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Part II

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Part II

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Summary

A bilateral exposure programme has been carried out along the Norwegian-Russian border in 1990–1991, 1992–1993 and 1993–1994, in order to provide a quantitative evaluation of the effect of sulphur pollutants on the atmospheric corrosion of important materials in sub-arctic climate.

The results of the corrosion tests of metal materials have shown that also in sub-arctic climate the metal corrosion is dependent of the atmospheric corrosivity, which is caused by man-made emissions. Dry deposition of sulphur is the main reason for the accelerated atmospheric corrosion of metals in the region along the Norwegian-Russian border. Dry deposition of Cl makes its own contribution to the processes of corrosion at Viksjøfjell and Karpdalen. Sea-salt aerosols are the important Cl source.

The kinetics of corrosion of steel and zinc as a function of time were characterized by the reduction of the corrosion rate with 60–70% at the less polluted areas and only with 20–50% in an atmosphere of sulphur dioxide and chlorides or in significantly SO_2-polluted areas. The second year corrosion rate of copper was characterized by the reduction of corrosion rate with 60–80% at all test sites.

The time of wetness is an important parameter for the prediction of atmospheric corrosion of metals even for a regional scale. For monitoring purposes and for trend-effect analysis it is most important to determine the corrosivity of SO_2 as a function of time of wetness, either by the average corrosion rate caused by SO_2 or by the average total corrosion rate during the period.

The yearly corrosion rates (C) of steel and zinc are best described by the dose/ response functions which combined the effects of SO_2 and time of wetness (TOW)

$$C = A_1 + A_2 [SO_2] TOW$$

$$C = (A_1 + A_2 [SO_2]) TOW$$

In accordance with dose/response functions obtained, the yearly corrosion rate for steel and zinc are higher for the areas with higher contents of dry deposition of Cl than for areas with similar climate, but only SO_2 containing atmosphere.

The temperature limit for time of wetness found on the basis of the data of monthly programme is below 0°C. For defining more precise temperature limits for the corrosion processes on a yearly basis, it is necessary to have a larger database from a larger region where the differences in the time of wetness linked to temperature are larger.

Atmospheric corrosion tests along the Norwegian-Russian border

Part II

1. Purpose of the bilateral exposure programme

The purpose of the programme is to evaluate quantitatively the effect of sulphur pollutants on the atmospheric corrosion of important metals in sub-arctic climate. The programme is based on a bilateral exposure programme at test sites along the Norwegian-Russian border and was carried out in co-operation between the Norwegian Institute for Air Research (NILU) and the Institute of Physical Chemistry of the Russian Academy of Sciences.

2. The main results of the first part of the programme

The first part of the bilateral exposure programme has been carried out along the Norwegian-Russian border in 1990–1991 and the results obtained published in Henriksen et al. (1992) and Henriksen et al. (1995).

The results of the corrosion tests of metal materials have shown that also in sub-arctic climate the metal corrosion is dependent of the atmospheric corrosivity. The monthly corrosion rate (C) of steel was best described by dose-response functions which combined the effects of SO_2 and time of wetness (TOW)

$$C = (a_1 + a_2 [SO_2]^{a3}) [TOW]^{a4}$$

where the exponential terms a_3 and a_4 did not differ greatly from 1. The yearly corrosion rate of metals like steel, galvanized steel, zinc, “aluzinc” and steel coated with “galfan” and aluminium were described by the simple equation

$$C = a_1 + a_2 [SO_2]$$

with good correlation. The time of wetness factor lost its importance because the temperature wetness characteristics at the different sites as well as the precipitation on them differed insignificantly. To obtain a more universal dose-response function the time of wetness must be included.

Dry deposition of Cl at the test sites increased in the sequence Viksjøfjell > Karpdalen > Svanvik and the Cl/Mg ratio measured has shown that sea-salt aerosols are the important Cl source. Dry deposition of Cl made its own contribution to the processes of atmospheric corrosion at Viksjøfjell and partly at Karpdalen. Accordingly the corrosion rates at Viksjøfjell and Karpdalen were higher than expected compared to the rest of the test sites. Figure 1 shows the test sites.

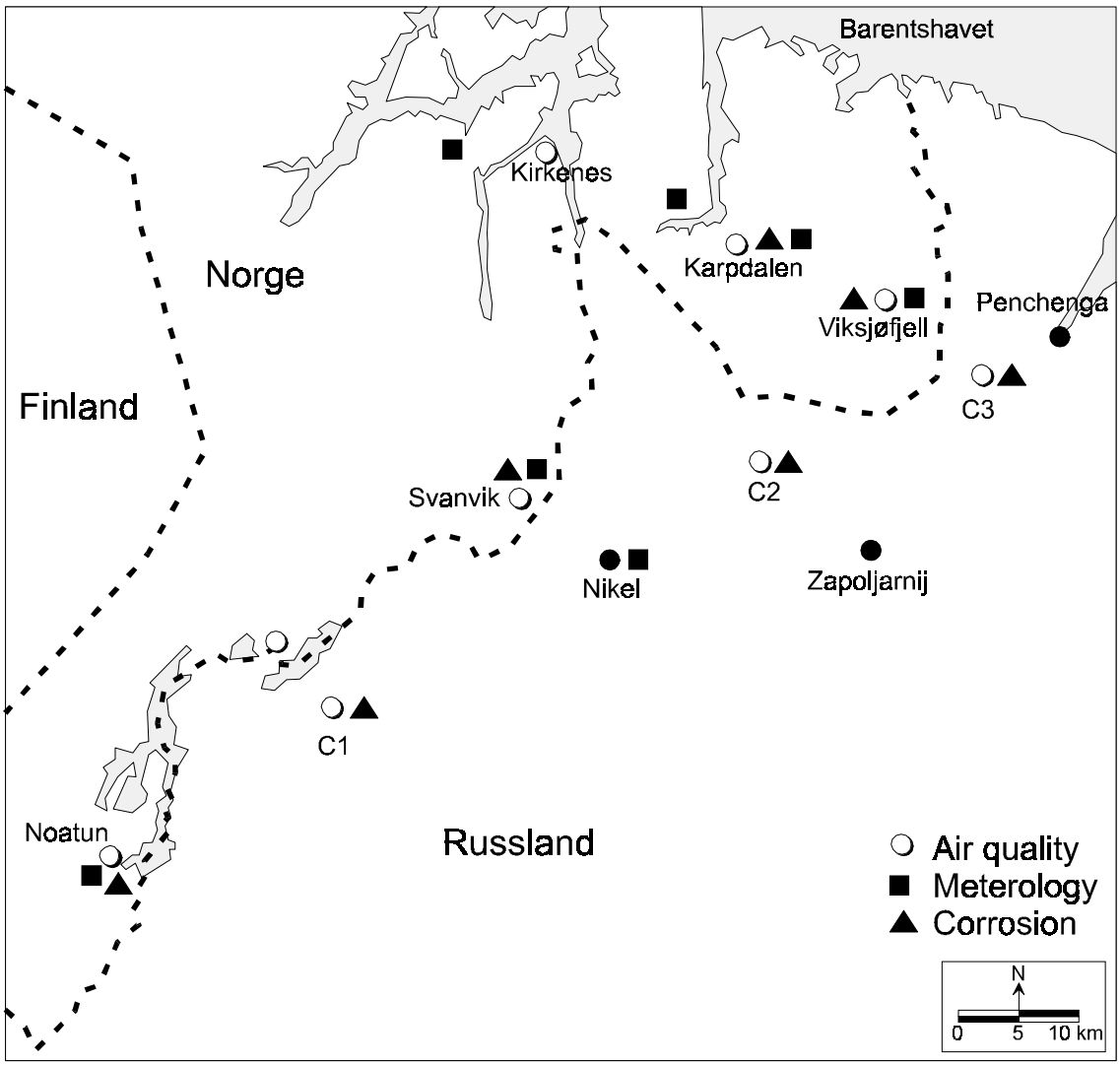


Figure 1: Map of the test sites and the type of measurements performed at the sites.

Because of the temperature range found in the sub-arctic, the importance of defining the real time of wetness on the surface will increase. The common approximation of assuming the time of wetness to be defined by relative humidity above 80% and temperatures above 0°C works well in temperature climate, but a more detailed and refined definition is needed in sub-arctic climate, where long periods with temperatures close to 0°C are more frequent.

3. Description of the second exposure part of the bilateral programme

The second part of the bilateral exposure programme has been carried out along the Norwegian-Russian border in 1992–1994.

This part of the programme involved the 1 and 2 year exposures of the flat samples (10 x 15 cm) of carbon steel, zinc and copper at the sites Svanvik, Viksjøfjell (Norway) and C1, C2 and C3 (Russia). The same materials were also used in the first part of the programme. The steel used follows the Swedish standard SIS 141316.

The panels were facing south with a 45° angle.

The mass loss determinations were carried out in one laboratory (NILU).

The regular air pollution measurements in this period were carried out at the sites Svanvik, Viksjøfjell, Karpdalen, Nikel and C2.

4. Experimental results and discussion

4.1 Temperature, relative air humidity, time of wetness

The temperature and relative humidity in the air were measured at Viksjøfjell and Svanvik. The monthly and yearly data for temperature, relative air humidity and time of wetness (TOW: RH >80% and T >0°C, T >-2°C and T >-4°C) for the period 1992–1994 are given in Annex A, Tables A1–A3. Yearly values for time of wetness for the period of one year of exposure in 1990–1991, 1992–1993 and 1993–1994 are given in Table 1. The results show that the temperature wetness data in the region differ significantly from year to year and for the different test sites for the same period. The yearly values of time of wetness obtained for different temperature limits also differ for the same test sites. In most cases the dependence of $TOW_T = f(T_{limit})$ are strongly linear. The slope of curves did not differ greatly, see Annex B, Figure B1.

Table 1: Time of wetness (TOW = RH >80% and T >0°C, T >-2°C and T >-4°C) at Svanvik and Viksjøfjell.

	Svanvik			Viksjøfjell[1)]		
	TOW, hour/year RH >80% and			TOW, hour/year RH >80% and		
Period	T >0°C	T >-2°C	T >-4°C	T >0°C	T >-2°C	T >-4°C
1990/1991	1752	2101	2417	1691	2086	2551
1992/1993	2279	2716	3086	2627	3339	4091
1993/1994	1718	2140	2448	2176	3122	3829

1) For the periods 06–07/90, 12/90 and 01/91 the TOW data of Svanvik were used for the calculation of the yearly TOW values at Viksjøfjell.

4.2 Sulphur dioxide and wind

The SO_2 levels at the test sites are depending on the emissions, speed and direction of the wind, as well as the distance from the sources. The wind conditions are responsible also for transfer of aerosols, contained Cl-ions, which has corrosive impact on metals.

Average monthly and average maximum daily SO_2 levels, µg/m³, from August 1992 up to July 1994 are given in Annex A, Table A4. Annual average SO_2 levels for the first and second periods of exposure of materials are given in Table 2. The highest annual average SO_2 levels were measured at Nikel, which has the main source for SO_2 emissions in the area: 66 µg/m³ for 1992–1993 and 57 µg/m³ for 1993–1994. At the Norwegian sites the SO_2 levels decreased in 1993–1994 compared to the period 1990–1991. The decrease at Viksjøfjell, Karpdalen and Svanvik were 34%, 33% and 36% respectively. The decrease of SO_2 at the site C2 in 1992–1993 was insignificant.

Table 2: Annual average SO_2 levels, µg/m³, in 1990–1991, 1992–1993 and 1993–1994.

Period	C2	C3	Viksjøfjell	Karpdalen	Svanvik	C1	Noatun
1990–1991	56.9	43.1	37.1	21.3	13.0	9.9	5.9
1992–1993	54.8	–	25.6	15.5	10.6	–	–
1993–1994	–	–	24.4	14.3	8.3	–	–

The NO_x pollutant level is low in this region. Therefore the measurements of NO_2 were not included in the programme.

The wind parameters (wind speed and wind direction) were measured at Viksjøfjell and at Svanvik. The distribution of wind direction and wind speed in 1992–1994 is given in Annex A, Tables A5 and A6. The wind conditions at Viksjøfjell in this period were characterized by the prevailing 210°–240° directions during the period from October to May. In the period from June to September winds prevailed of the 30°–180°and 360° directions. Relatively strong winds (> 6 m/s) prevailed during this period. Calm conditions did practically not occur.

The wind conditions at Svanvik were characterized by the prevailing 180°–240° directions during 9–10 months (from August to April–May). In the period from May to September the wind directions 30°–60° and 360° also prevailed. The calm periods during 8 months accounted for 10–32% of the time.

On the whole the wind conditions in 1992–1994 were approximately the same as in 1990–1991.

4.3 Precipitation

Precipitation has been measured regularly at Svanvik and Karpdalen. Some important corrosion parameters of precipitation are given in Table A7. The amount of precipitation in 1992–1993 was higher than in 1990–1991. This may be the reason for increasing values of the time of wetness at the test sites in 1992–1993. The three months' pH values were all below 5. The precipitation was characterized by increasing acidification and sulphur concentration when moving from the south to the north in the area. According to the results obtained in an international research programme carried out under UN/ECE Convention on long-range transboundary air pollution, the wet deposition (total amount of $[H^+]$ in precipitation) is one term in the dose/response functions for unsheltered zinc, copper and calcareous stones (Kucera et al., 1995; Kucera and Fitz, 1995). However, as it was concluded in the first part of the work, it is difficult to evaluate the quantitative role of acidity of the precipitation on corrosion due to the minor differences in the pH values for test sites.

The concentration of Cl in precipitation at Karpdalen was usually a factor of 2–3 higher than at Svanvik and sometimes it even increased abruptly. The Cl-ions accelerate the corrosion processes at Viksjøfjell and Karpdalen, and the corrosion is shown to have better correlation with dry than with wet deposition of Cl.

The concentration of NO_3^- was generally low, and increased insignificantly with increasing concentration of sulphate.

4.4 Analysis of corrosion data

The results of the corrosion tests during two years of exposure in 1992–1994 are given in Table 3. The mass losses of metals at all sites except Svanvik decreased in the order steel → zinc → copper. At Svanvik mass losses of copper were higher than zinc. The mass losses of all metals during the second year of exposure decreased compared to the first year, especially for copper, Annex B, Table B1. The most significant reduction of corrosion rate (on 60–70%) was observed at the less polluted test sites (Svanvik and C1). The reduction of the corrosion rate of steel and zinc the second year in presence of SO_2 and Cl-ions (Viksjøfjell) and at the significantly polluted test sites (C2 and C3) are only 20–50%. The second year corrosion rate of copper was reduced on 60–80% at all test sites. The low corrosion rate of copper at the test site C2 and the large reduction of the corrosion rate for the second year (by 80%) were unexpected, because of high concentration of SO_2 (54.8 µg/m^3) at the site.

The results of the yearly corrosion of metals during exposure in 1992–1993 and 1990–1991 are given in Table 4. The yearly mass losses of steel in 1992–1993 increased at all test sites compared with the period 1990–1991, in spite of the decrease of SO_2 levels. The yearly mass losses of zinc decreased at Viksjøfjell and at Svanvik, increased at the test sites C1 and C2 and did not change at the test site C3. The explanation for this phenomenon may be obtained on the basis of the analysis of the results of the two year exposures.

Table 3: Mass losses of steel, zinc and copper, g/m², after one (8/92–7/93) and tow years (8/92–7/94) of exposure.

	Viksjøfjell		Svanvik		C1		C2		C3	
Material	1	2	1	2	1	2	1	2	1	2
Steel	347	539	145	206	163	220	306	466	264	392
Zinc	18.0	26.8	7.1	9.5	8.3	11.2	21.3	33.4	15.1	27.1
Copper	12.1	16.4	10.1	12.8	8.2	–	8.9	10.7	–	–

Table 4: Mass losses of steel and zinc, g/m², after yearly exposure in 1990–1991 and 1992–1993.

Period	Material	Viksjøfjell	Karpdalen	Svanvik	Noatun	C1	C2	C3
1990/91	Steel	308	180	108	78	93	261	214
1992/93	"	347	–	145	–	163	306	264
1990/91	Zinc	24	12	9.6	5.4	6.4	19	15
1992/93	"	18	–	7.1	–	8.3	21	15

In accordance with the results of the UN/ECE ICP Programme (Kucera et al., 1995; Kucera and Fitz, 1995), the dose/response functions (DRF) for an unsheltered 4 year exposure of weathering steel and zinc in absence of significant amount of aerosols with Cl-ions can be written as:

$$ML_{steel} = a_1 + a_2\, TOW\, [SO_2][O_3] + a_3\, TOW \quad (1)$$

$$ML_{Zn} = a_1 + a_2\, TOW\, [SO_2][O_3] + a_3\, [Rain][H^+] \quad (2)$$

where ML – mass loss;
TOW – time of wetness = RH >80%, T >0°C;
$[SO_2]$ and $[O_3]$ – average annual concentrations;
Rain – amount of precipitation;
$[H^+]$ – annual concentrations;
a_1–a_3 – constant terms.

For urban and industrial areas in the UN/ECE ICP programme the annual ozone concentration has been estimated by the $[NO_2]$ concentration in accordance with the equation:

$$[O_3] = a_1 \exp(-|a_2|\,[NO_2]) \quad (3)$$

For the investigated region the level of NO_2 is low and all test sites except Nikel are located in rural areas. Therefore we can assume that $[O_3]$ = constant for all test sites. If we take into account that the differences between $[H^+]$ in precipitation is insignificant, we can also assume that $[Rain][H^+]$ = constant. In this case the equations (1, 2) can be written as

$$ML = A_1 + A_2\, TOW\, [SO_2] + A_3\, TOW \quad (4)$$

$$ML = A_1 + A_2\ TOW\ [SO_2] \quad (5)$$

From the first part of this programme (Henriksen et al., 1992; Henriksen et al., 1995) the dose/response function (DRF) observed can be written as:

$$ML_{steel} = (a_1 + a_2\ [SO_2] + a_3\ [Cl]) \cdot TOW \quad (6)$$

Dry deposition of Cl makes its own contribution to the corrosion rate at Viksjøfjell and Karpdalen. However, dry deposition of Cl was not measured during the second exposure of materials, therefore the statistical evaluation in this report is made on the basis of SO_2 and TOW data assuming that dry deposition of Cl at Viksjøfjell during the 1992–1993 exposure was approximately the same as for the 1990–1991 exposure. In this case it is possible to transform equation (6) to equation (7)

$$ML = (A_1 + A_2\ [SO_2]) \cdot TOW \quad (7)$$

It is obvious, that for constant TOW equations (4, 5, 7) transform to equation

$$ML = B_1 + B_2\ [SO_2] \quad (8)$$

which was used in the first part of the work for the statistical evaluation of yearly mass losses of metals.

The plan for statistical evaluation has been to investigate equations (4, 5, 7) as possible dose/response functions for steel and zinc. The regression analysis was made for two different sets of test sites:

A) Noatun, C1, Svanvik, Karpdalen and Viksjøfjell (1990/91), Svanvik and Viksjøfjell (1992/93);
B) Noatun, C1, Svanvik, C2 and C3 (1990/91), Svanvik and C2 (1992/93).

Set (A) contain test sites with higher content of dry deposition of Cl (Viksjøfjell and Karpdalen).

The results of the statistical evaluation are shown in Tables 5 and 6. All equations are characterized by high values of R^2. However, for equation (4) the constant term A_1 for steel and the term A_3 for zinc are negative. The main reason for this phenomenon is that for the research region the time of wetness did not change greatly and a high (negative) correlation between A_1 and TOW is observed (in all cases $R^2 > 0.9$). It means that one of the terms (A_1 or A_3 TOW) is unnecessary to use in the regression, and equation (4) can be transformed to equation (5) or (7). Both equations, (5) and (7), predict well the yearly corrosion rate of steel and zinc (see Tables 5 and 6). These are illustrated also on Figures 2–7.

Table 5: Equation constants for the calculation of yearly corrosion rates of carbon steel vs. SO_2 in air and time of wetness:

A) for test sites: Noatun, C1, Svanvik, Karpdalen and Viksjøfjell (1990/91), Svanvik and Viksjøfjell (1992/93);
B) for test sites: Noatun, C1, Svanvik, C2 and C3 (1990/91), Svanvik and C2 (1992/93).

	TOW: RH >80%	A_1	A_2	A_3	R^2
ML = A_1 + A_2 TOW[SO_2] + A_3 TOW					
A	T > 0	–27.0	40.0	230	0.994
	T > –2	–15.2	31.0	167	0.994
	T > –4	–6.0	24.7	134	0.993
B	T > 0	9.8	16.3	293	0.985
	T > –2	–1.9	13.5	292	0.988
	T > –4	–27.3	11.6	337	0.991
ML = A_1 + A_2 TOW[SO_2]					
A	T > 0	16.4	41.7	–	0.990
	T > –2	22.5	32.5	–	0.989
	T > –4	27.5	26.5	–	0.989
B	T > 0	70.0	16.8	–	0.976
	T > –2	69.7	14.1	–	0.976
	T > –4	69.1	12.2	–	0.974
ML = (A_1 + A_2 [SO_2]) TOW					
A	T > 0	97	40.1	–	0.989
	T > –2	91	32.0	–	0.989
	T > –4	105	25.4	–	0.989
B	T > 0	326	16.7	–	0.986
	T > –2	268	14.0	–	0.989
	T > –4	235	12.0	–	0.988

ML = g/(m^2year), SO_2 – µg/m^3, TOW – time fraction.

The regression analyses of equations (5) and (7) for yearly steel and zinc corrosion for three variants of time of wetness (RH >80% and T >0°C or T >-4°C) gives approximately the same R^2 for both metals. This is in contradiction with the results from the monthly test programme in this region and in the town Sulitjelma in Norway reported earlier (Henriksen, 1989; Henriksen et al., 1992; Henriksen et al., 1995). However, when we take into consideration that on the yearly basis the variation in the time of wetness is between 5–15% for the three variants of TOW, while the variation in the monthly values can be as high as a factor of 500, these results are easier to accept. To define temperature limits for the corrosion processes on a yearly basis we need a larger database from a larger region where the differences in the time of wetness is higher. For the monthly values the size of the region is very well suited for defining the temperature limits. SO_2 and time of wetness are the only factors we need to take into consideration and with the fairly high corrosion rates observed during the winter, a temperature limit below 0°C is obvious.

Table 6: Equation constants for the calculation of yearly corrosion rates of zinc vs. SO_2 in air and time of wetness:

A) for test sites: Noatun, C1, Svanvik, Karpdalen and Viksjøfjell (1990/91), Svanvik and Viksjøfjell (1992/93);
B) for test sites: Noatun, C1, Svanvik, C2 and C3 (1990/91), Svanvik and C2 (1992/93).

	TOW	A_1	A_2	A_3	R^2
$ML = A_1 + A_2\ TOW[SO_2] + A_3\ TOW$					
A	T > 0	12.0	3.0	–54.0	0.977
	T > –2	12.5	2.5	–47.0	0.977
	T > –4	12.7	2.0	–40.3	0.981
B	T > 0	8.1	1.3	–17.7	0.981
	T > –2	7.7	1.1	–13.8	0.981
	T > –4	7.5	0.9	–11.0	0.979
$ML = A_1 + A_2\ TOW[SO_2]$					
A	T > 0	1.6	2.6	–	0.891
	T > –2	2.0	2.0	–	0.878
	T > –4	2.4	1.6	–	0.879
B	T > 0	4.4	1.2	–	0.975
	T > –2	4.4	1.0	–	0.976
	T > –4	4.4	0.9	–	0.976
$ML = (A_1 + A_2\ [SO_2])\ TOW$					
A	T > 0	1.2	3.0	–	0.915
	T > –2	2.1	2.4	–	0.900
	T > –4	3.6	1.9	–	0.886
B	T > 0	24.0	1.2	–	0.962
	T > –2	20.0	1.0	–	0.964
	T > –4	17.4	0.8	–	0.963

ML = $g/(m^2 year)$, SO_2 – $\mu g/m^3$, TOW – time fraction.

The temperature wetness parameters in regional areas may differ from year to year. Time of wetness, which determine the duration of dry deposition of sulphur and the possibility of electro-chemical processes on metal surfaces, is an important parameter for the prediction of atmospheric corrosion even in regional areas. The results obtained show that the yearly mass loss of metals, especially steel, is practically linear with the sulphur dioxide concentration multiplied by the time of wetness (see Figures 2, 4B, 5 and 7B).

On the other hand, during exposure period 1992–1993 the average hourly corrosion rates during the time of wetness at the test sites decrease compared to 1990–1991 exposure and are in a good agreement with the decrease of the yearly mean SO_2 concentration in air (see Figures 3, 4A, 6 and 7A).

Figure 2: Yearly corrosion rate for carbon steel vs. the yearly mean concentration of sulphur dioxide multiplied with the yearly time of wetness in terms of time fraction:
1) TOW: RH >80% and T >0°C;
2) TOW: RH >80% and T >-2°C;
3) TOW: RH >80% and T >-4°C;
A) for test sites: Noatun, C1, Svanvik, Karpdalen and Viksjøfjell (1990/91), Svanvik and Viksjøfjell (1992/93);
B) for test sites: Noatun, C1, Svanvik, C2 and C3 (1990/91), Svanvik and C2 (1992/93).

Figure 3: Corrosion rate for carbon steel per hour of wetness vs. the yearly mean concentration of sulphur dioxide:
1) TOW: RH >80% and T >0°C;
2) TOW: RH >80% and T >-2°C;
3) TOW: RH >80% and T >-4°C;
A) for test sites: Noatun, C1, Svanvik, Karpdalen and Viksjøfjell (1990/91), Svanvik and Viksjøfjell (1992/93);
B) for test sites: Noatun, C1, Svanvik, C2 and C3 (1990/91), Svanvik and C2 (1992/93).

Figure 4: Average corrosion rate for carbon steel per hour of wetness vs. the yearly mean concentration of sulphur dioxide (A) and yearly corrosion rate for carbon steel vs. the yearly mean concentration of sulphur dioxide times yearly time of wetness in terms of time fraction (B) for TOW: RH >80% and T >0°C;

1) *for test sites: Noatun, C1, Svanvik, Karpdalen and Viksjøfjell (1990/91), Svanvik and Viksjøfjell (1992/93);*
2) *for test sites: Noatun, C1, Svanvik, C2 and C3 (1990/91), Svanvik and C2 (1992/93).*

Figure 5: Yearly corrosion rate for zinc vs. the yearly mean concentration of sulphur dioxide times the yearly time of wetness in terms of time fraction:

1) TOW: RH >80% and T >0°C;
2) TOW: RH >80% and T >-2°C;
3) TOW: RH >80% and T >-4°C;
A) for test sites: Noatun, C1, Svanvik, Karpdalen and Viksjøfjell (1990/91), Svanvik and Viksjøfjell (1992/93);
B) for test sites: Noatun, C1, Svanvik, C2 and C3 (1990/91), Svanvik and C2 (1992/93).

Figure 6: Average corrosion rate for zinc per hour of wetness vs. the yearly mean concentration of sulphur dioxide: RH >80% and T >0°C;
1) TOW: RH >80% and T >0°C;
2) TOW: RH >80% and T >-2°C;
3) TOW: RH >80% and T >-4°C;
A) for test sites: Noatun, C1, Svanvik, Karpdalen and Viksjøfjell (1990/91), Svanvik and Viksjøfjell (1992/93);
B) for test sites: Noatun, C1, Svanvik, C2 and C3 (1990/91), Svanvik and C2 (1992/93).

Figure 7: Average corrosion rate for zinc per hour of wetness vs. the yearly mean concentration of sulphur dioxide (A) and yearly corrosion rate for zinc vs. the yearly mean concentration of sulphur dioxide times the yearly time of wetness in terms of time fraction (B) for TOW: RH >80% and T >0°C;

1) for test sites: Noatun, C1, Svanvik, Karpdalen and Viksjøfjell (1990/91), Svanvik and Viksjøfjell (1992/93);

2) for test sites: Noatun, C1, Svanvik, C2 and C3 (1990/91), Svanvik and C2 (1992/93).

Thus two corrosion characteristics are important:

1) general atmospheric corrosivity – the total yearly corrosion rate;
2) atmospheric corrosivity of SO_2. This characteristic can be determined from the two dose/response functions as the average corrosion rate caused by SO_2 during the periods were corrosion can occur (time of wetness) in the same way as for the determination of acceptable SO_2 levels (Kucera et al., 1995; Kucera and Fitz, 1995; UN/ECE, 1996):

$$A_2\left[SO_2\right] = \frac{\left(ML - A_1\right)}{TOW} \text{ from equation (5)} \quad (9)$$

$$A_2\left[SO_2\right] = \frac{\left(ML\right)}{TOW - A_1} \text{ from equation (7)} \quad (10)$$

or as a first approximation for local region, the average total corrosion rate during the period divided with time of wetness $\left(\frac{ML}{TOW}\right)$. The determination of the corrosivity of SO_2 will therefore be the most important factor for corrosion monitoring and for trend-effect analysis.

The dose/response functions obtained can be recommended for the prediction of yearly corrosion rate of carbon steel and zinc in sub-arctic climate in absence of significant dry deposition of Cl by using data-set B. The dose/response functions are obtained for the range of SO_2: 5–57 µg/m^3, and for the range of TOW (RH >80%, T > 0°C): 0.19–0.26 time fraction of a year

		R^2
ML_{steel}	= 70 + 16.8 [SO_2] TOW	0.976
ML_{steel}	= (326 + 16.7 [SO_2]) TOW	0.986
ML_{Zinc}	= 4.4 + 1.2 [SO_2] TOW	0.975
ML_{Zinc}	= (24.0 + 1.2 [SO_2]) TOW	0.962

The dose/response functions obtained by using data-set (A), contain test sites with higher content of dry deposition of Cl (Viksjøfjell and Karpdalen) and can be used only for this region with the assumption that dry deposition of Cl does not differ greatly from one year to the next. The dose/response functions obtained for the range of SO_2: 5–37 µg/m^3, and for the range of TOW (RH >80%, T >0°C): 0.19–0.30 time fraction of a year

		R^2
ML_{steel}	= 16.4 + 41.7 [SO_2] TOW	0.990
ML_{steel}	= (97 + 40.1 [SO_2]) TOW	0.898
ML_{Zinc}	= 1.6 + 2.6 [SO_2] TOW	0.891
ML_{Zinc}	= (1.2 + 3.0 [SO_2]) TOW	0.915

The R^2 values for zinc for the data-set (A) are lower than for set (B). This indicates the need for taking into account in dose/response functions other environmental parameters, in particular the dry deposition of Cl.

In accordance with dose/response functions obtained, the yearly corrosion rates of steel and zinc were higher for the areas with higher contents of dry deposition of Cl (Viksjøfjell and Karpdalen). This can be shown by plots of corrosion versus the term $[SO_2]$ (see Figures 4 and 7).

The dose/response functions obtained can be used for the assessment of the corrosivity and for mapping of the corrosion rates of steel and zinc and acceptable SO_2 levels in this region in accordance with methodology elaborated (Kucera et al., 1995; Kucera and Fitz, 1995) and recommended by the UN/ECE (1996).

5. Conclusion

The results of corrosion tests of metals along the Norwegian-Russian border in 1990–1991 and in 1992–1994 show:

1. Dry deposition of sulphur is the main reason of the accelerated atmospheric corrosion of metals in the region along the Norwegian-Russian border. Dry deposition of Cl makes its own contribution to the processes of corrosion at Viksjøfjell and Karpdalen. Sea-salt aerosols are the important Cl source. The corrosivity of acid precipitation is certain but not possible to represent as a function in our study due to the small differences observed in the pH values for the different test sites.

2. The kinetics of corrosion of steel, zinc and copper are characterized by a reduced corrosion rate after one year of exposure at all test sites. The most significant reduction of the corrosion rate (by 60–70%) are observed at the less polluted areas (test sites C1 and Svanvik), while the reduction of the corrosion rate of steel and zinc in a presence of SO_2 and Cl-ions (Viksjøfjell, the C2 and C3), are only 20–50%. The second year corrosion rate of copper was reduced by 60–80% at all test sites.

3. Time of wetness is an important parameter for the prediction of atmospheric corrosion of metals even for a regional scale. Therefore for monitoring purposes and for trend-effect analysis it is most important to determine the corrosivity of SO_2, either as the average corrosion rate caused by SO_2 or as the average total corrosion rate during the period, with time of wetness. The dose/response functions for the yearly mass losses of steel and zinc are obtained on the basis of average annual SO_2 concentration in the air and time of wetness. These dose/response functions can be written in the general form:

$$ML = A_1 + A_2 [SO_2] TOW$$

$$ML = (A_1 + A_2 [SO_2]) TOW$$

In accordance with dose/response functions obtained, the yearly corrosion rate for steel and zinc are higher for the areas with higher amounts of dry deposition of Cl (test sites Viksjøfjell and Karpdalen) than for areas with analogous but only SO_2-containing atmosphere.

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Annex A

Tables

Table A1: Monthly temperature, relative humidity and time of wetness results for the period January–December 1992 at Svanvik and Viksjøfjell.

Svanvik

	T	RH	RH > 80% and T >0°C	RH > 80% and T >-2°C	RH > 80% and T >-4°C
	°C	%	in hours	in hours	in hours
January	-10	80	48	63	114
February	-8	82	1	22	105
March	-4	78	53	108	173
April	-6	71	14	14	38
May	5	68	131	179	193
June	10	66	173	177	182
July	9	80	426	431	431
August	8	81	416	429	429
September	7	89	576	580	581
October	-8	87	106	144	188
November	-12	86	14	55	108
December	-6	85	43	122	194
Year	-1	79	2001	2324	2736

Viksjøfjell

	T	RH	RH > 80% and T >0°C	RH > 80% and T >-2°C	RH > 80% and T >-4°C
	°C	%	in hours	in hours	in hours
January	-7	90	80	127	201
February	-6	93	3	24	121
March	-5	90	22	166	306
April	-6	85	40	58	83
May	3	79	217	295	318
June	7	75	342	367	367
July	8	86	515	515	515
August	7	86	531	531	531
September	7	93	643	650	650
October	-6	94	106	167	246
November	-9	93	7	34	104
December	-5	92	33	144	259
Year	-1	88	2539	3078	3701

Table A2: Monthly temperature, relative humidity and time of wetness results for the period January–December 1993 at Svanvik and Viksjøfjell.

Svanvik

	T	RH	RH > 80% and T >0°C	RH > 80% and T >-2°C	RH > 80% and T >-4°C
	°C	%	in hours	in hours	in hours
January	-10	82	0	17	62
February	-10	78	5	26	41
March	-9	80	13	31	94
April	-4	75	16	61	107
May	2	78	176	308	339
June	5	84	445	474	474
July	12	82	469	469	469
August	10	85	538	541	541
September	1	91	310	418	493
October	-3	83	134	228	279
November	-5	81	16	64	121
December	-11	80	0	23	31
Year	-2	82	2122	2660	3051

Viksjøfjell

	T	RH	RH > 80% and T >0°C	RH > 80% and T >-2°C	RH > 80% and T >-4°C
	°C	%	in hours	in hours	in hours
January	-8	91	1	19	115
February	-8	91	4	43	115
March	-7	89	9	46	118
April	-5	87	62	150	241
May	1	86	197	397	554
June	3	91	522	646	646
July	10	83	512	512	512
August	8	87	581	581	581
September	1	89	341	587	602
October	-4	94	90	237	369
November	-6	93	1	41	157
December	-10	94	0	0	30
Year	-2	90	2320	3259	4040

Table A3: Monthly temperature, relative humidity and time of wetness results for the period January–December 1994 at Svanvik and Viksjøfjell.

Svanvik

	T	RH	RH > 80% and T >0°C	RH > 80% and T >-2°C	RH > 80% and T >-4°C
	°C	%	in hours	in hours	in hours
January	-17	80	0	0	1
February	-11	78	6	9	33
March	-7	75	0	5	35
April	0	75	130	210	231
May	2	69	69	136	168
June	8	74	288	288	288
July	13	69	227	227	227
August	12	73	273	281	281
September	6				
October	0				
November	-7				
December	-5				
Year	-1	74	993	1156	1264

Viksjøfjell

	T	RH	RH > 80% and T >0°C	RH > 80% and T >-2°C	RH > 80% and T >-4°C
	°C	%	in hours	in hours	in hours
January	-11	93	0	0	1
February	-10	92	19	43	87
March	-7	92	0	10	70
April	-1	87	149	389	465
May	-1	85	119	291	524
June	5	85	473	549	549
July	10	80	394	394	394
August	10	79	325	325	325
September	4	88	517	565	567
October	-3	93	106	265	438
November	-7	94	6	42	104
December	-6	95	0	11	150
Year	-1	89	2108	2884	3674

Table A4: Average monthly and average maximum daily SO_2 levels in µg/m³ from August 1992 to July 1994.

	Viksjøfjell		Svanvik		Karpdalen		Nikel		C2	
Month/Year	Aver.	Max.	Aver.	Max.	Aver.	Max.	Aver.	Max.	Aver.	Max.
8/92	22	100	8	56	9	43	72	350	32	182
9/92	24	132	5	42	12	92	102	727	42	313
10/92	10	159	4	36	7	162	67	354	61	552
11/92	57	227	31	288	44	208	99	698	142	596
12/92	35	158	3	23	21	189	13	163	–	–
1/93	31	186	3	36	16	70	22	124	75	280
2/93	34	174	2	21	10	83	24	229	66	376
3/93	41	210	23	155	37	152	31	175	110	563
4/93	24	133	14	113	12	84	40	609	32	134
5/93	16	117	7	64	8	51	58	665	17	126
6/93	4	47	10	54	5	44	148	656	4	21
7/93	9	60	17	103	5	20	136	652	22	181
8/93	18	121	8	59	11	56	139	1127	41	188
9/93	15	83	3	27	5	62	27	127	51	256
10/93	29	304	2	20	6	54	44	452	86	389
11/93	42	141	3	37	14	89	9	81	–	–
12/93	25	76	19	172	33	149	30	246	–	–
1/94	45	234	10	151	22	108	38	197	*	321
2/94	13	96	2	21	9	119	23	243	25	111
3/94	36	187	11	126	32	137	24	162	52	266
4/94	34	202	10	130	14	68	22	194	–	–
5/94	11	62	11	86	4	65	90	377	–	–
6/94	7	25	13	64	6	42	149	440	–	–
7/94	18	141	8	89	15	52	94	378	–	–

* too few values for an average calculation.

Table A5: Distribution of wind speed and wind direction at Svanvik.

Station: Svanvik

Variation of wind directions, %

Month/year	08/92	09/92	10/92	11/92	12/92	01/93	02/93	03/93	04/93	05/93	06/93	07/93
Direction*	Wind-rose, %											
30	4.0	13.7	1.5	5.8	0.7	0.5	0.7	1.5	2.6	9.5	8.6	15.9
60	12.6	9.9	2.3	8.3	0.7	0.3	0.3	2.6	10.9	8.3	11.1	14.2
90	7.0	2.8	0.8	2.2	0.0	0.5	0.3	1.6	5.6	5.8	4.0	6.4
120	3.8	2.8	1.5	0.6	0.7	0.5	0.3	1.5	5.3	4.9	1.5	3.6
150	8.0	10.2	2.2	2.1	9.0	7.3	1.8	9.1	4.6	4.0	1.7	4.4
180	19.2	13.2	4.0	14.3	14.7	19.9	19.0	16.1	12.1	13.3	5.3	5.5
210	14.1	11.3	24.4	16.6	27.7	22.2	32.2	16.5	13.9	10.0	2.8	4.4
240	2.9	5.9	10.8	2.2	13.4	12.4	6.6	7.3	14.3	5.8	1.0	2.1
270	3.6	2.6	8.7	0.7	6.9	3.9	8.7	2.0	5.4	7.4	3.3	2.1
300	6.3	4.2	7.7	1.2	4.8	3.6	7.8	5.1	5.4	9.6	6.4	3.5
330	2.5	2.2	4.0	1.3	7.3	5.3	5.1	3.0	6.1	10.1	6.7	3.0
360	5.1	2.6	3.6	3.1	1.1	3.0	0.7	2.8	5.0	4.6	46.4	321
calm	10.9	18.5	28.1	31.6	13.2	20.5	16.5	30.9	8.1	6.7	0.6	2.7

* This number indicates central direction sector.

Distribution of wind speed, %

Class I: Wind speed 0.5 – 2.0 m/s
Class II: Wind speed 2.1 – 4.0 m/s
Class III: Wind speed 4.1 – 6.0 m/s
Class IV: Wind speed > 6.0 m/s

Month/year	08/92	09/92	10/92	11/92	12/92	01/93	02/93	03/93	04/93	05/93	06/93	07/93
Class	Wind speed, %											
calm	10.9	18.5	28.1	31.6	13.2	20.5	16.5	30.9	8.1	6.7	0.6	2.7
I	46.3	45.5	41.2	39.6	26.9	30.9	27.8	37.0	42.2	35.8	35.2	41.8
II	37.9	30.4	26.4	20.0	30.6	19.3	23.1	21.6	34.1	46.7	52.6	43.2
III	5.0	5.5	4.0	5.5	20.0	16.4	20.5	7.7	13.5	8.9	11.4	11.2
IV	0.0	0.1	0.3	3.4	9.3	12.9	12.1	2.8	2.1	1.8	0.1	1.1

Table A5, cont.

Station: Svanvik

Variation of wind directions, %

Month/year	08/93	09/93	10/93	11/93	12/93	01/94	02/94	03/94	04/94	05/94	06/94	07/94
Direction*	Wind-rose, %											
30	18.7	7.7	6.9	0.4	4.3	0.3	3.6	1.6	3.5	10.6	24.7	19.7
60	6.2	2.4	2.2	1.1	3.6	1.7	0.5	5.6	8.5	8.7	7.9	3.2
90	2.3	2.6	0.1	0.3	3.0	0.4	0.0	2.7	1.7	5.2	2.8	3.0
120	1.9	1.8	0.1	0.1	5.7	0.4	0.7	3.8	0.6	2.7	1.5	2.2
150	9.3	10.0	4.7	1.7	7.5	2.1	6.0	14.3	3.1	3.6	8.8	12.4
180	13.7	6.8	13.6	41.4	26.4	13.9	13.0	31.5	19.0	6.9	8.2	14.7
210	6.1	12.0	26.0	36.4	12.1	13.7	26.2	15.1	16.4	6.9	6.3	7.9
240	2.8	4.9	6.5	4.2	2.2	7.6	8.5	6.5	4.4	1.2	1.3	2.2
270	2.6	12.5	14.3	4.5	1.7	5.0	10.3	3.0	6.5	2.4	6.7	5.2
300	5.1	13.1	15.5	1.8	0.4	5.0	9.4	0.7	3.5	3.9	1.7	6.6
330	6.3	7.4	3.1	0.7	0.9	2.2	4.9	0.5	1.7	3.8	4.2	3.6
360	19.4	5.3	2.7	0.4	2.3	5.3	3.6	0.1	1.4	8.7	15.7	9.7
calm	5.5	13.5	4.3	7.0	29.9	42.3	13.4	14.4	29.9	35.3	10.3	9.7

* This number indicates central direction sector.

Distribution of wind speed, %

Class I: Wind speed 0.5 – 2.0 m/s
Class II: Wind speed 2.1 – 4.0 m/s
Class III: Wind speed 4.1 – 6.0 m/s
Class IV: Wind speed > 6.0 m/s

Month/year	08/93	09/93	10/93	11/93	12/93	01/94	02/94	03/94	04/94	05/94	06/94	07/94
Class	Wind speed, %											
calm	5.5	13.5	4.3	7.0	29.9	42.3	13.4	14.4	29.9	35.3	10.3	9.7
I	55.7	60.9	44.9	23.1	34.1	37.3	37.8	30.9	33.8	35.8	37.3	48.6
II	34.9	23.4	34.9	34.1	19.7	13.7	37.0	37.1	30.6	21.0	44.7	35.0
III	3.8	2.1	13.5	30.9	7.5	5.2	7.5	11.3	5.8	6.6	7.4	6.6
IV	0.1	0.1	2.4	5.0	8.9	1.5	4.4	6.3	0.0	1.3	0.3	0.1

Table A6: Distribution of wind speed and wind direction at Viksjøfjell.

Station: Viksjøfjell

Variation of wind directions, %

Month/year	08/92	09/92	10/92	11/92	12/92	01/93	02/93	03/93	04/93	05/93	06/93	07/93
Direction*	Wind-rose, %											
30	10.2	6.7	1.0	1.2	0.9	0.3	2.1	0.6	2.9	6.5	15.7	11.6
60	5.0	8.3	5.0	8.0	0.1	0.5	1.2	2.8	7.8	5.5	12.3	18.7
90	14.1	5.3	2.2	7.7	1.0	1.6	0.4	3.9	9.2	6.2	6.3	15.2
120	11.6	12.4	2.7	10.6	5.0	2.5	1.0	5.6	9.3	6.7	3.2	16.0
150	14.9	15.0	0.2	13.3	10.3	9.8	0.2	11.5	6.4	5.8	3.7	4.8
180	12.1	8.3	0.7	12.5	7.6	12.1	3.3	4.9	5.6	7.0	3.5	2.7
210	5.8	16.1	6.8	17.1	19.5	21.6	22.0	21.8	11.2	11.3	1.3	3.8
240	6.5	9.7	35.4	15.8	29.4	27.1	34.6	28.0	24.0	10.3	2.1	4.3
270	6.0	6.0	22.7	2.2	7.2	7.6	13.1	7.2	9.6	11.6	3.1	1.3
300	5.1	3.3	6.3	1.0	4.8	6.8	15.1	5.9	6.1	8.3	4.5	1.5
330	3.6	4.6	4.3	1.9	10.9	4.5	4.1	5.1	5.1	10.2	15.8	4.3
360	5.1	4.3	2.7	2.4	3.2	5.3	2.7	2.1	2.6	10.5	28.5	15.9
calm	0.0	0.0	10.0	6.3	0.0	0.3	0.0	0.6	0.1	0.3	0.0	0.0

* This number indicates central direction sector.

Distribution of wind speed, %

Class I: Wind speed 0.5 – 2.0 m/s
Class II: Wind speed 2.1 – 4.0 m/s
Class III: Wind speed 4.1 – 6.0 m/s
Class IV: Wind speed > 6.0 m/s

Month/year	08/92	09/92	10/92	11/92	12/92	01/93	02/93	03/93	04/93	05/93	06/93	07/93
Class	Wind speed, %											
calm	0.0	0.0	10.0	6.3	0.0	0.3	0.0	0.6	0.1	0.3	0.0	0.0
I	7.8	6.0	18.7	21.7	4.8	2.8	2.3	9.0	4.7	5.8	9.6	6.0
II	24.7	28.9	33.1	35.1	14.4	11.7	14.7	18.7	20.6	17.2	20.6	30.9
III	31.6	28.6	11.2	12.7	14.2	9.3	12.7	20.1	19.4	29.6	26.7	34.8
IV	35.9	36.5	27.0	24.2	66.5	75.9	70.3	51.6	55.1	47.2	43.2	28.2

Table A6, cont.

Station: Viksjøfjell

Variation of wind directions, %

Month/year	08/93	09/93	10/93	11/93	12/93	01/94	02/94	03/94	04/94	05/94	06/94	07/94
Direction*	Wind-rose, %											
30	17.1	4.6	1.2	0.0	1.2	3.8	6.5	1.1	2.6	12.2	17.2	11.6
60	9.3	2.8	8.6	0.3	2.0	1.2	0.6	4.4	4.0	10.9	7.9	4.2
90	7.1	1.5	1.8	0.8	3.7	0.5	0.4	6.7	5.7	10.1	6.0	4.2
120	11.3	3.2	0.6	1.7	16.7	2.6	0.3	9.3	8.8	7.8	6.8	8.7
150	18.1	8.1	1.2	4.3	7.9	8.9	5.4	13.8	8.6	4.6	7.2	12.4
180	4.4	4.9	6.7	11.1	19.1	13.3	4.2	21.1	17.2	7.5	8.6	10.1
210	3.4	9.0	12.6	38.3	14.2	15.3	8.3	21.6	19.2	11.0	7.2	8.3
240	3.9	17.6	33.4	35.1	23.0	18.6	39.0	18.3	11.9	9.3	3.1	6.0
270	0.8	11.5	7.7	4.2	2.2	15.9	13.2	2.6	11.4	4.2	9.3	5.9
300	1.6	14.9	15.0	3.3	1.9	5.0	9.7	0.4	2.4	4.8	2.5	9.1
330	9.0	14.0	10.7	0.6	2.4	8.1	9.7	0.3	6.1	7.9	7.2	7.1
360	13.6	7.9	0.3	0.0	0.8	4.0	8.9	0.4	2.1	9.1	16.9	12.4
calm	0.4	0.0	0.0	0.3	4.9	2.8	3.4	0.0	0.0	0.5	0.0	0.0

0,0

* This number indicates central direction sector.

Distribution of wind speed, %

Class I: Wind speed 0.5 – 2.0 m/s
Class II: Wind speed 2.1 – 4.0 m/s
Class III: Wind speed 4.1 – 6.0 m/s
Class IV: Wind speed > 6.0 m/s

Month/year	08/93	09/93	10/93	11/93	12/93	01/94	02/94	03/94	04/94	05/94	06/94	07/94
Class	Wind speed, %											
calm	0.4	0.0	0.0	0.3	4.9	2.8	0.0	0.0	0.0	0.5	0.0	0.0
I	8.9	9.2	4.0	6.5	19.9	20.2	6.1	9.1	4.7	8.5	6.5	11.4
II	35.6	44.9	15.0	20.0	19.8	25.7	20.7	21.6	21.0	22.6	25.0	32.8
III	29.4	25.6	9.8	16.9	14.2	24.9	19.0	17.1	24.9	29.4	28.5	29.2
IV	25.7	20.4	71.2	56.3	41.2	26.4	54.2	52.2	49.4	39.0	40.0	26.6

Table A7: Some precipitation parameters at Svanvik and Karpdalen.

Parameter		Rain	Cond.	pH	SO_4	Cl	NO_3
Test site	Period	mm	µs/cm		mg/l	mg/l	mg/l
Svanvik	07/92–09/92	227	16	4.61	2.1	0.5	0.5
	10/92–12/93	49	27	4.83	1.9	4.2	1.2
	01/93–03/93	29	32	4.78	1.8	5.8	0.8
	04/93–06/93	172	21	4.57	2.5	1.1	0.7
	07/93–09/93	61	21	4.72	2.8	1.4	0.5
	10/93–12/93	80	17	4.79	1.3	1.5	1.1
	01/94–03/94	51	22	4.77	1.0	2.7	1.0
Karpdalen	07/92–09/92	226	33	4.32	3.8	1.8	0.7
	10/92–12/93	74	50	4.68	3.4	9.0	1.1
	01/93–03/93	43	83	4.64	4.2	16.3	1.6
	04/93–06/93	141	86	4.14	4.6	3.9	1.1
	07/93–09/93	57	69	4.34	6.1	12.1	1.1
	10/93–12/93	84	27	4.80	1.3	4.2	1.0
	01/94–03/94	83	35	4.78	2.2	5.8	1.2

Annex B

Tables

Table B1: Ratio of the mass losses of metals during second and first year of exposure, $\left[\left(\frac{ML_2 - ML_1}{ML_1}\right)\right] \cdot 100\%$.

Material	Viksjøfjell	Svanvik	C1	C2	C3
Steel	55	42	35	52	48
Zinc	49	34	35	57	79
Copper	36	27	–	20	–

Figure B1: The yearly values of time of wetness at Svanvik and Viksjøfjell, defined as a time at: RH >80% and T >0°C, T >-2°C, T >-4°C vs. temperature limit for calculation.

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ABSTRACT
A bilateral exposure programme has been carried out along the Norwegian-Russian border in 1990–94. The results show that also in sub-arctic climate the corrosion is strongly effected by man-made pollution emission. A statistical analysis shows that SO_2 and time of wetness is the dominating factors for the corrosion. The influence of chloride and pH in precipitation is also obvious.

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