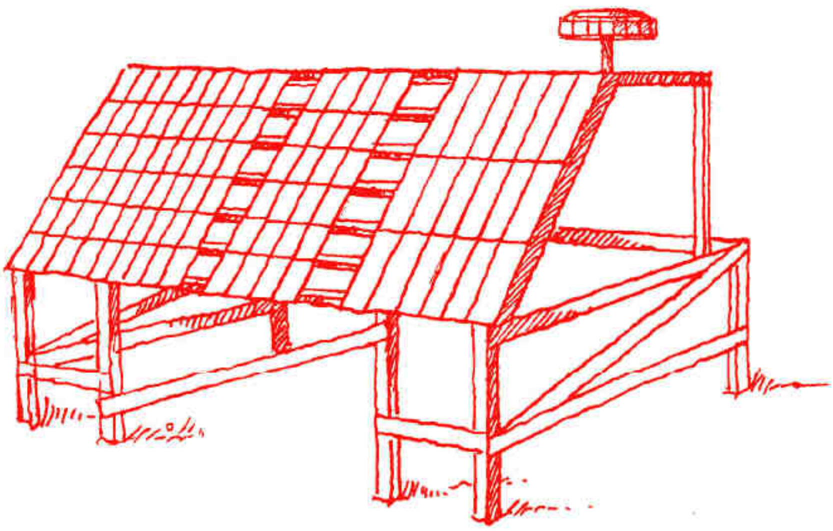
CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

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



Report No. 42

RESULTS FROM THE MULTI-POLLUTANT PROGRAMME
CORROSION ATTACK ON CARBON STEEL AFTER 1, 2 and 4 YEARS OF EXPOSURE (1997-2001)

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Summary

This report details the experimental method and gives results of evaluation of carbon steel corrosion after exposure in unsheltered and sheltered position at 30 test sites for 1 year, 2 years and 4 years in period 1997- 2001 in frame of the UN ECE ICP Effects on Materials. The report summarises the results of evaluation of corrosion gains, corrosion losses and evaluation of selected corrosion active water soluble compounds in rust layers. The preliminary results of 1 year and 2 years´ exposure had been presented in Report No 35.

The results for corrosion mass loss for 1, 2 and 4 years exposure are presented in Table 12-13 and below the mean values.

Mean and limited values of corrosion loss of carbon steel in period 1997-2001 ($g.m^{-2}$):

	1 year	2 years	4 years
open exposure			
Mean	154	210	309
Min.	53	82	147
Max	324	462	677
shelter exposure			
Mean	50	81	138
Min.	13	27	53
Max	103	176	303

In the first phase of programme carbon steel samples had been exposed only for 1 year period so there are no data to compare. This situation make difficult to perform a systematic validization of previous formulated D/R function.

Analysis of corrosion active compounds of rust layer is significant information of interaction between environment and corroded material. Rust water extract pH values are not characteristic parameter for evaluation of rust layers properties from different environmental exposures. The conductivity of rust water extract is much significantly affected by environmental conditions. The most concentrated soluble ions in adherent rust layer both in open and shelter exposure are sulphates. The second significant ion in rust layer is chloride. The concentration is higher for shelter exposure in all cases. The concentration of nitrate in adherent rust layer both in shelter and open exposure was non-significant.

Contents

Introduction

The UN ECE International Co-operative Programme was performed to 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. The programme was based on an international field exposure on 39 test-sites in a wide geographical zone of the 13 Signatories of the Convention on Long-Range Transboundary Air Pollution. The basic field exposure was performed in 1987-1995.

Within 1985 - 1995 the environmental situation have been changed. The SO_2 concentrations significantly decreased in many European countries and the pollution situation changed to multipollutant. This phase of exposure programme (1997-2001) is focused on the possible synergetic effects of NO_x, SO_2 and O_3 on a range of materials including carbon steel, zinc, copper, bronze, painted steel, glass and calcareous stone. The following list names the responsible sub-centres of this programme:

- Swedish Corrosion Institute, Stockholm, Sweden (main centre)
- SVUOM Ltd. , Prague, Czech republic
- Swiss Federal Laboratories for Material Testing and Research, Dübendorf, Switzerland
- Bavarian State Department of Historical Monuments, Munich, Germany
- Norwegian Institute for Air Research
- Building Research Establishment, Garston Watford, United Kingdom
- Institute for Chemistry, Academy of Fine Art, Vienna, Austria

SVUOM has been subcentre responsible for exposure and evaluation of samples of carbon steel in the frame of programme. The corrosion of unalloyed carbon steel is influenced to an high extent by environmental conditions mainly by acidifying airborne pollutants. Other results of evaluation of degradation of other materials exposed in this programme are reported by responsible sub-centres [1 - 6].

1. Methods

1.1. Characterisation of samples

Plates of unalloyed carbon steel (with C < 0.2 %, P < 0.07 %, Cr < 0.07 % according to CSN 11373) with dimensions 100 x 150 x 0,5 mm were used, triplicate per exposure period.

Before the exposure the samples were degreased in alkaline degreaser, rinsed with ethanol, dried and weighed.

1.2. Exposure of samples

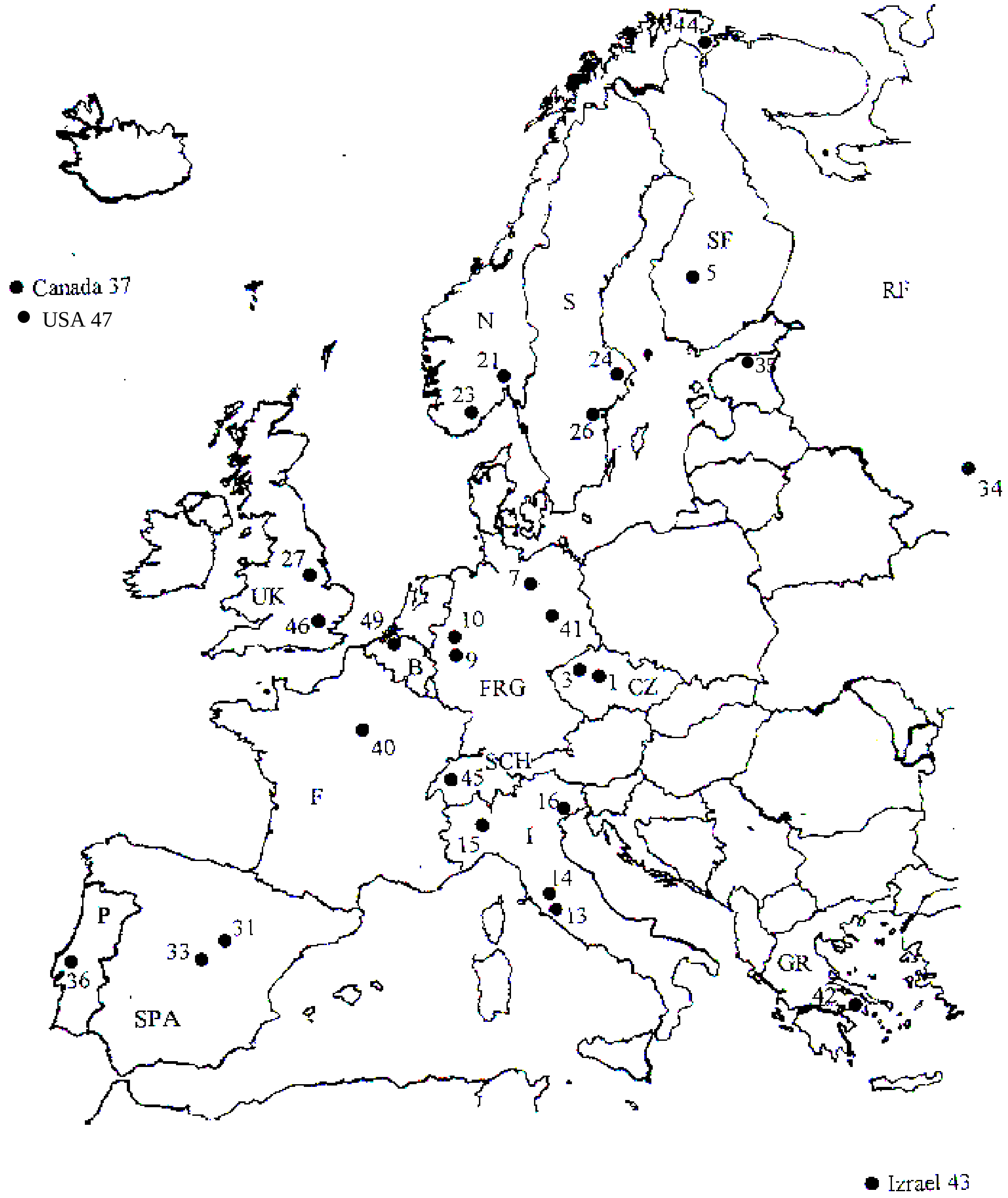
Methods prescribed in the Technical manual to the UN ECE International Co-operative Programme on Effects on Materials including Historic and Cultural Monuments [7] were applied for exposure of samples on test sites. Samples were exposed on racks in open atmosphere (unsheltered exposure) according to ISO 8565 and at special ventilated shelters which prevented rainfall reaching the samples. For each exposure there had been used triplicate samples.

The list of test sites for the multi pollutant programme is in Table 1 and Figure 1. Exposure period has been 1, 2 and 4 years (1997-2001).

Table 1 - The list of test sites

Country	Test site	Type of atmosphere
the Czech Republic	1 Prague 3 Kopisty	urban-industrial industrial
Finland	5 Ahtari	rural
the Federal Republic of Germany	7 Waldhof-Langenbrugge 9 Langenfeld 10 Bottrop 41 Berlin	rural rural industrial urban
Italy	13 Rome 14 Casaccia 15 Milan 16 Venice	urban rural urban-industrial urban
Norway	21 Oslo 23 Birkenes 44 Svanvik	urban rural rural
Sweden	24 Stockholm South 26 Aspvreten	urban rural
the United Kingdom	27 Lincoln Cathedral 46 London	urban urban
Spain	31 Madrid 33 Toledo	urban rural
the Russian Federation	34 Moskow	urban-industrial
Estonia	35 Lahemaa	rural
Portugal	36 Lisbon	urban
Canada	37 Dorset	rural
France	40 Paris	urban
Israel	43 Tel Aviv	urban
Switzerland	45 Chaumont	rural
USA	47 Los Angeles	urban-marine
Belgium	49 Antverps	urban-marine

Figure 1 – Map showing location of test sites



1.3. Measurement of environmental data

Basic climatic parameters (temperature, relative humidity and intensity of sunshine radiation), concentration of gaseous pollutants (SO_2, NO_x, O_3) and precipitation (amount, pH, conductivity, amount of SO_4^{2-}, NO_3^-, Cl^-, and NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+} if available) were measured on each test site. All data were reported to, and completed by the Norwegian Institute for Air Research - NILU, which also checked the quality of the data [8].

The environmental data collected in the course of the multi-pollutant programme confirms the decreasing concentration of sulphur dioxide in atmosphere.

1.4. Evaluation of corrosion attack

The visual evaluation of layer of corrosion products was done to indicate non uniform corrosion process.

The basic information about corrosion behaviour of carbon steel in different environmental conditions gives the value of corrosion gain and mass loss. After exposure samples were weighed and the corrosion products were removed using pickling method according to ISO 8407 (Annex A - solution C3.5. and C9.5.). In consecutive pickling cycles the corrosion layer was completely removed without dissolving the base metal. The repetition of the procedure stopped if the surface appears clean. The corrosion losses had been obtained by gravimetric method.

For selection samples of carbon steel the amount of water soluble salts in corrosion products was performed by spectrophotometric analysis. There were analysed corrosion products from samples exposed at test sites No 1, 3, 10, 27, 40, 41, 43, 46 and 49, it means test sites with high corrosion losses and test site 33 as the one with low corrosivity.

1.5. Evaluation of corrosion active characteristics of rust layer

Analysis of corrosion active components and evaluation of some other characteristics of rust layers gives an important information on interaction of environment with the steel surface and on expected function of rust in corrosion system including possible protective coatings. Analysis was performed on two rust sub-layers separate.

Non-adherent rust sub-layer had been got by mechanical removal by fine steel brush separately for upper and ground side of exposed samples. The content of active components had been analysed after extraction by deionised water for 24 hours.

The sample with adherent rust layer was immersed in deionised water for 24 hours and the water extract had been analysed. The concentration of soluble ions was determined by spectrophotometric method. The pH value and conductivity were measured too.

2. Results

2.1. Visual evaluation

An illustrative evaluation was done in combination with a digital photo of each sample. The visual evaluation of carbon steel samples after 1 and 2 years of exposure is presented in Report No 35.

2.1.1 Samples exposed at open atmosphere (unsheltered)

The layers of corrosion products of carbon steel had formed a typical structure, colour and thickness according exposure conditions. The surface layer of samples of carbon steel exposed on test site No. 43 had been affected by erosion (sand storm) - Figure 2.

The layer of corrosion products had very firm structure from test site with relatively "dry" climate (test site No 10, No 15, No 21, No 43) and on the other hand very rough structure from test sites with relatively "wet" climate (test site No 16, No 27).

2.1.2 Samples exposed at shelter

After 4 years of exposure there are samples with corrosion layer formed on 80 - 95 % of surface - there are samples from test sites: No 5, No 7, No 21, No 24, No 26, No 31, No 33, No 35 and No 45 - Figure 3.

The samples at test site No 47 had been exposed at open atmosphere only.

2.2. Mass gains of corroded carbon steel

Mass gains of exposed samples represent differences of mass of corrosion products originated at impact of environment and part of them removed by run-off erosion and fall out of non adherent particles and sub-layers. Mass increase of exposed steel samples gives a complex and not well-defined information. Mass changes of exposed samples of carbon steel exposed at open atmosphere and under shelter are summarised in Tables 2 - 5 and Figures 4 and 5.

For exposure at open atmosphere the negative values of corrosion mass gain were found for test sites:

exposure	test site No
1 year exposure	43
2 years exposure	10, 16, 27, 36, 43, 44, 46
4 years exposure	1, 3, 7, 9, 10, 16 23, 24, 27, 34, 36, 41, 43, 44, 46, 49

For exposure under shelter the negative values of corrosion mass gain were found for test sites:

exposure	test site No
1 year exposure	3, 10, 36, 49
2 years exposure	1, 3, 10, 36, 41, 44, 49
4 years exposure	1, 3, 10, 15, 27, 34, 36, 40, 41, 43, 44, 46, 49

Figure 2 - Samples from No 43 exposed at open atmosphere

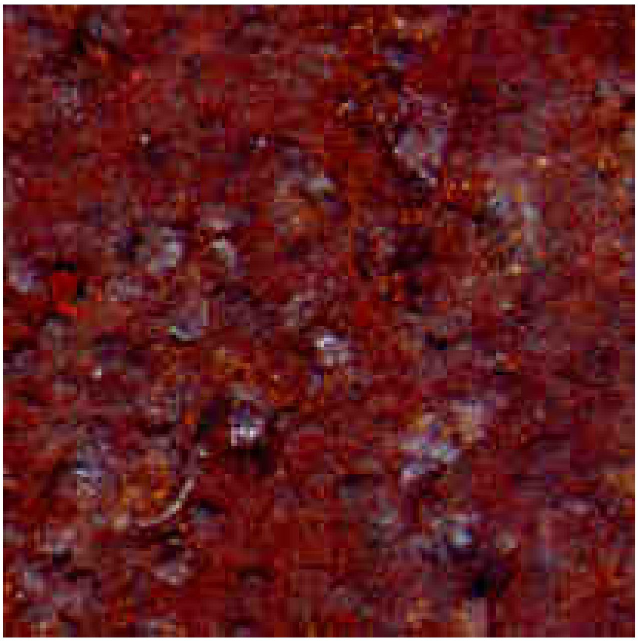


Figure 3 - Samples exposed under shelter - the surface partly covered by corrosion products - examples

No 5 No 21 No 26

No 31 No 35 No 45

Table 2 - Mass gain of carbon steel after 4 years of exposure at open atmosphere

Test site	MC_{57} (g)	MC_{58} (g)	MC_{59} (g)	average (g)	MC ($g.m^{-2}$)
1 Prague	-0,1482	-0,0377	-0,0701	-0,09	-2,84
3 Kopisty	-1,1166	-0,6685	-0,7861	-0,86	-28,57
5 Ahtari	1,0254	0,9996	0,9996	1,01	33,61
7 Waldhof-Langenbrugge	-0,1467	-0,3178	-0,2274	-0,23	-7,69
9 Langenfeld	-1,3862	-1,1613	-1,2094	-1,25	-41,74
10 Bottrop	-5,3415	-5,3017	-6,0303	-5,56	-185,26
13 Rome	-	-	-	-	-
14 Casaccia	-	-	-	-	-
15 Milan	0,8618	0,8793	5,0338	2,26	75,28
16 Venice	-1,5074	-1,1810	-1,1277	-1,27	-42,40
21 Oslo	0,7618	1,0043	1,1113	0,96	31,97
23 Birkenes	-0,0110	-0,3153	-0,4861	-0,27	-9,03
24 Stockholm South	-0,2471	-0,2014	-0,0994	-0,18	-6,09
26 Aspvreten	0,9786	1,0005	0,9514	0,98	32,56
27 Lincoln Cathedral	-4,4213	-4,104	-4,2802	-4,27	-142,28
31 Madrid	1,2021	1,2776	1,3304	1,27	42,33
33 Toledo	0,9262	0,9796	1,0838	1,00	33,22
34 Moskow	-0,0829	-0,0384	-0,094	-0,07	-2,39
35 Lahemaa	0,3815	0,4314	0,2136	0,34	11,41
36 Lisbon	-3,9448	-3,2435	-3,3649	-3,52	-117,26
37 Dorset	0,0879	0,1011	0,0363	0,08	2,50
40 Paris	-0,1799	0,1803	0,2280	0,08	2,54
41 Berlin	-0,3262	-0,0079	-0,2686	-0,20	-6,70
43 Tel Aviv	-10,404	-10,5060	-10,0860	-10,33	-344,40
44 Svanvik	-0,8833	-0,7475	-0,9189	-0,85	-28,33
45 Chaumont	0,9062	0,4209	0,8922	0,74	24,66
46 London	-1,8895	-1,7446	-0,8109	-1,48	-49,39
47 Los Angeles	1,9133	2,0011	2,6514	2,19	72,95
49 Antverps	-1,3799	-0,2969	-0,0965	-0,59	-19,70

Table 3 - Comparison of mass gain after 1, 2 and 4 years of exposure at open atmosphere

Test site	MC_1 ($g.m^{-2}$)	MC_2 ($g.m^{-2}$)	MC_4 ($g.m^{-2}$)
1 Prague	55,7	36,3	-2,8
3 Kopisty	79,7	36,7	-28,6
5 Ahtari	23,3	31,0	33,6
7 Waldhof-Langenbrugge	40,0	25,3	-7,7
9 Langenfeld	23,0	0,7	-41,7
10 Bottrop	18,7	-79,0	-185,3
13 Rome	30,0	18,3	-
14 Cassacia	47,0	63,3	-
15 Milan	36,7	36,0	75,3
16 Venice	6,3	-14,0	-42,4
21 Oslo	38,7	43,3	32,0
23 Birkenes	33,3	31,7	-9,0
24 Stockholm South	38,3	32,7	-6,1
26 Aspvreten	-	37,0	32,6
27 Lincoln Cathedral	9,0	-56,7	-142,3
31 Madrid	33,7	37,0	42,3
33 Toledo	26,0	31,7	33,2
34 Moscow	34,0	21,0	-2,4
35 Lahemaa	31,7	38,0	11,4
36 Lisbon	6,0	-43,7	-117,3
37 Dorset	51,7	40,0	2,5
40 Paris	28,0	22,0	2,5
41 Berlin	57,3	23,3	-6,7
43 Tel Aviv	-48,7	-136,7	-344,4
44 Svanvik	53,7	-7,3	-28,3
45 Chaumont	30,3	38,7	24,7
46 London	10,0	-16,7	-49,4
47 Los Angeles	58,7	78,7	73,0
49 Antverps	51,7	25,7	-19,7

Table 4 - Mass gain of carbon steel after 4 years of exposure at shelter

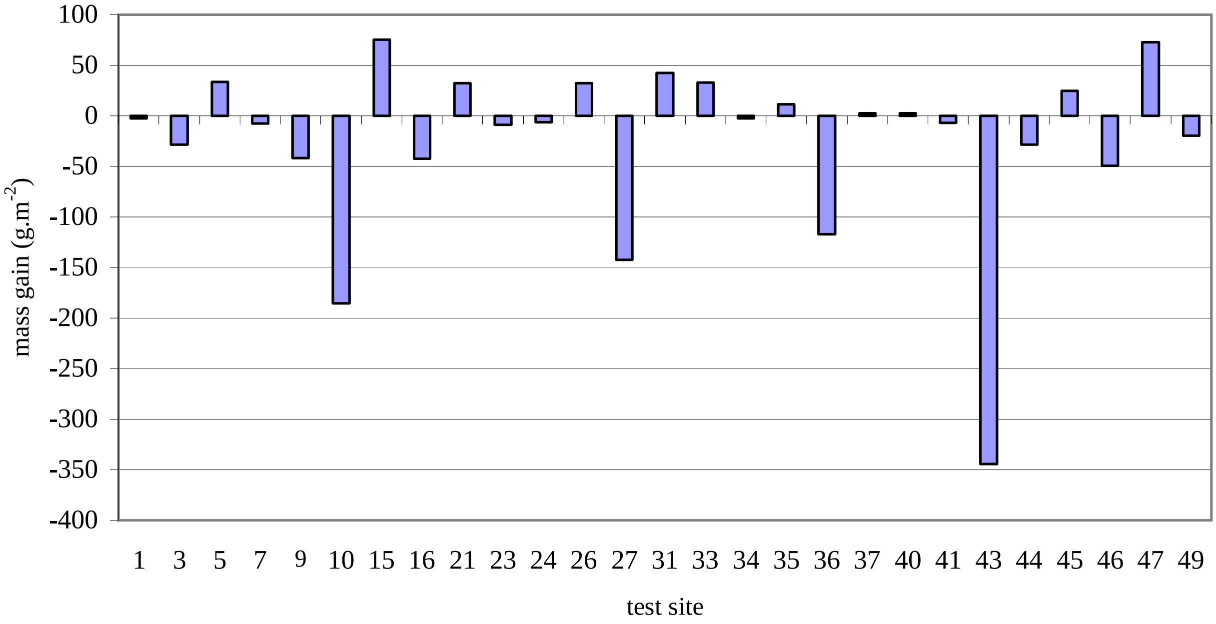
Test site	MC_{57} (g)	MC_{58} (g)	MC_{59} (g)	average (g)	MC ($g.m^{-2}$)
1 Prague	-0,9503	-0,9298	-1,1169	-1,00	-33,30
3 Kopisty	-2,0258	-2,0710	-2,1079	-2,07	-68,94
5 Ahtari	0,7548	0,7752	0,7858	0,77	25,73
7 Waldhof-Langenbrugge	1,0101	1,1255	1,0567	1,06	35,47
9 Langenfeld	0,4760	0,5077	0,3829	0,46	15,18
10 Bottrop	-3,5708	-3,4557	-3,407	-3,48	-115,93
13 Rome	-	-	-	-	-
14 Casaccia	1,3534	0,4324	1,6008	1,13	37,63
15 Milan	-0,8351	-0,6210	-0,9067	-0,79	-26,25
16 Venice	-0,0360	0,2480	0,2113	0,14	4,70
21 Oslo	0,4844	0,4866	0,4966	0,49	16,31
23 Birkenes	0,8207	0,8269	0,7681	0,81	26,84
24 Stockholm South	0,6971	0,7551	0,7811	0,74	24,81
26 Aspvreten	0,5751	0,5547	0,5716	0,57	18,90
27 Lincoln Cathedral	-0,9251	-0,9356	-1,1255	-1,00	-33,18
31 Madrid	0,3166	0,3080	0,2621	0,30	9,85
33 Toledo	0,8081	0,7167	0,7591	0,76	25,38
34 Moscow	-0,3462	-0,8398	-0,2951	-0,49	-16,46
35 Lahemaa	0,8882	0,7150	0,8200	0,81	26,92
36 Lisbon	-1,1193	-1,3901	-1,3410	-1,28	-42,78
37 Dorset	0,0042	0,1138	0,0441	0,05	1,80
40 Paris	-0,5829	-0,5693	-0,6391	-0,60	-19,90
41 Berlin	-0,2798	-0,2683	-0,3313	-0,29	-9,77
43 Tel Aviv	-0,6914	-0,5525	-0,9295	-0,72	-24,15
44 Svanvik	-1,1804	-1,2215	-1,2693	-1,22	-40,79
45 Chaumont	1,9988	0,9781	0,9493	1,31	43,62
46 London	-0,9860	-1,5035	-1,6899	-1,39	-46,44
47 Los Angeles	-	-	-	-	-
49 Antverps	-2,1912	-2,1598	-2,0809	-2,14	-71,47

Table 5 - Comparison of mass gain after 1, 2 and 4 years of exposure at shelter

Test site	MC_1 ($g.m^{-2}$)	MC_2 ($g.m^{-2}$)	MC_4 ($g.m^{-2}$)
1 Prague	1,0	-5,0	-33,3
3 Kopisty	-4,3	-31,7	-68,9
5 Ahtari	11,0	16,3	25,7
7 Waldhof-Langenbrugge	22,7	32,7	35,5
9 Langenfeld	21,3	19,0	15,2
10 Bottrop	-3,7	-42,3	-115,9
13 Rome	22,0	22,7	-
14 Cassacia	43,7	45,3	37,6
15 Milan	10,0	6,0	-26,3
16 Venice	17,0	12,7	4,7
21 Oslo	11,3	15,0	16,3
23 Birkenes	9,0	15,7	26,8
24 Stockholm South	20,7	27,3	24,8
26 Aspvreten	6,3	11,7	18,9
27 Lincoln Cathedral	21,7	8,7	-33,2
31 Madrid	12,0	14,3	9,9
33 Toledo	9,3	18,0	25,4
34 Moscow	17,7	13,0	-16,5
35 Lahemaa	-	-	26,9
36 Lisbon	-10,7	-42,3	-42,8
37 Dorset	15,3	17,0	1,8
40 Paris	13,0	8,0	-19,9
41 Berlin	57,3	-6,3	-9,8
43 Tel Aviv	9,0	9,0	-24,2
44 Svanvik	-0,3	-2,0	-40,8
45 Chaumont	13,0	26,3	43,6
46 London	12,0	5,7	-46,4
47 Los Angeles	-	-	-
49 Antverps	-3,7	-25,3	-71,5

Figure 4 - Mass gain of carbon steel after 4 years of exposure

open atmosphere



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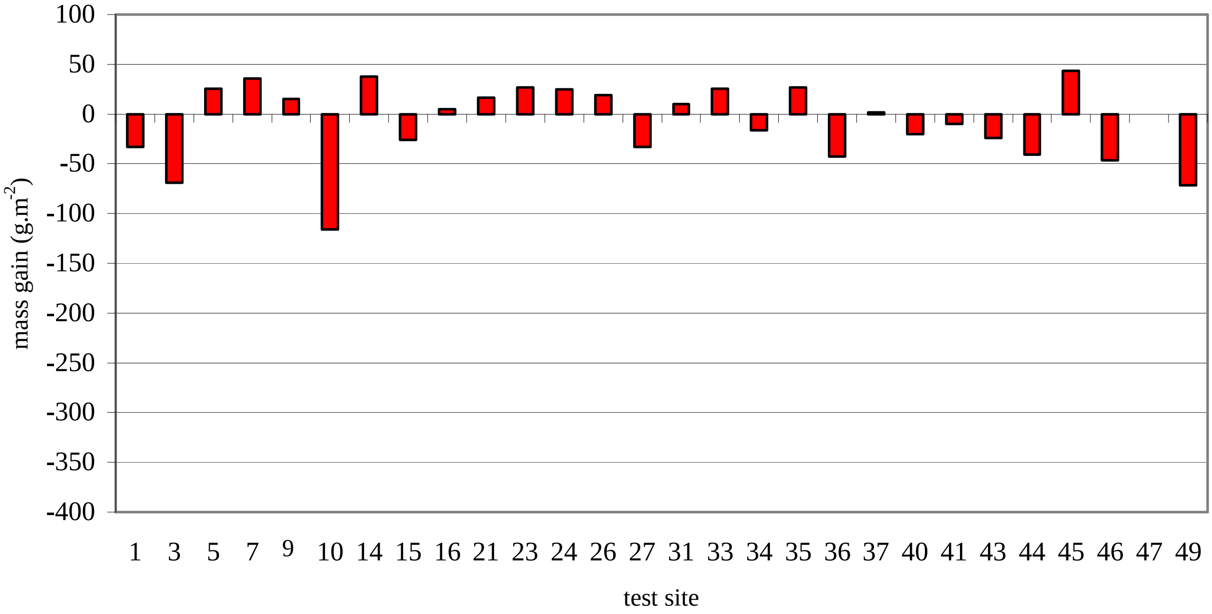
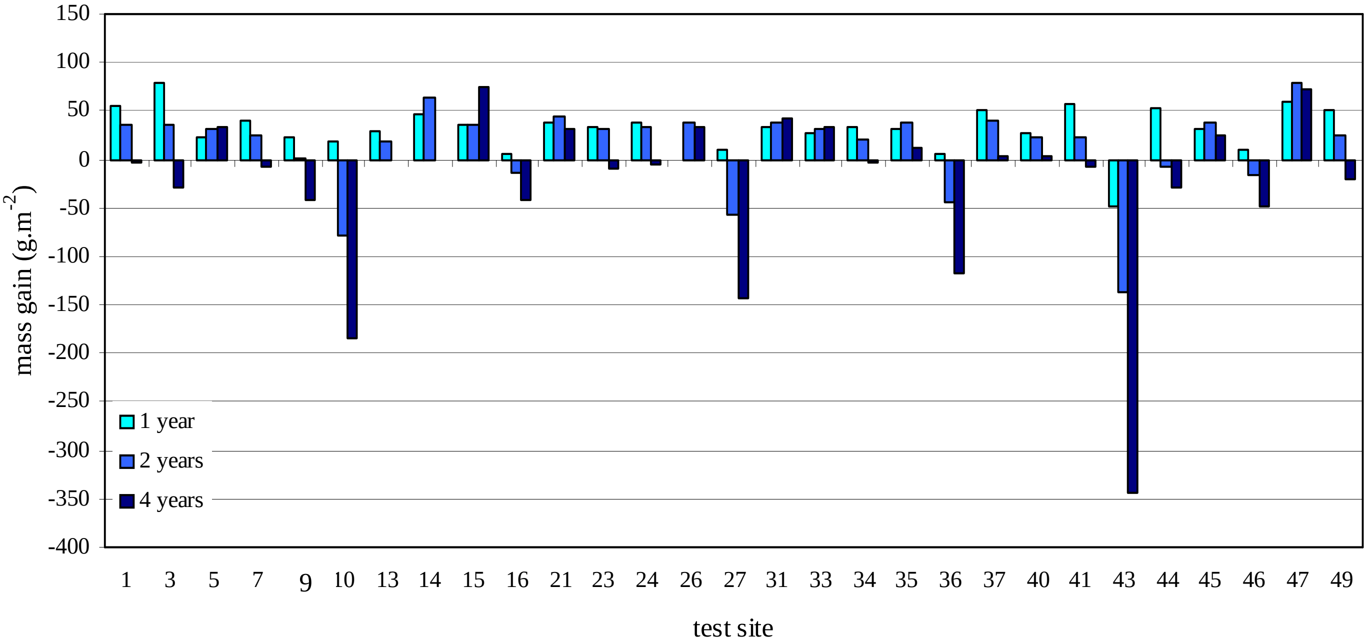


Figure 5 - Comparison of mass gain after 1, 2 and 4 years exposure

open atmosphere



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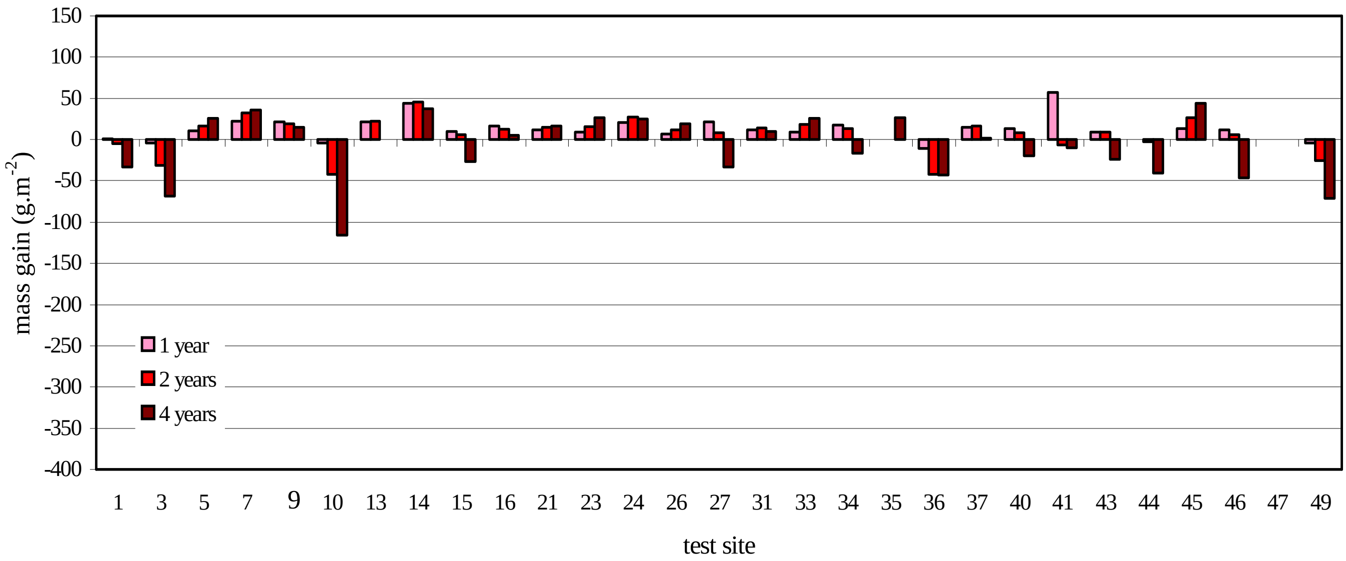
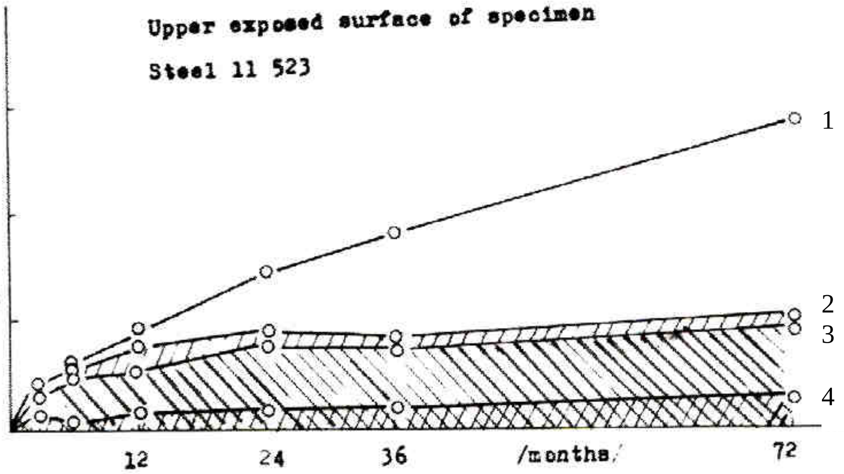
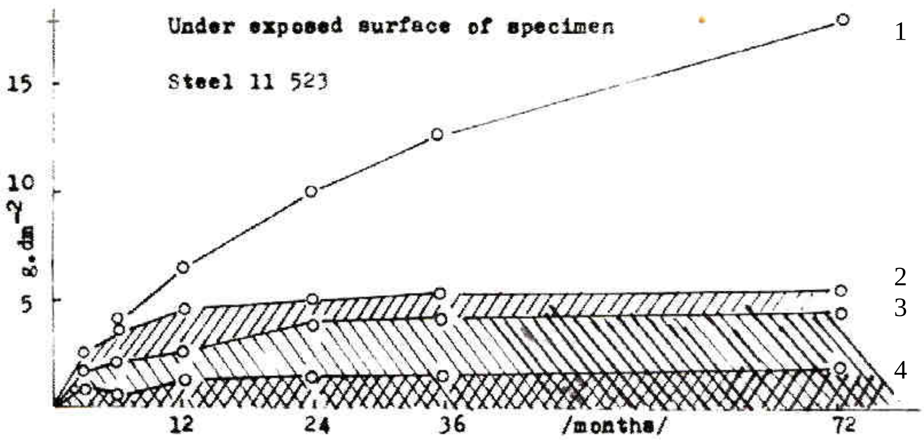


The rust layer is not an homogeneous material. The detailed systematic evaluation of the properties of rust layers is being performed in SVUOM on steel with a range of composition from various atmospheric exposures [9 - 12]. Quantity of rust in the individual underlayers (fall - 1, upper non adherent layer - 2, middle semiadherent layer - 3, under adherent layer - 4) was determined. The part of fall in the complex rust layer after outdoor exposure is very high. An example is given on Figure 6. The quote of fall in the total mass of created rusts is growing with time of exposure and corrosivity of exposure conditions. The part of fall of rust on carbon steel after 5 years of outdoor exposure for upper exposed surface was 50% of all formed rust, for under surface it was even higher.

Figure 6 – Quantity of rust in the individual underlayers





A systematic study of rust layers is laborious and it was not possible to perform it within the ICP programme. Certain information on mass changes in rusts layers gives Figure 5 making possible the relative comparison for rusts from outdoor and shelter exposures. The part of fall is very high on the most aggressive test sites (No 1, 3, 10, 27, 36, 44, 46 and 49). The fall of loosen rust during outdoor exposure is realized periodically in layers and fluent in scales, what is more typical for fall of rust during sheltered exposure. Relative part of non-adherent and adherent rust sub-layers on steel samples after 4 years exposure under shelter in presented in Table 6. The adherent rust layer forms as significant part of total rust layer from ca 75% to ca 95%.

Table 6 – Comparison of non-adherent and adherent parts of rust layer in shelter exposure

test site	non-adherent part* ($g.m^{-2}$)	adherent part ($g.m^{-2}$)	non-adherent part (%)	adherent part (%)
1	19,0	92,4	17,1	82,9
3	39,6	137,4	22,4	77,6
10	18,9	134,3	12,4	87,6
27	61,3	191,6	24,2	75,8
33	19,7	72,9	21,3	78,7
40	12,2	92,7	11,6	88,4
41	26,4	126,2	17,3	82,7
43	5,9	73,1	7,5	92,5
46	18,1	137,8	11,6	88,4
49	7,2	120,6	5,7	94,3

Note: part removed from samples after exposure by fine steel brush. This part of rust layer does not include fall of rust during exposure.

2.3. Corrosion losses of carbon steel

Corrosion losses for individual samples of carbon steel exposed in open atmosphere and under shelter evaluated for 4 years´ exposure (1996/2001) are summarised in Table 7 and Table 8 and presented in Figure 7. After 4 years of exposure in open atmosphere in this period test sites with the greatest corrosion losses of samples were No. 43 (Tel Aviv) and No. 10 (Bottrop).

Table 7 - Corrosion losses (g/m²) of carbon steel after 4 years exposure in open atmosphere (period 1997/2001)

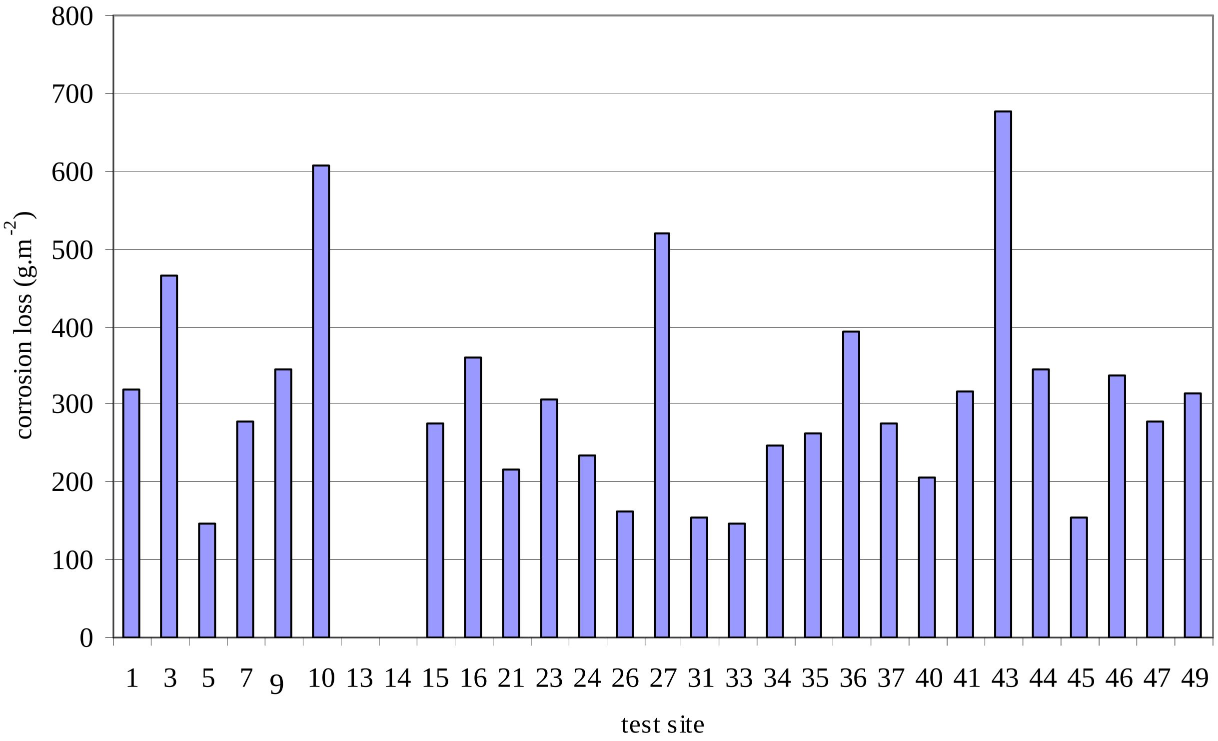
Test site	ML_{57}	ML_{58}	ML_{59}	ML
1 Prague	317,73	319,28	318,32	318,44
3 Kopisty	476,65	461,69	460,41	466,25
5 Ahtari	143,18	159,10	137,23	146,50
7 Waldhof-Langenbrugge	277,29	277,70	280,93	278,64
9 Langenfeld	351,24	341,87	344,79	345,97
10 Bottrop	593,97	606,36	621,60	607,31
13 Rome	-	-	-	-
14 Cassacia	-	-	-	-
15 Milan	289,00	293,98	245,48	276,15
16 Venice	363,34	370,24	346,17	359,91
21 Oslo	224,89	218,43	201,65	214,99
23 Birkenes	303,88	302,41	312,73	306,34
24 Stockholm South	232,21	238,89	232,25	234,45
26 Aspvreten	163,18	164,42	162,04	163,21
27 Lincoln Cathedral	526,40	516,39	514,92	519,24
31 Madrid	155,18	154,12	153,84	154,38
33 Toledo	130,02	152,54	157,90	146,82
34 Moscow	256,14	261,74	221,22	246,37
35 Lahemaa	276,87	271,91	237,93	262,24
36 Lisbon	395,95	391,41	390,09	392,48
37 Dorset	273,63	274,05	275,74	274,48
40 Paris	205,75	202,81	207,92	205,49
41 Berlin	315,29	307,98	323,13	315,47
43 Tel Aviv	670,99	690,97	669,59	677,18
44 Svanvik	331,99	356,25	348,49	345,58
45 Chaumont	150,94	161,29	151,18	154,47
46 London	348,61	356,26	307,32	337,40
47 Los Angeles	261,66	292,94	280,15	278,25
49 Antverps	313,63	316,21	310,46	313,43

Table 8- Corrosion losses (g/m²) of carbon steel after 4 years exposure under shelter (period 1997/2001)

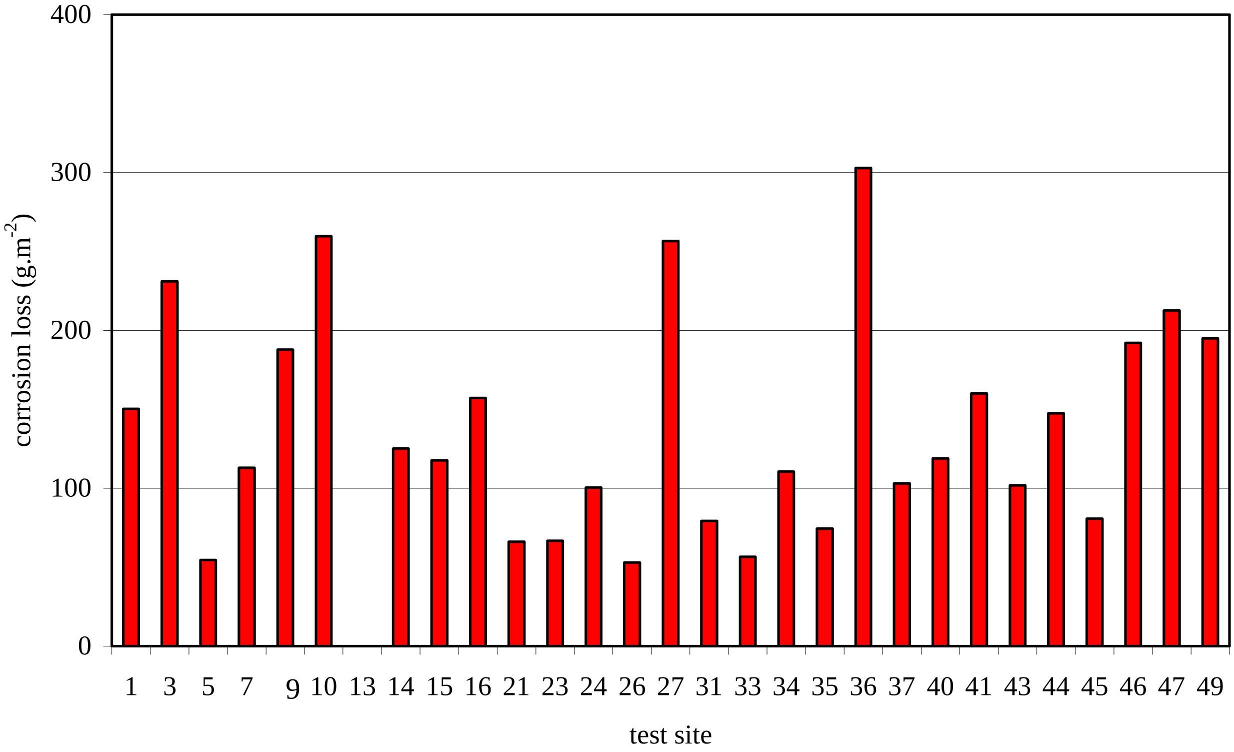
Test site	ML_{67}	ML_{68}	ML_{69}	ML
1 Prague	143,11	144,44	163,46	150,34
3 Kopisty	244,54	221,76	227,08	231,13
5 Ahtari	53,98	53,58	56,22	54,59
7 Waldhof-Langenbrugge	114,35	111,9	112,74	113,03
9 Langenfeld	189,50	189,80	184,36	187,89
10 Bottrop	275,64	255,11	248,23	259,66
13 Rome	-	-	-	-
14 Cassacia	111,05	144,08	120,45	117,59
15 Milan	119,71	148,75	163,84	157,18
16 Venice	158,95	148,75	163,84	157,18
21 Oslo	66,11	66,04	66,37	66,18
23 Birkenes	67,32	67,13	65,99	66,81
24 Stockholm South	100,84	100,01	100,34	100,40
26 Aspvreten	53,01	51,96	54,06	53,01
27 Lincoln Cathedral	283,70	243,46	242,92	256,69
31 Madrid	76,69	81,50	79,80	79,33
33 Toledo	65,71	51,91	52,28	56,63
34 Moscow	106,60	122,41	102,75	110,59
35 Lahemaa	75,81	72,87	74,86	74,51
36 Lisbon	300,80	302,78	305,08	302,89
37 Dorset	105,11	101,77	102,33	103,07
40 Paris	124,34	114,59	117,89	118,94
41 Berlin	161,90	157,80	160,69	160,13
43 Tel Aviv	102,05	98,34	105,04	101,81
44 Svanvik	146,93	147,82	147,65	147,47
45 Chaumont	52,36	81,21	80,22	80,72
46 London	188,74	190,23	197,36	192,11
47 Los Angeles	207,32	211,29	218,89	212,50
49 Antverps	200,91	191,29	192,75	194,98

Figure 7 - Corrosion loss of carbon steel exposed 4 years

open atmosphere (unsheltered)



shelter exposure



2.4. Analysis of corrosion products

Analysis of corrosion active compounds of rust layer is significant information of interaction between environment and corroded material. In rust layer the corrosive agents are cumulated in adherent layer.

The two analysis had been performed – for non-adherent and adherent rust sub-layers. The results are in Table 9 - 11 and in Figure 9. The pH value, conductivity and concentration of soluble ions (sulphates, chlorides and nitrates) were evaluated in water extract of corrosion products of selected samples of carbon steel exposed in period 1997/01 (test sites with relatively highest pollution of environment only). The concentration of soluble salts in extracts was determined by spectrophotometric method.

Rust water extract pH values are not characteristic parameter for evaluation of rust layers properties from different environmental exposures. During extraction, strong changes in pH value occur, pH values obtained by measurement after 24 hours of extraction. Non-adherent rust layer pH values are less acid (5,0 – 6,7 for open exposure and 4,8 – 6,6 for shelter exposure with exception of No. 1) than for adherent rust layer (3,1 – 4,0 for open exposure and 3,8 – 4,7 for shelter exposure).

The conductivity of rust water extract is much significantly affected by environmental conditions. Conductivity of non-adherent rust layer for open exposure ranges from 8 to 33 μS/cm and for shelter exposure from 25 to 60 μS/cm. Conductivity of adherent rust layer for open exposure ranges from 115 to 613 μS/cm and for shelter exposure from 145 to 545 μS/cm. There is one exception – test site No. 1.

The non-soluble part of non-adherent rust layer is about 95 – 96% for open exposure and about 98,5% for shelter exposure. Test sites with the highest soluble fraction in rust layer had been No. 40 and No. 41.

In Tables 10 and 11 the comparison of amount of soluble salts are summarized.

The amount of soluble salts contained in non-adherent rust layer is expressed as percentage in 1 g of rust product. The most concentrated ions in adherent rust layer both in open and shelter exposure is sulphate about 0,40%. The second significant ion in rust layer is chloride about 0,05%. The concentration of nitrate was non-significant about 0,01%. Higher concentration of sulphates and nitrates was found in upper non-adherent rust layer on the contrary to higher concentration of chlorides in adherent rust layer.

The most concentrated soluble ions in adherent rust layer both in open and shelter exposure are sulphates. The amount of sulphate is higher in shelter exposure in majority cases. The highest value was found for test site No 46 – ca 630 mg/m^2. The second significant ion in rust layer is chloride. The concentration is higher for shelter exposure in all cases. The highest value was found for test site No 27 and No 46 – ca 75 mg/m^2. The concentration of nitrate in adherent rust layer both in shelter and open exposure was non-significant – below 20 mg/m^2. Also the concentration of ammonium ion is very low from 0,1 to 3,3 mg/m^2.

Table 9 - Comparison of pH and conductivity of rust layers

test site	exposure	sample side	rust layer	pH	conductivity (µS/cm)
1	open	upper	non-adherent	6,40	8
		ground	non-adherent	5,53	8
		-	adherent	3,70	115
	shelter	-	non-adherent	3,40	230
		-	adherent	4,70	59
3	open	upper	non-adherent	6,03	8
		ground	non-adherent	5,47	9
		-	adherent	3,80	198
	shelter	-	non-adherent	4,90	25
		-	adherent	4,20	145
10	open	upper	non-adherent	5,19	11
		ground	non-adherent	5,05	13
		-	adherent	4,00	305
	shelter	-	non-adherent	5,50	32
		-	adherent	3,80	304
27	open	upper	non-adherent	5,61	9
		ground	non-adherent	5,54	10
		-	adherent	3,20	583
	shelter	-	non-adherent	6,20	60
		-	adherent	3,80	496
33	open	upper	non-adherent	6,00	11
		ground	non-adherent	5,53	10
		-	adherent	3,60	200
	shelter	-	non-adherent	6,60	14
		-	adherent	4,20	208
40	open	upper	non-adherent	5,51	13
		ground	non-adherent	5,61	19
		-	adherent	3,10	613
	shelter	-	non-adherent	4,80	36
		-	adherent	3,90	500
41	open	upper	non-adherent	5,68	12
		ground	non-adherent	6,76	15
		-	adherent	3,80	231
	shelter	-	non-adherent	5,70	52
		-	adherent	3,90	393
43	open	upper	non-adherent	6,32	33
		ground	non-adherent	5,69	17
		-	adherent	3,80	198
	shelter	-	non-adherent	4,80	25
		-	adherent	3,80	454

Table 9 - Continue

46	open	upper	non-adherent	5,60	11
		ground	non-adherent	5,26	18
		-	adherent	3,60	436
	shelter	-	non-adherent	5,20	32
		-	adherent	4,00	545
49	open	upper	non-adherent	6,72	32
		ground	non-adherent	5,29	31
		-	adherent	3,90	156
	shelter	-	non-adherent	5,70	21
		-	adherent	3,90	359

Table 10 - Comparison of soluble ion amount in non-adherent rust layer

Test site	exposure	sample side	Amount of soluble ions in adherent rust layer (%)			
			SO_4^{2-}	Cl^-	NO_3^-	NH_4^+
1	open	upper	0,20	0,02	0,010	0,010
		ground	0,40	0,02	0,004	0,009
	shelter	-	1,02	0,10	0,017	0,010
3	open	upper	0,30	0,02	0,020	0,007
		ground	0,30	0,02	0,020	0,009
	shelter	-	0,10	0,03	0,010	0,004
10	open	upper	0,20	0,02	0,010	0,008
		ground	0,50	0,02	0,006	0,009
	shelter	-	0,20	0,05	0,021	0,005
27	open	upper	0,30	0,02	0,010	0,006
		ground	0,20	0,03	0,020	0,010
	shelter	-	0,08	0,05	0,001	0,001
33	open	upper	0,90	0,03	0,020	0,020
		ground	0,30	0,02	0,007	0,010
	shelter	-	0,06	0,07	0,016	0,005
40	open	upper	0,60	0,04	0,020	0,030
		ground	0,30	0,03	0,003	0,010
	shelter	-	0,50	0,15	0,009	0,019
41	open	upper	0,10	0,04	0,040	0,010
		ground	0,40	0,02	0,030	0,009
	shelter	-	0,20	0,06	-	0,003
43	open	upper	0,40	0,03	0,020	0,010
		ground	0,30	0,03	0,008	0,010
	shelter	-	0,70	0,30	-	0,045
46	open	upper	1,10	0,06	0,060	0,030
		ground	0,40	0,04	0,020	0,010
	shelter	-	0,10	0,09	-	0,007
49	open	upper	0,40	0,05	0,030	0,090
		ground	0,50	0,02	0,020	0,020
	shelter	-	0,5	0,14	-	0,031

Table 11 - Comparison of soluble ion amount in adherent rust layer

Test site	exposure	Amount of soluble ions in adherent rust layer (mg/m^2)			
		SO_4^{2-}	Cl^-	NO_3^-	NH_4^+
1	open	72,0	12,7	15,3	3,3
	shelter	34,3	18,3	7,3	1,7
3	open	137,3	13,0	7,3	3,3
	shelter	104,7	15,3	4,7	3,3
10	open	192,0	18,0	8,7	3,3
	shelter	291,7	24,3	10,3	2,7
27	open	470,0	32,7	11,3	3,3
	shelter	480,3	75,0	5,7	> 0,1
33	open	89,3	30,0	19,0	3,3
	shelter	156,0	54,0	7,3	3,3
40	open	442,3	28,3	9,7	3,3
	shelter	607,7	60,0	11,7	> 0,1
41	open	202,3	20,0	11,0	3,3
	shelter	336,0	69,0	6,3	3,3
43	open	240,0	28,3	5,0	3,3
	shelter	533,3	39,3	12,3	> 0,1
46	open	419,3	40,7	8,0	0,3
	shelter	629,0	74,7	6,0	> 0,1
49	open	113,7	19,0	10,0	3,3
	shelter	414,0	29,0	8,0	1,3

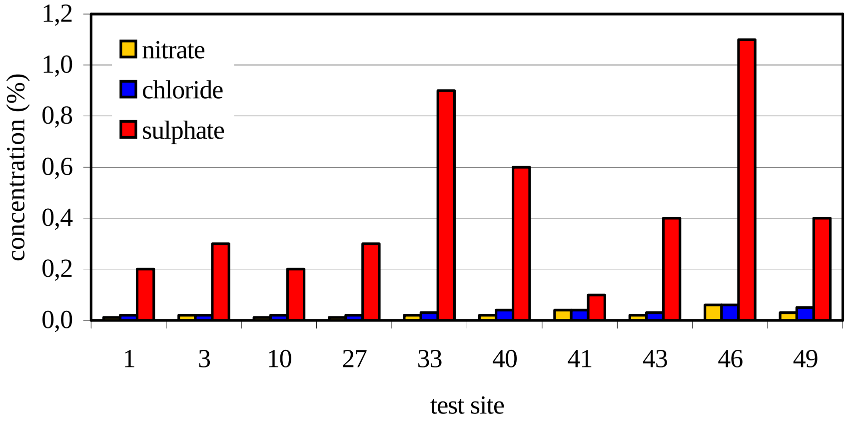
Analysis of corrosion active components of rust represents an important information not only on interaction of environment with the metal but can serve for looking on alternatives of surface preparation and choice of effective anticorrosion measures. Summary (complex) characterization of stimulate activity of electrolytes on corroded steel surfaces give evaluation of conductivity and pH of water extracts.

Content of sulphates represents still the dominating component of soluble ions in rust. Content of soluble ions is not in real relation to atmospheric corrosivity. Temperature – humidity complex and/or not measured parameters are very important too.

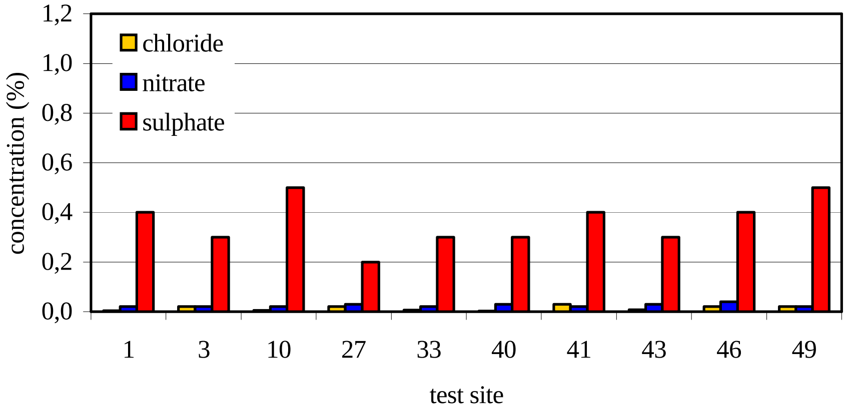
The real stimulative action of rust layers depends on activity of sulphate or chloride nests. Ions in nests are very stabile and may be not satisfactory extracted.

Figure 8 - Content of water soluble ions in corrosion products in non-adherent rust layer

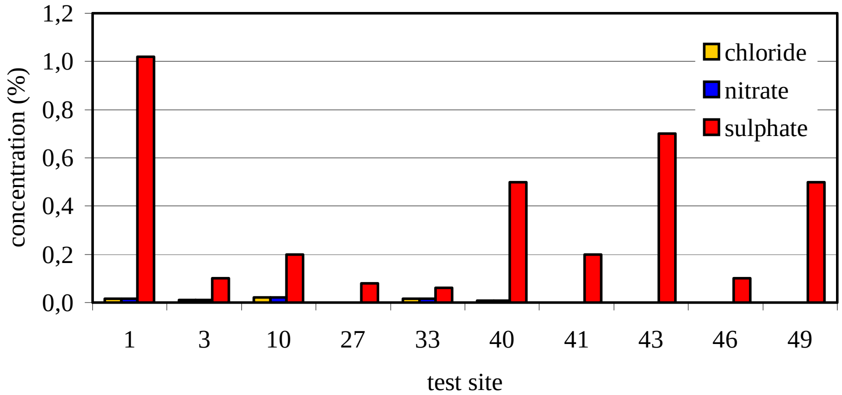
open exposure - upper non-adherent layer



open exposure - ground non-adherent layer



shelter exposure – non-adherent layer



3. Treatment of results

3.1. Comparison of corrosion losses after 1, 2 and 4 years

In Tables 12 and 13 there is a comparison of corrosion losses after 1, 2 and 4 years of exposure in open atmosphere and under shelter. In Tables 14 and 15 and Figure 10 corrosion rate on individual test sites is listed from the highest to the lowest one. There is seen from this that corrosion rate of carbon steel is decreasing during exposure time on all test sites.

Table 12 - Comparison of corrosion losses (g/m^2) of carbon steel after 1, 2 and 4 years´ exposure in open atmosphere (period 1997/2001)

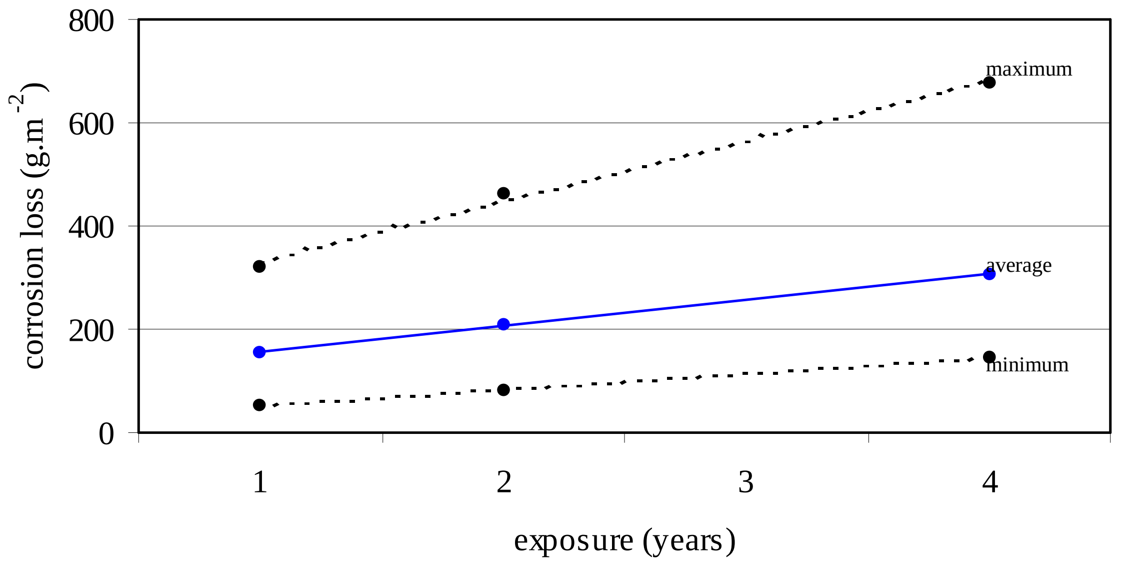
Test site	exposure (years)		
	1	2	4
1 Prague	182	236	319
3 Kopisty	239	333	466
5 Ahtari	53	82	147
7 Waldhof-Langenbrugge	144	193	279
9 Langenfeld	204	234	346
10 Bottrop	311	462	607
13 Rome	134	156	-
14 Cassacia	125	148	-
15 Milan	173	187	276
16 Venice	211	259	360
21 Oslo	93	137	215
23 Birkenes	101	164	306
24 Stockholm South	125	173	234
26 Aspvreten	62	100	163
27 Lincoln Cathedral	270	383	519
31 Madrid	72	115	154
33 Toledo	54	84	147
34 Moscow	135	157	246
35 Lahemaa	106	156	262
36 Lisbon	214	324	392
37 Dorset	116	166	274
40 Paris	137	159	205
41 Berlin	179	235	315
43 Tel Aviv	324	446	677
44 Svanvik	166	227	346
45 Chaumont	66	111	154
46 London	177	235	337
47 Los Angeles	136	183	278
49 Antverps	171	234	313

Table 13 - Comparison of corrosion losses (g/m^2) of carbon steel after 1, 2 and 4 years´ exposure under shelter (period 1997/2001)

Test site	exposure (years)		
	1	2	4
1 Prague	53	90	150
3 Kopisty	82	134	231
5 Ahtari	20	32	55
7 Waldhof-Langenbrugge	45	71	113
9 Langenfeld	51	91	188
10 Bottrop	72	148	260
13 Rome	50	68	-
14 Cassacia	101	106	125
15 Milan	47	65	118
16 Venice	59	83	157
21 Oslo	22	42	66
23 Birkenes	19	36	67
24 Stockholm South	42	64	100
26 Aspvreten	13	27	53
27 Lincoln Cathedral	91	161	257
31 Madrid	23	50	79
33 Toledo	16	33	57
34 Moscow	38	64	111
35 Lahemaa	-	-	75
36 Lisbon	103	176	303
37 Dorset	52	78	103
40 Paris	48	69	119
41 Berlin	59	95	160
43 Tel Aviv	48	52	102
44 Svanvik	37	73	147
45 Chaumont	25	55	81
46 London	74	120	192
47 Los Angeles	-	-	213
49 Antverps	70	104	195

Figure 9 - Comparison of average values of corrosion loss with limit values after 1, 2 and 4 years of exposure

open atmosphere (unsheltered)



shelter exposure

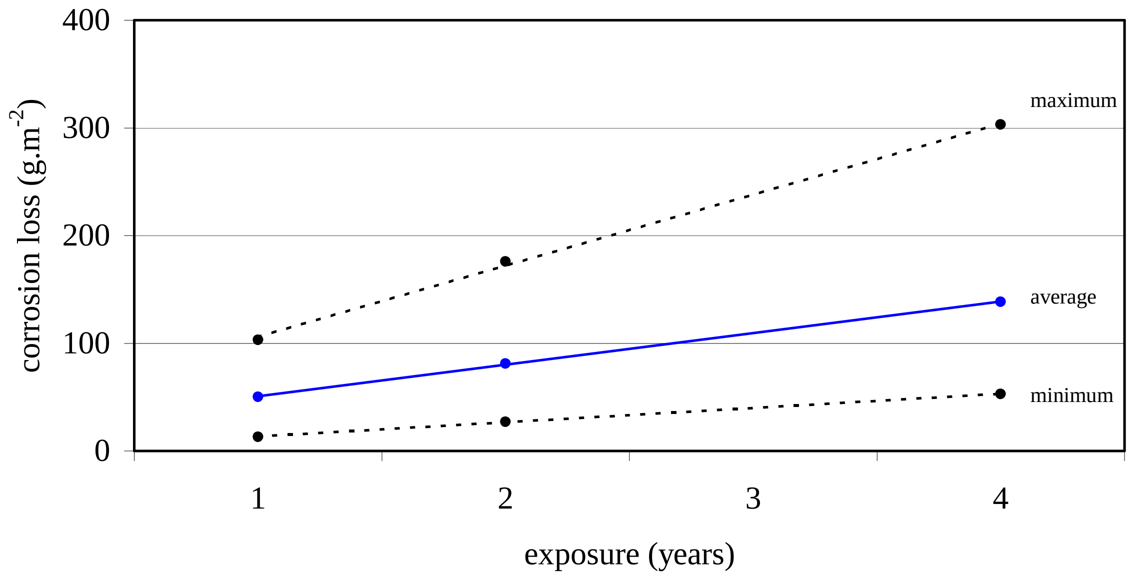


Table 14 - Comparison of corrosion rates (g/m^2 a) of carbon steel after 1, 2 and 4 years´ exposure in open atmosphere (period 1997/2001)

Test site	exposure (years)		
	0 - 1	0 - 2	0 - 4
5 Ahtari	53 C 2	41	37
33 Toledo	54 C 2	42	37
26 Aspvreten	62 C 2	50	41
45 Chaumont	66 C 2	56	39
31 Madrid	72 C 2	58	39
21 Oslo	93 C 2	69	54
23 Birkenes	101 C 2	82	77
35 Lahemaa	106 C 2	78	66
37 Dorset	116 C 2	83	69
14 Cassacia	125 C 2	74	-
24 Stockholm South	125 C 2	87	59
13 Rome	134 C 2	78	-
34 Moscow	135 C 2	79	62
47 Los Angeles	136 C 2	92	70
40 Paris	137 C 2	80	51
7 Waldhof-Langenbrugge	144 C 2	97	70
44 Svanvik	166 C 2	114	87
49 Antverps	171 C 2	117	78
15 Milan	173 C 2	94	69
46 London	177 C 2	118	84
41 Berlin	179 C 2	118	79
1 Prague	182 C 2	118	80
9 Langenfeld	204 C 3	117	87
16 Venice	211 C 3	130	90
36 Lisbon	214 C 3	162	98
3 Kopisty	239 C 3	167	117
27 Lincoln Cathedral	270 C 3	192	130
10 Bottrop	311 C 3	231	152
43 Tel Aviv	324 C 3	223	170

C 2, C 3 …..corrosivity category according to ISO 9223

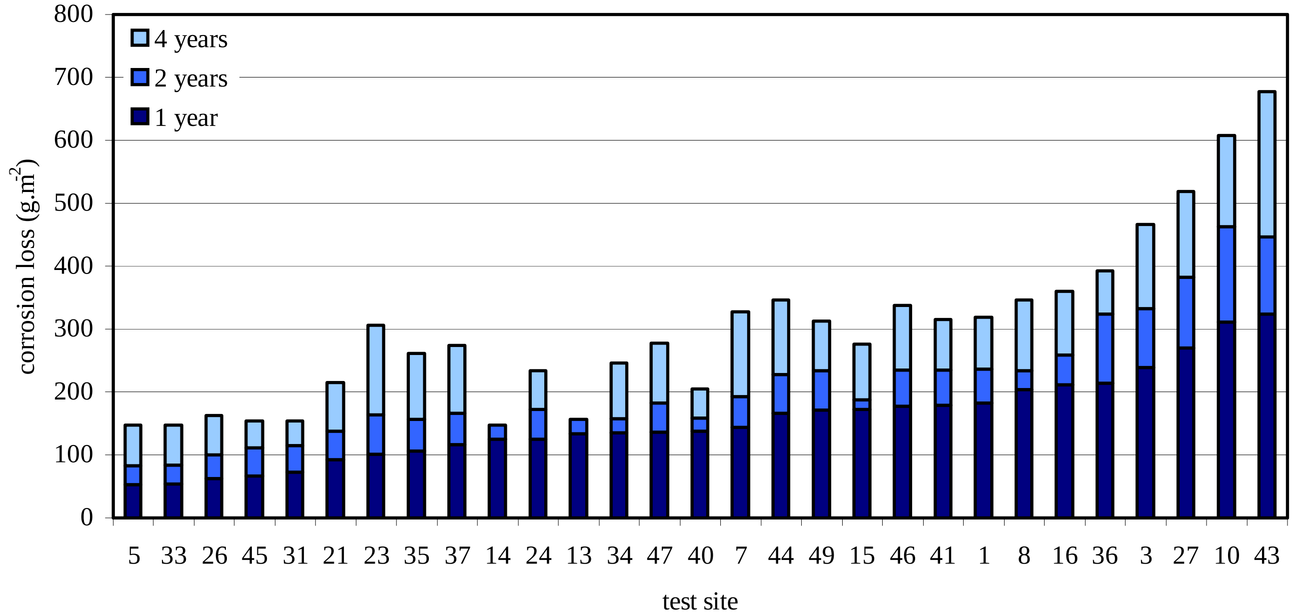
Table 15 - Comparison of corrosion rates ($g/m^2 a$) of carbon steel after 1, 2 and 4 years´ exposure under shelter (period 1997/2001)

Test site	exposure (years)		
	0 - 1	0 - 2	0 - 4
26 Aspvreten	13 C 2	14	13
33 Toledo	16 C 2	17	14
23 Birkenes	19 C 2	18	17
5 Ahtari	20 C 2	16	28
21 Oslo	22 C 2	21	17
31 Madrid	23 C 2	25	20
45 Chaumont	25 C 2	28	20
44 Svanvik	37 C 2	37	37
34 Moscow	38 C 2	32	28
24 Stockholm South	42 C 2	32	25
7 Waldhof-Langenbrugge	45 C 2	36	28
15 Milan	47 C 2	33	30
43 Tel Aviv	48 C 2	26	26
40 Paris	48 C 2	35	30
13 Rome	50 C 2	34	-
9 Langenfeld	51 C 2	46	47
37 Dorset	52 C 2	39	28
1 Prague	53 C 2	45	38
16 Venice	59 C 2	42	39
41 Berlin	59 C 2	48	40
49 Antverps	70 C 2	52	49
10 Bottrop	72 C 2	74	65
46 London	74 C 2	60	48
3 Kopisty	82 C 2	67	58
27 Lincoln Cathedral	91 C 2	81	64
14 Cassacia	101 C 2	53	31
36 Lisbon	103 C 2	88	76
35 Lahemaa	-	-	19
47 Los Angeles	-	-	53

C 2, C 3 …..corrosivity category according to ISO 9223

Figure 10 - Comparison of corrosion losses (g.m^{-2})

open exposure (unsheltered)



shelter exposure

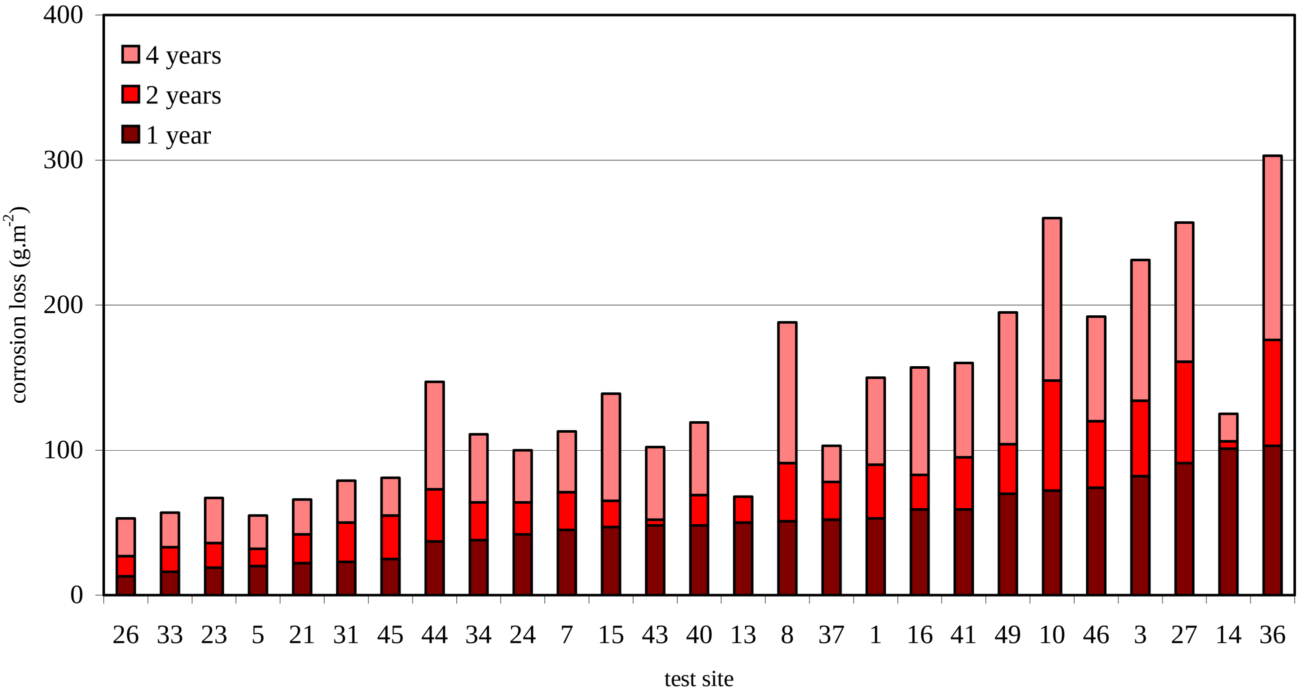
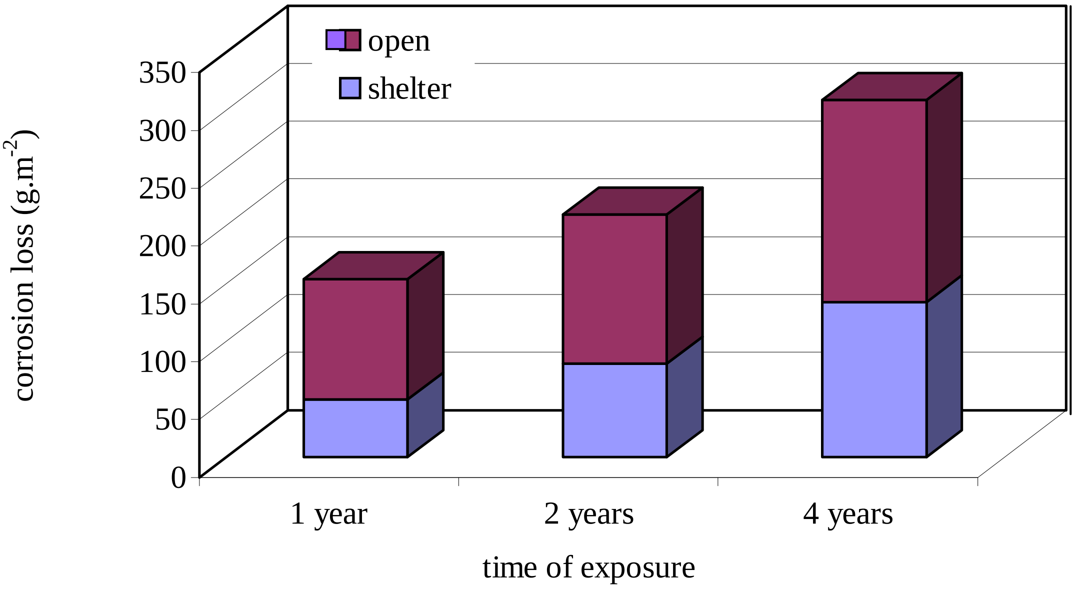
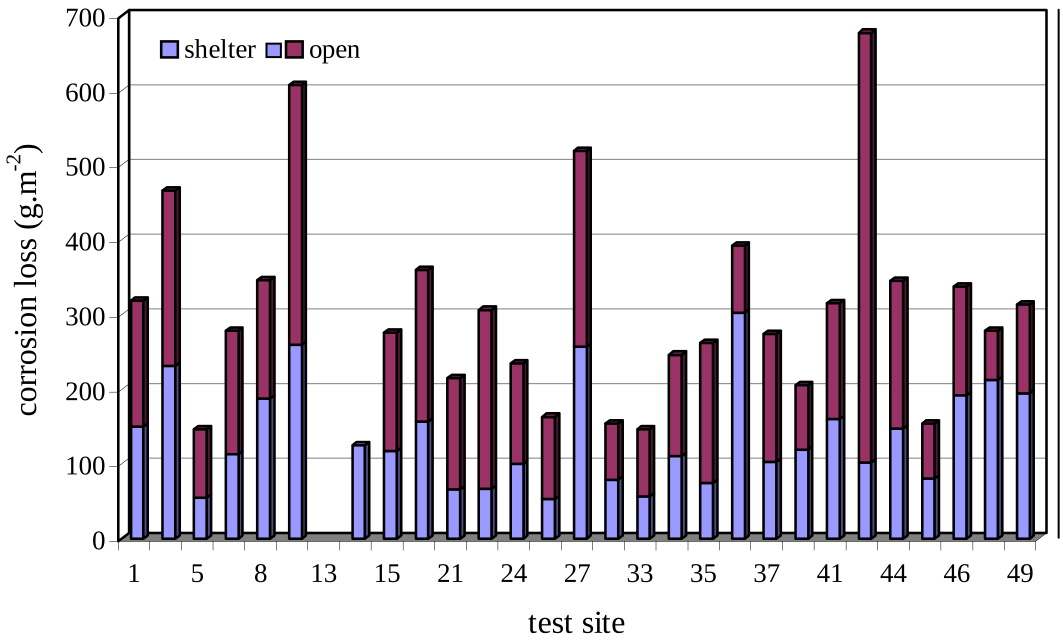


Figure 11 – Differences between corrosion losses of carbon steel in shelter and open exposure

Average values for 1, 2 and 4 years of exposure



Results after 4 years of exposure for individual test site



3.2. Environmental data

In Tables 16 - 18 there are summarized environmental data for 1, 2 and 4 years of exposure [8]. The pollution of SO_2 had been significantly lower in the second phase of exposure programme than in the first one, but the reduction was smaller than during the first phase of programme. NO_x had been much more significant gaseous pollutant that others. The amount of O_3 was rather remaining.

Table 16 - Average environmental parameters for exposure period 1997/98

Test site	CLIMATE			GASES			PRECIPITATION					
	Temp ^{0}C	Rh %	Sun MJ/m^2	SO_2 µg/m^3	NO_2 µg/m^3	O_3 µg/m^3	mm	pH	SO_4^{2-} mg/l	NO_3^- mg/l	Cl^- mg/l	Cond µS/cm
1 Prague	9,9	76	2971	15,3	23,7	48	522	5,56	11,34	2,19	1,95	27,6
3 Kopisty	9,9	76	3921	18,3	32,6	55	420	4,62	34,03	2,77	1,73	44,6
5 Athari	3,5	80	2889	0,9	3,0	60	742	4,74	0,25	0,21	0,15	10,7
7 Waldhof-Langenbrugge	9,5	83	3104	2,1	8,7	48	786	5,04	0,64	0,57	0,73	17,6
9 Langenfeld	10,9	80	2494	8,3	33,5	33	930	4,92	0,89	0,57	1,55	
10 Bottrop	11,5	81	2531	24,6	38,2	30	1044	4,84	0,99	0,46	1,20	22,1
13 Rome	19,4	65	4360	3,7	37,8	33	1125					
14 Casaccia	14,5	74	5178	5,2	21,0	30						
15 Milan	14,5	69	4940	15,4	83,9	38	1077					
16 Venice	13,5	83	4999	7,4			742	6.10				
21 Oslo	6,6	79	2521	4,1	27,5	36	523	5,20	0,85	0,55	0,87	20,7
23 Birkenes	6,2	79	2626	0,2	1,1	55	1744	4,50	0,61	0,47	1,50	25,5
24 Stockholm South	6,7	76	3048	2,6	20,3	44	463	4,63	0,54	0,38	0,48	17,1
26 Aspvreten	5,9	86	3301	0,6	2,9	51	479	4,59	0,41	0,37	0,57	17,3
27 Lincoln Cathedral	10,2	81	3224	8.4	19.1	51	708	4,61	1,64	0,56	3,56	
31 Madrid	12,9	61	5722	11,8	22,1	56	765	6,05	0,77	0,37	1,03	16,0
33 Toledo	14,0	59	5905	1,5	11,3	89	872	5,80	0,56	0,26	0,92	10,7
34 Moscow	6,5	74		31.5	28,0	42		6,68	1,42		1,57	45,8
35 Lahemaa	5,4	82	3238	0.5	0,7	55	859	5,16	1,64	0,24	0,78	19,4
36 Lisbon	17,9	63		17,7	42,0	12	252	5,98	13,30	5,02	13,30	75,3
37 Dorset	7,4	75	4435	2,4	9,7	62	788	4,31	0,76	0,52	0,11	24,2
40 Paris	13,4	67	4250	14,2	70,0	31	572	5,71	1,81	0,72	2,47	43,7
41 Berlin	10,4	77	3113	10,9	37,7	22	486		6,98	4,34	2,09	
43 Tel Aviv	24,6	83		35,0	38,3	40	485	5.64	0.47	0.44	3.53	
44 Svanvik	0,2	80	1967	7,5	0,9	54	344	4,77	0,57	0,12	1,87	20,7
45 Chaumont	6,9	77	4388	1,3	7,7	86	1053	4,99	0,27	0,21	0,18	9,4
46 London	12,2	70	3228	6.3	45.3	36	706	5,65	0,54	0,26	4,07	
47 Los Angeles	17,4	61		0,6	21,7	48		5.77				
49 Antverps	11,4	76	3027	22,8	52,8	28		5.07	1.46	0.47	3.86	35.6

Table 17 - Average environmental parameters for exposure period 1997/99

Test site	CLIMATE			GASES			PRECIPITATION					
	Temp	Rh	Sun	SO_2	NO_2	O_3	mm	pH	SO_4^{2-}	NO_3^-	Cl^-	Cond
	^0C	%	MJ/m^2	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$			mg/l	mg/l	mg/l	µS/cm
1 Prague	9,8	76	3025	14,2	22,9	48	464	5,2	8,4	1,4	2,3	27,9
3 Kopisty	9,7	77	4028	18,1	32,4	57	417	4,5	24,2	1,8	1,6	50,0
5 Athari	4,1	80	3052	0,9	3,1	62	678	4,7	0,3	0,2	0,1	11,6
7 Waldhof-Langenbrugge	9,5	81	3416	1,8	8,8	52	644	5,1	0,7	0,6	1,1	19,3
9 Langenfeld	11,1	79	2690	7,4	32,6	35	863	5,2	0,9	0,6	1,5	
10 Bottrop	11,6	81	2751	22,5	37,3	32	934	5,0	1,0	0,6	1,3	22,1
13 Rome	19,3	65	4224	3,7	40,3	32	1125					
14 Casaccia	15,5	70	4921	4,1	26,1	34						
15 Milan	14,5	69	4940	15,4	83,9	38	1077					
16 Venice	13,7	82	5129	6,5		45	683					
21 Oslo	6,8	79	2575	4,7	30,0	38	706	4,9	0,7	0,5	0,8	20,8
23 Birkenes	6,2	81	2681	0,3	1,4	57	1716	4,5	0,6	0,5	1,7	26,1
24 Stockholm South	7,4	77	3361	2,9	19,9	48	471	4,7	0,5	0,4	0,4	15,7
26 Aspvreten	6,2	85	3422	0,7	2,8	57	398	4,6	0,5	0,4	0,6	18,0
27 Lincoln Cathedral	10,2	81	3426	9,8	22,5	51	719	4,6	1,6	0,6	3,6	
31 Madrid	13,5	58	5152	9,2	23,5	55	563	6,1	0,7	0,3	1,1	15,2
33 Toledo	14,0	57	6107	1,9	11,2	84	628	5,9	0,5	0,2	0,9	10,3
34 Moscow	6,8	72		23,6	24,7	42	611	6,6	1,5		1,4	44,8
35 Lahemaa	5,9	81	3457	1,7	1,2	59	738	5,0	1,6	0,3	0,6	18,4
36 Lisbon	17,5	66		16,5	36,6	12	220	6,3	14,5	5,1	13,8	105,2
37 Dorset	7,9	74	4360	2,4	7,0	62	788	4,3	0,8	0,5	0,1	24,2
40 Paris	13,6	67	4382	12,7	61,1	33	565	5,8	1,8	0,9	2,5	44,8
41 Berlin	10,6	76	3316	10,9	40,8	24	450		5,6	3,8	1,7	
43 Tel Aviv	25,6	86		47,7	41,6	45	403					
44 Svanvik	1,0	78	1901	7,6	1,2	58	408	4,8	0,5	0,1	1,3	16,6
45 Chaumont	6,6	79	4329	1,3	7,9	85	1128	5,0	0,3	0,2	0,2	9,7
46 London	12,3	70	3397	7,6	48,2	39	679	5,7	0,5	0,3	4,1	
47 Los Angeles	16,9	62	6135	0,6	21,7	48						
49 Los Angeles	11,7	76	3259	19,7	50,7	29						

Table 18 - Average environmental parameters for exposure period 1997/2001

Test site	CLIMATE			GASES			PRECIPITATION					
	Temp ^0C	Rh %	Sun MJ/m^2	SO_2 $\mu g/m^3$	NO_2 $\mu g/m^3$	O_3 $\mu g/m^3$	mm	pH	SO_4^{2-} mg/l	NO_3^- mg/l	Cl^- mg/l	Cond $\mu S/cm$
1 Prague	9,8	76	3073	12,5	22,7	46,8	513	5,3	6,7	2,5	2,3	37,2
3 Kopisty	9,7	77	4073	17,5	29,4	52,5	463	4,5	16,3	3,2	1,6	49,2
5 Athari	4,5	80	3083	0,8	3,0	60,3	713	4,7	0,3	0,2	0,2	11,1
7 Waldhof-Langenbrugge	9,5	80	3405	1,7	8,5	52,0	617	5,0	0,6	0,6	1,0	19,0
9 Langenfeld	11,2	80	2764	6,3	31,7	34,0	918	5,1	0,9	0,6	1,2	21,4
10 Bottrop	11,6	81	2800	20,3	35,0	31,8	906	4,9	1,4	0,6	1,4	26,7
13 Rome	18,9	65	4119	3,7	42,6	30,8	1125					
14 Casaccia	15,9	67	4694	3,9	26,1	32,0						
15 Milan	14,9	70	4833	14,5	76,5	39,3	1024					
16 Venice	14,4	82	5190	6,8		38,5	696					
21 Oslo	7,1	77	2600	4,0	28,2	37,3	840	4,8	0,6	0,5	0,8	19,3
23 Birkenes	6,5	82	2701	0,3	1,6	55,5	1896	4,5	0,6	0,5	2,2	26,4
24 Stockholm South	7,7	78	3306	2,5	19,0	47,5	508	4,7	0,5	0,3	0,4	15,5
26 Aspvreten	6,6	85	3457	0,6	2,7	57,5	534	4,5	0,5	0,4	0,6	19,4
27 Lincoln Cathedral	10,0	81	3593	8,4	22,4	50,3	756	4,6	1,6	0,6	3,6	
31 Madrid	14,4	59	4858	5,9	18,6	54,3	505	6,3	0,7	0,4	1,1	15,5
33 Toledo	13,5	61	6038	1,7	8,6	87,0	570	6,1	0,6	0,3	1,1	12,2
34 Moscow	6,8	71		23,6	23,6	42,0	693	6,6	1,4		1,3	52,8
35 Lahemaa	6,4	81	3439	1,5	1,7	59,8	698	4,9	0,8	0,3	0,5	15,4
36 Lisbon	17,4	66		16,5	36,6	13,7	196	6,2	14,4	5,7	12,9	100,8
37 Dorset	7,2	76	4360	2,4	6,8	61,0	788	4,3	0,8	0,5	0,1	24,2
40 Paris	13,1	70	4206	11,6	54,7	32,8	651	5,5	1,5	1,0	2,1	39,1
41 Berlin	10,8	78	3378	9,7	41,8	25,8	450		4,7	3,5	1,4	
43 Tel Aviv	23,7	78		27,9	30,4	33,8	383					
44 Svanvik	1,4	79	1844	6,6	1,4	55,5	402	4,8	0,6	0,1	1,3	18,4
45 Chaumont	6,8	79	4281	1,2	7,5	83,5	1152	5,0	0,3	0,2	0,2	9,2
46 London	12,2	70	2902	6,4	46,2	35,7	730	5,7	0,5	0,3	4,1	
47 Los Angeles	16,9	64	6561	0,6	21,7	48,0						
49 Antverps	11,8	76	3367	17,4	49,4	29,5	1000	5,0	1,2	0,5	2,4	27,1

Conclusion

Evaluation of corrosion attack of carbon steel after 1, 2 and 4 years represents an important step in the ICP on materials activities as such exposure of this material was not included in the first phase of exposure programme. Repeated one-year exposures of carbon steel were realized only in that period.

The evaluation presented in this report implicated:

- visual evaluation of exposed samples,
- evaluation of mass gain of corroded samples,
- evaluation of corrosion losses after 4 years of exposure,
- analysis of corrosion layers,
- comparison of 1, 2 and 4 years corrosion losses.

Data base for later statistical treatment was summarized. Preliminary statistical treatment of corrosion losses of carbon steel after 1 and 2 years exposure had been presented in Report No. 35. Systematic statistical treatment of data including one-year data from the first phase of the ICP Effect on Materials is relatively simple including as parameters SO_2, RH and T only (chlorides and acidity pf precipitation have been not found as decisive).

The equation for weathering steel was presented:

$$ML = 34\,[SO_2]^{0,33}\,\exp\{0,020\,RH + f(T)\}t^{0,33}$$

where $f(T) = 0,059(T-10)$ when $T \leq 10^0C$, otherwise $f(t) = -0,036(T-10)$.

Treatment of the ISOCORRAG data gives D/R function for carbon steel based on one-year exposure data but the environmental base was not complex enough in this case – TOW, T, SO_2, salinity had been only measured. There were presented two equations for carbon steel:

$$CR = 0,091[SO_2]^{0,56}\,TOW^{0,52}\exp(f_{Fe}(T)) + 0,158[Cl^-]^{0,58}\,TOW^{0,25}\exp(0,050T),$$
$N = 125$, $R^2 = 0,85$

where $f_{Fe}(T) = 0,103(T-10)$ when $T \leq 10^0C$, otherwise $f_{Fe}(T) = -0,059(T-10)$.

$$CR = 1,77[SO_2]^{0,52}\exp(0,020RH)\exp(f_{Fe}(T)) + 0,102[Cl^-]^{0,62}\exp(0,033RH + 0,040T),$$
$N = 128$, $R^2 = 0,85$

where $f_{Fe}(T) = 0,150(T-10)$ when $T \leq 10^0C$, otherwise $f_{Fe}(T) = -0,054(T-10)$.

Parameters used in ISOCORRAG dose/response functions are listed in Table 19. All parameters are expressed as annual average.

Table 19 – ISOCORRAG environmental parameters

Symbol	Description	Interval	Unit
T	Temperature	-17,1 – 28,7	^{0}C
RH	Relative humidity	34 – 93	%
SO_2	Sulphur dioxide deposition	0,7 – 150,4	$mg.m^{-2}.d^{-1}$
Cl^-	Chloride deposition	0,4 – 760,5	$mg.m^{-2}.d^{-1}$

The statistical treatment performed by SVUOM Ltd. As sub-centre will be concentrated on deeper evaluation of the single and combined environmental effects in relation to analytical data published in this report.

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- VTT Manufacturing Technology, Espoo, Finland
- Bayrishes Landesamt fur Denkmalpflege, Munchen, Germany
- ENEA - Environmental Depatment, Rome, Italy
- NILU - Norwegian Institute for Air Research, Kjeller, Norway
- SCI - Swedish Corrosion Institute, Stockholm, Sweden
- BRE - Building Research Establishment Ltd., Watford, United Kingdom
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- Institute of Physical Chemistry, Academy of Sciences, Moscow, Russian Federation
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- Getty Conservation Institute, Museum Service, Los Angeles, USA
- UIA - University of Antwerpen, Department Chemistry, Wilrijk, Belgium

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Reference

1. Report No 43 Results from the multipollutant programme: Corrosion attack on zinc after 1, 2 and 4 years of exposure (1997-2001), 2003

2. Report No 44 Results from the multipollutant programme: Corrosion attack on copper and bronze after 1, 2 and 4 years of exposure (1997-2001), 2003

3. Report No 45 Results from the multipollutant programme: Corrosion attack on limestone after 1, 2 and 4 years of exposure (1997-2001), 2003

4. Report No 46 Results from the multipollutant programme: Corrosion attack on painted steel after 1, 2 and 4 years of exposure (1997-2001), 2003

5. Report No 47 Trends of corrosivity based on corrosion rates and pollution data. Part 3., 2003

6. Report No 48 Results from the multipollutant programme: Evaluation of the decay to glass samples after 1, 2 and 4 years of exposure (1997-2001), 2003

7. Report No 1, June 1988, Technical manual

8. Report No 41 Final Environmental data report for the multi pollutant programme: November 1997 to October 2001, 2003

9. Kukurs O., et al in Proceedings, 3rd International CMEA Congress on Corrosion, Warsaw, Vol. 4, 1980, p. 191

10. Knotkova D., Kuchynka D., Rossler K., Baum H., Neue Hutte, Vol. 24, No. 1, 1979, p. 26

11. Honzak J., Kuchynka D., Werkstoffe und Korrosion, Vol. 21, 19 , p. 342

12. Honzak J., Corrosion Important Components of Rust, Ph.D. Dissertation, Prague, 1974