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MULTI-POLLUTANT EXPOSURE PROGRAMME: RESULTS AFTER ONE YEAR OF EXPOSURE

Summary report by the Main Research Centre of the International Cooperative Programme on Effects of Air Pollution on Materials, including Historic and Cultural Monuments

I. INTRODUCTION

1. The first exposure programme of the International Cooperative Programme on Effects of Air Pollution on Materials, including Historic and Cultural Monuments (ICP Materials), which started in 1987, was followed from the end of 1997 by the new multi-pollutant exposure programme. To improve its efficiency and to take into account the new multi-pollutant situation, changes were made to the programme's network of test sites, the exposed materials and the characterization of the environment before the first exposure. The programme now includes 29 test sites in 15 European countries, Israel, Canada and the United States (fig. I). Withdrawals of material specimens were made after one and two years of exposure.

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2. Results from the first year of exposure in the multi-pollutant programme are now becoming available. From a corrosion perspective, one year is a relatively short time. However, the potential of the new data is enhanced by using the previous database for comparison. The present report (i) describes the creation of the database (chap. II); (ii) provides the characteristics of the new test sites, indicating, in particular, how they complement and extend the previous network (chap. III); and (iii) evaluates trends in corrosion of new materials by comparison with values from the first year of exposure in the original programme (chap. IV). For some materials this is the only comparison of trends which it is possible to make, while for limestone, steel and zinc, additional exposures and assessments of trends will follow. The inclusion of limestone as a new material (besides the metals zinc and carbon steel) in the "trend exposure" experiments constitutes an important contribution to the understanding of trends of the effects of air pollution on the deterioration of objects of cultural heritage.

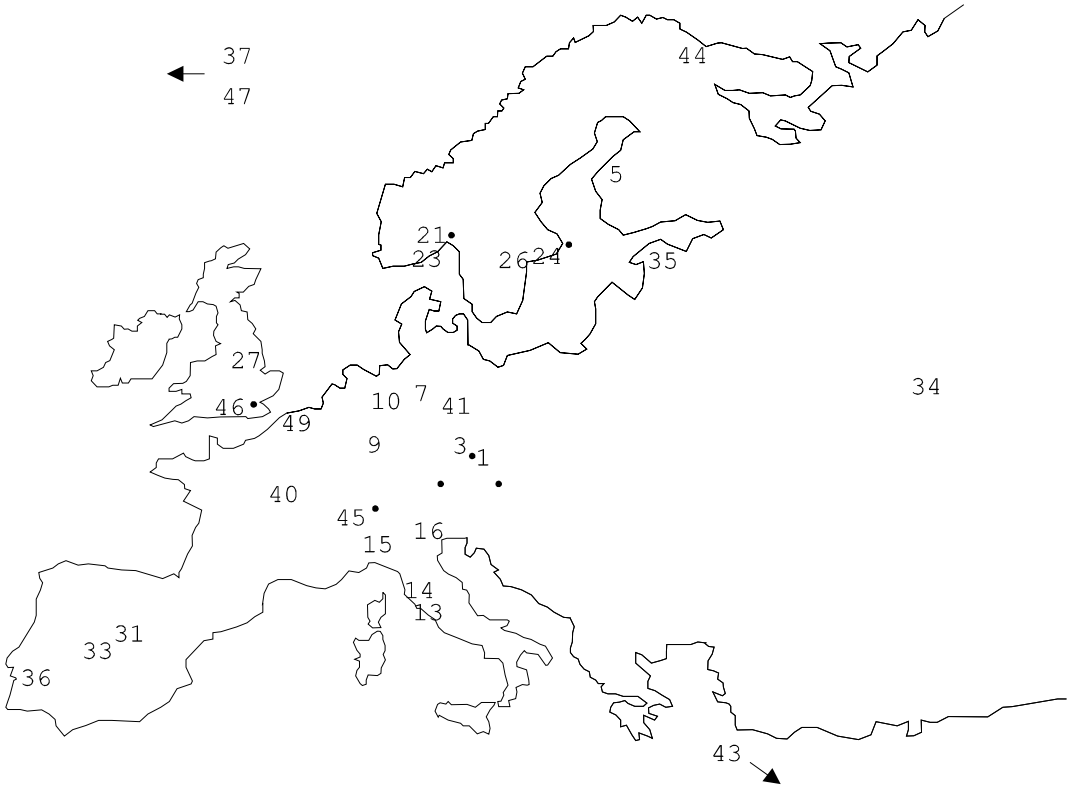

Figure I
Map showing approximate locations of European sites used in the multi-pollutant exposure programme (see table 1). The research centres, responsible for the evaluation of materials, are also indicated (•)

II. ESTABLISHMENT OF A DATABASE

3. Table 1 and figure I show the network of test sites used in the multi-pollutant programme. After careful examination of the extensive database obtained in the original exposure programme,

18 sites were considered redundant and excluded from the network. Keeping only 21 of the original 39 test sites and adding 8 new test sites with new pollutant situations and new combinations of climate and pollution parameters not only significantly improved the efficiency of the programme, but also better corresponded to its multi-pollutant character (see chap. III). These changes also increased the share of urban sites from 14 out of 39 to 16 out of 29 (by including, for example, new sites in Berlin, Paris and London).

Table 1
List of test sites used in the multi-pollutant exposure programme showing number, name, country and type. Sites 1-39 were also used in the original exposure programme and sites 40-49 are new test sites

No	Name	Country	Type
1	Prague-Letnany	Czech Republic	Urban
3	Kopisty	Czech Republic	Industrial
5	Ähtäri	Finland	Rural
7	Waldhof-Langenbrügge	Germany	Rural
9	Langenfeld-Reusrath	Germany	Rural
10	Bottrop	Germany	Industrial
13	Rome	Italy	Urban
14	Casaccia	Italy	Rural
15	Milan	Italy	Urban
16	Venice	Italy	Urban
21	Oslo	Norway	Urban
23	Birkenes	Norway	Rural
24	Stockholm South	Sweden	Urban
26	Aspvreten	Sweden	Rural
27	Lincoln Cathedral	United Kingdom	Urban
31	Madrid	Spain	Urban
33	Toledo	Spain	Rural
34	Moscow	Russian Federation	Urban
35	Lahemaa	Estonia	Rural
36	Lisbon	Portugal	Urban
37	Dorset	Canada	Rural
40	Paris	France	Urban
41	Berlin	Germany	Urban
43	Tel Aviv	Israel	Urban
44	Svanvik	Norway	Rural
45	Chaumont	Switzerland	Rural
46	London	United Kingdom	Urban
47	Los Angeles	United States	Urban
49	Antwerp	Belgium	Urban

4. The reporting of environmental data has been improved by using electronic communication, by reporting only monthly data and by replacing the not easily available parameter “time of etness” with temperature and relative humidity.

5. For the development of dose-response functions it is important that the concentrations of the pollutants at the compared sites are significantly different. Table 2 shows that the distribution

of concentration values for the gaseous pollutants is fairly good.

Table 2
Percentage of test sites with concentrations in different ranges based on annual SO_2, NO_2 and O_3 data for the first year

Concentration range, µg/m^3	SO_2	NO_2	O_3
≤10	63%	30%	0%
10 to 30	30%	30%	13%
30 to 50	7%	26%	52%
>50	0%	13%	35%

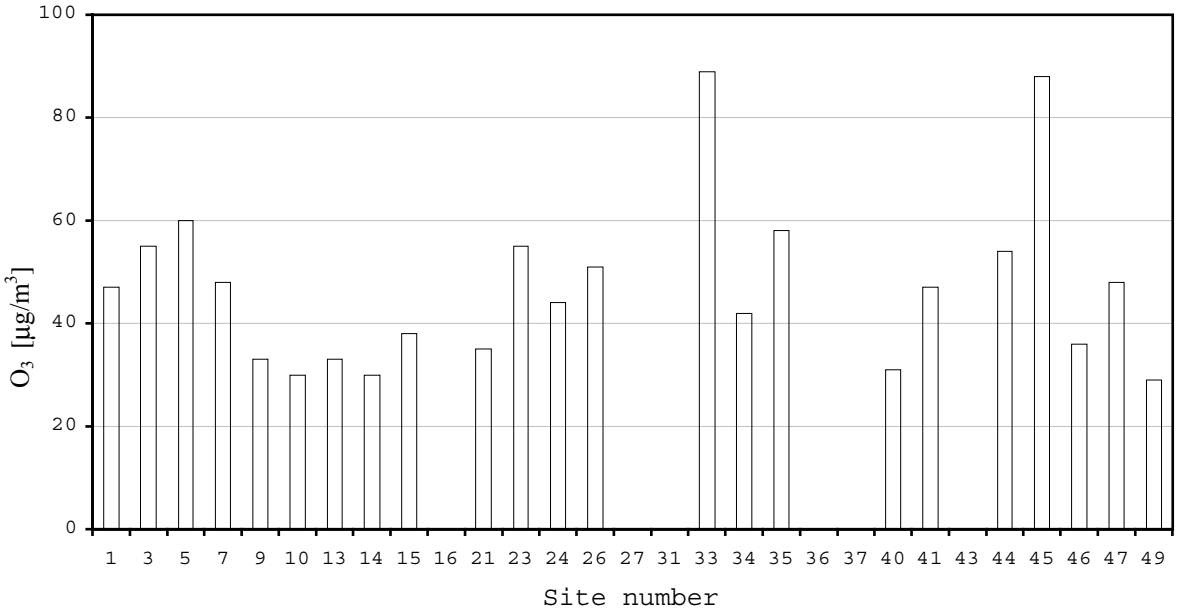

Figure II
Average O_3 concentration for the first year of the multi-pollutant exposure programme. Site numbers are explained in table 1 and figure I

6. SO_2 values range from about 30 µg/m^3 to 0.2 µg/m^3 at the Scandinavian background (EMEP) stations. As could be expected, low values dominate since the total amount of sulphur emitted in Europe has been reduced during the years of ICP Materials activities. NO_2 values range from about 80 µg/m^3 to 0.7 µg/m^3. Low values dominate, but the spread of values is significant. O_3 values range from about 90 µg/m^3 down to 30 µg/m^3. As can be seen in figure II, low values are observed in the big cities and high values in rural areas in the south and at high altitudes in the alpine area.

7. Corrosion effects on materials are evaluated by standardized or well-established procedures at dedicated/appointed programme sub-centres. Each sub-centre is responsible for a material, or group of materials, for which it performs all corrosion analyses regardless of where samples were exposed. The sub-centres are:

- SVÚOM, Prague, Czech Republic, responsible for the structural metals: carbon steel, weathering steel, zinc (1987-1995) and aluminium, and the materials for trend analysis: unalloyed carbon steel and zinc (since 1987);
- Bavarian State Department of Historical Monuments, Munich, Germany, responsible for the structural metals: copper and cast bronze, including pre-treated bronzes;
- Building Research Establishment (BRE), Garston, Watford, United Kingdom, responsible for the stone materials: limestone (also for trend analysis) and sandstone;
- Norwegian Institute for Air Research (NILU), Lilleström, Norway, responsible for the paint coatings: coil-coated galvanized steel with alkyd melamine, steel panel with alkyd, wood panel with alkyd paint and wood panel with primer and acrylate;
- Swedish Corrosion Institute, Stockholm, Sweden, responsible for the electric contact materials: nickel, copper, silver, tin and credit card connectors of three performance classes, and the polymer materials: polyamide and polyethylene;
- Institute of Chemistry, Academy of Fine Arts, Vienna, Austria, responsible for glass materials representative of medieval stained glass windows including potash-lime-silica glass M1 (sensitive) and potash-lime-silica glass M3;
- EMPA, Corrosion/Surface Protection, Dübendorf, Switzerland, responsible for the structural metal: zinc (since 1997).

8. The materials withdrawn after one year of exposure include carbon steel, zinc, copper, cast bronze, limestone and steel panel with alkyd. Glass materials are also included in the multi-pollutant programme but the first withdrawal will be made after three years of exposure at the end of 2000. As an example of results, figure III shows the corrosion attack values of unsheltered bronze obtained within the multi-pollutant programme, compared with values obtained a decade earlier within the original programme.

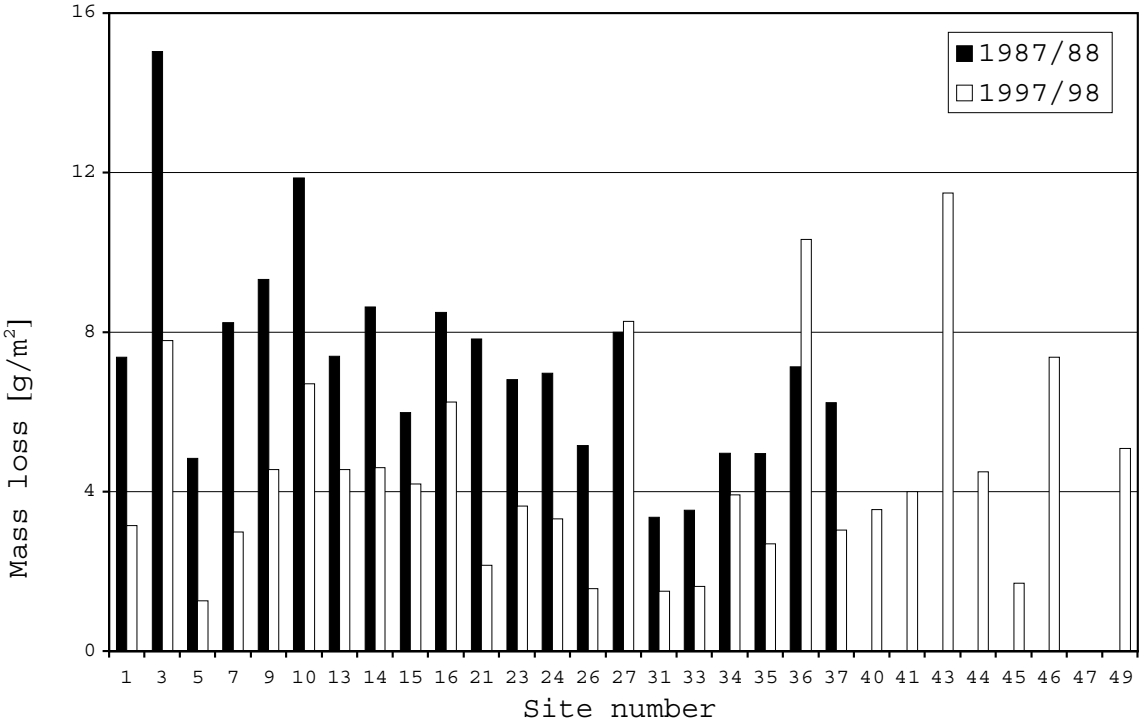

Figure III
Corrosion attack on unsheltered bronze after one year of exposure during 1987/88 and 1997/98. Site numbers are explained in table 1 and figure I

III. CHARACTERISTICS OF NEW SITES

9. The list of test sites was given in table 1. The new sites are urban sites in Paris, Berlin, Tel Aviv, London, Los Angeles and Antwerp, and rural sites in Svanvik and Chaumont.

A. Paris

10. With respect to both climate and pollution, Paris is similar to Milan. It is relatively warm and dry, with very high NO_2 concentrations. In the original programme, Milan was considered as an extreme site due to the high NO_2 concentration but with the inclusion of Paris a gap in experienced NO_2 concentrations between Milan and the remaining sites was filled. Compared to Milan, Paris has a lower amount of precipitation of lower acidity; thus the estimated relative contribution of dry deposition is higher. The corrosion values are normal with the exception of lower values for copper, probably due to the low O_3 concentrations. Copper is the only metallic material for which a clear correlation with O_3 concentration has been established in the field. Inclusion of the test site in Paris was also important for overall evaluation, since it is one of 5-10 sites having SO_2 concentrations higher than 10 $\mu g/m^3$.

B. Berlin

11. With respect to both climate and pollution Berlin is very similar to Prague. It has slightly lower SO_2 values but higher NO_2 values. The corrosion values are also similar with the exception of unsheltered limestone, for which the value is significantly lower.

C. Tel Aviv

12. The corrosion values are very high, similar to Bottrop, except for sheltered copper, for which it is very low. The environmental data are extreme: Tel Aviv is the warmest site in the network, with an annual average temperature of 25° C and it also has the highest annual average SO_2 concentration of 35 $\mu g/m^3$, compared to 25 $\mu g/m^3$ in Bottrop.

D. Svanvik

13. The climate is very cold, with an annual average temperature of about –2° C, which is unique in the programme's test sites network. Otherwise it is similar to the EMEP sites in Aspvreten, except for the higher SO_2 values. The corrosion values are similar or higher than in Aspvreten except for limestone, for which it is lower.

E. Chaumont

14. Chaumont is relatively similar to Ähtäri, a background site in Finland. It is warmer, with an annual average temperature of about 7° C. Compared to Ähtäri, it has higher NO_2 values combined with higher O_3 values, which is unique and probably due to its location in the mountains. The corrosion values are slightly higher except for limestone, for which they are much higher than those for samples exposed in Ähtäri.

F. London

15. So far climatic data are not available but with respect to pollution London is similar to Rome. The corrosion values are generally higher than those in Rome, probably due to the more humid climate.

G. Los Angeles

16. Los Angeles is truly unique, it is not like any other site in the programme. The pollution situation is like Stockholm but with even lower SO_2 concentration, less than 1 $\mu g/m^3$. The climate on the other hand is more like Madrid, warm and dry. So far, few corrosion values have been evaluated but the existing values are all higher than those obtained in Stockholm as well as in Madrid.

H. Antwerp

17. Antwerp is relatively similar to both Milan and Paris but the NO_2 concentrations are less extreme, about 50 µg/m^3 compared to 70 µg/m^3 in Paris and 90 µg/m^3 in Milan. The corrosion values are similar to those obtained in Milan.

IV. TRENDS

18. The "trend exposures" consist of repeated one-year exposures of material samples on the test sites starting and ending in the autumn. Their aim is to confirm the existing, and to provide new, information on the environmental effects of previous reductions in acidifying air pollutants achieved under the Convention. They are also a method for identifying other extraordinary environmental changes that result in damage to materials.

19. The results from trend exposures of unalloyed carbon steel and zinc were recently published in the Working Group on Effects report on Trends in Impacts of Long-range Transboundary Air Pollution [1/]. The new results achieved so far within the multi-pollutant exposure programme have not yet provided sufficient additional information to merit, already at this stage, a re-analysis of the steel and zinc data. Instead, more attention is given to new materials that have not previously been subject to trend analysis: copper, bronze, limestone and painted steel. However, the main results achieved for carbon steel and zinc within the original programme are also presented for comparison.

20. Figure IV shows some results of the previous trend analysis that confirmed clear trends in observed values of the environmental parameters SO_2, NO_2 and H^+ and in the corrosion of steel and zinc exposed in both unsheltered and sheltered position. No trend was observed in the O_3 concentration. The analysis also shows that SO_2 concentration is the most important parameter contributing to the decrease in atmospheric corrosion. For unsheltered materials, the decrease in corrosion rate is also partly related to decreasing H^+ in precipitation. However, the contribution of this parameter is on average, but not on all sites, much smaller than that of dry deposition.

21. The same methodology as applied for carbon steel and zinc was used for calculating average corrosion values for copper, bronze, limestone and painted steel. Table 3 shows the calculated trend values based on data for sites kept from the original programme. As in previous analyses, clear trends are observed for SO_2, NO_2 and H^+ of precipitation but not for O_3. The trends are also clear for the corrosion attack of all materials, however to a varying extent. (It should nevertheless be noted that on a few sites the values of some environmental parameters and of corrosion of some materials were actually increasing.)

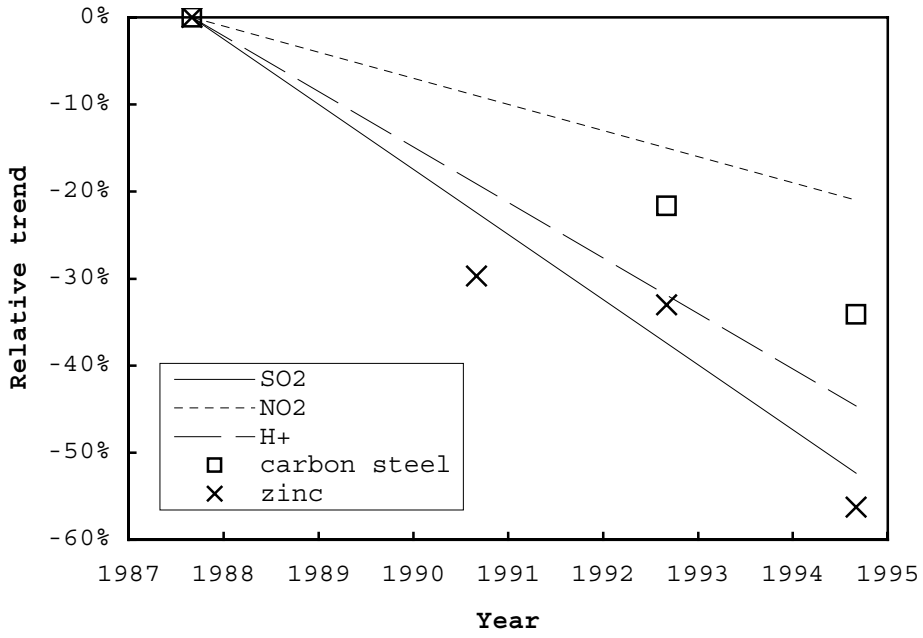

Figure IV
Relative trends in SO_2, NO_2, acidity (H^+), and corrosion of unsheltered unalloyed carbon steel and zinc. All values are expressed relative to the initial (1987/88) value. For environmental data. the average trend during the eight-year period is indicated instead of the individual annual averages

Table 3
Trends illustrated by average values from 1987/88 and 1997/98 of SO_2, NO_2, acidity, corrosion of unsheltered and sheltered copper and bronze, and corrosion of unsheltered limestone and painted steel. The values are based on data from the sites common to the original and multi-pollutant exposure programme

Parameter	**unit**	**1987/88**	**1997/98**	**Sites with increasing values**
SO_2	$\mu g/m^3$	16	5.3	1 of 18
NO_2	$\mu g/m^3$	29	22	2 of 16
H^+	mg/l	0.043	0.015	0 of 10
Copper, unsheltered	g/m^2	9.9	6.8	3 of 19
Copper, sheltered	g/m^2	6.3	4.0	3 of 19
Bronze, unsheltered	g/m^2	6.9	3.5	0 of 19
Bronze, sheltered	g/m^2	2.3	1.5	2 of 19
Limestone	µm	12	6.4	2 of 19
Paint on steel	mm	2.1	1.0	2 of 19

22. Figure V shows the relative decrease in the same manner as was presented in figure IV and

based on the values given in table 3. Note that the resulting values are not necessarily comparable to those obtained in the previous trend analysis due to the different selection of test sites. However, the trends in SO_2, NO_2 and H^+ seem to fit relatively well with figure IV, which makes a comparison possible. The average reduction is for most materials between 30% and 50% for the ten-year period, with the lowest value for unsheltered bronze (compare fig. III).

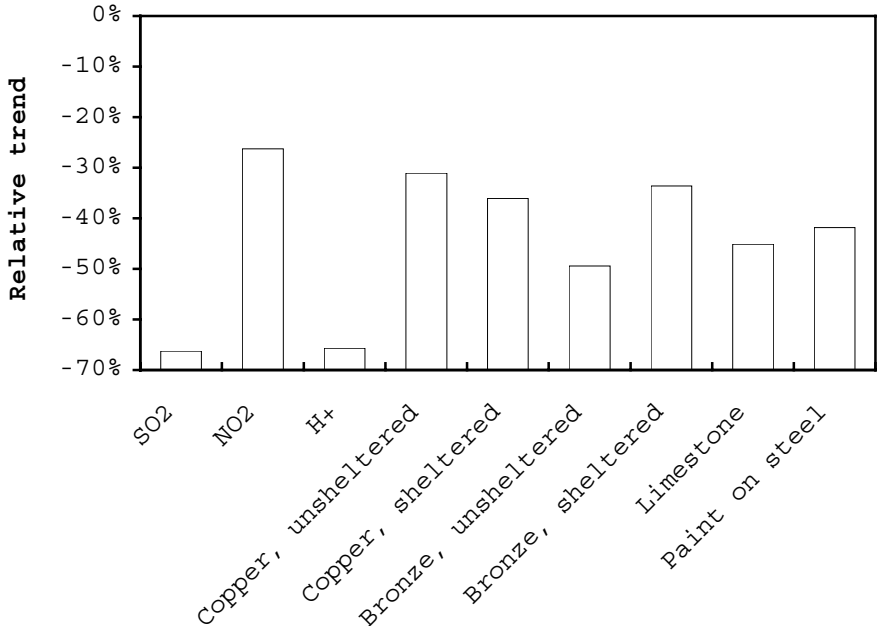

Figure V
Relative trends during the period 1987/88 to 1997/98 in SO_2, NO_2, acidity (H^+), corrosion of unsheltered and sheltered copper and bronze, and corrosion of unsheltered limestone and painted steel

V. CONCLUSIONS

23. A database of environmental and corrosion data based on the results after one year of exposure in the multi-pollutant exposure programme has been created and used for comparison with data obtained after one year of exposure in the original exposure programme.

24. Compared to the original exposure programme, 18 redundant sites were excluded, 21 original sites kept, and 8 new test sites added. The data on climate, pollution and corrosion from the new sites show clearly that they constitute a significant contribution to the programme by incorporating new pollutant situations and new combinations of climate and pollution.

25. Trends of decreasing pollution parameters (for SO_2, NO_2, H^+) and corrosion of unalloyed carbon steel and zinc exposed both in sheltered and in unsheltered positions were previously established using data from the original exposure programme. The recent results confirm trends of

decreasing values for SO_2, NO_2 and H^+, as well as decreasing corrosion rates for additional materials: unsheltered and sheltered copper and cast bronze, and unsheltered limestone and

painted steel. The reductions are on average about 30% to 50% during the period 1987 to 1997, depending on the material and exposure conditions. No trend was observed in the O_3 concentration.

Note

1/ Trends in Impacts of Long-range Transboundary Air Pollution. Technical report prepared by the Bureau and the International Cooperative Programmes of the Working Group on Effects. ISBN 1 870393 52 X, 1999.