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ENVIRONMENTAL SCIENCE

ICP Materials: long-term studies at the Lahemaa monitoring station, Estonia

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Abstract. The UNECE International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments (ICP Materials) is an ongoing research programme in the framework of which air pollution and the effect of climate on the corrosion and soiling of various natural and synthetic materials, among them on historic 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 observed. The present article is based on annual data on the corrosion of carbon steel, zinc, and limestone and the soiling of modern glass in the air at the Estonian Lahemaa observation station from the period 2008–2009 and the relevant environmental data (pollution and climate). For comparison the material corrosion data from the Lahemaa station for 1997–2006 are used. In 2002–2003 the corrosion loss of zinc and in 2005–2006 the loss of Portland limestone increased at Lahemaa. The data from the Lahemaa station for 2005–2006 and 2008–2009 indicate that the estimated corrosion rate exceeds the 2020 target for limestone, which is 8 μm per year.

Key words: air pollution, corrosion, soiling, carbon steel, limestone, modern glass, Lahemaa station.

1. INTRODUCTION

In Europe air pollution causes serious damage to materials and buildings, including historic and cultural monuments. The UNECE International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments (ICP Materials) was launched in 1985. In the first joint programme, which lasted for 8 years, 39 observation stations and 12 European states as well as one station in the USA and one in Canada participated. The cycles of the ICP Materials programme differ significantly, extending from one year (since the beginning of 2005) to eight years (first cycle 1987–1995) (Leygraf and Kucera, 1989; Tidblad, 2009).

A wide range of materials have been exposed over the years. An overview of the performed corrosion exposures for the period 1987–2009 for individual materials and groups of materials is given in (Tidblad et al., 2012) and for Lahemaa station in (Roots, 2008; Roots et al., 2011). The Estonian Lahemaa monitoring station has participated in the ICP Materials programme since 1987 (Leygraf and Kucera, 1989).

The main aim of the programme is to perform a quantitative evaluation of the effects of pollutants such as sulphur and nitrogen compounds, ozone, particulates, and other major pollutants, including the effects of low concentrations of these pollutants, as well as climate parameters on the atmospheric corrosion and soiling of important materials, among these materials used in objects of historic and cultural heritage, and to assess the trends of corrosion, soiling, and pollution. In this article the focus is on the measurements made at the Lahemaa station in 2008–2009.

2. METHODS

In 2005 a new trend exposure programme was started, and exposures of main indicator materials were planned to take place every third year together with collection of

data on environmental parameters. The studies are performed following the suggestions in the *Technical Manual for the Trend Exposure Programme 2008–2009* compiled by the Swedish Corrosion Institute (currently the Corrosion & Metals Research Institute, KIMAB) (Tidblad, 2009). The obtained results are presented later by the corresponding research institutions as reports (http://www.corr-institute.se/ICP-Materials/web/page.aspx?refid=11). National focal points (NFP) are responsible for carrying out the tasks as described in the manual (Tidblad, 2009) in connection with exposure and withdrawal of specimens. The NFPs are also responsible for the collection and reporting of environment data and sending the results of the measurements of the above-mentioned parameters to the Norwegian Institute for Air Research (NILU), which is the coordinator for ambient air observations (Grøntoft et al., 2007). A list of test sites over time for the ICP Materials project is given in Table 1.

2.1. States and observation stations participating in the ICP Materials programme

The corrosion observation stations can be divided into four groups:

1. The main observation stations and project coordinator, which have been located in Sweden since the start of the project. In 2005, Italy was added as a second coordinator.
2. The centre for the collection and processing of environmental air pollution data located in Norway.
3. Research centres that send sample materials to observation stations for corrosion testing and later perform analysis of the samples (Czech Republic, France, Italy, Norway, Switzerland, and United Kingdom).
4. States whose observation stations participated in corrosion research from the beginning of 1987 (*see* Mezinskis et al., 2004; Roots, 2008; Tzanis et al., 2009, 2011; Varotsos et al., 2009; Roots et al., 2011).

The Lahemaa background monitoring station lies 80 km east of Tallinn. Long-range transported pollutants are the major pollution source there. The first exposure started in 1987 when the station was included in the ICP Materials programme. Since then the racks have not been moved.

2.2. Parameters measured

At each ICP Materials observation station, the following parameters are measured: ambient air temperature, relative humidity, intensity of solar radiation; concentrations of gaseous pollutants SO_2, NO_x, and O_3; amount, conductivity, and concentration of SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} in precipitation. The mandatory programme for ICP Materials includes passive particle collection in an unsheltered position (bimonthly sampling) and a passive particle collector in a sheltered position. The unsheltered samplers are mounted under a metal disc approximately 3 m from the ground in order to protect them from precipitation and direct sunshine. Every two months the samplers are removed and replaced (Ferm et al., 2005). The sheltered samplers are mounted in a box for sheltered exposure and exposed for one year (Tidblad, 2009). Measurements of ozone were added to the ICP Materials programme at the beginning of 1997 and nitric acid measurements from 2002 (Ferm at al., 2005; Final Report, 2005). Due to the increasing importance of particulate matter (Ferm et al., 2006), modern glass was officially included as a trend material for soiling of materials in the 2005–2006 and 2008–2012 exposures (Lombardo and Ionescu, 2009).

At the Lahemaa air monitoring station the following parameters are measured: ambient air temperature, relative humidity, and broadband solar radiation; wind speed and direction; concentrations of gaseous pollutants SO_2, NO, NO_2, NO_x, CO, and O_3; concentrations of particles PM2.5 and PM10 and heavy metals (As, Cd, Ni, Pb) in PM10; amounts, pH, conductivity, and concentrations of SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} ions in precipitation.

An overview of the currently used measurement equipment at the Lahemaa observation station alongside with the characteristic parameters with their detection limits and measurement frequency is given in (Roots, 2008; Roots et al., 2009, 2011; Kabral et al., 2012). Also random measurements of persistent organic pollutants in the ambient air have been performed at the Lahemaa station using passive samplers (Roots and Sweetman, 2007; Roots et al., 2010).

2.3. Materials investigated

Material samples are kept in the territory of the Lahemaa monitoring station on holding stands constructed for this purpose (Fig. 1). Different countries provide the Lahemaa station with test materials for investigating corrosion and soiling as well as with passive samplers. The materials investigated at the Lahemaa station within the framework of the corrosion programme from 2008 to 2009 and the supplying countries are listed in Table 2. Over the course of that year all sample plates from the Lahemaa station were sent to the corresponding research centres for analysis. Table 3 gives an overview of the performed exposures for some materials in the Lahemaa station from 1987, when the first exposure started, to 2008.

Table 1. List of all ICP Materials test sites showing number, name, country site type, year with available data, and participation in the 2011–2012 trend exposure (Tidblad et al., 2011)

No.	Name	Country	Site type	Available data	2011–2012 exposure
1	Prague-Letnany	Czech Republic	Urban	1987–2009	X
2	Kasperske Hory	Czech Republic	Rural	1987–1995	
3	Kopisty	Czech Republic	Industrial	1987–2009	X
4	Espoo	Finland	Urban	1987–1995	
5	Ähtäri	Finland	Rural	1987–2003	
6	Helsinki-Vallila	Finland	Industrial	1987–1995	
7	Waldhof-Langenbrügge	Germany	Rural	1987–2003	
8	Aschaffenburg	Germany	Urban	1987–1995	
9	Langenfeld-Reusrath	Germany	Rural	1987–2003	
10	Bottrop	Germany	Industrial	1987–2009	X
11	Essen-Leithe	Germany	Rural	1987–1995	
12	Garmisch-Partenkirchen	Germany	Rural	1987–1995	
13	Rome	Italy	Urban	1987–2009	X
14	Casaccia	Italy	Rural	1987–2009	X
15	Milan	Italy	Urban	1987–2009	X
16	Venice	Italy	Urban	1987–2009	X
17	Vlaardingen	Netherlands	Industrial	1987–1995	
18	Eibergen	Netherlands	Rural	1987–1995	
19	Vredepeel	Netherlands	Rural	1987–1995	
20	Wijnandsrade	Netherlands	Rural	1987–1995	
21	Oslo	Norway	Urban	1987–2009	X
22	Borregard	Norway	Industrial	1987–1995	
23	Birkenes	Norway	Rural	1987–2009	X
24	Stockholm South	Sweden	Urban	1987–2009	X
25	Stockholm Centre	Sweden	Urban	1987–1995	
26	Aspvreten	Sweden	Rural	1987–2009	X
27	Lincoln Cathedral	United Kingdom	Urban	1987–2009	
28	Wells Cathedral	United Kingdom	Urban	1987–1995	
29	Clatteringshaws Loch	United Kingdom	Rural	1987–1988	
30	Stoke Orchard	United Kingdom	Industrial	1987–1993	
31	Madrid	Spain	Urban	1987–2009	X
32	Bilbao	Spain	Industrial	1987–1995	
33	Toledo	Spain	Rural	1987–2009	X
34	Moscow	Russian Federation	Urban	1987–2003	
35	Lahemaa	Estonia	Rural	1987–2009	X*
36	Lisbon	Portugal	Urban	1987–2003	
37	Dorset	Canada	Rural	1987–2006	
38	Research Triangle Park	USA	Rural	1987–1995	
39	Steubenville	USA	Industrial	1987–1995	
40	Paris	France	Urban	1997–2009	X
41	Berlin	Germany	Urban	1997–2009	X
43	Tel Aviv	Israel	Urban	1997–2001	
44	Svanvik	Norway	Rural	1997–2009	X
45	Chaumont	Switzerland	Rural	1997–2009	X
46	London	United Kingdom	Urban	1997–2003	
47	Los Angeles	USA	Urban	1997–2001	
49	Antwerpen	Belgium	Urban	1997–2003	
50	Katowice	Poland	Industrial	2000–2009	X
51	Athens	Greece	Urban	2005–2009	X
52	Riga	Latvia	Urban	2005–2009	X
53	Vienna	Austria	Urban	2008–2009	X
54	Sofia	Bulgaria	Urban	2008–2009	X
55	St Petersburg	Russian Federation	Urban	–	X

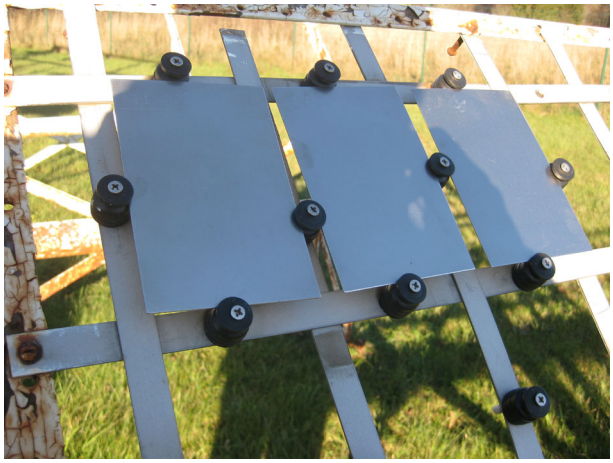
* Only modern glass exposure.

(a)

(b)

(c)

(d)



(e)

Fig. 1. Lahemaa corrosion observatin station (a), passive samplers for HNO_3 and particulate matter protected from wind and precipitation (b), a carousel on which rock samples are attached (c), materials plates exposed to the weather (d), and box for investigating the soiling of modern glass (e).

Table 2. Purpose of the investigation and materials used in the trend exposure at Lahemaa station in 2008–2009

Purpose	Material and number of samples	Label	Supplier country
Corrosion	Unalloyed carbon steel (C < 0.2%, P < 0.07%, S < 0.05%, Cu < 0.07%)* (3 samples)	A	Czech Republic
	Zinc (>99.9%)* (3 samples)	C	Czech Republic
	Zinc (>99.9%)* (3 samples)	D	Switzerland
	Portland limestone (mainly $CaCO_3$)* (3 samples)	M	United Kingdom
Soiling	Modern glass** (1 sample)	T	France
	Two passive samplers (4 samples for HNO_3 and 4 samples for particulate matter)***		Sweden

Exhibition: * exposed to weather conditions; ** sheltered from weather conditions; *** sheltered from wind and precipitation.

Table 3. One-year (trend) exposures of carbon steel, zinc (two not directly comparable samples), and limestone performed within ICP Materials, 1987–2008 (Tidblad et al., 2008)

Material	1987	1989	1992	1994	1996	1997	2000	2002	2005	2008
Carbon steel	X		X	X	X	X	X	X	X	X
Zinc[a]	X	X	X	X	X		X			X
Zinc[b]						X	X	X	X	X
Limestone	X					X		X	X	X

[a] Responsible centre SVUOM Ltd., Czech Republic.
[b] Responsible centre EMPA, Switzerland.

3. RESULTS AND DISCUSSION

In 1987 the focus was on the impact of SO_2 and climate. Later the programme was enlarged to include quantitative evaluation of the effect of NO_x, O_3, HNO_3, and particulate matter. These were introduced in combination with climate parameters to study their effect on the atmospheric corrosion and soiling of important materials (Final Report, 2005; Tidblad et al., 2012). The average trends are quite different for the gases (Fig. 2). The concentrations of O_3 increased at ICP Materials stations during the 1990s, but NO_2 and SO_2 concentrations decreased. The concentrations of SO_2 and O_3 were relatively constant after the year 2000 (Tidblad et al., 2008). At the Lahemaa station SO_2, NO_2, and O_3 concentrations in the ambient air were relatively low between 2000 and 2008 (the highest concentrations in the ambient air were measured there for 2005–2006) (Kabral et al., 2012). The year 2006 could be considered as a 'high-ozone' year (Roots et al., 2009, 2011; Kabral et al., 2012). Monthly values for the Lahemaa monitoring station sent by the Estonian national contact person (the author of this article) to the Norwegian Institute for Air Research (NILU) are presented in Table 4.

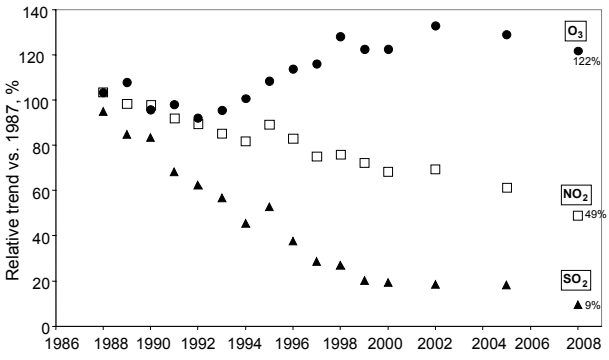


Fig. 2. Average SO_2, NO_2, and O_3 trends relative to the year 1987 at ICP Materials test sites (Tidblad et al., 2011).

Very few long-term measurements of atmospheric concentration of nitric acid have earlier been performed despite the fact that this compound causes corrosion and degradation of many materials. Its concentrations were the highest in Southern Europe, London, and Paris and very low in Northern Europe. The HNO_3 concentration was higher in urban areas than in rural areas (Ferm et al., 2005). The concentrations of HNO_3 in the Lahemaa station were also lower during the 2008–2009 campaign compared to 2002–2003 and were still low at all ICP Materials stations in comparison with the level of NO_2 content measured at those stations (Ferm et al., 2005; Tidblad et al., 2008). The highest concentrations of HNO_3 in the air at the Lahemaa station were analysed from February to April (Table 5). In addition to HNO_3 in the ambient air, the deposition of particles during a month was measured both in unsheltered from weather conditions and wind and precipitation and in sheltered positions (Tables 4 and 5). The mass of particulates deposited on all passive samplers of the observation station varied from <1 μg cm^{-2} per month (detection limit) to 417 μg cm^{-2} per month (Ferm et al., 2006).

Table 4. Monthly values of gaseous pollutants and concentrations in precipitation at the Lahemaa test site for the exposure period

Sampling period		Mandatory[a]																				Optional													
		Climate[b]				Gases[b]						Precipitation[c]										Precipitation[c]										Particles[d]			
		Temp		RH		SO_2		NO_2		O_3		Amount		H^+		SO_4^{2-}		NO_3^-		Cl^-		Conduct-ivity		NH_4^+		Na^+		Ca^{2+}		Mg^{2+}		K^+		Conc. PM10	
Year	Month	C degrees	Availability (%)	%	Availability (%)	µg m^{-3}	Availability (%)	µg m^{-3}	Availability (%)	µg m^{-3}	Availability (%)	mm	Availability (%)	pH	Availability (%)	mgS L^{-1}	Availability (%)	mgN L^{-1}	Availability (%)	mgCl L^{-1}	Availability (%)	µS cm^{-1}	Availability (%)	mgN L^{-1}	Availability (%)	mgNa L^{-1}	Availability (%)	mgCa L^{-1}	Availability (%)	mgMg L^{-1}	Availability (%)	mgK L^{-1}	Availability (%)	µg m^{-3}	Availability (%)
2008	10	10.6	86.0	88	86.0	0.49	86.0	1.6	86.0	44.6	85.9	79.8	61.3	4.82	38.7	0.28	61.29	0.23	61.29	0.34	61.29	8.8	38.7	0.12	61.3	0.25	61.3	0.45	61.3	0.06	61.3	0.02	61.3	4.9	100
2008	11	5.2	78.7	90	78.7	0.50	92.2	2.3	92.2	43.6	91.8	87.6	50.0	4.89	20.0	0.20	50.00	0.19	50.00	0.84	50.00	8.0	20.0	0.05	50.0	0.43	50.0	0.27	50.0	0.08	50.0	0.02	50.0	5.6	100
2008	12	2.4	100.0	92	100.0	0.71	100.0	3.2	100.0	36.9	100.0	42.0	41.9	4.80	32.3	0.34	41.90	0.32	41.90	0.39	41.90	15.6	32.3	0.14	41.9	0.27	41.9	0.36	41.9	0.04	41.9	0.03	41.9	6.4	100
2009	1	0.3	100.0	88	100.0	1.70	82.4	3.6	98.8	46.3	99.1	27.9	22.6	4.68	16.1	0.30	22.58	0.34	22.58	0.29	22.58	7.3	16.1	0.13	22.6	0.19	22.6	0.17	22.6	0.03	22.6	0.03	22.6	6.4	100
2009	2	−1.8	100.0	89	100.0	2.70	99.7	3.8	100.0	53.7	100.0	16.9	28.6	4.64	17.9	0.52	28.57	0.57	28.57	0.41	28.57	16.8	17.9	0.19	28.6	0.29	28.6	0.24	28.6	0.03	22.6	0.04	22.6	9.1	100
2009	3	1.7	99.1	82	99.1	1.90	97.6	2.4	98.9	72.7	99.1	29.8	25.8	5.20	19.4	0.45	25.81	0.30	25.81	0.20	25.81	8.9	19.4	0.26	25.8	0.14	25.8	0.82	25.8	0.04	25.8	0.03	25.8	7.3	100
2009	4	7.5	100.0	67	100.0	1.30	98.6	2.5	99.6	78.4	100.0	5.1	10.0	4.91	6.7	0.61	10.00	0.72	10.00	0.22	10.00	14.5	6.7	0.86	10.0	0.17	10.0	0.31	10.0	0.02	10.0	0.05	10.0	7.3	100
2009	5	13.0	99.9	67	99.9	1.00	99.2	2.0	99.9	73.1	99.9	11.4	22.6	5.96	22.6	0.69	22.58	0.71	22.58	0.48	22.58	23.0	22.6	0.88	22.6	0.36	22.6	2.78	22.6	0.27	22.6	0.53	22.6	8.8	100
2009	6	16.1	86.9	74	86.9	0.73	84.6	1.7	86.3	58.1	87.1	105.1	46.7	4.35	33.3	0.16	46.67	0.08	46.67	0.27	46.67	5.0	36.7	0.10	46.7	0.80	46.7	0.59	46.7	0.06	46.7	0.09	46.7	6.6	100
2009	7	18.5	100.0	77	100.0	0.64	96.9	1.1	97.2	50.7	99.7	119.3	54.8	4.35	48.4	0.22	54.80	0.09	54.84	0.11	54.84	<10	48.4	0.07	54.8	0.13	54.8	0.57	54.8	0.04	54.8	0.11	54.8	7.3	100
2009	8	17.5	100.0	80	100.0	0.57	99.9	1.1	95.4	43.2	100.0	60.9	38.7	4.67	29.0	0.15	38.71	0.08	38.71	0.31	38.71	<10	29.0	0.07	38.7	0.26	38.7	0.41	38.7	0.04	38.7	0.06	38.7	6.4	100
2009	9	14.9	99.4	83	99.4	0.50	99.3	1.3	99.6	46.8	99.7	54.1	46.7	4.78	46.7	0.21	46.67	0.06	46.67	0.51	46.67	<10	46.7	0.07	46.7	0.33	46.7	0.45	46.7	0.08	46.7	0.06	46.7	6.9	100
2009	10	7.2	94.4	88	94.4	0.85	89.7	1.5	94.2	37.7	94.4	144.7	71.0	4.53	67.7	0.26	71.00	0.13	71.00	0.58	71.00	<10	67.7	0.11	71.0	0.36	71.0	0.11	71.0	0.04	71.0	0.05	71.0	6.5	100

[a] Results for HNO_3 and particles are presented in Table 5.
[b] Measured hourly.
[c] Measured daily.
[d] Measured weekly.

Table 5. Nitric acid concentrations at the Lahemaa observation station (protected from precipitation) and deposition of particles on passive samplers (exposed sheltered from weather conditions) in 2002–2009 (Ferm et al., 2005; Roots 2008; Roots et al., 2010; Tidblad et al., 2008, 2011)

Beginning of exposure	End of exposure	Number of days	Temperature, °C	HNO_3, μg m^{-3}, STP*	Particulate mass, μg cm^{-2} per month
2008–2009					
09.10.2008 12:00	16.12.2008 10:00	68	−4.0	0.25	7
16.12.2008 10:10	11.02.2009 12:30	57	−4.0	0.27	27
11.02.2009 12:40	07.04.2009 9:30	55	2.0	0.45	5
07.04.2009 9:40	04.06.2009 11:30	58	6.0	0.32	14
04.06.2009 11:40	28.07.2009 13:10	54	21.0	0.14	12
28.07.2009 13:20	06.10.2009 11:00	70	9.0	0.11	7
2005–2006					
09.11.2005 11:30	03.01.2006 14:15	55	0.0	0.38	10
03.01.2006 14:30	21.03.2006 14:18	77	−4.0	0.80	4
21.03.2006 14:20	17.05.2006 13:55	57	2.0	0.52	21
17.05.2006 14:00	12.07.2006 10:50	56	14.0	0.36	18
12.07.2006 11:00	07.11.2006 11:00	118	12.6	0.19	7
2002–2003					
12.11.2002	14.01.2003	63		0.31	4
14.01.2003	12.03.2003	57		0.88	5
12.03.2003	21.05.2003	71		0.48	6
21.05.2003	30.07.2003	70		0.21	12
30.07.2003	11.09.2003	43		0.14	6
11.09.2003	20.11.2003	70		0.20	2

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

Table 6. Corrosion losses and soiling of modern glass (haze in %) after 1 year of exposure to open weather conditions at the Lahemaa observation station in 1997–2008 (Final Report, 2005; Kreislova et al., 2007; Reiss and Faller, 2007; Yates, 2007; Roots, 2008; Tidblad et al., 2008, 2011, 2013; Lombardo and Ionescu, 2009; Lombardo et al., 2010; Roots et al., 2011)

Exposure year	Unalloyed carbon steel* (SVUOM Ltd), g m^{-2}	Zinc (SVUOM Ltd), g m^{-2}	Zinc (EMPA), g m^{-2}	Portland limestone (BRE), μm $year^{-1}$	Modern glass (LISA), haze in %***
1997	106		7.3	5.5	
2000	95	5.1	7.7		
2002**	96		10.2	8.9	
2005	88		7.3	10.6	1.6
2008	58	2.8	7.2	8.3	1.6

* Tolerable level for carbon steel corrosion loss is 157 g m^{-2} (Kreislova et al., 2007).
** Exposure in the framework of the EU project MULTI-ASSESS (http://www.corr-institute.se/MULTI-ASSESS).
*** Haze is defined as the ratio between the diffuse transmitted light and the direct transmitted light (Lombardo and Ionescu, 2009; Lombardo et al., 2010).

Even though air pollution has continuously declined in the ambient air at the Lahemaa station, no significant reduction in corrosion on the displayed plates was observed there (Table 6). On the contrary, in 2002–2003 the corrosion loss of zinc and in 2005–2006 the loss of Portland limestone increased at Lahemaa. The corrosion attack to Portland limestone was much higher in 2005–2006 than in 2002–2003 (Roots et al., 2011). The environmental pollution and corrosion data for the Lahemaa station samples from 2005–2006 and 2008–2009 indicate that the estimated corrosion rate exceeds the 2020 target for limestone, which is 8 μm per year (Doytchinov et al., 2012).

The procedure for deriving dose–response functions (DRF) and trends in corrosion and soiling from the measured material deterioration at different exposure

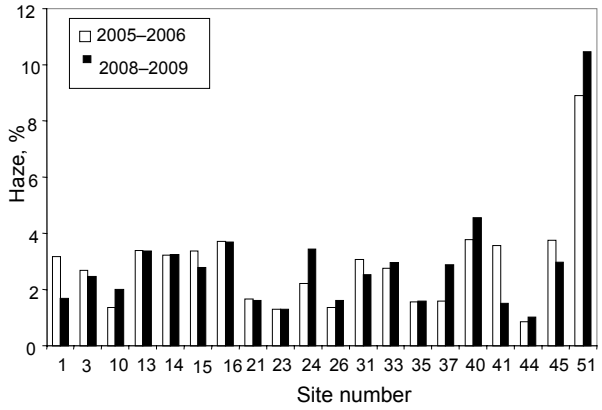


Fig. 3. Soiling of modern glass at ICP Materials test sites (Tidblad et al., 2012).

sites is described in (Reiss, 2004; Final Report, 2005; Tidblad et al., 2011, 2012, 2013). For example, the DRF for Zn in the sulphur dioxide-dominating situation that takes into account combined effects of climate change and air pollution on metal corrosion developed by ICP Materials (Economic Commission for Europe, 2008) is

$$\mathrm{ML} = 1.4\,[\mathrm{SO_2}]^{0.22} e^{0.018\,Rh} e^{f(T)} t^{0.85} + 0.029\,Rain[\mathrm{H^+}]t,$$

where ML is the mass loss in g m^{-2}, $[\mathrm{SO_2}]$ is the sulphur dioxide concentration in μg m^{-3}, e is Euler's number, Rh is the relative humidity in per cent, $f(T)$ is a function of temperature in °C equal to $0.062(T-10)$ when T is lower than 10 °C and $-0.021(T-10)$ when T is higher than 10 °C, t is the time in years, $Rain$ is the amount of annual precipitation in mm, and $[\mathrm{H^+}]$ is the hydrogen ion concentration in precipitation in mg L^{-1}.

Soiling of the modern glass has been assessed through an optical measurement (Fig. 3). Haze is currently used in the glass industry to measure the transparency of a product. Haze over 1% indicates the visual nuisance felt by human eyes looking through a 'dirty' glass plate (Lombardo and Ionescu, 2009; Lombardo et al., 2010; Verney-Carron et al., 2012). Although DRFs of the soiling of modern glass are currently being evaluated, no final functions are available yet because results after four years of exposure (2008–2012) will have to be included (Lombardo et al., 2010; Tidblad et al., 2011).

4. CONCLUSIONS

The present article is based on annual data on the environment (pollution and climate), corrosion of carbon steel, zinc, and limestone and soiling of modern glass for the period 2008–2009 acquired from the results of the Estonian State Ambient Air Monitoring Programme with individual ICP Materials reports. For comparison material corrosion data from the Lahemaa station for the period 1997–2006 were used.

The concentrations of SO_2, NO_2, and O_3 have decreased in the ambient air at Lahemaa as indicated by the latest trend exposure in 2008–2009. Nitric acid concentrations were measured at the Lahemaa observation station in 2002–2003, 2005–2006, and 2008–2009. This comparison revealed a 42% decrease from 2005–2006 to 2008–2009. However, only three exposure periods are not sufficient for far-reaching conclusions. It can be seen that even though air pollution continuously declined at the Lahemaa station, no significant reduction in corrosion on the displayed plates was observed there. On the contrary, in 2002–2003 the corrosion loss of zinc (Reiss and Faller, 2007) and in 2005–2006 the loss of Portland limestone increased at Lahemaa. Based on the environmental pollution and corrosion data from the Lahemaa station samples for 2005–2006 and 2008–2009 the corrosion estimated rate exceeds the 2020 target for limestone, which is 8 μm per year (Doytchinov et al., 2012). A tolerable corrosion rate should serve primarily for the protection of the so-called sensitive zones with objects of high cultural value such as medieval towns or objects included in the UNESCO World Heritage List (e.g. the Old City of the Estonian capital Tallinn).

Some of the crumbling deterioration could be due to a change in environmental conditions (highest concentrations of SO_2, NO_2, and O_3 in the ambient air at the Lahemaa station analysed for 2005–2006), but another explanation might be that the stone material was of different quality (Yates, 2007; Roots et al., 2011). The corrosion of carbon steel and zinc has decreased exponentially at the Lahemaa site since the beginning of exposures (Kreislova et al., 2007; Tidblad et al., 2011, 2012, 2013). Modern glass as an indicator for soiling has only been exposed at the Lahemaa station for two periods: 2005–2006 and 2008–2009. On average, there was no difference in the results of the soiling of modern glass at the Lahemaa station between the two periods. According to the material corrosion measurements, the Lahemaa station belongs to the group of the so-called background stations.

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REFERENCES

Doytchinov, S., Screpanti, A., and Leggeri, G. 2012. *UNECE International Co-operative Programme on Effects on Materials, Including Historic and Cultural Monuments*. Report No. 70. Pilot study on inventory and condition of stock of materials at risk at United Nations Educational, Scientific and Cultural Organization (UNESCO) cultural heritage sites. Part II: Determination of stock of materials at risk for individual monuments. Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), September 2012, 1–32.

Economic Commission for Europe. 2008. *Report by the Programme Centre of the International Cooperative Programme on Effects of Air Pollution on Materials, including Historic and Cultural Monuments*. ECE/EB.AIR/WG.1/2008/8, 9 July 2008, 1–12 http://www.unece.org/fileadmin/DAM/env/documents/2008/EB/WGE/ece.eb.air.wg.1.2008.8.e.pdf (accessed 07.11.2014).

Ferm, M., De Santis, F., and Varotsos, C. 2005. Nitric acid measurements in connection with corrosion studies. *Atmospheric Environment*, **39**, 6664–6672.

Ferm, M., Watt, J., O'Hanlon, S., De Santis, F., and Varotsos, C. 2006. Deposition measurement of particulate matter in connection with corrosion studies. *Analytical and Bioanalytical Chemistry*, **384**, 1320–1330.

Final Report, 2005. 2005. EU 5FP RTD Project. Model for multi-pollutant impact and assessment of threshold levels for cultural heritage. http://www.corrinstitute.se/MULTI-ASSESS (accessed 07.11.2014).

Grøntoft, T., Arnesen, K, and Ferm, M. 2007. *UNECE International Co-operative Programme on Effects on Materials, Including Historic and Cultural Monuments*. Report No. 52. Environmental data report. October 2005 to December 2006. Norwegian Institute for Air Research (NILU), Kjeller, Norway.

Kabral, N., Pauklin, T., and Teinemaa, E. 2012. Õhusaaste kauglevi seire ja uuringud. Eesti Keskkonnauuringute Keskus, Leping 4-1/39. Tallinn.

Kreislova, K., Knotkova, D., Kvapil, J., and Divisova, H. 2007. *UNECE International Co-operative Programme on Effects on Materials, Including Historic and Cultural Monuments*. Report No. 53. Results from the multi-pollutant programme – Corrosion attack on carbon steel after 1 year of exposure (2005–2006). Institute for Protection of Materials (SVUOM Ltd), Prague.

Leygraf, C. and Kucera, V. 1989. *UNECE International Co-operative Programme on Effects on Materials, Including Historic and Cultural Monuments*. Report No. 2. Description of test sites. Swedish Corrosion Institute, Stockholm, Sweden.

Lombardo, T. and Ionescu, A. 2009. *UNECE International Co-operative Programme on Effects on Materials, Including Historic and Cultural Monuments*. Report No. 59. Soiling of exposed materials and dose-response functions for modern glass. Laboratoire Interuniversitaire des Systèmes Atmosphérique (LISA), Paris.

Lombardo, T., Ionescu, A., Chabas, A., Lefèvre, R.-A., Ausset, P., and Candau, Y. 2010. Dose–response function for the soiling of silica–soda–lime glass due to dry deposition. *Sci. Total Environ.*, **408**, 976–984.

Mezinskis, G., Sidrabe, I., Yates, T., and Lusis, R. 2004. Stone and concrete in the multi-assess project. In *Cultural Heritage in the City of Tomorrow. Developing Policies to Manage the Continuing Risk From Air Pollution* (Kucera, V., Tidblad, J., and Hamilton, R., eds), pp. 135–143. Bulletin 110E. Stockholm Swedish Corrosion Institute.

Reiss, D. 2004. Use of the MULTI-ASSESS results for assessing threshold levels of pollutants. In *Cultural Heritage in the City of Tomorrow. Developing Policies to Manage the Continuing Risk From Air Pollution* (Kucera, V., Tidblad, J., and Hamilton, R., eds), pp. 229–234. Bulletin 110E. Stockholm Swedish Corrosion Institute.

Reiss, D. and Faller, M. 2007. *UNECE International Co-operative Programme on Effects on Materials, Including Historic and Cultural Monuments*. Report No. 54. Results from the UN ECE zinc trend exposure: Corrosion attack on zinc after 1 year of exposure (November 2005–November 2006). Swiss Federal Laboratories for Materials Testing and Research (EMPA), Dübendorf, Switzerland.

Roots, O. 2008. Materials corrosion and air pollution. Long-term studies at the Lahemaa monitoring station, Estonia. *Proc. Estonian Acad. Sci.*, **57**, 107–116.

Roots, O. and Sweetman, A. 2007. Passive air sampling of persistent organic pollutants in two Estonian monitoring stations. *Oil Shale*, **24**, 483–494.

Roots, O., Roose, A., Eerme, K., and Teinemaa, E. 2009. Developing long-term monitoring of ozone in Estonia: the mandate of the Montreal Protocol. *Int. J. Remote Sens.*, **30**, 4181–4194.

Roots, O., Roose, A., Kull, A., Holoubek, I., Cupr, P., and Klanova, J. 2010. Distribution pattern of PCBs, HCB and PeCB using passive air and soil sampling in Estonia. *Environ. Sci. Pollut. R.*, **17**, 740–749.

Roots, O., Roose, A., and Eerme, K. 2011. Remote sensing of climate change, long-term monitoring of air pollution and stone material corrosion in Estonia. *Int. J. Remote Sens.*, **32**(24), 9691–9705.

Tidblad, J. 2009. *UNECE International Co-operative Programme on Effects on Materials, Including Historic and Cultural Monuments*. Report No. 58. Technical manual for the trend exposure programme 2008–2009. Swerea KIMAB AB, Stockholm, Sweden.

Tidblad, J., Grøntoft, T., Kreislova, K., Faller, M., and Yates, T. 2008. *UNECE International Co-operative Programme on Effects on Materials, Including Historic and Cultural Monuments*. Report No. 56. Trends in pollution and corrosion of carbon steel, zinc and limestone 1987–2006. Swerea KIMAB AB, Stockholm, Sweden.

Tidblad, J., Ferm, M., Grontoft, T., Kreislova, K., Faller, M., Yates, T., and Lombardo, T. 2011. *UNECE International Co-operative Programme on Effects on Materials, Including Historic and Cultural Monuments. Description of Test Sites*. Report No. 66. Trends in pollution, corrosion and soiling 1987–2009. Swerea KIMAB AB, Stockholm, Sweden.

Tidblad, J., Kucera, V., Ferm, M., Kreislova, K., Brüggerhoff, S., Doytchinov, S., Screpanti, A., Grøntoft, T., Yates, T., de la Fuente, D., Roots, O., Lombardo, T., Simon, S., Faller, M., Kwiatkowski, L., Kobus, J., Varotsos, C., Tzanis, C., Krage, L., Schreiner, M., Melcher, M., Grancharov, I., and Karmanova, N. 2012. Effects of air pollution on materials and cultural heritage: ICP materials celebrates 25 years of research. *Int. J. Corrosion*, **2012**, article ID 496321, 1–16.

Tidblad, J., Gordon, A., Kreislova, K., Faller, M., Fuente, D., Yates, T., and Verney-Carron, A. 2013. *UNECE International Co-operative Programme on Effects on Materials, Including Historic and Cultural Monuments. Description of Test Sites*. Report No. 72. Results of corrosion and soiling from the 2011–2012 exposure programme for trend analysis. Swerea KIMAB AB, Stockholm, Sweden.

Tzanis, C., Varotsos, C., Ferm, M., Christodoulakis, J., Assimakopoulos, M. N., and Efthymiou, C. 2009. Nitric acid and particulate matter measurements at Athens, Greece, in connection with corrosion studies. *Atmos. Chem. Phys.*, **9**, 8309–8316.

Tzanis, C., Varotsos, C., Christodoulakis, J., Tidblad, J., Ferm, M., Ionescu, A., Lefevre, R.-A., Theodorakopoulou, K., and Kreislova, K. 2011. On the corrosion and soiling effects on materials by air pollution in Athens, Greece. *Atmos. Chem. Phys.*, **11**, 12039–12048.

Varotsos, C., Tzanis, C., and Cracknell, A. 2009. The enhanced deterioration of the cultural heritage monuments due to air pollution. *Environ. Sci. Pollut. R.*, **16**, 590–592.

Verney-Carron, A., Dutot, A. L., Lombardo, T., and Chabas, A. 2012. Predicting changes of glass properties in polluted atmospheric environment. *Atmos. Environ.*, **54**, 141–148.

Yates, T. 2007. *UNECE International Co-operative Programme on Effects on Materials, Including Historic and Cultural Monuments*. Report No. 55. Results from the 2005–2006 trend exposure programme. Corrosion attack of limestone after 1 year of exposure. Building Research Establishment Ltd. (BRE), Garston, Watford, UK.

Materjalide korrosioon ja õhusaaste. Pikaajalised uuringud Lahemaa seirejaamas

Ott Roots

Lahemaa seirejaam on osalenud ÜRO Euroopa Majanduskomisjoni rahvusvahelises korrosiooniuuringute programmis selle algusest 1987. aastast alates. Programmi eesmärgiks on olnud Euroopa eri regioonide materjalide korrosiooniuuringud, lähtudes kohalikust kliimast ja õhusaastetasemest. Samuti on antud soovitusi, milliseid materjale kasutada erinevates saaste- ja kliimatasemega tingimustes nii ehitusel kui ka ajaloo- ning kultuuripärandi restaureerimisel. Varasemates uuringutes (Roots, 2008; Roots et al., 2011) võtsime vaatluse alla korrosiooniuuringud Lahemaa seirejaamas programmi algusest kuni aastateni 2005/2006. Käesolevas artiklis on põhiline tähelepanu koondunud aastatele 2008/2009. Kuigi Euroopas ja ka Eestis on õhusaaste alates 1990. aastatest kahanenud, pole Lahemaal osa eksponeeritud materjalide korrosioon oluliselt vähenenud. Näiteks on tsingi korrosioonitase aastatel 2008/2009 jäänud aastate 1997/1998 tasemele. Suhteliselt kõrge on Portlandi lubjakivi korrosioon Lahemaa seirejaamas alates 2002. aastast, ületades Itaalia korrosiooniuurijate (Doytchinov et al., 2012) ajaloo- ja kultuurimälestistele soovitusliku korrosioonitaseme piirväärtuse kõigi kolme viimase mõõtmisperioodi jooksul. Aastatega 2005/2006 võrreldes on aastatel 2008/2009 Lahemaa õhus märgata nii osooni kui ka osakeste (PM10) sisalduse vähenemist. Esmapilgul tundub, et tänapäevase klaasi nn korrosioonitase / klaasi hägusus on jäänud aastatel 2005/2006 ja 2008/2009 samale tasemele. Siiski võib olukord muutuda, kui saame Prantsusmaa uurijatelt Lahemaa seirejaama viimase nelja aasta nüüdisaegse klaasi korrosioonitaseme / klaasi hägususe analüüside tulemused. Autor jätkab materjalide korrosiooniuuringuid Lahemaa seirejaamas ka aastatel 2014/2015. Lahemaa seirejaam on programmis tähtis kui üks foonijaamadest, kus õhusaastetase on suhteliselt madal.