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Item 4 of the provisional agenda

RECENT CORROSION TRENDS AND MEASUREMENT OF PARTICULATES AND HNO_3 FOR THE MULTI-POLLUTANT EXPOSURE PROGRAMME

Technical report 2004 of the International Cooperative Programme (ICP) on Effects of Air Pollution on Materials, including Historic and Cultural Monuments (ICP Materials)

Introduction

1. The first part of this report shows recent corrosion trends based on a comparison of results from the original and the multi-pollutant programmes as well as results from recent trend exposures. The second part reports results of measurements of particulates and HNO_3 which have been used to extend the database of environmental parameters in the multi-pollutant programme.

I. TRENDS IN CORROSION

2. Trend exposures have, from the beginning of the Programme, been one of the main activities within ICP Materials. They consist of repeated one-year exposures of selected materials. These materials should be well documented regarding the important parameters responsible for corrosion and should also give reliable corrosion data already after one year of exposure. From the start carbon steel and zinc were selected as trend materials and at a later stage limestone was also

included in order to give complementary information. In the future it is envisaged that trend exposures will continue to take place every third year at a reduced network of test sites. This will be done to elucidate the environmental effects of pollutant reductions achieved under the Convention and identify extraordinary environmental changes that result in unpredicted materials damage.

3. Besides the planned trend exposures performed by exposing carbon steel, zinc and limestone, the one-year exposure of the original programme (1987-1988) and the multi-pollutant exposure programme (1997-1998) are two sets of one-year exposures that can be used to evaluate trend effects for all the materials included in both of the exposure programmes. The results of a comparison of the programmes are illustrated in figure I, which shows average trends for the entire network. It is worth noting that when looking at individual sites a decreasing trend is found at both high and low polluted sites. On average, the decrease in both corrosion and pollution is about 50% for this 10-year period. However, marked exceptions are zinc and SO_2, with a larger decrease compared to the other materials/pollutants, and copper and ozone with a smaller decrease.

4. The trends in corrosion and pollution concentrations had already started between 1960 and 1980, though this was dependent on location. It was the result of the successful implementation of, inter alia, central heating and a decrease of sulphur content in oil. More interesting today, however, is to investigate the most recent trends in corrosion and pollution and to identify locations where trends are no longer obvious. The remaining part of this chapter will illustrate this based on results of carbon steel and will show recent trends in Scandinavia and a comparison with southern Europe.

5. Table 1 shows the result of trend exposures up until 2000-2001 in Finland, Norway and Sweden. It is evident that there is a change in the trends from clearly decreasing (until 1992) to almost constant (1995 onwards). Even after the stop in the decrease there is still a marked difference between urban and rural areas. This can be observed when comparing the rural sites of Aspvreten and Stockholm in Sweden, which are situated close to each other and have similar climatic conditions.

Table 1. Corrosion attack of carbon steel (μm) in unsheltered position after one year of exposure at sites in Finland, Norway and Sweden

	1987-1988	**1992-1993**	**1994-1995**	**1996-1997**	**1997-1998**	**2000-2001**
Ähtäri, Finland	17	6	8	7	7	7
Oslo, Norway	29	17	13	13	12	12
Birkenes, Norway	25	17	14	15	13	
Stockholm S., Sweden	34	15	13	13	16	15
Aspvreten, Sweden	19	10	10	9	8	9

6. When looking more closely at the two sites Aspvreten and Stockholm it is worth noting that, even though the corrosion has reached a constant value, the SO_2 concentration has continued to decrease during the same period (fig. II). This means that other pollutants are responsible for the difference in corrosion between these two sites.

7. When investigating the trend at other sites in Europe the picture is more complicated. At some sites the corrosion is still decreasing while at others it has reached a constant value (fig. III). However, a significant number of sites no longer have decreasing corrosion values. Therefore, in order to find out the most appropriate measures to decrease the significant differences that still exist between urban and rural areas, it is important to identify and quantify the effects of other pollutants besides SO_2 in the multi-pollutant situation. This was realized within ICP Materials several years ago and was the motivation for launching the multi-pollutant exposure programme. One important part of this programme is the measurement of additional environmental parameters (HNO_3 and particulates), which is presented in the chapter below.

II. MEASUREMENT OF PARTICULATES AND HNO_3

8. In order to extend the measurement and evaluation of these important pollutants, additional financing was needed. The source of this has been the European Union Fifth Framework Programme project "Multi-pollutant impact and assessment of threshold levels for cultural heritage" MULTI-ASSESS. This has supported the extended one-year ICP Materials multi-pollutant / trend exposure programme (2002-2003).

9. Passive sampling was performed at all sites for gaseous HNO_3 (two samplers per site per exposure period) and for particulate matter (two samplers per site per exposure period). Sampling in unsheltered positions was performed on a bimonthly basis, i.e. samplers were exchanged every second month. The total sampling period was one year resulting in a total of six bimonthly sampling periods.

10. Annual average HNO_3 values for the six sampling periods are shown in figure IV. Regarding seasonal variation, the sites can be classified into two groups, one with a maximum in winter (northern Europe) and one with a maximum in summer (southern Europe). It should be noted that the database of HNO_3 values is the first of its kind. The HNO_3 values range between 0.1 and 2.5 $\mu g/m^3$, which may seem low but preliminary results from laboratory exposures show that the effect of HNO_3, compared to SO_2 at equal concentrations, is several times higher.

11. Measurements with passive samplers have been performed giving results of particulate matter deposition of the ions SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+} and Mg^{2+}. Figure V shows an overview of the results and it is clear that soluble as well as non-soluble particles need to be considered. Of the soluble particles, the marine component has a significant share as well as the non-marine sulphate and nitrate.

12. As an example of the variation between sites, figure VI shows the annual averages of particulate SO_4^{2-} deposition. High values are observed for Lisbon, Berlin and London. The marine contribution is significant for Lisbon but small for the other two sites.

13. The data for HNO_3 and particulate matter have been merged with the data from the multi-pollutant exposure programme. A complete statistical evaluation is now in progress with the aim of developing new dose-response functions adapted to the multi-pollutant situation. The first stage of the analysis will be reported to the Task Force at its twentieth meeting, to be held on 9 June 2004 in London.

III. CONCLUSIONS

14. Both corrosion and SO_2 concentrations have decreased since 1980, on average about 50% for the ten-year period but values depend on the material and location.

15. Since about 1995 corrosion in the Nordic countries has ceased to decrease even though SO_2 concentrations are still falling. In other parts of Europe, but not all, corrosion continues to decrease.

16. There is still a significant difference in corrosion between urban and rural areas; this prompts continued efforts to develop dose-response functions adapted to the multi-pollutant situation.

17. Passive sampling of gaseous HNO_3 and particulate matter (total amount and SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+} and Mg^{2+}) has been performed at all sites. This has resulted in an extended database suitable for the development of dose-response functions adapted to the multi-pollutant situation.

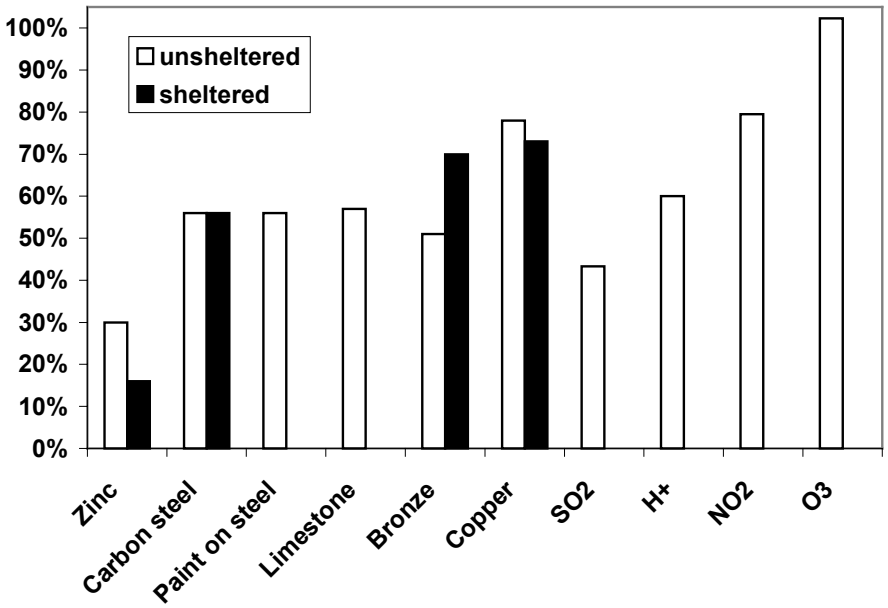

Figure I. The 1997/1987 relation between first year corrosion loss of materials and pollutant concentrations as averages in the original network (1987) and corresponding sites in the multi-pollutant network (1997) of ICP Materials

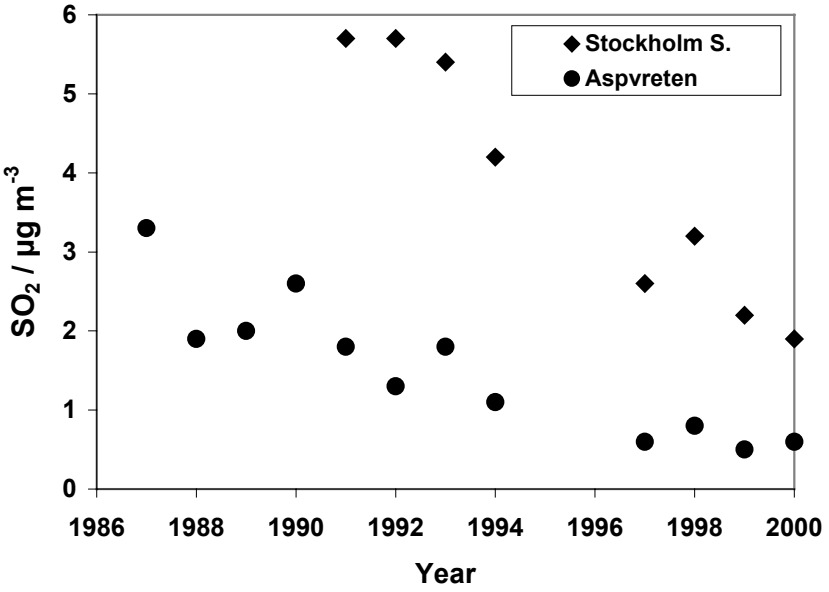

Figure II. Annual averages of SO_2 concentration in two sites in Sweden, Aspvreten (rural) and Stockholm (urban)

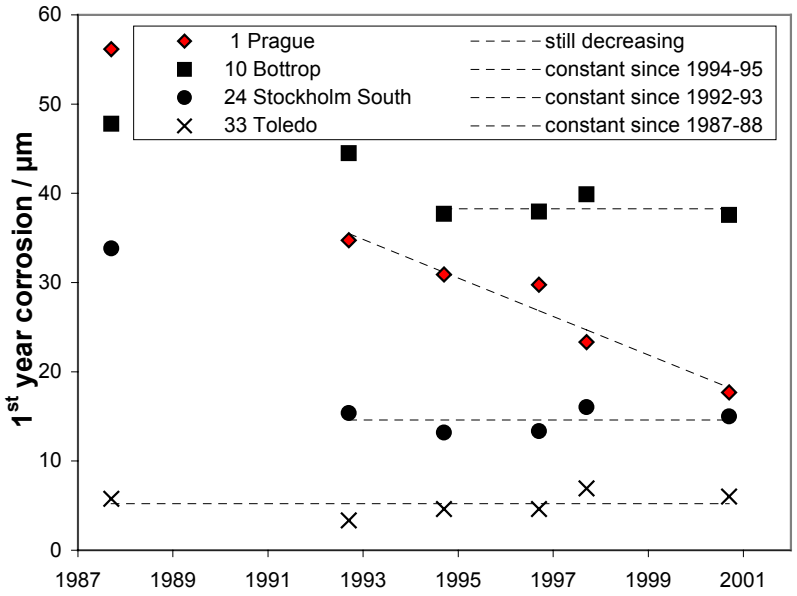

Figure III. Corrosion attack of carbon steel in unsheltered position after one year of exposure at selected sites in Europe

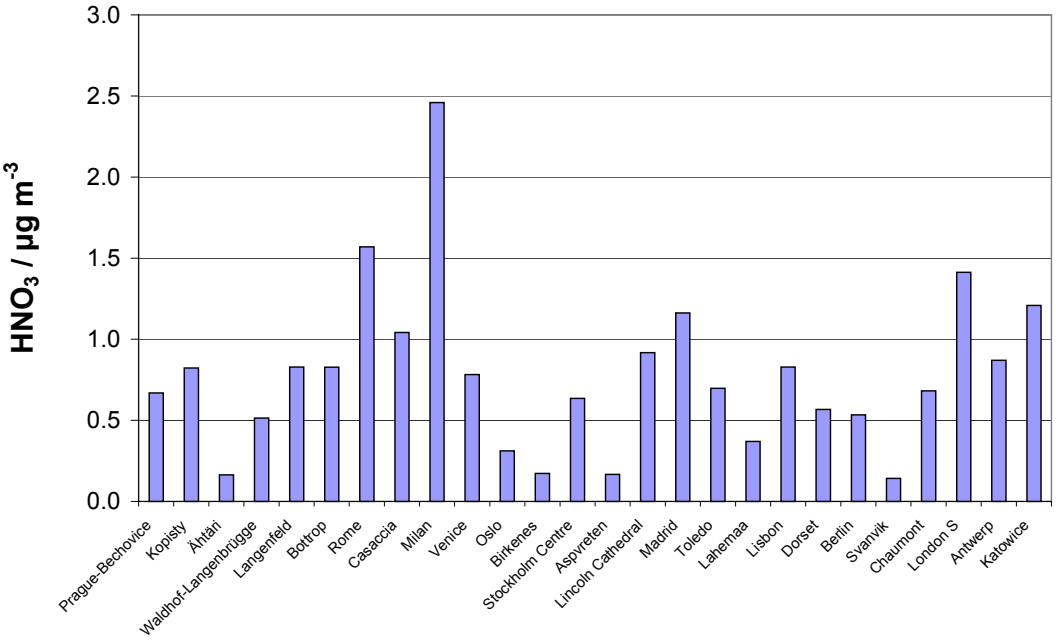

Figure IV. Results after one year of exposure (2002-2003) from passive sampling of HNO_3

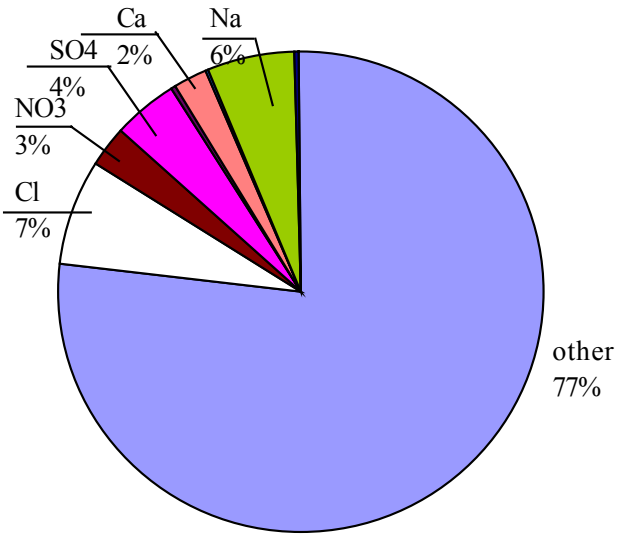

Figure V. Average chemical composition (mass %) of water-soluble particles deposited at the passive samplers exposed based on ICP Materials and targeted MULTI-ASSESS test sites

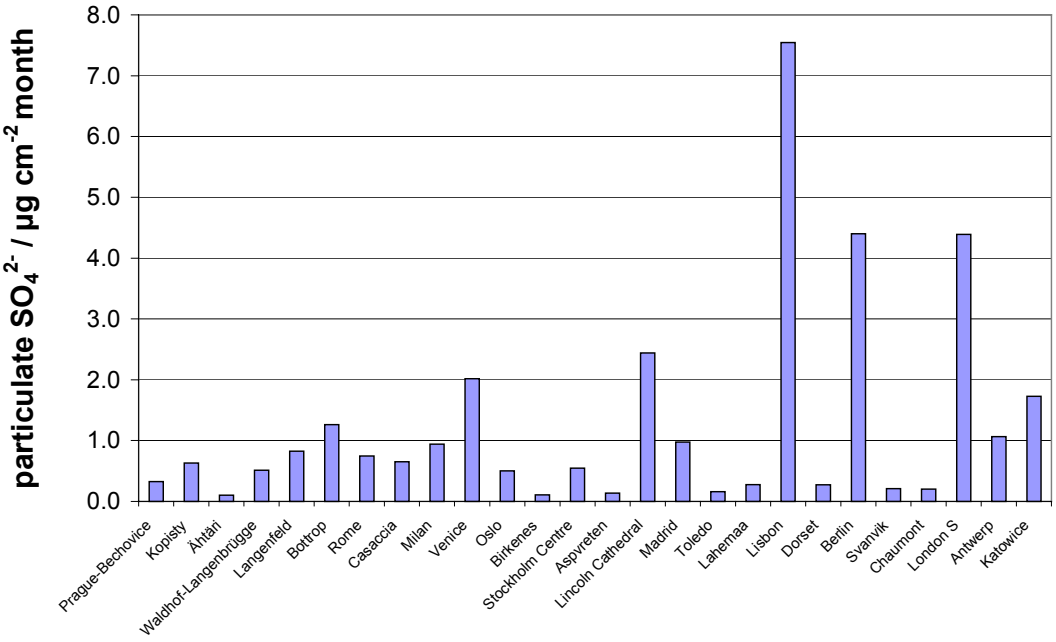

Figure VI. Results after one year of exposure from passive sampling of particulate SO_4^{2-}