



## Materials corrosion and air pollution. Long-term studies at the Lahemaa monitoring station, Estonia

Ott Roots

Estonian Environmental Research Institute, Estonian Environmental Research Centre, Marja 4D, 10617 Tallinn, Estonia;  
[ott.roots@klab.ee](mailto:ott.roots@klab.ee)

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**Abstract.** The Estonian Lahemaa monitoring station has participated in the International Co-operative Programme (ICP) on Effects on Materials, including Historic and Cultural Monuments (ICP Materials) since 1987. ICP Materials is an ongoing research programme in the framework of which air pollution and the effect of climate on the corrosion of various natural and synthetic materials, including on historical and cultural monuments, is studied. So far these studies have revealed that even though air pollution has continuously declined in Estonia, no significant reduction in corrosion on the displayed sample plates at the Lahemaa test site could be noticed. Just the opposite – in 2001–2002 the corrosion loss of zinc was greater compared with 1997–1998. It may have been caused by the fact that the reduction in air pollution has significantly affected the acidity of the precipitation and the decreased pH of the precipitation has in turn affected the corrosion of materials exposed at the Lahemaa monitoring station.

**Key words:** environmental science, air pollution, corrosion, materials, Lahemaa station, Estonia.

### INTRODUCTION

In Europe air pollution causes serious damage to materials and buildings, including historic and cultural monuments. In 1985, the International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments (ICP Materials), was started, based on the United Nations Economic Commission for Europe Convention on Long-Range Transboundary Air Pollution (CLRTAP). The programme is carried out in cycles. Until now four cycles have been completed. In the period 2002–2005 research was also conducted within the European Union's fifth framework programme – MULTI-ASSESS programme (Model for multi-pollutant impact and assessment of threshold levels for cultural heritage) (Final Report, 2005).

The objectives of the international materials corrosion observation are:

1. To provide information to the governments of European states on the concentrations of pollutants in the air and precipitation, as well as to assess the extent and effects of their long-distance transfer on the corrosion of materials.

2. To obtain source data for the preparation of a model on the long-distance transfer of air pollutants and for determining and charting hazardous corrosion areas.
3. To determine which materials could be used in the restoration of historical and cultural monuments.
4. To assess the monetary extent of corrosion damage caused by air pollution.

The main aim of ICP Materials is to perform a quantitative evaluation of the effects of multi-pollutants such as sulphur and nitrogen compounds, ozone, and particulates as well as climate parameters on the atmospheric corrosion of important materials, including materials used in objects of cultural heritage.

### MATERIAL AND METHODS

In the framework of the ICP Materials research programme, the tests conducted on various materials have been periodically changed in accordance with the objectives set in the research subprogramme. Programme cycles differ significantly, extending from one year (last cycle) to eight years (first cycle). The first cycle took

place in 1987–1995, the second in 1997–2000, the third in 2002–2003, and the fourth in 2005–2006. Hereafter cycles are planned to be repeated every three years. The studies are performed on the basis of the ‘Technical manual for the trend exposure programme 2005–2006’ developed by the Swedish Corrosion Institute (currently the Corrosion & Metals Research Institute – KIMAB) (Report No. 51, 2006). Material samples are kept on the territory of the monitoring station on holding stands constructed specifically for this purpose (Fig. 1). Standard specimens of carbon steel, zinc, copper, bronze, limestone, paint coated steel, and glass representative of medieval stained glass windows were exposed in unsheltered and for some materials in sheltered position on racks (Final Report, 2005).

### Parameters measured

At each observation station, the following parameters are measured: ambient air temperature, relative humidity, and intensity of solar radiation; concentrations of gaseous pollutants  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{O}_3$ ; amount, conductivity, and concentration of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  in precipitation. All results of the measurements of the above-mentioned parameters (Report No. 52, 2007) are sent by the national contact persons to the Norwegian Institute for Air Research (NILU), which is the co-ordinator for ambient air observation data. Measurements of ozone and particulate matter were added to the programme beginning in 1997, and nitric acid measurement from 2002.

### Materials investigated

Over the course of a year all sample plates (Table 1) must be sent to the corresponding research centre for analysis. The obtained results are presented later by the corresponding research institutions as reports.

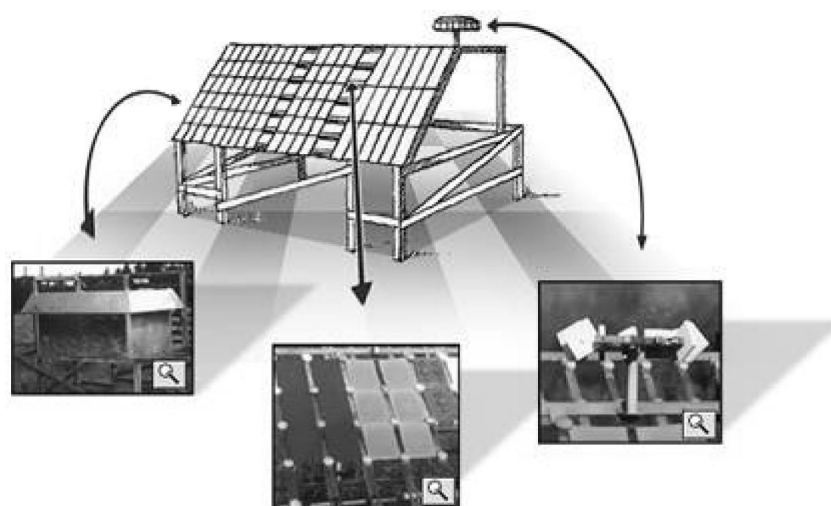
### States and observation stations participating in the programme

In the first cycle of the joint programme, which lasted for 8 years (1987–1995), 39 observation stations and 12 European states and one station in the USA and one in Canada participated. The fourth cycle, which lasted for two years, involved 24 (23 in Europe) observation stations from 15 states (Table 2). Together with the Lahemaa station, 21 stations have participated in the programme since its beginning in 1987.

**Table 1.** Materials for which corrosion was investigated at research centres within the framework of the fourth corrosion programme in 2005–2006 (Report No. 51, 2006)

Material investigated	Research centre	Description of material
Metal	Czech Republic	Pure non-alloy steel ( $\text{C} < 0.2\%$ , $\text{P} < 0.07\%$ , $\text{S} < 0.05\%$ , $\text{Cu} < 0.07\%$ )*
Metal	Switzerland	Zinc ( $>99.9\%$ )*
Rocks	England	Portland limestone (primarily $\text{CaCO}_3$ )*
Glass	France	Modern glass**

Exhibition: \* exposed to weather conditions; \*\* sheltered from weather conditions.



**Fig. 1.** Corrosion observation station. *Bottom left:* a box that protects the passive sample collectors from wind and precipitation; *bottom right:* a carousel on which rock samples are attached; *bottom centre:* test sample material plates that are exposed to the weather (<http://www.corr-institute.se/ICP-Materials/html/testsites2.html>).

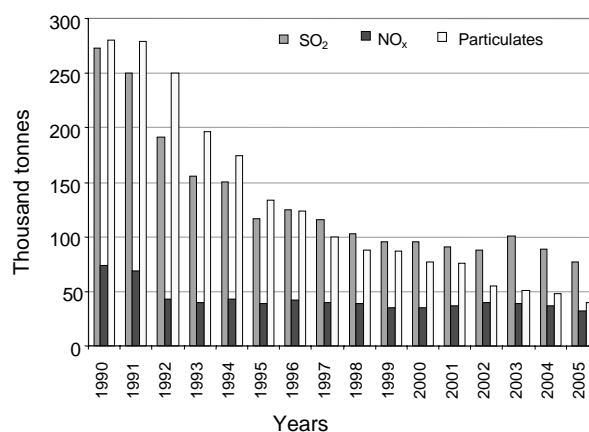
**Table 2.** Observation station numbers and locations, by state, that participated in the 2005–2006 corrosion programme

Station No.	Location of observation station	State
1	Prague	Czech Republic
3	Kopisty	Czech Republic
10	Bototrop	Germany
13	Rome	Italy
14	Casaccia	Italy
15	Milan	Italy
16	Venice	Italy
21	Oslo	Norway
23	Birkenes	Norway
24	Stockholm	Sweden
26	Aspvreten	Sweden
27	Lincoln	England
31	Madrid	Spain
33	Toledo	Spain
35	Lahemaa	Estonia
37	Dorset	Canada
40	Paris	France
41	Berlin	Germany
44	Svanvik	Norway
45	Chaumont	Switzerland
50	Katowice	Poland
51	Athens	Greece
52	Riga	Latvia
53	Vienna	Austria

## RESULTS AND DISCUSSION

### State of air pollution in Estonia

Over the period 1980–2000 the emission of sulphur dioxide decreased in Estonia by nearly 60% and that of NO<sub>x</sub> by 40% (Liblik and Karu, 2005). In comparison with 2005, emissions from stationary sources in Estonia also decreased in 2006 for particulates (by 5962 tonnes), nitrogen oxides (by 1002 tonnes), and sulphur dioxide (5770 tonnes) (Fig. 2). In comparison with the years 1980–1990 the emission of pollutants has significantly decreased, especially that of solid particles and sulphur dioxide.

**Fig. 2.** Emission of sulphur dioxide, nitrogen oxides, and particulates in Estonia in 1990–2005. (Source: Ministry of the Environment, Environmental Information Centre.)

### Measurements performed in the Lahemaa international corrosion monitoring station

The Lahemaa monitoring station in Estonia has participated in the observation work since 1987, when the first ICP Materials programme was started (Roots, 1992). The year of the restoration of the Republic of Estonia – 1991 – fell within the period of the first cycle of corrosion observations of 1987–1995 and the organization of the state observation programme (Roots and Saare, 1996). Ambient air observation data from the Lahemaa station are missing for the years 1991–1993, but data for the years 1987–1990 are available from the first cycle of the corrosion programme (Table 3) for the period September 1987 to August 1990. In 1994, together with the starting up of the national environmental observation programme, modernization of the equipment of the Estonian ambient air monitoring station began. Already the same year a modern ambient air observation station meeting international requirements started operation at Lahemaa (Roots and Saare, 1996; Saare et al., 2001). Comparison of the concentrations of pollutants in precipitation at the Lahemaa observation station in 1994–1997 and 1998–2001 reveals a significant reduction in sulphates, chlorides, magnesium ions, and inclusive cations (Table 4).

**Table 3.** Average monthly pollutant concentrations (mg/L) in precipitation and sulphur and nitrogen dioxide concentrations in the air ( $\mu\text{g}/\text{m}^3$ ) of the Lahemaa observation station during the period 1987–1990 (Report No. 21, 1997)

Research period*	Precipitation, mm	pH	SO <sub>4</sub> -S	Cl	NO <sub>3</sub> -N	NH <sub>4</sub> -N	Ca	Na	Mg	K	SO <sub>2</sub> , $\mu\text{g}/\text{m}^3$	NO <sub>2</sub> , $\mu\text{g}/\text{m}^3$
1987/88	447.8	4.66	1.11	0.61	0.3	0.28	0.88	0.39	–	–	0.9	2.9
1988/89	588.5	4.5	0.87	0.61	0.3	0.23	0.29	0.56	–	–	0.3	3.8
1989/90	532.7	4.65	0.75	0.81	0.31	0.2	0.51	0.55	0.08	0.42	0.6	6.5

\* 1987/88 = September 1987–August 1988;

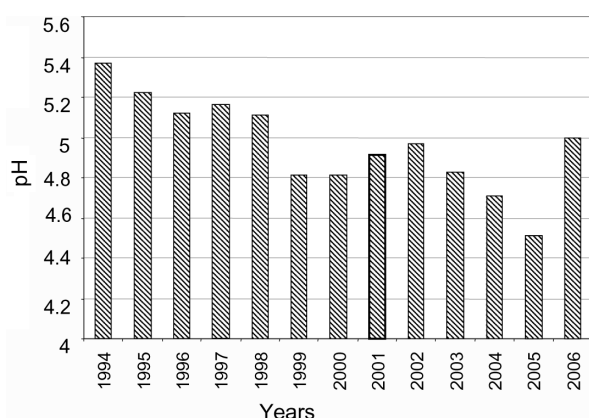
1988/89 = September 1988–August 1989;

1989/90 = September 1989–August 1990.

**Table 4.** Average monthly concentration of ions in precipitation (mg/L, except for H<sup>+</sup>, which is in µeq/L) and standard bias (in parentheses) for the periods 1994–1997 and 1998–2001 observed in the Lahemaa observation station (Treier et al., 2004)

Research period	H <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>
1994–1997	11.2 (11)	2.8 (1.2)	1.3 (1.5)	3.4 (1.0)	1.3 (1.4)	0.4 (0.3)	0.2 (0.21)	0.21 (0.08)
1998–2001	15.8 (14)	1.4 (0.5)	0.5 (0.3)	1.5 (0.8)	0.6 (0.2)	0.06 (0.02)	0.06 (0.02)	0.1 (0.04)

The dominating wind direction in Estonia is from south-west (Kimmel et al., 2002). As the sources of pollution are located primarily in North-East Estonia, the highest concentrations were measured at the Lahemaa observation station in the case of north-eastern and south-eastern winds. The reduction in air pollution has significantly affected the acidity of the precipitation at the Lahemaa observation station (Fig. 3). The pH of precipitation has considerably decreased, which has in turn affected the corrosion of materials set up at Lahemaa. The statistical parameters of concentrations of

**Fig. 3.** The pH of precipitation at the Lahemaa station in 1994–2005. (Source: Estonian Environmental Research Centre.)

hourly values at Estonian air monitoring stations in 1994–1999 are given in (Kimmel et al., 2002).

An overview of the currently operating measurement equipment at the Lahemaa observation station and detection limits, measurement frequency, and characteristic parameters can be found in Table 5.

The focus of the first phase of ICP Materials was on sulphur pollutants but with the decreasing levels of SO<sub>2</sub> it soon became evident that other pollutants need to be taken into account (Tidblad and Kucera, 1996; Kucera et al., 2005). Therefore after 1997 the following aim was formulated: to perform a quantitative evaluation of the effects of multi-pollutants such as sulphur and nitrogen compounds, O<sub>3</sub>, and particles as well as climate parameters on the atmospheric corrosion of important materials, including materials used in objects of cultural heritage. Ozone and particulate measurements were added to the programme beginning in 1997, and nitric acid measurement from 2002 (Final Report, 2005; Kucera et al., 2005).

Particular attention is paid to the recent spread of nitric acid and particulates in Europe and their effects on materials. Only a few laboratories in Europe possess measurement data on nitric acid concentrations in the ambient air over a longer period of time (Ferm et al., 2005; Final Report, 2005). At the Lahemaa station passive sample collectors for nitric acid as well as for particulates were installed for the first time in 2002–2003, and sample testing was started. Part of the passive

**Table 5.** Pollutants measured within the framework of the Estonian ambient air observation programme, Lahemaa station (Kesanurm, 2007)

Pollutant	Frequency of measurement	Type of equipment	Equipment detection limit	Year of manufacture of equipment
SO <sub>2</sub>	Continuous	Fluorescence analyser Horiba APSA 360 CE	0.5–500 ppb	2000
NO, NO <sub>2</sub> , NO <sub>x</sub>	Continuous	Chemiluminescent analyser Horiba APNA 360 CE	0.5–100 ppb	2000
O <sub>3</sub>	Continuous	UV-absorption analyser Horiba APOA 360 CE	0.5–1000 ppb	2000
CO	Continuous	IR analyser Horiba APMA 360 CE	0.05–100 ppb	2000
PM <sub>10</sub>	Random	DHI-80 gravimetric analysis	0.5–10 000 µg/m <sup>3</sup>	2005
Fine dust particles below 10 µm	(once per week)			
Heavy metals (As, Cd, Ni, Pb)	Random	DHI-80 gravimetric analysis and ICP AAS	0.1 ng/m <sup>3</sup>	2005
PM <sub>10</sub> in fractions	(once per week)			

samplers were switched every two months, some were left up for the entire year. In 2005–2006 passive samplers were ordered for nitric acid and particulates from the Swedish Environmental Institute (IVL). For the first time, results obtained from passive samplers were published in 2002–2003.

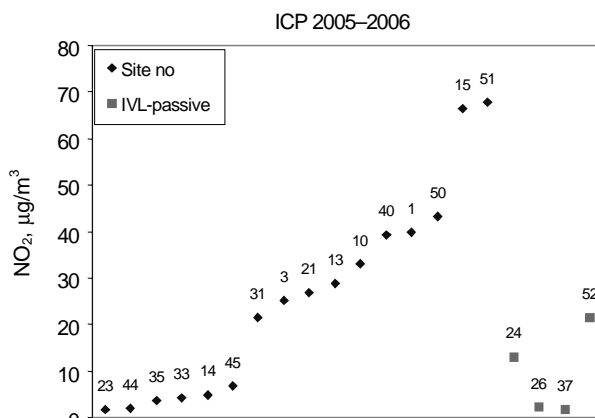
Table 6 presents the nitric acid concentrations in the air at Lahemaa during the period 2005–2006. The mean level of nitric acid was  $0.43 \mu\text{g}/\text{m}^3$  in 2005–2006, whereas in 2002–2003 the level was  $0.37 \mu\text{g}/\text{m}^3$ . How-

**Table 6.** Nitric acid concentrations at the Lahemaa observation station (protected from precipitation)

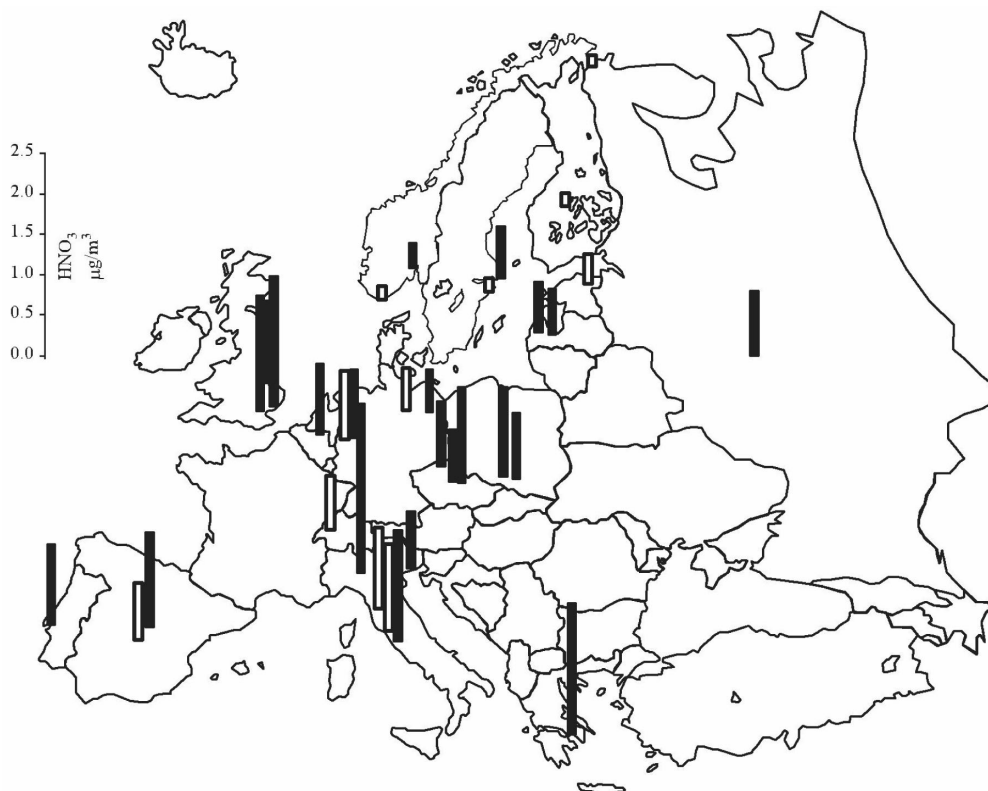
Beginning of exposure	End of exposure	Number of days	Temperature, °C	HNO <sub>3</sub> , $\mu\text{g}/\text{m}^3$ , STP*
9.11.2005 11:30	3.01.2006 14:15	55	0.0	0.38
3.01.2006 14:30	21.03.2006 14:18	77	-4.0	0.80
21.03.2006 14:20	17.05.2006 13:55	57	2.0	0.52
17.05.2006 14:00	12.07.2006 10:50	56	14.0	0.36
12.07.2006 11:00	7.11.2006 11:00	118	12.6	0.19

\* STP = Standard Temperature and Pressure (standard conditions), 20°C, 1013 hPa.

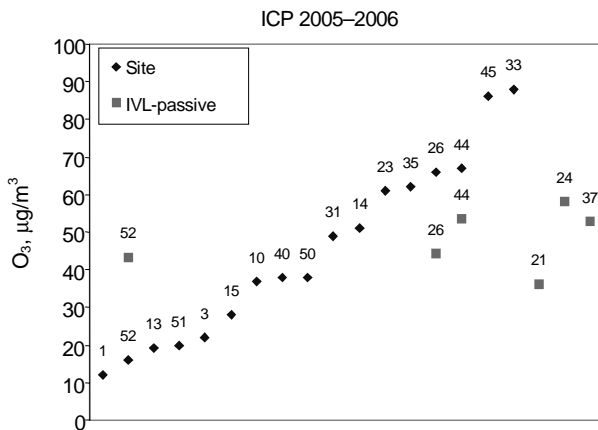
ever, in comparison with the level of NO<sub>2</sub> (Fig. 4), the concentration of HNO<sub>3</sub> was still low at all European test stations. While sulphur and nitric acid (Fig. 5) concentrations in the ambient air at the Lahemaa station are relatively low, the ozone level (Fig. 6) is one of the highest (Report No. 52, 2007).



**Fig. 4.** Comparison of the measured NO<sub>2</sub> concentration at the Lahemaa station (No. 35) with results from other observation stations (Report No. 52, 2007). Squares show concentrations measured with passive samplers.



**Fig. 5.** Comparison of the concentration of nitric acid measured at the Lahemaa station with other monitoring stations (Ferm et al., 2005; Final Report, 2005). Black columns and white columns denote respectively the cities and rural areas (background stations) where observation stations are located.



**Fig. 6.** Measured  $O_3$  concentration at the Lahemaa station (No. 35) in comparison with other observation station results (Report No. 52, 2007). Squares show concentrations measured with passive samplers.

In addition to the measurement of  $HNO_3$  in the ambient air, the deposition of particulates during the month was measured in both exposed to weather conditions and sheltered positions (Table 7). The samplers exposed to weather conditions were switched every two months for new ones, while the samplers sheltered from weather conditions for the collection of particulate deposition were out for a period of one year. The deposition of particulates on passive samplers at Lahemaa had increased in 2005–2006 by nearly one half in comparison with 2002–2003. The mass of particulates deposited on all observation station passive samplers varied in the range from  $<1 \mu\text{g}/\text{cm}^2$  per month (detection limit) to  $417 \mu\text{g}/\text{cm}^2$  per month. Two months

**Table 7.** Deposition of particulates on passive samplers at the Lahemaa observation station (\* exposed to and sheltered from weather conditions) in 2002–2003 (Final Report, 2005) and 2005–2006

Beginning of exposure	End of exposure	Number of days	Particulate mass, $\mu\text{g}/\text{cm}^2$ per month
09.11.2005	03.01.2006	55	10
03.01.2006	21.03.2006	77	4
21.03.2006	17.05.2006	57	21
17.05.2006	12.07.2006	56	18
12.07.2006	07.11.2006	118	7
*09.11.2005	07.11.2006	363	11
12.11.2002	14.01.2003	63	4
14.01.2003	12.03.2003	57	5
11.03.2003	21.05.2003	71	6
21.05.2003	30.07.2003	70	12
30.07.2003	11.09.2003	43	6
11.09.2003	20.11.2003	70	2
*12.11.2002	20.11.2003	374	6

of measurement gave the average mass of deposited particulates as  $32 \mu\text{g}/\text{cm}^2$  per month. The result of year-long measurement was on average  $4\text{--}138 \mu\text{g}/\text{cm}^2$  per month (Ferm et al., 2006).

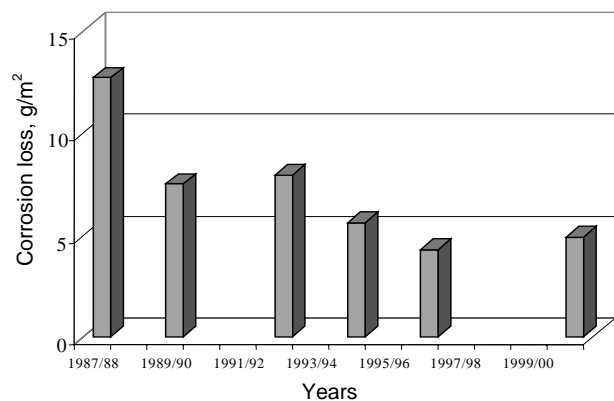
Monthly values for the Lahemaa test site for the last exposure period sent by national contact persons to the Norwegian Institute for Air Research (NILU) are presented in Table 8. Also random measurements of organic compounds in the ambient air have been made using passive samplers at the Lahemaa station (Roots and Sweetman, 2007).

### Effect of air pollution on materials

During the course of the first cycle of the corrosion programme pollutants were determined at Lahemaa only in the first three years. Corrosion measurement results from Lahemaa are given in Table 9.

From Table 9 it can be seen that even though air pollution continuously declined in Estonia (Fig. 2), no significant reduction in corrosion on the displayed sample plates at the Lahemaa station was observed. On the contrary, in 2001–2002 the corrosion loss of zinc increased in Estonia (Table 9) as well as elsewhere in Europe (Fig. 7) compared with the years 1997–1998.

Measurement results showed that at the Lahemaa station, non-alloy steel corrosion in 2005–2006 exceeded the so-called non-alloy steel corrosion background level (Report No. 53, 2007). It is not clear what the situation is in other regions of Estonia. In the future, the effects of climate conditions and pollutants on various local building materials, such as dolomite and limestone, should be observed in Estonia. There is an especially pressing need for research on Saaremaa dolomite. Within the framework of the MULTI-ASSESS project it became clear that of the stone samples studied that had been displayed for exposure in Athens, Krakow, London, Riga, Prague, and Rome the most sensitive to crumbling were



**Fig. 7.** Average corrosion loss of zinc (20 European observation stations; Kreislova et al., 2005).

**Table 8.** Monthly values of gaseous pollutants and concentrations in precipitation at the Lahemaa test site for the exposure period

Site No.	Sampling period		Mandatory														Optional					
			Climate			Gaseous				In precipitation							In precipitation					Particulates
			Temp, °C	RH, %	SO <sub>2</sub> , µg/m <sup>3</sup>	NO <sub>2</sub> , µg/m <sup>3</sup>	O <sub>3</sub> , µg/m <sup>3</sup>	Rain, mm	pH	SO <sub>4</sub> <sup>2-</sup> , mgS/L	NO <sub>3</sub> <sup>-</sup> , mgN/L	Cl <sup>-</sup> , mgCl/L	Cond., µS/cm	NH <sub>4</sub> <sup>+</sup> , mgN/L	Na <sup>+</sup> , mgNa/L	Ca <sub>2</sub> <sup>+</sup> , mgCa/L	Mg <sub>2</sub> <sup>+</sup> , mgMg/L	K <sup>+</sup> , mgK/L	Conc. PM <sub>10</sub> , µg/m <sup>3</sup>			
35	2005	11	2.4	91	1.7	3.9	42	39.3	4.43	0.32	0.25	0.61	13.3	0.27	0.40	0.23	0.07	0.05	9.83			
35	2005	12	-3.9	93	4.1	5.2	43	29.4	3.11	0.20	0.14	0.52	131.3	0.09	0.20	0.19	0.02	0.04	9.44			
35	2006	1	-5.9	89	8.3	4.8	51	9.8	4.33	0.58	0.43	0.95	35.7	0.28	0.32	0.42	-0.10	0.19	10.33			
35	2006	2	-9.9	90	10.4	6.1	65	24.8	4.86	0.22	0.27	0.22	7.5	-0.08	-0.10	0.30	-0.10	-0.10	13.40			
35	2006	3	-6.4	85	11.0	5.6	81	37.9	4.73	0.20	0.29	0.24	8.0	0.09	0.14	0.24	-0.10	-0.10	10.55			
35	2006	4	4.6	71	2.6	3.4	91	15.9	4.98	0.48	0.61	0.52	10.0	0.49	0.26	0.44	-0.10	0.12	14.98			
35	2006	5	10.4	63	4.0	3.0	83	33.1	5.22	0.39	0.33	0.45	10.2	0.50	0.21	0.68	-0.10	0.52	18.13			
35	2006	6	15.6	68	0.9	2.4	69	23.6	5.40	0.26	0.25	0.26	10.7	0.12	0.11	0.87	0.11	0.20	18.10			
35	2006	7	17.9	61	1.4	1.9	68	0.5		0.34	0.01	0.29		0.05	0.64	2.48	0.19	0.40	14.80			
35	2006	8	17.0	75	1.9	2.7	59	65.4	5.61	0.36	0.08	0.08	9.3	0.11	0.07	0.53	0.04	0.03	20.53			
35	2006	9	13.1	85	0.7	2.3	52	13.5	5.53	0.27	0.02	0.33	3.8	0.01	0.19	0.42	0.04	0.03	11.86			
35	2006	10	7.5	93	0.8	2.5	37	109.6	4.94	0.25	0.20	0.45	9.9	0.15	0.41	0.22	0.05	0.06	7.63			
35	2006	11	1.3	94	0.6	3.3	44	48.5	4.73	0.39	0.27	0.79	11.5	0.15	0.55	0.18	0.09	0.07	6.15			

**Table 9.** Corrosion losses after different times of exposure to open weather conditions at the Lahemaa observation station in 1987–2006

Exposure time	Non-alloy <sup>a</sup> steel, g/m <sup>2</sup>	Zinc <sup>b</sup> , g/m <sup>2</sup>	Portland <sup>c</sup> limestone, µg/y
1 year			
1987–1988	185	–	9.90
1990–1991	–	9.4	–
1997–1998	106	7.27	5.40
2000–2001	95	7.66	–
2002–2003 <sup>d</sup>	96	10.54	8.91
2005–2006	88	7.36	10.65
2 years			
1987–1989	–	9.5	–
1997–1999	–	10.44	–
4 years			
1987–1991	–	17.1	–
1997–2001	–	21.74	–

<sup>a</sup> Report No. 53, 2007.<sup>b</sup> Report No. 54, 2007.<sup>c</sup> Report No. 55, 2007.<sup>d</sup> Exposure in the framework of the EU project MULTI-ASSESS (<http://www.corr-institute.se/MULTI-ASSESS/>).

Saaremaa dolomite and Baumberger sandstone (Kucera et al., 2004). Additional information on research conducted on Saaremaa dolomite and other building materials, such as Carrara marble, Portland limestone, Baumberger sandstone, and Gotland sandstone, can be found in the MULTI-ASSESS conference materials (Kucera et al., 2004; Final Report, 2005).

### Further development directions in corrosion observation and the corrosion programme

The results obtained so far indicate that the economic damage to Europe (including to Estonia) due to corrosion of materials caused by air pollution can be assessed and, if needed, opportunities can be found to improve the situation. The final results showed that in order to protect the area from corrosion, reference figures for particulates have to be developed in addition to SO<sub>2</sub> limits. The aim of ICP Materials was to perform a quantitative evaluation of the effects of multi-pollutants such as sulphur and nitrogen compounds, ozone, and particulates as well as climate parameters on the atmospheric corrosion of important materials, including materials used in objects of cultural heritage. The corresponding indicators are listed in Tables 10 and 11 (Final Report, 2005).

**Table 10.** Tolerable corrosion rates based on background corrosion rates,  $n = 2.5$  (Final Report, 2005 – <http://www.corr-institute.se/MULTI-ASSESS/>)

Material	Background corrosion rate, µm/y	Tolerable corrosion rate*, µm/y
Limestone	3.2	8
Sandstone	2.8	7
Copper	0.34	0.8
Bronze	0.25	0.6
Zinc	0.46	1.1
Carbon steel	8.5	20

\* Tolerable rate: the maximum level at which a tolerable response occurs. Tolerable response should be based on experiences from restoration/maintenance work for cultural heritage objects.

**Table 11.** Most important parameters and recommended reference figures for materials (Final Report, 2005 – <http://www.corr-institute.se/MULTI-ASSESS/>)

Effect	Material	SO <sub>2</sub>	HNO <sub>3</sub>	PM <sup>a</sup>	Tolerable effect	Target SO <sub>2</sub> level <sup>b</sup>	Target PM <sub>10</sub> level
Corrosion	Zinc	X	X		1.1 µm/y	10 µg/m <sup>3</sup>	
	Carbon steel	X		X	20 µm/y		
	Limestone	X	X	X	8 µm/y		
Soiling	Painted steel			X	35% loss of reflectance		15 µg/m <sup>3</sup>
	White plastic			X			
	Limestone			X	in 10–15 years		

<sup>a</sup> Solid particles. PM is not a crucial parameter for the corrosion of materials, but its main effect is connected with soiling.<sup>b</sup> Concentration that ensures 80% regional protection. Hereafter, when calculating the combined effects, the effects of nitrogen pollution should be included, especially the effect of HNO<sub>3</sub>.



A list of MULTI-ASSESS dose–response functions, including the temperature function, for unsheltered materials is presented in (Final Report, 2005). As an example, consider the developed dose–response function for Portland limestone (Final Report, 2005):

$$R = 3.1 + \{0.85 + 0.0059[\text{SO}_2]\text{RH}_{60} + 0.054\text{Rain}[\text{H}^+] + 0.078[\text{HNO}_3]\text{RH}_{60} + 0.0258\text{PM}_{10}\}t,$$

where R – surface recession, in  $\mu\text{m}$

RH – relative humidity

Rain – mm

t – time (years)

$\text{H}^+$  – of precipitation, mg/L

$\text{SO}_2$ ,  $\text{HNO}_3$  – gaseous pollutants,  $\mu\text{g}/\text{m}^3$ .

In the future, the corrosion project should be expanded to corrosion observation in Tallinn and other Estonian towns and villages in cooperation with the national ambient air observation programme. As the Estonian Environmental Research Centre has facilities for the measurement of air pollution on site (measurement bus), it is especially necessary to acquire an overview of which parameters should be measured in the research on the corrosion of various materials.

## CONCLUSIONS

From the above it can be seen that regardless of the continuous decline of air pollution in Estonia, no significant reduction in corrosion on the displayed sample plates at the Lahemaa station was recorded. Quite the opposite was observed: compared with the years 1997–1998 in 2001–2002 the corrosion loss of zinc increased in both Estonia and elsewhere in Europe. At the Lahemaa observation station the reduction in air pollution has significantly affected the acidity of precipitation. The decreased pH of precipitation has in turn affected the corrosion of materials set up at Lahemaa.

An overview of how the air pollution level and meteorological conditions affect the rate of corrosion in materials, and what should be done to reduce the corrosion of materials, is especially needed in the case of historical and cultural monuments. As an end result, the programme should provide an opportunity to assess the economic damage caused by corrosion and not only on historical and cultural monuments. There are 387 sites in Europe on the UNESCO World Heritage list, including the Old Town of Tallinn as one object. Corrosion research in Tallinn would be extremely important since the number of cars in the city has tremendously increased.

In conclusion, it can be said that besides being harmful to health, polluted air damages the environment and materials.

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## Materjalide korrosioon ja õhu saastumine. Pikaajalised uuringud Lahemaa seirejaamas

Ott Roots

Õhu saastumine mõjutab oluliselt materjalide, sealhulgas ajaloo- ja kultuurimälestiste korrosiooni. Lahemaa õhu-seirejaam on osalenud ÜRO/Euroopa Majanduskomisjoni rahvusvahelises korrosiooniuringute programmis (ICP Materials) alates selle algusest 1987. aastal. Programmi eesmärgiks on olnud Euroopa eri regioonide materjalide korrosiooniuringud, lähtudes kohalikust kliimast ja õhusaaste tasemest. Praegu osaleb programmis 15 riiki 24 seirejaamaga (23 Euroopas ja 1 Kanadas). Kuigi Euroopas ja Eestis on õhusaaste alates 1990. aastatest alanenud, pole Lahemaal eksponeeritud materjalide korrosioon oluliselt vähenenud. Näiteks suurenes uuritavatest materjalidest tsingi korrosioon aastail 2001–2002, võrreldes aastail 1997–1998 tehtud mõõtmistega. Üheks põhjuseks võib olla, et õhusaaste vähenemisel Eestis on Lahemaa sademed muutunud happelisemateks. Õhus on suurenenud ka lämmastik-happe sisaldus, mida esmakordselt analüüsiti Lahemaal aastail 2002–2003. Materjalide korrosiooniuringuid jätkatakse Lahemaa seirejaamas ka aastail 2008–2009.