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RESULTS AFTER FOUR YEARS OF EXPOSURE IN THE MULTI-POLLUTANT PROGRAMME AND FURTHER DEVELOPMENT OF THE PROGRAMME

Note prepared by the Main Research Centre of the International Cooperative Programme on Effects of Air Pollution on Materials, including Historic and Cultural Monuments (ICP Materials)

Introduction

1. This note presents preliminary results from the withdrawal after four years of exposure in the multi-pollutant programme (1997-2001). Plans for future activities of the programme are also described with particular emphasis on synergisms between ICP Materials and the MULTI-ASSESS project within the European Union's fifth framework programme, which started in January 2002.

I. MULTI-POLLUTANT EXPOSURE PROGRAMME

2. Withdrawals in the multi-pollutant exposure programme (1997-2001) were made after one, two and four years of exposure. The programme included 30 test sites with ongoing measurements

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in 16 European countries, and in Canada, Israel and the United States. The latest addition to the programme is site number 50 in Katowice, Poland, which was included in the latest trend exposure (2000-2001) (table 1).

3. Corrosion effects on materials are evaluated by standardized or well-established procedures. Also, corrosion effects on materials are evaluated at dedicated sub-centres, each responsible for a material, or group of materials, and for performing all corrosion analyses of this material regardless of where it was exposed [1-5]. Glass materials are also included in the multi-pollutant programme but with withdrawals after three and four years of exposure. The following research sub-centres have participated in the programme:

(a) The Institute for Research and Testing Corrosion and Corrosion Protection (SVÚOM), Prague; responsible for the structural metals (carbon steel, weathering steel, zinc) (1987-1995) and aluminium and the trend materials (unalloyed carbon steel and zinc) (since 1987);

(b) The Bavarian State Department of Historical Monuments, Munich, Germany; responsible for the structural metals (copper and cast bronze including pretreated bronzes);

(c) The Building Research Establishment (BRE), Garston, Watford, United Kingdom; responsible for the stone materials (limestone (also as trend material), and sandstone);

(d) The Norwegian Institute for Air Research (NILU), Kjeller, 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);

(e) The Institute of Chemistry, Academy of Fine Arts, Vienna; responsible for glass materials representative of medieval stained glass windows (including potash-lime-silica glass M1 (sensitive) and potash-lime-silica glass M3);

(f) The Swiss Federal Laboratories for Materials Testing and Research (EMPA), Corrosion/Surface Protection, Dübendorf, Switzerland; responsible for the structural metal zinc (since 1997).

4. The selected results for zinc, bronze, limestone and paint-coated steel are shown below. The results derived within ICP Materials can, in addition to quantifying the total corrosion attack, also be used to assess the metal release (run-off) as is illustrated in figure I for unsheltered zinc. As a result of the weathering of roofs, facades and other constructions, which is accelerated due to acidifying pollutants, a significant part of the metals are emitted to the biosphere. High levels of heavy metals in sludge used as fertilizer, in bottom sediments or in drinking water may in the long run have adverse effects on biological systems and human health.

5. Since the concentration of sulphur dioxide in many European countries has decreased significantly while the concentrations of nitrogen pollutants and ozone remain high, the relative effects of NO_x, ozone and particulate matters are becoming more important. In figure II a trend for unsheltered bronze is evident. Even so, the differences between urban and rural regions are still significant, as can be seen by comparing the values for Stockholm South and Aspvreten, a rural site about 80 km south of Stockholm. The urban value is more than twice the rural value.

Table 1. List of ICP Materials test sites showing number, name, country, type and period in use

No	Name	Country	Site type	Period in use
1	Prague-Letnany	Czech Republic	Urban	1987-
2	Kasperske Hory	Czech Republic	Rural	1987-1997
3	Kopisty	Czech Republic	Industrial	1987-
4	Espoo	Finland	Urban	1987-1997
5	Ähtäri	Finland	Rural	1987-
6	Helsinki-Vallila	Finland	Industrial	1987-1997
7	Waldhof-Langenbrügge	Germany	Rural	1987-
8	Aschaffenburg	Germany	Urban	1987-1997
9	Langenfeld-Reusrath	Germany	Rural	1987-
10	Bottrop	Germany	Industrial	1987-
11	Essen-Leithe	Germany	Rural	1987-1997
12	Garmisch-Partenkirchen	Germany	Rural	1987-1997
13	Rome	Italy	Urban	1987-
14	Casaccia	Italy	Rural	1987-
15	Milan	Italy	Urban	1987-
16	Venice	Italy	Urban	1987-
17	Vlaardingen	Netherlands	Industrial	1987-1997
18	Eibergen	Netherlands	Rural	1987-1997
19	Vredepeel	Netherlands	Rural	1987-1997
20	Wijnandsrade	Netherlands	Rural	1987-1997
21	Oslo	Norway	Urban	1987-
22	Borregard	Norway	Industrial	1987-1997
23	Birkenes	Norway	Rural	1987-
24	Stockholm South	Sweden	Urban	1987-
25	Stockholm Centre	Sweden	Urban	1987-1997
26	Aspvreten	Sweden	Rural	1987-
27	Lincoln Cathedral	United Kingdom	Urban	1987-
28	Wells Cathedral	United Kingdom	Urban	1987-1997
29	Clatteringshaws Loch	United Kingdom	Rural	1987-1997
30	Stoke Orchard	United Kingdom	Rural Industry	1987-1997
31	Madrid	Spain	Urban	1987-
32	Bilbao	Spain	Industrial	1987-1997
33	Toledo	Spain	Rural	1987-
34	Moscow	Russian Federation	Urban	1987-
35	Lahemaa	Estonia	Rural	1987-
36	Lisbon	Portugal	Urban	1987-
37	Dorset	Canada	Rural	1987-
38	Research Triangle Park	United States	Rural	1987-1997
39	Steubenville	United States	Industrial	1987-1997
40	Paris	France	Urban	1997-
41	Berlin	Germany	Urban	1997-
43	Tel Aviv	Israel	Urban	1997-
44	Svanvik	Norway	Rural	1997-
45	Chaumont	Switzerland	Rural	1997-
46	London	United Kingdom	Urban	1997-
47	Los Angeles	United States	Urban	1997-
49	Antwerp	Belgium	Urban	1997-
50	Katowice	Poland	Industrial	2000-

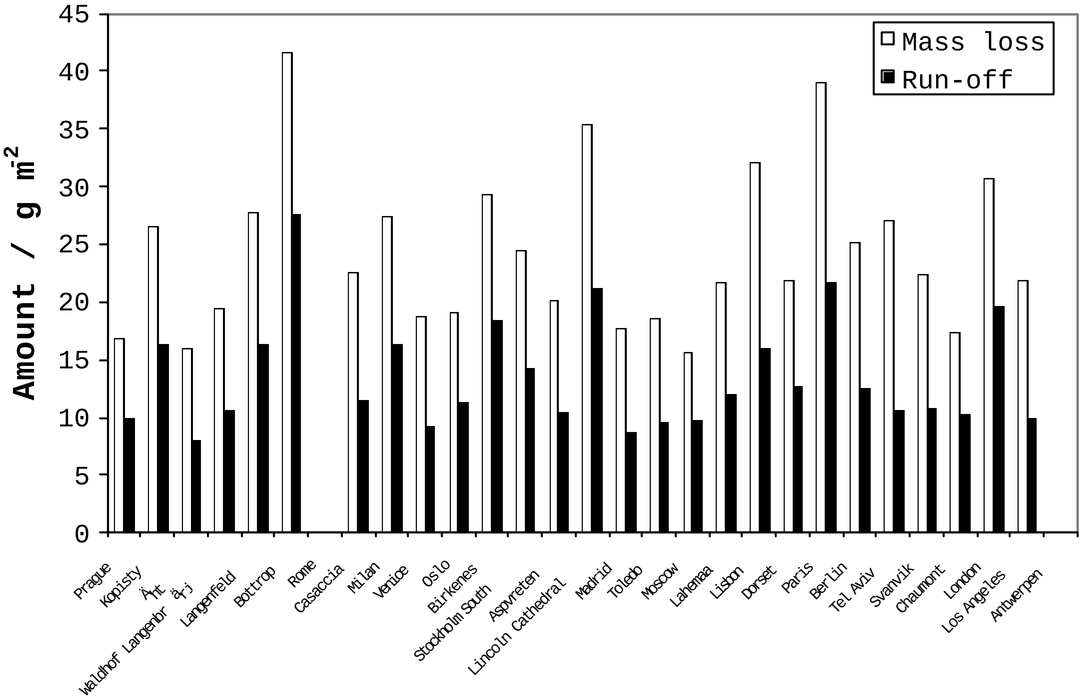

Figure I. Run-off and total corrosion attack (mass loss) for unsheltered zinc after four years of exposure in the multi-pollutant programme

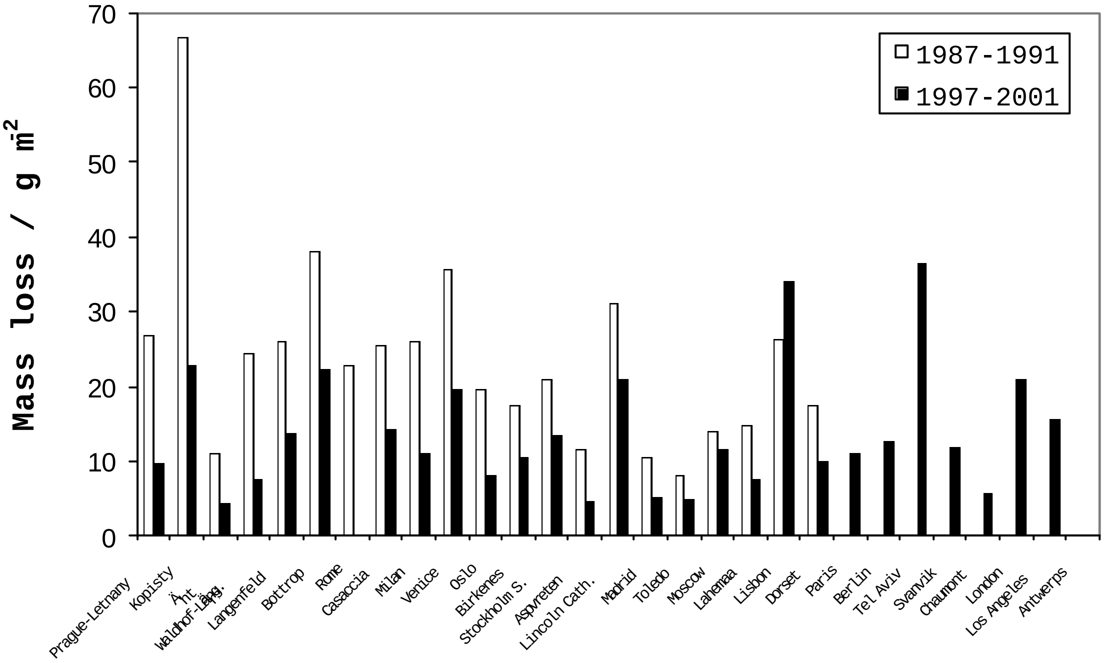

Figure II. Corrosion attack for unsheltered bronze after four years of exposure in the multi-pollutant programme

6. Values of corrosion attack for Portland limestone after 1, 2 and 4 years of exposure are given in figure III and values for the exposed paint system are given in table 2. The kinetic information will be used when constructing the dose-response functions and the incorporation of time in these functions makes it possible to estimate the lifetime of technical constructions and objects of cultural heritage.

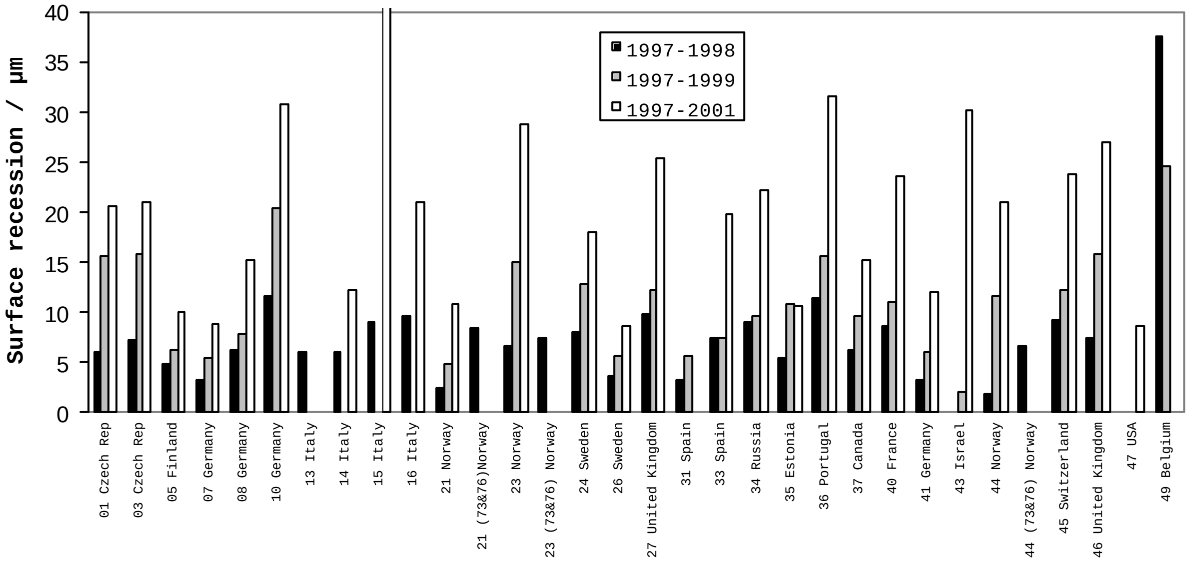

Figure III. Corrosion attack of unsheltered limestone after one, two and four years of exposure in the multi-pollutant programme

Table 2. Corrosion attack (damage from cut in mm) of unsheltered alkyd painted steel panels after one, two and four years of exposure in the multi-pollutant programme

Site	Country	Place	One year (97/98)	Two years (97/99)	Four years (97/01)
01	Czech Republic	Prague- Bechyne	3	4	6
03	Czech Republic	Kopisty	4	6	7
05	Finland	Ähtari	3	4	4
07	Germany	Waldhof L.	3	4	5.5
09	Germany	Langenfeld	3	4	5
10	Germany	Bottrop	3	5	7
13	Italy	Rome	2.5	2.5	*
14	Italy	Casaccia	3	3	3.5
15	Italy	Milan	3	3	4
16	Italy	Venice	2	3	3
21	Norway	Oslo	2	2.5	3
23	Norway	Birkenes	4	6	8
24	Sweden	Stockholm	3	3	3
26	Sweden	Aspvreten	4	4.5	5.5
27	United Kingdom	Lincoln Cathedral	5	6	5
31	Spain	Madrid	1.5	2	2.5
33	Spain	Toledo	1.5	2	3
34	Russian Federation	Moscow	3.5	3.5	3
35	Estonia	Lahemaa	3	5	6
36	Portugal	Lisbon	5	4	5
37	Canada	Dorset	3.5	3.5	6
40	France	Paris	1.5	3	2
41	Germany	Berlin	4	3	4
43	Israel	Tel Aviv	2.5	3	3
44	Norway	Svanvik	3	3.5	7
45	Switzerland	Chaumont	2	2.5	5
46	United Kingdom	London	5	4	5
47	United States	Los Angeles	2.5	2.5	2.5
49	Belgium	Antwerp	2.5	3	*

* = missing samples

II. FUTURE DEVELOPMENT OF THE PROGRAMME

7. Air pollutants cause severe damage to materials in buildings and monuments. The most efficient policy measure for safeguarding objects of cultural heritage is a reduction in emissions of harmful pollutants. To prevent or reduce the effects on human health and the environment as a whole, Council Directive 1999/30/EC has recently been issued relating to limit values for sulphur dioxide, oxides of nitrogen, particulate matter and lead in ambient air. The limit values for effects on materials have not been included even though limit values for SO_2 intended to protect health and ecosystems may not be sufficient for preventing damage to cultural heritage. The absence of material limit values is a serious shortcoming for the sustainable protection and management of Europe's cultural heritage.

8. The decreasing SO_2 levels in most parts of Europe and the increasing car traffic causing high levels of N compounds, ozone and particulates have created a new multi-pollutant situation. This was acknowledged in the activities within the UNECE Convention on Long-range Transboundary Air Pollution, with its "multi-pollutant, multi-effect" Gothenburg Protocol. In contrast to SO_2, the effects of O_3 and N compounds, and in particular the total effects of car traffic, are not well documented. This is especially true for nitric acid (HNO_3), as well as particulates, which can damage materials both by increasing the rate of degradation and by soiling.

9. In order to extend the measurements and evaluation of these important pollutants, which required additional financing, an application for the project Model for multi-pollutant impact and assessment of threshold levels for cultural heritage (MULTI-ASSESS) was submitted to the European Union's fifth framework programme within the key action "City of tomorrow and cultural heritage". The project was favourably evaluated and started on 1 January 2002. The main objectives of the MULTI-ASSESS project are:

(a) To develop multi-pollutant deterioration and soiling models of dry and wet deposition of gases and particulates on materials used in cultural heritage objects and to obtain dose-response functions quantifying the effects;

(b) To use the dose-response functions for assessing pollution thresholds to be implemented in the future development of European Union directives on urban air quality in order to minimize the pollution effects on cultural heritage objects and for mapping areas exceeding thresholds in Europe; and

(c) To adapt and validate passive samplers for measuring concentrations of nitric acid and particles and to develop a kit for the rapid assessment of the deterioration risk to objects of cultural heritage.

10. In MULTI-ASSESS, deterioration and soiling models resulting in dose-response functions for materials used in objects of cultural heritage will be developed including the effects of HNO_3 and particulates as well as other pollutants (SO_2, NO_2, O_3), climate (temperature, relative humidity and sun radiation), and characteristics of precipitation (pH, amount and ion analysis). Passive samplers for HNO_3 and particles will be developed and validated. They will be included in a kit for the rapid low-cost assessment of the deterioration risk to objects of cultural heritage, consisting of a package of selected material specimens and passive samplers for pollutants. The performance of this ambitious and innovative project will be possible as MULTI-ASSESS completes and extends

the work of ICP Materials. The broad field exposure will be performed using the network of 30 test sites in 15 European countries and Canada, Israel and United States. In addition, targeted field exposures will be performed in Athens, London, Prague and Rome with selected extensive analyses of environmental parameters, corrosion attack and soiling. The field exposures will be complemented by targeted laboratory exposures in climate chambers.

11. The dose-response functions will be used for the assessment of pollution thresholds for the future development of European Union directives on urban air quality in order to minimize the pollution effects on historic and cultural objects and for mapping areas in Europe with increased risk of damage. The kit will be useful for people in heritage management, which will enable them to undertake this type of work for their own requirements. For example, monuments on the world heritage list of the United Nations Educational, Scientific and Cultural Organization have special monitoring requirements. Figure IV gives an overview of the expected synergistic effects between ICP Materials and MULTI-ASSESS.

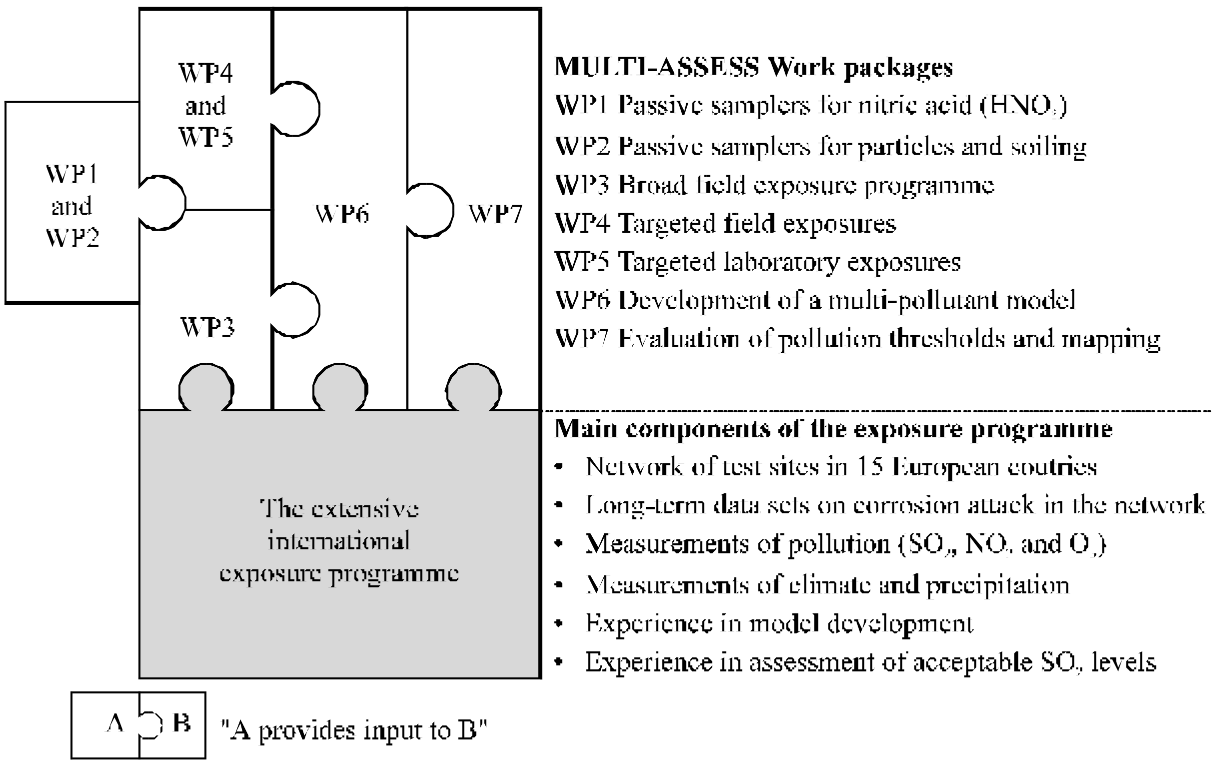

Figure IV. Schematic view of the relations and synergism between ICP Materials (the extensive international exposure programme) and MULTI-ASSESS

12. At the beginning of 2002 an application was submitted to the European Union's fifth framework programme within the key action "City of tomorrow and cultural heritage" with the aim of incorporating newly associated States to the project. The project was favourably evaluated and negotiations will soon start with the European Commission. The incorporation of partners from Poland and Latvia in the project will especially strengthen the WP4 element by incorporating several different stone materials and concrete in addition to Portland limestone, which has been

used in ICP Materials as a trend material, and by adding a new targeted site in Cracow, Poland, characterized by comparatively high SO_2 levels.

13. With the inclusion of Poland and Latvia, MULTI-ASSESS includes 15 partners from 13 countries. In addition to the Main Research Centre all six research sub-centres of ICP Materials are among these partners. Table 3 shows an overview of the partners of MULTI-ASSESS.

Table 3. Overview of participants showing participant number (No), acronym, role, organization's name and city/country

No	Role[#]	Organization's full name	Country/city
1	CO[##]	Korrosionsinstitutet Swedish Corrosion Institute AB	Sweden / Stockholm
2	AC[##]	Academy of Fine Arts	Austria / Vienna
3	AC[##]	Bavarian State Department for Historical Monuments	Germany / Munich
4	AC[##]	Swiss Federal Labs. for Materials Testing and Research	Switzerland / Dübendorf
5	CR	Swedish Environmental Research Institute Ltd.	Sweden / Gothenburg
6	AC	CNR Institute for Atmospheric Pollution	Italy / Rome
7	AC	University of Athens	Greece / Athens
8	CR	Middlesex University	United Kingdom / London
9	CR[##]	SVUOM Ltd.	Czech Republic / Prague
10	CR[##]	Building Research Establishment Ltd.	United Kingdom / Watford
11	CR[##]	Norwegian Institute for Air Research	Norway / Kjeller
12	AC	Institute of Precision Mechanics	Poland / Warsaw
13	AC	Riga Technical University	Latvia / Riga
14	SC	LISA - Université Paris XII	France / Paris
15	SC	EEIC - Estonian Environment Information Centre	Estonia / Tallinn

Notes:
[#]CO: coordinator; CR: principal contractor; AC: assistant contractor; SC: subcontractor.
[##]Main research centre / sub-centre of ICP Materials.

III. CONCLUSIONS

14. Results are available from the multi-pollutant exposure programme after one, two and four years of exposure. While results are still preliminary in anticipation of the statistical evaluation of four-year results and the results obtained in connection with synergistic actions with MULTI-ASSESS (fifth framework programme), the following conclusions can be made:

(a) The decreasing trends in corrosion are evident also for four-year exposures in addition to the previously evaluated two-year and one-year exposures;

(b) Despite the decreasing trends there are still significant differences in corrosion attack when comparing polluted and unpolluted sites in urban and rural areas;

(c) The results achieved can also be used for assessing the release of metals to the environment due to pollution;

(d) The incorporation of time in the dose-response functions makes it possible to estimate the lifetime of technical constructions and objects of cultural heritage.

IV. REFERENCES

Report No 35. Results from the multi-pollutant programme: Corrosion attack on carbon steel after 1 and 2 years of exposure (1997-1999).

Report No 36. Results from the multi-pollutant programme: Corrosion attack on zinc after 1 and 2 years of exposure (1997-1999).

Report No 37. Results from the multi-pollutant programme: Corrosion attack on copper and bronze after 1 and 2 years of exposure (1997-1999).

Report No 38. Results from the multi-pollutant programme: Corrosion attack on limestone after 1 and 2 years of exposure (1997-1999).

Report No 39. Results from the multi-pollutant programme: Corrosion attack on painted steel after 1 and 2 years of exposure (1997-1999).

Note: The references have been reproduced as received by the secretariat.