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CORROSION IN SO_2 POLLUTED COLD CLIMATE ATMOSPHERES IN NORTHERN NORWAY AND AT THE BORDER BETWEEN NORWAY AND RUSSIA

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ABSTRACT

The impact of SO_2 to the corrosion of metals in cold climate has been studied in two separate field studies. In Sulitjelma in Northern Norway the SO_2-emission came from a copper smelter and along the border between Norway and Russia close to the town of Nikel it came from the nickel production. The strong influence of average SO_2 for the test period on corrosion of all exposed metals was confirmed in both studies and in the study around Nikel the impact from chloride was also shown at some of the test sites.

In Sulitjelma the SO_2 effect was illustrated in two different ways. The copper smelter responsible for the SO_2 values was shut down during the summer for the three first years of exposure. This gave a reduction in the SO_2 concentrations from around 600 $\mu g/m^3$ to 10 $\mu g/m^3$ during the summer and a reduction of corrosion rate of carbon steel from 60 g/m^2 per month to 10 g/m^2. The last year the smelter was shut down permanently. This gave a yearly mean value for SO_2 of 2 $\mu g/m^3$ and a reduction of yearly corrosion of carbon steel from 500 g/m^2 to 60 g/m^2.

The influence of temperature was clearly documented in both studies and in a new joint evaluation. For carbon steel the evaluation of the monthly carbon steel results gave a freezing point retention of 4°C. Based on the best available equations for the dose-response equations for carbon steel and zinc, mapping of the corrosivity along the Norwegian-Russian border has been carried out for an area of 110x100km.

Keywords: cold climate, corrosivity mapping, atmospheric corrosion, SO_2 pollution.
Introduction

The main knowledge about corrosion is obtained in the moderate climate zone. In cold regions the studies have been rather few. In many countries the interests for the corrosion in cold climate has been focusing on chloride induced corrosion since a large part of the activity in the northern areas has been linked to the sea. However both in Norway and Russia there have been mining and metal production in the cold climate for many years with tremendous impact both on the surrounding vegetation as well as for the materials used in the area. The largest ecological effect caused by the industry in Norway has been in the copper production town Røros with production from 1646-1977. The wooden built town is now on the UNESCO's world heritage list. After these mines were closed the largest single emission source in Norway was from the copper production in Sulitjelma from 1886-1987, (67° 8' North). Today one of the areas with the highest air pollution in Norway is along the border between Norway and Russia caused by the nickel production on the Russian side of the border, in the towns Nikel and Zapoljarnij (69° 20' North). This production was started in the 1930ies and is still going on.

For corrosion scientist the Sulitjelma area and the Norwegian – Russian border were two very interesting fields for studying the corrosion due to sulphur dioxide in a cold climate. One important factor was that besides the emissions from the production there are very small amounts of other pollutants in the area, and for most of the area the influence from chloride is also low. The areas should therefore be very suitable for studying the climatic influence on sulphur dioxide corrosion. The Sulitjelma and the Norwegian-Russian border studies have been published earlier [1-3].

This time a joint evaluation of the two studies has been performed together with a modelling of the corrosion situation along the Norwegian - Russian border based on the corrosion equations obtained and the emission dispersion model CONDEP [4].

THE SULITJELMA STUDY

The study was started in February 1984 and continued to 1 March 1988 and was carried out on three test sites in the area: Sandnes, Furulund and Lomi. It was connected to the Norwegian surveillance programme that was responsible for all environmental data obtained. The amount of data collected changed to some degree from one year to the next and covered two sites for 1984 and 85, three in 1986 and two in 1987. The surveillance programme was closed in April 1987 because the copper smelter exploded on 3 February 1987 and the copper production never opened again. Besides the normal fluctuation in the meteorological parameters the sites had large variations in the monthly SO_2 levels, from an average value up to 600 $\mu g/m^3$ in the winter months and down to 6$\mu g/m^3$ in the summer time, when the smelter was closed. After the explosion the SO_2 level was fairly constant around 2 $\mu g/m^3$.

The corrosion test programme included monthly exposures of carbon steel to cover the variation in climate and pollution levels. For the general yearly corrosion steel, zinc, copper and aluminium was exposed.

THE NORWEGIAN – RUSSIAN BORDER STUDY

The Norwegian surveillance programme has included measurements along the border between Norway and Russia from 1974. A bilateral comprehensive investigation of air quality, precipitation chemistry and various environmental impacts was started in 1990.As a part of this programme a corrosion study was carried out in two periods, June 1990 to May 1991 and August 1992 to July 1994. In the first period corrosion tests were carried out at 5 sites in Norway and 3 sites in Russia, in the second period 2 sites in Norway and 3 sites in Russia were included. Figure 1 gives a rough map of the area including the name or code name for the test sites.

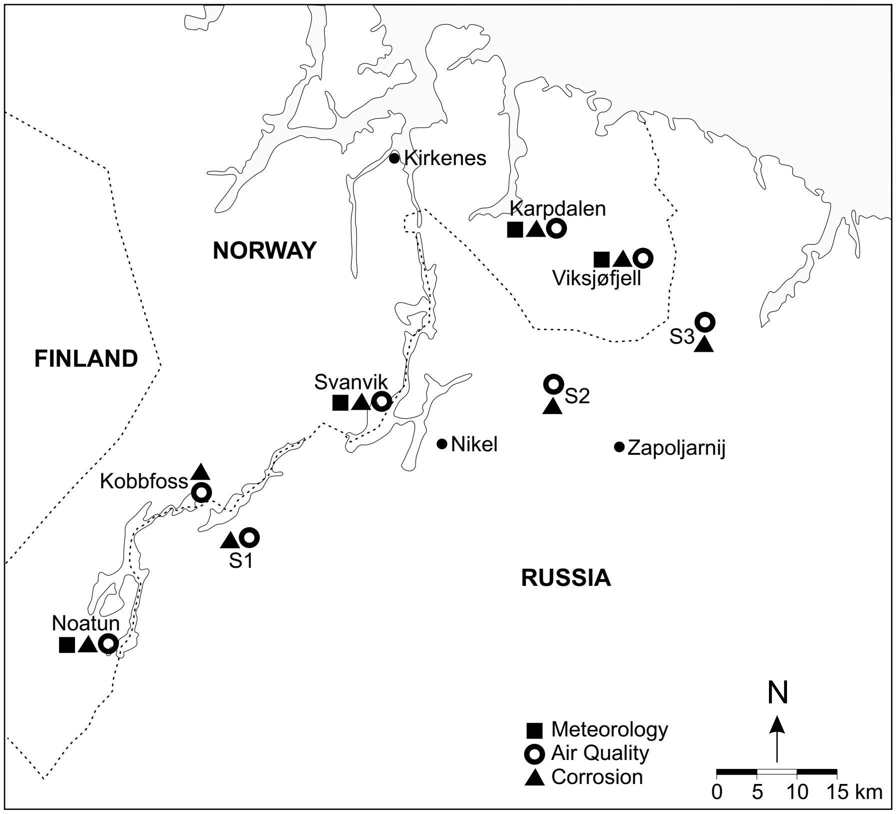

Figure 1 - Map of the test area along the Norwegian – Russian border with the test sites shown on the map

The investigation had different goals in the two phases. In the first phase the influence of the seasonal climatic variation was tested by exposure of 1 month and 3 months steel panels. Yearly panels for steel, zinc, galvanized steel and "Aluzinc" (1) coated steel and open helix specimens of aluminium, galvanized steel and "Galfan" (2) coated steel. The helix specimens were tests of suitable materials for the reindeer fences along the border. The results from the first period have been reported earlier[2].

The second phase was linked more to longer exposure effects and included steel, zinc and copper panels for one and two years of exposure[3].

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(1) Aluzinc is 55% aluminium zinc coated steel
(2) Galfan is 5% aluminium zinc coated steel

EARLIER PUBLISHED RESULTS

Sulitjelma:

The results (Table 1) from the yearly exposures in 1984-86 with high SO_2 levels compared to the 1987 data after the closing of the smelter show the dominating effect of SO_2 for the corrosion rate. The same trend is observed for all test sites and for both steel and zinc.

The effect is not that obvious for copper. However in the programme “Economical Commission for Europe international co-operative programme on effects on materials, including historic and cultural monuments” (UN ECE/ICP materials) it is also observed that copper oxidise fairly much the first year in unpolluted areas but levels quickly off while the copper corrosion increases in the next years [5]. To show the SO_2 effect on copper a longer exposure time than one year is needed.

Table 1 - One year of corrosion of steel zinc and copper (g/m^2) for three test sites in Sulitjelma

	Steel			Zinc			Copper		
Time	Sandnes	Furulund	Lomi	Sandnes	Furulund	Lomi	Sandnes	Furulund	Lomi
01/84-01/85	592	493		61	60		9.0	6.8	
01/85-01/86	449	431		46	50		10.4	9.4	
03/86-03/87	549	511	488	50	43	33	7.3	6.5	5.8
03/87-03/88	67	60	66	3	3	4	5.5	5.8	5.5

For zinc and steel the simple regressions between the corrosion and SO_2 are:

$$ML\ (steel) = 1.2\ SO_2 + 63 \quad (1)$$

$$ML\ (Zn) = 0.12\ SO_2 + 4.1 \quad (2)$$

ML= mass loss in g/m^2

No climatic effect could appear for the yearly evaluation since the climate is the same inside the whole valley. The climatic effect was studied by the monthly steel samples exposed in1986. The SO_2 concentration was measured on a daily basis and the precipitation on a monthly basis during the whole project. However the climatic parameters Temperature (T) and Relative Humidity (RH) were only measured in 1986. A comparison between the monthly mean values for SO_2 and the steel corrosion in the same period showed clearly that the effect of SO_2 was reduced at low temperature, particularly for November and December 1986 (see Figure 2). December was a very cold month with an average monthly temperature of –10.2°C and the corrosion was drastically reduced.

To compensate for the temperature effect a new parameter “effective” SO_2 concentration (C_{eff}) was introduced. The daily SO_2 value (C_d) was reduced to C_{eff} by multiplying the measured value with the fraction of the day where the temperature had been above a defined value, expected to be the freezing point of the surface wetness. $C_{eff} = C_d * (t/24)$

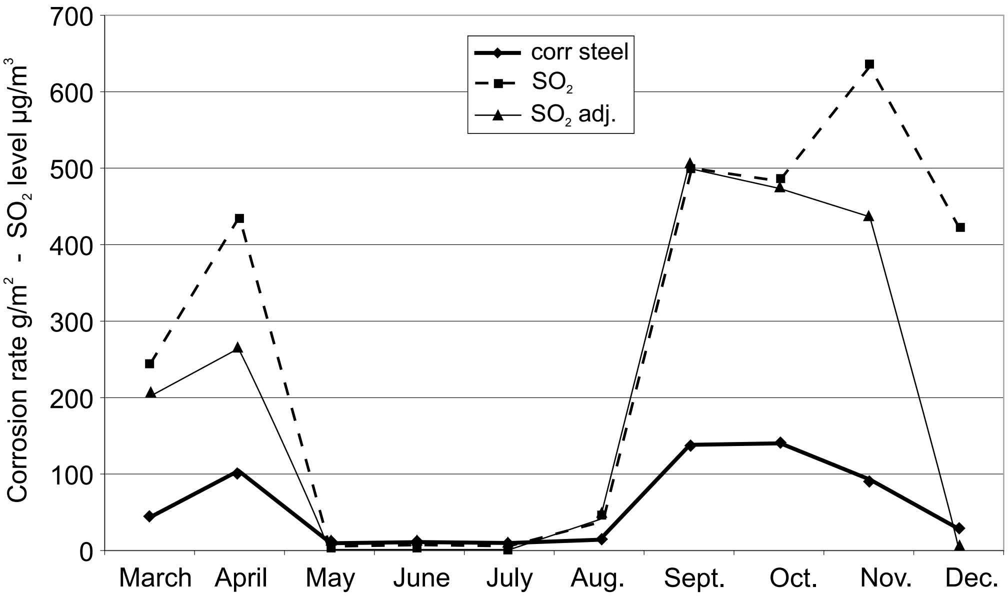


Figure 2 - Plot of monthly steel corrosion in g/m^2 together with the monthly SO_2 values and the "effective" SO_2 values using -4°C as the limit for corrosion

Regression analysis of the corrosion against "effective" SO_2 concentrations using temperature limits 0°C, -2°C, -4°C and -6°C was carried out to test this hypothesis. The results of this analysis are shown in Table 2

Table 2 - Equations from the linear regression for monthly corrosion results in Sulitjelma with and without freezing point adjustment of the SO_2 effect

Adjusted SO_2 values	Equations for linear regression	R-squared values
SO_2 without freezing point adjustment	$ML = 0.19*SO_2+9.1$	0.74
SO_2 with freezing point adjustment 0°C	$ML = 0.27* SO_2+20.8$	0.84
SO_2 with freezing point adjustment -2°C	$ML = 0.27* SO_2+13.2$	0.94
SO_2 with freezing point adjustment -4°C	$ML = 0.24* SO_2+13.1$	0.92
SO_2 with freezing point adjustment -6°C	$ML = 0.23* SO_2+14.3$	0.89

ML = mass loss in g/m^2

The improvement in the coefficient of determination R^2 indicates that a reduced effect of SO_2 occurs at lower temperature and that the freezing limit is around -2°C to -4°C.

Norwegian – Russian border

The test area used along the Norwegian – Russian border was much larger that the Sulitjelma area. The climatic conditions are changing inside this area and in the northern part the influence of sea salt is observed. By plotting the yearly corrosion for the year 1990-91 against SO_2 it is easy to see the additional chloride effect on the corrosion for the Norwegian site Viksjöfjell. The existence of the chloride was measured by monthly collected samples of a specially designed aerosol trap. The results showed that the amount of chloride was 4 times higher on that site compared to the average of the sites sheltered from the sea. The one-year corrosion rates for all test sites for the first phase of the study is given in Figure 3.

The results from the monthly exposed steel samples were evaluated in a similar manner as the corrosion data from Sulitjelma. However this time the temperature effect was evaluated by selecting different limits for the time of wetness factor (TOW). To include the chloride impact, the results from the Norwegian site Viksjöfjell were used for the evaluation. The results of these linear regressions are given in Table 3.

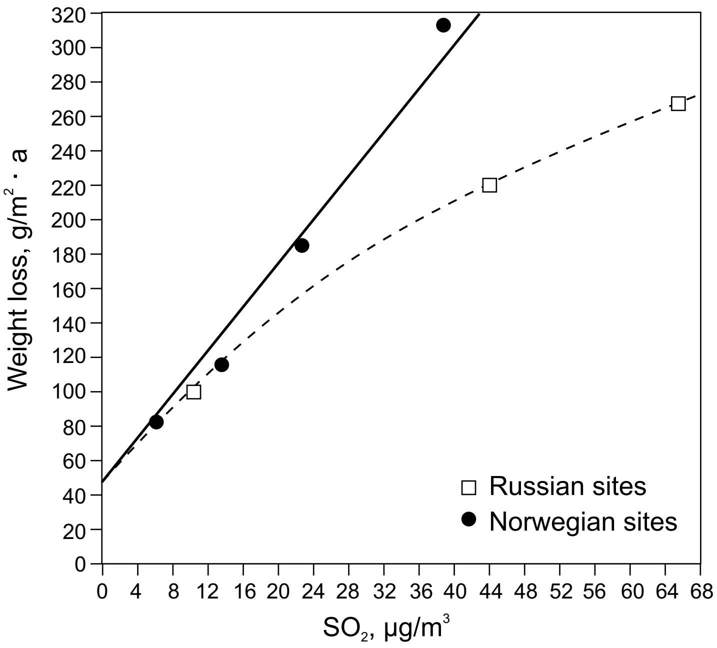


Figure 3 - Annual loss of carbon steel versus annual average sulphur dioxide concentration along the Norwegian – Russian border

Table 3 - The equation from the linear regression with different limits for the time of wetness

Temperature limits for TOW	Equation for the linear regression	R-squared values
T>-2°C	ML= $(-0.26+0.0088^* SO_2+0.0001^*Cl)^*TOW$	0.79
T>-4°C	ML= $(-0.16+0.0077^* SO_2+0.00004^*Cl)^*TOW$	0.96
T>-6°C	ML= $(-0.07+0.0067^* SO_2+0.00001^*Cl)^*TOW$	0.81

ML = mass loss in g/m^2

The evaluation of the monthly corrosion values in the two studies both indicates freezing point retention due to the pollutants in the area. However since the equations from the Norwegian - Russian border have a negative first factor the equations will not be valid below a threshold value.

In the second phase of the field test the same approach were used with different limits for the TOW values, when the evaluation of the one-year corrosion results should be performed. The test sites were divided into two groups Group A contained all the Norwegian sites and the Russian site closest to the border S1 and also covered sites influenced by the sea salt and following the steepest line in Figure 3. Group B included all Russian sites and the Norwegian sites with very low influence by chloride and followed the lower line in Figure 3. The results for both steel and zinc were evaluated using different combinations of pollution and climatic parameters. The selection of combinations was based upon the knowledge obtained after the four years evaluation of the international exposure programme ECE/ICP Materials [6]. The results are shown in Table 4 and Table 5

Table 4 - Equations from linear regression analysis of yearly steel corrosion, based on three different equation, three temperature limits and the data set in group A and B

	TOW: RH>80%	A_1	A_2	A_3	R^2
$ML = A_1 + A_2TOW[SO_2] + A_3TOW$					
A	T > 0°C	-27.0	40.0	230	0.994
	T > -2°C	-15.2	31.0	167	0.994
	T > -4°C	-6.0	24.7	134	0.993
B	T > 0°C	9.8	16.3	11.6	0.985
	T > -2°C	-1.9	13.5	292	0.988
	T > -4°C	-27.3	11.6	337	0.991
$ML = A_1 + A_2TOW[SO_2]$					
A	T > 0°C	16.4	41.7		0.990
	T > -2°C	22.5	32.5		0.989
	T > -4°C	27.8	26.5		0.989
B	T > 0°C	70.0	16.8		0.976
	T > -2°C	69.7	14.1		0.976
	T > -4°C	69.1	12.2		0.974
$ML = (A_1 + A_2[SO_2])TOW$					
A	T > 0°C	97	40.1		0.989
	T > -2°C	91	32.0		0.989
	T > -4°C	105	25.4		0.989
B	T > 0°C	326	16.7		0.986
	T > -2°C	268	14.0		0.989
	T > -4°C	235	12.0		0.988

ML = mass loss in g/m^2
TOW = fraction of the year with temperature equal to the temperatures in the table and relative humidity higher than 80%

Table 5 - Equations from linear regression analysis of yearly zinc corrosion, based on three different equations, three temperature limits and the data set in Group A and B

	TOW:	A_1	A_2	A_3	R^2
$ML = A_1 + A_2TOW[SO_2] + A_3TOW$					
A	T > 0°C	12.0	3.0	-54.0	0.977
	T > -2°C	12.5	2.5	-47.0	0.977
	T > -4°C	12.7	2.0	40.3	0.981
B	T > 0°C	8.1	1.3	-17.7	0.981
	T > -2°C	7.7	1.1	13.8	0.981
	T > -4°C	7.5	0.9	11.0	0.979
$ML = A_1 + A_2TOW[SO_2]$					
A	T > 0°C	1.6	2.6		0.891
	T > -2°C	2.0	2.0		0.878
	T > -4°C	2.4	1.6		0.879
B	T > 0°C	4.4	1.2		0.975
	T > -2°C	4.4	1.0		0.976
	T > -4°C	4.4	0.9		0.976
$ML = (A_1 + A_2[SO_2])\ TOW$					
A	T > 0°C	1.2	3.0		0.915
	T > -2°C	2.1	2.4		0.900
	T > -4°C	3.6	1.9		0.886
B	T > 0°C	24.0	1.2		0.962
	T > -2°C	20.0	1.0		0.964
	T > -4°C	17.4	0.8		0.963

ML = mass loss in g/m^2
TOW = fraction of the year with temperature equal to the temperatures in the table and relative humidity higher than 80%

By splitting the test sites into two groups an extremely good fit of equations including the two parameters SO_2 and TOW was obtained. The group B should give equations suitable for areas with SO_2 as the dominating pollutant while the equations for group A could be useful for areas with chloride impact in the same magnitude as in the data base. For both groups we had not sufficient data for observing the same temperature effect as for the monthly values the R-square values was almost identical for all the temperatures tested. The R-square values for zinc group A indicate that chloride should probably have been taken into account, but chloride was only measured on the Norwegian test sites in the project.

JOINT EVALUATION OF THE TWO STUDIES

Based on the last results from the ECE/ICP materials programme [7], it was decided to make an evaluation of the monthly steel corrosion results using a similar technique. Two differences from the previous evaluation were obvious.

- First: The parameter TOW was replaced with the parameters temperature (T) and relative humidity (RH).

- Second: A non-linear regression analysis between some of the parameters was tested, since it came out as the best approach in the ECE/ICP materials programme.

Time of wetness is still believed to be an important parameter for the corrosion process. However the TOW parameters used in the literature are a substitute for the real wetness, and are generated from meteorological observations of T and RH. It is therefore a good correlation between the three factors [5]. On a worldwide base the parameter TOW is costly and complicated to obtain, while T and RH on a monthly and yearly base are easily available from most meteorological stations in the world. The use of T as a factor has also been shown to have another advantage. Based on the results from the ECE/ICP material programme database it is shown that the surface wetness more quickly dries out at higher average temperature than 10°C. In the database in this study the limits for the temperature effect on the lower end were sought.

One limiting factor for this new evaluation was to regenerate the complete data set. The corrosion data exist, but the measured data for the environmental parameters to some degree only exist as treated data. The final result was that 111 data sets for monthly values for the parameters SO_2, T and RH were obtained. For the analysis the Marquardt programme was adapted. The best equations for monthly corrosion with $R^2 = 82.9\%$ turned out to be:

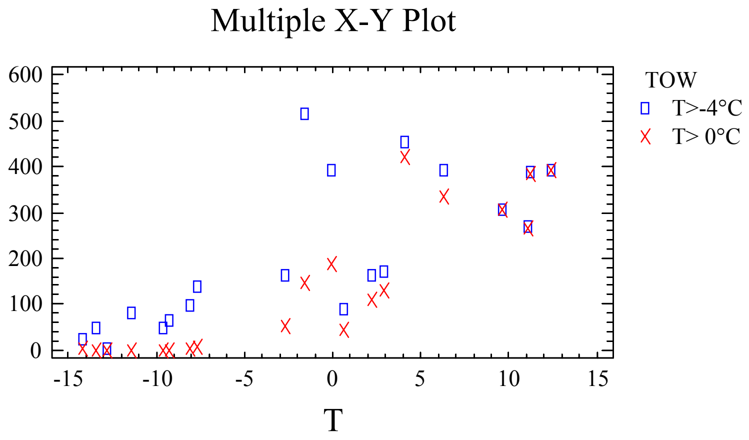
$$ML = 0.084[SO_2]^{0.53}\exp\{0.053RH+0.1(T-1)\} \quad \text{when } T \leq 1°C \qquad (3)$$

$$ML = 0.084[SO_2]^{0.53}\exp\{0.053RH\} \quad \text{when } 1< T \leq 5°C \qquad (4)$$

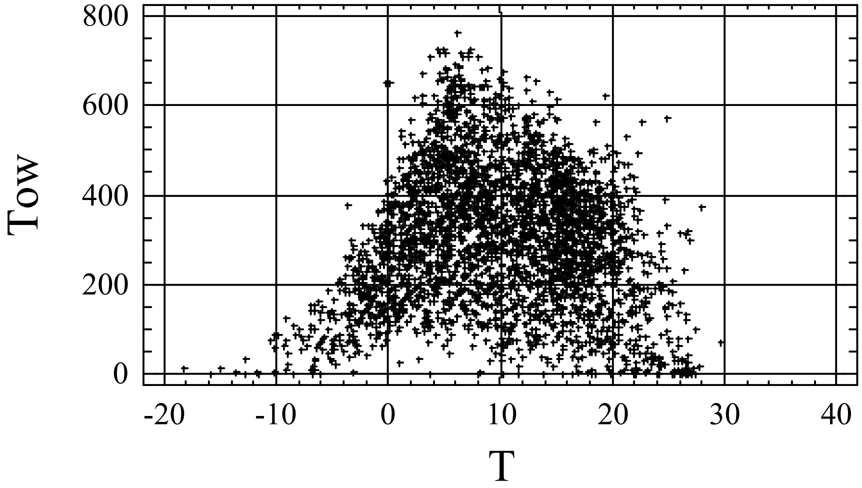
$$ML = 0.084[SO_2]^{0.53}\exp\{0.053RH-0.036(T-5)\} \quad \text{when } T> 5° \qquad (5)$$

ML = mass loss in g/m^2

Two temperature limits are observed based on this non-linear regression analysis. There is no temperature dependence from +1 to +5°C. By comparing the upper limit +5°C with the traditional time of wetness calculation, it can be observed that +5°C is the temperature where TOW has its highest value. Higher temperature is therefore a sign for reduced TOW values and not for reduced influence of the temperature as such. The limit observed in these studies also occurred in the ECE/ICP materials programme as illustrated in Figure 4.



a) Data from the Sulitjelma and the Norwegian/Russian study



b) Data from the ECE/ICP material programme

Figure 4 – Plot of the Time of Wetness (TOW) versus Temperature T for the monthly values

The lower limit of +1°C indicates that the high TOW value may occur down to a monthly mean value of +1°C. In the same way as +5°C gives the highest TOW value with T>0°C and RH>80%, +1°C will give the highest TOW value for the limits T>-4°C and RH>80%. The new statistical treatment using both the Sulitjelma and the Norwegian –Russian border results verifies that a reduced corrosion rate is obtained due to freezing point depreciation at low temperature and that the limit seems to be close to T=-4°C.

The freezing point retention observed should be valid for areas where the domination pollutant is SO_2. In areas dominated by other ions like Chloride another limit will be expected. Other materials than steel will also give other limits. The present database is too small and not the best for detecting other limits. There are some indications about the Chloride influence on Zinc but not sufficient for making any conclusion.

MODELLING OF THE CORROSIVITY ALONG THE NORWEGIAN – RUSSIAN BORDER

There has been large interest for mapping the pollution distribution in areas with high pollution levels during the last decades. However the main interest for this exercise is because of its impact on the environment. The corrosivity of the atmosphere is an important factor for risk assessment linked to abatement strategies in an area. As a part of the bilateral investigation along the Norwegian – Russian border modelling of SO_2 concentration in a grid of 110x100km has been carried out. The CONDEP model[4] used calculates long-term sector average concentrations for twelve 30° -sectors in specified receptor points or in a given grid. Inside the modelling area concentrations have been calculated for grid squares of 5x5km. The model uses a long-term frequency- matrix for wind direction and stability classes and is suited for industry emission sources up to 50 point sources. Along the border 11 high sources and 31 low sources mainly on the Russian side have been used.

For modelling the steel corrosion in the area, a set of equations from Table 4 and Table 5 have been used. The selected equation has the form $ML = A_1 + A_2TOW[SO_2]$ with a temperature limit of -4°C. The equation from group A was used for the southern part of the area and the one for group B in the northern part where the sea salt influence is more distinct. Figure 5 and Figure 6 show the results for steel and zinc respectively. The SO_2 concentrations in the grid are taken from modelling of the period summer 1998 and winter 1998/99 [8].

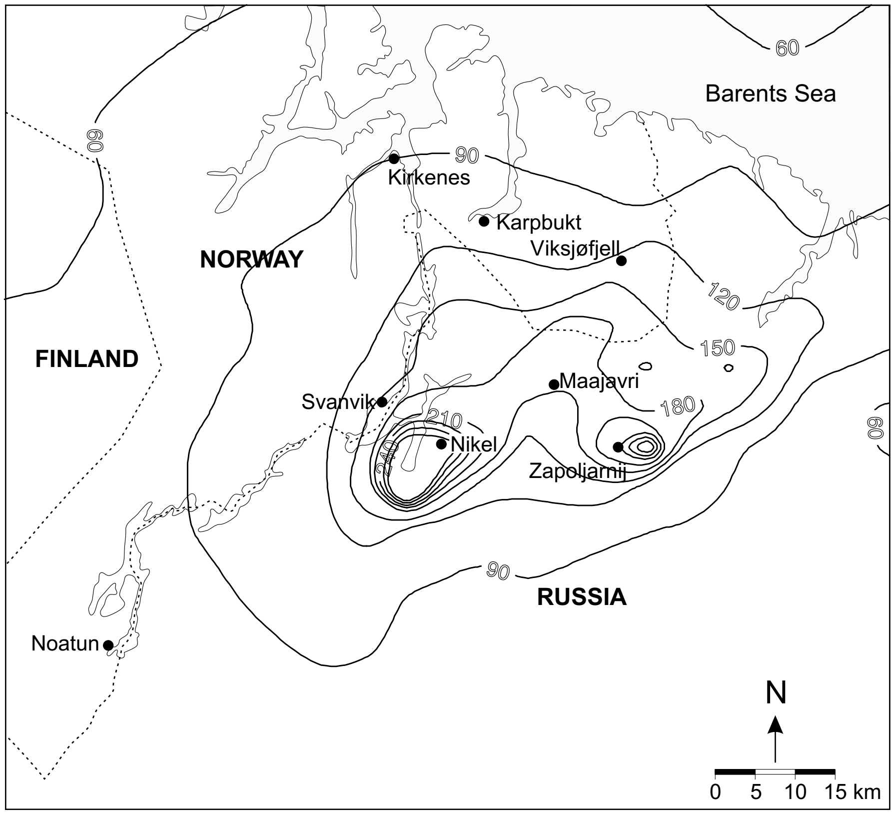


Figure 5 - Map of the first year of corrosion for steel inside a modelling area of 110x100km along the Norwegian – Russian border (corrosion in g/m²•year).

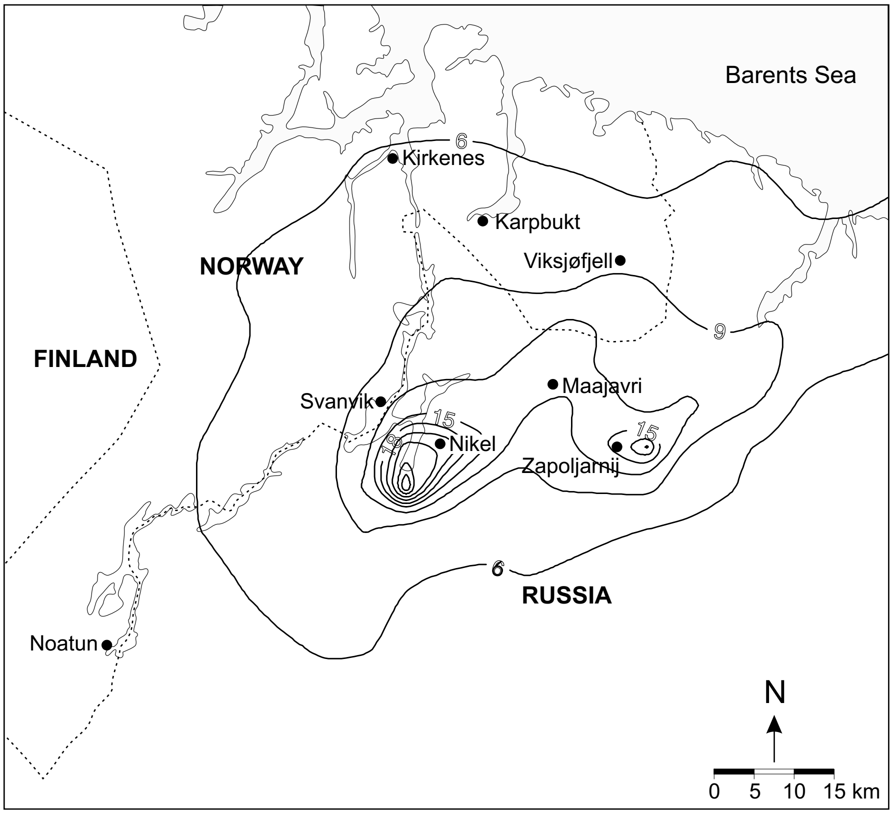


Figure 6 - Map of the first year of corrosion for zinc inside a modelling area of 110x100 km along the Norwegian – Russian border (corrosion in g/m^2•year).

Both materials have the same pattern with the highest corrosion rates on the Russian side of the border close to the two nickel production factories in Nikel and Zapoljarnij. The highest emission and the highest corrosion rates are observed in the Nikel area. The highest yearly grid square value is for steel 457g/m^2 and for zinc 33g/m^2. The equation used for the modelling includes only SO2 and TOW as determining factors. The estimates corrosion rates will therefore be correct in parts of the area without any large corrosion contribution from sea salt. In the neighborhood of the Barents Sea and in the ocean the corrosion rate calculated will underestimate the real corrosion.

CONCLUSIONS

In previous analysis of the corrosion behaviour of steel in cold climate polluted with SO_2 two different approaches have been used. In Sulitjelma a term “effective SO_2” $(C_{eff)}$ was introduced, where the fraction of a day with temperature above a selected limit was used to define the active SO_2 concentration, $C_{eff} = C_d * (t/24)$. In the study along the Norwegian – Russian border the expected reduced corrosion at low temperature was investigated by using lower temperature in the “Time of wetness” definition. For monthly corrosion values for steel the conclusion was almost the same in the two studies. The equations obtained had their best fit at a temperature limit between –2 to –4°C.

The yearly corrosion data for all materials tested had a good correlation either with SO_2 alone like in Sulitjelma or with SO_2 and TOW along the Norwegian –Russian border. The temperature effect could not be illustrated for the yearly values in the same way as for the monthly values since the data from the meteorological sites had a good correlated for yearly values. All the equations obtained can be used for modelling the corrosivity in the area. The type chosen for the modelling done has been ML = $A_1 + A_2$TOW[SO_2] with TOW at temperature limit -4°C.

The joint analysis of the monthly data using the approach from the ECE/ICP material programme with monthly mean values for temperature and relative humidity instead of TOW gave other limits for the temperature effect than the earlier results. The best fit was obtained by this set of equations

$$ML = 0.084[SO_2]^{0.53}\exp\{0.053RH+0.1(T-1)\} \qquad \text{when } T \le 1°C \qquad (6)$$

$$ML = 0.084[SO_2]^{0.53}\exp\{0.053RH\} \qquad \text{when } 1< T \le 5°C \qquad (7)$$

$$ML = 0.084[SO_2]^{0.53}\exp\{0.053RH-0.036(T-5)\} \qquad \text{when } T> 5° \qquad (8)$$

The limit $T \le 1°C$ is comparable to a freezing point depreciation of T=-4°C and since this limit is reached in two different studies and from evaluations made with three different techniques it would appear to be well justified. The upper limit T> 5° is linked to high TOW values and may be expected to change if a new data set from another area is used

Today equations exist that describe the corrosion of metals as a function of environmental parameters. The first year corrosion equations obtained for steel and zinc for the Norwegian – Russian border is useful for estimation of the corrosivity of the area if the SO_2 concentrations and the TOW values are known. Based on dispersion models, modeling of SO_2 distribution inside an area is possible to day. For the Norwegian-Russian border an industry module CONDEP was used for modeling SO_2. For other areas like a city or even for the European level other models are available.

REFERENCES

1. Henriksen J. F. and Fossestøl B. (1989) Corrosion in Sulitjelma, a copper mining town in Norway In: 11th Scandinavian Congress, Stavanger 1989. Proceedings. Stavanger, Høgskolesenteret i Rogaland, 1989 (Paper F48)

2. Henriksen J. F., Mikhailov A. A. and Mihailovski Y. N. (1995) Atmospheric corrosion tests on metals along the Russian-Norwegian border. Protection of Metals, 31, No1, p5-15 1995

3. Henriksen J. F. and Mikhailov A. A. (1997) Test for atmospheric corrosion of metals along the Russian-Norwegian border.2. Protection of Metals, 33, No4, p327-332 1997

4. Bøhler T. (1987) Users guide for the Gaussian type dispersion models CONCX and CONDEP. Lillestrøm (NILU TR 8/87)

5. Stöckle B., Krätschmer A., Mach M. and Snethlage R. (1998) UN/ECE ICP on effect on materials, including historic and cultural monuments. Corrosion attack on copper and cast bronze. Evaluation after eight years of exposure. Report No 23, Bavarian State Conservation Office, Munich, Germany 1998

6. Kucera V., Tidblad J. Henriksen J., Bartonova A and Mikhailov A. A. (1995) UN/ECE ICP on effect on materials, including historic and cultural monuments. Statistical analysis of 4

year materials exposure and acceptable deterioration and pollution levels. Report No 18, Swedish Corrosion Institute, Stockholm, Sweden 1995

7. Tidblad J., Kucera V and Mikhailov A. A. (1998) UN/ECE ICP on effect on materials, including historic and cultural monuments. Statistical analysis of 8 year materials exposure and acceptable deterioration and pollution levels. Report No 30, Swedish Corrosion Institute, Stockholm, Sweden 1998

8. Hagen L. O., Sievertsen B., Arnesen K. and Innset B. (2000) Air Quality Monitoring in the Border Areas of Norway and Russia- Progress Report April 1998- March 1999. Kjeller (NILU OR 2/2000) (in Norwegian)