



**ATMOSPHERIC CORROSION EFFECTS OF AIR POLLUTION
ON MATERIALS AND CULTURAL PROPERTY IN ASIA AND AFRICA**

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ABSTRACT

This project is part of the Swedish International Development Co-operation Agency (Sida) funded Program on Regional Air Pollution in Developing Countries (RAPIDC). The Program is managed on Sida's behalf by the Stockholm Environment Institute (SEI) and the corrosion project is coordinated by Swerea KIMAB AB. Corrosion attack after one (2002-2003 and 2005-2006), two (2002-2004) and four (2002-2006) years of exposure are presented for 12 test sites in Asia (India, Vietnam, Thailand, Malaysia, and China including Hong Kong) and four test sites in Africa (South Africa, Zambia and Zimbabwe). Materials exposed are carbon steel, zinc, copper, limestone and paint coated steel. At each test site, the environment is characterized by SO₂, NO₂, HNO₃, O₃, particles, amount and pH of precipitation, temperature and relative humidity. Preliminary results are also given from the enlargement of the network (2006-) by inclusion of five new test sites in Asia (Taj Mahal/India, Iran, Nepal, Sri Lanka and Maldives) and two new test sites in Africa (Mozambique and Tanzania). SO₂ is the most important parameter but acid rain is also important for all materials while HNO₃ show correlation to corrosion of zinc and limestone, much similar to the situation in Europe. Attempts to predict corrosion values using dose-response functions developed in Europe have failed, especially for limestone.

Keywords: Air pollution, corrosion, painted steel, carbon steel, zinc, copper, limestone, tropical

INTRODUCTION

There is and has been a concern that the high pollution levels combined with the elevated temperature levels and high amount of precipitation observed in many developing sub-tropical and tropical countries will result in higher corrosion rates than previously observed in Europe, Canada and the United States. A review of available data and exposure programs in sub-tropical and tropical regions¹ showed that either the environmental characterization is limited to SO₂ or the exposure time is relatively short.

In order to fill this gap a network of test sites was developed in Asia and Africa under the framework of the 2001-2004 Swedish International Development Cooperation Agency (Sida) funded program on Regional Air Pollution in Developing Countries (RAPIDC). The Program was managed on Sida's behalf by the Stockholm Environment Institute (SEI). The corrosion project was coordinated by the Swedish Corrosion Institute. Corrosion data after 1 year of exposure in the network of test sites was reported at the 2005 Acid Rain conference in Prague². The present paper will present results from the 2002-2008 RAPIDC corrosion project coordinated by Swerea KIMAB AB (former Swedish Corrosion Institute). It includes data after 1, 2 and 4 years of exposure, data on trends in pollution and corrosion and first results from the enlargement of CORNET, the Corrosion Network.

The aim of RAPIDC is to facilitate the development of agreements / protocols to implement measures that prevent and control air pollution and its role model is the Convention on Long-Range Transboundary Air Pollution (CLRTAP). In South Asia, the "Malé Declaration on Control and Prevention of Air Pollution and its Likely Transboundary Effects" is in effect while the African counterpart is the "Air Pollution Information Network for Africa" (APINA). The focus of the corrosion study was to investigate the response of materials to pollutants under Asian and African conditions and build capacity amongst researchers and practitioners in the countries involved to undertake corrosion studies. The focus on air pollution has resulted in preferable selection of inland test sites and, consequently, chloride corrosion effects are not covered by the present study.

EXPERIMENTAL PROCEDURE

The experimental methods were explained in detail in connection with the publication of the 1-year data², and only the most important aspects as well as an update on the development of the network are given here.

Exposure Racks and Test Sites

The exposure racks were fabricated in Sweden and shipped to the different test sites and personnel from Swerea KIMAB AB were present at the start of each exposure. Figure 1 shows a photograph of the rack in Nepal with samples of carbon steel, zinc, copper, painted steel and limestone on a carousel. In the background, a glimpse of another rack type can be seen attached to the white wall. This is a so-called kit for rapid assessment of corrosion originally developed in the EU 5FP project MULTI-ASSESS³. Ten kits of this type have been exposed in the Kathmandu valley and the results will form part of a separate publication.



FIGURE 1 – Rack installed at the roof of the International Centre for Integrated Mountain Development (ICIMOD), Nepal, Kathmandu

Table 1 shows a list of test sites including the responsible organizations and start of first exposure and Figure 2 shows a map of the test sites. Two groups of test sites are presented, the original network consisting of 12 sites in Asia and 4 sites in Africa and the enlargement of the network consisting of 5 sites in Asia and 2 sites in Africa. In total 23 test sites in 14 countries are included in the present network.

Characterization of the Environment

Passive sampling was performed on all sites for the gaseous pollutants SO₂, NO₂, O₃ and HNO₃ and for particulate matter. Sampling was performed on a bi-monthly basis i.e., samplers were exchanged each second month. Complementary data on temperature, relative humidity, amount of rain and its pH were collected by the partners at a nearby meteorological station.

TABLE 1 – List of test sites including country, name, responsible organization and start of first exposure (2002 – original network; 2006-2007 – enlargement of network)

Country	Test site name	Responsible organisation	Start
India	Bhubaneswar-u	Regional Research Laboratory	25 May 2002
India	Bhubaneswar-r	Regional Research Laboratory	25 May 2002
Thailand	Bangkok	Thailand Institute of Scientific and Technological Research	10 June 2002
Thailand	Phrapradaeng	Thailand Institute of Scientific and Technological Research	11 June 2002
Vietnam	Hanoi	Institute of Materials Science	23 July 2002
Vietnam	Ho Chi Minh	Ho Chi Minh Branch of the Institute of Materials Science	26 July 2002
Vietnam	Mytho	Ho Chi Minh Branch of the Institute of Materials Science	27 July 2002
China	Chongqing	Chongqing Institute of Environmental Science and Monitoring	20 July 2002
China	Tie Shan Ping	Chongqing Institute of Environmental Science and Monitoring	20 July 2002
China	Hong Kong	Environmental Protection Department	18 July 2002
Malaysia	Kuala Lumpur	Malaysian Meteorological Service	13 June 2002
Malaysia	Tanah Rata	Malaysian Meteorological Service	14 June 2002
South Africa	Johannesburg	Council for Scientific and Industrial Research	21 August 2002
Zambia	Kitwe	University of Zambia	27 August 2002
Zambia	Magoye	University of Zambia	25 August 2002
Zimbabwe	Harare	University of Zimbabwe	30 August 2002
India	Taj Mahal	Central Pollution Control Board	25 November 2006
Iran	Teheran	Environmental Research Center	20 November 2006
Sri Lanka	Battaramulla	Central Environmental Authority	27 November 2006
Nepal	Kathmandu	International Centre for Integrated Mountain Development	14 November 2006
Maldives	Hanimadhoo	Department of Meteorology	23 January 2007
Mozambique	Maputo	Eduardo Mondlane University	8 September 2006
Tanzania	Dar Es Salaam	University of Dar es Salaam	15 September 2006

Sample Preparation and Evaluation of Corrosion Attack

For each of the materials and exposure periods, a set of three identical samples was prepared and exposed. At the start of exposure, nine samples were exposed for each material, sufficient for three exposure periods. For the original network (Table 1), an additional set of three samples per material was exposed in 2005 and withdrawn together with the 4-year sample in 2006. By comparing this set (2005-2006) with the first 1-year exposure (2002-2003) information on trends in corrosion and pollution can be obtained.

All flat samples, carbon steel (Dc 04, SS – EN 10 130), zinc (Z1 – DIN EN 1179), copper (Cu DHP, SS 5015) and painted steel were cut to dimensions 100 x 150 mm². The thickness of all flat samples was 1 mm except for steel, which had a thickness of 2 mm. The painted steel had two layers of alkyd (90 µm), the first consisting of a 50 µm alkyd based primer and the second of a 40 µm and glossy acrylic modified alkyd topcoat.

The corrosion attack of the metal samples was evaluated with 10 minutes consecutive pickling using Clarke’s solution for steel, 250 g glycine and distilled water to make 1000 ml saturated solution for zinc and 50 g amidosulfonic acid and distilled water to make 1000 ml for copper. Painted steel was evaluated by visual examination of the spread of corrosion attack in both directions from the 1 mm cut but expressed as the average spread in one direction, excluding the width of the cut.

Portland limestone specimens of dimensions 50 x 50 x 8 mm³ were obtained from the Building Research Establishment Ltd, United Kingdom, where also the corrosion attack was evaluated as mass change during exposure. The mass change was then recalculated to surface recession.

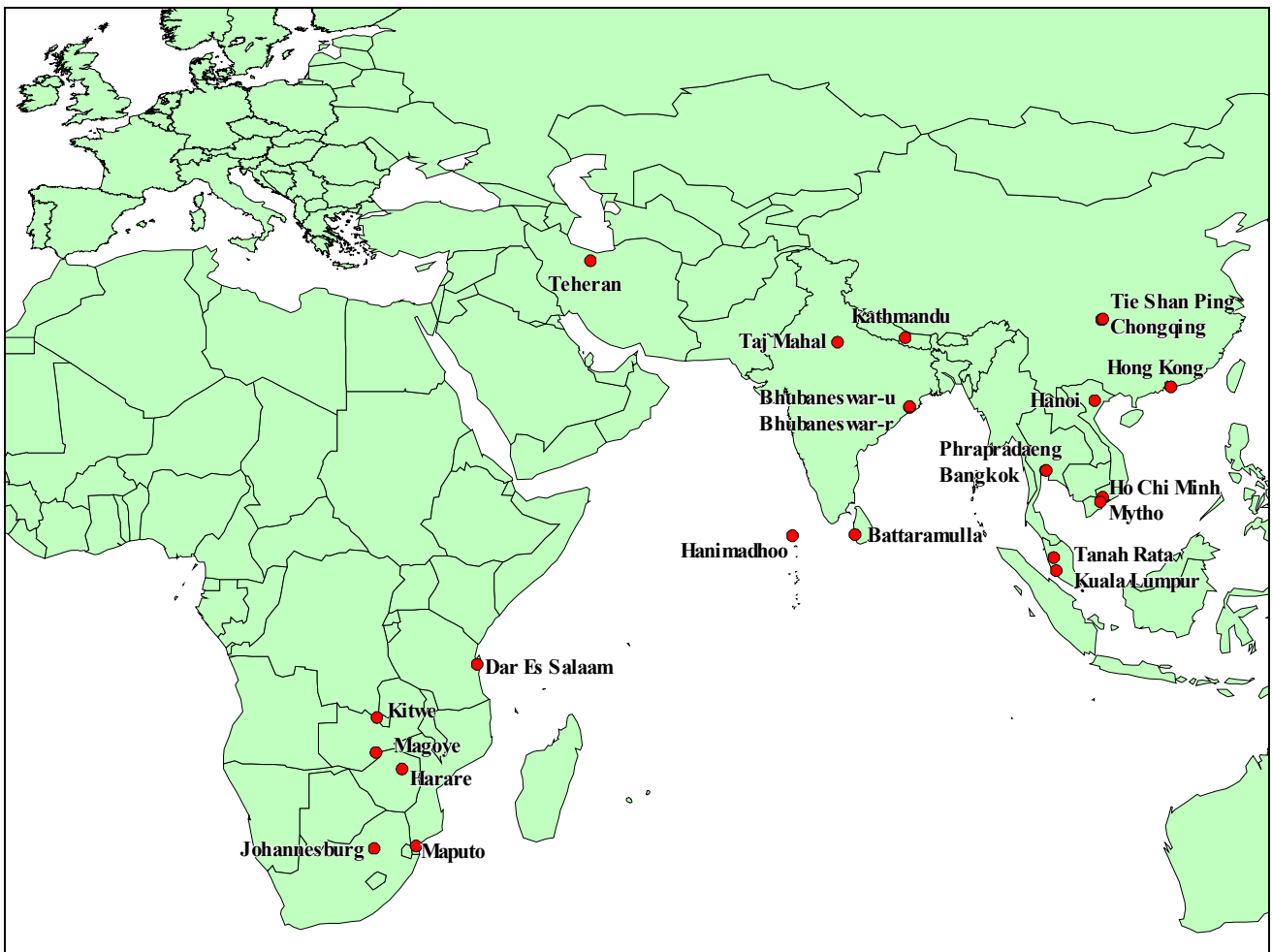


FIGURE 2 – Map of test sites

RESULTS AND DISCUSSION

The main part of the results are based on the original network (Table 1) where data after 1 (2002-2003 and 2005-2006), 2 (2002-2004) and 4 (2002-2006) years of exposure are available. The exposures at the enlarged network sites are on-going and at present time no corrosion data and only limited environmental data are available.

Status of the Environment

The environmental data for the period 2002-2006 are given in Table 2 and the selected parameters temperature, amount of precipitation and SO₂ concentration are in addition given in Figure 3. The values for these three parameters are generally higher compared to European conditions while the values for the other parameters are similar. Relative humidity is observed to be above 70 % for all Asian sites but around 60% for all African sites except Johannesburg.

Regarding SO₂, four extreme sites can be observed: Phrapradaeng, Chongqing, Tie Shan Ping, and Kitwe. Although Tie Shan Ping is a rural site, its distance is only 25 km from the Chongqing urban center. The highest precipitation values, about 3000 mm year⁻¹, are observed in Malaysia, where two stations are located, Kuala Lumpur and Tanah Rata. The latter has generally very low pollution levels while the highly trafficked Kuala Lumpur has high HNO₃ and NO₂ levels. NO₂ is also high for the other traffic intensive cities Bangkok, Chongqing and Hong Kong.

TABLE 2 – Environmental data (average 2002-2006) including temperature (T), relative humidity (Rh), precipitation (total amount (Rain) and pH), gaseous pollutants (HNO₃, SO₂, NO₂ and O₃), total particulate (PM) and ion deposition (Cl⁻, NO₃⁻ and SO₄²⁻)

Name	T °C	Rh %	Rain mm	pH	HNO ₃	SO ₂ µg m ⁻³	NO ₂	O ₃	PM	Cl ⁻ µg cm ⁻² month ⁻¹	NO ₃ ⁻	SO ₄ ²⁻
Bhubaneshwar-u	26.9	75	1499	6.3	1.5	5	10	66	117	3.5	1.7	2.4
Bhubaneshwar-r	26.9	75	1499	6.3	1.2	5	7	67	43	1.1	0.7	1.0
Bangkok	29.3	76	1465	6.8	2.2	9	37	42	41	0.4	2.6	1.8
Phrapradaeng	29.3	72	1446	5.7	1.4	59	32	52	89	1.5	2.1	8.1
Hanoi	24.5	79	1533	5.7	0.9	16	18	52	55	0.4	1.1	3.7
Ho Chi Minh	28.1	75	1585	6.1	1.0	18	19	46	35	0.4	0.9	2.0
Mytho	26.9	83	1341	6.1	0.4	2	8	38	57	2.3	0.6	1.3
Chongqing	18.5	74	1110	4.7	1.3	100	70	50	137	0.6	1.6	16.9
Tie Shan Ping	17.6	88	1191	4.0	2.0	56	16	73	56	0.2	1.1	7.2
Hong Kong	22.9	77	1957	4.5	1.8	18	47	32	41	0.6	2.3	1.8
Kuala Lumpur	27.9	77	3199	4.3	3.4	10	43	39	24	0.2	1.4	1.1
Tanah Rata	18.0	91	2751	4.9	0.2	0.2	1	34	7	0.1	0.2	0.1
Johannesburg	17.3	77	426	4.6	1.5	16	26	44	21	0.1	0.6	0.7
Kitwe	22.3	58	1251	4.7	0.9	87	-	71	62	0.2	0.6	6.1
Magoye	22.6	63	737	7.0	0.5	0.4	2	51	20	0.1	0.2	0.1
Harare	18.9	62	781	6.3	0.6	13	13	56	30	0.1	0.4	1.1

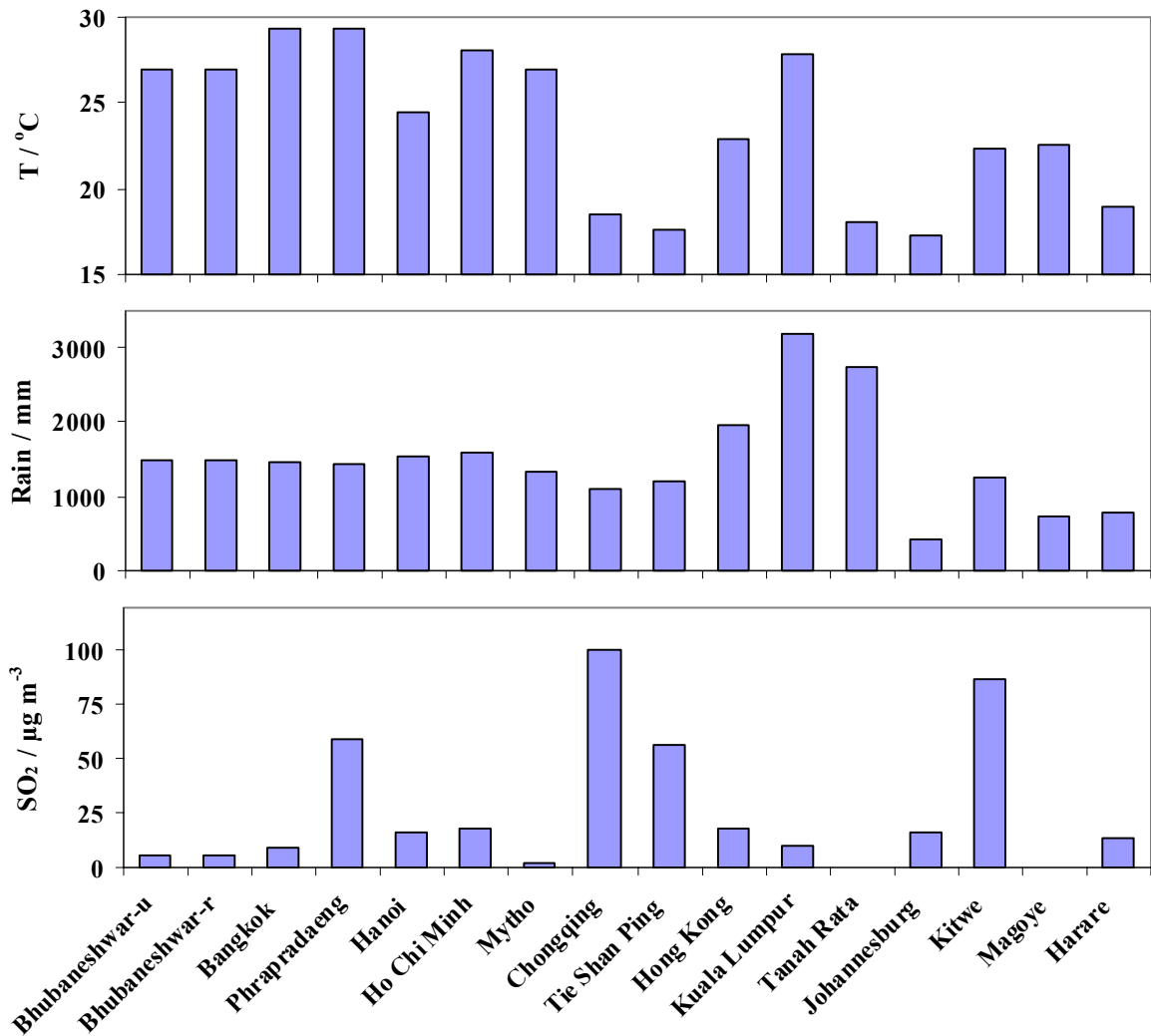


FIGURE 3 – Average (2002-2006) temperature (T), amount of precipitation (Rain) and SO₂ concentration

Corrosion Attack after 1, 2 and 4 Years of Exposure

Corrosion data after 2 years of exposure for all materials are given in Table 3 and corrosion for carbon steel and zinc after 1, 2 and 4 years of exposure is presented in Figure 4. High values of corrosion are generally observed when SO₂ is high (Chongqing and Kitwe). Comparing Chongqing and Kitwe, the values are generally higher in Chongqing with the exception of zinc. The high corrosion level of zinc in Kitwe is so far not explained but an unconfirmed suspicion is that it is related to particulate copper deposition. Kitwe is located in the copper belt mining areas of Zambia.

When looking at Figure 4, the different kinetics of carbon steel and zinc is evident. The corrosion rate of carbon steel is decreasing and the 4-year carbon steel value is on average slightly more than 50% compared to 4 times the 1-year value. The corrosion rate of zinc is constant while the kinetics for copper (not shown) is somewhere between zinc and carbon steel.

TABLE 3 – Corrosion attack after 2 (2002-2004) years of exposure of painted steel (spread from cut), carbon steel, zinc, copper and limestone

Name	Painted steel Mm	Steel g m ⁻²	Zinc g m ⁻²	Copper g m ⁻²	Limestone µm
Bhubaneswar-u	2.1	252	8.6	15.2	24.3
Bhubaneswar-r	1.2	270	7.9	19.4	17.3
Bangkok	0.6	161	7.6	26.3	25.4
Phrapradaeng	1.7	417	11.3	28.6	47.9
Hanoi	1.4	279	11.6	11.4	27.6
Ho Chi Minh	0.8	214	11.3	15.1	20.0
Mytho	2.3	298	8.5	20.1	9.9
Chongqing	8.2	1201	19.9	46.0	75.6
Tie Shan Ping	6.7	769	24.8	36.5	55.6
Hong Kong	0.7	201	11.4	12.4	25.3
Kuala Lumpur	0.9	181	15.8	19.3	35.9
Tanah Rata	0.8	90	11.0	20.0	15.8
Johannesburg	0.6	168	4.3	9.0	-
Kitwe	4.0	561	47.5	19.3	61.2
Magoye	0.6	70	3.3	10.2	9.7
Harare	1.5	267	6.3	7.6	14.5

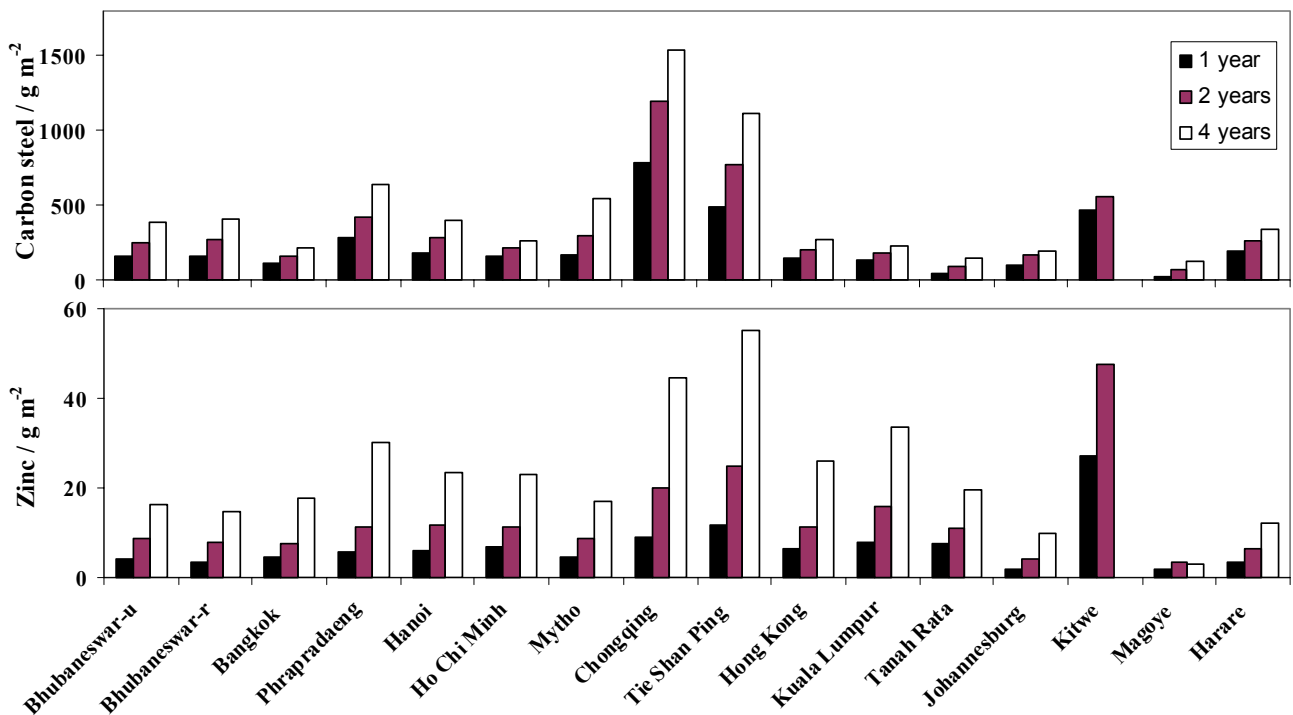


FIGURE 4 – Corrosion of carbon steel and zinc after 1, 2 and 4 years of exposure.

Correlation between Environmental and Corrosion data

Correlations between corrosion and important pollution parameters are shown in Table 4. A similar correlation analysis² performed on data after only one year of exposure showed significant correlations between limestone and all parameters, as in Table 4, but otherwise only carbon steel vs SO₂ and zinc vs pH. It is evident from Table 4 that both dry deposition (SO₂ and in some cases HNO₃) and wet deposition (pH) is important for all materials. Not surprising, carbon steel shows the highest correlation to SO₂ and zinc the highest correlation to pH. Regarding HNO₃, a gaseous pollutant that has recently received increased attention and is more corrosive than SO₂ as shown in laboratory experiments⁴, correlations are only present for zinc and limestone. This is in agreement with findings in the temperate zone (Europe) where HNO₃ was included in dose-response functions for zinc and limestone but not in functions for carbon steel, copper and bronze⁵.

TABLE 4 – Significant (95%) rank correlations between pollution and corrosion data

	SO ₂	HNO ₃	-pH
<i>Paint coated steel</i>	0.42		0.33
<i>Carbon steel</i>	0.73		0.40
<i>Zinc</i>	0.45	0.22	0.61
<i>Copper</i>	0.28		0.30
<i>Limestone</i>	0.49	0.40	0.53

Comparison with European conditions

As showed in the previous section, the most important pollution parameters (dry deposition of SO₂, acid rain and for some materials possible HNO₃) seem to be the same in subtropical/tropical climates as well as in temperate climate. However, the relative importance of the effects as well as the influence of climate can still be different. Therefore, it has some merit to compare further the present data to similar data obtained in Europe. To this purpose, data from the “International Co-operative Programme on effects on Materials including historic and cultural monuments” (ICP Materials)⁵ is used since the program uses identical methodology in almost every aspect. Two types of comparisons have been made, the first to compare the corrosion data as is, in order to answer the question if the corrosion problems in Asia/Africa poses a greater threat than in Europe. The second is a lightly more sophisticated comparison aiming at answer the question if dose-response functions developed in Europe can be used to predict corrosion attack in Asia/Africa.

Comparison of corrosion levels in Europe and Asia/Africa. Figure 5 shows box-and-whisker plots for ICP Materials and RAPIDC data sets after 4 years of exposure. Note that individual sample values, not averages for each exposure, are shown in the figure. For zinc, the median is slightly lower in Asia/Africa while for copper and carbon steel the median is slightly higher. Note that in Europe, copper values are generally lower than zinc values but this is not the case for Asia/Africa. For painted steel, the median is about the same but there are some extreme values in Asia/Africa but not in Europe. Limestone shows the highest difference with significantly higher values in Asia/Africa, the median is about three times higher.

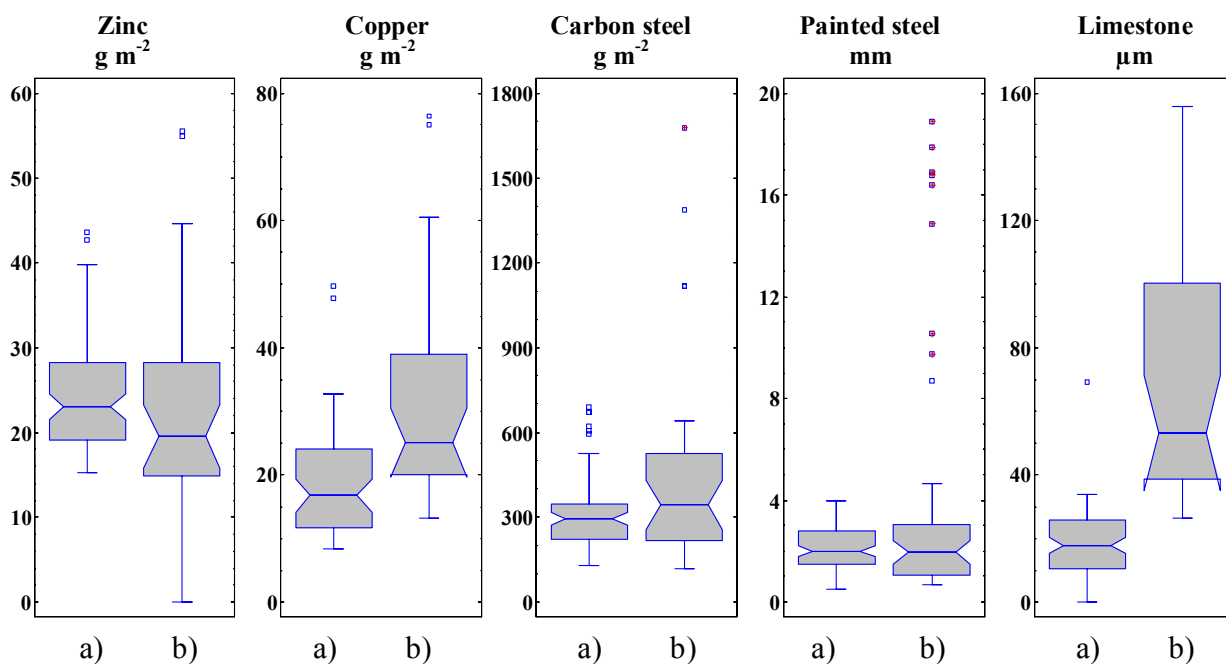


FIGURE 5 – Comparison of data after 4 years of exposure: a) ICP Materials; b) RAPIDC

Prediction of corrosion levels in Asia/Africa using dose-response functions developed in Europe. Is it possible to understand the differences shown in Figure 5 based on quantitative relations between corrosion and environmental data developed for European conditions? These quantitative relations are named dose-response functions. Within the work of ICP Materials, two sets of functions have been developed: dose-response functions for the SO₂ dominating situation⁶ and dose-response functions for the multi-pollutant situation⁵. The first set of functions was developed when SO₂ was still high and included only the effect of SO₂ and acid rain. The second set of functions was developed recently and is valid for the present situation in Europe when SO₂ is relatively low (it is not possible to give an absolute limit) and includes in addition HNO₃ and particulate matter. For the present situation in Asia/Africa SO₂ is the dominating pollutant and it is therefore appropriate to use the dose-response functions for the SO₂ dominating situation in order to answer the proposed question. However, but only for discussion purposes, the dose-response function for limestone for the multi-pollutant situation is also included in the comparison given in Table 5. No ICP Materials dose-response function for the SO₂ dominating situation exists for carbon steel and it is therefore not included in the discussion. The dose-response functions are not repeated here because, as it will turn out, they are not suitable for predicting corrosion in Asia/Africa.

Starting with zinc, the observed and predicted values are both in the range between 0.5 to 4.5 μm after 2 years of exposure with the exception of Kitwe, which has an extreme observed corrosion level (discussed above). A regression between observed and predicted values, with Kitwe excluded, show however that the observed values are on average a factor 0.80 times the expected values, i.e. the observed values are usually a bit lower than the predicted. For copper, on the other hand, the observed values are on average higher than predicted, a factor of 1.47, and in addition, the correlation between observed and predicted is generally poor. For limestone, the agreement is very poor, especially for the dose-response function for the SO₂ dominating situation, a factor of 2.35, but also for the function for

the multi-pollutant situation, a factor of 1.52. We suspect that the main reason for all discrepancies can be related to how temperature is included in the models. In any case, it is evident that new dose-response functions are needed for Asia/Africa, especially for limestone but also for the other materials.

TABLE 5 – Observed and predicted zinc, copper and limestone corrosion attack (μm) after 2 (2002-2004) years of exposure

Name	Zinc		Copper		Limestone		
	Observed	Predicted ^a	Observed	Predicted ^b	Observed	Predicted ^c	Predicted ^d
Bhubaneshwar-u	1.2	1.3	1.7	0.9	24	7	22
Bhubaneshwar-r	1.1	1.2	2.2	0.9	17	6	12
Bangkok	1.1	1.6	2.9	0.8	25	9	16
Phrapradaeng	1.6	2.1	3.2	1.7	48	22	22
Hanoi	1.6	2.0	1.3	1.4	28	13	16
Ho Chi Minh	1.6	1.8	1.7	1.2	20	13	14
Mytho	1.2	1.3	2.2	0.5	10	4	12
Chongqing	2.8	3.3	5.2	3.1	76	35	41
Tie Shan Ping	3.5	4.4	4.1	4.8	56	29	48
Hong Kong	1.6	2.5	1.4	1.6	25	15	22
Kuala Lumpur	2.2	3.1	2.2	2.7	36	16	39
Tanah Rata	1.5	1.4	2.2	0.7	16	3	10
Johannesburg	0.6	2.3	1.0	1.7		15	15
Kitwe	6.7	2.2	2.2	2.7	61	31	13
Magoye	0.5	0.6	1.1	0.3	10	2	7
Harare	0.9	1.6	0.8	1.5	15	14	7

^aBased on the zinc dose-response function for the SO₂-dominating situation from ICP Materials. Ref. 6

^bBased on the copper dose-response function for the SO₂-dominating situation from ICP Materials. Ref. 6

^cBased on the limestone dose-response function for the SO₂-dominating situation from ICP Materials. Ref. 6

^dBased on the limestone dose-response function for the multi-pollutant situation from ICP Materials. Ref. 5

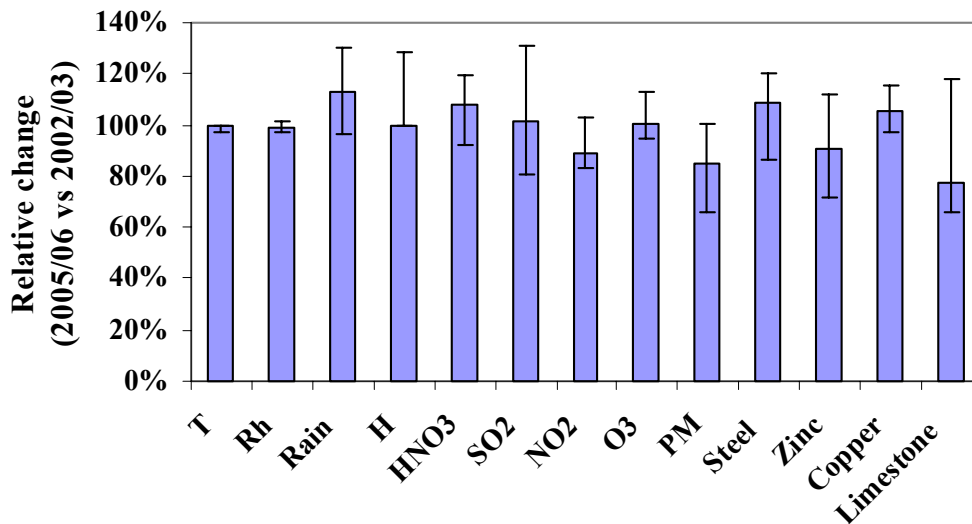


FIGURE 6 – Relative change in environmental and corrosion data based on 16 test sites in Asia and Africa

Trends in Pollution and Corrosion

Having access to data for the two periods 2002-2003 and 2005-2006, it has an interest, from an environmental policy and development point of view, to investigate if corrosion and/or pollution are increasing or decreasing. In Europe, the decrease in corrosion started between the 1960s and 1980s depending on location⁷. Based on only two points it is not possible to draw definite conclusion and continued trend exposures are therefore necessary in order to show if a similar trend in Asia/Africa has started. Figure 6 shows the ratio of the 2005-2006 value to the 2002-2003 value for both environmental and corrosion parameters. Individual test sites are not shown, only the median and upper/lower quartiles of the ratios. The value 100%, i.e. no change, is included in the range from lower to upper quartile, for all parameters in Figure 6. The change is generally small and it is not possible to say that corrosion or pollution in general either increases or decreases.

Preliminary Results from the Enlargement of the Network

The first exposure of the enlarged network (Table 1), was concluded in November 2007 but at writing moment all samples has not arrived at Swerea KIMAB AB. Therefore, it is only possible to show results from passive sampling of pollution, Figure 7. The highest SO₂ value was measured in Teheran but combining with data in Figure 3 this site is only ranked fifth from the top. Regarding HNO₃, the relative situation is similar. In all, the new sites complement the existing and provide a valuable contribution to the network taking into account geographical distribution (Figure 1), climate and pollution.

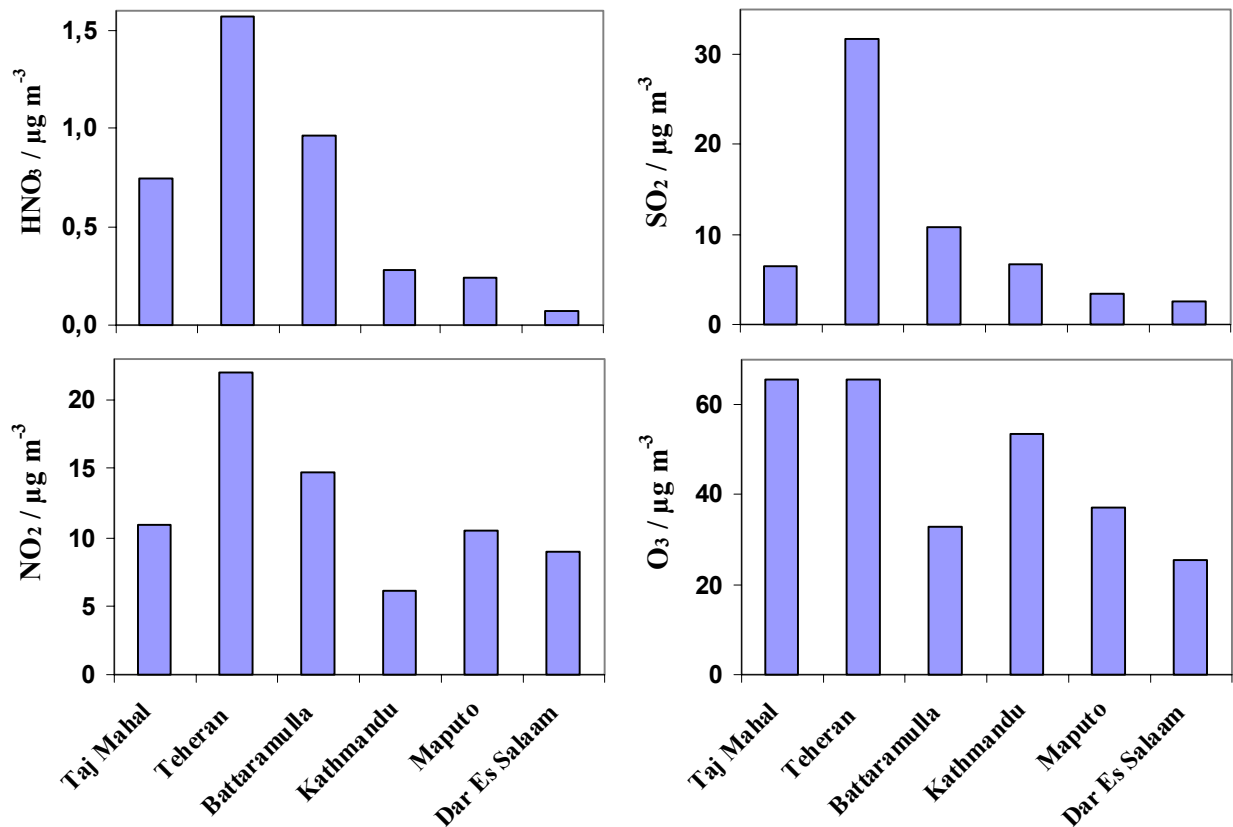


FIGURE 7 – Average concentrations (2006-2007) of HNO₃, SO₂, NO₂ and O₃.

CONCLUSIONS

Results of corrosion of carbon steel, painted steel, zinc, copper and limestone after 1, 2 and 4 years of exposure and extensive environmental characterization including pollution in a network of Asian (12 sites in India, Thailand, Vietnam, China including Hong Kong and Malaysia) and African (4 sites in South Africa, Zambia and Zimbabwe) sites was presented. Preliminary results from an enlargement of the network including sites in India, Iran, Sri Lanka, Nepal, Maldives, Mozambique and Tanzania was also presented.

Dry deposition of SO₂ is the most important parameter but acid rain is also important for all materials while HNO₃ show correlation to corrosion of zinc and limestone, much similar to the situation in Europe. When comparing further with European conditions the absolute corrosion values of the metals (zinc, copper and carbon steel) show systematic but not very large differences. For zinc, the median is slightly lower in Asia/Africa while for copper and carbon steel the median is slightly higher. For painted steel and limestone, however, the situation is more alarming. For painted steel extreme values can be seen at individual sites in Asia/Africa, while corrosion of limestone is generally much higher in Asia/Africa compared to Europe. Attempts to predict corrosion values using dose-response functions developed in Europe have failed, especially for limestone, but predicted values for zinc and copper also show systematic differences to observed values. We suspect that the main reason for all discrepancies can be related to how temperature is included in the models. Trends in corrosion and pollution have been investigated but it is not possible to show significant increases or decreases during the period 2002-2006.

The policy implications of our research is that corrosion is at least as important an issue in Asia and Africa as it has been in Europe. It is clear that the levels of corrosion experienced in these countries will give rise to significant economic losses. The next step and publication is to extend the analysis and put the data into perspective in order to develop dose-response functions for the materials based on the discussed data, possibly combined with similar data obtained in Europe, from ASTM and ISO.

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