

Plots of corrosion data, such as bar graphs on individual sites including corrosion data after 1, 2, 4, and 8 years of exposure were given as illustrations. This applies also for probability plots including number of observations (N) and statistical tests for normality.

2.2 Statistical analysis of corrosion data

Correlation analysis and multiple linear regression were the basis for the statistical analysis. For regression analysis the explained variability (R^2) and the significance of individual parameters (T-values) were given. Principal component analysis (PCA) and other projection techniques were sometimes used.

In preliminary analyses the conductivity of precipitation resulted frequently in dose-response functions with high explained variability. However, conductivity is a parameter highly correlated to SO_2 . This may lead to a decrease in the estimated SO_2 effect when conductivity is added to an equation, i.e., the SO_2 effect is underestimated. Therefore, it was decided to exclude conductivity from the final statistical analysis.

The difficulty and cost in obtaining time of wetness (TOW) data lead to the exclusion of TOW from the final statistical analysis. Also the general relevance of the way TOW is calculated ($RH > 80\%$ and $T > 0^\circ C$) was questioned, especially for other materials than metals for purpose of which the concept was originally developed.

2.3 Evaluation of time dependence

For each material and exposure condition it was clearly stated if the average corrosion rate decreases, is constant or increases. If the kinetics are approximately linear the data can be examined for the purpose of finding effects of decreasing pollution concentrations in Europe.

When evaluating the time dependence, several procedures were used. First, the same type of dose-response relation was evaluated for different exposure times and the time dependence of the estimated parameters investigated. Second, the four data points (1, 2, 4 and 8 years of exposure) from each site were used to obtain new parameter(s) which were then analyzed. For example, the data were fitted to the expression At^n with A and

n as the new parameters. The third possibility was to use time as a parameter no different from the others, i.e., a data table with 4x39 observations was created, and e.g. time or ln(time) used as an explanatory variable in the regression.

2.4 Treatment of extreme values, outliers and missing values

The term 'extreme value' is used to describe a deviation from the mean value of a set of observations. The term 'outlier' is used to describe an observation that has a large distance to the current model that is discussed. In other words, outliers are the extreme values of the residuals (differences between observed and predicted values) for a given model. Outliers or extreme values were excluded for reasons described below.

The site Clatteringshaws Loch was excluded from the statistical evaluation due to lack of environmental data. This is the only site excluded prior to the evaluation.

Obvious errors in raw data, evident after inspection of laboratory notes were a reason for exclusion from the evaluation. Appropriate information was included in the report.

If the resulting dose-response relation that includes the outlier(s) only expresses the difference between the outlier(s) and the main bulk of observations an alternative equation was frequently calculated without the outlier(s). This was for example the case when the outlier also was an extreme value not coinciding with the remaining trend in the data.

2.5 Requirements for all final dose-response relations

The physical/chemical interpretations of the dose-response functions are discussed in the text. The number of observations (N), the explained variability (R^2) and the reason for excluding data points (lack of environmental data, outliers, etc.) are also included as well as plots of observed vs. predicted values.

3 Description of data

3.1 Environmental data

At or nearby each site environmental data were continuously measured. This includes data for gaseous pollutants (SO_2 , NO_2 and O_3), precipitation (amount, conductivity and concentration of the ions H^+ , SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , Ca^{2+} , Mg^{2+} and K^+) and climatic parameters (temperature, relative humidity, time of wetness, sunshine hours and sunshine radiation). All environmental measurements were reported and compiled by the Norwegian Institute for Air Research (NILU), Lilleström, Norway, which also controlled the quality of the data [1]. Table 1 shows the 8-year averages for the most important environmental parameters at all test sites. The data from site 29 is completely missing and this site was therefore excluded from the statistical analysis.

Table 1 List of test sites and mean values of selected environmental parameters during the eight year exposure period, September 1987 to August 1995.

Country	No Site	Climatic parameters				Gases			Precipitation						
		Temp °C	Rh %	Tow h/yr	Sun MJ/m ²	SO ₂ ←-- μg/m ³	NO ₂ μg/m ³	O ₃ --→	Rain mm	H ⁺ mg/l	SO ₄ ²⁻ mgS/l	NO ₃ ⁻ mgN/l	Cl ⁻ mg/l	Cond μS/cm	NH ₄ ⁺ mgN/l
Czech Republic	1 Prague-Letnany	9.6	75	2970	3393	53.3	29.1	41	514	0.05	7.20	2.76	2.11	52.3	
	2 Kasperske Hory	6.9	75	3103		17.1	10.2	52	798	0.09	3.78	1.97	1.21	26.2	
	3 Kopisty	9.5	73	2532	3328	67.0	34.2	38	469	0.04	15.48	3.73	2.16	80.0	
Finland	4 Espoo	5.7	79	3574	2600	8.8	22.8	45	674	0.04	1.96	0.76	1.37	31.8	
	5 Ähtäri	3.3	80	3028	2403	2.4	4.2	56	646	0.03	0.51	0.27	0.24	16.3	0.25
	6 Helsinki-Vallila	6.2	78	3512	2596	11.8	35.4	37	644	0.04	2.01	0.88	1.78	36.4	
Germany	7 Waldhof-Langenbrügge	9.5	81	4573	3094	9.6	11.0	57	572	0.04	2.03	1.79	1.60	31.4	1.04
	8 Aschaffenburg	11.7	68	3438	3369	14.8	39.5	32	667	0.02	1.99	1.22	1.60	52.2	2.20
	9 Langenfeld-Reusrath	10.9	79	4674	3128	19.4	41.5	32	728	0.03	1.43	0.66	1.49	40.2	1.07
	10 Bottrop	11.2	77	4351	3172	44.8	43.4	32	758	0.03	1.89	0.64	2.41	46.5	1.07
	11 Essen-Leithe	10.9	78	4430	3172	24.0	39.8	34	717	0.03	1.43	0.66	1.73	38.4	1.00
	12 Garmisch-Partenkirchen	7.4	83	4434	3469	5.9	13.5	53	1287	0.01	0.68	0.47	0.23	16.7	0.50
Italy	13 Rome	17.7	64	1759	4163	24.5	53.4	19	604	0.02				23.0	
	14 Casaccia	14.8	72	3577		6.0	13.7	34	717	0.01	0.83	0.13	3.16	27.6	
	15 Milan	14.8	71	3289	4782	52.8	103.6	21	975	0.04	8.56	3.88	3.47	39.2	1.64
	16 Venice	13.6	82	5005	4663	15.7	44.9	25	562	0.00	3.13	1.02	3.78	57.1	
Netherlands	17 Vlaardingen	10.6	83	5439	3176	28.2	50.7	29	817	0.03	1.42	0.56	5.08	47.1	0.92
	18 Eibergen	9.9	81	4927	3053	7.7	23.6	40	817	0.01	1.25	0.54	2.05	27.9	1.56
	19 Vredepeel	10.4	81	5074	3157	8.9	30.6	38	746	0.01	1.58	0.57	1.98	31.6	1.74
	20 Wijnandsrade	10.5	81	4948	3216	10.2	28.3	39	703	0.01	1.33	0.54	1.54	28.9	1.21
Norway	21 Oslo	7.7	71	2689	2641	8.3	52.2	27	624	0.02	1.39	0.60	1.71	30.6	0.52
	22 Borregard	6.9	76	3448		34.2	18.0	47	658	0.08	2.35	0.69	3.27	57.4	1.08
	23 Birkenes	6.5	77	3965	2826	0.9	2.8	56	1472	0.05	0.86	0.56	2.56	33.7	0.52
Sweden	24 Stockholm South	7.7	71	2993	2679	8.4	27.1	45	513	0.03	0.79	0.39	0.45	24.3	0.73
	25 Stockholm Centre	7.8	72	2993	2679	8.5	32.3	39	513	0.03	0.79	0.39	0.45	24.3	0.73
	26 Aspvreten	6.5	80	3698	2737	2.0	4.0	54	459	0.04	0.93	0.50	0.65	27.2	0.51
United Kingdom	27 Lincoln Cathedral	10.1	83	5894	3059	17.6	32.7	39	411	0.03	2.71	1.11	3.89	50.0	0.80
	28 Wells Cathedral	11.5	83	6152	3150	5.7	23.0	44	545	0.02	2.67	0.88	6.02	67.3	3.07
	29 Clatteringshaws Loch														
	30 Stoke Orchard	10.3	76	4995		14.6	38.1	35	595	0.18	1.78	0.40	3.97		0.96
Spain	31 Madrid	14.6	62	2022	4945	11.7	25.4	26	324	0.00	1.58	0.57	0.71	30.1	0.54
	32 Bilbao	14.7	74	4408	3739	24.2	34.4	38	1095	0.01	10.22	2.83	8.19	65.6	1.83
	33 Toledo	14.2	59	1766	4931	5.7	15.7	77	508	0.00	0.55	0.18	0.61	14.1	0.22
Russian F.	34 Moscow	5.9	74	2248	2810	24.3	47.1	30	710	0.00	2.34	0.15	0.65	34.0	0.60
Estonia	35 Lahemaa	6.1	82	4076	2656	0.6	3.8	56	533	0.02	0.87	0.29	0.61	17.2	0.20
Portugal	36 Lisbon	17.6	63	1181		14.1	33.6	34	743	0.00	9.51	2.16	7.61	62.4	0.65
Canada	37 Dorset	4.7	78	3265	3753	2.8	1.7	59	767	0.05	0.76	0.51	0.11	25.1	0.35
USA	38 Research Triangle Park	15.5	67	2918	4887	9.8	25.5	51	1049	0.04	0.67	0.28	0.34	21.8	0.20
	39 Steubenville	11.7	64	1736	4059	49.4	40.9	38	854	0.11	1.88	0.48	0.53	50.0	0.38

3.2 Corrosion data

Subcentres in different countries have been appointed, each responsible for their own group of materials. Each subcentre has, in addition to the evaluation of corrosion attack by established methods, performed a statistical analysis of their materials. The results from these analyses have been described in substantive reports [2-9]:

Sub-centre	Materials	Ref.
SVÚOM Praha a. s. Prague Czech Republic	<i>Structural metals</i> weathering steel zinc aluminium	2
Bavarian State Conservation Office Munich Germany	<i>Structural metals</i> copper cast bronze	3
Building Research Establishment (BRE) Garston, Watford United Kingdom	<i>Stone materials</i> limestone sandstone	4
Norwegian Institute for Air Research (NILU) Lilleström Norway	<i>Paint coatings</i> coil coated galv. steel with alkyd melamine steel panel with alkyd wood panel with alkyd paint wood panel with primer and acrylate	5
Swedish Corrosion Institute Stockholm Sweden	<i>Electric contact materials</i> nickel copper silver tin Eurocard connectors	6
Institute of Chemistry Academy of Fine Arts Vienna, Austria	<i>Glass materials</i> potash-lime-silica glass M1 (sensitive) potash-lime-silica glass M3	7
Swedish Corrosion Institute Stockholm Sweden	<i>Polymer materials</i> polyamide polyethylene	8
SVÚOM Praha a. s. Prague Czech Republic	<i>Corrosion trends</i> unalloyed carbon steel zinc	9

Table 2 shows corrosion values taken from these reports for selected materials after 8 years of exposure.

Table 2 Corrosion attack after 8 years of exposure for selected materials.

Country	No Site	w steel		zinc		aluminium		copper		bronze		limestone		sandstone		paint ^a		nickel			
		unsh	sh	unsh	sh	unsh	sh	unsh	sh	unsh	sh	unsh	sh	unsh	sh	unsh	sh	unsh	sh		
Czech Republic	1 Prague-Letnany	397	738	153	24	3.4	6.1	63.8	32.8	48.3	33.7	113.6	9.3	126.1	9.9	5.7		2598			
	2 Kasperske Hory	288	421	100	14	2.2	3.9	56.4	35.9	34.1	19.4	45.7	11.6	50.7	1.1	6.3		212			
	3 Kopisty	356	1338	184	76	5.2	8.2	109.3	86.4	117.4	72.0	156.0	13.1	145.1	-5.1	4.4		3615			
Finland	4 Espoo	431	300	109	53	3.1	3.4	30.4	15.6	25.7	14.0	48.6	-3.2	38.4	2.2	5.8		112			
	5 Ahtari	249	160	75	44	2.3	2.2	30.9	29.0	17.6	7.6	33.9	-11.0	25.1	-0.3	6.1		16			
	6 Helsinki-Vallila	497	470	136	49	5.6	7.3	30.7	19.6	36.2	20.0	82.1	-1.9	82.8	6.8	6.4		205			
Germany	7 Waldhof-Langenbrügge	494	407	110	43	2.8	4.2	63.6	37.2	36.1	30.9	44.4	6.0	47.7	4.3	5.8		135			
	8 Aschaffenburg	341	244	105	40	2.5	3.2	42.1	11.5	29.4	16.7	38.4	5.3	45.8	4.2	5.4		500			
	9 Langenfeld-Reusrath	467	336	130	22	3.6	6.3	35.5	13.5	40.3	18.7	77.7	9.9	62.8	6.6	6.1		328			
	10 Bottrop	478	517	82	19		7.2	64.7	23.6	65.2	27.1		9.3	99.6	10.0	5.2		1243			
	11 Essen-Leithe	482	460	66	24	4.5	11.1	47.4	21.0	48.2	26.3	105.9	9.1	79.8	7.7	6.0		382			
	12 Garmisch-Partenkirchen	182	209	32	5	1.8	2.7	34.9	23.4	21.0	8.1		1.9			3.5		38			
Italy	13 Rome	237	175	80	14	3.3	5.5	27.9	13.2	37.2	14.0	54.1	7.0	50.4	5.1	9.7		497			
	14 Casaccia	350	275	63	23	3.1	4.6	35.1	18.8	36.2	17.8	29.7	3.5	30.0	2.5	6.5		214			
	15 Milan	337	373	118	23	4.2	4.0	44.7	24.5	43.1	18.8	113.5	11.7	123.8	12.8	4.7		1560			
	16 Venice	399	411	70	25	4.7	8.3	58.2	45.6	53.0	36.7	58.6	11.1	58.2	11.4	5.7		290			
Netherlands	17 Vlaardingen	497	555	143	20	4.9	13.6	37.5	22.7	51.3	23.6	86.3	8.8	40.7	11.3	5.6		733			
	18 Eibergen	352	268	75	13	2.7	2.9	60.9	29.2	25.5	21.7	38.0	7.3	33.3	4.3	5.8		85			
	19 Vredepeel	461	395	35	20	4.3	10.9	54.0	68.1	42.9	35.1	66.3	16.7	47.6	7.7	5.6		218			
	20 Wijnandsrade	380	289	127	15	3.6	4.6	46.3	20.2	30.0	15.5	51.3	8.0	40.0	7.3	5.7		234			
Norway	21 Oslo	311	175	109	17	4.6	2.5	24.3	7.6	28.2	6.9	41.4	5.8	45.9	4.2	6.1		173			
	22 Borregard	673	1205	163	88	15.7	32.8	75.9	61.7	115.6	40.8	191.6	11.1	208.4	5.5	5.5		1296			
	23 Birkenes	368	219	93	14	2.2	2.0	45.9	21.5	25.9	9.5	68.6	0.7	41.6	0.5	5.3		17			
Sweden	24 Stockholm South	396	237	80	23	3.9	5.7		13.1	32.3	14.7	65.7	6.2	65.4	5.6	7.4		245			
	25 Stockholm Centre	400	195	65	20	4.0	6.1	21.1	10.4	25.1	10.5	51.8	5.6	51.0	4.9	7.6		390			
	26 Aspvreten	284	201	167	11	1.9	3.0	33.6	23.4	16.9	9.8	22.3	2.6	25.5	1.1	6.1		27			
United Kingdom	27 Lincoln Cathedral	943	644	204	24	9.8	19.3	38.0	31.3	54.5	24.4	76.8	9.5	75.9	9.5	6.5		1081			
	28 Wells Cathedral	458	396	188	25	3.6	15.9	24.7	24.4	42.1	23.0	54.4	7.9	53.2	5.5	6.7		275			
	29 Clatteringshaws Loch	457	505	122	19	4.5	10.6	36.8	50.0	69.4	52.4	113.4	-16.8	58.0	-12.8	5.2		67			
	30 Stoke Orchard	507	446	107	21	4.8	16.5	30.0	21.7	52.4	22.8	63.4	7.0	68.3	5.4	6.1		491			
Spain	31 Madrid	210	199	78	16	1.7	3.3	19.8	9.7	19.3	10.4	69.1	7.5	83.8	5.1	7.6		890			
	32 Bilbao	382	240	125	20	8.1	5.2	41.8	20.6	61.4	25.1	187.8	12.7	143.7	13.6	5.4		2138			
	33 Toledo	144	105	15	11	2.8	2.5	16.7	8.6	13.3	7.3	23.6	0.1	22.9	0.5	14.6		34			
Russian F.	34 Moscow	283	195	40	20	2.9	2.6	23.8	7.2	24.0	10.6	60.0	5.1	57.4	1.3			348			
Estonia	35 Lahemaa	288	240	27	14	1.9	3.5	34.5	42.6	22.6	14.2	41.8	2.8	34.1	0.0			68			
Portugal	36 Lisbon	363	353	52	21	3.5	9.0	22.9	20.8	39.8	28.1	50.9	7.1	61.6	6.6	10.2		410			
Canada	37 Dorset	211	212	44	11	2.8	2.2	42.3	24.6	27.2	14.5	41.9	2.2	39.2	1.4	6.1		29			
USA	38 Research Triangle Park	337	330	92	20	4.7	3.0	44.1	16.1	30.8	15.0	49.2	4.6	49.4	4.0	5.6		198			
	39 Steubenville	287	309	76	22	2.7	5.1	97.3	26.3	82.2	44.7	130.0	9.2	142.1	7.7	4.5		2058			
	Unit																				
																		g/m ²	µm	yr ^b	µg/cm ²

^aSteel panel with alkyd

^bLifetime based on damage from cut

4 Uniform statistical evaluation

This section is a summary of two reports describing the relationship between temperature, relative humidity and time of wetness [10] and the uniform statistical evaluation of materials [11] prepared by the main research centre the Swedish Corrosion Institute in cooperation with the Institute of Physical Chemistry of the Russian Academy of Sciences. The main aim of the uniform statistical evaluation was to estimate dose-response functions suitable for mapping purposes and calculation of costs. This poses restrictions on the parameters that can be used in the final dose-response functions. Depending on the aim of the analysis and the parameters available alternative functions may be used for other purposes.

4.1 On the relationship between T, Rh and Tow

As was described in a previous section it was decided to use relative humidity and temperature in the analysis instead of time of wetness. A prerequisite for the decision was the assumption that if temperature is really important it should automatically be selected in the regression procedure. Therefore, a detailed analysis was performed on the relationship between time of wetness as calculated in the programme, relative humidity and temperature. This analysis included the development of a new improved relationship for estimating time of wetness from relative humidity and temperature based on probability distributions [10].

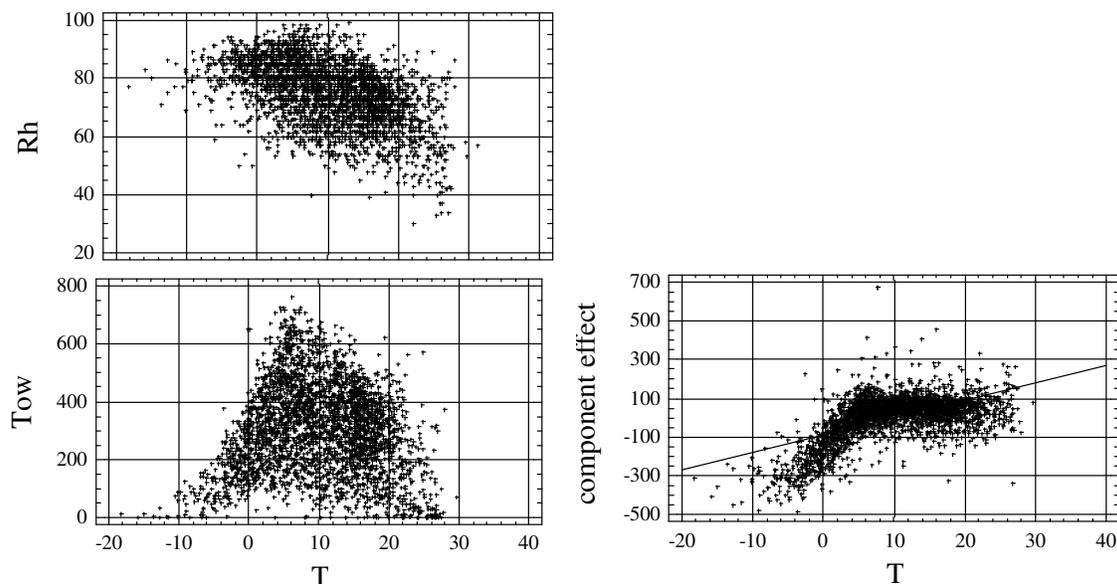


Figure 2 The relationship between time of wetness (Tow), temperature (T) and relative humidity (Rh) for monthly averages showing Rh vs. T (top panel), Tow vs. T (lower left panel) and the component effect of Tow vs. T, i.e. the temperature dependence that would be obtained if relative humidity was independent on temperature (lower right panel).

Figure 2 shows the relationship between time of wetness, temperature and relative humidity, illustrated by monthly averages from all test sites. When comparing time of wetness and temperature directly there is a positive correlation up to about 8 °C and a negative correlation above about 8 °C. The apparent negative correlation between T_{ow} and T at higher temperatures is due to the negative correlation between T and Rh . Rh also influences T_{ow} and the relationship is approximately linear. The net effect that would have been obtained if relative humidity was constant is shown as the component effect in figure 2. It shows that T_{ow} increases with T up to 8 °C and above that remains constant. A similar analysis based on annual data has shown that this temperature limit is between 10 and 13 °C.

4.2 Choice of environmental parameters

The measured environmental data includes climatic parameters (temperature, relative humidity, time of wetness, sunshine hours and sunshine radiation), gaseous pollutants (SO_2 , NO_2 and O_3) and precipitation (amount, conductivity and concentration of the ions H^+ , SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , Ca^{2+} , Mg^{2+} and K^+). Not all of these are used in the final dose-response relations and the motives will be briefly discussed.

The climatic data consists of the parameters temperature (T), relative humidity (Rh), time of wetness (T_{ow}) and sunshine radiation (Sun). Due to the general difficulty in obtaining T_{ow} and Sun data for mapping at different scales these two parameters are excluded from the final equations. Correlations between parameters make it possible to use only T and Rh as an explanation for climatic effects. However, in preliminary analyses Sun is also included for unsheltered exposure. For example, for high temperatures there sometimes exists a negative influence of Sun which could be interpreted as a decrease of the surface time of wetness due to an increase of the surface temperature relative to the ambient air temperature. In the equations, this effect is expressed as a negative temperature dependence since T and Sun are correlated. The substitution of Sun with T generally gives a lower R^2 value.

The gaseous pollutants SO_2 , NO_2 and O_3 are all included in the statistical analysis. However, there exists a negative correlation between NO_2 and O_3 such that O_3 is high when NO_2 is low (rural sites) and *vice versa* (urban sites). This results in a difficulty of separating the effects of NO_2 and O_3 . Therefore, NO_2 and O_3 are not included in a dose-response relation simultaneously.

Of the precipitation data the amount and the H^+ and Cl^- concentrations are included in the final equations for unsheltered materials. Table 3 shows all parameters included in the final dose-response relations.

In general care shall be taken when extrapolating the equations outside the intervals of environmental parameters used for their calculations (table 3). This is especially true for the Cl^- concentration since this parameter is used in the equations as a substitute for salinity, for which the parameter only is an indirect measure of.

Table 3 Parameters used in final dose-response functions including symbol, description, interval measured in the programme and unit. All parameters are expressed as annual averages.

Symbol	Description	Interval	Unit
t	Time	1-8	year
T	Temperature	2-19	°C
Rh	Relative humidity	56-86	%
[SO ₂]	SO ₂ concentration	1-83	µg/m ³
[NO ₂]	NO ₂ concentration	1-121	µg/m ³
[O ₃]	O ₃ concentration	14-82	µg/m ³
Rain	Rainfall	327-2144	mm
[H ⁺]	H ⁺ concentration	0.0006-0.13	mg/l
[Cl ⁻]	Cl ⁻ concentration	0.1-12	mg/l

4.3 Choice of mathematical form for dose-response relations

For unsheltered positions the materials damage is usually discussed in terms of dry and wet deposition. Wet deposition includes transport by means of precipitation and dry deposition transport by any other process. One important task for the programme has been to estimate the relative contribution of dry and wet deposition to the degradation of materials. Therefore, and also because it makes sense from a mechanistic point of view, only one type of dose-response relation was considered in which the corrosion attack, K, is described in terms of dry, f_{dry} , and wet, f_{wet} , deposition separated as additive terms

$$K = f_{dry} + f_{wet} \quad [4.1]$$

For dry deposition previous analyses have used a term like

$$f_{dry} = k[SO_2]^A Tow^B \quad [4.2]$$

This form has been used in the present analysis except that Tow has been replaced with a combined (multiplicative) Rh and T function. The Rh functions tested include linear, exponential or power functions but the form of the T function is more complicated. The temperature dependence is schematically illustrated in figure 3. The effect of temperature has for many materials a maximum at about 9-11 °C. The increasing part (a) can be related to the time of wetness as defined in the programme and this effect was illustrated in figure 2. The decreasing part (b) is due to a surface temperature above the ambient temperature, partly related to sun radiation, and therefore causing a decrease in true time of wetness. The net result from a statistical analysis including sites from the whole temperature range is often insignificant and therefore temperature is not normally included in the functions even though it could add to the explained variability. Two possibilities were considered, to use a complicated temperature dependence or to use simple linear functions with the possibility of different slopes in the high and low temperature region, as illustrated in figure 3. The later alternative was chosen, primarily because the analytical form of the temperature dependence (b) is not known. The increasing part (a) is quite complicated in itself [10].

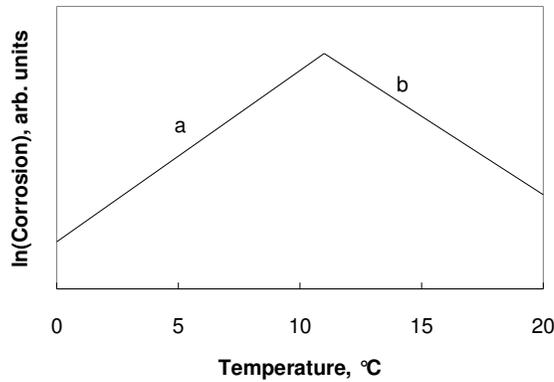


Figure 3 Schematic representation of the observed temperature dependence for many materials: a) increase of corrosion with temperature in the low temperature range and b) decrease of corrosion with temperature in the high temperature range.

The wet deposition term describes the influence of rain and its acidity. The acidity has been expressed as

$$f_{\text{wet}} = k \cdot \text{Rain}[\text{H}^+] \quad [4.3]$$

where k is a constant, Rain is the amount of precipitation and $[\text{H}^+]$ is the hydrogen ion concentration in precipitation. The k -value for the acidity load may be positive or negative. A negative value is an indication that the so-called washing effect, i.e. washing of pollutants from the surface by rain, is prevailing.

The chloride load in precipitation has been expressed as

$$f_{\text{wet}} = k \cdot \text{Rain}[\text{Cl}] \quad [4.4]$$

where $[\text{Cl}]$ is the chloride ion concentration in precipitation.

Several ways of estimating the time dependence were used. The main approach was to use data from all exposures simultaneously and to use time dependencies in accordance with earlier atmospheric corrosion modeling attempts

$$K = f_{\text{dry}} \cdot t^k + f_{\text{wet}} \cdot t^m \quad [4.5]$$

where t is the time and k and m are constants. Due to the form of this equation nonlinear regression has to be used for the general case.

4.4 Dose-response relations for different materials

The abbreviations of environmental parameters are specified in table 3. Some of the dose-response functions presented in this section have been verified outside the intervals occurring in the programme for SO_2 . A conclusion from these tests was that the use of exponential functions for gaseous pollutants is not recommended due to the extreme values obtained even with a moderate extrapolation. Therefore, power functions have generally been used even if they in some cases results in a slightly lower explained variability. Another general aim has been to obtain stable models, i.e., models that do

not change substantially if subsets of the data are used. In order to verify the stability of the equations several different subset of parameters (SO₂, time, temperature, temperature limit, and for some materials Cl⁻ and H⁺) have been used. For example different variants including only 1 and 8, 1 and 2, 2 and 8 years, etc, have been used.

4.4.1 Structural metals

The following functions have been obtained, where R² denotes the explained variability and N the number of sites included in the analysis. The corrosion attack is expressed as mass loss (ML) in g/m².

Weathering steel, unsheltered (N=148, R²=0.68)

$$\ln(\text{ML}) = 3.54 + 0.33\ln(t) + 0.13\ln[\text{SO}_2] + 0.020\text{Rh} + 0.059(\text{T}-10); \quad \text{T} \leq 10^\circ\text{C} \quad [4.6\text{a}]$$

$$\ln(\text{ML}) = 3.54 + 0.33\ln(t) + 0.13\ln[\text{SO}_2] + 0.020\text{Rh} - 0.036(\text{T}-10); \quad \text{T} > 10^\circ\text{C} \quad [4.6\text{b}]$$

Weathering steel, sheltered (N=148, R²=0.76)

$$\ln(\text{ML}) = 2.01 + 0.66\ln(t) + 0.24\ln[\text{SO}_2] + 0.025\text{Rh} + 0.048(\text{T}-10); \quad \text{T} \leq 10^\circ\text{C} \quad [4.7\text{a}]$$

$$\ln(\text{ML}) = 2.01 + 0.66\ln(t) + 0.24\ln[\text{SO}_2] + 0.025\text{Rh} - 0.047(\text{T}-10); \quad \text{T} > 10^\circ\text{C} \quad [4.7\text{b}]$$

Zinc, unsheltered (N=98, R²=0.84)

$$\text{ML} = 1.35[\text{SO}_2]^{0.22}\exp\{0.018\text{Rh} + 0.062(\text{T}-10)\}t^{0.85} + 0.029\text{Rain}[\text{H}^+]t \quad \text{T} \leq 10^\circ\text{C} \quad [4.8\text{a}]$$

$$\text{ML} = 1.35[\text{SO}_2]^{0.22}\exp\{0.018\text{Rh} - 0.021(\text{T}-10)\}t^{0.85} + 0.029\text{Rain}[\text{H}^+]t \quad \text{T} > 10^\circ\text{C} \quad [4.8\text{b}]$$

Zinc, sheltered (N=91, R²=0.80)

$$\text{ML} = 0.058[\text{SO}_2]^{0.16}\text{Rh} \exp\{+ 0.039(\text{T}-10)\}t^{0.49} \quad \text{T} \leq 10^\circ\text{C} \quad [4.9\text{a}]$$

$$\text{ML} = 0.058[\text{SO}_2]^{0.16}\text{Rh} \exp\{- 0.034(\text{T}-10)\}t^{0.49} \quad \text{T} > 10^\circ\text{C} \quad [4.9\text{b}]$$

Aluminium, unsheltered (N=106, R²=0.74)

$$\text{ML} = 0.0021[\text{SO}_2]^{0.23}\text{Rh} \exp\{+ 0.031(\text{T}-10)\}t^{1.2} + 0.000023\text{Rain}[\text{Cl}^-]t \quad \text{T} \leq 10^\circ\text{C} \quad [4.10\text{a}]$$

$$\text{ML} = 0.0021[\text{SO}_2]^{0.23}\text{Rh} \exp\{- 0.061(\text{T}-10)\}t^{1.2} + 0.000023\text{Rain}[\text{Cl}^-]t \quad \text{T} > 10^\circ\text{C} \quad [4.10\text{b}]$$

Copper, unsheltered (N=95, R²=0.73)

$$\text{ML} = 0.0027[\text{SO}_2]^{0.32}[\text{O}_3]^{0.79}\text{Rh} \exp\{+ 0.083(\text{T}-10)\}t^{0.78} + 0.050\text{Rain}[\text{H}^+]t^{0.89} \quad \text{T} \leq 10^\circ\text{C} \quad [4.11\text{a}]$$

$$\text{ML} = 0.0027[\text{SO}_2]^{0.32}[\text{O}_3]^{0.79}\text{Rh} \exp\{- 0.032(\text{T}-10)\}t^{0.78} + 0.050\text{Rain}[\text{H}^+]t^{0.89} \quad \text{T} > 10^\circ\text{C} \quad [4.11\text{b}]$$

Copper, sheltered (N=98, R²=0.53)

$$\text{ML} = 0.00045[\text{SO}_2]^{0.28}[\text{O}_3]^{1.16}\text{Rh} \exp\{+ 0.033(\text{T}-10)\}t^{0.78} \quad \text{T} \leq 10^\circ\text{C} \quad [4.12\text{a}]$$

$$\text{ML} = 0.00045[\text{SO}_2]^{0.28}[\text{O}_3]^{1.16}\text{Rh} \exp\{+ 0.019(\text{T}-10)\}t^{0.78} \quad \text{T} > 10^\circ\text{C} \quad [4.12\text{b}]$$

Cast Bronze, unsheltered (N=144, R²=0.81)

$$\text{ML} = 0.026[\text{SO}_2]^{0.44}\text{Rh} \exp\{+ 0.060(\text{T}-11)\}t^{0.86} + (0.029\text{Rain}[\text{H}^+] + 0.00043\text{Rain}[\text{Cl}^-])t^{0.76} \quad \text{T} \leq 11^\circ\text{C} \quad [4.13\text{a}]$$

$$\text{ML} = 0.026[\text{SO}_2]^{0.44}\text{Rh} \exp\{- 0.067(\text{T}-11)\}t^{0.86} + (0.029\text{Rain}[\text{H}^+] + 0.00043\text{Rain}[\text{Cl}^-])t^{0.76} \quad \text{T} > 11^\circ\text{C} \quad [4.13\text{b}]$$

Cast Bronze, sheltered (N=148, R²=0.71)

$$\text{ML} = 0.014[\text{SO}_2]^{0.41}\text{Rh} \exp\{+ 0.063(\text{T}-11)\}t \quad \text{T} \leq 11^\circ\text{C} \quad [4.14\text{a}]$$

$$\text{ML} = 0.014[\text{SO}_2]^{0.41}\text{Rh} \exp\{- 0.053(\text{T}-11)\}t \quad \text{T} > 11^\circ\text{C} \quad [4.14\text{b}]$$

The temperature dependence is generally different for low and high temperatures and two temperature coefficients are given for each equation. The temperature limit is 10 °C, except for bronze where it is 11 °C. Wet deposition (Rain[H⁺]) is generally important for unsheltered conditions except for weathering steel and aluminium. For aluminium there is an effect of chlorides which also applies for bronze. For coastal regions with high load

of chlorides the use of Rain[Cl] may give erroneous results since this parameter is then not directly correlated with chloride deposition. For dry deposition SO₂ is the most important pollutant except for copper where O₃ is also important. The exponent is generally lower than unity ranging from 0.13 for weathering steel to 0.44 for bronze, i.e., the relations are nonlinear with respect to SO₂.

Generally all sites have been included except site 22 and site 29. Exceptions are for zinc, unsheltered aluminium and copper. For zinc, some values were obviously wrong and observations were excluded using different procedures including comparisons of values for different years, comparison of values in sheltered and unsheltered positions, and comparisons with corrosion values for other materials. For aluminium the values from the first year of exposure were not reliable due to low corrosion rates. For copper, the first year of exposure was excluded due to the high rate of oxide formation for many sites. Also sites 23 and 35 were excluded as outliers. However, problems still exist with the copper equations due to the difficulty in describing the combined SO₂ and O₃ effects correctly which affects the stability of the model with respect to SO₂.

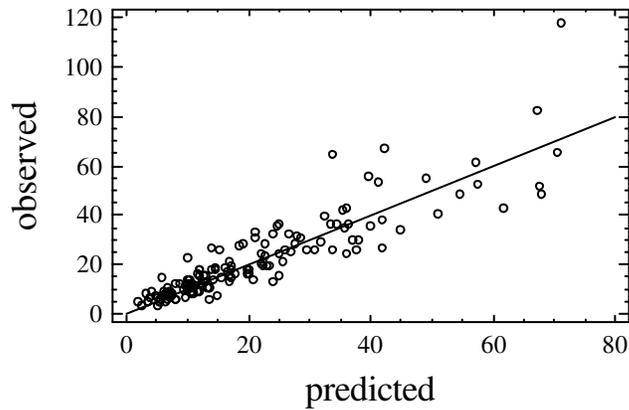


Figure 4. Observed vs. predicted values for mass loss of unsheltered bronze using equation 4.13.

4.4.2 Stone materials

The following functions have been obtained, where R² denotes the explained variability and N the number of sites included in the analysis. The corrosion attack is expressed as surface recession, R, in μm.

Portland limestone, unsheltered (N=100, R²=0.88)

$$R = t^{0.96} (2.7[\text{SO}_2]^{0.48} \exp\{-0.018T\} + 0.019\text{Rain}[\text{H}^+]) \quad [4.15]$$

White Mansfield sandstone, unsheltered (N=101, R²=0.86)

$$R = t^{0.91} (2.0[\text{SO}_2]^{0.52} + 0.028\text{Rain}[\text{H}^+]) \quad T \leq 10^\circ\text{C} \quad [4.16a]$$

$$R = t^{0.91} (2.0[\text{SO}_2]^{0.52} \exp\{-0.013(T-10)\} + 0.028\text{Rain}[\text{H}^+]) \quad T > 10^\circ\text{C} \quad [4.16b]$$

Values from the first year of exposure have not been used due to specific behavior at short times. The temperature dependence for limestone is negative throughout the entire temperature region, in contrast to the temperature effect for metals. This may be due to the correlation between average temperature and the number of frost-thaw cycles. If this interpretation is correct it would be extremely dangerous to extrapolate the relation below 0 °C. For sandstone the temperature effect in the low temperature region is insignificant which may be due to its higher resistance to frost-thaw cycles.

For sheltered materials no equation has been obtained. The corrosion values have both positive and negative values depending on the test site and this makes it difficult to build a dose-response relation.

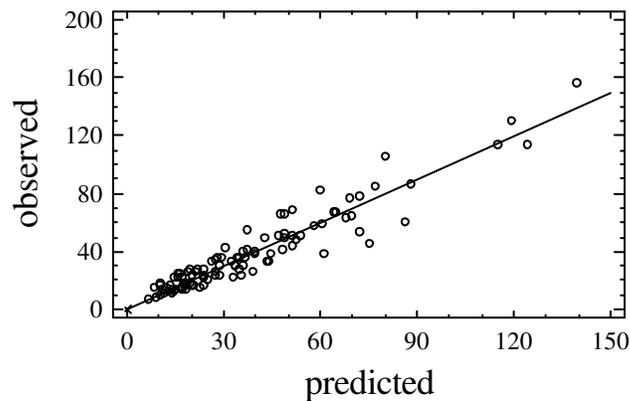


Figure 5 Observed vs. predicted values for surface recession for unsheltered Portland limestone using equation 4.15.

4.4.3 Paint coatings

The following functions have been obtained, where R^2 denotes the explained variability and N the number of sites included in the analysis. ASTM rankings from 1 to 10 of the damage from cut were used where 10 means a fresh sample and 1 a completely degraded.

Coil coated galv. steel with alkyd melamine, unsheltered (N=138, R²=0.73)

$$(10\text{-ASTM}) = t^{0.43} (0.0084[\text{SO}_2] + 0.015\text{Rh} + 0.040(\text{T}-10) + 0.00082\text{Rain}) \quad \text{T} \leq 10^\circ\text{C} \quad [4.17\text{a}]$$

$$(10\text{-ASTM}) = t^{0.43} (0.0084[\text{SO}_2] + 0.015\text{Rh} - 0.064(\text{T}-10) + 0.00082\text{Rain}) \quad \text{T} > 10^\circ\text{C} \quad [4.17\text{b}]$$

Steel panels with alkyd, unsheltered (N=139, R²=0.68)

$$(10\text{-ASTM}) = t^{0.41} (0.033[\text{SO}_2] + 0.013\text{Rh} + 0.015(\text{T}-11) + 0.0013\text{Rain}[\text{H}^+]) \quad \text{T} \leq 11^\circ\text{C} \quad [4.18\text{a}]$$

$$(10\text{-ASTM}) = t^{0.41} (0.033[\text{SO}_2] + 0.013\text{Rh} - 0.15(\text{T}-11) + 0.0013\text{Rain}[\text{H}^+]) \quad \text{T} > 11^\circ\text{C} \quad [4.18\text{b}]$$

The ASTM values as such have no specific meaning but the functions can be transferred into lifetime equations using the criterion

$$\text{ASTM} = 5 \text{ when } t = \text{lifetime} \quad [4.19]$$

which is a generally accepted maintenance criterion.

4.4.4 Electric contact materials

The following functions have been obtained, where R^2 denotes the explained variability and N the number of sites included in the analysis. The corrosion attack is expressed as weight increase (WI) in $\mu\text{g}/\text{cm}^2$.

Nickel, sheltered in ventilated box (N=150, R²=0.87)

$$\ln(WI) = 2.13 + \ln(t) + 1.19\ln[\text{SO}_2] + 0.171(T-9) \quad T \leq 9^\circ\text{C} \quad [4.20a]$$

$$\ln(WI) = 2.13 + \ln(t) + 1.19\ln[\text{SO}_2] - 0.047(T-9) \quad T > 9^\circ\text{C} \quad [4.20b]$$

Tin, sheltered in ventilated box (N=150, R²=0.68)

$$\ln(WI) = -0.70 + \ln(t) + 0.47\ln[\text{O}_3] + 0.11T \quad [4.21]$$

Nickel is the material which has the highest correlation to SO₂ but in addition a large temperature effect is noted.

For tin, ozone is the only pollution parameter that is included. Additional analyses show that chloride in precipitation also correlates but it can only be indirectly related to the corrosion attack since the box is completely sheltered from rain. The temperature is positive in the entire temperature region in contrast to other metals.

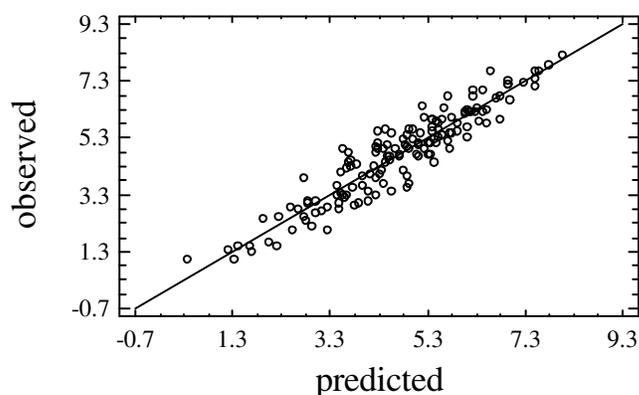


Figure 6 Observed vs. predicted (logarithmic) values for weight increase of nickel using equation 4.20.

6.4.5 Glass materials

The following functions have been obtained, where R² denotes the explained variability and N the number of sites included in the analysis. The corrosion attack is expressed as fraction of covered surface (CS) in % and depth of leached layer in nm.

Glass M1, sheltered, 0.5 year of exposure (N=20, R²=0.79)

$$\ln(\text{CS}) = 1.95 + 0.72\ln[\text{NO}_2] + 0.37(T-1) \quad T \leq 1^\circ\text{C} \quad [4.22a]$$

$$\ln(\text{CS}) = 1.95 + 0.72\ln[\text{NO}_2] - 0.15(T-1) \quad T > 1^\circ\text{C} \quad [4.22b]$$

Glass M1, sheltered, 1 year of exposure (N=21, R²=0.49)

$$\ln(\text{CS}) = 2.61 + 0.50\ln[\text{NO}_2] + 0.22(T-8) \quad T \leq 8^\circ\text{C} \quad [4.23a]$$

$$\ln(\text{CS}) = 2.61 + 0.50\ln[\text{NO}_2] - 0.14(T-8) \quad T > 8^\circ\text{C} \quad [4.23b]$$

Glass M1, unsheltered (N=46, R²=0.56)

$$\text{LL} = 0.013[\text{SO}_2]^{0.49}\text{Rh}^{2.75}t \quad [4.24]$$

Glass M3, sheltered (N=38, R²=0.53)

$$\ln(\text{LL}) = -0.98 + 0.45\ln(t) + 0.37\ln[\text{NO}_2] + 1.36\ln(\text{Rh}) + 0.041(T-10) \quad T \leq 10^\circ\text{C} \quad [4.25a]$$

$$\ln(\text{LL}) = -0.98 + 0.45\ln(t) + 0.37\ln[\text{NO}_2] + 1.36\ln(\text{Rh}) - 0.101(T-10) \quad T > 10^\circ\text{C} \quad [4.25b]$$

For glass M1, which is the most sensitive, in sheltered position the equations for 0.5 and 1 years of exposure are given separately since the temperature dependence was qualitatively different. For unsheltered position temperature was not significant and a time dependence could be obtained. It should be stressed, however, that the estimation of the time dependence only includes two exposure times and is thus uncertain.

Also worth noting is that NO₂ gives a much higher explained variability for sheltered position whereas SO₂ explains more for unsheltered position. The reason for this will be further investigated in the multipollutant exposure programme.

A dose-response relation for unsheltered glass M3 is at present stage not available. The behavior of this glass was very unexpected and often completely opposite to the other glass materials.

4.4.5 Polymer materials (polyamide and polyethylene)

No dose response relation has so far been obtained that includes gaseous pollutants. The final withdrawal of specimens was performed 2 years later for these materials compared to all other materials and the results are still subject to analysis.

5 Acceptable deterioration and pollution levels

Atmospheric corrosion and deterioration of materials is a cumulative, irreversible process which proceeds even in the absence of pollutants. The critical loads/level approach used for ecosystems has to be modified in relation to degradation of materials as even the lowest concentration of pollutants causes an increase in the deterioration rate. This leads to the concepts of acceptable corrosion rates and pollution levels.

5.1 Background corrosion rate

The acceptable corrosion rate must be determined by technical and economic considerations based on the specific application of a material. For model calculations, however, and for the purpose of comparing different materials with respect to their pollution sensitivity, different levels of acceptance can be defined by relating the corrosion rate to corrosion rates in areas with 'background' pollution. It has proven to be useful to define a dimensionless number, n

$$n = \frac{K_a}{K_b} = \frac{K_a}{K_{10\%}} \quad [5.1]$$

where K_a is the acceptable corrosion rate and K_b is the background corrosion rate, here calculated as the lower 10-percentile from the ICP Materials data set ($K_{10\%}$). Figure 7 shows the $K_{10\%}$ values for unsheltered bronze as a function of exposure time. As indicated in the figure, the points can be fitted to a line using the expression

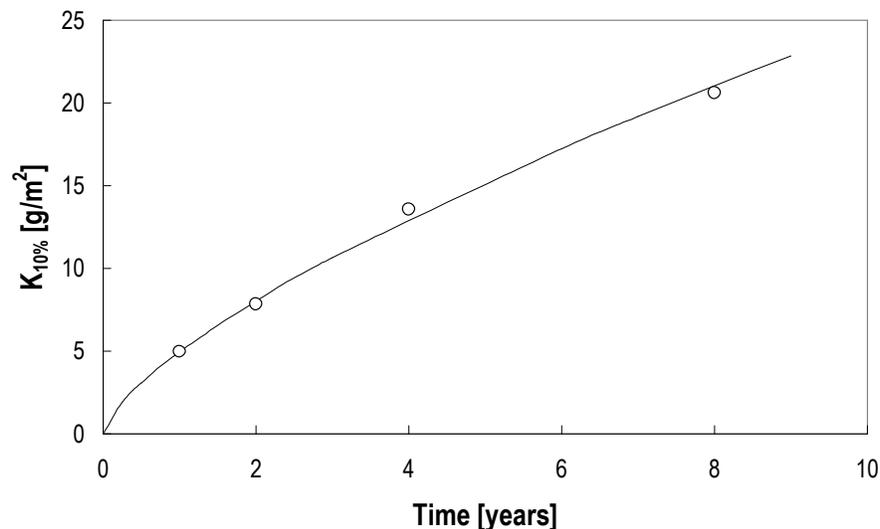


Figure 7 Background corrosion attack $K_{10\%}$ for unsheltered bronze vs. time of exposure. The solid line corresponds to fitting the points to the function $K_{10\%} = At^k$ where A and k are constants.

$$K_{10\%} = At^k \quad [5.2]$$

where A and k are constants.

Table 4 gives the $K_{10\%}$ values for all materials as a function of time. For the paint coatings no functions are given since the functions give lifetimes directly. Using the given dose-response functions and the average environmental data after 8 years of exposure background lifetime values, $L_{90\%}$, were calculated to be 22 and 20 year for coil coated steel with alkyd melamin and steel with alkyd paint, respectively. For the glass materials no background corrosion rate as a function of time is given since the time dependence is not fully evaluated due to lack of data.

Table 4 Average background corrosion rates calculated as 10-percentiles from the program, $K_{10\%}$, as a function of time of exposure (see figure 7).

	w steel	zinc	alu- minium	copper	bronze	lime- stone	sand- stone	nickel	tin
Unsheltered	$138t^{0.28}$	$6.6t^{0.8}$	$0.16t^{1.20}$	$5.1t^{0.75}$	$5.0t^{0.70}$	$6.7t^{0.80}$	$5.5t^{0.83}$		
Sheltered	$63t^{0.56}$	$4.7t^{0.41}$	$0.13t^{1.42}$	$2.0t^{0.76}$	$1.3t^{0.93}$	a	a		
Sheltered Al. box								5.0t	$3.2t^{1.20}$
Unit	g/m ²	µm	µm	µg/cm ²	µg/cm ²				

^aA mix of positive and negative values prevents the calculation of a meaningful 10-percentile

5.2 Acceptable corrosion rate

Previous calculations of the acceptable level used the corrosion values after 4 years of exposure [12]. The dose-response functions available at that time did not include the time of exposure as an independent variable. With the new dose-response functions and the background corrosion values, however, it is possible to calculate many different types of acceptable values. As an example will be given here the calculation of acceptable corrosion rates after 8 years of exposure. Using the $K_{10\%}$ time functions in table 4 it is possible to calculate the background corrosion rate, here called $r_{10\%}$, after 8 years of exposure, i.e., the slope of the curve at 8 years of exposure:

$$r_{10\%} = dK_{10\%}/dt = kAt^{k-1} = kA8^{k-1} \quad [5.3]$$

The $r_{10\%}$ values are shown in table 5 as background corrosion rates in µm/year. In this treatment, acceptable values are given for n values of 1.5, 2.0 and 3.0 independent of material. As stated above, however, the proper way to determine K_a , the acceptable corrosion rate, is from technical and economic considerations.

Table 5 Average background and acceptable corrosion rates, $r_{10\%}$, in $\mu\text{m}/\text{year}$ after 8 years of exposure (see figure 7).

Corrosion rates	w steel		zinc		aluminium		copper		bronze		limestone		sandstone	
	<i>unsh</i>	<i>sh</i>												
background, n=1	1.0	1.8	0.49	0.08	0.11	0.16	0.26	0.10	0.20	0.12	3.5	a	3.2	a
acceptable, n=1.5	1.5	2.7	0.74	0.13	0.16	0.24	0.39	0.15	0.30	0.19	5.3		4.8	
acceptable, n=2.0	2.1	3.6	0.98	0.17	0.21	0.32	0.52	0.20	0.40	0.25	7.0		6.4	
acceptable, n=3.0	3.1	5.4	1.47	0.25	0.32	0.48	0.77	0.30	0.61	0.37	10.5		9.6	

^aA mix of positive and negative values prevents the calculation of a meaningful 10-percentile

5.3 Acceptable pollution levels

Continuing the example, for a fixed n level it is now possible to calculate acceptable pollution levels, assuming that dose-response relations are available. The acceptable corrosion rate, r_a , is estimated by the derivative of the dose-response relations with respect to time at 8 years:

$$r_a = nr_{10\%} = (dK([SO_2]_a, [O_3]_a, [H^+]_a, \dots)/dt)_{t=8} \quad [5.4]$$

This relation implicitly defines an acceptable pollution situation but this situation can be reached by different combinations of the pollutants. Consider the case of unsheltered limestone (equation 4.15)

$$WL = t^{0.96} (2.7[SO_2]^{0.48} \exp\{-0.018T\} + 0.019\text{Rain}[H^+]) \quad [5.5]$$

An acceptable SO_2 level, $[SO_2]_a$ can be calculated for otherwise unchanged conditions if the n value is given

$$r_{a,\text{limestone}} = 3.5n = 0.96 \cdot 8^{-0.04} (2.7[SO_2]_a^{0.48} \exp\{-0.018T\} + 0.019\text{Rain}[H^+]) \quad [5.6]$$

Measured values of temperature and acid load are used in order to calculate an acceptable SO_2 level. This implies that H^+ in precipitation is independent of the SO_2 concentration, which is not necessarily true. Other types of calculations are also possible if more pieces of information are available. Table 6 shows a summary of calculated acceptable SO_2 values for different n values based on acceptable corrosion rates after 8 years of exposure.

Table 6 SO_2 mean acceptable values in $\mu\text{g}/\text{m}^3$ based on dose-response functions after 8 years of exposure and acceptable corrosion rates. For the test sites the background (10-percentile) and average SO_2 concentrations are 2.7 and 17.8 $\mu\text{g}/\text{m}^3$, respectively.

SO_2	w steel		zinc		aluminium		copper		bronze		limestone		sandstone	
	<i>unsh</i>	<i>sh</i>												
acceptable, n=1.5	5	9	12	10	10	b	7	5	5	5	7	b	8	b
acceptable, n=2.0	45	31	49	63	39	b	33	19	12	10	12	b	15	b
acceptable, n=3.0	a	a	a	a	a	b	131	80	34	28	30	b	34	b

^aCalculation of an acceptable value would imply extreme extrapolation of the dose-response function

^bDose-response function not available

5.4 Effect of temperature on the acceptable levels

New in most dose-response functions is the explicit inclusion of temperature compared to the previous implicit when only time of wetness was included. The new functions makes it possible to calculate different acceptable levels depending on the climatic region. Table 7 shows a relative comparison of acceptable levels for different materials as a function of temperature.

Table 7 Relative mean acceptable values of SO₂ concentration in cold and warm regions calculated from dose-response functions.

Region	w steel		zinc		aluminium		copper		bronze		limestone		sandstone	
	<i>unsh</i>	<i>sh</i>												
cold, 5 °C	1.3	1.3	1.4	1.2	1.2	a	1.5	1.2	1.4	1.5	0.9	a	1.0	a
moderate, 10 °C	1.0	1.0	1.0	1.0	1.0	a	1.0	1.0	1.1	1.1	1.0	a	1.0	a
warm, 15 °C	1.2	1.3	1.1	1.2	1.4	a	1.2	1.1	1.3	1.2	1.1	a	1.1	a

^aDose-response function not available

Generally, a higher SO₂ level can be accepted in cold and warm regions compared to moderate regions and the difference can be as large as 50%, see table 7. Special care should be taken, however, to extrapolate these values to extreme temperatures.

6 Evaluation of corrosion attack at sub-centres

Before the uniform statistical analysis, comprehensive analysis has also been performed at the individual subcentres (see section 3.2 Corrosion data). The interested reader should consult these reports for further reference when information on specific materials is sought. As an introduction to these reports this section summarizes the essential results and procedures of evaluation.

Unless otherwise stated, the symbols presented in table 3 have been used. However, exceptions exist, especially concerning the units used for the parameters Rain and $[H^+]$. Therefore, the units of these parameter are given in each individual case.

6.1 Weathering steel, zinc and aluminium

The sub-centre responsible for the evaluation of unalloyed carbon steel, weathering steel, zinc and aluminum is SVÚOM Praha a. s.. The following is a brief summary of their results [2].

Corrosion products were removed from weathering steel, zinc and aluminum specimens and the corrosion attack was expressed as mass loss (ML) in g/m^2 . Weathering steel behaves in a different way than an ordinary carbon steel at prolonged exposure and the corrosion rate is stabilized at fairly low levels since a protective rust layer forms during the first 2-4 years of exposure. The decrease of the SO_2 influence with time for unsheltered weathering steel is a known fact for this material and this is shown in table 8. Sheltered weathering steel is relatively sensitive to SO_2 even after 8 years of exposure and the effect of time of wetness for sheltered samples is not so evident.

Table 8 Comparison of correlation coefficients for corrosion losses of weathering steel and important environmental factors after 1, 2, 4 and 8 years of exposure.

	parameter	1 year	2 years	4 years	8 years
Unsheltered	[SO_2]	0.62	0.56	0.40	0.12
Unsheltered	Tow[SO_2]	0.74	0.69	0.54	0.39
Sheltered	[SO_2]	0.64	0.70	0.68	0.69
Sheltered	Tow[SO_2]	0.63	0.66	0.64	0.69

For zinc exposed outdoors, the experimental corrosion rates show unexpectedly high values at some sites. Also, the expected linear kinetics were not followed. Therefore, these sites were excluded in the analysis. Aluminium shows almost linear kinetics. The corrosion attack on aluminium is of local nature due to pitting formation especially on test sites with industrial pollution and salinity where the pit depth was up to 100 μm .

6.1.1 Dose-response relations

The aim of the programme, *i.e.*, to perform a quantitative evaluation of the effect of sulfur pollutants in combination with other pollutants and climatic parameters, was the basis for the statistical analysis and the determination of the dose-response relations. When applying a stepwise regression procedure for selecting a relation the estimated SO₂ effect decreases when more factors are added to the model. This is due to the correlation of environmental parameters. The final dose-response relations are therefore not those with the highest explained variability but instead those which preserves a sufficient SO₂ effect and still have a relatively high explained variability. For other aims, the selection procedure for the determination of the dose-response relations may be modified.

Another effect of the correlation of environmental parameters is that it makes the regression function unstable. Therefore, selected environmental parameters were investigated with principal component analysis (PCA). At least five factors were identified and the five-factor model explained 84% of the total variance. [SO₂], Tow, Rain and pH of precipitation, were important factors. It is unclear if the last factor should include the NO₂/O₃ pair or conductivity (Cond) and/or [Cl].

The estimated dose-response relations are shown in table 9.

Table 9 Coefficients for dose-response relations, for weathering steel, zinc and aluminum. The form of the dose response relations is $\ln(1+ML) = \ln(A) + B\ln(1+[SO_2]) + C\ln(1+Tow)$. Sites 22 and 29 were excluded from the analysis.

Material	exp.	years	A	B	C	R ²					
w. steel	unsh.	1	5.8	0.26	1.38	0.55					
		2	7.0	0.22	1.39	0.55					
		4	7.5	0.17	1.86	0.53					
		8	7.8	0.14	2.28	0.51					
	sh.	1	3.6	0.34	1.54	0.41					
		2	5.4	0.25	1.28	0.41					
		4	5.9	0.28	1.60	0.39					
		8	5.9	0.35	2.15	0.53					
Zn	unsh.	1	2.1	0.10	0.70	0.19					
		2	2.0	0.26	1.70	0.44					
		4	2.7	0.25	1.07	0.51					
		8	3.6	0.28	2.17	0.32					
	sh.	1	1.7	0.14	1.53	0.20					
		2	1.8	0.19	1.02	0.36					
		4	1.9	0.19	0.99	0.48					
		8	2.7	0.21	0.27	0.32	A	B	C	D	^aR²
Al	unsh.	1					1.0	0.10	0.56	0.06	0.24
		2	1.0	0.11	0.67	0.23	1.0	0.15	0.87	0.16	0.40
		4	1.0	0.19	1.27	0.36	1.0	0.15	0.87	0.16	0.40
		8	1.3	0.18	1.19	0.38	1.4	0.13	0.77	0.18	0.45
	sh.	1									
		2	1.0	0.16	0.90	0.29	1.0	0.10	0.48	0.48	0.38
		4	0.8	0.28	2.76	0.46	0.9	0.17	1.67	1.67	0.60
		8	1.1	0.29	2.72	0.45	1.1	0.20	1.92	1.92	0.55

^aAlternative equation $\ln(1+ML) = \ln(A) + B\ln(1+[SO_2]) + C\ln(1+Tow) + D\ln(1+[Cl])$

An additive logarithmic model was selected since strong deviations from the normal distribution were observed. SO_2 and T_{ow} are the decisive factors of corrosion. SO_2 is also the only parameter that decreases significantly during the 8-year exposure period. The effect of ozone was investigated thoroughly using partial correlations and other methods and it was concluded that the effect was negligible and/or undetectable. The equation derived for weathering steel cannot be applied for carbon steel since there is a specific kinetic influence of the rust layers formed. Worth noting is that the addition of conductivity frequently increases the explained variability with 10%-units or more, both for unsheltered and sheltered weathering steel and zinc.

6.2 Copper and cast bronze

The sub-centre responsible for the evaluation of copper and cast bronze is the Bavarian State Conservation Office, Munich, Germany. The following is a brief summary of their results [3].

The most important corrosion parameter for metals is the mass loss (ML), *i.e.*, the metal consumed by the degradation process. Besides, the difference between the mass of an exposed sample and the original mass, the weight change (WCH), is also very informative and can be positive or negative, depending on the conditions. Both ML and WCH are expressed in g/m^2 .

Two processes governs the development of the corrosion products, the uptake of material from the environment and the runoff of dissolved metal or patina components, the last process being effective only for unsheltered samples. The first process increases the weight because the oxygen of the oxides and the anions, mainly the sulphates, are absorbed from the environment, whereas the runoff decreases the weight. The weight change is thus always positive for sheltered samples but can be positive or negative for unsheltered samples. This is illustrated in figure 8 which shows the weight change as a function of time. After an initial buildup of corrosion products the weight starts to decrease, resulting in a negative linear trend. All curves of weight change of copper and bronze are pointing downward after 8 years of exposure.

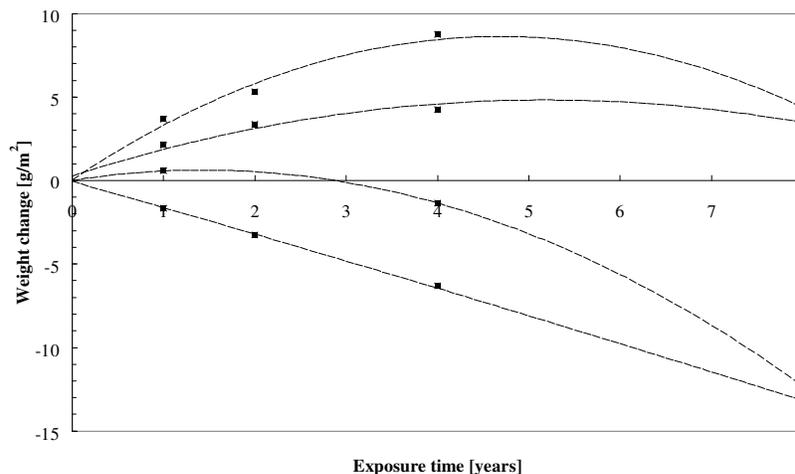


Figure 8 Weight change of unsheltered copper vs. time of exposure for four selected test sites with site number 9, 10, 2 and 16 (from bottom to top).

The weight changes of sheltered samples and the mass losses of sheltered and unsheltered samples can generally be fitted to the time dependence at^b , where a and b are constants and t is the exposure time in years. The factor a is almost identical to the 1-year value, *i.e.*, a can be regarded as the initial rate. The factor b is smaller than unity for the majority of the test sites; the rates are decreasing with exposure time. Small b values indicate a significant decrease of the reaction rates with time.

For copper exposed at typical rural sites the a value is high and the b value is low which means that a passive oxide layer is generated at a very early stage of exposure. These high values of the corrosion rate after 1 year of exposure observed at the rural test sites are not found for bronze. The difference between copper and bronze is due to the large initial formation of cuprite that seems to be specific for copper. The formation is influenced by humidity and the presence of ozone, which is generally high at the rural test sites. For the sheltered specimens the percentage of metal in the corrosion products can be calculated:

$$\%Me = 100ML/(ML+WCH) \quad [6.1]$$

Calculations using molecular weights show that copper oxides have high %Me values whereas the %Me values for basic copper sulfates are significantly lower. Thus, the formation of cuprite results in a higher mass loss values or corrosion rates compared to basic sulfates. This, together with the fact that cuprite formation is favored at rural sites explains the difficulty in obtaining reliable dose-response relations for copper at an early stage of the exposure.

6.2.1 Dose-response relations

O₃ was continuously measured at only 23 of the 39 test sites. At the other sites, ozone was calculated from NO₂ values using an empirical relationship. Because of the narrow relation of these gases, only one of the two was selected for each multiple regression.

Principal component analysis (PCA) shows that the mass loss of bronze is related to SO₂ and conductivity whereas the mass loss of copper is related to high wetness parameters and high ozone values. With time, copper changes its characteristics gradually and becomes more and more similar to bronze. The obtained dose-response relationships are valid for the entire exposure period, 1-8 years:

	R²	N	
$\ln ML_{Cu,unsh} = -0.45 + 0.74\ln t + 0.013[SO_2] + 0.025Rh + 0.010[O_3] + 2.56Rain[H^+]$	0.76	149	[6.2]
$\ln ML_{Cu,sh} = -3.48 + 0.76\ln t + 0.014[SO_2] + 0.050Rh + 0.025[O_3]$	0.67	152	[6.3]
$\ln ML_{Br,unsh} = +0.57 + 0.80\ln t + 0.011[SO_2] + 0.012Rh + 0.084[Cl^-] + 3.81Rain[H^+]$	0.85	148	[6.4]
$\ln ML_{Br,sh} = -0.85 + 0.99\ln t + 0.013[SO_2] + 0.016Rh + 0.103[Cl^-] + 2772[H^+]$	0.80	148	[6.5]

In these equations [H⁺] is expressed in mol/l. Otherwise, the symbols are according to table 3.

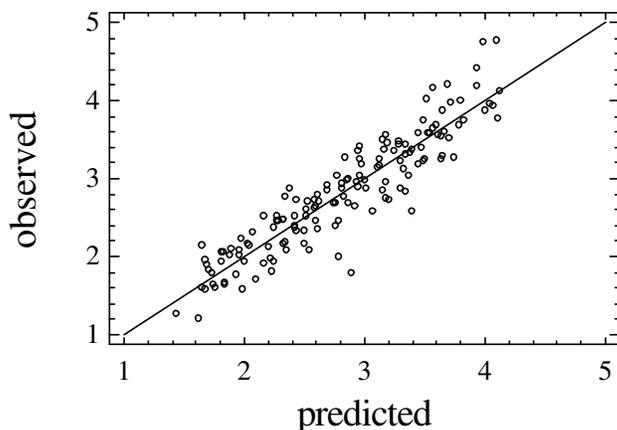


Figure 9 Observed vs. predicted values for mass loss of unsheltered bronze based on equation 6.4.

6.3 Calcareous stone materials

The sub-centre responsible for the evaluation of calcareous stone materials is the Building Research Establishment (BRE), Garston, Watford, United Kingdom. The following is a brief summary of their results [4].

The weight loss data were compiled from measurements for each of the 39 sites and for two stone types, Portland limestone and Mansfield sandstone. Three weight changes were recorded for each site of each of the years 1, 2, 4 and 8. Triplicate weight changes were averaged to give the weight loss at each site. These are reported as the erosion in microns per year from the surface of the tablets.

The weight data for both limestone and sandstone could be split into a trimodal distribution consisting of low, medium and high weight loss. However, breaking the data into groups does not significantly alter the conclusions about the manner in which the data are correlated and the low number of sites in the high and medium data sets makes the analysis of the subsets dubious. No attempt has been made to normalise the data using logarithmic transformations. Comparison of limestone and sandstone weight losses show that the two data sets follow an almost identical pattern, *i.e.*, the two data sets are virtually the same and the expectation is that the same trends will be observed in both data sets with minor changes in the coefficients. Weight losses against time were shown to be linear for both stone types across the eight year period with few exceptions, apart for year one.

Inspection of the environmental data indicated that the majority of the site conditions did not vary significantly across the eight year period, or at least remained within the order of one or two standard deviations. Thus, statistically the environmental data could be taken to be static with respect to time. The only exception to this was the sulphur dioxide data which showed substantial changes (mostly decreases) across the eight year period. Furthermore, any variable measuring the amount of moisture/ water can be used within the analyses since they are all interrelated. Also, gaseous emissions are often characterized by general simultaneous fluctuations of the components. Last, the conductivity is a good indirect indicator of the pH, gaseous absorption and the mineral content of the rainwater, all of which will affect the rate of dissolution. However, it is not the prime cause of damage. The strength of the correlation would affect the correlation coefficients when multiple regression techniques are used. On the grounds of that the

conductivity is substituting for the true variable sulphur dioxide the conductivity has been left out of the regression analyses.

6.3.1 Dose-response relations

Sulphur dioxide is the main contributor to the degradation of calcareous stones in areas of high pollution. Wet deposition and natural dissolution of stone are important, particularly in places where pollution concentrations are low. Linear dose-response relations have been formulated from the unsheltered samples which show moderately good predictive capabilities within the existing data set.

Multiple linear regression of the weight losses against the environmental data indicates that the major correlation rests entirely with the sulphur dioxide and with rainfall (or one of the indicators for rainfall) as an explanatory variable for the residuals once the effect of sulphur dioxide is taken into account. An important finding is that the R² values for individual time periods are very good but much worse when applied to the whole data set. The equations were therefore developed as below having converted weight percentage loss into a rate per year and including time as a variable. Four forms of the equation were examined using multiple linear regression:

$$A[\text{SO}_2] \quad [6.6]$$

$$A[\text{SO}_2] + B \cdot \text{pH} \quad [6.7]$$

$$A[\text{SO}_2] + B \cdot \text{Rain} \quad [6.8]$$

$$A[\text{SO}_2] + B \cdot \text{pH} + C \cdot \text{Rain} \quad [6.9]$$

Equation 6.6 gave the poorest fit whilst equations 6.7, 6.8 and 6.9 were almost equal in the degree of fit measured using R². Equation 6.8 was slightly better than equation 6.7. Introduction of a third term in equation 6.9 increased the goodness of fit marginally, as would be expected with extra terms added. However, the confidence limits on the coefficients of the equations were severely reduced. Thus, equation 6.8 is the preferred form. This analysis departs slightly from the previous 4 year data analysis in which the pH was included to account for a dissolution, but gives overall a better correlation than before. The resulting dose-response relations for the total thickness decrease of unsheltered stone samples (Th) in µm over time, t, are:

$$\text{Th}_{\text{Sandstone, unsh}} = -30t(0.0085[\text{SO}_2] + 1.9 \times 10^{-4} \text{Rain}) \quad [6.10]$$

$$\text{Th}_{\text{Limestone, unsh}} = -30t(0.0071[\text{SO}_2] + 2.4 \times 10^{-4} \text{Rain}) \quad [6.11]$$

where Rain is expressed in mm. A physical explanation for the marginal nature of the rainfall term is that the average rain volumes in the data set represent about 1% - 3% of the recorded weight loss, based on solubility arguments. On the basis of this estimate the rain term is a minor adjustment to the estimate based on sulphur dioxide alone.

For sheltered samples there is a correlation of SO₄²⁻ content with weight gain and SO₂ concentration. Soluble salts analysis on sheltered samples confirms the predominance of SO₂ as the most reacting pollutant. There is also evidence in some sites of marine and industrial influences. Dose-response relations were obtained for both limestone and sandstone where only SO₂ was significant and with the R² coefficient being again better for individual years than for the whole data set. The resulting equations for the sheltered samples are

$$\text{Th}_{\text{Sandstone, sh}} = 30t \cdot 0.0013[\text{SO}_2] \quad [6.12]$$

$$Th_{\text{Limestone, sh}} = 30t \cdot 0.0014[\text{SO}_2]$$

[6.13]

If the sheltered samples had been placed in a box of more open structure, perhaps giving a better simulation of stone in a sheltered position on the outside of a building, it is likely that weight changes, and hence degradation, would have been greater. The sheltered situation is complicated by increases in weight resulting from more than one factor, *i.e.*, particulate deposition as well as reaction with SO_2 . As particulate deposition is not measured it is difficult to make further developments of the dose-response relations for sheltered samples other than on mechanistic grounds.

6.4 Paint coatings for wood, steel and galvanized steel

The sub-centre responsible for the evaluation of paint coatings is the Norwegian Institute for Air Research (NILU), Lilleström, Norway. The following is a brief summary of their results [5].

Four different paint systems were tested: coil coated galvanized steel with alkyd melamine (*G*), alkyd on steel (*H*), alkyd on wood (*I*) and acrylate on wood (*K*). The evaluation has followed the available ASTM standards which results in a ranking from 10 (no attack) to 1 in the parameters general appearance, dirt, chalking, fungus, flaking, cracking, checking and gloss. For the metal paint systems (*G* and *H*), corrosion attack starting from an artificial cut through the paint was also evaluated and this parameter is called 'damage from cut'.

It is to some degree complicated to select the right damage parameter for the development of response relations. General appearance is often the parameter which in practice is used to decide when maintenance shall start. However, this parameter is largely affected by the environmental conditions immediately before inspection. After a dry, hot and dusty period the appearance may be influenced by dirt which is later washed away. The detailed information about the climatic changes that is required to evaluate this parameter is not available in the programme. Instead, fungus (*F*) has been used for the general degradation for all four paint systems (*G*, *H*, *I* and *K*). In addition, cracking has been used for the wood systems (*I* and *K*) and damage from cut has been used for the metal systems (*G* and *H*). Cracking (*C*) has been observed on most of the wood samples while other parameters only are affected after 8 years of exposure and only for a small number of sites. Damage from cut (*D*) is an irreversible parameter and is therefore useful for dose-response studies. Even after 8 years of exposure it was not possible to detect a thickness reduction on the undamaged area of the metal systems.

6.4.1 Dose-response relationships

The scale used in the visual ASTM evaluation of damage to paint systems is based on pictures and verbal descriptions, and the linearity of the scale can not be validated. However, an empirical function relating the ASTM evaluation to the length of exposure, can be estimated, and used to calculate lifetime. The lifetime may then be related to environmental parameters.

The statistical analysis was done in two steps. First, the functional relationship between ASTM rating and time of exposure was estimated using the equation

$$11 - \text{ASTM} = \exp\{\beta \cdot t\}$$

[6.14]

where β is a constant and t is the exposure time in years. The pre-exponential factor has been fixed to unity in order to ensure that the initial condition

$$\text{ASTM}_{t=0} = 10 \quad [6.15]$$

is satisfied. The lifetime, L_v , was then defined as the time at which the damage evaluation is classified as ASTM rating 5, as suggested by the paint industry, and calculated using the relationship

$$L_v = \ln(6)/b \quad [6.16]$$

where b is an estimate of β . Example of the procedure is shown in figure 10.

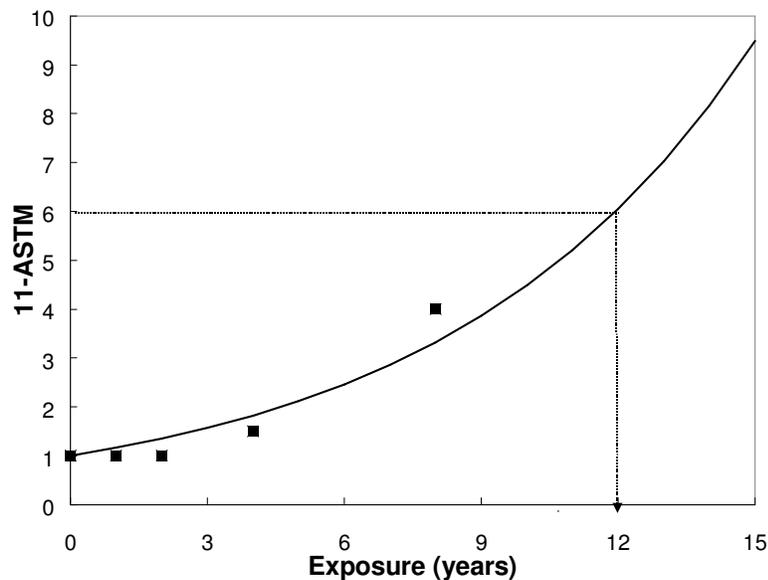


Figure 10 Prediction of lifetime from ASTM rating and maintenance action at ASTM rating 5.

In the second step of the analysis, the lifetime (L_v) was related to selected environmental parameters. Two sets of parameters were considered. In the first set (a) parameters were included that describes a number of processes contributing to the deterioration of the paint systems while the second set (b) was restricted and only included parameters with a straight-forward physical or chemical explanation:

extended set (a)	restricted set (b)
Tow, Sun, Sun·Tow	T, Rh, Sun (cracking)
[SO ₂], [SO ₂]Tow	[SO ₂]
[NO ₂], [NO ₂]Tow, [SO ₂][NO ₂]Tow	
[O ₃], [SO ₂][NO ₂][O ₃]	
Rain, [H ⁺], Rain[H ⁺]	Rain
[Cl ⁻]	[Cl ⁻] (fungus)

The symbols are according to table 3 with a few exceptions and additions. The solar radiation (Sun) is measured in MJ/m² and the time of wetness (Tow) is measured in time

fractions. Ozone is included in two variants, measured or calculated based on a relationship with NO₂. Finally, Rain is measured in mm and [H⁺] in mol/l.

Eight-year averages of the environmental parameters were related to the estimated lifetime Lv, using stepwise linear regression with backward elimination of parameters. In order to account for differences in statistical fit when estimating the model parameter two variants were used, unweighted and weighted using parameters of the regression fit. However, the difference in the results was minimal, and therefore, only the weighted results are presented here for the restricted set (b) with R² of the model for the extended set (a) in parentheses for comparison. Life-time equations are available for four paint systems: alkyd melamine on galvanized steel (G), alkyd on steel (H), alkyd on wood (I) and acrylate on wood (K)

Damage from cut:

Lv(G) =	17.2 - 0.0299[SO ₂] - 0.105Rh - 0.00249Rain	R ² =0.55 (0.93)	N=36	[6.17]
Lv(H) =	21.7 - 0.0473[SO ₂] - 0.168Rh - 0.00271Rain	R ² =0.58 (0.91)	N=36	[6.18]

Fungus:

Lv(H) =	51.5 - 0.582Rh + 1.9[Cl ⁻]	R ² =0.36 (0.46)	N=31	[6.19]
Lv(G) =	17.6 - 0.00983Rain	R ² =0.11 (0.58)	N=26	[6.20]
Lv(K) =	67.7 - 0.639Rh - 1.26T + 2.71[Cl ⁻]	R ² =0.41 (0.65)	N=33	[6.21]
Lv(I) =	29.2 - 0.252Rh - 0.367T + 0.484[Cl ⁻]	R ² =0.29 (0.54)	N=34	[6.22]

Cracking:

Lv(I) =	18.0 - 0.0861Rh - 0.00134Rain - 0.00072Sun	R ² =0.55 (0.57)	N=33	[6.23]
Lv(K) =	49.9 - 0.339Rh - 0.00365Sun	R ² =0.50 (0.31)	N=33	[6.24]

Results obtained from models using the first set of variables are promising, but complicated. Generally, the interaction terms are acting as modifiers of effects of individual variables, as expected. However, there is a complicated correlation structure in these variables, which complicates the interpretation further. In practice, the results obtained using the first parameter set need further analysis before they can be applied to estimating changes in damage connected to development in exposure parameters.

The second parameter set, explains the variability in lifetime for damage from cut and cracking reasonably well despite the much reduced number of parameters. SO₂ is the only air pollutant used, and it is associated only with damage from the cut (on both paint systems). A decrease of 5 µg/m³ of SO₂ (8-year average), increases the estimated lifetime by 0.2 years for system H and 0.1 years for system G. Cracking is only influenced by climatological parameters. Fungus shows positive association with Cl⁻ for all paint systems except G. For fungus on system G, no satisfactory relationship was established using the restricted parameter set.

6.5 Electric contact materials

The sub-centre responsible for the electric contact materials is the Swedish Corrosion Institute, Stockholm, Sweden. The following is a brief summary of their results [6].

The electric contact materials group contains nickel, copper, silver, tin and Eurocard connectors. These are exposed in rain sheltered position and inside a sheltering aluminum box to simulate the conditions for unheated storage of electronic devices. The materials can be separated in two different groups, one containing nickel, silver and

Eurocard connectors, and the other containing copper and tin. The corrosion of the first group is mostly related to the SO₂ concentration and to a limited extent to other parameters while the corrosion of the second group is more difficult to explain.

Analysis of nickel shows that it relates mainly to the SO₂ concentration. The corrosion products consists of basic nickel sulfates of different crystallinity. The protective ability increases with crystallinity which in turn increases with exposure time.

The weight increase of silver was due to the formation of Ag₂S and due to the deposition of chemical species, possibly ammonium chloride and/or ammonium sulfates, and organic contaminants. Since H₂S is not measured within the programme it has not been possible to estimate its contribution to the total Ag₂S formation compared to the contribution from SO₂.

The weight increase of copper is high both at low polluted sites, where O₃ is the main gaseous pollutant, and at high polluted sites, dominated by SO₂ and NO₂. Sulfate, nitrate, chloride and cuprite were detected on the copper surfaces. Nitrate was often found at the most polluted sites, whereas, cuprite was found at the low polluted sites. Sulfate was often dominating, both at high and low polluted sites. This is confirmed in a statistical analysis of mass loss and weight increase data that reveal that cuprite dominates at humid rural sites with high O₃ values.

The weight increase of tin did not correlate to the measured environmental data except chloride concentration in precipitation and the corrosion products consisted of oxides with different stoichiometries. Traces of particulate ammonium sulfate were also detected as it was on the other metals. Tin behaves similarly to copper in that both forms oxides. The general difficulty in describing tin corrosion, and also copper corrosion, may be due to the difficulty of quantifying oxide formation under field atmospheric conditions.

The Eurocard connectors consist of a base material (brass) covered with layers of nickel and gold in the μm-range. It is difficult to evaluate the corrosion attack on Eurocard connectors but it is evident that the attack after 8 years of exposure correlates with corrosion attack on nickel in general and mostly to the 1 year nickel exposure. This means that the exposure of a pure underplating material may be appropriate for simulating the behavior of Eurocard connectors, however, a time delay depending on the gold thickness may be present. The visual examination after 8 years of exposure correlates with SO₂ concentration times time of wetness but the trend is only clear at low and high polluted sites, not at medium polluted sites.

All metals (Ni, Cu, Ag, and Sn) show almost linear kinetics. The positions in the aluminum box are not equivalent due to concentration and mass transport differences but by assuming that nickel has a linear kinetics or SO₂ dependence it is possible to quantify the differences. By comparing different types of nickel box factors the effect of decreasing SO₂ concentrations in Europe was detected.

6.5.1 Dose-response relations

The weight increase (WI) of nickel in the aluminum box can be predicted, within a factor of two, for all stations and the entire exposure period, 1-8 years, by using the SO₂ concentration in the ambient air, an SO₂ deposition velocity of 0.34 cm/s, a shelter/box concentration ratio of 5 and a molecular weight ratio of 1.95 g weight increase/g SO₂.

The uncertainty in the prediction depends largely on the variation in mass transport conditions and concentration differences within the box. The corrosion rate for nickel can thus be estimated with the equation

$$ML_{Ni} = 2.4t[SO_2] \quad [6.25]$$

where ML_{Ni} is the mass loss in $\mu\text{g}/\text{cm}^2$, t is the time in years and $[SO_2]$ is the concentration in $\mu\text{g}/\text{m}^3$. This equation is based on a regression of weight increase on SO_2 , see figure 11, and a comparison of weight increase and mass loss values. It should be stressed that the SO_2 concentration used in the equation is measured outside the aluminium box and that the concentration inside the box, where the samples were exposed, is approximately 5 times lower.

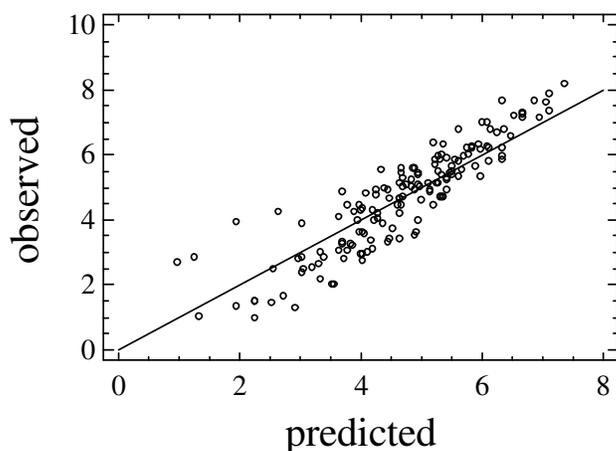


Figure 11 Observed vs. predicted (logarithmic) values for weight increase of nickel in $\mu\text{g}/\text{cm}^2$ and a dose-response function $Wl_{Ni} = At[SO_2]$.

Mass loss and weight increase values of copper after 8 years of exposure indicates that the corrosion products either can be dominated by cuprite or basic sulfates and that the variation between sites in this respect is substantial. Cuprite dominates at humid rural sites with high ozone values. After 8 years of exposure sites 14, 28 and 37 show considerable corrosion attack even though the corrosion attack was minor for shorter exposure times. The only model obtained for copper does not include these sites and involves many factors including gaseous, climatic and precipitation parameters. Therefore, no equation suitable for mapping and calculation of costs have been derived for copper exposed inside the aluminium box.

The equation obtained for silver involves SO_2 concentration and NH_4^+ concentration in precipitation. With multiple linear regression (MLR) the relative importance of NH_4^+ is overestimated, compared to partial least squares (PLS) and the predictive ability of the model decreases with exposure time. This is most likely due to the fact that Ag_2S is the dominating corrosion product. Ag_2S is related to H_2S which is not measured within the programme. Therefore, no equation suitable for mapping and calculation of costs has been derived for silver.

In the uniform statistical evaluation (section 4.4.4) a dose-response relation was derived including ozone as an explanatory parameter. In the original analysis, however, no equation involving gaseous pollutants was obtained for tin but there is a low correlation

to the chloride concentration in precipitation. However, chloride was not detected on the tin samples while it was detected on all other metals and tin forms oxides as dominating corrosion products. The chloride concentration in rain can only be an indirect measure of a corrosive specie, as the samples are well protected from rain.

6.6 Glass materials

The sub-centre responsible for the evaluation of glass materials is the Institute of Chemistry, Academy of Fine Arts, Vienna, Austria. The following is a brief summary of their results [7].

Potash-lime-silica glass was used predominantly in the Middle Ages for stained glass windows in cathedrals, churches or other historic buildings. These artifacts, consisting of numerous pieces of glass colored with metal oxides, show accelerated deterioration, particularly on their exterior surfaces. Therefore, the atmospheric attack of glass samples with a chemical composition similar to medieval stained glass was studied under natural conditions. Two types of glasses were used, one with a high amount of network modifiers to increase the sensitivity towards atmospheric attack (glass M1) and one with a higher chemical stability (glass M3). 23 test sites were selected from the original network to obtain a wide range of SO₂ and NO₂ concentrations, and of the relative humidity. Due to the different stabilities glass M1 was exposed for ½ and 1 year whereas glass M3 was exposed for 1 and 2 years.

As for metals, two types of processes can be distinguished in the glass weathering process, development of corrosion products and rain-induced removal of corrosion products for unsheltered conditions. Glass has ion exchange properties and the first step in the degradation process is the exchange of alkali ions in the glass network with hydrogen ions, which results in a pH-increase in the aqueous adlayer. In general, this ion exchange process leads to the formation of a leached layer on the glass surface. For sheltered conditions, where the alkaline solution is not removed, hydrolysis of siloxane bonds can result in destruction of the glass network if the pH is approximately above 9 depending on the composition of the glass. Therefore, different measures of the corrosion attack were used for samples exposed in unsheltered and sheltered conditions. However, scanning electron microscopy (SEM) was used to examine the morphological identification of weathering products for both sheltered and unsheltered samples.

The sheltered samples were characterised by the weathering products' degree of covering on the glass surface which was evaluated by SEM analysis in combination with image processing. The ratio of the area covered by products to the total image area (CS-covered surface) was used. The use of this parameter implies that densities of corrosion products are constant and homogeneous which did not occur in all cases in practice.

The unsheltered samples were characterised by the depth of the leached layer (LL). The thickness of this layer was up to 22 µm for glass M1 and approximately 1 µm for the more resistant M3 glass. The leached layer of glass M1 was evaluated in cross section by SEM in combination with energy dispersive x-ray microanalysis (EDS). The evaluation of the depth profiles of calcium and potassium resulted in different depths of the leached layers. The leaching of potassium ions proceeded into deeper regions of the glass than the leaching of calcium. Since the depths of the potassium profiles were similar to those obtained from backscattered electron images the potassium depth values were used. Unfortunately, the lateral resolution of SEM was insufficient to obtain depths for the leached layers of glass M3, which had to be analysed by nuclear reaction analysis (NRA).

This latter technique gives the hydrogen depth distribution from the outermost region of the sample surface. The change of the hydrogen content was then used to obtain the depth of the leached layer.

To summarize, the leached layers for glass M1 were determined by SEM-EDS using the depletion of potassium whereas the leached layers for glass M3 were determined by NRA using the enrichment of hydrogen.

6.6.1 Dose-response relations

The probability of normal distribution of the corrosion parameters was rather low in most cases. Therefore, the logarithmic values were used in the dose-response relations and the same was true for the SO₂ concentration.

The dominating factor for the weathering of glass M1 is the SO₂ concentration and the influence of humidity is negligible compared to this effect. Also, an NO₂ effect is observed which is rare in the programme. A correlation analysis with the purpose of examining the redundancy of cross terms leads to the conclusion that cross terms including more than one gaseous pollutant could be excluded from the analysis. However, the cross term [NO₂]RH was included since it resulted in a slightly better fit than [NO₂] only. Attempts using multiple regression showed higher significance when using RH compared to TOW. The following dose-response relations were obtained for the leached layer (LL) and the covered surface (CS) for ½, 1 and 2 years of exposure:

				R ²	n	
$\ln(^{1/2}\text{LL}_{\text{M1,unsh}})$	= -0.14 + 0.57ln[SO ₂]	+ 10.2Rain[H ⁺]		0.79	18	[6.26]
$\ln(^1\text{LL}_{\text{M1,unsh}})$	= -2.76 + 0.44ln[SO ₂]	+ 1.6E-3Rain[H ⁺]	+ 4.6E-2RH	0.64	18	[6.27]
$\ln(^{1/2}\text{CS}_{\text{M1,sh}})$	= 2.11 + 0.43ln[SO ₂]	+ 1.7E-4[NO ₂]RH		0.52	20	[6.28]
$\ln(^1\text{CS}_{\text{M1,sh}})$	= 0.46 + 0.23ln[SO ₂]	+ 3.9E-4[NO ₂]RH	+ 2.4E-2RH	0.46	20	[6.29]
$\ln(^1\text{LL}_{\text{M3,sh}})$	= 5.17	+ 2.6E-4[NO ₂]RH		0.51	15	[6.30]
$\ln(^2\text{LL}_{\text{M3,sh}})$	= 5.24 + 0.24ln[SO ₂]	+ 1.1E-4[NO ₂]RH		0.35	20	[6.31]

where Rain is measured in mm and [H⁺] in mol/l. For unsheltered M3 glass samples, however, negative SO₂ and NO₂ coefficients were observed. One possible explanation of this result can be leaching and consequently network dissolution of the leached layer. However, SEM images show a smooth and rather unweathered glass surface. Another explanation of the negative influence could be the formation of a protective layer on the M3 glass surface. Further investigations will be necessary to explain these unexpected results.

6.7 Polymeric materials (polyamide and polyethylene)

The sub-centre responsible for the polymeric materials is the Swedish Corrosion Institute, Stockholm, Sweden. The following is a brief summary of their results [8].

The present summary is based on evaluation of mechanical properties of polyethylene samples (PE) and polyamide samples (PA) exposed 0.5, 1, and 2 years in open and sheltered positions and from measurements of IR spectra of polyethylene samples exposed for 1 year. The results are preliminary in anticipation of the final evaluation of samples from the withdrawal after 4 years of exposure performed in October 1997.

Figure 12 shows typical tensile stress vs. strain curves for non-exposed PA and PE samples. Four measures of the mechanical properties have been evaluated for each stress-strain curve: Young modulus (MO), Energy to break point (EN), Tensile strength (BT) and Elongation (BE). The modulus is the initial slope of the curve expressed in MPa and the energy is the total area under the curve expressed in J. The tensile strength and elongation are the coordinates of the break point.

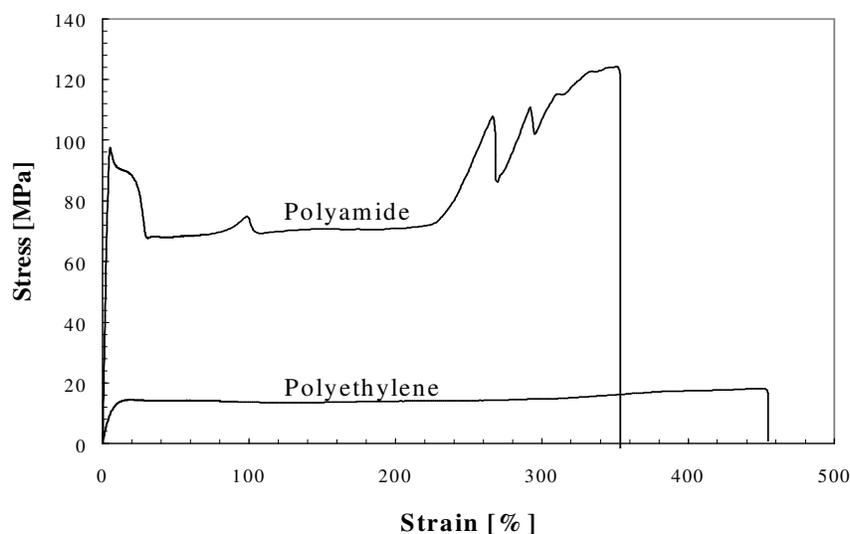


Figure 12 Typical stress-strain curves for unexposed polyamide and polyethylene samples.

Elongation (BE) is the best measure of degradation of the four parameters investigated (modulus, energy, tensile strength, and elongation). Furthermore, polyethylene is more resistant to attack than polyamide and the sheltered samples are more resistant to attack than the open. For shorter exposure times, elongation and strength are positively correlated but becomes, after a transition time, negatively correlated resulting in very hard samples that breaks easily. The exposure of polyethylene results in the formation of carbonyl and vinyl groups in the polymer and this formation is correlated to the degradation of the material.

6.7.1 Dose-response relations

Polyethylene exposed in open position can be described by a dose-response relation containing temperature and sunshine radiation. Temperature is the most important parameter and higher temperatures relates to more degraded samples as is shown by regression of infrared (IR) data for polyethylene (PE) exposed in open position for one year (O1):

$IR_{PEO1} = 0.00 + 0.050T$	R²	n	
	0.90	16	[6.32]
$IR_{PEO1} = -0.12 + 0.045T + 0.00005Sun$	0.91	16	[6.33]

In addition, it is possible to estimate service life times from elongation (BE) but this parameter is difficult to correlate to environmental parameters:

$\tau_{PEO}(BE) = 1.22 - 0.038T$	R²	n	
	0.38	19	[6.34]

where the life time, τ , is measured in years. The constant 0.038 is measured in year/°C which means that the effect of temperature is a life time decrease of approximately 2 weeks/°C for open polyethylene. It should be stressed that the explained variability in eq. 3 is rather low and this is due to the fact that the real relationship between τ and T is not linear.

At almost all test sites, polyamide exposed in open position was severely degraded already after 0.5 years of exposure. At all test sites, polyethylene exposed in sheltered position was relatively unaffected even after 2 years of exposure. Also, no dose-response relation was found for polyamide exposed in sheltered position. So far, it has not been possible to quantify the effect of gaseous pollutants.

7 Evaluation of trends

7.1 Environmental trends

The environmental sub-centre, the Norwegian Institute for Air Research (NILU), is responsible for the evaluation of trends of environmental parameters. The following is a summary of their findings [1].

The analysis of trends in SO₂ concentration has been based on yearly averages and also on mean values of the winter months December, January and February which give similar conclusions. Table 10 shows the trend lines for SO₂, NO₂ and acid load based on annual averages for all test sites during the period September 1987 to August 1995. Of the

Table 10 Trend lines showing the slope (a), intercept (b) and explained variability (R²) for SO₂, NO₂ and acid load from precipitation as a function of time. SO₂ and NO₂ concentrations are expressed in µg/m³, Rain in mm, [H⁺] in mol/l and t in years where 1 refers to the 1987/88 average and 8 refers to the 1994/95 average.

Country	No Site	[SO ₂] = at + b			[NO ₂] = at + b			10 ³ Rain[H ⁺] = at + b		
		a	b	R ²	a	b	R ²	a	b	R ²
Czech Republic	1 Prague-Letnany	-6.6	83	0.92	-2.7	42	0.73	-2.4	35	0.08
	2 Kasperske Hory	-0.9	21	0.23	-1.3	16	0.68	-1.7	81	0.00
	3 Koprstý	-6.8	98	0.85	-2.0	43	0.84	1.5	10	0.19
Finland	4 Espoo	-2.1	18	0.77	1.1	18	0.44	-1.9	35	0.66
	5 Åhtäri	-0.7	6	0.70	0.0	4	0.00	-1.1	22	0.58
	6 Helsinki-Vallila	-2.4	23	0.79	0.6	33	0.08	-2.9	36	0.57
Germany	7 Waldhof-Langenbrügge	-1.2	15	0.79	-0.5	13	0.67	-1.3	26	0.25
	8 Aschaffenburg	-1.5	22	0.64	0.2	38	0.02	-1.5	17	0.14
	9 Langenfeld-Reusrath	-2.0	29	0.88	-1.7	49	0.69	-0.6	24	0.14
	10 Bottrop	-2.7	57	0.65	-1.9	52	0.86	-0.1	21	0.00
	11 Essen-Leithe	-1.8	32	0.90	-2.0	49	0.96	-0.4	21	0.05
	12 Garmisch-Partenkirchen	-1.4	12	0.75	-0.1	14	0.03	-2.4	23	0.63
Italy	13 Rome	-5.2	44	0.63	-7.0	84	0.81	-1.2	14	0.54
	14 Casaccia	-0.5	9	0.61	-0.4	15	0.06	-0.1	7	0.01
	15 Milan	-8.0	89	0.89	-3.2	118	0.40	-2.0	45	0.08
	16 Venice	-2.6	28	0.86	3.1	37	0.60	-1.0	7	0.74
Netherlands	17 Vlaardingen	-2.1	38	0.96	-1.6	58	0.66	-1.3	31	0.20
	18 Eibergen	-0.7	11	0.76	-0.8	27	0.60	2.8	-6	0.36
	19 Vredepeel	-1.0	13	0.90	-0.7	34	0.35	0.3	3	0.05
	20 Wijnandsrade	-0.9	14	0.75	-0.7	31	0.44	-1.4	15	0.69
Norway	21 Oslo	-1.5	15	0.91	1.3	47	0.40	-2.5	25	0.49
	22 Borregard	-2.8	47	0.48	0.2	18	0.09	-9.6	95	0.49
	23 Birkenes	-0.1	1	0.69	-0.3	4	0.76	-7.3	99	0.55
Sweden	24 Stockholm South	-1.6	15	0.79	-1.0	32	0.55	-1.2	23	0.36
	25 Stockholm Centre	-2.4	20	0.67	-3.4	48	0.76	-1.2	23	0.36
	26 Aspvreten	-0.2	3	0.61	-0.3	5	0.86	-1.0	23	0.25
United Kingdom	27 Lincoln Cathedral	-1.3	22	0.45	-8.2	68	0.90	-0.5	15	0.03
	28 Wells Cathedral	-0.5	8	0.69	-0.1	24	0.04	5.1	-5	0.09
	29 Clatteringshaws Loch									
	30 Stoke Orchard	-0.1	14	0.00	-8.5	70	0.70	2.3	85	0.00
Spain	31 Madrid	-1.8	20	0.86	-0.1	26	0.00	-0.3	2	0.40
	32 Bilbao	-6.2	50	0.76	-2.1	42	0.50	-1.8	19	0.38
	33 Toledo	-0.7	9	0.19	0.6	13	0.11	-0.4	3	0.62
Russian F.	34 Moscow	-0.7	27	0.10	-6.7	78	0.92	-0.4	3	0.15
Estonia	35 Lahemaa									
Portugal	36 Lisbon	0.4	12	0.01	0.8	30	0.09	-0.1	2	0.06
Canada	37 Dorset	-0.2	4	0.33	0.0	2	0.01	-0.2	48	0.01
USA	38 Research Triangle Park	0.0	10	0.00	-0.2	27	0.21	-1.9	52	0.12
	39 Steubenville	-3.3	65	0.55	-0.6	44	0.04	-5.5	104	0.27

analyzed test sites all but two, sites 36 and 38, show a decreasing SO₂ trend. For site 36, Lisbon, the trend is disturbed by local building activities during the years 1991 and 1992. For site 38, Research Triangle Park the level is quite constant during the project period. In general, the highest reductions are observed at sites with high initial values. For Bilbao, site 32 in Spain, the reason for the very substantial decrease in pollution is that several important metallurgical industries have been closed during the latest years of the programme. The SO₂ concentration has dropped 78% from a four year average for 1987-91 of 37 µg/m³ down to 8 µg/m³ for the last four years. Even for several of the low concentration rural sites the SO₂ level has dropped. If the drop is calculated in percentage during the period 1987/88 to 1994/95 it is above 70% for all sites in Finland, for Stockholm (75%), site 24 and 25, and Oslo (80%), site 21, in Scandinavia, for Garmisch-Partenkirchen (74%), site 12, in Germany and for Rome (80%), site 13, in Italy.

Similarly, also the trend of NO₂ concentration has been analyzed both based on annual averages and on averages for winter months (table 10). Since the NO₂ level is affected both by stationary as well as mobile sources, local regulations could influence the results at the test sites differently. However, for some countries and sites the trend is quite clear. In many of the cities a trend of reduction is obvious. The strongest reduction is observed in UK: Lincoln, site 27, and Stoke Orchard, site 30. The reduction for Rome, site 13, is also high, but the amount of data is small for a definite conclusion. Large reductions are also observed for Moscow, site 34, Stockholm, site 25 and Milan, site 15. The same trend is observed at all sites in the Czech Republic, and for many sites in Germany and the Netherlands. The highest increase is observed for Oslo, site 21 and Venice, site 16. The results for site Lisbon, site 36 are influenced by the construction work, as was the case for SO₂. Finland is also a country where no reduction of NO₂ was observed.

The O₃ level has only been measured at 22 of the test sites in the programme. Not all of these registered O₃ values during the entire programme and gaps were quite frequent. When analysing the data no specific trends were observed, either increasing or decreasing.

Table 10 shows also the trend lines for acid load. The trend is decreasing for most sites but the fluctuation is larger compared to the gases. Even so, the trend of H⁺ reduction is observed at most of the test sites.

7.2 Corrosivity trends

The sub-centre responsible for the trend analysis is SVÚOM Praha a. s., Prague, Czech Republic. The following is a brief summary of their results [9]. The statistical analyses of trend results have been carried out by SVÚOM and by the Swedish Corrosion Institute in cooperation with the Institute of Physical Chemistry of the Russian Academy of Sciences.

The aim of the trend exposures is to serve as a confirmation of the environmental effects of previous pollutant reductions achieved under the Convention, as well as a method for identifying extraordinary environmental changes that result in materials damage.

The trend exposures consist of repeated 1-year exposures of carbon steel and zinc on all test sites starting and ending in the fall. In general, the exposure periods have been 1987-88, 1992-93 and 1994-95 with the exception of unsheltered zinc where the first

exposure period was replaced with a repeated exposure 1990-91. The reason for using carbon steel and zinc is that ISO 9223 recommends these metals for classification purposes and accordingly data from earlier exposures are available from many sites.

There are comparatively few exposure periods for assessment of the corrosion effect while pollution data are available each year. In order to present the results on a common scale all values are compared to the initial value, corresponding to the 1987/88 period (100%) and the results are presented in figure 13. The corrosivity change is substantial, resulting in a reduction in corrosion rate of carbon steel of 34% which is, however, relatively smaller than the SO₂ reduction (52%).

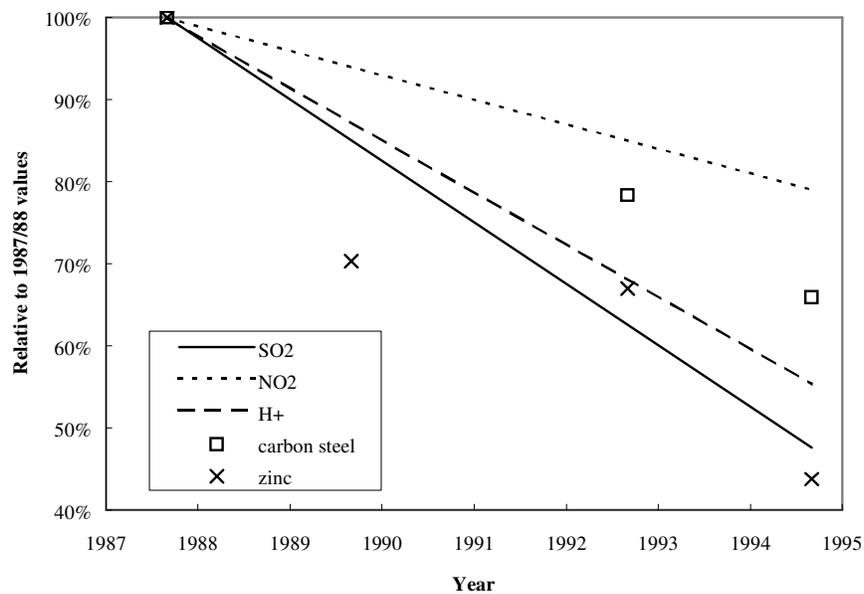


Figure 13 Trends of SO₂, NO₂, acidity (H⁺), and corrosion of unsheltered unalloyed carbon steel and zinc. All values are expressed relative to the initial (1987/88) value. For environmental data the average trend during the 8-year period is indicated instead of the individual annual averages.

Table 11 show the trends in mass losses of unalloyed carbon steel and zinc. Trends for both materials and exposure conditions, i.e. unsheltered and sheltered, are statistically significant. As indicated in figure 13, the average reduction is larger for zinc compared to carbon steel. If instead calculating the percentage reductions the greatest reductions for unsheltered materials are observed in Italy, for Rome, site 13 (35%) and Casaccia, site 14 (31%) for zinc while for steel the reductions are largest in the nordic countries, i.e. for Oslo, site 21 (44%), and Stockholm, site 25 (36%).

Table 11 Trend lines showing the slope (a), intercept (b) and explained variability (R²) for unalloyed carbon steel and zinc in unsheltered and sheltered position. All trend lines are expressed as $ML = at + b$ where ML is the mass loss in g/m² and t is the time in years where 1 refers to the 1987/88 average and 8 refers to the 1994/95 average.

Country	No Site	Unalloyed carbon steel						Zinc					
		unsheltered			sheltered			unsheltered			sheltered		
		a	b	R ²	a	b	R ²	a	b	R ²	a	b	R ²
Czech Republic	1 Prague-Letnany	-29	462	1.0	-20	197	0.6	-0.2	8.0	0.3	-1.2	12.4	0.9
	2 Kasperske Hory	-11	232	1.0	-3	84	0.2	-0.9	10.9	0.9	-0.6	8.4	1.0
	3 Kopisty	-33	588	0.9	-7	256	0.9	0.1	11.1	0.8	-0.5	11.8	0.3
Finland	4 Espoo	-23	288	1.0	-6	88	0.9	-0.8	10.4	0.9	-1.0	9.2	1.0
	5 Ähtäri	-12	142	0.8	-3	33	0.8	-0.6	9.6	0.9	-1.1	9.0	0.9
	6 Helsinki-Vallila	-13	272	0.7	-8	115	0.7	-0.8	11.1	0.9	-1.4	15.1	0.9
Germany	7 Waldhof-Langenbrügge	-13	285	0.8	-7	117	0.7	-0.6	10.6	0.4	-2.6	23.1	1.0
	8 Aschaffenburg	-12	217	0.7	-4	58	0.9	-0.1	5.1	0.2	-2.5	19.9	0.9
	9 Langenfeld-Reusrath	-12	304	1.0	-5	85	0.8	0.3	6.3	0.3	-3.3	26.4	0.9
	10 Bottrop	-11	393	0.8	2	78	0.4	-0.4	13.4	0.1	-2.4	23.4	1.0
	11 Essen-Leithe	-13	359	0.9	-5	116	0.4	-0.4	11.8	0.3	-1.7	16.5	1.0
	12 Garmisch-Partenkirchen	-7	139	1.0	-5	61	0.7	-0.6	9.7	0.7	-0.4	5.1	0.9
Italy	13 Rome	-13	229	1.0	-2	51	1.0	-1.2	13.4	1.0	-0.5	5.7	1.0
	14 Casaccia	-12	242	1.0	-7	103	1.0	-1.4	14.0	1.0	-0.6	5.7	1.0
	15 Milan	-24	390	1.0	-7	108	1.0	-1.3	16.0	1.0	-0.8	8.6	1.0
	16 Venice	-5	250	1.0	-7	78	1.0	-0.3	8.6	1.0	-0.6	6.2	1.0
Netherlands	17 Vlaardingen	-12	360	0.9	-4	118	1.0	-1.0	15.1	0.7	-0.4	8.5	0.6
	18 Eibergen	-15	273	0.9	-4	58	1.0	-0.6	10.4	0.7	-1.1	9.8	0.9
	19 Vredepeel	-14	302	0.9	-4	102	0.8	-0.5	11.4	0.2	-1.0	11.4	1.0
	20 Wijnandsrade	-12	273	1.0	-2	58	0.9	-0.7	13.1	0.4	-1.5	13.6	1.0
Norway	21 Oslo	-18	247	1.0	-3	47	0.7	-0.4	7.3	0.3	-3.5	27.0	0.9
	22 Borregard	-14	440	1.0	-5	270	0.9	-0.9	19.9	0.8	-4.4	42.0	1.0
	23 Birkenes	-12	206	1.0	0	26	0.1	-0.6	11.2	0.3	-1.9	15.4	1.0
Sweden	24 Stockholm South	-25	286	1.0	-9	98	0.9	-0.4	7.1	0.9	-0.8	8.7	0.9
	25 Stockholm Centre	-26	284	0.9	-4	69	0.9	-0.4	6.6	0.8	-0.8	7.6	0.9
	26 Aspvreten	-10	153	0.9	-3	44	0.7	-0.2	6.8	0.2	-0.5	5.3	0.9
United Kingdom	27 Lincoln Cathedral	-8	327	0.5	-13	162	1.0	-1.0	15.8	0.9	-0.4	8.2	0.3
	28 Wells Cathedral	-8	260	1.0	-5	91	1.0	0.4	5.1	1.0	-0.3	6.4	0.7
	29 Clatteringshaws Loch												
	30 Stoke Orchard	-15	322	1.0				0.0	8.5	1.0	-0.6	8.5	1.0
Spain	31 Madrid	-9	223	1.0	-3	54	1.0	-0.5	6.4	1.0	-0.5	6.6	0.9
	32 Bilbao	-10	337	0.8	-4	84	0.6	-0.8	13.3	1.0	-0.1	6.1	0.1
	33 Toledo	-2	45	0.5	0	15	0.0	-0.4	5.5	0.7	-0.2	2.2	1.0
Russian F.	34 Moscow	-9	190	1.0	-3	50	1.0	-0.8	11.1	1.0	-1.0	11.0	1.0
Estonia	35 Lahemaa												
Portugal	36 Lisbon	1	240	0.0	2	69	0.6	-2.4	24.8	1.0	-0.2	6.0	0.2
Canada	37 Dorset	-7	153	1.0	-5	53	1.0	0.0	6.1	0.1	-0.5	5.5	0.8
USA	38 Research Triangle Park	-19	238	0.6	-5	77	1.0	-1.5	17.3	0.9	-0.4	6.2	0.7
	39 Steubenville	-9	218	0.1	-7	93	0.6	-1.1	14.3	1.0	-0.5	6.6	1.0

The results clearly show established trends for the environmental parameters SO_2 , NO_2 and H^+ as well as for carbon steel and zinc in both unsheltered and sheltered position. SO_2 is the most important parameter for atmospheric corrosion of steel and zinc and should be responsible for a large part of the decrease in corrosion attack.

The next part of the analysis was to quantify the SO_2 contribution to the trends in corrosion and investigate if the remaining part can be associated with NO_2 , H^+ or unknown sources, in particular to estimate the contributions of dry and wet deposition. Figure 14 show a summary of such an attempt assuming that dry deposition can be described by the parameter $\text{TOW}[\text{SO}_2]$ and wet deposition by the parameter $\text{mm}[\text{H}^+]$.

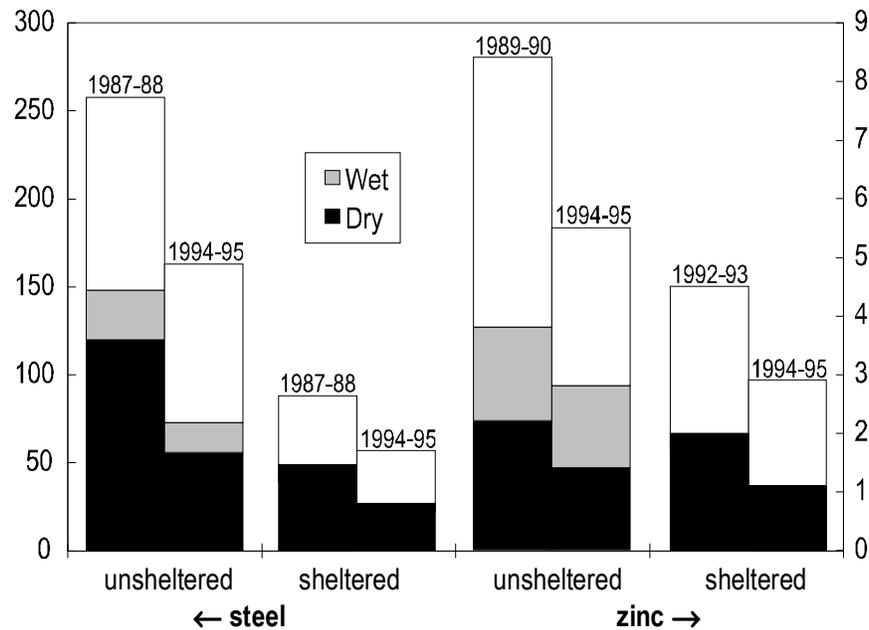


Figure 14 Mass loss of unalloyed carbon steel and zinc in g/m^2 , averaged over all ICP Materials test sites for one year exposure in unsheltered and sheltered positions. Each bar consists of the quantified parts corresponding to dry and wet deposition, and a blank part. The blank part covers unexplained effects, for example dry deposition of particles and/or HNO_3 .

8 Conclusions

- The UN ECE ICP Materials comprises an extensive field exposure programme which started in 1987 and involves 39 exposure sites in 12 European countries and in the United States and Canada. The final withdrawal of specimens was performed after 8 years of exposure.
- The aim of the programme was to perform a quantitative evaluation of the effects of sulphur pollutants in combination with NO_x and other pollutants as well as climate parameters on the atmospheric corrosion of important materials.
- The following materials groups were investigated in the individual research subcentres: structural metals, painted surfaces, electronic materials, calcareous stones, glass representative for medieval painted windows and polymer materials.
- The results of the materials exposure and of the environmental measurements create a data bank which is suitable for quantification of the effects of acidifying air pollutants on corrosion of materials.
- The statistical evaluation of the results for the materials involved was performed by the responsible research subcentres and published in separate reports.
- A unified approach for the statistical evaluation was then adopted in order to develop dose-response relations suitable for mapping purposes and calculations of cost of corrosion damage.
- The effect of dry and wet deposition has been expressed as additive terms in the unified dose-response relations which makes it possible to separate their individual contributions to the total corrosion attack.
- The effect of temperature has been included in a systematic way in the unified dose-response functions and the corrosion attack often shows a maximum in the temperature range 9 – 11 °C.
- Using this unified approach, dose-response relations have been obtained for copper, bronze, weathering steel, zinc, aluminum, nickel, tin, limestone, sandstone and glass.
- The decreasing trend in the concentration of acidifying air pollutants found in the network of urban and rural sites of ICP Materials has resulted in a decreasing trend of corrosion rate of exposed materials.
- The trend materials exposed, i.e., unalloyed carbon steel and zinc show strong negative trends in the corrosion rate, both in unsheltered and sheltered positions. The decrease in corrosivity occurred first in Scandinavia, between 1987-88 and 1989-90, and later in the western and central Europe, between 1989-90 and 1992-93.
- SO₂ is the largest single contributing factor to the decreasing trend of corrosivity.
- For unsheltered materials the decrease in corrosivity relates also partly to decreasing H⁺ in precipitation, however, the contribution is, on average but not on all sites, much smaller than that of dry deposition.

- The decrease in corrosivity is generally larger than what would be expected from the decreases in SO₂ and H⁺ concentrations. This part can not be directly related to a specific pollutant, but reflects the multipollutant character of the process of materials degradation. Likely contributors are particulates, not measured in the original programme and synergistic effects of SO₂ and NO₂ and/or O₃.
- The activity of the ICP Materials has also resulted in the development of the concept of acceptable corrosion rates and acceptable pollution levels/loads.
- The acceptable corrosion rates are based on results from the exposure programme. Using the developed dose-response relations acceptable SO₂ levels have been calculated. They have been included in the materials chapter of the UN ECE Mapping manual and are used for mapping of areas with elevated corrosion attack at different pollution scenarios and for calculation of cost of damage caused by pollution to materials.

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10 References

1. "UN/ECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No. 21: Final environmental data report September 87 to August 95.", Norwegian Institute for Air Research (NILU), Lilleström, Norway, 1997.
2. "UN/ECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No. 22: Corrosion attack on weathering steel, zinc and aluminium. Evaluation after 8 years of exposure.", SVÚOM Praha a. s., Prague, Czech Republic, 1998.
3. "UN/ECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No. 23: Corrosion attack on copper and cast bronze. Evaluation after 8 years of exposure.", Bavarian State Conservation Office, Munich, Germany, 1998.
4. "UN/ECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No. 24: Evaluation of decay to stone tablets: Part 3. After exposure for 8 years", Building Research Establishment (BRE), Garston Watford, United Kingdom, 1998.
5. "UN/ECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No. 25: Evaluation of decay to paint systems for wood, steel and galvanized steel after 8 years of exposure.", Norwegian Institute for Air Research (NILU), Lilleström, Norway, 1998.
6. "UN/ECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No. 26: Corrosion attack on electric contact materials. Evaluation after 8 years of exposure.", Swedish Corrosion Institute, Stockholm, Sweden, 1998.
7. "UN/ECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No. 27: Evaluation of decay to glass samples after 1 and 2 years of exposure.", Institute of chemistry, Academy of fine arts, Vienna, Austria, 1998.
8. "UN/ECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No. 28: Evaluation of decay to polymer samples after 4 years of exposure.", Swedish Corrosion Institute, Stockholm, Sweden, draft.
9. "UN/ECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No. 29: Trends of corrosivity based on corrosion rates. Part 2.", SVÚOM Praha a. s., Prague, Czech Republic, 1998.
10. J. Tidblad , A. A. Mikhailov and V. Kucera, "A relative humidity and temperature model for time of wetness prediction", to be published.
11. "UN/ECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No. 31: Statistical analysis of environmental data, corrosion attack and trends for the 8 year materials exposure.", Swedish Corrosion Institute, Stockholm, Sweden, draft.
12. "UN/ECE International co-operative programme on effects on materials, including historic and cultural monuments. Report No. 18: Statistical analysis of 4 year materials exposure and acceptable deterioration and pollution levels", Swedish Corrosion Institute, Stockholm, Sweden, 1995.