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Review Article

Effects of Air Pollution on Materials and Cultural Heritage: ICP Materials Celebrates 25 Years of Research

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An overview is given of all results from the International Co-operative Programme on Effects on Materials including Historic and Cultural Monuments (ICP Materials), which was launched in 1985. Since then, about twenty different materials have been exposed repeatedly in a network of test sites consisting of more than twenty sites with an extensive environmental characterisation and more than sixty official reports have been issued. Recent results on trends in corrosion, soiling, and pollution show that corrosion of carbon steel, zinc, and limestone is today substantially lower than 25 years ago, but while corrosion of carbon steel has decreased until today, corrosion of zinc and limestone has remained more or less constant since the turn of the century. Unique data are given on measured HNO_3 concentrations from 2002-2003, 2005-2006, and 2008-2009, and the relative average decrease was about the same from 2002-2003 to 2005-2006 as it was from 2005-2006 to 2008-2009.

1. Introduction

ICP Materials or "the International Co-operative Programme on Effects on Materials including Historic and Cultural Monuments" was launched in 1985 and had its first Task Force Meeting in March 10-11, 1986, Watford, United Kingdom. Since then, more than sixty reports in the official report series have been issued [1–66].

The history of ICP Materials [67] begins, however, with the history of the Convention on Long-range Transboundary Air Pollution (CLRTAP, LRTAP Convention or simply "the Convention"). In 1979, the Member States of the United Nations Economic Commission for Europe (UNECE) adopted the Convention as a response to acid rain, brought on by contamination of the air, killing forests and lakes even in remote places far from industrial facilities [68]. The Convention has been extended by eight protocols that identify specific measures to be taken by their 51 Parties to cut their emissions of air pollutants [69]. Worth mentioning in this context are the 1985 Protocol on the Reduction of Sulphur Emissions or their Transboundary Fluxes by at least 30 per cent, the 1994 Protocol on Further Reduction of Sulphur Emissions, and the 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone. The last of these is also named the "Gothenburg Protocol" or the "multipollutants/multi-effects protocol".

Already in 1980, Vladimir Kucera was approached by UNECE with a request to provide a short summary of the state of knowledge concerning the effects of sulphur compounds on materials. The reason for selecting Sweden was most likely due to Sweden's well-received case study for the United Nations conference on the human environment published in 1971 [70]. This led to the development of a proposal in 1983 for an international exposure program where Sweden declared its willingness to be lead country. A decision to launch the program was made by the Executive Body of the Convention during its third session in Helsinki, July 1985. Later the same year an unofficial planning meeting took place in Stockholm, December 1985 with participation from research subcentres from the countries Czechoslovakia, Norway, Federal Republic of Germany, and United Kingdom.

The first phase of ICP Materials (1987–1995) was marked by a focus on development of dose-response functions where long-term data on corrosion and pollution is required. During this time, SO_2 concentrations were still relatively high but decreasing, so it was in 1996 realised that a new exposure programme was needed, the multipollutant exposure (1997–2001). The aim of this program was to quantify not only the effect of SO_2, but also other important "new" pollutants such as HNO_3 and particulate matter. In connection with this, an EU proposal was submitted by the group with the aim of strengthening the multipollutant exposure. This proposal was, however, rejected but was successfully resubmitted and in 2002 the 40-month MULTI-ASSESS project could start with the first extensive measurements of HNO_3 and PM in the program [71].

In 1996, there was also a turning point with the first ICP Materials workshop "Economic Evaluation of Air Pollution Damage to Materials," January 23–25, 1996, Stockholm, Sweden. This emphasis on the use of results for policy purposes was further strengthened with the launch of a subcentre for the assessment of stock of materials at risk and cultural heritage in 2005, together with the close cooperation with the 2004–2007 EU 6FP CULT-STRAT project on management strategies that resulted in a textbook on the effects of air pollution on materials and cultural heritage [72], and even more with the significant involvement of ICP Materials in the revision of the Gothenburg protocol, 2011.

The aim of the present paper is first to present a complete overview of all results that are available from the ICP Materials programme, including references to original data and publications. During the last 25 years, there are many individual results that are more or less well known, and even though these results have been published to varying degrees they are now for the first time presented in one single paper. The second aim is to give new results on trends in corrosion, soiling, and pollution. The exposure of materials for trend analysis has been one of the key activities of ICP Materials from the beginning in 1987, with the addition of limestone for corrosion and modern glass for soiling as new trend materials in 2005, in addition to the original trend materials: carbon steel and limestone. Regarding pollution, the focus in this paper will be on N pollutants, especially HNO_3, where unique data from the period 2002–2009 are presented.

2. Exposure of Materials (1987–2009)

A wide range of materials has been exposed over the years and an overview of the performed corrosion exposures for the period 1987–2009 for individual materials/materials groups are given in Figure 1. Note that modern glass is not included in the figure since it is a material exposed for evaluation of soiling (see Section 6.3). The main exposure with the widest range of materials was the original 8-year exposure (1987–1995). This was later complemented in the multipollutant 4-year exposure (1997–2001). Since 2000, only so-called trend exposures, that is, repeated one-year exposures with the aim of establishing trends in corrosion and pollution, have been performed for selected indicator materials. The individual materials are described in more detail in the following with references to original publications and data sources.

Recently, soiling is also included as an important effect on materials next to corrosion, and since 2005 modern glass has been exposed in sheltered position as a trend material for evaluation of soiling effects.

2.1. Carbon Steel. The subcentre responsible for evaluation of carbon steel was SVUOM, Czech Republic. Several materials, including carbon steel, were in addition to the unsheltered exposure also exposed under shelter, but not in all exposures. One-year data of unalloyed carbon steel

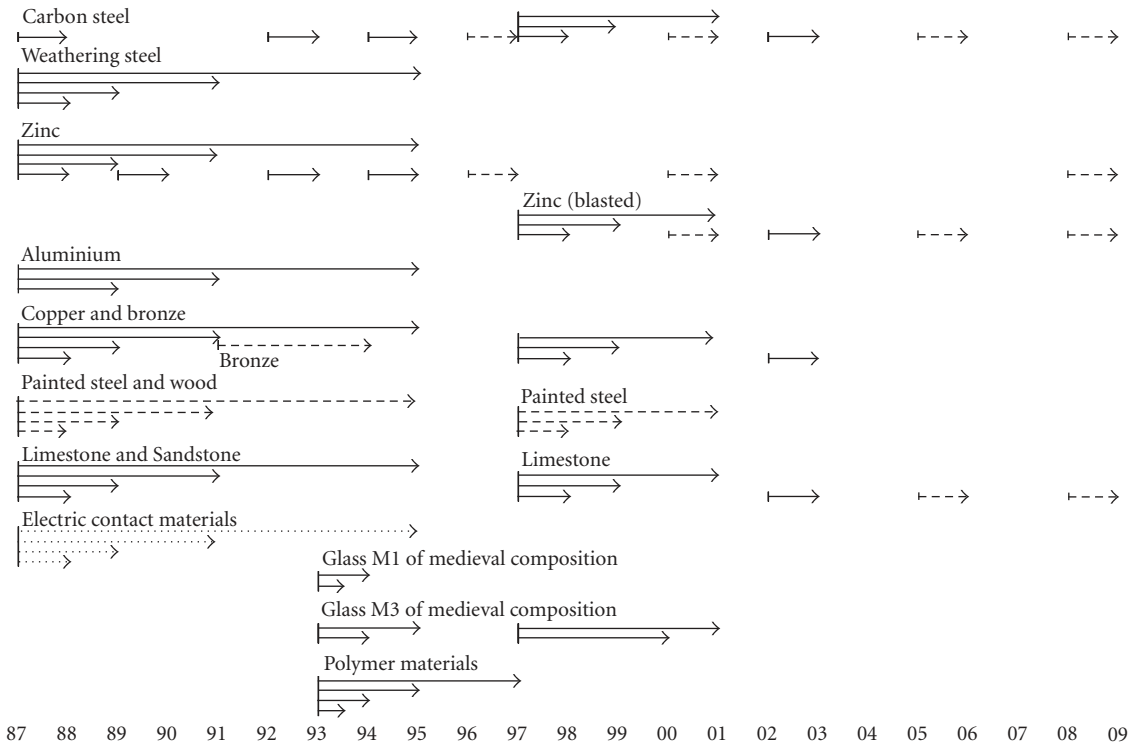

Figure 1: Overview of performed corrosion exposures within ICP Materials (solid arrows: unsheltered and sheltered exposure; dashed arrows: unsheltered exposure; dotted arrows: sheltered exposure inside an aluminium box).

(C < 0.2%, P < 0.07%, S < 0.05%, Cu < 0.07%) exposed in unsheltered position are available for the exposure years 1987-1988, 1992-1993, and 1994-1995 [29], 1996-1997 [46], 1997-1998 [41], 2000-2001 [46], 2002-2003 [73], 2005-2006 [52], and 2008-2009 [61]. One-year data for sheltered position are available for 1987-1988, 1992-1993, and 1994-1995 [29], 1997-1998 [41], and 2002-2003 [73]. Carbon steel was not exposed for longer periods than one year in the original exposure (1987–1995) but were in addition exposed both in unsheltered and sheltered positions in the multipollutant exposure, 1997–1999 and 1997–2001 [41], see Figure 1.

2.2. Weathering Steel. The subcentre responsible for evaluation of weathering steel was SVUOM, Czech Republic. Weathering steel (C < 0.12%, Mn 0.3–0.8%, Si 0.25–0.7%, P 0.07–0.15%, S < 0.04%, Cr 0.5–1.2%, Ni 0.3–0.6%, Cu 0.3–0.55%, Al < 0.01%) was exposed in unsheltered as well as sheltered position in the original exposure for the periods 1987-1988, 1987–1989, 1987–1991, and 1987–1995 [22], and an analysis of the results was later presented at the International workshop on atmospheric corrosion and weathering steels, Cartagena, 2004 [74].

2.3. Zinc. Two variants of zinc samples have been exposed, one "traditional" suitable for corrosivity classification and one that was blasted as a surface preparation prior to exposure resulting in slightly higher corrosion rates.

The subcentre responsible for evaluation of traditional zinc was SVUOM, Czech Republic. Zinc (>98.5%) was exposed in the original exposure for the periods 1987-1988, 1987–1989, 1987–1991, and 1987–1995, both in unsheltered and sheltered positions [22]. Additional data for one-year exposures are available for unsheltered position for the years 1989-1990, 1992-1993, and 1994-1995 [29], 1996-1997, and 2000-2001 [46], and 2008-2009 [61], and for sheltered position for the years 1987-1988, 1992-1993, and 1994-1995 [29], see Figure 1.

The subcentre responsible for evaluation of blasted zinc was EMPA, Switzerland. The first exposures were the multipollutant exposures in 1997-1998, 1997–1999, and 1997–2001 where samples were exposed in unsheltered as well as sheltered positions [42]. After that, blasted zinc has replaced traditional zinc as a trend material with exposures in 2000-2001 [42], 2002-2003 [73], 2005-2006 [53], and 2008-2009 [61]. In the year 2002-2003, sheltered samples were exposed as well [73].

2.4. Aluminium. The subcentre responsible for evaluation of aluminium was SVUOM, Czech Republic. Aluminium (>99.5%) was exposed in the original exposure program for the periods 1987-1988, 1987–1989, 1987–1991, and 1987–1995, both in unsheltered and sheltered positions. However, results are only available after 2, 4, and 8 years of exposure since the corrosion attack after 1 year of exposure could not be evaluated [22].

2.5. Copper, Cast Bronze, and Pretreated Bronzes. The subcentre responsible for evaluation of copper, bronze, and pretreated bronzes was the Bavarian State Department of Historical Monuments, Germany. Copper was of quality SF Cu, DIN 1787 (Cu 99%, P 0.015–0.04%) and cast bronze Cu Sn6Pb7Zn5, ISO/R 1338 (Cu 81%, Sn 5.8%, Pb 6.7%, Zn 4.5%, Ni 1.6% + trace elements). Both copper and cast bronze were exposed in unsheltered as well as sheltered positions in the original exposure program for the periods 1987-1988, 1987–1989, 1987–1991, and 1987–1995 [23] and later also in the multipollutant exposure program for 1997-1998, 1997–1999, and 1997–2001, and last in 2002-2003 [73].

In addition, recycled 1- and 2-year bronze specimens from the original exposure were grinded and then exposed in unsheltered position as untreated, waxed, patinated, and patinated/waxed for the period 1991–1994 [31].

2.6. Painted Steel and Wood. The subcentre responsible for evaluation of paint coatings was NILU, Norway. Four coatings were exposed, two painted on wood and two on steel: coil coated steel with alkyd melamine, steel panel with silicon alkyd, wood panel with alkyd, and wood panel with primer and acrylate. All these were exposed in unsheltered, but not sheltered, position in the original exposure program for the periods 1987-1988, 1987–1989, 1987–1991, and 1987–1995 [25]. One of these, the steel with silicon alkyd was then later also exposed in the multipollutant exposure program for 1997-1998, 1997–1999, and 1997–2001 [45].

2.7. Sandstone and Limestone. The subcentre responsible for evaluation of stone materials was BRE, UK. Portland limestone and white Mansfield dolomitic sandstone were exposed in unsheltered as well as sheltered positions in the original exposure program for the periods 1987-1988, 1987–1989, 1987–1991, and 1987–1995 [24].

In subsequent exposures limestone only was exposed. It was included in the multipollutant exposure in unsheltered and sheltered positions for 1997-1998, 1997–1999, and 1997–2001 [44] and also in 2002-2003 [73]. It is now classified as one of the indicator materials and was exposed in subsequent trend exposure in unsheltered position in 2005-2006 [54] and 2008-2009 [61].

2.8. Electric Contact Materials. The subcentre responsible for evaluation of electric contact materials was the former Swedish Corrosion Institute, now Swerea KIMAB. Nickel, copper, silver, and tin as well as Eurocard connectors of three different qualities were exposed in sheltered positions inside an aluminium box in the original exposure program for the periods 1987-1988, 1987–1989, 1987–1991, and 1987–1995 [26]. Several publications resulted from the evaluation including but not limited to [75–79].

2.9. Glass of Medieval Composition. The subcentre responsible for evaluation of glass of composition representative for medieval stained glass windows was the Institute of Sciences and Technology in Art, Academy of Fine Arts, Austria. Glass of two compositions were exposed, the more sensitive M1 (SiO_2 48%, K_2O 25.5%, CaO 15%, MgO 3%, Al_2O_3 1.5%, P_2O_5 4%, and Na_2O 3%) and M3 (SiO_2 60%, K_2O 15%, CaO 25%). Glass M1 was exposed for half a year (1993-1994) and one year (1993-1994) in both unsheltered and sheltered positions and in the same program glass M3 was exposed in unsheltered and sheltered positions for one (1993-1994) and two years (1993–1995) [27].

In the multipollutant exposure, only M3 was exposed for the periods 1997–2000 and 1997–2001 (3 and 4 years). However, by partly exposing samples already exposed for one and two years in the previous exposure (1993–1995) for the period 1997–2001 the final reports for sheltered [47] and unsheltered [48] exposure were able to contain results after 3, 4, 5, and 6 years of exposure. Several publications, Ph.D. and Diploma Theses resulted from these systematic investigations [80–87].

2.10. Polymer Materials. The subcentre responsible for evaluation of electric contact materials was the former Swedish Corrosion Institute, now Swerea KIMAB. Polyamide and polyethylene were exposed in unsheltered and sheltered positions for 0.5 (1993-1994), 1 (1993-1994), 2 (1993–1995), and 4 (1993–1997) years [28]. An analysis of the results was later presented at the 1st European Weathering Symposium, 2004 [88].

2.11. Modern Glass. The sub-center responsible for the evaluation of soiling on glass was LISA, France. Silica-soda-lime float glass (70 to 72% of SiO_2, about 14% of Na_2O, and about 10% of CaO, and other oxides) currently used as windows glass, as well as in building facades, was exposed in sheltered position inside an aluminium box for 1 year (2005-2006 and 2008-2009).

3. Network of Test Sites

A complete list of sites used for the previously described exposures is given in Table 1. The first thirty-nine sites (1–39) were used in the original exposure (1987–1995). When the multipollutant exposure (1997–2001) was started eight, new sites were added (40–49) but at the same time several sites were removed that were part in the original exposure. One of the criteria for keeping sites was that they should be measuring ozone, which during this time changed status from optional to mandatory (see below). Subsequent individual additions/removals of test sites have been made in connection with trend exposures as specified in Table 1.

4. Measurements of Environmental Data

Environmental data has been the back-bone of the program, and the extensive environmental characterisation is perhaps what most distinguishes this corrosion program from other. In fact, some of the reported environmental data (see HNO_3 below) is unique, even from the perspective of environmental research.

NILU, Norway has been responsible for the reporting of environmental data and data for individual years have

Table 1: List of ICP Materials test sites showing number, name, country site type, and years with available data 1987–2009.

Name	Country	Site type[a]	Available data
(1) Prague-Letnany	Czech Republic	Urban	1987–2009
(2) Kasperske Hory	Czech Republic	Rural	1987–1995
(3) Kopisty	Czech Republic	Industrial	1987–2009
(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
(11) Essen-Leithe	Germany	Rural	1987–1995
(12) Garmisch-Partenkirchen	Germany	Rural	1987–1995
(13) Rome	Italy	Urban	1987–2009
(14) Casaccia	Italy	Rural	1987–2009
(15) Milan	Italy	Urban	1987–2009
(16) Venice	Italy	Urban	1987–2009
(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
(22) Borregard	Norway	Industrial	1987–1995
(23) Birkenes	Norway	Rural	1987–2009
(24) Stockholm South	Sweden	Urban	1987–2009
(25) Stockholm Centre	Sweden	Urban	1987–1995
(26) Aspvreten	Sweden	Rural	1987–2009
(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
(32) Bilbao	Spain	Industrial	1987–1995
(33) Toledo	Spain	Rural	1987–2009
(34) Moscow	Russian Federation	Urban	1987–2003
(35) Lahemaa	Estonia	Rural	1987–2009
(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
(41) Berlin	Germany	Urban	1997–2009
43) Tel Aviv	Israel	Urban	1997–2001
(44) Svanvik	Norway	Rural	1997–2009
(45) Chaumont	Switzerland	Rural	1997–2009
(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
(51) Athens	Greece	Urban	2005–2009
(52) Riga	Latvia	Urban	2005–2009

Table 1: Continued.

Name	Country	Site type[a]	Available data
(53) Vienna	Austria	Urban	2008-2009
(54) Sofia	Bulgaria	Urban	2008-2009

[a]The characterisation of test sites as rural/urban/industrial is in some cases a difficult decision and is not an indication of the corrosivity of the test site.

been reported for 1987–1989 [3], 1989-1990 [9], 1990-1991 [10], 1991-1992 [16], 1992-1993 [17], 1993-1994 [20], 1987–1995 [21], 1995–1998 [33], 1998-1999 [39], 1997–2001 [40], 2002-2003 [49], 2005-2006 [51], and 2008-2009 [66]. Table 2 gives an overview of the reported environmental data for the period 1987–2009.

Temperature and relative humidity have always been included as a representation of the climatic conditions. Time of wetness was included from the beginning but has not been reported since 1995, with the reason being that this parameter is not given from meteorological institutions but needs to be calculated from highly time-resolved data of temperature and relative humidity, which is not always practical. Also the additional information contained in this variable, compared to what is already included in annual averages of temperature and relative humidity, is very limited. Sunshine data was also included from the beginning but has not been reported since 2005. This is a parameter that is especially important for polymeric materials and paint coatings, which were not exposed in the 2005-2006 and 2005-2006 trend exposures.

The gaseous pollutants SO_2 and NO_2 were included from the beginning as mandatory parameters, and in connection with the multipollutant exposure more emphasis was also put on O_3. A special campaign was launched in connection with the MULTI-ASSESS project in 2002-2003 [71], and since then HNO_3 and particulate matter has been included as mandatory parameters.

5. Dose-Response Functions

One of the main aims of ICP Materials from the beginning has been to "perform a quantitative evaluation of the effects of multipollutants such as S and N compounds, O_3 and particles, as well as climate parameters, on the atmospheric corrosion and soiling of important materials, including materials used in objects of cultural heritage". This has been done by developing dose-response functions. Of all the functions that have been developed through the years, some have been selected as suitable for mapping effects on materials. These are given in the UN ECE Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels; and Air Pollution Effects, Risks and Trends [89]. As described in the manual, two sets of functions have been developed. One for the SO_2 dominating situation [90], based on data from the original exposure (1987–1995) and one for the multipollutant situation [91], based on data from the multipollutant exposure (1997–2001). The dose-response functions given in the mapping manual are valid for unsheltered conditions, see Table 3.

6. Trends in Pollution, Corrosion, and Soiling

6.1. Trends in Pollution and Corrosion (1987–2009). The average absolute pollutant levels have changed during the period 1987–2009 not only because of changing pollutant concentrations, but also because of ICP Materials test site selection. Figure 2 shows average relative SO_2, NO_2, and O_3 concentrations at ICP Materials sites, corrected for site selection. The average trends are quite different for the gases. O_3 increased during the 1990s but has been relatively constant after this period. NO_2 has decreased and continues to decrease over the entire period, while the decrease in SO_2 ceased during 2000 to 2006 with a slight decrease in the most recent exposure in 2008-2009. Corrosion of materials has decreased during the same period, mainly due to the decreasing SO_2 concentration, but to varying degrees depending on the material. Figure 3 shows the surface recession of limestone for the exposure periods 1987-1988, 1997-1998, 2002-2003, 2005-2006, and 2008-2009.

Compared to the first exposure, the values today are obviously lower, but there is significant year to year variation and there is no obvious decrease since 1998. The same is true for zinc (Figure 4). In Figure 4, it is an obvious difference between traditional and blasted zinc, with use of the latter resulting in corrosion values on average almost twice that of traditional zinc. Therefore, blasted zinc values are shown in a different scale (Figure 4, right) in order to make a complete visual impression of the relative zinc trends. For carbon steel, however, the decrease in corrosion is in principle following an exponential decay with corrosion halving its value each 12th year in industrial/urban areas and each 16th year in rural areas (Figure 5).

6.2. Recent Trends in N Pollutants (HNO_3, NO_2, and Particulate NO_3^-). Nitric acid and particulate nitrate are the most stable forms when the primary pollutants nitric oxide and nitrogen dioxide are transformed in the atmosphere. There are very few reported measurements of HNO_3 and particulate NO_3^- in urban air in Europe and elsewhere. Nitric acid is a strong acid and its salts are very hygroscopic. It can, therefore, lead to increased atmospheric corrosion [92]. In the EU project MULTI-ASSESS [71], a diffusive sampler was validated for HNO_3 and a surrogate surface for particulate deposition was chosen for air quality measurements in connection with corrosion studies [72]. Nitric acid is rapidly adsorbed on most surfaces and, therefore, has a very high dry deposition velocity. Nanoparticles and coarse particles, but not accumulation mode particles, also deposit fast to surfaces. Nanoparticles generally represent a negligible fraction of the total airborne particle mass.

Table 2: Reported environmental data from ICP Materials test 1987–2009: X: mandatory; (X): optional; —: not reported.

Parameter	Symbol	Unit	1987–1995	1995–2001	2002-2003	2005–2009
Temperature	T	°C	X	X	X	X
Relative humidity	Rh	%	X	X	X	X
Time of wetness	Tow	h	X	—	—	—
Sunshine	Sun	h	X	—	—	—
Sunshine[a]	Sun	MJ m^{-2}	X	X	X	—
SO_2 concentration	SO_2	$\mu g\ m^{-3}$	X	X	X	X
NO_2 concentration	NO_2	$\mu g\ m^{-3}$	X	X	X	X
O_3 concentration	O_3	$\mu g\ m^{-3}$	(X)	(X)	X	X
HNO_3 concentration	HNO_3	$\mu g\ m^{-3}$	—	(X)[b]	(X)	X
Precipitation: amount	Prec	mm	X	X	X	X
(i) conductivity	Cond	$\mu S\ cm^{-1}$	X	X	X	(X)
(ii) pH	pH	—	X	X	X	X
(iii) SO_4^{2-}, NO_3^-, Cl^-	varies	$mg\ L^{-1}$	X	X	X	X
(iv) $HN4^+$, Na^+, Ca^{2+}, Mg^{2+}, K^+	varies	$mg\ L^{-1}$	(X)	(X)	(X)	(X)
Particulate matter	PM	$\mu g\ cm^{-2}\ month^{-1}$	—	(X)[b]	(X)	X

[a]Calculated from sunshine hours and latitude.
[b]Only data at a few test sites reported.

Table 3: Materials for which dose-response functions are given for the SO_2 dominating situation (top) and the multipollutant situation (bottom) in the UNECE Mapping Manual and the required environmental data.

Material	T	Rh	SO_2	O_3	HNO_3	PM10	Prec	pH	Cl^-
Weathering steel	X	X	X						
Zinc	X	X	X				X	X	
Aluminium	X	X	X				X		X
Copper	X	X	X	X			X	X	
Bronze	X	X	X				X	X	X
Limestone	X		X				X	X	
Sandstone	X		X				X	X	
Coil-coated steel with alkyd melamine	X	X	X				X		
Steel panel with alkyd	X	X	X				X		
Carbon steel (multipollutant)	X	X	X			X	X	X	
Zinc (multipollutant)	X	X	X		X				
Bronze (multipollutant)	X	X	X			X	X	X	
Limestone (multipollutant)		X	X		X	X	X	X	

Therefore, deposited particulate nitrate are mainly associated with coarse particles. Coarse particles are often alkaline and can also contain sodium chloride. These properties make them a sink for nitric acid. The reaction can either take place in the atmosphere or on already deposited particles.

Nitrogen oxides are mainly emitted as nitric oxide, but a small fraction is also emitted as nitrogen dioxide. The directly emitted nitrogen dioxide fraction from vehicles has increased during the last decades partly due to modern diesel engines. Nitric oxide forms nitrogen dioxide by reaction with ozone (R1):

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (R1)$$

$$NO2 + OH \xrightarrow{M} HNO_3 \quad (R2)$$

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \longleftrightarrow N_2O_5 \quad (R3)$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

$$2NO_2 + H_2O \longrightarrow HONO + HNO_3 \quad (R4)$$

The main reaction for oxidizing NO_2 to HNO_3 is the daytime gas-phase oxidation with OH radicals (R2). NO_2 can also be oxidized during nighttime by ozone through a series of reactions involving nitrate radicals and dinitrogen pentoxide (R3). Further, NO_2 adsorbed on a wet surface can recombine giving nitrous acid, HONO, and HNO_3 (R4).

HNO_3 was measured with diffusive samplers [93] and nitrate on deposited particles with a surrogate surface [94].

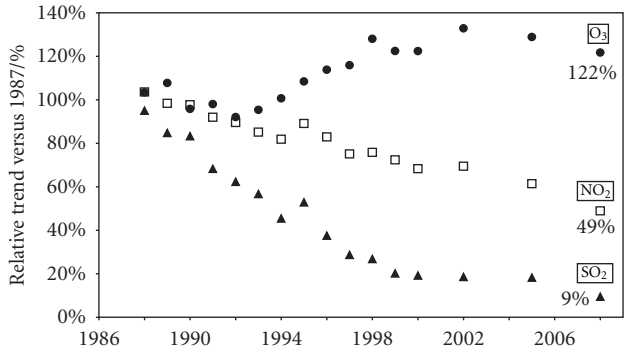

Figure 2: Average SO_2, NO_2 and O_3 trends relative to the year 1987 at ICP Materials test sites.

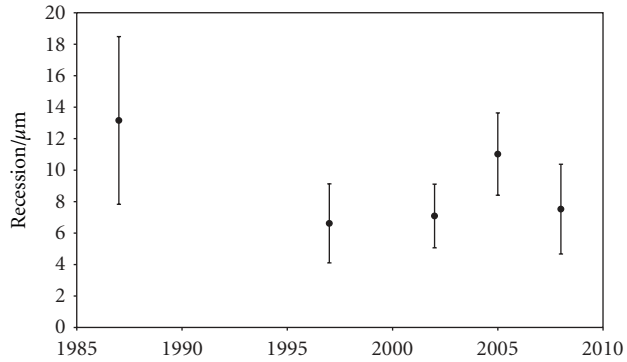

Figure 3: Averages and ranges (standard deviations) of limestone surface recession at ICP Materials test sites (one year exposures).

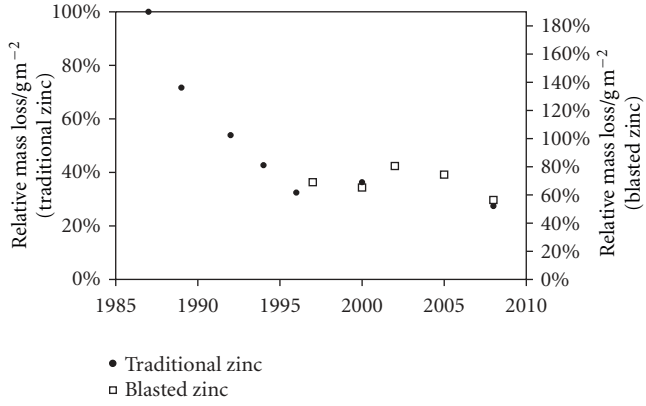

Figure 4: Average relative zinc corrosion at ICP Materials test sites. Values for both traditional and blasted zinc have been normalised to the 1987-1988 value for traditional zinc before averaging.

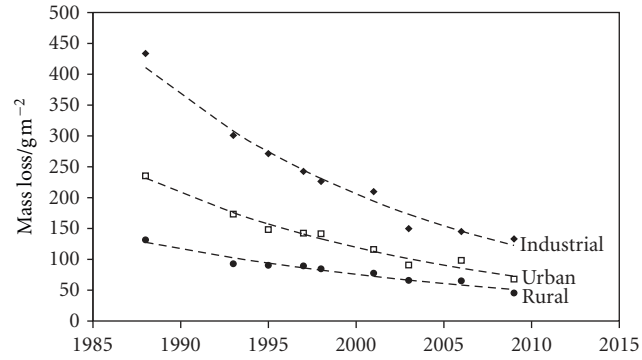

Figure 5: Carbon steel corrosion for industrial, urban, and rural ICP Materials test sites.

The exposure time was generally 2 months and each campaign lasted one year for the periods 2002-2003, 2005-2006, and 2008-2009. Two precursors to HNO_3, namely, NO_2 and O_3, were in the 2002-2003 exposure measured with diffusive samplers, or with other methods depending on exposure time and site. Most sites in ICP Materials used chemiluminescent and UV-instruments, respectively, to measure NO_2 and O_3. Monthly averages are available from these measurements. Some sites used, however, the same diffusive samplers as in 2002-2003.

Since only 17 stations (12 urban and 5 rural) did nitric acid measurements in all three campaigns, the nitric acid concentrations are compared between two campaigns at a time, in order to use all data and to see if there is a trend or random changes, as presented in Figure 6. The results are well correlated between the campaigns except for a few odd sites, which were excluded in the linear regression lines. The decrease in nitric acid concentrations seems to be substantial, on the average about 20% per three-year period, which would correspond to about 50% for a 10-year period, should the decrease continue at the same rate.

The concentrations of the precursors NO_2 and O_3 were also lower during the campaign 2008-2009 compared to 2002-2003, see Figure 7. As can be seen from the figure, the annual average concentration of these precursors has also decreased during this period (see also Figure 2 presented above). Since particulate nitrate requires a counter ion, it is not likely that the deposited particulate nitrate formation rate is proportional to the nitric acid concentration in air. A small decrease in particulate nitrate deposition was, however, observed between the first and latest campaigns.

To illustrate the correlation between HNO_3 concentration and its precursors, the concentrations were plotted against the latitude of the sites. Figure 8 shows that the HNO_3 concentration decreases from south to north, while the precursors' concentrations are not well correlated with latitude. This suggests that the photochemical formation of nitric acid (R2) is the most important. This is also supported by Figure 9, which shows the average seasonal variation of the HNO_3 concentration. Nitric acid and ozone both show a seasonal trend with maximum during the brightest time of the year and minima during the darkest.

At four places in the network, a rural site is quite close to a corresponding urban site. At these sites (Toledo-Madrid, Birkenes-Oslo, Aspvreten-Stockholm, and Casaccia-Rome) the HNO_3 concentrations are much higher at the urban sites than the rural except for Casaccia-Rome where they are quite similar. The NO_2 concentrations were always much lower at the nearby rural sites.

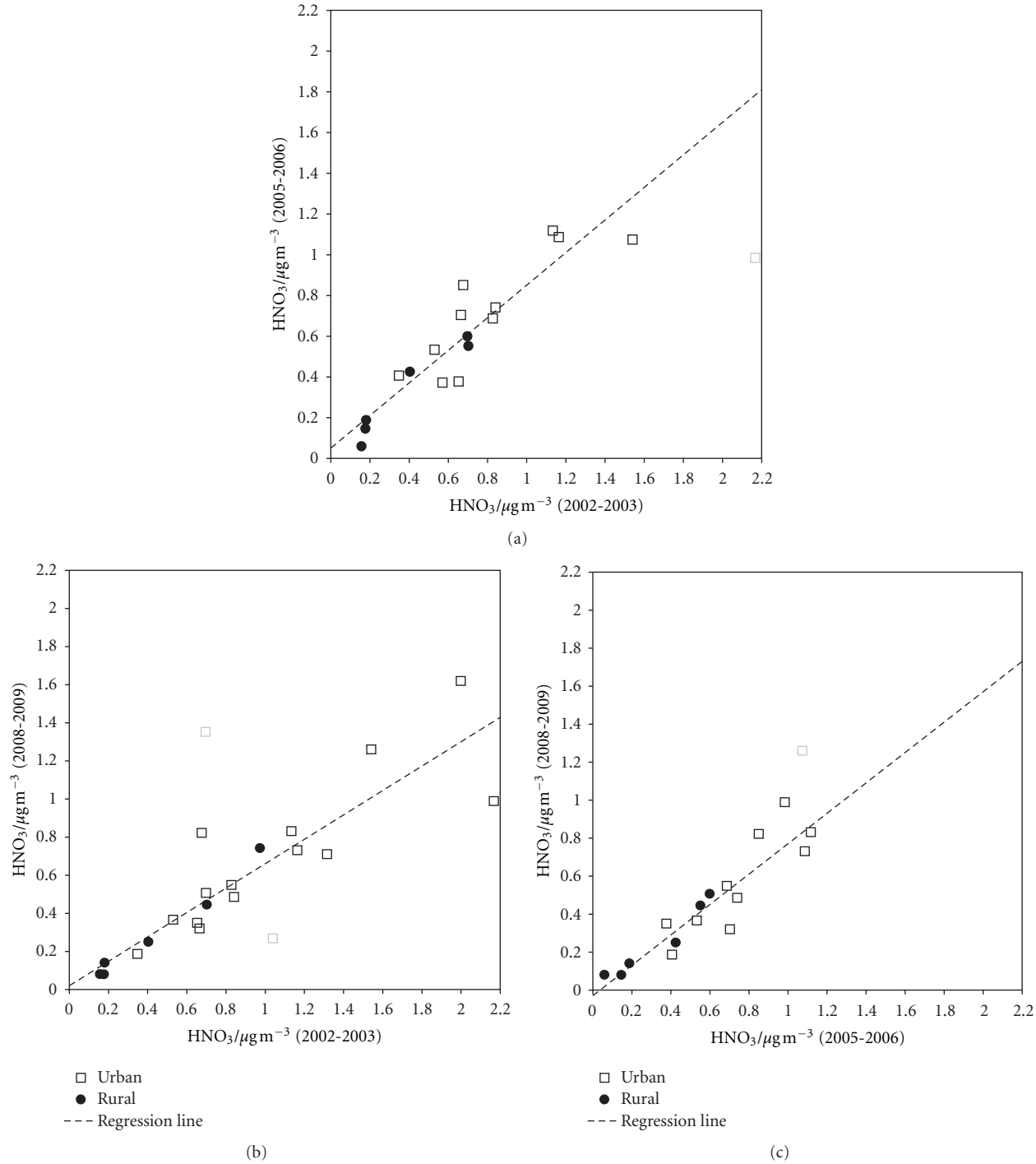

Figure 6: Annual average HNO_3 concentration at ICP Materials test sites for the three one-year campaigns 2002-2003, 2005-2006, and 2008-2009. The grey squares have been excluded when calculating the linear regression lines $y = 0.80x + 0.05$ (2005-2006 *versus* 2002-2003), $y = 0.80x - 0.03$ (2008-2009 *versus* 2005-2006), $y = 0.64x + 0.02$ (2008-2009 *versus* 2002-2003).

6.3. Recent Trends in Soiling of Modern Glass. Due to the increasing importance of particulate matter, modern glass was officially included as a trend material for soiling of materials in the 2005-2006 exposure, so this means that only two exposure periods are available. Dose-response functions are currently being evaluated [58, 95], but the final functions will not be available until end 2013 and will include results also after four years of exposure (2008–2012). Figure 10 shows soiling of modern glass measured by the haze parameter, which is the ratio between the diffuse and direct transmitted light. Taking into account the accuracy of the measurements, it is not possible to say that soiling, on

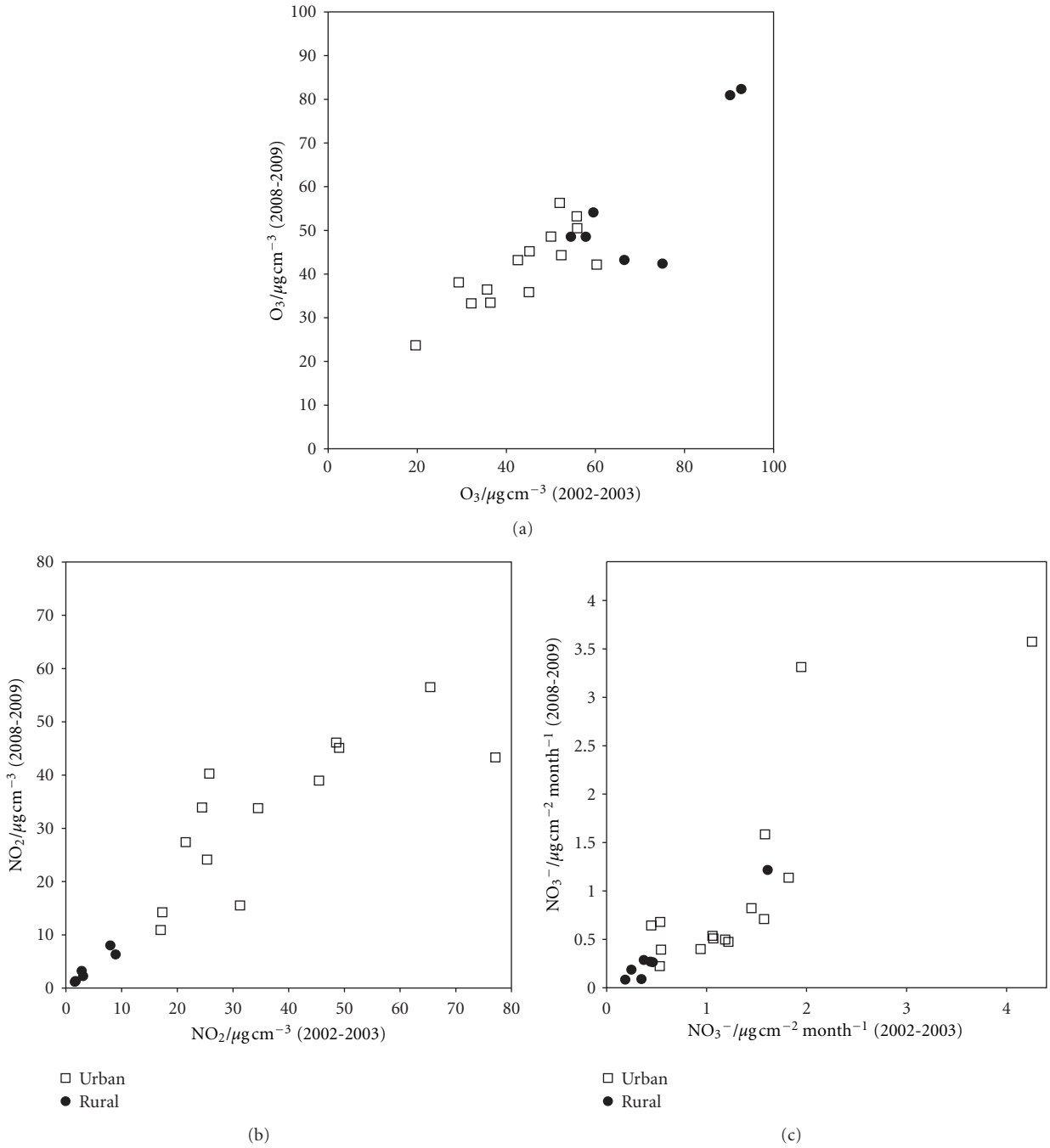

Figure 7: Annual average O_3 concentration, NO_2 concentration, and NO_3^- deposition at ICP Materials test sites for the two one-year campaigns 2002-2003, and 2008-2009.

average, has increased or decreased when comparing the two exposure periods 2005-2006 and 2008-2009.

7. Use of Results for Policy Purposes

The last main aim of ICP Materials is to "use the results for mapping areas with increased risk of corrosion and soiling, and for calculation of cost of damage caused by deterioration of materials". This was put high on the agenda in 2005 when Italy was selected as responsible for a new subcentre on the assessment of stock of materials at risk and cultural heritage, and Sweden and Italy started to share the position as chairs of ICP Materials.

The main results from ICP Materials in this area are the case studies on assessment of stock at risk and mapping areas of increased corrosion risk in Madrid [56, 96] and Italy [59, 62], and recent reviews of available data on stock of materials at risk [60] and economic evaluations [64]. Also

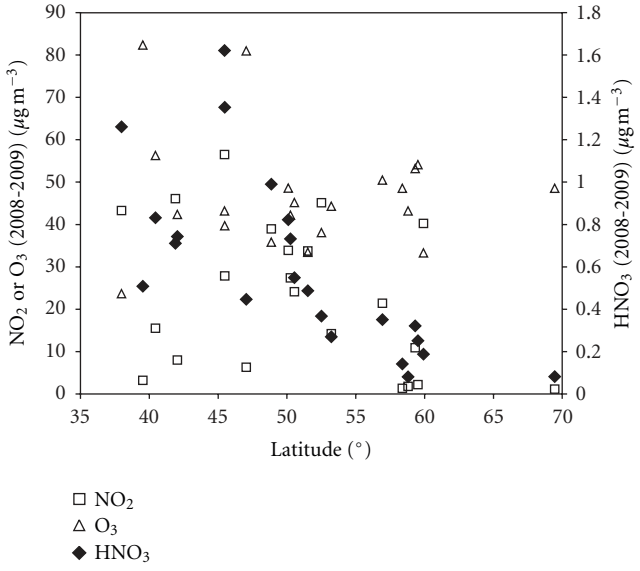

Figure 8: The concentration of nitric acid during 2008/09 and two of its precursors as a function of latitude.

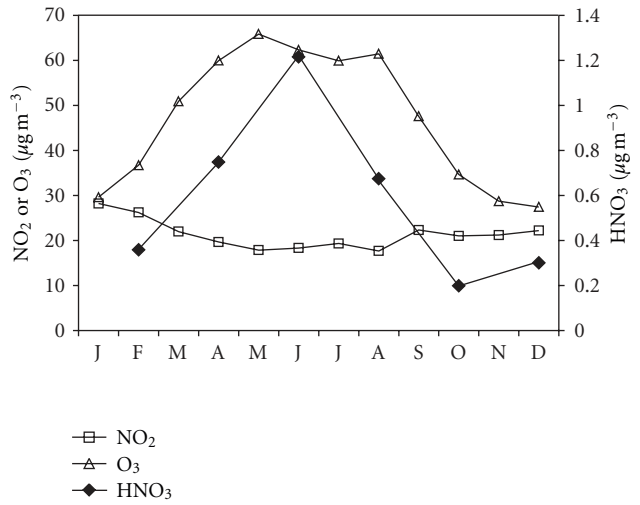

Figure 9: Seasonal cycle of nitric acid and two of its precursors during 2008/09.

there was a close link between ICP Materials and the CULTSTRAT project, which resulted in a book on effects of air pollution on cultural heritage, which included significant parts from the ICP Materials project, including stock at risk studies and discussion on the use of results for policy purposes [72].

At least two separate ways are possible in order to use the results for policy purposes, as outlined in the recent report on economic assessment [64]. The first, and most preferable if all data are available, is to perform a complete evaluation of cost savings (as part of a cost-benefit analysis) for materials and cultural heritage due to reductions in air pollution based on assessment of stock of materials at risk, data on maintenance practices, and costs and mapped

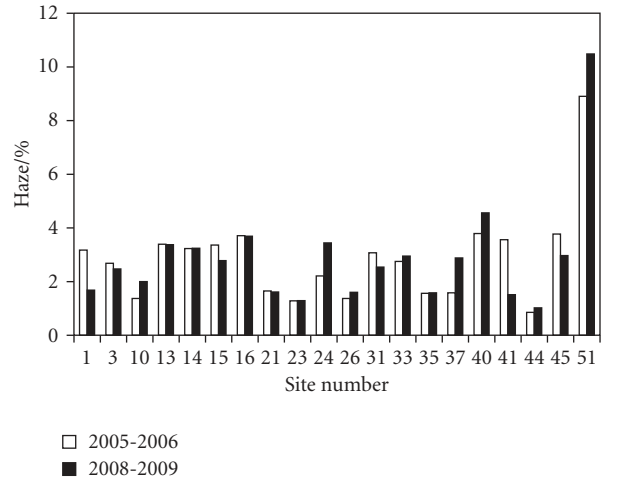

Figure 10: Soiling of modern glass at ICP Materials test sites (see Table 1).

areas of corrosion risk. The other approach is to use the concept of tolerable corrosion/soiling and pollution levels for indicator materials. The last approach is currently used in the evaluation of results from the working group on effect in connection with the current revision of the Gothenburg protocol [97].

Figure 11 shows a selected map [59] of calculated corrosion values for limestone. As is evident from the figure, the scale on which the original data is presented has a large impact on the results. If the scale is too coarse to capture the variation in urban areas, where cultural heritage is located, then the calculated corrosion attack can be significantly underestimated.

8. Plans for Future Exposures

A new trend exposure will start in the fall of 2011. Besides the usual trend exposures of carbon steel, zinc, limestone and modern glass, which are now part of the on-going three-year cycle of trend exposures, additional exposures will start including 4-year samples of these materials (2011–2015) as well as corresponding exposures for weathering steel, copper, and possibly aluminium. In addition, a new test site will be launched in St Petersburg. The incorporation of countries in Eastern Europe, Caucasus, and Central Asia (EECCA countries), that is, Armenia, Azerbaijan, Belarus, Georgia, Kazakhstan, Kyrgyzstan, Moldova, Russian Federation, Tajikistan, Turkmenistan, Ukraine, and Uzbekistan, is a high priority of the Convention.

9. Conclusions

An overview of available results from ICP Materials has been presented. Since the main focus of the programme has been to use the results for development of the policy process within the Convention on Long-range Transboundary Air Pollution, there are still significant parts of the results that

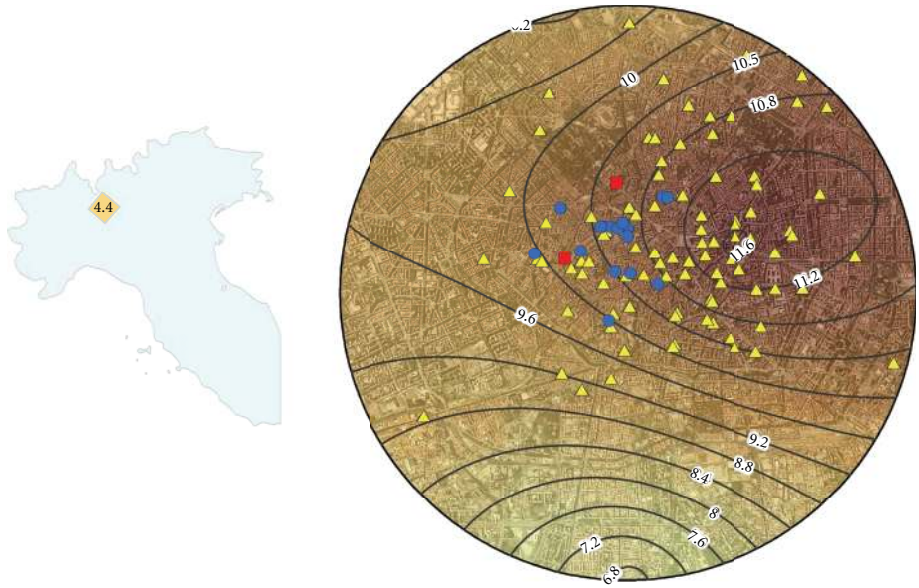

FIGURE 11: Calculated surface recession of limestone in μm (one-year exposure), based on the dose-response function for the SO_2 dominating situation, for the Milan city centre, reported either as one single value based on the EMEP 50 km × 50 km grid cell (left, 4.4 μm) or as a map of the city centre based on local data (right, 6.8 to 11.6 μm). Coloured symbols (blue, red, and yellow) in the map to the right indicate different types of cultural heritage [59].

have not been published outside the official UNECE ICP Materials report series.

Results on recent trends in corrosion, soiling, and pollution have been presented for the indicator materials carbon steel, zinc limestone, modern glass, and for the gaseous pollutants SO_2, NO_2, O_3, and HNO_3.

(i) Carbon steel corrosion has since the beginning of exposures (1987) decreased exponentially at industrial, urban, and rural sites so that the corrosion has been halved about each 12th year for industrial/urban sites and each 16th year for rural sites.

(ii) Zinc and limestone corrosion have decrease substantially compared to the levels in 1987, but since the turn of the century there is no obvious average trend in the ICP Materials network of test sites.

(iii) Modern glass as an indicator for soiling has only been exposed for two periods so far, 2005-2006 and 2008-2009, and when comparing the results from these periods, there is no average difference in the results. However, more exposures are needed before long-term trends can be established.

(iv) Nitric acid concentrations were measured in 2002-2003, 2005-2006, and 2008-2009. When comparing these three periods, the relative decrease was about the same from 2002-2003 to 2005-2006 as it was from 2005-2006 to 2008-2009, corresponding to about 50% for a 10-year period, should the decrease continue at the same rate. However, only three exposure periods are not sufficient to rule out that this apparent trend is not instead part of a natural year-to-year variation.

Acknowledgments

Coauthors to this paper are those who are currently active in the work of ICP Materials. However, during the years many researchers and organisations have come and left and the work would not have been possible without them. Since the list would otherwise most likely be incomplete, only previously involved organisations are listed here: (i) Technical Research Centre of Finland (VTT), (ii) Bavarian State Department of Historical Monuments, Germany, (iii) TNO Division of Technology for Society Department of Environmental Chemistry, the Netherlands, (iv) Institute of Physical Chemistry, Russian Academy of Sciences, Russian Federation, (v) Institute of Technology, Laboratory of Mineralogy and Petrology, Portugal, (vi) National Research Council of Canada and the Ministries of the Environment of Canada and of Ontario, (vii) United States Environmental Protection Agency, (viii) Israel Antiquities Authority, Conservation Department, and (ix) Department of Chemistry, University of Antwerp, Belgium. This compilation work was financed by the Swedish Environmental Protection Agency. However, ICP Materials has been and is financed by numerous sources and these can be found in the original papers referenced in this publication.

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